

## Electrochemical Performance of $\text{Li}_2\text{FeSiO}_4$ as Anode Material for Lithium-ion Batteries

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The conventional cathode material  $\text{Li}_2\text{FeSiO}_4$  (lithium iron orthosilicate) crystallites are synthesized by a solid state reaction, and used as the anode material for lithium-ion batteries. During the initial discharge,  $\text{Li}_2\text{FeSiO}_4$  irreversibly decomposes and transforms. Although the resulted anodes hardly contain  $\text{Li}_2\text{FeSiO}_4$  crystal phase, they show nice capacities and well cycling stability. At a current density of  $50 \text{ mA g}^{-1}$ , the anode exhibits an initial discharge/charge of  $799/569 \text{ mAh g}^{-1}$ , and keeps a discharge/charge capacity of  $550/542 \text{ mAh g}^{-1}$  after 60 cycles with 95.3% charge capacity retention. At a current of  $1000 \text{ mA g}^{-1}$ , the anode shows a charge capacity of  $191 \text{ mAh g}^{-1}$  with 99.5% coulombic efficiency during the 300th cycle. The anode material after 300 cycles presents many microcrystal structures. It is proposed that the  $\text{Li}_2\text{FeSiO}_4$  anodes transfer energy via a reversible conversion reaction.

**Keywords:** Lithium iron orthosilicate; anode material; lithium-ion battery; cycling stability

### 1. INTRODUCTION

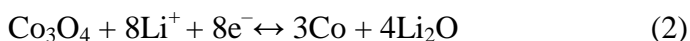
During the past 25 years, carbon materials always dominate the anode material market for lithium-ion batteries (LIBs). Graphitic carbon gives a safe insertion host for the unstable metallic lithium, and has a theoretical capacity of  $372 \text{ mAh g}^{-1}$  [1, 2]. Although some porous hard carbons exhibit excellent capacities, their stability and repeatability need further tested [3].

Compared with graphite, some Li-containing alloy anode materials have rather high theoretical capacities [4], such as 410 mAh g<sup>-1</sup> for LiZn, 993 mAh g<sup>-1</sup> for LiAl, and even 3579 mAh g<sup>-1</sup> for Li<sub>15</sub>Si<sub>4</sub>. But high-capacity Li-alloy anodes often suffer from the drastic volume variation and capacity fading during cycling. For example, crystalline Si is pulverized into amorphous Si after a single discharge/charge cycle due to a 280% volume expansion after full lithiation [5].

Apart from the lithium insertion/extraction and alloying mechanisms, some other anode materials act the lithiation/delithiation mechanisms in the reversible conversion reactions, where the transition metal comprising compounds (MX<sub>y</sub>, M=Co, Ni, Cu, Fe, etc; X=P, S, O, F, Cl, etc.) are electrochemically reduced into metal (M<sup>0</sup>) nanoparticles. As being charged, the metal nanoparticles are converted into their original states (MX<sub>y</sub>) [2, 6–8]. Theoretically, MX<sub>y</sub> compound anodes often have high capacities. For example, the CoO anode has a theoretical capacity of 715 mAh g<sup>-1</sup> caused by a reversible reaction mechanism as follows.



Additionally, the Co<sub>3</sub>O<sub>4</sub> anode has a higher theoretical capacity (890 mAh g<sup>-1</sup>) as metal ions are completely reduced [8].



Compared with Li-alloys, the reversible reaction mechanism of MX<sub>y</sub> anode may induce the smaller volume variation during cycling. Nevertheless, it still is not enough for keeping the cycling stability of binary oxides. It was reported that the capacity of FeO anode fades from 730 to 300 mAh g<sup>-1</sup> after 50 cycles at a discharge/charge rate of 0.2 C [6].

Except for the traditional anode materials such as graphite, silicon or other Li-alloys, and binary oxides [2–11], some polyanionic compounds, such as LiFePO<sub>4</sub>, Li<sub>2</sub>MnSiO<sub>4</sub>, and Li<sub>2</sub>FeSiO<sub>4</sub>, are studied to be used as the anode material and exhibit unexpectedly high capacities and cycling stability [12–16]. Among them, the Li<sub>2</sub>FeSiO<sub>4</sub> shows prominent anode performance [14]. The reported LiFeSiO<sub>4</sub> anode delivers an initial discharge/charge capacity of 880/618 mA g<sup>-1</sup> at a current density of 50 mA g<sup>-1</sup>, and a discharge capacity of ~449 mAh g<sup>-1</sup> at 100 mA g<sup>-1</sup> after 173 cycles. The capacities are much higher than that of Li<sub>2</sub>FeSiO<sub>4</sub> as cathodes [15–22]. Due to its low-cost raw materials, multivalence of Fe, and complicated polyanionic crystal structure, the anode performance of Li<sub>2</sub>FeSiO<sub>4</sub> needs further investigation.

In this work, the carbon-coated Li<sub>2</sub>FeSiO<sub>4</sub> crystallites are synthesized via a solid state reaction from a precursor prepared by a modified sol–gel method. The synthetic Li<sub>2</sub>FeSiO<sub>4</sub> crystallites are used as the anode material for LIBs. Amphiphilic carbonaceous material (ACM) is used as the reducing agent during the formation of Li<sub>2</sub>FeSiO<sub>4</sub>, and simultaneously forms the carbon coating on Li<sub>2</sub>FeSiO<sub>4</sub> crystallites. Differing from the other carbon sources such as citric acid or glucose, ACM mainly consists of aromatic molecules, and facilely forms the well carbon coating and connecting the Li<sub>2</sub>FeSiO<sub>4</sub> crystallites after carbonization. The coating carbon improves the electrochemical performance of active materials for LIBs in previous investigations [11, 23].

It is found that the  $\text{Li}_2\text{FeSiO}_4$  crystallites as anode material irreversibly decompose during the initial discharge. Though the resulted anodes hardly contain  $\text{Li}_2\text{FeSiO}_4$  crystal phase, they shows nice capability and well stability during cycling. The  $\text{Li}_2\text{FeSiO}_4$ -derived anode material contains many microcrystal structures after 300 cycles. Their lithiation/delithiation mechanism is discussed.

## 2. EXPERIMENTAL

### 2.1. Synthesis of $\text{Li}_2\text{FeSiO}_4$ crystallites

The precursor of  $\text{Li}_2\text{FeSiO}_4$  was prepared by a modified sol–gel process [16]. The main raw materials include  $\text{CH}_3\text{COOLi}\cdot 2\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ , and  $\text{SiO}_2$  fine powder (CAB-O-SIL M5). First, citric acid, ethylene glycol, and  $\text{SiO}_2$  in a molar ratio 1/3/3 were orderly dissolved and dispersed into deionized water to form a  $\text{SiO}_2$  suspension under stirring. Then, two aqueous solutions of  $\text{CH}_3\text{COOLi}\cdot 2\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  were respectively added into the suspension. After the mixture having been stirred at 80 °C for 12 h, ACM (20% of the theoretical mass of  $\text{Li}_2\text{FeSiO}_4$ ) was added. The new mixture was stirred at 80 °C until a gel formed. The gel was dried, ground, and then heated at 700 °C in  $\text{N}_2$  flow for 10 h to synthesize  $\text{Li}_2\text{FeSiO}_4$  crystallites.

### 2.2. Characterization

The precursor of  $\text{Li}_2\text{FeSiO}_4$  was analyzed by thermogravimetric analysis and differential scanning calorimetry (TG–DSC, STA 409 PC/PG, NETZSCH) from room temperature to 800 °C in  $\text{N}_2$  flow. The carbon content of the synthetic carbon-coated  $\text{Li}_2\text{FeSiO}_4$  crystallites was measured by TG–DSC analysis in air flow. The pristine, discharged, and charged anodes were analyzed by a powder X-ray diffractometer (XRD, D/MAX-2500, Rigaku) using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15406$  nm). The anode materials' morphology and microstructures were recorded by a field emission scanning electron microscope (SEM, Nanosem 430, FEI) and a high-resolution transmission electron microscope (HRTEM, Tecnai  $\text{G}^2$  F20, FEI). The cycled anode material was carefully scraped off the copper current collector, and analyzed by HRTEM and XRD.

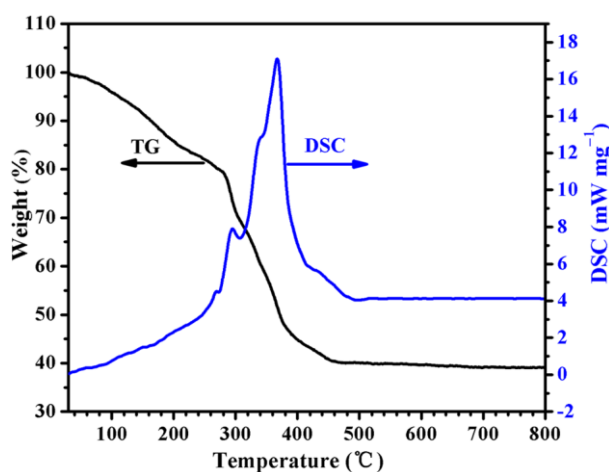
### 2.3. Electrochemical measurements

The electrochemical performance of the  $\text{Li}_2\text{FeSiO}_4$ -derived anodes was tested within CR2430-type coin cells. Metallic lithium was used as the counter electrode. The synthetic carbon-coated  $\text{Li}_2\text{FeSiO}_4$ , Super P carbon black, and polyvinylidene fluoride were mixed in a weight ratio of 80/10/10 using N-methyl-2-pyrrolidone (NMP) as solvent. The slurry was coated onto copper foil, and vacuum-dried at 80 °C for 12 h. 1.0 M  $\text{LiPF}_6$  in ethylene carbonate–dimethyl carbonate (EC–DMC, 1:1 in volume) was used as electrolyte. A polypropylene microporous film (Cellgard 2400) was used as the separator. The discharge/charge tests were performed on a battery program control test system (LAND CT2001A, China) between 3.0 and 0 V. The cyclic voltammetry (CV) was measured using an

electrochemical workstation (CHI604A, CH Instruments, China) at a scan rate of  $0.1 \text{ mV s}^{-1}$  between 3.0 and 0 V.

### 3. RESULTS AND DISCUSSION

Fig. 1 displays the TG–DSC curves of the precursor (without ACM) of  $\text{Li}_2\text{FeSiO}_4$ . Below  $460^\circ\text{C}$ , the total weight loss is about 60%. A sharp weight loss between  $280$  and  $460^\circ\text{C}$  with two exothermic peaks at  $295$  and  $367^\circ\text{C}$  corresponds to the decomposition of citric acid and the reactions among acetate, nitrate, and  $\text{SiO}_2$ . Above  $500^\circ\text{C}$ , there is no obvious weight loss and endothermic/exothermic peaks. It indicates that the  $\text{Li}_2\text{FeSiO}_4$  crystallites already formed before  $500^\circ\text{C}$ . The experimental results are similar with previous reports [17, 18]. Hence, the  $\text{Li}_2\text{FeSiO}_4$  crystallites were synthesized at  $700^\circ\text{C}$  in this work.



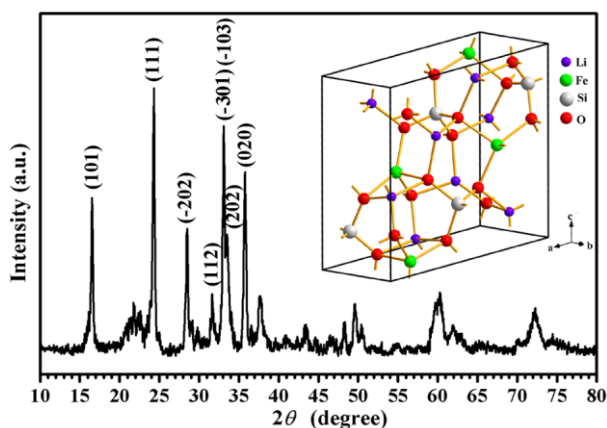
**Figure 1.** TG–DSC curves of the precursor of  $\text{Li}_2\text{FeSiO}_4$ .

Fig. 2 presents the XRD pattern of the synthetic carbon-coated  $\text{Li}_2\text{FeSiO}_4$ . Almost all diffraction peaks are indexed to a monoclinic  $\text{Li}_2\text{FeSiO}_4$  structure (ICSD 246132, S.G.  $P2_1/n$ ,  $a = 8.2407\text{\AA}$ ,  $b = 5.0132\text{\AA}$ ,  $c = 8.2302\text{\AA}$ , and  $\beta = 99.03^\circ$ ), which is quite consistent with previous reports [14, 19–22]. The unit cell of  $\text{Li}_2\text{FeSiO}_4$  is illustrated in Fig. 2. It consists of alternating layers being perpendicular to the  $b$  axes. In each layer, the atoms of Li, Fe, Si, and the O atoms between them are arranged in an uneven honeycomb lattice. Half of Li atoms respectively connect with three O atoms, and the rest Li atoms form  $\text{LiO}_4$  tetrahedra. The alternating layers are connected by MO ( $M = \text{Li, Fe, or Si}$ ) bonds along the  $b$  axes of  $\text{LiO}_4$ ,  $\text{FeO}_4$ , and  $\text{SiO}_4$  tetrahedra. The pattern of  $\text{Li}_2\text{FeSiO}_4$  unit cell is helpful to image the after-mentioned products of  $\text{Li}_2\text{FeSiO}_4$  decomposition.

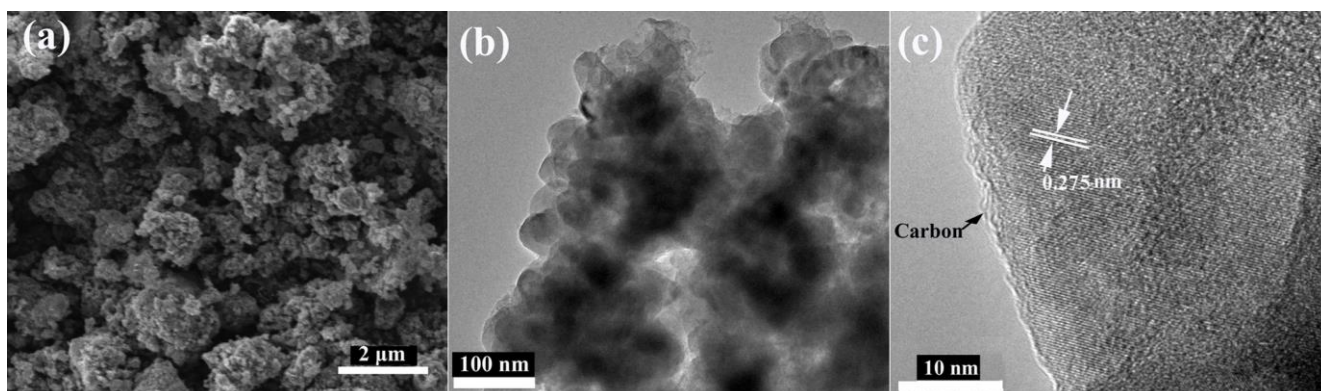
The mean size of the synthetic  $\text{Li}_2\text{FeSiO}_4$  crystallites is about 28 nm calculated by Scherrer formula. Although the carbon-coated  $\text{Li}_2\text{FeSiO}_4$  has a carbon content 13.4 wt% which results from the carbonization of reducing agents, no distinct diffraction peaks for ordered carbon are detected. The residual carbon should be amorphous.

As shown in Fig. 3a, the as-prepared  $\text{Li}_2\text{FeSiO}_4$  consists of aggregated particles. Fig. 3b exhibits the overlapping particles with sizes of less than 100 nm. In Fig. 3c, a magnified crystallite

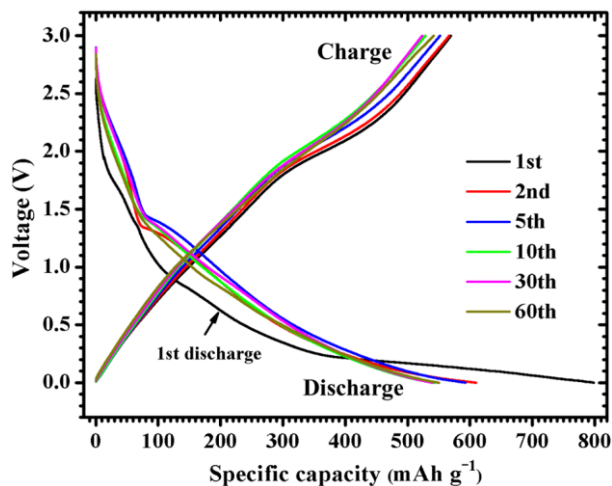
exhibits the well-ordered crystal planes with a lattice distance of 0.275 nm, corresponding to the diffraction peak (-301) or (-103) for  $\text{Li}_2\text{FeSiO}_4$  shown in Fig. 2. The crystallite is coated with a thin layer (thickness <1.0 nm) of amorphous carbon.



**Figure 2.** XRD pattern of the synthetic  $\text{Li}_2\text{FeSiO}_4$ . The insert is the unit cell of  $\text{Li}_2\text{FeSiO}_4$ .

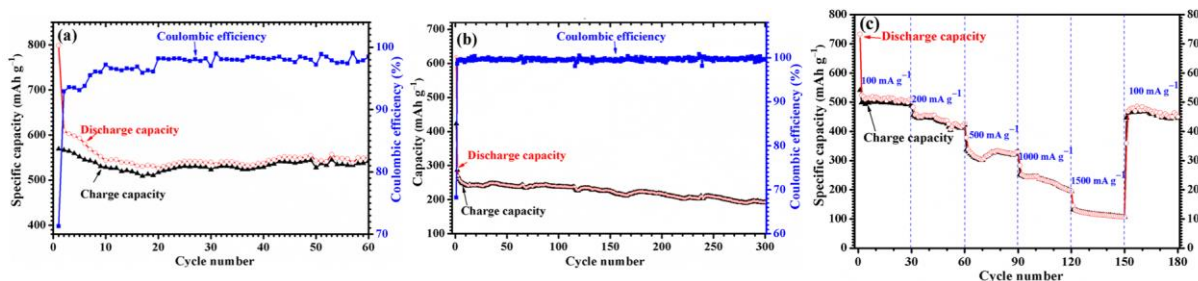


**Figure 3.** SEM and HRTEM images of the synthetic  $\text{Li}_2\text{FeSiO}_4$ : (a) SEM image, (b) HRTEM image of the aggregated particles, and (c) HRTEM image of a magnified crystallite.



**Figure 4.** Discharge/charge curves of  $\text{Li}_2\text{FeSiO}_4$ -derived anode at a current density of  $50 \text{ mA g}^{-1}$ .

Fig. 4 exhibits the discharge/charge curves of the  $\text{Li}_2\text{FeSiO}_4$ -derived anode. It delivers an initial discharge/charge capacity of  $799/569 \text{ mAh g}^{-1}$  at a current density of  $50 \text{ mA g}^{-1}$ . The initial capacity loss  $230 \text{ mAh g}^{-1}$  is mainly attributed to the lithium loss caused by the irreversible reduction of  $\text{Li}_2\text{FeSiO}_4$  and the formation of solid electrolyte interface (SEI) layers. After the initial charge, the subsequent discharge/charge curves show similar profiles, implying the anode's well reversibility. The charge plateaus at  $\sim 2.0 \text{ V}$  and the discharge plateaus at  $\sim 1.4 \text{ V}$  indicate redox reactions occurring.



**Figure 5.** Electrochemical performance of  $\text{Li}_2\text{FeSiO}_4$ -derived anodes: (a) cycling performance at a low current density of  $50 \text{ mA g}^{-1}$ , (b) cycling performance at a high current of  $1000 \text{ mA g}^{-1}$ , (c) rate performance at current densities varied from 100 to  $1500 \text{ mA g}^{-1}$ .

As shown in Fig. 5, the anode exhibits nice capabilities and cycling stability. At a low current density of  $50 \text{ mA g}^{-1}$  (Fig. 5a), it presents an initial charge capacity of  $569 \text{ mAh g}^{-1}$ , and keeps a charge capacity of  $542 \text{ mAh g}^{-1}$  during the 60th cycle, corresponding to 95.3% charge capacity retention. At a high current density of  $1000 \text{ mA g}^{-1}$  (Fig. 5b), the anode keeps a charge capacity of  $191 \text{ mAh g}^{-1}$  with a coulombic efficiencies of 99.5% during the 300th cycle.

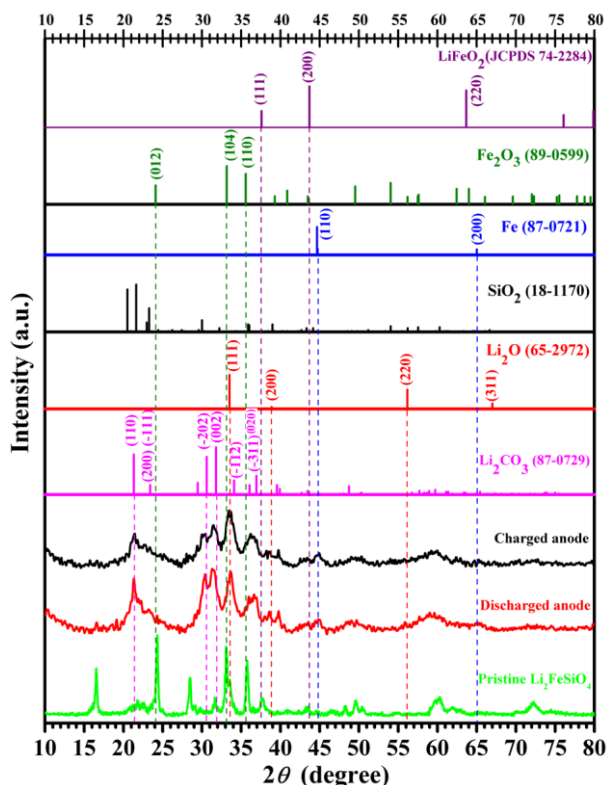
The  $\text{Li}_2\text{FeSiO}_4$ -derived anode shows a discharge/charge capacity of  $550/542 \text{ mAh g}^{-1}$  during the 60th cycle. Partial capacity should be attributed to the conductive carbons including Super P carbon black and coated carbon, which are hard carbons or non graphitizable carbons. It was reported that the discharge/charge capacity of a Super P anode is  $610/518 \text{ mAh g}^{-1}$  [24]. Generally, hard carbons have anode capacities between 200 and  $600 \text{ mAh g}^{-1}$  [25]. According to the contents and capacities of conductive carbons, the capacity of the  $\text{Li}_2\text{FeSiO}_4$ -derived active material is around  $520 \text{ mAh g}^{-1}$ .

The anode exhibits well rate capabilities and stability at a current density varied from 100 to  $1500 \text{ mA g}^{-1}$ . As shown in Fig. 5c, the reversible capacities are 541, 456, 338, 253 and  $132 \text{ mAh g}^{-1}$  at the start cycle at current densities of 100, 200, 500, 1000 and  $1500 \text{ mA g}^{-1}$ , respectively. After 150 cycles and the current density returned back to  $100 \text{ mA g}^{-1}$ , the anode has a reversible capacity of  $446 \text{ mAh g}^{-1}$  with a coulombic efficiency of 99.1%.

To investigate the lithiation/delithiation mechanism of the  $\text{Li}_2\text{FeSiO}_4$ -derived anodes, the discharged and charged anodes were analyzed by XRD and HRTEM. CV spectra of the anode were also studied.

As shown in Fig. 6, just after the initial discharge, most diffraction peaks for  $\text{Li}_2\text{FeSiO}_4$  crystallites irreversibly disappear. The broad peaks indicate that the  $\text{Li}_2\text{FeSiO}_4$  crystallites have decomposed and transformed. Both discharged and charged anodes show the similar XRD spectra.

They both exhibit the predominated diffraction peaks for  $\text{Li}_2\text{CO}_3$ , which is an ever-present component of SEI layers as carbonate-based non-aqueous electrolyte is used [14]. The broad diffraction peaks near  $21^\circ$  and  $60^\circ$  are indexed to the amorphous  $\text{SiO}_2$  resulting from the decomposition of  $\text{Li}_2\text{FeSiO}_4$  [26]. Two peaks (111) and (220) for  $\text{Li}_2\text{O}$  mainly appear in the XRD spectrum of the discharged anode.

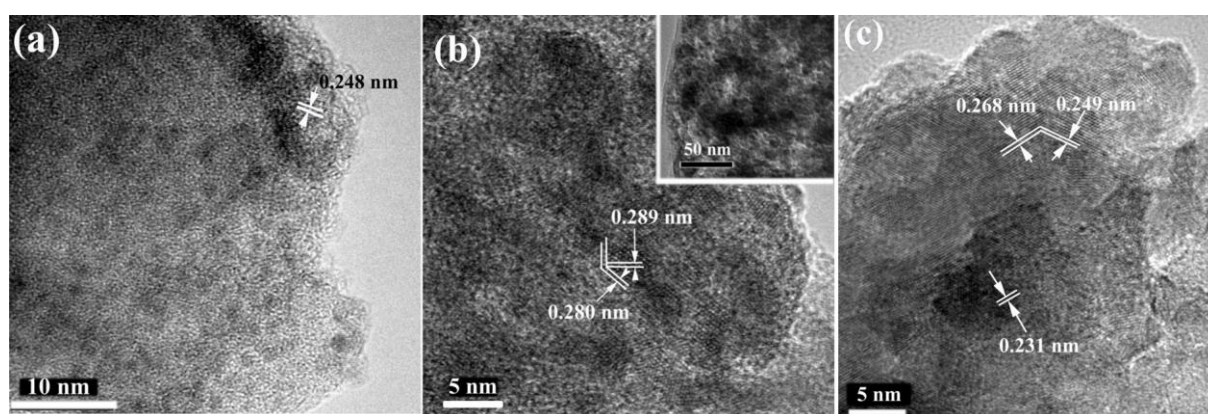


**Figure 6.** *Ex-situ* XRD patterns of  $\text{Li}_2\text{FeSiO}_4$ -derived anodes after the initial discharge/charge at a current density of  $10 \text{ mA g}^{-1}$ . The standard XRD patterns of  $\text{Li}_2\text{CO}_3$ ,  $\text{Li}_2\text{O}$ ,  $\text{SiO}_2$  (tridymite), Fe,  $\alpha\text{-Fe}_2\text{O}_3$  (hematite), and  $\text{LiFeO}_3$  are shown for comparison.

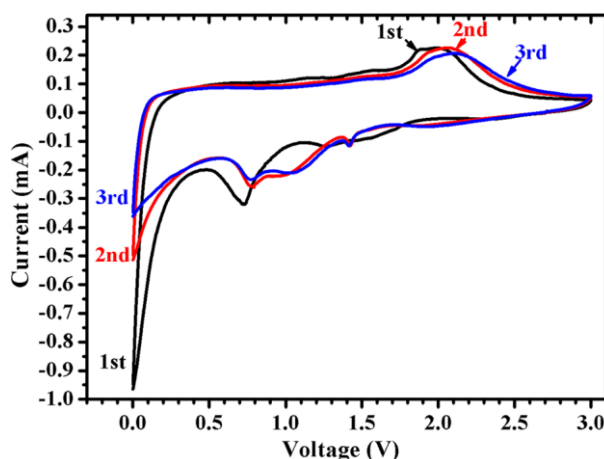
Metallic Fe and Fe-containing compounds play a key role for the anodes' energy conversion. However, due to the broad and overlapped diffraction peaks caused by the nanosized and/or amorphous particles, it is difficult to identify the metallic Fe by XRD results. Similar situation had ever been reported during the investigation on CoO anodes [6]. There are no obvious diffraction peaks for metallic Co because the presumed nanosized metallic Co nanoparticles are smaller than the X-ray coherence length. The charged anode shows a more intense diffraction peak at  $33^\circ$ , which is attributed to a mixed peak consisting of (104) peak for  $\alpha\text{-Fe}_2\text{O}_3$  and (111) peak for  $\text{Li}_2\text{O}$ . No obvious diffraction peaks for  $\text{LiFeO}_2$  are found. According to Fig.6, there possible is trace metallic Fe exists in both discharged and charged anodes.

Fig. 7 shows HRTEM images of the cycled anode materials. No  $\text{Li}_2\text{FeSiO}_4$  microcrystal structures are found in the particle after the initial discharge (Fig. 7a). As the anode was charged during the 1st cycle, the insert in Fig. 7b indicates that the material contains many tiny particles (mean size  $<6.0 \text{ nm}$ ), which exhibit microcrystal structures shown in the enlarged image (Fig. 7b). After 300 cycles, the charged anode material also shows many microcrystal structures (Fig. 7c). Many

microcrystal structures are indexed to  $\text{Li}_2\text{CO}_3$ , which more often has wider lattice spaces than  $\alpha\text{-Fe}_2\text{O}_3$ . At the particle edge shown in Fig. 7a, a lattice space of 0.248 nm is indexed to the (020) diffraction peak for  $\text{Li}_2\text{CO}_3$ . In Fig. 7b, the lattice spaces 0.289 and 0.280 nm respectively result from the (-202) and (002) planes of  $\text{Li}_2\text{CO}_3$ . Noticeably, the lattice spaces of 0.268 and 0.249 nm shown in Fig. 7c are respectively attributed to the (104) and (110) planes of  $\alpha\text{-Fe}_2\text{O}_3$ . The 0.231 nm lattice space possibly originates from the (200) planes of  $\text{Li}_2\text{O}$ , which reflects residual  $\text{Li}_2\text{O}$  in the charged anode. Many lattice spaces shown in Fig. 7 are difficult to be indexed by certain crystal phases. It reflects the mixed microcrystal phases and their ongoing phase transits involving  $\text{Li}_2\text{CO}_3$ ,  $\text{Li}_2\text{O}$ , Fe,  $\alpha\text{-Fe}_2\text{O}_3$ , etc. Nevertheless, the charged anode keeps ordered microcrystal structures after 300 cycles at a high current density of  $1000 \text{ mA g}^{-1}$ . It also corresponds to the anode's 99.5% coulombic efficiency shown in Fig. 5b.



**Figure 7.** HRTEM images for the powder scraped from the cycled anodes: (a) after the initial discharge at a current density of  $10 \text{ mA g}^{-1}$ , (b) after the initial charge at  $10 \text{ mA g}^{-1}$  (the insert is a low magnified image), and (c) after the 300th charge at  $1000 \text{ mA g}^{-1}$ .



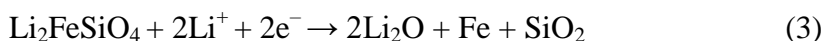
**Figure 8.** CV spectra of  $\text{Li}_2\text{FeSiO}_4$ -derived anode.

Fig. 8 presents the anode's CV spectra, which is simple explained according to literature. During the initial discharge from 3 to 0 V, the reduction peak at 0.72 V (vs  $\text{Li}^+/\text{Li}$ ) is associated with

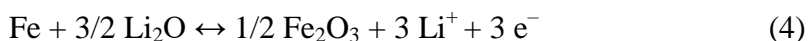


the reduction of  $\text{Fe}^{2+} \rightarrow \text{Fe}^0$  along with  $\text{Li}_2\text{FeSiO}_4$  decomposition [6, 27]. The sharp reduction peak at just above 0 V results from the formation of SEI layers, and the interfacial metallic lithium storage [14, 28, 29]. During the initial charge from 0 to 3 V, the peak at  $\sim 1.95$  V corresponds to the oxidation of metallic Fe [30–34]. From the 2nd cycle, the new reduction peaks around 1.42 V are assigned to the reduction of  $\text{Fe}^{3+}$ . The CV spectra are different with that of a  $\text{Li}_2\text{FeSiO}_4$ /activated carbon hybrid supercapacitor [35], and hence reveal that the  $\text{Li}_2\text{FeSiO}_4$ -derived anodes have no obvious capacitance behaviors. The oxidation/reduction peaks in CV curves reflect the redox reactions within the anodes during cycling.

As the above-mentioned results of XRD and HRTEM,  $\text{Li}_2\text{FeSiO}_4$  crystallites promptly disappear after the initial discharge. The discharged anode contains  $\text{Li}_2\text{CO}_3$ , amorphous  $\text{SiO}_2$ ,  $\text{Li}_2\text{O}$ , and possible metallic Fe. There is a reduction peak at 0.72 V (vs  $\text{Li}^+/\text{Li}$ ) in the CV spectra. So we propose that  $\text{Li}_2\text{FeSiO}_4$  decomposed during the initial discharge as follows.



$\text{Li}_2\text{FeSiO}_4$ -derived anodes show high charge capacities ( $>500$  mAh  $\text{g}^{-1}$ ) in literature [14] and this work. Their capacities likely correspond to the valence state change of iron between  $\text{Fe}^0$  and  $\text{Fe}^{3+}$ . We propose the anodes transferring energy via a reversible conversion reaction being simplified as follows.



$1/2 \text{Li}_2\text{O}$  per  $\text{Li}_2\text{FeSiO}_4$  remains due to its excess for reacting with Fe.

In this mechanism,  $\text{Li}_2\text{FeSiO}_4$ -derived anodes have a theoretical capacity of 497 mAh  $\text{g}^{-1}$ , which is higher than the theoretical capacity of graphite.

The performance of  $\alpha\text{-Fe}_2\text{O}_3$  anode has widely been investigated [31–34], and can be used to compare with the results of  $\text{Li}_2\text{FeSiO}_4$ -derived in this work.  $\text{Li}_2\text{FeSiO}_4$  anode material has an advantage over  $\alpha\text{-Fe}_2\text{O}_3$ . It forms amorphous  $\text{SiO}_2$  during the initial discharge. Amorphous  $\text{SiO}_2$  may buffer the anode volume variation during cycling, and improve the anodes' cycling stability. Additionally, the excess  $\text{Li}_2\text{O}$  in reaction (3) possibly favors the formation of  $\text{Fe}^{3+}$  (i.e.,  $\text{Fe}_2\text{O}_3$ ), which benefits the high capacities of anodes. In literatures, more redox peaks appeared in the CV spectra of  $\alpha\text{-Fe}_2\text{O}_3$  anodes, and indicate various valence states of iron during charge/discharge process. Partial oxygen in  $\alpha\text{-Fe}_2\text{O}_3$  is robbed to form the SEI layers. It induces the decrease of anodes' capacity due to the valence state change between  $\text{Fe}^{2+}$  and  $\text{Fe}^0$ .

#### 4. CONCLUSIONS

The conventional cathode material  $\text{Li}_2\text{FeSiO}_4$  crystallites are synthesized and used as the anode material for LIBs.  $\text{Li}_2\text{FeSiO}_4$  crystallites decompose during the initial discharge. The resulted anodes hardly contain  $\text{Li}_2\text{FeSiO}_4$ , but show well capability and high cycling stability. At a current

density of  $50 \text{ mA g}^{-1}$ , the anode keeps a charge capacity of  $542 \text{ mAh g}^{-1}$  and 95.3% charge capacity retention during the 60th cycle. At  $1000 \text{ mA g}^{-1}$ , the anode still presents a charge capacity of  $191 \text{ mAh g}^{-1}$  and 99.5% coulombic efficiency during the 300th cycle. It is proposed that the  $\text{Li}_2\text{FeSiO}_4$ -derived anodes transfer energy via a reversible reaction involving metallic Fe and  $\text{Fe}^{3+}$ .

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