

# CARBON AEROGELS WITH CONFORMAL, ELECTROACTIVE POLYMER COATINGS AS HIGH-PERFORMANCE ELECTROCHEMICAL CAPACITORS

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## Introduction

Carbon aerogels are attractive electrode structures for electrochemical applications due to their high surface areas, through-connected porosity, and high electrical conductivity [1,2,3]. The synthetic and processing conditions for carbon aerogels are also highly flexible, with effective control of both the predominant pore sizes in the structure, ranging from micropores to macropores, as well as the overall density of the final structure. These conductive nanoarchitectures are particularly useful as electrode platforms in electrochemical capacitors, where the inherent mesopore/macropore network of the carbon aerogel facilitates the transport of solvent and ions throughout the structure, enabling rapid charge-discharge reactions. However, the overall energy-storage capacities for carbon aerogels are limited, as they store charge primarily by a double-layer capacitance mechanism.

We extend the versatility and performance of carbon aerogels by modifying them with ultrathin ( $< 15$  nm), conformal, electroactive polymer coatings based on the self-limiting electropolymerization of *o*-methoxyaniline and related arylamine monomers. The electrodeposition conditions are deliberately chosen so that the through-connected pore network of the initial carbon aerogel is retained in the resulting polymer-carbon-aerogel hybrid [4]. Although grown under insulating conditions, these polymer coatings become electroactive when exposed to aqueous acid electrolytes. The overall energy-storage capacities of the resulting hybrid structures are greatly enhanced via the faradaic pseudocapacitance reactions of the polymer coatings. These hybrids will be designed to exploit the functions of both the polymer and carbon aerogel components to achieve electrode structures that exhibit stability, high energy density and high power density when used as electrochemical capacitors.

## Experimental

Carbon aerogels are prepared according to literature methods [5,6]. Working electrodes for electrochemical measurements are performed by immobilizing a pre-weighed (2 – 7 mg) piece of carbon aerogel in a stainless steel basket electrode, which serves as a current collector. The aerogel is carefully equilibrated with aqueous electrolyte prior to measurements to ensure that the porous structure is completely

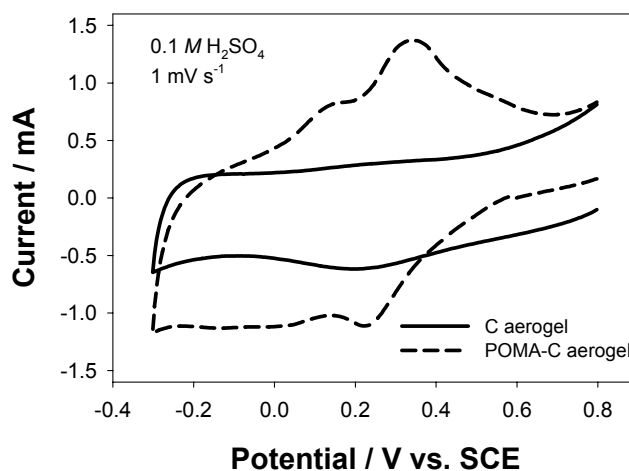
filled. The electrodeposition of self-limiting polymer coatings onto the carbon aerogel is performed in a buffered aqueous electrolyte (pH 2 – 9) containing the desired monomer, such as *o*-methoxyaniline. The electropolymerization is initiated uses a series of potential pulses, alternating between oxidizing and rest potentials. The polymer-coated carbon aerogel is then transferred to an acidic electrolyte, typically 0.1 M H<sub>2</sub>SO<sub>4</sub>, for electrochemical testing. The carbon aerogel may also be harvested for further characterization by thermal analysis, electron microscopy, or spectroscopy.

## Results and Discussion

The careful electrodeposition of ultrathin polymer coatings onto pre-formed, monolithic carbon aerogels results in hybrid nanoarchitectures that exhibit characteristics of both the electroactive polymer and carbon aerogel structure. The highly porous morphology of the carbon aerogel is preserved even after the exhaustive deposition of the polymer coating, as confirmed by scanning electron microscopy. The polymer component can be quantified by performing thermogravimetric analysis (TGA) under conditions where the polymer degrades and volatilizes but the carbon aerogel is inert. Using TGA measurements we have demonstrated that our initial polymer-carbon-aerogel hybrids contain between 10 and 26% polymer by mass. The polymer loading is dependent on a number of factors including the electrodeposition conditions as well as the particular carbon aerogel morphology. The presence of the polymer component and its chemical identity are confirmed by infrared, Raman, and X-ray photoelectron spectroscopy.

The addition of ultrathin electroactive polymer coatings to carbon aerogel electrodes leads to hybrid nanoarchitectures that exhibit significantly increased energy-storage capacity. A typical set of cyclic voltammograms for an uncoated and polymer-coated carbon aerogel is shown in Figure 1. In this case the polymer is poly(*o*-methoxyaniline), POMA, but similar results are observed for a number of other polymers. Whereas the uncoated carbon aerogel exhibits the featureless voltammogram expected for a double-layer capacitance mechanism, the POMA-coated carbon aerogel shows peaks characteristic of a faradaic pseudocapacitance mechanism.

Figure 1. Cyclic voltammograms for a 2.4-mg carbon aerogel monolith before (—) and after (---) the application of a POMA coating. The electrolyte is 0.1 M H<sub>2</sub>SO<sub>4</sub> and the voltammetric scan rate is 1 mV s<sup>-1</sup>.



Galvanostatic charge-discharge measurements are used to assess the energy-storage parameters of these electrode structures as a function of current demand. A typical data set is shown in Figure 2, where the half-cell electrochemical capacitance of a carbon aerogel is measured before and after the application of a conformal POMA coating. Even after taking into account the addition mass of the polymer component, the gravimetric (specific) capacitance of the electrode is significantly increased by the presence of the POMA coating at all current demands studied. An even greater enhancement is observed when the volumetric capacitance is considered. This is due to the fact that the polymer deposition occurs primarily within the volume of the porous carbon aerogel. Thus additional capacitance is achieved without increasing the bulk volume of the electrode structure. Due to the ultrathin, conformal nature of the polymer coatings, these enhancements in energy-storage capacity are maintained even under increased current demands.

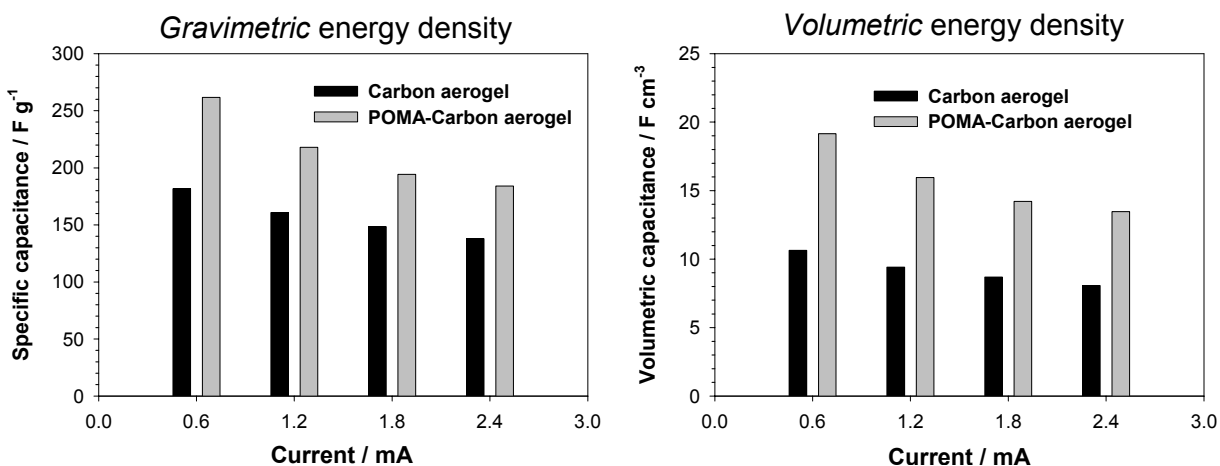


Figure 2. Capacitance values for a 2.4-mg carbon aerogel monolith before and after the application of a POMA coating. Measurements are taken in a half-cell configuration in 0.1 M H<sub>2</sub>SO<sub>4</sub>, and refer only to a single electrode.

We are currently extending this concept to include a variety of different polymer coatings, as well as different carbon aerogel morphologies. The resulting hybrids will be incorporated into two-electrode electrochemical capacitors in either a symmetric or asymmetric configuration, depending on the desired power and energy parameters.

## Conclusions

With deliberate design of the electrodeposition conditions, we can produce polymer-coated carbon aerogel electrode structures that retain the desirable porosity of the initial carbon aerogel, while also exhibiting enhanced energy-storage capabilities via the faradaic reactions of the polymer component. This hybrid design will be particularly beneficial for addressing the volumetric energy-storage requirements of many new devices where high pulse power is also desired.

## References

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