Inorganic Chemistry

Communication

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Advances in Understanding the Mechanism and Improved Stability of the Synthesis of Ammonia from Air and Water in Hydroxide Suspensions of Nanoscale Fe_2O_3

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Supporting Information

ABSTRACT: We report a mechanism of electrochemical ammonia (NH_3) production via an iron intermediate in which H_2 and NH_3 are cogenerated by different electron-transfer pathways. Solar thermal can contribute to the energy to drive this synthesis, resulting in a STEP, solar thermal electrochemical process, for NH_3. Enhancements are presented to this carbon dioxide (CO_2)-free synthesis, which uses suspensions of nano-Fe_2O_3 in high-temperature hydroxide electrolytes at nickel and Monel electrodes. In a 200 °C molten eutectic $Na_{0.5}K_{0.5}OH$ electrolyte, the 3 Faraday efficiency per mole of synthesized NH_3, η_{NH_3}, increases with decreasing current density, and at $j_{electrolysis}$ = 200, 25, 2, and 0.7 mA cm^{-2}, η_{NH_3} = 1%, 7%, 37%, and 71%, respectively. At 200 mA cm^{-2}, over 90% of applied current drives H_2, rather than NH_3, formation. Lower temperature supports greater electrolyte hydration. At 105 °C in the hydrated $Na_{0.5}K_{0.5}OH$ electrolyte, η_{NH_3} increases and then is observed to be highly stable at η_{NH_3} = 24(+2)%.

A low-carbon-footprint alternative is needed for the Haber–Bosch process to mitigate associated climate effects. We recently presented a carbon dioxide (CO_2)-free electrochemical pathway in which ammonia (NH_3) is produced by electrolysis of air and steam in a molten hydroxide suspension of nano-Fe_2O_3.[1] Haber–Bosch production of NH_3 is one of the world's most pervasive industrial processes, but it is energy-intensive and has a high carbon footprint, so an alternative is needed.[2,3] The process annually converts over 120 million tonnes of N_2 from the atmosphere[3] while emitting 200 million tonnes of CO_2.[4] Increased production of synthetic NH_3 for fertilizer parallels the explosive increase in the world population from 2 billion in 1930 to 7 billion today. The process is the origin of approximately one in two nitrogens within our bodies (microorganism nitrogen fixation is the other source). Currently, 0.7–0.8 CO_2 are emitted per NH_3 produced.[4]

Several electrochemical processes have been pursued for consideration as alternative syntheses of NH_3.[1,5−8] We observed high NH_3 generation rates when a 200 °C molten hydroxide (NaOH/KOH) electrolyte is mixed with high-surface-area Fe_2O_3, and N_2 and water vapor are electrolyzed in the cell (between a planar nickel anode and a mesh nickel–Monel cathode). Both water-saturated, CO_2-scrubbed air and 99.999% N_2 yielded similar efficiencies of NH_3 generation.[1]

The observed efficiency of NH_3 formation by electrolysis was lower at higher current densities. NH_3 by electrolysis refers to the global reaction of N_2, water, and electrons to form NH_3 (and oxygen). The efficiency, η_{NH_3}, is calculated based on the moles of electrons consumed compared to the $3e^-/NH_3$ equivalents generated. At higher current densities, the electrolysis cogenerates H_2. At 200 °C in a eutectic $Na_{0.5}K_{0.5}OH$ electrolyte with suspended nano-Fe_2O_3, we observed that 2 mA cm^{-2} NH_3 is produced at a Coulombic efficiency of η_{NH_3} = 35%, which decreases to 7% at 25 mA cm^{-2}.[1] Constant current electrolysis at 2 or 25 mA cm^{-2} is driven respectively at 1.2 or 1.4 V, producing NH_3 at maximum respective rates of 2.4×10^{-9} and 6.7×10^{-9} mol of NH_3 s^{-1} cm^{-2}. Here we show conditions of improved rates, Coulombic efficiency, and stability of NH_3 production. Details of the measured NH_3 formation rate and electrolysis efficiency are delineated in the Supporting Information.

The left side of Figure 1 presents the observed rate of NH_3 formation at high current 2000 mA (200 mA cm^{-2}) from N_2 and water using a 10 cm^2 nickel anode and a 10 cm^2 Monel mesh cathode. At 200 mA cm^{-2}, NH_3 is formed at 2.4 V in molten $Na_{0.5}K_{0.5}OH$ with suspended nano-Fe_2O_3 at 200 °C. The electrolysis is water-limited, constrained by the maximum solubility of water (∼10% by weight) in this molten hydroxide at 200 °C. Despite bubbling of water-vapor-saturated N_2 into the cell, the system dehydrates over time. As seen when water is added at the seventh hour (15 g of water added to the initial 70 g of hydroxide electrolyte), the rate of NH_3 production doubles compared to that in hours 4–6. Another path to hydrate the system is through lowering of the temperature, which supports higher dissolution of water in alkali hydroxide. At 105 °C, the NH_3 synthesis was conducted in both 30% (by mass) water in $Na_{0.5}K_{0.5}OH$ and 50% water in CsOH. As seen on the right side of Figure 1, the higher fraction of allowed water at 105 °C yields up to double the observed NH_3 generation rate compared to 200 °C. At 105 °C and 200 mA cm^{-2}, NH_3 is formed at 2.5 or 2.3 V respectively in $Na_{0.5}K_{0.5}OH$ containing 30% water or in CsOH containing 50% water.

In Figure 1 at the lowest applied current of 0.7 or 1 mA cm^{-2} (7 or 10 mA over 10 cm^2), the NH_3 production rate is stabilized. Interestingly, at this low current, only NH_3, and *no* H_2, product is detected. The lack of a cogenerated H_2 is related to the

Received: August 19, 2014
Published: September 23, 2014

dx.doi.org/10.1021/ic5020048 | *Inorg. Chem.* 2014, 53, 10042−10044

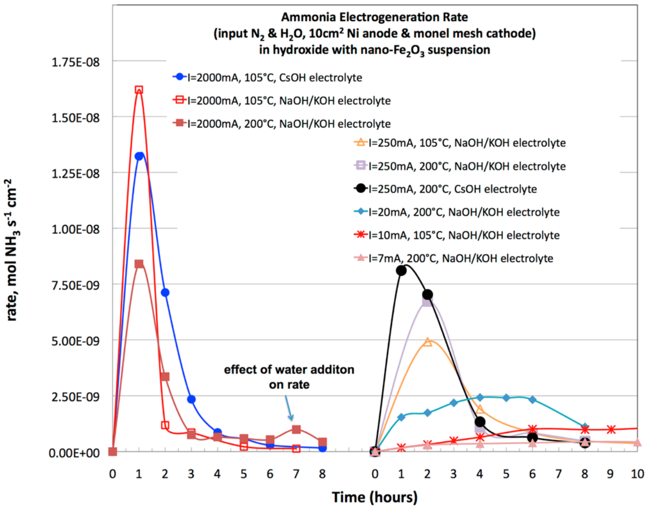

Figure 1. NH_3 formation rate by electrolysis from N_2 and water in suspensions of nano-Fe_2O_3 in a hydroxide electrolyte. In this one-pot synthesis, water-saturated N_2 gas was bubbled into the electrolyte, and a constant current was applied between 10 cm^2 nickel−Monel electrodes. The NH_3 product was quantitatively compared to the applied integrated electrolysis charge to determine the NH_3 production rate.

electrolysis potential, observed to be 1.2 V at 1 mA cm^{-2} in this 105 °C $Na_{0.5}K_{0.5}OH$ with 30% water electrolyte. This value equals the thermodynamic potential of 1.2 V for water splitting at this temperature and is too low to supply the additional overpotential that is necessary to drive the formation of H_2. At lower current, even at 200 °C, the electrodes without activation act in a sluggish manner and the observed efficiency is $\eta_{NH_3} = 18\%$ at 7 mA (0.7 mA cm^{-2}). However, when the electrodes are activated by a short burst of current, the maximum electrolysis rate of NH_3 formation is significantly higher, specifically 3-fold higher subsequent to a 30 min 250 mA current burst. In both the 15 and 30 min current-burst experiments in Figure 2, care was taken to flush the system (with NH_3 and no applied current) to ensure that all current-burst NH_3 produced was exhausted in the water trap prior to the initiation of electrolysis. The current efficiency of NH_3 formation is 51% subsequent to a 15 min 250 mA current burst, and the efficiency is 71% subsequent to a 30 min 250 mA current burst. Without the current burst, or subsequent to the current burst, the electrolysis at a constant current of 7 mA occurs at 1 V in the 200 °C molten $Na_{0.5}K_{0.5}OH$ electrolyte, and unlike at higher applied current densities, H_2 is not cogenerated with the NH_3 product. Specifically, the potential gradually increases from 1.00 to 1.04 during the first 8 h of electrolysis and then increases gradually to 1.18 V by hour 20.

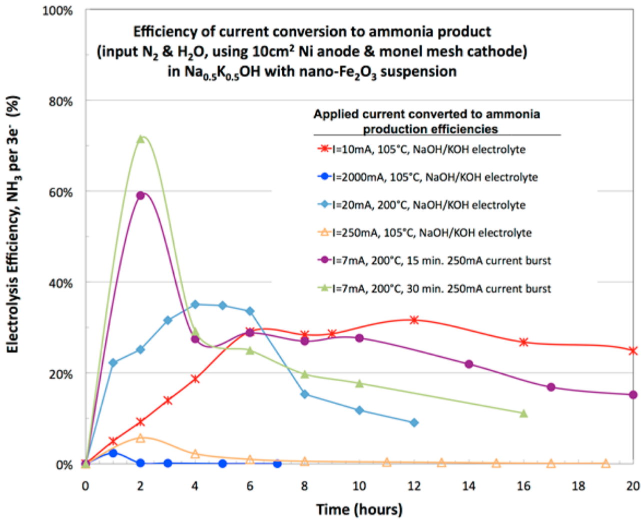

Figure 2. Charge efficiency, η_{NH_3}, of NH_3 formed by electrolysis of N_2 and water in suspensions of nano-Fe_2O_3 in molten $Na_{0.5}K_{0.5}OH$ electrolytes. To measure η_{NH_3}, the analyzed NH_3 product is compared to the applied, integrated electrolysis charge.

Figure 2 probes the stability of the NH_3 electrolysis efficiency over 20 h. Lower current density and lower temperature improve the stability of the rate of NH_3 formation, and the rate subsequent to the shorter current burst is more stable than that after the higher duration current boost. At 10 mA and 105 °C, the NH_3 electrolysis efficiency increases over the first 5 h (without current-burst activation) and is nearly stable at 24(+2%) over the next 15 h of electrolysis.

To synthesize NH_3 by electrolysis in hydroxide, water, N_2 (or air), and nanoscopic Fe_2O_3 are simultaneously required. The rates and electrolysis potentials at which H_2 formed hydroxide are not significantly perturbed when nanoscopic iron oxide is suspended in the electrolyte.[1] No H_2 is generated at potentials of less than the thermodynamic water potential. At higher electrolysis potentials, cogenerated H_2 formed by water splitting does not appear to significantly participate in the observed NH_3 formation process. Interestingly and was previously evidenced,[1] the potential of H_2 evolution is not affected, and the H_2 rate is only diminished by the extent of NH_3 evolution.

Without an applied electrolysis current, *no* significant chemical reaction is observed to occur between either N_2 and H_2 or N_2 and water in the presence of Fe_2O_3. Alternatively, we observe that iron metal powder, N_2, and water chemically react to form NH_3; the reaction accelerates with decreasing iron particle size. Specifically, water-saturated N_2 was bubbled into a 200 °C molten $Na_{0.5}K_{0.5}OH$ electrolyte containing either ∼70 μm, 1−3 μm, or 10−30 nm iron powder. With ∼70 μm iron, NH_3 was formed at 3.4×10^{-7} mol of NH_3 h^{-1} per g of the iron powder during the first 2 h, decreasing to 0.87×10^{-7} after 14 h. With 1−3 μm iron, the NH_3 formation rate was 3.6×10^{-5} mol of NH_3 h^{-1} g^{-1} during the first 2 h, decreasing to 0.21×10^{-5} after 16 h and to 0.0054×10^{-5} after 26 h. With 10−30 nm iron, the reaction was too fast and violent to be measured, forcing molten electrolyte into the gas outlet of the reaction chamber.

The experimental observations are consistent with an NH_3 formation mechanism in alkali hydroxide media, in which the iron oxide is reduced at the cathode and chemically reacts with the N_2 and water as

$$\text{cathode:} \quad Fe_2O_3 + 3H_2O + 6e^- \rightarrow 2Fe + 6OH^- \tag{1}$$

$$\text{chemical:} \quad 2Fe + 3H_2O + N_2 \rightarrow 2NH_3 + Fe_2O_3 \tag{2}$$

$$\text{anode:} \quad 6OH^- \rightarrow \frac{3}{2}O_2(g) + 3H_2O + 6e^- \tag{3}$$

$$\text{net:} \quad N_2 + 3H_2O \rightarrow 2NH_3 + \frac{3}{2}O_2 \tag{4}$$

Preferential electron transfer from iron to nitrogen is discussed in the Supporting Information. At high current densities, water splitting and the iron cathodic reaction run concurrently to cogenerate H_2 and NH_3 (and anodic O_2). At low current densities (at potentials less of than or equal to the water-splitting potential), only the iron cathodic reaction (1) contributes to the electrolysis. In this case, NH_3 and not H_2 is formed. Above the water-splitting potential, the global reaction also forms zH_2 from $2NH_3 + zH_2$ using $6 + 2z$ electrons, in the presence of nano-Fe_2O_3:

$$N_2 + (3 + z)H_2O \rightarrow 2NH_3 + zH_2 + \frac{3 + z}{2}O_2 \qquad (5)$$

Using the known enthalpy and entropy of the product and reactant species, we have recently calculated that the thermodynamic conditions in the reactions of water and air to form NH_3 and H_2 are endothermic and will benefit from the introduction of heat into the system.[1] Previous studies delineate outdoor solar experiments that use such endothermic elevated temperature conditions for our solar thermal electrochemical process (STEP). STEP has demonstrated that sub-band-gap solar thermal energy in sunlight is sufficient to heat and drive a variety of chemical reactions that would be energetically forbidden at lower temperature. STEP uses solar thermal energy to facilitate the electrochemical synthesis of societal staples, carbon capture, and water treatment without CO_2 emissions.[9−14] In ongoing experiments, the new NH_3 electrolyzer will be integrated into our outdoor STEP test heliostat platform.[12] The platform consists of a 39% efficient Spectrolab CPV with maximum power at 2.7 V, sufficient to drive two (at 1.35 V) or three (at 0.9 V) in-series solar-thermal-heated NH_3 electrolyzers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental methods and extended discussion and data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Partial support of this research was provided by NSF Grant 123072.

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