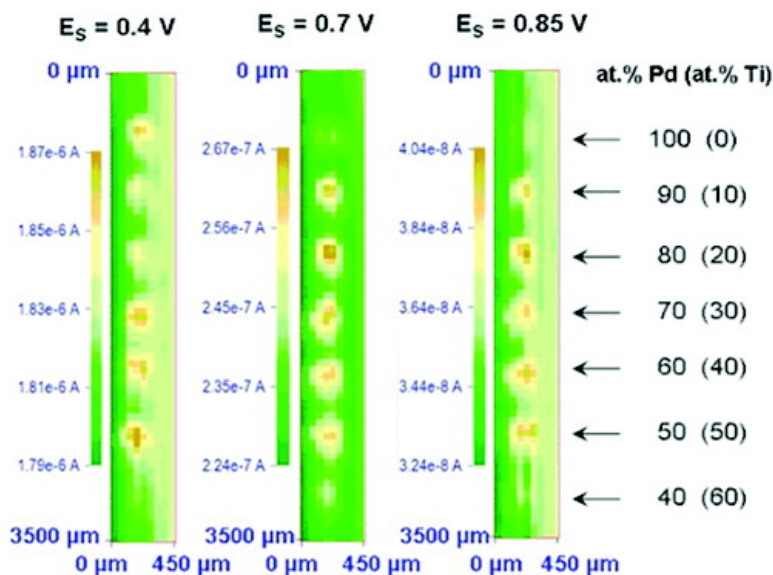


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## Pd–Ti and Pd–Co–Au Electrocatalysts as a Replacement for Platinum for Oxygen Reduction in Proton Exchange Membrane Fuel Cells

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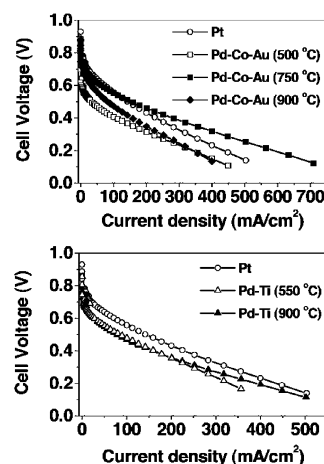
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We report two new catalysts, Pd–Co–Au and Pd–Ti, that show essentially equal or slightly better performance than the more expensive Pt currently used for the oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFC). We also demonstrate that the previously described high throughput screening method based on scanning electrochemical microscopy (SECM)<sup>1</sup> is indeed a good predictor of electrocatalyst performance in a PEMFC. Pt has been the cathode electrocatalyst of choice since the first fuel cell experiments in 1839 by Grove,<sup>2</sup> and there has been an intense search for less expensive, more abundant non-platinum electrocatalysts<sup>3</sup> that can offer acceptable performance.

These electrocatalysts were found using the previously described<sup>1</sup> guidelines and rapid screening of selected metal combinations (for example, Pd with Co, Au, and Ti) over a wide range of compositions using a SECM-based combinatorial approach<sup>4</sup> to identify suitable metal combinations with optimum compositions that exhibit good activity for ORR.<sup>1</sup> This screening technique is based upon producing an array of bimetallic or trimetallic catalyst spots with different compositions on a glassy carbon (GC) support. A small ultramicroelectrode tip is used to generate oxygen at a constant current as the tip is scanned above the array of spots, with the GC held at different potentials, so that each spot registers a current proportional to the rate of oxygen reduction at that location (GC, which is a poor oxygen reduction catalyst, does not produce a significant response at these potentials). The screening in 0.5 M H<sub>2</sub>SO<sub>4</sub> by SECM led to the identification of Pd-based compositions, Pd–Co–Au (70:20:10 atom %) and Pd–Ti (50:50 atom %), as those exhibiting good catalytic activity for the ORR (see Figure S1 in the Supporting Information).

Such screening techniques are useful in identifying candidate materials, but tests more closely related to the fuel cell operating conditions (e.g., supports, preparation conditions) are required to demonstrate electrocatalysis. Therefore, the identified compositions were then prepared on a carbon support, with a metal loading of 20 wt %, by a reverse microemulsion route for the Pd–Co–Au ternary system (Pd–Co–Au/C) and an impregnation method for the Pd–Ti binary system (Pd–Ti/C) and optimized by heat treatments in a flowing reducing atmosphere (90% Ar/10% H<sub>2</sub>).

The performance of the membrane electrode assemblies (MEAs) in PEMFC with the Pd–Co–Au/C and Pd–Ti/C as cathodes, with commercial Pt/C, 20 wt % platinum on carbon, Johnson Matthey (JM) as anodes, and Nafion 115 as electrolyte were evaluated in a single-cell PEMFC and compared to commercial platinumized carbon (20 wt % platinum on carbon, JM) (Figure 1). The Nafion 115 electrolyte was sandwiched between the cathode and anode by hot pressing. Both the Pd–Co–Au/C catalyst heat treated at 750 °C and the Pd–Ti/C catalyst heat treated at 900 °C exhibited performances that are remarkably equal or better than that of the



**Figure 1.** Comparison of steady-state polarization curves of the various heat treated carbon supported Pd–Co–Au (Pd:Co:Au = 70:20:10 atom %) and Pd–Ti (Pd:Ti = 50:50 atom %) catalysts for ORR in single-cell PEMFC with that of a commercial (JM) Pt catalyst at 60 °C with a metal(s) loading of 0.2 mg/cm<sup>2</sup>. The data were collected with Nafion 115 membrane, Pt anode catalyst loading of 0.2 mg/cm<sup>2</sup>, humidifier temperature of 60 °C, and hydrogen and oxygen pressures of 18 and 20 psi, respectively. The current density values given are with respect to geometric electrode area.

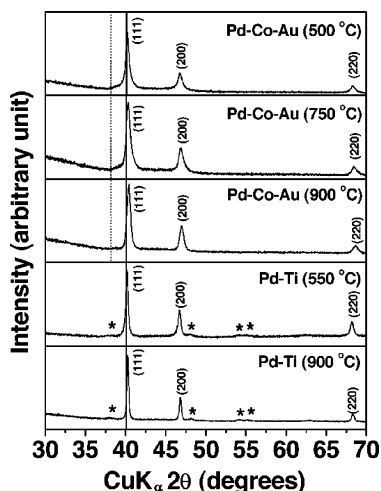
commercial Pt catalysts at the same loading (Figure 1). Both catalysts showed open circuit voltages of ~0.89 V, which is close to that found with commercial Pt catalysts.

For practical applications, in addition to high catalytic activity, good fuel cell stability is essential. A preliminary examination of stability was carried out with the 750 °C Pd–Co–Au/C and 900 °C Pd–Ti/C cathodes by recording the polarization curves before and after polarizing the cell at 200 mA/cm<sup>2</sup> for 12 h (Figure S2). The cell with the Pd–Ti/C cathode showed essentially stable performance within this test period, while that with the Pd–Co–Au/C sample degraded, perhaps because of possible leaching of Co in the fuel cell environment, as has been suggested with Pt–Co catalysts.<sup>3</sup>

Structural characterization of the compositions was carried out by X-ray diffraction (Figure 2). The 500 °C Pd–Co–Au sample showed well-defined reflections corresponding to a face centered cubic (FCC) phase. The shifting of these to higher angles compared to those for pure Pd metal and the absence of reflections corresponding to pure Au or Co suggests alloying of Pd with Co and Au. The reflections shift further to slightly higher angles on heating the sample at 750 and 900 °C, suggesting a slight improvement in the extent of alloying. The 550 °C Pd–Ti/C sample showed reflections corresponding to predominantly a FCC phase with a slight shift to higher angles compared to those expected for Pd metal and a small amount of TiO<sub>2</sub>. The shift of the reflections to higher angles increased slightly on heating at 900 °C, suggesting an increase in the extent of alloying with Ti and a further contraction

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**Figure 2.** X-ray diffraction patterns of Pd–Co–Au (Pd:Co:Au = 70:20:10 atom %) and Pd–Ti (Pd:Ti = 50:50 atom %) before and after heat treating at various temperatures. The solid and broken lines refer, respectively, to the standard  $2\theta$  values corresponding to the (111) reflections of Pd and Au metals. The very weak reflections marked with \* in the Pd–Ti samples refer to the  $\text{TiO}_2$  (anatase) phase.

of the lattice. The crystallite sizes estimated from the XRD data using Scherer's equation were about 12–15 and 24–33 nm, respectively, for the heat treated Pd–Co–Au/C and Pd–Ti/C samples.

The decrease in the catalytic activity from the 750 to 900 °C sample (Figure 1) could be due to an increase in particle size and consequent decrease in the electrochemically active surface area, and the lower catalytic activity of the 500 versus 750 °C sample could be due to a lower degree of alloying of Pd with Co and Au, as indicated by the XRD data in Figure 2. The catalytic activity depended on the amount of Au present in the sample, with the Pd–Co–Au/C sample with 10 atom % Au showing the highest catalytic activity (Figure S3). With the Pd–Ti/C system, the 900 °C sample exhibited slightly better performance than the 550 °C sample despite a slight particle growth, perhaps because of the incorporation of more Ti into the Pd–Ti alloy phase as indicated by the X-ray diffraction data (Figure 2).

In direct methanol fuel cells (DMFC), the oxidation of methanol that crosses into the cathode compartment of the fuel cell causes a

significant polarization loss in the ORR on Pt-based cathodes. Therefore, the tolerance of the cathode catalysts to methanol oxidation at the cathode is critical to achieving better cell performance and operational life in the DMFC. A cyclic voltammetric characterization of the Pt/C, Pd–Co–Au/C, and Pd–Ti/C catalysts in 1 M  $\text{H}_2\text{SO}_4$ , both with and without methanol, indicates that the methanol oxidation current densities on the Pd-based catalysts (Pd–Co–Au/C and Pd–Ti/C) are significantly lower or even negligible compared to that on the Pt/C catalyst (Figure S4), suggesting that these catalysts may be more tolerant to methanol compared to Pt/C, and may also find use in DMFC.

This study demonstrates the feasibility of developing non-platinum alloy compositions that offer catalytic activity similar to that of platinum. Comparison of the electrochemical properties of these new non-Pt alloy catalysts with that of Pt may also help to develop a better understanding of the mechanisms involved in the oxygen reduction reactions. The significantly lower cost of the Pd–Co–Au and Pd–Ti catalysts and the relative abundance of these metals compared to that of Pt could enhance the commercial viability of the fuel cell technology.

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**Supporting Information Available:** Additional figures, references, and experimental procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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