Accurate electronic properties and intercalation voltages of olivine-type Li-ion cathode materials from extended Hubbard functionals

Iurii Timrov[1], Francesco Aquilante[1], Matteo Cococcioni[2], Nicola Marzari[1]

[1]Theory and Simulation of Materials (THEOS), and National Centre for Computational Design and Discovery of Novel Materials (MARVEL), Ecole Polytechnique Federale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland
[2]Department of Physics, University of Pavia, via Bassi 6, I-27100 Pavia, Italy

The design of novel cathode materials for Li-ion batteries requires accurate first-principles predictions of their properties. Density-functional theory (DFT) with standard (semi-)local functionals fails due to the strong self-interaction errors of partially filled d shells of transition-metal (TM) elements. Here, we show for phospho-olivine cathodes that DFT with extended Hubbard functionals correctly predicts the "digital" change in oxidation states of the TM ions for the mixed-valence phases occurring at intermediate Li concentrations, leading to voltages in remarkable agreement with experiments [1]. This is achieved thanks to the use of onsite and intersite Hubbard parameters computed from density-functional perturbation theory with Lowdin-orthogonalized atomic orbitals [2]. We thus show that the inclusion of intersite Hubbard interactions is essential for the accurate prediction of thermodynamic quantities when electronic localization occurs in the presence of inter-atomic orbital hybridization.

[1] I. Timrov et al., PRX Energy **1**, 033003 (2022).
[2] I. Timrov et al., PRB **103**, 045141 (2021).