Solar electrochemical thermal process (STEP) ammonia: 
Optimization of the electrolysis conditions

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Abstract

In the solar thermal electrochemical process (STEP), sunlight is split into visible (for photovoltaic electricity) and thermal (unused, sub-bandgap) radiation using the full solar spectrum to efficiently drive high temperature electrolyzes. Electrolysis conditions for STEP ammonia are investigated. A mixed molten carbonate/hydroxide electrolyte with iron oxide catalyzes ammonia formation from water (steam) and air (nitrogen) via an iron intermediate. The higher temperature required for effective iron formation needs to be balanced by the lower temperature for effective hydration of the electrolyte. STEP ammonia is illustrated at a nickel anode and steel cathode at 650 °C in Li1.6Ba0.3Ca0.1CO3 with 6m LiOH and 1.5m Fe2O3.
The Haber-Bosch ammonia process uses $\text{H}_2$ as a reactant, principally produced by natural gas steam reformation ($\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow 4\text{H}_2 + \text{CO}_2$). Ammonia production was $1.45\times10^8$ tons in 2014; emitted $2\times10^8$ tonnes of the greenhouse gas $\text{CO}_2$. Ammonia is a critical resource to produce the world’s fertilizer. $^2$ CO$_2$-free alternatives are needed to synthesize ammonia directly from air and water. $^3-9$ We utilized Fe$_2$O$_3$ as an electrocatalyst in molten hydroxides for such an electrolysis. $^4$ Metallic iron was determined as the chemical intermediate, $^8$ and the Fe$_2$O$_3$ ammonia electrocatalyst can be isolated on activated carbon. $^9$

We introduced an alternative solar energy conversion, STEP (solar thermal electrochemical process) to drive CO$_2$-free chemical syntheses. $^{10-12}$ For example, STEP cement converts limestone to lime without CO$_2$ emission, $^{12,13}$ similarly STEP fuels, $^{14-18}$ STEP iron, $^{19-23}$ STEP carbon, $^{14,24-33}$ etc. $^{34,35}$ STEP uses full insolation, including solar thermal, driving hot electrolysises to desired products. Solar to chemical efficiencies as high as 50% have been observed for CO$_2$ splitting using photovoltaics and applying their (unused) solar thermal lowering the electrolysis potential. $^{14}$

STEP ammonia combines our previous STEP iron (electrolysis of iron oxide to iron in molten salts) and ammonia (electrolysis of air, $\text{N}_2$, and water to ammonia) chemistries as illustrated in Figure 1. Incident sunlight is split into PV visible and thermal (unused, sub-bandgap) radiation. The solar thermal component heats the electrochemical couple, while the solar PV visible component generates electronic charge to drive electrolysis of the heated electrochemical redox couple. The electrolysis forms anodic oxygen, and cathodic iron (from Fe$_2$O$_3$) which reacts with water and nitrogen to form ammonia (and Fe$_2$O$_3$, renewed to iron in the next cycle).

In this communication, we focus on the electrolysis component for STEP ammonia. STEP requires high temperature with molten carbonate to deposit and reform the iron catalyst necessary for sustainable iron. $^{19-23}$ Molten hydroxide can be added to establish a foundation for proton availability ($2\text{MOH} \rightleftharpoons \text{M}_2\text{O} + \text{H}_2\text{O}$). However, high temperature dehydrates the electrolyte. Here, a “goldilocks” intermediate temperature range is established in which STEP ammonia is sustainable in a mixed molten carbonate/hydroxide electrolyte. High electrolysis currents ensure small, reactive iron particles facilitating higher rates of ammonia generation.
Figure 1. STEP ammonia. Incident sunlight is concentrated and split. The visible is incident on a solar cell, such as a CPV, which drives an electrolysis chamber heated by the solar thermal. The electrolysis drives iron formation from Fe$^{3+}$, reacting with nitrogen and water to ammonia.

**Experimental**

From Alfa Li$_2$CO$_3$, Li$_2$O, LiOH, BaCO$_3$, and CaCO$_3$ are combined to form various molten electrolytes. Fe$_2$O$_3$ was added to the molten electrolytes.

The electrosynthesis chamber comprises cathode and anode in a molten carbonate mixture housed within an alumina crucible sealed to allow gas inlet and outlet; reactants: mixed air and water vapor are bubbled in. The anode and cathode are wound Ni and steel wire positioned horizontally and separated by 1cm. $^4$ Electrolyzes are driven galvanostatically.

The combined gas products exit through the chamber head space, and are sparged through an ammonia trap consisting of a 500mL 0.001M H$_2$SO$_4$ solution, changed regularly for ammonia analysis. Ammonia concentration was determined redundantly by: (1) UV/vis absorption, (2) potentiometric analysis and (3) test strips as previously described.$^8$
Results and Discussion

Nanoparticles of Fe$_2$O$_3$ catalyse ammonia generation with air and steam during molten hydroxide electrolysis: $^{4,8}$

Electrochemical: Fe$_2$O$_3$ → 2Fe+3/2O$_2$ [1]
Chemical: 2Fe + N$_2$ + 3H$_2$O → 2NH$_3$+ Fe$_2$O$_3$ [2]
Net: N$_2$+3H$_2$O → 2NH$_3$+ 3/2O$_2$ [3]

Fe$_2$O$_3$ is highly insoluble in hydroxide electrolyte and the iron oxide pathway of ammonia generation decreases in time as the integrity of the reformed Fe$_2$O$_3$ particles degrades. $^{4,8,9}$ Another pathway is Li$_2$CO$_3$ is to enhance the electrolytic solubility of ferric species, to permit the sustained, renewable cathodic growth of iron catalysts for ammonia electrocatalysis. We had separately demonstrated, STEP iron occurring in lithiated molten carbonate electrolytes. $^{19-23}$ Fe$_2$O$_3$ has low solubility (on the order of ppm) in molten Na/KOH carbonates, but Li$_2$O is soluble, forms highly Fe$^{3+}$ in Li$_2$CO$_3$, and can form metallic iron at the cathode by electrolysis in which there is no net consumption of Li$_2$O: $^{20}$

Dissolution: Fe$_2$O$_3$ + Li$_2$O* → 2LiFeO$_2$* (*soluble in molten Li$_2$CO$_3$) [4]
Electrolysis: 2LiFeO$_2$ → 2Fe + Li$_2$O + 3/2O$_2$ [5]
Net: Fe$_2$O$_3$ → 2Fe + 3/2O$_2$ [6]

STEP iron deposited particle size is inversely proportional to applied electrolysis current; low current density electrolysis 20mA cm$^{-2}$ form 500 µm particles, while high 1Acm$^{-2}$ produces 10 µm iron particles; shorter electrolysis time and added Li$_2$O further decreased the observed iron size. $^{23}$

A combination of the observed production of ammonia in molten hydroxides from water and nitrogen, combined with the efficient production of small particle iron catalysts in molten carbonates, suggests a mechanistic pathway for the STEP production of ammonia. However, molten hydroxides dehydrate at higher temperature, $^{18}$ while molten carbonates iron reduction is ineffective at lower temperatures. $^{22}$ Here, three molten carbonate electrolytes and temperature domains are explored: a low temperature domain window (< 400°C) opened up
by use of a low melting point mixed alkali (Li,Na,K,CO) carbonate eutectic, a high
temperature domain electrolyte based on the higher melting point Li,CO (mp 723°C), and an
intermediate alkali earth/ Li,CO mix functional as an electrolyte in the 600°C range. The
potassium component of a Li,Na,K,CO is corrosive to the oxygen evolving anode,35 rate.

Unlike, K,CO, and as with Li,CO, neither calcium nor barium carbonate are
corrosive to nickel.24,35 LiOH and Ba(OH) maintain better hydration at higher temperature,
leading to higher coulombic efficiencies for water electrolysis than sodium and potassium
hydroxide electrolytes.18 BaCO and Li,CO are fully miscible and exhibit a eutectic melting
point of 609°C.24 Here, 650°C mixtures of Li, Ba, Ca,CO, with 6m LiOH, and 1.5m Fe,O, are
explored at electrolysis currents of either 0.25A or 2.5A applied (J, current density, =
0.5A or 0.05Acm); higher J can decrease the iron catalyst particle size formed at the cathode.
Figure 2 presents SEM of the high current electrolysis iron product. The product is 2-10 µm
in size, and the effect of water from the 2LiOH to LiO equilibria induces an overlayer of
Fe,O (EDS analysis, and octahedral magnetite).

**Figure 2.** SEM of the iron product after 2.5A 650°C Li, Ba, Ca,CO, electrolysis with 6m
LiOH and 1.5m Fe,O, iron is analyzed titrametrically and by PHENOM EDS SEM.
Cathodic iron and octahedral magnetite, Fe,O are observed.32 The effect of water is evident
as oxidized iron.

Eutectic mixes of alkali cations, as binary and ternary carbonates, provide a path to
decrease carbonate’s melting point. As an alternative to maintain hydration electrolyses were
studied at lower temperature, 370°C molten Li,Na,K,CO with 6m (m =moles/kg
carbonate) LiOH, and 0.5m Fe$_2$O$_3$. (i) The added Fe$_2$O$_3$ was observed to be a suspension and not to be soluble and (ii) as shown in Figure 3 the measured generation ammonia rate was low and fell over time. A higher temperature 480°C run caused nearly complete anode loss in the Li$_x$Na$_y$K$_z$CO$_3$/LiOH/Fe$_2$O$_3$ consistent with K$_2$CO$_3$ additive nickel corrosion.$^{35}$

![Ammonia Electrogeneration Rate](image)

**Figure 3.** The rate of ammonia formation by electrolysis at low and intermediate temperatures in mixed hydroxide/carbonate electrolytes containing Fe$_2$O$_3$.

Ammonia electrolysis was investigated in Li$_2$CO$_3$ based electrolytes in higher temperature domains (such as > 700°C) in which STEP Iron remains effective. However under such higher temperature conditions, while high coulombic efficiencies of the reduction of iron oxide to iron metal are achieved, water availability for the ammonia reaction becomes less available. For example, in pure LiOH, due to dehydration, the coloumbic efficiency of water splitting drops from over 90% at 500°C to only 4% or 0% respectively at 700°C or 800°C. $^{18}$ While Fe$_2$O$_3$ is highly soluble in Li$_2$CO$_3$ as LiFeO$_2$, $^{20}$ without water availability to provide hydrogen for the ammonia synthesis, the observed ammonia generation rate in Figure
3 at 730°C is low and rapidly decreases.

We observe that a Li$_{1.6}$Ba$_{0.3}$Ca$_{0.1}$CO$_3$ with 6m LiOH and 1.5m Fe$_2$O$_3$ electrolyte is molten and not viscous at 650°C. This intermediate temperature mix exhibited the highest and most stable rate of ammonia generation during a 250mA electrolysis in Figure 3. As shown in the figure, even higher ammonia generation rates are observed in this 650°C electrolyte, when the same total electrolysis charge is applied, but pulsed at ten-fold higher current (2.5A) for 1/10 the time, over each 2h cycle (12 minutes 2.5A followed by 108 minutes 0A, repeat cycle) although this configuration passivates rapidly as observed in the sharp tail-off of the observed ammonia generation rate. Experiments in progress indicate that higher pressure can simultaneously improve hydration and iron formation for the STEP production of ammonia, and will be reported in an expanded study.

Summary

A mixed molten carbonate/hydroxide electrolyte can effectively generate small iron and Fe$_2$O$_3$ particles by electrolysis to catalyze ammonia formation from water and air. The higher temperature required for effective iron formation needs to be balanced by the lower temperature required for effective hydration of the electrolyte. Future experiments will explore a high-pressure domain to simultaneous improve hydration and iron formation for the STEP production of ammonia.

Acknowledgments

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References


