Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

A new, high performance $CuO/LiNi_{0.5}Mn_{1.5}O_4$ lithium-ion battery

Roberta Verrelli and Jusef Hassoun*

Department of Chemistry, University Sapienza of Rome, Italy

Attila Farkas, Timo Jacob and Bruno Scrosati*

Helmholtz Institute Ulm, Germany

SUPPLEMENTARY INFORMATION

The CuO electrode. Introduction.

Tarascon and co-workers[1] reported a detailed microscopy study of CuO particles and of their cycling mechanism in a lithium cell. However, no data were shown on cycle life and rate capability. Li *et. al.* [2] have investigated the electrochemical behavior of Li_2O/CuO nanocomposite electrode, however limited to 16 cycles and at a single rate. Mai *et.al.*[3] focused their attention on CuO/graphene composite electrodes showing capacity and cycling performance comparable with those reported in this work, while no data are reported on the rate capability. The synthesis of a 3D CuO urchin-like structure/graphene nanocomposite characterized by good cycling performances at different c-rates has been reported by Wang *et. al.*[4] but its behavior in a full lithium ion cell has not yet been tested. CuO-CNT composites have been studied by Park, Jeong and co-workers[5] but, although their cyclability and rate capability have been demonstrated in lithium half cells, their use as anode in a full battery has not yet been reported. Huang and co-workers[6] showed that good electrochemical performances may be obtained by CuO/C microspheres; on the other hand these electrode materials are obtained by a synthesis procedure much more complicated than that used in this work for the preparation of our CuO-MCMB composites. Qian and co-workers[7] described the synthesis and performance of bundle-like CuO nanusctructures, showing good capacity delivery and rate capability. Although not specifically mentioned in their paper, the tap density of this electrode is expected to be low, this probably reflecting in a low volumetric density. Finally, Yuan *et.al* [8] showed that sponge-like mesoporous CuO ribbon clusters can operate as high rate electrode materials. Also in this case, however, some concern may remain in the value of the tap density. An high performance CuO nanoribbons array electrode was prepared by Ke et. al.[9] but again no data are available on its behaviour when combined to a cathode in a full LIB.

This brief review of the most recent literature addressed to CuO-based electro materials confirms the novelty of this work in introducing a CuO- MCMB composite electrode exhibiting comparable if not higher performances and, in particularly, in demonstrating its practical value as anode in an advanced lithium-ion battery.

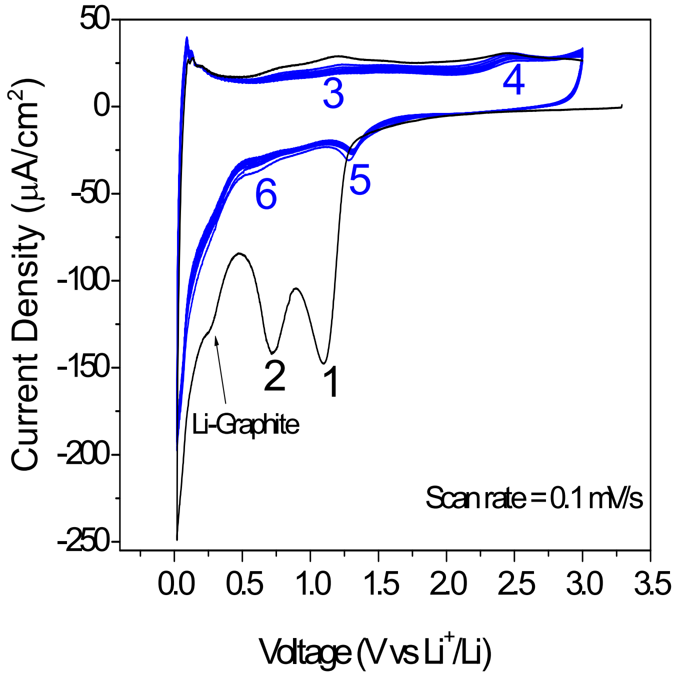
The CuO electrode. Electrochemical characterization.

The electrochemical conversion processes of transition metal oxides (M_aO_b, M= Fe, Co, Cu, Ni, etc.) in a lithium cell may be generally written as:[1]

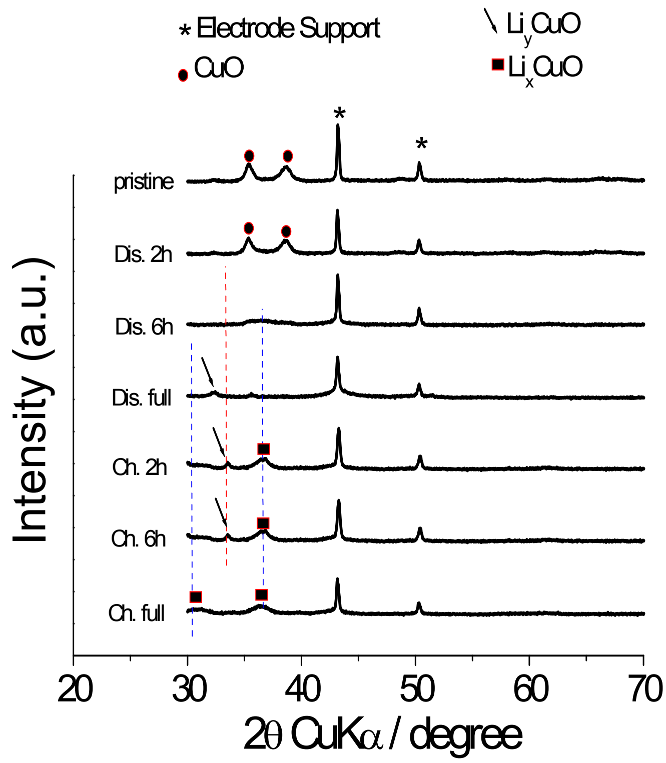
$$M_aO_b + 2b\,Li^+ + 2b\,e^- \leftrightarrows a\,M + b\,Li_2O \qquad (1)$$

According to this process, the M_aO_b oxide is electrochemically reduced to a mixture formed by metal nanoparticles dispersed in a Li_2O matrix, having a high reactivity towards Li_2O decomposition, thus ensuring the reversibility of the overall redox process.[10] However, a major drawback , namely , the large volume changes associated with the chemical conversion reaction that in turn can cause pulverization of the electrode, contact loss and, ultimately severe capacity fading upon cycling, may limit the performances and applicability of transition metal oxides in lithium batteries.

To address this issue we dispersed copper oxide in a MCMB (Mesoporous Carbon Micro Beads) carbon matrix, in order to form a CuO-MCMB composite material characterized by a submicrometric structure. It is in fact expected that this composite configuration may be effective in buffering the volume changes of the oxide particles, as well as of enhancing the bulk conductivity by promoting inter- and intra-particles electrical contact.



A



B

Figure 4: Cyclic Voltammetry of the CuO-MCMB composite (A) and XRD analysis on a fully cycled electrode (B) in a lithium cell. Electrolyte: EC:DMC 1:1 1M $LiPF_6$ solution. Cycling rate: at 0.1 mV/s. Voltage range: 0.02-3V vs Li^+/Li. Room temperature

Figure 4A shows the cyclic voltammetry (CV) of the CuO-MCMB electrode extended over ten cycles. The trend of the first cycle evidences three peaks, at approximately 1.2, 0.7 and 0.25 V, respectively, vs. Li. We assume that the first peak (marked as 1) at 1.2V is associated with the process:

$$CuO + xLi \rightarrow LixCuO\ (x<1) \qquad (2)$$

where, in the case that x reaches 1, one obtains LiCuO, namely a Cu_2O- Li_2O mixture.

The process at the second peak at 0.7V (marked as 2) may be written as:

$$LixCuO + (y\text{-}x)Li \rightarrow LiyCuO\ (1<y<2) \qquad (3)$$

where, in the case that y reaches 2, one obtains Li_2CuO, namely the expected Cu- Li_2O mixture. This interpretation is also supported by literature[1-3].

We finally assume that the third peak at 0.25V is due to lithium intercalation in the MCMB.

The CV curves clearly evidence the irreversibility of the two cathodic peaks followed, however, by a reproducible trend in the following nine cycles. We propose, in accordance with reactions (2) and (3), that this trend is associated with the following overall reversible process:

$$Li_yCuO \leftrightarrows (y-x)Li + Li_xCuO \quad (x<1,\ 1<y<2) \qquad (4)$$

represented in the CV of Fig. 4A by the sequence of the peaks marked as 3 and 4 in charge and of the peaks marked as 5 and 6 in discharge.

In the case when x=0 and y=2, the (4) becomes:

$$Li_2CuO \leftrightarrows CuO + 2Li \qquad (5)$$

hence, formally, and in the CuO reduction direction:

$$2Li + CuO \leftrightarrows Cu + Li_2O \qquad (6)$$

to which is associated a theoretical specific capacity of 670 $mAhg^{-1}$. The reaction mechanism proposed above is supported by the ex-situ XRD analysis on a fully cycled electrode reported in Fig. 4B. One may in fact clearly see that the peaks associated with CuO vanishes upon discharge, with the concomitant appearance of those associated with Li_yCuO and, in the following charge, of those of Li_xCuO.

This study on CuO, in addition to literature papers including other metal oxides [11-12], suggest the suitability of Li-conversion composite materials as advanced anode for lithium ion battery.

References

1. A. Dèbart, L.Dupont, P.Poizot, J-B.Leriche, J.M. Tarascon, *J. Electrochem. Soc.* **2001**, 148, A1266
2. T. Li, X.PAi, H.X.Yang, *J. Phys. Chem. C* **2011**, 115, 616.

3. Y.J. Mai, X.L. Wang, J.Y. Xiang, Y.Q. Qiao, D. Zhang, C.D. Gu, J.P. Tu, *Electrochim. Acta* **2011**, 56, 2306.
4. B. Wang, X.L. Wu, C.Y. Shu, Y.G. Guo, C.R. Wang, *Journal of Material Chemistry* **2010**, 20, 10661.
5. S. Ko, J.I. Lee, H.S. Yang, S. Park, U. Jeong, *Advanced Materials* **2012**, 24, 4451
6. X.H. Huang, C.B. Wang, S.Y. Zhang, F. Zhou, *Electrochimica Acta* **2011**, 56, 6752
7. L. Wang, W. Cheng, H. Gong, C. Wang, D. Wang, K. Tang, Y. Qian, *Journal of Materials Chemistry* **2012**, 22, 11297
8. Y.F. Yuan. Y.B.Pei, J.Fang, H.L.Zhu , J.L.Yang, S.Y.Guo, M*aterials Letters* **2013**, 91.
9. F.S. Ke, L. Huang, G.Z. Wei, L.J. Xue, J.T. Li, B. Zhang, S.R. Chen, *Electrochimica Acta* **2009**, 54, 5825.
10. S. Grugeon, S. Laurelle, R. Herrera-Urbina, L. Dupont, P. Poizot, J.M. Tarascon, *Journal of the Electrochemical Society* **2001**, 148 (4), A285.
11. J. Wang. N. Yang, H. Tang, Z. Dong, Q. Jin, M. Yang, D. kisailus, H. Zhao, Z. Tang, D. Wang, Angew. Chem. Int. Ed. 2013, 52, 6417–6420
12. X. Lai, J. E. Halpert, D. Wang, Energy Environ. Sci., 2012, 5, 5604 – 5618

.