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# Nafion–titanate nanotubes composites prepared by *in situ* crystallization and casting for direct ethanol fuel cells

B.R. Matos<sup>a,\*</sup>, R.A. Isidoro<sup>a</sup>, E.I. Santiago<sup>a</sup>, A.C. Tavares<sup>c</sup>, A.S. Ferlauto<sup>b</sup>,  
R. Muccillo<sup>a</sup>, F.C. Fonseca<sup>a</sup>

<sup>a</sup> Instituto de Pesquisas Energéticas e Nucleares, IPEN, Av. Prof. Lineu Prestes, 2242, São Paulo, SP 05508000, Brazil

<sup>b</sup> Universidade Federal de Minas Gerais, Departamento de Física, UFMG, Avenida Antônio Carlos, 6627, Belo Horizonte, Minas Gerais 31270901, Brazil

<sup>c</sup> Institut National de la Recherche Scientifique, Énergie, Matériaux et Télécommunications, INRS-EMT, 1650 Boulevard Lionel-Boulet, Varennes, Québec J3X 1S2, Canada

## ARTICLE INFO

### Article history:

Received 21 October 2014

Received in revised form

13 November 2014

Accepted 18 November 2014

Available online 17 December 2014

### Keywords:

Direct ethanol fuel cell

Nafion

Composite

Water retention

## ABSTRACT

The physical properties relevant for the application of Nafion–titanate nanotubes composites in electrochemical devices such as water absorption capacity, ion conductivity, and thermal stability are reported. The nanocomposites were prepared by *in situ* hydrothermal conversion of anatase into titanate nanotubes in Nafion matrix and by casting of nanotube suspensions in Nafion. Composites were characterized by differential scanning calorimetry (DSC), dynamic vapor sorption (DVS), X-ray diffraction (XRD), transmission electron microscopy (TEM), proton conductivity, and tested in direct ethanol fuel cells (DEFC). Nafion–titanate nanotubes displayed higher water retention capacity in comparison with Nafion–titania composites as revealed by DSC and DVS. The ion conductivity at intermediate temperatures (80–130 °C) for Nafion–titanate nanotube composites is higher than Nafion–titania composites indicating that the hydrophilicity and conduction properties of the titanate phase contributed to the improvement of the membrane electrical properties. The Nafion–titanate nanotube composites prepared by *in situ* sol–gel exhibited improved electric and electrochemical performance at high temperatures compared to the composite prepared by casting. The combined XRD, DSC, and TEM data indicated that at RH = 100% Nafion–titanate nanotubes are thermally stable up to 130 °C, but for higher temperatures the titanate nanotubes are converted to rutile nanorods.

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## Introduction

Direct ethanol fuel cells (DEFCs) have been considered to be cleaner and more efficient energy converters as compared to

conventional fossil-fueled devices [1–3]. However, several drawbacks such as short-term durability of DEFCs components, high ethanol crossover through the polymer electrolyte, and sluggish ethanol oxidation and oxygen reduction

\* Corresponding author.

E-mail address: [brmatos@usp.br](mailto:brmatos@usp.br) (B.R. Matos).  
<http://dx.doi.org/10.1016/j.ijhydene.2014.11.102>

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reactions severely reduce their conversion efficiency. Such hurdles have postponed the commercialization of this type of fuel cell [1]. One approach to improve the DEFC performance is to increase the operating temperature and lifetime by replacing the traditional polymer membrane for a mechanically robust and a high-proton conducting electrolyte [4,5].

The proton conductivity in hydrated Nafion membranes is strongly dependent on the dynamics of absorbed water molecules [6–8]. At 80 °C and high relative humidity (RH = 100%), Nafion exhibits high proton conductivity as a result of the predominant structural diffusion over the vehicular transport of protons in the electrolyte [9]. Such feature results in high power density outputs in polymer electrolyte fuel cells running on hydrogen [2]. In addition, perfluorosulfonate ionomers, such as Nafion, are known to have superior thermo-mechanical properties and chemical stability when compared to conventional polymers [8,10]. However, Nafion membranes have a high permeability to alcohol fuels such as methanol and ethanol, which decreases dramatically the fuel cell efficiency due to the alcohol oxidation reaction at the cathode [1,2,4,5]. Moreover, such solvent molecules act as plasticizers thereby reducing the mechanical stability of ionomer electrolytes during fuel cell operation [11].

The DEFC operation without appropriate electrocatalysts and at a low temperatures is hindered by incomplete ethanol oxidation that results in the formation of substantial amounts of by-products such as acetic acid and acetaldehyde [12–14]. Several studies have concentrated on the development of new electrocatalysts to improve ethanol oxidation and increase the DEFC efficiency [12–14]. It has been demonstrated that efficient operation of DEFC is attained in the 110–130 °C temperature range by using high-performance electrocatalyst alloys [12–14]. More recent results have shown that the efficiency of DEFC, using Polybenzimidazole (PBI) electrolytes and electrocatalysts based on Platinum alloys, increases as the operation temperature increases in the 130–260 °C range [15,16]. Thus, the increase of DEFC operation temperature has been a subject of great interest for increasing the ethanol oxidation efficiency, while enhancing the both water and heat managements of the device [17]. However, fewer studies have dedicated to tailor new electrolyte membranes in order to increase the DEFC efficiency. The increase of the operation temperature is limited by the standard polymeric electrolyte (Nafion), which, in its pristine form, does not possess the thermal stability and the water retention necessities to sustain high temperature conditions [5]. Indeed, to increase the DEFC temperature above 100 °C has been a hard task. As an alternative, PBI membranes with high thermal stability and high proton conductivity at high temperatures have been used as electrolytes allowing the operation of DEFC at higher temperatures [15,16]. However, PBI membrane shares some common deficiencies with Nafion, such as ethanol crossover and the reduction of the proton conductivity due to the leaching out of the charge carriers, which drastically reduces the DEFC performance [18]. The performance of fuel cells directly fed with alcohols using different electrolyte such as solid acid proton conductors ( $T \sim 243$  °C) [19,20] and PBI ( $T \sim 200$  °C) [15] and Nafion based composites ( $T \sim 130$  °C) [4,5,27] the reported power densities are of the order of  $\sim 35$  mW cm<sup>-2</sup>,  $\sim 10$ –60 mW cm<sup>-2</sup> and  $\sim 20$ –50 mW cm<sup>-2</sup>. In this framework, the increase of the DEFC efficiency cannot be only met by

increasing the operation temperature and must be accompanied by the development of electrolyte materials with low fuel crossover, low thickness, high and stable proton conductivity at high temperature [21–24].

In order to overcome such limitations, the addition of inorganic hydrophilic fillers (TiO<sub>2</sub>, SiO<sub>2</sub>, etc) to Nafion has been considered. However, such materials have relatively low superficial ion conductivity ( $\sim 10^{-4}$  S cm<sup>-1</sup>) and, thus, significant reductions in the proton conductivity of the composite membranes are usually observed [4,26]. In this sense, the use of proton conducting fillers such as titanate nanotubes (H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>·nH<sub>2</sub>O) can improve the mechanical stability and lower the alcohol permeability without drastically reducing the conductivity of the composite [26,27]. Recently-developed titanate nanotubes have high specific surface area, high hydrophilicity, and high proton conduction at high relative humidity ( $\sim 10^{-2}$  S cm<sup>-1</sup>– $10^{-3}$  S cm<sup>-1</sup>), thus good candidates to be used as fillers in Nafion membranes [28].

In a previous report, we showed that the Nafion–titanate nanotube composites, prepared *in situ* by the crystallization of 1D structures directly inside Nafion, have enhanced properties with respect to Nafion–titania composites that resulted in a significant boost of DEFC performance at 130 °C [27]. However, DEFC performance at high temperatures has been associated with different parameters, such as thermal stability, morphology, water retention, ethanol crossover, and proton conductivity [4]. Thus, the present study investigates the influence of the synthesis method on relevant properties of composite electrolytes, such as thermal stability and water absorption and retention capacities. These properties directly affect the proton conductivity and fuel cell performance and are relevant to advance the understanding of Nafion-based composite electrolytes.

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## Experimental

### Membrane synthesis

Titania (TiO<sub>2</sub>) nanofillers in acid Nafion membranes (N115/H) were prepared *in situ* by the sol–gel method. The methodology consisted of the controlled hydrolysis of titanium tetraisopropoxide embedded in Nafion commercial membranes (N115) using a hydrogen peroxide solution [29]. The resulting Nafion–titania (N–TiO) composite membranes were washed and protonated [29]. For the titania to titanate nanotubes conversion, the N–TiO composite membranes ( $4 \times 4$  cm<sup>2</sup>) were immersed in 50 mL of a concentrated basic solution (NaOH/10 mol L<sup>-1</sup>) and placed inside a Teflon covered stainless steel reactor. A microwave-assisted hydrothermal process was performed by placing the reactor in a microwave oven at 140 °C for 180 min. The resulting Nafion–titanate nanotubes membranes in the sodium form (Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>·nH<sub>2</sub>O – N-TN/Na) were copiously washed with distilled water at 70 °C to remove excess of sodium hydroxide. Ion exchange was carried out overnight at room temperature to convert the membranes to the proton form (H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>·nH<sub>2</sub>O – N-TN/H) by immersing the N-TN/Na in a 400 mL dilute solution of HCl (0.1 mol L<sup>-1</sup>) and subsequently washed with distilled water to remove excess of chemicals. The N-TN composite samples in the proton and sodium forms were synthesized with volume fractions of  $\sim 16$  vol% and  $\sim 15$  vol%,

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