



Electrochemical ammonia compression†

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Every year a large amount of ammonia is mechanically compressed with a low efficiency (~65%) as an environmentally friendly chemical for fuel storage, transportation, food preservation and air conditioning. Electrochemical compression with a high efficiency (93%) offers an opportunity for substantial energy savings. But ammonia is never considered electrochemically compressible because of the known decomposition at high applied potentials. The concept of using a carrier gas to co-compress ammonia was proposed but never experimentally validated. Here for the first time, we realized electrochemical compression of ammonia by using a proton exchange membrane as an NH_4^+ conductor and hydrogen as a carrier to avoid decomposition. The ammonia transfer mechanism and kinetics in a Nafion membrane was investigated and verified using electro-analytical methods, and the continuous electrochemical ammonia compression at a constant voltage of 200 mV with a stable current density for 7 hours has been demonstrated. NH_4^+ transports in the Nafion membrane by hopping and vehicular mechanisms with a high NH_4^+ conductivity of $4 \times 10^{-2} \text{ S cm}^{-1}$ at 50% RH and 70 °C, and a constant transfer ratio of 2 between NH_3 and H_2 ensure a stable and high compression rate.

Ammonia is the second most produced chemical in the world. It is considered as a promising carbon neutral fuel for energy storage and delivery because of its low cost, high energy density, and facile storage as a liquid.¹ It is also used as an environmentally friendly refrigerant in a vapor compression refrigeration system. Ammonia can be either directly combusted as a fuel or indirectly consumed as a source of hydrogen for proton exchange membrane fuel cells (PEMFC).^{1,2} As a hydrogen carrier, ammonia plays an important role in advancing the frontier of fuel cell electric vehicles and hydrogen economy.³ Additionally, an ammonia related compound such as borazane is an effective hydrogen storage material for PEMFC at low temperatures.^{4,5}

Therefore it is critical to develop a simple and effective ammonia compression process to ensure efficient on-board ammonia storage and delivery. Currently, ammonia can only be mechanically compressed with a low efficiency around 65% for small or medium sized compressors.⁶ In contrast, the electrochemical compression can achieve a high isothermal compression efficiency of 93%. To date, hydrogen is the only electrochemically compressible gas reported in the literature.^{7–11} And ammonia is never considered electrochemically compressible due to decomposition. Bahar *et al.*¹² proposed a concept of using H_2 as a carrier to electrochemically compress ammonia. But there has been essentially no experimental study to demonstrate the feasibility of the concept, and no detailed study on an electrochemical compression mechanism. The previous research on NH_3 in the PEMFC system considered ammonia as a contaminant.^{13–16} Traces of ammonia introduced into the H_2 anode may not poison the Pt catalyst but reduce the proton conductivity of the Nafion membrane by forming NH_4^+ .^{13–16} Therefore, all the previous literature studies have focused on minimizing the NH_3 contamination and crossover, and there has been no detailed investigation on the electrochemical transfer of a large amount of ammonia across the membrane. But the formation of NH_4^+ in the Nafion membrane demonstrated the feasibility of electrochemical compression of NH_3 with H_2 as a carrier gas.

Here for the first time we electrochemically compressed ammonia by taking advantage of the H^+ interaction with NH_3 to form NH_4^+ (Fig. 1). When NH_3 and H_2 are fed to the anode, H_2 is electrochemically oxidized to H^+ on an anode Pt catalyst. NH_3 then combines with H^+ to form NH_4^+ . The overall process is shown in reactions (1) and (2).

Anode reaction:



NH_4^+ is then transported across the Nafion membrane at external voltage. At the cathode, NH_4^+ is converted back to

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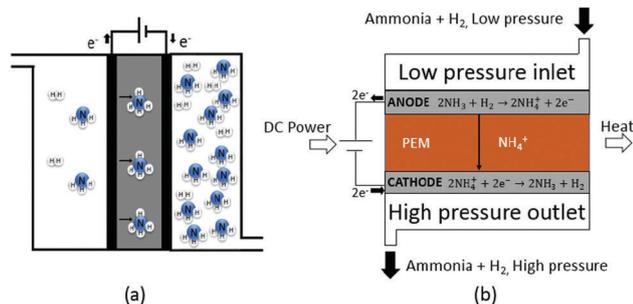


Fig. 1 (a) Electrochemical NH_3 compression using H_2 as a carrier gas. (b) Reaction mechanism, NH_4^+ travels across the membrane.

NH_3 and H^+ , H^+ is then electrochemically reduced back to H_2 on the Pt catalyst at higher pressure (reactions (3) and (4)).

Cathode reaction:



The standard voltage potentials for reactions (1) and (4) are the same as those for the hydrogen evolution reaction, which are normally smaller than 200 mV. Therefore NH_3 decomposition will not occur.¹⁵ The drag coefficient between NH_3 and H^+ is fixed at 1 due to the formation of NH_4^+ (reaction (2)). Therefore, the transfer ratio between NH_3 and H_2 is 2, since one hydrogen releases two protons. The overall compression reaction:



The schematic diagram of the electrochemical compression cell is shown in Fig. 2. The MEA is the commercially available product (Nafion 115). This simple compression device is in the solid state without moving parts, demonstrating a huge advantage over the state-of-the-art. The electrochemical compression efficiency is highly dependent on the NH_4^+ conductivity in electrolytes. The NH_4^+ conductivity in Nafion 115 at 30% and 50% relative humidity was measured using a standard 4-electrode device (BekkTech BT-112, Fig. S4 and S5, ESI[†]). The NH_4^+ conductivity in Nafion 115 in a temperature range between 35 °C and 70 °C at 30% and 50% RH is shown in Fig. 3. The NH_4^+ conductivity in Nafion 115 is in the range between 0.02 and 0.04 S cm^{-1} at 50% RH, which is 4–10 times lower than the conductivity of H^+ in Nafion at the same temperature and RH. These data agree with the NH_4^+ conductivity in a Nafion

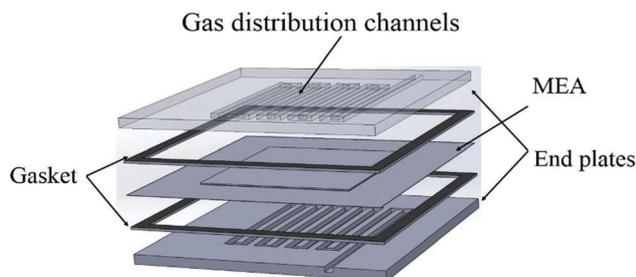


Fig. 2 Schematic diagram of segmented cell parts for electrochemical compression.

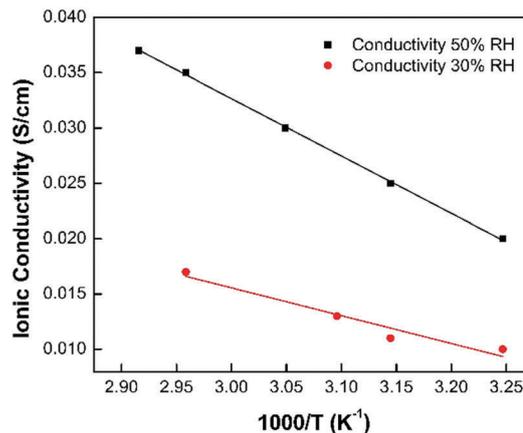


Fig. 3 The relationship between NH_4^+ conductivity in Nafion and temperature at 30% RH and 50% RH.

105 membrane reported by Uribe *et al.*, which is 0.033 S cm^{-1} .¹³ The reduced conductivity is due to the larger size of NH_4^+ than that of H^+ . Nevertheless, the high NH_4^+ conductivity in Nafion ensures the high kinetics for electrochemical NH_3 compression.

The mechanism of electrochemical NH_3 compression (reactions (1)–(4)) was investigated by feeding a gas mixture of NH_3 and H_2 to the anode side at varied molar ratios (from 1.0 to 4.0). The operating process schematic of electrochemical NH_3 compression is shown in Fig. S1 in the ESI[†] while the testing facility is shown in Fig. S2 (ESI[†]). The electrochemical NH_3 compression takes place upon operating the cell at a constant voltage, operated with a back pressure and the outlet gas stream is directed to gas chromatography (GC) and titration to determine the molar ratio between H_2 and NH_3 (Fig. S1 and S3, ESI[†]). GC gives an instantaneous composition of the outlet gas mixture, while titration determines the cumulative amount of ammonia over a period of time (5–10 min). Based on the proposed electrochemical reactions (1)–(4), the NH_3 and H_2 composition ratio in the EC outlet should always be maintained around 2. As shown in Table 1, second column, the measured ratio of NH_3 to H_2 in outlet gas ranges from 1.84 to 2.3 even when the feed gas ratio widely changed from 1.0 to 4.0, which is also backed up by titration measurements (Table S1, ESI[†]). The slight deviation of an outlet gas molar ratio from 2.0 was investigated and it is attributed to NH_3 crossover through the Nafion membrane due to the concentration gradient of the NH_3 between the inlet and the outlet. However, when a feed gas molar ratio is 1.0, H_2 is in excess based on reactions (1) and (2), and some NH_4^+ attached to the sulfonic acid group is exchanged by H^+ , therefore the outlet gas composition ratio is slightly less than 2.0.

Table 1 Comparison of the mixed gas in the inlet and outlet

Inlet ratio	Outlet gas composition ratio (NH_3/H_2) measured by GC	Outlet gas composition ratio adjusted
4.0	2.30	2.03
2.5	2.16	2.00
2.0	2.04	2.04
1.0	1.84	1.84

The amount of NH₃ and H₂ crossover in the Nafion membrane was measured using gas chromatography (GC) and the detailed deriving procedure is shown in the ESI† and Table S2. The anode and cathode were both maintained at around 1 atm during measurements. The adjusted ratio of NH₃ to H₂ is around 2.0 (Table 1, third column), which confirmed the compression reaction mechanism (reactions (1)–(4)). The NH₃ crossover in the Nafion membrane due to the concentration gradient is only 10% of the total NH₃ transfer. The H₂ crossover, however, is even much smaller than NH₃, due to the low solubility of H₂ in water (0.00016 g/100 g of water) compared to NH₃ in water (53 g/100 g of water).¹⁷ The ammonia crossover can be offset by increasing the cathode back pressure. When the compression takes place at a sealed cathode with back pressure, the concentration of H₂ and NH₃ on both sides of the membrane will reach equilibrium at the supplied voltage, satisfied by the Nernst equation. The concentrations on both sides are not expected to deviate from the initial values. NH₃ was reported to be electrochemically decomposed to N₂ and nitrogen oxide at potentials over 0.65V_{RHE}.¹⁵ However the oxidation/reduction of H₂ to protons requires smaller potential, due to the low activation over potential for the hydrogen evolution reaction (HER) on the anode and cathode side.¹⁸ Therefore NH₃ does not decompose during electrochemical compression, as evidenced by detection of no traceable N₂ GC. The formation of NH₄⁺ fixes the drag coefficient of NH₃ to H⁺ at 1, resulting in a constant transfer ratio between NH₃ and H₂ of 2 independent of the temperature. As shown in Fig. S6 (ESI†), the transfer ratio remains constant at temperatures ranging from 30 °C to 90 °C based on GC measurements. The relationship between the pressure ratio and voltage for electrochemical compression in a closed system should satisfy the Nernst equation when the system reaches the equilibrium, defined in eqn (6).^{18,19}

$$U_{\text{Nernst}} = E_0 + \frac{RT_{\text{EC}}}{nF} \ln \left(\left(\frac{P_{\text{H}_2, \text{outlet}}}{P_{\text{H}_2, \text{inlet}}} \right)^{\frac{1}{2}} \times \left(\frac{P_{\text{NH}_3, \text{outlet}}}{P_{\text{NH}_3, \text{inlet}}} \right) \right) \quad (6)$$

where the partial pressures of compressed hydrogen and ammonia at both the cathode (outlet) and anode (inlet) were measured and calculated, and n is the number of electrons each gas molecule releases, in our case $n = 1$ since one H⁺ combines with one NH₃ to form NH₄⁺. $T_{\text{EC}} = 40$ °C is the operating temperature of the device, and E_0 is equal to zero because the half reactions on both sides of the membrane are opposite. Once a voltage is charged to an EC with the cathode sealed, the current should gradually decrease to zero when equilibrium has been reached, and the compression ratio and voltage relationship can be obtained from eqn (6). However, for a continuous compression process at a constant voltage, the current gradually decreases to a steady-state value, which represents the flow rate across the EC membrane. The current density decreases with time at four different voltages in continuous compression processes are shown in Fig. S7 (ESI†), when the anode pressure is maintained around 0.1 MPa. Fig. 4 shows that the natural log scale of the partial pressure ratio follows a linear increase trend with respect to the cell voltage although the partial pressure ratio is lower than that calculated using Nernst equation (eqn (6)) for a sealed system due to

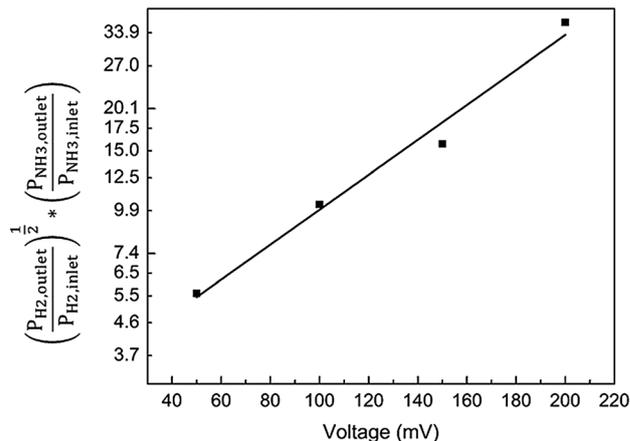


Fig. 4 Partial pressure ratio versus cell voltage based on the Nernst equation, where $P_{\text{outlet}}/P_{\text{inlet}}$ is the pressure ratio measured from the cathode and anode.

continuous compression flow. The cathode pressure increases with respect to time at each constant voltage operation in a continuous compression process are shown in the ESI† (Fig. S8–S11).

The compression efficiency at 50 mV is shown in Table 2, and the detailed calculations are shown in the ESI.† The efficiency would remain the same as EC is scaled up by stacking multiple units in parallel to increase the flow rates. Therefore the electrochemical ammonia compressor has an advantage over mechanical compressors in terms of efficiency. The NH₃ transfer rate is also measured in an open cell using titration over time and compared to the calculated rate using Faraday's Law (eqn (7)).²⁰

$$\frac{dn}{dt} = \frac{I}{nF} \quad (7)$$

where I is the current, n is the number of electrons released per gas molecule (n is 2 for H₂, and 1 for NH₃), and F represents Faraday's constant. As shown in Table S3 (ESI†), the flow rates measured are in the same order of magnitude as compared to the theoretical values. The small discrepancies between the theoretical and measured values are 16–18% for hydrogen and 22–25% for ammonia mainly due to the titration measurement error (shown in the table) and the crossover. The titration measured NH₃ flow rate is about 2 times as much as the measured H₂ flow rate, which further confirms the proposed reactions (1)–(4). The current density and voltage relationship determined by linear voltage sweep at 0.5 mV s⁻¹ from 50 mV to 200 mV is shown in Fig. S12 (ESI†). The linear sweep process is continuous without reaching the steady state. A similar technique was applied by Strobel *et al.* to understand the current density and voltage relationship for electrochemical hydrogen compression.⁹ In addition,

Table 2 Compression efficiency vs. voltage

Current density (A cm ⁻²)	Voltage charge (mV)	Nernst voltage (mV)	Cathode pressure (MPa)	Efficiency
0.010	50	47	0.28	93%

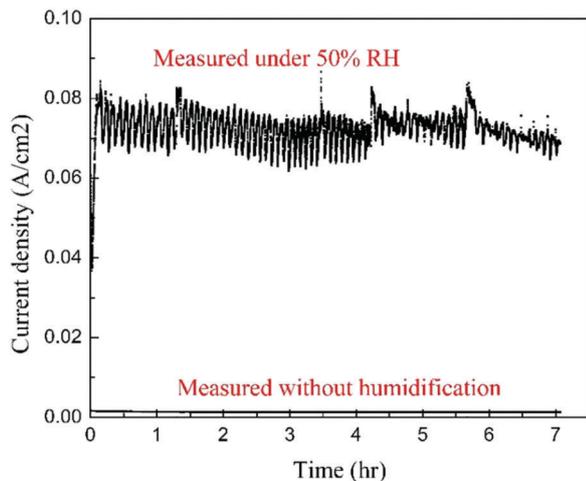


Fig. 5 Stabilized current density at a constant voltage of 200 mV measured over time with and without humidification (H_2 and NH_3 supplied to anode).

continuous electrochemical compression operation of 7 hours has been achieved with stable performance (Fig. 5).

Three mechanisms, including the Grotthuss mechanism, proton hopping and vehicular mechanism (mass diffusion), have been proposed for proton transfer in the Nafion membrane.²¹ While in the anion exchange membrane, hopping and vehicular mechanisms were determined for OH^- ions by Chen *et al.*²² Similarly, the transfer for NH_4^+ in Nafion may also be caused by hopping and vehicular mechanisms. The Grotthuss mechanism represents the H^+ mobility in water.²³ Without water, NH_3 alone cannot provide H^+ mobility in the Nafion membrane, as evidenced by almost zero current in electrochemical ammonia compression at a constant voltage with dry ammonia and hydrogen in Fig. 5. In contrast, a high current density of 0.07 A cm^{-2} is observed at 50% RH (Fig. 5). It is because water weakens the bonding between NH_4^+ and the Nafion sulfonic acid group (R-SO_3^-). The Nafion membrane was ion exchanged from H^+ to NH_4^+ by soaking in NH_3 solution, which gives the membrane an alkaline environment. H^+ does not exist in an alkaline environment. Therefore, the Grotthuss mechanism does not play a major role. Instead H^+ only transfers together with NH_3 in the form of NH_4^+ . Similarly, NH_3 transfer in the Nafion membrane is also facilitated by H^+ by forming NH_4^+ . If no H^+ is created by supplying H_2 on the anode, NH_3 alone cannot go through the membrane, which is verified by the very low current density measured by supplying humidified ammonia to the anode (Fig. S13, ESI[†]). The hopping mechanism represents the cation hopping between sulfonic acid groups on the membrane surface,²¹ which can be the transfer mechanism of NH_4^+ . The vehicular mechanism represents the mass diffusion of cations under external voltage influence, which may be one of the mechanisms NH_4^+ undergoes as well. The NH_3 in the Nafion membrane largely remains in an NH_4^+ form if NH_3 and H_2 are

continuously supplied to the anode side based on Le Chatelier's principle in reaction (2).

We successfully demonstrated electrochemical ammonia compression through Nafion with H_2 by forming NH_4^+ . The mechanism at both the anode and cathode is validated by (1) a fixed transfer ratio of 2 between NH_3 and H_2 molecules at the outlet which is independent of inlet composition as well as the operating temperatures, (2) the good agreement between the experimentally measured NH_3 and H_2 flow rates and the rates calculated from measured current using Faraday's Law. (3) The experimentally concluded hopping and vehicular transfer mechanisms of NH_4^+ in a proton exchange membrane. The high NH_4^+ conductivity in Nafion ensures a high compression efficiency of 93%. This technology can be applied to delivering compressed ammonia as a carbon neutral fuel. It can also be used to replace the mechanical compressor in the ammonia vapor compression refrigeration system.

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