



# Oxygen reduction and evolution reactions of air electrodes using a perovskite oxide as an electrocatalyst



Koji Nishio <sup>a,\*</sup>, Sergio Molla <sup>a</sup>, Tomohiko Okugaki <sup>a</sup>, Shinji Nakanishi <sup>b</sup>, Iwao Nitta <sup>b</sup>, Yukinari Kotani <sup>b</sup>

<sup>a</sup> Graduate School of Engineering, Kyoto University, Nishikyo, Kyoto 615-8510, Japan

<sup>b</sup> Battery Research Division, Toyota Motor Corporation, 1200, Mishuku, Susono, Shizuoka 410-1193, Japan

## HIGHLIGHTS

- Two types of gas-diffusion electrodes are used for electrochemical examinations of  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ .
- Distinguished differences of carbon-free and carbon-containing perovskite electrodes are revealed.
- Peroxide reduction/decomposition on the perovskite oxide is very fast in spite of its relatively low surface area.
- Properties of carbon give remarkable effects on oxygen reduction reactions of perovskites.
- Cycling durability of perovskite electrodes is also dependent on properties of carbon species.

## ARTICLE INFO

### Article history:

Received 20 October 2014

Received in revised form

17 December 2014

Accepted 21 December 2014

Available online 23 December 2014

### Keywords:

Air electrode

Oxygen reduction reaction

Oxygen evolution reaction

Perovskite

Electrocatalyst

## ABSTRACT

The oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) of air electrodes consisting of  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  and/or carbon in the electrocatalyst layer are studied by using two types of gas diffusion electrodes. Cyclic voltammetry and square wave voltammetry studies reveal very low ORR activity of carbon-free perovskite and remarkably enhanced ORR of perovskite-carbon composites. The ORR current density at  $-0.5$  V vs. Hg/HgO is higher than  $200 \text{ mA cm}^{-2}$  in a wide range of perovskite-carbon composition, suggesting good peroxide reducing capability of the perovskite. The ORR mechanisms of perovskite-carbon composites are consistent with the 2+2-electron mechanisms. The ORR and OER properties of perovskite-carbon composite electrodes are significantly influenced by the carbon species. The electrode exhibits a higher ORR current density, but inferior cycling performances when a carbon material with a higher specific surface area is used, and vice versa. Under a current density of  $20 \text{ mA cm}^{-2}$  and ORR and OER durations of 30 min, a gas diffusion type electrode consists of  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  and a low surface area carbon are capable of more than 150 cycles.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Metal-air batteries have attracted much attention as next-generation high capacity batteries because of their high theoretical specific energy. Among various cell configurations, aqueous alkaline electrolyte type batteries represented by zinc-air systems are expected as a near-term option which has advantages of low material cost and superior safety [1–5]. In order to achieve a compact cell and a high energy density, the air electrode is desired

to be bifunctional [6]; namely, the same electrode should be used for both the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER).

The ORR mechanisms of air electrodes in an alkaline electrolyte have been studied by many researchers [7–11]. It has been reported that oxygen is reduced by two typical pathways: a 4-electron reduction (Eq. (1)) and a 2-electron reduction (Eq. (2)), depending on the electrode materials. The peroxide species produced in Eq. (2) could be further reduced by the reaction in Eq. (3). The total reaction of 2+2-electron reduction (Eq. (2) + Eq. (3)) is substantially the same as that of the 4-electron ORR reaction in Eq. (1). The peroxide species could be chemically decomposed in the reaction in Eq. (4).

\* Corresponding author. Present address: Office of Society-Academia Collaboration for Innovation (SACI), Kyoto University, Gokanosho, Uji, Kyoto 611-0011, Japan.  
E-mail address: [k-nishio@saci.kyoto-u.ac.jp](mailto:k-nishio@saci.kyoto-u.ac.jp) (K. Nishio).



Platinum is known as a good electrocatalyst which facilitates the reaction in Eq. (1). An electrocatalyst composed of fine platinum particles dispersed on a high surface area carbon support (Pt/C) is known as a typical material for the cathode of proton exchange membrane fuel cells (PEMFCs) [12,13]. Unlike this type of cells using an acidic electrolyte, non-precious metal electrocatalysts could be used in an alkaline electrolyte, and various transition metal oxides, especially those with the ABO<sub>3</sub>-type perovskite structure, have been extensively studied in the past few decades [14–19].

Rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) setups are frequently used as useful tools for elucidation of ORR and OER mechanisms on perovskite oxides with or without carbon addition [20–26]. In this type of experimental setups, a thin electrocatalyst layer is formed on the disk electrode, and oxygen gas dissolved in the electrolyte is supplied as the reactant for ORR. In a study on electrocatalytic activities of La<sub>0.6</sub>Ca<sub>0.4</sub>CoO<sub>3</sub> in some different conditions by Li et al., for example, the authors conclude that ORRs on pure La<sub>0.6</sub>Ca<sub>0.4</sub>CoO<sub>3</sub> and La<sub>0.6</sub>Ca<sub>0.4</sub>CoO<sub>3</sub>-carbon are understood as 4-electron and 2+2-electron pathways, respectively [21]. Electrochemical activities of perovskite oxides based on other B-site elements have also been reported [25,26].

It is important to study the effect of carbon on the ORR and OER characteristics of oxide electrocatalysts because an addition of carbon not only increases the electronic conductivity but also enhances the porosity of the electrode. Moreover, the carbon material, which itself is an electrocatalyst, also contributes to the ORR. Poux et al. have studied the ORR properties of various compositions of LaCoO<sub>3</sub>, La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> and carbon using an RDE, and concluded that carbon plays a dual role in the composite electrodes, namely electronic conductivity enhancement and peroxide formation [22]. In the studies using RDE or RRDE setups, however, the measured ORR current density values are usually limited in a range of several mA cm<sup>-2</sup>, since the reactant is supplied as oxygen dissolved in the electrolyte. Besides, different porous structures of various electrode materials are considered to be not well represented in a thin film rotating disk electrode. Therefore, it is assumed that electrocatalytic activities of different materials, such as perovskite oxides, carbon, perovskite-carbon composites, Pt/C, are not accurately evaluated by the ORR current density values.

Gas-diffusion electrodes, typically with a dual-layer structure consisting of an electrocatalyst (active) layer and a gas diffusion layer, have also been used for evaluation of the ORR and OER performances of air electrodes [14,27–31]. Shimizu et al. [14] have reported an excellent ORR current density of ca. 3000 mA cm<sup>-2</sup> for a gas diffusion electrode in which La<sub>1-x</sub>Ca<sub>x</sub>CoO<sub>3</sub> and a high surface area carbon are employed as the active layer. In some other papers [31–35], ORR current densities of 300–500 mA cm<sup>-2</sup> are reported for Mn-based perovskite electrocatalysts, although direct comparison of the current densities is not meaningful due to different experimental conditions. Arai et al. [27] analyzed ORR mechanisms of air electrodes using La<sub>0.6</sub>Ca<sub>0.4</sub>CoO<sub>3</sub> and carbon in detail by an ac impedance method. The authors also pointed out fast degradation of electrodes containing high surface area carbon which was attributed to oxidative corrosion of the carbon material. Constant current ORR-OER cycling performances of perovskite oxide

electrodes have been reported by some other authors [35–37], however, the influences of different carbon species on the cycling performances have not been thoroughly studied.

The aim of this study is to clarify the effects of carbon materials on bifunctional properties of a perovskite oxide, La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub>. For this purpose, we prepared two types of gas diffusion electrode. Slurry-coated electrodes were used for basic evaluation of ORR and OER properties, and rolled-sheet electrodes were used for long-term ORR-OER cycling tests.

## 2. Experimental

### 2.1. Materials

The electrocatalyst La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> (hereafter “LSCO”) powder was synthesized by an organic acid precursor method. Reagent grade La<sub>2</sub>O<sub>3</sub>, SrCO<sub>3</sub>, CoCO<sub>3</sub> and malic acid were employed as starting materials. Malic acid was added to a dispersion of La<sub>2</sub>O<sub>3</sub>, SrCO<sub>3</sub>, CoCO<sub>3</sub> in deionized water and the mixture was kept at 50–60 °C. The resultant malic acid salt was first calcined at 600 °C for 10 h, and subsequently at 1200 °C for 6 h in air. The calcined oxide was pulverized by a ball-mill.

Three kinds of carbon materials, Vulcan XC-72<sup>®</sup> (“Vulcan”, Cabot Corp.), C-ENERGY Super C65<sup>®</sup> (“C65”, Timcal Corp.) and Ketjenblack<sup>®</sup> EC600JD (“KB”, Lion Corp.) were used as conducting additives, 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.

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. The phase purity of the LSCO was analyzed by an X-ray diffractometer (RINT-TTR III, Rigaku) using CuKα radiation.

### 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 layer, namely a slurry-coated type and a rolled-sheet type, were formed on the gas-diffusion layer. The slurry-coated catalyst layer was prepared by coating a slurry containing LSCO, carbon and PTFE (10 wt%) on a disk-shaped carbon paper having diameter of 24 mm. The rolled-sheet catalyst layer was prepared by roll-pressing a mixture of LSCO, carbon and PTFE (40: 40: 20, wt%) into a sheet of about 150 μm, punching the sheet into a disk having a diameter of 24 mm, and pressing onto a carbon paper of the same diameter. Both types of electrodes were heat-treated at 375 °C in vacuum for 20 min.

### 2.3. Electrochemical measurements

A two-compartment cell, each compartment having inner diameter of 20 mm and length of 52 mm, was used for electrochemical measurements of the air electrodes. The cell structure is similar to that reported in a previous paper [38]. The air electrode was sandwiched between two compartments, and the compartment in the electrocatalyst layer side was filled with 8 mol dm<sup>-3</sup> KOH aqueous solution. Air was supplied to the other compartment at a rate of 50 cm<sup>3</sup> min<sup>-1</sup>. A platinum plate and an Hg/HgO electrode were used as the counter and reference electrodes, respectively. A potentio/galvanostat (VMP-3, Biologic Inc.) was used for electrochemical measurements. Cyclic voltammetry (CV) was

Download English Version:

<https://daneshyari.com/en/article/7733924>

Download Persian Version:

<https://daneshyari.com/article/7733924>

[Daneshyari.com](https://daneshyari.com)