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Hydrogen-Bonding-Mediated Structural Stability and Electrochemical Performance in Iron Fluoride Cathode Materials

Zuosheng Li, Beizhou Wang, Chilin Li, Jianjun Liu*, Wenqing Zhang

Numerous lithium ions battery cathode materials containing trace amounts of water accommodated in Li⁺ transportation tunnels have been experimentally synthesized. However, the impact of water on structural stability and electrochemical performance of cathode materials is still unclear so far. Here, the first-principles calculations combining thermodynamics analysis for Li₄FeF₆•0.33H₂O were performed to unravel interaction mechanism among framework FeF₃, H₂O, and Li⁺. The FeF₃ framework structure distortion is mitigated by hydrogen bonding between isolated H₂O and F⁻ ions, bringing opposite effects in stability of hydrogen bonding and instability of structural distortion. The hydrogen bonding strength of F⁻–H₂O can further be mediated by the Li⁺-inserted amount, which indirectly results in a wide discharge voltage window from 2.2 to 3.6V. Li⁺ transportation barrier in cooperative mode is also tuned by the flexible hydrogen bonding strength due to different occupied positions. Liₓ(FeF₃)•0.33H₂O is determined as the most stable species and more Li⁺ insertion directly leads to the conversion reaction FeF₆³⁻ → FeF₆²⁺ + 2F⁻. Therefore, to stabilize Fe−F bonds and reduce octahedral chain distortion play an important role in improving their electrochemical performance of FeF₃ cathode materials with water.

1 Introduction

Rechargeable lithium-ion batteries (LIBs) have attracted tremendous attention due to their vast potential market for electric vehicles and portal electronic devices. Improving electrochemical performance of cathode materials by optimizing microstructure and tailoring composition, though very challenging, plays an important role in realizing LIB practical application with satisfactory power and energy densities as well as low cost. Compared with layered intercalation compounds only transferring one electron at most per formula during discharge-charge cycle, transition metal fluorides based on conversion reaction in which multiple electrons can be transferred, offer a tremendous advantages in energy and power densities. Among all M₂Fe₃ compounds, iron trifluoride (FeF₃) is the most promising cathode material because of its superior intrinsic characteristics such as high theoretical specific capacity (712 mAh g⁻¹ in the potential interval 1.5-4.5 V vs. Li⁺/Li⁻), low toxicity and cost, and good thermal stability. However, its practical application as LIB cathodes material has been severely prevented by its low electronic conductivity and sluggish kinetics closely associated with the high ionicity of Fe−F bonds.

Besides FeF₃-carbon nanocomposition, structural expansion, fabricating open framework FeF₃ is considered as a possible strategy to increase ionic conductivities. Li et al. firstly synthesized FeF₃ with trace amounts of water (FeF₃•0.33H₂O and FeF₃•0.5H₂O), which was demonstrated to have an improved electrochemical performances such as a larger reversible capacity and good cycle performance in voltage range 1.7–4.5 V. Such an open framework materials also provide new opportunities for Na and Mg batteries. Although the expanded structure possesses a significant potential to increase Li⁺ storage capacity and to enhance Li⁺ transport kinetics as compared with the poorly conductive ReO³-type FeF₃, most electrochemical studies only concentrate on 1e⁻ transfer with no conversion reaction involved. The excessive discharge after 1e⁻ transfer will result in occurrence of amorphous structure from ordered framework structure. Very importantly, a wide discharge voltage window (1.6-3.4V) was presented in FeF₃•0.33H₂O and FeF₃•0.5H₂O. A trace amount of water accommodated in cathode materials has been reported in many publications. However, an impact of water on electrochemical performance has not been studied so far. It is of significant importance to reveal open framework structure stability mechanism and understand electrochemical role of water.

Li et al synthesized FeF₃•0.33H₂O with a unique one-dimensional tunnel by using the low-temperature ionic-liquid-based synthesis method. Its discharge capacity is measured as 153 mAh g⁻¹ at the sixth cycle and decreased to 130 mAh g⁻¹ after 30 cycles at a current density of 14 mA g⁻¹. The further nanocomposition materials such as FeF₃•0.33H₂O/SWNT, FeF₃•0.33H₂O/MoS₂, and FeF₃•0.33H₂O/V₂O₅ exhibited an improved rate capacity and cycle performances. However, these studies did not provide enough information on underlying mechanism in structural stability and electrochemical effect induced by water. To the best of my knowledge, no theoretical study on FeF₃•0.33H₂O is reported so far.

In this work, the first-principles calculations combining thermodynamic analysis were performed to reveal the role of water...
in tuning structural stability and electrochemical performance of \( \text{FeF}_3 \cdot 0.33\text{H}_2\text{O} \). Our calculations indicate that hydrogen bonding between \( \text{H}_2\text{O} \) and \( F^- \) can be mediated by occupied positions and amount of \( \text{Li}^+ \) ions, which directly affects discharge voltage and \( \text{Li}^+ \) transport behaviour of \( \text{Li}_x\text{FeF}_3 \cdot 0.33\text{H}_2\text{O} \). We predict that stabilizing \( \text{Fe} \rightarrow \text{F} \) bonds and reducing octahedral chain distortion play an important role in improving electrochemical performance of \( \text{FeF}_3 \cdot 0.33\text{H}_2\text{O} \).

2 Computational Methods

The first-principles calculations were conducted within the formalism of spin-polarization density functional theory (DFT) and the generalized gradient approximation (GGA) of the exchange-correlation function as formulated by Perdew, Burke, and Ernzerhof.\(^24\) The valence electron-ion interaction was treated by the projector augmented wave (PAW) potential\(^25\) in the Vienna Ab initio Simulation Package (VASP).\(^26,27\) To take into account the strong correlated character of the d-electrons of \( \text{Fe} \), a Hubbard-like correction \( \text{GGA} + U \) is used. Within the \( \text{GGA} + U \) approach, only the difference between \( U \) and \( J (U_{\text{eff}}=U-J) \) is meaningful. An effective interaction parameter \( U_{\text{eff}}=5 \text{ eV} \) was used in our calculations, which is consistent with the previous publications.\(^29,30\)

The van der Waals-augmented density functional theory (vdW-DFT) was used to modify exchange and correlation energies.\(^31\) The functional \( \text{optB88-vdW} \) was chosen to accurately describe the behaviour of water.\(^32\) Klimes et al. demonstrated that the \( \text{optB88-vdW} \) could obtain more accurate vdW weak interaction energies in a variety of dispersion and hydrogen bonding systems than other exchange functionals such as \( \text{optPBE-vdW} \) and \( \text{optB86-vdW} \).\(^33\) The wave functions were expanded in plane-wave basis set up to a kinetic energy cutoff of 400 eV. Brillouin-zone integrations were performed by using the \( k \)-point sampling of the Monkhorst-Pack scheme\(^34\) with a \( 3 \times 3 \times 3 \) grid. The convergence of total energy with respect to the kinetic energy cutoff and the \( k \)-point sampling has been carefully examined. Minimization of the total energy was realized with a full relaxation of the atomic positions and cell parameters for each structure. According the results of experiments,\(^35\) the iron fluoride system in this work displayed strictly noncollinear antiferromagnetic (AFM) ground states along \( c \) axis below the \( \text{Néel} \) temperature (TN) 129 K with the magnetic moments \( \mu = 4.07 \mu_B \).\(^36,37\) The migration mechanisms were calculated by using the climbing image-nudged elastic band (CI-NEB),\(^38\) which is a reliable approach to search the minimum-energy path (MEP). The electrical conductivity is calculated by means of the Kubo-Greenwood approach,\(^39\) which is a very general formulation for the conductivity.\(^40\) In this approach, the electrical conductivity \( \sigma \) can be obtained by extrapolating to zero frequency:

\[
\sigma = \sigma(0) = \lim_{\omega \to 0} \sigma(\omega)
\]

with \( \sigma(\omega) \) computed as a configurational average of

\[
\sigma(\omega, \mathbf{R}_i) = \frac{2ne^2}{3m^2\omega^2} \sum_{\mathbf{R}_i} \langle f_i - f_i \rangle \left| \langle \psi_i | p | \psi_i \rangle \right|^2 \delta(E_i - E_i - \hbar \omega)
\]

where \( e \) and \( m \) are the electronic charge and mass, \( \mathbf{p} \) is the momentum operator and \( \psi_i, E_i \) are the electronic DFT eigenstates and eigenvalues, calculated for the ionic configuration \( \mathbf{R}_i \), at a single \( k \)-point of the Brillouin Zone.

3 Results and Discussion

3.1 Open Framework Structure Stability of \( \text{FeF}_3 \cdot 0.33\text{H}_2\text{O} \)

Several experimental studies\(^36-37,41,42\) have determined that \( \text{FeF}_3 \cdot 0.33\text{H}_2\text{O} \) is in a HTB (Hexagonal Tungsten Bronze) structure with space group \( \text{Cmcm} \) (space group \( \text{137} \)) and six \( \text{FeF}_3 \) perovskites are connected via corner-sharing to form a huge hexagonal cavity. The local structures of water interacting with open framework structure are difficult to be experimentally determined due to mobility of \( \text{H} \) atoms. This is directly related to the interaction between water molecules and the hexagonal cavity, even to the insertion sites and migration path of lithium ions.

![Fig. 1 The side and top views of relaxed FeF$_3$•0.33H$_2$O structures due to different orientation of water molecules. Fe, F, O and H atoms are presented by earthy yellow, blue gray, red, and light brown balls, respectively; the relaxed cell volumes (Å$^3$) and relative energy (eV) also are listed here.](image)

All optimized structures and relative energies of \( \text{FeF}_3 \cdot 0.33\text{H}_2\text{O} \) are shown in Fig. 1. According to relative positions of hydrogen atoms, three possible local structures of water interacting with cavity \( \text{FeF}_3 \) are considered. First of all, the hydrogen atoms of two water molecules are toward opposite directions in a unit cell. Two relaxed structures in which water molecules are in (001) and (100) planes were displayed in Fig. 1 C1 and C2, respectively. They have orthorhombic symmetry with the space group of \( \text{Cmcm} \). Herein, two relaxed structures are labelled as C1 and C2 according to their corresponding space group symmetry (the first letter) combined with the order of stability, which is also applied in the other relaxed structures (A3 and P4). In these structures, hydrogen atoms occupy 8g site in C1 and 8f site in C2. Secondly, four hydrogen atoms of two water molecules point one direction along b axis, as shown in Fig. 1 A3. The relaxed structure displays an orthorhombic symmetry with the space group of \( \text{Amm2} \). Hydrogen atoms in this structure are all in (001) plane and occupy 4d and 4e positions. Thirdly, two waters in tunnel approach each other to form a cluster structure due to strong hydrogen bonding, as shown in Fig. 1 P4. The relaxed P4 structure has a low symmetry with the space group \( \text{P1} \). As shown in Fig. 1, the orthorhombic structure C1 was found to have the lowest energy and smallest cell volume in all four relaxed structures. Our calculated structure symmetry and cell volume are qualitatively consistent with experimental measurement.\(^13\) Therefore, the C1 structure is considered in the following electrochemical calculations.
Table 1 The relaxed lattice parameter (Å), unit cells volume (Å³), the experiment data, diameter of hole (van der Waals radius of fluoride atom used 1.40 Å), and hydrogen bonding energy of each water of FeF₃, FeF₃•0.16H₂O, FeF₃•0.33H₂O, and FeF₃•0.66H₂O.

<table>
<thead>
<tr>
<th></th>
<th>FeF₃(SO)</th>
<th>FeF₃•0.16H₂O</th>
<th>FeF₃•0.33H₂O(Exp.)</th>
<th>FeF₃•0.66H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>a(Å)</td>
<td>7.15</td>
<td>7.16</td>
<td>7.43(7.42/7.42)</td>
<td>7.28</td>
</tr>
<tr>
<td>b(Å)</td>
<td>12.04</td>
<td>12.17</td>
<td>12.83(12.82/12.73)</td>
<td>12.59</td>
</tr>
<tr>
<td>c(Å)</td>
<td>7.11</td>
<td>7.16</td>
<td>7.59(7.46/7.53)</td>
<td>7.53</td>
</tr>
<tr>
<td>V(Å³)</td>
<td>612.5</td>
<td>623.5</td>
<td>723.5(709.3/711.2)</td>
<td>690.6</td>
</tr>
<tr>
<td>Diameter(Å)</td>
<td>5.02/5.25</td>
<td>5.08/5.32</td>
<td>5.15/5.55(5.23)</td>
<td>5.16/5.47</td>
</tr>
<tr>
<td>Fe-F chain 1</td>
<td>1.92/1.90/1.90</td>
<td>1.91/1.90/1.88</td>
<td>1.94/1.93/1.92</td>
<td>2.03/1.99/1.92</td>
</tr>
<tr>
<td>Fe-F chain 2</td>
<td>1.92/1.90/1.90</td>
<td>1.91/1.90/1.89</td>
<td>1.93/1.93/1.93</td>
<td>1.96/1.92/1.89</td>
</tr>
<tr>
<td>E_H₂O/H₂O(eV)</td>
<td>--</td>
<td>-0.37</td>
<td>-0.46</td>
<td>-1.23</td>
</tr>
</tbody>
</table>

According to our calculations, introducing waters in lattice not only leads to torsion angle reduced, but also forms hydrogen bonding between H₂O and FeF₃. Therefore, the FeF₃•nH₂O (n=0, 0.16, 0.33 and 0.66) with different water content were calculated to reveal the relationship between stability and water content. The optimized lattice parameters and unit volumes of different water content were presented in Table 1. Our calculated lattice parameters and volumes are in good agreement with experimental measurement. Based on van der Waals radius of F atom, the diameters of two holes in FeF₃•0.33H₂O were estimated as 5.15 and 5.55 Å, which are also consistent with experimental value (5.23 Å). An obvious feature with increasing water content in lattice is volume expansion by FeF₃ hexagonal torsion. As shown in Fig. 2, water insertion into the framework structure mitigates the torsion of the FeF₃ chain, which is probably originated from Jahn-Teller effect. As shown in Fig. 2(a), the reduced torsion directly leads to instability of framework structure. Particularly, the Fe−F bond in FeF₃•0.33H₂O are elongated as comparison with those of FeF₃•0.16H₂O and FeF₃. On the contrary, insertion of water also enhances stability of FeF₃•nH₂O due to hydrogen bonding energies between water and F. Therefore, there exists two opposite effects in FeF₃•nH₂O due to hydrogen bonding.

It is interesting to elucidate how much hydrous water can be accommodated in one-dimension cavity in FeF₃. Based on the frame structure of FeF₃•0.33H₂O, the possible FeF₃•nH₂O (n=0.0, 0.16, 0.33, and 0.66) structures with the different water content were calculated. The relative formation energy ΔEᵣ is defined to describe the strength of hydrogen bonding according to the following equations:

\[ ΔEᵣ = E_{FeF₃•nH₂O}^f - E_{FeF₃}^f \]  

\[ E_{FeF₃•nH₂O}^f = E_{FeF₃•nH₂O}^{tot} - E_{Fe} - 3E_F - nE_{H₂O} \]  

\[ E_{FeF₃}^f = E_{FeF₃}^{tot} - E_{Fe} - 3E_F \]

where \( E_{FeF₃•nH₂O}^f \) is formation energy for per FeF₃•nH₂O formula unit, \( E_{FeF₃•nH₂O}^{tot} \) is the energy of per FeF₃•nH₂O formula unit, \( E_{H₂O} \) is the energy of one water molecule, \( E_{FeF₃}^{tot} \) is the formation energy of per FeF₃ unit and \( E_{FeF₃}^f \) is the energy of per FeF₃ formula unit.
while \( \Delta E \) represent stability change of per FeF\(_3\) unit after hydrous water insertion. The calculated formation energies, hydrogen bonding energies, and relative energies with water content change were displayed in Fig. 2 (a). In comparison, FeF\(_3\)•0.16H\(_2\)O and FeF\(_3\)•0.33H\(_2\)O are found to have lower formation energy than FeF\(_3\) and FeF\(_3\)•0.66H\(_2\)O, indicating FeF\(_3\)•0.16H\(_2\)O and FeF\(_3\)•0.33H\(_2\)O is very likely to be experimentally observed.

Fig. 3 The band structure and density of states (total and partial DOS, TOTDOS and PDOS) of FeF\(_3\), FeF\(_3\)•0.33H\(_2\)O, FeF\(_3\)•0.66H\(_2\)O, Li\(_{0.67}\)FeF\(_3\)•0.33H\(_2\)O and Li\(_{0.67}\)FeF\(_3\)•0.66H\(_2\)O. All energies are relative to the Fermi energies respectively (red dot line).

3.2 Electronic and Magnetic Properties of FeF\(_3\)•0.33H\(_2\)O

Both electronic structure properties of FeF\(_3\) and FeF\(_3\)•0.33H\(_2\)O have been calculated by GGA+U method for comparison. Their band structures and the corresponding density of states (DOS) are shown in Fig. 3. Iron fluoride is a standard ionic crystal with a large band gap width. By using PBE functional, the band gap of FeF\(_3\) with open framework structure is calculated as 4.01 eV which is slightly smaller than that of bulk FeF\(_3\) (4.3 eV). The electronic structure change induced by microscopic structure change may lead to a significant improvement on electrochemical properties. The band gap of FeF\(_3\)•0.33H\(_2\)O can be further reduced to 0.95 eV because of the introduction of intermediate band. The electron transition from valence band to intermediate band is easier than to conduction band. This situation is similar to solar cell in which the intermediate band is designed to favour electron transition. In this framework, the intermediate band could improve conductivity in an electrochemical condition.

With the water concentration increased, the band gap of FeF\(_3\)•nH\(_2\)O becomes smaller, changing from 0.95 eV in FeF\(_3\)•0.33H\(_2\)O to 0.39 eV in FeF\(_3\)•0.66H\(_2\)O. When Li ions are inserted in the hole, the band gaps of Li\(_{0.67}\)FeF\(_3\)•0.33H\(_2\)O and Li\(_{0.67}\)FeF\(_3\)•0.66H\(_2\)O are increased to 1.53 eV and 1.04 eV, respectively. Based on the Kubo-Greenwood formula, the electric conductivities of FeF\(_3\)•0.33H\(_2\)O (7.0×10\(^{-8}\) S cm\(^{-1}\)), Li\(_{0.67}\)FeF\(_3\)•0.33H\(_2\)O (1.0×10\(^{-9}\) S cm\(^{-1}\)), FeF\(_3\)•0.66H\(_2\)O (2.8×10\(^{-7}\) S cm\(^{-1}\)) and Li\(_{0.67}\)FeF\(_3\)•0.66H\(_2\)O (7.0×10\(^{-8}\) S cm\(^{-1}\)) were calculated to evaluate the electron transport property as cathode materials. Our calculated value for FeF\(_3\)•0.33H\(_2\)O is in excellent agreement with the experimental result (1.4×10\(^{-8}\) S cm\(^{-1}\)) measured by Li et al. In general, the order of electronic conductivity is accordance with the band gap. Because the band gap is increased with Li\(^+\) insertion, the electric conductivity of Li\(_{0.67}\)FeF\(_3\)•0.33H\(_2\)O is significantly reduced, which is a possible reason for relatively high overpotential (0.4-0.5 V) in experiment. As a result, tailoring band gap of Li\(_{0.67}\)FeF\(_3\)•0.33H\(_2\)O plays an important role in reducing charging voltage.

FeF\(_3\) crystal with HTB (Hexagonal Tungsten Bronze) structure undergoes long-range ordering to a noncollinear antiferromagnetic G-type structure, which has been observed experimentally. The predicted total magnetic moments of Fe in FeF\(_3\)•0.33H\(_2\)O is about 4.48 \(\mu\)B which agrees reasonably well with experimental data 4.07 \(\mu\)B. The spin direction of three magnetic sublattices is at 120° one from each other in 001 plane.

3.3 Li\(^+\) Insertion into FeF\(_3\)•0.33H\(_2\)O

As mentioned above, the crystal structure of FeF\(_3\)•0.33H\(_2\)O belongs to space group Cmcm with orthorhombic symmetric structure. The wall of hexagonal cavity consists of fluoride atoms while the water molecules are alternately arranged in opposite directions. Except water and FeF\(_3\) octahedral, the symmetrically distinct sites for Li ions insertion are only possible at Wyckoff position as 4a, 4c, 8f, 8d, 4c and 8e sites are all in the perpendicularly bisecting plane. 4c is on the side of oxygen atom, while 8e is on the side of hydrogen atoms. 4a is at the middle point of every two adjacent oxygen atoms. 8f is at the middle point between 4a and 4c.
molecule are in the same plane and 8g is contrary to the hydrogen atom position, relative to the oxygen atom.

The site preference for inserted Li+ was investigated in a dilute approximation by calculating energy change of inserting a single Li+ in the possible distinct binding sites. The formation energies in which FeF3$\cdot$0.33H2O was used as a reference state were calculated and displayed in Fig. 4 (a). According to formation energy of Li ions insertion, the insertion positions in fully lithiated Li0.56FeF3$\cdot$0.33H2O should be at 4c due to the lowest formation energy at the dilute limit. In order to reveal the possible effect of water on Li+ insertion, the possible lower-energy site position of Li+ inserted after Li0.56FeF3$\cdot$0.33H2O is the most stable insertion site for Li ion, regardless of whether there is water molecule in channel.

In order to estimate the structural stability associated with Li+ concentration, the cohesive energies ($\Delta E^f$ = $E_{Li+FeF_3•0.33H_2O} - E_{Li^+} - E_{FeF_3} - E_{0.33H_2O}$) of Li+ inserted into the cavity structure of FeF3$\cdot$0.33H2O were calculated. The cohesive energies with a change of Li+ concentration were displayed in Fig. 5 (a). The relaxed Li+FeF3$\cdot$0.33H2O ($x$=0.0, 0.33, 0.50, 0.66, 0.83, and 1.00) structures also were presented in Fig. 5 (a) to describe structural change induced by Li+ insertion. Obviously, the cohesive energies of Li+ in the cavity are gradually decreased with increasing Li+ concentration. Interestingly, our calculations showed that the maximum capacity of Li+ under maintaining the FeF3$\cdot$0.33H2O cavity structure may be 0.66, reaching the most stable species of Li0.56FeF3$\cdot$0.33H2O. This calculated result is qualitatively consistent with the experimental measurement. When more Li+ ions are inserted after Li0.56FeF3$\cdot$0.33H2O, an octahedral chain (Chain 1 in Fig. 2) undergo transition from octahedral structure (FeF3$^{2-}$) to tetrahedral structure (FeF3$^{2-}$) and LiF, describing as the conversion reaction of Li0.56FeF3$\cdot$0.33H2O to LiFeF4+2LiF. It indicates that a slightly excessive discharge may lead to a significant structure change and therefore should be avoided in the practical operation.

![Fig. 5 (a) The relative formation energy and structural transition with Li+ concentration change of Li0.56FeF3$\cdot$0.33H2O (0.0≤x≤1.0). From x=0.66 to x=0.83, the octahedral FeF3$^{2-}$ undergoes structural transition to tetrahedral FeF3$^{2-}$ and 2F⁻; (b) the calculated voltage plateaus of Li0.56FeF3$\cdot$0.33H2O and fitted voltage curve (in black) and the experimental discharge potential profile for comparison.]

To describe quantitatively such a structural transition and its mechanism, the primitive cell volumes (V), bond lengths of Fe–F (rFe–F), and Bader charge of Fe ions were presented in Table 2 for comparison. First of all, the Li+ insertion leads to a significant volume shrinkage. The structural analysis shows that Li+ insertion directly induces decreasing torsion angles of octahedral chains probably due to a weakened hydrogen bonding between H2O and F⁻. The torsion angles of Chain 1 and Chain 2 in FeF3$\cdot$0.33H2O→Li0.56FeF3$\cdot$0.33H2O are calculated as 9.8°→21.1° and 9.8°→17.5°→19.5°, respectively. Hydrogen bonding strength is reduced from -0.46 eV in FeF3$\cdot$0.33H2O to -0.01 eV in Li0.56FeF3$\cdot$0.33H2O. This indicates that Li+ insertion introduces electrostatic interaction of Li+−F and Li+–H2O pairs. In meanwhile, hydrogen bonding strength of F–H2O is reduced with increasing Li+ concentration. The distortion of octahedral chains might directly result the shrinkage of lattice constants and volumes. The unit cell volume change during the charge/discharge processes is 8.3%, which rather comparable to that of LiFePO4 (6.5%). Actually, a similar situation also appears in other open framework battery material.

Table 2 The unit cell volumes (Å³), average bond length of Fe–F (rFe–F), and Bader charge (cBader) in bracket of Fe in Chain 1 and Chain 2 as shown in Fig. 2.

<table>
<thead>
<tr>
<th>Species</th>
<th>V (Å³)</th>
<th>rFe–F (Å)</th>
<th>cBader (±)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li0.56FeF3•0.33H2O</td>
<td>361.8</td>
<td>1.93 (±2.0)</td>
<td>1.93 (±2.0)</td>
</tr>
<tr>
<td>Li0.66FeF3•0.33H2O</td>
<td>348.1</td>
<td>2.03 (±1.5)</td>
<td>2.03 (±1.5)</td>
</tr>
<tr>
<td>Li0.75FeF3•0.33H2O</td>
<td>358.6</td>
<td>2.02 (±1.4)</td>
<td>2.02 (±1.4)</td>
</tr>
<tr>
<td>Li0.83FeF3•0.33H2O</td>
<td>364.1</td>
<td>2.01 (±1.5)</td>
<td>2.01 (±1.5)</td>
</tr>
<tr>
<td>Li0.91FeF3•0.33H2O</td>
<td>370.1</td>
<td>2.00 (±1.5)</td>
<td>2.00 (±1.5)</td>
</tr>
<tr>
<td>LiFeF3•0.33H2O</td>
<td>376.8</td>
<td>2.01 (±1.5)</td>
<td>2.01 (±1.5)</td>
</tr>
<tr>
<td>LiFeF3+2LiF</td>
<td>389.1</td>
<td>2.00 (±1.5)</td>
<td>2.00 (±1.5)</td>
</tr>
<tr>
<td>LiFeF3•2LiF</td>
<td>396.8</td>
<td>2.00 (±1.5)</td>
<td>2.00 (±1.5)</td>
</tr>
</tbody>
</table>

Further, the structural transition associated with the conversion reaction of Li0.56FeF3→FeF3+2LiF can be characterized by the bond length change of Fe–F as shown in Table 2. From FeF3$\cdot$0.33H2O to LiFeF3$\cdot$0.33H2O, the bond lengths of Fe–F in Chain 1 are not changed too much, whereas those in Chain 2 have a sharp stretching from 1.91 Å (Li0.56FeF3$\cdot$0.33H2O) to 2.48 Å (Li0.56FeF3$\cdot$0.33H2O). Our Bader charge analysis indicates that such a structural transition is closely associated with the charge state of Fe ion. The charge state change from +3 to +2 directly induces the bond stretching of Fe–F in Chain 1. In contrast, the similar charge change from FeF3$\cdot$0.33H2O to Li0.56FeF3$\cdot$0.33H2O does not lead to the bond elongation. Therefore, it is predicted that enhancing bond strength of Fe–F in Chain 2 plays an important role in increasing Li+ storage capacity.

Based on our thermodynamic calculations, it is very necessary to further calculate the intercalation/deintercalation voltage of cell in comparison with experimental measurement. For any intercalation system, the total Gibbs free energy change can be written as:

\[ dG = -SdT + VdP + \mu_LdN_L + \mu_{FeF_3•0.33H_2O}dN_{FeF_3•0.33H_2O} \]  (6)

where G is the Gibbs free energy, S is the entropy, T is the temperature, V is the volume, P is the pressure, $\mu_L$ and $N_L$ are the chemical potential and amount of electrode materials, respectively. When the operating temperature and pressure are kept constant, the equation (4) can be simplified as $d\mu = \mu_{Li}dN_{Li}$. Therefore, the chemical potential of Li+ further can be written as $\mu_{Li} = dG/dN_{Li}$. According to the Nernst equation, the voltage of cell can be expressed as $V_{cell} = -\mu_{Li}^{(cathode)} - \mu_{Li}^{(anode)}/Z$, where Z is the valence (+1) of Li+. With the reference of anode material (Li metal), the voltage thus is calculated according to the following formula:

\[ V = -2/3 \]  (7)
calculated Li given. It is noted that our NEB calculations include all atoms in the compared with the initial minimum structure. This process can be transportation mechanism. For the former, two transition states are has a lower transition state energy than the knock-off

Fig. 6 The CI-NEB-calculated potential energy curves of Li transportation paths are displayed in Fig. 6. In order to reveal the detailed transportation mechanism, all transition state and minimum structures with emphasis on H2O-Li interaction are also given. It is noted that our NEB calculations include all atoms in the calculated LiFeF2•0.33H2O lattice.

3.4 Li Transportation Mechanisms

The CI-NEB and DFT methods have been successfully applied to determine lithium migration paths and energy barriers for electrode materials.46,47 Both knock-off migration and cooperative migration mechanisms were investigated in solid-state electrode and electrolyte materials. The typical knock-off mechanism is an asynchronous migration process in which Li migrates into a neighboring vacancy followed by nearby Li further migrates into the newly-generated vacancy. In contrast, the cooperative mechanism presents a synchronous migration mode in which the nearby Li ions replaced one another. In this work, the CI-NEB method based on DFT-PBE was used to calculate reaction paths of Li transportation considering the possible knock-off migration and cooperative migration mechanisms. In terms of knock-off migration mechanism, a Li vacancy is generated at 4a position which has a higher site energy than 4c position. It is predicted that lithium ions occupying 4a and 4c positions in tunnel follow a zigzag path around water molecules along c axis direction. The energy profiles of two Li transportation paths are displayed in Fig. 6. In order to reveal the detailed transportation mechanism, all transition state and minimum structures with emphasis on H2O-Li interaction are also given. It is noted that our NEB calculations include all atoms in the calculated LiFeF2•0.33H2O lattice.

It is obvious that the cooperative transportation mechanism has a lower transition state energy than the knock-off transportation mechanism. For the former, two transition states are symmetric and have the same relative energy of 0.29 eV as compared with the initial minimum structure. This process can be described as stepwise migration of Li ions from 4a and 4c positions to 8f positions. Based on position preference calculations in Fig. 4 (a), it is found that 4Li ions migrations from 4a/4c position to 8f position require surmounting an energy barrier of 0.44 eV. Correspondingly F-H2O hydrogen bonding strengths in 4a/4c and 8f positions are calculated as −0.01 and −0.14 eV, respectively. This indicates that the mediated F-H2O hydrogen bonding effectively reduce Li migration barrier. Therefore, the electrostatic attraction between Li ions and H2O play an important role in fast ionic transportation. A relatively lower transition state energy of Li transportation indicates that LiFeF2•0.33H2O has a good electrochemical performance with a fast charging/discharging rate. In contrast, the knock-off mechanism has the activation barrier of 0.46 eV.

4 Conclusions

The DFT-based first-principles calculations were carried out to study the impact of water on structural stability and electrochemical performance of LiFeF2•0.33H2O as cathode material. The water molecules are isolated in the tunnels and form strong hydrogen bonding with F ions, which directly results in octahedral FeO6 distortion and destabilizes FeF3 framework structure. The most stable species are predicted as FeF3nH2O (n=0.16-0.33). Li+ insertion into water-accommodated tunnel further changes torsion angle of FeO6 octahedral chains, leading to a wide discharge voltage window of 2.2-3.6V. The species of LiFeF2•0.33H2O is the most stable with the maximum amount of Li+ ions. More Li+ insertion leads to the Fe-F bond cleavage and occurrence of conversion reaction of FeF2F3−→FeF3+2F−. As a result, to stabilize Fe-F bonds and reduce octahedral chains by mediating hydrogen bonding play an important role in improving the electrochemical performance of FeF3nH2O materials.

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References

Graphical Abstract

The tunable $\text{H}_2\text{O}$-$\text{F}^-$ hydrogen bonding is crucial to structural stability and electrochemical performance of $\text{FeF}_3\cdot0.33\text{H}_2\text{O}$ cathode material.