



# Manganese Dioxide-based Bifunctional Oxygen Reduction/Evolution Electrocatalysts: Effect of Perovskite Doping and Potassium Ion Insertion



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## ABSTRACT

Non-precious metal bifunctional oxygen reduction and oxygen evolution reaction (ORR and OER, respectively) catalysts are of great interest for rechargeable metal/air batteries and regenerative alkaline fuel cells. We investigate the initial stage activities and the electrocatalytic durability of bifunctional catalysts composed of MnO<sub>2</sub> and perovskite (LaNiO<sub>3</sub> or LaCoO<sub>3</sub>) in a 1:1 weight ratio. Gas diffusion electrodes (GDE) with a catalyst layer composed of MnO<sub>2</sub>:co-catalyst (LaNiO<sub>3</sub> or LaCoO<sub>3</sub>):Vulcan XC-72 were prepared and studied in O<sub>2</sub> saturated 6 M KOH. The initial stage bifunctional activities of MnO<sub>2</sub>-LaCoO<sub>3</sub> and MnO<sub>2</sub>-LaNiO<sub>3</sub> are markedly superior compared to either MnO<sub>2</sub> or perovskite alone, demonstrating a synergistic effect. Furthermore, we show for the first time that the degradation of the bifunctional electrocatalytic activity of the MnO<sub>2</sub>-perovskite electrodes during extensive potential cycling can be fully restored by resting the electrodes at open-circuit potential in 6 M KOH. A hypothesis is proposed to explain this catalytic promotion and 'healing' effect based on XPS results showing potassium ion incorporation in the electrocatalyst structure. Lastly, a thorough comparison of the results obtained in the present work with those reported in the literature with a variety of bifunctional catalysts is presented, demonstrating the effectiveness of the MnO<sub>2</sub>-perovskite electrodes.

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## 1. Introduction

The development of a bifunctional catalyst for both oxygen reduction (ORR) and evolution (OER) reactions is of great interest for electrochemical power sources such as regenerative fuel cells and rechargeable metal/air batteries [1–3]. Manganese dioxide has been intensely investigated as a catalyst for ORR in alkaline batteries and fuel cells due to a unique combination of properties, i.e., low cost, abundance, environmental friendliness and promising electrocatalytic activity for ORR [4–7]. Among the commercially readily available MnO<sub>2</sub> types, Gyenge and Drillet have demonstrated that the Sigma-Aldrich MnO<sub>2</sub> (structurally a  $\gamma$ -MnO<sub>2</sub>) is the most active for ORR [4]. However, pertinent to the bifunctional cathode, some issues such as low electrocatalytic activity for OER, poor recharging and complex charge-discharge behavior, limits the application of MnO<sub>2</sub> as a lone catalyst for both OER and ORR [2,8,9].

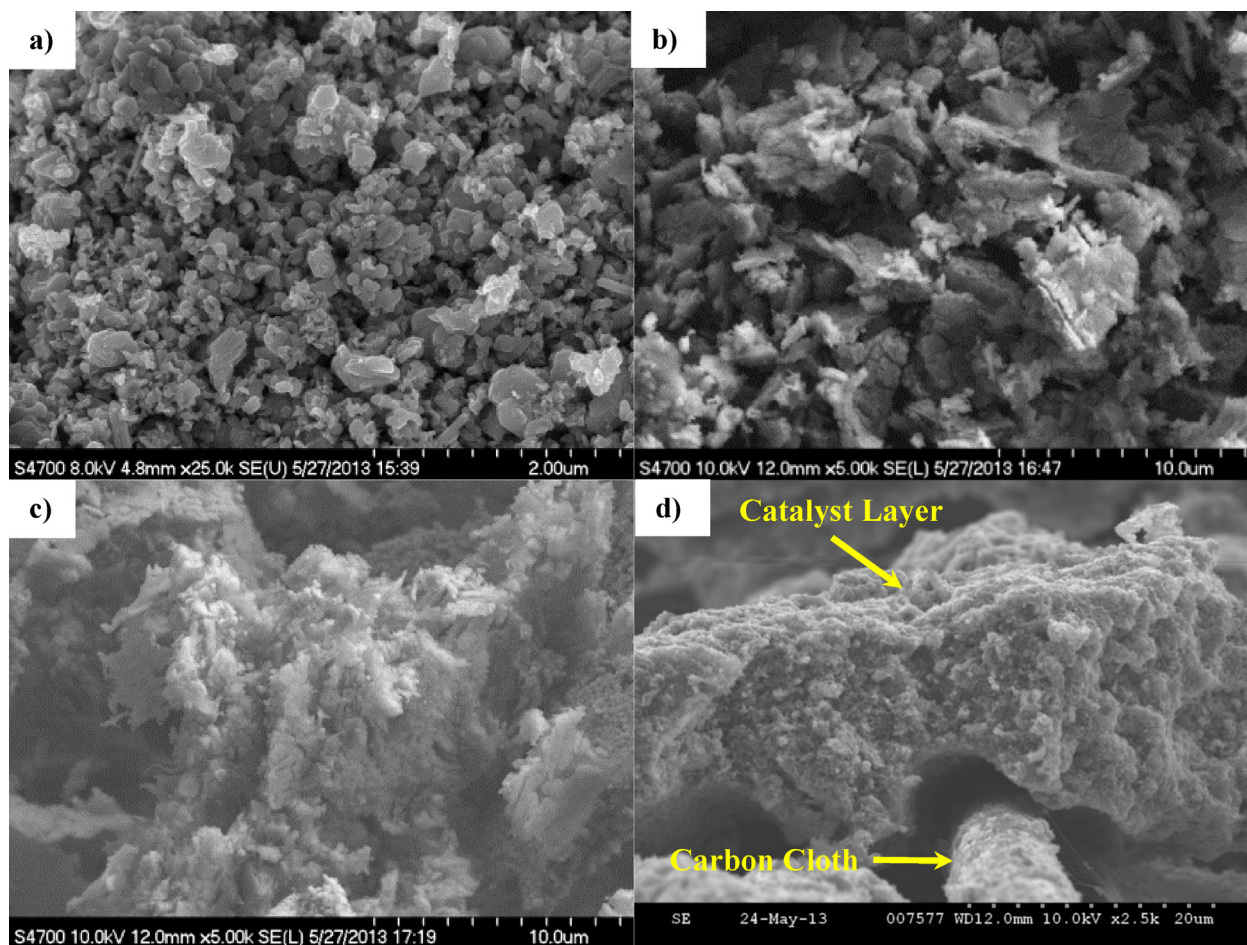
Another important class of non-precious metal electrocatalysts for oxygen cathodes are perovskites. These are catalysts of great diversity because of the wide range of ions and valences that the

structure can accommodate [10–12]. Different types of perovskites have been synthesized and reported to possess improved physical properties as well as good electrocatalytic activity for ORR and OER in alkaline electrolytes [12–17]. Lee et al. revealed that La<sub>0.6</sub>Ca<sub>0.4</sub>CoO<sub>3</sub> prepared by the amorphous citrate precursor process, calcined at 650 °C followed by rapid quenching, has a high surface area of 33 m<sup>2</sup> g<sup>-1</sup>. They reported that 10 mg cm<sup>-2</sup> of this catalyst can provide a significant bifunctional performance, i.e. -280 mA cm<sup>-2</sup> for ORR and 300 mA cm<sup>-2</sup> for OER at 600 and 1600 mV (vs. RHE) in 30 wt% KOH at 298 K, respectively, when the GDEs are exposed to pure oxygen [16]. In another study, Li et al. reported fast ORR kinetics for La<sub>0.6</sub>Ca<sub>0.4</sub>CoO<sub>3</sub>-Carbon composites with low Tafel slope of -60 mV dec<sup>-1</sup> and relatively high exchange current density of 5.8 × 10<sup>-11</sup> A cm<sup>-2</sup> in O<sub>2</sub>-saturated 6 M KOH [17]. Even though perovskite-type oxides show high electrocatalytic activity toward OER, their relatively low conductivity and surface area, as well as poor electrocatalytic activity toward ORR, compared to other non-precious compounds like MnO<sub>2</sub>, limits their use as bifunctional electrodes in concentrated alkaline solutions [4,17].

The present study is aimed at the development of highly active and durable MnO<sub>2</sub>-based catalysts for both ORR and OER by doping MnO<sub>2</sub> (Sigma-Aldrich Inc.) with two perovskite-type oxides, i.e. LaNiO<sub>3</sub> and LaCoO<sub>3</sub>, respectively. The performance of

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**Fig. 1.** SEM images of: a) commercial Sigma-Aldrich  $\text{MnO}_2$  powder, b) synthesized  $\text{LaCoO}_3$  powder, c) synthesized  $\text{LaNiO}_3$  powder and d) Catalyst layer consisting of  $\text{MnO}_2$ - $\text{LaCoO}_3$  sprayed on a 40wt% PTFE treated carbon cloth.

the mixed catalysts toward OER and ORR and the promoter role of potassium species are investigated by a combination of surface structural characterization methods and half-cell electrochemical techniques.

## 2. Experimental Methods

### 2.1. Preparation of the Perovskite- $\text{MnO}_2$ /Carbon cloth gas diffusion electrode (GDE)

Two different co-catalysts, i.e.,  $\text{LaNiO}_3$  and  $\text{LaCoO}_3$ , were synthesized via a co-precipitation method [18]. The  $\text{LaNiO}_3$  powder was made by preparing a solution of 0.2 M lanthanum (III) nitrate hexahydrate ( $\text{La}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$ ) and 0.2 M nickel(II) nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ ) and adding ammonium hydroxide 5% ( $\text{NH}_4\text{OH}$ ) as a precipitating agent until the pH reached 9.25. The solution was then heated 3 hrs at  $70^\circ\text{C}$  followed by a heating sequence of: 3 hrs at  $110^\circ\text{C}$ , 1 hr at  $300^\circ\text{C}$  and another 2 hrs at  $700^\circ\text{C}$  in air using a box furnace. Afterwards, the solution was left to cool down to room temperature in the furnace. The heating rate for all segments was  $5^\circ\text{C}/\text{min}$ . For  $\text{LaCoO}_3$  synthesis, a similar procedure was carried out except that  $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$  was replaced with cobalt(II) nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ ).

In order to produce the  $\text{MnO}_2$ -perovskite/carbon cloth GDEs, various catalyst inks were prepared by 1 hr sonication of a mixture composed of  $\text{MnO}_2$  (Sigma-Aldrich GmbH manganese (IV) dioxide), Vulcan XC-72, co-catalysts (i.e.  $\text{LaNiO}_3$  or  $\text{LaCoO}_3$ , whenever applicable), isopropanol, water, 5 wt% Nafion solution and

60 wt% PTFE (polytetrafluoroethylene) suspension. The  $\text{MnO}_2$ :co-catalyst:Vulcan weight ratio in the catalyst layer was always 1:1:1. The Vulcan:isopropanol:water weight ratio was kept at 1:50:16 in all catalyst inks. Furthermore, the PTFE and Nafion content of the catalyst layer was the same, namely, 14.8 wt% each, for all samples. Next, specified volume of the catalyst ink (10–20  $\mu\text{L}$ ) was drop-casted on a 6 mm diameter punch cut 40% PTFE treated carbon cloth from Fuel Cell Earth Co. such that to achieve a  $\text{MnO}_2$  and perovskite loadings of  $0.5 \text{ mg cm}^{-2}$  each. Afterwards, the GDEs were dried in an oven at  $70^\circ\text{C}$  for 1 hr.

### 2.2. Electrochemical Measurements

A quick-fit exchangeable sample holder from Radiometer Analytical (#A35T450) was used to insert the circular GDE (geometric area  $0.283 \text{ cm}^2$ ) in a rotating disk electrode (RDE) test setup for electrochemical measurements. Cyclic voltammetry tests were performed in  $\text{O}_2$  saturated 6 M KOH at 293 K using a conventional three-electrode setup where the working electrode was the GDE, the reference electrode was  $\text{Hg}/\text{HgO}/0.1 \text{ M KOH}$  (abbreviated as MOE), and the counter electrode was Pt mesh. The electrodes were connected to a computer-controlled VoltaLab 80 bi-potentiostat and its associated RDE set-up. The electrocatalytic activity of the doped  $\text{MnO}_2$ -based catalysts for both OER and ORR was investigated in the potential range between  $-700$  and  $750 \text{ mV}$  vs. MOE with a scan rate of  $5 \text{ mV s}^{-1}$ . The durability of the electrodes was also investigated during one hundred cycles in the potential range of  $-300$  to  $700 \text{ mV}$  in 6 M KOH at 293 K using the same scan rate of  $5 \text{ mV s}^{-1}$ .

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