Electrochemically-driven transition of crystallization morphologies in Li-O$_2$ batteries

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Lithium-oxygen (Li-O$_2$) batteries are a potential alternative to conventional combustion technologies in the mobility sector. However, the development of Li-O$_2$ cells is still at an early stage and a list of challenges needs to be addressed.

Compact solid discharge products in aqueous[1] and non-aqueous[2] Li-O$_2$ batteries enable energy storage devices with high gravimetric and volumetric energy densities, but solid deposits can disturb charge transport and induce mechanical stress. The formation of the electronically isolating solid reaction product Li$_2$O$_2$ in the cathode during discharge is an important design problem for non-aqueous Li-O$_2$ batteries. It limits the cell performance, especially if a film of Li$_2$O$_2$ forms.[3]

However, experiments at low surface specific rates have revealed that Li$_2$O$_2$ can be deposited in particles of complex morphology.[4–6] In our experiments, aligned carbon nanofiber and carbon nanotube electrodes serve as a platform for clear visualization of the morphological evolution of Li$_2$O$_2$ as a function of discharge/charge depth, discharge/charge rates and electrode chemistry using ex situ SEM and TEM techniques, providing new critical mechanistic insights.
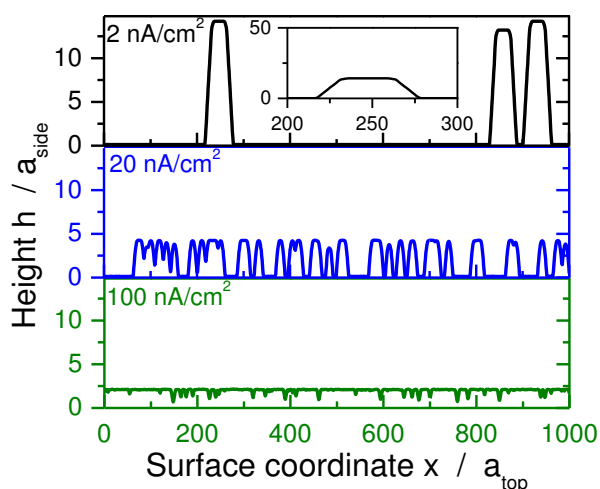

Figure 1: Transition from particle-growth to film-growth with increasing current

We developed a model to describe the spatial structure of electrochemically deposited Li$_2$O$_2$ within the cathode.[7] We make use of a consistent phase-field theory, which is based on an electrochemical Allen-Cahn reaction equation, that was shown to capture lithiation of LiFePO$_4$ nanoparticles.[8–12] Our model predicts that the transition between these surface growth modes occurs close to the exchange current density of the oxygen reduction reaction (see Figure 1). We validated our prediction with independent measurements of the exchange current density. Fundamental understanding of the structure and morphology of electrochemically deposited Li$_2$O$_2$ can allow for the optimization of air electrodes and reveal promising directions for electrode designs.

Metallic lithium anodes are required to profit from the huge energy density of lithium-oxygen cathodes. Growth of lithium dendrites during charge, however, significantly reduces their cyclability and prevents their widespread application. Models for lithium dendrites discuss growth at the top[13] or at the bottom[14] limited by diffusion[15] or by reaction kinetics[16]. We develop a phase field model to describe the growth morphology of dendrites.

1   B. Horstmann, T. Danner, W. G. Bessler, Energy & Environmental Science, 2013, **6**, 1299.

2   J. P. Neidhardt, D. N. Fronczek, T. Jahnke, T. Danner, B. Horstmann, W. G. Bessler, Journal of The Electrochemical Society, 2012, **159**, A1528.

3   V. Viswanathan, K. S. Thygesen, J. S. Hummelshøj, J. K. Nørskov, G. Girishkumar, B. D. McCloskey, A. C. Luntz, The Journal of Chemical Physics, 2011, **135**, 214704.

4   R. R. Mitchell, B. M. Gallant, C. V. Thompson, Y. Shao-Horn, Energy & Environmental Science, 2011, **4**, 2952.

5   Y.-C. Lu, B. M. Gallant, D. G. Kwabi, J. R. Harding, R. R. Mitchell, M. S. Whittingham, Y. Shao-Horn, Energy & Environmental Science, 2013, **6**, 750.

6   B. M. Gallant, R. R. Mitchell, D. G. Kwabi, J. Zhou, L. Zuin, C. V. Thompson, Y. Shao-Horn, The Journal of Physical Chemistry C, 2012, **116**, 20800.

7   B. Horstmann, B. M. Gallant, R. R. Mitchell, W. G. Bessler, C. V. Thompson, Y. Shao-Horn, M. Z. Bazant, 2013, to be submitted.

8   P. Bai, D. A. Cogswell, M. Z. Bazant, Nano Letters, 2011, **11**, 4890.

9   D. A. Cogswell, M. Z. Bazant, ACS Nano, 2012, **6**, 2215.

10   D. A. Cogswell, M. Z. Bazant, 2011, 1–10.

11   M. Bazant, Accounts of Chemical Research, 2013, DOI 10.1021/ar300145c.

12   T. R. Ferguson, M. Z. Bazant, Journal of the Electrochemical Society, 2012, **159**, A1967.

13   C. Monroe, J. Newman, Journal of The Electrochemical Society, 2003, **150**, A1377.

14   J. Yamaki, S. Tobishima, K. Hayashi, Y. Nemoto, M. Arakawa, Journal of Power Sources, 1998, **74**, 219.

15   J. Chazalviel, Physical Review A, 1990, **42**, 7355.

16   D. R. Ely, R. E. Garcia, Journal of the Electrochemical Society, 2013, **160**, A662.