Electronic supplementary information

Ammonia synthesis from water and nitrogen using electricity with hydrogen-permeable membrane electrochemical cell with Ru catalysts and molten hydroxide electrolyte: Integration with ammonia separation and unreacted gas recirculation.

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1. Vapor pressure of NH_3 in NH_3 separation system

The vapor pressure of NH_3 is the essential thermodynamic parameter for the gas/liquid separator. In the gas/liquid separator, the vapor pressure of NH_3 exists in the gas phase and the remaining portion of the NH_3 is liquefied. The vapor pressure curve of NH_3 is plotted in Fig. S1, where the individual data are obtained from NIST Chemistry Webbook.[1] In this study, the gas/liquid separator was kept at -75°C and NH_3 at 7 kPa remains in the gas phase.

2. Dissolution equilibrium of H_2O in NaOH-KOH

The electrolyte used in this study is a NaOH-KOH eutectic molten salt (1:1 molar ratio) in contact with humidified Ar. Since the melting point of the NaOH-KOH eutectic molten salt is 171°C, it remains in a liquid state under the experimental condition of 250°C. When this molten salt is exposed to a certain partial pressure of water vapor, it reaches a gas-liquid dissolution equilibrium. According to a literature on solubility, the dissolution equilibrium can be described by the following equation, with the Henry's law constant (k) being 0.0095 atm mol^{-1} kg at 250°C.[2-4]

$$P_{H2O} = k\, N_{H2O}$$

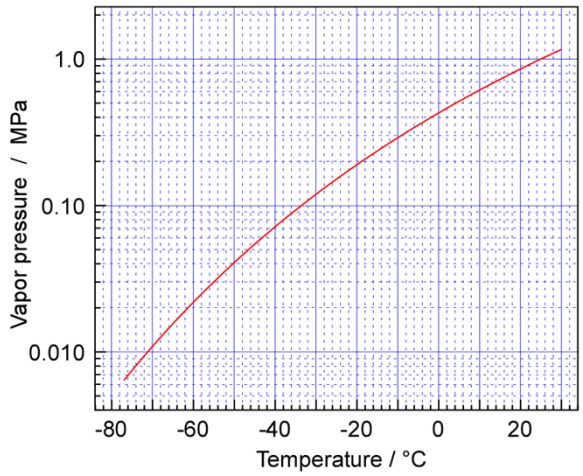

Fig. S1. Vapor pressure of NH_3 against temperature.

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Where P_{H2O} and N_{H2O} are partial pressure of H_2O in atm and amount of H_2O dissolved in melt in mol kg^{-1}. By plotting the amount (kg) of dissolved water against the amount (kg) of the NaOH-KOH eutectic molten salt as a function of the partial pressure of H_2O vapor and, Fig. S2 is obtained. In this study, the concentration of H_2O in Ar+H_2O is 38 vol%. From this graph, it is possible to determine how much water the NaOH-KOH eutectic molten salt contains under operating pressure condition. It should be noted that the data in the literature is for NaOH-KOH melt (63.1:36.9 mol%), so that the ratio of NaOH-KOH is not exactly same.

References

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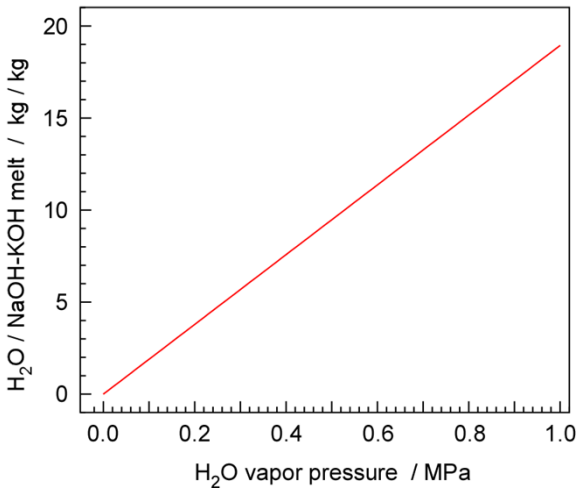

Fig. S2. Amount of H_2O dissolved in NaOH-KOH melt as a function of H_2O vapor pressure.