TECH HIGHLIGHTS

A 64-Channel Combinatorial Electrochemical Cell

In materials applications where interfacial properties dictate the system performance (*e.g.,* catalysts, corrosion barriers, sensors, etc.), subtle changes in interfacial composition can result in dramatic improvement or deterioration in behavior. Although incentives exist for fine-tuning these properties, the research effort required for optimization can be daunting when binary, ternary, or higher order combinations must be evaluated. With recent advances in multichannel potentiostats and increasing access to lithographic techniques, researchers are turning toward combinatorial discovery methods as a means of reducing the experimental burden imposed by traditional sequential testing. Recently, Fleischauer *et al.* at Dalhousie University in Canada combined combinatorial thin-film sputtering techniques with parallel electrochemical evaluation to demonstrate the applicability of combinatorial techniques to the development of Li-ion battery electrodes. A sixty-four channel cell was patterned onto a Cu thin film over a glass substrate using standard photolithographic techniques. A shadow-mask approach was then used to restrict the deposition of active material to the prescribed electrode areas. The combinatorial test array was shown to have good site-to-site reproducibility, and excellent agreement with results from a conventional test cell was reported. The time to assemble the sixty-four channel test structure was about double that required to assemble a single conventional cell, demonstrating the improvement in research efficiency offered by this approach.

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On the Error Structure of Impedance Measurements

As part of a continuing collaboration, researchers at the University of Florida and the University of South Florida recently examined the manner in which frequency domain errors arise from time domain measurements. In this particular study, error propagation brought about by the frequency response analyzer algorithm is analyzed. The error structure is expressed in terms of three components: errors due to the model, systematic experimental bias errors, and stochastic errors. The origin of the noise in time domain signals is discussed in terms of the specific components of the electrochemical cell and instrumentation. Simulations of the measurement technique were presented using a variety of generated time-domain signals. These signals were produced by intentionally adding noise to otherwise clean input and response signals, and these were then used to calculate the resulting electrochemical impedance spectra. Four specific cases were considered: (1) nominally clean signals; (2) normally distributed, additive errors; (3) skewed, additive errors; and (4) proportional errors. Errors in the frequency domain were found to be normally distributed under all conditions evaluated. For additive errors in the frequency domain, the variances of the real and imaginary components of the impedance were found to be uncorrelated. The statistical characteristics of the results correlated well with experimental observations.

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In Situ NMR Study of Li Insertion into Carbon

The development of *in situ* spectroscopic techniques to study electrochemical processes, where the system is probed while simultaneously performing electrochemistry, has received a great deal of attention in recent years. For batteries, where the properties of materials can be altered when removed from their local environment, these techniques provide a significant step forward compared to the oft-used *ex situ* methods. Chevallier and colleagues from CNRS-Université and Université de Picardie Jules Verne, both in France, and the Poznan University of Technology in Poland, have, for the first time, demonstrated the use of *in situ* ^{7}Li-nuclear magnetic resonance (NMR) to study carbon/Li cells during galvanostatic charge-discharge. The carbon electrode was prepared by carbonization of a viscose fabric followed by a coating of pyrolitic carbon. By combining NMR results with transmission electron microscopy imaging, the authors proposed a model for Li intercalation involving two kinds of sites corresponding to different interval sizes between the graphitic-type layers. Lithium is thought to first intercalate into the smallest intervals between the layers, followed by penetration into the nanopores with resultant formation of quasi-metallic clusters.

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SPEEK Membranes for Direct Methanol Fuel Cells

Due to its excellent chemical, mechanical, and thermal stabilities and high proton conductivity in the hydrated state, Nafion, a perfluorosulfonic acid membrane, is currently used as the polymer electrolyte in both proton exchange membrane fuel cells and direct methanol fuel cells (DMFCs). However, Nafion membranes are expensive and have limitations with respect to operating temperature (<100°C). In addition, its high methanol permeability reduces the overall cell potential and fuel efficiency for DMFCs. These limitations have created enormous interest in the development of alternate fluorine-free ionomer membranes. A promising candidate under active investigation is sulfonated poly(ether ether ketone) (SPEEK), which possesses good thermal and mechanical properties. To date, experimental studies of SPEEK have focused mainly on physical properties such as swelling, thermal stability, and proton conductivity. Recently, researchers at the University of Texas at Austin investigated the electrochemical performance of this polymer membrane in DMFCs. SPEEK membranes with a degree of sulfonation around 50% exhibit performances comparable to or exceeding that of Nafion due to lower methanol crossover; however, the operating temperature must be limited to <65°C. The lower cost and improved methanol crossover performance compared to Nafion make SPEEK membranes promising alternatives for DMFCs. However, further work is needed to fully assess long-term stability in DMFCs.

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Contamination of HfO_2, ZrO_2, and SiO_2 Dielectrics

HfO_2 and ZrO_2 are high-*k* materials with the potential to replace SiO_2 as a gate dielectric material in future generations of integrated circuits. Control of moisture and organic contamination is essential to realizing the performance benefits of these oxides. Moisture diffuses through ultrathin HfO_2 and ZrO_2 films and forms oxides or silicates at the oxide-silicon interface, resulting in a decrease in the net dielectric constant. Further, incorporation of organics within these dielectrics can result in a deterioration of breakdown characteristics and an increase in leakage currents. Researchers at the University of Arizona and ASM America used atmospheric pressure ionization mass spectroscopy to study the interaction of moisture and organics on thin film dielectric materials and discovered that HfO_2 and ZrO_2 adsorbed higher amounts of moisture and isopropanol than SiO_2 under similar conditions. Multilayer adsorption models were developed and fitted to the experimental desorption data, and quantitative descriptions of the affinity of these oxides for moisture and organics were generated. The results show that HfO_2 is less susceptible to moisture and organic contamination compared to ZrO_2, an important result when considering these oxides for potential use in future gate dielectric applications.

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