

Nanoscale Solid Polymer Electrolytes and Integrated Nanostructured Energy-Storage Architectures Obtained from Electropolymerization

Christopher P. Rhodes, Jeffrey W. Long, Michael S. Doescher and Debra R. Rolison

Naval Research Laboratory
Surface Chemistry Branch, Code 6170
Washington, DC 20375

The development of nanometer-scale battery and fuel cell systems requires new methods to generate and assemble electrode and electrolyte components with effective control on the nanoscale. Electropolymerization offers a route to generate nanoscale (<50 nm) solid electrolytes on planar and non-planar (3-D) systems,¹ and represents a fabrication strategy to obtain electrochemical energy-storage systems with nanoscale (<50 nm) distances between the cathode and anode² (Fig. 1). The study of these systems contributes to our understanding of *nano-ionics* and bridges the important area between molecular and conventional electronics.

Nanoscale solid electrolytes offer improved performance in terms of energy and power densities by reducing the ohmic drop across the electrolyte and by reducing the mass and volume of the non-electroactive components. In the regime where the distance between the electrodes is <50 nm, simulations show that dramatically different ionic transport mechanisms are operative compared to thicker systems, due to the overlapping electrical double layers that create a space charge within the electrolyte.² In these nanoscale systems, the importance of the electrolyte's low electronic conductivity and high dielectric strength is magnified so as to prevent self-discharge and dielectric breakdown, respectively.

To generate nanoscale solid electrolytes, we chose to explore electropolymerization. Although most studies of electrodeposited polymers have considered electronically conducting polymers, electropolymerization can yield highly insulating films that when functionalized with ions yield ionically conducting *and* electronically insulating films. Electropolymerization has advantages over self-assembly for creating ultrathin defect-free films, and over chemical vapor deposition for coating three-dimensional systems in a conformal fashion. Under controlled conditions, electrodeposited polymers are ultrathin, inherently pinhole free and generated directly at the electrode surface, which yields a system with desirable interfacial contact between the electrode and electrolyte.

Nanoscale (20–80-nm thick), pinhole-free films are electrodeposited on both planar (indium-tin oxide) and mesoporous (MnO₂ and carbon) substrates from phenol and substituted-phenol monomers from either basic acetonitrile or methanol electrolytes.³ Ions are incorporated within the electrodeposited films by solvent casting methods or electro-oxidizing substituted phenols with ionic functionality. The film thickness and morphologies are determined using atomic force microscopy. X-ray photoelectron spectroscopy and impedance

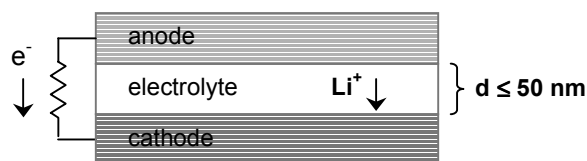


Figure 1. Representation of a nanobattery with an electrolyte thickness ≤ 50 nm

measurements are used to verify the presence of ions in the electrodeposited films.

Solid-state electrical measurements of electrodeposited poly(phenylene oxide) and related polymers on ITO and Au substrates are made in a two-electrode configuration using soft ohmic contacts, such as Hg or slowly evaporated Au or Al, as the top electrode. Impedance and DC measurements are used to determine the electronic conductivity, ionic conductivity, and dielectric strength. Impedance measurements confirm that the polymers contain mobile ions in the solid-state ($\sigma_{\text{ion}} \geq 10^{-10} \text{ Scm}^{-1}$), and DC measurements verify that the films are highly electronically insulating ($\sigma_{\text{elec}} \leq 10^{-12} \text{ Scm}^{-1}$).

Deposition of a metal oxide directly on the nanoscale, electrodeposited polymer is then investigated in order to fabricate an anode or cathode, but in a manner that does not electrically short the ultrathin film. Ruthenium dioxide (RuO₂) nanoparticles are deposited directly on polymer films from a solution of RuO₄ in hexane. The deposited RuO₂ is characterized by electrical and spectroscopic methods. Solid-state impedance measurements verify that the deposition of RuO₂ does not electrically short the ultrathin polymer film. Experiments are currently underway to assess whether such RuO₂ deposits can function as Li-ion-insertion electrodes in an all-solid-state battery configuration, in combination with the nanoscale solid electrolytes described here.

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