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HYDROGEN ISOTOPE RECOVERY USING PROTON EXCHANGE MEMBRANE ELECTROLYSIS (PEME) OF WATER

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A critical component of tritium glovebox operations is the recovery of high value tritium from the water vapor in the glove box atmosphere. One proposed method to improve existing tritium recovery systems is to replace the disposable hot magnesium beds used to separate the hydrogen and oxygen in water with continuous use Proton Exchange Membrane Electrolyzers (PEMEs). This study examines radiation exposure to the membrane of a PEME and examines the sizing difference that would be needed if the electrolyzer were operated with a cathode water vapor feed instead of an anode liquid water feed.

I. INTRODUCTION

The glovebox system used in tritium handling at the Savannah River Site (SRS) has been described in detail in previous publications.[1, 2] Tritiated water vapor is recovered from the glovebox gas system by absorption on zeolite beds. After a zeolite bed reaches capacity, it is purged and the water vapor from the bed is cracked in a magnesium bed to produce magnesium oxide and a mixture of gaseous hydrogen isotopes according to Eq. (1).

$$Mg + HTO \rightarrow MgO + HT \qquad (1)$$

The magnesium bed is disposed of when it has been completely oxidized. With the magnesium bed system, expansions in glovebox system capacity require more frequent changes of the magnesium bed and thus increase operating costs.

A modification of the system has been envisioned where a Proton Exchange Membrane Electrolyzer (PEME) could be used in place of the magnesium beds to separate the water into hydrogen and oxygen. The overall reaction for water electrolysis is shown in Eq. (2). At the anode, water is oxidized according to Eq. (3) to produce oxygen gas, hydrogen ions, and electrons. At the cathode, the hydrogen ions are recombined with electrons to form hydrogen gas as expressed in Eq. (4).

$$2HTO \rightarrow 2HT + O_2 \qquad (2)$$

$$2HTO \rightarrow O_2 + 2H^+ + 2T^+ + 4e^- \qquad (3)$$

$$2H^+ + 2T^+ + 4e^- \rightarrow 2HT \qquad (4)$$

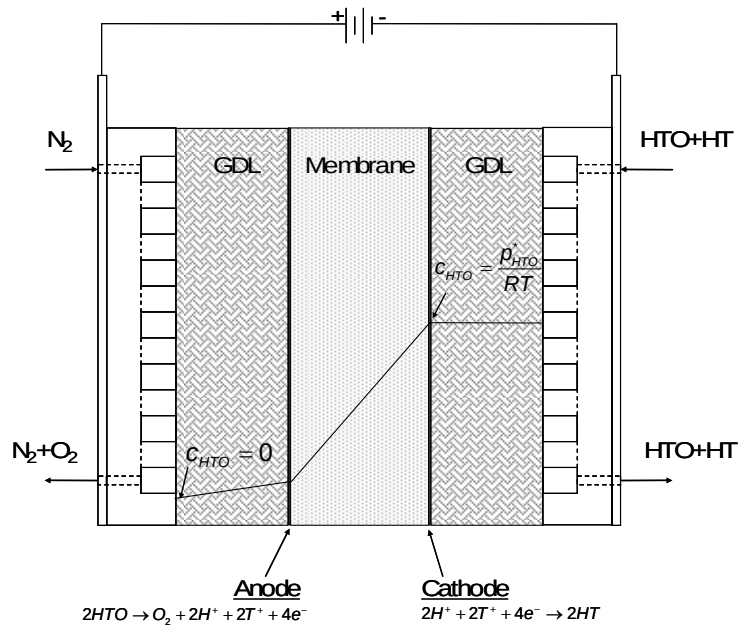

Fig. 1. Cell schematic for a saturated cathode water vapor feed electrolyzer.

Figure 1 illustrates the mass transport and chemistry occurring inside a cathode water vapor feed PEME that is operating near limiting current. Saturated tritiated water vapor enters the cathode. The tritiated water is transported across the membrane by diffusion and electroosmotic drag. The application of a voltage above the equilibrium of Eq 2. (1.23 V) to the anode will cause oxidation of the tritiated water vapor. A $PtIrO_2$ black catalyst is used in the Anode Catalyst Layer (ACL) to activate the electrochemical reaction. To reduce the activation barrier for this reaction, a Pt black catalyst is used in the Cathode Catalyst Layer (CCL). Hydrogen gas is produced at the cathode and oxygen gas is produced at the anode. The Nafion® membrane will segregate the product gases and prevent explosive mixtures of hydrogen and oxygen. Due to the slight solubility of hydrogen and oxygen in water small amounts of these gases will diffuse across the membrane.

The concentration profile for tritiated water in the cell illustrates how the water will diffuse across the membrane. Due to operation near the mass transfer limiting current, the concentration of water exiting the anode will be negligible since nearly all of it is oxidized at the ACL.

Using a PEME to electrolyze the water would allow continuous operation of the tritium recovery system by eliminating the need for changes of the magnesium beds. A similar PEME system has been proposed for use by the ITER project in their Water Detritiation System (WDS)[3, 4]. It has been proposed to use a cathode water vapor feed electrolyzer in the SRS Glovebox tritium recovery operation. Feeding the water on the cathode should minimize water recovery from the cathode oxygen stream, but increase system size. Two main questions about the system feasibility are: (1) what will be the maximum annual radiation dose rate of the Nafion® and (2) what will be the size difference for a cathode vapor feed electrolyzer. This paper uses literature models on Nafion water absorption and transport to predict answers to these questions.

II. MEMBRANE RADIATION EXPOSURE CALCULATION

The Nafion® membranes in the PEME stack may be degraded by the beta radiation emitted as tritium decays. The beta radiation is low energy and is easily shielded by thin layers of most metals. Therefore, the Pt and $PtIrO_2$ black electrodes on the anode and cathode will shield the membrane from radiation coming from other parts of the cell. The radiation exposure of the membrane will come from decay of the tritium in the membrane. To estimate the maximum possible radiation dosage to a PEME, the Nafion® membrane should be assumed to be in contact with liquid water.

The total tritium content of the membrane is the sum of the tritium ions associated with the sulfonic acid sites in the membrane and the tritium that is in the water absorbed in the membrane. The amount of water absorbed in a liquid water saturated membrane can be calculated using the data and model of Springer et al.[5] In their paper, Springer et al.[5] measured that the water content of a membrane saturated with liquid water, λ_{sat}, was 22 moles of water per mole of SO_3^- sites. This value together with the density of the membrane, ρ_{Nafion}, and the equivalent weight of the membrane, $M_{eq,Nafion}$, can be used to calculate the amount of hydrogen isotopes absorbed in a specific volume. Using this nomenclature, the atomic concentration of hydrogen isotopes in the membrane, $c_{(H+T)}$, is:

$$c_{(H+T)} = \frac{\rho_{Nafion} \cdot (1 + 2\lambda_{sat})}{M_{eq,Nafion}} \qquad (5)$$

Table 1 contains the values of these properties for a Nafion® 117 membrane. An estimate of the liquid phase tritiated water radioactivity that will be used in the PEM electrolyzer is 600 Ci/L. If it is assumed that 1 mole of atomic tritium has a radioactivity of 29,012 Ci, then it can be shown that the annual radiation dose of the membrane will be 24 Mrad/yr. Given that the radiation dose will vary proportionally with the radioactivity of the water, a more useful value may be found by normalizing this dose rate by the activity of the water. For liquid water saturated Nafion®, this value is 0.04 Mrad*L/(yr*Ci). This value is 2.7 times less than the annual activity normal radiation dosage estimated by Iwai et al.[3] However, it is not known if their calculation took into account the water absorption characteristics of Nafion® membranes. The smaller estimate for the annual radiation dosage to the membrane means that PEME system lifetimes may be longer than previously anticipated.

TABLE I. Properties of a Nafion® 117 Membrane

ρ_{Nafion}	2
$M_{eq,Nafion}$	1100
λ_{sat}	22
$D_{H_2O,\lambda=14}$	1.30E-06
t_{Mem}	0.018

III. LIMITING CURRENT CALCULATION

Inside a PEM membrane, water is not generated or consumed. The transport of water through the membrane can be considered one dimensional if it is assumed that there is planar symmetry in the membrane. Therefore, the conservation of mass expression inside the membrane is:

$$\frac{dN_{H_2O}}{dz} = 0 \qquad (6)$$

where N_{H_2O} is flux of water through the membrane and z is the direction that is orthogonal to the membrane surface. In a PEM membrane, water is mainly transported by diffusion and electroosmotic drag[6]. The electroosmotic drag will act in the direction of the protonic current in the membrane and for the case of a cathode vapor feed electrolyzer this flux will be in the opposite direction as the diffusional flux of water:

$$N_{H_2O} = N_{H_2O,diff} - N_{H_2O,drag} \qquad (7)$$

where $N_{H_2O,diff}$ is the diffusive flux of water through the membrane and $N_{H_2O,drag}$ is the flux of water through the

membrane due to electroosmotic drag. The diffusive flux of water through the membrane is assumed to follow Fick's law[6]:

$$N_{H_2O,diff} = -D_\lambda \frac{dc_w}{dz} \qquad (8)$$

where D_λ is the diffusion coefficient of water absorbed in the membrane and c_w is the concentration of water absorbed in the membrane. The electroosmotic drag flux through the membrane is proportional to the current by the electroosmotic drag coefficient and can be written as[6, 7]:

$$N_{H_2O,drag} = \xi \frac{i}{F} \qquad (9)$$

where ξ is the electroosmotic drag coefficient, and i is the current density. Thus, the water flux in the membrane can be rewritten as:

$$N_{H_2O} = -D_\lambda \frac{dc_w}{dz} - \xi \frac{i}{F} \qquad (10)$$

Fuller and Newman[8, 9] have empirically determined ξ to have a value near 1 for $\lambda > 5$. However, it should be noted that other authors have determined values of ξ up to 2.5 in water equilibrated membranes[7].

When the reaction rate per unit area (i.e. current density) in an electrochemical system is limited by the mass transfer in the system it is said to be at its limiting current density. The water reaction rate per unit area, r_{H_2O}, is proportional to the system current density by the relationship:

$$r_{H_2O} = \frac{i}{nF} \qquad (11)$$

At the limiting current density, $i_{\lim}$, the water reaction rate is equal to the flux of water through the membrane:

$$\frac{i_{\lim}}{nF} = -D_\lambda \frac{dc_w}{dz} - \xi \frac{i_{\lim}}{F} \qquad (12)$$

Solving this equation for the limiting current density gives:

$$i_{\lim} = -\frac{nF}{(1+n\cdot\xi)} D_\lambda \frac{dc_w}{dz} \qquad (13)$$

In the PEM membrane, the concentration of water of absorbed water can be expressed as a function of the equivalent weight of the membrane, the density of the membrane material, and the water content of the membrane per equivalent[5]:

$$c_w = \frac{\lambda \cdot \rho_{Nafion}}{M_{eq,Nafion}} \qquad (14)$$

The water content of the membrane, λ, will vary through the membrane while the other terms of this equation are constant. Thus, the limiting current expression can be rewritten:

$$i_{\lim} = -\frac{nF\rho_{Nafion}}{M_{eq,Nafion}(1+n\cdot\xi)} D_\lambda \frac{d\lambda}{dz} \qquad (15)$$

Since there is no consumption of water in the membrane, the gradient in the membrane is linear and the limiting current equation can be rewritten:

$$i_{\lim} = -\frac{nF\rho_{Nafion}}{M_{eq,Nafion}(1+n\cdot\xi)} D_\lambda \frac{\Delta\lambda}{t_m} \qquad (16)$$

where $\Delta\lambda = \lambda_{an} - \lambda_{ca}$ and t_m is the thickness of the membrane. If the anode of the electrolyzer is fed dry gas and all of the water transported from the cathode to the anode is consumed at the anode, then $\lambda_{an} = 0$. Since the cathode is saturated with water vapor, λ_{ca} is 14 according to the empirical data of Springer et al.[5] Given these values and the properties of Nafion® listed above, the limiting current density at 30°C can be calculated to be 0.12 A/cm^2.

Since the reaction rate of an electrolyzer is proportional to the current, the ratio of the current densities at which two electrolyzers operate will give you the ratio of active areas that are needed with the two configurations to achieve the same overall reaction rate. Typical operating current densities for anode liquid feed PEMEs are around 1.0 A/cm^2. Therefore, a cathode water vapor feed system will need to be around 8.3 times larger to electrolyze the same amount of water.

IV. CONCLUSIONS

Models that account for the detailed structure of Nafion® were used to predict the annual radiation dose rate of a membrane saturated with liquid water. For a liquid water tritium activity of 600 Ci/L, the annual membrane radiation dose rate was 24 Mrad/yr. On an activity normalized basis, this was shown to be 2.7 times less than previous literature estimates of the dose rate of Nafion®. A model of the water transport of the membrane was used to estimate the limiting current of a cathode vapor feed electrolyzer operating at 30°C to be 0.12 A/cm^2. Using this value, it was estimated that a cathode vapor feed system would need to be approximately 8 times larger than an equivalent anode liquid feed system.

V. NOMENCLATURE

c_w - Concentration of water in absorbed in the membrane, $\frac{mol}{cm^3}$

D_λ - Diffusion coefficient of the absorbed water in Nafion®, $\frac{cm^2}{s}$

F - Faraday's Constant, $96{,}485 \frac{C}{mol \quad e^-}$

i - Current density, $\frac{A}{cm^2}$

$M_{eq,Nafion}$ - Equivalent weight of Nafion®, $\frac{g}{mol}$

n - Moles of e- per mole of water, 2

N_{H_2O} -Flux of water through the membrane, $\frac{mol}{cm^2 \cdot s}$

$N_{H_2O,diff}$ - Diffusive flux of water through the membrane, $\frac{mol}{cm^2 \cdot s}$

$N_{H_2O,drag}$ - Flux of water through the membrane due to electroosmotic drag, $\frac{mol}{cm^2 \cdot s}$

r_{H_2O} - Water reaction rate per unit area, $\frac{mol \quad H_2O}{cm^2 \cdot s}$

t_{Mem} - Thickness of the dry membrane material, cm

T_{cell} - Cell temperature, K

z - Direction orthogonal to the membrane, cm

λ - Water content of the membrane, $\frac{mol \quad H_2O}{mol \quad eq.}$

$\lambda_{vap,sat}$ - Water content of a water vapor saturated membrane, $\frac{mol \quad H_2O}{mol \quad eq.}$

ρ_{Nafion} - Density of dry Nafion® membrane material, $\frac{g}{cm^3}$

ξ - Electroosmotic drag coefficient

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