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## Journal of Membrane Science

journal homepage: [www.elsevier.com/locate/memsci](http://www.elsevier.com/locate/memsci)

# Effect of pressure on through-plane proton conductivity of polymer electrolyte membranes

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## ARTICLE INFO

## Article history:

Received 4 March 2012

Received in revised form

20 June 2012

Accepted 22 June 2012

Available online 3 July 2012

## Keywords:

Polymer electrolyte membranes

Electrochemical impedance spectroscopy

Through-plane conductivity

Anisotropic conduction

Contact resistance

## ABSTRACT

This study reports an electrochemical analogy with the invention of a 2-electrode impedance cell oriented to analyze through-plane ionic conductivity of polymer electrolyte membranes. The membranes are utilized under varied pressures in assembled membrane stacks for water treatment, energy conversion, and storage devices. In addition, polymeric membranes are a viscoelastic material, which allow their shape to change according to the external pressure. Therefore, the impedance under controlled pressure is crucial information for analyzing their electrochemical properties. In this regards, an apparatus is designed to indicate the absolute pressure in the sample and the resulting thickness of the sample while measuring the impedance. As a model analysis, we employ a proton conducting membrane, Nafion<sup>®</sup>117, Nafion<sup>®</sup>115, and Nafion<sup>®</sup>112. The membrane thickness in a wet state was found to be significantly variable with the pressure, and the impedance spectra showed a clear dependence on the pressure. Therefore, this new approach facilitates a precise impedance analysis, since the exact sample thickness is indicated, along with the absolute pressure in the sample. As such, this technique could be a useful tool for analyzing the through-plane conductivity of polymer electrolyte membranes with high accuracy.

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## 1. Introduction

Polymer electrolyte membranes (PEMs) have been used in a diverse range of electrochemical water treatment and energy conversion-storage systems, including capacitive deionization [1], electrodialysis [2], reverse electrodialysis [3], fuel cells [4], secondary batteries [5], redox flow batteries [6], dye sensitized solar cells [7], and others. In such electrochemical systems, the general requirements of these membranes, such as ion-exchange capacity, water contents, swelling behaviors, mechanical properties, and thermal and chemical durability should be satisfied according to electrochemical specifications in the target system. In addition, the ionic conductivity of a PEM has been considered a primary parameter for estimating system performance, as PEM resistivity is the predominant reason for the potential drop in particular for a fuel cell [8,9]. To estimate proton conductivity under specific conditions, a number of galvanostatic alternating current (ac) electrochemical impedance spectroscopic (EIS) techniques have been well documented, based on equivalent circuits corresponding to the electrochemical impedance cells [10–23].

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To date, conventional 4-electrode cells have been universally used and analyzed for in-plane proton conductivity, due to advantageous features such as the geometrically large cell constant, negligible electronic resistance, and the interfacial contact between the membrane surface and thin platinum wires [12,13]. In addition, recent efforts have evolved analytical approaches for through-plane conductivity due to the increasing concerns of anisotropic proton conduction in the membranes [14,20,24]. It has also been posited that measuring proton conductivity in the through-plane direction may enable the precise estimation of PEM fuel cell performance, since the practical proton conduction occurs in the through-plane direction of a PEM. Indeed, several electrode arrangements have been reported for through-plane conductivity analyses [12,14,20,21,23] however, systematic investigations of through-plane impedance data under the influence of controlled pressure on a polymeric membrane and its viscoelastic behavior under pressure are sparse, and have yet to be strongly emphasized with the exploration of anisotropic proton conducting materials.

In an effort to precisely obtain the through-plane resistance, we report here the invention and application of a technically improved 2-electrode electrochemical cell [25] and a novel analogy of impedance data for the through-plane conductivity of Nafion<sup>®</sup> membranes. This cell is designed to indicate the

absolute pressure applied to the sample as well as the corresponding thickness of the sample during the through-plane EIS analysis. Within the best of our knowledge, previous works have neglected to include the thickness changes of a PEM under pressure, though this change may significantly affect the hydration rate (or water content) and proton conductivity of a suppressed PEM.

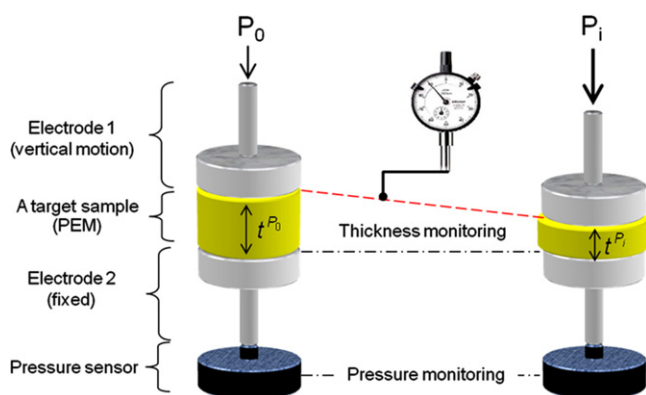
## 2. Experimental

### 2.1. Materials

Two disc type stainless steel electrodes were fabricated, each having an effective area of 1 cm<sup>2</sup>. A dial indicator (No. 2113S-10, Mitutoyo Manufacturing Co., Ltd., Japan) was used for the thickness measurement. A load sensor (SML-30L, Curiosity Technology Co., Ltd., Korea) having a maximum 66 pound-force capacity was calibrated (and communicates) with a digital indicator (MI-830, MiGun ST Co., LTD, Korea) as the pressure sensor. The polymer electrolyte membranes (Nafion<sup>®</sup>117, Nafion<sup>®</sup>115, and Nafion<sup>®</sup>112, DuPont, USA) were prepared after being treated with a 1 mol/l HCl solution for 5 h. Then, in order to examine the practical compression pressure for a membrane in a fuel cell and the apparatus system, two types of pressure sensitive film (Pressurex<sup>®</sup>, SPI Inc., USA) – “Superlow” for the range of 70–350 psi and “Low” for 350–1400 psi – were assembled instead of using a traditional membrane. A video microscope (SV-32, Sometech Co., Korea) was temporarily used to visually observe the thickness change of the membrane under specific pressures, and the photographed thickness was obtained using image tracer software (IT-Pro3.0, Sometech Co., Korea).

### 2.2. Cell configuration and instrumentation

Two disc electrodes were placed horizontally (see Fig. 1) for a through-plane EIS analysis of the polymeric membranes. As illustrated, electrode 2 on the bottom was fixed to the apparatus body (made by aluminum pillar), whereas electrode 1 was designed to allow only vertical motion, induced by the externally applied vertical compression force. Therefore, the electrode 1 provides a certain compression pressure to the target sample placed on electrode 2, and the apparatus was mechanically designed to exert the force to the load sensor through a static bypass aluminum frame. Finally, the absolute pressure was indicated by the calibrated digital indicator. Concurrently, the membrane thickness was monitored via the dial gauge. The device is



**Fig. 1.** Schematic of electrode structure for the 2-electrode cell used for the through-plane EIS analysis. A target sample is compressed by the external pressure from  $P_0$  to  $P_i$ , and the thickness of a viscoelastic PEM is reduced from  $t^{P_0}$  to  $t^{P_i}$ .

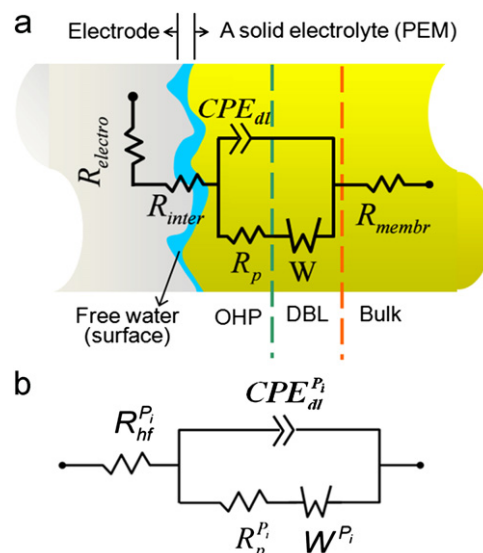
designed to indicate the membrane thickness directly by the distance between the two electrodes. The dial indicator was mechanically set-up to monitor the vertical position of electrode 1, and thus could readily monitor the distance of electrode 1 from the fixed electrode 2. The details on the technical reliability were discussed in the operational data.

### 2.3. Equivalent circuit model for through-plane EIS measurement

Two critical advances of this 2-electrode cell are the ability to exactly control the pressure applied to a PEM and to monitor the reduced thickness of a viscoelastic PEM under a stationary pressure. The pressure profile of a PEM obtained by the sandwiched electrodes significantly affects the impedance data, particularly due to variation of the physical interfacial contact resistance ( $R_{inter}$ ) between the electrode and PEM surfaces [20]. Then, at the interface of the PEM surfaces, an electrochemical double layer accompanies the polarization resistance ( $R_p$ ) in parallel with a constant phase element ( $CPE_{dl}$ ) within the outer Helmholtz plane (OHP) [19], and Warburg impedance ( $W$ ) is exhibited by a diffusion boundary layer (DBL) at the PEM surfaces. These electrochemical phenomena are described in Fig. 2(a), in which the electronic components include the electronic cell resistance ( $R_{electro}$ ) and membrane resistance ( $R_{membr}$ ). Among the components, only  $R_{electro}$  is independent to the pressure load; hence, the equivalent circuit can be modelled at a pressure  $i$  ( $P_i$ ), as shown in Fig. 2(b).

### 2.4. Through-plane proton conductivity via an electrochemical impedance measurement

Each swollen Nafion<sup>®</sup> membrane in deionized water was assembled between the two electrodes. The EIS analyses were carried out using a potentiostat/galvanostat (Autolab PGSTAT 30, Eco Chemie, Netherlands), and operated via a galvanostatic method under a 0.1 mA ac amplitude over a frequency range of 1 MHz to 10 Hz by using a frequency response analyzer. The EIS analysis was carried out under ambient conditions at room temperature and there was no additional humidification. Also, every membrane was analyzed at the same time and inside of a copper shield net in order to minimize the variation of temperature and humidity, and the signal interruption of high frequency from other electrical equipments, respectively. As



**Fig. 2.** (a) Impedance components based on electrochemical behaviors between the electrode and a swollen PEM. (b) Simplified equivalent circuit model as a function of pressure on a PEM.

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