



Proton-exchange membranes based on sulfonated poly(ether ether ketone)/polyaniline blends for all- and air-vanadium redox flow battery applications



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ABSTRACT

Thin and mechanically stable proton-exchange membranes with high V(IV) barrier properties and good proton conductivity have been fabricated by polymer blending of sulfonated poly(ether ether ketone) with polyaniline. V(IV) diffusion coefficient of blended membranes in a wt. ratio of 80/20 was 2.6 and 6 times lower than for pure sulfonated poly(ether ether ketone) and Nafion 112 membrane, respectively. This behaviour is assumed to be caused by a densified polymer matrix given by acid/base interactions between the two polymers. Blended membranes in a wt. ratio of 80/20 had a good proton conductivity of 54.15 mS cm⁻¹ and ion exchange capacity of 1.44 mmol g⁻¹. The membranes were also characterized in all-vanadium redox flow battery, where only slightly higher efficiencies were achieved than for pure polymer. Slow PANI degradation determines a decrease in membrane performance, reaching values close to the starting polymer (SPEEK-E600). Therefore, the application of blended membranes in the all-vanadium redox flow battery is not advantageous. However, the improved barrier properties are likely to be beneficial for their application in vanadium/air-redox flow battery in order to reduce oxygen crossover. In the latter, no V(V) ions can oxidize the blend polymer.

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1. Introduction

Redox flow batteries (RFBs) have gained much interest in recent years [1,2]. They are promising candidates for energy storage systems due to their ability to store large amounts of energy within the electrolytes. RFBs generally employ solutions with ability of redox reactions, such as iron or vanadium. The working principle of all-vanadium systems (VRFB) is based on two vanadium electrolyte solutions: VO₂⁺/VO²⁺, i.e. a V(IV)/V(V) solution as the positive electrolyte and a V(II)/V(III) solution is used as the negative electrolyte. Recent research focuses on the development of vanadium/air-redox flow battery (VARFB) where humidified air replaces the V(IV)/V(V) redox couple in order to increase the weight specific power output [3]. One of the main research areas in both systems is regarding the proton-exchanging membranes [4–8]. A suitable proton-exchange membrane should have low

area resistance for good voltage efficiencies and at the same time should have low vanadium and oxygen crossover, but these are dichotomic characteristics. Membranes used in VRFB need to be stable under the strong oxidative conditions given by V(V) ion. In VARFB membrane chemical stability is less demanding since the V(IV)/V(V) electrolyte solution is replaced by humidified air.

Generally, perfluorinated sulfonic acids such as Nafion membranes (DuPont) are used as proton-exchanging membranes due to their excellent proton conductivity and chemical stability under extreme conditions. Nevertheless, drawbacks such as low vanadium/proton ion selectivity and high cost determine many researchers to focus on the development of more suitable materials for this application. Sulfonated aromatic polymeric membranes have been suggested as proton-exchanging membranes in early 2000s for RFBs [9]. Sulfonated poly(ether ether ketone) (SPEEK) membranes have low production costs due to the aromatic backbone, high enough proton conductivity, and higher selectivity between vanadium and protons as a result of the tighter polymeric structure [9]. High degree of sulfonation gives a higher proton conductivity but directly affects the mechanical stability of the membranes. High degree of sulfonation increases the swelling

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ratio of the membranes due to an increase in membrane hydrophilicity. This can lead to losses in membrane dimensional stability or even to solubilization in water [10]. In this work we suggest to improve material properties of a highly sulfonated SPEEK membrane by SPEEK polymer blending with polyaniline (PANI). Solution blending of PANI with sulfonated polymers has already been used in an effort to produce materials with combined electrical and mechanical properties [11–14]. PANI belongs to the intrinsically electronically conductive polymer class [15]. PANI-based membranes and films are applied for actuators [16], gas separation [17], pervaporation [18], organic solvent nanofiltration [19], and rechargeable batteries [20]. Polymer blends between SPEEK and PANI are homogeneous for up to 30 wt.% of PANI [14]. Polymer compatibility is based on an acid–base reaction between one protonated sulfonic group of SPEEK and 2 basic nitrogen atoms, per PANI repeating unit [21]. This gives practically a physical crosslinking of SPEEK by PANI which is assumed to lead to a densified polymer matrix and, therefore, to improved mechanical stability and higher membrane barrier properties to vanadium ions or oxygen diffusion. The protonation reaction sacrifices part of SPEEK sulfonic groups; nevertheless proton conductivity is expected to remain close to pure SPEEK, as previously reported for up to 33 wt.% PANI load [14].

SPEEK membranes coated on both sides with PANI by polymerization (i.e. composite membranes) have already been produced for methanol fuel cell applications [22]. The composite SPEEK/PANI membrane had reduced methanol permeability when compared to pure SPEEK membrane. In VRFB application, similar composite membranes (Nafion/PANI) showed reduced crossover of cations [23]. Nevertheless, PANI dissolution during battery cycling in a VRFB system was observed. As far as we know, the chemical stability of PANI in V(V) solutions was never assessed and PANI dissolution might have been caused by simply mechanical delamination of PANI layer during battery operation. In contrast with the composite design, we suppose that mixing between SPEEK and PANI at molecular scale may protect PANI from being leached out from the membrane.

In resume, the hypothesis of this work is that SPEEK/PANI blends would give proton-exchange membranes improved mechanical stability and higher barrier properties against vanadium ions and oxygen crossover in VRFB and VARFB. These are highly important for long time system operation and consequently for scale-up and extensive commercialization. Testing of the properties in VRFB and improved short time properties are indicative of an improved property in the VARFB system.

2. Materials and methods

2.1. Materials

Sulfonated poly(ether ether ketone), SPEEK-E600 and SPEEK-E700, with different sulfonation degrees were kindly provided by FuMA-Tech GmbH. Polyaniline (PANI) was synthesized according to a procedure reported in [24]. The reaction time was reduced to half, i.e. to 8 h, by doubling the rate of oxidant addition. The reaction was left running for a total time of 24 h at $-15\text{ }^{\circ}\text{C}$. *N*-Methylpyrrolidone (NMP, 99 wt.%, Acros Organics) was used as solvent for membrane preparation. Prior to use, the polymers were dried in a vacuum oven at $30\text{ }^{\circ}\text{C}$ for 14 h; all other chemicals were used without further treatment. Other commercial membranes used were: Fumapen 14100 (FuMA-Tech GmbH) and Nafion 112 (DuPont).

2.2. Membrane preparation

Dense polymeric membranes were prepared from SPEEK and PANI blends of different weight ratios, as shown in Table 1.

Table 1

SPEEK-E600/PANI polymer blend weight ratios used for membrane fabrication.

SPEEK-E600 (wt.%)	PANI (wt.%)
100	0
98	2
95	5
80	20

A Pyrex[®] vessel with mechanical stirring (engine: Heidolph RZR 2052, centrifugal stirrer: Rotilab[®] YT27.1, 40 rot min⁻¹) was used to prepare 15 wt.% polymer blend solutions in NMP, at $50\text{ }^{\circ}\text{C}$. An air condenser was used to avoid solvent evaporation. After mixing for at least 8 h the dope solution was filtered through a $15\text{-}\mu\text{m}$ sintered metallic filter (Bekipor STAL3 Bekaert) and degassed for 1–2 h under vacuum.

Membranes with comparable thicknesses ranging from $23\text{ }\mu\text{m}$ to $40\text{ }\mu\text{m}$ were prepared by casting the polymer solution on a dust- and scratch-free glass plate using a casting knife. Dry films of comparable thicknesses were prepared by using a casting knife with a gap size of $500\text{ }\mu\text{m}$ for the bare SPEEK polymer, while a casting knife with a gap size of $200\text{ }\mu\text{m}$ was used for the blends. The cast membranes were dried for 24 h at room temperature under nitrogen atmosphere. Then, the cast membranes were further dried in a vacuum oven at $60\text{ }^{\circ}\text{C}$ and 90 mbar for minimum 3 days. The dried membranes were detached from the glass plate using water.

2.3. Pre-treatment

Membrane pre-treatment was done in 3 vol.% H_2O_2 solution at $60\text{ }^{\circ}\text{C}$ for 1 h. Afterwards, the membranes were immersed in 0.5 M H_2SO_4 for at least 48 h for full protonation of sulfonated groups.

2.4. Membrane characterization methods

In view of the membrane's application in VRFBs or VARBs, basic membrane properties such as swelling degree, water uptake, proton-exchange capacity, proton conductivity and vanadium diffusion coefficient were measured. These experiments have been carried out for three different samples of the same membrane. In addition, the VRFB performance was also evaluated.

2.4.1. Vanadium permeation through the membranes

The V(IV) diffusion rate through the membranes was determined using an H-Type cell. A pre-treated membrane, with an active area of 5.72 cm^2 , was placed between the two compartments of the cell. One compartment was filled with 100 ml of 1.0 M $\text{VOSO}_4/2.5\text{ M H}_2\text{SO}_4$ solution and the other with 100 ml of 1.0 M $\text{MgSO}_4/2.5\text{ M H}_2\text{SO}_4$ solution. MgSO_4 was added to equalize the ionic strengths and osmotic pressure between the compartments [25]. Mixing was provided by recirculating each solution with a peristaltic pump (Masterflex L/S Cole Parmer) at a flow rate of 100 mL min^{-1} . Samples of solution from the MgSO_4 compartment were taken at regular intervals and the concentration of V(IV) was measured in a UV-Visible Spectrophotometer (Genesys 10S), at a wavelength of 750 nm. The diffusion coefficients of vanadium ions across different membranes were calculated according to a reported method [25] using Eq. (1):

$$-\ln\left(1 - \frac{C_t}{C_0}\right) = \frac{D \times a}{l \times v} \times t \quad (1)$$

where C_t is the vanadium concentration in the MgSO_4 compartment in mol L^{-1} , C_0 the initial concentration of the vanadium in the vanadium compartment in mol L^{-1} , D the diffusion coefficient in $\text{cm}^2\text{ s}$, a the area of the membrane exposed to the solution in cm^2 ,

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