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$K_{0.67}Ni_{0.17}Co_{0.17}Mn_{0.66}O_2$: A cathode material for potassium-ion battery

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ABSTRACT

A novel layered ternary material $K_{0.67}Ni_{0.17}Co_{0.17}Mn_{0.66}O_2$ has been fabricated via a co-precipitation assisted solid-phase method and further evaluated as a cathode for potassium-ion batteries for the first time. Highly reversible K^+ intercalation/deintercalation is demonstrated in this material. It delivers a reversible capacity of 76.5 mAh/g with average voltage of 3.1 V and shows good cycling performance with capacity retention of 87% after 100 cycles at 20 mA/g. This work may give a new insight into developing cathode materials for potassium-ion batteries.

1. Introduction

Intermittent renewable energy sources (e.g., wind, solar) should be integrated into power grid by sustainable storage technologies to satisfy the growing energy demand of modern society [1,2]. Currently, among various energy storage technologies, lithium-ion batteries (LIBs) technology is the most suitable one for storing electricity in the form of chemical energy due to its dexterity and high-energy conversion efficiency [3–5]. However, the shortage, increasing cost and uneven global distribution of lithium resources has limited its comprehensive large-scale application [6]. Recently, due to similar electrochemical principles, sodium-ion batteries (NIBs) and potassium-ion batteries (KIBs) have gained extensive attention to renewable energy and electrical grid in large-scale energy storage applications owning to high natural abundance and low cost of these elements resources [3,7,8]. In comparison to the low abundance of only 0.0017 wt% of lithium element, sodium and potassium elements occupy 2.36 wt% and 2.09 wt% in the Earth's crust, respectively [9]. In the past few years, NIBs have been intensively investigated, while KIBs are less studied and still in the initial stage of research.

To date, only a few potassium insertion materials for cathode such as layered K_xMO_2 (M = Mn, Co, Fe, Ti) [10–13], polyanionic compound [14–17], prussian blue [8,18], organic materials [19,20] have been evaluated. Vaalma et al. reported $K_{0.3}MnO_2$ as a cathode, which showed an initial capacity of 136 mAh/g, however, its reversibility was poor at high potential [10]. To our knowledge, a class of layer-structured ternary materials such as $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ [21], $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ [22], $Li[Ni_{1-x-y}Co_xMn_y]O_2$ [23], $Na[Ni_{0.61}Co_{0.12}Mn_{0.27}]O_2$ [24] and $Na_{0.67}[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2$ [25] as the most promising cathode for LIBs and NIBs have been widely investigated. However, ternary materials containing potassium element have not been studied for KIBs yet.

Herein, we synthesized $K_{0.67}Ni_{0.17}Co_{0.17}Mn_{0.66}O_2$ by a very simple method and investigated its electrochemical potassium-ion storage properties for KIBs for the first time.

2. Experimental

$K_{0.67}Ni_{0.17}Co_{0.17}Mn_{0.66}O_2$ was synthesized by co-precipitation assisted solid-state reaction. An aqueous solution of $NiSO_4$, $CoSO_4$ and $MnSO_4$ (cation molar ratio of 0.17:0.17:0.66) with a concentration of 2 mol/L was pumped into reactor. Meanwhile, 1 mol/L Na_2CO_3 and 0.3 mol/L $NH_3{\cdot}H_2O$ were also fed into the reactor at 50 °C. The pH value was controlled at 8.0 ± 0.2 and stirring speed was set at 500 rpm. After extensively washed by de-ionized water, precipitate was dried at 120 °C overnight, then pre-heated in air at 550 °C for 5 h to form an oxide compound. Afterward, a 5% excess amount of K_2CO_3 was mixed with the oxide powders and calcined in air overnight at 750–900 °C.

XRD patterns were collected on a Rigaku instrument with Cu K_α radiation. Rietveld refinement was performed using GSAS software package. Particle morphology was observed by scanning (SEM, ZEISS SUPRA55) and transmission (TEM, Tecnai G2F20) electron microscopy. Chemical compositions were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Optima 4300 DV). Elements distribution was analyzed with electron diffraction spectroscopy (EDS).

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Oxidation state of key elements was studied by X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250Xi).

The cathode was prepared by mixing 80 wt% active material, 10 wt % acetylene black and 10 wt% poly(vinylidene fluoride) in *N*-methyl-2-pyrrolidinone. Then the slurry was coated on Al foil and vacuum-dried overnight at 120 °C. The electrode film was roll-pressed and punched into disks with a diameter of 10 mm and mass loading was approximately 2.0 mg/cm^2. CR2032 coin cells were assembled in an Ar-filled glovebox. Potassium metal (Aladdin Ltd) was used as counter/reference electrode, a glass-fiber (Whatman GF/D) as separator and 0.8 M KPF_6 (Aladdin Ltd) in ethylene carbonate/diethyl carbonate (1:1 by volume) as electrolyte. Galvanostatic charge-discharge cycles were tested on Land CT2001A battery testing systems between 2 and 4.3 V at 20 mA/g at room temperature. Cyclic voltammetry (CV) measurements were performed on a CHI 660C electrochemical workstation (Shanghai Chenhua, China).

3. Results and discussion

XRD patterns of as-prepared samples and the Rietveld-refined results are displayed in Fig. 1a and b. The intensity of main diffraction peak increases gradually with the increase of sintering temperature, suggesting higher crystallinity. Rietveld analysis demonstrates the formation of the desired $K_{0.67}Ni_{0.17}Co_{0.17}Mn_{0.66}O_2$ stabilizing into a triclinic structure (ICSD 152290, space group: R-3 m) with lattice parameters: a = 2.860(8) Å, c = 20.628(6) Å, α = 90°, β = 90°, γ = 120° and *Vol* = 146.2(1) Å^3. The small value of Rwp (< 6%) suggests the reasonable refinement results. Moreover, this material shows larger c value than that of the counterpart Na cathode such as $Na_{0.67}Mn_{0.72}Ni_{0.14}Co_{0.14}O_2$ [26], which could result in enlarged K^+ diffusion path and enhanced migration rate of K^+.

As shown in Fig. 1c, most of samples are spherical secondary particles with average diameter of 8 μm and each consists of several primary grains. With the increase of sintering temperature, particles grow up and crystallinity is improved. SEM image of sample synthesized at 850 °C displays a uniform, sphere-like crystal structure that consists of regularly multilayered sheets with size about 2 μm. The observation from SEM is further verified by a TEM image shown in Fig. 1e. The EDS mapping images demonstrate the existence and uniform distribution of K, Ni, Co and Mn elements (Fig. 1d). Furthermore, ICP-AES and EDS results confirm a K:Ni:Co:Mn ratio of 0.67:0.169:0.168:0.662, which is close to the designed stoichiometry. Fig. 1f shows fine crystalline lattice fringes with spacing of 3.43 Å, corresponding to (006) plane of R-3 m structure.

Fig. 2 shows the XPS spectra of $K_{0.67}Ni_{0.17}Co_{0.17}Mn_{0.66}O_2$. The presence peaks of K, Ni, Co, Mn and O in the survey spectrum can be assigned to $K_{0.67}Ni_{0.17}Co_{0.17}Mn_{0.66}O_2$, consistent with EDS results. The Ni $2p_{3/2}$ peak at 854.62 eV is smaller than the peak in Ni_2O_3, indicating that Ni ions are + 2. In Fig. 2c, the two major peaks at 779.9 and 794.8 eV are attributed to Co $2p_{3/2}$ and Co $2p_{1/2}$, which are consistent with the literature data on $LiCoO_2$ [27], demonstrating that Co ions are mainly + 3. In Fig. 2d, the Mn $2p_{3/2}$ peak located at 642.5 eV is close to that of Mn^{4+} in MnO_2, indicating the dominant Mn^{4+} cation. However, a couple of less prominent peaks at 641.8 and 653.3 eV correspond to

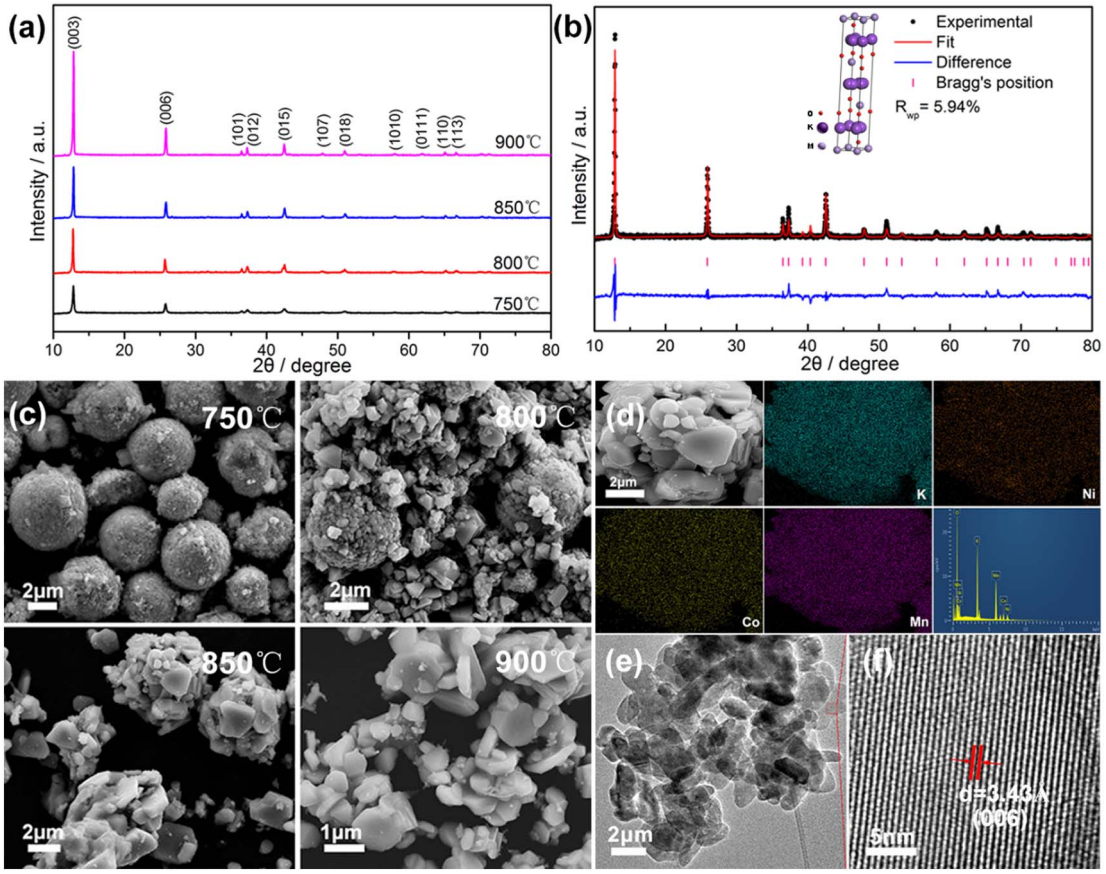

Fig. 1. XRD (a) and SEM (c) of $K_{0.67}Ni_{0.17}Co_{0.17}Mn_{0.66}O_2$ synthesized at different temperatures. Rietveld refinement result (b), EDS (d), TEM (e) and HRTEM (f) of $K_{0.67}Ni_{0.17}Co_{0.17}Mn_{0.66}O_2$ synthesized at 850 °C.