



Short communication

The influence of metal ions on the conductivity of Nafion 112 in polymer electrolyte membrane fuel cell

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ARTICLE INFO

Article history:

Received 28 April 2008

Received in revised form 23 May 2008

Accepted 26 May 2008

Available online 7 June 2008

Keywords:

Membrane conductivity

Metallic ions

PEMFC

Nafion

ABSTRACT

Nafion 112 membranes were soaked in 1 M H₂SO₄ solutions containing variable amounts of Fe and Cr ions, either individually or mixed. An even distribution of the metal ions on the surface of the membranes was observed with electron probe microanalysis (EPMA) mapping. The proton conductivity of the soaked membranes was investigated using a conductivity cell. For Fe ions, the conductivity was almost constant until the Fe-ion solution concentration reached 300 ppm. Over the 300-ppm threshold, the conductivity decreased significantly. Similar results were obtained with Cr ions in the membrane, but here the threshold was approximately 200 ppm in the solution. Mixed metal ions were found to decrease these threshold values due to the additive effect of the two metals.

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1. Introduction

A polymer electrolyte membrane fuel cell (PEMFC) combines hydrogen fuel and oxygen/air, generating dc electricity with by-products of water and heat [1]. If the hydrogen is obtained from renewable resources, the PEMFC is a clean energy conversion device with zero emissions. This attractive attribute generates a lot of attention and makes PEMFCs the leading candidates for the next generation automotive power plants and many stationary applications. However, the high cost of the PEMFC components restricts its commercial viability.

One of the challenges is the cost and manufacturability of bipolar plates for the PEMFC stack. Traditional PEMFCs used graphite plates for the bipolar plate material, resulting in high cost from the necessary machining of the gas distribution channels on both sides of the plate. Molded bipolar plates using graphitic powders and a binder or resin typically require a thick plate to obtain the necessary gas impermeability for the application. This is problematic for the automobile industry where small volumes and cost effectiveness are essential. Stainless steel and other metallic bipolar plates provide an alternative due to their wide choice of composition, ease of manufacturing, and high corrosion resistance in the acidic environment of a PEMFC, as well as for economic reasons [2–13]. However, two challenges are encountered with stainless steels as bipolar plate material: (1) the material will develop a passive film

on its surface in the PEMFC environment that could lead to higher interfacial contact resistance and lower fuel cell performance; (2) dissolved metallic ions coming from corrosion may contaminate the membrane, resulting in additional performance degradation.

We have shown progress in meeting these challenges by modifying the surface of candidate stainless steels via thermal nitridation. This results in excellent corrosion resistance and low contact resistance for AISI446 steel [14,15]. However, even with the modified surface, some metallic dissolution still occurs as measured by inductive-coupled plasma (ICP) analysis. In this paper we will show the influence of the dissolved metallic ions (Fe³⁺ and Cr³⁺) on the conductivity of a Nafion 112 membrane.

2. Experimental

2.1. Materials and solutions

De-ionized (DI) water with a specific resistivity of 18.2 MΩ cm was used to prepare all solutions. 96.5% H₂SO₄ from J.T. Baker, Cr₂(SO₄)₃·xH₂O, and Fe₂(SO₄)₃·xH₂O from Aldrich were used as received to prepare 1 M H₂SO₄ solutions containing up to 500 ppm Fe³⁺ and up to 300 ppm Cr³⁺. This range was selected based on the analysis, by means of ICP, of the solutions collected after polarization experiments of the metallic bipolar plates in simulated PEMFC environments [16,17]. The metal ion concentration of the prepared solution was verified by ICP. Calibration standard solutions of 1 M H₂SO₄ containing 100 ppm of each metallic ion were purchased from Inorganic Ventures, Inc. The ICP system was Varian Liberty 150 ICP Emission Spectrometer controlled by a PC.

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The Nafion 112 membranes were purchased from Ion Power, Inc., and had a thickness of 51 μm and a specific conductivity of 0.083 S cm^{-1} at 25°C according to manufacturer's literature. The membranes were cut into samples of $2.5 \text{ cm} \times 5.0 \text{ cm}$. Then they were pre-treated for 2 h in 3% H_2O_2 aqueous solution at 80°C , followed by rinsing in DI water. This is a standard membrane pre-treatment to remove organic residue contamination [18–20]. The Nafion 112 samples were then soaked in the prepared 1 M H_2SO_4 solutions, with or without metallic ions, for 24 h at 80°C . Finally, the membrane was rinsed again with DI water and stored in DI water prior to the conductivity test. The membrane sample was cut into ca. 5-mm-wide strips for proton conductivity test. The absorption mappings of Fe and Cr ions on the surface of soaked membrane samples were determined by means of electron probe microanalysis (EPMA).

In our previous experiments on metallic bipolar plates, we used a solution of 1 M $\text{H}_2\text{SO}_4 + 2 \text{ ppm F}^-$ to simulate an aggressive environment in the PEMFC [8–10,14–17]. After polarizing the stainless steel coupons, the solutions were collected and analyzed by means of ICP to determine the concentration of the dissolved metallic Fe and Cr ions stemming from the polarization process. The Nafion 112 samples were also soaked in these solutions, with the same procedure as above, to investigate the influence of the mixed metal ions on the proton conductivity.

2.2. Conductivity cell and conductivity measurements

The conductivity cell was purchased from BekkTech LLC, and was specially designed to use Fuel Cell Technologies 5 cm^2 fuel cell test hardware. The cell is schematically shown in Fig. 1. The membrane is sandwiched between two Teflon clamps (Fig. 1a). The Pt wires V1 and V2 (Fig. 1b) serve as terminals to read the voltage generated by the ion current and the membrane resistance. The distance

between the V1 and V2 wires – an important parameter in the conductivity cell – is known to be 0.425 cm. The Pt wires A and B serve as terminals to apply a voltage for the hydrogen reaction and as current collectors to complete the circuit. Two pieces of Pt gauze on wires A and B are used as the contact for the proton generation.

The conductivity cell was installed into the CompuCell GT Fuel Cell Station (Globe Tech), and controlled by a PC. Cell temperature was controlled with an OMEGA CSC 32 thermometer. The humidifier temperature was controlled with a Fuel Cell Load Unit 890 (Scribner Associates, Inc.). According to the calibration, the humidifier at a temperature of 80°C gives 100% relative humidity (RH). To simplify the test, all the conductivity tests were carried at 100% RH with a cell temperature of 80°C . Hydrogen gas was fed into the conductivity cell at 16.7 mL s^{-1} (1 L min^{-1}) with a back pressure of 0.103 MPa (15 psi). The voltage scan from -1 V to 1 V is applied between the two Pt wires (A and B) by means of Gamry's PC4 Potentiostat Board (Gamry Instruments, Inc.) controlled by Gamry Instruments Framework software (v.4.35). The scanning rate was 10 mV s^{-1} . The current response is collected from the terminals A and B and plotted against the voltage measured between V1 and V2. The conductivity of the membrane is calculated according to:

$$\text{Conductivity} = \text{Slope} \times \frac{\text{Length}}{\text{Width} \times \text{Thickness}} \quad (1)$$

in which the Slope (in the unit of ampere/voltage) is obtained from the linear portion of the current–voltage plot, the Length is the distance of the two Pt wires V1 and V2 (0.425 cm), the Width and the Thickness are the width and the thickness of the membrane; the later was 0.0051 cm.

3. Results and discussion

3.1. Solution calibration with ICP and EPMA analysis

To verify the ppm levels of the metal ions, the concentrations of all the prepared solutions were checked by ICP and plotted as a function of the nominal concentrations (not shown). As expected, both give straight lines. The relation coefficients are better than 0.99 for both cases, though the ICP measurements give slightly higher Fe contents than the nominal concentrations and slightly lower Cr contents than the nominal values. ICP measurements indicate the validity of the prepared solution, so we will use the nominal metallic ion concentrations in the following discussion.

After the membranes were soaked in the various metallic ion-containing solutions, the surface Fe and Cr ions were mapped by EPMA. An even distribution of Fe and Cr ions was obtained (Fig. 2) indicating even absorption on the membrane. Moreover, the membrane soaked in the Cr-bearing solution shows a much higher intensity than the one soaked in the Fe-containing solution, suggesting that Cr ions are absorbed more readily by the membrane than Fe ions. In other words, Cr ions would be more detrimental to the membrane conductivity in PEMFC environments. Therefore, a low dissolution rate for Cr is critical for the application of stainless steels as PEMFC bipolar plates. It should be mentioned that in this case, EPMA gives only a qualitative analysis; this is due to the high electrical resistance of the membrane.

The fact that Cr ions are absorbed more readily than Fe ions was also observed by Shores and co-workers, though the authors did not give further explanation [6]. Previously, Yeager had conducted a series of experiments with a Nafion membrane to determine the absorption selectivity when immersed in solutions containing mixed cations [21]. It is interesting that ion with the lowest surface charge density (or with the largest sphere radius) was preferentially absorbed into Nafion. Recent detailed experimental and modeling studies by Tandon and Pintauro proved this selective uptake of the

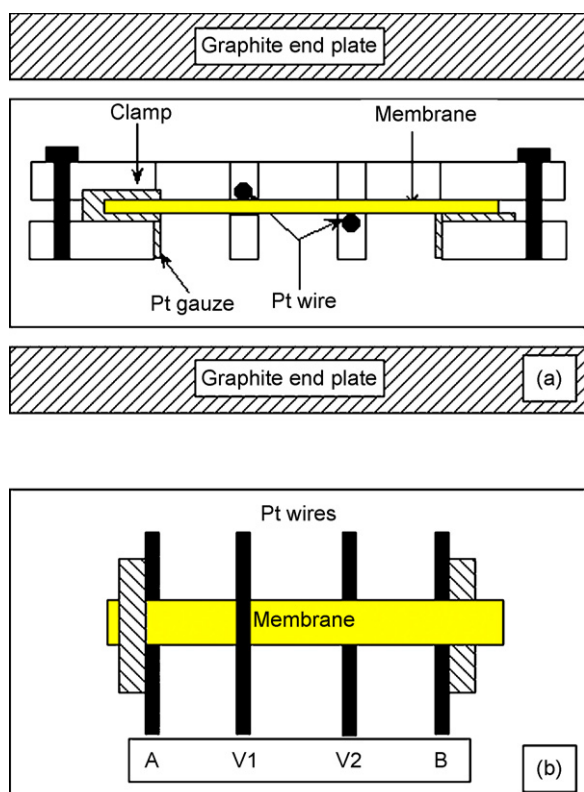


Fig. 1. Schematic view of the conductivity test cell: (a) cross-section; (b) top view.

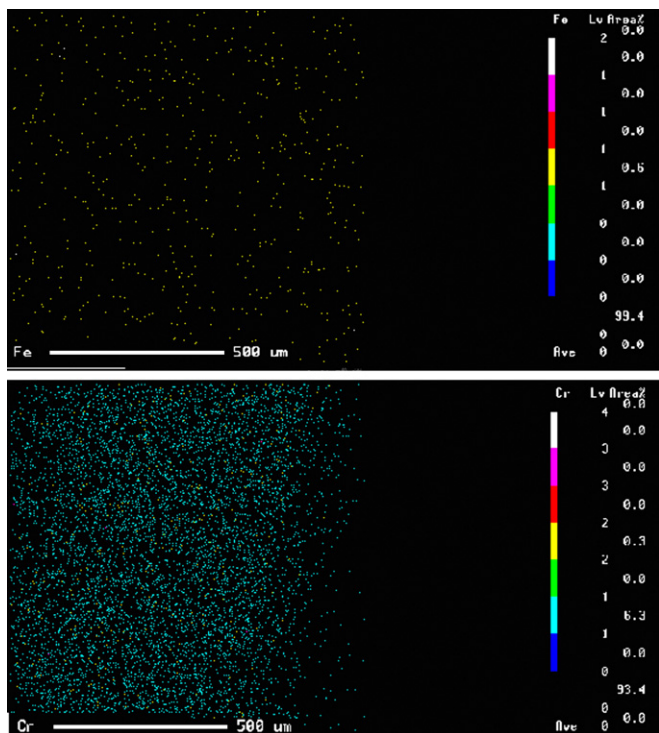


Fig. 2. EPMA images of the Fe^{3+} (above) and Cr^{3+} (bottom) ions in the Nafion 112 membrane. Both membranes were soaked in solutions contains 50 ppm metal ions.

monovalent cations by a Nafion membrane, though some modification in the model was made for the divalent cations [22]. By adopting that the radii of Cr^{3+} and Fe^{3+} ions are 0.62 Å and 0.55 Å, respectively [23], the preferential absorption of Cr ions over Fe ions by the Nafion membrane could be explained by the same model.

3.2. Conductivity of Nafion 112

Fig. 3 shows the typical results, with a forth and back voltage scan of a conductivity experiment for a fresh, Nafion 112 membrane; a linear current–voltage plot is obtained and a conductivity value of 102 mS cm^{-1} is calculated from Eq. (1). Although there are scattered data reported for the Nafion's conductivity, they are

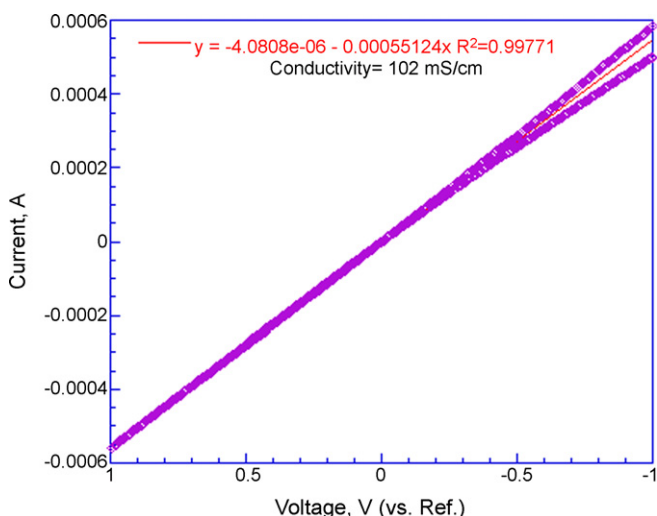


Fig. 3. Conductivity result of a control Nafion 112 sample at 80°C cell temperature and RH 100% with back hydrogen pressure of 0.103 MPa (15 psi).

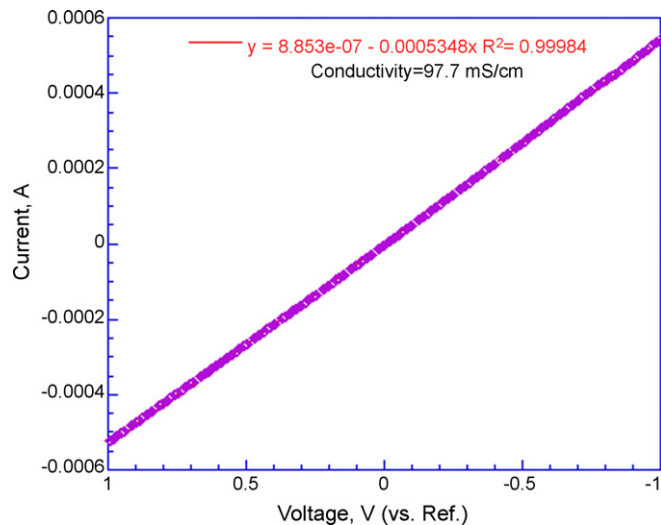


Fig. 4. Conductivity result of a Nafion 112 membrane soaked 24 h in $1 \text{ M H}_2\text{SO}_4 + 20 \text{ ppm Fe}^{3+}$ at 80°C . The test was made at 80°C cell temperature and RH 100% with back hydrogen pressure of 0.103 MPa (15 psi).

more or less related to the pre-treatment of the membrane and the experimental conditions [19]. Most of these measurements were conducted in aqueous solutions at different temperatures with dc or ac (impedance) methods. However, only a few papers applied the real fuel cell conditions to the conductivity measurement [24,25]. Wakizoe et al. obtained a conductivity of 74 mS cm^{-1} for Nafion 115 at 95°C in fuel cell operating conditions [24]. Buchi and Scherer measured a conductivity of 104 mS cm^{-1} for Nafion 117 at 60°C using a single fuel cell [25]. Slade et al. [19] reported the conductivity of ca. 80 mS cm^{-1} for Nafion 112 in PEMFC conditions at 80°C , and they also reported on the validity of the measurements in aqueous solutions at room temperature. This supports many measurements that indicate the conductivity of Nafion is around 100 mS cm^{-1} [18,26–28], and the conductivity measured here is in excellent agreement with the previous data obtained under similar conditions, as well as the manufacturer's literature.

3.3. Effect of metal ions on the conductivity of Nafion 112

Results were obtained with Nafion 112 soaked in solutions containing low concentrations of Fe ions. A typical result for 20 ppm Fe (with a forth and back voltage scan) is shown in Fig. 4. A conductivity value of 97.7 mS cm^{-1} is obtained according to the slope of the curve. A 20-ppm Fe-ion concentration in the solution does not affect the conductivity. Plotting the membrane conductivity against the Fe-ion concentration in the solution, Fig. 5 is the result. The inset of Fig. 5 gives the results in a linear scale. We see that conductivity is almost constant, approximately 95 mS cm^{-1} , at Fe-ion concentrations below 300 ppm. It slightly decreases at 300 ppm Fe. Significant conductivity decrease occurs at 500 ppm. 300 ppm could then be taken as the threshold for the Fe ions to influence the conductivity of the membrane. Below this threshold, the membrane acts the same as the uncontaminated one. Above this threshold, the absorbed Fe ions will have a significant impact on reducing the conductivity.

When the membrane was soaked in Cr-bearing solutions, similar linear current–voltage relationships were obtained. Plotting the conductivity against the Cr ion concentration, we obtained a trend in Fig. 6 similar to Fig. 5. The conductivity is not impacted below 200 ppm Cr. A decrease in the conductivity is noticed at 200 ppm and it is significantly reduced at 300 ppm Cr. Comparing Fig. 6 with

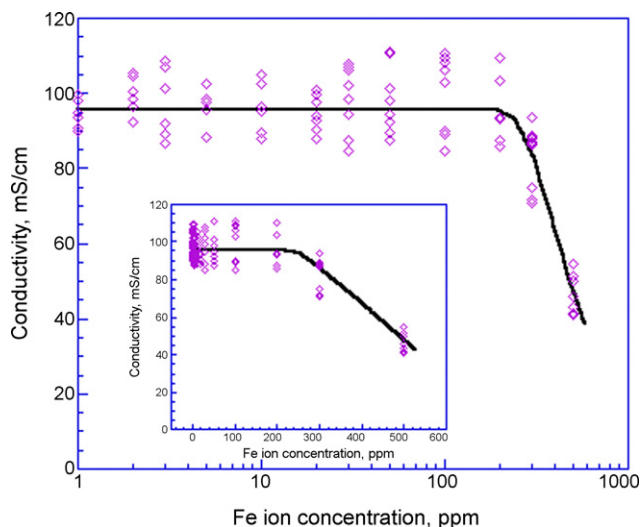


Fig. 5. Influence of Fe-ion concentration of the soaked solution on the conductivity of Nafion 112 membrane at 80 °C cell temperature and RH 100% with back hydrogen pressure of 0.103 MPa (15 psi). Inset shows the same behavior in linear scale of Fe-ion concentration.

Fig. 5, we see that at the same concentration level, the influence of Cr ion in solution on the conductivity of the membrane is much larger than that of the Fe ion in solution. This is in agreement with the EPMA mapping in which Cr ions are more readily adsorbed on the membrane than the Fe ions. In this way, Cr ions are more detrimental than Fe ions for the membrane. This result is also in agreement with a previous observation that Cr ions have a greater effect on degrading the membrane’s conductivity than Fe ions [6].

Solutions with mixed Fe and Cr ions, obtained from the polarization of lower grade stainless steel alloys in simulated PEMFC environments, were used to assess the impact of mixed metal-ion containing solutions on membrane conductivity. Test membranes were soaked as above and the results are shown in Fig. 7. We observed a conductivity trend similar to that seen in Figs. 5 and 6. Comparing Fig. 7 with Fig. 5, we see that the decrease in conductivity occurs at a lower Fe-ion concentration. This is surely related to the addition of Cr ions. It is interesting that the dissolved Fe–Cr

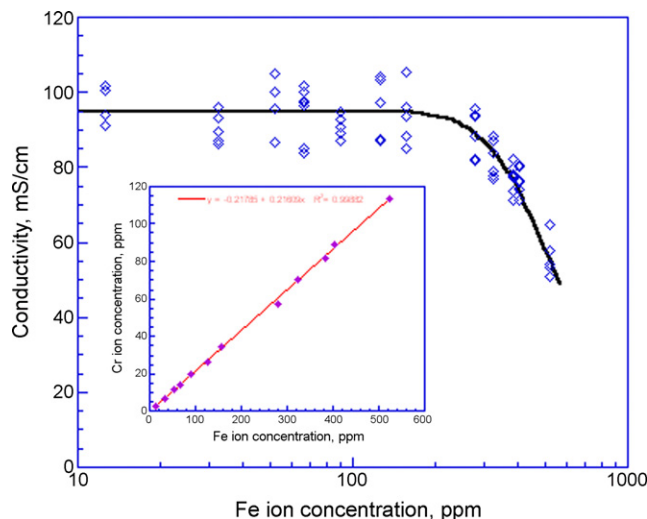


Fig. 7. Influence of mixed Fe and Cr ions on the conductivity of Nafion 112 membrane at 80 °C cell temperature and RH 100% with back hydrogen pressure of 0.103 MPa (15 psi). Inset shows the relationship of the dissolved Fe and Cr ions in the same solutions.

ions in the solutions follow a linear relationship for those stainless steels, inset of Fig. 7. The linear slope is approximately 0.22, meaning that the concentration of Cr ions is 0.22 times that of Fe ions in the same solution. In other words, Fe dissolved 4.6 times faster than Cr did for these steels in PEMFC environments, independent of the Fe:Cr ratio in the bulk steels. This selective dissolution of Fe has been described in other environments [29–31]. We should mention, however, that the dissolved Fe ions of our recommended stainless steels (349, AISI446, and 2205) in PEMFC environments were less than 5 ppm [16,17], with no dissolved Cr ions. So, the application of such steels in PEMFC environments will be acceptable. Our results are also in agreement with previous long-term tests (over 2000 h) with stainless-steel bipolar plates showing that the performance of the PEMFC was not degraded [3]. Therefore we suggest that not all of the metal ions absorbed in the membrane tied up functional sites. This could be also the case in the present situation.

4. Conclusions

Nafion 112 membranes were soaked in 1 M H₂SO₄ solutions containing Fe and Cr ions, either individually or mixed. An even distribution of the metal ions on the surface of the membranes was seen with EPMA mapping. The proton conductivity of the soaked membrane was investigated at 80 °C cell temperature and 100% RH with a hydrogen back pressure of 0.103 MPa (15 psi). For Fe ions, the conductivity was almost constant until the Fe-ion solution concentration reached 300 ppm. Over the 300 ppm threshold, the conductivity decreased significantly. Similar results were obtained with Cr ions in the membrane, but here the threshold was approximately 200 ppm. Mixed metal ions were found to decrease these threshold values due to the combination. Since the dissolved Fe ions for our candidate stainless steels (349, AISI446, and 2205) in PEMFC environments was below 5 ppm [16,17], with no detectable Cr, this confirms the suitability of these for PEMFC bipolar plates as far as membrane conductivity is concerned.

Note, we did not study the lifetime of the absorbed ions in the membrane when exposed to pure water. At high current densities, the generated water in the cathode side may leach out some contaminants [6] (depending on the acidity of the metal ions and the pH of the water) thus slow the accumulation of the ions into the

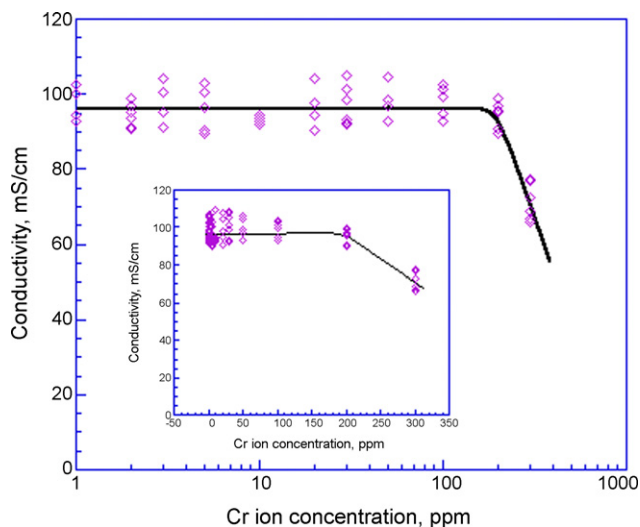


Fig. 6. Influence of Cr ion concentration of the soaked solution on the conductivity of Nafion 112 membrane at 80 °C cell temperature and RH 100% with back hydrogen pressure of 0.103 MPa (15 psi). Inset shows the same behavior in linear scale of Cr ion concentration.

membrane. In case of a higher pH, hydroxide complexes could form that release protons and subsequently replace the metal ions.

Acknowledgements

The authors thank Dr. Bobby To for the help in EPMA analysis. This work was supported by the US Department of Energy's Hydrogen, Fuel Cells & Infrastructure Technologies Program.

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