Electronic Supplementary Information (ESI)

Chemical Mechanism of the High Solubility Pathway for the Carbon Dioxide Free Production of Iron (Chemical Communications)

Stuart Licht,*a Hongjun Wu,a Zhonghai Zhang,a Hina Ayuba

aDepartment of Chemistry/Solar Institute, George Washington University, Washington, DC 20052, USA.
*CORRESPONDING AUTHOR EMAIL ADDRESS: slicht@gwu.edu

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LiFeO2 can be formed from Fe2O3 and Li2CO3 at < 400°C as measured by x-ray diffraction, XRD from the ball milled reactants.ESI-1 Another also salt forms spontaneously from lithiated hematite, Fe2O3. The ferrospinel LiFe5O8 was first reported by Hoffman who prepared the compound and measured its XRD.ESI-2 MFe5O8 preparation: At lower reaction temperatures pure LiFe5O8, size controlled (9-900 nm), has been prepared by sol gel/calcine synthesis or via hydrothermal ball milling.ESI-3 Here, the penta-iron octaoxides are prepared by ball milling of an equivalent ratio of 5 parts Fe2O3 (Baker, 98%) to 1 part of the alkali carbonate (Alfa Aesar 99% Li2CO3 or BDH 99.5% Na2CO3) for 2 hours at 500 rpm in a Retsch PM100 planetary ball mill, in stainless media, followed by sintering at 800°C for 2 hours. Ball mill of the Fe2O3: alkali carbonate 5:1 equivalent mix, prior to heating leads to complete reaction as measured by mass loss of 1 equivalent of CO2.

Determination of solubility in the molten carbonate Low melting points of carbonates are achieved through a eutectic mix of alkali carbonates (Tmp Li2CO3: 723°C, Na2CO3: 851°C, K2CO3: 891°C; Li1.07Na0.93CO3: 499°C; Li0.85Na0.61K0.54CO3: 393°CESI-6,7): Solubility is determined from multiple measurements including compositions, both approaching saturation, and also in compositions containing excess ferric oxide salts. When these salts are in excess in the molten mix, it is observed to descend to the bottom of the molten mix, and is not removed with the molten liquid. The molten liquid is removed from the molten mix and analyzed. The extracted liquid is cooled, ground and mixed with water. The carbonate component is water soluble, while the alkali iron oxide component is not, and is removed by filtration and dried at 100°C to determine the mass fraction of the ferric oxide salt that dissolved in the molten carbonate.

In molten Li2CO3 containing dissolved Fe(III), we observe that iron is readily deposited on the cathode with applied potentials as described in Figure 3. Electrolysis cell bodies are straight wall 20 ml nickel crucible (VWR), protected from air oxidation by argon. The anode is the internal cell wall, which when filled with ~15 ml of electrolyte, has a surface area of 30 cm2, and comprises a cylinder which surrounds an 0.5 cm2 area, coiled, 1.5 mm diameter iron wire cathode. As noted in Figure 3, in one experiment a 30 cm2 flat platinum sheet, rolled into a cylinder is used in lieu of the nickel anode, and an alumina crucible is used in lieu of the nickel crucible. In this study the full cell electrolysis potential is measured using the oversized anode to focus on cathode (iron reduction electrode) effects. We have also reported initial anode results2,
and other anode effects will be the focus of a future study. The electrolysis potential, as a function of concentration, temperature and current density is presented in Figure 3.

Hy-STEP iron production apparatus: In this demonstration a 31.5”x44.5” Fresnel lens (Edmund Optics) concentrates sunlight to provide temperatures of over 950°C, and a Sunforce-44444 400 W wind turbine provides electronic charge, charging series nickel metal hydride, MH, cells at 1.5V). Each MH cell, provides a constant discharge potential of 1.0-1.3 V, which are each used to drive the one or two, series connected iron electrolysis cells as indicated in the Figure 4. The electrolysis cells produce iron at 950°C in lithium carbonate electrolyte containing 14 molal Fe(III), added as Fe₂O₃, and Li₂O.

Electrolysis potentials in Figure 2 are calculated from the thermochemical data (only at unit activity) reported for Fe, Fe₂O₃, LiFe₂O₄, Li₂O, Li₂CO₃, CO₂, CO, and O₂. As noted in equation 4, other than unit activity coefficients can prevail in various concentrated electrolytes. Alternatively ion association effects can decrease activity coefficients. High Fe(III) activity coefficients, α_{Fe(III)} > 1, would further decrease the thermodynamic potential to produce iron.

It is interesting to note that the observed electrolysis potential at low current density is considerably smaller than the expected thermodynamic potential of 0.8V at 950°C. This is, at least in part, explained by the high, non-unit activity of the dissolved iron (14 m) providing significant voltage and energy savings. While a nickel anode appears stable during extended electrolyses, it is thermodynamically unstable. We have already reported initial anode results, and other anode effects will be the focus of a future study, and we note in the rights side of Figure 3, that when the nickel anode is replaced by a platinum electrode there is an observed increased in the measured electrolysis potentials, particularly at high current density.

The chemistry of LiFeO₂ and LiFe₅O₈

The corrosion product of iron containing alloys in lithium containing eutectic molten carbonates at 650°C is LiFeO₂. Of significance, this oxide had been reported as highly insoluble, with a solubility on the order of parts per million. That is beneficial for molten carbonate fuel cells, MCFC’s, electrode stability and has been the basis for a number of LiFeO₂ coatings or bulk material for MCFC electrodes. However, that insolubility of LiFeO₂ in Li₂CO₃ would not provide a basis for iron production by electrolysis of dissolved iron oxide salts. Collongues and Chaudron concluded that LiFeO₂ and LiFe₅O₈ are the limiting members of the solid solutions formed by the replacement of 2Fe²⁺ by Li⁺Fe³⁺ in 2FeO or 2Fe₃O₄, respectively.

The synthesis of solid LiFe₅O₈ from the complete reaction of a 5:1 mole ratio of powdered Fe₂O₃ and Li₂CO₃, or 10:1 ratio of Fe(NO₃)₂ and Li₂CO₃, occurs at elevated temperature and is accelerated under microwave irradiation, and LiFe₅O₈ remains stable up to 1000°C, although on heating it has been reported that lithium ions in the solid state LiFe₅O₈ lattice become disordered at temperatures above 755°C, and return to an ordered lattice state the system is cooled at 735°C.

The chemistry of the CO₂/Li₂O equilibrium in Li₂CO₃

Experimentally, we observe the facile reaction of CO₂ and Li₂O in molten Li₂CO₃. Here, thermodynamically, we also determine the equilibrium conditions between the CO₂, Li₂O and Li₂CO₃ species in the system:

\[
\text{Li}_2\text{CO}_3 + \text{Li}_2\text{O} + \text{CO}_2 \quad (1)
\]

Using the known thermochemistry of Li₂O, CO₂ and Li₂CO₃, we calculate the reaction free-energy of equation 1, and from this calculate the thermodynamic equilibrium constant as a function of temperature. From this equilibrium constant, the area above the curve in Figure ESI-1 presents the thermodynamic wide domain in which Li₂CO₃ dominates, that is where excess CO₂ reacts with Li₂O such that \( p_{\text{CO}_2} \cdot a_{\text{Li}_2\text{O}} < \)
This is experimentally verified in the measured thermogravimetric analysis of Li₂CO₃, Figure ESI-2, and when we dissolve Li₂O in molten Li₂CO₃, and inject CO₂(gas). Through the measured mass gain, we observe the rapid reaction to Li₂CO₃. Hence, CO₂ is flowed into a solution of 5% by weight Li₂O in molten Li₂CO₃ at 750°C, the rate of mass gain is only limited by the flow rate of CO₂ into the cell (using an Omega FMA 5508 mass flow controller) to react one equivalent of CO₂ per dissolved Li₂O. As seen in the thermogrametric analysis in Figure ESI-2, the mass loss in time of heated lithium carbonate heated in an open atmosphere (~0.03% CO₂) is slow up to 850°C, but accelerates at 950°C. However the mass loss falls to nearly zero, when heated under pure (1 atm) CO₂. Also in accord with Eq. 1 added Li₂O shifts the equilbrium to the left and inhibits carbonate decomposition. As seen in the figure in the open atmosphere, molten 100% Li₂CO₃ at 850°C loses mass, while a mixture of 90% by weight Li₂CO₃ and 10% Li₂O exhibits little mass loss in time.

Figure ESI-1. Species stability in the lithium carbonate, lithium oxide, carbon dioxide system as calculated from the thermochemical data for Li₂CO₃, Li₂O, and CO₂.¹⁰

Figure ESI-2. Thermogravimetric analysis of lithium carbonate. The measured mass loss in time of Li₂CO₃.
The chemistry of LiFeO\textsubscript{2} and LiFe\textsubscript{5}O\textsubscript{8} in Li\textsubscript{2}CO\textsubscript{3}

LiFe\textsubscript{5}O\textsubscript{8} dissolves rapidly in molten Li\textsubscript{2}CO\textsubscript{3}, however it reacts with the molten carbonate as evident in the mass loss of the solution. Similarly, Fe\textsubscript{2}O\textsubscript{3}, reacts with molten Li\textsubscript{2}CO\textsubscript{3}, resulting in a mass loss due to the evolution of CO\textsubscript{2} proportional to the quantity of Fe\textsubscript{2}O\textsubscript{3} contained in the Li\textsubscript{2}CO\textsubscript{3} mix. As seen in Fig. ESI-3, over a wide range of temperature and mass fractions of Fe\textsubscript{2}O\textsubscript{3} in Li\textsubscript{2}CO\textsubscript{3}, the system process to release one equivalent of CO\textsubscript{2} for each equivalent of Fe\textsubscript{2}O\textsubscript{3}, to form a steady state concentration of LiFeO\textsubscript{2} in accord with:

\[
\text{Fe}_2\text{O}_3 + \text{Li}_2\text{CO}_3 \rightarrow 2\text{LiFeO}_2 + \text{CO}_2
\]  

(2)

Alternatively, the dissolution of 1 equivalent of Li\textsubscript{2}O and 1 equivalent of Fe\textsubscript{2}O\textsubscript{3} in molten Li\textsubscript{2}CO\textsubscript{3} can drive the direct dissolution of LiFeO\textsubscript{2} mole without the reactive formation of CO\textsubscript{2} in accord with:

\[
\text{Fe}_2\text{O}_3 + \text{Li}_2\text{O} \rightarrow 2\text{LiFeO}_2
\]  

(3)

Figure ESI-3. Thermogravimetric analysis of a mix of lithium carbonate with ferric oxide. The measured mass loss in time of Li\textsubscript{2}CO\textsubscript{3}. As indicated in the figure legend, the mixture is composed of either 20, 40 or 60 weight percent of Fe\textsubscript{2}O\textsubscript{3} in Li\textsubscript{2}CO\textsubscript{3}. The mass loss over time is measured at the indicated constant temperature of either 650, 750 or 950°C, and corrected for CO\textsubscript{2} evolution measured from the 100% Li\textsubscript{2}CO\textsubscript{3} melt, then converted to moles of CO\textsubscript{2}, and finally normalized by the moles of Fe\textsubscript{2}O\textsubscript{3} in the lithium carbonate ferric oxide mix.

Eq. 3 is of particular significance to the electrolysis of Fe\textsubscript{2}O\textsubscript{3} in molten carbonate. As LiFeO\textsubscript{2} is reduced to iron metal, Li\textsubscript{2}O is released (2LiFeO\textsubscript{2} → 2Fe + Li\textsubscript{2}O) facilitating the continued addition and dissolution Fe\textsubscript{2}O\textsubscript{3} without CO\textsubscript{2} release, and without a change in the electrolyte. As indicated in Fig. ESI-2, a molar excess, of greater than 1:1 of Li\textsubscript{2}O to Fe\textsubscript{2}O\textsubscript{3} in molten Li\textsubscript{2}CO\textsubscript{3}, will further inhibit the Eq. 1 disproportionation of lithium carbonate.

Description of STEP energy conversion

Previously, we demonstrated a solar, carbon dioxide-free process for the production of iron, the STEP (Solar Thermal Electrochemical Photo) iron process\textsuperscript{2}. In that process, solar energy is split into IR (thermal) and visible bands, to respectively provide heat and electronic energy to drive the iron electrolysis. Hy-STEP, hybrid Solar
Thermal Electrochemical Production provides a synergy of renewable energy driven charge transfer, solar thermal, and electrolysis processes, by applying sunlight to heat a class of (endothermic) reactions, which require less energy at higher temperature. An energy diagram is presented in Figure ESI-4, which compares an energetically forbidden process at room temperature to a generalized energetically permitted STEP or hy-STEP process. Our first experimental example of a STEP process was driving water splitting, which is a 1.2V process at room temperature, which was instead driven by a single small band-gap (1.1V Si) semiconductor, at low potential at high temperature in a molten hydroxide electrolyte. Our previous demonstrations of STEP consisted of solar, rather the new wind-solar, hy-STEP process, which replaces solar with wind driven electronic charge transfer. The basis for improved efficiencies using the STEP or hy-STEP process is:

(i) The energy to drive many reactions to decrease greenhouse emissions, such as water splitting to generate hydrogen fuel, CO₂ splitting for carbon capture, or metal oxide reduction to form useful metals, is excessive at room temperature.
(ii) Concentrated solar thermal energy can be used to increase the temperature of endothermic electrolysis processes. The electrolysis potential is lowered at higher temperature, substantially improving system efficiency.

Expanded theoretical details of the STEP process are given in reference 3, and expanded experimental details are given in references 2 and 5. This communication focuses on novel aspects of the iron electrolysis cell, while the remaining wind (electric) and solar thermal (to T > 1000°C) components of Hy-STEP iron are mature technologies. An array of flat mirrors reflecting to a central tower, such as demonstrated by Brightsource can achieve temperatures of 550°C; individual parabolic heliostat can achieve temperatures over 800°C; short focal length, plastic fresnel generating optical concentrations of 500-1000 suns have been deployed for concentrator photovoltaics, such as demonstrated by Amonix, while better mirrors and secondary optics, can achieve temperatures over 1000°C.

Figure ESI-4. The complete solar spectra drives electrolysis in the STEP process. Redirected solar thermal heat incoming reactants to reduce the energy for an electrolysis, which is driven by visible light (hv) PV charge transfer. As one example, the energy of photodriven charge transfer is insufficient (left) to drive (unheated) electrolysis, but is sufficient (right) to drive endothermic in the solar heated STEP process.

Author Contributions. S. L. designed the Hy-STEP process, and together with H. W. and Z. Z conducted the solubility, electrochemical and Hy-STEP measurements analyses. H A. helped S. L. with the iron oxide and CO₂ thermodynamic calculations in the Fig. ESI-1.
Electronic Supplementary Information References

note: numbered references in the ESI text denoted as “x” rather than “ESI-x” refer to references listed in the Chem. Comm. text.


ESI-22. Fresnel solar concentrator technologies are described at: amonix.com, energyinnovations.com/sunflower.