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Evaluation of transport properties of cation exchange membranes for application in alkali concentrators

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Conductivity and transport properties of commercially available cation exchange membranes were investigated for their application in an electrochemical alkali concentrator. Among the three membranes studied, Nafion®* 961 was found to have high conductivity, high sodium ion transport and lower water transport characteristics which are the desired characteristics for fabrication of an alkali concentrator. The effect of concentration gradient between anolyte and catholyte on the overall transport properties is also reported.

1. Introduction

During the operation of an alkaline hydrogen/oxygen fuel cell, excess cationic species (H^+) are generated near the anode (due to hydrogen gas oxidation) and excess anionic species (OH^-) are generated near the cathode (oxygen reduction). If these two electrodes are effectively separated by a cation exchange membrane which can selectively transport Na^+ cation, the concentration of alkali in the cathode compartment may increase while that in the anode compartment becomes diluted. Hence, selection of an efficient cation-exchange membrane with desirable characteristics to be used between the fuel cell electrodes and fabrication and evaluation of an alkali concentrator based on the fuel cell described earlier [1, 2] became the objective of the present work.

Among the cation exchange membranes [3, 4] the Nafion®* brand of perfluorinated membranes were the earliest to enter the market and are also readily available. Among these membranes, three specific cation exchange membranes, namely Nafion 315, Nafion 901 and Nafion 961, were selected for the present investigations. Nafion 315 is a reinforced perfluorinated composite membrane containing only sulfonate groups. Nafion 901 and Nafion 961 are reinforced bilayer membranes containing a thick sulphonate layer and a thin carboxylate layer on either side of the membrane backbone. The carboxylate layer is relatively less hydrophilic and hence resists water transport through the membrane.

For application in an alkali concentrator, it is necessary to evaluate the conductivity and transport properties in chloride free alkaline environments. Only a handful of reports are available on the transport properties of perfluorinated cation exchange membranes in concentrated alkaline solutions [5–9]. Taylor *et al.* [8–11] have also reported wide variations in the values of voltage drop (0.2–1.0 V) for a series of proprietary membranes. The transport properties of the recently introduced Nafion 961 cation exchange membrane in these environments have not been studied. Thus it was felt desirable to evaluate the conductivity and transport properties of a few commercially available membranes in view of their use in alkali concentrators.

2. Experimental details

The voltage drop across membranes, which is inversely proportional to the conductivity of the membrane, may be studied by either a.c. or d.c. methods [6–9, 12, 13]. In the present study, the simple method of measuring the voltage drop between the electrodes placed on either side of the membrane, with and without the presence of the membrane under a constant d.c. load was employed. The cell employed for measuring the membrane voltage drop consisted of anode and cathode compartments which were easily assembled with or without the membrane. A flexible and stable neoprene rubber was used as gasket. The cell was also provided with suitable arrangements for electrolyte overflow as well as electrolyte drainage. Stainless steel and TSIA (titanium substrate insolube anode) electrodes were employed as cathodes and anodes, respectively. These electrodes were mounted on a non-conducting bar made of PVC which was positioned over the cell, thereby immersing the electrodes inside the electrolyte. This arrangement was made to provide constant interelectrode distance irrespective of the presence or absence of the membrane.

The electrochemical cell used earlier [1, 2] for the evaluation of fuel cell performance was modified by including a further electrolyte compartment and was used for the study of transport characteristics of the membranes. For the evaluation of Na^+ ion transport and water transport properties, constant current electrolysis was carried out for 8 h. The electrolyte flow

* Nafion® is a registered trademark of E.I.Du Pont deNemours & Company.

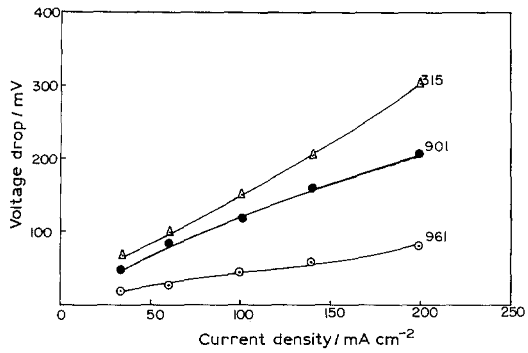

Fig. 1. Membrane voltage drop of Nafion (●) 901, (⊙) 961 and (△) 315 at different current densities. Anolyte and catholyte: 30 wt % NaOH; Temperature: 353 K.

was maintained using a duostatic (peristatic) pump. By measuring the change in concentration of Na^+, H_2O and the total current passed, the transport of sodium ions and the water was calculated [9] using the following relationships:

$$t_{Na^+} = \frac{\Delta W_{NaOH} F}{M_{NaOH} it}$$

and

$$t_{H_2O} = \frac{\Delta W_{H_2O} F}{M_{H_2O} it} / t_{Na^+}$$

where ΔW_{NaOH} is the weight change (g) of sodium hydroxide, and M_{NaOH} is the molecular weight of NaOH (40 g mol^{-1}). The remaining terms are : F, the Faraday constant (96 485 C mol^{-1}), t, the time of current passage (s), i, the current (A), ΔW_{H_2O}, the weight change (g) of water, and M_{H_2O}, the molecular weight of water (18 g mol^{-1}).

3. Results and discussion

The relative performance of Nafion 315, 901 and 961 were evaluated at different current densities, with a constant electrolyte concentration (30 wt % NaOH) and temperature (353 K). Then, the effect of electrolyte concentration and temperature on the performance of Nafion 961 was evaluated.

3.1. *Transport and conductivity of Nafion 315, 901 and 961*

The dependence of the voltage drop of the three Nafion membranes on the impressed current is presented in Fig. 1. Since the electrodes [1, 2] could function effectively only up to 200 mA cm^{-2}, no attempt was made to evaluate the transport properties beyond this current density. Within this limit, the current–potential response of the membrane was found to be linear for all three membranes. The voltage drop of the membranes were also found to decrease in the order Nafion 315 > Nafion 901 > Nafion 961. In Nafion 961 even at a current density of 200 mA cm^{-2} the voltage drop was less than 0.1 V. For Nafion 315, the value was as much as 0.3 V.

The transport number of Na^+ ions was found to decrease linearly with current density (Fig. 2). Again Nafion 961 was found to be the most efficient among the three membranes and in this case t_{Na^+} was found to be greater than 0.9 even at a current density of 200 mA cm^{-2}. The Na^+ ion transport number is slightly lower in Nafion 901. In the case of Nafion 315 which is more hydrophilic in nature, back migration of ions is more probable and the transport number reduces to 0.8 at this current density (Fig. 2).

The water transport is closely connected with Na^+ ion transport in perfluorinated cation exchange membranes which are highly hydrophobic in nature and water molecules diffuse through the membranes mainly through the solvation sheath of the alkali metal cation. Hence Nafion 315, which is more hydrophilic in nature, allows maximum water transport (Fig. 3). The water transport once again decreases with current density, as in the case of Na^+ ion transport. Among the three membranes, Nafion 961 is found to carry minimum water.

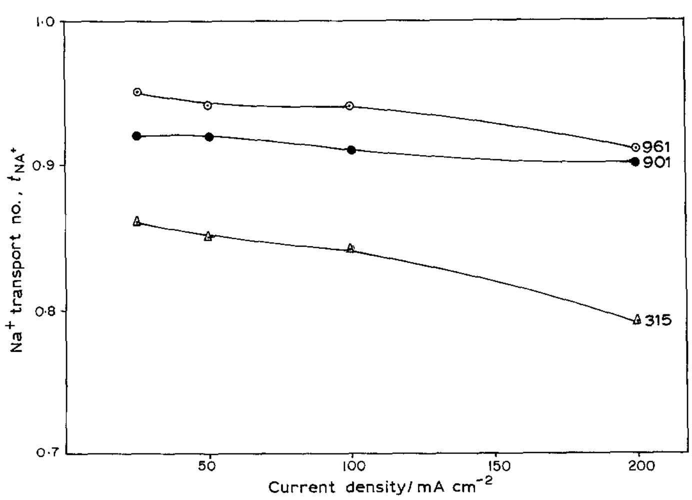

Fig. 2. Transport number of sodium ion in Nafion (△) 315, (●) 901 and (⊙) 961 at different current densities. Anolyte and catholyte: 30 wt % NaOH; Temperature: 353 K.

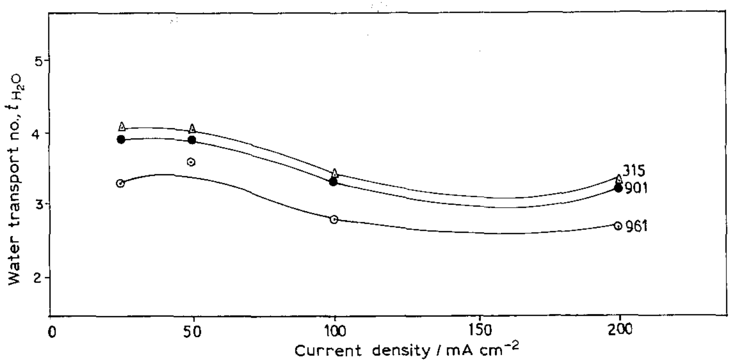

Fig. 3. Water transport number of Nafion (△) 315, (●) 901 and (⊙) 961 at different current densities. Anolyte and catholyte: 30 wt % NaOH; Temperature: 353 K.

Table 1. Electrochemical characteristics of Nafion 315, 901 and 961 cation exchange membranes in 30 wt % NaOH at 353 K, at two different values of current densities

Membrane	*Membrane voltage drop/V*		t_{Na^+}		t_{H_2O}	
	100 mA cm^{-2}	*200 mA cm^{-2}*	*100 mA cm^{-2}*	*200 mA cm^{-2}*	*100 mA cm^{-2}*	*200 mA cm^{-2}*
Nafion 315	0.150	0.300	0.84	0.79	3.4	3.3
Nafion 901	0.118	0.206	0.91	0.90	3.3	3.2
Nafion 961	0.045	0.080	0.94	0.91	2.8	2.7

The experimental results obtained from the three series of experiments at two different current densities are compared in Table 1. It is apparent from this Table that the membrane voltage drop is almost three times lower with Nafion 961 when compared with Nafion 315 at a current density of 100 mA cm^{-2}. The Na^+ ion transport number is also high and the relative number of water molecules transported is lower for this membrane. Hence a Nafion 961 membrane was chosen as the preferred membrane for the construction of the alkali concentrator. Further studies were confined to this membrane.

3.2. *Effect of experimental conditions on the performance of Nafion 961 membranes*

The voltage drop across Nafion 961 was measured at 303, 323 and 353 K and as expected it was found to decrease with increasing temperature. Temperature, however, was found to exert opposite effects on Na^+ ion transport and water transport. Beyond 323 K, a sudden increase in the transport number of Na^+ ions was noticed (Fig. 4). In 30 wt % NaOH solutions the Na^+ transport number approached 0.94 even at a current density of 100 mA cm^{-2}. The increase in current density led to a slight decrease in the Na^+ transport number. Interestingly, it was noticed that the relative water transport decreased with increasing temperature (Fig. 5). This inverse relation between the rate of Na^+ ion and water transport can be understood by recalling that the hydration number of Na^+ ions decrease with temperature and water primarily passes through the membrane as water of hydration. Decreasing hydration with increasing temperature naturally leads to increase in Na^+ ion transport and, hence, decrease in water transport.

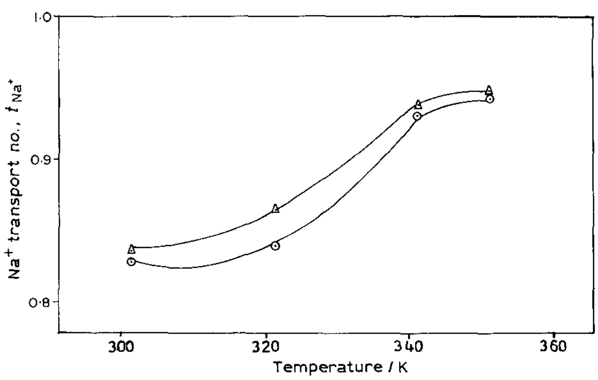

Fig. 4. Effect of temperature on sodium ion transport through Nafion 961 at (△) $i = 50$ mA cm^{-2} and (⊙) $i = 100$ mA cm^{-2}. Anolyte and catholyte: 30 wt % NaOH.

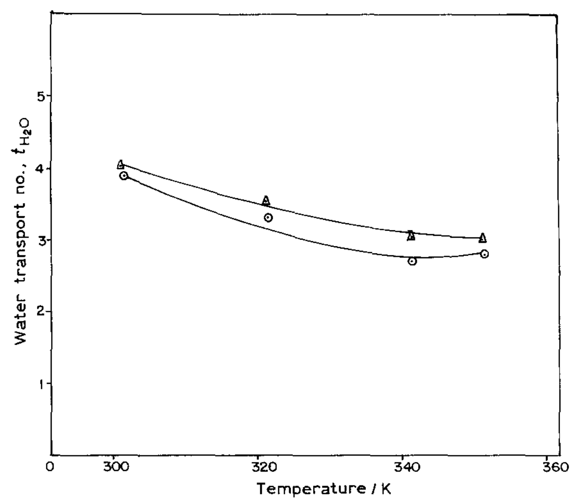

Fig. 5. Effect of temperature on water transport through Nafion 961 at (△) $i = 50$ mA cm^{-2} and (⊙) $i = 100$ mA cm^{-2}. Anolyte and catholyte: 30 wt % NaOH.

Table 2. Transport characteristics of Nafion 961 membrane at different anolyte and catholyte concentrations at 353 K

S	*Anolyte concentration/ wt % NaOH*	*Catholyte concentration/ wt % NaOH*	*Concentration gradient/ wt % NaOH*	t_{Na^+}		t_{H_2O}	
				50 mA cm^{-2}	*100 mA cm^{-2}*	*50 mA cm^{-2}*	*100 mA cm^{-2}*
1	25	35	10	0.91	0.90	4.5	4.4
2	25	40	15	0.84	0.82	4.8	4.7
3	20	40	20	0.68	0.68	5.1	5.0
4	20	50	30	0.55	0.56	5.6	5.3

The voltage drop in the membrane did not vary significantly with alkali concentration. The maximum variation in membrane voltage drop at any current density was around 10 mV only. Similar variations were also noticed when different alkali concentrations were used in the anode and cathode compartments. However, the Na^+ ion and water transport properties show substantial differences when concentration gradients were introduced at the beginning of the electrolytic process (Table 2). When the concentration gradient between anolyte and catholyte compartments exceeded 15 wt %, the Na^+ ion transport number decreased substantially and even fell, to approaching 0.55, when the initial anolyte and catholyte concentrations were 20 wt % and 50 wt %, respectively. The number of water molecules transported for each Na^+ ion also increased substantially. The substantial decrease in t_{Na^+} revealed higher OH^- ion diffusion in the opposite direction, indicating a lower performance of the alkali concentration.

4. Conclusion

Nafion 961 cation exchange membranes were found to be the best among the three membranes investigated for application in an alkali concentrator. This membrane can function efficiently even at a current density of 200 mA cm^{-2} with wide variations in the alkali concentration of anode and cathode compartments with a membrane voltage drop below 0.1 V. Although high temperatures favour better transport response, practical fuel cell operating conditions would allow the alkali concentrator to operate around 353 K only. A significant decrease in the Na^+ transport number and an increase in water transport are observed when the difference in the alkali concentrations of anolyte and catholyte compartments exceeds 15 wt %.

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