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# Mixed-phase mullite electrocatalyst for pH-neutral oxygen reduction in magnesium-air batteries

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ABSTRACT

Magnesium-air battery is a promising energy storage device because of its high theoretical voltage, high specific energy, low cost, and greater safety. Due to the passivation of Mg surface with $Mg(OH)_2$ in alkaline electrolyte (pH > 11) prevents further reaction of the anode, Mg-air battery typically works in pH-neutral aqueous electrolyte. However, developing electrocatalysts for pH-neutral oxygen reduction with high activity at low cost remains a significant challenge. Here, we report a mixed-phase mullite ($SmMn_2O_5$) electrocatalyst as an efficient substitute for Pt/C in pH-neutral oxygen reduction reaction (ORR). The mixed-phase mullite exhibits similar catalytic activity but superior stability to Pt/C in 1 M NaCl solutions. Density functional theory simulations reveal that the catalytic activity is correlated to the strength of *p-d* hybridization between octahedral Mn and lattice O in the mullite structure, which results in a moderate bond strength between adsorbed O atoms and square-pyramidal Mn dimer sites. The presence of $CeO_2$ phase also facilitates the adsorption and diffusion of oxygen atoms on mullite surface. Finally, the feasibility of utilizing mixed-phase mullite catalyst is demonstrated by fabricating Mg-air batteries to power a red light-emitting diode.

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## 1. Introduction

Driven by the ever-increasing demand of energy storage for renewable energy storage, metal-air batteries have attracted extensive attention due to the high theoretical energy density and environmental benignity [1–5]. Among many types of metal-air batteries, Li-air and Zn-air batteries have attracted the most attention [3,6–10], while magnesium-air batteries have been much less explored. Mg-air batteries could become a viable energy storage technology due to the low toxicity, high safety, and earth abundance of Mg. In fact, Mg-air batteries have been used commercially in reserve batteries, marine lifejacket lights, buoys, and undersea power supplies, etc. [11]. Although the present Mg-air battery is a primary battery, it could become mechanically rechargeable by replacing used Mg anode and electrolyte with fresh ones or eventually become electrochemically rechargeable once major technical challenges could be successfully resolved [4].

Mg-air batteries involve following reactions:

$$\text{Cathode: } O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (1)$$

$$\text{Anode: } Mg \rightarrow Mg^{2+} + 2e^- \quad (2)$$

$$\text{Overall: } 2Mg + O_2 + 2H_2O \rightarrow 2Mg(OH)_2 \quad (3)$$

During the discharge process, Mg anode is oxidized to $Mg^{2+}$ and $O_2$ is reduced to $OH^-$ via a four-electron transfer reaction. In the alkaline electrolyte (pH > 11), $Mg(OH)_2$ forms a passivation layer on Mg surface, which prevents further reaction of the anode. When pH < 11, corrosion reaction takes place as the side reaction: $Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$. While $Mg(OH)_2$ has a low solubility in water with a $K_{sp}$ of $1.5 \times 10^{-11}$, which is large enough that it will partially dissolve to produce ions in the solution forming the suspension. Therefore Mg-air batteries require a pH-neutral aqueous electrolyte [4]. Due to the low lying redox potential of $Mg/Mg^{2+}$ (−2.37 V vs. SHE), the theoretical voltage of a Mg-air battery is 3.1 V and the specific energy density is calculated to be

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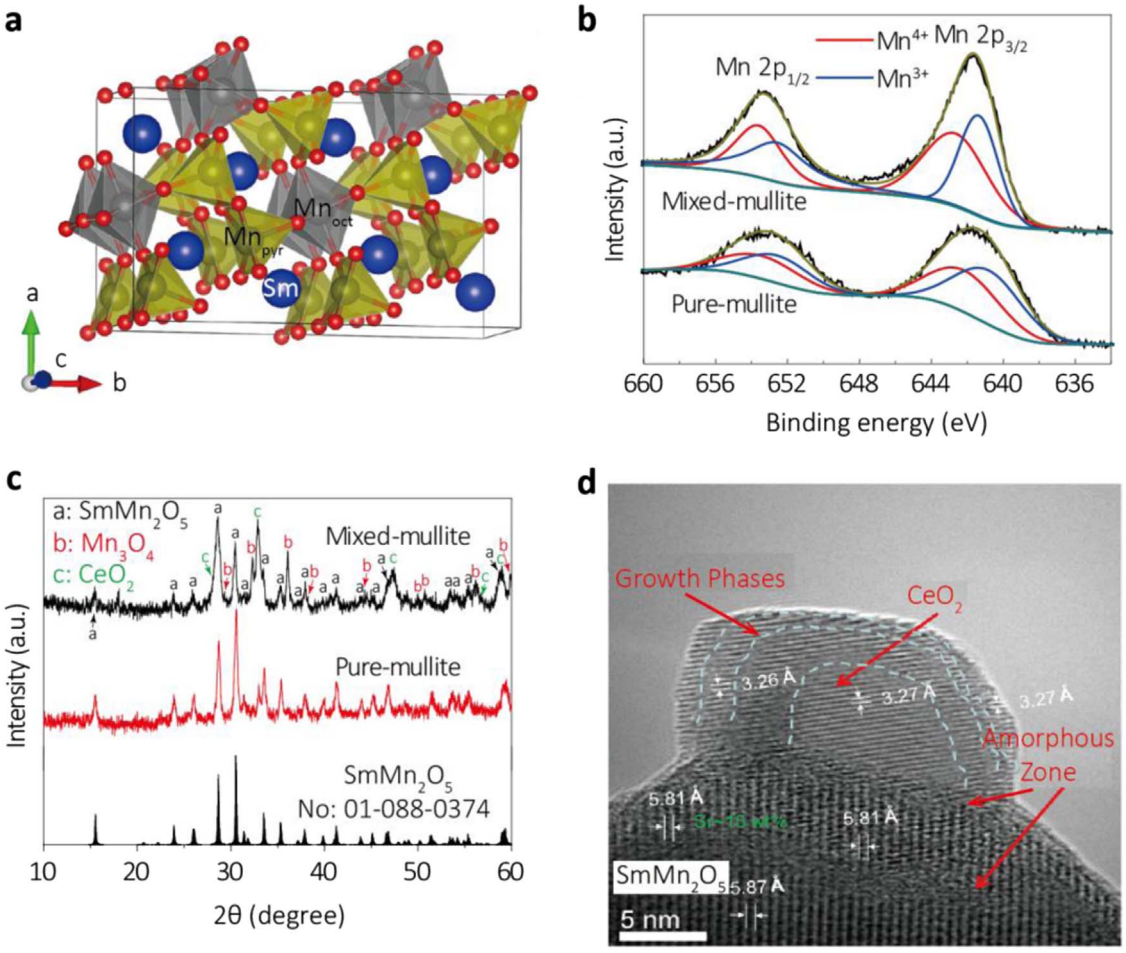


**Fig. 1.** (a) Crystal structure of $SmMn_2O_5$. O, Mn and Sm atoms are colored in red, purple, and grey. The $Mn_{pyr}$ and $Mn_{oct}$ complexes are displayed as yellow and grey polyhedra, respectively. (b) XPS spectra of Mn 2p peaks show $Mn^{3+}$ and $Mn^{4+}$ components. (c) XRD spectra of $SmMn_2O_5$ standard PDF (No: 01-088-0374), pure-, and mixed-mullite. $SmMn_2O_5$, spinel $Mn_3O_4$, and fluorite $CeO_2$ phases are identified in the mixed phase. (d) HRTEM image reveals lattice fringes of $SmMn_2O_5$ (110) and $CeO_2$ (200) and amorphous region.

6.8 kWh/kg. However, in reality, the working voltage is usually below 1.4 V due to two main challenges: corrosion of Mg metal and sluggish kinetics of oxygen reduction in pH neutral electrolyte. The first challenge has been studied in many reports with deeper understanding of the corrosion mechanism and novel Mg-Zn-Al alloys to alleviate the corrosion [12,13]. However, less progress has been made for the latter challenge, i.e, developing efficient oxygen reduction reaction (ORR) catalysts that are highly active and selective under pH-neutral condition. Such a catalyst has also been found important in microbial fuel cells [14]. Since the kinetics of oxygen reduction strongly depends on the $OH^-$ concentration of aqueous solution, ORR becomes very sluggish at neutral electrolyte when compared to the acid or alkaline electrolyte [15]. Noble metals such as platinum, palladium or iridium have the high catalytic performance and are traditionally used in Mg-air batteries [16,17].

Recently, low-cost alternatives have been actively explored to replace noble metals. Perovskite-based oxides, such as $LaMnO_3$ [18], $CaMnO_3$ [19], $La_{1-x}Sr_xMnO_3$ [20], $Sr_{0.95}Ce_{0.05}CoO_{3-\delta}$ [21], and $LaSr_3Fe_3O_{10}$ [22], attracted significant attention in the past few years. Most studies report high ORR catalytic activity in the alkaline electrolyte (0.1 M KOH) [23–25], however, their performance at pH-neutral electrolyte is not very well understood. A family of mullite oxide ($SmMn_2O_5$) has recently been reported by one of the authors with remarkable catalytic activity and durability towards $NO_x$ oxidation [26]. Breaking $O_2$ molecules into atomic O on the catalyst surface is an essential step in $NO_x$ oxidation process [26]. The same oxygen-bonding breaking might also be important in oxygen reduction, we are therefore inspired to explore the ORR catalytic activity with mullite oxide and explore its application in Mg-air batteries at pH-neutral electrolyte.

In this work, we synthesized the pure-phase (pure-mullite) and mixed-phase mullite (mixed-mullite) samples. The mixed-mullite exhibits similar catalytic activity but superior stability to Pt/C in 1 M NaCl solutions. Its performance compares favorably to Perovskite based catalysts. Density functional theory (DFT) simulations are employed to identify the catalytic mechanism for oxygen reduction and provides new insights to fine tune the Mn–O* bonding strength to optimize the rate limiting steps in ORR reactions.

## 2. Experimental

### 2.1. Preparation of pure- and mixed-mullite samples

All reagents (analytical grade) were purchased from Alfa-Aesar and used without further purification. Pure-mullite (SmMn2O5) was synthesized following Ref. [26]. To synthesize mixed- mullite, 7.7914 g of $Mn(CH_3CO_2)_2 \cdot 4H_2O$, 0.4205 g of $Sr(NO_3)_2$, 1.7255 g of $Ce(NO_3)_3 \cdot 6H_2O$, 0.8831 g of $Sm(NO_3)_3 \cdot 6H_2O$ and 0.2751 g of polyvinyl alcohol (PVA) (80% hydrolyzed) were dissolved in water. 15 mL of 25% TMAH was added until the pH reached 12. Then 0.2755 g of oxalic acid was dissolved in 2 mL of warm water (80 °C) in a separate container, and added to the above suspension.