

Determination of Low-temperature Electrochemical Properties of Selected Cation-exchange Membranes for Cathodic Protection Analysis

Moonyoung Ko, Byeongmin Kwon, Byungpyo Hong, and Hongsik Byun[†]

Department Chemical System Engineering, Keimyung University, Daegu, Korea
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Abstract: The electrochemical properties of Nafion type membranes as a function of temperature to examine the key factors affecting the cathodic protection process at low temperatures was investigated in this study. Variable temperature experiments for AC impedance, DC resistance were conducted. The resistances of 3 Nafion membranes (N 324, N 450, N MAC) were measured in 30% KOH (aq) for a range of temperatures between -30°C and room temperature. Membrane resistance increases exponentially with decreasing temperature. This behaviour is most significant at operational temperatures below 0°C. These membranes are stable under the low temperature and caustic conditions of the heat exchange system, but they place a much higher restriction on the cathodic protection of the stainless heat exchange stack. N 450 has the lowest AC impedance and DC resistance at temperatures below 0°C and consequently is most suitable membrane of the three, for low temperature applications.

Keywords: Nafion membrane, cathodic protection, heat exchange unit, low temperature

1. Introduction

A cryogenic operation utilizes a bath of 30% CaCl₂ (aq) at approximately -30°C. Low temperatures are achieved using a stainless steel heat exchanger [1-3]. Stainless steel plates stacked to form a network of channels that support the flow of a liquid cooling agent (compressed ammonia) comprise the heat exchange unit that is fully immersed in the brine [4,5]. Oxidation results in the corrosion of the stainless steel plates. Cathodic protection is second only to the use of protective coatings as a means of corrosion control [6]. Cathodic protection is employed to preserve the life of the stack. An electrolysis is applied to the brine such that cathodic reactions at the stainless steel produce reducing conditions that retard the oxidation process. In CaCl₂ (aq) the anodic reactions involve the evolution of Cl₂ (g) as a toxic gas [7]. As a preventative

measure, the anode is not placed directly into the brine, but in a 30% KOH (aq) solution that is separated from the CaCl₂ (aq) by a cation-exchange membrane. The system is still capable of carrying sufficient current to protect the stainless steel cathode [8,9].

The heat exchange system described above has been implemented for industrial applications using a Nafion membrane [10]. The purpose of this study is to investigate the electrochemical properties of Nafion type membranes as a function of temperature to examine the key factors affecting the cathodic protection process at low temperatures.

2. Experimental

2.1. Reagents and Membranes

All solutions used for experimental analysis were prepared from reagent grade chemicals. To obtain KOH (aq) in a 30% mass ratio, 110 g of solid KOH pellets were dissolved in 250 mL of deionized water.

[†] Author for all correspondences
(e-mail : hsbyun@kmu.ac.kr)

An N₂ (g) purge was used to prevent the absorption of CO₂ (g) prior to use. To obtain CaCl₂ (aq) in a 30% mass ratio, 146 g of solid CaCl₂ · 2H₂O was dissolved in 250 mL of deionized water. The pH of CaCl₂ (aq) was measured using an Orion model 720A pH meter and was adjusted to a value of 9.0 at room temperature by drop wise addition of 8.0 M NaOH (aq). The brine was filtered by gravity prior to use to remove precipitates such as Ca(OH)₂ (s).

Three Nafion membranes (N 324, N 450 and one unknown labeled N MAC) manufactured by DuPont Company and a Flemion CMF membrane obtained from Asahi Glass Company were used for electrochemical analysis. Each membrane was conditioned over a 48 h period by soaking in alternate solutions of 1.0 M NaOH (aq) and 1.0 M HCl (aq). The membranes were soaked in each solution five times and rinsed with deionized water prior to each soaking. The membranes were stored in 1.0 M HCl. Before using, each membrane was cut to the appropriate size and placed in deionized water.

2.2. AC Impedance Measurements

The electrochemical cell was used to measure the AC impedance of each membrane in 30% KOH (aq). The cell was assembled with the membrane in place and both compartments were filled slowly and simultaneously with 30% KOH (aq) using two 10.0 mL syringes to minimize the build up of pressure on either side of the membrane. The inlet and outlet tubes were plugged with glass stoppers and the cell was agitated to remove any air trapped in each compartment. Air was released by removing the stoppers and filling the excess tubing with KOH before replacing the stoppers. The electrodes of the cell were connected to an electrolytic conductivity bridge (Leeds & Northrup model 4959) which used a wheatstone bridge current to measure resistance. A schematic of the bridge is shown in Fig. 1, where R_x is the resistance of the electrochemical cell measured, and R₁, R₂, and R₃ are independent resistances. R₁ and R₂ were adjusted to a 10:1 or 100:1 ratio and R₃ was adjusted in small increments to

balance the potentials of points B and D. When the bridge was balanced, the galvanometer showed a reading of zero and R₁ and R₂ were equal; like-wise, R₃ and R₄ were equal. The resistance of the cell (R₄) was obtained from the relationship $R_x/R_1 = R_3/R_2$ [1]. Approximately 1000 Hz of AC current was applied and the resistance of the cell was measured at room temperature. The cell was placed in methanol previously cooled to about -60°C. A Flexi-cool cold finger was used to stabilize the temperature between -35 and -32°C. The cold finger was removed and the cell insulated with glass wool as the temperature of the cell gradually increased. The resistance of the cell was measured for a range of temperatures between -30°C and room temperature (~24°C). The procedure was repeated for each membrane and then without a membrane to determine the resistance of the cell.

2.3. DC Resistance Measurements using Electrochemical Cell

The electrochemical cell was used to conduct variable and constant temperature electrolysis experiments. The cell was assembled with the membrane in place and both compartments were filled slowly and simultaneously using two 10.0 mL syringes. The cathode compartment was filled with 30% CaCl₂ (aq) and the anode compartment was filled 30% KOH (aq). The cell was sealed and air was released as discussed above. To vent any H₂ (g) and O₂ (g) gases that evolved at the cathode and anode respectively, the outlet stoppers were replaced with an extended tube open to the atmosphere. The electrodes of the cell were connected to a rectifier. Two multimeters (Hewlett Packard model 3478A) were also connected, one in series to measure the applied current and the other in parallel measure to applied potential across the membrane as shown in figure API-4. A constant DC current of less than 5.0 mA was applied and the resulting voltage was measured. The electrochemical cell was placed in methanol previously cooled to about -60°C. The cell was stabilized at a temperature between -35 and -32°C. The temperature of the cell was gradually

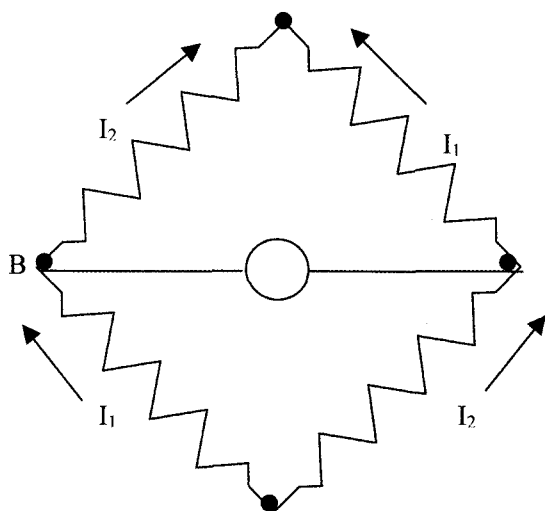


Fig. 1. Schematic diagram of wheatstone bridge.

increased, and the cell potential was measured for a range of temperatures between -30°C and room temperature.

For constant temperature analysis the electrochemical cell was assembled with the membrane in place. Inlet tubes were extended to pass through a peristaltic pump to the base of a 250 mL graduated cylinder used as a reservoir for each of the catholyte and anolyte solutions. Outlet tubes were extended to the mouth of each graduated cylinder. Each reservoir was filled with 150 mL of the appropriate solution. The cathode and anode chambers were slowly filled with 30% CaCl_2 (aq) and 30% KOH (aq) respectively. The cell was agitated to remove trapped air and the solutions slowly circulated by the pump. A DC rectifier and two multimeters (Hewlett Packard model 3478A) were connected as described above and a constant direct current of approximately 5.0 mA was applied. The cell potential was measured over a 56 h period. The pump and rectifier were disconnected for two days; the current was reapplied to the cell and the cell potential measured over a 24 h period.

3. Result and Discussion

3.1. Analysis of Membrane Resistance

The resistances of three Nafion membranes were

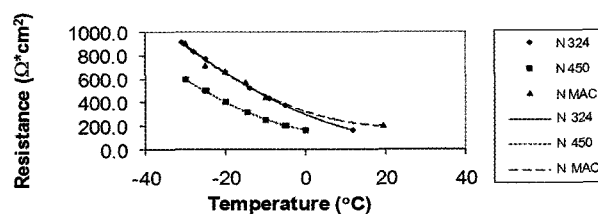


Fig. 2. Membrane resistance in 30% KOH (aq) as a function of temperature.

measured in a caustic environment of 30% KOH (aq). The resistance of each membrane was also measured for a range of temperatures between -30 and 25°C to observe how the frigid conditions of the application affect membrane resistance. An electrolytic conductivity bridge with an output of 1000 Hz of AC current was used to measure membrane resistance without polarization of the cell. Resistance was measured within an error of approximately 3, which is an estimation based on the comparison of the measured membrane resistance in 0.6 M KCl (aq) to values found in the literature. The major source of error was due to the resolution of the instrument.

Membrane resistance is plotted as a function of temperature for N 324, N 450 and N MAC in Fig. 2. The relationships obtained for each membrane correspond to second order polynomial functions. Extrapolation of these functions indicate a room temperature resistance of 90.0, 148.8 and 198.0 Ω/cm^2 for each membrane in their respective order. The resistance of the membranes in 0.6 M KCl (aq) at room temperature is in the range of 40 to 50 Ω/cm^2 . This is consistent with analysis on Chlor-Alkali membranes by Hine *et al.* [2] that show that at higher electrolyte concentrations, membrane resistance increases. The resistance of 30% KOH (aq) was also measured without a membrane and was found to be negligible over a similar range of temperatures.

Membrane resistance increases exponentially as temperature decreases. This trend is most significant as the temperature drops below 0°C . This is important to consider for low temperature applications as the one presented because an increase in resistance increases the voltage across the membrane obtained for a con-

stant current electrolysis. Analysis of membrane resistance indicate that N 450 is most likely the best candidate for such an application because it demonstrated the lowest resistance of three membranes. At -30°C , N 450 had a resistance of $\sim 600 \Omega/\text{cm}^2$ compared to $\sim 1000 \Omega/\text{cm}^2$ for N 324 and N MAC. The Nafion membranes tested are stable under the low temperature and caustic conditions of the heat exchange unit, but their resistance dramatically increases as temperatures are lowered below 0°C .

3.2. Analysis of DC Resistance using Electrochemical Cell

The electrochemical cell was also used to duplicate the conditions of the actual heat exchange system and obtain values for DC cell resistance. The cathode chamber was filled with 30% CaCl_2 (aq), and the anode chamber was filled with 30% KOH (aq); the solutions were separated by a membrane. The cell was polarized by the application of a constant DC current and the resulting voltage across the membrane was measured for a range of temperatures between -30°C and room temperature. The resistance of the cell was calculated using Ohm's Law and is plotted as a function of temperature in Fig. 3.

The resistance versus temperature relationships for electrolysis using the Nafion membranes are linear, inverse functions. The general trend of increasing resistance with decreasing temperature is consistent with the AC impedance measurements in 30% KOH (aq). Membrane resistance is a major contributing factor to cell resistance. One significant variation, however, is that the DC resistance of the electrochemical cell is an order of magnitude greater than the AC impedance of the corresponding membrane in 30% KOH (aq). This is most likely due to the polarization of the cell by the applied DC current and the difference in junction potentials at the membrane solution interfaces.

The trend of increasing DC resistance for the Nafion membranes in the order of N 450, N 324, and N MAC reflects the trend observed for AC impedance measurements. This illustrates that the AC impedance of the

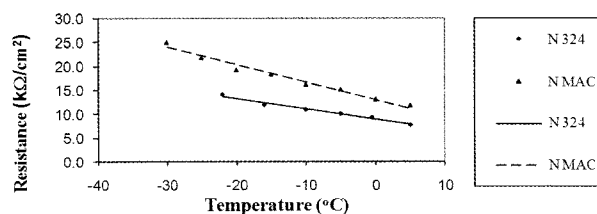


Fig. 3. Electrochemical cell: resistance during constant current electrolysis as a function of temperature (Catholyte - 30% CaCl_2 (aq); Anolyte - 30% KOH (aq)).

membrane makes an important contribution to cell resistance. A comparison of the DC resistance versus temperature curves shown in Fig. 3 demonstrates that N 450, having the lowest DC resistance is the most suitable membrane for low temperature applications.

A fourth membrane, Flemion CMF was obtained from the Asahi Glass Company, and was tested under the same conditions as the Nafion membranes to measure the DC resistance of the electrochemical cell. The results showed that the Flemion membrane behaved similarly to N 324 at temperatures above -15°C . However at temperatures below -15°C the DC resistance increases at a much faster rate. This behavior may be due to a high water content in the Flemion membrane. Consequently, Flemion CMF is not suitable for the low temperature application presented.

The DC resistance of the electrochemical cell with N MAC was also conducted at a constant temperature to determine if the resistance varied over time. A peristaltic pump was used to circulate the catholyte and anolyte solutions from their respective reservoirs through the appropriate chambers to observe the formation of precipitate and evolution of gases. The electrolysis was run for 56 h as shown in the resistance versus time plot of Fig. 4. There was no precipitate formed over this period, however significant amounts of gases were evolved at each electrode surface as expected. The initial increase in resistance was due to the building up of H_2 (g) and O_2 (g) gases in the cathode and anode chambers, respectively, which was observed extending through the tubing that connected each chamber to their respective reservoirs. The tubes were shortened and elevated to vent the gases. The resistance stabilized

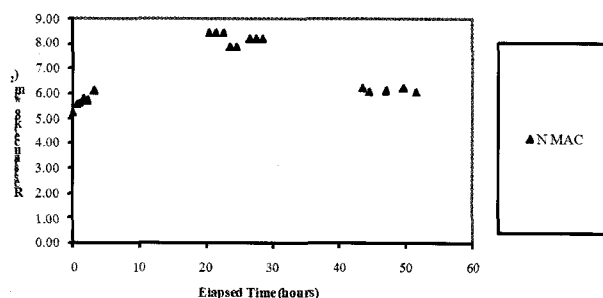


Fig. 4. Electrochemical cell: resistance during constant current electrolysis as a function of time (Catholyte - 30% CaCl_2 (aq); Anolyte - 30% KOH (aq)).

at its initial value as shown in the latter portion of the graph. The evolution of such large volumes of gas is due a higher applied current compared to the previous electrolysis experiments. The applied current and circulation of the solutions were halted and the cell left stagnant. After about 60 h the current and circulation were reapplied. There was no evidence for the formation of precipitate due to diffusion across the membrane and after some fluctuation in the resistance, it again stabilized at its initial value. Cell resistance does not vary over time provided the electrolyte compositions remain unchanged.

4. Conclusions

The AC impedance of Nafion type membranes in caustic conditions increases exponentially as temperature decreases. The DC resistance measurements during an electrolysis of 30% CaCl_2 catholyte and 30% KOH (aq) anolyte are consistent with the low temperature behavior of the membranes. It is evident that membrane resistance is a key contributing factor to cell resistance. The polarization due to the applied DC current and

varying junction potentials of the electrolysis increase the cell resistance by more than an order of magnitude compared to the AC impedance in 30% KOH (aq). Among the membranes tested, N 450 exhibited the lowest AC impedance in 30% KOH (aq) and the lowest DC resistance in the electrochemical cell over the range of temperatures tested. Consequently N 450 is best suited for the heat exchange application of the membranes tested.

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