Bimetal Oxide Nanoparticles Embedded in rGO as Catalyst for Rechargeable Zinc-Air Battery

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Rechargeable zinc-air batteries (ZAB) are promising for energy storage thanks to their environmental friendliness, abundant zinc reserves, high capacity, and safe operation.[1] One of their current limitations relates to low oxygen reduction reaction (ORR) in discharging and high overpotential of oxygen evolution reaction (OER) in charging at the air cathode. Catalysts are, thus, indispensable for high-rate performance.[2] Earth-abundant binary transition metal oxides have been emerging as potential catalysts for both ORR and OER to substitute the expensive and scarce ones (noble Pt and IrO_2).[2] Recent findings reveal the synergetic catalytic activities of bimetal oxides compared with the monometallic oxide counterparts.[3] When the binary oxide catalysts were applied to rechargeable ZAB, however, the cycle stability and power density have been reported only for low current densities (≤ 30 mA cm^{-2}) in short time per cycle.[4] Stable performance of ZAB at high current densities is significant for high-rate and large-scale harvesting renewable energies and grid application. Therefore, we developed binary metal oxides of Fe, Co, and Ni embedded on reduced graphene oxide (rGO), i.e., FeCo/rGO and CoNi/rGO, as ORR/OER bifunctional catalysts. For the first time, we evaluated them in ZAB at high current density (100 mA cm^{-2}) for 1 h each charge and discharge and set light on the structure-performance relation and issues associated with high-rate ZAB.

Our results revealed that the ORR/OER catalytic activities depended on the metal feeding ratio and metal loadings. The equimolar metal feedings resulted in the synergistic ORR catalytic effect. This ratio was found to enable the most abundant and the highest Co-rich bimetallic oxide nanocrystals in CoNi/rGO, which delivered high ORR activities. The lowest charging voltage of ZAB over cycles also belonged to the catalyst of equimolar metal feeding, suggesting the synergistic OER performance at high current density. At equimolar metal ratios, the loading of bimetallic oxide on rGO was found important for uniformly dispersing oxide catalyst on the conductive rGO substrate. Medium catalyst loading levels correlated with stable charging performance of ZAB by lowering the cathode corrosion using both FeCo/rGO and CoNi/rGO compared with only rGO and only metal oxides. The loading level was found to vary not only the dispersion but also the crystal structure of the bimetal oxides. The best cycle stability was more than 40 cycles for consecutive 80 h at 100 mA cm^{-2} while maintaining 90 % discharge capacity.

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