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# PAPER

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## 1. Introduction

The demand for cost-competitive LIBs with enhanced energy density and high safety has motivated extensive research into various advanced cathode materials.<sup>1-4</sup> In this context, the discovery and commercial success of olivine LiFePO<sub>4</sub> has been instrumental in directing considerable research activities on cathode materials built on three-dimensional frameworks of polyanions ( $XO_4^{n-}$ , X = Si, P, and S).<sup>5</sup> The positive attributes of polyanionic frameworks include their structural stability, increased redox potential as a result of inductive effect, and

# Unveiling the mechanism of improved capacity retention in $Pmn2_1$ Li<sub>2</sub>FeSiO<sub>4</sub> cathode by cobalt substitution<sup>†</sup>

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Li<sub>2</sub>FeSiO<sub>4</sub> (LFS) is a sustainable Li-ion cathode material composed of earth-abundant elements with potentially high energy density but suffers from limited reversible storage capacity (less than one Li), low intrinsic conductivities, and cycling instability. In search of deeper understanding of the structural chemistry of LFS towards overcoming some of these challenges, the viability of Fe-site doping by Co and other dopants in *Pmn*2<sub>1</sub> LFS is investigated using both first-principles calculations and experimental testing. Computational results suggest that the formation of Li<sub>2</sub>Fe<sub>1-x</sub>Co<sub>x</sub>SiO<sub>4</sub> is energetically favorable, predictions confirmed by successful hydrothermal synthesis. Substitution of Co in LFS is revealed to have a dual effect; firstly catalyzing faster electrochemically induced phase transformation to the stable inverse-*Pmn*2<sub>1</sub> phase; and secondly enabling the formation of a low-resistant, uniform and stable fluorine-rich cathode-electrolyte interphase (CEI) layer that inhibits detrimental reactions between the cathode and electrolyte. As a result, Co-substituted LFS displays enhanced reversibility with 95% capacity retention after 50 cycles as compared to 80% of the undoped LFS.

versatility toward cation and anion substitution.<sup>5</sup> LiFePO<sub>4</sub>, however, has reached its limitation of energy density.<sup>6</sup> In search of higher capacity polyanionic materials, transition metal orthosilicates, particularly Li<sub>2</sub>FeSiO<sub>4</sub> (LFS), are promising candidates as they can accommodate two Li-ions per transition metal, so theoretically having capacity of ~330 mA h g<sup>-1</sup>, twice the capacity of LFP.<sup>7-16</sup> Yet, the attainment of such high theoretical capacity from LFS has been hindered by several obstacles including low intrinsic electronic and ionic conductivities,<sup>10</sup> high voltage (~4.8 V vs. Li<sup>+</sup>/Li) required for accessing the above one-Li-capacity,<sup>17</sup> which could cause decomposition of the electrolyte,<sup>18-20</sup> and plausible participation of oxygen redox associated with structural instability.<sup>14,15</sup>

One strategy that has been pursued to overcome these material challenges with the electrochemical performance of  $\text{Li}_2\text{FeSiO}_4$  is  $\text{Fe}^{2+}$ -site cation doping. In this regard, various cations have been evaluated as dopants for the monoclinic LFS phase,  $P2_1/n$ , but not for the less common orthorhombic  $Pmn2_1$  phase. Among the dopants evaluated for  $P2_1/n$  are divalent cations such as  $\text{Mg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Sr}^{2+}$ , and sinvalent cations such as  $\text{Mg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Sn}^{4+}$ .<sup>21-34</sup> Some of these cations were found to improve the electrochemical properties of  $P2_1/n$  LFS. For example, aliovalent doping with  $\text{Ti}^{4+}$  was reported to profoundly enhance the structural stability and electrochemical activity of  $P2_1/n$  LFS, attributed to the strong hybridization between Ti 3d and 4s orbitals and O 2p orbital.<sup>32</sup> On the other hand,  $\text{Co}^{2+}$  was found to be the most effective divalent dopant in improving the rate

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<sup>†</sup> Electronic supplementary information (ESI) available: Fig. S1 containing Le Bail refinement results of powder X-ray diffractograms, Fig. S2 showing charge–discharge curves and SEM-EDS images of MgLFS, Fig. S3 showing charge–discharge curves of LFS and CoLFS at C/30, Fig. S4 illustrating the calculated total energies, voltages, and volume changes upon delithiation in LFS and CoLFS, Fig. S5 showing cyclic voltammetry measurements on LFS and CoLFS, Fig. S6 showing XPS spectra of Li 1s, Fe 2p, and Co 2p from the pristine and cycled electrodes of LFS and CoLFS. Table S1 listing the calculated total energies of Li<sub>2</sub>Fe<sub>0.94</sub>M<sub>0.06</sub>SiO<sub>4</sub>, Table S2 listing the calculated energies above the hull and potential decomposition phases, Table S3 tabulating the calculated voltage with comparison to the literature, Table S4 listing chemical diffusion coefficient  $D_{Li^+}$  of LFS and CoLFS, and Table S5 listing atomic percentages of C, O, F, P, and Si analysed from XPS spectra. See DOI: 10.1039/c9ta10287f

capability of LFS,<sup>24</sup> as in the case of  $\text{Co}^{2+}$  doping in Li<sub>2</sub>MnSiO<sub>4</sub> (ref. 35) and LFP.<sup>36</sup> The beneficial effect of  $\text{Co}^{2+}$  substitution in these previous studies have been attributed mainly to enhanced electronic and ionic conductivities *via* the introduction of defects.<sup>24</sup> But this conductivity enhancement effect does not shed light as to the structural stabilization effect  $\text{Co}^{2+}$  is known of and which is important to understand in our pursuit of Cofree cathode materials.<sup>37</sup>

It is the scope of this work to address this mechanistic gap in our understanding of the complex material chemistry effects Co substitution has by focusing on another important polymorph of LFS, i.e. a low-temperature orthorhombic structure in S.G. Pmn21.13 Pmn21 LFS has been found to be less electrochemically active in terms of capacity and cyclability than P21/n LFS9 and suffer also from capacity fading - the origin of which has not been elucidated,<sup>38,39</sup> hence offering an interesting intercalation host structure to study the effect of Co doping. Other than seeking to enhance its electrochemical performance and more generally the Co-doping chemistry of Pmn2<sub>1</sub>, it is of interest to examine how the solubility of Co substitution may differ from one LFS phase to the other and how it is influenced by the synthesis temperature.<sup>40,41</sup> In this context, first-principles DFT calculations can provide useful guideline for the selection of dopants via examination of the thermodynamic stability and other properties of the cation-substituted LFS compounds.42-45

In this work, we carried out first-principles calculations to examine the solubility of various cation dopants in Pmn21 LFS and subsequently prepared them via hydrothermal synthesis.46 As per computational guidelines, high-purity Li<sub>2</sub>Fe<sub>0.94</sub>Co<sub>0.06</sub>-SiO<sub>4</sub> (denoted as CoLFS) and Li<sub>2</sub>Fe<sub>0.94</sub>Mg<sub>0.06</sub>SiO<sub>4</sub> (denoted as MgLFS) were successfully prepared and electrochemically tested. In the meantime, Ni<sup>2+</sup> or Sr<sup>2+</sup>-substituted Pmn2<sub>1</sub> LFS could not be synthesized due to their high formation energies compared to other competing phases. A preliminary evaluation on the electrochemical performance of MgLFS revealed that the cyclability of MgLFS was even worse than the undoped LFS. Therefore, we focused on CoLFS which showed promise in enhancing the electrochemical performance and offering the opportunity to shed light on the stabilization effect Co doping plays. Galvanostatic charge-discharge, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) were applied to unveil the role of Co-substitution in improving the cyclability of LFS. Surface characterization by X-ray photoelectron spectroscopy (XPS) and Fourier Transform Infrared (FTIR) spectroscopy provided evidence of cobalt-enabled formation of a protective thin cathode-electrolyte interphase (CEI) contributing to cathode stability. DFT calculations provided insight as to the structural and electrochemical effects of cobalt in terms of energetics, redox potential, and structural changes during Liextraction in both Pmn21 and inverse-Pmn21 polymorphs.

### 2. Experimental

#### 2.1. Materials preparation

 $Li_2FeSiO_4$  and  $Li_2Fe_{0.94}M_{0.06}SiO_4$  (M = Mg, Co, Ni) were prepared by employing a hydrothermal method.<sup>46</sup> The starting materials used were lithium hydroxide monohydrate (98%) Paper

 $LiOH \cdot H_2O$ ), fumed silica (99%  $SiO_2$ ), iron(II) sulfate heptahydrate (98%  $FeSO_4 \cdot 7H_2O$ ), magnesium sulfate heptahydrate (98% MgSO<sub>4</sub> $\cdot$ 7H<sub>2</sub>O), cobalt(II) sulfate heptahydrate (98% CoSO<sub>4</sub>·7H<sub>2</sub>O), and nickel sulfate hexahydrate (99% NiSO<sub>4</sub>-·6H<sub>2</sub>O). For the preparation of Li<sub>2</sub>Fe<sub>0.94</sub>Sr<sub>0.06</sub>SiO<sub>4</sub>, Fe and Sr precursors were iron(II) chloride tetrahydrate (99%  $FeCl_2 \cdot 4H_2O$ ) and strontium chloride hexahydrate (99% SrCl<sub>2</sub>·6H<sub>2</sub>O) because of the limited solubility of strontium sulfate in water. All the chemicals were purchased from Sigma-Aldrich and used without purification. In a typical synthesis, SiO<sub>2</sub> powder was dissolved in LiOH aqueous solution.46 Mixed-metal solutions were prepared by mixing the required metal salts and dissolving them in water. The mixed-metal solution was then drop wisely added to the LiOH/SiO<sub>2</sub> solution. The concentration of Li<sup>+</sup> was 0.8 M in the precursor solution. The molar ratio of Li : (Fe + M) : Si was kept at 4 : 1 : 1 for all the syntheses. The as-formed precursor suspension was loaded to a 450 mL PTFE-lined stirred autoclave (Parr Instrument Company, Moline, IL). All these preparation steps were performed in a nitrogen-filled glovebox to avoid the oxidation of Fe(II) in alkaline solution. Hydrothermal synthesis was performed at 200 °C for 6 hours at a stirring speed of 300 rpm. A Parr 4848 reactor controller was used to control and monitor the temperature and pressure within the autoclave. After the completion of hydrothermal precipitation, the autoclave was cooled down to room temperature within 30 min. The obtained beige-greyish slurry was separated by centrifugation. The wet solid was rinsed with deoxygenated LiOH solution for two times and with acetone for one time, followed by drying in a vacuum oven at 80 °C for 12 hours. The obtained powders of LFS, CoLFS, and MgLFS were further subjected to annealing at 400 °C for 6 hours under Ar atmosphere and subsequently quenched to room temperature in a tube furnace. All the products were stored in glovebox to prevent the exposure to oxygen and moisture.

#### 2.2. Material characterization

X-ray Diffraction (XRD) characterizations were performed with a Bruker D8-Advantage powder diffractometer using Co-Ka radiation ( $\lambda = 1.78892$  Å, 35 kV; 15 mA) from  $2\theta = 15$  to  $100^{\circ}$  in a step size of 0.01°. XRD patterns were refined by Le Bail method with TOPAS Academic V.5.0 program to extract lattice parameters of the unit cell and check phase purity. A Hitachi SU-8230 cold-field emission Scanning Electron Microscope (CFE-SEM) (Hitachi High Technologies, Rexdale, Canada) was employed for morphology characterization and Energy-Dispersive X-ray Spectroscopy (EDS). X-ray Photoelectron Spectroscopy (XPS) measurements were performed on a PHI 5500 system using monochromatized Al-Ka at 1486.6 eV. The applied X-ray spot size was 400 µm. Electron flood gun was used for charge compensation. The spectrometer energy scale was calibrated using C 1s characteristic peak at 284.8 eV (C-C). Spectra of C 1s, O 1s, F 1s, P 2p, and Si 2p were fitted with single or multiple peaks. XPS data processing was performed with Thermo Avantage Software. Fourier Transform Infrared (FTIR) spectroscopy was carried out with Bruker's ALPHA platinum module in the wavenumber range of 400 to 4000  $\text{cm}^{-1}$ .

#### 2.3 Electrochemical measurements

The pristine powders collected after annealing were mixed with acetylene black (AB) in a weight ratio of 0.8 : 0.2 and ball-milled at 250 rpm for 3 hours using a planetary micro mill (Fritsch, Pulverisette 7 premium line). The working electrodes were prepared by spreading slurry of the ball-milled LFS (BM-LFS), acetylene black, and poly (vinylidene difluoride) (PVDF) in a weight ratio of BM-LFS: AB: PVDF = 0.8: 0.1: 0.1 onto aluminum foil. The resultant composite contains 64 wt% of active materials (LFS, MgLFS, or CoLFS), 26 wt% of AB, and 10 wt% of PVDF. Each final electrode contains approximately  $2.5 \text{ mg cm}^{-2}$  of active materials. Electrochemical testing was performed on Swagelok type half-cells using metallic lithium as the counter and reference electrode and two pieces of polypropylene film (Celgard 2200) as the separator in a standard electrolyte solution made of 1 M LiPF<sub>6</sub>/ethylene carbonate (EC)/ dimethyl carbonate (DMC) (1:1 by volume). Galvanostatic charge-discharge was conducted with an Arbin battery cycler at C/10 (16.6 mA  $g^{-1}$ ) or C/30 (5.5 mA  $g^{-1}$ ) rate in the voltage range between 1.5-4.5 V. The reported capacity values are based on the weight of active materials, excluding acetylene black and PVDF. Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) measurements were carried out on an electrochemical workstation (Bio-Logic). CV was performed between 1.5–4.5 V at a scan rate of 0.2 mV s<sup>-1</sup> for the first ten sweeps and then scanned at 0.1, 0.2, 0.3, 0.4, and 0.5 mV s<sup>-1</sup> successively. EIS measurements were made in the potentiostatic mode at open circuit voltage (OCV) after a 6 hour rest before and after the CV test. The frequency of EIS was between 1 MHz and 20 mHz. All the electrochemical measurements were performed at 45 °C.

For the *ex situ* characterizations of the cycled electrodes after CV tests, Swagelok cells were disassembled in an argon-filled glovebox. The electrodes were rinsed with DMC solvent and dried inside the antechamber under vacuum for 12 hours. The dried electrodes were then sealed and stored in the glovebox for further analyses.

## 3. Computational

Spin polarized density functional theory (DFT) calculations were performed in the Vienna *ab initio* simulation package (VASP) using the projector augmented wave (PAW) method.<sup>47,48</sup> Generalized gradient approximation Perdew–Burke–Ernzerhof (GGA-PBE) functional was employed.<sup>49</sup> Hubbard parameter correlation (GGA+U) was used to correct the interactions inside the d-orbitals of the transition metals. U values for Co, Fe, Mn, and Ni are 3.32, 5.3, 3.9, and 6.2 eV, respectively.<sup>50,51</sup> The cutoff energy was kept at 700 eV for all the calculations. A calculation is treated as converged if the forces on all of the nuclei were smaller than 0.01 eV Å<sup>-1</sup>.

The initial atomic configurations of  $Pmn2_1$  and inverse- $Pmn2_1$  Li<sub>2</sub>FeSiO<sub>4</sub> for the present calculations were adopted from Eames *et al.*<sup>52</sup> The difference between  $Pmn2_1$  and inverse- $Pmn2_1$ is that in inverse- $Pmn2_1$  half of the Li-ions interchange positions with all of the Fe-ions. Doping with a series of dopants, namely,

divalent Mg, Mn, Co, Ni, and Sr and aliovalent Ti and Zr were envisaged here.  $2 \times 2 \times 2$  supercells were constructed, and in each supercell one Fe was substituted by one dopant, giving a doping concentration of 6.25 atom% (shown in Fig. 1). This doping concentration was chosen as a comprise between the effectiveness of doping and the theoretical specific capacity; too low content of dopants may dilute the effect of doping while too high content would sacrifice the capacity from Fe<sup>2+</sup>/Fe<sup>3+</sup> redox reaction. The nominal formula of a doped Li<sub>2</sub>FeSiO<sub>4</sub> is represented as Li2Fe0.94M0.06SiO4, where M denotes the doping element. To evaluate the phase stability of the doped structures, all of the competing phases under the Li-Fe-Si-O-M compositional space were involved to build the energy convex hull.<sup>50</sup> In this case, the energy above the hull represents the thermodynamic driving force for a compound to decompose into the competing phases at the hull. This will therefore offer more accurate description about the stability and the potential phase transition of the compounds during synthesis. The structures of all the potential competing phases were taken from Materials Project database50 with followed-up DFT relaxation to ensure higher precision criterion as described above. In the assessment of delithiation process, particularly energy and volume changes, one or two Li-ions per formula unit was removed from Li2-FeSiO<sub>4</sub>, resulting in LiFeSiO<sub>4</sub> or FeSiO<sub>4</sub>. All of the structures were fully relaxed prior to further calculations. Note that in the delithiated inverse-Pmn21 LiFeSiO4, Li-ion occupies the original Li-site, which means it is the Li-ion on the Fe-site that has been removed from the host structure of Li<sub>2</sub>FeSiO<sub>4</sub>. Same approach was applied on Li2Fe0.94Co0.06SiO4 to understand its delithiation process.

## 4. Results and discussion

# 4.1. DFT-guided screening of potential dopants and experimental validation

First the theoretical feasibility of synthesizing a series of M doped-LFS in Pmn21 symmetry with 6.25% dopant concentration was evaluated using DFT calculations. The evaluated dopants (M) include divalent Mg, Mn, Co, Ni, Sr, and aliovalent Ti and Zr. The atomic configuration of Pmn2<sub>1</sub> Li<sub>2</sub>Fe<sub>0.94</sub>M<sub>0.06</sub>SiO<sub>4</sub> is shown in Fig. 1a. The  $Pmn2_1$  phase has a lower energy than the inverse-Pmn21 phase for all the dopants considered according to DFT calculations (results reported in Table S1<sup>+</sup>), hence we have assumed the Pmn21 will likely form during synthesis regardless of the dopant type. The experimental synthesis results presented later proved this hypothesis. Energies above the hull calculated for  $\text{Li}_2\text{Fe}_{0.94}M_{0.06}\text{SiO}_4$  are depicted in Fig. 1a. The values of energies and the potential decomposition phases are listed in Table S2.† As shown in Fig. 1a, doping of Zr is associated with extremely high energy above the hull of approximately 583 meV per atom. As energy above the hull represents the thermodynamic driving force for a compound to decompose into its competing phases at the convex hull, it is suggested that Zr-doped LFS is unlikely to form, even if higher synthesis temperatures and low doping concentrations are applied. Ti-doped LFS also shows a relatively high energy above the hull of about 33 meV per atom. An estimation based on



Fig. 1 Synthesis of different metal-substituted LFS compounds. (a) Energy above the hull of  $Pmn2_1 Li_2Fe_{0.94}M_{0.06}SiO_4$  (M = Mg, Mn, Co, Ni, Sr, Ti, and Zr) calculated by DFT. The inset shows atomic configuration of  $Pmn2_1 Li_2Fe_{0.94}M_{0.06}SiO_4$ , in which one Fe atom is replaced by one dopant in a 2 × 2 × 2 supercell. (b) XRD of Mg, Co, Ni, or Sr-involved Li<sub>2</sub>FeSiO<sub>4</sub> samples obtained by hydrothermal synthesis at 200 °C. Sticks at the bottom belong to the reference pattern of  $Pmn2_1 Li_2FeSiO_4$  (PDF# 01-080-3671). Stars and diamonds represent the impurities observed in Sr-LFS and Ni-LFS, respectively.

Boltzmann distribution<sup>53</sup> suggests that only 0.2% of Ti is possible to be doped into LFS at accessible hydrothermal temperatures (e.g. 200 °C). However, if the temperature is raised to 700 °C, the doping concentration can be increased to 4.3%. This may explain why Ti-doped  $P2_1/n$  LFS materials were reported by studies using high-temperature synthesis method.<sup>32,33</sup> Nevertheless, doping with high-valence cations seem to be limited to very low concentrations. Interestingly, a computational study on doping in the related LiFePO<sub>4</sub> system revealed that the substitution of high-valence dopants on either Li- or Fesite is highly unfavorable.<sup>40</sup> Sr- or Ni-substituted LFS possesses moderate energies above their competing phases. The lowest energies are found for substitution by Mn, Co, and Mg, which are less than 10 meV per atom above their energy hulls. This result suggests the possibility of doping a certain concentration of Mn, Co, or Mg into Pmn21 LFS under hydrothermal conditions. This finding is in agreement with a reported experimental study on  $Li_2Fe_{1-x}Mn_xSiO_4$  (x = 0-1) in which solid solutions were found to form by hydrothermal synthesis at 180 °C.54

To further validate this prediction, we examined experimentally the dopants identified to have relatively low formation energies (i.e. Mg, Co, Ni, and Sr that have less positive E above hull) with a nominal composition  $Li_2Fe_{0.94}M_{0.06}SiO_4$  (M = Mg, Co, Ni, Sr) via hydrothermal synthesis at 200 °C. XRD patterns of the as prepared powders are shown in Fig. 1b. Le Bail method was employed to refine the unit cell and check phase purity (see Fig. S1<sup>†</sup>). As shown in Fig. 1b and S1,<sup>†</sup> Mg- and Co-doped LFS materials have similar patterns as LFS, with all the diffraction peaks ascribed to Li<sub>2</sub>FeSiO<sub>4</sub> in space group Pmn2<sub>1</sub>. The similarity in XRD patterns suggests that Mg and Co being doped into LFS host lattice, which will be further evidenced by EDS elemental mapping presented in later section. As a comparison, XRD patterns from Ni- and Sr-involved samples show obvious signals from other Ni- or Sr-containing phases. The solubility of Ni in LFS is probably limited by the preferred formation of other compounds such as NiFe2O4 and NiO which are more stable

under the synthesis condition. As for Sr it formed a separate phase,  $SrSiO_3$ , rather than becoming incorporated in LFS lattice. These experimental results are consistent with the calculated formation energies (Fig. 1a), proving the validity and usefulness of the DFT calculations using in predicting new materials and material properties.

To this end, only MgLFS and CoLFS are concluded to be synthesizable by the hydrothermal process. A moderate postannealing at 400 °C was conducted on the hydrothermally synthesized powders with the aim to achieve improved electrochemical performance without changing the *Pmn*2<sub>1</sub> crystal structure. However, preliminary electrochemical evaluations revealed that the cyclability of MgLFS was even worse than the undoped LFS (Fig. S2†). Severe capacity loss associated with enlarging polarization were observed in MgLFS cycled at C/10. The cause for the observed adverse effect of Mg doping in LFS remains unclear. We chose CoLFS to further study the electrochemical performance of doped-LFS and compared it to LFS.

#### 4.2. Structural characterization

XRD patterns of the annealed LFS and CoLFS, shown in Fig. 2a, prove that both retained the Pmn21 crystal structure after annealing at 400 °C for 6 hours. It is consistent with previous studies that the Pmn21 phase of LFS is stable up to 500 °C.55 We constructed a quaternary phase diagram of the Li-Fe-Co-Si-O system (Fig. 2b) via the first principles DFT method. The thermodynamically stable phases within this chemical space are noted in the phase diagram. We can see from Fig. 2b that the major competing reaction for the formation of Li<sub>2</sub>Fe<sub>1-x</sub>Co<sub>x</sub>SiO<sub>4</sub> solid solution is its phase separation into a mixture of Li2FeSiO4 and Li<sub>2</sub>CoSiO<sub>4</sub>. This indicates that even if Co cannot be introduced into Li<sub>2</sub>FeSiO<sub>4</sub> lattice, it could still combine with other elements and form Li2CoSiO4, and this will give rise to a similar XRD pattern as  $Li_2Fe_{1-x}Co_xSiO_4$  due the similar electron densities between Co<sup>2+</sup> and Fe<sup>2+</sup>. Thus, SEM and EDS mappings were used to further confirm the substitution of Co in LFS



**Fig. 2** Structural and morphological characterizations of LFS and CoLFS. (a) X-ray diffraction patterns of LFS and CoLFS prepared by hydrothermal synthesis at 200 °C followed by annealing at 400 °C. The enlarged 2theta area from 25 to 45 degree are shown at the bottom. Sticks at the bottom belong to a reference pattern of *Pmn*2<sub>1</sub> Li<sub>2</sub>FeSiO<sub>4</sub> (PDF# 01-080-3671). Different peak intensities associated with (010), (011), and (200) planes are observed. (b) Calculated quaternary phase diagram of the Li–Fe–Co–Si–O system in accordance to Li<sub>2</sub>O, FeO, CoO, and SiO<sub>2</sub>. Dashed red line in the phase diagram presents Li<sub>2</sub>Fe<sub>1-x</sub>Co<sub>x</sub>SiO<sub>4</sub> (x = 0-1), in which the star presents the composition of Li<sub>2</sub>Fe<sub>0.94</sub>Co<sub>0.06</sub>SiO<sub>4</sub>. (c) Scanning electron microscopy images of LFS and CoLFS. (d) Energy dispersive spectroscopic mappings of Fe, Co, Si, and O in CoLFS.

lattice. SEM images in Fig. 1c reveal that LFS and CoLFS particles exhibit similar crystal size and morphology – both crystallized as mesocrystals (~1  $\mu$ m) assembled by irregular nanoplates. Details about the hydrothermal formation of LFS mesocrystals can be found in our precious work.<sup>46</sup> EDS elemental mappings on CoLFS particles (Fig. 2d) demonstrate uniform distributions of Fe, Co, Si and O, confirming that Co has been successfully incorperated to the host matrix of LFS, rather than forming separated Li<sub>2</sub>CoSiO<sub>4</sub> particles.

Although XRD patterns of both LFS and CoLFS can be indexed to the  $Pmn2_1$  symmetry, a careful comparison between these two patterns reveals that several peaks exhibit different intensities between LFS and CoLFS. As demonstrated in the enlarged 2theta region (Fig. 2a), three peaks at 19.1°, 28.4° and 33.1° in CoLFS have lower intensities than those in LFS. In *Pmn2*<sub>1</sub> polymorph, peaks at 19.1°, 28.4° and 33.1° ( $\lambda = 1.7889$  Å) correspond to the reflections from (010), (011) and (200) lattice planes, respectively. The difference in the peak intensity indicates that LFS and CoLFS have different electron densities in the corresponding lattice planes. Considering that Fe<sup>2+</sup> and Co<sup>2+</sup> have similar electron densities, variation in peak intensities would originate from different amount of Fe/Li and/or Co/Li antisite defects.<sup>56</sup> The lower XRD peak intensities from CoLFS than LFS suggest that there are more antisite defects in CoLFS than LFS. To confirm this hypothesis, we simulated the XRD patterns of CoLFS in ideal *Pmn2*<sub>1</sub> structure where Co sits on the

Fe-site *vs.* CoLFS with a local Co/Li antisite defect (one Co exchanges site with one Li) using VESTA software.<sup>57</sup> As shown in Fig. 3, the presence of Co/Li antisite defect results in lower



**Fig. 3** Effect of the position of Co on the corresponding peak intensities in XRD. (a) Crystal structures of  $Pmn2_1$  Li<sub>2</sub>Fe0.<sub>94</sub>Co<sub>0.06</sub>SiO<sub>4</sub> (CoLFS) in which Co occupies Fe-site (left) vs. CoLFS with a Co/Li antisite defect (right). Li (green), Fe (brown), Si (blue), O (red), and Co (purple). Co/Li antisite is pointed out by arrows. (b) Simulated X-ray diffraction patterns by VESTA software.<sup>57</sup> The existence of Co/Li antisite defect results in lower reflection intensities from (010), (011), and (200) planes.

reflection intensities from (010), (011), and (200) planes. The simulation results (Fig. 3b) agree very well with the experimental XRD (Fig. 2a). From the energetic point of view, we calculated the total energies of Li<sub>2</sub>FeSiO<sub>4</sub> and Li<sub>2</sub>CoSiO<sub>4</sub> in both *Pmn*2<sub>1</sub> and inverse-*Pmn*2<sub>1</sub> structures. Inverse-*Pmn*2<sub>1</sub> is formed when all the Fe and Co exchange sites with Li. Interestingly, the stable structure for Li<sub>2</sub>FeSiO<sub>4</sub> is *Pmn*2<sub>1</sub>, which has energy ~0.04 eV per f.u. lower than inverse-*Pmn*2<sub>1</sub> (*i.e.* -53.13 eV per f.u. *vs.* -53.09 eV per f.u.). On the contrary, Li<sub>2</sub>CoSiO<sub>4</sub> is more stable in inverse-*Pmn*2<sub>1</sub> structure rather than in *Pmn*2<sub>1</sub> structure (-51.68 eV per f.u. *vs.* -51.65 eV per f.u.). This energy difference suggests that when Co is incorporated into LFS matrix during synthesis, it may prefer to take the Li-site and leads to the formation of a Co/Li antisite.

#### 4.3. Electrochemical properties

The influence of Co substitution on the electrochemical activity of  $Pmn2_1$  LFS was evaluated by galvanostatic charging–discharging of LFS and CoLFS half-cells using Li metal as the counter and reference electrodes. Fig. 4a and d present the voltage profiles of LFS and CoLFS during galvanostatic cycling at C/10 in the range of 1.5–4.5 V, respectively. Both cells delivered discharge capacity of about 100 mA h g<sup>-1</sup> in their initial cycles, corresponding to the intercalation of 0.6 Li per f.u. The low material utilization at C/10 is a consequence of poor intrinsic electronic and ionic conductivities that result in high polarizations as can be observed in Fig. 4a and d. At a lower current rate of C/30, higher capacities up to 125 mA h g<sup>-1</sup> can be achieved (see Fig. S3<sup>†</sup>). Fig. 4b and e show



**Fig. 4** Electrochemical cycling performance of LFS and CoLFS. (a and d) Voltage profiles in the  $1^{st}$ ,  $2^{nd}$ ,  $10^{th}$  and  $50^{th}$  cycles at C/10 between 1.5 - 4.5 V at  $45 \,^{\circ}$ C. (b and e) Discharge capacity retention (solid symbols, left) and coulombic efficiency (open symbols, right) of LFS (blue) and CoLFS (red) in 50 cycles cycled at C/10 between 1.5 - 4.5 V at  $45 \,^{\circ}$ C. (c and f) Differential capacity, dQ/dV vs. voltage corresponding to (a) and (d), respectively. Arrows point out the shift of charge and discharge voltages in the initial cycles.

that LFS encountered serious capacity loss that there was only 80% capacity retention after 50 cycles at C/10, while CoLFS exhibited correspondingly at least 95% capacity retention. The same phenomenon of capacity loss in  $Pmn2_1$  LFS has been reported in other studies,<sup>38,39</sup> but an in-depth elucidation of the underlying mechanism responsible for this behavior remains unclear.

It is noticed that the charge voltage profiles of both LFS and CoLFS shift downward after the formation cycle. Similar voltage drop is quite typical in  $P2_1/n$  LFS, as a result of phase transformation to inverse-Pmn21 phase based on experimental and computational studies.58 Such electrochemically induced phase transformation is driven by the energy difference (~0.3 eV per f.u.) between  $P2_1/n$  and inverse-*Pmn2*<sub>1</sub> symmetries in the delithiated LFS with composition LiFeSiO<sub>4</sub>, hence resulting in a ~0.3 V voltage drop after the phase transformation. We hypothesized that similar phase transformation, from the mother matrix of  $Pmn2_1$  to the inverse-*Pmn2*<sub>1</sub> phase, would occur as well upon cycling. This indeed is supported by our calculation results. We calculated the energetics of  $\text{Li}_{y}\text{Fe}_{1-x}\text{Co}_{x}\text{SiO}_{4}$  (x = 0, 0.0625; y = 0, 1, 2) and found a similar energy trend as that in  $P2_1/n$  LFS. Fig. S4<sup>†</sup> shows that for the fully lithiated composition, *i.e.*  $Li_2Fe_{1-x}Co_xSiO_4$ , the total energy of inverse-Pmn21 phase is only about 0.04 eV per f.u. higher than the Pmn21 phase. These similar energies could explain why a certain content of Fe/Li or Co/Li antisite is found in the as-synthesized LFS. On the contrary, when one Li is extracted, corresponding to the composition  $LiFe_{1-r}Co_rSiO_4$ , the total energy of inverse-Pmn2<sub>1</sub> is about 0.3 eV per f.u. lower than that of *Pmn2*<sub>1</sub>. Because of the substantial lower energy, phase transformation from Pmn21 to inverse-Pmn21 could take place upon delithiation. Cell voltages (vs. Li<sup>+</sup>/Li) can be calculated from total energies according to the following equations.

$$E (y = 2 \rightarrow 1, V) = E_t (\text{Li}_2\text{Fe}_{1-x}\text{Co}_x\text{SiO}_4, eV) - E_t (\text{LiFe}_{1-x}\text{Co}_x\text{SiO}_4, eV) - E_t (\text{Li}, eV)$$
(1)

$$E (y = 1 \rightarrow 0, V) = E_t (\text{LiFe}_{1-x}\text{Co}_x\text{SiO}_4, eV) - E_t (\text{Fe}_{1-x}\text{Co}_x\text{SiO}_4, eV) - E_t (\text{Li}, eV)$$
(2)

The calculated cell voltages are shown in Fig. S4<sup>†</sup> and listed in Table S3<sup>†</sup> together with the reported values in the literature for comparison. As the cell voltage is proportional to the energy change associated with (de)lithiation, the voltage of  $Fe^{2+}/Fe^{3+}$ redox couple in inverse-*Pmn2*<sub>1</sub> is about 0.3 V lower than that in *Pmn2*<sub>1</sub>. After doping with Co, the calculated cell voltage is slightly higher than the undoped compound, while the difference between two phases remains as ~0.3 V.

Crystal structure stability is one of the key factors that affect capacity retention. To evaluate the structural stability of LFS and CoLFS in the one-Li extraction region, volume changes between Li<sub>2</sub>FeSiO<sub>4</sub> and LiFeSiO<sub>4</sub> in either *Pmn*2<sub>1</sub> or inverse-*Pmn*2<sub>1</sub> structure were calculated by DFT and plotted in Fig. S4.† It is found that upon the removal of one Li, Li<sub>2</sub>FeSiO<sub>4</sub> undergoes 1.68% and 3.19% volume expansions in its *Pmn*2<sub>1</sub> and inverse-*Pmn*2<sub>1</sub> polymorphs, respectively. It is consistent with the results reported by Eames *et al.* that the inverse structure was found to go through larger volume expansion than the normal  $Pmn2_1$ .<sup>52</sup> In regard to Li<sub>2</sub>Fe<sub>0.94</sub>Co<sub>0.06</sub>SiO<sub>4</sub>, its  $Pmn2_1$  structure expands by 1.68%, whereas its inverse- $Pmn2_1$  structure expands by 3.16% upon the removal of one Li. If the assumption of taking inverse- $Pmn2_1$  as the cycled structure is true, the minor volume changes infer that LFS and CoLFS in either  $Pmn2_1$  or inverse- $Pmn2_1$  are structurally stable when removing one Li. Within the applied voltage range (*i.e.* 1.5–4.5 V), only the first Li charged was compensated by Fe<sup>2+</sup>/Fe<sup>3+</sup>. In this regard then, irreversibility caused by plausible oxygen redox activity could be ruled out.

#### 4.4. Electrochemically-induced structural evolution

The voltage-capacity profiles in Fig. 4a and d reflect a progressive variation in the initial 10 cycles during charge, which suggest the cathode compounds have experienced an electrochemical activation process. Such electrochemical activation is enabled by the phase transformation in the bulk and surface reconstruction. To understand this activation process more clearly, dQ/dV curves (Fig. 4c and f) were derived from the corresponding voltage profiles. Upon the first charge cycle from the open-circuit voltage at  $\sim$ 2.8 V to the cut-off voltage at 4.5 V, a rather diffused peak appears at  $\sim$ 3.6 V for LFS and  $\sim$ 3.5 V for CoLFS, respectively. Considering that the theoretical charge voltage is at  $\sim$ 3.0 V (Fig. S4<sup>†</sup>), the average overpotential due to internal resistances is about 0.5 V and 0.4 V for LFS and CoLFS, respectively. Such diffused peaks associated with high overpotentials indicate very sluggish and complex kinetics of Li transport in the formation cycle. In a previous study, we found spontaneous reaction between LPF6-EC/DMC electrolyte and uncharged LFS prior to any cycling treatment that resulted in de-lithiation and Fe oxidation to Fe<sup>3+</sup>.59 Moreover, pristine LFS particles synthesized by hydrothermal method have always been found to contain a certain level of Fe<sup>3+</sup> even though a careful handling was taken.13,46 A deactivated surface will not only obstruct the mass transfer through the surface but also interfere with intercalation in the bulk. This also explains why the coulombic efficiency (CE) in the first cycle is larger than 100% (i.e. discharge capacity > charge capacity) for either of LFS or CoLFS (Fig. 4b and e). Thus, a surface reconstruction process is required to reactivate the delithiation and the subsequent relithiation process. After the formation cycle, the charge peak at 3.5 V/3.6 V transforms into a broad shoulder appearing in the range of 2.5–4 V. In the  $10^{\text{th}}$  cycle, dQ/dV curve of charge shows a peak at  $\sim 2.8$  V, corresponding to the inverse-*Pmn*2<sub>1</sub> phase which has theoretical charge voltage at  $\sim$ 2.7 V. The better resolved peak and the lowered overpotential reflect that upon cycling, re-ordering between Fe and Li gives rise to betterestablished channels that have low energy barriers for Li-ion diffusion, and thus enhanced delithiation kinetics.

Contrary to the variation observed in charge voltage profiles, the evolution of discharge profiles is relatively stable with only subtle changes for both LFS and CoLFS. The asymmetric shape of charge and discharge voltage curves (Fig. 4a and d) implies that the kinetics of Li-ion storage and phase transformation during lithiation (discharge) are completely distinct from the delithiation (charge) process. The corresponding dQ/dV curves

(Fig. 4c vs.Fig. 4f) confirm the steady discharge process upon cycling while notably, obvious distinction between LFS and CoLFS during discharge is revealed. As it is shown, CoLFS reached a stable discharge voltage at  $\sim$ 2.7 V even in the first cycle, whereas LFS proceeded through a progressive voltage drop from  $\sim$ 2.9 V to  $\sim$ 2.6 V. This indicates that CoLFS may complete the phase transformation in the first cycle and avoid unnecessary intermediate phases, while the un-doped LFS experienced rather slow phase transformation across multiple intermediate stages between the initial and the final structures. Such structure-dependent phase transformation kinetics have been reported previously for the three polymorphs of LFS:  $P2_1/n$ and Pmnb exhibited faster phase transformation than Pmn21 due to higher disorder degrees in the cation connectivity.<sup>13</sup> It is therefore reasonable to assume that, for the present study, substituting a small amount of Co for Fe induces more TM/Li antisite defects in the as-synthesized material (Fig. 1a), and these pre-existing TM/Li antisite defects work as nuclei that facilitate the phase transformation to inverse-Pmn21 as a consequence of cation rearrangement upon cycling. Evidence of creation of antisites serves as nucleation "catalyst" in phase transformation of  $P2_1/n$  to inverse  $Pmn2_1$  has been noted also by Lu et al.14 A rapid phase transition is preferred because it could avoid the formation undesired intermediate phases that would cause blockage of Li diffusion and unnecessary energy losses.

The distinction between charge and discharge as well as the difference between LFS and CoLFS are further revealed by cyclic voltammetry (CV), shown in Fig. 5. CV was conducted at a scanned rate of 0.2 mV s<sup>-1</sup> from 1.5 V to 4.5 V for ten sweeps. In the voltage window of 1.5-4.5 V vs. Li<sup>+</sup>/Li, the only redoxactive couple in the active materials is Fe<sup>2+</sup>/Fe<sup>3+</sup> because the oxidation of Co<sup>2+</sup> would require a voltage higher than 4.5 V.<sup>60</sup> For either LFS or CoLFS (Fig. 5a and b), a wide but well-resolved cathodic (=reduction) peak is shown. This peak remains stable upon cycling, which is similar to the steady discharge voltage profiles shown in Fig. 4, although the peak shift observed in LFS is only slightly reflected in its CV curves. On the contrary, the anodic (=oxidation) curves go through significant changes in shape and intensities in the first 10 sweeps. This is again, consistent with the general trend observed in galvanostatic charge voltage profiles (Fig. 4). For both LFS and CoLFS, it takes about six CV scans for the anodic curves to become stable. The 1<sup>st</sup> scan, giving rise to poorly resolved anodic peaks, confirms that the starting structures are nearly electrochemical inactive. After a few cycles, multiple peaks can be observed along with enhanced intensities, demonstrating a progressive activation process. The existence of multiple anodic peaks and their evolution can be attributed to the continuous surface reconstruction and phase transformation occurring during cycling which ultimately affect the kinetics of Li-ion diffusion. As discussed earlier, such phase transformation could be promoted by the TM/Li cation mixing.

The asymmetry between anodic and cathodic curves indicate different diffusion mechanisms during delithiation and lithiation processes. Different to the delithiation process, the lithiation process is more stable and progresses at enhanced kinetics from the beginning. This could be attributed to surface reconstruction taking place in the preceding delithiation cycle and also to the Li-vacancies that are generated after delithiation, both factors facilitating Li-ion transport. This phenomenon is also reflected in the galvanostatic charge-discharge results (Fig. 4a and b), where most of changes take place during charging rather than discharging process.

To demonstrate the evolution of anodic peak more clearly, the anodic curves of the 1st, 2nd, 5th, and 10th cycles were deconvoluted to four Gaussian peaks denoted as A1, A2, A3, and A<sub>4</sub> and shown in Fig. 5c and d. Detailed deconvolution process can be found in ESI.† The four peaks can be seen there to be centered at approximately 2.5 V, 2.9 V, 3.5 V, and 3.8 V, respectively. In the 1<sup>st</sup> sweep, A<sub>4</sub> occupies the largest area, with the other three peaks sharing similar areas. The dominant presence of A<sub>4</sub> is seen slightly more pronounced in LFS than that in CoLFS. In the following cycles, one can see that A4 slowly fades out till the 10<sup>th</sup> anodic sweep in LFS, while it almost disappears from the  $2^{nd}$  sweep in CoLFS. Simultaneously,  $A_3$  (at  $\sim$ 3.5 V) increases with scanning cycles, and the buildup of A<sub>3</sub> seems related to the reduction of A<sub>4</sub>. The A<sub>4</sub>, centering at  $\sim$ 3.8 V, is considered to be associated to the delithiation (oxidation) reaction occurring in the initial surface of the active particles. Thus, the decreasing intensities of A<sub>4</sub> imply structural reconstruction in the surface layer, which is apparently much faster in CoLFS than LFS. The  $A_3$  (~3.5 V) could be linked to the delithiation reaction from the Pmn21-dominant bulk region, whereas the  $A_2$  (~2.9 V) can be assigned to inverse-*Pmn*2<sub>1</sub>dominant region. A<sub>2</sub> grows with number of cycles due to continuous phase transformation. Again, the relatively fast kinetics in CoLFS is attributed to the pre-existing TM/Li antisite defects - created by Co substitution - that function as nuclei for phase transformation. The fundamental cause for  $A_1$  (~2.5 V), the peak at the lowest voltage, is still unclear, implying that some crystallographic information is missing. Nevertheless, the difference between LFS and CoLFS reveals that the electrochemical activation process is strongly correlated to the local structural changes caused by Co incorporation.

Fig. S5<sup>†</sup> shows the variation of CV at various scan rates from 0.1 mV s<sup>-1</sup> to 0.5 mV s<sup>-1</sup>. The chemical diffusion coefficient of Li<sup>+</sup> ( $D_{\text{Li}^+}$ ) can be estimated from the slope of the linear lines of the peak current, *i.e.*,  $I_{\text{C}}$ ,  $I_{\text{A}_2}$ , or  $I_{\text{A}_3}$ , *vs*. the square root of the scan rate  $\nu^{1/2}$ . The calculated results are listed in Table S4.<sup>†</sup> As it can be seen, diffusion coefficient of lithiation is larger than that of delithiation for both LFS and Co-LFS, although all the calculated  $D_{\text{Li}^+}$  are around  $10^{-13}$  cm<sup>2</sup> s<sup>-1</sup>.

Electrochemical impedance spectra (EIS) before and after CV tests were measured and presented in Nyquist format in Fig. 5e. We focus firstly at the unfinished loop that cut at 20 mHz, which is ascribed to the impedance related to solid-state diffusion of  $\text{Li}^+$  which is coupled with phase transformation.<sup>61</sup> This information is of great importance because the transport of Li-ions in LFS crystals will be correlated with the movement of grain boundaries between different phases. From the equivalent circuit model fitting (showing later in Fig. 6b), the resistance from phase transformation (denoted as  $R_{\text{PT}}$ ) declines from 17 k $\Omega$  to 7 k $\Omega$  in LFS, while more dramatically, from 14 k $\Omega$  to 2 k $\Omega$  in CoLFS. These results clearly point out two benefits brought by

0.15

0.2 mV/s



Re(Ζ') (Ω)

0.1

1.5 20

CoLFS

10<sup>th</sup>

5<sup>th</sup>

2<sup>nd</sup>

1<sup>st</sup>

1.5 2.0

LFS-fresh

LFS-cycled

CoLFS-fresh

2500

3000

CoLFS-cycled

CoLFS

10<sup>t</sup>

25 30 3.5 40 4 5

Voltage vs. Li\*/Li (V)

2.5 Voltage vs. Li<sup>+</sup>/Li (V)

4.0

Fig. 5 Structural evolution activates electrochemical properties. Cyclic voltammograms of (a) LFS and (b) CoLFS in the first 10 cycles at a scan rate of 0.2 mV s<sup>-1</sup> between 1.5–4.5 V. (c and d) Anodic (oxidation) curves fitted by three-four peaks for the 1<sup>st</sup>, 2<sup>nd</sup>, 5<sup>th</sup>, and 10<sup>th</sup> cycles corresponding to (a and b). (e) Electrochemical impedance spectra of LFS (blue) and CoLFS (red) cells before and after cycling in a frequency range of 1 MHz to 20 mHz. Solid and dashed lines represent the fitting results. Grey-filled half-circle represents the fitted resistance of CoLFS-cycled.

Co substitution: (i) improved phase transformation kinetics and (ii) enhanced electrochemical activation. Such electrochemical activation by structural evolution during cycling has been observed in other materials that involve TM/Li re-ordering, such as LiFeSO<sub>4</sub>F.<sup>62</sup> Thus, incorporation of Co in LFS can effectively suppress the formation of unnecessary intermediate phases, hence making the transformation pathway more energetic efficient.

#### 4.5. CEI formation on cycled electrodes

It is noted that at high voltage region, a rising oxidation tail starting from  $\sim$ 4.2 V is observed in both dQ/dV and CV curves (Fig. 4 and 5). This tail could be attributed to electrolyte oxidation that contributes a parasitic charge capacity fraction. Electrolyte oxidation has been observed in multiple cathode materials when charging above 4.2 V and the starting voltage for the parasitic oxidation is highly dependent on the nature of the electrode



**Fig. 6** Characteristics of the cathode-electrolyte interphases (CEIs) and the surface of electrodes. (a) Nyquist plots in the high-to-medium-frequency region of EIS spectra of LFS and CoLFS half-cells before and after cycling in LiPF<sub>6</sub> EC-DMC electrolyte at 45 °C. Arrows indicate increases of impedances upon cycling. (b) Equivalent circuit used to fit the Nyquist plots. (c) Deconvolution results of the loop composed of two depressed half-circles: one from CEI resistance ( $R_{CEI}$ ) and the other from charge-transfer resistance ( $R_{CT}$ ). (d) FTIR spectra of the pristine and cycled electrodes. Noted that "fresh" electrodes are those in the half-cells before cycling, while "pristine" electrodes are those electrodes that have not been in contact with electrolyte.

materials.18 The most common parasitic electrolyte oxidation reaction is the oxidation of ethylene carbonate (EC), which could go through ring-opening leading to evolution of CO2/CO gas.63 As the oxidation tail is the most significant in the 1<sup>st</sup> cycle subsequently fading out with cycling, one can assume that the extent of parasitic electrolyte oxidation is reduced with successive cycling. The presence of this extra capacity fraction results in low coulombic efficiencies (CEs) from the  $2^{nd}$  to  $\sim 15^{th}$  cycle in both LFS and CoLFS (see Fig. 4c and f). Surprisingly, LFS reaches  $\sim$ 100% CE which then remains stable, but CoLFS possesses rather poor CE ( $\sim$ 95%) till the 50<sup>th</sup> cycle. However, CoLFS has substantially better discharge capacity retention than LFS (95% vs. 80%). This contradiction implies that the fundamental cause for the continuous capacity loss in LFS is not the electrolyte oxidation. Indeed, more detrimental side reactions between electrode and electrolyte can come from the electrolyte decomposition associated with PF6<sup>-</sup>-based species.<sup>64</sup> More specifically,  $PF_6^{-}$  in the electrolyte is sensitive to moisture and heat, which can generate HF acid. HF could attack the cathode and result in the loss of active materials.<sup>20,65</sup> Simultaneously, a surface film, called cathode electrolyte interphase (CEI), will form on the surface of the cathode. The functionality of this CEI depends on its composition, thickness, and structure. Thus, a desired CEI could work as a protection buffer layer that prohibit further attack from HF while allow Li<sup>+</sup> to pass through. On the other hand, an undesired CEI may be incapable of blocking detrimental reaction while even worse, been resistive to Li<sup>+</sup> transport.

Fig. 6a shows the Nyquist plots of LFS and CoLFS EIS measurements which can be interpreted using a common equivalent circuit model as shown in Fig. 6b for a Li half-

cell.<sup>66-68</sup> It should be noted that Fig. 6a is a magnification from the high-to-medium frequency range in Fig. 5a. The fitted spectra are the convolution of two depressed semicircles, followed by a tail with  $\sim 60$  degree angle. The semicircle at high frequency can be assigned to the contact resistance between cathode interface (CEI layer) and current collector, denoted as  $R_{\text{CEI}}$ . The semicircle at medium frequency is ascribed to the charge-transfer resistance at the surface of cathode, denoted as  $R_{\rm CT}$ . Fig. 6c shows the fitting results of LFS and CoLFS before and after CV tests. LFS electrode exhibits larger overall impedance than CoLFS before and after cycling, more specifically in both  $R_{CEI}$  and  $R_{CT}$ . Upon cycling,  $R_{CEI}$  in CoLFS increases from about 12  $\Omega$  to 25  $\Omega$  while  $R_{CT}$  almost remains at about 20  $\Omega$ . As a comparison, LFS goes through a small increase in R<sub>CEI</sub> from 40 Ω to 44 Ω, whereas its  $R_{CT}$  is almost doubled from 34 Ω to 60 Ω upon cycling. CoLFS exhibits lower and more stable  $R_{\rm CT}$  than LFS. This means that Co substitution helps to establish a wellstructured CEI/CoLFS interphase that facilitates charge transfer. It has been reported that in  $P2_1/n$  LFS, Co-doping could introduce more defects and enhance the electronic and ionic conductivities.<sup>24</sup> In other materials, such as LiFePO<sub>4</sub> (ref. 36) and LiMn2O4,69 doping small amount of Co was found to decrease the charge-transfer resistance.

FTIR (Fig. 6d) was employed to reveal compositional and structural features of the surface on LFS and CoLFS and the CEI layer formed after cycling. In the pristine LFS electrode (denoted as LFS-pristine), the characteristic vibration bands from SiO<sub>4</sub> polyanion can be observed in the range of 400–1000 cm<sup>-1</sup>, which contains stretching vibrations at ~835 cm<sup>-1</sup> and ~870 cm<sup>-1</sup> and bending vibrations at ~510 cm<sup>-1</sup> and

 $\sim$ 580 cm<sup>-1</sup>. CO<sub>3</sub> in Li<sub>2</sub>CO<sub>3</sub> contributes to the bending vibration at  $\sim 900 \text{ cm}^{-1}$  and the stretching vibration at  $\sim 1400 \text{ cm}^{-1}$ .<sup>70</sup> Stretching band of C-F from PVDF binder is found at  $\sim$ 1150 cm<sup>-1</sup>.<sup>71</sup> After the CV tests at 45 °C between 1.5–4.5 V, all the features found in LFS-pristine remains in LFS-cycled but with changes in their relative intensities. The most noticeable changes are from the vibrations of SiO<sub>4</sub> which show substantial intensity reduction at  $\sim$ 510 cm<sup>-1</sup> while intensity growth at  $\sim$ 870 cm<sup>-1</sup>. This change implies that the surface chemistry of LFS has changed significantly upon cycling in the electrolyte. In the meantime, a small band at  $\sim 1000 \text{ cm}^{-1}$  emerges in LFScycled, which can be designated to Si-F stretching vibration.71 The formation of Si-F bonds should originate from the attack by HF acid that is produced by the decomposition of LiPF<sub>6</sub>. The reaction between LFS and HF was evidenced in a previous study and Li<sub>2</sub>SiF<sub>6</sub> was found to be the product.<sup>72</sup> Moreover, among the three common polymorphs of LFS, Pmn21 was the least stable polymorph upon the attack by HF.72

As shown in Fig. 6d, substituting 6% Co for Fe leads to insignificant variations in the FTIR spectra of the pristine electrodes (CoLFS-pristine *vs.* LFS-pristine), but the evolution of FTIR spectra upon cycling are different. In CoLFS-cycled, bending vibrations from SiO<sub>4</sub> in the range of 400–700 cm<sup>-1</sup>

almost disappear, while stretching vibrations from SiO<sub>4</sub> in the range of 800–900 cm<sup>-1</sup> diminish. Considering SiO<sub>4</sub> signals are only from the bulk of the electrode particles, reduction of SiO<sub>4</sub> vibrations could be attributed to a complete coverage of CEI layers on CoLFS particles. In addition, it is worth noting that there is only a diffused shoulder from Si–F vibration at ~1000 cm<sup>-1</sup>, suggesting that the content of Si–F-bearing species in CoLFS-cycled is considerably less than that in LFS-cycled. Therefore, the lower quantity of Si–F found in CoLFS indicates that CoLFS has an improved tolerance towards HF.

FTIR data in combination with the EIS results suggest that CoLFS formed relatively conductive and well-constructed CEI layers, whereas un-doped LFS appeared to have formed resistive, porous or even fractured CEI layers. It is also revealed that  $Li_2CO_3$  is one of the major components in the CEIs on both LFS and CoLFS.  $Li_2CO_3$  is a common component found in CEIs and SEIs, which can form during air exposure before electrochemical tests. With an appropriate content of  $Li_2CO_3$ , CEIs would have better interfacial stability and kinetics of carrier transport at the CEI/electrode interphases as well as endow the electrodes with improved high-temperature tolerance.<sup>73</sup>

XPS was applied to elucidate the surface chemistry and structures of CEIs. It is noted that XPS spectra usually represent



Fig. 7 XPS surface analysis of the pristine and cycled electrodes of LFS and CoLFS. Top left figure is the elemental percentages of C, O, F, P, and Si derived from XPS. The rest of the figures show XPS spectra of F 1s, P 2p, O 1s, C 1s, and Si 2p of the pristine and cycled electrodes.

surface chemistry in the top 1-10 nm layers from the studied substances.<sup>74</sup> Fig. 7 compares the XPS spectra of pristine and cycled electrodes of LFS and CoLFS (view from bottom to top). From the schematic summary of the chemical compositions of each sample given in the bar chart in Fig. 7, new signals from element P emerge and increasing signals from element F show up after cycling, both of which can be attributed to decomposition of the LiPF<sub>6</sub>-based electrolyte. Spectra on the right and bottom provide more specific information of the components and their changes after cycling. It is shown that signals belonging to LiF (~685.5 eV) and  $\text{Li}_x \text{PO}_v \text{F}_z$  (~135 eV) emerge in F 1s and P 2p spectra only after cycling.72,75 In the pristine electrodes, F 1s spectra are dominated by a peak at ~688 eV which is attributed to CF<sub>2</sub> from the binder PVDF, *i.e.*  $-(C_2H_2F_2)_n$ -. After cycling, the newly formed Li<sub>x</sub>PO<sub>y</sub>F<sub>z</sub> contributes additional signals to the peak at 688 eV in F 1s and that at 135 eV in P 2p. There is more LiF in the CEI of CoLFS than that in LFS after cycling by comparing F 1s spectra between the two cycled electrodes. More specifically, as summarized in Fig. 7 and Table S5,† CoLFS-cycled contains 24% of F, whereas LFS contains 19.2% of F in the sum of C, O, F, P, and Si. Remarkably, LiF in CoLFS-cycled (13.6%) is almost double of that in LFScycled (7.2%). CoLFS-cycled also bears higher P content (5.9%) than LFS-cycled (3.6%), which also reflects a higher content of  $\text{Li}_x PO_v F_z$  in CoLFS. LiF and  $\text{Li}_x PO_v F_z$  (e.g.  $\text{LiPO}_2 F_2$ ) derive from the decomposition of LiPF<sub>6</sub> in the electrolyte triggered by moisture and thermal sensitivities.20,76,77 Recent studies have revealed that the presence of fluorine species in the surface layer of electrode materials have positive impact on Раре

electrochemical performance.<sup>19,76–78</sup> The presence of  $Li_2CO_3$ , which was detected by the FTIR results, was also confirmed by XPS in C 1s and O 1s spectra.

As discussed above, FTIR (Fig. 6d) shows a sign of newly formed Si-F bonds as a result of reaction between LFS and HF. As shown in Fig. 7, Si 2p peak shifts to higher energy after cycling. This suggests formation of new Si-containing compounds that have higher-binding-energy bonds such as Si-F. Ensling et al.79 reported the formation of Si-F groups (at 103 eV if using C-C at 284.8 eV as reference) in the LFS/C cells cycled at 55 °C in LiPF<sub>6</sub> electrolyte. Our previous work<sup>59</sup> also showed that spontaneous reactions can occur even between the uncharged LFS and LiPF<sub>6</sub> electrolyte at room temperature, resulting in the reduction of electrolyte components and oxidation of Fe<sup>2+</sup>. Not only the attack of HF on LFS is responsible for material degradation such as mass loss of the active material but also is responsible for an increase of internal resistance, and consequently diminished capacity observed in various Li-ion intercalation compounds, such as Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, LiCoO<sub>2</sub>, LiNiO<sub>2</sub>, LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>, and LiFePO<sub>4</sub>.65 Moreover, compared with the oxides, the affinity of F- to Si-O bonds in LFS would lead to more detrimental effect on the degradation of LFS and electrolyte.

The CEI layers, which is usually only a few nanometers thick, also affects the performance of the electrodes.<sup>80,81</sup> By analyzing the ratio of XPS signals between LiF plus  $\text{Li}_x \text{PO}_y F_z$ , which are part of the CEI layer, and Fe plus  $\text{SiO}_4$ , which are part of the bulk electrode particles (Fig. 7 and S6†), it can be seen that CoLFS-cycled contains more signals from CEI than from the bulk,



**Fig. 8** Electrochemical structural activation mechanism: schematic illustration of structural evolution, surface reactivation, and formation of CEIs in LFS and CoLFS upon charge–discharge cycling in LiPF<sub>6</sub> EC/DMC electrolyte.

while LFS-cycled does not. As listed in Table S5,<sup>†</sup> the atomic percentage of Si in LFS almost remains the same (5.9% vs. 5.5%) before and after cycling. On the contrary, Si detected from CoLFS decreases from 7.3% to 4.2% after cycling, indicating that there is less amount of Si in the XPS sensitive region due to the coverage of the CoLFS surface by the better formed CEI layer. In addition, the SiO<sub>4</sub> vibration detected by FTIR (Fig. 6d) becomes significantly weaker in CoLFS-cycled due to the coverage of CEI. Combined with the EIS results where CoLFS was found to have lower CEI resistance than LFS, we believe that CoLFS was covered with more complete and thinner CEI layers that allowed Li-ion transport while adequately protecting the active particles from further detrimental reactions with electrolyte. By contrast undoped LFS formed a fractured CEI which failed to serve as protection layer.

Based on the results and discussions above, we propose a schematic illustration presented in Fig. 8 for the cobaltcatalyzed electrochemical activation and CEI formation in CoLFS and LFS during cycling. We find that substituting a small amount of Co for Fe induced more TM/Li antisite defects in the pristine materials, thus facilitating the phase transformation to the cycled structure and avoiding unnecessary intermediate phases. Surface reconstruction is progresses with cycling and is completed faster in CoLFS than LFS. Moreover, Co in LFS catalyzed the formation of more conductive and wellconstructed CEI layers that serve as a protection film to prevent further attack by HF. The CEI layers are mainly composed of LiF,  $Li_r PO_\nu F_2$ , and  $Li_2 CO_3$ . We hypothesize that Co ions on the surface may play catalytic site roles that favor the formation and deposition of conductive CEI components. This protection layer leads to enhanced capacity retention of CoLFS vis-a-vis the unprotected LFS. Nevertheless, the presence of Co also leads to some parasitic electrolyte oxidation which although does not diminish the discharge capacity still consumes electrolyte. Therefore, some electrolyte additives are still needed to optimize the electrolyte/CoLFS interphases.

## 5. Conclusions

In this work, we demonstrate the effect of Co-substitution on LFS via theoretical modeling and experimental testing. Li<sub>2</sub>-Fe<sub>0.94</sub>Co<sub>0.06</sub>SiO<sub>4</sub> solid solution in Pmn2<sub>1</sub> polymorph was successfully synthesized by hydrothermal method. Larger quantities of pre-existing TM/Li antisite defects were found in CoLFS, which during cycling served as nuclei for the phase transformation from Pmn21 to the electrochemically induced phase. The surface of both LFS and CoLFS was degraded upon contact with electrolyte thus exhibiting sluggish kinetics in the initial cycles, but upon cycling the surface was reconstructed. By careful examination of the surface on the cycled electrodes, we found that the substitution of Co tuned the CEI formation ability and resulted in a coverage of conductive and uniform protecting layer over the active particles. This CEI layer, mainly composed by LiF,  $Li_2CO_3$  and  $Li_xPO_vF_z$ , not only helped to prevent the active materials from corrosion attack by HF, but also possessed lower interphase resistance thus facilitating charge-transfer. As a consequence, CoLFS showed profoundly

enhanced capacity retention performance compared to undoped LFS (95% vs. 80%). We attempted to synthesize LFS doped with other elements according to their theoretical synthesizability predicted by DFT calculations. However, only Mg was successfully substituted into LFS under hydrothermal condition, but the presence of Mg introduced severe capacity loss, probably due to the lack of protective CEI layer. The new insight provided in this work opens new optimization avenues for LFS *via* investigation of surface coating with compatible and robust materials.

# Conflicts of interest

There are no conflicts to declare.

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