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Development of Polymer Nanocomposites as Electrolyte Membranes

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Summary: Confidence in the potential of hydrogen as an energy vector and fuel bring the opportunities for enhancing electrolyzer performance. The aim of this paper is to develop new polymer nanocomposites as electrolyte membranes for PEM-electrolyzer. A series of nanocomposite membranes, including GEFC/TiO_2, GEFC/CNTs, and GEFC/TiO_2CNTs have been developed and characterized by FT-IR spectroscopy and AFM. The application of polymer nanocomposite membranes in electrochemical cells for water electrolysis was investigated. Experimental results obtained with respect to performance are reported and discussed related to GEFC membrane.

Keywords: ion exchangers; membranes; nanocomposites; nanostructures; PEM-electrolyzer

Introduction

Electrolyzer technology may be implemented at a variety of scales wherever there is an electricity supply to provide hydrogen and/or oxygen for nearly any requirement. The increasing demand for hydrogen produce by latest advances in fuel cell technology are driving the need for the development of materials involved in H_2/O_2 proton exchange membrane (PEM) electrolyzer. Well-proven and long-lived PEM electrolyzer is an alternative to systems based on liquid alkali electrolytes. The operation of a PEM electrolyzer depends on the use of efficient metal catalysts and a solid polymeric electrolyte that operates acidic electrochemistry conveying protons. Desirable properties of those electrolytes include chemical and electrochemical stability, high proton conductivity, zero electronic conductivity, very low permeability to reactant gases, mechanical strength, stability for ease of assembly.[1,2]

Most successful proton conducting membranes are made from organic polymers that contain a significant contribution of covalently bonded fixed ionic groups, with the advantages of good flexibility, toughness, and separation properties. The two types of polymers actually used are: 1. styrene/divinylbenzene copolymers or vinylpyridine/divinylbenzene copolymers; 2. copolymers of a perfluorinated alkene and a substituted perfluorinated alkene.[3] Widely employed in PEM electrolyzers applications is Dupont's fluorocarbon-based ionomer known as Nafion.[1,4]

Organic–inorganic composite membranes of Nafion modified by inorganic additives (SiO_2, TiO_2, ZrO_2) have been also developed and studied with the main objective of increasing the proton conductivity of the membrane and the efficiency of power devices.[5–7]

Hybrid materials can combine basic properties of organic and inorganic materials and offer particular advantages for the synthesis of composite membranes with improved performances, good thermal and chemical resistance.[8,9] Titanium oxide is good hydrophilic filler for the composite polymer membranes because it allows a proper hydration of the membrane under electrolyzer operative conditions to be maintained.[10] The attention is oriented also on introducing CNTs into polymer matrices in order to obtain composites for

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high performance materials as tremendous promise in improving the performance of power devices.[11,12] The use of CNTs in PEM fuel cells or PEM electrolyzers has been a recent pursuit with the potential for significant enhancement of some distinctive properties. Reported results do not show an increasing of proton conductivity by CNTs addition, but the response in the higher performance to improve properties as water management, gas permeability, and thermal stability was observed for the CNTs–Nafion composite membrane.[13]

Experimental Part

The polymer nanocomposites have been prepared by using commercial perfluorinated proton exchange solution, 5 wt.% GEFC-510 (equivalent weight (EW) = 1000 g/mol, Golden Energy Fuel Cell Co., Ltd., Beijing), TiO_2 (190–290 m^2/g surface area and particle size <15 nm, anatase form, Sigma Aldrich) and CNTs ($d < 10$ nm, length: 5–15 μm, P: ≥95%, specific surface area: 40–300 m^2/g, Shenzhen Nanotech PortoCo., Ltd., China). The surface of the CNTs was modified with an acid treatment by refluxing with HNO_3 (3 M) (Merck reagent) for 24 h, followed by washing with de-ionized water until neutral pH and then the sample were dried in air for 30 min at 100 °C.[14]

The samples were prepared by the following procedure. An appropriate amount 5 wt. % GEFC-510 solution was mixed with TiO_2, CNTs or TiO_2/CNTs powders in an ultrasonic bath for 30 min. The mixed solutions were casted in a glass model and heated at 70 °C till the solvent was evaporated. Then, the recast polymer nanocomposite electrolyte membranes were detached from the glass model by adding some de-ionized water. Finally, the samples were purified by heating at 80 °C in the solution of 3% H_2O_2 for 1 h, de-ionized water for 2 h, 0.5 M H_2SO_4 for 1 h and in de-ionized water for 2 h, respectively.

A series of polymer nanocomposites, which have 5 wt. % or 10 wt. % TiO_2 and 2.5 wt. % or 5 wt. % CNTs compared with the dry GEFC-510 were denoted as 5TiO_2-GEFC, 10TiO_2-GEFC, 5TiO_2-2.5CNTs-GEFC, 10TiO_2-5CNTs-GEFC, 2.5CNTs-GEFC, and 5CNTs-GEFC, respectively. Samples without TiO_2 and CNTs addition (matrix samples) were also obtained for comparison and indexed as GEFC.

Fourier transform infrared (FT-IR) spectra were collected using a Jasco FT/IR – 6200 spectrometer with VeeMAX^{TM} II (Pike technology) accessory – variable angle specular reflectance at 45 grades with single reflection ATR crystals, and 8 cm^{-1} resolution. Surface topography of the recast membranes was measured by atomic force microscopy (AFM) using STM platform Ntegra Prima, in semicontact mode.

Energy efficiency and Faraday efficiency of a PEM electrolyzer were determinate towards to investigate the behavior of polymer nanocomposite and GEFC recast membranes during operating conditions as PEM electrolyte. The electrolyzer (cell active area - 9 cm^2) has been connected directly to an external power source (DC power) to produce hydrogen and oxygen from water. To ensure the same condition for electrolyzer testing, the 20 wt. % teflonised Toray carbon paper (E-TEK Division), were used on both the anode and the cathode. The catalyst ink consisted of 20 wt. % Pt/VXC72 (QuinTech) in isopropyl alcohol. The anode and cathode loading were 1 mg/cm^2.

Results and Discussions

The characteristic of FT-IR spectra for obtained polymer nanocomposites are shown in Figure 1 (A and B). The peaks that observed at 1055–1056 and 975–980 cm^{-1} are attributed to the stretching vibrations of SO_3– and C–O–C, respectively. The characteristic peaks in the region 1100–1400 cm^{-1} can be attributed to C–F bond (C–F stretching vibrations of GEFC backbone).[15] The band 1740 cm^{-1} is assigned to C=O stretching. The characteristic peaks corresponding to C–H

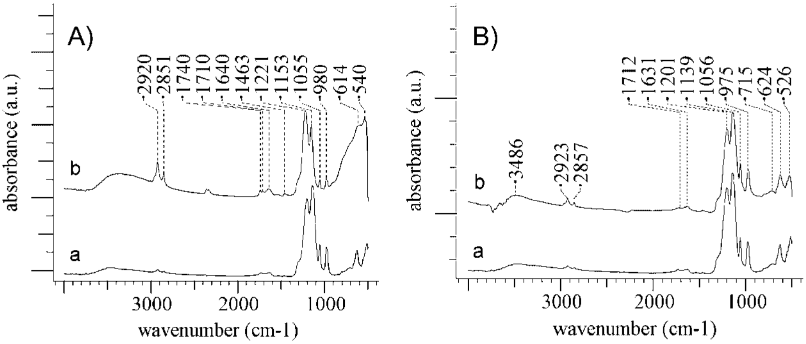

Figure 1.
FT-IR spectra for: (A) – GEFC (a), $10TiO_2$-GEFC (b) and (B) – GEFC (a), 5CNTs-GEFC (b).

stretch vibrations modes in alkyl chain are also found at ~2850 cm^{-1} and ~2920 cm^{-1}. In the region 3200–3500 cm^{-1}, O–H stretching vibrations were observed.[15] The existence of two absorption bands at 1712 cm^{-1} and 3486 cm^{-1} for the infrared spectrum of 5CNTs-GEFC are considered an indicative for the acid-treated CNTs contribution. The band at 3486 cm^{-1} is more obviously, at some intensities of bands found at ~2850 cm^{-1} and ~2920 cm^{-1}, due to CNTs contribution partly cover on the contribution of O–H stretching vibrations and polymer structure. Two new small bands are evidenced at 540 cm^{-1} and 614 cm^{-1} for $10TiO_2$-GEFC and can be assigned to interaction between TiO_2 anatase form and polymer matrix.

The AFM offers a method for directly observing the three dimensional structure of membranes. Using the AFM, individual nanostructures and groups of nanostructures can be visualized, providing spatial distribution information on nanocomposite materials. The surface topography evidenced by AFM, for obtained polymer nanocomposites show distinctive features. A random disposition of polymer chains concentration due to of lack of the ordering factor is observed for GEFC (Figure 2a). The recast polymer nanocomposite films with nano-sized TiO_2 show a different morphology (Figure 2b). The graft potential of polymer chains on TiO_2 nanoparticles is bigger one and the three dimensional shape of those is in charge to macromolecules arrangement as bundles around of TiO_2 nanoparticles. The arrangement leads on multi-segment channels because of spherical interfaces of macromolecular bundles. Thus, the multi-segment channels involved to polymer nanocomposites with an increasing porosity degree comparing to GEFC. The change of nanostructures type from tridimensional (TiO_2) to fibrillar (CNTs) leads to changes of membrane morphology with a preponderant orientation of macromolecules along CNTs (Figure 2d). The porosity degree is lower as linear interfaces among polymer macromolecules. As can be shown in Figure 2c, the surface of TiO_2-CNTs-GEFC samples becomes a mixture of above-mentioned characteristics as a result of both tridimensional and fibrillar components. Above-mentioned results are supported also by calculated average roughness values (GEFC: 210.49 nm, $10TiO_2$-GEFC: 151.48 nm, $10TiO_2$-2.5CNTs-GEFC: 290.88 nm, 5CNTs-GEFC: 125.12 nm).

Membrane electrode assemblies (MEAs) have been performed and tested to provide some preliminary performance data of PEM electrolyzer as well as polymer nanocomposite membranes performance in operating conditions (atmospheric pressure and room temperature). The time, voltage and current values have been recorded in Table 1 for certain volume (10 cm^3 in our case) of hydrogen gas produced. The

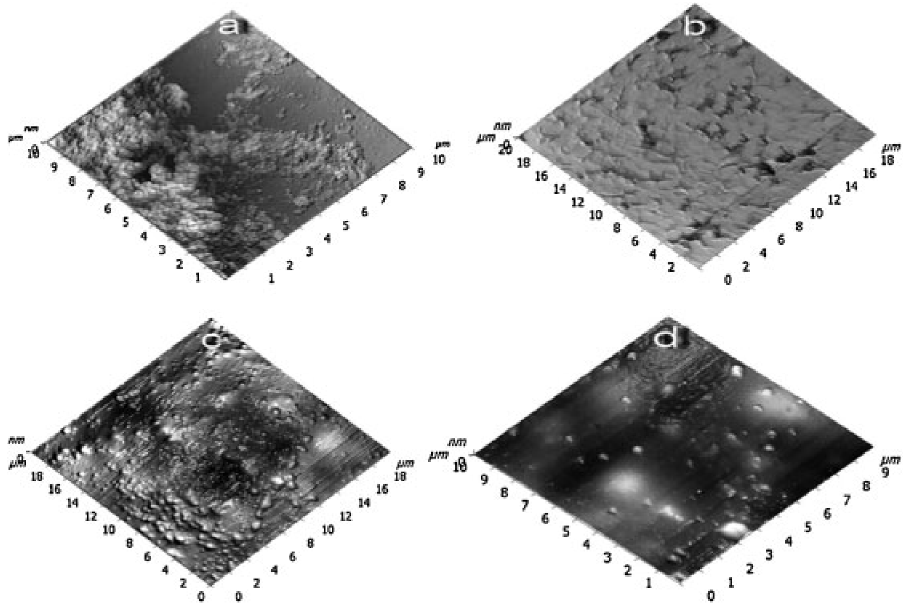

Figure 2.
AFM surface topography for GEFC (a), 10TiO_2-GEFC (b), 10TiO_2-2.5CNTs-GEFC (c), 5CNTs-GEFC (d).

Table 1.
Results of PEM electrolyzer test.

Sample	I (mA)	U (V)	t (s)	Faraday efficiency	Energy efficiency (%)
GEFC	470	3	151	84.96	55.98
5TiO_2-GEFC	470	2.9	146	87.87	59.90
10TiO_2-GEFC	470	3.1	150	85.53	54.54
5TiO_2-2.5CNTs-GEFC	470	2.8	165	77.76	54.89
10TiO_2-5CNTs-GEFC	470	3.1	216	59.40	37.87
2.5CNTs-GEFC	470	2.8	630	20.36	14.37
5CNTs-GEFC	470	3.1	773	16.59	10.58

addition of nano-sized TiO_2 particles improves the Faraday and energy efficiency of the PEM electrolyzer. Increasing the TiO_2 amount in the same experimental conditions, the electrolyzer performance is a little bit lower and close to that for GEFC membrane. How it can be observed in Table 1, addition of CNTs leads to a drastic decreasing of electrolyzer performance. The results show that the addition of adequate quantity of nano-sized TiO_2 particles can reach to an improved electrolyzer performance.

Conclusions

Polymer nanocomposites membranes, TiO_2-GEFC, TiO_2-CNTs-GEFC and CNTs-GEFC, were prepared by use of commercial perfluorinated proton exchange solution (GEFC) and nano-sized structures (TiO_2 and CNTs) followed by solution casting. The polymer nanocomposite membranes were characterized by FT-IR and AFM as well as PEM electrolyzer performance. AFM analysis shown that TiO_2-GEFC samples have the biggest porosity degree according with results from PEM electrolyzer tests. We show that the addition of an adequate amount of TiO_2 nano-sized particles in GEFC solution leads to a better performance of PEM electrolyzer with TiO_2-GEFC electrolyte.

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[1] P. Sivasubramanian, R. P. Ramasamy, F. J. Freire, C. E. Holland, J. W. Weidner, *Int. J. Hydrogen En.* **2007**, *32*(4), 463.

[2] I. Radev, E. Slavcheva, E. Budevski, Proceedings of the International Workshop "Portable and Emergency Energy Sources – from Materials to Systems" 16–22 Sept. 2005, Primorsko, Bulgaria.

[3] T. A. Davis, J. D. Genders, D. Pletcher, A first course in Ion Permeable Membranes, Alresford Press, UK **1997**.

[4] Y. Zhang, C. Wang, N. Wan, Z. Liu, Z. Mao, *Electrochem. Comm.* **2007**, *9*(4), 667.

[5] N. H. Jalani, K. Dunn, R. Datta, *Electrochim. Acta* **2005**, *51*, 553.

[6] M. Watanabe, H. Uchida, Y. Seki, M. Emori, P. Stonehart, *J. Electrochem. Soc.* **1996**, *143*(12), 3847.

[7] M. Watanabe, H. Uchida, M. Emori, *J. Phys. Chem. B* **1998**, *102*, 3129.

[8] Y. Yang, P. Wang, *Polymer* **2006**, *47*, 2683.

[9] C. Guizard, A. Bac, M. Barboiu, N. Hovnanian, *Sep. Purif. Technol.* **2001**, *25*, 167.

[10] A. Sacca, A. Carbone, E. Passalacqua, A. D'Epifanio, S. Licoccia, E. Traversa, E. Sala, F. Traini, R. Ornelas, *J. Power Sources* **2005**, *152*, 16.

[11] P. W. Lu, E. R. Garcia, R. L. Ammon, *J. Appl. Electrochem.* **1981**, *11*(3), 347.

[12] S. Motupally, A. J. Becker, J. W. Weidner, *J. Electrochem. Soc.* **2002**, *149*(5), D63.

[13] R. Jiang, H. R. Kunz, J. M. Fenton, *J. Membrane Sci.* **2006**, *272*, 116.

[14] J. F. Colomer, P. Piedigrosso, A. Fonseca, J. B. Nagy, *Synth. Met.* **1999**, *103*, 2482.

[15] Z.-G. Shao, P. Joghee, I.-M. Hsing, *J. Membrane Sci.* **2004**, *229*, 43.