



	Experiment title: Real time observation of the growth of individual Li_2O_2 grains in the Lithium-Air (Li-O_2) battery	Experiment number: MA1925
Beamline:	Date of experiment: from: 20-02-2014 to: 25-02-2014	Date of report: 24-08-2016
Shifts:	Local contact(s): J.P. Wright	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Marnix WAGEMAKER*, TU Delft, Applied Sciences, Delft, The Netherlands Niels VAN DIJK*, TU Delft, Applied Sciences, Delft, The Netherlands Swapna GANAPATHY*, TU Delft, Applied Sciences, Delft, The Netherlands Maria ANASTASAKI*, TU Delft, Applied Sciences, Delft, The Netherlands Jon WRIGHT*, ESRF, Grenoble, France		

Report:

The rechargeable 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 Li_2O_2 on the surface of the carbon composite cathode. On charge the oxygen evolution reaction (OER) takes place wherein the Li_2O_2 decomposes into its constituent Li and O_2 gas. Fundamental research into 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 Li_2O_2 in a working 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 Li-O_2 battery performance.

Two types of Li_2O_2 were studied, (a) electrochemically generated Li_2O_2 toroids comprised of Li_2O_2 platelets formed at a discharge current density of $65 \mu\text{A}/\text{cm}^2$ (E- Li_2O_2) and (b) commercial Li_2O_2 that was incorporated into a carbon electrode (C- Li_2O_2). The most obvious difference between the two types of Li_2O_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 Li_2O_2 crystallites in both E- Li_2O_2 and C- Li_2O_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° with an exposure time of 60 s for the E- Li_2O_2 sample and 15 s for the C- Li_2O_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 Li_2O_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- Li_2O_2 (9.7 h for C- Li_2O_2). This results in an average local current density per crystallite of about 200 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 Li_2O_2 decomposition rate limits the charging rates of these Li- O_2 batteries and highlights the importance of using redox mediators in solution to charge the cell [1].

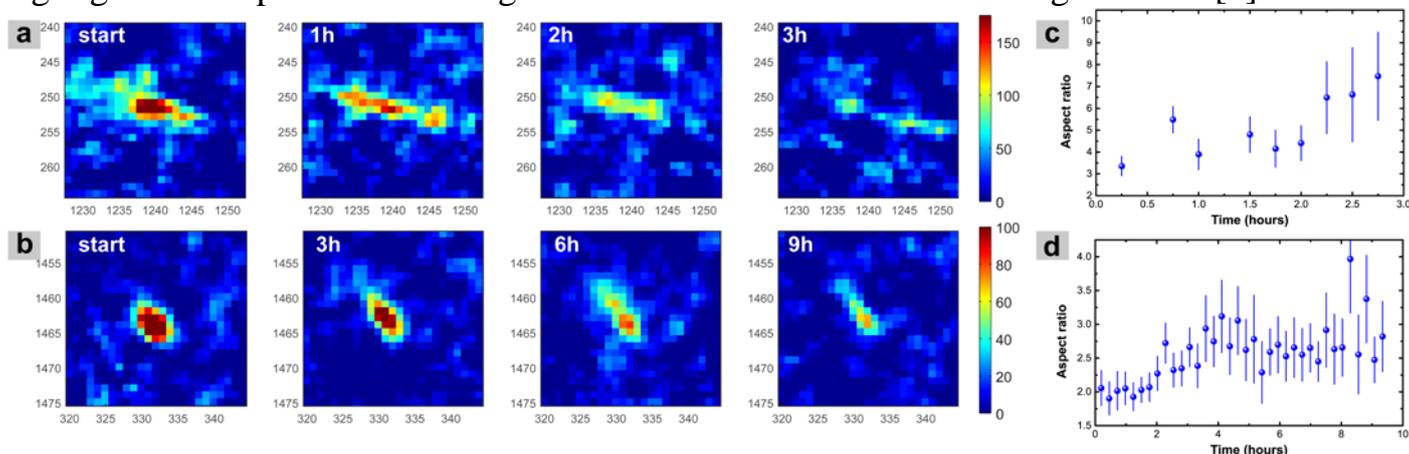


Figure 1. Time evolution of the (110) peak intensity and aspect ratio of the long and short dimensions of two individual Li_2O_2 crystallites during the initial charge stages for (a)/(c) E- Li_2O_2 and (b)/(d) C- Li_2O_2 as a function of the charge time [1].

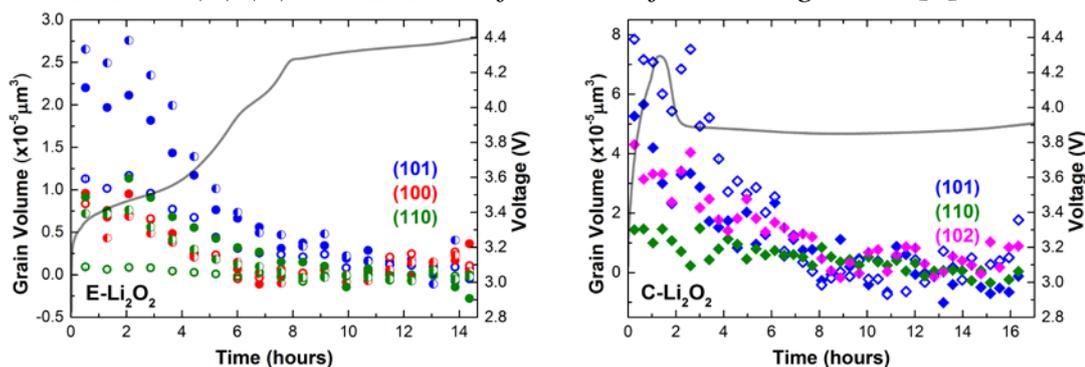


Figure 2. Examples of the evolution of grain volume as a function of charge time for various reflections of E- Li_2O_2 (left) and C- Li_2O_2 (right) along with the corresponding galvanostatic voltage curves recorded during operando synchrotron X-ray diffraction. Current densities of 100 and $135 \mu\text{A/cm}^2$ were used for E- Li_2O_2 and C- Li_2O_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 Li_2O_2 grains in a nonaqueous Li- O_2 battery*, Journal of Physical Chemistry Letters 7 (2016) 3388-3394.