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Characteristics of potassium iron oxide for high-powered anode materials for lithium-ion batteries

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ABSTRACT

Here, the electrochemical properties of layered-structure $KFeO_2$ anode material for lithium-ion batteries (LIBs) are reported for the first time in the literature. The even-sized $KFeO_2$ compounds were synthesized by the thermal diffusion of potassium into Fe_2O_3 nanoparticles produced using high temperature calcination of a graphene substrate. With the help of potassium, unlike typical iron oxide electrodes, the redox conversion between Fe^0 and Fe^{2+}/Fe^{3+} in the $KFeO_2$ electrode became gradually decreased, whereas the interfacial charging/discharging of lithium ions through the layered-structure increased as charge/discharge was repeated. In addition, the continuous cycle led to potassium desertion from $KFeO_2$ phases, forming well-dispersed layered-structure Fe_2O_3 nanoparticles less than 2 nm throughout the electrode. Such a favorable scenario gave rise to a significant reversible capacity of 2564 mAh g^{-1} after 1000 cycles at an extremely high current rate of 18.56 A g^{-1}.

1. Introduction

There is great interest in the development of novel anode materials for high-performance lithium-ion batteries (LIBs). Generally, novel anode materials for LIB should meet several specifications such as high theoretical and low irreversible capacities, small volume change during lithium insertion/desertion, a facile manufacturing process, and a low price if possible. Recently, transition metal oxides (MOs) and their alloys have attracted much attention as emerging anodic materials due to their higher gravimetric lithium storage capacities than conventional graphite [1–6]. Numerous examples are available; cobalt oxide [2], copper oxide [3], iron oxide [4], manganese oxide [5], and nickel oxide [6]. Unfortunately, early studies found that many MO anodes had high initial irreversible capacities and rapid capacity fade during cycling due to large volumetric change and cracking and pulverization of active particles, ultimately leading to severe damage in the electrical network of electrodes. Since 5nanosized materials easily release the extreme stress that develops within the materials during charge/discharge, the majority of the recent studies on MO anodes have focused on modification methods to synthesize structurally stable nanosized MOs such as nanoparticles, nanorods, nanofibers, and nanocomposites [3–10]. The crystal structure and morphology of nanosized MOs play significant roles in the charge/discharge characteristics including rapid lithium ion transport kinetics. Nevertheless, nanosized MOs are accompanied by undesirable side reactions at the numerous interfaces with liquid electrolyte. Additionally, nanosized MOs and their composites require very complicated and high-cost synthesis procedures.

Iron oxides (IOs) and their composites have been extensively studied since they could be formed by a relatively simple manufacturing process, with a low price as a result of an abundance of natural resources [10–17]. Iron reacts easily with oxygen in a normal environment, and mainly forms three types of oxides according to their oxidation states; magnetite (Fe_3O_4), hematite (Fe_2O_3), and wüstite (FeO). In particular, Fe_3O_4 and Fe_2O_3 have attracted considerable attention as anode materials for LIBs due to their high capacities of approximately 1000 mAh g^{-1}. In addition, to some extent, alkali metals such as sodium and potassium form unique lamella structures with iron oxide nanosheets, resulting in extra capacity than that theoretically calculated, although the cyclic performance is still poor. In very recent years, we have shown that potassium-added IO particles, with or without a graphene substrate, had superior anodic performance by forming electrochemically active and strong lamellar structures [18,19]. A portion of Fe_2O_3 crystals was transformed to $KFeO_2$ phases, orthorhombic $KGaO_2$-type structures with a *Pbca* space group [20–22], by

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thermal potassium diffusion into the Fe_2O_3 lattice. These phases had vacancies and broad d-spacing when compared to Fe_2O_3 crystal structures, leading to higher lithium storage performance than typical IOs. We believe that the unique crystal structure of $KFeO_2$ makes it an appropriate anode material for LIBs. The crystal structure and magnetic properties of the $KFeO_2$ phase have been previously reported in the literature [21,22], whereas its possibility as an anode material for LIBs has not been extensively investigated. In the present study, therefore, the electrochemical characterization of the $KFeO_2$ anode was thoroughly examined using a variety of physical and electrochemical characterization tools; x-ray diffraction (XRD), transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and cyclic charge/discharge analysis.

2. Experimental

2.1. Synthesis of nanosized $KFeO_2$ using Fe_2O_3/graphene composite

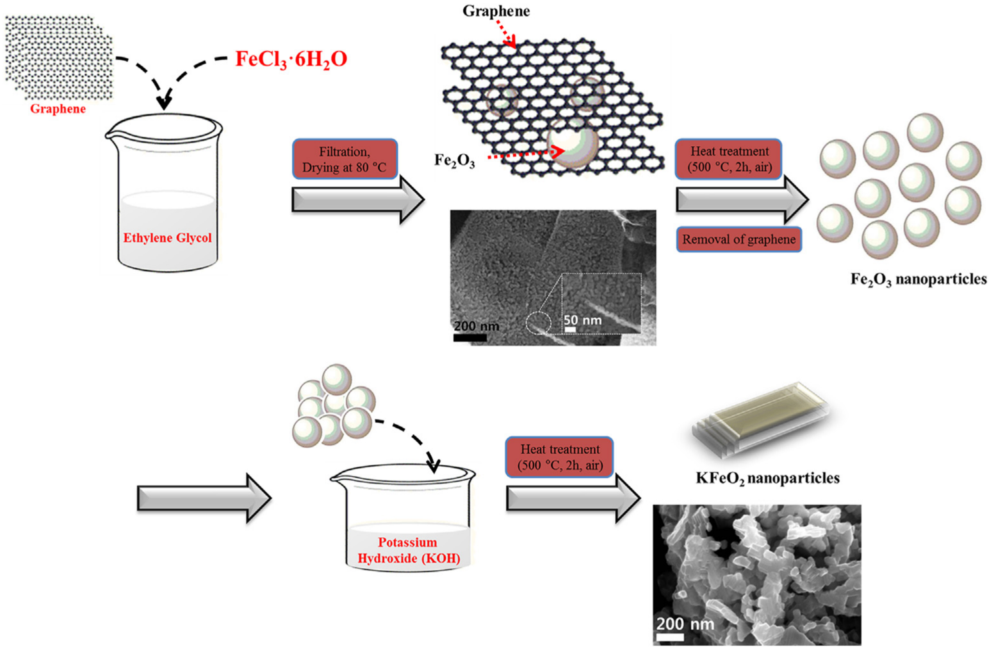
The schematic procedure for the synthesis of $KFeO_2$ is illustrated in Scheme 1. To synthesize even-sized Fe_2O_3 nanoparticles with a high-density, a graphene sheet was initially used as a substrate, and removed at the final stage of the procedure. 4.9 g iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, Junsei chemical Co.), dissolved in 40 ml ethylene glycol (EG), was added to 350 ml EG solution containing 0.2 g graphene (Angstron materials, N002-PDR). The solution was heated to 180 ± 10 °C after sonication in an ultrasonic bath for 10 min. 40 ml 1 M NaOH, dissolved in EG, was added dropwise to the mixture in order to adjust pH to 10, and was subsequently stirred for 3 h. This suspension was washed with deionized water and ethanol, and then dried in a vacuum oven at 80 °C. The iron oxide/graphene composite was subsequently annealed in air at 500 °C for 2 h, leading to the transformation of iron oxides to Fe_2O_3 and the removal of the graphene substrate by its oxidation in air. A mixture of 0.28 g Fe_2O_3 nanoparticles and 0.27 g potassium hydroxide (KOH, 30%, Alfa-Aesar) was sonic-distributed for 10 min, and the resultant was washed in deionized water and ethanol, dried in a vacuum oven at 80 °C, and finally calcined again at 500 °C for 2 h in an air atmosphere.

2.2. Physical characteristic analysis

The chemical composition of the as-synthesized $KFeO_2$ sample was identified by an electron probe microanalyzer (EPMA, Shimadzu, EPMA-1400). The crystal structures and morphologies of the synthesized Fe_2O_3 and $KFeO_2$ samples were characterized using an x-ray diffractometer (XRD, Rigaku, RAD-3C) with CuKα sources ($\lambda = 1.541$ Å), a transmission electron microscope (TEM, Jeol, Jem-2010), and a scanning electron microscope (SEM, Carl Zeiss, Supra 40). X-ray photoelectron spectroscopy (XPS) spectra were obtained using an Escalab 250 (Thermo Fisher Scientific, U.K.) with a 500-μm spot size, 15-kV x-ray energy, and equipped with a monochromated Al Kα ($h\nu = 1486.6$ eV) source. Argon ion-etching spectra were performed for 10 s to remove the solid electrolyte interface (SEI) on the electrode surface prior to obtaining XPS.

2.3. Electrochemical characteristic analysis

The electrochemical performance was evaluated through two-electrode coin half-cells (CR2016 type), with the working electrode containing the nanosized particles. The working electrode was composed of 30 wt% active materials, 50 wt% super-P carbon, and 20 wt% polyvinylidene fluoride (PVDF, Solef5130, Belgium) binder dissolved in n-methyl-2-pyrrolidone. Although this formulation deviated from the composition of commercial electrodes, it was necessary in order to investigate the possibility of using the newly developed $KFeO_2$ as a high-capacity and high-powered anode material. The electrode slurry was coated on copper foil current collector, and dried in a convection oven at 130 °C for 30 min. Subsequently the working electrode was dried again in a vacuum oven at 80 °C for 12 h to remove residual moisture and solvent before assembled in an argon-filled glove box. The density of the working electrode was approximately 0.5 g cm^{-3} and the loading amount of active material in the electrode was 0.7 mg cm^{-2}. Thick lithium foil was used as a counter and reference



Scheme 1. Procedure for the synthesis of $KFeO_2$ nanoparticles.