Evidence of Oxygen Intercalation and Mobility at Room Temperature in Oxides: An Electrochemical Quartz Microbalance Study of Intercalation in La_2CuO_4

N. Casañ-Pastor,* C. Zinck, C. R. Michel, E. M. Tejada-Rosales, and G. Torres-Gómez

Institut de Ciencia de Materials de Barcelona, CSIC, Campus UAB, 08193 Bellaterra, Barcelona, Spain

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This paper offers direct evidence for the electrochemical intercalation of oxygen in an oxide with the K_2NiF_4 structure, namely, La_2CuO_4, at room temperature. Organic solvents, as well as water, allow that reaction to occur. The charge-to-mass ratio evaluated from a comparison with fluoride intercalation implies that either OH^- or $O^{\delta-}$ species are being intercalated. Comparison with previous work seems to favor the latter. If an oxygen with lower charge is moving, that could indeed explain why oxygen conductivity can be observed at such low temperatures.

Introduction

The control of oxygen stoichiometry in oxides, in particular superconducting cuprates, has been achieved traditionally by thermal methods under oxygen flow, as in the case of $YBa_2Cu_3O_7$, or by methods that involve high pressure of oxygen, as in the case of La_2CuO_4.[1,2] In both cases, the oxygenation process can be considered an intercalation process in which oxygen anions diffuse through the structure while a redox change is occurring in the material. Electrochemical control of the oxygen content in these oxides has also been achieved at high temperatures using solid-state cells with yttrium-stabilized zircone (YSZ) as the electrolyte and oxide ion conductor and with the oxide to be doped as the electrode.[3] The possibility of electrochemical control was established by showing that the oxide was behaving as a mixed electronic−ionic conductor under those conditions. In 1990 and the following years,[4−8] the first evidence appeared that an oxide such as La_2CuO_4 could also be oxidized, with simultaneous intercalation of oxygen, at room temperature. With this finding, a new possibility arose. Not only was it the case that the superconducting phase, $La_2CuO_{4+\delta}$, had been prepared at room temperature from its precursor La_2CuO_4. There was another equally important feature. Oxygen ion mobility had been always assumed to require high temperatures, as most oxygen ion conductors show.[9] Until these low-temperature experiments were reported, the general field of intercalation chemistry at low temperature was overwhelmingly configured by cation intercalation studies, with the atypical exception of graphite intercalates.

Many other oxides have been oxidized at room temperature and up to 200 °C in fused nitrates by this low-temperature electrochemical method. Some examples are $SrFeO_{2.5}$, $Ca_{2-x}Ln_xMnO_4$, and $Ln_2Ba_2Cu_2Ti_2O_{11}$, all with perovskite-related structures.[10−12] However, La_2CuO_4 remains the most studied phase because of one physical property of the doped materials, superconductivity, that can be used as a probe of the extent of oxidation. Among the many features of the superconducting material, $La_2CuO_{4+\delta}$, prepared at low temperature by electrochemical methods, many groups, including our own, reported that the values of T_c achieved by this method were significantly higher than those obtained by alternative high oxygen pressures at high temperature. We reported, soon after, the existence

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of an inconsistency between the two methods of chemical analysis that were used to evaluate the amount of oxygen inserted, namely, TGA analysis in Ar/H_2 (a thermal method) and iodometry, and proposed an explanation for that discrepancy based on the nature of the oxygen anion intercalated in the oxide at room temperature.[6] Our reasoning involved the fact that peroxide-type oxygen reacts very slowly with iodide and that heating will tend to decompose this type of oxygen. Therefore, an internal equilibrium of charge between copper and oxygen could explain the observed data, if the peroxide-type oxygens were stable at room temperature but oxidized the copper when heated to 100 °C and above. Other groups also reported the analytical inconsistency.[5] Neither of these observations can be made for high-temperature–high-pressure doped samples. It is therefore quite possible that we are dealing with different phases in the low-temperature and high-temperature regimes. Neutron diffraction refinements indicate, however, that extra oxygen is intercalated within the Cu–O layers in both cases.[5b]

The apparent possibility of oxygen intercalation at such low temperatures presented, from our point of view, a new question. La_2CuO_4 behaves as a mixed electronic–oxygen ion conductor when acting as the electrode in an electrochemical cell, and the fact that oxidation is achieved in the bulk implies that oxygen diffusion is taking place (even with low diffusion rates). Therefore, the chemical nature of this oxygen could be the underlying reason that the oxygen anions were moving in a solid at room temperature, when all previously reported oxygen conductors had shown conductivity at much higher temperatures (500 °C for bismuth oxides and 800–1000 °C for cobaltates or stabilized ZrO_2).[9] Since then, we have attempted to study the characteristics of this type of oxygen and that of the charge carriers, not forgetting the important implications that oxygen mobility at low temperatures could have in sensors, separators, fuel cells, etc.

Thus, we have studied oxygen intercalation in solvents in which no free oxygen species are available. In this paper, we report that oxidation also occurs in organic solvents such as methanol and propylene carbonate. Fused nitrates (known to stabilize peroxides and superoxides) at 150 °C, using electrolytes with no free OH^- or O^{2-}, have also been shown to support the same oxidation.[10,12] Therefore, we are observing a phenomenon with a widespread range of occurrence that is not restricted to very specific conditions.

When the oxidation is carried out at room temperature, the number of actual charge carriers (type p) in the oxide remains constant, according to Seebeck measurements, up to 200 °C, at which point it begins to decrease.[7] At such temperatures, mass losses related to the loss of intercalated oxygen are detected by TGA. However, even at 235 °C, it is possible to induce oxygen intercalation in La_2CuO_4 using fused nitrates to yield superconducting properties, although a simultaneous partial oxide decomposition to paramagnetic CuO takes place.[10] Such decomposition can be prevented by oxidation in fused nitrates at 150 °C. Finally, for oxides electrochemically doped at room temperature, critical temperatures are dependent on measuring electrical current values, implying that there is a change in physical properties during the measurements, as if the measuring device were inducing an electrochemical cell in a mixed conductor. That would only be possible if the oxide showed ionic mobility.[7]

In this paper, we have investigated the intercalation process using a technique that allows for the evaluation of mass changes simultaneously with changes in electrochemical reaction parameters (e.g., charge, current, etc.). The electrochemical quartz microbalance bases its response in the frequency changes suffered by the gold-plated quartz electrode as the mass (actually pressure) on it changes during the electrochemical reaction. This technique should be able to determine whether there is an actual mass increase during the electrochemical doping of oxides and whether it is possible to observe the inverse mass loss by reduction, and it could even allow for a quantitative determination of the mass change. If such a mass change value is compared with the charge used electrochemically to induce the oxidation, the charge/mass ratio for the intercalated species could be determined. Of course, that would only be possible if a single reaction, with no interference, were being studied. The first studies performed in water showed[6,7] that either water or OH^- was being oxidized simultaneously with the oxidation of the material, and therefore, alternative solvents that do not interfere with the study at room temperature were investigated. Quartz crystals and the required Teflon holders cannot withstand the temperatures needed for the investigation of the same reaction in fused nitrates.

The vibration of quartz crystals in such an electrochemical environment is known to follow the Sauerbrey equation as the mass load on them changes (eq 1) when a series of conditions are fulfilled.[13–17] The actual changes in frequency must be small compared to the fundamental frequency. The mass load cannot surpass a certain value, and the ratio of the thickness to the surface of the quartz crystal must be minimal. Once those conditions have been met, according to the Sauerbrey equation, there is a direct relationship between the frequency changes and the mass change per unit area in the electrode. From the change of mass in the electrode, Δm, and the total charge passed during the reaction, Q, we can evaluate the number of electrons per anion (eq 2) in molar or atomic units, which will be dependent on the actual molar mass of the intercalated species.

$$\Delta m = -(\Delta f N r_q S)/f_o^{\,2} \tag{1}$$

$$\#\ e^-/\text{anion} = \frac{Q/96\,487}{\Delta m/M_{\text{anion}}} \tag{2}$$

where f_o is the resonance frequency of the fundamental mode of the quartz crystal in that medium, Δf is the change in frequency upon mass change over the quartz crystal, Δm is the mass change on the quartz, N is the shear modulus of quartz (1.67 MHz cm), r_q is the density of quartz (2.649 g/cm^3), and S is the exposed surface

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area of the electrode on which the electrochemical reaction occurs.

A crucial problem in using eq 1 is posed when the actual active area, *S*, is not known. This is a real problem when dealing with sintered pellets or porous or nonuniform surfaces. We have tried two approaches to solve this problem. On one hand, we determined the exposed area by the BET method[18] using nitrogen adsorption, and on the other, we tried to use an alternative anion as a reference point for the experiments in such a way that a relationship between the numbers of electrons per mole of each type anion can be obtained. The second approach should correct differences between the BET area, which implies gas absorption, and the actual area exposed during electrochemical experiments in solution, which could be different. Given the large electronegativity and small size of fluorine, fluoride seemed to be an appropriate anion for use as a reference. Thus, if the mass calculations were made relative to fluoride, we could eliminate the area of the electrode from the final calculation, according to eqs 3 and 4

$$\frac{\#\ e^-/O}{\#\ e^-/F} = \frac{Q_O \Delta m_F/19}{Q_F \Delta m_O/16} \qquad (3)$$

and

$$\frac{\#\ e^-/O}{\#\ e^-/F} = \frac{(Q_O/19)(-\Delta f_O N r_q S/f_{oO}^{\ 2})}{(Q_F/16)(-\Delta f_F N r_q S/f_{oF}^{\ 2})} = Q_O \Delta f_O 16 f_{oF}^{\ 2}/Q_F \Delta f_F 19 f_{oO}^{\ 2} \qquad (4)$$

To compare oxygen and fluoride intercalation, fluoride intercalation must be demonstrated and must be carried out in a medium in which competition from oxygen intercalation is eliminated. Thus, fluoride intercalation is performed in organic solvents with no oxygen available and with dissolved electrolytes that do not contain oxygen. Its intercalation is demonstrated by the appearance of superconductivity.

As will be shown below, the charge-to-mass ratio obtained from these calculations during oxygen intercalation (that is, the number of electrons removed to intercalate 16 atomic units) is very low. That could result from a very low charge on the oxygen atom, from protonation, or from the same solvation in terms of mass in all solvents investigated, and all these aspects will be discussed below.

Experimental Section

La_2CuO_4 was prepared as described previously by solid-state reaction of the precursor oxides, La_2O_3 (Aldrich, 99.9%, dried at 900 °C to remove humidity and absorbed CO_2) and CuO (Aldrich, 99.9%), in stoichiometric proportions and by heating in air to 1050 °C in the form of a pellet. The pellet was reground and treated again in air at the same temperature until no residual oxides were observed by X-ray powder diffraction. The final product was not superconducting. For use in the quartz electrochemical microbalance, pellets of 7-mm diameter were prepared with masses between 20 and 100 mg and were sintered at 1050 °C. The density of such pellets was 80% of the theoretical density for a single crystal, and their superficial area was calculated by BET methods (using nitrogen) in a Micrometritics ASAP 2000 system to be on the order of 15.3 m^2/g. Quartz microbalance studies were performed with a QCA-917 instrument from Seiko-EG&G coupled to a potentiostat (273A, EG&G) and controlled with software 270. Quartz AT-cut crystals that were 7 mm in diameter and plated with gold on both sides were used as the substrate for the oxide pellets. The pellets were held physically by a Teflon holder on top of the gold-plated quartz crystal. Electrical contact was optimum in this setup. The use of conducting binders has always resulted in spurious noise and capacitance factors derived from elastic vibrations. Usually, a 5.3-Hz low-pass filter was used in the experiments, but the results were checked with different filters. Ag/AgCl electrodes were used as the reference and were set up within a saline bridge (3 M KCl) to protect them from the basic and organic solutions. The counter electrodes used were platinum wires with approximately 1 cm^2 areas. The three-electrode electrochemical cell and the electrometer were protected inside a Faraday cage from external noise. The entire setup (cell and Faraday cage) was set up inside a fume hood to avoid possible danger from fluoride oxidation or solvent vapors. The potentiostat and balance were connected to a SAI system (AC−DC−AC converter based on batteries) to stabilize the input current to the potentiostat and the resonator. No magnetic stirring was used.

Electrolysis solutions were prepared in deionized−distilled water (1 M KOH), methanol (0.1 M $TMAOH{\cdot}3H_2O$, 97%, or TMAF, 99%, where TMA means tetramethylammonium), and propylene carbonate (0.1 M $TMAOH{\cdot}3H_2O$) and were deoxygenated by bubbling with argon prior to use in the experiments. TMAF reacted with propylene carbonate, which made the intercalation of fluoride impossible in this solvent. Magnetic measurements were performed on a Quantum Design SQUID magnetometer, using a 10-G magnetic field under zero field cooling.

Large extent (bulk) electrolyses were carried out prior to the microbalance experiments in the same range of conditions and using the same precursor oxide. In all cases, we observed superconductivity for the doped samples, regardless of the solvent and intercalated anion. Some examples of those results are shown in Figure 1.

The signal from the quartz microbalance system was tested by electrodepositing copper from a 0.01 M $CuSO_4$ aqueous solution onto a gold-plated AT-cut quartz crystal of the same dimensions. The results were in good agreement with the theoretical constant from the Sauerbrey equation. The signal was found to be more stable when the experiment was performed in the Faraday cage and when no hydrogen coming from water reduction was involved.

The electrochemical experiments performed were cyclic voltammetries and constant-potential electrolyses, under conditions previously studied in standard cells where oxidation was shown to occur using chemical analyses and physical measurements.[6,7]

The electrochemical current (*I*) and microbalance frequency were corrected prior to calculations in order to subtract capacitive currents and to adjust real frequency origins. (Immersion induces a shift in frequency as do initial capacitive currents.) Charge-to-mass ratios were calculated in the form of number of moles of electrons per mole of intercalated anion assuming atomic weights of 16 for oxygen and 19 for fluorine. Such calculations should show deviations from the charge used for intercalation if a secondary reaction exists, as well as possible variations in the molecular weight of the intercalated species. The ratio between fluoride and oxygen ratios is also calculated in the same solvent to evaluate the influence of any error present in the mass coming from the BET surface determination. Fluoride experiments were performed only in methanol because of the large reactivity of this anion versus propylene carbonate and the competition with oxygen that could exist in water. Electrolyte salts for the organic media

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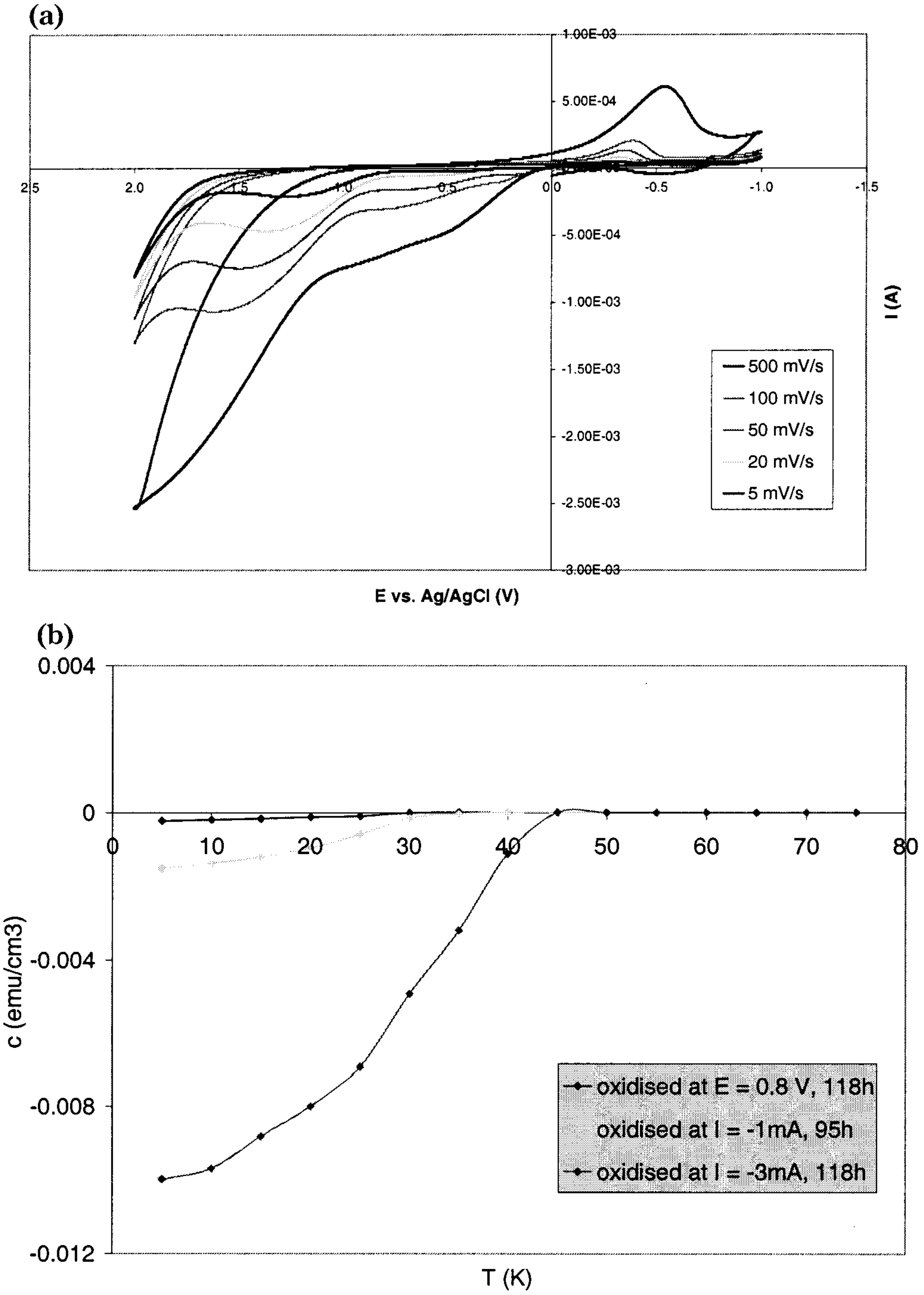

Figure 1. (a) Cyclic voltammetry (CV) of La_2CuO_4 in 1 M TMAOH propylene carbonate at different scan rates. More intense CV corresponds to faster scan rates. (b) Magnetic susceptibility of different pellets oxidized at constant potential or current. (A larger superconducting fraction is observed for constant-current electrolyses.) The total charge used on oxidation of material cannot be known in this case.

were chosen to contain a common cation for oxygen and fluoride intercalations, as well as the minimum hydration water and adequate solubility.

Results and Discussion

All electrochemical experiments, cyclic voltammetries (henceforth CVs), and electrolyses at constant potential or current have shown the possible presence of secondary or parallel reactions in all of the solvents tested. This reaction is particularly stronger in water, and it develops with the production of gas, implying that water oxidation to O_2(g) always occurs to some degree, along with the oxidation of the cuprate. The best way to evaluate the presence of additional reactions is to examine the calculated ratio between the charge used in the reaction and the mass change observed during the process. Thus, we observed that, at certain overpotentials or after certain electrolysis times, there is a large increment in charge without the corresponding mass increase that one would expect for an intercalation reaction. This is seen in the form of a sharp divergence in the charge-to-mass ratio and seems to indicate that a secondary reaction exists, sometimes with a long induction period.

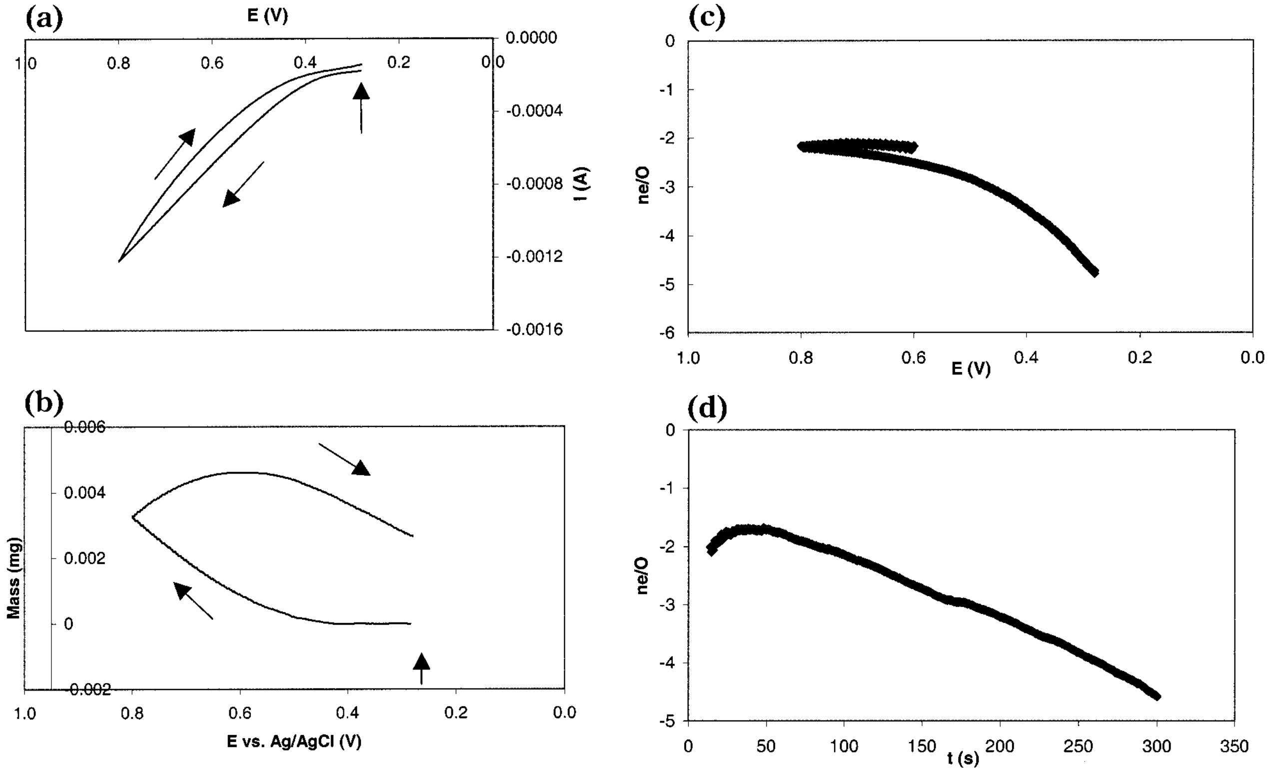

Figure 2. (a) CV of La_2CuO_4 in 7-mm setup for quartz microbalance, 1 M KOH (H_2O). Arrows indicate the direction of the potential sweep; vertical arrows indicate rest or open circuit potentials. (b) Mass change derived from frequency changes. (c) Number of electrons per oxygen for the CV process. (d) Number of electrons per oxygen for chronoamperometry at 0.6 V vs Ag/AgCl.

Initial cyclic voltammetry experiments also showed that there was a threshold negative potential below which the intercalation behavior of the solid changed sign when reoxidized, and therefore it was concluded that an irreversible phenomenon, not studied here, was taking place at negative overpotentials. The CVs recorded for the calculations, shown in the figures, correspond to small potential ranges in order to avoid such secondary effects, and so, they do not show diffusion-limited maxima.

Figure 1 shows the cyclic voltammagrams observed for pellets of larger dimensions obtained prior to the quartz microbalance studies, as well as the superconducting signal observed by oxidation of bulk samples under various conditions. These results agree with previously reported data on La_2CuO_4 oxidation.[4-8] Figures 2a–5a show the cyclic voltammagrams (CVs) obtained on the 7-mm pellets attached to the quartz resonator, and the corresponding mass changes observed simultaneously (calculated from frequency changes using the BET area). The ratio of charge to mass calculated from both signals are shown in Figures 2c–5c for each solvent (water, methanol and propylene carbonate) and anion (oxygen and fluorine). Cyclic voltammetry and electrolysis experiments performed in aqueous solutions reproduce older results performed in the absence of a Faraday cage. However, the experiments carried out within the Faraday cage showed less noise. Fluoride intercalation perfomed in methanol, in the absence of oxygen anions, was shown to occur by the appearance of superconductivity in bulk oxidation samples. More studies corresponding to such intercalation are being performed.

Constant-potential electrolyses performed on the quartz crystal microbalance were carried out on the same pellets after the CV experiments. The corresponding charge-to-mass ratios, in the form of the number of electrons per unit of atomic mass of the anion, are shown in Figures 2c–5c for the CV experiments and 2d–5d and 5e for the constant-potential electrolyses (chronoamperometries, CA). The conclusions that can be derived from both types of experiments, CV and CA, are similar.

In water, there is a mass increase upon oxidation that is not reversible when the initial potential is restored in CV, or even when much more negative potentials are applied (Figure 2b). When the ratio of mass to charge (number of electrons per mole of oxygen) is obtained (Figure 2c) using the BET area of the pellet, the initial oxidation regime shows a great deal of noise that eventually stabilizes at 0.6 V vs Ag/AgCl near the value of 2 electrons per oxygen. However, such a value is greatly increased in an exponential way afterward, implying the existence of a charge that is not used in the intercalation process (Figure 2c). When a constant-potential electrolysis is carried out at a mild potential, 0.5 V vs Ag/AgCl, it can be observed that the charge-to-mass ratio, originally near 2, increases steadily. This confirms a time evolution that is related to the accumulation of charge used in another process, possibly catalized by the oxide. In the case of water, this process very well could be water oxidation to form $O_2(g)$.

The behavior of La_2CuO_4 pellets in methanol (0.1 M TMAOH) or propylene carbonate (1 M TMAOH) is quite different from that in water solutions, and it is reproducible. The mass increase observed upon oxidation is

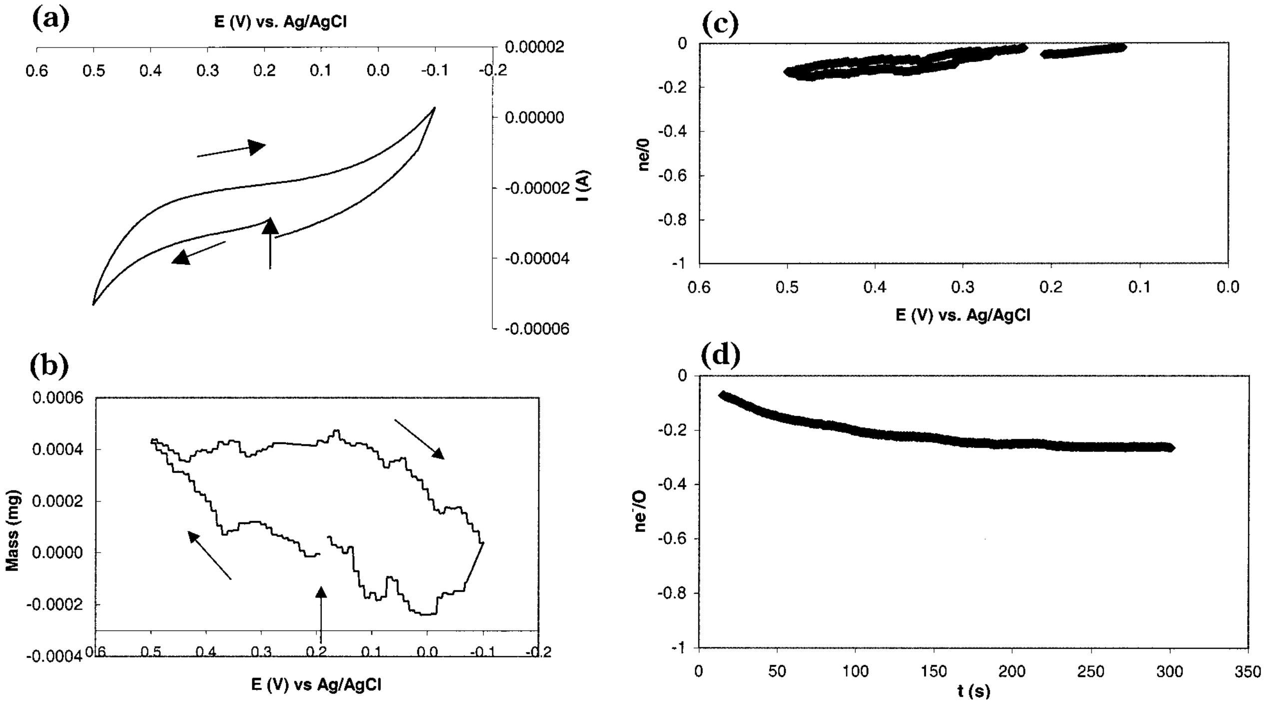

Figure 3. (a) CV of La_2CuO_4 in 7-mm setup for quartz microbalance, 0.1 M TMAOH in methanol. Arrows indicate the direction of the potential sweep. (b) Mass change derived from frequency changes. (c) Number of electrons per oxygen for the CV process. (d) Number of electrons per oxygen for chronoamperometry at 0.5 V vs Ag/AgCl.

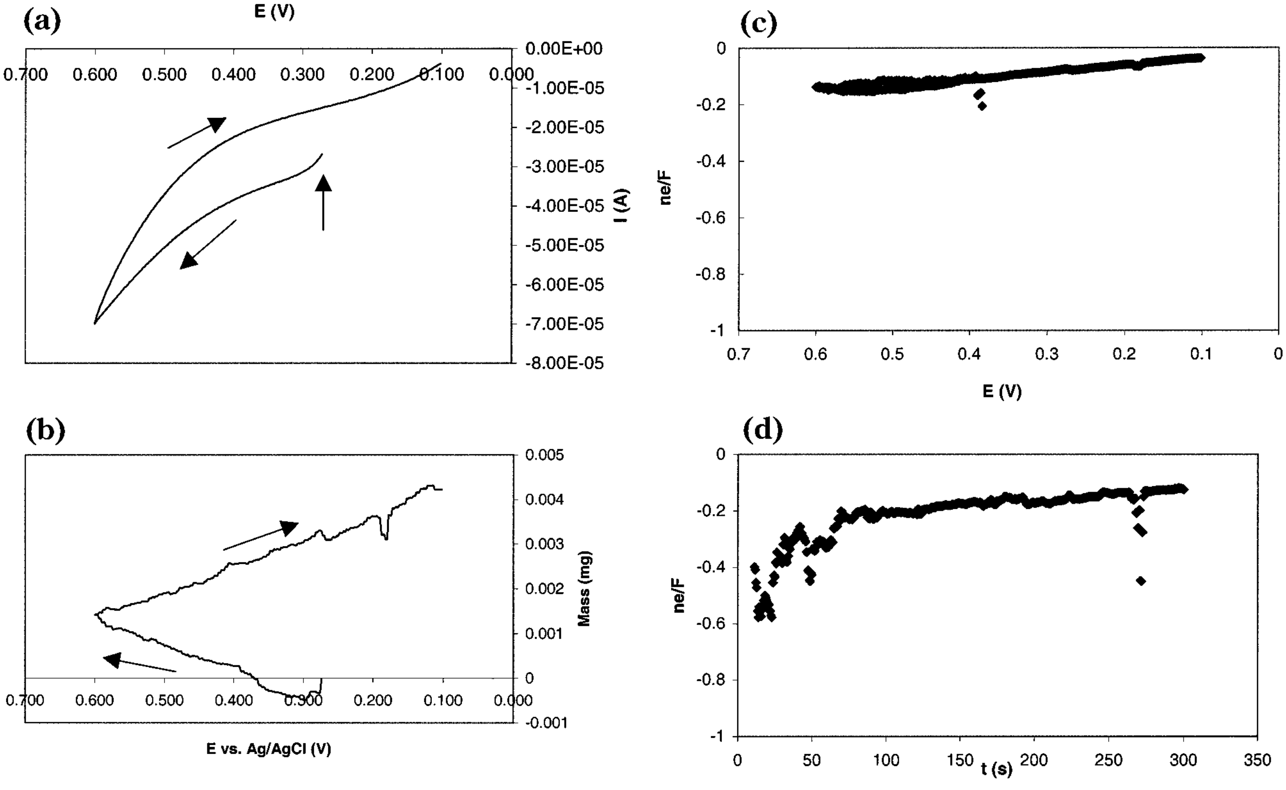

Figure 4. (a) CV of La_2CuO_4 in 7-mm setup for quartz microbalance, 0.1 M TMAF in methanol. Arrows indicate the direction of the potential sweep. (b) Mass change derived from frequency changes. (c) Number of electrons per oxygen for the CV process. (d) Number of electrons per oxygen for chronoamperometry at 0.5 V vs Ag/AgCl.

lost in a completely reversible form when the original applied potential is restored [Figures 3b (methanol) and 5b (propylene carbonate) for oxygen and 4b (methanol) for fluorine]. This reflects a reversible process within this potential scale, independently of the uncertainty affecting the calculation of mass changes from frequency changes due to the uncertainty in *S*. Figure 3c shows the charge-to-mass ratio for the CV performed in 0.1 M TMAOH in methanol when the maximum potential applied reached only 0.5 V. If the upper limit of the applied potential is increased in CV, as is shown, for example, in carbonate propylene up to 1.5 V, eventually

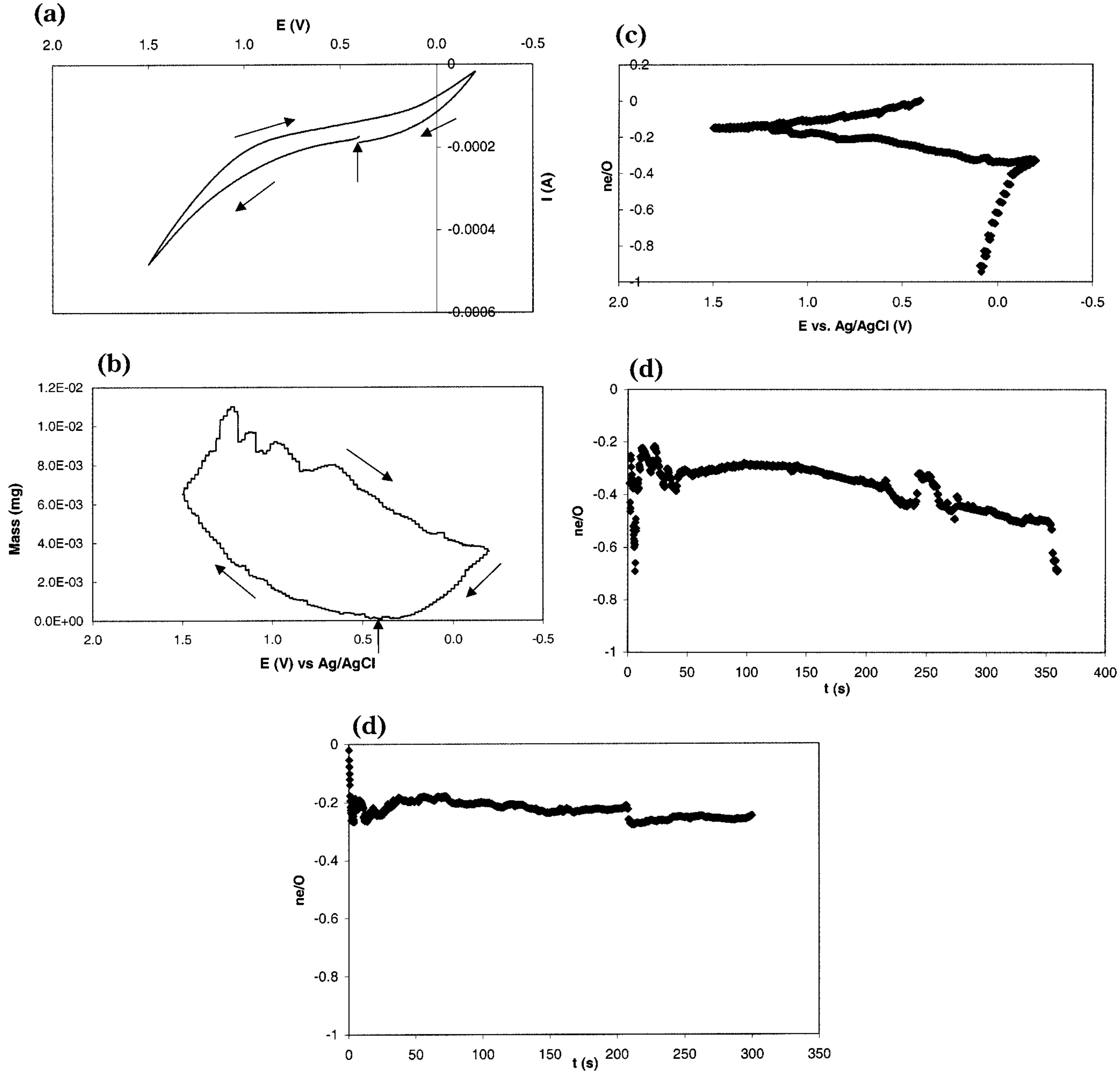

Figure 5. (a) CV of La_2CuO_4 in 7-mm setup for quartz microbalance, 1 M TMAOH in propylene carbonate. Arrows indicate the direction of the potential sweep. (b) Mass change derived from frequency changes. (c) Number of electrons per oxygen for the CV process. (d) Number of electrons per oxygen for chronoamperometry at 0.8 V vs Ag/AgCl. (e) Same as d but at 0.5 V vs Ag/AgCl.

the charge-to-mass ratio follows the same behavior as it does in water, possibly because solvent oxidation is involved. Also, in constant-potential electrolysis, a sharp increase in the charge-to-mass ratio is observed after a certain time in propylene carbonate if the applied potential is high, in a way that could resemble the effect seen in water at shorter times.

When the applied potentials are restricted to 0.5 V vs Ag/AgCl, a steady signal is observed in the electrolysis over time, indicating that a single process is taking place (Figure 3d and 5e). In such cases, in the absence of water, the charge-to-mass ratio is near 0.2 (±0.03) electrons per oxygen when the BET area is used. Fluoride intercalation, shows the same results, both qualitative and quantitatively (Figure 4d). This implies that oxygen intercalation consumes the same charge as fluoride intercalation per anion. If the charge on fluoride is taken to be −1, then the charge consumption for oxygen will also be approximately 1 electron per atom of oxygen intercalated.

Therefore, in the absence of secondary reactions coming from the solvent or the electrolyte, quartz microbalance experiments on oxygen intercalation imply a charge-to-mass ratio corresponding to 1 electron per anion, the anion weighing 16−17 atomic units. This mathematical result can derive from several possibilities. There are two possible routes to explain a charge of 1 electron per intercalated oxygen that the quartz microbalance studies cannot differentiate. First, a significant possibility, suggested by Schöllhorn in 1991,[19] is that the intercalated oxygen anions are really OH^-. This hypothesis can explain the quartz microbalance

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studies shown here but cannot explain the high mobility of oxygen at low temperatures or the analytical inconsistencies observed by various groups between iodometries and thermogravimetric analyses, which can be accounted for only if intermediate oxidation states are present for oxygen or if, formally assigning the oxidation to copper, Cu^{3+} transfers part of its positive charge to oxygen.

On the other hand, the second possibility is that intermediate oxidation states for oxygen are formed, which would explain other experimental data. Such oxygen ions must be formed during the oxidation process or immediately thereafter. If all intercalated oxygen in the partial oxidation state, $O^{-(2-\delta)}$, comes from the reaction of O^{2-} with the oxidized material, formally Cu^{3+}, the charge-to-mass ratio is expected to be 1 electron per oxygen, independently of the proportion of Cu^{3+} reacting. This can be schematically shown by the equations

$$La_2Cu^{2+}O_4 \rightarrow La_2Cu^{2+}{}_{1-x}Cu^{3+}{}_xO_4 + xe^-$$

electrochemical reaction at anode

$$La_2Cu^{2+}{}_{1-x}Cu^{3+}{}_xO_4 + \frac{x}{(2-\delta)}O^{2-} \rightarrow La_2Cu^{2+}O_4O^{-(2-\delta)}{}_{x/(2-\delta)}$$

reaction and intercalation

In this scheme, the number of electrons per oxygen is $x/[x/(2-\delta)] = (2-\delta)$

If only a fraction of Cu^{3+} were formed, both the charge and the mass would be affected, and the ratio would remain the same. (However, if only a fraction of Cu^{3+} reacted, the total charge consumption would be larger with respect to the mass change, and a larger number of electrons per oxygen would result. The same would happen if the oxygen in intermediate oxidation states were formed by a direct electrochemical reaction at the electrode, without chemical reaction with Cu^{3+}: a total final charge greater than that used in the intercalation process would be observed.)

Therefore, the electrochemical quartz microbalance experiments show that oxygen is not being intercalated as O^{2-}. Oxygen intercalation, as compared with fluoride intercalation is explained if the intercalated species is OH^- or $O^{\delta-}$ with $|\delta| < 2$, possibilities that cannot be distinguished by this technique given the small difference in molecular weight between the two species. To differentiate the two cases, we need to take into account the inconsistencies observed by several research groups between two types of analytical techniques that evaluate the oxidation state, namely, iodometry and TGA in hydrogen,[6,7] and the interpretations given for them.[6] It is the whole set of experiments, and the fact that oxygen species are moving at such low temperatures in the solid state, that can elucidate and clearly suggest the existence of oxygen in intermediate oxidation states.

If this is so, then a phenomenon is being observed in which the material being oxidized is, itself, the catalyst of the reaction that will produce the anions being intercalated and that will occupy interstitial sites of its structure, drastically modifying the electronic structure and the physical properties of the material.

As the applied potential is increased, in all of the solvents studied, additional electrochemical reactions occur in larger yield that contribute with charge but without a corresponding mass change and that need to be related to solvent or electrolyte oxidation. Thus, through the simultaneous measurement of charge and mass on the electrode, we are able to observe the different stages of the oxidation process that are not visible by other techniques such as cyclic voltammetry and to verify that there is high-yield anion intercalation at low overpotentials and pure electrochemical reaction without mass change at larger overpotentials.

A point that needs consideration is the possible solvation of the intercalated anion. The structural changes observed are very small,[4−8] and because no vacancies exist in the structure and interstitial sites need to be occupied, this possibility is not really plausible from a chemical point of view. In addition, the parallel results obtained in methanol and propylene carbonate require the same mass contribution from the solvent, which does not seem realistic as the two solvents have quite different molecular weights.

Another point is the absolute value of the charge for the intercalated anion. Severely restricted by the accurate measurement of the surface area, the relationship between frequency changes and actual mass changes in pellets is not easy, unless a reference experiment can be found. On the other hand, using fluoride as a comparison experiment, the values obtained using BET areas obtained in nitrogen show that the mass might have been overestimated (and the charge-to-mass ratio underestimated) because of an overestimated surface area. Both calculations would coincide if the real surface in contact with the electrolyte solution were 5 times smaller than the value obtained by nitrogen absorption (BET method) under vacuum and heating experiments. That conclusion agrees with the expected behavior of a sintered pellet in the presence of a gas or a liquid with much more viscous properties and reinforces any conclusion derived from the comparison of oxygen with fluoride.

Conclusions

Electrochemical intercalation of oxygen at room temperature, monitored by an electrochemical quartz microbalance, occurs with a mass increase. Such a mass increase is not reversible in the case of water, where the mass decreases upon reduction but never returns to its original value. A secondary reaction, presumably water oxidation to O_2, is occurring. Thus, the charge measured during the oxidation of La_2CuO_4 is larger than expected if only the material were being oxidized. This prevents a true evaluation of charge-to-mass ratios in water. On the other hand, if the process is carried out in methanol or propylene carbonate, it is possible to find a potential window in which the mass increase due to the electrochemical intercalation of oxygen is reversibly lost upon reduction. The charge-to-mass ratio for this process is calculated to be the same as that for fluoride intercalation. This similitude suggests that oxygen is being intercalated as a −1 anion, e.g., OH^- or O^-. Previous experiments based on chemical analysis of iodometry−TGA comparisons, as well as transport measurements, support the last possibility. Fluoride intercalation also occurs in those conditions. The range of conditions in which oxidation, followed by oxygen or fluoride intercalation, occurs has also been shown to include other solvents.

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