

Combined DFT and DEMS study on the role of CO<sub>2</sub> poisoning on the electronic conduction and overpotentials in Li-Air batteries

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Li-air batteries hold the potential to surpass the energy density of the Li-ion technology by up to an order of magnitude [1], but Li-air batteries face significant challenges in terms of high overpotentials [2], low current densities [3], degradation and poisoning, e.g., by CO<sub>2</sub> [4]. A detailed atomic level understanding of the fundamental mechanisms governing the electronic conduction, electrode-electrolyte interface reactions and degradation is needed to resolve these challenges.

Here, we present a combined Density Functional Theory (DFT) and Differential Electrochemical Mass Spectroscopy (DEMS) investigation of the interaction of CO<sub>2</sub> with Li<sub>2</sub>O<sub>2</sub> formed at the cathode during discharge of aprotic Li-air batteries (see Figure 1).

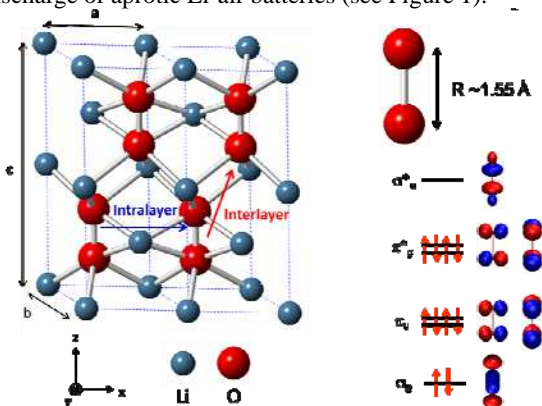


Figure 1: The unit cell of Li<sub>2</sub>O<sub>2</sub> repeated twice along the [100] direction. The intralayer (red arrow) and interlayer (blue arrow) paths for the polaron hopping are also shown. Structure and frontier orbitals of the O<sub>2</sub><sup>2-</sup> peroxide ion. [5].

The Li<sub>2</sub>O<sub>2</sub> growth mechanisms and overpotentials are investigated computationally with and without CO<sub>2</sub> at different nucleation sites such as steps, kinks and terraces on the (1-100) Li<sub>2</sub>O<sub>2</sub> surface. CO<sub>2</sub> is found to bind weakly at steps and kinks on the Li<sub>2</sub>O<sub>2</sub> surface, forming a type of lithium coordinated carbonate species (Li<sub>n</sub>CO<sub>3</sub>); effectively reducing the discharge potential. Trace amounts of CO<sub>2</sub> can also affect the morphological

growth directions of Li<sub>2</sub>O<sub>2</sub>, due to blocking of nucleation centers.

The charge/discharge processes are found to be limited by poor electronic conduction through the insulating Li<sub>2</sub>O<sub>2</sub> deposits [5] and the formation Li<sub>2</sub>CO<sub>3</sub> resulting from, e.g., CO<sub>2</sub> poisoning may worsen this problem [4]. We also present DFT+U calculations, which determine the formation and transport of hole and electron polarons in Li<sub>2</sub>O<sub>2</sub> and Li<sub>2</sub>CO<sub>3</sub>. For both materials, we find that the formation of polarons (both hole and electron) is stabilized with respect to the delocalized states for all physically relevant values of U. We find a much higher mobility for hole polarons than for the electron polarons, and we show that the poor charge transport in Li<sub>2</sub>CO<sub>3</sub> compared to Li<sub>2</sub>O<sub>2</sub>.

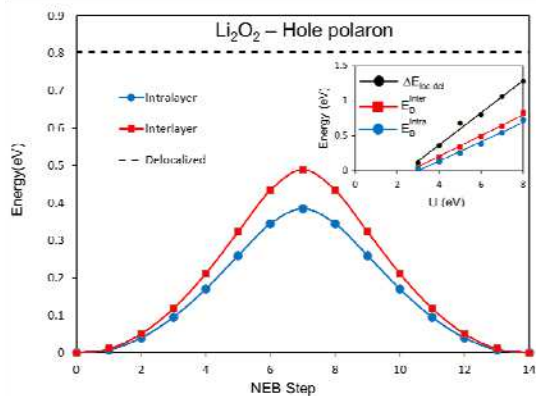


Figure 2: Calculated total energy along the intra- (blue circles) and interlayer (red squares) hopping paths in a 4x4x2 Li<sub>2</sub>O<sub>2</sub> supercell using U=6 eV for a hole polaron. Energies of the delocalized states are also shown [5].

A combination of computational and experimental results will be presented in this presentation.

#### References

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