Dramatic Change in Magnetic Properties of Manganates $Ca_{2-x}Ln_xMnO_4$ by Low-Temperature Electrochemical Oxidation in Fused Nitrates

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Electrochemical oxidation or reduction allows modification of the charge distribution within a solid with simultaneous intercalation/deintercalation of positive or negative charges in or out of the structure and consequent changes in physical properties. Cation insertion has been studied for a long time with many applications that involve batteries, electrochromic devices, etc. Anion intercalation (mainly halide) has only been reported much more recently. Although perovskites and other oxides are known to modify their oxygen content as a function of temperature and oxygen partial pressure, this type of redox process has never been considered as an intercalation reaction, since oxygen itself changes its oxidation state. Simple intercalation processes for oxygen anions had not been observed until the electrochemical oxidation of $SrFeO_{2.5}$ and La_2CuO_4 were reported, using an aqueous basic medium at room temperature.[1,2] The former phases have structures related to that of the perovskite, and at least La_2CuO_4 had previously been oxidized by high-temperature treatments at high oxygen pressure.[3]

In the first case, $SrFeO_{2.5}$, electrochemical oxidation filled the oxygen vacancies, yielding $SrFeO_3$. In La_2CuO_4, intercalated oxygens need to occupy interstitial vacancies, leading to an overstoichiometric phase, $La_2CuO_{4+\delta}$, that turned out to be superconducting with a T_c dependent on the doping extent with a maximum value 10K higher than the one obtained by the high-pressure synthesis. Phase segregation was observed in the form of complex Meissner transitions,[4,5] possibly coming from a shell distribution of oxygen content within each grain.

At any temperature, certain structural requirements as well as good oxygen mobility within the structure are required if oxygen intercalation is to occur. Along those lines, we have carried out systematic studies on a series of phases related to the perovskite structure, but with different degrees of complexity and a variety of metallic components.[6−8] We have observed evidence that suggests that oxygen intercalated at room temperature behaves chemically more like a peroxide or superoxide than as an oxide ion and that this behavior changes with temperature, as expected from the high reactivity of those species.[4,5] To verify this, we tested an alternative medium that would stabilize peroxide and superoxide species: fused alkali nitrates that allow one to work as low as 150 °C in one of the eutectics.[8] By doing so, we observed that this media also offers a larger electrochemical window for oxidation,[8] which, in turn, has allowed us to oxidize some materials for which oxidation had not been possible before in basic aqueous solutions. In this paper we give a preliminary report of the dramatic change in magnetic properties that can be achieved in manganates with the K_2NiF_4 structure when they are electrochemically oxidized at very low temperatures. The changes observed are so considerable that they could be of interest from a practical point of view.

The precursor oxides $Ca_{1-x}Ln_xMnO_4$ (Ca_2MnO_4, $Ca_{1.5}Nd_{0.5}MnO_4$, $Ca_{1.7}Y_{0.3}MnO_4$, $Ca_{1.7}Dy_{0.3}MnO_4$) were prepared by solid-state reaction of the simple oxides and carbonates according to ref 9. The reagents used were $CaCO_3$ (Baker, 99.95%), Mn_2O_3 (Aldrich, 99%), Y_2O_3, Dy_2O_3, Gd_2O_3, Sm_2O_3 (Aldrich, 99.99%), $Tb_2O_3{\cdot}H_2O$ (Aldrich 99.9%), and Nd_2O_3 (Aldrich, 99.9%). All oxides, except Mn_2O_3, were treated previously at 900 °C over 8 h to remove carbonates and water. Stoichiometric amounts for each case were mixed in an agate mortar and heated in an alumina crucible. A first thermal treatment was done at 1250 °C (24 h; heating and cooling rates 150 °C/h). The resulting powder was ground again, pressed into pellets 16 mm in diameter, and sintered at the same temperature for 40 h with the same heating and cooling rates. The purity of the precursor samples was tested by Xray powder diffraction (see Supporting Information) and compared with previously reported data,[9] as well as by iodometry. The stoichiometry of the precursor phases according to iodometry (assuming oxide ions) was as follows: $Ca_{1.5}Nd_{0.5}Mn_{0.34}{}^{3+}Mn_{0.66}{}^{4+}O_{4.08}$, $Ca_{1.7}Dy_{0.3}Mn_{0.24}{}^{3+}Mn_{0.76}{}^{4+}O_{4.03}$, $Ca_{1.7}Y_{0.3}Mn_{0.58}{}^{3+}Mn_{0.42}{}^{4+}O_{3.86}$. Undoped Ca_2MnO_4 (Mn^{4+}) is an insulating material with a resistivity larger than 20 MΩ cm, which prevents its use as working electrode in electrochemical oxidation. For that reason, only cation-doped materials, with manganese in a mixed-valence state, have been oxidized; therefore, the observed changes occur presumably among two mixed-valence materials with different number of carriers.

The pellets (density 80% of the theoretical) were set up as working electrodes in three-electrode electrochemical Teflon cells, using silver paint (Agar Sci. Ltd.) contacts protected with epoxy and Teflon tape. The

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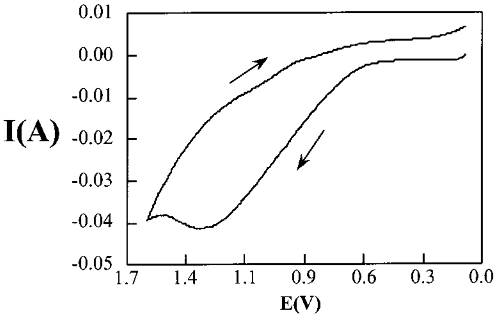

Figure 1. Cyclic voltammogram of $Ca_{1.5}Nd_{1.5}MnO_4$ in fused nitrates (150 °C, 0.2 M NaOH). Scan rate 20 mV/s

oxidation of silver contacts was determined to contribute less than 1% to the total current in a series of parallel experiments,[8] and does not show up in the recorded cyclic voltammograms. Ag and Pt wires were used as quasireference and counter electrodes, respectively. The eutectic $LiNO_3-NaNO_3-KNO_3$ (0.30:0.17:0.53 molar ratio; melting point 125 °C) was used in all experiments with a working temperature of 150 °C to prevent solidification. The electrochemical cells were bubbled with argon for up to 12 h when using fused nitrates, to remove oxygen and humidity and ensure homogeneity. Addition of solid NaOH to achieve 0.2 M concentrations was performed as soon as the nitrates were melted. Pellets of the oxides were introduced into the baths, and the rest potential was equilibrated within a few hours. No change was observed in properties due to immersion alone. Cyclic voltammograms (CVs) (see a representative one in Figure 1; the remainder can be found in the Supporting Information) were run to evaluate the appropriate value of the applied potentials during constant potential electrolysis. A more detailed study of the CVs and their reversibility is being carried out for a wider set of samples. After electrochemical oxidations involving 1×10^6 C/mol of Mn (5, 16, and 66 h, respectively, for the Nd-, Dy-, and Y-doped samples), the samples were quenched from 150 °C to room temperature or liquid nitrogen temperatures using water or liquid nitrogen, with no apparent changes observed among the two types of cooling. The samples were characterized in different parts of the pellet, as previously described,[6–8] by X-ray powder diffraction, chemical analysis, and measurement of their magnetic properties. Chemical analysis involved elemental analysis of K, Li, and Mn (by ICP and atomic absorption) and redox analysis by iodometry. Redox analysis in particular turned out to be difficult and ambiguous for electrochemically oxidized materials, as described previously[4–6,8] (solubility problems in sulfuric acid, impurities of nitrates (that prevent TGA analysis), and the lack of reactivity vs iodide being indicative of the existence of peroxide or superoxide). According to iodometric analysis, the oxygen content remains constant after electrochemical oxidation for the Dy and Nd derivatives and increases for the Y derivative (see Table 1). On the contrary, magnetic measurements show that a significant change has occurred. Elemental analysis showed the presence of Li and K nitrates in the oxide (up to 2 wt % in the case of K) that could not be removed effectively by washing.

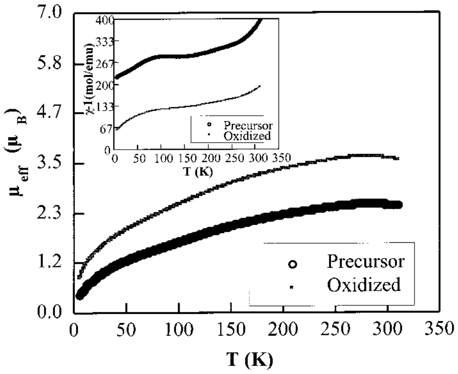

Figure 2. μ_{eff} vs T for $Ca_{1.7}Y_{0.3}MnO_4$ [$H = 10000$ G; μ_{eff} calculated as $(8\chi_M T)^{1/2}$]. Measured in field-cooled, ramp mode. Inset: inverse molar susceptibility.

Table 1. Experimental Parameters of Precursor, Oxidized Materials, and Oxidation Parameters

	iodometry-based O content					
metal	precursor	oxidized	E_{appl} V vs Ag	I_{range} (A)	ρ_{prec} (Ω cm)	ρ_{ox} (Ω cm)
Nd	4.08	4.08	1.3	0.01−0.05	surf. corr	
Dy	4.03	4.03	1.2	0.01	surf. corr	
Y	3.86	3.96	1.2	0.006−0.02	1.08	10.2

Magnetic measurements for the precursor and electrochemically oxidized samples were performed on a SQUID magnetometer at fields of 2000 and 10 000 G. Experiments were run under field-cooled conditions, from 5 to 300 K using ramp mode sequences. Molar susceptibilities were calculated from experimental magnetization values as $\chi_M = M/(Hm)$MW; μ_{eff} values were calculated as $(8\chi_M T)^{1/2}$. No fittings to eliminate temperature independent susceptibility have been applied. The room temperature and liquid nitrogen resistivity was measured in Y derivatives using the Van der Paw method (four contacts). Surface corrosion in the Dy and Nd derivatives allowed us to make just an estimation of resistance changes based on two contacts. The room-temperature resistivity changes observed are from 1 Ω cm (precursor) to 10 Ω cm (oxidized). The 77 K resistivity remains nearly unchanged at 1.3 MΩ cm. X-ray powder diffraction patterns[6] (Supporting Information) for precursor and electrochemically oxidized samples do not present any appreciable differences, neither they show decomposition of the material.

Inverse susceptibility plots show that all curves tend to zero at low temperatures. However, extrapolation of the high-temperature data is complex. If the highest temperature range is taken, the intercept is positive, but that rapidly changes to a negative intercept when the set of data is expanded slightly, even above 250 K. This is evidence for a complex behavior that is currently the subject of study on a wider set of samples.

On the other hand, the effective magnetic moment at room temperature, calculated as $\mu_{eff} = (8\chi T)^{1/2}$ (where χ is the experimental molar susceptibility), shows an appreciable change in the case where the only magnetic element is $Mn^{3+,4+}$. Thus, for $Ca_{1.7}Y_{0.3}MnO_4$, the room-temperature magnetic moment changes from 2.6 μ_B in the precursor to 3.5 μ_B in the oxidized sample. Since the contributions from isolated Mn^{3+} and Mn^{4+} should be 4.8 and 3.8 μ_B, respectively,[10] an increase in Mn^{4+}

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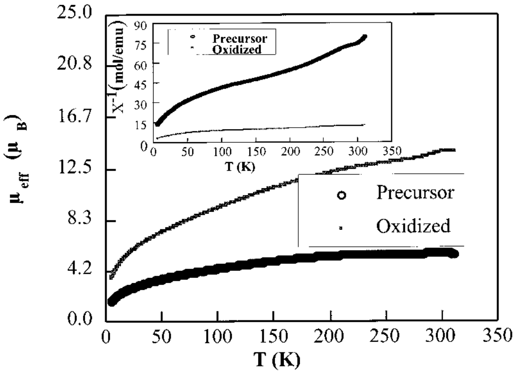

Figure 3. μ_{eff} vs T for $Ca_{1.5}Nd_{0.5}MnO_4$ [H = 10000 G; μ_{eff} calculated as $(8\chi_{M}T)^{1/2}$). Measured in field-cooled, ramp mode. Inset: inverse molar susceptibility.

content due to oxidation should lower the value of μ_{eff}. The opposite case is observed. Given the antiferromagnetic (AF) coupling existing in the precursor, the increase in moments implies a partial breaking of the AF coupling. The temperature dependence of the moment vs T shows (see Figure 2) that antiferromagnetic coupling among Mn ions exists after oxidation, but the moment is always higher than that of the precursor.

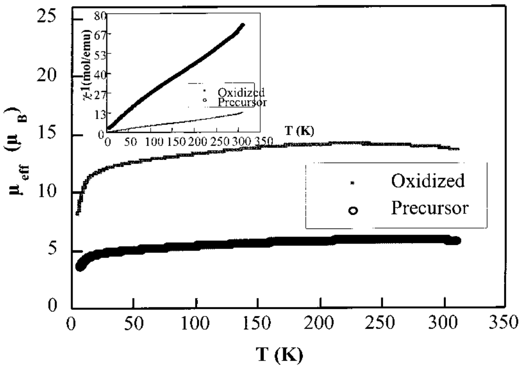

Figure 4. μ_{eff} vs T for $Ca_{1.7}Dy_{0.3}MnO_4$ [H = 2000 G; μ_{eff} calculated as $(8\chi_{M}T)^{1/2}$]. Measured in field-cooled, ramp mode. Inset: inverse molar susceptibility.

The change in magnetic properties upon electrochemical oxidation in the two cases in which the lanthanide is also magnetic is much more dramatic: 300% in the room-temperature effective moment (See Figures 3 and 4). In the case of $Ca_{1.5}Nd_{0.5}MnO_4$, μ_{eff} at room temperature changes from a value near 5.0 μ_B to 13.5 μ_B upon oxidation. For $Ca_{1.7}Dy_{0.3}MnO_4$, the change is from 6 to 13.9 μ_B at a lower field (2000 G). Taking into account the individual ion contribution to the magnetic properties (4.8, 3.8, 3.7, and 10.6 μ_B for Mn^{3+}, Mn^{4+}, Nd^{3+}, and Dy^{3+}, respectively at room temperature[10]), the expected values of μ_{eff} if the AF coupling is broken should be 5.06 μ_B in the first case (Nd^{3+} doping) and 7.36 μ_B in the second case (Dy^{3+} doping). Therefore, the difference between the expected maximum μ_{eff} values (no antiferromagnetic coupling) and the experimental ones is considerable. While these data alone seem to imply some type of ferromagnetic contribution, the temperature dependence of the moment is more consistent with the existence of a decreased antiferromagnetic coupling. A possible explanation is the existence of a random exchange ferromagnetic contribution (RKKY type) to the magnetic properties, caused by the itinerant holes introduced by electrochemical oxidation. A preliminary study shows a large dependence of the magnetic susceptibility with the applied magnetic field (room temperature μ_{eff} doubles) in the range 2000−10 000 G.

The possible practical relevance of this magnetic change, as well as the reversibility of the process, is being studied. Also the study is being extended to a larger set of isostructural manganese oxides.

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Supporting Information Available: X-ray powder diffraction patterns for precursor and oxidized materials and CV for all precursor materials (7 pages). See any current masthead page for ordering information and Internet access instructions.

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