

Abstract

The thesis entitled *Heteroatom-Doped Carbon Encapsulated Transition Metal Phosphide (TMP) Nanostructures for Rechargeable Zn-Air Battery and Water Splitting* describes the synthesis of various TMPs such as cobalt phosphide (CoP), iron phosphide (FeP), nickel phosphide (Ni₂P) and cobalt phosphide tailored with Ru (CoP-Ru) for the development of rechargeable Zn-air batteries (ZAB) and water splitting. A novel universal approach, the *carbothermal reduction of transition metal poly-pyridyl complex* for the synthesis of TMP is developed for the first time and the encapsulation of TMP with heteroatom doped carbon is achieved in a single step. The counter anion hexafluorophosphate (PF₆⁻) of the precursor complex is used as a phosphidating agent. The electrocatalytic activity of these nanostructures towards the oxygen reduction reaction (ORR), oxygen evolution reaction (OER), and hydrogen evolution reaction (HER) is examined. The catalysts N-doped carbon embedded CoP (NC-CoP) and N, P-dual doped carbon encapsulated Ni₂P (N₂P@NPC) exhibits decent and very good bifunctional oxygen activity, respectively. The atomic percentage of carbon dependent growth of NC-CoP is demonstrated. The generation of P-vacancies in Ni₂P@NPC by surface engineering via acid treatment is demonstrated. These catalysts exhibit poor performance towards HER. On the other hand, N, P- dual doped carbon encapsulated FeP (FeP@NPC) exhibits excellent bifunctional oxygen activity and decent HER activity. The carbothermal reduction temperature largely controls the composition, morphology, porosity, surface area and overall electrocatalytic performance of FeP@NPC. The surface tailored CoP@NC with Ru (CoP@NC-Ru) exhibits excellent activity towards ORR, OER, and HER. The charge transfer interaction of encapsulated NC with core CoP and surface tailored Ru nanoparticles is demonstrated for the enhanced electrocatalytic performance after surface tailoring. The performance of all the catalysts for ZAB is evaluated in terms of open circuit voltage (OCV), peak power density, specific capacity and galvanostatic cycling stability. Among all the catalysts FeP@NPC and CoP@NC-Ru shows superior ZAB performance with peak power densities of 170 and 175 mW cm⁻², and specific capacities of 785 and 780 mA h g_{Zn}⁻¹ with negligible voltaic efficiency loss. CoP@NC-Ru exhibits remarkable water splitting performance with overall water splitting voltage of only 1.47 V at 10 mA cm⁻² current density.

Keywords: Transition metal phosphide, heteroatom-doped carbon, carbothermal reduction, oxygen electrocatalysis, Zn-air battery, water splitting.