

Short communication

Effects of Nafion as a binding agent for unsupported nanoparticle catalysts

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Abstract

We studied the effect of Nafion on the formic acid oxidation reactivity of three unsupported nanoparticle catalysts: Pt black, Pt/Ru black, and Pt/Pd. The catalysts were prepared by physisorption deposition of the nanoparticles on Au both with and without Nafion as an adhesive. The results indicate that Nafion lowers both the apparent surface area and the formic acid oxidation current by blocking surface sites. Surface areas obtained with Nafion binding agent were suppressed by 13, 8, and 22%, while formic acid oxidation currents were attenuated by 40, 13 and 27% for Pt black, Pt/Ru black and Pt/Pd, respectively. When comparing the effects of Nafion on the surface areas, and comparing these results to the respective voltammograms, Nafion displays some selective site blocking effects as well.

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1. Introduction

The study of fuel cell catalysts has been an integral part of electrochemical research in recent years [1]. Much of the focus has centered on nanoparticle catalysts, which generate high net current due to large active surface area [2–7]. However, scientists and engineers have encountered a problem with studying and using these catalysts, namely applying the catalysts in such a manner that they form a stable, reproducible fuel cell catalyst. This problem has been solved in most facilities by using a polymer to bind the nanoparticles to a proton-conducting support to create a membrane electrode assembly (MEA). Nafion usually serves as such proton-conducting support and an electrolyte between the anode and cathode, and is readily available as a solution, it has also become the adhesive agent of choice for MEAs prepared from nanoparticle catalysts. A disk shaped electrode made of a noble metal may also serve as a Nafion-coated support in the laboratory practice, as reported further. Nafion has been incorporated into the catalyst in three distinct ways: (1) deposition on top of the nanoparticles [8–10], (2) deposition both above and below the nanoparticles (including sputtering the nanoparticles into a membrane) [8,11–13], and (3) mixture

into the nanoparticle ink [8,11,14–17], with the last method being generally preferred. The electrochemical effects of Nafion, predominantly noted as improving proton conduction or as impairing mass transfer to the electrode, have been studied in various formats, but have not been thoroughly established for nanoparticle catalysts [18–23]. In our group, we use a physisorption deposition method whereby we can adhere unsupported nanoparticles to a Au disc electrode, without the use of a binding agent [6]. This allows us to unequivocally determine the effect of Nafion on electrochemical properties of fuel cell catalysts. We studied the effects of Nafion as a binding agent for methods (1) and (3) described earlier, and compared the results to the unmodified catalysts.

Formic acid is used as a probe of the activity of the three catalysts studied in this paper due to its high activity for each catalyst. Formic acid is also of interest as an alternative fuel in micro fuel cells. The direct formic acid fuel cell (DFAFC), although not currently envisioned as a universal replacement to the direct methanol fuel cell (DMFC), holds a promise of high performance in diverse applications [24].

2. Experimental

Experiments were carried out in a standard three-electrode electrochemical cell. The counter electrode was a platinized

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Pt mesh. The reference electrode was Ag/AgCl/3M NaCl, but all potentials are reported versus the reversible hydrogen electrode (RHE). Electrolyte was 0.1 M H₂SO₄ prepared using concentrated sulfuric acid (double-distilled from Vycor, GFS) and Millipore deionized water (Milli-Q, 18.2 MW/cm²). Formic acid of 0.1 M (double-distilled, 88%, GFS) in 0.1 M H₂SO₄ was the solution from which formic acid oxidation occurred. Pt black and Pt/Ru black were obtained from Johnson Matthey. The Pt/Pd catalyst was produced as described previously [7]. Experiments were performed using either a Solartron SI 1287 potentiostat or Par 283 potentiostat, under control of CorrWare software.

3. Results and discussion

3.1. Procedure for phase I: Nafion deposition on top of the nanoparticles

The surface area for Pt/Ru black catalyst was determined by integrating the CO-stripping peak. Namely, the catalyst surface was first characterized via two cyclic voltammograms (CV) to document a clean and stable surface. Next, ultrapure CO was bubbled through the cell at 0.05 V for 40 min. The cell was purged with Ar for 20 min to remove any CO from solution and the adsorbed CO was stripped from the catalyst surface by cyclic voltammetry (Figs. 1–3). In the case of Pt black and Pt/Pd, surface area was determined by integrating the hydrogen adsorption and desorption peaks from the characterization CV. Specific surface areas were in excellent agreement with manufacturer's reported data for the Pt black and Pt/Ru black, and with previously reported data for Pt/Pd.

Experiments were carried out in two phases. In phase I, the effect of Nafion applied using method (1) was studied (see Section 1). Nanoparticle catalysts were deposited onto a polished Au disc electrode. Once the real surface area had been determined as described earlier, the electrode was carefully removed from the cell and the surface dried under a heat lamp. Approximately 10 ml of Nafion was applied to the surface and the electrode was again dried under a heat lamp. The experiment was repeated in the same manner to determine the effect of Nafion.

3.2. Procedure for phase II: Nafion mixed into the nanoparticle ink

In phase II, the effect of Nafion applied using method (3) described in the Section 1 was studied. For each catalyst, nanoparticles were diluted in Millipore water to a concentration of 4 mg/ml. The particle suspension was split in half and Nafion was added to one half to yield a final concentration of 4 mg/ml catalyst with 10% Nafion by mass.

The catalysts were sonicated for 15 min and deposited on the Au disc. Nafion containing samples were sonicated in an ice–water bath. The electrodes were dried under a heat lamp,

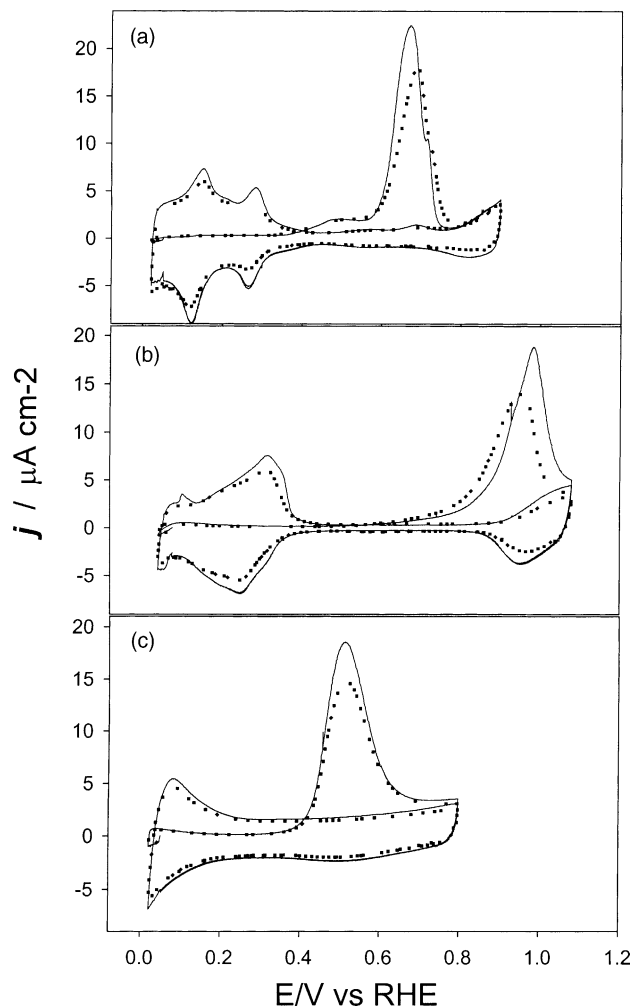


Fig. 1. Cyclic voltammograms of the three nanoparticle catalysts both with (dotted line) and without (solid line) Nafion as a binder deposited atop the nanoparticles. (a) Johnson Matthey Pt black nanoparticles; (b) Pd spontaneously deposited on Pt black (JM); (c) Johnson Matthey Pt/Ru black alloy. Scan rates were 5 mV/s. Loading was 0.5 mg/cm² in each case.

and inserted in the three-electrode cell. Catalyst surface area was determined as in phase I, then the activity was tested via chronoamperometry for 2 h.

3.3. Surface area effects

In the phase I of the experiment, Nafion adhesive was applied to a previously characterized electrode. This allowed the real surface area of the nanoparticle electrode to be determined. The cyclic voltammograms were then plotted concurrently, and normalized to the true surface area (Fig. 1). Fig. 1 clearly demonstrates that Nafion applied as a relatively thick film covering the membrane alters the shape and peak position of the CV. The changes indicate that Nafion application resulted in an average surface area decrease of 22, 15 and 19% for Pt black, Pt/Ru black and Pt/Pd, respectively. This current attenuation appeared in the hydrogen adsorption/desorption region for all CVs, and also in the

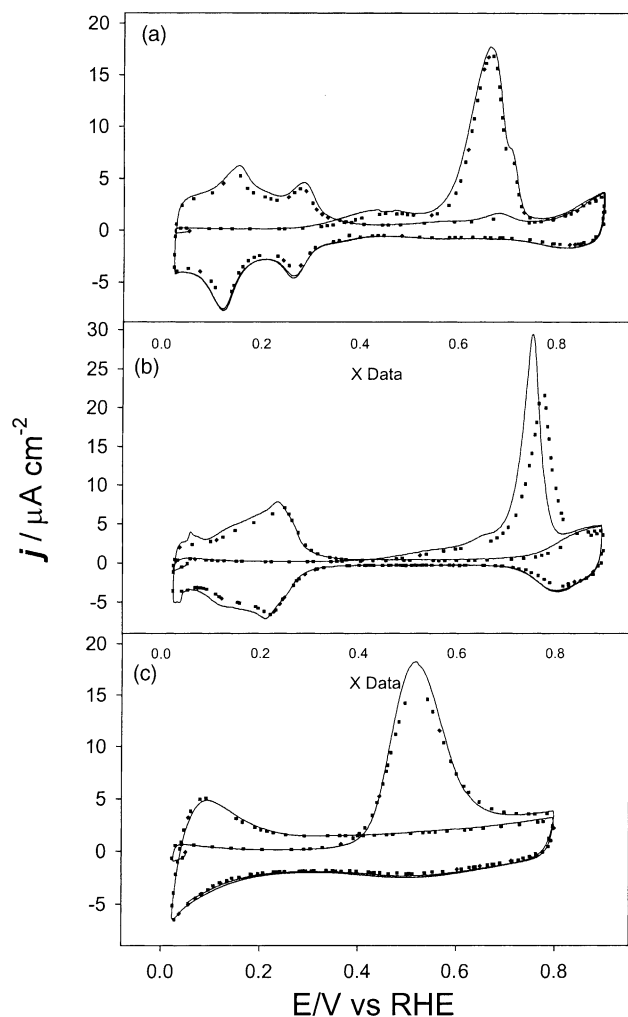


Fig. 2. Cyclic voltammograms of the three nanoparticle catalysts both with (dotted line) and without (solid line) Nafion as a binder mixed within the nanoparticle ink. (a) Johnson Mathey Pt black nanoparticles; (b) Pd spontaneously deposited on Pt black (JM); (c) Johnson Mathey Pt/Ru black alloy. Scan rates were 5 mV/s. Loading was 0.5 mg/cm² in each case.

CO oxidation region on the CO-stripping CV. This technique yielded high scatter and required many repetitions to establish acceptable reproducibility. This can be accounted for by the difficulty in controlling the thickness of Nafion layer on top of the catalyst.

In the second phase of the experiment, Nafion effect was analyzed by comparing electrodes made from pure catalyst ink versus those made from ink that also contained 10% Nafion in suspension. As seen in Fig. 2, the shape of the curves remained essentially unchanged, with the major difference being an overall peak current reduction. The Pt/Pd CV, however, showed a preferential hydrogen adsorption deactivation, with the peak located around 0.25 V being affected more than the peak located at 0.13 V. This phenomenon also appears in CV concerning the Pt black/Nafion formulation. In contrast, this peak does not appear at all on CV for Pt/Ru. Since the Pt/Ru surface is also the least affected by Nafion, this may indicate that Nafion has the

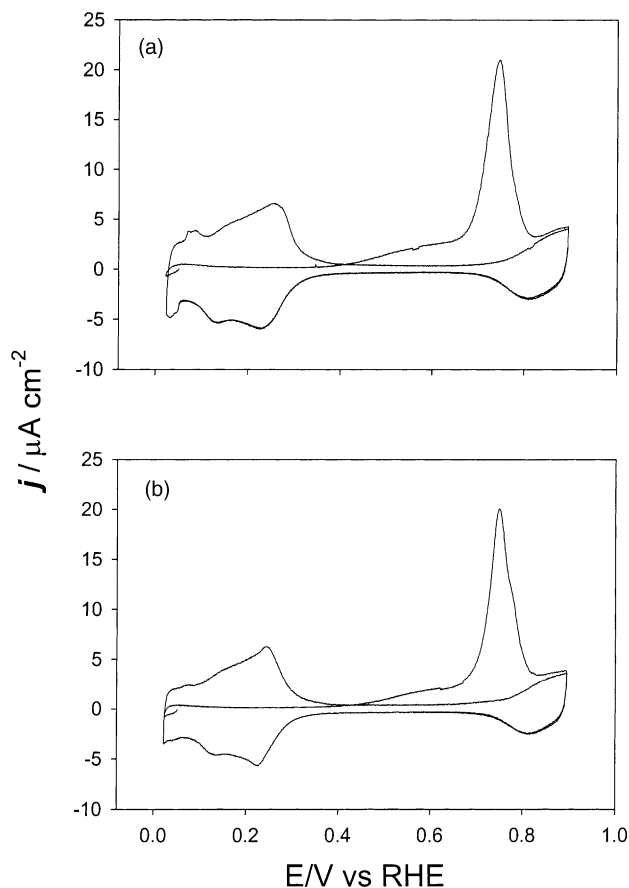


Fig. 3. Comparison of (a) Pt/Pd with a lower catalyst loading and (b) Pt/Pd with 10% Nafion in the ink. Suppression of the H₂ adsorption peak located at ~0.25 V, relative to the peak at ~0.13 V diminishes some of the Pd character of the CV. Scan rate was 5 mV/s and catalyst loading was 0.5 mg/cm², in both instances.

greatest effect on the feature of the catalyst that leads to the hydrogen adsorption/desorption at this potential. This selective site blocking has not been previously reported.

Nafion application using method (3) resulted in an average surface area decrease of 13, 8, and 22% for Pt black, Pt/Ru black and Pt/Pd, respectively. These results showed much greater reproducibility, suggesting that mixing Nafion into the ink helps form a polymer layer of consistent thickness surrounding the catalyst.

It is important to note that the effect of Nafion can easily be overlooked because the lower Nafion-covered surface area corresponds closely to the lower current. When the CV for catalyst/Nafion is normalized to its own hydrogen charge (as is typically the case) the CV will overlap exactly with the non-Nafion CV (however, except for Pt/Pd, Fig. 2b). This suggests that Nafion simply blocks a percentage of surface sites, yielding a lower surface area electrode. In the case of Pt/Pd, Nafion may preferentially deactivate Pd sites, thereby changing not only the overall current, but also the shape of the curve. The comparison between the Pt/Pd/Nafion catalyst and a Pt/Pd catalyst with the lower Pd loading prepared

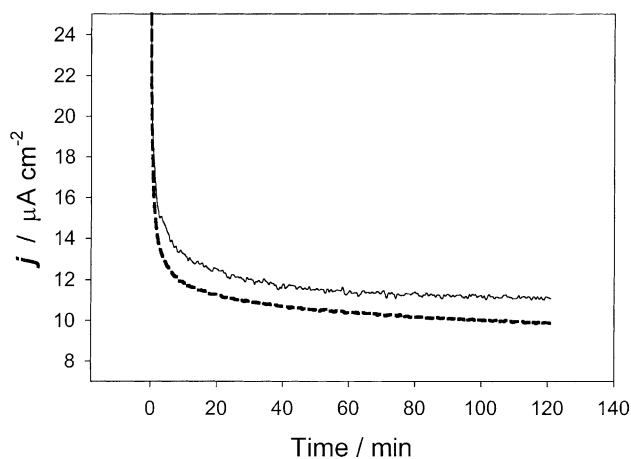


Fig. 4. Current vs. time curves for the oxidation of formic acid by Pt/Ru black catalyst, with (dashed) and without (solid) Nafion as a binder. Formic acid concentration was 0.1 M. Potential was 0.4 V vs. RHE.

by our group shows a striking similarity in the shape of all the peaks (Fig. 3).

3.4. Activity effects

Chronoamperometry was employed to determine whether the surface sites deactivated towards hydrogen adsorption would also be inert to formic acid oxidation. Formic acid was used as the molecule to be oxidized due to its high activity for the three catalysts chosen in this study. The potential was maintained at +0.4 V versus RHE, and formic acid concentration was set at 0.1 M.

We found that Nafion effect on the catalytic oxidation varied. A typical figure to illustrate our procedure is Fig. 4, which shows the current density—time curves for the Pt/Ru black catalyst, with and without Nafion as a binder in the ink. (Data for oxidation of formic acid for Pt black and Pt/Pd were presented elsewhere [7]). The current density is referring to the real surface area. With Nafion in the ink as a binder, the difference in the current density for HCOOH oxidation is reflected in a loss of between 1 and 2 mA cm⁻² for the three catalysts. Due to the lower relative activity that Pt black exhibits towards the organic molecules, this results in a larger percentage decrease for Pt black than for the Pt/Ru and Pt/Pd catalysts (Table 1). For Pt/Ru and Pt/Pd, the oxidation currents after 2 h at 0.4 V were diminished by only a few more percentages than the area reduction, 13 and 27%

Table 1

Relative decrease in surface area of the nanoparticle catalysts and in formic acid oxidation current (%) due to the application of Nafion (see text)

	Pt black (%)	Pt/Ru (%)	Pt/Pd (%)
Surface area, Nafion atop	22	15	19
Surface area, Nafion mix in ink	13	8	22
Oxidation current, Nafion in ink	40	13	27

The oxidation current was measured at 0.4 V vs. RHE after 2 h.

respectively. However, for Pt black the oxidation current was reduced by approximately 40% with the addition of Nafion, while the active surface area was only reduced ~13%. A similar result was reported for bulk Pt electrodes with methanol as the fuel. Gojkovic et al. interpreted the discrepancy between the percentage decrease in surface area (i.e. surface sites deactivated toward hydrogen adsorption) and the decrease in methanol oxidation current as due to methanol oxidation requiring three Pt sites per methanol molecule in the initial oxidation step [19]. This affect was not noted for Pt/Ru black and Pt/Pd, suggesting different oxidation mechanisms for the modified catalysts.

4. Conclusion

Nafion, whether applied on top of a catalyst or mixed into solution with the catalyst, reduces the active catalyst surface area. For Pt/Ru black and Pt/Pd nanoparticles, the drop in the oxidation efficiency mirrors approximately the reduction in the active surface area, but for the Pt black, the oxidation efficiency is lowered nearly three times as much as the active surface area. Depositing Nafion on top of the catalyst not only reduces the number of active surface sites, but also obscures the hydrogen peak shapes. For the three catalysts studied, only the Pt/Pd showed a change in the shape of the CV when Nafion was mixed in with the catalyst ink. These results agree with those by Wilson and Gottesfeld [16], suggesting that when Nafion is used in electrochemical experiments to help maintain a stable catalyst layer, Nafion should be mixed in with the catalyst ink, rather than deposited on top. However, surface areas and specific surface areas obtained from hydrogen peak integration will be underdetermined in these cases.

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