Electron microscopic characterization of Li-O_2 batteries: Clean, green electrochemical energy storage

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Keywords: Low-Voltage Electron Microscopy, Li-Air Batteries, Irradiation Effects

Lithium-based batteries have become one of the most important groups of rechargeable batteries in portable electronic devices owing to their high gravimetric energy-density. An increasing scientific and technological interest in further improving the energy-capacity and the number of charge-discharge cycles has provided significant impetus for further innovations in the field of Li-Air batteries [1, 2]. However, one of the most severe limitations in the commercialization of the Li-Air batteries is that the oxygen reduction reaction (ORR) during discharging and oxygen evolution reaction (OER) during charging must have fast kinetics. In order to enhance the ORR and OER reaction kinetics and to suppress any parasitic reactions, innovations in developing suitable electrocatalysts as well as suitable characterization techniques are also necessary.

In the current work, we employ aberrations-corrected high-resolution TEM and electron energy-loss spectroscopy (EELS) to characterize the reaction products and the electrocatalysts in order to gain a deeper understanding of the underlying reactions and their mechanisms to improve reaction efficiencies.

The TEM experimental challenges in this study are two-fold: Firstly, the typical end products of the ORR, i.e., lithium oxides (Li_2O_2 and/or Li_2O) tend to react with CO_2 in air and a fraction of the oxides could possibly transform to carbonates (Li_2CO_3). Thus, they must be studied ideally without exposure to air during preparation and loading of the sample. Secondly, a technically challenging issue arises from the fact that Li is a light-element and hence severe electron-irradiation-damage, may occur during TEM investigations, via radiolysis or/and atom knock-out. Thus, structural and chemical characterization must be performed at suitable low-voltage and low-dose conditions to minimize these effects.

We used both C_S-corrected Titan (operating at 80 kV) and the Sub-Angstrom Low-Voltage Electron Microscope (SALVE [3]) (operating at 20 and 40 kV) to study voltage-dependent irradiation damage on various Li based compounds. Operating at lower voltages offers two major advantages. Firstly, the total energy deposited by the incident electron is lower, thereby reducing knock-on damage. But, radiolysis can be the predominant damaging mechanism, which can counteract the benefits of lower deposited energy [4, 5]. Secondly, the inelastic scattering cross-section is higher at lower voltages, allowing better EELS signal [5]. However, one of the main challenges arising for low-voltage microscopy is preparing sufficiently thin sample to satisfy the weak-phase object condition. Additionally, since the inelastic mean-free path of the incident electron is a voltage-dependent quantity, care must be taken to have appropriate thicknesses for suitable voltages so that t/λ is in the range of 0.5 [5].

Several interesting initial observations have been made which needs to be evaluated precisely. For instance, we noticed the transformation of single-crystalline Li_2O_2 (hexagonal) to polycrystalline Li_2O (cubic) upon investigation at 80 kV electron beam (Fig. 1). This observation is qualitatively consistent with the Li-O_2 phase-diagram wherein a transformation from Li_2O_2 to Li_2O is predicted at elevated temperature [6]. Additionally, we found that Li_2O is stabler, even at 80 kV, to be imaged at high-resolution (Fig. 1). This is also consistent with the phase-diagram showing a higher melting point (thus, strong bonding) in comparison to Li_2O_2.

In parallel, we are also investigating other Li olivine phosphates, such as $LiNiPO_4$ to understand the irradiation effects. In our contribution, we will share our latest results from this on-going research work on mechanistic understanding of electrochemical reaction products and optimized imaging conditions.

References

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[7] The authors gratefully acknowledge funding from the German Federal Ministry of Education and Research (BMBF) under the project '*Strom aus Luft und Li*'.

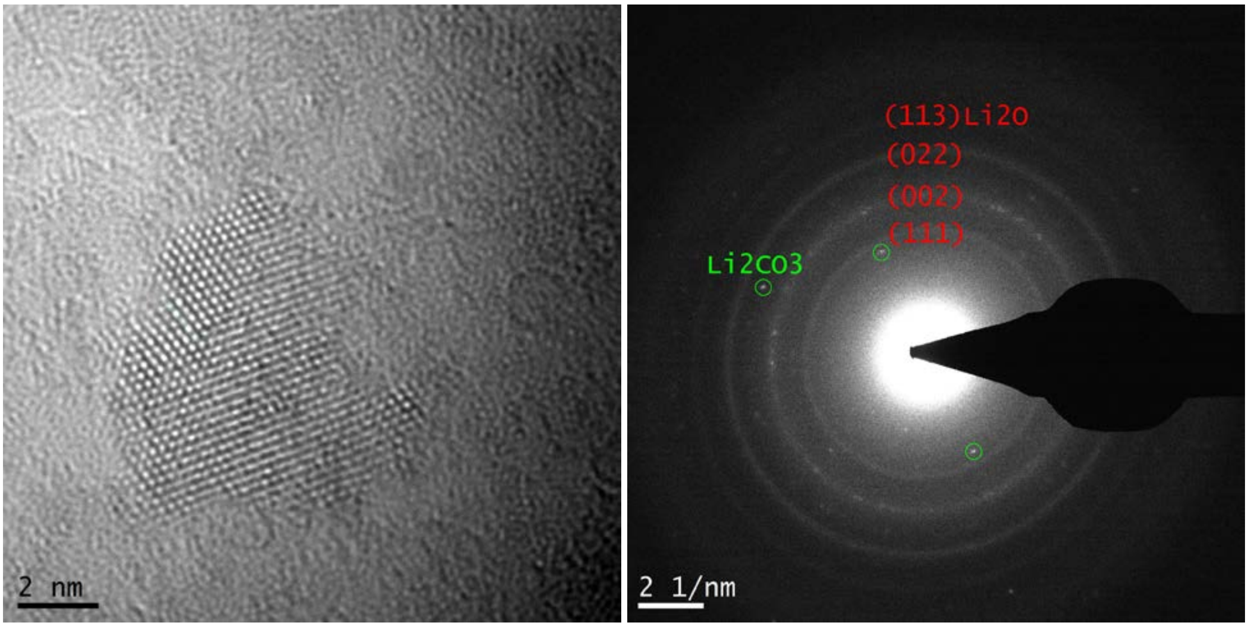

Figure 1. *(Left) HRTEM image (at 80 kV) of Li_2O crystal, an apparent product of irradiation induced transformation from original Li_2O_2 sample. (Right) Post-irradiation powder diffraction pattern from a collection of particles indicating that the Li_2O is the predominant phase.*