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Sulfur Mismatch Substitution in Layered Double Hydroxides as Efficient Oxygen Electrocatalysts for Flexible Zinc–Air Batteries

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Although layered double hydroxides (LDHs) are extensively investigated for oxygen electrocatalysis, their development is hampered by their limited active sites and sluggish reaction kinetics. Here, sulfur mismatch substitution of NiFe–LDH (S–LDH) is demonstrated, which are in-situ deposited on nitrogen-doped graphene (S–LDH/NG). This atomic-level sulfur incorporation leads to the construction of the tailored topological microstructure and the modulated electronic structure for the improved catalytic activity and durability of bifunctional electrocatalysts. The combined computational and experimental results clarify that the electron transfer between the sulfur anion and Fe^{3+} generates the high-valence Fe^{4+} species, while the mismatch substitution of the sulfur anion induces the metallic conductivity, an increased carrier density, and the reduced reaction barrier. Consequently, the as-fabricated Zn–air battery achieves a high power density of 165 mW cm^{-2}, a large energy density of 772 Wh kg_{Zn}^{-1} at 5 mA cm^{-2}, and long cycle stability for 120 h, demonstrating its real-life operation.

1. Introduction

The development of advanced energy storage technologies has become a research hotspot owing to the gradually increasing energy demand for renewable energy storage and electric vehicles.[1] Particularly, rechargeable Zn–air batteries are considered a promising candidate to satisfy this growing energy demand owing to their high theoretical energy density, safety, and inexpensiveness.[2] However, the commercialization of these batteries is severely limited by the sluggish electrokinetics of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in their discharge/charge processes.[3] Thus far, novel metal-based electrocatalysts, such as Pt- and Ir/Ru-based compounds, have been intensively investigated for ORR and OER owing to their high cata-