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Gas-Diffusion Electrodes for Oxygen Reduction Loaded with Large Surface Area $La_{1-x}Ca_xMO_3$(M=Co,Mn)

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Oxygen reduction performances of gas-diffusion type carbon electrodes loaded with perovskite-type oxides $La_{1-x}Ca_xMO_3$(M=Co,Mn) were examined in 30 wt% KOH at 25 °C. The highest electrode performance, i.e., 2600 mA/cm^2 at -125 mV vs. Hg/HgO, was obtained with large surface area $La_{0.6}Ca_{0.4}CoO_3$ prepared by an amorphous precursor method.

Electrochemical reduction of oxygen in an alkaline solution is especially important in energy-related systems such as H_2-O_2 fuel cells and metal-air batteries. These systems usually utilize a PTFE (poly-tetrafluoroethylene)-bonded gas diffusion carbon electrode as an air cathode. However, as the overpotential of a pure carbon electrode for oxygen reduction is high, a practical air cathode must be added with an active electrode catalyst. Rather many materials have been studied as the electrode catalysts, such as noble metals,[1,2] oxides,[3] organometal compounds,[4] nitrides[5] and so on. Among these, perovskite-type oxides[6] seem to be attractive because of high activity and low cost. In fact, we have reported that perovskite-type oxides such as $La_{1-x}Sr_xFe_{0.6}Co_{0.4}O_3$(x=0.2, 0.4) and $La_{1-x}Sr_xCoO_3$(x=0.2,0.4) can be promising catalysts for the electrochemical reduction of oxygen.[7] It has also been noticed that the performance of the carbon electrode increases as the specific surface area of the oxide catalyst increases. Recently it was reported that perovskite-type oxides with large surface area could be prepared by an amorphous citrate precursor (ACP) method.[8,9] We adopted these large surface area oxides to the oxygen electrodes and found that they gave far better performances than those reported so far. This paper deals with the oxygen reduction characteristics of the PTFE-bonded carbon electrodes loaded with large surface area oxides of $La_{1-x}Ca_xMO_3$(M=Co,Mn).

Preparation of perovskite-type oxides by the ACP method was carried out as follows.[9] Stoichiometric amounts of nitrates of constituent metals were dissolved in an aqueous solution of citric acid. The solution was evaporated at 70 °C in a vacuum oven to form a solid precursor. The precursor was heated at about 650 °C for 2 h in an ambient atmosphere. The formation of perovskite-type oxides was confirmed by means of X-ray diffraction (XRD) analysis (Rigaku Denki, D4011). For comparison, preparation by a conventional acetate decomposition (AD) method was also carried out; an aqueous solution dissolving constituent acetates was evaporated to dryness and calcined at 850 °C for 10 h in air. The gas-diffusion electrodes fabricated here were composed of a pair of carbon layers (a gas supply layer and an active layer) with a nickel screen (100 mesh, a current collector) sandwiched in between, a structure essentially the same as one developed by Motoo et al.[1] Carbon Black #3000B (Mitsubishi Chemical Ind.) and Denka Black (Denki Kagaku Kogyo) were used for the active and the gas supply layers, respectively. Both carbon layers were treated with 23-25 wt% PTFE dispersion (Daikin Kogyo , D-1), while only the active layer was loaded with a perovskite-type oxide catalyst by 25 wt%. The entire electrode was then hot-pressed into a thin disc, 15 mm in diameter and 0.4 mm thick, at 370 °C for about 10 s under a pressure of 64 MPa. The cathodic polarization curves of the electrodes were measured in 30 wt% KOH aqueous solution at 25 °C under a pure oxygen flow by using a Pt-plate counter electrode (20 x 20 mm). The electrode potential was controlled with a potentiostat (Hokuto Denko, HA-305) and an Hg/HgO (KOH) reference electrode. The activities of the perovskite-type oxides for the catalytic decomposition of HO_2^- were evaluated from the rates of O_2 generation rate in the H_2O_2 decomposition in an alkaline solution.[7]

Figure 1 compares the cathodic polarization curves of various carbon electrodes. All the electrodes loaded with $La_{0.6}Ca_{0.4}CoO_3$ or $La_{0.8}Ca_{0.2}MnO_3$ exhibited far higher performance than the unloaded electrode, indicating that these oxides are active for the electrochemical oxygen reduction. Among the oxide-loaded electrodes, electrode activity apparently depended very much on the oxide preparation method. That is, each oxide prepared by the ACP method gave far greater activity than the same oxide prepared by the AD method: at a potential of -125 mv vs. Hg/HgO, for example, current densities were about 4 times larger on the former oxides. As shown in Table 1, the specific surface area (BET method) of perovskite-type oxides prepared by the ACP method were about 5-9 times larger than those prepared by the AD method. Therefore, such high activities evidently result from the large surface area of the oxides prepared by the ACP method. It was also noted that, when prepared in the same methods,

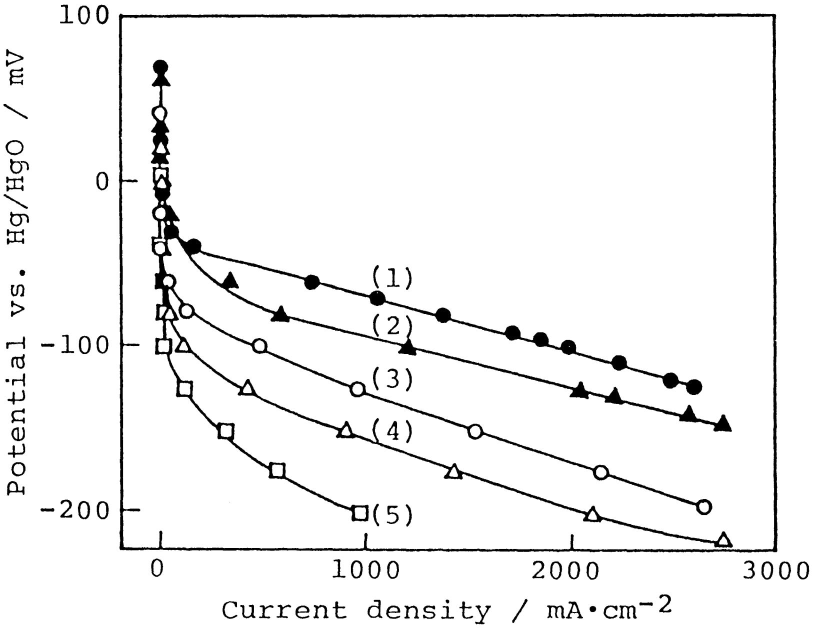

Fig. 1. Polarization curves of gas-diffusion carbon electrodes loaded with oxide catalysts.
(1) $La_{0.6}Ca_{0.4}CoO_3$ (ACP) (2) $La_{0.8}Ca_{0.2}MnO_3$ (ACP)
(3) $La_{0.6}Ca_{0.4}CoO_3$ (AD) (4) $La_{0.8}Ca_{0.2}MnO_3$ (AD)
(5) none

$La_{0.6}Ca_{0.4}CoO_3$ was always more active than $La_{0.8}Ca_{0.2}MnO_3$. Although little has been known about the catalytic activity of $La_{1-x}Ca_xCoO_3$ system, present study reveals the potentiality of the oxide system as an electrode catalyst. Thus the highest cathodic performance was marked by the electrode loaded with 25 wt% $La_{0.6}Ca_{0.4}CoO_3$ prepared by the ACP method; the attained current density was as high as 2600 mA/cm^2 at -125 mV vs. Hg/HgO (+800 mV vs. RHE) in 30 wt% KOH at 25 °C.

Table 1. Specific surface area of perovskite-type oxides prepared by the ACP and AD mehtod

Sample	ACP m^2/g	AD m^2/g
$LaMnO_3$	40	7.3
$La_{0.8}Ca_{0.2}MnO_3$	27	2.9
$La_{0.6}Ca_{0.4}MnO_3$	30	—
$La_{0.4}Ca_{0.6}MnO_3$	30	—
$La_{0.2}Ca_{0.8}MnO_3$	30	—
$LaCoO_3$	11	2.2
$La_{0.8}Ca_{0.2}CoO_3$	14	—
$La_{0.6}Ca_{0.4}CoO_3$	17	1.9
$La_{0.4}Ca_{0.6}CoO_3$	14	—

The system $La_{1-x}Ca_xCoO_3$ was examined further by changing the calcium content, Fig. 2 shows the current densities (at -125 mV vs. Hg/HgO) of the electrodes loaded with a series of $La_{1-x}Ca_xCoO_3$ (X = 0 - 0.6) prepared by the ACP method. The highest electrode performance was achieved at x = 0.4. It is known that the electrochemical reduction of oxygen on carbon in an alkaline solution produce hydrogen peroxide ions by the 2-electron reduction: $O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$ ($E^o = -0.076$ V vs. NHE). The HO_2^- ions produced, however, can not easily undergo the decomposition ($HO_2^- \rightarrow OH^- + (1/2)O_2$), unless an active catalyst is present nearby. As the present gas-diffusion electrodes contain carbon, the HO_2^- ions should be produced on the carbon surface especially in the higher overpotential (current density) range, necessitating the presence of a decomposition catalyst. Therefore an electrode catalyst should be not only active for a direct 4-electron oxygen reduction ($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$, $E^o = 0.401$ V vs. NHE) but also active for the HO_2^- decomposition. The activities for the HO_2^- decomposition were estimated from the rates of catalytic decomposition of H_2O_2. The rate constants of the decomposition

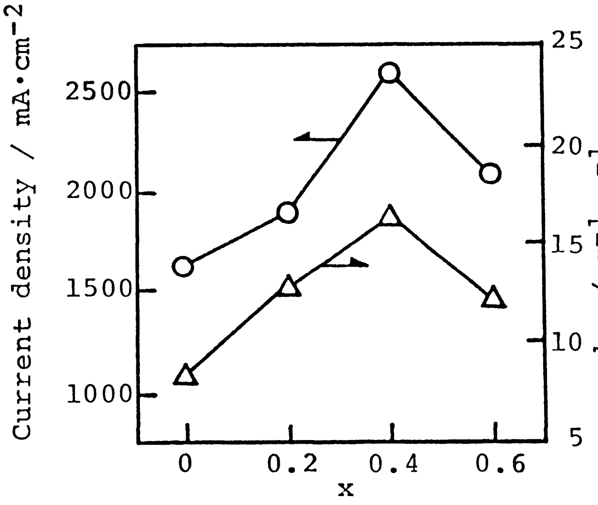

Fig. 2. Electrode performance at -125 mV vs. Hg/HgO and kinetic parameter (k_d) for HO_2^- decomposition on $La_{1-x}Ca_xCoO_3$ as a function of x.

(k_d) over $La_{1-x}Ca_xCoO_3$ system are also plotted in Fig. 2. The maximum decomposition activity appears at x = 0.4, in coincidence with the behavior in electrode performance. The parallelism between the electrode activity and the H_2O_2 decomposition activity suggests strongly that the high electrode performance attained with $La_{1-x}Ca_xCoO_3$ is deeply related with their high activities for the HO_2^- decomposition. However, as many perovskite-type oxides are known to be also active for the 4-electron reduction of oxygen, the present electrode performance may be partly assisted by the 4-electron reduction activity. Further studies are necessary to discuss the electrode activities more quantitatively.

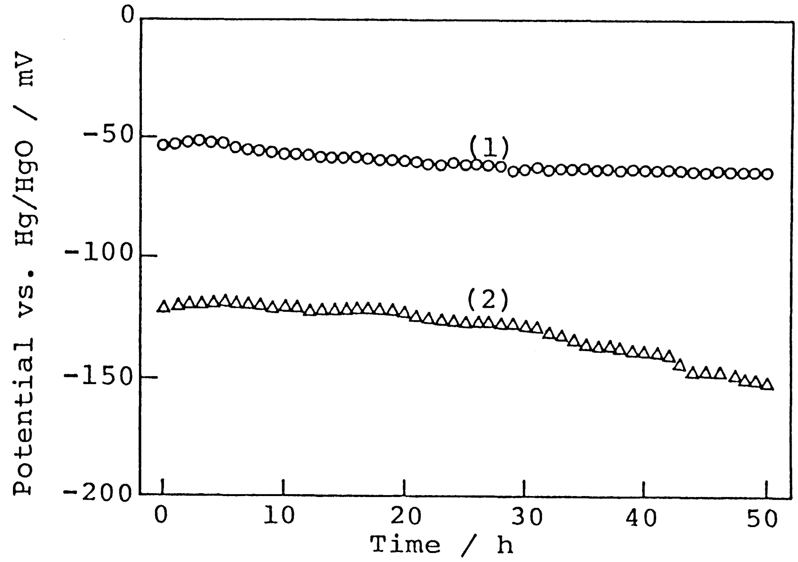

Fig. 3. Short-term stability test of gas-diffusion carbon electrodes with or without catalyst for O_2 reduction (300 mA/cm^2, 25 °C).
(1) 25wt% $La_{0.6}Ca_{0.4}CoO_3$ (2) none-catalyst

A short-term stability test was carried out in the galvanostatic conditions at 300 mA/cm^2 in 30 wt% KOH at 25 °C. As shown in Figure 3, the electrode loaded with $La_{0.6}Ca_{0.4}CoO_3$ was fairly stable in operation potential during 50 h, while the catalyst-unloaded electrode showed clear degradation after 20 h operation. This again suggests that the present electrode is promising as a practical oxygen reduction electrode.

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