

Progression of the silicate cathode materials used in lithium ion batteries

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Poly anionic silicate materials, which demonstrate a high theoretical capacity, high security, environmental friendliness and low-cost, are considered one of the most promising candidates for use as cathode materials in the next generation of lithium-ion batteries. This paper summarizes the structure and performance characteristics of these materials. The effects of different synthesis methods and calcination temperature on the properties of these materials are reviewed. Materials that demonstrate low conductivity, poor stability, cationic disorder or other drawbacks, and the use of various modification techniques, such as carbon-coating or compositing, elemental doping and combination with mesoporous materials, are evaluated as well. In addition, further research topics and the possibility of using these kinds of cathode materials in lithium-ion batteries are discussed.

lithium-ion batteries, silicate cathode materials, synthesis, performance optimization

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For the past few years, lithium transition-metal orthosilicates (Li_2MSiO_4 , $\text{M} = \text{Fe}, \text{Co}, \text{Mn}$) have been characterized as potential cathode materials for use in Li-ion batteries by some researchers. The strong Si-O bond allows this material to demonstrate good security. These orthosilicates are different from lithium transition-metal phosphates which only have one Li ion per formula unit. Li_2MSiO_4 with two Li ions per formula unit ($\text{M}^{2+} \rightarrow \text{M}^{4+}$) could have a theoretical capacity that is $>300 \text{ mA h g}^{-1}$. Therefore, its theoretical capacity and excellent safety performance could allow Li_2MSiO_4 to be used in potential toward the development of Li-ion batteries [1–6]. $\text{Li}_2\text{CoSiO}_4$ has a high theoretical capacity, but its second Li-ion deintercalation voltage plateau at about 5.0 V makes this difficult to achieve [1]. In addition, Co is expensive and environmentally toxic. So $\text{Li}_2\text{MnSiO}_4$ and $\text{Li}_2\text{FeSiO}_4$ have attracted more attention. This paper reviews the past few years of research progress in the field of $\text{Li}_2\text{Mn}/\text{FeSiO}_4$ materials, and summarizes the

methods that could be used to improve their electrochemical properties.

1 Overview of $\text{Li}_2\text{Mn}/\text{FeSiO}_4$ cathode materials

Generally, the extraction of Li atoms from $\text{Li}_2\text{FeSiO}_4$ is not possible due to electron-redox coupling of $\text{Fe}^{2+}/\text{Fe}^{3+}$. The theoretical capacity is considered to be 166 mA h g^{-1} and the voltage platform is 3.1 V. Phase-pure $\text{Li}_2\text{FeSiO}_4$ was successfully prepared by Nyten et al. [2]. The initial charge capacity of 165 mA h g^{-1} (99% of the theoretical value) can be stabilized to around 140 mA h g^{-1} (84% of the theoretical value) after a few cycles, and the initial discharge capacity is 130 mA h g^{-1} . The results of the cyclic voltammogram suggest that phase transition is more stable after the first cycle. This involves a structural ordering process from a solid solution to a long-range-ordered structure. Li_2MSiO_4 ($\text{M} = \text{Mn}, \text{Fe}$) was successfully prepared using a modified Pechini process by Dominko et al. [3]. During the process

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of charging/discharging, the structure of $\text{Li}_2\text{FeSiO}_4$ demonstrates only minor changes, equivalent of two fully reversible phase changes, so this material demonstrates good cycling performance. Deng et al. [4] suggested that the changes induced by exposure to air are entirely reversible. Air-exposed $\text{Li}_2\text{FeSiO}_4$ regenerates by calcining at 700°C for 4 h, demonstrating a similar structure, surface and electrochemical characteristics as the original sample. However, $\text{Li}_2\text{FeSiO}_4$ demonstrates very low electrical conductivity in the insulator range [5] and a value of $6 \times 10^{-14} \text{ S cm}^{-1}$ at room temperature has been reported. This leads to the poor rate capacity of $\text{Li}_2\text{FeSiO}_4$ materials, which is the main problem researchers are currently facing [6].

$\text{Li}_2\text{MnSiO}_4$ is another cathode material that possesses a high theoretical capacity of 333 mA h g^{-1} , and it is possible to extract two Li atoms at least theoretically from $\text{Li}_2\text{MnSiO}_4$ (Mn[II]/Mn[III] and Mn[III]/Mn[IV]), and it is theoretically easier to achieve a high specific capacity in cathode materials. $\text{Li}_2\text{MnSiO}_4$ was successfully prepared using a modified Pechini process by Dominko et al. [3]. The fact is that under the present conditions (C/30, 60°C) only about 0.6 Li is reversibly exchanged in the first cycle. In the next cycles, the reversible capacity fades considerably to only about 0.3 reversibly exchanged Li by the fifth cycle. $\text{Li}_2\text{MnSiO}_4/\text{C}$ composite materials were successfully prepared by Paromita et al. [7], and cyclic voltammetry demonstrated two oxidation/reduction couplings at 3.6/2.9 and 4.5/4.3 V with good reversibility. At the present, $\text{Li}_2\text{MnSiO}_4$ cathode materials demonstrate poor cycle stability and low conductivity. In the long run, silicate materials have good developmental prospects.

2 Structure and performance characteristics of $\text{Li}_2\text{Mn/FeSiO}_4$

Three possible $\text{Li}_2\text{MnSiO}_4$ forms have been considered for crystallizing the $Pmnb$, $Pmn2_1$ ($\beta\text{-Li}_3\text{PO}_4$ derivatives) and $P2_1/n$ ($\gamma\text{-Li}_3\text{PO}_4$ derivatives) space groups. Politaev et al. [8] synthesized $\text{Li}_2\text{MnSiO}_4$ and found that the crystal structure of $\text{Li}_2\text{MnSiO}_4$ is monoclinic within space group $P2_1/n$ ($a=6.3368[1]$, $b=10.9146[2]$, $c=5.0730[1]$ Å, $\beta=90.987^\circ[1]$). Arroyo de Dompablo et al. [9,10] pointed out that the denser $Pmn2_1$ polymorph can be obtained by high-pressure and high-temperature treatment of the $P2_1/n$ and $Pmnb$ polymorphs or their mixtures, but $Pmn2_1$ is still stable even at 80 kbar and 900°C . Therefore, $\text{Li}_2\text{MnSiO}_4$ is usually described as an orthorhombic structure within space group $Pmn2_1$. As shown in Figure 1, it can be considered that the $[\text{SiMnO}_4]$ layer infinities along the ac , and the LiO_4 tetrahedron is linked together along the b -axis. In these layers, the SiO_4 tetrahedron and MnO_4 tetrahedron are connected by total points. The Li ion holds two $[\text{SiMnO}_4]$ layers of the tetrahedron between these positions. In such a structure, where three LiO_4 tetrahedron O atoms are in the same layer,

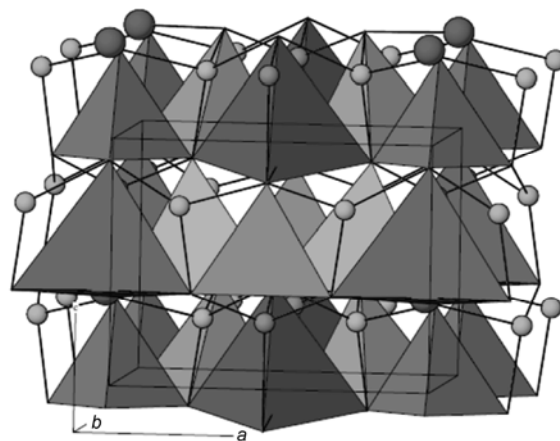


Figure 1 Crystal structure of $\text{Li}_2\text{MnSiO}_4$ shown in its polyhedral representation. Reprinted from [3] with permission from Elsevier.

the fourth ion is in the adjacent layer of O. The LiO_4 tetrahedron, with its total points along the axis linked together, allows the Li ion to complete the embedded emergency response. $\text{Li}_2\text{FeSiO}_4$ is isostructural with $\text{Li}_2\text{MnSiO}_4$ crystallizing the $Pmn2_1$ space group, demonstrating better stability during the processes of charging and discharging.

The strong Si-O bond allows poly anionic silicate materials to demonstrate good security. Dominko et al. [11] studied $\text{Li}_2\text{FeSiO}_4/\text{C}$ and $\text{Li}_2\text{MnSiO}_4/\text{C}$ cathode materials and found that the oxidation state of Mn in $\text{Li}_2\text{MnSiO}_4/\text{C}$ cathode materials changes from the initial Mn(II) state to Mn(III) with a potential range of 4.0 to 4.5 V. During oxidation, the short Mn-O bond decreases from 2.04 to 1.87 Å in correlation with the increase in the Mn valence state, while the larger Mn-O distance of the MnO_4 tetrahedron remains unchanged. This indicates that the related changes in the local environment of Mn are irreversible. The position of Fe in the slightly distorted O tetrahedra shifts as the valence changes accompanies the removal of Li, therefore, the cycling stability of $\text{Li}_2\text{FeSiO}_4/\text{C}$ has been confirmed. Dominko et al. [12] reduced the particle size of synthesized $\text{Li}_2\text{MnSiO}_4$, observing structural changes during the first charge that indicated the complete loss of peaks when reaching the nominal composition of ca. $\text{Li}_1\text{MnSiO}_4$. These peaks were not recovered during subsequent cycles. It is believed that the extraction of Li causes significant structural changes, so that the resulting material is only able to reversibly exchange a limited amount of Li. Kokalj et al. [13] considered that during the delithiation of $\text{Li}_2\text{MnSiO}_4$, phase separation of $\text{Li}_2\text{MnSiO}_4$ and MnSiO_4 may occur. Because the latter is amorphous-like, amorphization can be observed upon the removal of small amounts of Li, which can explain the drop in the reversible capacity during cycling. The visible, stability of the material structure, in order to avoid structural collapse is a key factor in improving the material properties of $\text{Li}_2\text{MnSiO}_4$. Nyten et al. [14] studied $\text{Li}_2\text{MnSiO}_4$ using XRD refinement and found that in the process of charging and discharging, parts of Mn and Li are

exchanged. Belharouak et al. [15] also reached a similar conclusion that the cationic mixing of Li^+ and Mn^{2+} ions at their mutual crystallographic sites is the main impediment to achieving the full theoretical capacity of $\text{Li}_2\text{MnSiO}_4$.

3 Performance optimization method of silicate materials

3.1 Optimization of synthesis

(1) Solid-state synthesis. Solid-state reactions are considered a traditional milling technology, though they are considered poorly efficient and are easily mixed with impurities, but due to the preparation process they are simple and inexpensive, so they are still commonly used to synthesize orthosilicate. $\text{Li}_2\text{FeSiO}_4$ was recently synthesized using the traditional solid-phase method described by Nyten et al. [2] for the first time. Ren et al. [16] prepared $\text{Li}_2\text{FeSiO}_4$ using solid-state reactions, and the particles of $\text{Li}_2\text{FeSiO}_4$ prepared using this method were evenly dispersed, demonstrating granularity between 300–400 nm. When the cycling rate is 0.1 C at room temperature, the first discharge capacity is 170 mA h g^{-1} . Xiang et al. [17] synthesized $\text{Li}_2\text{FeSiO}_4$ at different temperatures using solid-state reactions, and electrochemical tests showed that the first specific discharge capacity of $\text{Li}_2\text{FeSiO}_4/\text{C}$ synthesized at 650°C was $144.8 \text{ mA h g}^{-1}$, and the discharge capacity was $136.5 \text{ mA h g}^{-1}$ after 10 cycles. Nanoscale carbon-coated $\text{Li}_2\text{MnSiO}_4$ powder was prepared by Karthikeyan et al. [18] using the conventional solid-state method and the negative electrode of a $\text{Li}_2\text{MnSiO}_4/\text{activated carbon (AC)}$ hybrid super capacitor. The cell exhibits excellent cycle performance with >99% coulombic efficiency and maintains 85% of its initial capacitance after 1000 cycles. $\text{Li}_2\text{Fe}_{1-x}\text{Mn}_x\text{SiO}_4/\text{C}$ cathode materials were synthesized by Guo et al. [19] using a mechanically activated solid-state reaction. Under optimal conditions (650°C calcined for 16 h, Li/Si ratio of 2.04) synthetic $\text{Li}_2\text{Fe}_{0.9}\text{Mn}_{0.1}\text{SiO}_4/\text{C}$ demonstrated good electrochemical performance with an initial discharge capacity of $158.1 \text{ mA h g}^{-1}$ and a capacity retention ratio of 94.3% after 30 cycles.

(2) Microwave synthesis. Compared with conventional heat synthesis, heat synthesis in a microwave field has the advantages of increased efficiency, integrity, selectivity and non-thermal effects, thus the microwave process demonstrates a faster response, higher efficiency, lower energy consumption and is more environmentally friendly and conducive to the formation of pure substances and fine grains. Muraliganth et al. [20] synthesized nanostructured $\text{Li}_2\text{FeSiO}_4$ and $\text{Li}_2\text{MnSiO}_4$ cathodes using facile microwave solvothermal synthesis. To improve crystallinity and enhance electronic conductivity, the resulting samples were mixed with sucrose and heated to 650°C for 6 h in an argon atmosphere. The $\text{Li}_2\text{FeSiO}_4/\text{C}$ sample exhibits a high rate capability and stable cycle life, with discharge capacities of 148 mA h g^{-1} at room temperature and 204 mA h g^{-1} at

55°C . Although $\text{Li}_2\text{MnSiO}_4/\text{C}$ demonstrates higher discharge capacities of 210 mA h g^{-1} at room temperature and 250 mA h g^{-1} at 55°C , it suffers from poor rate capability and drastic capacity fade. A $\text{Li}_2\text{FeSiO}_4$ cathode material was prepared by Peng et al. [21]. The highly pure product with a fine particle size and narrow size distribution was successfully obtained by mechanical ball-milling and microwave processing and the obtained sample demonstrates good electrochemical performance, cycling stability, and an initial discharge capacity of $116.9 \text{ mA h g}^{-1}$ at 60°C . Peng et al. [22] using super-P carbon as the microwave absorber powder, were able to quickly synthesize a $\text{Li}_2\text{FeSiO}_4/\text{C}$ olivine-phase material by microwave processing at 650°C for 10 min. The obtained material exhibited uniform and fine particle sizes and good electrochemical properties. The initial discharge capacity of the prepared $\text{Li}_2\text{FeSiO}_4/\text{C}$ material is $121.7 \text{ mA h g}^{-1}$ at 60°C , after 10 cycles and the discharge capacity can be maintained at $119.2 \text{ mA h g}^{-1}$.

(3) Hydrothermal synthesis. The characteristics of hydrothermal synthesis allow the production of high-quality particles with good dispersion and good crystals that are easily controlled with less thermal stress and fewer internal defects. The factors that impact hydrothermal synthesis include the temperature, heating speed, stirring speed, reaction time, etc. $\text{Li}_2\text{CoSiO}_4$ was prepared by Gong et al. [23] via hydrothermal reaction for the first time. Solid solutions with Fe and Mn cations in $\text{Li}_2\text{Fe}_z\text{Mn}_{(1-z)}\text{SiO}_4$ were successfully prepared by Dominko et al. [24] using hydrothermal synthesis. Three different synthesis techniques (hydrothermal synthesis, modified Pechini synthesis and Pechini synthesis) were successfully used to prepare $\text{Li}_2\text{FeSiO}_4$ samples by Dominko et al. [25]. The obtained samples demonstrate some differences in morphology and particle size, and fewer impurities were found in the samples that did not contain any *in situ* carbon that was prepared via hydrothermal synthesis. $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites contain the highest amounts of impurities (e.g. Fe_2O_3 , SiO_2 , Li_2SiO_3) and only 68.8 at. % of Fe is in the form of Fe (II).

(4) Sol-gel synthesis. The sol-gel method uses compounds with highly chemically active precursors that are mixed together in the liquid phase under hydrolysis, thereby allowing condensation reactions to form a stable and transparent sol system. Sol, following the slow polymerization of colloidal particles, forms a 3-dimensional structural gel. After drying, sintering curing prepares the molecules and even the nanostructure materials. Using sol-gel, Du et al. [6] first synthesized $\text{Li}_2\text{MnSiO}_4$ materials. $\text{Mg}_{1.03}\text{Mn}_{0.97}\text{-SiO}_4$ was prepared by Feng et al. [26] using a sol-gel method, which was then evaluated for use as an intercalation electrode material in rechargeable magnesium batteries. Using a ball mill in the presence of acetylene black, the resulting composites demonstrated an increased discharge specific capacity (92.9 mA h g^{-1} at C/50). An adipic acid-assisted sol-gel route was employed to prepare phase-pure $\text{Li}_2\text{MnSiO}_4$ under optimized conditions by Aravindan et al. [27]. The

morphological features confirmed the appearance of evenly dispersed $\text{Li}_2\text{MnSiO}_4$ spherical nanoparticles with a size of approximately 30 nm. The $\text{Li}/\text{Li}_2\text{MnSiO}_4$ cell exhibited an initial discharge capacity of 161 mA h g^{-1} and delivered a stable discharge capacity profile of up to 50 cycles (125 mA h g^{-1}). $\text{Li}_2\text{MSiO}_4/\text{C}$ composites (M=Mn and/or Fe) prepared by Dominko [28] via Pechini synthesis generally demonstrate large, 30–50 nm sized particles that are embedded in the carbon matrix, as shown in Figure 2. The amount of carbon in the composite is close to 10 wt% of the $\text{Li}_2\text{FeSiO}_4/\text{C}$ composite and slightly $>5 \text{ wt\%}$ of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ composite.

(5) Supercritical solvothermal method. The supercritical solvothermal method allows the progression of hydrothermal reactions. One or more precursors is dissolved in a non aqueous solvent, under liquid or supercritical conditions, and the reactants are dispersed in solution and become active. Accordingly, the reactant (usually a solid) is dissolved, allowing the decentralization process and chemical reactivity to significantly improve or increase. This allows the reaction to occur at lower temperatures. As far as we know, during calcinations, particles might strongly aggregate, which affects the intrinsic conductivity of the cathode material and results in severe capacity fade. Materials prepared using this method demonstrate the advantages of uniform particle size, good dispersion and high crystallinity.

Kempaiah et al. [29] recently published a paper that describes monodispersed $\text{Li}_2\text{MnSiO}_4$ and PEDOT/ $\text{Li}_2\text{MnSiO}_4$ nanoparticles (PEDOT with a simple molecular structure, small energy gap, and high conductivity) that were synthe-

sized using the supercritical solvothermal method at 300°C for 5 min. The as-synthesized nanoparticles had a diameter of 15–20 nm. Samples prepared using the present method demonstrate several advantages over other methods, including good crystallinity at low temperatures; this includes the first synthesis of an almost 100% pure-phase $\text{Li}_2\text{MnSiO}_4$. The electrochemical performances of the PEDOT/ $\text{Li}_2\text{MnSiO}_4$ electrodes were compared with metallic Li in the presence of LiClO_4 in EC and DMC at 0.05 C. PEDOT/ $\text{Li}_2\text{MnSiO}_4$ nanoparticles demonstrated remarkably high discharge capacities of 293 and 313 mA h g^{-1} at room temperature and at 40°C , respectively, equal to the nearly 2.0 Li extraction from the $\text{Li}_2\text{MnSiO}_4$ structure. In addition, the discharge capacity of 240 mA h g^{-1} was retained after 20 cycles. The high discharge capacity is due to its high phase purity and monodispersed particles with 15 nm diameters that facilitate short reaction pathways for the Li insertion/extraction process, which when coupled with high-conductive PEDOT material compounds, not only enhances the conductivity of the material, but also reduces irreversible changes in the structure, while avoiding the reunion of particles.

(6) Influence of the calcination temperature on materials. The calcining temperature plays a decisive role on the growth of the material's particle. The candidate cathode material $\text{Li}_2\text{MnSiO}_4$ for use in Li-ion cells was synthesized by Belharouak et al. [15] using an all-acetate precursor sol-gel method under a reducing atmosphere at 600, 700, and 800°C , and the material prepared at 700°C was the purest. Scanning electron microscopy of $\text{Li}_2\text{MnSiO}_4$ showed

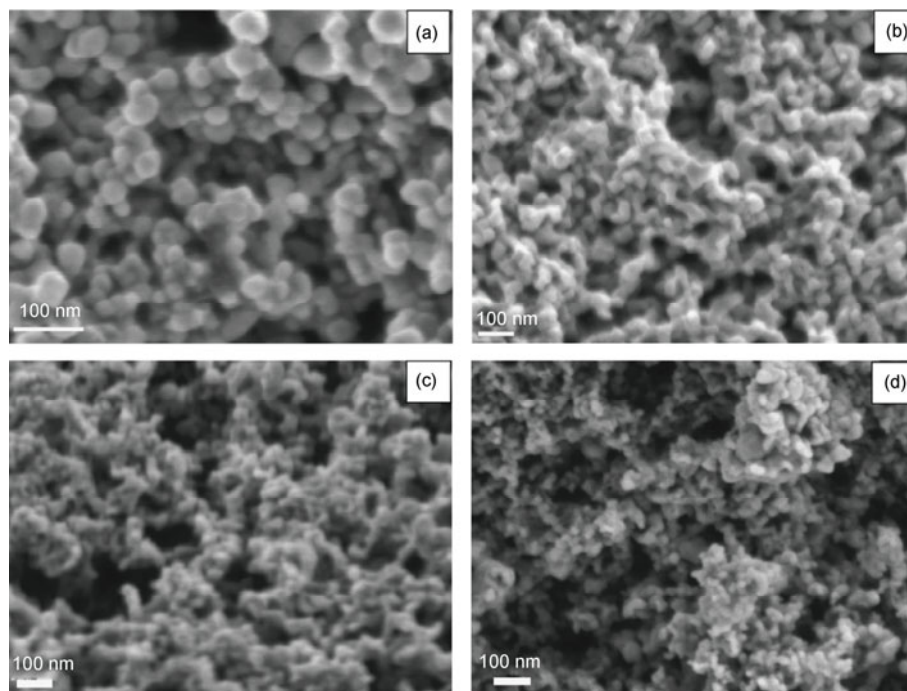


Figure 2 SEM micrographs of samples obtained using the Pechini method. (a) $\text{Li}_2\text{FeSiO}_4/\text{C}$ composite; (b) $\text{Li}_2\text{Mn}_{0.25}\text{Fe}_{0.75}\text{SiO}_4/\text{C}$ composite; (c) $\text{Li}_2\text{Mn}_{0.5}\text{Fe}_{0.5}\text{SiO}_4/\text{C}$ composite; (d) $\text{Li}_2\text{MnSiO}_4/\text{C}$ composite. Reprinted from [28] with permission from Elsevier.

large aggregates (10–50 μm) that were composed of nanosized particles (100–200 nm). Liu et al. [30] synthesized the $\text{Li}_2\text{MnSiO}_4/\text{C}$ composite through a polyol process that was following by heat-treatment at temperature of 500, 600, 700°C. The particle size increased from 5–20 to 20–40 nm as the temperature increasing from 500 to 700°C. Electrochemical experiments revealed that the sample that was treated at 600°C demonstrated the highest electrochemical performance with an initial discharge capacity of 132.4 mA h g^{-1} and a capacity retention ratio of 80% during the tenth cycle. Li et al. [31] synthesized $\text{Li}_2\text{FeSiO}_4/\text{C}$ cathodes by combining the wet-process method and the solid-state reaction. The primary particle size increases as the temperature increases from 600 to 750°C. The $\text{Li}_2\text{FeSiO}_4/\text{C}$ sample that was synthesized at 650°C demonstrates good electrochemical performances and an initial discharge capacity of 144.9 mA h g^{-1} and the discharge capacity remains at 136.5 mA h g^{-1} after 10 cycles. Li et al. [32] reported that $\text{Li}_2\text{FeSiO}_4$ can be prepared via the solid-state reaction using $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and Li_2SiO_3 , which can be synthesized using the sol-gel method at high temperatures. The calcination temperature plays an important role in the final properties of the Li_2SiO_3 samples. Samples calcined at 700°C provide 97% pure Li_2SiO_3 with good morphology that can be used as a precursor for the production of $\text{Li}_2\text{FeSiO}_4$. These samples consist of primary particles that are 1–3 μm in diameter, and the primary particle clusters form agglomerates with a loose and porous appearance. The effect of the sintering temperature on the performance of these materials was studied by Liu et al. [33]. $\text{Li}_2\text{MnSiO}_4$ materials synthesized via the traditional solid-state reaction, which are heated to 900°C for 20 h demonstrated the best initial specific discharge capacity (118 mA h g^{-1}). Yang et al. [34] synthesized the $\text{Li}_2\text{MnSiO}_4/\text{C}$ composite via the sol-gel method at temperatures of 500, 600 and 700°C. Electrochemical tests indicate that the $\text{Li}_2\text{MnSiO}_4/\text{C}$ composite that was synthesized at 600°C for 10 h demonstrates the best electrochemical performance, including an initial discharge capacity of 124.2 mA h g^{-1} , theoretical capacity of 74.5%, and a discharge capacity of 71.5 mA h g^{-1} after 30 cycles.

3.2 Carbon composites and coated materials

Low electrical conductivity is one of the main problems that leads to the poor electrochemical performance of silicate materials, and the use of composite or coated materials with high conductivities could not only improve the overall conductivity of the whole composite, but also prevent the reunion of the particles, which would facilitate short reaction pathways for the insertion/exertion of Li. The application of materials with specific morphologies could enhance the structure of these materials, thus, improving the cycling performance.

(1) Selection of the carbon source. Moskon et al. [35] reported that the use of citrate precursors can provide pretty

good conductivity (approximately 30 S cm^{-1}) after a 10 h of heat treatment at $\geq 700^\circ\text{C}$, while the conductivity plateau of the whole composite was observed at 0.1 S/cm . At that level, the carbon phase forms a well-distributed 3-dimensional electrical network within the composite. Li et al. [36] choose sucrose to prepare the $\text{Li}_2\text{MnSiO}_4/\text{C}$ composite, resulting in crystalline $\text{Li}_2\text{MnSiO}_4$ particles that were surrounded by a very thin film of amorphous carbon. At a current density of 5 mA g^{-1} , the material provides an initial discharge capacity of 209 mA h g^{-1} , but attenuation was very serious, as shown in Figure 3, resulting in a discharge capacity being still low at a high ratio.

$\text{Li}_2\text{MnSiO}_4$ cathode powders were synthesized by Paromita et al. [7], and the as-synthesized powder was ball-milled with acetylene black (0–20 wt%) to form the $\text{Li}_2\text{MnSiO}_4/\text{C}$ composite. The addition of acetylene black resulted in drastic changes in the morphology of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ composites, which consisted of uniform grains that were approximately 50 nm in diameter. The electrochemical discharged capacity as well as the rate capability of $\text{Li}_2\text{MnSiO}_4$ also dramatically improved as the amount of conducting carbon (acetylene black) increased in the matrix, resulting in values as high as 164 mA h g^{-1} and a current density of 0.01 mA cm^{-2} . Impedance spectroscopy showed that the addition of acetylene black decreases the charge-transfer impedance and balances the growth of cell impedance during cycling. $\text{Li}_2\text{MnSiO}_4$ was treated by carbon coating using a precursor to cellulose carbon by

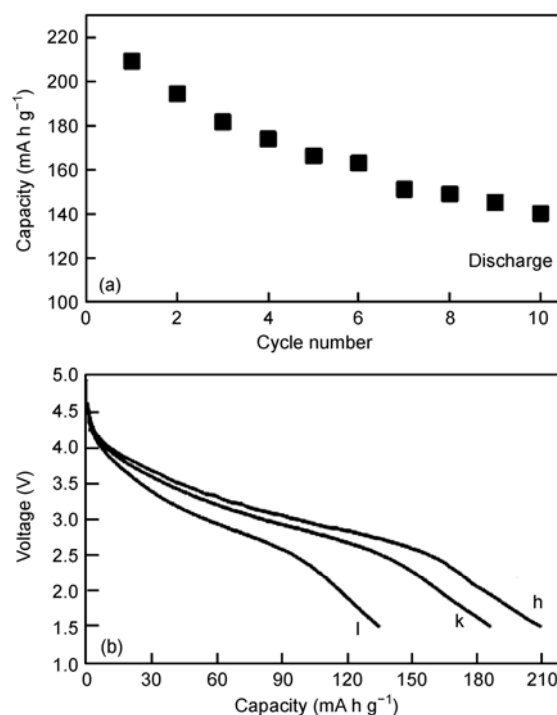


Figure 3 (a) Cycling performance of the material between 1.5–4.8 V at 5 mA g^{-1} . (b) First discharge curves at different current densities: h, 5 mA g^{-1} ; k, 30 mA g^{-1} ; l, 150 mA g^{-1} . Reprinted from [36] with permission from Elsevier.

Belharouak et al. [15], and the carbon-coated materials demonstrated a charge capacity of 190 mA h g^{-1} . A $\text{Li}_2\text{MnSiO}_4/\text{C}$ cathode material was synthesized by Liu et al. [37] using the traditional solid-state reaction method and sucrose as the carbon source. The product of $\text{Li}_2\text{MnSiO}_4/\text{C}$ has a smaller particle size (approximately 30–80 nm), which is beneficial for Li-extraction/insertion kinetics. The initial charge capacity of $\text{Li}_2\text{MnSiO}_4/\text{C}$ is 256 mA h g^{-1} (about 1.5 Li^+ per unit formula extracted) or 129 mA h g^{-1} (about 0.77 Li^+ per unit formula), which can be reversibly exchanged during the first cycle at a rate of $C/16$. Ahn et al. [38] found that by applying nanocoated polyaniline nanodisks as the cathode material, the discharge capacity improved by about 15% and the cyclability was enhanced, reducing the continuous structural distortion that occurs during extended charge-discharge cycling. $\text{Li}_2\text{MnSiO}_4$ was synthesized by Aravindan et al. [39] via the solid-state reaction method using adipic acid as the source material for carbon. The $\text{Li}/\text{Li}_2\text{MnSiO}_4$ cell delivered an initial discharge capacity of 160 mA h g^{-1} at $C/20$. After a few initial cycles, the cell exhibited stable discharge behavior of approximately 140 mA h g^{-1} and a coulombic efficiency that was $>90\%$. For the first time, the $\text{Li}_2\text{MnSiO}_4$ electrode demonstrated stable discharge behavior.

(2) Influence of carbon content. The carbon content has significant influence on the properties of materials, and an increase in carbon can improve the conductivity of the material; however too much will increase the distance between the active substances, thereby blocking the transfer of Li ions. Aravindan et al. [40] used adipic acid as the carbon source, and the concentration varied during the synthesis process between 0–1.0 mol (0, 0.05, 0.1, 0.2, 0.5, 1.0) against the total metal ions presents in $\text{Li}_2\text{MnSiO}_4$; 0.2 mol (0.92 wt%) adipic acid produced the highest-performing material. Figure 4 illustrates how adipic acid was carbonized and formed as carbon at the surface, which prevents the growth of particles and enhances the electronic conductivity

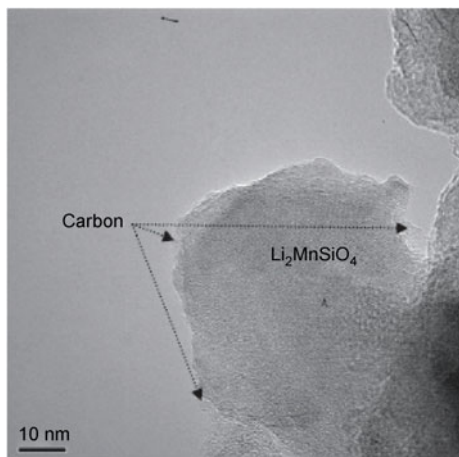


Figure 4 High resolution-transmission electron microscopic image of $\text{Li}_2\text{MnSiO}_4$ nanoparticles containing 0.2 mol adipic acid. Reprinted from [40] with permission from Elsevier.

of the material. Using sucrose as the carbon source, a $\text{Li}_2\text{FeSiO}_4/\text{C}$ composite was synthesized by Guo et al. [41], and the carbon content and the properties of the $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites were investigated. As carbon content increases to the range of 5%–20%, the amount of Fe_3O_4 impurities decreases. The $\text{Li}_2\text{FeSiO}_4/\text{C}$ composite, which contains 14.5% carbon, demonstrates good electrochemical performance, an initial discharge capacity of $144.8 \text{ mA h g}^{-1}$ and a capacity retention ratio of 94.27% after 13 cycles.

3.3 Elemental substitution

(1) Substitution of the M sites in Li_2MSiO_4 . Metal doping is an efficiency way to improve the electrochemical performance of the cathode material in Li-ion batteries. $\text{Li}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{SiO}_4$ ($x = 0, 0.3, 0.5, 0.7, 1$) cathode materials were synthesized by Deng et al. [42], as shown in Figure 5, and the prepared $\text{Li}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{SiO}_4$ samples can all be indexed based on the orthorhombic unit cell in space group $Pmn2_1$ and their lattice parameters are similar. Nanoparticles have been observed in these samples. The maximum discharge capacity was obtained when $x = 0.5$. However, the cycling performance of the $\text{Li}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{SiO}_4$ samples decreases as x increases. At the same time, Mn substitution lowers the electrochemical reversibility of the $\text{Li}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{SiO}_4$ samples.

Li et al. [31] improved the performance of $\text{Li}_2\text{FeSiO}_4/\text{C}$ by modifying Ni substitution. The $\text{Li}_2\text{Fe}_{0.9}\text{Ni}_{0.1}\text{SiO}_4/\text{C}$ composite cathode has an initial discharge capacity of $160.1 \text{ mA h g}^{-1}$, and the discharge capacity remains at $153.9 \text{ mA h g}^{-1}$ after 10 cycles. The diffusion coefficient of Li in $\text{Li}_2\text{FeSiO}_4/\text{C}$ is $1.38 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$, while that of $\text{Li}_2\text{Fe}_{0.9}\text{Ni}_{0.1}\text{SiO}_4/\text{C}$ reaches $3.34 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$. $\text{Li}_2\text{Fe}_{0.97}\text{Mg}_{0.03}\text{SiO}_4$ was synthesized via the sol-gel method by Zhang et al. [43], and Mg^{2+} has been doped into the structure of $\text{Li}_2\text{FeSiO}_4$ without destroying its lattice structure. Mg doping improves the discharge capacity and cycle stability of $\text{Li}_2\text{FeSiO}_4$. Electrochemical impedance analysis shows that Mg doping decreases the charge-transfer resistance of $\text{Li}_2\text{FeSiO}_4$, and moreover, Mg doping increases the Li-ion diffusion

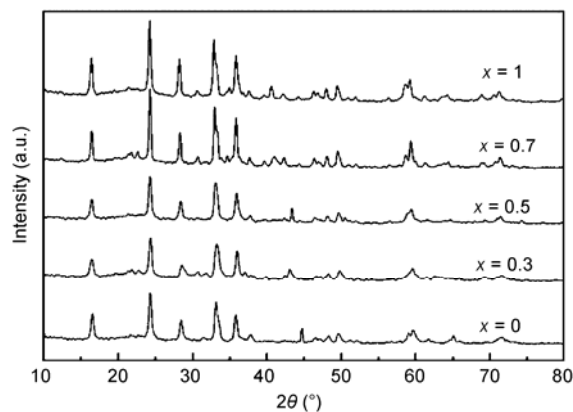


Figure 5 XRD patterns of the $\text{Li}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{SiO}_4$ samples. Reprinted from [42] with permission from Elsevier.

coefficient of $\text{Li}_2\text{FeSiO}_4$ by 1 order of magnitude. Cr-doped $\text{Li}_2\text{FeSiO}_4$ was prepared by Zhang et al. [44], who reported that the highest capacity that could be obtained by Cr doping was 3%. The $\text{Li}_2\text{Fe}_{0.97}\text{Cr}_{0.03}\text{SiO}_4$ sample demonstrates faster activation, a higher reversible capacity, and a better rate capability, which could be attributed to the smaller particle size and larger surface area as well as the crystal defects that are induced by Cr doping. DFT calculations were presented by Larsson et al. [45], which describe the effects of low-concentration Mn substitution on the Fe sites in $\text{Li}_2\text{FeSiO}_4$. The $\text{Li}_x\text{Fe}_{0.875}\text{Mn}_{0.125}\text{SiO}_4$ system could be produced by replacing 12.5% of the Fe-sites in the $2\times 2\times 1$ and $2\times 2\times 2$ supercells with Mn ions. Clear structural distortions can be seen in the Mn-sites following delithiation, suggesting possible structural instabilities that increases capacity in $\text{Li}_2\text{Fe}_{1-y}\text{Mn}_y\text{SiO}_4$ through >1 electron redox reactions, though this may not be readily attainable in practice. Attempts to dope Zn^{2+} , Cu^{2+} , Ni^{2+} into $\text{Li}_2\text{FeSiO}_4$ were attempted by Deng et al. [46]. The discharge capacity of the Zn-doped sample was 3.9% higher than that of the undoped sample, and the Zn-doped sample demonstrated the highest cycling stability; however, Ni^{2+} and Cu^{2+} cannot be doped into the lattice of $\text{Li}_2\text{FeSiO}_4$. An $\text{Li}_2\text{Al}_{0.1}\text{Mn}_{0.9}\text{SiO}_4$ cathode material was synthesized by Liu et al. [47], but a small amount of impurities was present. The particle size of the $\text{Li}_2\text{Al}_{0.1}\text{Mn}_{0.9}\text{SiO}_4$ sample was 100–500 nm and the morphology of the particle shape was not spherical. The reversible capacity and cycle life of the cathode sample improved with Al doping, and the mechanism illustrates that Al doping can stabilize the microstructure of the $\text{Li}_2\text{MnSiO}_4$ cathode material. Liu et al. [48] also synthesized $\text{Li}_2\text{Ti}_{0.1}\text{Mn}_{0.9}\text{SiO}_4$, which was similar to $\text{Li}_2\text{Al}_{0.1}\text{Mn}_{0.9}\text{SiO}_4$. The multicomponent olivine cathode material, $\text{LiMn}_{1/3}\text{Fe}_{1/3}\text{Co}_{1/3}\text{PO}_4$, was prepared by Park et al. [49] via a novel coprecipitation method that used a mixed transition-metal oxalate. The electrochemical activity of each transition metal in olivine that was synthesized via this method was clearly enhanced. Three distinctive contributions from Mn, Fe, and Co redox couples were reversibly detected in multiple charge/discharge processes. In the later experimental doping studies, substitution of the M sites in the orthosilicate material can be performed using materials other than metal ions, resulting in the performance of different ion synergies to improve the electrochemical properties of the material.

(2) Substitution of the O sites in Li_2MSiO_4 . First principles calculations were used to anticipate the electrochemistry of polyoxoanionic materials consisting of $\text{XO}_{4-y}\text{A}_y$ (A = F, N) groups by Armand et al. [50]. For example, this work focused on the effects of N and F on O substitution and the electrochemical properties of $\text{Li}_2\text{FeSiO}_4$. Within the $Pmn2_1$ - $\text{Li}_2\text{FeSiO}_4$ structure, virtual models of $\text{Li}_2\text{Fe}_2^{2.5+}\text{SiO}_{3.5}\text{N}_{0.5}$ and $\text{Li}_{1.5}\text{Fe}^{2+}\text{SiO}_{3.5}\text{F}_{0.5}$ were analyzed. They predicted that the Li deinsertion voltage is associated with $\text{Fe}^{3+}/\text{Fe}^{4+}$ redox coupling, which was decreased by both substituents. $\text{Li}_{1.5}\text{Fe}^{2+}\text{SiO}_{3.5}\text{F}_{0.5}$ demonstrates a lower specific capacity

than is inherent to F substitution. Substitution of N/F for O will respectively improve/worsen the electrode characteristics of $\text{Li}_2\text{FeSiO}_4$. Armand and Arroyo-de Dompablo [51] further investigated the effect of N for O substitution on the electrochemical properties of $\text{Li}_2\text{FeSiO}_4$. Within the $\text{Li}_2\text{FeSiO}_4$ structure, hypothetical models of N-substituted $\text{Li}_2\text{FeSiO}_3\text{N}$ and $\text{Li}_2\text{FeSiO}_{3.5}\text{N}_{0.5}$ were analyzed. The computational results indicate that the lithium deinsertion voltage associated with $\text{Fe}^{3+}/\text{Fe}^{4+}$ redox coupling could be decreased by N substitution (4.86 V in $\text{Li}_2\text{FeSiO}_4$, 4.7 V in $\text{Li}_2\text{FeSiO}_{3.5}\text{N}_{0.5}$ and 4.1 V in $\text{Li}_2\text{FeSiO}_3\text{N}$). The high theoretical specific capacity of $\text{Li}_2\text{FeSiO}_4$ (330 mA h g^{-1}) could be retained in N-substituted silicates due to the oxidation of N^{3-} anions. In light of the potential benefits of N substitution for O, experimental research is encouraged, in particular studies that investigate the reversibility and overpotential of the N redox reaction.

(3) Substitution of the Si sites in Li_2MSiO_4 . Defect chemistry, doping behavior, and Li-diffusion paths in $\text{Li}_2\text{MnSiO}_4$ were investigated using advanced modeling techniques. Kuganathan and Islam [52] found that the most favorable dopant incorporation was for Al^{3+} at the Si site in the monoclinic structure with Li interstitial compensation. Li/Mn anti-site defects or cation exchange can be improved by introducing extra Li in order to form the $\text{Li}_{2+x}\text{MnSi}_{1-x}\text{Al}_x\text{O}_4$ system, although the exact amount of Al that is incorporated cannot be predicted. Of course, the ideal scenario would be $x = 1.0$ for a solid solution consisting of $\text{Li}_{2+x}\text{MnSi}_{1-x}\text{Al}_x\text{O}_4$, which permits the removal of two Li^+ from the structure when accompanied by the oxidation of Mn^{2+} to Mn^{4+} , thereby yielding a high capacity for storing charge (approximately 300 mA h g^{-1}).

(4) Substitution of the Li sites in Li_2MSiO_4 . Na-substituted dilithium orthosilicate $\text{Li}_2\text{CoSiO}_4$ was investigated by performing density-function theoretical calculations within the GGA+U framework. The effects of Na-substitution on the electronic structures and structural properties of $\text{Li}_2\text{CoSiO}_4$ were presented by Wu et al. [53]. The results showed that Na-substitution at the Li sites in $\text{Li}_2\text{CoSiO}_4$ lowers the conduction bands and narrows the band gaps, which could enhance electrical conductivity. On the other hand, the Na-substitution of the Li ions in $\text{Li}_2\text{CoSiO}_4$ could lead to the expansion of the interlayer spaces within the adjacent corrugated layers. This lattice-expansion effect would benefit Li-ion diffusion.

3.4 Porous materials

A porous $\text{Li}_2\text{FeSiO}_4/\text{C}$ composite was synthesized by Fan et al. [54]. The $\text{Li}_2\text{FeSiO}_4/\text{C}$ composite is characterized by a large amount of particles that are approximately $5 \mu\text{m}$ in size. These particles are composed of a large number of smaller crystal grains that are approximately 100 nm, which are combined in many irregular pores. This structure not only offers channels for the infiltration of liquid electrolytes,

but also avoids the aggregation of nanoparticles during synthesis and/or electrochemical cycling. Although the $\text{Li}_2\text{FeSiO}_4/\text{C}$ cathode demonstrates a lower initial discharge capacity of 134 mA h g^{-1} , this improves to 155 mA h g^{-1} after 190 electrochemical cycles, as shown in Figure 6. Nanoembossed mesoporous LiFePO_4 microspheres were first synthesized by Qian et al. [55] using a template-free hydrothermal process. These microspheres demonstrate a uniform size distribution of approximately $3 \mu\text{m}$ and are composed of many densely aggregated 100 nm nanoparticles and interconnected nanochannels. This mesoporous structure allows sucrose to easily penetrate into the spheres and generate a thorough carbon coating on the surfaces of the nanoparticles on the interior of the spheres. These microspheres as a cathode-active material demonstrate a high tap density (1.4 g cm^{-3}), excellent rate capability (115 mA h g^{-1} , 10 C), and cycle stability.

Mesoporous magnesium manganese silicate as a cathode material used in rechargeable Mg batteries, was prepared by Nuly et al. [56] using mesoporous silica MCM-41 as both the template and silicon source. The mesoporous material exhibits better electrochemical performance with lower polarization for Mg de-intercalation and intercalation, larger discharge capacity and higher discharge flat plateau compared with the corresponding bulk material. At 0.2 C , the initial discharge capacity and discharge voltage plateau of

the mesoporous material can reach $241.8 \text{ mA h g}^{-1}$ and 1.65 V , respectively. The larger surface area of the mesoporous material favors efficient contact between the active material and the electrolyte, thereby providing additional active sites for electrochemical reactions, that are conducive to the transfer of the Li-ions, and for protecting the structure of the material during the processes of charging and discharging. This mesoporous structure may provide new approaches that could improve the reaction activity of the cathode materials used in rechargeable Mg batteries.

4 Summary and prospects

Poly anionic silicate materials that demonstrate high theoretical capacities, high levels of security, environmental friendliness and low cost attract the attention of many researchers, but this type of material was developed relatively recently and is relatively rare. The structures and properties of this material are still uncertain, and it is difficult to synthesize high-purity materials. Therefore the focus of future research should include in-depth studies of this material in order to clearly understand its structure, determine the mechanisms of capacity fade, optimize its synthesis, determine the best conditions for the synthesis of pure orthosilicate materials, improve the material's charge and discharge

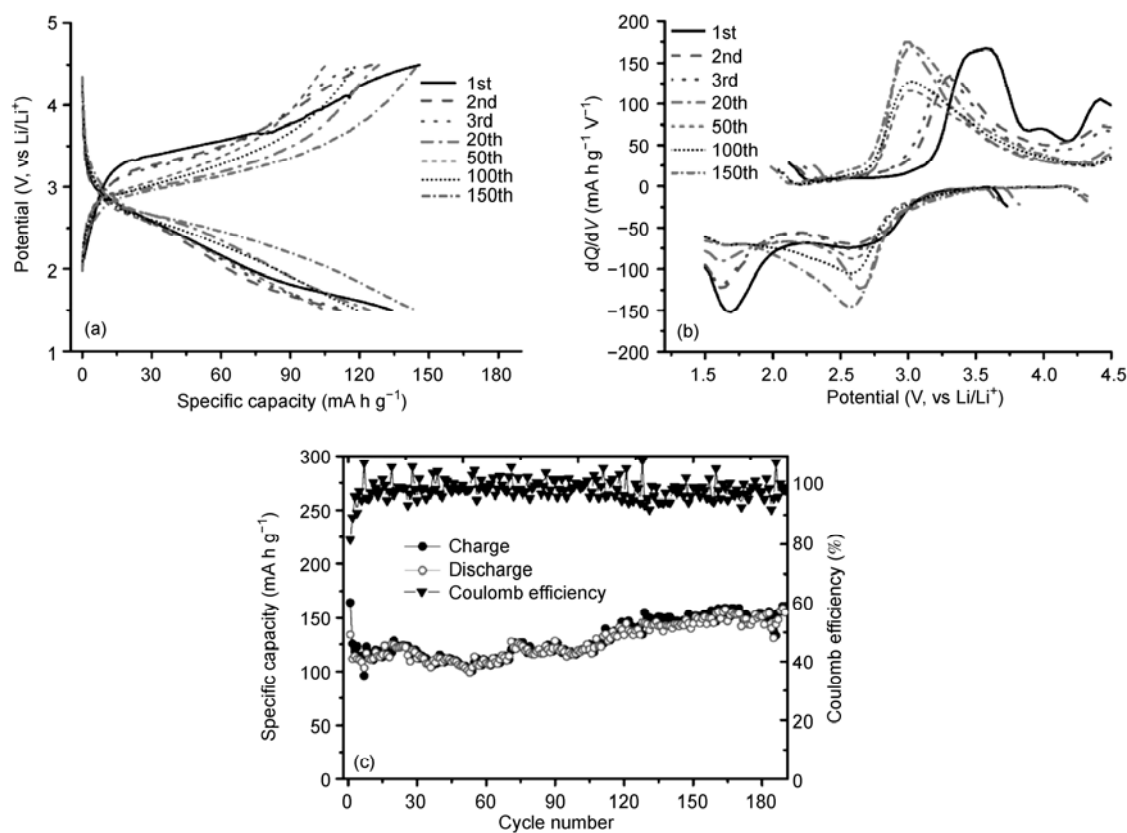


Figure 6 (a) Charge/discharge, (b) differential capacity, and (c) cycleability curves of $\text{Li}_2\text{FeSiO}_4/\text{C}$ composite. Reprinted from [54] with permission from Elsevier.

capacity and cycling performance (e.g. reduce the material's particle size, improve metal doping techniques, and elucidate its special morphology), and improve its low conductivity, such as by seeking suitable carbon sources and by optimizing carbon coating and composite conditions.

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