Supporting Information

Mechanistic study of Na-ion diffusion and small polaron formation in Kröhnkite $Na_2Fe(SO_4)_2{\cdot}2H_2O$ based cathode materials

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The effect of Hubbard U parameters

In this work, PBE+*U* exchange correlation functional is mainly employed as it can handle the self-interaction error of *d* orbitals and it requires reasonable computing cost compared to HSE06. It is crucial that the Hubbard *U* parameter is carefully chosen. Thus, we optimize the primitive structure with different U parameters from 3.5 to 6.5 eV, and then compare the resulting band gap (E_g) and Fe magnetic moment (μ_{Fe}) with those calculated with HSE06. Based on the consistency of E_g, the $U = 4.7$ eV is determined to give the similar value of E_g as shown in Fig.S1. Also, the density of states (DOS) calculated with this *U* value and with HSE06 are well corresponding as displayed in Fig.S2. Moreover, the DOS calculated with PBE clearly indicates that PBE cannot capture an electronic structure of this material.

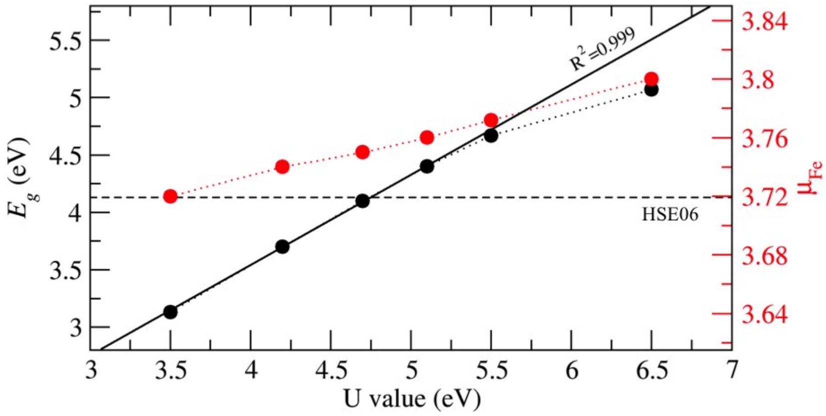

Fig. S1 The effect of Hubbard *U* parameter toward electronic band gap of $Na_2Fe(SO_4)_2{\cdot}2H_2O$. Dashed-lines refer to those parameters calculated with HSE06.

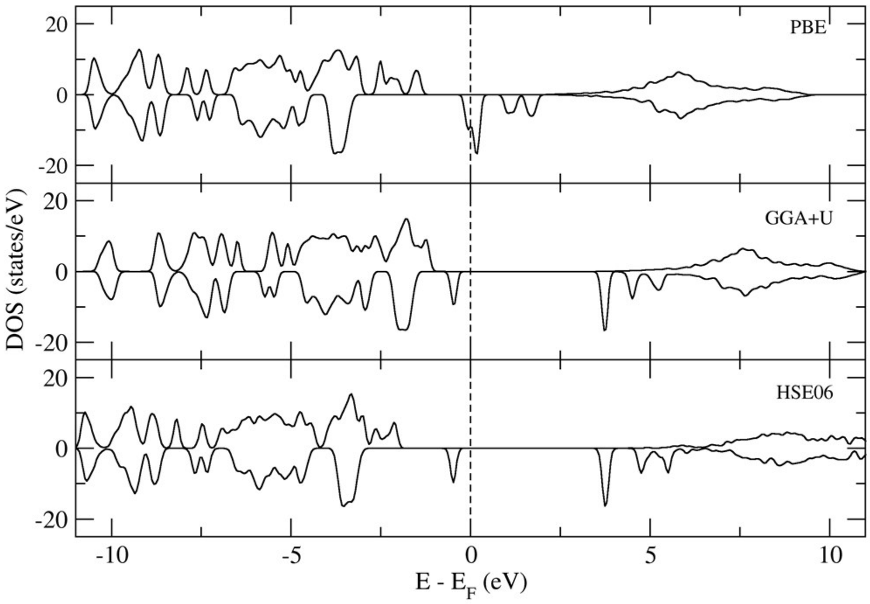

Fig. S2 Total-DOS of fully-sodiated structure calculated with PBE, PBE+*U*, and HSE06 exchange correlation functionals. The energies are referenced with the Fermi level (E_F).

The second sodium de-intercalation

After first sodium de-intercalation is completed, we found that the redox potential will occur via the oxidation transition of oxygen, whereas there is no significant change on H^+ ions. The DOS of fully-desodiated structure is displayed in Fig.S3. All PDOS are corresponding to those obtained for half-desodiated structure, except O-DOS. Thus, it implies the possibility of the evolution of oxygen in second sodium de-intercalation.

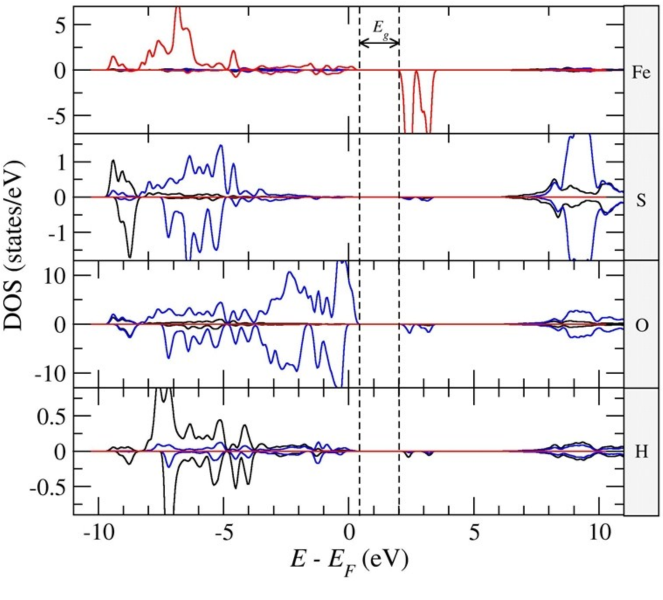

Fig. S3 The density of states of fully-desodiated $Fe(SO_4)_2 \cdot 2H_2O$. Black, blue, and red denote the electron distribution associated with *s*-, *p*-, and *d*-orbitals.

The effect of D2 correction on energy

The influence of vdW correction (D2) is presented in the view of energy variation and interlayer spacing as illustrated in Fig.S4. We find that there is a binding between each pseudolayer (27.8 meV/atom) for the calculations with and without D2 correction. Using the correction leads to an increase in the binding energy ~22.4 meV/atom (higher than that in non-vdW case) and a shorter equilibrium interlayer spacing. Thus, the stronger layered-binding is relevant to the higher intercalation voltage when PBE+*U*+D2 is employed.

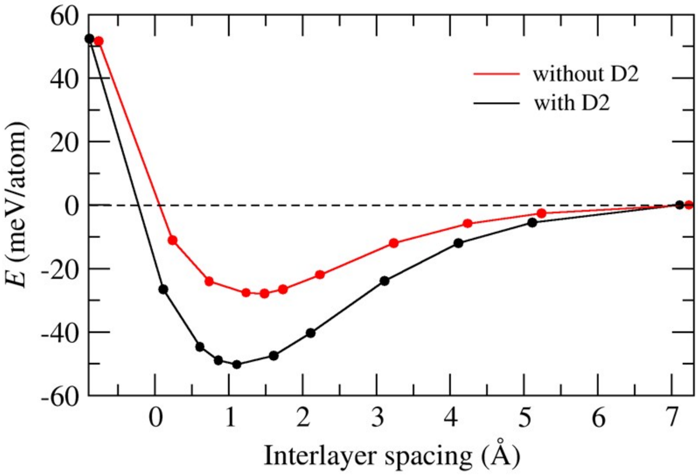

Fig. S4 Energy profile of $Na_2Fe(SO_4)_2 \cdot 2H_2O$ as a function of interlayer spacing calculated using PBE+*U* with and without D2 correction. The given energy is referenced with infinite separation (E=0eV).