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Preparation of carbon-supported nano-sized $LaMnO_3$ using reverse micelle method for energy-saving oxygen reduction cathode

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Abstract

Two ways of reverse micelle (RM) method were investigated to prepare carbon-supported nano-sized $LaMnO_3$ with high oxygen reduction activity. Hydrolysis precipitation in reverse micelle (HP-RM) method could give nano-sized particles of $LaMnO_3$ easily because the particles size decreased with decreasing R_w (=[H_2O]/[surfactant]) value as well as nitrate concentration. The electrode prepared by the resulting particles showed high oxygen reduction activity as compared with that prepared by mechanical mixing-method. Furthermore, it was found that new RM method (ROP-RM) using $KMnO_4$ as an oxidizer gave higher oxygen reduction activity than the HP-RM method, although particle size of $LaMnO_3$ obtained by the ROP-RM method was almost same as that by RM-HP method.

Keywords: Nanoparticle; Reverse micelle method; Oxygen reduction activity

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1. Introduction

High performance of gas-diffusion-type oxygen reduction cathode is of importance for applications to metal-air battery, fuel cell, energy-saving-type brine electrolysis and so on. Conventionally, this cathode has been made of an electrocatalyst and carbon support. Among the various kinds of electrocatalysts investigated so far, noble metals like Pt, Pt-alloy and Ag have been shown to be highly active [1–11]. However less expensive electrocatalysts, if available, would definitely be more desirable, and this motivated many researchers to pay attention on single- and mixed-oxides of transition metals. The potentiality of perovskite-type oxides as oxygen reduction electrode has been pointed out by Meadowcroft [12]. Since then, much research has accumulated on these oxides. We have reported that A- and B-sites partially substituted lanthanum manganites such as $La_{1-x}Sr_xMn_{1-y}Fe_yO_{3+\delta}$ and $La_{1-x}Ca_xMn_{1-y}Fe_yO_{3+\delta}$ are most promising from the viewpoints of activity and stability [13,14]. Conventionally, the neat perovskite-type oxide thus synthesized at high temperatures has been mixed into carbon powder mechanically to prepare the carbon-supported oxide. However, we noticed a technical difficulty in dispersing these oxides in carbon support, because the particles of oxide and carbon are usually coagulated heavily with each other. Under this situation, we proposed that oxide preparation by a reverse micelle (RM) method is of particular interest, because nano-sized solid precursors by RM method are dispersed well in carbon support. Then we reported that carbon-supported perovskite-type oxide ($LaMnO_3$) was successfully prepared in this way and that the carbon-oxide composite obtained gave a surprisingly good electrode performance as compared with the conventionally prepared one [15–17]. This RM method is considered to be one of the candidates to give high performance cathode.

In order to obtain highly active cathode, both the reduction of particle size and the high dispersion of particles on carbon matrix are very important. In the case of RM method, it is well known that the ability of RM formation depends on a balance of hydrophilic and hydrophobic groups in a surfactant [18–20] and also that the diameter of reverse micelle depends on molar ratio of [H_2O] to [surfactant], which is called “R_w value” [21,22]. However the detail, especially the relationship between concentration of salt and particle size obtained, is not still clear for perovskite-type oxide.

In this study, we investigated RM-method for preparation of nano-sized peroveskite-type oxide with electrochemical activity. As a result, we proposed new precipitation method that

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$LaMnO_3$-precursor was prepared by reduction–oxidation reaction between Mn^{2+} ($Mn(NO_3)_2$) and Mn^{7+} ($KMnO_4$). The new method is abbreviated as ''ROP-RM (reduction–oxidation precipitation in reverse micelle) method'', although the conventional reverse micelle method is abbreviated as ''HP-RM (hydrolysis precipitation in reverse micelle) method''. In the case of HP-RM, oxidation of Mn^{2+} seems to occur in precipitation or calcination processes. On the other hand, it is considered that addition of $KMnO_4$ into HP-RM process increases number of high valence state of Mn in precipitates as compared with the conventional hydrolysis reaction.

2. Experiment

2.1. Preparations of precursor by RM-HP and RM-ROP methods

The preparation procedure of $LaMnO_3$-precursor by HP-RM method is schematically shown in Fig. 1. Two kinds of RM solutions (RM-A, RM-B) were prepared by using hexaethyleneglycol nonylphenyl ether (NP-6) and cyclohexane, surfactant and solvent, respectively. RM-A contained an aqueous solution of an equimolar mixture of $La(NO_3)_3$ and $Mn(NO_3)_2$ (0.02, 0.2, 1.5 M each), while RM-B contained an aqueous solution of tetramethylammonium hydroxide (TMAH, 10 wt%, coprecipitator). The ratio of water to surfactant was set in the range of 3–18 in both solutions. When RM-A was poured into RM-B under agitation by stirring, a brown colored transparent solution, which could be an RM solution including mixed hydroxides of La^{3+} and Mn^{2+}, was obtained. On the other hand, the preparation procedure of $LaMnO_3$-precursor by ROP-RM method is shown in Fig. 2. RM-A and RM-B were prepared by the same process in HP-RM method. However, additional reverse micelle solution containing 0.2 M $KMnO_4$ (RM-C) was prepared and poured into RM-B to obtain reverse micelle solution containing TMAH and $KMnO_4$ solution (RM-BC). RM-BC and RM-A were mixed together and gave brown colored transparent solution as a result. Each system was stirred at 7 °C for 2 h to obtain transparent dispersions. It seems that the addition of $KMnO_4$ to TMAH solution in reverse micelle leads La and Mn ions to precipitation with high valence through oxidation–reduction reaction between Mn^{2+} in $Mn(NO_3)_2$ and Mn^{7+} in $KMnO_4$.

The particle distributions of reverse micelles obtained by HP-RM and ROP-RM methods were measured by dynamic laser scatting (DLS, ELS-8000, Otsuka Electronics Ltd.).

2.2. Preparation of carbon-supported $LaMnO_3$

For carbon-supported $LaMnO_3$, carbon black (EC600-JD, 1280 m^2/g, Ketjen Black international Co.) dispersed in cyclohexane was added into the reverse micelle solutions containing $LaMnO_3$-precursor under ultrasonic agitation. The resulting black suspension was stable, but the reverse micelles, when ethanol was added to these solutions, were broken down to precipitate carbon-supported $LaMnO_3$-precursor. The precipitation was collected by filtration, washed with ethanol, and dried at 120 °C for 3 h. The obtained powders were calcined at 600 °C for 5 h under N_2 flow to prevent combustion of carbon. The oxide loading was fixed to be 17 mass% of the composites. The crystalline phase of $LaMnO_3$ (orthorhombic, $a = 5.536$, $b = 5.726$, and $c = 7.697$, JCPDS card No. 33-713) was confirmed by X-ray diffraction analysis (XRD, Cu Kα, RINT2100, Rigaku Denki). To measure the distribution and the average of particle size, $LaMnO_3$ powder, after carbon-support was eliminated by calcining at 400 °C under air flow, was observed by FE-SEM (JSM-6340F, JEOL).

2.3. Preparation and evaluation of oxygen reduction electrode

Gas-diffusion-type electrodes (GDE), shaped into around a sheet of 7 mm in diameter (1.54 cm^2 in geometric surface area) and 0.4 mm in thickness, were composed of reaction layer (about 0.1 mm thick) and gas-supply layer (about 0.1 mm thick) on Ni mesh current collector. For the reaction layer, the carbon-supported $LaMnO_3$ powder was suspended with 15 mass% polytetrafluoroethylene (PTFE, binder, 32J, Daikin industries Ltd.) in *n*-buthanol containing water under ultrasonic agitation, followed by filtrating and drying at 120 °C. For gas-supply layer, commercial carbon black (AB-7, 47 g/m^2, Denki Kagaku Inc.) was mixed with 30 mass% PTFE in deionized water using Triton-X [poly(oxyethylene)$_{10}$-octhylphenyl ether, surfactant, Wako pure chemical industries Ltd.]. The surfactant was removed by a heat-treatment at 280 °C for 2 h in air. The powders obtained thus were pressed at 32 MPa into a thin sheet

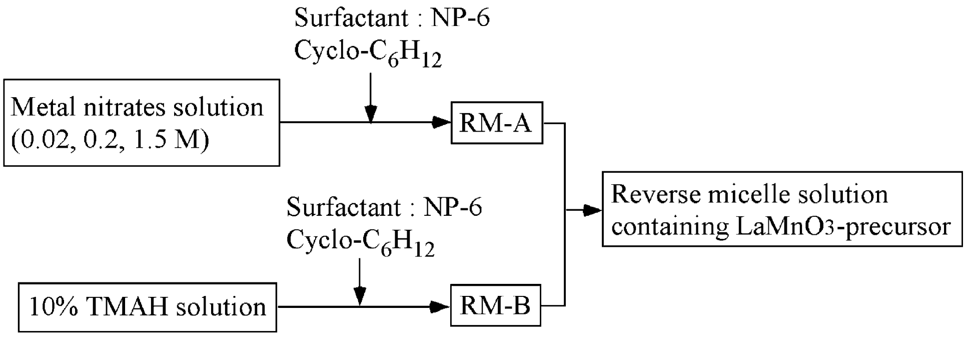

Fig. 1. The preparation scheme of $LaMnO_3$-precursor by HP-RM method.

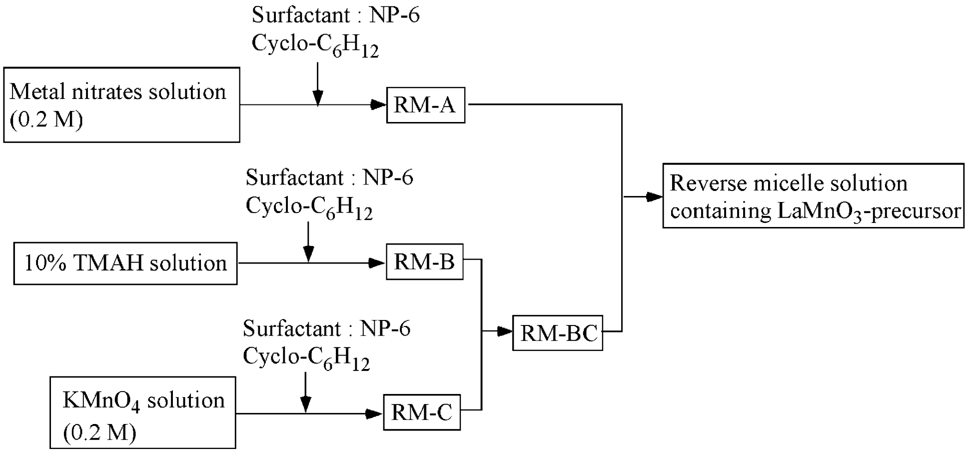

Fig. 2. The preparation scheme of $LaMnO_3$-precursor by ROP-RM method.

of the designated geometry on Ni mesh. Finally, the sheets of reaction layer and gas-supply layer were bonded together by hot pressing at 360 °C, which is a melting point of PTFE, under a pressure of 64 MPa. The amount of perovskite-type oxide in each electrode was set to be 2.0 mg/cm^2 unless otherwise noted.

Obtained GDE was attached vertically to the window of a PTFE-made cell, inside which 9 M NaOH solution at 80 °C was placed together with Pt counter electrode. Cathodic polarization curves were measured at 80 °C under O_2 flow by potentio/galvanostat (HA-305G, Hokuto Denko Co., Ltd.) based on Hg/HgO reference electrode.

3. Results and discussions

3.1. $LaMnO_3$ prepared by RM-HP method

Table 1 shows the mean particle size of solutions prepared by HP-RM to each R_w value (R_w = $[H_2O]/[\text{surfactant}]$) at various

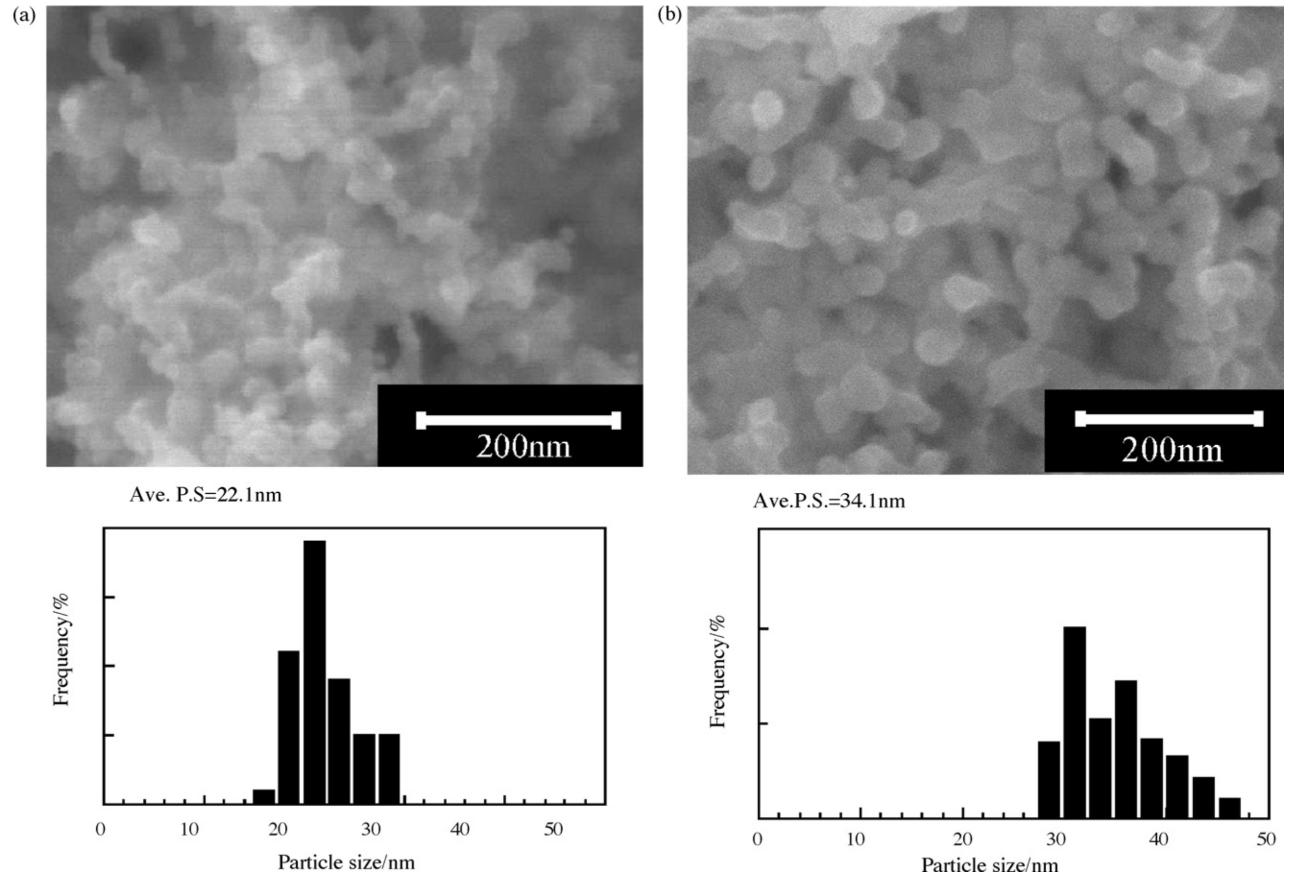

Fig. 3. SEM images and particle size distributions of $LaMnO_3$ prepared at nitrate concentration of 0.2 M by HP-RM method. (a) $R_w = 3$; (b) $R_w = 12$; (c) $R_w = 18$.

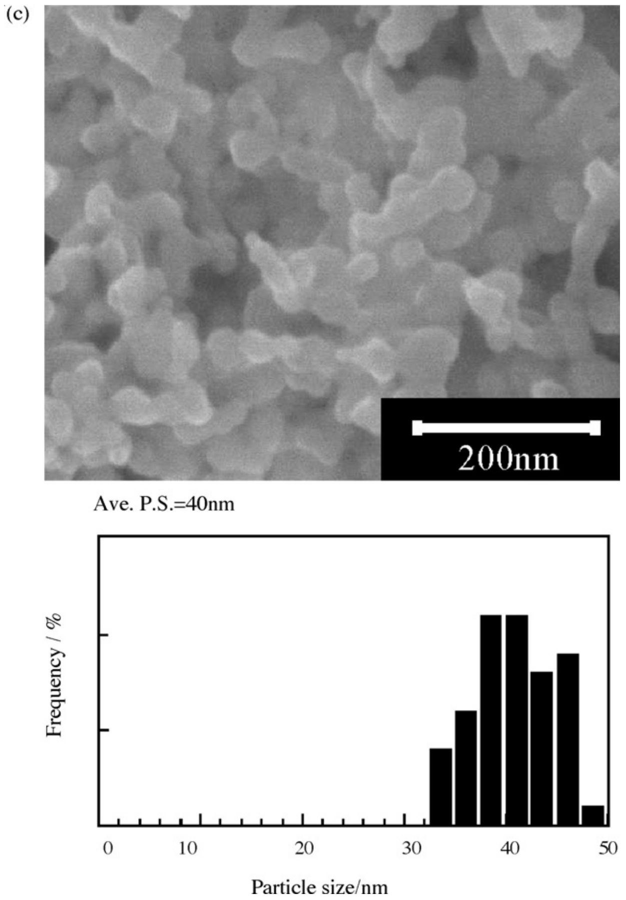

Fig. 3. (*Continued*).

nitrate concentrations. Particle size increased with increasing R_w value at each nitrate concentration. However, the particle size did not increase with increasing nitrate concentration at each R_w value. If DLS measurement indicates particle size of $LaMnO_3$-precursor inside reverse micelle, the values should increase with nitrate concentration. This means that the measured value was not particle size of $LaMnO_3$-precursor inside reverse micelle but diameter of reverse micelle. In these measurements, the preparation conditions of $R_w = 12$ and 18 at nitrate concentration of 1.5 M gave turbid solution because $LaMnO_3$-precursor particles seemed to agglomerate. This indicates that the precursor particle was too large to be covered with reverse micelle. From these results, it seems that $LaMnO_3$-precursor can be stable and nano-sized in reverse micelle under optimal condition.

Table 1
Mean particle size of reverse micelles prepared by HP-RM method

Concentration of nitrate solution (M)	R_w			
	3	9	12	18
0.02	[a]	8.5	11.5	15.0
0.2	3.8	7.8	8.5	12.2
1.5	3.5	12.1	[b]	[b]

[a] Out of range in DLS measurement (<3 nm).
[b] Agglomerated.

Fig. 3(a–c) show the SEM images and the particle distributions of $LaMnO_3$ particles prepared by HP-RM method at $R_w = 3$, 12, and 18, respectively, at nitrate concentration of 0.2 M. The average of particle size for each $LaMnO_3$ was 22, 34, and 40 nm at $R_w = 3$, 12, and 18, respectively. It was found that the particle size increased with increasing R_w value. However, particle sizes of obtained $LaMnO_3$ were much lager than those of reverse micelles shown in Table 1. Therefore, a whole lot of $LaMnO_3$-precursors seem to agglomerate through preparation process. We investigated the degree of agglomeration from the number of reverse micelles based on the measured micelle size and the volume of used water, and from the number of $LaMnO_3$ particles based on the average size of $LaMnO_3$ particle, the mole number of obtained $LaMnO_3$ and the volume of unit cell ($LaMnO_3$: orthorhombic, $a = 0.5536$ nm, $b = 0.5726$ nm, and $c = 0.7697$ nm). As the result of calculation, it seems that the preparation conditions of $R_w = 3$, 12 and 18 gave agglomeration of 330, 85 and 46 precursor particles, respectively. Agglomeration of precursor seems to be occurred when ethanol was added into reverse micelle solution for loading $LaMnO_3$ precursor on carbon-support. However, the particle size of obtained $LaMnO_3$ became smaller when the nitrate concentration was reduced to 0.02 M. Fig. 4 shows the SEM image and the particle distribution of $LaMnO_3$ prepared at nitrate concentration of 0.02 M at $R_w = 3$. Compared with average particle size of $LaMnO_3$ prepared by 0.2 M solution, that of $LaMnO_3$ prepared by 0.02 M solution was reduced by 6 nm. There is no difference in the number of

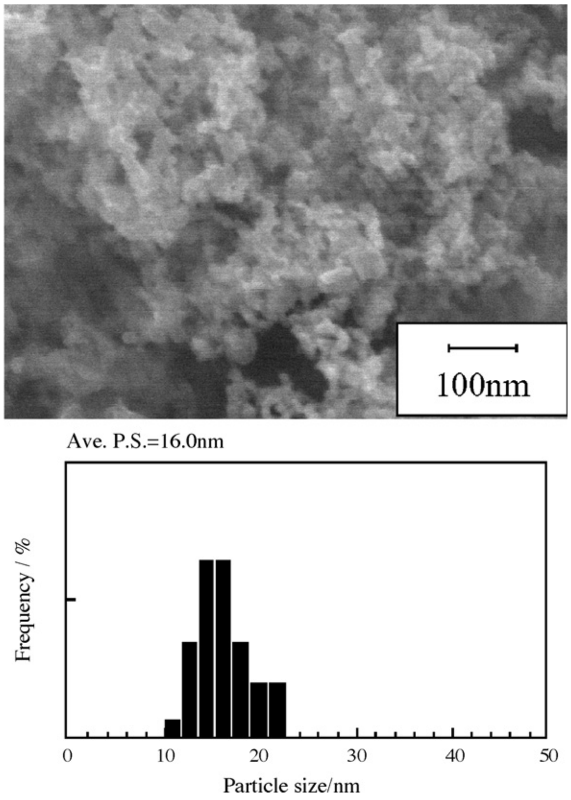

Fig. 4. SEM image and particle size distribution of $LaMnO_3$ prepared at nitrate concentration of 0.02 M by HP-RM method.

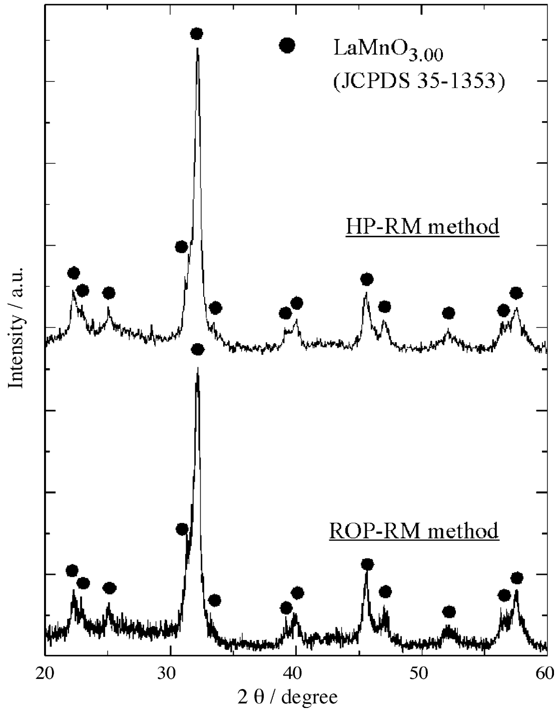

Fig. 5. XRD patterns of obtained oxides prepared by HP-RM and ROP-RM methods.

reverse micelle particle between 0.2 and 0.02 M solutions, although the nitrate concentrations were different. From the above results, it is found that optimal control of R_w as well as nitrate concentration is important to obtain finer particle.

3.2. $LaMnO_3$ prepared by ROP-RM method

ROP-RM method was compared with HP-RM method. Fig. 5 shows the XRD patterns of carbon-supported oxides prepared by HP-RM and RM-ROP methods. From the XRD result of obtained oxide, it was found that the ROP-RM method gave a single phase of $LaMnO_{3.00}$ (JCPDS 35-1353) without impurities. In addition, there was no difference in crystalline size between the two methods. Fig. 6 shows the SEM image and the particle distribution of $LaMnO_3$ prepared at nitrate concentration of 0.2 M at $R_w = 3$ by ROP-RM method. The obtained $LaMnO_3$ was the fairly same particle size as that prepared by HP-RM method, as shown in Fig. 3(a). The use of $KMnO_4$ seems not to affect $LaMnO_3$ in particle size and crystal structure except properties of oxygen-reduction electrode, as shown later.

3.3. Evaluation of oxygen reduction activity

Electrocatalytic activities of carbon-supported $LaMnO_3$ electrodes prepared by HP-RM method (nitrate concentration: 0.02, 0.2 M) and ROP-RM method (nitrate concentration: 0.2 M) were investigated. Fig. 7 shows the cathodic polarization curves of the resulting electrodes in 9 M NaOH solution at 80 °C under oxygen flow. Among the electrodes tested, it was found that the electrodes prepared by RM methods obviously show outstanding performances. It is likely that oxides prepared by RM methods were dispersed well with the carbon powder. This seems to be responsible for the high performances. Especially the electrodes prepared by HP-RM method using 0.02 M nitrate solution showed predominant property in oxygen reduction activity because of the smaller particle size of $LaMnO_3$. On the other hand, the activity of electrode prepared by ROP-RM method using 0.2 M nitrate solution was almost same as that of electrode prepared by HP-RM method using 0.02 M nitrate solution although the former was rather

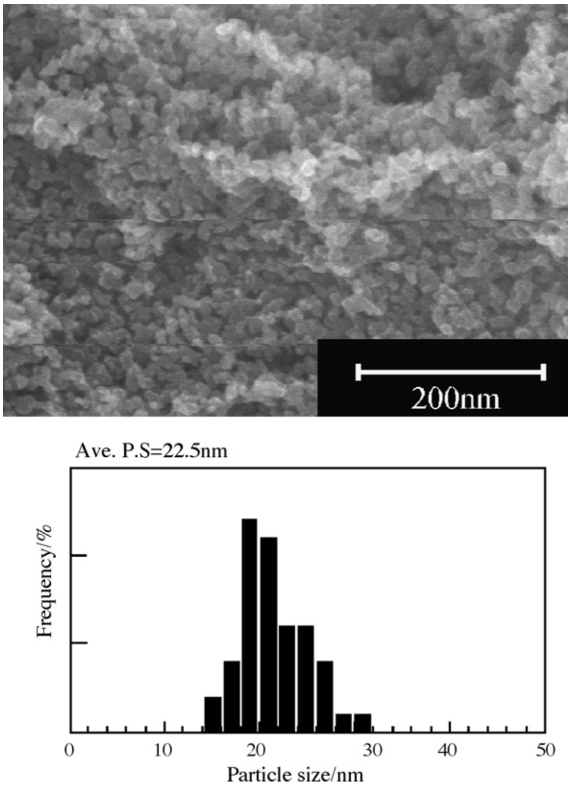

Fig. 6. SEM image and particle size distribution of $LaMnO_3$ prepared at nitrate concentration of 0.2 M by ROP-RM method.

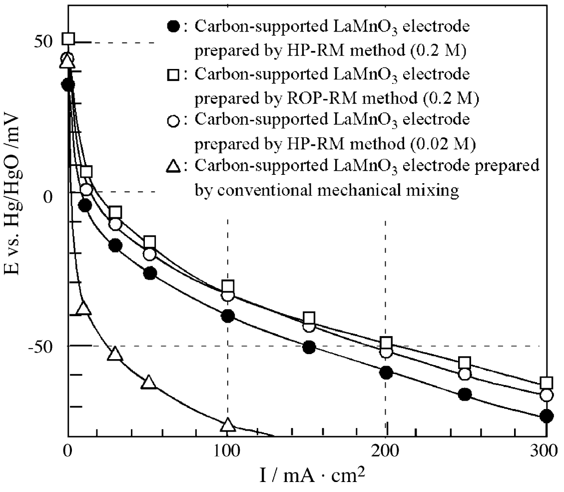

Fig. 7. Cathodic polarization curves of gas-diffusion-type oxygen electrodes using carbon-supported $LaMnO_3$ prepared by HP-RM method (0.2 and 0.02 M) and ROP-RM method (0.2 M). IR was not compensated.

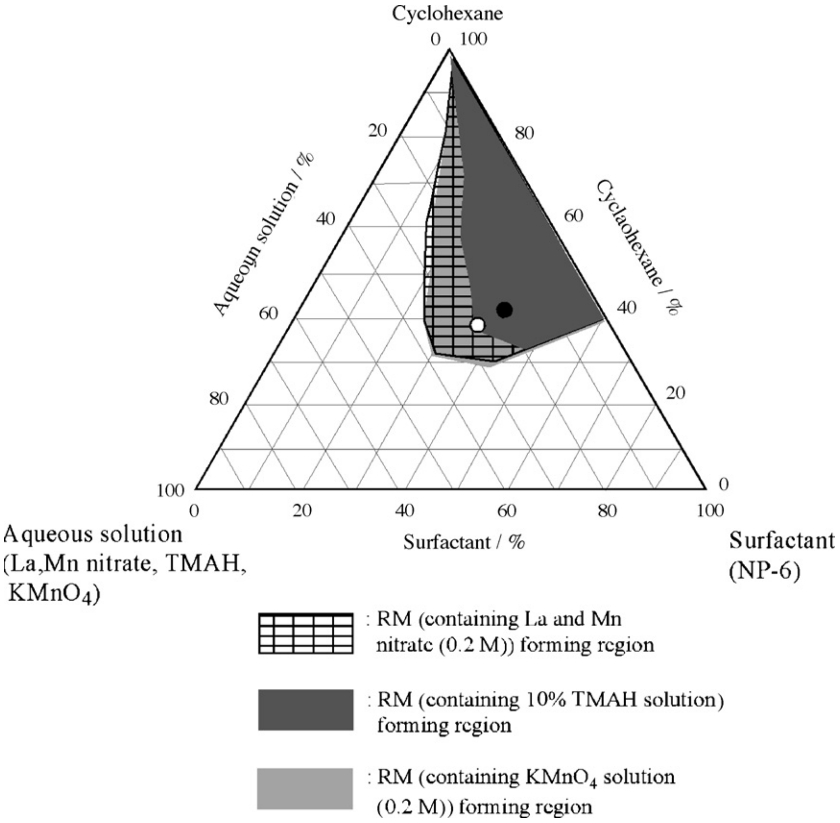

Fig. 8. Ternary phase diagram for cyclohexane-aqueous solution-surfactant.

lager in particle size than the latter. Such high activity seems to be due to high valence state of Mn introduced by the ROP-RM method using $KMnO_4$. In order to define relation between the ratio of high valence state and the efficiency, however, future investigations may be required.

3.4. Ternary phase diagram of RM solution

To know the limit of RM-forming, meaning how many catalyst can be prepared in solution, is important for practical use. The RM method uses nano-sized space, which is restricted by organic solvent, surfactant and water phases, as a reaction place. Therefore, the property of RM-forming is usually revealed by using ternary phase diagram. In this study, we used cyclohexane, NP-6 and various aqueous solutions (including La and Mn nitrate, TMAH or $KMnO_4$) as organic solvent, surfactant and water phases, respectively. The limit of RM-forming was investigated as follows. Each aqueous solution (La and Mn nitrate solution (0.2 M), 10% TMAH solution or $KMnO_4$ solution (0.2 M) was titrated into the mixture of cyclohexane and surfactant (NP-6). Then if the resulting solution is transparent, it is recognized that reverse micelle could be formed in the solution. This experiment was tried at various mass ratio of ternary phase. Fig. 8 shows the ternary phase diagrams obtained. Region of mass ratio obtained successfully reverse micelle solution is discriminated by meshed or colored domains. The domain of reverse micelle for La and Mn nitrate solution (meshed domain) agreed with that for $KMnO_4$ solution (light-gray-colored domain). On the other hand, however, the domain of reverse micelle for TMAH solution (deep-gray-colored area) was smaller, as compared with those for La and Mn nitrate solution and $KMnO_4$ solution. Such a difficulty of RM-forming may be due to strong alkalinity. Because it is thought that a lot of OH^- in TMAH weakens the forming force of reverse micelle, which is related to hydrogen bond between hydrogen in surface water and oxygen in hydrophilic group of surfactant.

As mentioned above, we have to calculate maximum yield of $LaMnO_3$ in RM method. In Fig. 8, maximum yield of $LaMnO_3$ was pointed by open circle (La and Mn nitrate solution: 0.2 M) and closed circle (La and Mn nitrate solution: 1.5 M). It is found that 12 and 52 g of $LaMnO_3$ can be obtained from 1 L solution of 0.2 and 1.5 M, respectively. These yields are acceptable for practical use because about 2 mg/cm^2 of catalyst is required for making the electrode.

4. Conclusion

In this study, we investigated RM-method for preparation of nano-sized peroveskite-type oxide with electrochemical activity and compared conventional RM-method (HP-RM) with new MR-method (ROP-RM). The following matters were made clear.

(1) In HP-RM method, particles size of obtained $LaMnO_3$ decreased with decreasing R_w value as well as nitrate

concentration. It was found that $LaMnO_3$-precursors, when reverse micelle was broken, agglomerate together and that the agglomerated size reflects particles size of obtained $LaMnO_3$.

(2) As a new RM-method, ROP-RM method using $KMnO_4$ was compared with HP-RM method. Although particle size of $LaMnO_3$ obtained by ROP-RM method was almost same as that by HP-RM method, the electrode prepared by ROP-RM method ($R_w = 3$ and nitrate concentration = 0.2 M) showed high oxygen-reduction activity as same as the electrode loaded smaller $LaMnO_3$ particles by HP-RM method ($R_w = 3$ and nitrate concentration = 0.02 M).

(3) Phase diagram, for which reverse micelle is stably prepared, was investigated. The stable domain for La and Mn nitrate solution agreed with that for $KMnO_4$ solution. On the other hand, however, the stable domain for TMAH solution was smaller than previous one. For maximum yield of $LaMnO_3$ in HP-RM method, it was found that 12 and 52 g of $LaMnO_3$ can be obtained from 1 L solution of 0.2 and 1.5 M, respectively.

Acknowledgement

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