

# The effect of ferric ions on the conductivity of various types of polymer cation exchange membranes

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Received: 9 January 2007 / Revised: 27 February 2007 / Accepted: 14 March 2007 / Published online: 17 April 2007  
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**Abstract** Recently, rejuvenated interest to fuel cells has posed a number of problems regarding the polymer electrolyte membrane properties and their behaviour in different electrolyte solutions. This work was dedicated to study the conductivity of  $H^+$ -,  $Fe^{3+}$ - and mixed  $H^+/Fe^{3+}$ -forms of cation exchange membranes Neosepta CMS, Nafion 112, 115 and 117 and Selemion HSF under conditions similar to these in the  $Fe^{3+}/Fe^{2+}-H_2/H^+$  fuel cell in the range of current densities 0–90 mA/cm<sup>2</sup>. It was found that the conductivities of these membranes in 1.09 M  $H_2SO_4$  solution decrease in the following order: Selemion HSF > Nafion 117 ≈ Nafion 115 ≈ Neosepta CMS > Nafion 112. Conductivities of perfluorinated membranes were discussed in terms of Hsu and Gierke percolation theory [20]. The  $Fe^{3+}$ -forms of Nafion membranes studied displayed a monotonous decline in the resistance when current increased, which is a manifestation of gradual conversion of the  $Fe^{3+}$ -form into  $H^+$ -form of these membranes. Unlike the Nafion membranes, the  $Fe^{3+}$ -forms of Neosepta CMS and Selemion HSF membranes exhibited a sharp jump of resistance at relatively high current densities (more than 70 mA/cm<sup>2</sup>) that is most probably a result of concentration polarization.

**Keywords** Polymer electrolyte membrane · Membrane conductivity · Membrane resistance · Ferric ions

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## Introduction

Transport properties of polymer electrolyte membranes being equilibrated with different electrolyte solutions are quite important with relevance to their permeability when applied in chlor-alkali electrolysis [1], electro dialysis [2, 3], redox flow fuel cells [4–7], as well as addressing the contamination problems of membranes in polymer electrolyte membrane (PEM) electrolyzers [8] and PEM fuel cells [9, 10]. Investigations of ion and water transport characteristics of different ion exchange forms of perfluorosulfonated membranes involving mainly alkali, alkaline earth and some transition metal ions have been performed [11–13]. It was reported that ferric ions have higher preference to the membrane compared to protons ( $H^+$ ), and thereby the higher the preference of metal cations ( $M^{n+}$ ), the steeper the decline of the membrane ionic conductivity as a function of a metal ion fraction was observed. It was found that the order of  $H^+$ -form membrane affinity for transition metal cations is  $Fe^{3+}$  >  $Ni^{2+}$  >  $Cu^{2+}$  [11, 12]. Yoshida et al. [13] showed that for mixed cationic forms, the specific resistance of the membrane significantly increases if the metal ion fraction exceeds 40%. Beyond that, metal cations have a different influence on the mobility of hydrogen ions within the mixed-form membrane. In particular, the  $H^+$ -ions mobility in the presence of  $Fe^{3+}$  ions decreases to a considerable extent, whereas the  $Ni^{2+}$  ions do not alter the  $H^+$ -ions mobility [11, 12]. In contrast, the introduction of  $Cu^{2+}$  ions into the solution leads to an increase in  $H^+$  mobility, while the mobility of metal cations is not affected by the presence of  $H^+$ -ions [12].

However, study of the behaviour of the  $Fe^{3+}$ - and mixed  $Fe^{3+}/H^+$ -forms of the above membranes under direct currents in the region of 0–90 mA/cm<sup>2</sup> has not been performed yet. Thus, the principal purpose of the present work was to study

the effect of ferric ions on the conductivity of Nafion®, Neosepta® and Selemion® membranes.

## Experimental

### Materials

The proton selective Nafion 112, 115 and 117 membranes of DuPont (thicknesses of 51, 125 and 175  $\mu\text{m}$ , respectively) used in the experiments were purchased from Fuel Cell Store (USA). The double-layer proton selective membrane Selemion® HSF (thickness of 130  $\mu\text{m}$ ) was purchased from Asahi Glass (Japan). The samples of Neosepta CMS reinforced proton-selective membrane (thickness of 150  $\mu\text{m}$ ) of Tokuyama Soda were kindly provided by Eurodia Industrie S.A. (France). The anion exchange membrane Excellion I-200 was kindly supplied by Electro-pure EDI (USA).

The Nafion 112, 115 and 117 membranes were pre-treated first in 2%  $\text{H}_2\text{O}_2$  at about 100  $^\circ\text{C}$  for 1 h, and then washed with deionised water at 80  $^\circ\text{C}$  for 1 h [11]. According to the recommendations of Asahi Glass [14], after an installation in the measuring cell, the Selemion HSF membrane was kept in deionised water for 24 h, after which the anodic and cathodic compartments were filled with working solutions. The aqueous solutions of 1.09 M  $\text{H}_2\text{SO}_4$ , 0.45 M  $\text{Fe}_2(\text{SO}_4)_3$  in 1.09 M  $\text{H}_2\text{SO}_4$  and 0.45 M  $\text{Fe}_2(\text{SO}_4)_3$  were utilised as the working solutions. To obtain  $\text{H}^+$ -,  $\text{Fe}^{3+}$ - and mixed forms of the membranes, the Nafion and Neosepta CMS membranes were kept for 1 week in solutions of sulphuric acid, ferric sulphate or both, respectively.

The solutions of ferric sulphate, sulphuric acid and potassium chloride were prepared using deionised water and reagents of analytical purity purchased from Aldrich and Sigma, respectively.

### Ionic conductivity measurements

To determine the ionic conductivity of the membranes, a galvanostatic four-point-probe electrochemical impedance spectroscopy and direct current four-point-probe techniques are usually employed [15, 16]. Good agreement between the conductivities obtained by the two methods was achieved, with mean error of less than  $\pm 7\%$  [16]. Because the impedance technique requires longer measurement times, even for a limited frequency range, the conductivity measurements in this work were performed by a direct current two-point-probe method [17] using the cell, shown in Fig. 1. The cell was made of plexiglas and consisted of four separate compartments (two central compartments of 200 ml each and two auxiliary ones of 500 ml). The

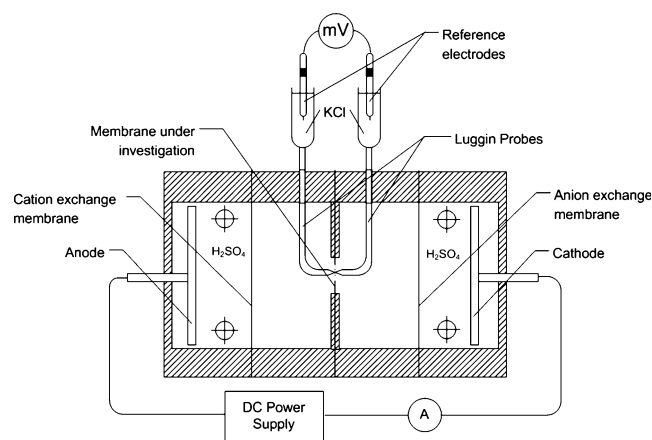


Fig. 1 Scheme of the experimental setup

auxiliary compartments contained the working electrodes, which were used to apply an electric field. The cathode was made of tantalum foil, and the anode was made of lead coated with lead dioxide. The central membrane was the membrane under investigation (Fig. 1), while the other two (Nafion 117 and an I-200 membranes were installed from the anodic and the cathodic compartments, respectively) were used to prevent the transport of water dissociation products formed at the working electrodes to the central compartments. The voltage drop across the studied membrane, installed in round windows having open areas of 11.3  $\text{cm}^2$ , was measured by a pair of Luggin capillaries. The capillaries were filled with saturated aqueous solution of potassium chloride ( $\text{KCl}_{\text{sat}}$ ) and each of them was connected to a test tube filled with  $\text{KCl}_{\text{sat}}$ , having Ag/AgCl,  $\text{KCl}_{\text{sat}}$  reference electrode in it. The reference electrodes were connected to a pH-meter/mV-meter ORION 420A for measuring the potential difference. The compartments containing anode and cathode (Fig. 1) were filled with circulating 10%  $\text{H}_2\text{SO}_4$  solution ( $\sim 1,000$  ml each). The circulation was achieved by peristaltic pumps with flow rates of 1,500 ml/h. To keep the constant temperature, the measuring cell and extension vessels with  $\text{H}_2\text{SO}_4$  solution were placed in a room with precise temperature control of  $22 \pm 0.2$   $^\circ\text{C}$ . The voltage drop ( $\Delta U$ , mV) across the studied membrane was measured as a function of the current density ( $i$ ,  $\text{mA}/\text{cm}^2$ ) in the range of 0–90  $\text{mA}/\text{cm}^2$ , while stepwise increasing the current applied. The area resistances ( $R$ ,  $\Omega \text{cm}^2$ ) of the membranes (Tables 1, 2 and 3) were determined as a slope of the linear parts on the  $\Delta U$ - $i$  plots. The conductivity values ( $\sigma$ ,  $\Omega^{-1}\text{cm}^{-1}$ ) were calculated as:

$$\sigma = \frac{l}{R},$$

where  $l$  was the membrane thickness in cm.

During the measurements, the membranes were equilibrated with the working solutions during a 2-h period.

The solutions in auxiliary compartments and a central compartment from the cathodic side remained the same

**Table 1** Conductivity data for membranes immersed in a solution of 1.09 M H<sub>2</sub>SO<sub>4</sub> at 22 °C

Membrane	Thickness of swollen membrane (μm)	Range of current density (mA/cm <sup>2</sup> )	Area resistance (Ωcm <sup>2</sup> )	Conductivity (Ω <sup>-1</sup> cm <sup>-1</sup> )
Nafion 112	65	0–40	0.37	1.8 10 <sup>-2</sup>
		40–90	0.66	1.0 10 <sup>-2</sup>
Nafion 115	160 [12]	0–90	0.67	2.4 10 <sup>-2</sup>
Nafion 117	220 [12]	0–90	0.84	2.6 10 <sup>-2</sup>
Selemion HSF	200	0–90	0.49	4.1 10 <sup>-2</sup>
Neosepta CMS	200	0–90	0.88	2.3 10 <sup>-2</sup>

(1.09 M H<sub>2</sub>SO<sub>4</sub>) for all the experiments, while the central anodic compartment was filled with corresponding working solutions.

The experiments were conducted at 22 °C.

## Results and discussion

The relationships between voltage drop and current density obtained are shown in Figs. 2, 3 and 4. As can be seen in Fig. 2, the voltage drop in the case of 1.09 M sulphuric acid solution is a linear function with respect to the current density. The only exception from the linear behaviour was observed with Nafion 112 membrane, because in that case, the  $\Delta U-i$  have different slopes at current densities above and below 37 mA/cm<sup>2</sup>. Besides, the highest voltage drop for Selemion membrane is observed at the lowest current density (~5 mA/cm<sup>2</sup>) and is more than five times larger than that for the rest of the membranes (Fig. 2). Unlike the Nafion membranes, Selemion belongs to the double-layer type of membranes; therefore, the Donnan potentials, establishing between each side of the membrane and the adjacent solution, significantly differ that, in turn, results in establishing a considerably high membrane potential [18]. Figures 3 and 4 represent the  $\Delta U-i$  relationships for the membranes studied in the 0.45 M Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in 1.09 M H<sub>2</sub>SO<sub>4</sub> and 0.45 M Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, respectively. As can be seen from Fig. 3, slopes of the linear sections of the curves decrease for all the membranes, compared to those obtained in the pure acid solutions (Fig. 2). The comparison of the

dependences represented in the Figs. 2, 3 and 4 show that the Fe<sup>3+</sup> ions have a significant influence on the slope of  $\Delta U-i$  line and as a result, on the membrane resistance. The strongest effect was registered in the case of 0.45 M ferric sulphate solution with a pH of 1.0 (Fig. 4). The largest voltage drop, when increasing current density, was observed for Neosepta CMS and Selemion HSF membranes. In particular, it sharply increases from about 320 to 680 mV within the range of 65–80 mA/cm<sup>2</sup>, indicating that limiting current density has been reached. Irrespective of the presence of other ions in the solution, the basic charge carriers are protons in the virtue of their high mobility. Thereby, at a certain current density, the solution close to the membrane, on the cathodic side, becomes depleted of protons. This phenomenon is referred to as the concentration polarization and is a cause of limiting current density [19]. The values of conductivities obtained may be interpreted and analysed in terms of modern knowledge on a chemical and three-dimensional nano-scale structure of the membranes. Because the Nafion membranes consist of strongly hydrophilic sulfonic acid groups attached to a strongly hydrophobic polytetrafluoroethylene backbone by perfluorinated ester side-chains, these have a phase-segregated morphology in terms of an inverted micellar structure in which the hydrophilic sulphonated groups are separated from the fluorocarbon backbone, and thereby form spherical clusters (pores), which are connected by short narrow channels [20, 21]. When the membrane is in a dry state, an average cluster has a radius of about 1.8 nm, but in the swollen state, the diameter increases up to about 4 nm and

**Table 2** Conductivity data for membranes separating two solutions: 0.45 M Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in 1.09 M H<sub>2</sub>SO<sub>4</sub> from anodic and 1.09 M H<sub>2</sub>SO<sub>4</sub> from cathodic side at 22 °C

Membrane	Thickness of swollen membrane (μm)	Range of current density (mA/cm <sup>2</sup> )	Area resistance (Ωcm <sup>2</sup> )	Conductivity (Ω <sup>-1</sup> cm <sup>-1</sup> )
Nafion 112		0–56	0.79	8.2 10 <sup>-3</sup>
		56–90	0.52	1.3 10 <sup>-2</sup>
Nafion 115	160	0–26	1.39	1.2 10 <sup>-2</sup>
		26–90	0.98	1.6 10 <sup>-2</sup>
Nafion 117	220	0–32	1.43	1.5 10 <sup>-2</sup>
		32–90	1.24	1.8 10 <sup>-2</sup>
Selemion HSF	200	0–26	1.13	1.8 10 <sup>-2</sup>
		26–60	0.98	2.0 10 <sup>-2</sup>
		60–90	0.74	2.7 10 <sup>-2</sup>

**Table 3** Conductivity data for membranes separating two solutions: 1.09 M H<sub>2</sub>SO<sub>4</sub> from the cathodic and 0.45 M Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> from the anodic side at 22 °C

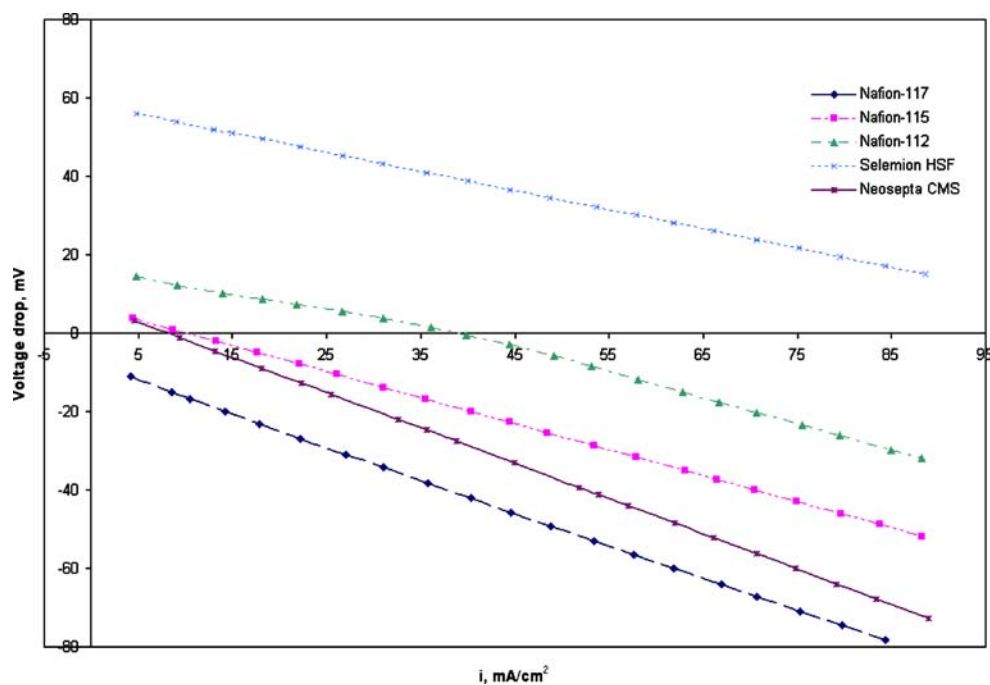
Membrane	Thickness of swollen membrane (μm)	Range of current density (mA/cm <sup>2</sup> )	Area resistance (Ωcm <sup>2</sup> )	Conductivity (Ω <sup>-1</sup> cm <sup>-1</sup> )
Nafion 112	65	0–38	1.84	3.5 · 10 <sup>-3</sup>
		38–90	0.82	7.9 · 10 <sup>-3</sup>
Nafion 115	160	0–50	2.86	5.6 · 10 <sup>-3</sup>
		50–90	1.54	1.0 · 10 <sup>-2</sup>
Selemion HSF	200	0–53	4.45	4.5 · 10 <sup>-3</sup>
Neosepta CMS	200	0–53	4.45	4.5 · 10 <sup>-3</sup>

each pore is filled with about 1,000 water molecules; the connecting channels have both diameter and length of about 1 nm [20]. According to the percolation theory of Hsu and Gierke [21], the membrane conductivity correlates with the water content, and there exists a critical content of water, below which ionic transport becomes drastically hindered because of the absence of extended pathway. Zawodzinski et al. [22] established the correlation between the conductivity of Nafion 117 membrane and its water content, measured in λ units (λ is equal to the number of water molecules per sulphonate group in the polymer). In turn, the λ value is a function of the water activity [23], which was reported to be equal to 0.95 in 1.09 M solution of sulphuric acid [24]. This value corresponds to λ ≈ 10 [23] and the conductivity of Nafion 117 of about 4 · 10<sup>-2</sup> Ω<sup>-1</sup>cm<sup>-1</sup> at 30 °C [22], which is relatively close to that obtained in our work (Table 1). The difference between these results could be because of a temperature effect: our experiments were performed at 22 °C rather than 30 °C. It should be noted that the obtained values of ionic conductivity for Nafion 117 membrane (Table 1) in 1.09 M H<sub>2</sub>SO<sub>4</sub> are fairly close to the data reported by Sumner et al. [15]

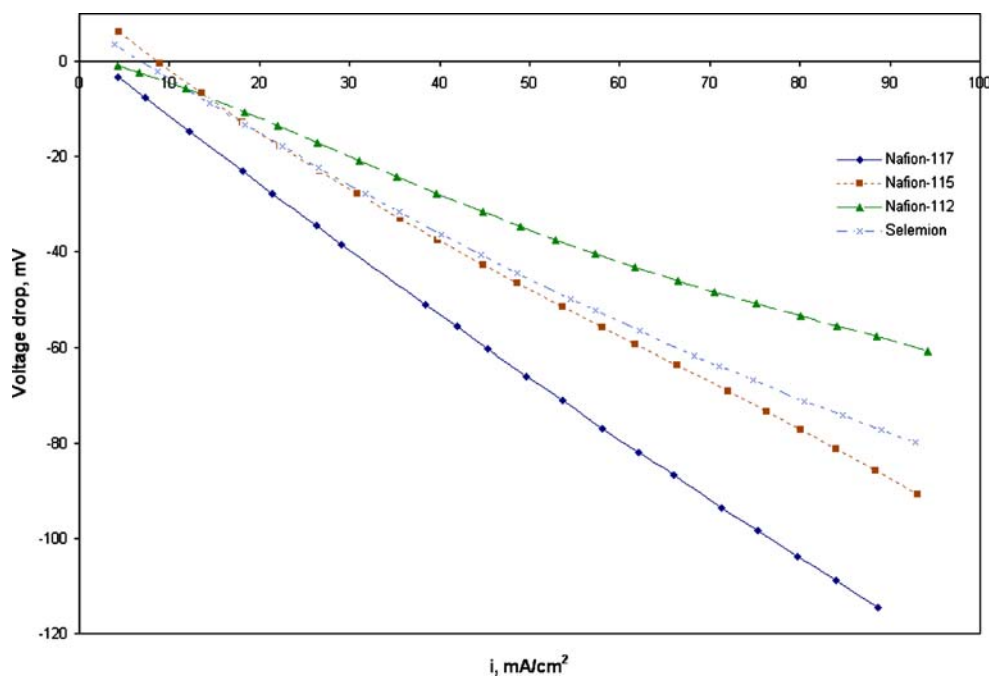
(2.8 · 10<sup>-2</sup> Ω<sup>-1</sup>cm<sup>-1</sup> for 81% relative humidity). The difference in water activity can also explain the difference observed in the measurements of an area resistance at 22 °C for Selemion HSF membrane in sulphuric acid solutions: 0.30 [14] and 0.49 Ωcm<sup>2</sup> in 0.5 M and 1.09 M H<sub>2</sub>SO<sub>4</sub>, respectively.

The results dealing with the influence of Fe<sup>3+</sup> ions on the Nafion membranes conductivity (Tables 2 and 3) are in good agreement with the data obtained by Okada et al. [12]. In particular, the conductivity of Fe<sup>3+</sup>-form of Nafion 115 membrane was found to be 5.6 · 10<sup>-3</sup> Ω<sup>-1</sup>cm<sup>-1</sup> as compared to 6.7 · 10<sup>-3</sup> Ω<sup>-1</sup>cm<sup>-1</sup> at 25 °C [12]. Using a dependence of conductivity on the ionic fraction of H<sup>+</sup>-form for Nafion 115 membrane [12], we have found out that in the solution containing both hydrogen and ferric ions in the ratio of H<sup>+</sup>/Fe<sup>3+</sup> equal to 2.4 (Table 3), the ionic fraction of Fe<sup>3+</sup>-form is equal to about 0.83. A difference between the resistances of Fe<sup>3+</sup>- and H<sup>+</sup>-forms of the membranes can be interpreted in terms of the ion transfer mechanisms: hopping mechanism that is typical for hydrogen ions and vehicle mechanism, which is characteristic for metal ions [12, 25, 26].

**Fig. 2** Effect of the voltage drop across the membrane on current density with 1.09 M H<sub>2</sub>SO<sub>4</sub> at the cathode



**Fig. 3** The relationship between the voltage drop and current density for membranes separating 0.45 M  $\text{Fe}_2(\text{SO}_4)_3$  in 1.09 M  $\text{H}_2\text{SO}_4$  and 1.09 M  $\text{H}_2\text{SO}_4$  solutions

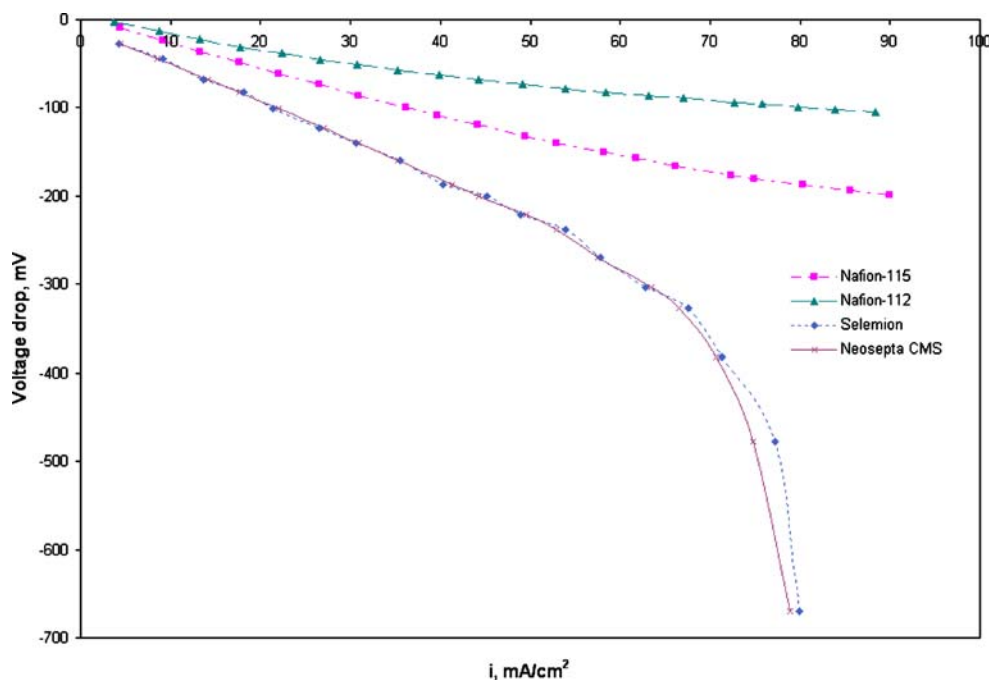


The data on the resistance of Neosepta CMS membrane available in the literature is quite limited. Strathmann et al. [27] established that the surface resistance of Neosepta CMS membrane in sodium chloride solutions falls in the range between 1.5 and 2.5  $\Omega\text{cm}^2$ . Experimentally, measured resistance of this membrane equilibrated with 0.45 M  $\text{Fe}_2(\text{SO}_4)_3$  solution showed a reasonably higher value, which was found to be 4.45  $\Omega\text{cm}^2$ . The difference in a resistance for  $\text{Na}^+$ - and  $\text{Fe}^{3+}$ -forms of Neosepta CMS membrane can be readily explained in terms of ion mobility. It is known that the mobility of the sodium ions

within Nafion 117 membrane [28] is almost six times higher in comparison with that for ferric ions [12]. However, in our case (when  $\text{Fe}^{3+}$ -form of Neosepta CMS membrane is in contact with sulphuric acid solution), hydrogen ions might take part in the process of a charge transfer along with ferric ions, that boosts conductivity and thereby results in the membrane resistance not much higher than that in sodium chloride solution.

The sharp increase in a voltage drop on the  $\Delta U-i$  dependences for Neosepta CMS and Selemion HSF membranes (Fig. 3) at reaching the limiting current density

**Fig. 4** Dependences of the voltage drop on current density for membranes separating 0.45 M  $\text{Fe}_2(\text{SO}_4)_3$  and 1.09 M  $\text{H}_2\text{SO}_4$  solutions



indicates that concentration polarization takes place, as was mentioned above. Similar behaviour was observed by Krol [19] for Neosepta CMS membrane in a sodium chloride solution. This phenomenon was not observed in the case of Nafion membrane. For this membrane, an increase in the current density leads to a gradual decline in the resistance up to values common for the  $H^+$ -form. This can be explained by a progressive substitution of  $Fe^{3+}$  ions by hydrogen ions from the cathodic compartment (Fig. 1) when the current density increases: apparently, the  $Fe^{3+}$  ions in perfluorosulfonated membranes are “pushed” (under direct current) by  $H_3O^+$  ions along the membrane channels. An indirect proof of this mechanism can be provided by the observed decolouration of the  $Fe^{3+}$ -forms of membranes after applying high current densities.

## Conclusions

The experimental data of the membrane conductivity study allowed us to make the following conclusions, in terms of their practical applications:

1. The highest conductivity among the studied  $H^+$ -form membranes has Selemion HSF. The comparison of the ionic conductivities of the membranes was as follows: Selemion HSF  $\succ$  Nafion 117  $\approx$  Nafion 115  $\approx$  Neosepta CMS  $\succ$  Nafion 112.
2. The ionic conductivity of the  $Fe^{3+}$ -form of all the membranes studied is approximately one order of magnitude lower than that of the  $H^+$ -form. The mixed  $H^+/Fe^{3+}$ -forms had the conductivity about two to three times lower than that for the corresponding  $H^+$ -forms.
3. Ferric ions have the least influence on the conductivity of the Nafion 115 under direct current at  $\sim$ pH 1.0, compared to the rest of the membranes studied.
4. Selemion HSF membrane had the lowest sensitivity to contamination by  $Fe^{3+}$  ions in the strong acidic media (1 M sulphuric acid).

**Acknowledgements** This work was supported financially by the Natural Science and Engineering Research Council of Canada, the Premier’s Research Excellence Award of Ontario, and the Western Innovation Fund of the University of Western Ontario. Authors also would like to thank Mrs. F. Lutin (Eurodia Industrie S.A., France) and Mr. L. White (Electropure EDI, USA) for kindly supplying us with membrane samples.

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