

REVERSE MICELLE BASED PREPARATION OF PARTIALLY SUBSTITUTED LANTHANUM MANGANITES SUPPORTED ON CARBON FOR AIR CATHODE

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Carbon-based gas diffusion-type electrodes have been investigated for air electrodes of metal-air batteries and new-type brine electrolysis cells. Some kinds of perovskite-type oxides, especially A- and B-sites partially substituted manganites such as $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{1-y}\text{Fe}_y\text{O}_3$, have been shown to be promising candidates for the oxygen reduction electrocatalysts. Since the perovskite-type oxides usually crystallize at high temperature, however, there has been a difficulty in dispersing the oxides well in carbon matrix by using conventional methods. We have shown for a carbon-supported LaMnO_3 system that this difficulty can be greatly mitigated by adopting a reverse micelle method, by which nano-sized particles of the precursor (mixed hydroxide) of the aimed oxide can be dispersed on carbon particles in liquid phase. This study aims at extending this method for $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{1-y}\text{Fe}_y\text{O}_3$ (x and y up to 0.2).

Carbon supported-oxide precursors were prepared through the same procedures as reported elsewhere. Cyclohexane and polyoxyethylene-(5)-rauryl ether were used as a solvent and surfactant, respectively. A reverse micelle dispersion containing a mixed solution of nitrates of constituent metals, i.e., La, Mn, Sr and Fe was mixed with another reverse micelle dispersion containing a solution of tetra methyl ammonium hydroxide (TMAH). The resulting reverse micelle dispersion containing a precipitate of mixed hydroxides (precursor) was further mixed with carbon black dispersed in cyclohexane under ultrasonic wave agitation. Ethanol was then poured to this mixture to break the reverse micelles and the resulting, precipitate of carbon-precursor composite was collected by filtration. The precipitate was calcined in N_2 atmosphere at 550-700°C for 5-15h. Gas diffusion type electrodes were prepared conventionally. A reaction layer consisting of the calcined composite obtained above and PTFE was stacked with a gas supply layer consisting of carbon black and PTFE by a hot press method. The amount of oxide was fixed to be 16wt% of the carbon-oxide composite and 1.9mg/cm² of electrode. The polarization curves were measured in 8M KOH at 60°C under air or oxygen flow by using a potentiostat.

Figure 1 shows the XRD patterns of the three carbon-oxide composites prepared in this study. It is seen that LaMnO_3 and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ were formed as a single phase after calcinations at 600°C and 550°C, respectively. However, these phases were decomposed more and less when calcination temperature was raised by 100 or 50°C, respectively. Such decomposition takes place as a result of reaction of the oxides or their precursors with carbon when calcination temperature is too high. The above result indicates that the A-site partially substituted oxide is less stable than the unsubstituted one. In contrast, the partial substitution of B-site for Fe was very effective for stabilization, allowing the aimed phase, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ to form stably even after

calcination at 700°C. Figure 2 shows polarization curves under air flow for the electrode using the respective carbon-oxide composite. Obviously, $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ were more active than LaMnO_3 , in agreement with the report of Shimizu et al., that A-site partial substitution for Sr improves oxygen reduction activity. Remarkably, the partial B-site substitution for Fe scarcely affected the activity, thus allowing the oxide to be endowed with both high activity and improved chemical stability. In conclusion, the reverse micelle method could be applied successfully for preparing the partially substituted lanthanum-manganites supported on carbon.

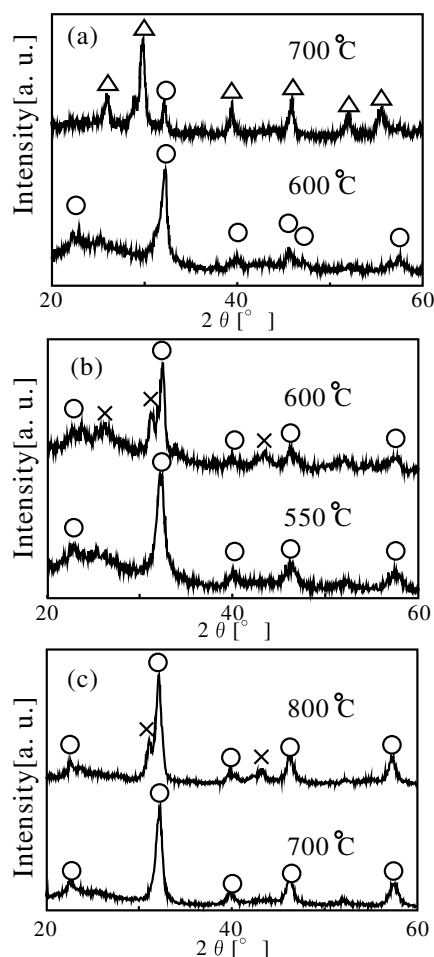


Fig.1 XRD pattern of carbon-supported $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{1-y}\text{Fe}_y\text{O}_3$
(a) x,y = 0, (b) x=0.2, y=0,
(c) x,y=0.2
○: perovskite phase
△: La_2O_3 ×: unknown

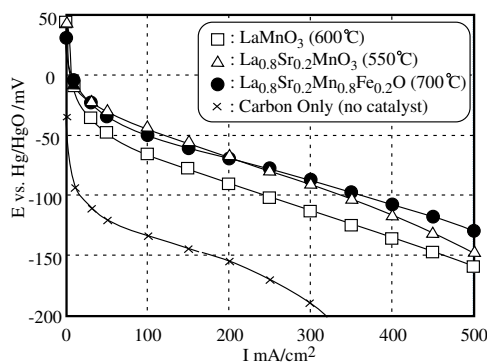


Fig. 2 Polarization curve of electrodes using carbon-supported $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{1-y}\text{Fe}_y\text{O}_3$ (each calcined at indicated temperature)

REFERENCES

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