Insight into cobalt-doping in Li$_2$FeSiO$_4$ cathode material for lithium-ion battery

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**Highlights**
- Co-doped Li$_2$FeSiO$_4$/C composite was successfully synthesized via a solid-state reaction assisted with refluxing.
- Co-doping does not change the monoclinic structure of Li$_2$FeSiO$_4$ and the oxidation state of Fe.
- XPS confirms that Co has been successfully doped into the lattice of Li$_2$FeSiO$_4$.
- Co-doping increases the defect concentration and the electronic conductivity of Li$_2$FeSiO$_4$.
- Co-doping can effectively improve the electrochemical performance for Li$_2$FeSiO$_4$.

**Abstract**
This study presents the preparation and electrochemical performance of cobalt-doped Li$_2$FeSiO$_4$/C (Co-doped LFS/C) composite by using a solid-state reaction assisted with refluxing process. The Co-doped LFS/C composite delivers a higher discharge capacity of 142.5 mAh g$^{-1}$ at 3.0 C even after 100 cycles compared with pristine LFS/C. A clear feature of cobalt-doping in Li$_2$FeSiO$_4$ has been specified by X-ray powder diffraction, X-ray photoelectron spectroscopy coupled with Ar-ion sputtering, X-ray absorption spectroscopy, and positron annihilation lifetime spectroscopy. It is confirmed that Co has been successfully doped into the lattice of LFS and the oxidation state of Fe. Positron annihilation lifetime spectroscopy analysis further demonstrates that Co-doping increases the defect concentration and the electronic conductivity of LFS. The results clarify the nature of cobalt-doping in LFS and are helpful for understanding the enhancement mechanism of the electrochemical performance of LFS and other cathode materials.

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**1. Introduction**
With the widespread application in electric vehicles or hybrid electric vehicles, rechargeable lithium-ion batteries (LIBs) have been one of the most developing power sources due to its higher energy density, longer cycle life, and memory-absence effect [1–4]. Polyanion-based cathode materials, such as LiMPO$_4$ and Li$_2$MSiO$_4$ (M = Fe, Mn) have been widely investigated as candidates for cathode materials because of their excellent safety, low cost, and environmental friendliness [5–10]. Among these polyanion cathode materials, lithium iron silicate (Li$_2$FeSiO$_4$) has been highlighted as one of the most promising cathode materials for large-size lithium-ion batteries owing to its high theoretical capacity and abundant raw materials [11–14]. However, as a polyanion cathode material, Li$_2$FeSiO$_4$ also suffers from the low intrinsic electronic conductivity and the slow diffusion of lithium ion. Therefore,
tremendous efforts have been made to solve this problem, such as carbon incorporation, particle size reducing, and metal ion doping [11–24]. Compared to other modification methods, metal ion doping has attracted more attention, because doping appears to be an effective method to improve electrochemical property of Li2FeSiO4. In spite of some controversy about the doping mechanism, the doping effect of Mn, Cr, Mg, Zn, Cu, Ni, and V on the electrochemical performance of Li2FeSiO4 has been investigated [19–24], but the effect of Co-doping for Li2FeSiO4 has not yet been reported. On the other hand, the positive effect of Co-doping for other cathode materials (i.e., LiFePO4, LiV2(PO4)3, LiMn2O4, etc.) has been confirmed by some researchers [25–27]. It is commonly believed that Co doping can not only decrease the charge-transfer resistance and enhance the Li+ ion diffusion coefficient [25,27], but also improve the structural stability of cathode material and moderate the volume changes (expansion/contraction) during the reversible Li+ extraction/insertion [26]. Furthermore, Li2CoSiO4 (with the same structural characteristics as triphylite) is also a potential candidate for cathode material of lithium ion batteries (with the same structural characteristics as triphylite) is also a potential candidate for cathode material of lithium ion batteries due to its high charge-discharge potential (higher than 4.1 V) [28–30].

In this study, cobalt-doped Li2FeSiO4/C (Co-doped LFS/C) composite was synthesized via a solid-state reaction assisted with refluxing process, and the effect of Co-doping on physicochemical property and electrochemical performance of Li2FeSiO4 was studied. The mechanism of Co-doping in Li2FeSiO4 was also proposed based on the results of X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), and positron annihilation lifetime spectroscopy (PALS) measurements.

2. Experimental

Co-doped Li2FeSiO4/C (Co-doped LFS/C) composite was synthesized via a solid-state reaction assisted with refluxing process. Lithium acetate, ferrous oxalate, cobalt acetate and tetraethyl orthosilicate at a molar ratio of 2:0.97:0.03:1 were successively dissolved in ethanol. The above solution was stirred sufficiently, and then transferred to the reflux system. The above mixture was maintained at 80 °C for 24 h. After evaporating ethanol and vacuum drying, the obtained dry gel was mixed with a certain amount of sucrose in acetone by ball-milling. The resulting precursor was dried at 50 °C and then calcined at 350 °C for 5 h, followed by 650 °C for 10 h in nitrogen atmosphere to obtain the Co-doped LFS/C powders. For comparison, pristine Li2FeSiO4/C (LFS/C) composite was synthesized via the same process without cobalt acetate.

X-ray diffraction patterns were obtained using X-ray powder diffraction (XRD, Rigaku Ultima IV) with Cu-κα radiation (λ = 1.5406 Å). Diffraction data were collected over the range of 2θ between 10° and 80° in step of 0.02°. The morphology was obtained with a field emission scanning electron microscope (FESEM, JSM-7500F, JEOL) coupled with an energy dispersive X-ray (EDX) detector and a transmission electron microscope (TEM, JEM-2100, JEOL). Carbon coating in both samples was characterized by Raman spectrometry (LabRAM HR800, Horiba JobinYvon), and carbon content was determined by a carbon sulfur analyzer (CS600, LECO, US). Electrical conductivity was measured with a standard four-probe method by RTS resistivity measurement system (RTS-8, China) on disk-shaped pellets with diameter of 8 mm and thickness of about 1.0 mm.

The oxidation state of key elements (Fe and Co) in LFS/C and Co-doped LFS/C samples was studied by X-ray photoelectron spectroscopy (XPS, PHI Quantera, U-P). In order to investigate the distribution of key elements (Fe, C, and Co) on the surface and/or in the interior of the samples, Ar-ion sputtering was also used in XPS analysis. The valences of Fe and Co were also studied by X-ray absorption fine structure (XAFS) measurements. The valences of Fe and Co were also studied by X-ray absorption spectroscopy (XAS). The Fe and Co K-edge XAS data were taken in fluorescence and transmission modes at beam line X-19A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. A standard (FeO for Fe K-edge and CoO for Co K-edge, respectively) was run simultaneously with the samples for energy calibration. A double-crystal Si(111) monochromator was used for energy selection and was detuned by reducing the incident photon flux 20% from its maximum value to suppress contamination from harmonics. The energy resolution (ΔE/E) of the X-19A beam line was 2 × 10^-4, corresponding to about 1.4 eV at Fe K-edge and 1.5 eV at Co K-edge. The XAS spectra presented in this paper were background subtracted and normalized to unity in the continuum region about 100 eV above the edge.

Positron annihilation lifetime spectroscopy (PALS) measurement was performed by using a high resolution positron annihilation lifetime spectrometer. PALS was carried out using an ORTEC fast-slow coincidence system with a BaF2 as the detector with a time resolution of 198 ps. The sample powders were pressed into a disk (diameter: 8 mm, thickness: ~1.0 mm). 22Na was chosen as the positron source and sandwiched between two identical sample disks. A fitting software LT9.0 was used to analyze the obtained spectra.

The working electrodes were prepared by mixing active materials (LFS/C and Co-doped LFS/C) with PVDF and acetylene black in a weight ratio of 75:15:10 in N-methyl pyrrolidinone solvent. The mixed slurry was coated onto an aluminum foil (20 μm in thickness) using an automatic film-coating equipment. The resulting film was dried under an infrared light to vaporize volatile solvent, punched into disks (14 mm), and then pressed under a pressure of 6 MPa. After drying at 120 °C for 12 h in vacuum, the disks were transferred into an argon-filled glove box (Super 1220/750,
Mikrouna) and assembled as the working electrodes in a 2025 coin cell using Celgard 2400 as the separator and lithium foil as counter and reference electrodes. A solution of 1 mol L$^{-1}$ LiPF$_6$ in EC/DMC (LB-301, China) was employed as the electrolyte. Galvanostatic charge/discharge measurements were performed between 1.5 and 4.6 V on a cell testing system (LAND CT2001A, China).

Electrochemical impedance spectra (EIS) and cyclic voltammetry (CV) measurements were performed on an electrochemical working station (CHI614C, China). EIS spectra were obtained over a frequency range from 0.01 Hz to 100 kHz, and CVs were tested at a scanning rate of 0.05 mV s$^{-1}$ within a voltage range of 1.5–4.6 V. All experiments were carried out at a temperature of 25 ± 0.5 °C.

### 3. Results and discussion

The XRD patterns of pristine and Co-doped LFS/C composites are displayed in Fig. 1. It could be seen that some weak peaks for Li$_2$SiO$_3$ (PDF: 83-1517) and Fe$_2$SiO$_4$ (PDF: 87-0320) impurities appeared in

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFS/C</td>
<td>8.1965</td>
<td>4.9970</td>
<td>8.2729</td>
<td>338.84</td>
</tr>
<tr>
<td>Co-doped LFS/C</td>
<td>8.1878</td>
<td>4.9609</td>
<td>8.1950</td>
<td>332.87</td>
</tr>
</tbody>
</table>

Table 1

Lattice parameters of LFS/C and Co-doped LFS/C.

**Fig. 2.** XPS spectra of the as-prepared samples: (a1–a3) LFS/C, and (b1–b4) Co-doped LFS/C.
the XRD pattern of Co-doped LFS/C, but the main diffraction peaks in the XRD pattern of Co-doped LFS/C are well identified by the monoclinic Li₂FeSiO₄ with a space group of P2₁, which is similar to that of the pristine LFS/C. This result indicates that Co-doping does not change the monoclinic structure of LFS. A full Rietveld refinement was carried out on LFS/C and Co-doped LFS/C samples, and the refined lattice parameters are listed in Table 1. The best refinement model was chosen from a P2₁ space group. Because the reliability factor of s is less than 2, and R_w is less than 15% (for LFS/C, the reliable factors are R_w = 10.73%, s = 1.22; and for Co-doped LFS/C, the reliable factors are R_w = 12.68%, s = 1.18), the Rietveld refinement results are reliable in the following analysis of crystal structure. Obviously, after Co-doping, the unit cell volume slightly decreases because of the substitution of Co²⁺ (radius: 0.074 nm) for Fe²⁺ (radius: 0.076 nm). So, we employed XPS and PALS measurements for further analysis, as discussed later. It should be noted that no diffraction peaks from carbon or any Co-containing composite are detected, indicating that the carbon yielded from pyrolysis of sucrose is amorphous, and the Co-doping content is too low to be detected. The measured residual carbon content in LFS/C and Co-doped LFS/C is 8.70 and 9.47 wt.%, respectively.

Table 2
Positron annihilation lifetime and relative intensity of LFS/C and Co-doped LFS/C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>t₁ (ps)</th>
<th>I₁ (%)</th>
<th>t₂ (ps)</th>
<th>I₂ (%)</th>
<th>t₃ (ps)</th>
<th>I₃ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFS/C</td>
<td>213.2</td>
<td>53.21</td>
<td>413.3</td>
<td>43.26</td>
<td>2203</td>
<td>3.53</td>
</tr>
<tr>
<td>Co-doped LFS/C</td>
<td>198.1</td>
<td>44.60</td>
<td>379.4</td>
<td>53.70</td>
<td>2200</td>
<td>1.72</td>
</tr>
</tbody>
</table>

Table 3
The electronic conductivity of LFS/C and Co-doped LFS/C composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>LFS/C</th>
<th>Co-doped LFS/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic conductivity (S cm⁻¹)</td>
<td>2.8 × 10⁻⁴</td>
<td>5.6 × 10⁻⁴</td>
</tr>
</tbody>
</table>

The XAS K-edge spectra for LFS/C, Co-doped LFS/C, and some reference compounds: (a) Fe K-edge and (b) Co K-edge.

Fig. 3. XAS K-edge spectra for LFS/C, Co-doped LFS/C, and some reference compounds: (a) Fe K-edge and (b) Co K-edge.

X-ray photoelectron spectroscopy (XPS) is an important surface analysis technique to resolve the controversy about whether or not metal ion is doped into the crystal structure [31,32]. In order to determine the oxidation state of Fe and Co, and the distribution of key elements (Fe, C, and Co) on the surface or in the interior of LFS/C and Co-doped LFS/C samples, XPS spectra shown in Fig. 2 have been used for the characterization of the samples. The binding energy for
each specimen obtained in the XPS analysis was referenced by setting the BE of C1s to 284.5 eV. As shown in Fig. 2a2 and b2, the intensity of C1s on the surface is much stronger than that in the interior, which reveals that carbon is just coated on the surface of the LFS particles. Instead, the intensity of Fe2p1/2 and Fe2p3/2 main peak (Fig. 2a3 and b3) on the surface is much lower than that in the interior due to the carbon coating. Though two main peaks of Fe2p are present at slightly lower energies due to the Fe-reduction during Ar-ion sputtering process (Fig. 2a3 and b3), the binding energies of Fe2p for Co-doped LFS/C (Fig. 2a3) are very close to that for LFS/C (Fig. 2a3), which indicates that Co-doping doesn’t change the oxidation state of Fe. From Fig. 2b4, it is worthwhile to note that Co2p3/2 main peak is clearly observed in the interior but almost disappears on the surface. Therefore, it is reasonable to believe that Co enters into the lattice of LFS rather than coats on the surface of LFS. Considering that the binding energy is intimately associated with the chemical environment in which the atoms exist, so it is difficult to determine accurately the oxidation state by XPS.

Consequently, XAS analysis was further performed to definite the real oxidation state of Fe and Co in the two samples.

We show in Fig. 3a the Fe K-edge spectra for the LFS/C and Co-doped LFS/C samples along with the spectra of three reference compounds. The spectra for the LFS/C and Co-doped LFS/C samples are almost identical, indicating that the valence value for Fe is the same for both of them. The formal valence values for Fe are: +2 for FeO; +3 for LaSrFeTiO6; and +4 for SrFeO3. The detailed 4p-related features at the near edge rise and peak energy can vary substantially due to variations in the local transition-metal/ligand crystalline environment. Fig. 3a shows that compared with the edge energies of the Fe2+, Fe3+, and Fe4+ standard compounds, the edge energy of the Fe K-edge for the pure and Co-doped Li2FeSiO4 spectra place them in a regime roughly halfway between Fe2+ and Fe3+, which is indicative of the existence of Fe3+ as well as Fe2+ in both samples. The Li+ ion in our products is nonstoichiometric due to the volatilization of lithium salt during sintering process. Furthermore, the presence of defects (such as vacancies) has been
proven by the following PALS analysis. Considering the stability of SiO₄ tetrahedra, it is difficult to form an oxygen vacancy; therefore, Li₂Fe₂⁺Fe³⁺SiO₄ would be formed to keep the charge balance. The existence of Li₂Fe₂⁺Fe³⁺Fe³⁺SiO₄ sheds a brilliant light on the existence of Fe³⁺. In addition, the pre-edge feature of these Li₂Fe-SiO₄ spectra (labeled P in Fig. 3a) is clearly enhanced. This is consistent with the non-centrosymmetric tetrahedral coordination allowing p/d hybridization and introducing dipole transitions into the pre-edge states. The standard compounds are octahedrally coordinated and have mostly weaker quadrupole transition matrix elements into the pre-edge d-state related features. Fig. 3b shows the Co K-edge spectra for the Co-doped LFS/C sample and four Co reference compounds: Co²⁺O, La₂Co²⁺VO₄, LaCo²⁺O₃, and SrCo⁴⁺O₃. It can be seen from Fig. 3b that with increase of the Co formal valence from +2 to +3 and then to +4, there is a substantial chemical shift to higher energy. The strong variation between the edge onset features is also evident when comparing the edge sharing octahedral environment in CoO to the double perovskite, corner sharing octahedra in La₂CoO₃. This variation leads to an energy elongated region for the onset behavior for Co²⁺⁴. It is observed from Fig. 3b that both the chemical shift and the broadened onset feature for the Co K-edge of the Co-doped Li₂FeSiO₄ are similar to the CoO standard. The Fe-edge onsets for the same compound seen in the previous figure were similar of the two step broadened type. Again the Co K-pre-edge feature (labeled P in Fig. 3b) is enhanced. The assignment of the Co²⁺⁴ state for substituted Co in Li₂FeSiO₄ is supported by the chemical shift of the edge. Moreover, based on the shape of the edge rise and the pre-edge enhancement, it is probable that the Co goes onto tetrahedral sites (similar to the Fe) in the crystal structure.

Positron annihilation lifetime spectroscopy (PALS) is a useful tool to study defects in solids, which can provide useful information about the size, type, and relative density of various defects [33–35]. To further investigate the effect of Co-doping on the structure of LFS, PALS measurements were also performed for LFS/C and Co-doped LFS/C samples. Table 2 lists the lifetime components (t₁, t₂, and t₃) and corresponding relative intensities (I₁, I₂, and I₃) for both samples. The longest component t₃ is due to the annihilation of orthopositronium atoms formed in the pores present in the material [33]; moreover, the relative intensity I₃ is the weakest (<4%), so it will not be discussed in the present work. The shortest component t₁ corresponds to the free annihilation of positrons in defect-free crystal and those trapped by small defects [34]. The intermediate lifetime t₂ is assigned to the annihilation events from the imperfect crystal with large number of defects (such as vacancies, pores and cavities, etc.) present in the material [33,35], which relative intensity I₂ quantifies the abundance of defects [34].

As can be seen in Table 2, for both samples, the intensity distribution of I₁ or I₂ is close to 50%, which demonstrates that the positron annihilation mechanism is not single, i.e., the positron annihilation occurs not only in the interior of the grains, but also in the defect position (such as vacancies, pores and cavities, etc.). For both samples, t₂ is longer than t₁, indicative of the existence of large defects in the two LFS composites. It is interesting to find that, after Co-doping, the ratio of I₂/I₁ increases from 0.81 to 1.20, indicating the change of the main annihilation mechanism from free capture to defect capture and the increase of large defects concentration. The increased defects are more conducive for Li⁺ ions diffusion [36]. Compared with LFS/C, Co-doped LFS/C exhibits shorter positrons annihilation lifetime t₁ and intermediate lifetime t₂, which indicates Co-doping makes not only the size of small defects but also the size of large defects decrease. It is generally known that positron annihilation lifetime is inversely proportional to electron density. That is to say, the shorter positron annihilation lifetime, the higher the electron density is. Therefore, the shortened positron annihilation lifetime implies a higher electronic conductivity. As shown in Table 2, compared with LFS/C, Co-doped LFS/C shows shorter t₁ and t₂, which means that Co-doped LFS/C sample should exhibit higher electronic conductivity, which agrees well with the measured electronic conductivity in Table 3 (i.e., 2.8 × 10⁻⁴ S cm⁻¹ for LFS/C, and 5.6 × 10⁻⁴ S cm⁻¹ for Co-doped LFS/C).

Fig. 4 shows the FESEM images of LFS/C and Co-doped LFS/C samples. LFS/C particles are to some extent agglomerated with a wide size distribution from 100 nm to 500 nm. There is no obvious difference in morphology after Co-doping, but Co-doped LFS/C sample shows less agglomeration and smaller particle size. The
structure and morphology of Co-doped LFS/C powders were further confirmed by TEM. As shown in Fig. 5a, it is obvious that the Co-doped LFS/C composite material is composed of many nanocrystals embedded in amorphous carbon network, resulting in an increased electronic conductivity for LFS. The clear crystal planes (with a d-spacing of 0.633 nm corresponding to the (010) planes and a d-spacing of 0.253 nm corresponding to the (022) planes for Co-doped LFS/C) can be observed in Fig. 5b, which indicates that high crystallinity of Co-doped LFS/C is obtained after the calcination process. The intensity ratio of D and G bands for graphitization of pyrolytic carbon is usually used to evaluate the graphitization degree of carbon. The intensity ratio of D and G bands of the residual carbon in both samples, respectively, are calculated to be 1.72 and 1.68, respectively. The intensity ratio of D (sp3-type) and G (sp2-type) bands of the residual carbon in both samples are 1.72 and 1.68, respectively.

Two intense broad bands at ~1350 and ~1600 cm\(^{-1}\) are assigned to the D (sp\(^3\)-type) and G (sp\(^2\)-type) bands of the residual carbon in both samples, respectively [37]. The intensity ratio of D and G bands is usually used to evaluate the graphitization degree of carbon. The lower \(I_D/I_G\) ratio means more carbon with sp\(^2\)-type in sample, that is to say, the lower \(I_D/I_G\) ratio, the higher the electronic conductivity of the residual carbon is. In this case, the \(I_D/I_G\) ratio of LFS/C and Co-doped LFS/C are calculated to be 1.72 and 1.68, respectively. The lower \(I_D/I_G\) for Co-doped LFS/C is ascribed to catalytic activity of Co for graphitization of pyrolytic carbon [38–41], leading to higher electronic conductivity. This result is in good agreement with the measured electronic conductivity shown in Table 3.

The first two charge–discharge cycles and the cyclic performance of LFS/C and Co-doped LFS/C samples are shown in Fig. 8. Both charge and discharge processes are conducted with a current rate of 0.1 C in a voltage range of 1.5–4.6 V. As shown in Fig. 8a, two potential plateaus (~3.2 V and ~4.5 V) can be observed in the initial charge curves for both samples, which are in good agreement with previous reports [12,13]. The first potential plateau at ~3.2 V is associated with the Fe\(^{3+}/Fe^{2+}\) redox couple [12,13]. However, compared with pristine LFS/C electrode, Co-doped LFS/C electrode exhibits a more obvious potential plateau at ~3.2 V due to less polarization. Subsequently, the potential plateau at ~3.2 V shifts to ~2.8 V in the second charge process, which can be explained by a structural rearrangement in which some of the Li ions (in the 4b site) and Fe ions (in the 2a site) become interchanged [42], which is also consistent with the result from DFT calculations [43]. The second voltage plateau at ~4.2 V corresponds to the Fe\(^{3+}/Fe^{2+}\) redox couple proved by D. Lv et al. [14]. In the second charge/discharge process, 1C-rate was carried out for 10 cycles. From Fig. 9a, it is found that, in all cases, the discharge capacity of Co-doped LFS/C is higher than that of LFS/C. The cycling performance of LFS/C and Co-doped LFS/C at a high C-rate, i.e., 3 C, was also investigated. As seen in Fig. 9b, after 50 cycles, Co-doped LFS/C still delivers a reversible capacity of 162.5 mAh g\(^{-1}\), whereas LFS/C exhibits a capacity of 138.2 mAh g\(^{-1}\).

Fig. 9 shows the rate capability of LFS/C and Co-doped LFS/C, which was tested in a mode such that all cells were charged under a small rate of 0.1 C (0.1 C = 16.6 mA g\(^{-1}\)) to 4.6 V and then discharged at different C-rate (0.5 C, 1 C, 2 C, 5 C and 0.5 C) to 1.5 V, and each C-rate was carried out for 10 cycles. From Fig. 9a, it is found that, in all cases, the discharge capacity of Co-doped LFS/C is higher than that of LFS/C. The cycling performance of LFS/C and Co-doped LFS/C at a high C-rate, i.e., 3 C, was also investigated. As seen in Fig. 9b, the discharge capacity gradually decreases in the first several cycles for both samples because of the structural rearrangement, but slightly increases with increasing cycle number in the subsequent cycles due to the gradual penetration of electrolyte into the electrode and the structural stability of LFS. After 100 cycles, Co-doped LFS/C electrode delivers a much higher discharge capacity of 142.5 mAh g\(^{-1}\) than LFS/C (75.7 mAh g\(^{-1}\)). Obviously, Co-doping can effectively improve the electrochemical performance of LFS/C.

To further study the electrochemical behavior of LFS/C and Co-doped LFS/C, we have performed CV tests at a slow scanning rate of 0.05 mV s\(^{-1}\). As can be seen in Fig. 10, for LFS/C, two obvious anodic peaks at ~3.10 V and ~4.20 V corresponds to the successive two steps of oxidation of Fe\(^{2+}/Fe^{3+}\) to Fe\(^{3+}/Fe^{4+}\) [44], and the cathodic peaks at ~2.58 V and ~3.85 V are associated with the reduction reaction of Fe\(^{3+}/Fe^{2+}\) and Fe\(^{2+}/Fe^{3+}\), respectively. The Fe\(^{3+}/Fe^{4+}\) redox is indicative of more than one Li\(^+\) ion extraction/insertion [12,45,46]. Noting that, larger current at ~4.20 V for Co-doped LFS/C is indicative of the more second Li\(^+\) ion extraction/insertion. Of course, we can't exclude the possibility of overlap of the anodic peak corresponding to Co\(^{2+}/Co^{3+}\) [30]. Besides, both samples exhibit an obvious anodic peak at ~4.56 V, which might be ascribed to the...
Corresponds to the solution resistance of the cell (cells at open-circuit potential). The small intercept at high frequency corresponds to the solution resistance of the cell ($R_s$); the depressed semicircle at medium frequency is attributed to the charge-transfer resistance at the electrode/electrolyte interface ($R_{ct}$) and the double-layer capacitance between the electrolyte and cathode ($C_d$); the inclined line at low frequency is assigned to a Warburg impedance related to the diffusion of lithium ions within the electrode ($Z_m$) [31]. The semicircle in the medium frequency range is related to the charge transfer resistance. The smaller the semicircular diameter, the lower the charge-transfer resistance is. The lower charge-transfer resistance is advantageous for intercalation/deintercalation of Li ions to give a better electrochemical performance. From Fig. 11, it is obvious that the Co-doped LFS/C electrode shows a much lower charge-transfer resistance. Furthermore, Li$^+$ ion diffusion in the cathode materials can be calculated from the relationship between $Z'$ and the reciprocal square root of the lower angular frequencies ($\omega^{-1/2}$) [18, 49]. Table 4 lists the Li$^+$ ion diffusion coefficient for both samples. It can be seen that the lithium ion diffusion coefficient for Co-doped LFS/C is higher than that of LFS/C, which indicates that Co-doping can effectively improve the lithium ion mobility of LFS/C.

Fig. 11. (a) Nyquist plots, and (b) The relationship between Z' and $\omega^{-1/2}$ in the low-frequency range of the as-prepared samples.

4. Conclusions

Co-doped Li$_2$FeSiO$_4$/C composite was successfully synthesized via a solid-state reaction assisted with refluxing method, and its physicochemical properties and electrochemical performance were also investigated. XRD results confirm Co-doping cannot change the monoclinic structure of LFS. XPS and XAS results reveal that Co successfully entered into the lattice of LFS and Co-doping does not change the oxidation state of Fe. PALS analysis demonstrates that Co-doping can increase the defect concentration, and the defect capture is the main annihilation mechanism in Co-doped LFS/C material. Electrochemical tests indicate that the Co-doped Li$_2$FeSiO$_4$/C exhibits higher reversible capacity at any C-rate compared to pristine Li$_2$FeSiO$_4$/C. The enhancement in the electrochemical performance is attributed to the reduced particle size, the increased defect concentration, the improved electronic conductivity, the decreased charge-transfer resistance, and the enhanced Li$^+$ ion diffusion coefficient. Our work indicates that this Co-doped Li$_2$FeSiO$_4$/C is a promising alternative for next-generation lithium ion batteries.

Acknowledgments

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References


Table 4

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<tr>
<th>Samples</th>
<th>LFS/C</th>
<th>Co-doped LFS/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{Li} (\text{cm}^2 \text{s}^{-1})$</td>
<td>$5.37 \times 10^{-13}$</td>
<td>$1.20 \times 10^{-12}$</td>
</tr>
</tbody>
</table>