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Effects of chlorides on the performance of proton exchange membrane fuel cells

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ABSTRACT

This paper investigates the effects of cathode gases containing chloride ions on the proton exchange membrane fuel cell (PEMFC) performance. Chloride solutions are vaporized using an ultrasonic oscillator and mixed with oxygen/air. The salt concentration of the mixed gas in the cathode is set by varying the concentration of the chloride solution. Five-hour tests show that an increase in the concentration of sodium chloride did not significantly affect the cell performance of the PEMFC. It is found that variations in the concentration of chloride do not show significant influence on the cell performance at low current density operating condition. However, for high current density operating conditions and high calcium chloride concentrations, the chloride ion appears to have a considerable effect on cell performance. Experimental results of 108-h tests indicate that the fuel cell operating with air containing calcium chloride has a performance decay rate of 3.446 mV h^{-1} under the operating condition of current density at 1 A/cm^2 . From the measurements of the I–V polarization curves, it appears that the presence of calcium chloride in the cathode fuel gas affects the cell performance more than sodium chloride does.

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1. Introduction

Fuel cells, which convert the chemical energy of the fuel directly to electricity with high efficiency, are considered to be the ultimate technology for the clean generation of power. Proton exchange membrane fuel cells (PEMFCs) are promising power sources for electrically powered vehicles and distributed power generation in the near future [1–3]. However, one of the main technological issues of the PEMFC is the limitation of lifetime under typical operating conditions, even under the operation with pure hydrogen. For automotive, portable, and residential applications, fuel cells are required to be reliable,

inexpensive and durable. Durability of the fuel cell targets exceed 5000 h for automotive applications and 40 000 h for stationary applications [4,5].

Taiwan is an island on the west Pacific Ocean with the coastline of 1137 km. When an ocean wave breaks, droplets of salt water interact locally with air and diffuse into the air. Eventually they would be blown inland by offshore winds. The salt (sodium chloride–NaCl; and potassium chloride–KCl) content of the sea air and subsequently the soil is approximately 0.046–0.455%. This salt mist can be detected as far as 25–55 km inland with the influence of typhoons in summer or north-eastern seasonal wind in winter. Consequently, the

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Nomenclature		Subscripts	
m	mass, g	g	for gas consumed per hour
T	temperature, °C	s	for sodium chloride in 1 L of chloride solution
t	total operation time, h	C	for chloride solution consumed per hour
V	voltage, V	w	for 1 L of chloride solution

cathode gases would contain significant levels of chloride, if fuel cells are located near the coastline. With higher levels of chloride concentration, the metal parts of the fuel cell would corrode and produce additional free metal ions in the air after a long period of operation. As a result, metal ions would enter into the membrane of the cells through the fuel gases in the cathode. This leads to the contamination of the membrane, in turns, a considerable impact on the membrane conductivity and the water transfer coefficient.

Mass transport is another important issue in cell performance of PEMFC. The mass transport properties degrade as a result of the accumulation of excess water. Furthermore, various impurities can affect the cell performance [6]. However, the failure modes for PEM fuel cells have not yet been well documented, and the causes and mechanisms of degradation are not fully understood. The long-term fuel cell tests are often performed in very specific conditions (in terms of temperature, gas humidification, nature of the catalyst, gas pressure, etc.) with precise and reliable comparison of the results reported in literature [7–11] on different membranes lifetime. Some studies suggest that degradation is induced at the anode [7,8] whereas some others conclude that it occurs at the cathode [9,10] or homogeneously through the membrane thickness [11].

Okada et al. [12] presented a one-dimensional model of linear water transport in a membrane, and analyzed the water concentration distribution, net water flux and the membrane resistance. Their results showed that the current density, humidification and membrane thickness were crucial parameters in determining the water concentration of the membrane. In addition, these results also showed that even if contamination was restricted to the membrane surface, severe dehydration of the membrane would occur. Their proposed one-dimensional model for water transport in the membrane was extended to consider contamination of either the anode [13] or cathode side [14], analyzing the water concentration distribution in the membrane. The results indicate that the membrane performance will decrease significantly due to contamination.

Xie and Okada [15] observed that the smaller ions would increase the transference coefficients due to the larger hydrological radii upon hydration. Zawodzinski et al. [16,17] found that if there is more water in a membrane, the diffusion effect will be more apparent. Chen et al. [18,19] numerically examined the water transport of proton exchange membrane fuel cells (PEMFC) and showed that severe dehydration occurs in the membrane as the membrane is fouled by foreign ions. Also, the time requires for the system to reach steady state will be prolonged.

The membrane maybe fouled during the manufacturing process or during cell operation, as the input gas may contain foreign ions, and hydrogen contaminated vapor. Okada et al. [20] found that water transference coefficient, defined as the

number of moles of water transported per Faraday through the membrane, is governed by two effects: an electrostatic effect between ion and water dipoles, and an effect due to the size of cations. Furthermore, Okada and his colleagues also suggested that other cations, such as Ca [21], Na [22], Fe, Ni, Cu, [23] Li, K, Rb, Cs [24], may have an influence on the characteristics of the membrane. As long as the membrane is contaminated, the water content, conductivity, and water permeability of the membrane decline rapidly.

From the literatures cited above, it is noted that previous researches have shown anions and cations in a membrane would affect the characteristics of the membrane. However, investigation of the effect of chloride content in cathode fuel gas on PEM fuel cell performance has not been well examined. This motivates the present study. In this work, the primary objective was to study the influence of cathode gases containing different chloride ions on cell performance of the PEM fuel cells.

2. Experiment setup and methodology

2.1. Fuel cell

The materials of the proton exchange membrane fuel cell used in these experiments are specified as below:

(1) Proton exchange membrane

The PEM is made of GORE, PRIMERA type 5621, with a reaction area of $5 \times 5 \text{ cm}^2$.

(2) Catalyst layer

The catalyst layer is also made of GORE. The platinum alloy content on the anode side is 0.45 mg/cm^2 whilst the platinum alloy content on the anode side is 0.6 mg/cm^2 . The combined thickness of the catalyst layer and PEM is $35 \text{ }\mu\text{m}$.

(3) Gas diffusion layer

The gas diffusion layer is made of carbon cloth GORE-TEX structures with a surface area of $5 \times 5 \text{ cm}^2$ and thickness of 0.4 mm .

(4) Flow field plate

The flow field plate is a graphite plate with a total surface area of $10 \times 10 \text{ cm}^2$ with plate thickness of 1 cm . A serpentine flow field was configured in both the anode and cathode sides. Both width and depth of the flow channels were 1 mm .

(5) Collector plate

The collector plate is made of copper. The copper surface is gilded to reduce corrosion and contact resistance between the plates. The collector plate has dimensions of $10 \times 10 \text{ cm}^2$ with the thickness of 0.4 cm. The end plate is made from Aluminum 7075, and has dimensions of $10 \times 10 \text{ cm}^2$ with the thickness of 1 cm.

2.2. Experimental setup

Schematic view of the experiment test system is shown in Fig. 1. The test bench mainly includes five parts, which are gas supply system, flow rate control system, temperature control system, humidity system and electric load system. The gas supply system supplies hydrogen, oxygen and air as the anode and cathode reactant gas in the fuel cell, and supplies nitrogen for removing the residual gas in the pipeline before and after experiments. The flow rate control system controls the gas inlet flow rate following stoichiometry and minimum flow mode. As for the temperature control system, heating rod, T-type thermocouple and CN76000 temperature controller are employed to control the cell temperature. The humidity system forces the

gases through humidification bottles and regulates the temperature of the humidified fuel gases. The electric load system has the maximum power output of 600 W, the maximum current of 120 A and the maximum voltage of 60 V.

The chloride salt solution is mixed with oxygen/air in a sealed bottle using an ultrasonic oscillator and mixing vessel. The chloride solution is sprayed to form water droplets in the form of a fine mist, which mixes with oxygen/air in the mixing vessel. The final mixture is fed into the fuel cell as the fuel reactant.

2.3. Analysis of gas chloride concentration

In order to investigate the effect of concentration of chloride on PEMFC performance, the concentration of chloride in the cathode gases is calculated by the following equation.

$$\text{Chloride concentration(ppm)} = \frac{\dot{m}_c \times \frac{m_s}{m_w}}{\dot{m}_g + \dot{m}_c} \times 10^6 \quad (1)$$

Where m_w is the mass of chloride solution, \dot{m}_g is the consumed mass of gas per h, \dot{m}_c is the consumed mass of chloride solution per h, m_s is the mass of chloride in the chloride solution. For clarity, all the measured and average values are

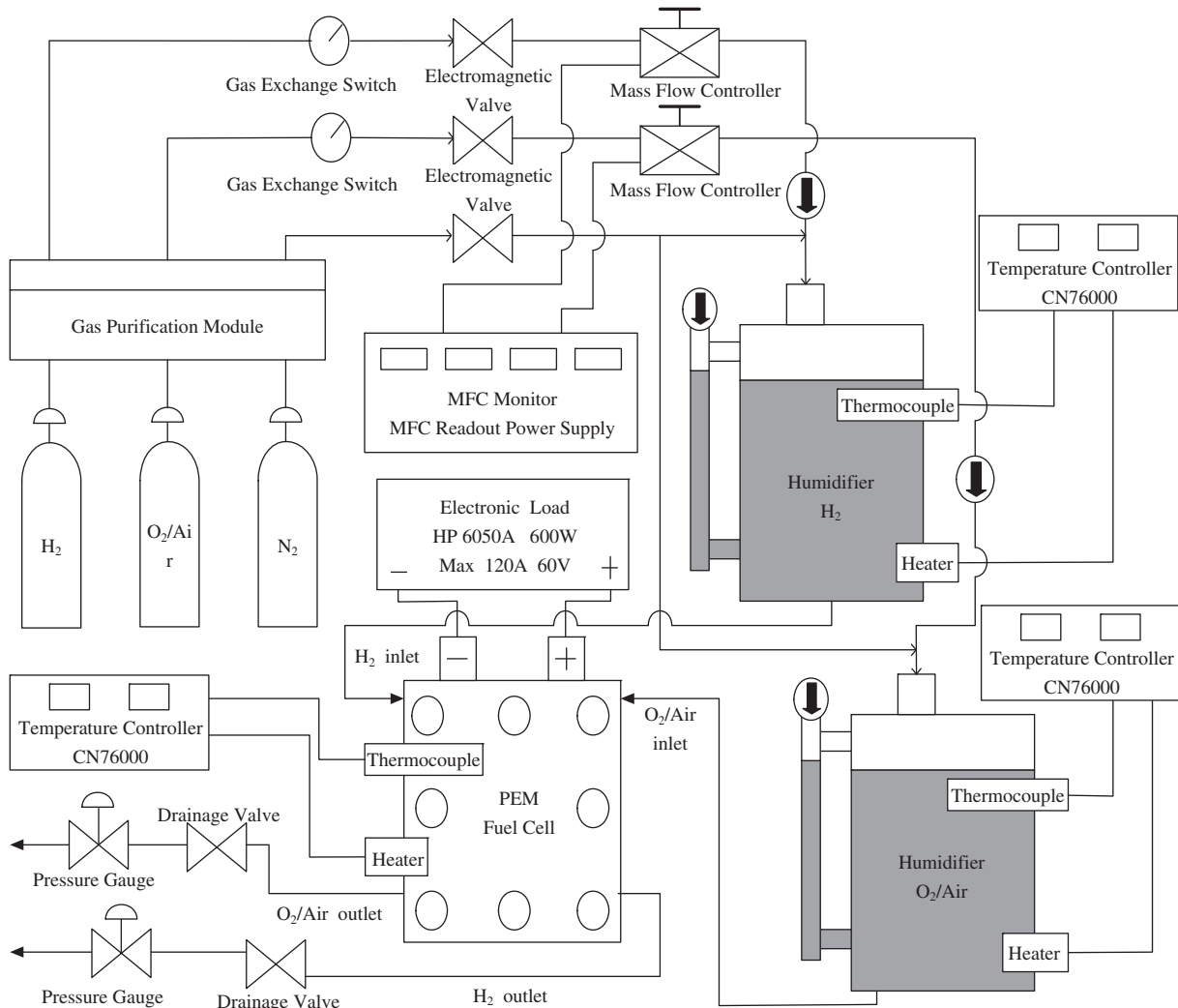


Fig. 1 – Schematic diagram of the experimental setup.

Table 1 – Experimental parameters for oxygen cathode gas and a volume flow rate of 8.33 cm³/s.

Chloride concentration	Operating current (A)	\dot{m}_c (g/hr)	\dot{m}_g (g/hr)	Concentration (ppm)	Average concentration (ppm)
0.1 M NaCl	20	13.4	42.87	1393	1409
	35	13.7	42.87	1417	
	50	13.7	42.87	1417	
1 M NaCl	20	10.8	42.87	11 353	11 323
	35	11.2	42.87	11 686	
	50	10.3	42.87	10 929	
2 M NaCl	20	10.1	42.87	20 770	20 546
	35	10.1	42.87	20 770	
	50	9.7	42.87	20 099	
0.1 M CaCl ₂	20	13.3	42.87	2619	2634
	35	13.5	42.87	2649	
	50	13.4	42.87	2634	
0.5 M CaCl ₂	20	11.1	42.87	11 013	10 960
	35	11.2	42.87	11 091	
	50	10.8	42.87	10 775	

presented in Table 1, and hereafter all the concentration mentioned refer to average concentration.

3. Results and discussion

In the present study, both effects of chloride salt concentration and the type of chloride salt on the PEM fuel cell performance are under investigation. The fuel cell is maintained at the temperature of 65 °C. The anode fuel gas was hydrogen, with the volume flow rate of 8.33 cm³/s and humidification temperature of 80 °C. The cathode gas was oxygen/air mixed with various chlorides concentrations (shown in Table 1), with the volume flow rate of 8.33 cm³/s and no humidification.

Fig. 2 shows the effect of NaCl concentrations on the potential of PEM fuel cell with different current densities. It is observed that the potential decreases as time increases during the 5 h testing. It is noticed that the concentration of NaCl does not show significant influence on the potential, especially for lower current densities. Nevertheless, it does show that the

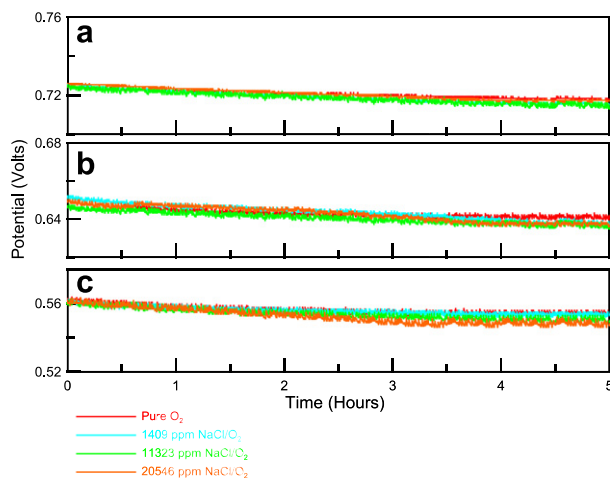


Fig. 2 – Effects of NaCl concentration on the cell performance of PEMFC as a function of time in 5 h with various current densities (a) 0.8 A/cm²; (b) 1.4 A/cm²; (c) 2 A/cm².

potential decreases as the concentration of NaCl increases. Effect of CaCl₂ concentrations on the PEM fuel cell performance with different current densities is presented in Fig. 3. The same trends as Fig. 2 can be observed in Fig. 3. However, significant effect of CaCl₂ concentrations on the potential of PEM fuel cell is noticed in lower operation current densities.

A second test was carried out to evaluate the effect of NaCl and CaCl₂ concentration on the PEMFC performance in a pattern of continuous operation. The fuel cell was operated for 12 h with current density of 1 A/cm² and then stop for 12 h daily. The anode fuel gas was hydrogen with a volume flow rate of 8.33 cm³/s and humidification temperature of 80 °C; the cathode gas was air mixed with chloride salt with a volume flow rate of 16.67 cm³/s and the humidification temperature at room temperature. The fuel cell operating temperature was 65 °C. A control test using pure air was performed prior to the experiment. Fig. 4 shows the voltage changes with operation time for operation time up to 108 h using pure air as the cathode gas. A suitable linear equation relating voltage to operation time was obtained according to the experimental data:

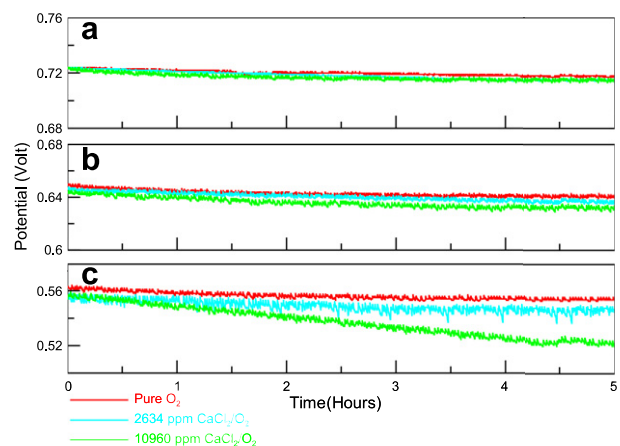


Fig. 3 – Effects of CaCl₂ concentration on the cell performance of PEMFC as a function of time in 5 h with various current densities (a) 0.8 A/cm²; (b) 1.4 A/cm²; (c) 2 A/cm².

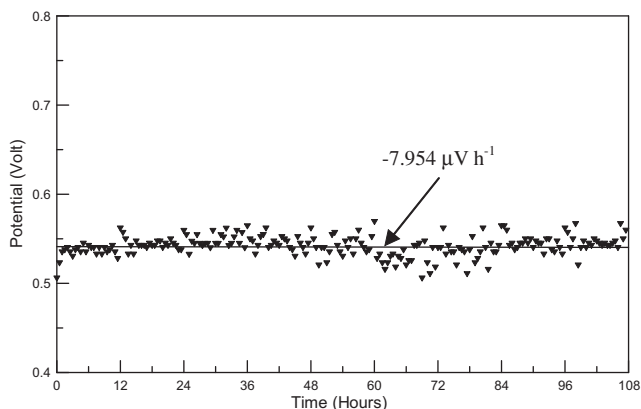


Fig. 4 – Electric potential versus total time using pure air as the cathode gas with current density of 1 A/cm^2 and cell operation for 12 h then stop for 12 h daily.

$$V = -7.954 \times 10^{-6}t + 0.541 \quad (2)$$

Where V is voltage and t is the operation time. The decay rate was found to be $7.954 \mu\text{V h}^{-1}$, a very low rate. After 108 h, the cell performance was stable. Extrapolating formula (2), we find that the voltage will reach zero after $\sim 68\,000$ h.

Fig. 5 presents the same test as Fig. 4, while the cathode gas was 10,043 ppm NaCl in the air. In Fig. 5, another linear relationship between voltage and operation time is established:

$$V = -1.082 \times 10^{-3}t + 0.601 \quad (3)$$

At $t = 0$, $V_0 = 0.601 \text{ V}$ and the voltage is stable for about the first 20 h. After 20 h of operation, the voltage began to decrease linearly with time. After 108 h of operation, the voltage becomes 0.49 V, corresponding to a voltage drop of approximately 0.111 V. The decay rate was calculated to be 1.082 mV h^{-1} using linear regression. This indicates that the NaCl/Air gas mixture significantly affects the cell performance. It can be estimated that the lifetime of a fuel cell using the NaCl/air mixture as the cathode fuel gas, is about 555 h (i.e. the time it takes V to equal zero). Furthermore, 9391 ppm CaCl_2 in air was used as the cathode gas for the same test, the voltage–time relationship variation is

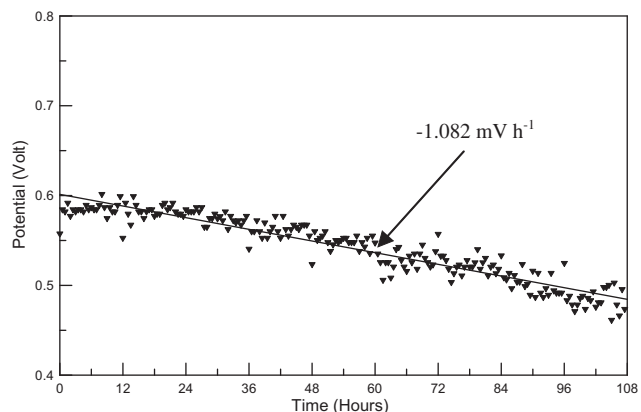


Fig. 5 – Electric potential versus total time using 10043 ppm NaCl/air as the cathode gas with current density of 1 A/cm^2 and cell operation for 12 h then stop for 12 h daily.

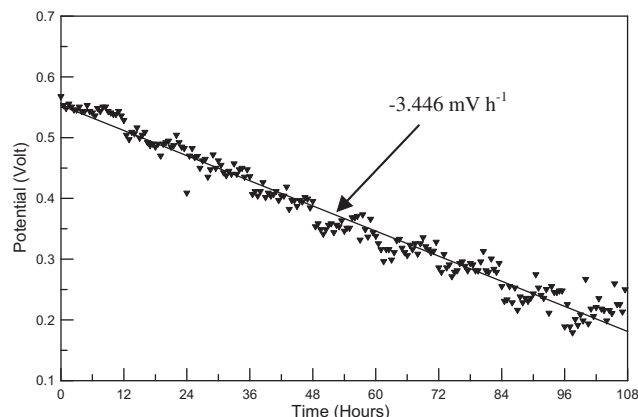


Fig. 6 – Electric potential versus total time using 9391 ppm CaCl_2 /air as the cathode gas with current density of 1 A/cm^2 and cell operation for 12 h then stop for 12 h daily.

shown in Fig. 6. The linear equation relating voltage to operation time is obtained:

$$V = -3.446 \times 10^{-3}t + 0.553 \quad (4)$$

The rate of decay is calculated as 3.446 mV h^{-1} , suggesting CaCl_2 in air will affect the cell performance to a far greater extent than NaCl in air does. In fact, by extrapolating the linear equation the lifetime of the fuel cell was estimated to be about 160 h, a significant reduction compared to that using NaCl/Air gas.

After all the experiments were completed, cupric oxide was found on the cathode bipolar and collector plates due to the chloride salts. Therefore, the gaseous diffusion layer, (also carbon cloth) was analyzed and screened using SEM. Fig. 7 shows the configuration of the carbon cloth with and without chloride salt in the cathode fuel gas. It is observed that the carbon fibers in the carbon cloth adhered with certain material, and as such an EDS analysis was conducted to understand the adsorption interaction. Results from EDS analysis reveal that most of the cloth is consisted of carbon (C), followed by fluorine (F), which was likely due to the manufacture method of carbon fiber inside the carbon cloth. The experimental data show that the cell performance is affected by varying the concentration of chloride salt. The activation energy of the cathode catalyst layer at the interface between the platinum catalyst and the macromolecular polymer bodies (membrane phase) is increased by the foreign ions as they allow the ion and water molecular structure to change. The macromolecular structure will influence the transfer of charge on the platinum surface. An increased overpotential is therefore required, which will also affect the performance.

The polarization curves can be used to establish the main factors and the extent of cell performance that is affected. Fig. 8 presents the total operation time of the polarization curve using 10043 ppm NaCl/Air in the cathode. It can be seen that an increase in operating time at low densities does not have a significant impact on cell performance. However, it does show significant influence for higher current densities. The decrease in cell performance may be explained by the fact that contact resistance between the cathode bipolar plate and collector plate

increases. The polarization curves using 9391 ppm CaCl_2/air in the cathode for several operation periods are shown in Fig. 9. It depicts that the increase of operation period results in a significant drop in voltage for lower current densities. This indicates that the activation energy of the cathode catalyst layer is affected by CaCl_2 . Comparing Figs. 8 and 9, it is clearly observed that the effect of CaCl_2 concentration on PEM fuel cell

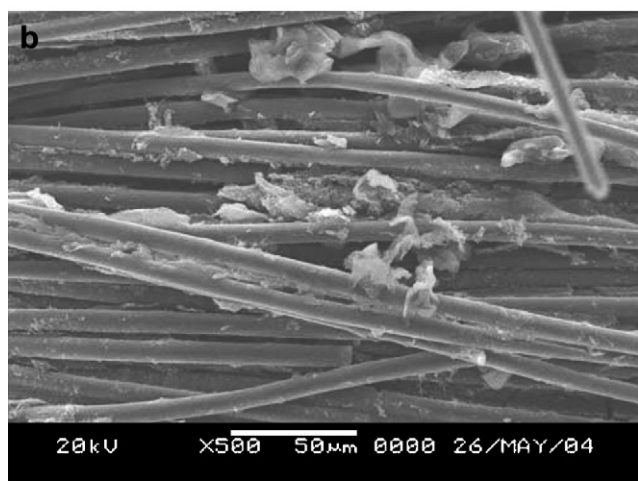
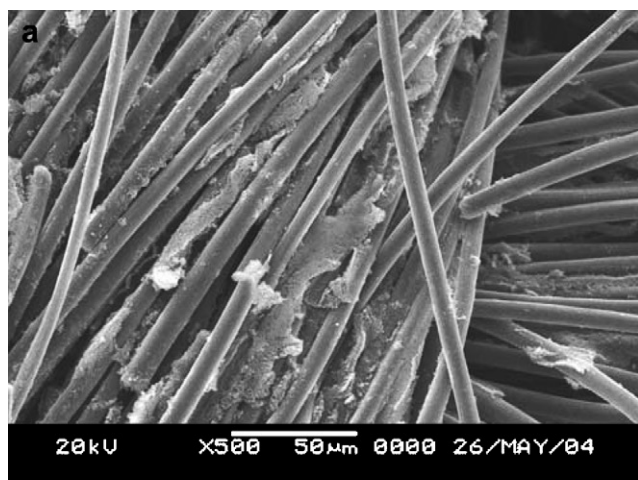


Fig. 7 – The structure of the gas diffusion layer observed using SEM (a) without chloride (b) with NaCl and (c) with CaCl_2 .

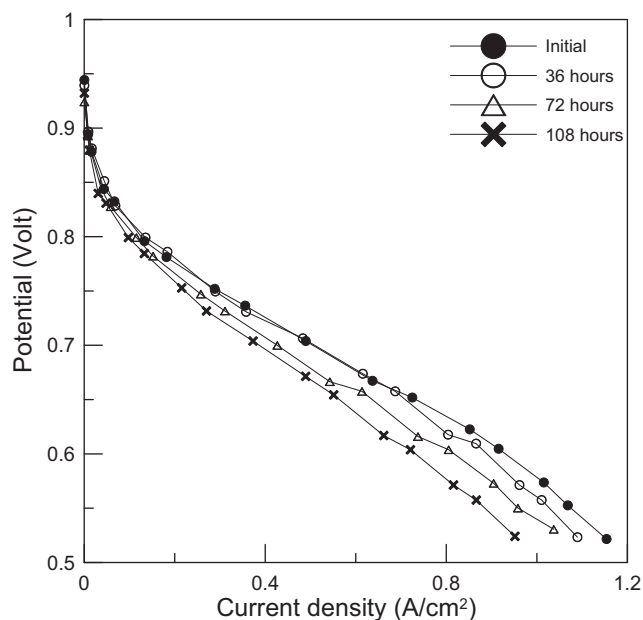


Fig. 8 – Polarization curves for various operating times using 10043 ppm NaCl/Air as the cathode gas.

performance is more dramatic than that of NaCl . The calcium ion has a valency of 2+, whereas the sodium ion has a valency of 1+, so the bonding force of a calcium ion to the macromolecular structure is stronger than that of a sodium ion. Stronger bonding forces create greater polarization. While calcium creates a greater polarization, the contact resistance is not affected significantly. From the 72 and 108 h polarization curves, it should be noted that the generation of limiting current corresponds to greater contamination, agreeing with Okada's [21] findings that calcium ions have a greater effect on the cell performance than sodium ions do.

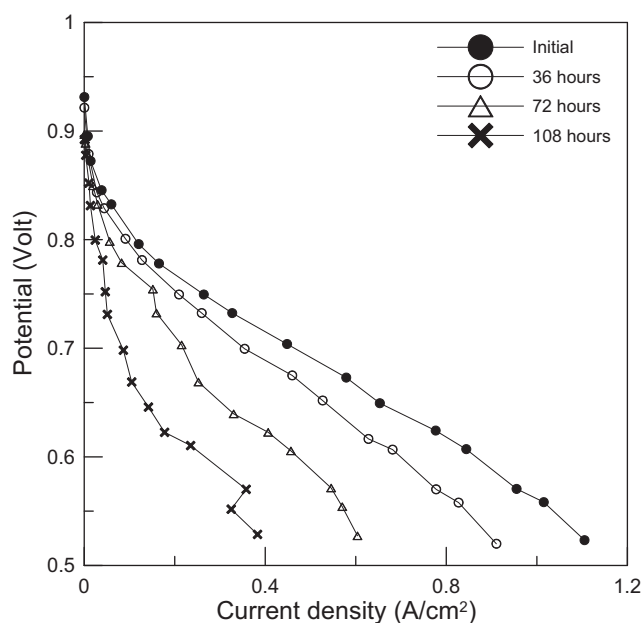


Fig. 9 – Polarization curves for various operating times using 9391 ppm CaCl_2/Air as the cathode gas.

4. Conclusion

The effects of chloride ions on the PEM fuel cell performance have been investigated in detail. Both sodium chloride and calcium chloride are used in the experiment. Effect of chloride concentration on the PEM fuel cell performance is also studied for both short and long operation times. Summaries are given below:

1. For a relatively short operation time, the increase in NaCl concentrations in the cathode does not show significant influence on the potential of the fuel cell. Furthermore, variations in current density do not show significant influence on the potential of fuel cell.
2. The increasing in CaCl₂ concentrations in the cathode depicts insignificant influence on the cell potential for a relatively short operation time. However, as the current density increases, the influence of CaCl₂ concentration on cell performance becomes significant. A dramatic reduction in cell performance is resulted with larger current densities and chloride concentration.
3. In the presence of chloride ion, PEMFC performance declines for a relatively long operation time. The declination rate is 1.082 mV h⁻¹ for NaCl/air fuel gas mixture, and 3.446 mV h⁻¹ for CaCl₂/air fuel gas mixture, respectively.
4. For a relatively long operation time, the effect of CaCl₂ on cell performance is more severe than that of NaCl. In addition, higher concentration of CaCl₂ was found to increase the decay rate of performance.

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