Synthesis and characterization of novel nanocomposite polymer electrolyte membranes for fuel cell applications

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ABSTRACT

The fuel cell technology has increased rapidly during the last two decades. The polymer electrolyte membrane fuel cells (PEMFC) are the most promising of all the types of fuel cells due to operating inexpensively in temperatures 60–80°C with great efficiency up to 60%. However, in this temperature range face problems including poor carbon monoxide tolerance and heat rejection. These drawbacks can be overcome by increasing the operating temperature range up to 120–130°C. In this temperature two opposite effects come into play: i) improved electrocatalytic kinetics and ii) decreased proton conductivity of the electrolyte. In order to reduce these overpotentials, properties such as stable water uptake and high proton conductivity are essential for the electrolyte. At the moment, Nafion (a perfluorosulfonate ionomer membrane) is the most widely used polymer electrolyte due to its unique mix of chemical inertness, mechanical and thermal stability and high proton conductivity. A common strategy that has been adopted to improve the water retention capacity is to integrate hygroscopic materials in the polymer obtaining nanocomposites. Over the last decade, attention has been focused on study of organic-inorganic hybrid materials as possible solution to enhance the hydration properties of the solid electrolytes at high temperatures. The fillers can be one dimensional materials like nanotubes, two dimensional such as layered silicate minerals (clays) and three dimensional such as inorganic particles.

In this thesis, inorganic layered structures such as (i) smectite clays (synthetic and natural)with different structural and physical parameters (Laponite and two montmorillonites: Kunipia and SWy-2), (ii) swellable graphene oxide (GO),prepared by oxidizing powdered graphite, and (iii) layered double hydroxides (LDHs) with different compositions (various combinations of metal cations, interlayer anions and molar ratios of divalent to trivalent cations), were tested as 2D nanofillers in order to create Nafion nanocomposites. Hybrid nanocomposites were synthesized in different fillers to polymer loadings (1, 3, 5 wt %). Furthermore, functionalization of clays and GO with organo-surfactants having different terminal groups (5-aminovaleric acid, 3-amino-1-propane sulfonic acid, N-[tris(hydroxymethyl)methyl]-2-aminoethanesulfonic acid and serine) was also performed in order to increase the number of acid sites and consequently the water retention of the produced nanocomposites membranes. Solution intercalation was followed for the synthesis of the above hybrid membranes. The type of solvent and the temperature for membrane preparation were examined in order to determine the optimum conditions for the preparation of highly homogeneous nanocomposite membranes. The samples were characterized by a combination of powder X-ray diffraction, FTIR and Raman spectroscopies, thermal analysis (DTA/TGA), scanning electron microscopy and dynamic mechanical analysis. Results showed that highly homogeneous exfoliated nanocomposites were created in most cases where the individual layered nanofillers are uniformly dispersed in the continuous polymeric matrix. The study of the water transport mechanism, consequently of the H^+ ions within the electrolyte membrane, is one of the key aspects in the evaluation of these materials. The Pulse Field Gradient (PFG) NMR technique was used in this work to obtain a direct measurement of the water self-diffusion coefficients either in pure Nafion membrane or in the final nanocomposites. A remarkable behaviour at high temperature is observed for all samples, where composite membranes maintain stable and unwavering diffusion for many hours and in conditions of not humidification, proving the exceptional water retention property of these materials. Finally the hybrid membranes are much stiffer and can withstand higher temperatures compared to pure Nafion, hence both these characteristics are highly desirable for use in fuel cell applications.

Keywords: nanocomposite membranes; graphene oxide; clays; surface modification; organo-graphenes; organoclays; layered double hydroxides; Self-diffusion; NMR; PEMFC.