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CO tolerance of nano-architectured Pt–Mo anode electrocatalysts for PEM fuel cells

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ABSTRACT

PEM fuel cell membrane electrode assemblies with Nafion electrolytes and commercial Pt-based cathodes were tested with $Pt_{0.8}Mo_{0.2}$ alloy and MoO_x@Pt core–shell anode electrocatalysts for CO tolerance and short-term stability to corroborate earlier thin-film RDE results. Polarization curves at 70 °C for the $Pt_{0.8}Mo_{0.2}$ alloy in H_2 with 25–1000 ppm CO showed a significant increase in CO tolerance based on peak power densities in comparison to PtRu electrocatalysts. MoO_x@Pt core–shell electrocatalysts, which showed extremely high activity for H_2 in 1000 ppm CO during RDE studies, performed relatively poorly in comparison to the $Pt_{0.8}Mo_{0.2}$ and PtRu alloys for the same total catalyst loading on a per area basis in MEA testing. The discrepancy is attributed to residual stabilizer from the core–shell synthesis impacting catalyst-ionomer interfaces. Nonetheless, the MoO_x@Pt electrochemical performance is superior on a per-gram-of-precious-metal basis to the $Pt_{0.8}Mo_{0.2}$ electrocatalyst for CO concentrations below 100 ppm. Due to cross-membrane Mo migration, the stability of the Mo-containing anode electrocatalysts remains a challenge for developing stable enhanced CO tolerance for low-temperature PEM fuel cells.

1. Introduction

Reducing the poisoning effects of CO on anode electrocatalysts for low-temperature, Nafion-based PEM fuel cells (PEMFCs) opens numerous market opportunities for PEMFC systems operating with hydrocarbon fuel reformers. Low-temperature PEMFCs integrated with hydrocarbon reformers require some form of H_2 purification process, such as a preferential CO oxidation (PROx) reactors, Pd-based membrane purifiers, or pressure-swing absorption beds. All of these H_2 purification strategies complicate the PEMFC system at the expense of economic viability, system weight and size, and overall system efficiency. Thus, efforts have sought to find ways to increase CO tolerance with higher temperature stacks [1,2] or novel anode electrocatalysts, which would reduce the need for H_2 purification.

Although there has been significant effort to develop multimetallic Pt-based anode electrocatalysts with higher CO tolerance [3–8], the common use of PtRu bimetallic catalysts for anodes only permits less than 100 ppm CO in the anode inlet [5,9,10]. PtRu catalysts can tolerate slightly higher CO concentrations with lower anode overpotentials by employing mitigation strategies such as small air bleeds for *in situ* CO removal [11]. However, such mitigation strategies also have negative impacts on system efficiencies and architecture. Thus, research and development efforts have sought alternative electrocatalysts such as Pt–Mo electrocatalysts which have slightly higher CO tolerance, with reasonable

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overpotentials up to 100 ppm CO [4,5,12]. Nonetheless, challenges remain because Mo-containing catalysts have shown poor durability due to leaching of the base metal Mo into the acidic Nafion-impregnated environment and subsequent crossover to the cathode catalyst layer [13,14].

Some efforts to improve durability and performance of bimetallic catalysts in PEMFC have sought to take advantage of well-controlled electrochemical or liquid-phase synthesis techniques, which can provide structures such as core–shell nanoparticles with only durable Pt on the outer catalyst particle surfaces [15,16]. Theoretical DFT studies suggest that such core–shell architectures with Pt shells on various metal/metal oxide cores may provide enhanced activity for CO oxidation due to core-modified electronic structure of the Pt surface [17,18]. Furthermore, the shell has the potential to provide improved durability of the base metal-containing catalysts with the Pt shell. These findings motivated an initial study which utilized RDE experiments to compare CO and H_2 oxidation on well-defined MoO_x@Pt core–shell and $Pt_{0.8}Mo_{0.2}$ nanoparticle electrocatalysts [16]. The results from the RDE study suggested that in CO-laden acidic solutions the MoO_x@Pt core–shell electrocatalysts had much lower CO overpotentials due to the MoO_x core altering the Pt surface favorably for enhanced CO oxidation. While it can be claimed that RDE experiments are adequate measures of electrocatalyst performance in full PEMFC membrane electrode assemblies (MEAs) for O_2 reduction [13], it is not clear that lower CO oxidation overpotentials in RDE experiments translate into better anode performance in MEA testing. Thus, this study presents MEA testing of previously identified MoO_x@Pt core–shell and $Pt_{0.8}Mo_{0.2}$ alloy electrocatalysts for comparison with standard PtRu electrocatalysts for H_2 oxidation laden with CO up to 1000 ppm. The results provide an initial assessment of the effectiveness of the core–shell and well-defined $Pt_{0.8}Mo_{0.2}$ alloy electrocatalysts to improve anode performance with higher CO tolerance and durability. Successful demonstration of these electrocatalysts – particularly the core–shell with its relatively low precious metal content – could motivate development of more CO-tolerant low-temperature PEMFCs for more efficient, cost-effective integration with hydrocarbon fuel reformers.

2. Materials and methods

$Pt_{0.8}Mo_{0.2}$ alloy and MoO_x@Pt core–shell nanoparticles were prepared in-house by liquid-phase synthesis as previously described in detail in the earlier reference [16]. Solution-based syntheses of Pt-Mo alloy nanoparticles are challenging due to the large negative redox potential of Mo^{n+}/Mo^0 couple and the low miscibility of Pt and Mo. For this synthesis, co-reduction of $MoCl_3$ and $Pt(acac)_2$ in phenyl ether was used with sodium triethylborohydride and oleic acid as the reducing agent and capping agent, respectively. The $Pt_{0.8}Mo_{0.2}$ alloy nanoparticles were heat treated in a reducing environment to remove the oleic acid after supporting the nanoparticles on a carbon support.

For the MoO_x@Pt core–shell synthesis, $NaBH_4$ reduction of $MoCl_3$ in ethylene glycol was employed in conjunction with the weakly-coordinating polyvinylpyrrolidone (PVP) stabilizer to form MoO_x nanoparticles. These particles were then reacted with $PtCl_2$ in ethylene glycol to give MoO_x@Pt core–shell nanoparticles containing *ca.* 1 ∼ 2 layers of Pt shells over MoO_x cores [16]. For the core–shell catalysts, the PVP stabilizer near the catalyst surface was not removed by heat treatment because of the high-temperatures required for PVP oxidation and concerns about high-temperature particle restructuring. The RDE tests suggested that the residual PVP did not impact catalyst performance in the liquid solution experiments, but as discussed below, impacts of the stabilizer on the Nafion/catalyst interface necessary for functioning PEMFC MEAs can be significant with respect to electrocatalyst utilization and electrode overpotentials.

Both Mo-containing catalysts were supported on XC-72 carbon at a 30 wt% metal loading. Commercial 1:1 PtRu alloy catalyst, also 30 wt% metal on XC-72, was also purchased from BASF Fuel Cell (Somerset, NJ), and used for comparison. Catalyst performance was characterized in 5 cm^2 single-cell MEAs. PtRu and $Pt_{0.8}Mo_{0.2}$ catalyst inks were prepared using a carbon-supported catalyst to 5% Nafion solution to isopropyl alcohol weight ratio of 1:12:31. For the MoOx@Pt catalyst 20 parts water were also added to the ink to improve the catalyst dispersion. After sonicating to break up chunks and disperse the nanoparticle catalyst, the ink was mixed continuously with a micro stir bar throughout the fabrication process. The anode catalyst layer was formed by brushing the catalyst ink onto a carbon-cloth GDL (BASF Fuel Cell) and drying at 60 °C between successive layers, until a total metal loading of 0.5 mg cm^{-2} was obtained.

Nafion 212 electrolyte membranes (Ion Power, New Castle DE) were treated in H_2O_2 and H_2SO_4 to remove impurities and convert to H^+ form. The same commercial Pt cathode GDE with 0.5 mg cm^{-2} loading (BASF Fuel Cell) was used as the cathode for all MEAs. MEAs were formed by hot-pressing the anode, membrane, and cathode together at 140 °C and 9.0 MPa for 2 min.

A Scribner Associates (Southern Pines, NC) 850e test stand was used to provide humidified flows and record measurements during MEA testing. H_2/CO mixtures with up to 1000 ppm CO (on a dry basis) were used as anode feeds, while air was the cathode oxidant. CO mixtures at 100 and 1000 ppm were obtained from Airgas and diluted using mass flow controllers. The cell was operated at 70 °C, with 2.0 barg back pressure on both sides and with both cathode and anode flows humidified to saturation at the same temperature as the cell. Thus, inlet partial pressures of anode H_2 and cathode O_2 for the fully humidified flows were $p_{H_2,\text{anode}} = 2.68$ bar and $p_{O_2,\text{cathode}} = 0.56$ bar respectively for all conditions in this study. Flow stoichiometry (defined as molar inlet flux divided by rate of moles consumed by current) was set at 2.2 on both sides of the MEA, with minimum flow rates of 56 and 133 sccm on the anode and cathode, respectively, to facilitate water removal.

MEAs were conditioned overnight at a constant 0.6 V before testing. CO-contaminated H_2 was then introduced and the cell was poisoned for 1.5–2.5 h while maintaining 0.6 V, until a constant current density was sustained for 2 h. *V-i* curves were recorded after this steady-state was reached, at intervals of 50 mA cm^{-2} after 20 s at each point to stabilize. Ohmic resistance of the cell was measured by the current-interrupt