Final Scientific/Technical Report

On-Demand Designing of Cathode Internal Surface Architecture for Dramatic Enhancement of SOFC Performance and Durability

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Abstract

This project is aimed to design and modify the internal surfaces of porous composite cathode from currently commercially viable Solid Oxide Fuel Cells (SOFCs), using additive manufacturing process of Atomic Layer Deposition (ALD). The material systems being investigated are commercial composite electrodes complex three-dimensional topographies. In term of the chemistry of the ALD layer applied on the internal surface of the porous cathode, this project has employed commercially relevant electrolyte, electrocatalyst and noble metal materials set. Such materials are fully compatible with the commercial fuel cells, and this project has developed special nanostructure on the surface of the commercial composite cathodes. The formation of the designed nanoarchitecture on the surface of SOFC cathode has been achieved through precise control of ALD parameters and their effect on overall cell performance and resultant electrochemical reaction mechanism of cathodes has been investigated through full cell electrochemical performance testing and nanostructure characterization by transmission electron microscopy (TEM). Under the support of this award, following has been achieved: (1). For cathode materials in solid oxide fuel cells (SOFCs), such as perovskite mixed conductor $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-x}$ (LSCF), cation surface segregation and consequently losing conductivity and active sites for the oxygen reduction reaction (ORR) are problematic. To mitigate the cation segregation and enhance SOFC durability, further decorating the internal backbone surface using the desired electrocatalysts could be a promoting approach. Commonly, the cation segregation such as Sr is very volatile, so the effective surface decoration is ideally conformal. Nevertheless, the conformal surface coating would inevitably alter the ORR pathways that initially take place on the surface of the backbone. To reveal the impact of the conformal coating on both the catalytic activity and the conductivity of the cathode, the unary electrocatalyst of Pt or CoO_x, was applied to the LSCF/SDC composite electrode of inherently functional SOFCs, respectively. Both ALD coating layers evolve strong interaction with the LSCF composite cathode. Upon operations, the Pt coating layer remains conformal on LSCF grain surfaces but turns into discrete particles on SDC grain surfaces. Meanwhile, CoO_x conformal coating grows to be the discrete nanograins on both the LSCF and SDC grains. ALD coating of the cathode alone reduces the ohmic resistance up to 28 % for the entire cells. The increased conductivity induced by the ALD coating of Pt or CoO_x is ascribed to different mechanisms. For the inherent functional SOFCs, the present study presents a novel and feasible approach to apply a conformal, dense coating layer on the surface of a mixed conductor, simultaneously increasing the conductivity and durability of the SOFC cathode.

(2). High resistance of the oxygen electrode still significantly hinders the state-of-the-art Solid Oxide Fuel Cells (SOFCs). In particular, for an oxygen electrode consisting of mixed electronic and ionic conductors, such as perovskite lanthanum strontium cobalt ferrite (LSCF), it deteriorates due to its low chemical stability of the grain surface. Such degradation is often associated with the segregation of cations. To prevent the cation surface segregation and its resultant perovskite phase decomposition, we demonstrate a conformal ultra-thin (7-10 nm) surface heterogeneous coating layer consisting of subjacent discrete nanoparticles capped with a superjacent fully dense conformal layer. The performance studies indicate the ALD coating reduces the cell series resistance by up to 40 %. The conformal layer consists of randomly orientated but single-layered nanograins, with high-density intergranular and surface grain boundaries serving as the electrochemical reaction sites and facilitating mass transport. The conformal coating layer appears to have successfully suppressed the Sr outward diffusion and confined the Sr enriched layer to a ~ 2 nm interface perovskite phase between the coating layer and the LSCF grain surface. Moreover, this ultra-thin Sr enriched perovskite layer presumably possesses high oxygen vacancy and high ionic conductivity and further imposes tensile strain to the LSCF grain surfaces. With the combination of a conformal nanoionics, Sr enriched layer, and its strained interface, the ALD coating induced surface layer is estimated to have a conductivity of ~ 1.27×10^4 S/cm, which is over two orders magnitude of that from LSCF at 750 ºC.

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2 Executive Summary

This project is aimed to design and modify the internal surfaces of porous composite cathode from currently **commercially** viable **Solid Oxide Fuel Cells** (SOFCs), using additive manufacturing process of Atomic Layer Deposition (ALD). The proposed work focuses on improving the power density and durability of commercial cells through tailoring the nanostructure of the surface of cathodes that possess complex three-dimensional topographies, using **simple one-step ALD coating**. The commercial SOFCs to be investigated through this project are with cathode composing of mixed ionic and electronic conducting $La_xSr_{1-x}Co_yFe_{1-y}O_{3-\delta}$ (LSCF) and Sm_2O_3 doped CeO_2 (SDC). The emphasis will be towards applications at temperatures of 650-800 ºC. The formation of the designed nano- architecture on the surface of SOFC LSCF/SDC cathode will be achieved through precise control of ALD parameters, and judicious selection of the ALD layer chemistry to form the engineered nano-architecture. The formation of the engineered nanoscale architecture/scaffold on the surface of LSCF/SDC cathode, their effect on overall cell performance, and resultant electrochemical reaction mechanism of cathodes will be investigated through full cell electrochemical performance testing and nanostructure characterization by TEM. Under the support of this award, following has been achieved: (1). Enhance the electrocatalytic activity and cell durability of commercial cells, through the formation of nanoscale single phase **metallic electrocatalyst Pt** on the surface of LSCF/SDC cathodes. Enhance the electrocatalytic activity and cell durability of commercial LSCF/SDC cathode through the formation of the ***Pt-free*** single phase transition metal oxide electrocatalyst of Co_3O_4. Through this project, it has been identified that there is significant interaction between the backbone phases and the ALD Pt or CoO_x layers during the electrochemical operations. Both the Pt and CoO_x went through the re-assembly after the electrochemical reaction. Although the Pt and

CoO_x undergo completely different nanostructure evolution, they share the same feature of a bimodal distribution on different grain surfaces. The re-assembly depending on the ALD layer chemistry and, most importantly, depends on the conductivity and electrochemical reaction electrical activity of the surface of the backbone grains and the related local oxygen partial pressure. When the electrochemical reactions are facial reactions, it is feasible to apply an electrocatalytic conformal layer to prevent cations out-diffusion and to mitigate the degradation related to the cation surface segregation. This study also unveils that the series resistance of the entire Cell can be dramatically reduced by applying a nanoscale thin film on the mixed conducting cathode backbone. This offers remarkable tuneability of the conductivity by further engineering the architecture from the internal surface of a porous electrode.

(2). Design a nanocomposite scaffold consisting oxide electrocatalyst of oxide and metallic electrocatalyst. The ability to manipulate the surface chemistry of the mixed conductor and suppress its degradation related to the intrinsic Sr surface segregation is critical for the SOFCs. The present work demonstrates that, for the inherent functional SOFC with a mixed conducting composite cathode, the electrocatalytic nanoionics with high-density grain boundaries could be precisely introduced onto the cathode backbone. The conformal thin-film surface nanoionics can be controlled to have the single-layered, randomly orientated nanograins to maximize the contribution of surface grain boundaries and the interface strains to the conductivity and the electrocatalytic activities. The conformal ALD layer completely shifted the ORR reduction pathways. It also serves as the effective barrier layer for backbone cations outward diffusion. Most importantly, the ALD coating turns the original perovskite surface that is vulnerable to cation segregation and degradation into an embedded strained interface phase with enormous conductivity. For the first time in the field of SOFC, our study demonstrates an effective approach for solving multiple-problems for successfully suppressing the Sr surface segregation of mixed conductors, preventing Cr contamination, and simultaneously increasing the conductivity. The high-density surface and intergranular grain boundaries of the strained ALD layer provide an enormous surface area and interface area for facilitating multiple mass transport and catalytic reactions. It opens new research directions in terms of the fundamental design of the grain boundaries and strained critical interface for electrochemical reactions at elevated temperatures.

3 Comparison of the actual accomplishment with the goals and objectives

Proposed goals and objectives: **With optimized design of the surface nanostructure, the technical achievement is cell power density for commercial operation throughout the entire SOFC** operation temperature range of 650-800ºC. On the other hand, using the versatile **on-demand design** of different nano-scaffold architectures enabled by ALD infiltration, the architecture/scaffold structures on the internal surface of with **LSCF/SDC cathode** integrates **multi-functions.** Those multi-functions include (1) Dramatically **improving the cell performance** for the commercial cells; (2) Dramatically **increasing the cell longevity** for being **stable nanostructure,** at the internal surface of porous cathode, upon high temperatures cell operation; (3) Dramatically **increasing the cell longevity** by potentially **preventing** the microstructure evolution and **grain coarsening of the cathode (4)** Dramatically **improving contamination resistance** for being an excellent protection coating layer **sealing off the Chromium contamination**. Overall, this project will provide **a simple solution** to **simultaneously** enhancing power density, and increasing reliability, robustness and endurance of commercial SOFCs, over the entire operational temperature range of 650-800 ºC.

Actual Accomplishment: In term of the chemistry of the ALD layer, this project has employed commercially relevant electrolyte, electrocatalyst and noble metal materials set. Such materials are fully compatible with the commercial fuel cells, and this project has developed special nanostructure on the surface of the commercial composite cathodes. Under the support of this award, following has been achieved:

Accomplishment -1: (1) Enhance the electrocatalytic activity and cell durability of commercial cells, through the formation of nanoscale single phase **metallic electrocatalyst Pt** on the surface of LSCF/SDC cathodes. Enhance the electrocatalytic activity and cell durability of commercial LSCF/SDC cathode through the formation of the ***Pt-free*** single phase transition metal oxide electrocatalyst of Co_3O_4. Through this project, it has been identified that there is significant interaction between the backbone phases and the ALD Pt or CoO_x layers during the electrochemical operations. Both the Pt and CoO_x went through the re-assembly after the electrochemical reaction. Although the Pt and CoO_x undergo completely different nanostructure evolution, they share the same feature of a bimodal distribution on different grain surfaces. The re-assembly depending on the ALD layer chemistry and, most importantly, depends on the conductivity and electrochemical reaction electrical activity of the surface of the backbone grains and the related local oxygen partial pressure. When the electrochemical reactions are facial reactions, it is feasible to apply an electrocatalytic conformal layer to prevent cations out-diffusion and to mitigate the degradation related to the cation surface segregation. This study also unveils that the series resistance of the entire cell can be dramatically reduced by applying a nanoscale thin film on the mixed conducting cathode backbone. This offers remarkable tuneability of the conductivity by further engineering the architecture from the internal surface of a porous electrode.

Accomplishment -2: Design a nanocomposite scaffold consisting oxide electrocatalyst of oxide and metallic electrocatalyst. The ability to manipulate the surface chemistry of the mixed conductor and suppress its degradation related to the intrinsic Sr surface segregation is critical for the SOFCs. The present work demonstrates that, for the inherent functional SOFC with a mixed conducting composite cathode, the electrocatalytic nanoionics with high-density grain boundaries could be precisely introduced onto the cathode backbone. The conformal thin-film surface nanoionics can be controlled to have the single-layered, randomly orientated nanograins to maximize the contribution of surface grain boundaries and the interface strains to the conductivity and the electrocatalytic activities.

Overall, this project demonstrated a time efficient and scalable ALD coating to improve the power density of as-fabricated commercial cells. The conformal ALD layer completely shifted the ORR reduction pathways. It also serves as the effective barrier layer for backbone cations outward diffusion. Most importantly, the ALD coating turns the original perovskite surface that is vulnerable to cation segregation and degradation into an embedded strained interface phase with enormous conductivity. For the first time in the field of SOFC, our study demonstrates an effective approach for solving multiple-problems for successfully suppressing the Sr surface segregation of mixed conductors, preventing Cr contamination, and simultaneously increasing the conductivity. The high-density surface and intergranular grain boundaries of the strained ALD layer provide an enormous surface area and interface area for facilitating multiple mass transport and catalytic reactions. It opens new research directions in terms of the fundamental design of the grain boundaries and strained critical interface for electrochemical reactions at elevated temperatures.

The approaches utilized in this project could enable increased electrical power of SOFCs at low operating temperature. The success of this project demonstrated the commercial scalability of the ALD processing with minimal impact to the cost structure of the cells and the stacks.

4 Conformal Surface Film Utterly Shifting Oxygen Reduction Reaction Pathways and Increasing Conductivity in Solid Oxide Fuel Cell

4.1 Introduction

In comparison with the solar, wind, and tidal power that is site-specific and intermittent, solid oxide fuel cells (SOFCs) offer unrivaled high efficiency and excellent fuel flexibility. However, current SOFC technology is still hindered by high production costs and insufficient durability. For utility-scale stationary power systems, the SOFCs are expected to have durability towards 40,000 h (5 years) continuous operation. The low conductivity and the sluggish electrode kinetics in SOFC cathodes are still causing significant ohmic and polarization losses over the prolonged operation at elevated temperatures. Currently, the perovskite $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-x}$ (LSCF) serves as one of the most promising cathode materials because of its high electrical and ionic conductivity at an intermediate temperature of ~ 750 ºC. [1] Unfortunately, LSCF based cathodes have been found to experience substantial long-term degradation [2,3] which is frequently associated with Sr enrichment at the LSCF surface. The insulating nature of segregated Sr species blocks the oxygen reduction reaction (ORR) active sites or passivates the entire surface of the cathode. The Sr surface segregation is also accompanied by a reduction in transition metal concentration in the perovskite phase, causing the deterioration and decomposition of the LSCF backbone. [4,5,6,7,8,9] Surface modification through solution infiltration has been extensively investigated to enhance cathode surface functionality while retaining the advantageous qualities of the cathode backbone. [10,11,12] However, the effect of the infiltration largely depends on the microstructure of the infiltrate and its interaction with the backbone. The solution infiltration often ends up with discrete particles and uncontrolled distribution of infiltrated materials. Accordingly, the impact of infiltration of discrete catalyst to suppress the Sr surface segregation is limited. In addition to the solid-state phase segregation, Sr surface segregation also leads to volatile Sr species [13, 14] such as SrO, $Sr(OH)_2$, $SrCO_3$, and their further interaction with volatile Cr evaporated from the interconnects of SOFC stacks. [15] To effectively mitigate the LSCF degradation associated with the Sr surface segregation, the surface coating layer on LSCF should be conformal over the entire internal surface of the cathode.

Because the LSCF surface provides the electrocatalytic active site for the ORR at elevated temperatures, the protective conformal coating layer needs to be both Sr-inert and electrocatalytic. Among the electrocatalyst, Pt 16 and CoOx 17 could be the appropriate candidates for forming a conformal coating layer. Catalytic Pt is immiscible with SrO with limited cation exchange with all elements in LSCF and provides a block of the Sr outward diffusion. On the other hand, CoOx may have cation exchange with Fe from LSCF. CoOx has limited diffusion of La or Sr at operating temperatures. Therefore, a CoOx topping layer could also block the Sr cation outward diffusion. However, the catalytic activity of CoOx on different cathode backbone remains controversial. CoOx is an effective ORR for LSM. 18 However, for the thin film La0.6Sr0.4CoO3-δ, performance degradation was even observed upon coating CoOx by atomic layer deposition (ALD) 19,20 and its catalytic impact on LSCF is not clear. Regardless of the catalytic activity, the as-deposited conformal coating applied to the backbone surface could interact with the backbone materials, evolve structure evolution, and lose the conformity on the backbone surfaces at elevated temperatures.

Furthermore, once a coating layer is managed to be conformal, it will inevitably shift the ORR pathways and potentially introduce additional either electrical or ionic pathways and affect the conductivity. Here we studied the ALD 21,22 coatings of conformal Pt or CoO_x layer, respectively, onto the internal surface of LSCF/SDC cathode of inherent functional cells, and explored the possibility of forming an appropriate conformal coating layer and its resultant reaction pathway changes on the backbone surface. Upon the electrochemical operation, the ALD coated cell has resulted in the reduction of both the ohmic resistance (R_s) and polarization resistance (R_p). The electrochemical and nanostructure origin of the SOFC performance enhancement was systematically investigated using the combination of electrochemical impedance spectroscopy, the corresponding impedance spectra deconvolution, and post-operation nanostructure imaging and chemistry study.

4.2 Experimental section

Commercially available, anode-supported solid oxide button cells fabricated by Materials and Systems Research, Inc. (MSRI, Salt Lake City, UT) were employed for all the experiments described in this paper. MSRI cells are composed of five layers as follows, starting from the anode: a ~700 µm thick Ni/YSZ cermet layer which supports the cell structure; a ~10 µm thick Ni/YSZ active layer; a ~10 µm thick YSZ electrolyte; a thin (2-3 µm), dense Sm_2O_3-doped CeO_2 (SDC) barrier layer, a ~10 µm thick LSCF/SDC active layer; and a 50 µm thick, pure LSCF current collecting layer. The cell active area (limited by the cathode) is 2 cm^2. The exposure area of the anode to fuel is about 3.5 cm^2.

The ALD coatings were performed in a commercial GEMStar-8 ALD reactor (Arradiance Inc). The precursors used in this study were all purchased from Strem Chemicals, Inc. The (trimethyl)methylcyclopentadienylplatinum(IV), (99 %) and the deionized water were used as Pt precursor and oxidant for depositing Pt layer; and the bis(cyclopentadienyl)cobalt (II), (min. 98 % cobaltocene) and ozone were used as Co and oxidant, respectively, for CoO_x layer growth. During the deposition, the (trimethyl)methylcyclopentadienylplatinum and bis(cyclopentadienyl)cobalt containers were maintained at 75 ºC and 90 ºC, respectively; and the reactor chamber was set at 300 ºC. Total 90 cycles were performed for each element deposition, leading to an ALD coating of ~ 7 nm Pt, or 7 nm of CoO_x, respectively. No masking or specific treatment is applied on the NiO/YSZ anode of the as-received cells before ALD processing. In practice, the thick and very dense NiO/YSZ anode prevents precursor penetration during the ALD processing, and the impact of ALD coating on the Ni/YSZ anode is negligible. No surface pretreatment was applied to the cells, and no heat-treatment was applied before or after the ALD coating either. The cell electrochemical operation was carried out directly after the ALD coating.

Three cells, including one baseline cell (cell no. 1), one with the ALD coating of Pt (Cell no. 2), and one with the ALD coating of CoO_x (Cell no. 3), were examined. All cell tests were performed on a test stand. The platinum mesh was used for anode and cathode lead connections.

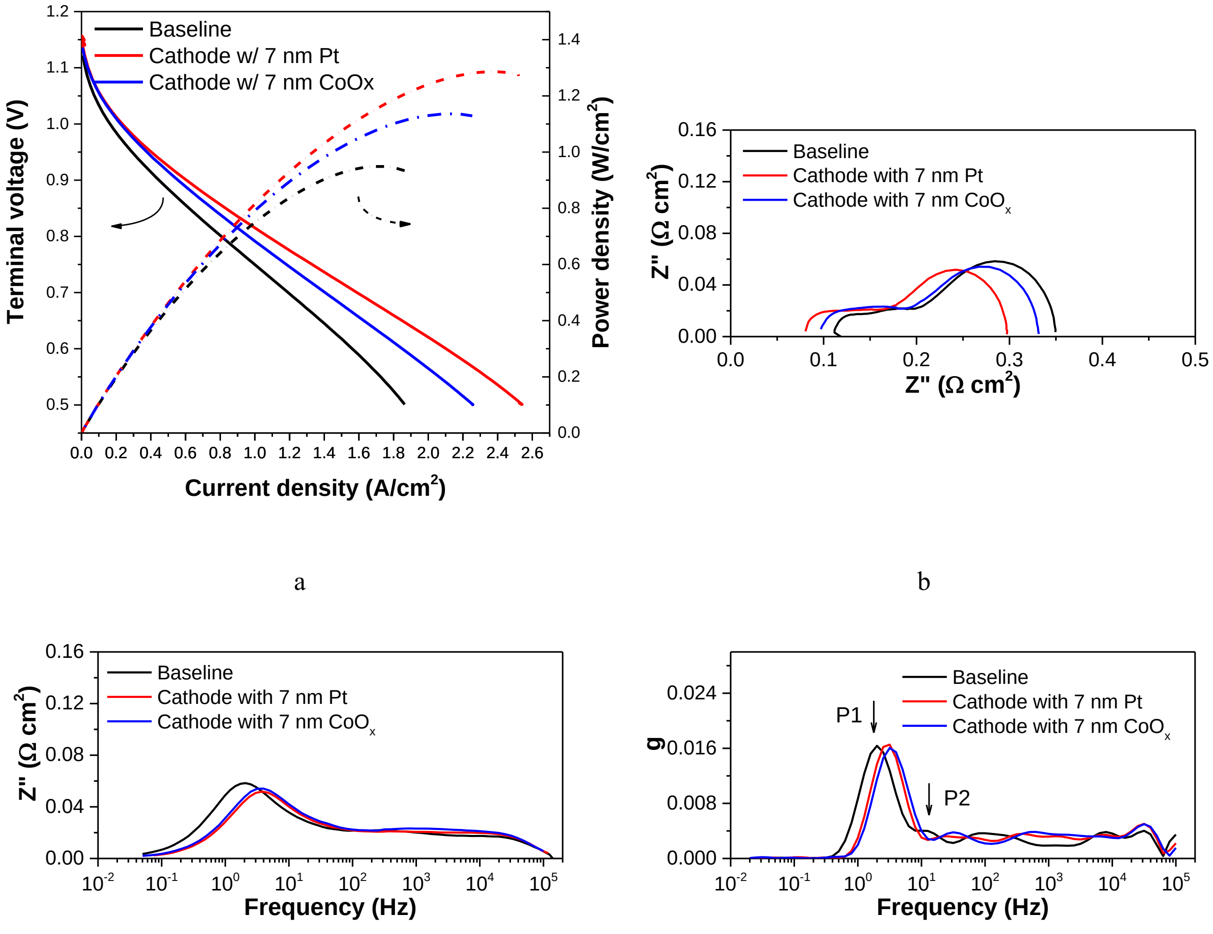
The fuel and air stream flow rates were controlled separately using mass flow controllers. Cell testing was performed at 750 °C. During the operation, a 400 mL/min air flow rate and a 400 mL/min fuel flow rate were used. Before any electrochemical measurements, both cells were current-treated for approximately ~15 h under a small current density of 0.1 A/cm^2 to ensure they were activated. The samples were loaded at a constant current of 0.3 A/cm^2 for 24 h, and then the cyclic voltammetry and impedance data were collected. The cell performance was examined using a TrueData-Load Modular Electronic DC Load, which guarantees voltage and current accuracies of 0.03 % FS of the range selected +/-0.05 % of the value. The cell impedance spectra were examined using a potentiostat/galvanostat (Solartron 1287A) equipped with a frequency response analyzer (Solartron 1260). Impedance measurements were carried out using a Solatron 1260 frequency response analyzer in a frequency range from 50 mHz to 100 KHz. The impedance spectra and resistances (R_s and R_p) presented are those measured under a DC bias current of 0.3 A/cm^2. On a Nyquist plot, R_s is determined by the intercept at the higher frequency end, and R_p is determined by the distance between two intercepts.

After the electrochemical operation, the ALD coated cells were sectioned and subjected to nanostructural and crystallographic examination using high resolution (HR) Transmission Electron Microscopy (TEM). All the TEM examinations were conducted in the cathode active layer. TEM samples were prepared by mechanical polishing and ion milling in a liquid-nitrogen-cooled holder. Electron diffraction, diffraction contrast, and HRTEM imaging were performed using a JEM-2100 operated at 200 kV. Chemical analysis was carried out under TEM using energy dispersive X-ray Spectroscopy (EDS).

4.3 Results and Discussion

4.3.1 Increased conductivity and shifted ORR pathway introduced by ALD coating of Pt

As shown in Figure 1, upon the electrochemical operation at 750 °C for 24 h, the baseline cell no. 1 possesses a peak power density of 0.949 W/cm^2, with R_s of 0.111 Ω cm^2 and R_p of 0.238 Ω cm^2. By contrast, at 24 h operation, Cell no. 2 with ALD coating of Pt on the cathode backbone shows the immediate higher peak power density of 1.286 W/cm^2, which is 136 % enhancement in comparison to that of the baseline.



a

b

c

d

Figure 1 Power density and impedance plots for the baseline cell no. 1, Cell no. 2 LSCF cathode backbone with 7 nm Pt layer, and Cell no. 3 LSCF cathode backbone with 7 nm CoO$_x$ layer. a Terminal voltage as a function of current density for the cells at 750 °C. b Nyquist plots of four cells at a constant current of 0.3 A/cm^2. c Bode plots of cells at a constant current density of 0.3 A/cm^2. d Corresponding deconvolution spectra of the impedance data collected from two cells. Two major arcs with the frequency ranging at 2-4 Hz and 20–40 Hz are indicated by P1 and P2, respectively.

Table 1 Impedance and peak power density of the baseline cell no. 1, Cell no. 2 with 7 nm Pt layer, and Cell no. 3 with 7 nm CoO$_x$.

Cell no.	**Operating time**	**Cathode architecture**	**Rs**	**Rp**	**Peak Power density**

	h		Ω cm2	Ω cm2	W/cm2
1	24	Baseline	0.111	0.238	0.949
2	24	With 7 nm Pt	0.080	0.217	1.286
3	24	With 7 nm CoOx	0.094	0.238	1.136

The power density increase is accompanied by the simultaneous reduction of R_s to 0.080 Ω cm^2 by 28 %, and R_p to 0.217 Ω cm^2 by 8.8 %, as shown in Table 1. The enhanced conductivity in the electrode can be seen by the decrease in R_s in the Nyquist plot. To identify the physical origin of polarization resistance changes, we retrieved the dynamic constant in the impedance data by evaluating the relaxation times and relaxation amplitude of the impedance-related processes using deconvolution [23,24,25,26] (shown in Figure 1d). The cells exhibit two arcs P1 and P2, with the frequency ranging at 2-4 Hz and 20-40 Hz, respectively, and the P1 is dominating. The P1 of ALD coated cell shifts to the higher frequency end compared to that of the baseline. In general, the physical processes occurring at the characteristic frequencies of 1-150 Hz range could be assigned to cathode activation polarization ORR. Depending on the cell backbone chemistry, the peaks could shift slightly to either direction under the identical cell operation conditions. [27] Since the baseline and ALD coated cells possess similar anode structures and operated under identical conditions, the slightly decreased P1 arc at 2-4 Hz is attributable to a decrease of gas diffusion and higher ORR resistance in the cathode.

The increased conductivity and change in the polarization resistance reveals that the ORR kinetics have been significantly altered in Cell no. 2. The ORR and oxygen ion transport kinetics are largely affected by the nanostructure and chemistry of active electrode surfaces where the reactant gas species meet and the electrode processes happen. The nanostructure and chemistry of the ALD coated Cell no. 2 are thus subjected to the TEM imaging and analysis.

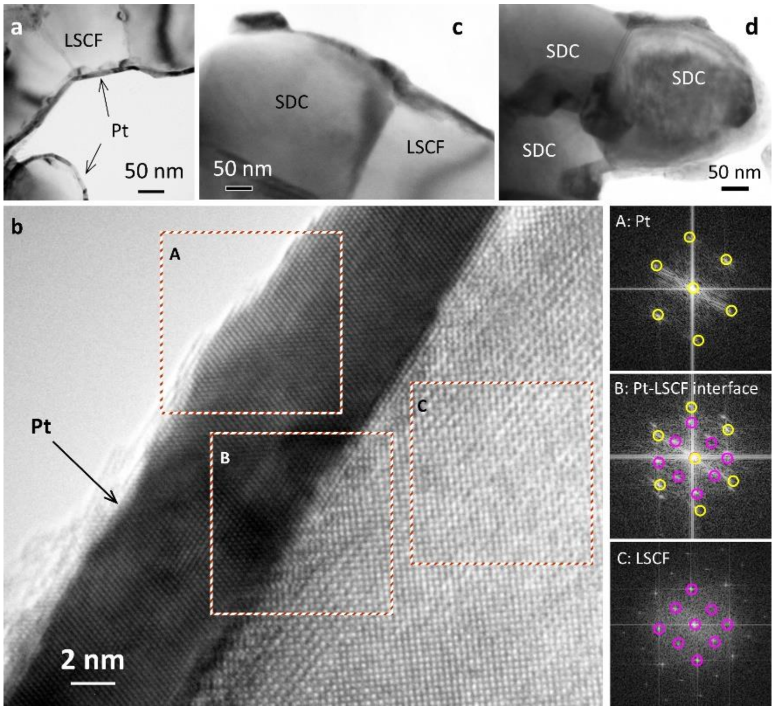


Figure 2 TEM examination of the operated Cell no. 2 with 7 nm Pt coating. a Conformal fully dense Pt film covering the LSCF backbone. b High-resolution TEM image and the related Fourier transformation showing the Pt layer is epitaxial with LSCF grain. The LSCF/Pt interface is highly strained due to the lattice mismatch. c Pt extended from the LSCF grain to the SDC grain surface. d Pt accumulated at the SDC surface grain boundaries.

As shown in Figure 2, Pt remains ~ 7 nm thick conformal coating layer after cell operation and covers the entire LSCF phase. Pt presents the indifference deposition between the LSCF grains and grain boundaries. The Pt layer keeps well defined atomic-scale binding with the LSCF grains. Moreover, there is a well-defined crystal orientation relationship between the LSCF and Pt phases in the local interface region, as shown in the Fourier Transformation. Therefore, due to the large lattice parameter difference, the interface from the well-epitaxial film is highly strained.

At the LSCF/SDC surface interfaces, the conformal coating layer extends to the SDC grains for ~100 nm. Pt phase becomes discrete further away from the LSCF/SDC surface interface. And the Pt discrete particles grew to ~ 70 nm in size on the SDC surface grain boundaries. According to the nanostructure analysis, the distribution of Pt in Cell no. 2 is schematized in Figure 3.

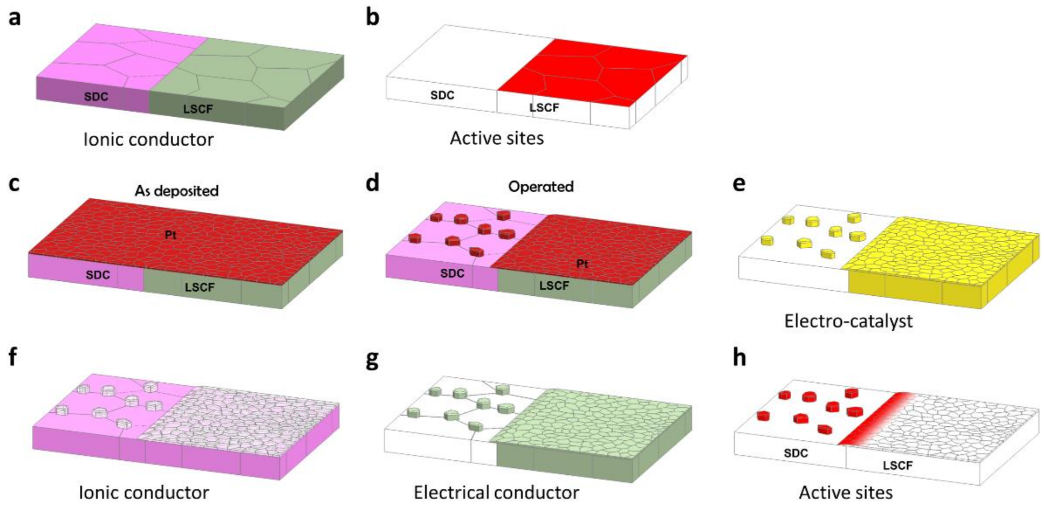


Figure 3 Schematic of the surface architecture of the baseline cell no. 1 and Cell no. 2 LSCF cathode backbone with 7 nm Pt layer. (a) Baseline LSCF phase and SDC phase and their phase boundary (interface). (b) Active ORR sites for baseline cell no. 1. (c) cell no. 2 cathode backbone with as-deposited conformal Pt layer. (d) Distribution of Pt surface layer after the electrochemical operation at 750 ºC. (e) Distribution of electrocatalyst after the operation. (f) Distribution of ionic conductor after the operation. (g) Distribution of electrical conductor after the operation. (h) Expected cathode active ORR sites for Cell no. 2.

There is no cation exchange between Pt and LSCF/SDC backbone. However, the bimodal nanostructure distribution of Pt indicates that the as-deposited conformal Pt layer must have undergone a self re-assembly procedure and developed strong interaction with LSCF/SDC backbone during the electrochemical reactions. According to the Pt-O_x phase diagram, the as-deposited ALD nano Pt could be vaporized as Pt-O gas species in the air at elevated temperatures. However, Pt-O_x is readily reduced during the ORR and re-assembled preferentially at the electrochemically active sites, where the oxygen partial pressure is the lowest on the cathode internal surface. [28,29,30,31] In an LSCF/SDC cathode, the oxygen adsorption and dissociation reactions take place on the LSCF surface. Subsequently, reduced oxide ions transport to the vicinity of the ionic conductor through either surface or bulk diffusion pathways. This creates a reduced atmosphere on the LSCF local surface upon the electrochemical reactions. Therefore, once the Pt is coated on LSCF, Pt remains as a dense conformal layer on the LSCF grain surfaces.

As shown in Figure 3d, the LSCF phase and Pt phase formed an atomic bonding interface.

The LSCF backbone surface seems to lose its activity for the ORR since it is entirely covered by the dense conformal Pt layer. Correspondingly, the cathode ORR sites and the related mass and charge transfer are entirely altered. The oxygen adsorption, dissociation, and the ORR take place on the Pt surfaces instead. When the Pt surface is enriched with negative oxygen ions, the dissociated oxygen ion could go through the Pt surface diffusion, through the "spillover" mechanisms, to the LSCF/SDC interface since the Pt has very low intragranular oxygen ion permeability. 32 This is consistent with Figure 2, showing the conformal Pt layer is stable across the LSCF/SDC interface and extends ~100 nm onto the SDC surface, which is the electrochemically active region that can be extended through polarization.

Interestingly, there is an accumulation of the Pt on the SDC surface grain boundaries, as shown in Figure 2c. In general, the SDC is an excellent ionic conductor with negligible electrical conductivity in the air. Since the Pt is deposited solely on the electrochemical reaction sites with reduced local atmosphere, the distribution of Pt grains reveals that the SDC/SDC surface grain boundaries are the active sites for the oxygen reduction reaction and SDC/SDC surface grain boundaries are carrying the sufficient electrical conductivity. Furthermore, it is well-known that the SDC is a mixed conductor under a reducing atmosphere due to the mixed-valence state of Ce^{4+} changes to Ce^{3+}. 33 The electrical conductivity along the SDC surface grain boundaries is expected to be further enhanced due to the deposition of the Pt and subsequent further oxygen reduction reactions taking place at the SDC surface grain boundaries. 34 In other words, for the SDC surface that is originally not active for electrochemical reactions, the existence of catalytic nano-Pt on the SDC surface enabled the formation of the electrochemically active sites over the entire surface of SDC for enhanced electrochemical reactions and reduced polarization resistance.

R_s of the ALD coated cell is also decreased. At elevated temperatures, Pt shows much higher electrical conductivity (~2.7×10^6 S/m for Pt at 750 ºC, extrapolated data) 35 and negligible ionic conductivity compared to LSCF. The reduced R_s could be attributed to the additional faster electrical pathway from the Pt layer. Meanwhile, it is worth pointing out that the Pt and LSCF have atomic-scale bonding, and the LSCF grains are significantly strained due to the large lattice mismatch between the LSCF and Pt, as shown in Figure 3. Since the Pt is with a lattice parameter of 3.912 Å and smaller than LSCF lattice parameter of ~3.925 Å, there is a compressive strain imposed on LSCF grain surface. Such compressive strain would decrease the local ionic conductivity of LSCF surface layer and offset the conductivity increased by the Pt layer. [36,37] For the LSCF/SDC coated with Pt, all reaction steps other than the transport of oxide ions in the mixed ionic and electrical conducting electrodes are facile. Once the conformal layer itself carriers higher conductivity, even if it is very thin such as ~ 7 nm, it would substantially lower the R_s of the cathode and, consequently, the entire Cell. This is very different from the impact of discrete nano-particles introduced by solution-based infiltration. To the best of our knowledge, all the effective solution-based infiltrations for the cathode only result in the reduction of the polarization resistance, not the series resistance. For the LSCF/SDC mixed conducting cathode backbone, our result of the conformal coating of Pt unveils that R_s of the entire Cell can also be significantly reduced by applying a nanoscale thin film on the mixed conducting cathode backbone. This conclusion offers remarkable tuneability of the conductivity by further engineering the internal surface of inherent functional SOFC.

Overall, the Pt coating has introduced two distinct ORR pathways on the LSCF grain surfaces and SDC grain surfaces, respectively, as shown in Figure 3. On the SDC grains, there are active sites along the SDC surface grain boundaries. On the LSCF backbone, the ORR sites are lifted from the original LSCF surfaces to the Pt surfaces. However, due to the low oxygen ion permeability in Pt and the conformality of Pt, the active sites on the LSCF backbone are limited to the LSCF/SDC interface region. Lower oxygen partial pressure of the LSCF grains could stabilize the Pt to a metallic state, ensuring the long-term stability of the LSCF without the Sr surface segregation. So, covering the LSCF with a conformal ALD layer appears feasible to prevent the Sr surface segregation and effectively increase the power density.

4.3.2 Strained Interface for Accelerated ionic conductivity introduced by ALD coating of

CoOx

The different Pt interaction with LSCF than that of the SDC is presumably due to their different conductivity, especially the locally different surface properties and different local oxygen partial pressure on the grain surfaces. Such impact of the catalytic and conductivity of the backbone surface on the nanostructure evolution of the ALD thin film is further manifested by the ALD coating of a CoO_x layer on the Cell with identical LSCF/SDC cathode.

Cell no. 3 with a 7 nm CoO_x layer shows the immediate higher peak power density of 1.136 W/cm^2, which is a 20 % enhancement compared to that of the baseline cell no. 1. The power density increase is accompanied by the reduction of R_s to 0.094 Ω cm^2 by ~18 %, while the R_p of 0.238 Ω cm^2 remains unchanged to the baseline cell.

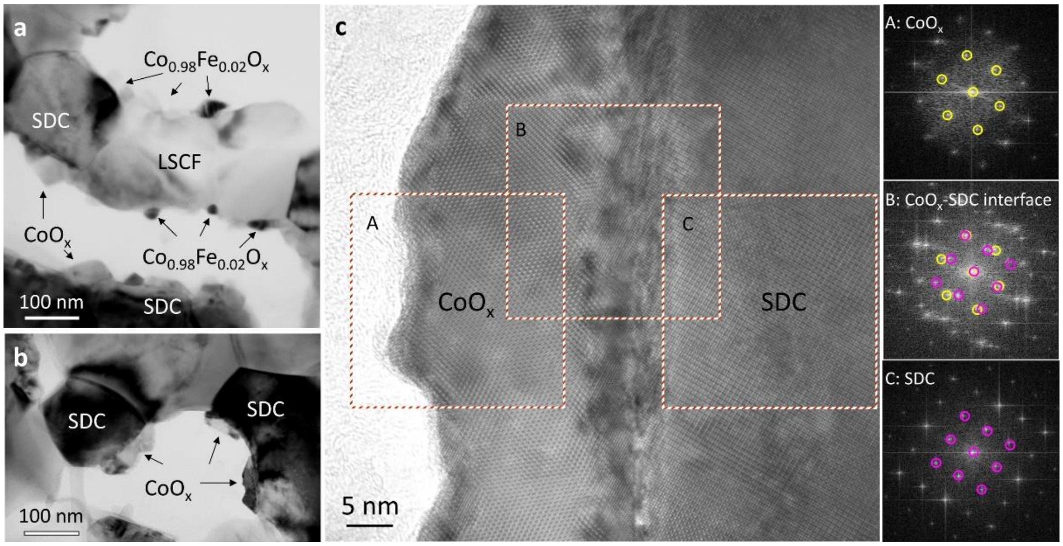


Figure 4 TEM examination of the operated Cell no. 3 with 7 nm CoOx coating. (a) CoOx interacts with LSCF, discrete (Co0.98Fe0.02)Ox, pinned on LSCF. (b) CoOx discrete nanograins on the surface of mixed conductor SDC. (c) High-resolution TEM image and the related Fourier transformation show that the CoOx layer is epitaxial with SDC grain, and the CoOx/SDC interface is highly strained due to the lattice mismatch.

The as-deposited CoO_x layer is polycrystalline with a grain size of ~ 10 nm, and the layer thickness is ~ 7 nm over the backbone surface. 38 The CoO_x coating layer interacts strongly with the backbone upon the operation and experiences different morphology evolution depending on backbone phases. After the operation, the CoO_x layer grew into discrete nano-particles with smaller

~20 nm CoO_x grains on the LSCF surfaces (in Figure 4 a) but much larger ~100 nm CoO_x islands on the SDC surfaces (in Figure 4 b). Specifically, the CoO_x on the LSCF surface is high density and is close to the neighboring grains. EDS examination indicates the CoO_x grains on the LSCF surface is doped with Fe of ~ 2 %.

The nanostructure evolution of the CoO_x layer and the resultant electrical and ionic pathway changes on the LSCF/SDC backbone are schematized in Figure 5. The ALD coated cell remained the same polarization resistance as that of the baseline, and this is because the CoO_x possesses inferior catalytic activity than LSCF. When the discrete CoO_x is covering the LSCF grain surface, it reduces the catalytic activity of LSCF. Meanwhile, there is no solubility of Co inside the SDC grains. When the CoO_x sits on the mixed conducting SDC grain boundaries, the SDC surface conductivity could be further enhanced during the oxygen reduction reactions due to the change of Ce^{4+} to Ce^{3+}. The SDC surface decorated with CoO_x becomes the active site for oxygen reduction reaction and compensates for the increase of the polarization resistance on the LSCF grain surface. Overall, the ALD coated cell depicts the comparable polarization resistance in comparison with that of the baseline.

On the other hand, R_s of the CoO_x coated Cell is decreased by 18 %. Such a reduction is smaller than that of Cell no. 2 with Pt coating. Considering the discrete nature of the CoO_x phase on both the LSCF/SDC grains, such a reduction of R_s is impressive. On the LSCF surface, the CoO_x grains is with a minimal amount of Fe, implying cation exchange between deposited Co and Fe from LSCF may occur. For the perovskite LSCF, Co ions on the Co/Fe sites have smaller binding energy for oxygen than that with Fe ions. Increasing the Co content in LSCF could increase the electrical conductivity of the LSCF backbone. [1] Simultaneously, the deposited CoO_x layer on the SDC surface developed into the larger CoO_x grains. The discrete CoO_x grains exhibit a well-defined crystal orientation relationship with the underneath SDC phase, as shown in the Fourier Transformation in Figure 4 c.

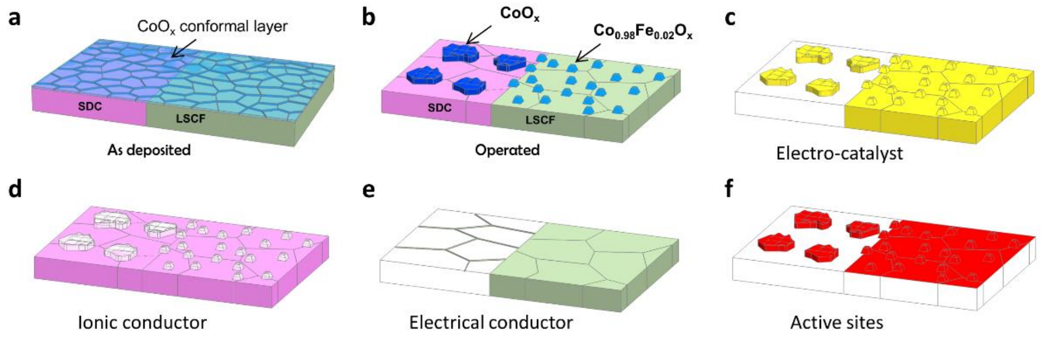


Figure 5 Schematic of the surface architecture of Cell no. 3 LSCF cathode backbone with 7 nm CoO_x layer. (a) Cell no. 3 cathode backbone with as-deposited conformal CoO_x layer. (b) Distribution of surface discrete CoO_x particles after the electrochemical operation at 750 ºC. (c) Distribution of electrocatalyst after the operation. (d) Distribution of ionic conductor after the operation. (g) Distribution of electrical conductor after the operation. (h) Expected cathode active ORR sites for Cell no. 3.

Due to the large lattice parameter difference, the interface from the well-epitaxial CoO_x grains is highly strained. The strained interface between the SDC and CoO_x might also provide fast ionic conducting pathways and increased electrocatalytic activity. 39 However, the CoO_x on SDC grain surface is discrete. So the effectiveness of the increased conductivity due to CoO_x coating on SDC could be much inferior to that of Pt coating. R_s is expected to be further lowered if the CoO_x can be managed to be a continuous layer.

4.4 Summary

There is significant interaction between the backbone phases and the ALD Pt or CoO_x layers during the electrochemical operations. Both the Pt and CoO_x surface layers went through the re-assembly during the electrode reaction. Although the Pt and CoO_x undergo completely different nanostructure evolution, they share the same feature of a bimodal distribution on different-phase surfaces. The surface layer re-assembly depends on the ALD layer chemistry, the electrochemical activity of the LSCF/SDC backbone surface, and the related local oxygen partial pressure. For the ORR taking place on the LSCF/SDC electrode surface, it is feasible to apply an electrocatalytic conformal layer to prevent cations out-diffusion and mitigate the cation surface segregation. This study also unveils that the series resistance of the entire Cell can be reduced by applying a nanoscale thin film on the mixed conducting cathode backbone. This offers remarkable tuneability of the conductivity by further engineering the architecture from the internal surface of a porous electrode.

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6 Technical effectiveness & economic feasibility of ALD processing developed through this project

Solid oxide fuel cells offers high energy conversion efficiency, minimize emissions compared to combustion-based electrical power generation methods, and features excellent fuel flexibility. The cells are modular and scalable. SOFCs are with broad applicability including stationary power supply fueled by natural gas for residential use and portable power supplies in transportation applications. There are three primary segments of the market: stationary applications, transportation applications, and portable applications. The global solid oxide fuel cell market was estimated at approximately $175 million in 2017 and is expected to increase significantly to an estimated $1.4 billion by 2025. [86]

Growth in the market is expected to be driven by increased awareness about alternative energy applications, the global energy crisis. Most importantly, growth in the market is expected to be driven by the increased market competitiveness of SOFC technology in term of the cell power density, cell longevity, and cell/stack fabrication and maintenance cost.

6.1 State-of-the-art solution based cathode infiltration and its technical barrier

One of the most reliable and efficient ways to further improve the performance of the SOFC cathodes is to modify the surface of the state-of-the-art cathodes to achieve enhancement in activity and stability. Electrode fabrication and modification by infiltration 87[88,89,90,91] of active components into a porous scaffold can achieve outstanding electrochemical performance. Over the past several years, solution-based infiltration processes have been developed for deposition of both discontinuous (discrete particle) and continuous (dense) coatings of catalysts into the state-of-the-art $La_{1-x}Sr_xMnO_3$ (LSM) and $La_xSr_{1-x}Co_yFe_{1-y}O_3$ (LSCF) cathodes, to enhance the surface electrocatalytic activity and stability 92, 93. Although solution based infiltration of electrode/catalyst materials into a cathode scaffold may allow the use of a wide range of catalyst materials, several concerns need to be carefully considered. (1) Introducing the nanoscale electrocatalyst has been very challenging for the SOFCs because of the difficulty of penetration into the active layer, which is ~50 microns below the current collecting layer. In addition, sufficiently thick coatings must be introduced to ensure low sheet resistance for efficient current collection, which is more important for larger cells or cell stacks. The need for large amounts of catalysts adds cost with respect to both fabrication with repeated infiltration steps and materials. (2) The degradation associated with the coarsening and sintering of nano-sized catalyst particles is potentially acute. Coarsening of the nanoparticles over the high temperature operation and loss of surface area and surface activity are problematic. (3) Due to the above, manufacturing scale-up of cathode infiltration is challenging, particularly in developing a low cost process with simple processing requirement that remains versatile enough to accept many form features in materials.

6.2 Uniqueness of ALD and its technical challenge for SOFC applications

Uniqueness of ALD processing on SOFCs: ALD is a **chemical vapor deposition** technique that sequentially applied atomic monolayers to a substrate, typically alternating compounds to produce a locally balanced atomic distribution of the target material. [94] ALD is uniquely suitable for depositing uniform and conformal films on complex three-dimensional topographies with high aspect ratio. The indifference of ALD to substrate shape makes it particularly promising for applications to SOFCs, which presses porous active structure with complex three-dimensional topographies, and with electrode performance strictly depending on the surface properties. ALD processing is large batch and features easy scale-up and simplified handling precursors. Such capacity of ALD processing permits the simultaneous processing of hundreds of SOFCs.[95]

Technical challenges: Although ALD possesses significant promise as SOFC processing techniques, insufficient research has been completed to assure success in commercial applications. Recent work was reported for ALD coated symmetric cells[96,97] and some showed that the ALD coating symmetrical cells was detrimental to the cathode performance. [98, 99] Similar to conventional cathode infiltration, judicious selection of the ALD coating layer chemistry and crystal structure is critical achievement of the high cell performance. Several ALD coated material has been demonstrated detrimental for the cell performance, including SrO, CeO_2 and Al_2O_3.

6.3 Technical effectiveness & economic feasibility of ALD developed through this project

Determination efficacious materials and structures for application to commercial cells is imperative to support commercial cell modifications using ALD. The results from this project have shown that significantly enhanced performance can be acheieved by ALD infiltration of commercial cathodes. The ability to manipulate the surface chemistry of the mixed conductor and suppress its degradation related to the intrinsic Sr surface segregation is critical for the SOFCs. The present work demonstrates that, for the inherent functional SOFC with a mixed conducting composite cathode, the electrocatalytic nanoionics with high-density grain boundaries could be precisely introduced onto the cathode backbone. The conformal thin-film surface nanoionics can be controlled to have the single-layered, randomly orientated nanograins to maximize the contribution of surface grain boundaries and the interface strains to the conductivity and the electrocatalytic activities.

Overall, this project demonstrated a time efficient and scalable ALD coating to improve the power density of as-fabricated commercial cells. The conformal ALD layer completely shifted the ORR reduction pathways. It also serves as the effective barrier layer for backbone cations outward diffusion. Most importantly, the ALD coating turns the original perovskite surface that is vulnerable to cation segregation and degradation into an embedded strained interface phase with enormous conductivity. For the first time in the field of SOFC, our study demonstrates an effective approach for solving multiple-problems for successfully suppressing the Sr surface segregation of mixed conductors, preventing Cr contamination, and simultaneously increasing the conductivity. The high-density surface and intergranular grain boundaries of the strained ALD layer provide an enormous surface area and interface area for facilitating multiple mass transport and catalytic reactions. It opens new research directions in terms of the fundamental design of the grain boundaries and strained critical interface for electrochemical reactions at elevated temperatures.

The ALD processing developed through this project features the following (1) Simple and straightforward one step processing and time efficient. (2). Highly repeatable and controllable manufacturing processing. (3). Cost-effective. The surface architecture/scaffold possesses engineered nanostructure but features commonly used electrocatalyst materials. The developed surface layer possesses a minimum thickness of 10-20 nm and is solely designed to maximize the TPB density. The fabrication methods offer precise structural control for maximum power density with minimum materials consumption. The ALD processing developed through this project thus bears immediate breakthrough on the SOFC technology since the applied ALD processing is scalable to both the single cells and SOFC stacks. Overall, the success of this project demonstrated the commercial scalability of the ALD processing with minimal impact to the cost structure of the cells and the stacks.

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7 Project conclusion

This project is aimed to design and modify the internal surfaces of porous composite cathode from currently **commercially** viable **Solid Oxide Fuel Cells** (SOFCs), using additive manufacturing process of Atomic Layer Deposition (ALD). The proposed work focuses on improving the power density and durability of commercial cells through tailoring the nanostructure of the surface of cathodes that possess complex three-dimensional topographies, using **simple one-step ALD coating**. The commercial SOFCs to be investigated through this project are with cathode composing of mixed ionic and electronic conducting $La_xSr_{1-x}Co_yFe_{1-y}O_3$ (LSCF) and Sm_2O_3 doped CeO_2 (SDC). The emphasis will be on applications at temperatures of 650-800ºC.

Actual Accomplishment: In terms of the chemistry of the ALD layer, this project has employed commercially relevant electrolyte, electrocatalyst and noble metal materials set. Such materials are fully compatible with the commercial fuel cells, and this project has developed a special nanostructure on the surface of the commercial composite cathodes. Under the support of this award, the following has been achieved:

Accomplishment -1: (1). Enhance the electrocatalytic activity and cell durability of commercial cells through the formation of nanoscale single-phase **metallic electrocatalyst Pt** on the surface of LSCF/SDC cathodes. Enhance the electrocatalytic activity and cell durability of commercial LSCF/SDC cathode through the formation of the ***Pt-free*** single phase transition metal oxide electrocatalyst of Co_3O_4. Through this project, it has been identified that there is significant interaction between the backbone phases and the ALD Pt or CoO_x layers during the electrochemical operations. Both the Pt and CoO_x went through the re-assembly after the electrochemical reaction. Although the Pt and CoO_x undergo completely different nanostructure evolution, they share the same feature of a bimodal distribution on different grain surfaces. The re-assembly depending on the ALD layer chemistry and, most importantly, depends on the conductivity and electrochemical reaction electrical activity of the surface of the backbone grains and the related local oxygen partial pressure. When the electrochemical reactions are facial reactions, it is feasible to apply an electrocatalytic conformal layer to prevent cations out-diffusion and to mitigate the degradation related to the cation surface segregation. This study also unveils that the series resistance of the entire Cell can be dramatically reduced by applying a nanoscale thin film on the mixed conducting cathode backbone. This offers remarkable tuneability of the conductivity by further engineering the architecture from the internal surface of a porous electrode.

Accomplishment -2: Design a nanocomposite scaffold consisting oxide electrocatalyst. The ability to manipulate the surface chemistry of the mixed conductor and suppress its degradation related to the intrinsic Sr surface segregation is critical for the SOFCs. The present work demonstrates that, for the inherent functional SOFC with a mixed conducting composite cathode, the electrocatalytic nanoionics with high-density grain boundaries could be precisely introduced onto the cathode backbone. The conformal thin-film surface nanoionics can be controlled to have the single-layered, randomly orientated nanograins to maximize the contribution of surface grain boundaries and the interface strains to the conductivity and the electrocatalytic activities.

Overall, this project demonstrated a time-efficient and scalable ALD coating to improve the power density of as-fabricated commercial cells. The conformal ALD layer completely shifted the ORR reduction pathways. It also serves as the effective barrier layer for backbone cations outward diffusion. Most importantly, the ALD coating turns the original perovskite surface that is vulnerable to cation segregation and degradation into an embedded strained interface phase with enormous conductivity. For the first time in the field of SOFC, our study demonstrates an effective approach for solving multiple-problems for successfully suppressing the Sr surface segregation of mixed conductors, preventing Cr contamination, and simultaneously increasing the conductivity. The high-density surface and intergranular grain boundaries of the strained ALD layer provide an enormous surface area and interface area for facilitating multiple mass transport and catalytic reactions. It opens new research directions in terms of the fundamental design of the grain boundaries and strained critical interface for electrochemical reactions at elevated temperatures.

The approaches utilized in this project could enable increased electrical power of SOFCs at low operating temperatures. The success of this project demonstrated the commercial scalability of the ALD processing with minimal impact to the cost structure of the cells and the stacks.

The ALD processing developed through this project features the following (1) Simple and straightforward one-step processing and time-efficient. (2). Highly repeatable and controllable manufacturing processing. (3). Cost-effective. The surface architecture/scaffold possesses engineered nanostructure but features commonly used electrocatalyst materials. The developed surface layer possesses a minimum thickness of 10-20 nm and is solely designed to maximize the TPB density. The fabrication methods offer precise structural control for maximum power density with minimum materials consumption. The ALD processing developed through this project thus bears immediate breakthrough on the SOFC technology since the applied ALD processing is scalable to both the single cells and SOFC stacks. It also bears immediate breakthrough on the SOFC technology since the applied ALD processing is scalable to both the single cells and SOFC stacks. Overall, the success of this project demonstrated the commercial scalability of the ALD processing with minimal impact to the cost structure of the cells and the stacks.

<u>This project demonstrated that</u> **with the optimized design of the surface nanostructure, the technical achievement is cell power density for commercial operation throughout the entire SOFC operation temperature range of 650-800ºC. On the other hand, using** the versatile <u>on-demand design</u> of different nano-scaffold architectures enabled by ALD infiltration, the architecture/scaffold structures on the internal surface of with <u>LSCF/SDC cathode</u> integrates multi-functions. Those multi-functions include (1). Dramatically improving the cell performance for the commercial cells; (2). Dramatically increasing the cell longevity for being stable nanostructure, at the internal surface of porous cathode, upon high temperatures cell operation; (3). Dramatically increasing the cell longevity by potentially preventing the microstructure evolution and grain

coarsening of the cathode (4). Dramatically improving contamination resistance for being an excellent protection coating layer sealing off the Chromium contamination. **Overall, t**his project will provide a simple solution to simultaneously enhancing power density and increasing reliability, robustness, and endurance of commercial SOFCs, over the entire operating temperature range of 650-800ºC.

In addition to SOFCs, the novel on-demand design approach and creation of multifunctional heterogeneous architecture on the electrode surface presented in this work opens further research for their application in other types of fuel cells, batteries, and sensors for which electrochemical reactions on the surface are similarly critical.