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Hybrid Density Functional Calculations of Redox Potentials of Transition Metal Compounds RICKARD ARMIENTO, VINCENT CHEVRIER, SHYUE PING ONG, GERBRAND CEDER, Massachusetts Institute of Technology — Prior works have shown that density functional theory (DFT) with the DFT+U method resolves the underestimation of redox potentials calculated by conventional functionals for a number of transition metal compounds relevant for battery applications, including the olivine Li_xMPO_4 (M = Fe, Mn, Co, Ni), layered Li_xMO_2 (M = Co, Ni) and spinel-like $Li_xMn_2O_4$. We show that the redox potentials of these compounds are also well reproduced by the hybrid density functional by Heyd-Scuseria-Ernzerhof (HSE06). Hybrid functionals combine a conventional DFT functional with a part of Hartree-Fock (HF) exchange. While the HF part increases the computational expense by at least one order of magnitude, it provides, in contrast to DFT+U, a correction for the self-interaction error that does not rely on special treatment of the occupancies of the orbital states of ions or species-specific parameters. We compare the accuracy of regular DFT, DFT+U and HSE06 for the redox potentials, lattice constants, and other properties. Examples of electron delocalization problems connected to the self-interaction error in the systems are discussed, and shown to be resolved both by the hybrid functional and DFT+U methods. Comments are made on the possibility to approach the delocalization problem with a semi-local functional.

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