

# Thursday Morning, November 1, 2012

## Energy Frontiers Focus Topic

Room: 15 - Session EN+NS-ThM

## Batteries and Fuel Cells

Moderator: Y. Wu, Purdue University

### 8:00am EN+NS-ThM1 Advanced Polymer Electrolyte Materials for Fuel Cell Applications, A.M. Herring, Colorado School of Mines INVITED

Proton exchange membrane (PEM) fuel cells are still the most desirable component of future zero emission, high efficiency automobiles fueled with hydrogen. However, their unit cost, ease of operation, and reliability must be reduced which includes eliminating the humidifier from the fuel cell system. Currently the commercial PEM is fabricated from a perfluorosulfonic acid (PFSA) polymer such as Nafion<sup>®</sup>. Unfortunately PFSA ionomers must be fully hydrated to achieve practical levels of proton conductivity which can only be achieved in vehicles operating at an inlet RH of 85% which still necessitates the use of a humidifier and undesirable complex water management and recovery. To achieve the goal of a PEM that can operate at temperatures from freezing to 120°C using dry inlet gases it will be necessary to develop new PEMs that are based on new chemistries or dramatically improved morphologies of existing chemistries. The versatility of the polymer electrolyte fuel cell could be expanded to more complex fuels with the use of an anion exchange membrane (AEM). An AEM fuel cell could potentially utilize less expensive metal catalysts and have the ability to oxidatively cleave carbon-carbon bonds.

Ionomers are generally perceived as being phase separated materials. However, the optimal morphology that an ionomer should adopt and that would be practical is still being debated. This situation is not helped by the uncertainty of the morphology adopted under operating fuel cell conditions of the incumbent material. Here I will describe a study that contrasts fully amorphous materials with materials designed to have phase separated morphologies of known symmetries and dimensions. While the designed materials allow us to probe certain concepts of ion conduction with pore shape and size, they do not necessarily out perform the amorphous materials. Curiously we show that the role of water has more to do with morphological changes in flexible materials than enhancing ion conduction in non-sulfonic acid based materials. This has implications for the fabrication of thin robust films that will be needed for an operating fuel cell. In the case of AEMs while a cation has yet to be found that is stable under hot and dry operation, water may be a necessary evil rather than an enhancer of anion conduction.

### 8:40am EN+NS-ThM3 Rational Design of Competitive Electrocatalysts for Hydrogen Fuel Cells, S. Stolbov, M. Alcántara Ortigoza, University of Central Florida

The large-scale commercial application of hydrogen fuel cells requires efficient and cost-effective electrocatalysts for the oxygen reduction reaction (ORR), which occurs on the cathode. We demonstrate that rational design can render electrocatalysts possessing both virtues. In this work, by unifying the knowledge on surface morphology, composition, electronic structure and reactivity, we find that tri-metallic sandwich-like structures are an excellent choice for optimization. Their constituting species are designed to couple synergistically rendering reaction-environment stability, cost-effectiveness and high catalytic activity. This cooperative-action concept enabled us to predict two Pt-free ORR electrocatalysts: Pd/Fe/W(110) and Au/Ru/W(110) [1]. Density functional theory calculations of the reaction free-energy diagrams indicate that these materials are more active toward ORR than the so far best Pt-based catalysts.

1. S. Stolbov and M. Alcántara Ortigoza; *J. Phys. Chem. Letts.* **3**, 463 (2012)

### 9:00am EN+NS-ThM4 Nanocomposite Materials for Lithium Ion Batteries, G. Yushin, Georgia Institute of Technology INVITED

High power energy storage devices, such as supercapacitors and Li-ion batteries, are critical for the development of zero-emission electrical vehicles, large scale smart grid, and energy efficient cargo ships and locomotives. The energy storage characteristics of supercapacitors and Li-ion batteries are mostly determined by the specific capacities of their electrodes, while their power characteristics are influenced by the maximum rate of the ion transport. The talk will focus on the development of nanocomposite electrodes capable to improve both the energy and power storage characteristics of the state of the art devices. Carbon-polymer and carbon-metal oxide nanocomposites have been demonstrated to greatly

exceed the specific capacitance of traditional electrodes for supercapacitors. Selected materials showed the unprecedented ultra-fast charging and discharging characteristics. Intelligently designed silicon-carbon-polymer composites showed up to 8 times higher specific capacity than graphite, the conventional anode material in Li-ion batteries, and stable performance for over 1000 cycles. In order to overcome the limitations of traditional composites precise control over the materials' structure and porosity at the nanoscale was required.

### 9:40am EN+NS-ThM6 Engineering Li<sub>x</sub>Al<sub>y</sub>Si<sub>z</sub>O Ionic Conductive Thin Films by Atomic Layer Deposition for Lithium-ion Battery Applications, Y.-C. Perng, J. Cho, D. Membreno, N. Cirigliano, B. Dunn, J.P. Chang, University of California, Los Angeles

Lithium (Li)-ion batteries have drawn much attention for their outstanding performance in portable electronics applications with the potentials to function as a power source for further miniaturized devices, including micro-systems through the utilization of 3-dimensional electrodes based on high aspect ratio pillars. To realize this potential, an ultra-thin and highly conformal electrolyte layer is needed to coat the 3D electrode array. The ionic conductor lithium aluminosilicate (LiAlSiO<sub>4</sub>) synthesized by atomic layer deposition (ALD) is a promising electrolyte material for 3D battery applications not only due to its high ionic conductivity along its c-axis resulting from channels formed by the alternating tetrahedra of aluminum-oxygen (Al-O) and silicon-oxygen (Si-O), but also expected to provide similar improved cell cyclability, as reported in the preliminary studies of ultra-thin metal-oxide ALD coatings on electrodes.

The self-limiting characteristic of ALD allows for precise control of thickness and composition of complex oxides and results in a highly conformal and pinhole-free coating suitable in 3D micro-battery applications or electrolyte surface coatings. The metal precursors used in this work are tetraethyl orthosilicate (TEOS), trimethylaluminum (TMA) and lithium t-butoxide (LTB). These precursors, along with water vapor as the oxidant, were used to deposit SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Li<sub>2</sub>O, with the deposition rates in the range of 0.8~2Å/cycle, respectively. The deposition rate of stoichiometric LiAlSiO<sub>4</sub> was ~20Å/cycle at a temperature of 290°C. The concentration of each metal element in Li<sub>x</sub>Al<sub>y</sub>Si<sub>z</sub>O (LASO) thin films was found to correlate closely to ALD cycles and the associated incubation times. The crystallinity of the films after post-deposition rapid thermal annealing (RTA) was a function of cation atomic percentage. Li-ionic conductivities and the activation energy of as-deposited LASO films with respect to lithium contents as well as their relation to the film thickness were studied. The LASO ALD coating on 3D features, such as NWs and nanoparticles (NPs), were confirmed to be conformal and uniform by transmission electron microscopy (TEM) imaging. The cell performance as well as cyclability enhancement from Li<sub>x</sub>Al<sub>y</sub>Si<sub>z</sub>O was investigated for a silicon-nanowire 3D microbattery, where SiNW was used as an anode, to explore the potentials of a solid-state SiNW battery with a solid-oxide electrolyte.

### 10:40am EN+NS-ThM9 Titanium Oxide and Lithium Titanium Oxide Coated 3D Nanoelectrodes for Li-ion Microbatteries, G. Pattanaik, J. Haag, M.F. Durstock, Air Force Research Laboratory

Titanium oxide based materials, including both Li-titanates and various TiO<sub>2</sub> polymorphs are promising alternatives to carbonaceous anode materials for Li-ion rechargeable batteries because of their higher voltage operation (enhanced safety), relatively small volume expansion upon lithiation, minimal electrode/electrolyte interface reactivity (nonexistent SEI layer), inexpensive and biocompatible non-toxic nature. Nanoscale three-dimensional (3D) architectures of current collectors for microbatteries would significantly increase the areal capacity over their planar counterparts, if the active Li-insertion electrode material could be coated conformally. The nanoscale thickness of the active electrode layer in combination with an electronically conducting 3D nanoarchitecture of the current collector should enable high areal capacity and fast charge-discharge rates.

Atomic layer deposition (ALD) is capable of growing conformal ultra thin films on complex 3D surface morphologies. We have used ALD to grow conformal layers of titanium oxide and lithium titanium oxide on various 3D nanoarchitectures including high aspect ratio nanoporous Al<sub>2</sub>O<sub>3</sub> templates, template-electrodeposited 3D metal nanowire arrays and carbon nanotube buckypapers. The precursors for ALD used in this study include lithium t-butoxide, tetrakis(dimethylamido)titanium (TDMAT) and water. We have been able to grow conformal layers with controllable thickness at nanometer scale uniformly coated around the high aspect ratio features.

A significant increase in areal capacity (up to two orders of magnitude) was obtained in anatase TiO<sub>2</sub> coated Ni nanowire arrays over 2D thin film

electrodes of a similar footprint. ALD TiO<sub>2</sub> coated buckypapers showed specific capacities in excess of 200 mAh/g at C/10, with 70% of the capacity retained at 5C. At 1C, 95% of the initial capacity is retained after 500 charge/discharge cycles. ALD deposition of LiOx and TiOx and subsequent thermal annealing leads to a combination of TiO<sub>2</sub> and spinel lithium titanium oxide (Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>) phases. The presence of these phases is reflected in XRD as well as electrochemical charge-discharge curves. This presentation will discuss a systematic study of the ALD growth of 3D titanium oxide and lithium titanium oxide nanostructures and their electrochemical characterization.

11:20am **EN+NS-ThM11 The Contribution of Auger Electron Spectroscopy to a Better Understanding of the Lithiation Process Occurring in Si-based Anodes Designed for Li-ion Batteries**, E. Radvanyi, E. De Vito, W. Porcher, S. Jouanneau, CEA Grenoble, France

With a specific capacity of almost 3580 mAh.g<sup>-1</sup> at room temperature (corresponding to the Li<sub>15</sub>Si<sub>4</sub> alloy), silicon is a promising element for designing new efficient anodes in Li-ion battery technology. However, because of huge material volumic expansion (around 300%) during the lithiation process<sup>1</sup>, leading to a quick pulverization of the electrode<sup>2</sup>, silicon has been used only as an additive to graphite in commercial cells so far<sup>3</sup>. In order to improve Si-based electrodes cyclability, a better understanding of the lithium insertion mechanisms is among the key issues<sup>4</sup>. The study of the lithiation process in silicon particles is particularly challenging. Indeed, a complete amorphization of the material during cycling<sup>4</sup> makes difficult the use of surface characterization techniques based on beam diffraction (e.g. X-rays or electrons). In this study, we have used Auger Electron Spectroscopy (AES) to study these mechanisms. Poor attention has been focused on AES in the battery research field so far<sup>5,6</sup>. In this work we emphasize its interest, notably for the study of the lithiation mechanisms in silicon particles. The first part of this work is dedicated to the study of Li-Si alloys by using AES. Several crystalline Li<sub>x</sub>Si alloys (Li<sub>7</sub>Si<sub>3</sub>, Li<sub>13</sub>Si<sub>4</sub> and Li<sub>22</sub>Si<sub>5</sub>) have been synthesized and characterized by X-Ray diffraction and AES. It appears that the atomic relative concentrations obtained by AES for the elements Li and Si are accurate with a tolerance of approximately 10%. The effect of Ar<sup>+</sup> sputtering has also been investigated. After this initial work, six electrodes based on silicon particles have been analyzed by using AES for different "State Of Charge" (SOC) within the first electrochemical cycle.

For each SOC, several silicon particles have been investigated individually. Li and Si depth concentration profiles have been achieved by following Li (KLL) and Si (LVV) Auger transitions. Thanks to the good spatial resolution (17 nm at 10kV/InA), it is possible to detect inhomogeneities of Li concentration at the particle surface. Based on the results obtained on different silicon particles at several SOC, a lithiation model is proposed and discussed.

(1) Beaulieu, L. Y.; Hatchard, T. D. ; Bonakdarpour, A. ; Fleischauer, M. D.; Dahn, J. R. *J. Electrochem. Soc.* **2003**, *150*(11), A1457-A1464

(2) Kasavajjula, U.; Wang, C.; Appleby, A. J. *J. Power Sources* **2007**, *163* (2), 1003-1039

(3) www.hitachi.com

(4) Zhang, W. J. *J. Power Sources* **2011**, *196* (1), 13-24

(5) Morigaki, K. I.; Ohta, A. *J. Power Sources* **1998**, *76* (2), 159-166

(6) Kim, Y. J., Lee, H.; Sohn, H. J. *Electrochem. Comm.* **2009**, *11* (11), 2125-2128

11:40am **EN+NS-ThM12 Organic/Inorganic Composite Materials as Anodes for Lithium Ion Batteries**, M. Thakur, R.B. Permites, Rice University, M. Isaacson, Lockheed Martin Space Systems, M.S. Wong, Rice University, S.L. Sinsabaugh, Lockheed Martin MS2, S.L. Biswal, Rice University

Silicon continues to draw great interest as an anode material for lithium ion batteries due to its large specific capacity for lithium. Electrochemical etching silicon is one of several anode materials of interest, but its energy density is oftentimes limited due to its attachment to an unreactive silicon substrate. Here, we present a novel "liftoff" method by which a freestanding macroporous silicon film (MPSF) is electrochemically detached from the underlying bulk silicon and combined with pyrolyzed polyacrylonitrile (PAN), a conductive polymer. We report the performance of these silicon thin films with and without pyrolyzed PAN.

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