Enhanced Oxygen Evolution in Lithium-Oxygen Battery using RuO₂ Nanoparticles and its Mechanism

Eda Yilmaz, Hye Ryung Byon

Byon Initiative Research Unit, RIKEN 2-1 Hirosawa, Wako-shi, Saitama 351-0198, Japan

Rechargeable non-aqueous lithium-oxygen (Li-O₂) battery providing theoretically high specific-energy-density calculated as $\sim 3 \text{ kWh kg}^{-1}_{\text{cell}}$ is a promising future energy storage system. However, the energy loss, indicated by an over-potential, during Li-O₂ electrochemical process $(2Li^+ + O_2(g) + 2e^- \leftrightarrow Li_2O_2(s))$, $E_{rev} = 2.96$ V vs. Li⁺/Li) is considerably severe, which is one of the great challenges for implementation of practical battery systems. The over-potential is prominently caused by the difficulty of decomposition of insulating Li₂O₂ during the oxygen evolution reaction (OER, $\text{Li}_2\text{O}_2(s) \rightarrow 2\text{Li}^+ + \text{O}_2(g) + 2e^-$) on recharge.² In addition, byproducts, e.g., lithium carbonate (Li₂CO₃) and lithium acetate formed due to degradation of non-aqueous electrolyte have required further energy to be decomposed.³

Many efforts for suppression of the over-potentials during discharge and recharge have been devoted by incorporation of metal and metal oxide structures to the carbon cathodes. However, there has been still a lack of deep understanding for the role of these metal and metal oxide structures. The functions of these structures have been interpreted diversely such as an electrocatalyst,⁴ a promoter enhancing the movement of Li_2O_2 species,⁵ a decomposer degrading electrolyte greatly⁶ and a stabilizer improving cyclic stability⁵.



Fig.1 First cycle discharge/charge curves with RuO₂/CNT and CNT cathodes using 0.5 M of LiTFSI in tetraglyme electrolyte at 0.05 mA/cm² current rate.

Here, we present improved OER performance of $Li-O_2$ cells using ruthenium oxide (RuO₂) nanoparticles (NPs) dispersed on multi-walled carbon nanotube (CNT) (RuO₂/CNT) and suggest the role of RuO₂ NPs. When RuO₂ NPs are used in the CNT cathode the over-potential during recharge is decreased to ~0.50 V as shown in **Fig.1**. The electrical efficiency of RuO₂/CNT cathode is 74%, much higher than that of CNT cathode only, which is 58%. X-ray absorption near edge structure (XANES) spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses of the discharge product reveal formation of poorly crystalline Li₂O₂ in the presence of RuO₂ NPs. In addition, shapeless Li₂O₂ layer structure having a large contact area with CNT electrode

is observed on the RuO₂/CNT electrode, which can be completely decomposed at low OER potential. This study reveals the role of RuO₂ NPs in the non-aqueous Li-O₂ electrochemical reaction and offers a guide to improvement of the electrical efficiency in the Li-O₂ battery.

References

1) Bruce, P. G.; Freunberger, S. A.; Hardwick, L. J.; Tarascon, J. M. Nat. Mater. 2012, 11, 19.

2) Hummelshoj, J. S.; Blomqvist, J.; Datta, S.; Vegge, T.; Ross- meisl, J.; Thygesen, K. S.; Luntz, A. C.; Jacobsen, K. W.; Nørskov, J. K. J. Chem. Phys. 2010, 132, 071101.

3) McCloskey, B. D.; Bethune, D. S.; Shelby, R. M.; Mori, T.; Scheffler, R.; Speidel, A.; Sherwood, M.; Luntz, A. C. J. Phys. Chem. Lett. 2012, 3, 3043.

4) Shui, J.-L.; Karan, N. K.; Balasubramanian, M.; Li, S.-Y.; Liu, D.-J. J. Am. Chem. Soc. 2012, 134, 16654.

5) Oh, S. H.; Black, R.; Pomerantseva, E.; Lee, J.-H.; Nazar, L. F. Nat. Chem. 2012, 4, 1004. (b) Black, R.; Lee,
6) McCloskey, B. D.; Scheffler, R.; Speidel, A.; Bethune,
D. S.; Shel- by, R. M.; Luntz, A. C. J. Am. Chem. Soc. 2011, 133, 18038.