CATALYTIC NANOCOMPOSITE MEMBRANES FOR CO ABATEMENT IN FUEL CELL APPLICATIONS

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Abstract

Catalytic nanocomposite membranes have been prepared by ion exchanging Pt^{2+} for Li^{+} in a synthetic hectorite clay and dispersing this inorganic component within a polymeric matrix. Transparent, self-supporting membranes from the polymer-clay nanocomposite are then made. The reduction of Pt^{2+} to Pt(0) nanoclusters is accomplished by thermal reduction under H_2 at temperatures higher than 120°C. Loadings are in the 1-2 wt% Pt range. The size of the Pt(0) nanoparticles is determined by in situ small angle x-ray scattering (SAXS) techniques at about 5 nm. The membranes are stable to 200°C. These membranes have been tested for H_2 and CO diffusion at room temperature. Without any other reactive gases present (such as O_2), a selectivity enhancement from 1:1 to 3:1 H_2:CO is observed through the membrane.

Introduction

A major hurdle in current fuel cell technology is to provide a high purity gas feed. Fuel cells that operate at relatively low temperatures (<130°C) are adversely affected by even low levels of carbon monoxide (CO). Production of H_2 from the reforming of natural gas (or possibly other carbon reserves) and the water gas shift reaction yields CO as a byproduct at levels that poison fuel cell anodes. Therefore, additional technology is required to decrease the CO to ppm levels.

Current methods for removing residual CO include pressure-swing adsorption, preferential oxidation, and catalytic methanation, all of which add cost and complexity to the fuel processing system[1]. A call for basic research to supply alternative solutions to this problem was recently made, including more active catalysts for the low-temperature water-gas shift reaction, better gas stream separation processes and membranes, and CO-tolerant catalysts at the fuel cell anode[1].

We are currently testing the separation and oxidation of CO from a H_2-rich gas by taking advantage of decreased permeation of CO over H_2 through a polymer-clay nanocomposite membrane and simultaneous catalytic CO oxidation via Pt(0) nanoclusters that are supported by the membrane. It is envisioned that such a membrane would be placed just before the fuel cell.

Experimental

Synthesis of Catalytic Membranes. The preparation of synthetic lithium hectorite (SLH) clay has been reported in detail[2]. Loading of Pt(II) is accomplished by adding 0.5 gm SLH to a 2.5 mM aqueous $Pt(NH_3)_4Cl_2$ solution and stirring for 24 hr. This yields a material that has 65% of the cation exchange capacity loaded with Pt(II), or 4.65 wt% Pt. The desired amount of poly(ethylene oxide) (PEO) is then added and the mixture is stirred for another 24 hr, with a final loading of 2.4 wt% Pt on a 1:1 nanocomposite. Films were prepared by puddle-casting the slurries onto Teflon-coated glass plates and air-drying. Further drying is carried out at 120°C under an inert atmosphere for 24 hr. The ion-exchanged membrane is then reduced in a flow of H_2 at 200°C for 3 hr.

In Situ Small Angle X-Ray Scattering (SAXS). *In situ* SAXS was carried out at the Sector 12 of the Advanced Photon Source at Argonne National Laboratory. Monochromatic x-rays (18 keV) were scattered and collected on a 15 x 15 cm^2 CCD camera. The scattering intensity is corrected for adsorption and instrument background. The differential scattering cross section is expressed as a function of scattering vector *q*. The value of *q* is proportional to the inverse of the length scale ($Å^{-1}$). The instrument was operated with a sample to operator detector distances of 228 cm and 390 mm to obtain data at $0.01 < q < 0.3$ $Å^{-1}$ and at $0.08 < q < 2.3$ $Å^{-1}$, respectively. For these studies, a specially designed sample holder was used to heat the sample and collect SAXS data at the same time. Films of about 1.25 cm in diameter and 40 □m in thickness were placed in the sample holder and held using Kapton tape. The furnace temperature program was set to ramp from room temperature to 200°C at 5°C/min, and the gas flow of H_2 and He was started at room temperature.

Reactor Design. A new s.s. tubular reactor that consists of a catalytic membrane in the middle of the reactor standing perpendicular to flow was designed. Special temperature-resistant O-rings were used to eliminate the possible leaks during the experiments. The experimental setup consists of a reactor, a feed and exhaust lines, flow meters, flow controllers, temperature controller, and safety and check valves (see Figure 1). Gases are fed into the reactor tube and the temperature can ramp to 250ºC. A thermocouple is placed in the reactor bed. The reactor is housed in a clamshell furnace controlled by an Omega oven controller (TIC-500) equipped with a temperature limit switch set for 30ºC higher than the reaction temperature. From the reactor tube, the feed gas flows into saltwater/ice bath where the products and remaining reactants are condensed and collected for analysis. The collector can be isolated from the reactor and removed to collect the sample. The reactor is designed to handle a variety of conditions under continuous flow conditions at ambient pressure. The feed from the top of the reactor consists of He, CO, and H_2. The oxygen source will be air added in countercurrent flow with respect to CO and H_2.

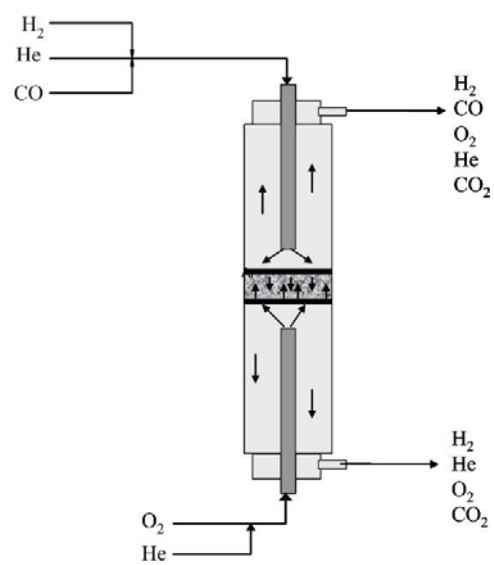

Figure 1. Reactor design for testing of catalytic membranes.

Results and Discussion

In Situ Pt Reduction. The Pt^{2+} reduction process was monitored under either H_2 (reducing) or He (inert) flow at different temperatures with simultaneous collection of SAXS data. When the

membranes were heated under a He flow (see Figure 2), the SAXS data could be fit using one structural layer throughout the entire temperature range in the so called general unified fit (GUF). This fitting procedure is explained in detail by Beaucage et al.[3]:

$$I(q) \approx G\exp\left(\frac{-q^2R_g^2}{3}\right) + B\left[\frac{\left(erf\left(qR_g/\sqrt{6}\right)\right)^3}{q}\right]^P$$

where G is the Guinier prefactor, B is the prefactor specific to the type of power-law scattering, q is the momentum transfer, Rg is radius of gyration and P is a constant. The derived Rg values are provided in Table 1.

This is a general equation developed to describe scattering functions that contain multiple length-scales (Guinier regimes) separated by power-law scattering regimes. Under He, scattering from the membrane itself should dominate. In contrast to the results with He, the addition of H_2 at relatively high temperatures produces significant changes in the SAXS results (see Figure 3). Under these conditions, the data fit better to two structural levels, with an additional length-scale added as seen in Table 1. This is presumbed to arise from the reduction of Pt^{2+} to Pt(0) nanoclusters. Harrison et al.[4] have claimed that the reduction of Pt^{2+} occurs at 140°C. Our SAXS measurements indicate that Pt(0) nanoparticles with a diameter of 4.8 nm form at 120°C. Diameters of the particles are calculated by multiplying the radius of gyration, which is derived from fitting results, by a constant of 2.6 (Rg = R/1.29 for spherical particles). The results also show that further heating to 200°C does not form significantly larger agglomerates.

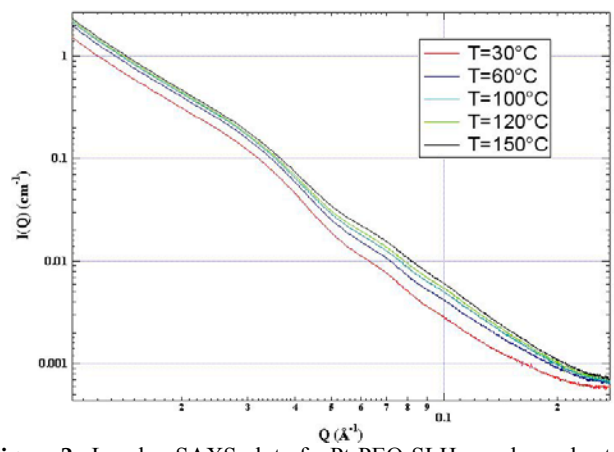

Figure 2. Log-log SAXS plot of a Pt-PEO-SLH membrane heated to various temperatures under He (non-reducing) flow.

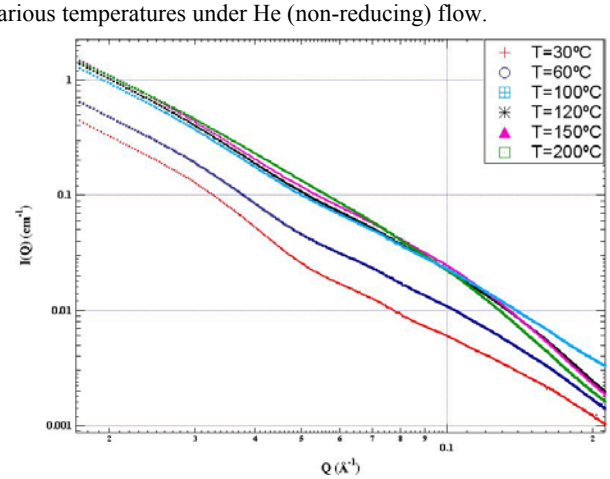

Figure 3. Log-log SAXS plot of a Pt-PEO-SLH membrane heated to various temperatures under H_2 flow.

Table 1. Microstructural Beaucage GUF SAXS Analysis of Pt-PEO-SLH Catalytic Membranes under Various Atmospheres

	Rg (Å)		
Temp. (°C)	He	H_2	
	Layer 1	Layer 1	Layer 2
30	81.3	80.0	-
60	79.2	81.9	-
100	79.7	84.2	-
120	81.7	88.1	18.6
150	82.0	90.5	19.0
200	89.8	104.7	19.8

Membrane Testing for H_2 and CO Performance. H_2-rich gas is fed from one end of the reactor. Permeation through the membrane alone acts to reduce the CO concentration. A selectivity enhancement from 1:1 H_2:CO to 3:1 H_2:CO has been observed upon feeding through a reduced Pt-PEO-SLH membrane at room temperature. Future experiments will feed a dilute CO stream with a countercurrent flow of O_2 at elevated temperature to convert the CO to CO_2 catalytically. The rates of CO oxidation depend on a variety of factors such as the thickness of the catalyst layer, its catalytic activity, and reaction conditions. Experimentation is directed toward formulating, evaluating, and establishing catalytic solids that promote the oxidation of CO with O_2.

Conclusions

A Pt-PEO-SLH catalyst is reduced successfully by thermal reduction under a H_2 flow at temperatures higher than 120°C. SAXS results (not shown) confirm that the reduction process does not degrade the polymer structure, although the polymer relaxes from crystalline to amorphous at >60°C. At low temperatures, CO poisons Pt(0). This is unfortunate because at higher temperature, Pt(0) is active for the catalytic oxidation of CO to CO_2. This is a higher temperature reaction than the operating temperature of low-temperature (<130°C) fuel cells, however, so this reaction cannot be exploited in current cells. It is envisioned that by using a membrane separator outside of the fuel cell, the possibility of catalytic oxidation of CO becomes a possibility. Low-temperature fuel cells are unstable above 135°C because of the Nafion. The PEO-membranes described here can go to 200°C. In the future, more thermally stable polymers will be tested. Pure clay could be used (laponite makes excellent films, for example), but the speculation is that the polymer helps to solvate the metal clusters and keep them from aggregating[5].

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References

1. "Basic Research Needs for the Hydrogen Economy", report from the DOE-BES Workshop on Hydrogen Production, Storage, and Use, held May 13–15, 2003; available on www.sc.doe.gov/bes.
2. Carrado K. A., *Appl. Clay Sci.*, **2000**, *17*, 1.
3. Beaucage G., Schaefer D. W. *J. Non-Cryst. Solids*, **1994**, *172-174*, 797.
4. Harrison J. B., Berkheiser V., Erdos G. W., *J. Catal.*, **1988**, *112*, 126.
5. P. Balbuena, personal communication.