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Electrospinning a versatile tool for designing hybrid proton conductive membrane

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ABSTRACT

The development of efficient hybrid membranes for high temperature Proton Exchange Membrane Fuel Cell (PEMFC) is currently under investigation. Here, we show that the electrospinning process combined with the sol-gel chemistry conduces to membranes with protonic conductivity similar to Nafion, at high temperature under the relative humidity of 90%, and with anisotropic mechanical properties due to the presence of long-range anisotropic object. The electrospun membranes' morphology is also highly dependent on the sol-gel chemistry (with/without additives) as well as the processing parameters including relative humidity, applied electrical field, temperature, rotating electrode's speed... Our hybrid fibers are based on poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP)/ SO₃H-silica networks that combines the ability to mimic the nano structural phase separation observed in hydrated Nafion with major feature, that is, array of orientated ionic nano channels intermingled within a locally aligned polymer, where proton can easily diffuse in this tubular nanostructure.

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1. Introduction

Proton exchange membrane fuel cells (PEMFC) have attracted great interest for future energy supply [1,2]. PEMFCs are a promising energy source for automobiles, portable electronics and residential power generation owing to their high power density, energy efficiency and low environmental impact [3]. Perfluorosulfonic acid polymer membranes [4] namely Nafion, are typically the reference materials for fuel cell membranes due to their excellent chemical, mechanical, and thermal stability as well as their high electrochemical properties [5,6]. However, PEMFCs have several drawbacks that need to be overcome, including high cost, high catalyst loading and low carbon monoxide (CO) tolerance [1,7]. Increasing their operation temperatures will be highly beneficial for improving their tolerance to CO and other impurities, thus facilitating their integration for automotive development [8]. Nevertheless at high temperature and low humidity conditions (100 °C and 50% RH) Nafion is dehydrated,

consequently decreasing its proton conductivity [9,10]. Additionally, its mechanical properties start to degrade due to its T_g value of 150 °C [11]. All of these conditions give rise to poor mechanical properties and high ohmic losses that consequently, decrease the fuel cell performances [12].

The developments of perfluorosulfonic acid membranes with a high conductivity at high temperature and low relative humidity generate a great interest [13,14]. One approach is to increase the ion capacity exchange (IEC) of the polymer by reducing the equivalent weight of the polymer. For example, 3M Company developed several PFSA polymers with low equivalent weight (EW). One interesting example is cast membrane obtained from 580 EW ionomer. The proton conductivity of this membrane is higher than 0.10 S/cm at 80 °C and 50% RH. Nevertheless, the membrane presents high swelling, poor mechanical properties and became soluble in liquid water at elevated temperature due to the loss of polymer crystallinity (for polymer below 800 EW).

To overcome these issues, various approaches have been developed including the development of organic-inorganic hybrid membranes [4,15,16]. Numerous studies were focused on the design of organic-inorganic membranes, as they are expected to play an important role in high temperature fuel cell development [17,18]. By contrast with Nafion, these membranes present the

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advantage of exhibiting proton conductivity less dependent on their hydration level as the inorganic component serves as a pump for water [19,20]. The distribution and size of the inorganic component in the polymer highlight the necessity of having hierarchically organized hybrid organic/inorganic interfaces for keeping both good mechanical and conduction properties [21,22]. For example, 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. These membranes exhibit proton conductivity of 10⁻² S cm⁻¹ at 20 °C [23].

Although the structure-function relationship in hybrid organic/inorganic membrane is fundamental, the design of long-range ordered organic/inorganic interfaces have been neglected in the literature. Owing to the systematic use of casting process (evaporation of solvent from the hybrid solution), huge phase separation between these two components has been reported. These conditions lead to poor mechanical properties as well as low proton conductivity, specifically when the function for proton conductivity is mainly supported by the inorganic network.

Choi et al. [24] developed nanofiber-based polymer/particles composite membrane. These membranes are composed by electrospun nanofibers composed of sulfonated poly(arylene ether sulfone) (sPAES) with sulfonated polyhedral oligomeric silsesquioxane (sPOSS) (loading 40 wt%) as a proton conductivity enhancer. The proton conductivity at 120 °C and 50% RH is 0.1 S/cm (2.5 times higher than Nafion[®]) but membrane conductivity degraded after immersion in liquid water due to dissolution of sPOSS. Other strategy based on electrospinning consists in designing sulfated zirconia fibers. Inorganic fibers served as long-range ionic channels via the agglomeration of functional groups, giving rise to improve proton conductivity of PEMs [25].

To address these shortcomings, Maneeratana et al. [26] recently proposed to synthesize new hybrid membranes composed of functionalized silica and hydrophobic polymer, PVDF-HFP, by combining sol-gel chemistry and electrospinning. This novel approach permits the mixing at the nanoscale of two opposite components that are hydrophilic and hydrophobic, respectively. More interestingly, the use of this process allows a fairly good control of the proton pathway throughout the membrane and proton conductivity as high as 1 S/cm under relative humidity of 80% to be achieved at 120 °C. Additionally, this work demonstrates even if the surface of the membrane appears to be porous, the membrane is dense, as fuel cell test was possible [26].

In contrast to Maneeratana studies that was mainly focussed on the impact of processing (casting vs. electrospinning), here we report in more details the influence of the sol chemistry (the chemical additives and the nature of the functionalized silicon precursor, as well as the processing parameters of the electrospinning process (flow rate) on the morphology of the fibers and their impacts on the proton conduction and the mechanical behaviour of the hybrid membrane (HM). For example, varying the CSPTC (2-(4-chlorosulfonylphenyl)ethyltrichlorosilane)/tetraethyl orthosilicate (TEOS) ratio has a drastic impact on the sol-gel chemistry as it influences the local pH and then the size of the silica clusters and in fine their assembly in the hybrid fibers. This parameter was not systematically studied previously [26]. The flow-rate-induced alteration in the fiber diameter yields an extension of the array of ionic nanochannels which are intermingled within a locally aligned polymer [27]. We also show that structuring the organic/inorganic interfaces at the nanoscale contribute to the mechanical properties of the membrane as well as proton conduction.

2. Experimental section

2.1. Materials synthesis

The materials used in this work were Poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) (solvay@21216, Mn=570–600), tetraethyl orthosilicate (TEOS) (sigma aldrich, 99.999% trace metal basis), 2-(4-chlorosulfonylphenyl)ethyltrichlorosilane (50% in methylene chloride, contains 30% free sulfonic acid and small amounts of silylsulfonic acid condensation products) (CSPTC) (ABCR), PEO (sigma Aldrich, MW = 100 × 10⁶ g mol⁻¹, n₂₀/D=1.4539), PVDF-2-hydroxy (specific polymer, Mn=392.16) and N,N-Dimethylformamide (sigma Aldrich, purity 99.9%). These materials were used as received without further purification.

Preparation of the hybrid solutions: For a solution with an inorganic volume percentage of 61 and a molar ratio of 1/2 in terms of TEOS/CSPTC, the following protocol was used. First, 600 mg of PVDF-HFP is dissolved in 7 mL of DMF. Then, 340 mg of polyethylene glycol, 312 mg of PVDF-2-hydroxy, 361 mg of TEOS and 347 mg of CSPTC (diluted at 50% in methylene chloride) are added. No additional water was added; hydrolysis and condensation reactions occur via the water present in DMF. The resulting solution is stirred for 3 h at 70 °C before electrospinning.

Synthesis of the electrospun hybrid membranes: Briefly, 2 mL of the hybrid solution was electrospun at 26 kV and with a flow rate of 0.1 mL/min in air with a relative humidity ranging from 20 to 40% under ambient temperature (25 °C). A white, flexible membrane was deposited onto aluminium foil that plays the role of counter electrode (deposited onto rotating electrode). Finally, the electrospun membranes were dried during 24 h at 70 °C. The electrospun membrane is then pulled out from the support and a homogenous self-standing membrane is achieved.

2.2. Material Characterization

Scanning Electron Microscopy: Membranes morphologies were observed by FEG-SEM with Hitachi S-3400N while the element mappings were performed with an energy dispersive X-ray (EDX) detector Oxford Xmax.

HR-TEM: The TEM images was performed on a JEOL 2100 F TEM/STEM microscope, operating at 200 kV and equipped with a probe corrector and a GIF Tridium energy Filter.

Small-Angle Neutron Scattering: SANS experiments were carried out with the PAXY spectrometer in the Leon Brillouin Laboratory (Laboratoire commun CEA-CNRS, Saclay, France). Three sample-to-detector distances (SDD) and neutrons wavelengths (λ) were used to cover magnitudes of the scattering vector modulus q from 0.04 to 4 nm⁻¹ ($\lambda=1.2$ nm, SDD =6.75 m; $\lambda=1.2$ nm, SDD=3 m and $\lambda=0.5$ nm, SDD=1 m). Note that the resulting flat level of the scattering intensity at the high q values is of the order of magnitude of the experimental background. The error in the slope (α), being due to the errors in the intensities has an average of 0.1.

¹H NMR: NMR experiments in the solid state were performed on a Bruker AVANCE 700 spectrometer III (Bo = 16.4 T, $\nu_0(^1\text{H})=700.13$ MHz) with a Bruker MAS probe 1.3 mm Double HX resonances. The samples were rotated at the magic angle in ZrO₂ rotors and at a rotation frequency of 60 kHz.

²⁹Si NMR: NMR experiments in the solid state were performed on a Bruker AVANCE 700 spectrometer III (Bo = 7 T, $\nu_0(^1\text{H})=300.29$ MHz and $\nu_0(^{29}\text{Si})=59.65$ MHz using a MAS probe Bruker 4 mm double-resonance MQ 1H-X. The samples were rotated at the magic angle in ZrO₂ rotors. The use of 4 mm diameter rotor was necessary thereby increasing the acquisition time required to perform quantization of the different species of silicon.

Conductivity: Proton conductivities of the electrospun hybrid

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