Tech Highlights

Effect of Morphology on the Response of Polyaniline-based Conductometric Gas Sensors

Various methods have been developed to produce polyaniline nanostructures such as nanofibers, nanotubes, and nanoshells. Applications in conductometric sensor technologies are being pursued under the hypothesis that these nanomaterials will provide advantages compared to a conventional thin film. Researchers at the National Institute of Standards and Technology and the Georgia Institute of Technology have reported a systematic comparison of the properties of polyaniline sensing layers with well-defined morphologies. They developed a convenient method for progressively transforming the morphology of polyaniline layers based on varying the solvent composition of the casting solution. When cast from pure methanol, the deposited film retained the nanofiber structure of the original, electrochemically synthesized starting material. When formic acid/methanol mixtures were used, the nanofibers agglomerated and interconnected. resulting in a more densely packed cast film. Formic acid concentrations greater than 90% produced a continuous thin film. Surprisingly, sensors using nanofiber layers had lower sensitivity to neutral molecules such as water and methanol than those based on a continuous thin film. The authors attribute this to the higher density of analyte-binding sites (of the sort that contribute to the sensor signal) and to the lower contact resistance of the thin film material, among other factors.

From: Electrochem. Solid-State Lett., 7 (10), H44 (2004).

Preparation of Fuel Cell Membrane Electrode Assemblies Using an Electrophoretic Deposition Process

Fabrication of membrane electrode assemblies (MEAs) used in polymer electrolyte fuel cells (PEFCs) usually involves a hot press of a catalyst ink onto a membrane such as Nafion. The performance of the fuel cell is dependent on the thickness, density, and composition of the polymer layer as well as the properties of the catalyst-polymer interface. Therefore, improved control of this step in the fabrication process will improve control over fuel cell behavior. Morikawa and coauthors at Tokyo Metropolitan University have demonstrated the successful application of electrophoretic deposition as an alternative means for preparation of MEAs. In the electrophoretic fabrication process, a Nafion 117 membrane was used to separate anode and cathode chambers and a high electric field (e.g., 125 V cm⁻¹) was used to drive a mixture of catalysts and Nafion polymer to the membrane where attachment occurred. Repeating the process for the other side of the membrane results in a complete MEA fabricated via

electrophoretic deposition. The authors found that good control could be exercised over the catalyst layer thickness, density, and composition by manipulation of cell voltage and electrolyte composition. Performance of the MEA generated by the electrophoretic process was comparable (if not better) than a comparable MEA generated using a hot press method.

From: J. Electrochem. Soc., 151 (10), A1733 (2004).

An Atomistic Description of Dealloying

Dealloying phenomenologically occurs when the selective dissolution of one or more alloy components results in a nanoporous microstructure enriched in the more noble component. Porosity evolution has been qualitatively identified with high dissolution rates above an experimental (empirical) critical potential. Jonah Erlebacher from The Johns Hopkins University developed a kinetic Monte Carlo model composed of the two significant contributions to morphology development: site coordination-dependent surface diffusion of all alloy components, and site coordination-dependent dissolution of the lessnoble atoms. The model closely simulates the features of selective dissolution phenomena, including parting limits and critical potentials, and describes the varying morphological changes accompanying stages of dissolution and passivation. However, the intrinsic critical potential was consistently a few hundred millivolts below the empirical critical potential. This difference was speculated to stem from insufficient experimental time for porosity to evolve, wherein dissolution of the less noble component(s) is not permitted to reach a steady state for potentials above the intrinsic critical potential. Additionally, the author presents a procedure to arrive at the enthalpy of dissolution of a terrace atom at the alloy/ electrolyte interface by extraction from experimental polarization curves, since analysis of the contributions of the various n-coordinated sites revealed that dissolution from terrace sites controls overall dissolution.

From: J. Electrochem. Soc., 151 (10), C614 (2004).

Hydrogen Adsorption and Absorption in Pd Films

Though the palladium - hydrogen system has been extensively studied via both gaseous and electrochemical methods, there is still no universally accepted model of the hydrogen insertion process. A number of theories, some of which contradict one another, have been proposed for this process; however, none of these treatments capture all of the intricacies of the process. In this series of papers, Gabrielli et al.

present a mathematical model describing the hydrogen insertion process which captures both single and dual step mechanisms, diffusion into the bulk metal, and the presence of trap sites within the metal. Experimental confirmation experiments presented in the second paper demonstrated that thin films of palladium differ in behavior from the bulk material. Cyclic voltammetry experiments were used to demonstrate that for thin films, absorption of hydrogen into the alpha and beta phases of palladium, along with the alpha/beta phase transition, could be resolved. This level of detail could not be resolved with bulk samples of the metal. The final paper presents the results from electrochemical impedance spectroscopy experiments that were used to verify the model and quantify associated kinetic parameters. From: I. Electrochem. Soc., 151 (11). A1925, A1937, A1943 (2004).

C-MEMS for the Manufacture of 3D Microbatteries

The growing use of miniature portable electronic devices such as smart cards and remote sensors has spurred research into the development of microbatteries. A significant obstacle is the inability to maintain energy and power during scale-down due to the difficulty in decreasing the weight and volume of the packaging correspondingly. 3D battery architectures with high aspect ratio (10:1) electrode elements offer a possible solution. Wang and co-workers from the University of California campuses at Irvine and Los Angeles have adapted their previous work on carbon-microelectromechanical systems (C-MEMS) to develop carbon electrodes of thicknesses ~350 µm. The process involves spin coating a negative tone photoresist (NANO SU-8 100) onto a substrate. Subsequently, the substrate was masked, exposed to UV light, developed, and finally pyrolyzed to convert the SU-8 to carbon. The procedure resulted in electrodes in the form of cylindrical posts of 80-275 µmin height Galvanostatic charge-discharge and cyclic voltammetry of the resulting electrode in a lithium perchlorate-based electrolyte showed capacities of 0.125 mAh/cm² The values obtained were reported to be 80% larger than corresponding unpatterned films. The authors believe that this improvement resulted from the larger active volume in the patterned electrodes.

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