<u>Tech Highlights</u>

Electrochemical Study of Hemosorption

Hemosorption is an extracorporal detoxification method that involves perfusing or passing a patient's arterial blood through a column filled with a sorbent, with the subsequent return of the blood into a patient's vein. Researchers from several universities in Russia and the United States recently studied the electrochemical features of hemosorption, based on an electrochemical mechanism of interaction between activated carbon (the sorbent, which also serves as the electrode) and blood (which serves as the electrolyte). The electrochemical system revealed a linear correlation between the stationary potential of activated carbon and the platelet count at the carbon/blood interface. A "threshold" potential of E = 0.04 V, corresponding to the point of indifference of carbon toward platelets, was obtained. A considerable effect of activated carbon potential on the adsorption of 1,2-dichloroethane and sodium barbital was found. A nonfaradaic method of external direct polarization of activated carbon in blood was realized by a special cylindrical column with granular activated carbon. Changes in hematological, morphological, and rheological indexes of blood subsequent to blood perfusion through activated carbon were investigated. The carbon potential was found to be the only determining factor in the carbon-blood interaction. The way of polarization of activated carbon had no influence on this interaction.

From: J. Electrochem. Soc., 153 (8), J91 (2006).

Nano/Micro Hierarchical Fe₂O₃ on Ni Mesh Structure for High-Rate Li-Ion Battery

A high specific capacity at high charge/ discharge current rates was achieved for a lithium ion battery negative electrode by forming a nanocrystalline and mesoporous Fe₂O₃ film on nickel wire mesh. Japanese researchers employed a chemical bath deposition method followed by pyrolytic transformation of the FeOOH-based film. Electron microscopy revealed a nestlike morphology consisting of an assembly of nanoflakes on the Ni wire weave. The resultant structure allowed for increased distributed electronic and ionic conductivity combined with decreased active material particle size to minimize the required diffusion length for the Li ion insertion and extraction processes. Furthermore, the high surface area resulted in lowered specific current density. Constant current discharge/charge curves revealed a specific capacity greater than the theoretical 6 Li per Fe₂O₃ formula unit, part of which is attributed to concurrent formation of NiO during the heating process. For all three current rates reported (0.78, 7.3, and 13 A/g), the capacity was maintained at 80, 70, and 55%, respectively, at the 20th cycle. For this number of cycles, the Coulomb efficiency remained above 95%. The authors propose that the nano/micro hierarchical structured

Fe₂O₃/Ni electrode yields lower volume changes arising from insertion/ extraction cycles and is a promising architecture for high rate battery electrodes.

From: J. Electrochem. Soc., 153 (7), A1273 (2006).

Application of Freestanding Perforated Diamond Electrodes for Efficient Ozone-Water Production

There has been recent interest in ozone generation technologies due to its possible use in sterilization, deodorization, and decolorization. Electrochemical techniques not only allow for generation of pure concentrated ozone, but also allow miniaturization over the presentlyused electrical discharge units. However, the choice of anodes for this reaction is limited due to the greater efficacy of the competing oxygen evolution reaction. In addition, the electrodes typically used in the literature are prone to erosion during electrolysis. Arihara and coworkers at the Central Japan Railway Company solve both of these issues via the use of a diamond electrode for ozone generation. The authors show that in sulfuric acid solution the production of ozone in diamond electrodes exceeds that on platinum electrodes by a factor of two at any given current density, demonstrating the superior behavior of this anode. In order to test the use of this anode for direct electrochemical ozonewater production, the authors make use of a freestanding perforated diamond electrode in an electrolytic cell consisting of a Nafion membrane and a Pt cathode with pure water in both the anode and cathode chambers. Results suggest that at a current of 10 A the amount of ozone produced is sufficient for sterilization in practical uses. In addition, a current efficiency of 29% was recorded for the reaction at 1 A. These results, combined with the expected stability of diamond toward dissolution. show the usefulness of this anode for electrochemical ozone production.

From: Electrochem. Solid-State Lett., 9 (8), D17 (2006).

The Relationship Between Pit Chemistry and Pit Geometry Near the Critical Pitting Temperature

Stainless steels in chloride solutions exhibit a critical pitting temperature (CPT) above which pitting will occur when the material is polarized above the critical pitting potential. For temperatures below the CPT, pitting will not initiate at any applied potential. In this paper, the importance of non-uniformity of the dissolution rate within a pit is demonstrated. The authors state that it is not the ability of the pit base to keep dissolving that is critical, but the ability of the pit to undercut the surface, forming a lacy metal cover that hinders outward diffusion. The pit stability product (essentially the diffusivity times the solubility of the relevant specie) is proportional to the product of the limiting current density and the depth of the pit for a cylindrical pit (pencil electrode experiments). The pit stability products as a function of temperature were determined for a series of austenitic stainless steels *via* artificial pit (pencil electrode) experiments. Several degrees below the CPT, stability products are initially low, indicating occlusion of the pit, then, as the pit propagates, rise to values consistent with an open hemispherical pit just prior to passivation. Near the CPT, where large metastable pit transients occur, the stability product rises to an extremely large value due to a geometric effect. Correcting for this geometric effect, the later stages of the pit growth kinetics become more consistent with anodic diffusion control, and the stability product does not rise higher than levels consistent with the artificial pit experiments.

From: J. Electrochem. Soc., 153 (8), B330 (2006).

An Innovative Technique for Electroless Deposition of Ultrathin Barriers for Copper Metallization

Electrochemical deposition of copper is a well-established technique in the Damascene process for fabrication of copper interconnects in multi-level integrated circuits. A thin barrier film of a transition-metal nitride, e.g. TaN or TiN, is typically deposited between the copper metallization and the dielectric layer to prevent unwanted chemical reactions or interdiffusion processes. These barrier films are typically deposited by physical vapor deposition. Recently, electroless deposition of other types of barrier layers (Co-P, Co-W-P, etc.) has been the subject of numerous studies because this approach provides highly selective deposition of conformal layers which will be necessary as feature sizes shrink below 65 nm. Researchers at Feng Chia University and the Hsiuping Institute of Technology in Taiwan recently described an innovative electroless deposition process for deposition of ultrathin Co-B and Co-W-B layers on SiO₂-based dielectric layers. These "seed" layers are then used to catalyze the growth of Co-P or Co-W-P barrier layers and copper films using electroless plating methods. The authors used electron microscopy and atomic force microscopy to analyze film properties during the early stages of growth of both the catalytic seed layers and the barrier layers. Among other key results, the authors report that the thermochemical stability and diffusionbarrier properties of Co-B films can be enhanced significantly by incorporating a small amount of tungsten into the film.

From: Electrochem. Solid-State Lett., 9 (8),C141 (2006).

Tech Highlights was prepared by Venkat Srinivasan of Lawrence Berkeley National Laboratory; Zenghe Liu of Abbott Diabetes Care; and David Enos, Donald Pile, and Mike