Current Density Dependence of Discharge Termination Mechanisms in Lithium-Oxygen Secondary Batteries

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Lithium-oxygen secondary batteries (Li-O_2 batteries) have attracted attention as a next-generation secondary battery due to their high theoretical gravimetric energy density. In this system, lithium peroxide (Li_2O_2), a solid with poor electrical conductivity, forms on the positive electrode during discharge. Ideally, this Li_2O_2 should be completely decomposed via oxidation at a low charging voltage; however, in reality, the charging voltage is high, and the cycle performance and energy efficiency of Li-O_2 batteries remain low. To address this issue, it is crucial to systematically understand the formation behavior of Li_2O_2 during the discharge process. In this study, we focused on the discharge termination mechanisms. Fig. 1 shows the discharge profiles at two different current densities. At a low current density (1 μA cm^{-2}), the discharge capacity reached 50 μA h cm^{-2}. In this experiment, second discharge tests were conducted under the same conditions immediately after the first discharge termination. The second discharge at low current density ceased almost immediately. According to the conventional understanding of the discharge determination in Li-O_2 batteries, this result is interpreted as being caused by the irreversible blockage of the cathode surface by Li_2O_2 deposition. On the other hand, at high current density (50 μA cm^{-2}), the discharge capacity reached 5 μA h cm^{-2}. Notably, the first and second discharge curves at high current density overlapped, a phenomenon that cannot be explained by the conventional understanding. This observation indicates that the cathode after discharge at high current density does not remain blocked by Li_2O_2 and is, in fact, reversible. These findings reveal two distinct discharge termination mechanisms that are dependent on the current density.

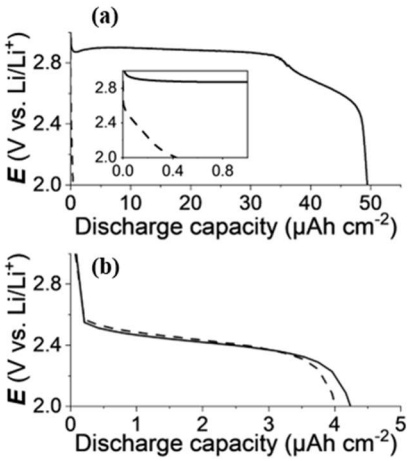

Fig. 1. Discharge profiles at (a)1 μA cm^{-2} and (b) 50 μA cm^{-2}. The solid and dashed lines show the first and second discharge, respectively.