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Electrochemical Fluorination of La_2CuO_4: A Mild "Chimie Douce" Route to Superconducting Oxyfluoride Materials

M. H. Delville,[*,†] **D. Barbut,**[†] **A. Wattiaux,**[†] **J. M. Bassat,**[†] **M. Ménétrier,**[†] **C. Labrugère,**[†,‡] **J. C. Grenier,**[†] **and J. Etourneau**[†]

[†]*CNRS, Université de Bordeaux, ICMCB, 87 avenue du Dr. A. Schweitzer, Pessac, F-33608, France, and*
[‡]*CeCaMA, Université de Bordeaux, ICMCB, 87 avenue du Dr. A. Schweitzer, Pessac, F-33608, France*

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The fluorination of La_2CuO_4 was achieved for the first time under normal conditions of pressure and temperature (1 MPa and 298 K) via electrochemical insertion in *organic* fluorinated electrolytes and led to lanthanum oxyfluorides of general formula $La_2CuO_4F_x$. Analyses showed that, underneath a very thin layer of LaF_3 (a few atomic layers), fluorine is effectively inserted in the material's structure. The fluorination strongly modifies the lanthanum environment, whereas very little modification is observed on copper, suggesting an insertion in the La_2O_2 blocks of the structure. In all cases, fluorine insertion breaks the translation symmetry and introduces a long-distance disorder, as shown by electron spin resonance. These results highlight the efficiency of electrochemistry as a new "chimie douce" type fluorination technique for solid-state materials. Performed at room temperature, it additionally does not require any specific experimental care. The choice of the electrolytic medium is crucial with regard to the fluorine insertion rate as well as the material deterioration. Successful application of this technique to the well-known La_2CuO_4 material provides a basis for further syntheses from other oxides.

Introduction

Since the discovery, in 1987, of high-T_C cuprate superconductors, the effect of fluorine doping in these materials has been extensively investigated. A few research groups reported a surprising enhancement in T_C above 140 K.[1-3] These reports generated accelerated research on the fluorination of various cuprates. Although their surprising results were not confirmed by other researchers,[4-7] fluorine doping into cuprates has continuously attracted much attention. The discovery of several new high-T superconductors containing fluorine has been reported. They include $La_2CuO_{4-\delta}F_y$ (T_C = 40 K),[8,9] $Nd_2CuO_{4-x}F_x$ (T_C = 27 K),[10] $Sr_2CuO_2F_{2+\delta}$ (T_C = 46 K),[11] $La_{0.7}Sr_{1.3}Cu(O,F)_{4+\delta}$ (T_C = 55 K),[12] and $Sr_2Ca_{n-1}Cu_nO_{2n+\delta}F_{2\pm y}$ (T_C = 99 K for n = 2, 111 K for n = 3).[13]

There are many techniques of fluorination; they mainly use high temperatures, toxic reactants, and specific safety setups.[14]

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*To whom correspondence should be addressed. E-mail: delville@icmcb-bordeaux.fr.

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A very standard one is preparation by solid-state reactions: the starting materials, generally oxides, or carbonates ($BaCO_3$, $SrCO_3$, $CaCO_3$, CuO, Y_2O_3, Bi_2O_3, etc.) are replaced by the corresponding fluorides or oxyfluorides (BaF_2, SrF_2, CaF_2,[2,15] CuF_2,[16] YF_3,[16a] BiOF,[17] YOF,[18] etc.). Additionally, $La_2CuO_4F_x$ thin films were generated on $SrTiO_3$[19,20] by laser-ablation techniques on La_2CuO_4. Some experiments were also performed with inorganic fluorinating agents such as NH_4F or transition metal difluorides.[21]

Another process is fluorination by solid–gas reactions, which are generally performed at temperatures around 300 °C using a fluorinated gas such as NF_3[6,22] or F_2.[8,16,23] Such a fluorination has attracted considerable attention as a technique to introduce carriers for inducing superconductivity, resulting in drastic changes in structures and superconducting properties.[8,11] However, great care is required in handling the toxic F_2 gas.[24] To solve this problem, fluorination by ionic bombardment with a fluoride beam has been developed.[16,25]

Another efficient way to overcome this disadvantage was sought in chemical fluorination based on the use of fluorinating reagents such as NH_4F,[18,26–28] but here the temperature is still higher than 200 °C and generates the release of fluorine by thermal decomposition. In this method, starting materials are simply heated together with the reagent. HF was also used in organic media.[29] However, all of these methods were not so easy to handle, with consequences on the results such as various divergences in the literature, as pointed out by Fadeeva et al. in their review paper.[14] Besides these techniques, electrochemical fluorination was investigated since it is a method which exhibits, among others, the following advantages: (i) hazardous or toxic reagents can be avoided; (ii) this fluorination can be carried out with relatively simple equipment under mild conditions; (iii) fluorination processes can be easily controlled by the applied potential, current, and electricity; (iv) it is an economic method, where a fluoride salt can be used as the fluoride ion source and supporting electrolyte.

Electrochemical fluorination has scarcely been approached in inorganic chemistry and was used essentially in organic chemistry using either the Simons or the Philips process.[30,31] As an example, the fluorination of yttrium barium copper oxide ($YBa_2Cu_3O_{7-x}$) was reported using a solid-state electrochemical method at 400 °C.[32] The preparation of low-temperature fluorinated oxides by anodic oxidation in dilute hydrofluosilicic acid (H_2SiF_6) solution was also performed to yield SiO_2.[33]

As a matter of fact, we have also been developing for nearly two decades now[34,35] an electrochemical insertion of anions such as oxygen ones, a process which can be carried out in the air, at room temperature, in alkaline media and which allowed the preparation of noteworthy materials, some having never been obtained with classical synthesis routes used in solid-state chemistry. Even if most of these oxides with high oxidation states for metal cations show a rather high chemical stability with respect to the electrolytic solution, these experiments often require long polarization times (a few hours to several days), and mechanical or chemical degradation of the materials may occur due to the combined action of water (hydrolysis) and carbonate anions (carbonatation) present in strong alkaline solutions. Thus, some materials, for example, could never been prepared this way ($YBa_2Cu_3O_7$, $BaFeO_3$). In order to kill this degradation, we developed this electrochemical insertion in nonaqueous electrolytes, using organic media.[36,37]

We have shown, in a previous paper,[38] that organic media without any external source of oxygen (KO_2 or H_2O) could be used to induce the electrochemical oxidative intercalation of oxygen in the well-known La_2CuO_4 material. Various electrochemical processes occur, implying not only the decomposition of the "oxygen-bearing" solvents but also that of the supporting salt, leading to the formation of oxygen species as O^- or $O^\bullet$, able to oxidize the material. Dimethylsulfoxide (DMSO) associated with $n Bu_4NClO_4$ appeared to be the most relevant electrolyte for oxidizing La_2CuO_4 into $La_2CuO_{4.10}$. The use of fluorine-containing salts during electrochemical insertion led to materials which exhibited electronic properties different from those obtained in fluorine-free salts. Insertion of fluorine in their structure was suggested.[38]

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In this work, we intend to illustrate the potentiality of this approach to generate fluorinated phases playing with the nature of the solvent and the electrolytic salt. Fluorination usually takes place with the formation of fluorinated species (F^-, $F^\bullet$) on the surface of the working electrode.[39] The choice of the electrolyte/solvent couple is therefore crucial. The model compound $La_2CuO_{4+\delta}$ was chosen since its electronic properties, depending on the Cu^{3+} ratios, are perfectly referenced in the literature.[34,35] The anodic polarization conditions and their impact on the final products as well as the full physical and chemical characterizations of a lanthanum copper oxyfluoride obtained in a N,N-dimethylformamide (DMF)/nBu$_4$NBF$_4$ medium are presented in this paper.

Experimental Procedure

The "nitrate–citrate" route[40] was used for synthesizing $La_2CuO_{4.01}$ starting from dried La_2O_3 and CuO. After a final annealing at 1000 °C for 24 h, the powder was ground and pressed as a pellet ($10 \times 5 \times 2.5$ mm^3, 400 mg), which was sintered at 1050 °C for 6 h. The as-prepared porous ceramics (75%-density) exhibit good mechanical properties. LaF_3 (99.99%) was supplied by Aldrich, and LaOF was synthesized according to the literature.[41]

Electrochemical insertion of fluorine was performed under both galvanostatic and potentiostatic modes with a Tacussel PRT 6 × 20–0.2 VA potentiostat and a potentiostat–galvanostat (Tacussel PJT 24–1). The electrochemical experiments were performed in an airtight glass cell, under a mild dry argon flow at 293 K, using a classical three-electrode system. The working electrode was an as-prepared ceramic one with an immersed part of 1 cm^2. The counterelectrode was a gold foil (≈ 3 cm^2), and the reference electrode was a Pt wire ($\varnothing = 0.5$ mm). The electrolyte salt concentration was constant (0.1 M) for all of the experiments.

Samples were systematically characterized before and after electrochemical treatment. X-ray diffraction (XRD) was performed using a Philips 1710 diffractometer (Cu Kα radiation); the unit cell parameters were obtained from powder XRD data using a whole-pattern decomposition and the Le Bail method using the Fullprof software.[42]

The Cu^{3+} content (τ) in the starting material ($La_2Cu_{1-\tau}{}^{2+}Cu_\tau{}^{3+}O_{4+\tau/2}$) was determined by chemical analysis (iodometric titration with an accuracy of ±0.01). Fluorine titration of the samples was carried out on polished and then ground ceramics. The chemical titration of fluorine is based on the distillation of the fluorosilicic acid. It consists of an alkaline fusion of the sample. The separation of fluorine from the other elements is performed by reaction with silica in the presence of concentrated H_2SO_4 to form fluorosilicic acid, which is then distilled at 240 °C. The titration was carried out using a fluorine-specific electrode (single crystal of LaF_3).[43] Results for the fluorine titration are given with an accuracy of ±0.05.

X-ray photoelectron spectroscopy (XPS) spectra obtained before and after electrochemical treatment were readjusted in energy with regard to the O1s peak located at 531.0 eV (Table 1); the validity of this shift was confirmed by the positioning of the C1s carbon peak at the expected binding energy of 284.8 ± 0.2 eV. Ionic sputtering (Ar^+) was performed under identical conditions for all samples. High-resolution spectra were recorded after 0, 60, 120, 300, and 480 s. The Auger electron spectroscopy (AES) experiments were performed with an Auger VG Microlab 310F.

Table 1. Binding Energies of the Different Elements for the Fluorinated Sample and the References

	binding energy (eV ± 0.2)[a]			
	$La3d_{5/2}$	$Cu2p_{3/2}$	F1s	O1s
La_2CuO_4	834.6 (large)	932.8		530.1 528.1
	[837.7, 833.6]			[528.1]
LaF_3	835.9		684.5	532.2
LaOF	839, 837. (d)		685.4	532.4
	[838.6, 834.6 (d)]			[532 + 529.9 (sh)]
CuF_2		942.6[b], 934.1	683.9	531.9
sample	835.5	932.2	684.0	531.2
	[838.6, 834.5 (d)]	[932.8]	[684.8]	[531.2 + 529.8]

[a] Values in brackets are those obtained after 480 s of etching when different from the surfaces values. (+) Detection of an extra signal; d, doublet; sh, shoulder. [b] Satellite.

The electrical resistivity of the ceramics was measured using the aligned four-probe method in the temperature range $4.2 \leq T \leq 300$ K using a 181 Keithley nanovoltmeter and a 220 Keithley current source.[44,45] X-ray photoelectron spectra were obtained using a VG 220i-XL Escalab spectrometer, employing a nonmonochromatized Mg Kα source ($h\nu = 1253.6$ eV). The X-ray gun was operated at 10 kV and 20 mA (pressure: 10^{-8} Pa).

Measurements of magnetic properties were also used to characterize the intercalation process. The thermal variation of the magnetization was measured using a SQUID magnetometer (Quantum Design MPMS2) under 0.01 T, at increasing (zero-field-cooled) and decreasing (field-cooled) temperature in order to determine the superconducting transition temperature T_C.

Electron spin resonance (ESR) measurements were performed between 4.2 and 300 K with a Bruker EMX X band (9.46 GHz) spectrometer, equipped with an Oxford ESR-900 helium cryostat.

^{19}F NMR data were recorded at 470.5 MHz with a Bruker Avance 500 spectrometer (11.7 T magnet) with magic angle sample spinning (MAS) of the sample at 15 kHz. The pulse sequence is a Hahn echo synchronized with the rotor rotation period suitable for refocusing electron–nucleus dipolar interactions.[46] The spectral width is 1 MHz with a 90° pulse duration of 4 μs and a recycling time of 2 s. The chemical shifts are given with respect to the signal of $CFCl_3$.

Results and Discussion

A set of experiments was performed on $La_2CuO_{4.01}$ for 48 h in various media for different current densities (100–800 μA cm^{-2}). The most characteristic AES depth profile analyses of the sample surfaces are shown in Figure 1 after polarized treatment in DMSO/nBu$_4$NBF$_4$ (300 μA/cm^2), CH_3CN/nBu$_4$NF (100 μA/cm^2), and DMF/nBu$_4$NBF$_4$ (600 μA/cm^2).

In all cases, the presence of a fluorine-rich surface layer is evidenced. This fluorine content more or less rapidly decreases upon etching with a concomitant increase of the oxygen amount (Figure 1a,b). DMSO has been shown to be a source of oxygen in such electrochemical treatment, leading

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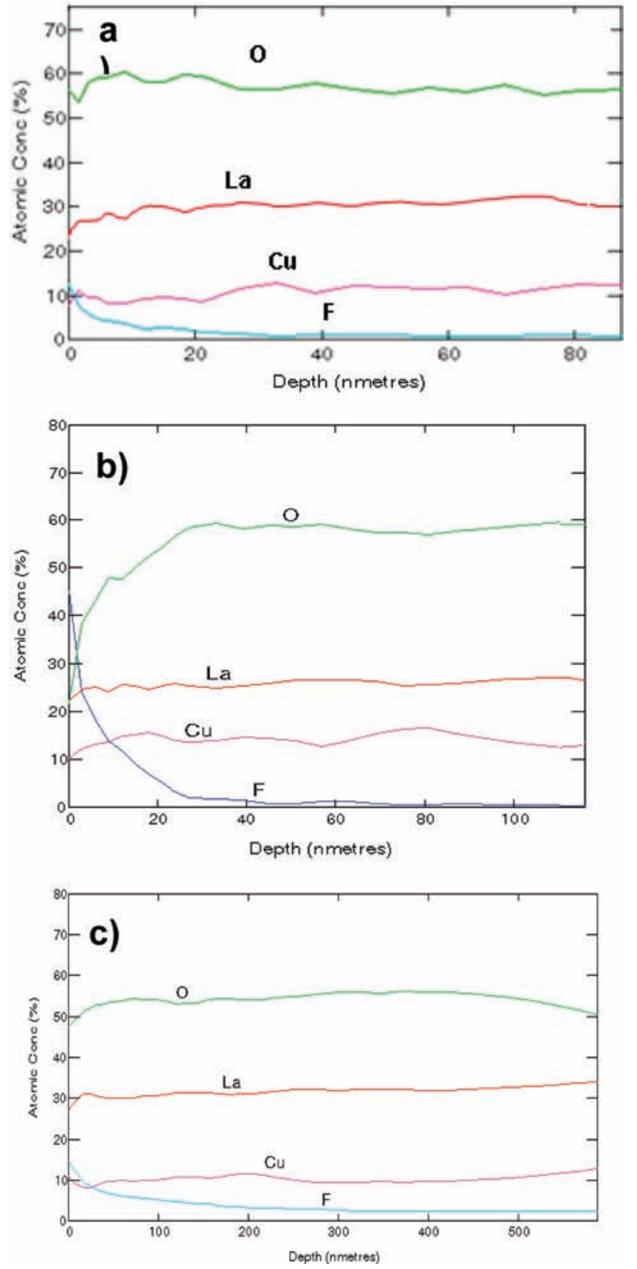

Figure 1. Auger depth profile of the elements present in the La_2CuO_4-(O,F) phases prepared (48H) at (a) 300 $\mu A/cm^2$ in DMSO/$n$$Bu_4NBF_4$ (0.1 M), (b) 100 $\mu A/cm^2$ in CH_3CN/nBu_4NF (0.1 M), and (c) 600 $\mu A/cm^2$ DMF/$n$$Bu_4NBF_4$ (0.1 M).

to preferential insertion of oxygen as compared to fluorine.[38] The very high amount of fluorine on the outer surface of some materials (see Figure 1b for example) shows that even such a low current density induces partial surface decomposition, especially with $n$$Bu_4NF$ as a salt. A reaction performed at a higher current density (600 $\mu A/cm^2$) led to a higher degradation rate, with the formation of a fluorinated material identified as LaF_3 down to 200 nm (results not shown).

To promote the reaction, experiments with high current densities (600−800 $\mu A/cm^2$) in solvents such as DMF with $n$$Bu_4NBF_4$ were also carried out. It seemed (Figure 1c) to be the solvent of choice with an apparent very thin fluorine-rich layer and a steady 3 atom % content all along the depth profile.

The resulting conclusion is that the optimized conditions require solvents such as DMF, salt electrolytes such as $n$$Bu_4NBF_4$, and maximum current densities of 600 $\mu A/cm^2$. With lower current densities, the experiments took nearly a month, resulting in a high amount of chemical degradation; with higher ones, the corrosion processes were detrimental. Thus, experiments carried out in galvanostatic mode in DMF/0.1 M $n$$Bu_4NBF_4$ under 600 $\mu A\ cm^{-2}$ yielded a fluorinated phase. Thermal variation of the electronic resistivity is reported in Figure 2 for different polarization times. It shows significant changes with respect to the starting material ($t = 0$ h, (∗), blue curve; Figure 2a).

The starting material $La_2CuO_{4.01}$, after 130 h, gave a product with electronic properties which did not change any more, indicating that, under these anodic polarization conditions, the fluorination reached its maximum. The value of the magnetic susceptibility shows that this sample becomes diamagnetic below a critical temperature (T_C) of 39−40 K (Figure 2b), slightly lower than that observed (44 K) for the $La_2CuO_{4.10}$ compound obtained after the electrochemical insertion of oxygen under the same conditions.[36] In addition, in the temperature range 50 K ≤ T ≤ 300 K, the compound exhibits a decrease of its electrical resistivity with the polarization time, suggesting an increasing amount of Cu^{3+} as shown for $La_2CuO_{4+\delta}$,[34,35] However, the electrical resistance tends to zero at 25 K. No such transition is observed on the magnetic susceptibility curve, which could mean that the volume of this superconducting phase is far too small to induce percolation phenomena and therefore be seen by magnetic properties. This can be explained by a compositional heterogeneity.

The X-ray diffractogram of this material after grinding (Figure 3) shows the presence of a single phase, with no detectable sign of additional phases, which might have resulted from the material decomposition.

The X-ray data were indexed in the *Fmmm* space group. The lattice parameters obtained from a least-squares refinement were a = 5.348(1) Å, b = 5.402(1) Å, c = 13.205(1) Å, and V = 381.48 Å^3. These values show some differences as compared to those of the $La_2CuO_{4.01}$ starting material (a = 5.359(1) Å, b = 5.410(1) Å, c = 13.141(1) Å, V = 380.99 Å^3).[47] Indeed, a very weak decrease of the a and b parameters as well as an increase of the c one are observed, as already shown for the superoxygenated $La_2CuO_{4.10}$ (a = 5.328 Å, b = 5.4060 Å, c = 13.187 Å, and V = 379.827 Å^3).[48] The decrease of a and b is due to the presence of the Cu^{3+} cations in the CuO_2 layers of the structure, whereas the c parameter increase is related to the insertion of species in the La_2O_2 blocks.

Comparison of the cell volume of the three materials shows that, when that of the superoxygenated one decreases by 0.3%, that of the fluorinated one does slightly increase (+0.13%) with regard to the starting material. Therefore, the cell shrinking which was observed in $La_2CuO_{4.10}$ and due to the presence of the Cu^{3+} cations responsible for the superconductivity is largely compensated by the larger radius of the fluorine anion in the fluorinated phase. A chemical titration of fluorine gave a composition of "$La_2CuO_4F_{0.18}$"

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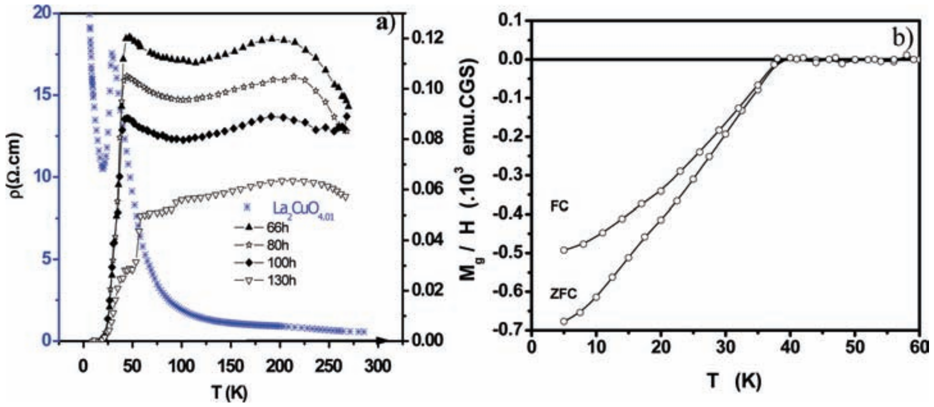

Figure 2. (a) Thermal variation of the electrical resistance of $La_2CuO_{4.01}$ (starting material, (∗)) after electrochemical treatment in DMF/nBu$_4$NBF$_4$ (600 μA cm^{-2}), for various times of polarization (66 h $\leq t_{ox} \leq$ 130 h). (b) Thermal variation of the magnetic susceptibility of the inserted sample obtained after 130 h. FC, field-cooled; ZFC, zero-field-cooled.

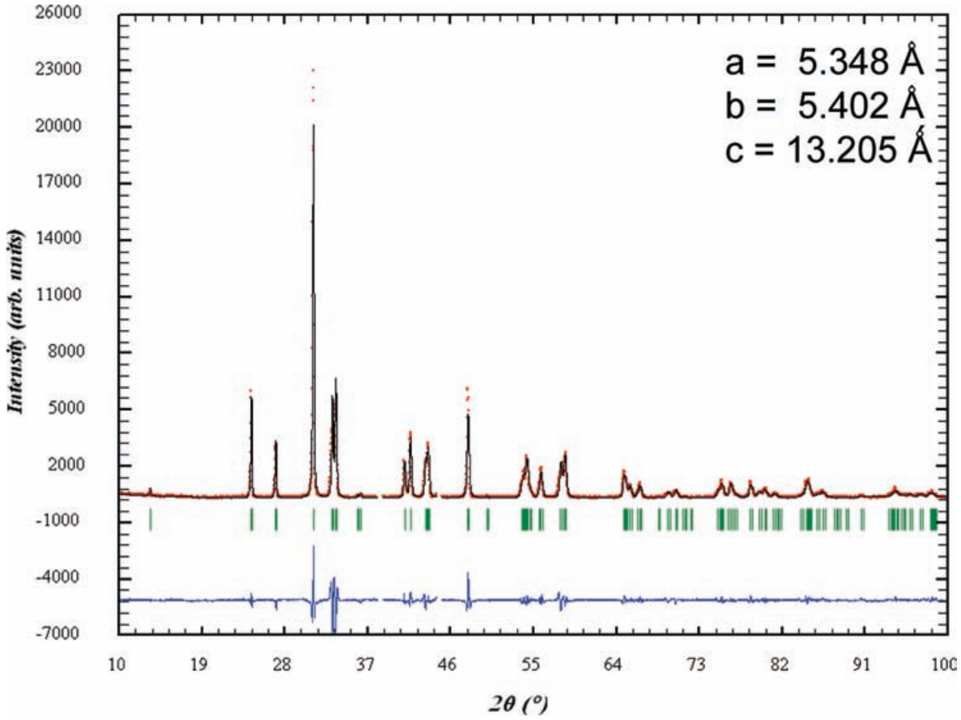

Figure 3. X-ray diffractogram of the fluorinated sample electrochemically treated in DMF/nBu$_4$NBF$_4$.

consistent with the X-ray analysis as well as the thermal variation of the magnetic susceptibility and the conductivity.

Since AES showed the presence of some impurities and XRD is poorly sensitive to impurities and could not detect them, we undertook some depth profile XPS analyses.

XPS Data. XPS analysis of the surface environment of the copper and lanthanum atoms within the sample was analyzed, and comparisons were made with reference materials such as LaF_3,[49] LaOF,[50] and CuF_2,[51] which could result from degradation, and with the starting material $La_2CuO_{4.01}$[52,53] High-resolution spectra (La3d$_{5/2}$, Cu2p$_{3/2}$, O1s, F1s, and C1s) were obtained from the extreme surface to about a few hundred nanometers depth after Ar$^+$ etching times of 0, 60, 120, 300, and 480 s (corresponding to a stabilization of the fluorine amount in the material, as also seen by AES). Tables 1 and 2 gather the values of the binding energy maxima and an atomic quantification for the different compounds.

Comparison of the Cu2p$_{3/2}$ signature of the two samples with that of CuF_2 definitely excludes the formation of such a phase in the bulk material during the electrochemical intercalation (absence of the shakeup satellite peak usually found at 943.0 eV in CuF_2).[51] On the other hand, the fluorine response does not differ

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Table 2. XPS Quantification (atom %; XR non-monochromatized Mg source, Ep = 20 eV, Scofield correction, relative incertitude 5−10%)

	C (atom %)	O (atom %)	F (atom %)	La (atom %)	Cu (atom %)
fluorinated sample	28.9	23.4	30.8	14.9	2.1
fluorinated sample (480 s etching)		43.6	15.3	31.7	9.5
LaF_3 surface	18.9		59.8	21.3	
LaF_3 (480 s etching)			65.8	34.2	
LaOF surface	31.8	40.7	13.4	14.1	
LaOF (480 s etching)		47.9	17.4	34.7	
La_2CuO_4 surface	58.8	29.0		8.1	4.0
La_2CuO_4 (480 s etching^2)		55.4		30.7	13.9

much from one sample to the other, as already mentioned in the literature.[50]

Since neutron diffraction and EXAFS measurements at the La LIII X-ray absorption edge have already shown that, when fluorinated at high temperature (200 °C), the La_2CuO_4 structure contains additional anions between consecutive LaO layers,[9] our focus will be concentrated of the La element. Figure 4 shows the surface and bulk $La3d_{5/2}$ spectra of the sample, and of the different references. The surface binding energy of $La3d_{5/2}$ evidences a modification of the La environment as compared to that of the starting material (834.6 eV in La_2CuO_4[52]) and the presence of La−F-type peaks (max. at 835.7 eV, close to those of LaF_3 values[49,54]).

After an etching time of 480 s, a different behavior is observed (Figure 4).

Below the characteristic LaF_3 outmost surface layer, we observe a $La3d_5$ peak with a binding energy corresponding to a lanthanum located in a mixed environment (close to what is observed in LaOF (Figure 4b)) with the classical two-level splitting for oxides. The modifications of the $La3d_{5/2}$ peak shape after four successive etching times (60, 120, 300, and 480 s) clearly illustrate the change in the environment of this atom (Figure 4c) with, after 300 s of etching, a peak enlargement and a transition from LaF_3 to a phase where the lanthanum is coordinated to both oxygen and fluorine. The Cu2p peak located at 932.2 eV does not vary very much with the depth profile; neither does the F1s one (684.8 eV).

According to the previous results, we can conclude that this room-temperature electrochemical fluorination is an efficient method which can compete with already known fluorination processes, yielding samples which, underneath a very thin layer of LaF_3, mainly exhibit a fluorine insertion in the host lattice of the starting material illustrated by the modification of the lanthanum chemical state. The fluorine insertion is then assumed to take place in the La_2O_2 block.[9]

ESR Data. ESR spectra of the sample and CuF_2 are shown in Figure 5. The absence of an ESR signal characteristic of the Cu^{2+} ion in semiconducting oxides such as $La_2CuO_{4.01}$ was attributed in the literature to the existence of strong two-dimensional antiferromagnetic couplings localized in the CuO_2 planes.[55,56]

The strong absorption observed at low field ($H < 0.08$ T; 20 mT) is a clear signature for the presence of a superconducting phase.[56] In contrast with what is observed in $La_2CuO_{4.10}$, the fluorinated phase exhibits a line centered at $H = 0.328$ T attributed to small quantities of Cu^{2+}

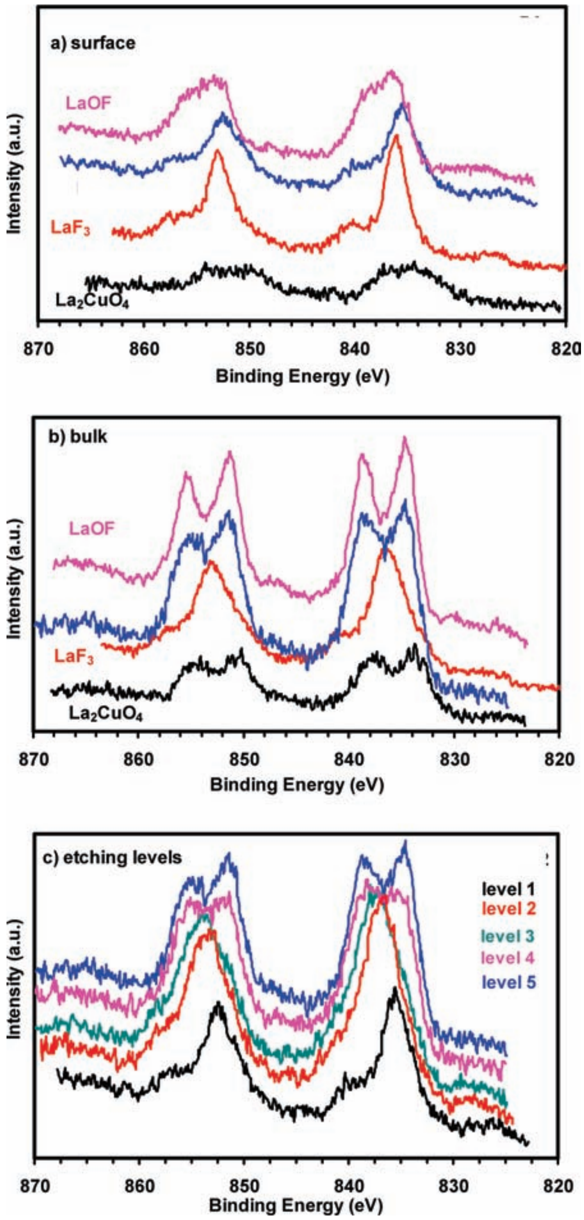

Figure 4. La3d high-resolution XPS spectra of (a) the surface of the fluorinated sample (blue), LaF_3, LaOF, and $La_2CuO_{4.01}$; (b) the bulk of the fluorinated sample (blue), LaF_3, LaOF, and $La_2CuO_{4.01}$; and (c) fluorinated sample: depth profile analysis after 0, 60, 120, 300, and 480 s etching times.

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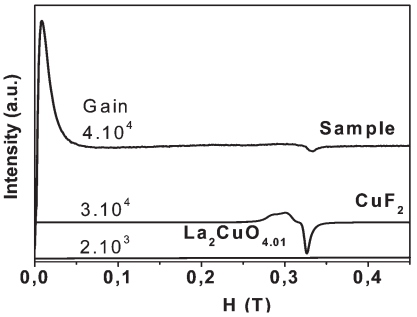

Figure 5. ESR spectra carried out at 4.2 K (9.46 GHz). For the fluorinated sample, $La_2CuO_{4.01}$ and CuF_2.

species,[57] which are not involved in the process of superconductivity (these Cu^{2+} ions being either isolated or slightly magnetically correlated with the network of the CuO_2 square). Note that, if these ions were not correlated at all, the signature would be that of the well-known isolated Cu^{2+} ions, that is, a less broad and anisotropic peak, as highlighted for example in CuF_2, with a significant absorption line at about 0.27 T. This major difference in signature between CuF_2 and the sample confirms the absence of CuF_2 in the fluorinated cuprates, as already observed by XPS, the limit of detection being much lower for ESR.

NMR Data. In order to understand both the nature and the localization of the fluoride species, ^{19}F MAS NMR measurements were also performed on the sample and compared to the LaF_3 reference. The spectrum of the latter exhibits narrow signals, well-separated into spinning side bands (Figure 6).

LaF_3 exhibits three isotropic signals as well as the associated spinning side bands corresponding to the three types of fluorine species (A, B, C) encountered in the P_{-3cl} space group structure.[58] Type A fluorine, corresponding to the most intense signal at 25 ppm, is located in the 12g site and is surrounded by four lanthanums ($d_{\mathrm{La-F_A}}$ = 2.42 Å). The coordination polyhedra of the other two fluorine atoms (B and C) are made of three La's with $d_{\mathrm{LaF_B}}$ = 2.46 Å and $d_{\mathrm{LaF_C}}$ = 2.44 Å. The spectrum of LaOF characterizes a single isotropic signal whose chemical shift is identical to the most intense one of LaF_3. Indeed, in the structure of LaOF (space group R_{-3mR}), the coordination polyhedron of fluorine is made of four lanthanum atoms (d_{LaF} = 2.42 Å), as in LaF_3. The ^{19}F MAS NMR spectrum of the sample (Figure 6) shows a small quantity of fluorine in the sample, together with a parasitic signal from the polytetrafluoroethylene surrounding of the probe. Besides this parasitic probe signal, two other signals are indeed detected. The first is a very broad one close to 0 ppm, not separated into spinning side bands spreading over nearly 400 ppm. The width of this signal despite magic angle spinning suggests that fluorine is incorporated in the host lattice. Indeed, it implies strong hyperfine interaction, namely, dipolar interaction with electron spins resulting from the conducting electrons at the Fermi level (Pauli paramagnetism). This dipolar interaction shows the proximity of F with the electron spin, that is, the presence of F in the bulk of the material.

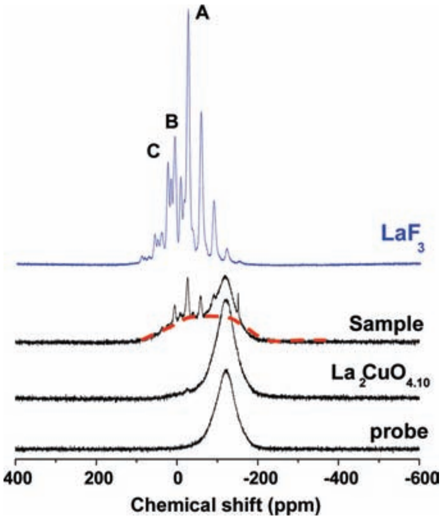

Figure 6. ^{19}F MAS NMR spectra of LaF_3, $La_2CuO_{4.10}$, the fluorinated sample, and the probe (T = 300 K).

However, there is no shift of the NMR line as compared to the references, showing that there is no transfer of electron spin or of delocalized electrons from Cu to F, which is in very good agreement with an insertion of F in the La_2O_2 blocks.[59] Such a low fluorination level and low temperature synthesis is known to prevent any ordering of the interstitial anions.[60]

In addition to the broad signal, there are also traces of narrow signals similar to those of LaF_3, suggesting a small amount of such an impurity in the samples, in agreement with XPS results. These signals are slightly broader than those of the model compounds: this is due to a weak dipolar interaction with electron spins on Cu. Indeed, this F species is in a diamagnetic impurity phase outside the material, but in very close contact with it; therefore, the distance with the electron spins present in the material is sufficiently short to lead to weak dipolar interactions. In comparison, the dipolar interactions with electron spins that cause the considerable width of the main signal are obviously much larger, which further confirms that the latter signal originates from F much closer to the electron spins (or conducting electrons), in other words, within the material itself.

Finally, no ^{19}F NMR signals (except the parasitic probe signal) were observed for the sample $La_2CuO_{4.10}$ prepared electrochemically in DMSO/$n$$Bu_4NBF_4$, which is indeed not expected to be fluorinated.[38]

Conclusion

The studies performed in this work have shown that, depending on the chemical nature of the electrolytic solution, it is possible to carry out an electrochemical fluorination of La_2CuO_4, leading to lanthanum oxyfluorides of the general formula $La_2CuO_4F_x$ with low corrosion processes. The various analyses showed that, underneath a LaF_3 layer thinner than 20 nm (<0.1% of the total volume of the ceramics), fluorine is inserted in the structure of the material.

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Table 3. Synthesis Conditions, Lattice Parameters, and Superconductivity for La_2CuO_4 before and after Fluorination

sample processed temperature and conditions	lattice parameters (Å)			T_C (K)	ref
La_2CuO_4	5.359	5.410	13.141		46
flowing O_2, NH_4F, 240 °C	5.319	5.442	13.20	42	28
1.3 bar, F_2, 200 °C, 20 h	5.342	5.436	13.192	40	9b
flowing 5 % F_2, 250 °C, 8−24 h	5.329	5.420	13.170	39	9f
1.3 bar N_2/F_2, 200 °C, 20 h	5.328	5.427	13.190	40	9d
1.3 bar N_2/F_2, 200 °C, 20 h	5.334	5.451	13.207	42	9e
F_2 gas on laser ablated La_2CuO_4			13.256, 13.196	36	19a
flowing 10% F_2/N_2 160 °C, 10 min			13.206, 13.260	38	19b
electrochemical insertion, Ar atmos., DMF/*n*Bu_4NBF_4, 25 °C 130 h	5.348(1)	5.402 (1)	13.205(1)	40	this work

Both XPS and MAS NMR confirmed this fluorine insertion in La_2CuO_4 and suggest its localization in the "LaO" sheets. The fluorine insertion breaks the translation symmetry and introduces a long-distance disorder, as shown by ESR.

The amount of inserted fluorine (0.18) leading to a formulation of $La_2CuO_4F_{0.18}$ would mean a Cu^{3+} content slightly lower than in the over-oxygenated compound, which corroborates the lower observed T_C. The lanthanum ion is in a mixed environment, while that of copper is not modified.[60] The extent of LaF_3 decomposition under these conditions is very low. This means that, by a strict control of the electrochemical parameters, we are able to develop a new route toward cuprate oxyfluorides. The choice of BF_4^- as a fluorine source is more judicious than that of F^- since, even with high current densities, it is possible to avoid the starting material degradation.

These results highlight the *efficiency* of electrochemistry as a new low-cost and safe technique for fluorination of solid-state materials under normal conditions of temperature and pressure (see Table 3 for comparison). Performed at room temperature, it additionally does not require any specific experimental precautions. These preliminary results provide a basis for further syntheses from oxides other than La_2CuO_4.

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