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Product Performance

Composites Nafion-titania membranes for Polymer Electrolyte Fuel Cell (PEFC) applications at low relative humidity levels: Chemical physical properties and electrochemical performance

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A B S T R A C T

The incorporation of inorganic compounds into the polymeric Nafion matrix represents a possible solution to improve the mechanical characteristics of the polymeric membranes when drastic operative conditions (higher temperatures and/or lower relative humidity levels) are adopted in a Polymer Electrolyte Fuel Cell (PEFC). On the basis of previous investigations, different commercial anatase titanium oxide (TiO_2) loadings were used to prepare composite membranes with the aim of reducing the humidification levels for a PEFC stack. Membranes with three different TiO_2 contents (5, 10, 15 wt.%) were cast and characterized in terms of chemical-physical and electrochemical behaviour. The influence of filler was highlighted resulting in a swelling reduction of the composite membranes if compared to a pristine recast Nafion membrane cast with the same method and used as a reference. A good proton conductivity was observed for all composite Nafion-titania (N-TiO2) membranes with values ranging $1.3–1.9 \cdot 10^{-2}$ S cm^{-1} at 60 °C and 50%RH against a value of $1.5 \cdot 10^{-2}$ S cm^{-1} related to the reference membrane. The composite membrane containing a 10 wt.% of TiO_2 has shown an improved performance respect to the reference membrane, especially at low levels of humidification and a higher stability during the accelerated stress test (AST) carried out in drastic conditions (60 °C and 50%RH), probably due to the filler capability to reduce the swelling and give stiffness to the polymeric matrix.

1. Introduction

Polymer Electrolyte Fuel Cells (PEFCs) systems represent a highly efficient and environmentally clean electric power supply for stationary and mobile applications. In the recent past, the need to develop PEFC operating at low or without any humidification with water vapour partial pressures below 0.5 bars became more and more evident, especially for the automotive sector.

A typical PEFC device utilizing polymer membranes based on perfluorosulfonic acid (PFSA), such as Nafion® as an electrolyte, supplies an excellent proton conduction and chemical stability when the membrane operates in a water-swollen state. Against, such perfluorosulfonic acid membranes have several critical limitations. First of all, the proton conductivity of standard Nafion membranes using a 30% of relative humidity (*RH*) is less than 10% of the value obtained with an 80%RH [1]. This means that must be provided and managed a large amount of water in order to ensure a high performance since the proton conduction mechanism of Nafion polymer proceeds thanks to the hydronium ions presence (H_3O^+). In low RH conditions, when the hydration of polymer is lowered, the proton conductivity strongly decreases provoking an increase of ohmic over-potential [2] and a consequent drop of the electrochemical performance. This phenomenon is obviously more evident when the fuel cell temperature increases. In-fact, in this case, it is essential to increase the pressure in the device over the water vapour pressure to maintain a fully hydration of the membrane [3]. Operating with fully humidified reactants, the water formed at the cathode side can flood the gas flow channels, hindering the gas diffusion and causing an important swelling phenomenon of the membrane. Such event provokes important dimensional modifications of the membrane as a function of the adsorbed water from the polymer. The consequence could be an excessive internal pressure of the membrane opposed by the

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electrodes and the gaskets [3]. Both the cell flooding and membrane swelling can be limited operating under a low RH, but this condition implies the membrane dehydration that reduces the proton conductivity and causes a certain brittleness of the film with a consequent failure of the cell performance. In these drastic conditions, it is highly desirable to enhance the proton conductivity and maintain an appropriate amount of water inside the perfluorosulfonic (PFS) membrane, so to achieve an appreciable electrochemical performance. In order to maintain an adequate proton conductivity and preserve the integrity of Nafion membranes from the state of dryness, under low RH conditions, hygroscopic and/or proton conductor ceramic inorganic fillers, such as SiO_2 [4–8], TiO_2 [3,9–22] ZrO_2 [23–26], hetero-polyacids [27–30], zeolites [31,32] and zirconium phosphates [33,34], etc. are often incorporated into the membrane. In fact, the hygroscopic fillers retain water in the molecular framework maintaining the appropriate amount of water for proton conduction.

Moreover, they preserve the membrane from the swelling assuring the mechanical properties of the polymer chain operating in drastic conditions and to prevent its degradation mechanism. In addition, the insolubility of these compounds in aqueous media also hinders their leaching out from the membrane [35]. In particular, titanium dioxide nanoparticles (TiO_2 - rutile and anatase) have been employed as fillers with the aim of improving the mechanical strength of the membranes [3]. It has been shown that the TiO_2/water interface is positively charged under acidic conditions and is characterized by a very high concentration of adsorbed protons [2].

Adjemian et al. [36] have suggested that a chemical interaction between the metal oxide surface and the Nafion polymer occurs. The metal oxide particles act to crosslink the Nafion polymer chains with an increase in the glass-transition temperature (*Tg*). They found good results at reduced relative humidity levels for titanium metal oxides composite membranes. Anatase-type Titania nanoparticles were synthesized in situ in a Nafion solution by Ye et al. [11]. The glass transition temperature of the formed Nafion-titania composite membranes was about 20 °C higher than that of pristine Nafion membrane and, moreover, Nafion-titania nano-composite membranes showed a higher water uptake ability and an improved proton conductivity compared to a pure Nafion membrane at elevated temperature and low relative humidity. Composite Nafion membranes loaded with a 10% and 20 wt.% of commercial TiO_2 showed a considerable improvement over un-modified Nafion membranes in the PEFC performance at 120 °C, 3 abs. bar and with a reduced humidification level in H_2/O_2 [21]. Titanium dioxide fillers have been used in a tubular morphology to enhance the water diffusion [37]. The proton conductivity of the composite Nafion-TNT (tubular titania) membranes was found to be higher than that of the recast Nafion and commercial NRE-212 membranes in all humidity ranges. In any case, a higher performance respect to the recast Nafion has been found both for TNT and nanoparticles Titania (TNP) membranes at different humidity levels. Composite membranes containing functionalized titanium oxide [22] showed improved mechanical properties, superior conductivity and improved electrochemical performance respect to that obtained for an unfilled Nafion with an increment of 100% of the power density.

In a previous work [10], composite Nafion membranes obtained through the addition of preformed synthesized anatase Titania nanoparticles were investigated. The performance was evaluated in a fuel cell in the temperature range of 80–130 °C in pure hydrogen and air. A composite membrane with a 3 wt% of Titania loading reached a power density of about 0.254 W cm^{-2} at 0.5 V and 100% RH. The present paper describes the Nafion® polymer matrix modification using a commercial treated anatase TiO_2. Composite membranes with different TiO_2 loadings were developed and characterized in terms of structural, morphological and chemical-physical properties (water uptake-*Wup*, Ion Exchange Capacity-*IEC*, lambda–λ, H^+ concentration-[H^+] and mobility-μ) in order to investigate their behaviour as a function of filler content. The electrochemical characterization on all samples was carried out with different humidification levels (50, 75%, 100%*RH*) at 60 and 80 °C as cell temperatures. The results in terms of polarisation curves have been evaluated and compared to a pristine Nafion membrane (named Nrecast), prepared with the same method, after a preliminary comparison with a commercial Nafion (NR212) membrane demonstrating the good quality of Nrecast, used as a reference. On the basis of the results, a cell temperature of 60 °C was selected for the final evaluation on composite N-TiO2 membranes as an optimal temperature condition for lower relative humidity levels. Regarding the supplied electrochemical performance, the membrane with a 10 wt.% of filler has shown an improved performance respect to the Nrecast reference. At the end, an Accelerated Stress Test (AST) at 60 °C and 50%RH (1.5 abs. bar) was carried out to verify the enhanced mechanical stability of the composite membranes obtaining a more stable and durable behaviour for composite than pristine membrane. The H_2 crossover measurements effected during the AST supported the obtained results.

2. Experimental

2.1. Preparation of membranes

A commercial powder of TiO_2 (Titanium (IV) oxide, anatase - powder, 99.8% trace metals basis supplied by Aldrich) was used as filler for the preparation of composite Nafion membranes. In order to obtain a homogeneous gran size, the filler was previously treated before to be inserted in the polymer matrix: the powder was milled in a ball milling for 1hr with isopropyl-alcohol (0.5 ml IPA/g) to form a paste that was successively desiccated in an oven at 80 °C for 90 min. IPA was used as degreasing solvent to eliminate any contaminants on TiO_2 surface [36] and to help the hydrophilic property of the powder. A 5 wt.% Nafion® alcoholic solution (Ion Power - Liquion LQ 1105 1100 EW 5 wt.%) was selected to manufacture the films, as described elsewhere [7,8,10]. The obtained dispersion was used to prepare a recast pristine Nafion membrane as a reference membrane (named Nrecast) and three composite membranes using three Titania loadings (5, 10 and 15 wt.%). At first, filler was dispersed in DMAc (5 ml) at room temperature under stirring and then added to a 20 wt.% Nation/DMAc solution. Such a dispersion was treated in an ultrasonic bath for 30 min and successively, through a slow re-concentration at 80 °C under magnetic stirring, suitable viscosity solutions were obtained and stratified on a glass plate by Doctor-Blade casting technique. The obtained membranes were dried on the hot plate at $T = 80$ °C for 3 h s. to eliminate the original solvent and, then, detached from the glass with distilled water. The films underwent a thermal treatment up to $T = 155$ °C to enhance the crystalline phase of the polymer and to improve the mechanical properties [38]. A chemical treatment in HNO_3/H_2O (1:1 vol), 1 M sulphuric acid solutions with intermediate boiling steps in distilled water were carried out [10]. Composite and recast membranes, having a comparable thickness of 50–60 μm, were used both for chemical-physical and electrochemical characterizations.

2.2. Membranes and TiO_2 characterization

2.2.1. Morphological characterization

The oxide morphology (surface SEM on filler) and its distribution within the polymeric matrix (cross-section SEM on composite