Energy Harvesting & Storage
Room Mauka - Session EH-WeP

Energy Harvesting & Storage Poster Session

EH-WeP1 Multifunctional Polymeric Binder for Silicon Anode in Li-ion Battery, ***Ja-Hyoung Ryu,*** Ulsan National Institute of Science and Technology, Republic of Korea

Silicon as an anode material in lithium-ion batteries has great potentials due to its high charge capacity. However, the practical application of Si is quite challenging because severe volume change during charging/discharging process results in breaking anode film and fading the reversible charge capacity. Therefore, the efficient polymeric binder to stably accommodate active materials in the anode is highly demanded. We demonstrated the systematic molecular design and synthetic approaches of novel binder is one of the solution which is capable of preserving electrode integrity and maintaining electrical contact during expansion/contraction of silicon anode. We have introduced multifunctional group-containing poly(acrylic acid-*co*-vinyl alcohol) copolymer binders. Polymeric binders with three different functional groups, namely, carboxylic acid (COOH), carboxylate (COO–), and hydroxyl (OH), in a single polymer backbone have been synthesized and characterized via 1H NMR and FTIR spectroscopies. A systematic study that involved varying the ratio of the functional groups indicated that a material with an acid-to-alcohol molar ratio of 60:40 showed promise as an efficient binder with an initial columbic efficiency of 89%. The strong interaction of the polymer binder with Si nanoparticle from PAA, and high viscosity form PVA could give a synergetic effect on making uniform anode film. Further more, three dimensionally interconnected networks provide sufficient mechanical properties to prevent the destruction of the electrode during numerous cycling.

EH-WeP3 Strain imaging of a LiCoO2 Cathode in a Li-ion Battery, ***Keisuke Nakayama,*** Kansai University, Japan

In recent years, world's energy consumption has been steadily increasing, and prompt efforts are needed to decrease CO_2 and other greenhouse gas emissions. Li-ion batteries are becoming increasingly important in the world market of energy storage and conversion devices. Compared with other commonly used batteries, Li-ion batteries have advantages including high energy density, high output voltage, and the absence of the memory effect, and so are recognized as promising candidates for energy storage. Li-ion batteries are applied to mobile electronic devices and these are an essential part of the full hybrid electric vehicles (HEVs) and/or plug-in electric vehicles (PHEVs) owing to their high energy densities and low weight-to-volume ratios.

Li-ion batteries are operated by the Li ions migration. Therefore, it is important to observe the migration of lithium-ions with a high spatial resolution and non-destruction.

The active materials in the electrodes of the lithium-ion batteries have been generally used $LiCoO_2$ cathode and graphite carbon anode that were layered materials. Graphitic materials, which are representative of carbon materials have been used the most for anode materials because of their low working potential, which is close to the metallic lithium anode. During charging and discharging, Li-ions migrate between $LiCoO_2$ and graphite, and intercalation/deintercalation are induced. Intercalation/deintercalation induce changes in volume. Scanning probe microscopy (SPM) can allow high resolution imaging of these volume changes, which enables us to investigate Li-ion migration without destruction.

Our samples to observe were as follows. $LiCoO_2$ particles around 10 µm in diameter were coated with the Al current collector. The thickness of the coated layer was around 30 µm. A 20-µm-thick polypropylene separator with the electrolyte was sandwiched between the $LiCoO_2$ cathode and the graphite anode.

We observed volume changes in the $LiCoO_2$ cathode using SPM, and successfully imaged the distribution of the volume changes corresponding to the $LiCoO_2$ particles. Volume changes in the interspace were significantly larger than those in the particles. Therefore, the large volume changes are caused by electrolyte flux induced by changes in concentration of Li ions.

EH-WeP4 Imaging of dry-out in a $LiCoO_2$ Cathode in a Li-ion Battery, ***Yukiho Okuno,*** Kansai Universisity, Japan

Lithium ion batteries have attracted an attention in the field of portable electronic devices and electric vehicles due to high energy density, high output voltages, and no memory effect. Therefore, Li-ion batteries are recognized as promising candidates for energy storage.

The main elements of Li-ion batteries are positive electrodes, negative electrodes, separators, and electrolytes. $LiCoO_2$ and graphite that are layered materials are commonly used as electrode materials for Li-ion batteries.

Lithium ion batteries operate through migration of Li-ions between the electrodes. During charging and discharging, Li-ions migrate between $LiCoO_2$ and graphite, and Li-ions are inserted into or extracted from particles of electrode materials. Insertion/extraction of Li-ions induce changes in volume. The volume change causes dry-out of electrolyte.

Dry-out of electrolyte is one of the most important issues in Li-ion batteries. The volume changes of the electrode materials induce dry-out of electrolyte, which greatly degrades the batteries. Our samples to investigate dry-out were as follows. $LiCoO_2$ particles around 10 µm in diameter were coated with the Al current collector. The thickness of the coated layer was around 30 µm. A 20-µm-thick polypropylene separator with the electrolyte was sandwiched between the $LiCoO_2$ cathode and the graphite anode.

We observed volume changes in the $LiCoO_2$ cathode using SPM. The observed volume changes are caused by electrolyte flux induced by changes in concentration of Li-ions. However, the volume changes were greatly reduced when the electrolyte dried out. The dry-out and infiltration of electrolyte between the $LiCoO_2$ particles and the current collector spread out with the procedure of degradation of the batteries. The boundaries between the dry-out and infiltration regions acted as barriers of electrolyte flux.

EH-WeP5 Application of XPS and UPS to the Characterization of LixPOyNz Surfaces, ***David Surman,*** Kratos Analytical Inc.*; J. Counsell, S.J. Coultas,* Kratos Analytical Ltd., UK*; C. Moffitt,* Kratos Analytical Inc.*; C.J. Blomfield,* Kratos Analytical Ltd., UK

Lithium ion batteries are commonly found in home electronic equipment. In recent times there have been significant efforts to improve the durability, cycle time and lifetime decay of the batteries and in particular the electrode/electrolyte material. Novel materials have been developed that also increase the energy storage density. Lithium phosphorus oxynitride (LiPON) has become one of the most commonly used solid electrolyte thin-films in energy storage devices. Obviously, due to the widespread use of this material, there is significant interest in understanding the characteristics and properties with a view towards optimization.

We have applied both XPS and UPS to explore the surface and bulk properties of several $Li_xPO_yN_z$ surfaces prepared via atomic layer deposition ALD [1]. The distribution of elements below the surface is explored using ion and angular-resolved depth profiling methods. This technique has been used extensively across a broad range of applications however the damage caused by impinging ions on the structure of the analyzed material has always been a concern for the analyst. Recently Argon gas cluster ion sources have been employed to reduce the chemical damage of organic materials and broaden the range of materials amenable to this type of analysis. Here we extend the application of cluster ions beyond organics to inorganic oxides. We will present how, with the use of Ar250-3000+ ions, where the energy per atom can be 2.5-40 eV, it is possible to obtain more accurate information regarding the true nature of the LiPON thin-film. A comparison is made with conventional monatomic depth profiles and in particular the differences in stoichiometry that is obtained with the two different ion sources. Ion implantation is also discussed as are the unfortunate chemical effects of carbon deposition from organic cluster ions. We will demonstrate how the analyst can now confidently depth profile through inorganic metal oxide thin-films without the worry of reduction or preferential sputtering.

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EH-WeP6 Study on Double Perovskite as a Solid Oxide Regenerative Fuel Cell Cathode Material, ***Youngjin Kwon,*** *J.M. Bae,* Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

It has been increasing interest in hydrogen(H_2) as an alternative energy carrier. Because the H_2 has high energy density, pure emission and it is easy to be transported by using a pipeline. But H_2 doesn't exist on the earth as a fuel. For this reason, it must be generated. There are several ways of producing H_2 such as by photocatalytic water splitting, gasification of biomass, solar thermochemical water splitting and water electrolysis driven by solar cell or wind turbine. Among these technologies, Solid oxide regenerative fuel cell(SORFC) is a practical and efficient method for the industrial field. High operating temperature improves the electrode kinetics and reduce the SORFC electrolyte resistance, leading to lower losses in cell performance.

Due to similarity to Solid oxide fuel cell(SOFC), advances have been made in the development of SORFC based on cell assemblies with structure nickel-yttria stabilized zirconia(Ni-YSZ) fuel electrode / YSZ electrolyte / lanthanum strontium manganite-YSZ(LSM-YSZ) air electrode. The previous study show that the performance discrepancies of the cell in operation between the electrolytic and galvanic modes could be varied, depending on the electrode materials. Moreover, the Ni-YSZ most widely used fuel electrode has several problems even though its great catalytic performance. One of them is degradation of the fuel electrode because of Ni particle's redox reaction and agglomeration. Therefore it is necessary to develop an alternative fuel electrode material.

Double perovskite electrode material is one of the promising candidate for the fuel electrode of the SORFC because of its high catalytic performance and stability at SOFC mode. In this study, We studied on the Double perovskite $Pr_{0.5}Br_{0.5}MnO_{3-\delta}$(PBMO) as a fuel electrode material of SORFC. PBMO was infiltrated into the scaffold structure of the electrolyte, $La_{0.8}Sr_{0.2}Ga_{0.85}$ $Mg_{0.15}O_{3-\delta}$ (LSGM) and synthesized at the low temperature because second phase generated when it annealed at high temperature. The Half cell test was conducted to investigate the electrochemical performance of the electrode material at the steam rich atmosphere.

EH-WeP8 Unoccupied Surface State Induced by Ozone and Ammonia on H-Terminated Diamond Electrodes for Photo-Catalytic Ammonia Synthesis*, I. Boukahil, P.S. Johnson,* University of Wisconsin Madison, USA*; R. Qiao,* Advanced Light Source, LBNL, USA*; J. Bandy, R.J. Hamers,* ***Franz Himpsel,*** University of Wisconsin Madison, USA

Recently, the use of H-terminated diamond electrodes for photo-catalytic conversion of N_2 to NH_3 in aqueous solution was demonstrated [1]. This concept uses energetic electrons, created in diamond by UV-light and injected into the solution. The negative electron affinity of H-terminated diamond surfaces makes them efficient electron emitters [2], and their chemical inertness enables applications as electrodes in reactive environments [1]. A limiting factor was the build-up of O at the interface during the photo-catalytic reaction.

We investigated the surface electronic structure of H-terminated, polycrystalline diamond films prepared the same way as those used for ammonia synthesis in [1], before and after treatment with ozone or ammonia. X-ray absorption spectroscopy (XAS) served as atom- and bond-specific probe (compare [3] for the methodology). For ozone treatment, a sharp C1*s* transition to an unoccupied surface state is found at -2.5 eV below the onset of the bulk conduction band transitions (289.2 eV). A similar transition is found at -2.6 eV after ammonia treatment.

It is surprising to obtain such a well-defined surface state at complex, real-life electrode materials. That suggests a characteristic local bonding configuration. An extensive comparison with spectra from reference molecules reveals two compatible configurations for the ozone-treated surface, a keto group (>C=O) and a hydroxyl group attached to π-bonded carbon (=C-OH). Both lead to low-lying π* transitions similar to those observed at the C1*s* and O1*s* edges.

Possible roles of the surface state in the photo-injection of electrons from diamond into electrolytes are discussed. Thereby the electron-hole interaction [4] is taken into account which affects both the position of the surface state in the core level spectra and the barrier for electron injection.

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EH-WeP9 Improved Thermo-stability of $(NH_4)_2SiF_6$ Fluorescent Microparticles with the Phosphoric Acids*,* ***Aoi Tokiwa,*** Tokyo Denki University, Japan

Ammonium hexafluorosilicate ($(NH_4)_2SiF_6$) microparticles, are one of novel phosphor, possess excellent features such as a high-efficient fluorescence and robust photo-stability, compared to other silicon (Si)-based ones. Because of these advantages, they are a promising candidate for the applications to light emitting diodes (LEDs), opto-electronic integrated circuits (OEICs) and solar cells. However, the microparticles may be restricted the adaptable environment so as to cause the rapid degradation of fluorescence intensity under temperature above 200°C Therefore, the improvement of heatproof temperature is of crucial importance. As a one of the heat-resistance materials, the phosphoric acids are known to have effective features for the products such as flame-retardant plastics and rubber. In this presentation, we will discuss the thermo-stable effect of the $(NH_4)_2SiF_6$ fluorescent microparticles with the phosphoric acids. The fluorescent microparticles were synthesized by the chemical reaction of vaporized hydrofluoric nitric acid with Si powders and P powders in closed container. The obtained microparticles had a mean diameter of approximately 10 - 30 µm, and were composed of $(NH_4)_2SiF_6$/phosphorus oxide composites as major ingredients. To investigate the thermo-stability of the fluorescent microparticles, they were annealed from room temperature to 300 °C for 30 min in the atmosphere. The microparticles could be dramatically enhanced the heatproof temperature by adding the phosphoric acids, showing the stable fluorescence even after 300 °C annealing. It is clarified from Fourier transforms infrared (FT-IR) analysis that the improved thermos-stability is mainly due to the formation of Si-O bond with the stronger binding energy at the interface region between the $(NH_4)_2SiF_6$ and the phosphorus oxide. It should be noted that the annealed microparticles at 300 °C could be visible to the naked eye. Therefore, the introduction of the phosphoric acids into the $(NH_4)_2SiF_6$ fluorescent microparticles would become a dominant tool for the development of the thermally stable phosphor.

EH-WeP10 Optimization of Si Quantum Dot Arrays in Inorganic-organic Solar Cells*,* ***Yuuki Sugano,*** Tokyo Denki University, Japan

Currently, silicon (Si)-based solar cells have been used extensively because of the possession of greater advantages such as high performance and high reliability. To expand the versatility and to reduce the production cost of the solar cells, inorganic-organic solar cells that combine Si quantum dots (SiQDs) with conducting organic polymers have been developed over the past several years. In the design of the highly efficient solar cells, the usage of strong wavelength range, i.e., 450-520 nm of sunlight is of crucial importance. The SiQDs can be freely controlled the bandgap width by the variation of size, enabling the selective absorption of sunlight. Therefore, it is necessary to uniform form the SiQDs on the substrate so as to maximize the potential abilities of the SiQDs. In this presentation, we will discuss the correlation between the morphology of the substrate surface and the configuration state of the SiQDs. The uniform arrangement of the SiQDs could be achieved by the formation of the micro-textured structures onto the substrate surface. Additionally, to investigate the absorbance characteristics of the substrates with SiQD arrays, we conducted the UV-vis analysis. As a result, the substrates with the SiQD arrays led to the higher absorbance compared to substrates without the SiQD arrays. Therefore, the optimizing the arrangement of the SiQDs becomes the most important factor in the performance improvement of SiQDs based on the inorganic-organic solar cells.

EH-WeP11 Upgradation in Photoelectrochemical Performances and Stability of CdS cased $ZnIn_2S_4/TiO_2$ Heterojunction *via* Improved TiO_2/FTO Interface and $Ni(OH)_2$ Cocatalyst*, M.A. Mahadik, P. Shinde,* Division of Biotechnology, Brain Korea 21 Plus Program, Advanced Institute of Environment and Bioscience, College of Environmental and Bioresource Sciences, Chonbuk National University, Republic of Korea*;* ***David Selvaraj,*** Division of Biotechnology, Brain Korea 21 Plus Program, Advanced Institute of Environment and Bioscience, College of Environmental and Bioresource Sciences, Korea*; H.H. Lee,* Pohang Accelerator Laboratory (PAL), Pohang University of Science and Technology (POSTECH), Republic of Korea*; M. Cho, J.S. Jang,* Division of Biotechnology, Brain Korea 21 Plus Program, Advanced Institute of Environment and Bioscience, College of Environmental and Bioresource Sciences, Chonbuk National University, Republic of Korea

A simple and effective strategy was used to fundamentally improve the performance of a $Ni(OH)_2$ loaded CdS cased $ZnIn_2S_4/TiO_2$ heterostructured photoanode. TiO_2 nanorods grown hydrothermally on fluorine-doped tin oxide (FTO) and annealed at 500°C yielded an optimal photocurrent density of ~ 988 µA cm^{-2} at 0.1 V vs. Ag/AgCl under simulated one sun illumination. The annealing effect minimized the defects in TiO_2 and assisted the formation of compact contacts between the FTO and TiO_2 nanorods for efficient electron transport. The stepwise introduction of $ZnIn_2S_4$ and CdS on annealed TiO_2 enhanced the absorption in the visible spectrum range and electron/hole separation in CdS cased $ZnIn_2S_4/TiO_2$. Additionally, the $Ni(OH)_2$ cocatalyst functioned in hole trapping and improved the stability of the photoelectrode through timely consumption of the photogenerated charges, particularly the holes. The photoelectrical performances studied under AM1.5G illumination shows the 3D heterostructure generate a photocurrent of approximately 1.9 mA cm^{-2}, and is stable up to 60 min.

EH-WeP12 Surfaces And Interfaces Of Methylammonium Lead Halide Perovskite/ Graphene Oxide Films Studied By Spectroscopy*, **Muge Acik**, S.B. Darling,* Argonne National Laboratory, USA

Power conversion efficiency in perovskite-based solar cells has recently improved to ≥20%, however, there is insufficient understanding of the underlying optoelectronic device function. Among all perovskite materials as candidates for the light harvesters in such solar devices, organolead halide perovskites, $MAPbX_3$ (X=I, Br, Cl), have stood out with their outstanding optoelectronic properties such as tunable bandgaps, long electron-hole diffusion length and high electron/hole mobility. Indeed, replacement of ETL/HTL with graphene-derived materials (graphene oxide, reduced graphene oxide, n/p-doped graphene, etc.) has emerged as a pathway to improve device performance. Nevertheless, unclear film growth, nucleation and degradation mechanisms at the graphene/perovskite hybrid interfaces require understanding of interfacial mechanisms during perovskite growth. Moreover, graphene/perovskite structure-property relationships are not well understood due to unclear chemistry/poor characterization at the interfaces of ETL/perovskite/HTL hybrids. To explore interfacial working mechanisms and perovskite film formation in graphene-derived perovskite solar cells, we performed variable temperature (≤600°C) *in situ* spectroscopy (infrared absorption, micro-Raman, UV-vis-NIR, x-ray photoelectron and luminescence), and *ex situ* XRD, SEM, TEM, and AFM for film morphology studies. Our studies targeted perovskite/graphene interfaces and perovskite growth mechanisms to overcome detrimental effects of stability factors such as incomplete lead precursor conversion, inconsistent crystallite formation/film uniformity, and weak cation-anion-solvent coordination. Effect of film thickness, stoichiometry control, underlayer/overlayer composition, and perovskite growth temperature were optimized. To address film scalability and stability, we studied opto-thermal changes in reduced graphene/graphite oxide (RGO) upon halide-based ($CH_3NH_3PbI_3$, $CH_3NH_3PbBr_3$, $CH_3NH_3PbCl_3$) perovskite deposition, and performed spectroscopic analysis derived from the intensity and peak areas of perovskite vibrational modes of C-H (~2800-3200 cm^{-1}) and N-H (~2000-2800 cm^{-1}). Controlled perovskite formation was achieved at room temperature for bromide/chloride-based perovskites resulting improved chemical stability with heat (*vs.* iodide derivative). Poor perovskite formation was monitored on RGO resulting in film degradation in air (O_2, H_2O) by *in situ* characterization. (1) M Acik, SB Darling. J. Mater. Chem. A (2016) 4, 6185-6235. (2) J Gong, SB Darling, F You, Energy Environ. Sci. (2015) 8, 1953-1968. (3) M Acik, G Lee, C Mattevi, M Chhowalla, K Cho, YJ Chabal. Nature Mater. (2010) 9 (10), 840-845.

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EH-WeP13 Kesterite Cu_2ZnSnS_4 (CZTS) Thin Films Using Sn/Cu/ZnS Stack Layers and H_2S Sulfurization*, M.S. Choi, D.H. Lim, Y.J. Kim, H.H. Han, S.K. Son, J.H. Lee,* Hanyang University, Seoul, Korea, Republic of Korea*; R.C. Choi,* Inha University, Incheon, Korea, Republic of Korea*; **Changhwan Choi**,* Hanyang University, Seoul, Korea, Republic of Korea

We synthesized and characterized Cu_2ZnSnS_4 (CZTS) thin film as an absorber layer using hybrid physical vapor deposition methods with a Sn/Cu/ZnS stack order on the Mo coated SLG (Soda lime glass) or SLG substrates. Considering melting temperature of each element, the first Sn layer was thermal-evaporated, followed by deposition of Cu and ZnS layers using Radio-Frequency (RF) magnetron sputtering. For the complete precursor, the final sulfurization process was carried out at 550 ^oC for 1 hour under the mixture gases of N_2 + H_2S (5%). ZnS was intentionally adopted to provide more sulfure into the film instead of using single Zn because some sulfur is lost during thermal processing. In order to investigate the effects of the elemental composition ratio within CZTS thin film on the structural, electrical and optical properties, the ratio of Sn: Cu: ZnS was modulated by adjusting the thickness of each element layers as following: (1) Sn (110 nm)/Cu (97 nm)/ZnS (243 nm), (2) Sn (132 nm)/Cu (109 nm)/ZnS (209 nm), (3) Sn (135 nm)/Cu (117 nm)/ZnS (198 nm), (4) Sn (134 nm)/Cu (138 nm)/ZnS (178 nm), and (5) Sn (134 nm)/Cu (158 nm)/ZnS (158 nm).

The CZTS thin film was turned out to be kesterite structure and the strongest preferred (112) orientation peak was detected to Cu/(Zn+Sn) ratio with 1.04. The Cu/(Zn+Sn) ratio substantially affects the peak intensity as well as growth and creation of secondary phases in the kesterite-structured CZTS films. In addition, the optical energy band gap (E_g) is significantly influenced by the composition ratio. Generally, increasing Cu/(Zn+Sn) ratio induced the growth of CZTS particle size leading to surface morphology improvement while the E_g was reduced. The moderate Cu/(Zn+Sn) ratio in the range between 0.53 and 1.04 led to enhance the kesterite structure of CZTS single crystal phase and reinforce growth direction of (112) preferred orientation. However, the Cu-rich films having Cu/(Zn+Sn) ratio greater than 1.0 showed much larger grain size due to agglomeration with adjacent grains. The Cu-rich CZTS thin film exhibited high carrier concentration (1.60×10^{20} cm^{-3}) and hall mobility (9.8 $cm^2/V\cdot sec$), but lower (1.18 eV) was attained. Instead, the E_g of Cu-poor CZTS thin film was 1.53 eV, favorable to the optimal CZTS absorber layer. Our results indicate that the optical energy band gap, an indicator to determining the optical properties of the CZTS thin film, is very sensitive to the composition ratio of constituent elements and PVD-based CZTS thin film should be carefully processed to get the optimum optical properties.

EH-WeP14 Charge Transfer Dynamics between Carbon Nanotubes and Hybrid Organic Metal Halide Perovskite Films*, **Philip Schulz**, M. Yang, R. Ihly, K. Zhu, J.L. Blackburn, J.J. Berry,* NREL, USA

The ongoing development of hybrid organic inorganic perovskite photovoltaics has revealed that the numerous interfaces in perovskite solar cells (PSC) play crucial roles for device efficiency and stability. Importantly, many critical interfacial properties are still poorly understood, a deficiency that often limits efforts to improve device performance. Carbon nanotubes have been identified as viable transport layer components in high efficient PSC with enhanced cell characteristics. In this talk I will present our most recent results exploring the mechanisms by which carbon nanotubes enable advantageous charge carrier extraction from the absorber layer and how carbon nanotube interlayers can ideally be embedded in the device geometry.

First, we demonstrated in a detailed photoemission spectroscopy study of semiconducting single-walled carbon nanotubes (s-SWCNT) on top of methlyammonium lead iodide ($MAPbI_3$) absorber films that the formation of an interfacial dipole leads to beneficial band bending in the s-SWCNT film. This observed alignment allows for rapid hole extraction at this interface from the absorber onto the s-SWCNT transport layer as seen from the clear spectroscopic signatures of both phases ($MAPbI_3$ and s-SWCNT) in transient absorption spectroscopy.[1] Subsequently, we were able to show that this enhanced hole extraction process impacts the kinetics of charge transfer at multiple interfaces within the device stack by unambiguously tracking charge carrier dynamics with a combination of time resolved photoluminescence, transient absorbance and time resolve microwave conductivity measurements.[2] Eventually, we showed that integrating a thin s-SWCNT interlayer between the $MAPbI_3$ absorber and a conventional organic hole transport layer leads to a significant improvement of device characteristics and cell performance. In my outlook I will sketch how the ensemble of these studies opens up an avenue to tailor-made charge carrier extraction interlayers for the next generation of transport layers in PSC.

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[2] R. Ihly, Anne-Marie Dowgiallo, Mengjin Yang, Philip Schulz, Noah Stanton, Obadiah G. Reid, Andrew. J. Ferguson, Kai Zhu, Joseph J. Berry, Jeffrey L. Blackburn. *Energy & Environ. Sci.***2016**, 9, 1439–1449

EH-WeP15 Combinatorial Reactive Sputtering of In_2S_3 as an Alternative Contact Layer for Thin Film Solar Cells, ***Sebastian Siol***, NREL, USA*; T. Dhakal,* Binghamton University, USA*; G. Gudavalli, P. Rajbhandari,* Binghamton University, USA*; C. DeHart, L. Baranowski, A. Zakutayev,* NREL, USA

High-throughput computational and experimental techniques have been used in the past to accelerate the discovery of new promising solar cell materials. An important part of the development of novel thin film solar cell technologies, that is still considered a bottleneck for both theory and experiment, is the search for alternative interfacial contact (buffer) layers. The research and development of contact materials is difficult due to the inherent complexity that arises from its interactions at the interface with the absorber. A promising alternative to the commonly used CdS buffer layer in thin film solar cells that contain absorbers with lower electron affinity can be found in β-In_2S_3. However, the synthesis conditions for the sputter deposition of this material are not well established.

Here, In_2S_3 is investigated as a solar cell contact material utilizing a high throughput combinatorial screening of the temperature-flux parameter space, followed by a number of spatially-resolved characterization techniques. It is demonstrated that by tuning the sulfur partial pressure, phase pure β-In_2S_3 could be deposited using a broad range of substrate temperatures between 500°C and ambient temperature [1]. Combinatorial photovoltaic device libraries with Al/ZnO/In_2S_3/Cu_2ZnSnS_4/Mo/SiO_2 structure were built at optimal processing conditions to investigate the feasibility of the sputtered In_2S_3 buffer layers and for an accelerated optimization of the device structure. The performance of the resulting In_2S_3/Cu_2ZnSnS_4 photovoltaic devices is on par with CdS/Cu_2ZnSnS_4 reference solar cells with similar values for short circuit currents and open circuit voltages.

Overall, these results demonstrate how a high-throughput experimental approach can be used to accelerate the development of contact materials and facilitate the optimization of thin film solar cell devices.

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EH-WeP16 Higher Voltage Li-rich Cathode Materials for Lithium-ion Battery Applications, *Chandrasekar M Subramaniyam*, *H.K. Liu, S.X. Dou,* Institute for Semiconducting and Electronic Materials AIIM facility, Innovation Campus, University of Wollongong, Australia

- Li-rich layered cathode material exhibited excellent specific capacity (250 mAh/g) over 100 cycles exhibiting 95-99% coulombic efficiency.
- Therefore, these materials in combination with appropriate electrolytes are expected to perform at high voltage (up to 5 V) which in turn could foresee the requirement for plug-in/ hybrid electric vehicles

A quest to replace fossil fuels so as to ignite the automotive and electronic devices with high-performing, economical and safe power storage simulates R&D in the field of chemical power sources. The past two decades research on lithium-ion batteries (LIBs) proven it to be robust technology in electrify electronic devices and in developing plug-in and hybrid electric vehicles as they delivers high energy and power capabilities. However, the present R&D aimed at beefing up it's the current state-of-art technology to develop "5 V" cell without sacrificing high specific charge capacity, excellent cyclability and safety[1-4]. Therefore, the current focus is on the development of cathode materials as the anode materials possess working voltage approximately close to Li metal.

In order to foresee these objectives, herein, we have attempted to synthesis spinel-layered[4-7] Li-rich Li-Mn-M-O based composites as cathode material for lithium-ion batteries applications via simple, low temperature - solvothermal method. Both as-obtained and annealed samples were characterized for their phase, morphology using x-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM), respectively. When electrochemically tested against Li^+/Li^0 between 2.0 – 4.8 V, the annealed Li-rich spinel-layered exhibited excellent specific capacity and rate capability even at high current density, making it as a probable next generation cathode material for LIBs.

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EH-WeP17 High-Resolution Observation of Electronic Properties of an Anode Material in a Lithium-Ion Battery, *Yuki Matsushita,* Kansai University, Japan

The electrochemical energy storage devices have attracted an attention in the field of mobile electric devices and electric vehicles. Lithium-ion batteries are one of the most significant devices because of high energy density, high output voltage, and no memory effect. The primary components of a lithium-ion battery are negative-electrode material, positive-electrode material, separator, and electrolytes along with current collectors. Lithium-ion batteries operate through the migration of lithium- ions between the electrodes. During charging and discharging, electrode reactions occur in the active materials corresponding to lithium-ion migrations.

The active materials in the electrodes of the lithium-ion batteries have been commonly used $LiCoO_2$ and graphite that were layered materials. Also, the electrolyte is a lithium salt in an organic solvent. The lithium-ion batteries based on graphite are approaching the theoretical limit for capacity. Therefore, Si particles have attracted an attention. Si has a high theoretical specific energy density for anode materials in lithium-ion batteries. However, the cycle life of batteries with Si anode is poor as large volume changes are associated with the lithiation and delithiation cycle according to electrode reactions, resulting in the pulverization of the electrode. In addition, lithium-ion batteries have a risk of ignition because of using flammable organic liquid electrolyte. All-solid-state lithium-ion batteries using the non-flammable inorganic solid electrolyte instead of flammable organic liquid electrolyte have been attracted an attention to improve safety. Lithium-ion batteries have been widely studied for additional improvement of performance and safety.

When Si or Li_2TiO_3 particles lithiated or delithiated with lithium ions in a battery, the electrons also are transferred to maintain charge neutral. Therefore, the anode materials in the electrodes of the lithium-ion batteries are required to both electronic conductivity and ionic conductivity. We focused on change in electronic properties of the anode materials especially Si due to the chemical reactions with lithium ions. We present results in observation of changes in electric properties of Si particles in the anode corresponding to the lithium-ion concentrations, which were obtained via a scanning probe microscope.

EH-WeP18 Activated Carbon-like Graphene Assembly for Supercapacitor Applications, *Kwang Bum Kim,* Yonsei University, Korea, Republic of Korea

Graphene has been extensively stuided as an electrode material for supercapacitors due to its large specific surface area, high electrical conductivity and excellent chemical/mechanical stabiity. Due to the 2D nature, however, graphene tends to easily restack to form layered microstructures on a current collector during electrode fabrication. Restacking of the graphene sheets in an electrode greatly reduces the effective surface area of graphene and limits ion transport within a graphene electrode, which in turn leads to a decrease in the specific capacitance.

Here, we developled new approaches to improve capacitive properties of graphene: nanomesh graphene and activated graphene microsphere. The activated graphene microsphere is like an activated carbon-like graphene assembly which is prepared through graphene assembly into microspheres followed by an activation treatments.

In this study,we report on the activated carbon-like graphene assembly as high specific capacitance electrode materials for supercapacitor applications. Detailed synthetic procedure and electrochemical properties of the activated graphene microsphere assembly will be discussed in the meeting.

EH-WeP19 Flexible and Stackable All-solid-state PPy/CNT-web Paper Supercapacitors, *Heejoon Ahn, S. Ahn,* Hanyang University, Republic of Korea

Increasing demand for wearable and portable electronic devices facilitates development of flexible energy storage systems such as Li-ion batteries and supercapacitors. Carbon nanotubes (CNTs) have a great potential for supercapacitors due to their great electrical properties and excellent flexibility, making them appropriate materials to be used in the backbone of flexible devices. However, low specific capacitance of CNTs limits their practical application in supercapacitors. Combination of CNT and conductive polymer is an effective way to improve the performance of supercapacitors. Among conductive polymers, polypyrrole (PPy) is a promising material for supercapacitor electrodes because of its high capacitance, facile synthesis, and low cost. However, there are several demerits such as poor rate capability and cycling stability of PPy. To overcome these drawbacks, in this study, PPy is deposited onto an ultra-thin CNT paper. Ultra-thin CNT-web paper is prepared by using chemical vapor deposition and direct spinning method, and PPy is electrochemically deposited on the CNT-web paper. Electrochemical characterization of the PPy/CNT-web paper electrodes has been carried out by means of cyclic voltammetry and galvanostatic charge/discharge. They exhibit high specific capacitance of 396 Fg^{-1} at a scan rate of 2 mVs^{-1} and retain the specific capacitance of 208 Fg^{-1} at a scan rate of 500 mVs^{-1}, which indicates the high rate capability of the electrodes. All-solid-state flexible symmetric supercapacitor is assembled with two PPy/CNT-web paper electrodes, and the symmetric supercapacitor devices can be stacked to form high-density energy devices. Electrochemical performance of the single and stacked PPy/CNT-web paper supercapacitors will be discussed in the presentation.

EH-WeP20 Thin Film Metallic Glass as an Effective Diffusion Barrier for Microelectronic Packaging and CIGS Solar Cell*, W. Diyatmika, L. Xue, C. Yu, C. Lee,* ***Jinn P. Chu,*** National Taiwan University of Science and Technology, Taiwan, Republic of China

Thin film metallic glass (TFMG) with its amorphous nature is of great interest owing to its unique properties, including high strength, large elastic limits, excellent corrosion, and wear resistance. Grain boundaries are generally considered as atomic diffusion path. Therefore, TFMG, possessing grain boundary-free structure, is thought to efficiently mitigate atomic diffusion.

In this presentation, we will report two examples of TFMG as the diffusion barrier on (1) Sn whisker mitigation in the Cu-Sn couples as well as (2) copper indium gallium selenide (CIGS) solar cells on stainless steel (SS). We found that TFMG effectively blocks the Cu/Sn interaction and thus minimizes Sn whisker formation, even with the thickness as thin as 25 nm. In addition, with very thin thickness, the introduction of TFMG underlayer is expected to yield insignificant degrees of compressive stress, which is anticipated to occur when the samples are exposed to thermal cycling. Furthermore, the detrimental iron diffusion from SS into CIGS is found to be effectively hindered by the introduction of a 70-nm-thick TFMG barrier; the cell performance is thus improved. Compared with the 2.73% of CIGS on bare SS, a higher efficiency of 5.25% is obtained for the cell with the TFMG barrier. Thin thickness and amorphous nature of TFMG are considered beneficial to make TFMGs as a promising diffusion barrier for Sn whisker and Fe diffusion mitigation in microelectronic packaging and flexible CIGS Solar Cell, respectively.

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