Composition Dependence of Ethanol Oxidation at Ruthenium-Tin Oxide/Carbon Supported Platinum Catalysts

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Pt nanoparticle catalysts supported on carbon black coated with mixtures of Ru and Sn oxides (Pt/Ru-Sn oxide/C) have been screened for their activity and stoichiometry for ethanol oxidation. The compositions, loadings, and properties of the mixed Ru + Sn oxide support layers were varied by changing the concentration of base used during their deposition. Cyclic voltammetry at ambient temperature showed that Ru oxide alone provided a significant increase in activity at low potentials over Pt/C, while a small amount of Sn provided a large additional benefit. The most active catalyst had Ru and Sn loadings of 17% and 1.2% by mass, respectively. This was also the most active catalyst for ethanol oxidation at 80 °C in proton exchange membrane electrolysis cells, where it provided four times more current than a commercial Pt/C catalyst at 0.25 V vs. a hydrogen evolving cathode. This is comparable to the performance of commercial PtRu/C, and the Pt/Ru-Sn oxide/C catalyst was more selective for the complete oxidation of ethanol to CO₂. Thus, in direct ethanol fuel cells, Pt/Ru-Sn oxide/C catalysts would provide greatly increased current and power densities over Pt/C, and improved efficiencies over PtRu/C.

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Experimental

Materials.—Anhydrous ethanol (Commercial Alcohols Inc.), sulfuric acid (Fisher Scientific), K₂RuO₄ (Alfa Aesar), SnCl₄·2H₂O (Alfa Aesar), H₂PtCl₆·6H₂O (Pressure Chemical Co.), sodium citrate (Sigma-Aldrich), potassium hydroxide (ACP Chemical Inc.), sodium borohydride (BDH Chemicals), carbon supported Pt (Pt/C; HiSPECF 13100, 70% Pt; Alfa Aesar), and Nafion solution (5% DuPont) 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. Distilled and deionized water was used throughout all experiments.

Preparation and characterization of the catalysts.—All of the catalysts were prepared by the reaction of K₂RuO₄ and SnCl₄ with carbon black in water or aqueous KOH, followed by deposition of Pt nanoparticles by reduction of H₂PtCl₆ with NaBH₄ in the presence of sodium citrate.2,3 Table I summarizes the conditions employed. In the catalyst descriptors, the targeted mass percent of the catalytic Pt nanoparticles is provided, followed by an identifier for the support (Sx) with a subscript related to the synthesis conditions. The support is taken to be the carbon + oxide composite, since these composites did not show significant activity for ethanol oxidation in the absence of Pt.

To deposit the mixed oxide, a mixture of K₂RuO₄ and SnCl₄ in aqueous KOH (or water) was added dropwise to a suspension of carbon black in water or KOH(aq). Following stirring for 24 h (or 30 min for S₁0.30), the Ru-Sn oxide/C powder was collected by filtration, rinsed several times with water, and dried in air overnight. Pt nanoparticles were deposited onto an aqueous suspension of the Ru-Sn oxide/C support by adding H₂PtCl₆ in 10 mL of water, stirring for 0.5 h, followed by dropwise addition of 50 mM trisodium citrate (12 mL), stirring for 1 h, dropwise addition of sodium borohydride (0.0902 g in 20 mL of water) and stirring for 3 h. The Pt/Ru-Sn oxide/C catalyst was collected by filtration, washed several times with water, and allowed to dry overnight. For comparison purposes, a Pt/Ru oxide/C catalyst was prepared in the same way as 25%Pt/S₁₁₀, without SnCl₄.

Although direct ethanol fuel cells (DEFC) are potentially an important future technology for many applications,4,5 they are currently impractical because of the low efficiencies of their anode catalysts and the production of incomplete oxidation products.6 The development of catalysts for ethanol oxidation has focused on increasing activities to produce higher power densities and voltage efficiencies, but this has generally led to lower selectivity for the complete oxidation to carbon dioxide.5–8 For example, PtSn based catalysts can provide attractive power densities, but the production of acetic acid and acetaldehyde as the main products results in low faradaic efficiencies and harmful emissions.5–7

Early work on the development of electrocatalysts for ethanol oxidation focused on the use of PtRu, PtSn, and PtRuSn based materials,9 while recent work has shifted toward PtRh and PtNi based systems.10–12 Alloying of Rh with Pt has been shown to promote cleavage of the C-C bond of ethanol, leading to increased selectivity for complete oxidation to CO₂.13,14 Activities have been increased by adding a third metal or an oxide phase, and control of the nanostructure.5,15 Mo,16 W,17 Ru,18 and Sn19 oxides have been employed with Pt and/or PtRh nanoparticles.

The high conductivity and stability and RuO₂ makes it an attractive component for electrolytic systems, and its co-catalytic effect on the oxidation of CO and methanol is well known.19–21 RuO₂ alone has been reported to have a small activating effect on Pt for ethanol oxidation,22,23 and it can be used in combination with SnO₂ to prepare very active and stable ethanol oxidation catalysts.23 Codeposition of SnO₂ with RuO₂ onto a carbon black support, followed by deposition of Pt nanoparticles, to produce a Pt/Ru-Sn oxide/C catalyst, has been shown to increase the low potential activity for ethanol oxidation relative to Pt black (higher voltage efficiency) and also increase the faradaic efficiency.23

The purpose of the work reported here was to explore the effects of the synthesis conditions and composition of Pt/Ru-Sn oxide/C catalysts on their activity and stoichiometry for ethanol oxidation. The objective was to control the nanostructure of these materials in order to optimize the balance between activity at low potentials and selectivity for the complete oxidation of ethanol to CO₂. Electrochemical measurements were made at ambient temperature in a conventional liquid electrolyte cell and in proton exchange membrane (PEM) electrolysis cells at 80 °C. Ultimately, this will allow optimization of the energy efficiency of DEFCs with Pt/Ru-Sn oxide/C anodes.
Table I. Summary of conditions for preparation of the catalysts reported in this work. The catalyst name includes the targeted Pt loading (mass %) and the key characteristic of the method for synthesis of the support (Sx). The reaction time for preparation of the support was 30 min for S_{110-30}, and 24 h for all others.

| Catalyst          | C (g)/KOH (ml, M) | SnCl$_4$ ·H$_2$O (g)/KOH (ml, M) | KRUO$_4$ (g)/KOH (ml, M) | Pt | Ru | Sn | Pt particle diameter (nm) |
|-------------------|-------------------|---------------------------------|-------------------------|----|----|----|--------------------------|
| 25%Pt/S_{110-30}  | 0.699/45, 0       | 0.265/30, 0.1                   | 0.158/30, 0.1           | 24.9 | 5.7 | 1.1 | 3.5                      |
| 25%Pt/S_{110}     | 0.650/45, 0       | 0.268/30, 0.1                   | 0.156/30, 0.1           | 30.4 | 3.4 | 1.2 | 4.4                      |
| 70%Pt/S_{110}     | 0.650/45, 0       | 0.268/30, 0.1                   | 0.156/30, 0.1           | 67.4 | 2.6 | 0.5 | 7.2                      |
| 25%Pt/S_{57nmM}   | 0.599/45, 0.057   | 0.265/30, 0.057                 | 0.152/30, 0.057         | 24.9 | 6.5 | 1.0 | 4.6                      |
| 30%Pt/S_{SLC}     | 0.087/10, 0       | 0.205/24, 0.1                   | 0.118/30, 0.1           | 30.2 | 17.0 | 1.2 | 6.4                      |
| 25%Pt/S_{O2.2M}   | 0.301/23, 0.2     | 0.132/15, 0.2                   | 0.078/15, 0.2           | 23.6 | 6.5 | 0.1 | 4.4                      |
| 25%Pt/S_{water}   | 0.297/23, 0       | 0.131/15, 0                     | 0.076/15, 0             | 30.5 | 5.3 | 7.4 | 4.3                      |

Powder X-ray diffraction (XRD) measurements were made on a Rigaku Ultima IV using a Cu-Kα source (1.5418 Å). Transmission electron microscopy was carried out at the University of New Brunswick (The Microscopy and Microanalysis Facility) using a JEOL, 2011 200 keV scanning transmission electron microscope.

**Electrochemical measurements.**—Cyclic voltammetry was carried out in a conventional three electrode glass cell with a Pine Instruments RDE4 Potentiostat. Glassy carbon working electrodes (0.071 cm$^2$) were coated with the catalysts as follows. The catalyst ink was applied to a glassy carbon electrode that had been polished with 0.3 μm alumina. A calomel (SCE) reference electrode and Pt wire counter electrode were used.

**PEM cells.**—Cells with nine separate 5 cm$^2$ anodes or a single 5 cm$^2$ anode, a single 5 cm$^2$ Pt black cathode, and a Nafion proton conducting membrane electrolyte (Nafion 117 for the 9-anode cell and Nafion 115 for the single anode cell) were used. Each cell was based on a commercial (ElectroChem Inc.) PEM fuel cell. The anode current collectors in the nine-anode cell were graphite rods embedded in a Bakelite plate. Anodes were prepared by painting a catalyst ink onto carbon fiber paper (CFP; Toray TGP-H-090). For the 5 cm$^2$ anode, the CFP (wet proofed with 10 wt% PTFE; E-TEK, Inc.) was first coated with a carbon black layer prepared with an ink consisting of carbon black (10.2 mg) dispersed in a mixture of 1-propanol (100 μL) and Nafion solution (50 μL), and the resulting ink was sonicated for 1 h (Branson Ultrasonic Corporation Model 1510R-MTH, 70 W at 42 kHz). Then, 3.0 μL of ink was applied to a glassy carbon electrode that had been polished with 0.3 μm alumina. A calomel (SCE) reference electrode and Pt wire counter electrode were used.

Results and Discussion

**Synthesis of the catalysts.**—The reaction of KRUO$_4$, with carbon black to form a Ru oxide coating should be conducted under basic conditions to avoid precipitation of Ru oxide due to oxidation of water. A solution of KRUO$_4$ in 0.1 M KOH has been used in previous work, and the previously reported method for preparation of Ru-Sn oxide/C employed a mixture of KRUO$_4$ and SnCl$_4$ in 0.1 M KOH. However, a hydrous Sn(IV) oxide slowly precipitates from 0.1 M KOH due to hydrolysis. This would be expected to influence the composition, structure, homogeneity, and morphology of the resulting Ru-Sn oxide deposit, and thereby modulate the effect of the Ru-Sn oxide/C support on the catalytic activity of the Pt/Ru-Sn oxide/C catalyst. In order to investigate this, the KOH concentration of the precursor solutions was varied, as shown in Table I. The aim of these experiments was to optimize the composition, loading, and structure of the Ru-Sn oxide. It was thought that controlling the solubility of hydrous Sn oxide would significantly influence the amount of Sn that would be incorporated into the Ru oxide deposit, and that precipitation of hydrous SnO$_2$ could lead to a homogeneous mixed oxide with discrete Sn oxide particles.

The compositions of the catalysts, measured by ICP-OES, are listed in Table I. The catalyst name indicates the targeted Pt loading. The supports (S_x) for the 25%Pt/S_{110-30}, 25%Pt/S_{110} and 70%Pt/S_{110} catalysts were prepared following a previously reported procedure, in which solutions of KRUO$_4$ and SnCl$_4$ in 0.1 M KOH were mixed and then added to a suspension of carbon black in water. The reaction time was 30 min for S_{110-30} and 24 h for S_{110} and all other supports. A black precipitate began to form when the KRUO$_4$ and SnCl$_4$ were mixed, and the resulting change in concentration of KOH was monitored. When this mixture was added to the carbon suspension in water, it could cause further precipitation of Sn oxide during the reaction. In order to investigate whether this change in the KOH concentration produced a significant effect, the support for the 25%Pt/S_{57nmM} catalyst was prepared with all of the precursors in 57 mM KOH. It can be seen from the Ru and Sn loadings reported in Table I that neither the increase in reaction time (relative to S_{110-30}) nor the dispersion of the carbon in water had a large influence on the Ru or Sn loading.

In order to increase the oxide loading, the amount of carbon was decreased by 40% for preparation of the low carbon (LC) support for 30%Pt/S_{LC}. This resulted in a large increase in the Ru content of the catalyst and large increase in the Ru:Sn mass ratio (from 5.2:1 for...
25%Pt/S_110 (to 14:1). Additional supports were prepared in 0.2 M KOH for the 25%Pt/S_0.2M catalyst and in the absence of base for the 25%Pt/S_water catalyst. Since, hydrous Sn oxide dissolves as Sn(OH)_4^{2-} in 0.2M KOH, there should have been no precipitation of Sn oxide during formation of S_0.2M, and this was confirmed by the very low Sn content of 25%Pt/S_110. In contrast, SnCl_4 slowly forms a precipitate of hydrous Sn oxide in water, and so the 25%Pt/S_water catalyst had a high Sn content, resulting in a low Ru:Sn mass ratio of 0.72:1.

The Pt loadings of the catalysts, listed in Table I, were very close to the target values, except for 25%Pt/S_110 and 25%Pt/S_water which had higher measured Pt contents, presumably due to loss of oxide during Pt deposition. Apart from 70%Pt/S_110 and 30%Pt/SLC, which had very broad. These are close to the (101) and (211) peaks for pure SnO_2 at 33.8° and 35.0°, respectively, which is consistent with the high Sn content of this catalyst (Table I) and the precipitation of hydrous Sn oxide at the neutral pH used for synthesis of the support. It can be seen in Fig. 1 that the predominantly SnO_2 peaks for 25%Pt/S_water were at significantly lower angles than the predominantly RuO_2 peaks for S_110.

A TEM image of the 30%Pt/SLC catalyst is shown in Fig. 2. It can be seen that the Pt particles (dark circles) were distributed reasonably uniformly over the support, while the morphology of the carbon black (agglomerates of ~50 nm diameter spheres) was not changed significantly by the deposition of the oxides and Pt. This is consistent with the expectation that the Ru oxide would deposit uniformly as a thin layer over the carbon. X-ray mapping by STEM (not shown) indicated that the Ru and Sn distributions mirrored the secondary electron image, but the resolution was insufficient to show whether the darker regions (10–20 nm) in Fig. 2 were due to thicker oxide deposits. The average diameter of the Pt particles from TEM was 5.0 ± 1.2 nm, which is similar to the average value of 6.4 ± 0.9 nm measured by XRD for two samples of 30%Pt/SLC prepared in the same way.

Electrochemical measurements in a 3-electrode liquid electrolyte cell.—Fig. 3 compares voltammograms of a Ru-Sn oxide/C support

![Figure 1. X-ray diffraction of a 25%Pt/S_110,30 (a) and 25%Pt/S_water (b) catalysts, and S_110 after (c) and before (d) annealing in air at 200 °C for 24 h.](image1)

![Figure 2. TEM image of a 30%Pt/SLC catalyst.](image2)

![Figure 3. Cyclic voltammogram (100 mV s^{-1}; 1 M H_2SO_4(aq)) of a 30%Pt/SLC catalyst (solid line) and a scaled (see text) voltammogram of S_LC (dashed line). The dotted line shows the difference between the two voltammograms.](image3)
with a Pt/Ru-Sn oxide/C catalyst in 1 M H₂SO₄(aq). Both voltammograms show broad redox waves at ca. 0.43 V that can be attributed primarily to the Ru/IV/III couple of the oxide layer on the carbon. These are similar to the voltammograms reported for Ru oxide deposited in the same way on carbon nanotubes and carbon fabric. The main differences between the voltammogram of the catalyst and the support in Fig. 3 are in the −200 to +100 mV region where the catalyst shows well-defined peaks for hydrogen adsorption and desorption at the Pt nanoparticles. The charges passed during these processes are proportional to the electrochemically active area (0.21 m² cm⁻²), which allows the Pt utilization (percentage of the total area that is active) to be estimated. In order the measure this charge more accurately, the voltammogram of the support, after appropriate scaling, was subtracted from the voltammogram of the catalyst as shown in Fig. 3. The scaling factor was determined by trial and error to produce a difference “Pt” voltammogram (dotted line) that was most representative of the Pt 5d band vacancy and thereby promote ethanol oxidation. \[ \text{Current (A gPt}^{-1}) \]

![Figure 4](image1.png)  
**Figure 4.** First cycle voltammograms (10 mV s⁻¹) of Pt/Ru oxide/C (green (a); 32 μg), 70% Pt/C (black (b); 30 μg), and 30%Pt/S₁C (red (c); 29 μg) electrodes in 1 M H₂SO₄ (aq) containing 0.1 M ethanol. Dotted lines show the reverse (cathodic) scan.

![Figure 5](image2.png)  
**Figure 5.** Linear sweep voltammograms (10 mV s⁻¹) of 30%Pt/S₁C (——; 29 μg), 25%Pt/S₁10,30 (---; 32 μg), 25%Pt/S₄water (----; 30 μg), 25%Pt/S₂M (-----; 33 μg), and 70% Pt/C (……; 30 μg) electrodes in 1 M H₂SO₄ (aq) containing 0.1 M ethanol.

dation under alkaline conditions. The work reported here is focused on the use of mixed Ru-Sn oxide layers, rather than Ru oxide alone, since they provide higher electrochemical activities at low potentials. However, the results in Fig. 4 show that Pt/Ru oxide/C catalysts should also be considered for DEFCs.

It should be noted that the voltammograms shown in Fig. 4 are all for the first cycle. In all cases, currents prior to the 0.64 V peak were lower on the 2nd and subsequent forward scans. This has been previously documented and discussed for Pt nanoparticles on bare and oxide modified glassy carbon electrodes. It has been attributed to the oxidation of pre-adsorbed species during the 1st scan and instability of the oxide layers at high potentials. Since the effects of pre-adsorbed species should be similar for each catalyst, but stability is not, it is most instructive to compare the 1st scans. Chronoamperometry at lower potentials has shown that the stability of the oxides is good over the potential range that would be encountered in a DEFC, and this was confirmed by the experiments in PEM cells reported below.

The reverse scans in the voltammograms in Fig. 4 are all quite similar (the higher peak at ca. 0.5 V for the Pt/Ru oxide/C catalyst is not significant based on the variability between electrodes prepared with the same catalyst). The peak is due to the oxidation of ethanol at the clean Pt surface that is formed when the oxide layer is reduced at ca. 0.5 V on the reverse scan (see the difference CV in Fig. 3). The similarity of the reverse scan between the three catalysts therefore shows that the Pt nanoparticles are similar, and that the differences seen in the forward scan are due to differences in poisoning by adsorbed intermediates such as CO.

![Figure 5](image2.png)

**Figure 5.** Linear sweep voltammograms (10 mV s⁻¹) of 30%Pt/S₁C (——; 29 μg), 25%Pt/S₁10,30 (---; 32 μg), 25%Pt/S₄water (----; 30 μg), 25%Pt/S₂M (-----; 33 μg), and 70% Pt/C (……; 30 μg) electrodes in 1 M H₂SO₄ (aq) containing 0.1 M ethanol.

Incorporation of Sn into the Ru oxide layer (curve c in Fig. 4) resulted in a large additional enhancement of the ethanol oxidation current at low potentials (0.1 to 0.4 V), and this has been attributed to an enhanced electronic effect of the oxide on the Pt nanoparticles. Electronic effects between metal nanoparticles and metal oxides have recently been reviewed, and it has been shown that a SnO₂ support can increase the Pt 5d band vacancy and thereby promote ethanol oxidation under alkaline conditions. The work reported here is focused on the use of mixed Ru-Sn oxide layers, rather than Ru oxide alone, since they provide higher electrochemical activities at low potentials. However, the results in Fig. 4 show that Pt/Ru oxide/C catalysts should also be considered for DEFCs.

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Ethanol electrolysis in a multi-anode PEM cell at 80 °C.—Although cyclic voltammetry of ethanol in H₂SO₄(aq) at ambient temperature is useful for initial screening of catalysts, the results are not necessarily indicative of the performance that will be achieved in a DEFC. In order to investigate the correlation, selected Pt/Ru-Sn oxide/C catalysts were evaluated in a nine-anode PEM cell at 80 °C. The cell was operated as an electrolysis cell to avoid interference from oxygen, and in cross-over mode to compare activities under controlled mass transport conditions. Thus, 0.1 M ethanol in water was supplied to the cathode and N₂ was passed through the anode flow field. Ethanol diffusing through the Nafion membrane was oxidized at the anode, while protons were reduced at the cathode to create a dynamic hydrogen pseudo-reference electrode (DHE). Evaluation of catalysts in this way allows the anode potential to be controlled much more accurately than in a DEFC, and the mass transport control provided by diffusion of ethanol through the membrane allows the number of electrons transferred (nₑ) to be estimated.

Fig. 6 shows polarization curves for ethanol oxidation at 25%Pt/S₁₁₀, 70%Pt/S₁₁₀, and 70% Pt/C anodes in a nine-anode PEM electrolysis cell. Three electrodes prepared with each catalyst were used, in order to statistically assess the differences between the catalysts. It can be seen that the onset of ethanol oxidation occurred at a significantly lower potential (ca. 0.15 V) for both Pt/Ru-Sn oxide/C catalysts relative to the commercial Pt/C catalyst (ca. 0.3 V), while the Pt/C catalyst provided higher currents at high potentials. The currents at the two Pt/Ru-Sn oxide/C anodes were not statistically different (t test at 95% confidence) at any potential, but the differences relative to the Pt/C anode were significant at 0.35 V, 0.4 V, and potentials above 0.5 V.

The lower onset of ethanol oxidation at the Pt/Ru-Sn oxide/C catalysts and higher currents at up to 0.45 V are consistent with the voltammetric results in Figs. 4 and 5. This demonstrates that voltammetric screening provides a useful indication of fuel cell performance for these catalysts. It also shows that the catalysts have significant durability (>3 h of operation) under DEFC conditions. The lower currents at the Pt/Ru-Sn oxide/C anodes at potentials above 0.5 V indicate that the stoichiometry (nₑ) was lower than at the Pt/C anodes. The current for Pt/C in this region is limited by diffusion of ethanol though the cathode and membrane, and so is proportional to nₑ. The decrease in this mass transport limited current with increasing potential has been shown to be due to a decreasing nₑ. A similar trend is seen for the Pt/Ru-Sn oxide/C anodes.

Polarization curves for several other Pt/Ru-Sn oxide/C catalysts are shown in Fig. 7. The 30%Pt/SLC catalyst stands out here as the best, particularly over the 0.2 to 0.4 V potential range that is most relevant to DEFCs. Over this range it is statistically superior (95% confidence t test) to all of the other catalyst that were tested. This is consistent with the voltammetric results in Fig. 5, although the superiority is more pronounced in the PEM cell. The average current at the 30%Pt/SLC anodes was statistically higher than at the Pt/C anodes up to 0.45 V, but statistically lower at potentials above 0.5 V. This again indicates that nₑ was lower than at the Pt/C anodes.

Ethanol electrolysis and product analysis in a PEM cell at 80 °C.—Full evaluation of catalysts for ethanol oxidation requires measurement of the product distribution, in order to determine their faradaic efficiency and the amounts of acetaldehyde and acetic acid by-products. To do this accurately, the area of the anode needs to be relatively large. Fig. 8 shows polarization curves for ethanol electrolysis at 30%Pt/SLC and Pt/C anodes in a 5 cm² PEM cell, together with data for a commercial 75% PtRu/C catalyst (HiSPEC 12100 from Alfa

Figure 6. Polarization curves for ethanol oxidation (0.1 M) at 25%Pt/S₁₁₀, 70%Pt/S₁₁₀, and 70% Pt/C anodes in a nine-anode PEM electrolysis cell at 80 °C. Averages and standard deviations are shown for 3 electrodes of each type.

Figure 7. Polarization curves for ethanol oxidation (0.1 M) at 25%Pt/S₁₁₀, 70%Pt/S₁₁₀, 30%Pt/SLC, 25%Pt/S₅₇mM, and 70% Pt/C anodes in a nine-anode PEM electrolysis cell at 80 °C. Averages, and selected standard deviations, are shown for 2 or 3 electrodes of each type.

Figure 8. Polarization curves for ethanol oxidation (0.1 M at 0.5 mL min⁻¹) at 30%Pt/SLC, 70% Pt/C anodes, and 75% PtRu/C in a 5 cm² PEM electrolysis cell at 80 °C.
with monitoring the CO2 in the combined anode and cathode exhausts, low potential performance over Pt/C. In addition, there is much scope both intermediate between the values for Pt/C and PtRu/C. Thus the performance of the 30%Pt/SLC anode was comparable to that of PtRu/C and 0.50 V and that currents were similar a higher potentials. The enhancement in low potential performance for 30%Pt/SLC is similar to that previously reported for a 30%Pt/S110-30 anode in a DEFC.23 The performance of the 30%Pt/SLC anode was comparable to that of PtRu/C at low potentials and superior at potentials above 0.35 V.

Table II reports the results of product analysis experiments at 0.45 and 0.50 V, together with data for a PtRu/C anode25 that was obtained under the same conditions. The cell was operated at constant potential with monitoring the CO2 in the combined anode and cathode exhausts, and collection of liquids in a cold trap. The average current during product collection is reported together with the chemical yields of each product. As observed in the polarization curves (Fig. 8), the current at 0.45 V in these longer timescale (ca. 50 min at each potential) experiments was higher at 30%Pt/SLC than at Pt/C, while the current at 0.5 V was higher at Pt/C. The sustained high currents observed for the 30%Pt/SLC catalyst in these experiments indicate that it has high stability at 80 °C under DEFC conditions (>15 h of operation over a 10 day period).

The product distributions show that the yield of CO2 was lower at the 30%Pt/SLC anode than for Pt/C, while the acetic acid yield was much higher. The 30%Pt/SLC anode produced much less acetaldehyde and so would decrease harmful emissions from a DEFC.4 From an efficiency perspective, the low CO2 yields for the 30%Pt/SLC catalyst are partially offset by the higher acetic acid to acetaldehyde ratio. Stoichiometries (nν) and faradaic efficiencies (εν) calculated from the product distributions25 are included in Table II. It can be seen that nν, and consequently εν, for the 30%Pt/SLC catalyst were both intermediate between the values for Pt/C and PtRu/C. Thus the increased electrochemical performance of 30%Pt/SLC over Pt/C comes at a lower trade-off in faradaic efficiency than for PtRu/C.

Overall, the 30%Pt/SLC catalyst represents a significant advance in the development of catalysts for DEFCs, with an increase in efficiency over a commercial high performance PtRu/C catalyst, and increase in low potential performance over Pt/C. In addition, there is much scope for improvement by further optimizing the composition and synthesis method for the Ru-Sn oxide/C, and the Pt deposition method. In particular, alloying of the Pt nanoparticles with Rh13 and/or Nt11 would be expected to increase the efficiency for breaking the C-C bond of ethanol.

Conclusions

The compositions, loadings, and properties of mixed Ru + Sn oxide layers on carbon black, deposited from solutions of K2RuO4 and SnCl4, can be varied by changing the concentration of KOH added. This consequently changes the activities for ethanol oxidation of PtRu-Sn oxide/C catalysts prepared using these supports. Similar differences in electrocatalytic activities have been observed in both a liquid electrolyte cell at ambient temperature and polymer electrolyte electrolysis cells at 80 °C. Cyclic voltammetry showed that the increased low potential activities of PtRu-Sn oxide/C over Pt/C were due to the presence of both Ru and Sn in the oxide support layer, with the highest activity corresponding to the highest Ru loading and a Ru:Sn atomic ratio of 12. The superiority of this catalyst was more pronounced in a PEM cell at 80 °C, where the onset potential for ethanol oxidation was >100 mV lower than at Pt/C and the current at 0.25 V vs. DHE was four time higher. These improvements in activity come at the cost of decreased selectivity for the complete oxidation of ethanol to CO2, although the best Pt/Ru-Sn oxide/C catalyst gave much higher CO2 yields than PtRu/C. Overall, it can be concluded that Pt/Ru-Sn oxide/C catalysts are potentially better than both Pt/C and PtRu/C for use in direct ethanol fuel cells and ethanol electrolysis cells.

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Table II. Chemical yields of products, stoichiometries, and faradaic efficiencies for ethanol oxidation (0.1 M at 0.2 mL min-1) at 30%Pt/SLC, 70%Pt/C, and 75%PtRu/C25 anodes in a 5 cm2 PEM electrolysis cell at 80 °C.

| cell potential/V | anode catalyst | current/mA | CO2 | acetic acid | acetaldehyde | nν | εν |
|------------------|---------------|------------|-----|-------------|-------------|----|----|
| 0.45             | 70%Pt/C       | 78         | 37.6% | 48.2% | 14.1% | 6.7 | 56% |
| 0.45             | 30%Pt/SLC     | 95         | 13.5% | 82.5% | 2.9% | 5.3 | 44% |
| 0.45             | 75%PtRu/C     | 107        | 7.0%  | 84.1% | 8.9% | 4.5 | 38% |
| 0.50             | 70%Pt/C       | 116        | 50.2% | 46.4% | 3.5% | 7.9 | 66% |
| 0.50             | 30%Pt/SLC     | 110        | 15.6% | 84.7% | 1.7% | 5.0 | 42% |
| 0.50             | 75%PtRu/C     | 117        | 6.9%  | 92.4% | 0.8% | 4.5 | 38% |

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