

SULFUR-FUNCTIONALIZED CARBON AEROGEL SUPPORTS FOR NOBLE-METAL FUEL-CELL CATALYSTS

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Introduction

Carbon aerogels offer several advantages over traditional carbon supports for fuel-cell catalysis including large surface areas (typically > 500 m²/g), high-fractional-mesoporous pore volumes for analyte transport, synthetic control over structural properties such as density and pore-volume distribution, and availability in monolithic forms. Carbon aerogels, which were introduced in the late 1980s, are prepared via a base-catalyzed condensation reaction between resorcinol (R) and formaldehyde (F) leading to gel formation that is accelerated by curing [1, 2]. Critical-point drying of the RF gel is followed by pyrolysis to produce a conductive carbon aerogel. The carbon aerogel morphology may be tailored by varying such parameters as the resorcinol/catalyst ratio (R/C), the curing temperature, and the reactant concentration [1, 2, 3, 4].

Previous reports of carbon-aerogel-based fuel-cell electrodes have focused on the development of fiber-reinforced carbon aerogels onto which noble-metal-catalyst films are deposited [5, 6]. Because poor catalyst distribution limits fuel-cell performance and diminishes the advantages associated with a high-surface-area support, it is desirable to develop more homogeneous electrode architectures. The objective of this project is to prepare carbon aerogels having well-dispersed Pt nanoparticle catalysts and to explore their use as catalytic electrode materials. Carbon aerogel supports were modified with thiophene functionalities in the RF state, and then the dried, pyrolyzed, ground carbon aerogels were exposed to pre-formed Pt colloids. The sulfur-mediated binding of Pt metal in the carbon aerogel mimics the noble-metal binding strategy of commercially available Vulcan carbon. The Pt-modified carbon aerogels were investigated for electrochemical addressability of the catalyst particles and for oxygen reduction reaction (ORR) activity.

Experimental

Traditional resorcinol/formaldehyde condensation chemistry and a low-temperature curing strategy are employed to prepare the RF gels [2, 3]. Heterocyclic sulfur is incorporated into the carbon aerogel by modifying resorcinol-formaldehyde (RF) gels with 3-thiophenecarboxaldehyde prior to critical-point drying and pyrolysis, as shown in Figure 1. The thiophene-modified RF aerogel retains its sulfur functionality following pyrolysis, allowing for Pt-nanoparticle binding. The chemical bond between

the noble-metal particle and the sulfur group will also discourage particle ripening during fuel-cell operation.

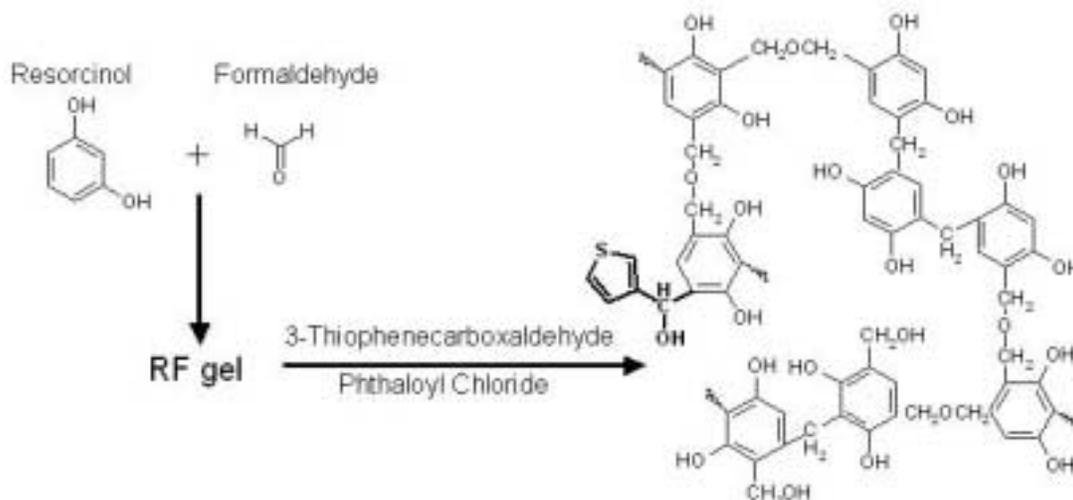


Figure 1. Synthetic strategy for preparing sulfur-modified carbon aerogels.

Powdered forms of sulfur-functionalized (C~S) and sulfur-free carbon aerogels were stirred with a 2.5-nm Pt sol. The Pt sol visibly decolorized upon mixing with the ground C~S powder, while the sulfur-free powder only minimally decolorized the Pt sol. This result illustrates the efficacy of the Pt-S binding mechanism and the accessibility of the sulfur-binding sites to the Pt sol.

The ground materials were characterized by TEM and XPS (on Sn foil). Electrochemical analyses were performed on Nafion-coated thin film samples adhered to a 5-mm-diameter glassy carbon electrode. The thin films were prepared using a sample preparation strategy developed for analyzing supported-catalyst powders [7]. CO-stripping voltammetry and oxygen-reduction measurements were done in 1.0 M H₂SO₄ at 25°C.

Results and Discussion

The immobilization of the Pt colloid by the sulfur-modified carbon aerogel is further illustrated by the TEM data shown in Figure 2. The micrograph indicates that most of the Pt adheres to the surface of the mesoporous carbon aerogel powder. The 2.5-nm average Pt colloid diameter should not adsorb on surfaces within electrochemically inaccessible micropores, thereby improving catalyst utilization.

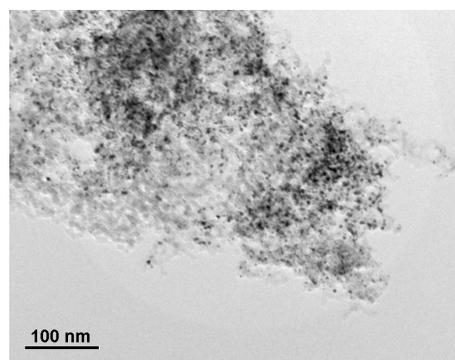


Figure 2. TEM of Pt colloid supported on C~S aerogel (R/C 200).

The XPS spectra obtained from a C~S aerogel modified with Pt colloid (Pt/C~S) are shown in Figure 3. The peaks in the S 2p region (Figure 3a), which are not observed for carbon aerogels with no thiophene modification, show the successful inclusion of sulfur in the aerogel architecture. The S 2p peak at 162.1 eV is indicative of either elemental or thiophene-like sulfur while the large signal at 168.8 eV is typical of sulfate. The chemical origin of the sulfate signal is currently under investigation. The combined sulfur signal for our C~S samples ranges from 0.1 to 1.0 atm % relative to the integrated C 1s peak, similar to measured values for Vulcan carbon [8, 9]. The adsorption of Pt colloid is also confirmed in the XPS spectra (Figure 3b). Platinum 4f peaks centered at 72.0 and 74.9 eV are observed for the C~S samples which have been mixed with the colloidal sol.

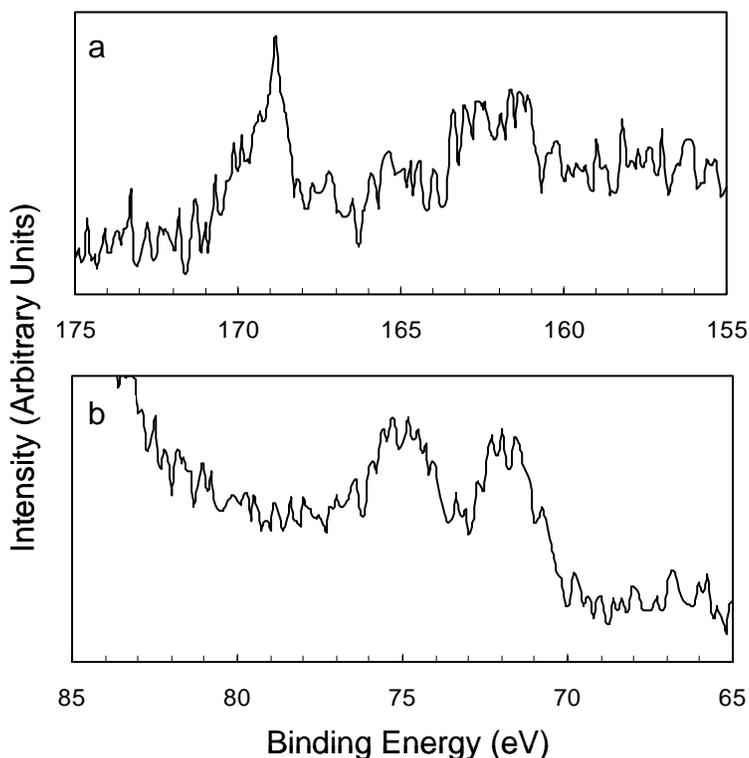


Figure 3. XPS of (a) S 2p and (b) Pt 4f regions of Pt/C~S sample (R/C 500).

Figure 4a depicts the voltammetric stripping of CO which has been chemisorbed on a Pt/C~S aerogel powder (10 wt% Pt, R/C 500). Platinum-free C~S powder shows only capacitive current in the CO oxidation region (not shown), indicating that the carbon aerogel possesses no significant CO binding sites. These voltammetric measurements demonstrate that the tethered Pt colloid is electrochemically addressable and in this particular case, exhibits 19% surface-atom accessibility for CO adsorption. Higher surface-atom accessibility (up to 78%) has been observed for Pt/C~S R/C 200 and the causes for this variation are under investigation [9]. Figure 4(b) shows that the C~S/Pt material exhibits catalytic activity for oxygen reduction in an oxygen-saturated acid electrolyte. In contrast, voltammograms obtained from Pt-free C~S aerogels (not shown) show no measurable response for oxygen reduction in the same potential window. Preliminary mass-normalized activities show that the Pt/C~S ground powders have similar catalytic activities as commercially available Pt/C catalysts [9]. These results indicate that an optimized Pt/C~S architecture, particularly one that possesses the advantages of a monolithic form, may yield performance advantages over traditional fuel-cell electrode materials.

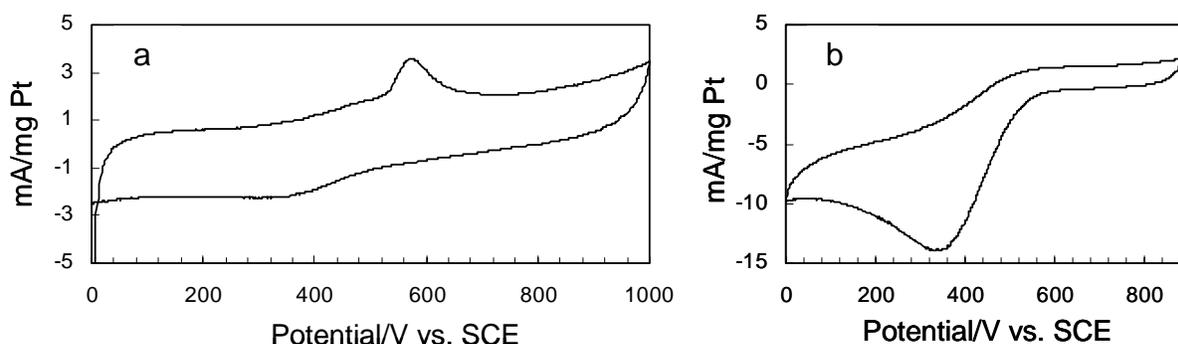


Figure 4. Cyclic voltammetry of (a) Pt/C~S sample after exposure to CO and an Ar purge to remove solution-phase CO (scan rate: 5 mV/s) and (b) Pt/C~S sample in an oxygen-saturated solution (scan rate: 5 mV/s). Pt/C~S samples are 10 wt % in Pt and were prepared using R/C 500.

Conclusions

The modification of carbon aerogel architectures with sulfur functionalities has been achieved by reacting the gel in its wet RF state with 3-thiophenecarboxaldehyde in the presence of phthaloyl chloride. The thiophene sulfur is retained in the aerogel architecture upon critical-point drying and pyrolysis, and the sulfur content is similar to that of commercially available Vulcan carbon, as evidenced by XPS. Platinum nanoparticles spontaneously adsorb to ground C~S aerogel powders, but not to sulfur-free carbon aerogels, and TEM data show that the Pt is well distributed on the surface of the carbon aerogel. Voltammetric stripping of adsorbed CO shows that the Pt colloids are electrochemically accessible and oxygen reduction data demonstrate that the materials have promise for potential fuel-cell applications.

References

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