

Ti-doped $\text{Fe}_{1-x}\text{Ti}_x\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposite as an ultrahigh rate capability cathode materials of lithium ion batteries

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The conductivity problem of $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ is the main constraint on development and application of this next-generation cathode material for lithium/sodium ion batteries. It has been found in our previous theoretical calculation that Ti-doping can dramatically improve the conductivity $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$, and thus improving its electrochemical performance. Herein, Ti-doped $\text{Fe}_{1-x}\text{Ti}_x\text{F}_3 \cdot 0.33\text{H}_2\text{O}$ ($x = 0, 0.06, 0.08, 0.10$) compounds have been successfully synthesized via a liquid-phase method. Subsequently, a ball milling process with acetylene black (AB) has been used to form $\text{Fe}_{1-x}\text{Ti}_x\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ ($x = 0, 0.06, 0.08, 0.10$) nanocomposite. The chemical composition and elemental distribution of the Ti-doped $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ samples were investigated by X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDXs). The results show that Ti can effectively dope into the samples, and replace partially Fe^{3+} ions in the $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ crystal. Especially the $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposite achieves an initial capacity of $460.15 \text{ mAh g}^{-1}$ and retains a discharge capacity of $294.86 \text{ mAh g}^{-1}$ after 40 cycles in the voltage range of 1.5–4.5 V. Besides, the as-prepared material shows excellent rate capability, it can deliver a discharge capacity of $146.06 \text{ mAh g}^{-1}$ even at 2 C.

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1. Introduction

In order to improve lithium ion batteries (LIBs) performance with satisfactory power and energy density, masses of new cathode materials have been explored [1]. Currently, the conversion reactions between alkali metals and electrode materials, which do not primarily rely on the size of alkali cations, seems to be a promising strategy to achieve high capacity of electrodes materials for LIBs. Among them, multi-electron materials, especially transition metal uorides, have attracted substantial interest because all oxidation states of the active material can be utilized and high specific capacities are supplied, which is quite different from cathode materials based on intercalation mechanism [2–4]. Since the iron tri uoride (FeF_3) was firstly reported for LIBs by Arais's, it has attracted extensively attention due to its high voltage plateau, high theoretical specific capacity (712 mAh g^{-1} for $3 e^-$ transfer), low cost, and environmental friendliness [1,5]. In addition, the strong Fe-F ionic bonds in the FeF_3 sample is expected to provide a

high discharge capacity and high redox voltage when applied in cathode materials for LIBs [6,7]. However, the high ionicity is the main problem restricting its practical application of cathode material, which induces a large bandgap of Fe-F, leading to a poor

improve the electrochemical property of the iron fluoride. For example, Li et al. [12–17] developed a series of iron fluoride with open framework. Among them, nanoscale $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ has attracted tremendous attention due to its unique tunnel structure [15–17]. The tunnel structure is beneficial to facilitate electrolyte penetration and Li^+ transport. By hybridizing FeF_3 with a conductive additive phase (such as SWNTs, 3DOM, CNHs, rGO, ordered mesoporous carbon and carbon nanohorns) can provide a facile electron pathway. Zhang et al. synthesized three-dimensionally ordered macroporous (3DOM) FeF_3/poly (3,4-ethylenedioxythiophene) (PEDOT) composite through in situ polymerization method. It has been found that the composite can deliver 210 mAh g^{-1} at 20 mA g^{-1} and a good rate capability of 120 mAh g^{-1} at 1 A g^{-1} in a voltage range of 2.0–4.5 V [18]. Li and his co-workers prepared SWNTs/ $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ in the BmimBF₄ medium via a precipitation method, which exhibit remarkable rate performance (220 mAh g^{-1} at 0.1 C and 80 mAh g^{-1} at 10 C, $1 \text{ C} = 237 \text{ mA g}^{-1}$) and better cycling performance (143 mAh g^{-1} at 0.1 C after 30 cycles) between 1.7 and 4.5 V [17]. Namely, the introduction of conductive polymer or carbon can greatly improve the electrochemical performance of iron fluoride. However, it is not worthwhile for the aspect of cost since BmimBF₄ ionic liquid and SWNTs are very expensive. Additionally, when relating to polymer, it will inevitably involve the harmful organic solvents usage, cumbersome synthesis process and post-processing. Our group has successfully prepared the mixed conducting matrices, such as $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{MoS}_2$ [19], $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{V}_2\text{O}_5$ [20], $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{ACMB}$ [21], FeF_3/G [22], $\text{FeF}_3 \cdot x\text{H}_2\text{O}/\text{G}$ [23], $\text{Fe}_2\text{F}_5 \cdot \text{H}_2\text{O}/\text{G}$ [24] and $\text{Fe}_2\text{F}_5 \cdot \text{H}_2\text{O}/\text{rGO}$ [25] cathode materials for LIBs and sodium ion batteries (SIBs), which showed some promising results. However, the capacity and cyclic property of $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposite are still required to be improved.

In addition, the substitution of elements such as Co [26], N [27] and -OH [28] for iron and fluorine elements is another effective strategy to improve the intrinsic electronic conductivity and crystal structural stability of FeF_3 cathode materials, thus it can evidently enhance their electrochemical performance. Generally, TiF₃ has the same crystal structure as FeF_3 and shows similar electrochemical activity [29,30]. In the studies of the LIBs cathode materials, Ti is usually applied as doping element due to its polyvalence and strong bond with nonmetalloid, but it has rarely been reported as the doping element of $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ [31–34]. In our previous work, the first-principles calculation was used to investigate the properties and electronic structures of Ti-doped $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$, it can be found that the crystal volume of Ti doped $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ was slightly increased with the increase of Ti-doping concentration. The band gap of $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ and $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}$ is 0.78 eV and 0.66 eV, respectively. Therefore, the electronic conductivity of $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ can be improved by Ti doping. These results can be ascribed to the substitution of large radius Ti^{3+} (6.70 Å) for small radius Fe^{3+} (6.45 Å), which can enlarge the structure of the lattice crystal, thus resulting in improving the electrochemical performance of $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ cathode materials [35].

In this work, we report a facile strategy for the synthesis of Ti-doped $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposite as ultrahigh rate LIBs cathode material. The $\text{Fe}_{1-x}\text{Ti}_x\text{F}_3 \cdot 0.33\text{H}_2\text{O}$

2.3. Electrochemical measurements

The electrochemical performance of the as-synthesized material was characterized using 2025 type coin cells, in which $\text{Fe}_{1-x}\text{-Ti}_x\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposite was used as a cathode active material and a lithium disk as cathode for LIBs. The cathodes for testing cells were fabricated by mixing the cathode materials, acetylene black, and polyvinylidene fluoride (PVDF) binder with a weight ratio of 80:10:10 in N-methyl pyrrolidone (NMP), which were then pasted on aluminum foil followed by drying under vacuum at 110 °C for 24 h. The testing lithium cells were assembled with the

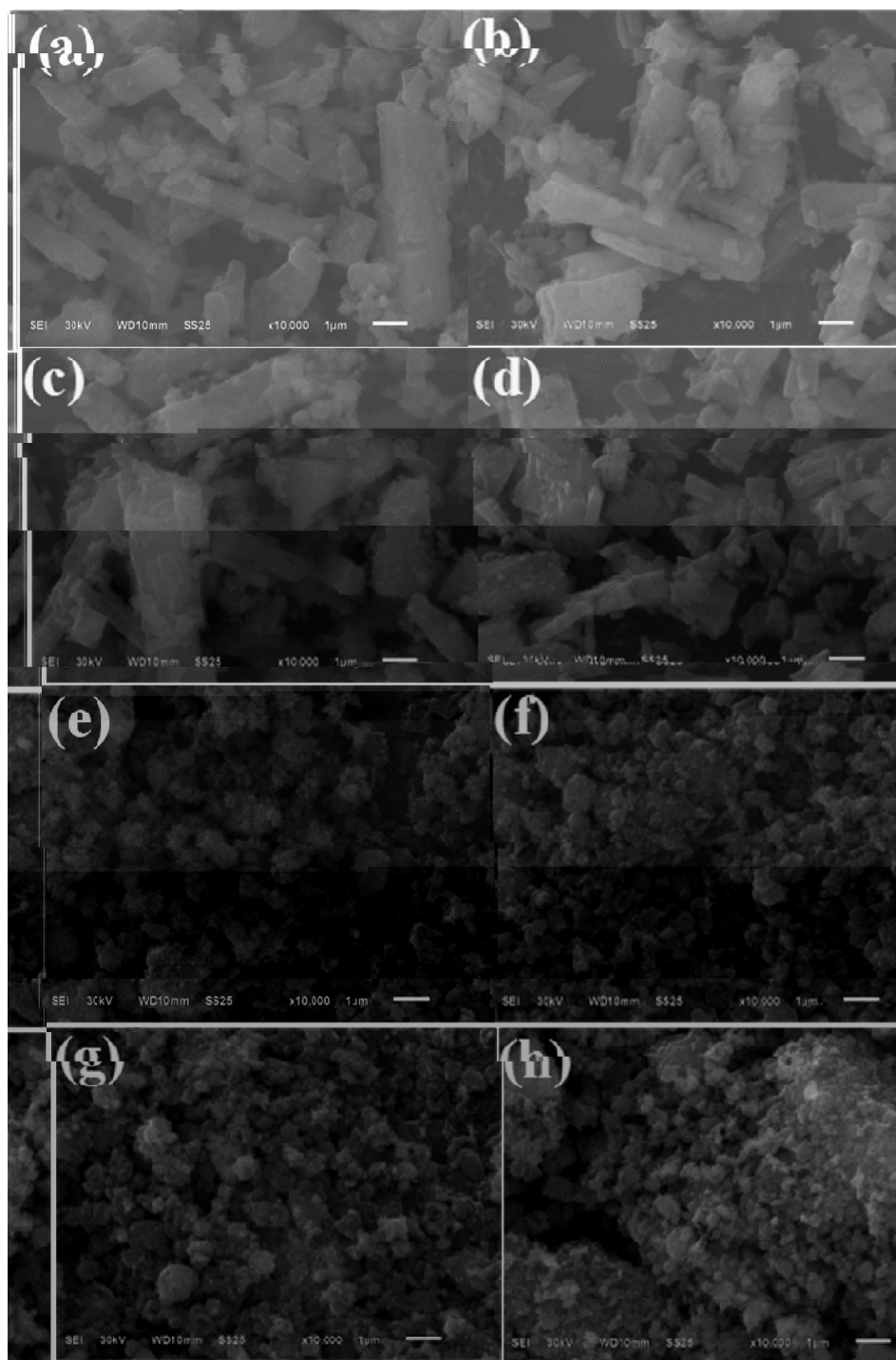


Fig. 1. (a) SEM images of $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$; (b) $\text{Fe}_{0.94}\text{Ti}_{0.06}\text{F}_3 \cdot 0.33\text{H}_2\text{O}$; (c) $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}$; (d) $\text{Fe}_{0.90}\text{Ti}_{0.10}\text{F}_3 \cdot 0.33\text{H}_2\text{O}$; (e) $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$; (f) $\text{Fe}_{0.94}\text{Ti}_{0.06}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$; (g) $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$, and (h) $\text{Fe}_{0.90}\text{Ti}_{0.10}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ composite.

$\text{Fe}_{1-x}\text{Ti}_x\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposite, which are further confirmed by the following electrochemical performances.

The crystallographic view of orthorhombic $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ along the direction of [001] was illustrated in Fig. 2c, as being seen, there is a special huge hexagonal cavity formed six Fe octahedral via corner-sharing, which can result in a larger cell volumes (~71 nm). The trace amount of water in $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ exist stably in the huge hexagonal cavity, it can be used as a structural stabilizer to stabilize the huge hexagonal cavity and avoid structure collapse during Li^+

insertion and extraction processes [15,26]. Therefore, $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ provide the space for accommodation and transport Li^+ .

The TEM and HRTEM are performed to accurately observed the morphology and detailed crystal structures of as-prepared materials. It can be clearly seen in Fig. 3a that the $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposite is composed of large clusters, which is made of many smaller particles. As illustrated in Fig. 3b, HRTEM images shows that the $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}$ (2–6 nm) nanocrystalline is encapsulated by an amorphous carbon matrix after ball milling.

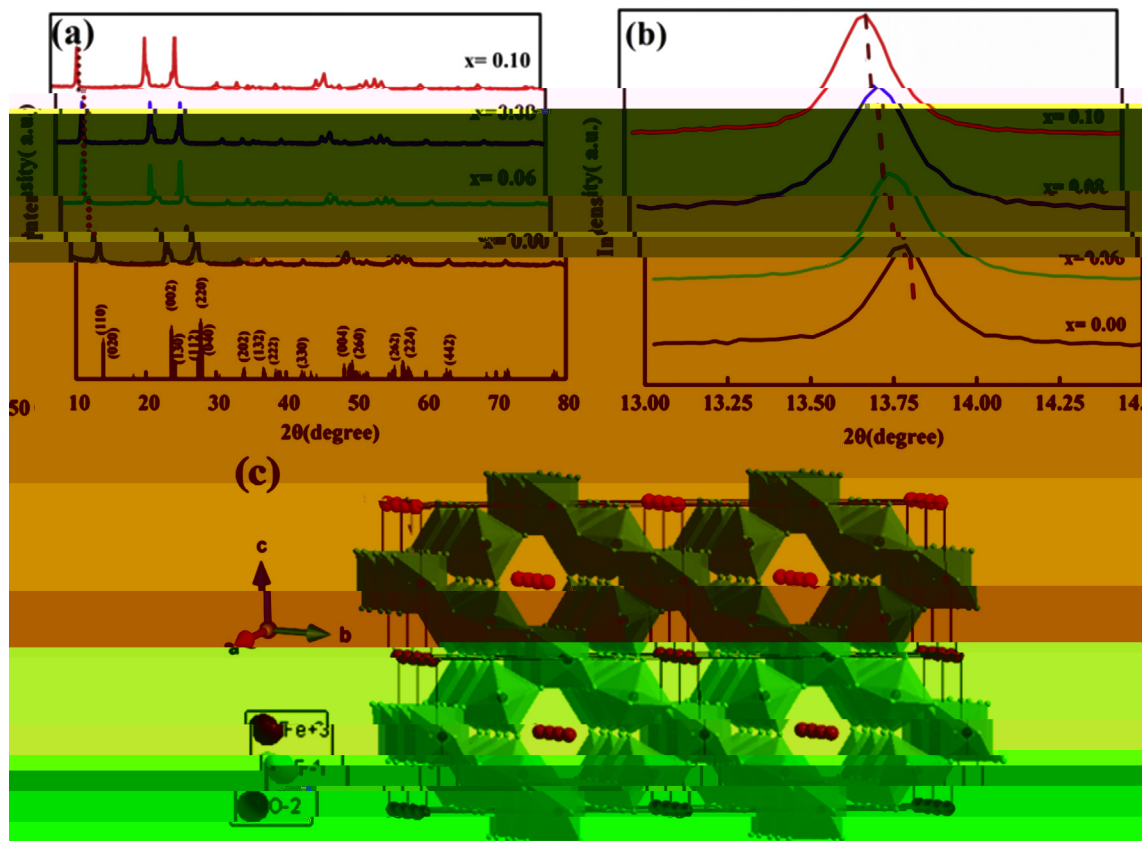


Fig. 2. (a) XRD patterns of $\text{Fe}_{1-x}\text{Ti}_x\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ ($x = 0, 0.06, 0.08, 0.10$) nanocomposites; (b) Magnification of the (110) XRD peak at around $2\theta = 13.8^\circ$; (c) Projections of $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ along the direction of [001].

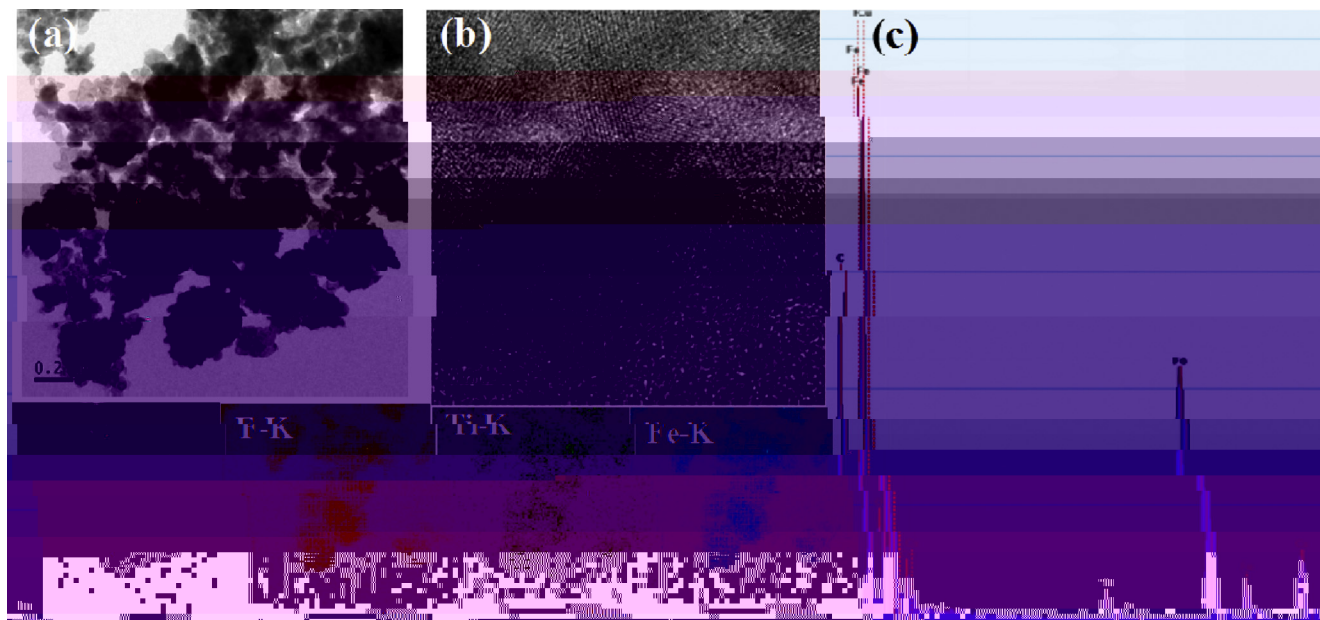


Fig. 3. (a) TEM and (b) HRTEM images of $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposite, (c) EDXs spectrum (c) and corresponding EDXs mapping images (F, Ti and Fe) of $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposite.

Besides, $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposite has the smallest particle size and best network structure, which is considered to be in favor of electrolyte penetration into the electrode and it can provide more interface between the electrode material and the

electrolyte. In order to further investigate the elemental distributions and compositions of the $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposite, the TEM images and corresponding EDXs mappings are shown in Fig. 3c. The Cu peaks come from a copper collector. The

average molar ratios for Fe, Ti, and F (Fe: 0.912, Ti: 0.077, F: 2.928) are in agreement with the nominal ratios. The result indicates that the Ti ions have been completely introduced into the $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposite via liquid phase method.

To further investigate the reason of improvement in the electrochemical performance for Ti-doping, the EIS analysis of $\text{Fe}_{1-x}\text{Ti}_x\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposites ($x = 0.0, 0.08$) is carried out, as shown in Fig. 4a and b. The shapes of the Nyquist plots for each cycle are similar. The EIS is recorded during 1st to 100th charge/discharge cycles at room temperature. The EIS pattern is composed of a semicircle within high-frequency region and a sloped straight line at low-frequency region. The semicircle is mainly ascribed to the charge transfer resistance (R_{ct}), which reflects the reaction kinetics of the electrodes; while the sloping line represents the Warburg impedance (Z_w), which is related to lithium ion diffusion in the solid matrix. The corresponding equivalent circuit model is shown in Fig. 4c, apparently, the fitting patterns are in good agreement with the experimental EIS data. As shown in Table 1, it can be found that the R_s value for all electrodes is almost the same. Besides, the R_{ct} values of $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ electrode at different cycle numbers are 220.4, 285.0, 449.3 Ω at 1st, 50th, 100th cycles, respectively. By contrast, the R_{ct} values for the $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ electrode after 1st, 50th, 100th cycles are 195.9, 263.3, 319.1 Ω , respectively. Thereby, the introduction of Ti can effectively decrease the charge transfer resistance and thus enhance the electrochemical performance of iron based fluoride cathode material. It can be found from Table 1 that the R_{ct} value of $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposite is less than that of $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposite, implying that the $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposite has higher conductivity and faster lithium ion diffusion kinetics than $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ sample.

The 1st and 40th charge/discharge profiles of $\text{Fe}_{1-x}\text{Ti}_x\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposites ($x = 0.00, 0.06, 0.08, 0.10$) are recorded at 0.1 C ($1\text{ C} = 237\text{ mA g}^{-1}$) rate in the voltage range of 1.5–4.5 V (vs. Li^+/Li), as shown in Fig. 5a–d. The $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ electrode delivers a low initial discharge capacity of 299.98 mAh g^{-1} , which is attributed to its poor electronic conductivity. Obviously, the Ti-doped materials show higher discharge capacity than

Table 1

R_s and R_{ct} values of $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ and $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ samples after different cycles in Li half-cells.

Samples	$\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$			$\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$		
	1 st	50 th	100 th	1 st	50 th	100 th
$R_s(\Omega)$	5.999	6.151	6.350	2.140	2.391	2.568
$R_{ct}(\Omega)$	220.4	285.0	449.3	195.9	265.3	319.1

$\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$. The initial discharge capacities when $x = 0.06, 0.08, 0.10$ are 361.70 mAh g^{-1} , 460.15 mAh g^{-1} , 399.48 mAh g^{-1} , respectively, thus Ti-doping with an optimal content can improve the specific capacity. Particularly, $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ delivers the highest specific capacity and exhibits an excellent cycling performance compared with other three nanocomposites. In addition, the $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposite exhibits also the highest discharge voltage plateau and lowest charge voltage plateau from the 1st to the 40th cycles. As shown in Fig. 5e, the $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ cell shows excellent cycling performance, it can provide an initial discharge capacity of 460.15 mAh g^{-1} at 0.1 C and a discharge capacity of 294.86 mAh g^{-1} after 40 cycles. By contrast, the $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ cell can reach an initial discharge capacity of 299.98 mAh g^{-1} at 0.1 C, but the discharge capacity of $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ is only 162.66 mAh g^{-1} after 40 cycles. In addition, the voltage fading of $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ cell is distinctly lower than $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ cell with the increase of the cycle number. As expected, the discharge specific capacity of the nanocomposites is superior to those of the recently reported results. For example, Rao et al. prepared $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{rGO}$ composite via a solvothermal route and obtained a discharge capacity of 165.0 mAh g^{-1} at 0.1 C after 30 cycles [44]. Xu et al. synthesized $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposite by one-step solid state method, and it only maintained a low discharge capacity of 157.4 mAh g^{-1} at 20 mA g^{-1} after 50 cycles [45]. Apparently, the $\text{Fe}_{1-x}\text{Ti}_x\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposite in this work exhibits much better excellent electrochemical performances.

In addition to the excellent cycling performance, the $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ cell displays also good rate capability compared

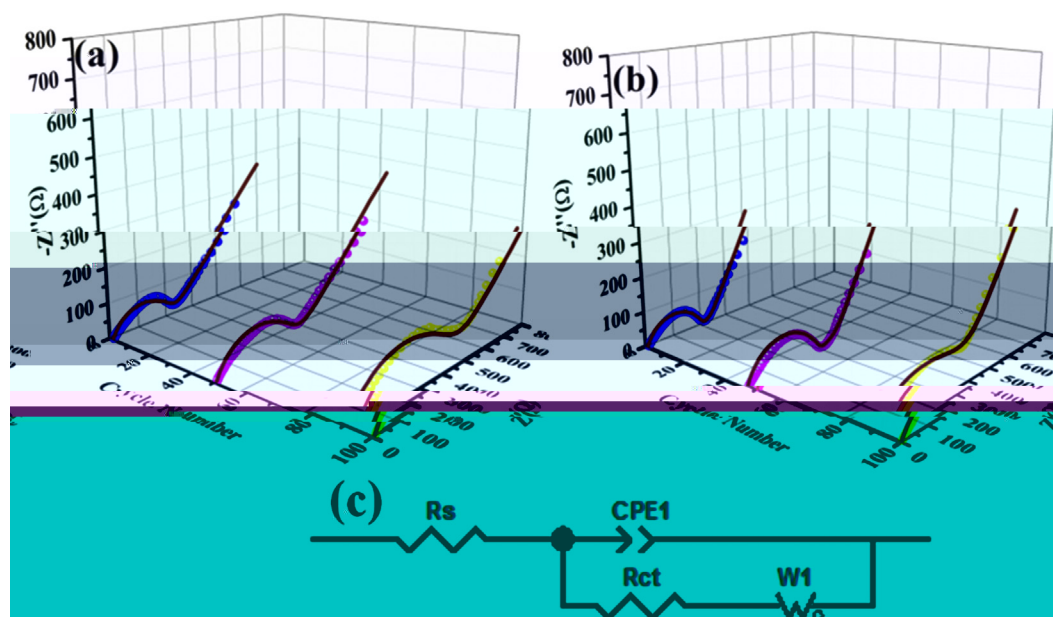


Fig. 4. Three-dimensional Nyquist plots measured for (a) $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ and (b) $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ samples after cycling for different cycles at 1 C in Li half-cells; (c) the equivalent circuit model.

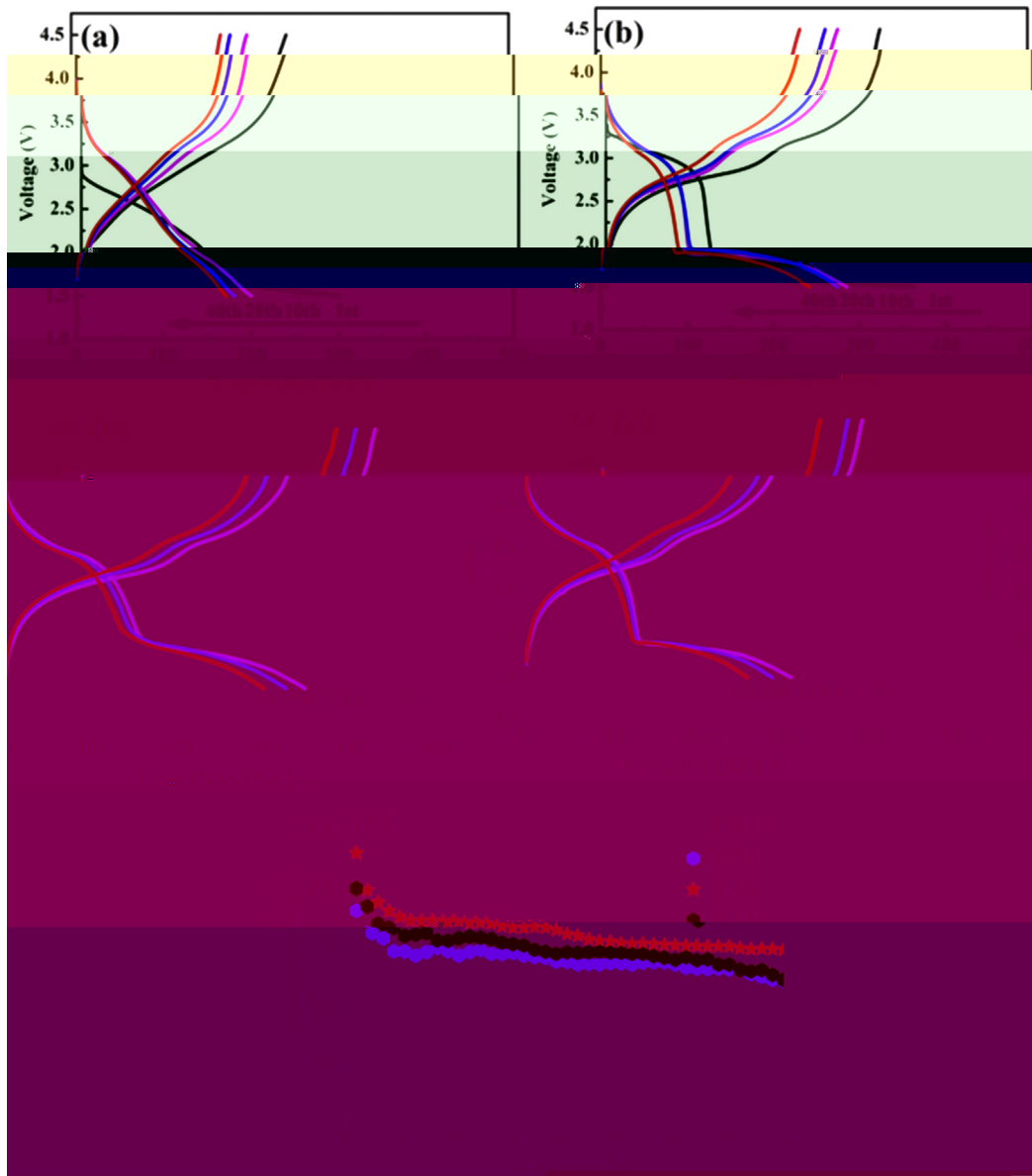


Fig. 5. Discharge and charge profiles of (a) $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$; (b) $\text{Fe}_{0.94}\text{Ti}_{0.06}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$; (c) $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$; (d) $\text{Fe}_{0.90}\text{Ti}_{0.10}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$; at 0.1 C at different cycles (1st, 10th, 20th, 40th); (e) Discharge capacity vs. cycle number for 0.00, 0.06, 0.08, 0.10 at 0.1 C in the voltage range of 1.5–4.5 V.

with the $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ cell. As illustrated in Fig. 6a, the rate capabilities of the $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ and $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposite are examined at 0.1 C, 0.2 C, 0.5 C, 1 C and 2 C rates for 10 cycles, respectively. The initial discharge capacity of $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ cell can reach as high as $470.51 \text{ mAh g}^{-1}$ at 0.1 C. The average discharge capacity of $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ cell is $366.06 \text{ mAh g}^{-1}$ at 0.1 C. And the subsequent average discharge capacity are about $314.34 \text{ mAh g}^{-1}$, $257.92 \text{ mAh g}^{-1}$, $200.25 \text{ mAh g}^{-1}$ and $146.06 \text{ mAh g}^{-1}$ at rate of 0.2 C, 0.5 C, 1 C and 2 C, respectively. Apparently, with increasing C-rate, $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ gives much higher discharge capacity and much better rate capability than $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$. Additionally, there is a slight capacity fading for the $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ electrode when the current density decreases from 2 C to 0.1 C, but the capacity of the $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ electrode can be recovered quickly. When the rate backs to 0.1 C after 50 cycles, a capacity of $261.74 \text{ mAh g}^{-1}$ can be resumed.

To further study the cycling performance of $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ and $\text{Fe}_{0.75}\text{Ti}_{0.25}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ electrodes at high rate, the samples were cycled at 1 C in the voltage range of 1.5–4.5 V, as shown in Fig. 6b–d. It can be found that a discharge capacity of $179.62 \text{ mAh g}^{-1}$ can be remained after 60 cycles for the $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ electrode and the capacity retention is 85.9%. On the contrary, the $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ electrode suffers a fast capacity fading and it only delivers $144.54 \text{ mAh g}^{-1}$ with a capacity retention of 72.2% after 60 cycles. The good electrochemical performance of $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ electrodes is probably due to the large increase of the lattice parameters after Ti doping, which can enhance the diffusion coefficient of Li^+ and lower the activation barrier of Li^+ diffusion with the increasing current rate. In addition, the Ti substitution for Fe can also stabilize the crystal structure of the material, which can provide a stable pathway for Li^+ to both insertion and conversion reactions [46,47].

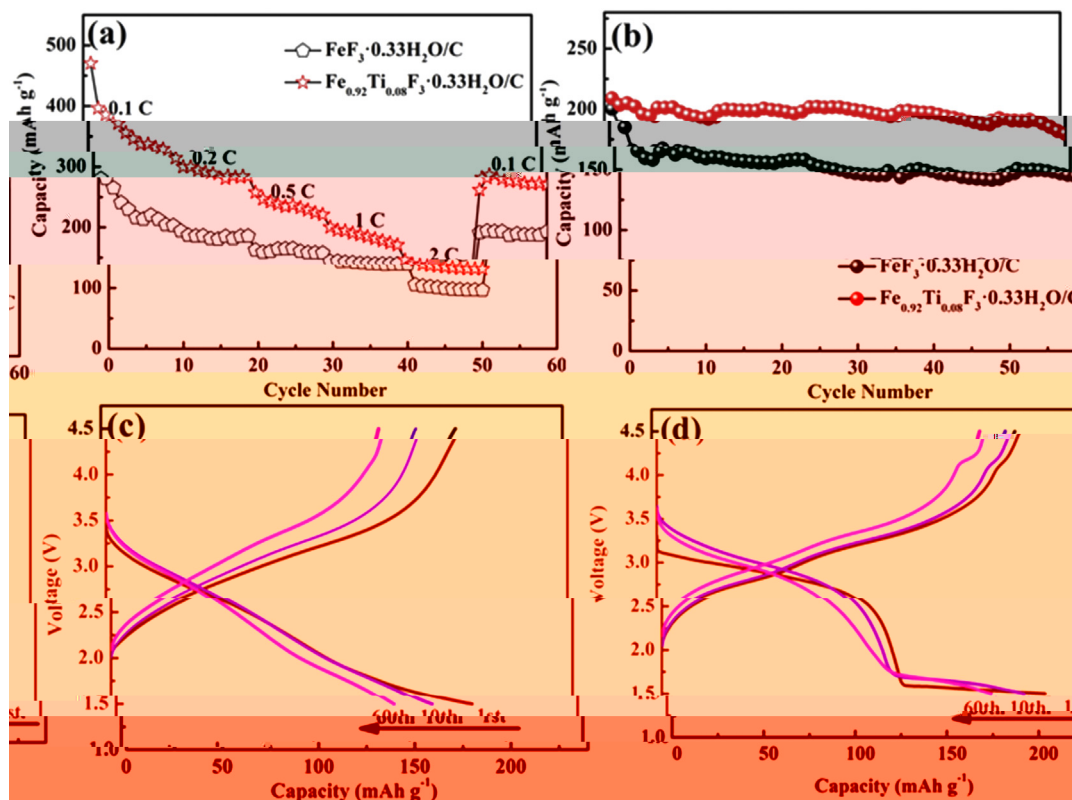


Fig. 6. Rate capabilities of (a) $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ and $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$

4. Conclusions

$\text{Fe}_{1-x}\text{Ti}_x\text{F}_3 \cdot 0.33\text{H}_2\text{O}$ has been successfully prepared through a simple liquid-phase method and followed by a heat-treatment process, and then mixed with carbon black by ball-milling to obtain $\text{Fe}_{1-x}\text{Ti}_x\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposite as cathode materials of LIBs. Smaller particles size, faster lithium ion diffusion rate and less polarization confer the Ti-doped $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposite outstanding electrochemical performance. Moreover, Ti can effectively and equably doped into $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ crystal, and replace partially Fe^{3+} site in the $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ crystal. Ti-doping can not only decrease apparently the charge transfer resistance of $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$, but also notably enhance the discharge capacity and cycling stability. Especially, the $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ material exhibits a highest initial discharge specific capacity of $460.15 \text{ mAh g}^{-1}$ and retains a discharge capacity of $294.86 \text{ mAh g}^{-1}$ after 40 cycles at 0.1 C among all samples. In addition, the $\text{Fe}_{0.92}\text{Ti}_{0.08}\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposite also shows good excellent rate capability, it can provide a discharge capacity of $146.06 \text{ mAh g}^{-1}$ even at 2 C. Therefore, Ti-doping will be of general interest and contribute meaningful guidance for designing high performance metal fluoride cathode for LIBs.

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