Operando Liquid-electrochemical TEM for Monitoring Growth and Dissolution Steps of NaO$_2$ Cubes in Na-O$_2$ Battery

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The recent development of liquid cell for TEM [1, 2] enables an exciting opportunity to explore [3, 4] and even quantify [5, 6] complex electrochemical reactions occurring inside batteries during operation. Indeed, the miniaturization of new electrochemistry echips (Protochips) [7] with complex electrode designs (3-electrodes cell) adds the capability to perform true *in situ/operando* quantitative electrochemical reactions, which can be followed using TEM multi-techniques.

Compared to conventional Li/Na-ion batteries, in which reversible energy storage relies on the use of redox active transition metal oxides as positive electrodes, the metal-O$_2$ battery systems would theoretically offer greater energy density owing to the use of the redox of gaseous oxygen using conductive and light carbon electrodes. Although in sodium−oxygen (Na−O$_2$) batteries show promise as high-energy storage systems, this technology is still the subject of intense fundamental research, owing to the complex reaction by which it operates. To understand the formation mechanism of the discharge product, sodium superoxide (NaO$_2$), liquid- electrochemical TEM holder has been used (Poseidon 510) [7].

Here we present for the first time the use of a "Na-O$_2$ microbattery" using a liquid aprotic electrolyte (liquid cell) coupled with fast imaging TEM (Oneview camera) and HAADF-STEM to visualize, in real time, the mechanism of NaO$_2$ nucleation/growth. The electrolyte (NaPF$_6$/DME) was saturated with ultrapure O$_2$, prior to inject into the liquid TEM cell, to induce the reaction $Na^+ + O_2 + e^- -> NaO_2$ using electrochemical echips with a glassy carbon electrode (in the observation window) as working electrode (with two others Pt electrodes).

We observe that the formation of NaO$_2$ cubes [8] onto the glassy carbon electrode during reduction occurs by a solution-mediated nucleation process. The cyclic voltammetry response obtained during discharge and charge of the Na-O$_2$ microbattery exhibits two peaks corresponding to the reduction and oxydation processes. We visualized the solution-mediated growth of NaO$_2$ in real-time and identified that the 3D growth process is governed by the equilibrium between NaO$_2$(solv) $\leftrightarrow$ NaO$_2$(solid). Based on the fast imaging acquisition (30 frames/s) of this phenomenon, we quantified the kinetics of growth of NaO$_2$ cubes and demonstrated the strong impact of O$_2$ diffusion in the liquid electrolyte on the NaO$_2$ cube growth. By HAADF-STEM imaging the charge process, we demonstrated that the same solvation−desolvation equilibrium is responsible for the dissolution of the NaO$_2$ discharge product, which consumes the NaO$_2$ cubes from the NaO$_2$−electrolyte interface toward the electrode.

Finally, we observed the formation of parasitic shell around NaO$_2$ cubes during the cycling of a Na-O$_2$

battery, in which the fast imaging TEM revealed the chemical reactivity of NaO_2 at the interface with the electrolyte. Parasitic products continuously accumulate on the cube surface to form a thick shell surrounding the NaO_2 cubes, which passivate the electrode surface. This information is vital for optimization of the battery, since this parasitic shell is responsible for its poor cyclability by preventing crucial O_2 redox and further nucleation of NaO_2. The assessment of the discharge−charge mechanistic in Na-O2 batteries through operando liquid-electrochemical TEM visualization should facilitate the development of this battery technology [8].

References:
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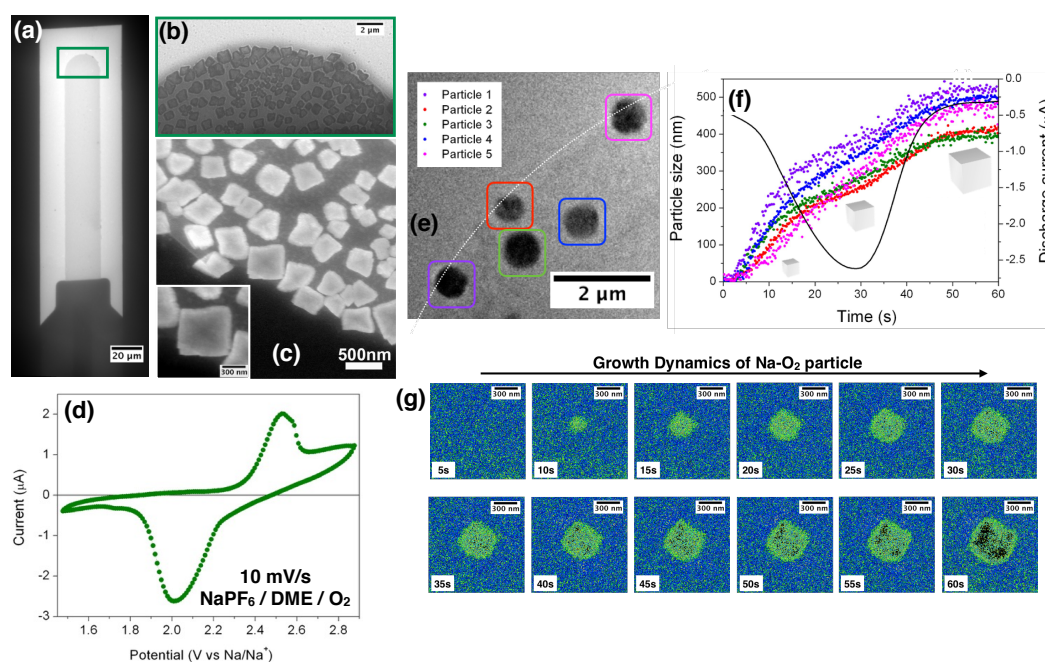[8] L Lutz et al., Nano Lett., **18** (2018), p. 1280.

Figure 1. (a) Low-magnification TEM image of the GC working electrode used in the in situ Na−O$_2$ microbattery cell. (b,c) TEM and HAADF-STEM overview images in the presence of liquid electrolyte showing NaO_2 cubes covering the GC electrode after discharge. (d) Curve of voltammetry cyclic measured inside the *in situ* electrochemical cell in which peaks of oxidation and reduction of Na-air micro-battery system is exhibited. (e) TEM image extracted from the growth study of several cubes (pink, blue, green, red, and black circles) forming during discharge. (f) The size-evolution analysis of these cubes reveals a nonlinear growth with intermittent plateaus demonstrating the $NaO_{2(solv)}$ diffusion dependency of this process. The black line indicates the anodic current response obtained during discharge. (g) Time-resolved and animated operando TEM images illustrate the morphological evolution of the NaO_2 product during discharge, featuring a nucleation event (10 s) and the subsequent growth of NaO_2 cubes, following a solution-mediated growth-process (11−60 s).