

Flexible, Solid Electrolyte-Based Lithium Battery Composed of LiFePO_4 Cathode and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Anode for Applications in Smart Textiles

The rigidity of electronic components and their powering sources remains a fundamental barrier to making truly wearable smart textiles. Researchers from Ecole Polytechnique de Montréal of Canada recently reported the fabrication of a flexible and stretchable Li-ion battery. The anode and cathode of the battery were made from conventional $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiFePO_4 powders, respectively, separated by a solid polyethylene oxide (PEO) electrolyte layer. The key enabling technology for the flexibility and stretchability was the use of large quantities of thermoplastic PEO as the binder material for electrode and separator fabrication. Using an optimized ratio of conducting carbon and polymer binder material for the electrodes, the authors demonstrated that flexible batteries could be fabricated by first casting as sheets, followed by cutting into thin strips, and finally integrating into a textile using conventional weaving techniques with conductive threads. The final woven batteries had a soft leather-like feel and appearance. Their electrochemical performance was poorer compared to batteries made of pressed powder tablet electrodes and liquid electrolytes. High internal resistance was found to be part of the reason for the compromise. Nonetheless, this study represents a noteworthy progress toward a fully extrudable/drawable battery system for textile applications.

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Energy Storage in Electrochemical Cells with Molten Sb Electrodes

Various energy storage solutions have been investigated for electrical grid load leveling. Among the electrochemical devices considered, flow batteries, and the very similar technology of reversible fuel cells, have been researched and promoted. A team of researchers from the University of Pennsylvania and University of Delaware have proposed a new type of flow battery based on the $\text{Sb-Sb}_2\text{O}_3$ system. These researchers investigated this system at 973 K and stirred operating conditions. Mixing is important to prevent long-range phase separation of the two liquids due to the difference in their densities and to approximate flow conditions within the eventual battery. A scandia-stabilized zirconia (O^{2-} -conducting) solid electrolyte separated the molten anode from the zirconia/ $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ (LSF) composite cathode. The authors measured $V-i$ curves at set increments of the extent of Sb amount converted to Sb_2O_3 . The linearity of these curves in both the fuel cell and electrolyzer modes demonstrated that the cell impedance was not dependent on the current density. Negative electrode impedances were

estimated by subtracting a literature value for the oxygen electrode from the impedance measurements made by the authors. Above 70% extent of Sb oxidation, the impedances increased – even more for the cell in electrolyzer mode since the Sb_2O_3 reactant is less conductive.

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Hysteresis of In Situ CCVD-Grown Graphene Transistors

With the rise of graphene electronics dependent on easier, more cost-efficient and controllable methods of realizing CMOS-compatible devices, transfer-free graphene deposition is garnering significant attention. Researchers from Technische Universität Darmstadt and the Fraunhofer Institute in Freiburg, Germany, successfully grew graphene directly on thermally grown SiO_2 using conventional silicon substrates, eliminating the need for expensive alternative materials or those incompatible with CMOS process technology. Additionally, they demonstrate that monolayer graphene field-effect transistors (MoLGFETs) and bilayer graphene field-effect transistors (BiLGFETs) can be grown directly on the oxidized silicon substrates. BiLGFET devices showed ultra-high on/off-current ratios of 10^7 , which appears to be the highest reported value for *in situ* CCVD grown BiLGFET, by several orders of magnitude. Corresponding transfer characteristics of full MoLGFETs and BiLGFETs show back gate bias-dependent hysteresis on the order of $\sim 18 - 20$ V. The team shows that the low gate field strength does not explain all device characteristics and postulates that intensive interactions between bilayer graphene and silicon dioxide are responsible for bandgap enhancement, a phenomenological interaction that was previously used to explain the substrate-induced bandgap opening in epitaxial graphene. With this novel fabrication method, hundreds of BiLGFETs are realized simultaneously with this transfer-free method on one 2" wafer by *in situ* CCVD in a silicon CMOS-compatible process.

From: Electrochem. Solid-State Lett., 15, K31 (2012).

Radiation-Induced Corrosion of Copper in Anoxic Aqueous Solution

As countries prepare to dispose spent nuclear fuel, the repository designs being considered are dictated by regional geology. For granite-based designs, such as those considered by Sweden, Finland, and Canada, copper has been selected as a potential material for the container walls. The anticipated environment at the container surface for such repositories is anoxic, low ionic content water. Under such conditions, it is expected that copper will be thermodynamically stable. However, water in contact with a disposal container will be subjected to a high radiation flux, undergo radiolysis, and form a variety of oxidizing and reducing

species that may have a profound impact on the corrosion process. Despite this fact, relatively few studies have been performed on the radiation-induced corrosion of copper, and those that are available in the literature have somewhat contradictory results, likely due to variations in the experimental conditions that were utilized. The goal of the work performed by the authors in this paper was to study specifically the behavior of copper under the conditions expected in a deep geological repository. Gamma radiation was found to cause significant corrosion of metallic copper in anoxic, high purity water. Deposits of corrosion product (predominantly Cu_2O) and circular cavities were observed on the copper surface. While the extent of attack increased with increasing radiation dose, the size and size distribution of the aforementioned features did not.

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Electrochemical Detection of Sodium Borohydride

A direct borohydride fuel cell (DBFC) is a type of alkaline fuel cell that uses sodium or potassium borohydride as the fuel and either air/oxygen or hydrogen peroxide as the oxidant. This is a relatively new type of fuel cell that is of considerable interest because of the theoretical ability to produce high specific energy levels (as high as $9,000 \text{ Wh kg}^{-1}$ with a cell potential of 1.64 V when oxygen is used as the oxidant). Recently, researchers at Virginia Tech published a report on the development of a method for electrochemical detection of sodium borohydride in alkaline media (0.5 M NaOH), with possible DBFC-relevant applications as (i) a sensor for determining membrane crossover rates for borohydride fuel, and (ii) a concentration monitor for borohydride fuel. They performed cyclic voltammetry and chronoamperometry experiments at a gold working electrode to probe the rather complex electrochemical-chemical oxidation mechanism, and developed a chronoamperometric method that allowed detection with good detection limits ($50 \mu\text{M}$) and sensitivity ($0.016 \mu\text{A}/\mu\text{M}$) within the investigated range of concentrations (1-100 mM). These results demonstrated that gold, normally considered inactive towards heterogeneous hydrolysis of borohydride, is capable of electrochemical hydrolysis of borohydride.

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Tech Highlights was prepared by Zenghe Liu of Google Inc.; David Enos and Mike Kelly of Sandia National Laboratories; Colm O'Dwyer of University College Cork, Ireland; and Donald Pile of Dow Kokam LLC. Each article highlighted here is available free online. Go to the online version of Tech Highlights, in each issue of Interface, and click on the article summary to take you to the full-text version of the article.

A High-Performance Rechargeable Iron Electrode for Large-Scale Battery-Based Energy Storage

Despite their low cost, robustness and eco-friendliness, iron anode-based rechargeable batteries have two major disadvantages—low charging efficiency due to hydrogen evolution and slow discharging rate because of electrode passivation—that have limited their application and further development since the 1970s. Recently, researchers at the University of Southern California reported new approaches to address these disadvantages. In their work, the iron electrode was fabricated with a simple “pressed-plate” method to press high-purity carbonyl iron powder and a polymer binder together. A small amount of bismuth was also incorporated by electro-reduction of added bismuth sulfide. The new electrode showed far superior performance compared to a commercially available iron electrode. A ten-fold reduction in hydrogen evolution rate, a high charging efficiency of 96%, a high discharge capacity of 0.3 Ah g⁻¹, and also a twenty-fold increase in capacity for the two-hour discharge rate were achieved. The study found that the high level of purity of carbonyl iron combined with the *in situ* produced bismuth suppressed hydrogen evolution, while the *in situ* formation of mixed-valent conductive iron sulfides facilitated high discharge rates. The performance was stable over the 25 cycles studied. These results make iron anode-based batteries promising candidates for low-cost, durable, and efficient large-scale electrical energy storage systems.

From: *J. Electrochem. Soc.*, **159**, A1209 (2012).

Thin Composite Films of Mussel Adhesive Proteins and Ceria Nanoparticles on Carbon Steel for Corrosion Protection

Corrosion inhibitors are widely used in coatings as a means to enhance their ability to protect the underlying substrate. Unfortunately, many of the traditional chemistries present health and safety concerns which render them undesirable. As a result, there has been a considerable push to develop “green” corrosion inhibitors that can provide a high degree of corrosion protection without introducing any potential health and safety concerns to those who work with them or the environment in general. In this work, a combination of two such chemistries was pursued—an adhesive protein from the marine mussel *Mytilus edulis* and ceria (CeO₂) nanoparticles. Individually, both have been demonstrated to provide protection to a variety of materials, though the effects were short lived, particularly for the adhesive protein. A composite coating was formed on a carbon steel surface via alternating immersion in aqueous solutions of each constituent. The resulting film consisted of a smooth, compact layer of adhesive protein and ceria nanoparticles, and was subsequently exposed to a mildly

acidic chloride solution. The protective nature of this film was found to increase with time, and was hypothesized to be the result of formation of an iron complex with the adhesive protein, increasing its bond to both the metal surface and the ceria nanoparticles.

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Determination of Conformational Behavior of DNA by Electrochemical Impedance Spectroscopy

A thorough understanding of DNA conformational changes is critical for continued advancements in gene therapy. Conformational transitions are typically characterized by rheological measurements of the viscoelastic response of dilute solutions of DNA biopolymers. These measurements can be used to determine the overlap concentration (C*, where polymer molecules in solution begin interacting with one another) and the entanglement concentration (C_e, where polymer molecules become entangled). Recently, researchers at Centro Universitario UTEG and Universidad de Guadalajara in Mexico reported an alternate approach to probing the dynamics of DNA solutions. The authors performed electrochemical impedance spectroscopy (EIS) in a 2-electrode cell at open circuit in an aqueous buffer (pH 7.3), and showed that the complex capacitance response could be modeled in an equivalent circuit containing a double layer capacitance (C_{dl}), adsorption capacitance (C_{ad}), adsorption resistance (R_{ad}), diffusion impedance (Z_{w,ad}), and charge transfer resistance (R_{ct}). Fitting the experimental complex capacitance data for DNA calf-thymus (13 kbp) produced values for all of the circuit elements, and plotting the values for C_{dl}, C_{ad}, and R_{ad} as a function of DNA concentration revealed noticeable changes at 0.4 and 1.5 mg/mL, which the authors associate with C* and C_e and which agree fairly well with literature values (0.35 and 2.0 mg/mL) determined by rheology.

From: *ECS Electrochem. Lett.*, **1**, G1 (2012).

Magnetic Graphene Nanoplatelet Composites Toward Arsenic Removal

The two major challenges faced while designing filtration materials are stability against the irreversible degradation of materials and the difficulty in reclamation and reactivation of the filter media after adsorption of pollutants. Nanomaterials are good candidates for removal of pollutants by adsorption due to their high surface area. However, they are found to be unstable and difficult to recycle. Researchers from Lamar University, Louisiana State University and Texas A&M University studied iron-iron oxide nanoparticles decorated on magnetic graphene nanoplatelet composites (MGNCs) for arsenic (III) removal. They used Fe-Fe₂O₃ core-shell particles that were synthesized on the high surface area MGNC by using a thermal decomposition method. The core-shell iron-iron oxide nanoparticles have higher stability and are easy to separate in a

continuous flow system by using a magnetic field. The Langmuir and Freundlich models were used to study the adsorption isotherm. The physical model exhibited a significantly higher adsorption capacity (11.34 mg/g) than the other adsorption values reported on the conventional iron oxide-based adsorbents (~1 mg/g). The equilibrium adsorption capacity calculated by using a pseudo-second-order kinetic equation was higher than that of the adsorption isotherm. The initial adsorption rate of 0.68 mg/g·min was slightly higher than that previously reported in the literature. The authors demonstrate nearly complete As(III) removal within 1 ppb using the Fe-Fe₂O₃-decorated MGNC material.

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The Effect of HfO₂ Overlayer on the Thermal Stability of SiGe Substrate

High dielectric constant (high κ) materials are now widely used in next-generation CMOS microelectronics and are crucial for the 22 nm technology node. For technologies at these length scales, HfO₂ is an important gate oxide. This material, however, suffers from complex interface formation which forms due to temperature-induced chemical reactions with the underlying substrate, and can become exacerbated under high performance (high mobility, high power) conditions. For faster devices, SiGe substrates offer a higher hole mobility channel, but compared to Si, comparatively less is known about temperature-induced chemical alterations at the substrate-gate dielectric interface during typical post deposition annealing (PDA) steps. Researchers from the Technion and Tower Semiconductor in Israel studied the interfacial chemical bonding state of the substrate-gate dielectric interface using X-ray photoelectron spectroscopy. Their work shows that the use of atomic layer deposited HfO₂ on a Si_{0.8}Ge_{0.2} substrate stabilizes the low oxidation states of strained Ge₂O₃. The finding is poignant since it shows that HfO₂-to-HfSi₃ silicide formation occurs when strained SiO₂ decomposes above 1000 °C; at PDA temperatures lower than this, however, a relatively clean (low interface trap density) SiGe-SiO₂-HfO₂ stack is maintained, which is important for low leakage current, high quality device performance in sub-100 nm node CMOS technologies, both on Si and on higher hole mobility SiGe substrates.

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