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Influence of temperature on the electrokinetic properties and power generation efficiency of Nafion® 117 membranes

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HIGHLIGHTS

- Electrokinetic energy conversion is investigated experimentally.
- High electrokinetic energy conversion efficiency in Nafion membrane is found.
- Power density and efficiency increases with temperature.
- Temperature dependence of pore size in Nafion are estimated from transport properties.

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ABSTRACT

In the present study we investigate the transport properties of Nafion® 117 membranes in temperatures ranging from ambient temperature up to 70 °C. The hydraulic permeability, streaming potential and ion conductivity have been measured as function of temperature in 0.03 M LiCl solutions in purposely designed, non-conductive set-ups. In particular, the apparent activation energies of the processes have been retrieved: 29.4 kJ mol^{-1}, 9.3 kJ mol^{-1} and 22.9 kJ mol^{-1} for the hydraulic permeability, streaming potential coefficient and ion conductivity respectively. Based on the knowledge of the temperature dependence of these three independent properties the *figure-of-merit* of the electrokinetic energy conversion process has been calculated obtaining a monotonous increase of the efficiency with temperature. At 70 °C the electrokinetic efficiency is rather high about 26.6%:50% higher with respect to the one found at room temperature. The electrokinetic transport properties were also used to esteem the average pore size of the water channels in the polymer matrix resulting in pore diameters ranging approximately from 2.0 (25 °C) to 2.8 nm (70 °C).

1. Introduction

The increasing demand of energy and the need of decentralized power generation systems combined together with the urgency of emission reductions encouraged the researchers' interests in developing new, efficient and more environmental friendly energy production systems. Polymer electrolyte fuel cells, PEMFCs, are potentially among the most efficient devices for power generation, and a large amount of specific literature has been published in the last decades focusing, especially, in developing new solid polymer electrolyte materials with enhanced properties [1–6]. However, despite the efforts devoted in this direction the reference membrane for fuel cell applications still remains Nafion®, produced by DuPont, due essentially to the high chemical, mechanical and thermal stability and high proton conductivity during fuel cells operation. Another attractive, still not well investigated, way of energy conversion in ion conductive membranes is the direct conversion of kinetic energy into electrochemical energy. The electrokinetic energy conversion has been studied both theoretically [7–10] and experimentally focusing the attention mostly on the properties of straight nanochannels with reported efficiencies up to 10% [11–16]. In literature, a few studies of the electrokinetic properties of ion conductive membranes have been reported. A non-mechanical pressurization system based on Nafion® 117, in the following referred to as Nafion, in tetrapropylammonium iodide and iodine in DMF solutions has been proposed by Evans et al. [17], while we have reported the electrokinetic properties of Nafion at room temperature in a previous work [18]. However a more systematic experimental investigation of the electrokinetic properties of ion conductive membranes is still missing. The basic mechanism behind the electrokinetic power generation is the potential

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difference generated by a pressure gradient applied across a membrane, i.e. streaming potential, separating two compartments filled with aqueous solutions having the same salt concentration. The streaming potential is a consequence of the coupling between ions and solvent (hydration) and whenever a pressure difference drives a volume flux through the membrane, ions are dragged along, whereby creating a potential difference. One of the key advantages of electrokinetic energy conversion is that moving mechanical stages are not required. Nonetheless, high conversion efficiency along with high power density are fundamental parameters in comparisons to e.g. electromagnetic actuators that represent the state-of-the-art of commercially available units that convert kinetic energy into electrical energy.

Based on measurements of the hydraulic permeability (κ_H), streaming potential coefficient (ν) and ion conductivity (σ) the electrokinetic *figure-of-merit* $\beta_{EK} = \nu^2 \cdot \sigma / \kappa_H$ is retrieved and can be used for calculation of the electrokinetic conversion efficiency $\eta_{EK} = [(1+\beta_{EK})^{1/2} - 1]/[(1+\beta_{EK})^{1/2} + 1]$. For a more detailed discussion the reader is referred to refs. [7,8,16,19].

In previous studies we demonstrated that the maximum efficiency of 18 ± 2% for Nafion [18] is significantly higher with respect to the non- or low-charged membranes [16,18], for which a maximum of about 7% for Cyclopore and Nucleopore membranes has been found [16]. These results indicate that ion conductive membranes could represent a possible pathway for high-efficiency electrokinetic energy conversion. The high electrokinetic efficiency observed in ion conductive membranes with respect to non-charged membranes could be explained by the high surface charge density, $\sigma_q \sim 0.2$–1 C m^{-2} for Nafion [20,21], of the nanoporous hydrophilic network. In its swollen state, an ion exchange membrane can be depicted as a hydrophobic PTFE-like matrix and a network of more or less interconnected water nano-channels in which the transport of water and ions takes place [22–27]. Besides the fixed charge density, the electrokinetic properties of such a system strongly depend on the average pore dimensions and channel tortuosity [28,29]. Several ways to modify the pore structure of Nafion, to increase the ion exchange capacity, the water retention and the mechanical and thermal stability have been proposed in the literature. This includes e.g. addition of hygroscopic materials (Al_2O_3, SiO_2, clays, silicophosphate gels etc.) obtaining inorganic-polymer composite membranes [30], use of dendrimers [31]. On the other hand it is well known from the literature that by increasing the temperature, Nafion membranes show higher dimensional swelling [32], liquid water uptake [33–35] and hydraulic permeability [36,37]. These latter experimental evidences indicate a more open structure with higher water content and larger average pore size. It is anticipated that all the three transport properties that enter the expression for $\beta_{EK} = \nu^2 \cdot \sigma / \kappa_H$ increase with the pore dimensions and thus with temperature. Still, the expected temperature dependence of β_{EK} is not known and depends on whether the nominator ($\nu^2 \cdot \sigma$) has a larger increase with temperature with respect to the denominator (κ_H). Therefore the main objective of this work is to experimentally determine the temperature dependence of κ_H, ν and σ in Nafion membranes and to get more detailed insight on the electrokinetic conversion efficiency as function of temperature.

2. Materials and methods

2.1. Membranes

Nafion 117, with a nominal thickness of 178 μm, was bought from Ion Power Inc, US. Before use membrane samples were pretreated by boiling in demineralized water. The membranes were then heated in 3wt% of H_2O_2 water solution for 60 min at $T \sim 90$ °C, transferred in boiling demineralized water, and then heated up to 90 °C for 60 min in 0.5 M H_2SO_4 water solution. Finally the membranes were washed in warm (~70 °C) demineralized water for ten minutes; the last step was repeated four times. After pretreatment the membrane samples were stored in 0.5 M LiCl solutions to obtain Nafion in Li^+ form. All measurements have been carried out in 0.03 M LiCl aqueous solutions, and to avoid any increase in the concentration in the measurement cells the membranes were carefully rinsed in 0.03 M LiCl before being tested. The membrane thickness in both the dry and swollen states was measured with a digital micrometer (Diesella, resolution 1 μm).

2.2. Hydraulic permeability and streaming potential apparatus

The experimental set-up for the measurement of the hydraulic permeability and streaming potential as a function of the temperature is schematically shown in Fig. 1. It consists of two jacked borosilicate glass chambers of about 400 cm^3 volume separated by two membrane holders made in Teflon. The custom-made holders had 4 ports each for instruments' connection (e.g. thermocouples and electrodes). The temperatures in the two cells were independently controlled by two different water baths (Eco Gold Lauda DE, temperature stability 0.01 °C) feeding the chambers' jackets, and monitored through two thermocouples type K (Omega US, 1/16 inch) placed at approximately 5 mm from the membrane surfaces. To reduce concentration polarization at the membrane/solution interface and to have a more uniform and constant temperature, two inert magnetically coupled stirrers (Büchi CH, Cyclone *i*) have been employed. The stirrers, having all the wet parts in PFA and glass, are rated to work up to 6 bar of pressure and temperature up to 180 °C and they were connected through GL 32 ports to the two Teflon lids of the two chambers. The absence of the shaft rotation ensures a small leakage of the system which was further reduced by using an additional O-ring (Seals DK, Silicon) along the shaft axis. The two chambers were filled with identical aqueous solutions by first applying vacuum (Vacuumbrand DK rotary pump) in both chambers (valves V3, V6 and V7 close, all the others open), and, subsequently by opening the outlet valves (V1–V5 close, V6 and V7 open), which were beforehand connected with a solution reservoir. After the system reached the thermal stability the low pressure chamber was connected to a calibrated capillary and pressure was applied in the high pressure chamber by using an Ar gas cylinder (V3 and V5 open, V7 close), and was monitored, in each cell, by the use of pressure transducers (Druck DE, range 1–11 bar). The glass reactors were designed to work above 6 bar in pressure, and in order to avoid any unexpected increase two additional rupture discs (Büchi CH, wet part in graphite and PFA 6 bar) were connected to the two cells.

The active area for the membrane transport was 3.14 cm^2. To avoid any deformation of the membrane due to the applied pressure, a screen (Sartorius US, coarse grid Teflon coated stainless steel) has been used in the low pressure compartment. The streaming potential was measured through the use of two Ag/Ag–Cl electrodes (0.25 mm in diameter) placed close to the membranes surfaces and mounted through the two membranes holders with PEEK 1/16 inch connector (Mikrolab DK) and purposely designed Teflon ferrules. The electrodes were prepared from 0.25 mm diameter silver rod (Alfa Aesar DE, 99.9985% metal basis) following the same procedure reported in a previous publication [18]. The hydraulic permeability was monitored following the movement of the liquid meniscus over time in the calibrated capillary (Teflon, inner diameter 0.75 mm).

All the fitting, valves and tubing were in Teflon and bought from Swagelok, with the exception of the GL connection of the cells (PFA) and the vacuum fittings and valves which were purchased form