Proton-Conducting Solid Electrolyte via Ozonolysis of Cationic Ammonium Organoalkoxysilane Surfactant-Templated MCM-41

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Fuel cells have gained worldwide attention because of their ability to efficiently convert chemical energy directly into electrical energy with zero or near-zero emissions. The direct methanol fuel cell (DMFC) in particular is one in a family of five distinct types of fuel cells that operates at low temperature (80−90 °C) with easy refueling capabilities. The polymer electrolyte membrane (PEM) is a pivotal component of the DMFC because it maintains charge balance by selectively facilitating proton transport between the anode and cathode. The most widely used PEMs are hydrated perfluosulfonic acid polymers, such as Nafion. Nafion exhibits excellent proton conductivity when hydrated. However, at high temperatures, the polymer suffers a loss in conductivity due to dehydration and a loss of fuel separation due to polymer swelling (leads to methanol cross over). In the past decade, several solid proton conductive materials have been proposed as alternatives to Nafion. Some of these include sulfonated polymers such as sulfonated polysulfone,[1] poly(ether ether ketone),[2] polyimides,[3] and poly(benzene-imidazole).[4] Although each material has its advantages, they all fail to curb methanol diffusion because of the swelling of their soft polymeric backbone upon hydration.

In an effort to circumvent the polymer swelling problem, several groups have investigated a new class of PEMs based on proton-conductive sulfonated mesoporous silicas.[5−7] These organically modified silica mesostructures, typically prepared by surfactant-templated hydrothermal synthesis, have several properties amenable to their use as solid electrolytes. Some of these properties include high specific surface areas, zero electrical conductivity, open ordered channels of variable dimensions, and high chemical, structural, and mechanical stability. More specifically, their condensed silica wall structure prohibits swelling when hydrated. These materials that typically contain sulfonated aromatic groups, which are placed onto the silica surface via grafting or through co-condensation of organosilanes with the silica precursores used in the synthesis, suffer from desulfonation and low loadings (<1.8 mmol/g). In order to overcome these limitations, preparation methods involving alkyl sulfonation[5] and the use of other acidic groups such as phosphoric acids[8] and doped nitrogen heterocycles[9] have been examined.

Here, we report on the synthesis of densely packed carboxylic acid groups within MCM-41 as a way to enhance proton conductivity in these types of solid electrolytes. Our strategy involves the use of functional surfactants that can be permanently attached to the pore walls during MCM-41 synthesis. These modified surfactants have a siloxane head group capable of being incorporated into the pore walls during the assembly of the mesoporous structure and a cleavable olefin unit embedded within the hydrophobic surfactant tail to generate the desired acid group after MCM-41 formation. This approach, by virtue of the assembly mechanism, will place the organic groups exclusively on the inner pore walls of MCM-41 at a high loading unattainable by either grafting or co-condensation.

The functional surfactant with the olefin at the C-4 position was prepared as shown in Scheme 1. Details of the synthesis are provided in the Supporting Information.

The functional surfactant, **8**, was dissolved in water under vigorous stirring at room temperature followed by simultaneous addition of tetramethylammonium hydroxide (TMAOH) and tetraethyl orthosilicate (TEOS). The resulting gel with a composition of 1:0.4:0.4:80 TEOS:surfactant:TMAOH:H_2O was aged at 100 °C for 24 h. The white precipitate formed was filtered and washed with deionized water and acetone and dried overnight at room temperature. Cleavage at the olefin functional group was carried out via ozonolysis by bubbling ozone through a suspension of the hybrid MCM-41 material in dichloromethane at −78 °C. Subsequent oxidation of the resulting solid with formic acid and hydrogen peroxide in water followed by a 1N hydrochloric acid post-treatment gave the corresponding pendent alkyl carboxylic acid groups. The solids were then washed with ethanol at 50 °C and dried to remove adsorbed species.

The powder XRD pattern of the as-made material before ozonolysis shows three well-resolved peaks in the low-angle diffraction region that can be indexed to the 100, 110, and 200 diffractions characteristic of the well-ordered two-dimensional hexagonal structure of MCM-41 (Figure S-1 in the Supporting Information). A similar diffraction profile is obtained after ozonolysis albeit of lower intensity than in the as-made material, indicating a slight loss in structural integrity (Figure S-2 in the Supporting Information). Nevertheless, the existence of the characteristic low-order peaks indicates preservation of long-range order after ozonolysis and acid treatment.

The structural details of the encapsulated functional surfactant and pendent acid chain upon ozonolysis in the

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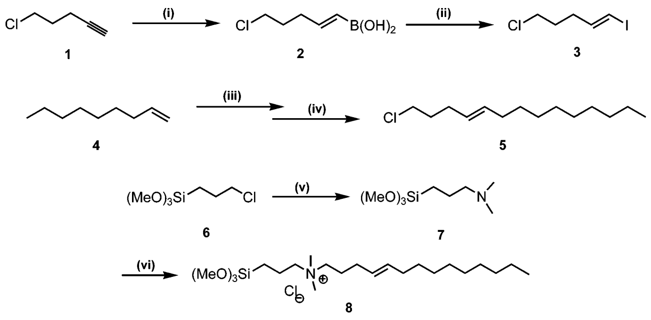
Scheme 1. Synthesis of C_4 Functional Surfactant



(i) a. Catecholborane, neat, 100 °C, 3 h; b. H_2O, 70 °C, 2 h. (ii) Iodine, NaOH, ether, 0 °C, 0.5 h. (iii) 9-BBN, THF, 0 °C to r.t., 6 h. (iv) $PdCl_2$(dppf), NaOH, reflux, 16 h. (v) dimethylamine, MeOH, 95 °C, 24 h. (vi) 5, MeOH, 95 °C, 84 h.

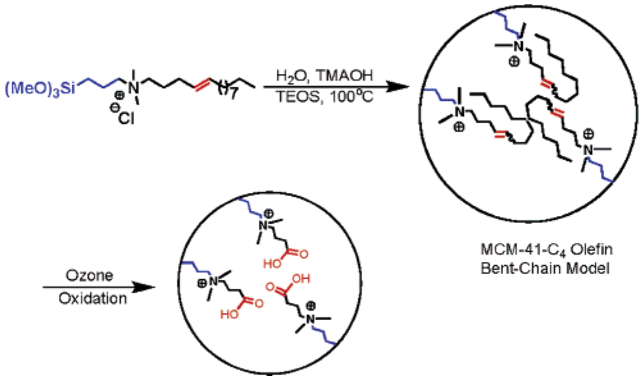


Figure 1. Schematic diagram of the preparation of MCM-41-C_4-acid

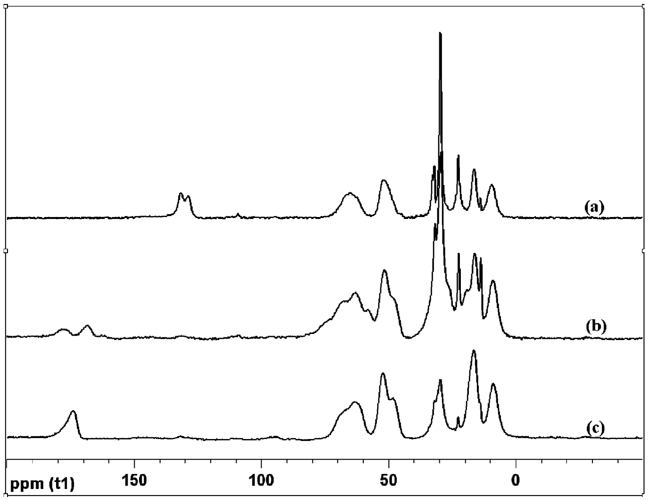


Figure 2. ^{13}C CP MAS NMR of (a) as-synthesized hybrid material, (b) after ozonolysis, and (c) after 1 N HCl treatment.

MCM-41 materials were investigated by ^{13}C cross polarization (CP) magic angle spinning (MAS) NMR. The chemical shift of the functional surfactant in the as-synthesized composite material is dominated by a strong resonance at 30 ppm attributed to the methylene carbons on the surfactant tail (Figure 2a). The olefin carbons appear at 129 and 132 ppm, respectively, whereas the other characteristic surfactant peaks mirror those of **8** in the liquid phase ^{13}C NMR (Figure S-3 of the Supporting Information). These data show that the functional surfactant **8** is stable to the hydrothermal alkaline hydrolysis conditions.

After ozonolysis, the two olefin peaks dissappear and are replaced by two carbonyl peaks at 174 and 168 ppm (Figure 2b). The peak at 168 ppm corresponds to the acid anhydride, whereas that at 174 ppm represents the free acid. The presence of the anhydride, formed via condensation of two pendent acid groups, highlights the proximity of the acid groups to one another within the MCM-41 material. Further acid treatment converts the anhydride groups into their respective free acids, as shown by the single carbonyl peak in Figure 2c. Titration of the ozone-treated material confirmed the presence of acid groups. The acid content of 2.1 meq H^+/g determined by titration is in good agreement with the estimated organic loading of 2.2 mmol/g from thermogravmetric data (Figure S-4 in the Supporting Information). This organic loading exceeds the values obtained from grafting and co-condensation preparation methods.[6,10−12]

Polymerization of the surfactant head group into the walls of MCM-41 was confirmed by ^{29}Si CP/MAS NMR (Figure S-5 in the Supporting Information). The two broad resonance peaks at −58 and −65 ppm are assigned to the Si species covalently bonded to carbon atoms T^2 [C-$\boldsymbol{Si}$(OH)$(OSi)_2$] and T^3 [C-$\boldsymbol{Si}$$(OSi)_3$] respectively, whereas those at −88, −97, and −108 ppm represent the silica sites Q^2 [$\boldsymbol{Si}(OH)_2(OSi)_2$], Q^3 [$\boldsymbol{Si}(OH)(OSi)_3$], and Q^4 [$\boldsymbol{Si}(OSi)_4$], respectively. The large ratio of T to Q sites supports the large organic incorporation estimated by both the TGA and columetric titration methods. The nitrogen adsorption isotherm (Figure S-6 in the Supporting Information) shows negligible adsorption. This can be rationalized by assuming a bent-chain configurational model (Figure 1) as opposed to a straight chain model (Figure S-7 in the Supporting Information). An estimate of 27 Å (using d_{100} from XRD Data) obtained for the pore diameter by assuming a typical MCM-41 pore wall thickness of 10 Å[13] is consistent with the estimated aggregate diameter of 25 Å predicted by the bent-chain model as depicted in Figure 1. Cleavage of the olefin functional group based on this model as shown in Figure 1 would lead to a nonporous MCM-41-C(4)-acid. An investigation into pore expansion and mesoporosity via the use of organic auxiliaries is currently underway.

Proton conductivity measurements were performed on thoroughly water-washed solid samples at 100% R.H. using two-electrode impedance spectroscopy (details provided in the Supporting Information). The MCM-41-C(4)-acid gives a conductivity of ca. 0.6 mS cm^{-1} (Figure 3) under ambient conditions. This value is an order of magnitude higher than both the nonporous as-synthesized material (C(4)-olefin) and mesoporous MCM-41, and illustrates the importance of the acid groups toward conductivity. The carboxylic acid grafted MCM-41 (0.85 mmol/g; Scheme S-1 in the Supporting Information) gives a 5-fold decrease in conductivity compared to the MCM-41-C(4)-acid and shows that the conductivity is not a linear function of acid concentration.

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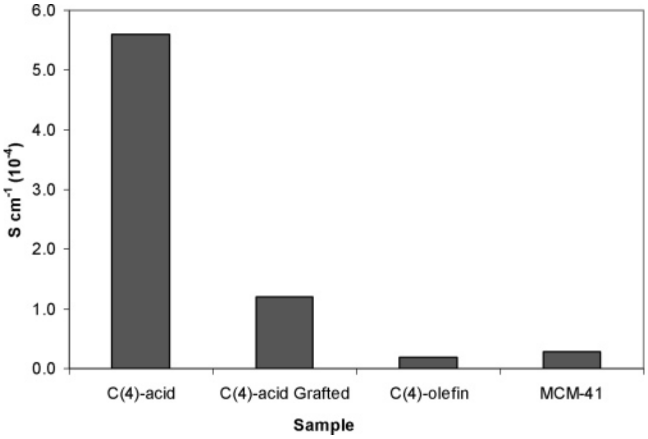

Figure 3. Proton conductivity at room temperature. Each data point represents an average of nine experiments.

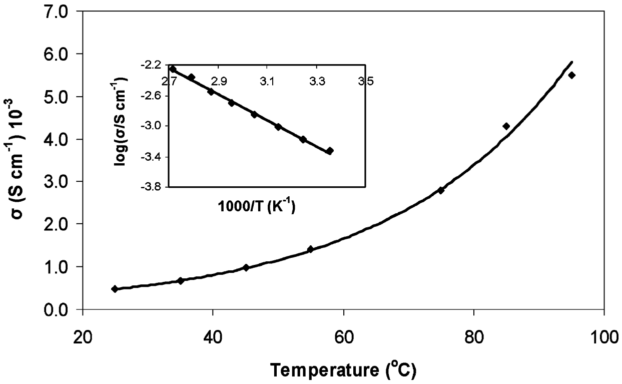

Figure 4. Proton conductivity of the C_4-acid between 25 and 95 °C. Insert: Arrhenius plot of the conductivity of the C_4-acid. Each data point represents the average conductivity over a 5 min period.

To probe the proton-transfer mechanism, we performed a temperature-dependent study on the MCM-41-C(4)-acid. As shown in Figure 4, the conductivity of this material increases exponentially with temperature to ca. 6 mS cm^{-1} at 95 °C. Mesoporous materials typically show a decrease in conductivity with increasing temperature due to evaporation of water within their pore channels.[14] The higher conductivities of the MCM-41-C(4)-acid at elevated temperatures indicate that either the material has a strong affinity for water or there is an alternate form of proton transport other than the vehicular mechanism. The former can be discounted on the basis of the fact that TGA results show negligible water adsorption even at room temperature (ca. 9 mg H_2O/g composite material). These results, along with the fact that proton transport does not scale linearly with acid concentration at room-temperature, suggest the presence of an alternate or additional form of proton transport such as structral diffusion, which is typical of materials containing well-oriented carboxylic acid groups.[15] The activation energy (E_a) was determined from the Arrhenius plot (Figure 4, insert) to be 14.2 kJ/mol.

In conclusion, we have synthesized a new surfactant with a siloxane head group and a cleavable olefin unit at the C(4) position within the surfactant tail and have demonstrated its use toward the synthesis of MCM-41. Ozonolysis of the as-synthesized MCM-41-C(4)-olefin generates a nonporous proton-conducting solid acid with a moderate conductivity of 6 mS cm^{-1} at 95 °C. The lack of porosity and a potentially low methanol uptake in the MCM-41-C(4) acid, along with an increased acid density and thus conductivity (cf. to materials prepared via conventional methods), makes inorganic−organic acid hybrid materials prepared via this methadology promising alternatives for PEMs in DMFCs. The synthetic method described herein for the introduction of new functionalities at high concentrations selectively within the pore walls of MCM-41 may lead to alternative designs of new solid-state polymeric inorganic−organic materials exhibiting interesting transport properties.

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Supporting Information Available: Detailed experimental procedures for the preparation of **8**, electrochemical impeadance spectroscopy setup and conditions, Figures S-1−S-7 and Scheme S-1. This material is available free of charge via the Internet at http://pubs.acs.org.

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