

SYMPOSIUM ET07

Advanced Processing and Manufacturing for Energy Conversion, Storage and Harvesting Devices
November 26 - November 29, 2018

Symposium Organizers

Corie Cobb, University of Washington
Jianlin Li, Oak Ridge National Laboratory
Wilhelm Pfleging, Karlsruhe Institute of Technology
Pu Zhang, Navitas Systems

* Invited Paper

SESSION ET07.01: Material Innovations for Energy
Session Chairs: Jianlin Li and Liyuan Sun
Monday Morning, November 26, 2018
Hynes, Level 3, Room 312

8:30 AM *ET07.01.01

Materials Science Challenges for Future High Energy Lithium Batteries [Jun Liu](#); Pacific Northwest National Laboratory, Richland, Washington, United States.

Lithium (Li)-ion batteries are widely used for many applications today, but there is an increasing demand to increase their specific energy (Wh kg^{-1}) and energy density (Wh L^{-1}). Among the many options, Li metal is considered one of the most promising electrode materials for future batteries. When coupled with a high capacity cathode material, such as high-nickel-content lithium nickel manganese cobalt oxide (high-Ni NMC) or sulfur (S), rechargeable Li metal batteries have the potential to achieve a specific energy much higher than 350 Wh kg^{-1} . However, achieving such goals requires fundamental breakthroughs and new knowledge to optimize and integrate of all active inactive components on relevant scales with appropriate cell architectures. This talk will discuss the materials science and materials chemistry challenges, along with potential solutions, of using Li metal anodes based on the system level requirements of a high-energy cell. The important relationships between the Li anode and other cell components, such as high cathode loading and restricted amounts of electrolyte and Li, are reviewed in order to inspire new ideas to effectively address the grand challenges in rechargeable Li metal batteries.

9:00 AM *ET07.01.02

Materials Innovations for Emerging Energy Technologies [Liangbing Hu](#); University of Maryland, College Park, Maryland, United States.

I will start by giving an overview of active research activities in my research group located at University of Maryland Energy Research Center, including wood materials toward sustainability, 3000K high temperature materials and processing, and beyond-Li ion batteries (solid state, Na-ion). Then I will focus on our recent development on:

garnet-based solid-state Li-metal batteries including interface engineering to improve the wetting between Li metal anode and Garnet solid-state electrolyte (Nature Materials 2016; JACS 2016; Advanced Materials 2017; Science Advances 2017); Garnet based 3D Li ion conductive framework toward high energy density Li-S batteries (EES 2017); Garnet nanofiber based flexible, hybrid electrolyte with a high Li ion conductivity (PNAS 2016). assembly and functionalization strategies of **wood nanocellulose** aimed at specific properties, with an eye toward high impact applications including energy, electronics, building materials and water treatment, including nanomanufacturing and light management in transparent nanopaper for optoelectronics (as a replacement of plastics); mechanical properties of densely packed nanocellulose for lightweight structural materials (replacement of steel, Nature 2018); artificial tree for high-performance water desalination and solar steam generations; mesoporous, three-dimensional carbon derived from wood for advanced batteries (replacement of metal current collectors for beyond Li-ion batteries).

9:30 AM ET07.01.03

Influence of Molecular Structure of Extractor Molecules on Electrochemical Performance of Supercapacitors Electrodes Fabricated by Liquid-Liquid Extraction of MnO_2 Particles [Ri Chen](#)^{1,2}, Rakesh P. Sahu¹, Igor Zhitomirsky² and Ishwar K. Puri^{1,2}; ¹Mechanical Engineering, McMaster University, Hamilton, Ontario, Canada; ²Materials Science and Engineering, McMaster University, Hamilton, Ontario, Canada.

The growing interest in using manganese dioxide (MnO_2) for supercapacitor (SC) electrodes is attributed to its high theoretical specific capacitance (1400 F g^{-1}), relatively large voltage window, natural abundance and environmental friendliness. However, the low electronic conductivity of MnO_2 impedes its further development in commercial applications. Normally, the conductive additives such as multiwalled carbon nanotubes (MWCNT) are introduced to enhance the electronic conductivity of MnO_2 for the fabrication of SC electrodes. However, it is critical to achieve a high electrochemical performance of SC with high active mass loading at high charge-discharge scan rates. The important task is to avoid agglomeration of MnO_2 nanoparticles and MWCNT. New strategies are developed to address this problem. In this work, liquid-liquid extraction method (LLEM) is developed to prepare non-agglomerated small sized MnO_2 nanoparticles with porous surface and improved mixing of MnO_2 and MWCNT. Head-tail (HT) surfactants, containing amine, phosphonate or carboxylic groups, are used as extractors for extraction of MnO_2 nanoparticles. Moreover, it was found that conceptually new multifunctional head-tail-head (HTH) surfactants containing one phosphonate end and one carboxylic end can be used as efficient extractors for LLEM. Furthermore, HTH surfactants can be used as dispersing and charging agents to prepare stable MnO_2 suspension for electrophoretic deposition (EPD) of thin film. The influence of molecular structure of different extractor molecules such as hexadecylamine (HDA), hexadecylphosphonic acid (HDEPA), palmitic acid (PA) and 16-phosphonohexadecanoic acid (16PHA) on the electrochemical performance of SC electrodes have been investigated

systematically. Various interactions between nanoparticles and extractor molecules such as covalent, ion-pair or electrostatic interactions play role in preparing the non-agglomerated MnO₂ nanoparticles. Compared to other HT surfactants such as HDA, HDBA and PA, the HTH surfactant 16PHA used as extractor for fabrication of SC electrodes with active mass loading of 37mg cm⁻² showed highest capacitance of 5.7 F cm⁻² (157 F g⁻¹) and 2.5 F cm⁻² (67 F g⁻¹) at a scan rate of 2 mV/s and 100mV/s, respectively. Additionally, MnO₂ particles extracted by 16PHA, are negatively charged and deposited on the anode surface by EPD forming a relatively smooth, dense and agglomerate-free thin film. The conceptually new strategy using multifunctional HTH surfactants as extractor for preparation of non-agglomerated nanoparticles by LLEM paves the way for the fabrication of different functional nanomaterials for advanced applications.

9:45 AM ET07.01.04

Electrochemical Supercapacitor Based on Co₃O₄-MnO₂-Graphene Oxide Nanocomposite Dipali S. Patil, Sachin A. Pawar and Jae Cheol Shin; Yeungnam University, Gyeongsan-si, Korea (the Republic of).

Various metal oxide nanostructures of RuO₂, MnO₂, NiO, Co₃O₄, SnO₂, MoO₃, and V₂O₅ have been used widely as promising electrode materials for supercapacitor applications. Among these Cobalt oxide (Co₃O₄) is believed to be one of the best materials among transition metal oxides for supercapacitors owing to its high theoretical capacitance (3560 Fg⁻¹), environmental friendliness, and better electrochemical performance. On the other hand, MnO₂ is one of the most favorable pseudo-capacitor electrode materials because of its low cost, environmentally friendly characteristics, and excellent capacitive performance. The intrinsically low conductivity of MnO₂, however, limits its practical applications as a pseudo-capacitive material. Several strategies have been employed to improve the electrical conductivity of MnO₂ based electrode. One simple strategy is to combine MnO₂ with other metal oxides to form hybrid nanostructure with sufficient electrical conductivity. Another approach is to integrate it with electrically conducting materials like carbon materials or graphene to enhance the electrochemical stability and electric conductivity of the electrode. In the present study, we developed new Co₃O₄- MnO₂-graphene oxide-based electrode by simple hydrothermal technique. The synthesized electrode materials are characterized by, XRD, XPS, FE-SEM, TEM, HRTEM etc. The supercapacitor performance of all the prepared electrodes was assessed by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge/discharge measurements. The important parameters of electrochemical supercapacitor like specific capacitance, energy density and electrochemical stability are measured in this work.

10:00 AM BREAK

10:30 AM *ET07.01.05

Design and Development of Sodium-Ion Batteries Based on Layered Transition Metal Oxide Cathode Material Zifeng Ma; Shanghai Electrochemical Energy Devices Research Center, Department of Chemical Engineering, Shanghai Jiao Tong University, Shanghai, China.

Rechargeable Li-ion batteries have been considered as a promising power source for the electric vehicles and the grid energy storage systems. However, lithium resources are limited and will restrict the huge applications of Li-ion batteries. It is of great significance to develop eco-friendly sodium ion batteries which employ abundant sodium resources. Recently, we developed the large-scale synthesis route of NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂ (NFM) by using hydroxide co-precipitation combined with solid-state reaction, and the optimization reaction condition was studied by using in situ XRD. The metastable structure change of NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂ during electrochemical sodium ion intercalation which cycled at 0.1C rate between 2.0 to 4.0V, and 2.0 to 4.3V, were studied by using in operando TXM-XANES and XRD, and the thermal decomposition behavior and structure evolution of charged NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂ cathode material during heating process was measured by using in situ high-energy X-ray diffraction (HEXRD) technique. The effect of Ca-substitution in Na sites on the structural and electrochemical properties of Na_{1-x}Ca_{x/2}NFM (x=0, 0.05, 0.1). X-ray diffraction patterns of the prepared Na_{1-x}Ca_{x/2}NFM samples show single α-NaFeO₂ type phase with slightly increased alkali-layer distance as Ca content increased. The cycling stabilities of Ca-substituted samples are remarkably improved. The Na_{0.9}Ca_{0.05}NFM cathode delivers capacity of 116.3 mAh g⁻¹ with capacity retention of 92% after 200 cycles at the 1C rate. In operando XRD indicates a reversible structural evolution through an O3-P3-P3-O3 sequence of the Na_{0.9}Ca_{0.05}NFM cathode during cycling. Compared to NaNMF, the Na_{0.9}Ca_{0.05}NFM cathode shows wider voltage range in pure P3 phase state during charge/discharge process and exhibits better structure recoverability after cycling. The superior cycling stability of Na_{0.9}Ca_{0.05}NFM makes it a promising material for practical applications in sodium ion batteries. A new portable energy storage device based on SIB has been designed and assembled. Layered oxide NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂ and hard carbon were used as cathode and anode, respectively. The SIB pouch cell has been designed and the electrochemistry and safety performance were tested.

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11:00 AM *ET07.01.06

Evaluation of Li-Ion Batteries Built with Recycled NCM 111 Cathode Jun Wang¹, Paul Gionet¹, Dennis Bullen¹, Ronnie Wilkins¹, Ian O'Connor¹, Leslie Pinnell¹, Derek C. Johnson¹, Zhangfeng Zheng², Mengyuan Chen² and Yan Wang²; ¹A123 Systems LLC, Waltham, Massachusetts, United States; ²Mechanical Engineering, Worcester Polytechnic Institute, Worcester, Massachusetts, United States.

Recycling of Li-ion batteries that have reached end-of-life (EOL) becomes increasingly critical to long term sustainability of electrochemical energy storage ecosystem, as the number of Li-ion battery powered portable devices and vehicles continues to increase rapidly. Many components incorporated in commercial Li-ion batteries face limited raw materials supply, such as Lithium, Nickel and Cobalt. Recovering those elements from spent batteries serves a dual purpose of reducing the environmental impact of hazardous materials disposal as well as providing a stable stream of the necessary metals to meet ever-growing manufacturing demand.

This research focused on evaluating nickel cobalt manganese oxide (NCM 111) cathode powder regenerated from a closed loop recycling process which targets end-of-life electric vehicle Li-ion batteries.^[1-2] This process starts with spent batteries regardless of cathode chemistry, produces stoichiometric LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ (NCM 111) cathode material with electrochemical properties rivaling commercial control NCM 111. Prismatic pouch cells consist of recycled NCM 111 were fabricated at small and large capacity, 1.0 Ah and 11.0 Ah, respectively. Subsequent performance benchmarking against control cells was conducted through an array of metrics including rate capability HPPC, cold crank, cycle life and calendar life. Cells built with recycled NCM 111

demonstrated similar cyclability to control at >2500 cycles to 80% retention under +1C, -2C cycling conditions, and no obvious difference was observed for cold crank, HPPC and calendar life between commercial control and recycled cells. The rate capability, however, seems to slightly favor recycled cell at rates above 2C. Those results undoubtedly validate the recycled NCM 111 cathode as a legitimate contender for commercial electric vehicle Li-ion battery applications.

References:

1. Gratz, E., Sa, Q., Apelian, D., Wang, Y., J. Power Sources 2014, 262, 255-262.
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11:30 AM ET07.01.07

High-Performance Energy Storage from Biomass Materials Yunya Zhang and Xiaodong Li; Mechanical and Aerospace Engineering, University of Virginia, Charlottesville, Virginia, United States.

Considering the irreversible environmental damages and the huge cost induced by fossil fuel consumption and Co/graphite mining, it is environmentally and socially significant to produce energy storage devices from low cost and renewable materials. In order to achieve lightweight, mechanical robustness, and various functionalities, nature often constructs hierarchically porous structures or thin films. These delicate structures, if well utilized, can largely improve the performances of energy storage devices. Thusly, a rational design strategy is to derive high-performance electrodes from biomass materials. Banana peels, as the inedible part of the most popular fruit, have a typical porous structure. After treated by NiNO₃, the micron sized pores on activated banana peel (ABP) effectively enhanced the accessibility of electrolyte, nanopores immobilized and encapsulated polysulfides, and graphene coated Ni nanoparticles improved conductivity, leading to a high specific capacity of the assembled Li-S batteries. To increase the utilization efficiency of graphene, graphene oxide sheets were incorporated with activated paper carbon (APC) via capillary method. Thin graphene layer were coated around cellulose fibers with nano sized bulges and wrinkles, which not only increased sulfur loading, but also encapsulated polysulfides and buffer volume fluctuations, rendering an ultra-long lifespan of 1000 cycles with over 60 % capacity retention rate of Li-S batteries. In addition to optimize the performance of biomass derived electrodes, we also seek holistic utilization of biomass materials. An all-solid, flexible supercapacitor was fabricated from a whole egg. Eggshell was used as templates and egg white/yolk was employed as carbon source for 2D graphene like carbon films. Solid electrolyte was produced by egg white/yolk and KOH. Egg shell membrane was then used as separator. The assembled supercapacitors exhibited superior performances.

11:45 AM ET07.01.08

Controlling Charge Transport in Spinel Oxides through Manipulation of Cation Site Occupation Anuj Bhargava and Richard Robinson; Cornell University, Ithaca, New York, United States.

Ternary spinel oxides are actively used and researched for applications ranging from electronics, sensors, catalysis, data storage, to energy storage due to their useful magnetic, catalytic, and electronic properties. One intriguing nanomaterial is the non-stoichiometric p-type spinel Co_xMn_{3-x}O₄, in which cation site occupation is an important determinant of materials properties. Therefore, by manipulation of cation configurational disorder, properties such as the charge carrier density and the associated electrical conductivity can be easily controlled. The manipulation of cation configuration disorder is carried out by changing the Co to Mn ratio (or the 'x' value in Co_xMn_{3-x}O₄), which leads to the variation of (1) atomic distribution of Co and Mn atoms present at tetrahedral (Td) and octahedral (Oh) sites in the spinel system, and (2) oxidation states of the cations. In this work, we utilize a new technique to characterize the configurational disorder in spinels. We demonstrate that x-ray emission spectroscopy (XES) is a more reliable method than traditionally used K-edge x-ray absorption spectroscopy (XAS) to extract cation site occupation. Comparison between the XAS and XES techniques reveal that XES provides not only the site occupation information that XAS reports, but also additional information on the valence states of the cations at each site. We show that the XES error is lower than the EXAFS error in all cases, by up to ~20%. Additionally, the error for EXAFS is as high as 35% whereas for XES, the error determined is consistently smaller than 10%. Furthermore, we correlate the extracted site occupation data to the electrical conductivity and the supercapacitor performance and observe a strong correlation between structural properties and electronic properties of spinels. We show that the number of hole acceptor/donor pairs of Mn²⁺/Mn³⁺ at Oh sites is proportional to both the electrical properties and the energy density of the supercapacitors. Finally, via the optimization of configurational order in the Co_xMn_{3-x}O₄ nanoparticles system, we were able to increase the energy density and specific capacitance of the supercapacitors by 2x as compared to previously reported values.

SESSION ET07.02: Materials Processing
Session Chairs: Sergiy Kalnaus and Jianlin Li
Monday Afternoon, November 26, 2018
Hynes, Level 3, Room 312

1:30 PM *ET07.02.01

The Processing Science and Engineering Research Portfolio for Advanced Vehicle Batteries at the U.S. Department of Energy Peter W. Faguy; Vehicle Technologies Office, Department of Energy, Washington, District of Columbia, United States.

The widespread adoption of electric vehicles using advanced battery technologies and the development of their manufacturing base in the United States are critically important goals for the US economy and therefore a major focus of research and development sponsored by DOE's Office of Energy Efficiency and Renewable Energy. Materials development is often touted as the most important enabling activity, however in a rank of major cost items, manufacturing costs ranks just below the cathode components. In addition to the need to reduce costs, US R&D should also focus on new, yet-to-be-scaled processing technologies that, when developed and implemented in the US provide both a strong component of US energy security and US-based employment in a field expected to grow to over \$100B in the next twenty years.

Processing science and engineering has traditionally been underrepresented in federally funded electrochemical energy storage R&D. Over the last eight years, the Vehicle Technologies Office (VTO) has been building an advanced processing R&D portfolio. This includes competitively funded research at universities, small businesses, and large corporations as well as programs supported across the array of the national laboratory complex. This presentation will provide an overview of the sub-program's history and some examples of early successes. Future research directions and scenarios for possible funding opportunities will also be discussed.

2:00 PM ET07.02.02

Colloidal Control of Percolating Conductive Networks and Short-Range Electronic Contacts for High-Rate Battery Performance Maureen Tang, Samantha Morelly and Nicolas Alvarez; Drexel University, Philadelphia, Pennsylvania, United States.

Despite the societal and economic importance of advanced batteries, the complicated relationships between electrode processing, structure, and performance are still poorly understood. In this work, we combine fundamental rheological and electrochemical studies to investigate the relationships between slurry microstructure, electrode morphology, and battery rate capability at industrially-relevant compositions of inactive material. In one example of our approach, dry-mixing $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ (NMC) with carbon black decreases the free carbon concentration and consequently the ability of the slurry to form a gel network, as revealed by small-angle oscillatory shear measurements. Less free carbon weakens the strength of the slurry's viscous and elastic moduli and is also reflected by a decrease in electronic conductivity of the dried electrode. Despite a clear dependence of slurry moduli and electronic conductivity on free carbon concentration, there is no obvious relationship between in-plane electronic conductivity and battery rate capability, demonstrating that short-range electronic contacts are more important than either ion transport or long-range electronic conductivity to cathode rate capability [1]. We further explain this finding by measuring the critical gelation concentration of carbon black and showing that it is independent of the NMC volume fraction, indicating that active material resides in the interstitials of the percolating carbon network [2].

Our identification of short-range electronic contacts as the key parameter for electrode performance motivates the development of new methods to observe and quantify these contacts. We use SEM-EDS to quantify the carbon black heterogeneity and show its sensitivity to a variety of manufacturing parameters, including the impact of polymer chain scission during mixing. In order to adapt this approach for carbonaceous active materials such as graphite, we substitute carbon black with commercial carbon-coated Fe nanoparticles as a contrast-enhancing agent that permits spectroscopic distinction between active material, conductive additive, and binder [3]. The Fe nanoparticles further enable nano x-ray computed tomography (XCT) to obtain three-dimensional images of the active material and carbon-binder-domains with 126 nm voxel resolution. Future work will discuss the relationships between the observed microstructure and the battery performance in more detail, as well as our efforts towards alternative electrode designs with optimal carbon connectivity.

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[3] Morelly et al, in revision, (2018).

2:15 PM ET07.02.03

A Systematic Approach for Characterizing the Surface Free Energy of Composite Electrodes for Li-Ion Batteries Ali Davoodabadi¹, Jianlin Li², David Wood² and Congrui Jin¹; ¹Mechanical Engineering Department, Binghamton University, The State University of New York, Binghamton, New York, United States; ²Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

One of the crucial steps in battery manufacturing is the electrolyte wetting step which typically requires a relatively long time to be completed. It is known that the relationship between polar and dispersive components of the electrolyte surface tension and the electrode surface free energy (SFE) plays a vital role in the extent of wetting and, thus, tuning the SFE can accelerate the wetting step in battery manufacturing.

This work developed and validated a systematic approach to characterize surface free energy of composite electrodes for lithium-ion batteries, which has never been reported in literature. We introduced two main surface parameters, r and f , that represent the surface roughness ratio and surface solid fraction, respectively. These parameters are crucial in determining the so called actual SFE of the electrodes.

The effect of slurry formulation and electrode porosity on the SFE of electrodes were investigated. It is demonstrated that the SFE of $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ cathode was higher than the graphite anode. Replacing the conventional Polyvinylidene fluoride (PVDF) with water soluble binder significantly increased the polar component of the electrodes surface free energy. The increased polar component is expected to enhance the wetting of the electrodes toward different common electrolytes. The results from this work provide insights in slurry formulation for optimal slurry wetting on current collector and electrolyte wetting on dry electrodes.

2:30 PM ET07.02.04

Enhancement of Cost Effective Pt-Based Catalyst Activity and Durability for Proton Exchange Membrane Fuel Cell Application Ali Abdelhafiz², Jianhuang Zeng¹, Bote Zhao² and Meilin Liu²; ¹South China University of Technology, Guangzhou, China; ²Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Proton exchange membrane fuel cells (PEMFCs) have tremendous potential to be the preferred power sources for many emerging technologies, from electric vehicles to portable/mobile devices and smart grids, because of their numerous inherent advantages such as high efficiency, high energy density, low emissions, and fast start-up and shut-down capability. While PEMFCs are expected to use platinum group metal (PGM)-based catalysts in the near-term, the cost of the Pt-based catalyst alone constitutes over 40% of the fuel cell stack cost. Enormous efforts have been devoted to reducing the high cost of catalyst. To date, the catalysts can be classified into three groups according to the active component used: PGM-based catalyst (supported on carbon or other supports); PGM-based catalysts that are modified or alloyed with other metals such as Cu, Co, and Ru; and PGM-free catalysts such as non-noble metals and organometallic complexes. PGM-free catalysts are attractive for cost reduction of PEMFC technology, however, in reality is still a long way to go to before they can be used to run actual fuel cell application. Here in, we are proposing a facile, one-step, synthesis of Pt-based alloy nanoparticles for cost effective low temperature oxygen reduction reaction electrocatalysis at industrial scale.

Direct Pt nanoparticles synthesis is performed under room temperature to form a branched triple and quadruple-pods particles with an average size of ~ 3.5 nm, as confirmed by X-ray diffraction (XRD) and Scanning transmission electron microscope (STEM) analysis. Rotating disc electrode (RDE) setup is used to probe ORR. Results showed that synthesized Pt-nanoparticles superior catalytic activity for oxygen reduction reaction compared to state of the art Pt-XC/72R commercial catalyst. Pt-nanoparticles periphery are conformed of high index family crystallographic planes, as observed by STEM analysis. High index planes contain lower density of kinks, which optimize the adsorption/desorption energies to be neither too weak nor too strong. Pt-nanoparticles under accelerated durability testing (ADT) outperform their state of the art commercial catalyst counterparts, surviving 81% of electrochemical active surface area (ECSA) after 10,000 testing cycles.

Using a catalyst coated membrane (CCM) technique membrane electro assembly (MEA) was prepared to test Pt nanoparticles under actual PEMFC operation conditions (i.e. temperature and humidity). MEA prepared using the synthesized Pt-nanoparticles outperformed their counterparts prepared by Pt-XC/72R state of the art commercial catalyst with 27% enhancement factor. The reported Pt-based nanoparticles propose a competitive and more efficient synthesis route to prepare large scale commercial catalyst without the need of sophisticated apparatus or special heating conditions.

2:45 PM BREAK

3:15 PM *ET07.02.05

Modeling and Characterization for Processing and Manufacturing of Li-Ion Cells Sergiy Kalnaus, Srdjan Simunovic, A. Kumar, Srikanth Allu and

John A. Turner; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Li-ion batteries are complex systems whose electrochemical performance depends on properties and design of many components that are combined to make a cell. Manufacturing of these components involves complicated processing, from slurry preparation, to casting and drying, to electrode calendaring. Each step depends on several variables, for example drying rate or calendaring pressure. Relationships between these variables and the resulting performance of the electrochemical cell has not been completely established. This talk reports on efforts towards establishing such relationships through characterization and mathematical modeling. Methods for computing elastic and inelastic properties of battery electrodes from their microstructure will be presented and the results will be correlated with degree of electrode compression during calendaring. Predictive capabilities of the models in terms of electrochemical performance will be discussed.

This research at Oak Ridge National Laboratory, managed by UT Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725, was sponsored by the Vehicle Technologies Program for the Office of Energy Efficiency and Renewable Energy.

3:45 PM ET07.02.06

Light-Driven BiVO₄-C Fuel Cell with Simultaneous Production of H₂O₂ Xinjian Shi and Xiaolin Zheng; Stanford University, Stanford, California, United States.

Photoelectrochemical (PEC) systems have been researched for decades for their great promise to convert sunlight to fuels. Majority of the research on PEC has been focusing on using light to split water to hydrogen and oxygen, and its performance is limited due to the need of additional bias. Another research direction on PEC focuses on using light to decompose organic materials while producing electricity. In this work, we report a new type of unassisted PEC system that uses light, water and oxygen to simultaneously produce electricity and valuable hydrogen peroxide (H₂O₂) on both photoanode and cathode, *i.e.*, $light + 2H_2O + O_2 = electricity + 2H_2O_2$. This new PEC system is essentially a light-driven fuel cell with H₂O₂ as the main product on both electrodes, and it consists of BiVO₄ photoanode where water is oxidized to H₂O₂ and carbon cathode where O₂ is reduced to H₂O₂. In addition to producing H₂O₂, this PEC system also generates electricity, achieving a maximum power density of 0.194mW/cm², an open circuit voltage of 0.61V, and a short circuit current density of 1.09mA/cm². The electricity output can be further used as a sign for cell function when accompanied by a detector such as an LED light or a multimeter. This is the first work that shows H₂O₂ two-side generation with strict key factors study on such system, with clear demonstration on electricity output ability for it using low-cost earth abundant materials on both sides, which represents an exciting new direction for PEC systems.

4:00 PM ET07.02.07

Monomer Derived Poly(Furfuryl)/BaTiO₃ 0–3 Nanocomposite Capacitors—Maximization of the Effective Permittivity Through Control at the Interface Frederick A. Pearsall^{1,2}, Julien Lombardi¹ and Stephen O'Brien^{1,2}; ¹Chemistry, City College of New York, New York, New York, United States; ²Chemistry, The Graduate Center of the City University of New York, New York, New York, United States.

Frequency stable, high permittivity nanocomposite capacitors produced under mild processing conditions offer an attractive replacement to MLCCs derived from conventional ceramic firing. Here, 0–3 nanocomposites were prepared using gel-collection derived barium titanate (BTO) nanocrystals, suspended in a poly(furfuryl alcohol) matrix, resulting in a stable, high effective permittivity, low loss dielectric. The nanocrystals are produced at 60 °C, emerging as fully crystallized cubic BTO, 8 nm, with a highly functional surface that enables both suspension and chemical reaction in organic solvents. The nanocrystals were suspended in furfuryl alcohol where volume fraction of nanocrystal filler (v_f) could be varied. Polymerization of the matrix in situ at 70–90 °C resulted in a nanocomposite with a higher than anticipated effective permittivity (up to 50, with v_f only 0.41, from 0.5–2000 kHz), exceptional stability as a function of frequency, and very favorable dissipation factors ($\tan \delta < 0.01$, $v_f < 0.41$; $\tan \delta < 0.05$, $v_f < 0.5$). The increased permittivity is attributed to the covalent attachment of the poly(furfuryl alcohol) matrix to the surface of the nanocrystals, homogenizing the particle–matrix interface, limiting undercoordinated surface sites and reducing void space. XPS and FTIR confirmed strong interfacial interaction between matrix and nanocrystal surface. Effective medium approximations were used to compare this with similar nanocomposite systems. It was found that the high effective permittivity could not be attributed to the combination of two components alone, rather the creation of a hybrid nanocomposite possessing its own dielectric behavior. A nondispersive medium was selected to focus on the frequency dependent permittivity of the 8 nm barium titanate nanocrystals. Experimental corroboration with known effective medium approximations is evident until a specific volume fraction ($v_f \approx 0.3$) where, due to a sharp increase in the effective permittivity, approximations fail to adequately describe the nanocomposite medium.

4:15 PM ET07.02.08

Simple Process for Preparing Core-Shell Type Hybridized Nanoparticles for Polymer Electrolyte Membrane Akito Masuhara^{1,3}, Keiji Shito¹, Yuki Takahashi¹, Satoshi Sekine¹, Kazuki Koseki¹, Keisuke Tabata¹, Tomohiro Nohara¹ and Toshihiko Arita²; ¹Yamagata University, Yonezawa, Japan; ²IMRAM, Tohoku University, Sendai, Japan; ³Roel, Yamagata University, Yonezawa, Japan.

We designed a novel polymer electrolyte membrane (PEM) for PEFC using inexpensive materials and fabricating precise nanostructures. Hence, we have focused on general inorganic filler filling method, which has advantage on improvement of heat resistance and gas barrier properties of the membrane. Novel model PEM consists of silica nanoparticles (NPs) with proton conductive polymer layer prepared by Reversible Addition-Fragmentation chain Transfer Polymerization with Particles (RAFT PwP)¹ on its surface. RAFT PwP can prepare precisely adsorbed hydrophilic polymer layer on particles surface, 2D ion-conductive channel consist of weak acids can be effectively prepared². RAFT PwP of acrylic acid and styrene with spherical silica NPs successfully synthesized, and coated poly(acrylic acid) and polystyrene block copolymers (PAA-*b*-PS) on the spherical silica filler particles (silica@PAA-*b*-PS)³.

Silica@PAA-*b*-PS was synthesized by the RAFT PwP. Silica@PAA-*b*-PS measured by ¹H NMR, GPC, FT-IR, XPS, TGA, SEM, and TEM. Proton conductivity of the silica@PAA-*b*-PS was measured under 98% RH with different temperature by impedance analyzer. The dried particles were processed into pellets of 1.3 mm diameter under a pressure of about 7 ton and porous gold paint was coated on quarter-circle onto both side of the pellet for the impedance measurements.

PAA-*b*-PS were determined to be $M_n = 32000$, PAA:PS = 61:39 by ¹H NMR and GPC. Silica@PAA-*b*-PS was successfully prepared by RAFT PwP. As the result of PAA-*b*-PS coating on the silica surface, pelletized silica@PAA-*b*-PS expressed relatively large proton conductivity of $1.22 \times 10^{-4} \text{ S cm}^{-1}$ (at 60 °C and 98% RH) as PAA based electrolyte with the activation energy of 0.21 eV. This low activation energy suggests proton conductive mechanism is under Grotthuss mechanism. By coating with PS layer, it is possible to maintain proton conduction under low humidity condition. The particle developed can be useful to build novel and further improved filler filling PEM for polymer electrolyte fuel cells (PEFC).

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[3] T. Arita, A. Masuhara, et. al., Japanese Unexamined Patent Application Publication

4:30 PM ET07.02.09

Low-Temperature Plasma Exfoliated Graphene for Supercapacitors Application [Keliang Wang](#)¹ and Qi H. Fan²; ¹Fraunhofer USA, Center for Coatings and Diamond Technologies, Michigan State University, East Lansing, Michigan, United States; ²Michigan State University, East Lansing, Michigan, United States.

Radio frequency (RF) dielectric barrier discharge plasma was used to exfoliate graphite oxide (GO) into graphene. The GO was synthesized from a modified Hummers method. The exfoliation occurred swiftly once the RF power and gas pressure reached a level that enabled sufficient energy transfer from the plasma to the GO. X-ray diffraction (XRD) and transmission electron microscopy (TEM) confirmed that graphene or carbon nanosheets were successfully prepared. The plasma exfoliation mechanism was revealed based on the microstructure characterization and optical emission spectroscopy, which indicated that oxygen was released at the moment of exfoliation. Inspired by the success of GO exfoliation, N-doping was realized by treating pyrrole-modified GO with plasmas. The N concentration in the resulted graphene depended strongly on the plasma gas. Of the gases studied, CH₄ treated pyrrole-modified GO (GO-PPY-CH₄) contained considerable concentration of N that was beneficial to electrical double layer capacitors (EDLCs). Supercapacitors made of the N-doped graphene exhibited promising capacitive characteristics. Electrochemical measurements showed that the GO-PPY-CH₄ presented an initial specific capacitance of ~312 F g⁻¹ under 0.1 A g⁻¹ charge/discharge current and ~100% retention after 1000 consecutive cycles under currents ranging from 0.1 to 10.0 A g⁻¹ in 6 mol L⁻¹ KOH electrolyte. This study demonstrated that the plasma exfoliation was an efficient approach to fabricating graphene and N-doped graphene that had promising potential to be high-performance electrode materials for EDLCs. Furthermore, flexible solid-state supercapacitors featuring lightweight and large capacitance have many attractive applications in portable and wearable electronics. The study demonstrates a magnetically enhanced dielectric barrier discharge that has the potential to efficiently exfoliate polyaniline-modified graphene at low input power. The plasma exfoliated N-doped graphene is subsequently used to fabricate flexible solid-state supercapacitors, which exhibit large specific capacitance of 45 mF/cm² at 0.2 A cm⁻² charging rate, ~100% capacitance retention after 1000 charge/discharge cycles at different current densities, and outstanding mechanical flexibility. The magnetically enhanced plasma exfoliation of graphite oxide offers a potentially cost-effective approach to producing high-quality carbon nanomaterials for energy storage.

SESSION ET07.03: Poster Session I: Energy Storage

Session Chairs: Jianlin Li and Pu Zhang

Monday Afternoon, November 26, 2018

8:00 PM - 10:00 PM

Hynes, Level 1, Hall B

ET07.03.01

Solution-Processable Conducting Polymers for Macroscale High-Rate Energy-Storage Devices [Ashley N. Hoffmaster](#)¹, [Megan B. Sassin](#)¹, [Jeffrey W. Long](#)¹, [Chi Kin Lo](#)², [Anna Österholm](#)² and [John R. Reynolds](#)²; ¹Naval Research Laboratory, Washington, District of Columbia, United States; ²Georgia Institute of Technology, Atlanta, Georgia, United States.

Conducting polymers (CPs) have been extensively investigated as prospective charge-storage materials for electrochemical capacitors. However, the methods typically used to fabricate CP-based electrodes (e.g., electrodeposition for 2D thin-film electrodes or solution-based synthesis followed by processing into composite-electrode formulations) severely limit their footprint-normalized capacity and rate performance, hindering their technological relevance. As an alternative, Reynolds and co-workers recently developed synthetic methods that yield gram-scale quantities of solution-processable CPs based on ProDOT and EDOT.^{[i],[ii]} The ability to solubilize these CP variants makes them amenable to incorporation into advanced 3D electrode architectures. We demonstrate scalable solution-based deposition methods to incorporate these CPs as conformal thin films at loadings of ≥ 30 wt.% throughout macroscopically thick 3D carbon-paper electrodes. The resulting 3D electrode design maintains the inherently fast charge-storage kinetics of the CP, yet greatly enhances the footprint-normalized capacitance by a factor of 120, from 0.4 mF cm⁻² for the 2D thin film to 48 mF cm⁻² for the 3D electrode. To demonstrate the technological relevance of these CP-3D carbon paper electrodes, we assess their rate-dependent capacitance/capacity, self-discharge, and cycle life in two terminal devices.

[i]. Ponder Jr., J. F.; Österholm, A. M.; Reynolds, J. R. "Designing a Soluble PEDOT Analogue without Surfactants or Dispersants," *Macromolecules* **49**, 2106 (2016).

[ii]. Österholm, A. M.; Ponder Jr., J. F.; Kerszulis, J. A.; Reynolds, J. R., "Solution Processed PEDOT Analogues in Electrochemical Supercapacitors," *ACS Appl. Mater. Interfaces* **8**, 13492 (2016).

ET07.03.02

Improved Mixed Transition Metal Oxide Thin-Films Supercapacitor Electrodes by Photonic Synthesis [Madhu S. Gaire](#)¹, [Sijun Luo](#)², [Binod Subedi](#)¹, [Kurt Schroder](#)³, [Stan Farnsworth](#)³ and [Douglas Chrisey](#)¹; ¹Physics, Tulane University, New Orleans, Louisiana, United States; ²Novacentrix, Austin, Texas, United States.

Transition metals oxides have attracted attention due to their high pseudocapacitance and excellent performance in electrochemical applications. More recently, the research has focused on fabrication of the mixed transition metal oxides, because of their wide working voltage range, resulting in enhanced specific capacitance. Our research has focused on preparation of manganese-cobalt based mixed oxides (Mn-Co); specifically, we hypothesize that Co addition hinders the dissolution of Mn into the electrolyte, resulting in enhanced capacitance and long cycle-life. By using photonic curing system (PulseForge 1300, Novacentrix, with fluence value of 7.5 J/cm²) for the pulsed Xe light irradiation of spray-coated (Mn-Co)-acetylacetonate solid precursor films under ambient whereby we have instantaneously synthesized films on commercial Pt-coated Si-substrates for potential use as electrode materials in supercapacitor devices. We have shown that the first two pulses of irradiation of (Mn-Co)-acetylacetonate molecules result in self-assembly and crystallization of nanocomposite thin films while subsequent pulses improve the crystallinity of nanocomposite film and evaporate the carbon component. We characterized our films using Scanning Electron Microscopy, X-ray Diffraction, and Raman Spectroscopy. Electrochemical characterization, i.e., cyclic voltammetry and charge-discharge cycling, were carried out in three-electrode cell configuration (where Hg-HgO, Pt, and our sample are the reference, counter and working electrodes respectively) with 1 M KOH as the electrolyte. The presence of redox peaks in cyclic voltammetry curves confirms the pseudocapacitive behavior of the sample while identical CV curves even at higher scan rates further suggest excellent rate

capability and ideal supercapacitor behavior. The galvanostatic charge-discharge measurements (GCD) performed at 0.25 mA current resulted in specific capacitance as high as 12 mF/cm² for the electrode prepared with 2-pulses of irradiation. After performing GCD measurements for 5000 cycles, we found that the electrode retains as high as 80% capacitance, which shows that as prepared electrode possesses excellent stability and long cycle-life. Next steps will be the work on other mixed oxides electrodes, such as Ni-Mn oxides, Mn-Fe oxide and thicknesses and different fluence values during irradiation.

ET07.03.03

CNT Flexible Membranes for Energy Storage and Conversion Systems Cullen Kaschalk⁴, Sean Spratt⁵, Kofi Adu^{2,1}, Ramakrishnan Rajagopalan^{3,1} and Clive Randall¹; ¹Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania, United States; ²Physics, The Pennsylvania State University, Altoona, Altoona, Pennsylvania, United States; ³Engineering, The Pennsylvania State University, DuBois, DuBois, Pennsylvania, United States; ⁴Electrical Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States; ⁵Physics, The Pennsylvania State University, University Park, Pennsylvania, United States.

We have successfully employed charge transfer mechanism to nanoengineer the surface of CNT powder and converted into CNT flexible membranes. The processing protocol has limited or no impact on the intrinsic properties of the CNTs. The CNT membranes have bulk mass density greater than that of water (1.0g/cc). We have demonstrated the use of the CNT membranes as electrode in a pristine and oxidized single/stacked solid-state capacitor as well as pristine interdigitated microcapacitor that show time constant of ~ 32 ms with no degradation in performance even after 10,000 cycles. The capacitors maintained very excellent performance even at temperature up to 90°C. We will present these results including the specific capacitance, leakage current, energy and power densities, as well the effects of flexing on these properties.

ET07.03.04

Stretchable Wire-Shaped Supercapacitor Based on Biodegradable Metal and Polymer Hanchan Lee, Geumbee Lee and Jeong Sook Ha; Korea University, Seoul, Korea (the Republic of).

Recently, there has been extensive interest in transient devices which experience the complete biodegradation after use for certain desired time since they can contribute to the realization of environmentally friendly electronic devices, wearable/implantable devices, or various transient systems for internet of things.

In this study, we report on a facile fabrication of stretchable wire-shaped supercapacitor (WSC), in which all components are completely resorbable in water or biofluid; water-soluble molybdenum (Mo) wire as a current collector, molybdenum oxide as a pseudocapacitive electrode, polyvinyl alcohol containing sodium chloride as an electrolyte, and poly (1,8-octanediol-co-citrate) (POC) film as an encapsulant as well as a deformable substrate. Mo oxide film is grown on the Mo wire surface via electrochemical oxidation by application of constant voltage of 0.8 V to Mo wire in electrolyte. Along with the duration time for applied bias voltage, the thickness of the oxide layer increases. Such fabricated WSC exhibits areal capacitance of 4.15 mF/cm² at a current density of 0.05 mA/cm² and a total cell capacitance increases in proportion to a cell length. Compared to the bare Mo, the capacitance increases dramatically by 47 times with electrochemically grown Mo oxide owing to the pseudocapacitance. A free-standing WSC maintains stable electrochemical properties under various deformation of bending, knotting, coiling and a wavy WSC embedded in the stretchable POC films also maintains initial capacitance after repetitive stretching cycles. Finally, electrochemical performances of the WCS decreases with time in phosphate-buffered saline (0.01 M, pH 7.4) at body temperature, confirming the biodegradable WSC.

This work suggests a facile way to fabricate a high performance transient WSC with a stretchability.

ET07.03.05

Vertically Aligned Insulating Nanotubes as a Structural Separator for Multifunctional Energy Storing Composites Luiz Acauan, Yue Zhou and Brian L. Wardle; Aeronautics and Astronautics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

The use of carbon fiber reinforced polymers (CFRP) as multifunctional structural supercapacitors has been limited by the low ionic conductivity and/or mechanical properties of the insulator separator. Here we propose a novel type of “structural separator” based on aligned insulating nanowires “nanostitched” between carbon microfiber laminates. Proof-of-concept composites were fabricated using aligned alumina nanotubes (ANTs) as well as standard commercial separators between carbon CF prepregs. ANTs nanostitched-composite laminates showed similar mechanical properties as the structural composite with no separator, while the commercial separator exhibited reduced strength due to interface failure. ANTs embedded in polymer electrolyte revealed 2X higher ionic conductivity than the pure electroactive polymer due to the nanowires disrupting the polymer semi-crystallinity. This new structural separator architecture allows standard CFRP structural composites to act as a multifunctional energy storage device, with the potential to enhance energy storage capabilities due to the process-structure coupling in ionically-conductive polymer.

ET07.03.06

Microstructure Engineering to Improve Wettability of Thick, Porous Electrodes for Energy Storage Katherine Stoll, Thomas Carney and Fikile Brushett; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Rechargeable batteries are well suited for energy storage due to their high energy density and efficiency. However, these devices are limited to the use of electrodes less than 300 μm thick to avoid diffusion limitations. Thin electrodes significantly increase the number of inactive components needed for the battery to function, leading to high costs as well as low energy and power densities. Transitioning to thicker electrodes requires novel electrode and cell architecture design to simultaneously enable sufficient ion transport through the flooded pores of the electrode and electron transport through the solid-phase material. Here, we investigate the permeability and wettability of different engineered electrodes as well as the compatibility of various electrode-electrolyte combinations with an overarching goal of enabling low-resistance thick electrodes. Specifically, we examine the electrolyte surface tension and viscosity as well as the electrode microstructure (e.g., porosity, pore size, pore geometry, and topology) in accordance with the Lucas-Washburn equation,¹ to determine the effect on battery performance.

We employ two methods, varying the particle size and altering the binder material, to fabricate electrodes with tailored microstructure. Theoretical models indicate that electrodes with graded porosity decrease resistance and improve capacity retention^{2,3}. Inks of varying particle size will be systematically combined to produce electrodes with controlled non-uniform porosity and pore size. Changing the electrode binder material impacts how the electrolyte wets the electrode and can also alter electrode microstructure (e.g., pore size, morphology). Coupled electrochemical testing and SEM imaging will be utilized to optimize the pore size distribution and total porosity, while contact angle goniometry will be used to quantify the electrolyte-electrode interactions as a function of pore geometry, surface chemistry, and applied voltage. The electrode permeabilities will be characterized using pressure drop testing in accordance with Darcy’s law⁴. The methods developed in this work are portable and can be applied to a wide range of materials and energy storage devices.

References

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ET07.03.07

Effect of Rheological Properties on Microstructure and Electrochemical Performance of Si Composite Electrodes Jiazhi Hu and Yang-Tse Cheng; University of Kentucky, Lexington, Kentucky, United States.

Silicon has been intensively studied as one of the high capacity negative electrode materials for lithium-ion batteries (LIBs). Typically, a silicon electrode is prepared by a wet coating process during which a slurry is made by mixing the components in a solvent and then casted onto a current collector, followed by a drying process. Thus, the rheological properties and stability against sedimentation may affect the microstructure and the electrochemical performance of the electrode. In this work, slurries consisting of Si nano-particles, carbon black (CB), and Na-carboxymethyl cellulose (Na-CMC) with various solid loading were prepared in an aqueous medium, and their rheological properties were compared. The effects of rheological properties on the microstructure and electrochemical performance of electrodes were investigated as well. The results show that, due to the formation of an internal network of solid particles bridged by polymer chains, slurries with higher than 6% solid loading are solid-like. With decreasing solid loading, the slurries become more liquid-like. The Si/CB/Na-CMC electrodes prepared using slurries with high solid loading are more uniform in microstructure than that prepared using low viscosity slurries. The propensity to aggregation, porosity, and the adhesion of the electrode laminate are also influenced by the rheological properties of the slurries. This work demonstrates the importance of slurry property on the microstructure and electrochemical performance of silicon electrodes.

ET07.03.08

Aluminum–Air batteries with Ultrahigh Energy Density Sangjin Choi and Wooyoung Shim; Yonsei University, Seoul, Korea (the Republic of).

There is growing interest in high-performance energy storage systems to meet the strong needs for high-energy-density and high-power devices. Metal-air battery systems could offer a low cost, environmental friendliness, and outstanding energy-storage capability. In particular, aluminum-air batteries are attractive systems due to their safe and energy-dense property. However, actual performances of them are far below the theoretical performances. Here, we show aluminum-air batteries adopting a sparked graphene oxide/silver nanoparticle cathode. The spark reaction makes the graphene oxide very porous structure that can provide a wide oxygen diffusion path. Moreover, silver nitrate is co-reduced by the reaction and becomes a silver nanoparticle which acts as a catalyst for the oxygen reduction reaction. The resultant aluminum-air cell shows very remarkable electrochemical performance close to the theoretical value, and showed enough power to turn on a smart watch when connected in series. This work represents an advancement in aluminum–air batteries using a facile one-step spark reaction concept, showing a practical applicability of aluminum-air batteries.

ET07.03.09

Fabrication of All-Solid-State Lithium-Ion Batteries Simon E. Hafner^{1,3}, Lei Cao¹, Hyukkeun Oh³, Harvey Guthrey², Sehee Lee³ and Chunmei Ban²; ¹National Renewable Energy Laboratory, Golden, Colorado, United States; ³Mechanical Engineering, University of Colorado, Boulder, Colorado, United States.

The complexity and expense of manufacturing all-solid-state batteries has long hindered the development of large-scale solid-state batteries for transportation and grid storage applications. Electrolyte-electrode interfacial resistance, air stability, and mass production capabilities pose particular challenges.

In our work, we demonstrate a new battery manufacturing method that overcomes the challenges of scaling and interfacial resistance by depositing very dense cathode, solid-state electrolyte, and anode layers directly on top of one another. This method enables using a variety of battery and solid-state electrolyte materials and manufacturing all-solid-state batteries in an ambient environment. Furthermore, the approach could ensure a straightforward transition to a roll-to-roll process and incorporate a wide range of materials for future large-scale manufacturing. This presentation will discuss the manufacturing process and electrochemical cycling performance of the as-fabricated all-solid-state batteries.

ET07.03.10

Photofuel Cells Consisting of a Particulate TiO₂ Photoanode with Using Cellulose as a Direct Fuel Takumi Yoshimura, Yosuke Kageshima and Hiromasa Nishikiori; Department of Engineering, Graduate School of Science and Technology, Shinshu University, Nagano, Japan.

Recent population growth and the resultant increase of energy consumption have caused the serious energy and environmental issues, that is, global warming and depletion of fossil resources. Renewable energy sources, such as solar energy and biomass, have been regarded as one of the promising alternatives to supply reliable electricity.

Fuel cells have been intensively studied as clean energy systems with less environmental load. However, since H₂ utilized as the fuel is typically produced by steam reforming of the fossil fuels, the conventional fuel cells are not truly environmentally friendly. The alternative direct fuel cells with using biomass-derived fuels, such as methanol,¹ glucose,² and cellulose³ have been also developed. Above all, cellulose can be expected as one of the most attractive biomass-derived fuels, since a tremendous amount of cellulose is disposed without effective reuse or recycle and is free from worry about competition against biological resources for edible use. It should be noted that the reports of the direct fuel cells with using cellulose as a fuel are still limited due to rigid crystalline structure of cellulose and its resulting insolubility in solvents. Most of the cellulose-based fuel cells are designated to use a large quantity of expensive enzyme.³ Y. Sugano *et al.* reported a novel method for direct electrochemical oxidation of cellulose dissolved in strong alkaline aqueous electrolyte on the inorganic metal electrode.⁴

In the present study, we demonstrated a photofuel cell consisting of a particulate TiO₂ photoanode, where cellulose is oxidized on the photoanode to generate electricity in an external circuit. The TiO₂ particles (P25, Nippon Aerosil) were coated on an FTO/glass substrate and evaluated as a photoanode. Cellulose was fed to the photofuel cells as a direct fuel by several methods: 1) with covering the photoanode surface by cellulose thin film or 2) by dissolving cellulose in a strong alkaline electrolyte. In the presentation, (photo)electrochemical investigations for cellulose oxidation, influence of methods for cellulose supply, effects of photoelectrode preparation conditions, and performances of the photofuel cells will be discussed in detail.

References

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ET07.03.11

Mussel-Inspired Polydopamine Treated Reinforced Membranes with Self-Supported CeO_x Radical Scavengers for Highly Stable PEMFC Ki Ro Yoon¹, Kyung-Ah Lee¹, Sun-Hee Cho¹, Seung-Ho Yook¹, Il Doo Kim² and Jin Young Kim¹; ¹Fuel Cell Research Center, Korea Institute of Science and Technology (KIST), Seoul, Korea (the Republic of); ²Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, Korea (the Republic of).

The physical and chemical degradations of proton exchange membranes (PEMs) in fuel cells induced by the harsh operation environments such as high humidity, high pressure, and repeatable wet/dry conditions and the free-radical attacks are critical factors limiting long-term operation of the PEMFCs. Mussel-inspired polydopamine (PD) with defective ceria nanoparticles (CeO_x NPs) is introduced into porous polytetrafluoroethylene (PTFE) substrates for highly durable and chemically stable composite membranes in proton exchange membrane fuel cells (PEMFCs). The hydrophilic functionalities of PD coated PTFE (PD@PTFE) films enable uniform coating of Nafion ionomer dispersion during blade casting and allow strong mechanical adhesion between PTFE and Nafion layers in PD@PTFE membrane (m-PD@PTFE). Furthermore, the redox properties of catechol at PD surface render the cerium salts to be self-supported CeO_x NPs as sustainable radical scavengers. Improved properties of prepared CeO_x and PD coated PTFE membrane (m-CePD@PTFE) were characterized via water uptake, dimensional stability, proton conductivity, elongation test, Fenton's test, and ex-situ observation. Finally, it was found that m-CePD@PTFE shows superior mechanical stability and long-term cell performance during repeated wet/dry cycling tests (6,000 cycles) *via* suppressed physical fracture and radical attacks on PFSA ionomer.

ET07.03.12

"Nanoscale Nucleation" *In Situ* Polymerization Method for Preparing Dielectric Nanocomposites with High Energy Density Tao Zhang, Yang Shen and Ce-Wen Nan; Tsinghua University, Beijing, China.

Polymer nanocomposite dielectrics, composed of polymer matrix with high breakdown strength and nanofillers with high dielectric constant, can achieve outstanding energy density. However, the large electrical mismatch between polymer and nanofillers will lead to poor compatibility and thus damage dielectric properties of the composites. Introducing a transition layer to the filler surface can significantly reduce the degree of mismatch. In this work, a "nanoscale nucleation" *in-situ* polymerization method was developed to successfully synthesize a series of BaTiO₃-based nanofillers with core-shell structure. Due to the "nucleation" role of the nano-BT particles, the polymerized monomers tend to form a stable coating layer on their surfaces. Nano-BT particles coated with three different monomers (TFEMA, HFPMA, DFHMA) were fabricated, respectively. The results demonstrate that the core-shell structures are all successfully achieved and the thickness of shell can controlled between 2 to 7 nm. With great interfacial compatibility and thus alleviate electrical mismatch, BT@PDFHMA-P(VDF-HFP) nanocomposite with 1 wt.% BT@PDFHMA fillers showed higher energy density of ~18 J cm⁻³ compared with the conventional solution blended BT nanocomposites BT-P(VDF-HFP) (~12 J cm⁻³). We consider that this novel and versatile method can be widely used in the preparation of core-shell structures in dielectric nanocomposites.

ET07.03.13

MXene/Carbon Nanotube Yarn Supercapacitor Jong Woo Park and Seon Jeong Kim; Hanyang University, Seoul, Korea (the Republic of).

Development of wearable electronics and flexible energy harvesters such as piezoelectric or triboelectric energy harvesters largely demand flexible and wearable energy storage devices especially, supercapacitors. Yarn type supercapacitors which are flexible, knittable, and stretchable are receiving large interests. However, the energy density of the yarn supercapacitors should be increased when their limited footprints are considered. The asymmetric configuration of yarn electrodes is one of the strategies to increase the energy storing performance, the low capacitance of conventional carbon materials such as activated carbon, graphene, and carbon nanotube (CNT) hinders the overall performance of the asymmetric supercapacitor. To accomplish high capacitance of the negative electrode, there have been reported some other materials such as PPy, VN, MoS₂, recently. MXene, especially Ti₃C₂T_x in which T_x denotes surface functional groups is an emerging material for its high volumetric capacitance in aqueous electrolyte and high electrical conductivity. The high volumetric capacitance makes this material great candidate for the active material of yarn structured supercapacitors. Also, MXene could be utilized for the negative electrode in asymmetric supercapacitors owing to its potential range. In this work, MXene was bisrolled with CNT sheets to form a high-performance yarn electrode. The bisrolled MXene/CNT yarn exhibited high areal and volumetric capacitance in 1 M sulfuric acid electrolyte. Using the MXene/CNT yarn as the negative electrode, MnO₂/CNT yarn as the positive electrode, and PVA/LiCl gel as a solid electrolyte, resulted yarn-type asymmetric supercapacitor could operate up to 2 V and store high energy density. The all-solid-state yarn supercapacitor could be woven into commercial cotton textile and perform without degradation under mechanical deformations.

ET07.03.14

Direct Urea Fuel Cells Based on CuNi Plated Polymer Cloth as Anode Catalyst Keiichi Kaneto¹, Mao Nishikawa¹, Sadahito Uto¹ and Toshiyuki Osawa²; ¹Department of Biomedical Engineering, Osaka Institute of Technology, Osaka, Japan; ²Department of Environmental Engineering, Osaka Institute of Technology, Osaka, Japan.

Direct and passive type urea fuel cells were studied based on CuNi plated polymer cloth for the anode catalyst and current collector. Pt-black and cation exchange membrane were used as the cathode catalyst and polymer electrolyte, respectively. The output power was significantly enhanced by coating the CuNi cloth with a conducting polymer of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT*PSS). The cell exhibited the open circuit voltage (E₀), 0.68V and the maximum output power (P_{max}), 1.88 mWcm⁻² for 0.5 M urea solution. Similar results of E₀ = 0.65V and P_{max} = 1.74 mWcm⁻² were obtained for 0.5 M ammonia solution. The cell performances and mechanisms of anode reactions were discussed taking the results of various biofuel cells using the other conducting polymers and polymer electrolytes into consideration.

ET07.03.15

Direct Observation of Dehydrogenation of Mg₂FeH₆ by Using *In Situ* Transmission Electron Microscopy Hyunmin Kim⁴, Joseph Song⁴, Julien Fadonougbo¹, Jee-Hwan Bae⁴, Jaeyoung Hong⁴, Soongju Oh², Younghwan Choi², Jaeyoung Ahn⁴, Wooyoung Shim², Dongwon Chun⁴ and Jinyoo Suh¹; ¹High Temperature Energy Materials Research Center, Korea Institute of Science and Technology, Seoul, Korea (the Republic of); ²Korea University, Seoul, Korea (the Republic of); ³Yonsei University, Seoul, Korea (the Republic of); ⁴Advanced Analysis Center, Korea Institute of Science and Technology, Seoul, Korea (the Republic of); ⁵Electronic Materials Research Center, Korea Institute of Science and Technology, Seoul, Korea (the Republic of).

Magnesium-based ternary hydrides have been considered as a promising candidates in fuel cell and hydrogen transport in light of their high hydrogen capacity and cycling ability. ^[1] Understanding hydrogenation /dehydrogenation mechanism is, however, hampered by difficulties in the *in-situ* observation of nanostructured ternary hydrides. For example, rapid dehydrogenation process at high temperature hinders proving the decomposition mechanism of ternary hydrides through electron microscopy. Currently, developed equipment such as *in-situ* electron microscopy (EM) holder, high resolution/fast image acquisition (One-view charge-coupled device (CCD) camera, Gatan) and fast energy-dispersive X-ray spectroscopy (Super-EDS) have enabled studies of fast reaction phenomena through electron microscopy.

Here, we investigated the dehydrogenation process of Mg_2FeH_6 . The nanostructured Mg_2FeH_6 sample was loaded on the in-situ TEM holder (Fusion, Protochips) and heated the sample with temperature of 250 degrees - 400 degrees for 1 hour to trigger the decomposition of Mg_2FeH_6 by hydrogen desorption. We imaged dynamics and diffraction patterns of Mg_2FeH_6 on dehydrogenation by one-view camera, attached on the Titan (G2, FEI). 25 pictures were acquired every second. In addition, high-speed EDS analysis was performed by super-EDS embedded TEM (Talos F200X, FEI) before and after the dehydrogenation. We utilized profile analysis of the SAD pattern (PASAD) program for the quantitative analysis of diffraction patterns.^[2] Upon heating, intensities of Mg_2FeH_6 diffraction spots were decreased and eventually disappeared within a couple of minutes. Sequentially, diffraction spots of Fe and Mg were appeared and its intensity increased through the dehydrogenation process. This is because the phase segregation in immiscible elements of Fe and Mg by the hydrogen desorption from Mg_2FeH_6 . It is noteworthy that MgO diffraction spots were observed simultaneously after the extinction of Mg_2FeH_6 diffraction spots, which might be possibly due to the oxidation of segregated Mg in TEM column. Super-EDS results reveal that nanosized Mg and Fe were produced after the dehydrogenation of Mg_2FeH_6 which was not observed in the sample before dehydrogenation at a temperature below 300 degrees. On the contrary, at a temperature above 300 degrees, size of segregated Mg and Fe increased much. Also, chemical composition of Mg was decreased appreciably. This suggests induced Mg was evaporated even below its melting points, indicating high energy electron beam promotes Mg evaporation.

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SESSION ET07.04: Electrode Manufacturing
Session Chairs: Wilhelm Pfleging and Pu Zhang
Tuesday Morning, November 27, 2018
Hynes, Level 3, Room 312

8:30 AM *ET07.04.01

Towards High Energy Density Electrodes—Ultrathick Cathodes and Prelithiation Lukas Ibing², Florian Holtstiege², Tobias Gallasch², Tobias Placke², Falko Schappacher² and Martin Winter^{2,1}; ¹Helmholtz Institute Münster HI MS, Forschungszentrum Juelich GmbH, Münster, Germany; ²MEET Battery Research Center, University of Münster, Münster, Germany.

The production of cost effective, high energy and environmentally friendly electrodes is key for the success of lithium ion batteries (LIBs) to be used in electro-mobility or grid storage. To overcome the remaining drawbacks new ways towards cost effective processing of LIB electrodes and higher energy density battery cells are main topics of nowadays research. One way to combine both requirements is the preparation of ultra-thick electrodes using aqueous processing: Thick dry film thicknesses (large active mass loadings) allow an increase in energy density, while the relative reduction of copper and aluminum current collectors reduces the costs. However, compared to conventional processing, aqueous electrode formulation also goes along with disadvantages like surface crack formation and basic pH values accelerating active material degradation, especially in case of cathode materials like NMC ($LiNi_xCo_yMn_zO_2$, with $x \geq 0.33$ and $y, z \leq 0.33$). Our approach to successfully overcome mechanical electrode instability is to develop a suitable “binder package” combining the water soluble components polyacrylic acid (PAA), polyethylene oxide (PEO) and sodium-carboxymethylcellulose (CMC). This mixture combines high flexibility (PEO) with low viscosity (PAA) and sufficient adhesion (CMC) resulting in a superior water compatible binder system to manufacture ultra-thick cathode sheets. Using this binder composition it was possible to achieve NMC based cathodes free from cracks with high amounts of active material and active mass loadings up to 50 mg cm⁻² delivering discharge capacities of 120 mAh g⁻¹ at 0.2 C. A further issue, which decreases the gravimetric energy and volumetric energy density of LIBs is active lithium loss, caused by solid electrolyte interphase formation on the surface of the anode, occurring mainly in the first cycle of operation. In order to compensate the loss of active lithium, various pre-lithiation methods have been developed that result in an increased reversible capacity and, consequently, in a higher gravimetric energy and volumetric energy density. Thereby, the term “prelithiation”, describes the addition of lithium to the active lithium content (= reversibly transferable lithium ions between positive and negative electrode) of a LIB prior to battery cell operation. Therefore, with help of prelithiation it is possible to use novel active materials inside LIB full cells which otherwise could not be utilized due to high active lithium losses.

9:00 AM *ET07.04.02

New Approaches to Cathode Manufacturing to Meet Emerging Environmental Restrictions Stuart D. Hellring; PPG, Allison Park, Pennsylvania, United States.

NMP remains the most commonly used solvent in the lithium ion battery cathode manufacturing process. However, NMP faces mounting global regulatory pressure, and recently issued EU directives could effectively eliminate NMP usage by 2021. These new restrictions will place enormous challenges on the industry’s ability to locally manufacture lithium ion batteries for electric vehicles. Novel solutions will be needed to manufacture cathodes without NMP. PPG is actively engaged in developing innovative solutions to the challenges presented by this historic transition. These solutions address eco-friendly battery manufacturing as well as providing other performance improvements in energy storage. Applying these unique approaches for NMP-free cathode production enables the manufacturing of lithium ion batteries within this new regulatory environment to support the predicted growth EV production.

9:30 AM ET07.04.03

An Advanced Dry-Powder Manufacturing of Lithium-Ion Batteries Applicable to Various Electrode Designs Yangtao Liu¹, Jin Liu¹, Brandon Ludwig², Heng Pan² and Yan Wang¹; ¹Worcester Polytechnic Institute, Worcester, Massachusetts, United States; ²Mechanical Engineering, Missouri University of Science and Technology, Rolla, Missouri, United States.

The slurry casting method currently dominates the manufacturing of electrodes for lithium-ion batteries. There exists a recognized shortcoming of this conventional method that the liquid solvent, mostly as the organic (N-methyl-2-pyrrolidone), is indispensable to fluidize the electrode material during casting, which is toxic and high cost during the entire processing. To overcome this restriction, an advanced power-based technology was developed by us to fabricate electrodes of the lithium-ion batteries through additive manufacturing. Gas-driven spraying guns are chosen to address a direct dry-powder printing of electrode structures onto the current collectors without involving solvents. Therefore, the removal of solvents shortened the production time from days to seconds, analyzed to reduce 20% of production cost, and enabled a more precise control of electrode microstructure during manufacturing. We have demonstrated this technology with a wide range of compatibility on different electrodes design, including cathodes (LCO, LMO, NCM), anodes (Graphite), advanced architecture designs (Ultra-low binder recipe (<1%), High-energy thick electrodes (>280um), Layered structured). Based on our current study, the dry printed electrodes outperformed the reference slurry cast electrodes at a few performance parameters (80% capacity retained in 500

cycles), high bonding strength, high structural integrity, high materials homogeneity Integrity. Along with better electrochemical and physical properties, this dry-powder manufacturing method could be attractive and competitive for nowadays production of electrodes and has the potential for further design.

9:45 AM ET07.04.04

Dry Process for Fabricating Low Cost and High Performance Electrodes for Energy Storage Devices [Qiang Wu](#)¹, Jim Zheng¹, M. Hendrickson² and E.J. Plichta²; ¹Florida State University, Tallahassee, Florida, United States; ²U.S. Army Research Laboratory, Aberdeen Proving Ground, Maryland, United States.

We report a roll-to-roll dry processing for making low cost and high performance electrodes for lithium-ion batteries (LIBs) and lithium-ion capacitors (LICs). Currently, the electrodes for LIBs and LICs are made with a coating or slurry casting procedure (wet method). The dry electrode fabrication is a three-step process including: step 1 of uniformly mixing electrode materials powders comprising an active material, a carbonaceous conductor and the soft polymer binder; step 2 of forming a free-standing, continuous electrode film by pressing the uniformly mixed powders together through the gap between two rolls of a roll-mill; and step 3 of roll-to-roll laminating the electrode film onto a substrate such as a current collector.

A prototype hybrid lithium ion capacitor cell with lithium iron phosphate (LFP)/activated carbon (AC) composite cathode and Li doped hard carbon (HC) anode has been made by our dry method, which has a breakthrough energy density of ~30 Wh kg⁻¹, high power density of 2,000 W kg⁻¹, as well as long cycle life over 30,000 cycles (90% retention). LIBs of LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ (NMC622)/graphite and LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ (NMC622)/graphite-silicon also has 250 Wh kg⁻¹ and 300 Wh kg⁻¹ energy density, respectively.

Compared with the conventional wet slurry electrode manufacturing method, the dry manufacturing procedure and infrastructure are simpler, the production cost is lower, and the process eliminates volatile organic compound emission and is more environmentally friendly, and the ability of making thick (>120um) electrodes with high tap density results high energy density of final energy storage device.

10:00 AM BREAK

10:30 AM *ET07.04.05

Reduce Electrode Manufacturing Cost—Transition from Batch to Continuous Production [David Ventola](#); B&W MEGTEC LLC, De Pere, Wisconsin, United States.

The basics of Li-ion battery electrode manufacturing have not changed much in the last twenty years. Ten years ago, B&W MEGTEC developed a method to utilize their extensive knowledge and experience in flotation drying to enable simultaneous 2-side coating of Li-ion electrodes. This development included a unique slot die coating arrangement along with proprietary technology to stabilize the thin foil current collector substrate. These advancements enabled world class battery manufacturers to reduce costs of manufacturing and increase productivity. Simultaneous 2-side coating allows for a simplified factory layout which reduces total floorspace required and reduces material moves. Additionally, when compared to a more typical sequential coating process the 2-side coating and flotation dryer only requires roughly half of the utilities which greatly reduces the operating expenses.

The focus of this talk will be to leverage the benefits of 2-side coating and flotation drying; linking other unit operations to streamline the electrode manufacturing process. Specifically, the following technologies are usually separate and distinct unit operations each with varying levels of materials in que, WIP and material transfers between operations.

- Slurry Mixing
- Electrode Coating & Drying
- Calendaring / Roll Pressing
- Secondary Drying

These unit operations can be linked to create a streamlined continuous processing plant with a focus on increasing productivity, improving quality and reducing manufacturing costs.

Continuous mixing leads directly into simultaneous 2-side coating and flotation drying. Traditionally after drying the coated electrode rolls are removed, stored and put in queue to move on to the calendaring/pressing operation. This movement and storage is wasted effort and floorspace. Linking calendaring/pressing directly after drying in the processing line eliminates this waste. The new process methodology allows for the dried electrode to move directly to the inline calender/press, bypassing the intermediate rewind and unwind steps.

In many electrode manufacturing processes, a secondary drying step is required to achieve the final level of drying or residual solvent retained on a percent or parts per million scale. Typically, this is done by loading full rolls of coated electrodes into a drying chamber and essentially “baking” the electrode for an extended period. The period could be as short as 8 hours or as long as 24 hours. The mechanics of extracting solvent and/or water out of a coated electrode wound into several hundred if not a thousand layers are very difficult. A new approach exists to employ continuous secondary drying inline with the other unit operations presented. Inline secondary drying provides more consistent drying of the entire electrode surface area, which leads to a more consistent and higher quality electrode.

11:00 AM *ET07.04.06

Present and Future Methods of Li-Ion Battery Electrode Slurry Preparation [Bernhard Stalder](#); Buhler AG, Uzwil, Switzerland.

An overview over present and near future preparation methods of electrode slurries will be presented:

1. The traditional methods with batch mixers (usually planetary type mixers) which have been used from the very first of the Li-ion battery history. The method is well known and has advantages in R&D use but shows low hanging limitations as soon as mass production is considered: The scalability via the mixer size has reached its upper end. The only way for a further scale up has to be performed via the number of mixers which is very expensive. Further, the reproducibility of the slurry quality shows some challenges due to the batch operation method.

2. An advanced semi-continuous thin film method in combination with simple batch mixers or existing planetary mixers for increased throughput rates and improved reproducibility of the slurry quality. Mainly the reproducibility of the viscosity as a key property of a slurry is on a high level and allows an easy electrode coating process. The method can be used in R&D scale (some 10 milliliters) but can be scaled up to manufacturing size with throughput rates of more than 1000 liters per hour.

3. With regards to the present strong growth of the Li-ion battery business a novel fully continuous method will be presented and explained in detail. This method allows the use of all components as they are supplied without any intermediate process steps except filling of silos. The new method allows to prepare a ready to coat slurry within a residence time of approx. 60 seconds compared to up to 8 hours in a batch process.

Further, throughput rates of 2000 liters per hour or more are feasible, but also small units for R&D activities are available.

Advantages and challenges of each method will be discussed and compared.
Remarks concerning the interaction of slurry preparation and the subsequent coating process will be shared.

11:30 AM ET07.04.07

Roll-to-Roll Solution Based Manufacturing of Flexible Large Area Devices for Energy Conversion and Harvesting Pim Groen^{1,2}; ¹Holst Centre, Eindhoven, Netherlands; ²Aerospace Engineering, TU Delft, Delft, Netherlands.

Coating technologies for functional materials by solution based ("wet") processing methods are a highly promising approach for production upscaling towards industrial scales. The use of flexible polymer substrates not only allows the preparation of ultrathin bendable devices, but also enables roll-to-roll (R2R) manufacturing, with all its associated benefits such as high volume, large area and high throughput production. Whereas for certain sectors like the packaging and paper industries, R2R printing and wet coating have been the established standard already for decades, its use in more demanding application areas like printed electronics has only recently started to emerge. Within this branch of industry, energy conversion and storage devices are a core application area with intense research activity going on to introduce R2R production technologies. This contribution presents technical approaches for solution based R2R manufacturing methods which can be applied in the large scale fabrication of flexible printed electronics devices for energy conversion and harvesting. The development of a R2R line with two slot-die coating stations is presented which can deposit two functional layers consecutively in a single run ("tandem coating") at web speeds up to 30 m/min. Whereas slot die coating typically is a technology for the uniform deposition of continuous functional thin films, additional adjustments to the equipment also allow patterning both in the web transport direction (stripe coating) and perpendicular to it (intermittent coating). These patterning options are a crucial prerequisite for the manufacturing of properly encapsulated devices with high stabilities and long lifetimes. Particularly for functional inks with low viscosities, well controlled intermittent slot die coating with proper edge definition of the resulting patches is far from trivial. It requires specially designed ink supply systems able to actively remove (suck back) fluid from the die opening in a precisely timed manner to achieve a uniform and sudden start and stop of the coating process. It will be demonstrated how, employing this approach in combination with stripe coating, patterns can be produced at high R2R speeds with definitions in the millimetre range using inks relevant for the manufacturing of energy conversion and harvesting devices.

SESSION ET07.05: Electrode Architectures
Session Chairs: Corie Cobb and Jianlin Li
Tuesday Afternoon, November 27, 2018
Hynes, Level 3, Room 312

1:30 PM *ET07.05.01

A Flexible Multiscale Computational Platform for the Simulation of the Battery Fabrication Process Alejandro A. Franco^{1,2,3}; ¹Laboratoire de Reactivite et Chimie des Solides, Universite de Picardie Jules Verne, Amiens, France; ²Institut Universitaire de France, Paris, France; ³ALISTORE-European Research Institute, Amiens, France.

In this talk I present the recent progresses we achieved within the ERC Project ARTISTIC [1]. This pioneering project aims at developing a comprehensive, flexible and multiscale computational platform simulating the fabrication process of battery cells [2,3]. The project is supported on three pillars: 1) computational white box simulation tools, 2) experimental screening, and 3) black box machine learning techniques. I discuss in particular our recent results obtained by employing Coarse Grained Molecular Dynamics to simulate slurries, electrode self-organization upon solvent evaporation and the calendaring stage. The resulting predicted electrode mesostructures are incorporated into a performance simulator resolving in three dimensions the interplays between electrochemistry, transport and mechanical processes in an operating battery cell. I discuss in particular how different fabrication parameters impact the electrode mesostructure and the corresponding electrochemical response for graphite and NMC electrodes, in close comparison with in house experimental data. Finally, I discuss the impact of using innovative in house Virtual Reality tools to analyse the calculated and the imaged electrode mesostructures.

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2:00 PM ET07.05.02

Towards Computational Modeling of Solid-State Lithium-Ion Battery Architectures Corie L. Cobb² and Srikanth Allu¹; ¹Computational Sciences and Engineering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ²Department of Mechanical Engineering, University of Washington, Seattle, Washington, United States.

Solid-state Lithium-ion (Li-ion) batteries can revolutionize battery design and performance due to their potential safety, high voltage stability, and high conductivity. As the field grows, there is a need for computational tools that can enable battery engineers to explore the effects of material and geometry and their subsequent impact on performance, enabling optimization of a given battery design without expansive experimental tests. In this talk, we survey current research literature on modeling of solid-state Li-ion batteries and discuss the key components that are needed to enable a multi-physics modeling framework. A three-dimensional (3D) computational framework called AMPERES, developed at ORNL, is used as a case study to examine the requirements of modeling the electrode-electrolyte interface of solid-state Li-ion batteries. Because AMPERES enables one to model arbitrary battery and electrode configurations, we also discuss potential 3D architectures that can enhance interfacial stability and effective conductivity.

2:15 PM ET07.05.03

3D-Printing of Three-Dimensional Graphene Aerogels with Periodic Macropores for Supercapacitor Electrodes Tianyu Liu¹, Cheng Zhu², Eric B. Duoss², Christopher M. Spadaccini², Marcus A. Worsley² and Yat Li¹; ¹Department of Chemistry, University of California, Santa Cruz, Santa Cruz, California, United States; ²Lawrence Livermore National Laboratory, Livermore, California, United States.

Recent progress in developing three-dimensional graphene macro-structure has resulted in a diverse array of bulk graphene aerogels for a plethora of applications. However, these aerogels generally exhibit compromised electrochemical performance compared to their two-dimensional counterparts, particularly when engineering into supercapacitor electrodes. This drawback is due mainly to their highly tortuous and stochastic pore networks that retard ion diffusion throughout the entire electrode. These structural limitations can be well addressed by developing graphene-based architectures with ordered macropores to provide ions with straightforward diffusion "expressways". Our recently pioneering work developed a direct ink writing, one of the 3D printing techniques that manufactured the first group of 3D graphene aerogels with periodic macropores as supercapacitor electrodes. These aerogels, though possess thickness 10-100 times thicker than most other reported carbon-based supercapacitor electrodes, display exceptional capacitance retention of ~90% from 0.5 to 10 A/g, a performance that is comparable or even outperforms those of conventional thin film supercapacitor electrodes. This talk will first present the key factors in developing an extrudable graphene oxide-based ink for electrode printing. Another emphasis will be given to the electrochemical analyses elucidating the links between the 3D printed structure and the excellent rate capability performance. This presentation is expected to highlight the power of direct ink writing (or generally, 3D printing) as an advanced manufacturing technique to revolutionize the production of electrochemical energy storage devices.

2:30 PM ET07.05.04

Thick Co-Extruded Cathode Electrodes for High Energy Lithium-Ion Batteries [Ranjeet Rao](#)¹, Scott Solberg¹, Rahul Pandey¹, Kathryn Murphy¹, Marissa Wood², Jianlin Li² and David Wood²; ¹Palo Alto Research Center, Palo Alto, California, United States; ²Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Co-Extrusion (CoEx) is a high speed, scalable deposition process for creating finely patterned, interdigitated thick films. Our CoEx printhead is designed to be a drop-in replacement for slot-die heads on web coaters, enabling novel geometric structuring of electrodes with minor changes to existing battery electrode processing lines. Here, we present the use of CoEx to prepare thick (~120 μm) NMC cathode electrodes consisting of alternating regions of high lithium-ion transport and high lithium-ion storage capacity. By structuring the cathode electrode, we enable full lithium utilization at C/2, despite near doubling of the electrode thickness compared to conventional baseline electrodes. CoEx cathode electrodes are paired with thick, graded graphite anode electrodes and assembled into 1 Ah pouch cells for electrochemical testing. CoEx pouch cells demonstrate 10 – 20% improved energy density with respect to conventional electrodes and > 30% improved power density with respect to thick conventional (unstructured) electrodes at high discharge rates.

2:45 PM BREAK

3:15 PM *ET07.05.05

Direct Electrodeposition of High-Performance Lithium and Sodium-Ion Battery Electrodes [Paul V. Braun](#); University of Illinois at Urbana Champaign, Urbana, Illinois, United States.

Battery electrodes are nearly universally formed via tape casting of a slurry containing a mixture of active material, binder, and conductive carbon. However, the electrochemical and mechanical properties of slurry cast electrodes are often limited by weak interconnections between particles and between the particles and the substrate. We suggest conformal electrodeposition of high-quality electrode materials would provide opportunities to enhance battery performance (energy density, power density, and flexibility) and broaden the scope of available electrode form factors (size, shape, porosity, and 3D integration). We have now made considerable advances in the direct electrodeposition at modest temperatures of high performance tin-based Na and Li-ion anodes and LiCoO₂, NaCoO₂, LiMn₂O₄, and Al-doped LiCoO₂-based Na and Li-ion cathodes. The electrolytically active materials were formed either as solid films, or where significant volume changes upon cycling are present, via a templating process, as a 3D mesostructured film. The capacities are near-theoretical, and in the case of the electroplated oxides, the crystallinities and electrochemical capacities of the oxides are comparable to powders synthesized at much higher temperatures (700 ~ 1000 °C). The electrodeposition method significantly broadens the scope of battery form factors and functionalities, enabling a variety of highly desirable battery properties including microbatteries, and high energy, high power, and flexible designs.

3:45 PM ET07.05.06

Multiscale-Controlled 3D Electrodes for Lithium-Ion Batteries [Jie Li](#) and [Jonghyun Park](#); Missouri University of Science and Technology, Rolla, Missouri, United States.

A new concept for making battery electrodes to simultaneously control macro-/micro-structures of electrodes is developed to address present energy storage technology gaps and meet future energy storage requirements. This new fabrication process fully utilizes the benefits of additive manufacturing, which provides a pathway for inexpensive and flexible production of specialized products. Furthermore, the process allows a simultaneous control of the microstructure and macrostructure of electrodes which cannot be achieved via conventional manufacturing techniques. Modern batteries are fabricated in a form of laminated structures that are composed of randomly mixed constituent materials. Due to this randomness, there is an ample room in the conventional method to enhance performance by developing viable processing techniques to construct well-organized structures. The synergistic control of micro-/macro-structures is a novel concept in energy material processing that has considerable potential for providing unprecedented control of electrode structures and enhancing performance. Electrochemical tests show that the new electrodes exhibit superior performance in their specific capacity, areal capacity, and life cycle. It is concluded that the macro-micro-controlled structure showed 21%, 16%, and 7% more areal capacity than a structure with no control, a macro-controlled structure, and a micro-controlled structure, respectively. The proposed control of 3D structures, with a well-organized distribution of energy materials, demonstrated more superior properties and advantages than structures with randomly distributed materials.

4:00 PM ET07.05.07

Manufacturing and Characterization of Carbon-Coated Silicon/Graphite 3D Electrodes for High Energy Lithium-Ion Batteries [Yijing Zheng](#)¹, Peter Smyrek^{1,2}, Jan-Hendric Rakebrandt¹, Xiaopeng Cheng³, Yuefei Zhang³, Hans J. Seifert¹ and Wilhelm Pfleging^{1,2}; ¹Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany; ²Karlsruhe Nano Micro Facility, Eggenstein-Leopoldshafen, Germany; ³Beijing University of Technology, Beijing, China.

Silicon as high-energy anode material for next generation lithium-ion batteries has recently become of great interest. Graphite active material mixed with silicon nanoparticles is under development in order to increase significantly the practical capacity of commercial anodes and to overcome the drawbacks of silicon due to large volume changes during electrochemical cycling. However, it is well known that pure silicon will form a native oxide layer during exposure in ambient air. During battery operation, this native oxide layer will restrain the lithiation process and a drop in silicon capacity will be achieved. Therefore, carbon-coated silicon nanoparticles were applied in order to maintain a high specific capacity of 3579 mAh/g. In order to reduce the intrinsic mechanical stress of silicon/graphite electrodes and to improve the lithium-ion transport kinetic, free-standing electrode structures were generated by applying ultrafast laser ablation. For comparison, a thin alumina layer (thickness ~5 nm), which acts as an artificial solid electrolyte interphase, was coated on structured silicon/graphite electrodes by applying atomic layer deposition. Cyclic voltammetry measurements were performed to investigate the fundamental properties of carbon- and alumina-coated silicon/graphite electrodes. Galvanostatic measurements reveal that the cells with structured

electrodes exhibit excellent electrochemical properties and improved lithium-ion diffusion kinetics compared to cells with unstructured electrodes.

4:15 PM ET07.05.08

3D Architected Pyrolytic Carbon as Efficient Battery Electrode [Kai Narita](#), Michael Citrin, Heng Yang and Julia R. Greer; California Institute of Technology, Pasadena, California, United States.

Engineering optimal electrode architecture in rechargeable batteries can improve volumetric power and energy density by controlling factors such as diffusion path of ions in electrode and electrolyte, mass loading of active materials, thickness of electrodes and migration path of electrons. Electrode engineering has been incorporated into batteries, for example, by utilizing 3D current collectors, by aligning active materials by an external field and by employing sacrificial template methods. These efforts are still being developed because powder electrodes require having a binder and methods that involve sacrificial templates offer limited flexibility in local geometry.

Aiming at greater flexibility in electrode structure without such limitations, we developed a facile and scalable fabrication method of 3D architected carbon anodes using direct light processing (DLP) 3D printing with UV-curable resin and a subsequent pyrolysis process in an inert atmosphere. The architected pyrolytic carbon electrode is free-standing and binder-free enabled by the monolithic structure and electrical conductivity of carbon. The specific architecture of these electrodes is fully controllable over every length scale: from local geometry (micrometer-scale) to control tortuosity and mass loading, as well as global geometry (centimeter-scale), to intergrade into any device geometries.

We fabricated 1mm-thick 3D periodically architected carbon electrodes with simple cubic-like geometry and 12% relative density composed of ~30 mm-diameter beams. We characterized its electrochemical performance by constructing a half-cell against a lithium metal counter electrode. X-ray diffraction (XRD), energy dispersed spectroscopy (EDS), Raman spectroscopy and transmitted electron microscope (TEM) showed that the pyrolytic 3D lattice was mainly amorphous, with a few interdispersed sp^2 -hybridized regions. Battery cycling of these electrodes using a coin cell showed reversible capacity of ~230 mAh/g, which corresponds to 7 mAh/cm² at a current density of 16 mA/g or 0.6 mA/cm². Varying cycling rate from 0.6 to 10.1 mA/cm² revealed that the 3D carbon electrodes are capable of good performance enabled by low tortuosity of the periodic structure, for instance, ~3.5 mAh/cm² at 3.4 mA/cm². These electrodes showed stable capacity over 50 cycles at 16 mA/g.

This methodology offers a facile and scalable fabrication method of 3D architected carbon that can serve as an efficient approach to create high energy density battery electrodes that can potentially be intergraded into 3D interdigitated batteries.

4:30 PM ET07.05.09

Additive Manufacturing of Three-Dimensional (3D) Micro-Supercapacitors Based on MXenes [Jafar Orangi](#) and Majid Beidaghi; Materials Engineering, Auburn University, Auburn, Alabama, United States.

Energy storage devices are crucial for the future development of portable/wearable electronic devices, wireless sensors, and self-power microsystems. The first requirement for fabrication of energy storage devices with high energy and power densities is using electrode materials and electrolyte with superior electrochemical properties. Another critical requirement is to develop manufacturing methods that enable the assembly of the electrode material and electrolytes in structures that promote high electrical and ionic conductivities. Recently, a family of two-dimensional (2D) materials, referred to as MXenes, has been introduced as high performance electrode materials for electrochemical capacitors (ECs, also called supercapacitors). It is demonstrated that a MXene with the composition of Ti_3C_2Tx can deliver specific volumetric capacitances as high as ~1500 Fcm⁻³, which has set a new record for the electrochemical performance of EC electrodes. In this talk, we will present our recent research on using 2D MXenes as building blocks for the fabrication of three-dimensional (3D) supercapacitors using an additive manufacturing process. In this process, a water-based ink of MXene with viscoelastic properties was developed and directly used for extrusion-based 3D printing of supercapacitors. The fabrication process follows a layer-by-layer deposition of the MXene ink using a programmable printing machine. This process allows rapid fabrication of supercapacitors on a variety of substrates, while the thickness of the electrodes can be controlled by the number of deposited layers. The evaluation of the electrochemical performance of the printed devices shows their excellent electrochemical properties. For example, a flexible device fabricated using Ti_3CTx electrodes and a gel polymer electrolyte delivered an extremely high areal capacitance of ~1100 mFcm⁻². Our study suggests that due to its high electrical conductivity and electrochemical properties, MXene is an excellent choice as the building block for the fabrication of 3D energy storage devices.

4:45 PM ET07.05.10

Optimally Engineered Flow-Through Electrodes Using Topology Optimization and Additive Manufacturing [Victor Beck](#), Todd Weisgraber, Anna Ivanovskaya, Swetha Chandrasekaran, Bryan Moran, Seth Watts, Dan Tortorelli, Eric B. Duoss, Juergen Biener, Michael Stadermann and Marcus A. Worsley; Lawrence Livermore National Laboratory, Livermore, California, United States.

Flow batteries are a promising technology for large scale energy storage and load balancing from intermittent power sources, but their viability hinges on our ability to attain high-power outputs while minimizing costs and meeting performance constraints. Effective engineering of these systems is further complicated both by limitations on the control of the electrochemical cell component morphologies across scales and accurate modeling of the multiple, simultaneous physical processes. At Lawrence Livermore National Lab, we have pioneered a potential solution to this problem using additive manufacturing techniques which enable hierarchical structures controlled from the sub-micron through the centimeter length scales. Yet, even with this expanded design space, the complexity and tight coupling of the underlying physical processes remains as an obstacle to effective design: Apparently obvious choices can nevertheless lead to an unexpected adverse performance impact. To address this challenge, we present an automatic design methodology to optimize flow-through electrode topologies over precisely defined performance criteria. We combine forward physics solvers for the full, multidisciplinary electrochemical problem, including fluid flow, electrochemistry and mass transfer, with adjoint solvers to determine topological sensitivities. Our algorithms compute optimal electrochemical cell architectures which are then physically created using additive manufacturing techniques and post-processed to create carbon electrodes. We compare the predicted performance of computationally optimized designs against standard, bulk electrodes and focus on the tradeoff between high surface areas and pressure drop. Our work provides a systematic path toward rational design of cost-effective, high-power flow batteries and other porous electrode systems.

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ET07.06.01

Performance Enhancement in Planar Type Sb₂S₃ Solar Cells by TiO₂ Surface Treatment Sung-Ho Woo, Wook Hyun Kim, Kang-Pil Kim and Dae-Hwan Kim; DGIST, Daegu, Korea (the Republic of).

Recently, many inorganic metal chalcogenides based on earth abundant elements such as copper zinc tin selenide (CZTS), lead sulfide (PbS), copper(I) sulfide (Cu₂S), tin sulfide (SnS) and antimony sulfide (Sb₂S₃) have been investigated as an absorber material for solar cell. Among them, Sb₂S₃ has received intense attention as a light absorber material due to its suitable band gap (~ 1.7 eV), high absorption coefficient (>10⁵ cm⁻¹), low cost, less toxicity, and high air stability.¹⁻³

In this study, Sb₂S₃ was deposited through a simple spin-coating process previously reported by Wang et al. using an antimony-complex precursor solution prepared by dissolving antimony oxide (Sb₂O₃), carbon disulfide (CS₂), and n-butylamine in an ethanol solvent.⁴ In order to enhance the performance of Sb₂S₃ solar cells, we applied surface treatment on TiO₂ layer by Cs₂CO₃ solution to adjust the work function of TiO₂ to the conduction band of Sb₂S₃ light absorption layer. Figure 1(a) shows a scheme of the device architecture. The bottom layer is composed of compact TiO₂ layers acting as electron transporting. Light is absorbed by the Sb₂S₃ while holes are transported by the P3HT, and collected at the Au counter electrode.

As can be seen in figure 1(b), the power conversion efficiency (PCE) of 3.51% was obtained under AM1.5G illumination in a planar type device consisting of FTO/Cs₂CO₃ treated TiO₂/Sb₂S₃/P3HT/Au, which is significantly higher than that of the control device without Cs₂CO₃ treatment (2.48%). The higher PCE of planar type Sb₂S₃ solar cell based on Cs₂CO₃ treated TiO₂ is attributed to uniform surface formation, suitable energy level alignment, and efficient electron transport properties. We believe that this solution processable surface treatment can provide simple and effective way of device performance improvement in planar type inorganic metal chalcogenides solar cells.

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ET07.06.02

Enhancing the Performance of Conventional Organic Photovoltaic Devices via Integrating Combined Fluorescence and Plasmon Resonance Energy Transfer Jinyoung Han¹, Ju Won Lim¹, Yu Jin Jang², Kyungwha Chung³ and Dong Ha Kim¹; ¹Department of Nanoscience and Chemistry, Ewha Womans University, Seoul, Korea (the Republic of); ²Center for Integrated Nanostructure Physics, Institute for Basic Science, Suwon, Korea (the Republic of); ³Department of Energy Science, Sungkyunkwan University, Suwon, Korea (the Republic of).

Utilization of solar energy is one of the most promising ways to solve the energy problems today. Organic solar cells have been attracting attention because of their low absorption coefficient, low consumption of materials, efficient solution processes, and low manufacturing energy. In order to enhance the power conversion efficiency (PCE) of the organic solar cell, the quantum yield of the incident photon must be increased. However, in an ideal binary bulk heterojunction scheme, it has been reported that 50 % of energy is lost due to recombination of electrons and holes. Recently, Förster resonance energy transfer (FRET) phenomenon is used as a method to minimize this loss. By adding a substance that can induce FRET phenomenon in relation with the p-type semiconductor, the photon absorption range can be increased and the exciton yield can be improved. Previous studies have shown that inclusion of squaraine (SQ) molecules in conventional Poly(3-hexylthiophene-2,5-diyl) (P3HT):[6,6]-Phenyl C₆₁ butyric acid methyl ester (PCBM) bulk heterojunctions can contribute to additional exciton generation through FRET. The SQ-doped active layer exhibits an energy transfer efficiency of up to 96 % due to the wide overlap between the emission spectrum of P3HT and the absorption spectrum of SQ. In addition to FRET, SQ exhibits a high absorbance (about 3 × 10⁵ M⁻¹ cm⁻¹) in the infrared and near-infrared spectral regions and can act as a long wavelength absorber. As a result, PCE has been greatly improved from 3.27 to 4.51 %.

Here, we suggest that the efficiency of the organic solar cell can be improved by adding polythieno [3, 4-b] thiophene / benzodithiophene (PTB7) polymer to the P3HT:PCBM active layer. The emission of P3HT is overlapped with the absorption of PTB7, leading to the above-described FRET phenomenon. Also, the combined absorption spectrum of P3HT and PTB7 occupies a larger portion of the solar spectrum, thus allowing for more efficient absorption of sunlight compared with the device including neat P3HT.

The rate and range of FRET can be further extended by the generation of near-field and plasmon resonant energy transfer (PRET) by introducing plasmonic nanostructures. We have proposed a method to improve the PCE by adding gold nano-bipyramid (AuNBP) as plasmonic nanostructure to increase the light path by scattering as well as to augment the PRET efficiency via the localized surface plasmon resonance (LSPR) effect. It has been found that the AuNBP provides a stronger electric field compared with other conventional AuNPs and facilitates the overall electron excitation process of the organic photoactive layer.

ET07.06.03

Ionothermal Synthesis of Copper-Modified Graphitic Carbon Nitride—Synthetical Effects on Improved Photoelectrochemical Performance Bingjun Jin and Jong Hyeok Park; Yonsei University, Seoul, Korea (the Republic of).

Graphitic carbon nitride, as the most stable allotrope of binary carbon nitride materials, has attracted considerable attention in solar energy conversion owing to its delocalized bandgap, thermal stability and nontoxic feature. However, challenges still remain in the promotion of charge transfer due to the intrinsically sluggish kinetics. Herein, we developed a facile salt melt method to fabricate multiple-Cu-modified graphitic carbon nitride which used as an effective photocathode material. Characterizations show that the free CuCl comes from precursor and the coordinated Cu species are incorporated in the as-prepared sample simultaneously forming a novel heterostructure, which achieving coordination effect and then improving the crystallinity of graphitic carbon nitride synchronously. These special properties of the material could contribute to the significantly enhanced photocurrent density. The proposed strategy for synthesis of the multiple-Cu-modified graphitic carbon nitride can be also used as a “tool box” to produce other highly efficient photo-catalysts.

ET07.06.04

Accelerating the Production of Scalable Materials for Energy Device Production Through Open-Access User Facilities Michael B. Pomfret and John D. MacKenzie; Washington Clean Energy Testbeds, University of Washington, Seattle, Washington, United States.

The Washington Clean Energy Testbeds opened at the University of Washington in February of 2016. The Testbeds are a group of facilities that allow researchers from academia and industry to collaborate on clean energy solutions at low cost, representing an open-access model reducing risk and capital

outlays for developing commercial-scale, clean energy systems that get to market faster. Specifically, the Testbeds provide best-in-class fabrication and characterization for photovoltaic and energy storage material processing, device prototyping, pilot commercial scale manufacturing, performance verification, and systems integration. Fabrication of current state-of-the-art and next-generation photovoltaics and battery architectures is enabled through variety of advanced and additive manufacturing techniques, such as roll-to-roll printing, sheet coating, screen printing, and 3D printing with options for processing in controlled environments. A full suite of material analysis instrumentation allows for rapid iteration of novel material formations and manufacturing processes. Finished devices can be tested on industry-best solar simulators with NREL traceability, battery test channels, and/or integrated into simulated grid environments. The Testbeds serve as an innovation hub, providing access to key resources, including capital funding to startups, a relevant talent base, and new innovation programs for established companies. The presence of private companies and investors in the Testbeds represents a higher level of public-private coordination necessary to harvest the fruits of research and bring them to market faster than we see today. The Testbeds' first year of operation has provided early successes with UW spin-out companies, Battery Informatics and Membrion, achieving proof of concept, gaining early customers, and raising funds. Now in the second year of operation, the Testbeds management has evaluated a number of successful elements that will be key to helping researchers developing energy products. Facilities like the Testbeds are essential to ensuring that new materials and processing techniques make significant impact on the energy market.

ET07.06.05

Industry Scale Additive Manufacturing of Photovoltaic Devices Using Advanced Roll-to-Roll Processing Felipe J. Pavinatto, Phillip Cox, Michael B. Pomfret and John D. MacKenzie; UW-Washington Clean Energy Testbeds, Seattle, Washington, United States.

The Washington Clean Energy Testbeds provide researchers with a cost-effective solution for accelerating product development by offering pay-per-use open access to state-of-the-art R&D instrumentation. Our staff scientists have pioneered large-scale printing of both organic and perovskite photovoltaic materials using state-of-the-art additive manufacturing techniques. This expertise is essential to driving the development of scalable next-generation photovoltaic devices and systems. This know-how is passed on to Testbeds users from around the world through related proprietary work with industry partners and hands-on coatings workshops designed to train researchers on ink preparation and analysis, slot-die coating, screen printing, and film characterization. Using cutting-edge solution-processable solar materials such as PCE-11 polymer and methylammonium lead halide perovskites, users learn the latest techniques to scale up solar cell manufacturing. Workshops are fully customizable to accommodate specific interests and applications. Our unique industrial-scale roll-to-roll printer is specially designed to fabricate printed, flexible solar modules and is used to develop advanced methods for manufacturing the next generation of low-cost solar materials. By fine tuning crystal growth kinetics through innovative ink formulations and film drying methods, we demonstrate fast and effective conversion of methylammonium lead halide perovskite inks, yielding flexible perovskite films on meter length scales in just minutes. Furthermore, implementation of in-line characterization methods (e.g. light-scattering, photoluminescence and Raman spectroscopy) is underway for assessing film quality during printing. In addition to active solar material coatings, we demonstrate greater than 20 meter per minute flexographic printing of thin and smooth patterned silver electrodes on 12-inch-wide plastic substrates. High precision web guiding and registration offers the ability to print and coat full solar cell device stacks. Fabrication activities at the Testbeds are supplemented with industry-leading characterization equipment. A large suite of rapid-scan materials analysis equipment provides immediate, comprehensive feedback on formulations and fabrication processes. Completed devices can be thoroughly tested on world-class equipment against NREL traceable reference devices.

ET07.06.06

Optical Manipulation Using Microlens Array of Various Sizes in Organic Photovoltaics Dongwook Ko, Hyojin Song, Seobum Chu and Jongbok Kim; Kumoh National Institute of Technology, Gumi, Korea (the Republic of).

Organic photovoltaics (OPV) are attracting much attention because they can be made light and flexible. However, due to low power conversion efficiency (PCE) compared to silicon-based solar cells, much research is underway to improve the PCE. In order to improve the PCE, many researchers have tried to synthesize noble materials with high light absorptivity or to control a complex interface. However low charge carrier mobility of organic materials have not allowed increasing the PCE. As an alternative, researches have been conducted to introduce various physical structures such as microlens, wrinkle into OPV to control the optical path. Here, we fabricated the microlens of various diameter (0.5 μm ~ 20 μm) and confirmed that the optical path and PCE can be dramatically increased with microlens array of optimum diameter.

To study the optical manipulation with microlens array, we first prepared the microlens of various diameter (0.5 μm ~ 20 μm) by rubbing and water transfer printing method and then replicated them with Polydimethylsiloxane (PDMS). The replicated PDMS lens were analyzed by scanning electron microscope (SEM) and AFM to examine their surface morphology and by UV-VIS-NIR spectrometer to examine optical properties. The total transmittance was almost the same regardless of the diameter of microlens, but the specular transmittance was decreased by increasing diameter of microlens. It indicated that the dispersed light increased with increasing microlens diameter. Specifically, we found that dispersive transmittance was similar above 7 μm of microlens diameter. The increase of dispersive light resulted in the enhancement of the light extinction in photoactive layer. Similar to dispersed light, the light extinction was similar from 7 μm or more. Then, we measured J-V characteristic under the condition of AM 1.5G, 100mW / cm² to confirm the increase of dispersive light improve PCE in OPV. We observed that short circuit-current density (J_{sc}) increased with increasing microlens size, and it was similar from 7 μm diameter or more. We also confirmed that the PCE increased by 12% compared with the OPV without microlens.

As a result, we fabricated various diameter of lens (0.5 μm ~ 20 μm) through rubbing and water transfer printing method. Then, we confirmed that dispersive light and light extinction was increased with larger diameter of microlens. Similar to these optical properties, we confirmed that J_{sc} increases with microlens array and the PCE increases by up to 12%.

ET07.06.07

The Effect of Substrate Roughness on the Properties of Sputtered AZO Thin Film Kairi Hamada¹, Hideyuki Okumura¹, Takaya Ogawa^{1,2} and Keiichi N. Ishihara¹; ¹Socio-Environmental Energy Science, Kyoto University, Kyoto, Japan; ²The Hakubi Center for Advanced Research, Kyoto University, Kyoto, Japan.

Transparent conductive oxide (TCO) for thin film solar cells requires special features such as not only transparency and conductivity but also light scattering in order to increase optical path length and promote more photon absorption for its efficiency. Representative TCO material is indium tin oxide (ITO), while it contains scarce metal, indium (In), and is expensive. Al-doped ZnO (AZO) thin film, which has many advantages such as low cost, low sheet resistance, and high transmittance, is one of the most promising alternative candidates to replace ITO as transparent electrodes. However, AZO has the problem of low durability, and it is difficult to combine or satisfy dual properties i.e. the stability and light scattering of the film. In order to obtain simultaneously excellent light scattering characteristics and good stability of AZO film, here, we focus on roughness of the substrate as well as roughness of AZO film surface.

We prepared textured substrates and nontextured substrates, and compared them in terms of structural, optical, electrical properties and environmental stability. In addition, we employed different substrates including of quartz plate and various types of glass slides. The roughness of the substrate surface was formed by abrasive papers on a rotary polishing machine for 2 minutes, and on the roughened substrate AZO film was made with radio frequency magnetron sputtering.

We expected a high haze value of the textured sample, which is one of the widely known parameters to represent the light scattering capability of rough

surfaces. The visible haze value of the textured glass slide sample increases from 1.4% which nontextured glass slide sample showed to 39.2% with a sheet resistance of 8.0 Ω /sq and a visible transmission of 81.1%.

The notable result of this study is to change the absorption edges. For the AZO film on the glass slides, the absorption edge showed a red shift and the optical band gap changed from 3.66eV to 3.48eV by roughening. On the other hand, for the AZO on the quartz plate, the absorption edge showed a blue shift and the optical band gap changed from 3.56eV to 3.68eV by roughening. These results suggest a simple method to control a band gap of a material just by grinding surface of substrates.

The possible origin of these shifts can be the difference of thermal expansion coefficients among AZO, glass slides and quartz plate. The difference could cause the thermal stress, which leads to the occurrence of defects inside the film. These defects could change the Al content in the film, which may lead to the shift in the absorption edges due to the Burstein-Moss effect.

We will continue to study an origin of the altered absorption behavior through investigating more details to confirm above hypothesis and will discuss at the conference.

ET07.06.08

Solution-Processed, Shape-Controlled Sb₂Se₃ Light Absorber for Efficient Photoelectrochemical Water Splitting Wooseok Yang¹, Jaemin Park¹, Jaiwan Tan¹, Hyungsoo Lee¹, Yunjung Oh¹, Joosun Kim² and Jooho Moon¹; ¹Yonsei University, Seoul, Korea (the Republic of); ²Korea Institute of Science and Technology, Seoul, Korea (the Republic of).

Sb₂Se₃ is recently spurred great interest as a promising low-cost light-absorbing material for solar energy conversion applications, such as thin film solar cells and photoelectrochemical (PEC) water splitting. The properties of Sb₂Se₃ strongly depend on its crystallographic orientation and surface morphology due to the anisotropic crystal structure. In this study, we synthesized Sb₂Se₃ light absorbers with various morphological variation from thin films to 1-D nanostructures via a simple solution processing with two different Sb-Se molecular solutions. The first molecular solution is synthesized by using the solvent mixture of thioglycolic acid (TGA) and ethanolamine (EA) and the aspect ratio of 1-D Sb₂Se₃ nanostructures can be controlled by adjusting the relative mixing ratio of TGA and EA. In the other Sb-Se molecular solution using the mixture of 2-mercaptoethanol and ethylenediamine, adjusting the relative amount of the Se precursor with respect to the Sb precursor results in the significant morphological change. The growth mechanism of the various structures of Sb₂Se₃ was elucidated by liquid Raman spectroscopy. In addition, electrical and photoelectrochemical properties of the shape-controlled Sb₂Se₃ were investigated depending on the structures. After deposition of TiO₂ and Pt, an appropriately oriented Sb₂Se₃-based photocathode exhibits a significantly enhanced PEC performance; the photocurrent reached 12.5 mA cm⁻² at 0 V versus reversible hydrogen electrode under AM 1.5 G illumination.

ET07.06.09

Assessing Adhesive Degradation in Photovoltaic Backsheets Using the Single Cantilever Beam Test Scott Julien¹, Jae Hyun Kim², Xiaohong Gu² and Kai-Tai Wan¹; ¹Northeastern University, Boston, Massachusetts, United States; ²Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

The photovoltaic (PV) backsheet, a multilayered polymer sheet that is laminated to the back side of a PV module, is used for protecting the internal components from corrosion and insulating outside users from the internal electrical components. The backsheet is typically comprised of several layers of polymer, adhered or coextruded together. Over prolonged exposure to the elements (extreme temperatures and humidities, and UV radiation), these layers can undergo adhesive degradation, resulting in weakening of the interfaces or delamination, that cause reduced heat dissipation and provide sites for moisture collection. Testing methods are needed in the industry to assess the adhesive durability of new candidate backsheets, and predict their longevity.

In the present work, we assess the interlayer adhesive strength of a polyethylene terephthalate (PET)-based backsheet, using the single cantilever beam (SCB) test. Backsheet samples of PET/PET/ethylene co-vinyl acetate (EVA) were obtained, and exposed to artificial UV radiation in the integrating sphere-based weathering device, located at the National Institute of Standards and Technology (NIST) in Gaithersburg, Maryland, USA. Samples were exposed to between 290-400 nm of light for varying lengths of time, to simulate field-induced UV degradation. SCB tests were then conducted by adhering a titanium beam to the outer layer of the backsheet and pulling the beam at one end, generating delamination at the weakest interface. The applied force, beam end displacement, and location of the "delamination front" were measured, and used to compute the critical adhesion energy of the delaminating interface.

Preliminary results have been obtained for two types of unaged PPE backsheets, of identical model but acquired during different years. The results show a marked difference in adhesion between the two (250-300 J/m² vs. 1000-3000 J/m²), which illuminates the significant differences in adhesion that can occur with slight changes in manufacture or formulation. These results will be compared to those obtained from the UV-exposed samples, and the results will be used to correlate UV exposure with long-term adhesive durability. Ultimately, this knowledge is of critical need in the community, for developing predictive models of the longevity of PV backsheets deployed in the field.

ET07.06.10

Adhesive Durability of Photovoltaic Backsheets as a Function of Indoor Accelerated Weathering Exposure Scott Julien¹, Jianfeng Sun¹, Yu Wang², Andrew Fairbrother³, Xiaohong Gu³, Sophie Napoli⁴, Liang Ji⁵, Kenneth P. Boyce⁵, Mike Kempe⁶, Roger H. French², Laura S. Bruckman², Gregory S. O'Brien⁴, Adam W. Hauser⁴ and Kai-Tai Wan¹; ¹Mechanical and Industrial Engineering, Northeastern University, Boston, Massachusetts, United States; ²Materials Science & Engineering, Case Western Reserve University, Cleveland, Ohio, United States; ³Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland, United States; ⁴Arkema, Inc., King of Prussia, Pennsylvania, United States; ⁵Renewable Energy, Underwriter's Laboratories Inc., Northbrook, Illinois, United States; ⁶Photovoltaics Research, National Renewable Energy Laboratory, Golden, Colorado, United States.

Photovoltaic (PV) backsheets are polymer sheets used to protect the backside of a PV module from moisture and mechanical damage. They typically consist of multiple layers of polymers, adhered or coextruded together. Over prolonged exposure to harsh outdoor elements—extreme temperatures and humidity, and ultraviolet (UV) radiation—debonding between the layers of the backsheet can occur. The resulting interlayer voids diminish heat dissipation, reduce the effectiveness of the backsheet as a physical barrier, and serve as collection sites for moisture. There is a need within the PV community for methods to quantify the adhesive integrity of the backsheet.

In the present work, we apply a wedge test to measure the interlayer adhesion energy of backsheet samples exposed to indoor accelerated weathering. Test coupons are prepared by laminating a backsheet sample to a glass substrate, then exposing it to an indoor accelerated weathering protocol. Wedge tests were performed by adhering a titanium beam to the outer layer of the backsheet, then pulling the beam at one end, generating delamination at the weakest interface. A wedge subsequently inserted into interface was used to drive delamination in a displacement-controlled manner. The location of the

“delamination front” was measured at intermittent points, and used—in conjunction with the known elastic properties of the beam and wedge thickness—to compute the adhesion energy of the interface.

Tests were performed on backsheets of several different polymer types, and exposed to several different accelerated weathering conditions. Backsheet polymer types included polyamide (PA)-, polyvinyl fluoride (PVF)-, polyethylene terephthalate (PET)-, and polyvinylidene fluoride (PVDF)-based backsheets. Exposure conditions included several UV protocols (e.g. 65°C at 20% relative humidity (RH) with an irradiance of 0.8 W/m².nm at 340 nm) as well as “dark” protocols (e.g. 85°C at 85% RH). The results show a clear difference in adhesive strength among the different types of backsheet, as well as an observable decrease in adhesive strength with exposure time, for several backsheet types. Furthermore, they show a change in location of the delamination interface with prolonged exposure duration. The results are useful in developing correlations with adhesive degradation measured in field-deployed modules, and are currently being used as part of a large-scale study to develop predictive models for the long-term reliability of PV modules.

ET07.06.11

Optical and Electrical Properties of Bulk Heterojunction CISE Films [Aida Torabi](#); Texas A&M-Central Texas, Killeen, Texas, United States.

Bulk homojunction CISE films are being developed as a new candidate for PV applications. The structures of these films are complex with the fabrication process dictating film properties. Herein we present our study on the optical and electrical properties of these materials deposited via electrodeposition. Cathodoluminescence (CL), Electron beam-induced current (EBIC), and energy dispersive X-ray spectroscopy (EDS) were measured from different films. Photoluminescence (PL) measurements were also taken to study large areas of the film. We observed peaks in the luminescence which may correspond to both the n and p semiconductors as well as trap states. These responses were mapped across the film to determine possible fabrication improvements.

ET07.06.12

The Voltammetric Hysteresis Behavior and Potential Scan Rate Dependence of a Dye Sensitized Solar Cells T. M. W. J. Bandara¹, [Ajith DeSilva](#)², K. Vignarooban³ and L. N. Senavirathna³; ¹Physics, University of Peradeniya, Peradeniya, Sri Lanka; ²Physics, University of West Georgia, Carrollton, Georgia, United States; ³Physics, University of Jaffna, Jaffna, Sri Lanka.

During last three decades the field of dye sensitized solar cells (DSSCs) gained significant advancement; however, there are some unresolved issues related to characterization of DSSCs. For example, the voltammetric hysteresis such as current density versus cell potential (J - V) curves, is a serious concern because it is known that the performance of DSSCs depends on the direction and the rate of cell potential scan. The present work is focused on studying the dependence of solar cell performance on the direction and the rate of cell potential scan in a DSSC prepared with a novel gel polymer electrolyte. For this purpose, the photo electrode was prepared by sensitizing TiO₂ double layers with N719 dye. The new gel polymer electrolyte used in this work is based on polyacrylonitrile (PAN) (Mw. 150,000) tetrahexyleammonium iodide, KI, 4-tertbutylpyridine (4TBP), Butyl-3-methylimidazolium iodide (BMII) and plasticizers, propylene carbonate (PC) and ethylene carbonate. J - V characteristics of the cells were obtained by varying the scan rate (from 0.01 to 0.1 V s⁻¹) and the direction (from forward bias to reverse bias and reverse bias to forward bias). The quasi solid state DSSC prepared in this work exhibited short circuit current density, open circuit voltage and efficiency 13.63 mA cm⁻², 0.76 V and 6.4% respectively under 1000 W m⁻² irradiation. The energy conversion efficiency of the DSSC increased from 5.9 to 6.4% with the increase of the scan rate (from 0.01 to 0.1 V s⁻¹), when the scanning is conducted from forward bias to reverse bias direction. However, when the scanning direction is reversed a drop of the efficiency was observed with increasing rate of potential scan. Therefore, different trends of efficiency variation were exhibited with the change of the direction of potential scan. The properties of the electrolyte and the DSSC were characterized further by analyzing complex spectroscopic data. Present work emphasizes the importance of reporting the rate and direction of potential scan with solar cell performance parameter.

SESSION ET07.07: Surface and Interface Engineering for Energy Materials

Session Chairs: Guang Yang and Pu Zhang

Wednesday Morning, November 28, 2018

Hynes, Level 3, Room 312

8:15 AM *ET07.07.01

Scalable Surface Modification Approach for Stabilizing Battery Materials [Chunmei Ban](#); National Renewable Energy Laboratory, Lakewood, Colorado, United States.

Electrode materials determine the energy density of lithium-ion batteries, while electrochemical behavior and cycling performance rely on chemical and physical properties of the interphase for efficient charge/electron transfer at the interface. Atomic/molecular layer deposition (ALD, MLD) techniques have been successfully introduced into this field for modifying the surface chemistry and manipulating the chemi-physical properties of the electrode-electrolyte interphase for reversible electrochemical reactions. Combining structural and spectroscopic results, this presentation will present the ALD/MLD coating effects on electrochemical properties of electrode materials—including both transitional metal oxide cathodes and high-capacity silicon anodes. Furthermore, recent developments on the scalable surface modification strategies will be elaborated to exploit the complicate interphase chemistry at surface of battery electrodes. This study provides fundamental insights in chemistry of ALD/MLD-synthesized artificial electrode-electrolyte interphase, but also discusses coating strategies toward industrial applications.

8:45 AM ET07.07.02

Application of Mixed-Phase MnO₂/Nitrogen-Containing Graphene Composites to Flexible Asymmetric Solid-State Supercapacitors Hsin-Ya Chiu and [Chun-Pei Cho](#); National Chi Nan University, Nantou County, Taiwan.

The electrode active materials of supercapacitors in this work were prepared by a low-cost and facile hydrothermal method. The nitrogen-containing graphene/MnO₂ (x-NGM) composites were obtained by growing α - and γ -phase MnO₂ nanostructures on the surface of nitrogen-containing graphene. A PVA/LiCl electrolyte gel membrane was used as the separator between the two electrodes of the supercapacitors. By changing the Mn content and adjusting the mass loading of active materials, the capacitance parameters of various electrodes and devices were investigated. Excessive contents of Mn were discovered to be detrimental to ionic transport and Faradaic charge transfer, and inferior capacitance performance has thereby resulted. Mass overloads of active materials were demonstrated to reduce conductivity, leading to worse capacitor characteristics. After calculation by the CV results, the

asymmetric solid-state supercapacitor 3-NGM1//G1 exhibited the highest specific capacitance of 579 Fg⁻¹. Its corresponding energy and power densities were 73.6 Whkg⁻¹ and 4400.0 Wkg⁻¹, respectively, implying the good charge-discharge capacity. After 2000 bending cycles of GCD under the current density of 1 Ag⁻¹, the retention rate of specific capacitance was approximately 86.7 %. The high flexibility, cycling stability, and good capacitance properties could be ascribed to the synergistic effect of mixed-phase MnO₂ and nitrogen-containing graphene. By combining the electric double-layer material with a pseudocapacitance material, two charge storage mechanisms were in conjunction to improve charge transfer, conductivity, and thus capacitor performance.

9:00 AM ET07.07.03

Demonstration of a Self-Forming Solid State Rechargeable Li/I₂ Battery [Alyson Abraham](#)¹, Jianping Huang¹, Paul Smith¹, Amy C. Marschilok^{1,2}, Kenneth Takeuchi¹ and Esther Takeuchi^{1,2}; ¹Stony Brook University, Stony Brook, New York, United States; ²Brookhaven National Laboratory, Upton, New York, United States.

Lithium based battery systems are attractive due to their higher energy densities, however, safety issues resulting from use of organic electrolytes and formation of Li dendrites remain major concerns. Solid state electrolytes provide an alternative to organic electrolyte, but present their own challenges, including limits in ionic conductivity and the lithium/solid-state electrolyte interface. Self forming batteries, where the anode and cathode are formed upon charge from a single solid electrolyte, can be a promising avenue to address and reduce interfacial resistance. The Li/I₂ couple is an attractive target due to its high energy density (1536 Wh/L, 560 Wh/kg) and opportunity to self-heal. Notably, the primary Li/I₂ battery has been a successful technology as the power source for pacemakers.

Herein, we describe a fully self-forming solid state rechargeable battery based on the Li/I₂ couple using LiI rich lithium iodide-(3-hydroxypropionitrile)₂ electrolyte. To our knowledge, this is the first demonstration of a rechargeable fully self-forming solid state lithium battery with the inclusion of LiI(HPN)₂. Characterization to verify the formation of the self-forming active battery will be discussed. The impact of variables such as LiI and LiI(HPN)₂ ratio and charging condition on the resulting impedance of the battery system will also be described. These results show promise for the future development of high energy density solid state self-forming self-healing batteries.

9:15 AM ET07.07.04

3D Interconnected Binder-Free Electrospun MnO@C Nanofibers for Supercapacitor Devices [Nageh K. Allam](#); American University in Cairo, New Cairo, Egypt.

Rational design of binder-free materials with high cyclic stability and high conductivity is a great need for high-performance supercapacitors. We demonstrate a facile one-step synthesis method of binder-free MnO@C nanofibers as electrodes for supercapacitor applications. The topology of the fabricated nanofibers was investigated using FESEM and HRTEM. The X-ray photoelectron spectroscopy (XPS) and the X-ray diffraction (XRD) analyses confirm the formation of the MnO structure. The electrospun MnO@C electrodes achieve high specific capacitance of 578 F/g at 1 A/g with an outstanding cycling performance. The electrodes also show 127% capacity increasing after 3000 cycles. An asymmetric supercapacitor composed of activated carbon as the negative electrode and MnO@C as the positive electrode shows an ultrahigh energy density of 35.5 Wh/kg with a power density of 10.7 kW/kg. The device shows a superior columbic efficiency, cycle life, and capacity retention.

9:30 AM ET07.07.05

Electrochemical Supercapacitor Based on a Heterostructure of 1D Mo₆Te₆ Nanowires and Few Layer 2D 1T'-MoTe₂ [Sachin A. Pawar](#)¹, Dipali Patil¹, Donghwan Kim^{1,2}, TaeWan Kim² and Jae Cheol Shin¹; ¹Yeungnam University, Gyeongsan-si, Korea (the Republic of); ²Korea Research Institute of Standards and Science, Daejeon, Korea (the Republic of).

Transition metal dichalcogenides (TMDs) with the layered structures are an analogue of a graphite which consists stacked graphene monolayers. TMDs are having many technologically essential and scientifically amazing properties due to their anisotropy. The layered TMDs demonstrate the most favorable electrochemical properties owing to their better electrical conductivities due to intrinsically layered structure and large surface areas. Amongst all TMDs viz., S, Se and Te, Te-based TMDs display higher electrical conductivities which are advantageous to enhance the superior performance of electrochemical supercapacitors. The semiconducting nature in S, Se based TMDs and 2H phase largely hinders their electrochemical performance owing to poor electronic conductivity. Moreover, Te-based TMDs as supercapacitors are gaining a lot of attention nowadays with a few reports. Integration of one dimensional (1D) 1T'-Mo₆Te₆ nanowires (NWs) into few layered two dimensional (2D) 2H MoTe₂ thin film is not realized yet for the supercapacitive studies. Herein, we demonstrate the growth of 1D 1T'-Mo₆Te₆ NW/2D 2H MoTe₂ thin film heterostructure through metal organic chemical vapor deposition (MOCVD) on Si/SiO₂ and thereby successful transfer of these heterostructure on flexible nickel (Ni) foam current collector by simple chemical etching protocol for high performance supercapacitor. A layer by layer study of Mo₆Te₆/MoTe₂ heterostructure is carried out by varying the number of transfer layers on Ni foam. The resultant supercapacitors demonstrate a three fold enhancement in areal capacitance (1412 mFcm⁻¹) than a single layer transferred electrode with excellent electrochemical stability (96%) and high energy density (140.36 mWcm⁻²). These supercapacitors outperform the TMD based (Te-based) supercapacitors presented in the past portraying the abundant potential for energy conversion devices.

9:45 AM ET07.07.06

Golden, Grey and White Titania—Controlled Surface Oxidation Towards Visible Light Assisted Water-Splitting [Larissa S. Chapman](#), Fayna Mammari and Souad Ammar; ITODYS, Université Paris Diderot, Paris, France.

The search for energy alternatives to reduce our dependency on fossil fuels has been a very pressing topic for the last few decades. Despite significant advances, oil remains the most used fuel worldwide, while also being the fuel that emits the most CO₂, apart from coal. [1] In contrast, hydrogen rises as a carbon-free fuel with the highest known energy content, while producing only water as a byproduct. [2]

When comparing different routes for hydrogen production, unfortunately the ones that rely on fossil fuels are still the most economically viable, since the low efficiencies of routes that use renewable raw materials or energy sources result in a high cost. [2] The key to balance this equation is to improve the efficiency of cleaner routes such as photo electrolytic water-splitting to make the hydrogen production cheaper and more widespread as fuel alternative. In this work, we propose a controlled surface oxidation of metallic titanium plates as a mean to enable its use as photo anode in visible light assisted water-splitting systems. The different degrees of oxidation and predominant treating mechanisms led to different characteristics and photo electrochemical properties of the treated samples, allowing us to tune the oxidized layer and obtain very promising materials. By varying key parameters, we managed to increase the TiO₂'s visible light absorption band while keeping its semiconductor behavior, which is crucial to its application in photo electrolytic water-splitting systems.

We show, then, that the structural defects and composition variations generated during the productive process are an effective way to improve the photo catalyst's efficiency.

The proposed process consists of few and simple steps, uses easy-to-obtain reagents and relatively low calcination temperatures. In addition, the use of metallic plates with highly adhered oxide layers presents practical and environmental advantages when compared to unsupported photo catalysts or similar

materials. These characteristics indicate that an eventual optimization and upscaling of the process up to industrial level is a possibility worth considering in the future.

[1] International Energy Agency, Key World Statistics 2017

[2] Pavlos Nikolaidis, Andreas Poullikkas, A comparative overview of hydrogen production processes, Renewable and Sustainable Energy Reviews, Volume 67, 2017

10:00 AM BREAK

10:30 AM *ET07.07.07

Coating Ceramic Films onto Lithium-Ion Battery Electrodes Bryant J. Polzin, Stephen E. Trask, Alison R. Dunlop, Nancy L. Dietz-Rago and Andrew N. Jansen; Argonne National Laboratory, Lemont, Illinois, United States.

Lithium-ion batteries have steadily advanced over the last three decades with great advancements in energy density and cycle life, while still maintaining acceptable safety tolerances. Further advances will continue to rely on creative uses of materials' properties such as developing multi-layer electrode-separator systems. These coated electrodes will serve a variety of applications, such as:

- Replace polymer separator with ceramic separator (added safety)
- Getter undesirable decomposition products with ceramic/functional film
- Suppress formation of lithium dendrites with novel electrode architecture.

The Cell Analysis, Modeling, and Prototyping (CAMP) Facility at Argonne National Laboratory is developing the capability to coat specialty films onto electrodes (preferably the anode). The overall mission of the CAMP Facility is to enable the transition of new advanced battery chemistries invented in research laboratories to industrial production through independent validation and analysis in prototype cell formats (xx3450 pouch, xx6395 pouch, and 18650 rigid cells). It is an integrated team designed to support production of prototype cells using semi-automated cell fabrication equipment, and includes activities in materials validation, modeling, and diagnostics - it is ideally suited to address this new field of R&D.

Initial focus here is on coating ceramic-based films onto the negative electrode. Later efforts may include developing methods of coating functional materials and/or polymer films onto negative or positive electrodes. Two ceramic materials (Al_2O_3 and MgO) were chosen to scope out the techniques needed for coating onto graphite electrodes. These ceramics are relatively benign in a typical lithium-ion battery system, and could thus serve the purpose of functioning as an added safety refractory layer to support a standard polymer separator during thermal abuse, or as a complete replacement of the polymer separator. Other ceramic materials were used later. In the work presented here, a PVDF-based slurry was used to adhere the ceramic particles to the graphite electrode.

Early coating attempts used a hand coating (doctor blade) method. Attempts were made with a roll-to-roll reverse-comma coater, but process issues arose. Other coating technologies are needed to enhance the coating process, which will be discussed in the presentation. Successful coatings were used in various electrochemical tests in prototype cells (coin & pouch), with and without separators, versus cathodes and lithium counter electrodes. The results from these cell tests are promising. In addition, Argonne's state-of-the-art facility in battery failure analysis (Post-Test Facility - PTF) inspected the interface between the anode and ceramic layer. These results will also be discussed in more detail.

Support from Peter Faguy, Steven Boyd, and David Howell of the Department of Energy's Vehicle Technologies Office is gratefully acknowledged.

11:00 AM ET07.07.08

Electrospinning Process for Lithium-Ion Battery Separator Wisawat Keaswejareansuk¹, Jianyu Liang¹ and Xiang Wang²; ¹Worcester Polytechnic Institute, Worcester, Massachusetts, United States; ²Department of Material Science and Engineering, Wuhan University of Technology, Wuhan, China.

Electrospinning (ES) is a versatile and straightforward process to fabricate high porous membranes with high surface to volume ratio. It is a relatively simple and efficient technique to create continuous fibers at nanoscale. The electrospun fibers are collected in ranges of micro- and nano-meters. Although the ES has been widely studied and the electrospun membranes have been created for many biomaterial and energy applications, the electrospun separators have specific characteristics to meet with the requirements of lithium-ion battery (LIB) separators. The separators are electrochemically inactive but crucial for providing safety to the battery. The primary commercial separator materials for LIB are polyolefin, which is anisotropic. Because of the anisotropic characteristic, it is easily damaged by puncture force, tension force and dendrite growth in a certain direction (transverse). The damages allow internal short circuits leading to battery fire and explosion. Properties of the electrospun membranes in a form of non-woven mats are independent to the membrane directions. The operation principle of the ES is simply a high electric potential is applied to a spinneret, which is connected to a polymer solution syringe. Polymer solution is fed by a syringe pump and spun in the electric field. The charged spun solution is elongated to a fiber-like jet, and then collected on a collector. The characteristics and properties of the electrospun membrane can be customized by simultaneously adjusting the materials parameters and regulating the process parameters. The material parameters are types of polymer, solvent systems and concentration of polymer solution. The process parameters include electric potential, spinneret-to-collector distance, solution feed rate and collector configuration. In this presentation, we will briefly explain the requirements of LIB separators and discuss in detail the effects of material and process parameters, the process control, and characterizations for customized electrospun separators' characteristics and properties.

11:15 AM ET07.07.09

Ultra Lightweight, High Power Density Lithium-Ion Batteries Mihai Duduta, Sebastien de Rivaz, David Clarke and Robert Wood; Harvard University, Cambridge, Massachusetts, United States.

Existing fabrication technologies cannot be used to make lightweight, high power density lithium ion batteries (>300mg). The need is increasing for these small, powerful batteries, as advances in fabrication techniques push the limits of miniaturization in robotics, haptics, wearable and biomedical technologies, and mobile computing for the Internet of Things. Unfortunately, current fabrication methods for lithium ion cells force the end user to make a choice between high energy density and lightweight batteries. Supercapacitors can provide even higher power density (>10 kW/kg), but have very short discharge times (0.1- 5s) which limits the range of potential applications. To push the limits of performance, we have developed a hybrid manufacturing approach which uses commercially available lithium ion materials and a laser micro machining method to build lightweight (10-200 mg) high power density (>1 kW/kg) batteries.

11:30 AM ET07.07.10

Development of Novel Thermoelectric Alloy Systems Through Fine Tuning the Eutectic Microstructure Sireesha P; Indian Institute of Science-Bangalore, Bangalore, India.

Abstract:

Conversion of dissipated heat into electricity is the basic principle of thermoelectricity. It has wide variety of applications in the areas such as automobile engineering, refrigerating coolants, satellite etc. These days there is a high demand of materials which are efficient in converting heat in to electricity [1]. In search of such materials thermoelectrics has given wide scope to complex materials like Tellurides, Clathrates, Zintl compounds, Half Heusler alloys, Si-Ge, Skutterudite etc. The defining factor for thermoelectric materials is ZT, thermoelectric figure of merit. This attributes to the power factor (σ electrical conductivity S-Seebeck coefficient enhancement and thermal conductivity reduction. Band gap tuning, carrier concentration are a few ways to improve power factor where as in parallel, grain size reduction, point defects, dislocations are key ways to thermal conductivity reduction. These can be achieved experimentally through microstructural engineering and processing [2]. The issues existing with available thermoelectric materials are associated with stability of performance for a long range of temperatures. Fine tuning of microstructure is the key factor in overcoming the thermal stability issues. Currently we are exploring a program of microstructure- transport properties correlation of newly processed thermoelectric alloys by fine tuning the eutectic microstructure. In this current work, we have synthesized a set of thermoelectric alloys eutectic and off eutectic compositions in Sn-Te alloy system ($\text{Sn}_{1-x}\text{Te}_x$ (at%)) [3]. These as melted alloys show eutectic microstructure consisting of $\text{Sn}_{50}\text{Te}_{50}$ and Te phase with varied volume fraction. Variations of transport properties with respect to secondary phase fraction have also been studied. Eutectic microstructure with different phase boundary will always help in minimizing lattice thermal conductivity by disrupting phononic movement. Hypo and Hyper eutectic composition are ($\text{Sn}_{20}\text{Te}_{80}$ (at%)) and ($\text{Sn}_4\text{Te}_{96}$ (at%)).

The elemental distribution mapping and the compositional analysis using electron probe microanalysis (WDS), demonstrates that the matrix is rich in tellurium and the continuous phase has the composition of $\text{Sn}_{50}\text{Te}_{50}$ (at%). Transport properties of the current alloy are attractive in terms of standard thermoelectric material ($S \sim 133 \mu\text{V/K}$ and $P \sim 3 \mu\text{W/cm-K}^2$ at 420°K). We are presently calculating Figure of Merit and detailed structural characterization of this alloy. Further attempts are being made for achieving more improved properties by elemental additions and fine tuning the microstructure. The detailed microstructure-transport properties correlation will be presented.

Acknowledgement: The authors would like to acknowledge the facility of the AFMM.

References:

- [1]. Terry M. Tritt, Annu. Rev. Mater. Res. 2011. 41:433–48.
- [2]. G. Jeffrey Snyder, Eric S. Toberer, Nature materials, 2008, VOL. 7, 105.
- [3]. SOHRAB RABII, Physical Review, 1969, VOL 182, 3, 822.

SESSION ET07.08: Diagnostics and Characterization
Session Chairs: Peter Smyrek and Yuefei Zhang
Wednesday Afternoon, November 28, 2018
Hynes, Level 3, Room 312

1:45 PM *ET07.08.01

Direct 3D Elemental Mapping of Li-Ion Batteries Using Ultrafast Laser Ablation Spectroscopy Vassilia Zorba; Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Direct chemical imaging and analysis of Li-ion batteries provides important information on factors that determine their overall performance, including energy density, specific energy and cycle lifetime. Despite progress in the chemical analysis of Li-ion battery materials, significant challenges remain, including the ability to analyze samples in their inherent environments and to provide spatially-resolved chemical information. In this work we introduce femtosecond laser ablation-based optical emission spectroscopy coupled with advanced visualization capabilities for the elemental imaging of Li-ion battery components including anodes, cathodes and solid electrolytes. We also address the use of ultrafast optical vortex beams with varying orbital angular momentum as sampling tools in optical emission spectroscopy, and present the influence of topological charge on the analytical sensitivity. In addition, we demonstrate the ability to perform standoff elemental and isotopic analysis at extended distances through the incorporation of femtosecond laser filaments. Two-dimensional (2D) layer-by-layer mapping, 2D cross-sectional imaging and three-dimensional (3D) volume rendering of major and minor elements in Li-ion battery components are presented. Depth-resolved analysis of the solid-electrolyte interphase (SEI) layer is also presented ex situ. The elemental distributions are correlated to the electrochemical performance and serve to identify strategies to improve high energy density Li-ion technologies. These chemical imaging technologies allow a sophisticated understanding of the three-dimensional distribution of major and minor elements, and impurities.

2:15 PM ET07.08.02

Laser-Induced Breakdown Spectroscopy—A New Diagnostic Approach for Advanced Electrode Architectures Peter Smyrek^{1,2}, Yijing Zheng¹, Jan-Hendric Rakebrandt¹, Hans J. Seifert¹ and Wilhelm Pfleging^{1,2}; ¹Institute for Applied Materials - Applied Materials Physics, Karlsruhe Institute of Technology, Karlsruhe, Germany; ²Karlsruhe Nano Micro Facility, Eggenstein-Leopoldshafen, Germany.

Based on a recent technology approach, three-dimensional (3D) architectures were introduced in lithium nickel manganese cobalt oxide (NMC) cathodes by femtosecond laser ablation. Here, an increased active surface area was formed leading to an improvement of lithium-ion diffusion mobility. Additionally, a spontaneous and homogeneous liquid electrolyte wetting along the entire electrode could be realized. Especially for an electrode thickness larger than 100 μm , this technology enables an improvement in capacity retention and a reduction of cell impedance. For the characterization of electrodes after manufacturing and at various state-of-charge, the lithium distribution was quantitatively investigated by laser-induced breakdown spectroscopy (LIBS). For this type of application, LIBS is a rather new approach in order to obtain post-mortem data about chemical degradation of electrodes, achieved from the surface down to the current collector interface. Furthermore, LIBS provides a great potential for enabling advanced fundamental studies on 3D electrode micro-structures for discovering their impact on performance enhancement regarding battery life-time and capacity as a function of electrochemical cycling parameters. In general, the main objective is to develop an optimized 3D cell design with improved electrochemical properties,

which can be correlated to a characteristic lithium distribution along the laser generated 3D architectures. For this purpose, 3D elemental imaging and depth profiling was performed for the entire electrode. The measurements were carried out in ambient air, applying a multivariate calibration technique "Partial Least Squares Regression". It could be clearly shown that the generation of 3D architectures tremendously influences the electrochemical performance. Results achieved from post-mortem studies will be presented for cells with unstructured and laser-structured electrodes.

2:30 PM BREAK

3:30 PM *ET07.08.03

Critical Size Scale and Effects of Manufacturing Defects on Plating in Li-Ion Batteries [Craig B. Arnold](#); Princeton University, Princeton, New Jersey, United States.

Lithium plating is an important degradation mechanism in Li-ion batteries that not only reduces battery capacity, but also can lead to catastrophic failures. The plated lithium can turn into dendrites and gradually grow through the separator, leading to a short circuit. In this study, we show that certain types of manufacturing defects can create conditions favorable to enhanced lithium plating in these cells under normal cycling conditions due to transport gradients within the systems. In particular, we explore effects of defect size and distribution within the cell and the corresponding effect on the plating behavior. Below a critical defect size, plating is unlikely to occur and we develop a simple phenomenological approach to guide manufacturing and quality control in assessing this situation for a given battery cell. Such studies help elucidate the fundamentals behind heterogeneous plating and can provide practical insights into battery safety and product control.

4:00 PM *ET07.08.04

Observing the Volume Change Process of Si/C Electrode by *In Situ* SEM at Elevated Temperature [Yuefei Zhang](#)¹, Rui Wu¹, Huifeng Shi¹ and Yijing Zheng²; ¹Institute of Microstructure and Property of Advanced Materials, Beijing University of Technology, Beijing, China; ²Karlsruhe Institute of Technology, Karlsruhe, Germany.

Compared to the conventional graphite electrode, the silicon-carbon electrode has attracted much interest from researchers due to its high theoretical capacity. However, the Si/C composite electrode is still limited by the low rate capability and cyclability induced by the microstructural challenges such as mechanical failure, SEI crack, and low ions kinetics, et al. Since the volume expansion rate of silicon is about 300% during charging and discharging, while graphite only expands by 10%, the different expansion rate could lead to poor contact of the electrodes and even pulverization.

Among all the improved methods, 3D-structured electrode could potentially alleviate the structural damage caused by volume expansion through the empty space formed by the high-energy laser beam. Therefore, understanding the structural evolution mechanisms of 3D electrode under working conditions and its possible failure mode during the charge/discharge process helps researchers to improve the performance of batteries more purposefully.

The in-situ, real-time, dynamical studying of electrode can directly provide the evidence of structure evolution under charge-discharge cycles. Here, we use the self-developed joint SEM-electrochemical system with the temperature controller to observe the morphological evolution of 3D Si/C composites electrodes. According to the experiment results, we found the separation process of active materials from current collectors because of the electrode's volume expansion, which leads by the insertion of lithium ion, and the separation direction is from edge to center. As temperature rise from 20°C to 60°C, the discharge voltage platform and discharge time also increase due to the more intense ion movement. Besides, the electrode with 3D structured has better cycle performance than the ordinary plane electrode.

4:30 PM ET07.08.05

Geometry and Size Dependence of Transport Non-Uniformities on Localized Plating [Xinyi M. Liu](#), Alta Fang, Mikko Haataja and Craig B. Arnold; Princeton University, Princeton, New Jersey, United States.

Lithium plating, the formation of metallic lithium, is an important degradation mechanism that not only reduces battery capacity but also can lead to catastrophic failures. While most lithium plating can be prevented under normal cycling conditions, it is difficult to avoid localized plating. In previous work, we demonstrated that the heterogeneity of materials or defects in cells can create non-uniform ionic transport, leading to regions with high current densities and therefore induce plating [1]. In this work, we look further into the importance of the size scale and geometry of transport non-uniformity on localized plating, and directly relate the size scale to the capacity fade of a battery.

We create transport non-uniformities by mechanically compressing separators to close all the pores and cutting the compressed separators into different patterns and sizes. The compressed separator defects were then placed inside the coin cell along with a pristine layer of separator. After a number of cycles, cells were disassembled to record the amount of plating on the electrode surface.

In this work, we show that certain geometric features are more vulnerable to plating than others and localization strongly depends on size [2]. A single continuous feature in a separator induces more plating than a collection of smaller features with same total area. By defining a simple IE ratio, which is a characteristic of size and geometry, we relate the ratio to the propensity of plating. A region with a high IE ratio means more concentrated ionic flow and is more vulnerable to plating. A large defect feature induces more capacity fade of a battery than a small feature. We also demonstrate numerically and experimentally that there exists a critical size scale below which localized plating is unlikely to occur, and such critical size depends on the current density. Finally, we look into the interactions between multiple features that are spaced at various distances. This work not only elucidate the fundamentals behind localization, but also provide insights into battery safety and product control.

1. Cannarella, John, and Craig B. Arnold. "The effects of defects on localized plating in lithium-ion batteries." *Journal of The Electrochemical Society* 162.7 (2015): A1365-A1373.

2. Liu, Xinyi M., et al. "Size Dependence of Transport Non-Uniformities on Localized Plating in Lithium-Ion Batteries." *Journal of The Electrochemical Society* 165.5 (2018): A1147-A1155.

4:45 PM ET07.08.06

Laser-Engineering and -Analytics in Electrode Manufacturing for Lithium-Ion Batteries [Wilhelm Pflöging](#)^{1,2}, Peter Smyrek^{1,2}, Yijing Zheng¹, Jan-Hendric Rakebrandt¹, Yangping Sheng³, Marissa Wood³, David Wood³, Jianlin Li³ and Hans J. Seifert¹; ¹IAM-AWP, Karlsruhe Institute of Technology, Karlsruhe, Germany; ²Karlsruhe Nano Micro Facility, Eggenstein-Leopoldshafen, Germany; ³Energy & Transportation Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

So far, high production costs, restricted process reliability, small energy and power density, and short operational lifetime are the main issues of lithium-ion batteries (LIBs). Manufacturing of thick film electrodes is one suitable approach for achieving high-energy densities in LIBs. However, thick film electrodes suffer from electrolyte transfer limitations. Therefore, electrodes with film thickness of about 40-50 µm are currently used for high-power

operation while thick film electrodes (thickness $\geq 100 \mu\text{m}$) are developed for high-energy applications. LIBs with high-energy and high-power density can be realized by introducing a three-dimensional (3D) battery concept, which offers an improved electrolyte transfer in thick film electrodes and an improved lithium-ion transport kinetic. For developing next generation batteries, the 3D battery concept, originally invented for micro-batteries, will be transferred to LIBs with large footprint areas. For this purpose, laser materials processing was recently introduced in research and industry enabling advanced design rules for new and state-of-the-art electrode materials. A significant increase of active surface area in lithium-ion cells is achieved by direct ultrafast laser-assisted structuring of composite electrodes. 3D micro-structures and capillary features in thick film anodes and cathodes are formed in order to shorten the electrolyte diffusion distance and consequently for the improvement of rate performance. The electrochemical performance of lithium-ion cells (coin cells, pouch cells) with laser-structured electrodes were analyzed and compared to cells with unstructured electrodes. The 3D micro-structured electrodes demonstrate high rate capability and an improved liquid electrolyte wetting. Laser-induced breakdown spectroscopy was applied as an analytical tool for chemical characterization of entire electrodes. Elemental mappings were recorded for the development of coating processes. Additionally, post-mortem studies were carried out for investigating degradation processes related to thick film electrodes.

SESSION ET07.09: Poster Session III: Energy Conversion and Applications

Session Chairs: Corie Cobb and Yijing Zheng

Wednesday Afternoon, November 28, 2018

8:00 PM - 10:00 PM

Hynes, Level 1, Hall B

ET07.09.01

Diffusion Controlled Molecular Doping in Conjugated Polymers and Its Effect on Thermoelectric Power Jachong Park¹, Yeongkwon Kang¹, Sang Eun Yoon², So Yeon Noh³, Jeongwoo Park⁴, Dae Woon Lee², Taekyeong Kim⁴, Gun-Ho Kim³, Dong Wook Chang⁵, Jong H. Kim² and Bong-Gi Kim¹; ¹Department of Organic and Nano System Engineering, Konkuk University, Seoul, Korea (the Republic of); ²Department of Molecular Science and Technology, Ajou University, Suwon, Korea (the Republic of); ³School of Mechanical, Aerospace and Nuclear Engineering, UNIST, Ulsan, Korea (the Republic of); ⁴Department of Physics, Hankuk University of Foreign Studies, Yongin, Korea (the Republic of); ⁵Department of Industrial Chemistry, Pukyong National University, Busan, Korea (the Republic of).

The low dielectric constant of organic materials and inhomogeneous distribution of molecular dopants in a conductive matrix impose difficulties in populating free charge carriers in organic materials, leading to practical challenges in developing highly conductive organic materials. We designed two different CPs with long side chains and an electron-donating isoindoloindole derivative in a way that the CPs strongly interact with molecular dopant, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethan (F4-TCNQ), and the doping efficiency was further enhanced through sequential doping to promote the diffusion degree of F4-TCNQ. With these strategies, electrical conductivities of the doped CPs films were significantly improved (over 140 S cm^{-1}), much larger than that obtained from the conventional blending approach (5 S cm^{-1}). Furthermore, the doping level is scalable with the exposure duration in the F4-TCNQ solution as well as the solution's concentration. The diffusion degree of F4-TCNQ is systematically correlated with physical properties (glass transition temperature and crystallinity) of CPs through the characterization of electrical conductivity according to the thermal annealing temperature of the pre-deposited CP films for the sequential doping. Finally, we observed distinct relations between electrical conductivity and Seebeck coefficient depending on the morphology of the doped CPs films, which suggests the fundamental effects of film morphology on charge carrier transport.

ET07.09.02

Mustard Seed Based Triboelectric Nanogenerator Sachin K. Singh¹, Subas Muduli², Ramamurthy Boomishankar¹ and Satishchandra Ogale²; ¹Chemistry, Indian Institute of Science Education Research, Pune, India; ²Physics, Indian Institute of Science Education and Research, Pune, India.

Mechanical energy from a local domain is seldom recovered due to its fluctuating amplitude and low frequency and is therefore usually designated as "unsystematic" energy. With several new ideas and device schemes introduced by Z. L. Wang and coworkers as well as others, it has now become feasible to tap such energy systematically. Herein we introduce an idea of using mustard seeds as a vehicle for construction of a green Triboelectric Nano Generator (TEng). There have been only a few attempts to make such devices using natural materials.^{1,2} Mustard seeds shells charge highly by friction and hence are susceptible to charge separation, a property that we have utilized in our device.

ITO coated-PET and aluminum sheet were employed as electrodes in TEng for achieving flexibility. The whole process of TEng fabrication is natural, cost-effective and environmental-friendly. For the first time, a specifically chosen natural seed with rich surface texture is introduced in this respect. The seeds were dispensed on an Araldite film as an active friction surface for TEng operation. Mustard seeds and Polyvinyl difluoride (PVDF) were used in the construction of the flexible nanogenerator.

The flexible TEng furnished an impressive output voltage of 50 V and a maximum current of 5.25 μA . The seed-TEng with good adaptability rendered the maximum output power of $45 \mu\text{W cm}^{-2}$, which is capable of driving advertising LEDs and commercial electronic temperature sensors.

ET07.09.03

SLIPS-Designed Electrodes in Monolithic PV-Electrolysis Water Splitting System for Membraneless Gas Separation, Transport and Collection Ki Duk Han, Sangkuk Kim, Yongjae Jeung, Seunghyeon Baek, HyunSik Moon and Kijung Yong; Pohang University of Science and Technology, Pohang, Korea (the Republic of).

Recently, PV-electrolysis is attracting much attention as a potential method for hydrogen production by water splitting due to high solar to hydrogen conversion (STH) efficiency. Although there are remarkable advances in modular performance and multifunctional design of PV-electrolysis systems, this artificial leaf system still has critical issues associated with product gas separation. In current monolithic PV-electrolysis modules, the H_2 gas product is inevitably mixed with the O_2 gas. Therefore, in order to obtain pure H_2 gas fuel, additional energy is required for gas separation, such as application of high cost, complex membrane system. To overcome this problem, we invented a simple and very compact gas separation system for monolithic PV electrolysis, which is based on biomimetic surface design. The key idea is adopting slippery lubricant-impregnated porous surface (SLIPS) in designing hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) electrodes, which enables gas bubble manipulation, separation and collection. When H_2 and O_2 gases are generated at the respective SLIPS-edged, inclined HER and OER electrodes, buoyancy drives gas bubbles to move up along each slope of the electrode. In this process, SLIPS-tracks deposited on the lateral edges of each electrode catch and transport gas bubbles along the inclined electrodes surface to the collection port and prevent air bubbles from escaping and cross-over from the electrode surface. Due to this smart design of electrodes, most generated H_2 and O_2 gases could be selectively collected at each product port without crossing or loss. Our membraneless PV-electrolysis device could capture, transport and collect H_2 and O_2 gases very efficiently with a separation efficiency of over 90%. Furthermore we have realized a monolithic PV-

electrolysis system with membraneless gas separation by combining the interconnected CuInS₂ (CIS) PV cell with inclined HER/OER electrodes consisting of an inverted triangle configuration. This unique membrane-free artificial leaf encapsulates free space inside and can float on the surface of the water, providing additional benefits such as total light utilization and reusability.

ET07.09.04

Near-Surface Water Currents Based Triboelectric Nanogenerators [Abdelsalam Ahmed](#)¹, Islam M. Hassan¹, Ali Radhi¹ and Jean Zu²; ¹University of Toronto, Toronto, Ontario, Canada; ²Stevens Institute of Technology, Hoboken, New Jersey, United States.

This work presents an entirely parallel network of triboelectric nanogenerators (TEENGs) for functional hydrokinetic energy harvesting from near-surface water currents. To the best of our knowledge, this is the first report on using the near-surface water current as a potential energy source. The TEENG operates with a free-standing mode with low-cost fabrication and high throughput from incidental water currents. The device is designed for a single unit to contain four TEENG components operated in parallel for use within the neritic zone of the ocean. The hybridized TEENG parallel network within a single underwater TEENG unit attained a voltage of 400 V, a current of 0.8 mA and generated power of 0.2 W, approximately. The observed hydrokinetic power harvesting performance is one of the highest achieved with TEENG technology, suggesting significant potential for portable coastal and shallow water applications in sustainable and underwater self-powered sensors.

ET07.09.05

Synthesis and Photocatalytic Properties of Semiconducting Composite Powder [Kensuke Akiyama](#)^{1,2}, Sakiko Nojima¹, Ryo Takahashi¹, Hiroshi Funakubo² and Hiroshi Irie³; ¹Kanagawa Institute of Industrial Science and Technology, Ebina, Japan; ²Materials Science and Engineering School, Tokyo Institute of Technology, Yokohama, Japan; ³Clean Energy Research Center, University of Yamanashi, Kofu, Japan.

Photocatalytic water-splitting is an ideal method for solar energy harvesting. Some photocatalysts that can split water under UV light have been discovered. However, development of visible-light sensitive photocatalysts is indispensable due to the effective utilization of incoming solar energy. On the other hand, semiconducting iron disilicide (β -FeSi₂) has a band gap of approximately 0.80 eV and a very large optical absorption coefficient over 10⁵ cm⁻¹ at 1 eV. Moreover, it has recently been reported that this semiconducting material acts as a hydrogen-evolution photocatalyst. As a hydrogen-evolution photocatalyst, β -FeSi₂ is expected to enable the use of infrared light longer than 1300 nm, which is the longest wavelength of light to be utilized. This semiconducting material is composed of the elements which are naturally abundant and less toxic than the elements used in conventional compound semiconductors.

In this paper, we report on the novel fabrication method of β -FeSi₂/SiC composite powder by using metal-organic chemical vapor deposition (MOCVD) method which is general in semiconductor process technology. Moreover, we report on the hydrogen evolution over this composite powder under irradiation of not only UV but also visible light and near-infrared light from methyl-alcohol aqueous solution.

10-nm-thick gold (Au) was deposited on the surface of SiC powder, average diameter of 60nm, at room temperature by rf-sputtering. β -FeSi₂ was deposited on the Au-coated SiC powder by using metal organic chemical vapor deposition (MOCVD) method. Iron pentacarbonyl [Fe(CO)₅] and monosilane (SiH₄) were used as sources, and the substrate temperature was 923K and the deposition rate was 1.6 nm/min, respectively. XRD θ -2 θ scan profile showed the formation of poly-crystalline β -FeSi₂ phase for the powder after MOCVD deposition of 1 hour. From the SEM observation of this composite powder, the inhomogeneous grains with sizes of the order 10 nanometers were confirmed to be formed on the SiC surface. The hydrogen gas was evolved by irradiation of UV light (250-430 nm) from methyl-alcohol aqueous solution. Moreover, similar hydrogen evolution was confirmed under visible light (420-650 nm) and near-infrared light (1050-1600 nm) light irradiation.

ET07.09.06

Spectroscopic Study for Hydrophilic Surface of TiO₂ Photocatalysts Modified with Au Nanoparticles [Hayato Kondo](#), Yosuke Kageshima and Hiromasa Nishikiori; Department of Engineering, Graduate School of Science and Technology, Shinshu University, Nagano, Japan.

Semiconductor photocatalytic materials have attracted a great attention as a promising approach to solve worldwide energy and environmental issues derived from mass consumption of fossil fuels. Above all, there are tremendous reports about TiO₂ photocatalysts. It is well-known that TiO₂ exhibits high photocatalytic activity and durability and is capable of driving decomposition of organic compounds and formation of hydrophilic surface under illumination of UV light. These unique characteristics enable us to utilize TiO₂ for various applications of environmental cleanup¹ (i.e., air purification, water purification, and antibacterial self-cleaning), as well as energy conversion (i.e., dye-sensitized solar cells² and water splitting³). Although hydrophilic surface of TiO₂ under UV irradiation should play an important role for its photocatalytic properties, detailed mechanisms and processes for expression of hydrophilic TiO₂ surface are still unclear. Therefore, in this report, expression mechanisms of hydrophilic surface of TiO₂ photocatalysts modified with Au nanoparticles were studied via the spectroscopic measurements. Here, it should be noted that Au nanoparticles were modified in order to increase the sensitivity for spectroscopic measurements by surface plasmon resonance.

TiO₂ particles (P25, Nippon Aerosil) were coated by Au nanoparticles via the photodeposition method. The TiO₂ particles were suspended in an aqueous solution containing Au salt, such as AuCl₃, and irradiated by UV light for various duration, followed by filtration, drying, and annealing in air. The objective TiO₂ particles modified with Au were referred to as Au/TiO₂ hereafter. IR spectra of the surface hydroxyl group on Au/TiO₂ were obtained by FTIR spectrophotometer.

In the presentation, effects of photodeposition conditions, such as concentration of Au precursor and duration of UV irradiation, on surface plasmon resonance will be reported. Based on temporal change of the surface hydroxyl group on Au/TiO₂, expression mechanisms of hydrophilic surface will be discussed.

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ET07.09.07

High-Efficiency Power Conditioning System for Autonomous Triboelectric Nanogenerator Devices Aravind Ravichandran and [Marc Ramuz](#); EMSE-CMP, Gardanne, France.

With the rapid development of wearable electronics and sensor networks, batteries cannot meet the sustainable energy requirements due to their limited lifetime, size and degradation. With miniaturization leading to high-power and robustness, triboelectric nanogenerators (TEENGs) have been conceived as a promising technology by harvesting mechanical energy for powering small electronic systems. However, low output power conversion efficiency has restricted its practical application because of its own extremely high output impedance.

In this work, a state of the art high efficient power conditioning system is proposed which increases the conversion efficiency by 60% but also with lower

impedance matching. Our work represents a nomenclature in the process and experimental methods to achieve effective energy harvesting and storage by TENGs.

In order to solve the limited life problem of typical battery power supply, an autonomous device is conceptualized that is based on the environmental energy harvesting has emerged as an amazing power supply approach. In order to match the high output impedance of TENGs and increase the output power, this work presents a highly efficient power conditioning system, which is composed of a diode rectifier bridge, a control circuit, impedance matching circuit and an energy storage device. Experimental results show that, in less than 3secs, the storage capacitor reached a voltage of 5V by the proposed conditioning technique. The charging efficiency increased by 60%.

By considering these merits of simple fabrication, outstanding performance, robust characteristic and low-cost technology, we believe that advanced power management of TENGs can open up great opportunities not only for powering small electronics but can contribute to large-scale energy harvesting through engineering design being complementary to existing energy sources allowing clean and uninterrupted energy production.

ET07.09.08

Fabrication of Nanoscale Multilayered Thin Film Based Integrated Thermoelectric Devices [Alandria Henderson](#), Jovonte Kimbrough, Kenneth Davis, Zackary Duncan, John Elike, Sam Chance, Brandon Whitaker, Michael Howard, Michael Glenn, TeAndrea Wimbley and Zhigang Xiao; Electrical Engineering and Computer Science, Alabama A&M University, Normal, Alabama, United States.

We report the growth of nanoscale multilayered thermoelectric thin films and fabrication of integrated thermoelectric devices for high-efficiency energy conversion. Nanoscale multilayered thin films such as Sb/Sb₂Te₃ and Te/Bi₂Te₃ thin films were grown using the e-beam evaporation. Integrated thermoelectric devices were fabricated with the nanoscale multilayered thin films using the clean room-based microfabrication techniques such as UV lithography. X-ray diffraction and reflection and high-resolution tunneling electron micrograph (HR-TEM) were used to analyze the e-beam-grown nanoscale multilayered thin films. SEM was used to image and analyze the fabricated devices. The open-circuit voltage and output power produced from the fabricated devices will be measured and analyzed, and highly-efficient thermoelectric thin-film materials and integrated devices will be demonstrated and reported.

ET07.09.09

Triboelectrically Self-Powered, Structural Carbon-Fiber-Reinforced Composites [Seonghwan Lee](#)¹, Changyoon Jeong¹, Maria Q. Feng² and Young-Bin Park¹; ¹Mechanical Engineering, Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of); ²Columbia University, New York, New York, United States.

As fossil fuel depletion is accelerating and energy saving is becoming increasingly critical, intensive efforts are being made to develop environmentally friendly, ultra-lightweight materials for applications in weight-sensitive structures, such as automobiles, aircraft, ships and civil structures. Carbon-fiber-reinforced plastic (CFRP), which is an ultra-lightweight material with a density only a fraction of steel, is well suited for structural applications, where a high strength-to-weight ratio is demanded. Here, we present a proof-of-concept study and demonstration of multi-functional CFRPs that serve as the “structural electrodes” – owing to the high electrical conductivity of carbon fibers - in a triboelectric generator system. If a dielectric material is deposited on the CFRP electrodes and rubbed against one another, the surfaces of the two dielectrics become oppositely charged, and the change in the gap between the two dielectrics induces electrostatic induction. This leads to the accumulation of negative charges along the carbon fiber electrode, thus, generating the electrical energy. Harvesting energy from friction allows high efficiency at low frequency, affordability and low weight due to relatively simple mechanisms and implementation, and this adds a great value and functionality to lightweight, structural CFRPs. The self-powered CFRPs transform the abandoned mechanical energy into usable electrical energy, which will find numerous applications where repetitive loading-unloading is applied, including power-generating speed bumps, roads, railways, doormats, and vibrating structures.

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Ministry of Science and ICT, Korea (NRF-2017R1A5A1015311) and the 2018 Research Fund (1.180015) of UNIST (Ulsan National Institute of Science and Technology).

SESSION ET07.10: Novel Fabrication for Energy Devices
Session Chairs: Wilhelm Pfleging and Yijing Zheng
Thursday Morning, November 29, 2018
Hynes, Level 3, Room 312

8:30 AM *ET07.10.01

Challenges and Opportunities in Primary Electrodeposition of Lithium Films for Secondary Batteries [Daniel Steingart](#) and Wesley Chang; Princeton University, Princeton, New Jersey, United States.

In theory, a clear pathway to improving the energy density of lithium based electrochemical energy storage is replacing the intercalation or alloy host negative electrode with lithium metal itself. The challenges of realizing a version of this electrode suitable for secondary batteries are manifold and most are well documented. A practical aspect that receives less attention, however, is how one creates a lithium foil in a practical manner thin enough to leverage the energy density advantages without “overbuilding” the negative electrode.

Electrodeposition is a well established industrial process for creating metal films and foils of thicknesses from nanometers to millimeters, but the reactivity of lithium has made it difficult to use electrodeposition to produce lithium from an electro refining setup or a primary electro-winning process. In this presentation we demonstrate a multi-electrolyte system which can electrodeposit function lithium films from 5 nm to 20 nm, and explore the morphologies and electrochemical behaviors of these films.

9:00 AM *ET07.10.02

From Laboratory to Industrial Manufacturing—Scale-Up Production of Advanced Lithium-Ion Batteries [Marcus Jahn](#) and Corina E. Täubert; Austrian Institute of Technology GmbH, Vienna, Austria.

The rising need for advanced energy storage solutions due to the increased electrification of global car brands has not only highlighted the need for more

materials research, but also increased innovation to bring such novel materials into production. The often-non-trivial scale-up process has become more important and is bridging the gap along the chain of technology readiness levels that is observed between fundamental research efforts and innovation actions taken by industry. In this work the critical manufacturing steps and scale-up parameters for Lithium-Ion battery manufacturing are analysed. Influencing parameters from materials to process are portrayed with particular focus on advanced, as well as post-lithium ion battery materials. Conventional manufacturing techniques are presented and critical parameters are identified, which are often ignored during the fundamental research stage of materials development. Advanced mixing and coating technologies are presented as well as electrode design work applied in order to increase energy or power density at a cell level. There is a rising need for moving away from conventional manufacturing methods to accommodate novel systems, such as all-solid-state batteries, but also to fulfil the demanding requirements for current storage systems, which push the limits of modern day cell chemistries. The need for increased energy density can not only be addressed on a materials level, but also on a manufacturing and processing level, which is part of the work conducted at the Research Pilot Line at AIT. This work shows how research pilot lines for Lithium-Ion battery manufacturing have become increasingly important, especially in Europe, and are considered a key enabler of the future of electric vehicles and to the success of the research needed to meet tomorrow's demands in energy storage.

9:30 AM ET07.10.03

Thin Continuous Films Built Using Electrospray Atomization of Nanoparticle Aggregates Yaquan Zhu and Paul Chiarot; Mechanical Engineering, Binghamton University, Binghamton, New York, United States.

Using electrospray atomization, we have built thin continuous films with controllable micro- and nano-structure from nanoparticle aggregates. The aggregates were assembled in-flight (i.e. after electrospray emission) and delivered to a target substrate in a dry state. Our research provides insights into the nanoparticle aggregation and thin film deposition phenomena for varying aggregate sizes and morphologies. Titanium dioxide nanoparticles (p25, ~21 nm) were used as a model system given their importance in photovoltaic applications. We have discovered the relationship among all the essential operating parameters and the micro- / nano-structure of the aggregates and films. We reveal how properties such as nanoparticle concentration, solvent volatility, Taylor cone pulsation frequency, and substrate electrical properties (among others) govern the size and morphology of an individual aggregate. We then further report how the aggregate size and morphology governs the structure of the continuous film. Aggregates formed using electrospray possess an excess electric charge that can be maintained after deposition on to the target substrate. We found that this charge accumulation and its decay rate play a significant role in the film formation. For example, films on a conducting substrate are thick and exhibit periodic islands. In contrast, films on semiconducting and insulating substrates are thin and tend to be uniform. To further probe the influence of charge accumulation, we used "periodic printing" (i.e. periodically turning the electrospray on-and-off during deposition). The structure of the films was significantly different when printing periodically compared to continuous printing. This further highlights the strong influence of the excess charge on deposit structure.

9:45 AM ET07.10.04

Large-Scale Printing of Micro-Wire Electrodes for Roll-to-Roll Manufacturing of Transparent Electrodynamic Screen (EDS) Films for Self-Cleaning Solar Collectors Malay K. Mazumder¹, Caroline Ellinger², Kevin O'Connor², Sean Garner³, Julius Yellowhair⁴, Ryan Eriksen¹, Annie Rabi Bernard¹, Cristian Morales¹, Mark Horenstein¹ and Ramakrishnan Lakshmanan¹; ¹Boston University, Boston, Massachusetts, United States; ²Eastman Kodak Company, Rochester, New York, United States; ³Corning Research and Development Center, Corning, New York, United States; ⁴Sandia National Laboratories, Albuquerque, New Mexico, United States.

A Manufacturing process for producing transparent Electrodynamic Screen (EDS) films by flexographic printing of micro-wire electrodes on optically clear dielectric films is discussed. The EDS film consists of a series of parallel transparent electrodes embedded between two transparent dielectric layers, which can then be retrofitted or integrated onto the optical surfaces of solar collectors, such as CSP mirrors and PV Modules. Activation of the electrodes by phased voltage pulses creates a non-uniform electric field distribution on the EDS film surface, which charges and levitates the dust particles and then removes the dust layer by a sweeping action of the traveling electric field created by the three-phase drive. Application of EDS film provides water-free cleaning as frequently as needed to maintain high optical efficiency of solar mirrors and solar panels minimizing energy-yield losses caused by dust deposition. Silver nanowire (AgNW) and passivated Cu micro-wire (micro-wire) electrodes were used as scalable and durable inks for solar field applications of EDS films. We screen-printed AgNW ink electrode directly on Willow Glass (Corning) film for producing lab-scale EDS films. For commercializing the technology, an existing roll-to-roll production facility at Eastman Kodak was used. EDS films were produced in medium scale (26 cm x 30 cm) with catalyst electrodes using flexographic printing on PET films. After printing, the substrate is conveyed through a touchless plating line where electrodeless copper is deposited on the printed catalyst pattern. The deposited copper is treated in-line with an environmental passivation and darkening agent, simultaneously protecting the micro-wires from corrosion and minimizing front-side reflection with a neutral color, all without contacting a roller to minimize the risk of conveyance related defect formation. For laminating the film on an optical surface of a solar collector, the following architecture of the EDS film is used: Willow Glass (sun facing)/Optically Clear Adhesive (OCA)/ Kodak-printed EDS electrodes on PET substrate/ OCA laminated on a solar panel or a mirror. The electrodes of the EDS film are connected to a compact power supply unit. A single power supply unit may serve several heliostats or PV modules. Cleaning operation can be activated automatically or manually from a control room without any interruption of the plant operation or human labor. Laboratory- and field-evaluations show that the EDS films can be operated in a wide range of ambient temperature (range of PV module application), relative humidity (varying from 20 to 70% RH and RH cycling) in an environmental chamber used for simulating conditions of solar fields. Limited field evaluations were carried out at the National Solar Thermal Test Facility located at the Sandia National Lab in New Mexico and at the Atacama Desert solar fields in Chile. Experimental data taken with EDS film laminated solar collectors would be presented showing (1) dust removal efficiency $\geq 90\%$; for solar mirrors: (2) specular reflection (SR) efficiency $\geq 90\%$; (3) specular reflection restoration (SRR) efficiency $\geq 90\%$ and for solar panels: (4) the light transmission efficiency (TE) $\geq 90\%$; and (5) output power restoration (OPR) efficiency $\geq 95\%$. Each cleaning cycle requires less than two minutes and expends a negligible amount of energy (0.2 Wh/m²/cleaning cycle).

10:00 AM BREAK

10:30 AM *ET07.10.05

Investigation of Additive Distribution in Electrodes for Lithium-Ion Batteries Werner Bauer; Karlsruhe Institute of Technology, Eggenstein-Leopoldsh, Germany.

The performance of lithium-ion batteries is not only determined by the used active cathode and anode materials, as these components only set the maximum achievable values for capacity and rate capability. The energy and power densities actually achieved in the cells are influenced primarily by the inactive additives and by the processing conditions. In order to understand the impact of additives and processing on cell properties, it is necessary not only to know material specific properties but also to analyze the entire structure of the electrodes. From this, it is feasible to derive processing-structure-property relationships that can close the understanding gap between the applied processing conditions and the resulting electrodes properties. Structural and chemical investigations of electrodes can be carried out on different length scales. The study of interface effects, such as contact resistance or binder adhesion, is performed on the nanoscale range. For many macroscopic effects, however, distribution of components on meso- and microscopic orders of magnitude is relevant. On the one hand, the mesoscale formation of clusters between the binder and carbon black and their localization in the

proximity of the active particles is important for the fundamental mechanical and electronic properties of the electrode. On the other hand, the overall electrode properties are also determined by the distribution of binder and conductive additives on a microscale level, i.e., over the entire cross-section and surface of the electrode.

Investigations of the electrode structure are challenging not only by the different orders of magnitude of the structural units, but also by the large number of materials used. As a result, the standard method for structure elucidation of diverse electrodes does not exist. Instead of that, one must have a pool of methods available and make appropriate adjustments for various electrodes. Examples, which illustrate these limitations, as well as successful application of methods, will be shown for common cathode and anode systems. The focus is placed on determining the microscopic binder distribution of standard electrodes, as knowledge of this feature is an essential prerequisite for understanding and optimizing of drying conditions. Most investigations are performed by using SEM based methods, which are available in many laboratories. A rather new user-friendly approach applies laser-induced breakdown spectroscopy for achieving a 3D elemental mapping of the entire electrodes, which can be used either for a rapid screening of 3D binder distribution or for post-mortem analysis of electrochemical degradation processes.

11:00 AM *ET07.10.06

WITHDRAWN 10/31/2018 ET07.10.06 Al-Air Rechargeable Batteries on Flexible Polyimide Substrates Anming Hu^{1,2}; ¹University of Tennessee Knoxville, Knoxville, Tennessee, United States; ²Beijing University of Technology, Beijing, China.

We reported a rechargeable Al-air battery fabricated on polyimide substrates. For air anode, Pt decorated carbon particles mixed with TiC nanoparticles worked an OER/ORR catalyst. This combination has a better performance than individual Pt catalyst or TiC. Ionic liquid (1-ethyl-3-methylimidazolium chloride) mixed with AlCl₃ as electrolyte. For Al cathode, we have compared Al foils, later-nanostructured Al foils and 3D printed Al nanoparticles. A stable charge-discharge of capacity of 0.3 mAh/cm² is achieved for more than 100 cycles.

11:30 AM ET07.10.07

Wire-Shaped Supercapacitor Fabricated via Layer-by-Layer Assembly with Enhanced Voltage Window Kayeon Keum¹, Geumbee Lee² and Jeong Sook Ha^{1,2}; ¹Korea University, Seoul, Korea (the Republic of); ²KU-KIST Graduate School of Converging Science and Technology, Seoul, Korea (the Republic of).

As wearable electronics receives vast interest nowadays, various shapes and forms of wearable devices have been studied. Among them, wire-shaped supercapacitor (WSS) shows a great potential as a wearable energy storage device because its 1-dimensional structure makes it highly flexible and be easily incorporated into conventional textile substrates. Here, we report a thin, reproducible WSS fabricated via layer-by-layer (LbL) assembly of multi-walled carbon nanotubes (MWCNTs) with organic electrolyte of propylene carbonate (PC) – acetonitrile (ACN) – lithium perchlorate (LiClO₄) – poly-(methyl methacrylate) (PMMA), extending the voltage window to 1.6 V. LbL assembly gives uniformly deposited MWNTs on a curved surface of Au wire, resulting in linearly increased areal capacitance of the fabricated WSS. Vanadium oxide is encapsulated onto LbL-assembled MWCNTs electrode to induce pseudo-capacitance, enhancing overall capacitance of the fabricated WSS. Cyclic stability of the WSS is enhanced via optimizing the mixing ratio of PC to ACN in the electrolyte. As a result, the fabricated WSS exhibits areal capacitance of 5.23 mF cm⁻² at 0.2 mA cm⁻², energy density of 1.86 μWh cm⁻², and power density of 8.5 mW cm⁻², in addition to 94% capacitance retention after 10,000 galvanostatic charge-discharge cycles. Furthermore, the WSSs are easily integrated into a textile to drive integrated μ-LEDs. This work demonstrates a high potential of the scalable WSS as an energy storage device in application to high performance textile electronics.

SESSION ET07.11: Novel Energy Devices and Materials

Session Chairs: Peter Smyrek and Yuefei Zhang

Thursday Afternoon, November 29, 2018

Hynes, Level 3, Room 312

1:30 PM ET07.11.01

Fabrication and Performance Analysis of All-Solid-State Flexible Porous 3D Graphene/Waste Composite Micro-Supercapacitor Gourav Bhattacharya¹, Sam Fishlock², James McLaughlin² and Susanta Sinha Roy¹; ¹Department of Physics, Shiv Nadar University, Gautam Buddha Nagar, India; ²NIBEC, University of Ulster, Newtownabbey, United Kingdom.

Rapid depletion of non-renewable energy resources and ever-increasing demands for power made researches to focus into advanced energy materials for power generation and green energy storage. Among several other energy storage devices, supercapacitor has garnered large attention as an alternative portable power source and storage device. Recently, to encounter the huge global requirement of portable and wearable electronics, high-performance, flexible, inexpensive, and sustainable micro-supercapacitor systems are being studied. Herein by employing electrochemical technique, the potential application of an all solid-state flexible solid-state hybrid micro supercapacitor was investigated. A 3-D hierarchically porous graphene nano-ribbon structure (LIG) with high surface area, was synthesized on a flexible polymer substrate (polyamide) using Laser scribing technique. An industrial waste material red mud which is an abundant source of iron oxide (Fe₂O₃) was further mechanically processed to produce metal oxide nanoparticles. These nanoparticles were decorated on the LIG film and acted as the pseudocapacitor component of the hybrid electrode. The composite electrode material was further characterized using transmission electron microscopy (TEM), field effect scanning electron microscopy (FESEM), Raman spectroscopy, cyclic voltammetry (CV) etc. An interdigitated planar hybrid micro-supercapacitor device was fabricated over the polymer substrate where polymer-based composite ionic liquid-gel electrolyte was casted over the hybrid electrodes. Inkjet printing was further employed to print silver and was acted as the current collector. The performance of the device was monitored using CV, charging/discharging (CD) and electrochemical impedance spectroscopy (EIS). The device exhibited a high sp. capacitance within an active working potential of ~3.8 V which further enhances the energy density of it. The micro-supercapacitor also exhibited good long-term cyclic stability. The swift lateral ion movement in the planar device, more accessible electrochemically active surface area, better charge transfer kinetics, presence of composite electrolytes contributed to the high electrochemical performance of the device. The inexpensive, lightweight, easy to construct device is thus have a great potential and can offer new opportunity for integration of energy storage units with flexible electronic devices.

1:45 PM ET07.11.02

Ultra-High-Rate Aqueous Zinc-Ion Batteries for Shape-Conformal Integration of Wearable Electronics Chanhoon Kim³, Bok Yeop Ahn¹, Teng-Sing Wei¹, Yejin Jo², Sunho Jeong², Youngmin Choi², Il Doo Kim³ and Jennifer Lewis¹; ¹Harvard John A. Paulson School of Engineering and Applied Science, Harvard University, Cambridge, Massachusetts, United States; ²Division of Advanced Materials, Korea Research Institute of Chemical Technology, Daejeon, Korea (the Republic of); ³Department of Materials Science and Engineering, KAIST, Daejeon, Korea (the Republic of).

The push towards miniaturized electronics requires the development of smaller battery, which has typically been one of the biggest components in the small electronics. With the selective miniaturization, customized geometries of the batteries may allow unprecedentedly comfortable and form-fitting design in the miniaturized electronics as well as wearable electronics. Nevertheless, the conventional battery design is confined to the rigid shapes, limiting its versatility. Here, we introduce the customized battery geometries for miniaturized and wearable electronics by optimized combination of 3D printing, electrospinning, and laser micromachining techniques. Pursuing easy processing and high safety, we have devised aqueous zinc-ion battery (ZIB) system in the customized geometries which consist of a conductive polyaniline (PANI) coated carbon fiber cathode, a porous separator, and a zinc (Zn) anode. The highly conductive 3D structured CF mat facilitates fast electron transfer even for relatively thick cathodes (~320 μm) and the highly porous PANI conformally coated on the CF also significantly contributes to fast ion diffusion in cathode layers. By the virtue of the rationally designed cathodes, the ZIBs can be quickly charged to about 50 and 20% within about 2 min and 6 s, respectively. Moreover, we use laser micromachining for customizing cell components (electrodes, separator, and terminals) corresponding to the shapes of SLA-printed packaging geometries. Notably, this is the first demonstration of the SLA technique, which has been widely used in many fields for prototyping custom-shaped complex plastic structures in ~ 100 μm resolutions for designing small batteries. The ZIBs with various geometries, including rectangular, cylindrical, H-, and ring-shapes retained the excellent electrochemical performances. Furthermore, we fabricated a wearable photosensor by shape-conformally integrating a ring-shape battery pack with electronic components to demonstrate the merit of our approach. We believe that the ability to fabricate power sources in any shapes and sizes as needed may open new revenues to shape-conformal integration of miniaturized and wearable electronics.

2:00 PM ET07.11.03

Light-Assisted Polymer-Based Electrochemical Energy Storage Abdelaziz M. Gouda¹, Ri Xu¹, Francesca Soavi² and Clara Santato¹; ¹Engineering Physics, Ecole Polytechnique Montreal, Montreal, Quebec, Canada; ²Chemistry, University of Bologna, Bologna, Italy.

The development of efficient solar energy conversion/storage technologies is critical to limit the negative effects of the anthropogenic climate change on Earth. Electrochemical technologies have been widely investigated to capture the power generated from intermittent sources, like the Sun. High performance storage solutions, such as batteries and supercapacitors, make use of toxic electrode materials and organic electrolytes with limited environmental sustainability. Nature could be the source of abundant and environmentally benign materials to be used in next generation batteries and supercapacitors, paving a way towards a sustainable use of resources.

Among natural materials, eumelanin is a functional biomacromolecule found in flora and fauna with fascinating properties, such as strong broadband UV-visible absorption, redox activity, metal binding affinity, humidity-dependent electrical response as well as good thermal and photostability [1]. DHI (5,6-dihydroxyindole) and DHICA (5,6-dihydroxyindole-2-carboxylic acid) are the two building blocks of melanin. The synergy between the reduction/oxidation (redox) activity of the building blocks and the capability of several of their functionalities to reversibly bind cations constitutes the foundation for the use of eumelanin in energy storage systems [2]. Photoconductivity of melanin in different form such as pellets and thin films has been reported in the literature [3] motivating current efforts for using this photoactive bio-pigment in solar assisted electrochemical energy storing systems. [2][4][5]. We were capable to overcome the legendary limited processability of melanin by adopting a solid state polymerization strategy for its fabrication. In this way we were capable to keep the environmental friendliness of the melanin controlling its (supra)molecular structure and processability. In this work, we report about a two symmetric electrode-system based on chemically controlled melanin wrapped with PEDOT: PSS on carbon paper current collectors. PEDOT:PSS enhances electronic transport and intermolecular connectivity between the melanin chains [6]. The electrode materials are processed by simple, solution-based methods. The electrochemical storage properties are evaluated for different chemically controlled eumelanin: polyDHI, polyDHICA and polyDHI:polyDHICA in dark and light condition, using cyclic voltammetry and galvanostatic charge/discharge cycles.

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2:15 PM ET07.11.04

Electrodeposition of MoS₂ on Three-Dimensional Graphene/Nickel Foam for Electrocatalytic Water Splitting Narasimman Rajaram, Manmohansingh Waldiya, Indrajit Mukhopadhyay and Abhijit Ray; Pandit Deendayal Petroleum University, Gandhinagar, India.

Rapidly depleting fossil fuel and CO₂ emission from the utilization of fossil fuels lead to the development of sustainable, clean and renewable alternate energy sources. Hydrogen is considered as a suitable candidate because it is having high energy density and zero gas emission. Among the various methods of production of hydrogen, hydrogen evolution reaction (HER) in electrochemical water splitting is considered as the most promising and environmentally friendly approach. Noble metals like Pt, Pd, etc., are known to effectively catalyze the HER, however, scarcity and high-price is restricting the large-scale production of hydrogen. Transition metal dichalcogenides (TMDC) such as MoS₂, WS₂ are widely studied electrocatalysts for HER in acidic medium. Also, three-dimensional (3D) electrodes are advantageous because of the porous and interconnected structure which increases the surface area and effective mass transport. In this study, we have electrodeposited MoS₂ on to the graphene coated nickel foam (graphene/nickel foam). Graphene/nickel foam was prepared by APCVD technique at 800°C. The graphene was coated uniformly on nickel foam and it consists of 5-8 layers. The graphene/nickel foam was used as the electrode for the electrochemical deposition of MoS₂. The cathodic electrodeposition of MoS₂ on graphene/nickel foam was carried out by applying the potential of -1.2 V (vs. Ag/AgCl) for 20 mins. The morphology was evaluated by scanning electron microscopy and formation of MoS₂ was confirmed by Raman spectroscopy. Freshly prepared samples were evaluated for HER in 0.5 M H₂SO₄ by linear sweep voltammetry, Tafel slope and electrochemical impedance study.

2:30 PM ET07.11.05

Enhanced Photoelectrochemical Water Splitting of Heteroepitaxial Grown Hematite Nanowires Kirtiman D. Malviya and Avner Rothschild; Technion-Israel Institute of Technology, Haifa, Israel.

Hematite ($\alpha\text{-Fe}_2\text{O}_3$) is a promising photoanode candidate for photoelectrochemical (PEC) cells for solar water splitting due to a unique combination of visible light absorption, stability in alkaline aqueous solutions, low cost, and abundance. However, the performance of the hematite photoanode is reported to be low and therefore different nanostructuring, and novel design microstructure is adopted to improve PEC performance. A simple and optimal design to facilitate the charge transfer in bulk is paramount important to achieve enhanced solar to fuel efficiency. Herein we report a simple and highly reproducible method of fabrication of multilayer heteroepitaxial grown Nb-doped SnO₂/hematite film on c-plane Al₂O₃ single crystal substrate and a series of systematic experiments to elucidate the effect of the microstructural variation on the photoelectrochemical properties. The microstructure varies from dense film to nanowire to defected porous structure depending on the growth conditions. To the best of our knowledge first time, we are reporting the heteroepitaxial grown thin film hematite consists of dense nanowires (~10-30 nm diameter and ~600 nm length) with the photocurrents of 1.3 and 2.1 mA/cm² at reversible (1.23 V_{RHE}) and thermoneutral potentials (1.48 V_{RHE}) respectively with bare hematite. Also, the reported results are higher than the most of the

recently reported state-of-art fabrication methods. In this work, we have investigated the effect of polycrystalline/heteroepitaxial, film thickness, the deposition temperature, oxygen partial pressure and the dopant concentration and their effect on the bulk and surface charge separation and injections efficiency. The effect of the surface treatment and the deposition of co-catalyst can further enhance the PEC properties which will be discussed during the presentation.

2:45 PM BREAK

3:15 PM ET07.11.06

Exploration of V Doped SnO₂ Nanocrystals for Thermochemical H₂ Generation Vinod Kumar², Dinesh Gupta³ and Sachin Kumar Sharma¹; ¹Conversion & Catalysis Division, Indian Institute of Petroleum, Dehradun, India; ²Chemistry, Kirori Mal College, University of Delhi, Delhi, India; ³Chemical Engineering, Indian Institute of Technology Delhi, Delhi, India.

Production of energy is the global concern, which needs to be addressed soon; otherwise, we will be in great problem. Dihydrogen is one of the reliable green energy source having high calorific value. There are several techniques to generate hydrogen as a fuel such as electrolysis, photoelectrochemical, photocatalytic approach, thermochemical water splitting etc. However, practically mass production, economic value, storage and usage of hydrogen as a fuel is still a challenging task. The hydrogen generation by splitting of water using various metal oxides has been reported for many years but their use is not applicable on off-sun hours, cloudy or rainy day that restrict them for their commercialization. However practically mass production and usage of hydrogen as a fuel is still a challenging task. An alternative approach needed to be explored for commercial mass production of hydrogen. It is an hour of need to explore better approach for commercial and economical production of dihydrogen. Among these techniques, thermochemical water splitting can be utilized for mass production of hydrogen as a fuel. Several materials have been used for thermochemical water splitting especial binary metal oxides CeO₂, TiO₂, SnO₂, CuO₂, MnO etc. CeO₂ is having the good efficiency for 100 cycles but require high thermal energy. SnO₂ may be the promising material; in spite of the fact that the hydrogen production rate was lower, but high conversion rates can be obtained in controllable reactions [1-4]. In the current work, we have synthesized V doped SnO₂ nanoparticles with varying concentration of vanadium using solution-based route at lower temperature. Obtained nanoparticles were characterized using PXRD, SEM, TEM, etc. Investigations based on powder X-ray diffraction studies confirm the phase formation tetragonal rutile-structured SnO₂ matched with JCPDS file No. 41-1445. Further, behavior of thermochemical water splitting reactions were studied using these nanoparticles. Hence, we can established pilot set up for micro and macro scale production of hydrogen fuel using V doped SnO₂ at lower thermal energy and show good efficiency for 10 cycles.

Acknowledgement

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References

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3:30 PM ET07.11.07

Low Temperature Fabrication of Dense Y-Doped BaZrO₃ Electrolyte by Utilizing the Co-Firing with the Anode Substrate Shrinking Well for Proton Conducting Solid Oxide Fuel Cell Yuki Yamaguchi, Hiroyuki Shimada, Toshiaki Yamaguchi, Hirofumi Sumi, Katsuhiro Nomura and Yoshinobu Fujishiro; AIST, Nagoya, Japan.

Y-doped BaZrO₃ (BZY) is widely known as a proton conducting material which shows the high ionic conductivity at intermediate temperature between 400 and 700°C. Thus, it is promising candidate of electrolyte material for the intermediate temperature solid oxide fuel cells (IT-SOFC). BaZrO₃(BZO) base proton conducting material has a good durability for CO₂ compared with BaCeO₃ base materials. However, the sintering temperature of BZO is quite high. High temperature heat-treatment more than 1700°C is required to obtain the dense body of BZO. Particularly for the fabrication of anode supported type SOFC, an electrolyte layer was prepared by co-firing with anode substrate. When the cells are fired at higher temperature to obtain the dense electrolyte, the pores in anode will be disappeared due to the densification of anode. Therefore, we developed the low temperature fabrication process of the proton conducting SOFC by utilizing the fine powder of BZY having a good sinterability, in this study.

BZY powders were prepared by the novel low temperature synthesis which can prepare the BZO by only mixing the zirconia hydrous gel and the barium hydroxide octahydrate at 100°C for 12 h. The 20 mol% doped BZY had ca. 30 nm of primary particles with quite high crystallinity. Y doping amount could be controlled up to 30 mol% by the addition amount of Y ions to the zirconia hydrous gels. For the strongly shrinking anode substrate, Sr and Ti co-doped BZY powders were also prepared by the same method. It has been reported that the addition of some metal elements, such as Zn and Ni, were effective to decrease the sintering temperature of BZY. However, the cell voltage of BZY was decreased by the hole conduction in the electrolyte layer, because the holes were generated in the BZY electrolyte by the substitution of lower valence metal elements to Zr⁴⁺ sites.

In this study, Sr²⁺ and Ti⁴⁺ were substituted to Ba²⁺ and Zr⁴⁺ sites, respectively. The sintering temperature of Sr and Ti co-doped BZY (BSZTY) powder was 200°C lower than that of BZY. BSZTY could be sintered at 1400°C. Then, BZY electrolyte layers were fabricated on the anode substrates including BZY-NiO or BSZTY-NiO by firing at 1400°C. When the BZY electrolyte layer was fabricated on the anode including the BZY-NiO, the electrolyte layer could not densify due to insufficient shrinkage of the anode. In contrast, the dense BZY electrolyte on the anode substrate of BSZTY-NiO was successfully obtained by firing at 1400°C. Besides, the grain growth of BZY was also observed. It was considered that the large shrinkage of anode substrate including BSZTY enhanced the sintering the BZY electrolyte layer. Using the BSZTY for anode material, the proton conducting cell having BZY electrolyte could be obtained by co-firing at 1400°C. This cell showed a high open circuit voltage (OCV) more than 1.0 V at 600°C. It was considered that the excessive hole generation did not occur.

3:45 PM ET07.11.08

Titanium Oxynitride Thin-Films with Large Power Conversion Efficiency in Photovoltaic Solar Cells Nikhil R. Mucha¹, Michael Froeschle², Mark Anderson³, Panupong Jaipon¹, Hemali Rathnayake², Christian Binck⁴, Jeffrey Shield⁴ and Dhananjay Kumar¹; ¹North Carolina A&T State University, Greensboro, North Carolina, United States; ²Nanoscience, University of North Carolina at Greensboro, Greensboro, North Carolina, United States; ³Earth Science, University of Nebraska-Lincoln, Lincoln, Nebraska, United States; ⁴Physics, University of Nebraska-Lincoln, Lincoln, Nebraska, United States.

A novel Ti_xN_yO_z (Ti-N-O) material system in thin film form has been synthesized using a pulsed laser deposition method. The photovoltaic solar cells constructed out of Ti-N-O in ITO-TiNO-Cu configuration have yielded a maximum power conversion efficiency (PCE) of 12.5% with short circuit current density (J_{sc}) of 36.50 mA/cm², open circuit voltage (V_{oc}) of 0.21 V, and fill factor (FF) of 57.4%. This is the highest PCE reported to date for any derivative of thin film based-Ti-N-O system as an active layer material in bulk heterojunction (BHJ) solar cells. The extraordinarily high values of power conversion efficiency have been attributed to the existence of a multi-bandgap-mediated electron-hole transfer pathway. X-ray diffraction and x-ray photoelectron spectroscopy

measurements lends evidence in support of multi-bandgap mediated transfer of charge carriers by confirming the presence of Ti-N-O, Ti-N, and Ti-O chemical binding states. The titanium oxynitride ($\text{TiN}_{1-x}\text{O}_x$) system has the potential to absorb visible light in the full solar spectrum.

4:00 PM ET07.11.09

MnFe₂O₄ Nanoparticle-Pigmented High-Temperature, Thermodynamically-Stable, Long-Term Antioxidation Solar Selective Absorber Coatings Eldred Lee¹, Can Xu¹, Katerina Kekalo^{1,2}, Jifeng Liu¹ and Xiaoxin Wang¹; ¹Dartmouth College, Hanover, New Hampshire, United States; ²U.S. Air Force, Hanover, New Hampshire, United States.

Photovoltaic (PV) technology for solar electricity is in high demand but lacks the flexibility on long term energy storage. Therefore, concentrated solar power (CSP) systems need to complement the PV technology to increase energy output. The efficiency of CSP systems can improve with high absorption in the solar spectrum regime and low emittances in the infrared spectrum. However, CSP systems can be expensive. High-temperature, air-stable solar selective absorbers made with cermet composite materials that have optimal properties of both ceramic and metal can be the solution to this goal; however, this achievement has been difficult due to metal oxidation at high temperatures. Here, we demonstrate outstanding optical responses of thermodynamically-stable, high-temperature, low-cost long-term antioxidation cermet solar selective absorbers using MnFe_2O_4 nanoparticles (NPs) with silicone precursors as low-cost Si-rich matrices that undergo interdiffusion reaction with Stainless Steel 310 (SS310) and Inconel 625 substrates. Current state-of-the-art product such as the Pyromark® black paint has a significantly high solar absorptance (>95%) in the solar spectrum regime but also has a high emittance loss (~87%) in the infrared spectrum. To decrease the emittance while maintaining high absorptance, we have undergone antioxidation interfacial engineering in Ni/SiO_x by creating low-cost solution-processed Ni nanochain- SiO_x ($X < 2$) selective solar thermal absorber coatings. When these coatings are deposited on metal substrates, the oxidation of the metal as well as the interdiffusion between the coatings and the substrates can exceed the optical responses of the coatings themselves. As there are low-cost NPs that exceed the optical responses of Ni in the desired spectrum, further investigation has been done with interdiffusion-induced selectivity testing using silicone precursors with varying molecular weight as low-cost Si-rich matrices for interdiffusion reaction with different low-cost NPs that have metal-like optical absorption properties and ceramic-like chemical stability and metal substrates. Thin layers of various NP-silicone matrix coatings were deposited on metal substrates using market-available low-cost perfume sprays. To test the stability, the samples were annealed in air at 750°C up to 1000 hours. Up to this date, solar selective absorber coatings with 28nm MnFe_2O_4 NPs and a high molecular weight silicone matrix on SS310 and Inconel 625 substrates result in the most ideal absorption up to 97% in the solar spectrum regime and the reduction of emittance down to 30-40% in the infrared regime, which are confirmed by UV/VIS/NIR spectrophotometer and an FTIR spectrometer. These coatings on SS310 and Inconel 625 substrates were found to be stable in air in 750°C and the optical responses in the desired spectrum have either maintained or improved. Such solution can lead to a newer and innovative approach to create better low-cost CSP systems.

4:15 PM ET07.11.10

A Solvent Toolkit for Electrochemical Characterization of Hybrid Perovskite Films Mehedi Hasan¹, Dmitry Lyashenko¹, Jason D. Slinker² and Alex Zakhidov¹; ¹Texas State University, San Marcos, Texas, United States; ²The University of Texas at Dallas, Dallas, Texas, United States.

Organohalide lead (hybrid) perovskites have emerged as competitive semiconducting materials for photovoltaic devices due to their high performance and low cost. To further the understanding and optimization of these materials, solution based methods for interrogating and modifying perovskite thin films are needed. In this work, we report hydrofluoroether (HFE) solvent based electrolyte for electrochemical processing and characterization of organic-inorganic trihalide lead perovskite thin films. Organic perovskite films are soluble in most of the polar organic solvents and thus until now they were not considered suitable for electrochemical processing. We have enabled electrochemical characterization and processing tools for these materials utilizing highly fluorinated electrolytes based on HFE solvent. Our results show that chemically orthogonal electrolytes based on HFE solvents do not dissolve organic perovskite films and thus allow electrochemical characterization of the electronic structure, investigation of charge transport properties and potential electrochemical doping of the films with in situ diagnostic capabilities.

4:30 PM ET07.11.12

Spray-on “CdO:Mn:Sn/PbS:Na:CdS” Thermoelectric Energy Harvester Francisco Javier Gonzalez^{2,1}, Isaiah Oladeji^{2,3} and Robert E. Peale^{2,4}; ¹Universidad Autonoma de San Luis Potosi, San Luis Potosi, Mexico; ²Truvent LLC, Orlando, Florida, United States; ³SISOM Thin Film LLC, Orlando, Florida, United States; ⁴Physics, University of Central Florida, Orlando, Florida, United States.

Thermoelectric (TE) thin films have promise for harvesting electrical energy from waste heat, which could power wearable electronics and enable conformal application to complex surfaces for enhanced thermal coupling. We demonstrate an n-type CdO:Mn:Sn and p-type PbS:Na:CdS thin-film TE device that was deposited by aqueous spray deposition on glass and flexible Upilex S substrates using a shadow mask. With the junction at 100 deg C, the open circuit voltage between p- and n-type free ends at 25 deg C is +13.6 mV. The short circuit current is 15 nA, giving ~0.2 nW of power for the single junction and the given temperature difference. Several thermocouples connected electrically in series and thermally in parallel will multiply the output voltage. The Seebeck coefficient (thermoelectric power) for this first device is ~0.2 mV/C, which is comparable to known values for other semiconductor thermocouples and may be improved by optimization. Numerical simulations using COMSOL Multiphysics are used to obtain figures of merit for comparison to experimental results.

SESSION ET07.12: Poster Session IV
Thursday Afternoon, November 29, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

ET07.12.01

Synergy of Optimized Topological Structure and Phase-Composition Boosts Ultrahigh Discharge Efficiency in High-Energy-Density Polymer Nanocomposites Jianyong Jiang, Yang Shen and Ce-Wen Nan; Tsinghua University, Beijing, China.

Poly(vinylidene fluoride) (PVDF)-based dielectric polymers are in great demand for the future electronic and electrical industry because of their high dielectric constants and energy density. However, some issues that limit their practical applications remain unsolved. One of the most urgent issues is their high dielectric loss and hence low efficiency. In this contribution, we proposed and demonstrate that substantially enhanced discharge efficiency of PVDF-based polymers nanocomposites could be achieved by simultaneously optimizing their topological-structure and phase composition. In the poly(vinylidene

fluoride-co-hexafluoropropylene (P(VDF-HFP)) / poly(vinylidene fluoride-*ter*-trifluoroethylene-*ter*-chlorofluoroethylene) (P(VDF-TrFE-CFE)) multilayered nanocomposites fabricated by non-equilibrium process, an ultrahigh discharge efficiency of ~85% is achieved up to 600 MV/m, which is the highest discharge efficiency reported so far for any polar-polymer dielectric materials at such high electric field. By adjusting the quenching temperature, the phase-composition hence dielectric permittivity in the terpolymer layers could be tuned for suppressed ferroelectric loss. Results of phase-field simulations further reveal that local electric field is substantially weakened at the interfaces between the Co/Ter polymer layers, which will act as barriers to motion of charge carriers and give rise to much suppressed conduction loss and a remarkably enhanced breakdown strength. Synergy of the optimized topological-structure and phase-composition thus leads to a nanocomposite that exhibits an unprecedented high discharge efficiency of the multilayered nanocomposites that is comparable to the bench-mark biaxially oriented polypropylene (BOPP) at high electric field as well as a high discharge energy density that is over 10 times higher than that of BOPP.

ET07.12.02

Toward High Solar to Fuel Efficiency via Photonic Design of Monolithic Photoelectrochemical Cells Wen-Hui Cheng, Matthias H. Richter, Sisir Yalamanchili, Phillip Jahlka, Pin Chieh Wu and Harry A. Atwater; California Institute of Technology, Pasadena, California, United States.

Direct solar to fuel generation using a photocathode device design requires a light absorber that can provide enough photovoltage to overcome the thermodynamic potential (1.23V for H₂/O₂, 1.33V for CO/O₂) and additionally the catalyst overpotentials for both the cathode and anode reactions. Further, catalyst ensembles featuring high catalytic current densities and high transparency are necessary to maintain a catalytic current close to the light limiting photocurrent of a solar light absorber for overall high solar-to-fuel efficiency. We recently reported a record solar-to-hydrogen efficiency using a tandem III-V semiconductor photoelectrode based solar photoelectrochemical cell with an optically transparent but dense Rh metal nanoparticle catalyst layer¹. However, a different strategy is required for CO₂ reduction, due to the opaque nature and limited activity of most CO₂R catalysts. To overcome this constraint, we have developed two light management strategies to create highly active and but still effectively transparent catalyst layers: i) an effectively transparent catalyst consisting of micron-scale triangular cross-sectional silver grid fingers that redirect light to open areas of the PEC cell, and ii) a tailored mesophotonic dielectric cone structure used as a light coupler to efficiently guide incident light through an opaque catalyst into the light absorber. Calculations using full wave electromagnetic simulations performed using finite-difference time-domain methods (Lumerical FDTD) assess the effect of dimension variations on optical response. We find that the mesoscale silver grid with its triangular cross-section and metal coverage of > 50% exhibits less than 2% loss through reflection. For the nanostructure dielectric cone strategy, 90% transmission can be observed for metal coverage as high as 70%. Both catalyst design pathways will be detailed, including methods to print catalysts and passivation layers using conductive and dielectric inks, so as to identify efficient designs and scalable processes for photoelectrochemical solar fuels generation.

Reference

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ET07.12.03

Layer by Layer Self-Assembly for 2D Energy Storage Materials Mahiar M. Hamed¹, Weiqian Tian¹, Zhen Wang¹, Armin V. Mohammadi² and Majid Beidaghi²; ¹KTH, Stockholm, Sweden; ²Auburn University, Auburn, Alabama, United States.

2D materials, or nanosheets, saw a revival with the discovery of graphene, and in the past decades, many classes of layered materials (e.g. transition metal dichalcogenides, metal halides, transition metal oxides/or carbides) have been exfoliated to form 2D nanosheets.

By stacking different electrically and electrochemically active 2D materials into “2D heterogeneous structures” we can engineer new types of energy storage devices. The potential of 2D materials is that the entire material comprises an active ‘surface’ and the fast surface diffusion of ions replaces slow bulk diffusion and results in a much higher power density. At the same time, unlike highly porous structures, 2D materials also allow high packing density and show excellent volumetric density.

The problem, however, is that stacking of 2D materials at large scale and with high precision is difficult. It has been suggested that Layer-by-layer assembly of 2D materials from solution may allow fabrication of 2D heterostructures. There has not been any systematic study and attempt at developing a sustainable and general method for fabricating 2D heterostructures from solution.

Here we address this problem by combining the field of molecular self-assembly of charges species in water to fabricate two-dimensional heterostructures in new battery structures. We focus on MXenes as a template material and show how these can be prepared from water solutions and we show how we can systematically optimize these solutions for Layer-by-Layer self-assembly of multilayered pillared structures. These results can pave the way for large-scale production of 2D heterostructures.