

**Fundamental investigations of ultrathin,  
electroactive polymer coatings as components  
of hybrid electrode structures for  
electrochemical capacitors**

Todd M. McEvoy and Jeffrey W. Long  
Code 6170, Surface Chemistry Branch  
Naval Research Laboratory  
Washington, DC 20375

Electrochemical capacitors (comprising supercapacitors and ultracapacitors) are a class of energy-storage devices that deliver a promising combination of high energy density and high power density.<sup>1,2</sup> Supercapacitors store charge by a double-layer capacitance mechanism, and are typically designed with porous, high-surface-area carbon electrodes, including carbon aerogels, foams, and papers.<sup>3</sup> The double-layer capacitance mechanism is ideal for rapid charge-discharge conditions, but ultimately limits the total energy-storage density of a supercapacitor. Ultracapacitors store charge via the faradaic reactions (i.e., pseudocapacitance) of transitional metal oxides or conducting polymers. Because these reactions can be propagated through the bulk of the active materials, ultracapacitors exhibit higher energy-storage capacities, although often at the expense of high-rate capabilities.

We are designing hybrid electrode structures<sup>4</sup> that combine the desirable morphologies and electrical conductivities of carbon aerogels with the energy-storage capacities of electroactive polymers, such as poly(o-methoxyaniline), POMA, and poly(o-phenylenediamine), PPD. In our approach, the highly porous aerogel serves as a conductive template onto which ultrathin, conformal polymers are applied via electropolymerization. Conformal coatings are achieved by forming the polymer coatings under self-limiting growth conditions, where the polymer thickness does not exceed ~15 nm. The pseudocapacitance of these polymer coatings significantly enhances the energy-storage capacity of these hybrid structures, while the porous architecture of the carbon aerogel facilitates rapid charging and discharging.

Self-limiting polymerizations, the critical step to achieving such hybrid electrode structures, are accomplished by choosing conditions where the developing polymer is both electronically insulating and exhibits minimal swelling. For polymers based on arylamine monomers, this requires avoiding the acidic pH conditions that are normally used to deposit conducting polymers. When these ultrathin polymers are transferred to acidic electrolytes they exhibit electrochemical features that are characteristic of electroactive polymers. Although related examples of such polymers have been reported, important aspects of structure, growth mechanism, and electrochemical properties have not yet been fully addressed. The optimization of hybrid structures incorporating such polymers will require a more detailed understanding of their physical, chemical, and electrochemical properties.

For these fundamental investigations we are growing and characterizing polymer films on planar substrates, such as indium-tin-oxide and glassy

carbon. In particular, we are examining how these self-limiting films differ from electroactive polymers prepared by more conventional approaches (i.e., from acid media). Specular-reflectance IR spectroscopy indicates that self-limiting POMA films exhibit the quinoid-like and benzene-like functionalities that have been previously reported for conventional POMA films. Using fluorine-tagged agents that specifically bind with the terminal -NH<sub>2</sub> groups of these polymers, we have determined that self-limiting POMA films are composed of polymer chains with an average length of ~10 monomer units.

The electrochemical features for self-limiting polymers typically occur near the potentials of their conventional counterparts, but often in a more restricted potential range. Self-limiting polymers are also distinguished by their conduction mechanism, as assessed by the behavior of these films in the presence of redox probes, such as Fe(CN)<sub>6</sub><sup>3-</sup>. For example, ultrathin POMA acts as a mediating electrode for Fe(CN)<sub>6</sub><sup>3-</sup>, indicating "redox" polymer behavior that would arise from localized site-to-site electron hopping. Conversely, a conventional POMA film acts as a metallic interface toward Fe(CN)<sub>6</sub><sup>3-</sup>, which is indicative of a "conducting" polymer with a de-localized electron conduction mechanism.

We are also pursuing strategies to extend the functionality of self-limiting films by post-deposition thermal processing. Our initial studies indicate that heating POMA films at moderate temperatures under vacuum leads to cross-linking of the POMA chains. Thermally cured POMA exhibits new electrochemical features that are consistent with the formation of phenazine-like structures within the polymer film. This simple procedure increases both the capacity and the electroactive potential range of the polymer.

In order to address a greater portion of the available potential window, we have explored bilayer configurations where different polymers are grown in layers by sequential electropolymerization steps. This is accomplished by first generating an initial self-limiting polymer layer from a buffered aqueous electrolyte, followed by deposition of a second polymer layer from acidic electrolyte. The resulting bilayer exhibits voltammetric features characteristic of both polymer layers, while maintaining an ultrathin form.

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