

Short communication

Perovskite-type oxides $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ for cathode catalysts in direct ethylene glycol alkaline fuel cells

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Abstract

Carbon-supported $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM/C) was prepared by reversible homogeneous precipitation method, and its catalytic activities for oxygen reduction under the existence of ethylene glycol (EG) were investigated by using rotating disk electrode. LSM/C exhibited the high activity for oxygen reduction irrespective with the presence of EG, indicating that EG is not oxidized by LSM/C at the cathode side in the present system. Consequently, LSM/C can serve as a cathode catalyst in alkaline direct alcohol fuel cells with no crossover problem. Performance test for fuel cells operation also supported these results and showed cathodic polarization curves were not affected by the concentration of EG supplied to anode even at 5 mol dm^{-3} .

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1. Introduction

Electrochemical reduction of oxygen is an essential reaction involving in polymer electrolyte fuel cells. Among the various kinds of electrocatalysts, Pt [1], Pt-alloy [2,3] and Ag [4,5] are known to be fairly active for oxygen reduction. Precious metals, however, have some serious problems to be overcome before worldwide spread of fuel cells, such as economical cost, reproducibility and limited resources. Another problem evoked with cathode catalyst in direct methanol fuel cells (DMFCs) is methanol permeation through the electrolyte membrane, so-called “methanol crossover.” Permeated methanol is oxidized on cathode catalyst simultaneously with oxygen reduction. This combination of methanol oxidation and oxygen reduction results in open-circuit-voltage loss caused by a mixed potential. Moreover, total efficiency for fuel utilization becomes lower because of the consumption of methanol at cathode. Therefore, the requirement for cathode catalysts

in DMFC and other direct alcohol fuel cells is higher activity only for oxygen reduction with less activity for oxidation of alcohols.

These problems motivated many researchers to study for alternative catalysts besides a standard catalyst of Pt/C. Among proposed alternative catalysts, perovskite-type oxide is one of the promising candidates as a non-precious metal catalyst. Since Meadowcroft pointed out the catalytic activity of lanthanum–cobalt oxide for oxygen reduction [6], perovskite-type oxides become attractive materials as electrocatalysts. From the viewpoint of material resources, rare-earth metals and transition metals are more abundant and cheaper than platinum and other precious materials. Generally, perovskite-type oxide is formulated by ABO_3 , in which A is lanthanide material and B is transition metal. The catalytic activities of perovskite-type oxide are quite dependent of the elements of B and the ratios of A/B [7,8]. Many researchers have investigated the activities for oxygen reduction of the ABO_3 due to the attractive characters [7–10]. Although much work has been done on the reduction activities of perovskite-type oxides, very little work is currently available on the reductive activities of oxygen in the presence of alcohols. In particular, the direct ethylene glycol (EG) fuel

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cell has attracted much attention since it exhibited higher power densities than fuel cells using methanol, glycerin, erythritol and xylitol in alkaline solutions [11]. Then, it will be interesting to study the reductive activities of perovskite-type oxides in the presence of EG to improve the performance of the direct EG fuel cells.

2. Experimental

By referring the literature reported by Yamazoe et al. group, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (abbreviated as LSM) was prepared by using the reversible homogeneous precipitation method, in which mixed metal hydroxides are formed by adding solutions of metal salts into a strongly alkaline solution [12]. An aqueous solution of lanthanum nitrate, strontium nitrate and manganese nitrate (0.01 mol dm^{-3} , respectively) was prepared and was dropped into a solution of KOH (0.5 mol dm^{-3}) and tetrapropylammonium bromide (0.03 mol dm^{-3}), which was used as a stabilizer for nitrate ions. Thus obtained precipitate of mixed hydroxides was filtered and was dried for 6 h at 393 K, followed by calcinations for 5 h at 923 K in air. Carbon-supported LSM (LSM/C) was prepared by calcinating the filtered precipitate, which was obtained from the mixture of hydroxides and carbon (Vulcan XC72) in de-ionized water. The resultant powder of LSM and LSM/C were characterized by X-ray diffraction (XRD) and energy dispersive X-ray spectrometer comprising scanning electron microscope (SEM/EDX).

To evaluate electrocatalytic activities of LSM for oxygen reduction, linear sweep voltammetry was conducted in a solution of 1 mol dm^{-3} KOH with or without 0.1 mol dm^{-3} EG using a rotating disk electrode. The working electrode was rotated at 400–3600 rpm and the potential was swept at 10 mV s^{-1} . By a similar manner reported by Schmidt et al. [13], a suspension of catalysts in ultra-pure water was pipetted onto a glassy carbon electrode to obtain a working electrode.

To investigate the performance of fuel cells using a LSM/C cathode, a membrane-electrode assembly (MEA) was fabricated, consisting of anion-exchange membrane, LSM/C and Pt–Ru/C. Prior to the fabrication of MEA, a commercially available anion-exchange membrane (A-006, Tokuyama Co. Ltd.) was washed with de-ionized water and was immersed in 0.5 mol dm^{-3} KOH aqueous solution for 1 h at room temperature to replace Cl with OH in A-006. Pt–Ru/C coated on a carbon cloth (E-TEK, Pt–Ru loading amount: 4 mg cm^{-2}) was used as an anode. LSM/C, anion-exchange membrane and Pt–Ru/C were assembled with pressing by 1 MPa at 333 K to form a MEA. The cell test was conducted at 353 K with supplying of 1 mol dm^{-3} KOH solution containing EG at a flow rate of $10 \text{ cm}^3 \text{ min}^{-1}$ and ultra-pure oxygen gas humidified at 353 K at flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$ for anode and cathode, respectively. In addition to the cathode of LSM/C, the other two cathodes of Pt/C (E-TEK, Pt loading amount: 20 wt%) and Ag/C (E-TEK, Ag loading amount: 20 wt%) were also tested to compare their catalytic activities in direct EG fuel cells. The net amount of cathode materials (LSM, Pt and Ag) was uniformed at 1 mg cm^{-2} .

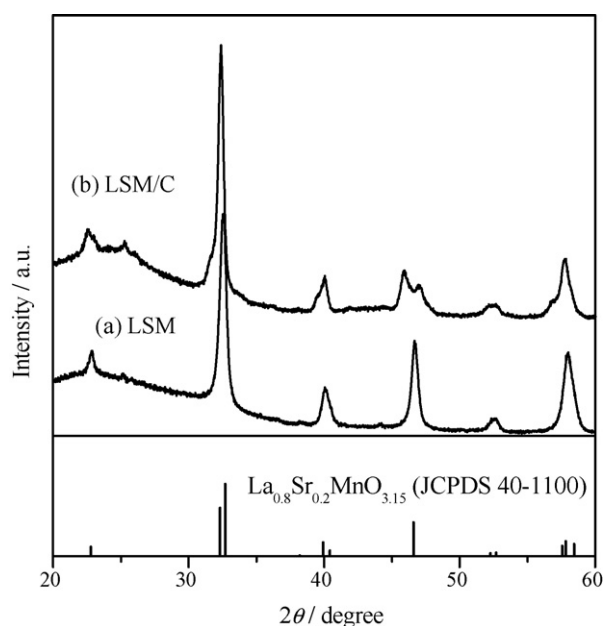


Fig. 1. XRD patterns of (a) $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM) and (b) carbon-supported LSM (LSM/C).

3. Results and discussion

XRD patterns of the resultant LSM and LSM/C are shown in Fig. 1. The diffraction patterns of LSM were almost identical with those of previously reported perovskite-type oxides such as $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3.15}$ [14] and did not show any other peaks due to impurities. The diffraction pattern of LSM/C was slightly shifted to the lower angles than that of LSM. It should be also denoted that the peak around 46° was split. These were explained by

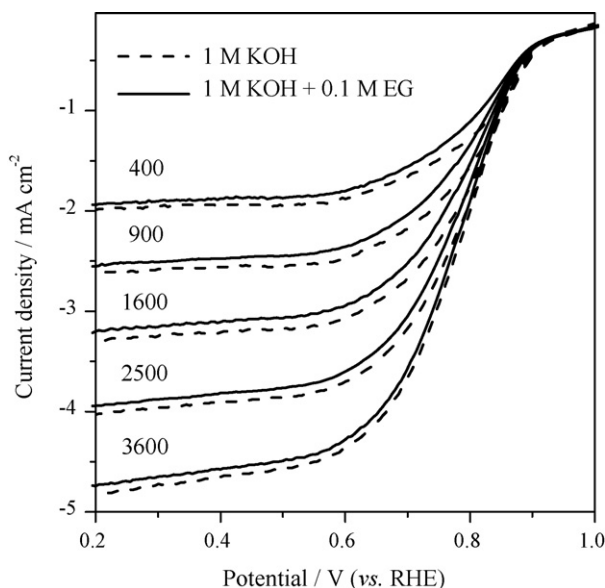


Fig. 2. Linear sweep voltammograms of LSM/C in 1 mol dm^{-3} (M) KOH with or without 0.1 M EG. Potential was swept at 10 mV s^{-1} , and cell temperature was maintained at 353 K. Inlitted number shows rotating speed of the disk electrode in rpm.

the oxygen deficiency of LSM caused by the addition of carbon [15]. Oxygen vacancy in LSM is expected to alter the electric structures of LSM and to improve the electron conductivity of the catalysts. The atomic ratio of the transition metals in LSM was determined by SEM/EDX to be 0.85:0.15:1.0 (La:Sr:Mn).

Fig. 2 shows linear sweep voltammograms of LSM/C in an aqueous solution of 1 mol dm^{-3} KOH with or without 0.1 mol dm^{-3} EG. There is no clear oxidative peak corresponding to EG oxidation within the present potential ranges. Although slight decrease of current densities for oxygen reduction was observed at all rotating rates in a solution of KOH with EG, the decrement was within a few percentages. Kutsche et al. reported that oxygen solubility in an aqueous solution of glycerol decreased as compared to the oxygen solubility in water [16]. Similarly, it is quite reasonable that the oxygen solubility decreases in a solution of EG. Therefore, the diffusion-controlled current density might be influenced by oxygen solubility in EG solution. Reductive activities of oxy-

gen on LSM/C was not influenced by the presence of EG in an electrolyte solution. This implies that LSM/C can be a promising candidate for cathode catalysts with high crossover tolerance.

The catalytic activities of LSM/C as cathode materials are shown in Fig. 3 together with those of Pt/C and Ag/C catalysts. Pt/C is used as a standard cathode catalyst in PEMFC, Ag/C is also one of the attractive catalysts in alkaline fuel cells since there is an advantage in cost and it works as a selective cathode catalyst for oxygen reduction without oxidizing permeated methanol. The maximum power densities of LSM/C, Ag/C and Pt/C were approximately evaluated to be 20, 21 and 25 mW cm^{-2} , respectively. Pt/C and Ag/C used in this work were commercially available catalysts, which should be well optimized to exhibit high catalytic activities. The particle sizes of Pt and Ag are less than a few nanometers. In contrast, the crystalline size of LSM is determined to be more than 10 nm by using a Scherrer equation. By considering these facts, the cat-

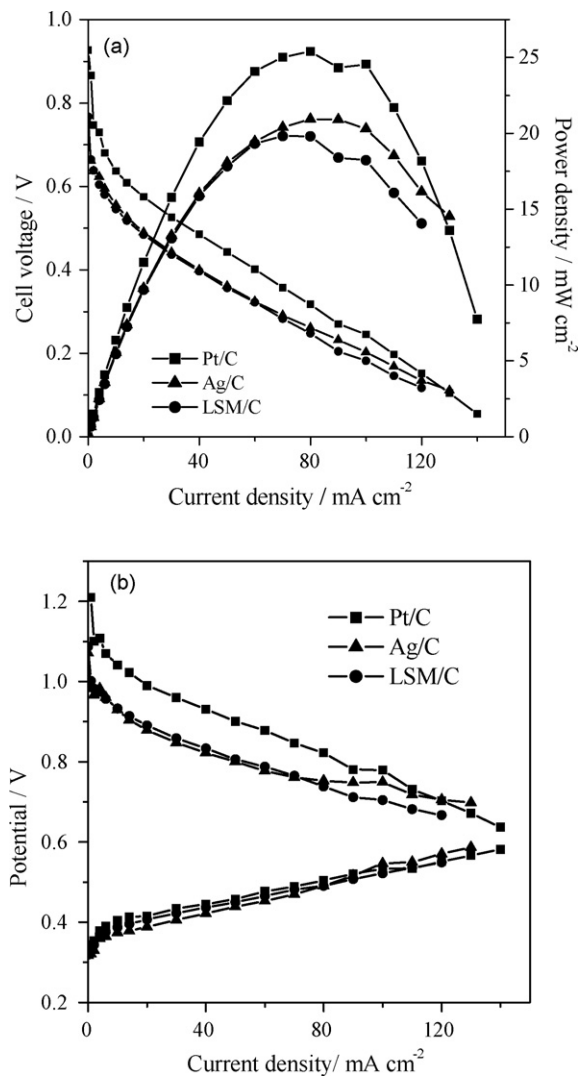


Fig. 3. (a) Cell voltages and power densities of direct EG alkaline fuel cells employing Pt/C, Ag/C and LSM/C as a cathode catalyst. (b) Polarization curves of the same fuel cells as in (a). Anode catalyst was Pt-Ru/C, and operating temperature was 353 K.

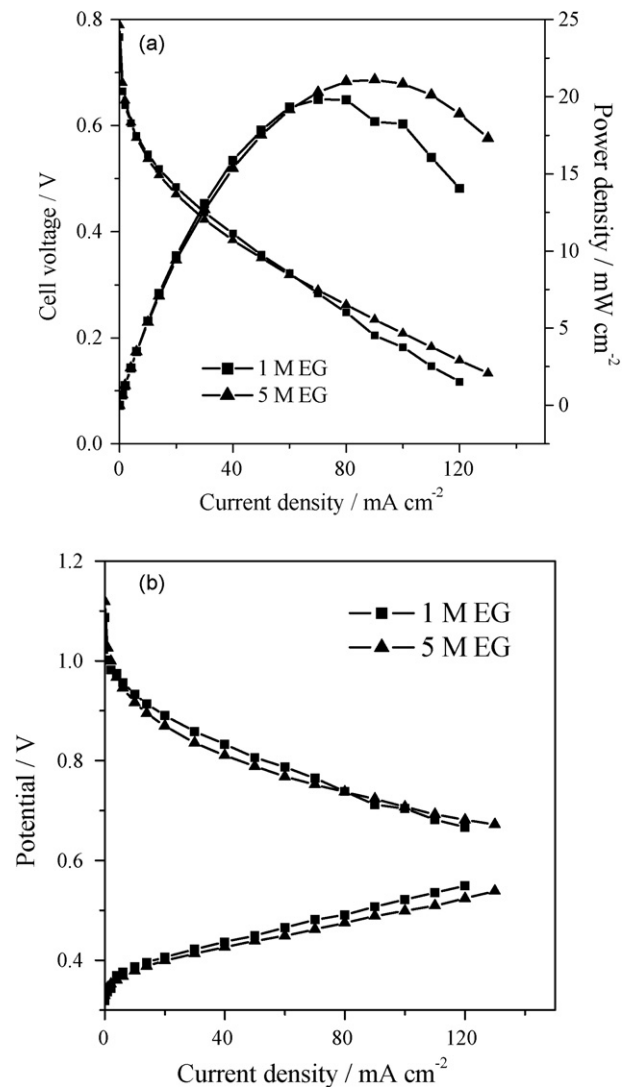


Fig. 4. (a) Cell voltages and power densities of direct EG alkaline fuel cells of LSM/C, supplied with 1 and 5 M EG with 1 M KOH solution. (b) Polarization curves of the same fuel cells as in (a).

alytic activities of LSM/C are superior to those of Ag/C. Fig. 3(b) illustrates polarization curves of anode and cathode electrodes. From this figure, LSM/C showed almost the same activities for oxygen reduction with Ag/C cathode. This result is quite consistent with the result that Ag/C and LSM/C showed almost the same power densities.

Fig. 4 shows the influence of EG concentration flowed into anode on the power density and the polarization of each electrode. Maximum power density increased with increasing concentration of EG. In Fig. 4(b), cathode polarizations remained unchanged regardless of the concentrations of EG, while anode polarization was improved by the increase of the concentration of EG. Condensed solution of fuel alcohol is preferable since higher energy density is obtained and it reduces the volume of fuel tank. Condensed solution of fuel, however, readily accelerates the permeation of alcohol through the electrolyte membrane. Ye et al. reported that open-circuit-voltage of DMFCs decreased with increasing methanol concentration due to the increase of methanol crossover [17]. Based on these results, we can conclude that LSM/C is an attractive cathode catalyst with high tolerance for EG crossover in alkaline fuel cells.

4. Conclusions

Carbon-supported $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM/C) was prepared by reversible homogeneous precipitation method, and its crossover tolerance under the existence of EG was evaluated with rotating disk electrode and fuel cell operation. As a result, oxygen reduction on LSM/C was not affected by the presence of EG in the electrolyte solution. Also, performance test demonstrated that fuel cell employing LSM/C as a cathode catalyst yielded the maximum power density of about 20 mW cm^{-2} , which was comparable to the power density using a commercially available Ag/C catalyst. Cathode polarization of LSM/C was not deteriorated by increasing the concentration of EG from 1 to 5 mol dm^{-3} . These results showed that LSM/C is a promising

material to possess high crossover tolerance used in direct EG alkaline fuel cells.

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