Ab initio modeling of electrode and electrode-electrolyte interfaces in post-Li batteries

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Energy storage technologies for current and foreseeable applications must rely on widespread and sustainable resources, with a particular attention on performances and safety issues [1]. The grand challenge is to control at the atomic level all the physico-chemical and electrochemical features at play. The objective is an effective implementation of a new paradigm of materials development based on solid scientific knowledge. To this end, first-principles modelling can provide an in-depth understanding of battery working mechanisms by offering an unbiased atomistic perspective on structure, stability and electron/ion transport. In this context, we present here our latest results on electrode systems, with a special focus on the outlined design strategies that can encourage the effective development of high-performing devices, including Li-ion, Na-ion and Li-air batteries. On the anode side, we address the capability of TiO_2 nanoelectrodes toward the reversible Na^+ uptake and storage and dissect the origin of Na^+ insertion activity at anatase nanocrystal facets [2-4]. Structural interfacial features are also shown to be key in determining migration efficiency in MoS_2/Graphene heterostructure [5]. DFT-based investigations on high-energy cathodes allows to unveil key features in their electrochemical behavior, such as the role of antisite defects in the capacity loss of $LiTMPO_4$ (TM = Co, Fe, Mn) [6] and the anionic redox activity in P2-type $Na_xNi_{0.25}Mn_{0.68}O_2$ layered oxide [7]. We also show the need of more accurate theoretical tools (within post-HF methods) for the detailed description of chemical processes involving highly correlated systems, such as the reversible formation of Li_2O_2 and the singlet O_2 release occurring along the Li-air battery functioning. All these results provide a new perspective on how materials design can be driven by theoretical tools, overcoming old trial-and-error approaches, and it is now essential to speed up the large-scale exploitation of advanced technology beyond lithium.

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