

Wednesday Evening, December 14, 2016

Energy Harvesting & Storage

Room Lehua - Session EH-WeE

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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