Novel Approach for Determining Microscale Electrochemical Behavior

A significant challenge associated with microscale electrochemical experiments is the precise determination of individual contributions to a measured current from samples comprising an assortment of grains, grain boundaries, precipitates, and other material features. The micro-capillary technique has historically been used for these types of studies, but has limitations that restrict its use in long duration experiments. Researchers at the United States Naval Academy and the Naval Research Laboratory recently published a report that describes a new approach for making electrochemical measurements on isolated microscale regions of metals and alloys. The method (Selective Masking by Photolithography) involves the spin coating application of a photoresist on the sample, followed by laser exposure of the resist in the region of interest (as determined by optical microscopy or electron backscatter diffraction). The region is mapped and exposed by translating the sample on a high-resolution X-Y stage as the resist is exposed to 355 nm laser pulses (40 µm spot size). The resist is subsequently developed and hard baked to produce a masked sample suitable for electrochemical impedance spectroscopy and DC polarization measurements. The authors demonstrated excellent sensitivity on exposed areas of less than 10^{-4} cm^2, including irregularly shaped regions such as dendritic fingers of the austenitic phases in Alloy 2205, a duplex stainless steel.

From: J. Electrochem. Soc., ***159****, C15 (2012).*

Cobalt Doping in Ru/Rutile-TiO2/Ru Capacitors to Minimize Leakage Current

The memory cell capacitors in 20 nm technology DRAMs require insulator materials with high relative permittivity and low leakage current density. Among insulator material candidates that fulfill permittivity goals, rutile-TiO_2 possesses a manufacturing advantage by having precursors that can be applied using atomic layer deposition. Utilizing ruthenium as the capacitor electrodes is appealing because ruthenium has a high work function and is compatible with semiconductor processes. Furthermore, rutile-RuO_2 and rutile-TiO_2 have similar crystal structures and lattice constants which facilitate crystallization of rutile-TiO_2 without high-temperature post-deposition annealing. Japanese researchers at Hitachi Ltd. characterized the crystal structure, permittivity, and leakage current exhibited by Ru/rutile-TiO_2/Ru and Ru/Co-doped-rutile-TiO_2/Ru capacitors. Raman spectroscopy confirmed the rutile TiO_2 crystal structure, and X-ray photoelectron spectroscopy revealed the presence of RuO_2—presumably formed by reaction with ambient air—on the surface of the ruthenium electrode. Cobalt doping significantly reduced the capacitor leakage current without decreasing the permittivity below the requirements for 20 nm technology DRAMs. Cobalt doping increased the Schottky barrier height which decreased leakage by thermionic emission; however, tunneling leakage increased as the depletion width decreased. The researchers calculated 0.3–0.6% as the optimal cobalt doping concentration that minimized the total leakage current from these two mechanisms.

From: J. Electrochem. Soc., ***159****, G1 (2012).*

Charge Trapping and Detrapping in nc-RuO Embedded ZrHfO High-k Thin Film for Nonvolatile Memory Applications

Nanocrystal-embedded high-k thin films form an important class of emerging gate dielectrics for high-density floating-gate non-volatile memory applications. This is due, in part, to their low power operation, but also because they have a high charge storage capability with long retention times for stored charge and thus stored memory. Ruthenium oxide (RuO) is a chemically and thermally stable conductive oxide with a usefully high work function (~5 eV), which makes it a viable deep charge trapping medium for dielectric films, particularly when applied to CMOS devices. Researchers from Texas A&M University successfully created a RuO nanocrystal-embedded Zr-doped HfO_2 (ZrHfO) high-k dielectric within a MOS capacitor. They show that the memory function of the capacitor is mainly contributed by hole trapping during the forward gate biasing and electron trapping during the reverse sweep. While the basic memory function has already been demonstrated, the researchers used detailed electrical measurements to quantify the role of charge trapping and retention which defines the memory window. They find that deeply-trapped holes and electrons at nanocrystal sites in the film can be retained, which is suitable for non-volatile memory. Their work identifies the role of charge traps facilitated by embedding dielectrics with oxide nanocrystals for high performance ZrHfO gate dielectric stacks in MOS-based memory devices.

From: J. Electrochem. Soc. ***159****, H214 (2012).*

Combining Structural and Electrochemical Analysis of Electrodes Using Micro-Computed Tomography and a Microfluidic Fuel Cell

The gas diffusion electrode (GDE) in a fuel cell consists of three layers – a catalyst layer, a microporous layer (MPL) of teflonized carbons, and a macroporous layer of carbon fibers – that function to deliver reactant gas, drain liquid water, and conduct electrons with low resistance. Fuel cell performance improvements are gained by optimizing this complex three-dimensional (3D) structure. Micro-computed tomography (MicroCT) is a non-destructive, 3D imaging technique that researchers at the University of Illinois at Urbana-Champaign employed to investigate the structure-activity relationships of these fuel cell electrodes that were hot-pressed at varying loads. The authors used a unique approach called the filament tracing method, which combines structural connectivity to grayscale thresholding to enable differentiation of the fibrous masses from void space. The same electrode volume was analyzed in the MicroCT after hot pressing and before testing in a microfluidic fuel cell. Electrode performance was affected (i) at low compression by subtle shifts in the catalyst and MPL layers, and (ii) at moderate compression by drastic structural densification of the highly porous carbon fiber layer. The authors demonstrated that this MicroCT-analytical protocol for obtaining more accurate quantification of the GDE structures enables direct correlation between electrode microstructural changes and the resulting electrochemical performance.

From: J. Electrochem. Soc. ***159****, B292 (2012).*

Particles and Polymer Binder Interaction: A Controlling Factor in Lithium-Ion Electrode Performance

Three components comprise the laminate coating of a positive electrode in a Li-ion battery: the active material (AM) particles, acetylene black (AB) particles, and the polymer binder. The composition and arrangement of the solid particles – AB particles for electronic conduction from the current collector to and around the AM particles – are important for the realizable electrode energy density and rate performance. Researchers from Lawrence Berkeley National Laboratory systematically changed the compositions of AB/polyvinylidene difluoride (PVDF) binder composites and AM/AB/PVDF composites of various compositions to investigate the effects on electrode performance. An effective conductivity equation was derived from experimental measurements on these composites. The physical model showed a competition for polymer binding exists between the AM and AB particles, due to their different surface areas and surface chemistries. A tradeoff exists for balancing the AM and AB amounts. For example, starting with a high binder ratio (AB:PVDF = 0.2:1), adding increasing amounts of AM causes binder to migrate to AM particles, which thereby increases the AB:PVDF matrix conductivity (as the originally high free binder content decreases). The authors suggest their physical model can be used as a tool for optimizing polymer-binder based Li-ion battery electrodes.

From: J. Electrochem. Soc. ***159****, A214 (2012).*

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