

Short communication

## Contaminant absorption and conductivity in polymer electrolyte membranes

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### Abstract

During its lifetime, the polymer electrolyte membrane of a fuel cell may be exposed to numerous impurities originating from sources such as materials used in various components of the fuel cell stack and contaminants in the coolant and reactant gas. The contamination of the membrane by cationic impurities has detrimental effects on membrane properties with regard to conductivity, water management and durability. Thus the measurement of absorption of contaminants into the membrane and the investigation of its relation to these detrimental effects is of interest.

Samples of Nafion 117 polymer electrolyte membrane were soaked in deionised water solutions containing part per million (ppm) concentrations of cation impurities, ranging from 0.1 to 100 ppm. Upon removal of the membranes from the soaking solutions, conductivity of the membranes and the effect of different cationic impurity concentrations on the conductivity was measured by impedance spectroscopy methods. Using atomic absorption spectrophotometry, the concentration of the cationic impurity species remaining in the soaking solutions was determined and the extent of ion absorption by the membranes calculated. Energy dispersive X-ray analysis was also employed and confirmed the presence of the contaminant ions in the membrane.

Impedance studies exhibited a loss of conductivity, while an increase in ion absorption into the membrane was observed, when membranes were soaked in solutions of higher contaminant concentration. In this study, the capacity for ion absorption into the membranes was determined and the extent of membrane contamination was compared and correlated with the loss in conductivity of the membrane for different levels of contamination.

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### 1. Introduction

The effect of contaminants on the energy output and durability of polymer electrolyte membrane (PEM) fuel cells is of concern due to the detrimental effect such impurities have on the fuel cell performance. The contamination can affect components such as the catalyst electrodes and the polymer

electrolyte membrane, with the result that the power output of the membrane electrode assembly (MEA), and thus of the fuel cell, is impaired. Contaminants may originate from different sources including materials used in other components of the fuel cell stack as well as entering the fuel cell via the gas supply or coolant. Transition metal ion contaminants must be considered as their presence in the fuel cell membrane can result in loss of conductivity, membrane dehydration and water management problems [1]. In order to regain optimum performance a thorough cleaning process must take place.

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Perfluorosulphonic membranes such as Nafion, which is of current interest as the proton conducting membrane in PEM fuel cells, are susceptible to loss of conductivity following exposure to cation impurities [2]. The effect of contaminant cations is to replace the protons in the membrane, and multiple charged cations displace protons for each charge on the cation. The sulphonic sites present in Nafion have a higher affinity for foreign cations than for  $H^+$ , while these impurity cations exhibit much lower mobility, thus decreasing conductivity [3].

In this study the extent of cation absorption by Nafion in solutions of different cation concentrations is investigated. This cation absorption into the membrane is correlated with the resultant effect on the measured conductivity. The affinity of the membrane for different cations is important to quantify as is the measurement of the response of the membrane to these different levels of contaminants.

## 2. Experimental

Solutions containing part per million (ppm) concentrations of cations were prepared from sulphate salts of the contaminant cations in deionised water. These cation solutions were prepared from sulphate salts of the cations. Cations considered in this study were  $Cu^{2+}$ ,  $Fe^{3+}$ , and  $Ni^{2+}$ . The Nafion 117 membrane, supplied by Fuel Cell Scientific of Stoneham, MA, was 7mil ( $1.778 \times 10^2 \mu m$ ) thick in the dry state. Nafion membrane samples were immersed and left soaking in individual 50 ml volumes of the solutions. Membrane samples, whose conductivity was subsequently measured by the four-probe impedance analysis method, were cut into strips 1 cm wide by 5.6 cm long. The membranes were immersed into the contaminant solutions and after 72 h of soaking in the immersion solutions, removed and their conductivity measured by the aforementioned impedance technique.

Following removal of the membrane, the immersion solutions were analysed by atomic absorption spectrophotometry to determine the concentration of the respective contaminant cations present in the solutions. Atomic absorption spectrophotometry was carried out with a Perkin-Elmer 5100 atomic absorption spectrophotometer (AAS) with a Zeeman 5100 detector. Contaminant containing solutions, in which no membrane had been immersed, were also analysed for reference. With this data the amount of cations absorbed into the membranes was then determined and the membrane cation content calculated.

Energy dispersive X-ray (EDX) analysis was also carried out on the contaminant ion containing membranes, in the dry state, to obtain further information on the ion absorption properties of the Nafion membrane. A Philips XL-30 environmental scanning electron microscope (ESEM) equipped with an EDAX CDU Leap detector was used for EDX analysis.

The use of four-probe measurements is an accurate means of measuring polymer electrolyte membrane conductivity [4,5]. Four-probe impedance studies were carried out with

an in-house fabricated four-probe cell and a Zahner Elektrik (Germany) IM6 impedance measurement unit. The four-probe conductivity cell, with two platinum foil outer current carrying electrodes and two platinum wire inner potential sensing electrodes, was used to measure the membrane resistance. In this method the alternating current is passed between the two outer electrodes and the resistance calculated from the ac potential difference between the two inner electrodes. The method is relatively insensitive to the contact impedance at the outer current-carrying electrodes [6] and therefore very appropriate for accurate ionic conductivity measurements. With the impedance analyser in galvanic mode, measurements were carried out with ac current amplitude of 0.01 mA over a frequency range of 0.1–20,000 Hz. The resistance was measured in the in-plane direction for all membranes and the conductivity calculated using the following expression [7]:

$$\sigma = l/(RS)$$

where  $\sigma$ ,  $l$ ,  $R$  and  $S$  are the ionic conductivity in  $S\text{ cm}^{-1}$ , distance between the potential probes, membrane resistance at 1 kHz and the cross sectional area of the membrane. A membrane, which had been immersed in deionised water, was also tested for reference. Conductivity measurements were carried out at room temperature ( $22^\circ\text{C}$ ), with the membrane in the fully saturated state (100% humidity).

## 3. Results and discussion

Atomic absorption spectrophotometry studies reveal that a large proportion of the ions present in the immersion solutions were absorbed by the membrane. The amounts of cations absorbed into the membrane are charted in Fig. 1. With increasing immersion solution concentration, the amount absorbed into the membrane increased.  $Cu^{2+}$  and  $Ni^{2+}$  appear to be almost completely absorbed into the membrane for each

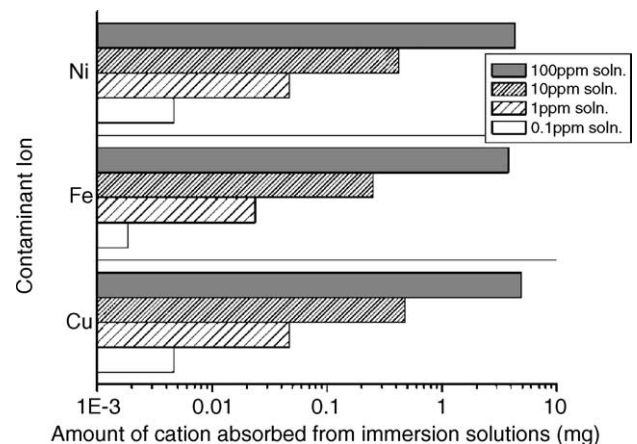


Fig. 1. Amount of contaminant cations absorbed into membrane from immersion solution.

Table 1  
Atomic ratio of contaminant to fluorine in membrane, as measured by EDX analysis

Immersion solution cation concentration (ppm)	Cu/F	Fe/F	Ni/F
0.1	$1.38 \times 10^{-3}$	$1.22 \times 10^{-3}$	$6.93 \times 10^{-4}$
1	$2.17 \times 10^{-3}$	$8.74 \times 10^{-4}$	$4.40 \times 10^{-4}$
10	$1.06 \times 10^{-2}$	$2.11 \times 10^{-3}$	$4.14 \times 10^{-3}$
100	$2.29 \times 10^{-2}$	$1.92 \times 10^{-2}$	$2.26 \times 10^{-2}$

concentration of immersion solution, however for samples contaminated with  $Fe^{3+}$ , less of the ions were absorbed into the membrane.

The data from EDX analysis are presented as an atomic ratio of contaminant ion to that of fluorine in the membrane and summarised in Table 1. Fig. 2 shows the EDX spectrum for a Nafion membrane, which had been immersed in a 100 ppm  $Cu^{2+}$  solution; the presence of contamination in the membrane is visible from the copper peaks detected. EDX results revealed that the contaminant cation to fluorine atomic ratio in the membrane increased with the increased concentration of soaking solution and the increased absorption of cation into the membrane. Less  $Fe^{3+}$  appears to be incorporated into the membrane than other cations while  $Cu^{2+}$  appears to have been absorbed into the membrane more readily, which is in agreement with the atomic absorption analysis. For the lower ratio values these trends are not as evident, which may be due to the difficulties in obtaining good quantitative analysis with the EDX at low membrane contaminant content.

Okada et al. [2] reported that the Nafion membrane has a higher preference for impurity cations over  $H^+$ , but the order of preference is  $Fe^{3+} > Ni^{2+} > Cu^{2+}$ . This seems to contradict our results, however it must be taken into account that in Okada's study, the membranes were soaked in impurity cation containing solutions for at least 1 month. The increased time of immersion would allow the less mobile iron ions to equilibrate through the membrane.

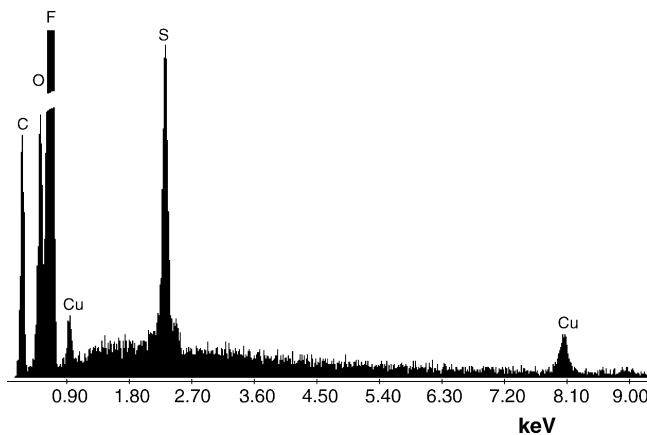


Fig. 2. EDX spectrum of Nafion 117 containing impurity, following immersion in a 100 ppm  $Cu^{2+}$  solution for 72 h.

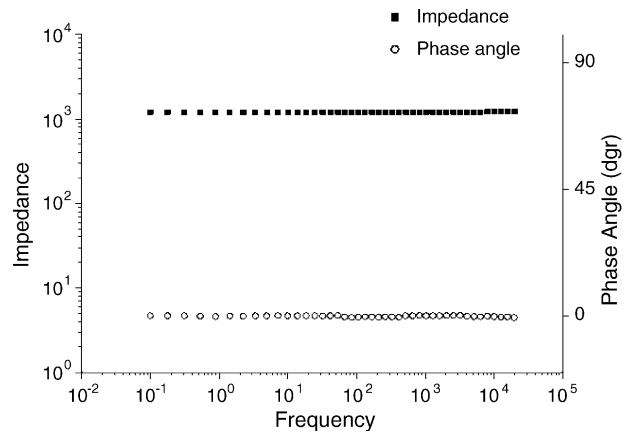


Fig. 3. Bode plot of the impedance response of a Nafion 117 membrane tested in the four-probe conductivity cell. This spectrum was measured for a membrane sample which had been immersed in a 10 ppm  $Fe^{3+}$  solution for 72 h.

As expected, four-probe conductivity studies revealed loss of conductivity with increasing contaminant concentration. Meanwhile the conductivity value for Nafion membrane soaked in distilled water was calculated to be  $0.077 S cm^{-1}$  and compared well with values reported [8,9]. Fig. 3 is a typical impedance spectrum obtained for a membrane sample, expressed as a Bode plot. The invariance of the impedance and the fact that the phase angle was at zero in this range of frequencies show that the membrane behaved as a pure resistor. Fig. 4 shows the decrease in conductivity with increased contaminant concentration in the immersion solution and this observed decrease agreed with results presented in a previous conductivity study carried out with microelectrodes [9]. Fig. 5 correlates the conductivity values to the cation content of the membranes. The conductivity of the membrane initially decreased slightly with increased ion absorption until an exponential decrease in conductivity is seen when the cation content in the membrane increases between 5 and 20  $mg cm^{-3}$ . Although the membranes contained lower

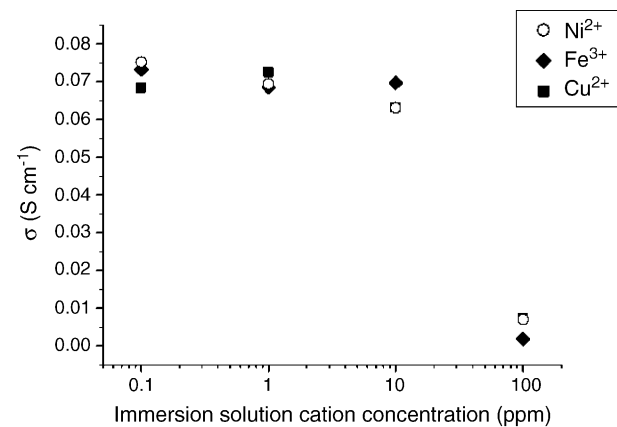


Fig. 4. Effect of immersion in contaminant containing cation solutions on membrane conductivity.

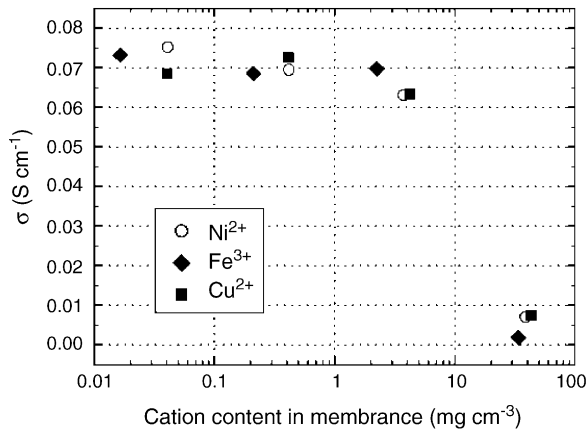


Fig. 5. Relationship between membrane contaminant ion content and conductivity.

$\text{Fe}^{3+}$  amounts, this contaminant often resulted in the greatest loss in conductivity; this is particularly evident in values for high membrane cation content. This characteristic behaviour may be as a result of the higher valence of the iron cations displacing more protons in the membrane [3].

#### 4. Conclusions

This study investigated the absorption of cations into a Nafion 117 membrane and showed, using impedance spectroscopy techniques, a detrimental effect of transition metal

ion contamination on ionic conductivity. Nafion membrane exhibited high affinity for the cations and absorbed most of the impurity ions from immersion solutions.  $\text{Cu}^{2+}$  was incorporated into the membrane more readily than  $\text{Ni}^{2+}$ , while  $\text{Fe}^{3+}$  was absorbed into the membrane at a lower rate, however  $\text{Fe}^{3+}$  contamination resulted in greater ionic conductivity losses.

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