



Tuning the ion channel network of perfluorosulfonated membranes via a facile sacrificial porogen approach



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ABSTRACT

The morphology in terms of the ion channel size, apparent porosity and tortuosity of perfluorosulfonated membranes was modified by using sulfonated polystyrene (SPS) as a sacrificial porogen. The precursor polymers were fabricated via solution-casting of the commercially available Nafion solution together with SPS. Upon swelling SPS was leached from the membrane matrix resulting in the formation of larger nanosized ion channels and clusters and hence a more open membrane matrix in fully hydrated conditions. Below a threshold value of 30% SPS, the membranes maintained high permselectivity and the porogen mainly increased the apparent porosity and network interconnectivity resulting in increased hydraulic permeability, streaming potential coefficient and membrane conductivity. Higher porogen contents resulted in larger characteristic hydrophilic domain sizes, quantified from SAXS/WAXS, and enhanced membrane conductivity up to 300% with only a slight decrease in the permselectivity in dilute LiCl solutions. These results together confirm the effective modification of the charged nanoscopic ion network and clearly indicate that SPS can efficiently be used for precise tuning of the PTFE-based membrane matrix to achieve tailored transport properties for specific electrochemical applications.

1. Introduction

Ion exchange membranes are a key component in a number of electrochemical applications that involve selective permeation of ions or protons such as proton exchange membrane fuel cells (PEM-FCs), (reverse) electrodialysis (RED/ED), pressure retarded osmosis (PRO), redox flow batteries (RFB) and electrokinetic energy conversion (EKEC) processes [1–7]. The transport properties of such membranes depend on the characteristics of the solvent swollen ion channel network (i.e. average channel diameter, porosity and tortuosity factor) and immobile charge density [8].

With respect to selectivity, immobile charges on the channel walls, e.g. sulfonate (SO_3^-) and other negatively charged groups in cation conductive membranes, exclude co-ions (anions) allowing the partitioning and permeation of mainly counter-ions (cations) [9]. The screening potential of the immobile charges in the proximity of the channel walls is an increasing function of the surface charge density and decays steeply towards the center of the ion channel, hence it is only effective up to a certain critical size [10–15]. In a simplified picture the ion channel provides an optimal permselectivity (Ψ) toward co-ions until the Debye screening length (λ_D) of the solution inside the

channel is larger or similar to the average channel radius (r_p). In these conditions the electrical double layers (EDLs) overlap and the potential profile is almost constant in the radial direction [16–18]. However, high permselectivity is a trade-off with the membrane conductivity (σ_m) that increases with r_p and the external solution concentration for a fixed surface charge density. Furthermore, the solution permeability and volume flux (j_v) is an increasing function of r_p [14,19,20]. Additionally, j_v and σ_m are extensive variables (i.e. dependent on the system geometry) and will for this reason increase with the porosity (ϕ) and decrease with the tortuosity factor ($\tau \geq 1$) at a fixed average ion channel dimension, while Ψ is an intensive variable and therefore independent of porosity and tortuosity factors.

The choice of membrane, as separator for a specific electrochemical application, is a trade-off between selectivity, membrane conductivity and the solution flux/permeability [21]. The membrane resistance (proportional to $1/\sigma_m$) should be kept as low as possible to minimize the parasitic ohmic resistances, still providing the required co-ion selectivity, while high j_v can either be an unwanted feature because volumetric crossover unbalances the reservoirs or, in other applications, required to maximize the power output [22,23]. For instance in RFBs a high σ_m improves the power density, cycle efficiency and even the

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capacity, however, volumetric crossover and crossover of redox active species must be kept at a minimum. On the other hand, in membrane-based EKEC a hydrostatic pressure load is converted directly into electrical energy [12,24] and a combination of high permselectivity and large ion channel radius has been shown to enhance the efficiency and power density significantly [25].

Nafion is a highly stable *state-of-art* cation exchange membrane because of its fluorinated backbone [9]. The phase separation between the highly hydrophobic fluorocarbon (PTFE based) and the highly hydrophilic ionic phase is very distinct [8,9]. Nonetheless in the solvent-swollen membrane the reorganization of these phases at a microscopic level is still under debate and several structural models have been proposed since the 1970s. These include Gierke's *cluster-network model* [8], *parallel cylindrical nanochannels model* [26], and *network models* [27,28], among others. As a consequence, only approximate structural features can be sketched: in particular, in fully hydrated conditions, the channel network is believed to have a characteristic r_p around 1–2 nm, relatively small porosity ($\vartheta \sim 0.3$ – 0.4) and high tortuosity factor ($\tau \sim 10$ – 20) [8,14,26].

In the following a facile sacrificial porogen approach to tune the nanosized network structure of Nafion is described. The polymer precursors were fabricated by casting the commercially available Nafion solution together with sulfonated polystyrene (SPS). The modified membranes were then obtained via a facile selective SPS leaching by swelling the cast membranes in methanol/water mixture. The successful modification was confirmed via SAXS/WAXS experiments and the transport properties were evaluated. At low SPS concentration the porogen mainly increased the apparent porosity and interconnectivity of the network thus enhancing the membrane conductivity by up to 60% with respect to the pristine membrane preserving the same permselectivity toward co-ions. At higher SPS content the porogen resulted in an evident modification confirmed by the characteristic spacing of the hydrophilic domains (up to approximately 7–8 nm from SAXS data). This resulted in enhanced membrane conductivities up to 300% with respect to the pristine membrane in LiCl with only a slight decrease in the membrane permselectivity in diluted LiCl solution. This ultimately indicates the effectiveness of SPS as sacrificial porogen to increase the apparent porosity and channel sizes of the hydrophilic network, still being in the nanoscopic range.

2. Materials and methods

2.1. Chemicals

Dimethylacetamide (DMAc, anhydrous 98.9%), diethyl ether (99.7%), hydrogen peroxide (30 wt% in H₂O) and methanol ($\geq 99.9\%$) were all used as received from Sigma Aldrich. Lithium chloride, sodium chloride and sulfuric acid (95%) were purchased from VWR and used as received. Sodium hydroxide (32%, technical grade) was obtained from Applichem. The alcohol-based Nafion solution (D2020, EW1000, 20 wt % in 1-propanol-water solution), obtained from Ion Power, was pre-cast in Teflon petri dishes overnight at room temperature before use. The sulfonated polystyrene (30% w/v aqueous solution, MW 75,000, $iec_{SPS} = 5.4 \text{ meq}_{H^+} \text{ g}^{-1}$) was obtained from Alfa Aesar and pre-treated by drying and re-dissolved in DMAc before use.

2.2. SPS modified Nafion

2 g of the pre-cast Nafion were dissolved in 30 mL DMAc at room temperature after which a desired amount of SPS (0–50 wt% compared to Nafion) was added. The solution was stirred until it turned turbid and poured into a Teflon petri dish (diameter 82 mm). The turbidity of the casting solution indicates the presence of hydrophilic micelles due to the presence of SPS, and to a much lesser extent from the water adsorbed from the atmosphere. The micelles were allowed to coalesce during the subsequent ~ 40 h curing process. First the membranes were

dried overnight at 50 °C before being carefully removed from the petri dishes and further dried under vacuum with the following temperature profile: 8 h ramp from 25 °C to at 110 °C, holding for 110 °C for 4 h and cooling down to room temperature in 12 h. Afterwards the membranes were swollen in a methanol/water mixture. Finally after being rinsed several times in milli-Q water ($\sim 18 \text{ M}\Omega \text{ cm}$), the membranes were chemically pre-treated in a three-step process involving 1 h in boiling H₂O₂ (3 wt%), 1 h in boiling sulfuric acid (1 M H₂SO₄), and 1 h in boiling demineralized water. The membranes were lithiated by immersion in a 0.5 M LiCl solution for at least 24 h.

2.3. Basic membrane characterization

The solution uptake was determined gravimetrically by weighing first the dry membranes and, after 24 h equilibration in 0.03 M LiCl, the wet membranes. The linear expansions (*in-plane* and *through-plane*) of the membranes in 0.03 M LiCl were determined by use of a micrometre screw gauge (thickness) and a Vernier calliper (diameter) on the dry and wet membranes. The ion exchange capacity was determined by pH-titration. The membrane in the H⁺-form was equilibrated in 1 M NaCl solution to exchange the counter-ions by Na⁺ and release the H⁺ ions to the solution. The ion exchange capacity (*iec*) was calculated (in the unit $\text{meq}_{H^+} \text{ g}_{\text{pol,dry}}^{-1}$) from the concentration of H⁺ in the NaCl solution determined by pH-titration with NaOH (Autotitrator 916 Ti-Touch, Metrohm). Details about the experimental procedure may be found in Ref. [21].

The glass transition temperature, T_g , of the modified Nafion membranes was assessed by using differential scanning calorimetry (PerkinElmer DSC 8000). Membrane samples in the H⁺ form were cut into disks with 2 mm in diameter (with a mass ranging between 2.2 and 2.8 mg depending on the membrane density and thickness) and mounted in 50 μl pans with holes. The samples were pre-treated with two thermal cycles (25 °C to 200 °C at a scan rate of 20 °C min⁻¹) to remove any trace of water inside the polymeric matrix. [29] Afterwards the T_g was determined from the specific heat measured in a third experiment (step scan of 5 °C min⁻¹ for temperatures ranging between 60 and 250 °C).

2.4. Small and wide-angle X-ray scattering (SAXS/WAXS)

The SAXS/WAXS experiments were performed on a SAXSess mc² instrument (Anton Paar, Austria). The instrument uses a GeniX Microfocus X-ray point source with a Cu anode (50 kV and 1 mA), single-bounce focusing X-ray optics, and an advanced collimation block. This configuration enables to measure in point collimation geometry only. Image plates together with the CyclonePlus[®] Reader (PerkinElmer, Inc.) were used for X-ray detection (2D). The sample exposure time was 10 or 20 min. The experiments were performed first on (i) vacuum-dried, (ii) humidified, and (iii) on swollen samples. The latter two sets of experiments were carried out in the SAXSess Humidity Cell which allows setting the relative humidity (RH) in the cell and the sample temperature independently.

- (i) First, the samples in H⁺ form were vacuum-dried for 24 h and then measured in vacuum without any thermal pre-treatment; selected samples were dried at 120 °C to remove all the water present in the polymers [29] and then measured in vacuum.
- (ii) The experiments in the humidity cell were carried out at RH $\sim 95\%$ and 23 °C. Before these measurements the originally dry samples were kept for 1.5 h in the humid atmosphere to allow a complete equilibration.
- (iii) One set of membranes were fully hydrated in demineralized water, surface water carefully removed followed by an immediate measurement in the humidity cell.

In all the experiments two pieces of membranes were stacked

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