# Hierarchically meso-macroporous LaMnO$_3$ electrode prepared by surfactant-templated method

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Zinc-air battery is a promising power source due to its high energy density (much higher than the Li-ion cells), low cost and nature friendly, which is already used in small devices like hearing aids. Recently, zinc-air battery has particularly attracted considerable attentions in development and commercialization for electric vehicles, indoor power generators, and industrial facilities [1]. The electrocatalysts on air electrodes of zinc-air battery are vital to the performance of metal-air battery; noble metals such as Ag, Pt, and its alloy as the oxygen reduction electrocatalysts of air electrodes have been widely investigated. Due to the significant cathodic over potential of the oxygen reduction reaction (ORR) and the rising cost of noble metal, the development of alternative and high oxygen reduction activity materials is of great importance [2,3]. One of the potential electrocatalysts used for air electrodes is metal oxides with perovskite structure. Perovskite metal oxides have been extensively studied due to their good redox properties, thermochemical stability, and tunable catalytic performances, which can be used as catalysts in the fields of environment protection and energy conversion. The general formula of perovskite oxides is ABO$_3$, having BO$_6$ octahedral with A$^{2+}$ cations inserted in the framework, in which the cation A is responsible for the thermal resistance whereas the cation B is responsible for the catalytic performance.

Among the ABO$_3$, LaMnO$_3$ showed good activities as oxygen cathodes in fuel cells and metal-air batteries. Suntivich et al. [4] reported that the quantitative correlation between the extent of σ*-antibonding orbital filling of surface transition-metal ions and the oxygen reduction reaction activity of perovskite oxides and found that LaMnO$_{3+\delta}$ prepared from an 800 °C heat treatment of LaMnO$_3$ in air exhibited an excellent oxygen reduction reaction activity. In general, the activity of the electrocatalyst closely depends on its preparation method, structure, and morphology. It is believed that porous structure and high specific surface area of ABO$_3$ are particularly effective to enhance its electrocatalytic activity. However, the LaMnO$_3$ prepared via the sol-gel citric acid-complexing method has relatively low surface area (<15 m$^2$/g) and nonporous, which limit the contact among reactants and active sites and strongly affect the derived catalysts's activity. There have been several reports on the preparation of mesoporous and high-surface-area ABO$_3$ by using the surfactant-templating method. For example, a mesoporous LaCoO$_3$ with a surface area of ca. 97 m$^2$/g via an ordered multi-step silica-nanocasting route. The multi-step silica-nanocasting route to obtain porous metal oxides involves the preparation of mesoporous silica template as first step, impregnation of the silica template with metal-containing precursors, followed by calcinations and removal the template. Mesoporous and high specific surface area of metal oxides could be obtained by the multi-step silica-nanocasting route; however, a high cost, longer processing time, and more complex procedures limits its commercial use. On the other hand, a facile approach using a triblock copolymer surfactant Pluronic P123 has been applied to obtain mesoporous ZrO$_2$ and provides enormous applications in terms of transportation or storage of fluids and gases, separation technology, and photoelectronics. The introduction of the P123 was beneficial for the generation of mesoporous materials incorporated with macropores to form a hierarchical pore structure; as a result, the macroporous channels could permit rapid transport of reactants or redox couples to the high surface area provided by the mesopores.

In this study, the relationships between the textural, structural, and electrical properties of the hierarchically structured LaMnO$_3$ electrode obtained by using P123 as the surfactant are investigated. The structural results indicate that P123 can be used as structure-directing agent for obtaining a cubic phase of LaMnO$_3$ and higher surface area with increase of additive ratios of P123 as shown in table 1. LMP_2(6,10,20) stands for LaMnO$_3$ with 2(6,10,20)% molar ratios of P123 addition as compared to La. The zinc air battery single cell measurement using LMP_2(6,10,20) as air cathode catalyst showed the same trend that more P123 resulted in higher discharge voltage. There was 5% voltage increase by applying LMP_10 (1.18V) compared to LMP_2 (1.12V). In summary, more P123 additions lead to higher specific surface area of perovskite metal oxides as electrochemical catalysts in a zinc air battery resulting in higher discharge voltages.

Table 1. Textural properties of samples with various amounts of P123.

| Sample | S$_{BET}$ (m$^2$/g) | V$_{pore}$ (cm$^3$/g) | D$_p$ (nm) |
|--------|------|------|------|
| LMP_2 | 8 | 0.04 | 21 |
| LMP_6 | 10 | 0.08 | 32 |
| LMP_10 | 20 | 0.14 | 30 |
| LMP_20 | 23 | 0.16 | 27 |

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