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Low-Temperature Synthesis of a PtRu/Nb_{0.1}Ti_{0.9}O₂ Electrocatalyst for Methanol Oxidation

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Niobium was doped into anatase TiO₂ support at 10 mol % (Nb_{0.1}Ti_{0.9}O₂) using sol-gel chemistry. A PtRu/Nb_{0.1}Ti_{0.9}O₂ catalyst was synthesized by LiBH₄ reduction in tetrahydrofuran. The methanol electro-oxidation activity of the catalyst shows that this oxide support was electrically conductive. The current (A/g_{Pt}) was 6% higher on the PtRu/Nb_{0.1}Ti_{0.9}O₂ catalyst compared to a commercial PtRu/C catalyst at 25°C. The electrochemically active surface area of the PtRu/C was 94% higher than PtRu/Nb_{0.1}Ti_{0.9}O₂, thus the current per active site was 100% higher on PtRu/Nb_{0.1}Ti_{0.9}O₂. A membrane electrode assembly with PtRu/Nb_{0.1}Ti_{0.9}O₂ had 46% higher current (A/g_{Pt}) than an equivalent E-TEK membrane electrode assembly at 70°C.
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Electrochemical cells that have porous electrodes require an electrically conductive matrix material to facilitate transportation of electrons between the electrodes. In many applications, the conductive matrix phase also serves as a support for catalyst particles that facilitate the reaction. Most traditional heterogeneous catalysts used for nonelectrochemical reactions are supported on insulating metal-oxide materials that have a high surface area and promote catalytic activity (i.e., enhanced catalyst-support interactions). In electrochemical applications (e.g., proton-exchange membrane fuel cells), the typical support material is carbon due to its high surface area and high electron conductivity rather than any enhanced catalyst-support interactions. However, carbon-supported electrodes that operate at voltages above ~0.9 V in the presence of water are known to undergo the carbon corrosion via the reaction¹



Figure 1 illustrates the three phase contact that is necessary in porous electrodes for an active reaction site and shows how carbon corrosion can deactivate the reaction site at high potentials. One method of increasing the durability of porous electrodes is the development of inert electrocatalyst supports.

Unfortunately, replacing carbon with traditional metal-oxide supports is not possible due to their electrical-insulating properties at temperatures below 200°C. However, metal oxides such as reduced oxidation state titania (e.g., Ti₄O₇ and Ebonex) and Niobium-doped TiO₂ (e.g., Nb_{0.1}Ti_{0.9}O₂) have shown promise for electrically conductive supports.^{2,3} Titanium-oxide-based supports may also provide catalytic advantages for the electrochemical oxidation of methanol because anatase TiO₂ is an active photocatalyst for the destruction of organic compounds.⁴ It has been shown that mixtures of NbO₂ and TiO₂ sintered at 1000°C lead to the formation of an electrically conducting material,^{3,5} with an electrical conductivity in the range of 0.2–1.5 S/cm and a surface area of ~1 m²/g.³ This high-temperature synthesis method shows promising results, but it leads to a low surface area material that requires long synthesis times. Because TiO₂ undergoes a phase transition from anatase to the less catalytically active rutile near 700°C,⁶ the high-temperature synthesis may also reduce some catalytic promotion of methanol oxidation by the support.

In this paper, a low-temperature synthesis route for Nb_{0.1}Ti_{0.9}O₂ via a surfactant templating method is presented. The support was characterized using Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), and transmission electron microscopy (TEM) techniques. A colloidal method was then used to deposit platinum and ruthenium nanoparticles onto the Nb-doped titania supports. Their catalytic activity toward the electrochemical oxidation of methanol

was compared to commercial PtRu on carbon via cyclic voltammetry (CV) on the catalysts deposited onto a disk electrode and direct methanol fuel cell (DMFC) test on the catalysts fabricated in membrane electrode assemblies (MEAs).

Experimental

Synthesis of an Nb_{0.1}Ti_{0.9}O₂ support.— The synthesis of the Nb_{0.1}Ti_{0.9}O₂ support was done through a modification of the procedure of Yan et al.⁷ First, 0.030 mol of the template, octadecylamine, were mixed in a 250 mL beaker with 75 mL of dehydrated ethanol for 30 min with magnetic agitation. Second, 0.010 mol of niobium(V) ethoxide was added to the solution and allowed to mix for 15 min. Then, 0.090 mol of titanium(IV) butoxide was added to the solution and mixed for 15 min. Next, 54 mL of deionized water was added to the beaker, stirring was stopped, and the gel was aged for 48 h. The gel was filtered and then the template was removed using solvent extraction. For the solvent extraction, 92 mL dehydrated ethanol and 8 mL of concentrated HCl were added to a round bottom flask containing the filtered sample. The mixture was then boiled under reflux for 12 h. The product of the solvent extraction was then mixed with 200 mL of dehydrated ethanol. This mixture was adjusted to a pH of 10 with NaOH. The resulting Nb_{0.1}Ti_{0.9}O₂ was then dried at 100°C in a vacuum oven for 12 h.

Synthesis of a 60 wt % 1:1 PtRu/Nb_{0.1}Ti_{0.9}O₂ catalyst.— To synthesize the PtRu catalyst on the Nb_{0.1}Ti_{0.9}O₂ a colloidal method was used. The tetrahydrofuran (THF) (400 mL) was heated to 40°C under reflux in a three neck flask and with magnetic agitation. RuCl₃ (6.04 mmol) and H₂PtCl₆ (3.02 mmol) in THF were added to the mixture. The Nb_{0.1}Ti_{0.9}O₂ (800 mg) was added to the mixture and allowed to mix for 1 h. Then, LiBH₄ (60 mmol, two times the va-

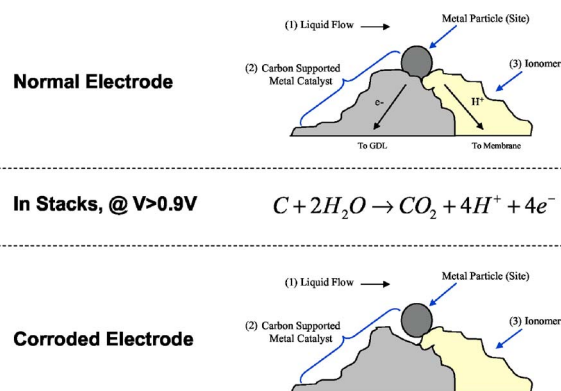


Figure 1. (Color online) Schematic showing the effect of carbon corrosion on reaction sites in the catalyst layer. If the metal particles lose contact with the carbon support, neither electrons nor protons can flow, making the site inactive.

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lence of the catalyst) in a 0.5 M solution with THF was added dropwise to the mixture. The solution was allowed to mix at 40°C for 12 h under reflux. The THF was evaporated from the mixture and the catalyst was washed with ethanol, benzene, and water. This same colloidal method was used to deposit PtRu on the Ketjenblack carbon.

Physical characterization.—TEM was performed on a Hitachi H-8000 to characterize the support particle size and the catalyst particle size. XRD was performed on a Rigaku 405S5 to examine the crystal structure of the $\text{Nb}_{0.1}\text{Ti}_{0.9}\text{O}_2$ support material and the PtRu/ $\text{Nb}_{0.1}\text{Ti}_{0.9}\text{O}_2$ supported catalyst. XRD patterns were compared with reference spectra using the software JADE (Materials Data, Inc.).

Electrochemical characterization.—CV was used to measure the methanol oxidation activity of PtRu/ $\text{Nb}_{0.1}\text{Ti}_{0.9}\text{O}_2$ films in a solution of 0.5 M H_2SO_4 and 1 M methanol. A catalyst ink was prepared by dissolving 6.0 mg of the catalyst in 3.0 mL of H_2O and 3.0 mL of isopropyl alcohol (IPA). This mixture was sonicated for 15 min and the catalyst ink was pipetted onto a glassy carbon electrode so that the catalyst film contained 37.5 nmol of Pt. To ensure film uniformity and integrity, the catalyst ink was applied in several aliquots with a maximum aliquot size of 5 μL . A binding solution was synthesized by diluting a 5 wt % Nafion in IPA solution with more IPA 1:20 by volume. After the catalyst film was applied, a 5 μL aliquot of binding solution was pipetted onto the electrode and allowed to dry.

The glassy carbon electrode was submerged in a reaction flask filled with the 0.5 M H_2SO_4 and 1 M methanol mixture. The solution was bubbled with N_2 for 15 min prior to testing. The counter electrode in the setup was a platinum wire electrode and the reference electrode was a Hg/HgSO₄ electrode with a Luggin capillary. The CV was conducted in a potential range between -0.7 and 0.6 V vs the Hg/HgSO₄ electrode (-0.02 to 1.28 V vs RHE) at a scan rate of 5 mV/s using a Princeton Applied Research 263A potentiostat controlled using the software package Corrware (Scribner Associates Inc.). The potential scans started at open circuit (~0.24 V), swept down to -0.7 V, swept up to 0.6 V, and swept back down to -0.70 V. The amount of active catalytic sites was determined by integrating the hydrogen desorption peak from a CV of the electrode in 0.5 M H_2SO_4 electrolyte using Corrware. The charge of the hydrogen desorption peak was converted to the moles of hydrogen desorbed via Faraday's law.

The MEA was constructed with a Nafion 117 membrane and E-TEK gas diffusion electrodes (GDEs) prepared according to the decal method of Wilson.⁸ The anode loading was 3.0 mg/cm² of 60 wt % 1:1 PtRu/ $\text{Nb}_{0.1}\text{Ti}_{0.9}\text{O}_2$ catalyst and the cathode loading was 1.0 mg/cm² of 40 wt % Pt/C catalyst. Current-voltage curves were obtained on a 25 cm² fuel cell from Fuel Cell Technologies. Before testing, the membrane was hydrated with water at 70°C for 24 h. Tests were conducted using an 890C load cell from Scribner Associates Inc. with a methanol fuel system and the software package FuelCell (Scribner Associates, Inc.) was used to control the station. The minimum flow rate for all experiments was 2 cm³/min on the anode and 20 standard cm³/min on the cathode. The anode methanol flow rate was 20 cm³/min and the cathode was operated at 20 stoich. Polarization curves between 0.2 V and open circuit were run at constant voltage and the current was allowed to equilibrate at each condition for 15 min before recording the current. The cell and inlet temperatures were 70°C.

Results and Discussion

Figure 2 shows the XRD diffraction pattern for the $\text{Nb}_{0.1}\text{Ti}_{0.9}\text{O}_2$ support material. The vertical lines in the figure show where peaks are expected for anatase TiO_2 structure from the JADE databases. The experimental XRD has peaks that appear at the same angles as the reference spectrum. A search was also conducted for niobium containing structures, but no distinct niobium oxide phases were

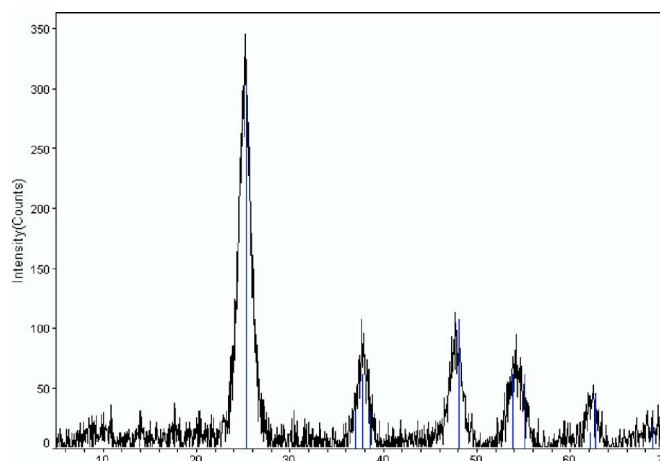


Figure 2. (Color online) XRD of the $\text{Nb}_{0.1}\text{Ti}_{0.9}\text{O}_2$ synthesized by solvent extraction.

found. A possible explanation for this result is that the niobium oxide is amorphous in the support material at low mole percents. TEM images of the material (not shown here) show that the $\text{Nb}_{0.1}\text{Ti}_{0.9}\text{O}_2$ formed small flakes that were about 10–20 nm and the flakes were arranged in multilayer structures.

BET surface area measurements were performed on the $\text{Nb}_{0.1}\text{Ti}_{0.9}\text{O}_2$ support. The surface area measured was 136 m²/g. This surface area is much higher than the value of 1.0 m²/g that was measured for a same synthesized at high temperature using the ceramic method.³ However, the surface area for the $\text{Nb}_{0.1}\text{Ti}_{0.9}\text{O}_2$ is lower than the 279 m²/g surface area measured by Yan et al.⁷ for a mesoporous TiO_2 support using a similar method. The inclusion of niobium in the support may have been responsible for this loss in surface area. Optimization of the Nb/Ti ratio may allow significant improvement of the surface area, conductivity, and catalytic activity.

The supported catalyst was also characterized by TEM images. A representative image of the supported catalyst is shown in Fig. 3. The TEM image for the PtRu/ $\text{Nb}_{0.1}\text{Ti}_{0.9}\text{O}_2$ is significantly different from that of typical PtRu/C catalysts. The PtRu/C catalysts usually have dark catalyst particles on a semitransparent carbon support. The Nb-doped TiO_2 support is generally darker than the carbon support in TEM images due to the larger, more densely packed Nb and Ti atoms. However, even with this lower contrast between the catalyst and the support, the metal catalyst particles do not appear to have enough connectivity to conduct current without a conductive support.

CV studies were performed on the PtRu catalysts deposited onto $\text{Nb}_{0.1}\text{Ti}_{0.9}\text{O}_2$ and carbon supports. The voltammograms, normalized by the mass of platinum deposited onto the disk, are shown in Fig. 4. Both voltammograms show a peak at 0.82 V, corresponding to the oxidation of methanol. The fact that methanol oxidation occurs on the electrocatalyst supported on $\text{Nb}_{0.1}\text{Ti}_{0.9}\text{O}_2$ means that the support is sufficiently conductive. Not only is this catalyst active, but the peak is approximately 6% higher than that on the PtRu/C synthesized by the same method. Even more impressive is that the hydrogen adsorption peak area was 94% higher on the PtRu/C than on the PtRu/ $\text{Nb}_{0.1}\text{Ti}_{0.9}\text{O}_2$. Therefore, each PtRu site was 100% more active on the PtRu/ $\text{Nb}_{0.1}\text{Ti}_{0.9}\text{O}_2$ catalyst.

DMFC tests were performed with the PtRu/ $\text{Nb}_{0.1}\text{Ti}_{0.9}\text{O}_2$ catalysts. Polarization results from tests at 70°C with 1 M methanol for the PtRu/ $\text{Nb}_{0.1}\text{Ti}_{0.9}\text{O}_2$ catalyst and a PtRu/C catalyst from E-TEK are shown in Fig. 5. Because both anodes have equal catalyst loadings (3.0 mg/cm²), the PtRu/ $\text{Nb}_{0.1}\text{Ti}_{0.9}\text{O}_2$ has 46% higher current per mass of Pt compared to the E-TEK PtRu/C at 0.40 V. This is

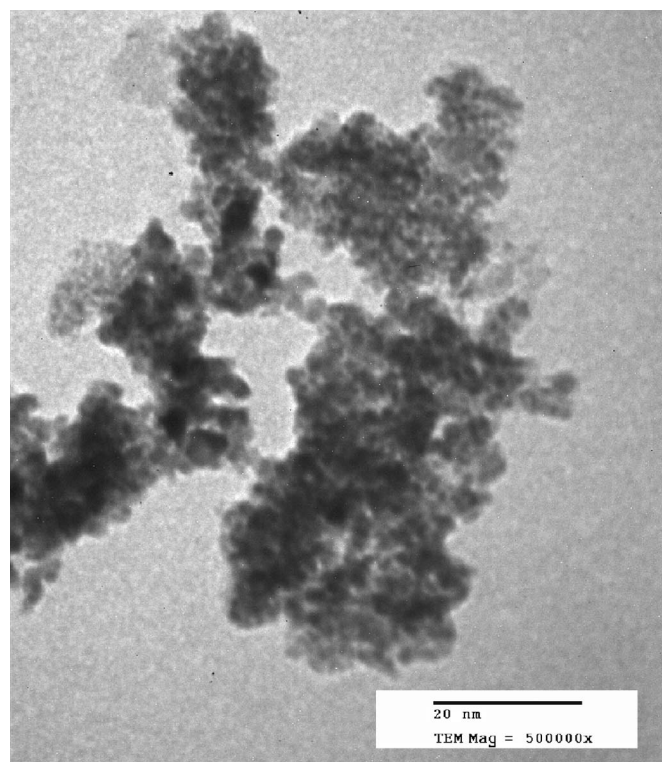


Figure 3. TEM image of the PtRu/Nb_{0.1}Ti_{0.9}O₂ supported catalyst.

significantly better than the 6% improvement seen on the disk electrode. Presumably, the MEA had better catalyst/Nafion mixing and dispersion.

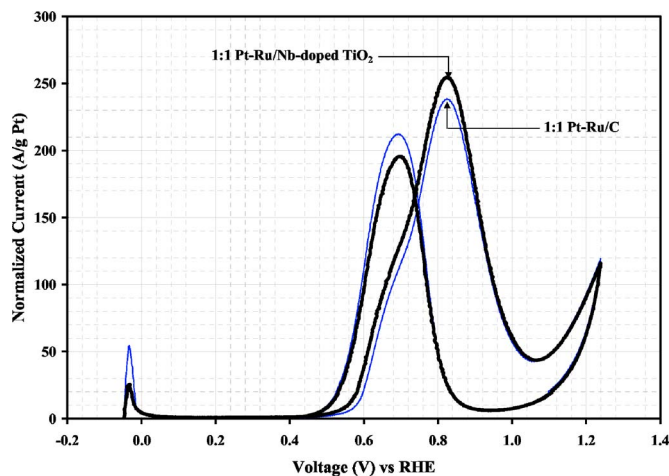


Figure 4. (Color online) Voltammograms for 60 wt % 1:1 PtRu catalysts supported on (-) carbon and (—) Nb_{0.1}Ti_{0.9}O₂ in 0.5 M H₂SO₄ and 1.0 M methanol at 25°C and 5 mV/s scan rate.

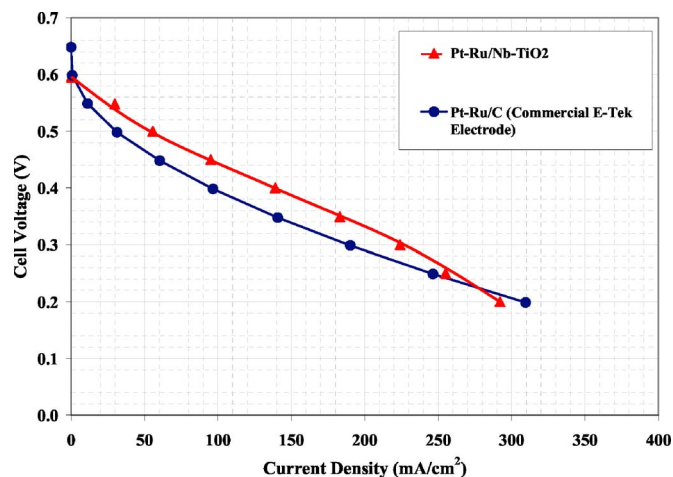


Figure 5. (Color online) Polarization curves at 70°C and 1.0 M methanol. The anode for each electrode had a PtRu loading of 3.0 mg/cm² of a 60 wt % 1:1 PtRu catalyst.

Conclusions

A Nb_{0.1}Ti_{0.9}O₂ catalyst support has been prepared via a low-temperature route. XRD results indicate the presence of anatase TiO₂ and do not show crystalline niobium oxide structures. A platinum-ruthenium catalyst supported on the Nb_{0.1}Ti_{0.9}O₂ appears to form catalyst particles that show a crystal structure similar to platinum. CV studies show that the supported catalyst is electrically conductive and has activity toward methanol oxidation.

At 25°C, the current per mass of platinum was 6% higher on the PtRu/Nb_{0.1}Ti_{0.9}O₂ catalyst compared to a commercial PtRu on carbon catalyst when deposited on a disk electrode. The electrochemically active surface area of the PtRu/C was 94% higher than PtRu/Nb_{0.1}Ti_{0.9}O₂, which means the current per active site was 100% higher on the PtRu/Nb_{0.1}Ti_{0.9}O₂ catalyst compared to the commercial PtRu/C catalyst when deposited on to a disk electrode. The current per mass of Pt from an MEA fabricated with the PtRu/Nb_{0.1}Ti_{0.9}O₂ was 46% higher than an equivalent E-TEK MEA at 70°C. These results suggest that the anatase titania support enhances the catalytic activity of the PtRu in ways that carbon cannot.

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