

Preview

Superior Oxygen Reduction Electrocatalyst: Hollow Porous Spinel Microsphere

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Developing robust oxygen reduction electrocatalysts is still a critical challenge for the commercialization of fuel cells and metal-air batteries. Recently in *Joule*, Lin and colleagues constructed hollow porous spinel AB_2O_4 microspheres (A = Zn, B = Mn/Co) as efficient and durable oxygen reduction electrocatalysts and found the importance of the electronic transition of the spin state of Co^{3+} in boosting the catalytic performance.

With the rapidly increasing energy demand and deteriorating environmental crisis, developing renewable-energy storage and conversion systems, such as fuel cells and metal-air batteries, has become a great and urgent challenge. Because of their high energy-conversion efficiency, safety, and reduced environmental pollution, developing fuel cell and metal-air batteries is a promising choice. Currently, the widespread practical application of these electrochemical devices mainly hinges on establishing an effective electrocatalyst system to accelerate the cathodic oxygen reduction reaction (ORR) because of its sluggish kinetics.¹ Generally, the noble metal Pt has been widely investigated as the most active ORR electrocatalyst. Despite its outstanding activity, its prohibitive cost, limited supply, poisoning, and questionable durability have seriously restricted the large-scale utilization of Pt-based electrocatalysts in the commercialization of fuel cell and metal-air batteries. Consequently, extensive research interests lie in exploring alternative electrocatalysts for fuel cell and metal-air batteries, which must meet three critical characteristics: low cost, high performance, and long-term durability.^{1,2}

In recent years, non-noble-metal-based materials, such as heteroatom-doped

carbon and transition-metal (Fe, Co, Ni, Mn, etc.) oxide, sulfide, and nitride, etc., have been widely proposed as the next generation of ORR electrocatalysts.¹ However, beyond their economical nature, these catalysts are still less competitive: (1) transitional-metal-based materials often suffer from inferior activity; (2) for carbon based materials, durability is the key problem for the long-term operation of fuel cell and metal-air batteries; and (3) the lack of recognition of active sites (especially the correlation between the electronic structure of the catalytic center and ORR activity) and of the ORR process on such catalytic centers greatly limits effective catalyst design. In response, the first step should be to carefully design an optimized elemental composition and interaction of different elemental parts given that these control the intrinsic active sites. In addition, the import of high-surface-area and abundant pores is necessary for the catalyst framework, which can ensure that the active sites are easily accessible for the electrolyte and afford sufficient mass transport during the ORR process.³ In terms of these two factors, a low-cost electrocatalyst with a high density of active centers and porous structure would effectively accelerate the ORR and promote the

practical operations of fuel cell and metal-air batteries.

Notably, among these innovative and promising alternatives, Co-based materials stand out by virtue of their earth abundance, low cost, adjustable electronic structure of the metal center, well-known active electrocatalytic activity, and excellent durability (in alkaline medium), etc. For instance, Co_3O_4 and $LaCoO_3$ have been verified as promising ORR electrocatalysts in alkaline electrolyte, wherein the electronic structure of Co^{3+} plays a key role in determining the ORR performance.^{4–7} Although tremendous efforts have been devoted to exploring effective and stable Co-based ORR electrocatalysts, the search for optimized Co-based electrocatalysts with activity comparable to and durability better than that of Pt-based catalysts for fuel cell and metal-air batteries is still ongoing and is also a great challenge.

Recently in *Joule*, Lin and colleagues developed a facile strategy for preparing hollow porous Co^{3+} -based spinel oxide AB_2O_4 microspheres (A = Zn, B = Mn/Co) as ORR electrocatalysts.⁸ When used in alkaline electrolyte, the hollow porous $ZnMnCoO_4$ microsphere exhibited excellent electrocatalytic activity (Figures 1A–1C), and the authors also established a correlation between the electronic structure of the Co^{3+} ion and the resulting ORR performance (Figures 1D and 1E). With the organic

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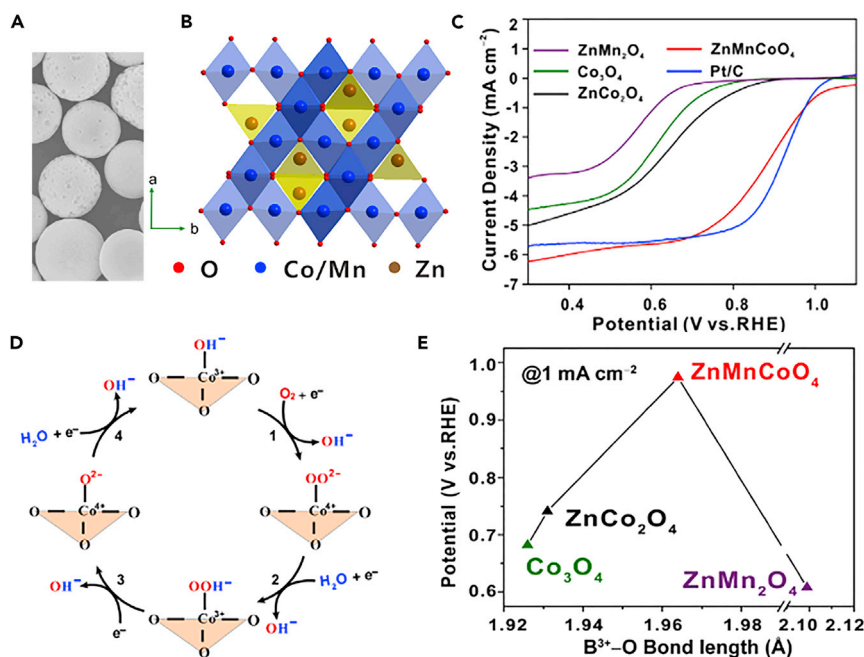


Figure 1. Schematic Illustration of the Hollow Spinel ZnMnCoO₄ Microsphere in Catalyzing the Oxygen Reduction Reaction

- (A) Scanning electron microscopy images of the hollow porous ZnMnCoO₄ microsphere.
 (B) Crystal structure of spinel ZnMnCoO₄.
 (C) Comparison of the ORR polarization curves among ZnCo₂O₄, ZnMn₂O₄, ZnMnCoO₄, solid Co₃O₄, and commercial Pt/C.
 (D) The proposed ORR process occurring on the surface of Co³⁺ ions.
 (E) The relationship between the ORR activity (onset potential) of a series of catalysts and the B³⁺-O (B = Co/Mn) bond length within the spinel oxide catalysts.

soft template polyvinyl pyrrolidone (PVP), the synthesized spinel oxide had a well-defined hollow porous framework (and thus high surface area and more pores), ensuring sufficient mass transport during the ORR process. Such a porous framework also had the benefit of exposing more active sites, effectively increasing the oxygen reduction current density. In spite of this, the authors optimized the elemental composition to create the intrinsically active sites. Among various Co-based spinel oxides, the ZnMnCoO₄ microsphere showed superior ORR performance, verifying the importance of the electronic structure in the catalytic ORR. Moreover, the half-wave potential of ZnMnCoO₄ was only 50 mV lower than that of the commercial Pt/C, and ZnMnCoO₄ microspheres were more durable and toler-

ated methanol better than Pt/C. In addition, its selectivity was excellent given that it catalyzed oxygen mainly via a four-electron ORR pathway. Such excellent activity and stability make ZnMnCoO₄ feasible for fuel cell and metal-air battery devices.

Combining experimental and theoretical studies, the authors also revealed the important role of the electronic structure of the transition B sites and the B-O character (e.g., bond length) in determining the ORR performance in alkaline medium. For example, in the commercial Co₃O₄, the Co²⁺ ion in the tetrahedral sites processes a high-spin state with an unpaired 3d electron, whereas the Co³⁺ ion in the octahedral sites has a low-spin state with all 3d electrons paired, which means that no electron occupied in the σ^* anti-

bonding orbital induces the strong Co³⁺/O₂ interaction (quite a stable Co⁴⁺-O₂²⁻ bond), and the ORR kinetics are thus slow. Because the Zn²⁺-O bond in ZnCo₂O₄ is stronger than the Co²⁺-O bond in Co₃O₄, Lin and colleagues replaced the Co with Zn to increase the bond length of Co³⁺-O, which caused the 3d electron to transition from the low-spin state of Co³⁺ in Co₃O₄ to the mixed low-spin and high-spin states of Co³⁺ in ZnCo₂O₄. This change indeed enhanced the ORR performance effectively. Furthermore, Co³⁺ was replaced with Mn³⁺ in ZnCo₂O₄, and the bond length of Co³⁺-O further increased because of the larger size of Mn³⁺, leading to a higher ratio of high-spin state to low-spin state for Co³⁺ in ZnMnCoO₄ and superior ORR performance. It is thus clear that the ORR activity of the spinel oxides can be greatly improved as the bond length of Co³⁺-O increases. DFT calculations also confirmed that ZnMnCoO₄ with a larger Co³⁺-O bond had more favorable binding energy with O₂ and oxygenated species and thus faster kinetics during the ORR process.

In summary, Lin and colleagues have developed an effective strategy for optimizing the d electron of Co sites to import intrinsically active sites (Co³⁺-O) and engineer the spinel ZnMnCoO₄ with a hollow porous structure to promote the mass transport of the Co-based spinel oxide electrocatalyst for ORR in alkaline medium. ZnCoMnO₄, which has shown outstanding activity and durability, is a promising ORR electrocatalyst for fuel cell and metal-air batteries, as well as other electrochemical devices. Additionally, the strategy of utilizing experimental and theoretical methods to investigate the relationship between the 3d electron in the Co³⁺ ion and the resulting ORR catalytic performance could also be expanded to other electrocatalyst designs and investigations.

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