Hybrid catalysts of polymer-wrapped pristine multi-wall carbon nanotubes and spinel oxides for oxygen evolution and reduction

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In recent years, the explosively increasing needs for portable electronic devices and electric vehicles have significantly stimulated the development of energy storage systems with high efficiency, low cost, and long life-circle. Compared to current lithium-ion rechargeable batteries, zinc-air batteries have very high theoretical energy density, low cost, less safety risk and thus have attracted tremendous attention in the past decade. One of the key challenges for zinc-air batteries is the bifunctional air electrode, on which the oxygen reduction and evolution reactions (ORR and OER) occur during discharge and charge processes with very sluggish kinetics, respectively.

Cobalt-based spinel oxides, such as Co_3O_4, $NiCo_2O_4$, and $MnCo_2O_4$, etc., have been intensively studied as the electrode materials for rechargeable zinc-air batteries and supercapacitors due to their high electrocatalytic activities. Since the electrical conductivity of these oxides is poor, they are usually supported on carbon or porous metals to act as electrocatalysts. In this work, we employed pristine multi-wall carbon nanotubes (MWNTs) as the support material because of the following advantages. Pristine MWNTs have excellent chemical stability and resistance to electro-oxidation even at high anodic potentials. Moreover, they are easy to be dispersed in some organic solvents, which allows MWNTs to easily form a free-standing film with sufficient gas diffusion path. Such a porous electrode structure will significantly benefits the practical oxygen reduction/evolution on electrode. Unfortunately, it is difficult to decorate pristine MWNTs with metal oxides because MWNTs have rare binding sites on the highly crystallized graphitic surface. The conventional way to create binding sites for MWNTs is to oxidize MWNTs in strong acid. As a result, the surface of MWNTs will be damaged, leading decrease in electrical conductivity and stability.

In this study, we propose a novel strategy for decorating polymer-wrapped pristine multi-wall carbon nanotubes (MWNTs) with metal oxides, including Co_3O_4, $MnCo_2O_4$, and $NiCo_2O_4$. Uniform $NiCo_2O_4$ and $MnCo_2O_4$ nanoparticles were homogeneously dispersed on the surface of pyridine-based polybenzimidazole (PyPBI)-wrapped pristine MWNTs via a solvothermal synthesis method. The resulted catalysts exhibited promising activity and durability as the bifunctional catalysts for zinc-air batteries. In particular, the MWNT/PyPBI/$NiCo_2O_4$ film electrode was used for a homemade zinc-air battery and a high cell voltage of 1.06 V was obtained at 20 mA cm^{-2} while the power density at 0.8 V achieved 51 mW cm^{-2}.