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Research Paper

The Factors Determining Charge Rate of Magnetite Electrode and the Functional Mechanism of Sulfide on the Reaction

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ABSTRACT

The electro-reduction of magnetite is important for many different industries. For example, it relates to the extraction of iron from iron ore and the charging of iron-based batteries. The sluggish electro-reduction reaction of magnetite affects the energy efficiency of iron extraction or the charge rate of iron-based batteries. However, what factors affecting the reduction rate is not well understood. In this study, electrochemical analysis, XRD, SEM, EDS mapping and XPS techniques are adopted to analyze the reaction, and it is proved that two factors determine the electro-reduction rate of magnetite electrode: O^{2-} diffusion inside the particles determines the electro-reduction rate of a single particle, and the electrical resistivity of electrode determines how many magnetite particles are involved in electro-reduction simultaneously. Contact resistance between particles is the dominant part of the electrical resistance of the magnetite electrode. The function mechanism of sulfide in the reaction is also revealed: a sulfide additive can react with magnetite to form amorphous or crystal FeS at different potentials. These compounds, especially crystal FeS, coat onto the surface of magnetite particles, and bond them together. The coating and bonding can decrease contact resistance significantly, thus enhancing the electro-reduction rate of magnetite to one order of magnitude.

1. Introduction

Iron-based batteries have attracted much attention for a long time due to their low cost, robust discharge/charge cycling, and environmental friendliness [1–3]. For large-scale battery applications, iron-based electrodes have two challenges: poor reversibility, and the parasitic H_2 evolution reaction [4]. Stagnant kinetics of the electro-reduction reaction is responsible for the poor reversibility. In the discharging process of iron-based batteries, FeOOH, one of the deeply discharged products, has very high electrical resistivity of $10^9\,\Omega\,cm$ [5], which leads to the sluggish reaction kinetics. To avoid the formation of FeOOH, the cut-off potential for discharge is below $-0.75\,V$ (vs. Hg/HgO), and magnetite is produced. However, magnetite also has an irreversible property [6], and to understand the reason of causing the property is very important. Unlike FeOOH, magnetite has very good electrical conductivity, and the resistivity is as low as $5 \times 10^{-4}\,\Omega$ cm [7]. This physical property benefits from its special structure of inverse spinel. In its face-center cubic unit cell, 16 Fe^{3+} ions evenly occupy cationic octahedral sites and tetrahedral sites, and 8 Fe^{2+} ions occupy the rest of cationic octahedral sites [8]. The electrons can hop between Fe^{3+} and Fe^{2+} in the octahedral sites, leading to as good electrical conductivity as metal [9]. Even with the high electrical conductivity, the capacity decay is directly related to the magnetite accumulation during the discharge/charge cycling of the iron electrode [6]. A recent study reveals that O^{2-} ion diffusion from the bulk of the crystal toward the outside is the limiting step for electro-reduction of a single hematite particle [10], and the same rule can also fit magnetite particle, which will be proved in another study [11]. However, the sluggish kinetics of electro-reducing magnetite inside iron-based batteries is still unclear. Narayanan reports that sulfide is an effective additive to eliminate magnetite accumulation and recover the fading capacity [6]. In the past decades, some research proposed different functional mechanisms of sulfide on the electro-redox of iron. For example, sulfide can mitigate the passivation layer [12,13], increase the electrical conductivity of iron oxides [4,6,14–16], enhance ionic diffusion inside the bulk of iron oxides [17,18], or suppress the H_2 evolution on the surface of iron electrode [19–22]. However, none of the above reports can give an unambiguous explanation about

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the function mechanism of sulfide, due to limited characterization techniques or other reasons.

In this study, ink electrode is adopted to study the reaction kinetics of electro-reduction of magnetite particles with and without sulfide, and the electrical resistivity of the magnetite particle layer is also evaluated. An advanced understanding about the sluggish reaction kinetics of electro-reduction of magnetite is the following: O^{2-} ion diffusion inside the particles determines the reduction rate of a single particle, and electrical resistance of the particle layer determines the thickness of the particle layer, which is involved in electro-reduction simultaneously. After adding sulfide, iron sulfide compounds are produced during the electro-reduction of magnetite, and the compounds (amorphous and crystal FeS) can coat on the particle surface and bond them together. The contact resistance is greatly reduced with the coating, and the reduction rate is enhanced one order of magnitude. This study provides fundamental understanding about the factors affecting the electrode reaction kinetics, and describes a detailed picture about how sulfide enhances the electro-reduction kinetics of magnetite.

2. Experimental

2.1. Preparation of Fe_3O_4 ink electrode and Fe_3O_4/carbon paper electrode

To preparing Fe_3O_4 ink electrodes, 50 mg nano-Fe_3O_4 particles (particle size: 20 nm) was added into 5 ml Nafion solution (0.05 wt % of Nafion in ethanol). The suspension was ultrasonically vibrated for 1 hour to form "Fe_3O_4 ink" and 5 μl of the "ink" was dropped on the surface of glass carbon electrode (diameter: 5 mm). The solvent was evaporated under infrared lamp, and Fe_3O_4 particles were bonded on the surface of glass carbon by Nafion polymer with the layer thickness of ~500 nm. To fabricate carbon paper electrode, carbon paper was cut into 1.2 cm × 2.5 cm dimension, and connected with silver wire by electrically conductive epoxy. The carbon paper was dipped into the "Fe_3O_4 ink", and dried under infrared lamp. The procedure was repeated for several times, and 50 mg Fe_3O_4 was coated on carbon paper eventually.

2.2. Electrochemical tests and material characterization

Electrochemical tests including cyclic voltammetry (CV), linear scanning voltammetry (LSV), and electrode charge/discharge were conducted in three-electrodes electrolytic cell. The main body of the electrolytic cell is four-necks flask (25 ml), with vacuum tight seal adapters in each neck. The counter electrode is Pt foil, and reference electrode is Hg/HgO. Electrolyte is 20 wt% of KOH solution (or with Na_2S) with N_2 gas bubbling through by gas dispersion tube. Because the bubbles are very fine, and the gas dispersion tube is far from the working electrode, the electrolyte around the working electrode is static. The cut-off potential is -1.25 V (vs. Hg/HgO) for charging, and -0.7 V (vs. Hg/HgO) for discharging. Before EIS test, LSV test was carried out for a new-prepared Fe_3O_4 electrode from open circuit potential to −1.011 V (vs. Hg/HgO) at a scan rate of 1 mV/s. EIS test was conducted at −1.011 V (vs. Hg/HgO). After that, the LSV test was conducted again from −1.011 V (vs. Hg/HgO) to −1.132 V (vs. Hg/HgO), and EIS test was then conducted at −1.132 V (vs. Hg/HgO). The frequancy range of EIS was from 100 kHz to 1 mHz, and the AC signal amplitude is 10 mV. For XRD testing of Fe_3O_4/carbon paper electrode, the electrode was transferred into air-tight holder (A100B33, Bruker) inside glove bag filled with N_2 gas before testing with Panalytical XRD machine with Cr as the X-ray tube. For SEM and XPS test, all the samples were stored inside vials filled with N_2 gas before they were transferred into SEM (JSM-7000F). XPS is Kratos Ultra brand, with Al Kα (1.486 KeV) monochromatic X-ray source.

3. Results and discussion

3.1. Electrochemical test for Fe_3O_4 ink electrode combining with SEM analysis

The CV profile of Fe_3O_4 ink electrode in Fig. 1(a) shows two cathodic peaks i, ii, and a cathodic current curve iii. Peak i and ii represent the reduction of Fe(III) to Fe (II) and Fe (II) to Fe inside Fe_3O_4, respectively [23], and curve iii represents H_2 evolution reaction. When the same CV test was conducted for the electrode with 0.01 M Na_2S added in the electrolyte, the current density of peak i′ in Fig. 1(a′) increases or decreases slightly depending on the scan rate. However, the current density of peak ii′ increases one order of magnitude. The peak potential of i and ii almost keeps the same value after adding Na_2S. Ex-situ SEM was adopted to analyze the morphology change of Fe_3O_4 particles on the surface of glass carbon, after LSV test from OCP to −1.20 V (vs. Hg/HgO) at 1 mV/s. Fig. 1(b) shows that most of Fe_3O_4 nano-particles maintained their original shape, and some micro-size hexagonal flakes formed on the surface of electrode. However, with 0.01 M Na_2S added in the electrolyte, not only were more hexagonal flakes produced but also some particles with ~100 nm were formed. Compared to the two SEM images, much more Fe_3O_4 particles were involved in the electro-reduction with 0.01 M Na_2S added. The quantity of Fe_3O_4 particles participating in electro-reduction was estimated according to the cathodic charge consumed for Fe_3O_4 reduction. The cathodic curve of the CV profile was integrated, and the integration value was divided by scan rate, then the charge from both Fe_3O_4 reduction and electric double layer was obtained. The CV test was carried out for glass carbon electrode with the same electrolyte and scan rate, and the integration of the cathodic curve of the CV profile corresponded to the charge from electric double layer. Therefore, the charge from Fe_2O_3 reduction can be obtained by subtracting the charge of electric double layer from the total charge. The method for the charge calculation was also introduced previously [10]. Without adding Na_2S, the charge for Fe_3O_4 reduction decreases gradually with increased scan rate, as shown in Fig. 1(c), and Fe_2O_3 ink electrode exhibits the same phenomenon [10]. After adding 0.01 M Na_2S, the charge for reduction increased one order of magnitude in comparison to the one without Na_2S, as shown in Fig. 1(c). However, the amount of the reduction charge is random, and the relationship between reduction charge and scan rate is not in a regular pattern. An experiment, described below, will explain the irregularity. Since more Fe_3O_4 particles were electro-reduced into Fe, and Fe is good catalyst for H_2 evolution, the cathodic current density (iii′) of H_2 evolution in Fig. 1(a′) increases one order of magnitude, in contrast with the current density (iii) in Fig. 1(a). These CV tests also give direct evidence that sulfide cannot suppress H_2 evolution on the surface of Fe_3O_4 during its electro-reduction. Fig. 1(c′) is the comparison of an electrode charge/discharge profile with and without adding sulfide, and the overpotentials for charging Fe_3O_4 and discharging Fe were reduced obviously, after adding sulfide. Without Na_2S, the specific discharge capacity of the Fe_3O_4 electrode was as low as 30 mA h/g, and with Na_2S, the specific discharge capacity reached to 205 mA h/g, which is compatible with a state-of-the-art commercialized iron electrode [6,12,16], but still much lower than the theoretical specific capacity of 693 mA h/g. The low utilization of Fe_3O_4 occurs because the thermodynamic potential of Fe_3O_4 reduction is lower than the thermodynamic potential of H_2 evolution. A part of the charge, especially in the later charging