JOURNAL OF
Materials
CHEMISTRY

Electrochemical oxidation of La_2CuO_4 in organic media: influence of the electrolyte composition

David Barbut, Alain Wattiaux, Marie-Hélène Delville, Jean-Claude Grenier and Jean Etourneau

Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB), CNRS-UPR 9048, Université Bordeaux I, 87 avenue du Dr. Albert Schweitzer, 33608 Pessac cedex, France

Received 20th June 2002, Accepted 3rd July 2002

The electrochemical intercalation of oxygen into La_2CuO_4 has been carried out in various anhydrous organic media: a variety of combinations of dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and acetonitrile (AN) as solvents, $NaClO_4$ or $^nBu_4NBF_4$ as supporting electrolytes, and the presence or absence of oxygen sources (H_2O, KO_2) have been studied. The various experiments show that the intercalated oxygen comes mainly from the solvent (DMSO, DMF), which plays a major role, leading, *via* its decomposition, to the formation of oxygen species able to oxidise the material. Anodic polarisation performed at room temperature gives rise to interesting materials with compositions up to $La_2CuO_{4.10}$, for which superconducting behaviour is observed below 42 K. The physical characterisations of the material (XRD, chemical composition, electronic properties) before and after controlled anodic polarisation are reported. This "*chimie douce*"-type intercalation proves to be as efficient as that previously performed in alkaline solution.

Introduction

During the last fifteen years, there have been many studies demonstrating that the electrochemical intercalation of oxygen into oxide host networks can be considered as an efficient "*chimie douce*" technique. Several oxides have thus been prepared and characterised,[1] some of them exhibiting quite original properties, such as superconductivity for $La_2CuO_{4.09}$ or change density ordering in $La_2NiO_{4.25}$.[2,3]

All these experiments were performed in alkaline solution (usually KOH 1 M), in air, at room temperature. The overall reaction can be simply written as shown in eqn. 1.

$$AMO_x + 2\delta\ OH^- \leftrightarrow AMO_{x+\delta} + \delta\ H_2O + 2\delta\ e^- \quad (1)$$

It should be noted that this process is reversible and oxygen atoms can be removed under cathodic polarisation, as in $La_2Ni_{1-x}Cu_xO_{4+\delta}$ compounds.[4]

Most of these oxides that contain high oxidation state metal cations show good chemical stability with respect to the electrolytic medium. However, these experiments often require long polarisation times—several days—and some degradation of the materials may occur. In addition, in some cases, electrochemical oxidation is impossible in such aggressive media, as it is, for instance, for compounds containing Ba or Bi cations.[5] Significant corrosion may result from the combined action of water (hydrolysis) and carbonate anions (carbonatation) present in strongly alkaline solutions.

Consequently, preliminary experiments were recently carried out with the aim of finding new electrolytic media in which these materials would be stable.[6] We proposed an anhydrous organic solvent, dimethyl sulfoxide (DMSO), in which a support salt ($NaClO_4$ or $^nBu_4NBF_4$) and an oxygen source (KO_2) were dissolved.

Galvanostatic experiments under 100 μA cm^{-2} were performed on La_2CuO_4. After anodic polarisation for 160 h, the material showed superconducting properties below 42 K and the composition was determined to be $La_2CuO_{4.08}$.

In this work, we report systematic studies concerned with the influence of various electrolytic media upon the electrochemical oxidation of the "model material" La_2CuO_4: the nature of the organic solvent, the nature of the supporting electrolyte, and the nature and concentration of the oxygen source will be examined. The electronic properties of La_2CuO_4 strongly depend upon its oxygen overstoichiometry, especially the superconducting properties. The magnetic properties will be more particularly used to characterise the grade of the intercalation process as a function of these various parameters.

Experimental

1 Preparation and characterisation of the samples

The La_2CuO_4 compound was prepared starting from a stoichiometric mixture of the starting materials La_2O_3 (Prolabo 99%), fired at 850 °C, and CuO (Merck 99%). After dissolving them in nitric acid solution (HNO_3, 8 M), citric acid was added (in the molar ratio 3 : 1 with respect to La_2CuO_4). Then, the solution was dehydrated at 120 °C and slowly heated until self-combustion occurred. The resulting fine powder was fired at 1000 °C for 24 h. After grinding, the powder was pressed into a pellet (10 × 5 × 2.5 mm^3, 400 mg) and, finally, sintered at 1050 °C for 6 h. The density of the ceramic was closed to 75%.

Samples were characterised before and after electrochemical treatment by X-ray diffraction using a Philips 1710 diffractometer (Cu-Kα radiation).

The chemical composition was determined by iodometric titration of the Cu^{III} content (τ) after dissolving the sample in acidic media under a nitrogen atmosphere. The oxygen overstoichiometry (δ) was calculated according to the formulation $La_2Cu^{2+}{}_{1-\tau}Cu^{3+}{}_{\tau}O_{4+\tau/2}$, with $\delta = \tau/2$.

The electrical resistivity of the ceramics was measured using the four-probe method in the temperature range $4.2 \leqslant T \leqslant 300$ K.

Magnetic measurements were performed using a SQUID magnetometer (Quantum Design MPMS2). The magnetisation was measured as a function of magnetic field ($0 \leqslant H \leqslant 5$ T) and/or of temperature ($4.2 \leqslant T \leqslant 300$ K). The sample was cooled under zero magnetic field; the linear field dependence of the magnetisation was checked in the range $0 \leqslant H \leqslant 0.01$ T. Then, the thermal variation of the magnetisation was measured under 0.01 T, at increasing (Z.F.C.) and decreasing (F.C.)

DOI: 10.1039/b205977k

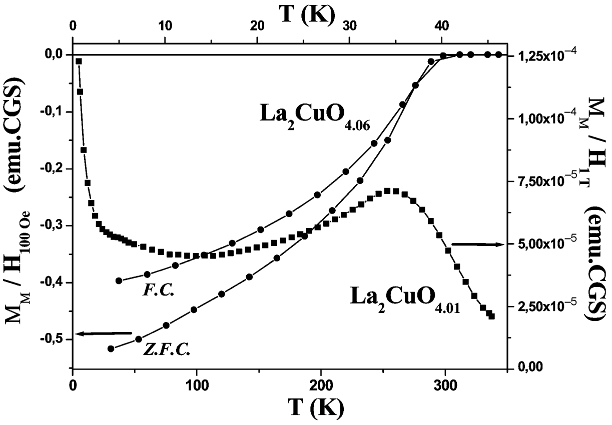

Fig. 1 Typical thermal variation of the magnetic properties of $La_2CuO_{4.01}$ (starting material, under 1 T) and $La_2CuO_{4.06}$ (electrochemically oxidised material, under 100 Oe).

temperature in order to determine the superconducting transition temperature T_C. The Meissner fraction was calculated with regard to the theoretical value given by the relation $M_V = -H/4\pi$, where M_V is the volume magnetisation. The particle size of the crystallites was considered to be the same for all samples with respect to the synthesis conditions.

Typical curves are presented in Fig. 1. The starting material, $La_2CuO_{4.01}$, shows paramagnetic behaviour at high temperature. The hump observed at about 250 K characterises the Néel temperature of the compound due to magnetic ordering. After oxidation, the compound whose composition is $La_2CuO_{4.06}$, exhibits diamagnetic behaviour below 40 K, typical of a superconducting material. The superconducting Meissner fraction for this material is about 12%.

In the following, the oxidised samples will be characterised using this technique. Provided that all the ceramics have similar morphology and texture, the Meissner fraction, or, in other words, the value of M_V/H (or M_M/H, M_M being the molar magnetisation), will represent the superconducting fraction of the material resulting from the electrochemical oxidation. These data will be used for analysing the effect of various parameters with respect to the electrochemical oxidation reaction.

2 Electrochemical experiments

The electrochemical experiments were carried out in an airtight glass cell under constant flowing argon dried over P_2O_5. A classical three-electrode system with a potentio-galvanostat (Tacussel PJT 24-1) was used. The reference electrode was made of Pt wire (Ø 0.5 mm), the counter-electrode was a gold foil (3 cm^2) and the working electrode was the as-prepared ceramic with an immersed area of 1 cm^2.

The electrolytic solution consisted of a mixture of three components. (i) A solvent, either dimethyl sulfoxide, $(CH_3)_2SO$ (DMSO, Aldrich 99.9%), dimethylformamide, $HCON(CH_3)_2$ (DMF, Aldrich 99.9%), or acetonitrile, CH_3CN (AN, Aldrich 99.93%), with water contents of less than 5 mmol L^{-1}, checked using a Metrohm 652KF Karl-Fisher coulometer. The choice of these solvents, known to be stable over a large range of potentials, is discussed later on. (ii) A supporting electrolyte, which provides the electrical conductivity and is assumed to be stable in the potential range of our experiments, either sodium perchlorate, $NaClO_4$ (Aldrich 99.9%), or tetrabutylammonium tetrafluoroborate, $^nBu_4NBF_4$, both dried at 80 °C under vacuum. (iii) An oxygen source, which is supposed to provide oxygenated species; potassium superoxide, KO_2 (Aldrich 99.9%), was used first, then the influence of H_2O as another source of oxygen was also examined.

The electrolytic solution was composed of 60 mL of solvent with 0.1 M supporting electrolyte, to which were added variable concentrations of the oxygen source. All the experiments were carried out in dry box in order to prevent any atmospheric pollution.

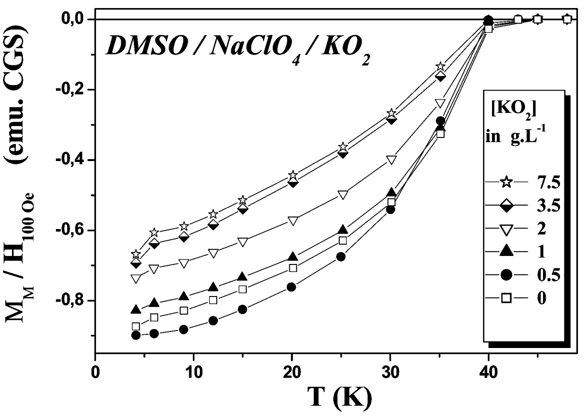

Fig. 2 Variation of the superconducting properties of La_2CuO_4 electrochemically oxidised in DMSO–$NaClO_4$ as a function of the concentration of KO_2 added as the oxygen source.

Results and discussion

The aim of the following experiments was to study the influence of the various constituents of the electrolyte upon the electrochemical intercalation. Experiments were performed on similar ceramics of the starting material $La_2CuO_{4.01}$, under a current density of 300 μA cm^{-2}, for a polarisation time of 170 h. Such conditions were determined on the basis of voltammetry studies.[7]

1 Influence of the oxygen source concentration

In a previous work that showed the feasibility of the electrochemical oxidation in an organic medium,[6] we used an electrolytic solution composed of DMSO and 0.1 M $NaClO_4$, to which KO_2 was added until saturation. Although the solubility of this superoxide is known to be low,[8,9] experiments were carried out with various controlled amounts of this oxygen precursor up to 7.5 g.L^{-1}. Fig. 2 shows the thermal variation of the magnetic susceptibility of the samples after oxidation: all of them exhibit a superconducting transition, T_C, at 42 K. In addition, it is observed that the Meissner fraction increases with decreasing KO_2 concentration. Such a result contradicts our basic assumption concerning the need for an additional oxygen source for the electrochemical reaction and suggests that the intercalated oxygen comes from another origin. Therefore, water was checked as another possible oxygen source.

Indeed, although careful attention was paid to this feature, it is well known that these polar solvents, as well as the salts used in these experiments, are highly hygroscopic, and hence the presence of traces of water able to play the role of oxygen source in the reaction is a possibility. Experiments were then carried out with controlled increasing amounts of H_2O in the DMSO–$NaClO_4$ (0.1 M) solution. Fig. 3 shows the Z.F.C. behaviour of samples oxidised in the presence of different water concentrations ($0 \leqslant [H_2O] \leqslant 10$ M). Again, it clearly appears that the lower the H_2O concentration, the higher the Meissner fraction of the samples. Indeed, for the highest concentration (10 M), the composition of the oxidised sample is $La_2CuO_{4.06}$ and its T_C is only 36 K, whereas for an H_2O concentration below the detection limit, the Meissner fraction reaches a maximum (20%); the composition of the material is $La_2CuO_{4.10}$ and $T_C = 42$ K.

It can be therefore be concluded from these studies that neither KO_2 nor H_2O can be considered as an oxygen source.

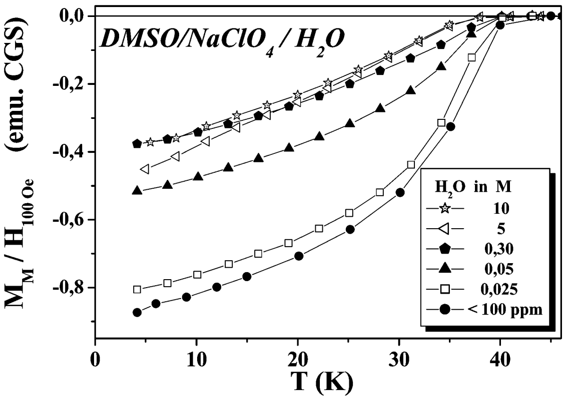

Fig. 3 Variation of the superconducting properties of La_2CuO_4 electrochemically oxidised in DMSO–$NaClO_4$ as a function of the concentration of H_2O added as the oxygen source.

They do not improve the electrochemical reaction and can even impede the process by consuming the intermediate species *via* ancillary reactions.

2 Influence of the supporting electrolyte

Therefore, either or both of the two remaining components, the solvent and the supporting electrolyte, must be involved in the electrochemical process.

Two different supporting electrolytes were used with DMSO as solvent: $NaClO_4$ was used as an "oxygenated" salt, while $^nBu_4NBF_4$ was selected because it obviously does not contain any oxygen species. All the starting compounds were water-free.

Magnetic data for the samples oxidised under 300 μA cm^{-2} for 170 h in DMSO–$NaClO_4$ (0.1 M) and DMSO–$^nBu_4NBF_4$ (0.1 M) are reported in Fig. 4 (white symbols). The results show the materials to be superconducting below the same T_C (42 K). Some differences are observed in the superconducting fractions and in the compositions; the oxidation performed with $NaClO_4$ appears to be somewhat more efficient, which means that $NaClO_4$ could act in the oxidation process.

However, since both supporting electrolytes lead to similar oxygen intercalation amounts, the main difference must result from the nature of the solvents. We therefore undertook a systematic study of the influence of various solvents.

3 Influence of the solvent

Among the solvents available for electrochemical studies,[10,11] three were selected according to the criterion of a large dielectric constant, allowing ion solubility and charge transport for long periods of time (a few days): dimethyl sulfoxide, dimethylformamide and acetonitrile (ε = 46.5, 36.7 and 36.0, respectively). Two of these solvents exhibit a potential oxygen source for intercalation in the ceramic, the last one, acetonitrile, being oxygen-free.

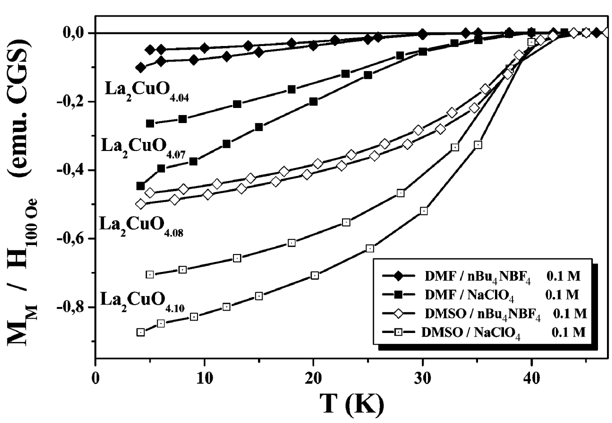

Fig. 4 Variation of the superconducting properties of electrochemically oxidised La_2CuO_4 as a function of the nature of the solvents (DMSO or DMF) or of the supporting electrolytes ($NaClO_4$ or $^nBu_4NBF_4$).

Electrochemical oxidations of $La_2CuO_{4.01}$ were performed using both the previously discussed supporting electrolytes. Magnetic data for the oxidised samples show that the oxidation occurs with both "oxygenated" solvents (Fig. 4). However, the oxidation rate appears somewhat higher with DMSO than with DMF for experiments of the same duration. Actually, after one week, the chemical composition of the sample obtained in DMSO is close to $La_2CuO_{4.10}$, whereas in DMF it is only $La_2CuO_{4.07}$ with $NaClO_4$ and $La_2CuO_{4.04}$ with $^nBu_4NBF_4$. This is confirmed by the low values of the superconducting fraction.

On the other hand, using AN, whatever the supporting electrolyte, does not lead to any superconducting material after a one week oxidation. In addition, magnetic studies, as well as the chemical composition of the resulting oxide, show that the starting ceramic has surprisingly being reduced down to $La_2CuO_{4.00}$. This could result from the electrochemical decomposition of the acetonitrile at either the anode or the cathode, leading to the presence at the anode surface of species able to chemically reduce $La_2CuO_{4.01}$. These experiments show the absence of activity of the oxygenated supporting electrolyte towards oxidation in this solvent.

Finally, from this study, it can be concluded that the organic solvent obviously plays the major role in the electrochemical process, since the electrochemical oxidation is only possible in "oxygenated" solvents and not in acetonitrile. A reaction mechanism leading to the formation of oxygen species able to oxidise the materials was proposed in alkaline medium, however, in these organic media, it is obviously different and this point will be clarified in the future.

4 Characterisation of the $LaCuO_{4.10}$

According to these studies, the optimal conditions for electrochemically oxidising La_2CuO_4 are 300 μA cm^2 over a period of 170 h in DMSO as solvent containing $^nBu_4NBF_4$ or, even better, $NaClO_4$ (Fig. 4) as supporting electrolyte. The final composition is $La_2CuO_{4.10}$.

The starting material was indexed with the *Bmab* space group and cell parameters $a = 0.5359 \pm 0.0005$, $b = 0.5409 \pm 0.0005$, $c = 1.3147 \pm 0.0005$ nm. The oxidised material has cell parameters very close to those previously reported for the compounds oxidised in alkaline solutions: $a = 0.5338 \pm 0.0005$, $b = 0.5406 \pm 0.0005$, $c = 1.3210 \pm 0.0005$ nm, in the *Fmmm* space group.[12]

The thermal dependence of the electrical resistivity is reported in Fig. 5 for both compounds: $La_2CuO_{4.01}$ exhibits semiconducting behaviour, while the oxidised sample $La_2CuO_{4.10}$ becomes metallic, showing superconducting behaviour below 42 K. The field dependence of the magnetisation (Fig. 6) shows a linear dependence up to $H_{C1} \approx 400$ Oe and the compound remains superconducting up to magnetic fields as high as 30 000 Oe. The Meissner fraction of this powdered sample is close to 18% for a particle size of about 1–3 μm. These results agree with previous studies concerning La_2CuO_4 samples electrochemically oxidised in alkaline solutions.[13]

Conclusion

These studies allow the following conclusions to be drawn. (i) Electrochemical oxidation is possible in organic media, *i.e.* in non-aqueous electrolytes, and the oxidation is at least as efficient as in alkaline solution. (ii) Neither KO_2 nor H_2O act as the oxygen source in the electrochemical process. (iii) The

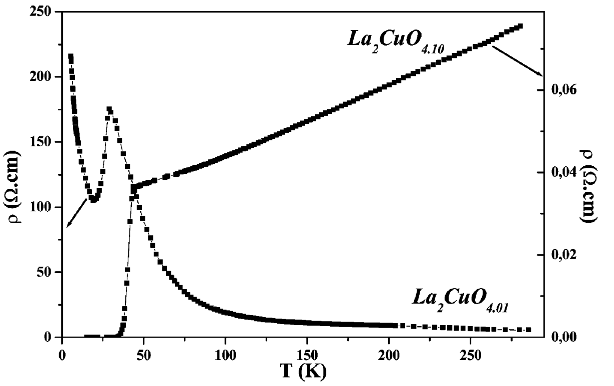

Fig. 5 Thermal variation of the electrical conductivity of $La_2CuO_{4.01}$ (starting material) and $La_2CuO_{4.10}$ (electrochemically oxidised sample in DMSO–$NaClO_4$, 300 μA cm^{-2}, 170 h).

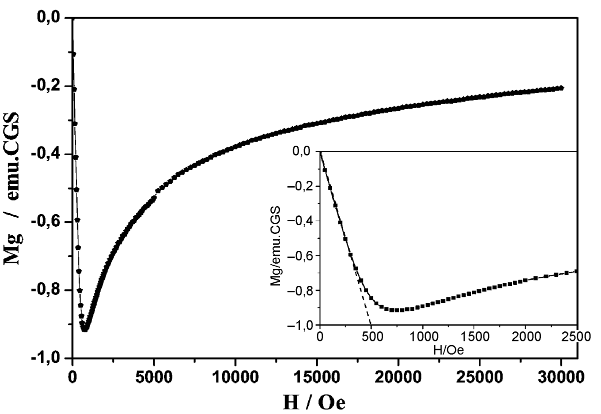

Fig. 6 Field dependence of the magnetisation of $La_2CuO_{4.10}$.

supporting electrolytes appear to be almost inert with respect to the electrochemical oxidation mechanism and the efficiency of the reaction. (iv) An oxygenated solvent, such as DMSO or DMF, seems to be mandatory for the electrochemical oxidation. (v) The mixture DMSO–$NaClO_4$ appears to be the most efficient medium for oxidising La_2CuO_4. The best electrochemical conditions were found to be 300 μA cm^{-2} for 170 h; under such conditions, the $La_2CuO_{4.10}$ composition was obtained. Its physical properties confirm that oxygen intercalation was achieved.

At this stage of our studies, the reaction mechanism is not yet fully elucidated and spectroscopic studies are in progress.

Acknowledgements

The authors are grateful to Rodolphe Decourt for his help with the electrical measurements.

References

1 J. C. Grenier, M. Pouchard and A. Wattiaux, *Curr. Opin. Solid State Mater. Sci.*, 1996, **1**, 233.
2 J. C. Grenier, A. Wattiaux, N. Lagueyte, J. C. Park, E. Marquestaut, J. Etourneau and M. Pouchard, *Physica C*, 1991, **173**, 139.
3 A. Demourgues, F. Weill, B. Darriet, A. Wattiaux, J. C. Grenier, P. Gravereau and M. Pouchard, *J. Solid. State Chem.*, 1993, **106**, 317.
4 J. C. Grenier, J. M. Bassat, J. P. Doumerc, J. Etourneau, Z. Fang, L. Fournès, S. Petit, M. Pouchard and A. Wattiaux, *J. Mater. Chem.*, 1999, **9**, 25.
5 J. C. Park, A. Wattiaux, J-C. Grenier, M. Pouchard and P. Hagenmuller, *Eur. J. Solid State Inorg. Chem.*, 1992, **29**, 361.
6 A. Jacob, D. Barbut, A. Wattiaux, M. H. Delville, J. C. Grenier, M. Pouchard and J. Etourneau, *J. Mater. Chem.*, 2000, **10**, 829.
7 D. Barbut, A. Wattiaux, M. H. Delville and J. C. Grenier, manuscript in preparation.
8 J. S. Valentine and A. B. Curtis, *J. Am. Chem. Soc.*, 1975, **97**, 224.
9 D. T. Sawyer and J. S. Valentine, *Acc. Chem. Res.*, 1981, **14**, 393.
10 H. Lund, in *Organic Electrochemistry*, ed. H. Lund and M. M. Baizer, Marcel Dekker Inc., New York, 1991, p. 253.
11 C. K. Mann, in *Electroanalytical Chemistry*, ed. A. J. Bard, Marcel Dekker Inc., New York, 1961, vol. 3, p. 57.
12 N. Lagueyte, F. Weill, A. Wattiaux and J. C. Grenier, *Eur. J. Solid State Inorg. Chem.*, 1993, **30**, 859.
13 J. C. Grenier, N. Lagueyte, A. Wattiaux, J. P. Doumerc, P. Dordor, J. Etourneau and M. Pouchard, *Physica C*, 1992, **202**, 209.