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Investigation of layered double hydroxide (LDH) Nafion-based nanocomposite membranes for high temperature PEFCs

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ABSTRACT

Hydrogen/air Polymer Electrolyte Fuel Cell (PEFC) are highly attractive as energy source for mobile applications, improving electrochemical kinetics rates, waste heat recovery and overcoming catalyst tolerance for reformed hydrogen at operating temperatures above 80 °C.

Layered double hydroxide (LDH) nanoparticles with Mg^{2+}/Al^{3+} metal cations (metal ratio 2:1) and different countervailing anions (CO_3^{2-}, ClO_4^-, NO_3^-) in the interlayer space were synthesized and tested as fillers for the creation of hybrid Nafion nanocomposites using a standardized casting method. The development of such nanocomposites will lead to a highly efficient H_2/air polymer electrolyte fuel cell operating at high temperatures. The produced hybrid membranes were characterized by a combination of powder X-ray diffraction, FTIR spectroscopy, and thermal analysis (DTA/TGA) that revealed the creation of homogeneous exfoliated nanocomposites. The water-transport properties were investigated by NMR spectroscopy (diffusion and relaxation time). Interlayer anions affect the lambda value (mol H_2O/mol SO_3H) showing better hydration with higher values compared to recast Nafion. Fuel cell tests performed in drastic conditions (1.5 abs. bar and 50% RH) at 100 °C highlighted the influence of the different interlayer anions in composite membranes. A good performance was obtained for membranes containing LDH-ClO_4^- with a power density of 300 mW cm^{-2} at 0.6 V at 100 °C.

1. Introduction

Nowadays, the demand of power generation using environmental friendly technologies has become one of the greatest priorities for researchers worldwide. In particular, fuel cells and especially Polymer Electrolyte Fuel Cells (PEFCs) are attractive candidates and thus well studied energy production technologies [1,2]. In fact, PEFCs are interesting due to their high electrical efficiency, low emissions and easiness to operate. The key component of a PEFC is the proton exchange membrane, which must have the following characteristics: high proton conductivity, electrical insulation, good separation between fuel and oxidant, good chemical and mechanical stability during operation.

Among several polymer membranes, Nafion (a registered trademark of E. I. du Pont de Nemours and Co.) is the most widely studied and used proton-conducting polymer. Nafion has a high proton conductivity at conventional operating temperatures (60–80 °C) while a drastic decrease occurs above this temperature and/or at low relative humidity [3]. One of the main targets for an automotive application is to maintain the good proton conductivity in drastic conditions of temperature and humidification [4–6]. However, high temperature operative conditions affect the mechanical stability of the polymer matrix because a softening/weakening effect occurs [7]. To overcome this drawback, several studies on the development of composite/hybrid membranes were carried out, by introducing organic/inorganic fillers with different shape and sizes [8–12]. The combination of inorganic and organic blocks produces membranes with improved physicochemical properties. The inorganic segments provide high mechanical and thermal stability while organic segments provide flexibility [13–25].

In this study we propose a new class of nano-sized compounds based on Layered Double Hydroxides (LDHs), belonging to the anionic clay class with a unique combination of physicochemical properties that make them versatile materials for different applications in various fields [26–30].

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Generally, the anionic clays (or hydrotalcite-type) are represented by the chemical structure $[M^{(II)}_{1-x}\,M^{(III)}_{x}\,(OH)_2]^{x+}[A^{m-}{}_{x/m}]\cdot nH_2O$, in which: $M^{(II)}$ is a divalent metal cation (Mg, Mn, Fe, Co, Ni, Cu, Zn, Ga), $M^{(III)}$ is a trivalent metal cation (Al, Cr, Mn, Fe, Co, Ni, and La) and A^{m-} represents an interlayer anion, such CO_3^{2-}, OH^-, NO_3^-, SO_4^{2-} or ClO_4^- [31]. Many fundamental properties of these compounds, such as anion exchange capacity, anion fixation, swelling ability, water retention, and high specific surface areas, are affected by the positive charge of the layers [32–34]. By introducing these nanofillers in the polymeric structure, composite membranes are developed which are suitable for fuel cell applications. In particular, LDHs introduction into the polymeric matrix produces: an increment of polymer tortuosity that reduces the permeation of the fuel (e.g. methanol) [35], an improvement of mechanical properties of polymers for high temperature operation, the maintenance of a suitable hydration due to a presence of surface hydroxyl groups [36–38].

In this work, LDHs with a 2:1 Mg^{2+}/Al^{3+} metal ratios and various interlayer anions (CO_3^{2-}, ClO_4^-, NO_3^-) were incorporated in a Nafion matrix, in order to evaluate the electrochemical performance of the final nanocomposite membranes. Structural characterization by powder X-ray diffraction, FTIR spectroscopy and thermal analysis (DTA/TGA) was performed both on the pristine materials and the resulted membranes. Transport properties of water confined in the nanocomposites were studied by diffusometry and relaxometry NMR spectroscopy [39–43]. Moreover, physico-chemical characterization was carried out to investigate the effect of the filler–polymer interaction at higher than conventional temperatures (above 80 °C), in particular on the water retention and distribution. Electrochemical tests were performed in order to investigate the proton conductivity and fuel cell performance as a function of the interlayer anions.

2. Experimental

2.1. Synthesis of inorganic fillers

Layered double hydroxide nanofillers have been synthesized by co-precipitation, in an aqueous solution of Na(OH) and Mg^{2+} and Al^{3+} salts. The magnesium/aluminium metal ratio was adjusted to 2/1 in 100 ml of an aqueous solution containing $Mg(NO_3)_2\cdot 6H_2O$ (0.05 mol), $Al(NO_3)_3\cdot 9H_2O$ (0.025 mol) and a sodium salt of carbonate or nitrate anions (Na_2CO_3 or $NaNO_3$: 0.045 mol). Next, an aqueous solution of NaOH (2.5 M) was added drop wise until a pH value of 10 was reached. For the synthesis of LDH with perchlorate as interlayer anions, the starting solution consisted of an aqueous solution (100 ml) containing $Mg(ClO_4)_2$ (0.05 mol) and $Al(ClO_4)_3\cdot 9H_2O$ (0.025 mol). The final precipitated LDH materials were stirred at 60 °C for 24 h and separated by centrifugation, washed several times with water and dried in air at 80 °C for 24 h. In the case of nitrate and perchlorate anions, the synthetic procedure was performed under a constant nitrogen gas flow and using decarbonated–deionized water.

2.2. Membranes peparation

A 5 wt% Nafion® solution (Ion Power LQ1105) was used to produce the membranes. The original solvents were completely eliminated by a rotary evaporator, in order to obtain a dry residue. Successively, it was diluted in dimethylformamide (DMF) as a solvent with a final concentration of 10 wt%. For the composite membranes preparation a nominal amount of 3 wt% of filler was added to the polymeric solution before the reconcentration step. Prior to use, the filler was dispersed in the same solvent of the polymer under magnetic stirring, for about 18 h at room temperature. The solutions were then slowly reconcentrated until a suitable viscosity was reached to be stratified with a doctor-blade. The obtained films were dried at 80 °C for 3 h to eliminate the solvent. All the prepared membranes underwent a thermal treatment up to 155 °C to increase the crystallinity of the polymer and thus improve the mechanical properties. Membranes with a thickness ranging from 50 to 70 μm were obtained.

Subsequently, the membranes were treated by rinsing in: (i) HNO_3 solution (1:1 vol) at 80 °C for 30 min. to oxidize the organic impurities as elsewhere reported [44], (ii) boiling deionized H_2O for 15 min., (iii) H_2SO_4 (1 M) at 80 °C for 30 min to remove any metallic impurities, (iv) boiling deionized H_2O for 15 min for three times to remove excess acid. According to MacMillan et al. [45] an ulterior purification procedure was performed in order to ensure the removal of paramagnetic contaminants which are particularly damaging to an NMR experiment, such as the presence of copper that we found by Electron Paramagnetic Resonance analysis. This procedure consists of soaking the membranes in an EDTA solution (0.001 M) for 1 day, followed by a thorough rinse. Then the membranes are soaked in 2 M HCl at a temperature of 80 °C for 2 h followed by boiling in fresh distilled–deionized water to remove any residual acids. Next, the treatment with EDTA is repeated. Finally, the membranes are rinsed in boiled deionized water three times to remove residual EDTA and stored at room temperature at fully hydrated state. In Table 1 the prepared membranes are reported.

2.3. Electrodes and MEAs preparation

The electrodes were produced by spraying [46] the catalytic ink onto a commercial Gas Diffusion Layer (SGL Sigracet-24BC). A 50% Pt/C (Alfa Aesar) was utilised as an electrocatalyst. The same Platinum (Pt) loading of 0.5 mg cm^{-2} for anodes and cathodes was used. Membrane-Electrode assemblies (MEAs) were manufactured by hot-pressing the electrodes onto the membranes at 125 °C and 20 kg cm^{-2}.

2.4. Characterization of nanofillers

The X-ray powder diffraction data were collected on a D8 Advanced Bruker diffractometer by using Cu Kα (40 kV, 40 mA) radiation and a sondary beam graphite monochromator. The patterns were recorded in a 2-theta range from 2° to 60°, in steps of 0.02° and counting time 2 s per step. Infrared spectra were measured with a FT-IR 8400 spectrometer, in the region of 400–4000 cm^{-1}, equipped with a DTGS detector. Thermogravimetric (TGA) and differential thermal (DTA) analysis were performed using a Perkin Elmer Pyris Diamond TG/DTA. Samples of approximately 5 mg were heated under air from 25 to 850 °C, at a rate of 10 °C/min.

2.5. Membranes characterization

2.5.1. NMR measurements

NMR measurements were performed on a Bruker NMR spectrometer AVANCE 300 Wide Bore working at 300 MHz on ^1H. The employed probe was a Diff30 Z-diffusion 30 G/cm/A multinuclear

Table 1
Developed membrane characteristics.

Membrane	Filler
N-recast	–
NLDH-NO_3	Mg/Al-LDH-NO_3^{2-}
NLDH-CO_3	Mg/Al-LDH-CO_3^{2-}
NLDH-ClO_4	Mg/Al-LDH-ClO_4^-