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Microwave-assisted hydrothermal synthesis of nanocrystalline lithium-ion sieve from biogenic manganese oxide, its characterization and lithium sorption studies

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ABSTRACT

Biogenic birnessite (BB) is a stable form of manganese oxide. It is widely distributed in the natural environment and originates from microbial oxidation. It has potential applications in functional material fabrication because of its unique morphology. Using a microwave-assisted hydrothermal method, nano-sized lithium-ion sieves were prepared from BB with a short reaction time. A combination of sorption experiments and structural characterization was used to compare Li uptake by nanoparticles with that by microparticles. X-ray diffraction (XRD) patterns showed that the nano- and microparticles had similar fundamental structures, but the lattice parameter of nanoparticles is smaller than microparticles. Mn K-edge X-ray absorption fine structure (XAFS) spectroscopy showed that the oxidation state of Mn increased from 3.50 to 3.69 with decreasing crystal size, and the Mn–Mn atomic distance decreased from 2.92 to 2.89 Å. Li extraction resulted in significant cleavage of the microparticle surfaces. The oxidation state of Mn increased to 4.0, and the Mn–Mn atomic distance decreased to 2.86 Å. XRD showed that dissolution of the polycrystalline phase of the nanoparticles occurred during acid washing. However, the EXAFS spectrum was similar to that of the original material before acid washing. The specific surface areas and Li-sorption capacities of the nano-sized lithium-ion sieves prepared from manganese carbonate were significantly higher than those of a similarly prepared micro-sized lithium-ion sieve. The results obtained in this work suggest that BB is a promising starting material for the energy-saving fabrication of functional materials for highly efficient Li recovery.

1. Introduction

Lithium, a key element in high-power lithium-ion batteries, is regarded as an energy metal in industry. Li production has attracted great interest globally, because of the increasing demand for portable electronic devices such as laptops and cell phones. The main Li resources are lithium-enriched minerals, seawater, and geothermal brine. One of the conventional processes for Li recovery from brine is evaporation, which consumes large amounts of water and solar energy, and gives low lithium-recovery efficiency. Another method for Li recovery from seawater or minerals is extraction. However, such processes are technically complex. New low-cost, simple, environmentally friendly techniques for Li recovery are therefore needed.

Manganese oxide spinel obtained by delithiation of spinel $LiMn_2O_4$ shows a high selectivity and high sorption capacity for Li, and is therefore used as a lithium-ion sieve. $LiMn_2O_4$ is also a promising cathode material for lithium-ion batteries (Kovacheva et al., 2002). Various approaches to $LiMn_2O_4$ production have been investigated. The lithium-ion sieve performance is closely related to the $LiMn_2O_4$ crystallinity, purity, and particle size (Chitrakar et al., 2000; Ma et al., 2011; Yu et al., 2013a,b). A simple solid-state reaction produces $LiMn_2O_4$ of high crystallinity, but requires a high temperature and long calcination period (Ammundsen et al., 1996). We successfully used biogenic birnessite (BB) as the starting material for the solid-state synthesis of lithium-ion sieves (Yu et al., 2013a,b). Unlike chemically synthesized manganese oxide, the poorly crystalline BB was transformed into spinel at low temperatures. In this method, powdery particles of BB were mixed with Li^+ solution, followed by evaporation and calcination. Calcination produced impurity phases along with spinel, because the mixture became inhomogeneous during evaporation. A number of soft chemistry methods have been developed for preparing spinel-type materials under mild conditions. Zhu et al. (2009) synthesized Zn_2SnO_4 spinel by a hydrothermal process using NaOH as an alkaline mineralizer. Zhao et al. (2008) prepared $CoFe_2O_4$ nanocrystals with a uniform particle size of 70 nm. LiMnO spinel with particles of diameter 200 nm was synthesized by a hydrothermal reaction in 4–48 h (Liu et al., 2004). Microwave-assisted synthesis of inorganic nanomaterials has recently attracted much interest, because microwave irradiation provides efficient and controlled heating, and the synthesis is much faster (Bilecka and Niederberger, 2010). In the present work, a microwave-assisted

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Abbreviation: BB, Biogenic birnessite.

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hydrothermal reaction was used for the rapid synthesis of nanocrystalline lithium-ion sieves from biogenic manganese oxides.

2. Experimental

2.1. Synthesis

BB was produced at pH 6.5 by a Mn-oxidizing fungus, *Paraconiothyrium* sp. WL-2 strain, as in our previous work (Yu et al., 2012). Nanocrystalline lithium-ion sieve were synthesized via a microwave-assisted hydrothermal treatment of BB with LiOH solution. The single phase $LiMn_2O_4$ can be obtained at appropriate concentrations of reactants, and the products with higher Li/Mn molar ratio shows smaller crystal sizes compared to that with lower Li/Mn molar ratio. Accordingly, two types of $LiMn_2O_4$ with different crystal sizes were prepared. Highly crystalline $LiMn_2O_4$, denoted by LMO-50, was prepared by adding 0.1648 g of BB to 75 mmol/L of LiOH (Wako Pure Chemical Industries Ltd., Osaka, Japan) with stirring, to give a total volume of 40 mL poorly crystalline $LiMn_2O_4$, denoted by LMO-10, was prepared by adding 0.4 g of BB to 2 mol/L of LiOH to give a total volume of 13 mL. For both samples, the mixture was transferred to a Teflon-lined stainless-steel autoclave to avoid vapor leakage and exposed to microwave irradiation for 0.5 h at 160 °C (Ethos Plus microwave, Milestone, Italy). After cooling to room temperature, the products were separated by centrifugation, washed three times with water and absolute ethanol, respectively, and dried at 60 °C for 6 h. LMO-50 or LMO-10 (50 mg) was mixed with 0.1 M HCl (8 mL, H/Li molar ratio = 2) for 12 h to obtain lithium-ion sieves, denoted by HMO-50 and HMO-10, respectively. The products were separated by centrifugation, washed with water, and dried at 60 °C for 6 h.

A micro-sized lithium-ion sieve, denoted by HMO-m, was synthesized using the method reported by Ammundsen et al. (1996). A finely ground mixture of lithium and manganese carbonate (Wako, Osaka, Japan), with an Li/Mn molar ratio of 0.5, was fired at 800 °C in air for 24 h to obtain bulk $LiMn_2O_4$, denoted by LMO-m. HMO-m was obtained by acid washing of LMO-m, using the same method as for HMO-50.

2.2. Characterization

The powdery samples were ground, and powder X-ray diffraction (XRD) patterns were obtained at room temperature and constant humidity (Cu Kα radiation, 40 mA, 40 kV, 2θ 0.02°, scanning speed 2 s; Multi Flex X-ray diffractometer (Rigaku, Akishima, Japan). Structural analysis was performed using a Rietveld calculation program PDXL 2 (Rigaku Co. Akishima, Japan).

The product morphologies before and after acid washing were examined using field-emission scanning electron microscopy (FE-SEM; Hitachi SU8000, Tokyo, Japan). N_2 adsorption/desorption isotherms were recorded at − 196 °C using a BELSORP-mini automatic adsorption analyzer (Bel Japan, Osaka, Japan).

Mn K-edge X-ray absorption extended fine structure (EXAFS) spectra were recorded in transmission mode at room temperature using BL 06 at the SAGA-Light Source (Tosu, Japan). A silicon (111) double-crystal monochromator was used to obtain the incident X-ray beam. All samples and references were analyzed in transmission mode. The intensities of the incident and transmitted X-rays were monitored using an ionization chamber. The energy was calibrated by adjusting the second pre-edge peak of δ-MnO_2 (synthesized) to 6539 eV. $MnCl_2$ (freeze-dried, special grade, Wako Pure Chemical Industries Ltd.), Mn_2O_3 (special grade, Wako Pure Chemical Industries Ltd.), and $Li_4Mn_5O_{12}$ (synthesized, Feng et al., 1992) were used as standards. All powder samples were lyophilized, diluted with BN (special grade, Wako Pure Chemical Industries Ltd.) to adjust the Mn content to 2 wt.%, and then pressed into tablets of 1 cm diameter. Only one spectrum was collected for each sample, to avoid the possibility of radiation damage. Sample homogeneity and lack of sample damage by X-ray radiation were confirmed by the reproducibility of the spectra. All spectra were analyzed using REX 2000 software (Rigaku). The absorbance background was subtracted from the spectrum using a Victoreen function ($C\lambda^3 - D\lambda^4 +$ constant), fitted over the pre-edge region, and μ_0 was calculated using the global cubic spline method, in the energy range 6600–7260 eV. The spectroscopic oscillation was multiplied by k^3 and filtered using the Hanning method before Fourier transformation. The phase shifts and amplitude functions for data simulation were calculated with FEFF7 (Ankudinov and Rehr, 1997), using $Li_{1.12}Mn_{1.88}O_4$ (space group *Fd3m*) (Strobel et al., 1998) as a structural model. The fitting was performed in the back *k*-space on the first and second shells using a single scattering model. The default value of the amplitude reduction factor ($S_0^2 = 1$) was used.

2.3. Sorption batch tests

The kinetic experiments were performed as follows. HMO (25 mg) was suspended in LiCl solution (100 mL) at 25 °C. The initial Li^+ concentration was adjusted to 10 mg/L. The initial pH was adjusted to 8.5, using 0.1 M NH_3/NH_4Cl buffer solution. Changes in the Li^+ concentration with time were monitored, using atomic absorption spectrometry (AAS), after filtration (0.2 μm membrane filter) of the supernatants. The experimental data were fitted to two kinetic models, i.e., a pseudo-first-order model (Eq. 1) and a pseudo-second-order model (Eq. 2):

$$\frac{1}{q_t} = \left(\frac{k_1}{q_1}\right)\left(\frac{1}{t}\right) + \frac{1}{q_1} \tag{1}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{t}{q_2} \tag{2}$$

where q_t (mg/g) is the Li^+ uptake at a given time, q_1 (mg/g) is the maximum adsorption capacity for pseudo-first-order adsorption, k_1 (1/h) is the pseudo-first-order rate constant for the adsorption process, q_2 (mg/g) is the maximum adsorption capacity for pseudo-second-order adsorption, and k_2 [g/(mg h)] is the rate constant for pseudo-second-order adsorption.

The Li^+ ion sorption isotherm was obtained as follows. HMO (10 mg) was suspended in LiCl solution (40 mL) at 25 °C for 24 h. The initial Li^+ concentration was adjusted to 5–100 mg/L. The initial pH was adjusted to 8.5 with 0.1 mol/L NH_3/NH_4Cl buffer solution. The sorption results were fitted to the Langmuir (Eq. (3) and Freundlich (Eq. 4) equations:

$$\frac{C_e}{Q} = \frac{1}{Q_{\max}} \cdot C_e + \frac{1}{Q_{\max} \cdot L} \tag{3}$$

$$\log Q = \frac{1}{n} \cdot \log C_e + \log K_F \tag{4}$$

where Q is the amount sorbed per unit weight (mg/g), C_e is the equilibrium concentration (mg/L), Q_{max} is the maximum sorbed mass (mg/g), L is the Langmuir isotherm constant (L/mg), and n and K_F are the Freundlich constants, indicating the relative capacity and adsorption intensity, respectively.

The effect of pH on the sorption of Li^+ by the HMOs was investigated as follows. The sorbent (10 mg) was added to LiCl solution (10 mg/L, 40 mL) and the mixture was shaken for 24 h. The initial pH was adjusted to 5–12 using NaOH and HCl solutions. The supernatant was separated by filtration and the Li^+ concentration was determined using AAS.