Transition Metal Oxides Nanomaterials for Aqueous Electrochemical Energy Storage

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Abstract: A key technical challenge for capacitive energy storage devices to rival the performance of lithium-ion batteries is to improve their energy density (E), which is proportional to the capacity (C) and square of potential window (V) as following equation shows: $E = ½ C V^2$. Therefore, the primary objective of this project is to develop the electrode materials with high capacity and/or wide potential window. Through this research support, the PI has been working on two major groups of metal oxides materials to tackle this challenge.

(i) The first group of materials are the manganese oxide-based nanoparticles (e.g., Mn_5O_8) having a kinetically stable potential window. Through hydroxylated interphase formed on the surface evidenced by synchrotron-based soft X-ray absorption analysis, such materials show high overpotential towards gas evolution reaction and enable a kinetically stable potential window (2.5 V in half cell and 3.0 V in full cell) for aqueous electrochemical energy storage, beyond the thermodynamically stable potential window (1.23 V). Besides the technological breakthrough, we have provided the fundamental understanding of this superior system by employing synchrotron-based soft X-ray spectroscopy, neutron scattering, electron microscope and density functional theory (DFT) calculations, as well as other hard X-ray and electrochemical tests. Our spectroscopic data reveals a well ordered ice-like surface hydroxyl layer that were only proposed in theory before. The unprecedented high voltage (3.0 V) and high-rate performance have been attributed to (i) high overpotential (> 0.6 V) of Mn_5O_8 towards HER and OER through interplay between Mn^{2+} terminated surface and this special hydroxylated interphase; (ii) the unique bivalence ($Mn^{2+}{}_2Mn^{4+}{}_3O_8$) structure that enables two-electron charge transfer via Mn^{2+}/Mn^{4+} redox couple; and (iii) facile pathway for Na-ion transport via intra-/inter-layer defects of Mn_5O_8.

(ii) The second group of the materials are the vanadium oxide-based (e.g., V_2O_5) disordered layered nanostructures having larger storage capacity. Through the engagement of structural water evidenced by neutron total scattering, such materials have exhibited a high capacity of towards K-ion storage in an aqueous electrolyte. we have implemented a complementary characterization package entailing performance measurement in device level, *in situ* synchrotron X-ray diffraction, and X-ray/neutron total scattering (pair distribution analyses), from which the roles of the structural water on the stability and performance of disordered V_2O_5 layered materials have been studied. We discovered that the hydration (intercalation of structural water) primarily causes structural rearrangements of the $[VO_6]$ octahedra that make up the V-O bilayers of the highly disordered V_2O_5 nanosheets. The disordered V_2O_5 nanosheets engaged with structural water exhibit superior high capacity and excellent stability for K-ion storage in an aqueous electrolyte. To our knowledge, this is one of the most stable and high capacity electrode materials ever reported for an aqueous K-ion storage. We believe our results will trigger more fundamental studies of the effects of structural water on stability and electrochemical performance of the disordered electrode materials.

1. Program Scope

There is an essential priority of developing large-scale stationary electrochemical energy storage (EES) systems efficiently and economically storing energy generated from renewable sources (e.g., solar or wind) in order to withstand the gaps between the peak production and peak consumption. Rechargeable non-aqueous lithium-ion batteries (LIBs) have advanced rapidly in the past twenty years with much improved energy density, widely used from portable electronics to electrical vehicle. However, high cost and safety concerns make the current LIBs less appealing for large-scale stationary EES, where the cost, safety, and cycle life become important in addition to mere energy density. Rechargeable EES devices using aqueous electrolytes and earth abundant cations (e.g., Na and K) as the charge carrier show several advantages compared with non-aqueous LIBs. For example, using non-flammable and environmentally benign water-based electrolytes not only mitigates the safety issue of non-aqueous LIBs, but also significantly lowers the production cost by avoiding rigorous manufacturing conditions. Moreover, compared with Li-ions, hydrated Na- or K-ions possess the smaller Stokes radius, defined as the total radius of the ion and bound water molecules, and thus greater transport properties in aqueous electrolytes. The utilization of aqueous Na-ion storage could fulfill essential requirements of large-scale stationary EES, where low cost and environmental sustainability become imperative. However, the current aqueous EES needs further improvement in the energy density in order to rival the performance of the non-aqueous LIBs. The energy density of aqueous EES is limited to its narrow voltage window and low storage capacity. To tacking these technical bottlenecks, the overall goals of the project are:

(i) Discover new aqueous EES material chemistry that enables metal oxide nanomaterials to be operated at the potential window beyond 1.23 V. Aqueous EES devices usually operate at or below 1.23 V. Beyond this thermodynamically stable potential window the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) occur. However, a voltage window of 1.23 V is too narrow to achieve high energy density and power density. The primary goal of the project is to discover a new type of materials that are not only redox active for charge storage, but also inert to HER and OER (high overpotential) thus a kinetically stable potential window higher than 1.23 V can be achieved.

(ii) Develop new metal oxide structures that reversibly store alkali cations in aqueous electrolyte via various charge storage mechanisms (e.g., capacitive and diffusion-limited redox). Our approach is through the design of layered electrode materials, from which the interlayer distance can afford nearly reversible insertion/extraction of alkali without causing structural degradation.

2. Research Outcomes:

2.1 The PI has discovered the formation of the hydroxylated interphase on the surface of Mn_5O_8 materials during the electrochemical cycling, which inhibits the HER/OER and thus enables a kinetically stable potential window of 2.5 V for aqueous Na-ion storage in half-cell (**Figure 1**).[1] This is the one of the most important achievements from PI's research. Monoclinic manganese oxide (Mn_5O_8, $Mn^{2+}{}_2Mn^{4+}{}_3O_8$) nanoparticles were synthesized using a wet chemistry method and discovered that this material forms a hydroxylated interphase upon the interaction with water during the electrochemical cycling. The theoretical calculations showed that the strong interaction between Mn^{2+} layer on the surface and water might account for the formation of such a hydroxylated interphase that increased the energy barrier for the consequent water decomposition processes. The hydroxylated Mn_5O_8 greatly suppressed gas evolution reactions (> 0.6 V

overpotential towards HER and OER) and delivered a kinetically stable potential window of 2.5 V in a half-cell (**Figure 1a**). An aqueous symmetric full cell using such electrodes demonstrated a stable potential window of 3.0 V, and good energy and power performance. The results offer a new paradigm for developing electrode materials with hydroxylated interphase for aqueous EES with a high voltage window.

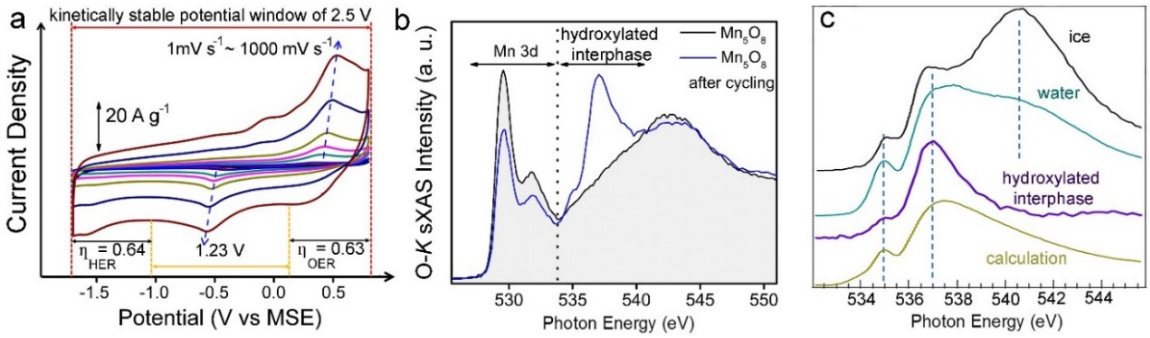

Figure 1. (a) Cyclic voltammetry (CV) of Mn_5O_8 materials in 0.1 M Na_2SO_4 solution between -1.7 to 0.8 V (vs MSE) in a half-cell. (b) Oxygen K-edge sXAS of Mn_5O_8 (pristine) and Mn_5O_8 after two CV cycles. The 535 and 537 eV peaks are fingerprints of the water. (c) A comparison of the oxygen K-edge features of the hydroxylated interphase with water, ice, and the reported calculation.

The PI conducted the oxygen K-edge soft X-ray Absorption Spectroscopy (sXAS) measurement on the pristine Mn_5O_8 and Mn_5O_8 after two cycles of CVs at beamline 8.0.1 at the Advanced Light Source (ALS) at Lawrence Berkeley National Lab (LBNL). Cycled Mn_5O_8 electrode displayed peaks at the 535 eV and 537 eV (**Figure 1b**), resembling the "pre-edge" and "main peak" fingerprints from water and indicating the formation of hydroxylated interphase on the surface of Mn_5O_8. **Figure 1c** shows the oxygen K-edge spectra after subtracting the Mn_5O_8 (pristine) signal. It is clear that the hydroxylated interphase layer is different from ice, by missing the high-energy hump from the saturated H-bonds in ice. It reproduces the "pre-peak" and "main peak" of liquid water, with the "main peak" at 537.5 eV dominating the spectrum. The enhancement of this main peak stems from a combination of an extended O-O distance and perfectly aligned H-bonds along the O-O direction.[2] DFT calculation was used to determine the activation energy of each intermediate reaction steps during the HER and OER on surfaces of hydroxylated Mn_5O_8, pure Mn_5O_8 and Mn_3O_4 (**Figure 2**). The activation energy of the rate determining step are all substantially high for OER, indicating that OER is intrinsically difficult. Particularly, activation energy of water dissociation ($H_2O^* \rightarrow H^* + OH^*$), the second catalytic step of gas evolutions, follows the order of hydroxylated Mn_5O_8 (1.41 eV) > Mn_5O_8 (0.45 eV) > Mn_3O_4 (~ 0 eV). Hydroxylated Mn_5O_8 shows about 1 eV higher in activation energy than that of Mn_5O_8, implying that the reaction rate at 300 K is at least 17 orders of magnitude slower according to the Arrhenius equation. Therefore, the DFT calculation directly confirmed the inhibitive role of the hydroxylated interphase on the HER and OER.

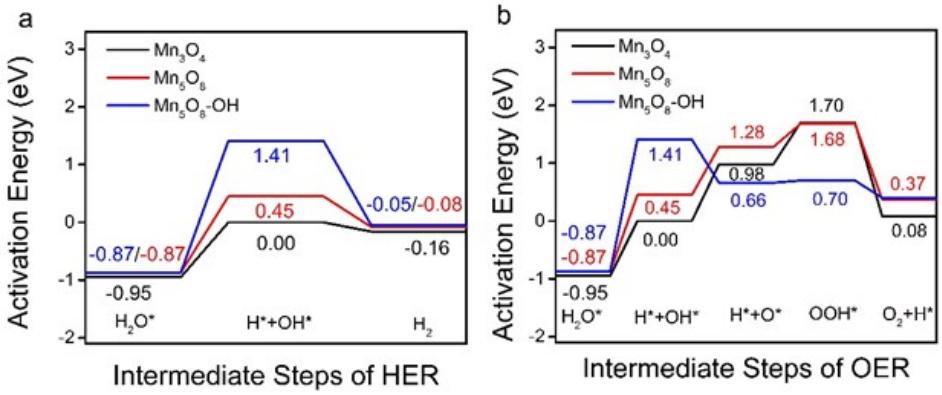

Figure 2. The activation energies of intermediate reaction steps of (a) HER and (b) OER on Mn_5O_8 with a hydroxylated interphase, Mn_5O_8 without interphase and Mn_3O_4 (the asterisk symbol denotes the adsorbed species on the surface).

2.2 The PI has studied the influences of the structural water on the stability and electrochemical performance of the disordered V_2O_5 nanostructures using neutron total scattering collected at Spallation Neutron Source (SNS) at Oak Ridge National Lab and pair distribution function (PDF) analysis as shown in **Figure 3a**.[3] The fully hydrated V_2O_5 material showed a much larger coherence length, the rearrangement of the local structure and larger occupancy of the water intercalated between the layers, compared with partially hydrated V_2O_5. These results indicated that disordered V_2O_5 could be stabilized via a strong interaction between O (from structural water) and V atoms. V_2O_5 engaged by structural water exhibited superior capacity (0.89 electrons transfer per vanadium atom) for aqueous K-ion storage in half-cell. *In situ* X-ray diffraction was conducted to examine the evolution of (001) diffraction peak upon the three cycles of cyclic voltammetry at 17-BM-B beamline at APS at Argonne National Lab. The results demonstrated that disordered V_2O_5 layered materials engaged with structural water showed more continuous expansion/contraction of (001) diffraction planes and a wider redox-active potential window during electrochemical cycling in a Contour plot (**Figure 3b**), compared with highly crystalline materials (**Figure 3c**). These results are important for designing a new type of disordered electrode materials stabilized by structural water for aqueous energy storage with a large storage capacity.

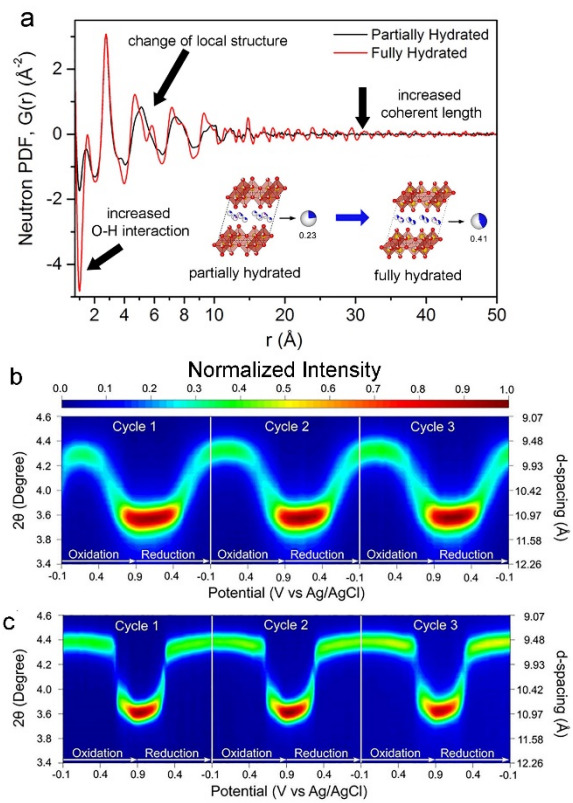

Figure 3. (a) Neutron PDFs of partially and fully hydrated disordered V_2O_5. The Contour plot of *in situ* XRD spectra of the (001) plane during CVs for (b) disordered V_2O_5 and (c) ordered V_2O_5 materials.

2.3 One of the research objectives is to understand the charge storage mechanism of transition metal oxides for aqueous EES with high storage capacity and long cycling life. By rational design of electrode materials with desired morphologies, sizes, compositions, storage capacity of electrode materials could be improved by enhancing both capacitive (including electrical double layer capacitance [EDLC] and pseudocapacitance) and diffusion-limited redox processes, while still sustained a plausible rate-performance. The PI developed a surfactant-free wet chemistry method to synthesize various metal oxide nanostructures.[4-7] Using this scalable method, the PI developed synthetic capability to prepare the multi-phase electrode materials with different morphologies. More importantly, with proper control of reaction conditions and post-synthesis thermal treatment, the local structures of the nanomaterials (e.g., cation/anion defect, disorder, bonding) can also been tuned. The PI reported the preparation of bi-phase Co-Mn-O nanostructures comprised of layered $MnO_2 \cdot H_2O$ birnessite and tetragonal $Co_xMn_{3-x}O_4$ spinel [$(Co_{0.83}Mn_{0.13}Va_{0.04})_{tetra}(Co_{0.38}Mn_{1.62})_{octa}O_{3.72}$; tetra: tetrahedral sites; octa: octahedral sites; Va: vacant site].[8] The layered MnO_2 phase significantly improved the capacitive charge storage process of Na-ions, while the Co-Mn-O spinel phase with predominant disorder in cation sites caused by cobalt insertion facilitated both storage capacity and ionic transport of Na-ion (**Figure 4**). Synergistic effect from layered and spinel bi-phase lead to the superior specific storage capacity for Na-ions (121 mAh g^{-1} in half-cell) and rate performance (81 mAh/g after 5000 cycles at 2 A/g in full-cell).

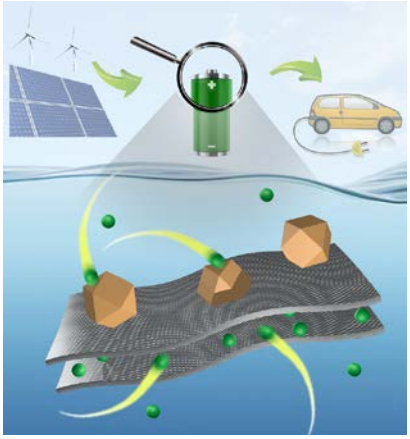

Figure 4. Bi-phase cobalt manganese oxide electrode materials comprised of layered MnO2 birnessite phase and $Co_{1.21}Mn_{1.75}O_{3.72}$ spinel phase

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8. Shan, X.; Charles, D. S.; Xu, W.; Feygenson, M.; Su, D.; Teng, X. W., Bi-phase Cobalt-Manganese Oxide with High Capacity and Rate Performance for Aqueous Sodium-ion Electrochemical Energy Storage. *Advanced Functional Materials* **2017**, 1703266.

Publications

(i) A list of papers and book chapters published in which DOE support is acknowledged

1). Shan, X., Charles, D.S., Xu, W., Feygenson, M., Su, D., Teng, X.W. *Bi-phase Cobalt-Manganese Oxide with High Capacity and Rate Performance for Aqueous Sodium-ion Electrochemical Energy Storage*. **Advanced Functional Materials**, 2017, 1703266, DOI: 10.1002/adfm.201703266

2). (Invited Contribution) Shan, X., Guo, F., Xu, W., Teng, X.W., *High purity Mn_5O_8 nanoparticles with a high overpotential to gas evolution reactions for high voltage aqueous sodium-ion electrochemical storage*. **Frontiers in Energy**, 2017, DOI: 10.1007/s11708-017-0485-3

3). Charles, D.S., Feygenson, M., Page, K., Neuefeind,J., Teng, X.W. *Structural Water Engaged Disordered Vanadium Oxide Nanosheets for High Capacity Aqueous K-ion Storage*. **Nature Communications** 2017, 7, 15520

4). Shan, X., Charles, D.S., Lei, Y., Qiao, R., Wang, G., Yang, W., Feygenson, M., Su, D., Xu, W., Teng, X.W. *Bivalence Mn_5O_8 with hydroxylated interphase for high-voltage aqueous sodium-ion storage*. **Nature Communications** 2016, 7, 13370

5). (Book Chapter) Guo, F., Gupta, N., Teng, X.W. *Enhancing pseudocapacitive process for energy storage devices: analyzing the charge transport using electro-kinetic study and numerical modelling*, Chapter in "**Supercapacitors - Theoretical and Practical Solutions**", Intech, New York, (2017) Editor: Lionginas Liudvinavičius

6). (Book Chapter) Charles, D. S., Teng, X.W.; *Vanadium Pentoxide Electrode for Aqueous Energy Storage: Understand Ionic Transport using Electrochemical, X-ray and Neutron Tools*, **Chapter** in "*Alkali-ion Batteries*", Intech, 2016, SBN 978-953-51-2395-8

7). (Book Chapter) Teng, X.W., Charles, D. S., Shan, X.Q., Wu, Y. T., "*In Situ Studies of Charge-Storage Mechanism of Manganese Oxide Nanomaterials for Electrochemical Capacitors*", Page 1-32. In book "*Supercapacitors: Electrochemical Properties, Applications and Technologies*", Nova, 2014, ISBN: 978-1-63321-019-6

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(ii) A list of Patents filed in which DOE support is acknowledged

1) Teng, X.W., Shan, X., *Sodium-Rich Manganese Hydrate with Capacity for Aqueous Na-ion Electrochemical Energy Storage*, **U.S. Provisional Patent**, Application Number: 62/587,060 (2017)

2) Teng, X.W., Charles, D.S., *Preparation of Intercalative Metal Oxide/Conductive Polymer Composites as Electrode Materials for Rechargeable Batteries*, **U.S. Provisional Patent**, Application Number: 62/585,031, (2017)

3) Teng, X.W. *Manganese Oxide Compositions and their Use as Electrodes for Aqueous Phase Energy Storage Devices*, **U.S. Non-Provisional Patent**, Application Number: 14/737,823 (2016)