

Atomic/Molecular Layer Deposition for Energy Storage and Conversion

Yang Zhao¹⁺, Lei Zhang¹⁺, Jian Liu²⁺, Keegan Adair¹, Feipeng Zhao¹, Yipeng Sun¹, Tianpin Wu³, Xuanxuan Bi⁴, Khalil Amine⁴, Jun Lu^{4*}, Xueliang Sun^{1*}

¹Department of Mechanical & Materials Engineering, University of Western Ontario, London, ON, N6A 5B9, Canada

²School of Engineering, Faculty of Applied Science, University of British Columbia, Kelowna, BC, V1V 1V7, Canada

3. X-ray Science Division, Advanced Photon Sources, Argonne National Laboratory, Lemont, IL, 60439, USA

⁴Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL, 60439, USA

Email: xsun9@uwo.ca (X. Sun), junlu@anl.gov (J. Lu)

+ These authors contributed equally to this work

Abstract

Energy storage and conversion systems, including batteries, supercapacitors, fuel cells, solar cells, and photoelectrochemical water splitting, have played vital roles in the reduction of fossil fuel usage, addressing environmental issues and the development of electric vehicles. The electrode materials fabrication and surface/interface engineering with the refined structures are indispensable for achieving optimal performance for the different energy-related devices. Atomic layer deposition (ALD) and molecular layer deposition (MLD) techniques, the gas-phase thin film deposition processes with self-limiting and saturated surface reactions, have emerged as a powerful technique for surface and interface engineering in energy-related devices due to their exceptional capability of precise thickness control, excellent uniformity and conformity, tunable composition and relative low deposition temperature. In the past decades, ALD and MLD have been intensively studied for energy storage and conversion applications with remarkable progress. In this review, we have a comprehensive summary of the development and achievements of ALD and MLD and their applications for energy storage and conversion, including batteries, supercapacitors, fuel cells, solar cells, and photoelectrochemical water splitting. Moreover, the fundamental understanding of the mechanisms involved in different devices will be deeply reviewed. Furthermore, the large-scale potential of ALD and MLD techniques are discussed and predicted. Finally, we will provide insightful perspectives on future directions for new material design by ALD and MLD and untapped opportunities in energy storage and conversion.

1. Introduction

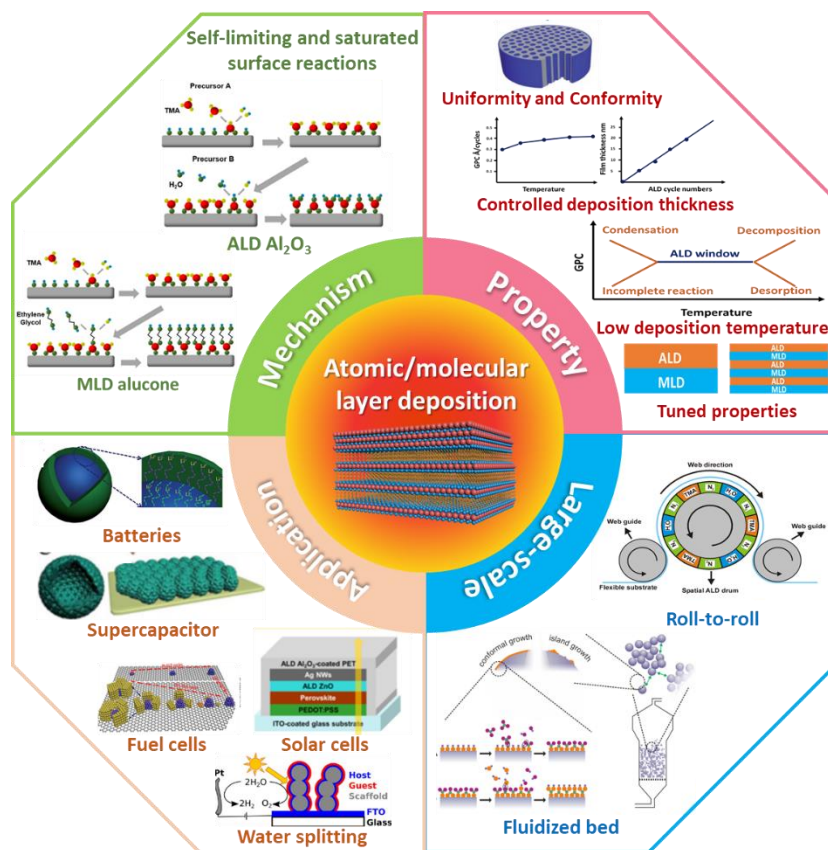


Fig. 1 The mechanism, properties, large-scale potentials, and the applications for energy storage and conversion, of ALD/MLD techniques.

Energy storage and conversion systems have played vital roles in the development of electric vehicles (EVs), reduction of fossil fuel usage, and addressing environmental issues¹. Among the various systems, Li-ion batteries (LIBs) and proton exchange membrane fuel cells (PEMFCs) are two of the most prominent technologies for powering electric vehicles due to their high energy and power density, high efficiency, room temperature operation, and zero emissions. However, the state-of-the-art LIBs and PEMFCs still need further improvement for higher energy density, longer durability, better safety, and lower cost to meet the increasing demands from automotive applications. Meanwhile, next-generation batteries, such as Li metal, Li-sulfur, and Li- O_2 batteries, solid-state Li batteries, Na batteries and beyond, have been intensively studied as promising alternatives to LIBs for large-scale energy storage applications due to their lower cost compared

to conventional LIBs²⁻⁵. Nevertheless, several formidable challenges inhibit the commercialization of these battery systems, including the detrimental structural changes and unfavourable side reactions at the surface and interface of electrode materials, which need to be addressed in order to prevent rapid capacity degradation and limited battery lifetime⁶⁻⁸. Therefore, it is necessary to rationally engineer the surface and interface of the electrode materials to prevent parasitic side reactions and thus enhance battery performance⁹⁻¹². For PEMFCs, the high cost and insufficient durability of Pt electrocatalyst is still a major barrier for their application in fuel cell vehicles. The degradation of the electrocatalytic properties of Pt could occur through the coalescence of Pt particles due to weak interactions between Pt and the support, Pt particle agglomeration, corrosion of the support material, and Ostwald ripening. Therefore, it is critical to design a strong interface between Pt and the support to preserve such structures in the harsh environment of PEMFCs while providing the three-phase boundary (catalyst, support, and reactants) required for performing multifunctional electrochemistry^{13, 14}. Moreover, renewable solar energy and solar fuels are regarded as the most promising alternative clean energy source for fossil fuels. Surface and interface engineering in a well-designed fashion are indispensable for obtaining desirable material structure and achieving optimal performance for the energy storage and conversion application. In this review, as shown in **Fig.1**, we will deeply discuss the unique techniques of atomic layer deposition (ALD) and molecular layer deposition (MLD) in the applications of energy storage and conversion. Particularly, we will summarize the mechanism, properties, wide applications and large scale potentials of ALD and MLD.

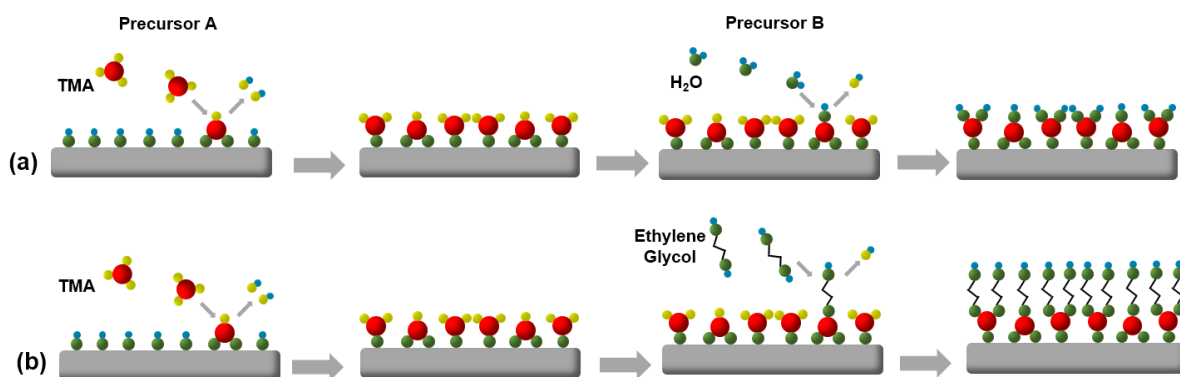


Fig. 2 Illustration of (a) ALD for inorganic films and (b) MLD for hybrid inorganic-organic films.

ALD has emerged as a powerful technique for surface and interface engineering in energy-related devices, such as rechargeable batteries, supercapacitor, fuel cells, solar cells, and electrochemical water splitting, due to its exceptional capability in controlling materials deposition with atomic-level precision¹⁵⁻¹⁷. During an ALD process, gas-phase precursors are sequentially exposed to the substrate, leading to self-limiting and saturated surface reactions (**Fig. 2a**). This reaction mechanism renders ALD-deposited inorganic thin films several advantages, including; precise thickness control, excellent uniformity and conformity, and tunable composition. These thin films have been employed as surface coating layers on the anode and cathode materials of LIBs to address structural and interfacial problems. Moreover, nanoparticles can also be deposited on substrates by ALD by controlling the nucleation sites on the substrate surface through pre-planted functional groups. This is because nucleation sites, such as hydroxyl groups, defect sites, and heteroatom-doping sites, are the prerequisites for ALD surface reactions to take place^{18, 19}. While ALD can traditionally deposit inorganic materials, MLD, the organic counterpart of ALD, can fabricate organic and hybrid inorganic-organic thin films (**Fig. 2b**). The incorporation of organic segments in the MLD process offers almost unlimited combinations for the film structure, which could lead to unique mechanical, optical, and thermal properties. These MLD thin films hold great promise for tackling surface and interfacial problems in energy storage and conversion systems.

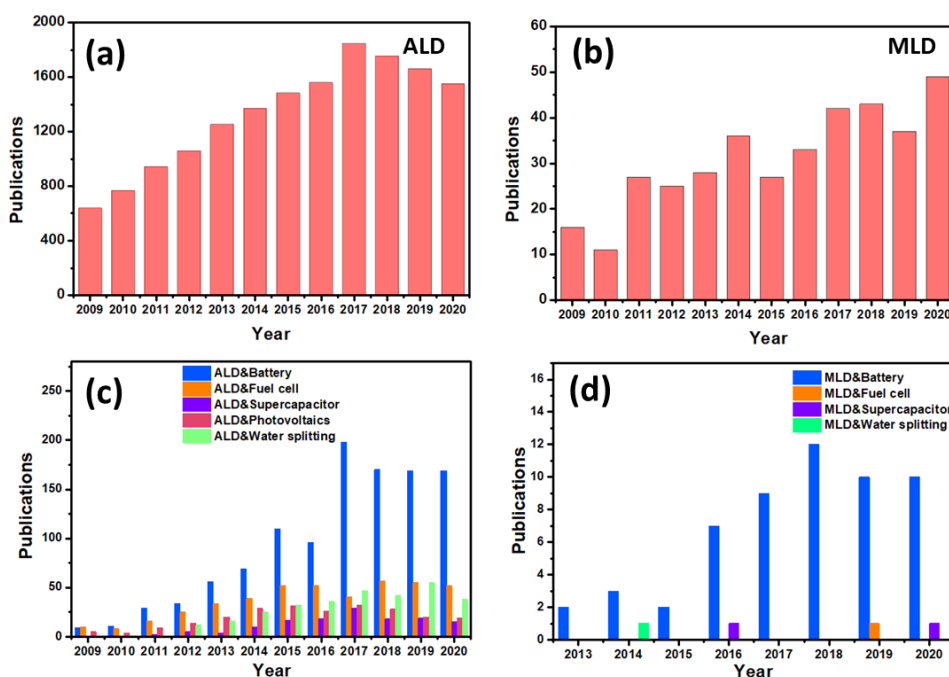


Fig.3 Publication numbers in the past ten years with the key words of (a) atomic layer deposition (ALD); (b) molecular layer deposition (MLD); (c) ALD & battery, ALD & fuel cell, ALD & supercapacitor, ALD & photovoltaics, ALD & water splitting; (d) MLD & battery, MLD & fuel cell, MLD & supercapacitor, MLD & photovoltaics, MLD & water splitting. (Based on Web of Science).

Since the development of ALD in the late 1970's (previously referred to as atomic layer epitaxy (ALE)), this advanced thin film deposition technique has received increasing attention for multiple applications, including catalysis, microelectronics, energy storage and conversion, and sensing²⁰⁻²². Various materials, including metal oxide, metal sulfide, metal fluoride, and metal phosphates can be deposited by ALD with precisely controlled thicknesses, compositions and structures^{23, 24}. Particularly in the past ten years, the fields of ALD and MLD for energy storage and conversion has grown rapidly. **Fig.3 (a)** shows the number of publications associated with atomic layer deposition from 2009 to date, with a significant increase in recent years. As an extension of ALD, MLD was later developed as the organic molecule equivalent. Although the publication numbers on MLD are not as large as that of ALD (**Fig. 3(b)**), the unique properties of MLD films are still attracting attention for different applications. Among the various applications, energy storage and conversion, especially batteries and fuel cells, are one of the most attractive areas for ALD and MLD (**Fig. 2(c, d)**). There are several excellent review papers that have summarized the fundamental chemistry and principles of ALD/MLD, and their application for LIBs and Li-S batteries²⁵⁻⁴⁴. However, there is no comprehensive review that summarizes both ALD and MLD in the applications of energy storage and conversion.

In this review, we focus on the development and achievements of ALD and MLD and their applications for energy storage and conversion. Different energy storage systems, including batteries and supercapacitors, are included in this comprehensive review. Moreover, the application of ALD/MLD for energy conversion systems including fuel cells, solar cells and photoelectrochemical water splitting, has been discussed in detail. Not only has the significant progress been summarized, but also a fundamental understanding of the mechanisms involved will be deeply reviewed. Finally, we will provide insightful perspectives on future directions for new material design by ALD and MLD and untapped opportunities in energy storage and conversion.

2. ALD/MLD for energy storage

2.1 ALD/MLD for batteries

2.1.1 ALD/MLD for Li-ion batteries

2.1.1.1 ALD/MLD for electrode fabrication

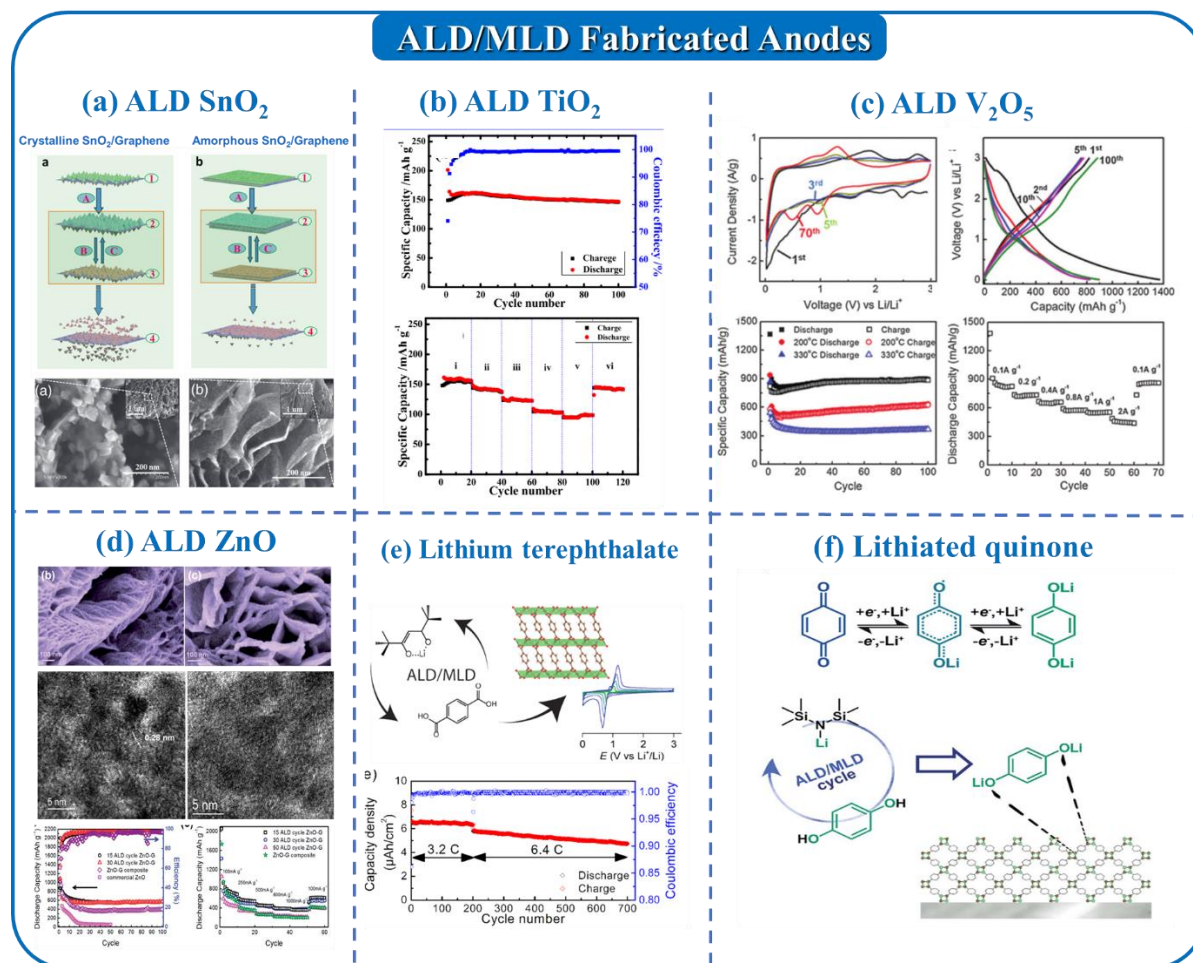


Fig.4 ALD and MLD metal oxide anodes: (a) ALD SnO_2 ; (b) ALD TiO_2 ; (c) ALD V_2O_5 ; (d) ALD ZnO ; (e) Lithium terephthalate; (f) lithiated quinone.

Metal oxides are the most popular films deposited by ALD and are promising candidates for electrode materials in LIBs. For example, SnO_2 has been extensively investigated due to its high specific capacity and energy density, relative to conventional graphite anodes. ALD SnO_2 was first demonstrated as an anode material for LIBs when deposited on graphene nanosheets (GNS)⁴⁵, as

shown in **Fig.4 (a)**. Benefitting from the unique properties of ALD, the structural phases of SnO₂ were precisely controlled by the ALD deposition temperatures, resulting in amorphous and crystalline SnO₂-GNS composites with sandwich nanostructures. The precursors used in this study were SnCl₄ and H₂O at two different temperatures of 200 °C and 400 °C. It is very interesting to note that the amorphous SnO₂-GNS showed higher electrochemical stability and Coulombic efficiency compared to the crystalline SnO₂-GNS. The amorphous SnO₂-GNS obtained a capacity of 793 mAh g⁻¹ after 150 cycles, which is higher than that of the crystalline SnO₂-GNS (499 mAh g⁻¹ after 150 cycles). It is believed that the amorphous SnO₂-GNS is more effective than the crystalline SnO₂-GNS in overcoming the large volume change of SnO₂ nanoparticles during electrochemical cycling. Subsequently, ALD SnO₂ was deposited on different substrates, including stainless steel⁴⁶, reduced graphene oxide⁴⁷, and MXene⁴⁸. The as-prepared ALD SnO₂ is uniform on different substrates with highly controlled structures and thicknesses^{49, 50}.

TiO₂ is another attractive anode material candidate for LIBs due to its chemical stability, low volume expansion during cycling, high rate capability and intrinsic safety. ALD TiO₂ is also a routine recipe for the ALD community, in which TiCl₄ and Titanium (IV) isopropoxide (TTIP) are widely used as precursors for Ti-based ALD processes^{51, 52}. Ban et al. firstly reported ALD amorphous TiO₂ on high surface area graphene (reduced graphene oxide) sheets for LIBs⁵³. The as-prepared ALD TiO₂ can effectively minimize the Li-ion diffusion coefficient of TiO₂, resulting in a stable and high capacity anode with high rate performances. Other matrices have also been used as substrates for ALD TiO₂, such as graphite, graphene, carbon nanotubes, anodic aluminum oxide (AAO) templates and Ni nanotubes⁵⁴⁻⁵⁸. Sun's group also fabricated ALD TiO₂ on worm-like GNS with high capacity and stability, as shown in **Fig.4 (b)**⁵⁹. Another interesting work has been demonstrated by Hong et al.⁶⁰, in which carbon black is used as a sacrificial template to create the mesoporous structure of TiO₂. As a result, the mesoporous TiO₂ exhibits a large specific surface area, high capacity, and good Coulomb efficiency.

Among the aforementioned metal oxides, ZnO shows various advantages, such as low cost, facile synthesis, chemically stable, and a high theoretical capacity of 978 mAh g⁻¹ in LIBs. ZnO has also been widely deposited by ALD, in which Zn(CH₃CH₂)₂ is the most widely used precursor⁶¹. Lian et al. firstly reported ALD ZnO on graphene layers as an anode material for LIBs, as shown in **Fig.4 (d)**⁶². In their study, the ZnO was deposited as quantum dots (QDs) on graphene with controllable sizes from 2 to 7 nm. Interestingly, the smaller ZnO QDs on graphene displayed

better electrochemical performance, in which a high reversible specific capacity of 960 mAh g⁻¹ is achieved. Another work has been reported using graphene frameworks as substrates for ALD ZnO⁶³. To achieve better electrochemical performance, another ALD Al₂O₃ layer was deposited on the ZnO-graphene electrode as a physical protection layer and an artificial ionically conductive SEI layer. As a result, the ALD Al₂O₃-wrapped ALD ZnO-graphene architecture provided the electrode with superior electrochemical performance with high capacity, excellent rate capability, and good cycling stability.

Some other metal oxides have also been deposited by ALD and used as anode materials for LIBs⁶⁴⁻⁶⁶, such as MoO₃, RuO₂, and V₂O₅. For example, as shown in **Fig.4 (c)**, V₂O₅ was deposited on graphene using vanadyl oxytriisopropoxide and water as precursors with a deposition temperature of 150 °C, achieving a growth per cycle (GPC) of 1 Å⁶⁴. The electrochemical results reveal a stable capacity of 892 mA h g⁻¹ can be achieved for the ALD V₂O₅-graphene composite with excellent cyclic stability. The authors believed that the highly conformal coating induced by the ALD process is the key to mitigating mechanical degradation and vanadium dissolution. Besides the popular metal oxides, other metal nitrides, metal phosphate, and metal sulfide deposited by ALD have also been reported⁶⁷⁻⁷⁴, including MoS₂, MoN, W₂N, WS₂, VP_x, AlS_x, and ZnS. The detailed ALD deposition parameters and performances of these materials as anodes in LIBs are shown in **Tab. 1**.

Tab.1 The detailed parameters and performances of the ALD-fabricated anode materials for LIBs

ALD materials	Precursors	Substrate	Deposition temperature	Electrochemical Performances	ref
	SnCl ₄ and H ₂ O	Graphene nanosheets	200 °C	793 mA h g ⁻¹ after 150 cycles	45
			400 °C	499 mA h g ⁻¹ after 150 cycles	
	Tin(IV)-butoxide and Plasma O ⁻	Stainless steel	200 °C	646 mAh g g ⁻¹ after 250 cycles	46

SnO₂	Tetrakis(dimethylamino) tin and H ₂ O	Reduced graphene oxide	150 °C	800 mAh g ⁻¹ after 200 cycles	47
	Tetrakis (diethylamido) tin and O ₃	MXenes	150 °C or 200 °C	843 mAh g ⁻¹ after 50 cycles	48
	Sn(C ₂ H ₅) ₄ and O ₂ plasma	Silicon and stainless steel	150 °C and 200 °C	650 mAh g ⁻¹ after 400 cycles	50
TiO₂	TiCl ₄ and H ₂ O	Reduced graphene oxide	120 °C	120 mAh g ⁻¹ after 400 cycles	53
	TiCl ₄ and H ₂ O	graphite	-	~ 230 mAh g ⁻¹ after 100 cycles	54
	Titanium tetraisopropoxide and H ₂ O	Graphene nanosheets	100 °C	140 mAh g ⁻¹ after 100 cycles	59
	TiCl ₄ and H ₂ O	Carbon nanotubes	120 °C	120 mAh g ⁻¹ after 1000 cycles	55
	TiCl ₄ and H ₂ O	Carbon black	200 °C	128 mAh g ⁻¹ after 100 cycles	60
	TiCl ₄ and H ₂ O	CNTs/CFP	120 °C	178 mAh g ⁻¹ after 400 cycles	56
ZnO	diethyl zinc and H ₂ O	Graphene nanosheets	120 °C	540 mAh g ⁻¹ after 100 cycles	62
	Zn(C ₂ H ₅) ₂ and H ₂ O	Graphene	150 °C	490 mAh g ⁻¹ after 100 cycles	63
	diethyl zinc and H ₂ O	Carbon black	150 °C	769 mAh g ⁻¹ after 500 cycles	61
MoS₂	Mo(CO) ₆ and H ₂ S	Carbon	170 °C	851 mAh g ⁻¹ after 50 cycles	67
MoN	Mo(CO) ₆ and NH ₃	Carbon	170 °C	700 mAh g ⁻¹ after 100 cycles	68
MoO₃	Mo(CO) ₆ and O ₃	Carbon nanotube	165 °C	150 mAh g ⁻¹ after 60 cycles	66

V₂O₅	vanadyl oxytriisopropoxide and H ₂ O	Graphene	150 °C	892 mAh g ⁻¹ after 100 cycles	⁶⁴
RuO₂	Ru(C ₉ H ₁₃) ₂ and O ₂	Carbon nanotube	210 °C-240 °C	~ 600 mAh g ⁻¹ after 100 cycles	⁶⁵
W₂N	W(CO) ₆ and NH ₃	Stainless steel	180-195 °C	25 uAh cm ⁻² after 200 cycles	⁶⁹
WS₂	W(CO) ₆ and H ₂ S	Stainless steel	180-195 °C	13 uAh cm ⁻² after 100 cycles	⁷⁰

Organic electrode materials for metal ion batteries have shown great potential due to their high theoretical capacity, flexible structure design, and environmental friendliness⁷⁵⁻⁷⁷. Generally, the redox reactions of organic electrode materials are based on the charge-state change of the electroactive groups⁷⁸. With this in mind, MLD can be used to fabricate organic electrodes for LIBs. Karppinen's group firstly reported the synthesis of lithium terephthalate (LiTP) by ALD/MLD for anode applications in LIBs⁷⁹. As shown in **Fig.4 (e)**, the LiTP was deposited using the precursors of Li(thd) (thd=2,2,6,6-tetramethyl-3,5-heptanedionate) and terephthalic acid (TPA) at 200 °C with a GPC of 3.0 Å. The ALD- LiTP presented the same layered crystal structure and high electrochemical activity. Moreover, they demonstrated in-situ deposition of the quinone cathode in its lithiated state by ALD/MLD, using LiHMDS and hydroquinone as the precursors, as shown in **Fig.4 (f)**⁸⁰. Furthermore, organic all-solid-state cells were successfully developed and fully functional without any conductive additives. However, the MLD-fabricated anode material is still in its infancy and the electrochemical performances of the MLD anode need to be further enhanced.

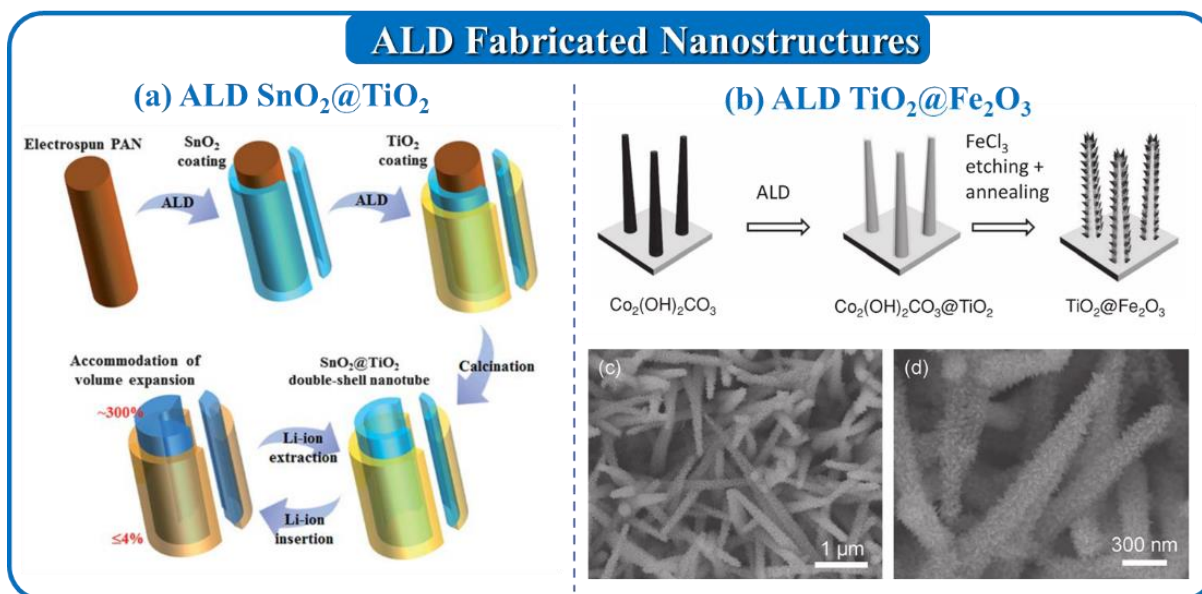


Fig.5 Nanostructured anodes fabricated by ALD: (a) $\text{SnO}_2@\text{TiO}_2$; (b) $\text{TiO}_2@\text{Fe}_2\text{O}_3$.

Nanostructured anode materials demonstrate various structure-dependent advantages, such as high surface area to mass/volume ratios and robust hierarchical structure^{81, 82}. In the past years, nanomaterials with different dimensions and structures have been synthesized via different methods^{83, 84}. Among them, ALD is also a powerful tool to design nanostructured materials^{85, 86}, especially with sacrificial templates⁸⁷⁻⁹³. For example, Jeun et al. fabricated $\text{SnO}_2@\text{TiO}_2$ double-shell nanotubes through a combination of electrospinning and ALD methods. As shown in the schematic diagram of **Fig.5 (a)**, the electrospun polyacrylonitrile (PAN) is chosen as a sacrificial template and two layers of SnO_2 (inner shell) and TiO_2 (outer shell) were deposited and precisely controlled by ALD⁸⁷. As a result, the TiO_2 outer shell can encapsulate the inner SnO_2 nanotube, leading to a hollow structure that can effectively relieve the volume expansion of SnO_2 during cycling and improved electrochemical performance. Their group further developed $\text{TiO}_2@\text{SnO}_2@\text{TiO}_2$ triple-shell nanotubes by a similar procedure⁹³. The diameter of the triple-shell nanotubes is around 200 nm with a shell thickness of 10 nm. Fan's group also developed a series of anode materials by ALD with rationally designed nanostructures^{56, 88, 90}. Generally, the sacrificial template materials are firstly synthesized through hydrothermal methods. Then, popular metal oxides (such as TiO_2 , ZnO , et al.) are deposited on the template materials by ALD. Finally, the templates can be removed by an ion-exchange method or acid etching method to achieve a

hollow nanostructure. For example, **Fig.5 (b)** shows a schematic diagram of the synthesis process and morphology of the $\text{TiO}_2@\text{Fe}_2\text{O}_3$ nanostructured anode materials.

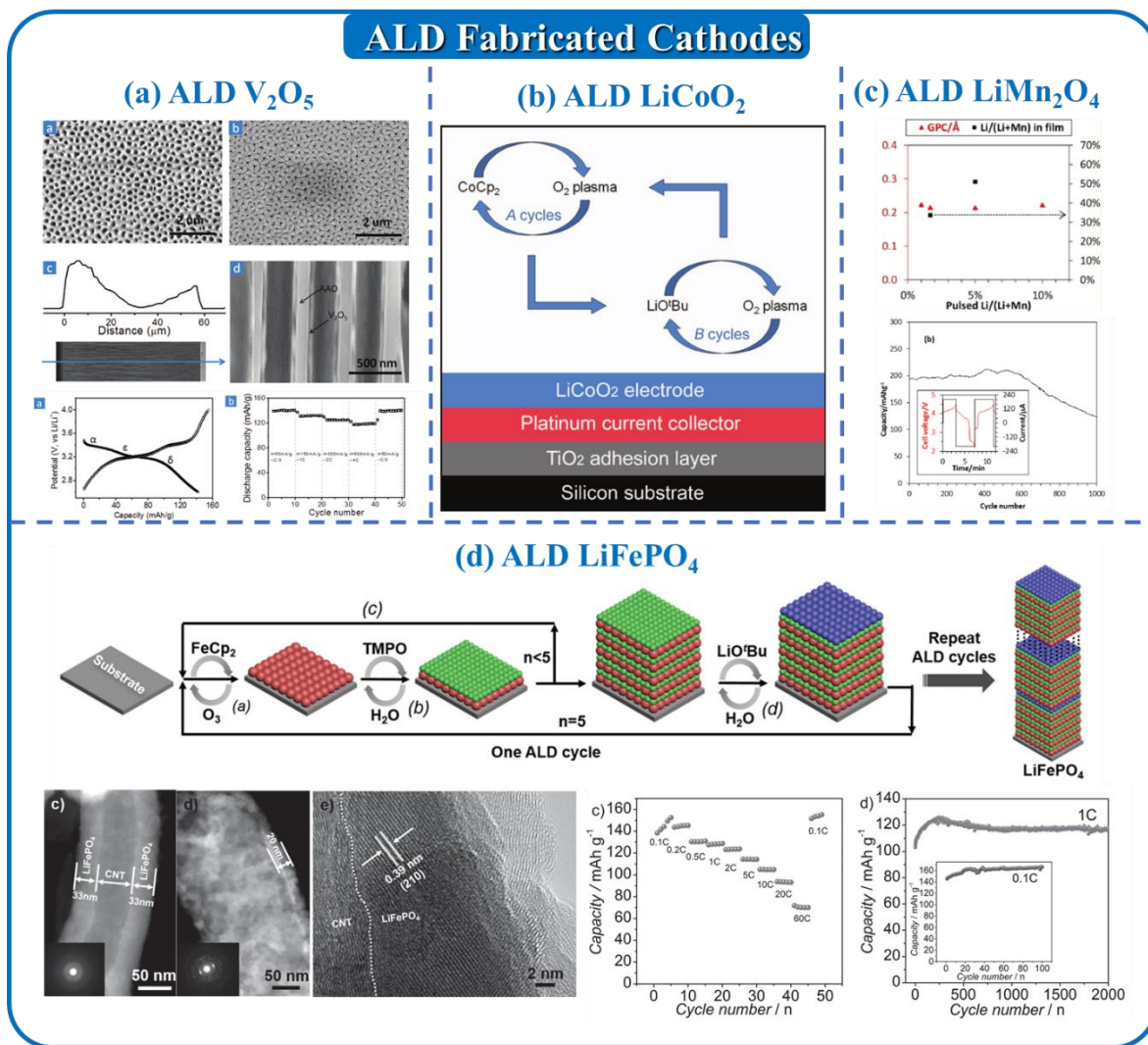


Fig.6 ALD-fabricated cathodes: (a) V_2O_5 ; (b) LiCoO_2 ; (c) LiMn_2O_4 (d) LiFePO_4 .

The cathode material is typically considered as the limiting factor in determining the energy density of LIBs. The popular cathode materials include LiCoO_2 , LiFePO_4 , LiMn_2O_4 , $\text{LiCo}_x\text{Ni}_y\text{Mn}_z\text{O}_2$ (NMC), $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) et al. However, the fabrication of complex oxides with more than three elements by ALD is relatively challenging compared to the binary oxides. The early work using ALD to synthesize cathode materials started from binary oxides of V_2O_5 . V_2O_5 presents a high reversible capacity of 147 mAh g^{-1} (at 2.6-4.0 V) and 294 mAh g^{-1} (at

2.0–4.0 V) as well as fast lithiation and enhanced safety.^{94–96}. In the last section, we have introduced examples using ALD V_2O_5 as anode materials within the potential range of 0–2 V. However, ALD V_2O_5 is more often used as a cathode material for LIBs^{97,98}. Rubloff's group firstly reported ALD V_2O_5 as a cathode material for LIBs⁹⁹, as shown in **Fig.6 (a)**. In their study, $VO(OC_3H_7)_3$ and O_3 are used as precursors within a deposition temperature range of 150 to 210 °C. The 30 nm thick ALD V_2O_5 film was deposited on Au-coated stainless-steel disks and used as the cathode in coin cell configurations. The electrochemical results indicated that the initial specific discharge capacity of ALD V_2O_5 is 142 mAh g⁻¹ at 2.6–4.0 V with outstanding rate and cycling performances. Furthermore, their group compared the ALD V_2O_5 recipes using O_3 and H_2O as oxidant precursors¹⁰⁰. As a result, polycrystalline V_2O_5 films were obtained by the O_3 -based process and amorphous V_2O_5 films were synthesized from the H_2O -based process. From the electrochemical performances, the polycrystalline V_2O_5 films delivered a higher storage capacity than the amorphous films because of their ability to incorporate up to three Li per V_2O_5 formula unit. In another study, Mattelaer et al. synthesized VO_2 using tetrakis[ethylmethylamino] vanadium and H_2O or O_3 as precursors¹⁰¹. This work provided a series of stable vanadium oxide phases in the VO_2 – V_2O_5 series fabricated under different oxygen partial pressures between ambient air and 3.7 Pa. It is found that the different vanadium oxide phases demonstrate different volumetric capacities in the order of $V_2O_5 < VO_2 (B) < V_6O_{13} < V_3O_7 < V_4O_9$ in the 1.5–4.5 V vs. Li^+/Li potential range.

$LiCoO_2$ is the most popular commercialized cathode material for LIBs. However, the development of complex oxides by ALD with three elements is complicated. Generally, the procedure is separated into two sub-cycles of Li compounds and Co compounds and the ratio between these two sub-cycles is controlled to achieve the desired composition. Donders et al. firstly reported the ALD $LiCoO_2$ process using $CoCp_2$ as the cobalt precursor, $LiOtBu$ as the lithium precursor and O_2 plasma as an oxidant source with a deposition temperature of 325 °C¹⁰². The schematic diagram is shown in **Fig.6 (b)** and the super-cycles of $LiCoO_2$ consist of two sub-cycles of Co_3O_4 and Li_2CO_3 . The crystalline $LiCoO_2$ was obtained after annealing at 700 °C for 6 minutes. The ALD-deposited $LiCoO_2$ electrodes were electrochemically active, revealing good electrochemical performance. Similar to $LiCoO_2$, $LiMn_2O_4$ is also an important cathode material for LIBs, especially for high-rate performances. The first report of ALD $LiMn_2O_4$ was from Miikkulainen et al. with a combination of binary ALD processes for ALD $Li_2O/LiOH$ and MnO_2

or MnO^{103} , as shown in **Fig.6(c)**. In their study, the Tris(dipivaloylmethanato)manganese ($\text{Mn}(\text{thd})_3$), $\text{Li}(\text{thd})$, and O_3 were used as precursors at the deposition temperature of 240°C . However, it is very challenging to obtain pure LiMn_2O_4 through the supercycles. Moreover, they further developed a conversion process for using $\text{Li}(\text{thd})/\text{O}_3$ and $\text{LiO}^t\text{Bu}/\text{H}_2\text{O}$ treatment to convert ALD- MnO_2 into $\text{Li}_x\text{Mn}_2\text{O}_4$, in which the obtained $\text{Li}_x\text{Mn}_2\text{O}_4$ films presented high electrochemical capacity and good cycling stability (Fig. 5(c)). There are other examples of the direct application of ALD MnO_2 as cathode¹⁰⁴ or converting the MnO/MnO_2 into LiMn_2O_4 through (electro)chemical methods^{105, 106}.

LiFePO_4 is one of the most popular cathode materials for commercialized LIBs because of the excellent cycling stability, environmentally friendly, and promising safety. Some important breakthroughs in recent years have allowed its successful commercialization¹⁰⁷⁻¹⁰⁹. The research of ALD LiFePO_4 started from FePO_4 as the base. Gandrud et al. firstly synthesized FePO_4 by ALD, combining two sub-cycles of FeO_x and PO_x ¹¹⁰. The precursors used in this recipe are trimethyl phosphate (Me_3PO_4) and $\text{H}_2\text{O}/\text{O}_3$ as oxygen sources for PO_x , while $\text{Fe}(\text{thd})_3$ (Hthd = 2,2,6,6-tetramethyl-3,5-heptanedionate) and O_3 are used for FeO_x . The as-deposited films are amorphous and a post annealing treatment at 600°C was required to obtain the crystalline trigonal FePO_4 . However, the amorphous FePO_4 was found to be electrochemically active and provide exceptional cyclability with a capacity of 178 mAh g^{-1} . Sun et al. also reported ALD-deposited FePO_4 on carbon nanotubes and other 3D carbon nanostructures for cathode applications in LIBs^{111, 112}. PE-ALD deposited FePO_4 was reported by Detavernier's group using Me_3PO_4 plasma, O_2 plasma, and tert-butylferrocene as precursors with an exceptionally high GPC of 1.1 nm/cycle ¹¹³. The as-deposited films were amorphous with a composition of $\text{FeP}_{1.5}\text{O}_{4.7}$ and further formed a trigonal FePO_4 after annealing to 700°C in air. Furthermore, Sun et al. developed ALD LiFePO_4 by a combination of Fe_2O_3 , PO_x , and Li_2O subcycles, which is the first report using ALD to fabricate complex compounds with four elements. **Fig.6 (d)** shows the schematic diagram of the ALD LiFePO_4 process, in which the ratio of the different subcycles is the key to obtaining the proper stoichiometry. Similarly, post-treatment is necessary to obtain the crystalline LiFePO_4 . The annealed $\text{LiFePO}_4/\text{CNTs}$ exhibited exceptional battery performance with excellent rate capability, high power density, and long lifetime. Other types of phosphates, such as vanadium phosphate and titanium phosphate, have been further developed by Detavernier's group via plasma enhanced-ALD (PEALD) and used as cathode materials for LIBs^{71, 114}.

In this section, the recent development of ALD-fabricated electrode materials, including both cathodes and anodes, has been summarized in detail. **1)** Metal oxides, including SnO_2 , ZnO , TiO_2 , et al., have been deposited by ALD and used as anode materials for LIBs. The morphology, structures, and thickness of the metal oxides are precisely controlled by ALD parameters. Some other compounds, including metal nitrides, metal phosphates, and metal sulfides, have also been fabricated by ALD and used as anode materials for LIBs. **2)** Organic electrode materials have been developed and deposited by MLD as anode materials for LIBs, however, the electrochemical performances of the MLD-derived organic electrodes still need to be further improved. **3)** Nanostructured materials, such as hollow structures and core-shell structures, were designed and realized by ALD with sacrificial templates. **4)** Several types of cathode materials, such as V_2O_5 , LiCoO_2 , LiMn_2O_4 , and LiFePO_4 , were synthesized by ALD. Although promising progress has been obtained and various electrode materials have been synthesized by ALD, it should be noted that there are still several drawbacks of ALD/MLD for electrode fabrication. The slow GPC of the ALD/MLD films is a major concern, which is in the $\text{\AA}$ /cycle range for most deposition processes. In the reported literature, hundreds or even thousands of ALD cycles are required to obtain electrodes with reasonable active material mass loading. However, the time-consuming process is less commercially viable for standard battery technologies, particularly when compared with composite/powder-based electrodes.

2.1.1.2 ALD/MLD for cathode/electrolyte interface engineering

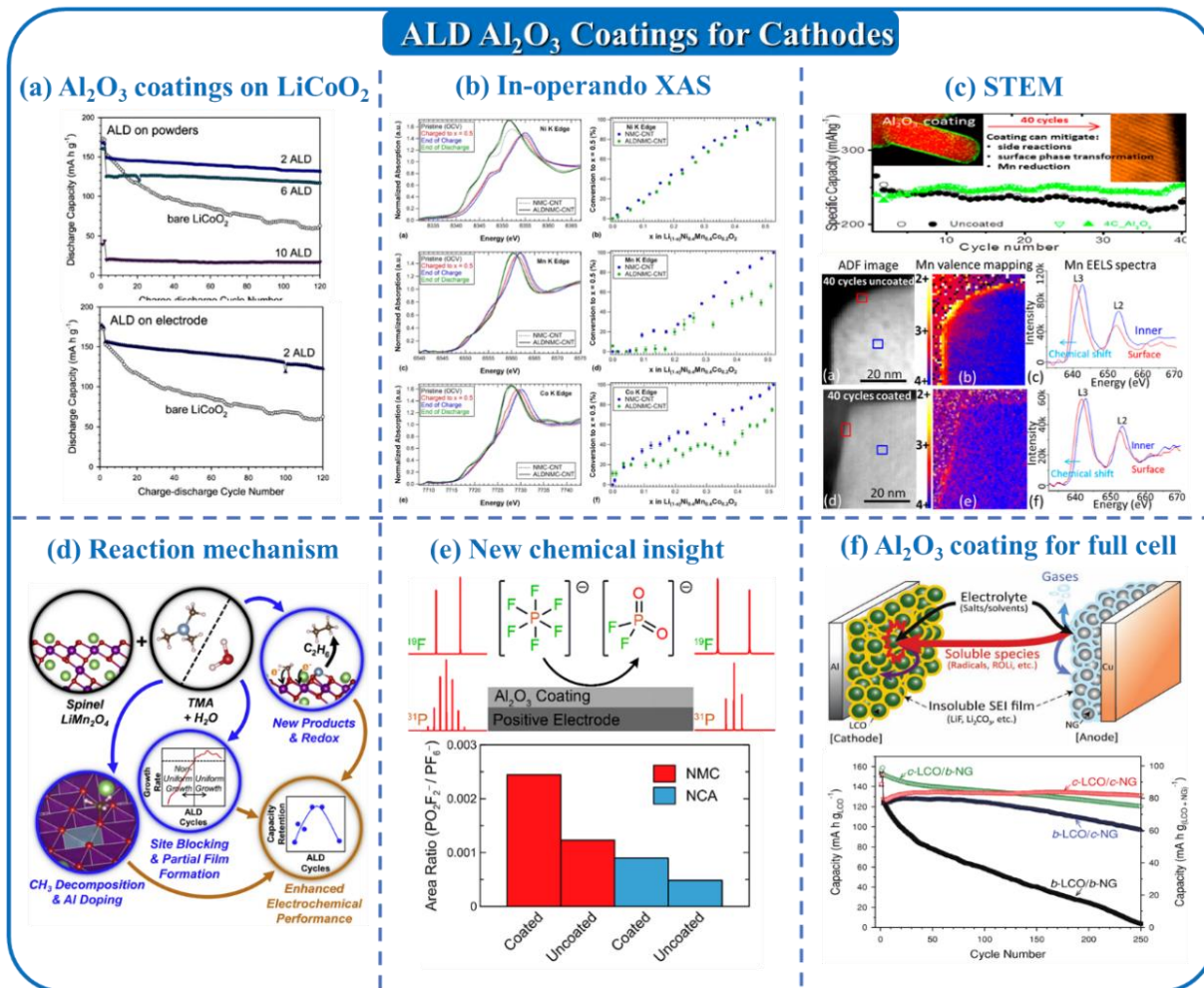


Fig.7 Characterization and application of ALD Al_2O_3 coatings for cathode materials: (a) comparison between ALD coating directly on powder and electrodes; (b) in-operando XAS for ALD coated cathode; (c) STEM for interface characterization; (d) reaction mechanism during ALD process for cathode application; (e) effects of ALD coating on chemical reactions; (f) Al_2O_3 coating for full cells.

Cathode materials are considered as the limiting factor for the energy density and capacity of LIBs. As discussed above, layered LiCoO_2 , spinel LiMn_2O_4 , and polyanion LiFePO_4 are the primary groups of cathode materials^{115, 116}. The layered LiCoO_2 is the first developed and most widely used cathode material for commercial LIBs. However, the high cost, toxicity, limited capacity and chemical instability in the deep charged state have prevented its further applications for transportation and stationary storage. Compared to LiCoO_2 , spinel LiMn_2O_4 shows the

advantages of material availability and environmental compatibility. However, the Mn dissolution of LiMn_2O_4 during electrochemical cycling leads to capacity fading especially when operating at temperatures above ambient. LiFePO_4 is another promising cathode material with low cost, low toxicity, high safety, and excellent cycling performance. The challenges for LiFePO_4 include poor rate performances and surface chemistry stability. More recently, $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ (NMC) and $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) have become popular because of their high operational voltage and specific capacities. For example, the NCA cathode possesses a high theoretical capacity of 265 mAh g^{-1} (0.95 Li^+ involving (re)-insertion), which is higher than other “4 V” cathode candidates. However, the Li transition metal oxide cathode still has serious challenges, such as phase transition, mechanical cracking, electrolyte decomposition, transition metal dissolution, conductivity, and air instability.¹¹⁷ Among these issues, the interface between cathode materials and electrolyte, which is referred to as the cathode electrolyte interphase (CEI), plays the most important role^{118, 119}. At high oxidation potentials, the electrolytes decompose to form an interface with side products on the cathode materials, which is referred to as the CEI. On one hand, a stable and dense CEI can enhance the stability of the cathode materials by preventing the interfacial reactions, HF etching and transition metal dissolution. On the other hand, unstable CEI may aggravate the interfacial reactions and cause an increase of the interfacial impedance and result in the fast degradation of battery performance¹²⁰. To address the interfacial challenges and achieve a stable CEI, surface modification of cathode materials is the most effective approach, especially to prevent the electrolyte decomposition and transition metal dissolution¹²¹. The basic requirements of the coating layers are 1) controllable thickness. On one hand, a coating that is too thick will affect Li-ion or electron transportation. On the other hand, coatings that are too thin cannot totally prevent side reactions. 2) Uniform, conformable and continuous coating on cathode materials. 3) Good mechanical properties^{122, 123}. To meet these requirements, ALD/MLD is the ideal technique due to its aforementioned attributes. Lee’s group firstly reported the enhanced stability of LiCoO_2 cathodes using surface coating by ALD, in which routine ALD Al_2O_3 was chosen as the coating materials¹²⁴. From their study, only two cycles of ALD Al_2O_3 with a thickness of 3~4 Å can effectively improve the electrochemical performances, exhibiting capacity retention of 89% after 120 charge-discharge cycles, as shown in **Fig.7 (a)**. Furthermore, they compared the performances of ALD coating directly on the electrode versus the powder. As a result, the capacity retention for ALD Al_2O_3 directly on the composite is slightly inferior to the

capacity retention of ALD on powders. Several questions relating to the reaction mechanism during the ALD process on cathode materials have been raised. Elam's group used in-situ and ex-situ experimental characterization coupled with DFT calculations to elucidate the mechanism for ALD Al_2O_3 on LiMn_2O_4 cathodes (**Fig.7 (d)**)¹²⁵. In situ Fourier transform infrared spectroscopy (FTIR), quadrupole mass spectrometry (QMS), and quartz crystal microbalance (QCM) measurements are combined to have a comprehensive study. It is very interesting to note that the ALD Al_2O_3 process on LiMn_2O_4 in the early cycles was different compared to the deposition on conventional substrates. The Al heteroatom bridged several oxygen atoms at the LMO surface initially, even doping into the LiMn_2O_4 surface. The initial few cycles of ALD Al_2O_3 leads to a reduction in the average Mn oxidation state, with a higher ratio of Mn^{3+} , resulting in higher capacities.

In the past years, several studies have reported the use of ALD Al_2O_3 as a surface coating for different types of cathode materials, such as LiCoO_2 , LiMn_2O_4 , $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ ¹²⁶⁻¹⁵⁵. Leung et al. provided insight into the mechanism of ALD coating on the interface of cathode materials by first-principles calculations¹⁵⁶. The results revealed that with the oxide coating, e^- tunnelling to the adsorbed ethylene carbonate (EC) falls within the nonadiabatic regime, resulting in reduced electrolyte decomposition. To better understand the mechanism of ALD Al_2O_3 coating for cathodes, *in-operando* synchrotron-based X-ray diffraction (XRD) and *in-operando* X-ray absorption near edge structure spectroscopy (XANES) were carried out to probe the structure and interfacial chemistry of cathode materials of $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ cathode during electrochemical cycling¹⁵⁷. The operando XRD results indicated that the ALD Al_2O_3 -coated electrodes displayed a higher level of reversibility in the shift of d-spacing following charge to 4.7 V. Moreover, as shown in **Fig.7 (b)**, the operando XANES data revealed that the ALD coating can suppress the transformation of Co and Mn at low capacities, which was attributed to the protection of the Ni by preventing side reactions of the highly reactive oxygen at the Ni sites with the electrolyte and enabling reversible cycling¹⁵⁷. Besides synchrotron-based X-ray techniques, electron microscopy is another powerful tool to study the structure and morphology of the coatings. Wang's group used aberration-corrected scanning transmission electron microscopy (STEM) and high-efficiency spectroscopy to characterize and understand the functions and roles of the ALD Al_2O_3 coating layer for the $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ cathode¹⁵⁸, as shown in **Fig.7 (c)**. The atomic-level imaging and nanoscale chemical composition analysis from STEM and EELS revealed that the ALD Al_2O_3

coating can mitigate the side reactions between cathode and electrolyte, eliminate the surface structure transformation, and suppress the reduction of Mn at the particle surface. Most of the reported studies believe that the ALD Al_2O_3 plays a role as a chemical scavenger of corrosive HF and the physical blockage of electrolyte decomposition. However, Dahn's group proposed a new mechanism recently, combining published thermochemistry data with new density functional theory calculations¹⁵⁹. As shown in **Fig.7 (e)**, ^{19}F and ^{31}P solution nuclear magnetic resonance spectroscopy were applied to understand the surface chemistry. Their results showed that the LiPF_6 -containing liquid electrolyte solution can chemically react with ALD Al_2O_3 cathode coatings to produce LiPO_2F_2 , which is a well-known and effective electrolyte additive. Moreover, it is a universal phenomenon observed in both NMC622 and NCA cathodes with ALD Al_2O_3 coating, in which LiPO_2F_2 is found in electrolyte solutions stored for 14 days.

Generally, ALD Al_2O_3 has been widely recognized and proven as an effective coating for various cathode materials with enhanced electrochemical performances. Potential mechanisms were proposed to explain the functions of the ALD Al_2O_3 layers. The most popular mechanism is that the ALD Al_2O_3 can prevent electrolyte decomposition, HF corrosion, and transition metal dissolution. However, recent literature suggests the potential for other possibilities. In this case, the functions and roles of ALD Al_2O_3 in performance enhancement is still worth further exploration.

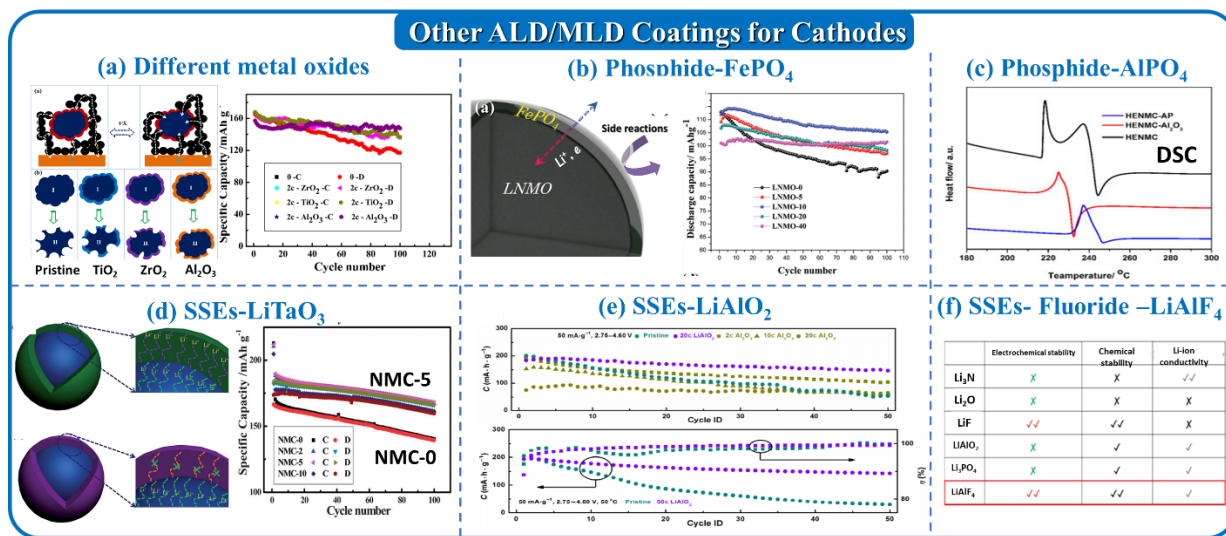


Fig.8 Other ALD/MLD coatings for cathode applications: (a) different metal oxides; (b) FePO₄; (c) AlPO₄; (d) LiTaO₃ solid-state electrolyte; (e) LiAlF₄ solid-state electrolyte; (f) LiAlO₂ solid-state electrolyte.

Besides ALD Al₂O₃, other metal oxides have also been used as coatings for various cathode materials, including ZrO₂, ZnO, TiO₂, CeO₂, Ga₂O₃, MgO and FeO_x¹⁶⁰⁻¹⁸². Most of these metal oxides showed similar functions with ALD Al₂O₃ and the electrochemical performances were enhanced with few cycles of ALD metal oxide. However, the comparison between different metal oxide coating is critical. Wang's group firstly studied ALD ZnO, ZrO₂, and Al₂O₃ as surface modification layers for LiMn₂O₄¹⁸³. All of the ALD-coated LiMn₂O₄ electrodes demonstrated improved cyclability compared to the bare electrode, in which ZnO is the most effective oxide coating. However, this conclusion is a bit different from the earlier work on ALD ZnO and Al₂O₃ for LiCoO₂, in which the Al₂O₃ coated LiCoO₂ delivered better performances than that of ZnO coated LiCoO₂. Sun's group also compared the different metal oxides, including Al₂O₃, TiO₂, and ZrO₂ as coatings for LiCoO₂ cathodes¹⁸⁴, as shown in **Fig.8 (a)**. From their results, the Al₂O₃ coating demonstrated the best cycling stability while the ZrO₂ coating contributes to the best rate capability. The reasons behind the observations can be attributed to multiple factors, including; 1) Al₂O₃ possesses the highest bandgap energy ($E_g=9.00$ eV) and is most effective in suppressing phase transitions during electrochemical cycling; 2) the better electrical conductivity of ZrO₂ leads to higher rate performances. One of the consensuses from this area of research is that ALD Al₂O₃ is the best coating among the different metal oxides in terms of cycling stability. Moreover, the electrical conductivity of metal oxide affects the rate performances of the cathode materials.

Phosphates, including FePO₄ and AlPO₄, is another family of coating material for cathodes, which have also been deposited by ALD¹⁸⁵⁻¹⁸⁷. For example, as shown in **Fig.8 (b)**, FePO₄ was developed by Sun's group as a coating for LiNi_{0.5}Mn_{1.5}O₄¹⁸⁵. When the LiNi_{0.5}Mn_{1.5}O₄ was coated with 40 cycles of ALD FePO₄, the capacity retention increased up to 100%. Compared to the regular metal oxides, ALD FePO₄ can provide both electron/ion diffusion across the surface. Another candidate material, AlPO₄, presented a much higher thermal resistivity than Al₂O₃, leading to the enhanced high-temperature electrochemical performances. The DSC profiles of the charged pristine high energy NMC (HEMNC), Al₂O₃-coated HENMC, and AlPO₄-coated HENMC are shown in **Fig. 8(c)**. The DSC results show that decomposition temperatures of pristine

high energy NMC (HEMNC), Al₂O₃ coated HENMC, and AlPO₄ coated HENMC are 219 °C, 223 °C, and 237 °C, respectively. The thermal stability improvement of AlPO₄ coating can be ascribed to the high thermal stability of phosphate, leading to better electrochemical performances at high temperatures.

The metal oxide coatings are still limited by their ionic conductivity and Li-ion transport across the interface of the electrode particles. In this case, the development of surface coatings with Li-ion conductivity is necessary and solid-state electrolyte thin films are the ideal candidates. As shown in **Fig.8 (d)**, Sun et al. firstly reported the ALD solid-state electrolyte (SSE) LiTaO₃ as a coating for NMC cathode¹⁸⁸. A 5 nm LiTaO₃ coating proved to be beneficial towards preventing transition metal dissolution into the electrolyte and aided in maintaining the microstructure of NMC. As a result, the electrochemical performance of NMC was significantly improved with as low as 5 cycles of LiTaO₃ coating. Meanwhile, another Li-ion conductive film, LiAlO₂, was also used as a surface modification for LiCoO₂ and NCA¹⁸⁹⁻¹⁹¹. For example, Cui's group developed a chemically inert and ionically conductive LiAlO₂ interfacial layer on LiCoO₂ by ALD. It was found that the LiAlO₂-coated LiCoO₂ cathode was able to deliver a much higher specific capacity than that of the Al₂O₃ coating, which can be attributed to the ionic conductivity of LiAlO₂. Moreover, the stability of LiAlO₂-coated LiCoO₂ cathode in an extended electrochemical window of 2.75–4.60 V showed significant improvement compared to bare LiCoO₂ cathode, as shown in **Fig. 8 (e)**. From these studies, it has been proven that Li-ion conductive films fabricated by ALD is more promising as a coating for cathode materials compared to metal oxide coatings. However, the currently developed ALD SSE films still present low ionic conductivity ($10^{-6}\sim 10^{-9}$ S cm⁻¹), which cannot meet the requirements for fast Li-ion transport across the interface. Moreover, the relationship between the ionic conductivity of the coating and the electrochemical performances is still unclear.

Based on computational simulations, fluoride materials have the widest electrochemical windows and are especially favoured for their high potential stability (up to 5 V)^{192, 193}. Fluoride chemistry has been widely studied in the ALD community, for either deposition or etching. Several types of fluorides, including MgF₂, AlF₃, and AlW_xF_y were deposited as a coating for high-voltage cathode materials, including LiNi_{0.5}Mn_{1.5}O₄ and LiCoO₂¹⁹⁴⁻¹⁹⁹. AlF₃ is the most popular fluoride ALD coating, which uses TMA as the Al precursor and another F contain compounds (HF, TaF₅ or hexafluoroacetylaceton) as the F precursor. As a result, the cathode materials coated with ALD

fluoride materials delivered remarkable performances at high voltage. However, the poor ionic conductivity of metal fluorides such as AlF_3 has limited their further improvement. In this case, Cui's group designed an ALD LiAlF_4 process to be applied for high Ni content NMC811²⁰⁰. Compared to other potential coatings such as Li_3N , Li_2O , LiF , LiAlO_2 , and Li_3PO_4 , LiAlF_4 demonstrates a wider electrochemical window and ideal chemical stability (**Fig.8 (f)**). The ionic conductivity of ALD LiAlF_4 is around $3.5 \pm 0.5 \times 10^{-8} \text{ S cm}^{-1}$, which is much higher than that of the metal fluoride of LiF and AlF_3 . The ALD interfacial layer is chemically and electrochemically stable as well as Li-ion conductive, resulting in the improved cycling stability and rate performances of NMC-811 cathode.

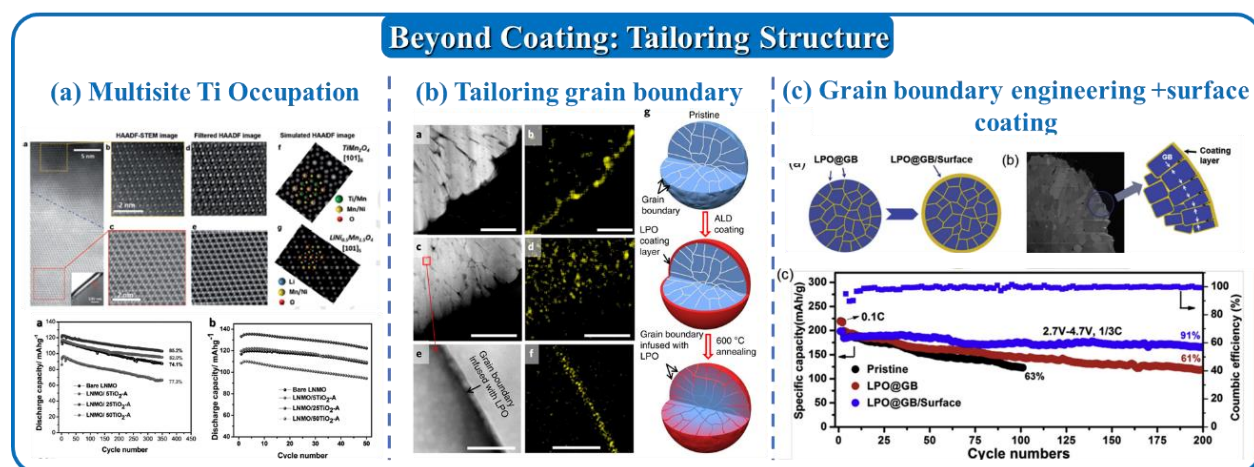


Fig.9 Function of ALD films more than coating. (a) Multisite Ti Occupation by ALD TiO_2 ; (b) Tailoring grain boundaries with ALD Li_3PO_4 ; (c) Dual functions of grain boundary engineering and surface coating.

Most ALD coatings are generally amorphous and used as deposited. The continuous ALD films will shrink and form island-like structures after high-temperature annealing²⁰¹. However, recent studies have discovered that post-treatment of ALD coatings can modify the structures of the cathode material itself. As shown in **Fig.9 (a)**, a two-step surface modification method was developed by Sun's group to deposit ALD TiO_2 on spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode material with a subsequent post-annealing treatment²⁰². A TiMn_2O_4 -like spinel phase was formed resulting from the reaction of TiO_2 with the surface $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The TiMn_2O_4 -like spinel phase can combat the impedance growth from continuous irreversible structural transition and alleviates the

electrolyte decomposition during electrochemical cycling. The electrochemical results revealed that 25 ALD TiO₂ cycles appeared to produce the optimal thickness that yields improved stability, Coulombic efficiency, discharge capacity, and rate capability.

Rather than the degradation of the cathode surface, the permeation and penetration of liquid electrolytes along the grain boundaries and cracks in the secondary particles is another serious issue that worsens the decay of electrochemical performances. Especially for the Ni-rich NMC (LiNi_xMn_yCo_{1-x-y}O₂) cathode, when the Ni content is above 0.8, there is a phase transition near the charge-end causing an abrupt anisotropic shrinkage (or expansion during discharge), which is similar to LiNiO₂. This phase transition has residual stress that causes internal microcracks and allows the cracks to propagate to the surface of the cathode particles, leading to the electrolyte penetration and degradation of the exposed ²⁰³. To address this challenge, the ALD solid-state electrolyte Li₃PO₄ was infused into the grain boundaries of a Ni-rich NMC cathode material²⁰⁴, as shown in **Fig.9 (b)**. 10 nm of Li₃PO₄ was firstly deposited on the surface of Ni-rich NMC by ALD. After annealing at 600 °C for two hours in the air, the Li₃PO₄ was successfully infused along the grain boundaries of the secondary particles. The infused solid-state electrolyte within the grain boundaries played several roles in improving the electrochemical performances, including; 1) providing fast channels for Li-ion transport; 2) preventing the penetration of the liquid electrolyte into the boundaries; 3) eliminating intergranular cracking and layered-to-spinel phase transformation. The capacity retention and voltage stability of the cathode were significantly improved with this grain boundaries modification. However, after thermal infusion, the ALD Li₃PO₄ almost completely disappeared from the surface of the NMC particles, resulting in exposure of the particle surface to the electrolyte. With this in mind, based on the Li₃PO₄ infused NMC cathode, another layer of ALD Li₃PO₄ was further deposited on the exterior surface²⁰⁵. With the dual functional grain boundary engineering and surface coating, superior cycling stability was achieved even with high voltage cut-offs (91% retention after 200 cycles at 2.7-4.7 V), as shown in **Fig. 9 (c)**.

Until recently, MLD coatings have rarely been reported as coatings for cathode materials. The major concern is the high voltage stability of the organic components in the MLD films. However, it is still interesting to explore the application of MLD coatings for cathode materials due to the unique properties of MLD, such as high flexibility. To extend the applicability of MLD-type coatings, new polymers with good electronic or ionic conductivity and high voltage stability

should be developed for cathode applications. Moreover, the films derived from MLD are another possibility for cathodes. For example, a uniform carbon- Al_2O_3 composite coating was deposited on NMC-622 by the pyrolysis of MLD alucone under argon²⁰⁶. The C- Al_2O_3 coated NCM-622 exhibited enhanced electrochemical performances with higher reversible capacity, better rate capability, and stability. In the MLD-derived composite coating, the Al_2O_3 plays the role in suppressing the undesirable side reactions and stabilizing the layered structure, and the conductive carbon in the composite enhances the transport of electrons.

In this section, we have summarized the application of ALD/MLD films in addressing the interfacial issues for different cathode materials. 1) ALD Al_2O_3 is the most popular coating for cathode materials and has been widely studied over the past ten years. The electrochemical performances are effectively enhanced with ultrathin Al_2O_3 coatings. Furthermore, the mechanism and interface evolution have been deeply understood using advanced characterization techniques. In addition, other metal oxides have also been deposited on cathode materials, and among them, ALD Al_2O_3 is generally considered as the best coating in terms of electrochemical performances. 2) solid-state electrolytes have been deposited by ALD as coatings for cathode materials, such as Li_3PO_4 and LiAlO_2 . Compared to the metal oxides, even with thicker layers, solid-state electrolyte coatings enable better Li-ion conduction across the interface and enhanced performances. 3) Other ALD materials, including phosphates and fluorides are developed to modify the interface. On one hand, the metal phosphates present higher thermal resistivity, which is beneficial for high-temperature applications. On the other hand, the metal fluoride demonstrates a wide electrochemical window for high voltage cathode materials. 4) Beyond surface modification, ALD films are further designed to tailor the structure of the cathode, such as preventing phase transition and grain boundaries engineering.

The general requirements of the coatings for cathode materials are discussed above, including controllable thickness, uniformity and conformity. These requirements can be achieved with ALD/MLD techniques, however, there are extra requirements for the application of ALD materials as coating layers. 1) A wide electrochemical window. The ALD coatings for cathodes are required to be electrochemically stable at high potential, preventing the decomposition of the liquid electrolyte. 2) Chemically stable with cathode and electrolyte. The ALD coatings on the cathode are required to be stable when deposited on the cathode and in contact with liquid

electrolytes. 3) High Li-ion conductivity. The fast Li-ion transport across the interface leads to low resistance and better rate performances. A thicker coating also can be realized with high Li-ion conductivity. 4) Good mechanical properties. The mechanical properties are also critical for maintaining the structure and volume expansion of the materials, which should be considered for the coating design²⁰⁷.

2.1.1.3 ALD/MLD for anode/electrolyte interface engineering

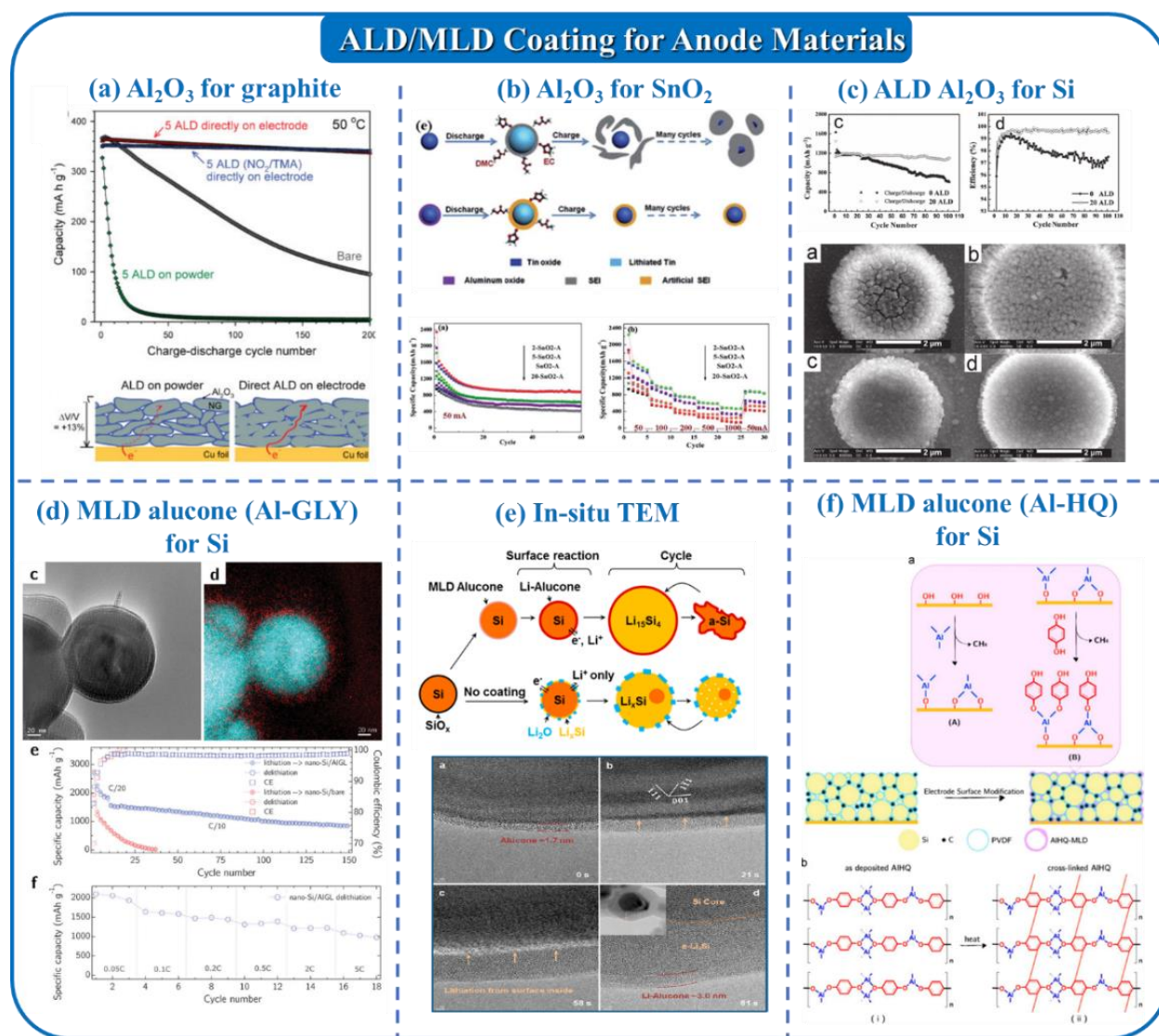


Fig.10 ALD/MLD coatings for anodes: (a) ALD Al_2O_3 for graphite; (b) ALD Al_2O_3 for SnO_2 ; (c) ALD Al_2O_3 for Si; (d) MLD alucone for Si.

The SEI layer on the anode materials is formed due to the decomposition of the electrolyte at the low electrochemical potential. The SEI continuously grows in these electron/electrolyte-participated reactions and the thickness direction of SEI layer is not homogeneous with dual-layer structure and various components. The generally recognized description of the SEI structure is the mosaic model, in which the layer closed to the anode surface contains species of low oxidation states of Li_2O , Li_3N , LiF , LiOH , and Li_2CO_3 . The outer layer near the surface consists of high oxidation states species such as ROCO_2Li , ROLi , and RCOO_2Li , which is related to the solvent decomposition process. It is widely regarded that the properties of SEI layer are the key factor determining the electrochemical performances of the anode materials. Graphite is a commercialized anode material that is widely used for its low electrochemical potential, minimal volume change, and low cost. The solid electrolyte interphase (SEI) layer related to the side reactions between anode materials with electrolyte is one of the key factors determining the overall electrochemical performance of the battery. Lee's group was the first to report ALD Al_2O_3 as a coating for graphite²⁰⁸, as shown in **Fig.10 (a)**. The graphite with ALD Al_2O_3 coating on both powder and electrodes were compared at an elevated temperature of 50 °C for charge-discharge cycling. The decomposition of the SEI at elevated temperature is exothermic and considered to initiate thermal runaway. The electrochemical data indicated that the Al_2O_3 coating on graphite electrodes presented much better cycling performances than that of Al_2O_3 coating directly on the powders. The mechanism is explained in the schematic diagram in **Fig.10 (a)**. When depositing Al_2O_3 on the powders, the graphite and current collector was isolated by the insulating Al_2O_3 film and the electrical conductivity was disrupted. Moreover, ALD Al_2O_3 coated directly on the electrode enables electrical pathways between interconnected particles, which is necessary for electronic conductivity. Another interesting work demonstrated the application of ALD Al_2O_3 coatings on both LiCoO_2 and graphite for full cells²⁰⁹, as shown in **Fig.7 (f)**. It was observed that the full cell with coating on both cathode and anode delivered better electrochemical performances compared to that of the bare electrodes and coating on an individual electrode. ALD and MLD coatings on other carbon anode materials, such as carbon nanotubes and carbon fibres, have also been reported to improve electrochemical performances²¹⁰⁻²¹².

Sn-based materials, including tin oxides, tin sulfides, and stannates, are also attractive anode materials for LIBs with high theoretical capacity and improved safety²¹³⁻²¹⁵. However, the large volume fluctuation of Sn-based materials is the biggest challenge limiting their further

application²¹⁶. The volume change during electrochemical cycling causes the continuous consumption of electrolyte and accumulation of a thick SEI layer, leading to the performance degradation of Sn-based materials. To address the issues, Sun's group demonstrated ALD Al₂O₃ coating on SnO₂ based anodes²¹⁷ (**Fig.10 (b)**). It was found that the particle sizes of the SnO₂ electrodes affected the volume change of the electrodes, resulting in the need for Al₂O₃ coating layers with optimized thickness. The well-defined ALD Al₂O₃ layer can 1) relieve the volume expansion and mechanical failure; 2) as the artificial interface to block the undesirable reactions and decompositions of the electrolyte, resulting in significantly enhanced cycling stability. Furthermore, other ALD films, such as HfO₂ and TiO₂ have also been deposited as protective coatings for Sn-based anodes, including Sn, SnO₂, and SnS₂²¹⁸⁻²²². Nevertheless, it has proven difficult for thin ALD coatings to accommodate the large volume fluctuation of Sn-based anodes. Fan's group designed a hollow wire-in-tube structure of SnO₂@TiO₂ on a carbon cloth with a high mass loading by ALD²²³. This hollow SnO₂@TiO₂ structure presented radically improved rate capability and cycling stability compared to both bare SnO₂ nanowires and solid electrodes. This study extends the application of ALD for anodes beyond surface coating to nanostructure engineering. Other kinds of anode materials, including Li₄Ti₅O₁₂, MoO₃, MnO_x, NiCo₂O₄, Fe₂O₃, and Fe₃O₄ et al, have also been studied as ALD coatings designed to improve the electrochemical properties of anode materials²²⁴⁻²³⁸.

Si is an excellent alternative for graphite due to its high theoretical capacity of 4200 mAh g⁻¹, low discharge potential (~ 0.2 to 0.3 V vs. Li/Li⁺), natural abundance, low cost and environmental friendliness²³⁹⁻²⁴³. Si and its composites have attracted enormous attention in recent years for industrial application. However, the alloying process of Si anodes leads to a large ~400% volume expansion during cycling, low ionic conductivity, and unstable SEI²⁴⁴. Similar to other anode materials, the SEI is a critical factor for Si-based electrodes, and ALD/MLD displays the great potential to stabilize the interface. Huang's group firstly reported ALD Al₂O₃ on patterned amorphous Si anodes for LIBs²⁴⁵. As shown in **Fig.10 (c)**, alumina-coated Si electrodes coated with 20 ALD cycles presented excellent cycling performance with an initial charge capacity of 1125 mAh g⁻¹ and a retained capacity of 1100 mAh g⁻¹ after 100 cycles. From the SEM images after cycling, cracks are observed on the bare Si columns. Remarkably, with the conformal ALD Al₂O₃ coating, the small cracks and pinholes of Si were reduced, resulting in high Coulombic efficiency and good cycling performance. The reduced cracking with ALD Al₂O₃-coated Si was

also investigated by in-situ atomic force microscopy (AFM) in detail²⁴⁶. It has been proven through first-principles investigations that the intrinsic ionic conductivity of ALD Al_2O_3 is very low, but the Li diffusion energy barrier becomes lower as lithiation proceeds and LiAlO_2 is formed²⁴⁷. To further improve the electrochemical performance, Hwang's group proposed multiple approaches combining the ALD technique with a vinylene carbonate (VC) electrolyte additive²⁴⁸. With the combination of these strategies, the stability of the Si anode was significantly improved due to the formation of a more stable SEI. Moreover, other ALD coatings, such as TiN, TiO_2 , and ZnO, were used for Si anodes and led to improved performances²⁴⁹⁻²⁵⁴. Mitlin's group provided a detailed comparison between Al_2O_3 , TiN, and TiO_2 coatings on the inner, the outer, or both surfaces of hollow Si nanotubes²⁵⁵. The optimum performance was achieved for Si nanotubes with ALD TiO_2 on both sides, enabling a capacity retention of 1700 mAh g^{-1} after 200 cycles at 0.2 C, which is significantly improved compared to the bare Si nanotubes. The TiO_2 layer, which consists of amorphous TiO_2 and cubic LiTiO_2 , displayed both high ionic and electronic conductivity leading to fast lithiation kinetics. However, ALD films with only high electronic (TiN) or only ionic (Al_2O_3) conductivity are not nearly as effective²⁵⁵.

In contrast to ALD materials, MLD layers have become more attractive as coatings for Si anodes. The MLD films, including organic-inorganic hybrid layers and polymer layers, are considered to be more mechanically robust and highly flexible, which is beneficial for relieving the large volume change of the Si anode during lithiation and delithiation²⁵⁶. Ban's group firstly applied MLD alucone for Si nanoparticles, using TMA and glycerol ($\text{C}_3\text{H}_5(\text{OH})_3$) forming the Al-GL hybrid films (**Fig. 10 (d)**)²⁵⁷. The Al-GL coating on Si anode provided significant improvement in cycling stability, rate, and CE. It was concluded that the Al-GL layers maintained a mechanically robust, resilient, and highly conductive network for the Si electrodes, and are stable against liquid electrolyte, allowing for long and stable cycle life. To understand the influence of MLD alucone coatings on the performances of Si nanoparticles, in-situ TEM analysis was carried out on both uncoated and alucone-coated Si nanoparticles, as shown in **Fig. 10(e)**^{258, 259}. The MLD alucone coating on Si nanoparticles can reduce the formation of Li_2O , resulting in fast and highly reversible lithiation kinetics. It was also clarified that the alucone coating possesses good mechanical flexibility and fast Li^+ conductivity²⁵⁸. Furthermore, the DFT calculations by Ma et al. revealed that the alucone film is electronically and ionically conductive after saturation with Li atoms, which is in agreement with the observed morphology and electrochemical analysis²⁶⁰. Rather than

alucone with glycerol linkers, another type of MLD alucone (Al-dioxybenzene, Al-HQ) was developed using TMA and hydroquinone as precursors (**Fig. 10(f)**)²⁶¹. During the MLD deposition and subsequent treatment, a longitudinal crosslinking reaction occurred between the aluminum-dioxybenzene chains. The 3D cross-linked network led to improved conductivity and mechanical properties. The high flexibility of the Al-HQ coating enabled the accommodation of volume expansion and maintenance of the mechanical integrity of the Si electrodes, resulting in excellent cycling performance and high rate capability with a reversible capacity of over 1500 mAh g⁻¹ after 200 cycles. More recently, Ban's group further developed a nanoscale polyamide coating by MLD on Si anode with excellent electrochemical performances²⁶².

In this section, we discuss the typical examples of ALD/MLD coatings for anode materials in LIBs, such as graphite, Sn-based materials, and Si anodes. The roles of ALD/MLD coatings are summarized as 1) forming a stable artificial SEI to prevent the side reactions between anodes and liquid electrolytes. 2) relieving the volume change of alloy-based anodes (Sn and Si). ALD Al₂O₃ is the most popular and widely developed coating for different anodes. However, due to the volume change of most anode materials, coatings with better mechanical properties are highly desired. In this case, MLD coatings with high flexibility are more promising as protective layers for anode materials, especially for Si anodes.

There is still significant room for exploring the engineering of electrode interfaces by ALD/MLD. Firstly, better mechanical properties, including flexibility and stiffness, are among the major requirements for accommodating the large volume changes. Secondly, both ionic and electronic conductivity are required to provide pathways for Li-ion and electrons across the surface of the electrodes. Thirdly, the chemical and electrochemical stabilities towards liquid electrolytes are the most basic requirements for a high-performance ALD/MLD coating.

2.1.1.3 ALD/MLD for 2D/3D micro-batteries

Additionally, as unique thin film deposition techniques, ALD/MLD are considered as promising approaches for the fabrication of thin-film batteries and 3D micro-batteries^{35, 263}. It is possible to deposit uniform electrodes and electrolytes on 2D flexible substrates (such as polymers) and more complex 3D substrates with these techniques.

A thin film solid-state battery (SSB) was demonstrated by Stewart et al., in which the tin oxynitride was deposited by ALD using tetrakisdimethylamido(tin), H₂O, and N₂ plasma as precursors.²⁶⁴ LiPON was deposited by ALD as SSEs and Li was deposited by e-beam evaporation. In the thin film SSBs, the SnNy anodes demonstrated more stable performances than the SnO₂ or SnOxNy films, which retained 75% of their capacity over 200 cycles compared to only 50% for SnO₂. Another example of thin film SSBs was reported by the same group, in which LiPON was deposited by ALD as a SSE and LiCoO₂ and Si were deposited as the cathode and anode, respectively.

Besides the 2D configuration, the 3D electrodes of hierarchical CNTs@FePO₄ architecture were designed by ALD. Compared to the 2D electrodes, the 3D CNTs@FePO₄ nanostructure displays 16 and 33 times higher areal capacity Li and Na ion batteries, which is 64 and 33 $\mu\text{Ah cm}^{-2}$ after 180 cycles, respectively¹¹². Lethien's group reported another 3D electrode design by ALD for micro-batteries, in which an anatase TiO₂ negative electrode was coated on 3D tubes with Li₃PO₄ as electrolyte²⁶⁵. A high surface capacity of 0.37 mAh cm^{-2} was achieved by this proposed approach.

Pearse et al. also demonstrated a 3D micro full cell by ALD, in which all the active battery components including electrodes, solid electrolyte, and current collectors were deposited by ALD onto Si wafers with arrays²⁶⁶. The 3D micro-battery fabricated by ALD utilized a prelithiated LiV₂O₅ as cathode, Li₂PO₂N as solid electrolyte, SnNx as anode and TiN and Ru as current collectors with a deposition temperature at or below 250 °C. Remarkably, the 3D micro-batteries fabricated by ALD exhibit a reversible capacity of 2.6 $\mu\text{Ah cm}^{-2}$ up to 100 cycles. Moreover, by using a 3D substrate with ALD deposition, the areal discharge capacity of the cell is 9.3 times higher than the integrating planar cells. This work provided a new opportunity for the realization of long-sought 3D micro-batteries by ALD techniques.

2.1.2 ALD/MLD for Next Generation Li batteries

2.1.2.1 ALD/MLD for Li-O₂ batteries

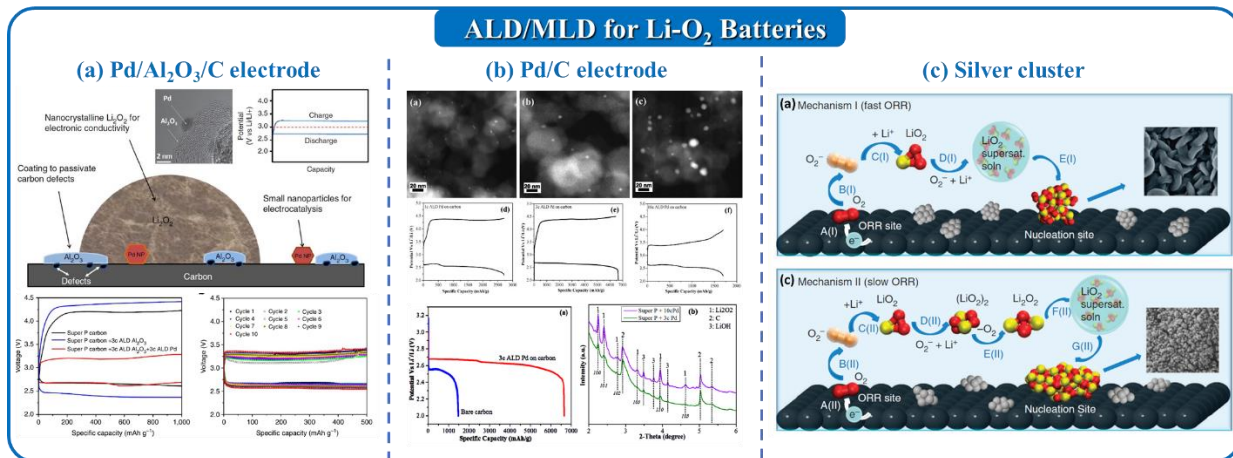
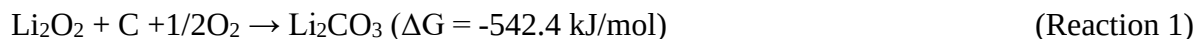


Fig.11 ALD/MLD for Li-O₂ air electrode design: (a) Pd/Al₂O₃/C; (b) Pd/C; (c) silver cluster

Li-O₂ batteries provide high theoretical energy densities up to 3-5 times larger than LIBs and have significant potential for application in EVs and large-scale energy storage systems²⁶⁷⁻²⁶⁹. However, the development of Li-O₂ batteries has been greatly hindered by the sluggish oxygen evolution reaction (OER) process during charge, which is caused by the poor charge conductivity of the discharge product, Li₂O₂. In addition, the liquid electrolyte is decomposed from reactive superoxide species during discharge, and Li₂O₂ suffers from side reaction with the defect sites on the carbon cathode^{270, 271}. A thin layer of Li₂CO₃ could be created in the interface of Li₂O₂ and carbon, as shown in Reactions 1 and 2.



The insulating nature of carbonate species generates high interfacial resistance, contributing to the large voltage polarization during discharge/charge²⁷². Hence, surface modification of the air electrodes is critical to prevent the accumulation of side products on the carbon surface and tune the formation mechanism of the discharge products. ALD enables uniform surface coating not only on flat surfaces but can also form thin films on 3D or mesoporous structures, which is ideal for modifying the air electrode in Li-O₂ batteries. We used ALD to deposit Al₂O₃ on super P conductive carbon particles to cover the defect sites, preventing unwanted side reaction of electrolyte with the carbon²⁷³. Then Pd nanoparticles were further coated on the carbon surface by ALD. Pd nanoparticles created active sites for crystalline Li₂O₂ formation and served as the catalyst during the Li₂O₂ decomposition (**Fig.11 (a)**). Compared to the charge overpotential of the

bare carbon-based cathode (over 1V), the ALD-coated material shows a much lower charge potential of 0.2 V. Density functional theory (DFT) calculations revealed that the Al_2O_3 was inert to TEGDME solvent and could prevent the dissociation of TEGDME molecules in the electrolyte.

Detailed studies (**Fig.11 (b)**) on $\text{Pd}/\text{Al}_2\text{O}_3/\text{C}$ materials with 1, 3 and 10 ALD cycles of Pd catalysts revealed the role of ALD in relation to the electrochemical performance of Li- O_2 batteries²⁷⁴. ALD enabled the formation of Pd nanoparticles in the range of 2-8 nm with uniform dispersion on the carbon substrate. Although with high charge overpotential, the $\text{Pd}/\text{Al}_2\text{O}_3/\text{C}$ electrode with 3 ALD cycles delivers a high capacity of 6600 mAh g^{-1} , suggesting that the full coverage of the carbon defects may prevent the decomposition of the electrolyte. For the case of the electrode with 10 ALD cycles, the cell shows a low charge overpotential of 3.3V, which is probably due to improved electronic conductivity and more crystallization sites created by the Pd nanoparticles on the electrode surface. Similar nano-architecture by ALD could also be expanded to other catalysts such as $\text{Pd}/\text{ZnO}/\text{C}$ ²⁷⁵. The catalyst further lowered the charge potential to 3.0 V, supporting the synergic effect of ZnO and Pd nanoparticles. Subsequently, other ALD metal oxides, including TiO_2 , In_2O_3 , Fe_2O_3 , and ZnO, were deposited either on carbon electrodes or catalysts to prevent the corrosion and side reactions between air electrodes and electrolyte²⁷⁶⁻²⁸¹. This electrode architecture achieved by ALD opened a new door for the prevention of side reactions and guided the new design of functional catalysts in Li- O_2 batteries.

The defect sites on the carbon could react with Li_2O_2 compromising the electrochemical performance, which is difficult to rule out when focusing on fundamental studies. We employed ALD to cover the surface defect sites and silver clusters are further loaded to probe the different scenarios during the discharge process in Li- O_2 batteries²⁸². Silver clusters with different sizes (3, 9, and 15 atoms) were deposited on ALD-modified carbon by the magnetron sputtering method²⁸³⁻²⁸⁶. It was found that the morphology of discharge products has a high dependency on the cluster size, and the Li_2O_2 formation is through a solution-mediated process (**Fig.11 (c)**). DFT results supported that superoxide species had a weaker bonding to Ag_{15} cluster and thus LiO_2 reached a supersaturated solution, growing on the nucleation sites as LiO_2 containing product and leading to the low charge overpotential. The form of LiO_2 was proved to be present in Li- O_2 cells and showed fast kinetics during charge²⁶⁷. Meanwhile, in Ag_3 and Ag_9 based electrodes, LiO_2 underwent a disproportionation reaction to form Li_2O_2 in the electrolyte and then deposited on the electrode surface, resulting in high charge potential in galvanostatic mode. Another effective catalysis

deposited by ALD for air electrodes for Li-O₂ batteries is Ru or RuO₂ nanoparticles²⁸⁷. Wang's group reported the selective deposition of Ru onto the b planes of TiSi₂ nanonets by ALD as a catalyst for Li-O₂ batteries²⁸⁸. The selective deposition was a result of different interface energetics proven by DFT calculations. As a result, extensive cyclability (>100 cycles) with confirmed Li₂O₂ formation and decomposition was obtained. Furthermore, Sun and his group further designed a 3D nanostructure using a conductive and porous matrix of Mn₃O₄ nanowires and carbon nanotubes composite film as substrates. Then, the ALD RuO₂ nanoparticles with an extremely low amount (just 2.84 wt%) were uniformly deposited on the matrix to form the composite electrode²⁸⁹. The Mn₃O₄/CNTs-RuO₂ electrode delivered a high specific capacity, improved round-trip energy efficiency, and ultra-long cycle life.

In this section, the recent results of the application of ALD for Li-O₂ batteries have been summarized and discussed. Several critical challenges for Li-O₂ batteries were effectively addressed by ALD. Firstly, catalysis was widely used to decrease the overpotentials for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). ALD is an ideal coating technique for catalysts in Li-O₂ batteries, especially for noble metals such as Pd and Ru. Secondly, the corrosion and side reaction between the carbon electrodes and electrolyte is one of the major issues limiting the performances of Li-O₂ batteries. Benefitting from the uniform coverage of ALD, thin metal oxides were used to protect the carbon electrode and catalysis with significantly improved cycling stability.

2.1.2.2 ALD/MLD for Li-S batteries

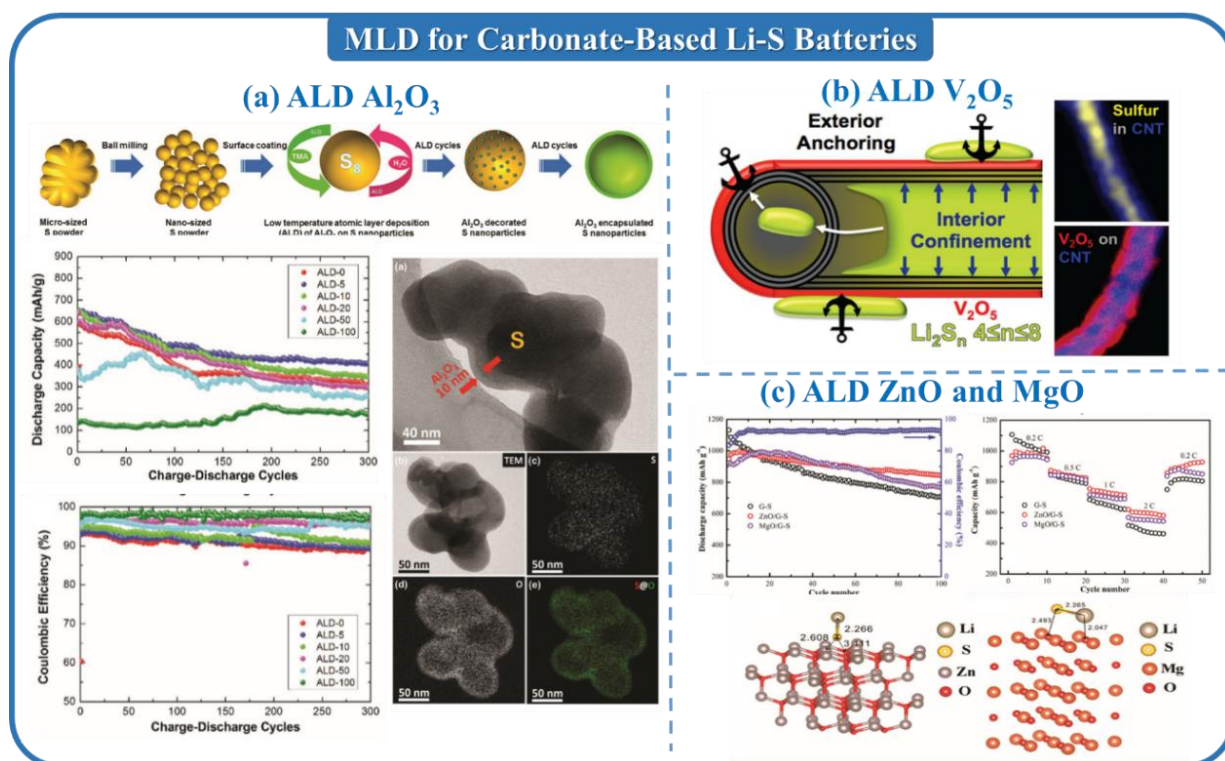


Fig.12 ALD for Li-S batteries: (a) ALD Al_2O_3 – encapsulated S cathodes for Li-S batteries. (b) ALD V_2O_5 coated CNTs for S confinement and adsorption. (c) ALD MgO and ZnO-coated rGO sulfur-composite aerogels for polysulfide trapping.

Li-S batteries are highly sought after for their high theoretical energy density of 2600 Wh/g and the wide abundance of elemental sulfur. However, several problems have plagued the development of Li-S batteries including poor electrical conductivity of sulfur, side reactions of electrode materials with electrolyte, Li dendrite formation, and dissolution of polysulfide species, leading to rapid capacity fade. ALD/MLD are promising techniques that have been shown to eliminate many of these issues through various mechanisms. For example, there have been several studies using ALD/MLD modified cathodes to prevent polysulfide dissolution²⁹⁰⁻²⁹⁷. Other cases have used ALD to modify the separator and trap dissolved polysulfides²⁹⁸. More recently, ALD has been applied to Li metal anode to further prevent side reactions and extend the cycling lifetime of Li-S batteries significantly, which will be discussed in detail in the following section. As a result, ALD/MLD are promising coating techniques for addressing the issues of Li-S battery systems.

As one of the earliest examples of ALD for S cathodes, Elam et al. utilized low-temperature ALD of Al_2O_3 on S_8 cathodes at 50 °C to improve the electrochemical performance of Li-S batteries (**Fig.12 (a)**)²⁹⁷. The low-temperature ALD process suppressed the sublimation of S, which is important for retaining the electrode capacity. Moreover, depending on the number of cycles in the ALD process, different morphologies ranging from Al_2O_3 nanoparticles to thin films can be obtained. The mechanism of improved performance is postulated to differ depending on the morphology of the ALD coating. For ALD nanoparticle Al_2O_3 , it is believed that they adsorb polysulfides, effectively eliminating the shuttling effect and improving Coulombic efficiency. In contrast, ALD Al_2O_3 thin films on S cathode act as a physical barrier to prevent the dissolution of polysulfides into the electrolyte.

As one of the primary roles of ALD coatings for Li-S batteries, many materials have been used to adsorb polysulfide species. Pint et al. recently used an ALD process for V_2O_5 on CNTs to anchor polysulfides and achieve long cycle life ²⁹⁵. After optimization of the ALD coating thickness, a balance between polysulfide anchoring and high S confinement within the CNT channels was achieved, leading to Li-S batteries with 73% capacity retention after 450 cycles (**Fig.12 (b)**). Several other ALD materials have been explored for application in Li-S batteries, such as MgO and ZnO, as exemplified by Shi et al²⁹³. They developed a reduced graphene oxide (rGO)-sulfur composite aerogel which was modified by ALD ZnO or MgO as an electrode for Li-S batteries (**Fig. 12(c)**). While batteries with both ALD coatings had enhanced electrochemical performance relative to the uncoated electrodes, it was found that ZnO was more effective than MgO. The authors carried out DFT calculations which revealed ZnO has a significantly higher binding energy towards Li-S* radical species (5.40 eV) compared to MgO (1.22 eV). Because of this, it is believed that ALD ZnO is more effective in inhibiting polysulfide shuttling. The ZnO-modified electrode could achieve a discharge capacity of 998 mAh g⁻¹ at a current density of 0.2C with minimal capacity fade after 100 cycles.

ALD has proven to be a powerful tool for application in Li-S batteries. The wide range of ALD chemistries can be applied on either the anode, separator, or cathode to directly enhance electrochemical performances. While multiple ALD coatings have been shown to interact with polysulfide species, there is still relatively little work studying the effects of different metal centers or how they may affect the interconversion of S species during electrochemical cycling.

Nevertheless, ALD chemistries often need reaction temperatures greater than 100 °C, which may cause S sublimation and reduce the capacity of electrodes. In this case, MLD coatings with lower deposition temperatures may prove vital for future improvements.

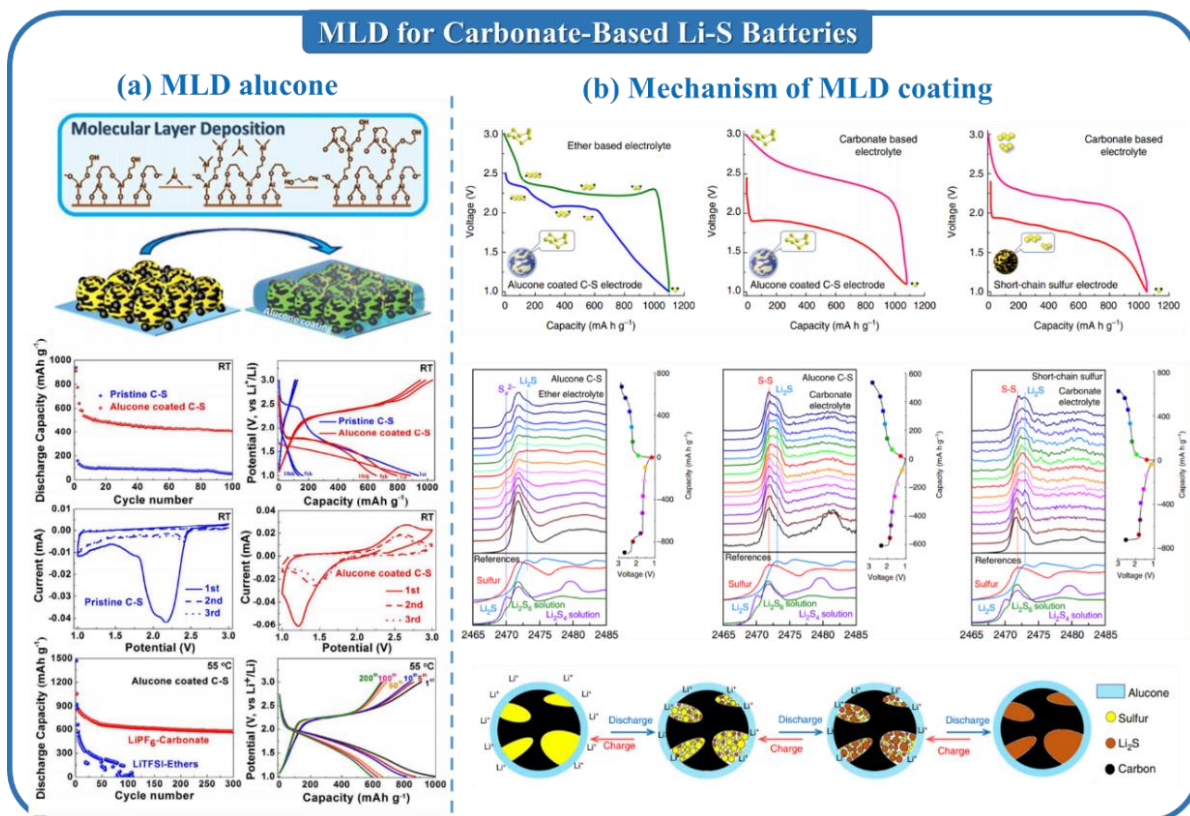


Fig. 13 MLD for Li-S batteries: (a) MLD Alucone coating on microporous S cathode can enable long cycle life in carbonate electrolytes. (b) The working mechanism of MLD coating on S cathodes in carbonate electrolyte studied by in-situ XANES showing solid-state interconversion between cyclo S₈ and Li₂S.

MLD has recently been shown to be advantageous for application in Li-S batteries. Traditionally, Li-S batteries have been cycled in ether electrolytes due to the reversible transformation between elemental S and Li₂S species through polysulfide intermediates. Nevertheless, ether electrolytes have narrow electrochemical stability windows and have low flash points which cause severe safety concerns. In an ideal scenario, Li-S batteries may be better suited for carbonate electrolyte systems due to their better thermal stability. However, conventional Li-S

batteries are unable to operate in carbonate electrolyte due to the irreversible side reactions between polysulfide intermediates and carbonate solvents.

Recently, Sun et al. discovered that MLD Alucone coatings on carbon-S cathode composites can enable stable electrochemical cycling of Li-S cells in carbonate systems²⁹⁴. The Alucone coating serves multiple functions including acting as a protective barrier against side reactions and play a role in the interconversion of S species. In a typical Li-S battery with ether electrolyte, two cathodic reactions occur at around 2.3V and 2.1V during the lithiation of sulfur corresponding to the reduction of cyclo-S₈ to long-chain polysulfides and short-chain sulfide species, respectively (**Fig.13 (a)**). In comparison, the pristine carbon-S cathode in carbonate electrolyte exhibits a broad CV peak at 2.5V that is irreversible in subsequent cycles, which can be attributed to the formation of long-chain polysulfides. However, upon applying as little as 10 cycles of MLD alucone on the carbon-S cathode, the Li-S batteries show reversible cycling of S species, albeit with electrochemical activity at different potentials compared to traditional Li-S voltages, suggesting an alternative reaction route. The Li-S cells were shown to not only cycle better with alucone coated cathodes in carbonate electrolyte at elevated temperatures, but the cells actually performed better than that with conventional ether electrolytes. This work highlighted the ability of MLD to enable Li-S batteries with longer life in new types of electrolyte systems, which is important for their commercialization.

Shortly after, Sun's group further revealed the working mechanism of alucone coated S in Li-S batteries by in-operando XANES studies²⁹⁹. S K-edge XANES of Li-S batteries with alucone-coated S cathodes revealed different reaction mechanisms found in ether versus carbonate electrolyte systems (**Fig.13 (b)**). In conventional ether electrolytes, the alucone coating does not affect the interconversion of S intermediates, following the traditional reaction scheme. However, in carbonate electrolyte, the in-operando S K-edge XANES reveals that the MLD coating enables cyclo-S₈ molecules are directly reduced to Li₂S in a solid-phase reaction without the formation of polysulfide intermediates. Moreover, high-performance Li-S pouch cells were fabricated with MLD-coated S cathodes in carbonate electrolyte for the first time. A first discharge capacity of over 1100 mAh g⁻¹ at a 0.05C rate was achieved, resulting in an energy density at the cell level of over 200 Wh Kg⁻¹. This work provided important information on the reaction mechanisms of Li-

S batteries in carbonate electrolytes and the role of MLD alucone coatings in achieving high electrochemical performances.

It is expected that new MLD coatings may provide alternative reaction chemistries for Li-S batteries and more work in the future should be focused on studying the effects of different MLD thin films and their interactions with S cathodes.

2.1.2.3 ALD/MLD for solid-state Li batteries

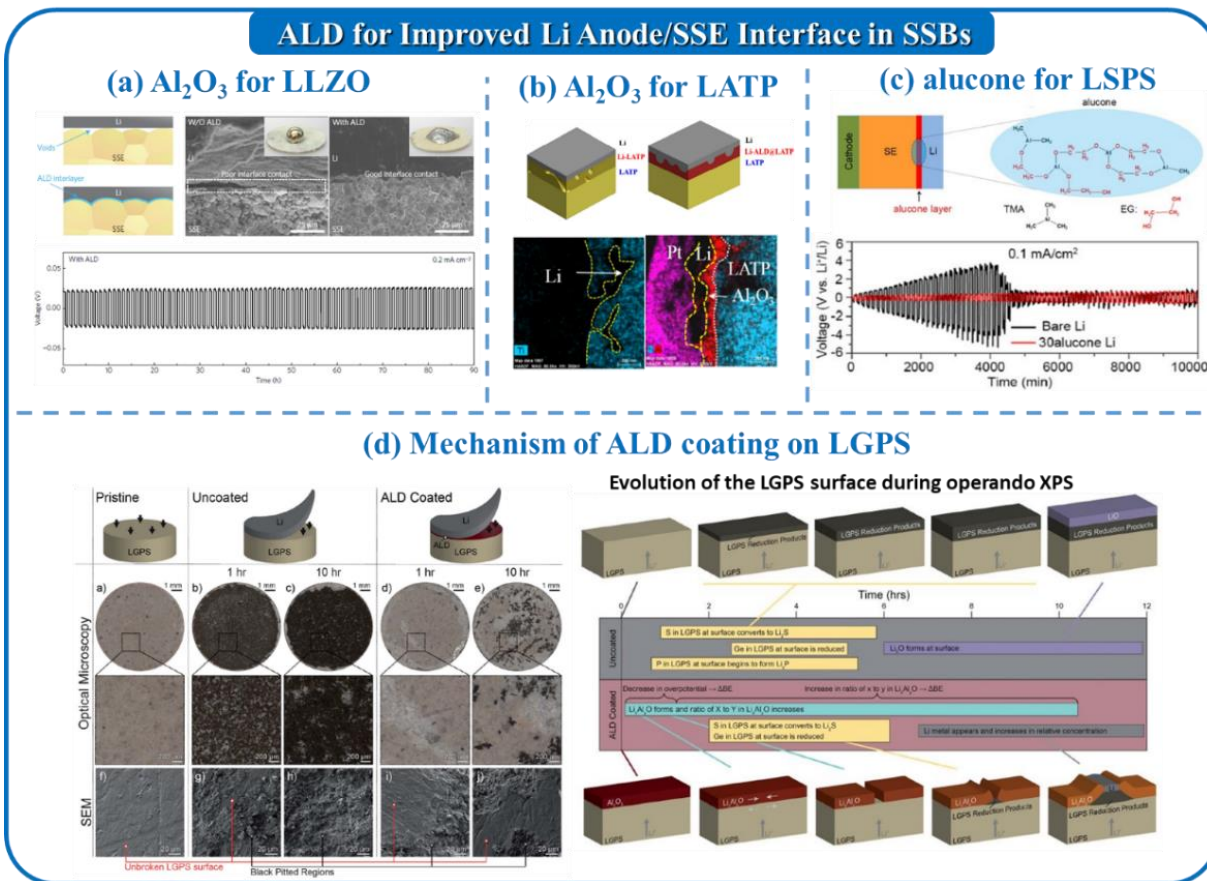


Fig 14. ALD for improved anode interface in SSBs (a) ALD Al_2O_3 for LLZO and Li metal; (b) ALD Al_2O_3 for LATP and Li metal; (c) MLD alucone for LSPS and Li metal; (d) Using operando microscopy and XPS to study the impact of the ALD- Al_2O_3 on the electro-chemo-mechanical degradation of LGPS.

All-solid-state Li batteries (ASSLBs) based on solid-state electrolytes (SSEs) have attracted significant attention recently due to their capability of achieving high energy density and improved

safety compared to liquid-based electrolyte systems. One of the major components of SSBs is the solid-state electrolyte (SSE), which requires a large voltage stability window and good ionic conductivity. Until now, several types of SSEs, including oxide, sulfide, halide, and polymer electrolytes, have been developed to replace the flammable liquid electrolyte in conventional batteries³⁰⁰⁻³⁰³. The organic polymer-based SSE poly(ethylene oxide) (PEO) is one of the earliest developed SSEs for SSBs. However, the low ionic conductivity of polymer SSEs at room temperature is generally in the range of $10^{-5}\sim 10^{-6}$ S cm⁻¹, which is still far away from practical application. An ionic conductivity of over 10^{-4} S cm⁻¹ can be achieved at high operation temperatures (65-80 °C). For the oxide SSEs such as perovskite (Li_{3.3}La_{0.56}TiO₃), NASICON (LiTi₂(PO₄)₃), and garnet (Li₇La₃Zr₂O₁₂), the ionic conductivities at room-temperature are around $10^{-5}\sim 10^{-3}$ S cm⁻¹. The sulfide-based SSEs possess the highest ionic conductivity of 10^{-2} S cm⁻¹ (Li₁₀GeP₂S₁₂) among all different types of SSEs. Although significant progress has been achieved for the development of high ionic conductive SSEs, the fabrication of thin film SSEs at the nanoscale is also important for thin film batteries, 3D micro-batteries and interface engineering of electrode materials. In the past years, various thin films SSEs, such as Li₃PO₄, LiTaO₃, LiNbO₃, LiSiO₄, Li₇La₃Zr₂O₁₂, and LiPON, have been fabricated by ALD^{201, 304-309}. However, the ionic conductivities of the developed ALD SSEs are around $10^{-8}\sim 10^{-9}$ S cm⁻¹, which cannot be directly used as SSEs for SSBs. Moreover, these ALD SSEs are generally amorphous and the high-temperature post-annealing can cause shrinkage of the films, resulting in island-like structures. A recent achievement from Dasgupta's group reported an amorphous lithium borate-carbonate (LBCO) film which can be prepared by ALD, yielding the highest Li-ion conductivity (2.2×10^{-6} S cm⁻¹ at room temperature) among all previously reported ALD-prepared Li-ion conductive compounds³¹⁰. Although it is difficult for the ALD LBCO films to be directly used as SSEs for SSBs, they are still promising as an interface modification between SSEs and cathode/anode electrodes.

One of the most inhibiting factors of ASSLBs is the side reaction between anode/cathode and the SSE. Surface modification of the interface with ALD/MLD techniques has been demonstrated as a promising strategy that can alleviate specific problems associated with parasitic side reactions. On the anode side, the direct use of Li metal in the ASSLBs has problems associated with poor contact, uncontrollable side reactions and the formation of Li dendrites. Hu et al.³¹¹ coated ALD-Al₂O₃ on a garnet electrolyte (Li₇La_{2.75}Ca_{0.25}Zr_{1.75}Nb_{0.25}O₁₂, LLCZN) to

increase the interfacial contact and reduce the interfacial impedance from $1,710 \Omega \text{ cm}^{-2}$ to $1 \Omega \text{ cm}^{-2}$. **(Fig 14 (a))** The intimate contact is derived from the high binding energy of Li with lithiated Al_2O_3 . In addition, the ultrathin lithiated Al_2O_3 can provide conductive Li^+ ions pathways and prevent the garnet decomposition. Sun et al. compared the ALD- Al_2O_3 coating process on the Li metal anode and the NASICON-type LATP $[\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3]$ ³¹². The results showed that the ALD coating on the electrolyte enables a much more stable Li/LATP interface. Both Li penetration and Ti reduction are prevented by the dense ALD- Al_2O_3 coating. **(Fig 14(b))** Apart from improving the interfacial stability of Li/oxide-based SSEs by coating ALD- Al_2O_3 , MLD-prepared inorganic-organic coating (alucone) has been developed as well to alleviate the interface problem between Li metal and $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ sulfide-based SSEs³¹³. **(Fig. 14 (c))** Alucone interlayer, as an artificial SEI, significantly suppresses the side reactions by blocking electron transfer. Very recently, Dasgupta et al. used a suite of operando microscopy and spectroscopy techniques to study the impact of the ALD- Al_2O_3 on the electro-chemo-mechanical degradation of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) sulfide electrolytes **(Fig. 14 (d))**. This ALD- Al_2O_3 interlayer was confirmed to delay degradation of the Li/LGPS interface by modifying the interphase chemistry and morphology³¹⁴.

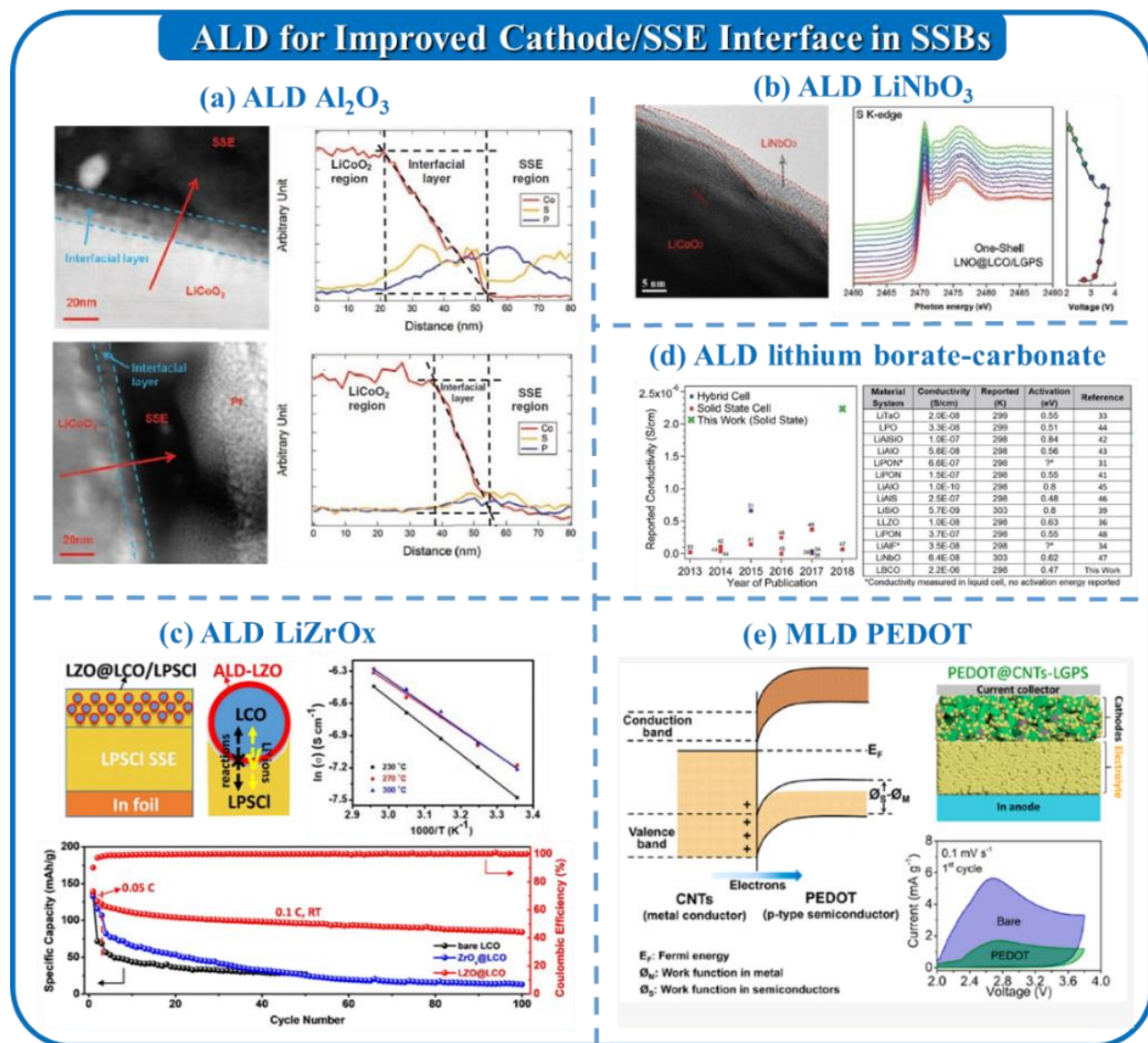


Fig. 15 (a) ALD Al_2O_3 for LiCoO_2 and SSEs; (b) ALD LiNbO_3 for LiCoO_2 and SSEs; (c) tuning the ionic conductive LZO coating via controlling the ALD process; (d) ALD deposited lithium borate-carbonate as SSEs; (e) MLD PEDOT coatings for additives in cathode composite to tune the electronic conductivity of the interface.

On the cathode side, the interfacial problem mainly exists between oxide cathode materials and sulfide-based SSEs. Due to the different affinities of Li^+ ions towards oxides and sulfides, the space charge effect is one of the main obstacles that render poor cycling stability. Moreover, the variable-valence-state transition metal elements in the cathode materials are reactive with sulfide electrolytes. It is recognized that the development of Li-ion conductive and

chemically/electrochemically inactive cathode coating materials is essential. Lee's group demonstrated that ALD- Al_2O_3 layers coated on LiCoO_2 (LCO) cathode materials can effectively prolong the cycle life of the ASSLBs³¹⁵. High-resolution TEM and EELS aided in observing that the ALD- Al_2O_3 layer can reduce the thickness of the formed interface. The interdiffusion of elements from LCO cathode materials and $\text{Li}_{3.15}\text{Ge}_{0.15}\text{P}_{0.85}\text{S}_4$ SSEs are also inhibited, as shown in **Fig. 15 (a)**. Sun et al. further demonstrated ALD processes for amorphous and Li-ion conductive LiNbO_x (LNO), LiPO_x (LPO), and LiZrO_x (LZO) coating layers on LCO and NMC cathode materials³¹⁶⁻³¹⁸. In-situ XANES results imply that the LNO shell can suppress the interfacial reactions between LCO and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ during the charging and discharging processes (**Fig. 15(b)**), and a similar functionality was also verified for the LPO-coated and LZO-coated cathode materials. It should be noted that ALD processes (i.e. sub-cycles and deposition temperatures) can be easily tuned to fabricate conformal cathode coating layers with different ionic conductivity, which is demonstrated in the LZO coating by Zhao et al. (**Fig. 15 (c)**). In addition to the binary and ternary coating materials, the amorphous ALD-LBCO (including Li, B, C, and O elements) layer was verified to work well in a thin film battery, which shows a very promising ionic conductivity of $2.2 \times 10^{-6} \text{ S cm}^{-1}$ at 25 °C (**Fig. 15 (d)**)³¹⁰. Therefore, ALD-LBCO is anticipated to be an ideal protection layer when applied to cathode materials for ASSLBs. In addition to the ionic conductivity of the interfacial layer, the electronic conductivity is also an important factor that can determine the battery performance. Recently, Deng et al. employed MLD to prepare poly(3,4-ethylenedioxythiophene) (PEDOT) as a semiconducting additive for cathode composites in the sulfide-based solid-state batteries³¹⁹ (**Fig. 15 (e)**). The MLD-PEDOT modification not only significantly suppresses the side reactions but also realizes effective electron transfer at the cathode/SSE/carbon three-phase interface.

SSBs are promising energy storage systems and the future target for the battery community. However, the development of SSEs and interfacial issues are the major hurdles that need to be overcome for practical applications. Meanwhile, the application of ALD and MLD for SSBs is still in the early stage. To play a more important role, new ALD and MLD films with high ionic conductivity, electronic conductivity, and wide electrochemical windows need to be developed.

2.1.2.4 ALD/MLD for Li metal anode

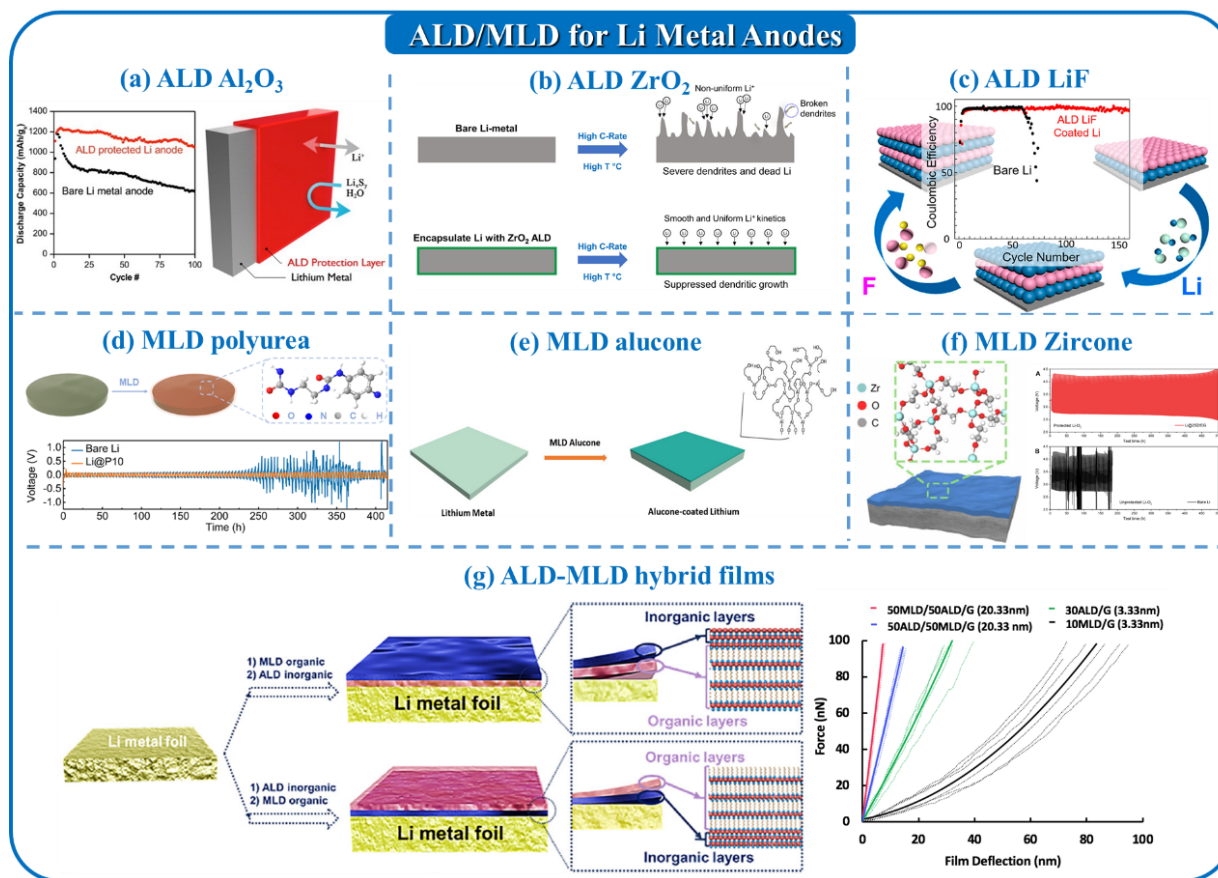


Fig.16 ALD/MLD for Li metal anodes: (a) ALD Al_2O_3 ; (b) ALD ZrO_2 ; (c) ALD LiF ; (d) MLD organic polyurea; (e) MLD hybrid inorganic-organic alucone; (f) MLD hybrid inorganic-organic zircono; (g) ALD-MLD dual protective layer.

The practical energy density of present LIBs ($\sim 240 \text{ Wh kg}^{-1}$) has nearly approached its physicochemical energy density limit with only a 7-8 % increase per year³²⁰. With a super high capacity (3860 mAh g^{-1}) and the lowest electrochemical potential (-3.04 V vs the standard hydrogen electrode), Li metal is strongly regarded as the most promising candidate for next-generation Li metal batteries (LMBs) beyond traditional LIBs. To date, some fundamental issues including poor safety and cycling stability still hinder the practical application of the Li metal anode. Firstly, the formation of dendrites during electrochemical plating/stripping can penetrate the separator, triggering the failure of the battery due to internal short circuits. The risk of thermal runaway and cell combustion arising from shorting will significantly increase. Secondly, The formation of unstable SEI components due to uncontrolled side reactions between Li metal and

liquid electrolyte leads to poor Coulombic efficiency. In addition, the large volume fluctuation of Li during electrochemical cycling owing to its hostless nature further causes the formation of “dead” Li deposits and further aggravates parasitic side reactions³⁵. The stability of the SEI is the most important factor that needs to be addressed in order to prevent further side reactions between Li and electrolyte. Nevertheless, naturally-formed SEI is heterogeneous with respect to composition, ionic conductivity, and mechanical properties, leading to fracture upon electrochemical cycling and continuous side reactions between Li and electrolyte^{321, 322}. Therefore, interphase design is critical to improving the stability of SEI and is considered to be an effective approach to enhance the performance of Li metal anodes. The functions of the artificial SEI are summarized as [1]: 1) A strong physical barrier against dendrite propagation; 2) Preventing the side reactions between Li metal and electrolyte; 3) Regulating the Li⁺ flux on the surface of Li metal and uniformizing the Li nucleation and deposition³²³. There have been many works reporting the construction of surface coatings on Li as a protective film, including metal oxides^{324, 325}, solid-state electrolytes^{326, 327}, and polymers^{328, 329}. These ex-situ strategies can be realized by various coating techniques, such as chemical vapor deposition³³⁰, wet chemical method³³¹, and physical vapor deposition³³². Among all of the coating methods, ALD is believed to be very promising due to its conformal coverage and accurate control over thickness in the nanoscale regime¹⁹. Ultra-thin protective films with homogeneous composition can be deposited on Li metal, and all the features achieved by ALD can be beneficial towards meeting the requirement of an ideal SEI. As an analogue technique to ALD, MLD is employed for the deposition of polymeric films rather than inorganic materials by ALD. As previously mentioned, MLD provides several unique advantages such as tunable electrochemical properties and improved mechanical performance while maintaining the advantages of ALD³³³.

The investigation of ALD metal oxides for Li metal protection was reported by Noked's group for the first time³²⁵. In their work, a ~14 nm thick ALD Al₂O₃ layer was coated on Li by plasma-enhanced ALD (PEALD) with trimethylaluminum (TMA) and O₂ plasma. When tested in Li-S batteries, the ALD-protected anodes showed improved capacity retention compared to bare Li for up to 100 cycles (**Fig.16 (a)**). Moreover, this Al₂O₃ layer can effectively prevent the corrosion of the Li surface when exposed to the atmosphere, sulfur, and electrolyte. Following this work, there have been other studies on the protective effects of ALD Al₂O₃ for Li. Dasgupta's group used TMA and H₂O as precursors to deposit an optimized ~2 nm ultrathin Al₂O₃ layer and

investigated the plating/stripping of symmetric Li-Li cells³³⁴. They observed a greatly improved lifetime enabled by the coating layer and a smooth Li surface after 1000 electrochemical cycles. This work demonstrated that Li can transport through Al_2O_3 during the Li plating process, which was confirmed from XPS results that indicated that Al still remained on the surface after Li plating. Based on their first work, Noked's group further studied the protective effects of ALD coating on Li against organic electrolyte quantitatively using mass spectrometry and in situ AFM³³⁵. They confirmed that both electrochemical degradation and solvent corrosion can be efficiently suppressed by ALD Al_2O_3 . Moreover, Elam's group investigated the growth mechanism of ALD Al_2O_3 deposition on Li by in situ quartz crystal microbalance and found enhanced wettability of Li surface towards electrolytes³³⁶. Promisingly, the cycling life of ALD protected Li was four times longer than bare Li when the volume of electrolyte was only 5 μL . Furthermore, Cui's group applied ALD Al_2O_3 on a 3D hollow carbon host, which can guide Li deposition inside the hollow carbon spheres and prevent direct electrolyte contact, resulting in a high coulombic efficiency of 99% over 500 cycles³³⁷. Other than Al_2O_3 , Cho's group recently reported a ZrO_2 encapsulation layer on Li metal by plasma-thermal activated ALD for the first time, as shown in **Fig.16 (b)**³³⁸. This conformal and ionically conductive ZrO_2 layer with high-k dielectric properties can suppress side reactions and stabilize Li metal. The protected Li also exhibited good heat tolerance up to 170 -180 degree °C due to the high thermal resistance of ZrO_2 .

The development of lithium-containing compounds via ALD is also considered as a promising strategy to stabilize the Li metal anode. Elam's group developed an ultrathin and ionically conducting ALD $\text{Li}_x\text{Al}_y\text{S}$ coating to stabilize the SEI and decrease the interfacial resistance³³⁹. In this ALD process, a newly developed coating of Al_2S_3 by tris(dimethylamido) aluminum(III) and H_2S is combined with a reported process for Li_2S by combining lithium tert-butoxide (LiO^tBu) and H_2S subcycles. The electrochemically deposited Li with $\text{Li}_x\text{Al}_y\text{S}$ coating was found to maintain a smooth surface, and the cycle life of Li-Cu cells was doubled compared to the bare Li. A new ALD process enabling the deposition of LiF (**Fig.16 (c)**) directly on Li was also developed recently by Elam's group³⁴⁰. In the synthesis of ALD LiF, LiO^tBu and HF/pyridine solution were used as precursors for deposition at 150 °C, which is below the melting point of Li. A high shear modulus of 58 GPa was detected by nanoindentation measurements, which is higher than that required to prevent the growth of Li dendrites. Owing to the high dielectric value and great stability of LiF, the protected Li showed a stable Coulombic efficiency of ~99.5% for 170

cycles. Furthermore, Cui's group demonstrated selective ALD LiF deposited on the defect sites of h-BN films³⁴¹. The LiF was primarily deposited on the defects of h-BN, thereby saturating the h-BN crystallites. As a result, the protected electrodes exhibit excellent cycling stability with more than 300 cycles at relatively high Coulombic efficiency in an additive-free carbonate electrolyte.

To date, polymeric films have been reported as effective coating materials for Li metal with some interesting and unique mechanical properties. The fabrication of various MLD nanoscale coatings on Li has been reported by Elam's group and Sun's group. Different from ALD coatings, MLD coatings have good flexibility, lower density, and high softness, which can lead to improved electrochemical performance when using artificial SEI. A type of pure polymeric coating of 'polyurea' was reported to stabilize the SEI by our group for the first time, as shown in **Fig.16 (d)**³⁴². Abundant polar groups in this polymer can redistribute the Li-ion flux and lead to a uniform Li plating/stripping process. Both XPS and TOF-SIMS results confirmed that nitrogen remained on the surface after electrochemical cycling, suggesting that the protective film is mechanically robust upon electrochemical cycling. As a result, a three-fold increase in cycle life was achieved in symmetric cells at a current of 3 mA cm⁻² and higher capacity retention was obtained in Li-LFP batteries for 200 cycles. A hybrid inorganic-organic MLD coating, alucone, has been reported by both Sun's group and Elam's group for the use of a protective layer for Li metal anodes (**Fig.16 (e)**)^{343, 344}. With a composition consisting of (-Al-O-CH₂-CH₂-O-)n repeating units, alucone is synthesized by the sequential reactions of TMA and ethylene glycol (EG). Our results showed that alucone-protected Li had superior electrochemical performance compared to that of ALD Al₂O₃ coatings³⁴³. The reason for improved performance was revealed by RBS measurements on both electrochemically cycled Al₂O₃ and alucone coated Li. The results demonstrated that the alucone coating was more effective than Al₂O₃ in preventing film fracture under the large volume change during Li plating/stripping. Elam's group also found a similar conclusion that alucone coating can stabilize Li against dendrite growth and minimize side reactions³⁴⁴. Their results showed the protected Li can yield longer cycle life and 39.5% higher capacity after 140 cycles in Li-S batteries with a high mass loading of ~5 mg/cm². Sun et al. recently reported the fabrication of MLD zirconium as a protective layer on Li metal at 130 °C using zirconium tertbutoxide and ethylene glycol as precursors, as shown in **Fig.16 (f)**³⁴⁵. In-situ synchrotron X-ray absorption spectroscopy was used to study the lithiation process of the zirconium thin films. Promisingly, the zirconium coated Li showed

a 10-fold increase in cycle life in Li-O₂ batteries compared to those with unprotected Li due to its excellent air stability.

The electrical and mechanical properties of MLD thin films are different compared with their ALD counterparts. When used as protective coatings on Li, dense ALD films are expected to block the electron transport and reduce unwanted side reactions, whereas porous MLD films are expected to better accommodate the volume changes during plating/stripping because of their improved flexibility. Recently reported by Sun et al., a dual protective layer for Li metal anodes was fabricated by combining ALD and MLD, leading to significantly enhanced electrochemical performances³⁴⁶. Inspired by natural SEI formation, this dual protective layer consisted of organic alucone as the outer layer and inorganic Al₂O₃ as the inner layer. The concept and design of the ALD/MLD recipe are shown in **Fig.16 (g)**. The mechanical properties of the protective layer were investigated by atomic force microscopy (AFM). The results showed both high strength and local flexibility, which are beneficial for suppressing crack formation upon electrochemical cycling. Results from SEM demonstrated that dendrite growth and dead Li formation can be effectively suppressed by the introduction of a dual-layer. Moreover, surface and interface analysis by both TOF-SIMS and RBS indicated an excellent robust feature of the protective layer. This work demonstrates the precise control over coating thickness and composition enabled by ALD and MLD techniques, which is difficult to achieve by other methods.

In this section, we have summarized the application of ALD/MLD coatings to address the challenges of Li metal anodes. The reasons for their enhanced electrochemical performances are mainly: 1) the electronically insulating properties of the coatings can induce Li deposition underneath the films. 2) The protective layers can serve as a physical barrier to suppress dendrite growth and/or accommodate volume change. 3) Side reactions between electrolyte and Li can be suppressed by coating. Ionic conductivity plays a crucial role in SEI as the Li-ion transport through interphase considerably affects the electrochemical performances³⁴⁷. However, there are still very few reports on the fabrication of ALD/MLD coatings with high ionic conductivity directly on lithium. We strongly believe the development of new ALD/MLD processes for ionically conductive coatings on Li is of great importance to realizing stable Li metal anodes for next-generation LMBs.

2.1.3 ALD/MLD for Na batteries and beyond

2.1.3.1 ALD/MLD for Na ion batteries

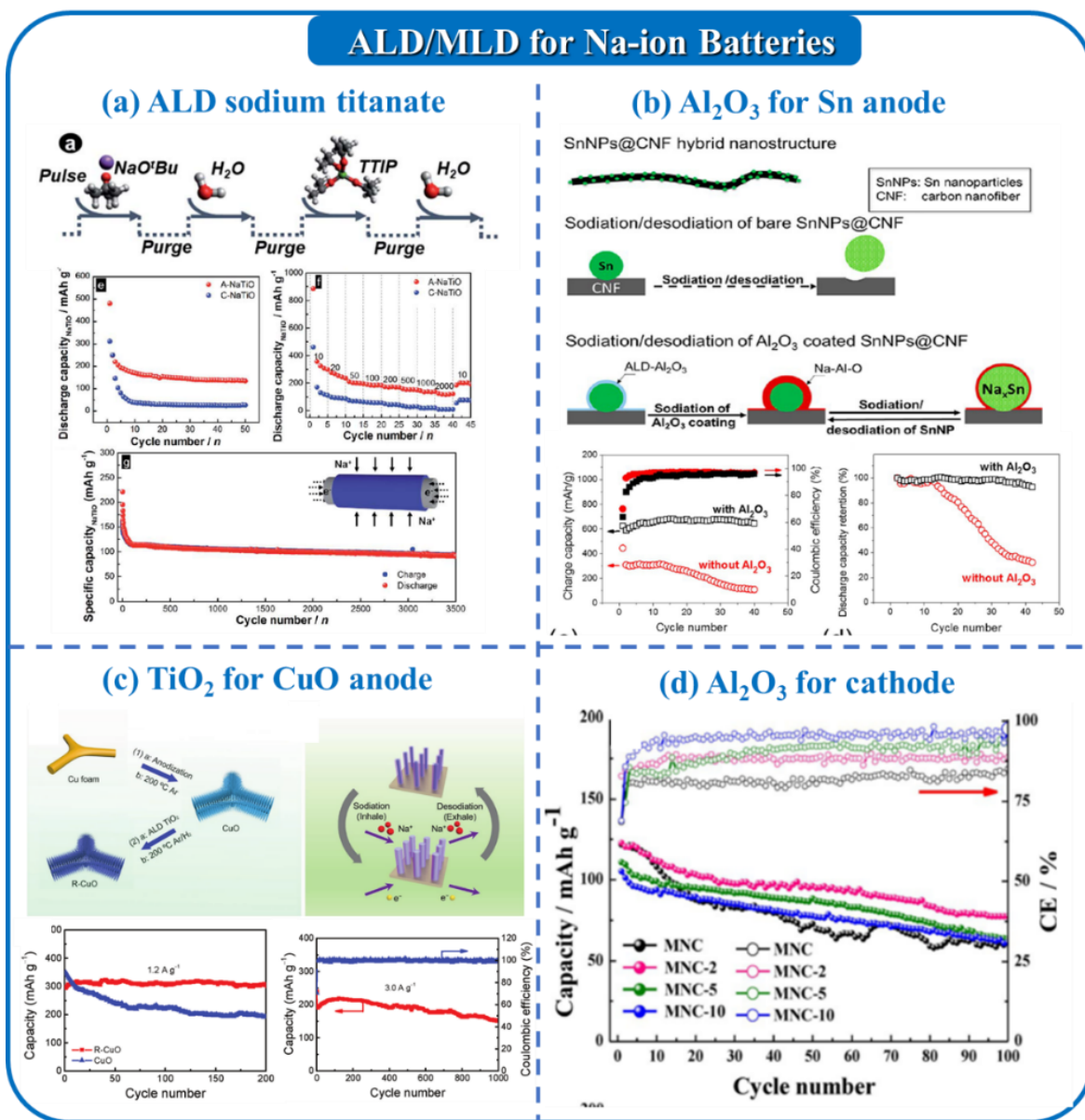


Fig.17 ALD/MLD for Na-ion batteries: (a) ALD fabricated sodium titanate; (b) ALD Al_2O_3 for Sn anode; (c) ALD TiO_2 for CuO anode; (d) ALD Al_2O_3 for $\text{Na}_{2/3}(\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13})\text{O}_2$.

With the continuous consumption of resources due to the large demand for Li-ion batteries, the availability of Li sources has been dramatically reduced. Thus, it is necessary to develop a new energy storage system to replace Li-based batteries^{348, 349}. Na batteries, including Na-ion batteries

(NIBs) and room temperature Na metal batteries, are recognized as promising alternatives to Li batteries due to the lower price, natural abundance of sodium, and similar intercalation chemistry to lithium³⁵⁰⁻³⁵². The electrodes, including both cathode and anode, are still the key components for high-performance Na batteries. ALD/MLD can be used for the fabrication of electrodes and engineering of the electrode/electrolyte interfaces. Sun et al. were the first to demonstrate an ALD-fabricated sodium titanate as anode for NIBs³⁵³. As shown in **Fig.17 (a)**, the NaO^tBu, titanium(IV) isopropoxide (TTIP), and H₂O were used as precursors at a deposition temperature of 200 °C-275 °C. One ALD supercycle consists of two ALD sub-cycles, which include NaO^tBu-H₂O and TTIP-H₂O. The as-deposited sodium titanate was amorphous, and crystalline Na_{0.23}TiO₂ was obtained after a post-annealing treatment. Carbon nanotubes (CNTs) were used as the substrate for electrode fabrication. The sodium titanates on CNTs delivered excellent electrochemical properties as anodes for NIBs with high energy density, exceptional rate performances and long lifespans. As shown in Fig. 17(a), the as-deposited amorphous sodium titanates demonstrated better electrochemical performances with high capacity compared to the crystalline Na_{0.23}TiO₂. Another work reported nitrogen-doped TiO₂ on CNTs (N-TiO₂/CNTs) fabricated by plasma-enhanced ALD using N₂ plasma³⁵⁴. Furthermore, Rao et al. have grown ultrathin crystalline epitaxial thin films of MoS₂ on c-sapphire by ALD³⁵⁵. The MoS₂ films showed a high density of nanowalls and exhibit a high surface to volume ratio. The cell with the ALD-grown MoS₂ nanowall network presented remarkable electrochemical performances in both LIBs and NIBs, delivering a specific capacity of 667 mAh g⁻¹ and 1710 mAh g⁻¹ for LIBs and NIBs, respectively.

Similar to their application in LIBs, ALD/MLD techniques are also used to modify the SEI layer for anode materials in NIBs. Hu's group designed a novel hybrid nanostructure (**Fig.17 (b)**), consisting of Sn nanoparticles (SnNPs) attached to carbon nanofibers (CNFs) with another thin layer of ALD Al₂O₃ for use as an anode in NIBs³⁵⁶. As shown in Fig. 17(b), without the ALD coating, the SnNPs detach and fall off from the underlying CNF substrate after sodiation/desodiation cycles. In contrast, the ALD Al₂O₃ coating could conduct sodium ions after forming the Na-Al-O layer, allowing for the uniform sodiation of the SnNP core. The volume change of SnNP during cycling was accompanied by a conformal swelling and shrinking of the Na-Al-O layer. It was verified by in-situ TEM that the ALD Al₂O₃ coating was robust and deformed coherently with the SnNPs during the sodiation/desodiation process, effectively limiting the volume changes during cycling. As a result, the electrochemical stability was improved with

the ALD Al_2O_3 coating. Liu et al. further demonstrate the concept using a composite anode of SnO_2 nanoparticles on carbon cloth (CC) with the surface coating layer of ALD Al_2O_3 ³⁵⁷. Moreover, the ALD metal oxides of Al_2O_3 and TiO_2 have also been deposited as a protective layer for conversion-type anodes such as CuO and NiCo_2O_4 ^{358, 359}. For example, Li's group demonstrated CuO nanowire electrode arrays grown on 3D Cu foams with ALD TiO_2 as protective coatings (as shown in **Fig.17 (c)**)³⁵⁹. The CuO nanowire arrays delivered a high specific capacity of 592 mAh g^{-1} and remarkable cycling performances with a high capacity retention of 82% over 1000 cycles.

On the cathode side, ALD Al_2O_3 was also used to engineer the interface for different cathode materials, such as $\text{Na}_{2/3}(\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13})\text{O}_2$, $\text{P2-Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ ³⁶⁰⁻³⁶⁶. For example, our group reported an ALD Al_2O_3 coating for P2-type $\text{Na}_{2/3}(\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13})\text{O}_2$ with an optimized thickness of 2 Al_2O_3 cycles, as shown in **Fig. 17 (d)**. Thick ALD Al_2O_3 can reduce the utilization of active materials and increased the charge-transfer resistance upon cycling³⁶⁰. The role of ALD metal oxide coating in NIBs is similar to that of LIBs, which prevent the side reactions between cathode and electrolyte; minimize the transition metal dissolution, and provide structural stability against mechanical stresses which occur during the cycling process.

2.1.3.2 ALD/MLD for Na metal batteries

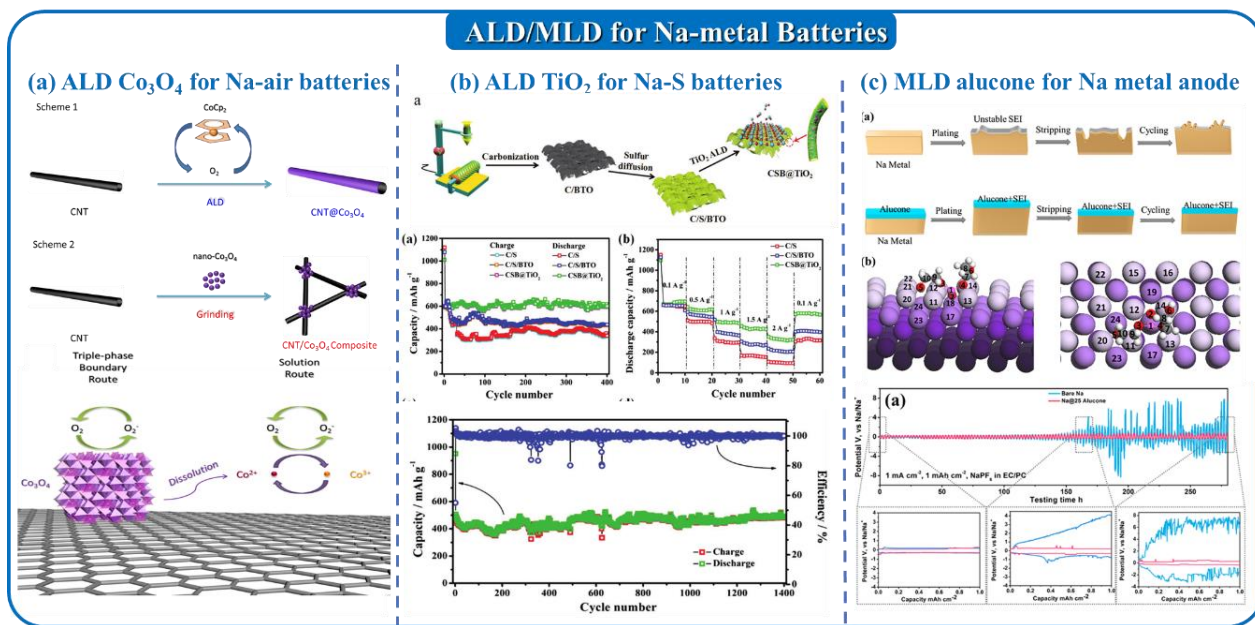


Fig. 18 ALD/MLD for Na metal batteries: (a) ALD Co_3O_4 as catalysis for Na-air batteries; (b) ALD TiO_2 for Na-S batteries; (c) MLD alucone for Na metal anode.

Room temperature Na metal batteries (NMBs), including Na-S, Na-Se, and Na-O₂ batteries, present higher energy densities compared to traditional LIBs and NIBs³⁶⁷⁻³⁷⁰. Sun's group demonstrated non-noble ALD Co₃O₄ catalysts on CNTs as an air electrode for Na-air batteries³⁷¹. As shown in **Fig. 18(a)**, a conformal layer of Co₃O₄ was formed on the CNTs substrates by ALD technique. In contrast, mechanically mixed CNT/Co₃O₄ nanocomposites were prepared for comparison. The ALD deposited Co₃O₄-CNTs air electrodes can effectively improve the utilization of the catalytic centers and orientate the growth of the discharge products, resulting in the increased capacity and extended lifespan. Furthermore, we designed another 3D structured air electrode for Na-O₂ batteries³⁷², in which graphene foam was used as the substrate and mesoporous Mn₃O₄ with ALD Pd deposition were decorated on the graphene foam. In this 3D air electrode, the mesoporous Mn₃O₄ and Pd nanoclusters acted as ORR and OER catalysts, respectively, resulting in a stable electrochemical performance for over 100 cycles in Na-O₂ batteries.

ALD has also been extended to Na-S and Na-Se battery applications. As shown in **Fig. 18(b)**, we designed a novel structured cathode material for Na-S batteries³⁷³. The C/S/BaTiO₃ composites were firstly fabricated via electrospinning and following the annealing process. Then, ALD TiO₂ was deposited on the C/S/BaTiO₃ composites as the protective layer. With the ALD TiO₂ coating, the electrode showed enhanced stability with a discharge capacity of 611 mAh g⁻¹ after 400 cycles. The ALD coating can effectively absorb the polysulfides, suppress the volume changes, reduce the interfacial resistance, and facilitate charge transfer and ion transport, resulting in improved electrochemical performances. Moreover, the ALD Al₂O₃-coated (Se/porous N-doped carbon nanofibers)@Se composites were rationally designed and fabricated as free-standing cathodes for Na-Se batteries. The ALD coated composite electrode with high Se loading (67 %) delivered the high specific capacity of 503 mAh g⁻¹ after 1000 cycles with almost 100 % capacity retention at the current density of 0.5 A g⁻¹. The major function of the ALD Al₂O₃ is to serve as an artificial barrier to limit the dissolution of sodium polyselenides and mitigate the shuttle effects in the electrolyte.

For room temperature Na metal batteries, the Na metal anode is another serious challenge that needs to be overcome. As an alkali metal, the issues of Na metal anode can be summarized as 1) Na dendrite growth; 2) unstable SEI and dead Na layer formation; 3) infinite volume change^{374, 375}. For the individual subcategories of Na metal batteries, there are other problems specific to the

full cell system. For example, the O_2 diffusion to the anode is also a critical issue in Na- O_2 batteries³⁷⁶. Our previous review has summarized the recent development of Na metal anodes in detail³⁷⁷. ALD/MLD can play an important role in addressing the interfacial issues. Hu's group and our group reported ALD Al_2O_3 as a protective layer for the Na metal anode^{378, 379}. The ultrathin Al_2O_3 coating serves as a stable artificial SEI for Na metal, resulting in both carbonate-based and ether-based symmetric cells with enhanced electrochemical performances. Furthermore, our group firstly demonstrated MLD alucone coatings for Na metal³⁸⁰. As shown in **Fig. 18(c)**, the MLD alucone presented strong surface bonding on the surface of Na metal. Fig. 18(c) also shows the electrochemical performances of the symmetrical cells for both Na@25alucone and the pristine Na foil at $1\text{ mA cm}^{-2}/1\text{mAh cm}^{-2}$ in the $NaPF_6$ -carbonate electrolyte. From the results, the Na@25alucone presented more stable plating/stripping performances with reduced dendrite growth and double the lifetime.

ALD was also used to fabricated SSEs for Na-based SSBs. Nuwayhid et al. firstly demonstrated a thermal ALD process for sodium phosphorus oxynitride (NaPON), a thin-film SSEs³⁸¹. In the ALD process, sodium tert-butoxide ($NaOtBu$) and DEPA were used as precursors with the deposition temperature at 250–400 °C. The ALD process produced a conformal film with a stoichiometry of Na_4PO_3N , corresponding to a sodium polyphosphazene structure. The ionic conductivity of the NaPON film was as high as $1.0 \times 10^{-7}\text{ S cm}^{-1}$ at 25 °C and up to $2.5 \times 10^{-6}\text{ S cm}^{-1}$ at 80 °C with an activation energy of 0.53 eV. Their promising result makes NaPON a viable SSE or passivation layer for Na-based SSBs.

2.1.3.3 ALD/MLD for other batteries

The application of ALD/MLD has also been extended to other battery systems, such as Al-ion, K-ion, and Zn-ion batteries³⁸²⁻³⁸⁵. For example, Huang's group demonstrated uniformly coated ALD amorphous V_2O_5 on CNTs as a cathode for K-ion batteries³⁸⁵. The $V_2O_5@CNT$ sponge cathode deposited by ALD exhibits the reversible capacity of 206 mA hg^{-1} and stable cycling performances in the carbonate-based electrolyte. Liu et al. utilized ALD Al_2O_3 coating to modify solid electrolyte interphase (SEI) on biomass carbon anode in K-ion batteries and improve the average CE from 99.0% to 99.6%³⁸⁶. ALD protection coatings were also proposed to be effective for Zn metal anodes, where ALD TiO_2 and Al_2O_3 was used as a demonstration³⁸⁷. The ALD layer can prevent the gas generation on the Zn metal anode and maintain effective contact between the Zn and electrolyte, resulting in enhanced Coulombic efficiency. The protected Zn metal anode can

be cycled in the Zn-MnO₂ batteries over 1000 cycles with a capacity retention of 85%. Furthermore, ALD was used to deposit nanoscale ZnO on the current collector as a binder-free cathode for rechargeable Al-ion batteries³⁸³. The electrochemical results showed that binder-free ALD grown ZnO cathode manifested a high initial discharge capacity of 2563 mAh g⁻¹, which was significantly higher than that of the cells fabricated with the ZnO powder as the cathode. However, the capacity decay is serious with only 245 mAh g⁻¹ at a current rate of 400 mA g⁻¹ after 50 cycles. Further efforts are needed to stabilize the cycling stability of this cathode material for Al-ion batteries.

In this section, the applications of ALD/MLD for Na batteries and beyond (including Na-ion batteries, Na-metal batteries, Al-ion batteries, Zn-ion batteries) have been discussed in detail. The studies on this topic are not as prominent compared to Li metal batteries, but promising progress has been reported. Firstly, several types of electrode materials were fabricated by ALD with controllable structure and thickness. Secondly, the ALD coating was deposited as a coating for both anode and cathode electrolyte in different battery systems. On the cathode side, the ALD layers were used to prevent side reactions and transition metal dissolution during cycling. On the anode side, the ALD coating served as a buffer layer to relieve the volume change and stabilize the SEI layer. Particularly, the ALD/MLD coatings were effective for metal anodes, such as Na metal and Zn metal anode. Thirdly, ALD was considered to synthesize the catalysis as an air electrode for Na-O₂ batteries.

2.2 ALD/MLD for supercapacitor

2.2.1 ALD for electrode fabrication

Supercapacitors are another important electrochemical energy storage system with higher power density compared to batteries³⁸⁸. However, the energy density of supercapacitor is not as high as traditional LIBs. This makes supercapacitor suitable for applications that require short power bursts but not necessarily high energy density^{389, 390}. Another great advantage of supercapacitors is the extremely long lifetime due to the charge storage mechanism, which is based on splitting charge at the surface of the electrodes in an electric double layer without chemical reactions³⁹¹⁻³⁹³. Moreover, supercapacitors are generally safer than batteries for high power-rating charging and discharging^{394, 395}.

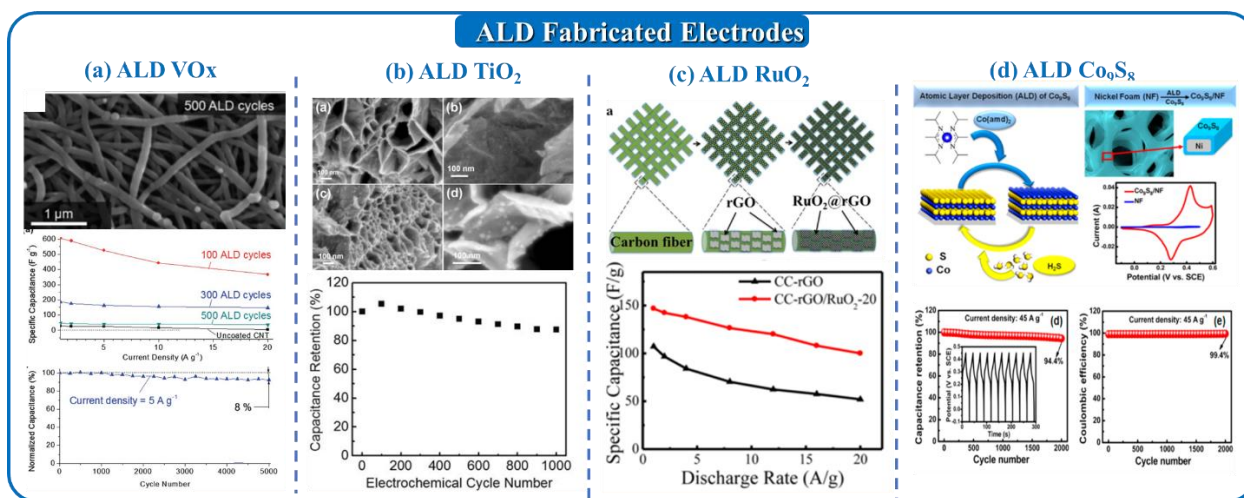


Fig.19 ALD fabricated electrodes for supercapacitors: (a) ALD VO_x³⁹⁶; (b) ALD TiO₂³⁹⁷; (c) ALD RuO₂³⁹⁸; (d) ALD Co₉S₈³⁹⁹.

The performance of supercapacitors is highly dependent on the surface/near-surface reactions on the electrodes, which is one of the most significant factors for determining the performance of the supercapacitor. ALD/MLD has been used to deposit active materials on different substrates to fabricate composite electrodes for supercapacitors^{230, 400, 401}. For example, Yushin's group fabricated VO₂/multi-walled carbon nanotube (MWCNT) composite electrodes by ALD with controlled thickness and porosity, greatly improving the electrical conductivity and cycling stability (**Fig.19 (a)**)³⁹⁶. The results show that the thin VO₂ films on the MWCNTs present higher capacitance, in which the 10 nm thick VO₂ exhibited the highest capacitance of 1550 F g⁻¹ at a current density of 1 A g⁻¹. Moreover, the charge-discharge tests show stable performance with high capacitance retention over 5000 cycles. TiO₂ is also a promising candidate with impressive capacitance behaviour. However, the low ion diffusion coefficient and high electrical resistance limit its further application^{402, 403}. To address these issues, Sun et al. deposit TiO₂ on graphene to prepare TiO₂-G composites for supercapacitors³⁹⁷. As shown in **Fig.19 (b)**, the surface of the wrinkled graphene is uniformly covered by TiO₂ nanoparticles, in which the particle size is 10 nm after 100 ALD cycles. The 50 cycles-TiO₂-G and 100cycle-TiO₂-G composites deliver the capacity of 75 F g⁻¹ and 84 F g⁻¹ at a scan rate of 10 mV, respectively. The composite electrode shows good cycling performance up to 1000 cycles at 2 A g⁻¹, as shown in **Fig.19 (b)**. The composite electrode

deposited by ALD possesses excellent conductivity for charge transfer and open structures for ion diffusion. Furthermore, their group demonstrated that ALD TiO₂ coated on CNT could lead to a higher capacitance of 135 F g⁻¹ at 1 A g⁻¹ with excellent stability over >1000 cycles⁴⁰⁴. Other transition metal oxides, such as NiO, Co₃O₄, Mn₃O₄, Fe₂O₃, WO₃, et al, were deposited by ALD on different conductive substrates to fabricate electrodes for supercapacitor⁴⁰⁵⁻⁴¹⁰. For example, NiO is one of the most popular electrode materials due to the high theoretical specific capacitance of 2573 F g⁻¹, environmental friendly and low cost. Qin's group applied the ALD technique to deposit NiO nanoparticles of various sizes on the nanoporous graphene (NG) as the electrode for supercapacitor⁴⁰⁵. The NiO/NG composite with 500 ALD cycles presented the best performance with a high specific capacitance of up to 1005.8 F g⁻¹ at current densities of 1 A g⁻¹. The ALD deposited metal oxides with controlled size and uniform coverage provide short ion diffusion pathways and the conductive substrate can significantly enhance the conductivity of the metal oxides. Moreover, noble metal oxides, such as RuO₂, are considered as one of the highest performing pseudocapacitive material candidates⁴¹¹. Realized by ALD, a very small amount of RuO₂ (~9.3 wt % Ru) leads to a 40% increase in capacitance for the graphene electrodes³⁹⁸, as shown in **Fig.19 (c)**. Moreover, the strong chemical bonding between RuO₂ and graphene results in excellent cycling stability with over 92% capacitance retention over 4000 cycles.

Additionally, metal sulfides and metal nitrides have also been used as electrode materials for supercapacitors⁴¹². This was exemplified by Wang's group, in which a Co₉S₈ film was deposited on a Ni foam electrode³⁹⁹. The deposition process used bis(N,N-diisopropylacetamidinato)cobalt (II) and H₂S as the precursors for the ALD Co₉S₈ process, as shown in **Fig. 19 (d)**. With 2000 ALD cycles, 54 nm Co₉S₈ was coated on the Ni foam to form the Co₉S₈/NF electrode. In the 2 M KOH aqueous electrolyte, the excellent specific capacitances of 1645, 1616, 1544, 1493, 1378, and 1309 F g⁻¹ can be obtained for the Co₉S₈/NF electrode at the current densities of 3, 6, 12, 15, 30, and 45 A g⁻¹, respectively. Furthermore, the prepared electrode exhibited stable long-term cycling performance with 94% retention at a current density of 45 A g⁻¹ up to 2000 cycles. Other metal sulfides, such as MoS₂ and SnS₂, were also developed by ALD as electrodes for supercapacitors^{413, 414}. For example, molybdenum hexacarbonyl [Mo(CO)₆] and H₂S were used as precursors to deposit MoS₂ on Ni foam substrates⁴¹³. A high areal capacitance of 3400 mF cm⁻² was obtained for the MoS₂@NF electrode with an optimized MoS₂ thickness of 400 ALD cycles at a current

density of 3 mA cm^{-2} . A high cyclic stability ($>80\%$ specific capacitance retention) was achieved for over 4500 cycles.

2.2.2 ALD for design of nanostructures

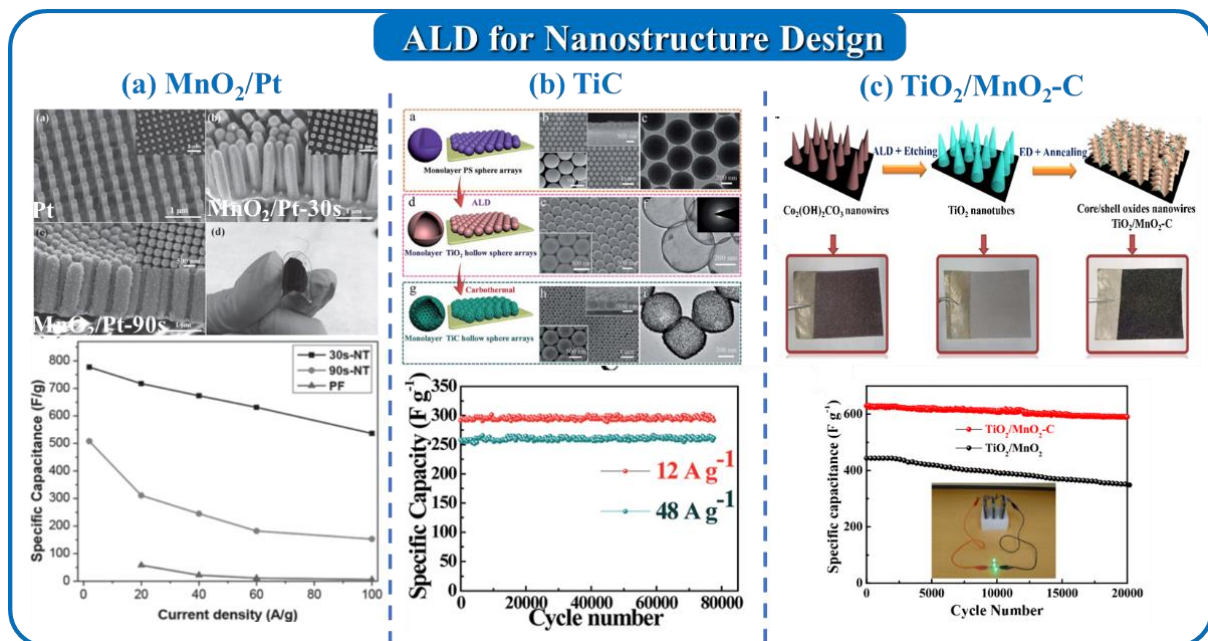


Fig.20 ALD-designed nanostructured electrodes for supercapacitors: (a) MnO_2/Pt ⁴¹⁵; (b) TiC ⁴¹⁶; (c) $\text{TiO}_2/\text{MnO}_2\text{-C}$ ⁴¹⁷.

To further improve the performance of supercapacitor electrodes, nanostructured materials need to be rationally designed in order to enhance surface area and porosity. ALD/MLD techniques are promising techniques that can be used to design various nanostructures by using sacrificial templates. Lei's group designed well-defined Pt nanotube arrays and Pt/ MnO_2 core-shell nanotubes by ALD in anodic alumina templates and used them as current collectors⁴¹⁵. In this process, the Pt NT array was first grown on the pre-patterned alumina template by ALD. Unlike the conventional ALD process for Pt deposition, an innovative ALD process for Pt was developed with a low N_2 filling step used after pulsing. In their ALD Pt deposition process, the nucleation delay phenomenon largely decreased, and half of the Pt precursor was saved to obtain a similar Pt film deposited by the conventional ALD process. After the Pt deposition, mixed polydimethylsiloxane (PDMS) solution was used on the surface of the template followed by dissolving the backside alumina template. Then, a thin MnO_2 layer was deposited on the Pt

nanotubes by electrodeposition. The diameter and length of the Pt nanotubes are 180 nm and 2 μm , respectively. The MnO_2 shells were electrodeposited on Pt cores and controlled by the deposition times, as shown in **Fig.20 (a)**. When the MnO_2 deposition time was 30 s, the tube diameter and the shell thickness was about 240 and 30 nm, while the diameter and thickness reach up to about 340 and 80 nm respectively for 90 s deposition time (**Fig. 20 (a)**). The Pt/ MnO_2 -30s delivered a higher capacity of 793 F g^{-1} at a current density of 2 A g^{-1} compared to the 530 F g^{-1} of Pt/ MnO_2 -90s. Moreover, the Pt/ MnO_2 presents good rate capability at different current densities, as shown in **Fig.20 (a)**, which was attributed to the superior surface area of the Pt nanotube that could enable fast and reversible Faradic reactions along with short ion diffusion paths. Another nanostructured TiC hollow sphere array was fabricated on a conductive substrate by the ALD-assisted template synthesis strategy⁴¹⁶, as shown in **Fig. 20 (b)**. In a typical process, close-packed PS spheres were used as a template on the graphite substrate. The ALD TiO_2 was deposited on the template and the PS spheres were dissolved by toluene. Finally, the monolayer of TiC hollow nanosphere arrays was successfully formed after a high-temperature carbothermal reaction. The designed electrode delivered excellent electrochemical performances with high capacitance, ultra-long lifespan over 75,000 cycles with a high capacity retention of 98% and promising rate capability. Another interesting structure of $\text{TiO}_2/\text{MnO}_2$ -C core/shell arrays were designed and fabricated using a combination of ALD and electrodeposition methods⁴¹⁷, as shown in **Fig.20 (c)**. A high specific capacitance of 880 F g^{-1} at 2.5A g^{-1} , exceptional rate performances of 735 F g^{-1} at 30A g^{-1} and excellent cycling stability of 94.3% capacitance retention after 20000 cycles were obtained for the $\text{TiO}_2/\text{MnO}_2$ -C electrodes. Some other nanostructures were further developed using ALD-assisted methods^{238, 417-423}. In a typical process, different types of templates are used to deposit ALD films. Afterwards, the templates are removed or transferred to create nanostructures by post-treatment processes. Then, the 3D nanostructures with high surface area and short ion diffusion paths are achieved with significantly improved electrochemical performances.

2.2.3 MLD for electrode design

MLD has also been reported as a fabrication method for electrode materials in supercapacitor. Because MLD films generally consist of pure polymers or organic-inorganic hybrid films, they are used to design porous metal oxides and carbon-containing composites with post-treatment methods. Qin's group was the first to demonstrate the use of MLD to design electrodes for supercapacitors, in which aromatic polyimide (PI) films were deposited on the surfaces of graphene and then

carbonized to produce a nitrogen-doped carbon layer on graphene⁴²⁴. The as-prepared N-doped carbon layer-coated graphene electrodes exhibited a high capacitance of 290.2 F g⁻¹ at 1 A g⁻¹ with excellent rate properties and stability. In another example, a gap shell structure with an ultrathin and conformal porous carbon coating was successfully constructed through ALD and MLD processes followed by annealing and etching⁴²⁵. The as-obtained composite electrode exhibited a high capacitance of 1034.6 F g⁻¹ at a current density of 1 A g⁻¹ with superior rate capability. The gap-porous carbon derived by ALD/MLD can not only maintain the electrochemical reactivity of nickel sulfide but also provide a protective layer with a buffer area for volume change.

In this section, we summarized the development of ALD/MLD techniques for supercapacitor applications. Firstly, different materials, including metal oxides, metal sulfides and metal nitrides, were deposited by ALD on various conductive substrates to fabricate composite electrodes for supercapacitors. The conductive substrates, such as graphene, carbon nanotube and Ni foam, provide improved electronic conductivity for the ALD-deposited materials. The nanoscale materials deposited by ALD can provide uniform coverage and short ion diffusion pathways, resulting in enhanced electrochemical performances. Secondly, by combining with other methods or using templates, ALD was used to design and fabricate nanostructured materials with high surface areas. Thirdly, MLD was used to create porous metal oxides and carbon-contained composite by post-treatment methods. However, the study of MLD films for supercapacitor applications is still in a state of infancy. This application of MLD is expected to be explored further in the future.

3. ALD/MLD for energy conversion

3.1 ALD/MLD for electrocatalytic reactions

3.1.1 ALD/MLD for proton-exchange membrane fuel cells

3.1.1.1 ALD of Pt on different substrates for improving ORR activity

Proton-exchange membrane fuel cells (PEMFC) are promising alternative power sources for transportation and portable applications due to their high efficiency in converting the chemical energy from hydrogen into electrical energy, near room temperature operation, and zero

emissions.⁴²⁶ During the operation of PEMFCs, the oxygen reduction reaction (ORR) is the rate-limiting reaction due to its inherently sluggish kinetics. Therefore, in order to achieve widespread commercial implementation of PEMFCs, developing a promising catalyst for enhanced oxygen reduction reaction (ORR) kinetics is of great significance. Platinum is reported as the most effective catalyst used for the ORR in PEMFC.^{427, 428} However, Pt is still meeting a great challenge for the commercial applications in PEMFCs due to its gradually increasing price and low abundance in the earth. ALD is a promising technique to solve the problems associated with reducing the cost. ALD can not only precisely control the particle sizes ranging from single atom, sub-nanometer clusters, or nanoparticles in high-aspect-ratio and porous materials, but can also be used to design novel structures through surface engineering of the substrate to improve the activity of Pt catalysts.⁴²⁹

Aaltonen et al. made great progress in ALD synthesis by deposition of Ru metal from RuCp₂ and O₂, and the process has been extended to other metals such as Pt, Rh, and Ir^{430, 431}. The intrinsic roughness of the surface induced by noble metal ALD processes can effectively increase the surface area of the catalyst, leading to a more efficient device.^{19, 432} Due to the self-limiting characteristic of ALD process, the precursor should be volatile and thermally stable. In addition, precursors must chemisorb on the surface or react rapidly with the substrates and react aggressively with each other.⁴³³ Until now, Pt precursors such as MeCpPtMe₃, Pt(acac)₂ (acac=acetylacetonato) and platinum(II) hexafluoroacetylacetonate [Pt(hfac)₂] have been investigated for the deposition of Pt. However, Pt(acac)₂ has lower thermal stability, which makes it an unsuitable precursor for thermal ALD.^{434, 435} When using Pt(hfac)₂ as the precursor, the formalin should be used as the reactants and the ALD process was found to be only effective at relatively high temperatures (200 °C).⁴³⁶ Therefore, MeCpPtMe₃ is the most widely used Pt precursors in ALD for the preparation of Pt NPs used in ORR. During the ALD Pt process, the island growth of Pt NPs occurs instead of thin film formation. In a whole Pt ALD cycle, the Pt precursors firstly bond with the functional groups on the surface of the substrates. Then the chemical ligands are removed by the introduction of O₂ or O₃. The formed Pt atoms might aggregate to small clusters due to the limited number of functional groups on the substrate surface, which leads to the formation of Pt NPs instead of a thin film on the substrates. Hence, the selection of substrate is of great importance for ALD Pt NPs, and it can significantly determine the ORR activity of the catalysts. Pt nanoparticles (NPs) are deposited on substrates such as oxides, carbon materials and other metals.

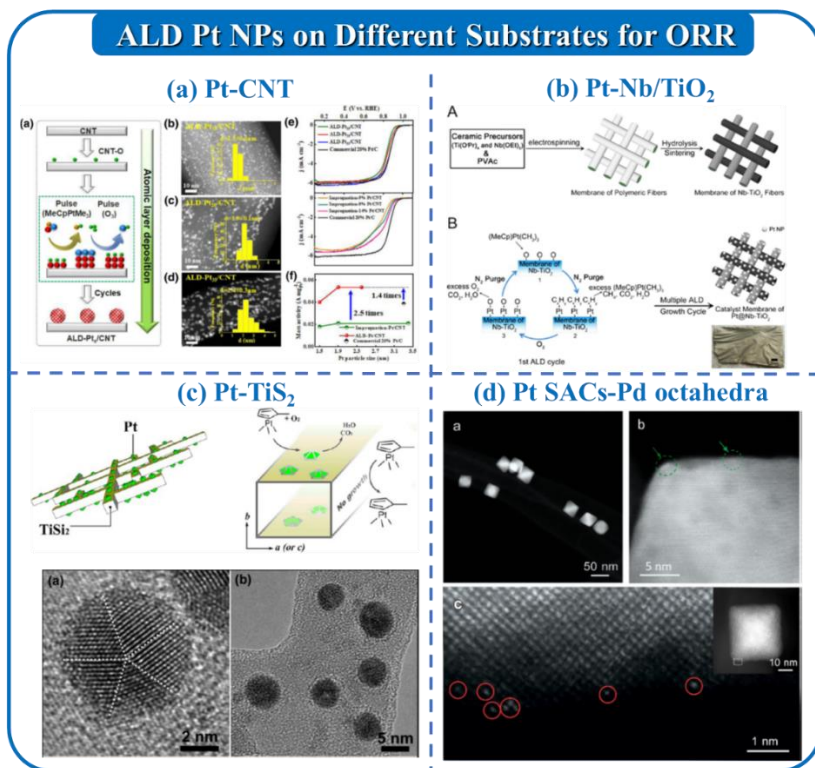


Fig. 21 ALD of Pt NPs on different substrates by using MeCpPtMe₃ for ORR: (a) Pt NPs on CNTs; (b) Pt NPs on Nb-TiO₂; (c) Pt NPs on TiS₂; (d) Pt single atoms on octahedral Pd NPs.

Carbon nanotubes (CNTs) are one of the most widely used carbon substrates for the deposition of Pt. Chen and co-workers prepared three carbon nanotube-supported Pt nanoparticles (Pt/CNT) with different sizes by tuning the number of ALD cycles (**Fig. 21 (a)**).⁴³⁷ In addition, they compared the ALD-prepared catalysts with those obtained by impregnation methods. During the ORR test, the ALD-Pt/CNT catalysts showed much higher activity and selectivity than the impregnation-Pt/CNT catalysts. It was found that the well-controlled Pt particle size and distribution, desirable Pt⁰ 4f binding energy, and the Cl-free Pt surfaces of the ALD-Pt/CNT catalysts contributed to the outstanding ORR performance. Besides carbon-based supports, Yang and co-workers fabricated fibrous membranes of niobium-doped titania-supported platinum catalysts (Pt@Nb-TiO₂) by a two-step approach (**Fig. 21 (b)**).⁴³⁸ Firstly, they synthesized Nb-TiO₂ fibrous membranes by electrospinning. Then the Pt NPs were deposited on Nb-TiO₂ by ALD. The as-prepared catalysts were further post-treated at 200 °C in 5% H₂ to improve the conductivity of Nb-TiO₂ fibres and obtain Pt NPs with better crystallinity. After the post-treatment, the ORR

activity could reach as high as 0.28 mA/cm² at 0.9 V (vs RHE) and it had very good stability with only a ~10% loss in ORR activity after 30 k cycles. When Pt is deposited on TiSi₂ nanonets, Pt nanoparticles were observed to only grow on the (020) planes and the NPs exhibited 5-fold twinned structures with planes exposed, as shown in **Fig. 21 (c)**.⁴³⁹ The interaction between Pt and the TiSi₂ nanonet b planes was the key to the formation of twinned Pt nanoparticles. At 0.9 V vs. RHE, the current density of the Pt/TiSi₂ catalysts was 0.16 mA cm⁻², which is considerably higher than that of Pt/C (0.1 mA cm⁻²). The availability of non-carbon electrode constructions, such as the Pt@Nb-TiO₂ and Pt/TiSi₂, permits fundamental studies to discern the role of carbon support in existing devices.

To improve the mass activity of Pt catalysts and thereby reducing the cost of the catalyst, one of the most direct routes is to increase their atom utilization efficiency (AUE) by reducing the particle size to clusters or even single atoms.⁴⁴⁰ However, the single atom Pt catalysts exhibit a 2 electron process instead of 4 electron process during the ORR.⁴⁴¹ DFT results indicate that the breaking of the O–O bond can readily occur on Pt nanoparticles. While for single atoms, the O₂ molecule is end-on adsorbed on isolated Pt atoms (which avoids O-O cleavage), resulting in the selective production of H₂O₂.^{442, 443} It has been reported that Pt single atoms can not only be deposited on carbon-based support^{444, 445}, but also on a metal surface, forming the single atom alloys (SAA). Sun et al. successfully deposited Pt single atoms on octahedral Pd NPs due to the similar lattice constants between Pd and Pt. To obtain Pt single atoms, we only conducted one cycle of ALD by using MeCpPtMe₃ and O₂ as precursors.⁴⁴⁶ The atomic-resolution STEM image (**Fig. 21 (d)**) clearly illustrates the presence of Pt-isolated atoms on the Pd (111) surfaces. With the formation of SAA structure, the Pt atoms on Pd exhibited more metallic state compared to that on NCNTs. The coordination number of Pt-Pd is fitted to be 0.8 in the EXAFS spectra, which further provides direct evidence on the presence of isolated Pt atoms on octahedral Pd particles. In ORR, the octahedral Pt/Pd SAA catalysts exhibited a mass activity of 1.09 A·mg⁻¹ normalized by the Pt mass at 0.9 V vs. RHE, which is 8.3 times greater than that of the Pt/C catalyst (0.13 A·mg⁻¹).

3.1.1.2 Improvement of ORR durability by area selective ALD and MLD

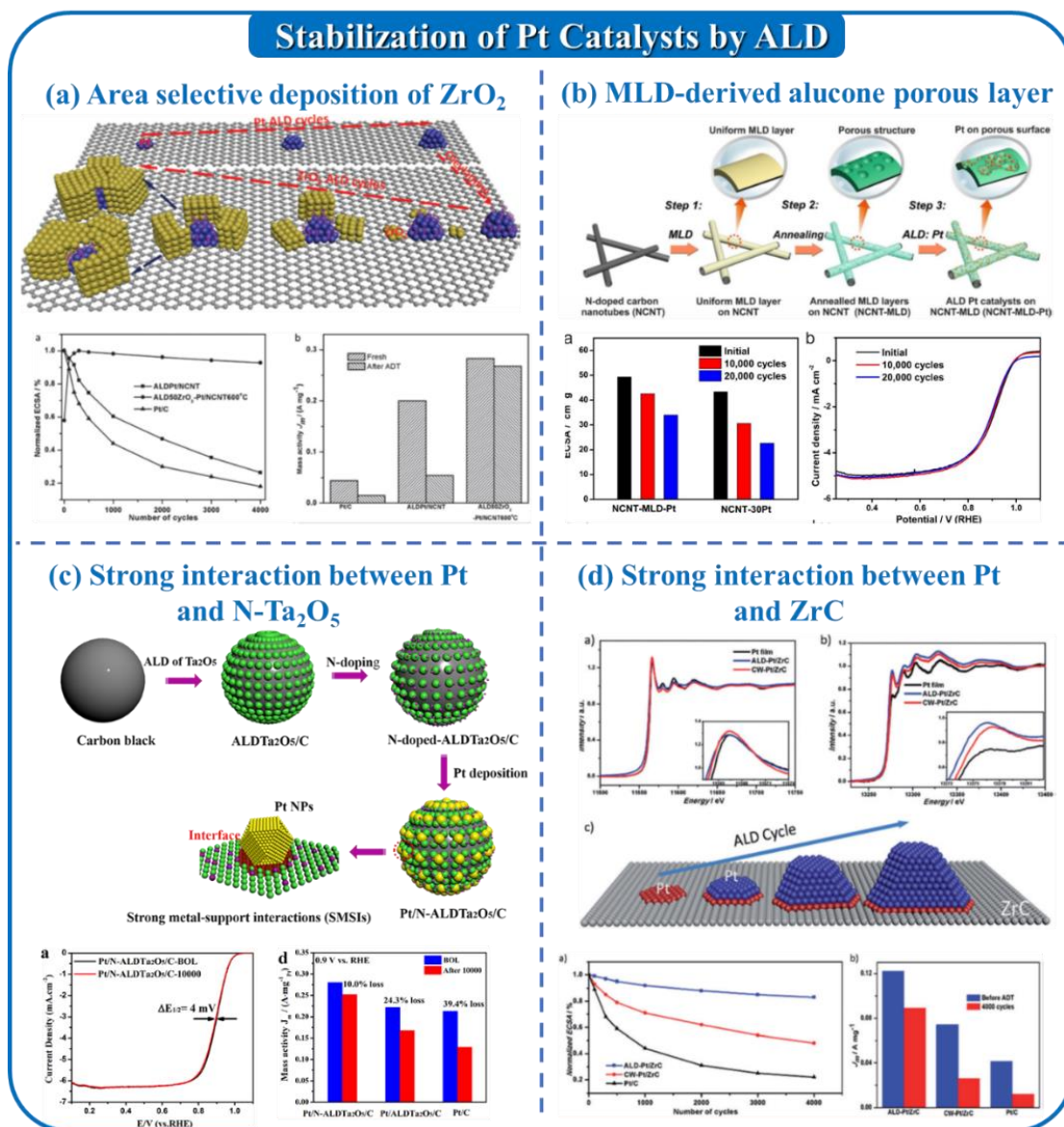


Fig. 22 ALD/MLD for Pt catalyst stabilization: (a) area-selective ALD of ZrO_2 ; (b) MLD alucone-derived porous carbon layer; (c) ALD of Pt on N-Ta₂O₅; (b) ALD of Pt on ZrC substrates.

In addition to the activity, durability is another important parameter for evaluating Pt catalysts. The harsh conditions (strong acid environment, high oxygen concentration, high humidity and etc.) at the cathode might gradually deactivate Pt catalysts, resulting in the loss of Pt performance due to Pt NP migration and agglomeration. Thus, there is a significant need for the development of highly active and durable Pt catalysts that can withstand harsh conditions for long-term testing. It has been reported that the creation of the porous layer of inorganic oxide is an

effective route for the stabilization of supported metal NPs. The surrounding oxide layer, which has weaker bonding to metal NPs, can provide an additional energy barrier to restrict the diffusion and migration of the metal NPs across the biphasic support surface. However, for many methods, precise control over the thickness of the porous overlayers is difficult to achieve and results in a decrease in ORR activity from mass transfer resistance. By using ALD, the thickness of the stabilizer can be precisely controlled. McNeary et al. stabilized carbon black-based Pt catalysts with ALD-deposited TiO_2 .⁴⁴⁷ They found that ten cycles of TiO_2 ALD on the functionalized substrate yielded well dispersed, locally homogenous TiO_2 structures that could surround the small Pt nanoparticles. The catalysts with the addition of TiO_2 ALD nanostructures maintained around 70% mass activity after the accelerated durability testing (ADT).

By manipulating the surface functional groups of Pt catalysts, area selective ALD can be achieved, which means that the location of deposited materials is precisely controlled, avoiding the coverage of Pt active sites.^{336, 448, 449} One of the most successful designs for highly stable catalysts is Pt catalysts encapsulated in zirconia nanocages by area-selective ALD.⁴⁵⁰ The synthetic strategy is depicted in **Fig. 22 (a)**. The ALD Pt NPs were firstly deposited on nitrogen-doped carbon nanotubes (NCNTs). Then oleylamine was attached to the Pt NPs surface as a blocking agent, which results in the selective deposition of zirconia around the Pt NPs, instead of on the Pt surface due to the blocking agent. The Pt catalyst encapsulated in zirconium nanocages showed very high activity and stability towards (ORR) in acid media. The novel catalyst exhibited 9 times higher stability than ALD-Pt on NCNTs without zirconia nanocage and 10 times high stability compared to the state-of-the-art commercial Pt/C catalyst. Pt NPs encapsulated in a zirconia nanocage also showed six times greater ORR activity than Pt/C catalyst. The remarkably stable performance with this novel catalyst is attributed to the presence of the zirconia nanocages, which prevent Pt NPs from migrating and agglomerating on the support. In addition, the higher surface area of small Pt NPs and the synergistic effects between Pt and ZrO_2 resulted in the enhanced activity of Pt/ ZrO_2 catalysts. Besides ZrO_2 , TaO_x has also been reported as an alloying additive that can enhance the activity and durability of various catalysts. Our group deposited TaO_x NPs on a commercial Pt/C catalyst by area-selective ALD.⁴⁵¹ Due to the blocking agent, TaO_x particles are selectively nucleated and grown around Pt NPs. With the formation of the triple-junction structure at the interface, the sample with 35 ALD cycles of TaO_x on the Pt/C surface exhibited superior stability compared with Pt/C. After 120 h ADT, the activity in a membrane electrode

assembly (MEA) maintained 88%. These examples show that it is critical to design novel Pt encapsulation catalysts with open or holey nanocage architectures by precisely controlling ALD metal oxide layers. The open or holey nanocage architectures are essential for achieving good performance because they allow reactants, such as oxygen and protons, to reach the Pt surface.

Molecular layer deposition (MLD), as an analogue of ALD, has been employed to produce inorganic–organic hybrid thin films with many advantages. Alucone is considered as a promising material as the interlayer to improve the stability of catalysts. However, the poor conductivity of MLD coating greatly hinders their application in electrochemical systems. Recently, Sun et al. prepared a porous structure by annealing the alucone MLD layer. With the deposition of Pt NPs on the porous structure, the Pt catalysts were anchored on the surface and exhibited good performance.⁴⁵² As shown in **Fig. 22 (b)**, 30 cycles of MLD alucone (TMA-GLY) thin film was firstly deposited on the NCNTs using sequential exposures of TMA and glycerol at 150 °C. After annealing the NCNT-MLD material at 400 °C for 3 h, Pt NPs are selectively deposited on the porous structure by ALD method. The Pt catalysts show significantly enhanced ORR activity and durability compared to that without the MLD interlayer.

3.1.1.3 Improvement of ORR durability by enhancing the interactions between Pt single atoms and supports

Carbon-based substrates have many advantages, such as large surface area, high electrical conductivity and well-developed pore structure, and thus have been widely applied as the support material in electrochemistry. However, the weak interactions between carbon support and metal particles lead to Pt NP migration and agglomeration, and eventually a rapid degradation of electrocatalyst performance. To solve these issues, enhancing the interaction between Pt NPs and carbon supports by ALD oxide has been proposed. The strong metal-support interactions (SMSIs) can improve the activity and durability of the Pt catalysts by tuning the electronic structure and hindering metal particle migration. In addition, the preparation of metal oxide-decorated carbon composites for the deposition of Pt NPs can maintain the good electroconductivity of substrates. By introducing metal oxide NPs to the position between Pt catalyst and carbon support, a stable and strong interface between the Pt and metal oxide can be achieved, which plays a significant role in preventing the rapid degradation of catalytic activity.

For example, Sun et al. synthesized extremely stable Pt NPs immobilized on carbon support via a bridge layer of nitrogen-doped tantalum oxide (N-Ta₂O₅).³³¹ Firstly, the Ta₂O₅ NPs were developed by ALD to decorate the carbon black surface. Then, NH₃ treatment of ALDTa₂O₅/C support was conducted to dope N species, leading to the formation of N-doped-Ta₂O₅/C with enhanced conductivity. Finally, a microwave-assisted ethylene glycol (EG) reduction method was used to deposit Pt NPs on different supports. X-ray absorption spectroscopy indicated that the total unoccupied density of states of Pt in the Pt/N-ALDTa₂O₅/C is higher than that of 0.826 for Pt/ALDTa₂O₅/C and 0.795 for Pt/C. This result provides the most direct evidence for the electronic effects and SMSIs formed between the Pt NPs and N-Ta₂O₅/C support. The as-prepared Pt/N-ALDTa₂O₅/C catalyst showed around two times higher mass activity compared to Pt/C after 10,000 cycles of ADT (**Fig. 22 (c)**). Another metal oxide used for increasing the interaction between Pt and support is ZrO₂. Cheng and co-workers synthesized ALD-ZrO₂/nitrogen-doped graphene nanosheets (ZrO₂/NGNs) as the support for Pt NPs.⁴⁵³ The unique triple-interface of ZrO₂-Pt-NGN induced strong interaction between Pt NPs and supports. As a result, the Pt-ZrO₂/NGNs catalyst exhibited 2.2 times higher durability than that of Pt/NGNs in ORR testing. These attempts provide more strategies for the preparation of well-dispersed, nanoscale metal compounds for carbon surface modification towards achieving controllable and well-defined metal-support interfaces.

In addition to the introduction of metal oxides between the carbon support and Pt NPs, the substitute for carbon-based support with other materials is another promising strategy for improving the durability of Pt catalysts. Among various supports, ZrC has many advantages, such as high conductivity, strong electrochemical corrosion resistance, high stability, and good thermal conductivity, which makes it as a good substitute for Vulcan XC-72 (carbon black) support. Based on this, Sun et al. used a ZrC support as a substitute for carbon-based support for the ALD of Pt NPs.⁴⁵⁴ As shown in **Fig. 22 (d)**, we synthesized a robust Pt-on-ZrC nanocomposite catalyst with strong metal-support interactions by ALD. The quantitative XANES results showed that the interactions between Pt and ZrC support by ALD is much higher than that prepared from the conventional chemical reduction method. Due to the strong interaction between Pt and ZrC, the exhibited ORR activity was 9 times greater than Pt/C after the extended durability test.

3.1.1.4 ALD for MEA systems

On the anode side, the fast hydrogen oxidation reaction (HOR) is driven by a small amount of Pt/C catalyst. However, when the Pt loading is lower than $0.025 \text{ mg}\cdot\text{cm}^{-2}$, the HOR performance would obviously decreased due to the very thin layer thickness. Therefore, the Pt loading at the anode needs to be further decreased for fuel cell automotive applications. Hsieh et al. directly deposited Pt NPs by ALD on a gas diffusion electrode consisting of CNT and GO. The MEA was fabricated using a ALD-Pt electrode as the anode to study the performance of a single cell, which offered improved catalytic activity.^{455, 456} Recently, Shu et al. deposited Pt NPs on gas diffusion layer by ALD method.^{457, 458} The formed catalyst layer exhibited around 2.5 times higher mass activity than that of the MEA with the anode prepared using the commercial catalyst. Perng and co-workers grew Pt NPs on nitric acid-treated CNTs with ALD for catalysis in PEMFCs.⁴⁵⁹ The Pt loading amount of anode and cathode (0.019 and 0.044 mg cm^{-2} , respectively) in the MEA is significantly reduced. In addition, the PEMFC test indicated that the specific power density of ALD-prepared MEA is 11 times higher than that made from commercial catalysts. This result revealed that ALD can significantly decrease the Pt loading of the electrodes in PEMFCs. To achieve extremely low Pt loading while maintaining high PEMFC performance and durability, Sun et al. prepared a series of membrane electrode assemblies (MEAs) with low Pt loading in the anode layer through the use of ALD.⁴⁶⁰ The best ALDPt-MEA with an ultralow anode Pt loading of $0.01 \text{ mg}\cdot\text{cm}^{-2}$ displays a high surface area of $155 \text{ m}^2\cdot\text{g}^{-1}_{\text{Pt}}$. During the PEMFC test, the ALDPt-MEA exhibited a power density of $0.78 \text{ W}\cdot\text{cm}^{-2}$, and maintained around 90% after ADT (**Fig. 23 (a)**). The above studies demonstrated that the application of ALD for Pt deposition directly on the carbon layer of the electrodes can effectively reduce the Pt loading while enhancing the Pt dispersion, utilization, and durability, thus enhancing their performance on MEA anodes.

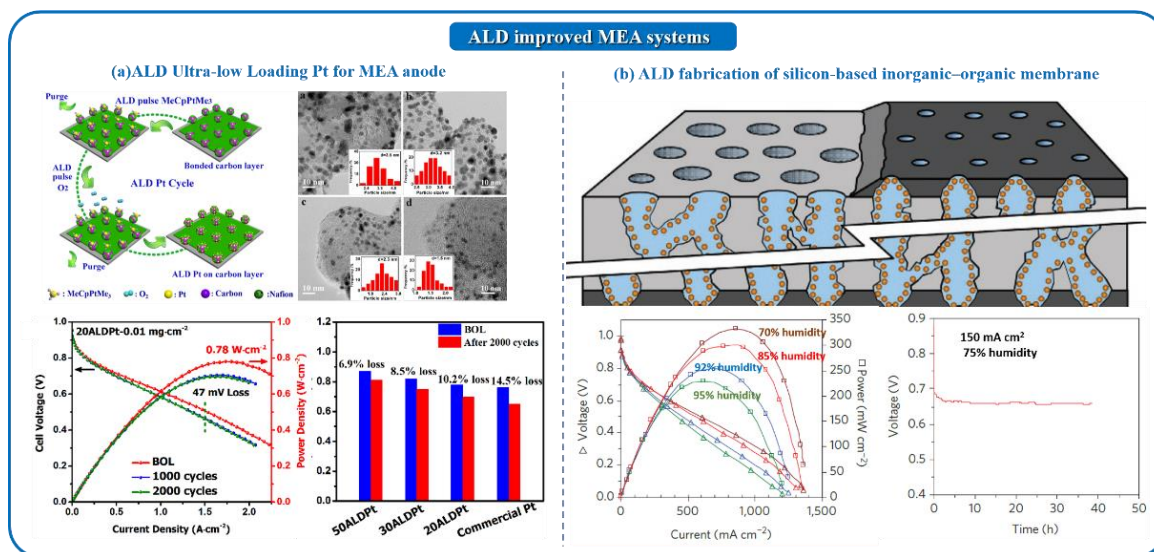


Fig. 23 The application of ALD towards the fabrication of MEA systems: (a) ALD fabrication of ultra-low Pt loading anode; (b) ALD-modified silicon-based inorganic-organic membrane.

In addition to the fabrication of active Pt catalysts, ALD has also been applied for the improvement of membrane properties. Moghaddam and Shannon prepared a silicon-based inorganic-organic membrane as a substitute for Nafion-based PEMFCs (**Fig. 23 (b)**).⁴⁶¹ Silicon-based inorganic-organic membranes have a number of advantages over Nafion, including higher proton conductivity, a lack of volume change, and membrane electrode assembly capabilities. A silicon membrane with pore diameters of $\sim 5\text{--}7$ nm was firstly fabricated, followed by the addition of a self-assembled molecular monolayer on the pore surface. The plasma-directed atomic layer deposition (PD-ALD) was employed to create a 2-nm thick hydrophilic silica aperture at the mouth of the pores. With the formation of the silica layer, the diameter of the pores is reduced, and the proton conductivity value is significantly increased, which is two to three orders of magnitude higher than that of Nafion at low humidity. The MEA with this membrane exhibited much higher power density than previously achieved with a dry hydrogen feed and an air-breathing cathode. Inside the membrane, the catalysts are expected to catalyze water production. The introduction of metal oxide nanoparticles that have hygroscopic properties, such as TiO_2 , can absorb the water produced in the cathode reaction. Uhm and Lee coated an ultrathin layer of hydrophilic TiO_2 on a hydrophobic microporous gas diffusion layer (GDL) at the cathode by ALD to maintain the power performance of PEFC cathodes operating under extremely low humidity.⁴⁶² They found that the

TiO₂-coated GDL resulted in higher performance than the as-received GDL at low humidity operation.

3.1.2 ALD for electrocatalytic small organic molecule oxidation

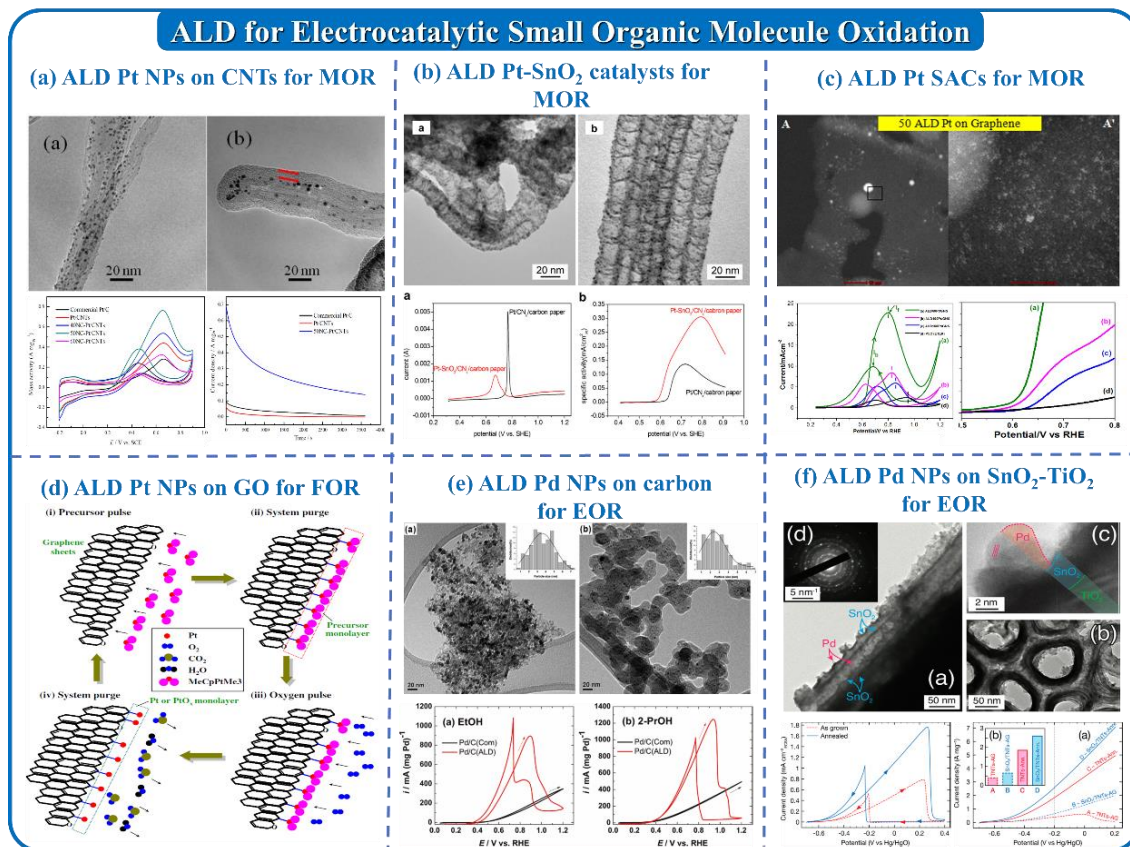


Fig. 24 ALD Pt and Pd NPs for electrocatalytic small organic molecule oxidation: (a) Pt-CNTs for MOR; (b) Pt-SnO₂ for MOR; (c) Pt SACs on graphene for MOR; (d) Pt NPs-GO for FOR; (e) Pt NPs on porous carbon for FOR; (f) Pd NPs on SnO₂-TiO₂ for EOR.

3.1.2.1 ALD for electrocatalytic methanol oxidation

The direct methanol fuel cell (DMFC) received more and more attention due to its high efficiency, high power density and short start-up transient-response time. Despite considerable advances in these points, the widespread application of DMFCs has been hindered by several technical and economical barriers. The low electrocatalytic activity of commercial Pt/C catalysts toward MOR and serious CO poisoning is the most severe challenges. By using ALD, Hsieh et al. fabricated Pt NPs on carbon powders, offering superior catalytic activity toward MOR. They found

that the ALD-Pt catalyst offers not only an improved catalytic activity toward methanol oxidation but also superior CO tolerance, as compared to commercial P/C. The substrates for Pt loading can also significantly affect the MOR activity.⁴⁶³ Qin and co-workers prepared a Pt/CNTs catalyst coated with N-doped carbon (NC-Pt/CNTs) by ALD (**Fig. 24 (a)**).⁴⁶⁴ Firstly, Pt NPs and polyimide (PI) are sequentially deposited on CNTs by ALD. Subsequently, the catalysts were annealed at 600 °C in a H₂ atmosphere, and the PI was carbonized to produce porous N-doped carbon. It was observed that the current density of NC-Pt/CNTs was 0.76 A mgPt⁻¹, which is 2.7 times higher than that of commercial Pt/C and 1.7 times higher than that of Pt/CNTs. The interactions between Pt and the N-doped carbon can weaken the Pt-CO bond, resulting in enhanced catalytic activity and durability for the MOR.

In addition to carbon substrates, metal oxide substrates have proven to be effective in minimizing the effect of CO poisoning. Peng and co-workers prepared Pt@ZnO catalyst on carbon cloth via ALD.⁴⁶⁵ Firstly, they deposited a ZnO seed layer on carbon cloth, followed by hydrothermal growth of high-density vertical aligned ZnO nanorods (NRs). To increase the surface hydrophilicity of the ZnO NR arrays, UV light irradiation was used prior to the deposition of Pt NPs on ZnO by ALD. XPS results indicated that Zn(OH)₂ species were formed on the ZnO NR arrays, which may enhance CO tolerance via a bifunctional mechanism. The negative binding energy shift of the Pt 4f peak and the positive shift of Zn 2p peak suggest that charge transfer occurs between the ZnO support and the Pt NPs. The electronic modification of surface Pt atoms via ligand effects could lower the adsorption energy of CO and improve the electrocatalytic activity on MOR. Thanks to the ZnO substrates, the catalysts exhibited 90% higher methanol oxidation activity than commercial Pt/C with the same Pt loading. Sun and co-workers deposited a 1.5 nm SnO₂ interfacial layer to anchor Pt NPs on CNTs by using SnCl₄ and H₂O as precursors (**Fig. 24 (b)**).⁴⁶⁶ In the electrochemical testing, the ECSA of Pt-SnO₂/CNTs is 1.36 times higher than that of Pt/CNTs. In addition, the Pt-SnO₂/CNTs also shows higher activity towards MOR than Pt/CNTs, as indicated by a 52 mV more negative onset potential, along with larger specific and mass activities. Recently, Mo₂C has also been used as an anode material for the direct oxidation of hydrocarbons in fuel cells. Chen and co-workers demonstrated a highly active and stable Pt nanoparticle/Mo₂C nanotube catalyst for methanol electro-oxidation.⁴⁶⁷ The peak current density of Pt NPs/Mo₂C for the MOR is 1.5 times higher than that of the commercial Pt/C catalysts.

A convenient way to modify the strong CO intermediate bonding interactions with the Pt catalyst is to make alloys or bi-metallic surfaces. To obtain bimetallic catalysts, the two metal precursors should have similar properties, as the ALD process is carried out using one precursor cycle followed by another precursor cycle. For example, Sairanen et al. prepared Pt-Co bimetallic catalysts by using $\text{Pt}(\text{acac})_2$ and $\text{Co}(\text{acac})_3$ as precursors.⁴³⁴ When compared with ALD mono-metallic Pt, the onset potential decreased by 50 mV and the current intensities of the Pt-Co catalysts were 1.5 times higher, which might be attributed to the electronic effect of Co on Pt. Another widely used catalysts for MOR are Pt-Ru bimetallic catalysts. It has been reported that the removal of CO is much faster on a Pt-Ru surface than on pure Pt.^{468, 469} For instance, Johansson and co-workers prepared highly dispersed Ru-decorated Pt nanoparticles using MeCpPtMe_3 , $\text{Ru}(\text{EtCp})_2$ and O_2 as the precursors.⁴⁷⁰ The Pt nanoparticles decorated with 5 ALD Ru cycles exhibited much better catalytic activity towards MOR compared with the undecorated Pt catalyst. Shim and co-workers synthesized Ru onto a porous Pt mesh by ALD and applied the heterogeneous Pt-Ru catalysts directly as the anode in direct methanol solid oxide fuel cells (DMSOFCs).⁴⁷¹ The obtained Pt/Ru catalyst after 100 ALD cycles outperformed pure Pt by more than 1 order of magnitude in terms of power output. The authors also deposited Ru by ALD on a porous Ni mesh to substitute Pt catalysts. The maximum power density of the Ni/ALD Ru sample was found to be comparable to that of the Pt/ALD Ru sample, despite the dramatic reduction (<10%) in precious metal catalyst loading.⁴⁷² The good performance of Ni/ALD Ru sample is due to the stabilizing effect of the Ni surface after ALD deposition of Ru and the prevention of carbon formation.

Decreasing the size of Pt nanoparticles is an effective route to increasing the surface area of Pt catalysts. In addition, the formation of clusters and single atoms can improve atom utilization to a new level. In 2013, Sun et al. reported a practical synthesis for single Pt atoms anchored to graphene nanosheets using the ALD technique.⁴⁷³ In this study, the Pt catalysts from single atoms, subnanometer clusters to nanoparticles were precisely controlled by ALD method. Among the three types of Pt catalysts, the single atom catalysts exhibited the best activity (**Fig. 24 (c)**). XAFS analysis revealed that the superior performance of single atoms was contributed by the low-coordination environment and partially unoccupied 5d states.

3.1.2.2 ALD for electrocatalytic formic acid oxidation

The fuel cells based on formic acid are particularly well-suited for applications related to room-temperature power generation and portable electronics. The performance of a direct formic acid fuel cell (DFAFC) is largely determined by the catalyst deposited on the anode for formic acid oxidation (FAO). Pt is an effective catalyst for FAO. Hsieh and co-workers fabricated Pt nanocatalysts supported on graphene oxide (GO) sheets by ALD and investigated their electrocatalytic performance in FAO.^{474, 475} The ALD-Pt atoms were decorated on the edges of the GO sheets with the presence of dangling bonds and oxygen functionalities (**Fig. 24 (d)**), which resulted in unique FAO catalytic activity. During the FAO process on Pt, the ratio of the current density of the first anodic peak (J_{1st}) to the second anodic peak (J_{2nd}) clearly provides a clue regarding the reaction pathway (direct or indirect oxidation). They found that the ratio of J_{1st}/J_{2nd} for Pt-GO catalyst is approximately 99.8%, and a high ratio of 93.7% can be reached after 100 CV cycles, indicating that the ALD-Pt catalyst displays the capability to regenerate the CO-adsorbed surface after cycling. The presence of Pt-O species can increase the anti-poisoning ability during FAO in addition to improvement of the catalytic activity. The Pt-O species can induce abundant Pt-O_{ads} and Pt-(OH)_{ads} to strip the CO-adsorbed sites (according to this reaction step: $\text{Pt}-(\text{CO})_{\text{ads}} + \text{Pt}-\text{O}_{\text{ads}} \rightarrow 2 \text{Pt} + \text{CO}_2$), thus resulting in a high CO tolerance.

Pd can substitute Pt for electrochemical FAO due to its good stability and high-power densities. In addition, the reaction pathway of formic acid is on Pd a direct dehydrogenation process without the formation of CO species. Santinacci et al. prepared three-dimensionally (3D) nanoarchitected Pd-Ni bimetallic catalysts by ALD on high-aspect-ratio nanoporous alumina templates.⁴⁷⁶ The deposition of NiO is carried out with the use of nickelocene and O₃ precursors and the formed NiO film is reduced to metallic Ni by a reductive annealing process under H₂ atmosphere. The growth of Pd clusters uses palladium hexafluoroacetylacetone (Pd(hfac)₂) and formaldehyde, which is commonly used for Pd ALD. The electron microscopy images show a homogeneous deposition of granularly-structured Pd onto the Ni substrate. The deposited Pt NPs preferred the growth along the [220] direction on the amorphous NiO film. The oxidized Ni is a more suitable substrate for obtaining three-dimensional growth of Pd islands, which are ideal for electrocatalytic applications. The FAO on the Pd/Ni nanocatalysts proceeds through a direct dehydrogenation mechanism according to the cyclic voltammetry curves. The as-prepared Pd/Ni bimetallic systems Pd (40 ALD cycles)/Ni(1000 ALD cycles) demonstrates a high activity of 0.83 A·mg⁻¹ toward the FAO, with a Pd loading amount of 0.06 ng cm⁻². The strong interaction between

Pd and Ni, the electronic effects between the alloyed Pd/Ni metals and the mass transport effect in 3D nanostructures might be the reason for the enhanced electrochemical properties. Besides the deposition of Pd on the substrates, ALD was also used to deposit a SiO₂ layer for stabilizing Pd-based catalysts for FAO. Zahmakiran et al. prepared trimetallic PdCoNi NPs supported on TiO₂ nanopowders (PdCoNi/TiO₂) by a wet-impregnation method. After the preparation, ALD was utilized to improve the catalytic durability of PdCoNi/TiO₂ by growing SiO₂ layers among the PdCoNi alloy NPs by using 3-aminopropyltriethoxysilane and oleylamine as the Si source and surface protection groups, respectively.⁴⁷⁷ Due to the existence of free -NH₂ functionalities, the resulting PdCoNi/TiO₂-ALD-SiO₂ nanocatalyst displays almost two times higher activity than PdCoNi/TiO₂ in FAO. The -NH₂ functionalities grafted onto the support might affect the formic acid adsorption/storage process. The O-H bond cleavage in formic acid is facilitated by the -NH₂ functionalities leading to the formation of metal-bound formate species which accelerate the dehydrogenation process and produce H₂ and CO₂. Moreover, the SiO₂ layer-protected PdCoNi alloy NPs showed unprecedented catalytic stability against sintering and leaching throughout the reusability experiments.

3.1.2.3 ALD for electrocatalytic ethanol oxidation

Ethanol has also been applied in the fuel cells, due to their low cost, easy storage, low toxicity and pollutant emission, high energy density. In addition, ethanol can be easily produced in large quantities by the fermentation of biomass from agriculture. However, the C–C bond is difficult to break at low temperature during the ethanol oxidation process. Hence, the development of highly active electrocatalysts is critical to achieving the commercialization of direct ethanol fuel cells (DEFCs). Hsieh et al. investigated the ethanol oxidation reaction (EOR) activity of ALD Pt NPs with different sizes and found that the ALD-Pt catalysts with smaller size exhibited relatively high catalytic activity, CO tolerance, and stability.⁴⁷⁸

However, the ethanol oxidation kinetics on Pt-based catalysts in acidic media is slow, incomplete, and mostly leads to the production of acetic acid and acetaldehyde. Pd is considered to be a promising alternative to Pt for EOR in alkaline medium due to it being relatively more abundant and having higher tolerance towards carbonaceous species from ethanol oxidation. Rikkinen and co-workers demonstrated that Pd nanoparticle catalysts on porous carbon support can be prepared with ALD.⁴⁷⁹ Due to the narrow size and good dispersion on carbon support (**Fig.**

24 (e)), the ALD-Pd/C exhibited better mass activity compared with the commercial material. Chen and Wang used a chemical vapor-deposited three-dimensional graphite-coated nickel foam as the substrates for the deposition of Pd NPs.⁴⁸⁰ Benefitting from the advantages of ALD, the Pd loading can be reduced to as low as 50 $\mu\text{g cm}^{-2}$. The peaking current density of ALD-Pd/GNF with 450 cycles was about 2.64 times (39.97 mA cm^{-2}) higher than that of commercial Pd/C (15.17 mA cm^{-2}). Nevertheless, carbon-based materials are not stable and corrode under these reaction conditions. TiO_2 is well-known for its high stability and its strong metal-support interaction with Pt group metals. Baranova and Santinacci grew Pd NPs with precisely controlled sizes on TiO_2 nanotubes (TNTs) by ALD.⁴⁸¹ They found that the EOR activity of Pd NPs can be enhanced by annealing the TiO_2 nanotubes, since anatase is more conductive than the amorphous TiO_2 . The 500 ALD cycle Pd/TNTs system showed the best catalytic activity and satisfactory stability in alkaline media. The peak current for ethanol oxidation can reach approximately 2.25 A mg^{-1} . In addition to TNTs, they also investigated the EOR activity of Pd NPs on SnO_2 -coated TNTs (**Fig. 24 (f)**). The XPS results indicated that the top surface of the SnO_2 layer is reduced to metallic Sn during the deposition of the Pd particles, which facilitated the ALD process of Pd.⁴⁸² The activity of Pd NPs for EOR was further enhanced on SnO_2 compared with that on TiO_2 surfaces. The positive impact of the addition of Sn species on Pd catalyst can be attributed to the preferred deposition of Pd on metallic Sn, facilitation of OH adsorption on the SnO_2 layer, and the strong metal-support interaction between Pd and SnO_2 . These works indicated that the use of ALD to grow metallic nanoparticles onto three-dimensional nanostructured substrates appears to be a very promising approach for the preparation of well-defined catalysts for ethanol and other alcohol electrooxidation.

3.1.3 ALD for electrocatalytic oxygen evolution reactions

The electrochemical oxygen evolution reaction (OER) is the core reaction process in water splitting for renewable energy conversion devices. However, due to the slow reaction kinetics of OER, the energy conversion efficiency was limited to a certain extent. At present, the commercial electrocatalysts for OER are RuO_2 catalysts. Unfortunately, high cost and poor durability have hindered their further development and applications. Therefore, it is of great importance to developing effective OER catalysts by various methods. Finke and Hoffmann reported that ALD fabricated TiO_2 coatings on IrO_2 , RuO_2 and F-doped SnO_2 can tune the surface charge density, and consequently tune the catalytic activity of electrocatalyst.⁴⁸³ For example, the $\text{TiO}_2/\text{IrO}_2$ catalyst

exhibited a current density of 0.9 mA cm^{-2} at 350 mV overpotential, which is 9-fold increase compared with that of IrO_2 . With the different ALD cycles of TiO_2 , the oxidation state of Ti and the potential of zero charge can be adjusted, which resulting in the tuned activity of the electrocatalysts.

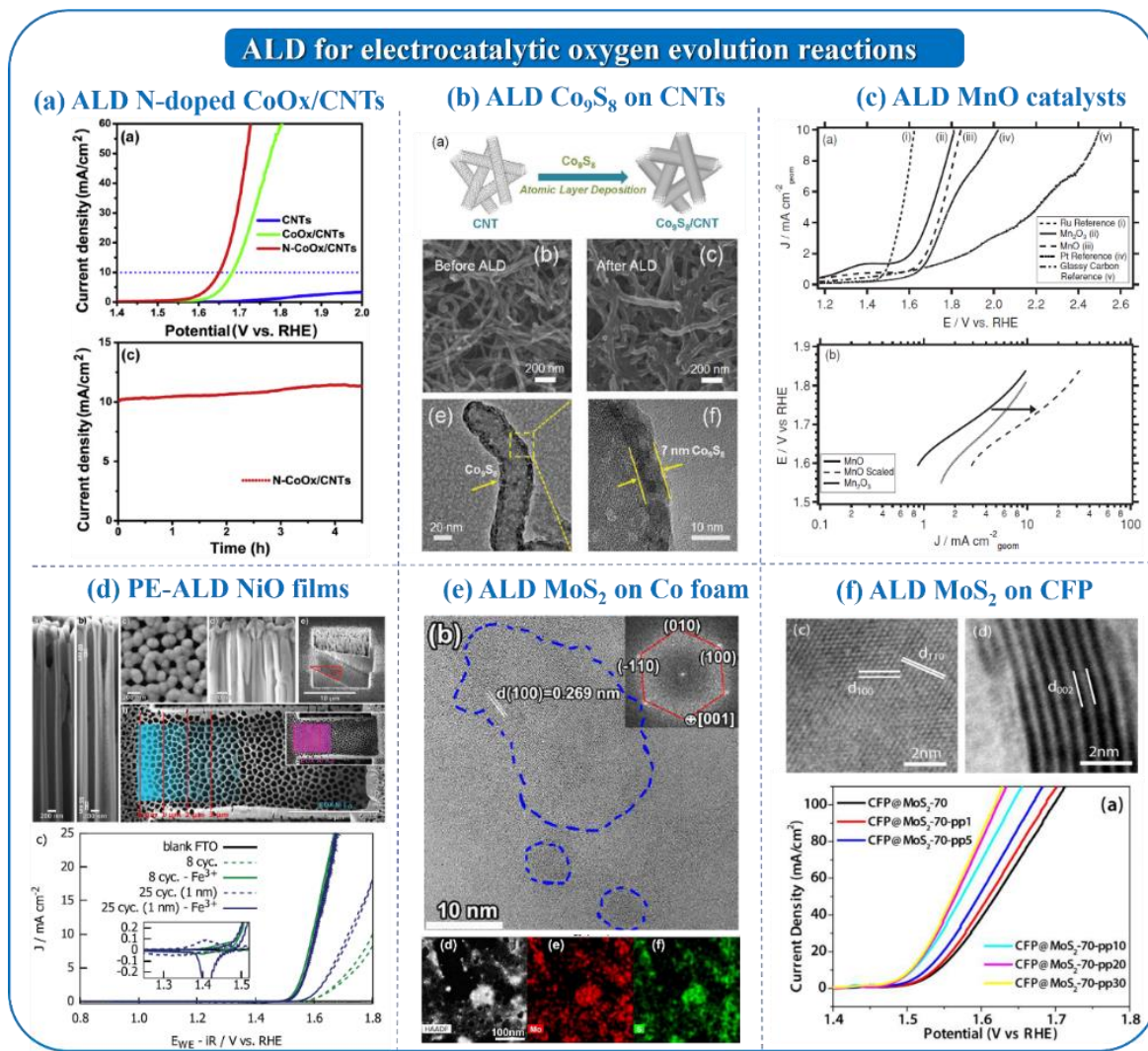


Fig. 25 ALD fabrication of OER catalysts: (a) N-doped CoO_x /carbon nanotubes; (b) Co_9S_8 on CNTs; (c) MnO catalysts; (d) NiO film; (e) MoS_2 on Co foam; (f) MoS_2 nanoflakes on CFP.

To substitute the noble metals, many researchers have developed highly catalytic and low-cost transition metal compounds. Nowadays, cobalt and cobalt oxides have been extensively applied in electrocatalysis, especially for OER, because of their high catalytic activity and good stability. By using ALD, the as-prepared Co-based catalysts can be uniformly deposited onto the

substrates and the thickness can be accurately controlled. Yilmaz and Uyar reported ALD of highly monodisperse Co_3O_4 nanocrystals of different sizes on N-doped electrospun carbon nanofibers ($\text{Co}@n\text{CNFs}$) for OER.⁴⁸⁴ The obtained $\text{Co}@n\text{CNFs}$ with an average Co_3O_4 particle size of 3 nm exhibited the turnover frequency (TOF) value of 0.14 s^{-1} at an overpotential of 550 mV, which is ca. 3 and ca. 15-fold higher than those of bulk Co and the standard state-of-the-art IrO_x catalyst, respectively. Li and co-workers synthesized a homogeneous N-doped cobalt oxide thin film on high-surface-area CNTs (N-CoOx/CNTs) by plasma-enhanced ALD at 200°C .⁴⁸⁵ The overpotential of OER for N-CoOx/CNTs electrocatalyst was only 420 mV at 10 mA cm^{-2} (**Fig. 25 (a)**). They found that the intrinsic crystal structure and chemical composition of cobalt oxides were tailored after N-doping and the resulting NCoOx/CNTs electrocatalyst displays remarkable electrocatalytic activity and stability towards the OER. In addition to oxides, a uniform thin layer of Co_9S_8 was synthesized on CNTs by using bis($\text{N,N}'$ -diisopropylacetamidinato)cobalt(II) and H_2S precursors.⁴⁸⁶ With the deposition of 200 ALD cycles, a 7 nm Co_9S_8 thin layer on the CNTs can be obtained as shown in **Fig. 25 (b)**. The ALD-synthesized $\text{Co}_9\text{S}_8/\text{CNT}$ catalyst exhibited an overpotential of 369 mV with a current density of 10 mA/cm^2 , which is much smaller than that of RuO_2 (409 mV), and CoO_x/CNT (431 mV). The Tafel slope of ALD-synthesized $\text{Co}_9\text{S}_8/\text{CNT}$ electrocatalyst was 58 mV/decade, indicating the Tafel kinetics of the $\text{Co}_9\text{S}_8/\text{CNT}$ electrocatalyst was favored during the OER process. In addition, the LSV curves were maintained well after the 2000 cycles scan, which indicated the good stability of the ALD-prepared Co_9S_8 electrocatalyst. Cobalt phosphate (CoPi)-based electrocatalysts have also exhibited good performance towards OER. Palma et al. deposited CoPi films by using bis(cyclopentadienyl)cobalt(II) (CoCp_2), trimethyl phosphate and O_2 as precursors.⁴⁸⁷ The Co-to-P atomic ratio can be controlled by tuning the ALD process and is found to significantly affect the activity of the prepared electrocatalyst. The current density increased from 1.77 mA/cm^2 to 2.89 mA/cm^2 at 1.8 V vs. RHE, concurrently with a Co-to-P ratio increase from 1.6 to 1.9. The results highlight the role of stoichiometric composition of Co in CoPi on its activity. Rongé et al. developed a plasma-enhanced process to obtain CoPi films without the need for a phosphidation step. The as-prepared CoPi films exhibited an overpotential of 509 mV with a current density of 10 mA/cm^2 , which is much smaller than Co_3O_4 ⁴⁸⁸. In addition, this catalyst can enable hydrogen evolution after either a thermal or electrochemical reduction step.

Besides Co-based transition metals, Mn- and Ni-based metal oxide were also prepared by ALD for OER. For example, Bent et al. prepared MnO catalysts on glassy carbon electrodes through the use of a $\text{Mn}(\text{EtCp})_2$ precursor.⁴⁸⁹ The as-deposited films of MnO can be converted to Mn_2O_3 via annealing. In OER testing, the Mn_2O_3 catalyst could reach a current density of 10 mA cm^{-2} at 1.81 V, while the MnO catalyst required 1.84 V, as shown in **Fig. 25 (c)**. The small differences in OER are attributable to differences in surface area. Following this study, the authors prepared NiO thin films using Nickelocene and O_3 at 275 °C.⁴⁹⁰ The ALD-grown NiO thin films were studied as an OER electrocatalyst with the incorporation of Fe from the electrolyte. They characterized the activity of NiO towards OER in both trace Fe and Fe-saturated 0.1 M KOH electrolytes and found that the Fe-saturated electrolyte significantly increases the OER activity of the NiO films. Bein further confirmed that when a 1 nm layer of the PE-ALD NiO catalyst is deposited on a porous transparent conductive oxide (TCO) substrate, their OER activity can be further improved (**Fig. 25 (d)**).⁴⁹¹

Mo-S sites along the edges of MoS_2 are very active for OER owing to the excellent chemisorption of the oxygen-containing intermediates. Liu and co-workers reported ALD of ultrafine MoS_2 nanocrystals over a porous Co foam by using $\text{Mo}(\text{CO})_6$ and H_2S as precursors (**Fig. 25 (e)**).⁴⁹² The ALD-derived Co@MoS_2 only requires an overpotential of 270 mV to reach a current density of 10 mA cm^{-2} . Furthermore, the Co@MoS_2 electrode exhibited excellent stability, showing no noticeable degradation after operating at 20 mA cm^{-2} for 50 hours and 100 mA cm^{-2} for additional 50 hours. In order to further improve the activity, plasma treatment was proved as an effective route to generate vacancies and structural disorders on the surface of MoS_2 , which can further increase the exposure of the active site. Liu et al. fabricated MoS_2 nanoflakes that were obtained by ALD using MoCl_5 and H_2S on a carbon fibre paper (CFP) surface (**Fig. 25 (f)**).⁴⁹³ When the CFP@MoS_2 was treated by plasma for 20 s, the current density increased to 80.42 mA/cm^2 at 1.6 V vs RHE, which is two times higher than that of CFP@MoS_2 (43.89 mA/cm^2). In addition, the Tafel slope decreased from 65.8 to 61.2 mV dec^{-1} when the plasma treatment time increases from 0 to 20 s, which further indicates that the plasma treatment can improve the activity of MoS_2 nanoflakes.

3.1.4 ALD for electrocatalytic hydrogen evolution reactions

3.1.4.1 ALD of Pt-based catalysts

Hydrogen is a clean fuel and can be applied as the energy source in PEMFCs. Water electrolysis is considered a promising green route for the production of hydrogen. The hydrogen evolution reaction (HER) is one half-reaction during water electrolysis, and Pt-based catalysts exhibited good activity during the hydrogen evolution process. The HER process on Pt particles contains two half-reactions, which are the Volmer reaction and the desorption reaction (Heyrovsky reaction or Tafel reaction). Many previous studies indicated that the Tafel mechanism usually occurs on Pt NPs due to the high H coverage on Pt surfaces. By using the ALD method, Pt-based catalysts have been synthesized to decrease the Pt content, and thus reducing the cost. Alshareef and co-workers report the fabrication of monolithic, self-standing, 3D graphitic carbon scaffolds with conformally deposited Pt by ALD (**Fig. 26 (a)**).⁴⁹⁴ The as-prepared Pt on a 3D network of laser-scribed graphene (Pt/LSG) electrode exhibited comparable activity with the benchmark Pt/C electrode. It should be noted that the mass loading (0.04 mg/cm^2) of Pt/LSG was much smaller than that of commercial Pt/C catalyst (0.5 mg/cm^2). The synergistic effect between the ALD Pt and the 3D network of the laser scribed graphene provides an avenue for maximized utilization of Pt loading and enhanced HER activity. Another reported strategy to lower Pt loadings by ALD is to use tungsten monocarbide (WC) as the support.⁴⁹⁵ Chen et al. deposited Pt onto WC powders using ALD to obtain a Pt-WC core-shell catalysts for the HER. The Pt-WC core-shell exhibited equivalent HER activities compared to bulk Pt catalysts; while the Pt loading amount is reduced 10 times.

Downsizing noble metal nanocatalysts to clusters or even single atoms is an effective strategy to significantly increase their catalytic activity and efficiency. In 2013, Sun et al. firstly reported isolated single Pt atoms anchored to graphene nanosheets by an ALD method for MOR. Subsequently, we synthesized Pt single atoms on N-doped graphene nanosheets (NGNs) through ALD method (**Fig. 26 (b)**).⁴⁹⁶ The HER activity and reaction mechanism on Pt single atoms were carefully investigated. At an overpotential of 0.05 V, the mass activity of the ALD50Pt/NGNs catalyst reached 10.1 A mg^{-1} , which was much greater than the ALD100Pt/NGNs catalyst and Pt/C catalyst. Synchrotron characterization and DFT analysis revealed that the Pt single atoms are strongly anchored on the substrates due to the SMSIs. In addition, according to the DFT results, the interaction between single Pt atoms and N-dopants is much larger than that of Pt atoms/C-substrates, indicating Pt atoms are bonded to N-sites. Due to the unique electronic structure of Pt single atom catalysts, several H could adsorb on one Pt atom, followed by the formation of H_2 on

the isolated Pt atom. According to the DFT calculation results, during the HER process, four H atoms can be adsorbed on Pt single atoms, and the interaction between the Pt and H atoms reduced the repulsion between the H atoms. The desorption process is similar to the Tafel reaction ($H_{ads} + H_{ads} \rightarrow H_2$), and leads to a Tafel slope that is similar to the Volmer–Tafel mechanism (29mV dec^{-1}).⁴⁹⁷

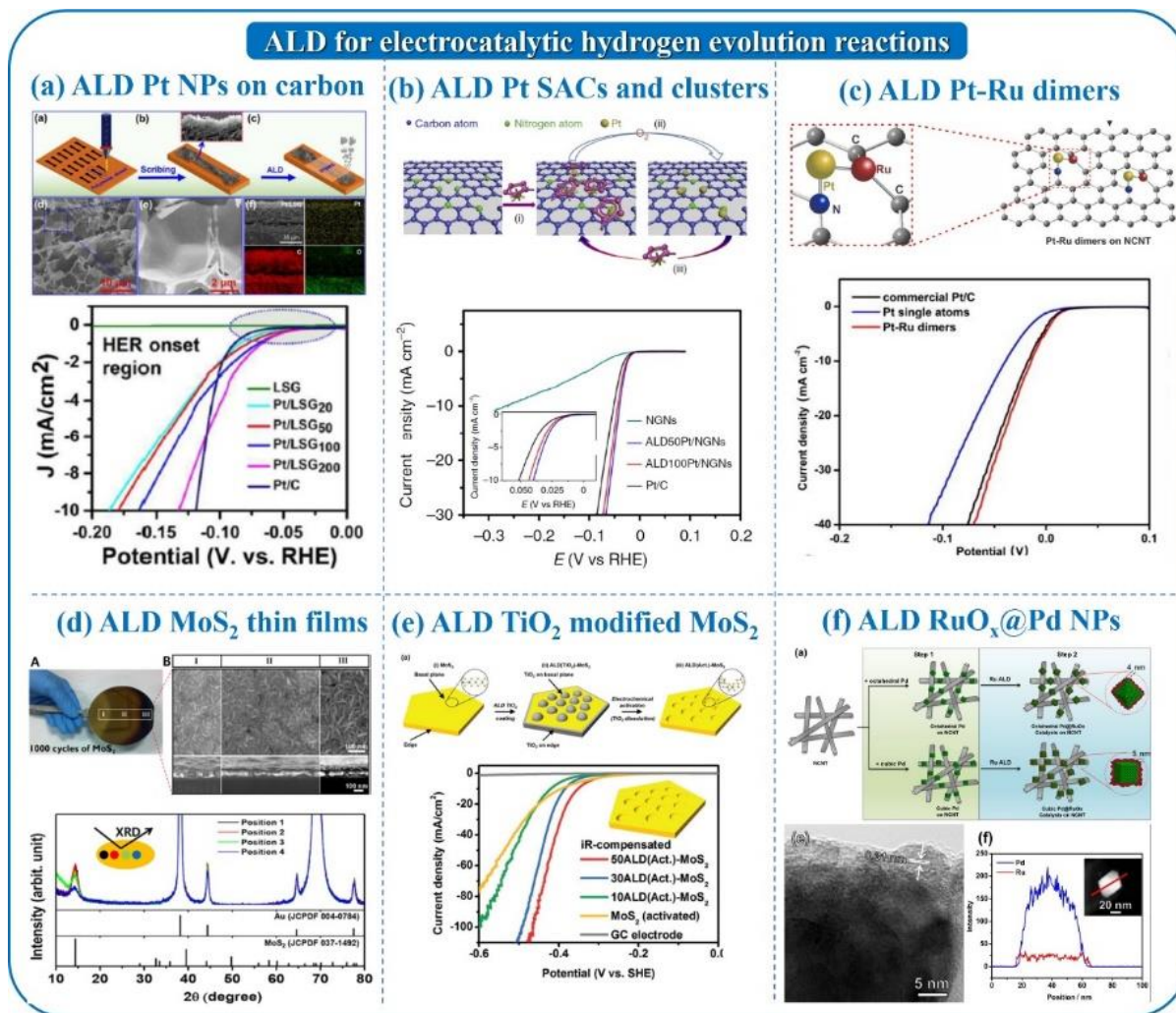


Fig. 26 ALD fabrication of HER catalysts: (a) Pt NPs on 3D graphitic carbon; (b) Pt single atoms and clusters; (c) Pt-Ru dimer catalysts; (d) MoS₂ thin films; (e) TiO₂ modified MoS₂ nanoflakes; (f) RuO_x@Pd NPs.

Recently, dual-metal catalysts were found to greatly enhanced catalytic performance due to the synergistic effects. The method by pyrolyzing two metal precursors simultaneously has been

reported as a successful route for the preparation of dual-metal catalysts. However, the detailed location of each metal site can hardly be controlled. The ALD technique provides the possibility to achieve atomically precise metal clusters, even bimetallic catalysts. Through careful control of the ALD deposition conditions, the second metal can be selectively deposited on the initial metal deposit sites, enabling the formation of bimetallic dimer structures. Very recently, Sun et al. successfully prepare high-quality one-to-one A-B bimetallic dimer structures (Pt-Ru dimers) by ALD. As shown in **Fig. 26 (c)**,⁴⁹⁸ the atomic resolution HAADF-STEM images illustrate that a dimer-like structure was successfully prepared by a two-step ALD process. The different contrast of the two atoms reflects that the dimer is composed of Pt and Ru. The EXAFS R space curve fitting results based on the Ru K-edge and Pt L3-edge indicated that the coordination number of Pt-Ru is close to 1, confirming the formation of Pt-Ru dimer structures. Benefiting from the unique bimetallic dimer sites, the Pt-Ru dimers exhibited 50 times higher HER activity compared to commercial Pt/C catalysts and the dimer structure maintained after the long-term durability test. The Pt-Ru dimer HER mechanism and reaction route were systematically explained by first-principle calculations. We found that when three hydrogen atoms connect with the Pt atom (3H-Pt), and three bonds with the Ru atom (3H-Ru), a hydrogen atom can be released from Ru atom. The Pt-Ru dimer generates a synergistic effect by modulating the electronic structure which evolves from metallic to semiconducting during the hydrogen adsorption, resulting in an increase in the unoccupied orbitals and a decrease of the bonding between the Ru and H, thus playing a vital role for the high HER activity. These findings demonstrate that the remarkable performance of the single Pt atoms and Pt-X dimer can be mainly attributed to their unique electronic structure. In addition, these ALD approaches for SACs provides a promising approach for the rational design of highly active and stable bimetallic dimers, which have great potential for application in various catalytic reactions.

3.1.4.2 ALD of MoS₂ catalysts

Recently, molybdenum disulfide (MoS₂) has attracted attention due to its biomimetic hydrogen evolving activity. It should be noted that MoS₂ has poor activity for the HER in its bulk form, which is due to the small amount of HER active sites at the basal planes. The HER activity of MoS₂ can be improved by tuning the exposed surface of the crystalline MoS₂ to increase the number of active edge sites. Min and co-workers prepared an amorphous MoS₂ catalyst on Au by ALD method. During the ALD process, the molybdenum hexacarbonyl (Mo(CO)₆) and

dimethyldisulfide ($\text{CH}_3\text{S}_2\text{CH}_3$) are employed as Mo and S precursors, respectively.⁴⁹⁹ The required overpotential for a designated current density of $100 \mu\text{A}/\text{cm}^2$ on the MoS_2 film is 165 mV. The turnover frequency on each active site of the amorphous MoS_2 film is calculated to be 3 H_2/s at 0.215 V. The Tafel slope is 47 mV/decade indicates the HER process follows the Volmer-Heyrovsky mechanism on the amorphous MoS_2 surface. However, the weak adhesion of MoS_2 on Au caused the unstable activity of the ALD- MoS_2/Au catalysts. The authors tried to use carbon fibre papers (CFPs) as the alternative to replace the Au substrate, as CFPs can provide a large surface area and strengthen the adhesion of the ALD MoS_2 .⁵⁰⁰ Different from the amorphous MoS_2 on a Au surface, the ALD- MoS_x on CFP exhibited a mixture of amorphous and nano-crystalline phases. Because of the formation of nano-crystalline MoS_2 , the turnover frequency of the MoS_x/CFP is smaller than that of the amorphous ALD- MoS_2/Au . However, the MoS_x/CFP catalyst exhibits very good stability with no obvious change in the polarization curves after 1000 CV cycles, due to the strong interaction between MoS_x and CFP. To achieve the direct growth of nanocrystalline MoS_2 by ALD, Bae and Shin demonstrated that the nonideal growth mode operates when MoS_2 is deposited by ALD on planar surfaces using MoCl_5 and H_2S as the precursors (**Fig. 26 (d)**).⁵⁰¹ This nonideal mode of growth shows that the growth thickness does not linearly increase with the number of cycles. Interestingly, the relative ratios of the edge sites and basal planes of MoS_2 can be controlled by tuning the ALD conditions. At low growth temperatures, the MoS_2 with mixed 2H and 1T phases can be deposited due to the incorporation of chlorine impurities. They found that the as-prepared planar MoS_2 films exhibited good HER performance, with a current density of 20 mA cm^{-2} at -0.3 V and a Tafel slope of 50–60 mV/decade.

To make the MoS_2 more active, many studies focused on synthesizing MoS_2 catalysts with more edge sites or to further improve the active edge sites by modification. Kim and Kuech attempted to make use of basal plane sites which account for the majority of the MoS_2 materials in bulk form.⁵⁰² They firstly ALD deposited TiO_2 on the bulk MoS_2 particles. A thin layer of TiO_2 is formed on the edge sites of the MoS_2 and TiO_2 islands are formed on basal planes. Then they dissolved the TiO_2 layers by an in situ electrochemical activation method. After this process, the localized surface distortions are created on the MoS_2 basal planes. The TiO_2 coatings on the basal planes and edge sites completely disappeared on the surface of MoS_2 catalysts after the electrochemical activation process, as shown in **Fig. 26 (e)**. In addition, the degree of surface distortion on the MoS_2 basal planes can be tuned by controlling the ALD TiO_2 coating cycles from

10 to 50. With the increase of the surface distortions on the MoS₂ basal plane, the HER catalytic activity was increased. The as-prepared MoS₂ catalysts exhibited a much smaller Tafel slope (80–90 mV dec⁻¹) compared with that of pristine MoS₂ (180 mV dec⁻¹). According to the DFT calculations, the hydrogen-binding energy is reduced on the local flexure of MoS₂ layers, which result in the improved HER kinetics. This result suggests that the ALD technique can be used for the decoration of the catalysts by induced physical changes including defects, defect-mediated strain, and flexure of surface layers.

3.1.4.3 ALD of other catalysts

Transition metal sulfides have high stability and conductivity, which allows them be applied s from catalysis to photovoltaics. Among them, nickel sulfide exhibited good activity for HER. Farha and Hupp constructed nickel sulfide (NiS_x) layers by using bis(N,N'-di-tert-butylacetamidinato)nickel(II) (Ni(amd)₂) vapor and hydrogen sulfide gas as the precursors.⁵⁰³ In situ quartz crystal microbalance (QCM) studies revealed a linear GPC of 9.3 ng/cm² per cycle growth behavior for NiS_x films. The ALD NiS_x catalysts exhibited the overpotential of 440 and 576 mV at a current density of 10 mA/cm² in acidic and pH 7 phosphate buffer aqueous reaction media, respectively. In addition to two binary sulfides, ternary sulfides can also be achieved by ALD method. For example, Fe_xCo_{1-x}S_y films were grown by ALD at 120 °C from the precursors, including bis(N,N'-diisopropylacetamidinato)-cobalt(II), bis(N,N'-diisopropylacetamidinato)iron(II), and H₂S.⁵⁰⁴ The ternary Fe_xCo_{1-x}S_y was achieved by repeatedly growing one or multiple cycles of FeS_y followed by one or multiple cycles of CoS_y. In addition, the elemental composition of the ternary sulfide Fe_xCo_{1-x}S_y can be tuned by controlling the cycle ratio of FeS_y and CoS_y. The as-prepared Fe_{0.54}Co_{0.46}S_{0.92}/CNTs/CC electrode achieved -10 mA/cm² at a overpotential of -70 mV in alkaline solution, which indicates the effectiveness of the ALD method. Transition-metal carbides (TMCs) have also attracted a lot of attention due to their peculiar electronic structures and their broad applications in electrocatalysis. Wang and co-workers synthesized smooth, pure, crystalline nickel carbide (Ni₃C) films on CNTs by using bis(1,4-di-tert-butyl-1,3-diazabutadienyl)nickel(II) and H₂ plasma with an ideal self-limiting ALD growth fashion.⁵⁰⁵ The as-prepared ALD Ni₃C/CNT catalyst showed an onset overpotential of -77 mV (at -0.1 mA/cm²), and an overpotential of -132 mV to reach -10 mA/cm² in 1 M KOH aqueous solution.

Recently, several studies reported that rational designed Ru-based catalysts exhibited good HER performance. For example, the anomalous crystalline structure of Ru on g-C₃N₄ was prepared by Qiao et al. and it exhibited comparable HER activity with Pt in alkaline solutions.⁵⁰⁶ By using ALD, Sun et al. fabricated Pd@RuO_x core-shell catalysts by using octahedral and cubic Pd NPs with two typical surface atom arrangements as the substrates (**Fig. 26 (f)**).⁵⁰⁷ Due to the similar lattice constants of Pd and Ru, Ru atoms were selectively deposited on Pd particles instead of N-doped CNT substrates by using bis(ethylcyclopentadienyl)ruthenium(II) and O₂ as precursors. The ALD cycles can easily tune the thickness of the RuO_x shell. The as-prepared octahedral Pd@RuO_x/NCNT exhibited better activity and stability for the HER in acid solution compared with the cubic one. According to the XAS and XPS results, the Ru shell consists of metallic Ru and Ru(IV). DFT calculation results indicated that the H* can be easily detached on the octahedral Pd@RuO_x, and resulted in a better HER activity.

3.2 ALD/MLD for photoelectrocatalysis

3.2.1 ALD/MLD for photovoltaics

3.2.1.1 ALD/MLD for Dye-Sensitized Cells (DSSCs)

Renewable solar energy is regarded as the most promising alternative clean energy source for fossil fuels. To realize cost-effective and competitively priced solar cells, dye-sensitized solar cells (DSSCs) have been extensively explored since 1991 and garnered increasing research attention over the past decades^{508, 509}. The advantages of DSSCs are their low cost, simple manufacturing process, lightweight, flexibility, low toxicity, et al. A typical DSSCs consists of several parts, including the photoanode on a conductive substrate, sensitizer, electrolyte and counter electrode^{510, 511}. The excited electrons are generated from the photoanode under the visible light irradiation when the photoanode experiences photo-excitation of the absorbed dye molecules. The electrons are then injected into the conduction band of a semiconductor and further to produce the electric current with an external. The dye is then restored to the original state by electron donation from the redox electrolyte. Moreover, the charge is returned from the external to the cycling circuit on the counter electrode in the cell⁵¹². The performances of the DSSCs are determined by each component in the cell. For example, the function of the photoanode in DSSCs is to support the sensitizer loading and transport the photo-excited electrons from the sensitizer to

the external circuit. In this case, both high surface area and fast charge transportation are the keys to achieving high-efficiency photoanodes for DSSCs.

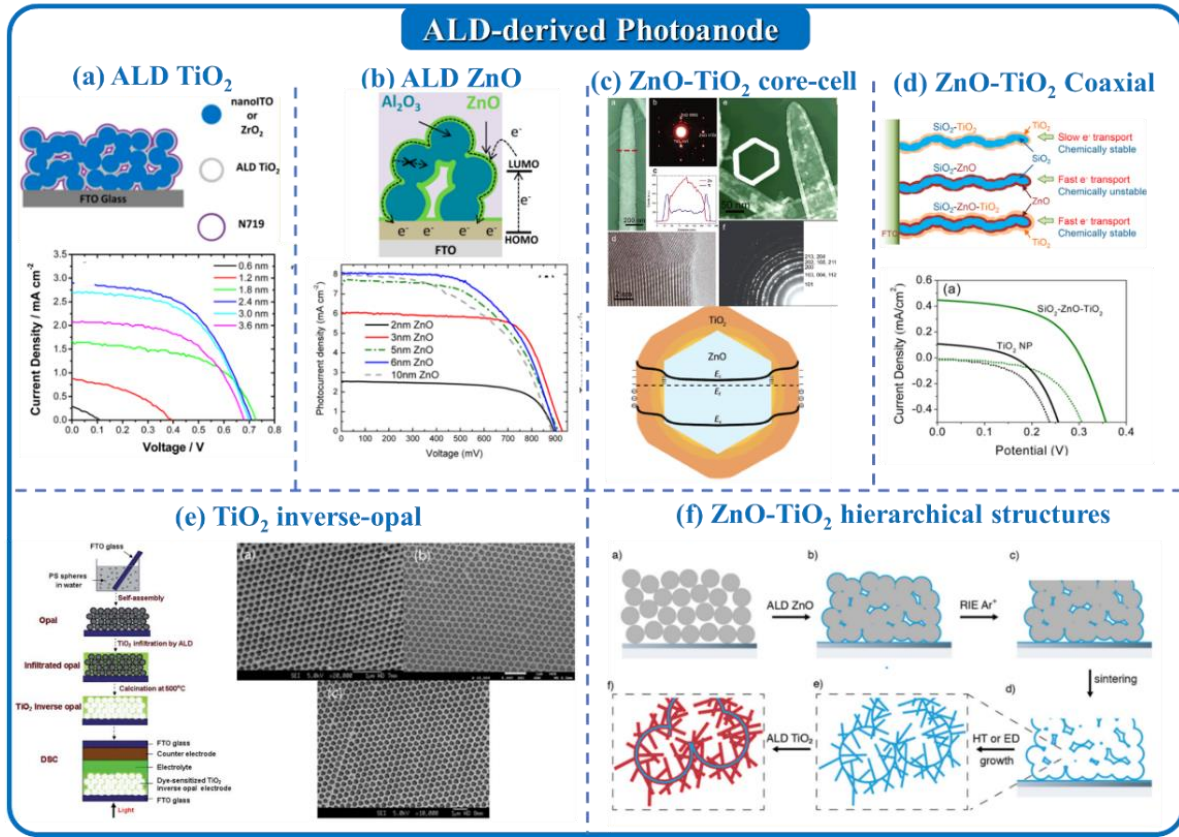


Fig.27 ALD-derived photoanodes for DSSCs: (a) ALD TiO_2 ; (b) ALD ZnO; (c) ZnO- TiO_2 core-shell; (d) ZnO- TiO_2 coaxial; (e) TiO_2 inverse-opal; (d) ZnO- TiO_2 hierarchical structure.

ALD and MLD techniques have been used to design and fabricate photoanode materials for DSSCs^{513, 514}. To minimize the time scale for transferring the injected electrons to the conducting oxide, a thin semiconductor oxide is required on the conductive substrate. ALD is an ideal technique to fabricate core-shell-structured photoanodes. TiO_2 is one of the most widely used semiconductor photoanode materials and can also be easily deposited by ALD techniques⁵¹⁵⁻⁵²³. As shown in **Fig.27 (a)**, a thin TiO_2 shell was deposited by ALD onto high surface area ITO and ZrO_2 core nanoparticles⁵²⁴. The ALD TiO_2 was deposited at 120 °C with a GPC of 0.6 Å using TiCl_4 and H_2O as precursors. With an N719 dye, the results indicate that with the increasing of the thickness on TiO_2 shell (to 1.8-2.4 nm), the short-circuit current densities, open-circuit voltages,

and back electron transfer lifetimes all increased. When further increasing the thickness of TiO₂ (>3 nm), electron trapping in the TiO₂ shell occurs, increasing back electron transfer (BET) and decreasing device efficiencies. In addition, ALD-designed core-shell photoelectrodes can provide a practical alternative for maximizing solar cell efficiencies by enhancing electron transport through mesoporous films. Another candidate metal oxide for photoanode application is ZnO, which is also a routine material deposited by ALD^{525, 526}. Grätzel's group fabricated a ZnO nanoshell by ALD on a 2.5 μm thick Al₂O₃ mesoporous scaffold and used it as a photoanode for DSSCs, as shown in **Fig.27 (b)**⁵²⁷. With a ZnO nanoshell of 3-6 nm, a maximum power conversion efficiency of 4% was achieved with the standard organic sensitizer and Co²⁺/Co³⁺ redox mediator. A high-power conversion efficiency (PCE) of 7% was achieved with the similar ZnO nanostructure in the CH₃NH₃PbI₃ based solid-state solar cells. The comparison of the photovoltaic performance and the electron transfer dynamics between different metal oxide photoanodes is also interesting. However, the morphological differences between the different metal oxides hamper the fair comparison. ALD techniques can circumvent this issue by depositing these oxides on an insulating mesoporous template and using them directly as photoanodes. Grätzel's group deposited different thicknesses of ZnO and TiO₂ on mesoporous alumina for photoanode applications in DSSCs⁵²⁸. The results showed that the best performance was achieved with 5 nm ZnO or TiO₂ overlayer films yielding a high-power conversion efficiency of 4.4%. Moreover, the transport rate of electrons through ZnO is faster compared to the TiO₂.

In addition, other types of core-shell structures were developed by ALD as a photoanode for DSSCs⁵²⁹⁻⁵⁴². In 2006, Yang's group demonstrated the core-shell structures of Al₂O₃ or TiO₂ shells on ZnO nanowires by ALD⁵⁴³, as shown in **Fig.27 (c)**. The results showed that the ALD Al₂O₃ could act as an insulating barrier regardless of thickness and that the cell V_{oc} could be improved at the expense of a larger decrease in J_{sc}. However, when the TiO₂ shell thickness was 10-25 nm, it caused an obvious increase in V_{oc}, resulting in an improvement in conversion efficiency up to 2.25%. Another similar TiO₂-ZnO core-shell structure was demonstrated with a TiO₂ shell on ZnO nanocrystallites⁵⁴⁴. The ultrathin layer of ALD- TiO₂ can effectively enhance the power conversion efficiency from 5.2% to 6.3%. The ALD-TiO₂ layer increases the open-circuit voltage and suppressed surface charge recombination without impairing the photocurrent density. Hupp et al designed a doubly coaxial photoanode architecture based on templated SiO₂ aerogels⁵⁴⁵. As shown in **Fig.27 (d)**, the first layer of ZnO was deposited on the template by ALD to create the

electronically interconnected, low density, high-surface-area, semiconductor framework. Then, another layer of thin conformal oxide of alumina, zirconia, or titania was further deposited via ALD to suppress the dissolution of ZnO. The doubly coaxial structure of SiO₂-ZnO-TiO₂ photoanode showed 2 orders of magnitude faster electron transport compared to the SiO₂-TiO₂ structure. The fast electron transport by the coaxial core-shell-shell structure enables good charge-collection efficiencies even with redox shuttles capable of rapidly intercepting injected electrons.

Surface area is an important parameter that affects the sensitizer loading and cell efficiency. The design of a hierarchical nanostructure is an effective approach to increasing the effective surface area. ALD has been used to fabricate hierarchical nanostructures using a sacrificial template or through the combination of other approaches. For example, 3D colloidal silica was used as a sacrificial template on a conductive substrate⁵⁴⁶. After the deposition of ALD TiO₂, the silica spheres were etched using a 2% HF solution to form the TiO₂ inverse opal photoanode. The Ta-doped TiO₂ films were deposited by repeated super-cycles of two groups of sub-cycles dedicated for Ta₂O₅ and TiO₂, respectively. The content of Ta in the TiO₂ films affects the cell performances. The photoconversion efficiency was effectively increased by Ta doping, which increased the electron concentration. However, excessive Ta doping decreased J_{sc} and photoconversion efficiency. The 3.4 atom%-doped TiO₂ inverse opal electrode presented a high photoconversion efficiency of 1.56%, which was 23% higher than that of pure TiO₂⁵⁴⁶. In another study, different sizes of polystyrene spheres were used as a template and then ALD was applied to deposit TiO₂ thin layers(**Fig.27 (e)**)⁵⁴⁷. The results showed that the TiO₂ inverse opal with a size of 288 nm demonstrated high power conversion efficiency of 2.22 %. The smaller size of the TiO₂ inverse opal with higher surface areas led to higher efficiency. More complex nanostructures were further designed for a novel self-assembled 3D ZnO nanostructure⁵⁴⁸. As shown in **Fig.27 (f)**, a poly(methylmethacrylate) (PMMA) micro-template was used to fabricate a ZnO 3D host backbone by ALD. Afterwards, ZnO nanowires were grown on the 3D host backbone via a hydrothermal method. Finally, another 10 nm dense TiO₂ overlayer was deposited throughout the 3D ZnO host by ALD. With an increased surface area attributed to the ZnO nanowires, the photocurrents increased to 4 mA cm⁻². The ALD TiO₂ overlayer can effectively reduce dark currents, recombine the photogenerated electrons from the conduction band of the semiconductor to the electrolyte and increase the transport rate.

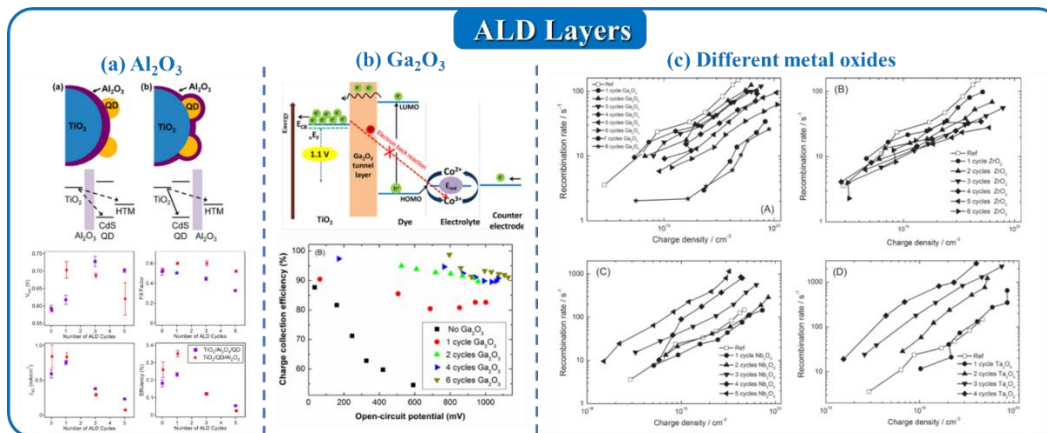


Fig.28 ALD layer modification for the interface in DSSCs: (a) Al_2O_3 ; (b) Ga_2O_3 ; (c) different metal oxides.

Beyond the design core-shell structure photoanodes, ALD has been more widely used to modify the interfaces in DSSCs, including passivation, barrier, and blocking layers. Different metal oxides have been demonstrated to engineer the interfaces in DSSCs. For example, ALD Al_2O_3 is one of the most popular and routine materials used for this purpose⁵⁴⁹⁻⁵⁵⁴. As shown in **Fig.28 (a)**, ALD Al_2O_3 was deposited on cadmium sulfide (CdS) quantum dot-sensitized solar cells as a barrier layer⁵⁵⁵. It was found that the ALD Al_2O_3 layer can suppress dark current and increase electron lifetimes with increasing Al_2O_3 thickness. The thickness of the ALD barrier layer affected the performance of the cell, in which the thin layer leads to an increase in open-circuit voltage and efficiency, however, the thicker layer resulted in a loss of photocurrent and decreased efficiency. Other metal oxides, such as Ga_2O_3 , TiO_2 , In_2O_3 , et al., were also developed to modify the interface of the photoanodes⁵⁵⁶⁻⁵⁵⁸. As shown in **Fig.28 (b)**, the surface of the porous substrate was passivated using a sub-nanometer-thick Ga_2O_3 tunnelling overlayer by ALD⁵⁵⁷. The ALD Ga_2O_3 leads to a high open-circuit potential of 1.1 V with an organic D- π -A sensitizer and a cobalt redox mediator. Moreover, the electron back reaction is effectively reduced with the Ga_2O_3 - overlayer, which leads to improved charge collection efficiency and fills factor up to 30% and 15%, respectively. To understand the influence of tunnelling layers on blocking the interfacial charge carrier recombination reaction, different metal oxides (**Fig.28 (c)**), the recombination characteristics, electronic properties on the surface, transport rate, and injection dynamics were investigated for different metal oxides of Ga_2O_3 , ZrO_2 , Nb_2O_5 , and Ta_2O_5 .⁵⁵⁹. The results showed

that both Ga_2O_3 and ZrO_2 are good candidates as tunnelling layers to limit the interfacial recombination of photogenerated carriers. Moreover, pentavalent oxides such as Nb_2O_5 and Ta_2O_5 introduce shallow donor levels below the conduction band of titanium dioxide⁵⁵⁹.

One of the issues of DSSCs is the charge loss which occurs at the interface between the conductive substrate and electrolyte. To suppress the substrate/electrolyte recombination, a thin oxide blocking layer is usually used on the surface of the conductive substrate. Different metal oxides, such as Al_2O_3 , HfO_2 , TiO_2 , et al., have been deposited by ALD and used as blocking layers⁵⁶⁰⁻⁵⁶⁷. For example, Parsons's group demonstrated an ALD TiO_2 layer as a blocking layer for DSSCs with significantly impeded charge recombination in functional DSSCs, leading to improved photocurrents, open-circuit photovoltages, and fill factors⁵⁶⁰. Compared to the blocking layer fabricated by other methods (hydrolysis and spin casting), with the thinner ALD films, a better performance was achieved, which is attributed to the lower pinhole density.

Besides the photoanode, the counter electrode is another important component of DSSCs. The electrons were transferred by the counter electrode from the external circuit back to the redox electrolyte, further catalyzing the reduction of the redox couple. Different conductive materials, such as Pt, Ru, metal sulfides, and metal nitrides et al. have been studied as counter electrodes for DSSCs^{510, 512, 514}. ALD was also applied to fabricate the counter electrode, including Pt, Ru, conductive polymers and MoS_2 , et al⁵⁶⁸⁻⁵⁷³. For example, Pt nanoparticles were deposited by ALD on indium tin oxide/polyethylene naphthalate substrates⁵⁶⁸. The ALD deposited Pt showed better performance compared to the electrodeposited and sputtered Pt counter electrodes with relative improvements in the efficiency of 19% and 29%, respectively. In addition, ALD was shown to be practical for fabricating a large area counter electrode with an efficiency of 3.1%.

3.2.1.2 ALD/MLD for Perovskite Solar Cells (PSCs)

The metal halide perovskite solar cells (PSCs) utilize novel thin-film photovoltaic technology and have attracted increasing attention over the past decade due to their remarkable PCE of over 25%^{574, 575}. Generally, the PSCs have a sandwich-type structure including a conductive substrate, perovskite layer, and charge transport layer (electron transport layer and hole transport layer)⁵⁷⁶⁻⁵⁷⁸. The cell performance and stability are determined by several factors, such as perovskite/contact interfaces, internal and external degradation, et al⁵⁷⁹⁻⁵⁸¹. The ALD fabrication method is regarded as a promising tool to address the challenges in PSCs.

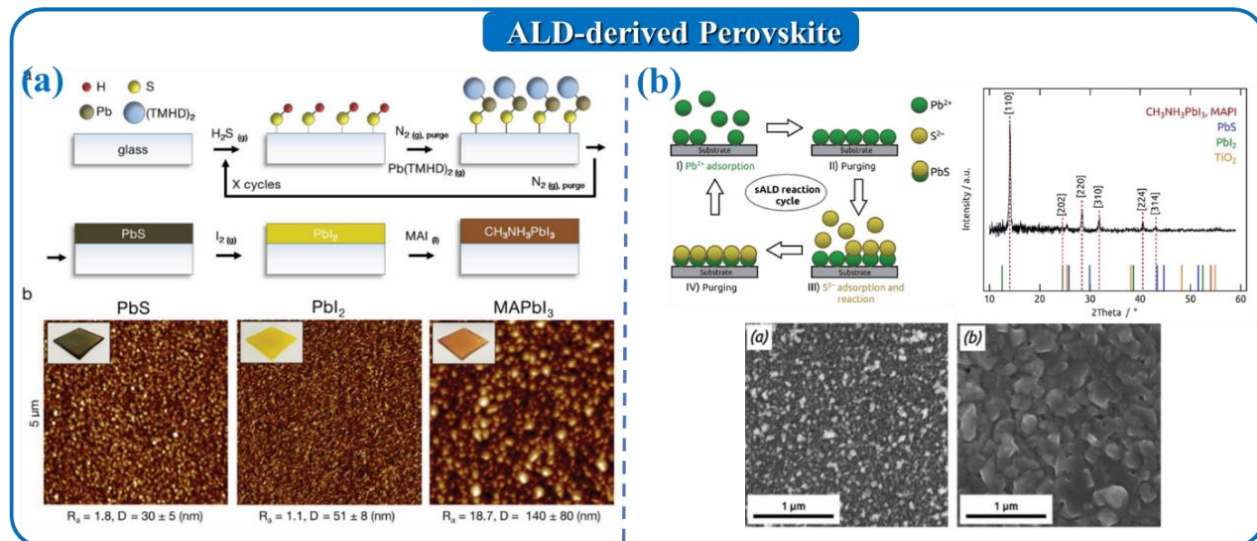


Fig.29 ALD-derived perovskite thin films of CH₃NH₃PbI₃.

ALD is ideal for the fabrication of perovskite thin films due to its advantages which include controllable thickness and uniformity. For ALD-derived perovskite, another advantage is the improved adhesion with a wide range of substrates. However, the direct growth of halide compounds by ALD is challenging. In 2015, Sargent's group demonstrated an ALD-assisted process to synthesize perovskite CH₃NH₃PbI₃ thin films⁵⁸². As shown in **Fig.29 (a)**, the ALD PbS was first deposited as a seed layer on the glass substrate, in which H₂S and Pb(tmhd)₂ were used as precursors. The GPC of PbS was ~ 1.3 Å. Afterwards, the PbS film was converted to PbI₂ through exposure to iodine gas. The PbI₂ was subsequently converted to CH₃NH₃PbI₃ through a 60 s dip in methylammonium iodide in IPA. The surface roughness and morphology are shown in the AFM images in **Fig.29 (a)**. The morphology of the final CH₃NH₃PbI₃ perovskite film is primarily determined by the methylammonium iodide treatment, and the thickness of the CH₃NH₃PbI₃ perovskite film is thicker than the initial ALD PbS film. Another similar process was reported by Julien et al.⁵⁸³, as shown in **Fig.29 (b)**. The PbS thin films were firstly deposited on planar and porous substrates by ALD, in which the polycrystalline p-type PbS films are found to be stoichiometric and pure. The CH₃NH₃PbI₃ perovskite film was obtained by annealing the ALD PbS film at 150 °C in the presence of vapors from methylammonium iodide. As seen in the XRD results, the perovskite CH₃NH₃PbI₃ was successfully synthesized by this multistep approach. The SEM images indicate that the grain size of the ALD PbS is approximately 40–70 nm and the converted perovskite film has a more densely packed layer with large grain sizes. The direct

synthesis of perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ has yet to be successful. However, Popov et al. have moved forward to fabricate metal iodides by ALD⁵⁸⁴, which are closer to the ALD perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$. In their process, lead silylamide ($\text{Pb}(\text{btsa})_2$) and SnI_4 were used as precursors and the deposition temperature was below 90 °C. The roughness of the substrate surface significantly affected the crystalline texture and morphology of the PbI_2 films, in which the films are dense on smooth substrates and porous on rough substrates. This ALD PbI_2 film presents high film quality, uniformity, and scalability.

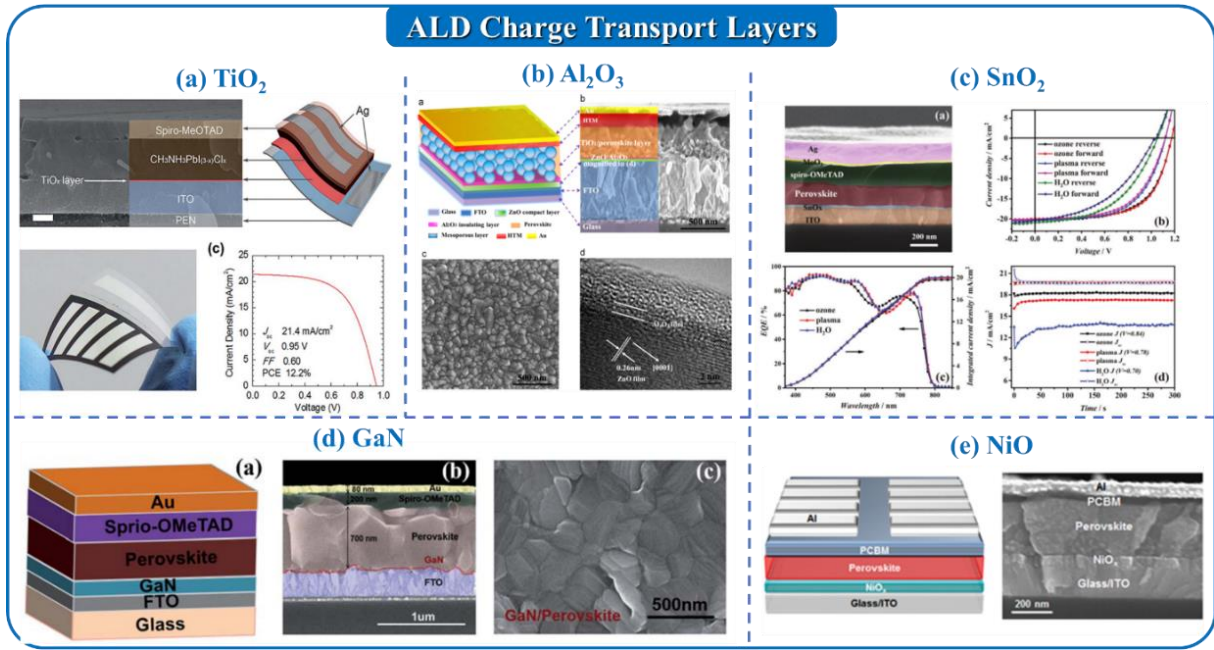


Fig.30 ALD deposited charge transport layers for PSCs: (a) TiO_2 ; (b) Al_2O_3 ; (c) SnO_2 ; (d) GaN ; (e) NiO .

The charge transport layers are essential for the performance and efficiency of PSCs^{585, 586}. The charge transport layer is used to selectively extract photo-generated charges from the perovskite layer and transport the electrons/holes to the electrodes^{587, 588}. The charge transport layers are generally divided into electron transport layers, which transport photo-excited electrons, and hole transport layers, which transport holes. The main characteristics required of an ideal charge transport layers include charge selectivity, high conductivity, chemical stability, transparency, and pinhole-free dense morphology⁵⁷⁸. Meanwhile, the thickness of the charge transport layers is required to be thin in order to reduce the charge transfer resistance of the photogenerated charges.

With this in mind, ALD is an ideal approach to deposit a charge transport layer with conformal and dense film growth. Among the different materials, TiO_2 has been extensively studied as a charge transport layer in PSCs. In the early studies, the ALD TiO_2 layers were deposited as a hole blocking layer in PSCs^{589, 590}. For example, Grätzel's group demonstrated the sub-nanometer ALD TiO_2 overlayer for high efficiency solid-state mesoscopic solar cells using a perovskite absorber, which effectively blocked the parasitic back reactions⁵⁸⁹. Subsequently, ALD- TiO_2 was further studied as an electron transport layers for PSCs^{507, 591-604}. Jung's group reported flexible perovskite solar cells with a high power conversion efficiency of 12.2 %. As shown in **Fig.30 (a)**, the amorphous and compact TiO_2 was deposited by ALD with a thickness of 20 nm. The fast electron transport leads to the excellent performance of the PSCs, which was proven by the time-resolved photoluminescence and impedance studies. Additionally, the flexibility of the device is remarkable, in which it can maintain 95% of the initial PCE after 1000 bending cycles with a bending radius of 10 mm. Afterward, Li's group further investigated the effect of TiO_2 thicknesses on the performance and clarified the mechanism behind the improved performance⁶⁰⁵. Different thicknesses of the TiO_2 film, ranging from 5 nm-20 nm, were optimized, in which a high efficiency of 13.6 % was achieved with the 10 nm thick TiO_2 layer. The optimized electron transport layer provided by ALD- TiO_2 delivered several advantages including high transmittance, low leakage current, and low charge transfer resistance and recombination rate⁶⁰⁵. The post-treatment process of the ALD- TiO_2 electron transport layer also influences cell performances. Martinson et al. explored two strategies which include annealing at 500 °C and UV- O_3 treatments for the ALD- TiO_2 electron transport layer³³⁹. The results showed that the room-temperature UV- O_3 treatment for ALD- TiO_2 is considered as a more effective way to improve the efficiency comparable to crystalline TiO_2 thin films synthesized by higher temperature methods. To show the advantages of ALD- TiO_2 , other methods were also investigated for the fabrication of TiO_2 electron transport layers. Tian's group demonstrated the comparison between ALD and spin-coating methods for the synthesis of TiO_2 electron transport layers⁶⁰⁶. Compared to the spin-coating, the ALD TiO_2 electron transport layer is more uniform, presented reduced interfacial charge accumulation, and accelerated electron transport. In another study, the ALD approach was proved to be superior to the spray pyrolysis and the sol-gel methods⁵⁶⁵. The results showed that high-temperature sintering is not mandatory to achieve high-performance PSCs and that low-temperature fabrication of compact layer by ALD can provide high efficiency on flexible substrates.

SnO₂ is another promising electron transport layer candidate for PSCs due to its deep conduction band, high electron bulk mobility, wide optical bandgap, and excellent chemical stability^{575, 607-611}. Hagfeldt's group firstly demonstrated the use of ALD SnO₂ instead of TiO₂ as an electron transport layer with an almost hysteresis-free efficiency of 18% and a high voltage up to 1.19 V⁶¹². Compared to TiO₂, the PSCs with SnO₂ as an electron transport layer delivered better performances with high voltages and remarkably good stability over time. A barrier-free charge transport across the SnO₂/perovskite interface was achieved, resulting in highly stable current densities. Moreover, the ALD deposition parameters have obvious influences on the properties of the deposited materials. As shown in **Fig.30 (c)**, Hu et al. studied different oxidant precursors, including H₂O, O₃, and O₂ plasma, for use in the deposition of ALD SnO₂ and their effects on the PSCs⁶¹³. The results showed that the ALD SnO₂ electron transport layer deposited using O₃ has the best performance with a stable PCE of 15.3% and a remarkably high V_{oc} of 1.17 V. During the ALD process, an interfacial layer of PbI₂ was formed between the SnO₂ and perovskite. Different oxidants precursors resulted in different extraction barriers at the interfaces, in which the barriers were the largest for H₂O-deposited SnO₂ and the smallest one is O₃-deposited SnO₂. The smaller barrier led to superior electron extraction. Another important parameter for the ALD process is the deposition temperature. Kuang et al. studied the ALD SnO₂ electron transport layer deposited at different temperatures in the range of 50-200 °C⁶¹⁴. The ALD-SnO₂ deposited at 200 °C contributed to cell stability, however, the efficiency decreased by approximately 50% for the counterpart device using the 50 °C SnO₂. The post-treatment of the ALD layers also have an influence on the cell performances. Jeong et al. demonstrated ALD-SnO₂ exposed to different post-annealing temperatures of 180 °C and 300 °C and used them as electron transport layers⁶¹⁵. As a result, the PSCs with the ALD SnO₂-180 °C layer showed the highest power conversion efficiency of 18.3 % and better reproducibility. The higher power conversion efficiency of ALD SnO₂-180 °C based PCSs compared to as-deposited SnO₂ was attributed to the enhanced electron-transport properties that improving the electrical conductivity. However, Although the conductivity of the ALD SnO₂-300 °C was highest, the poor hole blocking ability of ALD SnO₂-300 °C led to the lower power conversion efficiency. Another similar study was demonstrated by Wang et al.⁶¹⁶, in which the PSCs with a lower temperature (100 °C) post-treatment under air resulted in a higher power conversion efficiency of 20.3 % than that of the PSCs with the as-deposited SnO₂ and SnO₂ annealed at higher temperatures of 200 and 300 °C).

Some other materials, such as GaN, and Nb₂O₅, et al. have also been demonstrated as electron transport layers for PSCs⁶¹⁷⁻⁶¹⁹. For example, as shown in **Fig.30 (d)**, Wei et al. deposited a compact and amorphous n-type GaN layer by plasma-enhanced ALD at 280 °C to be used as an electron transport layer for PSCs⁶¹⁸. The GaN-based PSCs exhibited higher efficiency of 15.18% with less hysteresis than the GaN-free device (10.38% efficiency). The improved performance with the GaN layer can be attributed to the improved electron extraction and reduced recombination at the FTO/perovskite interface. In addition, the bilayer structure was further designed as an electron transport layer for PSCs⁶²⁰. As shown in **Fig.30 (b)**, an ultra-thin Al₂O₃ insulating layer was deposited between the electron transport layer of ZnO and perovskite for PSCs⁶²¹. This insulating layer with an electron transport layer can suppress the carrier's recombination process and improve the conversion efficiency of PSCs. The designed interface with ZnO/Al₂O₃ resulted in PSCs with high efficiency of 15.55%, in which the thickness of Al₂O₃ insulating layer is only 4 Å. Another bilayer structure of TiO₂/WO₃ was designed and fabricated by a combination of ALD and spin-coating processes on a conductive substrate to prevent the contact between the fluorine-doped tin oxide (FTO) and perovskite⁶⁰². The PSCs with the TiO₂/WO₃ electron transport bilayer exhibited an enhanced power conversion efficiency of up to 20.14%, which is much better than the single WO₃ or TiO₂ electron transport layer-based devices.

For the hole transport layers, NiO has proven to be one of the most popular materials due to its good optical transparency, high chemical stability, and ability to align the band edges of the perovskite layers^{575, 578}. The advantages of NiO as hole transport layers can be summarized as: 1) suitable work function and large bandgap; 2) efficient hole extraction and low electrode polarization restricted to the interface of NiO; 3) high transparency in the visible spectral range⁵⁸⁶. ALD holds obvious advantages in the fabrication of NiO hole transport layers compared to other methods, such as sol-gel process⁶²²⁻⁶²⁴. Seo et al. first demonstrated ultra-thin NiO by ALD as hole transport layers for PSCs⁶²⁵. The results showed that the work function and hole concentration of the thin NiO hole transport layers increased due to the overlap of the Debye length, resulting in an enhanced photovoltaic activity. A post-annealing process of the NiO layer can reduce the hydroxylated NiOOH on the surface, leading to higher electrical conductivity and better interfacial properties. The inverted planar PSCs with ALD NiO hole extraction layers exhibited a high efficiency of up to 16.40 % with negligible hysteresis. Similarly, another work also demonstrated the influence of the post-treatment of ALD NiO on the PSCs performances⁶²⁶. The PSCs with post-

annealed ALD NiO layers delivered a higher efficiency of 17.07% when compared to the pristine NiO-based device, which had an efficiency of 13.98%. To improve the device reliability for large-scale fabrication, an atmospheric pressure spatial ALD process was developed to deposit NiO hole extraction layers, as shown in **Fig.30 (e)**⁶²⁷. The PSCs with NiO hole extraction layers exhibited a high-power conversion efficiency of 17.1%. The NiO obtained by spatial ALD has improved uniformity with an average roughness of < 0.6 nm. Importantly, the simply prepared and high-quality ALD NiO films are compatible with the large-throughput fabrication of perovskite optoelectronics.

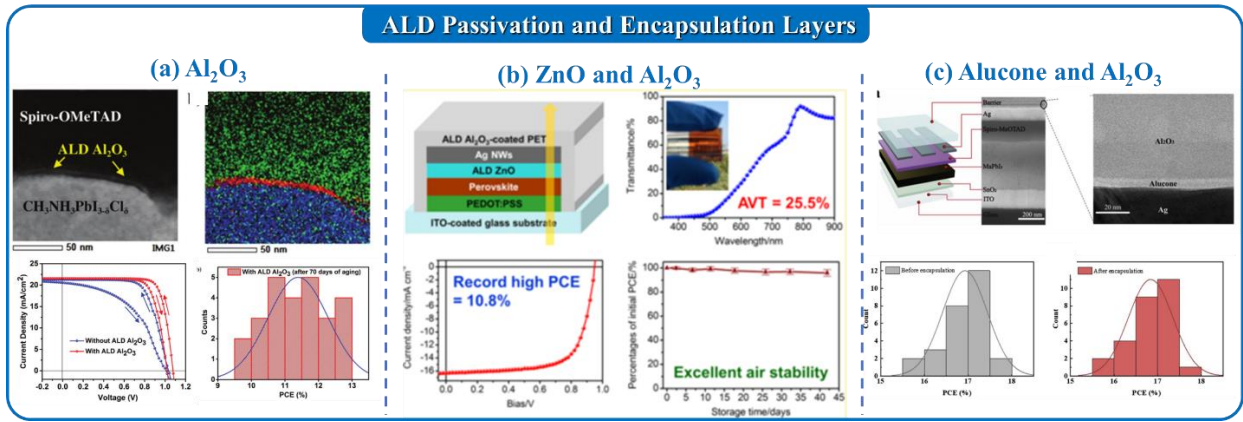


Fig.31 ALD deposited passivation and encapsulation layers: (a) Al_2O_3 ; (b) ZnO and Al_2O_3 ; (c) alucone and Al_2O_3 .

The passivation layers at the perovskite absorber and contact layer interfaces in PSCs are generally used to reduce the concentration of surface defects that induce undesirable carrier recombination. ALD Al_2O_3 is one of the most commonly used passivation layer materials for PSCs⁶²⁸⁻⁶³⁶. For example, as shown in **Fig.31 (a)**, a thin layer of ALD Al_2O_3 was deposited on $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ for PSCs to reduce the hysteresis loss and stabilize the devices against humid conditions⁶³⁷. As a result, the PSCs with the ALD Al_2O_3 layer exhibited a high efficiency of 18.8 % with a significantly reduced hysteresis. Furthermore, the Al_2O_3 passivation layer can significantly improve the PSCs stability against ambient humidity while retaining 60–70% of the initial efficiency after 70 days. However, the pristine cell without the Al_2O_3 layer suffered from a drastic fall to 12% of its initial PCE during the study period. In another study, two ALD layers were deposited for the PSCs; one being a ZnO passivation layer and another one being the Al_2O_3 encapsulation layer, as shown in **Fig. 31 (b)**⁶³⁸. The fabricated PSCs device showed a remarkable

efficiency of 16.5% with high reproducibility. The Al_2O_3 encapsulation layer can effectively enhance the ambient stability of the PSCs due to its ability to act as an effective gas diffusion barrier. To further improve the operational stability of PSCs in a humid environment, an alternating organic-inorganic encapsulation structure was deposited by ALD/MLD and found to exhibit an excellent water vapor transmittance rate, as shown in **Fig.31 (c)**⁶³⁹. The PSCs with the Al_2O_3 /alucone hybrid encapsulation layer survived at 80% relative humidity and 30 °C for over 2000 h while preserving 96% of its initial performance.

3.2.2 ALD/MLD for photoelectrochemical water splitting

Another important energy conversion device is the photoelectrochemical (PEC) water splitting cell, which splits water into H_2 and O_2 through the use of sunlight⁶⁴⁰⁻⁶⁴². It is a renewable approach to convert solar energy into storable fuels. In a PEC water-splitting cell, the photoelectrodes mainly consist of H_2 -evolving p and O_2 -evolving photoelectrodes. For the O_2 -evolving photoanode, n-type semiconductor materials are used to drive the holes to the interface between the semiconductor and electrolyte⁶⁴³⁻⁶⁴⁵. The electron-hole pairs are generated when the energy of the light is greater than the bandgap on the photoanode. The holes, where the water oxidation occurs, move to the surface. The protons are reduced to form molecular hydrogen and the electrons are collected at the metal cathode^{642, 646}. On the H_2 -evolving photocathode, the p-type semiconductor facilitates electron transfer to the electrolyte interface for the reduction reaction. The proton is reduced by the electrons to evolve hydrogen gas at the photocathode surface, and the holes move back to the counter electrode, where water oxidation takes place^{642, 646}. Therefore, the choice of semiconductor material is the key to achieving high-performance PEC water splitting devices⁶⁴⁷⁻⁶⁵⁰. The semiconductor generally requires a suitable bandgap, high conductivity, excellent stability, low cost, and should be environmentally friendly.

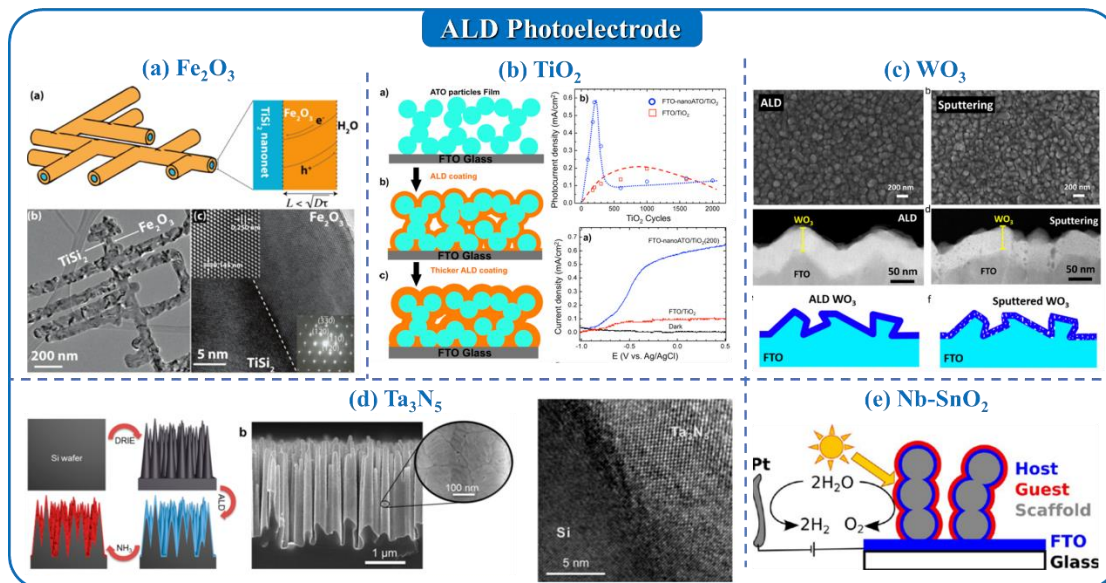


Fig.32 ALD-fabricated photoelectrodes for PEC water splitting devices: (a) Fe_2O_3 ; (b) TiO_2 ; (c) WO_3 ; (d) Ta_3N_5 ; (e) SnO_2 .

Fe_2O_3 possesses a suitable bandgap and low-cost, which makes it a desirable candidate as a photoelectrode for PEC water splitting devices⁶⁵¹⁻⁶⁵⁵. Wang's group demonstrated ALD Fe_2O_3 on a TiSi_2 nanonet as photoelectrode⁶⁵⁶, as shown in **Fig.32 (a)**. The TiSi_2 nanonet was used as a charge transport layer to improve the charge collection. The photocurrents of 1.6 and 2.7 mA cm^{-2} were achieved at 1.23 and 1.53 V (vs. RHE) without any additional oxygen-evolving catalysts. Another p- LaFeO_3 /n- Fe_2O_3 heterojunction structure was reported by Chen's group⁶⁵⁷. The La_2O_3 layer was first deposited on the β - FeOOH nanorods by ALD, followed by the formation of the p- LaFeO_3 /n- Fe_2O_3 heterojunction which was obtained by a post-annealing process. Because of the well-matched band levels of LaFeO_3 and α - Fe_2O_3 , the photocurrent density was promoted from 0.37 to 0.58 mA cm^{-2} at 1.23 V versus RHE. The significant improvement could be attributed to the accelerated charge separation within the space depletion layer induced by the built-in potential⁶⁵⁷.

TiO_2 was the first reported photoelectrode for water splitting, however, the solar-to-fuel conversion efficiency of it is the major limitation⁶⁵⁸⁻⁶⁶³. The main challenges for the TiO_2 photoelectrode are the carrier diffusion length, optical penetration depth, and inefficient electron collection. Peng et al. demonstrated an ALD TiO_2 layer on nano antimony-doped tin oxide

(nanoATO) films as photoelectrodes for PEC water splitting, as shown in **Fig. 32 (b)**⁶⁶⁴. The nanoATO-ALD TiO₂ photoelectrode delivered a high photocurrent density of 0.58 mA cm⁻² under 1.5 G AM (~sunlight of 100 mW cm⁻²), which is 3 times higher than that of the planar TiO₂ electrodes on FTO glass. It was further reported that the thickness of the ALD TiO₂ layer and post-treatment process are also critical factors that affect the water splitting capabilities⁶⁶⁵. ALD TiO₂ was deposited on hematite nanorod arrays as photoelectrodes. In this study, different post-annealing temperatures of 400, 650, 750 °C, were investigated. It was found that with an annealing temperature of 650 °C, significant photocurrent can be observed. Furthermore, the thicknesses of the ALD TiO₂ was optimized. Below a critical thickness, the PEC performance was steadily enhanced. If the thickness of the TiO₂ layer was too thick, the hole transfer from hematite to liquid was blocked because of the formation of a substantive heterojunction. With the optimized annealing temperature and thickness for the ALD TiO₂ layer, a high photocurrent of 1.9 mA cm⁻² at 1.23 V (vs RHE) under AM 1.5 simulated solar illumination was achieved.

In addition to TiO₂, other metal oxides, such as Ga₂O₃, SnO₂, ZnO, HfO₂, WO₃, et al., have been deposited by ALD on different substrates and used as effective photoelectrodes for PEC water splitting devices^{57, 666-677}. For example, as shown in **Fig.32 (c)**, Zhao et al. compared two different deposition techniques which included sputtering and ALD for the deposition of WO₃ thin film photoelectrodes⁶⁷⁸. For the sputtered WO₃, the film possessed obvious nanosized holes throughout the surface. Meanwhile, for the ALD WO₃ film, no obvious microholes or other physical defects were observed. The highest performance was achieved for WO₃ films deposited by ALD after annealing in air, which led to the fewest physical defects and an appropriate amount of oxygen vacancies⁶⁷⁸. Another Nb-doped SnO₂ was deposited by ALD and demonstrated by Grätzel's group (**Fig. 32 (e)**)⁶⁷⁹. The doped films were deposited using SnO₂ and Nb₂O₅ subcycles in which the content of Nb was controlled from 0-4%. The conductivity of the SnO₂ was improved with Nb-doping, in which the conductivity reached a maximum with 2% Nb in SnO₂. With another layer of hematite, the architecture showed a significant photocurrent plateau of 2.26 mA cm⁻² at 1.4 V vs RHE.

Besides the metal oxide, metal nitrides such as tantalum nitride have received increasing attention due to their favourable bandgaps and band edge positions that straddled both the reduction and oxidation potentials of water^{680, 681}. Narkeviciute et al. fabricated core-shell Ta₃N₅

on a Si substrate by ALD (**Fig.32 (d)**)⁶⁸⁰. The Ta₃N₅ was obtained by the nitridation of amorphous Ta₂O₅ under NH₃. The thinner Ta₃N₅ shells resulted in superior photocurrents and absorbed-photon-to-current efficiencies, indicating minimal carrier diffusion lengths on the order of tens of nanometers.

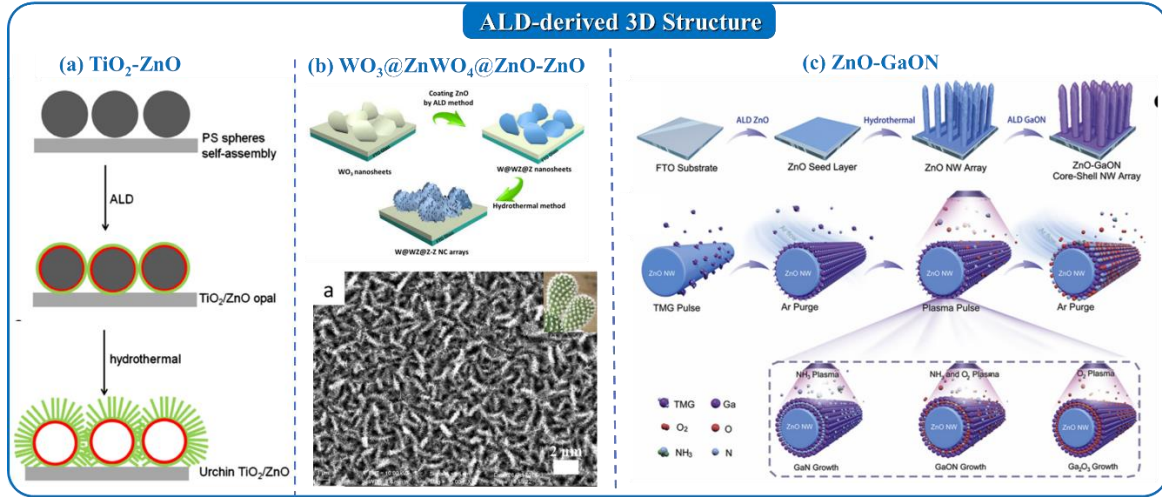


Fig.33 ALD-derived 3D structured photoelectrodes for PEC water splitting devices: (a) TiO₂-ZnO; (b) WO₃@ZnWO₄@ZnO-ZnO; (c) ZnO-GaON.

Similar to other applications, ALD is also used to design different 3D-structured photoelectrodes for PEC water splitting devices aimed towards achieving high specific surface area, direct electron transport pathways, and excellent light-harvesting abilities^{170, 682-691}. In an early study, Cheng's reported a 3D ordered urchin-like hollow TiO₂/ZnO nanorods structure on transparent FTO as a photoanode for photoelectrochemical hydrogen generation⁶⁹², as shown in **Fig.33 (a)**. In a typical process, a monolayer of PS microspheres was assembled onto the FTO substrate to act as a sacrificial template. Then, 20 nm of TiO₂ and 10 nm of ZnO were deposited onto the PS spheres by ALD. Afterwards, ZnO nanorods were grown onto the surface of TiO₂/ZnO hollow spheres with a hydrothermal approach. With a CdS sensitizer, a photocurrent of 3.6 mA cm⁻² (at 0 V vs Ag/AgCl) was generated by the urchin-like TiO₂/ZnO photoanode, which is much higher than that of the 2D and 1D structure. The higher surface area provided by the nanostructured electrode for quantum dot loading contributed to the enhanced light scattering ability. Another interesting 3D-structured cactus-like WO₃@ZnWO₄@ZnO-ZnO was demonstrated by Zhang's group, fabricated by combining ALD with a hydrothermal process⁶⁹³. As shown in **Fig.33 (b)**, the well-aligned WO₃

nanosheet array was grown on FTO glass by the hydrothermal method. Subsequently, the amorphous ZnO layer was coated on the WO₃ nanosheets by ALD and further annealed in air to form a ZnWO₄ buffer layer. Finally, another set of ZnO nanosheets was grown on the surface by a secondary hydrothermal process. As a result, the fabricated 3D photoelectrode photocurrent density was 3.8 times higher ($\sim 1.57 \text{ mA/cm}^2$) at 1.23 V vs. RHE than the pristine WO₃ photoanode after long-term continuous illumination. Their group further developed another ZnO-GaON core-shell nanowire structure by PE-ALD⁶⁹⁴, as shown in **Fig.33 (c)**. The ZnO nanowire was firstly grown on the FTO substrate via a hydrothermal method with an ALD ZnO seed layer. Afterwards, a GaON film was further deposited on the ZnO nanowire by a PE-ALD process. To grow the GaON film, NH₃ and O₂ gas were introduced simultaneously at a specific flow ratio in the plasma pulse step. The unique structure of ZnO-GaON core-shell nanowires with optimized ALD GaON shell thickness exhibited a significant electric field enhancement and light trapping ability, which improved the photocurrent from ~ 0.24 (pristine ZnO) to 2.25 mA cm^{-2} at 1.23 V versus RHE.

To improve the PEC device performance, numerous transition-metal/metal oxides, such as nickel (and NiO) and cobalt (and Co₃O₄), have been used as catalysts for oxygen-evolution. ALD was also widely reported as a method to deposit transition-metal catalysts on photoelectrodes for PEC water splitting^{609, 695-700}. Yang et al. fabricated a conformal, biphasic CoOx catalyst by PE-ALD and used it as a photoelectrode with high activity and compatibility⁷⁰¹. A compact and continuous nanocrystalline Co₃O₄ spinel was deposited by PE-ALD, which provides effective protection for the underlying substrate. Furthermore, disordered surface layers composing of Co(OH)₂ were obtained at a reduced deposition temperature and significantly improved electrocatalytic activity. This Co(OH)₂ layer promoted chemical and structural transformation, leading to a high concentration of catalytically active sites. As a result, the Co₃O₄/Co(OH)₂ thin films exhibited high activity towards water splitting with enhanced durability.

Passivation layers are widely used to suppress the surface recombination that occurs on photoelectrodes for PEC water splitting devices. ALD is an ideal technique to deposit the passivation layer, which has also been introduced in the above sections for solar cells. TiO₂ is one of the most popular materials as a passivation layer and has been deposited by ALD^{591, 702-710}. For example, Yang's group fabricated an epitaxial rutile TiO₂ shell by ALD on TiO₂ nanowires as the passivation layer⁷¹¹. When coated with a 150-ALD-cycle TiO₂ shell, the photocatalytic activity of

the 1.8 μm long TiO_2 nanowire was enhanced 1.5 times (1.5 V vs RHE) higher, reaching a current density of 1.1 mA cm^{-2} . This ALD TiO_2 coating improved the charge collection efficiency due to the passivation of surface states and an increase in surface area. Moreover, Paracchino et al., examined several factors that determine the performance and stability of Cu_2O photocathodes with ALD-deposited overlayers⁷¹². It was found that the ALD deposition temperature is critical towards the device performance, and determines the energy level positions as well as crystallinity. With a more crystalline overlayer, 62% stability over 10 hours of testing was achieved for the Cu_2O photocathodes. Some other metal oxides deposited by ALD, such as Al_2O_3 , SnO_2 , Ta_2O_5 , ZnO , et al., were also reported as passivation layers for PEC water splitting devices⁷¹³⁻⁷²⁰. For example, ALD Al_2O_3 was deposited on TiO_2 nanotubes as a passivation layer and was used as a photoanode for PEC water splitting⁷²¹. The optimized ALD coating exhibited an enhanced photocurrent density by 0.8 times compared to the pristine TiO_2 nanotubes. The improvement was mainly ascribed to the reduction of the electron-hole recombination and decreased surface defect density combined with the field-effect passivation induced by the ALD Al_2O_3 shells. In another work, 2 nm of ALD- ZnO was fabricated on the spin-cast PC71BM thin-film n-type organic semiconductor photoanode as a passivation layer⁷²². As a result, the passivated photoelectrode exhibited increased stability for 1000 s and a photocurrent of $30 \mu\text{A cm}^{-2}$ at $E = 1.23 \text{ V}$ versus RHE, which were nearly 300% and 600% of those in the un-passivated PC71BM, respectively. The results revealed that the ALD ZnO can tunnel the hole transfer through passivation layers and improve the adhesion to the organic semiconductor, thus lowering ohmic resistance.

4. Large scale ALD/MLD

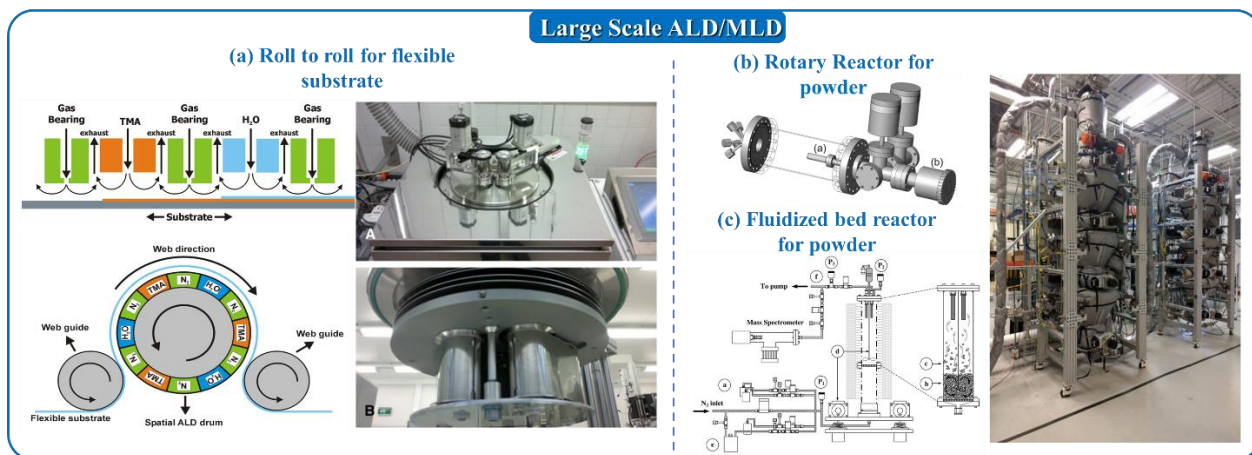


Fig.34 Large scale ALD/MLD: (a) roll-to-toll techniques for flexible substrates; (b) rotary reactor for powder; (c) fluidized bed reactor for powder.

With significant efforts from the community, ALD and MLD techniques have been widely proven as effective and promising tools for energy storage and conversion applications, particularly for the fields of batteries and fuel cells. However, one of the major concerns is the practicality of large-scale deposition for industrial applications⁷²³. To address this concern, large-scale spatial ALD systems have been proposed and developed⁷²⁴. In a spatial ALD process, the precursors are pulsed simultaneously and continuously, but at a different physical location in the reactor⁷²⁵⁻⁷²⁷. **Fig.34 (a)** shows the concept of roll-to-roll ALD, which uses a typical spatial ALD process. In this roll-to-roll process, the reactor is divided into individual spaces, exposing the precursors to the substrate in different regions and moving the substrates through the reactor⁷²⁸⁻⁷³¹. This roll-to-roll ALD process allows very high deposition rates while maintaining the desired ALD properties such as film quality and conformality. Subsequently, another roll-to-roll reactor was designed, consisting of a central drum that contains one or more half-reaction zones for individual precursors, as illustrated in **Fig.34 (a)**. This upgrade allows for the avoidance of the mechanical contact between the deposition side of the foil and the reactor and further minimizes the amount of moving parts⁷²⁸. These roll-to-roll ALD reactors are ideal for large scale flexible substrates requiring fast deposition rates⁷³². For energy storage and conversion applications, they are promising to carry out roll-to-roll ALD coatings on electrodes at the industrial levels.

Another reactor design is used for large scale powder depositions. It is also very important and practical for energy storage and conversion applications, such as ALD/MLD coatings on cathode/anode powders for batteries, and catalysis deposition on carbon powders for fuel cells. One of the options for ALD/MLD deposition on powders is the rotary reactor, which is presented in **Fig. 34(b)**. The rotary reactor allows for static reactant exposures that can utilize the ALD precursors more efficiently⁷³³⁻⁷³⁵. Another possibility is the fluidized bed reactor, which has been studied intensively for different ALD/MLD processes⁷³⁶⁻⁷⁴⁹. For example, **Fig. 34(c)** shows a typical fluidized bed reactor for ALD deposition on powder. This reactor allows for the optimization of the process variables at any scale. Combined with in-situ mass spectrometry, the precursors can be fully utilized to maximize precursor utilization and surface saturation. Some ALD companies have already commercialized the fluidized bed reactor with the capabilities of

process material at the ton level, as shown in **Fig. 34**⁷⁵⁰. Moreover, many types of films can be deposited in these reactors on virtually any particle substrate using this gas-phase reaction process⁷³⁸.

5. Conclusion

In this comprehensive review, we summarize the development and understanding of ALD/MLD techniques for energy storage and conversion applications, focusing on batteries, supercapacitor, fuel cells, solar cells and photoelectrochemical water splitting. In general, ALD/MLD are very promising techniques that can address the challenges for energy storage and conversion due to their unique properties such as precise thickness control, excellent uniformity and conformity, and tunable composition. The main content of this review is as follows:

1) ALD/MLD techniques are used to fabricate electrode materials for LIBs and NIBs. Various types of metal oxides (SnO_2 , ZnO , and TiO_2 , et al.) have been deposited on different substrates (such as graphene, carbon nanotubes, and stainless steel) as anode materials. Several Li/Na-containing compounds (LiCoO_2 , LiFePO_4 , and NaTiO_x) have been developed as cathodes for LIBs and NIBs. Meanwhile, MLD is proposed to synthesize organic electrodes for batteries. Benefitting from the advantages of ALD/MLD, the morphologies, structures, compositions, and particle sizes are precisely controlled by adjusting the ALD/MLD parameters, resulting in excellent electrochemical performances. However, as we discussed above, the drawbacks of ALD/MLD for electrode fabrication are also obvious. The major concern is the low GPC of ALD/MLD films, which is in the range of $\text{\AA}$ /cycle for most of the procedures. To reach a high enough loading of the active materials, hundreds or even thousands of ALD cycles are required to obtain a thick electrode. This time-consuming process has less commercial viability for standard battery technologies, particularly when compared with composite/powder-based electrodes. Nevertheless, it still needs to be pointed out that ALD/MLD is still promising for the design and fabrication of thin film batteries or micro-batteries with thin electrodes.

2) Rather than electrode fabrication, ALD/MLD is more promising for the engineering of the interface between the electrode and electrolytes in LIBs and NIBs, especially on the cathode side. ALD Al_2O_3 is the most popular coating layer used to modify the surface of cathode materials. The electrochemical performances of Al_2O_3 -coated cathode materials are significantly improved with

only a few cycles of ALD. The protection mechanism of ALD Al_2O_3 has been intensively studied by different approaches, such as in-operando XRD, in-operando XANES, and STEM-EELS. The most widely recognized explanation is that the thin ALD Al_2O_3 can prevent the electrolyte decomposition, HF corrosion, and transition metal dissolution. Some other metal oxides have been further investigated as a coating for cathode materials, in which ALD Al_2O_3 still performs the best among them. However, the metal oxides are generally non-ionic conductive, which will limit the Li-ion transport across the interface. In this case, Li-ion conductive solid-state electrolytes have been developed to replace the metal oxide coatings for cathode materials. The solid-state electrolyte coating enables fast Li transport and achieves even better electrochemical performances compared to their respective metal oxides. Beyond surface coating, ALD films are used to tailor the structures of the cathodes with further post-treatments, such as doping the lattice and modifying the grain boundary.

3) On the anode interface of LIBs and NIBs, the ALD/MLD coatings serve two purposes. On one hand, the ALD/MLD layers are deposited as artificial SEI to prevent the side reactions between anode materials and liquid electrolytes. On the other hand, the ALD/MLD surface coating can relieve the volume change of the anode materials during lithiation/delithiation. Generally, when depositing coating layers for anodes, MLD presents more promising properties and better electrochemical performances compared to ALD due to the enhanced flexibility for volume change accommodation. Beyond the conventional anode materials, Li metal and Na metal are excellent candidates for next-generation Li metal batteries and Na metal batteries, respectively. The application of ALD/MLD has also been extended to artificial SEI fabrication for Li and Na metal anodes. Similar to regular anodes, the MLD layers deliver better performances than that of ALD coatings for alkali metal anodes. Additionally, the organic-inorganic hybrid coatings have been proven to be ideal layers with excellent electrochemical, chemical and mechanical properties. Moreover, the ALD/MLD techniques have been applied to address the interfacial issues for SSBs, in which ALD/MLD layers are used to prevent the side reaction between the electrodes and SSEs.

4) ALD/MLD has also been used to deposit catalysis with controllable particle sizes for metal-air batteries and fuel cells. For metal-air batteries, precisely controlled catalysis is the key to tuning the discharge product composition and morphologies. Moreover, selective ALD deposition can be applied to stabilize the catalysts. For electrocatalytic applications, ALD has been shown to be an ideal technique to deposit catalysts with controllable particle sizes in high-aspect-ratio and porous

materials. It can be further used to design novel structures and modify the surface of the substrate to stabilize the catalysts. Moreover, ALD can be used to precisely deposit single atoms and even dimer catalysts on the different substrates, which improves the activity to a new level.

5) ALD/MLD has been used to develop nanostructure materials for different applications, such as batteries, supercapacitor, solar cell and photoelectrochemical water splitting. Generally, different types of templates are used to deposit ALD films. Afterwards, the templates are removed or transferred to create hollow nanostructures by post-treatment processes. Finally, the 3D nanostructures with high surface area and short ion diffusion paths are achieved with significantly improved performances for different energy-related devices.

6) For photovoltaics of DSSCs, Perovskite and photoelectrochemical water splitting, ALD/MLD is used to deposit the core-shell structure of photoelectrode with minimized electrons transferring way to the conductive substrate. Moreover, ALD has been more widely used to modify the interfaces in DSSCs, including passivation, barrier, and blocking layers, with significantly improved performances.

7) The potential of large scale ALD/MLD for energy applications has been further discussed. On one hand, the roll-to-roll ALD/MLD has been widely developed for flexible substrates and is suitable for battery electrodes, fuel cell membranes and solar cell substrates. On the other hand, the rotary and fluidized bed reactors are designed for the mass production of powder samples, which is ideal for cathode/anode material manufacturing.

6. Perspective

Significant progress in the fields of ALD/MLD for energy application has been reported over the past decade and ALD/MLD techniques are gradually becoming recognized by the energy storage and conversion communities as powerful and effective tools. However, the challenges still remain and need to be addressed, at the same time, enormous potentials are expected to be exploited. We list the detailed potential directions and perspectives below.

1) Extension of other ALD chemistries for energy applications. Currently, the most popular materials deposited by ALD for energy applications are various metal oxides and noble metals. In the ALD community, other types of materials, such as nitrides, sulfides, and fluorides, have been successfully synthesized by ALD (or PEALD). These materials have unique properties compared

to metal oxides and are expected to be applied in energy applications. For example, metal nitrides generally show higher electronic conductivity and chemical stability compared to metal oxides, and can be used as a substrate for fuel cell catalysis or as coatings for cathode/anode materials for batteries. Furthermore, metal fluorides have been predicted to have the widest electrochemical stability windows, especially at high potential. These materials would be ideal coatings for cathode materials in batteries. With this in mind, more opportunities and possibilities should arise for ALD/MLD chemistry in energy applications.

2) Development and application of new MLD chemistry. The developed MLD chemistry is also plentiful and attractive, however, their application in energy is still in an early stage. Firstly, the organic electrodes fabricated by MLD for Li and Na storage are interesting with various electrochemical active sites. Secondly, the fabrications of Li-ion and Na ion conductive MLD films is also challenging, putting forward the requirement for new MLD chemistries. Meanwhile, for fuel cell applications, highly conductive and catalytically active MLD thin films are expected to be explored as catalysts in fuel cells. Furthermore, the post-treatment of MLD films can be used to design and synthesize porous and carbon-containing films.

3) Investigation of the properties of ALD/MLD films. Although numerous materials have been synthesized by ALD/MLD techniques, their properties have not been fully studied, such as chemical stability, electrochemical stability, and mechanical stability. These properties are always predicted from simulations or inferred from the same bulk materials. However, the properties of ALD/MLD films at the nanoscale or atomic scale are relatively different compared to the bulk materials. In this case, the understanding and characterization of ALD/MLD films at the nanoscale are critical for the community.

4) Tuning of the mechanical properties of ALD/MLD films. Recent studies reveal that the mechanical properties also affect the electrochemical performances of the electrode, particularly the materials with large volume change. However, there are few examples of research focusing on the mechanical properties of the ALD/MLD films. Thus, it is also important to connect the mechanical properties of the coating layer to the electrochemical performances of the batteries.

5) Rationally designed of films by ALD/MLD. Various individual ALD/MLD films have been studied for energy applications. However, the individual film cannot meet all the requirements for

different applications. The combination of different ALD/MLD films for hybrid coating designs are required to meet the demands of specific applications.

6) Mechanistic insight behind the electrochemical performance. It has been widely proven that ALD/MLD is effective in improving the performances of various systems. However, functionality and mechanisms of ALD/MLD layers are still unclear. Thus, advanced characterization methods, especially in-situ techniques, are the key for providing a deep understanding and provide guidance towards future ALD/MLD material design.

7) Currently, it is time to demonstrate practical applications of ALD/MLD technologies in energy storage and conversion for large-scale production. In particular, it is urgent to realize the mass products of ALD coating on powder materials, such as cathode materials for batteries.

Acknowledgments

X. Sun would like to acknowledge the funding support by the Natural Science and Engineering Research Council of Canada (NSERC), the Canada Research Chair Program (CRC), the Canada Foundation for Innovation (CFI), Ontario Research Fund (ORF), Mitacs and the University of Western Ontario (UWO). Y. Zhao would like to acknowledge the Mitacs Elevate Postdoctoral Fellowship. J. Liu is grateful for funding support from NSERC, CFI, BC Knowledge Development Fund (BCKDF), and the University of British Columbia (UBC). The work at Argonne National Laboratory was supported from the U.S. Department of Energy (DOE), Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Office. Argonne National Laboratory is operated for DOE Office of Science by UChicago Argonne, LLC, under contract number DE-AC02-06CH11357.

Author contributions

Y. Zhao, L. Zhang, and J. Liu contributed equally to this work; X. Sun and J. Lu supervised the overall work; Y. Zhao, L. Zhang, J. Liu, K. Amine, J. Lu, and X. Sun designed the content of the review; J. Liu and Y. Zhao organized the introduction; L. Zhang wrote the electrocatalytic reactions for fuel cell application; K. Adair focused on the Li-S batteries application and edited the language for the whole manuscript; Y. Sun wrote the Li-metal anode application; F. Zhao was in charge of solid-state Li batteries application; T. Wu and B. Xuan focused on the Li-O₂ batteries

application; Y. Zhao organized and wrote all the other parts of Li-ion batteries, Na batteries and beyond, supercapacitors, and photoelectrocatalysis applications; All authors read and commented on the manuscript.

References

1. D. Larcher and J. M. Tarascon, *Nat Chem*, 2015, **7**, 19-29.
2. A. Manthiram, X. Yu and S. Wang, *Nature Reviews Materials*, 2017, **2**, 16103
3. Y. Li and J. Lu, *ACS Energy Letters*, 2017, **2**, 1370-1377.
4. T. Famprikis, P. Canepa, J. A. Dawson, M. S. Islam and C. Masquelier, *Nat Mater*, 2019, **18**, 1278–1291
5. Y. Liu, Y. Zhu and Y. Cui, *Nature Energy*, 2019, **4**, 540-550.
6. Y. Yuan, K. Amine, J. Lu and R. Shahbazian-Yassar, *Nature communications*, 2017, **8**, 15806
7. Y.-J. Wang, B. Fang, D. Zhang, A. Li, D. P. Wilkinson, A. Ignaszak, L. Zhang and J. Zhang, *Electrochemical Energy Reviews*, 2018, **1**, 1-34.
8. L. Xu, S. Tang, Y. Cheng, K. Wang, J. Liang, C. Liu, Y.-C. Cao, F. Wei and L. Mai, *Joule*, 2018, **2**, 1991-2015.
9. S. Kalluri, M. Yoon, M. Jo, H. K. Liu, S. X. Dou, J. Cho and Z. Guo, *Advanced Materials*, 2017, **29**, 1605807
10. J. Kim, H. Lee, H. Cha, M. Yoon, M. Park and J. Cho, *Advanced Energy Materials*, 2018, **8**, 1702028.
11. X. Li and X. Sun, *Advanced Functional Materials*, 2018, **28**, 1801323.
12. J. Song, B. Xiao, Y. Lin, K. Xu and X. Li, *Advanced Energy Materials*, 2018, **8**, 1703082.
13. Z. P. Cano, D. Banham, S. Ye, A. Hintennach, J. Lu, M. Fowler and Z. Chen, *Nature Energy*, 2018, **3**, 279-289.
14. N. Tian, B.-A. Lu, X.-D. Yang, R. Huang, Y.-X. Jiang, Z.-Y. Zhou and S.-G. Sun, *Electrochemical Energy Reviews*, 2018, **1**, 54-83.
15. M. Leskela and M. Ritala, *Thin Solid Films*, 2002, **409** 138–146.
16. M. Leskela and M. Ritala, *Angewandte Chemie*, 2003, **42**, 5548-5554.
17. M. Knez, K. Nielsch and L. Niinistö, *Advanced materials*, 2007, **19**, 3425-3438.
18. S. M. George, *Chemical Review*, 2010, **110**, 111–131.
19. R. W. Johnson, A. Hultqvist and S. F. Bent, *Materials Today*, 2014, **17**, 236-246.
20. M. Liu, X. Li, S. K. Karuturi, A. I. Tok and H. J. Fan, *Nanoscale*, 2012, **4**, 1522-1528.
21. C. Marichy, M. Bechelany and N. Pinna, *Advanced materials*, 2012, **24**, 1017-1032.
22. M. Noked, C. Liu, J. Hu, K. Gregorczyk, G. W. Rubloff and S. B. Lee, *Accounts of chemical research*, 2016, **49**, 2336-2346.
23. M. Mäntymäki, M. Ritala and M. Leskelä, *Coatings*, 2018, **8**, 277.
24. V. P. Prasad, N. Bahlawane, F. Mattelaer, G. Rampelberg, C. Detavernier, L. Fang, Y. Jiang, K. Martens, I. P. Parkin and I. Papakonstantinou, *Materials Today Chemistry*, 2019, **12**, 396-423.
25. X. Meng, X. Q. Yang and X. Sun, *Advanced materials*, 2012, **24**, 3589-3615.
26. K. X. Wang, X. H. Li and J. S. Chen, *Advanced materials*, 2015, **27**, 527-545.
27. X. Wang and G. Yushin, *Energy & Environmental Science*, 2015, **8**, 1889-1904.
28. B. Ahmed, C. Xia and H. N. Alshareef, *Nano Today*, 2016, **11**, 250-271.
29. C. Guan and J. Wang, *Advanced science*, 2016, **3**, 1500405.
30. L. Ma, R. B. Nuwayhid, T. Wu, Y. Lei, K. Amine and J. Lu, *Advanced Materials Interfaces*, 2016, **3**, 1600564.
31. W. Lu, L. Liang, X. Sun, X. Sun, C. Wu, L. Hou, J. Sun and C. Yuan, *Nanomaterials*, 2017, **7**, 325
32. X. Meng, *Journal of Materials Chemistry A*, 2017, **5**, 10127-10149.

33. B. Yan, X. Li, Z. Bai, X. Song, D. Xiong, M. Zhao, D. Li and S. Lu, *Journal of Power Sources*, 2017, **338**, 34-48.
34. Y. Zhao and X. Sun, *ACS Energy Letters*, 2018, **3**, 899-914.
35. Y. Zhao, K. Zheng and X. Sun, *Joule*, 2018, **2**, 2583-2604.
36. H. C. M. Knoops, M. E. Donders, M. C. M. van de Sanden, P. H. L. Notten and W. M. M. Kessels, *Journal of Vacuum Science & Technology A*, 2012, **30**, 010801.
37. X. Meng, *Energy Storage Materials*, 2020, **30**, 296-328.
38. O. Nilsen, V. Miikkulainen, K. B. Gandrud, E. Østreng, A. Ruud and H. Fjellvåg, *Physica Status Solidi (a)*, 2014, **211**, 357-367.
39. K. Share, A. Westover, M. Li and C. L. Pint, *Chemical Engineering Science*, 2016, **154**, 3-19.
40. Q. Sun, K. C. Lau, D. Geng and X. Meng, *Batteries & Supercaps*, 2018, **1**, 41-68.
41. O. Tiurin and Y. Ein-Eli, *Advanced Materials Interfaces*, 2019, **6**, 1901455.
42. F. Yu, L. Du, G. Zhang, F. Su, W. Wang and S. Sun, *Advanced Functional Materials*, 2019, **30**, 1906890.
43. J. Zhang, G. Zhang, Z. Chen, H. Dai, Q. Hu, S. Liao and S. Sun, *Energy Storage Materials*, 2020, **26**, 513-533.
44. Z. Zhao, Y. Kong, Z. Zhang, G. Huang and Y. Mei, *Journal of Materials Research*, 2019, **35**, 701-719.
45. X. Li, X. Meng, J. Liu, D. Geng, Y. Zhang, M. N. Banis, Y. Li, J. Yang, R. Li, X. Sun, M. Cai and M. W. Verbrugge, *Advanced Functional Materials*, 2012, **22**, 1647-1654.
46. V. Aravindan, K. B. Jinesh, R. R. Prabhakar, V. S. Kale and S. Madhavi, *Nano Energy*, 2013, **2**, 720-725.
47. M. Xie, X. Sun, S. M. George, C. Zhou, J. Lian and Y. Zhou, *ACS Applied Materials & Interfaces*, 2015, **7**, 27735-27742.
48. B. Ahmed, D. H. Anjum, Y. Gogotsi and H. N. Alshareef, *Nano Energy*, 2017, **34**, 249-256.
49. D. V. Nazarov, M. Y. Maximov, P. A. Novikov, A. A. Popovich, A. O. Silin, V. M. Smirnov, N. P. Bobrysheva, O. M. Osmolovskaya, M. G. Osmolovsky and A. M. Rumyantsev, *Journal of Vacuum Science & Technology A*, 2017, **35**, 01B137.
50. M. Y. Maximov, P. A. Novikov, D. V. Nazarov, A. M. Rumyantsev, A. O. Silin, Y. Zhang and A. A. Popovich, *Journal of Electronic Materials*, 2017, **46**, 6571-6577.
51. X. Meng, M. N. Banis, D. Geng, X. Li, Y. Zhang, R. Li, H. Abou-Rachid and X. Sun, *Applied Surface Science*, 2013, **266**, 132-140.
52. X. Meng, D. Geng, J. Liu, R. Li and X. Sun, *Nanotechnology*, 2011, **22**, 165602.
53. C. Ban, M. Xie, X. Sun, J. J. Travis, G. Wang, H. Sun, A. C. Dillon, J. Lian and S. M. George, *Nanotechnology*, 2013, **24**, 424002.
54. M.-L. Lee, C.-Y. Su, Y.-H. Lin, S.-C. Liao, J.-M. Chen, T.-P. Perng, J.-W. Yeh and H. C. Shih, *Journal of Power Sources*, 2013, **244**, 410-416.
55. M. Xie, X. Sun, C. Zhou, A. S. Cavanagh, H. Sun, T. Hu, G. Wang, J. Lian and S. M. George, *Journal of The Electrochemical Society*, 2015, **162**, A974-A981.
56. H. Wang, G. Jia, Y. Guo, Y. Zhang, H. Geng, J. Xu, W. Mai, Q. Yan and H. J. Fan, *Advanced Materials Interfaces*, 2016, **3**, 1600375.
57. J. Liu, P. Zhou, T. Han, J. Huang, J. Liu, J. Li and P. V. Braun, *Materials Letters*, 2018, **219**, 12-15.
58. S. K. Panda and H. Shin, *Materials Research Innovations*, 2015, **19**, S5-694-S695-699.
59. M. Li, X. Li, W. Li, X. Meng, Y. Yu and X. Sun, *Electrochemistry Communications*, 2015, **57**, 43-47.
60. K. J. Hong and S. O. Kim, *Energy Storage Materials*, 2016, **2**, 27-34.
61. S. Lu, H. Wang, J. Zhou, X. Wu and W. Qin, *Nanoscale*, 2017, **9**, 1184-1192.
62. X. Sun, C. Zhou, M. Xie, H. Sun, T. Hu, F. Lu, S. M. Scott, S. M. George and J. Lian, *J. Mater. Chem. A*, 2014, **2**, 7319-7326.
63. M. Yu, A. Wang, Y. Wang, C. Li and G. Shi, *Nanoscale*, 2014, **6**, 11419-11424.

64. X. Sun, C. Zhou, M. Xie, T. Hu, H. Sun, G. Xin, G. Wang, S. M. George and J. Lian, *Chemical Communications*, 2014, **50**, 10703-10706.
65. Keith E. Gregorczyk, A. C. Kozen, X. Chen, M. A. Schroede, M. Noked, A. Cao, L. Hu and G. W. Rubloff, *ACS nano*, 2015, **9**, 464-473.
66. S. Fleischmann, M. Zeiger, A. Quade, A. Kruth and V. Presser, *ACS Applied Materials & Interfaces*, 2018, **10**, 18675-18684.
67. D. K. Nandi, U. K. Sen, D. Choudhury, S. Mitra and S. K. Sarkar, *Electrochimica Acta*, 2014, **146**, 706-713.
68. D. K. Nandi, U. K. Sen, D. Choudhury, S. Mitra and S. K. Sarkar, *ACS Applied Materials & Interfaces*, 2014, **6**, 6606-6615.
69. D. K. Nandi, U. K. Sen, S. Sinha, A. Dhara, S. Mitra and S. K. Sarkar, *Physical Chemistry Chemical Physics : PCCP*, 2015, **17**, 17445-17453.
70. D. K. Nandi, U. K. Sen, A. Dhara, S. Mitra and S. K. Sarkar, *RSC Advances*, 2016, **6**, 38024-38032.
71. T. Dobbelaere, F. Mattelaer, P. M. Vereecken and C. Detavernier, *Journal of Vacuum Science & Technology A*, 2017, **35**, 041513.
72. X. Meng, Y. Cao, J. A. Libera and J. W. Elam, *Chemistry of Materials*, 2017, **29**, 9043-9052.
73. X. Meng, K. He, D. Su, X. Zhang, C. Sun, Y. Ren, H.-H. Wang, W. Weng, L. Trahey, C. P. Canlas and J. W. Elam, *Advanced Functional Materials*, 2014, **24**, 5435-5442.
74. M. Chen, X. Liu, M. Qi, J. Xiang, J. Yin, Q. Chen and X. Xia, *Materials Technology*, 2017, **32**, 888-892.
75. Y. Liang, Z. Tao and J. Chen, *Advanced Energy Materials*, 2012, **2**, 742-769.
76. Y. Liang, Y. Jing, S. Gheytani, K. Y. Lee, P. Liu, A. Facchetti and Y. Yao, *Nat Mater*, 2017, **16**, 841-848.
77. Y. Liang and Y. Yao, *Joule*, 2018, **2**, 1690-1706.
78. Y. Lu, Q. Zhang, L. Li, Z. Niu and J. Chen, *Chem*, 2018, **4**, 2786-2813.
79. M. Nisula and M. Karpinen, *Nano letters*, 2016, **16**, 1276-1281.
80. M. Nisula and M. Karpinen, *Journal of Materials Chemistry A*, 2018, **6**, 7027-7033.
81. Y. Fang, X.-Y. Yu and X. W. Lou, *Matter*, 2019, **1**, 90-114.
82. W. T. Jing, Y. Zhang, Y. Gu, Y. F. Zhu, C. C. Yang and Q. Jiang, *Matter*, 2019, **1**, 720-733.
83. Y. Zhao, X. Li, B. Yan, D. Xiong, D. Li, S. Lawes and X. Sun, *Advanced Energy Materials*, 2016, **6**, 1502175.
84. Y. Lu, L. Yu and X. W. Lou, *Chem*, 2018, **4**, 972-996.
85. C. G. Carvajal, S. Rout, R. Mundle and A. K. Pradhan, *Langmuir : the ACS journal of surfaces and colloids*, 2017, **33**, 11-18.
86. X. Wang, L. Fan, D. Gong, J. Zhu, Q. Zhang and B. Lu, *Advanced Functional Materials*, 2016, **26**, 1104-1111.
87. J. H. Jeun, K. Y. Park, D. H. Kim, W. S. Kim, H. C. Kim, B. S. Lee, H. Kim, W. R. Yu, K. Kang and S. H. Hong, *Nanoscale*, 2013, **5**, 8480-8483.
88. J. Luo, X. Xia, Y. Luo, C. Guan, J. Liu, X. Qi, C. F. Ng, T. Yu, H. Zhang and H. J. Fan, *Advanced Energy Materials*, 2013, **3**, 737-743.
89. X. Xia, Z. Zeng, X. Li, Y. Zhang, J. Tu, N. C. Fan, H. Zhang and H. J. Fan, *Nanoscale*, 2013, **5**, 6040-6047.
90. C. Zhu, X. Xia, J. Liu, Z. Fan, D. Chao, H. Zhang and H. J. Fan, *Nano Energy*, 2014, **4**, 105-112.
91. M. Kim, J. Lee, S. Lee, S. Seo, C. Bae and H. Shin, *ChemSusChem*, 2015, **8**, 2363-2371.
92. H. Zhang, W. Ren and C. Cheng, *Nanotechnology*, 2015, **26**, 274002.
93. J.-H. Jean, H. Kwak, W.-S. Kim, H.-C. Kim, K.-Y. Park, H. Kim, H.-S. Yang, W.-R. Yu, K. Kang and S.-H. Hong, *Journal of Solid State Electrochemistry*, 2017, **21**, 2365-2371.
94. B. Yan, X. Li, Z. Bai, Y. Zhao, L. Dong, X. Song, D. Li, C. Langford and X. Sun, *Nano Energy*, 2016, **24**, 32-44.
95. E. Østreng, K. B. Gandrud, Y. Hu, O. Nilsen and H. Fjellvåg, *J. Mater. Chem. A*, 2014, **2**, 15044-15051.

96. H. Jung, K. Gerasopoulos, A. A. Talin and R. Ghodssi, *Journal of Power Sources*, 2017, **340**, 89-97.
97. F. Mattelaer, K. Geryl, G. Rampelberg, J. Dendooven and C. Detavernier, *ACS applied materials & interfaces*, 2017, **9**, 13121-13131.
98. S. Fleischmann, D. Leistenschneider, V. Lemkova, B. Krüner, M. Zeiger, L. Borchardt and V. Presser, *Chemistry of Materials*, 2017, **29**, 8653-8662.
99. X. Chen, E. Pomerantseva, P. Banerjee, K. Gregorczyk, R. Ghodssi and G. Rubloff, *Chemistry of Materials*, 2012, **24**, 1255-1261.
100. X. Chen, E. Pomerantseva, K. Gregorczyk, R. Ghodssi and G. Rubloff, *RSC Advances*, 2013, **3**, 4294.
101. F. Mattelaer, K. Geryl, G. Rampelberg, T. Dobbelaere, J. Dendooven and C. Detavernier, *RSC Advances*, 2016, **6**, 114658-114665.
102. M. E. Donders, W. M. Arnoldbik, H. C. M. Knoop, W. M. M. Kessels and P. H. L. Notten, *Journal of The Electrochemical Society*, 2013, **160**, A3066-A3071.
103. V. Miikkulainen, A. Ruud, E. Østreng, O. Nilsen, M. Laitinen, T. Sajavaara and H. Fjellvåg, *The Journal of Physical Chemistry C*, 2013, **118**, 1258-1268.
104. F. Mattelaer, P. M. Vereecken, J. Dendooven and C. Detavernier, *Chemistry of Materials*, 2015, **27**, 3628-3635.
105. M. J. Young, H.-D. Schnabel, A. M. Holder, S. M. George and C. B. Musgrave, *Advanced Functional Materials*, 2016, **26**, 7895-7907.
106. H.-E. Nieminen, V. Miikkulainen, D. Settapani, L. Simonelli, P. Hönicke, C. Zech, Y. Kayser, B. Beckhoff, A.-P. Honkanen, M. J. Heikkilä, K. Mizohata, K. Meinander, O. M. E. Ylivaara, S. Huotari and M. Ritala, *The Journal of Physical Chemistry C*, 2019, **123**, 15802-15814.
107. J. Wang and X. Sun, *Energy Environ. Sci.*, 2012, **5**, 5163-5185.
108. J. Wang and X. Sun, *Energy & Environmental Science*, 2015, **8**, 1110-1138.
109. Y. Liu, J. Liu, J. Wang, M. N. Banis, B. Xiao, A. Lushington, W. Xiao, R. Li, T. K. Sham, G. Liang and X. Sun, *Nature communications*, 2018, **9**, 929.
110. K. B. Gandrud, A. Pettersen, O. Nilsen and H. Fjellvåg, *J. Mater. Chem. A*, 2013, **1**, 9054-9059.
111. J. Liu, B. Xiao, M. N. Banis, R. Li, T.-K. Sham and X. Sun, *Electrochimica Acta*, 2015, **162**, 275-281.
112. J. Liu, B. Wang, Q. Sun, R. Li, T.-K. Sham and X. Sun, *Advanced Materials Interfaces*, 2016, **3**, 1600468.
113. T. Dobbelaere, F. Mattelaer, J. Dendooven, P. Vereecken and C. Detavernier, *Chemistry of Materials*, 2016, **28**, 3435-3445.
114. T. Dobbelaere, F. Mattelaer, A. K. Roy, P. Vereecken and C. Detavernier, *Journal of Materials Chemistry A*, 2017, **5**, 330-338.
115. J. W. Choi and D. Aurbach, *Nature Reviews Materials*, 2016, **1**.
116. L. Wang, B. Chen, J. Ma, G. Cui and L. Chen, *Chemical Society Reviews*, 2018, **47**, 6505-6602.
117. B. Xiao and X. Sun, *Advanced Energy Materials*, 2018, **8**, 1802057.
118. C. Zhan, T. Wu, J. Lu and K. Amine, *Energy & Environmental Science*, 2018, **11**, 243-257.
119. Y. Ding, Z. P. Cano, A. Yu, J. Lu and Z. Chen, *Electrochemical Energy Reviews*, 2019, **2**, 1-28.
120. I. Takahashi, H. Kiuchi, A. Ohma, T. Fukunaga and E. Matsubara, *The Journal of Physical Chemistry C*, 2020, **124**, 9243-9248.
121. T. Li, X.-Z. Yuan, L. Zhang, D. Song, K. Shi and C. Bock, *Electrochemical Energy Reviews*, 2020, **3**, 43-80.
122. J. Liu and X. Sun, *Nanotechnology*, 2015, **26**, 024001.
123. X. Meng, *Nanotechnology*, 2015, **26**, 020501.
124. Y. S. Jung, A. S. Cavanagh, A. C. Dillon, M. D. Groner, S. M. George and S.-H. Lee, *Journal of The Electrochemical Society*, 2010, **157**, A75.
125. L. Chen, R. E. Warburton, K.-S. Chen, J. A. Libera, C. Johnson, Z. Yang, M. C. Hersam, J. P. Greeley and J. W. Elam, *Chem*, 2018, **4**, 2418-2435.

126. J.-T. Lee, F.-M. Wang, C.-S. Cheng, C.-C. Li and C.-H. Lin, *Electrochimica Acta*, 2010, **55**, 4002-4006.
127. D. Guan, J. A. Jeevarajan and Y. Wang, *Nanoscale*, 2011, **3**, 1465-1469.
128. L. A. Riley, S. Van Atta, A. S. Cavanagh, Y. Yan, S. M. George, P. Liu, A. C. Dillon and S.-H. Lee, *Journal of Power Sources*, 2011, **196**, 3317-3324.
129. I. D. Scott, Y. S. Jung, A. S. Cavanagh, Y. Yan, A. C. Dillon, S. M. George and S. H. Lee, *Nano letters*, 2011, **11**, 414-418.
130. Y. Seok Jung, A. S. Cavanagh, Y. Yan, S. M. George and A. Manthiram, *Journal of The Electrochemical Society*, 2011, **158**, A1298.
131. H.-M. Cheng, F.-M. Wang, J. P. Chu, R. Santhanam, J. Rick and S.-C. Lo, *The Journal of Physical Chemistry C*, 2012, **116**, 7629-7637.
132. D. Guan and Y. Wang, *Ionics*, 2012, **19**, 1-8.
133. D. Liu, Y. Liu, S. L. Candelaria, G. Cao, J. Liu and Y.-H. Jeong, *Journal of Vacuum Science & Technology A*, 2012, **30**, 01A123.
134. M. Bettge, Y. Li, B. Sankaran, N. D. Rago, T. Spila, R. T. Haasch, I. Petrov and D. P. Abraham, *Journal of Power Sources*, 2013, **233**, 346-357.
135. M. Choi, G. Ham, B.-S. Jin, S.-M. Lee, Y. M. Lee, G. Wang and H.-S. Kim, *Journal of Alloys and Compounds*, 2014, **608**, 110-117.
136. X. Fang, M. Ge, J. Rong, Y. Che, N. Aroonyadet, X. Wang, Y. Liu, A. Zhang and C. Zhou, *Energy Technology*, 2014, **2**, 159-165.
137. J. W. Kim, J. J. Travis, E. Hu, K.-W. Nam, S. C. Kim, C. S. Kang, J.-H. Woo, X.-Q. Yang, S. M. George, K. H. Oh, S.-J. Cho and S.-H. Lee, *Journal of Power Sources*, 2014, **254**, 190-197.
138. X. Dai, A. Zhou, J. Xu, B. Yang, L. Wang and J. Li, *Journal of Power Sources*, 2015, **298**, 114-122.
139. C. A. Kim, H. J. Choi, J. H. Lee, S. Y. Yoo, J. W. Kim, J. H. Shim and B. Kang, *Electrochimica Acta*, 2015, **184**, 134-142.
140. J. W. Kim, D. H. Kim, D. Y. Oh, H. Lee, J. H. Kim, J. H. Lee and Y. S. Jung, *Journal of Power Sources*, 2015, **274**, 1254-1262.
141. Y. Su, S. Cui, Z. Zhuo, W. Yang, X. Wang and F. Pan, *ACS Applied Materials & Interfaces*, 2015, **7**, 25105-25112.
142. Y. Shi, M. Zhang, D. Qian and Y. S. Meng, *Electrochimica Acta*, 2016, **203**, 154-161.
143. G. H. Waller, P. D. Brooke, B. H. Rainwater, S. Y. Lai, R. Hu, Y. Ding, F. M. Alamgir, K. H. Sandhage and M. L. Liu, *Journal of Power Sources*, 2016, **306**, 162-170.
144. M. Xie, T. Hu, L. Yang and Y. Zhou, *RSC Advances*, 2016, **6**, 63250-63255.
145. D. H. K. Jackson and T. F. Kuech, *Journal of Power Sources*, 2017, **365**, 61-67.
146. N. Dannehl, S. O. Steinmuller, D. V. Szabo, M. Pein, F. Sigel, L. Esmezjan, U. Hasenkox, B. Schwarz, S. Indris and H. Ehrenberg, *ACS applied materials & interfaces*, 2018, **10**, 43131-43143.
147. S. Neudeck, A. Mazilkin, C. Reitz, P. Hartmann, J. Janek and T. Brezesinski, *Scientific reports*, 2019, **9**, 5328.
148. H. V. Ramasamy, S. Sinha, J. Park, M. Gong, V. Aravindan, J. Heo and Y.-S. Lee, *J. Electrochem. Sci. Technol.*, 2019, **10**, 196-205.
149. H. Yu, Y. Gao and X. Liang, *Journal of The Electrochemical Society*, 2019, **166**, A2021-A2027.
150. W. Zhu, X. Huang, T. Liu, Z. Xie, Y. Wang, K. Tian, L. Bu, H. Wang, L. Gao and J. Zhao, *Coatings*, 2019, **9**, 92.
151. J. Song, X. Han, K. J. Gaskell, K. Xu, S. B. Lee and L. Hu, *Journal of Nanoparticle Research*, 2014, **16**.
152. S. Fang, D. Jackson, M. L. Dreibelbis, T. F. Kuech and R. J. Hamers, *Journal of Power Sources*, 2018, **373**, 184-192.
153. T. Teranishi, Y. Yoshikawa, M. Yoneda, A. Kishimoto, J. Halpin, S. O'Brien, M. Modreanu and I. M. Povey, *ACS Applied Energy Materials*, 2018, **1**, 3277-3282.

154. J. R. Croy, D. C. O'Hanlon, S. Sharifi-Asl, M. Murphy, A. Mane, C.-W. Lee, S. E. Trask, R. Shahbazian-Yassar and M. Balasubramanian, *Chemistry of Materials*, 2019, **31**, 3891-3899.
155. B. Huang, R. Wang, Y. Gong, B. He and H. Wang, *Frontiers in chemistry*, 2019, **7**, 107.
156. K. Leung, Y. Qi, K. R. Zavadil, Y. S. Jung, A. C. Dillon, A. S. Cavanagh, S. H. Lee and S. M. George, *Journal of the American Chemical Society*, 2011, **133**, 14741-14754.
157. A. M. Wise, C. Ban, J. N. Weker, S. Misra, A. S. Cavanagh, Z. Wu, Z. Li, M. S. Whittingham, K. Xu, S. M. George and M. F. Toney, *Chemistry of Materials*, 2015, **27**, 6146-6154.
158. P. Yan, J. Zheng, X. Zhang, R. Xu, K. Amine, J. Xiao, J.-G. Zhang and C.-M. Wang, *Chemistry of Materials*, 2016, **28**, 857-863.
159. D. S. Hall, R. Gauthier, A. Eldesoky, V. S. Murray and J. R. Dahn, *ACS applied materials & interfaces*, 2019, **11**, 14095-14100.
160. J. Zhao, G. Qu, J. C. Flake and Y. Wang, *Chemical communications*, 2012, **48**, 8108-8110.
161. J. Zhao and Y. Wang, *The Journal of Physical Chemistry C*, 2012, **116**, 11867-11876.
162. X. Zhang, I. Belharouak, L. Li, Y. Lei, J. W. Elam, A. Nie, X. Chen, R. S. Yassar and R. L. Axelbaum, *Advanced Energy Materials*, 2013, **3**, 1299-1307.
163. J. Zhao and Y. Wang, *Nano Energy*, 2013, **2**, 882-889.
164. J.-Z. Kong, C. Ren, G.-A. Tai, X. Zhang, A.-D. Li, D. Wu, H. Li and F. Zhou, *Journal of Power Sources*, 2014, **266**, 433-439.
165. H. M. Cho, M. V. Chen, A. C. MacRae and Y. S. Meng, *ACS applied materials & interfaces*, 2015, **7**, 16231-16239.
166. J.-Z. Kong, S.-S. Wang, G.-A. Tai, L. Zhu, L.-G. Wang, H.-F. Zhai, D. Wu, A.-D. Li and H. Li, *Journal of Alloys and Compounds*, 2016, **657**, 593-600.
167. M. R. Laskar, D. H. Jackson, Y. Guan, S. Xu, S. Fang, M. Dreibelbis, M. K. Mahanthappa, D. Morgan, R. J. Hamers and T. F. Kuech, *ACS applied materials & interfaces*, 2016, **8**, 10572-10580.
168. D. Mohanty, K. Dahlberg, D. M. King, L. A. David, A. S. Sefat, D. L. Wood, C. Daniel, S. Dhar, V. Mahajan, M. Lee and F. Albano, *Scientific reports*, 2016, **6**, 26532.
169. R. L. Patel, J. Park and X. Liang, *RSC Advances*, 2016, **6**, 98768-98776.
170. C. Qin, J. Cao, J. Chen, G. Dai, T. Wu, Y. Chen, Y. Tang, A. Li and Y. Chen, *Dalton transactions*, 2016, **45**, 9669-9675.
171. K. Sharma, D. Routkevitch, N. Varaksa and S. M. George, *Journal of Vacuum Science & Technology A*, 2016, **34**, 01A146.
172. M. Xie, X. Sun, H. Sun, T. Porcelli, S. M. George, Y. Zhou and J. Lian, *Journal of Materials Chemistry A*, 2016, **4**, 537-544.
173. J.-Z. Kong, H.-F. Zhai, X. Qian, M. Wang, Q.-Z. Wang, A.-D. Li, H. Li and F. Zhou, *Journal of Alloys and Compounds*, 2017, **694**, 848-856.
174. M. R. Laskar, D. H. Jackson, S. Xu, R. J. Hamers, D. Morgan and T. F. Kuech, *ACS Applied Materials & Interfaces*, 2017, **9**, 11231-11239.
175. F. Mattelaer, P. M. Vereecken, J. Dendooven and C. Detavernier, *Advanced Materials Interfaces*, 2017, **4**, 1601237.
176. S. Sarkar, R. L. Patel, X. Liang and J. Park, *ACS applied materials & interfaces*, 2017, **9**, 30599-30607.
177. Y. Gao, R. L. Patel, K. Y. Shen, X. Wang, R. L. Axelbaum and X. Liang, *ACS omega*, 2018, **3**, 906-916.
178. C.-C. Wang, J.-W. Lin, Y.-H. Yu, K.-H. Lai, K.-F. Chiu and C.-C. Kei, *ACS Sustainable Chemistry & Engineering*, 2018, **6**, 16941-16950.
179. C. Zhang, J. Su, T. Wang, K. Yuan, C. Chen, S. Liu, T. Huang, J. Wu, H. Lu and A. Yu, *ACS Sustainable Chemistry & Engineering*, 2018, **6**, 7890-7901.
180. J. Ahn, E. K. Jang, S. Yoon, S.-J. Lee, S.-J. Sung, D.-H. Kim and K. Y. Cho, *Applied Surface Science*, 2019, **484**, 701-709.
181. H. Gao, J. Cai, G.-L. Xu, L. Li, Y. Ren, X. Meng, K. Amine and Z. Chen, *Chemistry of Materials*, 2019, **31**, 2723-2730.

182. Y. Gao, Z. Shang, X. He, T. White, J. Park and X. Liang, *Electrochimica Acta*, 2019, **318**, 513-524.
183. J. Zhao and Y. Wang, *Journal of Solid State Electrochemistry*, 2012, **17**, 1049-1058.
184. X. Li, J. Liu, X. Meng, Y. Tang, M. N. Banis, J. Yang, Y. Hu, R. Li, M. Cai and X. Sun, *Journal of Power Sources*, 2014, **247**, 57-69.
185. B. Xiao, J. Liu, Q. Sun, B. Wang, M. N. Banis, D. Zhao, Z. Wang, R. Li, X. Cui, T. K. Sham and X. Sun, *Advanced science*, 2015, **2**, 1500022.
186. S. Deng, B. Xiao, B. Wang, X. Li, K. Kaliyappan, Y. Zhao, A. Lushington, R. Li, T.-K. Sham, H. Wang and X. Sun, *Nano Energy*, 2017, **38**, 19-27.
187. B. Xiao, B. Wang, J. Liu, K. Kaliyappan, Q. Sun, Y. Liu, G. Dadheech, M. P. Balogh, L. Yang, T.-K. Sham, R. Li, M. Cai and X. Sun, *Nano Energy*, 2017, **34**, 120-130.
188. X. Li, J. Liu, M. N. Banis, A. Lushington, R. Li, M. Cai and X. Sun, *Energy Environ. Sci.*, 2014, **7**, 768-778.
189. O. Srur-Lavi, V. Miikkulainen, B. Markovsky, J. Grinblat, M. Talianker, Y. Fleger, G. Cohen-Taguri, A. Mor, Y. Tal-Yosef and D. Aurbach, *Journal of The Electrochemical Society*, 2017, **164**, A3266-A3275.
190. J. Xie, J. Zhao, Y. Liu, H. Wang, C. Liu, T. Wu, P.-C. Hsu, D. Lin, Y. Jin and Y. Cui, *Nano Research*, 2017, **10**, 3754-3764.
191. J. S. Park, X. Meng, J. W. Elam, S. Hao, C. Wolverton, C. Kim and J. Cabana, *Chemistry of Materials*, 2014, **26**, 3128-3134.
192. W. D. Richards, L. J. Miara, Y. Wang, J. C. Kim and G. Ceder, *Chemistry of Materials*, 2015, **28**, 266-273.
193. Y. Zhu, X. He and Y. Mo, *ACS Applied Materials & Interfaces*, 2015, **7**, 23685-23693.
194. A. Kraysberg, H. Drezner, M. Auinat, A. Shapira, N. Solomatin, P. Axmann, M. Wohlfahrt-Mehrens and Y. Ein-Eli, *ChemNanoMat*, 2015, **1**, 577-585.
195. J. S. Park, A. U. Mane, J. W. Elam and J. R. Croy, *Chemistry of Materials*, 2015, **27**, 1917-1920.
196. D. H. K. Jackson, M. R. Laskar, S. Fang, S. Xu, R. G. Ellis, X. Li, M. Dreibelbis, S. E. Babcock, M. K. Mahanthappa, D. Morgan, R. J. Hamers, T. F. and T. F. Kuech, *Journal of Vacuum Science & Technology A*, 2016, **34**, 031503.
197. J. S. Park, A. U. Mane, J. W. Elam and J. R. Croy, *ACS omega*, 2017, **2**, 3724-3729.
198. Y. Zhou, Y. Lee, H. Sun, J. M. Wallas, S. M. George and M. Xie, *ACS Applied Materials & Interfaces*, 2017, **9**, 9614-9619.
199. A. Shapira, O. Tiurin, N. Solomatin, M. Auinat, A. Meitav and Y. Ein-Eli, *ACS Applied Energy Materials*, 2018, **1**, 6809-6823.
200. J. Xie, A. D. Sendek, E. D. Cubuk, X. Zhang, Z. Lu, Y. Gong, T. Wu, F. Shi, W. Liu, E. J. Reed and Y. Cui, *ACS nano*, 2017, **11**, 7019-7027.
201. E. Kazyak, K.-H. Chen, K. N. Wood, A. L. Davis, T. Thompson, A. R. Bielinski, A. J. Sanchez, X. Wang, C. Wang, J. Sakamoto and N. P. Dasgupta, *Chemistry of Materials*, 2017, **29**, 3785-3792.
202. B. Xiao, H. Liu, J. Liu, Q. Sun, B. Wang, K. Kaliyappan, Y. Zhao, M. N. Banis, Y. Liu, R. Li, T. K. Sham, G. A. Botton, M. Cai and X. Sun, *Advanced materials*, 2017, **29**, 1703764.
203. H.-H. Ryu, K.-J. Park, C. S. Yoon and Y.-K. Sun, *Chemistry of Materials*, 2018, **30**, 1155-1163.
204. P. Yan, J. Zheng, J. Liu, B. Wang, X. Cheng, Y. Zhang, X. Sun, C. Wang and J.-G. Zhang, *Nature Energy*, 2018, **3**, 600-605.
205. X. Cheng, J. Zheng, J. Lu, Y. Li, P. Yan and Y. Zhang, *Nano Energy*, 2019, **62**, 30-37.
206. J.-Z. Kong, Y. Chen, Y.-Q. Cao, Q.-Z. Wang, A.-D. Li, H. Li and F. Zhou, *Journal of Alloys and Compounds*, 2019, **799**, 89-98.
207. M. Amirmaleki, C. Cao, B. Wang, Y. Zhao, T. Cui, J. Tam, X. Sun, Y. Sun and T. Filletter, *Nanoscale*, 2019, **11**, 18730-18738.
208. Y. S. Jung, A. S. Cavanagh, L. A. Riley, S. H. Kang, A. C. Dillon, M. D. Groner, S. M. George and S. H. Lee, *Advanced materials*, 2010, **22**, 2172-2176.
209. Y. S. Jung, P. Lu, A. S. Cavanagh, C. Ban, G.-H. Kim, S.-H. Lee, S. M. George, S. J. Harris and A. C. Dillon, *Advanced Energy Materials*, 2013, **3**, 213-219.

210. I. Lahiri, S.-M. Oh, J. Y. Hwang, C. Kang, M. Choi, H. Jeon, R. Banerjee, Y.-K. Sun and W. Choi, *Journal of Materials Chemistry*, 2011, **21**, 13621.
211. A. J. Loebl, C. J. Oldham, C. K. Devine, B. Gong, S. E. Atanasov, G. N. Parsons and P. S. Fedkiw, *Journal of The Electrochemical Society*, 2013, **160**, A1971-A1978.
212. H.-Y. Wang and F.-M. Wang, *Journal of Power Sources*, 2013, **233**, 1-5.
213. Y. Zhao, Y. Huang, Q. Wang, K. Wang, M. Zong, L. Wang, W. Zhang and X. Sun, *RSC Advances*, 2013, **3**, 14480.
214. Y. Zhao, Y. Huang, X. Sun, H. Huang, K. Wang, M. Zong and Q. Wang, *Electrochimica Acta*, 2014, **120**, 128-132.
215. Y. Zhao, Z. Song, X. Li, Q. Sun, N. Cheng, S. Lawes and X. Sun, *Energy Storage Materials*, 2016, **2**, 35-62.
216. Y. Zhao, X. Li, B. Yan, D. Li, S. Lawes and X. Sun, *Journal of Power Sources*, 2015, **274**, 869-884.
217. D. Wang, J. Yang, J. Liu, X. Li, R. Li, M. Cai, T.-K. Sham and X. Sun, *Journal of Materials Chemistry A*, 2014, **2**, 2306.
218. N. Yesibolati, M. Shahid, W. Chen, M. N. Hedhili, M. C. Reuter, F. M. Ross and H. N. Alshareef, *Small*, 2014, **10**, 2849-2858.
219. D. Guan and C. Yuan, *Journal of Electrochemical Energy Conversion and Storage*, 2016, **13**.
220. M. Mao, F. Yan, C. Cui, J. Ma, M. Zhang, T. Wang and C. Wang, *Nano letters*, 2017, **17**, 3830-3836.
221. B. Joshi, E. Samuel, M.-W. Kim, S. Park, M. T. Swihart, W. Y. Yoon and S. S. Yoon, *Chemical Engineering Journal*, 2018, **338**, 72-81.
222. H. Zhang, Z. Chen, R. Hu, J. Liu, J. Cui, W. Zhou and C. Yang, *Journal of Materials Chemistry A*, 2018, **6**, 4374-4385.
223. C. Guan, X. Wang, Q. Zhang, Z. Fan, H. Zhang and H. J. Fan, *Nano letters*, 2014, **14**, 4852-4858.
224. M. Q. Snyder, S. A. Trebukhova, B. Ravdel, M. C. Wheeler, J. DiCarlo, C. P. Tripp and W. J. DeSisto, *Journal of Power Sources*, 2007, **165**, 379-385.
225. J.-H. Lee, M.-H. Hon, Y.-W. Chung and I.-C. Leu, *Applied Physics A*, 2010, **102**, 545-550.
226. J. Liu, X. Li, M. Cai, R. Li and X. Sun, *Electrochimica Acta*, 2013, **93**, 195-201.
227. T. Hu, M. Xie, J. Zhong, H.-t. Sun, X. Sun, S. Scott, S. M. George, C.-s. Liu and J. Lian, *Carbon*, 2014, **76**, 141-147.
228. A. L. Lipson, K. Puntambekar, D. J. Comstock, X. Meng, M. L. Geier, J. W. Elam and M. C. Hersam, *Chemistry of Materials*, 2014, **26**, 935-940.
229. B. Ahmed, M. Shahid, D. H. Nagaraju, D. H. Anjum, M. N. Hedhili and H. N. Alshareef, *ACS applied materials & interfaces*, 2015, **7**, 13154-13163.
230. C. Guan, Y. Wang, M. Zacharias, J. Wang and H. J. Fan, *Nanotechnology*, 2015, **26**, 014001.
231. M. H. Jung, *Journal of colloid and interface science*, 2017, **505**, 631-641.
232. W. Shi, H. Zhao and B. Lu, *Nanotechnology*, 2017, **28**, 165403.
233. X. Cheng, Y. Li, L. Sang, J. Ma, H. Shi, X. Liu, J. Lu and Y. Zhang, *Electrochimica Acta*, 2018, **269**, 241-249.
234. W. u. rehman, Y. Xu, X. Du, X. Sun, I. Ullah, Y. Zhang, Y. Jin, B. Zhang and X. Li, *Applied Surface Science*, 2018, **445**, 359-367.
235. S. Xie, D. Cao, Y. She, H. Wang, J. W. Shi, M. K. H. Leung and C. Niu, *Chemical communications*, 2018, **54**, 7782-7785.
236. J. K. Yoon, S. Nam, H. C. Shim, K. Park, T. Yoon, H. S. Park and S. Hyun, *Materials*, 2018, **11**.
237. Y. Jin, H. Yu, Y. Gao, X. He, T. A. White and X. Liang, *Journal of Power Sources*, 2019, **436**, 226859.
238. Y. Li, T. Liang, R. Wang, B. He, Y. Gong and H. Wang, *ACS Applied Materials & Interfaces*, 2019, **11**, 19115-19122.
239. K. Feng, M. Li, W. Liu, A. G. Kashkooli, X. Xiao, M. Cai and Z. Chen, *Small*, 2018, **14**.

240. Y. Gao, R. Yi, Y. C. Li, J. Song, S. Chen, Q. Huang, T. E. Mallouk and D. Wang, *Journal of the American Chemical Society*, 2017, **139**, 17359-17367.
241. Y. Li, K. Yan, H.-W. Lee, Z. Lu, N. Liu and Y. Cui, *Nature Energy*, 2016, **1**, 15029
242. J. Lu, Z. Chen, F. Pan, Y. Cui and K. Amine, *Electrochemical Energy Reviews*, 2018, **1**, 35-53.
243. H. Wu and Y. Cui, *Nano Today*, 2012, **7**, 414-429.
244. F. Dou, L. Shi, G. Chen and D. Zhang, *Electrochemical Energy Reviews*, 2019, **2**, 149-198.
245. Y. He, X. Yu, Y. Wang, H. Li and X. Huang, *Advanced materials*, 2011, **23**, 4938-4941.
246. C. R. Becker, S. M. Prokes and C. T. Love, *ACS applied materials & interfaces*, 2016, **8**, 530-537.
247. S.-Y. Kim and Y. Qi, *Journal of The Electrochemical Society*, 2014, **161**, F3137-F3143.
248. S. Hy, Y. H. Chen, H. M. Cheng, C. J. Pan, J. H. Cheng, J. Rick and B. J. Hwang, *ACS applied materials & interfaces*, 2015, **7**, 13801-13807.
249. A. Kohandehghan, P. Kalisvaart, K. Cui, M. Kupsta, E. Memarzadeh and D. Mitlin, *Journal of Materials Chemistry A*, 2013, **1**, 12850.
250. J. Li, X. Xiao, Y.-T. Cheng and M. W. Verbrugge, *The Journal of Physical Chemistry Letters*, 2013, **4**, 3387-3391.
251. E. Memarzadeh Lotfabad, P. Kalisvaart, K. Cui, A. Kohandehghan, M. Kupsta, B. Olsen and D. Mitlin, *Physical chemistry chemical physics : PCCP*, 2013, **15**, 13646-13657.
252. Y. Li, Y. Sun, G. Xu, Y. Lu, S. Zhang, L. Xue, J. S. Jur and X. Zhang, *J. Mater. Chem. A*, 2014, **2**, 11417-11425.
253. B. Zhu, N. Liu, M. McDowell, Y. Jin, Y. Cui and J. Zhu, *Nano Energy*, 2015, **13**, 620-625.
254. Y. Bai, D. Yan, C. Yu, L. Cao, C. Wang, J. Zhang, H. Zhu, Y.-S. Hu, S. Dai, J. Lu and W. Zhang, *Journal of Power Sources*, 2016, **308**, 75-82.
255. E. M. Lotfabad, P. Kalisvaart, A. Kohandehghan, K. Cui, M. Kupsta, B. Farbod and D. Mitlin, *J. Mater. Chem. A*, 2014, **2**, 2504-2516.
256. S. B. Son, Y. Wang, J. Xu, X. Li, M. Groner, A. Stokes, Y. Yang, Y. T. Cheng and C. Ban, *ACS applied materials & interfaces*, 2017, **9**, 40143-40150.
257. D. M. Piper, J. J. Travis, M. Young, S. B. Son, S. C. Kim, K. H. Oh, S. M. George, C. Ban and S. H. Lee, *Advanced materials*, 2014, **26**, 1596-1601.
258. Y. He, D. M. Piper, MengGu, J. J. Travis, S. M. George, S.-H. Lee, A. Genc, L. Pullan, J. Liu, S. X. Mao, J.-G. Zhang, C. Ban and C. Wang, *ACS nano*, 2014, **8**, 11816-11823.
259. L. Luo, HuiYang, PengfeiYan, J. J. Travis, Y. Lee, N. Liu, D. M. Piper, S. Zhang, C. Ban, S.-H. Lee, P. Zhao, S. M. George, J.-G. Zhang, Y. Cui and C.-M. Wang, *ACS nano*, 2015, **9**, 5559-5566.
260. Y. Ma, J. M. Martinez de la Hoz, I. Angarita, J. M. Berrio-Sanchez, L. Benitez, J. M. Seminario, S. B. Son, S. H. Lee, S. M. George, C. Ban and P. B. Balbuena, *ACS applied materials & interfaces*, 2015, **7**, 11948-11955.
261. D. Molina Piper, Y. Lee, S.-B. Son, T. Evans, F. Lin, D. Nordlund, X. Xiao, S. M. George, S.-H. Lee and C. Ban, *Nano Energy*, 2016, **22**, 202-210.
262. J. M. Wallas, B. C. Welch, Y. Wang, J. Liu, S. E. Hafner, R. Qiao, T. Yoon, Y.-T. Cheng, S. M. George and C. Ban, *ACS Applied Energy Materials*, 2019, **2**, 4135-4143.
263. J. Liu, H. Zhu and M. H. A. Shiraz, *Frontiers in Energy Research*, 2018, **6**, 10
264. D. M. Stewart, A. J. Pearse, N. S. Kim, E. J. Fuller, A. A. Talin, K. Gregorczyk, S. B. Lee and G. W. Rubloff, *Chemistry of Materials*, 2018, **30**, 2526-2534.
265. M. Létiche, E. Eustache, J. Freixas, A. Demortière, V. De Andrade, L. Morgenroth, P. Tilmant, F. Vaurette, D. Troadec, P. Roussel, T. Brousse and C. Lethien, *Advanced Energy Materials*, 2017, **7**, 1601402.
266. A. Pearse, T. Schmitt, E. Sahadeo, D. M. Stewart, A. Kozen, K. Gerasopoulos, A. A. Talin, S. B. Lee, G. W. Rubloff and K. E. Gregorczyk, *ACS nano*, 2018, **12**, 4286-4294.
267. J. Lu, Y. J. Lee, X. Luo, K. C. Lau, M. Asadi, H. H. Wang, S. Brombosz, J. Wen, D. Zhai, Z. Chen, D. J. Miller, Y. S. Jeong, J. B. Park, Z. Z. Fang, B. Kumar, A. Salehi-Khojin, Y. K. Sun, L. A. Curtiss and K. Amine, *Nature*, 2016, **529**, 377-382.
268. J. Lu, L. Li, J. B. Park, Y. K. Sun, F. Wu and K. Amine, *Chem Rev*, 2014, **114**, 5611-5640.

269. J. Wang, Y. Li and X. Sun, *Nano Energy*, 2013, **2**, 443-467.
270. A. C. Luntz, V. Viswanathan, J. Voss, J. B. Varley, J. K. Nørskov, R. Scheffler and A. Speidel, *The Journal of Physical Chemistry Letters*, 2013, **4**, 3494-3499.
271. J. B. Varley, V. Viswanathan, J. K. Nørskov and A. C. Luntz, *Energy Environ. Sci.*, 2014, **7**, 720-727.
272. B. D. McCloskey, A. Speidel, R. Scheffler, D. C. Miller, V. Viswanathan, J. S. Hummelshoj, J. K. Nørskov and A. C. Luntz, *J Phys Chem Lett*, 2012, **3**, 997-1001.
273. J. Lu, Y. Lei, K. C. Lau, X. Luo, P. Du, J. Wen, R. S. Assary, U. Das, D. J. Miller, J. W. Elam, H. M. Albishri, D. A. El-Hady, Y. K. Sun, L. A. Curtiss and K. Amine, *Nature Communications*, 2013, **4**, 2383.
274. Y. Lei, J. Lu, X. Luo, T. Wu, P. Du, X. Zhang, Y. Ren, J. Wen, D. J. Miller, J. T. Miller, Y. K. Sun, J. W. Elam and K. Amine, *Nano letters*, 2013, **13**, 4182-4189.
275. X. Luo, M. Piernavieja-Hermida, J. Lu, T. Wu, J. Wen, Y. Ren, D. Miller, Z. Zak Fang, Y. Lei and K. Amine, *Nanotechnology*, 2015, **26**, 164003.
276. J. Yang, D. Ma, Y. Li, P. Zhang, H. Mi, L. Deng, L. Sun and X. Ren, *Journal of Power Sources*, 2017, **360**, 215-220.
277. J. Yang, H. Mi, S. Luo, Y. Li, P. Zhang, L. Deng, L. Sun and X. Ren, *Journal of Power Sources*, 2017, **368**, 88-96.
278. Y. Bae, D.-H. Ko, S. Lee, H.-D. Lim, Y.-J. Kim, H.-S. Shim, H. Park, Y. Ko, S. K. Park, H. J. Kwon, H. Kim, H.-T. Kim, Y.-S. Min, D. Im and K. Kang, *Advanced Energy Materials*, 2018, **8**, 1702661.
279. C. Gong, L. Zhao, S. Li, H. Wang, Y. Gong, R. Wang and B. He, *Electrochimica Acta*, 2018, **281**, 338-347.
280. J.-W. Jung, D.-W. Choi, C. K. Lee, K. R. Yoon, S. Yu, J. Y. Cheong, C. Kim, S.-H. Cho, J.-S. Park, Y. J. Park and I.-D. Kim, *Nano Energy*, 2018, **46**, 193-202.
281. Z. Zhang, K. Tan, Y. Gong, H. Wang, R. Wang, L. Zhao and B. He, *Journal of Power Sources*, 2019, **437**, 226908.
282. J. Lu, L. Cheng, K. C. Lau, E. Tyo, X. Luo, J. Wen, D. Miller, R. S. Assary, H. H. Wang, P. Redfern, H. Wu, J. B. Park, Y. K. Sun, S. Vajda, K. Amine and L. A. Curtiss, *Nature communications*, 2014, **5**, 4895.
283. Y. Lei, F. Mehmood, S. Lee, J. Greeley, B. Lee, S. Seifert, R. E. Winans, J. W. Elam, R. J. Meyer, P. C. Redfern, D. Teschner, R. Schlögl, M. J. Pellin, L. A. Curtiss and S. Vajda, *Science*, 2010, **328**, 224.
284. G. Kwon, G. A. Ferguson, C. J. Heard, E. C. Tyo, C. Yin, J. DeBartolo, S. n. Seifert, R. E. Winans, J. Kropf, J. Greeley, R. L. Johnston, L. A. Curtiss, M. J. Pellin and S. Vajda, *ACS Nano*, 2013, **7**, 5808-5817.
285. S. Lee, L. M. Molina, M. J. Lopez, J. A. Alonso, B. Hammer, B. Lee, S. Seifert, R. E. Winans, J. W. Elam, M. J. Pellin and S. Vajda, *Angewandte Chemie*, 2009, **48**, 1467-1471.
286. S. Vajda, M. J. Pellin, J. P. Greeley, C. L. Marshall, L. A. Curtiss, G. A. Ballentine, J. W. Elam, S. Catillon-Mucherie, P. C. Redfern, F. Mehmood and P. Zapol, *Nat Mater*, 2009, **8**, 213-216.
287. H.-S. Shin, G. W. Seo, K. Kwon, K.-N. Jung, S. I. Lee, E. Choi, H. Kim, J.-H. Hwang and J.-W. Lee, *APL Material*, 2018, **6**, 047702.
288. J. Xie, X. Yao, I. P. Madden, D. E. Jiang, L. Y. Chou, C. K. Tsung and D. Wang, *Journal of the American Chemical Society*, 2014, **136**, 8903-8906.
289. C. Zhao, C. Yu, M. N. Banis, Q. Sun, M. Zhang, X. Li, Y. Liu, Y. Zhao, H. Huang, S. Li, X. Han, B. Xiao, Z. Song, R. Li, J. Qiu and X. Sun, *Nano Energy*, 2017, **34**, 399-407.
290. H. Kim, J. T. Lee, D.-C. Lee, A. Magasinski, W.-i. Cho and G. Yushin, *Advanced Energy Materials*, 2013, **3**, 1308-1315.
291. X. Li, A. Lushington, J. Liu, R. Li and X. Sun, *Chemical Communications*, 2014, **50**, 9757-9760.
292. M. Yu, W. Yuan, C. Li, J.-D. Hong and G. Shi, *Journal of Materials Chemistry A*, 2014, **2**, 7360.

293. M. Yu, A. Wang, F. Tian, H. Song, Y. Wang, C. Li, J. D. Hong and G. Shi, *Nanoscale*, 2015, **7**, 5292-5298.
294. X. Li, A. Lushington, Q. Sun, W. Xiao, J. Liu, B. Wang, Y. Ye, K. Nie, Y. Hu, Q. Xiao, R. Li, J. Guo, T. K. Sham and X. Sun, *Nano letters*, 2016, **16**, 3545-3549.
295. R. Carter, L. Oakes, N. Muralidharan, A. P. Cohn, A. Douglas and C. L. Pint, *ACS applied materials & interfaces*, 2017, **9**, 7185-7192.
296. Y. Chen, S. Lu, J. Zhou, X. Wu, W. Qin, O. Ogoke and G. Wu, *Journal of Materials Chemistry A*, 2017, **5**, 102-112.
297. X. Meng, Y. Liu, Y. Cao, Y. Ren, W. Lu and J. W. Elam, *Advanced Materials Interfaces*, 2017, **4**, 1700096.
298. X. Han, Y. Xu, X. Chen, Y.-C. Chen, N. Weadock, J. Wan, H. Zhu, Y. Liu, H. Li, G. Rubloff, C. Wang and L. Hu, *Nano Energy*, 2013, **2**, 1197-1206.
299. X. Li, M. Banis, A. Lushington, X. Yang, Q. Sun, Y. Zhao, C. Liu, Q. Li, B. Wang, W. Xiao, C. Wang, M. Li, J. Liang, R. Li, Y. Hu, L. Goncharova, H. Zhang, T. K. Sham and X. Sun, *Nature Communications*, 2018, **9**, 4509.
300. Z. Gao, H. Sun, L. Fu, F. Ye, Y. Zhang, W. Luo and Y. Huang, *Advanced materials*, 2018, **30**, e1705702.
301. F. Zheng, M. Kotobuki, S. Song, M. O. Lai and L. Lu, *Journal of Power Sources*, 2018, **389**, 198-213.
302. J. Liang, X. Li, Y. Zhao, L. V. Goncharova, W. Li, K. R. Adair, M. N. Banis, Y. Hu, T. K. Sham, H. Huang, L. Zhang, S. Zhao, S. Lu, R. Li and X. Sun, *Advanced Energy Materials*, 2019, **9**, 1902125.
303. A. Miura, N. C. Rosero-Navarro, A. Sakuda, K. Tadanaga, N. H. H. Phuc, A. Matsuda, N. Machida, A. Hayashi and M. Tatsumisago, *Nature Reviews Chemistry*, 2019, **3**, 189-198.
304. J. Liu, M. N. Banis, X. Li, A. Lushington, M. Cai, R. Li, T.-K. Sham and X. Sun, *The Journal of Physical Chemistry C*, 2013, **117**, 20260-20267.
305. B. Wang, J. Liu, Q. Sun, R. Li, T. K. Sham and X. Sun, *Nanotechnology*, 2014, **25**, 504007.
306. A. C. Kozen, A. J. Pearse, C.-F. Lin, M. Noked and G. W. Rubloff, *Chemistry of Materials*, 2015, **27**, 5324-5331.
307. M. Nisula, Y. Shindo, H. Koga and M. Karppinen, *Chemistry of Materials*, 2015, **27**, 6987-6993.
308. B. Wang, J. Liu, M. Norouzi Banis, Q. Sun, Y. Zhao, R. Li, T. K. Sham and X. Sun, *ACS applied materials & interfaces*, 2017, **9**, 31786-31793.
309. B. Wang, Y. Zhao, M. N. Banis, Q. Sun, K. R. Adair, R. Li, T. K. Sham and X. Sun, *ACS applied materials & interfaces*, 2018, **10**, 1654-1661.
310. E. Kazyak, K.-H. Chen, A. L. Davis, S. Yu, A. J. Sanchez, J. Lasso, A. R. Bielinski, T. Thompson, J. Sakamoto, D. J. Siegel and N. P. Dasgupta, *Journal of Materials Chemistry A*, 2018, **6**, 19425-19437.
311. X. Han, Y. Gong, K. K. Fu, X. He, G. T. Hitz, J. Dai, A. Pearse, B. Liu, H. Wang, G. Rubloff, Y. Mo, V. Thangadurai, E. D. Wachsman and L. Hu, *Nat Mater*, 2017, **16**, 572-579.
312. Y. Liu, Q. Sun, Y. Zhao, B. Wang, P. Kaghazchi, K. R. Adair, R. Li, C. Zhang, J. Liu, L. Y. Kuo, Y. Hu, T. K. Sham, L. Zhang, R. Yang, S. Lu, X. Song and X. Sun, *ACS applied materials & interfaces*, 2018, **10**, 31240-31248.
313. C. Wang, Y. Zhao, Q. Sun, X. Li, Y. Liu, J. Liang, X. Li, X. Lin, R. Li, K. R. Adair, L. Zhang, R. Yang, S. Lu and X. Sun, *Nano Energy*, 2018, **53**, 168-174.
314. A. L. Davis, R. Garcia-Mendez, K. N. Wood, E. Kazyak, K.-H. Chen, G. Teeter, J. Sakamoto and N. P. Dasgupta, *Journal of Materials Chemistry A*, 2020, **8**, 6291-6302.
315. J. H. Woo, J. E. Trevey, A. S. Cavanagh, Y. S. Choi, S. C. Kim, S. M. George, K. H. Oh and S.-H. Lee, *Journal of The Electrochemical Society*, 2012, **159**, A1120-A1124.
316. C. Wang, X. Li, Y. Zhao, M. N. Banis, J. Liang, X. Li, Y. Sun, K. R. Adair, Q. Sun, Y. Liu, F. Zhao, S. Deng, X. Lin, R. Li, Y. Hu, T. K. Sham, H. Huang, L. Zhang, R. Yang, S. Lu and X. Sun, *Small Methods*, 2019, **3**, 1900261.

317. X. Li, Z. Ren, M. Norouzi Banis, S. Deng, Y. Zhao, Q. Sun, C. Wang, X. Yang, W. Li, J. Liang, X. Li, Y. Sun, K. Adair, R. Li, Y. Hu, T.-K. Sham, H. Huang, L. Zhang, S. Lu, J. Luo and X. Sun, *ACS Energy Letters*, 2019, **4**, 2480-2488.
318. S. Deng, X. Li, Z. Ren, W. Li, J. Luo, J. Liang, J. Liang, M. N. Banis, M. Li, Y. Zhao, X. Li, C. Wang, Y. Sun, Q. Sun, R. Li, Y. Hu, H. Huang, L. Zhang, S. Lu, J. Luo and X. Sun, *Energy Storage Materials*, 2020, **27**, 117-123.
319. S. Deng, Y. Sun, X. Li, Z. Ren, J. Liang, K. Doyle-Davis, J. Liang, W. Li, M. Norouzi Banis, Q. Sun, R. Li, Y. Hu, H. Huang, L. Zhang, S. Lu, J. Luo and X. Sun, *ACS Energy Letters*, 2020, **5**, 1243-1251.
320. X.-B. Cheng, R. Zhang, C.-Z. Zhao and Q. Zhang, *Chemical Reviews*, 2017, **117**, 10403-10473.
321. C. Fang, X. Wang and Y. S. Meng, *Trends in Chemistry*, 2019, **1**, 152-158.
322. S. Shi, P. Lu, Z. Liu, Y. Qi, L. G. Hector, H. Li and S. J. Harris, *Journal of the American Chemical Society*, 2012, **134**, 15476-15487.
323. D. Lin, Y. Liu and Y. Cui, *Nat Nanotechnol*, 2017, **12**, 194-206.
324. L. Wang, L. Zhang, Q. Wang, W. Li, B. Wu, W. Jia, Y. Wang, J. Li and H. Li, *Energy Storage Materials*, 2018, **10**, 16-23.
325. A. C. Kozen, C.-F. Lin, A. J. Pearse, M. A. Schroeder, X. Han, L. Hu, S.-B. Lee, G. W. Rubloff and M. Noked, *ACS Nano*, 2015, **9**, 5884-5892.
326. W. Wang, X. Yue, J. Meng, J. Wang, X. Wang, H. Chen, D. Shi, J. Fu, Y. Zhou, J. Chen and Z. Fu, *Energy Storage Materials*, 2019, **18**, 414-422.
327. N.-W. Li, Y.-X. Yin, C.-P. Yang and Y.-G. Guo, *Advanced Materials*, 2016, **28**, 1853-1858.
328. N.-W. Li, Y. Shi, Y.-X. Yin, X.-X. Zeng, J.-Y. Li, C.-J. Li, L.-J. Wan, R. Wen and Y.-G. Guo, *Angewandte Chemie International Edition*, 2018, **57**, 1505-1509.
329. J. Luo, C.-C. Fang and N.-L. Wu, *Advanced Energy Materials*, 2018, **8**, 1701482.
330. D. Lin, Y. Liu, W. Chen, G. Zhou, K. Liu, B. Dunn and Y. Cui, *Nano Letters*, 2017, **17**, 3731-3737.
331. Z. Song, M. N. Banis, L. Zhang, B. Wang, L. Yang, D. Banham, Y. Zhao, J. Liang, M. Zheng, R. Li, S. Ye and X. Sun, *Nano Energy*, 2018, **53**, 716-725.
332. L. Wang, Q. Wang, W. Jia, S. Chen, P. Gao and J. Li, *Journal of Power Sources*, 2017, **342**, 175-182.
333. X. Meng, *Journal of Materials Chemistry A*, 2017, **5**, 18326-18378.
334. E. Kazyak, K. N. Wood and N. P. Dasgupta, *Chemistry of Materials*, 2015, **27**, 6457-6462.
335. C.-F. Lin, A. C. Kozen, M. Noked, C. Liu and G. W. Rubloff, *Advanced Materials Interfaces*, 2016, **3**, 1600426.
336. X. Liu, Q. Zhu, Y. Lang, K. Cao, S. Chu, B. Shan and R. Chen, *Angew Chem Int Ed*, 2017, **56**, 1648-1652.
337. J. Xie, J. Wang, H. R. Lee, K. Yan, Y. Li, F. Shi, W. Huang, A. Pei, G. Chen, R. Subbaraman, J. Christensen and Y. Cui, *Science Advances*, 2018, **4**, 5168.
338. P. K. Alaboina, S. Rodrigues, M. Rottmayer and S.-J. Cho, *ACS applied materials & interfaces*, 2018, **10**, 32801-32808.
339. I. S. Kim, R. T. Haasch, D. H. Cao, O. K. Farha, J. T. Hupp, M. G. Kanatzidis and A. B. Martinson, *ACS Appl Mater Interfaces*, 2016, **8**, 24310-24314.
340. L. Chen, K.-S. Chen, X. Chen, G. Ramirez, Z. Huang, N. R. Geise, H.-G. Steinrück, B. L. Fisher, R. Shahbazian-Yassar, M. F. Toney, M. C. Hersam and J. W. Elam, *ACS applied materials & interfaces*, 2018, **10**, 26972-26981.
341. J. Xie, L. Liao, Y. Gong, Y. Li, F. Shi, A. Pei, J. Sun, R. Zhang, B. Kong, R. Subbaraman, J. Christensen and Y. Cui, *Science Advances*, 2017, **3**, 3170.
342. Y. Sun, Y. Zhao, J. Wang, J. Liang, C. Wang, Q. Sun, X. Lin, K. R. Adair, J. Luo, D. Wang, R. Li, M. Cai, T.-K. Sham and X. Sun, *Advanced Materials*, 2019, **31**, 1806541.
343. Y. Zhao, L. V. Goncharova, Q. Sun, X. Li, A. Lushington, B. Wang, R. Li, F. Dai, M. Cai and X. Sun, *Small Methods*, 2018, **2**, 1700417.

344. L. Chen, Z. Huang, R. Shahbazian-Yassar, J. A. Libera, K. C. Klavetter, K. R. Zavadil and J. W. Elam, *ACS applied materials & interfaces*, 2018, **10**, 7043-7051.
345. K. R. Adair, C. Zhao, M. N. Banis, Y. Zhao, R. Li, M. Cai and X. Sun, *Angewandte Chemie International Edition*, 2019, **58**, 15797-15802.
346. Y. Zhao, M. Amirmaleki, Q. Sun, C. Zhao, A. Codireenzi, L. V. Goncharova, C. Wang, K. Adair, X. Li, X. Yang, F. Zhao, R. Li, T. Filleter, M. Cai and X. Sun, *Matter*, 2019, **1**, 1215-1231.
347. X.-B. Cheng, R. Zhang, C.-Z. Zhao, F. Wei, J.-G. Zhang and Q. Zhang, *Advanced Science*, 2016, **3**, 1500213.
348. Y. Liang, W. H. Lai, Z. Miao and S. L. Chou, *Small*, 2018, **14**.
349. M. Á. Muñoz-Márquez, D. Saurel, J. L. Gómez-Cámer, M. Casas-Cabanas, E. Castillo-Martínez and T. Rojo, *Advanced Energy Materials*, 2017, **7**, 1700463.
350. W. Luo, F. Shen, C. Bommier, H. Zhu, X. Ji and L. Hu, *Accounts of Chemical Research*, 2016, **49**, 231-240.
351. B. Xiao, T. Rojo and X. Li, *ChemSusChem*, 2019, **12**, 133-144.
352. B. Xiao, F. A. Soto, M. Gu, K. S. Han, J. Song, H. Wang, M. H. Engelhard, V. Murugesan, K. T. Mueller, D. Reed, V. L. Sprenkle, P. B. Balbuena and X. Li, *Advanced Energy Materials*, 2018, **8**, 1801441.
353. J. Liu, M. N. Banis, B. Xiao, Q. Sun, A. Lushington, R. Li, J. Guo, T.-K. Sham and X. Sun, *J. Mater. Chem. A*, 2015, **3**, 24281-24288.
354. J. Lin, D. Ma, Y. Li, P. Zhang, H. Mi, L. Deng, L. Sun and X. Ren, *Dalton transactions*, 2017, **46**, 13101-13107.
355. M. B. Sreedhara, S. Gope, B. Vishal, R. Datta, A. J. Bhattacharyya and C. N. R. Rao, *Journal of Materials Chemistry A*, 2018, **6**, 2302-2310.
356. X. Han, Y. Liu, Z. Jia, Y. C. Chen, J. Wan, N. Weadock, K. J. Gaskell, T. Li and L. Hu, *Nano letters*, 2014, **14**, 139-147.
357. Y. Liu, X. Fang, M. Ge, J. Rong, C. Shen, A. Zhang, H. A. Enaya and C. Zhou, *Nano Energy*, 2015, **16**, 399-407.
358. H. Kou, X. Li, H. Shan, L. Fan, B. Yan and D. Li, *Journal of Materials Chemistry A*, 2017, **5**, 17881-17888.
359. J. Ni, Y. Jiang, F. Wu, J. Maier, Y. Yu and L. Li, *Advanced Functional Materials*, 2018, **28**, 1707179.
360. K. Kaliyappan, J. Liu, A. Lushington, R. Li and X. Sun, *ChemSusChem*, 2015, **8**, 2537-2543.
361. J. Alvarado, C. Ma, S. Wang, K. Nguyen, M. Kodur and Y. S. Meng, *ACS applied materials & interfaces*, 2017, **9**, 26518-26530.
362. L. Dong, L. RuiXian, J. Feng, C. Long, G. Wang, H. Kou, M. Zhao, L. Dong, X. Li and D. Li, *Materials Letters*, 2017, **205**, 75-78.
363. K. Kaliyappan, J. Liu, B. Xiao, A. Lushington, R. Li, T.-K. Sham and X. Sun, *Advanced Functional Materials*, 2017, **27**, 1701870.
364. C. Luo, A. Langrock, X. Fan, Y. Liang and C. Wang, *Journal of Materials Chemistry A*, 2017, **5**, 18214-18220.
365. Y. Xu, M. Zhou, C. Zhang, C. Wang, L. Liang, Y. Fang, M. Wu, L. Cheng and Y. Lei, *Nano Energy*, 2017, **38**, 304-312.
366. S. Chu, X. Jia, J. Wang, K. Liao, W. Zhou, Y. Wang and Z. Shao, *Composites Part B: Engineering*, 2019, **173**, 106913.
367. H. Yadegari, Q. Sun and X. Sun, *Advanced materials*, 2016, **28**, 7065-7093.
368. Q. Sun, X. Lin, H. Yadegari, W. Xiao, Y. Zhao, K. R. Adair, R. Li and X. Sun, *Journal of Materials Chemistry A*, 2018, **6**, 1473-1484.
369. H. Yadegari and X. Sun, *Accounts of chemical research*, 2018, **51**, 1532-1540.
370. X. Lin, F. Sun, Q. Sun, S. Wang, J. Luo, C. Zhao, X. Yang, Y. Zhao, C. Wang, R. Li and X. Sun, *Chemistry of Materials*, 2019, **31**, 9024-9031.

371. Q. Sun, J. Liu, X. Li, B. Wang, H. Yadegari, A. Lushington, M. N. Banis, Y. Zhao, W. Xiao, N. Chen, J. Wang, T.-K. Sham and X. Sun, *Advanced Functional Materials*, 2017, **27**, 1606662.
372. H. Yadegari, M. Norouzi Banis, A. Lushington, Q. Sun, R. Li, T.-K. Sham and X. Sun, *Energy & Environmental Science*, 2017, **10**, 286-295.
373. D. Ma, Y. Li, J. Yang, H. Mi, S. Luo, L. Deng, C. Yan, M. Rauf, P. Zhang, X. Sun, X. Ren, J. Li and H. Zhang, *Advanced Functional Materials*, 2018, **28**, 1705537.
374. Y. Zhao, X. Yang, L. Y. Kuo, P. Kaghazchi, Q. Sun, J. Liang, B. Wang, A. Lushington, R. Li, H. Zhang and X. Sun, *Small*, 2018, **14**, e1703717.
375. Y. Zhao, J. Liang, Q. Sun, Lyudmila V. Goncharova, J. Wang, C. Wang, K. R. Adair, X. Li, F. Zhao, Y. Sun, R. Li and X. Sun, *Journal of Materials Chemistry A*, 2019, **7**, 4119-4125.
376. X. Lin, Q. Sun, H. Yadegari, X. Yang, Y. Zhao, C. Wang, J. Liang, A. Koo, R. Li and X. Sun, *Advanced Functional Materials*, 2018, **28**, 1801904.
377. Y. Zhao, K. R. Adair and X. Sun, *Energy & Environmental Science*, 2018, **11**, 2673-2695.
378. W. Luo, C.-F. Lin, O. Zhao, M. Noked, Y. Zhang, G. W. Rubloff and L. Hu, *Advanced Energy Materials*, 2017, **7**, 1601526.
379. Y. Zhao, L. V. Goncharova, A. Lushington, Q. Sun, H. Yadegari, B. Wang, W. Xiao, R. Li and X. Sun, *Advanced materials*, 2017, **29**, 1606663.
380. Y. Zhao, L. V. Goncharova, Q. Zhang, P. Kaghazchi, Q. Sun, A. Lushington, B. Wang, R. Li and X. Sun, *Nano letters*, 2017, **17**, 5653-5659.
381. R. B. Nuwayhid, A. Jarry, G. W. Rubloff and K. E. Gregorczyk, *ACS applied materials & interfaces*, 2020, **12**, 21641-21650.
382. N. D. Schuppert, S. Mukherjee, A. M. Bates, E.-J. Son, M. J. Choi and S. Park, *Journal of Power Sources*, 2016, **316**, 160-169.
383. D. Pal, A. Mathur, A. Singh, S. Pakhira, R. Singh and S. Chattopadhyay, *ChemistrySelect*, 2018, **3**, 12512-12523.
384. K. Zhao, C. Wang, Y. Yu, M. Yan, Q. Wei, P. He, Y. Dong, Z. Zhang, X. Wang and L. Mai, *Advanced Materials Interfaces*, 2018, **5**, 1800848.
385. F. Ye, D. Lu, X. Gui, T. Wang, X. Zhuang, W. Luo and Y. Huang, *Journal of Materiomics*, 2019, **5**, 344-349.
386. L. Tao, L. Liu, R. Chang, H. He, P. Zhao and J. Liu, *Journal of Power Sources*, 2020, **463**, 228172.
387. H. He, H. Tong, X. Song, X. Song and J. Liu, *Journal of Materials Chemistry A*, 2020, **8**, 7836-7846.
388. C. Zhong, Y. Deng, W. Hu, J. Qiao, L. Zhang and J. Zhang, *Chem Soc Rev*, 2015, **44**, 7484-7539.
389. A. González, E. Goikolea, J. A. Barrena and R. Mysyk, *Renewable and Sustainable Energy Reviews*, 2016, **58**, 1189-1206.
390. M. F. El-Kady, Y. Shao and R. B. Kaner, *Nature Reviews Materials*, 2016, **1**, 16033.
391. G. Wang, L. Zhang and J. Zhang, *Chem Soc Rev*, 2012, **41**, 797-828.
392. Y. Shao, M. F. El-Kady, L. J. Wang, Q. Zhang, Y. Li, H. Wang, M. F. Mousavi and R. B. Kaner, *Chem Soc Rev*, 2015, **44**, 3639-3665.
393. H. Liu, X. Liu, S. Wang, H.-K. Liu and L. Li, *Energy Storage Materials*, 2020, **28**, 122-145.
394. Y. Li, X. Han, T. Yi, Y. He and X. Li, *Journal of Energy Chemistry*, 2019, **31**, 54-78.
395. D. Chen, K. Jiang, T. Huang and G. Shen, *Advanced materials*, 2020, **32**, e1901806.
396. S. Boukhalfa, K. Evanoff and G. Yushin, *Energy & Environmental Science*, 2012, **5**, 6872.
397. X. Sun, M. Xie, G. Wang, H. Sun, A. S. Cavanagh, J. J. Travis, S. M. George and J. Lian, *Journal of The Electrochemical Society*, 2012, **159**, A364-A369.
398. F. Yang, L. Zhang, A. Zuzuarregui, K. Gregorczyk, L. Li, M. Beltran, C. Tollan, J. Brede, C. Rogero, A. Chuvilin and M. Knez, *ACS applied materials & interfaces*, 2015, **7**, 20513-20519.
399. H. Li, Y. Gao, Y. Shao, Y. Su and X. Wang, *Nano letters*, 2015, **15**, 6689-6695.
400. K. Hong, M. Cho and S. O. Kim, *ACS applied materials & interfaces*, 2015, **7**, 1899-1906.
401. L. Iglesias, V. Vega, J. Garc a, B. Hernando and V. c. M. Prida, *Frontiers in Physics*, 2015, **3**, 12.
402. P. Avasthi, A. Kumar and V. Balakrishnan, *ACS Applied Nano Materials*, 2019, **2**, 1484-1495.

403. F. Naeem, S. Naeem, Y. Zhao, D. Wang, J. Zhang, Y. Mei and G. Huang, *Nanoscale research letters*, 2019, **14**, 92.
404. X. Sun, M. Xie, J. J. Travis, G. Wang, H. Sun, J. Lian and S. M. George, *The Journal of Physical Chemistry C*, 2013, **117**, 22497-22508.
405. C. Chen, C. Chen, P. Huang, F. Duan, S. Zhao, P. Li, J. Fan, W. Song and Y. Qin, *Nanotechnology*, 2014, **25**, 504001.
406. C. Guan, X. Qian, X. Wang, Y. Cao, Q. Zhang, A. Li and J. Wang, *Nanotechnology*, 2015, **26**, 094001.
407. R. M. Silva, G. Clavel, Y. Fan, P. Amsalem, N. Koch, R. F. Silva and N. Pinna, *Advanced Materials Interfaces*, 2016, **3**, 1600313.
408. L. Yu, G. Wang, G. Wan, G. Wang, S. Lin, X. Li, K. Wang, Z. Bai and Y. Xiang, *Dalton transactions*, 2016, **45**, 13779-13786.
409. Z. Hai, M. Karbalaee Akbari, Z. Wei, C. Xue, H. Xu, J. Hu and S. Zhuiykov, *Electrochimica Acta*, 2017, **246**, 625-633.
410. M. Li and H. He, *Vacuum*, 2017, **143**, 371-379.
411. R. Warren, F. Sammoura, F. Tounsi, M. Sanghadasa and L. Lin, *Journal of Materials Chemistry A*, 2015, **3**, 15568-15575.
412. E. Kao, C. Yang, R. Warren, A. Kozinda and L. Lin, *Sensors and Actuators A: Physical*, 2016, **240**, 160-166.
413. D. K. Nandi, S. Sahoo, S. Sinha, S. Yeo, H. Kim, R. N. Bulakhe, J. Heo, J. J. Shim and S. H. Kim, *ACS applied materials & interfaces*, 2017, **9**, 40252-40264.
414. M. Z. Ansari, N. Parveen, D. K. Nandi, R. Ramesh, S. A. Ansari, T. Cheon and S. H. Kim, *Scientific reports*, 2019, **9**, 10225.
415. L. Wen, Y. Mi, C. Wang, Y. Fang, F. Grote, H. Zhao, M. Zhou and Y. Lei, *Small*, 2014, **10**, 3162-3168.
416. Y. Zhong, X. Xia, J. Zhan, Y. Wang, X. Wang and J. Tu, *Journal of Materials Chemistry A*, 2016, **4**, 18717-18722.
417. Q. Xiong, C. Zheng, H. Chi, J. Zhang and Z. Ji, *Nanotechnology*, 2017, **28**, 055405.
418. Y.-Q. Cao, X. Qian, W. Zhang, S.-S. Wang, M. Li, D. Wu and A.-D. Li, *Journal of The Electrochemical Society*, 2017, **164**, A3493-A3498.
419. L. Yu, G. Wan, Y. Qin and G. Wang, *Electrochimica Acta*, 2018, **268**, 283-294.
420. X. Zang, C. Shen, E. Kao, R. Warren, R. Zhang, K. S. Teh, J. Zhong, M. Wei, B. Li, Y. Chu, M. Sanghadasa, A. Schwartzberg and L. Lin, *Advanced Materials*, 2018, **30**, 1704754.
421. L. Yu, G. Wan, X. Peng, Z. Dou, X. Li, K. Wang, S. Lin and G. Wang, *RSC Advances*, 2016, **6**, 14199-14204.
422. S. A. Sherrill, J. Duay, Z. Gui, P. Banerjee, G. W. Rubloff and S. B. Lee, *Physical chemistry chemical physics : PCCP*, 2011, **13**, 15221-15226.
423. R. Wang, C. Xia, N. Wei and H. N. Alshareef, *Electrochimica Acta*, 2016, **196**, 611-621.
424. Y. Chen, Z. Gao, B. Zhang, S. Zhao and Y. Qin, *Journal of Power Sources*, 2016, **315**, 254-260.
425. J.-B. Fang, C. Liu, Y.-Q. Cao and A.-D. Li, *Journal of Materials Research*, 2019, **35**, 738-746.
426. B. C. Steele and A. Heinzl, *Nature*, 2001, **414**, 345-352.
427. L. Wei, Z. Y. Zhou, S. P. Chen, C. D. Xu, D. Su, M. E. Schuster and S. G. Sun, *Chem Commun (Camb)*, 2013, **49**, 11152-11154.
428. L. Zhang, K. Doyle-Davis and X. Sun, *Energy & Environmental Science*, 2019, **12**, 492-517.
429. N. Cheng, Y. Shao, J. Liu and X. Sun, *Nano Energy*, 2016, **29**, 220-242.
430. T. Aaltonen, A. Rahtu, M. Ritala and M. Leskelä, *Electrochemical and Solid-State Letters*, 2003, **6**, C130.
431. T. Aaltonen, M. Ritala, T. Sajavaara, J. Keinonen and M. Leskelä, *Chemistry of Materials*, 2003, **15**, 1924-1928.
432. S. D. Elliott, *Langmuir*, 2010, **26**, 9179-9182.
433. N. E. Richey, C. de Paula and S. F. Bent, *J Chem Phys*, 2020, **152**, 040902.

434. E. Sairanen, M. C. Figueiredo, R. Karinen, A. Santasalo-Aarnio, H. Jiang, J. Sainio, T. Kallio and J. Lehtonen, *Applied Catalysis B: Environmental*, 2014, **148-149**, 11-21.
435. M. Utriainen, M. Kröger-Laukkanen, L.-S. Johansson and L. Niinistö, *Applied Surface Science*, 2000, **157**, 151-158.
436. V. R. Anderson, N. Leick, J. W. Clancey, K. E. Hurst, K. M. Jones, A. C. Dillon and S. M. George, *The Journal of Physical Chemistry C*, 2014, **118**, 8960-8970.
437. J. Gan, J. Zhang, B. Zhang, W. Chen, D. Niu, Y. Qin, X. Duan and X. Zhou, *Journal of Energy Chemistry*, 2020, **45**, 59-66.
438. Q. Du, J. Wu and H. Yang, *ACS Catalysis*, 2013, **4**, 144-151.
439. J. Xie, X. Yang, B. Han, Y. Shao-Horn and D. Wang, *ACS Nano*, 2013, **7**, 6337-6345.
440. L. Zhang, L. T. Roling, X. Wang, M. Vara, M. Chi, J. Liu, S. I. Choi, J. Park, J. A. Herron, Z. Xie, M. Mavrikakis and Y. Xia, *Science*, 2015, **349**, 412-416.
441. C. H. Choi, M. Kim, H. C. Kwon, S. J. Cho, S. Yun, H. T. Kim, K. J. Mayrhofer, H. Kim and M. Choi, *Nat Commun*, 2016, **7**, 10922.
442. R. Shen, W. Chen, Q. Peng, S. Lu, L. Zheng, X. Cao, Y. Wang, W. Zhu, J. Zhang, Z. Zhuang, C. Chen, D. Wang and Y. Li, *Chem*, 2019, **5**, 2099-2110.
443. S. Siahrostami, A. Verdager-Casadevall, M. Karamad, D. Deiana, P. Malacrida, B. Wickman, M. Escudero-Escribano, E. A. Paoli, R. Frydendal, T. W. Hansen, I. Chorkendorff, I. E. Stephens and J. Rossmeisl, *Nat Mater*, 2013, **12**, 1137-1143.
444. Y. Chen, S. Ji, Y. Wang, J. Dong, W. Chen, Z. Li, R. Shen, L. Zheng, Z. Zhuang, D. Wang and Y. Li, *Angew Chem Int Ed Engl*, 2017, **56**, 6937-6941.
445. Y. Qu, Z. Li, W. Chen, Y. Lin, T. Yuan, Z. Yang, C. Zhao, J. Wang, C. Zhao, X. Wang, F. Zhou, Z. Zhuang, Y. Wu and Y. Li, *Nature Catalysis*, 2018, **1**, 781-786.
446. L. Zhang, H. Liu, S. Liu, M. Norouzi Banis, Z. Song, J. Li, L. Yang, M. Markiewicz, Y. Zhao, R. Li, M. Zheng, S. Ye, Z.-J. Zhao, G. A. Botton and X. Sun, *ACS Catalysis*, 2019, **9**, 9350-9358.
447. W. W. McNeary, A. E. Linico, C. Ngo, S. van Rooij, S. Haussener, M. E. Maguire, S. Pylypenko and A. W. Weimer, *Journal of Applied Electrochemistry*, 2018, **48**, 973-984.
448. J. Cai, J. Zhang, K. Cao, M. Gong, Y. Lang, X. Liu, S. Chu, B. Shan and R. Chen, *ACS Applied Nano Materials*, 2018, **1**, 522-530.
449. Y. Wen, J. Cai, J. Zhang, J. Yang, L. Shi, K. Cao, R. Chen and B. Shan, *Chemistry of Materials*, 2018, **31**, 101-111.
450. N. Cheng, M. N. Banis, J. Liu, A. Riese, X. Li, R. Li, S. Ye, S. Knights and X. Sun, *Advanced materials*, 2015, **27**, 277-281.
451. Z. Song, B. Wang, N. Cheng, L. Yang, D. Banham, R. Li, S. Ye and X. Sun, *Journal of Materials Chemistry A*, 2017, **5**, 9760-9767.
452. L. Zhang, Y. Zhao, M. N. Banis, K. Adair, Z. Song, L. Yang, M. Markiewicz, J. Li, S. Wang, R. Li, S. Ye and X. Sun, *Nano Energy*, 2019, **60**, 111-118.
453. N. Cheng, J. Liu, M. N. Banis, D. Geng, R. Li, S. Ye, S. Knights and X. Sun, *International Journal of Hydrogen Energy*, 2014, **39**, 15967-15974.
454. N. Cheng, M. Norouzi Banis, J. Liu, A. Riese, S. Mu, R. Li, T.-K. Sham and X. Sun, *Energy & Environmental Science*, 2015, **8**, 1450-1455.
455. C.-T. Hsieh, Y.-Y. Liu, D.-Y. Tzou and W.-Y. Chen, *The Journal of Physical Chemistry C*, 2012, **116**, 26735-26743.
456. Y.-C. Hsueh, C.-C. Wang, C.-C. Kei, Y.-H. Lin, C. Liu and T.-P. Perng, *Journal of Catalysis*, 2012, **294**, 63-68.
457. T. Shu, D. Dang, D.-w. Xu, R. Chen, S.-j. Liao, C.-t. Hsieh, A. Su, H.-y. Song and L. Du, *Electrochimica Acta*, 2015, **177**, 168-173.
458. T. Shu, S.-J. Liao, C.-T. Hsieh, A. K. Roy, Y.-Y. Liu, D.-Y. Tzou and W.-Y. Chen, *Electrochimica Acta*, 2012, **75**, 101-107.
459. C. Liu, C. C. Wang, C. C. Kei, Y. C. Hsueh and T. P. Perng, *Small*, 2009, **5**, 1535-1538.

460. Z. Song, M. Norouzi Banis, H. Liu, L. Zhang, Y. Zhao, J. Li, K. Doyle-Davis, R. Li, S. Knights, S. Ye, G. A. Botton, P. He and X. Sun, *ACS Catalysis*, 2019, **9**, 5365-5374.
461. S. Moghaddam, E. Pengwang, Y. B. Jiang, A. R. Garcia, D. J. Burnett, C. J. Brinker, R. I. Masel and M. A. Shannon, *Nat Nanotechnol*, 2010, **5**, 230-236.
462. M. Choun, S. Chung, H. Jeon, S. Uhm and J. Lee, *Electrochemistry Communications*, 2012, **24**, 108-111.
463. C.-T. Hsieh, D.-Y. Tzou and M.-T. Jiang, *Journal of Electroanalytical Chemistry*, 2017, **794**, 139-147.
464. H. Yang, B. Zhang, B. Zhang, Z. Gao and Y. Qin, *Chinese Journal of Catalysis*, 2018, **39**, 1038-1043.
465. C.-Y. Su, Y.-C. Hsueh, C.-C. Kei, C.-T. Lin and T.-P. Perng, *The Journal of Physical Chemistry C*, 2013, **117**, 11610-11618.
466. Y. Chen, J. Wang, X. Meng, Y. Zhong, R. Li, X. Sun, S. Ye and S. Knights, *International Journal of Hydrogen Energy*, 2011, **36**, 11085-11092.
467. K. Zhang, W. Yang, C. Ma, Y. Wang, C. Sun, Y. Chen, P. Duchesne, J. Zhou, J. Wang, Y. Hu, M. N. Banis, P. Zhang, F. Li, J. Li and L. Chen, *NPG Asia Materials*, 2015, **7**, e153-e153.
468. X. Jiang, T. M. Gür, F. B. Prinz and S. F. Bent, *Chemistry of Materials*, 2010, **22**, 3024-3032.
469. A.-C. Johansson, J. V. Larsen, M. A. Verheijen, K. B. Haugshøj, H. F. Clausen, W. M. M. Kessels, L. H. Christensen and E. V. Thomsen, *Journal of Catalysis*, 2014, **311**, 481-486.
470. A. C. Johansson, R. B. Yang, K. B. Haugshøj, J. V. Larsen, L. H. Christensen and E. V. Thomsen, *International Journal of Hydrogen Energy*, 2013, **38**, 11406-11414.
471. H. J. Jeong, J. W. Kim, K. Bae, H. Jung and J. H. Shim, *ACS Catalysis*, 2015, **5**, 1914-1921.
472. H. Jeong, J. W. Kim, J. Park, J. An, T. Lee, F. B. Prinz and J. H. Shim, *ACS Appl Mater Interfaces*, 2016, **8**, 30090-30098.
473. S. Sun, G. Zhang, N. Gauquelin, N. Chen, J. Zhou, S. Yang, W. Chen, X. Meng, D. Geng, M. N. Banis, R. Li, S. Ye, S. Knights, G. A. Botton, T.-K. Sham and X. Sun, *Scientific reports*, 2013, **3**, 1775.
474. C.-T. Hsieh, W.-Y. Chen, D.-Y. Tzou, A. K. Roy and H.-T. Hsiao, *International Journal of Hydrogen Energy*, 2012, **37**, 17837-17843.
475. C.-T. Hsieh, H.-T. Hsiao, D.-Y. Tzou, P.-Y. Yu, P.-Y. Chen and B.-S. Jang, *Materials Chemistry and Physics*, 2015, **149-150**, 359-367.
476. L. Assaud, E. Monyoncho, K. Pitzschel, A. Allagui, M. Petit, M. Hanbucken, E. A. Baranova and L. Santinacci, *Beilstein J Nanotechnol*, 2014, **5**, 162-172.
477. N. Caner, A. Bulut, M. Yurderi, I. E. Ertas, H. Kivrak, M. Kaya and M. Zahmakiran, *Applied Catalysis B: Environmental*, 2017, **210**, 470-483.
478. R.-S. Juang, C.-T. Hsieh, J.-Q. Hsiao, H.-T. Hsiao, D.-Y. Tzou and M. M. Huq, *Journal of Power Sources*, 2015, **275**, 845-851.
479. E. Rikkinen, A. Santasalo-Aarnio, S. Airaksinen, M. Borghei, V. Viitanen, J. Sainio, E. I. Kauppinen, T. Kallio and A. O. I. Krause, *The Journal of Physical Chemistry C*, 2011, **115**, 23067-23073.
480. Y. Jiang, J. Chen, J. Zhang, A. Li, Y. Zeng, F. Zhou, G. Wang and R. Wang, *RSC Advances*, 2016, **6**, 13207-13216.
481. L. Assaud, N. Brazeau, M. K. Barr, M. Hanbucken, S. Ntais, E. A. Baranova and L. Santinacci, *ACS Appl Mater Interfaces*, 2015, **7**, 24533-24542.
482. M. K. S. Barr, L. Assaud, N. Brazeau, M. Hanbücken, S. Ntais, L. Santinacci and E. A. Baranova, *The Journal of Physical Chemistry C*, 2017, **121**, 17727-17736.
483. C. E. Finke, S. T. Omelchenko, J. T. Jasper, M. F. Lichterman, C. G. Read, N. S. Lewis and M. R. Hoffmann, *Energy & Environmental Science*, 2019, **12**, 358-365.
484. M. A. Khalily, B. Patil, E. Yilmaz and T. Uyar, *Nanoscale Advances*, 2019, **1**, 1224-1231.
485. X. Sun, X. Yang, H. Xiang, H. Mi, P. Zhang, X. Ren, Y. Li and X. Li, *Electrochimica Acta*, 2019, **296**, 964-971.

486. H. Li, Z. Guo and X. Wang, *J. Mater. Chem. A*, 2017, **5**, 21353-21361.
487. V. Di Palma, G. Zafeiropoulos, T. Goldsweer, W. M. M. Kessels, M. C. M. van de Sanden, M. Creatore and M. N. Tsampas, *Electrochemistry Communications*, 2019, **98**, 73-77.
488. J. Rongé, T. Dobbelaere, L. Henderick, M. M. Minjauw, S. P. Sree, J. Dendooven, J. A. Martens and C. Detavernier, *Nanoscale Advances*, 2019, **1**, 4166-4172.
489. K. L. Pickrahn, S. W. Park, Y. Gorlin, H.-B.-R. Lee, T. F. Jaramillo and S. F. Bent, *Advanced Energy Materials*, 2012, **2**, 1269-1277.
490. K. L. Nardi, N. Yang, C. F. Dickens, A. L. Strickler and S. F. Bent, *Advanced Energy Materials*, 2015, **5**.
491. A. G. Hufnagel, A.-K. Henß, R. Hoffmann, O. E. O. Zeman, S. Häringer, D. Fattakhova-Rohlfing and T. Bein, *Advanced Materials Interfaces*, 2018, **5**.
492. D. Xiong, Q. Zhang, W. Li, J. Li, X. Fu, M. F. Cerqueira, P. Alpuim and L. Liu, *Nanoscale*, 2017, **9**, 2711-2717.
493. Y. Huang, L. Liu and X. Liu, *Nanotechnology*, 2019, **30**, 095402.
494. P. Nayak, Q. Jiang, N. Kurra, X. Wang, U. Buttner and H. N. Alshareef, *Journal of Materials Chemistry A*, 2017, **5**, 20422-20427.
495. I. J. Hsu, Y. C. Kimmel, X. Jiang, B. G. Willis and J. G. Chen, *Chem Commun*, 2012, **48**, 1063-1065.
496. N. Cheng, S. Stambula, D. Wang, M. N. Banis, J. Liu, A. Riese, B. Xiao, R. Li, T. K. Sham, L. M. Liu, G. A. Botton and X. Sun, *Nature communications*, 2016, **7**, 13638.
497. Y. Lei, Y. Wang, Y. Liu, C. Song, Q. Li, D. Wang and Y. Li, *Angew Chem Int Ed Engl*, 2020, **59**, 20794-20812.
498. L. Zhang, R. Si, H. Liu, N. Chen, Q. Wang, K. Adair, Z. Wang, J. Chen, Z. Song, J. Li, M. N. Banis, R. Li, T. K. Sham, M. Gu, L. M. Liu, G. A. Botton and X. Sun, *Nature Communications*, 2019, **10**, 4936.
499. S. Shin, Z. Jin, D. H. Kwon, R. Bose and Y. S. Min, *Langmuir*, 2015, **31**, 1196-1202.
500. D. H. Kwon, Z. Jin, S. Shin, W. S. Lee and Y. S. Min, *Nanoscale*, 2016, **8**, 7180-7188.
501. T. A. Ho, C. Bae, S. Lee, M. Kim, J. M. Montero-Moreno, J. H. Park and H. Shin, *Chemistry of Materials*, 2017, **29**, 7604-7614.
502. Y. Kim, D. H. K. Jackson, D. Lee, M. Choi, T.-W. Kim, S.-Y. Jeong, H.-J. Chae, H. W. Kim, N. Park, H. Chang, T. F. Kuech and H. J. Kim, *Advanced Functional Materials*, 2017, **27**, 1701825.
503. Y. Cimen, A. W. Peters, J. R. Avila, W. L. Hoffeditz, S. Goswami, O. K. Farha and J. T. Hupp, *Langmuir*, 2016, **32**, 12005-12012.
504. W. Xiong, Z. Guo, H. Li, R. Zhao and X. Wang, *ACS Energy Letters*, 2017, **2**, 2778-2785.
505. W. Xiong, Q. Guo, Z. Guo, H. Li, R. Zhao, Q. Chen, Z. Liu and X. Wang, *Journal of Materials Chemistry A*, 2018, **6**, 4297-4304.
506. Y. Zheng, Y. Jiao, Y. Zhu, L. H. Li, Y. Han, Y. Chen, M. Jaroniec and S.-Z. Qiao, *Journal of the American Chemical Society*, 2016, **138**, 16174-16181.
507. L. Zhang, Z.-J. Zhao, M. Norouzi Banis, L. Li, Y. Zhao, Z. Song, Z. Wang, T.-K. Sham, R. Li, M. Zheng, J. Gong and X. Sun, *Journal of Materials Chemistry A*, 2018, **6**, 24397-24406.
508. T. W. Hamann, R. A. Jensen, A. B. F. Martinson, H. Van Ryswyk and J. T. Hupp, *Energy & Environmental Science*, 2008, **1**, 66.
509. N. Tétreault and M. Grätzel, *Energy & Environmental Science*, 2012, **5**, 8506.
510. K. Fan, J. Yu and W. Ho, *Materials Horizons*, 2017, **4**, 319-344.
511. J. M. Cole, G. Pepe, O. K. Al Bahri and C. B. Cooper, *Chem Rev*, 2019, **119**, 7279-7327.
512. M. Ye, X. Wen, M. Wang, J. Iocozzia, N. Zhang, C. Lin and Z. Lin, *Materials Today*, 2015, **18**, 155-162.
513. A. F. Palmstrom, P. K. Santra and S. F. Bent, *Nanoscale*, 2015, **7**, 12266-12283.
514. D. H. Kim, M. D. Losego, Q. Peng and G. N. Parsons, *Advanced Materials Interfaces*, 2016, **3**, 1600354.

515. A. K. Chandiran, P. Comte, R. Humphry-Baker, F. Kessler, C. Yi, M. K. Nazeeruddin and M. Grätzel, *Advanced Functional Materials*, 2013, **23**, 2775-2781.
516. I. Dirnstorfer, H. Mähne, T. Mikolajick, M. Knaut, M. Albert and K. Dubnack, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 2013, **31**, 01A116.
517. X. Gao, J. Chen and C. Yuan, *Journal of Power Sources*, 2013, **240**, 503-509.
518. J. Y. Kim, K. H. Lee, J. Shin, S. H. Park, J. S. Kang, K. S. Han, M. M. Sung, N. Pinna and Y. E. Sung, *Nanotechnology*, 2014, **25**, 504003.
519. A. F. Palmstrom, G. E. Eperon, T. Leijtens, R. Prasanna, S. N. Habisreutinger, W. Nemeth, E. A. Gaulding, S. P. Dunfield, M. Reese, S. Nanayakkara, T. Moot, J. Werner, J. Liu, B. To, S. T. Christensen, M. D. McGehee, M. F. A. M. van Hest, J. M. Luther, J. J. Berry and D. T. Moore, *Joule*, 2019, **3**, 2193-2204.
520. D. H. Kim, H. J. Koo, J. S. Jur, M. Woodroof, B. Kalanyan, K. Lee, C. K. Devine and G. N. Parsons, *Nanoscale*, 2012, **4**, 4731-4738.
521. J. W. Lee, J. Lee, C. Kim, C. Y. Cho and J. H. Moon, *Sci Rep*, 2014, **4**, 6804.
522. W. Song, H. Wang, G. Liu, M. Peng and D. Zou, *Nano Energy*, 2016, **19**, 1-7.
523. J. Y. Kim, J. S. Kang, J. Shin, J. Kim, S. J. Han, J. Park, Y. S. Min, M. J. Ko and Y. E. Sung, *Nanoscale*, 2015, **7**, 8368-8377.
524. L. Alibabaei, B. H. Farnum, B. Kalanyan, M. K. Brennaman, M. D. Losego, G. N. Parsons and T. J. Meyer, *Nano Lett*, 2014, **14**, 3255-3261.
525. A. B. F. Martinson, J. W. Elam, J. T. Hupp and M. J. Pellin, *Nano Lett*, 2007, **8**, 2183-2187.
526. T. W. Hamann, A. B. F. Martinson, J. W. Elam, M. J. Pellin and J. T. Hupp, *Advanced Materials*, 2008, **20**, 1560-1564.
527. A. K. Chandiran, M. Abdi-Jalebi, A. Yella, M. I. Dar, C. Yi, S. A. Shivashankar, M. K. Nazeeruddin and M. Gratzel, *Nano Lett*, 2014, **14**, 1190-1195.
528. A. K. Chandiran, M. Abdi-Jalebi, M. K. Nazeeruddin and M. G. tzel, *ACS Nano*, 2014, **8**, 2261-2268.
529. J.-S. Jeong, B.-H. Choe, J.-H. Lee, J.-J. Lee and W.-Y. Choi, *Journal of Electronic Materials*, 2013, **43**, 375-380.
530. A. R. Pascoe, L. Bourgeois, N. W. Duffy, W. Xiang and Y.-B. Cheng, *The Journal of Physical Chemistry C*, 2013, **117**, 25118-25126.
531. T. R. Garvey, B. H. Farnum and R. Lopez, *Nanoscale*, 2015, **7**, 2400-2408.
532. R. R. Knauf, B. Kalanyan, G. N. Parsons and J. L. Dempsey, *The Journal of Physical Chemistry C*, 2015, **119**, 28353-28360.
533. H. Lu, W. Tian, J. Guo and L. Li, *Sci Rep*, 2015, **5**, 12765.
534. C. Wang, Z. Yu, C. Bu, P. Liu, S. Bai, C. Liu, K. K. Kondamareddy, W. Sun, K. Zhan, K. Zhang, S. Guo and X. Zhao, *Journal of Power Sources*, 2015, **282**, 596-601.
535. N. S. McCool, J. R. Swierk, C. T. Nemes, C. A. Schmittenmaer and T. E. Mallouk, *J Phys Chem Lett*, 2016, **7**, 2930-2934.
536. L. Alibabaei, R. J. Dillon, C. E. Reilly, M. K. Brennaman, K. R. Wee, S. L. Marquard, J. M. Papanikolas and T. J. Meyer, *ACS Appl Mater Interfaces*, 2017, **9**, 39018-39026.
537. C. Karam, C. Guerra-Nuñez, R. Habchi, Z. Herro, N. Abboud, A. Khoury, S. Tingry, P. Miele, I. Utke and M. Bechelany, *Materials & Design*, 2017, **126**, 314-321.
538. J. Maçaira, L. Andrade and A. Mendes, *Solar Energy*, 2017, **158**, 905-916.
539. D. Wang, B. D. Sherman, B. H. Farnum, M. V. Sheridan, S. L. Marquard, M. S. Eberhart, C. J. Dares and T. J. Meyer, *Proc Natl Acad Sci U S A*, 2017, **114**, 9809-9813.
540. C. Karam, R. Habchi, S. Tingry, P. Miele and M. Bechelany, *ACS Applied Nano Materials*, 2018, **1**, 3705-3714.
541. L. Tian, J. Fohlinger, Z. Zhang, P. B. Pati, J. Lin, T. Kubart, Y. Hua, J. Sun, L. Kloo, G. Boschloo, L. Hammarstrom and H. Tian, *Chem Commun*, 2018, **54**, 3739-3742.
542. J.-Y. Kim, K.-Y. Shin, M. H. Raza, N. Pinna and Y.-E. Sung, *Korean Journal of Chemical Engineering*, 2019, **36**, 1157-1163.

543. M. Law, L. E. Greene, A. Radenovic, T. Kuykendall, J. Liphardt and P. Yang, *J. Phys. Chem. B*, 2006, **110**, 22652-22663.
544. K. Park, Q. Zhang, B. B. Garcia, X. Zhou, Y. H. Jeong and G. Cao, *Adv Mater*, 2010, **22**, 2329-2332.
545. V. O. Williams, N. C. Jeong, C. Prasittichai, O. K. Farha, M. J. Pellin and J. T. Hupp, *ACS Nano*, 2012, **6**, 6185-6196.
546. J.-H. Choi, S.-H. Kwon, Y.-K. Jeong, I. Kim and K.-H. Kim, *Journal of The Electrochemical Society*, 2011, **158**, B749-B753.
547. L. Liu, S. K. Karuturi, L. T. Su and A. I. Y. Tok, *Energy Environ. Sci.*, 2011, **4**, 209-215.
548. P. Labouchere, A. K. Chandiran, T. Moehl, H. Harms, S. Chavhan, R. Tena-Zaera, M. K. Nazeeruddin, M. Graetzel and N. Tetreault, *Advanced Energy Materials*, 2014, **4**, 1400217.
549. C. Lin, F.-Y. Tsai, M.-H. Lee, C.-H. Lee, T.-C. Tien, L.-P. Wang and S.-Y. Tsai, *Journal of Materials Chemistry*, 2009, **19**, 2999.
550. T. P. Brennan, J. R. Bakke, I. K. Ding, B. E. Hardin, W. H. Nguyen, R. Mondal, C. D. Bailie, G. Y. Margulis, E. T. Hoke, A. Sellinger, M. D. McGehee and S. F. Bent, *Phys Chem Chem Phys*, 2012, **14**, 12130-12140.
551. T. P. Brennan, O. Trejo, K. E. Roelofs, J. Xu, F. B. Prinz and S. F. Bent, *Journal of Materials Chemistry A*, 2013, **1**, 7566.
552. X. Gao, D. Guan, J. Huo, J. Chen and C. Yuan, *Nanoscale*, 2013, **5**, 10438-10446.
553. W. Dong, L. Yang, T. Meng and Q. Chen, *Surface and Coatings Technology*, 2015, **276**, 116-120.
554. G. Natu, Z. Huang, Z. Ji and Y. Wu, *Langmuir*, 2012, **28**, 950-956.
555. K. E. Roelofs, T. P. Brennan, J. C. Dominguez, C. D. Bailie, G. Y. Margulis, E. T. Hoke, M. D. McGehee and S. F. Bent, *The Journal of Physical Chemistry C*, 2013, **117**, 5584-5592.
556. V. Ganapathy, B. Karunagaran and S.-W. Rhee, *Journal of Power Sources*, 2010, **195**, 5138-5143.
557. A. K. Chandiran, N. Tetreault, R. Humphry-Baker, F. Kessler, E. Baranoff, C. Yi, M. K. Nazeeruddin and M. Gratzel, *Nano Lett*, 2012, **12**, 3941-3947.
558. T. P. Brennan, J. T. Tanskanen, K. E. Roelofs, J. W. F. To, W. H. Nguyen, J. R. Bakke, I. K. Ding, B. E. Hardin, A. Sellinger, M. D. McGehee and S. F. Bent, *The Journal of Physical Chemistry C*, 2013, **117**, 24138-24149.
559. A. K. Chandiran, M. K. Nazeeruddin and M. Grätzel, *Advanced Functional Materials*, 2014, **24**, 1615-1623.
560. D. H. Kim, M. Woodroof, K. Lee and G. N. Parsons, *ChemSusChem*, 2013, **6**, 1014-1020.
561. L. Kavan, N. Tetreault, T. Moehl and M. Grätzel, *The Journal of Physical Chemistry C*, 2014, **118**, 16408-16418.
562. L. Li, S. Chen, C. Xu, Y. Zhao, N. G. Rudawski and K. J. Ziegler, *ACS Appl Mater Interfaces*, 2014, **6**, 20978-20984.
563. J.-H. Yum, T. Moehl, J. Yoon, A. K. Chandiran, F. Kessler, P. Gratia and M. Grätzel, *The Journal of Physical Chemistry C*, 2014, **118**, 16799-16805.
564. L. Li, C. Xu, Y. Zhao, S. Chen and K. J. Ziegler, *ACS Appl Mater Interfaces*, 2015, **7**, 12824-12831.
565. F. Di Giacomo, V. Zardetto, G. Lucarelli, L. Cinà, A. Di Carlo, M. Creatore and T. M. Brown, *Nano Energy*, 2016, **30**, 460-469.
566. V. Manthina and A. G. Agrios, *Thin Solid Films*, 2016, **598**, 54-59.
567. J. Song, A. Ge, B. Piercy, M. D. Losego and T. Lian, *Chemical Physics*, 2018, **512**, 68-74.
568. D. Garcia-Alonso, V. Zardetto, A. J. M. Mackus, F. De Rossi, M. A. Verheijen, T. M. Brown, W. M. M. Kessels and M. Creatore, *Advanced Energy Materials*, 2014, **4**, 1300831.
569. W. L. Hoffeditz, M. J. Katz, P. Deria, A. B. Martinson, M. J. Pellin, O. K. Farha and J. T. Hupp, *ACS Appl Mater Interfaces*, 2014, **6**, 8646-8650.
570. Y. Noh and O. Song, *Electronic Materials Letters*, 2014, **10**, 263-266.
571. S. Abdelnasser, M. A. Sakr and M. Serry, *Microelectronic Engineering*, 2019, **216**, 111045.
572. T. Jeong, S.-Y. Ham, B. Koo, P. Lee, Y.-S. Min, J.-Y. Kim and M. J. Ko, *Journal of Industrial and Engineering Chemistry*, 2019, **80**, 106-111.

573. D.-J. Yun, H. Ra, J.-M. Kim, E. Oh, J. Lee, M.-H. Jeong, Y. J. Jeong, H. Yang and J. Jang, *Organic Electronics*, 2019, **65**, 349-356.
574. K. O. Brinkmann, T. Gahlmann and T. Riedl, *Solar RRL*, 2019, **4**, 1900332.
575. J. A. Raiford, S. T. Oyakhire and S. Bent, *Energy & Environmental Science*, 2020, **13**, 1997-2023
576. K. Deng and L. Li, *Advanced Materials Interfaces*, 2016, **3**, 1600505.
577. B. Macco, H. C. M. Knoops, M. A. Verheijen, W. Beyer, M. Creatore and W. M. M. Kessels, *Solar Energy Materials and Solar Cells*, 2017, **173**, 111-119.
578. S. Seo, S. Jeong, H. Park, H. Shin and N. G. Park, *Chem Commun*, 2019, **55**, 2403-2416.
579. V. Zardetto, B. L. Williams, A. Perrotta, F. Di Giacomo, M. A. Verheijen, R. Andriessen, W. M. M. Kessels and M. Creatore, *Sustainable Energy & Fuels*, 2017, **1**, 30-55.
580. P. Rong, S. Ren and Q. Yu, *Crit Rev Anal Chem*, 2019, **49**, 336-349.
581. P. Schulz, D. Cahen and A. Kahn, *Chem Rev*, 2019, **119**, 3349-3417.
582. B. R. Sutherland, S. Hoogland, M. M. Adachi, P. Kanjanaboos, C. T. Wong, J. J. McDowell, J. Xu, O. Voznyy, Z. Ning, A. J. Houtepen and E. H. Sargent, *Adv Mater*, 2015, **27**, 53-58.
583. V. M. Koch, M. K. S. Barr, P. Büttner, I. Mínguez-Bacho, D. Döhler, B. Winzer, E. Reinhardt, D. Segets and J. Bachmann, *Journal of Materials Chemistry A*, 2019, **7**, 25112-25119.
584. G. Popov, M. Mattinen, T. Hatanpää, M. Vehkamäki, M. Kemell, K. Mizohata, J. Räisänen, M. Ritala and M. Leskelä, *Chemistry of Materials*, 2019, **31**, 1101-1109.
585. N. G. Park, *Advanced Energy Materials*, 2020, **10**, 1903106.
586. L. Xu, X. Chen, J. Jin, W. Liu, B. Dong, X. Bai, H. Song and P. Reiss, *Nano Energy*, 2019, **63**, 103860.
587. J. W. Lee and N. G. Park, *Advanced Energy Materials*, 2019, **10**, 1903249.
588. R. Wang, M. Mujahid, Y. Duan, Z. K. Wang, J. Xue and Y. Yang, *Advanced Functional Materials*, 2019, **29**, 1808843.
589. A. K. Chandiran, A. Yella, M. T. Mayer, P. Gao, M. K. Nazeeruddin and M. Gratzel, *Adv Mater*, 2014, **26**, 4309-4312.
590. Y. Wu, X. Yang, H. Chen, K. Zhang, C. Qin, J. Liu, W. Peng, A. Islam, E. Bi, F. Ye, M. Yin, P. Zhang and L. Han, *Applied Physics Express*, 2014, **7**, 052301.
591. A. Mettenbörger, Y. Gönüllü, T. Fischer, T. Heisig, A. Sasinska, C. Maccato, G. Carraro, C. Sada, D. Barreca, L. Mayrhofer, M. Moseler, A. Held and S. Mathur, *Nano Energy*, 2016, **19**, 415-427.
592. K. E. Roelofs, V. L. Pool, D. A. Bobb-Semple, A. F. Palmstrom, P. K. Santra, D. G. Van Campen, M. F. Toney and S. F. Bent, *Advanced Materials Interfaces*, 2016, **3**, 1600580.
593. A. E. Shalan, S. Narra, T. Oshikiri, K. Ueno, X. Shi, H.-P. Wu, Mahmoud M. Elshanawany, E. Wei-Guang Diao and H. Misawa, *Sustainable Energy & Fuels*, 2017, **1**, 1533-1540.
594. V. Zardetto, F. Di Giacomo, G. Lucarelli, W. M. M. Kessels, T. M. Brown and M. Creatore, *Solar Energy*, 2017, **150**, 447-453.
595. W. Tan, O. L. Hendricks, A. C. Meng, M. R. Braun, M. D. McGehee, C. E. D. Chidsey and P. C. McIntyre, *Advanced Materials Interfaces*, 2018, **5**, 1800191.
596. V. Zardetto, F. di Giacomo, H. Lifka, M. A. Verheijen, C. H. L. Weijtens, L. E. Black, S. Veenstra, W. M. M. Kessels, R. Andriessen and M. Creatore, *Advanced Materials Interfaces*, 2018, **5**, 1701456.
597. Y. Zhu, K. Deng, H. Sun, B. Gu, H. Lu, F. Cao, J. Xiong and L. Li, *Adv Sci (Weinh)*, 2018, **5**, 1700614.
598. D. Chen, A. Su, X. Li, S. Pang, W. Zhu, H. Xi, J. Chang, J. Zhang, C. Zhang and Y. Hao, *Solar Energy*, 2019, **188**, 239-246.
599. T. W. Kim, S. Uchida, T. Kondo and H. Segawa, *Applied Physics Letters*, 2019, **115**, 203902.
600. M. Kong, H. Hu, K. Qin, B. Dong, L. Wan and P. Guo, *Materials Research Express*, 2019, **6**, 095501.
601. S. Na, S. Lee, W.-G. Choi, C.-G. Park, S. O. Ryu and T. Moon, *Journal of Vacuum Science & Technology A*, 2019, **37**, 010902.

602. Y. You, W. Tian, L. Min, F. Cao, K. Deng and L. Li, *Advanced Materials Interfaces*, 2019, **7**, 1901406.
603. W. Zhu, W. Chai, Z. Zhang, D. Chen, J. Chang, S. Liu, J. Zhang, C. Zhang and Y. Hao, *Organic Electronics*, 2019, **74**, 103-109.
604. Y. Wang, D. Wang, H. Qu, J. Cheng, Y. Fang, C. Zhang and Q. Chen, *Thin Solid Films*, 2020, **696**, 137786.
605. H. Lu, Y. Ma, B. Gu, W. Tian and L. Li, *Journal of Materials Chemistry A*, 2015, **3**, 16445-16452.
606. L. Chen, J.-R. Wang, L.-Q. Xie, C. Zhan, Z. Qiu, J.-Z. Zhou, J.-W. Yan, B.-W. Mao and Z.-Q. Tian, *Electrochemistry Communications*, 2016, **68**, 40-44.
607. S. Albrecht, M. Saliba, J. P. Correa Baena, F. Lang, L. Kegelmann, M. Mews, L. Steier, A. Abate, J. Rappich, L. Korte, R. Schlattmann, M. K. Nazeeruddin, A. Hagfeldt, M. Grätzel and B. Rech, *Energy & Environmental Science*, 2016, **9**, 81-88.
608. C. Wang, D. Zhao, C. R. Grice, W. Liao, Y. Yu, A. Cimaroli, N. Shrestha, P. J. Roland, J. Chen, Z. Yu, P. Liu, N. Cheng, R. J. Ellingson, X. Zhao and Y. Yan, *Journal of Materials Chemistry A*, 2016, **4**, 12080-12087.
609. J. Kim, T. Iivonen, J. Hämäläinen, M. Kemell, K. Meinander, K. Mizohata, L. Wang, J. Räisänen, R. Beranek, M. Leskelä and A. Devi, *Chemistry of Materials*, 2017, **29**, 5796-5805.
610. L. Hoffmann, K. O. Brinkmann, J. Malerczyk, D. Rogalla, T. Becker, D. Theirich, I. Shutsko, P. Gorrn and T. Riedl, *ACS Appl Mater Interfaces*, 2018, **10**, 6006-6013.
611. Y. Lee, S. Lee, G. Seo, S. Paek, K. T. Cho, A. J. Huckaba, M. Calizzi, D. W. Choi, J. S. Park, D. Lee, H. J. Lee, A. M. Asiri and M. K. Nazeeruddin, *Adv Sci*, 2018, **5**, 1800130.
612. J. P. Correa Baena, L. Steier, W. Tress, M. Saliba, S. Neutzner, T. Matsui, F. Giordano, T. J. Jacobsson, A. R. Srimath Kandada, S. M. Zakeeruddin, A. Petrozza, A. Abate, M. K. Nazeeruddin, M. Grätzel and A. Hagfeldt, *Energy & Environmental Science*, 2015, **8**, 2928-2934.
613. T. Hu, T. Becker, N. Pourdavoud, J. Zhao, K. O. Brinkmann, R. Heiderhoff, T. Gahlmann, Z. Huang, S. Olthof, K. Meerholz, D. Tobbens, B. Cheng, Y. Chen and T. Riedl, *Adv Mater*, 2017, **29**.
614. Y. Kuang, V. Zardetto, R. van Gils, S. Karwal, D. Koushik, M. A. Verheijen, L. E. Black, C. Weijtens, S. Veenstra, R. Andriessen, W. M. M. Kessels and M. Creatore, *ACS Appl Mater Interfaces*, 2018, **10**, 30367-30378.
615. S. Jeong, S. Seo, H. Park and H. Shin, *Chem Commun*, 2019, **55**, 2433-2436.
616. C. Wang, C. Xiao, Y. Yu, D. Zhao, R. A. Awni, C. R. Grice, K. Ghimire, I. Constantinou, W. Liao, A. J. Cimaroli, P. Liu, J. Chen, N. J. Podraza, C.-S. Jiang, M. M. Al-Jassim, X. Zhao and Y. Yan, *Advanced Energy Materials*, 2017, **7**, 1700414.
617. A. Guerrero, G. Garcia-Belmonte, I. Mora-Sero, J. Bisquert, Y. S. Kang, T. J. Jacobsson, J.-P. Correa-Baena and A. Hagfeldt, *The Journal of Physical Chemistry C*, 2016, **120**, 8023-8032.
618. H. Wei, J. Wu, P. Qiu, S. Liu, Y. He, M. Peng, D. Li, Q. Meng, F. Zaera and X. Zheng, *Journal of Materials Chemistry A*, 2019, **7**, 25347-25354.
619. A. S. Subbiah, A. K. Dhara, N. Mahuli, S. Banerjee and S. K. Sarkar, *Energy Technology*, 2020, **8**, 1900878.
620. R. D. Chavan, M. M. Tavakoli, D. Prochowicz, P. Yadav, S. S. Lote, S. P. Bhoite, A. Nimbalkar and C. K. Hong, *ACS Appl Mater Interfaces*, 2020, **12**, 8098-8106.
621. H. Si, Q. Liao, Z. Zhang, Y. Li, X. Yang, G. Zhang, Z. Kang and Y. Zhang, *Nano Energy*, 2016, **22**, 223-231.
622. J. Tang, D. Jiao, L. Zhang, X. Zhang, X. Xu, C. Yao, J. Wu and Z. Lan, *Solar Energy*, 2018, **161**, 100-108.
623. M. Jošt, T. Bertram, D. Koushik, J. A. Marquez, M. A. Verheijen, M. D. Heinemann, E. Köhnen, A. Al-Ashouri, S. Braunger, F. Lang, B. Rech, T. Unold, M. Creatore, I. Lauermann, C. A. Kaufmann, R. Schlattmann and S. Albrecht, *ACS Energy Letters*, 2019, **4**, 583-590.
624. J. Tirado, M. Vásquez-Montoya, C. Roldán-Carmona, M. Ralaifarisoa, N. Koch, M. K. Nazeeruddin and F. Jaramillo, *ACS Applied Energy Materials*, 2019, **2**, 4890-4899.

625. S. Seo, I. J. Park, M. Kim, S. Lee, C. Bae, H. S. Jung, N. G. Park, J. Y. Kim and H. Shin, *Nanoscale*, 2016, **8**, 11403-11412.
626. D. Koushik, M. Jošt, A. Dučinskis, C. Burgess, V. Zardetto, C. Weijtens, M. A. Verheijen, W. M. M. Kessels, S. Albrecht and M. Creatore, *Journal of Materials Chemistry C*, 2019, **7**, 12532-12543.
627. B. Zhao, L. C. Lee, L. Yang, A. J. Pearson, H. Lu, X. J. She, L. Cui, K. H. L. Zhang, R. L. Z. Hoye, A. Karani, P. Xu, A. Sadhanala, N. C. Greenham, R. H. Friend, J. L. MacManus-Driscoll and D. Di, *ACS Appl Mater Interfaces*, 2018, **10**, 41849-41854.
628. W. Li, J. Li, L. Wang, G. Niu, R. Gao and Y. Qiu, *Journal of Materials Chemistry A*, 2013, **1**, 11735.
629. J.-J. Shi, W. Dong, Y.-Z. Xu, C.-H. Li, S.-T. Lv, L.-F. Zhu, J. Dong, Y.-H. Luo, D.-M. Li, Q.-B. Meng and Q. Chen, *Chinese Physics Letters*, 2013, **30**, 128402.
630. X. Dong, X. Fang, M. Lv, B. Lin, S. Zhang, J. Ding and N. Yuan, *Journal of Materials Chemistry A*, 2015, **3**, 5360-5367.
631. H. Wei, J. Shi, X. Xu, J. Xiao, J. Luo, J. Dong, S. Lv, L. Zhu, H. Wu, D. Li, Y. Luo, Q. Meng and Q. Chen, *Phys Chem Chem Phys*, 2015, **17**, 4937-4944.
632. M. Kot, C. Das, Z. Wang, K. Henkel, Z. Rouissi, K. Wojciechowski, H. J. Snaith and D. Schmeisser, *ChemSusChem*, 2016, **9**, 3401-3406.
633. D. Koushik, W. J. H. Verhees, D. Zhang, Y. Kuang, S. Veenstra, M. Creatore and R. E. I. Schropp, *Advanced Materials Interfaces*, 2017, **4**, 1700043.
634. Y. Lv, P. Xu, G. Ren, F. Chen, H. Nan, R. Liu, D. Wang, X. Tan, X. Liu, H. Zhang and Z. K. Chen, *ACS Appl Mater Interfaces*, 2018, **10**, 23928-23937.
635. D. Koushik, L. Hazendonk, V. Zardetto, V. Vandalon, M. A. Verheijen, W. M. M. Kessels and M. Creatore, *ACS Appl Mater Interfaces*, 2019, **11**, 5526-5535.
636. H.-S. Yun, K. Noh, J. Kim, S. H. Noh, G.-H. Kim, W. Lee, H. B. Na, T.-S. Yoon, J. Jang, Y. Kim and S.-Y. Cho, *physica status solidi (RRL) – Rapid Research Letters*, 2019, **14**, 1900573.
637. D. Koushik, W. J. H. Verhees, Y. Kuang, S. Veenstra, D. Zhang, M. A. Verheijen, M. Creatore and R. E. I. Schropp, *Energy & Environmental Science*, 2017, **10**, 91-100.
638. C.-Y. Chang, K.-T. Lee, W.-K. Huang, H.-Y. Siao and Y.-C. Chang, *Chemistry of Materials*, 2015, **27**, 5122-5130.
639. H. Wang, Y. Zhao, Z. Wang, Y. Liu, Z. Zhao, G. Xu, T.-H. Han, J.-W. Lee, C. Chen, D. Bao, Y. Huang, Y. Duan and Y. Yang, *Nano Energy*, 2020, **69**, 104375.
640. T. Wang, Z. Luo, C. Li and J. Gong, *Chem Soc Rev*, 2014, **43**, 7469-7484.
641. Y. He, T. Hamann and D. Wang, *Chem Soc Rev*, 2019, **48**, 2182-2215.
642. W. Yang, R. R. Prabhakar, J. Tan, S. D. Tilley and J. Moon, *Chem Soc Rev*, 2019, **48**, 4979-5015.
643. D. Bae, B. Seger, P. C. Vesborg, O. Hansen and I. Chorkendorff, *Chem Soc Rev*, 2017, **46**, 1933-1954.
644. D. Li, J. Shi and C. Li, *Small*, 2018, **14**, 1704179.
645. S. Shen, J. Chen, M. Wang, X. Sheng, X. Chen, X. Feng and S. S. Mao, *Progress in Materials Science*, 2018, **98**, 299-385.
646. S. Wang, G. Liu and L. Wang, *Chem Rev*, 2019, **119**, 5192-5247.
647. T. Yao, X. An, H. Han, J. Q. Chen and C. Li, *Advanced Energy Materials*, 2018, **8**, 1800210.
648. I. V. Bagal, N. R. Chodankar, M. A. Hassan, A. Waseem, M. A. Johar, D.-H. Kim and S.-W. Ryu, *International Journal of Hydrogen Energy*, 2019, **44**, 21351-21378.
649. S. Bellani, M. R. Antognazza and F. Bonaccorso, *Adv Mater*, 2019, **31**, e1801446.
650. S. Chandrasekaran, L. Yao, L. Deng, C. Bowen, Y. Zhang, S. Chen, Z. Lin, F. Peng and P. Zhang, *Chem Soc Rev*, 2019, **48**, 4178-4280.
651. M. T. Mayer, C. Du and D. Wang, *J Am Chem Soc*, 2012, **134**, 12406-12409.
652. L. Liu, *Materials Letters*, 2015, **159**, 284-288.
653. Q. Liu, F. Cao, F. Wu, W. Tian and L. Li, *RSC Advances*, 2015, **5**, 79440-79446.
654. L. Steier, J. Luo, M. Schreier, M. T. Mayer, T. Sajavaara and M. G. tzel, *ACS Nano*, 2015, **9**, 11775.

655. Gurudayal, R. A. John, P. P. Boix, C. Yi, C. Shi, M. C. Scott, S. A. Veldhuis, A. M. Minor, S. M. Zakeeruddin, L. H. Wong, M. Gratzel and N. Mathews, *ChemSusChem*, 2017, **10**, 2449-2456.
656. Y. Lin, S. Zhou, S. W. Sheehan and D. Wang, *J Am Chem Soc*, 2011, **133**, 2398-2401.
657. Q. Peng, J. Wang, Z. Feng, C. Du, Y. Wen, B. Shan and R. Chen, *The Journal of Physical Chemistry C*, 2017, **121**, 12991-12998.
658. I. A. Cordova, Q. Peng, I. L. Ferrall, A. J. Rieth, P. G. Hoertz and J. T. Glass, *Nanoscale*, 2015, **7**, 8584-8592.
659. D. Wang, H. Chen, G. Chang, X. Lin, Y. Zhang, A. Aldalbahi, C. Peng, J. Wang and C. Fan, *ACS Appl Mater Interfaces*, 2015, **7**, 14072-14078.
660. M. Pavlenko, K. Siuzdak, E. Coy, M. Jancelewicz, S. Jurga and I. Iatsunskyi, *International Journal of Hydrogen Energy*, 2017, **42**, 30076-30085.
661. A. N. El-Shazly, A. H. Hegazy, M. M. Rashad, M. F. El-Shahat and N. K. Allam, *Journal of Alloys and Compounds*, 2018, **739**, 178-183.
662. E. Kao, H. S. Park, X. Zang and L. Lin, *International Journal of Photoenergy*, 2019, **2019**, 1-8.
663. Y. Gun, G. Y. Song, V. H. Quy, J. Heo, H. Lee, K. S. Ahn and S. H. Kang, *ACS Appl Mater Interfaces*, 2015, **7**, 20292-20303.
664. Q. Peng, B. Kalanyan, P. G. Hoertz, A. Miller, D. H. Kim, K. Hanson, L. Alibabaei, J. Liu, T. J. Meyer, G. N. Parsons and J. T. Glass, *Nano Lett*, 2013, **13**, 1481-1488.
665. X. Li, P. S. Bassi, P. P. Boix, Y. Fang and L. H. Wong, *ACS Appl Mater Interfaces*, 2015, **7**, 16960-16966.
666. T. Hisatomi, J. Brillet, M. Cornuz, F. Le Formal, N. Tetreault, K. Sivula and M. Gratzel, *Faraday Discuss*, 2012, **155**, 223-232.
667. J. Ji, W. Zhang, H. Zhang, Y. Qiu, Y. Wang, Y. Luo and L. Hu, *Journal of Materials Science: Materials in Electronics*, 2013, **24**, 3474-3480.
668. M. Liu, C.-Y. Nam, C. T. Black, J. Kamcev and L. Zhang, *The Journal of Physical Chemistry C*, 2013, **117**, 13396-13402.
669. C. Li, T. Hisatomi, O. Watanabe, M. Nakabayashi, N. Shibata, K. Domen and J.-J. Delaunay, *Energy & Environmental Science*, 2015, **8**, 1493-1500.
670. M.-W. Kim, K. Kim, T. Y. Ohm, H. Yoon, B. Joshi, E. Samuel, M. T. Swihart, S. K. Choi, H. Park and S. S. Yoon, *Chemical Engineering Journal*, 2018, **333**, 721-729.
671. M. Li, X. Tu, Y. Wang, Y. Su, J. Hu, B. Cai, J. Lu, Z. Yang and Y. Zhang, *Nanomicro Lett*, 2018, **10**, 45.
672. S. Haschke, Y. Zhuo, S. Schlicht, M. K. S. Barr, R. Kloth, M. E. Dufond, L. Santinacci and J. Bachmann, *Advanced Materials Interfaces*, 2019, **6**, 1801432.
673. X. Huai, L. Girardi, R. Lu, S. Gao, Y. Zhao, Y. Ling, G. A. Rizzi, G. Granozzi and Z. Zhang, *Nano Energy*, 2019, **65**, 104020.
674. T.-G. Kim, B. Joshi, C.-W. Park, E. Samuel, M.-W. Kim, M. T. Swihart and S. S. Yoon, *Journal of Alloys and Compounds*, 2019, **798**, 35-44.
675. C.-C. Wang, C.-Y. Chou, S.-R. Yi and H.-D. Chen, *International Journal of Hydrogen Energy*, 2019, **44**, 28685-28697.
676. B. Alfakes, C. Garlisi, J. Villegas, A. Al-Hagri, S. Tamalampudi, N. S. Rajput, J.-Y. Lu, E. Lewin, J. Sá, I. Almansouri, G. Palmisano and M. Chiesa, *Surface and Coatings Technology*, 2020, **385**, 125352.
677. K.-I. Liu and T.-P. Perng, *ACS Applied Energy Materials*, 2020, **3**, 4238-4244.
678. Y. Zhao, S. Balasubramanyam, R. Sinha, R. Lavrijsen, M. A. Verheijen, A. A. Bol and A. Bieberle-Hütter, *ACS Applied Energy Materials*, 2018, **1**, 5887-5895.
679. M. Stefik, M. Cornuz, N. Mathews, T. Hisatomi, S. Mhaisalkar and M. Gratzel, *Nano Lett*, 2012, **12**, 5431-5435.
680. I. Narkeviciute, P. Chakthranont, A. J. Mackus, C. Hahn, B. A. Pinaud, S. F. Bent and T. F. Jaramillo, *Nano Lett*, 2016, **16**, 7565-7572.

681. H. Hajibabaei, D. J. Little, A. Pandey, D. Wang, Z. Mi and T. W. Hamann, *ACS Appl Mater Interfaces*, 2019, **11**, 15457-15466.
682. A. Kargar, K. Sun, Y. Jing, C. Choi, H. Jeong, G. Y. Jung, S. Jin and D. Wang, *ACS Nano*, 2013, **7**, 9407-9415.
683. Z. Li, C. Yao, F. Wang, Z. Cai and X. Wang, *Nanotechnology*, 2014, **25**, 504005.
684. W. Ren, H. Zhang, D. Kong, B. Liu, Y. Yang and C. Cheng, *Phys Chem Chem Phys*, 2014, **16**, 22953-22957.
685. Q. Nie, L. Yang, C. Cao, Y. Zeng, G. Wang, C. Wang and S. Lin, *Chemical Engineering Journal*, 2017, **325**, 151-159.
686. Z. Wang, X. Li, H. Ling, C. K. Tan, L. P. Yeo, A. C. Grimsdale and A. I. Y. Tok, *Small*, 2018, **14**, e1800395.
687. X. Chai, H. Zhang, Q. Pan, J. Bian, Z. Chen and C. Cheng, *Applied Surface Science*, 2019, **470**, 668-676.
688. N. Nasori, T. Dai, X. Jia, A. Rubiyanto, D. Cao, S. Qu, Z. Wang, Z. Wang and Y. Lei, *Journal of Semiconductors*, 2019, **40**, 052701.
689. Y. Fu, C.-L. Dong, W. Zhou, Y.-R. Lu, Y.-C. Huang, Y. Liu, P. Guo, L. Zhao, W.-C. Chou and S. Shen, *Applied Catalysis B: Environmental*, 2020, **260**, 118206.
690. W. Hu, N. D. Quang, S. Majumder, E. Park, D. Kim, H.-S. Choi and H. S. Chang, *Journal of Alloys and Compounds*, 2020, **819**, 153349.
691. K. R. Nandanapalli, D. Mudusu, J. S. Yu and S. Lee, *J Colloid Interface Sci*, 2020, **558**, 9-20.
692. C. Cheng, H. Zhang, W. Ren, W. Dong and Y. Sun, *Nano Energy*, 2013, **2**, 779-786.
693. K. Yuan, Q. Cao, X. Li, H.-Y. Chen, Y. Deng, Y.-Y. Wang, W. Luo, H.-L. Lu and D. W. Zhang, *Nano Energy*, 2017, **41**, 543-551.
694. H.-P. Ma, J.-H. Yang, J.-J. Tao, K.-P. Yuan, P.-H. Cheng, W. Huang, J.-C. Wang, Q.-X. Guo, H.-L. Lu and D. W. Zhang, *Nano Energy*, 2019, **66**, 104089.
695. X. Yang, C. Du, R. Liu, J. Xie and D. Wang, *Journal of Catalysis*, 2013, **304**, 86-91.
696. K. M. Young and T. W. Hamann, *Chem Commun*, 2014, **50**, 8727-8730.
697. S. Oh, S. Jung, Y. H. Lee, J. T. Song, T. H. Kim, D. K. Nandi, S.-H. Kim and J. Oh, *ACS Catalysis*, 2018, **8**, 9755-9764.
698. C.-C. Wang, P.-H. Chou, Y.-H. Yu and C.-C. Kei, *Electrochimica Acta*, 2018, **284**, 211-219.
699. J. Zhao, T. M. Gill and X. Zheng, *Nano Research*, 2018, **11**, 3499-3508.
700. S. A. Lee, T. H. Lee, C. Kim, M.-J. Choi, H. Park, S. Choi, J. Lee, J. Oh, S. Y. Kim and H. W. Jang, *ACS Catalysis*, 2019, **10**, 420-429.
701. J. Yang, J. K. Cooper, F. M. Toma, K. A. Walczak, M. Favaro, J. W. Beeman, L. H. Hess, C. Wang, C. Zhu, S. Gul, J. Yano, C. Kisielowski, A. Schwartzberg and I. D. Sharp, *Nat Mater*, 2017, **16**, 335-341.
702. J. Qiu, G. Zeng, P. Pavaskar, Z. Li and S. B. Cronin, *Phys Chem Chem Phys*, 2014, **16**, 3115-3121.
703. H. Wang, W. Zhu, B. Chong and K. Qin, *International Journal of Hydrogen Energy*, 2014, **39**, 90-99.
704. X. Yang, R. Liu, C. Du, P. Dai, Z. Zheng and D. Wang, *ACS Appl Mater Interfaces*, 2014, **6**, 12005-12011.
705. G. Yun, G. Y. Song, B.-E. Ahn, S.-K. Lee, J. Heo, K.-S. Ahn and S. H. Kang, *Applied Surface Science*, 2016, **366**, 561-566.
706. J. Yan, S. Wu, X. Zhai, X. Gao and X. Li, *Journal of Power Sources*, 2017, **342**, 460-466.
707. P. J. Reed, H. Mehrabi, Z. G. Schichtl and R. H. Coridan, *ACS Appl Mater Interfaces*, 2018, **10**, 43691-43698.
708. L. Meng, W. Tian, F. Wu, F. Cao and L. Li, *Journal of Materials Science & Technology*, 2019, **35**, 1740-1746.
709. Z. Wang, X. Li, C. K. Tan, C. Qian, A. C. Grimsdale and A. I. Y. Tok, *Applied Surface Science*, 2019, **470**, 800-806.

710. S. Choi, J. Hwang, T. H. Lee, H.-H. Kim, S.-P. Hong, C. Kim, M.-J. Choi, H. K. Park, S. S. M. Bhat, J. M. Suh, J. Lee, K. S. Choi, S.-H. Hong, J. C. Shin and H. W. Jang, *Chemical Engineering Journal*, 2020, **392**, 123688.
711. Y. J. Hwang, C. Hahn, B. Liu and P. Yang, *ACS Nano*, 2012, **6**, 5060-5069.
712. A. Paracchino, N. Mathews, T. Hisatomi, M. Stefik, S. D. Tilley and M. Grätzel, *Energy & Environmental Science*, 2012, **5**, 8673.
713. L. Kavan, L. Steier and M. Grätzel, *The Journal of Physical Chemistry C*, 2016, **121**, 342-350.
714. S. W. Shin, M. P. Suryawanshi, H. K. Hong, G. Yun, D. Lim, J. Heo, S. H. Kang and J. H. Kim, *Electrochimica Acta*, 2016, **219**, 470-481.
715. M. Zeng, X. Peng, J. Liao, G. Wang, Y. Li, J. Li, Y. Qin, J. Wilson, A. Song and S. Lin, *Phys Chem Chem Phys*, 2016, **18**, 17404-17413.
716. M. Forster, R. J. Potter, Y. Yang, Y. Li and A. J. Cowan, *ChemPhotoChem*, 2018, **2**, 183-189.
717. F. Haydous, W. Si, V. A. Guzenko, F. Waag, E. Pomjakushina, M. El Kazzi, L. Sévery, A. Wokaun, D. Pergolesi and T. Lippert, *The Journal of Physical Chemistry C*, 2018, **123**, 1059-1068.
718. R. Wang, X. Li, L. Wang, X. Zhao, G. Yang, A. Li, C. Wu, Q. Shen, Y. Zhou and Z. Zou, *Nanoscale*, 2018, **10**, 19621-19627.
719. J. Gao, X. Sun, Y. Wang, Y. Li, X. Li, C. Chen and J. Ni, *Applied Surface Science*, 2020, **499**, 143971.
720. M.-W. Kim, B. Joshi, E. Samuel, H. Seok, A. Aldalbahi, M. Almoqli, M. T. Swihart and S. S. Yoon, *Applied Catalysis B: Environmental*, 2020, **271**, 118928.
721. Q. Gui, Z. Xu, H. Zhang, C. Cheng, X. Zhu, M. Yin, Y. Song, L. Lu, X. Chen and D. Li, *ACS Appl Mater Interfaces*, 2014, **6**, 17053-17058.
722. L. Wang, D. Yan, D. W. Shaffer, X. Ye, B. H. Layne, J. J. Concepcion, M. Liu and C.-Y. Nam, *Chemistry of Materials*, 2018, **30**, 324-335.
723. J. M. Jarmo Maula, *Chinese Optics Letters*, 2010, **8**, 53-58.
724. P. Poodt, D. C. Cameron, E. Dickey, S. M. George, V. Kuznetsov, G. N. Parsons, F. Roozeboom, G. Sundaram and A. Vermeer, *Journal of Vacuum Science & Technology A*, 2012, **30**, 010802.
725. A. Goulas and J. R. van Ommen, *KONA Powder and Particle Journal*, 2014, **31**, 234-246.
726. D. Muñoz-Rojas, T. Maindron, A. Esteve, F. Piallat, J. C. S. Kools and J. M. Decams, *Materials Today Chemistry*, 2019, **12**, 96-120.
727. D. Muñoz-Rojas and J. MacManus-Driscoll, *Mater. Horiz.*, 2014, **1**, 314-320.
728. P. Poodt, R. Knaapen, A. Illiberi, F. Roozeboom and A. van Asten, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 2012, **30**, 01A142.
729. K. Ali, K.-H. Choi, J. Jo and Y. W. Lee, *Materials Letters*, 2014, **136**, 90-94.
730. K. Ali, K.-H. Choi and N. M. Muhammad, *Chemical Vapor Deposition*, 2014, **20**, 380-387.
731. T. Hirvikorpi, R. Laine, M. Vähä-Nissi, V. Kilpi, E. Salo, W.-M. Li, S. Lindfors, J. Vartiainen, E. Kenttä, J. Nikkola, A. Harlin and J. Kostamo, *Thin Solid Films*, 2014, **550**, 164-169.
732. P. S. Maydannik, T. O. Kääriäinen, K. Lahtinen, D. C. Cameron, M. Söderlund, P. Soininen, P. Johansson, J. Kuusipalo, L. Moro and X. Zeng, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 2014, **32**, 051603.
733. J. A. McCormick, K. P. Rice, D. F. Paul, A. W. Weimer and S. M. George, *Chemical Vapor Deposition*, 2007, **13**, 491-498.
734. K. Sharma, R. A. Hall and S. M. George, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 2015, **33**, 01A132.
735. D. J. Higgs, J. W. DuMont, K. Sharma and S. M. George, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 2018, **36**, 01A117.
736. L. F. Hakim, J. Blackson, S. M. George and A. W. Weimer, *Chemical Vapor Deposition*, 2005, **11**, 420-425.
737. L. F. Hakim, S. M. George and A. W. Weimer, *Nanotechnology*, 2005, **16**, S375-381.
738. D. M. King, J. A. Spencer, X. Liang, L. F. Hakim and A. W. Weimer, *Surface and Coatings Technology*, 2007, **201**, 9163-9171.

- 739. X. Liang, K. S. Barrett, Y. B. Jiang and A. W. Weimer, *ACS applied materials & interfaces*, 2010, **2**, 2248-2253.
- 740. D. M. King, X. Liang and A. W. Weimer, *Powder Technology*, 2012, **221**, 13-25.
- 741. C. L. Duan, X. Liu, B. Shan and R. Chen, *Rev Sci Instrum*, 2015, **86**, 075101.
- 742. S. Adhikari, S. Selvaraj and D.-H. Kim, *Advanced Materials Interfaces*, 2018, **5**, 1800581.
- 743. L. F. Hakim, J. H. Blackson and A. W. Weimer, *Chemical Engineering Science*, 2007, **62**, 6199-6211.
- 744. D. M. King, X. Liang, C. S. Carney, L. F. Hakim, P. Li and A. W. Weimer, *Advanced Functional Materials*, 2008, **18**, 607-615.
- 745. D. M. King, X. Liang, P. Li and A. W. Weimer, *Thin Solid Films*, 2008, **516**, 8517-8523.
- 746. D. M. King, X. Liang, Y. Zhou, C. S. Carney, L. F. Hakim, P. Li and A. W. Weimer, *Powder Technology*, 2008, **183**, 356-363.
- 747. D. Longrie, D. Deduytsche and C. Detavernier, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 2014, **32**, 010802.
- 748. J. R. Wank, S. M. George and A. W. Weimer, *Powder Technology*, 2004, **142**, 59-69.
- 749. J. R. Wank, S. M. George and A. W. Weimer, *J. Am. Ceram. Soc.*, 2004, **87**, 762-765.
- 750. <https://www.forgenano.com/products/morpheus/>

Biography of Each Author



Dr. Yang Zhao will join the Department of Mechanical and Materials Engineering at the University of Western Ontario as an Assistant Professor from Jan 2021. Dr. Zhao received his B.S. and M.S. degrees from Northwestern Polytechnical University (Xi'an, China) in 2011 and 2014, respectively. He obtained his Ph.D. degree under the supervisor of Prof. Xueliang (Andy) Sun from the University of Western Ontario in 2018. Then, he has his postdoc training at the University of Western Ontario with Prof. Sun and the Advanced Light Source of Lawrence Berkeley National Laboratory with Prof. Jinghua Guo in 2019-2020. His current research interests focus on atomic/molecular layer depositions, next-generation batteries, and synchrotron-based X-ray techniques.



Dr. Lei Zhang received his BS degree in Chemistry (2008) and PhD degree in Nanomaterial Chemistry (2014) from Xiamen University with Prof. Zhaoxiong Xie. He was a visiting graduate student at Georgia Institute of Technology in Prof. Younan Xia's group from 2012 to 2014. From 2015 to 2016, he worked as a Postdoc at the Collaborative Innovation Center of Chemical Science and Engineering in Tianjin University. He is currently a postdoctoral associate with Professor Xueliang Sun at the University of Western Ontario. His research interests include the design and synthesis of metal nanomaterials and single atom catalysts for fuel cells, carbon dioxide reduction, and water splitting devices.



Dr. Jian Liu is an Assistant Professor in the School of Engineering at the University of British Columbia (UBC) Okanagan campus, Canada. Dr. Liu received his Ph.D. materials science (2013) from the University of Western Ontario (Canada), and worked as a NSERC Postdoctoral Fellow at Lawrence Berkeley National Laboratory and Pacific Northwest National Laboratory prior to joining UBC in January 2017. His current research interests focus on advanced nanofabrication techniques, materials design for Li-ion batteries and beyond, and interfacial control and understanding in energy storage systems.



Dr. Khalil Amine is an Argonne Distinguished Fellow and the leader of the Advanced Battery Technology team at Argonne National Laboratory, where he is responsible for directing the research and development of advanced materials and battery systems for HEV, PHEV, EV, grid, satellite, military and medical applications. Dr. Amine is also the Deputy Director of the US/China clean energy research center and serves as a Fellow of the US National Academy of inventors and committee member of the U.S. National Research Council at US Academy of

Sciences on battery related technologies. He is an adjunct professor at Stanford University, and hold a joint appointment as Professor at the University of Chicago. Among his many awards, Dr. Amine is a 2003 recipient of Scientific America's Top Worldwide 50 Researcher Award, a 2009 recipient of the US Federal Laboratory Award for Excellence in Technology Transfer, 2013 DOE Vehicle technologies office award and is the six-time recipient of the R&D 100 Award. In addition, he was awarded the ECS battery technology and battery research award and the international battery association award. Dr. Amine holds over 207 patents and patent applications and has 632 publications with google h-index of 130. From 1998-2017, Dr. Amine was one of the most cited scientist in the world in the field of battery technology. He serves as the president of IMLB. He is also the chairmen of the international automotive lithium battery association, ECS fellow and associate editor of the journal of Nano-Energy.



Dr. Jun Lu is a chemist at Argonne National Laboratory. His research interests focus on electrochemical energy storage and conversion technology, with main focus on technology beyond Li-ion batteries. He received his bachelor's degree in chemistry physics from University of Science and Technology of China (USTC) in 2000. He completed his Ph.D. in material science from the Department of Metallurgical Engineering at University of Utah in 2009. Following a DOE-EERE postdoctoral fellow under Vehicles Technology Program, he joined the Division of Chemical Sciences and Engineering at Argonne National Laboratory as chemist in 2015.



Prof. Xueliang (Andy) Sun is a Canada Research Chair in Development of Nanomaterials for Clean Energy, Fellow of the Royal Society of Canada and Canadian Academy of Engineering and Full Professor at the University of Western Ontario, Canada. Dr. Sun received his Ph.D. in materials chemistry in 1999 from the University of Manchester, UK, which he followed up by working as a postdoctoral fellow at the University of British Columbia, Canada and as a Research Associate at L'Institut National de la Recherche Scientifique (INRS), Canada. His current research interests are focused on advanced materials for electrochemical energy storage and conversion, including solid-state batteries, solid-state electrolytes, Li-S batteries, metal-air batteries, single atom catalysts and low temperature fuel cells.