Emerging Materials
Room 104-106 - Session EM2-WeM

Battery and Energy Storage II

Moderators: Parag Banerjee, Washington University, St. Louis, Neil P. Dasgupta, University of Michigan

10:45am **EM2-WeM-12 Atomically-Precise Interfacial Engineering of Energy Conversion and Storage Materials by ALD*, Neil P. Dasgupta,*** University of Michigan **INVITED**

There has been a dramatic increase in research of nanoscale materials for energy conversion and storage devices due to several advantageous features such as high surface areas, short transport distances, and tunable material properties. However, with these benefits come challenges. In particular, the ability to precisely control the properties of surfaces and heterogeneous interfaces limits the performance of many of these devices, and requires novel approaches. Additionally, the ability to manufacture materials with precise control of heterogeneous features in three dimensions and at length scales spanning from atoms to meters is challenging, requiring complementary processing techniques. To bridge this gap requires novel approaches to design material systems across these length scales, allowing us to fabricate hierarchical structures with deterministic control of geometric and chemical properties.

To address this challenge, the Dasgupta Research Group at University of Michigan focuses on the atomically-precise modification of surfacesandinterfaces to control material assembly and transport phenomena across physical and chemical boundaries. Examples include surface passivation against undesirable reactions at electrode-electrolyte interfaces in batteries, integration of co-catalysts on semiconductor surfaces for solar-to-fuel conversion, and charge transport layers in photovoltaics. The key enabling technology that is used for surface modification is Atomic Layer Deposition (ALD). This atomic-scale modification of surfaces allows for precise control of interactions at heterogeneous interfaces, which can be used to direct self-assembly processes, provide tunability of the optical, electronic, thermal, and mass transport properties of integrated material systems, and encapsulate structures to promote their stability in a wide range of environments. In this talk, I will demonstrate examples of the ALD process for modification of electrode-electrolyte interfaces with an emphasis on “beyond Li-ion” batteries and solar-to-fuel conversion, and provide a perspective on how this versatile approach can lead to the design and manufacturing of hierarchical material systems with “designer” interfaces and interphases.

11:15am **EM2-WeM-14 Minimizing Polysulfide Shuttle Effect in Lithium-Ion Sulfur Batteries by Anode Surface Passivation via Atomic Layer Deposition*, Jian Liu,*** The University of British Columbia, Canada*; D Lu, J Zheng, P Yang,* Pacific Northwest National Laboratory*; B Wang, X Sun,* University of Western Ontario, Canada*; Y Shao, C Wang, J Zhang, J Liu,* Pacific Northwest National Laboratory

Lithium-sulfur (Li-S) batteries have grained increasing attentions as competitive power supply system for electric vehicles, due to their high energy density and low cost of sulfur [1,2]. During the past few years, encouraging progresses have been made to develop novel cathode structure to address the polysulfide shuttle effect and poor conductivity of sulfur. However, the problems associated with Li metal, such as Li dendrite and polysulfide corrosion, remain unresolved. To circumvent the problem, one promising route is to pair a non-Li anode with the sulfur cathode to develop Li-ion sulfur batteries [3,4]. Nevertheless, polysulfide shuttle reactions still occur when using non-Li anodes, leading to limited cycling life and low CE in Li-ion sulfur batteries.

In this work, we developed a surface passivation strategy to minimize polysulfide shuttle effect on those alternative anodes, in order to enable high-performance practical Li-ion sulfur batteries. We used an ultra-thin electron-insulating layer (Al_2O_3), deposited by atomic layer deposition (ALD), to passivate the surface of the non-Li anodes (graphite as an example), with the aim of blocking the electron transfer pathway and alleviating polysulfide shuttle (Figure 1). We found that with the optimal thickness of 2 nm Al_2O_3 coated on graphite anode, the Coulombic efficiency of the sulfur cathode was improved from 84% to 96% in the first cycle, and from 94% to 97% in the subsequent cycles (Figure 2). As a result, the discharge capacity of the sulfur cathode was increased to 550 mAh g^{-1} in the 100th cycle, as compared with 440 mAh g^{-1} when the pristine graphite anode was used. Mechanism study disclosed that the Al_2O_3 passivation layer minimized the formation of insoluble polysulfide (Li_2S_2, Li_2S) on the surface of graphite anode and improved the efficiency and capacity retention of the graphite-sulfur batteries. It is expected that this surface passivation strategy could be also applied to other sulfur based battery systems (with Li, Si, and Sn anodes), to reduce side reactions and enable high-performance sulfur batteries.

References

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11:30am **EM2-WeM-15 A Facial Way to Prepare Large Areal 3D Porous Carbon via Molecular Layer Deposition and its Application for Lithium Sulfur Batteries*, Yan-Qiang Cao,*** *W Zhang, A Li,* Nanjing University, China

Nowadays, rechargeable batteries with a high energy density and long life are needed in many applications, ranging from portable electronic devices to electric vehicles. Unfortunately, the state-of-the-art lithium ion batteries (LIBs) cannot satisfy these requirements now. Therefore, tremendous efforts are being dedicated toward developing “beyond-lithium-ion” batteries. Lithium sulfur (Li-S) batteries are one of the most promising next-generation energy storage systems with a high capacity of 1675 mAh/g and energy density of 2600 Wh/kg. However, significant issue must be overcome before Li-S batteries can be implemented, such as the highly insulating nature of sulfur and the high solubility/diffusivity of lithium polysulfides in the electrolyte. A great deal of scientific and technological innovations have been proposed to solve these problems, such as optimizing the electrolyte and fabricating composite electrodes of sulfur/polymer, sulfur/metal organic framework (MOF) or sulfur/carbon.

In this work, a novel and facial approach was proposed to synthesis the large areal three-dimensional (3-D) porous carbon. Inorganic-organic hybrid film via molecular layer deposition (MLD) was used as carbon precursor, while metal foam or metal oxide fiber was utilized as sacrifice template. Inorganic-organic hybrid films would be transformed into carbon/oxide by pyrolysis in inert atmosphere. After etching the oxide in carbon and template, 3D porous carbon of various shapes can be achieved. We can gain a large porous carbon of 10*10 cm at present. In addition, as-prepared porous carbon exhibits well flexibility.

Further, a composite cathode system for Li-S batteries was synthesized by loading sulfur onto 3D network of porous carbon via a sulfur melt infiltration method. The 3D porous carbon can offer excellent electrical conductivity, and an appropriate hierarchical pore structure containing the electro-active sulfur facilitates rapid electron/ion transport. More importantly, this cathode system does not require any additional binding agents or conductive additive. A Li-S battery with the sulfur-3D porous carbon cathode shows good electrochemical stability and high rate discharge capacity retention, which delivers a reversible capacity of about 930 mAh/g at the current density of 100 mA/g. Our results indicate the great potentials of MLD derived 3D porous carbon for high-performance batteries.

11:45am **EM2-WeM-16 Enhanced Metal-support Interaction of Ceria Supported Platinum Single Atoms and Subnanoclusters for Room Temperature CO Oxidation*, Xiao Liu,*** *Y Tang, B Shan, R Chen,* Huazhong University of Science and Technology, China

The CO poisoning effect is one of the critical problems plaguing platinum (Pt) catalyst, which can limit its activity by blockage of surface active sites and subsequent reaction steps under low temperatures.[1] Such phenomena is quite general considering that CO will be used as reactants or generated as reaction intermediates in many catalytic processes such as CO oxidation, water-gas shift reactions, and fuel cells.[2-3] In view of the high dispersion (smaller Pt nanoparticles) required for catalyst applications, CO poisoning will be only more pronounced, wherein large fraction of coordinately unsaturated edge and vertex sites over-bind CO molecules.[4] Here, we report a method to tackle the CO poisoning effect on high dispersed Pt clusters by enhancing the metal-support interaction. The Pt single atoms and subnanoclusters have been prepared on ceria (CeO_2) nanorods by optimizing the atomic layer deposition recipe and post-treatment annealing process. The copper doping at the interface of

Pt/CeO_2 has been performed to enhance the low temperature CO oxidation activity. The as-prepared copper-doped CeO_2 supported Pt subnanoclusters show excellent CO oxidation activity, which is significantly better than that of the reported subnanocluster and single atom catalysts in previous studies. The results of X-ray photoelectron spectroscopy, *in-situ* CO diffuse reflectance infrared absorption spectroscopy and density functional theory calculations show that the enhanced catalytic activity is due to the activation of lattice oxygen and the decrease of CO binding strength.

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