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Short communication

Effects of carbon on oxygen reduction and evolution reactions of gas-diffusion air electrodes based on perovskite-type oxides

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HIGHLIGHTS

- Electrocatalytic activities of some perovskite oxides are studied.
- Gas-diffusion type electrodes are employed for electrochemical measurements.
- All perovskite oxides examined show poor oxygen reduction activity without carbon.
- The results support the peroxide pathway of oxygen reduction mechanism.
- Oxygen evolution activity of electrodes depends on the perovskite species.

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ABSTRACT

Electrochemical properties of three perovskite oxides with different B-site elements, $LaMnO_3$, $La_{0.6}Sr_{0.4}FeO_3$ and $LaNiO_3$, are examined with and without carbon using gas-diffusion electrodes, in comparison with our previous results on $La_{0.5}Sr_{0.5}CoO_3$. Cyclic voltammetry studies reveal very low oxygen reduction current density of carbon-free perovskite oxides, indicating their poor catalytic activity on oxygen reduction reactions. By mixing carbon with perovskite oxides, the oxygen reduction current density is increased by about two orders. The results are consistent with the peroxide pathway mechanism in which the perovskite oxide is highly active on either electrochemical reduction or chemical decomposition. Electrochemical properties of a three-layered gas diffusion electrode demonstrate the peroxide pathway mechanism works even the perovskite oxide and the carbon exist in separate layers. Oxygen evolution reactions are prominently dependent on the oxide species and also on an addition of carbon. The electrode based on carbon-free $LaNiO_3$ or $La_{0.5}Sr_{0.5}CoO_3$ show moderate oxygen evolution activity, and the activity is further enhanced by an addition of carbon, while $LaMnO_3$ and $La_{0.6}Sr_{0.4}FeO_3$ show poor activity even with an addition of carbon.

1. Introduction

Development of a high-performance reversible air electrode is one of the most important issues for realization of high energy density, safe and inexpensive metal–air rechargeable batteries for automotive and power storage applications [1–5]. Air electrodes based on non-precious metal catalysts are highly expected as a practical cathode for metal–air rechargeable batteries because of their low material cost, and among such materials, transition metal oxides with perovskite-type crystal structures have been most extensively studied with regard to their synthesis method, chemical composition, crystal structure, and electrochemical properties [6–12]. Oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) mechanisms of various pure and carbon-containing perovskite oxide electrodes have been reported [9,13–23] and the results suggest that elucidation of the roles of oxide and carbon in an air electrode is of utmost importance for improvement of performances. Rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) setups have been often employed for the studies of ORR activities of carbon-free perovskite oxides [17–23].

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However, in RDE setups, evaluation of ORR activity is differences of electrode performances are often unclear due to low limiting current density originated from low concentration of dissolved oxygen. Therefore, in our previous study [24], we investigated ORR and OER activities of a perovskite type $La_{0.5}Sr_{0.5}CoO_3$ employing gas-diffusion type electrodes with a thin electrocatalyst layer, and demonstrated that ORR current density of $La_{0.5}Sr_{0.5}CoO_3$ with carbon was two orders of magnitude higher than that without carbon. For an OER electrocatalyst, $La_{0.5}Sr_{0.5}CoO_3$ without carbon shows moderate activity and it is enhanced by an addition of carbon. However, the ORR and OER properties of $La_{0.5}Sr_{0.5}CoO_3$ could not be generalized without further studies on other perovskite oxide materials, because properties of perovskite oxides are greatly influenced by the chemical composition, especially by the B-site elements [25–30].

In this study, we examine perovskite oxides with different B-site elements, $LaMnO_3$, $La_{0.6}Sr_{0.4}FeO_3$, $LaNiO_3$, as well as $La_{0.5}Sr_{0.5}CoO_3$ using gas-diffusion type electrodes, and influences of carbon on the ORR and OER properties are discussed.

2. Experimental

2.1. Materials

Perovskite type oxides, $LaMnO_3$, $La_{0.6}Sr_{0.4}FeO_3$ and $LaNiO_3$ were synthesized by the malic acid precursor method described in our previous study [24]. Reagent grade La_2O_3, $SrCO_3$, $MnCO_3$, iron(III) citrate n-hydrate, $NiCO_3$ corresponding to the perovskite compositions were used as starting materials. Malic acid salt precursors were first calcined at 600 °C for 10 h, and subsequently at 1200 °C for 6 h in air, except for the $LaNiO_3$ precursor which was first calcined at 600 °C for 10 h, and then at 900 °C for 6 h in oxygen atmosphere.

As a conducting carbon material C-NERGY Super C65® (hereafter "C65", Timcal Corp.) was used, and polytetrafluoroethylene (PTFE, Aldrich, 60 wt% dispersion) was used as a binder of air electrodes. A teflon-treated carbon paper (EC-TP1-120T, ElectroChem. Inc.) was used as the gas-diffusion layer.

2.2. Preparation of test electrodes

Gas-diffusion type air electrodes composed of two layers, an electrocatalyst layer and a gas-diffusion layer, were fabricated for evaluation of electrocatalysts. Two types of electrocatalyst layers, namely a slurry-coated type and a rolled-sheet type, were formed on the carbon paper gas-diffusion layer. The slurry-coated catalyst layer was prepared by coating a slurry consisting of perovskite oxide and PTFE (10 wt%) on a disk-shaped carbon paper having a diameter of 24 mm. The loading of perovskite oxide was adjusted to 3 mg cm^{-2}. For the viscosity control of the slurry, aqueous solution of polyvinyl alcohol (ca. 10 wt%) was used, which was completely removed by a heat treatment process. The rolled-sheet catalyst layer was prepared by roll-pressing a mixture of oxide, carbon (C65) and PTFE (40: 40: 20, wt%) into a sheet, punching the sheet into a disk having a diameter of 24 mm, and pressing onto a carbon paper of the same diameter. Thickness of the sheet was adjusted to 150–160 μm, with an oxide loading of about 7 mg cm^{-2}. Both types of electrodes were heat-treated at 375 °C in vacuum for 20 min.

A three-layered gas diffusion type electrode having carbon paper/carbon (rolled-sheet, C65)/$La_{0.5}Sr_{0.5}CoO_3$ (slurry-coated, without carbon) layers was used for evaluation of effects of carbon in a separate layer.

2.3. Measurement of crystal structure and physical properties of materials and electrodes

The crystal structure of the oxides was analyzed by an X-ray diffractometer (RINT-TTR III, Rigaku) using CuKα radiation. Average particle size and specific surface area of the materials were measured using a particle size analyzer (LA-950V2, Horiba) and an automatic surface area analyzer (BELSORP-mini II, BEL Japan, Inc.), respectively. Gas permeability of air electrodes were measured by a Gurley type densometer (No. 323-Auto, Yasuda Seiki). Electric conductivity of perovskite oxides was measured for pellets (diameter: 12 or 15 mm) of the samples containing 10 or 15 wt% PTFE. A field-emission type scanning electron micrograph (JSM-7000F, JEOL) was used for observation of the cross-section of the electrode.

2.4. Electrochemical measurements

The cell structure is similar to that reported in our previous papers [24,31]. A platinum plate and an Hg/HgO electrode were used as the counter and reference electrodes, respectively, and an aqueous solution of 8 mol dm^{-3} KOH was used as an electrolyte. The electrolyte may contain oxygen or air, since the electrolyte is not degassed and oxygen evolution occurs on the counter electrode during oxygen reduction on the working electrode. In this study, all electrode potential values are converted to the reversible hydrogen electrode (RHE) scale. Electrochemical measurements were conducted using a potentiostat/galvanostat (VMP-3, Biologic Inc.) at 50 °C under air supply. Current density data obtained in cyclic voltammetry are based on the geometric surface area of the electrode.

3. Results and discussion

Fig. 1 shows XRD patterns of $LaMnO_3$, $La_{0.6}Sr_{0.4}FeO_3$ and $LaNiO_3$ examined in this study. Perovskite structures are confirmed for all samples, but minor NiO impurity peaks are observed in $LaNiO_3$. Physical properties of perovskite oxides, including $La_{0.5}Sr_{0.5}CoO_3$

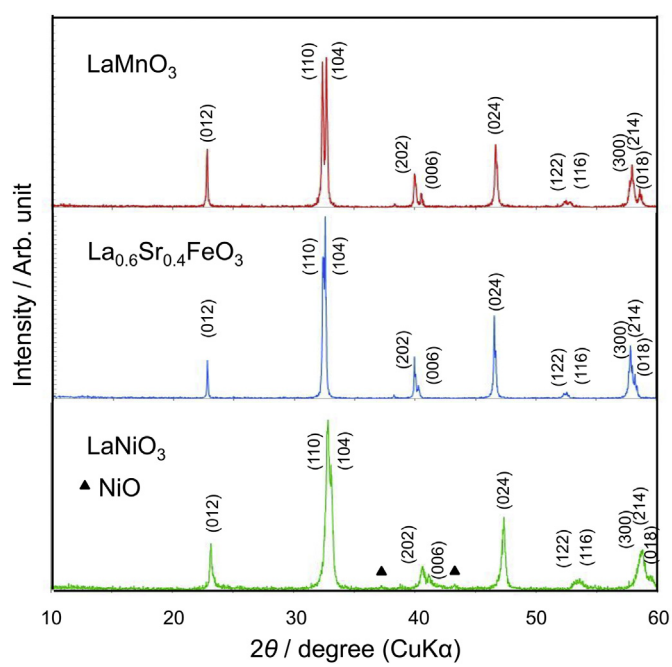

Fig. 1. X-ray diffraction patterns of $LaMnO_3$, $La_{0.6}Sr_{0.4}FeO_3$, and $LaNiO_3$ synthesized by an organic precursor method.