

ROOM TEMPERATURE ELECTROCHEMICAL  
INTERCALATION OF OXYGEN OR FLUORINE  
INTO  $\text{La}_2\text{CuO}_4$  USING ORGANIC ELECTROLYTES

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It is well known that oxygen can be electrochemically intercalated at room temperature into oxide host networks (1). Up to now these experiments were carried out in alkaline media, which sometimes involve some corrosion of the materials due to the high basicity of these solutions. Therefore we have investigated new anhydrous organic media. These electrolytes are combinations of an inorganic solvent such as the DMSO, DMF, acetonitrile AN, THF,... and  $\text{NaClO}_4$  or  $\text{nBu}_4\text{NBF}_4$  as supporting electrolytes. The presence of an additional oxygen source ( $\text{H}_2\text{O}$ ,  $\text{KO}_2$ ) has been shown to be unnecessary. Various experiments were carried out with the "model compound"  $\text{La}_2\text{CuO}_4$  (Fig. 1). Electrochemical experiments, ( $i$ ,  $E$ ) curves (Fig. 2), reveal the existence of an oxidation plateau. It has been shown that : i) the intercalated oxygen comes either from the anodic decomposition of  $\text{ClO}_4^-$  or mainly from the solvent (DMSO, DMF), which plays a major role via its decomposition leading to the formation of oxygen species  $\text{O}^*$  able to oxidise the material. A mechanism involving a 2 electron process is proposed ; ii) this reaction is reversible and oxygen can be deintercalated.

The anodic polarisation performed at room temperature gives rise to noteworthy materials having compositions up to  $\text{La}_2\text{CuO}_{4.10}$  for which a superconducting behaviour is observed below 42 K (Fig. 3). The physical characterisations of the material (XRD, chemical composition, electronic properties) before and after controlled anodic polarisation are reported.

In addition, for the first time, using electrolytes composed of DMF or AN with fluorinated salts as  $\text{nBu}_4\text{NBF}_4$  or  $\text{nBu}_4\text{NF}$ , the intercalation of fluorine has been successful. This "Chimie Douce"-type intercalation technique proves to be as efficient as that previously performed in alkaline solution and opens a new field of preparative chemistry.

1- J.C. Grenier, M. Pouchard, A. Wattiaux, Current opinion in Solid State and Materials Sciences, **1**, 233 (1996).

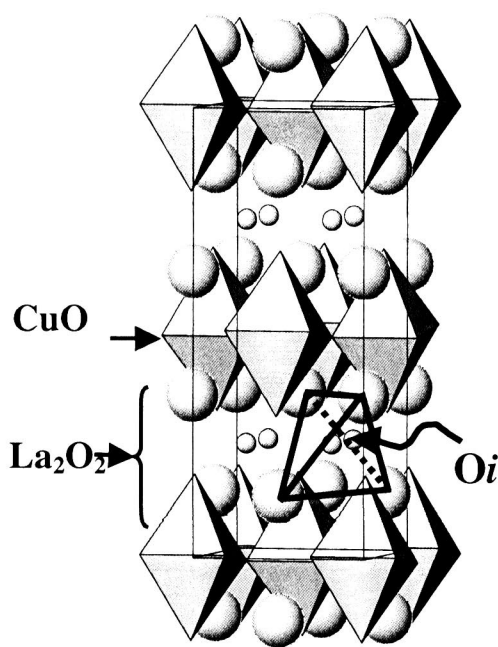


Fig. 1 Structure of  $\text{La}_2\text{CuO}_{4.10}$  showing the location of the inserted oxygen atoms.

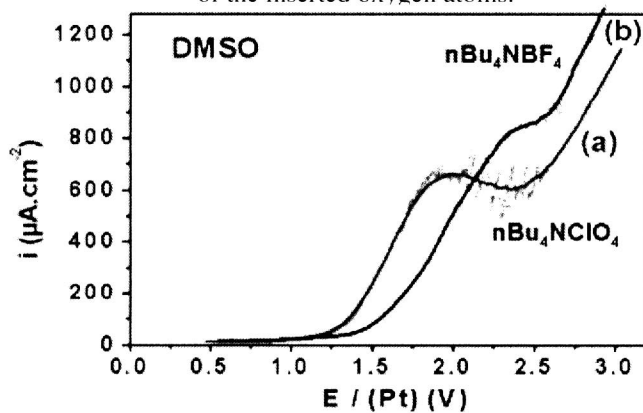


Fig. 2 Cyclic voltammograms ( $i$ ,  $E$ ; 100 mV/h) obtained for a  $\text{La}_2\text{CuO}_4$  ceramic in (a) DMSO /  $\text{nBu}_4\text{NBF}_4$ ; (b) AN /  $\text{nBu}_4\text{NBF}_4$

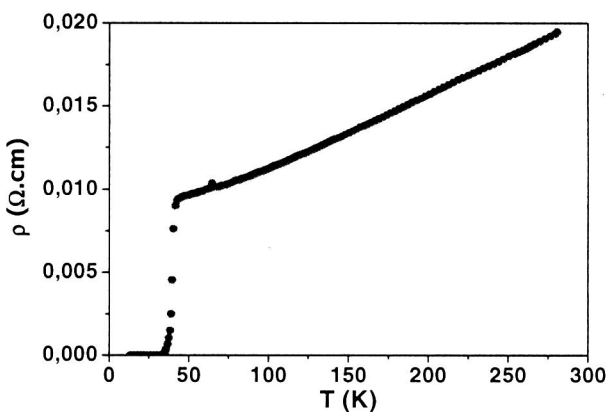


Fig. 3 Thermal evolution of the electrical resistivity for  $\text{La}_2\text{CuO}_{4.10}$  obtained by electrochemical oxidation in DMSO /  $\text{nBu}_4\text{NBF}_4$ .