



The influence of water channel geometry and proton mobility on the conductivity of Nafion[®]



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ABSTRACT

Water uptake of polymer exchange membranes (PEMs) such as Nafion[®] leads to water channels that are separated from the solid polymeric phase. In this study, the proton mobility in Nafion[®] and the influence of the water channel morphology on its overall conductivity are characterized by experimental approaches in combination with reported computational results. Using impedance spectroscopy with amplitude and frequency variation, the proton mobility was derived to be independent of the length scale of the proton permeation through fully hydrated Nafion[®], suggesting equal direct current (DC) and alternating current (AC) conductivities. The proton conductivities of aqueous solutions with equal proton concentrations as the aqueous phase of fully hydrated Nafion[®] membranes were measured to be approximately 6.0 ± 0.7 times higher than those of the membranes. Recently reported resistor network modeling results characterized the influence of the morphology of the aqueous phase on the proton permeation through fully hydrated Nafion[®] to approximately the same degree. By comparing these experimental and modeled result, the mean proton mobility in the aqueous phase of fully hydrated Nafion[®] was estimated to equal that in aqueous solutions.

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1. Introduction

In low-temperature fuel cells [1], water electrolyzers [2], and artificial leaves [3], polymer electrolyte membranes (PEMs) can be used to separate the anodic and cathodic compartment and to provide the ionic conductivity between the electrodes. The most stable and conducting PEMs are proton conducting perfluorosulfonic acids such as Nafion[®] [4,5]. In these materials, sulfonic acid groups are covalently bonded to the polymer matrix [6]. When in contact with liquid water or with a humidified atmosphere, the acidity leads to water uptake and the formation of an aqueous phase in which the protons can be dissolved [7]. The morphology of the aqueous phase in Nafion[®] was experimentally examined by methods such as cryo electron tomography [8], small angle scattering techniques [9,10], and atomic force microscopy [11]. Based on these measurements, a clear phase separation between the aqueous phase and the solid phase was reported [5,12]. Nafion[®] membranes

are fully hydrated when immersed in water. In the case of water uptake from a humidified ambient atmosphere lower hydration levels result [13–17]. As a consequence of the expansion of the water network with larger water sorption [18–22], the conductivity increases toward higher relative humidity [18,23].

By using computational simulations, the electrostatic force between the anions and the protons of the functional groups was reported to cause inhomogeneous distributions of the dissolved protons in the water channels of Nafion[®] [19,24–26]. This inhomogeneous distribution was modeled to reduce the proton mobility [19,26]. In addition, the influence of the sulfonated groups on the hydration, solvation, diffusion, and mobility of the protons was computationally modeled [27–34]. Most of these studies came to the conclusion that the proton mobility inside the aqueous phase of Nafion[®] is reduced compared to that of aqueous solutions while lowering the water content increases this effect. The influence of the morphology of the aqueous phase in Nafion[®] was estimated by various authors using resistor network modeling [18,21,19,35].

The aim of this study is to experimentally examine the influence of the interaction of protons with the pore walls of the water channels, the proton mobility, and the proton permeation through the morphology of the water channels on the proton conduction of Nafion[®] membranes. Within this aim, the response of the proton

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conduction of fully hydrated Nafion® membranes as a function of the length scale of the proton movement was examined using impedance spectroscopy with different excitation amplitudes and frequencies. Moreover, the differences between the proton conductivity of Nafion® membranes and aqueous solutions with similar acidity were examined, in order to relate the influence of the geometry of the water channels in fully hydrated state on the overall conductivity.

2. Methods

2.1. Experimental setups

The impedance of the aqueous solutions and the Nafion® membrane samples were measured using an impedance analyzer (Zahner, IM6) and two different setups. To measure the Nafion® membrane samples, a four-wire sensing configuration based on that proposed by Sone *et al.* [23] was used. This setup is in the following denoted as setup A and is illustrated in Fig. 1A. In this setup, membrane strips of 15 mm width were woven around four platinum wires in a parallel alignment that acted as the electrodes for the electrochemical impedance spectroscopy. These platinum wires were arranged with a distance of respectively 10 mm in an in-house made polytetrafluoroethylene (PTFE) cell. With reference to a standard four-wire sensing impedance measurement, an alternating current (AC) with a defined frequency was applied to the outer electrodes, while the voltage drop at the inner electrodes was measured. During the measurements, the cell with the membrane was immersed into a bath with deionized water (Millipore, Advantage A10, resistivity 18 MΩ cm). A weight of 100 g was used to keep the membrane sample taut and to press it onto the electrodes. To measure the influence of temperature on the conductivity, the water bath with the PTFE cell was heated in a self made oven with rates of 0.1 K/min. During this temperature variation, the high

frequency resistance² of the cell and the temperature of the water bath were simultaneously monitored over time. A Pt100 resistance thermometer (Electrotherm, K3-E-3LS-200) was immersed in the water bath and used to measure the temperature. Before measuring, the as-received Nafion® membranes were boiled for 20 min in deionized water. Additional boiling of the samples in acid (1 M H₂SO₄) and subsequent rinsing by boiling in deionized water did not markedly change the conductivity as the membranes were delivered in the protonated form.

In order to measure the ionic conductivity of aqueous solutions, these were filled into an in-house made 10 cm long PTFE block with a cylindrical hole of 2.2 cm diameter. Fig. 1B illustrates this setup, which is in the following denoted as setup B. The PTFE block was sandwiched between two electrodes made of carbon fleece (Freudenberg). These carbon fleeces were coated with Hispec 9100 (Johnson Matthey) carbon supported platinum catalyst (1 mg_{Pt} cm⁻²) in order to enlarge the surface areas of the electrodes and the related electrochemical capacitances. Catalyst ink was directly coated on the carbon fleeces following the procedure described in a previous study [37]. Based on the data of the HiSpec 9100 catalyst reported by the manufacturer [38] and the amount of the catalyst used, the surface area of the platinum catalyst was estimated to be approximately 850 times larger than that of the geometric electrode area. Graphite plates sealed and electrically contacted the porous carbon fleeces electrodes. Both carbon based materials were chemically resistant to corrosion by the hot acid solutions measured. Steel end plates were pressed onto the two graphite plates. These steel end plates were contacted by banana plugs with the impedance analyzer. Pseudo four-wire sensing was used, where two of the four wires were connected to one of the steel end plates, respectively. By using this configuration the impedance of the wires and contacts were eliminated. Besides the electrolyte resistance, also the resistances of the steel plates, graphite plates, and carbon fleece contributed to the measured impedance. These resistances of the apparatus were determined by reference measurements, where the impedance of the cell was measured without the PTFE cylinder, so that the carbon fleece electrodes were directly pressed onto one another. The resistance of this alignment was measured to be negligible, meaning that the influence of the resistances of the apparatus had a negligible contribution to the total impedance of the aqueous solutions measured. In order to control the temperature, the cell was immersed in an in-house made oven. To measure the temperature, a Pt100 thermometer (Unitherm) embedded in a heat shrink plastic tubing was in direct contact to the examined aqueous solution

The impedance measurements of the samples/solutions (measured with setup A or B) were carried out during variation of the temperature with upward and downward ramps. Thanks to the low rates of the temperature ramps of ±0.1 K min⁻¹, significant differences between the measured impedance of a sample/solution as a function of the temperature for the upward and downward ramps could not be observed. The temperature dependency of the impedance of a sample/solution as a function of temperature was obtained by averaging the data from up and down sweeps.

2.2. Interpretation of the impedance spectra

In order to describe the impedance spectra of the Nafion® membranes and the aqueous solutions measured, the equivalent circuit diagram illustrated in Fig. 2 was utilized. This equivalent circuit diagram is the most simple and frequently used approach to characterize electrochemical cells [36]. When both electrodes

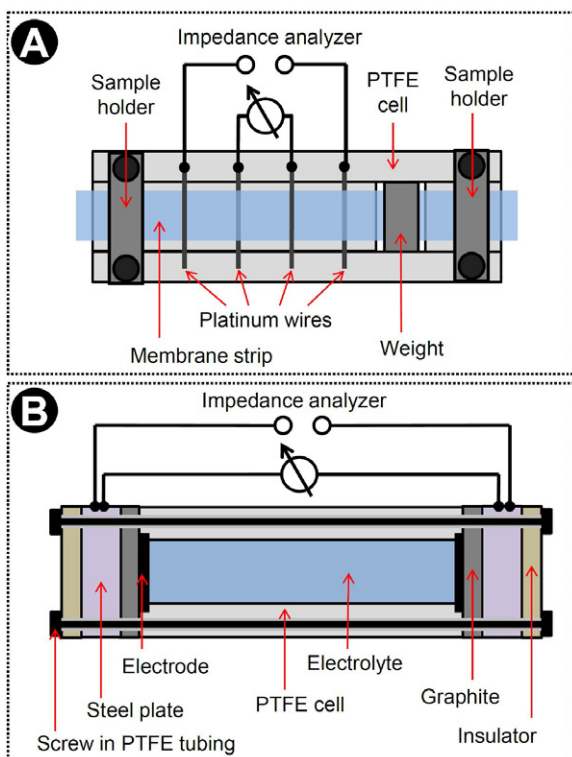


Fig. 1. Schematic illustrations of the setups used to measure the impedance of membrane samples (A) and aqueous solutions (B).

² The high frequency resistance of an electrochemical cell (typically in between 1 kHz and 100 kHz) is dominated by the ohmic resistance of the electrolyte [36].

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