

SYMPOSIUM ET09

Materials for Chalcogen Electrochemistry in Energy Conversion and Storage
November 26 - November 28, 2018

Symposium Organizers

Marine Cuisinier, Qatar Environment and Energy Research Institute
Jun Lu, Argonne National Laboratory
Yuyan Shao, Pacific Northwest National Laboratory
Jiajun Wang, Harbin Institute of Technology

* Invited Paper

SESSION ET09.01: Li-S Batteries: Design and Mechanism
Session Chairs: Kisuk Kang and Hongzhang Zhang
Monday Morning, November 26, 2018
Hynes, Level 3, Room 301

8:30 AM *ET09.01.01

Designing Lithium-Sulfur Batteries with Practically Necessary Parameters Arumugam Manthiram; The University of Texas at Austin, Austin, Texas, United States.

Sulfur has become appealing as a cathode in recent years as sulfur is abundant, is environmentally benign, and exhibits an order of magnitude higher charge-storage capacity than the currently used lithium-ion battery oxide cathodes. However, lithium-sulfur cells suffer from a few formidable challenges: (i) poor electronic and ionic conductivity of sulfur and its discharge product Li_2S , (ii) dissolution in the liquid electrolyte of the polysulfide intermediates and their shuttling between the cathode and anode, (iii) large volume changes occurring during charge-discharge cycling, and (iv) lithium-metal degradation during cycling due to continuous solid-electrolyte interphase (SEI) formation and electrolyte consumption. Efforts to overcome these difficulties around the world have shown enormous improvements in cycle life, but a vast majority of the published work has been with low sulfur content, low sulfur loading, and a high amount of liquid electrolyte, which will drastically reduce the practical energy density and make the lithium-sulfur technology uncompetitive with the current lithium-ion technology.

This presentation will focus on designing lithium-sulfur cells with practically necessary parameters to be competitive with lithium-ion technology. Innovative sulfur cathode architectures and novel cell configurations will be presented to realize the practically necessary parameters. For instance, lithium-sulfur cells with a coaxial-graphene-coated cotton-carbon as a substrate for sulfur cathode that display high performance with simultaneously a high sulfur loading ($\sim 50 \text{ mg cm}^{-2}$), high sulfur content (75 wt. %), and a low electrolyte/sulfur ratio ($4.2 \mu\text{L mg}^{-1}$) will be presented. Such a cell exhibits remarkably a high areal capacity (31 mA h cm^{-2}) and areal energy density (66 mW h cm^{-2}) with a capacity-retention of 68% over 200 cycles, exceeding the areal capacity (4 mA h cm^{-2}) and areal energy density (10 mW h cm^{-2}) of commercial LiCoO_2 cathode. Besides the challenging cycle life, lithium-sulfur cells also suffer from rapid self-discharge. With novel cell configurations, self-discharge data collected over an extended period of one year will be presented. Moreover, the roles of the porosity, electrical conductivity, and chemical interaction with sulfur of various carbons used in lithium-sulfur cells will be presented, which will help to choose the appropriate carbons. Finally, the areas that need to be addressed in the future to make the lithium-ion technology practically viable will also be presented. In addition, a comparison of the lithium-sulfur technology with other metal-sulfur batteries will also be provided.

9:00 AM *ET09.01.02

Directly Observing Electrochemical Reactions of Sulfur Cathodes by Transmission Electron Microscopy Kisuk Kang and Zheng-Long Xu; Seoul National University, Seoul, Korea (the Republic of).

Taken advantage of a high theoretical energy density of 2567 Wh kg^{-1} , lithium sulfur batteries (LSBs) have been considered promising candidates for next-generation energy storage systems. Tremendous efforts have been devoted to improving the battery performance by preparing smart nanostructures. However, detailed reaction mechanisms and the principles of tailoring reaction paths at nanoscale remain unclear. In-situ transmission electron microscopy (TEM) is a powerful technique to probe the dynamic processes of electrochemical reactions at a high spatial resolution and in real-time. Through in-situ TEM study with a solid cell (using $\text{Li/Li}_2\text{O}$ as lithium source and electrolyte, respectively), we find that carbon nanofibers activated at 550°C encapsulating sulfur particles (PCNF/A550/S) present a low volume expansion of $\sim 35\%$ and integrated structure upon full lithiation. In contrast, PCNF/A750/S prepared from carbon fibers activated at 750°C shows a larger volume expansion of 61 % and overflowing of Li_2S , due to the weak mechanical property and large pores of the carbon host, providing a testament to their different electrochemical performance. Further, we develop in-situ TEM techniques with a graphene-based liquid cell (GLC), where liquid electrolyte and TiN-C/S nanoparticles are encapsulated between two graphene sheets. When exposed to the electron beam, the liquid cells undergo chemical reactions, showing that sulfur particles disappear gradually and Li_2S particles nucleates and grows at the conductive and polar TiN substrate during lithiation. An interesting inward growth of Li_2S particles is observed in the TiN-C core-shell structure, suggesting effective immobilization of polysulfides by TiN inside of hollow carbon, leading to excellent cyclic stability of TiN-C/S cathodes. Now, we are trying to establish in-situ TEM with flow liquid cells undergoing electrochemical reactions. It is believed that in-situ microscopic investigation of sulfur cathodes would not only shed new light on understanding of reaction mechanisms but also provide fundamental guidelines to design better LSBs.

9:30 AM ET09.01.03

Sulfur Interaction with Porous Carbon Marie-Vanessa Coulet, Loic Goumelen and Renaud Denoyel; CNRS-Aix Marseille Univ, Marseille, France.

Sulfur is the most puzzling element in the chalcogen family, in the liquid as well in the solid state. It is the element of the periodic table with the highest number of allotropes in the solid state [1]. At the melting point ($T_m = 115^\circ\text{C}$), the liquid is essentially composed of S_8 rings and has a low viscosity. Around 159°C , a reversible polymerization transition is observed and the chain formation leads to an increase in the viscosity of almost four orders of magnitude [2]. At 445°C , the sulfur sublimates into vapor consisting of S_n molecules ($n = 2 - 10$) in proportions depending on temperature and pressure. Within the last decade, Sulfur has been considered as a promising component of electrode material for the next generation of Li-ion batteries since it would permit to obtain high energy density rechargeable batteries [3]. However the main drawbacks remains in the poor electrochemical cycle stability of the sulfur cathode because of the insulating nature of sulfur and the formation of highly soluble lithium polysulfides leading to the so-called shuttle effect. One of the methodologies to avoid those problems consists in reducing the polysulfide dissolution using barrier materials. Among the proposed methods, confinement of the sulfur into porous carbon materials is seen as a promising technique since the pores could retain the polysulfides. Various hosts are considered ranging such as mesoporous carbon [4], microporous carbon [5] or carbon nanotubes [6]. Our objectives are to understand the interaction between sulfur and porous carbon and the influence of confinement of sulfur thermodynamic properties. The confinement is realized using commercial porous carbon structures that differ from their specific surface area and pore-size distribution. Various carbon-sulfur composites are synthesized using different impregnation temperatures in the liquid (before and after polymerization) and in the vapor states. It is shown that sulfur loading in the porous carbon hosts is related to the impregnation temperature and to the pore-size distribution. The evidence for sulfur incorporation into the pores is demonstrated owing energy measurements. Using immersion calorimetry, the interaction energy between sulfur and carbon is evaluated for both meso- and microporous carbons. These results could make it possible to propose new ways of synthesis of the Li-S batteries in order to improve their capacities.

[1] R. Stuedel, "Solid Sulfur Allotropes," *Anion Sens.*, pp. 1–79, 2003.

[2] B. Meyer, "Elemental Sulfur," *Chem. Rev.*, 76(3) pp. 367–388, 1976.

[3] X. Ji, K. T. Lee, L. F. Nazar, *Nature Materials*, 8, pp. 500–506, 2009.

[4] N. Jayaprakash, J. Shen, Surya S. Moganty, A. Corona, L.A. Archer, *Angew. Chem. Int. Ed.* 50, pp. 5904–5908, 2011.

[5] S. Zheng, Y. Chen, Y. Xu, F. Yi, Y. Zhu, Y. Liu, J. Yang, C. Wang, *ACS Nano*, 7(12) pp 10995–11003, 2013.

[6] J. Guo, Y. Xu, C. Wang, *Nano Lett.*, 11, pp. 4288–4294, 2011.

9:45 AM ET09.01.04

A High Performance Cathode Scaffold for Room Temperature Sodium-Sulfur Battery [Ajit Kumar](#)^{3, 1, 2}, Arnab Ghosh^{1, 2}, Amlan Roy¹, Manas R. Panda^{3, 1, 4}, Maria Forsyth⁵, Douglas R. MacFarlane² and Sagar Mitra¹; ¹Energy Science and Engineering, Indian Institute of Technology Bombay, Mumbai, India; ²Chemistry, Monash University, Melbourne, Victoria, Australia; ³IITB Monash Research Academy, Mumbai, India; ⁴Material Science and Engineering, Monash University, Melbourne, Victoria, Australia; ⁵Institute for Frontier Materials, Deakin University, Melbourne, Victoria, Australia.

Sodium-sulfur (Na-S) battery, introduced by Ford Motors in 1960 and later the technology marketed by NGK, Japan, is known to be a primary source of large-scale electrochemical storage options. The only setback with this particular battery technology is high operating temperature and the associated technical glitches. The room-temperature sodium-sulfur battery (RT Na-S) is anticipated to overcome such glitches by means of reduced operating temperature. However, the RT Na-S batteries are still suffering from few major challenges such as rapid capacity decay caused by the polysulfides shuttle and low active material utilization due to insulating nature of sulfur and end discharge product. Here, we prepare a free-standing cathode using manganese dioxide decorated carbon cloth (CC@MnO₂) as electronically conducting substrate as well as polysulfide reservoir and sodium polysulfide (Na₂S₆) catholyte as the active material. Without incorporating any active interlayer and expensive ion-selective membrane (such as Nafion), this free-standing cathode exhibits an initial specific capacity of 938 mA h g⁻¹ with remarkable capacity retention of 65% after 500 cycles. The as-assembled RT Na-S cell operates at an average potential of 1.82 V and delivers an initial energy density of 946 W h kg⁻¹ and 855 Wh kg⁻¹ (based on the mass of sulfur and sodium) after 50 cycles.

10:00 AM BREAK

10:30 AM *ET09.01.05

Research and Development for Lithium-Sulfur Batteries with Super High Energy Density Xianfeng Li and [Hongzhang Zhang](#); Dalian Institute of Chemical Physics, Chinese Academy of Science, Dalian, China.

The lithium/sulfur (Li/S) battery has been attracting increasing attention due to their higher theoretical specific energy density (2,600 Wh kg⁻¹). However, the practical energy density of the Li/S battery (soft package) is still low, accompanied other unsolved problems as poor cycle life, low safety as well as worse rate capability. To solve these problems, much research effort has been engaged in developing better cathode materials (carbon/sulfur), cathode structure, electrolyte and separators. By improving the performance of key materials and structure, the energy density of the Li/S battery has been improved to over 900 Wh/kg and 1000 Wh/L. For another thing, the Li/S cathode could reach over 100 cycles with capacity retention of 70% (still over 800 mAh/g (S)) with initial energy density of 300 Wh/kg. In this presentation, the design and preparation of key materials for soft package batteries will be presented. The key issues and solutions that affect the cycle life and energy density of Li/S batteries would be discussed in detail.

11:00 AM DISCUSSION TIME

11:15 AM ET09.01.07

High Areal Capacity and Power Li-S Batteries Enabled by Mass-Produced Self-Assembled Porous Carbon Nanotube Electrodes [Jian Tan](#)¹, Peng Wu² and Choongho Yu^{1, 2}; ¹Mechanical Engineering, Texas A&M University, College Station, Texas, United States; ²Materials Science & Engineering, Texas A&M University, College Station, Texas, United States.

Li-S batteries featuring high areal capacity and high current density have been developed based on functionalized free-standing carbon nanotubes (CNT). Even though Li-S batteries can potentially deliver high energy density and power, the critical problems such as high loading of sulfur, polysulfide shuttle, and lithium dendrite formation still impede practical Li-S batteries. Furthermore, the state-of-the-art high-performance Li-S batteries use nanomaterials, which requires scalable synthesis processes and manufacturing processes with binders, which further hinder the commercial application of Li-S batteries. This study reports free-standing self-assembled CNT electrodes activated by functional groups and embedded nanoparticles. The nano-structure provides polysulfide-philic surfaces in the cathode to alleviate the shuttle problem and lithiophilic surfaces in the anode to lower lithium nucleation potential. The activated CNT sponge electrode tackles most critical problems on cathode and anode of Li-S battery. The reduced interfacial resistance and charge transfer resistance at cathode and anode improved the reaction kinetics and lowered the overpotential. A binder-free CNT sponge can be manufactured with a commercially viable roll-to-roll process and directly used as electrodes. The 3D connected CNT network are flexible, ultra-light weight, highly conductive, porous and low-cost. The meso-scale structure such as porosity and tortuosity was tuned to facilitate optimal accommodation of active material as well as fast electron and mass transfer. The functionalized CNT sponge demonstrated not only performance improvement of Li-S batteries, but also provided a commercially viable solution of nanomaterials that can be utilized in energy storage and beyond.

SESSION ET09.02: Energy Conversion and Storage
Session Chairs: Seok-Jin Kim and Ju Li
Monday Afternoon, November 26, 2018
Hynes, Level 3, Room 301

1:30 PM *ET09.02.01

Advancing Li-S and Li-O₂ Batteries Through New Electrolyte and Electrode Design Linda F. Nazar, Quan Pang and Chun Xia; University of Waterloo, Waterloo, Ontario, Canada.

Li-S and Li-oxygen batteries are both promising as alternatives to conventional lithium-ion technology due to the high energy density of their theoretical redox couples. For Li-S, extended battery life times have been demonstrated, but two notable challenges still exist to realize its full potential: overcoming the undesired high electrolyte/sulphur (E/S) ratio required for the catholyte-type mechanism that governs most cell configurations, and inhibiting Li dendrite growth and its parasitic reaction with the electrolyte that results in cell degradation. In this presentation we demonstrate that by tuning the electrolyte structure, the challenges at both electrodes can be tackled simultaneously. The sulfur speciation pathway transforms from a dissolution-precipitation route to a quasi-solid-state conversion in the presence of lowered solvent activity and an extended electrolyte network structure, curtailing the need for high electrolyte volumes. With such an optimized structure, the Li plates dendrite-free and shows 20-fold reduction in parasitic reactions with Li, avoiding electrolyte consumption and greatly extending the life time of a low E/S (5 $\mu\text{l}/\text{mg}$) sulphur cell. A new advanced electrolyte/electrode design for the Li-oxygen cell will also be presented that demonstrates exceptional Coulombic efficiencies of close to 100% with good cycle life.

2:00 PM *ET09.02.02

"Solid Oxygen" Cathodes Ju Li; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

As the energy ceiling ($\sim 700\text{Wh}/\text{kg}$) of conventional transition-metal oxide (LiMO₂, M=Ni,Co,Mn) Li-intercalation cathodes has been approached, hybrid anion- and cation-redox (HAC) cathodes are being actively pursued, to compete with purely anion-redox Li-S and Li-O cathodes [Nature Energy 1 (2016) 16111] as candidates for the next-generation Li ion battery. HAC cathode is a hybrid between traditional Li-ion (purely cation redox, intercalation-type) and Li-O (purely anion redox, conversion-type) cathodes. Here we show a scalable synthesis of new HAC material with energy density 858 Wh/kg at the end of the 100th cycle at 1C, compressed density 3.5 g/cm³, with very little oxygen release by differential electrochemical mass spectrometry and almost no voltage decay.

2:30 PM ET09.02.03

Neighboring Pt Atom Sites in 2D Ultrathin FePt Nanosheets as the High Performance Oxygen Reduction Reaction Electrocatalyst Wenlong Chen¹, Wenpei Gao², Hong Zhu¹, Tao Deng¹, Xiaoqing Pan², Hong Yang³ and Jianbo Wu¹; ¹Shanghai Jiao Tong University, Shanghai, China; ²University of California, Irvine, Irvine, California, United States; ³University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

The shape and morphology structure of catalyst can largely affect their reactive selectivity and activity. Recently, single atom catalyst and two-dimensional (2D) nanostructures have attracted much interests because of their optimized electronic structures and sufficient use of atoms. Generally, single atom catalysts show an improved cost efficiency because the abundant participate and exposure of the noble elements in the reaction. However, in some catalytic processes, such as the oxygen reduction reaction (ORR) in fuel cells, its fast four-electron reaction path usually required at least two neighboring Pt atomic sites to cooperate, which cannot be realized in the traditional isolated single Pt atoms catalysts. To this regard, the low loading of a single atom hinders the wide application in some catalytic reactions which need enough active sites for reactants or intermediates. The fabrication of densely dispersed single atom catalysts with adjacent atom sites available at the same time on a 2D metallic nanostructures matrix with a high surface area paves a feasible way but is still challenging and rarely studied. Here, we combined the advantages of 2D structure and single atom to fabricate 2D ultrathin FePt nanosheets (NSs) with 6.7 wt % neighboring Pt atoms dispersion. Different from the previous reported isolated Pt single atoms materials, these neighboring Pt sites in the ultrathin wrinkled FePt NSs showed a four-electron reduction pathway, a high electrochemical active surface area of 545.54 m² g_{Pt}⁻¹, and an improved 7 times mass activity than the commercial Pt/C in the ORR. The high performance to catalyze a fast ORR derived from the sufficient use and synergistically interaction of neighboring Pt atoms dispersed in a more packed spacing and exposed on the surface of ultrathin sheets. In conclusion, this "neighboring atom catalyst" not only reserves the advantages of the traditional single atom catalysts but also can synergistically cooperate to catalyze the reaction, which needs two or more nearby sites, contributing to a four-electron pathway of the ORR, which distinguished from the traditional isolated single Pt atom catalysts that usually showed a two-electron path to produce H₂O₂. Furthermore, we also proved its outstanding CO-tolerance performance in the ORR by the experiment and computational density functional theory (DFT) calculation method.

2:45 PM ET09.02.04

Optimization of Surface Chemistry for Electrocatalysis via Anion Exchange in Nanoparticles Andrew Nelson¹, Kevin Fritz¹, Shreyas Honrao^{1,2}, Richard Hennig^{1,2}, Jin Suntivich¹ and Richard Robinson¹; ¹Materials Science and Engineering, Cornell University, Ithaca, New York, United States; ²Materials Science and Engineering, University of Florida, Gainesville, Florida, United States.

The need for inexpensive high-activity materials in electrocatalytic applications such as water splitting has driven substantial research into the surface chemistry of non-noble metal catalysts, especially metal oxides. Great progress has been achieved in optimization of oxide electroactivity by the use of mixed metal oxides, which achieve the necessary physicochemical properties via controlled substitution of cation sites. Despite the obvious importance of the anionic partner in determining the catalyst electronic and surface structure, knowledge of the effects of anionic substitution in electrocatalysis is far less certain. We show that, by controlling the relative proportions of oxide and sulfide, the activity of cobalt oxysulfide nanoparticle electrocatalysts can be substantially increased. Cobalt oxide nanoparticles undergo anion exchange in the presence of ammonium sulfide at low temperatures, allowing access to thermodynamically unstable structures by preventing phase separation of immiscible oxides and sulfides. A lightly doped CoO_xS_{0.18} prepared in this way exhibits a metastable, S-substituted CoO structure and is 2-3 times more active in the hydrogen evolution reaction than either end-member of the oxide-sulfide series. We explain this result using density functional theory calculations, which reveal that S-substitution of the CoO surface increases the bonding strength of H to the surface. This binding energy reaches an optimum value at a low doping level, consistent with our observations. These results show that mixed-anion catalysts are accessible under mild conditions and provide an important strategy for controlling the physicochemical properties of electrocatalyst surfaces.

3:00 PM BREAK

3:30 PM *ET09.02.05

Efficient Anchoring of Polysulfides Using a Metal Oxide Interlayer in Li-S Rechargeable Batteries with High Mass Loading S-Cathodes Aninda J. Bhattacharyya and Subhra Gope; Indian Institute of Science, Bengaluru, India.

Over the last decade, there has been a paradigm shift towards usage of earth abundant and cost effective electrodes in rechargeable batteries. This strategy enhances the energy density by nearly one order of magnitude. The concept of sulfur as a positive electrode material was highlighted as early as 1962 by Herbet and Ulam. Sulfur delivers a high theoretical capacity of 1672 mAh g⁻¹, nearly one order higher compared to the intercalation oxide cathodes (IOC) used in conventional Li/Na-ion batteries. The high theoretical capacity originates from the possibility of two exchangeable Li-ions/S-atom as compared to only one Li⁺ ion/formula unit of IOC. In addition to high storage, S is cheap, highly abundant and non-toxic in nature. Despite these advantages, the chemical reactions determining the mechanism and quantum of electrical energy storage in Li-S battery pose a formidable challenge mainly due to the various intermediate polysulfides formed during the reversible conversion of elemental S₈ to Li₂S. Bulk of the work related to Li-S rechargeable battery revolves around materials design strategies of a suitable carbon/(non-carbon)-host matrix targeted towards the entrapment of S and prevention of leaching out of polysulfides into the electrolyte. This strategy however, limits the extent of S-loading and depending on the host may simultaneously increase the un-utilizable mass of S in the electrode. The presentation will discuss various hosts for the sulfur cathodes for rechargeable Li-S battery. Recently, usage of interlayers between conventional S/C composite cathode and separator has been demonstrated in Li-S batteries. This interlayer, mostly carbon or doped carbon, has been used to trap the polysulfides in between the interlayer and S-cathode. Instead of carbon, we demonstrate here an alternative and novel interlayer of metal oxide nanoparticles between cathode and separator to efficiently trap and arrest the polysulfides at the S-cathode. Oxide-based compounds exhibit superior ability to hold the lower order polysulfides towards the S-cathode by bonding interactions thereby, enhancing anode protection. In the presence of metal-oxide nanoparticle interlayer, an alternative pathway for S-reduction and oxidation takes place which simultaneously lead to a phenomenal reduction in the polysulfide shuttle effect, even at extremely high loadings of sulfur (up to 15 mg cm⁻²). The inhibition of the shuttle effect is studied by probing the battery separator and interlayer ex situ (cycled at various depths of discharge and charge). The conventional Li-S cell with S/C composite cathodes and metal oxide interlayers exhibits a remarkable improvement in cyclability and rate capability *vis a vis* the cell without any interlayer. The talk will also discuss some of our explorations in to other metal-sulfur chemistries viz. Na-S and Mg-S.

3:30 PM ET09.02.06

Modification of Back-Surface Contacts to Metal Chalcogenide Active Layers Using Carrier-Selective Thionated Perylene Derivatives Curtis W. Doiron, Alexander D. Carl, Emma Travassos and Ronald L. Grimm; Worcester Polytechnic Institute, Acton, Massachusetts, United States.

Sulfur-terminated organic functional layers were attached to TiO₂ surfaces through successive reactions of substrates with 3-aminopropyl triethoxysilane (APTES), perylene tetracarboxylic dianhydride (PTCDA), and Lawesson's Reagent (LR). X-ray photoelectron spectroscopy (XPS) quantified coverages of APTES and thionated perylene species. IRRAS confirmed chemical attachment of PTCDA to the APTES surface through the formation of the imide, and thionation yields on the exposed anhydride group of PTCDA were estimated by C=S features and the presence of sulfur in the XPS. Throughout the surface modification process, UPS studies observed changes in the HOMO-LUMO levels of the organic species at the TiO₂ surface that indicate the desired electron-transfer and hole-blocking characteristics for the modified perylene surface that could ultimately yield increased solar energy conversion efficiency in a tandem junction solar cell with deposited metal chalcogenides.

3:45 PM ET09.02.07

Encapsulation of Fe⁰ in 2D Fused Aromatic Networks as an Oxygen Reduction Electrocatalyst Seok-Jin Kim¹, Javeed Mahmood¹, Changmin kim¹, Gao-Feng Han¹, Seong-Wook Kim¹, Sun-Min Jung¹, Guomin Zhu², James J. De Yoreo², Guntae Kim¹ and Jong-Beom Baek¹; ¹Energy Engineering, Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of); ²Physical Science Division, Pacific Northwest National Laboratory, Richland, Washington, United States.

For oxygen reduction reaction (ORR), nonprecious iron (Fe)-based materials, such as Fe-N-C and Fe/Fe₃C have gained considerable attention as electrocatalysts. However, the poor stability hindered their practical application because of the defective protection of unstable Fe nanoparticles. Here, a synthesis strategy of a stable iron-based electrode catalyst is introduced using a two-dimensional phenazine-based aromatic porous organic network (Aza-PON). The bifunctional Fe@Aza-PON catalyst exhibited promising electrocatalytic activity and practical performance in a hybrid Li-air battery cell. Moreover, the Fe@Aza-PON displayed void-free encapsulation of vulnerable metallic nanoparticles for improved stability and tolerance against contamination (methanol and CO poisoning). The new design and synthesis of indirect-contact catalysts is promising for various additional applications.

SESSION ET09.03: Poster Session I: Energy Conversion
Monday Afternoon, November 26, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

ET09.03.01

Dispersion of Natural Molybdenum disulfide (MoS₂) Nanosheets for the Electrocatalytic Hydrogen Evolution Reaction (HER) Michaela Arcangel and Candy C. Mercado; University of the Philippines Diliman, Quezon City, Philippines.

Alkaline electrolysis has been considered in commercial applications as a clean and efficient technology for the growing demand for hydrogen fuel in fuel cell technologies. To speed up the Hydrogen Evolution Reaction (HER), several materials including precious metals with appropriate surface properties have been considered as catalyst. Difficulty in common synthesis of catalysts through chemical means with variations in morphology and higher economics brings the need for a more scalable and cost-effective approach. Natural molybdenum disulfide (MoS₂) in the form of the crystalline Molybdenite has been extracted from mine waste tailings (Residue Impoundment Sludge) in FCF Minerals Corp, Nueva Viscaya, Philippines through Rougher-Cleaner route of Oil-Agglomeration Froth Flotation with 99.97% final recovery and final grade of 74.80% Mo from a low grade Mo source (1.052% Mo) with ultrafine particles with interference of organic matter and silicates, with SEM/EDX photomicrographs of probable fine and flaky molybdenite particles on a silicate matrix. MoS₂ nanosheets were produced from exfoliation of Rougher (1st stage flotation) and Cleaner 2 (final stage flotation) concentrates in OAF flotation through high-shear milling in common household surfactant solution and the dispersion in varying concentrations of Ethanol (EtOH). Agglomeration due to the retained oil from OAF has no significant effect on particle size distribution of PBM products (Head sample, Rougher concentrate, Cleaner 1 concentrate and Cleaner 2 concentrate) with average Cumulant diameters of 26.27±66.56 nm, 25.69±50.40 nm, 25.93±67.58 nm and 25.51±61.23 nm, respectively. Exfoliated and dispersed Rougher (50%EtOH) and Cleaner 2 (20%, 50% and 80% EtOH) products were drop-casted onto a conductive

substrate (0.025 cm² NiO films) to serve as a cathode of in an electrolytic cell with 1 M KOH as electrolyte, Pt counter electrode and sat'd Ag/AgCl as reference electrode. Voltage bias of 0.5V at 0.1V/s at a range of -0.7 to 0.3V was applied to derive the Linear Sweep Voltammograms of each cathode at 4 trials. There was a significant difference between Rougher and Cleaner 2 (50%EtOH) cathodes with the former having a wider range of performance and instability with the progression of trials that may be due to the lower grade of Mo on the sample and unwanted reactions on the cathode surface. There was a significant difference in Cleaner 2 cathodes in varying EtOH concentrations. Best electrocatalytic performance among the three was found at 50%EtOH with the lowest average onset potential of -0.341V, while 20% and 80% EtOH having -0.354 and -0.352V, respectively. The higher onset potentials were due to the summative of either ineffective dispersion or lower MoS₂ concentration. Results show that the dispersed MoS₂ from OAF flotation of fine molybdenite from mine waste tailings is a viable source of HER electrocatalyst in alkaline medium.

ET09.03.02

Solution-Processed Lead Oxide Microcrystallites and Its Application as a Photoelectrode Dharini Bhagat, Manmohansingh Waldiya and Indrajit Mukhopadhyay; Pandit Deendayal Petroleum University, Gandhinagar, India.

In the recent years, metal oxide semiconductors have found its attention in PV (Photovoltaics) world as an absorber layer beyond its common use for electron transport layer. Lead oxides, commonly used in batteries and sensors, are one of those metal oxides which have been used in photovoltaics in recent years. Lead oxides exist mainly in two polymorphic forms, litharge (tetragonal alpha phase) and massicot (orthorhombic beta phase), among which alpha phase was found to be more photoactive according to literature. Hence, different methods are employed by researchers to obtain the tetragonal alpha phase of lead oxide.

In this work, Lead oxide (PbO) was synthesized chemically at an elevated temperature from lead acetate and sodium hydroxide solution. As prepared powder was polycrystalline in nature having alpha phase tetragonal symmetry. The average crystallite size of 70nm with lattice constants a=3.97Å, b=3.97Å, and c=5.02Å was obtained from X-Ray Diffraction analysis. Direct band gap of the PbO powder was found to be 1.9 eV by Uv-visible spectral analysis. Raman analysis confirmed the presence of pure alpha phase. Photoactivity of the prepared PbO powder was studied by employing it as a photoelectrode in photoelectrochemical cell. Photocurrent density value of about 0.5mA/cm² could be achieved by photoactive microcrystallites in ferrocyanide electrolyte.

ET09.03.03

Synthesis and Determination of the Activity of Mesoporous Sulfoselenides for the Hydrogen Evolution Reaction Shaylin A. Cetegen¹, Biswanath Dutta² and Yang Wu³; ¹Chemical Engineering, University of Connecticut, Storrs, Connecticut, United States; ²Chemistry, University of Connecticut, Storrs, Connecticut, United States; ³Institute of Materials Science, University of Connecticut, Storrs, Connecticut, United States.

Electrocatalysis of water provides a scalable and sustainable means of hydrogen (H₂) production. The drive for a clean energy future inspired us to develop a stable, readily producible, and highly active catalyst that can serve as a cheaper alternative to many pyrites. To achieve this, we adopt the approach of structural tuning by different metals/non-metals that has been found to be effective in several instances. We present one such effort by partial surface selenization of mesoporous metal sulfides produced by sulfurization of cobalt, iron, and nickel UCT-synthesized metal oxides. Using a variety of analytical techniques and electrochemical measurements, we analyze the morphology and demonstrate the enhanced electrochemical activity of these mesoporous sulfoselenides under acidic media, highlighting our catalysts superiority over most existing systems.

ET09.03.04

Improving Performance of Facile Preparing Antimony Selenide Sensitized Solar Cells by Interface Modification Bowen Zhao, Xingzhao Liu and Chunyang Jia; University of Electronic Science and Technology of China, Chengdu, China.

Sb₂Se₃ has received great attention for photovoltaic cells recently due to its excellent optical property, superior stability and eco-friendly nature. Herein, an efficient Sb₂Se₃ sensitized solar cell (SSC) is prepared for the first time through a solution-based successive ionic layer adsorption and reaction (SILAR) procedure which is flexible, low-cost and easy to access. Aiming to further improve the device performance, a novel approach based on TiCl₄ treatment on mesoporous TiO₂ has been introduced, which is found to optimize the growth condition of Sb₂Se₃ nanoparticles and improve the interfacial surface state, resulting in the better band alignment and the controlled recombination losses in Sb₂Se₃ SSCs. The TiCl₄ treated devices achieve the best photoelectric conversion efficiency of 1.22%, which is much higher than that of 0.46% for the solar cells without TiCl₄ treatment.

ET09.03.05

La_{1-x}Ca_xMnO₃ as Model Catalyst System for the Oxygen Evolution Reaction Raika Oppermann, Christoph Richter, David Kröck, Viet A. Chu, Bjoern Luerßen and Juergen Janek; Institute of Physical Chemistry, Justus-Liebig-Universität Gießen, Gießen, Germany.

The catalysis of the oxygen evolution reaction (OER) represents a key challenge in (photo)electrochemical water splitting, fuel cells and metal-air batteries. In nature, the large overvoltage of the energy-intensive reaction is circumvented through a calcium-manganese complex in photosystem II¹, which draws the attention to manganese oxides as earth abundant alternatives to the state-of-the-art catalysts such as IrO₂ and RuO₂.

One main issue of binary manganese oxide catalysts is the insufficient activity in OER due to their poor electric conductivity. Ternary perovskite materials like CaMnO₃ have shown a possibility to overcome this problem. Controlled defect formation due to doping or careful post processing under varying oxygen partial pressures led to increased electrocatalytic activities in OER.^{2,3}

We have systematically investigated the perovskite system La_{1-x}Ca_xMnO₃ (LCMO) as model nonstoichiometric electrocatalyst for OER in alkaline media. Powder samples over the whole composition range have been prepared by citrate route as well as the corresponding thin films by pulsed laser deposition (PLD). By varying the lanthanum to calcium ratio we could adjust the manganese oxidation state and the nonstoichiometry from an oxygen deficient to an oxygen excess material while changing the dominant defect species from oxygen to cationic defects.

Physicochemical characterisation (XRD, XPS, SEM, Raman spectroscopy) before and after catalysis has provided close insight into the correlation between the oxidation state of manganese and the catalytic activity. Our results have shown a clear trend in activity and stability during catalysis in LCMO thin films. Part of our current work is the defect chemistry adjustment of the materials by thermal treatment leading to a better understanding of the correlation between the major defect species and the catalytic activity.

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SESSION ET09.04: Li-S Batteries: Systems
Session Chairs: Philipp Adelhelm and Donghai Wang
Tuesday Morning, November 27, 2018
Hynes, Level 3, Room 301

8:30 AM *ET09.04.01

Nanoscale Design for Lithium-Sulfur Batteries Yi Cui; Stanford University, Stanford, California, United States.

Lithium sulfur (Li-S) batteries have high theoretical specific energy for portable and stationary storage application. However, Li-S batteries have many challenging issues at the materials level. Here I will present our recent progress on: 1) Nanoscale design of host and interface for Li metal anodes; 2) Discovery of sulfur cathode phase behavior, leading to new guidance to materials design.

9:00 AM *ET09.04.02

Stable Li Anodes Enabled by Interfacial Functionalization for Li-S Batteries Donghai Wang; The Pennsylvania State University, University Park, Pennsylvania, United States.

Lithium-sulfur (Li-S) batteries are promising high-energy storage devices due to high theoretical capacities of both the sulfur cathode and lithium (Li) metal anode. Considerable efforts have been made to improve sulfur cathodes. However, the issues associated with Li anodes such as low Coulombic efficiency (CE) remain unsolved due to poor stability of solid-electrolyte interphase (SEI) associated with excessive SEI accumulation and exacerbation of Li dendrite growth, leading to poor capacity retention and short cycling life of Li-S batteries. In this talk, I will present a strategy to reinforce the SEI with desired properties including good tolerance to the Li-based material volume change and efficient surface passivation against electrolyte penetration. The strategy works via introducing multiple functional components bonded to the Li-based material surface into the SEI. The SEI reinforced shows much better stability than the SEI reinforced by electrolyte additive strategy, which is the current state-of-art and commercially used solution to SEI stability issue. The durable SEI layer can suppress dendritic Li growth, enhance Li plating/stripping CE, and in turn, enable Li-S batteries with long cycling life and good capacity retention. We also demonstrate the reinforced SEI can improve Li metal efficiency in a carbonate-based electrolyte for Li-metal oxide batteries. This study provides a promising route to address the issues associated with Li metal anodes and promote the development of high-energy rechargeable Li metal batteries.

9:30 AM ET09.04.03

Sustainable Approach Towards WS₂ and MoS₂ Films via Single-Source Precursors for Lithium-Oxygen Batteries and Photochemical Water-Splitting Veronika Brune, Tim Ludwig, Lasse Jürgensen and Sanjay Mathur; Inorganic Chemistry, University of Cologne, Cologne, Germany.

The worldwide consciousness of the low-carbon economy and sustainable energy concept greatly promote the progress of chemical power sources such as batteries and fuel cells. With the rapid development of portable electronic devices and electric vehicles, the demand for research on advanced energy-storage and conversion systems with low cost, high power density, long cycle life and high energy density has significantly increased to optimize the traditional devices. Therefore, electrocatalytic layered materials and host materials, which success the task of separators in battery application, attracted great attention. Layered two-dimensional (2D) transition metal dichalcogenides (TMDCs) materials, like tungsten or molybdenum disulfide, are receiving increased interest due to their high specific surface area and versatile electronic structure. The direct bandgap of these monolayered materials is located in the visible light or near infrared range, which also make them promising for efficient solar energy conversion, water splitting applications as well as semiconductor utilization.

In this context, a new class of chalcogenide based transition metal single-source precursors of the formula [M^{IV}(SEtN(Me)EtS)₂] were designed in this work which enable a highly efficient approach towards crystalline 2D-structured transition metal disulfides (TMDSs). To synthesize mono- or few-layered WS₂ and MoS₂, volatile single-source precursors [W(SEtN(Me)EtS)₂] and [Mo(SEtN(Me)EtS)₂] were prepared based on the reaction of the chelating pincer type (HSEt)₂NMe-ligand with the tetravalent metals tungsten and molybdenum. Chemical vapor deposition (CVD) on various substrates including fibrous structures resulted in the formation of homogenous thin films, which were subjected to atomic scale imaging and x-ray analysis to confirm the synthesis of crystalline WS₂ and MoS₂ materials. The advantageous properties of WS₂ and MoS₂ combined with the flexible, controllable and sustainable synthetic route, developed in this work, is expected to be of significant interest for various energy storage and conversion applications including lithium-oxygen batteries and photochemical water-splitting.

9:45 AM ET09.04.04

Effect of the Solvate Electrolyte on Lithium-Sulfur Battery Performance and Reaction Mechanism Heng-Liang Wu; National Taiwan University, Taipei, Taiwan.

Solvate electrolytes such as acetonitrile-based solvate electrolyte have been proposed to suppress the polysulfide dissolution and enhance the capacity retention of lithium-sulfur (Li-S) batteries.(1-3) In this study, we report on our use of in situ spectroscopy including Raman and X-ray spectroscopy (X-ray diffraction and X-ray absorption spectroscopy) to investigate sulfur reaction mechanism and the interaction between polysulfide and electrolyte. Raman spectroscopy and cyclic voltammetry obtained from sulfur-carbon cathodes in the conventional ether-based electrolyte show that long chain polysulfides (S₈²⁻) are formed in the first reduction process at ~2.4 V vs Li/Li⁺ and short chain polysulfides such as S₄²⁻, S₄⁻, S₃⁻ and S₂O₄²⁻ are observed with continued discharge at ~2.3 V vs Li/Li⁺ in the second reduction process.(4-5) The elemental sulfur changes from orthorhombic phase to monoclinic phase in the conventional ether-based electrolyte during the first cycle. In acetonitrile-based solvate electrolyte, in situ spectroscopy results show that short chain polysulfides are formed at the early stage of discharge process and the formation of soluble long chain polysulfides is suppressed. Elemental sulfur with orthorhombic phase is reformed in acetonitrile-based solvate electrolyte during cycling. These results suggest that solvate electrolyte changes the sulfur reaction mechanism. The effect of solvate electrolyte on Li plating/stripping process was also studied. We next propose different solvate electrolytes with low polysulfide solubility and high stability toward Li metal to enhance the capacity retention of Li-S batteries.

References:

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10:00 AM BREAK

10:30 AM *ET09.04.05

From Insulating to Conductive, From Hard to Soft Materials—Sulfur and Chalcogenides (CuS, MoS₂) in Metal-Sulfur and Solid-State Batteries Philipp Adelhelm^{1,2}; ¹Institute of Technical Chemistry and Environmental Chemistry, Jena University, Jena, Germany; ²Center for Energy and Environmental Chemistry (CEEC Jena), Jena University, Jena, Germany.

Sulfur and chalcogenides are attractive materials for rechargeable batteries thanks to their generally high specific capacity. Other relevant properties such as conductivity, plasticity or volume expansion during lithiation/sodiation largely vary and depend on the specific compound of interest. Sulfur and the ideal discharge product Li₂S or Na₂S are insulating which requires a sophisticated electrode design with a porous carbon matrix. CuS, on the other hand, is both electronically and ionically conductive which generally benefits the reversibility of the cell reaction. Finally, MoS₂, is very soft which may be of advantage considering the large volume expansion during lithiation/sodiation. In this presentation, we will discuss specific properties of sulfur in contact with a porous carbon matrix combined with results on room-temperature sodium-sulfur cells. We also address the use of copper sulfide and molybdenum sulfide as electrode material for lithium/sodium solid state batteries which can show high capacity despite their large volume expansion during cell cycling.

11:00 AM ET09.04.06

Developing Air Cathodes Using ORR and OER Catalysts for Aqueous Lithium-Air Batteries Varun Rai and Daniel John Blackwood; National University of Singapore, Singapore, Singapore.

Lithium air batteries with aqueous acidic catholytes system have a high potential to attain theoretical energy density limits in energy storage devices because of high conductivity and solubility of discharge products along with low CO₂ solubility [1,2]. Therefore, the role of low cost, active, durable and noble free ORR and OER catalysts are very critical in improving charging and discharging cycles followed to addressing the problem in achieving high energy density for practical storage applications. Catalysts suitability as efficient air cathodes are determined by its electronic conductivity, non-solubility in aqueous acidic catholyte, optimal porosity for fast oxygen diffusion and selective adjustments of hydrophobic in ORR and hydrophilic property in OER processes. Transition metal oxides [3] shows fairly low conductivity in comparison to noble metal however by introducing dopant centers and hetero atoms like N, S, F etc significantly improve electronic conductivity and favorable redistribution of positive charges in the lattice for oxygen adsorption than pristine oxides. We would be presenting carbon black supported catalyst for better ORR performance with high current. As Carbon black improves the electron transfer among substrate, catalyst and electrode tip.

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11:15 AM ET09.04.07

Amorphous Superatom Molecular Cluster-Based Microspheres for Electrochemical Energy Storage and Conversion Boyu Qie¹, Andrew Pinkard², Xavier Roy² and Yuan Yang¹; ¹Applied Physics and Applied Mathematics, Columbia University, New York, New York, United States; ²Chemistry, Columbia University, New York, New York, United States.

Precisely tunable and programmable synthesis of materials that satisfy specific functions is one of the critical points of materials chemistry. One trend to design solid-state materials is using functional molecular clusters, so-called superatoms, to substitute single atoms in strategy design to create more applicable possibility like high porosity and novel nanomaterials. A rich library of different molecular clusters has been established in a variety of attractive properties, such as redox activity, large magnetic moments and luminescence. However, to our knowledge, there have been few attempts to use these building blocks to assemble new materials for energy purposes - alkali ion battery and water splitting. Here we report a new method to synthesize cobalt sulfides (Co₆S₈) and selenides (Co₆Se₈) based on molecular cluster building blocks. The products presented amorphous micron-size spherical shape with high porosity and surface area (~360 m²/g of Co₆S₈ and ~130 m²/g of Co₆Se₈), considering which, they could provide more channels/rooms for ion transport, to have better kinetics and less volume change during battery cycling in high-capacity conversion reaction. We successfully utilized these micron-sized spheres into lithium and sodium-ion batteries with high specific capacities (~650 mAh/g for Co₆S₈-Li-ion battery and ~450 mAh/g for Co₆Se₈-Na-ion battery), impressive rate capability, and reasonable reversibility (17% lost for 300 cycles in Li-ion battery and 10% lost for 100 cycles in Na-ion battery). Moreover, we also found that the super-based materials are efficient catalysts for the hydrogen evolution reaction (HER) with reasonable overpotential (the highest -0.184V vs. SHE at 10 mA/cm² in 0.5 M H₂SO₄ solution).

SESSION ET09.05: Catalysis in Energy Conversion and Storage
Session Chairs: Haoyi Li and Hui Xu
Tuesday Afternoon, November 27, 2018
Hynes, Level 3, Room 301

1:30 PM *ET09.05.01

High Capacity Cathodes Invoking Oxygen Redox Chemistry Peter Bruce; University of Oxford, Oxford, United Kingdom.

The energy stored by Li-ion batteries is limited by the cathode. State-of-the-art materials can deliver in the region of 180 mAh g⁻¹ of charge storage capacity. Such materials, e.g. LiFePO₄, are limited by storing electrons only on the transition metal ion (transition metal redox). It is now known that the oxide in so called lithium-rich transition metal oxides, e.g. Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O₂ can store charge (oxygen redox). To harness the opportunity of increased

charge storage that O-redox may offer it is important to understand the nature of O-redox processes and the factors that control them. O-redox in 3d transition metal oxides will be discussed, leading to a high capacity manganese based cathode that utilizes the full capacity of the Mn as well as charge storage on oxygen.

2:00 PM *ET09.05.02

Catalyzing the Charging Process in Li-O₂ Batteries Using Lithium Halides Graham Leverick, Michal Tulodziecki, Ryoichi Tatara, Shuting Feng and Yang Shao-Horn; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Non-aqueous Li-O₂ batteries have been the subject of intense research interest over the past decade or two, owing to their very high theoretical gravimetric energy density; potentially up to three times that of state-of-the-art lithium ion batteries. Despite this widespread effort, lithium oxygen batteries still suffer from a number of significant issues, including high overpotential on charge and poor cycle life. Part of this poor charging performance can be attributed to the insulating nature of the Li₂O₂ formed on discharge, which makes direct electrochemical oxidation challenging. While a number of approaches have been taken to try and catalyze the charging process of a Li-O₂ battery, soluble lithium halides, such as lithium iodide and lithium bromide, in particular, have shown very promising performance. Despite this promise, there has been serious ambiguities in literature relating to the influence of lithium iodide on both the discharge and charge processes. In this talk, strategies for controlling the thermodynamics of the chemical oxidation of Li₂O₂ during the charging progress are discussed, based on controlling solvation energy through solvent-ion interactions and the addition of water to the electrolyte, as well as through the formation of halide-complexes. This work shows promise that the charging process of a Li-O₂ battery can be optimized for both energy efficiency and effective oxidation of Li₂O₂ through systematic electrolyte and redox mediator design.

2:30 PM ET09.05.03

Systematic Design of Bifunctional Hybrid Electrocatalysts Comprised of 1T' MoS₂ and Fe, Co, Ni-Based Compounds for Overall Water Splitting Haoyi Li and Xun Wang; Department of Chemistry, Tsinghua University, Beijing, China.

Driven by the exigent demand for sustainable and renewable energy sources, a huge effort has been devoted to the development of efficient and accessible energy conversion technologies. Electrochemical water splitting – an environmentally-friendly and cost-effective technology for hydrogen production from electricity – has attracted great attention as a promising pathway to decrease social dependence on fossil fuels. The development of low-cost, high-performance electrocatalysts is necessary to enable water splitting as a functional and practical technology. As a means of lowering the driving overpotential and increasing the efficiency of catalytic water splitting, first, enhancing the intrinsic activity of catalytic sites in electrocatalysts requires an optimization of the adsorption free energy of reactants to speed the rate-determining step of the overall reaction. Second, the enhanced conductivity of electrode materials contributes to fast charge transfer, a requirement for which metallic materials have demonstrated superior ability. Third, the optimization of mass transfer properties has a tremendous effect on the ultimate efficiency of electrocatalysts. Innovative nanoarray and porous two-dimensional architectures can facilitate the dissipation of as-formed gas bubbles from the electrode surface. Finally, the increased density of catalytic active sites in the electrode material allows for the maximization of limited electrode surface area – porous nanostructures have a proven ability to facilitate increased surface area.

Herein we prepared the hybrid nanostructures integrating metallic 1T' MoS₂ with Fe, Co, Ni-based compounds for water splitting via integrated compositional and geometric structural design. Metallic 1T' MoS₂ was employed for its excellent electrode kinetics, fast charge transfer, and remarkable intrinsic electrocatalytic HER activity. Fe, Co, Ni-based compounds were utilized for their inherent and adjustable OER reactivity (a result of synergistic effects between metal ions). Lastly, nanotube-array and porous two-dimensional architectures were exploited for their porosity, high surface area, and uneven surface characteristics – a way to maximize catalytic active site density and facilitate mass transfer. Notably, the hybrid nanostructures deliver a current density of 10 mAcm⁻² at an overpotential of 58 mV for the HER and 184 mV for the OER while demonstrating outstanding durability (200 mAcm⁻² for 80-hour continuous operation). The low Tafel slopes of 37.5 mVdec⁻¹ and 49.9 mVdec⁻¹ for HER and OER demonstrate the fast reaction kinetics. Additionally, we utilize this electrode in a water splitting system as anode and cathode simultaneously, achieving a current density of 10 mAcm⁻² at a cell voltage of 1.429 V in alkaline media. Our results demonstrate substantial improvement in the design of high-performance electrodes for water electrolysis.

2:45 PM ET09.05.04

Developing Photoelectrochemical Water-Splitting Anodes with Iridium Oxide-Based OER Catalysts Micha Ben-Naim¹, Alaina L. Strickler¹, David W. Palm¹, Drew Higgins^{2,1}, Laurie King¹, Adam Nielander¹ and Thomas F. Jaramillo^{1,2}; ¹Chemical Engineering, Stanford University, Stanford, California, United States; ²SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, Menlo Park, California, United States.

Photoelectrochemical (PEC) water-splitting is a promising technology that uses solar radiation to split water into hydrogen and oxygen, providing a storable form of chemical fuel to pair with intermittent renewable electricity sources¹. Silicon shows promise as a small bandgap absorber material (1.1 eV) to use in tandem PEC devices¹. However, pairing catalysts with semiconductors has proven difficult due to poor energetic alignments and interfaces as well as stability concerns, which are especially limited in acid².

Many catalyst deposition techniques require high temperatures and complicated processing and are incompatible with some photoabsorber materials. Thus, we developed a spin coating procedure due to its inherently simple and versatile nature to synthesize amorphous iridium oxide and biphase strontium iridium oxide. Material structure is probed by SEM, XPS, AES, and XRD, while electrochemical performance was measured under illumination and in the dark by cyclic voltammetry, chronoamperometry, and electrochemical impedance spectroscopy.

The addition of strontium to the catalyst gives 550 mV of photovoltage, a 100 mV improvement upon iridium oxide. By probing a facile redox couple, we show that the strontium iridium catalyst forms a more beneficial electronic interface with silicon. A comparison of the as-prepared and post-test anodes via AES demonstrates that the predominant failure mechanism is film cracking and delamination, which originates from initial film heterogeneity.

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3:00 PM BREAK

3:30 PM *ET09.05.05

Creating High-Performance Heterogeneous Catalysts Through Surface Engineering Yu Huang; University of California, Los Angeles, Los Angeles, California, United States.

Noble metal-based nanocrystals have played important roles in heterogeneous catalysis due to their high activity and chemical stability. Owing to the large

surface to volume ratio at nanoscale slight changes in the surface structure of catalytic materials can have large impacts on the catalytic stability and activity. The composition, facet, and the topology of the top surface layers of a nanocatalyst eventually determine its performance in catalytic reactions. In this presentation, I will share our recent efforts on designing the surface compositions, structures and the overall morphology of noble metal catalysts to improve both catalytic activity and stability of nanocatalysts.

4:00 PM *ET09.05.06

Advanced Electrolysis for Renewable Energy Conversion and Storage Hui Xu; Giner Inc., Newton, Massachusetts, United States.

The utilization of renewable energy has substantially driven more attention into electrolysis technologies. As renewable energy emerges and penetrates further into the energy market, the storage of surplus “off peak” electricity has received widespread attention. An electrolyzer can utilize “off peak” electricity from solar or wind farms to produce hydrogen or other fuels. These chemicals can then be operated in a fuel cell mode to generate electricity when needed or used for other industrial applications. It is estimated that the water electrolyzer market can increase up to 300 GW over the next two decades. The power to gas market alone is poised to become a multi-billion-dollar market for on-site water electrolysis systems over the next decade. However, current hydrogen production from electrolysis comprises only a small fraction of the global hydrogen market due to the high costs that results from expensive materials even if “free” electricity from renewable energy can be acquired. Giner has been a world leader in researching, developing and manufacturing water electrolyzers and reversible fuel cells. We have been striving to address the challenges of these materials (catalyst, membrane, and bipolar) to improve electrolyzers’ performance, extend their lifetimes, and lower their capital costs. These efforts include: 1) lowering platinum-group metal (PGM) catalyst loading; 2) discovering non-precious metal catalysts; 3) improving membrane durability; 4) increasing corrosion resistance of separators and other hardware.

In addition to water electrolysis for hydrogen production, electrochemical synthesis of ammonia and CO₂ conversion to hydrocarbon fuels have also been extensively investigated at Giner. Advanced catalysts have been developed to enhance the conversion rate and boost the process efficiency. For example, the electrochemical production of ammonia from nitrogen and water has thus led to tremendous energy savings compared to the conventional Haber-Bosch process. The produced ammonia can be used as low-cost energy carrier for fuel cell vehicles. Some of these advances have been applied in our electrolyzer products, from single cell lab hydrogen generators to large stacks. The performance and efficiency of our electrolyzers are thus tremendously improved. The development and deployment of these large electrolyzer stacks will cultivate the large-scale application of a variety of renewable energy. Due to their high energy density and reduced cost, the electrolysis technologies may become strongly competitive and complementary to rechargeable batteries for renewable energy storage.

4:30 PM ET09.05.07

Activation of Ultrathin SrTiO₃ with Subsurface SrRuO₃ for the Oxygen Evolution Reaction Andrew Akbashev^{1,2}, Liang Zhang³, J. Tyler Mefford^{1,2}, William Chueh^{1,2} and Aleksandra Vojvodic³; ¹Department of Materials Science and Engineering, Stanford University, Stanford, California, United States; ²Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, California, United States; ³Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Designing simultaneous activity and stability of a catalyst during electrochemical water splitting is a significant challenge on the way to efficient energy conversion. A dream material for the oxygen evolution reaction (OER) should evince sufficiently high activity and maintain stability of the active surface. Although oxide materials hold great promise for the electrocatalysis applications owing to their high OER activity, their efficient operation is often hindered by structural instability. A core-shell design, where an active core catalyst is covered with a stable nanometers-thick shell, is an attractive solution to the problem of catalyst instability that is commonly employed in metal nanoparticles. However, the interaction between the core and shell of oxide materials during electrocatalytic reactions is not well understood. We hypothesize that the core material can act as a subsurface activator for the shell by introducing spatially accessible electronic states. We validate this hypothesis by studying single-crystalline oxide heterostructures (epitaxial thin films) as model core-shell architectures.

A highly OER-active SrRuO₃ undergoes rapid dissolution under OER conditions, which makes it an ideal material for a model active layer. On the contrary, SrTiO₃ is OER-inert and chemically stable and can serve as a shell material. We employ atomically-precise deposition to fabricate ultrathin heterostructures composed of bottom SrRuO₃ and capping SrTiO₃ layers.

We demonstrate that inserting as little as *one unit cell* of an active material (SrRuO₃) under a shell layer (SrTiO₃) activates the inert shell, while only *two unit cells* (1 nm) of SrTiO₃ is enough to fully protect the inherently unstable SrRuO₃ against dissolution. Using density functional theory calculations, we unravel the mechanism for the subsurface activation in oxide systems. Burying an active material under an ultrathin shell layer introduces new electronic states in the system, changing the electronic hybridization between the adsorbates and the shell layer and facilitating an easy transfer to the adsorbed intermediates.

Ultrathin heterostructures serve as a rigorous platform for screening core/shell nanoparticle combinations and thicknesses. Our study provides an insight into the role of atomic-level modification of the surface and subsurface layers of oxide electrocatalysts, opening up a rich playground for further discovery and design of active and stable materials.

4:45 PM ET09.05.08

Hierarchical Titanium Nitride Nanostructures as Stable Catalyst Supports for Low-Pt Content Fuel Cell Cathodes Andrea Perego^{2,1}, Giorgio Giuffredi^{2,1}, Piero Mazzolini², Rosaria Brescia³, Dinesh Sabarirajan⁴, Iryna Zenyuk⁴, Andrea Casalegno¹ and Fabio Di Fonzo²; ¹Department of Energy, Politecnico di Milano, Milan, Italy; ²Center for Nano Science and Technology @PolMi, Istituto Italiano di Tecnologia, Milan, Italy; ³Istituto Italiano di Tecnologia, Genova, Italy; ⁴Mechanical Engineering Department, Tufts University, Medford, Massachusetts, United States.

To overcome the high cost of the catalyst in Polymeric Electrolyte Fuel Cells (PEMFC) technology, research is moving towards the reduction in the Pt loading in the electrodes by increasing the electrochemical surface area through a proper catalyst support. To date, the state of the art of catalyst supports is dominated by mesoporous carbon, which shows high conductivity but suffers from stability issues especially on long term operation. As shown in various works in the literature, titanium nitride (TiN) has a metal-like conductivity with an outstanding chemical stability, making it a possible candidate to replace carbon.

In this contribution, we report about Pt-TiN catalysts support with self-assembled, hierarchical mesoporous nanostructure, grown by Pulsed Laser Deposition. This approach controls the gas dynamics of the nanoclusters-inseminated supersonic jet in order to differentiate the resulting impaction deposition, affecting the growth of the film. We demonstrate that with our technique, morphology can be controlled at the nanoscale to tune the pore size to a mesoporous range, already proven to be effective in fuel cell electrodes. Platinum catalyst is deposited on the tree-like structures either by electrodeposition and atomic layer deposition, tuning the process to achieve ultra-low Pt loading (<0.1 mg cm⁻²).

Electrochemical characterization towards ORR is carried out and shows it is possible to reach good value of the ECSA while controlling the porosity and the morphology of the material down to the nanoscale, reaching good current values. Stability of the scaffold is evaluated according to DOE Accelerated

Stress Test (AST) standard protocols, and the ECSA loss is registered to be around only 7% with respect to the 40% goal. The thin films fabricated this way are then transferred by decal method to a Nafion® membrane, to demonstrate their applicability to a fuel cell cathode. Despite the currents are fairly low, further optimization, focused in particular towards a better ionomer contact in the electrode, will improve the cell performance in the future. Our results show the potential of a PVD based technique that opens the doors of the nanoscale to the fabrication of highly stable electrodes whose morphological and electrochemical properties are easily tuned. This approach holds promises for a high platinum utilization and lower costs for PEMFC technology.

SESSION ET09.06: Poster Session II: Energy Storage
Tuesday Afternoon, November 27, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

ET09.06.01

Lithiated Metal Oxide Nanosheets Decorated Sulfur Microparticles for High-Performance Lithium-Sulfur Batteries Arnab Ghosh^{2,1}, Ajit Kumar^{2,1}, Amlan Roy², Manas R. Panda², Mega Kar¹, Douglas R. MacFarlane¹ and Sagar Mitra²; ¹Chemistry, Monash University, Melbourne, Victoria, Australia; ²Energy Science & Engineering, Indian Institute of Technology Bombay, Mumbai, India.

Due to high specific capacity and high energy density, lithium-sulfur batteries are considered as promising alternative to conventional lithium-ion batteries. Combining lithium and sulfur could yield as much as high specific energy of 2600 Wh/kg. However, some serious issues like dissolution of active sulfur and polysulfides into electrolyte and their shuttling between the anode and cathode impede the practical realization of lithium-sulfur batteries. In this work, lithiated metal oxide (LMO) nanosheets (with an average size of 100 nm) were decorated on the surface of sulfur microparticles of 50-80 μm . The LMO decorated sulfur shows lower rate of dissolution of active material sulfur as well as intermediate polysulfides into the ether-based electrolyte, leading to a low self-discharge rate and high cycling stability. The lithiated metal oxide (LMO) facilitates the transport of Li^+ ion throughout the cathode scaffold, resulting higher utilization of active material. At a current rate of 200 mA/g, the LMO decorated sulfur cathode delivers an initial reversible capacity of 788 mAh/g at second cycle and retains a capacity up to 657 mAh/g (83.4% of initial capacity) after 100 cycles. During the meeting discussion, I will elaborate the synthesis procedure and highlight the electrochemical performance of lithiated metal oxide decorated sulfur microparticles as cathode material in lithium-sulfur batteries.

ET09.06.02

MoSe₂ Anchored with N, P Dual Doped rGO for High-Performance Sodium-Ion Batteries Amlan Roy, Arnab Ghosh, Ajit Kumar and Sagar Mitra; IIT Bombay, Mumbai, India.

Although lithium-ion batteries excel for its sheer performance, sodium ion batteries have attracted more attention to the scientific community because of its low cost-per-storage and their vast abundance in the earth's crust. There is an immense need for the battery farms to store renewable energy like wind energy and solar energy, therefore, a suitable host material specifically anode is required, which can integrate large size of sodium cation (0.108 nm vs. 0.078 nm of Li^+) throughout the cycle. Graphite is a commercially available anode material for Li-ion batteries (LIB) but their limited capacity against sodium due to the discrepant interlayer distance between graphite layers because of the radius of Na^+ ion. Another anode material based on transition metals (TMD) has the unique 2D structure with excellent electronic property and high energy density as compared to graphite. Another most commonly used conversion based anode material MoS_2 for SIB has the interlayer distance of 0.62 nm, but major issues with this material are the utilization of less conductive S after full conversion of MoS_2 . MoSe_2 , the analogous structure of MoS_2 , have large interlayer distance (~ 0.64 nm) with higher conductivity as compared to MoS_2 . The major drawbacks with this TMD's are large volume expansion and layers agglomeration while cycling. Here, we improved cyclic performance as well as the stability of MoSe_2 by incorporating the heteroatom doped reduced graphene oxide (N, P doped rGO) in between the layers of MoSe_2 (denoted as MoSe_2/NPr) through single step method at the high temperature in the inert atmosphere. In MoSe_2/NPr , N and P dual dope boosts the conductivity of rGO sheets which improves the Na-ion transportation throughout the active material compare to bulk MoSe_2 electrode. The MoSe_2/NPr composite delivers 337 mA h g^{-1} at a current rate of 0.1 A g^{-1} and stable up to 100 cycles whereas MoSe_2 shows 63.2 mA h g^{-1} after 100 cycles at a same current density. Lastly, Sodium storage mechanism also investigated by several ex-situ physical and microscopic studies.

ET09.06.03

Nickel-Based Sulfide/Phosphide Electrocatalysts for Rechargeable Lithium-Oxygen Batteries Bobae Ju, Hee Jo Song, Gwang-Hee Lee, Hyunseok Yoon and Dong-Wan Kim; Korea University, Seoul, Korea (the Republic of).

Lithium-oxygen batteries are considered as another potential alternative to lithium-ion technology due to their high theoretical energy density of 3505 W h kg^{-1} . However, in spite of their high energy density, lithium-oxygen batteries are still faced with many issues such as sluggish O_2 redox kinetics and inferior Li_2O_2 /cathode contact interface on cathode, resulting in high oxygen reduction/evolution reaction (ORR/OER) overpotential, low round-trip efficiencies, short lifetimes, and poor rate capabilities. To overcome these obstacles, it is required to develop an effective electrocatalyst which is capable of inducing a reversible reaction between lithium-ion and O_2 at the cathode. So far, although carbon-based materials or carbon-supported noble metals, metal oxides are investigated as effective electrocatalysts, there still remain several unresolved drawbacks. Thus, it is necessary to develop the new efficient electrocatalyst for lithium-oxygen batteries. Transition metal sulfides/phosphides are known to be used as a hydrogen evolution reaction, oxygen evolution reaction electrocatalyst. However, the use of these materials has rarely been addressed as ORR/OER electrocatalysts for lithium-oxygen batteries in detail. In this study, therefore, we develop the nickel-based sulfide/phosphide electrocatalysts (NiS_2 and Ni_2P) for high-performance lithium-oxygen battery cathodes. Nanostructured $\text{Ni}(\text{OH})_2$ precursors are prepared via hydrothermal process, and then they are transformed to NiS_2 and Ni_2P via sulfidation/phosphidation process. Their microstructural and electrochemical activities are systematically investigated. Both NiS_2 and Ni_2P show the long-term cyclic stability over 200 and 150 cycles, respectively, at a current density of 500 mA g^{-1} and a fixed capacity of 1000 mA h g^{-1} in voltage range 2.0-4.8 V. Also, both electrocatalysts exhibit overpotential of 1.6 V even at the 100th cycle.

ET09.06.04

High-Capacity WS₂ Nanosheets Derived from WO₃ Nanocolloids for Lithium-Ion Battery Anodes Inha Kim, Sung-Woo Park and Dong-Wan Kim; Civil, Environmental and Architectural Engineering, Korea University, Seoul, Korea (the Republic of).

Recently, lithium ion batteries (LIBs) dominate the market of power sources for portable electronics, energy storage systems, electric vehicles. Depending

on the application, it is still necessary to enhance and optimize the electrochemical performances such as energy density, cycle stability, cost, safety, etc. Among the various factors to enhance the performances of LIBs, the development and design of new anode materials are being suggested. Due to limited capacity of 372 mAh g^{-1} (based on $\text{Li} + 6\text{C} \leftrightarrow \text{LiC}_6$) in commercial graphite anodes, transition metal dichalcogenides (TMDCs) MX_2 (M=Mo, W, V, Ti; X=S, Se) have a great attention as one of promising anode materials. The TMDCs have been most heavily investigated among the post-graphene 2-dimensional materials. Each monolayer comprising stacked 3-atom layers (X-M-X) in TMDCs is bonded by weak van der Waals forces. This 2-dimensional layer structure can facilitate intercalation and/or diffusion of Li^+ ion into TMDCs. In particular, WS_2 , stemming from its large interlayer spacing (0.62 nm, compared to 0.34 nm for graphite) can deliver a high capacity of 432 mAh g^{-1} as a possible anode for LIBs. In this study, uniform WS_2 nanosheets derived from WO_3 nanocolloids are successfully synthesized via underwater electrical wire explosion and subsequent sulfidation process. Firstly, to prepare WO_3 nanocolloids, a tungsten wire was exploded in deionized water as a surrounding medium at 320V, and then the obtained nanocolloids were freeze-dried. Secondly, the dried WO_3 nanocolloids were placed in an alumina crucible and underwent sulfidation at various temperatures from 400 to 600 °C. Thin uniform WS_2 nanosheets were successfully prepared without any residual WO_3 phase. These nanosheets exhibited an excellent Li-electroactivity, delivering of over 700 mAh g^{-1} at a current density of 50 mA g^{-1} .

SESSION ET09.07: Nano and Catalysis
Session Chairs: Xinliang Feng and Tae Yang Son
Wednesday Morning, November 28, 2018
Hynes, Level 3, Room 301

8:15 AM *ET09.07.01

Functional Energy Materials Based on Multifunctional Polymers and Carbon Nanomaterials Liming Dai; Case Western Reserve University, Cleveland, Ohio, United States.

Polymers have been traditionally used as electrically insulating materials: after all, metal wires are coated in plastics to insulate them. However, various *conjugated* macromolecules with alternating single and double bonds have been synthesized with unusual electrical and optical properties through the p-electron delocalization along their 1D backbones. A number of synthetic methods have also been devised to produce conjugated polymers with the processing advantages of plastics and the optoelectronic properties of inorganic semiconductors for energy conversion and storage, including polymer photovoltaic cells. Having conjugated all-carbon structures, carbon nanomaterials, including 1D carbon nanotubes and 2D graphene, also possess certain similar optoelectronic characteristics as conjugated macromolecules. Thus, carbon nanomaterials (*e.g.*, 1D carbon nanotubes, 2D graphene sheets, 3D carbon architectures) have been playing a more and more important role in the development of efficient energy conversion and storage devices.

In this talk, I will present some of our rational concepts for the design and development of functional conjugated polymers and multidimensional carbon nanomaterials for various energy-related applications, including polymer solar cells containing graphene nanosheets for improving charge transport, fuel cells and metal-air batteries with carbon nanomaterials as multifunctional metal-free catalysts, and supercapacitors with nanotube/graphene hybrid electrodes for energy storage.

8:45 AM *ET09.07.02

Carbon-Rich Electrocatalysts by Design and Nanostructure Engineering Xinliang Feng; Chemistry and Food Chemistry, Technische Universität Dresden, Dresden, Germany.

For universal utilization of hydrogen energy, development of high-efficiency, low cost and sustainable energy conversion technologies, especially fuel cells and electrochemical/photoelectrochemical water splitting devices, is of paramount significance. In order to enhance the energy conversion efficiency of water splitting and fuel cell systems, earth-abundant and stable electrocatalysts are essential for accelerating the sluggish kinetics of hydrogen and oxygen reactions. Up to now, noble metal (*e.g.*, Pt, Ir and Ru)-based materials still remain as the benchmark hydrogen and oxygen electrocatalysts. Unfortunately, high cost and scarce reserve of such noble metals seriously hinder their large-scale applications. Recently, intensive study on active centers and nanostructures of carbon-based materials have greatly advanced the rapid development of new classes of carbon-rich electrocatalysts, featuring defined electronic structures of active sites, for example, metal-free carbons, atomic metal-doped carbons, metal-organic frameworks (MOFs), as well as conjugated porous polymers. To explore earth-abundant and efficient carbon-rich electrocatalysts, it is pivotal to rationally design their active sites, electronic properties and nanostructures that can offer optimal active sites, abundant accessible surface area, and fast mass transport during the electrochemical processes.

In this lecture, we will present our recent efforts on the design and synthesis of carbon-rich nanomaterials as metal-free or noble-metal-free electrocatalysts for hydrogen and oxygen reactions, particularly including template-directed synthesis of metal-free and noble metal-free carbons, 2D metal organic framework nanosheets and Cu surface-mediated fabrication of carbon-rich nanofibers. We will highlight the great potential by tailoring active sites and nanostructures as well as to address the fundamental relationships associated with these carbon-rich electrocatalysts.

9:15 AM ET09.07.03

$\text{Cu}_2\text{BaSn}(\text{S,Se})_4$ -Based Photocathodes for Hydrogen Production Edgard Ngaboyamahina¹, Yihao Zhou¹, Donghyeop Shin², Betül Teymur¹, Charles Parker¹, David Mitzl¹ and Jeff Glass¹; ¹Duke University, Durham, North Carolina, United States; ²Korea Institute of Energy Research, Daejeon, Korea (the Republic of).

Photoelectrochemical cells (PEC) provide a prospective sustainable and environmentally benign route towards the generation of hydrogen and oxygen from water. Various chalcogenides ($\text{Cu}(\text{In,Ga})(\text{S,Se})_2$, CdTe , $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$) have been adopted as a photocathode for hydrogen evolution but several concerns and material limitation remain regarding scarcity/toxicity (*e.g.*, In and Ga/ Cd) and Cu-Zn anti-site disordering in earth-abundant $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ chalcogenides. Recently, the $\text{Cu}_2\text{BaSn}(\text{S,Se})_4$ (CBTSSe) system has attracted attention as an emerging chalcogenide semiconductor with desirable properties for solar energy conversion applications¹. The current study investigates how the introduction of Se into the parent compound, CBTS, influences its electronic and optical properties and overall photoelectrochemical performance.

It was found that the photocurrent of vacuum-processed CBTSSe photocathode increases significantly with increasing Se concentration due to larger grain size, reduced grain boundaries, and improved light absorption². In addition, the use of TiO_2/CdS protective overlayers creates a desirable band alignment for efficient charge extraction at the hetero-interfaces. This significantly improves the PEC performance of CBTSSe films, yielding a photocurrent of $12+ \text{ mA/cm}^2$ at 0 V/RHE, the highest value reported for CBTSSe-based PEC devices, as well as stable hydrogen evolution for 10+ hours³. Ultimately, the study

demonstrates that similar level of performance is achieved with high purity CBTSSe films synthesized in solution using inexpensive and commercially available precursors. The present results highlight the potential of CBTSSe materials as efficient, stable and low-cost photocathodes for solar water splitting.

1. Shin, D.; Saporov, B.; Zhu, T.; Huhn, W. P.; Blum, V.; Mitzi, D. B., BaCu₂Sn(S,Se)₄: Earth-Abundant Chalcogenides for Thin-Film Photovoltaics. *Chemistry of Materials* 2016, 28 (13), 4771-4780.
2. Shin, D.; Ngaboyamahina, E.; Zhou, Y.; Glass, J. T.; Mitzi, D. B., Synthesis and Characterization of an Earth-Abundant Cu₂BaSn(S,Se)₄ Chalcogenide for Photoelectrochemical Cell Application. *The Journal of Physical Chemistry Letters* 2016, 7 (22), 4554-4561.
3. Zhou, Y.; Shin, D.; Ngaboyamahina, E.; Han, Q.; Parker, C. B.; Mitzi, D. B.; Glass, J. T., Efficient and Stable Pt/TiO₂/CdS/Cu₂BaSn(S,Se)₄ Photocathode for Water Electrolysis Applications. *ACS Energy Letters* 2018, 3 (1), 177-183.

9:30 AM BREAK

10:00 AM ET09.07.04

Preparation and Characterization of poly(ether ether ketone) Containing Imidazolium Group for Anion Exchange Membrane Fuel Cell Application Tae Yang Son, Tae Ho Ko and Sang Yong Nam; Gyeongsang National University, Jinju, Korea (the Republic of).

In the case of proton exchange membrane fuel cell application, the cation exchange membrane and the platinum catalyst are expensive. However, in the anion exchange membrane fuel cell (AEMFC) using non-precious metal catalyst, the anion exchange membrane are key component. The anion exchange membrane should have high electrochemical and mechanical properties. The poly(ether ether ketone) (PEEK) based copolymer containing imidazolium group was synthesized. The synthesized PEEK had different contents of imidazolium group. For preparing free standing film, the various PEEK containing imidazolium group were dissolved in n-methyl-2-pyrrolidone (NMP). Then, the fully dissolved solution is poured into a Petri-dish. After the various PEEK films were prepared, the properties of films were evaluated. The ion exchange capacity was measured by back-titration method and the ion conductivity was calculated by membrane resistance method. The TGA and UTM were used to investigate the thermal and mechanical properties of the various PEEK films.

10:15 AM ET09.07.05

Organic Anions Intercalated NiFe Layered Double Hydroxides as Oxygen Evolution Reaction Catalysts in pH-Near-Neutral Electrolytes Yan Dong^{1,2} and Sridhar Komarneni²; ¹Department of Materials Science and Engineering, The Pennsylvania State University, State College, Pennsylvania, United States; ²Materials Research Institute and Department of Ecosystem Science and Management, The Pennsylvania State University, State College, Pennsylvania, United States.

Oxygen evolution reaction (OER), the anodic reaction of water splitting which involves the transfer of four electrons is kinetically sluggish and therefore, has become the main challenge to improve the efficiency and lower the energy cost of the water splitting process. Tremendous efforts have been made to develop cost-effective, highly efficient and robust OER catalysts to replace the scarce and expensive RuO₂ and IrO₂ catalysts. Among all the earth-abundant OER catalysts that have been developed which showed comparable or better performance than RuO₂ and IrO₂, many of them are layer-structured materials such as transition-metal hydroxides, layered double hydroxides (LDHs), layer-structured transition-metal oxides such as (Li,Na)Ni₄Fe₂O₂ and birnessite, layer-structured metal-organic frameworks (MOFs), and also the emerging MXene materials. Even for the transition metal oxides, sulfides, selenides, nitrides or phosphides as OER catalysts, studies have shown that the real active phase is the transition-metal hydroxide formed in-situ in the alkaline electrolyte during the reaction. Therefore, it is very important to study the structure-property relationships between the layered structures of these OER catalysts and their OER performance. The interlayer spacing of LDH could be modified by organic anions, which could affect their OER activity, especially when the interlayer spacing of the catalysts is larger than 1nm. In this work, NiFe LDH OER catalysts with an interlayer spacing ranging from 1.4nm-0.4nm were synthesized by intercalating a series of dicarboxylic acids of different carbon chain lengths. These LDHs with different interlayer spacing were tested as OER catalysts in a pH-near-neutral NaClO₄ electrolyte in which the interlayer spacing of the LDH was not changed during the reaction. The overpotential needed to generate a 10mA/cm² OER current density was used to characterize the OER activity of each sample. And the relationships between the OER performance and the interlayer spacing of these NiFe LDHs were studied. In addition, we found that the sebacate anions intercalated NiFe LDH is an excellent OER catalyst for the pH-near-neutral potassium borate electrolyte (pH=9.2) which can outperform RuO₂. To the best of our knowledge, this is the first time that anyone has reported a better performance of an earth-abundant OER catalyst than that of the precious RuO₂ in pH-near-neutral borate electrolytes. This study provides us with insights into the interlayer spacing effects on the OER activity of layer-structured OER catalysts and also opens up a new path to develop LDH type OER catalyst for pH-neutral or pH-near-neutral electrolytes.

10:30 AM ET09.07.06

Effects of Electrochemical Potential on Aliovalent Dopant Segregation on Perovskite Oxides Through Elastic and Electrostatic Interactions Dongha Kim, Roland Bliem and Bilge Yildiz; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

La-based perovskite oxides such as (La,Sr)CoO₃ and (La,Sr)MnO₃ have been extensively studied as cathodes in solid oxide fuel cells (SOFCs) due to their high oxygen reduction activity and good compatibility with the electrolyte materials. However, cathode performance is still regarded as one of the main bottlenecks in SOFC operation. In the case of perovskite cathodes, the activity for oxygen reduction and incorporation is impeded by the surface segregation of aliovalent dopants such as Sr. Our previous work assessed the role of temperature and oxygen pressure on segregation of dopants on perovskite oxide surfaces.^{1,2} The present study investigates the effect of electrochemical polarization on dopant segregation. This is important for electrochemical energy conversion applications because electrode material is under different electrochemical and oxygen chemical potentials when we run the system in electrolytic or fuel cell modes.

In order to resolve the electrochemical potential effect systematically, we applied a potential gradient parallel to the surface of thin films, (La,D)MnO₃ (D = Ba, Sr, Ca), as model cathodes, following a cell design by Huber et al.³ We chose dopants with different sizes ($R_{Ba} > R_{Sr} > R_{Ca}$) to investigate how different misfit elastic energies affect segregation. Applying potential changed the oxygen chemical potential and the local oxygen vacancy concentration across the surface. Accordingly, this modified the two key driving forces behind segregation, elastic energy minimization and electrostatic attraction. Changing oxygen chemical potential alters the lattice parameter and causes chemical contraction/expansion, affecting the elastic energy of the dopant in the material. It also changes the relative concentration of oxygen vacancies at the surface versus bulk, affecting the electrostatic attraction of the dopant to the surface. We applied -0.8 V and +0.8 V to the working electrode of each oxide and measured the local cation composition at four points ($\pm 0.16, \pm 0.32, \pm 0.48, \pm 0.64$ V) by X-ray photoelectron spectroscopy (XPS). The amounts of segregated dopants were calculated by deconvoluting the Ba 4d, Sr 3d, and Ca 2p peak into two doublet components: one for the surface species and the other for the original perovskite phase. On all three compositions, segregation of the dopant increased with increasing cathodic polarization. However, in case of (La,Ba)MnO₃ and (La,Sr)MnO₃ where the dopant has larger radius than La, segregation increased also with increasing anodic polarization. We attribute this to the increase in the elastic energy of Ba and Sr as their host lattice contracted under anodic bias. As a result, we found that the segregation behavior of perovskite oxide can be explained by the sum of the elastic and electrostatic energy drivers of segregation.

1. Lee, W. *et al.*, *J. Am. Chem. Soc.*, 135 (2013) 7909.
2. Tsvetkov, N. *et al.*, *Nat. Mater.*, 15 (2016) 1010.
3. Huber, T. M. *et al.*, *J. Electrochem. Soc.*, 164(7) (2017) F809.

10:45 AM ET09.07.07

Metal Deposition Affects the Surface Properties and Stability of Perovskite Oxide Cathode Materials [Roland Blicm](#), Dongha Kim and Bilge Yildiz; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Highly active doped ternary oxides, including perovskites, are common functional materials in energy conversion, catalysis, and information processing applications [1]. At elevated temperatures related to synthesis or operation, however, surface segregation of dopant cations is a common problem of state-of-the-art materials, such as the Sr-doped La-based transition metal perovskites (La,Sr)CoO₃, (La,Sr)FeO₃, and (La,Sr)MnO₃, used for example as solid oxide fuel cell cathodes. In these oxides, Sr segregation under operating conditions leads to degradation via the formation of an inactive surface oxide [2,3], blocking the oxygen reduction reaction [4]. This dopant segregation occurs due to two driving forces: strain and electrostatics [5]. While the size mismatch between Sr and La cations causes strain that can be released via segregation, the electrostatic driving force originates in the attraction of negatively charged dopants to the surface layer enriched in positively charged oxygen vacancies.

Here we relate the segregation in perovskite oxide cathodes to their surface properties, comparing the effects on surface structure and composition of as-grown thin films and metal-doped surfaces. We address the electrostatic driving force of segregation by depositing metals of different reducibility using electron-beam evaporation, thus modifying the local bond strength of oxygen in the surface region. Similar doping has proven successful in a previous study on solution-based metal deposition on (La,Sr)CoO₃ [6]. Here we demonstrate that this effect is not limited to one material and deposition method, but can be generalized to (La,Sr)MnO₃, an intrinsically different type of cathode material, modified using metal evaporation. Using in-situ ambient pressure photoelectron spectroscopy and X-ray absorption spectroscopy, we observe an improved stability under the influence of metals such as Hf and Ti. In combination with scanning probe microscopy and electrochemical performance measurements, we analyze the details of surface doping on structure and stability and explore its limitations. Identifying the nature of the surface phase and the changes due to metal deposition will provide a foundation for targeted approaches to inhibit segregation, facilitating the pathway towards higher long-term stability of doped perovskite oxide surfaces.

Support by the Fonds zur Förderung der Wissenschaftlichen Forschung (FWF, project J4099) and the Air Force Office of Scientific Research (AFOSR) is gratefully acknowledged.

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- [6] N. Tsvetkov, Q. Lu, L. Sun, E.J. Crumlin, and B. Yildiz, *Nat. Mater.* 15, 1010 (2016).

11:00 AM ET09.07.08

Optimization of Structure of CoO Nanoparticles and Its Application in Supercapacitors [Qingsong Huang](#), Xiaofeng Bi, Shuang Song, Wentao Liu and Ruifeng Qi; Sichuan University, Chengdu, China.

CoO nanoparticles doped with Ni were successfully synthesized with facile one-step solvothermal approach and its structure was optimized after being doped with Ni. Compared with pure CoO nanoparticles, the specific surface area increased to 57.83 m²/g to 36.48 m²/g, and the most probable aperture transferred to 3.78 nm from 8.757 nm after being doped with Ni, which created the basis for the optimization of electrochemical performance. Besides, NiO and CoO have similar redox reaction, which can produce synergistic effect during the faradic process. Typically, the specific capacitance of CoO nanoparticles after being doped with Ni increased to 273.9 F/g from 152.4 F/g at current density of 2 A/g and exhibits a ultrahigh capacity retention (106%) after 500 cycling test. Our findings have opened a new way to acquire better electrochemical performance of electrode materials for energy storage/conversion.

11:15 AM ET09.07.09

Photoelectrochemical (PEC) Water Oxidation Using Vertically Aligned Tin Disulfide (SnS₂) Nanoflakes [Binod Giri](#) and Pratap M. Rao; Worcester Polytechnic Institute, Worcester, Massachusetts, United States.

Tin disulfide (SnS₂) is a 2-dimensional material similar to MoS₂ and WS₂, with layers held together by weak Van der Waals forces. It has excellent optical and electronic properties that are suitable for a number of applications. It is derived from non-toxic and earth-abundant elements, and is stable under ambient atmosphere. Because of its high optical absorption coefficient, moderate band gap, and conduction and valence band edges that straddle the reduction and oxidation potentials of water, SnS₂ is a promising material for photoelectrochemical (PEC) water splitting. Several reports describing fundamental properties and synthesis methods have been published, however very few reports have successfully realized SnS₂-based photoanodes. In this work, vertically aligned 2D SnS₂ nanoflakes were grown directly on fluorine doped tin oxide-glass (FTO) substrates using a scalable close space sublimation (CSS) method. Vertical alignment in which the basal planes are perpendicular to the substrate, is superior to random alignment because it allows most of the charges to move effectively along basal planes instead of across them. Scanning electron microscopy revealed that our nanoflakes contain vertical tapered structures with high aspect ratios and high density of exposed edges. They exhibit an indirect bandgap of 2.28eV and are excellent photoabsorbers. Photoanodes consisting of these nanoflakes were synthesized and measured in aqueous pH7 buffer containing sodium sulfite as hole-scavenger. Photocurrents up to 4.5 mA/cm² were obtained at 1.23 V vs. the reversible hydrogen electrode under simulated sunlight. Using the regenerative iodide/triiodide redox couple, it was also shown that the high photocurrent was due to the vertical structure rather than physical degradation.

11:30 AM ET09.07.10

Intercalation/Conversion Hybrid Strategy for High-Energy-Density Li-S Batteries [Weijiang Xue](#)¹, Liumin Suo² and Ju Li¹; ¹Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²Institute of Physics, Chinese Academy of Sciences, Beijing, China.

Although intercalation and conversion battery chemistries have their own advantages in either gravimetric or volumetric energy densities, it is very challenging to achieve both simultaneously. Here, we develop an “intercalation+conversion” hybrid cathode by introducing electrochemically-active Chevrel-phase Mo₆S₈ with fast lithium intercalation reactions and high tap density to hybrid with sulfur to achieve high *full-cell* gravimetric-and-volumetric-energy-density *simultaneously*. The mechanically “hard” Mo₆S₈ with fast Li-ion transport, decent capacity contribution and the dramatically enhanced affinity for LiPS after lithium intercalation, is an ideal backbone to immobilize “soft” sulfur species and “unlock” their high gravimetric capacity. This material combination is akin to the relation between primer and TNT in explosives, one fast acting, the other with high gravimetric energy content. The cell using the hybrid cathode paired with Li metal anode delivers very high *full-cell* gravimetric and volumetric energy densities with good cycling

stability, surpassing both Li-S and Li-ion batteries. Our approach demonstrates the potential for such hybrid cathodes for high energy density applications.

11:45 AM ET09.07.11

Zn-Doped CdS Nano-Flower @ RGO/BN for High Performance Asymmetric Supercapacitor Application Chandan K. Maity and Ganesh Chandra Nayak; Indian Institute of Technology (Indian School of Mines), Dhanbad, India.

Transition metal sulphides with excellent electrochemical properties are proved to be an excellent electrode material for supercapacitor Application. In this work flower like Zn doped CdS has been grown over h-BN and reduced graphene oxide (RGO) by hydrothermal synthesis and explored the effect of Zn doped CdS on electrochemical activity. The samples were analyzed by FESEM, FTIR, XRD, XPS and RAMAN to access their morphology, interaction, growth and chemical nature. Flower like morphology has been grown on h-BN and RGO nanosheets. Zn doped CdS enhanced the compatibility and electrochemical performance of electrode material. Surface area of ternary composite of CdS/RGO/BN found to be enhanced as compared to binary composite which can be attributed exfoliation and stabilization of composite in presence of CdS. Maximum specific capacitance of 750 F/g at 1 A/g current density was obtained for Zn-CdS/BN/RGO composites in 1M KCl. The enhanced capacitive behavior is mainly due to smart combination of pseudocapacitance and double layer capacitance and synergistic effect of individual components. The ternary composite electrode material showed high energy density of 66.66Wh/kg at a power density of 404.68 W/kg and has 90% retention of specific capacitance after completion of 1000 cycles. For practical applicability, this electrode material has also been used for an asymmetric device and was able to glow 20 numbers of 2 V LED lights in parallel. These analysis showed that ternary composite of Zn doped CdS/RGO/BN can be a potential candidate for supercapacitor.

SESSION ET09.08: Li-Sulfur Batteries: Design and Applications

Session Chairs: Mei Cai and Feng Li
Wednesday Afternoon, November 28, 2018
Hynes, Level 3, Room 301

3:30 PM *ET09.08.03

Design of a High Energy Lithium-Sulfur Battery Ning Kang², Li Yang¹ and Mei Cai¹; ¹General Motors, Warren, Michigan, United States; ²Optimal CAE, Plymouth, Michigan, United States.

Li-S batteries has a theoretic energy density of 2510 Wh/kg and 2740 Wh/L, which is one of the most promising candidates for the next generation rechargeable batteries¹. Despite the great merits of the Li-S batteries such as high energy density and low cost, challenges, including polysulfide anions redox² and low lithium cycling efficiency, hinder its commercialization.

There has been great research effort devoted to the optimization of sulfur electrodes, the formulations of electrolytes as well as the ratios of electrolyte to sulfur. In this talk, we will address the impact of sulfur electrode porosity on the energy density of Li-S battery and the influence of electrolyte/sulfur ratio on the Li-S battery performance.

Based on our preliminary results, the total sulfur concentration [S] in the electrode increases exponentially with the decrease of the porosity. The [S] is 15 M at 70% porosity but increase to 30 M at 50% porosity, which may explain the reason for the 2nd discharge voltage plateau decay of the Li-S cells. The cycling performance of the lithium-selenium cells will also be discussed in this talk using different electrolyte formulations.

1) A. Manthiram, Y. Fu, S. Chung, C. Zu, Y. Su, *Rechargeable Lithium-Sulfur Batteries*, *Chem. Rev.*, 2014, 114 (23), pp 11751–11787

2) SS Zhang, *Improved Cyclability of Liquid Electrolyte Lithium/Sulfur Batteries by Optimizing Electrolyte/Sulfur Ratio*, *Energies* 2012, 5, 5190-5197

4:00 PM ET09.08.04

A Li-Li₂S₄ Battery with Improved Discharge Capacity and Cycle Life at Low Electrolyte/Sulfur Ratio Chao Shen^{1,2}, Jianxin Xie^{3,4}, Mei Zhang^{3,4}, Petru Andrei^{1,2}, M. Hendrickson⁵, E.J. Plichta⁵ and Jim Zheng^{1,2,6}; ¹Electrical and Computer Engineering, Florida A&M University and Florida State University, Tallahassee, Florida, United States; ²Aero-Propulsion, Mechatronics and Energy Center, Florida State University, Tallahassee, Florida, United States; ³Industrial and Manufacturing Engineering, Florida A&M University and Florida State University, Tallahassee, Florida, United States; ⁴High-Performance Materials Institute, Florida State University, Tallahassee, Florida, United States; ⁵Army Power Division, RDER-CCA, Aberdeen Proving Ground, Maryland, United States; ⁶Center for Advanced Power Systems, Florida State University, Tallahassee, Florida, United States.

Rechargeable lithium-sulfur (Li-S) batteries with a theoretical specific energy of 2,500 Wh kg⁻¹ are promising candidates to replace Li-ion batteries in many applications.¹ Even though Li-S batteries possess a high theoretical specific energy, several major technical challenges must be overcome. Many of these challenges are closely related to the formation of soluble lithium polysulfide (LiPS) intermediates. For instance, the irreversible redistribution of LiPS inside the battery leads to degradation of sulfur cathodes and passivation of Li metal anode. The uncontrolled LiPS relocation further leads to severe active material loss and self-discharge behavior of the batteries.

Ultimately, the most critical question for Li-S batteries is whether their high theoretical energy density can be practically delivered. The practical specific energy of Li-S batteries greatly depends on the electrolyte/sulfur (E/S) ratio of the batteries. To increase the energy density of rechargeable Li-S batteries, the E/S ratio should be decreased as much as possible. However, when the E/S ratio is decreased, multiple issues arise that degrade battery performance such as discharge capacity, cycle life, and rate capability. Very importantly, our group has recently found that once the electrolyte becomes saturated with liquid phase high-order LiPS, the solid phase LiPS cannot be further reduced and consequently does not contribute to the capacity of the cells at normal discharge rates.^{2,3} Therefore, the solubility of high-order LiPS can potentially lower the achievable specific energy of Li-S batteries to less than 500 Wh kg⁻¹, which becomes much less attractive for their commercialization.

To address the above mentioned challenges associated with conventional Li-S batteries, here we use the solid-state lower-order LiPS, i.e., Li₂S₄, as the cathode active material to construct a new type of Li-Li₂S₄ battery. By replacing the elemental sulfur with solid-state Li₂S₄ as the active cathode material, we avoid any solubility limitation previously encountered in the upper plateau of discharge. We found that in the lower plateau of discharge, the discharge capacity is not limited by the finite solubility of Li₂S₄, and much higher discharge capacity with a Li-Li₂S₄ cell is achieved under a higher sulfur content of 84% and a low E/S ratio of 4.4 ml g⁻¹. Moreover, the cycleability is also enhanced due to the reduced diffusion of high-order LiPS. We believe the reported results of our Li₂S₄ cathode open a new direction of cathode development for high energy density Li-S batteries.

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Electrochemical Study of Novel MoTe₂ Anode Based Lithium-Ion Full Cell Manas R. Panda^{1,2,3}, Anish Raj K², Arnab Ghosh², Ajit Kumar², Qiaoliang Bao³ and Sagar Mitra²; ¹IITB Monash Research Academy, Mumbai, India; ²Energy Science & Engineering, IIT Bombay, Mumbai, India; ³Material Science and Engineering, Monash University, Melbourne, Victoria, Australia.

Lithium-ion batteries (LIBs) are capable power sources for the convenient power electronic device, electric vehicle and space applications during last few years. However, the specific power density at high rate electrochemical test is still too poor to satisfy the industry needs. Hence, the development of high-performance rechargeable lithium-ion batteries becomes increasingly important. Transition metal dichalcogenides (TMDs) are considered as a promising anode for high-performance lithium-ion batteries due to their availability, low-cost, structural stability and layered structure for easy movement of lithium-ion into the host structure. Among TMDs, layered molybdenum ditelluride (MoTe₂) has the highest interlayer spacing and electronic conductivity which are the two key factors to provide more Li-ion storage property. However, their comprehensive study in lithium batteries is limited. Henceforth in the present study, the polycrystalline MoTe₂ powder has been prepared by a simple solid-state synthesis and characterized using XRD, FESEM, EDS, and HRTEM techniques. The physiochemical characterizations of the material prove the phase purity and crystallinity of the material. When the same material used as a working electrode for lithium battery, it gives a high reversible specific discharge capacity ~280 mA h g⁻¹ in the potential window of 0.1 V–2.8 V at a current density of 1.0 A g⁻¹. The above results stimulated us to construct a lithium-ion full cell using our synthesized anode against commercial LCO cathode for the first time. The electrochemical analysis of the MoTe₂/LCO full cell shows a competitive discharge capacity of ~140 mA h g⁻¹ at a current density of 500 mA g⁻¹ in the potential range of 1.75-3.75 V. The excellent cyclability of the full cell without capacity fading over 50 cycles was achieved with the coulombic efficiency ~100%. The obtained results positively open up the possibility of scaling up the technology for energy-storage applications.