**Materials Science Challenges for Future High Energy Lithium Batteries**

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 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.

**Materials Innovations for Emerging Energy Technologies**

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).
Electrochemical Supercapacitor Based on Co3O4-MnO2-Graphene Oxide Nanocomposite

Design and Development of Sodium-Ion Batteries Based on Layered Transition Metal Oxide Cathode Material

Evaluation of Li-Ion Batteries Built with Recycled NCM 111 Cathode

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 NaNi1/3Fe1/3Mn1/3O2 (NFM) by using hydroxide co-precipitation method with solid-state reaction, and the optimization reaction condition was studied by using in situ XRD. The metastable structure of NaNi1/3Fe1/3Mn1/3O2 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 NaNi1/3Fe1/3Mn1/3O2 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 Na1-xCax/2NFM (x=0.05, 0.1) demonstrate that X-ray diffraction patterns of the prepared Na1-xCax/2NFM 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 NaNi1/3Fe1/3Mn1/3O2 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 NaNi1/3Fe1/3Mn1/3O2 cathode during cycling. Compared to NaNMF, the NaNi1/3Fe1/3Mn1/3O2 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 NaNi1/3Fe1/3Mn1/3O2 makes it a promising material for practical applications in sodium ion batteries.

Research on recycling lithium-ion batteries in electric vehicles and other applications has 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 NaNi1/3Fe1/3Mn1/3O2 (NFM) by using hydroxide co-precipitation method with solid-state reaction, and the optimization reaction condition was studied by using in situ XRD. The metastable structure of NaNi1/3Fe1/3Mn1/3O2 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 NaNi1/3Fe1/3Mn1/3O2 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 Na1-xCax/2NFM (x=0.05, 0.1) demonstrate that X-ray diffraction patterns of the prepared Na1-xCax/2NFM 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 NaNi1/3Fe1/3Mn1/3O2 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 NaNi1/3Fe1/3Mn1/3O2 cathode during cycling. Compared to NaNMF, the NaNi1/3Fe1/3Mn1/3O2 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 NaNi1/3Fe1/3Mn1/3O2 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 NaNi1/3Fe1/3Mn1/3O2 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.


11:00 AM ET07.01.06

Evaluation of Li-Ion Batteries Built with Recycled NCM 111 Cathode

Jun Wang1, Paul Gionet1, Dennis Boulten1, 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 was 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. This process starts with spent batteries regardless of cathode chemistry, produces stoichiometric LiNi0.5Co0.2Mn0.3O2 (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 cranking, HPPC and calendar life between commercial control and recycled cells. The rate capability, however, seems to slightly favor recycled cell at rates above 2C. These results undoubtedly validate the recycled NCM 111 cathode as a legitimate contender for commercial electric vehicle Li-ion battery applications.

References:

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 Ni(NO3)2, 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 CoMn3-xO4, 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 CoMn3-xO4), 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 CoMn3-xO4 nanoparticles system, we were able to increase the energy density and specific capacitance of the supercapacitors by 2x as compared to previously reported values.
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 LiNi0.33Mn0.33Co0.33O2 (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].

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.

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 LiNi0.33Mn0.33Co0.33O2 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.

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 Liu1; 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-NC/72R commercial catalyst. Pt-nanoparticles periphery are conformal 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-NC/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.

Modeling and Characterization for Processing and Manufacturing of Li-Ion Cells

Serejiv Kalnaks, Srdjan Simunovic, A. Kumar, Srikanth Allu and

Y. Nagao, J. Matsui et. al., can be useful to build novel and further improved filler filling PEM for polymer electrolyte fuel cells (PEFC).

Simple Process for Preparing Core-Shell Type Hybridized Nanoparticles for Polymer Electrolyte Membrane
corroboration with known effective medium approximations is evident until a specific volume fraction (νf ≈ 0.3) where, due to a sharp increase in the
could not be attributed to the combination of two components alone, rather the creation of a hybrid nanocomposite possessing its own dielectric behavior.

Emerging as fully crystallized cubic BTO, 8 nm, with a highly functional surface that enables both suspension and chemical reaction in organic solvents.

Suspended in a poly(furfuryl alcohol) matrix, resulting in a stable, high effective permittivity, low loss dielectric. The nanocrystals are produced at 60 °C,
derived from conventional ceramic firing. Here, 0−3 nanocomposites were prepared using gel-collection derived barium titanate (BTO) nanocrystals,
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.

Frequency stable, high permittivity nanoparticle capacitors produced under mild processing conditions offer an attractive replacement to MLCCs
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emerging as fully crystallized cubic BTO, 8 nm, with a highly functional surface that enables both suspension and chemical reaction in organic solvents.
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).

The voltammetry curves confirms the pseudocapacitive behavior of the sample while identical CV curves even at higher scan rates further suggest excellent rate performance. Based on ProDOT and EDOT,[i],[ii] the ability to solubilize these CP variants makes them amenable to incorporation into advanced 3D electrode architectures. As an alternative, Reynolds and co-workers recently developed synthetic methods that yield gram-scale quantities of solution-processable CPs for the fabrication of conductive films and microparticles that can be used in conjunction with other high-capacity materials [e.g., transition metal oxides and graphene][iii]. This approach to producing high-quality carbon nanomaterials for energy storage.

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 EDO.[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.

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 performance.


**ET07.02.09**

**Low-Temperature Plasma Exfoliated Graphene for Supercapacitors Application**

Keliang Wang¹ 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). 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).

Super capacitors 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.
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**

CFL: Flexible Membranes for Energy Storage and Conversion Systems

Cullen Kaschka1, Sean Spratt1, Kofi Adu1,1, Ramakrishnan Rajagopalan1,1 and Clive Randall1;
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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 microporous electrode 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, power and energy densities, as well as 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/plantable 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 bioliquid; 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 Katherine Stoll, Thomas Carney and Fikile Brushett; 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 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 electrode thicknesses 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 equation1, 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 retention2-3. 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

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 Se/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.

References

ET07.03.07
Effect of Rheological Properties on Microstructure and Electrochemical Performance of Si Composite Electrodes Jiaxhi Hu and Yang-Tse Cheng; University of Kentucky, Lexington, Kentucky, United States.

ET07.03.08
Aluminum–Air batteries with Ultrahigh Energy Density Sangjin Choi and Wooyoung Shim; Yonsei University, Seoul, Korea (the Republic of).

ET07.03.09
Fabrication of All-Solid-State Lithium-Ion Batteries Simon E. Hafner1, 3, Lei Cao1, Hyukkeun Oh1, Harvey Guthrey2, Sehee Lee1 and Chunmei Bar1; 1National Renewable Energy Laboratory, Golden, Colorado, United States; 2Mechanical 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 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 spark generated 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.
Mussel-Inspired Polypolyamine Treated Reinforced Membranes with Self-Supported CeO2 Radial Scavengers for Highly Stable PEMFCs

Ki Ro Yoon1, Kyung-Ah Lee1, Sun-Hee Cho2, Seung-Ho Yook3, Il Doo Kim4 and Jin Young Kim4; 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 polypolyamine (PD) with defective ceria nanoparticles (CeO2 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 CeO2 NPs as sustainable radical scavengers. Improved properties of prepared CeO2 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) vs suppressed physical fracture and radical attacks on PFSA ionomer.

“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 alleviated electrical mismatch, BT@P(DFHMA-P(VDF-HFP)) nanocomposite with 1 wt.% BT@P(DFHMA 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.

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 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 Ti3C2Tx in which T 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 bisecteded with CNT sheets to form a high-performance yarn electrode. The bissculated 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.

Direct Urea Fuel Cells Based on CuNi Plated Polymer Cloth as Anode Catalyst

Keichi 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 (Eo) 0.68 V and the maximum output power (Pmax) 1.88 mW/cm2 for 0.5 M urea solution. Similar results of Eo = 0.65 V and Pmax = 1.74 mW/cm2 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.

Direct Observation of Dehydrogenation of Mg2FeH6 by Using In Situ Transmission Electron Microscopy

Hyunmin Kim1, Joseph Song2, Julien Fadonougbo3, Iee-Hwan Bae3, Jaeyoung Hong4, Soongju Oh5, Younghwan Choi3, Jaeyoung Ahn3, Wooyoung Chun3 and Jinwoo 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); 4Electronic Materials Research Center, Korea Institute of Science and Technology, Seoul, Korea (the Republic of); 5Advanced Analysis 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. 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 Mg₂FeH₆. The nanostructured Mg₂FeH₆ 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 Mg₂FeH₆ by hydrogen desorption. We imaged dynamics and diffraction patterns of Mg₂FeH₆ 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. 

Upon heating, intensities of Mg₂FeH₆ 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 Mg₂FeH₆. It is noteworthy that Mg₀ diffusion spots were observed simultaneously after the extinction of Mg₂FeH₆ 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 Mg₂FeH₆ 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. Almost all 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.

cycles), high bonding strength, high structural integrity, high materials homogeneity, and/or 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 Wu1, Jim Zheng1, M. Hendrickson2 and E.J. Plichta3; 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}O_{2} (NMC622)/graphite and LiNi_{0.6}Mn_{0.2}Co_{0.2}O_{2} (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
- Calendering / 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 calendrer/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 preparations 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 Groen1,2; Holst Centre, Eindhoven, Netherlands; Aerospace 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. Franco1,2,3,1 Laboratoire de Reactivité et Chimie des Solides, Université 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 calendering 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.

References
[1] ERC Consolidator Project ARTISTIC (Advanced and Reusable Theory for the In Silico-optimization of composite electrode fabrication processes for rechargeable battery Technologies with Innovative Chemistries), grant agreement #772873 (PI: Prof. Alejandro A. Franco).

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 expensive 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 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 Ranveet Rai1, Scott Solberg1, Rahul Pandey1, Kathryn Murphy2, Marissa Wood3, Jianlin Li4 and David Wood5, 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 rigid 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, NaNiO2, LiMnO2, and Al-doped LiCoO2-based Na and Li-ion cathodes. The electrochemically 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 capacitors 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, University of Missouri at 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 structures 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 Yinxue Zhong1, Peter Smyrek2, 3, Jan-Hendrik Rakebrandt1, Xiaopeng Cheng1, Yuefei Zhang1, Hans J. Seifert1 and Wilhelm Pfleging1, 2, 1Karlsruhe Institute of Technology, Egg-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 when silicon will form a native oxide layer due to 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 Architectured 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 electrodes 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 sp²-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 intergrated 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 Ti3C2Tx 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 Ti3C2Tx electrodes and a gel polymer electrolyte delivered an extremely high areal capacitance of ~1100 mFcm⁻², which is the highest reported to date.

4:45 PM ET07.05.10

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.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.
Performance Enhancement in Planar Type SbS3 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 (>10^5 cm^-1), low cost, less toxicity, and high air stability. In this study, SbS3 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. In order to enhance the performance of SbS3 solar cells, we applied surface treatment on TiO2 layer by Cs2CO3 solution to adjust the work function of TiO2 to the conduction band of SbS3 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 SbS3 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/SbS3/P3HT/Au, which is significantly higher than that of the control device without Cs2CO3 treatment (2.48%). The higher PCE of planar SbS3 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.

DGIST, Daegu, 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 × 10^5 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 polythioene [3, 4-b] thiophene / benzodithiofene (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 absorption.

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.

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.
with microlens array and the PCE increases by up to 12%.

The Effect of Substrate Roughness on the Properties of Sputtered AZO Thin Film

ET07.06.07

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 haze value, which is defined as the percentage of total light scattered within a certain angle, is a key factor for determining the optical properties of thin film solar cells. Therefore, it is important to optimize the surface roughness to achieve a good balance between light scattering and light absorption for maximum power output.

A high haze value means that a large portion of incident light is scattered within the substrate, which in turn reduces the amount of light reaching the active layer of the solar cell. To overcome this problem, we used a combination of different techniques such as chemical etching, mechanical polishing, and laser treatment to achieve the desired roughness profile.

The overall performance of the solar cells was measured under simulated sunlight conditions using a solar simulator. The results showed that the textured substrates produced higher power output compared to the flat substrates. The improvement in power output is attributed to the increased light scattering, which compensates for the lower light absorption caused by the textured substrate.

In conclusion, the use of textured substrates is a promising approach to improving the performance of thin film solar cells. Further research is needed to optimize the surface roughness and to investigate the effects of different processing conditions on the optical and electrical properties of the solar cells.
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.

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 Sb$_2$Se$_3$ Light Absorber for Efficient Photoelectrochemical Water Splitting
Wooseok Yang, Jeiwan Tan, Hyungsoo Lee, Yunjung Oh, Joosun Kim and Jooho Moon; Yonsei University, Seoul, Korea (the Republic of); Korea Institute of Science and Technology, Seoul, Korea (the Republic of).

Sb$_2$Se$_3$ 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 Sb$_2$Se$_3$ strongly depend on its crystallographic orientation and surface morphology due to the anisotropic crystal structure. In this study, we synthesized Sb$_2$Se$_3$ 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 Sb$_2$Se$_3$ 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 Sb$_2$Se$_3$ was elucidated by liquid Raman spectroscopy. In addition, electrical and photoelectrochemical properties of the shape-controlled Sb$_2$Se$_3$ were investigated depending on the structures. After deposition of TiO$_2$ and Pt, an appropriately oriented Sb$_2$Se$_3$-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 Julien, Jae Hyun Kim, Xiaohong Gu and Kai-Tai Wan; Northeastern University, Boston, Massachusetts, United States; Engineering 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/m$^2$ vs. 1000-3000 J/m$^2$), 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 Julien, Jianfeng Sun, Yu Wang, Andrew Fairbrother, Xiaohong Gu, Sophie Napolitano, Liang Ji, Kenneth P. Boyce, Mike Kempe, Roger H. French, Laura S. Bruckman, Gregory S. O'Brien, Adam W. Hauser and Kai-Tai Wan; Mechanical and Industrial Engineering, Northeastern University, Boston, Massachusetts, United States; Materials Science & Engineering, Case Western Reserve University, Cleveland, Ohio, United States; Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland, United States; Akemana, Inc., King of Prussia, Pennsylvania, United States; Renewable Energy, Underwriter’s Laboratories Inc., Northbrook, Illinois, United States; Photovoltaics 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 CIsSe Films**

Aida Torabi; Texas A&M-Central Texas, Killeen, Texas, United States.

Bulk homojunction CIsSe 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. Bandara, Aith DeSilva, K. Vignarohban and L. N. Senaviratna; Physics, University of Peradeniya, Peradeniya, Sri Lanka; Physics, University of West Georgia, Carrollton, Georgia, United States; Physics, 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 (BMI) 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**

*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 nanostuctures 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-ability on fossil. 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 Abraham¹, Jianping Huang¹, Paul Smith¹, Amy C. Marschilok¹, Kenneth Takeuchi² and Esther Takeuchi¹², Stony Brook University, Stony Brook, New York, United States; Brookhaven 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-hydroxyproprionitrile), 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 impedance of the resulting 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 Fg⁻¹ 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 196% 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. Pawar¹, Dipali Patil¹, Donghwan Kim¹², Tae Wan 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-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⁻²) than a single layer transferred electrode with excellent electrochemical stability (96%) and high energy density (140.36 mWhcm⁻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

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
Electrospinning Process for Lithium-Ion Battery Separator

Wisawat Keaswejiareansuk1, 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 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.
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 (electrical conductivity S-Seebeck coefficientenhancement 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 (Sn56Te44 (at%)) [3]. These as melted alloys show eutectic microstructure consisting of Sn50Te50 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 (Sn62Te38 (at%)) and (Sn30Te70 (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 Sn56Te44 (at%). Transport properties of the current alloy are attractive in terms of standard thermoelectric material (S−133µV/K and P−3µW/cm-K2 at 420ºK). 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:


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 new imaging technologies allow for an unprecedented 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 Smyrek1,2, Yijing Zheng1, Jan-Hendric Rakebrandt3, Hans J. Seifert1 and Wilhelm Pflueglinger1,2; 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 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 electrical 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 Zhang1, Rui Wu1, Huiheng Shi1 and Yijing
Zheng2; Institute 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 dissembled 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

4:45 PM ET07.08.06

Laser-Engineering -Analytics in Electrode Manufacturing for Lithium-Ion Batteries Wilhelm Pfieger1,2, Peter Smyrek1,2, Yijing Zheng1, Jan-
Hendric Rakebrandt2, Yangting Sheng3, Marissa Wood4, David Wood4, Jianlin Li5 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 ≥100 μm) 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 kinetics. 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.

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 Wook Lee2, Taekyeong Kim4, Gun-Ho Kim4, Dong Wook Chang2, Jong H. Kim2 and Bong-Gi Kim5; 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 isodindolindole 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 ET07.09.02 Mustard Seed Based Triboelectric Nanogenerator Sachin K. Singh1, Subas Muduli2, Ramamurthy Boomishankar1 and Satishchandra Ogale3; 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. 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. For the first time, a specifically chosen natural seed with rich surface texture is introduced in this respect. The seed-TENG with good adaptability rendered the construction of the flexible nanogenerator.

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 Jeun, 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 H₂ gas product is inevitably mixed with the O₂ gas. Therefore, in order to obtain pure H₂ 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 H₂ and O₂ 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 H₂ and O₂ gases could be selectively collected at each product port without crossing or loss. Our membraneless PV-electrolysis device could capture, transport and collect H₂ and O₂ 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 Ahmed1, Islam M. Hassan1, Ali Radhi2 and Jean Zu3; 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 (TENGs) 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 TENG 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 TENG components operated in parallel for use within the neritic zone of the ocean. The hybridized TENG parallel network within a single underwater TENG 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 TENG 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 Akiyama1, 2, Sakiko Nojima1, Ryo Takahashi2, Hiroshi Funakubo2 and Hiroshi Irie1; 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 10^5 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 metallic 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 0-20 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 the order of 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, Shinsyu 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 cleanup such as air purification, water purification, and antibacterial self-cleaning, as well as energy conversion (i.e., dye-sensitized solar cells and water splitting). 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 AuCl4-, 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. FTIR 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.

References


**ET07.09.07**

**High-Efficiency Power Conditioning System for Autonomous Triboelectric Nanogenerator Devices**

Aravind Ravichandran and Marc Ramazz; 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 (TENGs) 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, Joevonte 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 Sh/Shb2Te3 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 Lee1, 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).

SEÇÃO ET07.10: Fabricação de Dispositivos para Energia
Session Chairs: Wilhelm Pfleging e Yijing Zheng
Terça-feira, 29 de novembro de 2018
Hynes, Nível 3, Quarto 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 electrowinning process. In this presentation we demonstrate an 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 Yanmin 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, Carolina Ellinger1, Kevin O’Connor1, Sean Garner1, Julius Yellowhair1, Ryan Erikson1, 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; 5Sandia 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 electroless copper is deposited on the printed catalyst pattern. The deposited copper is treated in-line with an environmental passivation and darkening agent, protecting the micro-wires from corrosion and minimizing from-say protecting 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 ≥90%; for solar mirrors: (2) specular reflection (SR) efficiency ≥90%; (3) specular reflection restoration (SSR) efficiency ≥90% and for solar panels: (4) the light transmission efficiency (TE) ≥ 90%; and (5) output power restoration (OPR) efficiency ≥ 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-Leopoldshof, 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 nanoscopic range. For many macroscopic effects, however, distribution of components on meso- and microscopic orders of magnitude is relevant. On the one hand, the mesoscopic formation of clusters between the binder and carbon black and their localization in the
proximity of the active particles is important for the fundamental and 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 Hu1,2, *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 as OER/ORR catalyst. This combination has a better performance than individual Pt catalyst or TiC. Ionic liquid (1-ethyl-3-methylimidazolium chloride) mixed with AC13C as electrolyte. For AI 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 Kayeom Kernen1, Geumbee Lee1 and Jeong Sook Ha2,1, *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/cm2 at 0.2 mV/cm2, energy density of 1.86 mWh/cm2, and power density of 8.5 mW/cm2, in addition to 94% capacitance retention for more than 100 cycles.

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 Kim1, Bok Yeop Ahn1, Teng-Sing Wei1, Yevin Je1, Sunho Jeong1, Youngmin Choi1, Il Doo Kim1 and Jennifer Lewis2, *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 um) 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 routes to shape-conformal miniaturization of miniaturized and wearable electronics.

2:30 PM ET07.11.05
Light-Assisted Polymer-Based Electrochemical Energy Storage
Abdelaziz M. Gouda,1, Ri Xu,1, 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, and humidity-dependent electrical response as an ion-conducting medium [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.

In this way we were capable to keep the environmental friendliness of the melanin controlling its (supra)molecular structure and processability. In this way, 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 eumelans: polyDHI, polyDHICA and polyDHI/polyDHICA in dark and light condition, using cyclic voltammetry and galvanostatic charge/discharge cycles.


2:15 PM ET07.11.04
Electrodeposition of MoS2 on Three-Dimensional Graphene/Nickel Foam for Electrocatalytic Water Splitting
Narasimman Rajaram, Mannoohansingh Waldiya, Indrajit Mahkopadhyay 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 such a 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, et., are known to effectively catalyse the HER, however, scarcity and high-price is restricting the large-scale production of hydrogen. Transition metal dichalcogenides (TMDs) 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 (α-Fe2O3) 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 the further refinement of hematite 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 defective 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) and thermoneutral potentials (1.48 V) respectively than bare hematite. Also, the reported results are higher than the most of the
Y-doped BaZrO$_3$(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 intermediate temperature solid oxide fuel cells (IT-SOFC). BaZrO$_3$(BZO) base proton conducting material has a good durability for CO$_2$ compared with BaCeO$_3$ base materials. However, the sintering temperature of BZO is quite high. In this study, Sr$^{2+}$ and Ti$^{4+}$ were substituted to Ba$^{2+}$ and Zr$^{4+}$ sites, respectively. The sintering temperature of Sr and Ti co-doped BZY (BSZTY) powder was 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 electrolyte SOFC by utilizing the fine powder of BZY having a good sinterability, in this study. BSZTY powders were prepared by the novel low temperature synthesis which can prepare the BZO by only mixing the zirconia hydrate 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 Zr$^{4+}$ sites. In this study, Sr$^{2+}$ and Ti$^{4+}$ were substituted to Ba$^{2+}$ and Zr$^{4+}$ 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 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.
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 bonding states. The titanium oxynitride (TiN_{1-x}O_y) 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 Xu2, Katerina Kekalo1, Jifeng Liu2 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 MnFe2O4 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 absorbance, we have undergone antioxidation interfacial engineering in N2/So2 by creating low-cost solution-processed Ni nanochain-SO2 (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 MnFe2O4 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 Meheddi 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 toolset 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 Gonzalez2, 1, Isaiah Oladeji2, 3 and Robert E. Peale2, 4; 1Universidad Autonoma de San Luis Potosi, San Luis Potosi, Mexico; 2Truventric 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 Janyong 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) (PVDF)-based dielectric polymer nanocomposites, the electrical properties are in part controlled by the phase and interface chemical biding states. The titanium oxynitride (TiN_{1-x}O_y) system has the potential to absorb visible light in the full solar spectrum.
fluoride-co-hexafluoropropylene) (PVDF-HFP) / poly(vinylidene fluoride-ter-trifluoroethylene-ter-chlorofluoroethylene) (PVDF-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-Hai Cheng, Matthias H. Richter, Sisir Yalamanchili, Phillip Jahelka, 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 photocathode based solar photoelectrochemical cell with an optically transparent but dense Rh metal nanoparticle catalyst layer. 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 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 (Numerical 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