Journal of Power Sources 242 (2013) 357–364

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Crystal modification of iron oxide scale by potassium addition and its application to lithium-ion battery anodes

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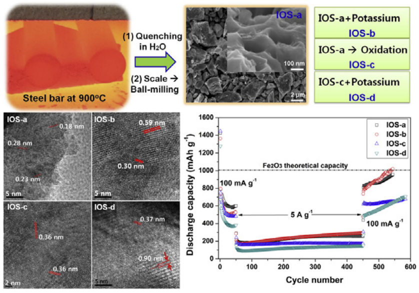
HIGHLIGHTS

- We suggest a simple method to reuse iron oxide scale (IOS) as anode materials in LIBs.
- The IOSs are successfully modified by KOH via a thermal diffusion process.
- KOH-treated IOS exhibits excellent cyclic capability and high reversible capacity.
- This improved performance is attributed to the unique structure of $KFeO_2$ crystals.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 April 2013
Received in revised form
20 May 2013
Accepted 21 May 2013
Available online 4 June 2013

Keywords:
Iron oxide scale
Potassium iron oxide
Anode active materials
Lithium-ion battery
Electrochemical characterization

ABSTRACT

This paper proposes a valuable method to reuse the iron oxide scale (IOS) often produced in the steel industry as an anode active material in lithium-ion batteries (LIBs). The IOS samples are prepared via quenching of carbon steel and simple oxidation at a high temperature with or without sequential treatment by potassium hydroxide. Morphological and physical characterizations confirm the formation of a lamellar structure of orthorhombic $KFeO_2$ with a high degree of crystallinity in the potassium-added IOSs. Additionally, the potassium addition decreases the particle size of the crystals and increases the d-spacing between crystal layers. Electrochemical performance tests show that the discharge capacities of the IOS samples monotonically increased with increasing number of charge/discharge cycles regardless of the existence of potassium. In addition, the rate of increase is larger in the potassium-added IOS samples containing the lamellar $KFeO_2$ structure. Consequently, after prolonged cycling (more than 500 cycles), the potassium-added IOS sample retains a discharge capacity of 1020 mAh g^{-1} with good cycling stability, while the IOS quenched sample only exhibits a capacity of 956 mAh g^{-1}. This result is attributed to the unique structure of the $KFeO_2$ crystals formed in the potassium-added IOS particles.

1. Introduction

Carbon steel is an alloy containing iron and carbon in which the carbon content is normally in the range of 0.2–2.1% by weight. Carbon steel is generally heat-treated to achieve suitable physical and mechanical properties as it responds rapidly to heating or cooling. Quenching is a rapid cooling process which produces steel with hard and strong microstructures and forms numerous iron oxide scales (IOSs) on the surface of the steel including magnetite (Fe_3O_4), hematite (Fe_2O_3), and wüstite (FeO). Most of the IOS is remelted to produce more steel, but this process requires large amounts of coke, limestone, and fossil fuels. Recently, Fe_3O_4 and Fe_2O_3 have attracted much attention as anode materials for lithium-ion batteries (LIBs) due to their high theoretical lithium

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http://dx.doi.org/10.1016/j.jpowsour.2013.05.091

storage capacities above 900 mAh g^{-1} [1–4]. Unfortunately, these materials experience large volumetric changes during charge/discharge processes with lithium ions, ultimately leading to rapid degradation of their anodic performance. This behavior is very dependent on the treatment of the IOSs.

In this study, we evaluated the anodic performance of IOSs pretreated by quenching and severe oxidation and propose a technique involving potassium doping to improve their anodic performance. Gleitzer et al. [5,6] reported that potassium ions trapped in the lattices of iron oxides accelerated oxygen exchange and increased the mobility of oxygen ions, resulting in smaller iron oxide particles with porous and locally-distorted surfaces. From the perspective of anodic performance, small and porous active particles give rise to a large surface area and short path lengths for electronic and ionic transports, resulting in a higher electrode/electrolyte contact area and quick charge/discharge current rates [7–9]. Additionally, the significant change in volume can be alleviated by using nano-sized active materials, which results in stable and improved cyclability over long-term use [1]. It is also known that an electrode containing potassium salt can improve LIB rate performance without any harmful effects such as electrode corrosion [10]. The positive effects of the addition of potassium ions on the anodic performance of IOS were thoroughly investigated in this study.

2. Experimental

Carbon steel (S45C, JIS G4051) was heated to 900 °C in air and rapidly quenched in de-ionized water at room temperature. The IOS collected through the quenching process was dried at 80 °C and separated from impurities by magnetic filtration. Three grams of the IOS was placed in a steel jar containing steel beads (10 mm: 3 EA, 5 mm: 12 EA) and was ball-milled using a vertical mini-mill (Pulverisette 23, Fritsch Co.) at 50 Hz for 20 min to reduce the particle size. The resulting material is referred to as IOS-a. The IOS-a was ultra-sonicated in potassium hydroxide (KOH) solution (30%, Alfa–Aesar Co.) for 10 min and dried in a convection oven at 80 °C overnight. The weight ratio of KOH to IOS-a was 1. The resulting material was calcined at 600 °C in a N_2 atmosphere for 5 h. The material produced is referred to as IOS-b. Additionally, a more oxidized sample, IOS-c, was synthesized by heating IOS-a at 570 °C in an air atmosphere for 3 h. This oxide was also used to produce potassium-doped and more oxidized iron oxide, IOS-d, by applying the same procedure as that used to generate IOS-b.

The crystal structures and phase composition of the treated IOS samples were determined using an X-ray diffractometer (XRD, Rigaku, RAD-3C) with a CuKα ($\lambda = 1.541$ Å) source. Morphological characterizations of the treated IOS samples were characterized using a scanning electron microscope (SEM, Carl Zeiss, Supra40) with a field emission gun, and a transmission electron microscope (TEM, JEOL, JEM-2100F).

The electrochemical characteristics of the samples as LIB anodes were evaluated in CR2016 coin cells with lithium metal as a counter and reference electrode. The working electrodes were composed of 50 wt.% treated IOS, 30 wt.% super-P as an electrically-conductive additive, and 20 wt.% polyvinylidene fluoride (Solef 5130, Belgium) as a binder. Their loading densities were 1.3 ± 0.1 mg cm^{-2}. As an electrolyte, 1 M $LiPF_6$ (Panaxetec Co., Korea) dissolved in a 1:1:1 (v/v/v) mixture of ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate was used. The coin cells were galvanostatically charged to 3 V and discharged to 5 mV at various current densities in a battery test system (PNE solution BCP50). Additionally, cyclic voltammetry (CV, Biologis VSP) and electrochemical impedance spectroscopy (EIS) were performed from 3 V to 0 V at a potential sweep rate of 0.5 mV s^{-1} and at a frequency range of 0.01 Hz–100 kHz, respectively.

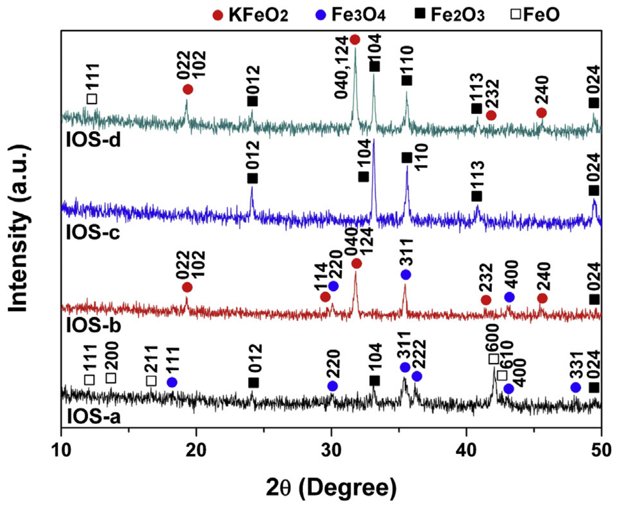

Fig. 1. XRD peaks of the treated IOS samples: IOS-a (quenching), IOS-b (quenching and potassium addition), IOS-c (quenching and oxidation), and IOS-d (quenching, oxidation, and potassium addition).

Some of the coin cells charged/discharged more than 300 times were disassembled in an argon-filled glove box and their anode materials were washed with dimethyl carbonated and stripped away from the copper foil. The remaining electrolyte and organic matters in the materials were eliminated by ultrasonication in a 1:9 (v/v) mixture of de-ionized water and ethanol for 20 min. The particles collected via filter paper were dried in a vacuum oven at 80 °C for 30 min and their crystal structures were investigated using XRD and TEM analyses.

3. Results and discussion

The crystal structures of the treated IOS samples were characterized by their XRD peaks, as shown in Fig. 1. The XRD pattern of IOS-a indicates that various iron oxide crystals such as Fe_3O_4 (JCPDS No. 87-2334), Fe_2O_3 (JCPDS No. 87-1165), and FeO (JCPDS No. 87-2316) were formed during the quenching process. As seen from the XRD peaks of the IOS-b sample in Fig. 1, the KOH treatment transforms some of iron oxides, especially Fe_2O_3, into an orthorhombic $KFeO_2$ compound (JCPDS No. 83-2153) with a high crystallinity. The IOS-c sample produced by an additional oxidation step showed a higher crystallinity than the IOS-a sample, and most of the XRD peaks are assigned to rhombohedral Fe_2O_3, clearly indicating that both Fe_3O_4 and FeO phases are transformed into a relatively high oxidation form of iron, Fe_2O_3. Thus, the XRD spectra of the IOS-d sample show peaks that can be assigned to the mixture of $KFeO_2$ and Fe_2O_3 only. Relative quantitative percentages of each crystalline phase in the IOS samples were determined from the comparison among integrated XRD peak areas and were listed in Table 1.

Table 1
Particle size and quantitative percentage of IOS samples estimated by the XRD peaks.

Samples	Quantitative percentage of crystalline phase (%)				Mean particle size (nm)
	$KFeO_2$	Fe_3O_4	Fe_2O_3	FeO	
IOS-a	0	43.9	18.9	37.2	64.8
IOS-b	50.8	44.0	5.2	0	23.3
IOS-c	0	11.0	89.0	0	53.2
IOS-d	41.3	0	55.3	3.4	49.1