DFT Contributions to the Understanding of Li-O$_2$ Battery Operation

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The Li-O$_2$ battery is a promising energy storage system that has generated much interest in the scientific community owing to its high theoretical energy density in view of the potential use in electric cars. In the last years, it has been intensively studied with the aim of finding solutions to the limitations that are preventing its practical implementation. The origin of the poor performance is mainly related to the insulating nature of the main discharge product, the lithium peroxide (Li$_2$O$_2$), which passivates the cathode during the discharge, limiting the capacity. On the other hand, it demands a high charging potential during the recharge that reduces its efficiency.

A profound knowledge of the electronic and transport properties of Li$_2$O$_2$, both in bulk and at the surface, is crucial to understanding battery operation and to propose new routes and strategies to circumvent the above mentioned difficulties.

In this talk, I will describe some of the DFT contributions on this matter.

Standard local DFT functionals induce spurious metallic states in the insulating Li$_2$O$_2$ upon lithium vacancy formation or at its non-stoichiometric surfaces. These metallic states have been interpreted as beneficial to the battery because a metallic behaviour of the Li$_2$O$_2$ surface could mitigate the electrical passivation of the cathode. I will comment on the crucial role of the intrinsic defects such as polarons and lithium vacancies in the physical properties of Li$_2$O$_2$ and I will show the importance of using the correct functionals for the exchange and correlation potential in the DFT calculations.

I will finally describe the effect of doping in the Li$_2$O$_2$ decomposition that takes place during the recharge, showing that Na-doping decreases the energy barrier of the limiting step in the electrochemical decomposition reaction, reducing the charging overpotential, in line with the experimental observations.