Abstract Submitted
for the MAR17 Meeting of
The American Physical Society

Understanding Birnessite MnO_2: Effects of Small Polaron and Local Dipole[1] HAOWEI PENG, JOHN P. PERDEW, Department of Physics, Temple University — Birnessite MnO_2, usually with cations like K and Na intercalated between layers, is a class of potential cheap oxygen evolution reaction (OER) catalyst. Using hybrid density functional calculations, we investigate the electronic structures of the layered MnO_2 with the intercalated cation modelled as a defect. We found that an electron small polaron will form when an extra electron is doped in the pure MnO_2, turning a Mn(IV) to a Mn(III) with a singly occupied e_g orbital located within the band gap, and the resulting small-polaron hopping conduction explains the observed low electric conductivity. The inter-layer doped K atom will donate one electron to one Mn ion as expected, and also contributes to a local dipole forming between K and the Mn(III), raising the electrostatic potential of the specific layer. With a certain spatial distribution of such local dipoles, the small-polaron e_g states become comparable in energy with the global conduction band minimum, and charge transfer occurs. This further results in a singly or partially occupied e_g orbital near the Fermi level, which has been regarded as a signal for an excellent OER catalyst. Our calculation helps understanding several experimental observations.

[1]This work was supported as part of the CCDM-EFRC funded by the U.S. DOE, Office of Science, Basic Energy Sciences.

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Date submitted: 11 Nov 2016 Electronic form version 1.4