

## A closer theoretical and experimental look at iodine in Li-air chemistry

Erlendur Jónsson<sup>ab</sup>, Rachel N. Kerber<sup>b</sup>, Tao Liu<sup>b</sup>, Gunwoo Kim<sup>b</sup> and Clare P. Grey<sup>b</sup>

<sup>a</sup> *Department of Physics, Chalmers University of Technology, 41296 Gothenburg, Sweden*

<sup>b</sup> *Department of Chemistry, University of Cambridge, Lensfield Road, CB21EW, Cambridge, United Kingdom*

E-mail: [ej311@cam.ac.uk](mailto:ej311@cam.ac.uk)

Increased scientific interest in lithium-air (Li-air) batteries has emerged from recent developments in materials science and technology. Li-air batteries are considered as “state-of-the-art” battery technology due to their theoretical energy density, which is ten times that of traditional lithium-ion.

Recent work [1] in our group showed the effect of using LiI and H<sub>2</sub>O as additives for a lithium-oxygen battery. Reversible LiOH formation and removal was shown. One intriguing question is why LiOH rather than the typical Li<sub>2</sub>O<sub>2</sub> discharge product forms under the experimental conditions. The work presented in this poster discusses the nature of the complexes formed in the wet organic electrolytes, which is critical to understanding the synergistic effect of water and LiI.

First, electrolytes with various water concentrations were investigated using molecular dynamics (MD), to reveal the corresponding Li<sup>+</sup> coordination, water clustering, etc. Density functional theory (DFT) was then used to calculate the cluster models extracted from MD simulations and to benchmark with experimental results (for example, NMR chemical shifts) obtained from various electrolytes.

Secondly, DFT was also used to calculate the standard Gibbs free energy change ( $\Delta G$ ) of relevant discharge reactions in both gas phase and as molecular complexes predicted from the MD simulations. These results reveal the local coordination environment of the Li-I pair and how water pushes dimethoxyethane out of the coordination shell, and shed light on how a four-electron oxygen reduction reaction to form LiOH is realized in an ether-based nonaqueous electrolyte via LiI.

### References:

[1] T. Liu, et al., *Science*, 350 (2015), 530-533