Tuning anionic/cationic redox chemistry in a P2-type $\text{Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_2$ cathode material via a synergic strategy

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ABSTRACT The anionic redox chemistry ($\text{O}^{2-} \rightarrow \text{O}^-$) in P2-type sodium-ion battery cathodes has attracted much attention. However, determining how to tune the anionic redox reaction is still a major challenge. Herein, we tune the activity and reversibility of both the anionic and cationic redox reactions of $\text{Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_2$ through an integrated strategy that combines the advantages of Li_2SiO_3 coating, Li doping and Si doping, and the initial capacity, rate performance and cycling stability are significantly improved. The in-depth modulation mechanism is revealed by means of neutron diffraction, X-ray absorption spectroscopy, *in situ* X-ray diffraction, electron paramagnetic resonance spectroscopy, first-principles calculations and so on. The Li_2SiO_3 coating alleviates the side reactions and enhances the cycling stability. Si^{4+} doping lowers the Na^+ diffusion barrier due to the expanded interlayer spacing. Additionally, Si^{4+} doping improves the structural stability, oxygen redox activity and reversibility. Li^+ doping in Na sites further increases the structure stability. The electron density maps confirm the greater activity of Na and O in the modified sample. Nuclear density maps and bond-valence energy landscapes identify the Na^+ migration pathway from Nae site to Naf site (the positions of the Na ions in the crystal structure). The proposed insights into the modulation mechanism of the anionic and cationic redox chemistry are also instructive for designing other oxide-based cathode materials.

Keywords: sodium-ion battery, P2-type cathode, anion redox, electron density nephogram, Li_2SiO_3 coating

INTRODUCTION

Lithium-ion batteries (LIBs) have been widely used in portable electronics and electric vehicles due to their high capacity, cycle stability and long life [1,2]. With the development of technological advances related to mobile energy storage, renewable energy integration and connection objects, human life will rely more on batteries than ever before [3–5]. Charge storage in traditional oxide-based cathodes for LIBs is limited to transition metal (TM) ions. However, an increasing number of studies indicate that charge can also be stored by the anion redox reaction, which plays a critical role in the specific capacity and cycling performance [6–10].

The cathode materials for sodium-ion batteries (SIBs) have a charging and discharging mechanism similar to that of LIBs, which has been considered one of the substitutions for LIBs owing to their abundant resources and low cost, especially P2-type Fe- and Mn-based $\text{Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_2$ layered transition metal oxide cathode materials [11–13]. The oxygen redox reaction in the cathodes of SIBs also has received increasing attention [14–18]. Maitra *et al.* [19] reported that the extra capacity originates from oxygen redox chemistry. Du *et al.* [20] reported a TM layered oxide cathode with a redox reaction near the top of $\text{O}-2\text{p}^6$. In a recent review, Xu *et al.* [21] summarized the anionic redox reaction in both Na-deficient and Na-rich materials. However, determining how to tune the activity and reversibility of the anionic redox reaction through a facile

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strategy as well as how to understand the underlying modulation mechanism is still a major challenge.

Herein, we proposed a facile “three-in-one” strategy of Li_2SiO_3 surface modification that combines the advantages of Li_2SiO_3 coating, Li doping and Si doping. The redox reaction activity of oxygen and the Mn ion has been significantly improved, which leads to a large enhancement of the initial capacity, rate capacity and cycling performance. Furthermore, the nano Li_2SiO_3 layer and the enhancement of the binding energy between the TM and oxygen also suppress lattice oxygen loss from the cathode surface. The underlying modification mechanism has been revealed based on the analyses of neutron diffraction, *ex situ* X-ray absorption spectroscopy (XAS), differential scanning calorimetry (DSC), cyclic voltammetry (CV), *in situ* X-ray diffraction (XRD), *ex situ* X-ray photoelectron spectrometry (XPS), *ex situ* electron paramagnetic resonance (EPR) spectroscopy and density functional theory calculations.

EXPERIMENTAL SECTION

Materials synthesis

The P2-type $\text{Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_2$ cathode material was synthesized *via* a facile sol-gel method. First, ethylene glycol (EG) and citric acid (CA) (4:1) were dissolved in deionized water at ambient temperature, and then, sodium acetate (3% excess sodium), manganese acetate, and nickel acetate were added in stoichiometric amounts. Second, after being aged at 80°C for 5 h in a constant-temperature drying box, the wet sol was dried to a xerogel at 150°C. Finally, after being ground into powder, the xerogels were calcined in air for 12 h at 900°C to obtain the final materials. All the chemical reagents above were analytically pure and purchased from China National Pharmaceutical Chemical Reagent Co., Ltd.

A wet chemistry method was used to coat Li_2SiO_3 on $\text{Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_2$ ($\text{Li}_2\text{SiO}_3\text{@MF}$). Stoichiometric ratios of CA and silicon(IV) acetate and lithium acetate salt were successively dissolved in 20 mL ethanol. We have confirmed that the solid materials obtained by the above method are indeed Li_2SiO_3 . The mass ratio of $\text{Li}_2\text{SiO}_3\text{/MF}$ was set at 1.5%. Then, the prepared solution was mixed with $\text{Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_2$ powder under stirring for 5 h and dried overnight. The mixture was annealed at 600°C for 5 h to obtain the final cathode materials with the Li_2SiO_3 coating ($\text{Li}_2\text{SiO}_3\text{@MF}$).

Electrochemical characterizations

Electrochemical capability measurements were tested

using coin cells (R2025) with a glass fiber (GF/D, Whatman) as the separator, a metal sodium plate as the counter electrode and 1.0 mol L^{-1} NaClO_4 in propylene carbonate (PC) as the electrolyte. The active material was mixed with super P carbon and poly(vinylidene fluoride) (PVDF) (75:15:10, mass ratio) in *N*-methylpyrrolidinone (NMP) to form the composite electrode slurry. The slurry was uniformly applied to the Al foil and dried overnight at 120°C in a vacuum drying box. The loaded mass of the active materials was approximately 2.0 mg. R2025 coin cells were fabricated in a glove box filled with Ar gas. Galvanostatic charge-discharge cycles were tested in the voltage range of 1.5–4.2 V *versus* Na^+/Na using an automatic galvanostat (NEWARE). The CV measurements, the potentiostatic intermittent titration technique (PITT) and electrochemical impedance spectroscopy (EIS) were performed on an electrochemical workstation (PGSTAT302N, Autolab).

Characterization techniques

Powder XRD (PXRD) was performed on a diffractometer (SmartLab, Cu K α) in the 2θ range of 10°–70° with a step width of 0.01°. The lattice parameters were refined using Fullprof software based on the Rietveld method. *In situ* and *ex situ* XRD was carried out on an X-ray diffractometer (SmartLab, Cu K α) in the 2θ range of 10°–50° with a step width of 0.01° and scan rate of $10^\circ \text{ min}^{-1}$. The X-ray absorption fine structure spectra were collected on the 1W1B beamline of Beijing Synchrotron Radiation Facility (BSRF Beijing, China). Scanning electron microscopy (SEM, Hitachi SU8010, Japan) and high-resolution transmission electron microscopy (HRTEM, Tecnai G2 F20 S-TWIN, 200 kV) were applied to observe the microstructures of the samples. The surface element compositions and valences were characterized by XPS (Thermo Scientific ESCALAB 250Xi, USA) with nonmonochromated Al K α X-ray radiation as the excitation source. The oxygen vacancies were evaluated by *ex situ* EPR spectroscopy (Bruker A300-10/12, Germany) to reveal the reversibility of the oxygen-based redox reaction. DSC analysis was carried out by using a DSC 200 PC system (NETZSCH, Germany) at a temperature scan rate of $2^\circ \text{C min}^{-1}$ in a flowing N_2 atmosphere. Neutron diffraction data were collected on a PKU-HIPD at the China Advanced Research Reactor (CARR), and the neutron diffraction wavelength was 1.4812 Å.

Calculation

First-principle calculations were performed by the density functional theory (DFT) using the Vienna *Ab-initio* Si-

mulation Package (VASP). The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was used to describe the electronic exchange and correlation effects. Uniform G-centered k -points meshes with a resolution of $2\pi \times 0.03 \text{ \AA}^{-1}$ and Methfessel-Paxton electronic smearing were adopted for the integration in the Brillouin zone for geometric optimization. The simulation was run with a cutoff energy of 500 eV throughout the computations. These settings ensure convergence of the total energies to within 1 meV per atom. Structure relaxation proceeded until all forces on atoms were less than $1 \text{ meV \AA}^{-1}$ and the total stress tensor was within 0.01 GPa of the target value. Due to the strong-correlation of d electrons in Mn and Fe, a U - J parameter (U is the Coulomb repulsion energy and J is the Honde coupling parameter) of 4.64 and 5.2 eV were applied.

For geometry optimization and electronic density of state (DOS) calculations, we built a $2 \times 2 \times 1$ supercell structure of the initial $\text{NaFe}_{0.5}\text{Mn}_{0.5}\text{O}_2$ rhombohedral layered oxide structure, which contains 8 formula units (f.u.), i.e., $\text{Na}_8\text{Fe}_4\text{Mn}_4\text{O}_{16}$. To evaluate the effect of silicon doping on structural stability and physical properties, a Si atom was substituted for a Mn atom in random position. The energy barrier for the diffusion of Na atom was calculated using the nudged elastic band (NEB) method based on $4 \times 2 \times 1$ supercell structure. The calculation parameters and convergence criteria were kept the same as in the ground state calculations.

RESULTS AND DISCUSSION

Crystal structure and morphology

The phase compositions of MF, $\text{SiO}_2\text{@MF}$, $\text{Na}_2\text{SiO}_3\text{@MF}$ and $\text{Li}_2\text{SiO}_3\text{@MF}$ cathode materials were determined by XRD. The main peaks of the four samples are similar, corresponding to the P2-type layered structure with a $P6_3/mmc$ (No. 194) space group, as shown clearly in Fig. 1a [22–24]. Furthermore, to demonstrate the difference between the XRD patterns of the MF, $\text{SiO}_2\text{@MF}$, $\text{Na}_2\text{SiO}_3\text{@MF}$ and $\text{Li}_2\text{SiO}_3\text{@MF}$ cathode materials, an enlarged view of the (002) peak is shown in Fig. 1b. The (002) peaks of $\text{SiO}_2\text{@MF}$, $\text{Na}_2\text{SiO}_3\text{@MF}$ and $\text{Li}_2\text{SiO}_3\text{@MF}$ all show a leftward shift, corresponding to an increase in the cell parameter c value. Compared with that of the MF samples, the (002) peak of the $\text{Li}_2\text{SiO}_3\text{@MF}$ sample shifts to a lower 2θ angle, indicating the expansion of the (002) slab due to Li^+ doping and Si^{4+} doping into the host structure [25–27]. Since Li^+ and Si^{4+} have smaller atomic radii than Na^+ (0.76 Å for Li^+ , 0.4 Å for Si^{4+} and 1.02 Å

for Na^+) and Na^+ vacancies exist in the P2-type cathode material, the Li^+ ions may prefer to enter the Na sites. Si^{4+} ions may prefer to enter the transition-metal sites because the valence state of the Si ion is higher and the ion can coordinate well with oxygen at the transition-metal sites. However, the (002) peaks of the $\text{SiO}_2\text{@MF}$ and $\text{Na}_2\text{SiO}_3\text{@MF}$ cathode materials show a much higher angle shift, which may lead to instability of the layered structure.

Rietveld refinements were performed to analyze the structural parameters of MF and $\text{Li}_2\text{SiO}_3\text{@MF}$, as shown in Fig. 1c, d, respectively; the fitting factor (R_p) values for the two samples are 2.91% and 4.01%, respectively. The weighted R_p (R_{wp}) values for MF and $\text{Li}_2\text{SiO}_3\text{@MF}$ are 3.94% and 4.94%, respectively, which indicates that the refinement data are acceptable. The atoms' occupancy information of the MF and $\text{Li}_2\text{SiO}_3\text{@MF}$ materials from Rietveld refinement is depicted in Tables S1 and S2. As shown in Table 1, a decrease in the V , the O–O bond length and the TM–O bond length are favorable to the stability of the layered structure. In particular, the shortening of the TM–O bond illustrates the enhancement of the binding energy between the TM and oxygen [28,29]. The increase in the Na–O bond length can reduce the electrostatic attraction between Na and O and facilitate Na^+ intercalation/extraction in $\text{Li}_2\text{SiO}_3\text{@MF}$ cathode materials compared with the MF cathode material. The increase in the interlayer spacing (d) also provides a wider channel for Na^+ intercalation/extraction during the charge/discharge process, which can lower the energy barrier of Na^+ diffusion during the intercalation/extraction process. As shown in Fig. 1c, the crystal structure model of each sample is constructed based on the Rietveld refinement results. In addition, we analyzed the electron density maps of all atoms (Na; TM; oxygen), as shown in Fig. 2a, b, especially the oxygen atoms in Fig. 2c, d. Compared with that in the MF sample, the electronic layers of sodium and oxygen both show greater activity, which enhances the migration of sodium ions and the activity of oxygen participating in the redox reaction. We also observe that the electronic layer of the TM in the $\text{Li}_2\text{SiO}_3\text{@MF}$ samples becomes weaker than that in the MF sample, as shown in Fig. 2e, f, which illustrates the enhancement of the layer structural stability. These calculated results are also highly consistent with the refined data, especially the d , leading to the higher rate capacity.

Compared with conventional PXRD, the neutron powder diffraction technique is more sensitive to the distribution of Mn and Fe and especially the light elements [30]. To further verify the doping effect of the Li^+

Figure 1 (a) The XRD patterns; (b) the (002) peaks of the materials; (c) the refinement results of bare MF materials and the Refined crystal structures; (d) the refinement results of $\text{Li}_2\text{SiO}_3\text{@MF}$ materials; the refinement results of the neutron powder diffraction of (e) bare MF and (f) $\text{Li}_2\text{SiO}_3\text{@MF}$.

and Si^{4+} ions, neutron powder diffraction and refinements were performed, as shown in Fig. 1e, f, and the lattice parameters are summarized in Table 2. The lattice parameters show a similar trend to the data derived from the PXRD. The crystal structures of the two samples are constructed as shown in Fig. S1, which illustrates that the Li^+ ions entered the Na sites and Si^{4+} ions entered the TM sites. The Si^{4+} ions in the transition-metal sites can stabilize the redox reaction of oxygen because the binding energy of $\Delta H_f^{298\text{K}}(\text{Si-O})$ (460 kJ mol^{-1}) is larger than that

of $\Delta H_f^{298\text{K}}(\text{Mn-O})$ (402 kJ mol^{-1}) and $\Delta H_f^{298\text{K}}(\text{Fe-O})$ (409 kJ mol^{-1}). The Rietveld refinement results of the neutron powder diffraction data are also simulated, which reflect the distribution of the nuclear density in the MF and $\text{Li}_2\text{SiO}_3\text{@MF}$ samples. As shown in Fig. 3a, b, the migration pathway of the sodium ions can be clearly identified by the bond valence energy landscape (BVEL) calculation, and sodium ions preferably migrate from the Nae site to Naf site because the sodium ions at the Nae site are more active and require less energy to migrate to

Table 1 The refined crystallographic parameters of the cathode materials by the XRD patterns

	MF	Li ₂ SiO ₃ @MF
<i>a</i> (Å)	2.9329(1)	2.9177(1)
<i>c</i> (Å)	11.2096(4)	11.2361(5)
<i>d</i> (Å)	3.5714	3.6072
<i>V</i> (Å ³)	83.51(5)	82.84(6)
Na–O (Å)	2.4609	2.4679
TMO ₂ (Å)	2.0334	2.0109
O–O (Å)	2.6462	2.6232
TM–O (Å)	1.975	1.962
<i>R_p</i> (%)	2.91	3.94
<i>R_{wp}</i> (%)	4.01	4.94

the Naf site (Na ions occupy two kinds of trigonal prismatic sites: the Nae site shares edges with the six TMO₆ octahedra, and the Naf site shares two faces with the lower and upper TMO₆ octahedra).

SEM was used to detect the morphology of the two samples of MF and Li₂SiO₃@MF, as shown in Fig. S2a, b, respectively. The whole morphology of the Li₂SiO₃@MF sample was not changed after Li₂SiO₃ coating. An HRTEM image of the Li₂SiO₃@MF sample is shown in Fig. 4a, and a heterostructure with two distinct layers can be clearly observed. The coating layer of Li₂SiO₃ is approximately 5 nm thick. To further confirm the thickness of the coating layer, HRTEM images with low magnifi-

Figure 2 Electron density nephogram of all atoms in the [110] direction: (a) MF sample; (b) Li₂SiO₃@MF sample. Electron density nephogram of the oxygen in the [001] direction: (c) MF sample; (d) Li₂SiO₃@MF sample. Electron density nephogram of the TM in the [001] direction: (e) MF sample; (f) Li₂SiO₃@MF sample.

Table 2 The refined crystallographic parameters of the cathode materials by the neutron powder diffraction

	MF	Li ₂ SiO ₃ @MF
<i>a</i> (Å)	2.9360(3)	2.9251(4)
<i>c</i> (Å)	11.2262(4)	11.2323(5)
<i>d</i> (Å)	3.5843	3.5868
<i>V</i> (Å ³)	83.80(6)	83.23(6)
Na–O (Å)	2.4668	2.4750
TMO ₂ (Å)	2.0288	2.02935
O–O (Å)	2.6437	2.6379
TM–O (Å)	1.9754	1.971
<i>R_p</i> (%)	2.16	3.65
<i>R_{wp}</i> (%)	2.66	4.58

cation were obtained, as shown in Fig. S3a, b. We can also observe a coating layer on the surface of the cathode materials, which was approximately 5 nm thick. The spacing of the outermost lattice fringes is approximately 0.25 nm, which corresponds to the (100) plane (*P6₃/mmc*) of the layered transition-metal oxide Li₂SiO₃@MF. As shown in Fig. 4b, c, the Fourier transform images corresponding to the symbols by the squares and the results from the fast Fourier transform (FFT) images are coin-

cident with the lattice spacing of 0.25 nm (*P6₃/mmc*). To directly observe the distribution of the Li₂SiO₃ coating layer on the surface of the MF cathode materials, energy dispersive spectrometer (EDS) mapping was performed, and the results are shown in Fig. 4d–i. The distributions of Na, Fe, Mn, Si and O are shown separately. The Si element is also uniformly distributed in the cathode material, which illustrates the doping of Si⁴⁺ into the host structure.

Electronic structure analysis

To further investigate the surface oxidation state of the elements in the cathode materials, MF and Li₂SiO₃@MF were analyzed by XPS, as shown in Fig. 5. The Mn 2p spectra show two characteristic peaks, which can be divided into Mn 2p_{3/2} (including two characteristic peaks: Mn³⁺ at 641.0 eV and Mn⁴⁺ at 642.3 eV) and Mn 2p_{1/2}, as shown in Fig. 4a [31,32]. As shown in Table 3, we can observe that the ratio of Mn³⁺ is reduced in the Li₂SiO₃@MF cathode material compared with the MF cathode material (57.9% for MF and 33.6% for Li₂SiO₃@MF), which indicates that the stability of the P2-type structure is enhanced due to reduction of the Jahn-Teller effect caused by Mn³⁺ [11,33]. As shown in Fig. 5b, the

Figure 3 Nuclear density nephogram of all atoms in the [001] direction: (a) MF sample; (b) Li₂SiO₃@MF sample. Nuclear density nephogram of the TM in the [001] direction: (c) MF sample; (d) Li₂SiO₃@MF sample.

Figure 4 (a) HRTEM image of the $\text{Li}_2\text{SiO}_3@\text{MF}$ sample; (b, c) the FFTs of the corresponding area in (a); (d) scanning TEM (STEM) image and (e–i) the EDS mapping images of the Na, Fe, Mn, Si, O.

Figure 5 XPS patterns of the cathode samples: (a) Mn, (b) Fe, (c) O, and (d) Si for the $\text{Li}_2\text{SiO}_3@\text{MF}$.

Table 3 The ratio of Mn^{3+} and Mn^{4+} in the cathode materials

	MF	$\text{Li}_2\text{SiO}_3\text{@MF}$
Mn^{3+}	57.9%	33.6%
Mn^{4+}	42.1%	66.4%

observed Fe 2p peaks located at 710.8 eV (Fe 2p_{3/2}) and 724.5 eV (Fe 2p_{1/2}) demonstrate that the surface oxidation state of Fe was trivalent (+3) in this layered transition-metal oxide [34,35]. The ratio of the lattice oxygen and surface oxygen was also further analyzed, and the result indicates that the ratio of lattice oxygen is increased in the $\text{Li}_2\text{SiO}_3\text{@MF}$ cathode material compared with the MF sample (16.3% for MF and 46.6% for $\text{Li}_2\text{SiO}_3\text{@MF}$) as shown in Table 4. This means that the binding energy between the oxygen and TM of the cathode material was enhanced by the Li_2SiO_3 coating and Si doping, which further strengthened the stability of the oxygen in the host structure and enhanced the reversibility of the oxygen redox reaction during the charge/discharge process. Additionally, the Si 2p_{3/2} peak at approximately 100.8 eV indicates the existence of Si^{4+} [36], which suggests that Li_2SiO_3 is successfully coated on the surface of the MF cathode material.

To reveal the activity of the oxygen atoms in the redox reaction and the stability of these atoms in the host structure, the *ex situ* O 1s XPS spectra and the DSC results of the two samples (MF and $\text{Li}_2\text{SiO}_3\text{@MF}$) charged at 4.2 V were collected, as shown in Fig. S4. In Table S3, compared with that in MF, the ratio of lattice oxygen is higher in $\text{Li}_2\text{SiO}_3\text{@MF}$, corresponding to the determined peak separation, as shown in Fig. S4a. The higher lattice oxygen content means better structural stability of the cathode materials when charged at 4.2 V due to the enhancement of the binding energy between oxygen and the TM. As shown in Fig. 6a, d, in the charged state (4.2 V), the existence of peroxo-like species O_2^{2-} was observed; these species disappeared at the 1.5 V discharge state and were converted to oxygen ions (O^{2-}) as shown in Fig. 6b, e. This result may be due to the redox reaction of oxygen during charge/discharge processes at high voltage [15,37,38]. Furthermore, compared with that of the MF cathode material, the ratio of the peroxo-like species O_2^{2-} in the $\text{Li}_2\text{SiO}_3\text{@MF}$ cathode material increased at the high-voltage charged state, as shown in Table 5, which indicates that the Li_2SiO_3 coating with a small amount of Si doping not only promotes the anion redox reaction of oxygen but also further strengthens the stability of the oxygen in the host structure. This conclusion was further confirmed by XPS evaluation of the bare MF electrode

Table 4 The ratio of surface O and lattice O in the cathode materials

	MF	$\text{Li}_2\text{SiO}_3\text{@MF}$
Surface O	83.7%	53.4%
Lattice O	16.3%	46.6%

(charged at 4.2 V) and $\text{Li}_2\text{SiO}_3\text{@MF}$ electrode (charged at 4.2 V) after being etched to 50 nm, as shown in Fig. 6c, f. It is obvious that compared with that in the bare MF, the ratio of the lattice oxygen (O_2^{2-}) in the $\text{Li}_2\text{SiO}_3\text{@MF}$ cathode material has been increased after charging at 4.2 V, which means that more lattice oxygen participates in the redox reaction and further reveals the improvements of the lattice oxygen activity.

To further test the stability of the oxygen in the host structure, DSC was performed, as shown in Fig. S4b. The thermal decomposition temperature of $\text{Li}_2\text{SiO}_3\text{@MF}$ was increased from 245.34 to 249.45°C, which illustrates that the strategy of the Li_2SiO_3 coating with a small amount of Si doping is a feasible way to inhibit the loss of lattice oxygen and further enhance the oxygen redox reversibility. The thermal stability results are also consistent with previous viewpoints that an enhancement of the binding energy between the TM and oxygen can also strengthen the stability of the oxygen in the host structure.

Ex situ EPR spectroscopy was performed to reveal the reversibility of the oxygen participation in the redox reaction during the charge/discharge process due to the occurrence of oxygen vacancies and the problem of oxygen precipitation. As shown in Fig. 6g, there are more oxygen vacancies in the $\text{Li}_2\text{SiO}_3\text{@MF}$ cathode material than in the MF cathode material due to secondary sintering during the Li_2SiO_3 post-coating process. However, the number of oxygen vacancies in MF is much higher than that in the $\text{Li}_2\text{SiO}_3\text{@MF}$ cathode material at the 4.2 V charged state, as shown in Fig. 6h, which illustrates that the oxygen evolution can be adequately alleviated by the Li_2SiO_3 coating and the enhancement of the binding energy between the TM and oxygen [39–41]. When discharged to 1.5 V as shown in Fig. 6i, there are still more oxygen vacancies in MF than in $\text{Li}_2\text{SiO}_3\text{@MF}$, which further reveals this issue in sodium-ion battery cathode materials and provides an effective strategy to suppress the oxygen evolution from the host structure.

To further explore the redox reaction of the TMs Mn and Fe during Na^+ extraction/insertion, *ex situ* XAS analysis of the MF and $\text{Li}_2\text{SiO}_3\text{@MF}$ cathodes in different states was carried out. The normalized X-ray absorption near-edge structure (XANES) spectra of the Mn and Fe

Figure 6 The *ex situ* XPS O 1s spectra collected for the (a) charged 4.2 V, (b) discharged 1.5 V and (c) etching to 50 nm after charged 4.2 V of the MF cathode material. The *ex situ* XPS O 1s spectra collected for the (d) charged 4.2 V (e) discharged 1.5 V and (f) etching to 50 nm after charged 4.2 V of the $\text{Li}_2\text{SiO}_3/\text{MF}$ cathode material. Comparison of the *ex situ* EPR results of the MF and $\text{Li}_2\text{SiO}_3/\text{MF}$ cathode materials: (g) pristine; (h) charged 4.2 V; (i) discharged 1.5 V.

Table 5 The ratio of peroxo-like species O_2^{2-} and the oxidation of O^{2-} in the charge 4.2 V state

	O_2^{2-}	O^{2-}
MF	42.2%	57.8%
$\text{Li}_2\text{SiO}_3/\text{MF}$	44.1%	55.9%

K-edges are shown in Fig. 7. Compared with that for the $\text{Li}_2\text{SiO}_3/\text{MF}$ cathode shown in Fig. 7c, when charged to 4.2 V, the Mn K-edge shows an obvious shift in the higher-energy region of the MF cathode, as shown in Fig. 7a, which corresponds to the XPS data that the ratio of Mn^{3+} is decreased in the $\text{Li}_2\text{SiO}_3/\text{MF}$ cathode material. When the MF and $\text{Li}_2\text{SiO}_3/\text{MF}$ cathodes were discharged

to 1.5 V, the valence of Mn decreased again to Mn^{3+} , which proved the capacity contribution of Mn during the charge/discharge process [42]. As shown in Fig. 7b, d, there is a slight shift of the Fe K-edge when the cathode is charged to 4.2 V, which means that the iron ion also participates in electrochemical oxidation by increasing its oxidation state during the charge process. We discovered that Fe^{4+} translates to Fe^{3+} during the discharge process, which indicates that the contribution of Fe to the capacity comes from the conversion of $\text{Fe}^{3+}/\text{Fe}^{4+}$ in the cathode materials during the charge/discharge process.

To understand the structural stability and charge compensation of the MF and $\text{Li}_2\text{SiO}_3/\text{MF}$ cathode ma-

Figure 7 The *ex situ* XANES spectra collected at different charge/discharge states: (a) Mn K-edge, and (b) Fe K-edge of the MF electrode; (c) Mn K-edge, and (d) Fe K-edge of the $\text{Li}_2\text{SiO}_3@\text{MF}$ electrode.

materials in the process of Na^+ extraction/insertion, especially for the reversibility of the oxygen redox reaction, DFT was carried out. As shown in Fig. 8e, f, the calculated densities of states of the MF and $\text{Li}_2\text{SiO}_3@\text{MF}$ samples show that the oxygen 2p state below the Fermi level is dominant [43]. It is obvious that the effect of Si^{4+} doping on the oxygen 2p orbital is more remarkable for $\text{Li}_2\text{SiO}_3@\text{MF}$ than for the MF cathode material. To reveal the migration of sodium ions during the charge/discharge process, schematic diagrams of sodium-ion migration are shown in Fig. 8. Compared with that of the MF cathode, the sodium-ion migration barrier of $\text{Li}_2\text{SiO}_3@\text{MF}$ was reduced from 1.35 to 0.81 eV.

Electrochemical performance

Fig. 9a–e shows the typical CV curves of the MF and $\text{Li}_2\text{SiO}_3@\text{MF}$ cathode materials measured in the voltage range from 1.5 to 4.2 V at a scan rate of 0.1 mV s^{-1} . The MF cathode material has two pairs of reversible redox peaks, namely, 2.6088 V/2.003 V and 3.8832 V/3.246 V, and the ΔV values are 0.6058 and 0.6372 V, respectively. The $\text{Li}_2\text{SiO}_3@\text{MF}$ cathode material also has two pairs of

reversible redox peaks, namely, 2.3923 V/1.9309 V and 3.8864 V/3.251 V, which correspond to the redox reactions of $\text{Mn}^{3+}/\text{Mn}^{4+}$ and $\text{Fe}^{3+}/\text{Fe}^{4+}$, respectively. The ΔV values decrease to 0.4614 and 0.6354 V, indicating a more reversible sodium insertion/deinsertion process. Furthermore, the results show that the polarization for the $\text{Li}_2\text{SiO}_3@\text{MF}$ cathode is reduced greatly and that the charge/discharge reversibility is improved. Compared with that of the MF cathode material shown in Fig. 9c, the redox reaction peak of the Mn ion was increased by approximately 0.2 V in the $\text{Li}_2\text{SiO}_3@\text{MF}$ cathode material due to the Si doping, which illustrates that the redox activity of the Mn ion was enhanced by Si doping. As is known, the Jahn-Teller effect is mainly caused by Mn^{3+} , and the increase in the redox peak potential can also indicate that the ratio of Mn^{3+} is reduced, which corresponds to the XPS results of Mn and further improves the stability of the layered structure. The peak at 4.163 V for MF and 4.15 V for $\text{Li}_2\text{SiO}_3@\text{MF}$ should be largely related to the oxygen redox couple of $\text{O}^{2-}/\text{O}_2^{2-}$, which illustrates that the O^{2-} species contribute to the specific discharge capacity. To verify the above result, we extend the voltage

Figure 8 Schematic diagrams of Na-ion migration in (a, b) MF and (c, d) $\text{Li}_2\text{SiO}_3@\text{MF}$. The element calculated density of states of (e) MF and (f) $\text{Li}_2\text{SiO}_3@\text{MF}$.

range from 1.5 V and measure 10 cycles of CV curves for MF and $\text{Li}_2\text{SiO}_3@\text{MF}$ cathode materials at a scan of 0.1 mV s^{-1} , as shown in Fig. 9d, e. We find that the redox reaction activity of Mn and oxygen is enhanced by the Li_2SiO_3 surface modification, and the redox reaction of oxygen always contributes to the discharge capacity. In addition, Si does not participate in the redox reaction, as shown in Fig. 9b, e, and c, f.

As shown in Fig. 10, the rate capacities at different current densities and the cycling capacities at 0.1 and 1 C ($1 \text{ C}=200 \text{ mA g}^{-1}$) were tested in the voltage range from 1.5 to 4.2 V. As shown in Fig. 10a, the rate capability of the $\text{Li}_2\text{SiO}_3@\text{MF}$ cathode material was greatly improved

compared with that of the MF cathode material. In addition, as shown in Fig. 10b, c, we observed that the charge/discharge curve of the $\text{Li}_2\text{SiO}_3@\text{MF}$ cathode material was smoother than that of the MF cathode material. The improvement of the rate capability can be largely attributed to the enlarged interlayer spacing (d : $3.5714 \text{ \AA}$ for MF, $3.5793 \text{ \AA}$ for $\text{Li}_2\text{SiO}_3@\text{MF}$) and increased Na–O bond length ($2.4609 \text{ \AA}$ for MF, $2.4705 \text{ \AA}$ for $\text{Li}_2\text{SiO}_3@\text{MF}$), which are favorable to the diffusion of Na^+ and further enhance the rate capability.

The cycling performances at 0.1 and 1 C were tested, as shown in Fig. 10d, e. The capacity retention ratios of MF and $\text{Li}_2\text{SiO}_3@\text{MF}$ cathode materials are approximately

Figure 9 The CV curves of the as-prepared cathodes from 1.5 to 4.2 V with the scan rate of 0.1 mV s^{-1} : (a) MF, (b) $\text{Li}_2\text{SiO}_3\text{@MF}$, (c) the second cycles CV curves of two samples. The CV curves of as-prepared cathodes from 1.5 to 4.5 V with the scan rate of 0.1 mV s^{-1} : (d) MF, (e) $\text{Li}_2\text{SiO}_3\text{@MF}$, (f) the second cycle CV curves of two samples.

66% and 80% at 0.1 C after 50 cycles, respectively. In addition, at a high current density of 1 C, capacity retention ratio values of MF and $\text{Li}_2\text{SiO}_3\text{@MF}$ are 35% and 62% after 50 cycles, respectively. The enhancement of the cycling stability can first benefit from the protection of Li_2SiO_3 and the alleviated side effects between the electrode and electrolyte by the Li_2SiO_3 layer, which stabilizes the P2-type layered structure. In addition, the decrease in the V, the O–O bond length and the TM–O bond length induced by Si^{4+} doping is favorable to the stability of the layered structure. In particular, the shortening of TM–O bond enhances the binding energy between the TM and oxygen. Furthermore, the Li^+ ions enter the Na sites, which also benefit the stability of the layered structure. Furthermore, the stability of the oxygen involved in the redox reaction contributes more capacity continuously.

To investigate the impacts of the surface modification on the interface between the cathode and electrolyte, EIS was performed at different frequencies ranging from 0 to 100 kHz, as shown in Fig. S5a. By the Nyquist curves of the MF and $\text{Li}_2\text{SiO}_3\text{@MF}$ cathode materials, we can obtain the internal ohmic resistance (R_{ele}) value and the electrochemical reaction resistance (R_{ct}) value by fitting the circuit in Fig. S5. The data are shown in Table S4. The charge transfer resistance of the $\text{Li}_2\text{SiO}_3\text{@MF}$ cathode material was significantly changed compared with that of

the bare MF. The increase in the R_{ele} value was due to the Li_2SiO_3 coating layer, representing the internal ohmic resistance and revealing the combined resistance of the liquid electrolyte, Na metal anode, and Al foil current collector. The semicircle at high frequencies along the Z' -axis and the linear part at low frequencies represent the R_{ct} and diffusion-controlled Warburg impedance, respectively. Furthermore, the EIS measurements revealed that the Li_2SiO_3 coating layer can effectively decrease the interparticle contact resistance. In addition, the PITT was performed to compare the Na^+ diffusion coefficient, as shown in Fig. S5b. We can see that the Na^+ diffusion coefficient is also increased by the Li_2SiO_3 surface modification, corresponding to the increase in the rate capability.

To study the layered structure evolution of the cathode materials during the Na-ion intercalation/extraction process, *in situ* XRD patterns were collected in the voltage range from 1.5 to 4.2 V at a scan rate of 0.2 mV s^{-1} . Furthermore, the CV curves are shown in Fig. S6; the sequence of every XRD pattern corresponds to every point from “1” to “34”. Except for the Al foil peaks in the cathode plate, no other new peaks appeared in the $\text{Li}_2\text{SiO}_3\text{@MF}$ cathode material during the Na-ion intercalation/extraction process, which indicated that the synergistic modification strategy could inhibit the phase

Figure 10 (a) Rate capabilities test at different current densities (MF, $\text{SiO}_2\text{@MF}$, $\text{Li}_2\text{SiO}_3\text{@MF}$, $\text{Na}_2\text{SiO}_3\text{@MF}$). Charge and discharge curves at different rates: (b) bare MF; (c) $\text{Li}_2\text{SiO}_3\text{@MF}$. Cycling performance of cathodes at different current densities and corresponding charge and discharge profiles: (d) cycling performance at 0.1 C; (e) cycling charge and discharge profiles of bare MF; (f) cycling charge and discharge profiles of $\text{Li}_2\text{SiO}_3\text{@MF}$; (g) cycling performance at 1 C; (h) cycling charge and discharge profiles of bare MF; (i) cycling charge and discharge profiles of $\text{Li}_2\text{SiO}_3\text{@MF}$.

transition and further stabilize the structure of the cathode materials. As shown in Fig. 11a, b, the (002) and (004) peaks clearly show a coincident change trend, which indicates that the change in the lattice parameter c value first increases and then decreases (the left deviation of the peak (002) and (004) indicates the increase in the c value; in contrast, the c value decreases). As shown by the *in situ* XRD spectra in Fig. 11c, d, the (002) peak of the $\text{Li}_2\text{SiO}_3\text{@MF}$ cathode material is still more apparent than that of the bare MF cathode material when charged to the highest voltage. In addition, the shifts of the (100), (102) and (103) peaks reflecting the changes in the lattice parameters a and b show similar trends. Therefore, the

structural change of the cathode material is a reversible process, which further indicates the higher structural stability of the $\text{Li}_2\text{SiO}_3\text{@MF}$ cathode material than the MF cathode material, especially when charged to the highest potential.

To prove the conclusion obtained by the *in situ* XRD results, *ex situ* XRD of the two samples was further performed, as shown in Fig. S7. We can observe that the $\text{Li}_2\text{SiO}_3\text{@MF}$ cathode material maintains its original P2-type phase structure at any potential, in contrast to the MF cathode material. However, some unknown peaks appeared near the (002) peak in the MF cathode material at discharge states of 3.3 and 2.0 V, which are not con-

Figure 11 (a) *In situ* XRD patterns collected during the cyclic voltammograms of bare MF with the scan rate of 0.2 mV s^{-1} . (b) *In situ* XRD patterns collected during the cyclic voltammograms of $\text{Li}_2\text{SiO}_3@\text{MF}$ with the scan rate of 0.2 mV s^{-1} . The (002) peak of the (c) bare MF and (d) $\text{Li}_2\text{SiO}_3@\text{MF}$.

ductive to the stability of the P2-type structure. As shown in Fig. S8, the variation curve of the refined crystallographic parameters from the *ex situ* XRD patterns collected during the charging and discharging of $\text{Li}_2\text{SiO}_3@\text{MF}$ cathode material at 0.05 C was gentler than that of the MF cathode material, especially the change in the d and V . The results show that the structural stability of $\text{Li}_2\text{SiO}_3@\text{MF}$ is better than that of the MF cathode material owing to the synergistic effects of Li doping, Si doping and Li_2SiO_3 coating.

CONCLUSIONS

In summary, a facile integrated strategy that combines Li doping, Si doping and Li_2SiO_3 coating has been proposed to improve the rate capability and cycling stability of a $\text{Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_2$ cathode. The redox reaction activity of the anion (oxygen) and the cation (Mn) has been significantly improved, leading to a significant enhancement of the initial capacity, rate capacity and cycling performance. The reversible transformation from the P2 to O2 phase at approximately 4.15 V was promoted, indicating an improvement of the oxygen redox reaction. Furthermore, the enhancement of the binding energy between the TM and oxygen can suppress lattice oxygen loss from

the cathode surface due to Si^{4+} doping, which was confirmed by electron density maps and *ex situ* EPR spectroscopy. The migration pathway of the sodium ions can be clearly identified by the BVCL calculation, which first migrated from the position of Nae to Naf because the sodium ions at the Nae site are more active and require less energy to migrate to the Naf site. This strategy reduces the ratio of Mn^{3+} and alleviates the negative impact of the Jahn-Teller effect, which further enhances the stability and improves the cycling performance. The DFT calculations show that the energy barrier of Na^+ migration was reduced from 1.35 to 0.81 eV , which increased the Na^+ diffusion coefficient and improved the rate capacity. The proposed strategy to tune the activity and reversibility of both the anionic and cationic redox reactions may also be helpful in the design of other layered oxide-based cathode materials.

Received 27 February 2020; accepted 24 March 2020;
published online 18 May 2020

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Acknowledgements This work was supported by the National Natural Science Foundation of China (11975238 and 11575192), the Scientific Instrument Developing Project (ZDKYYQ20170001), the International Partnership Program (211211KYSB20170060 and 211211KYSB20180020) and the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB28000000), and the Natural Science Foundation of Beijing Municipality (2182082). The support from University of Chinese Academy of Sciences is also appreciated.

Author contributions Liu X designed and guided the work; Kong W projected and performed the experiments. All authors contributed to the analysis of data and general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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通过一种协同策略调节P2型Na_{0.67}Mn_{0.5}Fe_{0.5}O₂正极材料的阴/阳离子氧化还原反应

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摘要 P2型钠离子电池正极材料中的阴离子氧化还原化学(O²⁻→O⁻)引起了广泛关注. 但是如何调节阴离子氧化还原反应仍然是一个很大的挑战. 本文通过一种集Li₂SiO₃包覆层、Li掺杂和Si掺杂三方优点的协同策略对正极材料Na_{0.67}Mn_{0.5}Fe_{0.5}O₂中阴、阳离子氧化还原反应的活性和可逆性进行了调控. 改性后正极材料的初始容量、倍率性能和循环稳定性都得到了显著改善. 通过中子衍射、同步辐射X射线吸收谱、原位X射线衍射、电子顺磁共振、第一性原理计算等手段深入揭示了调控机理. Li₂SiO₃包覆层减轻了电极表面的副反应, 提高了循环稳定性. Si⁴⁺掺杂扩大了钠层层间距, 降低了Na⁺扩散势垒. 此外, Si⁴⁺掺杂还增强了结构的稳定性以及氧的氧化还原活性和可逆性. Li⁺在Na位的掺杂进一步提高了结构的稳定性. 电子密度云图证实了改性样品中Na和O活性较高. 核密度云图和键价能谱确定了Na⁺从Na₁向Na₂的迁移途径. 本文所揭示的阴/阳离子氧化还原反应调控机理对其他氧化物正极材料的设计也具有指导意义.