

Energy Harvesting & Storage

Room Lehua - Session EH-MoM

Surfaces & Interfaces for Environmental Processes

Moderator: Jun Yoshinobu, ISSP, Univ. of Tokyo, Japan

8:20am EH-MoM2 In-situ FTIR Spectroscopy of Water Adsorption on Alkali-free Glass Surfaces, *Nicholas J. Smith, G.P. Agnello*, CORNING Incorporated

The adsorption of water on glass surfaces is believed to be critical in mediating a number of surface properties, and is particularly relevant for alkali-free multicomponent glasses used as display substrates when considering attributes like coating adhesion or electrostatic charging. Prior observations on similar glasses, as well as silica, have yielded intriguing observations about the capacity, the kinetics, and especially the structure of water that chemically or physically adsorbs on glass surfaces. In this work, we report on application of in-situ FTIR spectroscopy methods to experimentally investigate the nature of water adsorbed on planar alkali-free glass surfaces as a function of humidity and vacuum pre-treatment, shedding light on the content and structure of adsorbed water.

8:40am EH-MoM3 Nuclear-spin State Filtering and Conversion of H₂ with Solid Surfaces for Efficient Hydrogen Liquefaction, *G. Nakamura, K. Takeyasu, S. Ohno, D. Ivanov, S. Ogura, Katsuyuki Fukutani*, University of Tokyo, Japan

Hydrogen is a clean energy source, and storing hydrogen in a liquid form is a high-density storage method. Molecular hydrogen exists in nuclear-spin isomers of ortho and para species according to the total nuclear spin [1]. Since these species are correlated to the rotational states with even and odd rotational quantum numbers (J) because of the symmetry of the total wavefunction with respect to the permutation of the two nuclei, the stable state at the liquid hydrogen temperature is the para state. Although the ortho-para conversion in an isolated state is strictly forbidden, the conversion is promoted at solid surfaces [1], which has been used for efficient hydrogen liquefaction. Due to the symmetry of the H₂ molecule, on the other hand, the molecule-surface interaction is anisotropic depending on the molecular orientation, which can be analyzed with the J -state selective temperature-programmed desorption (TPD) [2]. In the present work, we have investigated the potential anisotropy of H₂ on a Pd(210) surface with resonance-enhanced multiphoton ionization (REMPI). With the anisotropic potential, furthermore, we propose that the ortho and para species can be separated by surface scattering, which is potentially used for efficient hydrogen liquefaction. We demonstrate such nuclear-spin state filtering on a TiO₂(110) surface.

When the Pd(210) surface is exposed to H₂ at ~30 K, H₂ is molecularly chemisorbed on a H-covered surface, which is revealed by a TPD peak at ~70 K [3]. When this desorption is J -state selectively detected, the $J=0$ para H₂ is desorbed at 74 K, while the $J=1$ ortho H₂ is desorbed at a higher temperature of 78 K. This indicates that the adsorption energy of the ortho species is larger than that of the para species. This is due to the lifting of the degeneracy of the ortho state induced by the potential anisotropy. From the population ratio of the ortho and para states, the ortho-para conversion time in this adsorption state is found to be shorter than ~10 s, which is much faster than Ag surfaces [1]. By applying a pulsed supersonic H₂ beam, the angular distribution of H₂ scattered from TiO₂(110) is state-selectively measured. Whereas the $J=1$ ortho H₂ reveals a broad distribution in the near-specular direction, the $J=0$ para H₂ shows a slightly shifted distribution. We discuss the scattering of H₂ via an anisotropic potential and resultant nuclear spin-state filtering.

References

- [1] K. Fukutani, T. Sugimoto, Prog. Surf. Sci. 88, 279 (2013).
- [2] T. Sugimoto, K. Fukutani, Phys. Rev. Lett. 112, 146101 (2014).
- [3] P. K. Schmidt et al., Phys. Rev. Lett. 24 87, 096103 (2001).

9:20am EH-MoM5 Chemical Gradients Formation on Polymer Surfaces for Directed Molecular Transport, *Hyung-Jun Koo*, Seoul National University of Science and Technology, Republic of Korea; *P.V. Braun*, University of Illinois at Urbana-Champaign, USA; *K.V. Waynant*, University of Idaho, USA; *C. Zhang*, University of Illinois at Urbana-Champaign, USA

Surfaces containing defined microscale chemical gradients are important for various applications including a sample library with an extremely dense variable set and a smart platform to direct 2D-molecular transport. In this

regard, reliable methods to form milli- to micron-scale chemical gradients are required. We present two facile microfluidic methods to form narrow surface chemical gradients in a tertiary amine functionalized polymer brush via a selective quaternization. Two methods are on the basis of different physical mechanisms: permeation into porous media vs. diffusion at liquid/liquid laminar interface. Concentration and separation as well as directional transport driven by surface-gradient on highly hydrated polymer films will be also demonstrated. Such a new concept to control 2D transport of molecules could generally be applied for signal enhancement in chemical sensors to detect tiny amount of harmful molecules, e.g., pollutants, toxins, etc..

References:

1. **H.-J. Koo**, K. V. Waynant, C. Zhang, R. T. Haasch, P. V. Braun, "General Method for Forming Micrometer-Scale Lateral Chemical Gradients in Polymer Brushes", *Chemistry of Materials*, 26, 2678 (2014).
2. **H.-J. Koo**, K. V. Waynant, C. Zhang, P. V. Braun, "Polymer Brushes Patterned with Micrometer-Scale Chemical Gradients using Laminar Co-Flow", *ACS Applied Materials & Interfaces*, 6, 14320 (2014).
3. C. Zhang, A. Sitt, **H.-J. Koo**, K. V. Waynant, H. Hess, B. D. Pate and P. V. Braun, "Autonomic molecular transport using hydrogel films containing programmed chemical potential gradients", *Journal of the American Chemical Society*, 137, 5066 (2015)

10:20am EH-MoM8 Activation of CO₂ using Heterogeneous Catalysts, *Junji Nakamura*, Tsukuba University, Japan

INVITED

Methanol synthesis by hydrogenation of CO₂ using Cu catalysts is one of the promising reactions to convert CO₂ into useful chemicals. Formate species is the pivotal intermediates formed as the initial step of CO₂ hydrogenation (CO₂ + H₂ → HCOO_a). The reaction rate of formate synthesis is very low and the reaction probabilities are about 10⁻¹² at 340K. The formate synthesis must be accelerated in order to convert CO₂ to methanol efficiently. Our previous kinetic measurements have suggested that formate is synthesized via Eley-Rideal typed mechanism, in which CO₂ molecules directly attack adsorbed hydrogen atoms on Cu surfaces. The structure insensitivity observed for formate synthesis experiments on Cu(111), Cu(100), and Cu(110) were well explained by the Eley-Rideal mechanism based on DFT calculations. In addition, sharp angular desorptions of CO₂ have been observed for formate decomposition as the reverse reaction of formate synthesis, indicating thermal non-equilibrium reaction. We thus performed molecular beam experiments to prove the Eley-Rideal typed mechanism, in which CO₂ molecules with controlling vibrational and translational energies were reacted with adsorbed hydrogen on cold Cu(111) and Cu(110) surfaces (TS =150-215 K). The formation of formate was found by infrared spectroscopy and temperature programmed desorption measurements of CO₂ and H₂ from decomposition of formate. We confirmed the formation of formate species on Cu(111) and Cu(110) with reaction probabilities of 10⁻⁵ by heating nozzle above 1000 K, while no formate is formed at nozzle temperatures below 1000 K. The results indicate the Eley-Rideal typed mechanism with thermal non-equilibrium character. DFT calculations also reproduce the Eley-Rideal typed mechanism, in which translational and vibrational excitations of CO₂ are required to overcome the barrier of formate synthesis, 0.6-0.7 eV. The understanding on dynamics of CO₂ activation is expected to apply for the state-to state chemistry of methanol synthesis. That is, selective energy supply for an energy-efficient methanol synthesis process.

Energy Harvesting & Storage Room Lehua - Session EH-TuM

Surfaces & Interfaces for Solar Cells and Solar Fuels

Moderator: Charles Eddy Jr., US Naval Research Laboratory, USA

8:00am **EH-TuM1 Electrospun Photoelectrodes for Dye-Sensitised Solar Cells**, *J. Macdonald*, University College London, UK; *D. Tune*, KIT, Germany; *R. Dewi*, Zeiss, Australia; *T. Gibson*, *G. Shapter*, Flinders University, Australia; **Thomas Nann**, Victoria University of Wellington, New Zealand
The performance of dye-sensitised solar cells (DSSCs) depends to a large degree on the material and surface structure of the photoelectrodes (most commonly only the anode is a photoelectrode). Electrospun photoelectrodes offer a very high surface area and inter-connectivity, which should be ideal for this particular application. We will present a study on electrospun titania and nickel oxide photoelectrodes and their application in DSSCs.

Titania (TiO₂) photoanodes are by far the most studied system for DSSCs. We have shown that the performance of electrospun titania (anatase) fibre-photoelectrodes can be significantly increased by forming a single walled carbon nanotube (SWCNT) composite material [1]. Figure 1 shows scanning electron micrographs (SEMs) of a typical photoanode of this type.

Photocathodes are much less efficient compared with anodes and are replaced by platinum group metal catalysts frequently. We have studied photocathodes that are based on nickel oxide (NiO). The base semiconductors have been 'sensitised' with quantum dots and organic fluorophores. The morphology and nanostructure of the materials have been varied and finally, electrocatalysts have been added. It was found that sensitising can improve the performance of some *p*-type photocathodes significantly, but even the best performing photocathodes did not compare with equivalent TiO₂ photoanodes.

References

[1] T. J. Macdonald, D. D. Tune, M. R. Dewi, C. T. Gibson, J. G. Shapter, T. Nann, *ChemSusChem* **2015**, *8*, 3396–3400.

8:20am **EH-TuM2 Combinatorial in-situ Photoelectron Spectroscopy Investigation of Sb₂Se₃/ZnS Heterointerfaces**, **Sebastian Siol**, *P. Schulz*, *M. Young*, *K. Borup*, *G. Teeter*, *A. Zakutayev*, NREL, USA

Energy band alignments at heterointerfaces play a crucial role in defining the functionality of semiconductor devices. The search for material systems with suitable electronic band alignments is one of the key challenges in developing novel photovoltaic technologies. Particularly the tuning of band offsets has enabled significant advances in efficiency for several state of the art thin film solar cell technologies. While the theoretical prediction of band alignments at semiconductor heterointerfaces is often very limited, interface experiments utilizing X-ray photoelectron spectroscopy (XPS) measurements can be employed to track the evolution of the electronic structure at the interface. In particular the V-IV binary chalcogenide Sb₂Se₃ has been identified as a prospective absorber material for the next generation of thin film solar cells [1], yet the understanding of interfacing this compound semiconductor to commonly employed buffer layers such as ZnS is still in its very infancy.

In recent years high throughput, combinatorial materials science methodology has gained tremendous interest [2]. In this work we demonstrate how combinatorial techniques can be utilized to increase the throughput of *in-situ* experiments to investigate the interface formation for respective semiconductor heterojunctions. Thin films are grown with intentional thickness gradients on the substrate, to minimize the required number of depositions and transfers. In addition, other deposition parameters such as the deposition temperature or composition can be systematically co-varied with thickness to cover several individual interface experiments on one substrate.

Using orthogonal thickness and temperature gradients a combinatorial *in-situ* interface experiment was set up, that provided a comprehensive dataset for the extensive investigation of the band alignment at the prototypical Sb₂Se₃/ZnS heterojunction. Our findings point to a large conduction band offset of $\Delta E_{CB} = 1.75 \pm 0.05$ eV along with a potentially detrimental interfacial reaction at the junction. With this result, the study reveals why the choice of a ZnS buffer layer would limit device parameters and gives initial guidelines for alternative buffer layer materials with smaller electron affinities.

The method presented in this contribution can easily be applied for other material systems and will enable other researchers to quickly acquire comprehensive data for a more accurate picture of electronic processes across potential device interfaces.

[1] Y. Zhou et al. *Nat. Photonics* **2015**, *9*, 409.

[2] M. L. Green et al. *J. Appl. Phys.* **2013**, *113*, 231101.

8:40am **EH-TuM3 High Performance Transparent Electrode Based on Silver Nanowires with Plasma Treatment for Flexible Solar Cell Applications**, **Sunghoon Jung**, *W. Ahn*, *D.G. Kim*, Korea Institute of Materials Science, Republic of Korea

The random networks of silver nanowires (AgNWs) have been noticed as next generation transparent electrode which satisfies the high conductivity, transmittance and flexibility at the same time. Thus, AgNWs have a great potential for replacement of indium-tin-oxide (ITO) transparent electrode which have been used most widely. Although the nature of the superb self-electrical, optical and mechanical properties, some disadvantages of the transparent electrode such as chemical, environmental stability and contact resistance are bottle-necks for practical applications.

A simple approach to improve the stability of AgNW electrode is to form low-reactive materials such as graphene, graphene oxide and alumina on the top of AgNWs as passivation layers. Chemical and environmental stability is increased and electrical resistance is decreased. However, there are some negative aspects which are losses of transmittance, increasing vertical electrical resistance and upper layer and unisotropic chemical etching.

In this study, plasma techniques are applied to augment the electrical and environmental properties of AgNWs transparent electrode. The electrical resistance is decreased and environmental stability is improved. Moreover, AgNWs with plasma treatment showed much improved thermal stability compared to untreated AgNWs. We applied the plasma treated AgNWs to flexible organic photovoltaic devices as transparent electrode, and its power conversion efficiency is similar to organic photovoltaics based on ITO/Glass.

9:00am **EH-TuM4 Visible Light Responsive Photocatalysts toward Solar Hydrogen Production**, **Ryu Abe**, Kyoto University, Japan **INVITED**

Water splitting into H₂ and O₂ using semiconductor photocatalysts has received much attention recently due to the potential for the clean production of H₂ from water utilizing solar energy [1]. Because almost half of all incident solar energy at the Earth's surface falls in the visible region, the efficient utilization of visible light remains indispensable for realizing practical H₂ production. We have developed a new type of photocatalytic water splitting system, mimicking the mechanism of photosynthesis in green plants [2-6]. In this system, the water splitting reaction is broken up into two stages: one for H₂ evolution and the other for O₂ evolution; these are combined by using a shuttle redox couple (Red/Ox) in the solution. Over a H₂ evolution photocatalyst, the photoexcited electrons reduce water to H₂ and holes oxidize a reductant (Red) to an oxidant (Ox). The Ox is reduced back to the Red by photoexcited electrons generated over an O₂ evolution photocatalyst, where the holes oxidize water to O₂. This system reduces the energy required to drive each photocatalysis process, allowing visible light to be utilized more efficiently than in conventional system. We have achieved water splitting using various visible light responsive photocatalysts, such as SrTiO₃ doped with Cr [3], tantalum oxynitrides (TaON or BaTaO₂N) [4], and organic dyes [5], which work as a H₂ evolution photocatalyst, combined with tungsten oxide (WO₃) for O₂ evolution in the presence of a shuttle redox mediator such as iodate/iodide. Some oxyhalides such as Bi₄NbO₈Cl have also been proven as stable and efficient O₂-evolving photocatalysts under visible light, enabling a Z-scheme overall water splitting with iron redox [6]. We have also demonstrated that the porous photoanodes of tantalum oxynitrides can stably oxidize water with significantly high quantum efficiency, after loading of IrO₂ or CoO_x nanoparticles as a cocatalyst; enabling water splitting under visible light with a relatively small applied bias [7].

References

[1] J. Photochem. Photobiol. C: Photochem. Rev. **11** (2011) 179.

[2] Bull. Chem. Soc. Jpn. **84** (2011) 1000.

[3] J. Phys. Chem. B **109** (2005) 16052.

[4] a) Chem. Commun. (2005) 3829; b) Chem. Mater. **21** (2009) 1543; b) J. Am. Chem. Soc. **132** (2010) 5858; c) ChemSusChem **4** (2011) 228.

[5] J. Am. Chem. Soc. **135** (2013) 16872.

[6] J. Am. Chem. Soc. 38 (2016) 2082.

[7] a) J. Am. Chem. Soc., 132 (2010) 11828; b) Energy Environ. Sci. 4 (2011) 4138; c) J. Am. Chem. Soc. 134 (2012) 6968; d) J. Am. Chem. Soc. 135 (2013) 10238.

9:40am EH-TuM6 *In Situ* Growth and Degradation Mechanisms in Methylammonium Lead Halide Perovskites for Graphene-Based Solar Cells, *Muge Acik, S.B. Darling*, Argonne National Laboratory, USA

High power conversion efficiency of perovskite-based solar cells offers promise for low-cost and scalable production of renewable energy. The need to harness solar energy has recently motivated the search to alternate ETL/HTL hybrid materials, specifically graphene/perovskite films. Hybrid organic-inorganic methylammonium lead halides, MAPbX₃ (X=I, Br, Cl)/mixed-halides (I_{3-x}Cl_x, I_{3-x}Br_x) have been reported as light harvesting layers with their superior optoelectronic properties: tunable bandgap, long electron-hole diffusion lengths and high electron/hole mobility. Nevertheless, halide-based perovskites require *in situ* investigation for film growth, degradation and perovskite formation mechanisms to overcome detrimental effects of incomplete lead precursor conversion, inconsistent crystallite formation/film uniformity, and weak cation-anion-solvent coordination. Graphene-derived hybrids have recently emerged as an ETL/HTL replacement in these devices, however understanding the origin of interfacial chemical reactions between deposited perovskite films over graphene-derived materials is still lacking, especially at the ETL/perovskite/HTL interfaces. Moreover, effect of film thickness, stoichiometry control, overlayer/ underlayer morphology/composition, stability issues and cation-anion electrostatic interactions ought to be examined for better charge transport. To address scalability and stability issues, we examined degradation, nucleation and growth mechanisms in reduced graphene/graphite oxide (RGO) upon halide-based (I, Cl, Br) perovskite deposition. Chemical interactions were interpreted at perovskite/RGO interfaces for the grain size, orientation, boundaries, and surface/bulk effects using variable-temperature ($\leq 600^\circ\text{C}$, Ar(g)) *in situ* spectroscopy (infrared absorption, micro-Raman, UV-vis-NIR, luminescence) and SEM, XRD, XPS, TEM, and AFM for morphology characterization. Controlled perovskite formation was achieved at room temperature for bromide/chloride-based perovskites resulting in improved chemical stability with heat (vs. iodide derivative). Overall, perovskite decomposition and oxygen-induced chemical reactions occurred at $\leq 150^\circ\text{C}$, eliminated hydroxyls/carboxyls in RGO, and maintained ethers/epoxides upon perovskite decomposition. Poor perovskite formation was observed on RGO due to varying electron affinity and reactivity of precursor halides, resulting in film degradation in air (O₂, H₂O). References: (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 Materials (2010) 9 (10), 840-845.

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10:20am EH-TuM8 Back Contact Passivation via Atomic Layer Deposition for Increased Device Performance of Earth-Abundant Cu₂ZnSn(S,Se)₄ Solar Cells, *Priscilla Antunez, D.B. Farmer, D.M. Bishop, R.A. Haight*, IBM T.J. Watson Research Center, USA

Thin film solar cell absorbers composed of earth-abundant elements such as Cu₂ZnSn(S,Se)₄ (CZTSSe) are particularly attractive due to their relative low toxicity and their record maximum power conversion efficiency of 12.6% using an antireflective coating. Despite rapid progress, further improvements in efficiency are needed to enable the commercial-scale implementation of CZTSSe as a solar cell absorber. Our recent efforts have identified the deleterious impact of recombination at the interface between the CZTSSe absorber and the molybdenum back contact, which results in decreased lifetime, compared to the bulk, and a reduced open circuit voltage (V_{oc}), compared to theoretical expectations. To address this limitation, we have employed two approaches designed to increase device

performance. The first approach involves the deposition of Al₂O₃, via ALD, onto the Mo/glass substrate prior to the CZTSSe growth. In the second approach, the CZTSSe device is exfoliated to expose the back surface of the absorber, and a thin Al₂O₃ layer is then deposited to passivate the back of the solar cell. The passivating ALD step is then followed by the deposition of a high work function back contact. The high work function material further reduces recombination by imposing an electrostatic field, which drives the separation of electrons and holes to increase device performance. These effects are supported by device simulations and confirmed with experimental results that show an increase in several performance parameters, like V_{oc} and J_{sc}, when high work function back contacts are employed in conjunction with careful control of absorber thickness. With this approach, along with the inclusion of the Al₂O₃ passivating layer designed to inhibit recombination, efficiencies as high as 11.6% have been achieved without the use of an antireflective coating.

10:40am EH-TuM9 Nanoscale Imaging of Charge Carrier Transport in Monoclinic Bismuth Vanadate Photoanodes Via Atomic Force Microscopy, *Johanna Eichhorn, J.K. Cooper, L.H. Hess*, Lawrence Berkeley Lab, USA; *D. Ziegler*, Scuba Probe Technologies LLC, USA; *D.M. Larson, M.K. Gilles, I.D. Sharp, F.M. Toma*, Lawrence Berkeley Lab, USA

Photoelectrochemical water splitting is a promising route for efficient conversion of solar energy to chemical fuel. Among different photoelectrode materials, bismuth vanadate (BiVO₄) is one of the most actively investigated oxide semiconductors due to its moderate bandgap, favorable conduction band position, and relatively long photocarrier lifetimes.[1] However, under relevant operating conditions, pristine BiVO₄ thin films are subjected to degradation at the exposed surface facets. The degradation process in solution is accelerated by photoexcitation, which causes trapping of photogenerated holes at localized surface sites.[2] Therefore, developing approaches to stabilize these efficient semiconductor nanostructures requires a detailed understanding and control of charge separation, transport, and recombination mechanisms at their relevant length scales.

Here, we use photoconductive atomic force microscopy in combination with Kelvin probe force microscopy to correlate local surface morphology with generated photocurrent and contact potential difference maps at individual grain facets in polycrystalline BiVO₄ films. Furthermore, we employ scanning transmission X-ray microscopy to trace the changes in local chemical structure and composition in pristine and photodegraded BiVO₄.

The photocurrent and contact potential difference maps reveal the impact of different working conditions, such as bias voltage, excitation energy or excitation power, on the local charge carrier dynamics. Both for excitation above the bandgap (405 nm) and sub-bandgap illumination (532 nm), the photocurrent maps resolve the contributions from individual grains with nanometer spatial resolution. The photoelectrochemical performance of BiVO₄ can be significantly enhanced by varying the oxygen vacancy defects and hydrogen impurities, through hydrogen annealing. Therefore, we compare the photocurrent generation of pristine and hydrogen annealed BiVO₄. This careful analysis allows us to identify locally the charge transfer and loss mechanisms in these materials which ultimately contribute to desired photocurrent generation or undesired photocorrosion.[3]

[1] J. K. Cooper et al., The role of hydrogen in defining the n-type character of BiVO₄ photoanodes, *Chem. Mater.* **2016**.

[2] F. M. Toma et al., Mechanistic insights into chemical and photochemical transformations of bismuth vanadate photoanodes, *Nat. Commun.* **2016**.

[3] J. Eichhorn et al., Nanoscale photocurrent imaging of monoclinic BiVO₄ films via atomic force microscopy, **2016** (in preparation).

11:00am EH-TuM10 Energy Level Alignment at Interfaces in Hybrid Lead Halide Perovskite Photovoltaics, *Philip Schulz, A.A. Dameron, P.F. Ndione, M. Yang, K. Zhu, J.J. Berry*, NREL, USA

Hybrid organic/inorganic perovskites define an emerging class of solar cell absorber materials which advances to the lead in maximum power conversion efficiencies in the area of thin-film solar cells.¹ In the photovoltaic device the electronic interaction between the perovskite absorber and adjacent charge extraction and transport layers is key to maximize cell functionality. We identified that device characteristics such as the open circuit voltage can be affected by the alignment of the electronic energy levels of an organic charge extraction layer with the electronic transport levels in the perovskite film.² Furthermore, we found that the doping characteristic of the underlying oxide substrate can be used to rigidly tailor the Fermi level position in a subsequently deposited

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perovskite film. For future applications such as the integration of a perovskite subcell into a tandem device, precise control over the electronic alignment processes is required.³

Here we present our recent findings in which we examine a selection of incrementally deposited oxide charge carrier transport layers on top of methylammonium and formamidinium lead iodide perovskite films. Functional *n*-type (e.g. TiO₂, MoO_x), *p*-type (e.g. NiO) and intrinsic oxides (e.g. Al₂O₃) are grown by pulsed laser and atomic layer deposition techniques on top of the perovskite absorber layer. We then use ultraviolet and X-ray photoemission spectroscopy (UPS/XPS) to determine the electronic energy level alignment at the oxide/perovskite interface while at the same time tracking changes in the interface chemistry. Using this approach we are able to explain band offset changes induced in the perovskite layer by chemical interactions with the oxide on top, changes in the electrostatic potential and the formation of defective surface layers. The results are not only used to give guidelines about how to embed oxide layers into perovskite photovoltaic devices but also inform to what extent the electronic structure of the perovskite is subject to extrinsic perturbations on a more universal scale.

[1] K. Emery, Best research-cell efficiencies. http://www.nrel.gov/ncpv/images/efficiency_chart.jpg, Ed. NREL: 2016

[2] P. Schulz, E. Edri, S. Kirmayer, G. Hodes, D. Cahen, A. Kahn, *Energy Environ. Sci.* **2014**, *7*, 1377

[3] P. Schulz, L. L. Whittaker-Brooks, B. A. MacLeod, D. C. Olson, Y.-L. Loo, A. Kahn, *Adv. Mater. Interfaces* **2015**, *2*, 1400532

11:20am **EH-TuM11 Facet-dependent Photovoltaic Efficiency Variations in Single Grains of Hybrid Halide Perovskite**, *Alexander Weber-Bargioni*, Lawrence Berkeley National Laboratory, USA

Photovoltaic devices based on hybrid perovskite materials have exceeded 22% efficiency due to high charge carrier mobilities and lifetimes. Properties such as photocurrent generation and open circuit voltage are influenced by the microscopic structure and orientation of the perovskite crystals, but are difficult to quantify on the intra-grain length scale and are often treated as homogenous within the active layer. Here, we map the topography, local short circuit photocurrent, open circuit photovoltage, and local powerconversion efficiency in state-of-the-art methylammonium lead iodide perovskite solar cells using photoconductive atomic force microscopy. We find, within individual grains, spatially-correlated heterogeneity in short circuit current and open circuit voltage up to 0.6 V. These variations are related to different crystal facet surfaces and have a direct impact on the macroscopic power conversion efficiency. We attribute this heterogeneity to a facet-dependent density of trap states at the surface [1]. These results imply that controlling crystal grain and facet orientation will enable a systematic optimization of polycrystalline and single crystal devices for photovoltaic and lighting applications.

[1] *Nature Energy* **1**, Article number: 16093 (2016)

11:40am **EH-TuM12 Atomic Scale Understanding of the CdS/Cu(In,Ga)Se₂ Interface in Alkali-incorporated Solar Cells**, *Mowafak Al-Jassim*, NREL, USA

Polycrystalline thin film technologies are rapidly evolving to be an important part of the solar energy portfolio and currently have about 10% of the photovoltaics market share. Cell efficiencies exceeding 22% have been reported for CIGS, which makes thin film solar cells competitive with wafer Si cells. However, this is still considerably lower than the theoretical efficiency limit. In this work we investigate carrier loss mechanisms in CIGS thin films associated with grain boundaries and interfaces. We combined scanning electron microscopy (SEM)-based cryogenic cathodoluminescence (CL) spectrum imaging and electron backscatter diffraction (EBSD) in order to map the spatial distribution of various atomic-level defects as a function of deposition and film processing. These investigations were complemented with atom probe tomography and high resolution STEM-EELS to study the chemical nature of the defects. In addition to investigating the structural and chemical properties of grain boundaries and interfaces in CIGS cells, considerable emphasis was placed on understanding the role of alkali post-deposition treatment in improving cell efficiency. These results will be presented and discussed.

Energy Harvesting & Storage Room Lehua - Session EH-TuE

Battery/Supercapacitor Coatings, egs., Li⁺ Batteries & Thermo-/Piezo-electrics

Moderator: Takuya Masuda, NIMS (National Institute for Materials Science), Japan

6:00pm EH-TuE2 Electrochemistry at Well-defined Interfaces in Organic Environments, *Nenad Markovic*, Argonne National Laboratory, USA

In recent years, improvements in the fundamental understanding of electrochemical interfaces and their role in electrocatalytic processes have started to revolutionize the development of alternative energy systems for clean energy production, storage and conversion. In many respects the subject of surface electrochemistry in aqueous environments is more advanced than the corresponding understanding of interfaces in organic solvents. This is due to a long-standing difficulty associated with developing in-situ methods that are capable of characterizing interfaces at atomic-/molecular levels in organic solvents. This intrinsic disparity in understanding, however, has a tendency to mask the inherently close ties that exist between interfacial phenomena in aqueous and organic environments [1]. In this presentation, by building a bridge between these two artificially differentiated types of interfaces will allow for us to define the landscape of parameters that control the coupled roles of surface structure, chemical identity, electrostatic field, solvation and other related factors that determine the functional links between activity, selectivity and stability of any electrochemical interface. Selected example will be discussed, ranging from oxygen electrochemistry to metal deposition of Mg all the way down to intercalation processes on well-defined single crystal oxide materials. We identify the profound impact of trace levels of H₂O (<3ppm) on the kinetics of Mg deposition as well Mg intercalation in a layered V₂O₅ compound. Two types of water has been found; a “bad water”, that via the formation of MgO and Mg(OH)₂ passive films inhibits Mg deposition as well as a “good water” that helps intercalation of Mg²⁺ into V₂O₅ structures [2]. We conclude that understanding the complexity of electrochemical interfaces would open new avenues for design and deployment of alternative storage systems.

References:

1. V.R. Stamenkovic, D. Strmcnik, P. Lopes, and N.M. Markovic, *Nature Materials* (2016), in press.
2. S. Tepavcevic, C. Johnson, N.M. Markovic and T. Rajh, *ACS Nano* 9 (2015) 8194.

6:20pm EH-TuE3 Coupling in-situ TEM and Ex-Situ Analysis to Understand Heterogeneous Sodiation of Antimony, *David Mitlin*, Clarkson University, USA

We employed an in-situ electrochemical cell in the transmission electron microscope (TEM) together with ex-situ time-of-flight, secondary-ion mass spectrometry (TOF-SIMS) depth profiling, and FIB - helium ion scanning microscope (HIM) imaging to detail the structural and compositional changes associated with Na/Na⁺ charging/discharging of 50 and 100 nm thin films of Sb. TOF-SIMS on a partially sodiated 100 nm Sb film gives a Na signal that progressively decreases towards the current collector, indicating that sodiation does not proceed uniformly. This heterogeneity will lead to local volumetric expansion gradients that would in turn serve as a major source of intrinsic stress in the microstructure. In-situ TEM shows time-dependent buckling and localized separation of the sodiated films from their TiN-Ge nanowire support, which is a mechanism of stress-relaxation. Localized horizontal fracture does not occur directly at the interface, but rather at a short distance away within the bulk of the Sb. HIM images of FIB cross-sections taken from sodiated half-cells, electrically disconnected and aged at room temperature, demonstrate non-uniform film swelling and the onset of analogous through-bulk separation. TOF-SIMS highlights time-dependent segregation of Na within the structure, both to the film-current collector interface and to the film surface where a solid electrolyte interphase (SEI) exists, agreeing with the electrochemical impedance results that show time-dependent increase of the films' charge transfer resistance. We propose that Na segregation serves as a secondary source of stress relief, which occurs over somewhat longer time scales.

6:40pm EH-TuE4 Polymer-based Piezoelectric Nanogenerators for Energy Harvesting Applications, *Sohini Kar-Narayan*, University of Cambridge, UK INVITED

Harvesting energy from ambient sources in our environment has generated tremendous interest as it offers a fundamental energy solution for ‘small power’ applications, including, but not limited to, ubiquitous wireless sensor nodes; portable, flexible and wearable electronics; biomedical implants and structural/environmental monitoring devices. Energy harvesting from ambient vibrations is particularly attractive as these are ever present and easily accessible, originating from sources such as moving parts of machines, fluid flow and even body movements. In this context, piezoelectric materials offer the simplest means of directly converting mechanical vibrations into electrical power and are well suited for microscale device applications, thus offering a means of superseding traditional power sources such as batteries that require constant replacing/recharging and that do not scale easily with size. In particular, nanoscale piezoelectric energy harvesters, or *nanogenerators*, are capable of converting small ambient vibrations into electrical energy, thus paving the way for the realisation of the next generation of self-powered devices. A recent review article from our group [1] highlighted the fact that nanogenerator research to date has mainly focused on traditional piezoelectric materials in the form of ceramics, but these are stiff and prone to mechanical failure. On the other hand, piezoelectric polymers [1-3], although less well studied, have several advantages over ceramics such as being flexible, robust, lightweight, easy and cheap to fabricate, lead free and bio compatible. However, they do suffer from inferior piezoelectric properties in comparison to ceramics. The field thus faces orthogonal difficulties associated with these two classes of materials. In this talk, I will discuss work from our group aimed at developing novel hybrid polymer-ceramic nanocomposites [2,4,5] combining the best of both materials, while developing scalable nanofabrication techniques for flexible, low-cost and highly efficient polymer-based nanogenerators and sensors.

[1] S. Crossley, R.A. Whiter & S. Kar-Narayan, *Materials Science and Technology* 30, 1613 (2014).

[2] R.A. Whiter, V. Narayan & S. Kar-Narayan, *Advanced Energy Materials* DOI: 10.1002/aenm.201400519 (2014)

[3] S. Crossley & S. Kar-Narayan, *Nanotechnology* 26, 344001 (2015).

[4] C. Ou, P. E. Sanchez-Jimenez, A. Datta, F. L. Boughey, R. A. Whiter, S.-L. Sahonta & S. Kar-Narayan, *ACS Applied Materials & Interfaces* DOI: 10.1021/acsami.6b04041 (2016)

[5] F. L. Boughey, T. Davies, A. Datta, R. A. Whiter, S.-L. Sahonta, S. Kar-Narayan, *Nanotechnology (Letters)* 27, 28LT02 (2016).

7:40pm EH-TuE7 High-Resolution Observation of Electronic Properties of a Cathode Material in a Li-ion Battery, *Ryuma Osaka*, Kansai University, Japan

Li-ion batteries are widely used in many portable electronic devices and are recognized to be energy storage devices for mass-produced electric vehicles. However, to improve of power density, durability and safety, it is crucial to optimize the structure of the electrode as well as exploring new materials because the kinetics of the electrode reaction depends on the structure of the composite electrode.

The main elements are positive electrodes, negative electrodes, separators, and electrolytes. The electrolyte is typically a nonaqueous mixture of organic carbonates containing complexes of Li ions, which are noncoordinating anion salts such as Li hexafluorophosphate (LiPF₆). The separator is, for example, monolayer polypropylene. The electrode materials hold the key to determine the performance of the batteries. They are generally intercalated lithium compounds. Depending on the materials, the voltages, capacities, and lifetimes of the batteries greatly change. Therefore, they have been actively investigated.

The cathode material is also an oxide such as lithium cobalt oxide (LiCoO₂). Concerning the cathode materials, some materials, Li₂MnO₃, Li_{1.2}Mn_{0.4}Fe_{0.4}O₂, LiNi_{0.3}Mn_{0.3}Co_{0.3}O₂, etc., have been proposed, developed, and investigated. Redox of the transition metal oxides or valence fluctuation of transition metals play important roles of charge neutral. Therefore, not only ionic conductivity but also electronic conductivity is important for battery operation. However, electric conductivity varies with valence fluctuation of the transition metals due to extraction or insertion of Li ions. We present results on a change in band structure of LiCoO₂ corresponding to the Li-ion concentrations, which were obtained via a scanning probe microscope.

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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-Hyung 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 CO₂ 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 LiCoO₂ 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 LiCoO₂ 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. LiCoO₂ 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 LiCoO₂ cathode and the graphite anode.

We observed volume changes in the LiCoO₂ cathode using SPM, and successfully imaged the distribution of the volume changes corresponding to the LiCoO₂ 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 LiCoO₂ Cathode in a Li-ion Battery, Yukiho Okuno, Kansai University, 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. LiCoO₂ 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 LiCoO₂ 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. LiCoO₂ 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 LiCoO₂ cathode and the graphite anode.

We observed volume changes in the LiCoO₂ 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 LiCoO₂ 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 Li_xPO_yN_z 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.

[1] Alexander C. Kozen, Alexander J. Pearce, Chuan-Fu Lin, Malachi Noked, Gary W. Rubloff, DOI: 10.1021/acs.chemmater.5b01654

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(H₂) as an alternative energy carrier. Because the H₂ has high energy density, pure emission and it is easy to be transported by using a pipeline. But H₂ doesn't exist on the earth as a fuel. For this reason, it must be generated. There are several ways of producing H₂ 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

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industrial field. High operating temperature improves the electrode kinetics and reduce the SOFC 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 SOFC 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 SOFC because of its high catalytic performance and stability at SOFC mode. In this study, We studied on the Double perovskite $\text{Pr}_{0.5}\text{Br}_{0.5}\text{MnO}_{3-\delta}$ (PBMO) as a fuel electrode material of SOFC. PBMO was infiltrated into the scaffold structure of the electrolyte, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{3-\delta}$ (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 Himpfel*, 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 C1s 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 ($>\text{C}=\text{O}$) and a hydroxyl group attached to π -bonded carbon ($=\text{C}-\text{OH}$). Both lead to low-lying π^* transitions similar to those observed at the C1s and O1s 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.

[1] D. Zhu et al., *Nature Materials* **12**, 836 (2013).

[2] F. J. Himpfel et al., *Phys. Rev. B* **20**, 624 (1979); J. Van der Weide et al., *Phys. Rev. B* **50**, 5803 (1994).

[3] I. Zegkinoglou et al., *J. Phys. Chem. C* **116**, 13877 (2012).

[4] P. S. Johnson et al., *J. Phys. Chem. C* **120**, 1366 (2016).

EH-WeP9 Improved Thermo-stability of $(\text{NH}_4)_2\text{SiF}_6$ Fluorescent Microparticles with the Phosphoric Acids, *Aoi Tokiwa*, Tokyo Denki University, Japan

Ammonium hexafluorosilicate ($(\text{NH}_4)_2\text{SiF}_6$) 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 $(\text{NH}_4)_2\text{SiF}_6$ 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 $(\text{NH}_4)_2\text{SiF}_6$ /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 thermo-stability is mainly due to the formation of Si-O bond with the stronger binding energy at the interface region between the $(\text{NH}_4)_2\text{SiF}_6$ 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 $(\text{NH}_4)_2\text{SiF}_6$ 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 $\text{ZnIn}_2\text{S}_4/\text{TiO}_2$ Heterojunction via Improved TiO_2/FTO Interface and $\text{Ni}(\text{OH})_2$ Cocatalyst, *M.A. Mahadiq, 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 $\text{Ni}(\text{OH})_2$ loaded CdS cased $\text{ZnIn}_2\text{S}_4/\text{TiO}_2$ heterostructured photoanode. TiO_2 nanorods grown hydrothermally on fluorine-doped tin oxide (FTO) and annealed at 500°C yielded an optimal photocurrent density of $\sim 988 \mu\text{A cm}^{-2}$ 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 $\text{ZnIn}_2\text{S}_4/\text{TiO}_2$. Additionally, the $\text{Ni}(\text{OH})_2$ cocatalyst functioned in hole trapping and improved the stability of the photoelectrode through timely consumption of the photogenerated charges, particularly the holes. The photoelectrochemical 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.

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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 $\geq 20\%$, 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 ($\leq 600^\circ\text{C}$) *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 ($\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{CH}_3\text{NH}_3\text{PbBr}_3$, $\text{CH}_3\text{NH}_3\text{PbCl}_3$) perovskite deposition, and performed spectroscopic analysis derived from the intensity and peak areas of perovskite vibrational modes of C-H ($\sim 2800\text{-}3200\text{ cm}^{-1}$) and N-H ($\sim 2000\text{-}2800\text{ cm}^{-1}$). 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 $\text{Cu}_2\text{ZnSnS}_4$ (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 $\text{Cu}_2\text{ZnSnS}_4$ (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°C for 1 hour under the mixture gases of $\text{N}_2 + \text{H}_2\text{S}$ (5%). ZnS was intentionally adopted to provide more sulfur 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 ($1.60 \times 10^{20}\text{ cm}^{-3}$) and hall mobility ($9.8\text{ cm}^2/\text{V}\cdot\text{sec}$), 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 methylammonium 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.

[1] P. Schulz, Anne-Marie Dowgiallo, Mengjin Yang, Kai Zhu, Jeffrey L. Blackburn, Joseph J. Berry. *J. Phys. Chem. Lett.* **2016**, 7, 418–425

[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

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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 $\text{Al}/\text{ZnO}/\text{In}_2\text{S}_3/\text{Cu}_2\text{ZnSnS}_4/\text{Mo}/\text{SiO}_2$ 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 $\text{In}_2\text{S}_3/\text{Cu}_2\text{ZnSnS}_4$ photovoltaic devices is on par with $\text{CdS}/\text{Cu}_2\text{ZnSnS}_4$ 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.

[1] S. Siol et al. *ACS Appl. Mater. Interfaces* **2016**, *8*, 14004.

EH-WeP16 Higher Voltage Li-rich Cathode Materials for Lithium-ion Battery Applications, *Chandrasekar M Subramaniam, 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 safety¹⁻⁴. 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-layered⁴⁻⁷ 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.

1. J.-M. Tarascon, M. Armand, *Nature* **414** 359 (2001)
2. B. Dunn, H. Kamath, J.-M. Tarascon, *Science* **334** 928 (2011)
3. J.B. Goodenough, Y. Kim, *Chem. Mater.* **22** 587 (2010)
4. Eun-Sung Lee, Ashfia Huq, Arumugam Manthiram, *J. Power Sources* **240** 193 (2013)
5. K. Amine, H. Tukamoto, H. Yasuda, Y. Fujita, *J. Electrochem. Soc.* **143**1607 (1996)
6. Q. Zhong, A. Bonakdarpour, M. Zhang, Y. Gao, J.R. Dahn, *J. Electrochem. Soc.* **144** 205 (1997)
7. D. Luo, Guangshe Li, C. Fu, Jing Zheng, J. Fan, Qi Li, Liping Li, *Adv. Energy Mater.* (1400062) **8** (2014)

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 studied as an electrode material for supercapacitors due to its large specific surface area, high electrical conductivity and excellent chemical/mechanical stability. 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 developed 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

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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.

Energy Harvesting & Storage

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Surfaces & Interfaces for Efficient Power Conversion

Moderator: Junji Nakamura, Tsukuba University, Japan

5:40pm EH-WeE1 Influence of Annealing Treatment on Optical, Electric and Thermoelectric Properties of MBE Grown ZnO, *Khalid Mahmood*, Government College University Faisalabad, Pakistan

In this paper, we have reported the influence of annealing temperature and annealing environment on optical, electrical and thermoelectric properties of MBE grown ZnO thin films on Si substrate. A set of grown ZnO thin films was annealed in oxygen environment at 500°C – 800°C with a step of 100°C and another set was annealed in different environments (vacuum, oxygen, zinc and successively annealed vacuum and zinc) for one hour in a programmable furnace. Room temperature Seebeck measurements showed that Seebeck coefficient and power factor increased from 222 to 510 $\mu\text{V/K}$ and 8.8×10^{-6} to 2.6×10^{-4} $\text{Wm}^{-1}\text{K}^{-2}$ as annealing temperature increased from 500 to 800 °C respectively. This observation was related with the improvement of crystal structure of grown films with annealing temperature. X-ray diffraction (XRD) results demonstrated that full width half maximum (FWHM) of ZnO (002) plane decreased and crystalline size increased as the annealing temperature increased. Photoluminescence study revealed that the intensity of band edge emission increased and defect emission decreased as annealing temperature increased because the density of oxygen vacancy related donor defects decreased with annealing temperature. This argument was further justified by the Hall measurements which showed a decreasing trend of carrier concentration with annealing temperature

6:00pm EH-WeE2 Hard X-ray Photoelectron Spectroscopy: Applications To Energy Materials, *Jeff Terry*, Illinois Institute of Technology

We have recently commissioned a new Hard X-ray Photoelectron Spectroscopy (HAXPES) system on the undulator beamline at the Materials Research Collaborative Access Team (MRCAT). This system was built to study materials of interest in energy storage and generation. There are a number of problems where knowledge of the electronic structure of materials is of great interest. Specific, how is the electronic structure modified due to chemistry, irradiation, structural change, disorder, etc. The MRCAT HAXPES system is designed to operate with photon energies between 6 keV and 12 keV. This will allow us to study the electronic structure of these materials as a function of depth. Our initial measurements have been on thin films utilized in lithium ion batteries and in claddings used in nuclear reactor fuels. We will discuss these results and describe other experiments that can be conducted at the new HAXPES facility.

6:20pm EH-WeE3 Bridging the Gap between Model Catalyst Systems and Industrial Type Fuel Cell Catalysts, *Matthias Arenz*, University of Bern, Switzerland

INVITED

An overview of our work is given which aims at characterizing and developing catalysts for proton exchange membrane fuel cells (PEMFCs). We investigate both model systems as well as applied catalysts, i.e. high surface area catalysts that can be used in industry or industrial samples. In our work, we focus on determining their activity for key electrochemical reactions as well as their electrochemical stability. The measurements are performed in electrochemical half-cells, which allows us to focus on a single electrode under relatively defined conditions as compared to measurements of membrane electrode assemblies (MEAs). Thereby we try to establish general trends and to reveal mechanistic information.

We argue that in many investigations there is still a large gap between the insight gained on model systems and its utilization in applied catalysts. To meet this goal, we strive to improve experimental methods and procedures for characterizing catalyst performance. We introduced for example the method IL-TEM to follow catalyst corrosion in more detail. More recently we started to develop a synthesis platform that allows systematic investigations of industrial type catalysts. We coined this a colloidal toolbox approach. In this presentation we discuss the benefits and limits of our approach to combine basic and applied research.

7:00pm EH-WeE5 First-Principles Study on Influence of Metal Oxide on Poisoning Tolerance of Pt Nano-Particle Catalyst in Polymer Electrolyte Fuel Cell, *Tsuyoshi Kaji*, Y. Ootani, T. Nishimatsu, Y. Higuchi, N. Ozawa, M. Kubo, Tohoku University, Japan

Platinum (Pt) catalyst is used in an anode of polymer electrolyte fuel cell. It is reported that carbon monoxide (CO) in the fuel adsorbs on an active site

of Pt catalyst and degrades the catalytic activity. Thus, a development of a CO tolerant catalyst is required. Some experiments show that an addition of metal oxide nano-particles improves the CO tolerance of the Pt-based catalyst[1]. This result may be due to a decrease in an adsorption energy of CO on the Pt-based catalyst, but the detail mechanism is under consideration. In order to develop a higher CO tolerant catalyst, it is necessary to reveal an effect of the metal oxide nano-particle on the CO tolerance. In this work, we calculated an adsorption energy of a CO molecule on a Pt₄ cluster on an anatase TiO₂(101) surface with first-principles calculation to investigate the effect of the metal oxide on the CO tolerance of the Pt catalyst.

First, we placed the Pt₄ cluster on the anatase TiO₂(101) surface with several configuration, and decided the stable configuration. The Pt₄ cluster had a tetragonal structure. Three Pt atoms adsorbed on two-coordinated O atoms on the TiO₂(101) surface. Then, we calculated the adsorption energy of the CO molecule on each adsorption sites of the Pt₄ cluster. The adsorption energies are defined by the difference of a total energy between the adsorption structure and dissociation structure. The largest adsorption energy of -49.31 kcal/mol was obtained for the on-top site on the Pt atom which is located on the undermost layer of the Pt₄ cluster. Whereas, the adsorption energy of the CO molecule on the on-top site of the isolated Pt₄ cluster is -68.66 kcal/mol. These results indicate that the adding of TiO₂ improves the CO tolerance of the Pt catalyst.

Next, we examined the effects of the doping elements on TiO₂. Since the doping modifies electronic structure of TiO₂, improvement of the CO tolerance of the Pt catalyst is expected. Thus, we substituted a F atom for the O atom or a Nb atom for the Ti atom of the TiO₂(101) surface. When we substituted the F atom and the Nb atom, the adsorption energies of the CO molecule on the Pt₄ cluster are -41.75 and -40.61 kcal/mol, respectively. These adsorption energies are lower than the adsorption energy on Pt₄ cluster on the undoped TiO₂(101) surface. Thus, we suggest that the substitution of F and Nb atoms improves the CO tolerance of the Pt cluster on the TiO₂ surface. At the conference, we discuss the reason why the doping of F and Nb atoms decrease the adsorption energy of a CO molecule on the Pt₄ cluster on the TiO₂(101) surface based on the density of states.

[1] T. Takeguchi et al., *Catal. Sci. Technol.*, **6**, 3214 (2016).

7:40pm EH-WeE7 In Situ Observation of Electrochemical Processes at Solid/Liquid Interfaces, *Takuya Masuda*, NIMS (National Institute for Materials Science), Japan

INVITED

In order to design highly efficient and durable materials for energy conversion devices such as fuel cells and batteries, it is important to understand the key electrochemical processes occurring at solid/liquid interfaces. We have utilized various x-ray techniques to investigate those interfacial processes under electrochemical potential control. In this talk, in situ XAFS studies on electron transfer reactions on electrocatalysts and development of an in situ electrochemical XPS apparatus for the solid/liquid interfaces will be presented.

The rate of oxygen reduction reaction (ORR) was significantly enhanced when cerium oxide (CeO_x) was utilized as a co-catalyst together with Pt catalyst. The promotion effect of CeO_x for ORR at Pt was investigated by in situ XAFS measurements of the Pt-CeO_x/C and a conventional Pt/C catalyst. Upon the incorporation of CeO_x into Pt, not only Ce⁴⁺ species corresponding to CeO₂ but also Ce³⁺ species were observed due to the formation of the Pt/CeO_x interface. After cleaning the Pt surface by oxidation/reduction cycles in an aqueous solution, Ce⁴⁺ species is preferentially eluted in the solution, so that 3–5 nm Pt nanoparticles coated with a few CeO_x layers were formed. At the Pt L₃ edge of the Pt/C, the white line intensity increased as the potential was made more positive than 1.0 V (vs. Ag/AgCl), showing the formation of Pt oxide because the white line intensity reflects the d-band vacancies. In contrast, for the Pt-CeO_x/C, the formation of Pt oxide was significantly suppressed by the CeO_x layer. This suggests that the intrinsic ORR activity of bare Pt was maintained at the Pt-CeO_x/C while the Pt surface is partly covered by insulating Pt oxide at the pure Pt/C. At the Ce L₃ edge of the Pt-CeO_x/C, a singlet peak due to the Ce³⁺ species formed at the Pt surface turned into a doublet peak characteristic to the CeO₂, suggesting that Ce³⁺ species was oxidized to Ce⁴⁺ species to inhibit the formation of Pt oxide.

XPS is a powerful technique to analyze the surface compositions and oxidation states. However, it is difficult to carry out *in situ* XPS analysis of electrode surfaces in contact with electrolyte solutions under electrochemical potential control because of requirement of vacuum. Recently, we constructed an *in situ* XPS apparatus, which is applicable to electrochemical processes at solid/liquid interfaces, using a micro-volume

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cell equipped with an ultrathin photoelectron window. Electrochemical growth of Si oxide in contact with water was observed as a first demonstration of the capability of this system and effect of potential and time on the thickness of Si and Si oxide layers was quantitatively determined.

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