



# Promotion of the bifunctional electrocatalytic oxygen activity of manganese oxides with dual-affinity phosphate

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## ABSTRACT

The search for low cost and high activity bifunctional electrocatalysts for the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) is a research priority in the development of rechargeable metal-air batteries. Manganese oxides are the current favorite, but their native activity needs to be substantially improved before they can be considered as the substitute of noble metals. We discovered phosphate modification as an effective strategy to increase the bifunctional oxygen activity of MnO<sub>2</sub> in ORR and OER. Specifically, the half-wave potential of phosphate-promoted  $\alpha$ -MnO<sub>2</sub> (PMO) for ORR is 0.85 V vs. RHE, ~70 mV more positive than  $\alpha$ -MnO<sub>2</sub> and the same as the benchmark 20 wt% Pt/C catalyst. The OER potential to maintain 10 mA cm<sup>-2</sup> of current density is 1.63 V, ~40 mV more negative than  $\alpha$ -MnO<sub>2</sub> and about the same as the benchmark 20 wt% Ir/C catalyst (1.60 V). The potential difference between ORR (at -3 mA cm<sup>-2</sup>) and OER (at 10 mA cm<sup>-2</sup>) is 0.79 V, a standard measure of bifunctional oxygen activity, notably surpasses the performance of  $\alpha$ -MnO<sub>2</sub> (0.91 V) and the noble metals (0.95 V for Pt/C and 0.93 V for Ir/C). Additional electrochemical measurements and density functional theory calculations suggest that the promoted bifunctional activity of PMO is due to the dual-affinity of phosphate for O and OH groups, which assists O<sub>2</sub>/OH adsorption in ORR/OER.

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## 1. Introduction

Oxygen electrocatalysis is essential for the development of efficient electrochemical energy devices based on the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) which have inherently slow kinetics [1,2]. The most active oxygen electrocatalysts are all noble metal-based (e.g., Pt for ORR and RuO<sub>2</sub>, IrO<sub>2</sub> for OER), but their prohibitively high cost has limited their utility in large-scale applications. In addition, noble metal catalysts are seldom bifunctional, while bifunctionality is a requirement for regenerative energy devices such as the rechargeable metal-air batteries [3–6]. The development of low cost bifunctional oxygen electrocatalysts is therefore a priority research area in oxygen electrocatalysis [7–10]. Among the non-noble metal alternatives

developed to date, manganese oxides have drawn the most interest because of their cost effectiveness, natural abundance, environmental benignity and most importantly; their activity for both ORR and OER [11–13]. The ORR activity of manganese oxides has been known for decades and extensively researched [14,15]. On the other hand, the discovery that the active sites in the oxygen evolving complex (OEC) of photosystem II (PSII) are m-oxido-Mn<sub>4</sub>Ca clusters [16–18] has energized much of the current interest in manganese oxides for OER. Many forms of manganese oxides (tunnel, birnesite, spinel and perovskite) have been examined for ORR and OER catalysis [19–24], and so are factors such as the surface area [25] and Mn oxidation state [26–28]. The ORR and OER activities of most of the manganese oxides examined to date are still not at the level of the noble metals. The oxygen bifunctionality of manganese oxides is also an area for improvement.

The main issues of manganese oxides in ORR and OER are their low electronic conductivity and their low affinity for O<sub>2</sub> and OH<sup>-</sup> capture [29,30]. The multi-valence character of manganese also leads to low stability, especially under the high anodic potential for

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oxygen evolution. Introducing an adjuvant component that can promote the adsorption of O<sub>2</sub> and OH<sup>-</sup> as well as stabilize the Mn active sites would be one method to improve the bifunctional performance of manganese oxides. In this context, the phosphate (PO<sub>4</sub><sup>3-</sup>) doping of manganese oxides may be a solution since P atoms can bond well with both O and OH groups; and PO<sub>4</sub><sup>3-</sup> is stable against oxidation [31]. In addition many metal phosphates are OER active [32–37]. The PO<sub>4</sub><sup>3-</sup> group was also found to facilitate the proton transfer in OER on perovskites [38]. It is likely that a similar assistive effect may also occur in OER on manganese oxides.

This is a report of our finding that the bifunctional oxygen activity of α-MnO<sub>2</sub> can be improved effectively by phosphate modification. α-MnO<sub>2</sub> was chosen because it is the most catalytically active phase of manganese oxides [21]. The potential difference between OER (at 10 mA cm<sup>-2</sup>) and ORR (at ~ -3 mA cm<sup>-2</sup>), a standard measure of oxygen bifunctionality, is reduced from 0.91 V for the α-MnO<sub>2</sub> to 0.79 V for the phosphate-promoted α-MnO<sub>2</sub> (PMO). Besides, the same ORR activity as Pt/C and similar OER activity as Ir/C makes PMO a very promising alternative to the noble metals. More importantly, DFT calculations show the good bifunctional performance of PMO is probably attributed to the effect of the phosphate group in increasing the adsorbed O<sub>2</sub> bond length in ORR and in promoting OH adsorption in OER.

## 2. Experimental section

### 2.1. Synthesis of phosphate-promoted α-MnO<sub>2</sub> (PMO)

In a typical synthesis, 0.2 g MnSO<sub>4</sub>·H<sub>2</sub>O (>99%, Alfa-Aldrich) and 50 mg NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (>98%, Alfa-Aldrich) were dissolved in 10 ml water and stirred for 10 min. Separately, 0.5 g KMnO<sub>4</sub> (99%, AMRESCO) was dissolved in 15 ml water. The KMnO<sub>4</sub> solution was then slowly added to the MnSO<sub>4</sub> and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> mixed solution under vigorous stirring. The resulting mixture was stirred for 2 h and then transferred to a 40 ml Teflon-lined autoclave. The autoclave was heated in an oven at 180 °C for 24 h. The solid product was removed by centrifugation, washed with water and dried in 60 °C in air overnight. For the preparation of PMO with different P contents, only the amount of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> was changed (25 mg, 100 mg, 150 mg, and 200 mg). The products formed are denoted as PMO-0.022, PMO-0.041, PMO-0.048 and PMO-0.060, respectively. Pure α-MnO<sub>2</sub> nanowires were also prepared by a similar procedure but without NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> [39].

### 2.2. Material characterization

Powder X-ray diffraction (XRD) measurements were conducted on a Bruker D8 Advance with Cu Kα radiation (λ = 1.5418) over the 5°–80° range. The X-ray diffraction data was refined by the RIETAN-2000 Rietveld refinement program [40]. Field emission scanning electron microscopy (FESEM) images were taken by a JEOL JSM-6700F. Field emission transmission electron microscopy (FETEM) images were taken by a JEOL 2010F with an EDS analyzer and operating at 200 kV accelerating voltage. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra DLD spectrometer. The measured binding energies were corrected by referencing the C1s peak of adventitious carbon to 284.5 eV. The Mn valence state was inferred from the multiplet splitting in the Mn 3s spectrum as well as the location of the Mn 2p<sub>3/2</sub> peak. Fourier Transform Infrared Spectroscopy (FT-IR) was carried out on a Bio-Rad FTS-3500 ARX FTIR Spectrometer. Raman spectroscopy was performed on a XploRA PLUS Raman microscope, Horiba/JY, France.

### 2.3. Electrochemical measurements

Electrochemical measurements were based on a three-electrode system consisting of a Ag/AgCl (in 3 M KCl, aq) reference electrode, a Pt foil counter electrode; and 0.1 M KOH aqueous solution saturated with high-purity O<sub>2</sub> as the electrolyte. The measured potentials were subsequently converted to the reversible hydrogen electrode (RHE) scale ( $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.21 + 0.059 \times \text{pH V}$ ). The working electrode was fabricated by depositing the catalyst ink onto a glassy carbon (GC, 5 mm in diameter) electrode. The catalyst ink was prepared as follows: 4 mg of PMO (or α-MnO<sub>2</sub>) and 1 mg of carbon powder (Ketjen black) were mixed in a mortar and ultrasonically dispersed in a mixture of Nafion solution (20 μl, Sigma-Aldrich), water (250 μl) and ethanol (750 μl) for 30 min. 12 μl of the suspension was then dispensed onto the polished GC electrode and dried overnight. The effective catalyst loading prepared as such was 0.30 mg cm<sup>-2</sup>. The carbon powder was used to improve the electrical conductivity of manganese oxides. In comparison tests, the GC electrode was loaded with the benchmark 20 wt% Pt/C and Ir/C catalysts to the same level (0.30 mg cm<sup>-2</sup>). Electrochemical measurements were carried out on an Autolab type III potentiostat/galvanostat using a rotating disk electrode (RDE) and a rotating ring disk electrode (RRDE). A μAutolab potentiostat/galvanostat with a FRA-attachment was used for the electrochemical impedance spectroscopy (EIS). The impedance measurements were carried out over the 100 kHz to 50 mHz frequency range at 0.84 V and 1.65 V vs. RHE at room temperature. The electron transfer number (*n*) was calculated by the Koutecky-Levich (K-L) equation:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} = \frac{1}{nFAkC^0} - \frac{1}{0.62nFAD_0^{2/3}\nu^{-1/6}C^0\omega^{1/2}} \quad (1)$$

where *i*, *i<sub>k</sub>*, and *i<sub>d</sub>* are the measured, kinetic, and diffusion-limited current, respectively. *n* is the overall electron transfer number, *F* the Faraday constant, *A* the geometric electrode area (cm<sup>2</sup>), *k* the rate constant for oxygen reduction, *C<sup>0</sup>* the saturated oxygen concentration in 0.1 M KOH, *D<sub>O<sub>2</sub></sub>* the diffusion coefficient of oxygen, *ν* the solution kinetic viscosity, and *ω* the rotation rate (rad s<sup>-1</sup>) of the electrode. In order to correct for the capacitance effect in the measurements, the polarization curves of samples in O<sub>2</sub>-saturated solution were subtracted from the polarization curves in N<sub>2</sub>-saturated solution.

The percentage of peroxide species (H<sub>2</sub>O<sub>2</sub>%) with respect to the total generated oxygen reduction products was calculated using the following equations:

$$\text{H}_2\text{O}_2\% = 200 \frac{I_r/N}{I_d + I_r/N} \quad (2)$$

where *I<sub>d</sub>* is the disk current, *I<sub>r</sub>* the ring current, and *N* the current collection efficiency of the electrode, which is 0.38.

### 2.4. Computational methods

The theoretical calculations were based on the CASTEP [41] density-functional software package in Materials Studio 2016. The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) was used to estimate the exchange-correlation effect [42]. Ultrasoft pseudopotential was supplemented with rotationally invariant “+U” description [43]. Only Gamma point was used in the calculations since the “+U” method is very time consuming. Energy cutoff was set as 500 eV. The Hubbard *U* value of Mn atoms was chosen to be 2.5 eV. Spin polarization calculation was carried out for all structural optimizations. The initial structures of PMO and α-MnO<sub>2</sub> were obtained from Rietveld

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