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Designed porous microstructures for electrochemical reduction of bulk hematite ceramics

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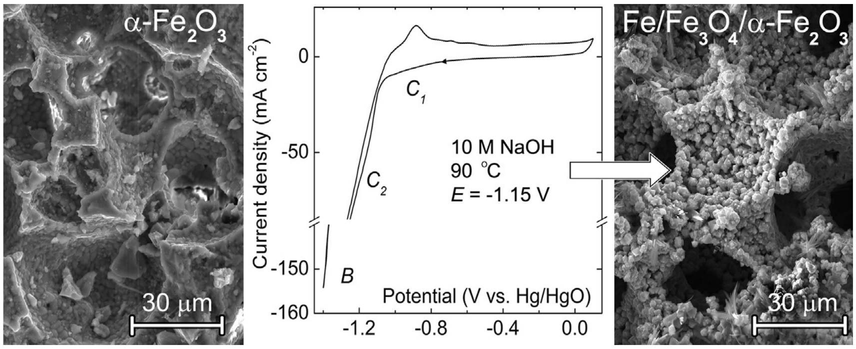
HIGHLIGHTS

- Controlled tuning of microstructure in hematite ceramic cathodes is achieved.
- Cathodic reduction of designed cellular ceramics is performed in aqueous medium.
- Cellular $Fe/Fe_3O_4/Fe_2O_3$ composites are obtained from hematite ceramic cathodes.

GRAPHICAL ABSTRACT



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ABSTRACT

This work proposes a new approach for electrochemical reduction of hematite to magnetite and/or metallic iron, based on ceramic cathodes with designed microstructures. The processing method, involving emulsification of concentrated aqueous ceramic suspensions with melted paraffin, enables preparation of cellular hematite ceramics possessing open porosity and pore interconnectivity controlled by simple process parameters. The obtained porous hematite ceramics were successfully used as cathodes for in situ electrochemical reduction in aqueous alkaline electrolyte. Electrochemical reduction converts the designed ceramic microstructure to corresponding cellular $Fe/Fe_3O_4/Fe_2O_3$ composites with adjustable phase distributions and high prospects for applications in heterogeneous catalysis or other applications, based on unique combinations of active functionalities of metallic Fe, magnetite and hematite.

1. Introduction

Hematite is the most common raw material for iron production. Traditionally, the metallurgical route is used for large-scale iron/steel production from oxide ores. However, this technology is one of the largest industrial contributions to green house gas emissions. Therefore, nowadays, alternative carbon lean technologies are pursued, with emphasis on electrochemical conversion of iron oxides [1], including electroreduction of solid iron oxide particles suspended in alkaline medium [2–6] and high-temperature pyroelectrolysis in molten oxide-based electrolytes [7–9].

Recently, an interesting approach exploring the use of iron oxide itself as a cathode in direct electrochemical transformation to metallic

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iron in alkaline media has been developed [2,10–13]. Within this approach, reduction of a single hematite particle (d ~ 1 mm) is described [10–11]. Other works are devoted to the electrochemical processes on thin oxide films, such as epitaxial magnetite on Au [14], passive films at corroded iron surfaces [15–18], sputtered oxide films [17,19] or freshly prepared hydroxide films [2]. Direct cathodic reduction of thick hematite electrodes faces difficulties due to low electric conductivity of this oxide at moderate temperatures (20–100 °C), impeding the charge transport and propagation of the electrochemical reaction. To overcome this, modification of hematite electrode with a conducting material may be performed. Indeed, successful reduction of micrometer thick layers of Fe_2O_3/Nafion® composite to metallic iron and magnetite is reported [12]. Another strategy to improve electrochemical activity of bulk hematite may be related to the morphology factor, namely, material porosity. Reduction of spherical Fe_2O_3 pellet electrodes (d ~ 3 mm) covered with porous Ni foil in concentrated alkali at 110 °C is discussed in [13], and the authors point the importance of electrode residual porosity for reduction. The success of reduction was also attributed to magnetite inclusion found in hematite samples (the amount of Fe(II) species was not specified by the authors). Recently, one showed [20] that thick (several mm) magnetite pellet cathodes (relative density within 55–85% of theoretical value) with diameter of about 1 cm were successfully reduced in situ to metallic Fe in aqueous alkaline electrolyte, the porosity promoting kinetics and Faradaic efficiency of the reduction. Mentioned facts allow one to suggest that microstructural design of bulk hematite ceramics intended for use as electrode in cathodic reduction might have a significant positive impact on the efficiency of electrochemical process. It is reasonable to assume that suitable ceramic electrodes should possess high porosity, good interconnectivity between pores and appropriate mechanical strength to be further handled as electrodes in aqueous electrolytes.

By now, different methods have been developed for fabrication of porous inorganic materials, with emphasis on ceramics, such as: replica method [21], template methods [21,22], freeze-casting [23,24], direct foaming of emulsified ceramic powder suspensions [21,25–27] and others. Recent works have proved the feasibility of direct foaming to obtain cellular Al_2O_3 [25,29], ZrO_2 [30], $MgAl_2O_4$ [31], $NiAl_2O_4$ [32] ceramics where the size of the cells is within several µm up to mm scale, and the microstructure is characterized by high interconnectivity between the cells. Thus, the microstructure of ceramics prepared by this method might be beneficial for enhanced electrochemical activity of bulk hematite electrodes.

Present study explores a novel methodology to promote direct electrochemical reduction in aqueous alkaline electrolyte by controlled tuning of the microstructural features in hematite ceramic cathodes. The work emphasizes the role of microstructural design of ceramic cathode as a tool to allow infiltration of electrolyte and to extend the effective area for electrochemical conversion. In present paper, one tunes the conditions for processing porous hematite ceramics by emulsification of melted paraffin in aqueous suspensions, aiming well-interconnected cellular microstructures. Selected porous Fe_2O_3 cathodes with designed microstructures are tested for electrochemical reduction in aqueous alkaline solutions.

2. Materials and methods

Hematite powder (<5 µm, Sigma Aldrich) was used as starting material. The powder was ball-milled to decrease the final particles sizes to the range of 100–200 nm, as assessed by scanning electron microscopy (SEM). Emulsification of hematite suspensions was used to process cellular Fe_2O_3 ceramics, following the already described procedure [28]. Paraffin (Merck, melting temperature of 58 °C) was used as a volatile organic component, Dolapix PC 67 (Zschimmer & Schwarz) as a dispersant, collagen (OXOID LP0008) as a gelling additive, and sodium lauryl sulfate (Sigma-Aldrich L-6026) as a surfactant. All solutions and suspensions in the work were prepared with distilled water. Emulsification was carried out at ambient pressure and included following steps: a) preparation of aqueous hematite suspension (50 vol%) stabilized by Dolapix PC 67 dispersant; b) mixing the hematite suspension with melted paraffin under vigorous stirring with addition of collagen as a consolidation agent (5 vol%) and sodium lauryl sulfate surfactant (5 vol%); c) pouring the resultant emulsion into a plastic mold, leaving the top surface exposed to the air, and cooling to room temperature to ensure paraffin solidification and to induce collagen gelling; d) soft thermal treatment of samples at 50 °C in air for water removal followed by heating at $2\ ^\circ C \cdot min^{-1}$, up to a plateau at 200 °C, for 10 h, for slow elimination of paraffin, to prevent collapse of the green ceramic body, and then heating at $5\ ^\circ C \cdot min^{-1}$ up to the final firing temperature at 1100–1200 °C for 3 h in air, to yield the cellular microstructures. The relative density (D) of the ceramic samples was estimated by the Archimedes' method [28–29,33], by immersion in distilled water at 22 ± 2 °C. Open (x_o) and total porosity (x_t) were calculated using the equations given below:

$$D = \frac{wt_1}{wt_2 - wt_3} \times \rho_w \times 100\% \tag{1}$$

$$x_o = \frac{wt_2 - wt_1}{wt_2 - wt_3} \tag{2}$$

$$x_t = 1 - \frac{\rho_w}{\rho_{th}} \times \frac{wt_1}{wt_2 - wt_3} \tag{3}$$

where wt_1, wt_2, wt_3 are the dry, wet (impregnated with water) and apparent (weighted being immersed in water) weight of the samples, respectively, ρ_w is the density of water at 22 °C and ρ_{th} is the theoretical density of hematite ($5.26\ g \cdot cm^{-3}$).

Prior to electrochemical studies, Fe_2O_3 samples were polished, washed in distilled water and ethanol, and dried in a flow of compressed air. Fe_2O_3 pellets with thickness of 3.0–5.5 mm were used as electrodes. Electrical contact was provided by Ni foil support attached to the back side of the pellet using Ag paste. Back and lateral sides of the electrode were isolated by a chemical-resistant lacquer to ensure that only the front side of Fe_2O_3 samples is exposed to the electrolyte. The values of the current densities are given vs. geometric area of the front side of the samples.

Electrochemical measurements were carried out in a teflon cell with Fe_2O_3 working electrode, a Pt wire as a counter electrode and Hg|HgO|NaOH(1 M) reference electrode (+0.098 V versus saturated hydrogen electrode) connected with electrolyte using Luggin capillary. The scheme of the experimental setup is given in Fig. 1. The Autolab potentiostat PGSTAT 20 was used as an electrochemical station. All the curves were recorded with a scan rate of $10\ mV \cdot s^{-1}$.

Before electrochemical studies, porous Fe_2O_3 electrodes were kept in electrolyte for 40 min to provide proper electrolyte infiltration into the open porosity. At the same time, the electrolyte was bubbled with a flow of pure N_2 to ensure the removal of dissolved O_2.

The morphology of the samples was studied by SEM using a Hitachi S-4100 microscope. The crystal structure was examined by X-ray diffraction (XRD) employing a Rigaku D/MAX-B diffractometer (CuKα). For XRD examination, the sample was detached from Ni substrate and ground to powder.

3. Results and discussion

3.1. Fabrication and microstructural characterization of cellular Fe_2O_3 ceramics

For successful processing of porous materials via emulsification of organic phase in water suspensions, several parameters of the preparation procedure need to be controlled [25,28]: i) solid load of the ceramic suspension and quantity of dispersant; ii) organic phase to ceramic