

In-situ XRD Study of Li-O₂ Electrochemical Reaction in Rechargeable Lithium-Oxygen Battery

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Understanding of electrochemical process in rechargeable lithium-oxygen (Li-O₂) battery has suffered from lack of proper analytical tool. Here we present simple and straightforward analytical method for simultaneously attaining chemical and quantified information of discharge product on full discharge and recharge process using *in-situ* X-ray diffraction (XRD) measurement. We explored Super P/binder cathode with ether-based electrolyte (triethylene glycol dimethyl ether (triglyme) and dimethoxyethane (DME)) for *in-situ* XRD analysis, and acquired dominant presence of Li₂O₂ with formation/decomposition rate by the monitoring of real-time Li₂O₂ peak-area change during discharge/recharge process.

Super P carbon and nafion[®] (mass ratio of 6/4) were used for cathode materials, which were mixed in alcohol using a planetary mixer, pasted on a polymer membrane, and dried in a vacuum at 60 °C overnight. The typical mass and diameter of cathode were 1.2 mg and 12 mm, respectively. This cathode was assembled with a metallic lithium, glassy-fiber separator, and total 200 μL of ether-based (triglyme (< 25 ppm of H₂O), or DME (< 25 ppm of H₂O)) or carbonate-based (PC/ DMC (1/1 in volume, < 10 ppm of H₂O)) electrolyte containing 0.5 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) into a home-made Li-O₂ battery cell (Li-O₂ XRD cell), in an Ar-filled glove box (< 1 ppm of H₂O). The O₂ gas (99.999%) was flowed into the Li-O₂ XRD cell via an O₂ tank (~70 mL of volume capacity) at 100 sccm for 15 min. The Li-O₂ XRD cell was then loaded in a parallel beam XRD instrument (Smartlab[®], Rigaku). *In-situ* XRD pattern was recorded in 30 - 45° of 2θ region at 0.5 degree min⁻¹ of scan rate. Electrochemical measurement in the Li-O₂ XRD cell was performed at 0.1 mA cm⁻²_{geometry} (0.114 mA) of current rate using a battery cycler (WPG 100e, WonATech) in 1 atm of O₂ at room temperature. The cut-off potential of discharge was 2 V vs. Li/Li⁺ and the recharge process was performed to deliver the same capacity amount of discharge.

By real-time monitoring of XRD peak area on solid state of discharge product, the accurate efficiency of discharge product and the number of electrons can be evaluated. The XRD pattern on cathode of Li-O₂ battery cell (**Fig. 1**) showed dominant Li₂O₂ and no evidence of other inorganic crystal in ether-based electrolyte. With chemical identification of discharge product, the real-time acquisition of Li₂O₂ XRD pattern allowed us to estimate increasing and decreasing Li₂O₂ peak-area change, which revealed the rates of formation and decomposition of solid-state Li₂O₂ during discharge and recharge, respectively. The number of electrons estimated from time-dependent Li₂O₂ peak-area change showed the constant rate of Li₂O₂ formation but non-linear rate of decomposition. The quantity of Li₂O₂ was limited to 60 - 70% after the first full discharge and further reduced after the second discharge (~40%) even though Li₂O₂ formed was completely decomposed after the first recharge.

References

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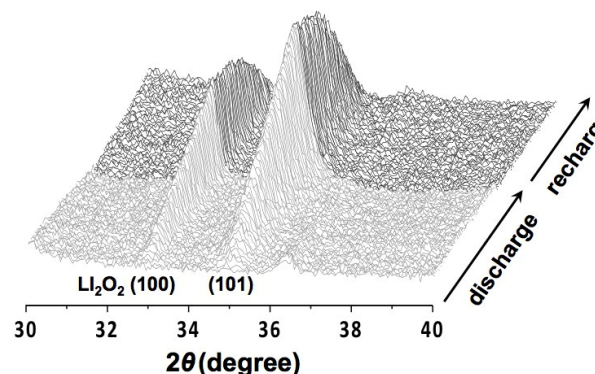


Fig. 1 *In-situ* X-ray diffraction patterns of Li₂O₂ (100) and (101) obtained with 0.5 M of Li salt in triglyme during discharge and recharge processes.