Oxidation mechanism of Li_2O_2 and its implication in Li-O_2 batteries

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Non-aqueous lithium-oxygen (Li-O_2) batteries have attracted intensive research attentions owing to their potential to provide gravimetric energy density 3–5 times that of conventional Li-ion batteries. In-depth understandings of the reaction mechanisms during discharge and charge are the prerequisites for further advancement of the Li-O_2 technology.

In this study, we report a solvent-dependent oxidation mechanism of Li_2O_2 (charging mechanism) by examining the charging overpotential and reaction intermediate species in solvents with a wide range of donor number (DN) via three-electrode cells, potentiostatic intermittent titration technique (PITT), thin-film rotating–ring disk electrode (RRDE) and synchrotron-based X-ray absorption near edge structure (XANES). We select two high-DN solvents 1-methylimidazole (Me-Im, DN=47) / dimethyl sulfoxide (DMSO, DN=29.8) and two low-donicity solvents, tetraethylene glycol dimethyl ether (TEGDME, DN=16.6) / diethylene glycol dimethyl ether (DG, DN=19.5). To remove solvent's influence on the Li anode potential and the junction potential, we exploit Li_2O_2-prefilled three-electrode system with a Ag reference electrode converting to a Fc/Fc^+ scale.

Figure 1 shows the galvanostatic charge voltage profiles of the Li_2O_2-prefilled three-electrode cells using the four model solvents. The Me-Im exhibits drastically lower charge voltage followed by DMSO, DG and TEGDME. The observed difference is more than 500 mV between Me-Im and TEGDME, which is much larger than differences made by many reported catalysts.

We will discuss solvent-dependent charging reaction pathways and mechanism responsible for differences in charging voltage.

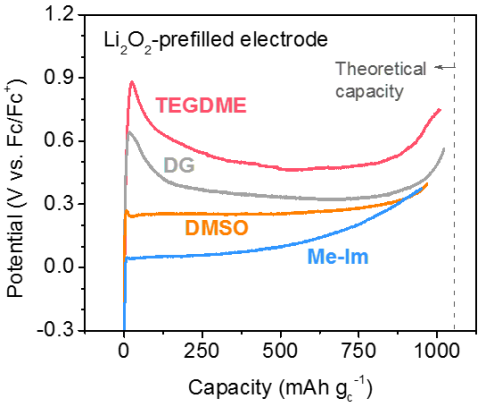

Figure 1. The galvanostatic charge voltage profiles of the Li_2O_2-prefilled three-electrode cells using the four model solvents Me-Im, DMSO, DG and TEGDME.

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