DESIGN AND DEVELOPMENT OF A TRITIUM-COMPATIBLE ELECTROLYZER

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Abstract

Proton exchange membrane (PEM) electrolysis is the process of cracking water into hydrogen and oxygen using a PEM electrolyzer. The PEM electrolyzer consists of a PEM, bipolar plates, insulators and end plates. In this study, a PEM electrolyzer is designed and developed for its application in the nuclear industry for tritium removal using the catalytic exchange electrolysis process. Tyne, in collaboration with CNL, has designed a tritium-compatible PEM electrolyzer with specially designed 20.3 cm active diameter electrodes which can withstand tritium better than ordinary Nafion® and with enhanced safety features. Electrochemical and hydrodynamic models are used in the design stage to determine various design parameters. A prototype with 1 Nm^3/hr design capacity is built and tested with Nafion® N-117. The polarization curve is experimentally determined at ambient temperature and pressure. The results showed that the required single cell potential is 3 V at 1.0 A/cm^2. As a second phase of the electrolyzer development, tritium-compatible membrane, specifically developed for tritium application at CNL, was soaked in tritiated water for 3 months and then detritiated for several months. The detritiated membrane has been then tested in a smaller unit. Compared to the soaked Nafion® membranes the specially designed and developed tritium-compatible membranes perform better and thus are to be used in final electrolyzer assembly.

1. Introduction

PEM electrolyzers can produce hydrogen at high pressure and high hydrogen purity. Advantages over alkaline electrolyzer and other hydrogen production technologies include fast response time and the ability to adapt to changes in the power supply. One of the most advantageous factors of the PEM based electrolyzer is its caustic-free environment. The electrolyzer has four main components, namely: Membrane Electrode Assembly (MEA), bipolar plates, sealing components and end plates. The MEA which is the heart of the electrolyzer, is composed of three components, namely: catalyst, membrane and gas diffusion layer. Figure 1 shows a typical representation of a PEM cell.

Tritiated water at the anode is oxidized to form oxygen, protons and tritium ions. The ions diffuse through the membrane (mass transfer) and are reduced to tritium gas. The reactions at the anode and cathode are given as

$$HTO \rightarrow O_2 + H^+ + T^+ + 2e^- \quad (1)$$

$$H^+ + T^+ + 2e^- \rightarrow HT \quad (2)$$

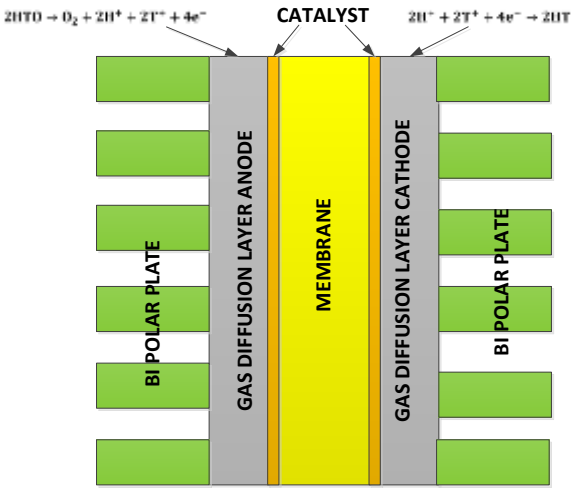

Figure 1 PEM Cell

Numerous different researchers have discussed different aspects of the PEM electrolyzer [1-3]. However, very few studies have been performed on design and development of tritium-compatible PEM electrolysis. Soreefan et al. have studied tritium enrichment parameters of commercially available PEM electrolyzers [4]. However, Nafion® membranes in commercially available electrolyzers are not really suitable for long term usage, especially at higher concentrations of tritium [5]. Boniface et al. [6] have laid down some of the criteria for the tritium-compatible electrolyzer in the Combined Electrolysis Catalytic Exchange (CECE) process. The objective of this study, is to present the design and test data of a tritium-compatible electrolyzer with Nafion® N-117 membranes and to compare the specially designed tritium-compatible membrane with Nafion membranes.

2. Modelling

Electrochemical, hydrodynamic and mechanical models were developed to assist the design of the electrolyzer. This includes finding the pressure drop in the electrolyzer, an electrochemical model to find the minimum required voltage, deflection calculations in order to find the deflection in the end plate. A brief description of the electrochemical model and the pressure drop calculation is given below.

2.1 Electrochemical Model

An electrochemical model is used to determine the required potential of the reaction. In water electrolysis, the net required potential (E_{Total}) is approximately the sum of equilibrium potential (E_{Nernst}), ohmic loss across the membrane (E_{Ohm}) and activation losses on anode (E_A) and cathode (E_C). This is given as:

$$E_{Totol} = E_{Nernst} + E_{Ohm} + E_A + E_C \tag{3}$$

The water decomposition voltage at which the thermal efficiency is 100 % (i.e. also known as thermoneutral voltage) can be computed as

$$E_{Nernst} = \frac{\Delta H}{nF} + \frac{\Delta S}{nF}(T_{cell} - T_{ref}) + \frac{RT_{cell}}{nF}\left(\ln\left(\frac{P_{H_2}}{101.325}\right) + \left(\frac{1}{2}\right)\ln\left(\frac{P_{O_2}}{101.325}\right)\right) \tag{4}$$

Where ΔH and ΔS represents the change in enthalpy and entropy of reaction.

The voltage loss across the membrane can be calculated as

$$E_{Ohm} = R_{Mem} I_D A \tag{5}$$

Where the R_{Mem} represents the resistance across the Nafion membrane and it is a function of cell temperature, current density and water content, I_D represents the operating current density and A is the total active area.

The activation losses across the anode and the cathode are computed as [7]

$$E_A = \frac{RT_{cell}}{\alpha_a nF} \ln\left(\frac{\frac{I_D}{I_{EA}}}{1-\frac{I_D}{I_L}}\right) \tag{6}$$

$$E_C = \frac{RT_{cell}}{\alpha_c nF} \ln\left(\frac{\frac{I_D}{I_{EC}}}{1-\frac{I_D}{I_L}}\right) \tag{7}$$

Where α_a and α_c represent the activity coefficient across anode and cathode respectively, I_{EC} and I_{EA} represent the exchange current density and I_L represent the limiting current density. Usually heat is generated in the electrolyzer. The net heat generated in each cell of the electrolyzer can be computed as

$$\dot{Q}_{Heat/cell} = I_D A(E_{Ohm} + E_A + E_C) \tag{8}$$

The number of cells required to produce any desired flow rate of hydrogen can be evaluated as

$$N_{cell} = \frac{\dot{V}_{Required}}{\frac{3.6 I_D A}{nF}} \tag{9}$$

Where $\dot{V}_{Required}$ (m^3/hr) is the design flow rate of hydrogen that needs to be produced, n represents the number of electrons taking part in reaction for a unit molecule of water ($n = 2$) and F is the faraday constant (96485 C/mol).

2.2 Hydrodynamics and Water Management in Electrolyzer

There are two different approaches to feed the water to the electrolyzer.

- Single Feed
- Dual Feed

In single feed system, water is fed only to the anode and it is usually adopted when the operating current density is small (typically less than 0.7 A/cm^2) [8]. In the dual feed system, water is fed to both the anode and the cathode, however only water at the anode is electrolyzed. Water at the cathode is used for cooling and to remove excess heat generated in the electrolyzer. As Tyne's tritium-compatible electrolyzer is

designed to operate at 1.0 A/cm^2 with a large active area, the dual feed system is adopted. Figure 2 shows the water management approach in Tyne electrolyzer.

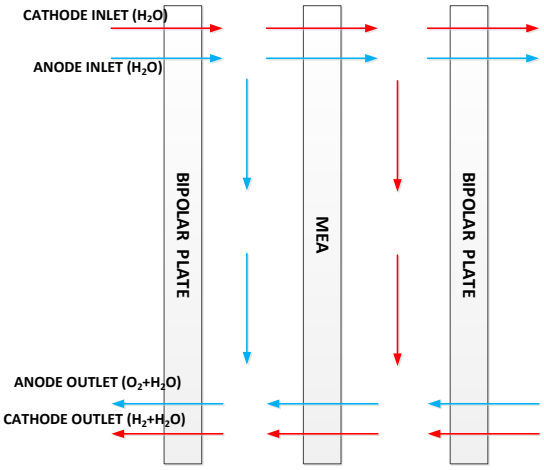

Figure 2 Water management approach used in Tyne electrolyzer

There are number of different flow patterns reported in literature. Each with its own strengths and weaknesses. The spiral flow pattern is selected for Tyne electrolyzer. This pattern is shown in Figure 3. Regardless of the flow pattern chosen, there is usually pressure drop across the plates and across the system.

The pressure drop across the electrolyzer is divided into three sections

- Pressure drop in the inlet water feed line (ΔP_{in})
- Pressure drop in the bi polar plate (ΔP_{CH})
- Pressure drop in the outlet line (ΔP_{out})

As Tyne electrolyzer is using dual feed water management system, so there are two inlet channels. The pressure drop in each of the inlet can be calculated using Hagen–Poiseuille equation

$$\Delta P_{in} = \frac{8\mu LQ}{\pi r^4} \tag{10}$$

Where μ (Pa.s) represents the viscosity of water, Q (m^3/s) represents the volumetric flow rate, L (m) represents the length of the electrolyzer and r (m) represents the radius of the circular channel.

Pressure drop in the spiral pattern across anode and cathode is computed using the correlation reported by Ali & Seshadri [7].

$$Eu.G = 49Re^{-0.67} \tag{11}$$

Where Eu represents the Euler number and G is the geometrical group number. They can be computed as represents as

$$G = \frac{p_t\sqrt{D_S}}{R_{max}^{\frac{3}{4}}(R_{max}-R_{min})^{\frac{3}{4}}} \tag{12}$$

$$Eu = \frac{\Delta P}{2\rho V^2} \tag{13}$$

Where ΔP (Pa) represents the pressure drop in the spiral, ρ (kg/m^3) represents the density of water and V represents the velocity (m/s), D_S is the depth of the channel in the spiral flow, p_t is the pitch, R_{max} is the maximum diameter and R_{min} is the minimum diameter. Re represents the Reynolds number.
The flow in the output line is also two phase flow and pressure drop in the output line can be computed as

$$\Delta P_{out} = 4f\left(\frac{Re_{eq}^2\mu_l}{2\rho_l}\right)\left(\frac{L}{D_{ch}^3}\right) \tag{14}$$

Where f represents the friction factor and Re_{eq} represents the Reynolds number for two phase flow. Bubble flow regime is assumed for calculation.

As the flow across both inlet channels is assumed the same, so the net pressure drop across the electrolyzer can be estimated as

$$\Delta P_{Ele} = 2\Delta P_{In} + \Delta P_{out,Anode} + \Delta P_{out,Cathode} + \Delta P_{CH,Anode} + \Delta P_{CH,Cathode} \tag{15}$$

Figure 3 Spiral flow pattern

2.3 Deflection Calculations

In an electrolysis process in a PEM cell, it is essential for the cell to have low-resistance electrical contacts between its components. Poor electrical contact would increase cell resistance. The central deflection in the end plate needs to be minimized to ensure uniform electrical contact between the components. The central deflection for uniformly-distributed pressure on the simply supported circular plate can be computed as:

$$y_c = -\frac{Pr^4(5+\nu)}{64\beta(1+\nu)} \tag{16}$$

Where P represents the design pressure, r presents the radius of the plate, ν represents the Poisson ratio and β represents the plate constant. The plate constant can be computed as:

$$\beta = \frac{Et^3}{12(1-\nu^2)} \tag{17}$$

Where t represents the thickness, E represents the Young's modulus.

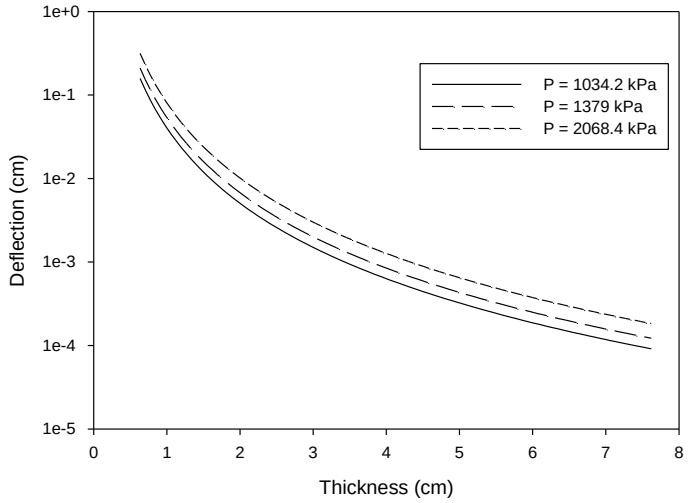

Figure 4 Deflection due to the fluid pressure in the end plate

Figure 4 shows the deflection of the end plate when subjected to three different pressures (calculated using equation 16 and 17). Stainless steel type 316 is used as a material. The graph indicates that at 0.5 inch thickness, the deflection is very high. However it decreases with increase in thickness. Based on given parametric study results, 3.8 cm thickness was selected and used for the Tyne electrolyzer. The resulted deflection at 3.8 cm thickness is negligibly small. (The overall deflection is less than the defined designed criteria deflection of 0.00254 cm). To reduce the total weight and hence the bulkiness of the electrolyzer, the minimum thickness to give the minimum acceptable deflection was used.

3. Design Features of Tyne Tritium-compatible Electrolyzer

Tyne in collaboration with CNL has designed and developed a tritium-compatible electrolyzer. It has 8 inch active diameter (active area 325 cm^2) electrodes and it is rated to work at 1.0 A/cm^2. The end plate is stainless steel type 316 of 1.5 inch thickness. There are several features which distinguish Tyne's

tritium PEM electrolyzer (TE) from other commercially available PEM electrolyzers for tritium application. TE has

- Double sealing between the bipolar plates (gaskets and outer O-ring)
- Outer container to capture any leaked tritiated water or gas from the stack.
- Specially developed tritium-compatible membrane for long term usage
- Ease of handling and replacement

Figure 5 is a 3-D representation of the TE,

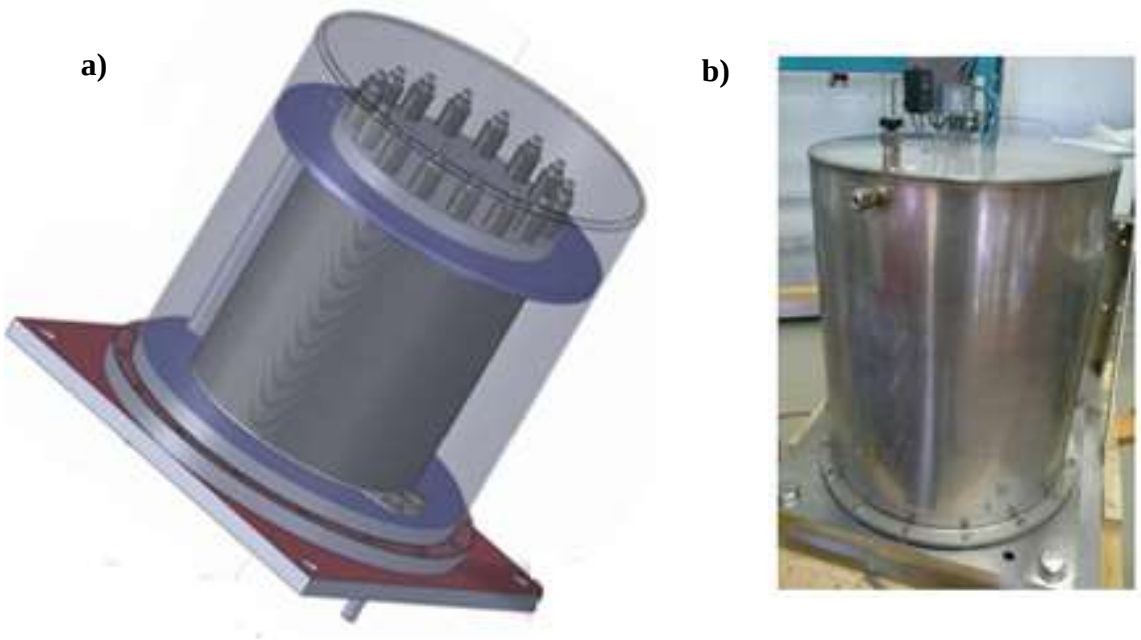

Figure 5 a) CAD Model b) Prototype Electrolyzer

4. Experimentation

4.1 Experimentation Using Nafion® N-117

Tyne built a prototype electrolyzer with a capacity of 1 Nm^3/hr (20 °C and 1atm) using seven MEAs. This prototype electrolyzer has eight active plates (i.e. bipolar plates) including two end electrode plates. Water was fed to the anode and cathode separately using a pump. The anode stream was heated using an immersion heater and cathode stream was used to remove the heat generated within the electrolyzer. Current, voltage, flowrates (of both anode and a cathode) and temperatures (both inlet and outlet streams) of anode and cathode were recorded. The water flow rate across both anode and cathode was 1 L/min.

4.2 Membrane Development

Membrane is a critical component of the electrolyzer. Specialized membranes were developed which can withstand tritated water significantly well as compared to Nafion® membrane. These membranes were soaked in high concentrated tritated water at CNL for approximately six months. The membranes were

then decontaminated and their performance was evaluated against commercially available Nafion membranes. The details of soaking the membrane and decontamination of these membranes are discussed below.

4.2.1 Exposure of CNL-100 Series Membrane to Tritium

CNL-100 series membranes were exposed to tritium in the Tritium Facility at CNL using titriated water in a stainless steel vessel. Figure 6 (Left) shows the membrane arrangement inside the vessel, while Figure 6 (Right) is a side view drawing of an assembled vessel. To load/drain the tritiated water, the Fill and Vent lines are connected to a loading rig designed for handling tritiated water.

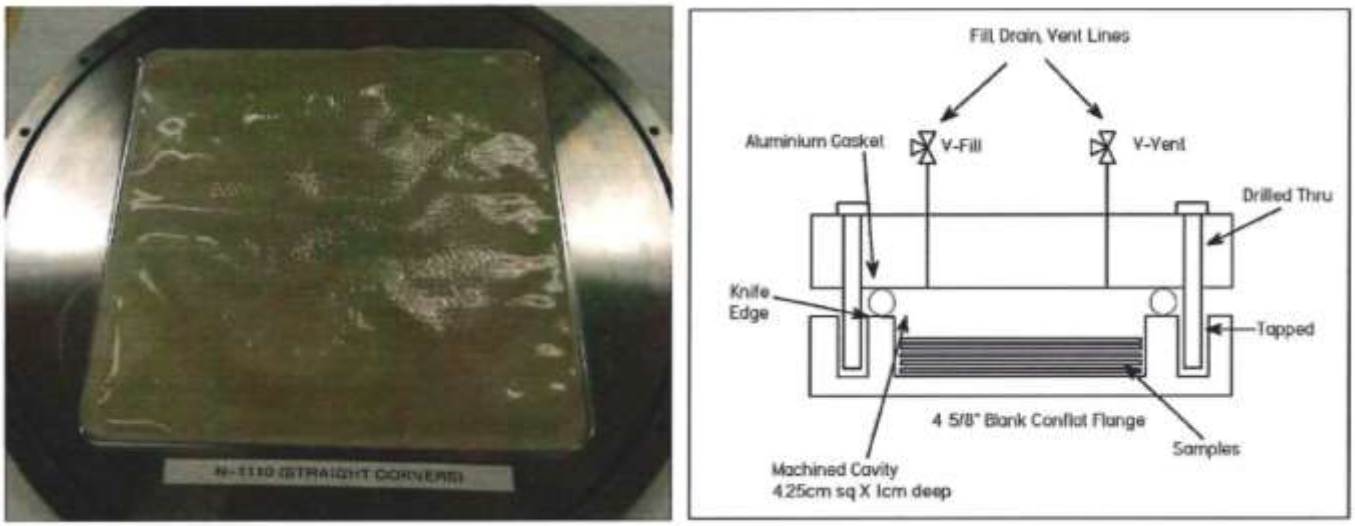

Figure 6 Exposure Vessel (Left) and Side View of Assembled Exposure Vessel (Right)

Samples of both CNL-100 series and commercial Nafion® N-1110 membranes were soaked in tritiated water at ambient pressure to receive the desired doses. The received doses of the exposed membranes were categorized into three levels: Dose A for 40-60 kGy, Dose B for 61-160 kGy and Dose C for 161-400 kGy. The membranes with dimensions of 25 cm x 25 cm were exposed to 775 Ci/kg tritiated water for 134 days in a chamber held at 60°C and received approximately 60 kGy of radiation. The fresh (i.e., as purchased or as manufactured) and the blank (which was soaked in non-tritiated water for the same period of time as the exposed membrane) membranes did not receive any radiation during the study. They were used as a reference/benchmark for comparison.

4.2.2 Decontamination of Exposed Membranes

Once the membranes in the exposure vessel reached the desired levels of exposure, the exposure vessel was re-connected to the loading rig to drain the tritiated water. The membranes were then decontaminated following the steps in Figure 7. During the in-situ decontamination, non-tritiated water was passed through the exposure vessel and flushed a few times. The tritium concentration in the flushed water from the vessel was monitored until its tritium concentration is reduced from above $10x10^{10}$ Bq/ml to about $10x10^{7}$ Bq/ml, typically after four flushes (shown in Figures 8).

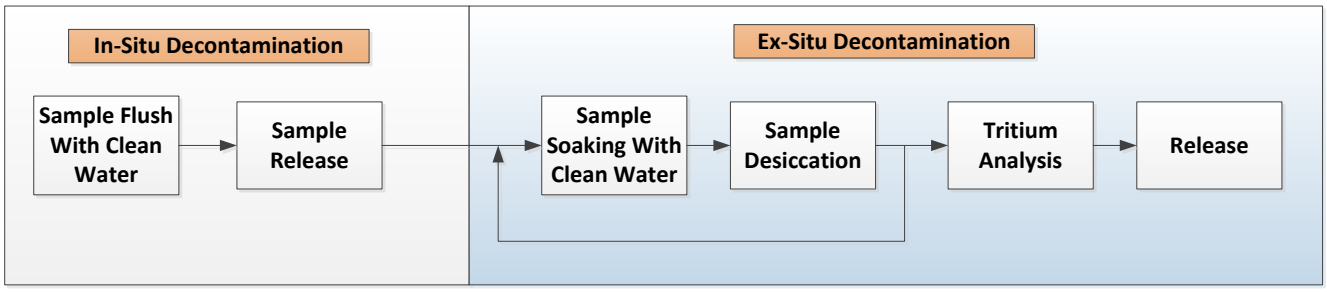

Figure 7 Decontamination Sequence

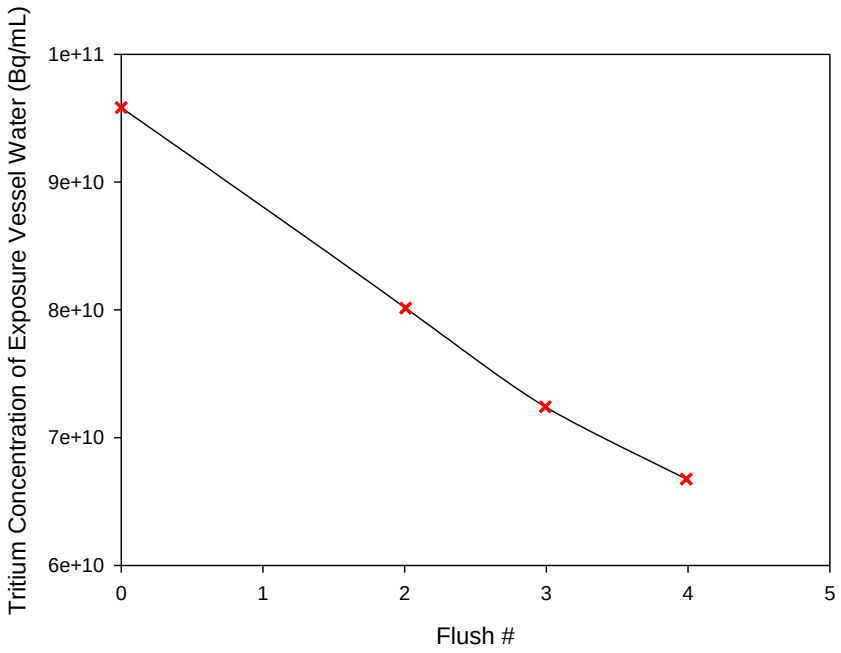

Figure 8 Typical Tritium Concentration during In-Situ Decontamination

5. Results and Discussion

5.1 The Seven-Cell Prototype Electrolyzer

Figure 9 shows the polarization curve of a seven-cell prototype electrolyzer with Nafion® N-117 membrane. The current is varied from 0 to 1.0 A/cm^3 which corresponds to a hydrogen production rate from 0 to 1 Nm^3/hr. The resulting voltage varied from an initial voltage of 1.7 V to 3 V per cell at 1.0 A/ cm^3. The increase in voltage is sharp in the beginning due to activation losses. As the current density increased further, its required voltage also increased but at a lower rate. The experiment was conducted at ambient temperature and pressure, however heating the feed water can significantly reduce the required voltage.

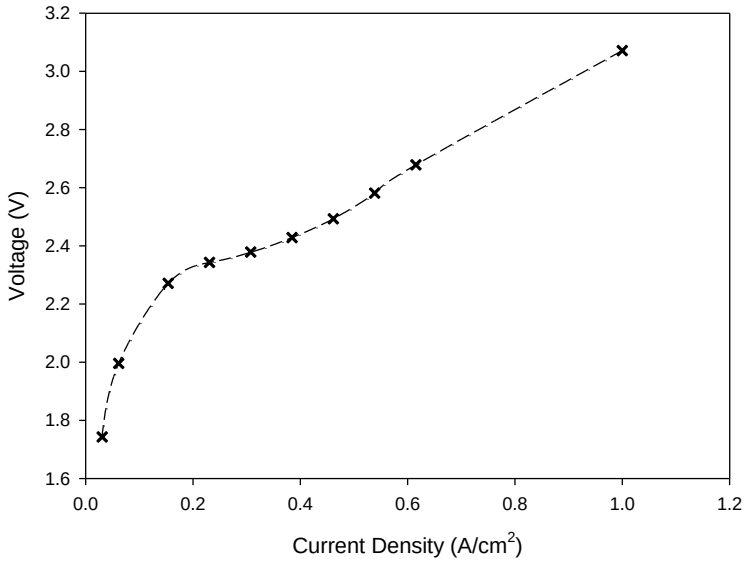

Figure 9 Polarization Curve at 1 LPM and at ambient temperature and pressure.

5.2 Characterization of CNL-100 Membranes after Tritium Exposure

In this section, results of tritium-compatible membrane which was soaked and then decontaminated will be presented and compared with a commercially available Nafion® membrane.

The physical characterization was performed using both exposed membrane samples and their respective blanks, all with a dimension of 4 cm x 4 cm. The physical characterizations examined the ion exchange capacity (IEC), mechanical and hydrolytic properties of the membranes. IEC measures the amount of available sulfonic acid sites ($-SO_3H$) per unit mass of total membrane. The higher the IEC, the more acid sites are available for proton conduction. IEC for Nafion® N-1110 showed 40% and 50% reductions at doses A and B respectively. This may suggest that beta radiation from tritiated water caused significant damage to the sulfonic acid groups in Nafion® initially, but the damage became less severe as the exposure time increases. Dose A resulted in a 40% reduction but dose B only resulted in an additional 10% loss of IEC. The CNL-100 series membrane showed similar degree of IEC loss at the same dose level. There is essentially no difference in IEC between the fresh and blank samples. This means that soaking of membrane in non-tritiated water had negligible effect on the IECs of the membranes analyzed thus far.

The mechanical properties that were investigated include modulus, ultimate stress and break strain. A high modulus represents a rigid material. At both Dose A and Dose B, CNL-100 membrane behaved quite differently from the Nafion® N-1110 membrane. The modulus for CNL-100 decreased after tritium exposure while the modulus for Nafion® N-1110 remarkably increased. Compared with the Nafion® N-1110 membrane, the break strain for CNL-100 membrane only changed slightly at all dose levels. Under electrolyzer operating conditions, the maximum pressure the membrane can hold is dependent on the membrane support structure. With Tyne's titanium disk-backed MEA, it is very likely the CNL-100 series membrane will function well at 100 psi.

The hydrolytic properties include membrane thickness change, water uptake and linear expansion after soaking. The thickness of CNL-100 series membranes generally increased upon tritium exposure while the thickness of Nafion® N-1110 membranes did not change much. However, the CNL-100 series membrane demonstrated superior in-plane stability. Its linear expansion was less than 5% regardless of soaking and radiation levels. Exposure of membranes in tritated water effects the water uptake. At Dose B, for example, the water uptake of CNL-100 membrane decreased from 53.83% (blank) to 9.23% whereas the water uptake of Nafion® N-1110 membrane only reduced from 34.97 (blank) to 10.98%.

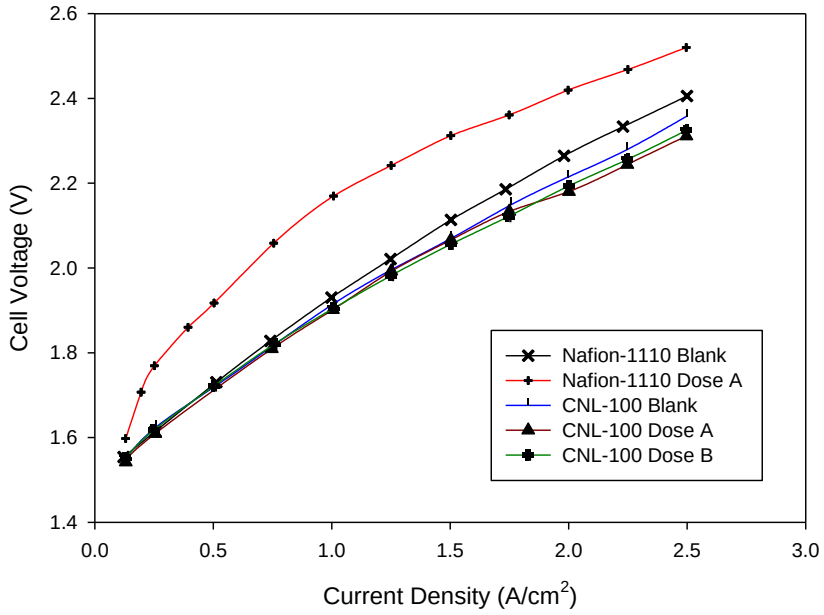

Figure 10: Comparison of CNL-100 series membrane and Nafion® N-1110 membrane at different current densities.

It is difficult to project how the changes in physical properties of the membrane would influence the actual electrolyzer performance unless these membranes are tested in an electrolyzer. The MEAs were made with both the Nafion® N-1110 and CNL-100 membranes (4 cm x 4 cm) and tested in an electrolyzer operating at 60°C and ambient pressure. The polarization curves of these membranes are shown in Figure 10. The voltages of exposed CNL-100 membranes were very close to that of the blank. Tritium exposure up to 159 kGy (Dose B) did not result in any performance deterioration for the CNL-100 membrane. On the contrarily, the exposed commercial Nafion® N-1110 membrane showed a cell voltage of about 200 mV higher than the blank at the current density of 1.0 A/cm^2. The CNL-100 membrane is clearly better than the commercial Nafion® N-1110 in terms of tritium compatibility.

6. Conclusions

The following conclusions can be drawn from this study:

- Tyne, in collaboration with CNL, has designed a tritium-compatible electrolyzer which has an active area of 325 cm^2. It can withstand tritium more effectively than commercially-available electrolyzers with Nafion® membranes.

- Though the actual designed capacity for hydrogen production is 10 Nm^3/hr, a prototype of 1 Nm^3/hr was fabricated using Nafion® N-117 membranes and tested at ambient temperature and pressure.
- An average voltage of 3 V per cell was required to achieve a current density of 1.0 A/cm^2.
- An end-plate thickness of 3.8 cm limited the deflection to less than 25 µm at a pressure of 2068 kPa (300 psi).
- CNL-100 series membranes show better cell voltage and durability in tritiated water than Nafion® N-1110 membranes.
  Further long-term electrolyzer testing at 80 ^oC is ongoing.

7. References

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