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Iron/carbon-black composite nanoparticles as an iron electrode material in a paste type rechargeable alkaline battery

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ABSTRACT

Iron/carbon-black composite nanoparticles were synthesized by chemically reducing the iron salt mixing with carbon black by adding $NaBH_4$ in the aqueous solution. Carbon-black particles, with a mean particle size of approximately 40 nm, function as the nucleation cores for iron deposition. Additionally, core–shell iron composite particles are observed to be 30–100 nm with spherical sharp. At the first time discharge, the iron/carbon-black composite nanoparticle discharged 1200 mAh g^{-1}(Fe) at plateau one and 400 mAh g^{-1} at plateau two at a high current density of 200 mA g^{-1}(Fe). The capacity is larger than the theoretical value, which is attributed to the formation of iron hydride (FeH_x) while the iron was reduced by $NaBH_4$, followed the hydrogen reaction as an active material while the battery discharge occurs. In further cycles, the iron/carbon-black composite iron electrode shows a good reversibility of about 600 mAh g^{-1}(Fe) when the nickel–iron battery operated between 1.65 and 0.8 V. XRD analysis results indicate that the carbon black in the core of the iron/carbon-black composite enhances the reduction/oxidation reactions of iron, as achieved by the carbon black forming an enhanced electronic conductive network while iron is discharged as the insulator species such as $Fe(OH)_2$ and Fe_3O_4. SEM images reveal that the iron/carbon-black composite keeps particle sizes smaller than 300 nm during the electrode cycling, indicating that carbon black also acts as the nucleation cores for the dissolution–deposition of iron.

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1. Introduction

Large scale batteries are widely discussed for use in electrical powered vehicles. Safe, low cost, and high energy density are the basic requirements of it. Of particular interest are lithium ion batteries, in which $LiFePO_4$ is used as the cathode material. Despite their attractiveness given the abundance of iron and the highly safe nature of $LiFePO_4$, lithium ion batteries are limited in safety owing to the flammable organic electrolyte contained inside. In contrast, alkaline rechargeable batteries satisfy safety concerns owing to their use of an aqueous electrolyte. The Ni–Fe rechargeable alkaline battery, in which iron is used as the anode and $Ni(OH)_2$ as the cathode material, was developed around 1900, and has a cycle life of 3000 cycles and a calendar life of about 20 years [1]. Despite its good resistance against overcharging, deep discharging, and mechanical shocks, this battery has been replaced owing to its relatively low power density, low energy density [2], and high self-discharge [3]. Alternatively, nickel–iron batteries are highly promising for large scale battery applications owing to their high theoretical capacity, inexpensiveness, and absence of toxic materials. Although the theoretical capacity of iron is 962 mAh g^{-1}, in previous studies, the iron electrode performed as low as 1/3 of the theoretical value [4–7], owing to the formation of a passive film [8]. While attempting to enhance the capacity and power density of iron active materials, our previous study [9] used the nanosized iron particle, in which the nanosized iron particle discharge capacity is about 700 mAh g^{-1}(Fe) during the first cycle, a capacity that was significantly higher than in other studies. However, the capacity of the active material decreases quickly to less than 300 mAh g^{-1} during the second or third cycle. Although other investigators made nanosized iron active materials, the reversibility was not improved [10–14]. This work describes a novel composite structure with carbon-black particle as the core and iron as the shell, via the formation of a good conductive network of carbon black to improve the reversibility of the active material.

2. Experimental

2.1. Preparation of active materials

Nanosized iron particles were synthesized by chemically reducing Fe ion by sodium borohydride. 0.025 mole of $FeSO_4{\cdot}7H_2O$

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(Showa, Japan) was dissolved in 200 ml D.I. water, followed by dissolution of 0.05 mole of $NaBH_4$ (Lancaster, England) in 50 ml D.I. water. The $NaBH_4$ solution was then pumped into the $FeSO_4$ solution of 5 ml min^{-1} with an ice bath. Next, composite iron nanoparticles were prepared by reducing Fe on the surface of carbon-black particles. The carbon black (40 nm, Timcal, Switzerland) was pre-mixed with the $FeSO_4$ solution, followed by pumping of the $NaBH_4$ solution into the $FeSO_4$ solution of 5 ml min^{-1} with an ice bath. Additionally, all reaction solutions were stirred continuously for 30 min to complete the reduction reaction. The synthesized iron particles were then washed by hot water (~90 °C) and separated by a magnet three times. After the unwanted reactants were removed, the samples were stored in acetone to prevent oxidation. Moreover, the samples were identified by X-ray diffraction (XRD; Rigaku, Japan), and the morphology was observed by scanning electron microscopy (SEM; S-4700, Hitachi, Japan). Cyclic voltammetry studies were conducted with a three-electrode cell assembly, in which iron electrodes were used as the working electrode, and nickel hydroxide as the counter electrode, Ag/AgCl as the reference electrode. Notably, the electrolyte was 8 M KOH + 1 M LiOH aqueous solution. Finally, cyclic voltammetry measurements were recorded at a sweep rate of 5 mV s^{-1} and in the range of −0.4 to 1.4 V.

2.2. Preparation of iron electrode and cell assembling

Paste type iron electrodes were prepared to evaluate the performance of iron active materials. The synthesized iron active materials, which contained 1.39 g of iron, were mixed with 0.028 g of Na_2S (Showa, Japan) and 0.14 g of PTFE (60% suspended solution, Aldrich, USA) to form the pastes. The pastes were then poured into nickel foam current collectors (80 mm × 40 mm × 1.8 mm, 110 ppi). Next, the iron electrodes were packed by non-woven PP cloth as separators. A miniature cell was assembled with a single iron electrode and two nickel electrodes with an excess capacity placed on both side; the cell was then packed in a case. The base electrolyte in the experiment is 8 M aqueous KOH solution containing 1 M LiOH. Additionally, the performance of the iron electrodes was evaluated based on its discharge capacity. Finally, the cells were cycled in the range of 0.8–1.65 V at a current density of 200 mA g^{-1}(Fe) at room temperature by a battery automatic tester (760B, Acutech System, Taiwan).

3. Results and discussion

3.1. Characteristics of synthesized iron nanoparticles

Fig. 1 shows the XRD patterns of the reduced pure iron and iron/carbon-black composite. The XRD pattern of the reduced pure iron reveals a weak and broad peak at Fe(1 1 0), indicating that the iron is obviously reduced and has a poor crystalline structure.

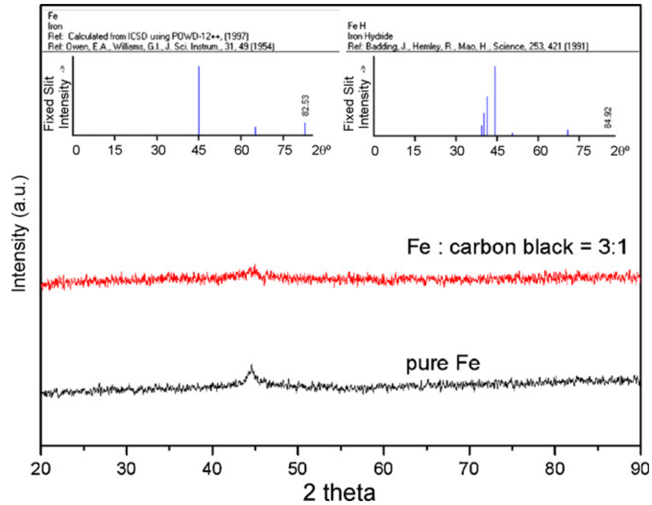

Fig. 1. XRD patterns of pure iron and iron/carbon-black composite nanoparticles as prepared.

The XRD pattern of the iron/carbon-black composite nanoparticle shows a weaker peak than that of pure iron, suggesting that the iron deposited on the surface of carbon-black particles decreases the grain size of iron.

ICP-MS analysis reveals that the boron residual in the iron particles was about 4.8 wt.% or 0.25(mol/mol) even after the samples were washed by D.I. water three times. Some studies suggest that the compound Fe_2B forms when iron is reduced by BH_4^- in an aqueous solution [15]. The reactions are shown as follows:

$$Fe^{2+}(aq) + 2BH_4^-(aq) + 2H_2O \rightarrow Fe(s) + B_2H_6 + H_2 \quad (1)$$

$$B_2H_6 + 6H_2O \rightarrow 2B(OH)_3 + 6H_2 \quad (2)$$

According to reaction (1), B_2H_6 is produced when the reduction reaction proceeded. The intermediate B_2H_6 then decomposes to B and H_2 and, then, the boron combines with iron. However, in an aqueous solution, B_2H_6 also reacts with H_2O subsequently producing $B(OH)_3$ and H_2 (Eq. (2)). Therefore, only a slight amount of Fe_2B is produced [15]. Additionally, a significant amount of hydrogen is produced during the reduction reaction, implying that the hydrogen is either trapped in the crystalline structure or adsorbed on the iron surface [16,17], subsequently forming the iron hydride (FeH_x). Comparing the XRD patterns in Fig. 1 reveals that, although the strongest peak shifts slightly to the peak of FeH (44.2°), this is not exactly the peak of pure iron. Therefore, we believe that the fresh sample of the reduction reaction closely resembles the mixture of Fe, FeH and $B(OH)_3$.

Fig. 2 shows the SEM images of these two iron particles. In Fig. 2(a), the pure iron particles strongly aggregate together and their particle sizes range from 50 to 150 nm. In contrast, the particle

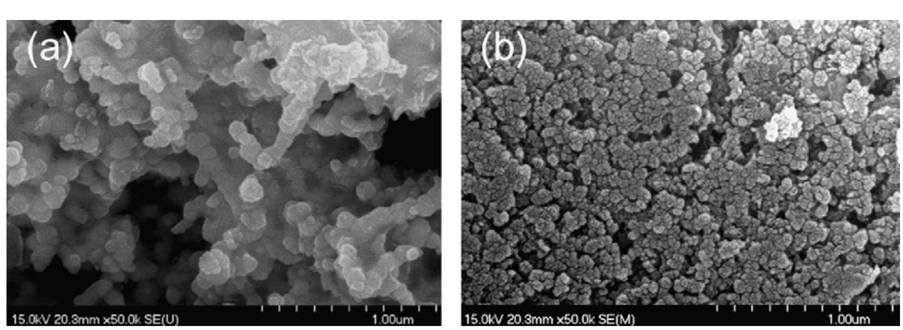

Fig. 2. SEM images of the iron nanoparticles as prepared: (a) pure iron and (b) iron/carbon-black composite.

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