



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/hydro

Functionalized Al₂O₃ particles as additives in proton-conducting polymer electrolyte membranes for fuel cell applications

Mario Branchi, Mirko Sgambetterra, Ida Pettiti, Stefania Panero, Maria Assunta Navarra*

Sapienza University of Rome, Chemistry Department, Piazzale Aldo Moro 5, 00185 Roma, Italy

ARTICLE INFO

Article history:

Received 2 April 2015
Received in revised form
15 June 2015
Accepted 7 July 2015
Available online xxx

Keywords:

Functionalized acidic alumina
Composite polymer membranes
Proton conducting electrolyte
Hydrogen fuel cells

ABSTRACT

This study reports on the synthesis and characterization of sulfated Al₂O₃ and of composite membranes, prepared by dispersing the functionalized oxide in Nafion, acting as electrolytes in proton-exchange membrane fuel cells.

Different synthetic routes were explored to obtain nanometric alumina particles with sulfate groups. Structural and morphological characteristics of the inorganic compounds and the nature of the bond of the sulfates with the oxide were investigated by x-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy, N₂ adsorption and thermal gravimetric analysis. Key properties of the hybrid membranes were elucidated in terms of thermal characteristics, water uptake and ionic exchange capacity. Functionality of the nanocomposite membranes, compared with plain Nafion, was tested in hydrogen-fed fuel cells. Polarization and power density curves and in-situ electrochemical impedance spectroscopy were accomplished to evaluate the effect of temperature on the cell performance.

It is shown that well-addressed variations in the synthetic routes are able to determine different morphologies and dimensions of the particles and different degrees of functionalization. The incorporation of alumina in Nafion changes the characteristics of the membrane, with special regard towards hydration. In-situ fuel cell electrochemical tests reveal improved electrode-composite membrane interface properties as the working temperature of the cell increases.

Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Sulfated metal oxides are a very attractive class of materials, known for their super-acidity. Among the solid acids, they

have a particularly high acid strength characterized by values on the Hammett function scale $H_0 > -12$, that is the acidity of sulfuric acid [1].

The acidity gained by a metal oxide upon sulfate functionalization can be related to the nature of the sulfate group

* Corresponding author.

E-mail address: mariassunta.navarra@uniroma1.it (M.A. Navarra).

<http://dx.doi.org/10.1016/j.ijhydene.2015.07.030>

0360-3199/Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

that increases overall Lewis acidity thanks to its electron-withdrawing effect. The Lewis points can easily convert to Brønsted acid points in the presence of water, so that the sulfated compound finally acts as proton donor [2,3]. These properties conferred the ability to some metal oxides, when sulfated, to catalyze reactions typical of very strong acid catalysts at low temperatures. Indeed, great attention has been devoted for example to Zr, Ti, Fe and Sn oxides with sulfate functionalization due to their great activity in different organic reactions, e.g. hydrocarbon skeletal isomerization or alkylation of paraffins [4,5].

Generally, sulfation is easily realized on the amorphous precursors of the oxides, such as hydroxides or oxyhydroxides, in order to result in high activity. Exception occurs with Al_2O_3 and little is known on the catalytic properties of nanosized sulfated alumina [6–9]. Arata et al. reported that sulfated alumina (S- Al_2O_3) prepared starting from $\gamma\text{-Al}_2\text{O}_3$ with high surface area is a superacid with $H_0 \leq -14.5$ [10].

Prompted by the interesting but still few studies on this compound, we decided to further investigate sulfated alumina in order to determine the appropriate conditions for its synthesis and the influence of sulfate content on some fundamental properties of the oxide. Moreover we were interested in the application of such sulfated particles as additives in Nafion membranes, with the aim of forming highly conductive composite polymer electrolytes, to be used in hydrogen-fed, high temperature fuel cells.

Indeed, one of the major issues still limiting the widespread commercialization of polymer electrolyte membrane fuel cells (PEMFCs) as clean and efficient energy conversion devices is related to the conventionally adopted benchmark Nafion electrolyte. Although having many positive characteristics, such as high proton conductivity, mechanical and chemical stability, Nafion most favorable properties are exhibited only under full humidification and limited temperatures ($T \leq 80\text{ }^\circ\text{C}$) [11,12]. A promising strategy to improve the performance of PEMs is based on the incorporation of nanometer sized particles of hygroscopic inorganic acids or oxides, which play the function of providing additional acid groups for proton conduction and/or enhancing water retention [13–20]. Due to their intrinsic super-acidity and tunable properties, sulfated metal oxides are very attractive candidates as additives to form hybrid, nano-composite membranes having adequate performances at low relative humidity (RH) and high temperature. We recently investigated sulfated zirconium [21–25], titanium [26] and tin oxides [27,28] as proton conductors or fillers in polymer systems. To our knowledge there is no study concerning the application of sulfated alumina in Nafion membranes. For this reason we propose here a double-task investigation. Firstly, the synthesis and characterization of sulfated aluminum oxide in terms of structure, morphology, acidic properties and degree of functionalization was performed. Secondly, the incorporation of selected S- Al_2O_3 particles within a Nafion matrix was realized, in order to evaluate the influence of the inorganic additive on the functional properties of composite polymer electrolytes.

Experimental section

Preparation of sulfated alumina

A two-step procedure, consisting of Al_2O_3 preparation followed by sulfation of the obtained powder, was addressed.

A sol-gel synthesis was adopted to obtain Al_2O_3 , starting from an alkoxide precursor, through the following steps: i) hydrolysis of the alkoxide; ii) peptization to sol; iii) gel formation; iv) calcination to oxide. In a first approach the sol was made by using nitric acid as the peptization agent, according to a synthesis procedure proposed by Yoldas et al. [29,30]. In a second approach, a polymeric template was used, according to a non-ionic peptization mechanism [31,32].

Details on the two syntheses for Al_2O_3 preparation are given below:

- 1) Al-isopropoxide (Aldrich) was added to hot water ($T = 80\text{ }^\circ\text{C}$) to form a mono-hydroxide precipitate during the hydrolysis. HNO_3 was added in the molar ratio alkoxide/ HNO_3 equal to 0.07 to obtain the sol. The water solvent was removed by evaporation bringing to gelation, after which calcination was conducted at $550\text{ }^\circ\text{C}$ for 3 h. Al_2O_3 powders obtained according to this synthesis will be labeled as Y.
- 2) A mixture of deionized water and isopropanol was added to a solution composed by Al-isopropoxide (Aldrich) and Pluronic 123 copolymer (Aldrich, $M_w \approx 5800$) in isopropanol, according to a molar relative composition of polymer: Al-isopropoxide: H_2O equal to 0.1: 1: 2. The mixture was left for 16 h at room temperature and a gel was obtained. The excess of polymer was washed off with ethanol. The complete removal of polymer occurred during the calcination step performed at $550\text{ }^\circ\text{C}$ for 3 h. Al_2O_3 powders obtained according to this synthesis will be labeled as M.

Sulfation procedure consisted of an impregnation of both synthesized oxides in sulfuric acid [33]. 1 g of powder was added to 10 ml of diluted sulfuric acid and kept under stirring for 10 min. Then, after separation and filtration, another calcination step was performed at $550\text{ }^\circ\text{C}$ for 3 h. For each alumina sample, sulfuric acid concentration, to be adopted in the sulfation process, was properly selected in order to reach a stable degree of surface sulfation as high as possible but, contemporarily, to avoid formation of undesired aluminum sulfates. With this respect, 0.8 M H_2SO_4 was used to sulfate Y powders and samples here after labeled as Ys were formed, being the sulfuric acid concentration here selected in accordance with the studies of Yang et al. [33]; differently, a reduced concentration of sulfuric acid, i.e. 0.4 M H_2SO_4 , was adopted for M powders, to obtain sulfated samples here after labeled as Ms.

Preparation of the composite membranes

Nafion membranes were prepared following a solvent casting procedure. The commercial Nafion dispersion (5 wt% in water/alcohol, E.W. 1100, Ion Power, GmbH) was treated with N,N-

Download English Version:

<https://daneshyari.com/en/article/7713858>

Download Persian Version:

<https://daneshyari.com/article/7713858>

[Daneshyari.com](https://daneshyari.com)