Inhibition of Bismuth Dissolution during Anode Catalyst Layer Pore Former Removal in a Direct Formic Acid Fuel Cell

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An in-situ method is presented that protects the submonolayer of Bi on Pt/C, for enhanced formic acid electrooxidation in a fuel cell, from oxidative dissolution due to elevated potentials during an acid leaching pore former removal process by maintaining a potential of 0 V vs RHE. Comparing the current density of the no pore former catalyst layer at 0.25 V to the uncontrolled ex-situ acid leached catalyst layer, there was a 65% loss in activity, while for the in-situ potential controlled acid leached catalyst layer with pore former a 20% increase in performance was measured.

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Direct liquid fuel cells have been under intense study as alternative power sources for portable electronics. These power sources, unlike batteries, offer continuous energy availability due to fuel replenishment allowing nearly 100% uptime without needing recharging and downtime. While a significant portion of the literature for liquid fuel cells revolves around methanol as a fuel, direct formic acid fuel cells (DFAFCs) are a potentially superior alternative as they can be run with pure/neat fuel because of their inherent lower fuel crossover through the proton conducting membrane (i.e. lower parasitic loss). They allow for easy leak detection and they have potentially higher power densities. Two major electro-oxidation pathways for formic acid exist; i.e. the direct pathway (1-step, dehydrogenation) and the indirect pathway (2-step, dehydration). On platinum (Pt), the limiting indirect pathway dominates. To enhance the dominance of the direct pathway, researchers have decorated the Pt surface with a sub-monolayer of bismuth (Bi). Bismuth has been shown to favorably promote the adsorption orientation of formic acid in the C-H down orientation through a ‘third-body effect’ and to a lesser degree a favorable electronic Pt d-band shift. In a previous formic acid electrooxidation study, it has been demonstrated in the Rice group that 54% Bi coverage (θBi) is optimal for enhanced performance on carbon supported platinum nanoparticles (Pt/C).

Liquid mass transport in the anode catalyst layer of DFAFCs has been a limiting factor in performance, but has been decreased with the use of a pore former to artificially produce a larger pore network. A common pore former used in direct methanol fuel cells is lithium carbonate, which is easily removed via acid leaching by immersing the entire membrane electrode assembly in a dilute sulfuric acid solution.

The initial objective of this work was to improve anode catalyst layer performance for DFAFCs by combining the Bi (θBi = 54%) modified carbon supported Pt (Pt/C) catalyst with the pore former to enhance activity and mass transport, respectively. The Bi modified catalyst used herein was found to be nearly entirely removed during the pore former acid washing step due to uncontrolled and elevated potentials resulting in oxidation and removal of the Bi. This paper presents the challenge at hand of maintaining catalyst performance and altering the catalyst layer structure by limiting the potential (below Bi oxide formation potential) during in-situ pore former removal which has practical applications in large scale production.

Experimental

Catalyst preparation.— The catalyst was prepared by modifying a commercially available 66.9 wt% Pt/C catalyst from Tanaka (TEC10E70TPM) using an approach previously developed. In brief, the method included controlled surface potential of the catalyst by sparging gaseous H2 in a centrifuge tube containing 150 mg Pt/C in 8 mL 0.5 M H2SO4 (double distilled 95–98%, GFS) for 20 min to set the Pt surface potential to 0 V. The suspension was subsequently purged with N2 for 10 min, then bismuth oxide (Bi2O3, 13.6 mg) was added and agitated using N2 sparging (for 60 min) to result in θBi = 54% on Pt. Subsequently, the suspension was again purged with H2 (for 20 min) to fully reduce the submonolayer of Bi. All gasses used in this and subsequent sections are UHP, Airgas. The suspension was segregated by sedimentation and washed via centrifugation and liquid exchange with Millipore water. The final catalyst was collected in a petri dish and dried in a vacuum oven (80°C, –127 mmHg) for 3 hours. The catalyst was then tested in one of two ways: as a catalyst layer in a membrane electrode assembly for in-situ half-cell fuel cell testing or as a thin film on a rotating disc electrode for ex-situ testing in an aqueous electrolyte.

In-situ testing.— A membrane electrode assembly was prepared using the modified catalyst in a catalyst ink suspension which was directly applied onto a Nafion HP (Ion-Power Inc.) membrane using an airbrush for the anode. An ink comprised of 150 mg modified catalyst, 0.9 mL Millipore water, 1.8 mL methanol, 0.87 mL of 5 wt% Nafion solution (Ion-Power Inc., D521) and 45 mg lithium carbonate was prepared. The catalyst, water and methanol are stirred for 3 hours. Nafion solution is added and allowed to mix >12 hrs. Finally, 0.5 hours before use, 30 wt% lithium carbonate pore former versus mass of Pt/C is added. While lithium carbonate is only partially soluble in water, changes in surface chemistry may occur after prolonged exposure. The prepared ink is directly sprayed onto the Nafion HP membrane using an airbrush with nitrogen as propellant. A Teflon fixture with 5 cm2 open window is used to suspend the membrane during spraying. The catalyst loading for the anode is determined gravimetrically. Prior to assembly, a 5 cm2 section of the gas diffusion electrode is prepared for the cathode and applied to the membrane using a thinly brushed layer of Nafion solution as adhesive. Three membrane electrode assemblies were prepared: (1) a baseline without pore former, (2) pore former removed by ex-situ acid leaching and (3) pore former removed by in-situ acid leaching.

During the experimental testing, two 5 cm2 Fuel Cell Technologies fuel cell fixtures with serpentine flow fields were utilized; a standard dual gas feed and a one specially designed to designed to restrict formic acid contact with metal components and the endplates, referred to herein as ‘dual gas feed’ and ‘liquid feed’ fixtures, respectively. The diffusion media used on the anode was non-hydrophobic (SGI 25AA, Ion Power, Inc.). The cathode was a combined gas diffusion electrode (Pt/C, Alfa Aesar, 45375). The cell temperature, reactant gas supply, dew point and applied loads were controlled via an 850E fuel cell...
test station (Scribner Associates, Inc.). The initial cell conditioning was performed at a cell temperature of 70°C at 70% relative humidity (RH), by cycling the cathode potential between N2 and air (21% O2) (0.5 L min⁻¹) while maintaining a constant feed of H2 to the anode (0.2 L min⁻¹). This allowed for simultaneous aging of the catalyst and hydration of the cell. Subsequently, H2/air polarization curves were performed by scanning the applied current from open circuit voltage (OCV) to 0.3 V, until stable performance was obtained.

For the membrane electrode assemblies with pore former in the anode catalyst layer, prior to conditioning, the acid leaching was either ex-situ or in-situ. The ex-situ acid leaching was performed by submersion in 50 mL of 0.5 M H2SO4 open to the atmosphere. While the in-situ acid leaching was done in the liquid feed fixture with 5 M formic acid on the anode. For the in-situ acid leaching approximately 100 mL of 5 M formic acid solution was passed through the anode at 2.5 mL min⁻¹ while 55% RH hydrogen was passed through the cathode. During this time the cell was shorted to maintain the potential near to 0 V. Water is then used to remove the formic acid in the anode catalyst layer.

Once the cells were conditioned, the membrane electrode assemblies were then switched to the liquid feed fixture for all electrochemical characterization with either Millipore water or 5 M formic acid (2.5 mL min⁻¹) versus 55% RH 4% H2 in an Ar balance (0.1 L min⁻¹) at a cell temperature of 40°C. The H2 established a dynamic hydrogen reference electrode (DHE) on the cathode. For all electrochemical measurements a Solartron 1287 potentiostat was used. Linear sweep voltammetry was performed from the negative formic acid open circuit potential around −0.025 V to 0.25 V vs. DHE at a sweep rate of 10 mV sec⁻¹. Directly after purging 10 min with Millipore water, carbon monoxide (CO) stripping was preformed from 0.05 V to 1.05 V vs. DHE at 50 mV sec⁻¹.

Ex-situ testing — To test the actual bismuth coverage and the stability in various gas-purged acid solutions, ex-situ characterization of the catalyst in a 3-electrode electrochemical cell was performed. A reversible hydrogen electrode (RHE) reference and a platinum gauze counter electrode were used in 0.1 M HClO4 electrolyte. A glassy carbon rotating disc electrode (5 mm diameter) with 10 μL catalyst ink comprised of (5 mg catalyst: 4 ml Millipore water: 1 mL isopropanol: 20 μL 5 wt% D521 Nafion solution) was prepared and electrochemical tests were performed.

The ex-situ testing is a simple protocol. A beginning of life cyclic voltammogram (0.025–1.2 V vs. RHE) was acquired at 10 mV sec⁻¹. The electrode was removed and immersed in a solution of 0.5 M H2SO4 for > 12hrs which is either non-purged (air saturated) or purged with H2. A quick rinse with an argon saturated HClO4 solution was performed to remove any residual H2SO4 and the electrode is re-immersed in the 3-electrode cell. Finally, an end of life cyclic voltammogram (0.025–1.2 V vs. RHE) is performed. The current densities of the ex-situ cyclic voltammograms were normalized, based on the beginning of life platinum electrochemically active surface area, calculated using the hydrogen desorption region of the cyclic voltammograms, assuming a 210 μC cm⁻² charge density for a monolayer of hydrogen.

Results and Discussion

In an attempt to increase direct formic acid fuel cell performance, a pore former (submicron sized lithium carbonate, Li2CO3) and a bismuth modified catalyst Pt(66.9 wt%)/C-Bi(θBi = 54%) were used simultaneously to promote the synergistic effects of improved mass transport in the anode catalyst layer and higher anode catalyst activity. Bismuth modified catalyst is commonly prepared using an electrochemical process, however recently it has been prepared in our laboratory using underpotential deposition using a simple gas controlled surface potential modulation technique amenable to future large-scale production. This catalyst has shown stability in formic, perchloric and sulfuric acid, with the caveat that above 0.75 V, oxidation and subsequent removal of bismuth resulting in decreased performance occurs. It is therefore critical that the anode potential be maintained below the onset of Bi oxidation to avoid performance losses.

Figure 1 shows the linear sweep voltammetry performance of the baseline membrane electrode assembly (MEA, No pore former) in 5 M formic acid vs. DHE. Based on Gibbs Free Energy the theoretical potential for formic acid electro-oxidation is −0.25 V15 therefore a relatively small onset potential is required to observed activity above 0 V as the reaction proceeds via the direct pathway. However the MEA prepared with 30 wt% pore former that was acid leached ex-situ shows a striking decrease in performance. The standard removal process was used, i.e. ex-situ immersion of the MEA in acid, followed by rinsing with Millipore water prior to assembly in a fuel cell fixture.12,13 The onset potential was extended to above 0.05 V and a 65% loss in current density at 0.25 V was observed. These trends were consistent with a non-optimized Bi coverage, which were confirmed with subsequent carbon monoxide (CO) stripping analysis.

Immediately following linear sweep voltammetry CO stripping was performed in Millipore water, Figure 2. For the baseline MEA (No pore former) two peaks were observed: (1) oxidation of CO at 0.66 V and (2) oxidation of BiOx at 0.86 V. The ex-situ acid leached MEA showed barely any trace of BiOx, demonstrating inadvertent removal. It was has been suggested that Bi loss was occurring due
to elevated potentials during acid washing due the atmospheric O\textsubscript{2} concentration in solution.

To test the hypothesis, an ex-situ testing experiment was conducted in a 3-electrode electrochemical cell. It has been found that lack of potential control during the pore former removal process results in removal of bismuth via oxidation. To assess Bi stability in the absence of potential control, the working electrode was removed from the 3-electrode cell and immersed in 0.5 M H\textsubscript{2}SO\textsubscript{4} under the following purge conditions for 12 hours: (1) air and (2) hydrogen gas. To maintain the catalyst surface potential below the oxidation potential of Bi, a hydrogen purged solution was used and showed nearly complete retention of bismuth through both examination of the Pt features (0.025–0.4 V vs RHE) and the BiOx peak ~0.86 V vs RHE. The results in Figure 3 clearly show nearly complete Bi removal when the working electrode was exposed to air. With respect to Pt, there was a 113% increase in Pt electrochemically active surface area (ECSA) with the air purged solution electrode while there was only a 14% increase in Pt ECSA with the electrode in the hydrogen purged solution. To detect the BiOx peak, the catalyst must be taken to a potential above its stable point where loss may occur as some surface BiOx may dissolve into the electrolyte. As such, the loss seen in Figure 3 ~0.86 V vs RHE is mostly due to oxidation during this process.

Based on the results from the ex-situ testing, an alternative in-situ pore former removal process was devised to maintain the anode potential near 0 V. This process, referred to herein as in-situ acid leaching, uses 5 M formic acid to remove the pore former on the anode in a liquid-feed fixture while maintaining a DHE on the cathode.

Presented in Figure 1 are linear sweep voltammograms comparing the performance differences between the baseline and the two acid leaching methods. The in-situ removed pore former shows enhanced catalyst activity owing to the synergistic effect of the increased anode porosity and promotion of the direct pathway using Bi adatoms. For the 3 different MEAs, the onset potential was 0 V for both the baseline (No pore former) and the in-situ acid washed pore former, while it was adversely increased to 0.05 V for the ex-situ acid washed pore former. Compared to the baseline, the current density at 0.25 V was increased by 20% for the in-situ acid washed pore former and decreased by 65% for the ex-situ acid washed pore former.

Future work will involve optimization of the pore former. Both the optimal size and amount will be investigated to improve mass transport.

**Conclusions**

We have presented a methodology for successful in-situ removal of an acid solvable pore former salt from a catalyst layer while maintaining potential control of aforementioned layer’s catalyst. This is specifically useful for retaining easily oxidized species such as Bi decorated on platinum catalyst, used in this study. Only 14% increase in platinum surface area (due to removal of Bi) was seen with the potential controlled method versus complete removal of Bi without potential control. A 20% increase in current density was realized due to the combined effects of the modified catalyst and pore former as shown though linear sweep voltammetry performance.

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