Solid State Ionics 322 (2018) 85–92

Contents lists available at ScienceDirect

Solid State Ionics

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

Properties of anion exchange membrane based on polyamine: Effect of functionalized silica particles prepared by sol–gel method

Narges Ataollahi[a,*], Elisa Cappelletto[a], Keti Vezzù[b], Vito Di Noto[b,c], Gianni Cavinato[d], Emanuela Callone[e], Sandra Dirè[e], Paolo Scardi[a], Rosa Di Maggio[a]

[a] Department of Civil, Environmental and Mechanical Engineering, University of Trento, Via Mesiano 77, 38123 Trento, Italy
[b] Section of Chemistry for Technology, Department of Industrial Engineering, University of Padova, Via Marzolo 9, 35131 Padova, Italy
[c] Institute of Condensed Matter Chemistry and Technologies for Energy (CNR-ICMATE), Via Marzolo 1, 35131 Padova, PD, Italy
[d] Department of Chemical Sciences, University of Padova, Via Marzolo 1, 35131 Padova, PD, Italy
[e] "Klaus Müller" Magnetic Resonance Lab., Department of Industrial Engineering, University of Trento, Via Sommarive 9, 38123 Trento, Italy

ARTICLE INFO

Keywords:
Polyamine
Modified silica
Membrane
NMR

ABSTRACT

Membranes of polyamine $(PA\text{-}SiNH_2)_m$, containing silica reacted with 3-aminopropyltriethoxysilane (APTES) in hydrolytic conditions were prepared *via* solution casting, followed by methylation and ion exchange process. The influence of amino-functionalized silica ($Si\text{-}NH_2$) on the properties of the obtained membrane was investigated. Fourier transform infrared spectroscopy (FTIR) and Nuclear magnetic resonance spectroscopy (NMR) were used to investigate the chemical features of the silica and its interaction with the polyamine polymer. The results of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the modified membrane confirmed it is stable up to 300 °C. The thermal stability is the result of the interaction of modified silica particles and polyamine polymer. It was demonstrated that the performance of the $(PA\text{-}SiNH_2)_m$ anion exchange membrane is greatly improved by incorporation of silica nanoparticles as compared with the anion exchange membrane (PK-PDAPm), which doesn't contain silica. Therefore, the $(PA\text{-}SiNH_2)_m$ is a suitable candidate for electrochemical applications.

1. Introduction

The main goal of this study is to obtain a new polymeric material in which amino-functionalized silica ($Si\text{-}NH_2$) contributes in a synergic way to the performance of the final composite, increasing both anion exchange properties and thermal stability.

This goal could be reached by surface modification of inorganic nanoparticles, which is of big interest due to the wide range of potential applications in the fields of chemistry, biology and physics including composite materials [1] drug delivery [2], coupling and immobilization of functional molecules and biomolecules [3] base-catalysis [4]. Moreover, the surface modification of inorganic nanoparticles leads to enhance the compatibility between organic and inorganic phases [5]. Metal oxides such as SiO_2 have been widely used as inorganic fillers in polymer composites [6–8]. This is due to the commercial availability of a wide range of particle size and morphology, the large number of surface hydroxyl groups suitable for further modification and finally the ease of *in situ* silica formation by the sol-gel process of silicon alkoxides under mild conditions [9,10]. Silica addition was also proved to strengthen the interface between nanoparticles and polymer matrices [11,12]. Basically, the functionalization of silica particle is a method for tailoring the surface properties of particles to fit the target applications [13,14] and 3-aminopropyltriethoxysilane (APTES) is often used if the aim is to insert anionic groups [15–18].

Recently, our research group reported the preparation of anion exchange membrane based on polyamine (PK-PDAPm), prepared by the modification of polyketone (PK) skeleton [19]. The polyamine consists of a stable pyrrole ring along the backbone, and a reactive pendant amino functional group [19]. In the present work, the hydroxyl groups of silica powder were exploited for the condensation reaction with 3-APTES under hydrolytic conditions [20–22], and the modified silica ($Si\text{-}NH_2$) was added to polyamine. It is expected that the amino functional groups ($Si\text{-}NH_2$), incorporated into the polyamine membrane, lead to a stable, homogeneous reinforcement effect by improving the filler-polymer interface, and, in turn, help in achieving improved ionic exchange capacity (IEC). As a consequence, the incorporation of $Si\text{-}NH_2$ within polyamine membranes to form $(PA\text{-}SiNH_2)$m, should help to increase its conductivity, maintain water retention at high temperatures

---

[*] Corresponding author.
E-mail address: narges.ataollahi@unitn.it (N. Ataollahi).

https://doi.org/10.1016/j.ssi.2018.04.022
Received 15 September 2017; Received in revised form 10 March 2018; Accepted 27 April 2018

and low relative humidity, improve thermomechanical properties and thermal degradation at high temperatures. The structural and thermal properties of the final products were assessed using FTIR, NMR, X ray diffraction (XRD), TGA and DSC, and the ion exchange ability was determined.

2. Materials and methods

2.1. Materials

3-Aminopropyltriethoxysilane (Aldrich, 99%), ammonium hydroxide (Carlo Erba, 30%), hydrochloric acid (Baker, 36–38%), iodomethane (ABCR GmbH, 99%), polyethylene glycol 200 (Sigma Aldrich, MW 190–210 g/mol), potassium hydroxide (VWR), absolute ethanol (VWR), 1,1,1,3,3,3,-hexafluoroisopropanol, (Sigma-Aldrich, 99%), were commercially available and used as received. Silica powder with average diameter of 6.20 μm was employed. Bi-distilled water was used in all procedures.

2.2. Methods

Synthesis of polyketone (PK) and amination of polyketone (PK-PDAP) were followed according to procedure reported in our previous work [19].

2.2.1. Modified silica (Si-NH_2)

100 mg of silica was suspended in 1.5 mL of APTES and 1.5 mL ethanol in the ultrasonic bath for 10 min. Then, 0.1 mL of distilled water was dropped into the reaction medium to facilitate APTES hydrolysis. After 1.5 h, 60 μL of NH_4OH catalyst was fed into the reaction mixture. Sonication was continued for 3 h. Gelation was allowed for 1 h. The gel was centrifuged and washed with ethanol and distilled water (3 × 5 min, 4000 rpm). The final material (Si-NH_2) was dried at 70 °C for 24 h [23].

2.2.2. Membrane preparation

The synthesis of polyamine (PK-PDAP) followed the Paal-Knorr reaction and was previously reported [19]. 30 mg of polyamine powder was weighted and grinded. Then, 15 mg of modified silica (Si-NH_2) previously grinded, was added and mixed with 7 mL HFIP solvent, stirred for 1 h at 40 °C, followed by addition of 50 w% of PEG200 (0.26 mL) to the solution. 60 mL NH_4OH was inserted into the solution by means of a syringe. The solution was homogenized by treatment in an ultrasonic bath at 40 °C for about 30 min, and it was left stirring overnight at 40 °C; finally, the solution was casted into a Petri dish leading to a homogeneous, free-standing membrane. The modified membrane was named as (PA-SiNH_2)m. In order to run the methylation reaction, (PA-SiNH_2)m was immersed in iodomethane for 24 h and then washed thoroughly with deionized water and dried at 40 °C in a vacuum for 24 h. The methylated membrane ((PA-SiNH_2)mI) exchanged to the hydroxide ion form ((PA-SiNH_2)mOH) in 1 M KOH solution for 1 h. This step was repeated three times. (PA-SiNH_2)mOH was washed with distilled water and stored under nitrogen atmosphere to prevent hydroxide anions to transform into carbonate and bicarbonate species by contact with atmosphere carbon dioxide.

2.3. Instrumental methods

Fourier Transform Infrared Spectroscopy (FTIR) was collected using a Nicolet FT-IR Nexus spectrometer by averaging 16 scans with a resolution of 4 cm^{-1} in the wavenumber range between 650 and 4000 cm^{-1}. Solid state NMR analyses were carried out with a Bruker 300WB spectrometer operating at a proton frequency of 300.13 MHz. ^{29}Si and ^{13}C Magic-Angle Spinning-NMR (MAS NMR) spectra were acquired with single pulse experiments (SP) and cross polarization (CP) pulse sequences under the following conditions. ^{29}Si frequency: 59.62 MHz, SP: π/4 pulse 2.25 μs, recycle delay 150 s, 3 k scans; CP: contact time 5 ms, ^{1}H π/2 3.2 μs, decoupling length 5.9 μs, recycle delay: 10 s, 5 k scans. ^{13}C frequency: 75.48 MHz, CP: contact time 2 ms, decoupling length 5.9 μs, ^{1}H π/2 3.2 μs, recycle delay 5 s, 20 k scans. Samples were packed in 4 mm zirconia rotors, which were spun at 7 kHz under air flow. Adamantane, Q_8M_8 was used as external secondary references. Si units were labelled according to the usual NMR notation, T^n and Q^n representing trifunctional ($SiCO_3$) and tetrafunctional (SiO_4) Si units respectively, and n the number of bridging O atoms. The lineshape analysis was run with the Bruker Topspin 3.2 software. Thermo-Gravimetric Analysis (TGA) was performed from 25 °C to 700 °C in N_2 and in air with a heating rate of 10 °C/min, using a Labsys SETARAM thermobalance. Differential Scanning Calorimetry (DSC) analyses were performed using a DSC92 SETARAM, equipped with a liquid N_2 cooling system. The data were collected in the temperature range between −100 °C and 400 °C with a heating rate of 10 °C min^{-1}. X-ray diffraction (XRD) measurements were made on a X'TRA diffractometer (Thermo ARL, Switzerland), based on conventional powder geometry and a solid-state Si–Li detector, using Cu Kα radiation. The data were taken at the diffraction angle 2θ from 1° to 60° at the scan rate of 0.025° s^{-1}. The water uptake (WU) of membranes was determined by measuring the difference in membrane weight before and after immersion in deionized water. In this study, the membranes (3 × 3 cm, 0.1 mm thick) were soaked in deionized water at room temperature for 24 h. Then, each sample was weighed immediately after removing the surface water on the membrane (W_{wet}). Membrane samples were then dried at 40 °C for 6 h and weighted again (W_{dry}). The water uptake was calculated by the following equation:

$$\text{Water uptake (\%)} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100$$

Ion exchange capacity (IEC) was determined by back titration method. A dried (PA-SiNH_2)mOH membrane was immersed into 30 mL of 0.1 M HCl solution for 24 h. NaOH (0.01 M) solution was used for back titration, using phenolphthalein as an indicator. The IEC was determined based on the following equation:

$$\text{IEC (meq/g)} = \frac{[(V_{0,NaOH} - V_{NaOH})]C}{m_{dry}}$$

where: $V_{0,NaOH}$ and V_{NaOH} are the volumes of NaOH solution consumed for back titration without and with the membrane, respectively; C is the concentration of NaOH solution, and m_{dry} is the weight of the dry membrane.

3. Results and discussions

3.1. FTIR

Fig. 1(a, b) shows the FTIR spectra in the 4000–650 cm^{-1} range collected on pristine silica (SiO_2), APTES, modified silica (Si-NH_2) and resulting modified membrane (PA-SiNH_2)m. The FTIR peak assignments shown in Table S1 (Supplementary Materials) were based on literature data.

Fig. 1(a) displayed the characteristic bands of silica, showing at 794, 1060 and 1217 cm^{-1} the stretching vibrations of Si—O—Si bonds, and Si—OH vibration at 957 cm^{-1} [24–27]. The band at 1647 cm^{-1} is assigned to the bending vibration of water molecules adsorbed on the surface of silica [24,27].

The characteristic functional groups of APTES included the absorption peak at 765–789 cm^{-1} assigned to Si—C stretching and in phase Si—O stretching vibration [28]. The peak assigned to the silanol groups [23] which was found at 953 cm^{-1} was shifted to 927 cm^{-1} after the reaction of silica and APTES. The intense peaks at 1073 and 1101 cm^{-1} of Si—O—C stretching of APTES [28] were replaced in Si-NH_2 spectrum by a broad band at 1095 cm^{-1} indicating the effective