

# Monday Evening, December 3, 2018

## Energy Harvesting & Storage

### Room Naupaka Salon 6-7 - Session EH-MoE

#### Process

**Moderator:** Paul Dastoor, University of Newcastle, Australia

5:40pm **EH-MoE1 Surface Engineered Smart Optical Nanostructures for Energy Saving and Thermal Control**, *Ludvik Martinu*, Montreal Ecole Polytechnique, Canada

**INVITED**

Optical coating (OC) applications represent a multibillion dollar market worldwide; they range from antireflective (AR) coatings found in most optical components and low emissivity windows in buildings and automobiles to narrowband optical interference filters used in telecommunications. As the range of applications of OCs continuously broadens and extremely attractive market opportunities arise, it is becoming increasingly important to develop new nanostructured thin film materials with specific multifunctional properties. Further progress in this fast evolving field is strongly stimulated by a simultaneous action of two forces: a) the “pulling force” represented by the economic, technological and societal needs, including sustainable development, and b) the “pushing force” related to the curiosity-driven nanotechnology combining new design concepts of materials and devices, fabrication processes and innovative characterization tools, where the only limitation frequently appears to be our imagination.

This presentation will describe a holistic approach to OCs based on a broad and in depth knowledge of the interplay between the design, material, process and performance with respect to specific applications and coating system durability. It will review the progress and future opportunities for the use of nanostructurally-controlled architectures, advanced deposition techniques including high power impulse magnetron sputtering (HiPIMS), atomic layer deposition (ALD), glancing angle deposition (GLAD) and tailored plasma- and ion-surface interactions, as well as complex systems implementing active (smart, tunable thermochromic and electrochromic) materials.

These trends will be illustrated by examples from the field of advanced glazings for energy saving using smart windows, and smart radiators with self-tuned emissivity for the thermal management in satellites

6:20pm **EH-MoE3 Carbon Capture by Metal Oxides: Unleashing the Potential of the (111) Facet**, *Ryan Richards*, Colorado School of Mines, USA; *S. Shulda*, National Renewable Energy Laboratory, USA; *G.A. Mutch*, Newcastle University; *J.A. Anderson*, *D. Vega-Maza*, University of Aberdeen  
Carbon capture, utilisation and storage is a portfolio of processes to combat climate change. The capacity of sorbents proposed for low temperature carbon capture is entirely limited to surface interaction, resulting in a race to produce ever increasing surface areas - exemplified by metal-organic frameworks.

Metal oxides have a diverse range of electronic and physical properties that make them useful for a variety of applications such as semiconductors in diodes, electro- and thermo-chromics, catalysis and Li ion batteries --to name a few. One of the simplest structures of metal oxides is the rock-salt structure that are face-centered cubic crystals with the metal ion surrounded by six nearest-neighbor oxygen ions and vice versa. Amongst the rock-salt metal oxides, MgO is the most widely studied and is the second most abundant compound in the Earth's crust at 35% (behind silica which is 42%).<sup>1</sup> Due to surface area reduction by sintering, solid metal oxides generally exhibit reduced adsorption capacity for carbon capture following high temperature exposure.

The preponderance of literature studies involving the properties of metal oxides has been conducted on the (100) surface because this surface is the most readily obtained and most thermodynamically stable form for most rock-salt metal oxides. The (100) surface is a checkerboard of alternating metal cations and oxygen anions. While most methods produce materials dominated by (100) surfaces, decomposition of metal hydroxides such as Mg(OH)<sub>2</sub> can initially yield materials with hydroxylated (111) surfaces via topotactic dehydration.<sup>1-3</sup> Following the development of techniques that allow for the deliberate preparation of materials with primarily (110) and (111) surfaces, came interest in potentially new properties of these surfaces.<sup>4,5</sup>

The (111) facet of MgO however, exhibits a high concentration of low coordinate sites.<sup>4,5</sup> In recent work, MgO(111) nanosheets displayed high capacity for CO<sub>2</sub>, as well as a  $\approx$  65% increase in capacity despite a  $\approx$  30% reduction in surface area following sintering (0.77 mmol g<sup>-1</sup>@ 227 m<sup>2</sup>g<sup>-1</sup> vs 1.28 mmol g<sup>-1</sup>@ 154 m<sup>2</sup>g<sup>-1</sup>).<sup>6</sup> These results, unique to MgO(111) suggest

intrinsic differences in the effects of sintering on basic site retention. Spectroscopic and computational investigations provided a new structure-activity insight; the importance of high temperature activation to unleash the capacity of the polar (111) facet of MgO. In summary, we present the first example of a faceted sorbent for carbon capture and challenge the assumption that sintering is necessarily a negative process; here we leverage high temperature conditions for facet-dependent surface activation.

6:40pm **EH-MoE4 Graphene Oxide-cellulose Nanocrystal Sponge as a Tunable Platform for Contaminant and Pathogen Removal from Water**, *Nathalie Tufenkji*, *N. Yousefi*, *R. Allgayer*, *A. Filina*, McGill University, Canada

Graphene oxide (GO) sponges are a new class of sorbents for removal of a diverse range of contaminants from water. The immobilization of GO in a solid porous macrostructure eliminates the requirement for removal of the otherwise stable colloidal GO from the treated water. Unlike colloidal GO, solid macrostructures can be easily stored, transported and manipulated. Although much progress has been made on forming high surface area and multifunctional GO sponges, synthesizing mechanically robust multifunctional sponges, especially in wet state, is a challenge. We report the preparation of an ultrastrong GO-based sponge strengthened with cellulose nanocrystal (CNCs) – natural nanorods isolated from wood pulp – using a green synthesis method with the aid of excess vitamin C (VC). VC acts as a natural reducing agent, whereas CNCs provide a scaffold that links the reduced GO (rGO) nanosheets together, resulting in an exceptionally stiff nanocomposite. During sponge synthesis, undissolved excess VC grains act as soft templates, yielding nanocomposites with hierarchical pore architecture, even in the core of large sponges as confirmed by micro and nano X-ray tomography. The use of ultra-large GO nanosheets, as well as the interconnected hierarchical pore structure translate into sponges with a high specific surface area and large removal capacity for a wide range of contaminants such as dyes, heavy metals, and pharmaceuticals. The GO-CNC sponges exhibit excellent contaminant removal from single and multicomponent waters, in batch and continuous removal modes. Additionally, we show that the sponges of this study can be readily functionalized with antimicrobial peptides and biopolymers to enhance removal and inactivation of bacteria from contaminated water supplies.

7:00pm **EH-MoE5 Surface Science Approach For Alumina Supported Hydrodesulphurisation Catalysts**, *Anne-Félicie Lamic-Humblot*, Sorbonne Université, France; *C. Bara*, Solvay; *R. Garcia de Castro*, Sorbonne Université, France; *E. Devers*, *G. Pirngruber*, *M. Digne*, IFPEN; *X. Carrier*, Sorbonne Université, France

Since 2009, the sulphur content need to be reduced to 10 ppm in gasoline. In order to achieve this goal, hydrodesulphurisation process is efficient for now, using sulfided molybdenum (doped or not by cobalt) deposited on alumina.

In order to optimize this process, a molecular-scale understanding of the adsorption of the active phase (metal ions) is of fundamental importance. However, this objective is difficult because of the high surface area developed by the support (g-alumina) and the large number of exposed sites. One way to simplify the system is to use oriented single crystals of alumina presenting a lower number of sorption sites and well defined surface sites. As single crystals of g-alumina do not exist, we use some of a-alumina commercial wafers in order to mimic the g-alumina exposed surfaces.

Ammonium heptamolybdate complexes were deposited on the surface using conventional aqueous routes (“equilibrium” adsorption and impregnation). The samples were then calcined and sulphided. The samples were characterised (XPS, AFM) after each thermal treatment.

The sulphurisation degree was determined with sulphurisation temperature, and a correlation between the exposed sites and molybdenum sulphide is discussed. GI-EXAFS allowed us to show that the exposed surface induce in some case a certain orientation of MoS<sub>2</sub>slabs on the surface.

Hence it is possible to conclude that the control of the industrial support morphology constitutes a way to tune the genesis of the hydrotreating catalysts sulfide phase.

7:40pm **EH-MoE7 Direct 3D Printing of Reactive Agitating Impellers for the Convenient Treatment of Various Pollutants in Water**, *Xueyan Sun*, Dalian University of Technology, China

Mass transfer plays a key role in the diffusion-controlled heterogeneous reactions. Varied efforts have been made to design the structure of

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catalysts and reactors to optimize the diffusion process. Herein, a facile strategy is reported to construct highly reactive agitating impeller (denoted as AI) by employing 3D printing and a facile surface activation treatment. On the one hand, experimental results and numerical simulation analysis reveal that the 3D printing AI with appropriate structure can not only effectively eliminate external diffusion but also conveniently be separated from heterogeneous reaction systems. On the other hand, surface activation helps to significantly promote the chemical reactivity of AI for Fenton and galvanic replacement reaction, which are used to treat organic and inorganic pollutants in water, respectively. Benefiting from these cooperative merits, the integrated catalytic AI delivers a catalytic performance toward Fenton reactions as high as a homogeneous catalyst, and the removal rate for heavy metal ions is nearly 100% through galvanic replacement. This 3D printing with surface engineering strategy should also be extended to other applications, and provide new field for preparing efficient and durable heterogeneous catalysts in a more economical way.

8:00pm **EH-MoE8 BN Films for Hydrogen Permeation Barrier, *Motonori Tamura***, The University of Electro-Communications (UEC-Tokyo), Tokyo, Japan

Cubic boron nitride (c-BN) has attracted much attention because of its outstanding physical and electrical properties. However, there are limited research data on hydrogen permeation of BN thin films that can be applied to

components of hydrogen fuel cells. Several techniques such as sputtering, laser ablation, ion-beam deposition, and plasma-enhanced chemical vapor deposition are used to synthesize c-BN films. To realize a stable c-BN structure and film stoichiometry, precise control of the plasma parameters is necessary. In this study, a magnetically enhanced plasma-ion-plating system was successfully designed and applied to produce stable c-BN films.

Hydrogen-permeation tests of BN-, SiC-, and TiN-coated Type 316L stainless steels were performed. A diffusion-limited permeation regime was confirmed on the coated samples at 573-773 K. The permeability depended on the test temperature, where high values of permeability data were obtained at high temperature. The hydrogen permeability data of SUS316L stainless steel in the temperature range of 573-773 K correlated well with results of a previous study. Our results indicate that the 1.5-micrometers-thick films of SiC, TiN, and BN were all effective in reducing the hydrogen permeability. In comparison with TiN and SiC coatings, the c-BN (cubic boron nitride) coating was most effective to reduce the rate of hydrogen permeation through stainless steel.

# Tuesday Afternoon Poster Sessions, December 4, 2018

## Energy Harvesting & Storage

### Room Naupaka Salon 1-3 - Session EH-TuP

#### Energy Harvesting and Storage Poster Session

Moderator: Satoshi Ishii, National Institute for Materials Science

**EH-TuP1 Oxygen Vacancies Boost  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> as High-Performance Electrode for Rechargeable Aqueous Batteries, TingTing Qin, W. Zhang,** State Key Laboratory of Automotive Simulation and Control, and School of Materials Science & Engineering, and Electron Microscopy Center, and International Center of Future Science, Jilin University, Changchun 130012, China

Metal oxides as electrode materials are of great potential for rechargeable aqueous batteries. However, they suffer from inferior cycle stability and rate capability because of poor electronic and ionic conductivities. Herein, taking vertically-orientated Bi<sub>2</sub>O<sub>3</sub> nanoflakes on Ti substrates as examples, we found that  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> electrode with plenty of intrinsic positively-charged oxygen defects have shown remarkably higher specific capacity (264 mAh g<sup>-1</sup>) and far superior rate capability than that of  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> with less oxygen vacancies. Through pinpointing the existence form and the role of oxygen vacancies within the electrochemical processes, we demonstrate that oxygen vacancies in  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> serve as central entrepots collecting OH<sup>-</sup> groups via electrostatic force effect, which has boosted the oxidation reaction and enhanced the electrochemical properties. Besides, oxygen vacancies can largely facilitate electronic conductivity. Our work merited an excellent Bi<sub>2</sub>O<sub>3</sub> negative electrode material via giving full play to the role of oxygen vacancies in electrochemical energy storage.

**EH-TuP3 Novel Cathode Nanomaterials and Electrolytes for Al-ion Batteries, Nicolò Canever,** Victoria University of Wellington, New Zealand; *N. Bertrand*, Ecole Nationale Supérieure de Chimie de Clermont-Ferrand, SIGMA Clermont, Aubière, France; *T. Nann*, Victoria University of Wellington, New Zealand

Battery-based energy storage could be a useful tool for transitioning to a fully renewable-based energy economy. Current battery technologies, however, often lack the cost-effectiveness [1] and safety [2] requirements necessary for large-scale grid energy storage applications. Aluminium-ion batteries (AIBs) are a very promising alternative to Lithium-based systems, thanks to the low cost, non-flammability, and three-electron redox chemistry of aluminium. [3] AIBs could, in principle, offer better cost-effectiveness, energy density [4] and safety, [5] than currently available energy storage technologies. This poster deals with the investigation of new electrode nanomaterials and electrolyte systems for Al-ion batteries, with the aim of improving the performance and cost-effectiveness of AIBs, and facilitate their commercial feasibility.

#### REFERENCES:

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**EH-TuP4 Study of Charge Transfer across C<sub>60</sub>/BCP and BCP/Ag Interfaces Using Core-Hole Clock Spectroscopy, Tetsuya Miyazawa,** SOKENDAI, Japan; *K. Ozawa*, Tokyo Institute of Technology, Japan; *K. Kanai*, Tokyo University of Science, Japan; *T. Sakurai*, Tsukuba University, Japan; *K. Mase*, KEK, Japan

Electronic properties at organic/metal and organic/organic interfaces affect the efficiencies of organic electronic devices such as organic solar cells, perovskite solar cells, and organic field effect transistors. Peuman *et al.* have found that the conversion efficiency of the organic solar cell is improved when bathocuproine (BCP) is inserted as buffer layer between the organic molecule of acceptor and negative electrode [P. Peuman *et al.*, *Appl. Phys. Lett.* 76, 2650 (2000)]. In order to reveal the role of buffer layers, we investigated C<sub>60</sub>/BCP and BCP/Ag layered systems by resonant photoelectron spectroscopy and X-ray absorption spectroscopy. A core-hole clock analysis was carried out to examine transfer times of an electron from C<sub>60</sub> to BCP and that from BCP to Ag. The sample was prepared by the procedure that monolayer of BCP was deposited on Ag thin film and then monolayer of C<sub>60</sub> was deposited on the BCP. The charge transfer times from

LUMO+1 of BCP to Ag and C<sub>60</sub> to BCP were calculated to be 2.5 fs and less than 60 fs, respectively. In the photoelectric conversion of organic solar cells, electrons generated by exciton separation transfer from organic molecule of acceptor to negative electrode. These results suggest that ultrafast charge transfers across C<sub>60</sub> to BCP and BCP to Ag are one of the role of buffer layers to improve conversion efficiency of organic solar cells.

**EH-TuP6 Structure and Optical Properties of HfO<sub>2</sub>-based Thermal Emitter Films for Thermophotovoltaic Energy Conversion Devices, Gregory Abadias, Y. Metayrek, A. Michel, J. Drevillon,** Institut Pprime, CNRS-Université de Poitiers, France

One of the key points for designing high-efficiency thermophotovoltaic (TPV) systems is to match the spectral emission of the radiator with the spectral range where photons are converted into electron-hole pairs inside the photovoltaic device. Recent studies have shown the potential offered by photonic crystals made of metal/dielectric stack of layers acting as Fabry-Pérot cavity, ensuring spectral selectivity to the emitter. Another material requirement is thermal stability in order to keep the same spectral emission at the operating temperature of the radiator. The Mo/HfO<sub>2</sub> system is a promising candidate material in this respect, as recently reported by Blandre *et al.* [1].

In this work we investigate the synthesis by magnetron sputtering of W/HfO<sub>2</sub> four-layer films for TPV applications. The individual layer thicknesses were optimized based on fluctuational electrodynamics calculations of thermal emissivity of one-dimensional layered media. Prior to the fabrication of the multilayer stack, the structure and optical properties of the transparent HfO<sub>2</sub> layer were investigated as a function of process parameters: substrate temperature  $T_s$  and O<sub>2</sub> flow rate.

Films were characterized by X-ray reflectivity, X-ray diffraction and wavelength dispersive spectroscopy. The optical indices ( $n$  and  $k$ ) were measured experimentally from variable angle spectroscopic ellipsometry in the visible and mid-infrared (MIR) range (up to 35  $\mu$ m). Results show that dense, crystalline HfO<sub>2</sub> layers with monoclinic structure can be formed by reactive magnetron sputtering at room temperature with optical index  $n$  close to 2.1 at 550 nm; however, crystallinity was improved by increasing  $T_s$  up to 500°C, with little variation on  $n$  and  $k$ . In the MIR, the optical properties of HfO<sub>2</sub> were consistent with the data reported by Bright *et al.* [2]. The optical reflectance of the W/HfO<sub>2</sub> stack was measured using spectrophotometer and a good agreement with theoretical predictions was found, attesting of the potential of this system for TPV emitters.

**EH-TuP7 Bimetallic Cobalt-Iron Hydroxide Encapsulated in Organic Ligand Derived Carbon Layers as an Efficient Electrocatalyst for Oxygen Evolution Reaction, Jian Du, F. Li,** Dalian University of Technology, China

Water electrolysis as one of the prospective approach to produce hydrogen is limited by the anodic oxygen evolution reaction (OER) due to its sluggish kinetics. Considering the practical application, the development of highly efficient non-noble OER catalysts is essential. Among the reported low-cost electrocatalysts, CoFe-based oxides or hydroxides are intriguing owing to the rich redox chemistry. However, the severe aggregation and intrinsically poor electronic conductivity hinder their electrocatalytic performance. Hybridizing cobalt-iron oxides or hydroxides with carbon materials can not only enhance the conductivity of the catalyst, but also facilitate the uniform distribution of metal species within carbon matrix, thus improving the electrochemical performance towards OER. In view of this, we report here the bimetallic cobalt-iron hydroxide encapsulated in carbon layers derived from organic ligand (Schiff base) via hydrothermal carbonization. In alkaline media, Co Fe/C loaded on GC electrode delivers a current density of 10 mA cm<sup>-2</sup> at an overpotential of 260 mV and exhibits a low Tafel slope of 45.2 mV dec<sup>-1</sup> as well as excellent durability. The remarkable OER performance outperforms those of CoFe-based electrocatalyst in the literature.

**Keywords:** Oxygen evolution reaction, cobalt-iron hydroxide, organic ligand, electrocatalyst

#### Results

As shown in Figure 1, the Co<sub>1.2</sub>Fe/C delivers a current density of 10 mA cm<sup>-2</sup> at an overpotential of 260 mV and exhibits a low Tafel slope of 45.2 mV dec<sup>-1</sup> as well as excellent durability in 1M KOH solution.

Figure 1 (a) LSV curves of GC, Co<sub>1.2</sub>Fe and Co<sub>1.2</sub>Fe/C; (b) Tafel plots of Co<sub>1.2</sub>Fe and Co<sub>1.2</sub>Fe/C; © Chronopotentiometric measurement of Co<sub>1.2</sub>Fe/C at 10 mA cm<sup>-2</sup>. All tests were carried out in 1 M KOH.

#### Conclusions

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The  $\text{Co}_{1.2}\text{Fe}/\text{C}$  exhibits excellent OER performance in alkaline media, which can be ascribed to the following factors: 1) the homogenous distribution of metal hydroxide within carbon matrix inhibits the aggregation of the active nanoparticles; 2) the excellent electronic conductivity enables fast electron transport during the OER process; 3) the synergetic effect between the  $\text{Co}_{1.2}\text{Fe}$  hydroxide and carbon species also contributes to the improvement of the electrochemical performance.

## Reference

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## **EH-TuP8 Anchoring Water Oxidation Catalysts on a DS-PEC via Pyridine Group for Light-Driven Water Splitting, Yong Zhu, F. Li, Dalian University of Technology, China; L. Sun, KTH Royal Institute of Technology, Sweden**

Dye-sensitized photoelectrochemical cell (DS-PEC) water splitting into hydrogen and oxygen is a potential approach to realize the conversion solar energy to chemical energy efficiently.  $\text{Ru}(\text{bda})$  (bda is 2,2'-bipyridine-6,6'-dicarboxylate) is one of the most efficient water oxidation catalysts in DS-PEC. Traditionally,  $\text{Ru}(\text{bda})$  have been anchored onto the dye-sensitized photoanode by modifying phosphoric acid or carboxylic acid groups. These complexes can reduce the overpotentials of water oxidation and exhibit highest turnover. However, the efficiency of the entire system is inhibited due to the strong recombination effect of electrons injected into the  $\text{TiO}_2$  bulk on the photosensitizer and catalyst in the oxidized state. Herein, we have replaced the anchor group of the water oxidation catalysts  $\text{Ru}(\text{bda})$  (bda is 2,2'-bipyridine-6,6'-dicarboxylate) from phosphoric acid to pyridine. Time-resolved transient absorption spectroscopy demonstrates that the pyridine anchor group have effect of inhibiting electron recombination. The photocurrent densities of 1.5-1.8  $\text{mA}/\text{cm}^2$  were achieved and produced an incident photon to current efficiency (IPCE) of 25.5% at 450 nm. Under  $\text{pH}=5.8$  under  $100\text{mW}/\text{cm}^2$  ( $>400\text{nm}$ ) illumination.

## **EH-TuP10 A steady-state thermoreflectance method to measure thermal conductivity, Jeffrey Braun, D. Olson, J. Gaskins, P. Hopkins, University of Virginia**

We demonstrate a steady-state thermoreflectance based optical pump-probe technique to measure the thermal conductivity of materials using a continuous wave laser heat source. The technique works in principle on leaving a pump laser on long enough to induce a steady-state temperature rise in a material. A probe beam is then used to detect the resulting change in reflectance, which is proportional to the change in temperature of the sample. Varying the power of the pump beam to induce larger temperature rises, Fourier's law is used to determine the thermal conductivity. We show that this technique is capable of measuring the thermal conductivity of a wide range of materials having thermal conductivities ranging from 1 to  $>2000\text{ W m}^{-1}\text{K}^{-1}$ , in excellent agreement to literature values. With a measurement length scale capable of reaching  $<10$  microns, this techniques is capable of measuring both bulk material and films.

## Energy Harvesting & Storage

### Room Naupaka Salon 5 - Session EH-WeM

#### Efficient Power Conversion/Cells

**Moderator:** Paul Braun, University of Illinois at Urbana-Champaign, USA

8:00am **EH-WeM1 Linear and Multi-photon Fluorescence of Thiophene based Copolymer as Novel Potential Material for Photovoltaics**, *L. Slusna*, Comenius University, Bratislava, Slovakia; *L. Haizer*, International Laser Center, Bratislava, Slovakia; *E. Jane*, Institute of Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia; *D. Bondarev*, Polymer Institute, Slovak Academy of Sciences, Bratislava, Slovakia; *V. Szocs*, *M. Drzik*, International Laser Center, Bratislava, Slovakia; *E. Nuskovicova*, Comenius University, Bratislava, Slovakia; *D. Lorenc*, International Laser Center, Bratislava, Slovakia; *M. Jerigova*, Comenius University, Bratislava, Slovakia; **Dusan Velic**, Comenius University, Bratislava, Slovakia

Currently, the most important applications for polythiophenes are in the area of solar cells, thin-film transistors, light-emitting diodes, sensors and nonlinear optics with low-cost and low-temperature processing [1]. On the other hand, polythiophenes show a great promise also in the area of nonlinear optics and photonics [2] with enhanced second and third order nonlinearities. Hence, dynamics of polythiophenes gained an increased interest, because it is providing detailed understanding of the complex processes occurring in  $\pi$ -conjugated polymers.

A novel copolymer (poly(thiophene-2,5-diyl-2,5-di-n-octyloxycarbonyl-1,4-phenylene)) denoted as P33 is introduced as a potential material for photovoltaics. P33 dissolved in chloroform was investigated by steady-state absorption, linear/non-linear fluorescence spectroscopies and time-resolved fluorescence spectroscopy.

Molar extinction coefficient of P33 was determined as  $18315 \text{ cm}^{-1} \cdot \text{M}^{-1}$ . The P33 fluorescence quantum yield and P33 singlet fluorescence lifetime were determined as 0.4 and 810 ps, respectively. The P33 fluorescence fast decay component shows decay times of 1.2 ps, 2.0 ps, and 0.5 ps for increasing wavelengths of 480 nm, 500 nm, and 520 nm, respectively. The fast component has been previously attributed to transport of nearly instantaneously formed excitons to localized states known as downhill energy transfer. Multi-photon excited fluorescence has been observed for the P33 solutions in chloroform and for 800 nm and 1200 nm pumping. The P33 TPA cross-section was evaluated as 6.9 GM. This spectroscopic study provides basic fluorescence characteristics of the novel thiophene copolymer P33.

This work was supported by VEGA 1/0400/16.

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8:20am **EH-WeM2 Novel Semi-Transparent Inorganic Sb<sub>2</sub>S<sub>3</sub> Thin Film Solar Cells**, *Shi-Joon Sung*, *S.-J. Lee*, *K.-J. Yang*, *J.-K. Kang*, *D.-H. Kim*, DGIST, Republic of Korea

In recent years, researches on transparent photovoltaics has been attracting immerse interests as a key component of multifunctional window applications. Until now, there were enormous researches on transparent photovoltaics were based on organic materials, such as dye sensitized solar cell (DSSC) or organic solar cell (OSC), because of wide bandgap of the organic materials. However, these organic-based transparent solar cells are still suffering from the stability problem, which is one of critical obstacles for the commercialization of organic-based solar cells. In order to overcome this problem, some researchers are nowadays interested in the inorganic-based transparent solar cell technologies, such as ultra-thin film solar cells, patterned aperture solar cells, and so on. However, in these cases, device fabrication process is complicated and the device performance is limited because of restricted physical dimensions.

Because inorganic Sb<sub>2</sub>S<sub>3</sub> has wide bandgap (1.6 ~ 1.8 eV) and higher absorption coefficient ( $10^5 \text{ cm}^{-1}$ ) compared with other inorganic materials, Sb<sub>2</sub>S<sub>3</sub> might be a good candidate for inorganic semi-transparent absorber materials. In our work, we adopted ultra-thin and high quality Sb<sub>2</sub>S<sub>3</sub> thin films as a semi-transparent absorber layer. The high quality Sb<sub>2</sub>S<sub>3</sub> thin films with different thickness were deposited using atomic layer deposition

(ALD) technique, which showed bandgap of 1.78 eV, absorption coefficient of  $1 \times 10^5 \text{ cm}^{-1}$ , and light transmittance up to 30 %. In order to fabricate semi-transparent solar cell devices, ALD Sb<sub>2</sub>S<sub>3</sub> thin film with 80 nm thick were firstly deposited on transparent TiO/ITO substrates. Transparent P3HT and ultra-thin transparent Au electrode were also deposited onto the ALD Sb<sub>2</sub>S<sub>3</sub> thin film. This semi-transparent Sb<sub>2</sub>S<sub>3</sub> solar cell device showed power conversion efficiency of 3.44% and average light transmittance (from 400 to 800 nm) of 13%. The semi-transparent Sb<sub>2</sub>S<sub>3</sub> solar cell device also showed excellent device stability over 180 days, which might be attributed to the inorganic Sb<sub>2</sub>S<sub>3</sub> absorber material. Semi-transparent inorganic thin film solar cells based on Sb<sub>2</sub>S<sub>3</sub> has a great potential to be a novel robust and stable transparent solar cell technology.

8:40am **EH-WeM3 In situ Scanning Tunneling Microscopy of the Electrocatalytic Reactions**, *Dong Wang*, ICCAS, China

The electrocatalytic reactions at the electrode/electrolyte interface play a critical role in the performance of electrochemical energy storage and conversion devices. Understanding the structure and reaction processes at solid/liquid interface is of great importance in surface science and electrochemistry. In view of the dynamic and complex nature of the interface, in situ research approaches can provide valuable information of interfacial phenomena. In situ scanning tunneling microscopy (STM) is a powerful technique used for the interfacial investigation of electrochemical energy devices.

In this presentation, we employed high resolution electrochemical STM to investigate the typical electrochemical catalytic reactions, such as oxygen reduction reactions, oxygen evolution reactions, using the model molecular catalysts. The self-assembled metal porphyrin and phthalocyanine compounds show notable electrocatalytic activity. The real-time STM imaging provides direct evidence to study the interfacial electrochemical reactions at molecular level.

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2. Cai, ZF; Wang, X; Wang, D; Wan, LJ. *ChemElectroChem*, 2016, 3, 2048-2051.

9:00am **EH-WeM4 Fabrication of Free-standing Thin Film by Injecting Polymer into Porous Substrate for Thin Film Solid Oxide Fuel Cells**, *Yusung Kim*, *S.W. Cha*, *W. Yu*, *W. Jeong*, *J.H. So*, Seoul National University, Republic of Korea

Free standing thin films were fabricated by injecting polymer into porous substrate for thin film solid oxide fuel cells (TF-SOFCs). To apply thin film on porous substrate with pores of more than 1 micrometer, anode functional layer (AFL) is needed to reduce pore size. However, it is difficult to supply gas when the AFL is thickened due to the reduced pore size and porosity. To solve this problem, free standing under 1 micrometer thin film AFL was fabricated on a porous support. Based on the Si-based free standing thin film soft, which is a field of TF-SOFCs, the pores of the porous NiO-YSZ support were blocked through injecting polystyrene, the NiO-YSZ thin film was deposited thereon, and the polystyrene was removed to make the free-standing thin film by pyrolysis. The pore blocking through the polymer was obviously a major influence on the thin film covering the pore. On the other hand, since the pore size of the support is about 10  $\mu\text{m}$ , the pore size is not reduced when the thin film is deposited without pore blocking. In the process of melting and solidifying into a liquid to insert the polymer, a nanoscale gap was created due to the volume change due to the phase change, and the thin film deposited thereon also has this shape. Also it is verified that the NiO-YSZ thin film was successfully fabricated on the porous NiO-YSZ substrate by FIB-SEM analysis.

9:20am **EH-WeM5 First-Principles Study on Influence of Metal Oxide on H<sub>2</sub>S Poisoning Tolerance of Pt Nano-Particle Catalyst in Polymer Electrolyte Fuel Cell**, *Kota Kuranari*, *N. Miyazaki*, *Y. Ootani*, *N. Ozawa*, Tohoku University, Japan; *M. Kubo*, Institute for Materials Research, Tohoku University, Japan

Pt catalysts are used as anode catalysts for polymer electrolyte fuel cell (PEFC). The fuel in PEFC contains a small amount of impurities such as CO and H<sub>2</sub>S. These impurities adsorb on active sites of Pt surfaces and degrade the hydrogen oxidation reaction activity of the anode catalyst. This loss of catalytic activity caused by impurities is known as impurity poisoning. Therefore, the development of the anode catalyst with the high impurity tolerance is strongly required. Takeguchi et al. experimentally found that adding SnO<sub>2</sub> as support material improves the CO tolerance of the Pt-based catalyst[1]. Furthermore, it is known that adsorbed impurities on the Pt catalyst can be removed by oxidation reaction. Kakati et al. reported that oxidation reaction by O and OH can recover from the H<sub>2</sub>S poisoning[2]. In

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order to develop the high impurity tolerant catalyst, it is necessary to reveal the effect of SnO<sub>2</sub> nano-particles on H<sub>2</sub>S tolerance and the recovery mechanism from H<sub>2</sub>S poisoning by oxidation reaction. In this study, we analyzed the adsorption states of H<sub>2</sub>S on Pt/SnO<sub>2</sub>(110) model and the recovery process from H<sub>2</sub>S poisoning by oxidation with OH using first-principles calculation.

For the calculation model, we put a Pt<sub>29</sub> cluster on SnO<sub>2</sub>(110). The Pt<sub>29</sub> cluster exposes Pt(111) on the top (See supplementary document Fig. 1). We calculated the adsorption energy of H<sub>2</sub>S on Pt/SnO<sub>2</sub>(110) and compared with the one on Pt(111) to reveal the effect of SnO<sub>2</sub> on H<sub>2</sub>S poisoning process. The adsorption energies of H<sub>2</sub>S were -18.38 and -24.73 kcal/mol on the Pt cluster of Pt/SnO<sub>2</sub>(110) and Pt(111), respectively. Thus, it was found that the adsorption of H<sub>2</sub>S on Pt is suppressed by addition of SnO<sub>2</sub>. Next, we analyzed the recovery process from H<sub>2</sub>S poisoning by OH generated from dissociation of H<sub>2</sub>O. It is known that H<sub>2</sub>S adsorption on Pt is dissociative and adsorbed sulfur atom is generated. The sulfur atom adsorbed on the surface decreases the activity of the Pt catalyst. In this study, we considered the reaction process (See supplementary document Fig. 2) based on the intermediate stable species during the H<sub>2</sub>S oxidation cascade in the gas phase[3] and calculated the activation energies of each elementary process. We found that the water dissociation is the rate-determining step on both Pt/SnO<sub>2</sub>(110) and Pt(111) and the activation energies were 18.78 and 23.70 kcal/mol, respectively. Therefore, we demonstrated that an addition of SnO<sub>2</sub> promotes an oxidation reaction of adsorbed sulfur on the Pt catalyst.

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

2) B. K. Kakati, et al., J. Power Sources 252, 317 (2014).

3) F. Tureček, et al., J. Am. Chem. Soc. 118, 11321 (1996).

**9:40am EH-WeM6 Impurity Tolerance of Pt/ Metal-Oxide Anode Catalyst for Polymer Electrolyte Fuel Cell: First-Principles Calculation, Nobuki Ozawa, K. Kuranari, M. Kubo, Tohoku University, Japan**

Polymer electrolyte fuel cell (PEFC) needs anode materials with high tolerance to poisoning by impurities such as CO, NH<sub>3</sub>, and H<sub>2</sub>S in the fuel, which degrades performance of the PEFC. Recently, a composite of Pt and WO<sub>3</sub> (Pt/WO<sub>3</sub>) is used as a catalyst in the anode, and this catalyst is effective for CO removal by oxidation [1]. For theoretical design of anode materials with high tolerance to impurity poisoning, the mechanism of high tolerance of Pt/WO<sub>3</sub> to CO should be revealed. In this study, we investigated CO oxidation processes on Pt/WO<sub>3</sub>(001) by first-principles calculation. At first, we calculated the adsorption energies of CO on Pt/WO<sub>3</sub>(001) and an isolated Pt cluster, to discuss an effect of WO<sub>3</sub> on CO tolerance of Pt. For a Pt/WO<sub>3</sub>(001) model, a Pt<sub>20</sub> cluster is put on a WO<sub>3</sub>(001) surface. The adsorption energy of CO on the Pt<sub>20</sub> cluster is 36.40 kcal/mol, while that on an isolated Pt<sub>20</sub> cluster is 45.65 kcal/mol. These results indicate that the combination of the WO<sub>3</sub> surface and Pt cluster decreases the adsorption energy of CO on the Pt cluster. To investigate the reason why the adsorption energy of CO decreases by the WO<sub>3</sub> surface, we calculated d-band center [2] of the Pt atom on Pt/WO<sub>3</sub>(001) and Pt cluster. In general, downward shift of the d-band center increases the adsorption energy of CO. Here, the d-band center values of the Pt atom on Pt/WO<sub>3</sub>(001) and isolated Pt cluster are -2.28 and -2.15 eV, respectively. This means that WO<sub>3</sub> modifies the electronic states of the Pt cluster and leads to the downward shift of the d-band center, which decreases the adsorption energy of CO. Next, we discuss CO oxidation on Pt/WO<sub>3</sub>(001). The CO oxidation by H<sub>2</sub>O proceeds as follows; (i) H<sub>2</sub>O → OH<sup>-</sup> + H<sup>+</sup> and (ii) CO + OH<sup>-</sup> → CO<sub>2</sub> + H<sup>+</sup> + 2e<sup>-</sup>. Here, we firstly investigated H<sub>2</sub>O dissociation on Pt/WO<sub>3</sub>(001). In this calculation, the H<sub>2</sub>O molecule adsorbs on the interface between the Pt cluster and WO<sub>3</sub>(001) surface, and dissociates to H<sup>+</sup> on the Pt atom and OH<sup>-</sup> at the interface. The activation energy for the H<sub>2</sub>O dissociation is 19.87 kcal/mol, which is lower than that on a pure Pt(111) surface (23.70 kcal/mol). Thus, we suggest that WO<sub>3</sub>(001) can decrease an adsorption energy of CO and activation energy for H<sub>2</sub>O dissociation on Pt catalyst during CO oxidation process.

[1] P.-Y. Olu, et al., *Electrochem. Commun.*, 71, 69 (2016).

[2] B. Hammer, et al., *Catal. Lett.*, 46, 31 (1997).

**10:20am EH-WeM8 Harvesting Sunlight for Photoelectric and Photothermal Conversions with Titanium Nitride Nanostructures, Satoshi Ishii, National Institute for Materials Science, Japan; S.L. Shinde, R.P. Sugavaneshwar, M. Kaur, T. Nagao, National Institute for Materials Science**

**INVITED**

Harvesting sunlight enables conversion of photon energy to electronic energy and thermal energy. Among different classes of materials, metals

have unique properties in light harvesting. Since metals are highly conductive and do not have bandgaps, metals can generate hot carriers even with low energy photons to be injected into an adjacent semiconductor. The excited hot carriers eventually become heat and heat the metals themselves and their surroundings. These photoelectric and photothermal effects can be enhanced by the optical resonances i.e. surface plasmon resonances. Hence, number of researches have taken advantage of plasmon resonances in photoelectric and photothermal conversions. As gold and silver are known to be excellent plasmonic materials, nanostructures made of these noble metals have been widely used in the recent studies.

In contrast, we have been working with titanium nitride (TiN) nanostructure to show that it can also be used in photoelectric and photothermal conversions. Titanium nitride is chemically stable and much cost-effective than gold or silver, making it a practical choice of material. In addition, TiN is plasmonic in visible and near infrared and superior to gold and silver in absorbing broad spectrum. In the first part, we present that TiN nanostructures can generate photocurrent by the irradiation of visible light, and can enhance the visible photocatalytic activities of carbon nitride which is a UV-active metal-free photocatalyst. In the second part, we show that TiN nanoparticles are efficient sunlight absorbers to generate solar heat. Since each TiN nanoparticle act as a nanoscale heater, solar heated TiN nanoparticles offer efficient water distillation and chemical reactions such as oxidation of carbon monoxide. Our results demonstrate that TiN nanostructures have the potential to replace gold and silver nanostructures in sunlight harvesting applications with better efficiencies.

**11:00am EH-WeM10 Solar Printing: From Benchtop to Rooftop, Paul Dastoor, University of Newcastle, Australia**

**INVITED**

Organic photovoltaics (OPV) are poised to play a major role in the global energy portfolio driven by their capability to be printed at high speeds across large areas using roll-to-roll (R2R) processing techniques; creating the tantalising vision of coating every roof and other suitable building surface with photovoltaic materials at extremely low cost. Indeed, recent full economic modelling of the balance of materials (BOM) and balance of system (BOS) costs, have highlighted the long-term commercial viability of OPV-based technology in today's energy marketplace.

However, the chlorinated solvents that are used in current OPV technology are under continual regulatory pressure due to their hazardous and toxic nature. Indeed, increasingly harsh technical requirements for using these solvents means that their implementation in high speed printing lines will be highly problematic if not economically impractical. In addition, tailoring device morphology across large areas is fraught with difficulty due to the challenge of controlling phase segregation of polymer mixtures using conventional printing. Water-based polymer nanoparticle dispersions (solar paint) offer the prospect of simultaneously controlling the nanoscale architecture of the active layer whilst eliminating the need for hazardous organic solvents during device fabrication. However, the behaviour of these nanoparticulate devices is complex and thus understanding their structure-function relationships requires characterisation techniques that can probe chemical structure on the nanoscale. In this paper we review our progress in understanding the structure-function relationships of organic electronic nanoparticulate thin films. In particular, I will discuss how scanning transmission X-ray microscopy is an invaluable tool for characterising these materials.

Finally, I will explore the future prospects and economics for large scale manufacture of solar cells based on printing. I will discuss our recent achievements in the development of a fully operating R2R printing line and the installation of several large scale (> 100 m<sup>2</sup>) demonstrations of printed solar modules.

# Thursday Morning, December 6, 2018

## Energy Harvesting & Storage

### Room Naupaka Salon 6-7 - Session EH-ThM

#### Batteries

**Moderator:** Ludvik Martinu, Polytechnique Montréal

**8:20am EH-ThM2 Real-Time TEM Observation of Electrochemistry and Failure in Battery Materials, Reza Shahbazian-Yassar,** University of Illinois at Chicago

Electrodes in rechargeable batteries undergo complex electrochemically-driven phase transformations upon driving Li ions into their structure. Such phase transitions in turn affect the reversibility and stability of the battery. This presentation gives an overview of the PI's research program on in-situ transmission electron microscopy (TEM) of ceramic battery materials. In-situ TEM has been shown to be a very powerful technique in shedding light to some of the mysteries in electrochemical performance of new materials. Various anode materials including SnO<sub>2</sub> and MnO<sub>2</sub> were subjected to lithiation process and the transport of Li ions was visualized within their atomic structure. For SnO<sub>2</sub> nanowires, it was observed that the Li ion transport results in local strain development preferably along (200) or (020) planes and [001] crystallographic directions. The lithiation behavior in the presence of twin boundary defects was completely different compared to pristine state with no twin boundary defect. We showed that twin boundaries in general provide a more accessible pathway for Li ion transport. Anisotropic plastic deformation was also observed along [010] directions of MnO<sub>2</sub> nanowires. Sb-based intermetallics which have been proved to be promising anode materials for Li-ion batteries, are also capable of storing of sodium ions. We investigated the microstructural changes and phase evolution of such intermetallic nanowires using in-situ TEM. These alloys also exhibit a new cubic alloying phase that form by intermixing of the ABAB atomic ordering in hexagonal lithiated phase due to Li inclusion in their lattices. Our results indicate that the reaction between these alloys and sodium proceeds through a different pathway during the first compared to the subsequent cycles.

**8:40am EH-ThM3 Reactive Ion Beam Etching of Piezoelectric ScAlN and LiTaO<sub>3</sub> for RF Filter Applications, Robinson James, Y. Pilloux, H. Hegde,** Plasma Therm

Etching piezoelectric Scandium Aluminum Nitride (ScAlN) and lithium tantalate (LiTaO<sub>3</sub>) films with controllable profile angle and very smooth surface is required for next generation Bulk Acoustic Wave (BAW) and Thin Film Surface Acoustic Wave (TF SAW) RF filter applications respectively. First part of the paper reports the facile etching of ScAlN with 15% Scandium concentration by Reactive Ion Beam Etching (RIBE) with very smooth surface of less than 5 nm average roughness and controllable profile angle between 60 to 80 degrees. Recent studies indicate that incorporating high concentration Sc into AlN improves the piezoelectric response of the device by five times and the band width of RF filters also improved. However, etching highly Sc doped ScAlN using traditional RIE and ICP based methods are extremely difficult. Moreover RIE and ICP etching methods exhibit low etch rate and results in rough surfaces when Sc concentration increases more than ~ 8% in ScAlN. Reactive Gas/Ar based RIBE processes were developed with highly controllable profile angle from 60 to 80 degrees, improved etch rate (~ 36 nm/min) and selectivity to photoresist mask (0.7:1), in comparison to conventional IBE. ScAlN selectivity to photoresist was improved significantly when using Reactive Gas/Ar compared to pure Ar based etching. Second part of the paper reports the optimization of LiTaO<sub>3</sub> etching with either RIBE or IBE. LiTaO<sub>3</sub> etch rate and selectivity were optimized by varying the Reactive gas/ Ar ratio and wafer tilt. LiTaO<sub>3</sub> etch rate of ~ 80 nm/min, 1.25: 1 selectivity to PR and a very smooth surface with roughness of ~ 2 nm was achieved. Further improvements in etch rate, selectivity are under investigation. Etching ScAlN and LiTaO<sub>3</sub> were characterized using scanning electron microscope (SEM) and white light interferometer (WLI) was used for measuring surface roughness. By varying wafer tilt, Reactive Gas/Ar ratio, beam voltage and current we achieved desired profile angle, etch rate, selectivity and smooth surface. This research has significant importance in fabricating ScAlN based BAW and LiTaO<sub>3</sub> based TF SAW RF filters for next generation mobile and wireless applications.

**9:00am EH-ThM4 Lead-free Epitaxial Ferroelectric Heterostructures for Energy Storage and Harvesting Applications, Amrit Sharma,** Center for Materials Research, Norfolk State University

Fast and rapid depletion of natural resources such as fossil fuel and coal is driving researchers to focus continuously on the development of new technologies and exotic materials having high energy density and efficiency

for both harvesting and storage of clean and green energy. In United States, nearly 68% of the primary energy produced is wasted as a heat each year. Energy harvesting for low power electronic devices using ferroelectric materials is one of the emerging areas of research because they possess excellent piezoelectric and pyroelectric coefficients. These materials are unique as they only sense time dependent temperature change to generate electric power. Temperature change can be obtained through different ambient sources such as waste-heat, solar radiation etc. We have grown lead free BaZr<sub>0.2</sub>Ti<sub>0.8</sub>O<sub>3</sub> (BZT)/ Ba<sub>0.7</sub>Ca<sub>0.3</sub>TiO<sub>3</sub> (BCT) multi-layer hetero structures and studied the structural, dielectric, ferroelectric, pyroelectric and energy density characteristics. The BZT/BCT multilayer epitaxial hetero-structures were grown on La Sr MnO (LSMO) buffered SrTiO (STO) single crystal substrate by optimized pulsed laser deposition technique. The ferroelectric phase transitions have been probed above room temperature with relaxor behavior. These heterostructures show large polarization change and high energy density characteristics due to interface effect even at low applied field and small temperature fluctuation which may be useful for both high energy storage density and thermal harvesting applications.

**9:20am EH-ThM5 Direct Electrodeposition of High-Performance Li-ion Battery Electrodes, Paul Braun,** University of Illinois at Urbana-Champaign, USA **INVITED**

Lithium-ion battery electrodes are nearly universally formed via tape casting of a slurry containing a mixture of active material, binder, and conductive carbon. However, the electrochemical and mechanical properties of slurry cast electrodes are often limited by weak interconnections between particles and between the particles and the substrate. We suggest conformal electrodeposition of high-quality electrode materials would provide opportunities to enhance battery performance (energy density, power density, and flexibility) and broaden the scope of available electrode form factors (size, shape, porosity, and 3D integration). We have now made considerable advances in the direct electrodeposition at modest temperatures of high performance tin-based Li-ion anodes and LiCoO<sub>2</sub>, NaCoO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, and Al-doped LiCoO<sub>2</sub>-based Li-ion cathodes. The electrolytically active materials were formed either as solid films, or where significant volume changes upon cycling are present, via a templating process, as a 3D mesostructured film. The capacities are near-theoretical, and in the case of the electroplated oxides, the crystallinities and electrochemical capacities of the oxides are comparable to powders synthesized at much higher temperatures (700 ~ 1000°C). The electrodeposition method significantly broadens the scope of battery form factors and functionalities, enabling a variety of highly desirable battery properties including microbatteries, and high energy, high power, and flexible designs.

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