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Structural changes and electrochemical properties of $Li_2Cu_{1-x}M_xO_2$ for lithium secondary batteries

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ABSTRACT

Li_2CuO_2 substituted by various cations, such as Co, Ni, Fe, Mn, and Ti, was examined to decrease the irreversible capacity of unsubstituted one. Among several kinds of cations tested, Ni and Co were found to be effective in improving the irreversible capacity. $Li_2Cu_{0.7}Ni_{0.3}O_2$ exhibited a reversible capacity of about 150 mAh/g, while the unsubstituted one exhibited a capacity of only about 100 mAh/g. The structural changes in the Cu-based oxides that occurred during the electrochemical reaction were investigated with ex-situ XRD measurements. The results indicated that the structural transformation behavior changed as a result of the cation substitution.

1. Introduction

Lithium secondary batteries including rocking-chair type lithium ion batteries (LIBs) are widely used as power sources for electronic tools such as cell phones and laptop computers. The use of large scale LIBs has spread to power sources for electric vehicles and energy storage tools for smart grid systems combined with recyclable energy such as solar and wind power [1,2]. The price of LIBs should be low, especially for large-scale utilization. However, most of the cathode materials used for the LIBs contain rare metals such as Mn, Ni, Ti and Co [3,4]. It is essential to greatly decrease the use of rare metals other than lithium. Cu-based oxides such as $LiCuO_2$, Li_2CuO_2 and $NaCuO_2$ have already been reported as rare metal-free cathode materials [5–12]. Copper element is a common and inexpensive metal element without concern on natural resource. These compounds have one-dimensional $[CuO_4]$ square chains, where copper is at the center of an oxygen rectangle. The $[CuO_4]$ chains in Li_2CuO_2 are located in a corrugated manner. This can be regarded as a layer-like structure, which enables smooth Li-ion diffusion in the oxide. Moreover, Li_2CuO_2 has a high theoretical capacity of 245 mAh/g corresponding to the following electrochemical reaction: $Li_2CuO_2 \rightarrow LiCuO_2 + Li^+ + e^-$. The electrochemical behavior of Li_2CuO_2 has been reported in detail by Arai et al. [8]. The Li_2CuO_2 (space group: Immm) was electrochemically oxidized to $Li_{1.5}CuO_2$ (C2/m) and it was finally oxidized to $LiCuO_2$ (C2/m) during charging. The first charge and discharge capacities were 250 and 130 mAh/g, respectively. The reversible capacity was 130 mAh/g after the second cycle. This reversible capacity corresponds to the reversible reaction between $Li_{1.5}CuO_2$ and $LiCuO_2$. The large irreversible capacity at the first cycle occurred so that the final discharge product, $LiCuO_2$, could not be electrochemically reduced to $Li_{1.5}CuO_2$ during discharging. This irreversible reaction might be due to relatively large structural changes in Li_2CuO_2, $Li_{1.5}CuO_2$ and $LiCuO_2$, although all these oxides have one-dimensional $[CuO_4]$ chains. Furthermore, Imanishi et al. reported that the first irreversible capacity was suppressed by substituting the Cu sites of Li_2CuO_2 by Ni and that $Li_2Cu_{0.6}Ni_{0.4}O_2$ exhibited a maximum first discharge capacity of about 320 mAh/g [9]. Love et al. also reported that $Li_2Cu_{0.5}Ni_{0.4}M_{0.1}O_2$ (M = Al, Ga) prepared by micro emulsion method exhibits better cyclability and capacity retention than unsubstituted Li_2CuO_2 [12]. These results indicate that the partial substitution of Cu sites is an effective way of improving the reversibility of Li_2CuO_2. There are no reports on the electrochemical properties of Li_2CuO_2 substituted by transition metals other than Ni. It is important to investigate effects of substitution with various kinds of metals to reduce the irreversible capacity of Li_2CuO_2.

In this study, we investigated the electrochemical properties and structural changes in Li_2CuO_2 substituted by various transition metal ions such as Co, Ni, Fe, Ti, and Mn, and examined its effect in suppressing the irreversible capacity at the first cycle and increasing the reversible capacity.

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2. Experimental

2.1. Synthesis of $Li_2Cu_{1-x}M_xO_2$ (M = Co, Ni, Fe, Mn, and Ti)

Lithium copper oxide (Li_2CuO_2) was synthesized by a simple solid state reaction involving a lithium source [lithium hydroxide monohydrate ($LiOH \cdot H_2O$, Kanto Chemical Co., Inc.)] and a high purity copper source [copper oxide (CuO, Kanto Chemical Co., Inc.)] at 850 °C for 24 h under O_2 gas flow. The resultant powder was then stored in a dry room with a dew point of less than −40 °C. The same procedure was used for the cation, M (M = Co, Ni, Fe, Ti, and Mn), -substituted oxides. Mono oxides (Kanto Chemical Co., Inc.) for M = Co, Ni, Mn and metal powders (Kanto Chemical Co., Inc.) for M = Fe and Ti were used as cation sources. The crystallographic structure of the resultant powder was characterized with an X-ray diffractometer (Rigaku, RINT2500) using CuK_α radiation under a constant power of 30 kV and 100 mA. The formation phases of the synthesized powder were identified using the database of the International Center for Diffraction Data (ICCD). The particle morphology was observed using a scanning electron microscope (SEM, SU1510, Hitachi High-Technologies Corp.).

2.2. Electrochemical measurements of $Li_2Cu_{1-x}M_xO_2$ (M = Co, Ni, Fe, Mn, and Ti)

Electrochemical measurements were carried out using a two-electrode coin-type test cell (type 2320). An electrode material mixture was prepared with Cu-based oxide (70 wt.%), Ketjen Black EC600JD (25 wt.%, Lion Co., Ltd.), and polytetrafluoroethylene (5 wt.%, Daikin Co., Ltd.). The mixture was then roll-pressed into a 0.5 mm thick sheet. This sheet was cut into a circle shape and used as a working electrode in a coin-type test cell. Lithium metal (0.3 mm thick) was used as a counter electrode. Microporous polypropylene film (Celgard), which was located between the two electrodes, was used as a separator. The electrolyte was 1 mol/L of $LiPF_6$ in an equal volume of ethylene carbonate (EC) and dimethyl carbonate (DMC) solution (Kishida Chemical Co., Ltd.).

The entire preparation and assembly process was carried out in a dry room with dew point of less than −40 °C. The tests on the coin-type cell were conducted in a constant temperature-controlled chamber maintained at 20 °C. The electrochemical measurement was carried out at a constant current density of 1 mA/cm^2 in a voltage range of 2.0–4.0 V, with a rest period of 10 min between each charge and discharge step.

2.3. Stability evaluation of $Li_2Cu_{1-x}M_xO_2$ (M = Co, Ni, Fe, Mn, and Ti)

An ex-situ evaluation of the discharged/charged electrodes containing the Cu-based oxides was carried out to study the stability of the crystal structure when it underwent an electrochemical process. Test cells were performed under the same condition as the electrochemical evaluation (current density: 1 mA/cm^2) but they were terminated under different conditions on the cut-off voltages or discharge/charge capacities. After the electrochemical evaluation, the cells were disassembled and the pellet electrode containing the Cu-based oxide was removed from the cell and washed several times with dimethylcarbonate solution (DMC, Kishida Chemical Co., Ltd.) to eliminate the lithium salt particles in the electrode. The pellet electrodes were dried and stored in a vacuum condition prior to the XRD measurements.

3. Results and discussion

Fig. 1 shows XRD patterns of $Li_2Cu_{0.9}M_{0.1}O_2$ [M = Cu (unsubstituted), Co, Ni, Fe, Mn, and Ti]. Almost all the peaks for the cation-substituted Li_2CuO_2 corresponded to PDF data #01-079-1975 (space group: Immm) for Li_2CuO_2, although there were some new peaks or peak shifts in the patterns. No peaks indexed to the raw materials of monoxides or metal were confirmed in the patterns. These results indicate that the cations can substitute the Cu sites in Li_2CuO_2.

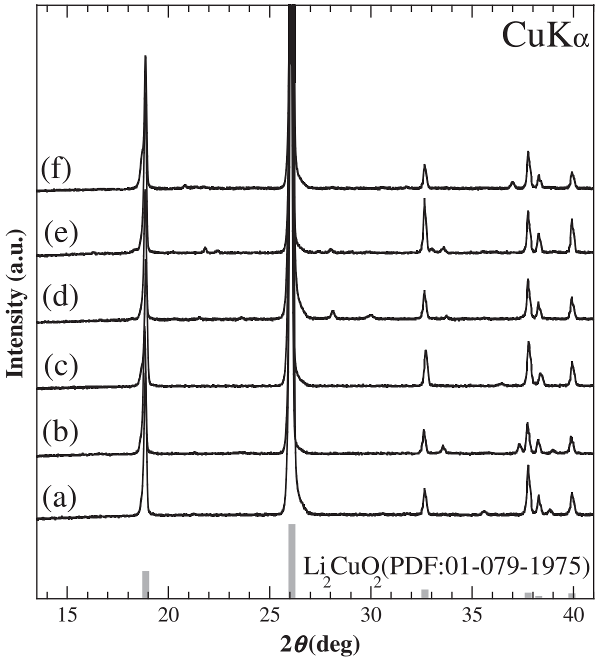

Fig. 1. XRD patterns of $Li_2Cu_{0.9}M_{0.1}O_2$ [M = (a) Cu (unsubstituted), (b) Co, (c) Ni, (d) Fe, (e) Ti, and (f) Mn].

Morphology changes in the cation-substituted Li_2CuO_2 were analyzed by SEM observation. Fig. 2 shows SEM images of $Li_2Cu_{0.9}Ni_{0.1}O_2$ as a typical cation-substituted Cu-based oxide compared with Li_2CuO_2. The Ni-substituted Li_2CuO_2 particles are more homogeneous and have a smooth shape without a sharp edge compared with Li_2CuO_2. This result suggests that the crystallization temperature became lower as a result of the cation substitution, and the sintering of the particles can proceed easily.

Fig. 3 shows the first charge and discharge curves of $Li_2Cu_{0.9}M_{0.1}O_2$ (M = Co, Ni, Fe, Ti, and Mn) electrodes compared with those of the unsubstituted Li_2CuO_2 electrodes. All the electrodes exhibited charge and discharge capacities of about 240 mAh/g and about 130 mAh/g, respectively. These values correspond to about 1.0 mol and about 0.6 mol equivalent of lithium in $Li_2Cu_{1-x}M_xO_2$. Moreover, irreversible capacities of about 110 mAh/g were observed in all oxides, regardless of the substituent metals. As for Li_2CuO_2, this first discharge capacity agreed well with that of 130 mAh/g reported by Arai et al. [8]. Consequently, no clear improvement in the irreversible capacity could be achieved with a cation-substitution content, $x = 0.1$. However, it can also be seen that Ni- and Co-substituted Li_2CuO_2 electrodes have slightly larger discharge capacities than unsubstituted Li_2CuO_2.

Fig. 4 shows the cycle properties of $Li_2Cu_{0.9}M_{0.1}O_2$ (M = Co, Ni, Fe, Ti, and Mn) electrodes compared with those of the unsubstituted Li_2CuO_2 electrodes. As shown in this figure, compared with the unsubstituted oxide, the Fe- and Mn-substituted oxides exhibited smaller discharge capacities and that of the Ti-substituted oxide was similar. On the other hand, the Ni- and Co-substituted oxides exhibited the larger discharge capacities than the unsubstituted oxide. In addition, the discharge capacities of the Ni-substituted oxide gradually increased as the cycle number increased. This unique behavior was not observed for any other cation-substituted oxide other than Ni. However, similar behavior has been observed in the cycle properties of $Li_2Cu_{0.8}Ni_{0.2}O_2$ as reported by Imanishi et al. [9], but they did not describe the reason for this behavior in detail.

Fig. 5 shows the correlation between the Ni- and Co-substitution content, x, and the first charge and discharge capacities of $Li_2Cu_{1-x}M_xO_2$

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