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# Electrochemical intercalation of oxygen into $La_2CuO_4$ using anhydrous organic electrolytic media

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**The electrochemical intercalation of oxygen into $La_2CuO_4$ has been carried out for the first time in anhydrous organic–inorganic media such as dimethyl sulfoxide (DMSO)/0.1 M $NaClO_4$ or $nBu_4NBF_4$. The electrochemical reaction needs the presence of an oxygen source ($KO_2$) even with potential oxidising supporting electrolytes ($NaClO_4$). The anodic polarisation is performed at room temperature, with the aim of replacing the usual efficient but sometimes aggressive alkaline media. This so-called *chimie douce* reaction gave rise to noteworthy materials having compositions up to $La_2CuO_{4.08}$ for which superconducting behaviour was observed below 42 K. The physical characteristics of the material (XRD, chemical composition, electronic properties) before and after controlled anodic polarisation are reported. The processes are time dependent and the oxygen stoichiometry could be controlled through reaction times.**

Oxides are usually synthesised at relatively high temperatures, under a controlled pressure of oxygen. The thermodynamic conditions are such that only the stable form of the compound is generally obtained.

In the past two decades, new so-called *chimie douce* (soft chemistry) methods have been developed for their ability to prepare metastable compounds. One of these new methods, initiated for the first time in 1989,[1] uses the electrochemical intercalation (or deintercalation) of oxygen, under controlled polarisation, in ternary or quaternary oxide networks of transition elements (Fe, Ni, Co, Cu) with perovskite or $K_2NiF_4$ related structures. This electrochemical intercalation carried out in air, at room temperature, in alkaline media gave rise to noteworthy materials never obtained before with classical treatments used in solid state chemistry.[1–13]

The electrochemical intercalation of oxygen in $La_2CuO_4$ is an illustration of this process. Materials could be prepared with compositions up to $La_2CuO_{4.09}$, for which superconducting behaviour has been observed below 44 K.[14] In the same way, fully oxidised materials such as the perovskites $SrMO_3$ (M = Fe or Co) have been obtained.[2,3,6]

However, the use of alkaline media (KOH 1 M) as well as long polarisation times (three months) may induce some degradation and corrosion of the materials due to dissolution–precipitation processes during the reaction. This destruction phenomenon limits or at least makes difficult and even sometimes impossible the intercalation of oxygen for some sensitive materials.[3]

Therefore new electrolytic systems are required and anhydrous organic–inorganic media are proposed and used for the first time. The lanthanum cuprate $La_2CuO_4$, which was reported for the first time as exhibiting superconducting behaviour after treatment under high oxygen pressure,[14] was chosen as a model material to investigate electrochemical oxidation in these new electrolytes. Its electronic properties as a function of the oxygen composition are relatively well known.[4,15] The physical characteristics of the material (XRD, chemical composition, and electronic properties) before and after controlled anodic polarisation are reported. A representation of the structure of $La_2CuO_4$ is given in Fig. 1. As shown by Chaillout *et al.* and explained later by Darriet *et al.*, the oxygen atoms are inserted into vacant sites of the $La_2O_2$ layers.[16,17]

The compound $La_2CuO_4$ was prepared starting from a ground stoichiometric mixture of $La_2O_3$ (previously dried in air, at 1123 K, for 15 h) and CuO. The mixture was annealed several times in air at 1323 K (24 h) and reground each time, finally leading to $La_2CuO_4$. Pellets (400 mg, diameter 8 mm, and thickness 2 mm) were pressed from this powder using a uniaxial pressure of 2 MPa. They were then sintered at 1323 K for 24 h and quenched. The as-prepared ceramics have good mechanical behaviour and a density of 80–85%. The characterisation of the samples before and after polarisation was achieved by X-ray powder diffraction with a Guinier–Häag chamber using Cu-Kα radiation. The oxygen content was deduced from the chemical analysis of the oxidation state of copper by iodometric titration. Electrical resistivity measurements were performed on the electrodes as a function of temperature ($4.2 \leqslant T \leqslant 293$ K) using a four-probe method. Magnetic measurements were carried out in the temperature range 4.2–300 K, using a SQUID Quantum Design MPMS2.

The electrochemical oxidation was performed using a three-compartment electrochemical cell with a three-electrode system. The reference electrode was a pseudo-reference one made of a platinum wire (diameter = 0.5 mm). The auxiliary

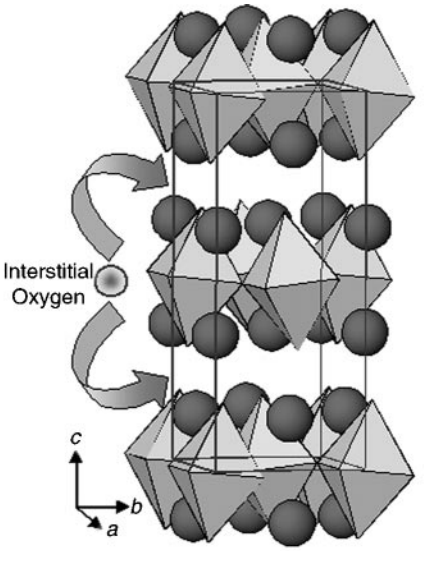

**Fig. 1** Structure of $La_2CuO_4$ showing the intercalation of oxygen into the "$La_2O_2$" layers.

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**Table 1** Electrochemical experimental conditions and physical characteristics of $La_2CuO_{4+\delta}$ before and after anodic polarisation ($I = 100\ \mu A$) at 298 K

| Experiment | Compound | Electrolytic solution | $t$/h | % $Cu^{3+}$ (atom.) | Electrical behaviour or $T_{onset}$/K[a] | $T_c$/K[b] | $\rho_{RT}$ at 290 K[c] |
|---|---|---|---|---|---|---|---|
| 1 | $La_2CuO_{4.01}$ starting material | | | 2 | Semicond. | | 0.48 |
| 2 | $La_2CuO_{4.01}$ | anhydrous DMSO/0.1 M $NaClO_4$ | 120 | 2 | Semicond. | | 0.59 |
| 3 | $La_2CuO_{4.03}$ | anhydrous DMSO/0.1 M $NaClO_4$/sat. $KO_2$ | 68 | 6 | 40 | 29 | 0.05 |
| 4 | $La_2CuO_{4.08}$ | anhydrous DMSO/0.1 M $NaClO_4$/sat. $KO_2$ | 160 | 16 | 48 | 42 | 0.02 |
| 5 | $La_2CuO_{4.00}$ | anhydrous DMSO/0.1 M $nBu_4NBF_4$ | 170 | 0 | Semicond. | | 0.79 |
| 6 | $La_2CuO_{4.03}$ | anhydrous DMSO/0.1 M $nBu_4NBF_4$/sat. $KO_2$ | 160 | 6 | 39 | 32 | 0.11 |

[a]$T_{onset}$ from electrical conductivity measurements. [b]$T_C$: diamagnetic superconducting temperature. [c]$\rho_{RT}$: electrical resistivity at room temperature.

electrode was a gold plate with a large area. The working electrode consisted of the ceramic material soaked in the electrolytic solution and connected to the potentiostat–galvanostat through a stainless steel grip. The electrolytic medium is described below. To avoid any trace of water, all experiments were performed at 298 K under an argon atmosphere predried over KOH pellets and then over $P_2O_5$.

The electrolytic medium consists of a solution of anhydrous dimethyl sulfoxide (DMSO, $\varepsilon = 47$) containing either 0.1 M $NaClO_4$ or $nBu_4NBF_4$ as supporting electrolytes[18–21] and saturated with $KO_2$ as an oxygen source. Pellets of the starting material prepared as described above (Table 1, row 1) were submitted to anodic polarisation ($I = 100\ \mu A$). The results are reported in Table 1. Experiments 2 and 5 were performed in the absence of $KO_2$. The results obtained under these reaction conditions underline the necessity of an oxygen source to achieve oxygen intercalation in the material. Indeed, no change is observed in the oxygen content even after polarisation times as long as 120 h. Neither $NaClO_4$ nor $nBu_4NBF_4$ were able, on their own, to induce any modification of the material or its degradation. This is understandable for $nBu_4NBF_4$,which is very often used in organic electrochemistry because of its highly inert character over a large range of potentials.[18,21] It was therefore used as a reference to test the behaviour of $NaClO_4$ which may be considered otherwise as an oxidising reagent.[19]

Anhydrous $KO_2$ was then added until saturation to these two electrolytic media in order to provide oxygen species to be intercalated in the material (Table 1, experiments 3, 4 and 6).

In each case, the pellets were analysed before and after polarisation, showing that the electrochemical oxidation of $La_2CuO_4$ is efficiently performed in anhydrous organic media. It is a time dependent phenomenon, the overstoichiometry increases from $\Delta\delta = 0.02$ for 68 h to 0.07 for 160 h in DMSO/$NaClO_4$/$KO_2$ with significant variation of the physical properties of the materials (Table 1, experiments 3 and 4). The use of DMSO/$nBu_4NBF_4$/$KO_2$ gives rise to a less efficient system (Table 1, experiment 6), since for the same polarisation time of 160 h the resulting material exhibits a $\Delta\delta$ of only 0.02 with $nBu_4NBF_4$ while it rises to a value of 0.07 with $NaClO_4$.

The lattice parameters $a$, $b$ and $c$ of the samples for experiments 1 and 4 are given in Table 2. Before the electrochemical treatment, the crystalline cell is orthorhombic (*Bmab*). After the anodic polarisation, the X-ray patterns show single well-crystallised phases. Samples 3 and 6 exhibit a pseudotetragonal symmetry and sample 4 an enhanced orthorhombic distortion. In addition, the $c$ parameter increases, which illustrates the intercalation of oxygen into the $La_2O_2$ layers as shown in Fig. 1. This is in very good agreement with previous results obtained for samples oxidised in alkaline solutions.[1,4,6] These structural modifications due to the increase of oxygen overstoichiometry induce remarkable changes in the electronic properties of the materials correlated to an increase of the oxidation state of copper. Fig. 2 and 3 illustrate the thermal variation of the electrical resistivity before and after electrochemical treatment respectively. Before polarisation, the starting material exhibits semi-conducting-type behaviour (the small peak around 30 K reveals filamentary superconductivity).[15] After polarisation (experiment 4), the material exhibits an abrupt decrease of the electrical resistivity by a factor of 1000 with zero resistivity below 30 K. The shape of the transition between 50 and 30 K as well as the presence of a hump at about 230 K reveal that the electrochemical oxidation is not completely achieved. In other words, the material is not homogeneous from an oxygen stoichiometry viewpoint, as shown in the inset of Fig. 3 (experiment 6).

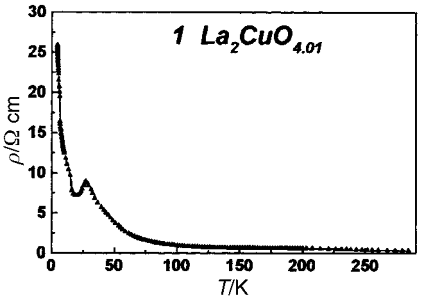

**Fig. 2** Thermal variation of the electrical resistivity of the starting material $La_2CuO_{4.01}$ (experiment 1).

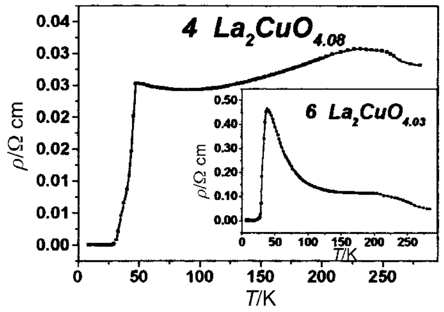

**Fig. 3** Thermal variation of the electrical resistivity of $La_2CuO_{4.03}$ and of $La_2CuO_{4.08}$ after anodic polarisation.

**Table 2** Crystallographic data of $La_2CuO_{4+\delta}$ samples before and after anodic polarisation

| Sample | $a$/nm ± 0.0005 | $b$/nm ± 0.0005 | $c$/nm ± 0.005 | $\delta \pm 0.01$ |
|---|---|---|---|---|
| 1 | 0.5359 | 0.5410 | 1.314 | 0.01 |
| 4 | 0.5354 | 0.5387 | 1.321 | 0.08 |

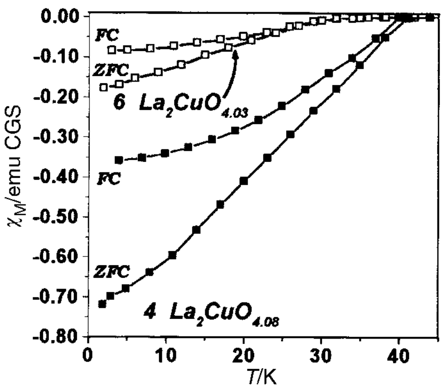

**Fig. 4** Thermal variation of the magnetic susceptibility of $La_2CuO_{4.03}$ (sample 6) and of $La_2CuO_{4.08}$ (sample 4) measured under $10^{-2}$ T.

In the same way, the thermal dependencies of the magnetic susceptibility (Fig. 4) for the compounds $La_2CuO_{4.08}$ and $La_2CuO_{4.03}$ confirm their superconducting behaviour with the onset of the transition temperatures $T_c = 42$ K and 32 K, respectively. All these results nicely agree with previous results reported for the electrochemical oxidation of this compound in alkaline aqueous solution.[1,4,6,15]

From these preliminary results, it can be concluded that anhydrous organic electrolytes are efficient replacements for alkaline media for the anodic intercalation of oxygen into oxide networks. Two new electrolytic media have been used, the source of oxygen being anhydrous $KO_2$. However, experimental conditions such as the working electrode, polarisation intensity current and time should be optimised. In fact, as observed from their physical properties, samples show some inhomogeneity compared to those previously obtained.[5] The presence of an oxygen source seems to be compulsory. The oxidation mechanism is under scrutiny: its determination requires, *inter alia*, the use of a stable reference electrode. Work is in progress to develop such electrolytic media, which will open a wide field of investigations for oxidising materials sensitive to aqueous media, such as $YBa_2Cu_3O_y$ or bismuth cuprates.

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## Notes and references

1 A. Wattiaux, J. C. Park, J. C. Grenier and M. Pouchard, *C. R. Acad. Sci. Paris*, 1990, **310**(II), 1047.
2 A. Wattiaux, L. Fournès, A. Demourgues, N. Bernaben, J. C. Grenier and M. Pouchard, *Solid State Commun.*, 1991, **77**, 489.
3 P. Bezdicka, A. Wattiaux, J. C. Grenier, M. Pouchard and P. Hagenmuller, *Z. Anorg. Allg. Chem.*, 1993, **619**, 7.
4 J. C. Grenier, N. Lagueyte, A. Wattiaux, J. P. Doumerc, P. Dordor, J. Etourneau, J. B. Goodenough, J. S. Zhou and M. Pouchard, *Physica C*, 1992, **202**, 209.
5 A. Demourgues, A. Wattiaux, J. C. Grenier, M. Pouchard, J. M. Dance and P. Hagenmuller, *J. Solid State Chem.*, 1993, **105**, 458.
6 J. C. Grenier, M. Pouchard and A. Wattiaux, *Curr. Opin. Solid State Mater. Sci.*, 1996, **1**, 33.
7 R. Mahesh, K. R. Kannan and C. N. R. Rao, *J. Solid State Chem.*, 1995, **114**, 294.
8 N. Casan-Pastor, P. Gomez-Romero, A. Fuertes, J. M. Navarro, M. J. Sanchis and S. Ondono, *Physica C*, 1993, **216**, 478.
9 P. G. Raedalli, J. D. Jorgensen, R. Kleb, B. A. Hunter, F. C. Chou and D. C. Jonhson, *Phys. Rev. B*, 1994, **49**, 6239.
10 W. Paulus, G. Heger, P. Rudolf and R. Schollhorn, *Physica C*, 1994, **235–240**, 861.
11 H. H. Feng, Z. G. Li, P. H. Hor, S. Bhavaraju, J. F. Di Carlo and A. J. Jacobson, *Phys. Rev. B*, 1995, **51**, 16499.
12 R. D. Sanchez, C. Gerber, A. Cretton, Y. Jaccard, E. J. Williams and E. Mächler, *Electrochim. Acta*, 1995, **40**, 209.
13 M. Itoh, Y. J. Shan, S. Sakamoto, Y. Inaguma and T. Nakamura, *Physica C*, 1994, **223**, 75.
14 J. Beille, R. Cabanel, C. Chaillou, B. Chevalier, G. Demazeau, F. Deslandes, J. Etourneau, P. Lejay, C. Michel, J. Provost, B. Raveau, A. Sulpice, J. L. Tholence and R. Tournier, *C. R. Acad. Sci. Paris*, 1987, **304**(II), 1097.
15 J. C. Grenier, A. Wattiaux and M. Pouchard, ed. K.A. Müller and G. Benedeck, *Phase Separation in Cuprates*, World Scientific, Singapore, 1992, p. 187.
16 C. Chaillout, J. Chenavas, S. W. Cheong, Z. Fisk, M. Marezio, B. Morosin and J. E. Schirber, *Physica C*, 1990, **170**, 87.
17 C. Dussarat, F. Grasset and J. Darriet, *Eur. J. Solid State Inorg. Chem.*, 1995, **32**, 557.
18 J. N. Butler, *J. Electroanal. Chem.*, 1967, **14**, 89.
19 D. T. Sawyer, A. Sobkowiak and J. L. Roberts, *Electrochemistry for Chemists*, Wiley, New York, 1995, p. 299.
20 J. L. Jones and H. A. Fritsche, *J. Electroanal. Chem.*, 1966, **12**, 286.
21 J. Simonet, *Organic Electrochemistry*, ed. H. Lund and M. M. Baizer, Marcel Dekker Inc., New York, 1991, p. 1217.

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