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Praseodymium–calcium manganites ($Pr_{1-x}Ca_xMnO_3$) as electrode catalyst for oxygen reduction in alkaline solution

T. HYODO, M. HAYASHI, S. MITSUTAKE, N. MIURA, N. YAMAZOE

Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Kasuga-shi, Fukuoka 816, Japan

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1. Introduction

Gas diffusion-type electrodes have potentiality in various energy-related fields, such as brine electrolysis, fuel cells and metal–air batteries. In practice, however, their use has been limited to low-power coin-type zinc–air batteries only. To be applied in a phosphoric acid fuel-cell or brine electrolyser, it is necessary to make the electrodes more powerful, and for this purpose various electrode catalysts have been tested under practical conditions. Apart from noble metals, such as Pt and Pt-alloy [1], less expensive materials have been examined for the electrode catalytic activity in alkaline solution, including spinel-type oxides [2], pyrochlore-type oxides [3, 4], perovskite-type oxides [5–7] and single-metal oxides [8, 9]. Our attention has been focused on the electrode activity of La-based perovskite-type oxides ($La_{1-x}A'_xBO_3$, $A' =$ Ca or Sr, $B =$ Co, Fe, or Mn) for oxygen-reduction [10–16]. It has been shown that the cobaltites ($B =$ Co) are unstable under the cathodic condition in concentrated alkaline solution, despite their quite high activity [14]. In contrast, the ferrites ($B =$ Fe) are very stable but hardly active [15]. The manganites ($B =$ Mn) seem to be better as practical electrode catalysts with rather high activity as well as acceptable stability under the same severe conditions. In the previous paper [16], we reported that oxygen-reduction activities of manganites, $LnMnO_3$ ($Ln =$ rare earth metal), increased monotonically with increasing ionic radius of Ln^{3+}, the highest electrode performances being with La^{3+} and Pr^{3+}. Unlike La-based perovskite-type oxides, Pr-based ones have been little investigated for oxygen-reduction activity in alkaline solution, though they have been tested for solid oxide fuel cells (SOFC) [17]. In this paper, Pr-based oxides with partial substitution of the alkaline earth metal for A-site, $Pr_{1-x}A'_xMnO_3$ ($A' =$ Ca, Sr, Ba), were examined for their cathodic catalytic activity and stability in gas diffusion-type oxygen electrodes.

2. Experimental details

$Pr_{1-x}A'_xMnO_3$ ($A' =$ Ca, Sr, Ba) were synthesized by an amorphous malate precursor method [18]. The amorphous precursors prepared from malic acid and the nitrates of constituent metals were calcined at 850 °C for 5 h in air. The formation of perovskite-type phase was confirmed by means of X-ray diffraction analysis (Rigaku Denki Co., RINT 2100). The gas diffusion-type electrodes were composed of a gas-supply layer (about 0.25 mm thick, carbon black (AB-7, Denki Kagaku Kogyo Co.) : PTFE (Daikin Kogyo Co.) = 7:3 in weight ratio) and a reaction layer (about 0.15 mm thick, perovskite-type oxide : carbon black (KB(EC600JD), Ketjen Black Int. Co.) : PTFE = 5:3.5:1.5 in weight ratio) with a nickel screen, as reported elsewhere [13]. The polarization curves were measured in 8 M KOH solution at 60 °C under air flow ($100\,cm^3\,min^{-1}$) by means of a potentiostat (Hokuto Denko Co. HA-305).

3. Results and discussion

The polarization curves of the gas diffusion-type oxygen electrodes loaded with or without $Pr_{0.8}A'_{0.2}MnO_3$ ($A' =$ Ca, Sr, Ba) are shown in Fig. 1. The electrode performances were improved significantly with the addition of these oxides, indicating their usefulness as oxygen-reduction catalysts. Among the oxides, the Ca-substituted one gave the highest electrode performance, closely followed by the Sr-substituted one, whereas the Ba-substituted electrode was no better than $PrMnO_3$. For the electrode using $Pr_{0.8}Ca_{0.2}MnO_3$, the current density at −150 mV (vs Hg/HgO), $I_{150\,mV}$, was $260\,mA\,cm^{-2}$, which was an improvement by up to 40% from that attained with $PrMnO_3$.

A series of Ca-substituted oxides, $Pr_{1-x}Ca_xMnO_3$, were subjected to further investigations of catalytic

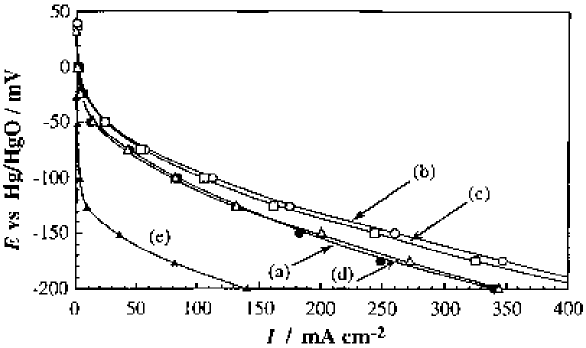

Fig. 1. Cathodic polarization curves of gas diffusion-type oxygen electrodes loaded with and without $Pr_{0.8}A'_{0.2}MnO_3$ ($A' =$ Ca, Sr, Ba, 50 wt %) in 8 M KOH aqueous solution at 60 °C under air flow. Key: (a) $PrMnO_3$; (b) $Pr_{0.8}Ca_{0.2}MnO_3$; (c) $Pr_{0.8}Sr_{0.2}MnO_3$; (d) $Pr_{0.8}Ba_{0.2}MnO_3$; (e) carbon only.

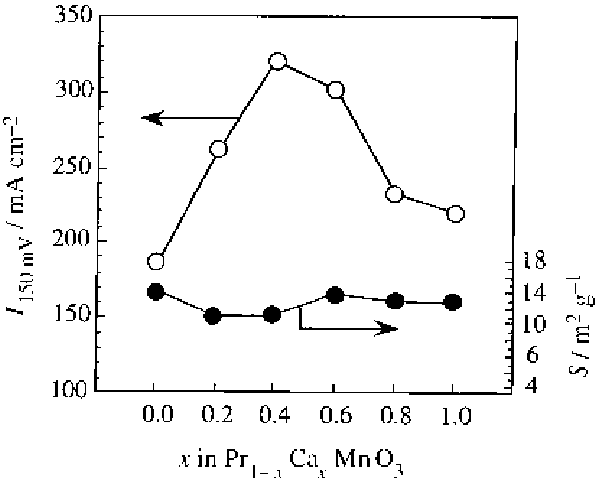

Fig. 2. Oxygen reduction performances ($I_{150\,mV}$) and specific surface area (S) as a function of x in $Pr_{1-x}Ca_xMnO_3$.

activity, as done for other perovskite-type oxides [19, 20]. Figure 2 depicts electrode performances over $Pr_{1-x}Ca_xMnO_3$ ($I_{150\,mV}$), as well as the surface areas of the oxides as a function of Ca content, x. With increasing x from zero, $I_{150\,mV}$ increased remarkably, going through a maximum at $x = 0.4$. It is noteworthy that the maximum $I_{150\,mV}$ value was as high as 320 mA cm^{-2} even under air (not pure oxygen) flow. The electrode performance often tends to increase with increasing catalyst specific surface area [13]. In the present case, however, the surface areas were almost similar, (about 12 m^2 g^{-1}) so that the electrode performances probably reflect the intrinsic catalytic activity of the oxides. The cause of the catalytic activity variations with x is now under investigation.

The stability of gas diffusion-type electrode loaded with $Pr_{0.6}Ca_{0.4}MnO_3$ was tested for a short term up to 200 h under galvanostatic condition at 300 mA cm^{-2} in 8 M KOH aqueous solution at 60 °C. Figure 3 shows the cathodic polarization data obtained (a), together with the reference data on $La_{0.6}Ca_{0.4}CoO_3$ (b). The former data, though fluctuating considerably with time, remained stable as a whole over the test period of 200 h. The latter data, in contrast, exhibited an obvious decay in catalytic activity with time, as seen from the increase in overpotential by 110 mV in 120 h. Figure 4 compares the XRD patterns of the perovskite-type oxides before and after the short-term stability test above. There were no noticeable changes in perovskite-structure for $Pr_{0.6}Ca_{0.4}MnO_3$ after the test, while $La_{0.6}Ca_{0.4}CoO_3$ had been decomposed largely to produce $La(OH)_3$ after the test. With such activity and stability, $Pr_{0.6}Ca_{0.4}MnO_3$ shows promise as an oxygen-reduction catalyst in alkaline solution.

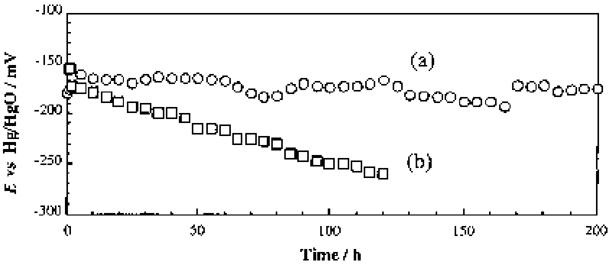

Fig. 3. Short-term stability test for gas diffusion-type oxygen electrodes loaded with $Pr_{0.6}Ca_{0.4}MnO_3$ (a) and $La_{0.6}Ca_{0.4}CoO_3$ (b) under the galvanostatic conditions of 300 mA cm^{-2} and air flow in 8 M KOH solution at 60 °C.

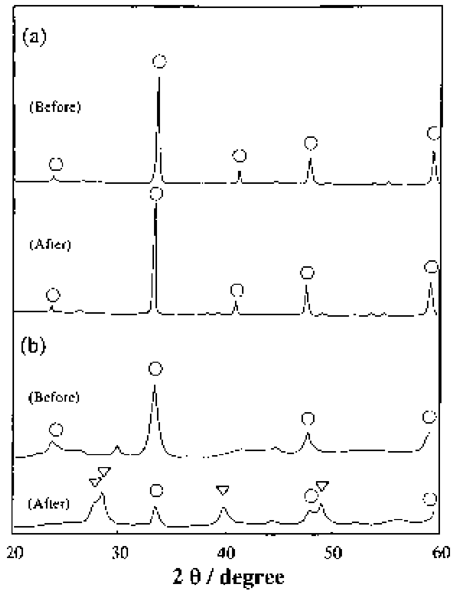

Fig. 4. XRD patterns of gas diffusion-type oxygen electrodes loaded with $Pr_{0.6}Ca_{0.4}MnO_3$ (a) and $La_{0.6}Ca_{0.4}CoO_3$ (b) before and after the stability test. Key: (○) perovskite phase and (▽) $La(OH)_3$.

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