

Sulfur-functionalized carbon aerogel supports for noble-metal fuel-cell catalysts

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Carbon aerogels and related nanofoams are sol-gel-derived nanoarchitectures that exhibit the desirable characteristics of high surface area, high porosity, excellent conductivity, and stable monolithic forms. This combination of properties makes carbon aerogels attractive as platforms for electrochemical applications, especially because the through-connected pore network of the aerogel facilitates transport of ions and molecules to the amplified electrochemical interface, while electronic conduction is promoted through the bonded solid network of the aerogel skeleton. Carbon aerogels have been extensively studied for electrochemical capacitors, and exhibit high specific capacitances and favorable charge-discharge characteristics relative to other forms of carbon.¹

The investigation of carbon aerogels for fuel-cell applications has been far more limited. Fricke and co-workers developed fuel-cell electrodes based on fiber-reinforced carbon aerogels, onto which noble-metal-catalyst films were deposited.^{2,3} However, this electrode design did not yield good performance for fuel-cell reactions, presumably because the catalyst was largely limited to the boundaries of the aerogel. In order to take advantage of the 3-D structure of the carbon aerogel, these electrodes should be designed so that the electrocatalyst is distributed throughout the aerogel nanoarchitecture.

The objective of this project is to generate carbon aerogels containing well-dispersed noble-metal nanoparticles that are useful for fuel-cell catalysis. The critical step in achieving this aim involves introducing functionalities onto the carbon aerogel surfaces that serve as anchoring sites for such nanoparticles. Our approach is to modify the precursor resorcinol-formaldehyde (RF) gels with 3-thiophenecarboxyaldehyde during the initial processing to form a polymer gel. Following supercritical-fluid extraction to obtain the highly porous RF aerogel, these materials are subsequently pyrolyzed, yielding the electronically conductive carbon aerogel. Thiophene-like sulfur functionalities are retained in the resulting carbon aerogel (designated as C~S aerogel), as indicated by X-ray photoelectron spectroscopy, with sulfur contents ranging from 0.1 to 1 atom %.⁴

Functional catalytic nanoarchitectures are achieved by stirring coarse powders of the C~S aerogel with colloidal suspensions of ~2-nm Pt. The C~S aerogel readily de-colorizes the brown Pt sol, indicating that Pt nanoparticles are immobilized on the carbon surface. By contrast, freshly prepared carbon aerogels without sulfur functionalization do not readily adsorb Pt colloids. This sulfur-mediated binding of pre-formed Pt colloids on the C~S aerogel mimics the behavior of commercially available Vulcan carbon, which is known to have thiophene-

like surface moieties.^{5,6} Transmission electron microscopy images show that the Pt nanoparticles are well-distributed over the surface of the C~S aerogel with minimal aggregation. These TEM studies further confirm that the Pt nanoparticles are located on surfaces exposed to mesoporous or macroporous pathways, where access to fuel/oxidant is optimized. This catalyst deposition strategy avoids the "hidden Pt" problem that occurs with other catalyst designs, where some Pt nanocrystallites become trapped and inaccessible within micropores, which are pervasive features in many high-surface-area carbons.

The electrochemical properties of Pt-modified C~S (Pt/C~S) aerogels were initially investigated under half-cell, flooded electrolyte conditions, both to assess the electrochemical accessibility of the catalytic sites, and to test the catalytic activity for the oxygen-reduction reaction (ORR). Using CO-adsorption stripping voltammetry we determined that up to 86% of the predicted surface atoms of Pt are electrochemically accessible. Preliminary tests also indicate the Pt/C~S aerogels exhibit ORR mass activities that are at least comparable to commercial Pt/Vulcan-carbon catalysts. In future studies we will focus on optimizing both the sulfur content and the pore-solid architecture (mesoporous vs. macroporous) of these aerogels in order to achieve desirable fuel-cell performance.

ACKNOWLEDGEMENTS

This work is supported by the Office of Naval Research.

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