Preparation of Carbon-Supported $LaMnO_3$ Electrocatalyst by Modified Reverse Homogeneous Precipitation Method

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A gas diffusion-type oxygen reduction electrode, potential to be utilized for metal-air battery, fuel cells and brine electrolysis, is required to allow high current density at low overpotentials. To fulfill this requirement, not only selection of a highly active electrocatalyst but also high dispersion of it on the carbon support are indispensable[1]. Previously, we showed that nano-sized particles of $LaMnO_3$ perovskite-type oxide could be dispersed on the carbon support finely by use of the reverse homogeneous precipitation (RHP) method[2]. However, the precursor sol formed as an intermediate in that method was not always stable enough to be kept for a long time. In later study, we found that a modification of RHP method by adding EDTA (ethylenediaminetetraacetic acid) to the starting solution of mixed nitrates of La and Mn was effective in stabilizing the precursor sol. This paper aims at reporting the modified RHP (MRHP) method to prepare carbon-supported $LaMnO_3$ composites.

Figure 1 shows the scheme of MRHP method. The mixed nitrates solution of La and Mn was mixed with EDTA prior to adding dropwise to the hydroxide solution (pH 13.5) under stirring. The resulting sol of mixed hydroxides of La and Mn was further mixed with a suspension of carbon powder dispersed in water and the whole system was agitated ultrasonically for 30 min. After filtration and desiccation, the deposit (carbon-supported precursor) was calcined at 650 °C in N_2 for 5 h and then incorporated into gas diffusion-type electrodes (apparent surface area: 1.54 cm^3), in a conventional way[3]. Polarization curves of the electrode were measured in 8 M KOH solution at 60 °C under O_2 flow by using a potentiostat.

Figure 2 shows the particle size distribution of a typical precursor sol as measured by a dynamic light scattering method. The particle sizes were distributed in a narrow range from 10 to 20 nm, with an average particle size of 13 nm. Figure 3 compares the cathodic polarization curves of the electrodes prepared by MRHP (A), or RHP (B) method. Electrode A indicated an excellent performance, giving 300 mA/cm^2 at -74 mV vs. Hg/HgO, while electrode B gave an almost comparable performance in this case. It is emphasized that electrode A was far more reproducible than electrode B because the precursor sol of MRHP was more stable than that of RHP. The dispersion state of the oxide precursor on the carbon-support was evaluated after the carbon was burnt off by calcination at 450 °C under air flow. As seen from an SEM image (Fig. 4), the oxide precursor particle formed in MRHP were as fine as about 10 ~ 15 nm in size, to be compared with 20 nm or above for those of RHP. These results indicate that MRHP method is more useful for preparing the oxide catalyst finely dispersed carbon electrode.

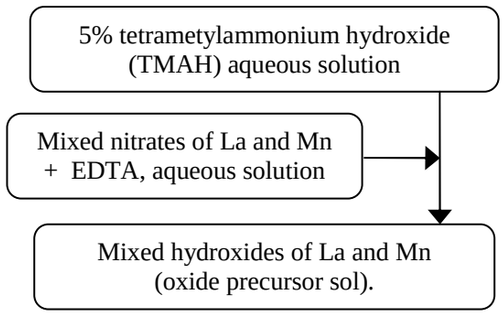

Fig. 1 Scheme of MRHP method (up to sol formation).

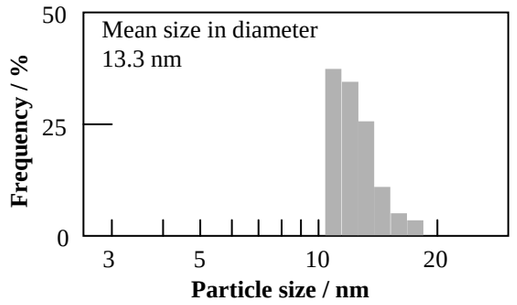

Fig. 2 Particle size distribution of the precursor sol.

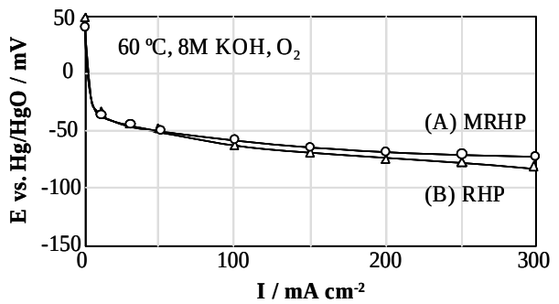

Fig. 3 Cathodic polarization curves of gas diffusion-type electrodes loaded with $LaMnO_{3.00}$ (30 wt.%) in 8 M KOH at 60 °C under O_2 flow.

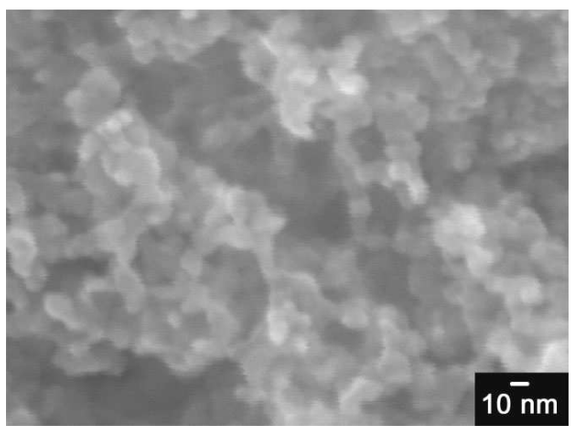

Fig. 4 SEM image of precursor particles prepared by MRHP method (after the carbon matrix was burnt off).

References
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