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ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · FEBRUARY 2005

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Preparation of Platinum–Nafion–Carbon Black Nanocomposites via a Supercritical Fluid Route as Electrocatalysts for Proton Exchange Membrane Fuel Cells

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Novel platinum–Nafion–carbon black nanocomposites were synthesized using supercritical deposition. The method consists of preparation of a Nafion–carbon black composite followed by impregnation of a platinum precursor (PtMe_2COD) into the composite via adsorption from a solution of supercritical carbon dioxide. Subsequently, the impregnated composite is subjected to thermal treatment resulting in a platinum–Nafion–carbon black composite. The platinum–Nafion–carbon black composite was characterized by hydrogen chemisorption, and the average size of the platinum metal particles was found to be around 2.6 nm. A preliminary cyclic voltammetry test demonstrated that the composite displayed promising electroactivity as an electrocatalyst for proton exchange membrane fuel cells. To investigate the effects of the impregnation under supercritical conditions at high pressures and subsequent thermal reduction at elevated temperatures on the Nafion structure, composite films of platinum–Nafion 112 were prepared by the same supercritical deposition method. The infrared spectra of the films indicated that the structure of Nafion 112 did not change significantly during processing.

1. Introduction

Fuel cells are promising alternatives to present power sources because they convert chemical energy directly into electrical energy with high efficiency and low pollutant emissions. Among several different types of fuel cells, proton exchange membrane fuel cells (PEMFCs) are particularly attractive since (i) they operate at low temperatures and thus can respond fast to changes in the demand for power, (ii) the electrolyte (proton conductor) is a solid membrane that minimizes safety concerns, and (iii) they exhibit high efficiencies and power densities. A PEMFC is comprised of a membrane electrode assembly (MEA) typically made of an ionically conducting polymeric membrane (usually Nafion) sandwiched between two electrically conductive electrodes (anode and cathode). The electrochemical reactions at each electrode (hydrogen oxidation at the anode and oxygen reduction at the cathode) are catalyzed by the finely divided platinum metal in the electrodes.

Reduction of the platinum loading in current electrodes is necessary to reduce the cost per kilowatt of the PEMFC to acceptable levels for commercialization.¹ One of the strategies used to reduce the platinum loading is to disperse the platinum on a porous carbon support before incorporating it into the electrode. This results in an increase of the active surface area of platinum per unit mass of platinum. Significant research efforts have been directed toward reducing particle diameters in carbon-supported platinum.^{2–4} Currently, carbon black supported platinum particles have average diameters ranging from 1.5 to 10 nm, as compared to 10–20 nm for unsupported platinum particles.⁵ Although the supported platinum particle

size has been significantly reduced, all of the platinum atoms at the surface of the platinum particles are not utilized in the electrochemical reactions. This is due to the fact that only the platinum particles at the electrolyte/catalyst interfacial region can be utilized since the carbon-supported platinum cannot conduct protons and the electrolyte cannot conduct electrons. Therefore, further improvements in platinum utilization were achieved by incorporating a certain amount of Nafion into the electrode with the hope that this will enable the transfer of the protons in the catalyst layer. Nafion has been incorporated into electrodes in several distinct ways:⁶ (i) brushing a Nafion solution onto the catalyst-loaded electrode surface to form a thin Nafion layer^{7–10} and (ii) mixing Nafion into the catalyst solution ink.^{8,11–15} The second method is generally preferred.

However, even with Nafion incorporation, the Pt utilization (defined as the ratio of the effective electrocatalyst surface area to the surface area obtained from XRD measurement) in current electrodes is low.⁶ Pasalacqua et al.⁹ found that, by the first method described above, the Pt utilization even in the best-performing electrodes ranged only from 10 to 25%. Cheng et al.¹¹ found that the platinum utilization of the thin film catalyst layer containing only Pt/C and Nafion was only 45.4%. Zecevic et al.¹⁰ showed that there was a 15–20% reduction in the effective electrocatalyst surface area due to deposition of Nafion. It was suggested that Nafion directly covered the particles or blocked the pores of the support where the catalyst particles resided, making these particles inaccessible. Furthermore, Nafion could also block the conduction of electrons. Therefore, substantial research efforts have been directed toward optimization of electrode structures consisting of Nafion, carbon, and platinum.^{11,16–18} In this study, we propose a novel method for preparation of a platinum–Nafion–carbon composite with a novel structure that may eventually lead to an improvement in Pt utilization.

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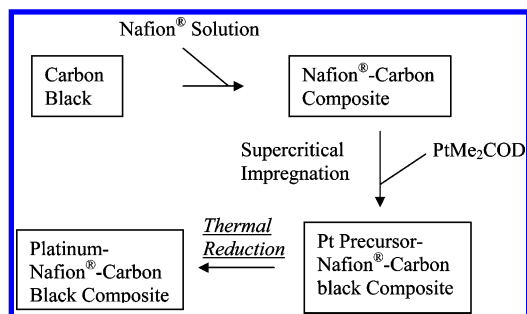


Figure 1. Scheme for synthesis of platinum-Nafion-carbon composite.

The synthesis method for the platinum-Nafion-carbon composite is shown in Figure 1, and it consists of the following steps:

- (1) preparation of a Nafion-carbon black composite
- (2) incorporation of platinum into the composite using supercritical deposition

Supercritical deposition involves impregnating the Nafion-carbon black composite with an organometallic platinum precursor, dimethyl(1,5-cyclooctadiene)platinum(II) (PtMe_2COD), from a scCO_2 solution. Subsequent thermal treatment of the impregnated composite results in a platinum-Nafion-carbon composite. Supercritical fluids (SCFs) are fluids that have been heated and compressed above their critical temperature and pressure. The thermophysical properties of SCFs are intermediate between those of a gas and a liquid and can be adjusted by slight changes in temperature and/or pressure. The liquid like densities enable SCFs to dissolve a wide range of organometallic precursors. High diffusivities in SCFs, combined with low viscosities, result in enhanced mass transfer characteristics as compared to organic solvents. Their low surface tension also facilitates rapid penetration into porous materials. Among the SCFs, supercritical carbon dioxide (scCO_2) ($T_c = 31.1\text{ }^\circ\text{C}$, $P_c = 71.8\text{ bar}$) is particularly attractive for a wide variety of applications including this one since it is chemically inert, nontoxic, environmentally acceptable, leaves no residue in the treated medium, and does not dissolve Nafion.

In this paper, the synthesis of the platinum-Nafion-carbon composite is described. The effects of the impregnation and thermal reduction on the structure of Nafion were investigated by Fourier transform infrared spectra (FTIR). The dispersion and the particle size of the platinum were characterized by H_2 chemisorption. The electrochemical activity was measured by cyclic voltammetry (CV) using membrane electrode assemblies (MEAs) prepared from this composite.

2. Experimental Section

2.1. Materials. PtMe_2COD was purchased from STREM, Inc. Carbon black (Vulcan XC-72R) was purchased from Cabot International. The 5% Nafion (an equivalent weight of 1100) solution was obtained from Solution Technology Inc. Nafion 112 film was purchased from Ion Power, Inc. All of the chemicals were used as received.

2.2. Composite Preparation. 2.2.1. Synthesis of Nafion-Carbon Black Composites. A total of 0.250 g of carbon black powder was mixed with 1.745 g of 5% Nafion solution in a vial and was kept in an ultrasonic bath (SF20, Fisher) for 24 h. Subsequently, the mixture

was spread on the surface of a flat dish. The dish was placed in the ultrasonic bath to keep the mixture uniform, and the solvent was evaporated overnight. Finally, the mixture was dried at $50\text{ }^\circ\text{C}$ under vacuum overnight.

2.2.2. Incorporation of PtMe_2COD into the Nafion-Carbon Black Composites. A total of 0.175 g of PtMe_2COD , a stirring bar, and Nafion-carbon black (0.331 g) were placed into a high-pressure vessel (internal volume of 54 cm^3) that was custom-manufactured from 316 stainless steel. The vessel had two sapphire windows (1-in. i.d., Sapphire Engineering, Inc.) and was sealed on both sides with PEEK O-rings (Valco Instruments, Inc.). It was equipped with a T-type thermocouple assembly (Omega Engineering, DP41-TC-MDSS), a pressure transducer (Omega Engineering, PX300-7.5KGV), a vent line, and a rupture disk assembly (Autoclave Engineers). The vessel was heated to $80\text{ }^\circ\text{C}$ using a bath circulator (Fisher, Isotemp model 90) via machined internal fluid channels and charged with carbon dioxide to the operating pressure of 27.6 MPa using an ISCO (model 260D) syringe pump. The adsorption of precursor from scCO_2 into Nafion-carbon black was continued at this condition for 24 h to ensure that equilibrium was reached. Subsequently, the vessel was depressurized through a restrictor into the atmosphere. During this process, the un-adsorbed PtMe_2COD was vented out of the vessel together with scCO_2 and collected in a glass vial. Although precipitation on the substrate during this process may occur, the amount of the precipitate was found to be very small as compared to the amount adsorbed within the substrate. After the vessel was cooled, the PtMe_2COD -Nafion-carbon black powder was taken out. The amount of the precursor adsorbed was determined by the weight change of the substrate using an analytical balance (Adventure model AR2140) accurate to $\pm 0.1\text{ mg}$; 0.441 g of powder was obtained indicating that 0.110 g of PtMe_2COD was adsorbed.

2.2.3. Thermal Reduction. The powder obtained as explained above was placed in a tube, which was placed into a furnace (model: F21125 Thermolyne tube furnace). The precursor in the Nafion-carbon black composite was reduced to platinum at $200\text{ }^\circ\text{C}$ under flowing N_2 ($100\text{ cm}^3/\text{min}$). The thermal reduction was carried out for a period of 2 h. Subsequently, the oven was turned off and cooled under flowing nitrogen. The platinum loading was calculated from the amount of the adsorbed precursor by assuming all the precursor was reduced to elemental platinum. Finally, 0.420 g of the composite powder consisting of 16.3 wt % platinum, 21.7 wt % Nafion, and 62.0 wt % carbon black was obtained.

2.2.4. Incorporation of Platinum into Nafion 112 Film. Platinum was incorporated into Nafion 112 film by the supercritical CO_2 deposition method. The details were similar to the procedure for incorporating platinum into the Nafion-carbon black composite.

2.3. Characterization. 2.3.1. Thermogravimetric analysis (TGA). TGA of Nafion 112 and PtMe_2COD was carried out over the ranges of $25\text{--}500\text{ }^\circ\text{C}$ and $25\text{--}600\text{ }^\circ\text{C}$, respectively, at a rate of $20\text{ }^\circ\text{C}/\text{min}$ under nitrogen using Hi-Res TGA 2950 thermogravimetric analyzer (TA Instruments).

2.3.2. Infrared Spectra. Infrared spectra of the pure Nafion 112 film and the platinum-incorporated Nafion films were recorded on a Bruker Vector22 Fourier transform infrared spectrometer in the $400\text{--}4000\text{ cm}^{-1}$

wavenumber range. 90 scans were taken at a scan velocity of 6 and resolution of 4 cm^{-1} . Each spectrum was obtained by subtracting the previously recorded background. The films were measured directly without any treatment.

2.3.3. Hydrogen Chemisorption. Hydrogen chemisorption measurements were carried out at $25\text{ }^{\circ}\text{C}$ using the Omnisorp 100CX instrument (Coulter Electronic, Inc). The sample was first reduced under hydrogen flow at $160\text{ }^{\circ}\text{C}$ for 1 h to reduce any oxidized platinum and subsequently evacuated at $160\text{ }^{\circ}\text{C}$ under a high vacuum of 10^{-5} bar for 1 h. Finally, it was cooled to $25\text{ }^{\circ}\text{C}$, and the first chemisorption isotherm (run 1) was obtained by incrementally adding hydrogen to the sample flask and measuring the pressures after equilibrium was reached. After this measurement, the sample was evacuated at room temperature for 1 h, and the procedure was repeated to obtain the second chemisorption isotherm (run 2) to account for physisorption and weak chemisorption. The chemisorbed hydrogen amount was determined by subtracting the adsorbed hydrogen amounts of run 2 from run 1 as determined by extrapolating the two chemisorption isotherms to zero pressure. The values of the metal dispersion were calculated by assuming that platinum particles were spherical and that the adsorption stoichiometry (H/Pt) was one.

2.3.4. Cyclic Voltammetry. The MEAs were prepared by spraying inks prepared from the composite powders and characterized by CV. Two kinds of catalyst ink were prepared: (a) by mixing a Nafion solution with isopropyl alcohol and the platinum–Nafion–carbon black composite powder and (b) by mixing methanol and the composite powder. The cathodes were prepared by spraying the resulting catalyst inks (a) or (b) onto Toray paper. The anodes were prepared by a similar procedure except that the catalyst ink was made from carbon black supported platinum powder (20 wt % Pt) from Tanaka (Kikinzoku Koguo K. K. Japan) and the platinum loading was 0.5 mg/cm^2 . The electrodes with Nafion 112 were hot-pressed to make the membrane-electrode assembly. The cyclic voltammograms were taken in situ (in fuel cell test fixtures) on the cathode by a potentiostat (Princeton Applied Research model 273A) in order to obtain the electrochemically active surface areas. Hydrated nitrogen was passed through the working electrode (fuel cell cathode) compartment, and hydrated hydrogen was passed through the counter electrode (fuel cell anode) compartment. The profiles were recorded at a scan rate of 30 mV/s .

3. Results and Discussion

For preparation of the composites using the method shown in Figure 1, the precursor selection is very important since the precursor needs to possess some specific properties. It should have a reasonably high solubility in scCO_2 in order to achieve appreciable rates of impregnation. It should partition favorably to the Nafion–carbon black composite phase in the presence of scCO_2 . Moreover, the precursor should have a low decomposition temperature so that the Nafion would not decompose during the conversion of the precursor to elemental platinum.

We recently reported on preparation of carbon aerogel (CA) supported platinum nanoparticles using supercritical deposition.¹⁹ We were able to prepare Pt/CA nanocomposites using PtMe_2COD as a precursor. PtMe_2COD has a relatively high solubility in scCO_2 at $80\text{ }^{\circ}\text{C}$

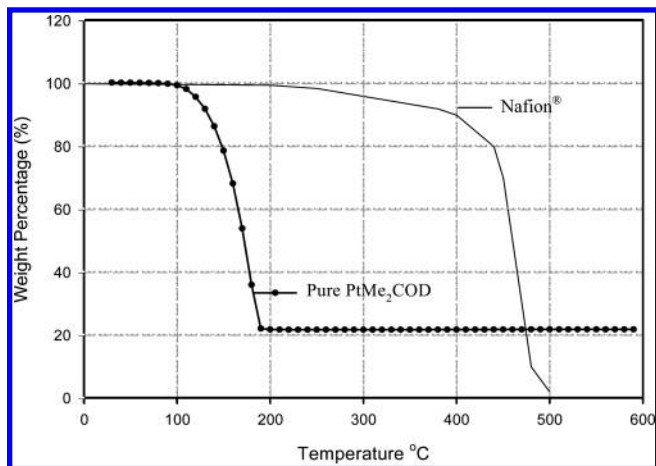


Figure 2. Thermogravimetric analysis (TGA) of Nafion 112 and PtMe_2COD in nitrogen.

and 27.6 MPa (higher than 14.9 mg/cm^3). Furthermore, the rates of impregnation of porous carbon aerogels with PtMe_2COD were found to be high. Therefore, we hypothesized that PtMe_2COD would also be suitable as a precursor for preparation of platinum–Nafion–carbon composites. To determine whether Nafion would decompose during thermal reduction, TGA tests were carried out. Figure 2 shows the TGA of Nafion, which demonstrates significant decomposition at temperatures higher than $240\text{ }^{\circ}\text{C}$. On the other hand, PtMe_2COD has a low decomposition temperature. The weight loss starts around $120\text{ }^{\circ}\text{C}$, and the decomposition is complete around $185\text{ }^{\circ}\text{C}$. Therefore, it should be possible to carry out the reduction of the PtMe_2COD at a sufficiently low temperature so that the Nafion in the carbon black–Nafion composite would not decompose. The low temperature should also prevent the sintering of metal particles, which leads to large particle sizes. Furthermore, we found out that when Nafion was contacted with a solution of PtMe_2COD dissolved in scCO_2 , a substantial amount of PtMe_2COD was adsorbed on Nafion. At equilibrium, the concentrations of PtMe_2COD in the Nafion phase and the scCO_2 phase were 333 mg/g substrate and $1.20\text{ mg/cm}^3\text{ scCO}_2$, respectively. Assuming that the equilibrium isotherm is linear, one can calculate a partition coefficient of $277.5\text{ cm}^3/\text{g}$ indicative that PtMe_2COD partitions favorably to the Nafion phase. Therefore, PtMe_2COD was selected as the precursor.

To investigate the effects of the high pressures used for impregnation and the elevated temperatures used for thermal reduction on the chemical structure of Nafion, composite films of platinum–Nafion 112 were prepared using supercritical deposition at the same conditions used for preparation platinum–Nafion–carbon composite. The changes in the chemical structure of Nafion 112 was monitored by FTIR. The IR spectra of pure Nafion 112 and PtMe_2COD is shown in Figure 3 a. The detailed assignment of IR peaks of Nafion 112 was given by Gruger et al.²⁰ The two plateaus between 1600 and 3800 cm^{-1} were assigned to water or acidic water (H_3O^+). The peak at 1058 cm^{-1} was assigned to sulfonic groups, which is one of the most important functional groups in Nafion. The IR spectrum of PtMe_2COD impregnated Nafion 112 after supercritical CO_2 deposition is also shown in Figure 3a. Based on this spectrum, although one of the plateaus assigned to water disappeared, the main structure of Nafion 112

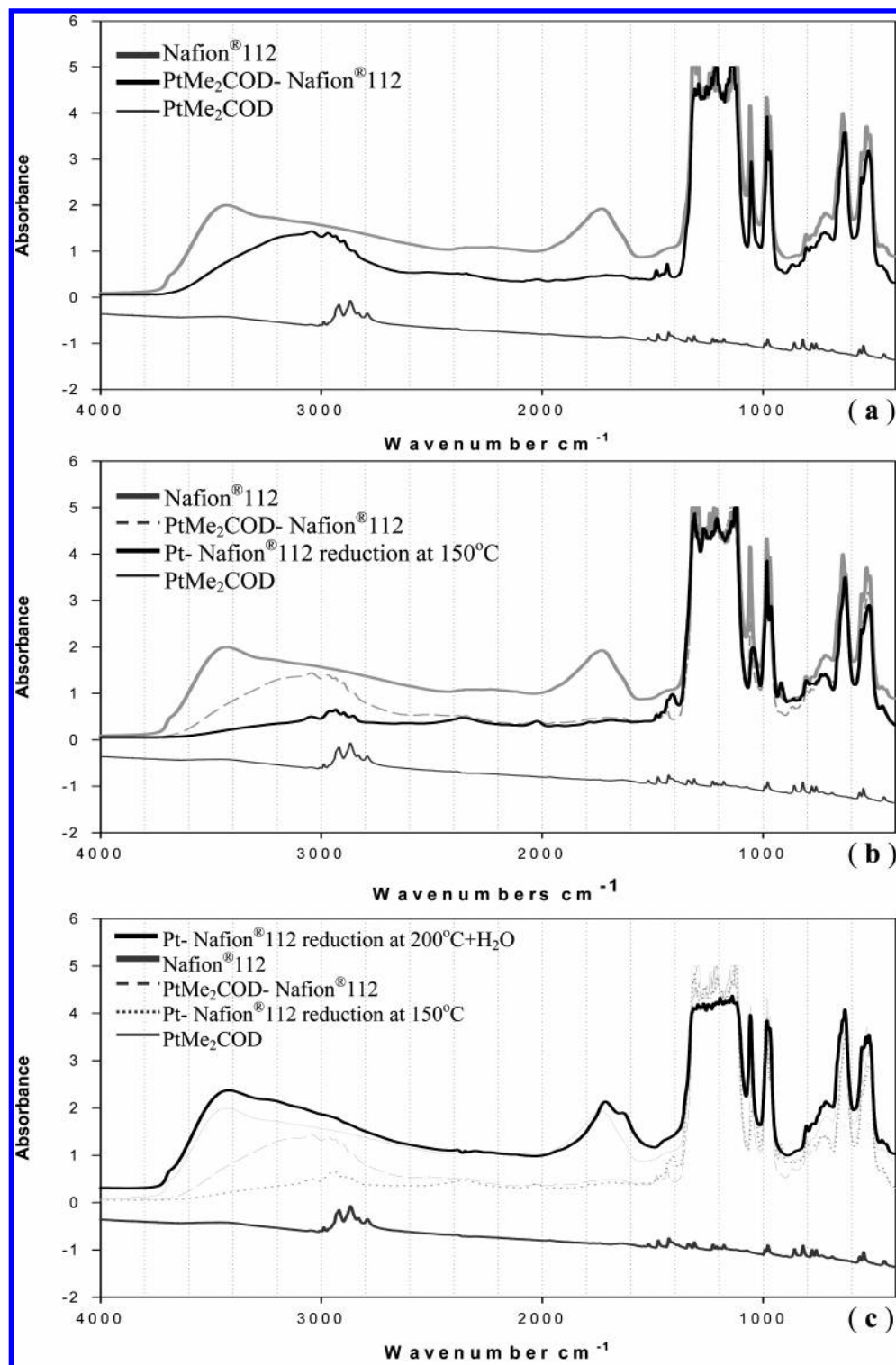


Figure 3. Effects of impregnation and thermal treatment on chemical structure. (a) The IR spectrum of Nafion impregnated with PtMe₂COD (compared with pure Nafion 112 and PtMe₂COD). (b) The IR spectrum of Nafion impregnated with PtMe₂COD and subjected to thermal treatment at 150 °C for 2 h. (c) The IR spectrum of Nafion impregnated with PtMe₂COD and subjected to heat treatment at 200 °C for another 2 h and saturated with water.

was intact. The new peaks that appeared around 1430, 1480, 2850, and 3050 cm⁻¹ were assigned to PtMe₂COD. The PtMe₂COD impregnated into Nafion 112 was subjected to thermal treatment at 150 °C for 2 h, and the IR spectrum of the resulting Pt–Nafion composite is shown in Figure 3b. The plateaus assigned to water disappeared completely, but the main structure of Nafion 112 was almost intact. However, the peaks assigned to PtMe₂COD were still apparent, indicating that PtMe₂COD did not decompose completely at 150

°C during the 2 h. Further thermal reduction was carried out at 200 °C for another 2 h. The resulting Pt–Nafion film was immersed in water for 24 h. After wiping the water off from the surface of the film by tissues, the IR spectrum of this film was taken and shown in Figure 3c. The structure of the Nafion is slightly changed. The plateaus assigned to water appeared again, which means after PtMe₂COD impregnation and thermal reduction, the Nafion film still has the ability to absorb water. The peaks assigned to

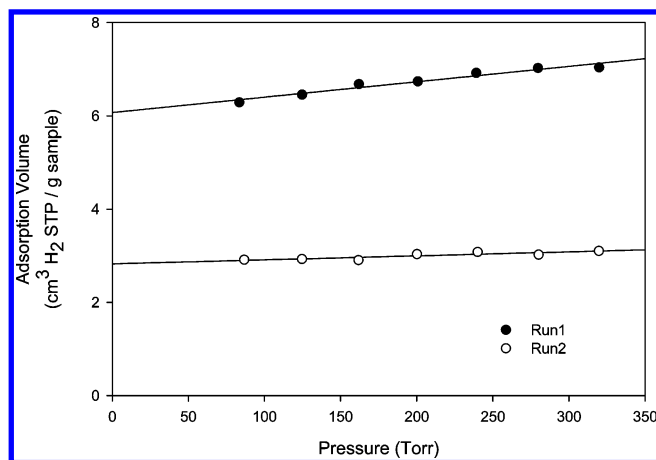


Figure 4. H₂ chemisorption isotherm of platinum–Nafion–carbon black composite. Run 1: total H₂ adsorption on platinum–Nafion–carbon black composite. Run 2: H₂ weak chemisorption on composite and physisorption on support. The H₂ chemisorption amount is determined by the adsorption difference between run 1 and run 2 at zero pressure.

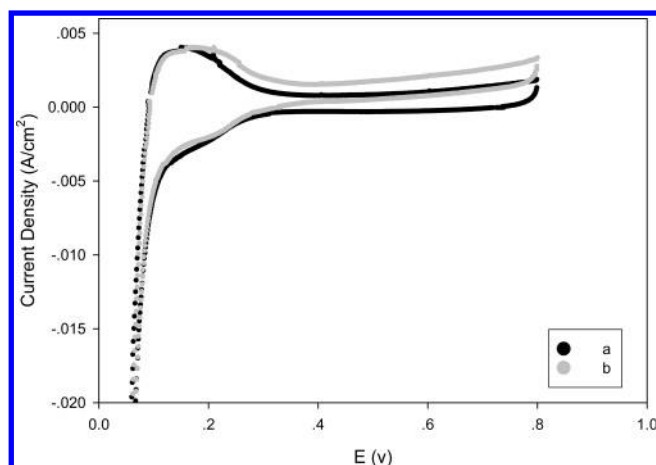


Figure 5. Cyclic voltammograms. (a) Extra 20% Nafion was incorporated in the Pt–Nafion–carbon composite during preparation of catalyst ink. Pt loading is 0.42 mg/cm². (b) Without extra Nafion incorporation during preparation of catalyst ink. Pt loading is 0.45 mg/cm².

PtMe₂COD disappeared completely, which indicates that the treatment at 200 °C for 2 h is sufficient to decompose PtMe₂COD completely.

Platinum (16.3 wt %)-Nafion (21.7 wt %)-carbon black (62.0 wt %) composites were synthesized and characterized by H₂ chemisorption and CV. The platinum dispersion (D_{Pt}), which is a measure of the fraction of platinum atoms that are exposed is given by the following equation:

$$D_{Pt} = 100\% \times 2 \times N_{H_2}/N_{Pt \text{ total}} \quad (1)$$

where N_{H_2} is the molar amount of adsorbed H₂ and $N_{Pt \text{ total}}$ is the total molar amount of platinum in the composite. Based on the isotherms of the H₂ chemisorption shown in Figure 4, D_{Pt} was calculated as 43%. The relevant active surface area of platinum was 106 m²/g. Assuming that the platinum particles are spherical, the particle diameter was calculated as 2.6 nm.

Membrane electrode assemblies (MEAs) prepared from platinum–Nafion–carbon composites as described in Section 2.3.4. were tested by cyclic voltammetry (CV) in a 5 cm² fuel cell hardware. The preliminary CV data are shown in Figure 5. The Coulombic charge (Q) was

used to calculate the active platinum surface area of the electrodes. The value of Q was calculated from the mean value between the amounts of charge exchanged during the electro-adsorption (Q') and desorption of H₂ on platinum site (Q''). The details on how to calculate Q' and Q'' from CV data are described in elsewhere.²¹ The electrochemical surface area (EAS) was calculated by:

$$EAS = Q/[Pt]/0.21 \quad (2)$$

where Q represents the Coulombic charge (mC/cm²); [Pt] represents the platinum loading (mg/cm²) in the electrode; and 0.21 represents the charge required to oxidize a monolayer of H₂ on bright platinum.²¹ The EAS of platinum was about 20 m²/g Pt for both electrodes made from catalyst ink (a) and (b). Further studies are underway to optimize the ratio of Nafion to carbon black, the platinum loading and reduction conditions. Carrying out the reduction in scCO₂ in the presence of H₂ may lead to increased dispersion due to substantially lower temperatures.

4. Conclusions

A novel Pt–Nafion–carbon black composite was prepared via a supercritical fluid route. Supercritical impregnation was found to be an effective way to incorporate metal nanoparticles into both Nafion and Nafion–carbon black composites. The average Pt particle size in the composite was found to be 2.6 nm from H₂ chemisorption measurement. Preliminary CV tests demonstrated that the Pt–Nafion–carbon black nanocomposite displayed promising electroactivity as an electrocatalyst for fuel cells. The electrochemical area can possibly be further increased by optimization of the preparation conditions and the ratio of Nafion to carbon black.

Acknowledgment

We gratefully acknowledge the financial support of the U.S. Army, CECOM-OT DAAB07-03-3-K415.

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Received for review September 1, 2004

Revised manuscript received December 3, 2004

Accepted December 7, 2004

IE049177I