

Master M2 Project (February-July 2017)

What Shall We Learn From Density Functional Theory About Lithium-Air Batteries?

Experimental context. Lithium-air batteries (LABs) have attracted much attention during the last years, as promising energy storage devices with theoretical specific capacities significantly larger than those of commonly commercialized lithium-ion batteries (LIBs) with two intercalation electrodes. However, cyclability issues related to several irreversible physical and chemical phenomena prevent their wide commercialization. During the charge processes, the recent experimental studies have pointed out the co-existence of thin films and particles of lithium oxides at the cathode. Those different material phases present different charge capacities and they decompose at various electrode potential. This should originate from competitive kinetics, of which elementary mechanisms are unknown yet.

Scientific objectives & timeline. In this work, we propose to investigate elementary processes of the discharge (nucleation and growth) and charge, with an atomistic approach based on density functional theory. Two different models will be examined for describing the complex interfaces of lithium oxides and graphite support at the atomic scale: isolated clusters (for particles) and extended surfaces (for thin films). The use of VASP and CRYSTAL computational codes on massively parallel supercomputers will be essential to develop these models. Those calculations will be performed on PSMN computational resources. In a first approximation, the organic-based electrolyte and the external electric field will be neglected in the models. More precisely, the adsorption properties of a superoxide LiO_2 complex on peroxide Li_2O_2 and of a peroxide Li_2O_2 complex on graphite will be studied in gas phase condition. Concerning the models of extended surfaces of lithium oxides, a special care will be devoted to the stability of the chosen surface terminations. Regarding the models of lithium oxide clusters, size effects will have to be considered cautiously. In a second step, the solvation effects at these interfaces (modeled by DMSO) will be evaluated by a continuum model (PCM), if time allows it. The DFT results provided in the project (adsorption energetics) will be useful parameters for upper working scales in the multiscale modeling, developed at LRCS, aiming to predict the working of LABs from numerical simulations. The final goal of this project is a rational design of more efficient and optimal LABs for industrial applications.

Partnership. This project will be financed in the context of a contract promoted by La Région Hauts-de-France and the FEDER (MASTERS project headed by Pr. A. A. Franco). It will thus be developed in collaboration with A. A. Franco (Laboratoire de Réactivité et de Chimie des Solides, Université de Picardie, Jules Verne, Amiens, email: alejandro.franco@u-picardie.fr), and also with Tangui Le Bahers (Laboratoire de Chimie, ENS Lyon, email: tangui.le_bahers@ens-lyon.fr). The recruited M2 student will be settled at ENS Lyon.