Evaluation of Nafion-SiO_2 Hybrids as Electrolytes in PEMFC operating at High Temperature

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Nafion-SiO_2 hybrid membranes were prepared by the incorporation of SiO_2 into commercial Nafion 115 and evaluated as electrolytes in H_2/O_2 proton exchange membrane fuel cells (PEMFC). Hybrid membranes were produced by *in-situ* sol-gel method with different SiO_2 contents by using Tetraethyl Ortosilicate (TEOS) as the silicon precursor. The catalytic parameters, such as the nature of alcohol (methanol, ethanol, and 2-propanol); concentration of the acid catalyst (HNO_3, 0.2-2.0 mol L^{-1}); reaction temperature (25-90ºC); and the precursor concentration (0.5-2.0 mol L^{-1}) were studied. Gravimetric analysis revealed that degree of incorporation of SiO_2 is in the 4-10 wt% range. The obtained values are strongly dependent, mainly, on both the alcohol nature and TEOS concentration. Energy dispersive X-ray analysis (EDX) showed that the inorganic phase is well distributed across the membrane thickness, indicating that the synthesis methodology provides homogeneous dispersion of the nanoparticles into the polymeric matrix. The stability of the hybrids was evaluated after successive washings in H_2SO_4 0,5 mol.L^{-1} and water at 70ºC employed to remove surface residues. The water uptake data have showed a ~50% increase for the hybrid membranes in comparison to Nafion 115. Gas diffusion electrodes were prepared with Pt/C catalyst (E-tek, 20 %wt) with a loading of 0.4 mg cm^{-2} for both anode and cathode. Polarization curves of fuel cells operating with water-saturated hydrogen and oxygen gases were obtained galvanostatically with 5 cm^2 electrode area single cells. Measurements were carried out in the 80 - 130ºC temperature range with total absolute pressure of 3 atm (RH=100%) and at 130 °C with reduced relative humidity (RH = 75 and 50%). The polarization curves using hidryds Nafion-SiO_2 5% (wt/wt) with electrolyte showed that the addition of a inorganic phase has not changed significantly the ohmic drop polarization of fuel cells and up to 120ºC both the pure Nafion and Nafion-SiO_2 hybrids display comparable performances. With further increase in the operating temperature to 130ºC the performance of the Nafion-SiO_2 hybrid was maintained and, in contrast, the unmodified Nafion showed a pronounced decrease of the performance. Such different temperature dependence represents a performance of ~40% superior of the Nafion-SiO_2 hybrid at 130ºC in comparation with unmodified Nafion. This response is probably attributed to the higher water retention capacity of the SiO_2 present in hybrids membrane, in agreement with the water uptake data.
In summary, hybrids based on Nafion-SiO_2 were effectively prepared by the incorporation of the inorganic phase into commercial Nafion by an optimized sol-gel route. A significant enhancement of the fuel cell performance was evidenced at 130ºC, indicating that ionic conductivity was sustained at high temperature, probably, due to the increase of the water retention capacity of the hybrids conferred by the hygroscopic property of the SiO_2.
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