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

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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.

Liu et al. (1) reported a “breakthrough” of Li-O2 battery. Their cathode was able to cycle 2000 times at a 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 Research Article was the reactions shown in Scheme 1. Adding the two charge reactions together will get the total charge reaction of

$$4\text{LiOH} \rightarrow 4\text{Li}^{+} + 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \quad (1)$$

This reaction is well known as the charge reaction of aqueous lithium-air batteries (4, 5). The potential of this reaction is widely agreed to be 3.84 V (versus Li+/Li) in neutral solutions or 3.42 V when 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 I3− species, which is a catalyst. The solvation effect of different solvents may bring a little difference to the charge potential, but it cannot explain a difference as large as 0.4 V. Liu et al. further claimed that, even with 45,000 parts per million of water, no appreciable change in the electrochemical profile was observed. The solvation situation in highly hydrated DME should be similar to 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).

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

$$6\text{C mol}^{-1} \times \frac{2}{3} = 0.89 \text{mAh}$$

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

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

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 because 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 section titled “Comparison of the Capacity Obtained with the I−/I3− Couple (in Ar) with that Obtained for the Li-O2 Cells” in Liu et al.’s supplementary materials does not support what they claimed, because the LiI was originally in its reduced state, so there was nothing to be further reduced and the discharge capacity was thus very small. They unfortunately did not show the

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Fig. 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 elected cycles. (C) XRD pattern of the cathode after 100 cycles of discharge and charge.
complete charge curve with LiI electrolyte in Liu et al.’s figure S3 and figure 1B.

On the whole, we believe that Liu et al.’s 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 reactions in Scheme 2.

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 whether the charge capacity is from the oxidation of the discharge product or from the side reactions.

REFERENCES AND NOTES

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