First principles analyses on the sodium iron pyrosilicate $Na_2Fe_2Si_2O_7$

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Sodium ion batteries attract much attention for large scale applications due to the abundance and low cost of sodium. As a cathode material, sodium iron silicate is ideal because all the constituent elements are naturally abundant. Recently, $Na_2Fe_2Si_2O_7$ has been successfully synthesized with the theoretical capacity 164.5 mAh/g, but very limited reversible capacity is observed at present [1]. Toward practical utilization, we apply density functional theory calculation to elucidate the intrinsic bulk properties of the $Na_2Fe_2Si_2O_7$ electrode.

All calculations were performed with the VASP code [2] using the PAW method and the GGA/PBE functional. To reduce the self-interaction error of GGA, a Hubbard U parameter (4.2 eV) on Fe site was used within the GGA+U framework. The carrier transport properties were calculated in the fully sodiated limit with a supercell (1×1×2). The activation energy of the Na vacancy migration and the polaron hopping were calculated by the CI-NEB method and by linearly interpolating initial and final configurations, respectively.

Assuming the following electrode reaction

$$Na_2Fe_2Si_2O_7 \rightleftarrows Fe_2Si_2O_7 + 2Na^+ + 2e^-,$$

we calculated an average voltage of 2.56 V in good agreement with the experimental result (2.7 V). The volume change is found to be 1.9% which shoud be small enough for smooth (de)sodiation. The localized 3*d* electron forms valence band maximum and conduction band minimum. Thus, Fe is the main redox center during the charge discharge process. Because of the large band gap (3.7 eV) and localized character of the Fe *d* electron, electronic conduction mainly arises from polaron hopping. The activation energies of the Na vacancy migration (0.56 eV) and the polaron hopping (0.29 eV) does not hinder electrode reaction at room temperature.

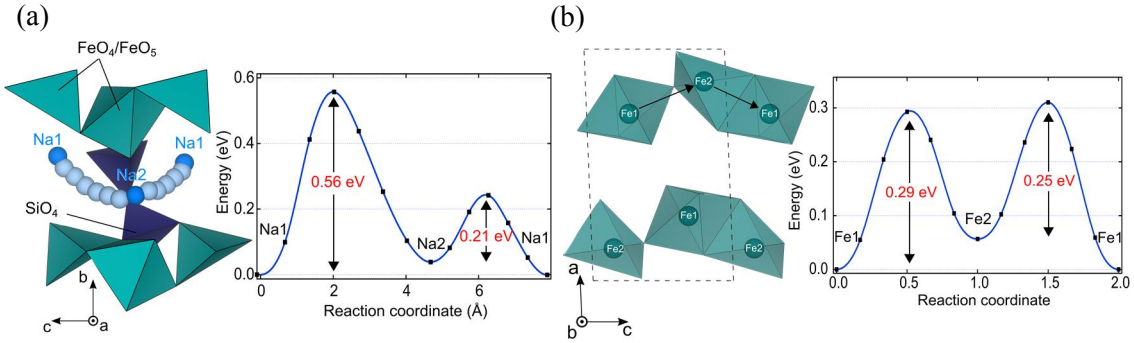

Fig. 1. (a) Atomic configuration during Na-vacancy migration and corresponding energy profiles. (b) Local geometry and energy barrier for polaron hopping.

References:

[1] A. Panigrahi, S. Nishimura, T. Shimada, E. Watanabe, W. Zhao, G. Oyama, A. Yamada, Chem. Mater. 29, 4361 (2017)

[2] G. Kresse and J. Furthmüller, Phys. Rev. B: Condens. Matter Mater. Phys. 54, 11169 (1996)