Hybrid polymer electrolytes Nafion-TiO$_2$ for PEMFCs: synthesis and characterization

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Abstract
Nafion based hybrid membranes containing titanium dioxide (TiO$_2$) nano particle was synthesized and characterized. Nafion-TiO$_2$ membranes were produced by using in-situ sol-gel technique on Nafion membrane at room temperature. Commercial Nafion membrane was impregnated in Titan tetraisopropoxide (TIP) and then treated in micro-wave. The X-ray diffraction (XRD) shows the crystallization of TiO$_2$ in anatase phase. The Infrared spectroscopy IR spectrum of hybrid membranes Nafion-titanium dioxide confirm the presence of bonds Ti-O-Ti and Ti-OH which proves that the hybridization of the membrane by sol-gel method is successful. Atomic Force Microscopy AFM confirmed the good dispersion of TiO$_2$ nano-particles. The interaction between the organic and inorganic phase is favorable for the improvement of the thermal stability of the hybrid membrane. The nano-TiO$_2$ film can be used to reduce the cross-over permeation of fuel through the PEM and increase electric power of the Fuel cells.

Keywords - Nafion, sol gel, TiO$_2$, fuel cell,

1. Experimental

The core element of a fuel cell is an ion conducting electrolyte membrane. Polymer electrolyte membrane fuel cells (PEMFC, also "proton exchange membrane fuel cells") are a sector where the use of organic-inorganic nanohybrids and nanocomposites is receiving growing attention. Up to date, the well-established perfluorinated polymer electrolytes (Nafion®, Flemion®, and Aciplex® families) are the materials of choice in the construction of commercial membrane-electrode assemblies (MEA) [1].

PEM fuel cells based on perfluorinated membrane electrolytes operate in the temperature range between 60 and 80 °C while elevating the operating temperature provides improved carbon monoxide tolerance, faster electrode kinetics and simpler thermal management [2-3]. However, high temperature results in dehydration of the polymer electrolyte leading to increased membrane resistance and degradation of the membrane–electrode interface. Addition of an inorganic material like SiO$_2$, ZrO$_2$, TiO$_2$ or other metal oxide can alter and improve the water uptake of a polymer electrolyte (such as Nafion) and enable high temperature and low relative humidity PEMFC operation [4-5].

One of the effective approaches is to incorporate hygroscopic metal oxide particles into the hydrophilic domains of the polymer electrolyte membrane to enhance the water retention of the Nafion [6-7]. Titanium dioxide is a good candidate for the hydrophilic filler for the Nafion because it provides suitable hydration of the membrane.
under fuel cell operation conditions. Studies on Nafion/TiO₂ composite membranes have attracted the attention of many research groups. Their results show that the morphological properties of the filler play a key role in the performance of the composite membranes at a high operating temperature [8–9]. Santiago et al. [10] incorporated TiO₂ into Nafion by sol–gel method to form a composite membrane that showed an improved cell performance at 130 °C. However, no morphological study has been reported in their work. Daiko et al. [11] synthesized Nafion composite membrane with combination of both TEOS and TBT alkoxides and tested them in direct methanol fuel cell. They concluded that infiltrated oxides improve the membrane barrier property for methanol. Barbora et al. [12] prepared Nafion/TiO₂ composite membranes with different loadings of TiO₂ by casting method for the possible application in direct ethanol fuel cell.

In this study Nafion/TiO₂ nanohybrid membranes were produced in different concentrations of TiO₂ particles by in situ sol–gel synthesis of titanium dioxide particles in preformed Nafion membranes. Furthermore, a sample is fabricated with TiO₂ particles by the solution casting method to compare different synthesis methods. The porous TiO₂ solution, were then, used as fillers to prepare the Nafion composite membrane. The performance of the membrane was obtained by using this composite [13]. Titan tetraisopropoxide (TIP) is used as precursor and ethanol as the solvent (optimising precursor to solvent weight ratio) for the synthesis of TiO₂ sol [14].

In this work, the fabrication and characterization of Nafion–TiO₂ hybrid electrolytes for proton exchange membrane fuel cell (PEMFC) operating at high temperature are reported. A low temperature sol–gel synthesis, based on the formation of a sol from Ti-peroxy complex, was used to effectively incorporate hydrophilic anatase TiO₂ nanoparticles into the Nafion matrix.

2. Experimental

2.1 Membrane preparation

Nafion–TiO₂ hybrids were produced by in situ sol-gel synthesis of TiO₂ into commercial Nafion 212 membranes. Nafion membranes were previously dried at 110 °C for 24 h and immersed in absolute ethanol. The membrane was added for 45 min to different percentage ([TiO₂]=0.6% and [TiO₂]=1.2%) of TiO₂ sol. In order to promote the formation of the Ti-peroxy sol, hydrogen peroxide was added. Then, the membrane-solution mixture was submitted to consecutive heat treatments at room temperature for 7 h in micro-wave. Finally, the produced membranes were exhaustively treated in 0.5 mol L⁻¹ H₂SO₄ and water at 70 °C to remove residues. To confirm the crystallization process of TiO₂ in the Nafion membrane at room temperature, we have characterized hybrid membranes.

2.2 Characterisation

The structure and morphology of the membrane was characterized by X-ray diffraction (XRD) spectra were recorded with an automated Bruker D8 advance X-ray diffractometer with CuK radiations (40 kV and 30 mA) for 2θ values over 5–80°. The spectra were obtained with a Fourier transform infrared spectrometer FT-IR was used to analyze the chemical and structural properties of membranes. In this work measurements are performed using a spectrometer VERTEX 80. Infrared analysis is performed in two parts: the mid-IR (4000 cm⁻¹ - 400 cm⁻¹) and far IR (700 cm⁻¹-50 cm⁻¹) with a resolution of 4 cm⁻¹. The surface morphology of membranes was studied by Topometrix TMX 2000 Explorer Atomic Force Microscopy (AFM). This deflection allows characterizing the surface morphology and measuring the surface roughness. The roughness can be characterized via the roughness RMS (Root Mean Square).

3. Results and discussion

3.1. X-ray diffraction (XRD):

Fig. 1 shows the XRD patterns of the Nafion and the hybrid membranes. The diffractograms of the hybrid Nafion membranes with different amounts of TiO₂ sol-gel method according to room temperature showed the presence of additional peak compared to the pure Nafion membrane. Indeed, for Nafion hybrid membrane with [TiO₂]=0.6%, we note the presence of peak at 12.32 ° but for the hybrid membrane with [TiO₂]=1.2%, it shows the presence of another two peaks at 22.82 and 25.57 °. This confirms that crystalline TiO₂ was present in the anatase phase.
3.2. **FT-IR ATR analysis:**

The characterization of pure Nafion and modified membranes with different concentrations of TiO$_2$ shows the presence of IR bands of TiO and TiO$_2$. The crystallization of titanium dioxide at anatase form confirms the results found by XRD as shown in Figure 2. The hybrid membranes of Nafion TiO$_2$ exhibit new bands compared to that of pure Nafion. Indeed, the membrane of hybrid nafion with [TiO$_2$]=0.6% present bands at 226, 242, 326, 336,385, 409, 421 cm$^{-1}$. When we varied the concentration of TiO$_2$ at 1.2% these bands become respectively at 221,239, 328, 336, 385,404 and 450 cm$^{-1}$ [15]. The reference spectrum of the TiO$_2$ hybrid membrane is identical to that of pure Nafion membrane up to 1500 cm$^{-1}$:

- The bands allocated to the CF$_2$ group are intense bands at 1155 and 1215 cm$^{-1}$ (stretching vibrations symmetric and antisymmetric of CF), and less intense bands at 520 and 637 cm$^{-1}$. [16, 17]
- The bands associated with hanging chain are present at 1065, 970 and 1295 cm$^{-1}$ (respectively stretching vibrations of SO$_3^-$, symmetric and antisymmetric stretching S = O of the group SO$_3^-$), and 982 cm$^{-1}$ (symmetric stretching vibration of CO group COC). [18, 19]

**Fig.1**: XRD patterns for: (a) pure Nafion$_{212}$ membrane; hybrid Nafion membrane with TiO$_2$: (b) for [TiO$_2$]=0.6% and (c) for [TiO$_2$]=1.2%.

**Fig.2A**: FT-IR ATR Nafion 212 difference spectrum of Nafion/(TiO$_2$) membranes; each spectrum is obtained by subtracting the FT-IR ATR spectrum of side: (a) pure Nafion$_{212}$ membrane; hybrid Nafion membrane with TiO$_2$; (b) for [TiO$_2$]=0.6% and (c) for [TiO$_2$]=1.2%.
The important fact is the apparition of pick at 430 cm\(^{-1}\) assigned for Ti-O-Ti bonds. Let’s note that J. Sabataityté et al had determined the strip of absorption of the Ti-O-Ti bonds at 440 cm\(^{-1}\) [20].

In general, lattice water absorbs at 2884-3420 cm\(^{-1}\) (antisymmetric and symmetric OH stretching) and at 1630-1600 cm\(^{-1}\) (HOH bending) [21, 22].

**Figure 2B** : FT-IR ATR spectrum of Nafion 212 membrane shown in the wave number range between 1300 and 4000 cm\(^{-1}\) : (a) pure Nafion 212 membrane; hybrid Nafion membrane with TiO\(_2\) : (b) for [TiO\(_2\)] = 0.6% and (c) for [TiO\(_2\)] = 1.2%.

3.3. Atomic force microscopy (AFM)

AFM is considered an appropriate technique to analyze the phase distribution of polymer/inorganic composite materials [23]. The following AFM images (Fig. 3) of the Nafion and the Nafion/TiO\(_2\) hybrid membranes show the change of Nafion morphology. This change is clearer observed with a percentage of 1.2% of TiO\(_2\).

Nafion hybrid membranes with TiO\(_2\) exhibit a surface topography is composed of groups of varying size TiO\(_2\) with irregular shapes. The irregular shape of nanoparticles is caused by low temperatures and the kinetic energy is not sufficient to induce the coalescence of grains. Surface morphological changes were observed in the hybrid nafion membranes with 1.2% of [TiO\(_2\)] nanoparticles are well separated and become more visible.

In the AFM micrographs, the TiO\(_2\) inorganic nanoparticles can be clearly observed in the hybrids membranes. AFM is considered an appropriate technique to analyze the phase distribution of polymer/inorganic hybrids materials. The high contrast of the color distribution in narrow diameters suggests that the "hard" TiO\(_2\) is well dispersed in the polymer electrolyte, while the relatively featureless boundary implies that many of the TiO\(_2\) nanoparticles are covered by the “soft” polymer ionomers. The harmonization between the inorganic phase and polymer phase decreases the contrast of the inorganic domains. The surface roughness of the composite membranes is presented in the 2D-height AFM images (Fig. 3). The surface of the composite membrane is clearly very smooth. In the presence of Nafion ionomers, self assembly would occur between the positively charged TiO\(_2\) and the negatively charged SO\(_3^-\) end groups of Nafion ionomers by the electrostatic force. The self-assembly of the Nafion and TiO\(_2\) nanoparticles also give the composite structure a good compatibility on the interface [24].
Fig. 3: AFM surface morphology images of membranes: (a) pure nafion membrane; hybrid nafion membrane with TiO$_2$: (b) for [TiO$_2$]=0.6% and (c) for [TiO$_2$]=1.2%.

4. Conclusion

The comparison between the spectrum of pure Nafion and hybrid with TiO$_2$ shows that the chemical structure of Nafion has been preserved in the memorandum of incorporation of TiO$_2$ nano-particles: All characteristic bands of Nafion are highlighted in the spectrum of the Nafion-TiO$_2$ hybrid membrane. Nafion–TiO$_2$ hybrid electrolytes were successfully prepared by sol–gel process at room temperature. This improvement is associated with more efficient water management at the electrode/electrolyte interface due to the hygroscopic properties of the oxide nanoparticles, as inferred from Infrared spectroscopy. The hybrid membranes was observed, indicating that the presence of the inorganic phase has an important contribution to Nafion, conferring to the hybrid membrane a better stability in severe fuel cell operating conditions.

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References


