

## Electrowinning of Iron in Aqueous Alkaline Solution Using Rotating Disk Electrode

Boyan Yuan and Geir Martin Haarberg

Dpt. of Materials Technology, Norwegian University of Science and Technology, Trondheim, Norway

[boyan.yuan@material.ntnu.no](mailto:boyan.yuan@material.ntnu.no)

In order to develop a new, efficient industrial process for producing high quality iron and steel without with significantly reduced carbon dioxide emissions, we investigated the electrowinning of iron from an iron oxide ore in aqueous alkaline solutions. Hematite ( $\text{Fe}_2\text{O}_3$ ) solid particles suspended in the concentrated aqueous sodium hydroxide (NaOH) solutions were transferred to the cathode (e.g., a rotating disk graphite electrode) and reduced to iron metal by applying a constant current; oxygen was evolved on the anode (e.g., a nickel screen mesh). Current efficiencies of above 90% with respect to iron deposition were consistently obtained under the specific conditions in a laboratory cell, and the corresponding energy consumptions were calculated to be around  $3 \text{ kWh}\cdot\text{kg}^{-1}$  iron. The deposited iron crystals were the oriented clusters of stacked six-fold twins in a tetrahedron-shape grew growing in a direction perpendicular to the cathode surface. Influences of rotation rates of the cathode, cathodic current density densities, contents of the  $\text{Fe}_2\text{O}_3$  particles in electrolytes, and concentrations of NaOH solutions on current efficiency efficiencies and morphology of deposits were studied.

### Introduction

It is widely accepted that the emissions of greenhouse gases, most notably  $\text{CO}_2$ , are responsible for climate change leading to global warming. In order to achieve the decided target on the reductions in  $\text{CO}_2$  emissions, enormous technological innovations in, especially, electric power-generation and heavy industries including steelmaking are required. Currently iron is produced almost exclusively by reducing iron ores by coke in a blast furnace at a temperature of around  $2000 \text{ }^\circ\text{C}$ . This carbothermic reduction process directly produces liquid metal with a high efficiency, but generates a large amount of exhaust gases containing  $\text{CO}_2$ . The production of iron and steel contributes to about 8% of the global emissions of  $\text{CO}_2$ . This industry is expected to continue growing in the near future especially due to the developments in China and India. Alternative ways of producing iron are studied in a large project (Ultra Low CarbonDioxide in Steelmaking (ULCOS)) supported by the European Commission and the steel industry in Europe. Electrolysis to decompose iron ore ( $\text{Fe}_2\text{O}_3$ ) using an inert oxygen evolving anode is an attractive alternative in terms of reducing  $\text{CO}_2$  emissions. However, the current blast furnace reduction process is highly efficient so an electrochemical process must be developed to be competitive.

Electrolytic processes, e.g., electrorefining of iron from a pig or cast iron anode in an aqueous  $\text{FeSO}_4\text{-FeCl}_2$  solution; disproportion of ferrous chloride ( $\text{FeCl}_2$ ) by electrolysis using an insoluble anode and a diaphragm cell; electrowinning of iron from an aqueous  $\text{FeSO}_4\text{-H}_2\text{SO}_4$  solution, were historically employed for producing iron at an industrial scale. These electrolytic processes can not be directly employed to produce iron from iron oxide ores. We investigated the electrowinning of iron from an iron oxide ore in aqueous alkaline solutions by using a

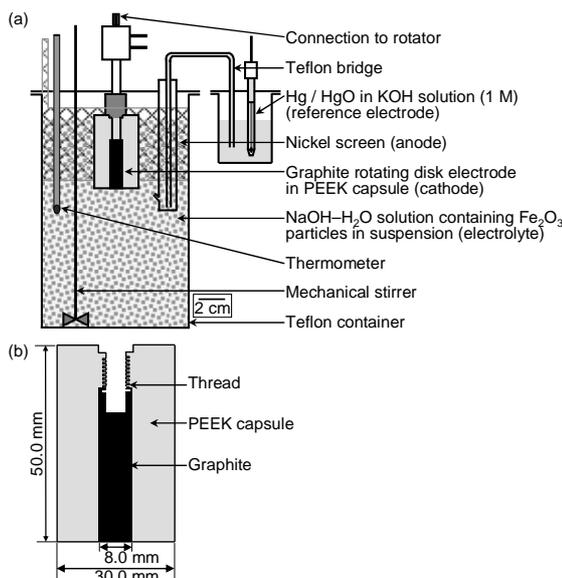
rotating disk electrode (cathode) in a laboratory cell. Hematite ( $\text{Fe}_2\text{O}_3$ ) solid particles suspended in concentrated aqueous sodium hydroxide (NaOH) solutions were transferred to the cathode (a rotating disk graphite electrode) and reduced to iron metal by applying a constant current; oxygen was evolved on an inert anode (a nickel mesh). In order to evaluate the feasibility of this process to be industrialized, we determined the current efficiency and the corresponding energy consumption of the process for producing iron. Moreover, we studied influences of cell operation parameters on the current efficiency and the morphology of deposits, and determined the optimum cell operation conditions under which compact iron deposits can be produced with high current efficiencies and productivities.

### Experimental

Figure 1 (a) schematically illustrates the experimental setup and (b) the sketch of the rotating disk graphite electrode (cathode) used in this study. A nickel mesh (anode;  $100 \times 100$  mesh,  $0.1 \text{ mm}$  line thickness,  $99.9 \text{ wt } \%$  purity;  $310 \text{ mm}$  length,  $50 \text{ mm}$  width) was attached to the wall of a teflon container ( $100 \text{ mm}$  diameter,  $160 \text{ mm}$  length) before adding chemicals. The electrolyte was typically a  $50 \text{ wt } \%$  ( $25 \text{ mol}\cdot\text{kg}^{-1}$ ) NaOH aqueous solution containing  $33 \text{ wt } \%$   $\text{Fe}_2\text{O}_3$ . The density of the  $50 \text{ wt } \%$  NaOH solution at  $114 \text{ }^\circ\text{C}$  was measured to be  $1.43 \times 10^3 \text{ kg}\cdot\text{m}^{-3}$ ; this data was reasonable as compared to the literature value of  $1.48882 \times 10^3 \text{ kg}\cdot\text{m}^{-3}$  at  $70 \text{ }^\circ\text{C}$ . The molarity of the NaOH solution calculated using the measured density value was  $18 \text{ mol}\cdot\text{L}^{-1}$  (M). The highly concentrated NaOH solution was used mainly in order to suppress the  $\text{H}_2$  evolution reaction at the cathode. The  $\text{H}_2$  evolution reaction caused reduced current efficiency for the iron deposition and also contributed to increased porosity of the product. The

content of  $\text{Fe}_2\text{O}_3$  was defined as the weight of  $\text{Fe}_2\text{O}_3$  divided by the total weight of  $\text{Fe}_2\text{O}_3$ ,  $\text{NaOH}$  and  $\text{H}_2\text{O}$ . The particle size distribution and specific surface area of the  $\text{Fe}_2\text{O}_3$  powder were analyzed by the laser light diffraction method (Mastersizer 2000, Malvern Instrument Ltd., United Kingdom); and they were  $d_{10} = 0.2 \mu\text{m}$ ,  $d_{50}$  (median diameter) =  $0.5 \mu\text{m}$ ,  $d_{90} = 1.5 \mu\text{m}$ ; and  $15 \text{ m}^2 \cdot \text{g}^{-1}$ , respectively.  $d_{10}$ ,  $d_{50}$ , and  $d_{90}$  are the equivalent particle diameters where the cumulative distribution percentages reach 10%, 50%, and 90% respectively; therefore 10%, 50%, and 90% of the  $\text{Fe}_2\text{O}_3$  particles were smaller than  $0.2 \mu\text{m}$ ,  $0.5 \mu\text{m}$ ,  $1.5 \mu\text{m}$ , respectively.  $\text{NaOH}$  (VWR International Ltd., 99%, 716.3 g, tablets) was dissolved in distilled water (716.3 g) gradually, and then the  $\text{Fe}_2\text{O}_3$  powder (Alfa Aesar GmbH & Co KG, 99.5%, 716.3 g) was added to the  $\text{NaOH}$  solution. The cathode disk was fabricated by embedding a graphite rod (8 mm diameter) in a plastic (Polyetheretherketone (PEEK)) capsule (30 mm diameter, 50 mm length). It was mounted to the shaft of a modulated speed rotator (AFMSRCE, Pine Research Instrumentation, USA) through the threads made in the capsule and the graphite (around 5 mm) in order to maintain an electrical contact between the shaft and the graphite electrode. The reference electrode was a commercial Hg / HgO electrode (XR400, Radiometer Analytical S.A., France), which was immersed in an aqueous potassium hydroxide (KOH) solution (1 M) in a teflon container. A teflon tube filled with an organic fiber was immersed in the KOH solution and the electrolyte; the fiber was wetted in the KOH solution beforehand. A mechanical teflon stirrer was rotated at a speed of 500 rpm in all experiments in order to keep the  $\text{Fe}_2\text{O}_3$  particles from settling at the bottom of the container. A lid with five inlets was equipped with the mechanical stirrer, the graphite disk electrode, the lead to the nickel mesh, a thermometer, and the teflon tube, and was attached to the electrolyte container. The cell was then placed in a thermal circulator (Julabo, Germany) filled with oil; the temperature of the electrolyte was maintained at  $114 \text{ }^\circ\text{C}$  in all experiments. A constant current was supplied by an electrochemical workstation (Zahner IM6, Germany) to perform the electrowinning experiments; the cell voltage was monitored using a multimeter. The deposited iron was peeled off from the graphite substrate and washed in distilled water by using an ultrasonic cleaner, and dried in a fume hood or a vacuum oven.

The produced iron deposits were weighed. The deposits were characterized by using an optical microscopy (Nikon SMZ800, Japan) and a scanning electron microscopy (SEM; JEOL Ltd., JSM-5600LV, Japan). The cross sections of the deposits without polishing were prepared by splitting them manually; and those after polishing were made by wet grinding the cross sections of the splits embedded in epoxy using various grades of silicon carbide paper; the cross sections were observed by using the SEM. The purity of the iron deposits at the cross section after polishing was analyzed by using the SEM-EDS (Energy Dispersive X-ray Spectroscopy).

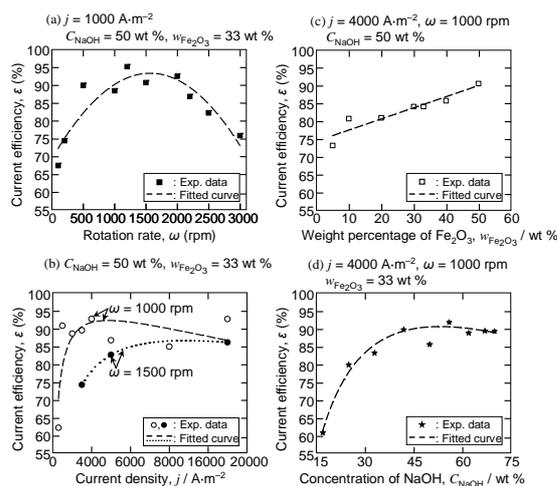


**Figure 1.** (a) Schematic illustration of experimental set-up and (b) mechanical sketch of rotating disk graphite electrode

## Results and Discussion

*Influence of rotation rate on the current efficiency.*— The current efficiency for iron deposition was calculated according to the Faraday's law using the weight of the obtained iron. Fig. 2 (a) shows the current efficiency in the 50 wt %  $\text{NaOH}$  solution containing 33 wt %  $\text{Fe}_2\text{O}_3$  at a current density of  $1000 \text{ A} \cdot \text{m}^{-2}$  and different rotation rates from 0 – 3000 rpm of the cathode. At the rotation rate of 0 rpm (stationary disk electrode): in most of the experiments, powdery deposits were produced and fell down into the electrolyte and the current efficiency was very low around 10%. However, in some cases smooth deposits were obtained at current efficiencies ranging from 86 – 94%. The experiments at 0 rpm rotation rate of the cathode (stationary disk electrode) were conducted multiple times (> 10). These experiments gave current efficiencies for iron deposition ranging from 10 – 94 %. The poor reproducibility is likely to be due to the random transfer of  $\text{Fe}_2\text{O}_3$  particles to the cathode surface. The particles primarily tend to settle at the bottom of the electrolyte when using a stationary cathode. Repeated use of the same electrolyte was found to change the homogeneity of the suspension, which may also affect the current efficiency. For rotation rates below 1000 rpm the current efficiency was found to vary from 60 – 95% with low reproducibility. At rotation rates from 1200 – 2000 rpm the current efficiency was above 90% in repeated experiments. When the rotation rates were further increased to above 2200 rpm, it was observed that in some of the experiments air bubbles might be dragged into the electrolyte, together with

the hydrogen gas evolved, these gas bubbles might partly or fully cover the cathode surface, and caused high cathode potentials (more negative than  $-4$  V vs. the Hg / HgO electrode). The current efficiency was found to decrease at high rotation rates, and at 3000 rpm it was 76%. The rotating disk electrode was positioned about 40 mm (length of plastic capsule: 50 mm) down into the electrolyte. The dragging of air into electrolyte might be due to the onset of turbulent flow for rotation rates above 2200 rpm (although theoretically it has a much higher value). Gas bubbles adhering to the cathode contributed to the passivation of the cathode surface. The problems arising from the passivation of the cathode due to accumulation of gas bubbles have not been examined in details. These problems are related to the use of a rotating cathode which will not be used in a real industrial cell. The cathode potentials and the cell voltages were from  $-1.13$  –  $-1.19$  V versus the Hg / HgO electrode and from  $1.4$  –  $1.9$  V, respectively. The corresponding energy consumption can be estimated to be about  $3$  kWh·kg<sup>-1</sup> iron. The optimum rotation rates under the above-mentioned conditions were determined to be from 1000 to 2000 rpm.



**Figure 2.** Variation of current efficiency with cell operation parameters

*Influence of current density on the current efficiency.*—Figure 2 (b) shows current efficiency of the iron deposition in a 50 wt % NaOH solution containing 33 wt % Fe<sub>2</sub>O<sub>3</sub> at rotation rates of 1000 and 1500 rpm and different cathodic current densities from 600 – 18000 A·m<sup>-2</sup>. When the current density was increased from 600 to 1000 A·m<sup>-2</sup>, the current efficiency increased sharply from 62% to 90%. Current efficiency above 88% was obtained at current densities from 1000 to 4000 A·m<sup>-2</sup>. At current densities above 4000 A·m<sup>-2</sup>, it was observed that the obtained deposits were fairly rough with big edges, and included some oxide particles; and the calculated current efficiency slightly decreased. The current efficiency at 1500 rpm was from 5 – 10% lower

than at 1000 rpm. This was possibly due to the high negative cathode potentials (more negative than  $-4$  V vs. the Hg / HgO electrode) caused by gas bubbles occurred frequently in the experiments at 1500 rpm. This suggests that the development of techniques for controlling the gas bubbles in the electrolyte is important in order to achieve high current efficiencies in this process. These results indicate that the high cathodic current density of 4000 A·m<sup>-2</sup> was applicable in the electrowinning cell; this resulted in the high productivity of the process: estimated to be 22 tones of iron per m<sup>2</sup> cathode area per year under the assumptions of continuous operations at the constant current efficiency of 92%.

*Influence of Fe<sub>2</sub>O<sub>3</sub> content on the current efficiency.*—Figure 2 (c) shows current efficiency of the iron deposition at a rotation rate of 1000 rpm, a current density of 4000 A·m<sup>-2</sup> and different contents from 5 – 50 wt% Fe<sub>2</sub>O<sub>3</sub> particles in a 50 wt % NaOH solution. The current efficiency increased linearly with content of Fe<sub>2</sub>O<sub>3</sub> particles in the solution. When the content of Fe<sub>2</sub>O<sub>3</sub> increased from 5 to 10 wt %, the current efficiency increased from 77% to 86%. Above 30 wt % the current efficiency was above 90%, and at 50 wt % Fe<sub>2</sub>O<sub>3</sub>, the current efficiency was 98%. These results indicate that the content of the Fe<sub>2</sub>O<sub>3</sub> particles in the solution had a significant influence on the current efficiency.

*Influence of the concentration of NaOH on the current efficiency.*—Figure 2 (d) shows the current efficiency of the iron deposition at a rotation rate of 1000 rpm and a current density of 4000 A·m<sup>-2</sup> and different concentrations of NaOH from 17 (6 M) – 71 (26 M) wt % containing 33 wt % Fe<sub>2</sub>O<sub>3</sub>. The pH of the solution and the solubility of the Fe<sub>2</sub>O<sub>3</sub> particles in the electrolyte were varied with the concentration of the NaOH solution. The current efficiency increased from 60 to 80 wt % when the concentration of NaOH was increased from 17 – 25 wt %; high current efficiencies were obtained at concentrations above 40 wt %.

Figure 3 shows SEM images of the iron deposit at (a) the surface, (b) the cross section of the center and (c) the cross section of the edge. The deposited iron crystal was composed of six-twin crystals; the twin crystals were tetrahedron-shaped and converged at an apex. At the center, the deposit tended to form crystals growing from and perpendicular to the graphite surface by an oriented layer-by-layer growth in a shape of a tetrahedron; on the other hand, at the edge, the deposit tended to form smaller crystals growing in radial directions with various angles, and contained large pores between the crystals. Close to the electrode surface, smaller grains were formed; however, bigger crystals were formed with the oriented crystal growth. The deposits shown in Figure 3 (b) were of columnar structure composed of six contacting twins, and these individual columns were spatially separated from each other. Crystal grows radially from the center forming a texture of smooth parallel lines. The rotating motion of the disk electrode, and the highest

local current density at the edge, influenced the direction of the growth of the crystals and hence its morphology.

In general solid deposits having good adherence to the carbon cathode substrate were obtained. At high rotation rates and high current densities edge effects were observed. The thickness of the deposits was fairly uniform. The phase transformation from iron oxide solid particles to iron bulk deposit involved the following processes: the mass transfer of the solid oxide particles to the graphite-cathode surface, the electro-reduction of oxide to metal phase, the nucleation and crystal growth. The overall diffusion and rearrangement processes of the reduced metal particles under the specific experimental conditions determined the texture of the metal produced, and these processes with the minimum Gibbs energy were thermodynamically preferred. The mass transfer of the solid particles was facilitated by thermal diffusion (random Brownian motion) of the particles combined with the transfer by fluid flow created by the rotating disk cathode. The distribution of the iron oxide particles on rotating disk and therefore that of the reduced iron atoms was not uniform across the disk substrate. Figure 2 shows SEM images of the cross sections of the iron deposits obtained at  $1000 \text{ A}\cdot\text{m}^{-2}$  current density in 50 wt % sodium hydroxide solution containing 33 wt %  $\text{Fe}_2\text{O}_3$  powder suspension at rotation rates of the cathode of 1500 and 3000 rpm, respectively. As shown in this figure, the random oriented small grains were usually formed in the initial stage of the nucleation and growth, especially at the higher rotation rate of the cathode. The oriented layer-by-layer growth was observed in both experiments of 1500 and 3000 rpm rotation rate of the cathode. However at 1500 rpm, the growth in the normal direction is bigger than that in the case of 3000 rpm rotation rate. At 3000 rpm, the growth in the lateral direction to the substrate surface is much larger than in the normal direction, so that compact layers and flat crystals were formed. The surface morphology was six-twin crystals pyramids converge at apex. Parameters that may influence this distribution contained the content of the iron oxide particles in the electrolyte, the dimension and the rotation rate of the rotating disk electrode, and the local current density distribution, and the hydrogen evolution reaction. In this system, the initial growth of the iron metal on the graphite substrate was random islands growth mode. After covering the graphite substrate, the oriented layer-by-layer growth continued on the iron metal substrate. The columnar structure depended on the ratio of the growth in the two directions: the higher the lateral growth, the flatter the crystal grains. The ratio of the nucleation rate to the growth rate defines the grain size. The formation of the contact twins was due to the stacking faults of the atoms in the process of nucleation and crystal growth.

The deposits shown in Figure 3 (b) were of columnar structure composed of six contacting twins, and these individual columns were spatially sepa-

rated from each other. Crystal grows radially from the center forming a texture of smooth parallel lines. The rotating motion of the disk electrode, and the highest local current density at the edge, influenced the direction of the growth of the crystals and hence its morphology. Porosity of the deposits decreased with increasing rotation rate of the cathode, decreasing current density, increasing content of  $\text{Fe}_2\text{O}_3$  particles and NaOH solution. Detailed results and discussions are reported in reference [1].

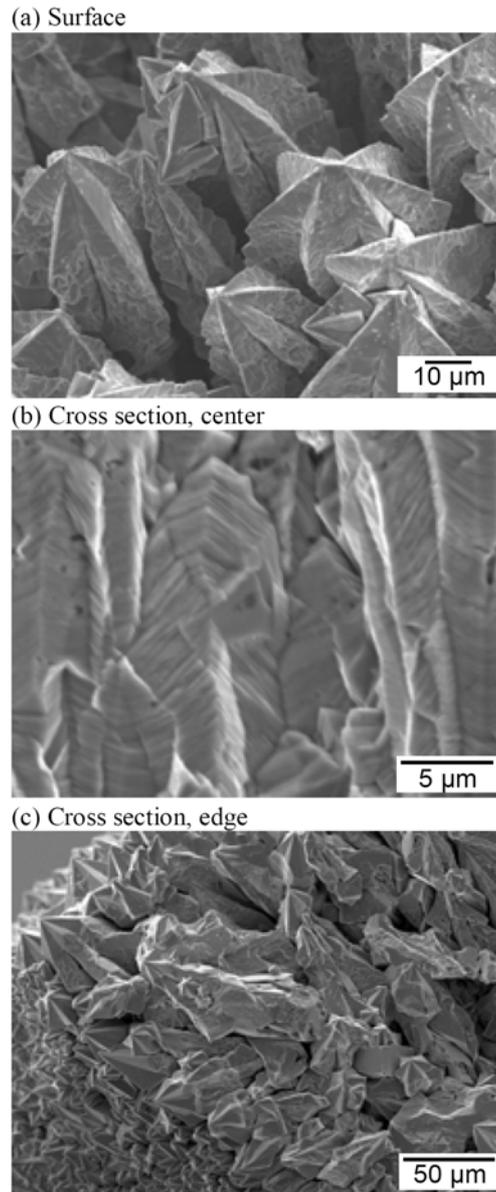


Figure 3. SEM images of iron deposit at cross section

## Conclusion

The electrowinning of iron in the aqueous alkaline solutions using a the rotating disk graphite electrode was investigated. The high cathodic current efficiency efficiencies and the corresponding energy consumptions were determined to be 90 ~ 95% and 2.6 ~ 3 kWh·kg<sup>-1</sup>, respectively, in the laboratory cell. The morphology of the iron deposits was the oriented clusters of stacked six-fold twins grew growing in the direction perpendicular to the cathode surface. The purity was approximately 99.98 wt %. The influences of the rotation rates of the cathode, the cathodic current densities, the contents of the Fe<sub>2</sub>O<sub>3</sub> particles in the electrolyte, and the concentrations of the NaOH solutions on the current efficiency and the morphology of the deposits were studied. The mechanism of the iron deposition from the Fe<sub>2</sub>O<sub>3</sub> particles suspended in the NaOH solutions is presently under investigation.

## Acknowledgements

The authors are grateful to the ULCOS SP13 partners: Drs. Jean-Pierre Birat, Herve Lavelaine, Antoine Allanore (Arcelormittal Maizieres les Metz, France), Chris Treadgold (Corus, The Netherlands), José Ignacio Barbero (Labein, Spain), Jorge Frade (University of Aveiro, Portugal), and Dr. Sverre Rolseth (SINTEF, Trondheim, Norway); Professor Jomar Thonstad (NTNU, Norway), Dr. Ana Maria Martinetz, and Ms. Karen S. Osen (SINTEF, Norway) for their valuable input.

The present work is part of the ULCOS program, which operates with direct financing from its 48 partners, especially of its core members (Arcelor-Mittal, Corus, TKS, Riva, Voestalpine, LKAB, Saarstahl, Dillinger Hütte, SSAB, Ruukki and Statoil), and has received grants from the European Commission under the 6<sup>th</sup> Framework RTD program and the RFCS program<sup>1</sup>.

## References

[1] B. Yuan, O.E. Kongstein, G.M. Haarberg, "Electrowinning of Iron in Aqueous Alkaline Solution Using a Rotating Cathode", *Journal of the Electrochemical Society*, 156, D64 (2009).

---

<sup>1</sup> Priority 3 of the 6<sup>th</sup> Framework Programme in the area of "Very low CO<sub>2</sub> Steel Processes", in co-ordination with the 2003 and 2004 calls of the Research Fund for Coal and Steel