Stability of Carbon-Supported Perovskite-Type Oxide under Cathodic Polarization in Strong Alkaline Media

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A gas diffusion-type oxygen reduction electrode has been investigated for applications to metal-air battery, brine electrolysis and fuel cell. We have investigated the electrocatalytic activity of perovskite-type oxides for the oxygen reduction, which was first pointed out by Medowcroft [1]. As a result, $LaMnO_3$ has turned out to be most promising in activity and stability in alkaline solution among the typical oxide. In addition, we have succeeded in preparing the electrode for which loading nano-sized particles of the oxide catalyst were dispersed finely on the carbon matrix by using reverse micelle method [2]. The oxygen reduction activity of the resulting electrode was almost as high as that of Pt-loaded carbon electrode as shown in Fig. 1. However, stability of such highly dispersed perovskite-type oxides in strong alkaline media has not always been clear yet. This study aimed at investigating the stability of La-Mn based oxides as correlated with calcination temperature, preparation method and oxide composition.

Two kinds of reverse micelle dispersions, RM-A and RM-B, were first prepared by using cyclohexane and NP-6 (polyoxyethylene (6) nonylphenyl ether) were used as oil phase and surfactant, respectively. RM-A contained a mixed nitrate solution of La, Mn and Fe at a designated ratio, while RM-B contained a 10% solution of tetra methyl ammonium hydroxide (TMAH). The two dispersions were mixed together to obtain a reverse micelle dispersion containing a precursor (mixed hydroxides) of the perovskite-type oxide aimed. Throwing carbon black powder into this dispersion followed by filtration, the precursor-loaded carbon was collected, which was further calcined at 550-700°C for 5-15h in N_2 atmosphere. The calcined powder was incorporated into PTFE bonded das diffusion type electrodes, as reported elsewhere [2]. Polarization curves were measured in 9M NaOH at 80°C under air or oxygen flow by using a potentiostat. After polarization, electrodes were subjected to chemical analysis for Mn and Fe to evaluate the amounts of perovskite-type oxide decomposed.

Figure 2 shows the amounts of $LaMnO_3$ decomposed under non-polarized (just immersed) and cathodically polarized (-100mV) conditions in strong alkaline solution (80°C 9M NaOH). The decomposition was always more extensive under the polarized condition than under the non-polarized one. This indicates that electrochemical decomposition is more prevailing than chemical decomposition. In each case, the decomposition tended to decrease remarkably with increasing calcination temperature as shown. Furthermore the decomposition tended to saturate when the immersion or polarization was elongated for more than 3 h. These results suggest that crystallization of $LaMnO_3$ from the precursor state goes more to completion as calcination temperature increases resulting in an increase in stability.

Figure 3 shows the decomposition behavior of $LaMn_{1-y}Fe_yO_3$ (calcined at 700°C) under the same conditions. Compared with the case of the unsubstituted oxide (y=0), decomposition tended to reduce remarkably with increasing y, under the polarized (circle) and non-polarized (triangle) conditions. Obviously the decomposition can be suppressed effectively by the partial substitution of Fe.

References

1. D. B. Medowcroft, *Nature*, **226**, 847 (1970).
2. M. Hayashi, H. Uemura, K. Shimanoe, N. Miura and N. Yamazoe, *Journal of the Electrochemical Society*, **151**, A158 (2004).

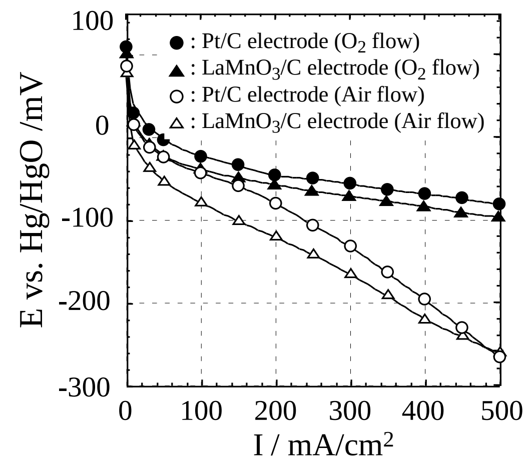

Fig.1 Polarization curves for $LaMnO_3$-loaded carbon electrode and Pt-loaded carbon electrode under O_2 and air flow. (Loading amount of Pt and $LaMnO_3$: 9.80wt% and 27.7wt%, respectively)

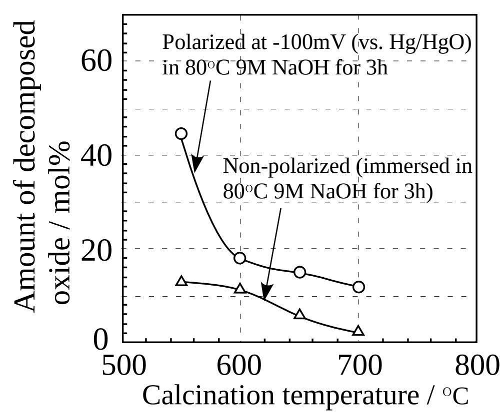

Fig.2 Amounts of $LaMnO_3$ decomposed under cathodically polarized and non-polarized conditions.

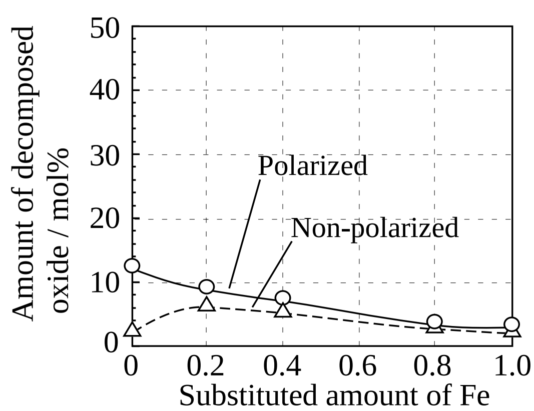

Fig.3 Amount of $LaMn_{1-y}Fe_yO_3$ (y=0 - 1.0) decomposed under the same conditions as adopted in Fig. 2.