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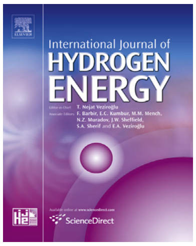

Composites membranes based on Nafion and PAMAM dendrimers for PEMFC applications

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ABSTRACT

The aim of this work consists in to incorporate organic compounds as PAMAM (Polyamidoamine) dendrimers into the polymeric Nafion matrix to prepare composite membranes as a possible alternative to reduce methanol crossover effect. Composite Nafion membranes were prepared using a 3 wt% of Generation-4 hydroxyl-terminated PAMAM (G4OH) dendrimers containing 64-terminal OH-functional groups. The influence of PAMAM-(G4OH) dendrimer on chemical–physical properties of the composite membrane was highlighted resulting in a reduction of the methanol permeability (1.05×10^{-6} cm^2 s^{-1}) if compared to a recast bare Nafion membrane (8.19 × 10–6 cm^2 s^{-1}), used as a reference. Good proton conductivity was also observed for PAMAM-(G4OH) composite membrane. The polarization curves carried out at 100 °C in the presence of 2 M methanol have revealed the higher performance of the PAMAM-(G4OH) membrane when compared to a recast Nafion membrane.

Introduction

Since 1960 fuel cells have emerged as an alternative to traditional systems for energy production, although their history began in 1839, more than a century had to pass to prove their practical technological value [1]. There are five main types of fuel cells such as phosphoric acid (PAFC), alkaline (AFC), molten carbonate (MCFC), solid oxide (SOFC) and proton exchange membrane (PEMFC). The system that has attracted the most interest consists in the PEMFC due to its wide range of power density (1×10^{-3}–100 kW), simplicity of components, facility to be used in portable applications and its friendly user operating conditions (30–100 °C). High purity hydrogen must be used as fuel if Pt is the catalyst used at the anode or hydrogen from reforming, which contains some pollutants as CO, can also be used if CO-poisoning resistant catalysts are used as Pt–Ru. For mobile applications, it is necessary to

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compress the fuel rendering it an impractical energy carrier. Direct Methanol Fuel Cells (DMFCs) appear as the alternative whereas a PEMFC is not suitable, since they possess the simplicity of storage and transportation of a liquid fuel [2]. DMFC is basically a PEMFC where a water-methanol solution is fed, instead of hydrogen. The use of another fuel involves technological challenges as the development of a low cost and efficient catalyst to carry out the methanol oxidation reaction as well as the development of proton conducting membranes impermeable to methanol and capable of operating at a higher temperature.

The thermodynamic potential of a DMFC is 1.21 V and it is determined by the methanol oxidation potential (0.02 V) and the oxygen reduction potential (1.23 V) reactions; however, this open circuit potential is barely reached due to methanol crossing through the membrane (usually Nafion®) from anode to cathode. The diffusion of fuel means that it will react at the cathode (Pt) and the corresponding six electrons from methanol oxidation will not be used to produce electrical work; hence, power density is lower than expected one. Methanol oxidation at the cathode also diminishes the electro-active area available for the oxidant reduction. In-fact, this reaction creates a mixed potential that lowers the fuel cell efficiency and increases oxygen requirement. Since the proton conductivity of the membrane is related to its water content and methanol is water soluble, the methanol crossover through the membrane section represents the most relevant hindrance to be solved. Several strategies have been employed to minimize the reagent diffusion from anode to cathode including: (1) operation at a low temperature and keeping the methanol concentration below 2 M [3,4]; (2) employment of more efficient electro-catalyst for methanol oxidation at the anode [5,6]; (3) usage of thicker membranes with a lower methanol crossover; (4) application of non-perfluorinated ionomer membranes alternative to Nafion®; (5) utilization of perfluorinated and non-perfluorinated membranes modified by organic or inorganic compounds [7–11] in order to increase the pathway tortuosity within the membrane and to reduce the methanol crossover. In-fact, the aim of Nafion® modification or substitution by another polymer is to develop a membrane with a lower methanol crossover ($<10^{-6}$ mol min^{-1} cm^{-1}), a good high proton conductivity (>80 mS cm^{-1}), a good chemical and mechanical stability ($T > 80$ °C) and low cost.

In the 1980s, Tomalia [12] and Newkome [13] independently succeeded in synthesizing new polymeric structures called dendrimers. Dendrimers are macromolecules hyperbranched, monodisperse and nanometer sized, with a large density of surface functional groups. In the structure of the dendrimer, three regions of interest can be distinguished: the core, surrounded by the dendritic branches; an intermediate region consisting of dendritic branches and the exterior comprising surface functional groups. Each region can be tailored for specific applications [14,15]: for fuel cells, dendrimers have been used to encapsulate the electro-catalysts [16,17], to modify the proton conducting membranes [18,19] and as components in the electro-catalytic ink [20]. It is worthy to be noticed that, in all these cases, PAMAM (poly-amidoamine) dendrimers have been used due to the presence of amino and amidic groups that can interact with ionic metal precursors; besides, amino group allows a subsequent functionalization, which expands its application potential. The evaluation of Pt encapsulated into PAMAM (G4OH) for a DMFC cathode [16] proved that at low concentrations of methanol, the dendrimer acts as a barrier that only allows the oxygen incoming, while methanol is kept away from the encapsulated catalyst. This protection avoids the unwanted methanol oxidation reaction. This information indicates that dendrimers could be used as membranes modifiers to avoid or reduce the methanol crossover.

The purpose of this work consists into investigating the prevention capability of methanol crossover of a composite membrane Nafion®/PAMAM-(G4OH) dendrimer, whereas G4OH indicates the generation 4 with 64 surface groups having –OH as a functional group. The physicochemical characteristics and transport properties of this composite membrane were compared with those of a bare recast Nafion membrane. At higher temperature, OH-functional groups of the dendrimer play an important role to keep the proton conducting properties of the membrane.

Experimental

Membrane preparation and treatments

Generation-4 hydroxyl-terminated PAMAM (G4OH) dendrimers with the highest available purity (10 wt.% in methanol) were obtained from Sigma–Aldrich and used without further purification.

The composite N-dendrimer membranes were prepared through a solution casting method: first, a 5 wt.% Ion Power Nafion® alcoholic solution (LQ1105) was selected to manufacture the film. The original solution was desiccated at $T = 40$ °C under vacuum using a rotating evaporator until obtaining a dry residue, successively solubilised in dimethylacetamide (DMAc) as a solvent in order to obtain a 20 wt.% polymeric solution. Such a solution was used to prepare a recast bare membrane (N-recast) used as a reference. For the composite membrane, an amount of 3 wt.% of PAMAM (G4OH) dendrimer compared to the dry Nafion resin was added to the polymeric solution and dispersed in an ultrasonic bath for 30 min before the re-concentration phase necessary for the casting procedure. Through a slow re-concentration at 80 °C under a magnetic stirring, suitable viscosity solutions were obtained and stratified using the Doctor Blade technique on a glass sheet. The obtained membranes were dried on the hot plate at $T = 80$ °C for 3 h to evaporate the solvent and, then, detached from the glass with distilled water. Successively, they underwent a thermal treatment until $T = 155$ °C (30 min) to enhance the crystalline phase of the polymer and, consequently, to improve the mechanical properties. A chemical treatment in HNO_3/H_2O (1:1, volume ratio) at 80 °C for 30 min was carried out on the membranes with intermediate boiling steps in distilled water (15 min). A successive treatment in a 1 M H_2SO_4 solution at 80 °C for 30 min was employed on all the membranes with final washings in boiling distilled water (three times – 15 min for each). This chemical treatment