

Growth of Li_2O_2 on carbon cathode in a Li-air cell: a self-assembly process

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Today's lithium-ion batteries do not provide sufficient energy for an acceptable driving distance, which has limited public interest in electric vehicles, particularly for long distance travel. Lithium-air cells can be considered the 'holy grail' of lithium batteries because they offer, in principle, a significantly superior theoretical gravimetric energy density approaching that of gasoline. It is generally accepted that the capacity of the non-aqueous Li-air battery is limited by its insoluble product, Li_2O_2 , in oxygen reduction reaction (ORR). Instead of the homogenous thin film coverage, Mitchell et al. found that Li_2O_2 particles formed "toroid" structures on the carbon surface during discharge. However, the underlying mechanism of formation of such toroids is not well understood yet. In this work, we reported, for the first time, that the growth of Li_2O_2 toroids on oxygen cathode during discharge is through a self-assembly process, likely caused by the magnetic properties of the Li_2O_2 surface. In order to investigate the formation/decomposition and morphological evolution of Li_2O_2 , non-aqueous Li-air cells were discharged and charged with different specific capacities (electrolyte: TEGDME/ LiCF_3SO_3 , current density: 100 mA/g_{carbon}, carbon loading per electrode: 0.8-1.2 mg). XRD results confirmed the formation and decomposition of Li_2O_2 upon discharge and charge, respectively. SEM observations showed clearly evidence that toroid Li_2O_2 particles (1~2 μm) are formed at later discharge (higher capacity), which consists of numerous small Li_2O_2 nanoparticles (30-50 nm). Upon charging, most of these toroid particles disappeared, indicating that a reversible reaction ($2\text{Li} + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2$) occurs on the cathode. The cell impedance increases upon discharge and decreases upon charge, due to the poor electron conductivity of Li_2O_2 . It should be also noted that the impedance cannot reach its origin value at the end of charge stage, and the difference became larger as the cell cycled at larger capacity. Our work could help to understand the morphological change of Li_2O_2 during the electrochemical cycle, and its effect on the impedance of the non-aqueous Li-air battery.