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Bi-functional Oxygen Electrode Using Large Surface Area Perovskite-type Oxide Catalyst for Rechargeable Metal-Air Batteries

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Gas-diffusion electrodes loaded with large surface area perovskite-type oxides, $La_{0.6}Ca_{0.4}Co_{0.8}B'_{0.2}O_3$ (B'=Mn,Fe,Co,Ni,Cu), were examined for the electrochemical reduction and evolution of oxygen in 7 M KOH at 25 °C. The oxide with B'= Fe gave the highest bi-functional performances, i.e., 200 mA/cm^2 for the oxygen reduction in air and 300 mA/cm^2 for the oxygen evolution at -150 and +620 mV vs. Hg/HgO, respectively, owing to its high catalytic activity for the decomposion of the HO_2^- intermediate.

Bi-functional oxygen electrodes, which are active for both the electrochemical reduction and evolution of oxygen, are indispensable for designing rechargeable metal-air batteries to be utilized for electric vehicles. Various PTFE-bonded carbon electrodes of a gas diffusion type, loaded with Ag,1) Ni+mixed oxide,2,3) or mixed oxides,4) have so far been tested for the bi-functionality, but the resulting performances are either unsatisfactory or not well reported. We have found that the Co- and Mn- based perovskite type oxides, $La_{0.6}Ca_{0.4}CoO_3$ and $La_{0.8}Ca_{0.2}MnO_3$, are both highly active as an electrode catalyst for the oxygen reduction, especially when their specific surface area are large.5,6) For the oxygen evolution, however, the Mn-based oxide was far less active than the other, suggesting that the Co-based family is better for the bi-functionality.7) Subsequent investigation has revealed that the bifunctional activity is improved when the Co based oxide has B-site cations partially substituted. This paper deals with the bi-functional activity of the carbon electrodes loaded with such partially substituted oxides of the Co-based family.

The B site-substituted oxides, $La_{0.6}Ca_{0.4}Co_{0.8}B'_{0.2}O_3$ (B'=Mn,Fe,Co,Ni,Cu), were synthesized by an amorphous citrate precursor (ACP) method.8) The precursor obtained from citric acid and the nitrates of constituent metals was heated at about 650 °C for 2 h in an ambient atmosphere. The resulting oxides had specific surface area as large as 17-28 m^2/g, except for B'=Cu, as shown in Table 1. The gas diffusion electrodes using PTFE bonded carbon were prepared and tested in the same way as already reported.5-7) Cathodic and anodic polarization curves were measured in 7 M KOH aqueous solution at 25 °C by the use of Pt-plate counter electrode and Hg/HgO(KOH) reference electrode. Dry synthetic air (21 kPa O_2) was supplied to the back side of the gas diffsion electrodes during the measurements. Rotating carbon-paste disk electrodes loaded with the perovskite-type oxides (50 wt%) were subjected to the measurements of cyclic voltammograms in the O_2-saturated aqueous solution of 1 M NaOH at 25 °C.6,7) The catalytic activities of the oxides for the decomposition of HO_2^- were evaluated from the rates of oxygen evolution from an alkaline solution dissolving H_2O_2 in 9 M NaOH at 80 °C.6,9)

Table 1. Specific surface area (S) of $La_{0.6}Ca_{0.4}Co_{0.8}B'_{0.2}O_3$ (B'=Mn,Fe,Co,Ni,Cu)

B'	Mn	Fe	Co	Ni	Cu
S (m^2/g)	18	28	18	17	4

Figure 1 shows the cathodic and anodic polarization curves of the electrodes loaded with the synthesized oxides by 25 wt%. Fairly good cathodic performances, i.e., current densities as large as about 200 mA/cm^2 at -150 mV vs. Hg/HgO, were exhibited by all electrodes except one using the oxide of B'=Cu which had an exceptionally small surface area (Table 1). The anodic performances were more dependent on the B' cations, resulting in the order of Fe>Co>Ni ≅ Cu>Mn at +600 mV vs. Hg/HgO , although the activity of the oxide of B'= Cu was degraded at the higher overpotentials. Further information on the properties of the oxides was collected by using the rotating disk electrodes. As shown in Fig. 2, the electrodes using the oxides of B'= Ni, Fe, and Co gave completely reversible cyclic voltammograms in the anodic region, while those using B'=Mn, and Cu gave large hysterisis. This suggests that the former oxides are resistant to electrochemical oxidation and reduction but the latter ones are not.

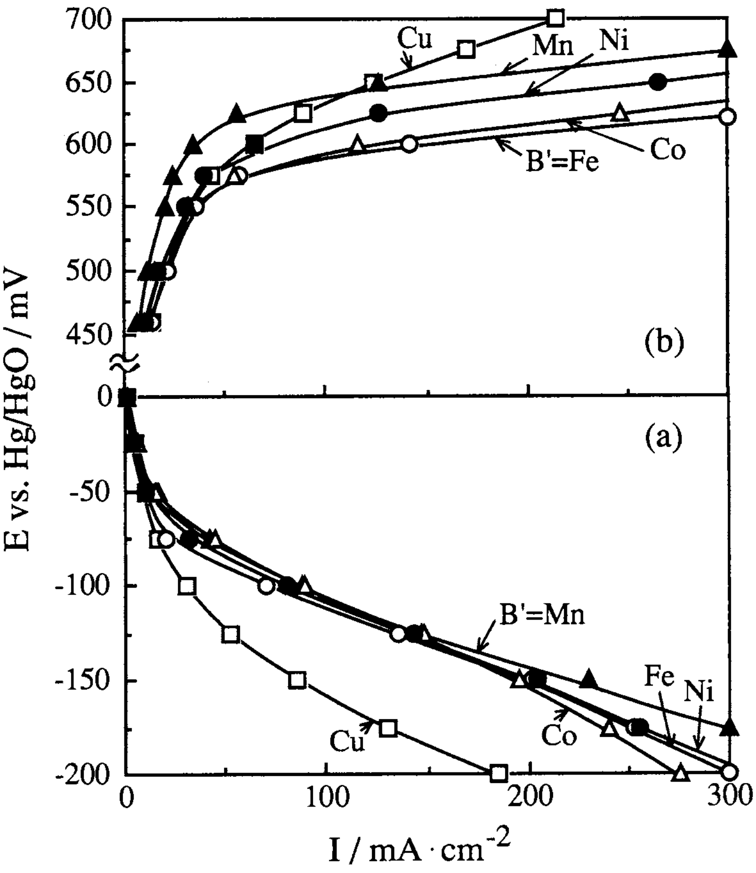

Fig. 1. Polarization curves of gas-diffusion electrodes loaded with 25 wt% $La_{0.6}Ca_{0.4}Co_{0.8}B'_{0.2}O_3$ (B'=Mn,Fe,Co,Ni,Cu) in 7 M KOH at 25 °C.

(a) Cathodic polarization in air (O_2 reduction)

(b) Anodic polarization (O_2 evolution)

These results lead to the conclusion that $La_{0.6}Ca_{0.4}Co_{0.8}Fe_{0.2}O_3$ is the best bi-functional electrode catalyst among the tested oxides. The electrode loaded with this oxide by 25% gave a cathodic current density of 200 (oxygen reduction in air) and an anodic one of 300 mA/cm^2 (oxygen evolution) at -150 and +620 mV vs. Hg/HgO, respectively. Moreover, this electrode could stand more than 240 cycles of charge-discharge test at a current density of ±100 mA/cm^2, as shown in Fig. 3.

Bockris et al.[10)] have proposed that the electrochemical oxygen evolution consists of a series of elemental reactions, as follows.

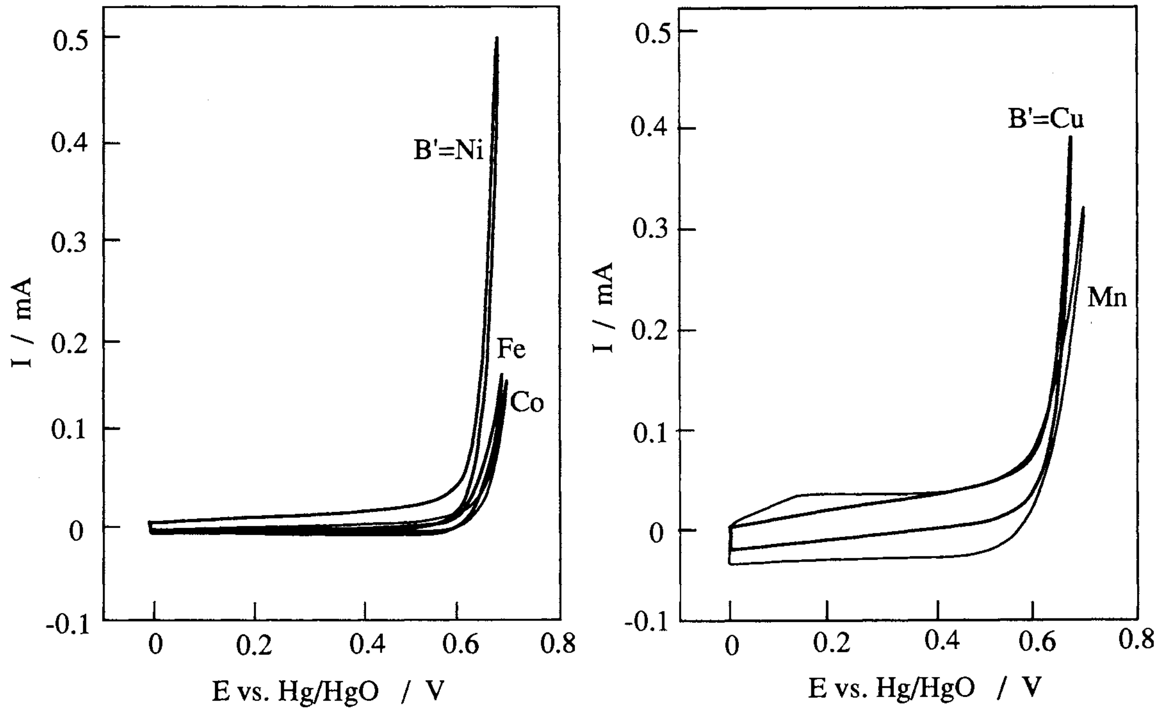

Fig. 2. Cyclic voltamograms of rotating carbon paste disks loaded with 50 wt% $La_{0.6}Ca_{0.4}Co_{0.8}B'_{0.2}O_3$ (B'=Mn,Fe,Co,Ni,Cu) (O_2-satulated 1 M NaOH, sweep rate: 5 mV/s, rotating rate 900 rpm)

$$M^Z + OH^- = M^Z\text{-}OH + e^-, \qquad (1)$$
$$M^Z\text{-}OH + OH^- = M^Z\text{-}H_2O_2 + e^-, \qquad (2)$$
$$M^Z\text{-}H_2O_2 = M^Z + H_2O_2, \qquad (3)$$
$$H_2O_2 + OH^- = HO_2^- + H_2O, \qquad (4)$$
$$H_2O_2 + HO_2^- = H_2O + OH^- + O_2, \qquad (5)$$

where M^Z is a trandision-metal ion of a valence Z. It is noteworthy that the formation and decomposition of HO_2^- (or H_2O_2) are included in the mechanism. The synthesized oxides were tested for their catalytic activities for the decomposition of HO_2^-. As shown in Fig. 4, the decomposition activities as expressed by the rates (k_w) of oxygen evolution from the H_2O_2 solution per gram of the oxides suspended could be correlated almost linearly with the anodic current densities of the electrodes

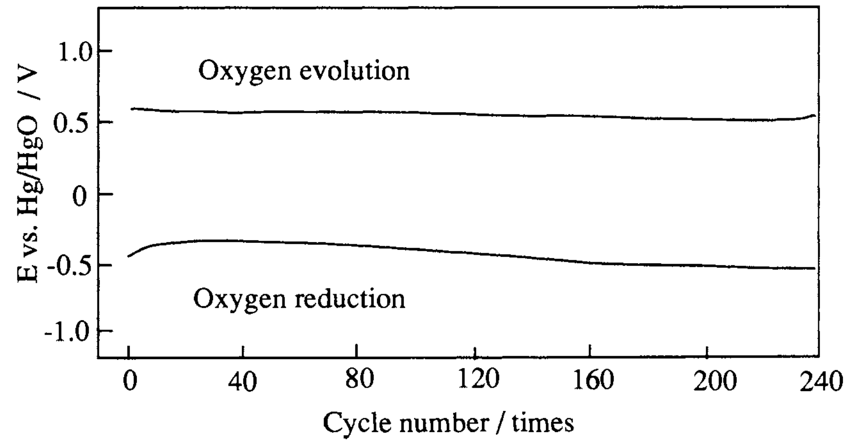

Fig. 3. Test of the gas-diffusion electrode loaded with 70 wt% $La_{0.6}Ca_{0.4}Co_{0.8}Fe_{0.2}O_3$ for the cycles of oxygen reduction (10 min) and evolution (10 min) at ±100 mA/cm^2 (25 °C in 7 M KOH).

using the oxides at +600 mV vs. Hg/HgO. This suggests that decomposition of HO_2^- is a key step of the oxygen evolution. It is stated that the decomposition of HO_2^- is also important for the oxygen reduction. As already revealed by the use of the rotating-ring-disk electrode technique, oxygen is reduced dominantly via the 2-electron mechanism, $O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$, in the practical current density region, the total rate being determined by the decomposition of HO_2^-, while the 4-electron O_2 reduction, $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$, prevails at very low overpotentials.[6] The high bi-functional activity of $La_{0.6}Ca_{0.4}Co_{0.8}Fe_{0.2}O_3$ thus seems to benefit from its activity to decompose HO_2^-, the intermediate commonly appearing in both oxygen reduction and evolution. Further investigation should be necessary to clarify the mechanism of the oxygen evolution on the oxide catalysts.

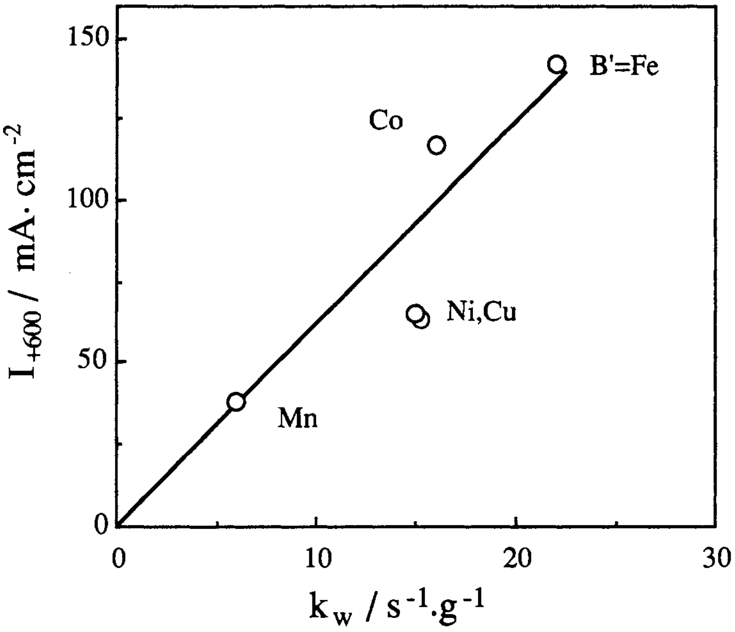

Fig. 4. The anodic current densities of oxide-loaded electrodes at +600 mV vs. Hg/HgO (I_{+600}) as correlated with the catalytic activities for the decomposition of HO_2^- (k_W).

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