

Electrochemical Oxygen Intercalation into Oxide Networks

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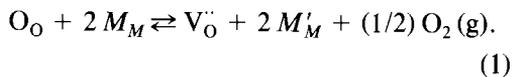
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DEDICATED TO P. HAGENMULLER ON THE OCCASION OF HIS 70th BIRTHDAY

The electrochemical oxidation of $Sr_2Fe_2O_5$ brownmillerite-type ferrite and La_2MO_4 ($M = Ni, Cu$) oxides is reviewed. The oxidation process appears as a very powerful method for preparing high oxidation states of transition-metal oxides. The characterization of the reaction products shows that they are well described as intercalation compounds of oxygenated anions. The fact that the intercalated species are the same as the host anions distinguishes these materials from most other intercalated compounds, in which guest species usually are chemically different from the host ions. The question of the nature and site of the intercalated species as well as that of their diffusion into the sample bulk is discussed on the basis of various characterizations and physical measurements, as well as within the scope of recent considerations of the electronic distribution in oxides of transition elements in a high oxidation state. © 1992 Academic Press, Inc.

Introduction

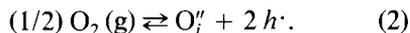
The interaction of oxygen with an oxide, such as the insertion of O^{2-} species into the network of non-stoichiometric oxides, is usually described in terms of heterogeneous equilibrium. For instance, for binary oxides such as MO_{2-x} ($M = Pr, Ce$) (1) with available oxygen vacancies, the following equilibrium may be written in the Kröger-Vink notation (2):



The formation of line phases as for PrO_y ($y = 1.714, 1.778, 1.800, 1.818, 1.833$) (1) shows that oxygen vacancies are generally ordered.

The occupancy of interstitial sites in overstoichiometric oxides, as for instance

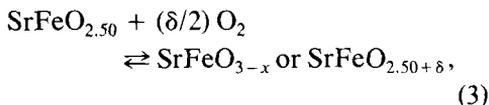
UO_{2+x} , may be expressed in the following way:



In the latter system, interstitial oxygen atoms are not randomly distributed, but form various types of complexes depending on the x value, as reported for example by Willis (3, 4).

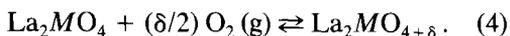
Recently some of us, using an electrochemical process in aqueous solution, succeeded in oxidizing ternary oxides of transition elements such as $Sr_2Fe_2O_5$ and La_2MO_4 ($M = Ni, Cu$). We showed that the oxidation leads to mixed-valence oxides containing (at least formally) high oxidation states such as Fe(IV), Ni(III), and Cu(III) (5-8). From the point of view of thermodynamics, the reaction can be formally described as a heterogeneous equilibrium as

previously mentioned. Referring to equilibrium (1) or (2), we may write for the oxidation of the brownmillerite $\text{Sr}_2\text{Fe}_2\text{O}_5$



where $\delta = 0.50 - x$.

For the La_2MO_4 -type oxides whose structures are related to that of K_2NiF_4 , equilibrium (2) is more relevant to the electrochemical oxidation.



However, an electrochemical reaction carried out at room temperature is supposed to belong to the "chimie douce" processes; therefore, it is not expected to lead systematically to the thermodynamically most stable phase as assumed for heterogeneous equilibria, which are generally investigated at high temperature. In other words, as clearly stated for instance in the case of room temperature lithium insertion into V_2O_5 (9), kinetics plays a very important role in the formation of metastable phases provided that their free energy is lower than that of the starting materials. Consequently, for the interpretation and rationalization of the experimental results, it seems much more appropriate to use the concepts and models worked out in the field of *intercalation*.

During the last ten years many works have been devoted to chemical or electrochemical intercalation (10-14). We will adopt here the definition of the term "intercalation" proposed by Wittingham (10): ". . . it describes the reversible insertion of guest species into a lamellar host structure with maintenance of the structural features of the host. The term can equally be applied to one- and three-dimensional solids. . . ."

Intercalation compounds may be classified according to the nature of the intercalated species or to that of the host material.

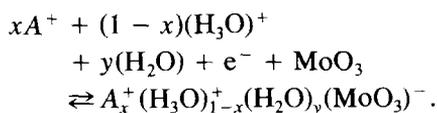
Intercalated species can be cations,

anions, or neutral species. The latter are generally polar molecules of the solvent, amines, or transition-metal halides. Intercalation of charged species usually involves a redox process between guest species and the host network: the insertion of an A^+ cation, for example, results from the ionization of the electropositive guest element A , which reduces the host matrix Z into Z^- . Well-known examples are those of alkali metals and hydrogen. An electronegative atom B or molecule B_2 may be ionized into B^- anions, leading to oxidation of the matrix to Z^+ .

Several kinds of intercalation compounds can be distinguished according to the host composition: those related to graphite, dichalcogenides of transition metals such as TiS_2 and TaS_2 , layered oxides such as MoO_3 , V_2O_5 , β -alumina and clays, layered oxychlorides such as FeOCl and FeMoO_4Cl , halogenides such as ZrCl and ZrCl_2 , and some metallic alloys such as LaNi_5 , which can intercalate hydrogen (10).

Whereas cationic and molecular intercalations are known and have been investigated for a long time, *anionic intercalation* implying the oxidation of the host matrix has been thoroughly studied only in the case of graphite salts containing anions such as HSO_4^- , NO_3^- , and MF_6^- ($M = \text{As, W, Re, Os, Ir, Pt, . . .}$) (11). Anionic intercalation involving an exchange reaction has also been mentioned for oxyhydroxide of transition elements such as NiOOH (15). However, to our knowledge, no example of room temperature intercalation of oxygen species—atomic, molecular, or anionic—has been reported before now.

Regarding electrochemical intercalation in aqueous solutions, cathodic reduction in acidic media of V_2O_5 and MoO_3 , for instance, have been extensively studied (12, 14). The reaction may be written as follows:



As mentioned above, the reaction product depends not only on the energetic, but also the kinetic balance as is usual in electrochemical reactions performed at room temperature.

Diffusion in the solid phase is the limiting step for kinetics. It depends on various parameters, but most authors consider the size effects as predominant: the smaller the inserted species and the larger the channels, the easier the diffusion. On this basis, one can readily predict that cationic intercalation must be easier than anionic intercalation, since removing electrons from an atom decreases its ionic radius whereas adding electrons makes it bigger. This assertion explains why in oxide-ion conductors, the mobility of the O^{2-} anions is noticeable only at high temperatures as in stabilized ZrO_2 (above $600^\circ C$) and in Bi-containing Aurivillius-type ($n = 1$) phases such as $Bi_4V_2O_{11}$ ($\sigma_{400^\circ C} \approx 10^{-3} \Omega^{-1} cm^{-1}$) (16). The values of the O^{2-} diffusion coefficient, \bar{D} , determined at $700^\circ C$ for nonstoichiometric perovskites, are close to 10^{-7} – $10^{-8} cm^2 s^{-1}$, but extrapolation to room temperature gives values as low as 10^{-14} or $10^{-15} cm^2 s^{-1}$ (17). However, some of us have clearly shown that electrochemical oxidation of dense ceramics having densities higher than 90% and containing

crystallites of about 1 – $100 \mu m^3$ leads to homogeneously oxidized materials; i.e., that the oxidation, and therefore oxygen insertion, indeed reaches the bulk.

The aim of the present paper is to show that electrochemical oxidation can be a powerful room temperature preparative method and to give evidence of oxygen intercalation into the bulk material on the basis of results obtained from various techniques such as X-ray diffraction (XRD), neutron diffraction, electron diffraction and microscopy (TEM), and Mössbauer spectroscopy. For this purpose, we have chosen two types of ternary oxides.

The first one is $Sr_2Fe_2O_5$; it has the brownmillerite structure and can be considered, as shown by Grenier and co-workers (18, 19), as the end member of a line-phase series of formula $A_nFe_nO_{3n-1}$ ($A = Ca, La$), where ($n - 1$) is the number of octahedral layers that are separated by one layer of FeO_4 tetrahedra; the oxygen vacancies are ordered along $[101]_c$ rows within the tetrahedral layers (Fig. 1). These authors have also experimentally shown that the reversible reaction of these compounds with oxygen, at high temperature, involves the formation of $(O_i)''$ species (20).

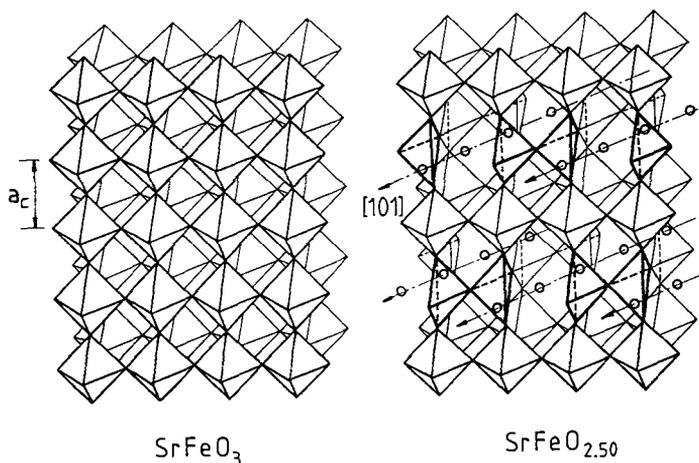


FIG. 1. Idealized structures of the perovskite $SrFeO_3$ and of the brownmillerite $SrFeO_{2.50}$.

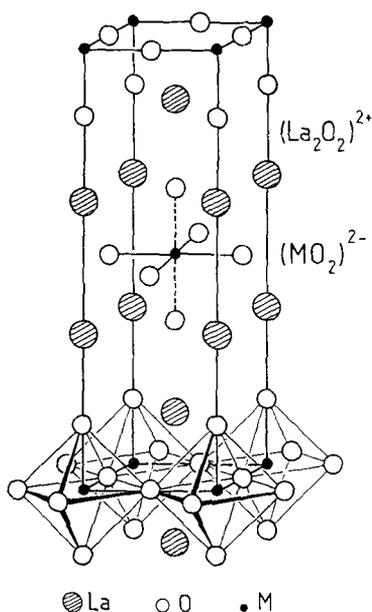


FIG. 2. Idealized structure of La_2MO_4 compounds (K_2NiF_4 -type).

The second family of compounds has the general formula La_2MO_4 ($M = \text{Ni}^{2+}, \text{Cu}^{2+}$); they exhibit a structure related to that of K_2NiF_4 (I_4/mmm), which can be described as a succession of $(\text{La}_2\text{O}_2)^{2+}$ rock-salt layers alternating with $(\text{MO}_2)^{2-}$ layers of MO_4 squares sharing corners with nearly 180° $M\text{-O-M}$ bonds (Fig. 2).

Electrochemical Experiments

Experimental

The procedure for the electrochemical measurement has been described elsewhere in detail (21). Experiments were performed at 25°C in air in a two-compartment cell filled with a 1N KOH solution with a three-electrode device.

—the reference electrode was HgO/Hg filled with 1N KOH ($E_{\text{th}} = +0.098 \text{ V}/\text{SHE}$). All potentials quoted in this work are referred to this electrode.

—the counter electrode was a gold foil of large area.

—a rotating disk electrode was used as the working electrode; the disk was a polished ceramic (ϕ 8–32 mm; ≈ 2 mm thick; 0.4–10 g). Reliable measurements required control of the textural characteristics of the electrodes, i.e., the roughness factor, the microstructure, and especially the density of the ceramics, which should be higher than 90% (21).

The cyclic voltammograms (I, E) were obtained by a potentiodynamical device. A typical voltammogram is given in Fig. 3. One can observe:

—an oxidation plateau (designated O_1) arising between 350 and 700 mV (depending on the nature of the 3d metal M); it corresponds to the following overall reaction:

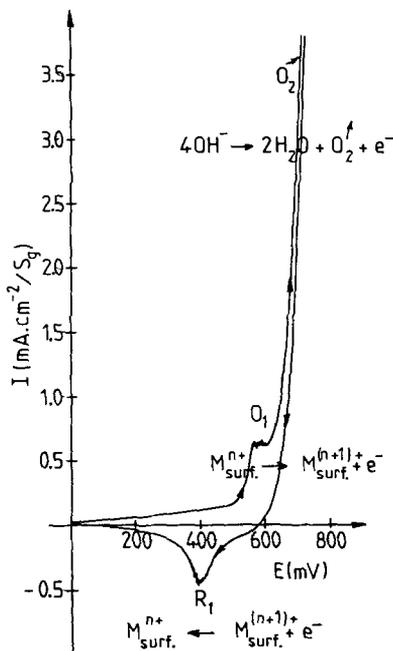
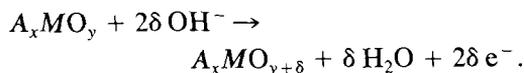


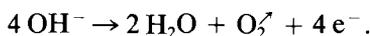
FIG. 3. Typical cyclic voltammogram (I, E) obtained on 3d transition-metal oxides.

TABLE I

CRYSTALLOGRAPHIC AND MÖSSBAUER RESONANCE DATA OF $\text{SrFeO}_{2.50}$ BEFORE AND AFTER ELECTROCHEMICAL OXIDATION

	Before polarization	After polarization
Chemical Analysis	$\text{SrFeO}_{2.53 \pm 0.02}$	$\text{SrFeO}_{3.00 \pm 0.02}$
XRD	Orthorhombic $a = 5.519 \pm 0.005 \text{ \AA}$ $b = 15.54 \pm 0.01 \text{ \AA}$ $c = 5.662 \pm 0.005 \text{ \AA}$ $(a_c = 3.930 \text{ \AA})$	Cubic $a = 3.845 \pm 0.005 \text{ \AA}$ $(a_c = 3.845 \text{ \AA})$
Mössbauer spectroscopy	50% Fe^{III} magnetic O_h T_d $\delta = 0.376$ $\delta = 0.189$ mm s^{-1} mm s^{-1}	100% Fe^{IV} paramagnetic O_h $\delta = 0.06$ mm s^{-1}

—above 700 mV, oxygen evolution occurs according to the reaction:



The applied potential for the electrochemical oxidation was usually chosen as that corresponding to the beginning of the plateau.

—a reduction peak in the 200–400 mV range is attributed to the reduction of $M^{(n+1)+}$ to M^{n+} .

Electrochemical Oxidation of $\text{SrFeO}_{2.50}$ (5)

The starting material $\text{SrFeO}_{2.68}$ was first prepared by firing a stoichiometric mixture of SrCO_3 and Fe_2O_3 in air at 1200°C . Then the $\text{SrFeO}_{2.50 \pm \epsilon}$ phase was obtained by annealing $\text{SrFeO}_{2.68}$ under flowing argon at 1000°C for 18 h. In order to achieve ceramics of high density, pelleted samples were sintered under flowing argon for 4 h at 1000°C and then quenched. The electrode was characterized with powder XRD, chemical analysis, and ^{57}Fe Mössbauer spectroscopy. The results (Table I) are in good agreement with those of previous authors (22, 23); the composition is close to $\text{SrFeO}_{2.51}$, and the XRD

pattern (Fig. 4) as well as the Mössbauer spectrum (Fig. 5) are characteristic of the brownmillerite-type phases; i.e., Fe^{III} ions are located in both octahedral and tetrahedral sites.

A preliminary electrochemical study has shown that the optimal conditions for oxidizing this compound were a polarization potential of 400 mV for 60 h. Under these conditions, the initial value of the open-circuit voltage (OCV) is equal to -120 mV; polarization increases the OCV to $+380$ mV. This potential corresponds to the oxygen chemical potential in the material; its strong evolution gives evidence of a drastic variation of the material composition at 400 mV.

XRD and Mössbauer resonance data for samples before and after anodic polarization (Figs 4 and 5 and Table I) show that the electrochemical treatment is a *bulk treatment* leading to a fully oxidized material. No trace of the starting $\text{SrFeO}_{2.51}$ could be detected. The XRD pattern is characteristic of the cubic perovskite; the unit-cell parameter $a_c =$

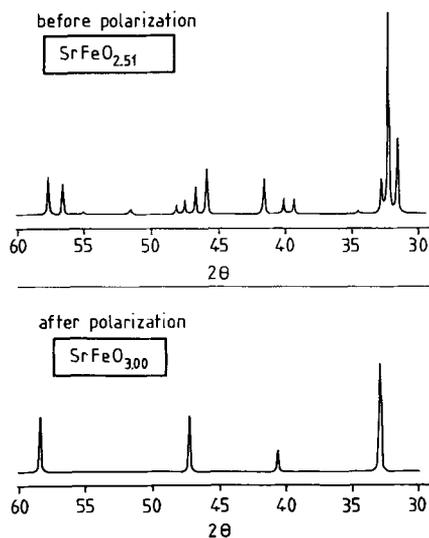


FIG. 4. XRD diffraction patterns of an $\text{SrFeO}_{2.51}$ -based electrode before and after electrochemical oxidation to SrFeO_3 .

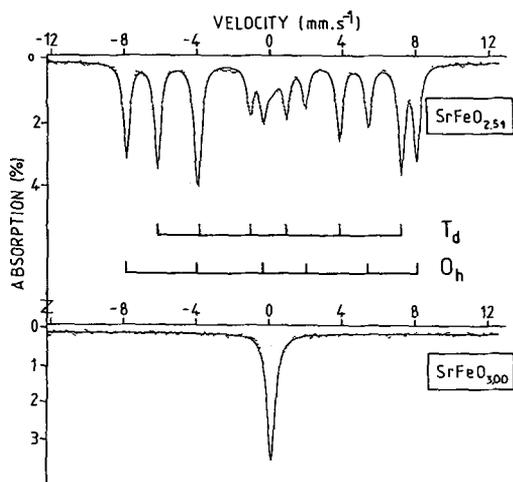


FIG. 5. Mössbauer spectra at 300 K of an $\text{SrFeO}_{2.51}$ -based electrode before and after electrochemical oxidation.

$3.845 \pm 0.005 \text{ \AA}$ is in good agreement with previous data reported for SrFeO_3 prepared under high oxygen pressure (23). In addition, the determination of the oxidation state of iron using a redox titration leads to 100% Fe(IV) after polarization, which corroborates the SrFeO_3 formulation.

Mössbauer resonance data nicely confirm these results: the spectra before and after polarization reveal a large evolution of the oxidation state and the iron coordination. After treatment, the spectrum characterizes iron in the exclusive oxidation state IV, in complete agreement with chemical analysis. Moreover the value of the quadrupole splitting ($\Delta = 0$) accounts for a symmetrical octahedral site of iron and fully supports the cubic symmetry detected by XRD.

Very recently similar results have been found for $\text{Sr}_2\text{Co}_2\text{O}_5$, which was oxidized into stoichiometric SrCoO_3 (24).

Electrochemical Oxidation of $\text{La}_2\text{MO}_{4+\delta}$ Phases ($M = \text{Ni}, \text{Cu}$)

The starting materials were prepared by an usual solid-state reaction of a stoichiometric

mixture of La_2O_3 (prefired at 900°C) and MO ($M = \text{Ni}, \text{Cu}$) oxides heated at 1050°C and ground repeatedly. They were also obtained from a solution of nitrates of lanthanum and 3d metal that was dehydrated at 150°C and slowly fired up to 1050°C .

After annealing at 1200°C in air and quenching, the determination of the nickel oxidation state and of the La/Ni ratio by chemical analysis led to a composition close to $\text{La}_2\text{NiO}_{4.14}$. Then the sample was annealed at 1300°C under argon for 24 h and quenched. Under these conditions, the $\text{La}_2\text{NiO}_{4.03}$ composition was reached.

The copper compound was annealed in air at 1050°C for 24 h and then quenched; the resulting composition was close to $\text{La}_2\text{CuO}_{4.01}$.

The product materials were finely ground and pressed into disks. They were then sintered in air at 1050°C for $\text{La}_2\text{CuO}_{4.01}$ —at 1300°C under argon for $\text{La}_2\text{NiO}_{4.03}$ —and finally quenched. The density of the ceramics was close to 95%. After polishing, the disks were used as working electrodes.

La_2NiO_4 was polarized at 600 mV for various times. The maximum oxidation state of nickel was 52% Ni^{III} ($\text{La}_2\text{NiO}_{4.26}$); it was reached after 7 days (6). In addition, an increase of E_{OCV} from -200 mV up to $+440$ mV was observed (Table II). Similarly after a polarization at 450 mV for 3 days, an oxidized material of $\text{La}_2\text{CuO}_{4.09}$ composition (18% Cu^{III}) was obtained (7, 8).

TABLE II
CRYSTALLOGRAPHIC DATA AND OCV POTENTIALS OF La_2MO_4 PHASES

	V (\AA^3)	c (\AA)	E_{OCV} (mV)
$\text{La}_2\text{CuO}_{4+\delta}$			
$\delta = 0.01$	380.2	13.139	350
$\delta = 0.09$	381.6	13.203	435
$\text{La}_2\text{NiO}_{4+\delta}$			
$\delta = 0.03$	377.2	12.609	-200
$\delta = 0.26$	377.2	12.681	440

The formation of mixed valency of the 3d cations obviously gives rise to drastic changes in the physical properties of these materials.

Thus $\text{La}_2\text{NiO}_{4.03}$ is a p-type semi-conductor; the thermal evolution of its electrical conductivity follows an Arrhenius-type law with a thermal activation energy $E_a = 0.07$ eV. Comparison of the thermal evolution of the Seebeck data with that of the conductivity indicates small-polaron conduction with a motional enthalpy $\Delta H_m \approx 0.05$ eV; a small excitation energy of the small-polaron holes is therefore indicated. During oxidation, the evolution of the Seebeck coefficient shows a progressive change into an n-type semi-conductor, and the non-Arrhenius thermal evolution of the electrical conductivity suggests that the motional enthalpy of the polarons increases with temperature.

The case of La_2CuO_4 is even more impressive. The starting material behaves as an antiferromagnetic, p-type semiconducting material; but, after oxidation, its electrical resistivity and thermoelectric power at 300 K strongly decrease by a factor of 50 and 10, respectively. Moreover, the thermal evolution of the resistivity of the oxidized material is typical of a metallic behavior and exhibits a superconducting transition around 50 K (Fig. 6) (8).

XRD data (Table II) show a relatively small increase—or even no variation—of the unit cell volume, but a significant enhancement of the c parameter (0.57% and 0.48% for the Ni and Cu compounds, respectively). This c -axis elongation is similar to that observed in fluorinated La_2CuO_4 (25); it can be attributed to the insertion of oxygenated species in the lattice.

Discussion

Obtaining highly oxidized materials at room temperature raises some basic questions such as:

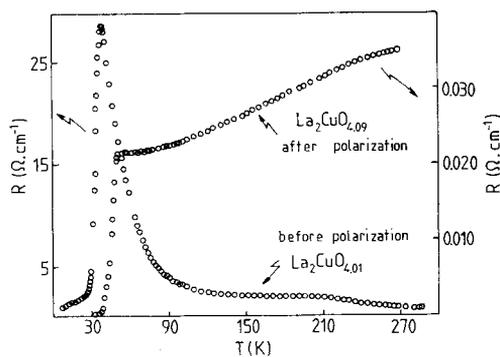


FIG. 6. Temperature dependence of the electrical resistivity of La_2CuO_4 before and after electrochemical oxidation.

(i) Can this reaction be considered as an intercalation process?

(ii) What are the nature of the intercalated species and of the occupied sites?

(iii) What is the mechanism of the electrochemical oxidation?

(i) At first it should be pointed out that the reaction is reversible as expected for an intercalation reaction. For instance $\text{La}_2\text{CuO}_{4.00}$ is recovered after a polarization at 200 mV, i.e., in the reduction-peak region (Fig. 3), for 12 h of the oxidized $\text{La}_2\text{CuO}_{4.09}$ phase. It is also interesting to notice that the starting material can always be recovered by thermal decomposition (TGA measurements and *in situ* IR studies (8, 26).

(ii) The complete transformation of the oxygen-deficient $\text{Sr}_2\text{Fe}_2\text{O}_5$ into the perovskite SrFeO_3 (or similarly of $\text{Sr}_2\text{Co}_2\text{O}_5$ into SrCoO_3) obviously demonstrates the intercalation of "foreign" species into the parent network. The structural evolution of the 2D La_2MO_4 phases is less striking although a significant c -axis elongation was observed.

For SrFeO_3 the chemical analysis as well as the Mössbauer resonance data indicated the presence of only Fe^{IV} . In addition, the XRD pattern was characteristic of the cubic perovskite structure, and the Sr/Fe ratio remained unity. Due to electrical neutrality,

these results rule out that the intercalated species are OH^- as might reasonably have been expected. In the same way the results of the chemical analysis and of the TGA measurements for $\text{La}_2\text{CuO}_{4+\delta}$ prove that the intercalated species are not OH^- in this case either (8). This conclusion is also corroborated by the absence of an OH-band in the IR spectra (27). In addition, NMR experiments have not revealed the presence of protons. On the other hand, our XPS measurements have not confirmed previous assumptions, which supposed the existence of unusual O_2^- or O_2^{2-} species. Therefore we believe that the inserted species are formally O^{2-} anions.

In the brownmillerite-type materials, intercalated O^{2-} anions can easily take place in vacant sites of the network (Fig. 1) without significant modification of the parent structure, i.e., of the cationic network. But when all these vacant sites are filled, as in SrFeO_3 or in SrCoO_3 , no difference can be observed between "guest" and "host" species. This feature makes the oxygen intercalation somewhat different from the well-known cationic intercalation in oxides. However, from this point of view the La_2MO_4 phases behave differently, as the normal sites of the K_2NiF_4 -type structure are completely occupied. Therefore overstoichiometric oxygen atoms must be located in interstitial sites. Various evidences have been given. For instance, neutron-diffraction experiments on $\text{La}_2\text{CuO}_{4.09}$ (28) have confirmed that the extra oxygen atoms are in the O_4 position (1/4, 1/4, 0.258) of the structural model of Chailout *et al.* (29). This O_4 site is located in the La_2O_2 planes in a position similar to that of the oxygen atoms in Nd_2CuO_4 (Fig. 7). The extra oxygen is surrounded by four lanthanum atoms and four oxygen atoms and causes local structural rearrangements; for instance, an increase of the lanthanum coordination number is observed by XPS (27).

Contrary to the general tendency in inter-

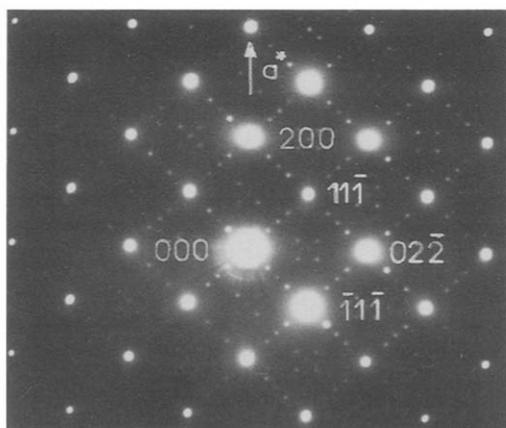


FIG. 7. Electron diffraction pattern of $\text{La}_2\text{NiO}_{4.26}$ along the $[101]$ zone axis showing extra spots due to intercalated oxygen atom ordering.

calated compounds, the unit-cell volume variations are small or even negative as for SrFeO_3 . A volume increase can be easily explained in the case of cation insertion, considering that both the intercalation of species and the eventual reduction of the host network contribute to an expansion of the material. Conversely in the case of oxygen intercalation, the creation of highly oxidized cations of smaller ionic radius act to compensate the rather big size of the intercalated species O^{2-} .

Finally, evidence of intercalation has come from TEM investigations. Figure 8 shows an electron-diffraction pattern of $\text{La}_2\text{NiO}_{4.26}$ along the $[101]$ zone axis. Extra spots can be observed along the $[111]$ and $[\bar{1}\bar{1}\bar{1}]$ directions. A structural model has been proposed by Demourgues *et al.*; it shows the direct correlation between the amount of intercalated oxygen and the type of superstructure or, in other words, the occurrence of various stages during the oxygen intercalation with the formation of microphases of definite composition (30).

(iii) The mechanism of electrochemical oxidation can be decomposed into two main steps:

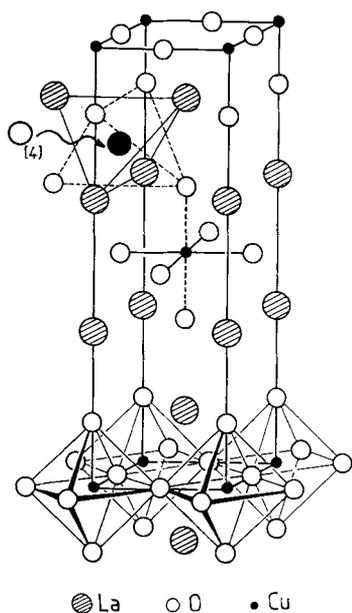


FIG. 8. Schematic representation of the location of the extra oxygen atom $O_{[4]}$ in $La_2CuO_{4+\delta}$.

—a surface oxidation involving electroactive species depending on the nature of the electrolyte.

—a bulk oxidation involving the diffusion of charged or non-charged species which eventually can be the same as the electroactive species occurring during the surface oxidation.

The diffusion phenomena strongly depend on such electrode features as structure, texture and physical properties.

For the electrochemical oxidation the potential was set at a value lying in the range of the diffusion plateau of Fig. 3. We may note that at such a potential the theoretical activity of oxygen at the surface is very large (theoretically several orders of magnitude). The oxidation mechanism is not presently known; its determination requires a further investigation now in progress. However, the mechanism of oxygen evolution at the surface of similar materials has been extensively studied during the last decade (31–33). More especially we have proposed

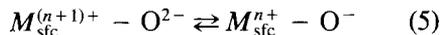
a mechanism involving 7 steps for the $La_{1-x}Sr_xFeO_{3-y}$ materials (34).

An alternative mechanism has been proposed by Goodenough *et al.* (35); these authors assume that:

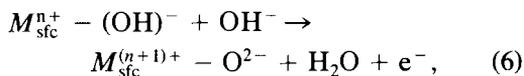
—the metal atoms of the oxide retain their full oxygen coordination throughout the reaction by binding oxygen from the water of the electrolyte and exchanging the protons of the bound water to come into equilibrium with the pH of the electrolyte.

—the surface charge on the oxide remains constant.

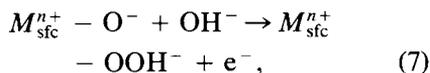
Finally, we also note with Goodenough that the oxygen-evolution reaction on oxides is found where the equilibrium



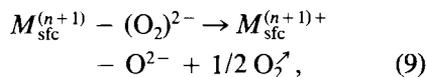
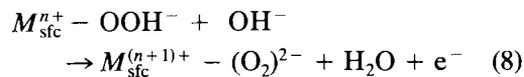
is not biased too strongly to the left. With these assumptions, the oxygen-evolution reaction proceeds as follows, where M is a transition-metal ion for which Eq. (5) is satisfied,



which, from Eq. (5), is followed by

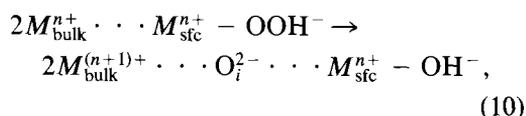


where equilibrium (5) has made the surface oxygen an active site for attack by an OH^{-} group of the solution. This equilibrium also makes possible the next two steps,



which returns the surface to equilibrium (5). Clearly the insertion of interstitial oxygen into the bulk can only occur between steps (7) and (8); therefore, the phenomenon is predicted to occur where equilibrium (5) is found and at potentials where the oxygen-

evolution reaction is just being initiated or is in competition. If step (8) is the rate-determining step of the oxygen-evolution reaction, then the competitive oxidation reaction is



which returns the surface to its condition in Eq. (6). In order for step (10) to compete with (8) + (9), it is necessary to be able to insert interstitial oxygen having a good mobility at room temperature. This condition appears to be satisfied in the K_2NiF_4 structure and in the oxygen deficient perovskites. It is also tempting to propose that equilibrium (5) is also playing an important role in the oxygen-diffusion mechanism. An electron transfer from O_i^{2-} to $M_{\text{bulk}}^{(n+)+}$ would create a more mobile O_i^- species, and the transferred electron could be returned after a diffusion jump so as to be carried with the mobile ion.¹

Conclusion

The results obtained on ceramics of ternary oxides of perovskite and K_2NiF_4 -type structures clearly show that electrochemical oxidation is a very powerful method for the preparation of materials containing high oxidation states of transition elements. The reaction products have been characterized, and various features have allowed us to describe them as intercalation compounds of oxygenated anions. However, the intercalated species being similar to the host anions, these materials appear somewhat original with respect to previous interca-

lated compounds in which guest species usually are chemically different from the host ions. The exact nature of the diffusion mechanism for the oxygen is not yet clearly stated. Further investigations are now in progress in order to clarify this point, as well as to extend this efficient electrochemical preparative method to other oxide series.

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¹ It is worthwhile to point out that, according to previous authors, we have observed that $\text{La}_2\text{CuO}_{4+\delta}$ ($\delta = 0.05$) undergoes a phase separation, namely "a spinodal decomposition," at ca. 240 K; such a behavior would also suggest an easy oxygen diffusion at low temperature (36-38).

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