

Tuesday Afternoon, December 9, 2014

Energy Harvesting & Storage

Room: Lehua - Session EH-TuE

Batteries, Capacitors & Storage Materials

Moderator: Stacey Bent, Stanford University, USA

5:40pm **EH-TuE1 Electrochemical Deposition of Organic-inorganic Composites for Supercapacitors**, *M. Bai, Xiaoxia Liu*, Northeastern University, China

Electrochemical Deposition of Organic-inorganic Composites for Supercapacitors

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Electrochemical capacitors (supercapacitors) are widely recognized as an important class of energy storage devices. Development of high performance supercapacitors is highly desirable to meet the increasing demand for energy storage devices. Conducting polymers, including polyaniline (PANI) and polypyrrole (PPy) have promising applications in a variety of technological fields, including supercapacitor. One-dimensional (1D) growth control of conducting polymer, directing to polymer nanofibers, has aroused great interest because an ordered arrangement of the polymer chains favours higher conductivity and better performance in charge storage. The growth of nanofibers is known to be intrinsic to PANI, however heterogeneous nucleation on the initially-formed PANI nanofibers would result in irregularly-shaped PANI particles. The suppression of this overgrowth on the surface active sites of initially-formed PANI nanofibers has been achieved by some chemical polymerization methods, including aqueous/organic interfacial polymerization, rapidly-mixed reactions, which led to the formation of nanofibrous PANI. However, only nonfibrous, granular powder PPy can be yielded by these methods since fibrillar structure is not intrinsic for PPy and so it is very hard for PPy to grow one dimensionally. Electrochemical deposition is very attractive due to the ability to anchor the product onto substrate materials in the desired quantity, shape and size in one single step, enabling the final application to be performed easier.

In this work, we will present the one-dimensional growth of conducting polymer through electrochemical co-deposition with inorganic oxide. Pseudocapacitive properties of the obtained composite films are studied as well. The local environment at the electrode surface for polymerization was tried to be controlled by the electrodeposition of inorganic oxide from their precursors like VO^{2+} , in which process proton may be released and some of the anodic charges may be consumed. Composites with improved electrochemical performance were obtained through 1D growth control of the conducting polymer, leading to increased surface area and organic-inorganic synergistic effect.

Acknowledgements

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6:20pm **EH-TuE3 Soft X-ray Operando Spectroscopy for Polymer Electrolyte Fuel Cells and Li Ion Batteries**, *Masaharu Oshima*, The University of Tokyo, Japan **INVITED**

In order to meet strong demands for electronic structure analysis of green devices, namely 1) power generation devices such as polymer electrolyte fuel cells (PEFC), 2) power efficient devices such as graphene FET and Resistive RAM, and 3) energy storage devices such as Li ion battery (LIB), we have developed two soft X-ray nano-spectroscopy systems at the Spring-8 University-of-Tokyo (UT) outstation. One is *operando* soft-X-ray emission spectroscopy (XES)¹ for PEFC cathode catalysts and Li ion battery, and the other is scanning photoelectron microscopy with 70 nm spatial resolution², which has been used to analyze graphene FET and organic FET *in operando*.

First, we analyzed electronic structures of carbon-related catalysts alternative to Pt for PEFC in order to elucidate the oxygen reduction reaction (ORR) mechanism. We prepared metal phthalocyanine-based carbon catalysts with 1-2% nitrogen and less than 1 % of Fe for PEFC. Photoelectron spectroscopy and first principles calculation revealed that zigzag edge carbons with neighboring graphite-like nitrogen are ORR active sites. Based on these analyses, we fabricated fuel cell stack for PEFC which showed comparable performance to Pt catalysts. Furthermore, we

have taken *operando* XES spectra of Fe $2p$ - $3d$ transition during power generation, revealing that Fe impurity may act as an ORR catalyst³.

Next, we analyzed the change of Fe $3d$ states accompanied with the Li intercalation/ deintercalation process by resonant photoemission spectroscopy. Since the battery voltage should reflect the energy difference between Li $2s$ and Fe $3d$ down-spin state, we measured the change in Fe $3d$ down-spin states for LiFePO_4 (3.4V) and $\text{Li}_2\text{FeP}_2\text{O}_7$ (3.6V) and found that 0.2 eV shift from PO_4 to P_2O_7 poly-anions directly reflects battery voltage. Furthermore, the *operando* XES method was applied to cathode materials LiMn_2O_4 in Li ion battery to reveal the electronic structure change of Mn with changing OCV (open circuit voltage). It was demonstrated that the Mn^{3+} and Mn^{4+} states are successfully distinguished using high-energy-resolution resonant XES⁴. Multiplet calculations⁵ have been performed to determine the electronic structures in comparison with *operando* XES spectra for both Fe and Mn chemical states in FC and LIB, respectively.

This work has been done in collaboration mainly with Y. Harada, H. Niwa, T. Aoki, Y. Nabae, Y. Nanba and D. Asakura.

References

- 1) Y. Harada *et al.*, Rev. Sci. Instrum. **83**, 013116 (2012).
- 2) K. Horiba *et al.*, Rev. Sci. Instrum. **82**, 113701 (2011).
- 3) H. Niwa *et al.*, Electrochemistry Com. **35**, 57 (2013).
- 4) D. Asakura *et al.*, SPring-8 BL07LSU Activity Report 2012.
- 5) Y. Nanba *et al.*, PCCP **14**, 7031 (2014).

7:40pm **EH-TuE7 Water as Promoter and Catalyst in Di-Oxygen Reactions at Aqueous and Organic Electrified Interfaces**, *Nenad Markovic*, Materials Science Division, Argonne National Laboratory, Argonne, IL 60439, USA

Understanding the role of water in di-oxygen electrochemistry at atomic and molecular levels is the key to driving technological innovations that are urgently needed to deliver reliable, affordable and environmentally friendly energy [1-4]. Surprisingly, all previous studies have treated the water molecule as reactants needed to satisfy the stoichiometry of the reaction, rather than as vital hydrogen-donor molecules that can promote the rates of transformation of oxygen intermediates to final products. It is the impact of water on di-oxygen electrochemistry that constitutes the focus of our paper. First, we introduce a universal model that is capable of rationalizing, and ultimately understanding, electrocatalysis of the oxygen reaction in aqueous media, as well as in Li-O_2 electrochemistry in organic environments. The model is based on the formation of $\text{HO}_{ad}\cdots\text{H}_2\text{O}$ (alkaline) and $\text{LiO}_2\cdots\text{H}_2\text{O}$ (organic solvents) complexes that place water in a configurationally favorable position for proton transfer to O_2^- and HO_2^- intermediates that are formed on neighboring active sites. We propose that monometallic electrodes modified by omnipresent oxygenated spectators such as OH_{ad} and LiO_2 are, in fact, bifunctional catalysts capable of facilitating different parts of the overall multi-electron process: providing adsorption sites for the formation of complexes as well as bare metal sites to facilitate the electron transfer to O_2 , O_2^- and HO_2^- .

Moreover, we demonstrate that water plays a dual role in Li-O_2 electrochemistry, acting simultaneously as a promoter in the production of Li_2O_2 and also as a *catalyst*, regenerating itself through a sequence of steps that include the recombination of H^+ and OH^- back to water. Water acting as a catalyst has not, to the best of our knowledge, previously been reported for any electrochemical reaction.

References:

1. N. M. Markovic; "Interfacing Electrochemistry"; *Nature Materials*, **12**(2013)101-102
2. R. Subbaraman, D. Tripkovic, K-C. Chang, D. Strmcnik, A. P. Paulikas, H.P. Hurinsit, M. Chan, J. Greeley, V. Stamenkovic and N. M. Markovic; "Trends in Activity for the Water Electrolyzer Reactions on 3d-M(Ni,Co,Fe,Mn)-Hydr(oxy)oxide Catalysts"; *Nature Materials*, **11** (2012) 550-557.
3. R. Subbaraman, D. Tripkovic, D. Strmcnik, K-C. Chang, M. Uchimura, A. P. Paulikas, V. Stamenkovic and N. M. Markovic; "Enhancing Hydrogen Evolution Activity in Water Splitting by Tailoring $\text{L}^+-\text{Ni}(\text{OH})_2$ -Pt Interfaces"; *Science*, **334** (2011) 1256-1260
4. H. Gasteiger and N.M. Markovic; Fuel Cells - "Just a Dream-or Future Reality", *Science*, **324** (2009) 48-49.

8:20pm **EH-TuE9 Electrochemical Reduction of CO₂ as a Way to Store Energy from Intermittent Sources**, *Paul Kenis*, University of Illinois at Urbana-Champaign

The desire to increase the utilization of sustainable energy sources such as solar and wind is hampered by their intermittent nature. Large scale energy storage capacity is needed to maximize utilization of these sources,

specifically to avoid large amounts of renewable energy being wasted when their supply exceeds demand.

Over the last years we have studied the electrochemical reduction of CO₂ to various value-added chemicals such as carbon monoxide (CO), formic acid, and methane. When coupled to renewable energy sources such as wind and solar, this process can produce carbon-neutral fuels or commodity chemicals, possibly providing a method for storage of otherwise wasted excess energy from intermittent renewable sources [1].

For this process to become economically feasible, more active and stable catalysts as well as better electrodes are necessary such that CO₂ electrolyzers can be operated at sufficient conversion (current density >250 mA/cm²), reasonable energetic efficiency (>60%), and sufficient product selectivity (Faradaic efficiency >90%). For CO production, a key reactant in the Fischer-Tropsch process, the best performance reported to date is current densities on the order of 90 mA/cm² and energy efficiencies up to 45%, when operating at ambient conditions [2]. This presentation will focus on new catalyst systems for efficient conversion of CO₂ to CO: (i) Ag nanoparticles supported on TiO₂ [3]; (ii) Au nanoparticles supported on multiwall nanotubes; and (iii) metal-free N-doped carbons. These catalysts have been characterized in a 3-electrode cell and in an electrolyzer. Current densities of between 100 and 250 mA/cm² as well as energy efficiencies of up to 70% were obtained. The electrodes in all these cases are prepared using automated airbrushing [2], which reduced catalyst loadings to 0.75 mg/cm² for Ag and 0.17 mg/cm² for Au. These performance levels, together with the lower cost due to low precious metal loading (due to the use of catalyst supports), or even the elimination of precious metals altogether (N-doped carbons), brings electrochemical reduction of CO₂ to CO closer to economic feasibility.

We also performed an economic / life-cycle analysis of this process, to determine whether this technology can become, economically viable for large scale application in the storage of energy from renewable sources, and/or in the reduction of greenhouse gas emissions.

References

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