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Supplemental Information for

Opportunities for intermediate temperature renewable ammonia electrosynthesis

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Methods

Kinetic Considerations

The reaction rate of the thermochemical reduction of nitrogen to ammonia is calculated by a modified form of the Temkin equation[1,2]. Due to the high temperatures and pressures, the activities of the gases are used instead of the partial pressures.

$$R_{NH_3} = 2*k*[K_a^2*a_{N_2}*(\frac{a_{H_2}^3}{a_{NH_3}^2})^{\alpha} - (\frac{a_{NH_3}^2}{a_{H_2}^3})^{1-\alpha}] \tag{1}$$

where a_{H_2}, a_{N_2}, a_{NH_3}, k, K_a, and α are the activity coefficients for nitrogen (a_{N_2}), hydrogen (a_{H_2}) and ammonia (a_{NH_3}) (eqn. 3 - eqn. 6), rate constant for the reverse reaction (eqn. 8), reaction equilibrium constant (eqn. 7), and constant ($\alpha = 0.5$).

The activity of a component (a_i) is defined as the ratio between the fugacity of the component at a particular chosen state (f_i) to the fugacity of the pure component at ambient pressure and a temperature equal to the system (f_i^*).

$$a_i = \frac{f_i}{f_i^*} \tag{2}$$

Additionally, the activity of a component in a mixture can be calculated using the molar fraction of the component (y_i), the fugacity coefficient of the component (Φ), and the pressure at which the reaction takes place (P).

$$a_i = y_i*\Phi_i*P \tag{3}$$

The fugacity coefficients for nitrogen[3,4], hydrogen[3,5], and ammonia[3,4] can be calculated using the following equations:

$$\Phi_{N_2} = 0.93431737 + 0.3101804*10^{-3}*T + 0.295895*10^{-3}*P - 0.270729*10^{-6}*T^2 + 0.4775207*10^{-6}*P^2 \tag{4}$$

$$\Phi_{H_2} = exp[e^{(-3.8402*T^{0.125}+0.541)}*P - e^{(-0.1263*T^{0.5}-15.980)}*P^2 + 300*[e^{(-0.011901*T-5.941)}]*(e^{(-P/300)}-1)] \tag{5}$$

$$\Phi_{NH_3} = 0.1438996 + 0.2028538*10^{-2}*T - 0.4487672*10^{-3}*P - 0.1142945*10^{-5}*T^2 + 0.2761216*10^{-6}*P^2 \tag{6}$$

The reaction equilibrium constant (K_a) can be calculated using the following equation[6]:

$$log(K_a) = -2.691122*log(T) - 5.519265*10^{-5}*T + 1.848863*10^{-7}*T^2 + \frac{2001.6}{T} + 2.67899 \tag{7}$$

Finally, the reaction rate constant (k) is calculated as a function of temperature using the Arrhenius equation:

$$k = A*e^{\frac{-Ea}{RT}} \tag{8}$$

where A is the frequency factor, Ea is the activation energy for the reaction, R is the universal gas constant, and T is the temperature of the reaction. The values for the catalyst properties used for ammonia synthesis are shown in the table below.

Table 1 Catalyst Kinetic Properties[2]

α	A (kmol*m^{-3})	Ea (kJ*kmol^{-1})
0.5	8.8490*10^{14}	1.7056*10^{5}

Finally, the rate equations presented above result is a rate with units of $kmol*m^{-3}*h^{-1}$. We transformed this rate to the preferred units of $mol*g^{-1}*s^{-1}$ by using the catalyst density (2.35 g/cm^3)[7].

Here, we study the effect variations of the constant α have in the rate equation for thermochemical synthesis(Fig. 1). We find that larger values of α coefficients lead to larger reaction rates. However, the trends temperature and pressure are the same regardless of the value of the constant α. Hence, we find the use of a $\alpha = 0.5$ appropriate as it simplifies the calculations.

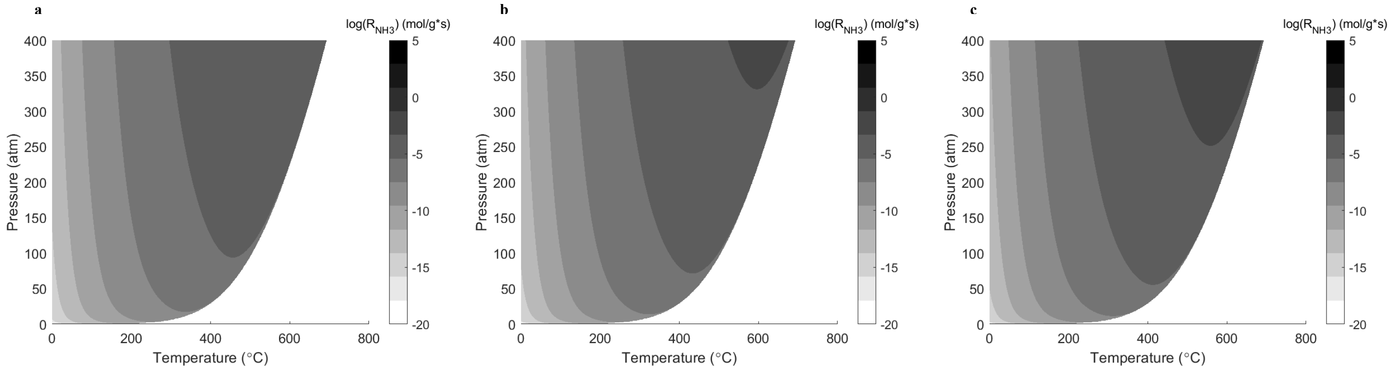

Fig. 1 Rate of ammonia produced at various temperatures and pressures for thermochemical synthesis with a constant $\alpha = 0.5$ (a), $\alpha = 0.6$ (b), and $\alpha = 0.7$ (c). The rate of the Haber-Bosch process is provided as a reference (red line)

For the electrochemical synthesis of ammonia, the rate is determined through the Butler-volmer equation

$$R_{NH_3} = k_c * e^{-\frac{\alpha*6*F*V}{R*T}} - k_a * e^{\frac{(1-\alpha)*6*F*V}{R*T}} \tag{9}$$

where k$_c$ and k$_a$ are rate constants for the reaction, F is Faraday's constant, α is the transfer coefficient, and V is the voltage. In order to find a parallel between the performance of electrochemical and thermochemical reactions we calculated the values for k$_c$ and k$_a$ using equation 12. The resulting equations used to calculate k$_c$ and k$_a$ are shown below:

$$k_c = 2 * k * K_a^2 * a_{N_2} * (\frac{a_{H_2}^3}{a_{NH_3}^2})^\alpha \tag{10}$$

$$k_a = 2 * k(\frac{a_{NH_3}^2}{a_{H_2}^3})^{1-\alpha} \tag{11}$$

Finally, the rate equations presented above result is a rate with units of $kmol * m^{-3} * h^{-1}$. We transformed this rate to the preferred units of $mol * g^{-1} * s^{-1}$ by using the catalyst density (2.35 g/cm^3)[7].

Here, we study the effect variations of the transfer coefficient have in the rate equation for electrochemical synthesis (Fig. 2) . We find that larger transfer coefficients lead to larger reaction rates. However, the comparison with the Haber-Bosch process (red line) falls in a similar location regardless of the transfer coefficient. Hence, we find the use of a symmetric transfer coefficient appropriate as it simplifies the calculations.

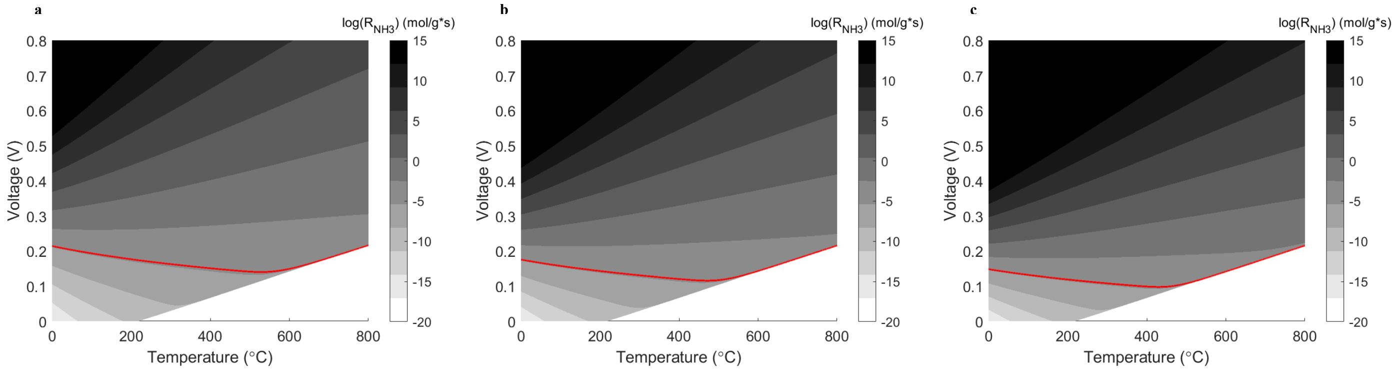

Fig. 2 Rate of ammonia produced at various temperatures and overpotential for electrochemical synthesis with a transfer coefficient (a) $\alpha = 0.5$, (b) $\alpha = 0.6$, and (c) $\alpha = 0.7$. The rate of the Haber-Bosch process is provided as a reference (red line)

Based on these calculations, the equivalent exchange current density is in the order of $10^{-8} A/cm^2$ at ambient temperatures.

$$i_o = n * k_c^{0.5} * k_a^{0.5} \tag{12}$$

where n is the number of electrons involved in the reaction (n = 6).

Energy Efficiency Considerations

Faradays law relates the current density (i) to the rate of ammonia produced (R_{NH_3}).

$$i = \frac{R_{NH_3} * n * F * m_l}{FE} \tag{13}$$

where R_{NH_3} is the production rate by unit mass of catalyst (mol/g*s), FE is the faradaic efficiency (as a decimal), n is the number of electrons per mole of ammonia (n = 3), F is Faraday's constant (F = 96,485 C/mol), m$_l$ is the catalyst loading (m$_l$ = $10^{-3} g/cm^2$).

The cell voltage is a combination of the open circuit voltage (V$_{OCV}$) and the cell overpotential (η_{total}) (the cell overpotentials are described in the following section and depend on the current density).

$$V = V_{OCV} + \eta_{total} \tag{14}$$

In an electrochemical system, the open circuit voltage (OCV) of the reaction is defined as the change in the Gibbs free energy (ΔG) divided by the number of electrodes involved in the reaction (n = 3) and the Faraday's constant (F = 96,485 C/mol).

$$V_{OCV} = \frac{\Delta G}{nF} \tag{15}$$

The reversible energy demand for an electrochemical reaction corresponds to the change in enthalpy of the reaction (ΔH), which is a combination of the electrical energy demand or the change in the Gibbs free energy (ΔG) and the thermal energy demand which is the change in the product's temperature times the entropy of the system ($T\Delta S$).

$$\Delta G = \Delta H - T\Delta S \tag{16}$$

The energy efficiency of the system (as a decimal) can be related to the rate of production, current density, and voltage.

$$\eta_{EE} = \frac{LHV * R_{NH_3} * m_l}{i * V + Q_{in}} \tag{17}$$

where LHV is the lower heating value of ammonia (318,000 J/mol), R_{NH_3} is the rate per unit mass of catalyst, m$_l$ is the catalyst loading (m$_l$ = $10^{-3} g/cm^2$), i is the current density, V is the cell voltage, and Q_{in} is the heat required to heat the reactants (N_2 and H_2O) to the operating temperature.

The heat required for the reactants to heat the reactants (Q_{in}) depends on the operating temperature of the electrolyzer, the molar flow of reactants, and the specific heat of the reactants.

$$Q_{in} = \dot{N}_{N_2} * Cp_{N_2} * \Delta T + \dot{N}_{H_2O} * Cp_{H_2O} * \Delta T \tag{18}$$

where Cp_{N_2} and Cp_{H_2O} are the specific heats for nitrogen gas and water vapor (Cp_{N_2} = 30 J/mol*K and Cp_{H_2O} = 37 J/mol*K). The molar flow of the reactants ($\dot{N}_{N_2}$ and $\dot{N}_{H_2O}$) depends on the molar flow of ammonia and the faradaic efficiency.

$$\dot{N}_{N_2} = \frac{R_{NH_3}}{2} \tag{19}$$

$$\dot{N}_{H_2O} = \frac{R_{NH_3} * 3}{2 * FE} \tag{20}$$

where R_{NH_3} is the molar flow of ammonia and FE is the faradaic efficiency as a decimal.

Finally, the change in temperature (ΔT) is the difference between the operating temperature and the ambient temperature ($T_{ambient}$ = 25 $°C$).

$$\Delta T = T - T_{ambient} \tag{21}$$

Electrolysis Cell Overpotentials

The energetic losses in an electrochemical reactor can be characterized by the reaction overpotentials and the operating current. The total cell overpotentials include the activation overpotential (η_{act}),the ohmic overpotential (η_{ohm}), and the concentration overpotential (η_{conc}).

$$\eta_{total} = \eta_{act} + \eta_{ohm} + \eta_{conc} \tag{22}$$

The activation overpotential (η_{act}) can be approximated using the Butler-Volmer equation. As discussed in the previous section, we have assumed that the reaction has symmetric electron transfer coefficient ($\alpha = 0.5$). This assumption is done to simplify the calculations.

$$\eta_{act} = \frac{RT}{n\alpha F} * sinh^{-1}(\frac{i}{2i_{0,c}}) + \frac{RT}{n\alpha F} * sinh^{-1}(\frac{i}{2i_{0,a}}) \tag{23}$$

where R is the universal gas constant (8.314 J/mol*K), F is the Faraday's constant, T is the reactor operating temperature, n is the number of electrons involved in the reaction (n = 6 for the cathodic reaction of NRR and n = 4 for the anodic reaction of OER), α is the electron transfer coefficient ($\alpha = 1/2$), i is the operational current and i_0 is the exchange current density. The exchange current density represents the electrode's readiness to initiate the reaction and it depends in the electrode's geometry and composition.

The exchange current density of a reaction improves with temperature. The relationship between the exchange current density and temperature can be modeled using the following equation:

$$i_0 = i_0^{ref} * exp((-Ea/(R*T)) * (1-(T/T_{ref})) \tag{24}$$

where i_0^{ref} is the reference exchange current density at ambient temperature, Ea is the activation energy (1.03*10^5 kJ*$kmol^{-1}$), R is the universal gas constant, T is the operating temperature, and T_{ref} is the reference temperature (T_{ref} = 298K). The cathode reference exchange current density ($i_{0,c}^{ref}$) varies between $10^{-9} A/cm^2$ and $10^{-11} A/cm^2$. The anode reference exchange current density ($i_{0,a}^{ref}$) is kept constant at $10^{-9} A/cm^2$.

The ohmic overpotential (η_{ohm}) can be described by the Ohm's law

$$\eta_{ohm} = i * R_{electrolyte} \tag{25}$$

where $R_{electrolyte}$ is the area specific resistance of the electrolyte. The area specific resistance of an electrolyte is

$$R_{electrolyte} = \frac{1}{\sigma} * L \tag{26}$$

where σ is the electrolyte conductivity and L is the electrolyte thickness. For low temperature electrosynthesis we used the conductivity of a Nafion membrane. For a fully humidified proton exchange membrane made of Nafion, the conductivity can be approximated by the following equation[8].

$$\sigma = 0.1098 * e^{1268*(\frac{1}{303} - \frac{1}{T})} \tag{27}$$

For solid electrolytes for intermediate temperature operations we used the relationship of conductivity and temperature shown in Figure 3[9].

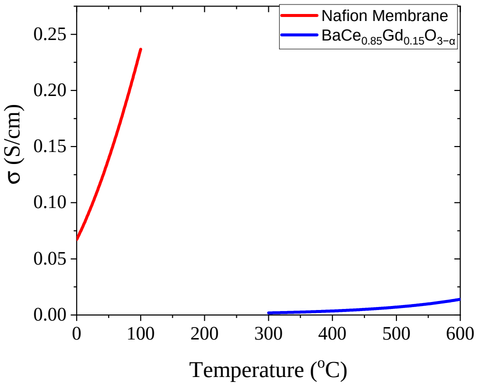

Fig. 3 Conductivity of electrolytes used at different operating temperatures

Finally, we assume that the concentration overpotential (η_{conc}) is negligible when compared to the other overpotentials at the studied current densities.

For Figure 3a, the lower edge of shaded region assumes the reference exchange current density is 10^{-9} A cm^{-2}, the middle of the shaded region assumes the reference exchange current density is 10^{-10} A cm^{-2}, the upper edge of the shaded region assumes a reference exchange current density of 10^{-11} A cm^{-2}. In each case, the liquid electrolyte ionic conductivity is 0.8 S cm^{-1}, the Nafion ionic conductivity is 0.1 S cm^{-1}, and the electrolyte thickness is 60 μm. The lower edge of the blue shaded region assumes a cell only with liquid electrolyte, the middle line assumes a cell only with a Nafion membrane, and the upper edge assumed a cell with a liquid electrolyte and a Nafion mebrane.

For Figure 3b, the lower edge of shaded region assumes the reference exchange current density is 10^{-9} A cm^{-2}, the middle of the shaded region assumes the reference exchange current density is 10^{-10} A cm^{-2}, the upper edge of the shaded region assumes a reference exchange current density of 10^{-11} A cm^{-2}. In each case the electrolyte ionic conductivity ranged from 0.014 S cm^{-1} at the upper edge to 0.05 S cm^{-1} lower edge, and the electrolyte thickness was 50 μm.

Notes and references

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