Li_2CuO_2 as an Additive in Positive Electrodes of Lithium Cells

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A common problem in lithium ion systems is a loss of the specific capacity when a fraction of lithium extracted from the positive electrode is bound irreversibly on the negative electrode in the initial charge of the cell. Many efforts have been made to minimise such irreversible capacity by stabilising the surface of the carbon based negative electrodes normally used in commercial lithium ion systems at present. An alternative way to balance the charge of both electrodes and to increase the overall specific capacity of lithium ion cells was proposed by West et al [1], who suggested adding lithium rich manganese oxide $LiMnO_2$ to the positive electrode. This provided the additional capacity required in the initial charge half-cycle, exhibiting up to 270 mAh/g to 4.5 V vs. Li. This work investigates the use of Li_2CuO_2 for the same purpose.

Former studies of lithium cuprates Li_xCuO_2 with x = 1, 1.5 and 2 [2] have shown that on lithium extraction, copper can only be oxidised as far as Cu^{3+} in the monoclinic $LiCuO_2$. As proven by XRD, further slow oxidation of this compound leads to irreversible formation of CuO, e.g., $2LiCuO_2 \rightarrow 2Li^+ + 2CuO + ½O_2 + 2e^-$. Accordingly, the initial charge capacity of ca. 330 mAh/g in orthorhombic Li_2CuO_2 (Fig. 1) consists of a reversible extraction of lithium up to $LiCuO_2$ followed by irreversible extraction to form CuO at 3.5-4.5V. The large discharge capacity of ca. 200 mAh/g is unfortunately not useful because a combination of slow lithium ion diffusion (10^{-12}-10^{-13} cm^2/s) and a rearrangement of the host lattice reduces the potential to around 2.4 V. Irreversible loss of energy is significant. Therefore Li_2CuO_2 is not efficient as a base material in positive electrodes of lithium ion cells. However, the easy preparation of Li_2CuO_2 in a reaction between inexpensive components CuO and LiOH at above 400 °C, its good stability under ambient conditions, and the large initial charge capacity make this material potentially superior for the additive application.

An example of performance of a composite electrode, consisting of 80 wt% of $LiMn_2O_4$ (115-120 mAh/g) and 20 wt% of Li_2CuO_2 (330 mAh/g in 1st charge only), is shown in Fig. 2. In the initial charge the electrode delivers almost exactly the theoretical 162 mAh per gram of total active material. On the following cycles the reversible capacity becomes 92 mAh/g corresponding to $LiMn_2O_4$ being the only material active in the range 3-4.5 V vs. Li.

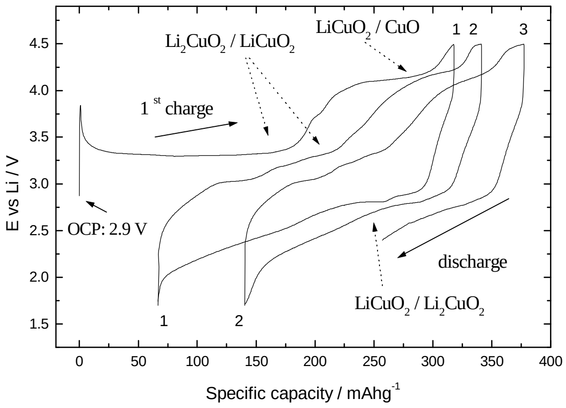

Fig. 1 Galvanostatic cycling of Li_2CuO_2 at the rate of 1 Li per 26h.

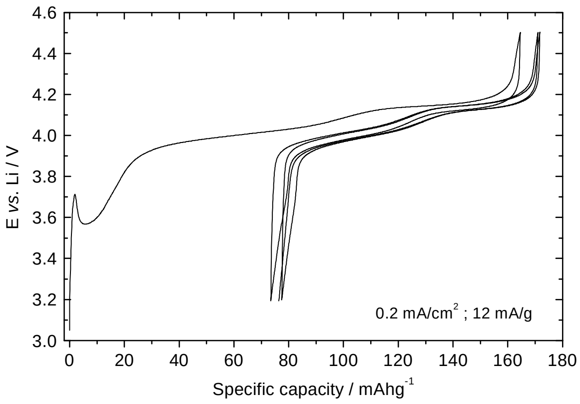

Fig. 2 Galvanostatic cycling of a 80% $LiMn_2O_4$ 20% Li_2CuO_2 electrode, showing the irreversible capacity of Li_2CuO_2 and reversible capacity of $LiMn_2O_4$ when cycled to a 3.2.V potential limit. (Rate = 1.2Li per 16h)

The benefit of the additive may be calculated by estimating the additional mass of positive electrode material required to counter the irreversible capacity of the negative. Each ampere-hour requires 8.3mg of additional $LiMn_2O_4$, whereas the equivalent amount of Li_2CuO_2 would only be 3.0mg. Therefore, in cases where irreversible capacity of the negative electrode requires the use of additional positive electrode material, substitution of an appropriate amount by the additive would result in a significant decrease in mass of the cell and a consequent increase in the specific energy.

[1] K. West, G. Vitins, and R. Koksbang, Electrochimica Acta 45 (2000) 3141-3149

[2] H. Arai, S. Okada, Y. Sakurai, J. Yamaki, Solid State Ionics 106 (1998) 45-53