Engineering the Active Sites of Bifunctional Electrocatalysts of Ternary Spinel Nickel-Cobalt Oxides, $M_xNi_{1-x}Co_2O_4$, for the Air Electrode of Rechargeable Zinc-Air Batteries

Chi-Chang Hu*, Yi-Ting Lu, Yu-Ju Chien, Ting-Hsuan You, Po-Chieh Li
Department of Chemical Engineering, National Tsing Hua University
101, Section 2, Kuang-Fu Road, Hsin-Chu 30013, Taiwan

*E-mail: cchu@che.nthu.edu.tw

Due to the sluggish kinetics of the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR), how to efficiently discover cost-effective catalysts with desirable functionalities for rechargeable metal-air batteries is one of the major scientific challenges in future energy storage/conversion technologies. Based on the octahedral site preference energy (OSPE) model, engineering the active sites of ternary $M_{0.1}Ni_{0.9}Co_2O_4$ for the OER and ORR in alkaline solutions is demonstrated in this work. From the X-ray photoelectron spectroscopic (XPS) and OSPE model, Fe-doped $NiCo_2O_4$ ($Fe_{0.1}Ni_{0.9}Co_2O_4$) provides the highest Co^{2+}/Co^{3+} ratio and the lowest Ni^{2+}/Ni^{3+} ratio, leading to the enhanced electrocatalytic activities toward both the OER and ORR in alkaline electrolytes from the rotating ring-disk electrode (RRDE) voltammograms. In addition, all ternary oxides are examined as bifunctional electrocatalysts for the air electrode of rechargeable zinc-air batteries from the polarization curves of the ORR and OER in 6 M KOH under the ambient air. The full-cell configuration using the $Fe_{0.1}Ni_{0.9}Co_2O_4$-coated air electrode exhibits the maximum power density of 150 mW cm^{-2} at a current density of 250 mA cm^{-2} under the ambient air and facilitates long-term cycle stability (over 66.7 h at 10 mA cm^{-2}). These results confirm the excellent bifunctional electrocatalytic activity of $Fe_{0.1}Ni_{0.9}Co_2O_4$ which is considered to be a practical catalyst for the air electrode of rechargeable Zn-air batteries.[1]

A novel configuration of two electrodes containing electrocatalysts for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) pressed into a bifunctional air electrode is designed for rechargeable Zn–air batteries. MOC/25BC carbon paper (MOC consisting of α-MnO_2 and XC-72 carbon black) and $Fe_{0.1}Ni_{0.9}Co_2O_4$/Ti mesh on this air electrode mainly serve as the cathode for the ORR and the anode for the OER, respectively. The morphology and physicochemical properties of $Fe_{0.1}Ni_{0.9}Co_2O_4$ are investigated through scanning electron microscopy, inductively coupled plasma-mass spectrometry, and X-ray diffraction. Electrochemical studies comprise linear sweep voltammetry, rotating ring-disk electrode voltammetry, and the full-cell charge–discharge–cycling test. The discharge peak power density of the Zn–air battery with the unique air electrode reaches 88.8 mW cm^{-2} at 133.6 mA cm^{-2} and 0.66 V in an alkaline electrolyte under an ambient atmosphere. After 100 charge–discharge cycles at 10 mA cm^{-2}, an increase of 0.3 V between charge and discharge cell voltages is observed. The deep charge–discharge curve (10 h in each step) indicates that the cell voltages of discharge (1.3 V) and charge (1.97 V) remain constant throughout the process. The performance of the proposed rechargeable Zn–air battery is superior to that of most other similar batteries reported in recent studies.[2]

References:

[1] Y.-T. Lu, Y.-J. Chien, C.-F. Liu, T.-H. You, C.-C. Hu, J. Mater. Chem. A. 5 (2017) 21016-21026.
[2] P.-C. Li, Y.-J. Chien, C.-C. Hu, J. Power Sources 313 (2016) 37-45.