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A high selectivity quaternized polysulfone membrane for alkaline direct methanol fuel cells

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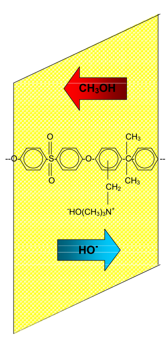
HIGHLIGHTS

- Alkaline membranes were synthesized via quaternization of a commercial polysulfone.
- Young's modulus of QPAES membranes alkalinized in 1 M KOH is similar to that of Nafion.
- Methanol permeability is much lower in QPAES than in Nafion membranes.
- Conductivies between 0.017 and 0.05 S cm^{-1} were measured at 30 < T (°C) < 70 °C.
- Methanol selectivity of the QPAES membranes is higher than that of Nafion 117.

GRAPHICAL ABSTRACT



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ABSTRACT

Alkaline membranes based on quaternized poly(arylene ether sulfone) (QPAES) were characterized in relation to their water and methanol uptake, methanol permeability, electrical conductivity, and mechanical properties. The performance of QPAES as electrolyte in alkaline direct methanol fuel cells was studied using a free-breathing single fuel cell at room temperature. Methanol uptake by QPAES membranes is lower than water, while their methanol permeability, determined in the temperature range from 30 °C to 75 °C, was much lower than for Nafion membranes. Young modulus of QPAES membranes decrease with the degree of alkalization of the membrane, although mechanical properties are still satisfactory for fuel cell applications for membrane alkalized with 2 M KOH, which additionally exhibit optimal hydroxide conductivity. Although the specific conductivity of QPAES membranes was lower than that reported for Nafion, its methanol selectivity (conductivity/methanol permeability ratio), is much higher than that reported for Nafion 117, and a commercial amminated polysulfone. In view of these results, QPAES membranes are expected to exhibit promising performance as an electrolyte in alkaline direct methanol fuel cells.

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1. Introduction

Methanol economy has been proposed by Olah et al. [1] as a previous step to a future hydrogen economy, because methanol is the simplest, safest, and easiest way to store and transport hydrogen as a liquid hydrocarbon. A methanol-based economy involves not only the conversion of methanol to synthetic hydrocarbons and their products that are essential part of our life, but also its use as a fuel in internal combustion engines or methanol direct proton exchange membrane (PEM) fuel cells (DMFC).

The use of methanol instead of hydrogen for feeding PEM fuel cells for electric vehicle transportation would have the advantage of facilitating fuel distribution and on-board storage, leading to a higher autonomy. However, the large-scale deployment of DMFC will probably starts through its use as power source of portable electronics, due to a high theoretical power density as compared with Li-ion batteries [2,3].

The high methanol crossover through Nafion and inorganic- or organic-Nafion composite membranes reduces the efficiency of DMFC in comparison with hydrogen fed PEM fuel cells, [4–6] thus triggering the search for novel proton exchange membranes with reduced alcohol permeability. [7,8] Nevertheless, anion exchange membrane (AEM) direct methanol fuel cells have numerous advantages over proton exchange membrane DMFC. For example, non-noble and low cost metal, such as silver and nickel, can be used as electro-catalysts due to the inherently faster kinetics of oxygen reduction reaction in alkaline media. Furthermore, methanol oxidation is more facile in alkaline media than in acidic one [9–13].

Although the ionic conductivity of AEM is not as high as that of PEM membranes, [14,15] they have several advantages, namely: can be synthesized from low cost materials, and exhibit less alcohol crossover that PEM because the electro-osmotic transport of water and alcohol occurs from the cathode to the anode, that is, in opposite direction that solvent transport in PEM DMFC [16–18].

Several types of AEM have been developed during the last decade aiming to improve the performance of H_2/O_2 AEM fuel cells running with aqueous KOH electrolyte, first demonstrated by Bacon in the 1930s and used in the NASA missions two decades later. The polymeric materials currently under investigation for H_2/O_2 solid AEM fuel cells have been recently reviewed by Couture et al., [19] while their performance in direct alcohol AEM fuel cells was also analyzed [20,21].

Varcoe and coworkers were pioneers in synthesizing AEM with quaternized ammonium groups for DMFC by radiation grafting vinylbenzyl chloride (VBC) onto stable materials such as poly (ethylene-co-tetrafluoroethylene) (ETFE). [18,22] Other AEMs based on polymers containing a quaternary ammonium group have been developed and their electrical conductivity and methanol permeability have been reported, and in some cases they were tested in alcohol direct alkaline fuel cells (ADAFC). Among these quaternized membranes are: poly(ether sulfone cardo) (QPES-C), [23] poly(ether ketone cardo) (QPEK-C), [24] poly(phthalazinone ether sulfone ketone) (QPPESK),16 poly(arylene ether sulfone) (QPAES), [12,25,26], QPAES cardo, [27] QPAES/crosslinked polyethylene, [28] and QPAES/ZrO_2 composites, [29] poly(arylene ether) (QPAE), [30] poly (arylether oxadiazole) (QPAEO), [31] polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (QSEBS), [32] poly(vinyl alcohol) (QPVA), [33] poly(vinyl chloride) (QPVC), [34] poly(vinylbenzyl chloride) (QPVBC), [35] and poly(vinylbenzyl chloride)-grafted-poly(ethylene-alt-tetrafluoroethylene) (QETFE-g-PVBC) [36].

C. C. Yang and coworkers and other authors have studied quaternized PVA (QPVA)-based membranes in relation to their methanol permeability and DMFC performance, including PVA cross-linked with sulfosuccinic acid (cPVA), [37] and composite membranes of QPVA with SiO_2, [38] quaternized SiO_2, [39] Al_2O_3, [40] chitosan, [41,42] and poly (epichlorohydrin) (PECH) [43].

Commercial AEM based on quaternary ammonium exchange groups have been developed by Tokuyama (Japan) on unknown backbone polymer (A201 membrane), by Solvay (Belgium) on cross-linked fluorinated polymer (Morgan ADP membrane), and by Fumatech (Germany) on polysulfones (FAA membrane). All of then have been tested in methanol and other ADAFC [44–54].

Membranes based on poly(arylene ether sulfone) with pendent quaternary ammonium (QPAES) have recently received much attention in relation to their use in solid-state alkaline fuel cell due to its relatively low cost and high electrical conductivity (up to 60–80 mS cm^{-1} at room temperature) [12,25]. Its high permselectivity is expected to be also useful for salinity gradient technologies, such as reverse electrodialysis. [55] Moreover, QPAES chemical stability seems to be compatible with the expected long operation lifetimes in alkaline fuel cell [56], and alkaline electrolyzer [57] applications.

The successful replacement of Nafion by quaternized AEM in DMFC strongly depend on the possibility of compensate the lower ion conductivity of the AEM with lower methanol permeability. In a previous work [12] we prepared a quaternized poly(arylene ether sulfone) membrane (QPAES) from a commercial polysulfone (Udel), quaternized by a trimethylamine treatment. The obtained AEMs exhibited good mechanical and conductivity, and sorbs more water but less methanol than Nafion over the whole range of water activities. Based on these results we claimed that QPAES membranes could exhibit promising barrier properties against methanol crossover in DMFC, although the permeability of methanol through these membranes was not studied.

In this work we determined the methanol permeability through QPAES membranes on a wide temperature range in order to confirm our expectations. We have also performed electrical conductivity measurements of QPAES membranes alkalinized with 2.0 mol dm^{-3} KOH at temperatures up to 71 °C, and the effect of the KOH concentration on the mechanical properties was evaluated using nanoidentation analysis to determine the Young's modulus of the AEMs. This parameter is related to the resistance of the material to be compressed, [58] which is relevant for fuel cell application. Finally, water and methanol uptake and partition coefficients were determined in bulky membranes, in order to compare with previous sorption results obtained using the quartz microbalance (QMB) technique on ultrathin (40 nm thickness) ones. [12] This analysis could help to decide whether the properties of bulky QPAES membranes differs from that of thin QPAES films, as those present in the three-phases region of the MEAs, as it was found in the case of Nafion [59].

In summary, the aim of this work is to characterize bulky QPAES membranes in order to obtain all the physico-chemical parameters needed for understanding the behavior of the membrane under direct methanol alkaline fuel cell conditions. These properties will be compared with those of Nafion® membrane properties, still the most used membrane in DMFC, and with those of a commercial alkaline membrane (A201®, Tokuyama).

2. Experimental

2.1. QPAES synthesis and membrane preparation

A commercial Udel® polysulfone was chloromethylated, amminated, and converted to the HO^- form, following a procedure described elsewhere. [12] Different KOH concentrations were used in order to analyze the effect of the HO^- counterion content on the membrane properties. Due to the Donnan equilibrium, the concentration of HO^- counterions in the membrane is that required to