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Nonstoichiometry in perovskite-type oxide $Ca_{1-x}Ce_xMnO_{3-\delta}$ and its properties in alkaline solution

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Nonstoichiometry in high conductivity perovskite-type oxide $Ca_{1-x}Ce_xMnO_{3-\delta}$ was investigated. At room temperature in air, the $3 - \delta$ value was determined to be 2.91 for $CaMnO_{3-\delta}$, which meant that 82% of manganese was tetravalent. Although the $3 - \delta$ value increased by increasing the cerium content, i.e. by doping of higher valent cation into the calcium site, the quantity of Mn^{4+} in the sample oxide essentially decreased with increasing x. The oxygen contents change reversibly with temperature in air. Change of oxygen content was also observed on discharging this oxide as the cathode material of a battery in alkaline solution. Surprisingly, the sintered ceramics of this oxide worked as a cathode without mixing with a conductive powder such as graphite. Considering the discharging performance, this oxide may be a candidate for the cathode material of the alkaline battery.

1. Introduction

Perovskite-type oxides having transition metals such as Fe, Co and Mn in the B sites are generally shown by the formula $ABO_{3-\delta}$, where δ is the number of oxygen deficiencies in the crystal. These oxides have lately attracted special interest for the redox catalyst and/or the electrode material of high temperature fuel cells [1–4], because these show fairly high electronic conductivity due to the valence change of B metal ions and easily varied oxygen contents in their lattices. Considering these properties, this type of oxide is also expected to be a candidate as a cathode material for alkaline batteries.

Recently, we reported that the substituted perovskite-type oxide ($Ca_{1-x}Ce_xMnO_{3-\delta}$) is a candidate for the air-electrode material of the SOFC [5]. The following results were obtained: (i) in the formula $Ca_{1-x}Ce_xMnO_{3-\delta}$, the samples of $x \leqslant 0.15$ showed X-ray diffraction patterns of the perovskite-type cubic crystal and the samples of $x > 0.2$ a mixed phase; (ii) these oxides are chemically stable and show fairly high electronic conductivities from room temperature to 1100° C; and (iii) the conductivity in this oxide system increased with increasing Ce content up to $x = 0.1$. The value for $Ca_{0.9}Ce_{0.1}MnO_{3-\delta}$ was $2.9 \times 10^2\,S\,cm^{-1}$ at room temperature. Further substitution of Ce for Ca decreased the conductivity. In this paper, based on the idea of using the oxides as a cathode material for alkaline batteries, the nonstoichiometry of $Ca_{1-x}Ce_xMnO_{3-\delta}$ and its properties in alkaline solution has been investigated.

2. Experimental details

The samples were prepared from reagent grade powders of $CaCO_3$, Mn_2O_3 and CeO_2. These materials were weighed in the defined molar ratios, mixed in an agate mortar, and fired at 1200° C in air for 5 h. Thereafter, the samples were finely powdered and used for various measurements. In order to get sintered porous samples as cathode materials for alkaline batteries, the finely powdered samples were mixed with some NH_4HCO_3, pressed ($600\,kg\,cm^{-2}$) into disc-shape (15–16 mm diam. by 2–3 mm thickness) and sintered at 1300° C in air for 5 h. The sample porosity was controlled by NH_4HCO_3 content (55–62% porosity for 33 wt % of NH_4HCO_3). TG measurement was performed to check the change of oxygen content in the samples.

In order to investigate the properties of the sample as a cathode active material for alkaline batteries, the test electrode was prepared as follows. First, the powdery sample mixed with graphte (23 wt %) was put into a polyethylene holder in which a filter paper had been previously placed in the bottom to prevent outflow of the sample. Next, this was pressed by a polyethylene cap with a platinum plate connected to a platinum lead. The sintered porous sample, with no graphite, was also used afterwards as an active material. These were immersed in the 15% KOH solution (Fig. 1), and current was passed between the test electrode (cathode material) and a counter electrode (Pt plate). In each case, the cathode potential was measured against a Hg/HgO electrode. From the discharge curves, the discharge capacities of the cathode

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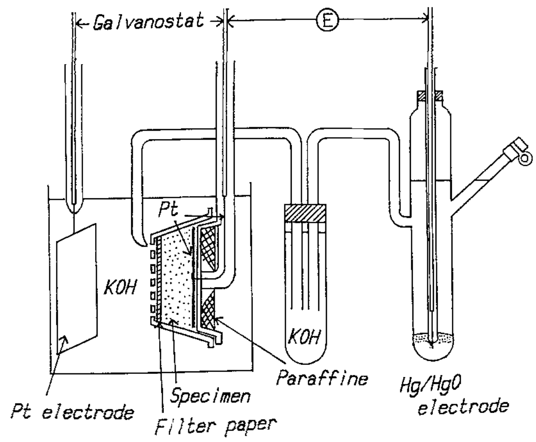

Fig. 1. Schematic diagram of a cell.

materials were calculated and compared with the TGA results as to nonstoichiometry of the samples.

3. Results and discussion

3.1. *Nonstoichiometry of samples*

From TG measurements made in air for the mixture of raw materials of each sample, the $3 - \delta$ values in $Ca_{1-x}Ce_xMnO_{3-\delta}$ can be calculated. For example, these are 2.91 and 2.93 for the $x = 0$ and $x = 0.1$ samples, respectively. The average valence of manganese in all samples could be also determined from the same TGA data, if the valence of cerium was exactly confirmed. Various methods were used for this such as chemical analysis (titration), ESCA etc. Although reliable data were not obtained in each case, it was concluded that the cerium was tetravalent from the discharge characteristics as mentioned below.

Figure 2 shows the variation of the average valence of manganese with cerium content at room temperature. All the manganese is not tetravalent even in the $x = 0$ sample fired in air. By increasing the cerium content in the $CaMnO_{3-\delta}$-type solid solution, the content of trivalent manganese increases and the average valence decreases. This behaviour is a natural result due to the substitution of tri- or tetravalent metal for the calcium sites. As reported previously, high electronic conduction based on a $Mn^{4+} \leftrightarrow Mn^{3+}$ hopping mechanism is observed in the $x = 0.10$ sample ($2.9 \times 10^{-2}\,S\,cm^{-1}$) [5].

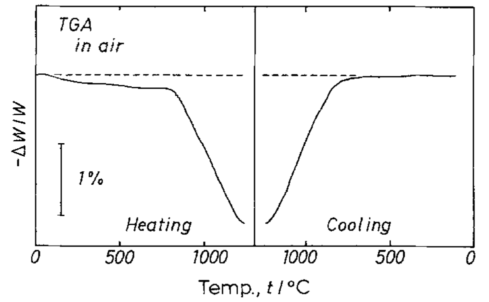

Fig. 3. TGA chart of $CaMnO_{3-\delta}$. Heating/cooling rate: $10°C\,min^{-1}$.

TG measurements were also carried out for the samples pre-fired in air. As indicated on the TGA charts of the $x = 0$ sample in Fig. 3, a reversible weight change was observed (some weight decrease on heating and some weight increase on cooling). In the other samples, $x = 0.05$, 0.10 and 0.15, similar results were obtained. As they were considered to correspond to oxygen transfer, these data were converted to the temperature dependence of the nonstoichiometry $(3 - \delta)$ in $Ca_{1-x}Ce_xMnO_{3-\delta}$ for the representative samples (Fig. 4). By TGA in the different oxygen atmospheres, the $3 - \delta$ value was also found to decrease with decreasing oxygen partial pressure, although, in a nitrogen atmosphere ($P_{O_2} = 1.2 \times 10^{-4}$ atm), a steady state was not achieved over 10 h, even at 1000° C. From these results, the oxygen contents in these oxides were considered to be changeable, which means that oxides may be usable as active materials for batteries.

3.2. *Electrode properties*

The electrodes mixed with the powdery sample and graphite showed fairly stable e.m.f.'s of 0–20 mV(Hg/HgO) at 25° C. Figure 5 indicates the discharge curves of representative samples. In each case, a sharp potential drop was initially observed. Thereafter, the potential recovered to several tens of millivolts. Further discharge lowered the potential with time, showing a

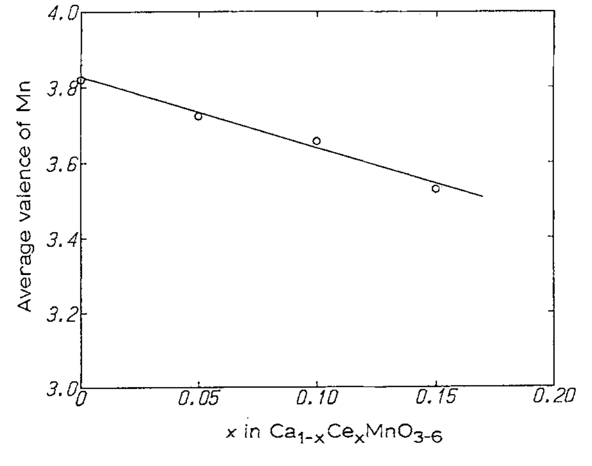

Fig. 2. Average valence of manganese in $Ca_{1-x}Ce_xMnO_{3-\delta}$ assuming all cerium being tetravelent at 25° C in air.

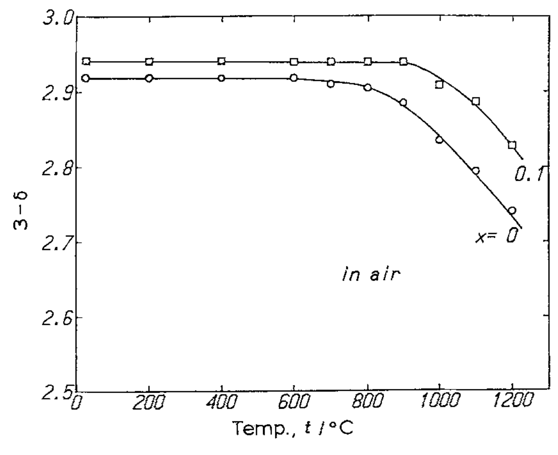

Fig. 4. Temperature dependence of non-stoichiometry in $Ca_{1-x}Ce_xMnO_{3-\delta}$.

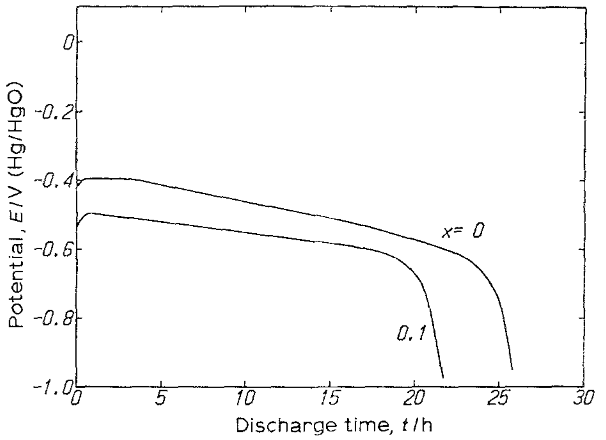

Fig. 5. Discharge curves of powdery oxide $Ca_{1-x}Ce_xMnO_{3-\delta}$ (1 g) mixed with graphite. Cathodic current 10 mA; temp. 25° C; 15% KOH.

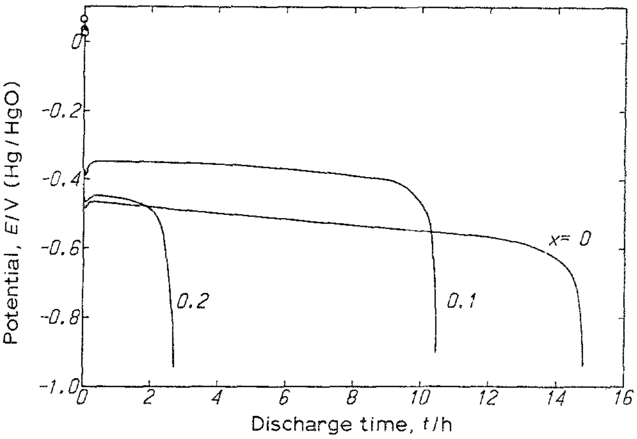

Fig. 6. Discharge curves of sintered porous oxide $Ca_{1-x}Ce_xMnO_{3-\delta}$ (1 g). Cathodic current 10 mA; temp. 25° C; 15% KOH.

pseudo plateau region. After about 20–25 h, the potential dropped suddenly to evolve hydrogen gas. At the end of the 24 h discharge for the $x = 0$ sample, the average valence of manganese was 2.56, that is about 45% of the manganese is reduced to divalent. Here, we exclude the reduction of Ce tetravalent to Ce trivalent state, since the electrode composed using CeO_2 mixed with graphite did not work as a cathode material at all. In the case of the $x = 0.1$ sample, the situation is almost the same as that of the $x = 0$ sample, although the discharge capacity decreases from 860 to 720 C g^{-1}.

After a series of discharge experiments, the sample oxides were found to become fairly stiff solids having good electrical conductivity due to the included graphite. In this condition, the good and inherent discharge performance was not obtainable due to its increased cathode polarization. Compared with the conventional cathode material, MnO_2, for alkaline batteries the oxides examined here showed a much higher electronic conductivity. Therefore, the use of these oxides as cathode materials without graphite was investigated. Sintered, rather than power, samples were used.

These electrodes showed a stable e.m.f. of about 50–80 mV (Hg/HgO) at 25° C. But, sintered samples having less than 20% porosity worked only as a hydrogen evolution electrode on galvanostatic discharging. Figure 6 represents the discharge curves of the porous oxide cathode (55–62% porosity) on 10 mA discharge. In all cases, sharp potential drops similar to that in Fig. 5 were initially observed. The $x = 0.1$ sample showed a plateau at about -380 mV for 10 h and thereafter the potential decreased again due to hydrogen evolution. Although the $x = 0$ sample showed a wider pseudo plateau region, the potential was about 100 mV lower than that of the $x = 0.1$ sample. This might be due to the fact that the electronic conductivity of the $x = 0$ sample is two orders of magnitude lower than that of the $x = 0.1$ sample at room temperature [5]. In the $x = 0.2$ sample with the mixed crystal phase, the discharge property was not so good and the plateau region was observed for only 2 h. Assuming the end potential of discharge to be -650 mV for $x = 0$ and -450 mV for $x = 0.1$, the discharge capacity for each sample was calculated to be 514 and 360 C g^{-1}. These data are different from those of Fig. 5 in two ways: (i) the plateau region becomes flatter and (ii) the time to hydrogen evolution becomes shorter. As to the first point, no explanation can be offered. As to the second point, the electronic conductivity of the samples was considered to play an important role, because it was found that the conductivity of the discharged oxide became several orders of magnitude lower. This meant that the sample oxide lost its own conductivity when the tetravalent manganeses were partly reduced to the lower valent state.

Based on the discharge capacity 514 C g^{-1} the average valence of manganese after discharge was calculated to be 3.06 for the $x = 0$ sample, which indicates that the discharge terminates when the tetravalent manganese almost totally changes to the trivalent state. As mentioned previously, as long as the conductivity is the main problem for discharge termination, the situation would be the same in the $x = 0.1$ sample. If we assume trivalent cerium, the average valence of manganese after discharge is 3.19, which is considerably higher than 3.06. In this valence state, 20% of manganese is tetravalent and the discharge capacity is expected to be retained. If we assume tetravalent cerium and no reduction of Ce^{4+} to Ce^{3+}, the average valence of manganese after discharge is calculated to be 3.09, which is close to 3.06 for the $x = 0$ sample. These results show the existence of the tetravalent cerium in the oxide crystal.

Table 1 summarizes the change in the average valence of manganese and the oxygen utilization by

Table 1. Change in valence of manganese and oxygen utilization in $Ca_{1-x}Ce_xMnO_{3-\delta}$ by discharge

Composition X	Average valence of Manganese		Oxygen utilization
	Before discharge	After discharge	
0.0	3.82	3.06	0.92
0.1	3.67	3.09	0.86

discharging. The oxygen utilization, 0.86, for the $x = 0.1$ sample means that 86% of the oxygen, which is changeable by the valence change of manganese, is used for the discharge. This is equivalent to 86% of Mn^{4+} in the initial oxide changing to Mn^{3+} during discharge. Comparing with the sample oxides mixed with graphite, the sintered porous sample showed lower discharge capacity by non-utilization of $Mn^{3+} \rightarrow Mn^{2+}$ reduction. When these high conductivity oxides are used as the cathode material in alkaline batteries, several advantages will accrue: (i) as the conductive powders such as graphite are unnecessary, the side reaction (for example, the reduction of the cathode oxide by graphite) can be avoided; and (ii) the oxides can be prepared by sintering only. However, the problem of the initial sharp potential drop, requires further investigation prior to actual application.

4. Conclusion

The nonstoichiometry in the perovskite-type oxide solid solution, $Ca_{1-x}Ce_xMnO_{3-\delta}$ ($x = 0$–0.15) fired in air was determined by TGA. The $3 - \delta$ values are present in the range 2.91–2.94 at room temperature in air. With increasing Ce content in the oxide, the $3 - \delta$ increases slightly but the average valence of Mn essentially decreases. On cathodic discharge in alkaline solution, the oxygen contents in the samples decrease, together with the reduction of manganese. The samples not only show fairly good discharge performance in the case of the powder mixed with graphite but also in the case of the porous ceramics. In the latter case, the cathodic discharge terminates when a greater part of tetravalent manganese is reduced to the trivalent state, and thereby, the hopping conductivity in the sample becomes much lower. From the discharge characteristics of the $x = 0$ and $x = 0.1$ ceramic samples, cerium in the sample oxide is considered to be tetravalent throughout the discharge. Considering the discharge capacity and the high electronic conductivity, the ceramic sample oxide $Ca_{0.9}Ce_{0.1}MnO_{3-\delta}$ containing no graphite is expected to be a candidate for the active material of the alkaline battery.

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