

Characterization and Analysis of New Catalysts for a Direct Ethanol Fuel Cell[†]

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A direct ethanol fuel cell offers an attractive, fairly high density, energy source, if an electrochemical system can be developed that efficiently carries out the 12-electron oxidation of ethanol to carbon dioxide and water. To that end, new catalyst systems must be developed along with fuel cell operating conditions that encourage the complete oxidation of ethanol, as opposed to the presently available platinum on carbon systems that tend to produce acetaldehyde (two-electron oxidation) or acetic acid (four-electron oxidation) products. It is found that a composite nanoparticulate catalyst containing platinum and tin oxide or platinum indium tin oxide allows the partial conversion of ethanol to its 12-electron oxidation products. Catalysts of this type can be formed using a modified polyol process. Elevation of the operating temperature of a proton exchange membrane fuel cell using the indicated catalysts to 130 °C facilitates the production of carbon dioxide and provides an improved current–voltage response.

Introduction

The direct 12-electron oxidation of ethanol to carbon dioxide and water in a fuel cell reactor offers a potentially attractive energy resource. In contrast to the much studied hydrogen–oxygen fuel cell, ethanol provides a volumetric energy density that approaches that of gasoline (21 MJ L⁻¹ for ethanol vs 31 MJ L⁻¹ for gasoline). As a liquid fuel, ethanol also avoids issues of storage associated with proposed hydrogen systems. Assuming that ethanol is bioderived, this material is considered to be carbon neutral. The direct ethanol fuel cell's (DEFC) primary disadvantage is the lack of a catalyst that can initiate complete oxidation at a high rate. In the absence of an electrocatalytic system that can efficiently deliver 12 electrons per ethanol molecule, the optimistic picture suggested above vanishes.

The electrochemical oxidation of ethanol is a difficult task because of the substantial increase in the number of reaction intermediates associated with this 12-electron process. More troublesome is the presence of the C–C bond, which is between two atoms with little electron affinity or ionization energy, thus making it difficult to access electrochemically.

Efforts to electro-oxidize ethanol in solution have been under investigation for nearly a century; however, serious ambiguity still exists about the mechanism. The exact onset potential of ethanol oxidation on a platinum surface is highly dependent on several factors,¹ primarily the configuration of the adsorbed ethanolic species.

There is a long list of catalysts that have demonstrated the ability to electrochemically oxidize small alcohols. Monocrystalline platinum is an obvious first choice for the oxidation of interest, and has been demonstrated by, among others, Morin.² All three low-index faces are shown to oxidize ethanol, but only up to acetaldehyde.³ The [111] and [110] planes demonstrate

more catalytic activity and more susceptibility to surface poisoning than polycrystalline platinum, which, in turn, out-performs the [100] face. More complete ethanol oxidation has been accomplished with binary alloys and intermetallics of platinum.⁴

The present study in part aims to demonstrate that the extent and rate of ethanol oxidation in a fuel cell environment can be substantially controlled by regulation of the cell temperature, along with catalyst composition. The initial elevated temperature studies of a DEFC performed by Arico⁵ showed improved performance, but there has been no work since then at these temperatures. That preliminary study showed reaction selectivity toward CO₂ at 145 °C. A recent review⁶ lists no other studies probing elevated temperature operation for DEFCs.

Catalytic systems under current investigation generally involve alloys or intermetallic compounds composed of platinum and a post-transition metal (Sn, Bi, or Pb). Typically, these materials have been evaluated at or near room temperature (and often in a classical electrochemical cell environment). The most prevalent systems involve Pt–Sn compositions. These materials have not been demonstrated to efficiently promote the 12-electron oxidation of ethanol to carbon dioxide. Additionally, little thought has been given to whether these materials maintain their initial stoichiometry, composition, or structure when formulated as a nanoparticulate supported catalyst and maintained in an active fuel cell environment. For example, the standard redox potential for the Sn/Sn²⁺ couple is –0.13 V versus SHE, and the redox potential for Sn²⁺/Sn⁴⁺ is +0.15 V versus SHE. Given that a direct ethanol anode operates at an open circuit potential of ~1.14 V versus SHE (see Table 1), it is likely that a tin containing catalyst system would convert to SnO₂ under the operational conditions of a DEFC. Thus, the active catalyst in a Pt/Sn system is reasonably envisioned as some type of Pt–SnO₂ composite, as suggested by Sun, who has recently proposed that the ethanol catalyst of interest is a supported Pt on tin oxide species.⁷ Thus, this study aims to better identify the necessary structure of the

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Table 1. Calculated Reaction Potentials of Partial Ethanol Oxidation, Assuming Products Desorb from the Surface

	stable desorbed products					
	H ₂ O + CH ₃ CHO	H ₂ O + CH ₃ COOH	H ₂ O + CO ₂ + CH ₃ OH	2H ₂ O + CO ₂ + CH ₂ O	2H ₂ O + CO ₂ + HCOOH	3H ₂ O + 2CO ₂
ΔG° (kJ)	-191	-413	-622	-803	-1044	-1324
n	2	4	6	8	10	12
E° (V)	0.99	1.07	1.07	1.04	1.08	1.14

catalyst and to solidify the importance of the metal oxide phase for the catalysis of ethanol.

To that end, the synthetic method of Sun⁷ is used to produce platinum on metal oxides. These particles have been incorporated as catalysts in an active DEFC and evaluated both electrochemically and in terms of oxidation product distribution.

Experimental Section

Membranes. Nafion 117 (Ion Power, Inc.) was cut into rectangles of approximately 3 × 4 cm. The membranes, up to 15 at a time, were boiled in successive solutions of 3% hydrogen peroxide, water, and 0.5 M sulfuric acid, and then in two baths of water. The hydrogen peroxide was used to oxidize any residual organic moieties retained from the fabrication process. This step changed the appearance of the membrane from slightly brown to uncolored. The first water bath served to expunge any remaining hydrogen peroxide. The sulfuric acid bath was used to ensure the sulfonate groups were completely protonated. Any metallic residues would be removed in this step, too. The final two water baths were performed to wash away excess sulfuric acid. The membranes were then stored in deionized water until needed.

Catalyst Formation: The Polyol Process. Stannous chloride in ethylene glycol (6–10 mM) and enough 10 M aqueous sodium hydroxide to bring the NaOH concentration to approximately 0.2 M were heated in a sand bath to 150° C with constant stirring until the solution became slightly yellow and cloudy. The solution was then allowed to cool to room temperature, at which point enough 0.2 M aqueous Na₂PtCl₆ was added to bring the platinum concentration to 3 times the tin concentration. This solution was slowly brought to 130° C, causing it to turn black. The reaction mixture was maintained at this temperature for 2 h after the color change occurred. Separately, XC-72 carbon black (Cabot Corp.) was suspended in water via sonication. The mass of carbon was 4 times the mass of platinum metal. With vigorous stirring, the platinum solution was slowly added to the carbon mixture; stirring was continued for 2 h afterward. The suspension was allowed to settle, the clear colorless supernatant was decanted, and fresh water was added. This was repeated four times. The black solid remaining after the fourth washing was centrifuged, and the supernatant was discarded. The solids were dried in air at 150° C for a day and then stored.

Ternary catalysts were made with nearly an identical preparation. At the first step, along with stannous chloride, a similar amount of indium (III) chloride (for example) was added. The amount of platinum in the next step was then 3 times the sum of the tin and indium concentrations.

Electrodes. LT-140 electrodes (Pt on carbon) were purchased from ETEK and used as fuel cell cathodes. The catalyst loading was 0.5 mg cm⁻². Anodes were prepared in house from a range of catalysts. Catalytic ink was suspended by sonication in reagent grade 2-propanol. The suspension was then sprayed using an artist's air brush onto the gas diffusion side of an A-6 ELAT single-sided electrode (ETEK). On top of this catalytic layer was sprayed a layer of solubilized Nafion (Ion Power, Inc.). Catalytic loadings of approximately 0.6 mg cm⁻² of platinum were achieved.

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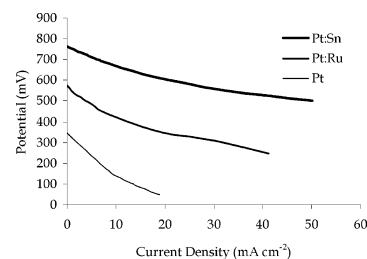


Figure 1. Steady-state polarization curves for three different MEAs thermostated at 120 °C based on different commercial catalysts supplied as pure. The Pt/Sn catalyst is composed of a 3:1 intermetallic compound, and the Pt/Ru catalyst is a 1:1 alloy. All catalysts were used at a loading of ~0.6 mg cm⁻². One molar aqueous ethanol flows through the anode compartment at a rate of 1 mL min⁻¹. An excess of oxygen was utilized at the cathode.

Membrane Electrode Assemblies (MEAs). A gasket (LGS Technologies, 3016), an anode, a membrane, a cathode, and a second gasket were assembled between two sheets of Teflon. The sandwich was heated from room temperature to 140 °C at approximately 8° min⁻¹. The assembly was then pressed at 245 psi for 60 s, after which it was allowed to quickly cool to room temperature under reduced pressure (2 psi).

Testing. Five square centimeter cells were assembled and interfaced to a modified Globe Tech test station. Liquid fuel flow through the anode chamber was achieved by a Waters M-45 solvent delivery system. One molar aqueous ethanol flowed over the anode at approximately 1 mL min⁻¹, and dry oxygen flowed through the cathode at approximately 100 mL min⁻¹.

Other Instrumentation. Product analysis was performed by extracting anode effluent immediately downstream from the cell and injecting it into a Hewlett-Packard 5890 gas chromatograph (GC) with a DB-WAX column (J&W Scientific). X-ray powder diffraction (XRD) was accomplished with Cu K_α radiation and a diffracted beam monochromator on a D8-Focus by Bruker. Atomic compositions were acquired with a Perkin-Elmer continuous double view inductively coupled plasma optical emission spectrometer (ICP). Transmission electron microscope (TEM) images and energy-dispersed X-ray (EDX) spectra of nanoparticles were acquired using a Philips CM200 field-emission TEM equipped with a PGT-IMIX EDX system operated at 200 keV.

Results and Discussion

Catalyst Characterization Analysis. Initially, existing commercial catalysts were used in the anode of a DEFC (Figure 1). The standard Pt catalyst for H₂/O₂ proton exchange membrane (PEM) cells yields an extreme overpotential for ethanol oxidation, which both brings the open circuit voltage down under 0.4 V and prevents the cell from generating current densities in excess of a few tens of milliamperes per square centimeter. The preferred DMFC catalyst, PtRu, does significantly better, but can only claim an open circuit potential (~500 mV) of half the theoretical potential. Pt₃Sn is, again, a significant improvement over PtRu, with an open circuit voltage near 0.8 V. Since the platinum/tin intermetallic produces the best response of available commercial catalysts, it is the foundation from which new catalysts were built.

In an effort to improve upon Pt₃Sn and Sun's previously reported platinum–tin oxide catalysts,⁷ ternary catalysts were made by selecting metals that, like tin, have multiple oxidation states near 0 V (In, Mo, V), or metals with previously demonstrated catalytic abilities toward small organics (Eu, La, Nb). Two catalysts were characterized in some detail: platinum–tin oxide (PtSnO) and platinum–tin–indium oxide (PtSnInO). These catalysts were designed to be close to 20 wt % platinum during the synthesis, and the weight percent of each was confirmed to

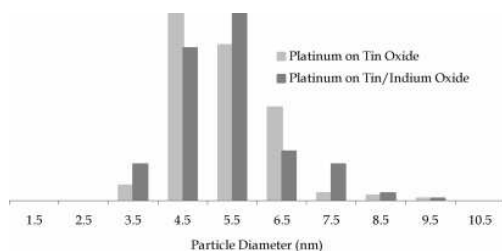


Figure 2. Particle size distributions for the two catalysts identified in this work. Each distribution included over 150 particles and was accomplished by measuring particle dimensions on TEM micrographs.

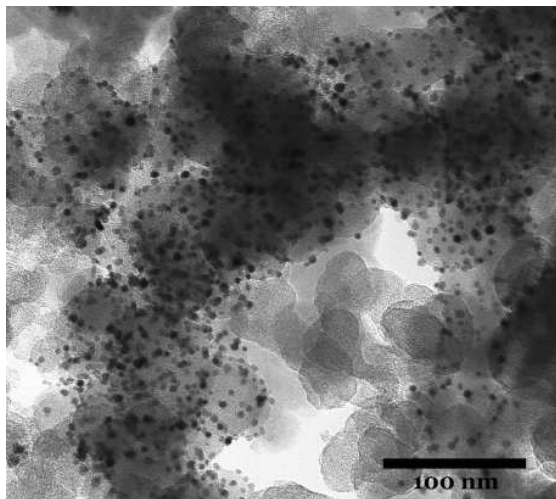


Figure 3. A TEM micrograph of the carbon-supported PtSnInO catalyst. The lighter regions are composed of XC-72 carbon. The dark spots are mainly composed of platinum.

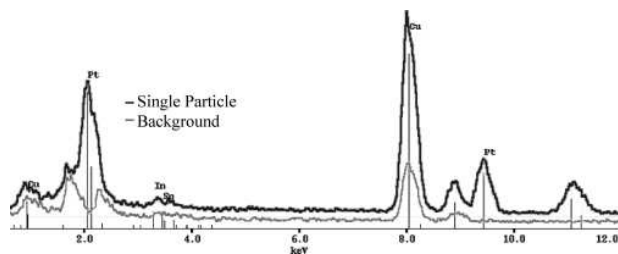


Figure 4. Single-particle and background EDX of the PtSnInO catalyst on a copper TEM grid. Platinum has strong signals at 2.0, 9.4, and 11.3 keV, indium has one signal at 3.3 keV, and tin has a signal at 3.5 keV. The unlabeled peaks near 2 keV are silicon.

be $21 \pm 2\%$ by ICP. The tin composition was found to be $2.5 \pm 1.2\%$ in PtSnO, while in PtSnInO it was $1.0 \pm 0.2\%$; the indium had an identical loading ($1.0 \pm 0.2\%$).

Particle size distribution of the catalysts yielded a narrow range with an average particle size of 5.3 nm, as shown in Figure 2. The catalytic particles were fairly uniformly distributed on the carbon support, as can be seen in a representative image (Figure 3).

The relative locations of the platinum, tin, and indium on the carbon support were determined by single-particle TEM–EDX (Figure 4). When the electron beam was masked so that it struck only a single 5 nm PtSnInO catalyst particle, the energy spectrum showed that it contained platinum, tin, and indium. There were no signals for these metals when a spectrum was taken of an area with only the carbon support. Analysis of high-resolution TEM images, however, showed only lattice fringes corresponding to

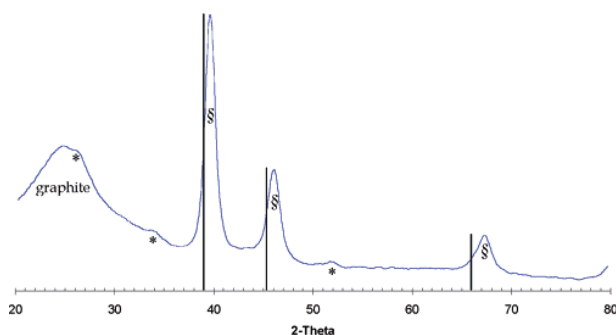


Figure 5. XRD of the PtSnO catalyst on a carbon support. Asterisks (*) mark the tetragonal tin oxide phase, (110, 011, and 211 reflections, left to right); § indicates the cubic platinum phase (111, 200, and 220 reflections, left to right); vertical lines show the position of the first platinum–tin intermetallic (Pt_3Sn) reflections.

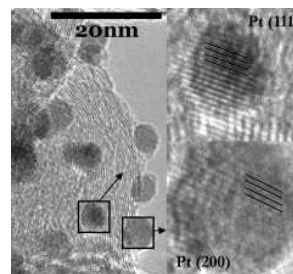


Figure 6. High-resolution TEM showing individual 5 nm catalyst particles on the carbon supports. Lattice spacings for both the carbon and the catalyst are observed. The lattice spacings of the catalyst particles (2.26 and 1.96 Å) identify these sites as primarily platinum with exposed [111] and [200] planes.

platinum (Figure 5). This is in contrast to the work done by Sun, in which fringes were also seen for tin oxide, and the lattice constant for the platinum was dilated. This lack of fringes resulting from tin is the combined result of there being far less tin than that in Sun's catalysts, and that the tin is distributed in particles too small to generate fringe lines in this instrumentation.

The catalysts were also analyzed by XRD (Figure 6). The reflections from the cubic phase indicative of platinum occur unshifted from those of pure platinum in all of the samples. Thus, platinum alloy formation is ruled out. The cubic Pt_3Sn intermetallic, which has previously been suggested as the catalytic element, has a noticeably enlarged unit cell from platinum in all three directions; the lack of such a shift in the 2θ plot indicates that this phase is not present. Additionally, the PtSnO pattern exhibits weak reflections for tin oxide. As indicated by the EDX data, these tin oxide crystals must be part of the same 5 nm particles as the platinum crystals. By extension, since platinum particles alone have only limited catalytic activity toward ethanol, it must be the interaction between the platinum and the tin oxide that provides the enhanced activity.

The PtSnO and PtSnInO catalysts we report here compare well against Sun's catalyst and the commercial Pt_3Sn catalyst. The polarization curve of a commercial Pt_3Sn (3:1) intermetallic catalyst is very similar to that of PtSnInO (18:1:1, metal ratio) (Figure 7). The exact role of the tin in the surface-bound catalysis of ethanol is not clear, but the electronic change induced by expanding the lattice parameters of platinum (from 3.92 to 4.00 Å) is unimportant, as catalysts are successful without the change. The small amount of tin that is present in the predominantly platinum crystalline particles must therefore be impacting the mechanism of the oxidation. Subsequently, the tin must be present at the surface of the platinum particles where ethanol can access

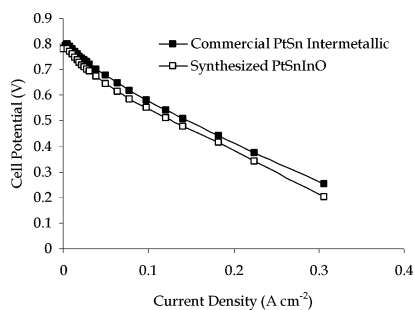


Figure 7. Polarization curves generated by a commercial PtSn (3:1) catalyst (■) and a PtSn(oxide)In(oxide) (18:1:1) catalyst (□) both operating at 130°C.

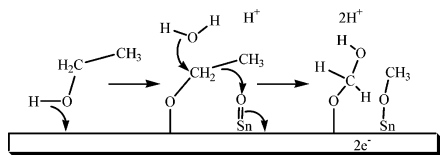


Figure 8. This is a proposed mechanism in which the electron affinity of tin oxide on a platinum surface is sufficient to pull the methyl group off the α -carbon of a surface-bound ethanol.

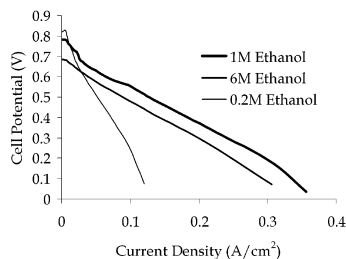


Figure 9. Polarization curves using a PtSnInO electrocatalyst at 130°C as a function of ethanol concentration.

the successful platinum/tin oxide catalytic sites. Because the expanded lattice of the successfully performing Pt_3Sn intermetallic catalyst has been shown to be inconsequential, this catalyst must employ the same kind of surface chemistry that makes the PtSnO catalyst successful. The critical part of the commercial intermetallic must be oxidized tin atoms at the surface of the catalytic particles.

Partial oxidation of ethanol will certainly occur at unadulterated pure platinum sites, and acetaldehyde (primarily) and acetic acid are products that will result from those reactions.⁸ A proposed first step in the complete oxidation of ethanol must include the platinum with the tin oxide phase. It can be shown (Figure 8) that if the carbon-carbon bond of ethanol is weakened as a result of the oxygen being bound to the platinum surface,⁸ a tin oxide moiety on the platinum surface may possess enough electron affinity to pull the methyl group off the α -carbon of the ethanol, whereas the platinum surface can only pull the hydrogens during a nucleophilic attack by free water. This mechanism is consistent with the observation that more complete oxidations occur on PtSnO than on a pure platinum catalyst or PtRu.

Catalyst Performance Analysis. The efforts of this study focused on catalytic effects and temperature effects. Little effort was expended to reduce poor performance as a result of high ethanol crossover through ethanol-swelled Nafion membranes. All subsequent discussion regards PtSnO and PtSnInO.

A study of the cell performance as a function of ethanol concentration yielded several notable results (Figure 9). Increasing the ethanol concentration from 1 M to 6 M does not affect the rate of the electrochemical reaction. This demonstrates that, at

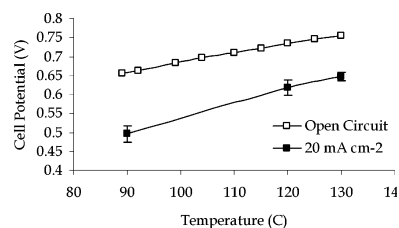


Figure 10. PtSnO-based cell potentials as a function of temperature: (□) open circuit and (■) galvanostated at 20 mA cm^{-2} . In both cases, a much stronger dependence on temperature is observed than can be explained by a simple Nernstian effect.

these concentrations, the oxidation is zeroth order in ethanol. The higher concentration decreases the open circuit voltage by ~ 100 mV, an effect easily ascribed to increased crossover through the alcohol-swelled membrane. Consistent with this conclusion, significant nonelectrochemical oxidation of ethanol is observed, indicating substantial crossover of O_2 into the anode half cell. Increasing the ethanol concentration from 1 M to 6 M approximately doubles the amount of oxidation products formed by O_2 crossover.

Decreasing the concentration from 1 M to 0.2 M improved the open circuit voltage (850 mV), which is consistent with decreased swelling of the membrane. The decreased concentration details other issues as well, though. At higher current densities, it becomes apparent that this low ethanol concentration affects the rate of the reaction. Increased ethanol flow rates were used to separate mass transport effects from suspected kinetic effects. These studies demonstrated that the cells do not experience mass transport losses. While current densities above 300 mA cm^{-2} at 100 mV are typical for cells operating with 1 M ethanol, the cells operating with 0.2 M ethanol only achieved 120–140 mA cm^{-2} , an indication that the reaction order is greater than zeroth order in ethanol when the ethanol concentration is 0.2 M. Since, at 1 M concentration, the reaction kinetics were ethanol-independent, the results reported here all utilize 1 M ethanol.

The open circuit voltage (Figure 10) of a DEFC as a function of temperature demonstrates the benefits of elevated temperature. The open circuit voltage at 130°C can be as high as 830 mV before crossover brings it down to an average of 800 mV. Using the formation energies of stable desorbed molecules to get a handle on reaction potential (Table 1), the reaction must proceed through the complete 12-electron oxidation (eq 1) to achieve an open circuit voltage above 0.8 V. This is assuming a 200 mV activation overpotential for the oxygen reduction reaction⁹ and an anodic overpotential of at least 130 mV.¹⁰



A pure Nernstian response would only provide ~ 0.5 mV/10°C increase in cell temperature. Since there is an observed increase in cell potential (approximately 25 mV for each 10°C increase), it is concluded that elevated temperature leads to more complete oxidation.

This effect is still obvious on cells that are pulling a load. The data in Figure 10 represents the average of results from nine

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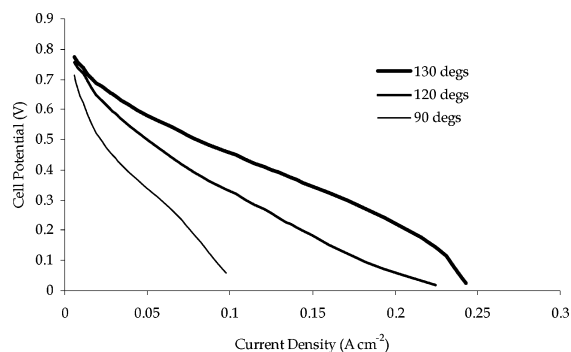


Figure 11. Steady-state polarization curves (2 s per point) using a PtSnInO-based MEA as a function of temperature. One molar ethanol is used.

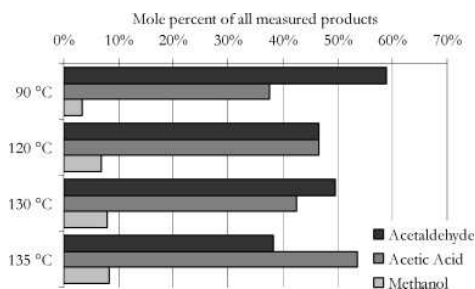


Figure 12. PtSnInO cell products as a function of temperature.

separate cells. In this experiment, the cells were galvanostated at 20 mA cm^{-2} , and cell voltage was recorded as a function of cell temperature. Figure 11 demonstrates that more complete oxidation is evident at all potentials. The polarization curves exhibit higher current densities for each increase in temperature.

Product analysis of the anode effluent reveals that the extent of reaction is indeed a function of temperature. Carbon dioxide, methanol, acetic acid, and acetaldehyde were all observed by GC analysis of the spent fuel. While the latter three species gave very reliable GC data, CO_2 results fluctuated as a result of atmospheric contamination. Results are summarized in Figure 12. At higher temperatures, the cell products in more oxidized states represent larger mole fractions of the total product distribution than they do at low temperatures. The mole fractions of acetic acid and particularly methanol climb as the temperature climbs, while the mole fraction of acetaldehyde drops. This shift toward more oxidized products at higher temperatures is the reason the potential is higher at higher temperatures, as well as the current.

Among the ternary catalysts generated for this study using the polyol method, the performance of only one was superior to that of the binary platinum–tin system. PtSnInO was able to generate current densities nearly 40% greater than those of PtSnO (Figure

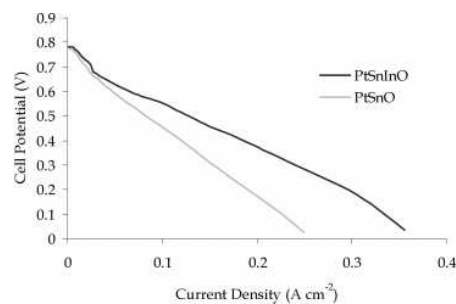


Figure 13. Polarization curves of a DEFC at 130°C for PtSnO compared to PtSnInO.

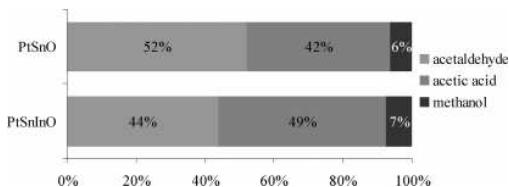


Figure 14. Anode product analysis of DEFCs operating at 130°C using PtSnO and PtSnInO.

13) at a cell temperature of 130°C , and the product analysis showed a significant shift toward higher oxidized products for the indium-containing catalyst (Figure 14). As discussed previously, this effect must come as a result of mechanistic routes made available as a result of configurations at the surfaces of the catalytic particles. The addition of indium to the platinum–tin oxide system must increase the ability of the surface to extract both hydrogen and methyl groups from ethanol's α -carbon, as depicted in Figure 8.

Conclusions

Temperatures elevated to above 130°C enable the complete 12-electron oxidation of ethanol on PtSnO and PtSnInO catalysts. The platinum–tin intermetallic (Pt_3Sn) is not a necessary catalytic phase for this reaction. The catalysis is performed equally well by pure platinum integrated with tin oxide. The amount of tin required to make the platinum properly catalytic is also far below reported values. Instead of requiring 25%, as little as 5% tin is sufficient to enable mechanisms yielding more completely oxidized products. These mechanisms are further favored by the addition of indium to the platinum–tin catalyst. The polyol process is a simple and adaptable synthetic method that can be used to build catalysts with very tunable characteristics.

Acknowledgment. We thank H. Ota for help obtaining the GC data presented here and for discussions related to the mechanism of alcohol oxidation.

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