



Performance of the direct formic acid fuel cell with electrochemically modified palladium–antimony anode catalyst

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ABSTRACT

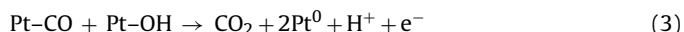
Previous work has shown that palladium catalysts are quite active for formic acid electrooxidation, but the catalysts need to be periodically regenerated to remove a CO impurity from the surface. The objective of this paper is to determine whether antimony additions could suppress the CO formation under fuel cell conditions. We find that antimony doubles the rate of reaction in an electrochemical cell, but the increase is less in real fuel cell conditions. The current that is produced at 0.6 V is approximately 14% greater for the fuel cell containing antimony additions than the palladium anode catalyst. In a constant-current test, we find that the fuel cell assembled with palladium–antimony anode catalyst produces 18% more voltage than the palladium anode catalyst after 9 h of operation. These results show that the antimony additions that significantly improve oxidation in the electrochemical cell have a much lesser impact in the formic acid fuel cell – they do not suppress CO formation in the fuel cell as anticipated.

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1. Introduction

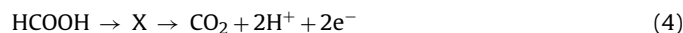
The direct formic acid fuel cell (DFAFC) has been studied recently as a means to provide high power density for portable devices without requiring connection to the electrical grid for device recharging [1–39]. The DFAFC power is comparable to that of a battery, and its performance at ambient temperature is stronger than a direct methanol fuel cell (DMFC), with less crossover [3,5,40,41]. Stronger performance and lower crossover rates result in higher energy density in the DFAFC, although its theoretical energy density is lower.

The first anode catalyst that was used in the DFAFC was platinum black, but the oxidation of formic acid on platinum occurs via an indirect pathway that includes a strongly bound CO intermediate [42–46]:



The CO builds up quickly on the platinum catalyst, poisoning the surface, and rapidly degenerating the fuel cell performance [47,48].

A more efficient catalyst is palladium black, on which the oxidation of formic acid occurs via a more direct pathway which involves a reactive intermediate, X, minimizing the buildup of CO on the catalyst surface [23,44,45,49,50]:



As expected, CO buildup is not observed in an electrochemical cell while oxidizing 1 M formic acid. However, in a commercial fuel cell using 22–24 M formic acid, CO slowly accumulates on the anode catalyst. Purification of formic acid to remove methyl formate and formic anhydride impurities leads to substantial reduction in the rate of CO buildup [30]. However, CO buildup has not been eliminated, and the anode catalyst must be regenerated periodically in an operating fuel cell [4–6,32].

At this point we do not know how the CO forms, but one possibility is that the presence of Nafion enhances the electrooxidation of formic acid via a CO intermediate. Gates and Schwab previously found that polystyrene sulfonic acid catalyzes the dehydration of formic acid to yield carbon monoxide and water [51]. The carbon monoxide could slowly adsorb on the palladium. Alternatively, the acid in the Nafion could cause steps to form on the palladium surface [52,53]. Such steps could be active for C–O bond scission in palladium [54–56] leading to CO formation. The CO pathway is well established during formic acid electrooxidation on platinum [43,48,49,57–62] and it can be inhibited by adatoms such as antimony, bismuth, cadmium, and lead [63–66]. CO adsorption is also inhibited. Recently, formic acid fuel cells have been developed using a *platinum* anode catalyst modified with lead and antimony [15,67].

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Although the adatoms slowed the buildup of CO poison, the fuel cell performance was still substantially lower than DFAFC performance using *palladium* black anode catalyst. Formic acid oxidation is also known to improve on smooth palladium when adatoms such as bismuth, cadmium, and lead are included [68], but these have not yet been shown in a DFAFC.

In this paper, we have studied the effects that adatoms have on the performance of a DFAFC. We find that antimony additions increase the rate of reaction in an electrochemical cell. The effect is less in an operating fuel cell but there is a small enhancement.

2. Experimental

2.1. Reagents

High surface area palladium black unsupported nanoparticles (99.8%, Aldrich) were used as the fuel cell anode catalyst and high surface area platinum black unsupported nanoparticles (HiSpec 1000, Alfa Aesar) were used as the fuel cell cathode catalyst. Sulfuric acid (Veritas® double distilled from Vycor, GFS) was diluted to 1 M H₂SO₄ as the supporting electrolyte for electrochemical modification. Antimony(III) oxide (99.999%, Alfa Aesar) was used to make ~1 mM Sb³⁺ in 1 M H₂SO₄. Ten molar formic acid was used for fuel cell testing as diluted from 50% formic acid (Fluka, HPLC grade). All solutions were made using 18 MΩ Milli-Q water as the solvent. Compressed air (S.J. Smith) was used for fuel cell testing.

2.2. Electrochemical modification

A standard three electrode electrochemical cell was used with a Solartron potentiostat (SI 1287) to modify the anode catalyst. The working electrode was a 4 cm² carbon paper with palladium black painted on one side, and this electrode was used in the fuel cell assembly. A platinum mesh was used for the counter electrode. The Ag/AgCl/sat'd KCl reference electrode (BAS) was calibrated by bubbling hydrogen gas (S.J. Smith) over a platinum mesh electrode in 1 M H₂SO₄.

2.3. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed using a PHI 5400 XPS system with an Mg Kα X-ray source. A sample of carbon paper (area 4 cm², as in the fuel cell assembly) was painted with palladium black and modified with antimony using the same parameters as those used in fuel cell preparation.

2.4. Electrochemical testing

A sample of carbon paper (area 0.5 cm²) with the same approximate catalyst ink loading as the fuel cell was tested in the three electrode cell. First, the current was measured after 5 min of formic acid oxidation in 3 M formic acid and 0.1 M sulfuric acid. Next, the electrode was modified in 1 mM Sb³⁺ and 1 M H₂SO₄ at 0.2 V for 2 and 5 min. Finally, the current was measured again after 5 min of formic acid oxidation.

2.5. Fuel cell testing

The membrane electrode assembly (MEA) used in fuel cell testing is shown in Fig. 1. The cathode consisted of approximately 10 mg cm⁻² platinum black painted directly onto a Nafion 117 membrane (Ion Power). Carbon cloth with single-sided wet-proofing (0.020" E-Tek) was used as the cathode gas diffusion layer (GDL). A very small amount of platinum (four paint layers; geometric coverage: 0.3 cm²) was also painted in an off-centered

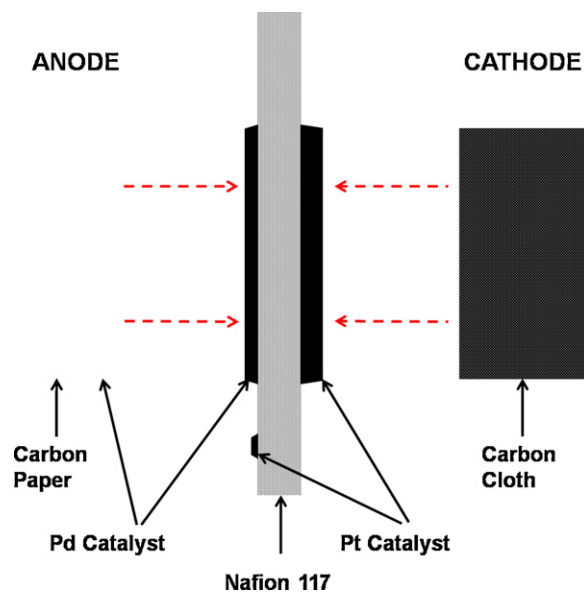


Fig. 1. Novel MEA design. This is a cross-section diagram of fuel cell MEA design that demonstrates the features of an MEA designed so that some of the anode catalyst can be electrochemically modified.

area on the anode side of the membrane for use as a reference electrode. Palladium black was painted onto the fuel cell anode for a total loading of approximately 10 mg cm⁻². Approximately half the anode catalyst was painted directly onto the Nafion, while the remainder was painted onto a carbon paper GDL (0.008", Spectracarb). The palladium that was painted on the carbon paper was then electrochemically modified at 0.45 V vs the reversible hydrogen electrode (RHE) during suspension in ~1 mM Sb³⁺ and 1 M H₂SO₄ in an electrochemical cell. This modified carbon paper then completed the MEA and was inserted into a fuel cell. This same MEA painting method was used without electrochemical modification to test the palladium black anode catalyst for comparison to antimony-modified palladium black anode catalyst.

Fuel cell current–potential tests were performed at 30 °C using the Solartron potentiostat running 1.0 mL min⁻¹ 10 M formic acid and 300 sccm air. Constant-current tests were performed with 0.15 mL min⁻¹ flow of formic acid. The formic acid fuel cell contained a reference electrode established by bubbling humidified hydrogen over platinum foil in contact with the platinum layer that had been painted off-center on the anode side of the Nafion membrane.

Anode polarization was measured at 30 °C by preparing carbon paper with palladium black catalyst as in the fuel cell assembly, except that no additional anode catalyst was painted onto the Nafion and the MEA was not hot pressed. Hydrogen at 300 sccm was passed over platinum catalyst on the other side of the Nafion as a reference, and 1.0 mL min⁻¹ formic acid was pumped on the anode.

3. Results

3.1. XPS characterization

Carbon paper (4 cm²) was painted with palladium black catalyst on one side. The paper was then modified in an electrochemical cell for 20 min at 0.4 V vs RHE in a solution of ~1 mM Sb³⁺ and 1 M H₂SO₄. The presence of antimony was confirmed by XPS, and the atomic composition was 62% Pd and 38% Sb.

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