Carbon-free Cathode for Li-O_2 Batteries with Long Life and High Efficiency

Xuecheng Cao, Xiangjun Zheng, Zhihui Sun, Ruizhi Yang*
[a] *Soochow Institute for Energy and Materials InnovationS, College of Physics, Optoelectronics and Energy & Collaborative Innovation Center of Suzhou Nano science and Technology, Soochow University, Suzhou, Jiangsu 215006, China*
E-mail: *yangrz@suda.edu.cn*

The fast development of electric transportation and grid-scale applications requires energy-storage systems with high energy density. The rechargeable nonaqueous Li-O_2 batteries have attracted a great deal of attention due to their highest theoretical energy density (11700 Wh kg^{-1}, without the mass of O_2) among the existing electrochemical energy-storage systems.[1] Carbon based material, a promising candidate for air electrode, has been extensively studied. However, the discharge product, such as Li_2O_2 and LiO_2, could react with carbon to form insulating lithium carbonate layer, resulting in cathode passivation and capacity fading in Li-O_2 batteries.[2,3] Therefore, to develop new carbon-free cathode with high capacity and long life to replace carbon-based cathode is still of great importance and remains a great challenge.

Herein, we have successfully synthesized $MnCo_2O_4$(MCO) nanoparticles anchored on Magnéli phase Ti_4O_7 and porous MoO_2 nanosheets grown on Ni foam (current collector) (MCO/MoO_2@Ni), repsectively, acting as a carbon-free cathode for Li-O_2 batteries, in an attempt to improve the electronic conductivity, electrocatalytic activity and stability. The dischrage/charge voltage gap of the as-prepared Ti_4O_7/MCO hybrid is only about 0.75 V, which is significantly lower than that of pure carbon, C+MCO and pristine Ti_4O_7 cathode. A high specific capacity (5400 mAh g^{-1} at 100 mA g^{-1}) and excellent cycling performance (100 cycles at a limited depth of discharge of 500 mAh g^{-1} under 200 mA g^{-1}) are obtained. The resulting MCO/MoO_2@Ni cathode gives a high specific capacity (4210 mAh g^{-1} at 200 mA g^{-1}) and low over-potential (0.28 V), enabling a Li-O_2 battery's operation for over 400 cycles and the columbic efficiency of higher than 85 %. The high performance of the Ti_4O_7/MCO and MCO/MoO_2@Ni cathode can be attributed to the improved electrical conductivity based on Ti_4O_7 or MoO_2, efficient oxygen diffusion and electrolyte transport, effective O_2/Li_2O_2 conversion and the synergistic interaction between MCO and Ti_4O_7 or MoO_2. This study demonstrates a new highly active carbon-free cathode and provides a new avenue for rational design of cathode for Li-O_2 batteries.

Acknowledgement:
This work is supported financially by National Natural Science Foundation of China (51572181), the National Key Research and Development Program of China (2016YFB0100200), Natural Science Foundation of Jiangsu Province, China (BK20151226).

References:
[1] J. Lu, L. Li, J.-B. Park, Y.-K. Sun, F.Wu, K.Amine, Chem. Rev. 114(2014)5611-5640.
[2] J.-B. Park, J. Lee, C. S.Yoon, Y.-K. Sun, ACS Appl. Mater. Interfaces 5(2013)13426-13431.
[3] M. M. O.Thotiyl, S. A.Freunberger, Z. Q. Peng,; P. G. Bruce, J. Am. Chem. Soc. 135(2013)494-500.