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A facile synthesis of proton-conducting organic–inorganic membranes

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ABSTRACT

Hybrid organic–inorganic proton conducting membranes based on arylsulfonic acid (Ar-SO₃H) groups and poly(ethylene glycol) (PEG) units were easily obtained in one step synthesis by co-hydrolysis and polycondensation of 2-(4-Chlorosulfonylphenyl)ethyl trimethoxysilane and bis-silylated polyethylene oxide. The hydrolysis of SO₂Cl groups into SO₃H was achieved during the sol–gel process by the in situ generated HCl acting as catalyst for the hydrolysis and polycondensation reactions. All membranes were characterized by ¹H, ¹³C and ²⁹Si MAS solid-state NMR, elementary analysis, Scanning Electron Microscopy (SEM) and X-ray photoelectron (XPS) spectroscopy. Their thermal and thermomechanical properties were investigated by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), respectively. The thermomechanical and conductive properties were found to be dependent on the PEG chain length and the PMMA amount. The proton conductivities of these materials were found to be approximately 10⁻² S cm⁻¹ at 20 °C.

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1. Introduction

Fossil fuel exhaustion and environmental problems caused by conventional power generation have triggered an intensification of research on renewable energies such as photovoltaic sources, fuel cells, wind generation, etc. Fuel cells, particularly the proton exchange membrane fuel cell (PEMFC), is considered to be one of the most significant alternatives to depleting fossil energy resources due to their green nature and high power density [1]. Desirable properties of PEMFCs include chemical and electrochemical stability, mechanic strength in the operating conditions and high proton conductivity to sustain large current densities [2]. Therefore, the development of alternative membranes with high mechanical strength, thermal, chemical and electrochemical stability as well as robust proton conductivity properties at elevated temperatures remains an important challenge for their large scale production [3].

Organic–inorganic hybrid materials have been regarded as promising materials for such requirements, in particular, silica-based organic–inorganic hybrid materials [4]. Such materials obtained by the sol–gel process [5] combine the remarkable functionality of organic materials with the stability of inorganic materials [6–8].

For example, a wide variety of bridged polysilsesquioxanes-organic hybrid materials including different functional organic units and spacers R' can thus be obtained starting from a bis-silylated precursors of general formula [(RO)₃Si]_mR' (m ≥ 2) [9–12].

In the last decade, numerous hybrid materials have been developed for fuel cells applications and their performance evaluated [4c]. Zoppi et al. [A. Zoppi, I.V.P. Yoshida, S.P. Nunes, Polymer 39 (1998) 1309–1315] and Mauritz et al. [K.A. Mauritz, Mater. Sci. Eng. C 6 (1998) 121–133] have in particular described the preparation of hybrid membranes made with in situ grown colloidal silica within Nafion. More recently, modified Nafion[®] membranes with phosphosilicate prepared by the sol–gel process with improved thermo-mechanical, water uptake and retention properties have been reported [13].

Another sulfonic conductive groups-based hybrid materials have been also developed. Membranes based on polystyrene sulfonic acid (PSSA) functionalized silica particles and poly(vinylidene fluoride) were prepared and a proton conductivity comprised between 2 and 10 × 10⁻² S/cm at room temperature was found for these materials [14]. Promising multi-component materials (PSSA/PEG and silica) for tailoring the hydrophobic and hydrophilic architectures and conductive PEMs were also described [15]. Perfluorinated polymers containing sulfonic groups-based hybrid membranes have been also synthesized. For example, crosslinked (poly(VDF-*ter*-PFSVE-*ter*-VTEOS)) terpolymers were obtained by a radical copolymerization and the sol–gel approach [16]. The hydrolysis of the sulfonyl fluoride group generates the sulfonic acid functions necessary for the proton

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conductivity. These membranes exhibited high proton conductivity (4×10^{-2} S/cm at 65 °C under 100% relative humidity) and high temperature stability.

Recently, we have reported the synthesis of SBA-15 functionalized in the pores with different acid groups ($-\text{CO}_2\text{H}$, $-\text{PO}(\text{OH})_2$ and $-\text{SO}_3\text{H}$) [17]. We have shown that the proton conductivity values depend on the pKa and the density of the functional groups attached to the mesopore surface. Sulfonic acid [18] and phosphonic acid [19] modified ordered mesoporous silica were used as inorganic fillers in Nafion[®] hybrid membranes fabrication. They show high proton conductivities at 80 °C and 50% relative humidity, which is six times higher than that of Nafion[®].

In 2012, we have also described the synthesis of hybrid organic–inorganic monolith silica containing poly(ethylene glycol) and sulfonic acid (SO_3H) groups [20]. 3-Mercaptopropyltrimethoxysilane was used as a source for sulfonic acid generation. We showed that whatever the conditions, the chemical modification (SH to SO_3H) were not complete (75%). In addition, the stability of the monolith remains questionable during the chemical treatment.

Herein, we report the easy synthesis (one pot approach) of highly flexible hybrid organic–inorganic membranes for proton conductivity. These materials based on polyether units, sulfonic acid groups (SO_3H) and silica network were prepared by co-hydrolysis and co-polycondensation of bis-silylated polyethylene glycol as hybrid matrix precursors and 2-(4-chlorosulfonyl-phenyl)ethyltrimethoxysilane (CSPETMS). The latter generates in situ the formation of SO_3H groups and HCl which acts as catalyst for the hydrolysis and polycondensation reactions during the sol–gel process. The obtained membranes were characterized by solid-state nuclear magnetic resonance (NMR) spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), Scanning Electron Microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). Their proton conductivities and mechanical properties were investigated and discussed. Based on these results, these membranes seem to be promising candidates for electrolyte solids applications in fuel cells.

2. Experimental part

2.1. Materials

All reactions were carried out under argon or nitrogen using standard high-vacuum and Schlenk techniques. Dry THF was obtained by distilling over CaH_2 , then Na/benzophenone. All polyethylene glycol (PEG) $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ ($M_n=400, 600$ and 1000) were purchased from Aldrich and used after drying under vacuum at 85 °C for 12 h. 2-(4-Chlorosulfonylphenyl)ethyltrimethoxysilane (CSPETMS, purity $\geq 95\%$) and 3-isocyanatopropyltriethoxysilane (ICPTES, purity $\geq 95\%$) were purchased from TCI Europe and Acros, respectively, and used as received. Polymethyl methacrylate (PMMA, $35,000 \text{ g mol}^{-1}$) was purchased from Aldrich.

2.2. Characterization methods

FT-IR spectra were recorded on a Thermo Nicolet Avatar 320 spectrometer in ATR in the range of $4000\text{--}400 \text{ cm}^{-1}$. ^{29}Si and ^{13}C Solid-state NMR spectra were recorded at 7.05 T on a Varian VNMRs 300 MHz spectrometer, using a 7.5 mm MAS probe spinning at 5 kHz. Single-pulse sequences with continuous-wave ^1H decoupling were used for ^{29}Si NMR experiment, with $2 \mu\text{s}$ $\pi/2$ pulse duration and a recycle delay of 60 s. For ^{13}C nucleus, CP-MAS experiments with a continuous-wave ^1H decoupling were acquired with 5 s recycle, $5 \mu\text{s}$ $\pi/2$ (^1H) pulse duration, and 3 ms contact time. Both nuclei were referenced to Tetramethylsilane (TMS). Scanning Electron Microscopy (SEM) images were obtained

with a Hitachi S2600N microscope. Thermogravimetric analyses (TGA) were carried out on a Netzsch STA 409 PC apparatus at $5 \text{ }^\circ\text{C min}^{-1}$ under air between 25 °C and 300 °C using ca. 10 mg samples in Pt pans. performed using a NETZSCH DSC 204F1 (Phoenix[®]) apparatus at a heating rate of $10 \text{ }^\circ\text{C/ min}$ between $-100 \text{ }^\circ\text{C}$ and $120 \text{ }^\circ\text{C}$ under a nitrogen flux (20 mL min^{-1}). All membranes were previously dried under vacuum before the thermal analyses. The DSC capsules containing the sample were drilled in order to avoid any variation in pressure within the capsule that could be due to the evaporation of the adsorbed phase. Energy dispersive spectroscopy (EDS) analyses were performed with an environmental SEM FEI Quanta 200FEG coupled with an Oxford INCA analyzer at the Service Commun de Microscopie Electronique of the University Montpellier 2. Elemental analyses (C, H, S and N) were carried out by the Service Mesures Physiques of the University Montpellier. The X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Thermo Electron ESCALAB 250. The excitation source is a monochromatic AlK_α line (1486.6 eV) working under a 100 W power. The analyzed surface has a diameter of 400 μm . The photoelectron spectra are calibrated in binding energy compared to the energy of the C–O bond component (PEG) carbon C1s at 286.5 eV. Spectra were recorded in high-resolution modes (pass energy of 20 eV). Each sample was analyzed at a photoelectron takeoff angle of 45°. The background signal was removed using the Shirley method [21]. The atomic surface concentrations were determined from photoelectron peaks areas using the atomic sensibility factors reported by Scofield [22]. The proton conductivity of the hybrid materials was recorded at 20 °C by Complex Impedance Spectroscopy (CIS) with a Novocontrol dielectric alpha analyzer, in the $10^{-1}\text{--}10^6 \text{ Hz}$ frequency range. Prior to any experiments, membranes were brought into contact with an atmosphere of saturated water vapor for 24 h at 25 °C to ensure the highest relative humidity. Finally, they were treated in situ at 20 °C for 30 min in order to remove the excess of physisorbed water. The dynamic mechanical behavior of each substrate was investigated using a stress-controlled rheometer (MCR301 from Anton Paar[®]) equipped with an environmental chamber. This apparatus allowed recording the evolution of the complex shear modulus $G^* = G' + jG''$ as a function of temperature from $-150 \text{ }^\circ\text{C}$ up to 200 °C. The heating rate was set at $3 \text{ }^\circ\text{C min}^{-1}$ and the oscillating angular frequency was fixed at $\omega = 1 \text{ rad/s}$. The component G' , called “storage modulus”, represents the mechanical rigidity of the sample (i.e. its elastic contribution) whereas the loss modulus G'' relates to the dissipated mechanical energy. Due to the material rigidity, all experiments were performed using rectangular torsion geometry. Typical dimensions of the samples were $45 \text{ mm} \times 10 \text{ mm} \times 1 \text{ mm}$. Rheological experiments were performed twice to check the reproducibility of the results.

2.3. Synthesis

Bis-silylated PEG **1** ($M_n=400, n=8$), **2** ($M_n=600, n=12$) and **3** ($M_n=1000, n=21$) were prepared in a similar manner by using ICPTES as a silylating agent following a method described in the literature [23].

2.3.1. General procedure for the synthesis of membranes **M-SO₃H** (**M**=400, 600 and 1000)

All membranes were prepared following the same procedure. Herein, the synthesis of **600-SO₃H** is described as an example. A solution containing 0.37 g (1.15 mmol) of 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane in EtOH (1.2 mL) was added to a solution of bis-silylated PEG **2** (1.26 g, 1.15 mmol) in EtOH (3 mL). After homogenization, 0.46 mL of water was added. The resulting clear solution was stirred for 2 h and exposed to ultrasound bath

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