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Nafion-SiO_2 Hybrids Combined with Pt-Sn/C Anodes for DEFC Operating at High Temperature

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Polymer electrolyte fuel cells (PEFCs) are particularly attractive for applications with variable electric load and intermittent operation, such as portable electronics, distributed power sources, and electric vehicles. Furthermore, such devices can operate with diverse fuels such as hydrogen, methanol, and ethanol. In particular, the direct ethanol fuel cell (DEFC) has been considered a promising energetic alternative due to low toxicity of ethanol compared with methanol, and the possibility of fuel production from renewable sources. However, the efficiency of DEFCs is substantially lower than for fuel cells fed with hydrogen or methanol mainly due to the lower anode activity.

An alternative to enhance the performance of DEFCs is to increase the operating temperature because the electrode reactions are thermally activated. However, pristine Nafion membranes are not suitable for such operating conditions because increasing the temperature, which decreases the level of hydration, results in severe loss of ionic conductivity [1]. Several approaches were proposed to prevent the conductivity loss of Nafion at high temperature. A straightforward approach is the addition of a hygroscopic phase, such as SiO_2 and TiO_2, within the perfluorosulfonic acid (PFSA) matrix to form a hybrid nanocomposite [2].

On the other hand, PtSn catalysts are currently considered the most efficient materials for ethanol oxidation, which activity is dependent on the amount of alloyed Sn and oxides [3].

In this context, the objective of this work is to evaluate Nafion-SiO_2 hybrids in combination with well-alloyed PtSn/C catalysts produced by a modified polyol method [4] for DEFC operating at high temperature (130 ^{o}C).

Nafion-SiO_2 hybrids were synthesized by *in situ* sol-gel reaction, by the incorporation of oxide directly into the ionic aggregates of Nafion membranes with different thickness (95, 125, and 175 µm) and conformation (casting and extrusion). The effect of synthesis parameters, such as sol-gel solvent, membrane thickness and silicon precursor concentration on silica incorporation degree, water and ethanol uptake, and mechanical stability, were also studied. Characterization of Nafion-SiO_2 hybrids showed an effective incorporation of SiO_2 particles in both hydrophilic and hydrophobic domains of Nafion template with a compositional range of 4 and 13 SiO_2 wt% depending on the silicon precursor concentration, sol-gel solvent, and Nafion thickness. In comparison to pristine Nafion, the hybrids exhibited higher water and ethanol uptakes.

Carbon-supported PtSn nanoparticles with different compositions were synthetized by a modified polyol method using two reducers. Characterization was carried out by X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). These studies showed rather large amounts of Sn incorporated into the PtSn alloyed phase compared with values usually reported in literature. The electronic properties of PtSn/C catalysts were studied by in situ X-ray absorption spectroscopy (XAS).

Polarization curves were obtained for 2 mL min^{-1} ethanol flow (1 mol L^{-1}). The oxidant was pure oxygen at 3 atm pressure. For the DEFC having a commercial PtSn/C (75:25) at the anode and unmodified Nafion 117 showed a rather poor performance, with a maximum power density of 40 mW cm^{-2} at operating temperature of 80^{o}C. Changing the electrolyte to Nafion 117-SiO_2 (13 wt%) hybrid and keeping the same anode catalyst resulted in a somewhat better performance at 80^{o}C. The cell performance improved at higher temperatures and a maximum power density of about 100 mW cm^{-2} was obtained. Finally, the optimized anode and electrolyte were evaluated in DEFC prototypes operating in the 80 – 130 ºC temperature range. For the DEFC composed by optimized PtSn/C prepared by a polyol method combined with the Nafion 117-SiO_2 (13 wt%) hybrid a significant performance improvement was observed, with a maximum power density of 125 mW cm^{-2} for the cell operated at 130^{o}C.

In summary, the combination of optimized catalysts and electrolytes allowed high operating temperatures that resulted in significant improvement of DEFC performance.

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