JOURNAL OF APPLIED ELECTROCHEMISTRY **26** (1996) 439–442

Control of oxygen deficiency in $Ca_{1-x}La_xMnO_{3-\delta}$ and its cathodic properties in alkaline solution

T. ESAKA, M. KAMATA, M. OHNISHI

Faculty of Engineering, Tottori University, Minami 4-101, Koyamacho, Tottori 680, Japan

Received 7 June 1995; revised 14 September 1995

Ceramic samples of composition $Ca_{0.9}La_{0.1}MnO_{3-\delta}$ having various oxygen contents were prepared by a quenching method under nitrogen atmosphere. As the $3-\delta$ value decreased from 2.97 to 2.79, the sample conductivity decreased from 10^2 to 10^{-1} S cm^{-1}. The porous ceramic samples showed good properties as cathode materials in alkaline solution without using conductive material such as graphite, but the discharge capacity decreased with decreasing sample conductivity. The discharge termination is explained by a simple model considering dissipation of the conductive path (high conductivity core) present in the porous sintered ceramic.

1. Introduction

Perovskite-type oxides ABO_3 having transition metals, whose valence in the B site is easily changeable, are generally known to show the following properties: (i) very mobile oxide ions in the crystal, (ii) easily variable oxygen contents and (iii) high electronic conductivity [1, 2]. The present authors reported that substituted perovskite-type oxides such as $Ca_{1-x}Ln_xMnO_{3-\delta}$ (Ln = La, Ce) show high electronic conductivity by a hopping mechanism due to the valence change of manganese and easily change the oxygen contents in their lattices [3, 4]. Moreover, these compounds can include high contents of Mn^{4+} (more than 80%) in ceramic bodies prepared by sintering in air. Considering these properties, these oxides are expected to be candidates as high electronic conductivity active materials in alkaline batteries. If they could be used as practical active materials without conductive agents such as graphite, the discharge capacities would be greater.

Recently the following results were obtained [5, 6]: (i) these perovskite-type oxides have properties which make them suitable as cathode materials for alkaline batteries, (ii) the discharge capacity is larger for $Ca_{0.9}La_{0.1}MnO_{3-\delta}$ than for $Ca_{0.9}Ce_{0.1}MnO_{3-\delta}$, and (iii) the discharge capacity is larger in LiOH solution than in KOH solution. These ceramic active materials include no conductive agents such as graphite, the discharge was considered to terminate when the conductivity of the ceramic itself fell below a certain threshold value. To examine the relation between conductivity and cathodic dischargeability, we prepared samples having various oxygen contents and investigated their discharge performances.

2. Experimental procedure

To investigate the cathodic properties of oxide samples having various oxygen contents, the present sample composition (cation ratio) was fixed as $Ca_{0.9}La_{0.1}MnO_{3-\delta}$. The sample was prepared from reagent grade powder of $CaCO_3$, Mn_2O_3 and La_2O_3. The materials were weighed in the defined molar ratios, mixed in an agate mortar and fired at 1200 °C in air for 5 h. To obtain dense samples for conductivity measurement, the finely ground samples were pressed into discs (about 15 mm diam. × 2 mm thickness) at a pressure of 200 MPa and sintered again at 1300 °C in air for 5 h. The porous samples were obtained for cathodic property measurements using almost the same process, but the NH_4HCO_3 powder was mixed in the ratio of 50 wt % to the ground sample before pressing at 65 MPa. TG measurements were performed to obtain the change in oxygen content in the samples under air and nitrogen. The oxygen content in the sample was controlled by sample quenching from various temperatures under nitrogen atmosphere.

To investigate the properties of the oxides as cathode active materials in alkaline batteries, each sintered porous sample (1 g, about 15 mm diam × 2 mm thickness), containing no graphite, was set in a polyethylene holder having a planar Pt terminal and was gradually immersed in 15% KOH solution. D.c. current was passed between the cathode material and a Pt plate prepared as a counter electrode in the KOH solution [4].

The electronic conductivity of the oxides was measured by the d.c. four terminal method using rectangular samples (about 2 mm × 2 mm area by 12 mm length) cut out from the dense disk-shapes mentioned above.

3. Results and discussion

According to TG measurement of the starting material mixture ($CaCO_3$, Mn_2O_3 and La_2O_3) corresponding to the composition $Ca_{0.9}La_{0.1}MnO_{3-\delta}$, the $3-\delta$ value was determined to be 2.97 for preparation

0021-891X © 1996 Chapman & Hall

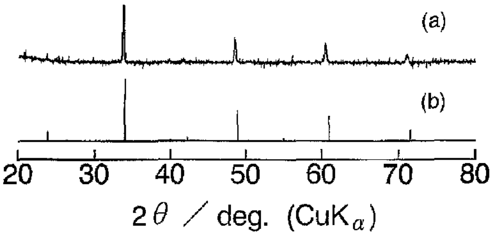


Fig. 1. Xray diffraction patterns. (a) $Ca_{0.9}La_{0.1}MnO_{2.97}$ (sintered sample) and (b) $CaMnO_{3-\delta}$ (JCPDS card).

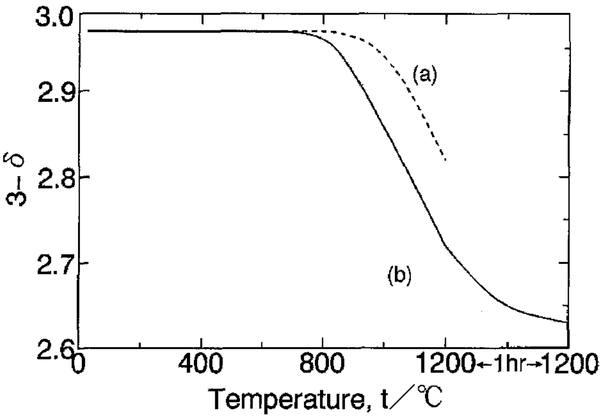
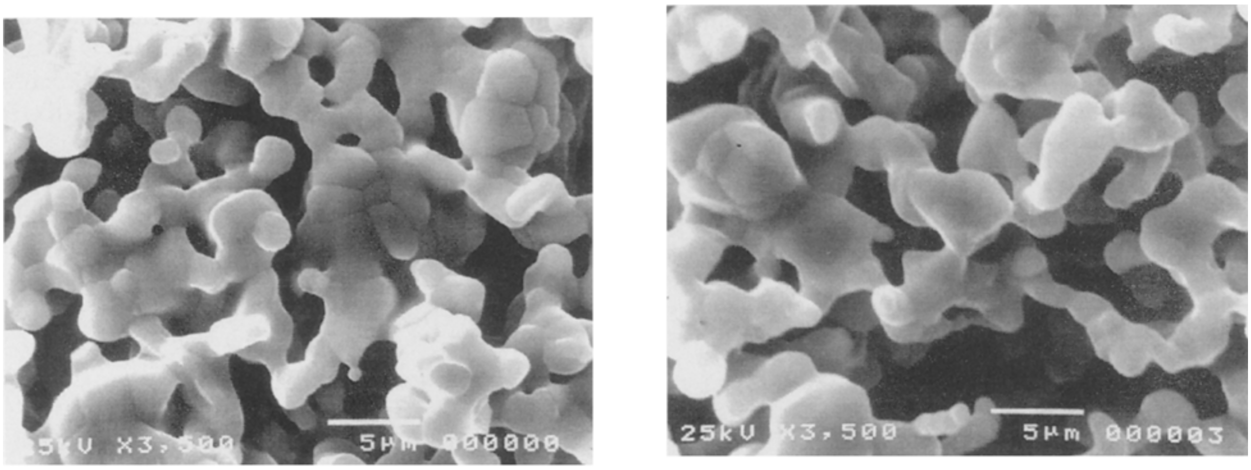


Fig. 2. Temperature dependence of nonstoichiometry of $Ca_{0.9}La_{0.1}MnO_{3-\delta}$. Heating rate: 10 °C min^{-1} (a) in air and (b) in nitrogen gas.

in air. Figure 1 shows the X-ray diffraction pattern together with that calculated from the JCPDS card. The good coincidence denotes that the substituted perovskite-type oxide phase is obtained by this experimental procedure. TG measurement was also carried out for the sample prefired in air. If the starting sample composition mentioned above and the sample weight used are known, the weight change with temperature is easily converted to the variation of nonstoichiometry $(3-\delta)$ of $Ca_{0.9}La_{0.1}MnO_{3-\delta}$. Figure 2 shows the temperature dependence of $3-\delta$ of $Ca_{0.9}La_{0.1}MnO_{3-\delta}$ in air and nitrogen. In both atmospheres, the $3-\delta$ values began to decrease at about 800 °C. The extent of decreasing oxygen is higher in nitrogen than in air. When the sample was kept in nitrogen at 1000 °C for 1 h, the oxygen content decreased further, as shown in the same Figure, which means the oxygen content does not reach an equilibrium value. Therefore, as mentioned in Section 2, it is possible to obtain samples having various oxygen contents by quenching from the corresponding temperature in nitrogen. In this case, the TG measurements were also carried out to check that the actual oxygen contents in the quenched samples coincided with the values expected.

Figure 3 shows the SEM photographs of representative samples. It is clear that grains are combined to form a network-like structure in the porous ceramics, and that oxygen deficiency does not cause apparent morphological changes. Furthermore, from X-ray diffraction patterns, these samples having various oxygen contents were found to have the perovskite-type crystal structure. The conductivity variation against the $3-\delta$ of the samples is presented in Fig. 4. The sample prepared in air has a $3-\delta$ value of 2.97 and shows high electronic conductivity above 10^2 S cm^{-1}. The conductivity decreases linearly with decreasing $3-\delta$ value in this semilogarithmic graph. The decrease in the $3-\delta$ value is associated with a decrease in the Mn^{4+} content due to reduction from Mn^{4+} to Mn^{3+}. Therefore, the decrease in the Mn^{4+} content is a reason for the conductivity decrease.

Figure 5 shows the discharge curves of the representative ceramic cathodes $Ca_{0.9}La_{0.1}MnO_{3-\delta}$ (about 60% porosity) on 10 mA discharge in KOH solution at 25 °C. The open circuit potential is 70 ~ 80 mV (vs Hg/HgO reference electrode) for each sample. When discharge starts, the sample of $3-\delta=2.97$ showed an initial sharp potential drop and a subsequent plateau region at about −360 mV for 14.2 h. Thereafter, the potential dropped suddenly to evolve hydrogen gas. The plateau region became shorter with decreasing $3-\delta$. The relationship between the discharge capacity and the $3-\delta$ value in $Ca_{0.9}La_{0.1}MnO_{3-\delta}$ is indicated in Fig. 6. A dashed line represents the ideal discharge capacity, which is obtained by considering that all Mn^{4+} present in



(a) (b)

Fig. 3. SEM photographs of $Ca_{0.9}La_{0.1}MnO_{3-\delta}$. (a) $3-\delta=2.97$ and (b) $3-\delta=2.66$.

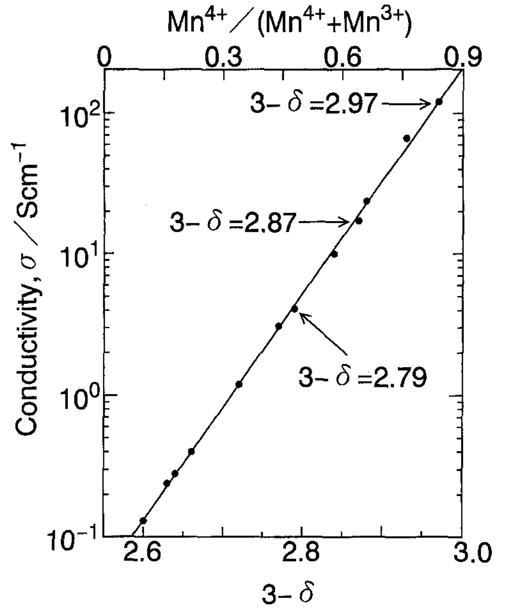


Fig. 4. Conductivity variation with $3-\delta$ value in $Ca_{0.9}La_{0.1}MnO_{3-\delta}$ at 25 °C.

each sample having various $3-\delta$ values, are reduced to Mn^{3+} at the end of discharge. The actual discharge capacity decreased with decreasing $3-\delta$ value and becomes almost zero at $3-\delta = 2.79$. Therefore, the discharge efficiency, calculated from the ratio of the actual capacity to the ideal one, similarly decreases with decreasing $3-\delta$ value. The reason for this is not yet clear, because although it has been found that the reduction of Mn^{4+} to Mn^{3+} is essential for the discharge [7], the cathodic reaction is not fully understood. The following hypotheses may be suggested: (i) the sample oxides examined here as active materials are not reduced homogeneously, (ii) the reducing reactions proceed gradually from the outside to the inside of grains in the porous oxides, and (iii) the reactions terminate when the conductance of the nontreated part (high conductivity core) in the active materials reaches a defined threshold value. It has been already confirmed that, although the surfaces of the discharged oxides show more than three orders of magnitude lower conductivities than those of the as-prepared oxides, the core portions of the discharged oxides maintain high conductivity, almost the same as that of the initial oxide surfaces.

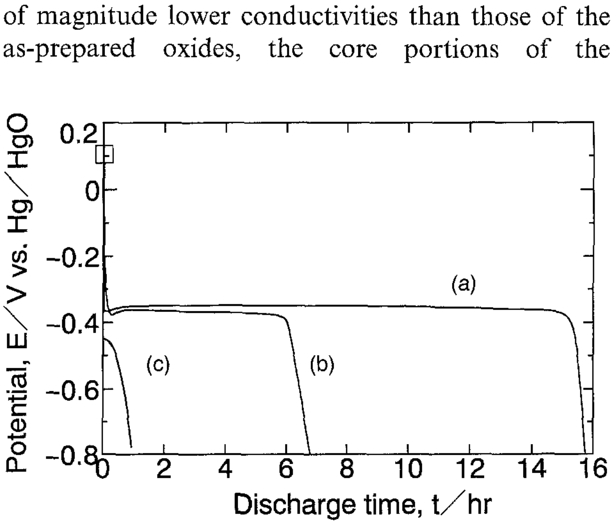


Fig. 5. 10 mA discharge curves for 1 g porous disc of $Ca_{0.9}La_{0.1}MnO_{3-\delta}$ in 15% KOH solution at 25 °C. (a) $3-\delta = 2.97$, (b) 2.87 and (c) 2.79.

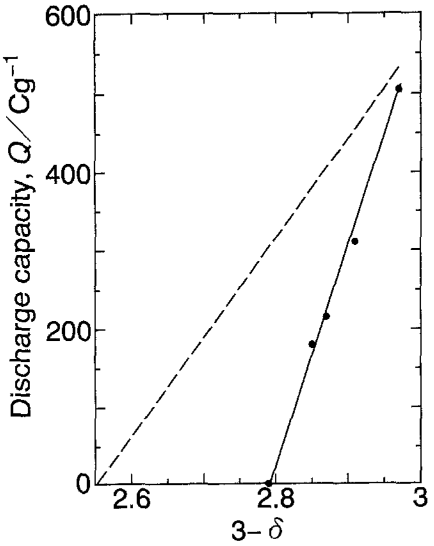


Fig. 6. Relationship between discharge capacity and $3-\delta$ in $Ca_{0.9}La_{0.1}MnO_{3-\delta}$. A dashed line shows an ideal line considering the reduction of all Mn^{4+} to Mn^{3+}.

This situation is schematically illustrated in Fig. 7, where the actual three-dimensional network structure is represented as a cylindrical pellet. When the cathodic reactions proceed according to the above assumptions, the reaction period for the high conductivity cathode material will be longer than the period for the low conductivity cathode material. To confirm this assertion by calculation, we focused on the $3-\delta = 2.87$ sample, the discharge efficiency of which is about 50%, and calculate the conductance of the nonreacted part (high conductivity core) remaining in the sample at the end of discharge from its actual discharge efficiency (53%) and its initial conductivity ($17.2\,S\,cm^{-1}$). In case of the $3-\delta = 2.87$ sample, the conductance is obtained as $17.2 \times (1-0.53) = 8.0$, whereas the conductivity values are taken as conductances to simplify the expression in uniform-shaped samples, 17.2 is the initial conductance of the oxide and 0.53 is the discharge efficiency. If the value of 8.0, a so-called threshold, is independent of the sample, the discharge capacity can be calculated for the other samples. For the $3-\delta = 2.97$ sample, for example, the initial conductivity is $120\,S\,cm^{-1}$. Therefore, from the equation, $(120-8)/120 = 0.93$, the discharge efficiency is 93%, which agrees well with the measured value. Using analogous calculations, discharge capacities were obtained over the whole range. The result is shown by the bold line in Fig. 8. Even though the model is simple, good coincidence is observed.

4. Conclusion

Oxygen contents in perovskite-type oxides $Ca_{0.9}La_{0.1}MnO_{3-\delta}$, was controlled by quenching from high temperatures in nitrogen. Although the ceramic oxides with porous structure have favourable properties as cathode materials for alkaline batteries,

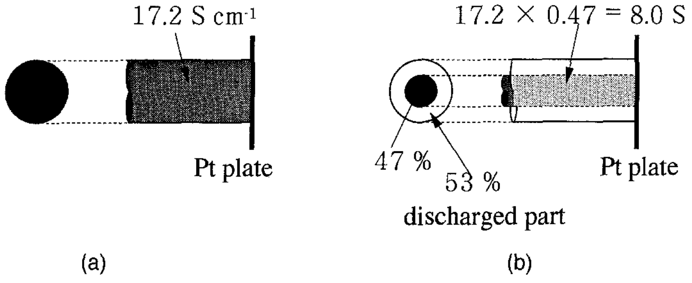


Fig. 7. Schematic illustration of dissipation of conductive path for the $3-\delta=2.87$ sample. (a) Before discharge and (b) after discharge.

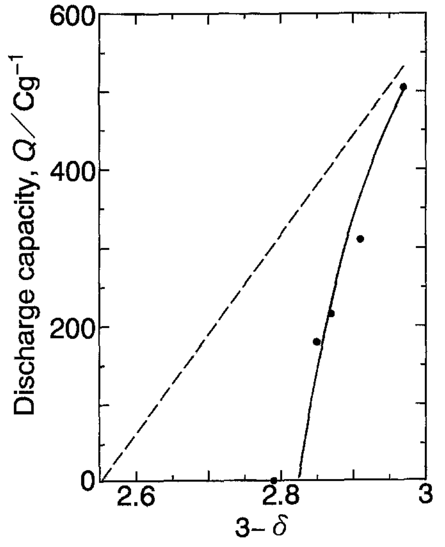


Fig. 8. Comparison of measured discharge capacity with the calculated one based on the conductive path model. The full line shows the calculated discharge capacity based on the assumption mentioned in the text.

the decrease in oxygen content causes, not only a decrease in discharge capacity, but a decrease in discharge efficiency. This is due to conductivity decrease caused by the decrease in oxygen content. This phenomenon has been explained by a simple model considering a conductive core in the porous oxide.

References

[1] V. Joshi, O. Parkash, G. N. Rao and C. N. R. Rao, *J. Chem. Soc. Faraday Trans.* **2** (1979) 75.

[2] N. F. Mott, *Adv. Phys.* **21** (1972) 785.

[3] H. Iwahara, T. Esaka and H. Hamajima, *Denki Kagaku* **57** (1989) 591.

[4] T. Esaka, H. Morimoto and H. Iwahara, *J. Appl. Electrochem.* **22** (1992) 821.

[5] T. Esaka, H. Morimoto and M. Kamata, *Denki Kagaku* **61** (1993) 1028.

[6] T. Esaka and H. Morimoto, *Prog. In Batt. & Batt. Mat.* **12** (1993) 1.

[7] H. Morimoto, M. Kamata and T. Esaka. *J. Electrochem. Soc.*, submitted.