

How initial nucleation influences discharge capacities of Li-O₂ cells

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The Li-O₂ system has been recognized as one of the candidates for next generation batteries. Several groups have reported Li-O₂ cells with high capacity and good cycle stability [1-3]. However, there are also concerns about chemical and electrochemical reactions that occur during discharge and charge in different solvents and electrolytes [4-5]. In particular, the gradual formation of organic deposits as a result of the side reactions by the reactive superoxide radical O₂^{•-} and Li₂O₂ with the solvents can impede the discharge and charge reactions. The rates of both the main cathode reaction and the side reactions are influenced by composition and morphology of the cathode surface. The overall energy density of a Li-O₂ cell is limited by the amount of solid Li₂O₂ formed at the cathode during discharge. Hence, it is important to understand if that amount only depends on structure and composition of the permanent cathode backbone (here: carbon), or if also its own growth history is relevant.

In this work, we will demonstrate that the morphology of Li₂O₂ layers formed on carbon cathodes at the beginning of discharge vary in roughness when grown at increasing kinetically relevant overpotentials.

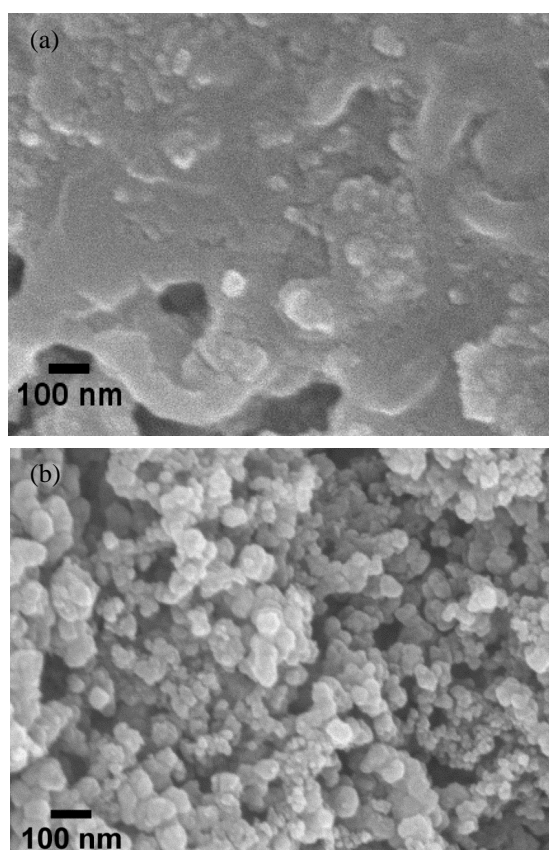


Fig.1. Discharge product deposits on carbon cathode after discharge to 400 mAh/g at (a) 2.6 V (b) 1.7 V.

According to the SEM images in Figure 1, a slow growth rate at 2.6 V leads to a much smoother surface as compared to a higher growth rate obtained at 1.7 V. In all cases, the seed layer has a volume equivalent to a cumulative capacity of 400 mAh/g (all current and charge densities are given per gram carbon). After formation of the initial seed layer, all cells were rested for 5 h at 2.9 V and then discharged at a rate of 50 mA/g. As an example, Figure 2a shows the time line for a cell pre-discharged at 2.3 V. For all cells, the discharge was stopped when the cell voltage dropped to below 2.0 V.

As illustrated in Figure 2b, the obtainable discharge capacity drastically decreases with the potential applied for the initial discharge to 400 mAh/g. Specifically, an initial discharge at 1.7 V decreases the overall discharge capacity by a factor of two as compared to an initial discharge at E > 2.3 V.

Based on electron microscopy, X-ray diffraction, and Raman spectroscopy, we will discuss in how far this pronounced history dependent capacity can be explained by the influence of the surface morphology on the growth kinetics and to which extend also the chemical composition and the physical properties of the seed layer are of relevance.

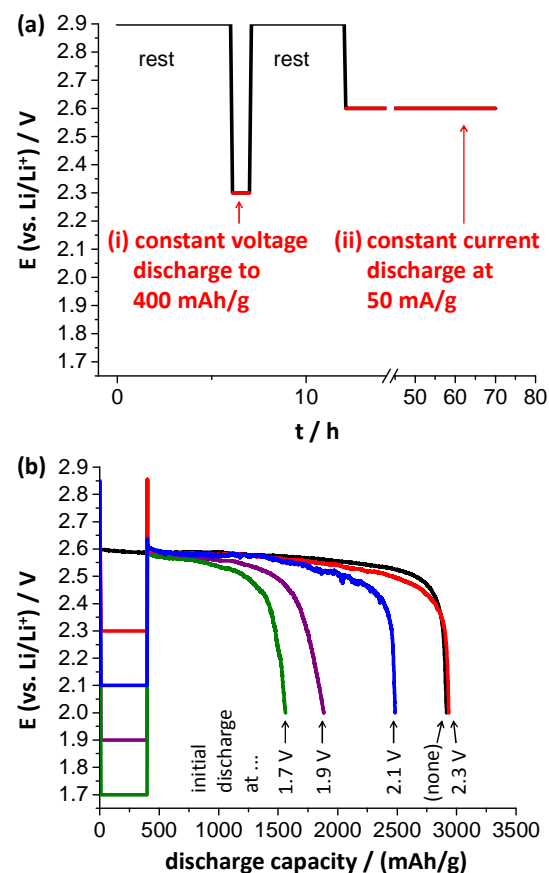


Fig. 2. (a) Voltage profile involving (i) initial discharge at 2.3 V followed by (ii) constant-current discharge at 50 mA/g; (b) discharge curves for various initial discharge voltages.

References

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