CARBON MONOXIDE TOLERANT ANODES FOR PROTON EXCHANGE MEMBRANE (PEM) FUEL CELLS.
II. ALLOY CATALYST DEVELOPMENT

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ABSTRACT

PEM fuel cells are highly attractive for distributed power and cogeneration systems. To be competitive, they must operate on fuel mixtures obtained by reforming of widely available natural gas. Such fuels invariably contain CO, a strong poison for Pt. Therefore, CO tolerant anode catalysts are essential for widespread PEMFC introduction. Ternary PtRuX alloy catalysts where X= Ni, Pd, Co, Rh, Ir, Mn, Cr, W, Nb, Zr, were synthesized and evaluated as fuel cell anodes in the presence of CO. The alloys were prepared as well defined thin films on standard TFE-bonded carbon substrates via a dc magnetron sputtering technique. W containing catalysts with substantially increased tolerance towards the presence of CO were developed.

INTRODUCTION

Recent advances in the performance of proton exchange membrane (PEM) fuel cells make them highly attractive for distributed power, cogeneration and transportation systems. They are efficient and function virtually without noise or pollution. To be economically competitive, PEM fuel cells must operate on H2 rich fuel mixtures obtained by reforming of widely available natural gas or liquid hydrocarbons. Reformed fuel gas mixtures invariably contain CO. Catalytic shift reactors can reduce the concentration to 10 to 100 ppm, but even at those levels CO is a strong poison for Pt (1-3). Therefore, CO tolerant anode catalysts are essential for widespread PEMFC introduction. Alloying with Ru facilitates the oxidative removal of adsorbed CO from Pt, and PtRu alloy catalysts represent the state of the art for anodes operating on reformed gas mixtures (4,5).

Our goal is to further improve the CO tolerance of fuel cell anodes with new, multi component, bi-functional transition metal catalysts. We aim to provide, in close proximity to Pt, surface sites which can adsorb -OH at cathodic potentials and facilitate oxygen transfer to the Pt-COads species and/or modify the Pt surface environment to reduce the coverage of COads. Specifically we explore here the catalytic activity of ternary PtRuX alloys where X represents the transition metals Ni, Pd, Co, Rh, Ir, Mn, Cr, W, Nb and Zr. To permit a truly comparative evaluation of the catalyst activity in a representative fuel cell configuration, we developed a new technique to synthesize multi-component alloy catalysts as well defined thin films on standard TFE-bonded carbon substrates via dc magnetron sputtering (6). The thin catalyst layer (e.g. 100 nm) is located at the electrode-membrane interface, permitting complete catalyst utilization.
difficult to achieve in conventional TFE bonded electrodes, where some parts are always inaccessible by either the gas or the electrolyte. Further, the catalysts are tested in an electrode structure which is identical for all alloy compositions and which has, due to its availability, become almost a standard in many fuel cell research laboratories.

EXPERIMENTAL

Electrode Catalyst Fabrication

The sputter deposition was performed with a custom designed Microscience IBEX-2000 system. A schematic of the IBEX deposition system is shown in Figure 1. The system permits simultaneous sputtering of up to four different metals with independent control of the deposition rate and hence the amount of each metal in the catalyst coatings. The substrates (2.5 x 5.0 cm glass slides and uncatalyzed carbon electrodes) are mounted on a circular plate that rotates at 105 rpm beneath the sputter guns. At this rotation rate, less that one monolayer of metal from each sputter gun is deposited during a single pass, ensuring that the films have homogeneous compositions. For the work described here, the catalysts are generally deposited at a pressure of 10 mTorr, and an Ar flow rate of 10 sccm, with the substrates mounted on the rotating planet. The substrates were at ambient temperature, and at a distance of 6.5 cm from the targets. The typical sputter time was 30 minutes following an equally long pre-sputtering period to condition and clean the target surfaces. During these periods the substrates were shielded. The metal deposition and thus the alloy composition was controlled by the power (current and voltage) applied to the respective targets.

Our principal substrate was a standard but uncatalyzed TFE-bonded carbon fuel cell electrode purchased from E-TEK. Simultaneously the alloy film was also deposited onto microscope glass slides. These were used for the alloy characterization including measurement of film thickness, crystal structure, and elemental composition.

Film thickness was measured with a Dektak profilimeter using an edge created by partially masking (e.g., painting an ink line on the substrate) the clean glass slide before catalyst deposition. This mask, along with the overlying film, was removed with a cotton swab dampened with isopropanol.

The crystal structure of the catalyst films was determined by X-ray diffraction in a Rigaku spectrometer using the Bragg-Brentano geometry.

The surface morphology of the deposited catalysts was evaluated via scanning electron microscopy (Cambridge Instruments, Stereoscan 120). Film composition was determined semi-quantitatively from energy dispersive X-ray spectroscopy (EDS) in the SEM.

Electrochemical Test Arrangement

Electrode performance was evaluated in the modified fuel cell arrangement illustrated in Figure 2. The fuel cell cathode was replaced by 0.5M H₂SO₄ electrolyte and
a Pt wire counter electrode. This permitted the unambiguous measurement of anode potentials against a dynamic H₂ reference electrode (DHE). The DHE consisted of a TFE bonded Pt black electrode (~0.2 cm²) to which a cathodic current of 0.2 mA was applied that maintained the reference electrode potential about 1 to 2 mV cathodic of the reversible H₂ potential. The test cell was constructed of Teflon with Viton O-ring seals. We pressurized the counter electrode compartment to 0.5 atm above atmospheric pressure to provide a uniform contact force between the back side of the anode and the graphite insert, that resulted in a low resistance electrical contact. The pressure was maintained independent of the H₂ evolution rate at the counter electrode by a pressure regulating vent.

Gas composition and gas flow were controlled via a system of mass flow controllers (Tylan) connected to compressed gas cylinders (H₂ grade 4.7, H₂ + 99 ppm CO, N₂ pre-purified from AIRCO). Gas flow rates were generally 0.5 to 2.0 cc/s, and the gas stream was humidified before use by passage through distilled H₂O held at the same temperature as the test cell. Potential and/or current was controlled by a potentiostat/galvanostat (EG&G PAR Mod. 363 and Universal Programmer Mod. 175). The ohmic resistance component of the measured potential was monitored continuously by a current interrupter (ESC Model 800 IR measurement system). Current, voltage, and resistance data were acquired with a computer-based data acquisition system. The experimental setup is schematically illustrated in Figure 3.

Electrode Test Procedures

For the electrochemical evaluation, the catalyzed electrodes were bonded to a proton exchange membrane Nafion 117 (DuPont). The membrane was hydrated by boiling in distilled water for 1h, followed by immersion in 5% H₂O₂ at 70°C to 80°C for 1 h and then in 1M H₂SO₄ at ~80°C for 0.5 h. Repeated treatments with boiling distilled water were performed until the pH of the rinse water indicated that all excess H₂SO₄ had been removed.

Catalyzed electrode discs (2.2 cm diameter) were die cut from the coated substrates. These specimens were impregnated with about 0.3 mg/cm² Nafion using an alcoholic solution of Nafion 117 (Aldrich) applied with a spray atomizer to the catalyzed side of the electrode. The catalyzed side was placed face-down onto a 4.5cm diameter wet Nafion membrane and the two components were bonded by hot pressing at 130°C and 80 atm for 90 seconds. The active electrode diameter in our test cell was 1.6 cm, and yielded an active electrode of 2 cm².

The anode performance characterization was generally carried out at 60°C with H₂ and H₂-CO gas mixtures containing 10 and 100 ppm CO. Selected tests were also performed with H₂ containing other CO concentrations. A standard test regime consisted of the following sequence: (1) slow anode polarization at 1 mV/s in pure H₂; (2) a sequence of cyclic voltage sweeps at 1 mV/s between 0 and 180 mV in H₂ + 10 ppm CO; (3) extended (~1h) polarization of the electrode at ~100 mV and monitoring of the
current to establish steady state conditions with H₂ + 10 ppm CO gas (4) slow (1 mV/s) cyclic voltage sweeps to ~600 mV or 1000 mA with H₂ + 10 ppm CO; (5) switch over and electrode equilibration in H₂ + 100 ppm CO; (6) slow (1mV/s) cyclic voltage sweeps to 180 mV and then to ~600 mV or 1000 mA with H₂ + 100 ppm CO; (7) change over to N₂ and then H₂ followed by polarization at 1 mV/s to 1000 mA. This test regime was developed to achieve reproducible, near steady state conditions, and to detect any time or test induced changes in electrode activity.

RESULTS AND DISCUSSION

Catalyst and Electrode Structure

The surface morphology of the catalysed electrode structures is illustrated in the scanning electron micrographs of Figure 4. At low magnification, the uncatalyzed electrode shows a tile-like pattern, and evidence of processing. Higher magnification reveals the agglomerates observed typically with Teflon-bonded carbon. SEM examination of all carbon substrates with deposited metals or alloys show surface structures identical to those for the Pt₀.₅₅Ru₀.₄₇ and Pt₀.₅₅Ru₀.₃₀W₀.₁₅ catalyzed electrodes. They are characterized by nearly spherical particles with diameters of 200 to 200 nm nucleated around the surface agglomerates. The morphology of the catalyst layer was clearly controlled by the substrate. Thus, a macroscopically two-dimensional but microscopically three-dimensional rough alloy catalyst interface was obtained. From Pt deposits of the same structure we determined, via H adsorption and stripping, surface roughness factors of 10 to 13. The catalyst surface area was found to be fairly insensitive to changes in deposit thickness, and agreed well with calculations based on dimensions obtained from the SEM photographs. Thus, a 100 nm Pt catalyst layer is equivalent to a 0.2 mg/cm² loading and a specific catalyst surface area of 5 m²/g.

The catalyst films were mostly crystalline, as indicated by X-ray diffraction. Figure 5 shows a comparison of the X-ray diffraction patterns obtained for Pt, Ru, Pt₀.₅₂Ru₀.₄₈, and Pt₀.₅₅Ru₀.₃₀W₀.₁₅, clearly demonstrating that we are depositing alloys as opposed to merely mixtures of the individual components. The pattern for Pt shows a strong, sharp, well-defined peak for the 111 plane, whereas those for the 222, 311, 220, and 200 reflections were weak. This is a result of the preferred orientation common to thin films. Pt has a cubic close-packed structure, while Ru is hexagonal close-packed. These structures are more compatible with each other than with the W structure. Consequently, PtRu alloys preserve the Pt lattice structure, with a shift toward higher angles. The main diffraction peak in the pattern for the PtRuW ternary is still shifted toward higher angle, but there is also a more significant reduction in the overall intensity of the diffraction. We have observed that the alloys have more amorphous character when the third constituent has a crystal structure that differs significantly from those of Pt and Ru.

Anode Catalyst Performance

Characteristic potential-current relationships measured with a Pt catalyzed anode in the absence and presence of CO are reproduced in Figure 6. For H₂ the IR corrected electrode polarization was very small. The addition of only 10 ppm CO changed the
potential–current behavior very dramatically. The anode polarized quickly beyond 400 mV. Higher current densities could be maintained only around 600 mV, where the surface $-\text{OH}_{\text{ads}}$ concentration on Pt was sufficient to allow effective oxidative removal of adsorbed CO. Clearly, such electrode polarizations are not acceptable in a practical fuel cell. The improvement achieved with a Pt-Ru alloy catalyst is demonstrated in Figure 7.

Again, in the absence of CO, H$_2$ oxidation occurred at very low polarization. The onset of substantial electrode polarization in the presence of CO was shifted to higher current densities. Also, the potential at which H$_2$ – CO mixtures could be oxidized at high rates was significantly reduced occurring now between 300 and 400 mV. This has been attributed to the facilitated oxidation of CO$_{\text{ads}}$ on Pt by the proximity of $-\text{OH}_{\text{ads}}$ at Ru sites.

We synthesized and characterized ternary PtRuX alloys where X=Ni, Pd, Co, Rh, Ir, Mn, Cr, W, Nb, Zr. All alloy catalysts showed low polarization with pure H$_2$. In the presence of CO, the potential-current relationships were fundamentally similar for all alloys and resembled those shown for PtRu in Figure 7. Differences were observed in the current density at which significant electrode polarization occurred and in the plateau voltage at which CO$_{\text{ads}}$ was effectively oxidized. These parameters are summarized for the alloys in Table 1. In general we found that the partial replacement of Ru by another transition metal lowered the alloy activity both in the low potential and the plateau regions. At low levels of Ru substitution the effect was small for most elements but it was quite significant for Pd, Ni and Nb. A striking exception was W where the partial substitution of Ru resulted in a significantly increased tolerance to the presence of CO at 10 and 100 ppm levels. A graphic representation of the results and a comparison with the binary alloys is shown in Figure 8.

In the presence of CO the binary PtRu and PtW alloy catalysts were far superior to pure Pt. Of the two, PtRu was better in the low potential region while PtW proved superior in the plateau region except at very high current densities. The performance of the ternary PtRuW alloy, however, exceeded both binaries in the low potential and the potential plateau regions. To probe whether our results are indeed representative for steady state conditions, we held the potential of the ternary catalyst at 100 mV and at 200 mV. The currents remained, except for minor fluctuations, flat at 85 mA and 250 mA respectively over the entire 90 min test period.

A similar series of potential-current curves for Ir containing Pt alloys is reproduced in Figure 9. Again, the ternary alloy catalyst was more active for H$_2$ oxidation in the presence of CO than any of the binary catalysts. Ru was, however, more effective than Ir in improving the CO tolerance as can be seen from the activity decrease when Ru was substituted by Ir in the PtRu alloy.
in improving the CO tolerance as can be seen from the activity decrease when Ru was substituted by Ir in the PtRu alloy.

To translate our results into the realm of practical fuel cells, we need to consider the relatively low surface area of our catalysts. A practical PEM fuel cell electrode may contain a loading of e.g. 1 mg/cm² of a catalyst with a specific surface area of 30 m²/g. This would translate into a real catalyst surface of 300 cm²/cm² of electrode. If 70% of the catalyst were accessible, such an electrode should, neglecting IR and transport limitations, be able to support about 20 times the current measured with our thin layer electrodes. Thus, with the goal of lower catalyst loadings in mind, our results up to ~100 mA/cm² would be most relevant for practical full size fuel cells.

CONCLUSIONS

Using a new technique we synthesized multi-component Pt–transition metal alloy catalysts as thin layers on standard fuel cell electrode substrates. This permitted a true comparative evaluation of catalyst activity for the oxidation of H₂ in the presence of CO. The partial substitution of Ru in PtRu by Ni, Pd, Co, Rh, Ir, Mn, Cr, Nb and Zr resulted in a moderate decrease in activity for H₂ oxidation in the presence of 10 or 100 ppm CO. The effect increased with increasing level of metal substitution. In contrast, PtRuW alloy anodes showed a substantially improved tolerance towards the presence of CO.

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| Alloy | H₂+10 ppm CO | H₂ + 100 ppm CO |
|------|-------------|-----------------|
|      | I (mA/cm²) | E (V) | I (mA/cm²) | E (V) |
|      | at 100 mV | at 100 mA/cm² | at 300 mA/cm² | at 100 mV | at 100 mA/cm² | at 300 mA/cm² |
| Pt₀.₅₃Ru₀.₄₇ | 57 | 0.256 | 0.311 | 19 | 0.309 | 0.364 |
| Pt₀.₅₅Ir₀.₄₅ | 29 | 0.314 | 0.489 | 11 | 0.446 | -- |
| Pt₀.₈₂W₀.₁₈ | 31 | 0.172 | 0.493 | 6.8 | 0.469 | 0.670 |
| Pt₀.₅₂Ru₀.₁₃Cr₀.₃₃ | 32 | 0.238 | -- | 14 | 0.316 | -- |
| Pt₀.₅₂Ru₀.₃₃Cr₀.₁₅ | 60 | 0.186 | 0.282 | 25 | 0.265 | 0.374 |
| Pt₀.₅₂Ru₀.₁₄Mn₀.₃₄ | 33 | -- | -- | 10 | 0.292 | 0.386 |
| Pt₀.₅₄Ru₀.₃₆Mn₀.₁₀ | 29 | 0.314 | 0.489 | 11 | 0.446 | -- |
| Pt₀.₄₄Ru₀.₁₄Zr₀.₄₂ | 26 | -- | -- | 5 | 0.362 | 0.421 |
| Pt₀.₅₂Ru₀.₁₃Zr₀.₁₄ | 52 | -- | -- | 13 | 0.333 | 0.350 |
| Pt₀.₄₀Ru₀.₁₇Ni₀.₅₀ | 25 | 0.294 | 0.342 | 4 | 0.414 | 0.471 |
| Pt₀.₄₇Ru₀.₁₃Ni₀.₄₀ | 38 | -- | -- | 10 | 0.324 | -- |
| Pt₀.₅₂Ru₀.₃₂Ni₀.₁₆ | 49 | 0.253 | 0.316 | 9.2 | 0.347 | 0.391 |
| Pt₀.₄₉Ru₀.₁₄Rh₀.₃₇ | 45 | -- | -- | 10 | 0.356 | -- |
| Pt₀.₄₉Ru₀.₁₃Rh₀.₁₈ | 50 | -- | -- | 18 | 0.340 | 0.371 |
| Pt₀.₄₆Ru₀.₁₃Co₀.₄₁ | 21 | 0.310 | 0.364 | 6.2 | 0.404 | 0.449 |
| Pt₀.₅₀Ru₀.₁₃Co₀.₁₇ | 35 | -- | -- | 17 | 0.316 | 0.364 |
| Pt₀.₅₄Ru₀.₃₂Ir₀.₁₇ | 57 | 0.233 | 0.304 | 24 | 0.308 | 0.372 |
| Pt₀.₆₆Ru₀.₂₁Ir₀.₂₂ | 36 | 0.266 | 0.326 | 9 | 0.339 | 0.406 |
| Pt₀.₅₄Ru₀.₁₄Pd₀.₃₂ | 35 | -- | -- | 13 | 0.433 | 0.462 |
| Pt₀.₅₁Ru₀.₁₄Pd₀.₁₅ | 35 | -- | -- | 13 | 0.364 | 0.415 |
| Pt₀.₅₇Ru₀.₃₃Nd₀.₀₇ | 39 | 0.354 | 0.454 | 12 | 0.411 | 0.551 |
| Pt₀.₅₃Ru₀.₁₃W₀.₁₅ | 85 | 0.142 | 0.248 | 34 | 0.251 | 0.385 |
| Pt₀.₅₃Ir₀.₁₈W₀.₂₉ | 57 | 0.132 | 0.255 | 33 | 0.206 | -- |
| Pt₀.₅₁Ir₀.₄₃W₀.₁₆ | 93 | 0.157 | 0.309 | 28 | 0.279 | 0.430 |
| Pt₀.₅₂Ir₀.₄₇W₀.₀₁ | 85 | 0.161 | 0.299 | 28 | 0.365 | 0.613 |
Figure 1. Schematic diagram of in-vacuo apparatus used for sputter deposition of alloy catalysts. For clarity only two sputter targets, Pt and Ru, are shown. Shields, masks, and substrate heaters are also omitted from the drawing.

Figure 2. PEM fuel cell anode test cell.
Figure 3. Test arrangement for fuel cell anode performance evaluation.

Figure 4. Scanning electron micrographs of (a,b) uncoated TFE-bonded carbon electrode, and electrodes catalyzed with (c) Pt$_{0.53}$Ru$_{0.47}$, and (d), Pt$_{0.55}$Ru$_{0.30}$W$_{0.15}$.
Figure 5. X-ray diffraction patterns of sputter deposited catalysts. The patterns are offset and intensities are in arbitrary units.

Figure 6. Polarization of a Pt catalyzed fuel cell electrode in H\textsubscript{2} (lower unlabeled trace) and H\textsubscript{2}-CO mixtures. 60°C, sweep rate 1 mV/s.
Figure 7. Polarization of a $\text{Pt}_{0.53}\text{Ru}_{0.47}$ catalyzed fuel cell electrode in $\text{H}_2$ (lower unlabeled trace) and $\text{H}_2$-$\text{CO}$ mixtures. 60°C, sweep rate 1 mV/s.

Figure 8. Comparison of anode polarization measured for electrodes catalyzed with Pt, PtRu, or PtW, and a PtRuW ternary in a mixture of $\text{H}_2$ with 10 ppm CO. Typical performance in pure $\text{H}_2$ is included for comparison.
Figure 9. Comparison of anode polarization for Pt, PtIr, PtRuIr, PtRu, and PtIrW alloys in pure H₂ and in a mixture of H₂ with 10 ppm CO.