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Comparative study of the cation permeability of protonic, anionic and ampholytic membranes

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ABSTRACT

The vanadium ion permeability of various ion-conducting polymer membranes was determined using a home-made apparatus. The study includes proton-conducting sulfonated poly(ether ether ketone) (SPEEK) with various cross-linking degrees, anion-conducting membranes, such as polysulfone with quaternary ammonium groups (PSU-QA) and sulfaminated PEEK (SA-PEEK), and amphoteric membranes based on PEEK containing both sulfonic and sulfonamide groups (SAM-PEEK) that can conduct both cations and anions. The polymer structure was investigated by NMR spectroscopy. The permeability of SPEEK decreases with the cross-linking degree and can be up to two orders below the permeability of a Nafion 117 reference membrane ($1.4 \cdot 10^{-6}$ cm^2 min^{-1}). The cation permeability of SA-PEEK attains values as low as $5.0 \cdot 10^{-10}$ cm^2 min^{-1}, whereas amphoteric SAM-PEEK has a cation permeability of $7.0 \cdot 10^{-10}$ cm^2 min^{-1}. A factor or merit is introduced, defined as the ratio of ion conductivity and ion permeability; the highest value, corresponding to the best compromise of high ion conductivity and low permeability of electrochemically active ions, is found for highly cross-linked SPEEK, SA-PEEK and SAM-PEEK membranes. The influence of the polymer backbone (PEEK or PSU), the degree of cross-linking, determined by NMR spectroscopy, and the grafted ionic groups (sulfonic acid, sulfammonium, and quaternary ammonium) on the cation permeability is discussed.

1. Introduction

Ion exchange membranes have many applications in various fields, including inverse osmosis, electrodialysis, and electrochemical energy technologies, such as fuel cells and redox flow batteries [1–6]. In most of these applications, the separator membrane must impede the cross-mixing of ionic solutions. For example, an ion exchange membrane is employed in different electrochemical devices to separate the positive and negative half-cells and to prevent the permeation of the electrochemically active species (e. g. vanadium ions in all-vanadium redox flow batteries) while presenting the required ionic conductivity by non-electrochemically active ions [7]. The membrane separator is a key material for commercialization of electrochemical energy technologies, because it determines the performance and its cost can be a main part of the whole system.

Important properties that a high performance ion exchange membrane should therefore present are [7,8] i) high ion conductivity, required to minimize the Ohmic loss and to increase the voltage efficiency in batteries, ii) high ion selectivity: the separator must be permeable to the charge balancing ions of the supporting electrolyte (e.g. protons, hydrogensulfate ions or others), but must prevent permeation of the electrochemically active ions, which leads to self-discharge in the case of the redox flow battery and reduces the Coulombic efficiency, and iii) mechanical stability, which is another requisite for an optimal performance of the membrane separator.

Many large scale electrochemical devices use expensive perfluorinated membranes (e.g. Nafion) as separator, given their excellent chemical stability and relatively high ionic conductivity [8]. However, it is well known that Nafion presents a relatively large cation permeability, a limited mechanical stability and a high price. Efforts have therefore been made to develop less expensive membranes with lower permeability and better mechanical properties [9–12].

Alternative non-fluorinated cation exchange membranes have been developed [13–15]. The family of sulfonated aromatic polymers (SAP [7,9,16,17]) is of particular interest, because it is well known that, in fuel cell devices, the gas permeability of SAP is below that of perfluorinated ionomers [18,19], due to more tortuous and less connected hydrated channels; the gas permeability can be further reduced by the presence of cross-link bonds [20]. The behavior of SAP with respect to the cation permeability and the effect of cross-linking is explored in this work.

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In principle, anion exchange membranes (AEM) can prevent cation permeation owing to the Donnan exclusion effect, reducing significantly the cation cross-over. The Donnan exclusion is due to the presence of ionic groups grafted on the polymer backbone that repulse ions with similar charge. For example, positively charged ammonium groups in anion exchange ionomers oppose cation permeation.

Ampholytic (amphoteric) ion exchange membranes (AIEM) have both cation and anion exchange groups, and might thus combine a relatively low cation and anion permeability [21,22].

We present in the following the vanadium permeability, the ionic conductivity and mechanical properties of various ion exchange membranes, including protonic (with various degree of cross-linking), anionic, and amphoteric ionomers and discuss the relationship with the type of grafted ionic groups (sulfonic acid, sulfammonium, quaternary ammonium) and the type of polymer backbone, such as poly(ether ether ketone) (PEEK) or polysulfone (PSU). Both aromatic polymers have a large strength and stiffness due to the rigid phenyl rings in the macromolecule. PEEK presents a slightly higher stiffness than PSU [23,24], due to the quaternary carbon in the PSU structure that increases the backbone flexibility. PSU results more permeable to hydrogen (788.4 vs 108.6 $cm^2\ min^{-1}$) [25,26] and oxygen (82.8 vs 6.6 $cm^2\ min^{-1}$) [25,27] gas.

The ionomer structure was characterized by NMR spectroscopy, which is also used for the determination of the cross-link density.

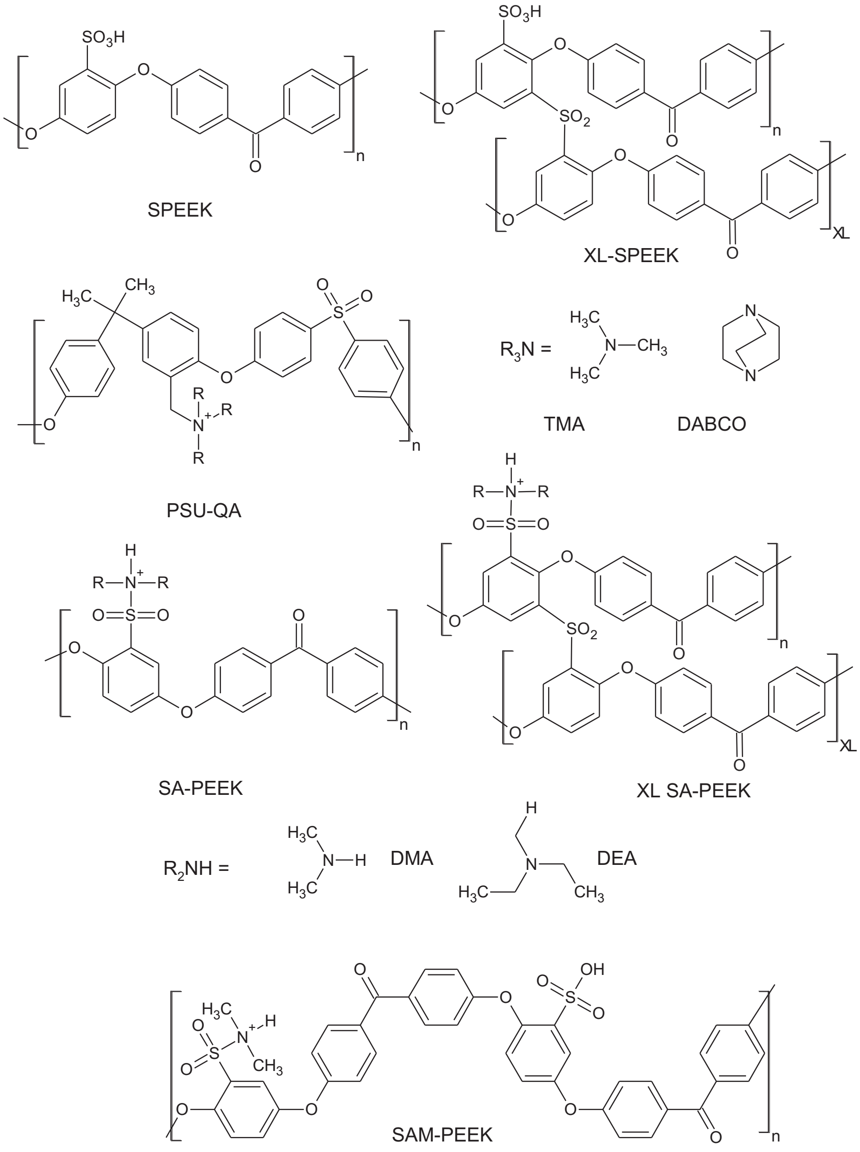
Vanadium was chosen as a model cation, because VO^{2+} ions can be easily observed by UV spectroscopy. Furthermore, vanadium is the active species in the All Vanadium Redox Flow Battery, one of the most promising large scale electrochemical storage systems.

2. Experimental

Nafion 117 (equivalent weight, EW = 1100 g/mol) was supplied by Sigma-Aldrich. Poly(ether ether ketone) (PEEK, 450P, MW = 38.300 g/mol)) and polysulfone (PSU, MW = 55.500 g/mol) were supplied by Victrex and Solvay, respectively. Other reagents were used as received from Sigma Aldrich.

2.1. Membrane synthesis

The repeat units of sulfonated poly(ether ether ketone) (SPEEK), polysulfone with quaternary ammonium (PSU-QA), sulfaminated poly(ether ether ketone) (SA-PEEK), and sulfonated and sulfaminated poly(ether ether ketone) (SAM-PEEK) are shown in Scheme 1. The



Scheme 1. Repeat units of investigated polymers.