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Comment on "cycling Li-O₂ batteries via LiOH formation and decomposition"

Abstract

Copyright 2016 by the American Association for the Advancement of Science; all rights reserved. Liu et al. (Research Article, 30 October 2015, p. 530) described a lithium-oxygen (Li-O₂) battery based on lithium iodide (LiI)-assisted lithium hydroxide (LiOH) formation and decomposition. We argue that LiOH cannot be oxidized by triiodide (I₃⁻). The charge capacity is from the oxidation of I⁻ instead of LiOH. The limited-capacity cycling test is misleading when the electrolyte contributes considerable parasitic reaction capacity.

Keywords

formation, decomposition, cycling, li, comment, o₂, batteries, via, lioh

Disciplines

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Comment on “Cycling Li-O₂ battery via LiOH formation and decomposition”

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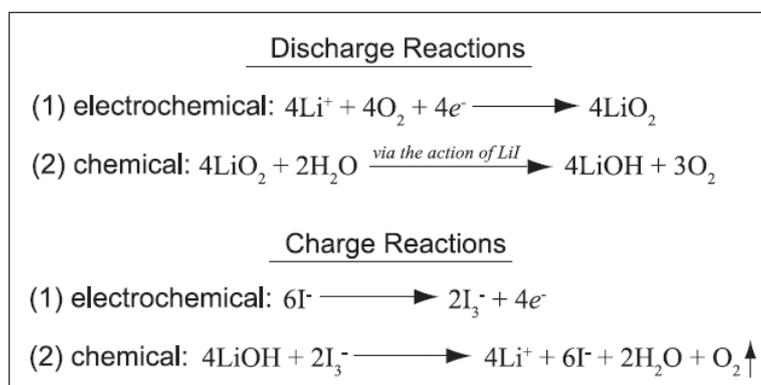
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Abstract: Liu *et al.* (Research Article, 30 October 2015, p.530) described a Li-O₂ battery based on LiI assisted LiOH formation and decomposition. We argue that LiOH cannot be oxidized by I₃⁻. The charge capacity is from the oxidation of I⁻ instead of LiOH. The limited capacity cycling test is misleading when the electrolyte contributes significant parasitic reaction capacity.

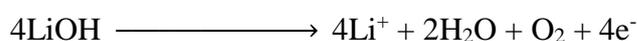
Main Text:

Liu *et al.* (1) reported a breakthrough” of Li-O₂ battery (LOB). Their cathode was able to cycle 2000 times at limited capacity of 1000 mAh g⁻¹ and the overpotential was as small as 0.2 V. In contrast to previous studies (2, 3), they claim that the excellent cycling stability is based on the formation and decomposition of LiOH. Small amounts of water and LiI depress the oxidation potential of LiOH down to 3.0 V.

The major conclusion in Liu *et al.*’s paper was the following reactions:



Adding the two charge reactions together will get the total charge reaction as:



This reaction is well known as the charge reaction of aqueous lithium-air batteries (4, 5). The potential of this reaction is widely agreed as 3.84 V (versus Li^+/Li) in neutral solutions or 3.42 V when $\text{pH}=12$, much higher than 3.0 V in Liu *et al.*'s paper. The equilibrium potential is a thermodynamic value; it cannot be influenced by the existence of I_3^- species which is a catalyst. The solvation effect of different solvents may bring a little difference to the charge potential. But it cannot explain the difference as big as 0.4 V. Liu *et al.* further claimed that even with 45,000 ppm of water, no appreciable change in the electrochemical profile was observed. The solvation situation in highly hydrated DME should be similar with the aqueous lithium-air batteries. Thus, the potential should not change very much. Therefore, LiOH cannot be oxidized at 3.0 V (versus Li^+/Li).

To determine the true charge reaction, a transparent battery was built to repeat the cycling experiment with similar weight ratio of the rGO cathode to electrolyte as in Liu's experiment (Fig. 1A). The charge potential was indeed lower than 3.2 V (Fig. 1B), but the electrolyte became darker after every charge process, indicating the concentration of I_3^- was increasing. This result is against Liu *et al.*'s mechanism, since they believe that the I_3^- should react with LiOH and transform back to colorless I^- . The cathode after 100 cycles of discharge and charge was measured with XRD, and the result confirmed the LiOH accumulation (Fig. 1C).

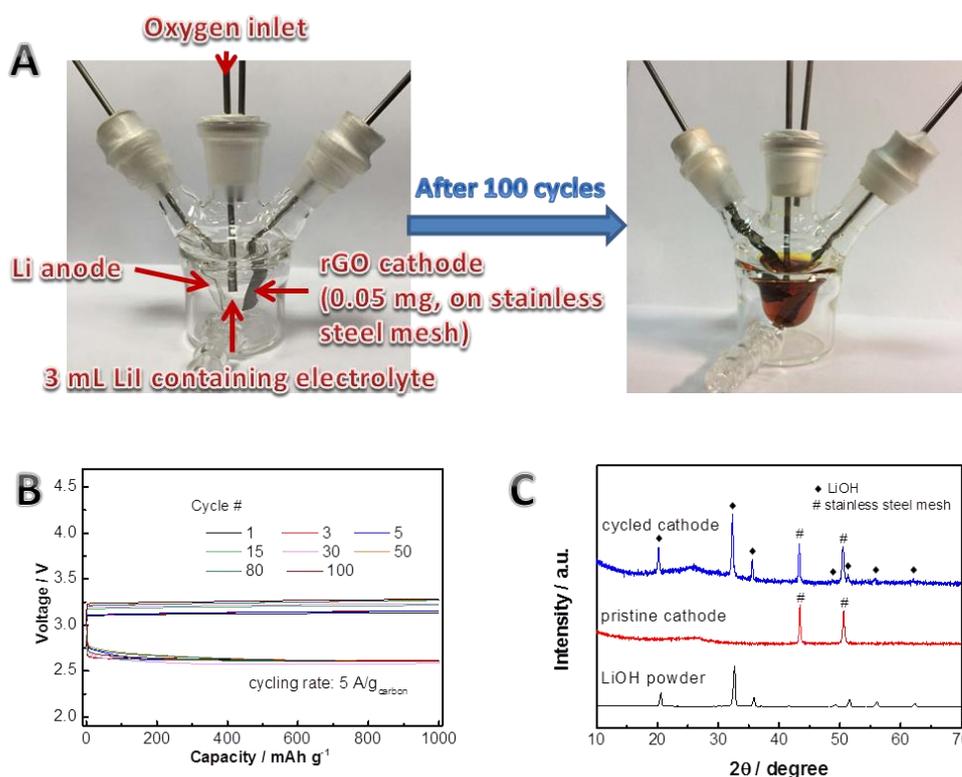


Figure 1. Cycling test of a transparent battery. (A) Photograph of the battery before and after 100 cycles. (B) Discharge-charge curves of the battery for selected cycles. (C) XRD pattern of the cathode after 100 cycles of discharge and charge.

In Liu *et al.*'s paper, the amount of electrolyte was 1 mL. The LiI concentration was 0.05 mol L⁻¹. Three I⁻ acquire two electrons to become I₃⁻. So, the capacity of the I₃⁻/I⁻ redox couple should be:

$$\frac{0.05 \times 10^{-3} \text{ mol} \times 96485 \text{ C mol}^{-1}}{3.6 \text{ C mAh}^{-1}} \times \frac{2}{3} = 0.89 \text{ mAh}$$

Meanwhile, the mass loading of Liu *et al.*'s rGO cathode (active materials) was as low as 0.01 mg. When the battery was cycling at a specific capacity limiting method of 1000 mAh g⁻¹, the capacity of the battery should be:

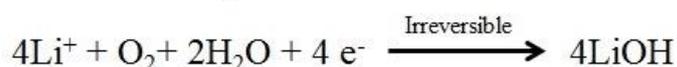
$$1000 \text{ mAh g}^{-1} \times 0.01 \times 10^{-3} \text{ g} = 0.01 \text{ mAh}$$

This value is only about 1% of the capacity of the I₃⁻/I⁻ redox couple. Thus, during charging, the LiOH does not need to be oxidized since the oxidation of I⁻ could sustain the charge reaction. The charge potential is very low simply because it is the I₃⁻/I⁻ redox reaction.

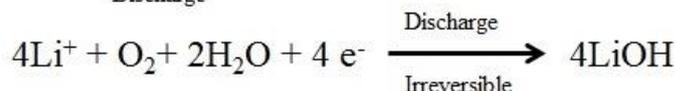
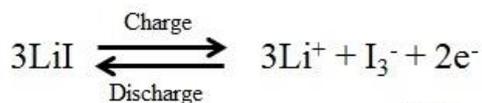
The "Comparison of the Capacity Obtained with the I⁻/I₃⁻ Couple (in Ar) with that Obtained for the Li-O₂ Cells" part in Liu *et al.*'s supplementary materials does not support what they claimed, because the LiI was originally in its reduced state and so there was nothing to be further reduced and the discharge capacity was thus very small. They unfortunately did not show the complete charge curve with LiI electrolyte in Liu *et al.*'s Fig. S3 and Fig.1 (B).

On the whole, we believe that Liu *et al.* proposed explanation of the reversible decomposition of LiOH is not scientifically sound. Their battery is actually a combination of an irreversible lithium-air battery and a reversible lithium-iodine battery, as shown in the following reactions:

Initial discharge



Following cycles



For lithium-oxygen batteries, limited capacity cycling test results can be misleading. They may conceal a large amount of parasitic reactions, especially when the weight ratio of the cathode material to the electrolyte is very small. It is necessary to use multiple techniques (6, 7) to confirm if the charge capacity is from the oxidation of the discharge product or from the side reactions.

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References and Notes:

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