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Short Communication A High-Performance Li₂FeSiO₄/C Cathode Enhanced by a

Novel Liquid-State Carbon Source

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A novel liquid-state carbon source, [2-[(2R,3S,4R)-3,4-dihydroxytetrahydrofuran-2-yl]-2-hydroxyethyl] dodecanoate (sorbitan monolaurat, Span-20, C₁₈H₃₄O₆), is used to synthesize Li₂FeSiO₄/C by thesol-gel method. X-ray diffraction and scanning electron microscope measurements are carried out todetermine the crystal structures, morphologies and particle sizes of the resulting products. The resultsshow that Li₂FeSiO₄/C has pure phase and the average particle size of Li₂FeSiO₄ is in 20-30 nm. Theresult of Raman spectroscopy measurement indicates that the liquid-state carbon source can be proneto generate the carbon materials with high-ordered structure compared to the solid-state carbon source.The Li₂FeSiO₄/C cathode delivers an initial discharge capacity of 187 mAh g⁻¹ at 0.1 C rate, and it alsoshows good rate performance and stable cycle performance, indicating that the liquid-state carbonsource helps to improve the electrochemical performance of the Li₂FeSiO₄/C cathode. By analyzingelectrochemical impedance spectra, it is concluded that the carbon coating layer generated from theliquid-state Span-20 enhances the electrode/electrolyte interface characterization and improves the Li⁺diffusion.

Keywords: Lithium-ion battery; Polyanion-type compound; Cathode materials; Lithium iron silicate; Liquid carbon source; Carbon coating

1. INTRODUCTION

During the past decade, lithium-ion batteries not only have been widely applied on various electronic products, such as cell phone, digital camera, laptop and portable power tools, but also have became a reliable power source for electric vehicles due to their highly efficient energy conversion, high energy density and low self-discharge [1]. Currently, the lithium-ion batteries have moved toward a practical application of large-scale energy storage, the major challenges of which were specific

capacity, cyclic stability, safety and cost of cathode materials [2]. Sparked by the pioneer work of the Goodenough group [3], polyanion-type compounds have been pursued as cathode materials because they have the advantages of low exothermicity and high safety, compared with lithium transition-metal oxide cathode materials, such as LiMn₂O₄, LiCoO₂ and Li[Ni,Co,Mn]O₂ [4,5]. Lately, lithium transition-metal orthosilicates (Li_2MSiO_4 , M = Fe, Mn and Co) have stood out from the polyanion-type cathode materials by virtue of their high theoretical capacity (approximately 330 mAh g⁻¹, corresponding to a 2 mol Li⁺ per formula unit exchange) [6-9]. Among the orthosilicates, intensive investigations focused on Li₂FeSiO₄ due to its good cycle performance, low cost and environmental friendliness [10-22]. However, Li₂FeSiO₄ suffered from low electronic conductivity and slow Li⁺ diffusion [6,11]. To overcome these obstacles, two effective approaches could be made to improve the electrochemical performance of Li₂FeSiO₄, including coating the Li₂FeSiO₄ with carbon materials and decreasing Li₂FeSiO₄ particle size [23-25]. Up to now, the sol-gel method combined with an *in-situ* carbon coating technique has been offered to prepare Li₂FeSiO₄/C with nano-scaled particle size. The Dominko group synthesized Li₂FeSiO₄/C using a sol-gel reflux method, which based on the soluble iron source ($Fe(NO_3)_3$) and insoluble silicon source (SiO_2), leading to the Fe_3O_4 and Li_2SiO_3 impurities generating in the resulting product [7]. If SiO₂ was replaced by the soluble silicane (TEOS), the Li, Fe and Si elements would achieve a molecular-level mixing in the xerogel precursors. Representatively, the Li₂FeSiO₄/C nanocomposites prepared by the microwave-solvothermal or hydrothermal-assisted sol-gel methods showed good electrochemical performance [2,12]. Recently, our group have prepared Li₂FeSiO₄/C using a template-assisted sol-gel method, and the resulting product showed stable cycle performance at different rates ranged from 0.1 C to 2 C [26,27].

In the sol-gel preparation process of the Li₂FeSiO₄/C cathode, polymers and small molecule compounds were two kinds of major carbon sources. Popularly, the polymer carbon sources were generated from the condensation reaction of functional monomers, such as citric acid and glycol, during the gel formation, and the porous carbon-coated Li₂FeSiO₄ could reversibly exchange more than 1 mol Li⁺ per formula unit [18,28,29]. Furthermore, some template-functional polymers (P123) (PEO₂₀PPO₇₀PEO₂₀), F127 (PEO₁₀₆PPO₇₀PEO₁₀₆) and Phenol-Formaldehyde Resin) were directly used, but the resulting products showed a relatively high carbon content (higher than 15 wt%), which was considered as an infaust factor to the energy density of the Li₂FeSiO₄ cathode [20,30]. For the small molecule compounds, some solid saccharides (sucrose and glucose) with low cost were used as carbon source. They were mixed with xerogel precursors followed by the calcinations so that the introducing of carbon source did not effect on the gel formation process [2,12,31]. However, the solid carbon source was difficult to be mixed uniformly with the xerogel precursors, influencing the state of carbon coating and the electrochemical performance of Li₂FeSiO₄/C cathode. In this work, Span-20 (sorbitan monolaurat, $C_{18}H_{34}O_6$), which was liquid state at room temperature, was used as a novel liquid-state carbon source to prepare Li₂FeSiO₄/C cathode. This Li₂FeSiO₄/C showed higher discharge capacity at 0.1 C and better rate performance compared with the Li₂FeSiO₄/C prepared by using sucrose as carbon source. It indicated that the liquid-state carbon source could be more beneficial for improving the electrochemical performance of Li₂FeSiO₄/C cathode compared to the solid-state carbon source. Finally, the effects of carbon source on the electrochemical performance of Li₂FeSiO₄/C cathode were investigated by using Raman spectroscopy and electrochemical impedance spectroscopy measurements.

2. EXPERIMENTAL

The xerogel precursors were synthesized by a hydrothermal-assisted sol-gel method [12], and the brown gel was transferred into a glass dish from the autoclave and dried in an oven at 80 °C for 8 h. The obtained xerogel (1.6 g) was mixed with Span-20 (0.3 g) and ethanol (4 mL) and the mixture was ground by ball-milling. After evaporating the solvent, the dry powder was calcined in a horizontal quartz tube oven at 600 °C for 10 h flowing an argon atmosphere to obtain Li₂FeSiO₄/C (LFS-So), For comparison, the sample prepared by sucrose (0.3 g) as carbon source under the same condition was labeled as LFS-Su. Two products were stored in a glove-box.

The crystal structures of the LFS-So and LFS-Su samples were characterized by X-ray diffraction (XRD, Bruker D8 Advance) measurement with Cu Kα radiation operated at 40 kV and 40 mA. The morphologies of two products were observed by scanning electron microscopy (SEM, NOVA NanoSEM 230) and transmission electron microscopy (TEM, JEOL JEM-2010HT). The carbon content in the resulting product was measured by high frequency carbon-sulfur infrared analysis (CSI, Shanghai Baoying Photoelectric Technology CS-206), and the values were 8.4 wt% and 9.4 wt% for the LFS-So and LFS-Su samples, respectively. The graphitization degree of carbon coating for the resulting product was characterized by Raman spectroscopy (Bruker, Senterra R200-L dispersive Raman microscope). Electrode preparations (cathode loading was ~3-5 mg cm⁻²) and charge-discharge measurements were performed as described in our previous report [26]. Electrochemical impedance spectroscopy (EIS, 0.01 Hz to 100 kHz) was carried out using a CHI 660b electrochemistry workstation (Shanghai Chenhua Instrument).

3. RESULTS AND DISCUSSION





Figure 1. (a) XRD patterns of the LFS-So and LFS-Su samples, SEM images of (b) the LFS-So and (c) LFS-Su samples.

The XRD patterns of the LFS-So and LFS-Su samples were showed in Fig. 1a, and all the diffraction peaks of Li_2FeSiO_4 were indexed by a orthorhombic structure with a *Pmn2*₁ space group, which results were in full accord with those reported previously [6,12,32]. No iron oxides, lithium silicates or other impurities phases were detected in the resulting products. It indicated that both LFS-So and LFS-Su samples exhibited high-purity phase. The diffraction peaks of carbon were not observed in the XRD patterns due to its amorphous state. SEM measurement was used to investigate the Li_2FeSiO_4 particle size, and the corresponding images were shown in Fig. 1b and c. It could be found that the LFS-So particle was significantly smaller than the LFS-Su particle. The particle size of the LFS-Su sample ranged from 20 to 30 nm (Fig. 1b), and the particle size of the LFS-Su sample was larger than 50 nm (Fig. 1c). It indicated that the liquid-state carbon source could be prone to decrease the Li_2FeSiO_4 particle size much more compared with the solid-state carbon source. Moreover, the LFS-So particles were interconnected tightly to from a three-dimensional conductive network, probably enhancing the electronic conduction and Li^+ diffusion.

Reference	Method	Carbon Source	Voltage Range (V)	Condition	Capacity (mAh g ⁻¹)
Muraliganth <i>et al</i> ^[2]	Microwave- solvothermal sol-gel	Sucrose	1.5-4.7	25 °C	~150 (C/20) ~105 (2 C)
Dominko et al ^[11]	Pechini sol-gel	Citric acid EG	2.0-3.8	60 °C	~120 (C/10)
Gong et al ^[12]	Hydrothermal- assisted sol-gel	Sucrose	1.5-4.8	30 °C	160 (C/16) 125 (2 C)
Zhang et al ^[13]	Sol-gel	Citric acid	1.5-4.8	25 °C	153 (C/16) 100 (2 C)
Fan <i>et al</i> ^[14]	Sol-gel	Citric acid	1.5-4.5	25 °C	155 (C/5)

 $\label{eq:table 1. Comparison of the electrochemical performance of the Li_2FeSiO_4/C cathodes synthesized by sol-gel method.$



Figure 2. (a) The initial and (b) second charge-discharge curves of the LFS-So and LFS-Su cathodes, (c) their corresponding discharge capacities continuously cycled at 1 C, 2 C and 5 C, and (d) the cycle performance of the LFS-So cathode at 1 C, 2 C, 5 C and 10 C.

Galvanoststic charge-discharge measurement was carried out to assess the electrochemical performance of the LFS-So and LFS-Su cathodes. Fig. 2a displayed the initial charge-discharge curves of the resulting products at 0.1 C. The LFS-So cathode delivered an initial discharge capacity of 187 mAh g⁻¹, corresponding to a reversible exchange of 1.13 mol Li⁺ per formula unit. By contrast, the LFS-Su cathode only showed an initial discharge capacity of 140 mAh g⁻¹. As shown in Fig 2b, the second charge plateau was obviously lower than the initial plateau for both LFS-So and LFS-Su cathodes, which suggested that a Li/Fe disordering process might be occurred during the initial cycle [33-35]. Rate performances of the LFS-So and LFS-Su cathodes were shown in Fig. 2c, and it could be

easily found that the LFS-So cathode exhibited higher discharge capacities at different rates compared with the LFS-Su cathode. The discharge capacities of the LFS-So cathode were 137, 123 and 89 mAh g^{-1} for 1 C, 2 C and 5 C, respectively. Table 1 listed the electrochemical performance of the Li₂FeSiO₄/C cathodes synthesized by sol-gel method. It could be found that the Li₂FeSiO₄/C cathode prepared with Span-20 as carbon source showed high discharge capacity and good rate performance. This result meant that liquid-state carbon source could be more beneficial than solid-state carbon source for improving the discharge capacity and rate performance of Li₂FeSiO₄ cathode, due to uniform carbon coating layer. The cycle performance of the LFS-So cathode at high rate was further assessed, and the corresponding discharge capacities were shown in Fig. 2d. The LFS-So cathode delivered the discharge capacity of 131 mAh g⁻¹ at 1 C in the 50th cycle, and approximately 95% of the initial capacity could be retained. The capacity retentions were close to 100% while the rates increased to 2 C, 5 C and 10 C.



Figure 3. Raman spectra of (a) the LFS-So and (b) LFS-Su samples. The two broad bands can be deconvoluted into four peaks (dotted-line, peak 1, peak 2, peak 3 and peak 4) from a Gaussian numerical simulation, which are attributed to four vibration modes of carbon.

Fig. 3 showed the Raman spectra of the two samples, and the intensity ratio (I_D/I_G) of disordered carbon band (D-band) and graphitized carbon band (G-band) was used to evaluate the degree of carbon materials with ordered structure [36]. The signals at round 1595 cm⁻¹ and 1339 cm⁻¹ were attributed to sp² type carbon and sp³ type carbon, respectively [2,20,28]. The I_D/I_G values of carbon in Li₂FeSiO₄/C were fitted to 0.55 and 0.76 for the LFS-So and LFS-Su samples, respectively, indicating the LFS-So sample showed a relatively high sp² type carbon content compared with the LFS-Su samples. The low I_D/I_G value meant high degree of carbon materials with ordered structure, which might be helpful to the electrochemical performance [37]. Therefore, it was speculated that the LFS-So cathode exhibiting batter rate performance could result from the higher degree of carbon materials with order structure compared with the LFS-Su cathode.



Figure 4. (a) Impedance responses of the cells for the LFS-So and LFS-Su cathodes and (b) linear relationship between Z and $\omega^{-1/2}$ in the low-frequency region.

EIS measurement was use to understand the kinetic characteristic of the Li₂FeSiO₄/C cathode, and the impedance responses of the cells were showed in Fig. 4a. An intercept along the Z' axis at high-frequency region corresponded to the electrolyte resistance (R_e), and a depressed semicircles from high-frequency to medium-frequency regions was assigned to the charge transfer resistance (R_{ct}). The R_{ct} value of the LFS-So cathode was much smaller than that of the LFS-Su cathode, indicating that the LFS-So cathode exhibited relatively faster kinetics in Li⁺ intercalation/deintercalation reactions at the electrode/electrolyte interface compared with the LFS-Su cathode. The straight line in low-frequency region was associated with the Li⁺ diffusion process in the Li₂FeSiO₄ bulk. The Warburg coefficient (σ_w) could be obtained from the low frequency plots according to the following equation [15,38]:

$$Z' = R_{\rm e} + R_{\rm ct} + \sigma_{\rm w} \omega^{-1/2} \tag{1}$$

where ω (2 πf) is the angular frequency, and both R_e and R_{ct} are kinetic parameters independent of frequency. As shown in Fig. 4b, Z' showed a good linear relationship with $\omega^{-1/2}$, and the slope of the fitting line represented σ_w , and their corresponding values were 90.9 and 140 4 Ω cm² s^{-1/2} for the LFS- So and LFS-Su cathodes, respectively. The Li^+ diffusion coefficient (D_{Li}) can be calculated according to the following equation [15,38]:

$$D_{\rm Li} = \frac{R^2 T^2}{2A^2 n^4 F^4 C_{\rm Li}^2 \sigma_{\rm w}^2}$$
(2)

In the equation, *R* is the gas constant (8.314 J mol⁻¹ K⁻¹), *T* is the test temperature (298.15 K), *A* is the area of electrode (1.54 cm²), *n* is the number of electrons per reaction species, *F* is the Faraday's constant (96500 C mol⁻¹) and C_{Li} is the Li⁺ bulk concentration in the electrode (0.04 mol cm⁻³ for Li₂FeSiO₄ [28]). The calculated D_{Li} value was 1.13×10^{-15} cm² s⁻¹ for the LFS-So cathode, which was one order of magnitude higher than that of the LFS-Su cathode (4.74×10⁻¹⁶ cm² s⁻¹). The result of ESI measurement indicated that the LFS-So cathode showed smaller electrode/electrolyte interface resistance and faster Li⁺ diffusion compared with the LFS-Su cathode, resulting in the enhanced discharge capacity and rate performance. Generally, the improvement of electrochemical performance for the Li₂FeSiO₄/C cathode synthesized by the liquid-state carbon source could be attributed to a coefficient result of the close packing of particles, the high degree of carbon coating layer with ordered structure, and the enhanced electrode/electrolyte interface characterization and Li⁺ diffusion capability.

4. CONCLUSIONS

The liquid-state Span-20 was used as a novel carbon source to synthesize Li_2FeSiO_4/C cathode material for the lithium-ion batteries. The product showed pure phase with a $Pmn2_1$ orthorhombic structure and its active material particle size was in 20-30 nm. The Li_2FeSiO_4/C cathode showed good rate performance. By investigating the morphologies and Raman spectra of the resulting products, it concluded that the liquid-state carbon source could be prone to decrease the Li_2FeSiO_4 particle size and generate a tightly connected three-dimensional conductive network with the high-ordered sp² type carbon structure. The carbon coating layer generated from the liquid-state Span-20 could decrease the charge transfer resistance and improve the Li^+ diffusion.

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