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ELECTROCHEMICAL COMPRESSION OF AMMONIA/ HYDROGEN BLENDS FOR HEAT PUMP APPLICATION

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Abstract

Ammonia is widely used as a refrigerant in air conditioning, food preservation and for fuel storage purposes. Ammonia is an attractive candidate for electrochemical compression (ECC). Electrochemical compressors can be an ideal replacement for mechanical compressors because of noiseless operation, higher efficiencies at lower voltages and the ability to operate without the use of Global Warming Potential (GWP) working fluids. This paper explores the electrochemical compression of ammonia with hydrogen as a carrier gas, using fuel cell type hardware. A perfluorosulfonic acid (PFSA) membrane allows the transfer of ammonia, using hydrogen as a carrier gas, by the conduction of NH_4^+ ions from anode to cathode. The ECC performance was evaluated using electrochemical methods using a single cell at STP. The effects of back-diffusion in the compression process are highlighted and suggestions to improve the ECC of ammonia-hydrogen blends are proposed.

Keywords: Ammonia; Hydrogen; Electrochemical compression; Nernst voltage; Diffusion; Compression Ratio

1. Introduction

Global energy demand is rising rapidly as we face the depletion of conventional sources of energy. There is a need to look for sustainable alternatives to traditional mechanical energy conversion devices such as heat pumps that account for a large and growing portion of the global demand for energy. The developments in fuel cell technology to generate electricity in a clean and environment-friendly manner has placed hydrogen as an important energy vector to meet both stationary and automobile power generation applications. Ammonia is a rich source of hydrogen and could also play a significant role as an energy vector in a hydrogen economy. Moreover, ammonia itself is widely used as a refrigerant in large scale industrial heat pump applications particularly in applications involving the food chain. Electrochemical compression of ammonia therefore can be used for conveying ammonia when used as a bulk energy vector but could also be an alternative to mechanical compressors for heat pump applications.

Electrochemical compression is superior to mechanical compression as it offers the potential to compress a working fluid at higher efficiency, noiseless operation, usage of green refrigerants, and greater reliability due to a lack of moving parts.

The first validation of the concept of an electrochemical compressor based on hydrogen was done by Sedlak et al. [1], who applied a potential difference to transfer protons across a proton exchange membrane and

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achieved higher pressures. Rohland et al. [2] and Strobel et al. [3] carried the idea forward to electrochemically transfer and purify hydrogen. All these studies were only focused on hydrogen compression until 2009, when the general idea of using electrochemical compression for heat pump applications was pioneered by Bahar et al. [4]. Bahar et al. [5] then proposed the use of ammonia in electrochemical compressors (ECC) using hydrogen as the carrier gas by engaging perfluorosulfonic acid (PFSA) membranes to electrochemically compress ammonia under a potential difference. An overall system analysis was favorably reported by Tao et al. [6] in 2017.

Ammonia is a well-established contaminant for PFSA membranes in fuel cell applications and is actively scrubbed out of reformed hydrogen gas streams used for fuel cells. Our challenge in this project was to understand and then develop transportation mechanisms for ammonium ions in ion-exchange membranes.

The hardware of an ECC is similar to that of a fuel cell and consists of a membrane-electrode-assembly (MEA) sandwiched between two graphite plates with flow fields for gas distribution, held together by end plates on either side. The entire assembly is held together by eight bolts, all maintained at a same torque (Figure 1).

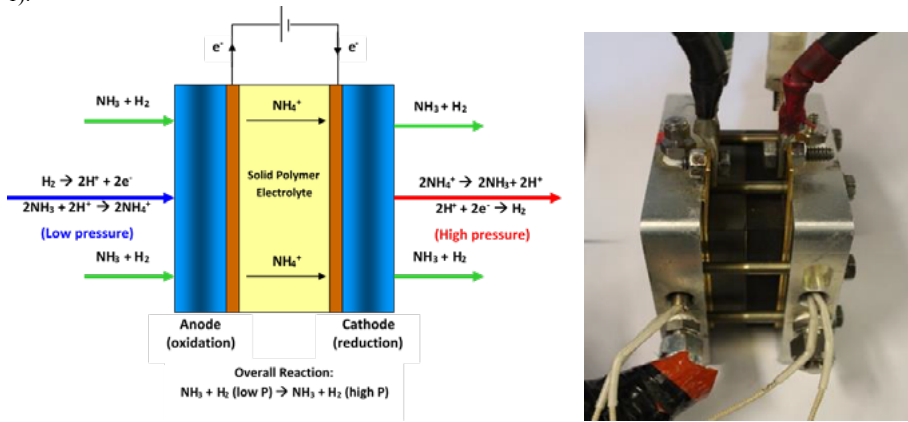


Fig. 1. Schematic of an electrochemical ammonia compressor (left); ECC hardware (right)

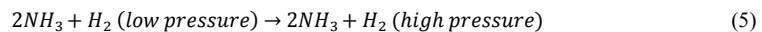
A mixture of ammonia and hydrogen gases is fed to the anode, where, by applying a DC voltage, hydrogen gets oxidized to protons (H^+), which combine with ammonia to form ammonium ions (NH_4^+), as in Equations 1 and 2.



The ammonium ions get transferred across the membrane to the cathode. Two electrons are required for this reaction to take place, as per Equation 1. The ammonium ions are reduced at the cathode to regenerate ammonia and hydrogen gases at a higher pressure, as shown in Equations 3 and 4.



The overall electrochemical reaction can be written as:



The production of protons facilitates the formation of ammonium ions which is the species conducted by the PFSA membrane. The membrane needs to be functionalized by soaking in aqueous ammonia solution overnight. In this paper, the use of ammonia as a working fluid in an electrochemical compressor (ECC) is

reviewed. The performance of the ECC is presented in the form of output pressures reached within the phase conversion pressure limits of gaseous ammonia at room temperature; cathode pressures and current densities are also plotted for all voltages tested.

The membrane used for experiments was a sulfonated tetrafluoroethylene-based fluoropolymer-copolymer membrane, 50 μm thick. The platinum (Pt) catalyst loading on the electrodes was 0.3 mg/cm^2 . The membranes were functionalized for ion exchange from H^+ to NH_4^+ by soaking in ammonia solution overnight, after which, they were thoroughly rinsed with deionized water and dried gently using paper towels. The membrane surface has residual ammonia and does not readily stick to the electrodes, so the membrane and electrodes were stacked together inside the ECC and assembled by tightening the bolts. The ECC was assembled with 25 cm^2 hardware.

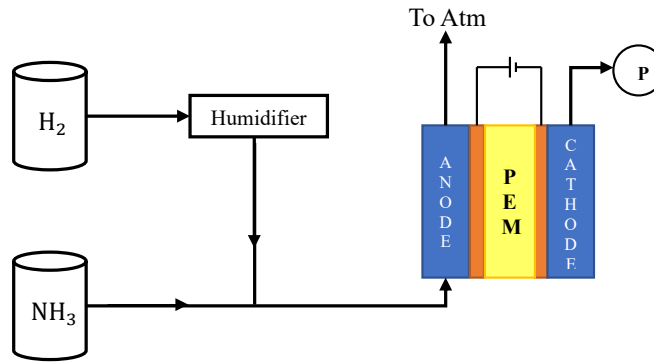


Fig. 2. Experimental setup of the electrochemical ammonia compressor

The ECC was tested at room temperature (22°C) and pressure (1 atm). The PFSA membranes used for experiments only function when properly hydrated [7, 8]. Hence, it is important to maintain adequate humidity in the system. The inlet gas stream at the anode consisted of a 50-50 mixture of fully hydrated hydrogen (100% RH at a flow rate of 100 cm^3/min) and dry ammonia (0% RH at a flow rate of 100 cm^3/min), resulting in an overall humidity around 50%, whereas, the cathode port terminated with a pressure transducer. A schematic of the experimental setup is shown in Figure 2. The ammonia inlet stream was kept dry as ammonia reacts with water to form ammonium hydroxide, which can precipitate inside the humidifier chamber. The anode outlet was open to the environment, hence the anode pressure was fixed at 1 atm. The ECC cell was tested using the fuel cell test station (FCTS) from Arbin Instruments. The experiments were performed at four different operating voltages: 0.025, 0.05, 0.075 and 0.1 V.

2. Results and Discussion

Before preparing the MEA, the membranes were soaked in ammonia solution, which makes them alkaline in nature implying that the contribution of H^+ to the generated current can be neglected, which is also evident by the almost zero current when the ECC was tested with only hydrogen at the anode. Also, the total amount of ammonia and hydrogen gases generated at the cathode can be expressed in terms of total current I :

$$\dot{n}_{\text{H}_2} = \frac{I}{2F} \quad (6)$$

$$\dot{n}_{\text{NH}_3} = \frac{I}{F} \quad (7)$$

where \dot{n}_{H_2} is the mol/s of hydrogen transferred across the membrane according to Faraday's law [9], \dot{n}_{NH_3} is the mol/s of ammonia transferred, and F is Faraday's constant.

The applied cell voltage E_{cell} is the sum of the Nernst potential, the activation overpotential, and ohmic (IR), mass transport and back diffusion losses [10]:

$$E_{\text{cell}} = E_{\text{Nernst}} + \Delta E_{\text{Activation}} + \Delta E_{\text{Ohmic}} + \Delta E_{\text{Transport}} + \Delta E_{\text{Back Diffusion}} \quad (8)$$

The activation overpotential $\Delta E_{Activation}$ is a sum of the overpotentials at the anode and the cathode. The ohmic losses ΔE_{Ohmic} arise mainly due to the membrane resistance and contact resistance between difference components of the ECC. At high current densities, mass transport losses denoted by $\Delta E_{Transport}$ could become significant due to the inability to maintain adequate reactant gas supply to the anode catalytic sites; however this loss term is not expected to be significant in the case of ammonia compression due to the small operating currents. $\Delta E_{Back\ Diffusion}$ represents losses due to back diffusion of ammonia and hydrogen from the pressurized cathode to the anode through the membrane. All of these losses cause the required voltage to exceed the Nernst voltage for a given compression ratio. The Nernst potential E_{Nernst} defined by the Nernst equation, Equation 9, depends logarithmically on the pressure ratio between the cathode (high) and anode (low). The total pressure at the anode and cathode can be expressed in terms of the partial pressures of hydrogen and ammonia.

$$E_{Nernst} = \frac{RT}{F} \ln \left\{ \left(\frac{P_{H_2,out}}{P_{H_2,in}} \right)^{\frac{1}{2}} \left(\frac{P_{NH_3,out}}{P_{NH_3,in}} \right) \right\} \quad (9)$$

where R is the universal gas constant, and T is the cell temperature in K.

The ECC performance at different operating voltages is presented in Figure 3. For each applied voltage, the current density (red curve) is the highest at the start of the operation and declines rapidly at first before gradually reaching an equilibrium value after a few hours. Concurrently, the cathode pressure (blue curve) rises rapidly at the start and eventually plateaus to an equilibrium value. Both the initial and equilibrium current densities increase with the applied voltage as shown in Figure 3. Similarly, the equilibrium pressures also increase with the applied voltage. The fact that the current is non-zero although the cathode pressure has equilibrated indicates that back-diffusion is occurring.

The backward diffusive flux (\dot{n}_b) as given by Fick's law is directly proportional to the difference in the concentration of individual species (ΔC) across the membrane and inversely proportional to the membrane thickness (d):

$$\dot{n}_{b,NH_3} = \mathcal{D}_{NH_3} A \frac{\Delta C_{NH_3}}{d}, \quad \dot{n}_{b,H_2} = \mathcal{D}_{H_2} A \frac{\Delta C_{H_2}}{d} \quad (10)$$

where \dot{n}_{b,NH_3} and \dot{n}_{b,H_2} are the backward diffusive fluxes for ammonia and hydrogen, respectively. \mathcal{D}_{NH_3} and \mathcal{D}_{H_2} are the diffusivities of ammonia and hydrogen, respectively, in the membrane. The concentration of ammonia and hydrogen at either face of the membrane is directly related to their partial pressures through Henry's law. Henry's constant (H) depends on the type of membrane and the gas in contact with the membrane [10].

$$C = HP \quad (11)$$

Combining Equations 10 and 11, we can express the diffusive fluxes as a function of cathode and anode pressures as:

$$\dot{n}_{b,NH_3} = (\mathcal{D}H)_{NH_3} A \frac{(P_c - P_a)_{NH_3}}{d} \quad (12)$$

$$\dot{n}_{b,H_2} = (\mathcal{D}H)_{H_2} A \frac{(P_c - P_a)_{H_2}}{d} \quad (13)$$

where $\mathcal{D}H$ is the permeability constant and depends on the nature of the gas and membrane. Denoting \dot{n}_n as the net molar flow rate to the cathode (= forward flux – back diffusive flux), and assuming that both ammonia and hydrogen follow the ideal gas law, we can write:

$$(\dot{n}_n)_{NH_3} = \dot{n}_{f,NH_3} - \dot{n}_{b,NH_3} = \frac{\dot{P}_{c,NH_3} V_c}{RT} \quad (14)$$

$$(\dot{n}_n)_{H_2} = \dot{n}_{f,H_2} - \dot{n}_{b,H_2} = \frac{\dot{P}_{c,H_2} V_c}{RT} \quad (15)$$

where \dot{P}_c is the rate of cathode pressure rise (Pa/s), and V_c is the pressurized volume on the cathode side (m^3). Substituting the expressions for forward and backward fluxes in Equations (14) and (15), the compression equations can be written as:

$$\text{Ammonia: } \frac{I}{F} - (DH)_{NH_3} A \frac{(P_{NH_3,c} - P_{NH_3,a})}{d} = \frac{\dot{P}_{NH_3,c} V_c}{RT} \quad (16)$$

$$\text{Hydrogen: } \frac{I}{2F} - (DH)_{H_2} A \frac{(P_{H_2,c}(t) - P_{H_2,a})}{d} = \frac{\dot{P}_{H_2,c} V_c}{RT} \quad (17)$$

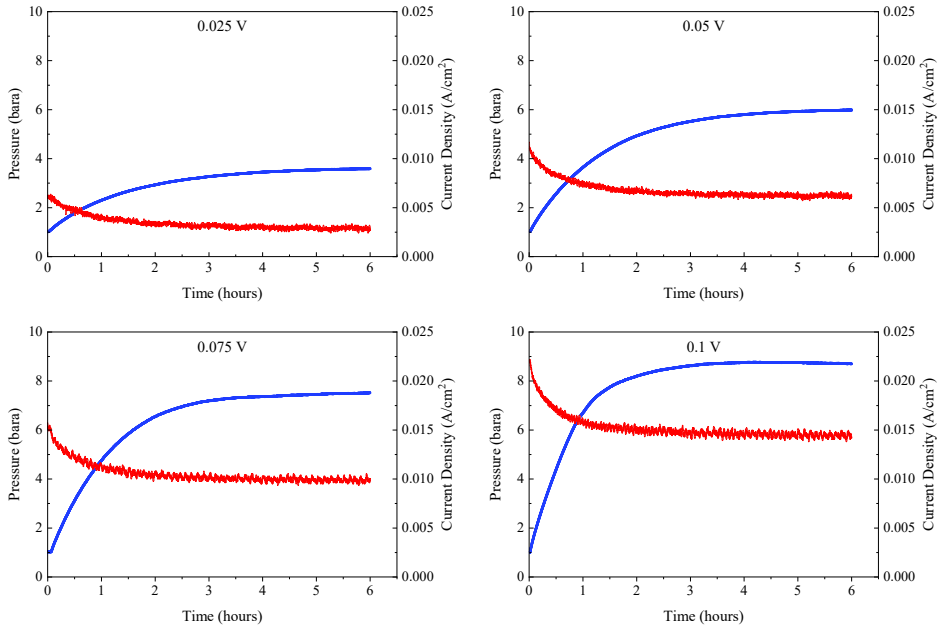


Fig. 3. Pressure (blue) and current density (red) vs. time for Nafion 212 at different applied voltages

Since ammonium is a much bulkier ion than a proton, the current density observed in this case is much less than in the case of a pure hydrogen compressor [7].

When the pressure reaches its equilibrium value, $\dot{P}_c = 0$, in an ideal scenario without back-diffusion, the equilibrium current would also reduce to zero. However, in reality, the forward flux equals the backward flux at steady state, and hence, there is an equilibrium current which maintains the cathode at equilibrium pressure ($P_{c,eq}$) given by Equations (18) and (19).

$$\frac{I_{eq}}{F} = \frac{(DH)_{NH_3} A (P_{c,eq} - P_a)_{NH_3}}{d} \quad (18)$$

$$\frac{I_{eq}}{2F} = \frac{(DH)_{H_2} A (P_{c,eq} - P_a)_{H_2}}{d} \quad (19)$$

As the pressure builds at the cathode, with the anode still at atmospheric pressure, it creates a pressure difference across the membrane, which in turn forces ammonia to permeate back through the membrane to the anode by back-diffusion. This poses a barrier in achieving higher pressures. The back-diffusion losses increase

as the pressure difference across the membrane increases, hence lowering the ECC efficiency at higher pressures.

The composition of the ammonia-hydrogen gas mixture at the cathode side was measured using the Nesslerization method at two different stages of compression – (i) cathode open and (ii) cathode closed. The cathode outlet stream containing the ammonia-hydrogen mixture was passed into a graduated cylinder (250 mL) which was completely filled with and held inverted in a 1250 mL beaker containing Nessler's reagent. Ammonia in the outlet stream immediately and completely reacts with Nessler's reagent to change its color from pale yellow to yellowish-brown [11,12], which was analyzed using a spectrophotometer (Vernier SpectroVis Plus). The hydrogen in the mixture is inert with respect to Nessler's reagent and was collected in the graduated cylinder using the downward displacement method.

First, the quantification of the cathode outlet stream was carried out when the cathode was open to the atmosphere. At this stage, both anode and cathode were maintained at the same pressure ($P_a = P_c$) and hence, back-diffusion losses were zero. In this case, the ratio of ammonia to hydrogen measured was 2, which is also the stoichiometric ratio of NH_3 and H_2 at the cathode as per Equations 1-4.

Next, the cathode outlet was closed and ECC was allowed to pressurize. After the pressure attained equilibrium, the quantification of the cathode outlet stream was carried out by slowly opening the outlet valve and passing the constituents to the Nessler's reagent solution. The ammonia-hydrogen ratio obtained in this case is plotted along with the results from the cathode open case for all four operating voltages in Figure 4.

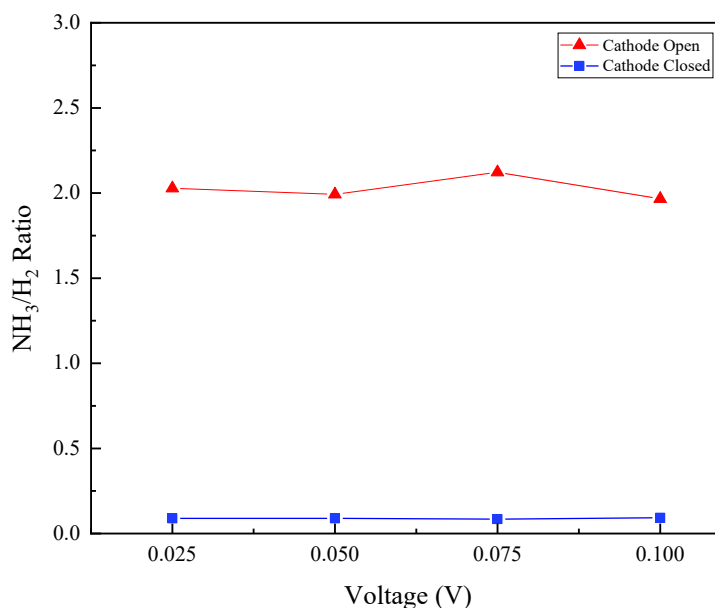


Figure 4. $NH_3:H_2$ volumetric ratios for 'cathode open' and 'cathode closed' cases for the four voltages tested

The $NH_3:H_2$ for cathode open case was measured to be 2. However, the ratio obtained in the 'cathode closed' case is only about 0.085. This means that the cathode chamber is predominantly composed of hydrogen in the 'cathode closed' case. Thus, one can conclude ammonia diffuses back to the anode at a significantly faster rate than hydrogen.

Furthermore, separate depressurization experiments were carried out to evaluate the permeability coefficients of both hydrogen and ammonia through the Nafion membrane. The cathode was initially pressurized by directly connecting it to the respective gas cylinders. The applied voltage was set to zero and the cathode was allowed to depressurize. The gas diffusing back from cathode to anode was detected by the formation of gas bubbles when the anode outlet tube was immersed in oil.

The rates of depressurization can be determined by setting $I = 0$, $P_{NH_3,a} = 0$, and $P_{H_2,a} = 0$ in Equations (16) and (17), which gives exponential expressions for the rates of depressurization:

$$P_{NH_3,c}(t) = P_{NH_3,c,i} \exp\left(-\frac{(DH)_{NH_3} ART}{dV_c} t\right) \quad (20)$$

$$P_{H_2,c}(t) = P_{H_2,c,i} \exp\left(-\frac{(DH)_{H_2} ART}{dV_c} t\right) \quad (21)$$

where $P_{NH_3,c,i}$ and $P_{H_2,c,i}$ are the initial cathode pressures of ammonia and hydrogen, respectively, at the start of depressurization.

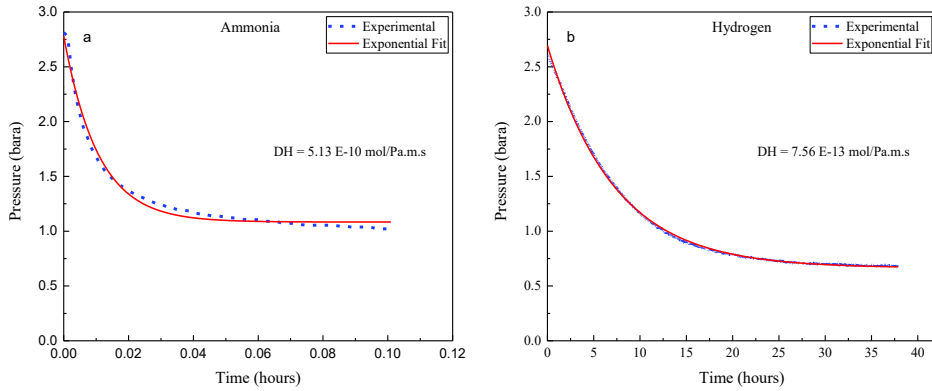


Figure 5. Cathode depressurization profiles for (a) ammonia, and (b) hydrogen

Figure 5 shows the measured depressurization curves (blue) obtained for both ammonia and hydrogen. The exponential curve fits (red) closely match the experimental curves for both gases as shown in Figure 5. Using the curve fits and substituting the known values of A , R , T , d , and V_c , into Equations (20) and (21), the values of the two permeability coefficients are obtained as:

$$(DH)_{NH_3} = 5.13 \text{ E} - 10 \text{ molPa}^{-1}\text{m}^{-1}\text{s}^{-1}$$

$$(DH)_{H_2} = 7.56 \text{ E} - 13 \text{ molPa}^{-1}\text{m}^{-1}\text{s}^{-1}$$

The permeability coefficients obtained here are similar to the values found for Nafion membranes for ammonia ($\sim 9 \text{ E} - 10 \text{ molPa}^{-1}\text{m}^{-1}\text{s}^{-1}$) in Refs. [12-14] and hydrogen ($\sim 3.5 \text{ E} - 14 \text{ molPa}^{-1}\text{m}^{-1}\text{s}^{-1}$) in Refs. [15-17]. Figure 5 shows that when $(DH)_{NH_3} \gg (DH)_{H_2}$, then the cathode chamber is mostly composed of hydrogen and ammonia is only present in trace quantities. The Nafion membrane functionalized in ammonia solution is highly permeable to molecular ammonia and hence, it is very difficult to pressurize ammonia using an ECC with the given set of materials and conditions. Nafion being a PFSA membrane, requires moisture to function properly. However, higher hydration levels also exacerbate back-diffusion. Therefore, a better candidate for ammonia compression could be a membrane that can operate at low humidity levels. Also, membrane chemistry could be optimized to enhance the conduction of ammonium ions while mitigating the diffusion of molecular ammonia. A thicker membrane could also reduce the rate of back-diffusion and improve the working process of compression.

3. Conclusion

This work discusses the advantages of an electrochemical ammonia compressor over a conventional mechanical compressor. Electrochemical compression hardware was used for the ECC of an ammonia-hydrogen blend; hydrogen was used as the carrier gas, which facilitates the generation of ammonium ions. The ECC was operated at various voltages using a single cell setup. When the cathode outlet is open, the amount of ammonia produced at the cathode is twice that of hydrogen. When the cathode is closed, the pressure rises rapidly and eventually plateaus to an equilibrium value. Similarly, the current is maximum at the start of the compression and drops to attain an equilibrium value. The quantification of cathode constituents during

equilibrium resulted in an ammonia:hydrogen ratio to be around 0.085, which is much smaller than the ideal value of 2. Separately conducted depressurization experiments for ammonia and hydrogen showed that the permeability coefficient of ammonia is about three orders of magnitude larger than that of hydrogen. This implies that ammonia back-diffuses much faster than hydrogen and hence, hydrogen contributes almost the entire cathode pressure. Successful ECC of ammonia would require an alternate membrane formulation that allows the forward transfer of ammonium ions while simultaneously reducing the back diffusion of molecular ammonia.

Acknowledgements

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