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Electrochemical properties and structures of the mixed-valence lithium cuprates $\text{Li}_3\text{Cu}_2\text{O}_4$ and $\text{Li}_2\text{NaCu}_2\text{O}_4$

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Abstract

The electrochemical performances of $\text{Li}_3\text{Cu}_2\text{O}_4$ and $\text{Li}_2\text{NaCu}_2\text{O}_4$ as cathode materials in lithium coin type batteries have been studied. In $\text{Li}_3\text{Cu}_2\text{O}_4$, the copper was oxidised to the III level when cycling. The replacement of the lithium by the sodium ions in the octahedral sites in $\text{Li}_2\text{NaCu}_2\text{O}_4$ might have an effect on the pathway of the lithium ions during the (de)intercalations. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Lithium-ion cells consisting of LiMeO_2 (Me: 3d-transition metal element) and carbon materials have been of interest because of their capabilities of operating thousands of cycles safely while retaining high energy densities. Candidate materials examined intensively as positive electrodes have included LiCoO_2 [1–4], LiNiO_2 [4–6], LiMn_2O_4 [7–9] and LiMnO_2 [10–12].

Copper is an abundant, fairly inexpensive transition metal; it is also of lower toxicity than cobalt and nickel. However, no complex oxide of the stoichiometry LiCuO_2 synthesised directly by a solid-state method has been reported, though a number of other ternary lithium copper oxides containing Cu^{I} , Cu^{II} and Cu^{III} , have been prepared. These include Li_2CuO_2 [13], Li_3CuO_3 [14], LiCu_2O_2 [15], LiCu_3O_3 [16] and $\text{Li}_3\text{Cu}_2\text{O}_4$ [17,18]. In previous electrochemical studies of Li_2CuO_2 [19] by Arai et al., it has been shown that the lithium cupric oxide Li_2CuO_2 could be oxidised by lithium extraction to formally reach LiCuO_2 and that the extraction proceeds via $\text{Li}_3\text{Cu}_2\text{O}_4$.

The structure of $\text{Li}_3\text{Cu}_2\text{O}_4$ has been solved by ourselves [20] from powder neutron data collected following synthesis under high oxygen pressure. In order to reveal the high voltage expected by the presence of Cu^{III} in LiCuO_2 ,

extraction of lithium-ion from the mixed-valence lithium cuprate $\text{Li}_3\text{Cu}_2\text{O}_4$ has been examined. We have also recently synthesised a new Cu^{III} -containing material in which lithium has been partially replaced by sodium to give $\text{Li}_2\text{NaCu}_2\text{O}_4$. We also report on the electrochemical extraction of lithium from this material.

2. Experimental

2.1. Materials

Phases $\text{Li}_2\text{ACu}_2\text{O}_4$ (A = Li, Na) were prepared from the binary oxides by heating at 700°C under ~ 250 atm oxygen for 4 h in a gold crucible. Excess Li_2O (20%) and Na_2O (30%) were added to overcome losses through volatilisation. The products, which were well-sintered grey-black powders, were slightly hygroscopic, possibly due to traces of unreacted alkali-metal oxide, so were handled in air only for short periods. Powder X-ray diffraction was performed with a Siemens D5000 diffractometer using $\text{Cu K}\alpha_1$ radiation. Patterns used for structure refinement were collected for 16 h over a 2θ range of 10 – 110° . Powder neutron data were collected for 2 h on the Polaris medium resolution diffractometer at the Rutherford Appleton Laboratory. The back-scattered detector data, with a time-of-flight range of 2000–19580 μs , were used for refinement of the structure of $\text{Li}_2\text{NaCu}_2\text{O}_4$. Lattice parameters were refined using CELL and full profile Rietveld analysis was carried out using the GSAS program suite.

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2.2. Electrochemical measurements

The electrochemical measurements were carried out using stainless steel coin type cells (Panasonic CR 2016). A dry blending technique was employed for the preparation of the porous electrodes using the $\text{Li}_3\text{Cu}_2\text{O}_4$ oxide powder having a nominal composition of 82 wt.% active material (the oxide), 8 wt.% super S carbon black (3 M) added for electronic conductivity, and 10 wt.% binder (polytetrafluoroethylene, Aldrich). Electrodes were pressed from this mixture. The pellets were cut (diameter: 16 mm; thickness: ca. 250 μm) and dried under vacuum at 100°C for 1 day. The electrolyte (Merck, Selectipur) was 1 M LiPF_6 dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume). A glass filter was used as the separator. A metallic lithium disk (diameter: 18 mm; thickness: 200 μm , Aldrich) was used as a counter electrode. The cells were constructed in an argon filled glove box (Unilab, Mbraun).

The cells were charged and discharged galvanostatically at room temperature. A home-made computer battery charge/discharge testing system was used. The apparent lithium contents in the cathode materials were calculated using the current passed and the electrode active mass.

3. Results and discussion

3.1. Neutron refinement of $\text{Li}_2\text{NaCu}_2\text{O}_4$

The similarity of the powder X-ray diffraction pattern of $\text{Li}_2\text{NaCu}_2\text{O}_4$ to that of $\text{Li}_3\text{Cu}_2\text{O}_4$ [20] was immediately apparent but with a significant shift in the reflection positions to higher d -spacings. Structure refinement using the powder neutron diffraction data was undertaken using with the initial atom positions and space group $C2/m$ taken from $\text{Li}_3\text{Cu}_2\text{O}_4$. Full details of this structure refinement will be presented elsewhere [21] but it was clear from this work that the (split) lithium on the octahedral site in $\text{Li}_3\text{Cu}_2\text{O}_4$ was replaced by a centrally placed sodium ion. No substitution for lithium on the tetrahedral site occurs.

3.2. Description of the structure

The structure of $\text{Li}_2\text{NaCu}_2\text{O}_4$ contains square-planar CuO_4 units parallel to the b direction which share opposite edges. This gives rise to infinite chains of the stoichiometry CuO_2 similar to those found in other alkali-metal cuprates. The copper–oxygen chains are separated by lithium atoms with the majority (two-thirds) of these occupying tetrahedral sites derived from co-ordination to oxygen atoms in three separate cuprate chains. In $\text{Li}_3\text{Cu}_2\text{O}_4$, the remainder (one-third) are disordered over two sites within an elongated octahedral oxide ion cavity. The sodium ions in $\text{Li}_2\text{NaCu}_2\text{O}_4$ occupy only the slightly elongated octahedral site (Fig. 1).

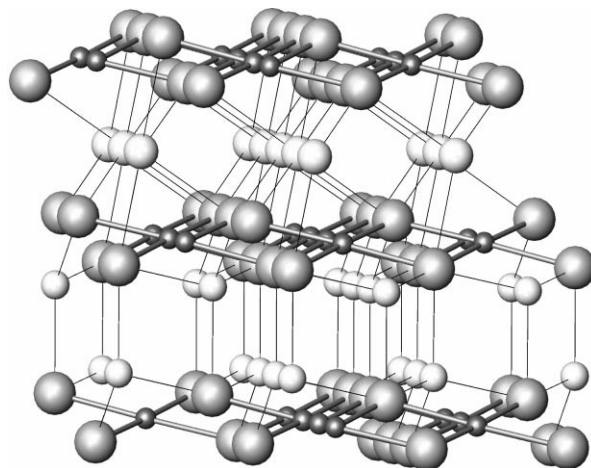


Fig. 1. Structure of $\text{Li}_2\text{NaCu}_2\text{O}_4$ showing the coordination geometries of Li (pale spheres), Na and Cu (small dark spheres) within the unit cell.

3.3. Electrochemical properties of $\text{Li}_3\text{Cu}_2\text{O}_4$ and $\text{Li}_2\text{NaCu}_2\text{O}_4$

The cycling behaviour of the $\text{Li}/\text{Li}_3\text{Cu}_2\text{O}_4$ and $\text{Li}/\text{Li}_2\text{NaCu}_2\text{O}_4$ cells was tested at a constant current density of 0.25 mA/cm^2 . The charge/discharge profiles are shown in Figs. 2 and 3 while all data obtained for $\text{Li}_2\text{NaCu}_2\text{O}_4$ is presented in Fig. 4. The open-circuit voltages of freshly assembled cells were 2.85 V for $\text{Li}_3\text{Cu}_2\text{O}_4$ and 3.10 V for $\text{Li}_2\text{NaCu}_2\text{O}_4$, respectively.

The first charge of $\text{Li}_3\text{Cu}_2\text{O}_4$ (Fig. 2) shows a gradual increase in potential, tending to a limit of about 4.1 V with no sign of an end-point. This was interpreted as an electrolyte decomposition reaction competing with ion extraction at this highest voltage, the former being aided by the catalytic effect of the copper oxide surface. The amount of lithium extraction may, however, be deduced from the subsequent discharge, where the potential–charge relation shows the sigmoidal shape typical of an insertion electrode with a capacity of about 90 mAh g^{-1} , corresponding to approximately 0.75 lithium ions per $\text{Li}_3\text{Cu}_2\text{O}_4$.

During the subsequent charge half-cycles, the potential behaviour was markedly different from the first, showing a plateau at around 3.3 V and a steep rise in potential after the passage of 80 mAh g^{-1} of charge; this corresponds to a theoretical extraction of 0.45 lithium ions from $\text{Li}_{1.15}\text{Cu}_2\text{O}_4$ (see Fig. 3). The following recharges showed a similar shape with a hysteresis of 1 V ascribed to lattice deformation.

The change in behaviour after the first cycle is reminiscent of the passivation phenomenon observed in negative electrodes, where excessive electrolyte decomposition on the first charge is avoided due to the growth of a protective layer of a solid electrolyte interface (SEI) [22]. No degradation in capacity was observed on extended cycling. In fact, the capacity appeared to increase slightly during the first 15 cycles.

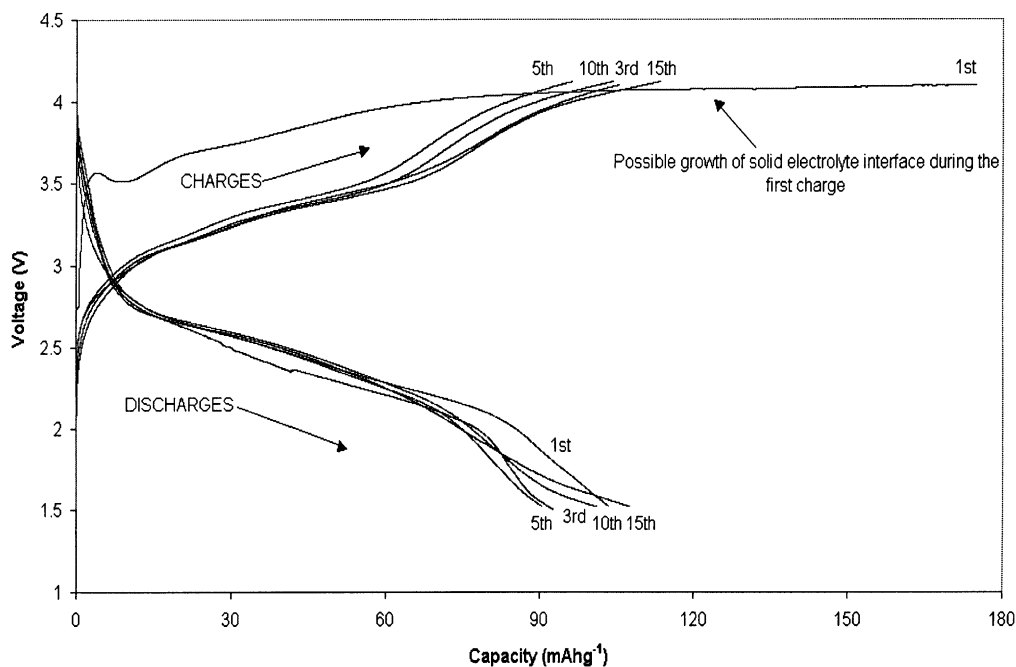


Fig. 2. Charge/discharge profiles of $\text{Li}/\text{Li}_3\text{Cu}_2\text{O}_4$ cell.

In Fig. 4, there is an absence of plateaux at 3.3 and 2.5 V during the charge and discharge processes of $\text{Li}/\text{Li}_2\text{NaCu}_2\text{O}_4$ cell. The charge voltage rose rapidly from the initial value of 3.1–4.1 V. The plateau between 4.1 and 4.3 V probably corresponds to the decomposition of the

electrolyte. In the discharging process, the voltage dropped to 1.5 V and the capacity was found to be only 30 mAh g^{-1} . The presence of sodium in the structure may disrupt the lithium ions pathways lead to the marked change in cell behaviour.

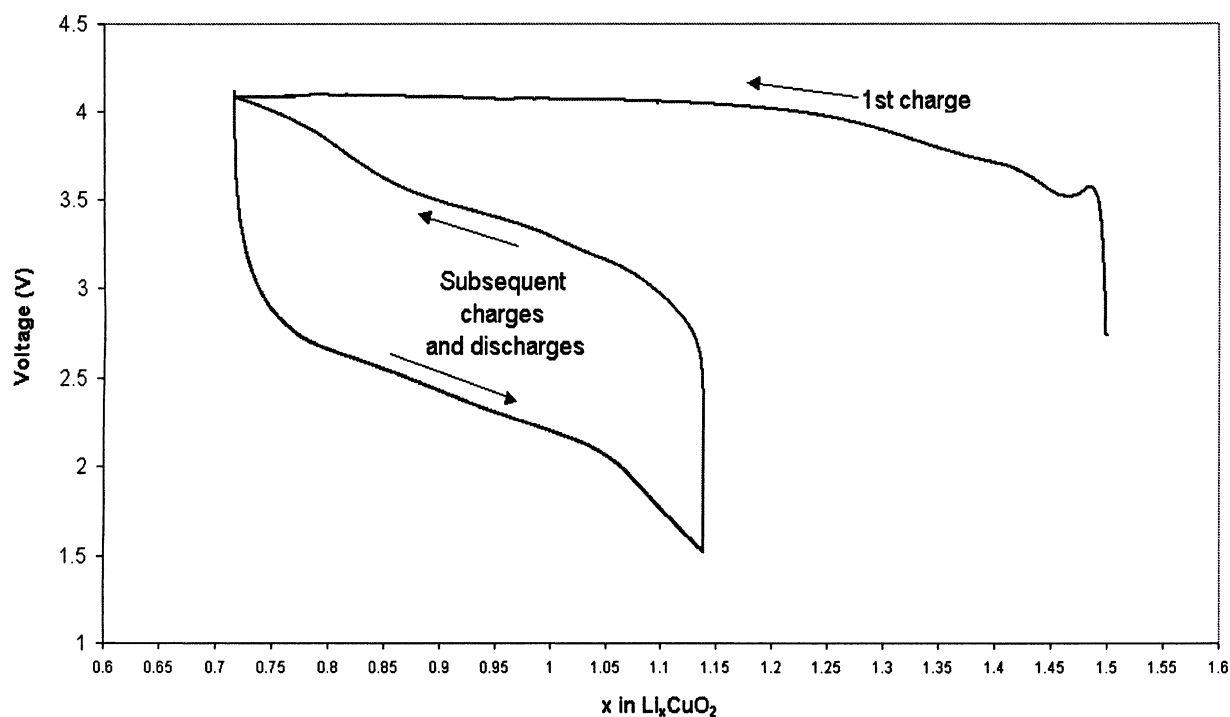


Fig. 3. Voltage cell of $\text{Li}/\text{Li}_3\text{Cu}_2\text{O}_4$ cell vs. lithium compositions, x during the charging/discharging processes.

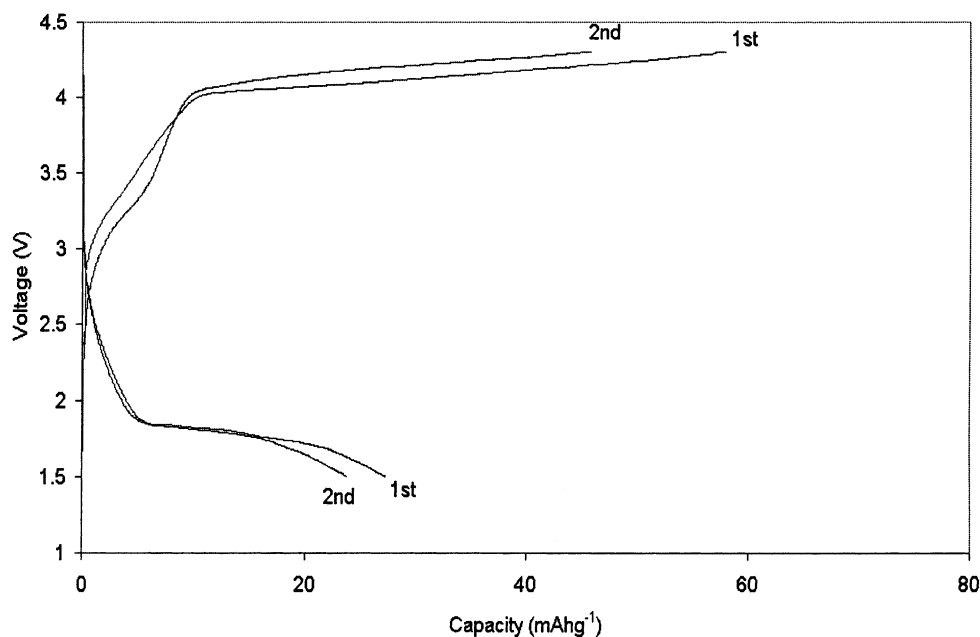


Fig. 4. Charge/discharge profiles of Li/Li₂NaCu₂O₄ cell.

4. Conclusion

It was revealed that the oxidation reaction of the redox couple Cu²⁺/Cu³⁺ processes at 3.3 V during the extraction of Li ions from Li₃Cu₂O₄. A hysteresis phenomenon of about 1 V ascribed to lattice deformation was observed during the discharge. After the first charge where a SEI might have grown at the highest potential, the cell showed good capacity and cyclability. The contrastory behavior of the Li/Li₂NaCu₂O₄ reflects problem with the presence of sodium occupying in the structure of the octahedral sites.

Acknowledgements

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