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New Oxygen Reduction Electrocatalysts Based on Lanthanum Manganite Oxides and Their Application to the Cathode of AEMFCs

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In recent years, anion-exchange membrane fuel cells (AEMFCs) have received increasing attention because of the availability of non-Pt-based catalysts, e.g. Ag/C [1] and Mn oxides [2], and an enhancement in the oxygen reduction reaction (ORR) in alkaline media. The use of non-precious metal and oxides can solve the problems of the cost and resources of Pt in the conventional proton-exchange membrane fuel cells (PEMFCs). In this study, we synthesized new Ketjen Black-supported perovskite oxide $La_{1-x}Sr_xMnO_3$ (LS_xM/KB) catalysts by a modified reverse micelle (RM) method [3] using a non-ionic surfactant, i.e. polyethylene-glycol mono-4-nonylphenyl ether. The ORR activities were examined by hydro-dynamic voltammetry (HV) using a rotating ring-disk electrode (RRDE) in 0.1 M KOH. Also, the single cell performances were evaluated for the catalysts with the highest ORR activities.

The LS_xM/KB catalysts were synthesized by the modified RM method[3]. The products were characterized by X-ray diffraction (XRD) analysis, transmission electron microscopy (TEM), an inductively coupled plasma (ICP) atomic emission spectrometer and thermo-gravimetry-differential thermal analysis (TG-DTA). The LS_xM/KB catalysts were loaded at 56.7 $\mu g_{(LSxM)}$ cm^{-2} on the GC disk electrode, on which an alkaline ionomer binder (AS-4, Tokuyama Co.) was coated and dried at room temperature. The ORR activity of the LS_xM/KB catalyst was evaluated by HV in the potential range of 0.05 to 1.00 V vs. reversible hydrogen electrode (RHE) in O_2-saturated 0.1 M KOH at 50°C. Commercially available catalysts of 50 wt% Ag/C (BASF) and 46 wt% Pt/C (TKK) and 45 wt% $LS_{0.23}$M/KB catalyst prepared by a co-precipitation (CP) method reported previously [4] were used as reference samples. AEMFC single cell performance on the MEAs of Pt/C anode (1 mg cm^{-2}) | AEM (Tokuyama Co.) | LS_xM/KB cathode (1 mg cm^{-2}) were also evaluated with an FC evaluation system (Chino Co., 5100 Model II) at 50°C.

Formation of the perovskite phases in the products was confirmed by XRD analysis. From the TEM images, the average diameter of LS_xM nanoparticles on KB supports was ca. 4-18 nm, which was easily changed by R_W value (molar ratio of water/surfactant). Figure 1 compares the ORR activity of 20 wt% $LS_{0.17}$M/KB prepared by the RM method (RM-$LS_{0.17}$M/KB, average particle size: 4.3 nm), 45 wt% $LS_{0.23}$M/KB catalyst synthesized by a CP method (CP- $LS_{0.23}$M/KB) reported in a previous study [4], and commercially available 50 wt% Ag/C and 46 wt% Pt/C. The 20 wt% RM-$LS_{0.17}$M/KB showed higher catalytic activity for ORR than Ag/C and CP-$LS_{0.23}$M/KB, though its activity is still lower than that of Pt/C. In addition, the RM-$LS_{0.17}$M/KB exhibited clear potential-independent limiting currents at potentials lower than 0.65 V as was observed for Pt/C, while the limiting current for Ag/C and CP-$LS_{0.23}$M/KB slightly increased with a drop in potential. This indicates that the RM-$LS_{0.17}$M/KB had a sufficient electronic conductivity as ORR catalyst, which is attributed to the high dispersion of $LS_{0.17}$M/KB nanoparticles on KB supports. The selectivity for the 4-electron ORR estimated using the Pt-ring current was around 98 % at 0.6 V, which is comparable to that of the Pt/C catalyst. Figure 2 shows I-V and I-P curves at 50°C of AEMFC single cells prepared with 20 wt% RM-$LS_{0.17}$M/KB, 45 wt% CP-$LS_{0.23}$M/KB [4], 50 wt% Ag/C, and 46 wt% Pt/C as cathode catalysts. The AEMFC single cell with 20 wt% RM-$LS_{0.17}$M/KB was stably operated and exhibited the maximum power density of ca. 130 mW cm^{-2}, which was comparable to that with the Pt/C catalyst (ca. 140 mW cm^{-2}). Therefore, the 20 wt% RM-$LS_{0.17}$M/KB is a promising candidate as a cathode catalyst for AEMFCs.

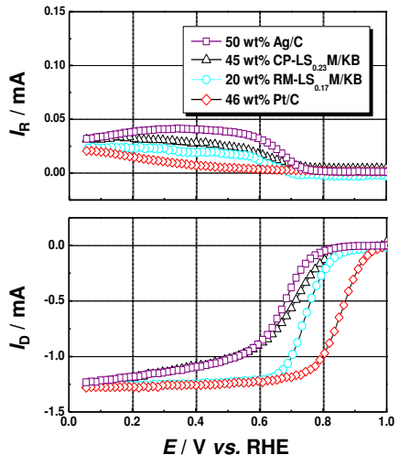

Fig. 1. HV curves for ORR at 20 wt% RM-$LS_{0.17}$M/KB in O_2 saturated 0.1 M KOH at 50°C. Data at 45 wt% CP-$LS_{0.23}$M/KB, 50 wt% Ag/C and 46 wt% Pt/C catalysts are also shown for comparison.

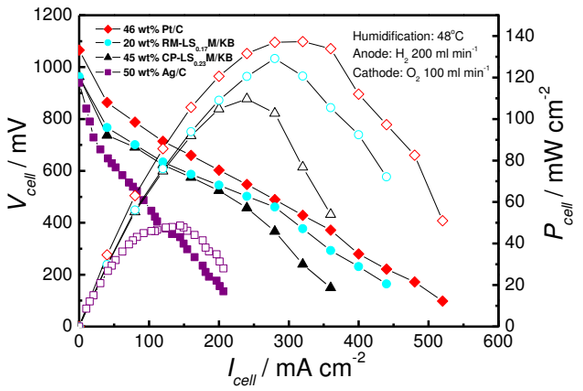

Fig. 2. Performance of the AEMFC single cells with 20 wt% RM-$LS_{0.17}$M/KB cathode catalysts at 50°C. Humidified H_2 and O_2 (RH = 100%) were supplied to anode and cathode, respectively.

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