Ceramic Supported Pt and Pt-Ru Catalysts for Methanol Oxidation

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Introduction

Pt and Pt-Ru are the primary catalysts used for electrodes in direct methanol fuel cells (DMFCs). Noble metals are expensive, and present a significant cost barrier to commercially viable fuel cells. Dispersing these catalysts onto support materials has effectively reduced the noble metal loading required for fuel cell electrodes and reduced fuel cell costs. High surface area carbon has been the most popular fuel cell catalyst support material. While relatively stable, carbon serves only to disperse the noble metal catalysts. No catalytic activity is displayed by the carbon support material, either directly or indirectly, toward methanol oxidation. Additionally, the density of carbon is low, hence a large volume of supported catalyst is required for higher Pt loadings needed for high power density DMFCs. Large volumes of supported catalysts impose detrimental mass transport effects on fuel cell performance through necessarily thick catalyst layers and limit DMFC power densities (1, 2).

Transition metal oxides have shown catalytic activity toward methanol oxidation in concert with noble metal catalysts (3). However, high degrees of electronic resistance within the oxide contribute to larger ohmic potential losses (3). We address the need for improved anode electrocatalysts for use in DMFCs by dispersing Pt and Pt/Ru onto high surface area conducting ceramic supports. Our approach investigates the catalytic activity of noble metal catalysts dispersed onto the surface of high surface area metal carbide and metal nitride support materials (4). These supported catalysts possess high catalytic activities due to dispersed noble metal sites in intimate contact with the electronically conductive ceramic support materials. Further, the support materials studied in this work are 3-5 times more dense than carbon, which reduces mass transport effects that limit the power density of the anode. The use of noble metal catalysts supported on high surface area conductive ceramics should therefore be useful for improving the performance and cost of direct methanol fuel cells.

Experimental

Preparation of high surface area ceramic support materials-

High surface area carbide and nitride support materials were prepared by temperature programmed reactions (TPR) under controlled atmospheres (5). Precursors used were either oxide or metal amide/imide powders. Precursors were heated in a 1 inch diameter quartz tube positioned in a horizontal tube furnace. Reactant gas compositions and flow rates were controlled through a manifold of Tylan precision mass flow controllers. Results will be presented for two carbides and a nitride support material (see Table I). Support material phases and compositions are considered proprietary and will not be identified.
Table I. Metal Carbides and metal nitride used as noble metal support materials.

| Support Material | Reference Code | with Pt dispersion | with Pt-Ru dispersion |
|------------------|----------------|--------------------|----------------------|
| T/J Metal Carbide I | MC1            | Pt/MC1             | Pt-Ru/MC1            |
| T/J Metal Carbide II | MC2           | Pt/MC2             | Pt-Ru/MC2            |
| T/J Metal Nitride      | MN1            | Pt/MN1             | Pt-Ru/MN1            |

Reference codes do not imply material stoichiometry.

Noble metal dispersion onto ceramic support materials-

Small platinum clusters were dispersed onto the surface of the high surface area ceramic supports using methods similar to those described by Watanabe et al. (6,7,8). 200 mL of chloroplatinic acid (0.5% by weight in water) was converted to platinum sulfite acid by slowly mixing in ~ 4 g of sodium bisulphite. The solution was diluted to 700 mL and the pH was adjusted to 5.0 by adding 1 M sodium carbonate solution. Binary Pt/Ru catalysts were prepared in a similar manner, except Ru salts (RuCl₃) were dissolved in water and then added to the Pt precursor solution to achieve the desired Pt:Ru ratio. Noble metal solutions were then converted to metastable oxide salts by slowly adding 30 wt % H₂O₂ while stirring. Solution pH was maintained at 5.0 by adding 1 M sodium carbonate solution when necessary. Noble metal particles were reduced onto the support materials by bubbling hydrogen gas through the solution overnight. The supported catalysts were collected and washed thoroughly with deionized water and then dried at 100°C.

Support materials characterization-

Support material phases and compositions were examined by x-ray diffraction using a Rigaku DMAX-B x-ray diffractometer with a Digital VAXstation II/GPX. Powder patterns were compared with existing x-ray diffraction files for identification. Surface areas were determined by single point BET using a Quantasorb Jr. Surface Area Analyzer with 29% N₂/He as adsorption gas and N₂ calibration gas. The weight % of noble metals in each supported catalyst was determined using atomic absorption spectroscopy. Prior to analysis, supported catalysts were dissolved in aqua regia and diluted to a known volume. Analyses were made with a Perkin Elmer 1100 B spectrometer.

Electrochemical measurements were made with the use of an EG&G Versastat Potentiostat/Galvanostat interfaced with a personal computer through an IEEE-488 interface board and run by M270 electrochemical software. Measurements were made in a three electrode glass cell with a Pt foil counter electrode and a reversible hydrogen electrode (RHE) in a separate compartment connected to the analyte through a ground glass frit and Luggin capillary. All experiments were run in 1.0 N H₂SO₄ at room temperature (23 ± 2°C). Solutions were purged of oxygen using argon gas unless otherwise stated. All voltages are reported vs. RHE.

Catalyst inks were prepared by mixing supported catalysts with Nafion (15% by weight, Nafion/catalyst) and diluting to an appropriate volume with isopropanol (9). Aliquots of ink were withdrawn with a micropipette and weighed after being allowed to dry. In this way the mass of solids per unit volume of ink was determined for each catalyst ink.
Electrochemical analyses were performed with carbon current collectors. Graphite rods (0.32 cm²) were cleaned on abrasive paper, sonicated in 18 MΩ water to remove polishing debris, and air dried. Appropriate volumes of each ink were withdrawn with a micropipette and carefully placed on the end of the graphite rods and then cured at 120°C for 30 minutes. After curing, the barrel of each electrode was wrapped with Teflon tape to prevent any interference from the graphite rod.

Results and Discussion

Surface area analysis-

MC1 and MC2 were produced with BET surface areas of 90 m²/g and 113 m²/g, respectively. MN1 displayed surface areas exceeding 100 m²/g. Surface areas were dependent on the precursors used and TPR profile followed. Pores of less than 10 nm were minimized in order to ensure adequate mass transfer of reactants to catalyst surfaces (10). Higher surface area support materials with pore size distributions optimized for DMFC applications will be produced in the future by further modifying reaction conditions.

X-ray diffraction-

Diffraction patterns for supported catalysts were highly dependent on the support material used. Noble metals dispersed onto MC1 generated no Pt diffraction patterns in conjunction with the diffraction pattern for the support material (see Figure 1). Subsequent electrochemical analysis, coupled with evidence from atomic absorption spectroscopy (vida infra), suggested that the noble metals were finely dispersed on the surface of MC1, either as Pt sites too small to be detected by x-ray diffraction, or as an amorphous species dispersed on the MC1 support (11).

![X-ray diffraction pattern for Pt/MC1](image.png)

Figure 1. X-ray diffraction pattern for Pt/MC1. Pt particle size estimation impossible, possibly due to amorphous Pt or very small Pt domains.
The diffraction pattern for Pt/MN1 allowed for an estimation of Pt particle sizes of ~9 nm. Pt catalysts supported on MC2 exhibited noble metal particle sizes of ~6 nm. Diffraction patterns for MC2 and MN1 become less pronounced following Pt dispersion (see Figure 2). Changes in diffraction patterns following dispersion indicates structural changes in MC2 and MN1 during the dispersion processes.

![X-ray diffraction pattern for Pt/MC2. Pt particle size estimated to be ~6 nm.](image)

**Figure 2.** X-ray diffraction pattern for Pt/MC2. Pt particle size estimated to be ~6 nm.

**Atomic absorption analysis**-

Atomic absorption analysis confirmed that noble metals were successfully dispersed onto the high surface area carbide and nitride support materials. Pt weight percentages exceeding the expected value (Pt/MC2, Pt/MN1) suggest dissolution of support materials during the dispersion process.

**Table II. Pt content of TZJ supported catalysts.**

| Catalyst Type | Pt Content (wt %) | Ru Content (wt %) |
|---------------|-------------------|-------------------|
| Pt/MCl        | 12                | --                |
| Pt-Ru/MCl     | 9                 | 4.5               |
| Pt/MC2        | 27                | --                |
| Pt/MN1        | 10                | --                |

*Expected Pt content of 10 wt %.
Cyclic voltammetry performed on supported catalyst inks revealed differences in catalytic activity toward methanol oxidation. Catalyst activity depended highly on the support material used. The Pt/MN1 catalyst demonstrated a high electrochemical surface area with no distinct voltammetric features (Figure 3). Methanol oxidation occurred in a manner typical for Pt catalysts, oxidizing methanol on both positive-going and negative-going sweeps. Current densities for the Pt/MN1 catalyst were less than current densities observed for equivalently produced Pt/C catalysts. Differences in activity may be due to inaccessible Pt sites within the MN1 support following dispersion. Future research will examine the effects of alternative dispersion methods on catalyst performance.

Figure 3. Cyclic voltammograms for the Pt/MN1 catalyst recorded at scan rates of 20 mV/s in 1 N H₂SO₄ with methanol concentrations of 0 mol/L and 1 mol/L. Currents are normalized by Pt content of catalyst (mA/mg Pt).

Platinum catalysts supported on MC2 displayed voltammetry indicating surface interactions between the carbide and noble metal domains (see Figure 4). Reversible waves observed in the potential region between 0.05 and 0.3 V suggested a high degree of hydrogen adsorption/desorption on this supported catalyst. The voltammetry in blank electrolyte differed significantly from the independent voltammetries of MC2 and Pt, indicating the electrochemical activity is due to the two species acting in concert. Methanol oxidation activity for the Pt/MC2 catalyst was comparable to Pt/C catalysts under equivalent conditions.
Figure 4. Cyclic voltammograms for the Pt/MC2 catalyst recorded at scan rates of 20 mV/s in 1 N H₂SO₄ with methanol concentrations of 0 mol/L and 1 mol/L. Currents are normalized by Pt content of catalyst (mA/mg Pt).

The most dramatic results were observed for the Pt/MCl supported catalyst (see Figure 5). Blank voltammetry clearly indicated intimate surface interactions between the MCl support and Pt particles in the hydrogen adsorption/desorption region. Waves due to Pt oxide formation and reduction were observed. The electrochemical surface area for this catalyst was high, supporting the assertion that Pt domains on this catalyst are small. The methanol oxidation activity for the Pt/MCl catalyst was significantly higher than for equivalently produced Pt/C supported catalysts.

Figure 5. Cyclic voltammograms for the Pt/MCl catalyst recorded at scan rates of 20 mV/s in 1 N H₂SO₄ with methanol concentrations of 0 mol/L and 1 mol/L. Currents are normalized by Pt content of catalyst (mA/mg Pt).

In addition to high catalytic activity, Pt/MCl supported catalysts displayed tolerance to poisoning by CO during methanol oxidation. Three consecutive scans following dosing
with methanol show a gradual shift in the overpotential for methanol oxidation at the Pt/MCl catalyst (see Figure 6a). In contrast, Pt/C catalysts develop almost the full overpotential for methanol oxidation after only the first scan (Figure 6b). These results indicate MCl promotes CO tolerance by Pt.

Figure 6. Cyclic voltammograms recorded at 25 mV/s for (a) Pt-MCl and (b) Pt/C catalysts in oxygen-free solutions of 1 M methanol in 1 N H2SO4. First scans (—) for each catalyst exhibit high activities. Scans 2 (—) and 3 (---) for the Pt/C catalyst (b) exhibit a large increase in overpotential for methanol oxidation, due to CO formation on Pt sites. The Pt-MCl catalyst (a) displays only small changes in overpotential for scans 2 and 3, indicating catalyst tolerance to CO. Methanol oxidation activities (normalized to mA/mg Pt) for the Pt-MCl catalyst are twice those observed for the equivalently produced Pt/C catalyst.

Further CO tolerance was imparted to the MCl supported catalysts through the dispersion of Pt-Ru instead of pure Pt. Similar to Pt-MCl supported catalysts, x-ray diffraction revealed no peaks due to Pt or Pt-Ru alloys on the surface of Pt-Ru/MCl catalysts, despite the presence of noble metal sites confirmed by both voltammetry and atomic absorption spectroscopy. Figure 7 shows differences in voltammetry between Pt-MCl and Pt-Ru/MCl supported catalysts. Voltammograms recorded for both supported catalysts exhibit waves indicative of hydrogen adsorption/desorption between 0.05 V and 0.3 V vs. RHE. The Pt-Ru/MCl supported catalyst showed reduction of Pt-oxides formed on the anodic sweep at a potential of ~100 mV cathodic of the Pt/MCl supported catalyst, due to the lower potentials for oxide formation on Pt-Ru alloys.
Figure 7. Cyclic voltammograms recorded at 20 mV/s in 1.0 N H₂SO₄. Data for Pt/MCl (dashed line) and Pt-Ru/MCl (solid line) catalysts shown. Peak positions for oxide reduction waves at 0.7 V and 0.8 V for the Pt-Ru and Pt supported catalysts, respectively, indicate a higher affinity of the Pt-Ru catalyst toward surface oxides.

A direct comparison of methanol oxidation activities was made between Pt-Ru/MCl supported catalyst produced at TJ and Pt-Ru/C catalysts purchased from major catalyst suppliers. In these tests, catalyst activity was determined by chronoamperometric methods using the potential waveform shown in Figure 8. The pulsed potential waveform electrochemically cleans working electrodes prior to methanol oxidation, ensuring a clean and reproducible surface for each experiment. Similar potential waveforms are commonly used in studies of organic oxidation reactions (12). Initially the working electrode was pulsed to 1.1 V for 10 s. At this potential carbon monoxide and other passivating species deposited on the working electrode during previous experiments are oxidized to CO₂ and removed from the working electrode surface. The poison-free electrode was then pulsed to a potential of 0.05 V for 10 s. At this potential Pt oxides are reduced to metallic Pt, the species responsible for the adsorption and subsequent oxidation of methanol. Finally, the working electrode was pulsed to the potential of interest (E₂) for 60 s. Currents were recorded before and after the addition of methanol. Current differences obtained at the end of E₂ were used to determine methanol oxidation currents for each type of catalyst.

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Figure 8. Schematic of the potential sequence used for chronoamperometric experiments.

Figure 9 shows Tafel plots constructed from current densities (normalized to mA/mg Pt) due to methanol oxidation at Pt-Ru/MCl and two commercially available Pt-Ru/C supported catalysts. At potentials below 0.4 V, the Pt-Ru/MCl supported catalyst produced at T/J Technologies is significantly more active than either of the Pt-Ru/C supported catalysts. We believe this is due to the greater dispersion of noble metals on the MCl surface and promotion of Pt activity by the support material. At potentials greater than 0.4 V, the Pt-Ru/MCl supported catalyst maintains activities equal to or slightly less than those observed for the carbon supported catalysts.

Future research will examine the activity of Pt-Ru/MCl catalysts as functions of temperature and Pt:Ru ratio. Pt-Ru black and carbon supported Pt-Ru realize an optimum level of methanol oxidation activity for an atomic ratio of 1:1 Pt:Ru at elevated temperatures. The catalytic promotion of Pt activity by the MCl support, as well as a degree of CO tolerance, may make it possible to increase the Pt-Ru ratio for noble metals dispersed on MCl supports. A higher Pt:Ru ratio is desirable, since Ru serves only to facilitate the oxidation of CO from Pt surfaces, and does not participate directly in methanol oxidation. Minimizing the amount of Ru will increase Pt site density and overall catalyst activity.
Figure 9. Tafel plots for the oxidation of 1 M MeOH in 1 N H₂SO₄. Catalysts composed of 15% Nafion inks on glassy carbon electrodes. — Non-optimized T/J Pt-Ru-Carbide I (6.7% Pt). — Purchased Pt-Ru/C catalyst (20% Pt). ----- Purchased Pt-Ru-C (10 % Pt). Methanol oxidation activity of the T/J catalyst is greater than the activity of either of the carbon supported catalysts for E < 0.45 V, the potential region most desirable for DMFC anode operation.

A further advantage conducting ceramic supports have over carbon supports is a higher density. Higher density support materials enable greater amounts of catalyst (mg catalyst/cm²) to be used without imposing diffusion limitations on electrode performance due to catalyst layer thickness. Experiments indicate diffusion limitations within the catalysts layer are less with the use of noble metal catalysts supported on MCI than for carbon supported catalysts. Further experiments will determine the electrode loadings possible without significant loss of performance due to diffusion limitations.

Conclusions

The catalytic promotion of noble metal catalyst activity toward methanol oxidation by high surface area conducting ceramic support materials has been demonstrated. Catalyst activity depends strongly on the composition of the ceramic support material. T/J Technologies has developed a carbide support material (MCI) upon which noble metal dispersion is very high, and support sites promote the activity of Pt. High catalytic activities toward methanol oxidation were displayed by the Pt/MCl supported catalyst, due to high dispersion of Pt sites. MCI was also observed to promote CO tolerance in the Pt supported catalyst. Tests with Pt-Ru/MCl supported catalyst indicate greater CO tolerance than observed for Pt/MCl. The higher density of MCl allows greater catalyst loadings to be applied without imposing diffusion limitations on DMFC anode performance. Hence, a highly active (mA/mg Pt) supported catalyst can be applied with sufficient noble metal loadings (mg Pt/cm²) to produce direct methanol fuel cells with higher power densities than are currently possible using carbon supported catalysts.
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