

Electronic Supplementary Information (ESI)

High Solubility Pathway for the Carbon Dioxide Free Production of Iron (Chemical Communications, 2010)

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Overview of iron history, mechanism & calculated decrease of CO₂ emissions with new STEP electrolysis

²⁰ Iron smelting, the reduction of iron oxide ores with carbon, started as early as 3000 BCE, and the Iron age began in the 12th century BCE, with the collapse of the Bronze Age as shortages of tin or copper arose.^{SEI-1} Commercial iron today continues to be produced by this millennia old carbothermal process. In the carbothermal process iron oxide is reduced by carbon, via carbon monoxide or hydrogen as intermediate reductants. The carbothermal process releases the greenhouse gas, CO₂, in the 3 electron reduction of Fe(III),
²⁵ accompanied by the 4 electron oxidation of carbon:

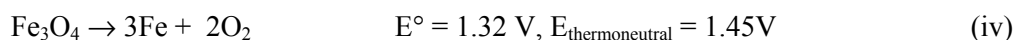
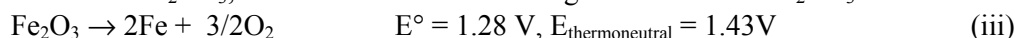


This Fe₂O₃ reduction reaction is endothermic. To sustain this reaction, heat, ΔH, is provided by the burning of
³⁰ over one additional carbon, with concurrent release of further carbon dioxide:



From a thermodynamic perspective the carbothermal process releases over one CO₂ per Fe formed (Equations i and ii). In practice, many more than one CO₂ per iron is released in the industrial formation of iron. Globally,
³⁵ the iron and steel industry accounts for about a quarter of direct CO₂ emissions from the industry sector, which total 27 x 10⁹ tonnes of CO₂ per year.^{SEI-2} Hence, 6.8 x 10⁹ tonnes of CO₂ is released in the annual production of 1.2 x 10⁹ tonnes of iron and steel,^{SEI-3} from ~2 x 10⁹ tonnes of iron ore,^{SEI-3} resulting in the emission of 7 CO₂ per Fe formed.

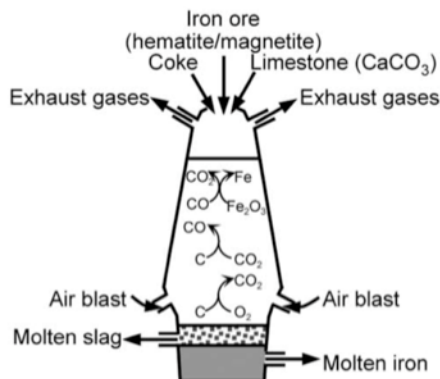
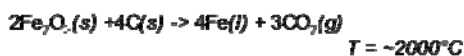
⁴⁰ As demonstrated in this study, iron may be formed at an electrolysis potential of as little as 0.9V from hematite in molten Li₂CO₃, or as little as 0.6V from magnetite in molten Li₂CO₃ as:



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The carbothermic and the new STEP iron production process in this study are compared in Figure 4.

carbothermic iron production



STEP CO₂-free iron production

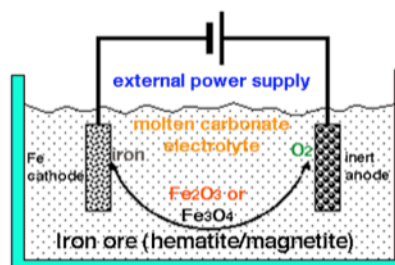
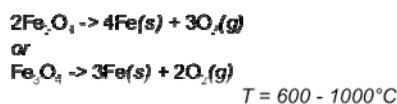


Fig. 4. Comparison of the industrial production of iron (left) and the STEP CO₂ free production of iron (right) presented in this study. The new process can utilize renewable or nuclear power to drive iron formation, and then is CO₂ free. The new process alternatively can also be driven by fossil fuel electrical power, which as described in the text generates less CO₂ than the carbothermic process. The left side of the figure is reproduced from reference SEI-4 with permission from the Electrochemical Society.

No CO₂ is released in this process when the heat and electronic charge is generated by renewable energy (solar, wind, hydro, geothermal) or nuclear energy. Alternatively, we can calculate the CO₂ release when fossil fuels are used to form the electricity. As demonstrated in this study, iron may be formed at an electrolysis potential of as little as 0.9V in molten Li₂CO₃. In Equation iii, the room temperature rest potential (calculated from the free energy of the reaction) is 1.28 V and the thermoneutral potential (calculated from the enthalpy of the reaction) is 1.43 V. The latter voltage is the energy required to prevent the system from cooling during electrolysis, and unlike the endothermic rest potential, is nearly constant with changing temperature, for example, E_{thermoneutral}(1200°C) = 1.40 V, and from Equation iii requires 6 Faraday per mole of iron. This is equivalent to 0.225 kWh / mol Fe (from F = 96,485 A sec, and 1 kW=1000 VA), and will be less if an alternate heat source is used to maintain the system electrolysis temperature. Currently, fossil fuels release ~11 mol CO₂ / kWh; specifically the natural gas, oil, and coal generation of electricity have respective stack emissions of 7.5, 12 and 15 mol CO₂ / kWh.^{SEI-5} Hence, even if fossil fuel, rather than renewable energy, is used to generate the heat and electricity and heat for iron by electrolysis, it will only emit 0.225 x 11 = 2.5 CO₂ per Fe generated. This is less than the 7 CO₂ per Fe emitted by the existing iron smelting processes. In summary:

Iron generation Process	CO ₂ emitted per Fe generated
conventional smelting	7
new Li ₂ CO ₃ electrolysis powered by fossil fuel electricity	2.5
STEP Li ₂ CO ₃ (solar) electrolysis	0

We hypothesize that five expanded mechanisms, all carbon neutral, are consistent with the observed facile iron oxide electrolysis in molten Li₂CO₃ in the main text. The mechanisms may act alone, or in concert, and will be probed in ongoing studies. They are described here for Fe₂O₃, and an analogous set can be considered for the reduction of Fe₃O₄. The first consists of simple dissolution and reduction of iron oxide, such as:



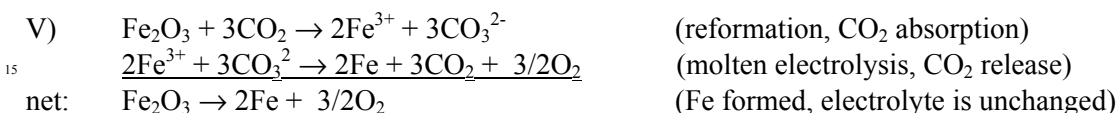
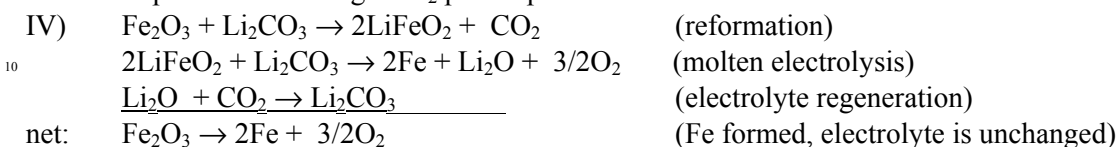
then there is the high oxide ion activity case:



5 the direct reduction of solid, suspended iron oxide ion in the molten carbonate case:



and the respective low or high CO_2 partial pressure cases:



20 From a historical perspective, the earliest attempt at electrowinning iron (the formation of iron by electrolysis) from carbonate appears to have been in 1944 in the unsuccessful attempt to electrodeposit iron from a sodium carbonate, peroxide, metaborate mix at 450-500°C, which deposited sodium and magnetite (iron oxide), rather than iron.^{1,2} Later attempts have focused on the electrodeposition of iron from molten mixed chloride/fluoride electrolytes, which has not provided a successful route to form iron.^{3,4} Compared to molten electrolysis, aqueous electrodeposition would require higher energy due to both the thermodynamics of a higher rest potential ($E^\circ=1.28$ V), and the diminished kinetics at low temperature, but requires less heat input into the electrolysis. Aqueous electrowinning of iron has been attempted for at least century in solutions including electrodeposition from aqueous chloride, sulfate and hydroxide solutions.^{SEI-4,SEI-6-8} However, due to the high thermodynamic potential, aqueous electrodeposition requires a working electrolysis potential of a minimum of 1.4 to over 2.0 V, and also additional mechanical energy to stir electrode or solution, and these very high 30 requisite energies impede viability or widespread commercial use. At higher temperatures, after an unsuccessful attempt at iron deposition in alternative molten electrolytes, the focus turned to molten halide electrolytes, which have been problematic and not led to a commercial process. An overview of the prior attempts of the art of iron electrolysis at higher temperatures, was provided in 2007 by Haarber, Kvalheim, Rolseth, Murakami, Pietrzyk and Wang, and is repeated verbatim here:²

35 “The earliest work on iron deposition was reported in 1944 by Andrieux and Weiss.¹ Electrolysis experiments were carried out in sodium peroxide, sodium carbonate and sodium metaborate using iron electrode at 450-500 °C and 10-25 A. Instead of iron deposits, sodium and magnetite were deposited on the cathode. In the 1960s Zulkiewitz et al.^{SEI-9,10} used eutectic KCl-LiCl-FeCl₂·4H₂O at 150-225 °C, and obtained iron deposits. However, 40 due to the dehydration of the melt, FeCl₂ sublimation and decomposition occurred. In their further study, LiCl was replaced by NaCl, which made the iron crystal size drop from 2-3 mm to 1-10 μm.^{SEI-11} Great efforts on the electrodeposition of iron from molten salts were made in the former Soviet Union for powder metallurgy applications, but the process was never commercialized. A. B. Suchkov et al.^{SEI-12} tested the electrorefining of scrap iron and pig iron. Dendritic iron was produced in NaCl-FeCl₂ (10wt %) melt at 850-900 °C and the current 45 efficiency decreased rapidly due to the dendritic growth of the deposit. By increasing the iron concentration of electrolytes and decreasing starting current, iron grains in the cathode grew coarsely.^{SEI-13} Electrorefining of iron from molten NaCl-KCl-FeCl₂-MgCl₂ and electrowinning of iron from molten NaF-KF, NaF-KF-NaCl, NaCl-KCl-FeCl₂, NaCl-KCl-FeCl₂-MgCl₂ and NaCl-KCl-Na₄P₂O₇-K₄P₂O₇ was also tried at 900-950 °C.^{SEI-14,15} In NaF-KF electrolyte iron deposit grains were about 0.5 – 0.1 mm and decreased with the addition of NaCl. The 50 iron deposits in the phosphate containing electrolyte were contaminated by phosphorus and the phosphorus content in the iron deposit was about 1.5% P, and no iron was deposited in NaCl-KCl-FeCl₂ electrolyte. In 1987, Demidov et al.^{SEI-16} studied the reduction of Fe₂O₃ and Fe₃O₄ in LiCl-KCl eutectic electrolyte by the cyclic

voltammetry method, and assumed the reduction Fe_3O_3 occurred in three steps. Haarberg et al.^{SEI-17,18} studied the electrochemistry of Fe_2O_3 dissolved in several chloride and fluoride containing electrolytes, and found that the solubility of Fe_2O_3 in CaCl_2 -NaCl melts was greatly enhanced upon additions of AlCl_3 , AlF_3 or MgCl_2 , but a divalent iron species was produced by an exchange reaction between hematite and aluminum chloride, and chlorine gas was evolved. In molten fluorides and mixed fluoride/chloride electrolytes CaCl_2 -KF (15-85 mol %), CaCl_2 -KF-NaF (7-39-54 mol %), KF-NaF (50-50 mol %) and LiF-KF-NaF (46.4-42.1-11.5 mol %), the exchange reaction was avoided. However, the solubility of hematite was more limited in the absence of an acidic substance such as AlCl_3 .^{SEI-17} In a novel process of producing titanium, Chen et al.^{SEI-19} used CaCl_2 as the main electrolyte due to the high solubility of CaO in the melt. The electrochemistry of iron in CaCl_2 - CaF_2 (80-20 mol %) was studied.²⁷

Description of solar thermal electrochemical photo energy conversion

STEP provides a synergy, of photovoltaic, solar thermal and electrolysis, and is capable of achieving solar energy efficiencies higher than PV or solar thermal alone, through the effective use of both visible and infrared sunlight. The energy diagram for a generalized STEP process is presented in Figure 5. The basis for improved efficiencies using the STEP process is^{5,6}

- (i) Most sunlight is not used in even the best solar cells, and is lost as waste heat.
- (ii) the “excess” heat can be used to increase the temperature of endothermic electrolysis processes, such as a CO_2 capture electrochemical cell, or within other electrolysis cells, and the electrolysis potential can be lowered at higher temperature, substantially improving system efficiency.

Expanded theoretical details of the STEP process are given in reference 5, and expanded experimental details are given in reference 6.

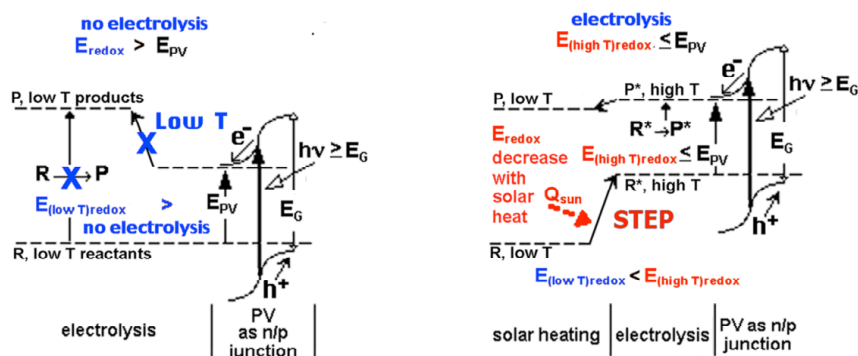


Fig. 5. The complete solar spectra drives electrolysis in the **STEP** process. Redirected solar thermal (Q_{sun}) heats incoming reactants to reduce the energy for an electrolysis, which is driven by visible light ($h\nu$) PV charge transfer. The energy of photodriven charge transfer is insufficient (left) to drive (unheated) electrolysis, but is sufficient (right) to drive endothermic in the solar heated STEP process. PV charge transfer, whether derived from single or multijunction sources is symbolized by a single pn junction.

Comparison of alkali carbonate electrolytes

Li_2CO_3 , Na_2CO_3 and K_2CO_3 , have respective melting points of 723 °C, 851 °C and 891 °C. Molten Li_2CO_3 has higher conductivity (6 S cm^{-1}) than that of Na_2CO_3 (3 S cm^{-1}) or K_2CO_3 (2 S cm^{-1}).^{SEI-20} Higher conductivity is advantageous as it leads to lower impedance potential losses during electrolysis. The mass transport is also improved at higher temperature; the conductivity increases from 0.9 to 2.1 S cm^{-1} with temperature increase from 650 °C to 875 °C for a 1:1:1 mixture of the three alkali carbonates.^{SEI-21} The availability of the three carbonated salts for electrolysis has recently been discussed in the supporting information of reference 6.

Electronic Supplementary Information References

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

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