

*Short Communication*

## **Test System For Through-Plane Conductivity Measurements of Hydrogen Proton Exchange Membranes**

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We present a simple test system for membrane through-plane conductivity measurements. In this design the catalyst layer is detached from the membrane and added to the gas diffusion electrode. Moreover, the humidifying gas is recycled after exiting the test cell making it more cost effective. To prove the test system applicability, electrochemical impedance spectroscopy (EIS) is used to determine the ionic conductivity of a model Nafion membrane at two different temperatures. Nyquist plots are used to analyze the impedance spectra. Equivalent circuit modeling of the EIS data is used to extract the Ohmic membrane resistance, which is in turn used to calculate the membrane ionic conductivity using self-developed fitting routines.

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**Keywords:** Ionic conductivity, through-plane, fuel cell, bare proton exchange membrane, EIS, Nyquist plot.

### **1. INTRODUCTION**

Proton exchange membrane fuel cells (PEMFCs) are one of the most promising clean energy technologies. They have certain potential advantages such as portable applications, power generation, and high efficiency [1-3]. One of the key components of a PEMFC is the proton exchange membrane (PEM), which is responsible for proton transportation from the anode to the cathode [4]. The current state-of-the-art PEM is a perfluorocarbon based polymer (Nafion) [5,6]. Major drawbacks of Nafion membranes include: low conductivity, poor performance under low humidification, drying at elevated temperatures (above 90 °C), and high methanol permeability. These factors together with the high cost of Nafion have triggered an extensive research for alternative PEM materials [7-15]. The primary demand on any potential PEM replacement is a high ionic (proton) conductivity. Systematic testing of

the membrane ionic conductivity under a wide range of conditions is essential in the process of developing new membranes to replace Nafion [16]. Therefore, it is desirable to have a simple and cost effective test system that allows conductivity measurements without using much of the costly platinum catalyst.

Proton conductivity is widely measured in the in-plane direction of the membrane because it is easily implemented [17, 18]. However, conductivity in the through-plane direction, along the membrane thickness, is more relevant for fuel cell applications, especially for membranes exhibiting morphological anisotropy [4]. In this respect, various apparatus for the through-plane conductivity measurement have been reported [19–28]. However, detailed information about the cell configuration and the data extraction methods are sparse. Recently, however, Cooper reported on an easily-implemented test system for evaluating the membrane through-plane conductivity over a broad range of temperature and humidity conditions [29]. On the basis of Cooper's work, Scribner Associates Inc. introduced a commercial membrane test system (MTS) that provides advanced testing features for electrochemical research [30].

In this article, we report a simple test system that has been designed and manufactured to measure through-plane ionic conductivity of bare (non catalyzed) PEMs at different temperature and humidity conditions. The design builds on Cooper's work, whereby the nanostructured Pt catalyst layer is detached from the membrane and added to the gas diffusion electrode (GDE). Emphasis is placed on recycling the humidifying gas after exiting the test cell making it more cost effective than Cooper's cell. To assess the manufactured cell's applicability, we used it to determine the ionic conductivity of a model Nafion membrane at different temperatures. Electrochemical impedance spectroscopy (EIS) was applied using a frequency range of  $10^{-1}$  to  $10^5$  Hz. Nyquist plots were used to analyze the impedance spectra. Equivalent circuit modeling of the EIS data was used to extract the Ohmic membrane resistance which was in turn used to calculate the membrane ionic conductivity using self-developed fitting routines.

## 2. EXPERIMENTAL

### 2.1. Instrumentation of the test cell

Figure 1 shows a schematic drawing of the test cell manufactured in this work. It comprises five units:

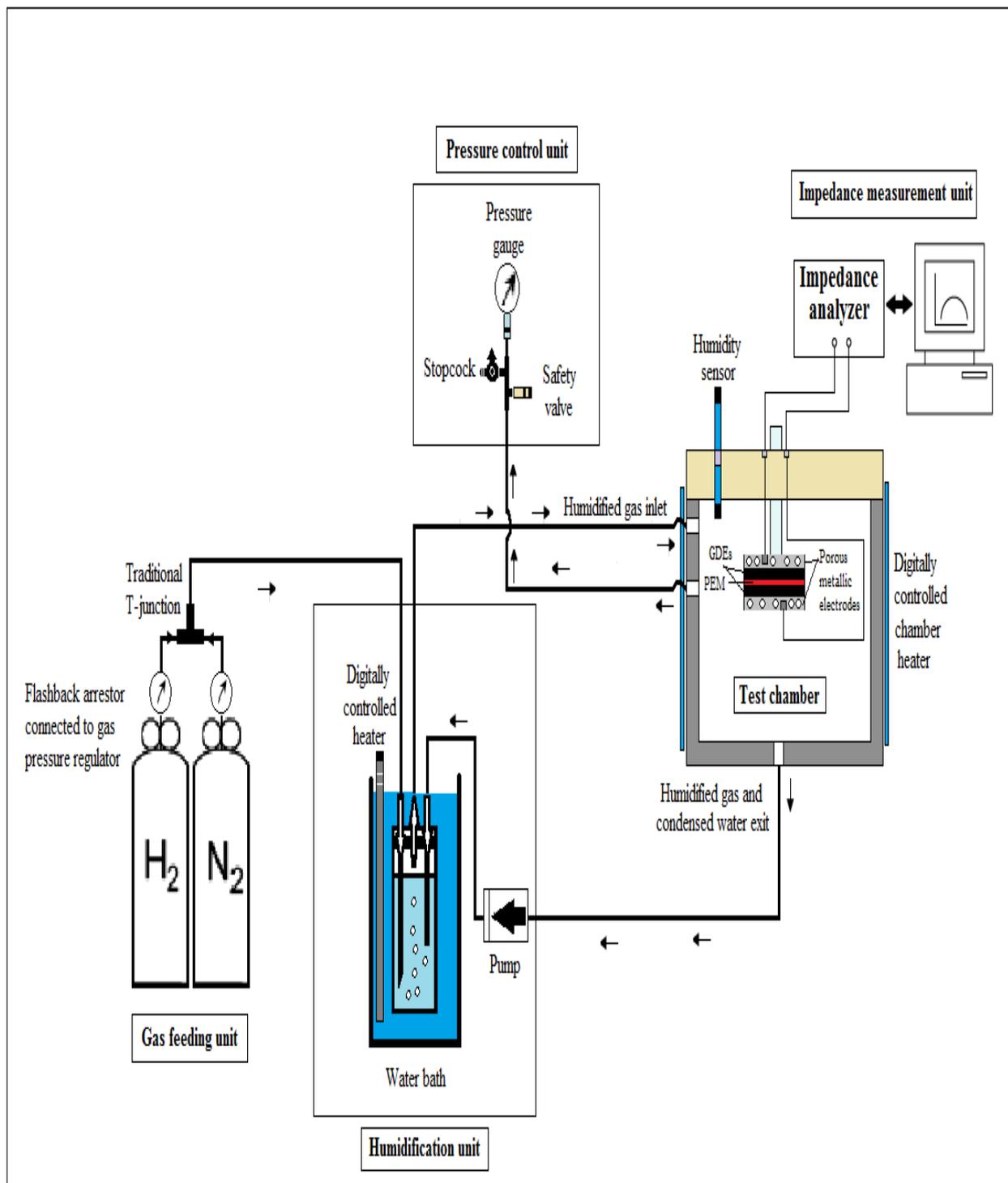
(i) Gas feeding unit:

This unit consists of two gas cylinders; one for hydrogen and another for nitrogen. Each cylinder is connected to a pressure regulator joint with a flashback arrestor. A traditional T-junction matches the two cylinders with the humidification unit to act as gas supplier.

(ii) Humidification unit:

A three-port closed water-filled glass bottle is immersed in a digitally heat-controlled water bath. The bottle has two inlets, one for  $N_2/H_2$  gas, and the other is connected with a pump to ensure a

one-directional flow of the humidifying gas. The third port is an outlet that feeds the test chamber with the humidifying gas.



**Figure 1.** Schematic drawing of the manufactured test system for membrane through-plane conductivity measurements.

Transportation of the humidified heated gas is realized through Teflon tubes. This results in a closed circulated humidification system and in turn recycling of the humidifying gas. It is worth noting that Cooper's cell does not have such a closed system, and instead water is condensed and then collected in a water trap.

(iii) Test chamber:

A closed chamber is insulated by glass wool and can be heated by a digitally controlled external heater. It has humidity, temperature, and pressure controllers. A Teflon holder is used to fix the membrane electrode assembly (MEA) to be tested inside the chamber. The exit at the bottom of the chamber is connected to a pump to ensure the one-directional flow of the humidified gas.

(iv) Pressure control unit:

Using this unit, the chamber can be flushed by either N<sub>2</sub> gas or a mixture of N<sub>2</sub>/ H<sub>2</sub> gases with an accurate percentage. It consists of a pressure gauge, stopcock, and safety pressure valve. Any excess gas pressure is released by the safety pressure valve.

(v) Impedance measurement unit:

The impedance of the MEA is measured by an HP 4192A impedance analyzer with two-terminal impedance spectroscopy over a range of frequency.

## 2.2. Operating procedure

The system is provided with a ground fault switch to prevent any electrical contact. The system is checked to be free from any gas leakage. Non-catalyzed membrane is sandwiched between the two sheets of the GDEs. The resulting MEA is then fixed inside the test chamber. The chamber is purged with pure nitrogen and then allowed to equilibrate at the desired temperature and relative humidity for 30 minutes. Electrochemical impedance spectroscopy (EIS) impedance data is collected over a frequency range of 10<sup>-1</sup> to 10<sup>5</sup> Hz. The membrane ionic conductivity,  $\sigma$ , is calculated using:

$$\sigma = \frac{L}{RA}, \dots \dots \dots (1)$$

where  $L$  corresponds to the electrode separation,  $A$  is the area of the electrodes, and  $R$  is the bulk membrane resistance. The reproducibility of the results is verified by repeating the measurements three times for a given membrane sample.

## 2.3. Gass diffusion layer (GDL) preparation

### 2.3.1. Pt deposition

Commercial carbon cloth was used as the GDL substrate to precipitate Pt catalyst layer. The carbon cloth sheet (5×5 cm<sup>2</sup>) was first immersed in ethanol for 6 min, and then rinsed with deionized water three times. After that it was sonicated for 6 min in ethanol aqueous solutions (5 vol % ethanol/water), and then immersed in an aqueous solution of H<sub>2</sub>PtCl<sub>6</sub> and formic acid at room temperature for 72 h. After completion of the Pt reduction reaction and the precipitation of Pt layer onto the substrates, the samples were rinsed with deionized water followed by ethanol and finally by

deionized water. Then the samples were dried using a stream of hot air for 30 seconds. The resulting GDL was then characterized by field emission scanning electron microscope (SEM) to characterize the Pt deposition.

### 2.3.2. Adding Nafion

In order to transform the GDL into a full GDE, Nafion was added. For every 0.9 g of solid sample containing Pt, 0.1g of Nafion ionomer (5% Nafion solution) was added. Carbon cloth loaded with Pt ( $4.0 \times 2.0 \text{ cm}^2$ ) was suspended on the top of two plastic edges and then 0.3 ml of Nafion solution (5 wt% solution) was added. The solvent evaporated from all sides leaving an even distribution of Nafion polymer on the carbon cloth.

### 2.4. Scanning electron microscopy (SEM)

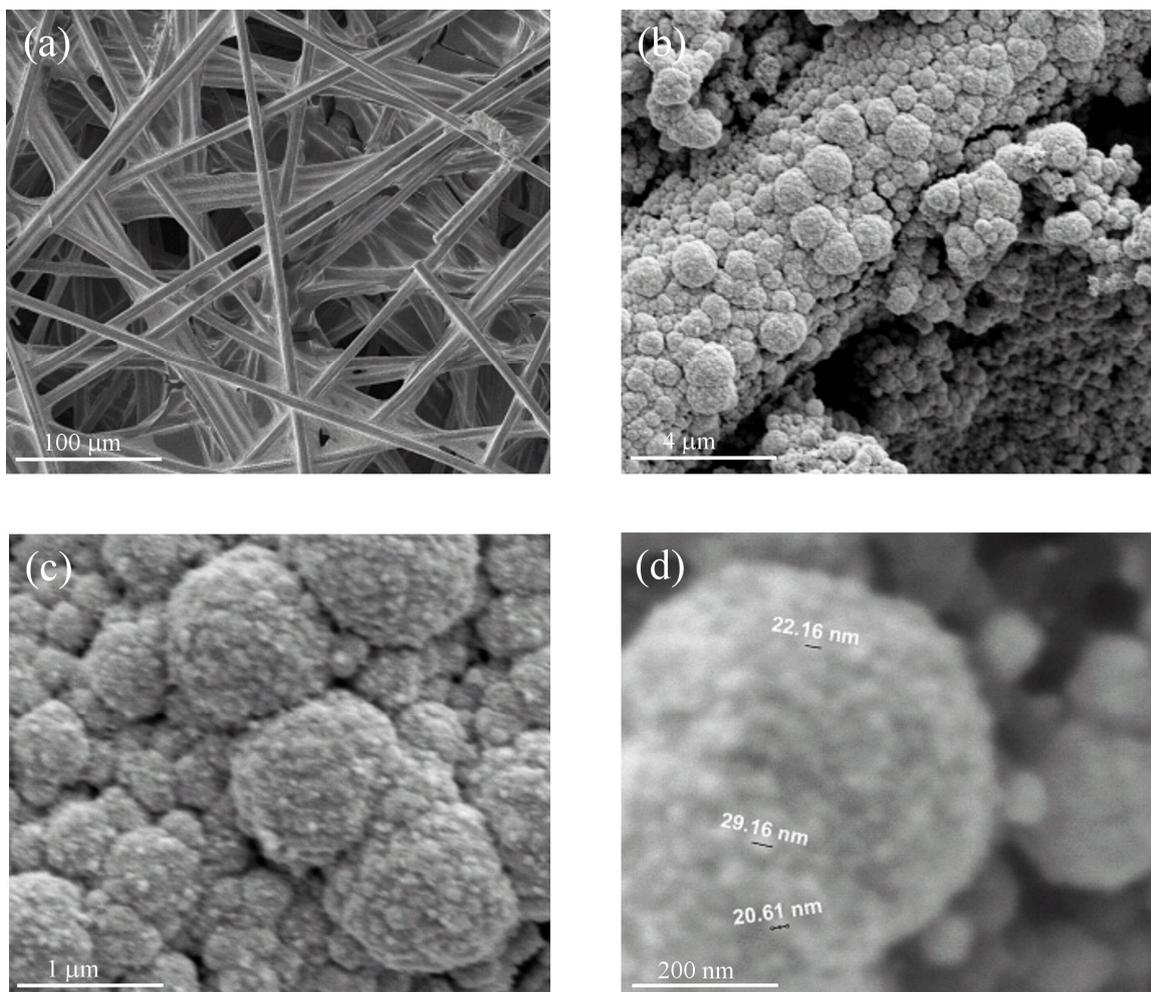
SEM analysis of the prepared GDLs were performed using high resolution field emission scanning electron microscope (Inspect F50/ FEG).

## 3. RESULTS AND DISCUSSION

### 3.1. The GDE morphology

As mentioned earlier, the platinum catalyst layer was detached from the PEM in the MEA and added to the GDE. GDE is an electrode interface between solid, liquid and gaseous phases. It also has an electrical conducting Pt catalyst that can support the electrochemical reaction without being part of the MEA. Electrons can be conducted by the carbon cloth, whereas protons are conducted by Nafion polymer.

To evaluate the Pt deposition on the carbon cloth, SEM images of the prepared GDLs were recorder as shown in Figure 2. The gray area represents the precipitated Pt layer. As can be seen, a nanostructured Pt layer is successfully precipitated and distributed evenly. At smaller scale, Figure 2 (c) and Figure 2(d), one can notice that the Pt nano particles form clusters. Nonetheless, the individual form of each nano particle seems to be preserved to a large extent, and therefore the exposed surface area of the catalyst per unit volume is increased. It is worth mentioning that the U.S. Department of energy suggests that one method of increasing the performance of Pt catalysts is to optimize the size and shape of the Pt particles. Decreasing the particle size increases the total surface area of the Pt nano particles and thus less of the costly Pt catalyst will be used.



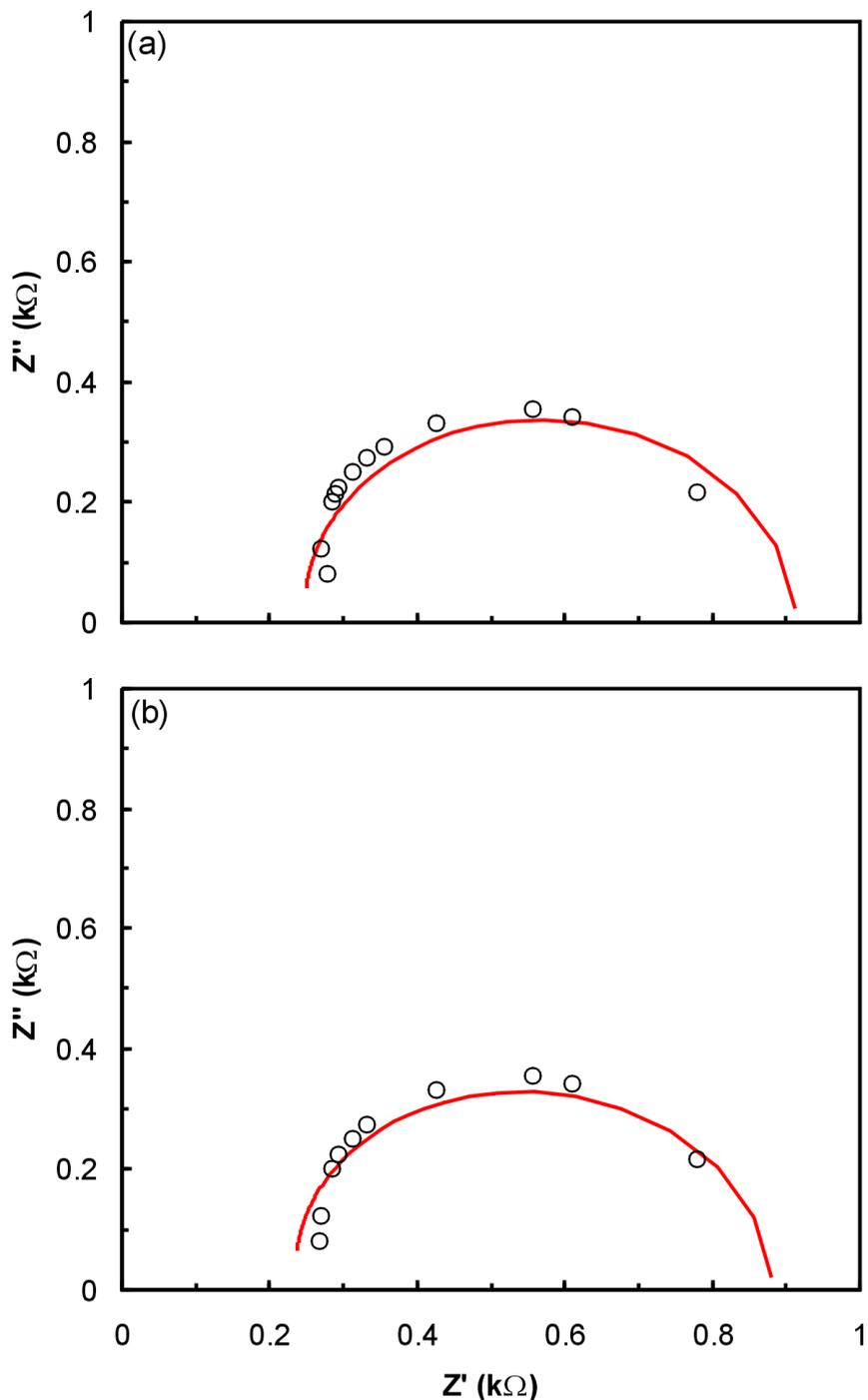
**Figure 2.** Typical SEM images of the prepared GDL.

### 3.2. Nafion membrane

We chose Nafion 117 membrane as a model PEM to assess the applicability of the manufactured test system. EIS measurements were performed on a sample having an area of 0.54867 cm<sup>2</sup> and a thickness of 171.5 μm at temperatures of 18, 36, and 42 °C and a relative humidity of 80%, according to the procedure described earlier. The obtained impedance spectra are shown in Figure 3 as Nyquist plots. As can be seen, all plots exhibit depressed single semicircle arcs.

### 3.3. EIS spectra analysis

Many studies determined the membrane resistance by simply taking the value of the impedance when the imaginary part of the impedance is equal to zero in the Nyquist plot [31-34]. However, a more accurate method is to fit the impedance data to equivalent circuit models. The equivalent circuit presented in Figure 4 provides reasonably good fits for the data presented in Figure 3.



**Figure 3.** Impedance spectra for a Nafion 117 membrane obtained at a relative humidity of 80% and temperatures of (a) 18 °C, and (b) 42 °C. The solid lines represent the fit data using the model shown in Figure 4.

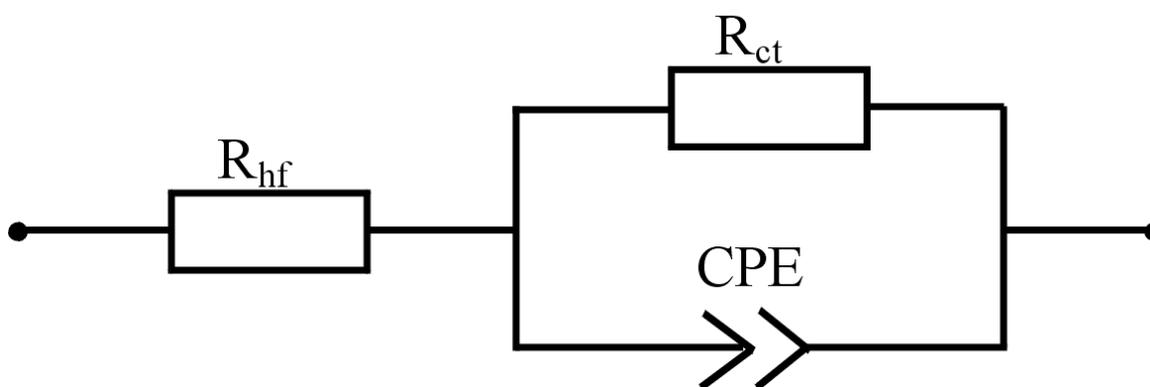
It consists of a parallel connection of a resistor,  $R_{ct}$ , and a generalized constant phase element (CPE) with an impedance of  $\frac{1}{(i\omega C)^n}$  in series with another resistor,  $R_{HF}$ , where  $\omega$  is the frequency and  $C$  corresponds to the polarization capacitance of the membrane. For  $n = 1$ , this model is known as

Randles model, where  $R_{ct}$  and  $R_{HF}$  represent the charge transfer resistance at the electrode-membrane interface and the bulk resistance of the membrane, respectively.

**Table 1.** Summary of the results obtained by fitting the impedance data with the equivalent circuit using a non-linear least square procedure.

Temperature (°C )	$R_{HF}$ (kΩ)	$R_{ct}$ (kΩ)	n	C (μF)	$\sigma$ (mS/cm)
18	0.247	0.670	0.993	785	0.126
42	0.234	0.650	0.989	785	0.133

Table 1 reports the data determined by fitting the impedance data to the equivalent circuit model shown in Figure 4 at the indicated temperatures.



**Figure 4.** Equivalent circuit model for analysis of the impedance spectra to determine the PEM ionic conductivity.

The fit was performed using self-developed routines using a non-linear least square procedure. The results reveal a slight decrease in the values of both  $R_{ct}$  and  $R_{HF}$  with increasing temperature. It is known that upon increasing temperature, the proton mobility increases and thus higher membrane conductivity is observed [33]. On other hand, increasing temperature speeds up the catalyst kinetics. This accelerates the charge transfer at the electrode-membrane interface. Consequently,  $R_{ct}$  gradually decreases as temperature increases.

#### 4. CONCLUSIONS

Systematic testing of the PEM ionic conductivity under a wide range of conditions is essential in the process of developing new membranes to replace Nafion. Therefore, it is desirable to have a

simple and cost effective test system that allows such measurements without using much of the costly platinum catalyst. To this end, we have designed and manufactured a test cell that allows measurements of PEM through-plane ionic conductivity at different humidity and temperature conditions. In this design the catalyst layer is detached from the membrane and added to the gas diffusion electrode. Moreover, the humidifying gas of the cell is recycled after exiting the test cell making it more cost effective. The applicability of the manufactured test system has been demonstrated using a model Nafion membrane at two different temperatures.

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