

## Novel High Temperature Polymer/molecular Sieve Composite Membranes for Direct Methanol Fuel Cells

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Proton exchange membrane fuel cells (PEMFC) occupy a prominent position as the next generation clean energy source for transportation and small-scale stationary power generation.<sup>1</sup> Methanol is an attractive fuel because it is relatively inexpensive, readily available, easily stored and transported. A key component of direct methanol fuel cells (DMFC) is the proton exchange membrane, which is required to have high proton conductivity at elevated temperatures (110-160°C)<sup>2</sup> and methanol barrier properties. Various perfluorosulfonic acid polymer membranes such as Nafion<sup>®</sup>, have been developed. However, these membranes need to be hydrated to retain high proton conductivity, which is a problem when operating at higher temperatures. Another disadvantage of perfluorosulfonic acid polymer membranes is their high methanol permeability, which lowers the fuel cell efficiency.

Here, we report the preparation of novel polymer/molecular sieve composites we are currently investigating for end use as membranes in DMFC applications. Anticipated advantages of this approach include thermal stability at elevated temperatures, low methanol uptake, and enhanced water retention.

Two types of materials have been prepared. The first is a polyaniline/mesoporous SBA-15 composite (PANI-SBA-15). To prepare this material, an aniline functionalized mesoporous molecular sieve in which the pore walls are decorated with aminophenylsilane was synthesized (aniline-SBA-15). After extraction of the block copolymer template, aniline monomers were introduced into the pores, and then polymerized in the presence of ammonium persulfate to form PANI-SBA-15. Powder X-ray diffraction patterns for both materials indicate well-ordered mesoporous structures with a  $d_{100}$ -spacing of  $\sim 9$  nm, which is similar to published literature.<sup>3</sup> A scanning electron micrograph (Figure 1) of the PANI-SBA-15 composite after the excess PANI was Soxhlet extracted with NMP shows small particles ( $\sim 1 \mu\text{m}$ ). IR spectra (Figure 2) of the aniline-SBA-15 and PANI-SBA-15 composites indicate the presence of polyaniline with characteristic bands at 1414 and 1514  $\text{cm}^{-1}$ . TGA reveals that the PANI-SBA-15 composite contains  $\sim 15\%$  PANI. Preliminary impedance spectroscopy studies show proton conductivity in the  $10^{-3}$  S/cm range.

The other composite material we are investigating utilizes linear polyethyleneimine (PEI)<sup>4</sup> in combination with cetyltrimethylammonium bromide as the template. This material yields an XRD pattern typical of a mesoporous material with a broad low angle reflection peak. SEM shows a material composed mainly of spheres.

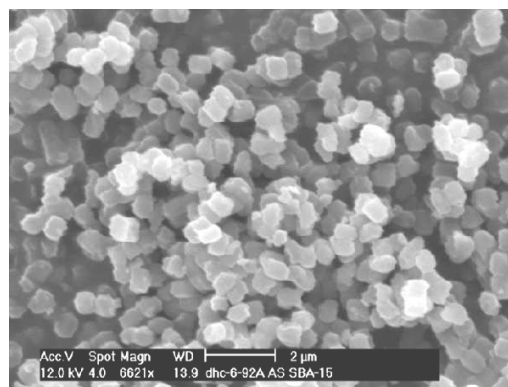


Figure 1. Scanning electron micrograph of PANI-SBA-15

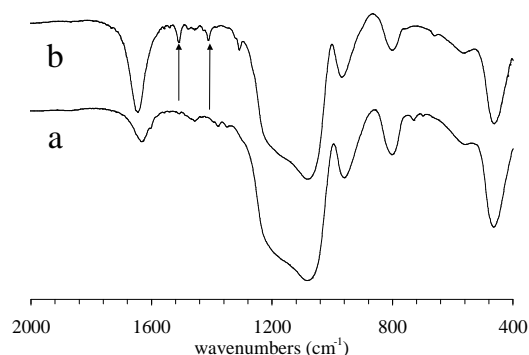


Figure 2. (a) Template-free aniline-SBA-15. (b) PANI-SBA-15 after Soxhlet extraction with NMP

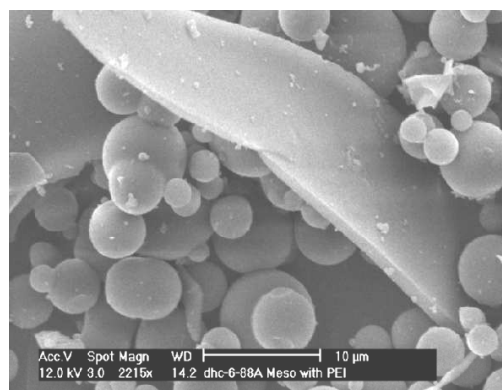


Figure 3. Mesoporous silica prepared with CTAB/PEI template.

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<sup>2</sup> G. Alberti, M. Casciola, L. Massinelli, B. Bauer, J. Mem. Sci., 2001, 185, 73-81.

<sup>3</sup> D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc.*, 1998, 120, 6024.

<sup>4</sup> R. Tanaka, H. Yamamoto, A. Shono, K. Kubo, M. Sakurai, *Electrochim. Acta*, 2000, 45, 1385-1389.