



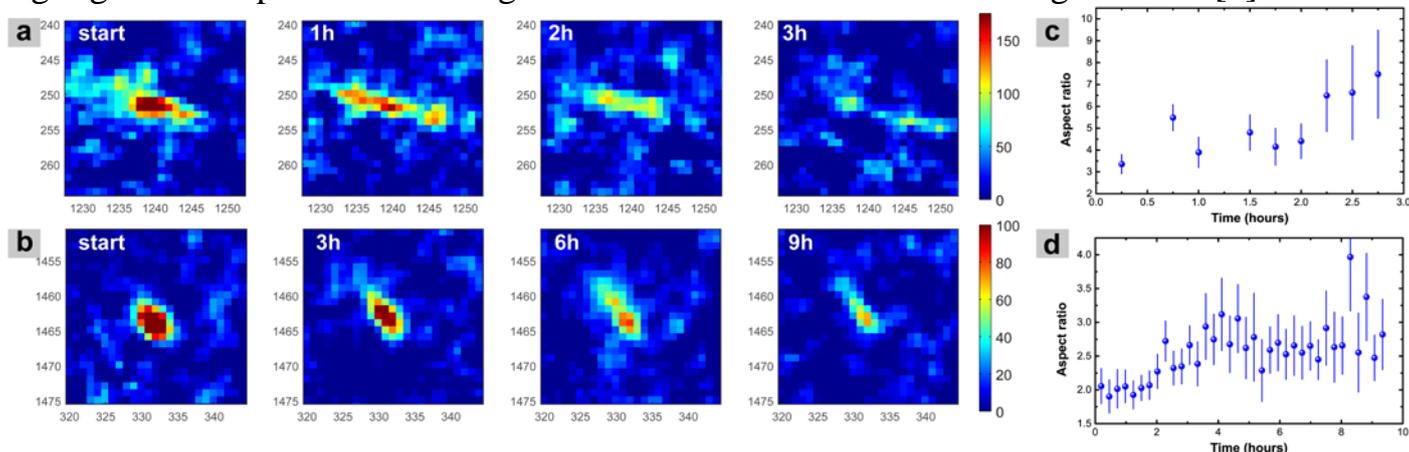
	<b>Experiment title:</b> Real time observation of the growth of individual $\text{Li}_2\text{O}_2$ grains in the Lithium-Air ( $\text{Li-O}_2$ ) battery	<b>Experiment number:</b> MA1925
<b>Beamline:</b>	<b>Date of experiment:</b> from: 20-02-2014 to: 25-02-2014	<b>Date of report:</b> 24-08-2016
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### Report:

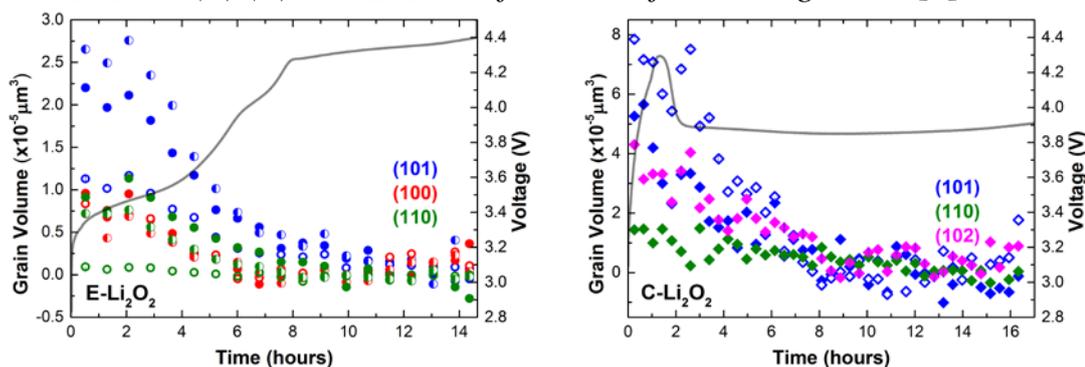
The rechargeable  $\text{Li-O}_2$  (Lithium-air) cell is a very promising large-scale energy storage system owing to its high theoretical energy density (energy per unit weight) and the possibility of using oxygen from air as a fuel source is very attractive. The cell reactions can be broadly classified as the oxygen reduction reaction (ORR) which takes place on discharge leading to the formation of  $\text{Li}_2\text{O}_2$  on the surface of the carbon composite cathode. On charge the oxygen evolution reaction (OER) takes place wherein the  $\text{Li}_2\text{O}_2$  decomposes into its constituent Li and  $\text{O}_2$  gas. Fundamental research into  $\text{Li-O}_2$  batteries is still in its infancy, and practical energy densities are far from the theoretical value. The experimental aim was to follow the evolution of individual grains of  $\text{Li}_2\text{O}_2$  in a working  $\text{Li-O}_2$  experiment where they are present in their native environment in a bid to help understand the high overpotentials and sluggish kinetics restricting  $\text{Li-O}_2$  battery performance.

Two types of  $\text{Li}_2\text{O}_2$  were studied, (a) electrochemically generated  $\text{Li}_2\text{O}_2$  toroids comprised of  $\text{Li}_2\text{O}_2$  platelets formed at a discharge current density of  $65 \mu\text{A}/\text{cm}^2$  (E- $\text{Li}_2\text{O}_2$ ) and (b) commercial  $\text{Li}_2\text{O}_2$  that was incorporated into a carbon electrode (C- $\text{Li}_2\text{O}_2$ ). The most obvious difference between the two types of  $\text{Li}_2\text{O}_2$  was the shape and size of the primary crystallites. The time-resolved information obtained by nanobeam synchrotron X-ray diffraction on the transformation of a number of individual  $\text{Li}_2\text{O}_2$  crystallites in both E- $\text{Li}_2\text{O}_2$  and C- $\text{Li}_2\text{O}_2$  made it possible to study the difference in the decomposition mechanism and decomposition rate. The measurements were performed using a monochromatic X-ray beam with an energy of  $E = 42 \text{ keV}$ , beam dimensions of  $260 \text{ nm} \times 5 \mu\text{m}$  and a FReLoN2k CCD detector. During exposure the sample was continuously rotated around the axis perpendicular to the X-ray beam over an angular range of  $7.5^\circ$  with an exposure time of 60 s for the E- $\text{Li}_2\text{O}_2$  sample and 15 s for the C- $\text{Li}_2\text{O}_2$  sample.

In **Figure 1** we show the time evolution of the aspect ratio (average long dimension divided by average short dimension) during charge. The short dimension tends to decrease faster than the long dimension (**Figure 1c,d**). This can be observed from the increase in the aspect ratio of the grain as a function of charge time, where during the initial stages of charging the elongated (110) reflection broadens significantly (**Figure 1a,b**), directly reflecting that the  $\text{Li}_2\text{O}_2$  platelet thickness decreases as a function of charging time. This implies that the particles preferentially decompose from the (001) facets, which have been determined to be the predominant interfacial facets between the platelet stack. In addition, the evolution of the crystallite volume was monitored as a function of charge time (**Figure 2**). This gives unique experimental insight into the average crystallite decomposition time  $\langle \Delta t \rangle$ , yielding 8.9 h for E- $\text{Li}_2\text{O}_2$  (9.7 h for C- $\text{Li}_2\text{O}_2$ ). This results in an average local current density per crystallite of about  $200 \text{ nA/cm}^2$ , two orders of magnitude larger than the exchange current density indicating that the overpotential is largely due to crystallite decomposition. This reflects that the  $\text{Li}_2\text{O}_2$  decomposition rate limits the charging rates of these Li- $\text{O}_2$  batteries and highlights the importance of using redox mediators in solution to charge the cell [1].



**Figure 1.** Time evolution of the (110) peak intensity and aspect ratio of the long and short dimensions of two individual  $\text{Li}_2\text{O}_2$  crystallites during the initial charge stages for (a)/(c) E- $\text{Li}_2\text{O}_2$  and (b)/(d) C- $\text{Li}_2\text{O}_2$  as a function of the charge time [1].



**Figure 2.** Examples of the evolution of grain volume as a function of charge time for various reflections of E- $\text{Li}_2\text{O}_2$  (left) and C- $\text{Li}_2\text{O}_2$  (right) along with the corresponding galvanostatic voltage curves recorded during operando synchrotron X-ray diffraction. Current densities of  $100$  and  $135 \mu\text{A/cm}^2$  were used for E- $\text{Li}_2\text{O}_2$  and C- $\text{Li}_2\text{O}_2$ , respectively [1].

## Reference

[1] S. Ganapathy, J.R. Heringa, M.S. Anastasaki, B.D. Adams, M. van Hulzen, S. Basak, Z. Li, J.P. Wright, L.F. Nazar, N.H. van Dijk, M. Wagemaker, *Operando nanobeam diffraction to follow the decomposition of individual  $\text{Li}_2\text{O}_2$  grains in a nonaqueous Li- $\text{O}_2$  battery*, Journal of Physical Chemistry Letters 7 (2016) 3388-3394.