Ruthenium-Tin Oxide/Carbon Supported Platinum Catalysts for Electrochemical Oxidation of Ethanol in Direct Ethanol Fuel Cells

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Carbon black coated with a mixture of Ru and Sn oxides has been used as a support for Pt nanoparticles (Pt/Ru-Sn oxide/C) in order to increase their activity for ethanol oxidation without a significant loss of selectivity. The mixed oxide layer was prepared by the spontaneous reaction of the carbon surface with KRuO₄ in the presence of Sn(IV). Pt nanoparticles were then deposited by reduction of H₂PtCl₆ with NaBH₄. The resulting catalyst provided higher electrochemical activities than Pt black for ethanol oxidation in both a liquid electrolyte cell at ambient temperature and a proton exchange membrane direct ethanol fuel cell at 80 °C. CO₂ yields from the fuel cell were similar for the Pt/Ru-Sn oxide/C and Pt black catalysts, while acetic acid to acetaldehyde ratios were much higher for Pt/Ru-Sn oxide/C. Consequently, the Pt/Ru-Sn oxide/C catalyst increased both the voltage efficiency and faradaic efficiency of the cell.

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Direct ethanol fuel cells (DEFC) are a very attractive future technology for efficient power generation from renewable resources.1-3 Use of a safe liquid fuel at moderate temperatures makes DEFC suitable for a wide range of applications, particularly in transportation and portable devices.4,5 However, the lack of high performance catalysts for ethanol oxidation5-7 means that DEFC are currently not competitive with hydrogen and methanol fuel cells. In particular, the selectivity toward complete oxidation of ethanol to carbon dioxide is poor, resulting in substantial efficiency losses and the production of large quantities of acetic acid and acetaldehyde as by-products.1,7 The commercial development of DEFC based on proton exchange membrane (PEM) technology will require substantial improvements in both the activity and selectivity of the anode catalyst, and this has led to significant advances in recent years.5-8 Of particular note are the use of PtRh alloys to increase the selectivity for breaking the carbon-carbon bond of ethanol,9 to produce CO₂, and the use of metal oxide supports to increase reaction rates without blocking the sites on the catalyst required for C-C bond activation.10,11 A variety of metal oxide supports have been shown to be effective for increasing the activities of both Pt and PtRh nanoparticles, including SnO₂,10 MoO₃,12 WO₃,12 RuO₂,13 and Sb₂O₅.14 Hydrous RuO₂ is an attractive support material for ethanol oxidation catalysts because it conducts both electrons and ions, is very stable in acidic media, and can catalyse the oxidation of CO, which is the main catalyst poison formed during ethanol oxidation. In addition, thin films of RuO₂ can easily be deposited on high surface area carbon supports by the spontaneous reduction of KRuO₄ at the carbon surface.15,16 These oxide layers can promote ethanol oxidation at Pt nanoparticles17 and be can be prepared as composites with other metal oxides18 that can modulate the catalytic activity.19 A mixture of Ru and Sn oxides was found to give the best balance of activity and stability for ethanol oxidation at Pt nanoparticles on oxide modified glassy carbon electrodes.13 The purpose of the work reported here was to prepare a fuel cell catalyst based on this methodology. Thus, a mixed Ru and Sn oxide layer was deposited onto a high surface area carbon support using a mixture of KRuO₄ and SnCl₄, and Pt nanoparticles were then deposited by reduction of H₂PtCl₆ with NaBH₄. Following characterization, the activity of the catalyst for ethanol oxidation was measured in a conventional electrochemical cell and a DEFC. Products from the fuel cell were analyzed in order to determine the selectivity.

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**Materials.**—Anhydrous ethanol (Commercial Alcohols Inc.), sulfuric acid (Fisher Scientific), K RuO₄ (Alfa Aesar), SnCl₂·5H₂O (Fisher Scientific), H₂PtCl₆·6H₂O (Alfa Aesar), sodium citrate (Anachemia), potassium hydroxide (ACP Chemical Inc.), Nafion solution (5% DuPont) and sodium borohydride (Sigma Aldrich) were used as received. Carbon black (Vulcan XC - 72, Cabot) was dispersed in 0.1 M H₂SO₄, then collected by filtration, and washed with water before use. Double distilled water was used throughout all experiments.

**Preparation and characterization of the catalyst.**—To prepare the mixed Ru-Sn oxide on carbon support, KRuO₄ (0.151 g; 0.025 M) was dissolved in 0.1 M KOH (30 mL), a 0.025 M solution of SnCl₂·5H₂O (0.267 g in 30 mL of 0.1 M KOH) was then added drop wise, and this Ru+Sn solution was then added to a suspension of 0.6 g of carbon black in 45 mL of water. Following vigorous stirring for 30 min, the Ru-Sn oxide/C powder was collected by filtration, rinsed several times with water, and dried under vacuum overnight.

Pt nanoparticles were deposited onto the Ru-Sn oxide/C support using a method similar to Yang et al.17 H₂PtCl₆ (0.1828 g) in 10 mL of water was added dropwise to an aqueous suspension of Ru-Sn oxide/C (0.208 g) and the mixture and stirred for 0.5 h. 50 mM trisodium citrate (0.0778 g; 12 mL) was then added dropwise. After mixing for 1 h, sodium borohydride 0.0902 g was added dropwise. Following stirring for 3 h, the Pt/Ru-Sn oxide/C catalyst (0.2521 g) was collected by filtration, washed several times, and allowed to dry overnight.

Inductively coupled plasma – mass spectrometry (Elan DRC II ICP-MS) gave a composition (mass%) of 32.6% Pt, 2.6% Ru, and 4.1% Sn.

Powder X-ray diffraction (XRD) measurements were made on a Rigaku Ultima IV using a Cu-Kα source (1.5418 Å). Scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX) was carried out using a Bruker XFlash dual 5030. Transmission electron microscopy was carried out at the University of New Brunswick (The Microscopy and Microanalysis Facility) using a JEOL 2011 200 kV scanning transmission electron microscope.

**Electrochemical measurements.**—A 5 cm² commercial cell (Fuel Cell Technology Inc.) was used for fuel cell testing. The cathode inlet and outlet were both modified to prevent the ethanol solution from contacting any metal parts of the hardware. The Pt/Ru-Sn oxide/C anode for the fuel cell was prepared with an ink consisting of 74.4 mg of the catalyst dispersed in 185 μL of 5% Nafion solution by sonication for 30 min. This ink was spread onto a 5 cm² piece of Toray carbon fiber paper with a spatula, and allowed to dry for 1 day. A catalyst loading of 9.74 mg cm⁻² (ca. 2.8 mg Pt cm⁻²) was obtained.
Membrane and electrode assemblies were prepared by hot pressing a 5 cm² anode and a 5 cm² cathode (4 mg cm⁻² Pt black on Toray carbon fiber paper) onto a Nafion 115 membrane (Ion Power) at a pressure of 200 kg cm⁻² at 135°C for 90 s. The fuel cell was operated with an anode feed of 0.50 M ethanol solution at 0.50 mL min⁻¹. The cathode feed was oxygen at 50 mL min⁻¹. Electrochemical measurements on the fuel cell were made using a Solartron 1287 potentiostat operated with Corrware software.

Cyclic voltammetry was carried out in a conventional three electrode glass cell with an EG&G PAR 273 A model potentiostat/galvanostat using M270 commercial software. Working electrodes were strips of catalyst-coated carbon fiber paper prepared in the same manner as the fuel cell electrodes.

Product analysis.—Both the anode solution and the cathode gas were passed into a 125 mL flask in order to include products that crossed through the membrane to the cathode. The O₂ stream was bubbled through the ethanol solution in the flask to collect CO₂ from the anode exhaust and then passed into a Telaire 7001 non-dispersive infrared (NDIR) CO₂ detector for analysis.¹⁸ Acetic acid measurements were made by titrating the solution collected in the flask with 0.01 M NaOH solution. Background CO₂ and acetic acid measurements, made at open circuit, were subtracted to account for their production by the chemical reaction of ethanol with O₂, due to crossover.¹⁹ Faradaic yields of CO₂ and acetic acid are reported, based on their measured amounts (moles) and the charge passed during operation of the cell at constant current.

Results

Characterization of the catalyst.—Fig. 1 shows XRD of the C/Ru-Sn oxide/Pt catalyst. The diffraction peak at ca. 25° represents the carbon (002) plane. The Pt peaks are at ca. 40.0°, 46.5°, 67.5°, 81.5° and 86.1°, representing the Pt(111), Pt(200), Pt(220), Pt(311) and Pt(222) planes, respectively. The mean Pt particle size was estimated from the width of the Pt(111) peak to be ca. 8.6 nm based on the Scherrer equation. The peaks at ca. 34–35° and 53° can be assigned to a mixed Ru-Sn oxide.²⁰ Both are very broad and shifted from the values of 35.1° and 54.2° for pure RuO₂ and 33.8° and 51.7° for pure SnO₂. This is consistent with a reported XRD pattern of a low crystallinity mixed Ru-Sn oxide.²⁰ The presence of both Ru and Sn was confirmed by ICP-MS and energy dispersive X-ray analysis (EDX) using both SEM and TEM.

TEM images of the C/Ru-Sn oxide/Pt catalyst are shown in Fig. 2. Fig. 2A shows extensive aggregation of the Pt nanoparticles (dark spots). Where individual Pt particles could be seen (Fig. 2B), the average diameter was 5.0 ± 1.1 nm, which is somewhat lower than the value of 8.6 nm indicated by XRD. This suggests that the Pt aggregates contained larger crystallites than the more dispersed Pt particles.

The TEM images shown in Fig. 2 do not show any features that can be attributed to Ru oxide, Sn oxide, or a mixed oxide. This can be explained by the mechanism of Ru oxide formation, which requires reduction of Ru(VII) to Ru(IV) at the carbon surface.¹⁶ The Vulcan XC-72 carbon black support consists of agglomerates of ~50 nm diameter nanospheres, and this is the structure of the modified support seen in Fig. 2. The persistence of the morphology of the carbon black indicates that the oxide was present as a thin layer coating the carbon. Based on the BET surface area of Vulcan XC-72 (~200 m² g⁻¹),¹¹ a uniform coverage of the measured loading of Ru and Sn would correspond to a mixed oxide layer of only ca. 0.1 nm. However, it is unlikely that the whole of the BET area is accessible, and so the actual oxide layer should be ca. 0.2–0.4 nm.¹¹ This interpretation of the structure of the oxide in the catalyst is supported by the similarity of the electrochemical results (below) with those obtained for mixed Ru-Sn oxide layers deposited on glassy carbon electrodes.¹³

Electrochemical measurements in a 3-electrode liquid electrolyte cell.—Fig. 3 compares voltammograms of Pt/Ru-Sn oxide/C (2.8 mg Pt cm⁻²) and Pt black (4.0 mg cm⁻²) electrodes in 0.1 M H₂SO₄(aq). In the -200 to 0 mV region the Pt/Ru-Sn oxide/C electrode showed significantly smaller H adsorption and desorption waves than the Pt

![Figure 1. X-ray diffraction of the Pt/Ru-Sn oxide/C catalyst.](image)

![Figure 2. TEM images of the Pt/Ru-Sn oxide/C catalyst.](image)
black electrode, which can be attributed to the lower Pt loading of ca. 2.8 mg cm$^{-2}$ relative to 4.0 mg cm$^{-2}$ for the Pt black. However, currents were much higher for the Pt/Ru-Sn oxide/C electrode at higher potentials due to the electrochemistry of the Ru and Sn oxides as well as the carbon support. A voltammogram of a Ru-Sn oxide/C support without Pt is shown as the dotted line in Fig. 3 to allow estimation of the charge for hydrogen adsorption (shaded area) on the Pt/Ru-Sn oxide/C electrode. Comparison with the hydrogen adsorption charge for the Pt black electrode shows that the active Pt surface area for the Pt/Ru-Sn oxide/C electrode was ca. 45% of the value for the Pt black electrode.

Fig. 4 compares voltammograms of the same electrodes in 0.1 M H$_2$SO$_4$(aq) containing 0.2 M ethanol. It can be seen that the Pt/Ru-Sn oxide/C electrode was much more active for ethanol oxidation at low potentials (< 600 mV) than the Pt black electrode. This can be attributed to the combined bifunctional and electronic effects of the Ru and Sn oxides. The voltammogram at the Pt/Ru-Sn oxide/C electrode in Fig. 4 is similar to voltammograms obtained by depositing Ru-Sn oxide and Pt nanoparticle onto glass carbon electrodes using similar methodology. The effects of potential cycling were similar, and the stability of those structures has been discussed.

**Figure 3.** Cyclic voltammograms (10 mV s$^{-1}$) of Pt/Ru-Sn oxide/C (solid line; 2.8 mg Pt cm$^{-2}$) and Pt black (dashed line; 4.0 mg cm$^{-2}$) and Ru-Sn oxide/C (dotted line) electrodes in 0.1 M H$_2$SO$_4$(aq). The voltammogram of the Ru-Sn oxide/C support has been scaled to approximately match the Ru-Sn oxide peaks for the Pt/Ru-Sn oxide/C electrode.

**Figure 4.** Cyclic voltammograms (10 mV s$^{-1}$; 2nd cycle) of Pt/Ru-Sn oxide/C (red (solid) line; 2.8 mg Pt cm$^{-2}$) and Pt black (black (dashed) line; 4.0 mg cm$^{-2}$) electrodes in 0.1 M H$_2$SO$_4$ (aq) containing 0.2 M ethanol. Dotted lines show the reverse (cathodic) scan. The differences in currents below −100 mV are due to the different lower potential limits employed.

**Figure 5.** Polarization curves for DEFC with Pt/Ru-Sn oxide/C (solid line; 2.8 mg Pt cm$^{-2}$) and Pt black (dashed line; 4 mg cm$^{-2}$) anode catalysts, at 80°C, with 0.5 M ethanol solution at 0.50 mL min$^{-1}$ and O$_2$ at 50 mL min$^{-1}$. Currents were measured after 300 s at each cell potential.

Direct ethanol fuel cell performances.—Fig. 5 shows polarization curves for DEFC with Pt/Ru-Sn oxide/C (2.8 mg Pt cm$^{-2}$) and Pt black (4.0 mg cm$^{-2}$) anode catalysts. It can be seen that the performance of the Pt/Ru-Sn oxide/C anode was significantly higher at all potentials than the Pt black anode, despite the lower Pt loading and significantly lower active Pt area indicated by the voltammograms in Fig. 3. The high activity of the Pt/Ru-Sn oxide/C anode demonstrates that the support effects observed in 0.1 M H$_2$SO$_4$(aq) at ambient temperature can also substantially increase performance in a fuel cell. Moreover, the sustained high performance of the Pt/Ru-Sn oxide/C anode at 80°C demonstrates good stability over a >1 h measurement period.

The high activity of the Pt/Ru-Sn oxide/C anode in the DEFC is not particularly notable in light of the large number of reports of Pt, Ru, and Sn based binary and ternary catalysts that provided higher performances than Pt alone. However, alloying or surface decoration of Pt with Ru and/or Sn decreases the selectivity for CO$_2$ formation, resulting in an overall loss of efficiency. The use of Ru oxide and/or Sn oxide supports to activate pure Pt nanoparticle therefore offers the potential of increasing their electrochemical performance (increasing the voltage efficiency of the DEFC) without loss of selectivity (decreasing the faradaic efficiency of the DEFC). Consequently, it is important to consider the product distribution in addition to the electrochemical performance.

**Product analysis and CO$_2$ selectivity.**—Cell voltages and product analyses for DEFCs operated at constant current with Pt/Ru-Sn oxide/C and Pt black anodes are compared in Table I. These experiments were performed at 80°C with product analysis over a 30 min period in each case. Average cell potentials and faradaic yields are reported. As in the polarization curves, the cell potential at each current was significantly higher at the Pt/Ru-Sn oxide/C anode than the Pt black anode. This further illustrates the durability of the Pt/Ru-Sn oxide/C catalyst, with the operation of the cell extended to >6 h over a period of days, and also demonstrates increased resistance to longer term poisoning relative to Pt black.

The CO$_2$ yields reported in Table I show only small decreases in selectivity for the complete oxidation of ethanol at the Pt/Ru-Sn oxide/C catalyst at 50 and 100 mA, while it was actually more selective.
Table I. Average cell potentials and faradaic yields from titration (acetic acid) and NDIR (CO2) measurements on the combined anode and cathode exhausts from DEFC at constant current. The cathode gas was O2 and the cell was operated at 80°C with 0.5 M ethanol solution.

| Catalyst        | Current/mL A | Potential/mV | CO2 yield | Acetic acid | Acetaldehyde* |
|-----------------|--------------|--------------|-----------|------------|--------------|
| Pt black        | 50           | 294          | 34%       | 30%        | 36%          |
|                 | 100          | 178          | 30%       | 37%        | 33%          |
| Pt/Ru-Sn oxide/C| 50           | 78           | 20%       | 41%        | 40%          |
|                 | 100          | 264          | 27%       | 55%        | 18%          |
|                 | 150          | 204          | 23%       | 47%        | 30%          |

*Acetaldehyde yields were calculated based on faradaic charge balance.

Table II. Voltage and faradaic efficiencies of the DEFC.

| Catalyst       | Current/mL A | Voltage efficiency | Faradaic efficiency |
|----------------|--------------|--------------------|---------------------|
| Pt black       | 50           | 26%                | 29%                 |
|                | 100          | 15%                | 29%                 |
| Pt/Ru-Sn oxide/C| 50           | 29%                | 26%                 |
|                | 100          | 23%                | 33%                 |
|                | 150          | 18%                | 29%                 |

the distribution of the Pt and oxides, optimizing the composition, and employing alloys such as PtRh that are more selective for oxidation of ethanol to CO2.

Conclusions

Deposition of Pt nanoparticles on a mixed Ru oxide + Sn oxide support on carbon black has significantly increased their electrochemical performance for ethanol oxidation in both a liquid electrolyte cell at ambient temperature and a polymer electrolyte fuel cell. In contrast to alloying and surface decoration, use of the Ru and Sn co-catalysts in this way does not significantly decrease the selectivity for the complete oxidation of ethanol to carbon dioxide. Thus use of a Pt/Ru-Sn oxide/C anode catalyst can increase the voltage efficiency of a DEFC while also increasing the faradaic efficiency.

The reaction of KRuO4 with the surface of carbon black allows the oxide support to be deposited as a thin film with high surface area, that can maximize contact and interactions with the Pt nanoparticles. This can decrease CO2 poisoning by providing surface –OH functionality (the bi-functional mechanism). In addition, Sn oxide can be co-deposited with the Ru oxide, presumably as a mixed oxide, to provide an electronic effect.13,31–33 By providing these activity enhancing effects via the support material, large areas of unmodified Pt can be maintained to facilitate cleavage of the C-C bond of ethanol.

This work highlights the importance of measuring both the electrochemical performance and reaction stoichiometry when catalysts for ethanol oxidation are evaluated. It demonstrates for the first time that an anode support material can increase the performance of a DEFC without sacrificing fuel efficiency.

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