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Development of Nafion-based composite electrolytes for applications in PEMFC at high temperature.

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Abstract – Composite membranes based on Nafion and inorganic particles with different morphologies (nanoparticles, mesoporous, and nanotubes) were prepared and evaluated as electrolytes in PEM fuel cell operating at high temperature (130°C) and using either hydrogen or ethanol as fuels. The experimental results revealed that the electrical, structural, and thermal properties of the composite electrolytes have a positive effect on the performance of fuel cells at high temperature. Fuel cells with composite electrolytes exhibit higher stability, enhanced water retention and management, which contribute to superior performance. In addition, by using adequate catalysts and composite membranes, direct ethanol fuel cells showed power output of ~50 mW cm^{-2} at high temperature.

Proton exchange membrane fuel cell (PEMFC) fed with pure hydrogen has emerged as a promising electrical supply for portable, vehicular, and stationary applications. However, problems associated with production, management, storage, and distribution of the gaseous hydrogen stimulate the search for alternative fuels [1]. Developments in the direct ethanol fuel cell (DEFC) technology are mostly concerned with both the fuel crossover and the incomplete oxidation of ethanol. In this context, the operation at high temperature (130-150°C) would significantly boost PEMFC performance, enhancing important parameters, such as electrode reaction kinetics, CO tolerance, and allowing an easier thermal management of the fuel cell system. However, the strong dependence of the proton transport on the water uptake in the state-of-art Nafion electrolyte restricts the operation temperature to ~80°C. Organic-inorganic membranes based on Nafion matrix and hygroscopic oxides, such as TiO_2, SiO_2, and ZrO_2, have been considered as a promising alternative for increasing PEMFC operating temperature due to high water retention capacity and better transport properties at high temperatures [2].

Nafion-based membranes with either TiO_2 or SiO_2 nanoparticles have been systematically fabricated, characterized, and tested in fuel cells. Both the fabrication method (cast composites or sol-gel hybrids), and nanoparticle morphology (spherical, mesoporous, and nanotubes) are found to result in composite electrolytes with different characteristics. The general properties of the produced membranes have been investigated by different techniques such as Fourier-transformed infrared spectroscopy (FT-IR), thermogravimetric analysis (TG), differential scanning calorimetry (DSC), electrochemical impedance spectroscopy (EIS), small angle X-ray scattering (SAXS), and scanning electron microscopy (SEM). Nafion composites were evaluated as electrolytes in PEMFC fed with either hydrogen or ethanol in 80-130°C temperature range and reduced relative humidity (RH).

The main results show that the enhanced properties of the composite electrolytes contribute to superior performance of fuel cells operating at high temperature and/or reduced RH. Figure 1 shows the H_2/O_2 fuel cell polarization curves for Nafion-titanate nanotube (TNT) composites with different inorganic phase contents at 130°C. An appreciable enhancement (~30%) is evidenced for Nafion-TNT (5 wt%) composites when compared to unmodified Nafion. Such a feature is related to a remarkable increase in the water absorption (up to 60%) for Nafion-TNT composites due the high surface area of the nanotubes. Figure 2 shows DEFC polarization curves for Nafion-mesoporous TiO_2 at 80 and 130°C. An enhancement of the performance of DEFC was observed when the operation temperature was increased from 80 °C to 130°C, reaching maximum power density of 50 mW cm^{-2}. Both higher glass-transition temperature of the composite membranes (Tg~130°C), inferred from DSC measurements, and no significant decrease in ionic conductivity of the composites with 10 wt% TiO_2 are likely to promote better fuel cell performance at high temperature.

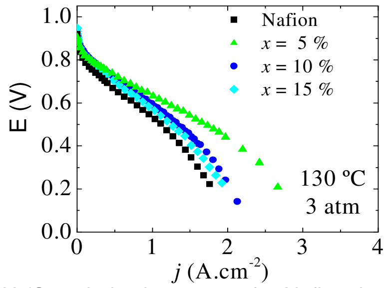

Figure 1: H_2/O_2 polarization curves for Nafion-titanate nanotubes with different compositions (x) at 130°C.

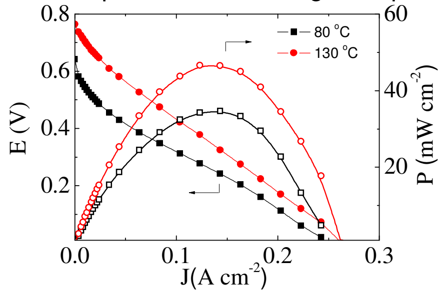

Figure 2: DEFC polarization curves (left axis) and power density curves (right axis) for Nafion-mesoporous TiO_2 (10 wt%).

[1] J. Larminie and A. Dicks, *Fuel Cell Systems Explained*, John Wiley & Son Ltd, Chichester, England (2000).
[2] B.R. Matos et al. *J. Electrochem. Soc.*, 154, B1358 (2007).