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Improving the catalytic activity of lanthanum manganese oxide with strontium doping for hydrogen peroxide reduction reaction in micro direct alcohol-hydrogen peroxide fuel cell

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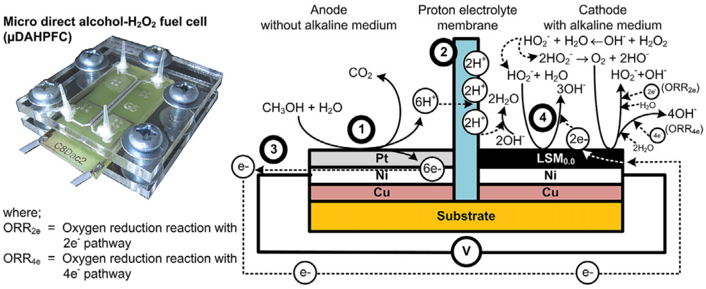
HIGHLIGHTS

- The performance of $La_{1-x}Sr_xMnO_{3\pm\delta}$ and thin-film Pt in the micro fuel cell is studied.
- O_2 and H_2O_2 reduction reactions occur on $La_{1-x}Sr_xMnO_{3\pm\delta}$ in alkaline solution.
- Increasing Sr-doping will increase Mn^{4+}/Mn^{3+} ratio in $La_{0.4}Sr_{0.6}MnO_{3\pm\delta}$ ($LSM_{0.6}$).
- $LSM_{0.6}$ has its catalytic activity on H_2O_2 reduction reaction closed to thin-film Pt.
- Reaction pathways in a micro direct alcohol-hydrogen peroxide fuel cell are proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

The work presents lanthanum manganese oxide with strontium doping written as $La_{1-x}Sr_xMnO_{3\pm\delta}$ (LSM_x; x = 0.0 and 0.6), using as an alternative catalyst for replacing high-cost platinum-based catalysts used for hydrogen peroxide reduction reaction (HPRR) applications in alkaline solution. Among LSM_x series, the $La_{0.4}Sr_{0.6}MnO_{3\pm\delta}$ ($LSM_{0.6}$) is chosen due to its highest catalytic performance from our previous study. It is compared with $LaMnO_{3\pm\delta}$ ($LSM_{0.0}$) and thin-film platinum as a representative of the platinum-based catalyst and as a reference catalyst. With Sr-doping, the ratio of Mn^{4+} to Mn^{3+} of $LSM_{0.6}$ increases and its catalytic activity improves. Both HPRR and oxygen reduction reaction (ORR) occur in micro direct alcohol-hydrogen peroxide fuel cell (μDAHPFC). As a cathode catalyst in μDAHPFC, although $LSM_{0.6}$ gives higher performance compared to $LSM_{0.0}$, it still exhibits lower performance compared to that of the thin-film platinum. The electrochemical impedance spectroscopy study also reveals that $LSM_{0.6}$ exhibits higher conductivity compared to $LSM_{0.0}$ but lower conductivity compared to that of the thin-film platinum. The main factors causing low open circuit voltage value could be the activation loss due to the charge transfer rate and mass transfer effect including the proton transfer across the casted proton electrolyte membrane and the fabrication of μDAHPFC.

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1. Introduction

A micro direct alcohol fuel cell (μDAFC) is an electrochemical energy conversion device which can directly convert the chemical energy stored in alcohols (such as methanol, ethanol, 2-propanol and ethylene glycol) into electricity [1–5]. The μDAFC is useful for portable electronic devices because of its many advantages, including compact structure, high energy density, easy fuel storage and fuel flexibility with a wide choice of feed [5,6]. However, to increase power density, hydrogen peroxide (H_2O_2) is used to replace oxygen (O_2) at the cathode side of fuel cells [7–16]. Compared with O_2, H_2O_2 can be dissolved at a higher concentration in an aqueous solution; therefore, it has a potential to enhance the power density of fuel cells. H_2O_2 is easy to handle and safer than a compressed O_2 in a gas tank. In addition, hydrogen peroxide reduction reaction (HPRR) involves 2-electron transfer and offers lower activation loss compared to the oxygen reduction reaction (ORR), involving both 2- and 4-electron transfer [17]. Therefore, the kinetic rate of HPRR should be faster than that of ORR. However, on non-noble metal catalysts, the kinetic of HPRR is slow and the side reaction of H_2O_2 decomposition occurs [18,19]. H_2O_2 decomposition produces O_2 gas or bubbles into the solution, leading to partial loss of H_2O_2 oxidant. The produced O_2 bubbles also block the oxidant laminar flow inside the micro fuel cell or attach to the cathode surface, causing a decrease in the electrode active area of the micro fuel cell, which is a cause of the decreasing power density [12,13].

ORR requires platinum-based catalysts, which are high-cost materials, to achieve the best performance at room temperature (RT). HPRR at RT can be catalyzed by noble metals (such as platinum, palladium, iridium, gold, silver, nickel, iron, cobalt and a combination of these metals) [17,20–24] and metal oxides (such as $LaMnO_3$, $LaNiO_3$, and $LaCoO_{3-\delta}$) [16,19,25–27]. Usually, noble metals exhibit high catalytic activity for HPRR, but they significantly catalyze the decomposition reaction of H_2O_2 to O_2 [5,19]. Meanwhile, metal oxides show lower catalytic activity for H_2O_2 decomposition reaction and they are inactive to crossover alcohol [5,19]. To overcome the slow kinetic problem, it is necessary to develop a highly active and alcohol tolerable low-cost catalyst for a cathodic reduction reaction in μDAFC.

ABO_3 perovskite-type metal oxides are studied as promising cathode materials for alkaline fuel cells (AFCs) and solid oxide fuel cells (SOFCs) due to their abundant, inexpensive, nontoxic and stable in an alkaline medium [3,28]. The physical and chemical properties of the perovskite oxide can be tuned by partially replacing the elements in either the A or B site. For AFC and SOFC applications, $LaMnO_3$, a perovskite oxide, and its family with the molecular formulae of $La_{1-x}Sr_xMnO_{3\pm\delta}$ were studied for ORR at high temperature [28]. For ORR in an alkaline medium at RT, the $La_{1-x}Sr_xMnO_3$ series was investigated and $La_{0.4}Sr_{0.6}MnO_3$ exhibited the best catalytic activity among them [29]. $La_{0.4}Sr_{0.6}MnO_3$ was also reported to give high catalytic activity toward HPRR in an alkaline medium at RT [16,30].

The aim of the work is the use of perovskite metal oxide as an alternative cathode catalyst to replace the platinum-based catalyst for the application of HPRR in alkaline solution. $La_{1-x}Sr_xMnO_{3\pm\delta}$ (LSM_x) was chosen and thin-film platinum was used as a representative of platinum-based catalysts. From our literature data of using LSM_x for HPRR or ORR applications at room temperature [16,30], x = 0.6 provided the best performance. Therefore, $La_{0.4}Sr_{0.6}MnO_{3\pm\delta}$ ($LSM_{0.6}$) was chosen and its catalytic performance was compared to those of $LaMnO_{3\pm\delta}$ ($LSM_{0.0}$) and the thin-film platinum. The $La_{1-x}Sr_xMnO_{3\pm\delta}$ (LSM_x; x = 0.0 and 0.6) and the thin-film platinum were also used as cathode catalysts in a micro direct alcohol-hydrogen peroxide fuel cell (μDAHPFC). Methanol and ethanol were employed as fuels and thin-film platinum was used as an anode catalyst. The LSM_x powders were characterized and their electrocatalytic activities on HPRR in an alkaline medium at RT were examined to compare with those of thin-film platinum. The μDAHPFC performance of LSM_x was evaluated with the optimum conditions and compared to that of thin-film platinum.

In the present work, there are three main objectives. One is to investigate the crystalline phase and the oxidation state of manganese species, as well as the porosity of $LSM_{0.6}$, which is characterized by X-ray diffraction (XRD), X-ray adsorption spectroscopy (XAS) and nitrogen sorption, compared to $LSM_{0.0}$. Another is to investigate the electrochemical behavior of the LSM_x and thin-film platinum catalysts using cyclic voltammetry (CV). And, the other is to evaluate the performance of LSM_x as the cathode catalyst of a μDAHPFC device compared to that of thin-film platinum, and to measure the total internal impedance of the device. For better understanding, the possible reaction pathways are proposed for a μDAHPFC with/without alkaline medium.

2. Experimental section

$LaMnO_{3\pm\delta}$ and $La_{0.4}Sr_{0.6}MnO_{3\pm\delta}$ powders were synthesized by a citric acid sol-gel precursor method according to the report by Rabelo et al. [31]. Starting reagents and calcination for catalyst preparation are described in Supporting Information. Phase identification was investigated by XRD. The oxidation state and phase composition of the LSM_x powders were characterized by XAS at Beamline 5.2 and 8, Synchrotron Light Research Institute (Public Organization), Nakhon Ratchasima, Thailand. The nitrogen sorption isotherm was performed and then specific surface area, pore size distribution, and total pore volume were calculated. Electrochemical properties of LSM_x and thin-film platinum electrodes were investigated by CV in a 0.5 M KOH electrolyte containing 0.1 M H_2O_2. For μDAHPFC studies, the μDAHPFCs were fabricated using LSM_x and thin-film platinum as catalysts in the cell. More details about this section are described in Supporting Information.

3. Results and discussions

3.1. X-ray diffraction

XRD patterns of LSM_x catalyst powders are shown in Fig. 1. Based on the Inorganic Crystal Structure Database (ICSD), Standard-$LaMnO_3$ (Std-$LaMnO_3$) diffraction peaks were correlated to the $LaMnO_3$ perovskite structure (CSD Number 433,498) with cubic symmetry. Fig. 1 shows that Std-$LaMnO_3$ contains a single phase of a cubic $LaMnO_3$ perovskite phase; $LSM_{0.0}$ consists of the perovskite phase and a La_2O_3 impurity phase; $LSM_{0.6}$ is composed of the perovskite phase and a $SrCO_3$ impurity phase.

The average crystallite sizes of all LSM_x samples were calculated from the peak at 2θ = ∼32.6° via the Scherrer's equation and were

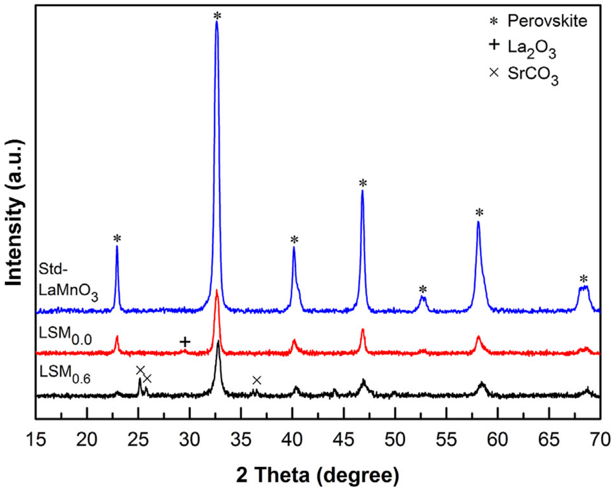

Fig. 1. XRD patterns of $La_{1-x}Sr_xMnO_{3\pm\delta}$ (x = 0.0 and 0.6) catalyst powders.