

High temperature operation of direct ethanol fuel cells with Nafion-TiO<sub>2</sub> membranes and PtSn/C electrocatalysts

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Ethanol has been considered a promising fuel for direct alcohol fuel cells due to its lower toxicity when compared to methanol, environmental friendliness, and production in large scale. However, the low power capacity at low temperature and the high permeability of ethanol through the Nafion electrolyte (crossover) hinder a wide use of direct ethanol fuel cells (DEFCs). The main reasons for poor overall DEFC performance at low temperature are incomplete ethanol oxidation, resulting from the difficulty of C-C bond cleavage, and the crossover effect, which leads to the adsorption onto the cathode of the fuel and its intermediates. Binary DEFC electrocatalysts based on platinum (Pt) and oxophilic elements (ruthenium or tin) have been reported as promising for the oxidation of ethanol and/or its intermediates (CO-like species) at lower potentials than Pt<sup>[1]</sup>.

An alternative to improve DEFC performance is increasing the operation temperature. In general, operating DEFCs at high temperatures is beneficial for accelerating the electrode kinetics, enhancing the CO tolerance, and improving the water and heat management. However, the operating temperature of proton exchange membrane fuel cell (PEMFC) is limited to 85°C due to the strong dependence of water on the proton transport by the state-of-the-art Nafion electrolyte. Organic-inorganic membranes based on Nafion matrix and hygroscopic oxides, such as TiO<sub>2</sub>, SiO<sub>2</sub>, and ZrO<sub>2</sub>, are a promising alternative for increasing PEMFC operating temperature due to high water retention capacity and better transport properties at high temperatures.

In this context, this study aims to evaluate the high temperature (130°C) performance of DEFC using composite electrolytes based on Nafion and mesoporous TiO<sub>2</sub>, and PtSn/C electrocatalysts.

The composite membranes were prepared by casting a mixture of Nafion solution (DuPont) and TiO<sub>2</sub> nanoparticles, using dimethylsulfoxide (DMSO) as a solvent. The resulting membranes, with different TiO<sub>2</sub> concentrations, were heat treated at 160°C for 5 h. The membranes were characterized by Fourier-transformed infrared spectroscopy (FT-IR), thermogravimetric analysis (TG), differential scanning calorimetry (DSC), and electrochemical impedance spectroscopy (EIS)<sup>[2]</sup>. PtSn/C electrocatalysts were synthesized by alcohol-reduction process<sup>[3]</sup>. In this methodology, platinum and tin precursors (chloroplatinic acid 6-hydrate and tin chloride, Aldrich), ethylene glycol, and carbon (Vulcan XC-72) were kept in reflux for 3 h. The electrocatalysts were washed with water and dried at 75°C for 24 h. The characterization of PtSn/C catalysts was carried out by X-ray diffraction (XRD) analysis, energy dispersive X-ray spectroscopy (EDS), and transmission electronic microscopy (TEM). The composite membranes and PtSn/C electrocatalysts were evaluated as electrolyte and anode, respectively, in DEFC at 80°C and 130°C. DEFC was fed with ethanol solution (2 molL<sup>-1</sup>, 2 mLmin<sup>-1</sup>) at the anode and oxygen at the cathode. The cathode was based

on Pt/C (HP 20%, BASF). A Pt loading of 1 mg cm<sup>-2</sup> was used for both anode and cathode. The oxygen pressure was 3 atm.

Fig. 1 shows the XRD patterns for PtSn/C catalysts with various compositions. The diffraction peaks of Pt (face-centered cubic) were observed for all the catalysts. The SnO<sub>2</sub> diffraction peaks were also detected for the samples with high tin content (PtSn/C 60:40 and 50:50). TEM analysis showed that the mean particle size was 2.5±0.5 nm with a rather narrow and homogeneous size distribution.

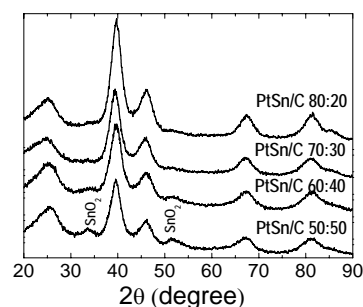


Fig. 1: XRD pattern for PtSn/C catalysts produced by alcohol-reduction process.

DSC findings showed that the glass-transition temperature of the composite membranes was T<sub>g</sub>~130°C, a value larger than that of Nafion. In addition, EIS data evidenced no significant decrease in ionic conductivity for the composites with 10 wt% TiO<sub>2</sub>. Both features are expected to contribute to a better fuel cell performance at high temperature. Fig. 2 shows the polarization curves of DEFC composed by PtSn/C-based anode and Nafion-TiO<sub>2</sub> (10wt%) composite performed at 80°C and 130°C.

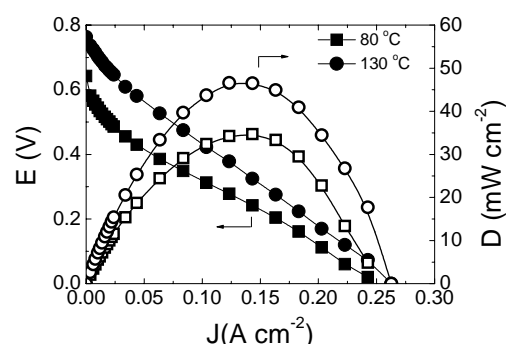


Fig. 2: Polarization (solid symbols, left axis) and power density (open symbols, right axis) curves for DEFC composed with PtSn/C (60:40) anode and Nafion-TiO<sub>2</sub> (10 wt%) electrolyte at 80°C and 130°C.

An enhancement in the performance of DEFC operating at 130°C, with a maximum power density of 50 mW cm<sup>-2</sup>, was clearly evidenced when compared to the power density obtained at 80°C. Such an increase is likely to be attributed to faster ethanol oxidation reaction, lower poisoning due to CO-like species, and a stable electrolyte.

In summary, an enhanced performance of DEFC made of PtSn/C anode and Nafion-TiO<sub>2</sub> electrolyte was achieved by the combination of both electrocatalyst and electrolyte properties during high temperature operation.

<sup>1</sup> F. Colmati et al., *J. Power Sources*, **157**, 98 (2006).

<sup>2</sup> B.R.Matos et al., *J. Electrochem. Soc.*, **154**, B1358 (2007).

<sup>3</sup> A. Oliveira-Neto et al., *J. Power Sources*, **166**, 87 (2007).