

## Why the charge overpotential in non-aqueous Li–O<sub>2</sub> batteries is so high and exhibits different rising trends?

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As one of the most promising candidates to replace the conventional lithium-ion batteries with super-high capacity, non-aqueous Li–O<sub>2</sub> batteries have attracted increasing attention [1]. However, the technology is still in its infant stages and widespread commercialization is hindered by several issues, particularly low round-trip efficiency and poor cycle performance—both of which can be largely attributed to the high charge overpotential in this type of battery. This perspective is to bring up a critical issue of why the charge overpotential is so high and exhibits different rising trends.

The commonly reported charge overpotential in typical non-aqueous Li–O<sub>2</sub> batteries is as high as 1.0 V [1]. More interestingly, though sharing the same trend in rise, the detailed charge curves reported in different experiments, even performed by the same research groups, showed significant variations. McCloskey et al. [2] demonstrated a curve with a rising slope (Fig. 1, curve a) and another one with an initially sloped region, followed by an area of plateau (Fig. 1, curve b) [3], whereas others reported a two-stage charging behavior (Fig. 1, curve c) [4]. Tremendous efforts have been made to explain the underlying mechanisms from both experimental and theoretical points of view, with the expectation to provide clues for catalyst design and utilization to reduce the high overpotential. There has yet to be a consensus.

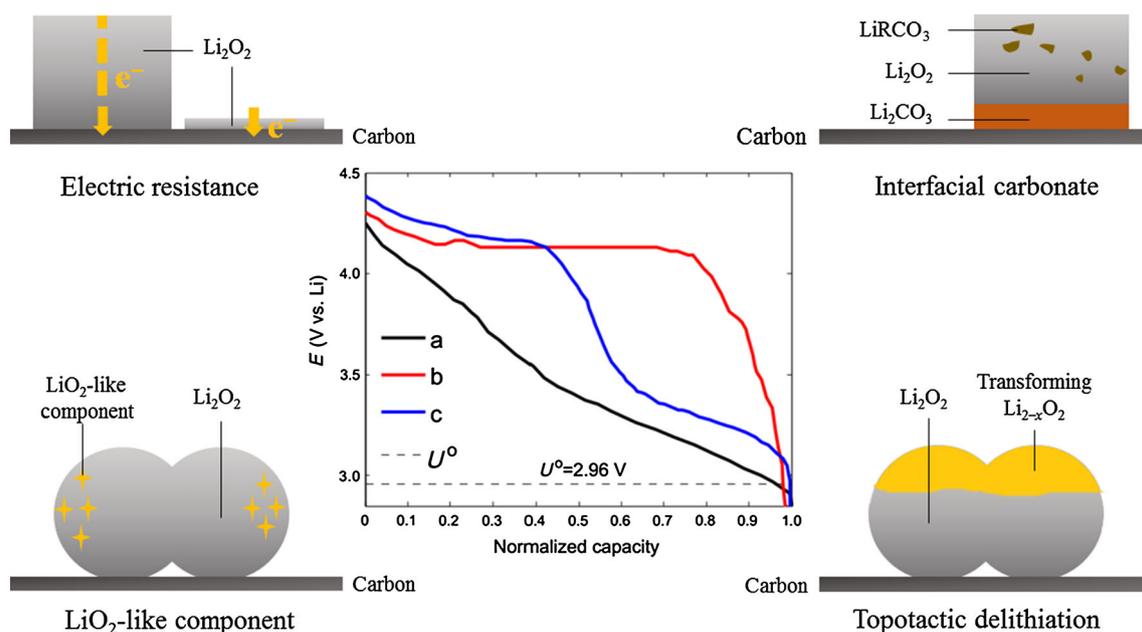
It is understood that the main discharge product in non-aqueous Li–O<sub>2</sub> batteries is solid-state Li<sub>2</sub>O<sub>2</sub>, which is a wide band gap insulator with poor electric conductivity [1]. Thus,

a natural chain of thought is to attribute the high charge overpotential to the large electric resistance. Radin and Siegel [5] studied the charge transport mechanism in Li<sub>2</sub>O<sub>2</sub> by first-principle modeling and proposed that for a thin-film layer of Li<sub>2</sub>O<sub>2</sub> with a thickness smaller than 10 nm, charge will transport through the electron tunneling mechanism, which can be completed with a small overpotential. Bulk Li<sub>2</sub>O<sub>2</sub>, however, transports via the polaron hopping mechanism, which requires a much higher overpotential. Yet, based on this explanation, the charge curve is expected to fall at the end of the charge process when the discharge product is thinner than 10 nm, which contradicts the experimental observations [1]. In addition, the decomposition of the outer shell of large Li<sub>2</sub>O<sub>2</sub> particles at relatively low overpotential was observed in some experiments [4]. These observations indicate that the large electric resistance of Li<sub>2</sub>O<sub>2</sub> may not be the only reason for the high charge overpotential and the various charging behaviors.

McCloskey et al. [2] investigated the relationship between the decomposition of parasitic discharge product and the charge overpotential. They observed that the interfacial carbonate formed from the reaction between Li<sub>2</sub>O<sub>2</sub> and electrolyte will decompose only at a higher charge overpotential, and thus concluded that the parasitic interfacial carbonate is responsible for the rising charge curve. However, the decomposition of parasitic discharge product can only explain the rising trend, but does not provide explanation for the reported two-stage charging behavior (Fig. 1, curve c) observed in other experiments [4, 6].

Different mechanisms have been proposed for the two-stage charging behavior. Zhai et al. [4] claimed a “LiO<sub>2</sub>-like component”, which is expected to be responsible for the low charge plateau. They found that the 1,123 cm<sup>-1</sup> peak in Raman spectrum, which represents the presence of

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**Fig. 1** Possible explanations for the charging behaviors of non-aqueous Li–O<sub>2</sub> batteries [2–4]

the LiO<sub>2</sub>-like component, can only be observed when the charge voltage is below 3.5 V. High-resolution TEM images further revealed that at the lower charge plateau, the outer part of the toroid particles decomposed first, which indicated the possible position of the LiO<sub>2</sub>-like component. However, the existence of such “LiO<sub>2</sub>-like component” is still being questioned as the LiO<sub>2</sub> crystal can only exist at very low temperatures [1]. The detailed composition and structure of these LiO<sub>2</sub>-components and the mechanisms of how they become involved during the charging process need further exploration.

Kang et al. [7] proposed a novel topotactic delithiation mechanism for the decomposition of Li<sub>2</sub>O<sub>2</sub> to explain the low charge overpotential at the initial plateau of the curve. First-principle calculations showed that this proposed delithiation mechanism can happen at about 3.3 V, which is consistent with the voltage of the plateau at the lower charge and can explain the observation of slight lattice parameter changes during the charging process [6]. However, this mechanism fails to explain the higher voltage plateau, since it is rather unreasonable to assume the existence of certain “activated Li<sub>2</sub>O<sub>2</sub>”, which will be charged following this facile mechanism, while the remaining Li<sub>2</sub>O<sub>2</sub> will be charged through a different mechanism.

From the above analyses, the high charge overpotential of non-aqueous Li–O<sub>2</sub> batteries is a complex topic and intimately related to the discharge process. The aforementioned proposed mechanisms can offer partial explanations to certain experimental observations, but are severely limited as none of them provide all-encompassing

explanations. In a real-life charge process, these reasons may be somewhat involved with certain mechanisms dominating others depending on the situation. New charging mechanisms may yet to be discovered. Understanding the charging behavior of non-aqueous Li–O<sub>2</sub> batteries is the first step in attempting to decrease the overpotential. In the future, tremendous efforts should be made to unify the controversy about the underlying charging mechanisms and to provide practical guidance to catalyst design and further system utilization.

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