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## Multimetallic Electrocatalysts of Pt, Ru, and Ir Supported on Anatase and Rutile TiO<sub>2</sub> for Oxygen Evolution in an Acid Environment

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Anatase and rutile TiO<sub>2</sub> were investigated as stable supports for different multimetallic nanoparticles (i.e., Pt:Ru, Pt:Ir, Pt:Ru:Ir, and Ir:Ru) and tested for activity toward the oxygen evolution reaction (OER). Overall, Ir:Ru had the highest activity toward OER (i.e., current per gram of metal) compared to the other multimetallic combinations studied. This bimetallic supported on anatase TiO<sub>2</sub> had a 53% higher current per gram of metal than an unsupported electrocatalyst of the same composition. The higher catalyst utilization of the supported electrocatalysts for OER is consistent with small, well-dispersed nanoparticles, which were observed in high resolution transmission electron microscopy images.

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The electrolysis of water is a convenient method to obtain pure hydrogen. Two commercial types of water electrolyzers are based on either an alkaline or a proton exchange membrane (PEM).<sup>1–7</sup> PEM electrolyzers have many advantages over the alkaline system such as higher power densities and efficiencies at low temperatures (80°C), compact stack design that allows high-pressure operation and excellent partial-load range, and rapid response to fluctuating power inputs.<sup>4,5</sup> Also, there is greater safety and reliability because no caustic electrolyte is circulated in the cell.<sup>6</sup> However, one of the main problems of a PEM electrolyzer is the high costs of the electrocatalyst,<sup>7</sup> because nonprecious metals are not stable in an acidic environment.

Electrocatalysts used for the oxygen evolution reaction (OER) consist of combinations of precious metals such as platinum, ruthenium, and iridium. Platinum forms a poorly conductive oxide film and shows a high overpotential.<sup>8</sup> However, electrocatalysts consisting of iridium and ruthenium<sup>9</sup> and their oxides<sup>9–12</sup> have been shown to possess high electroactivity for OER. Song et al.<sup>9</sup> argued that Ir and Ru oxide forms are preferred because unsupported metallic forms were observed to be unstable. Pure ruthenium metal in particular was shown to be the most active catalyst for OER, but very unstable. Iridium oxide was found to be the next most active and stable at higher current densities.<sup>9</sup> Based on these findings, Siracusano et al.<sup>17</sup> used IrO<sub>2</sub> as the anode electrocatalyst for a PEM electrolyzer. Several researchers found that mixtures of Ir and Ru oxides are even more active than pure IrO<sub>2</sub> for OER.<sup>12–14</sup> They added Ta<sub>2</sub>O<sub>5</sub>,<sup>12</sup> SnO<sub>2</sub>,<sup>13</sup> or MoO<sub>3</sub> (Ref. 14) to stabilize the structure of Ir:Ru oxide, because RuO<sub>2</sub> is less stable than IrO<sub>2</sub>. The addition of MoO<sub>3</sub> enhanced activity, but Ta<sub>2</sub>O<sub>5</sub> and SnO<sub>2</sub> reduced performance in a PEM electrolyzer compared to Ir:Ru oxide.

The use of a support for metal electrocatalysts used in OER was discussed by Ma et al.<sup>15,16</sup> They prepared iridium metals supported on titanium carbide. Using cyclic voltammetry (CV) and PEM electrolyzer tests, they found that supported iridium metals are more active and more stable than unsupported iridium. Still, it has not been studied extensively in the literature if a support can provide both stability for the metals and enhanced the electrochemical activity for OER. The main reason for using a support is to increase the dispersion of metals, thus increasing catalyst utilization. Unfortunately, the typical electrode support in fuel cells is carbon, which corrodes at high potentials.<sup>17</sup> This corrosion will cause a loss of electrical contact and agglomeration of the electrocatalyst, decreasing reaction activity. Due to these limitations, it is desirable to find a

support that can be stable at high potentials, possess high surface area to better disperse the catalyst, and is inexpensive.

Inexpensive metal oxides (e.g., SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) are generally used as supports in various heterogeneous catalysis applications. The advantages of these metal oxides are that they can enhance activity of the catalyst and are stable in an oxidizing environment. However, for electrochemical reactions most metal oxides are not considered because they are nonconductive. Attempts to impart conductivity in metal oxides have been tried by either doping Nb into TiO<sub>2</sub> (Ref. 18) or using reduced forms of TiO<sub>2</sub> (Ref. 18–20) (e.g., Ebonex). However, reduced forms of TiO<sub>2</sub> can be unstable, especially in oxidizing environments, and doped materials have a significantly lower surface area [about 1.4 m<sup>2</sup>/g (Ref. 18)]. High surface area materials are desired (i.e., more than 150 m<sup>2</sup>/g) to better disperse the metal, which provides less agglomeration and more reaction sites. We recently demonstrated that an electrode comprised of metal electrocatalysts (e.g., Pt) supported on a low conductive but a high surface area TiO<sub>2</sub> has sufficient conductivities suitable for electrochemistry as long as the metal loadings are above 40 wt % which is typical for supported electrodes.<sup>21,22</sup>

In this paper, combinations of platinum, ruthenium, and iridium electrocatalysts were supported on commercially available anatase and rutile TiO<sub>2</sub>. The objective was to investigate the performance for OER of dispersed nanoparticles supported on TiO<sub>2</sub>, and compare these to an unsupported equivalent. The electrocatalysts are characterized in high resolution transmission electron microscopy (HR-TEM) to compare dispersion of the nanoparticles on supported versus unsupported electrodes.

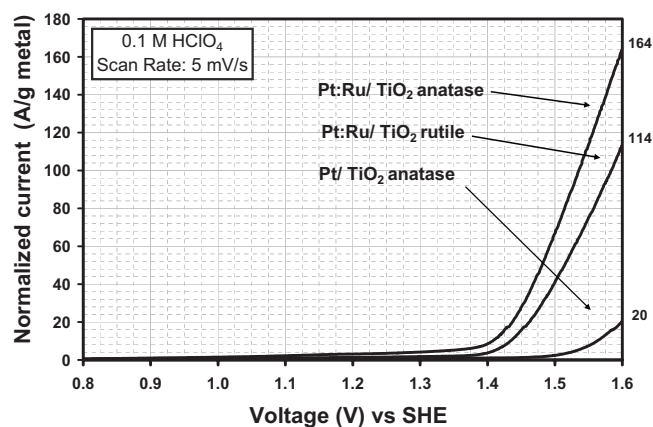
### Experimental

**Synthesis of supported and unsupported electrocatalysts.**—The electrocatalysts were synthesized using a modified ethylene-glycol colloidal procedure published by Bock et al.<sup>23</sup> A solution of 0.2 M sodium hydroxide in ethylene glycol (150 mL) was added in a round bottom flask, and the support was added to eventually obtain 60 wt % metal in the electrocatalyst. TiO<sub>2</sub> anatase and TiO<sub>2</sub> rutile were used as supports and were purchased from Sigma-Aldrich. The suspension was sonicated for 45 min to disperse the particles into solution. Under a nitrogen environment, the metal precursors [platinum (IV) chloride and ruthenium (III) chloride from Sigma-Aldrich; iridium (III) chloride from Alfa-Aesar] were added to the mixture in the following amounts: (1) 1:1 bimetallics, 2.04 mmol of each metal precursor; (2) 2:1 Ir:Ru bimetallic, 2.04 mmol of iridium chloride and 1.02 mmol of ruthenium chloride; (3) 1:1:1 trimetallic (Pt:Ir:Ru), 1.23 mmol of each metal precursor; and (4) pure Pt metal, 3.08 mmol of platinum chloride. The complete mixture was allowed to mix for 2 h, and subsequently heated to 175°C for 3 h. The sample was mixed with approximately 1000 mL of deionized

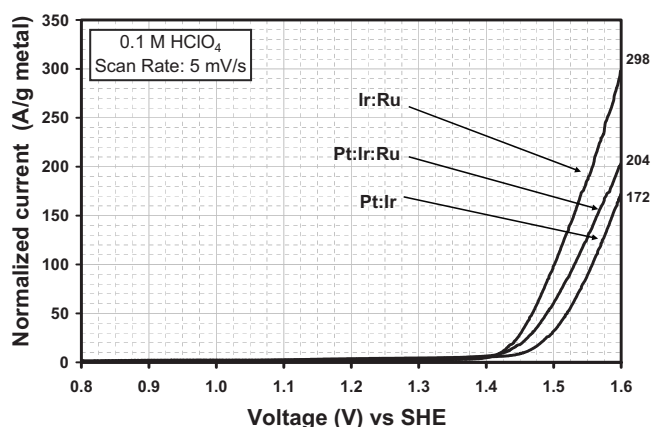
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**Figure 1.** Cyclic voltammograms of 60 wt % 1:1 Pt:Ru catalysts supported on TiO<sub>2</sub> with two different crystal structures and 60 wt % Pt supported on anatase TiO<sub>2</sub> at 25°C.



**Figure 2.** Cyclic voltammograms of 60 wt % electrocatalysts supported on anatase TiO<sub>2</sub>. The metals are in equal atomic ratios and the CVs were run at 25°C.

(DI) water, and nitric acid was added until pH reached  $\sim 1$ . The colloidal suspension was mixed for an additional 3 h. After allowing the solution to settle for 5 h, the sample was filtered and washed with several aliquots of water. The sample was dried at 110°C for 4 h under vacuum conditions. The resulting material was crushed with a pestle and mortar to obtain a fine powder. Unsupported catalysts were made following a similar procedure, except a support was not added and the solution was not sonicated. The amount of electrocatalyst obtained was approximately 1.3 g for supported Pt:Ir, 0.6 g for unsupported electrocatalysts, and 1.0 g for the rest.

**Materials characterization.**—HRTEM images were obtained on a JEOL 2100 F transmission electron microscopy (TEM) with accelerating voltage of 80–200 kV. Elemental analysis in a scanning electrode microscope with energy dispersive X-ray spectroscopy (SEM-EDX) was executed on a Quanta 200 FEI and confirmed the ratios of the supported and unsupported electrocatalysts. Cyclic voltammetry was performed using a Princeton Applied Research 263A potentiostat, with Corrware software used to record the data. The experiments were run at room temperature (25°C). The electrochemical cell consisted of a catalyst film on a 5 mm platinum disk as the working electrode, a luggin capillary Hg/HgSO<sub>4</sub> reference electrode, and a Pt wire as the counter electrode. A solution of 0.1 M HClO<sub>4</sub> was used as the electrolyte. The ink used for the catalyst film consisted of 6.0 mg of the electrocatalyst sonicated with 3 mL of DI water and 3 mL of isopropyl alcohol (IPA). A volume of 18.5  $\mu$ L was placed on the platinum disk and allowed to dry under a heat lamp. Then 5  $\mu$ L of 0.2 wt % Nafion solution with 2-propanol were added to the catalyst film and dried. Approximately 10 CV scans were run at 50 mV/s over the potential range of 0.00–1.60 V versus standard hydrogen electrode (SHE) until the CVs overlapped. The sweep rate was reduced to 5 mV/s and 3 additional scans were performed. All scans shown here are the third and final scans normalized by the amount of metal on the electrode. Each catalyst type was prepared and tested two to six times to establish the reproducibility of the results. The standard deviation from the average of each catalyst was calculated using the current at 1.6 V versus SHE for the final scan. A total of 23 experimental runs were used to obtain the standard deviation.

### Results and Discussion

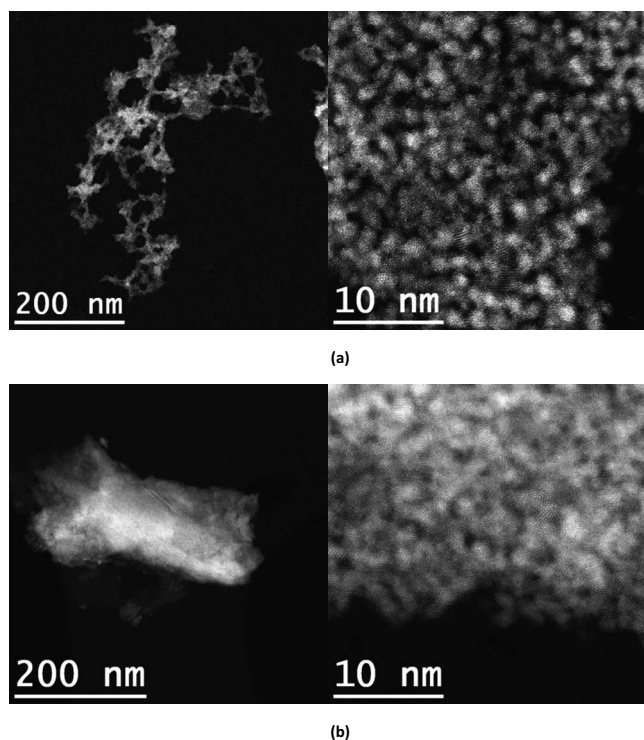
Figure 1 shows the final scans for 60 wt % Pt:Ru on anatase TiO<sub>2</sub>, 60 wt % Pt:Ru on rutile TiO<sub>2</sub>, and 60 wt % Pt on anatase TiO<sub>2</sub>. The platinum catalyst had the lowest activity toward OER, as expected from previous studies.<sup>8</sup> However, adding ruthenium to create the bimetallic Pt:Ru on anatase TiO<sub>2</sub> enhanced the OER by a factor of 8. Also, for two different structures of TiO<sub>2</sub>, Pt:Ru sup-

ported on anatase was 44% more active compared to Pt:Ru supported on rutile. This is consistent with the enhancement of activity observed for Pt:Ru with different supports for the methanol oxidation reaction that we previously reported.<sup>22</sup>

The activity toward OER for other metal combinations (i.e., 60 wt % Ir:Ru, Pt:Ir, and Pt:Ir:Ru) dispersed on anatase TiO<sub>2</sub> are shown in Fig. 2. At 1.6 V, all three of these supported electrocatalyst combinations had higher activities toward OER compared to Pt:Ru supported on anatase TiO<sub>2</sub>, shown in Fig. 1. Also it was observed that Ir:Ru supported on anatase TiO<sub>2</sub> had a 47% higher activity compared to the next most active electrocatalyst, Pt:Ir:Ru on anatase TiO<sub>2</sub>.

An unsupported electrocatalyst was prepared for the most active bimetallic (i.e., Ir:Ru) and HRTEM images were taken to observe the distribution of particles. Low magnification and high magnification images were acquired and an example is shown in Fig. 3 for (a) 60% 1:1 Ir:Ru supported on anatase TiO<sub>2</sub> and (b) unsupported 1:1 Ir:Ru. In the images, the bright spots are the nanoparticles consisting of ruthenium and iridium and the black areas are void space. The gray areas in Fig. 3a consist of the anatase TiO<sub>2</sub> support. As seen at low magnification, the supported catalyst is well distributed on the support. Going to a higher magnification, the electrocatalysts are seen dispersed and separated. This separation can provide more available sites for reaction and, hence, better catalyst utilization. On the other hand, when the material is unsupported, the nanoparticles tend to agglomerate and at low magnification it looks like a whole particle. Magnified, the particles are more tightly packed in the absence of a support.

Because Ir:Ru was found to be the highest active catalyst, atomic ratio variations were synthesized and tested toward OER. The oxidation currents at 1.6 V are presented in Fig. 4. A total of 23 experiments were performed for the results reported here, and the cumulative data sets were used to calculate a percent standard deviation. The percent standard deviation was at the average of  $\pm 12\%$  and is shown by error bars in Fig. 4. The bar graph shows: (1) atomic ratio variations of 1:1, 2:1, and 1:0 Ir:Ru (i.e., pure Ir) supported on anatase TiO<sub>2</sub>; (2) 1:1 Ir:Ru supported on rutile TiO<sub>2</sub>; (3) unsupported 1:1 Ir:Ru. The value reported on top of each bar in the graph are the averages of the experiments performed. In comparison, all supported Ir:Ru electrocatalysts resulted in higher currents per gram of catalysts compared to unsupported Ir:Ru. The best supported electrocatalyst (1:1 Ir:Ru on anatase TiO<sub>2</sub>) had 53% higher current per gram of metal compared to the unsupported Ir:Ru of the same atomic ratio. This increase in performance is believed to occur because of better particle dispersion on the support, and hence higher surface area, as observed in the HRTEM images (see Fig. 3). A more quantitative assessment of the catalyst surface area is difficult.

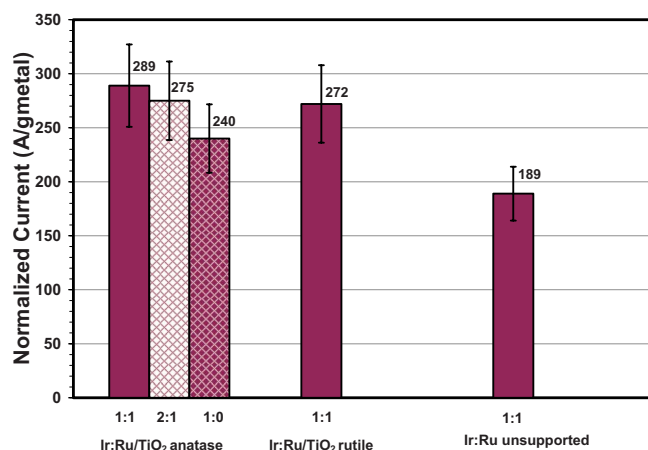


**Figure 3.** HRTEM images at low magnification (left) and high magnification (right) of (a) 60 wt % Ir-Ru on anatase TiO<sub>2</sub> and (b) unsupported Ir-Ru.

Therefore, it is not clear if the larger currents on the supported catalysts reported in Fig. 4 are due to enhanced dispersion alone (i.e., greater surface area), or if the support is providing additional enhancement to the activity of the catalyst. Furthermore, it is shown that the 1:1 Ir:Ru electrocatalysts supported on anatase TiO<sub>2</sub> had a slightly higher activity toward OER compared to the 2:1 Ir:Ru on anatase TiO<sub>2</sub> and pure Ir on anatase TiO<sub>2</sub> and 1:1 Ir:Ru supported on rutile TiO<sub>2</sub>.

### Conclusion

Anatase and rutile TiO<sub>2</sub> were investigated as stable supports for different multimetallic nanoparticles (i.e., Pt:Ru, Pt:Ir, Pt:Ru:Ir, and



**Figure 4.** (Color online) Normalized OER current on Ir:Ru electrocatalysts at 1.6 V and 25°C.

Ir:Ru) and tested for activity toward the OER. Overall, bimetallic Ir:Ru had the highest current per gram of metal than other multimetallic combinations studied. For example, Ir:Ru dispersed on anatase TiO<sub>2</sub> was 47% more active toward OER at 1.6 V versus SHE than the next best metal combination, Pt:Ir:Ru, on this support. Finally, a 1:1 ratio of Ir:Ru support on anatase TiO<sub>2</sub> was 53% and had a higher current per gram of catalyst toward OER compared to an unsupported electrocatalyst with the same atomic ratio and metal composition. The higher performance of the supported catalysts is consistent with small, well-dispersed nanoparticles, which were observed in HRTEM images. A more quantitative assessment of the catalyst surface area is difficult. Therefore, it is not clear if the larger currents on the support catalysts reported here are due to enhanced dispersion alone (i.e., greater surface area), or if the support is providing additional enhancement to the activity of the catalyst. Separating these effects will be pursued in further studies. In addition, the long-term stability of these electrocatalysts on the TiO<sub>2</sub> support for OER still needs to be tested, but this is beyond the scope of this study.

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