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Preparation of Macroporous Conductive Carbon Aerogels from Pyrolysis of Isocyanate-Crosslinked Resorcinol Formaldehyde Aerogels

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INTRODUCTION

Carbon aerogels combine typical aerogel properties such as high surface area and low density with electrical conductivity.¹ They are prepared by pyrolysis under N₂ or Ar at 600-2100 °C of resorcinol formaldehyde (RF) aerogels, which in turn are prepared via aqueous sol-gel chemistry.² Carbon aerogels are considered for numerous applications such as separation media in HPLC, as supercapacitors, as materials for hydrogen storage, as non-reflective materials, and as anodes in lithium-ion batteries.³⁻⁶

Meanwhile, porous carbons with high hydrophobic surface areas and large pore volumes are used as industrial adsorbents. In addition, macropores enhance mass transport for applications in energy storage and lithium intercalation batteries.⁷ It is well-established with silica that monodispersed polystyrene beads can be used to introduce ordered mesoporosity or macroporosity.^{8,9} In the same approach, polystyrene beads have been also incorporated as templates in RF sol-gel matrices and have been removed later by dissolving in toluene. Here, we report that RF gels crosslinked with isocyanates yield macroporous, electrically conducting carbon aerogels without need for templating.

EXPERIMENTAL

Preparation of Native RF Aerogels and their Crosslinking with Isocyanates. Wet RF gels were prepared by mixing at room temperature two solutions: solution "A" containing 0.337 g (0.003 mol) of resorcinol, 0.477 mL (0.006 mol) of the commercially available formaldehyde solution and 11.5 mL CH₃CN; and, solution "B" containing 0.636 mL CH₃CN and 0.03 mL (0.363 mmol) of concentrated HCl as reported earlier.¹⁰ The crosslinking solution was prepared by mixing 11 g of isocyanates (Desmodur N 3200 or Desmodur N 3300) oligomer in 94 mL of anhydrous acetone with 0.1172 mL (0.1% w/w) anhydrous triethylamine.¹¹ Wet RF gels, after washing with acetone (3x, 8 h, 20 mL each time), were placed in the crosslinking solution where the isocyanate crosslinker was allowed to diffuse into the wet gels and to equilibrate for 24 h. After heating at 55 °C for 24 h, the containers were cooled to room temperature and gels were removed and placed in fresh acetone. After washing with acetone (3x, 8 h, 20 mL each time), the gels were dried in an autoclave with liquid CO₂, taken out at the end supercritically to form crosslinked RF aerogels (X-RF aerogels), as shown in Scheme 1.

Preparation of Carbon Aerogel Derivatives of Native and Crosslinked RF Aerogels. Native RF aerogels and the X-RF gels crosslinked with Desmodur N3200 or Desmodur N3300 were pyrolyzed in a tube furnace in the presence of inert atmosphere of flowing Ar. Prior to the pyrolysis, Ar was flown for 10 min to replace the air in the tube. The X-RF aerogels in a tube furnace were heated to 800 °C with a heating rate of 5 °C min⁻¹. After 3 h of heating, the hot tube furnace was allowed to cool slowly under Ar.

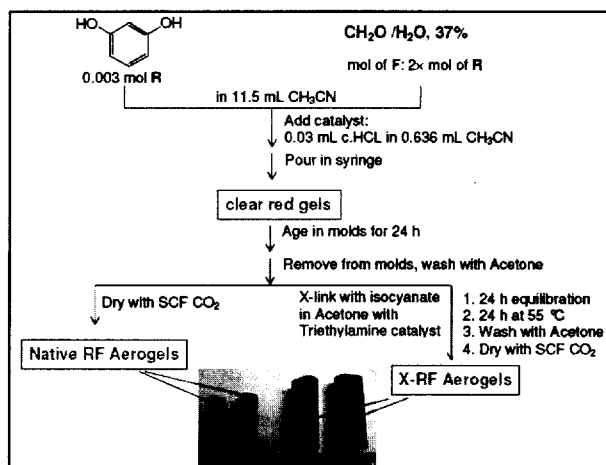
Preparation of High Porosity-High Conductivity Carbon Aerogels. Macroporous carbon aerogel chunks prepared by pyrolysis of X-RF aerogels prepared by crosslinking with Desmodur N3300 were immersed in an RF sol which gelled at room temperature in 2h. The composite gel was processed into a aerogel, which was further pyrolyzed under the same conditions as above to form a mesoporous carbon aerogel nested inside a macroporous carbon aerogel network.

RESULTS AND DISCUSSION

Shrinkage of RF aerogels during supercritical drying is a major issue during preparation of low density RF aerogels. Minimization of

that shrinkage has been demonstrated by crosslinking the RF wet gels with isocyanate. The di- or tri-isocyanate solution in acetone was introduced into the mesopores of acid catalyzed RF wet gels and was allowed to react with surface hydroxyls. Triethylamine, was used as base catalyst to increase the nucleophilicity of the aromatic hydroxyl groups.

Scheme 1. Preparation of X-RF aerogels.



As shown in photograph in Scheme 1, native RF aerogels shrink a lot whereas their crosslinked counterparts exhibit minimal shrinkage. All pertinent physical characterization data are summarized in Table 1.

Table 1. Physical Characterization Data for Native RF Aerogels and Isocyanate Crosslinked RF Aerogels Processed Under Various Conditions

Crosslinking Conditions (11 g of Isocyanate in 94 mL of Acetone)	Dia (cm)	Bulk Density (g cm ⁻³)	Skeletal Density (g cm ⁻³)	Porosity (% Void Space)	BET Surf. Area [avg. Pore Dia, b] (m ² g ⁻¹ [nm])	Particle Dia (nm)	% Shrink
-	0.65 ± 0.02*	0.136 ± 0.008*	1.363 ± 0.056	90	318 [14.7, 83.3]	13.8	39
N3200	0.83 ± 0.02*	0.135 ± 0.005*	1.288 ± 0.032	90	363 [7.5, 73.1]	12.8	21
N3200 + 0.1% TEA (w/w %)	0.89 ± 0.01*	0.126 ± 0.004*	1.2339 ± 0.017	90	396 [8.3, 72.0]	12.3	15
N3300	0.82 ± 0.01*	0.125 ± 0.006*	1.323 ± 0.039	91	387 [8.4, 74.9]	11.7	22
N3300 + 0.1% TEA (w/w %)	0.91 ± 0.01*	0.120 ± 0.005*	1.196 ± 0.023	90	396 [7.8, 75.7]	12.7	13

a: average of 3 samples;

b: by the $4V_{Total}/a$ method (where V_{Total} : mass specific total pore volume, a : mass specific surface area by the BET method). V_{Total} has been calculated by two methods, hence the two numbers cited for the Average Pore Diameter: first automatically by the system software from single point volume measurements of N₂ adsorbed, and second manually from the bulk and skeletal densities via $V_{Total} = (1/\rho_b) - (1/\rho_s)$, where ρ_b and ρ_s represent the bulk and skeletal densities, respectively).

Microscopically, both native and crosslinked aerogels look indistinguishable and consist of agglomerations of primary and secondary particles, akin to silica aerogels. The SEM data suggest that the polymer has coated the surfaces of the particles conformally, leaving the internal empty mesoporous space intact. The uptake of isocyanate by RF gels was confirmed by infrared (IR) spectroscopy and ¹³C CPMAS solid NMR. Scheme 2 shows that the pyrolysis of native RF aerogels and crosslinked RF aerogels, carried out under inert conditions, lead to carbon aerogels with different morphologies. The carbon aerogels prepared from native RF aerogels are brittle and with dull black color, whereas the carbon aerogels prepared with X-RF aerogels crosslinked with N3300 are sturdy, shiny and glassy in appearance.

The SEM of carbon aerogels derived from native RF aerogels show the mesoporous morphology inherited from RF aerogel precursors. This was confirmed by N_2 adsorption porosimetry isotherm by exhibition of characteristic type IV isotherms. The electrical conductivity measured with four probe conductivity meter on the flat surface of polished carbon aerogel shows surface conductivity of 27.6 mho/m. The SEM image of carbon aerogels derived from X-RF aerogels prepared by heating wet RF gels with N3300 in the presence of catalyst, shows the macroporous morphology may be assigned to the gases evolved with the isocyanate crosslinked polymer. The four probe conductivity measurement exhibited the surface conductivity of 57.1 mho/m, which is almost two times that of the carbon aerogels prepared from native RF aerogels. Table 2 shows the physical characterization of carbon aerogels derived from native RF and X-RF aerogels.

Scheme 2. Conversion of native RF aerogels and X-RF aerogels to carbon aerogels.

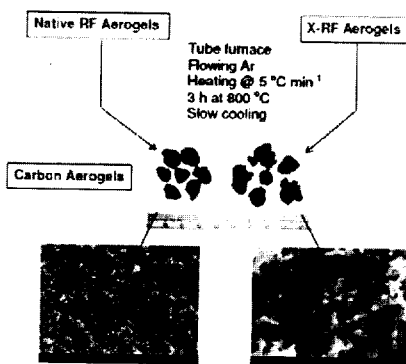


Table 2. Physical Characterizations of Carbon Aerogels Derived from Native RF and X-RF Aerogels

Carbon Aerogels Derived by Pyrolysis at 800°C from:	Bulk Density (g cm ⁻³)	Skeletal Density (g cm ⁻³)	Porosity (% void space)	BET Surf. Area [avg. Pore Dia] (m ² g ⁻¹ (nm))	Particle Diameter (nm)
Native RF aerogel	0.138 ± 0.024	2.146 ± 0.121	93	626[14.2]	4.46
X-RF aerogel (Crosslinked with N 3300)	0.254 ± 0.082	1.866 ± 0.011	86	17[18.7]	189

As shown in Figure 1, the oxidation of ferrocene (3 mM) was carried out with platinum disk electrode as well as carbon aerogel electrode derived from X-RF aerogel. The behavior of carbon aerogel was similar to that of Pt disk electrode.

oxidation of ferrocene (3 mM) in $CH_3CN/0.1$ M TBAP, 0.1 V s⁻¹

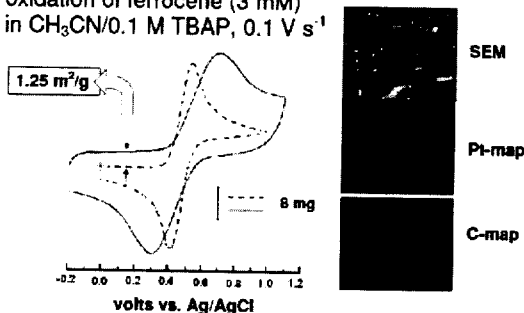
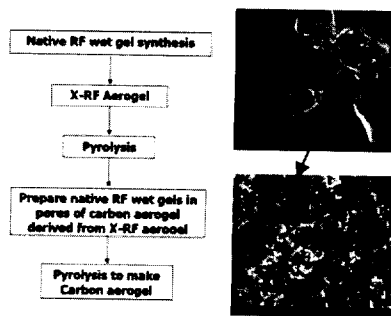


Figure 1. Oxidation of ferrocene with Pt disc electrode and carbon aerogel derived from X-RF aerogel, SEM image and EDS maps for carbon and platinum of carbon aerogel surface after electrodeposition of platinum.

The cyclic voltammogram of ferrocene with carbon aerogel electrode exhibits characteristic features of a high surface area electrode. The accessible surface area for electrochemistry was calculated as 1.25 m²/g. In order to prove the potential of carbon aerogel electrode in fuel cell application, we have electrochemically deposited platinum on the surface of carbon aerogel electrode from a solution of potassium tetrachloroplatinate (II) (3 mM) in water/KCl (0.1 M). The SEM image and the EDS spectra obtained by surface mapping show the presence of islands of platinum all over the surface.

The carbon aerogels derived from native RF aerogels have large surface area but low electrical conductivity (27.6 mho/m) and poor mechanical integrity. On the other hand, the carbon aerogels prepared from X-RF aerogels have low surface area but high electrical conductivity (57.1 mho/m) and very good mechanical integrity. In order to take advantage of the properties of both high surface area as well as high electrical conductivity, we nested mesoporous carbon aerogels in their macroporous counterparts by the method outlined in Scheme 3.

Scheme 3. Preparation of high porosity-high conductivity carbon aerogels



CONCLUSION

The crosslinked RF aerogels is a new class of materials, in which the macroporosity comes from gases (CO_2 , NO_2 , etc.) evolving during the pyrolysis process. These new materials could be used as efficient high surface area electrodes. RF aerogels are pursued in their own right (thermal insulation) but mostly as precursors of carbon aerogels. In turn, carbon aerogels are used in a variety of commercial applications such as supercapacitors, Li intercalation batteries, fuel cells, etc. The macroporous, high conducting carbon aerogels can be prepared easily and in short time without the use of external templating agents.

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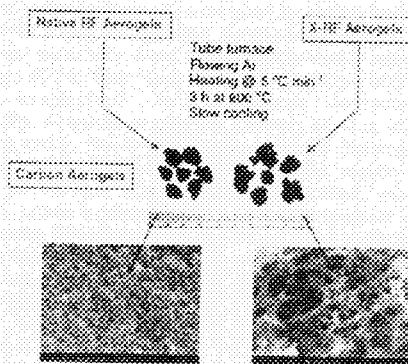


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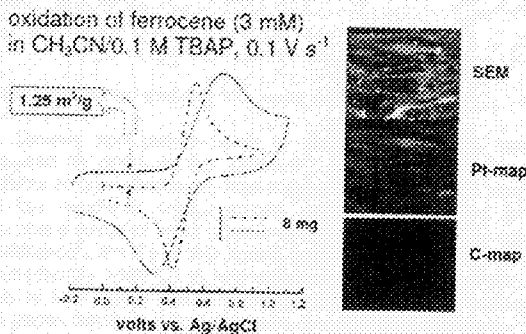
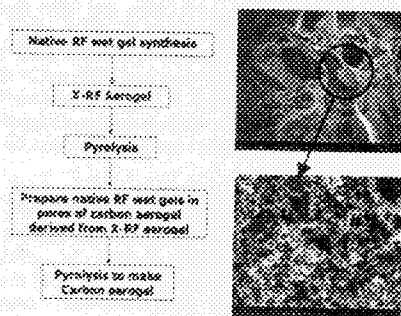


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