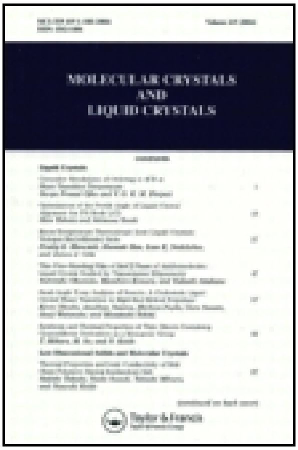

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

New “Chimie Douce” Oxidizing Processes: Electrochemical Oxidation and in situ Oxidation by NO_2

Jean-Claude Grenier [a], Jean-Pierre Doumerc [a], Yuji Muraoka [b], Stephane Petit [a], Michel Pouchard [a], Alain Wattiaux [a] & Fang Zhou [a]

[a] Institut de Chimie de la Matière Condensée de Bordeaux, C.N.R.S., Av. du Dr. Schweitzer, 33608, Pessac, FRANCE

[b] Institute for Material Research, Tohoku University, Katahira, Aoba-ku, Sendai, 980-77, JAPAN

To cite this article: Jean-Claude Grenier, Jean-Pierre Doumerc, Yuji Muraoka, Stephane Petit, Michel Pouchard, Alain Wattiaux & Fang Zhou (1998): New “Chimie Douce” Oxidizing Processes: Electrochemical Oxidation and in situ Oxidation by NO_2, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 311:1, 359-366

To link to this article: http://dx.doi.org/10.1080/10587259808042411

Mol. Cryst. Liq. Cryst., 1998, Vol. 311, pp. 359–366
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New "Chimie Douce" Oxidizing Processes : Electrochemical Oxidation and *in situ* Oxidation by NO_2

JEAN-CLAUDE GRENIER, JEAN-PIERRE DOUMERC, YUJI MURAOKA[a], STEPHANE PETIT, MICHEL POUCHARD, ALAIN WATTIAUX and FANG ZHOU
Institut de Chimie de la Matière Condensée de Bordeaux,
C.N.R.S., Av. du Dr. Schweitzer, 33608 Pessac, FRANCE
(a) Institute for Material Research, Tohoku University, Katahira, Aoba-ku,
Sendai 980-77, JAPAN

Two new oxidation processes are described : the electrochemical oxidation in alkaline solution uses the electrical potential as the driving force for intercalating oxygen, at room temperature, into oxide networks such as perovskites or Ln_2MO_4 (M = Ni, Cu) compounds. The second one is based on the *in situ* destruction of ammonium ions in oxide lattices by interaction with NO_2 gas, at moderate temperatures. Pictures of the reaction mechanisms are also proposed.

Keywords: electrochemical oxidation, oxygen intercalation, ammonium deintercalation, in situ nitrogen dioxide reaction

INTRODUCTION

Nowadays it is obvious that Chimie Douce has become a major field in the synthetic chemistry of new materials, especially for those that are highly metastable and that cannot be prepared by usual solid state chemistry. Chimie Douce supposes mild reaction conditions, typically at temperatures lower than 300 °C, which allows to keep a structural filiation between the so-called "mother" and "daughter phases" ; as a consequence it requires original synthetic routes.

Commonly one distinguishes two main types of reactions : the acid-base ones (*e.g.* ionic exchange, dehydration or hydrolysis, molecular intercalation,...) and the redox reactions implying electronic transfers that can be achieved using either a chemical agent or the electric potential. We report in this paper two new oxidizing processes belonging to the latter reaction type.

Lithium or proton (de)intercalation in iono-covalent compounds (*e.g.* chalcogenides or oxides) has been widely studied during the last twenty years in relation with applications for batteries or electrochromism. Often this reaction is rather easy to carry out as the oxidation of Li or H and the reduction of the host that captures electrons, simultaneously occur. In addition, due to the small ionic size of these cations, the intercalation does not require drastic structural changes of the parent structure. In this scope the migration of big species seems to be much more difficult especially in the considered temperature range. However one should mention that intercalating big species such as large molecules is possible in 2D layered compounds (the so-called pillaring or grafting techniques). It is almost unknown in tunnel or 3D deficient structures : our studies deal with (de)intercalation of big species such as O^{2-} ($r_i \approx 1.40$Å) and NH_4^+ ($r_i \approx 1.48$Å).

ELECTROCHEMICAL OXYGEN INTERCALATION

The use of electric field as the driving force of a redox reaction is often very fruitful, especially for preparing new materials at about room temperature. Thanks to the high oxygen activity obtained on electrodes under anodic potentials in alkaline solution, we could intercalate oxygen into oxide networks provided that a diffusion path exists[1]. Potentiostatic as well as galvanostatic experiments were carried out on ceramics, thin films or crystals, in the potential range preceding the oxygen evolution reaction. A bulk oxidation of the material was observed according to the global reaction :

$$A_xM_zO_y + 2\delta\, OH^- \longleftrightarrow A_xM_zO_{y+\delta} + \delta\, H_2O + 2\delta\, e^- \qquad (1)$$

Indeed it was clearly established that it is really oxygen which is inserted at room temperature. Mainly two kinds of oxides were thus overoxidized : oxygen deficient perovskites and K_2NiF_4-related oxides.

i)- **<u>oxygen deficient perovskites :</u>** strontium ferrites and cobaltites such as $Sr_2M_2O_5$ ($M = Fe_{1-x}Co_x$) or $Sr_2LaFe_3O_8$, belonging to the series $A_nM_nO_{3n-1}$ ($n \geq 2$) were fully oxidized into perovskite compounds (see the experimental conditions in Table 1). All the starting materials are almost insulators and after some days become metallic or almost metallic conductors. The X-ray diffraction (XRD) characterization of the samples shows that they remain well crystallized after the electrochemical oxidation : they exhibit a cubic perovskite-type pattern and a significant volume shrinkage (≈ 6%) due to the oxidation process and the occurrence of tetravalent Fe(IV) or Co(IV) ions whose ionic radii are somewhat smaller than those or Fe(III) or Co(III) ions present in the starting materials. The full oxidation was checked by chemical and physical analyses, more especially by Mössbauer spectroscopy that clearly evidences the presence of Fe(IV) in the treated material, its amount well agreeing with the chemical analysis[2].

Table I

Parent material	Electrochemical conditions	Final material	Cell parameter (a_C pm)	ΔV/V (%)
$Sr_2Fe_2O_5$	E = 400 mV ; 60 h.	$SrFeO_3$	383.5(2)	- 5.8
Sr_2FeCoO_5	I = 250 μA ; 240 h.	Sr_2FeCoO_6	383.7(2)	- 6.7
$Sr_2Co_2O_5$	E = 500 mV ; 180 h.	$SrCoO_3$	383.5(2)	- 5.8
$Sr_2LaFe_3O_8$	E = 500 mV ; 190 h.	$Sr_2LaFe_3O_{8.95}$	387.7(2)	- 5.2

ii) **Ln_2MO_4-related oxides :** intense researches were devoted especially to cuprates in relation with superconductivity. The most interesting results were obtained with $La_2CuO_{4+\delta}$ in which oxygen could be inserted up to $\delta \approx 0.10$, giving rise to metallic and superconducting properties[3]. Electrochemical oxidation was the only way for obtaining these oxidized cuprates that cannot be synthesized even under high oxygen pressures. Galvanostatic experiments exhibit very similar features with cationic intercalation as shown in Fig. 1 : two steps can be seen in the potential-composition curves (the composition being determined by coulometry). They reveal the formation of two different superconducting phases with T_C = 32 K and T_C = 44 K in which additional oxygen atoms are ordered in different ways. Such a succession of ordered phases characterizing different stages

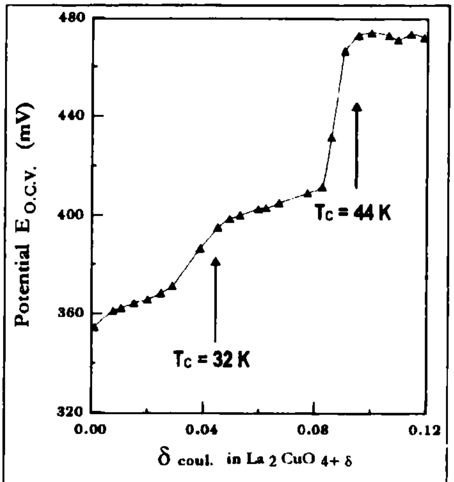

Fig. 1 Variation of the Open Circuit Voltage as a function of the oxygen excess calculated from coulometric experiments (I = 2 μA).

of intercalation has been also evidenced in $Ln_2NiO_{4+\delta}$ nickelates by electrochemical experiments as well as by structural characterizations (neutron diffraction, TEM studies, ...)[2].

***iii)* Structural aspects :** Intercalating oxygen appears rather surprising with regards to the size of oxygen anions. Clearly it requires diffusing paths in the material, the size of which must be large enough. In perovskite related materials (e.g. brownmillerite compounds), there exist channels with three different polygonal windows. From electrostatic considerations (Pauli repulsion and Madelung potential calculations), we showed that diffusing oxygen atoms experience the highest energy barriers at the triangular and trapezoidal windows, especially in the calcium compounds, which may explain why these materials cannot be electrochemically oxidized.

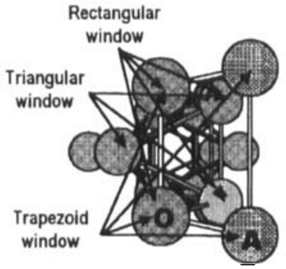

Fig. 2 View of the diffusion channels in an oxygen deficient perovskite of the series $A_nM_nO_{3n-1}$.

In Ln_2MO_4 compounds many controversies were raised about the oxygen excess location ; the description of the structure in terms of AO_3 hexagonal stacking clearly evidences the presence of vacancy files along the $[1\bar{1}0]_T$ direction within the $(114)_T$ planes of the tetragonal structure thus forming "empty" planes between "LaO" layers. These oxygen "vacancies" make possible the oxygen diffusion and ordering may appear as observed in $La_2NiO_{4+\delta}$ (i.e. $La_8Ni_4O_{17}$).

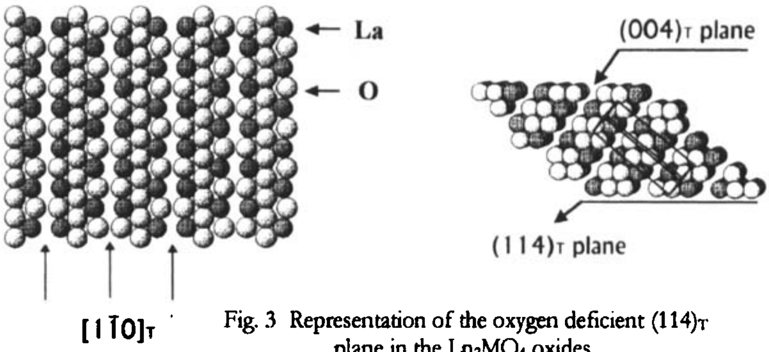

Fig. 3 Representation of the oxygen deficient $(114)_T$ plane in the Ln_2MO_4 oxides.

iv) **electronic aspects :** electrochemical studies have revealed that the electroactive species formed at the surface of the electrode are O^- anions that have a high diffusion coefficient ($D_{ox} \approx 10^{-12}$ cm^2.s^{-1}). In addition the diffusion of oxygen seems to occur only in oxides for which the energy of the cation d levels are close to those of oxygen, *i.e.* when the energy charge transfer Δ characterizing the equilibrium $M^{(n+1)+} + O^{2-} \Leftarrow\Rightarrow M^{n+} + O^-$ is close to zero. Many evidences of this easy oxygen diffusion have been given as for instance the fact that the complete deintercalation is also possible at room temperature [2-3].

IN-SITU DESTRUCTION OF AMMONIUM IONS BY NO$_2$

This second example deals with ammonium containing compounds. Due to the large size of the inserted ions, the structures of the starting materials are expected to be much different from those containing much smaller ions such as Li^+, H^+ or Na^+, which should lead to new structures for the - generally metastable - deintercalated phases. Various reactions can be used for "extracting" NH_4^+ : thermal decomposition, gas-solid reaction using O_2 or F_2, oxidation in solution (e.g. using H_2O_2). We have used a gas-solid reaction process involving the *in-situ* action of NO_2 [4, 5]. In the considered temperature range (T < 350 °C), NO_2 is stable and the expected reaction is :

$$NO_{2(g)} + NH_4^+ + e^- \rightarrow N_2^{\nearrow} + 2\,H_2O^{\nearrow} \quad (2)$$

Simple considerations show that using NO_2 is, from the thermodynamics viewpoint, more favorable than using O_2. In addition, one should point out that the reaction of NH_4^+ with NO_2 implies a mole-to-mole reaction leading to the formation of stable neutral molecules that can easily diffuse out of the parent network. This process has been tested on ammonium compounds having different structural types.

i) **Tunneled compounds : hexagonal WO$_3$ and MoO$_3$.**

The hexagonal ammonium tungsten bronzes $(NH_4)_xWO_3$ $(0.05 \leq x \leq 0.33)$, isostructural with the so-called Magneli bronzes K_xWO_3, have been prepared by controlled reduction of the hydrated ammonium paratungstate $(NH_4)_{10}W_{12}O_{41},5H_2O$ under Ar/H$_2$(5%), in the temperature range 350 < t <

380 °C. Then the reaction with NO_2 was carried out at temperatures ranging between 20 and 350 °C. The complete oxidation-deintercalation was obtained by heating at 250-300 °C for 3 h., which was confirmed by various physical-chemical characterizations such as the determination of the nitrogen content by the Kjeldahl method, I.R. spectroscopy, mass spectrometry, etc.... The final oxidized product is white and the XRD analysis shows that the material is well crystallized and that the deintercalation is topotactic, the hexagonal structure of the bronze being retained. TEM studies as well as the structure refinement by the Rietveld method confirm the doubling of the *c* parameter (a = 7.334 Å and c = 7.652 Å) caused by a tilting of the octahedra. This feature was not observed for the material previously prepared by Figlarz et al. [6], using a reconstructive reaction. Combined DTA/TGA analyses show the irreversible transition from hexagonal to stable monoclinic phase to occur at about 500°C.

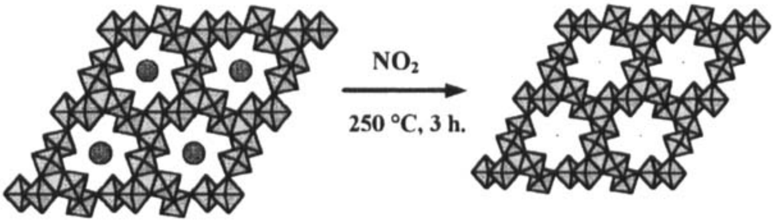

Fig. 4 Topotactic destruction of NH_4^+ in the ammonium molybdate

It is well known that it is difficult to prepare the hexagonal MoO_3 phase because of its high metastability. This compound was obtained in a similar way starting from the ammonium molybdate $(NH_4)_yMo_{6-x}O_{18}H_{6x-y}$ that was prepared by cationic exchange from Na_2MoO_4, $2H_2O$. Its composition was determined by analysis of the NH_4^+ content by the Kjeldahl method and TGA under O_2 up to 600 °C. XRD analysis of the as-prepared material $(NH_4)_{0.7}Mo_{5.3}O_{18}H_{3.5}$ showed a single phase with a hexagonal symmetry (Fig.4). The NO_2 treatment was carried out in the temperature range of 150-300 °C for 3 h.. Structural analysis showed that the hexagonal structure was kept and almost no NH_4^+ was detected by the Kjeldahl method or I.R. spectroscopy in the sample prepared at 300 °C.

However, TGA measurements reveal a small weight loss assigned to the loss of some remaining water in the structure, which would imply, as for WO_3, that an appropriate amount of H_2O in the matrix could be required to stabilize the hexagonal form of MoO_3 (Fig4).

ii) Lamellar structures 3 ammonium vanadates.

The first example deals with the mixed valent so-called Glemser's "black hydrate" $(NH_4)_2V_3O_8$ whose structure is represented in Fig. 5. In such a structure, NH_4^+ ions play the role of pillars between $(V_3O_8)^{2-}$ layers. This compound was prepared using an original way, the reduction of V_2O_5, at room temperature, by the sodium borohydride $NaBH_4$ in presence of an excess of NH_4Cl according to the reaction:

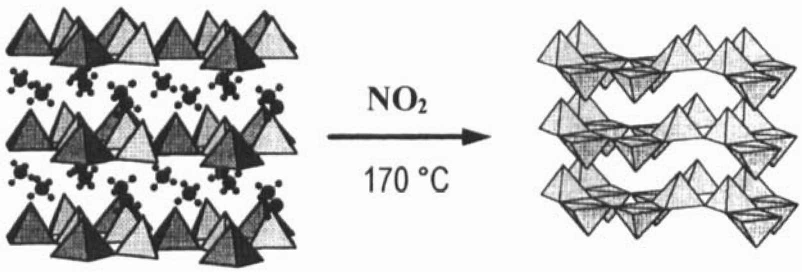

Fig. 5 Non topotactic destruction of NH_4^+ in the ammonium vanadate $(NH_4)_2V_3O_8$

$$12\,V_2O_5 + 16\,NH_4^+ + BH_4^- + 7\,H_2O \Longleftrightarrow H_3BO_3 + 8\,(NH_4)_2V_3O_8 + 15\,H^+$$

The reaction is completed after a few hours and the product shows a tetragonal symmetry with unit cell parameters close to those previously reported (a = 8.88 Å; c = 5.56 Å). Then the reaction with NO_2 is very fast even at room temperature and an orange amorphous product is formed. Above 170°C the reaction is instantaneous and the very well crystallized α-V_2O_5 is obtained. One should notice that, in this case, the reaction is not topotactic and that a rearrangement of the parent lattice occurs due to the destruction of interlayer NH_4^+ ions, which basically differs from the previous examples. A similar reaction was achieved with $(NH_4)_2V_2PO_8$ giving V_2PO_{75} (*i.e.* $V_{4/3}P_{2/3}O_5$) [5].

The action of NO_2 was also studied with the lamellar NH_4VO_3 (α-$NaVO_3$ type-structure). Again the destruction of NH_4^+ is observed within a few minutes, starting from 100 °C, leading to the formation of α-V_2O_5.

***iii)* <u>reaction process :</u>** for a mixed valence oxide, the electron involved in reaction *(2)* is supposed to come from the oxidation of the metal cation ($Me^{n+} \rightarrow Me^{(n+1)+} + e^-$). But when the metal cation is in its highest valence, the reaction still takes place and may result either from the direct oxidation of oxygen anions ($O^{2-} \rightarrow O^{\cdot} + 2e^-$) or from a two step process involving the evolution of NH_3 with the formation of an intermediate hydrate that is finally decomposed. In any case the reaction is very fast, exothermic and can be used for preparing either amorphous materials or finely divided powders. Such a reaction was used for preparing submicronic CeO_2 powers starting from cerium ammonium nitrate [5].

CONCLUSION

We described two original oxidizing processes that have been more especially used for (de)intercalating big species such as oxygen anions or ammonium cations. They do appear as new synthetic routes in the field of oxide chemistry as well as they provide new possibilities for technological applications in the materials sciences[7-8].

Acknowledgments : The authors thank Rhône-Poulenc company for its financial support.

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