Atomistic simulation of post lithium ion batteries

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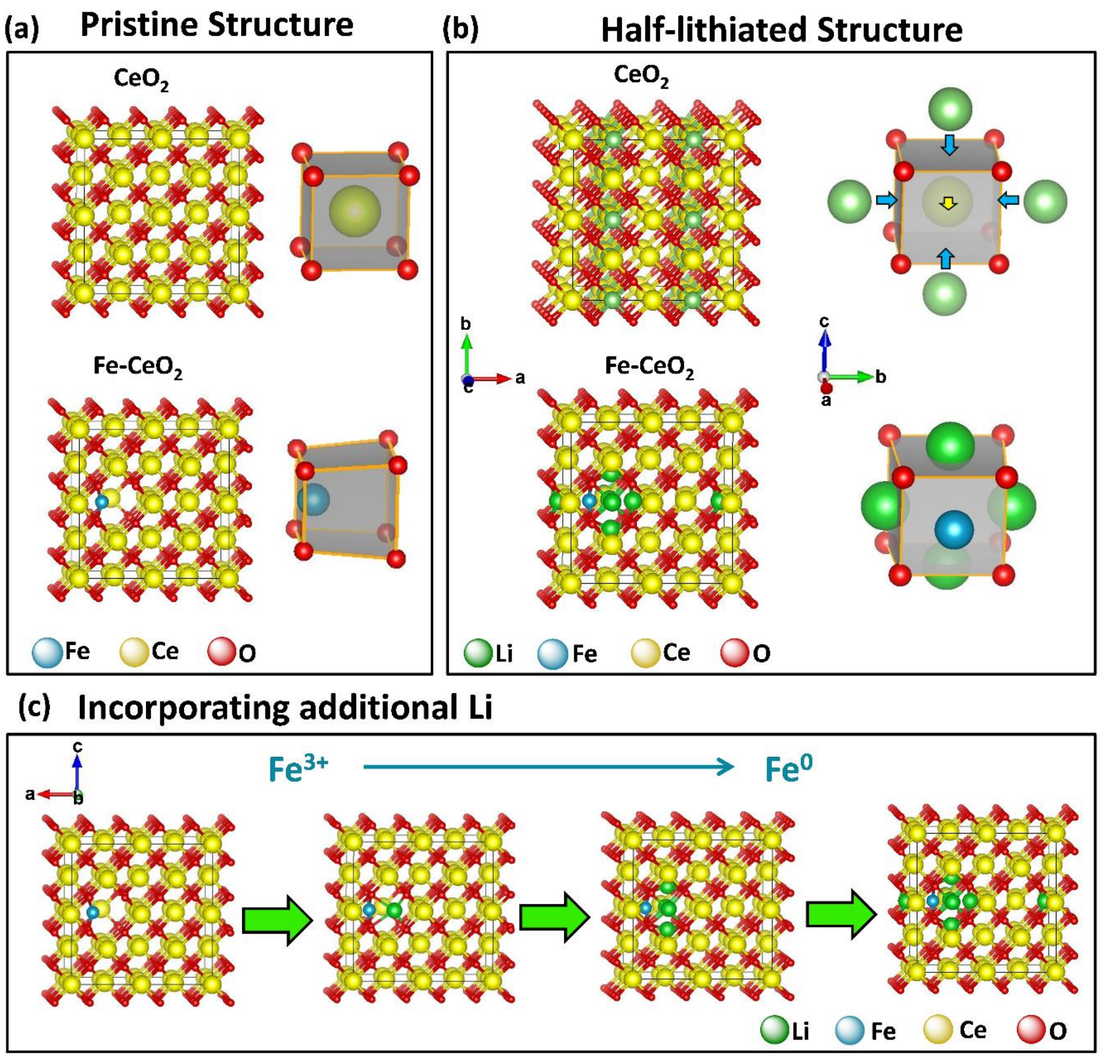
Introduction

Alternative electrode materials with high storage capacity are of utmost importance for next-generation lithium and post-lithium ion batteries. Here, the computational investigation of two electrode materials is presented. Fe-doped CeO_2 shows an unexpected reduction of the iron dopant to the metallic state, which is at the origin of a significant capacity increase for Li (and post-Li) storage at low potential, thus making it a promising anode material. δ-V_2O_5 on the other hand has been investigated as cathode material for aqueous Zn-ion batteries. Experimentally observed changes in the pH value of the aqueous solution could be shown to be a consequence of a H^+/Zn^{2+} exchange mechanism.

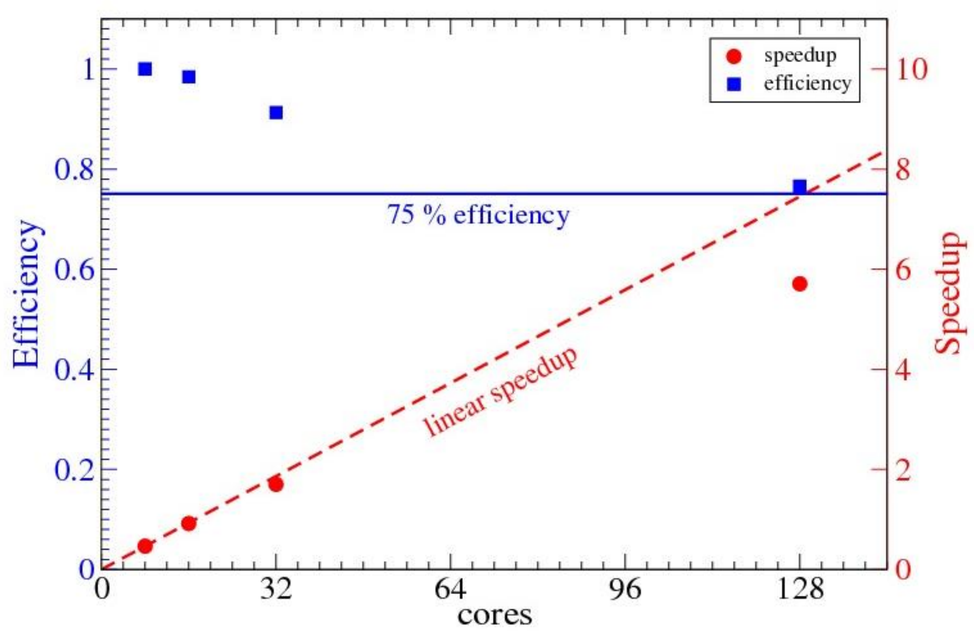
Fe-doped CeO_2 as new insertion-type electrode

Fe-doped CeO_2 as new insertion-type electrode for lithium and post-lithium ion batteries



- Fe-doping results in the off-centering of the dopant
- This creates additional space for intercalation
- Li intercalation results in a predominant reduction of Fe from Fe^{3+} to metallic Fe^0
- Confirms XRD and XANES results

Code Performance (VASP)



H^+/Zn^{2+}exchange mechanism in δ-V_2O_5

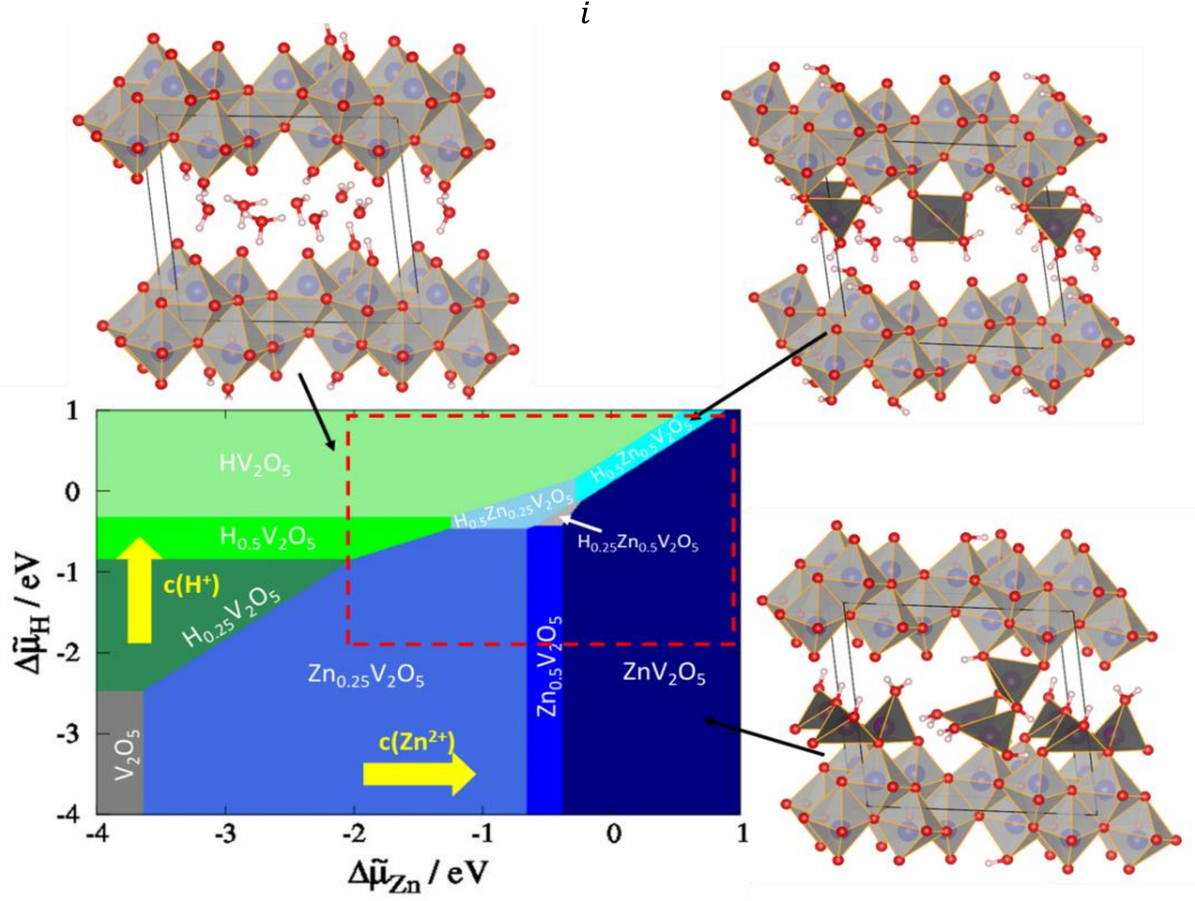
Computational hydrogen electrode (CHE)

The CHE allows for a grand canonical treatment without additional computational cost:

$$\tilde{\mu}_{H^+}(aq) + \tilde{\mu}_{e^-} = \frac{1}{2}\mu_{H_2}(g) - eU_{SHE} - k_B T ln(10) pH$$

$$\Delta\tilde{\mu}_H = \tilde{\mu}_{H^+}(aq) + \tilde{\mu}_{e^-} - \frac{1}{2}E_{H_2} = -eU_{SHE} - k_B T ln(10) pH$$

$$\Delta G = \Delta E_f - \sum_i n_i \Delta\tilde{\mu}_i\,(T, c_i, U)$$



- The resulting phase diagram indicates the possibility of a H^+/Zn^2 exchange mechanism
- Perfect agreement with experimentally observed changes in the pH value under electrochemical cycling

Computational Setup

- Density functional theory (DFT)
- Periodic plane wave code (VASP)
- PBE exchange correlation functional
- PAW method for electron-core interaction
- typically 50 to 100 atoms
- 20 to 40 cores

HIU – Joint research institute of KIT and Ulm University with associated partners DLR and ZSW
KIT – University of the State of Baden-Wuerttemberg and National Research Center of the Helmholtz Association