The Ferrocyanide/Stabilized Carbon System, a New Class of High Rate, Long Cycle Life, Aqueous Electrolyte Batteries

Along with the increasing integration of renewable energy sources into the energy distribution grid comes the urgent need for methods and systems to store such energies. Unlike conventional portable batteries, the storage devices for such purpose are required to have superior performances in terms of their power, cost, calendar and cycle lives, and safety. Professor Huggins of Stanford University recently described his group's work on a new class of aqueous electrolyte batteries for such purpose. The cathode of the batteries is based on a new family of hexacyanoferrate materials. Because of the open framework crystal structure of these materials, monovalent cations such as Li^+, Na^+, K^+, or NH_4^+ from aqueous electrolytes can be reversibly intercalated at high rates with very little crystallographic distortion. The anode side utilizes a new class of composite materials that combines electroactive polypyrrole with capacitive activated carbon. This combination offers this hybrid electrode the high rate capability of a capacitor, as well as the well-defined electrochemical potential of a battery electrode. Reduction of the polypyrrole with $NaBH_4$ can also lower the potential of the anode. Overall, the full cells possess very attractive kinetics and long cycle life, and can operate at aqueous electrolyte limited voltage.

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Alkanethiols as Inhibitors for the Atmospheric Corrosion of Copper Induced by Formic Acid: Effect of Chain Length

The atmospheric corrosion of copper has been studied for many years, due to its extensive use in a wide variety of industrial applications. Carboxylic acids, such as acetic and formic acids, are particularly aggressive towards copper, and are frequently present in indoor environments. In this work, self-assembled monolayers (SAMs) of organic materials were evaluated as corrosion inhibitors for copper when exposed to such accelerants. More specifically, the impact of the chain length of self-assembled n-alkanethiols on copper exposed to a humid, formic acid-containing environment was explored. While there exists a large body of research evaluating the performance of SAMs as corrosion inhibitors for copper and other metals, the majority of these studies have been performed under aqueous rather than atmospheric conditions. In this work, vibration sum frequency spectroscopy, a non-linear vibrational laser spectroscopic technique, was used to interrogate the interfacial reactions occurring between the SAM-protected copper substrate and the atmospheric environment. A detailed description of the corrosion process was developed based upon the GILDES model (a multi-regime model including the gaseous phase (G), the gas/liquid interface (I), the liquid phase (L), the deposition layer (D), the electrodic region near the surface (E), and the solid phase (S)). Performance increased with increasing chain length, with the SAMs hindering the ability of water, oxygen, and formic acid to reach the underlying copper substrate.

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p-InP Films for Light-Induced Hydrogen Evolution

Photoelectrochemical cells (PECs) are under study in many laboratories because of their potential to efficiently produce hydrogen gas using renewable energy (solar) as well as a resource (water) that is abundant in many regions of the world. A PEC uses a semiconducting working electrode where excitation of the electron-hole pairs and subsequent charge transfer processes can decompose water, thereby providing a source of hydrogen fuel. Researchers at the Helmholtz-Centre Berlin for Materials and Energy and the California Institute of Technology have reported that the energy conversion efficiency of thin film p-InP electrodes can be significantly enhanced by photoelectrochemical conditioning. Homoepitaxial (100) InP thin films were grown by metallorganic vapor phase epitaxy (MOVPE), and were subsequently conditioned into a device structure by a three-step process: etching in bromine/methanol, potentiodynamic cycling under illumination in 0.1 M HCl, and photoelectrochemical deposition of a thin layer of Rh from $RhCl_3$/NaCl/isopropanol. Photocurrent-voltage measurements showed a record light-to-hydrogen conversion efficiency of 14.5%. The authors performed extensive microscopic and spectroscopic characterization of the photoelectrodes, and attribute the excellent conversion efficiency to local In_2O_3-like structural regions that introduce energy levels near the conduction band edge which impart conductivity, as well as to an interfacial dipole attributed to chloride adsorption on segregated indium in the photoelectrode structure.

From: ECS J. Solid State Sci. Technol., **2**, Q51 (2013).

Cs-Corrected STEM Observation and Atomic Modeling of Grain Boundary Impurities of a Very Narrow Cu Interconnect

Impurity segregation near grain boundaries is well known to influence grain growth in Cu and related materials, and plays a crucial role in determining material properties for large scale integration (LSI) interconnects. If impurities from electroplating steps, and their tendency to segregate at grain boundaries, can be identified during annealing steps with very high accuracy, the understanding of their influence on grain growth processes during annealing can be significantly improved. Researchers at Ibaraki University in Japan used high resolution C_s (spherical aberration)-corrected scanning transmission electron microscopy (STEM) to analyze impurities in grain boundaries of very narrow Cu interconnects. One significant finding is that Cl introduced from a high purity plating bath specifically segregates in high concentrations. Analytical microscopy confirmed impurities were localized at grain boundaries in a Cu interconnect. The authors further confirmed this finding through *ab initio* simulations based on segregation energies of Cl at a Cu grain boundary. These findings are the first high resolution aberration-corrected STEM data on Cl segregation in Cu grain boundaries and may aid in the realization of very low resistivity and high electro-migration resistant Cu interconnects for future high speed and low power consumption device integration.

From: ECS Electrochem. Lett., **2**, H23 (2013).

High Capacity of SnO_2 Nanoparticles-Decorated Graphene as an Anode for Lithium Ion Batteries

Many recent efforts to improve the energy density of lithium ion batteries are devoted to investigating novel anode materials with higher specific capacity. Tin oxide is one of these anodes and has twice the lithium storage capacity as that of graphite anodes. Graphene/tin oxide (SnO_2) composites are emerging as one of the lithium ion battery materials for anodes due to high specific capacity of tin oxide coupled with the high electrical conductivity of graphene. A new approach to synthesize tin oxide-decorated graphene composite anode material is demonstrated in the present investigation by researchers at Tianjin University. The novel wet chemical synthesis method produces thin layers of graphene platelets separated from each other by the SnO_2 nanoparticles. The transmission electron microscopy observations show that the SnO_2 nanoparticles are uniformly distributed on the homogeneous graphene layers. High resolution TEM images confirm that the diameter of these nanoparticles is 4-6 nm. Raman spectra show the decrease in the average size of the sp^2 domain as a result of the reduction of graphene oxide to graphene. Galvanostatic charge/discharge cycling shows the first discharge capacity at 2751.4 $mAh \times g^{-1}$. The authors demonstrate excellent lithium storage capacity of the SnO_2/graphene nanocomposite compared to the graphite anodes.

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Tech Highlights was prepared by Vishal Mahajan of Dow Kokam LLC, 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. 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.