

The effect of discharge conditions on recharge profile of Li-Oxygen battery

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The formation of solid Li_2O_2 as the discharge (DC) product, which is a wide bandgap insulator, poses severe difficulties in Li-O₂ battery. Very poor ionic and electronic conductivities of Li_2O_2 prevent facile electron transfer from the electrode surface to the reaction site especially during recharge (RC) of the cell and as a result the charging overpotential in Li-O₂ battery is usually very high. A typical RC curve of a Li-O₂ battery consists of two parts; an initial low-voltage sloping region and a flat high-voltage plateau. Previous reports¹ show that the sloping region relates to the decomposition of nano-sized Li_2O_2 formed at high rate of DC, whereas, the high voltage plateau is for the decomposition of large toroid-like particles formed at low rate. But it is not known why both these parts coexist at all current densities. Although an operando X-ray diffraction study² of Li-O₂ cell further revealed that amorphous Li_2O_2 decomposes at low overpotential forming the sloping region, while the crystalline Li_2O_2 undergoes decomposition at the high-voltage plateau, still the mechanism of concurrent formation of amorphous and crystalline Li_2O_2 is not provided. However, these studies do indicate that structural and morphological modification of discharged Li_2O_2 may improve the RC efficiency of Li-O₂ battery, and for doing so, it is essential to know the formation mechanism of Li_2O_2 under different DC conditions. In this work, we try to understand how the DC conditions affect the physical properties of Li_2O_2 which in turn influence the RC profiles of Li-O₂ battery and find out a general explanation for recharge processes, irrespective of Li_2O_2 morphology and crystallinity.

Commercial ketjen black (KB) carbon and 1.0 M Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in tetraglyme (< 20 ppm H₂O) are used as the electrode and electrolyte, respectively. Discharge in this dry electrolyte yields film-like Li_2O_2 with similar degree of crystallinity over a wide range of DC current densities (25-200 mA g⁻¹). Despite the similarity in morphology and crystallinity of Li_2O_2 , RC curves of these cells are quite different and still consist of two parts. With increasing DC current, the overpotential of the sloping region decreases. Whereas, the potential of the flat RC plateau remains almost similar. Addition of known concentration of water grows Li_2O_2 in toroidal morphology and the RC overpotential becomes higher. But the shape of the RC curve looks similar to that of film-like Li_2O_2 grown in low DC current. Our studies show that the RC profile of Li-O₂ battery cannot be completely explained by bulk morphology of Li_2O_2 . Rather, fundamentally it depends on the surface area of Li_2O_2 in contact with both electrode and electrolyte as well as on the crystallinity of Li_2O_2 . Gradual changes in DC conditions that affect these parameters show continuous change in RC profile. Increase in the exposed surface of Li_2O_2 , which is believed to be nonstoichiometric with higher conductivity, possibly promotes delithiation during RC at low overpotential and the sloping region becomes predominant. Amorphous Li_2O_2 also shows similar effect during RC. On the contrary, decomposition of bulk crystalline Li_2O_2 occurs at the high-voltage plateau. This explanation is valid over a wide range of morphologies of Li_2O_2 where decomposition of amorphous conformal film of Li_2O_2 with large surface area and crystalline toroidal morphology with low surface to volume ratio become two limiting cases.

References:

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