Electronic Supplementary information

Electro-reduction of hematite using water as the redox mediator

Kaiyu Xie^a, Ali Reza Kamali *^{a,b,}

^a School of Metallurgy, Northeastern University, Shenyang 110819, China
^b Department of Materials Science and Metallurgy, University of Cambridge, CB3 OFS, UK
* Corresponding author at: School of Metallurgy, Northeastern University, Shenyang 110819, China
E-mail: ali@smm.neu.edu.cn

Experimental Information

Materials and the electrolysis setup. A given amount of Fe_2O_3 powders (Aladdin, F108317) and NH₄HCO₃ (Aladdin, A110536) were mixed in the mass ratio of 4:1, and then 2wt% PVA solution was added to the mixture followed by further mixing. After being dried out in air, the mixture was pressed into pellets of about 20 mm in diameter and 3 mm in thickness using a hydraulic press under a pressure of 20 MPa for 10min. The pellets were then heated for 4h at 400 °C to remove the PVA and NH₄HCO₃, and then at 800 °C for 2 h in air atmosphere to achieve sintered pellets of appropriate strength. For assembling of the cathode in a typical experiment, a sintered Fe_2O_3 pellet was attached to one end of a copper rod electrode lead of 6 mm diameter and 800 mm length sheathed with an alumina tube, using a thin Ni wire. The electrolysis cell consisted of a high-purity graphite crucible (internal diameter 55 mm, wall thickness 15 mm and height 140 mm) filled with about 250 g anhydrous LiCl (Sigma-Aldrich, V900067) and a molybdenum wire (diameter 1 mm, length 800 mm) served as the anode and the quasi-reference electrode, respectively, as well as the assembled cathode. In order to enclose the electrochemical cell, the graphite crucible was placed into a quartz tube, and the latter was positioned into an Inconel retort. This reactor configuration ensures the separation of the molten salt system from metallic parts of the reactor, preventing the corrosive attack from the evaporated salt during the electrolysis process. The experimental setup used in this study is shown in Fig. 1.

Constant voltage electrolysis process. In this study, all experiments were performed in a batch-mode. Typically, the electrolytic cell containing LiCl was heated to 660 °C by a ramp of 5 °C/min, around 50 °C higher than the nominal melting point of LiCl, under an argon gas flow of about 600 ml/min. When the target temperature was reached, the argon gas flow was re-directed to be passed through a U-shaped quartz tube containing distilled water, before entering into the reactor (see Fig. 1). Then, the electrolysis process was conducted under the humid Ar flow until the end of the electrolysis process, after which the humid Ar flow was replaced by the initial dry Ar flow, and the system allowed to be cooled down. Then, the crucible was washed by copious amounts of distilled water, leading to the dissolution of the salt and retrieving of the product, which was grounded and dried in vacuum oven before further characterization.

The electrolysis process was conducted at a constant cell voltage in the range 1-1.4 V for a period of 1-5 h. For the electrolysis, a DC power supply (IT6502D, ITECH) was employed and the current-time curve was simultaneously monitored during the process. The potential differences between both the cathode/anode and the Mo quasi-reference electrode were measured by two digital multimeters (Keysight, 34460A) during the process. A hydrogen sensor (Empaer, operating based on catalytic combustion) was employed to detect the concentration of hydrogen in the exhaust gas from the cell. The amount of water carried into the molten salt reactor was estimated by measuring the quantity of water in the U-shape tube, before and after the electrolysis process. It was found that a quantity of 1.19 g water could be introduced into the reactor by the humid Ar flow during 5 h of the electrolysis. In an ideal condition, this amount of water could produce 0.13 g H⁺ in the molten salt throughout the electrolysis. This could ideally lead to the reduction of about 3.5 g Fe₂O₃ to form about 2.4 g Fe. In our experiment, a Fe₂O₃ pellet of about 1.63 g was used as the initial material, and a quantity of around 1.12 g Fe was collected after the electrolysis (at 1.4V, 5h) , washing and filtering process. The amount of hydrogen injected to the system, therefore, was sufficient to explain the hydrogen reduction occurred by the electrochemical process.

Characterization. The obtained products were characterized by X-ray diffraction (XRD, MPDDY2094 with Cu-K_{α} radiation of λ =1.5405Å, PANalytical), scanning electron microscopy (SEM, Ultra Plus, ZEISS.) equipped with energy dispersive spectrometer (EDS, Shimadzu Corp.), and the infrared carbon and sulfur analyser (CS230, LECO).

Kinetic considerations

The overall kinetics, and also the rate of different steps involved in the electroreduction of Fe_2O_3 by the in-situ generated hydrogen, proposed in the present work, are influenced by various mass and charge transfer events throughout the molten salt process. These events include: (i) the hydrolysis of molten LiCl electrolyte, leading to the formation of protons and oxygen anions, and the subsequent transportation of the protons through the bulk of the electrolyte towards the cathode surface; (ii) the electron transfer at the interface between the electrolyte and the current collector, either the Ni wire or the cathode pellet. The latter becomes more pronounced after the partial reduction of the metal oxide surface, enhancing its electrical conductivity. Gradually, the mass/charge transfer at the boundaries among the electrolyte and the porosity within the metal oxide pellet play a more significant role in the overall process; (iii) the inward propagation of the reaction boundary and the transportation of protons through the porosity as well as the outward transportation of the reaction products through the pores; (iv) the dissolution of the generated H₂O into the electrolyte through the hydrolysis mechanism. The mass transfer of the reactive species and the reaction products in the cell may occur due to the gradient of either electrical potential and/or chemical concentration, as well as the forced convection taking place due to the bubbling of gaseous species. The process presented here deserves further investigations to correlate the physical and structural features, such as the morphology of the metal oxide reactant, the electrolysis duration, applied voltage, the electrolysis temperature, and composition of the electrolyte used with kinetics and transport properties of the electrochemical process, on one hand, and the properties and the yield of products, on the other. This is the subject of further investigations in our lab. **Table S1** A comparison between the molten salt electro-deoxidation methods used for the reduction of Fe_2O_3 with the method proposed in the present work.

Electrolyte system	Constant voltage/ V	Time / h	Temperature / °C	Current efficiency / %	Energy consumption /(kWh/kg-Fe)	Reference
CaCl ₂	1.8	15	800	80	3	Li et al ¹
Na ₂ CO ₃ -K ₂ CO ₃	2	12	750	93.6	3.08	Tang et al ²
Na ₂ CO ₃ -K ₂ CO ₃	1.9	11	750	95	2.87	Yin et al ³
NaOH	1.7	6	530	89	2.8	Cox et al ⁴
NaOH	1.7	16	500	30	8.1	Jiao et al ^{5,6}
LiCl	1.4	3.5	660	96	2.5	Present work



Fig. S1 XRD patterns of the Fe_2O_3 pellet sintered in air at 800 °C for 2 h, and the sintered pellet heated in LiCl melt at 660 °C for 1h under humid argon atmosphere.



Fig. S2 XRD pattern of the retrieved LiCl salt after the electrolysis under 1.4 V for 5 h.

References

- 1. G. Li, D. Wang and Z. Chen, J. Mater. Sci. Technol., 2009, 25, 767-771.
- 2. D. Tang, H. Yin, W. Xiao, H. Zhu, X. Mao and D. Wang, J. Electroanal. Chem., 2013, 689, 109-116.
- 3. H. Yin, D. Tang, H. Zhu, Y. Zhang and D. Wang, *Electrochem. Commun.*, 2011, **13**, 1521-1524.
- 4. A. Cox and D. J. Fray, J. Appl. Electrochem., 2008, 38, 1401-1407.
- 5. S. Wang, J. Ge, Y. Hu, H. Zhu and S. Jiao, *Electrochim. Acta*, 2013, **87**, 148-152.
- 6. D. Tian, H. Jiao, J. Xiao, M. Wang and S. Jiao, J. Alloy Compd., 2018, 769, 977-982.