

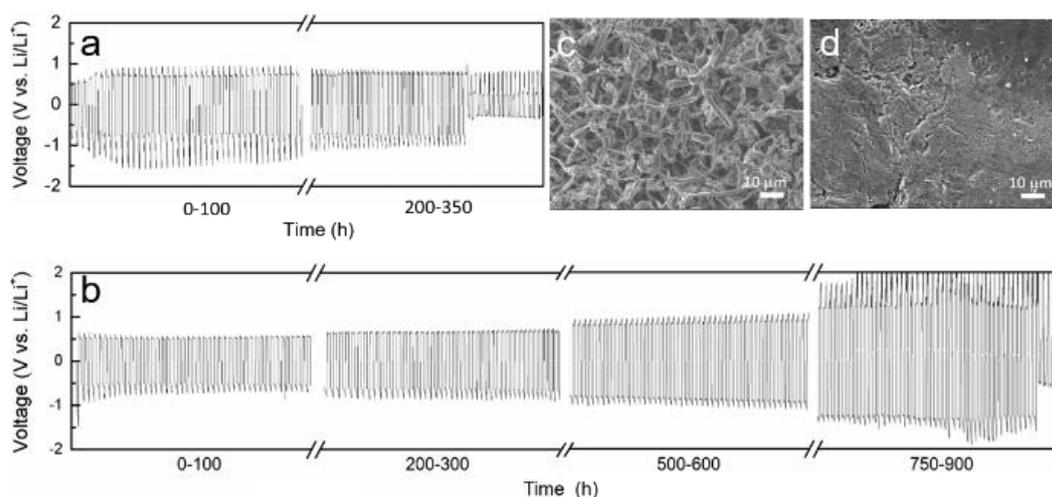
# Br<sup>-</sup>/NO<sub>3</sub><sup>-</sup> dual-anion electrolyte for suppressing charge voltage and dendrite formation of Li-O<sub>2</sub> Batteries

Xing Xin, Kimihiko Ito, Yoshimi Kubo

E-mail: XIN.xing@nims.go.jp

The main issues with Li-O<sub>2</sub> batteries are the high overpotential at the cathode and the dendrite formation at the anode during charging. Various types of redox mediators (RMs) have been proposed to reduce the charging voltage. However, the RMs tend to lose their activity during cycling owing to not only decomposition reactions but also undesirable discharge (shuttle effect) at the Li metal anode. Moreover, the dendrite growth of the Li metal anode is not resolved by merely adding RMs to the electrolytes. We have recently reported a simple yet highly effective method to reduce the charge overpotential while protecting the Li metal anode by incorporating LiBr and LiNO<sub>3</sub> in the electrolyte for Li-O<sub>2</sub> cells.<sup>1</sup> The Br<sup>-</sup>/Br<sub>3</sub><sup>-</sup> couple acts as an RM to oxidize the discharge product Li<sub>2</sub>O<sub>2</sub> at the cathode, whereas the NO<sub>3</sub><sup>-</sup> anion oxidizes the Li metal surface to prevent the shuttle reaction. Moreover, both anions work synergistically in the mixed Br<sup>-</sup>/NO<sub>3</sub><sup>-</sup> electrolyte to dramatically suppress dendrite formation by generating a solid Li<sub>2</sub>O thin film on the Li metal anode.<sup>1</sup>

In this work, we investigated the cycle life of the symmetrical Li | Li split-type cells in different electrolytes in O<sub>2</sub> atmosphere. In LiNO<sub>3</sub> alone electrolyte, a sudden drop in voltage caused by a dendrite-induced short circuit was found in around 300 h of operation as shown in Figure 1a. In contrast, the cells containing LiBr (Figure 1b) showed a similar short circuit failure after 850 h. Figure 1c and d exhibit the surface morphology of the charged (deposited) Li anode after cycled for 200 h. Although typical dendrite morphology was found for LiNO<sub>3</sub> alone electrolyte (Figure 1c), considerably smooth surface was observed for LiBr-LiNO<sub>3</sub> electrolyte (Figure 1d). These observations suggest a synergistic effect of Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and O<sub>2</sub> to suppress the dendrite formation by forming a thin and homogeneous SEI layer of Li<sub>2</sub>O.



**Figure 1.** Voltage versus time for a symmetrical Li | Li split-type cells during cycling in (a) 1 M LiNO<sub>3</sub> and (b) 0.05 M LiBr-1 M LiNO<sub>3</sub> with tetraglyme solvent at a current density of 0.5 mA cm<sup>-2</sup> in O<sub>2</sub> atmosphere. Each charge and discharge time is set as 1h. The corresponding top-view SEM images of the deposited Li metals in (c) 1 M LiNO<sub>3</sub> and (d) 0.05 M LiBr-1 M LiNO<sub>3</sub> after 200 h cycles.

## References:

[1] Xing Xin, Kimihiko Ito and Yoshimi Kubo, *ACS Appl. Mater. Interfaces* 9, 25976–25984 (2017).