

Designing 3-D polymer-carbon-nanoarchitecture hybrids for high-performance electrochemical capacitors

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Carbon aerogels, and related nanoarchitectures, are promising candidates as electrode platforms for batteries, fuel cells and electrochemical capacitors.^{1,2} These structures act as extended three-dimensional electrochemical interfaces, where through-connected networks of void volume promote the transport of ions and molecules to and from the amplified surface areas, and long-range electronic conduction is facilitated through the bonded solid network of the aerogel skeleton. The synthesis and processing methods for producing carbon aerogels are also highly flexible, and characteristics such as the average pore size and envelope density can be easily tuned to achieve a desired structure. Carbon aerogels offer the additional benefit of a stable monolithic structure, which mitigates the need for the binding agents often used in electrode construction.

Carbon aerogel electrodes have been extensively investigated for electrochemical capacitor applications. The structural characteristics of carbon aerogels lead to exceptional improvements in charge-discharge rate capabilities and increases in volumetric energy densities. However, because carbon aerogels store charge primarily in the electrical double-layer of the solid/electrolyte interface, they are limited to single-electrode capacitances of up to 150 F/g.³ The overall energy densities of carbon aerogels can be improved by incorporating additional functionalities that can undergo reversible faradaic reactions (i.e., pseudocapacitance), such as transition metal oxides⁴ or conducting polymers.⁵

We are creating high-performance electrode structures using carbon aerogels as 3-D templates onto which ultrathin (<15 nm), conformal polymer coatings are applied by electrodeposition.⁶ These polymer coatings are deposited under self-limiting-growth conditions so that the desirable through-connected mesoporous/macroporous pathways should be retained in the resulting hybrid structure. Although deposited under conditions where they are non-conducting, these polymer coatings become electroactive when exposed to aqueous acid electrolytes.

The self-limiting electrodeposition of conformal, ultrathin, electroactive polymers onto pre-formed, monolithic carbon aerogels yields hybrid electrode structures that exhibit characteristics of both components. Scanning electron microscopy and N₂ porosimetry measurements confirm that the initial porous morphology of the carbon aerogel is retained following the exhaustive electrodeposition of polymers such as poly(*o*-methoxyaniline), POMA. Polymer mass loadings of up to 26% have been achieved with this protocol, as shown by thermogravimetric analysis. The presence and structural identity of the resulting polymer coatings

are also confirmed by infrared, Raman, and X-ray photoelectron spectroscopy, and also by solid-state ¹³C-NMR analysis.

Figure 1 shows the voltammetric responses for a carbon aerogel before and after electrodeposition of an ultrathin polymer film of POMA. As expected for a double-layer capacitance mechanism, the voltammetric signature for an uncoated carbon aerogel is featureless. However, the POMA-coated carbon aerogel exhibits additional peaks characteristic of a faradaic pseudocapacitance mechanism.

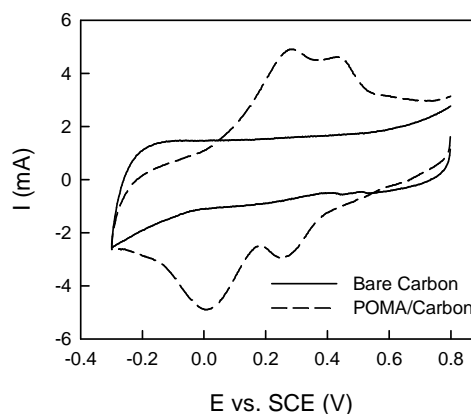


Figure 1. Voltammetric responses for bare carbon aerogel (solid line) and poly(*o*-methoxyaniline)-coated carbon aerogel (dashed line) electrodes. Scans acquired at 2 mV/s in 0.1 M H₂SO₄.

The energy-storage performance for these hybrid electrodes is substantially improved over a wide range of current demands when compared to native carbon aerogels. Galvanic charge-discharge measurements indicate that the gravimetric capacitances are increased by >50% but even greater enhancements (>100%) are observed for volumetric capacitances.⁶ In this hybrid design the greater energy-storage capacity can be introduced via the redox reactions of the ultrathin polymer coating without increasing the bulk volume of the electrode structure.

We are currently exploring new combinations of pore-solid architectures and electroactive polymers with the goal of achieving electrode structures that exhibit stability, high energy density and high power density when used as electrochemical capacitors.

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