

Comparison of Ethanol and Methanol Oxidation in a Liquid-Feed Solid Polymer Electrolyte Fuel Cell at High Temperature

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The electrochemical oxidation of ethanol and methanol in a liquid-feed solid polymer electrolyte fuel cell operating at 145°C was investigated. A composite membrane made of Nafion ionomer and silica was fabricated in order to maintain the advantageous water-retention properties of these materials at high temperature. A pressurized cell (4 atm, anode; 5.5 atm, cathode) employing carbon-supported Pt-Ru (1:1) and Pt catalysts with a Pt loading of 2 mg cm⁻² was investigated. The direct methanol fuel cell showed a peak power density of about 240 mW cm⁻² at 0.6 A cm⁻² and 0.4 V. The power density approached 450 mW cm⁻² in the internal resistance-free polarization curve, and the methanol crossover rate was about 4 × 10⁻⁶ mol min⁻¹ cm⁻². The direct ethanol fuel cell showed a maximum power density of about 110 mW cm⁻² at 0.32 V and 0.35 A cm⁻² with high selectivity toward CO₂ formation (≈95%).

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Liquid-feed solid polymer electrolyte fuel cells offer a promising alternative to hydrogen-consuming devices for traction applications because they allow easy handling and storing of the liquid fuel.¹⁻³ The main prerequisite of a liquid fuel for a solid polymer electrolyte fuel cell is a high electrochemical reactivity at relatively low temperatures. Furthermore, the fuel should be reasonably inexpensive, nontoxic, and largely available. At present, only methanol is actively investigated as a possible alternative to hydrogen in low-temperature fuel cells. Yet, in order to extend the practical applications of low-temperature fuel cells and to facilitate their penetration into the transport market it is desirable to increase the number of liquid fuels which can be employed in these systems. Among the possible candidates, ethanol appears to fulfill many of the above requirements. In particular, it can be obtained from renewable energy sources, e.g., through fermentation of agricultural products and from biomasses. Although the oxidation of ethanol to carbon dioxide requires the cleavage of the C-C bond, previous studies have shown that the electrochemical reactivity of ethanol on Pt-based catalysts is not significantly lower than methanol.⁴⁻⁶ It was observed that the main adsorbed species in the electrochemical oxidation of ethanol was linearly adsorbed CO, whereas CO₂ and acetaldehyde were the bulk products. A few electrochemical studies have pointed out that formation of acetaldehyde during ethanol electro-oxidation occurs through weakly adsorbed intermediates, whereas CO-like strongly adsorbed species are involved in CO₂ formation.⁷⁻⁹ Recently, Wang et al.¹⁰ have demonstrated that ethanol could be suitably employed in a polymer fuel cell based on phosphoric acid-doped polybenzimidazole electrolyte membrane at 170°C. These authors have also shown that acetaldehyde was the main reaction product (from 65 to 80%) whereas carbon dioxide was the secondary product (from 20 to 32%). This fact determines low electrical energy yield for ethanol oxidation and poses some environmental problems.

At present, perfluorosulfonic-based polymer electrolyte membranes are fairly developed and have been successfully used in H₂/O₂ and methanol/O₂ fuel cells. The main problems connected with these electrolytes are the membrane dehydration when the fuel cell works at high temperatures and the large methanol crossover in liquid-feed systems. The first drawback severely hinders the fuel cell operation at temperatures higher than 100°C which is a prerequisite for the suitable electro-oxidation of small organic molecules involving formation of strongly adsorbed reaction intermediates such as CO-like species.

Recently, Dahr,¹¹ Stonehart,¹² and Watanabe et al.¹³ have made an attempt to reduce the humidification constraints in solid polymer electrolyte fuel cells (SPEFCs) by using modified perfluorosulfonic membranes. A recast Nafion film sandwiched between the two electrodes

was first proposed by Dahr¹¹ for the realization of an internally humidified solid polymer fuel cell. Stonehart¹² suggested the inclusion of small amounts of silica powder into the recast film in order to retain the electrochemically produced water inside the membrane. Watanabe et al.¹³ have tried to exploit the H₂/O₂ crossover through the membrane to produce a chemical recombination to water on small Pt clusters inside the membrane. All of these membranes were operated with H₂/O₂ at 80°C and allowed the development of systems without assisted humidification or with near ambient humidification.

The basic idea of the present work was to use a composite silica recast Nafion membrane, similar to that developed by Stonehart,¹² in a liquid-feed fuel cell operating at a temperature (~150°C) well above that of a H₂/O₂ fuel cell, in order to enhance the kinetics of methanol and ethanol oxidation. In a liquid-feed fuel cell, water is supplied together with the fuel at the anode compartment and is produced at the cathode side during the electrochemical operation. Thus, we have sought advantage from the water-uptake properties of both recast Nafion and silica in order to allow fuel cell operation at 145°C with the oxygen humidifier and fuel conditioner maintained at 85°C. This system allowed us to compare the electrochemical oxidation of methanol and ethanol in the presence of a perfluorosulfonic membrane at suitable temperatures.

Experimental

Membrane.—Composite polymer electrolyte membranes were prepared by using a procedure similar to that developed by Stonehart¹² and Watanabe et al.¹³ for H₂-O₂ solid polymer electrolyte (SPE) fuel cells. An appropriate amount of Nafion ionomer (5% wt/wt, Aldrich) was mixed with 3% wt/wt SiO₂ (Aerosil 200, Degussa) in an ultrasonic bath for 30 min. This solution was cast^{14,15} in a Petri dish and heated at 80°C for 30 min. The recast composite Nafion film was detached from the Petri dish by addition of distilled water and allowed to dry for 15 h at room temperature. Afterward, it was cut to obtain a regular shape and then hot pressed between two polytetrafluoroethylene (PTFE) foils at a few bars and increasing temperatures. The final treatment was 160°C for 10 min. The latter step increased the crystalline fraction inside the composite membrane with consequent improvement of the mechanical properties. The thickness of the dry membrane was 80 μm. The membrane was purified by using the usual procedure.¹⁶ X-ray diffraction analysis revealed an increase of the ratio between the crystalline peak and the amorphous scattering,¹⁵ as well as a shift of the crystalline peak to higher Bragg angles in the composite membrane with respect to Nafion (Fig. 1).

Membrane-electrode (M&E) assembly.—The catalysts for methanol oxidation and oxygen reduction were 40% Pt-20% Ru/Vulcan XC 72 (E-TEK, Inc.) and 20% Pt/Vulcan XC 72 (Electrochem, Inc.), respectively. The physicochemical characteristics of these materials were pre-

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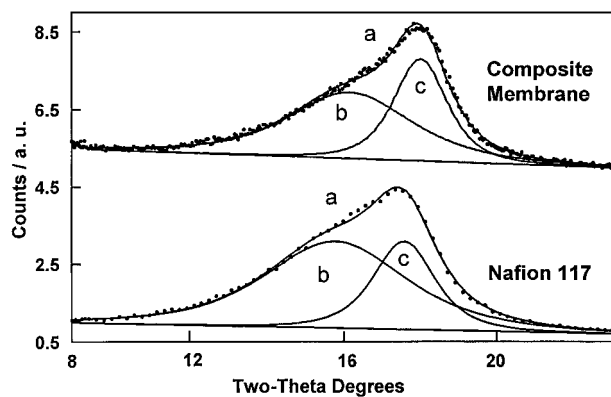


Figure 1. X-ray diffraction profiles for Nafion 117 and composite membrane in the protonic form and dry state. The measured data are shown by dots, whereas curves b (amorphous) and c (crystalline) are the deconvoluted profiles by the least-squares method, and curve a is the convolution of curves b and c.

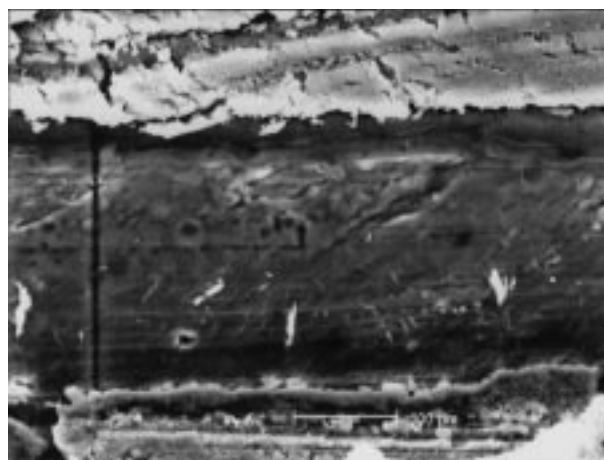


Figure 2. SEM micrograph of a cross section of the M&E assembly region. Anode, bottom; cathode, top.

viously investigated.^{17,18} The reaction layers were prepared by directly mixing a suspension of Nafion ionomer in water with the catalyst powder in an ultrasonic bath; the resulting paste was spread onto carbon cloth backings. The Pt loading was 2 mg cm^{-2} in both electrodes. The M&E assembly was manufactured by pressing the electrodes onto the composite membrane at 130° and 50 atm. A scanning electron micrograph (SEM) of the interface between the composite membrane and the electrodes is shown in Fig. 2. Good adhesion of the catalytic layers to the composite membrane is observed.

Single cell.—The M&E assembly was loaded into a single-cell test fixture (Globe Tech, Inc.) which was connected to an HP 6060B electronic load. Aqueous solutions of methanol or ethanol, as well as humidified oxygen were preheated at 85°C and fed to the cell. The operating temperature of the cell was 145°C . Oxygen humidification at significantly lower temperatures produced thermal gradients which resulted in some fluctuations during the electrochemical polarization. The outlet fluxes from anode and cathode compartments were measured on-line before being condensed in two separate reservoirs. The solutions were analyzed by a Carlo Erba VEGA series 2 GC 6000 chromatograph equipped with CarboPack 3% SP 1500 column and flame ionization detector. An appropriate experiment was devised to analyze the gas compositions at both anode and cathode outlets. The outlet stream composition was chromatographically analyzed by drawing a dried gas sample with a syringe. Water and methanol or ethanol from the stream were removed by a magnesium perchlorate bed while the gas sample was being drawn from a glass sampling bulb provided with a plug-type system. The gaseous products were analyzed with a Hewlett-Packard 5890A gas chromatograph equipped with two columns in series: (i) a 2.5 m Porapak QS 80/100 and (ii) a 2.5 m molecular sieve 5 A kept at 70°C and connected to a thermal conductivity detector (TCD).

Results and Discussion

Polarization experiments in direct methanol and ethanol-fed fuel cells.—A preliminary investigation showed that the optimal conditions for the methanol fuel cell were 2 M methanol concentration, 4.5 atm (abs) methanol back pressure and 5.5 atm (abs) cathode back pressure. Figure 3 shows the steady-state polarization curve of methanol (2 M) oxidation at 145°C . A high open-circuit potential (0.95 V) was recorded, indicating low methanol crossover. A significant potential drop of about 0.23 V was observed when a current density of 60 mA cm^{-2} was passed through the cell. This behavior indicates a strong activation control at low current densities, typical of the methanol-oxidation reaction. However, the potential losses due to the charge-transfer resistance appear to be about 100 mV lower than those measured at 95°C in the same range of current densities.¹⁷ At currents higher than 60 mA cm^{-2} the linear variation of potential vs. current indicates that the electrochemical behavior is mainly affected by the intrinsic ohmic resistance. The slope of

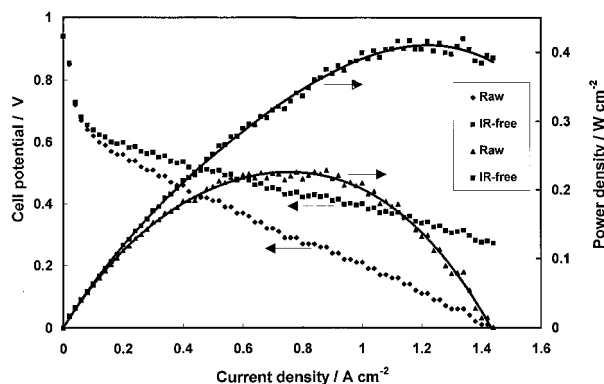


Figure 3. Raw and iR-free polarization and power density data for the direct methanol fuel cell at 145°C ; anode 2 M CH_3OH , 4.5 atm (abs); cathode 5.5 atm (abs) O_2 . Anode Pt-Ru (1:1)/C, 2 mg Pt cm^{-2} ; cathode Pt/C, 2 mg Pt cm^{-2} .

potential vs. current curve in the region from 0.06 to 1 A cm^{-2} is close to the value of uncompensated resistance, i.e., $0.18 \Omega \text{ cm}^2$ as determined by the current interruption method. Mass-transfer polarization becomes significant only at current densities higher than 1 A cm^{-2} , determining the last potential drop. A peak power density of about 240 mW cm^{-2} is obtained in the current range from 0.6 to 0.9 A cm^{-2} . It is observed that a limiting current density close to 1.5 A cm^{-2} is obtained at short-circuit conditions, revealing that mass transfer affects the cell performance only slightly. On the other hand, ohmic drop polarization strongly influences the fuel cell performance as the internal resistance (iR)-free curve shows power densities close to 0.45 W cm^{-2} .

The polarization curve for 1 M ethanol oxidation at 145°C is shown in Fig. 4. Preliminary investigation of the ethanol fuel cell operation showed that suitable conditions were 1 M ethanol, 4 atm (abs) anode back pressure and 5.5 atm (abs) oxygen pressure. The open-circuit voltage in the ethanol fuel cell is 0.82 V, compared to 0.95 V in the methanol cell. The potential losses in the activation-controlled region are more pronounced with respect to the methanol fuel cell (0.35 vs. 0.23 V) but they extend over a wider range of current densities (120 vs. 60 mA cm^{-2}). The ohmic drop is comparable in both systems ($0.18 \Omega \text{ cm}^2$) whereas the mass-transfer polarization appears to be more significant in the ethanol fuel cell, with diffusion limiting current of 0.62 A cm^{-2} . Power densities close to 110 mW cm^{-2} are obtained with ethanol; they are slightly higher (150 mW cm^{-2}) upon correction for the ohmic drop.

Stability, crossover, and product distribution in methanol and ethanol fuel cells.—The stability of both the methanol and ethanol fuel cells were investigated by discontinuous operation. The methanol fuel

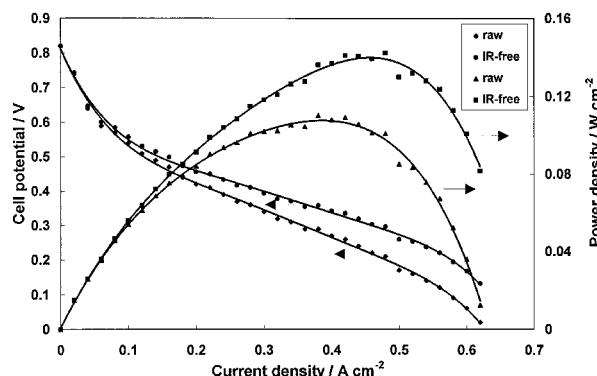


Figure 4. Raw and iR-free polarization and power density data for the direct ethanol fuel cell at 145°C; anode 1 M C₂H₅OH, 4.0 atm (abs); cathode 5.5 atm (abs) O₂. Anode Pt-Ru (1:1)/C, 2 mg Pt cm⁻²; cathode Pt/C, 2 mg Pt cm⁻².

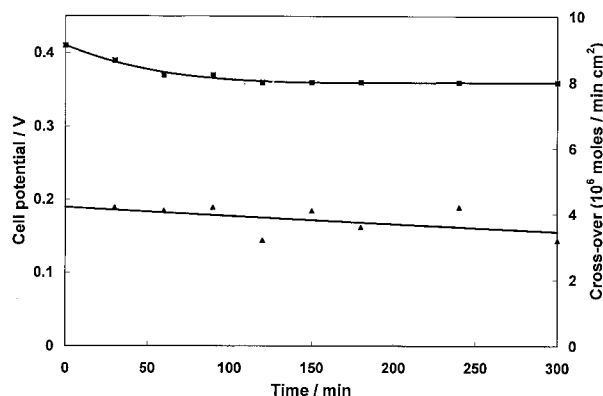
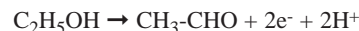
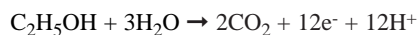


Figure 5. Variation of cell potential (■) and methanol crossover rate detected from the CO₂ production at the cathode outlet (▲) as a function of time during galvanostatic cell operation at 500 mA cm⁻² and 145 °C; anode 2 M CH₃OH, 3.5 atm (abs); cathode 5.5 atm (abs) O₂.

cell was galvanostatically operated at 500 mA cm⁻². It showed a voltage decay from 0.42 to 0.36 V in the first 2.5 h of operation, then the voltage remained constant up to 8 h (Fig. 5). The cell was discharged under short-circuit conditions in the presence of distilled water fed to the anode compartment before being shut down over night. The methanol fuel cell regained its initial performance of 0.42-0.41 V at 500 mA cm⁻² upon subsequent operation, showing that the performance decay was mostly due to anode poisoning under operating conditions. The adsorption of poisoning species appears to be reversible at 145°C since they can be removed during short-circuit discharging in the presence of water. The chromatographic analysis of the product distribution at the anode outlet showed the presence of water, unreacted methanol, and CO₂. The methanol crossing the membrane in part adsorbs on the electrode surface and in part is dragged out by the oxygen-water flow exiting from the cell. The methanol adsorbed on the electrode is catalytically oxidized to CO₂. In order to determine the amount of CO₂ formed at the cathode compartment and the unreacted methanol, two different experiments were devised during fuel cell operation at 500 mA cm⁻². The cathode outlet stream composition was chromatographically analyzed by on-line sampling a dried gas sample with a syringe in order to determine the rate of CO₂ formation. A value corresponding to 4 ± 0.5 10⁻⁶ mol min⁻¹ cm⁻² was determined for the methanol crossover rate (Fig 5). The unreacted methanol passed through the membrane, was collected in the cathode outlet reservoir, and was chromatographically analyzed every 30 min; a value of 2 ± 0.5 10⁻⁷ mol min⁻¹ cm⁻² was determined. Thus, the total average crossover rate of methanol through the membrane was close to that determined from the CO₂ production rate at the cathode.

Similar stability experiments were carried out with ethanol. It was observed that the potential decay at 200 mA cm⁻² was slightly

lower compared to methanol (40 mV in 8 h). A cell discharging under short-circuit conditions, in the presence of distilled water fed to the anode compartment, regained its initial performance upon subsequent operation. Chromatographic analysis of the product distribution at the anode outlet during stationary measurements revealed the presence of water, CO₂, unreacted ethanol, and acetaldehyde. Other compounds, in trace, were also detected but not identified. From an analysis of the electrical charge passed through the cell it was determined that only 4 ± 1% of the electrochemically reacted ethanol gave rise to the formation of acetaldehyde. The remaining part of the electrochemically reacted ethanol was almost entirely converted to CO₂, as confirmed by the chromatographic analysis of the CO₂ production rate at the anode during galvanostatic fuel cell operation at 300 mA cm⁻². Accordingly, the yield of CO₂ in the ethanol electro-oxidation reaction is about 96%. The high selectivity toward CO₂ is in contrast with that observed in the presence of acid-doped polybenzimidazole membrane.¹⁰ The most-intuitive explanation of these contrasting results resides in the different water/ethanol ratios fed to the anode. Wang et al.¹⁰ have recorded a decrease of the acetaldehyde yield from 80 to 65% as the H₂O/C₂H₅OH molar ratio was increased from 2 to 5 in their phosphoric acid-doped polybenzimidazole membrane fuel cell. In the present work, the optimal H₂O/C₂H₅OH molar ratio was found to be about 53, i.e., a diluted solution of 1 M ethanol was fed to the anode. According to the following ethanol electro-oxidation reactions



a large water content could result in a significant increase of the CO₂ yield. Wang et al.¹⁰ reported that an increase of the water/ethanol molar ratio above 5 caused diffusion limitations in their fuel cell. However, this effect appears to be compensated by the larger yield of CO₂ in the presence of perfluorosulfonated membranes. The performance of both ethanol-fed fuel cells based on the different electrolytes is similar. The lack of a significant increase in performance with the increase of CO₂ yield, in the Nafion-based fuel cell, seems to confirm the evidence that CO₂ evolution is hindered by the formation of strongly adsorbed intermediates.⁷⁻⁹

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