

Research Article

Effect of Hydrofluoric Acid Etching on Performance of Si/C Composite as Anode Material for Lithium-Ion Batteries

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The effect of hydrofluoric acid (HF) etching on the performance of Si/C anode was extensively studied in terms of the structural stability, morphology, element distribution, and electrochemical properties. XRD results show that the diffraction peaks of silicon got weakened after being etched by HF. SEM images reveal that the morphology of the composite became coarse after being etched by HF. EDS mapping illustrates the distribution of elements before and after HF etching. Electrochemical studies show that HF etching can improve the cycling performance of Si/C composite but exhibit a deleterious effect on capacity. The results indicate that HF etching could be a promising method for enhancing the performance of silicon-based materials.

1. Introduction

The increasing demands for electric vehicles (EVs) and hybrid electric vehicles (HEVs) have resulted in extensive research on the high-energy lithium-ion batteries (LIBs), considering that rechargeable LIBs almost dominate the portable electronic and electric vehicle markets [1–3]. Various methods have been reported to improve device performance [4–8]. However, as an important part of LIBs, commercialized graphite anodes have limited application because of their low theoretical specific capacity (372 mAh g^{-1}) and security issues, which cannot satisfy the growing demands of high-energy application fields [9].

Different types of anode materials are available, such as alloy anodes and transitional metal oxides. However, silicon-based materials have attracted extensive attentions among all anode materials due to their high theoretical specific capacity (3579 mAh g^{-1}), abundance in nature, and appropriately low working potential [10–13]. However, the extremely huge volume variations during the alloying/dealloying process, low electric conductivity of the silicon-based materials, and unstable solid electrolyte interphase (SEI) film formed on the silicon surfaces newly exposed to commercial

electrolyte are the impending challenges for the development of the silicon-based anode [14–16].

Great efforts have been made to overcome the shortcomings of silicon-based anodes, such as optimizing the structural stability of the materials [17–19], improving the binders and electrolytes [20, 21], and improving the fabrication technology of the cells [22] [23–25]. Furthermore, the employment of silicon oxide (SiO_x) material is also an effective way to improve the cycling performance of Si-based anode [26]. Besides, surface modification is an effective way to improve the performance of the silicon-based materials [27]. Yao et al. reported interconnected Si hollow nanospheres by chemical vapour deposition-template etching process to form hollow structure [28]. Zhou et al. reported Silicon@carbon hollow core-shell heterostructures by SiO_x template-HF etching process [29]. Hence, a simple and convenient method to improve the performance of silicon-based materials is very necessary. The structure of the material should be sufficiently flexible to restrain the tremendous volumetric effect during the discharge/charge processes.

This paper proposes a novel surface modification method to improve the performance of the silicon-based materials. Si/C composite was prepared and etched by hydrofluoric acid

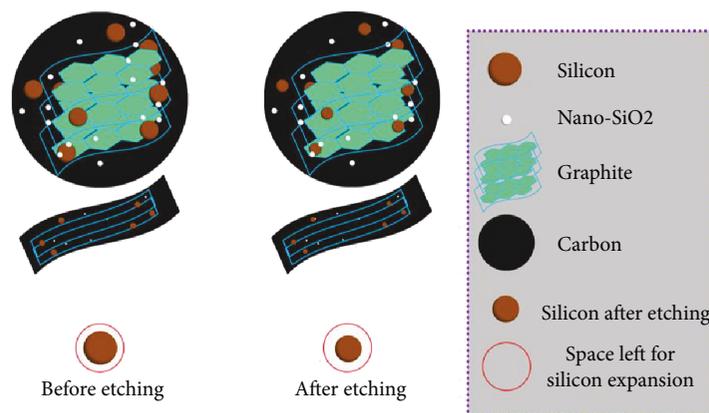


FIGURE 1: Structural representations of the composite.

(HF). This method is simple and easy and does not use expensive reagents. The performance of the effect of HF etching was investigated in detail; the composite is expected to exhibit enhanced electrochemical performance.

2. Experimental

Si/C-F composite was prepared by liquid-phase solidification combined with high-temperature pyrolysis method. The synthetic procedures can be briefly described as follows: (1) phenolic resin used as the source of disordered carbon was dissolved in alcoholic solution (5%); nanosilicon (nano-Si, >99.9%, ~30 nm, Shuitian Materials Technology Co., Ltd, Shanghai, China) and graphite (>99%, ~0.5 μm , Qingdao Tianhe Graphite Co., Ltd, Shandong, China) were added in the mass ratio of 1 : 4, and a small quantity of nanosilica sol (nano-SiO₂, 30 nm) was added as additive agent; (2) after being mixed uniformly, the mixture was evaporated at 80°C to get a solid precursor and dried in the oven at 120°C overnight; (3) pyrolyzed at 750°C for 2 h under argon atmosphere; (4) hydrofluoric acid (30 wt%) was diluted to 10 wt% by deionized water and then used to etch the Si/C composite for a certain time by gradient centrifuge method (3500 r min⁻¹ for 20 min) and washed several times by ethanol and deionized water (3500 r min⁻¹) to remove redundant HF; the desirable powders were dried at 120°C for 12 h and marked as Si/C-F for convenience. For comparison, the composite without HF etching was prepared and denoted as Si/C.

Powder X-ray diffraction (XRD, Rint-2000, Rigaku, Japan) measurements using Cu K α radiation were used to identify the crystalline phase of the as-prepared composite. Scanning electron microscopy (SEM, JEOL, JSM-5600LV) and transmission electron microscopy (TEM, FEI Tecnai G220) were used to observe the morphology and microstructure of samples.

The electrochemical characterization tests were performed using a CR2025 coin-type cell of Li | LiPF₆ (EC : EMC : DMC = 1 : 1 : 1 in volume) | anode. The anode is composed of 80 wt% anode material, 10 wt% Super P as conducting agent, and 10 wt% polyvinylidene fluoride (PVDF) as binder. After being mixed in *N*-methyl pyrrolidinone (NMP), the mixed slurry was spread uniformly on a copper foil and dried in vacuum for 12 h at 120°C. A polypropylene

microporous film was used as the separator. The assembly of the cells was performed in a dry argon-filled glove box. Electrochemical tests were carried out using a Neware battery tester (Neware, Shenzhen) with various cut-off potential ranges of 0.01–2.00 V (versus Li/Li⁺) at room temperature. The electrochemical impedance spectroscopy (EIS) were performed on a CHI660E electrochemical workstation (Chenhua Instruments, Shanghai, China) with AC amplitude of 5 mV from 0.01 Hz to 100 kHz.

3. Results and Discussion

The structural representations of the Si/C composite before and after etching are presented in Figure 1. Typically, in this composite, the graphite acts as a matrix to suppress the aggregation of silicon; silicon and silica nanoparticles are well dispersed in the graphite matrix, and disordered carbon is coated on the surface of the particles. Graphite will buffer the stress caused by volume change and provide sufficient electronic conductivity. SiO₂ also acts as dispersant to separate the silicon nanoparticles and buffer the volume expansion and shrinkage of silicon to a certain degree [30]. The size of nanosilicon decreases and the number of the bare silicon particles will reduce after etching, thereby improving the electrochemical performance of the Si/C composite.

The purpose of our research is to investigate the effect of HF etching on the performance of Si/C composite; XRD analysis was conducted to identify the phase structure of the as-prepared Si/C and Si/C-F powders, and the corresponding plots are demonstrated in Figure 2(a). Figure 2(a) compares the characteristic peaks of Si/C and Si/C-F composites. For Si/C composite, there only exist the crystalline diffraction peaks of nano-Si (JCPDS No. 27-1402) and graphite (JCPDS No. 41-1487) in addition to a broad diffraction peak around $2\theta = 23^\circ$ which is attributable to the amorphous phenolic resin-pyrolyzed carbon. No other phases, such as SiC, are observed. This indicates that the Si/C composite is the composite of silicon, graphite, and amorphous phenolic resin-pyrolyzed carbon. Since there are no obvious peaks for SiO₂, the existence of SiO₂ should be examined by other methods. It can also be seen that there is no noticeable structural changes, and diffracted intensity of graphite ($2\theta = 26.5^\circ$) was observed in the sample Si/C-F.

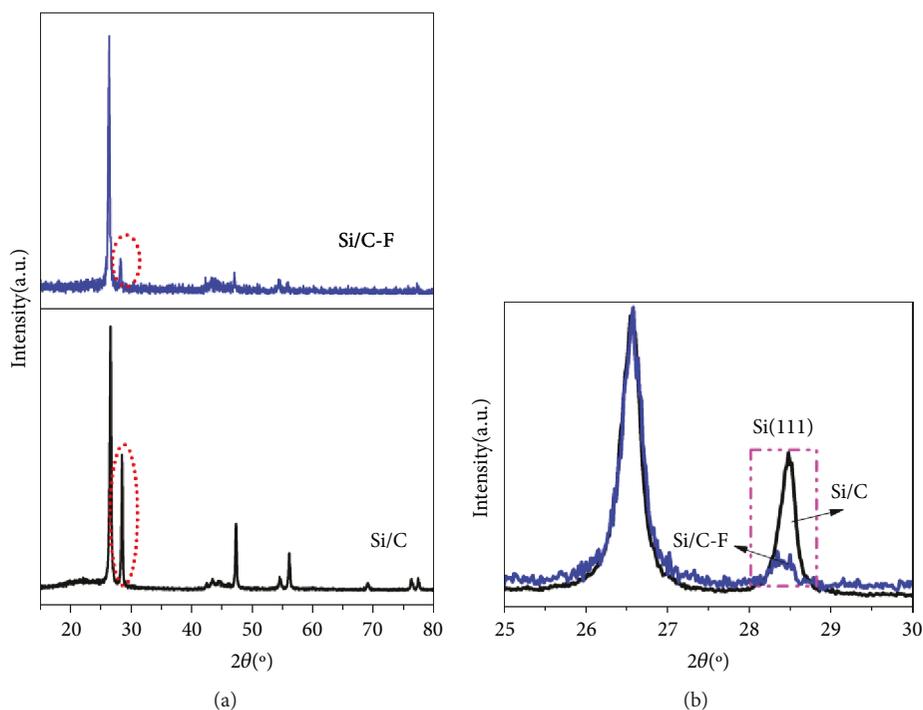


FIGURE 2: (a) XRD patterns of Si/C and Si/C-F powders; (b) comparison of silicon of Si/C and Si/C-F powders.

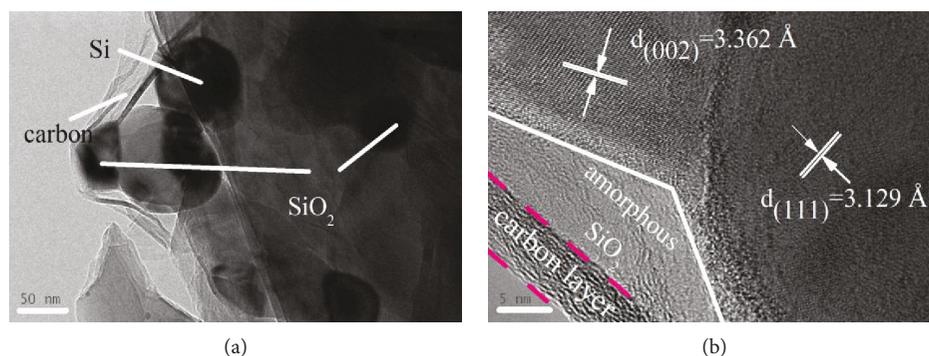


FIGURE 3: (a) TEM and (b) HRTEM images of Si/C composite.

However, the diffraction peaks of silicon ($2\theta = 28.4^\circ$) got weakened as shown in Figure 2(b), which proved that HF etching can reduce the content of the silicon in the composite. Those results could be attributed to the reactions between hydrofluoric acid and silicon, which will reduce the content of silicon.

In order to prove the existence of SiO_2 , TEM investigation was conducted. In Figure 3(a), it can be seen that SiO_2 consists in Si/C composite, and an amorphous carbon layer is coated on the surface of the Si/C composite and constructs the connection network of graphite and nano-Si particles. From the HRTEM picture of the Si/C composite as shown in Figure 3(b), the composite particles are composed of graphite ($d(002) = 3.362 \text{ \AA}$), nano-Si ($d(111) = 3.129 \text{ \AA}$), SiO_2 , and phenolic resin-pyrolyzed carbon, and SiO_2 is amorphous (as analyzed in the XRD patterns).

Figure 4 shows the SEM images of Si/C and Si/C-F samples. The morphology of the particles is both flaky in Figure 4(a) and Figure 4(b), which was possibly inherited

from the basic shape of graphite. The particles are firmly united in Figure 4(a), and the grain boundaries are smooth, and a great quantity of silicon is exposed and agglomerated on particle surface. Compared with Figure 4(a), the grain boundaries became coarse, and exposed silicon was reduced in Figure 4(b). These changes are associated with the structural representations of the Si/C composite before and after etching. The results revealed that silicon could be reduced after HF etching, which will affect the structure and morphology of the composite.

In order to investigate the interactions between HF and Si/C-F samples, it is necessary to study the element distribution on the surface of the as-prepared composite. Figure 5 shows the EDS results of elements Si, C, and O dispersed in the Si/C and Si/C-F composites. The element Si, O, and C dispersion state of the Si/C and Si/C-F composites is displayed in Figure 5. It can be seen from Figures 5(b) and 5(b') that the content of silicon significantly reduced after etching, which is in good agreement with the XRD results.

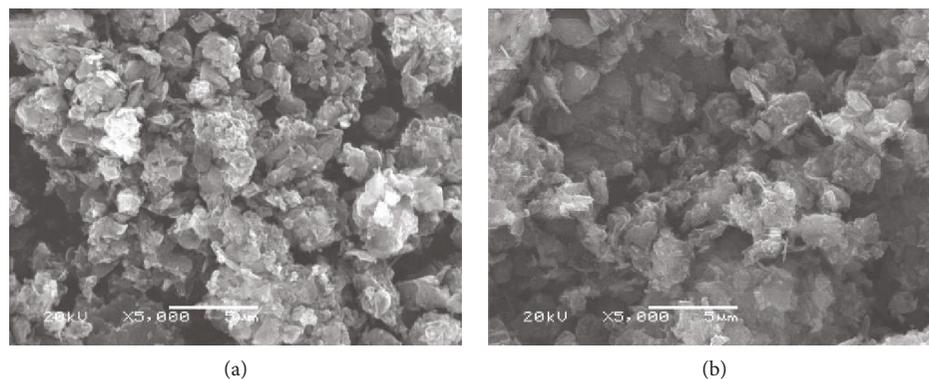


FIGURE 4: SEM images of (a) Si/C and (b) Si/C-F particles.

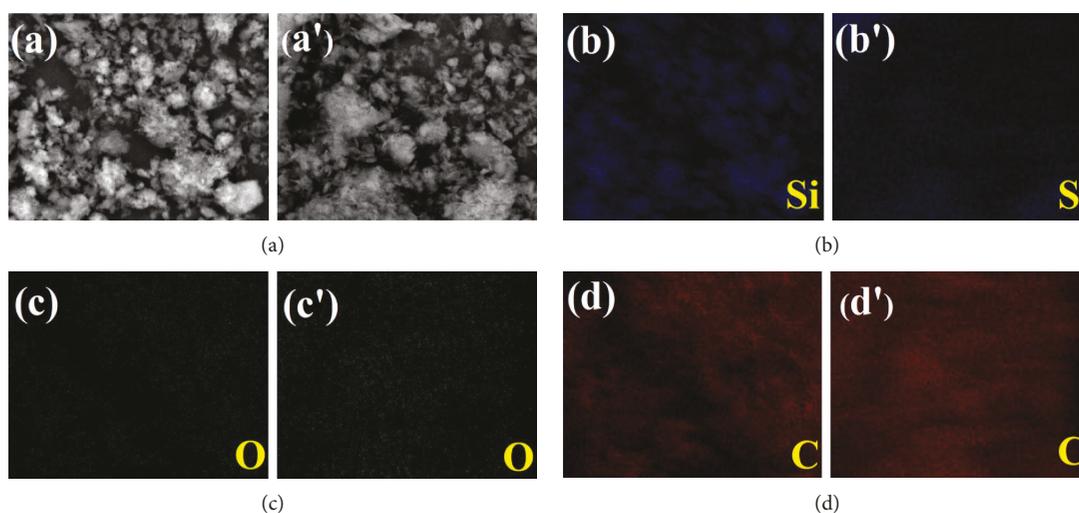


FIGURE 5: EDS maps of (b), (b') Si; (c), (c') O; (d), (d') C for Si/C and Si/C-F particles.

However, the contents of O (Figures 5(c) and 5(c')) and C (Figures 5(d) and 5(d')) show no obvious change. Those results show that silicon is the main element that was reduced during the etching process. The decrease in the amount of silicon is helpful to improve the cycling performance of the composite.

Figure 6(a) shows the initial discharge-charge curves of the Si/C and Si/C-F materials at the current density of 100 mA g^{-1} . It can be seen that the slope at around 0.6 V during the first discharge process is apparently higher after etching, indicating that high amounts of lithium were consumed to form SEI film [23]. The initial discharge capacity of the Si/C and Si/C-F composites are 1126.9 and $1083.9 \text{ mAh g}^{-1}$, respectively. Although the content of silicon decreased, the initial discharge capacity did not decrease significantly, which can be mainly ascribed to the improvement of electrochemical activity after being etched by HF. The initial charge capacity of Si/C and Si/C-F composites is 753.4 and 559.0 mAh g^{-1} , respectively. Compared with Si/C, the lower initial charge capacity and coulombic efficiency were observed for the Si/C-F composite, which could be partly attributed to the decreased amount of silicon by HF etching. The 50th charge-discharge curves for Si/C and Si/C-F samples are also shown in Figure 6(a).

Figure 6(b) shows the cyclic profiles of the Si/C and Si/C-F electrode at the current density of 100 mA g^{-1} , in which the cyclic performance was clearly enhanced by etching and remained stable after the first few cycles. Although the specific capacity of the Si/C-F electrode faded rapidly at the first three cycles, it exhibited a steady charge capacity with about 400.0 mAh g^{-1} after 50 cycles. Hence, HF etching was beneficial to improve the stability of the structure during the discharge/charge process.

The electrochemical impedance spectra (EIS) of Si/C and Si/C-F electrode after the 1st cycling process are presented in Figure 7, and the equivalent circuit model is inserted in the figure. It is remarkable that the EIS profiles are similar; both of them were composed of a semicircle in high frequency and a straight line in low frequency in the EIS spectra. In the circuit, R_1 presents the ohmic resistance between the electrolyte and electrode; R_2 is the charge transfer resistance in the electrode; CPE_1 is the double-layer capacitance and passivation film capacitance, and W_1 is the diffusion-controlled Warburg impedance [7, 31, 32]. The obtainable parameters related to equivalent circuit are recorded in Table 1. Apparently, the difference of R_1 is not striking between Si/C (2.0Ω) and Si/C-F (2.1Ω). However, Si/C-F delivers smaller R_2 (31.2Ω) than Si/C (35.8Ω), indicating that the Si/C-F

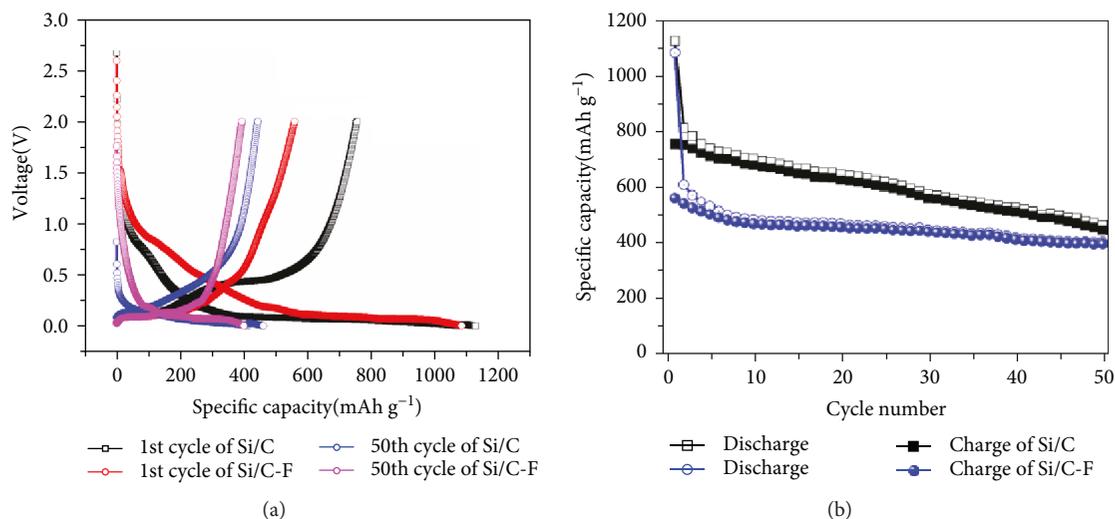


FIGURE 6: (a) Charge-discharge curves and (b) cyclic profiles of Si/C and Si/C-F composites.

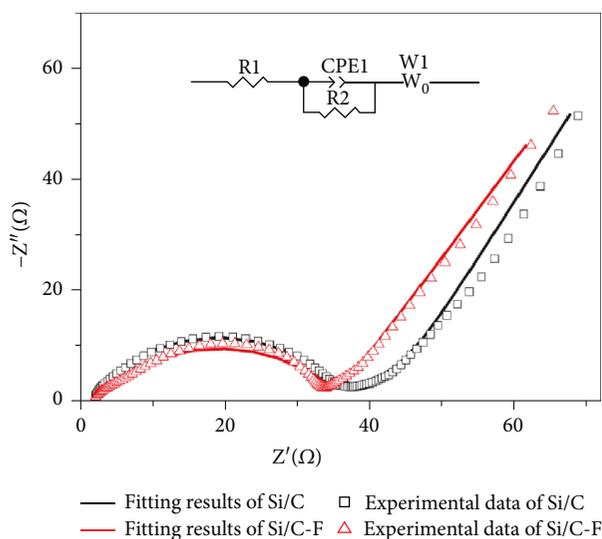


FIGURE 7: EIS of Si/C and Si/C-F composites.

TABLE 1: Electrochemical impedance parameters of samples.

Sample	R_1 (Ω)	R_2 (Ω)
Si/C	2.0	35.8
Si/C-F	2.1	31.2

electrode possesses lower charge transfer resistance, which may be caused by the low content of silicon and the stable structure of Si/C-F. The smaller R_2 possibly leads to better cycling, which is in accordance with the cycle performance.

4. Conclusion

In conclusion, the cycling performance and the structural stability of the Si/C composite were enhanced by HF etching, although it produced a deleterious effect on the

capacity of Si/C composite. The results of XRD and EDS analyses indicated that silicon was mainly etched, and its content reduced by the etching process. The etching of silicon can be helpful to construct a more stable structure and reduce charge transfer resistance. This method can significantly improve the performance of the as-prepared composite and deserves further investigation.

Data Availability

All authors can share the data that support the findings of the article by depositing them in a publicly available data repository wherever possible.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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References

- [1] Y. Liu, S. Zheng, Q. Wang et al., "Improvement the electrochemical performance of Cr doped layered-spinel composite cathode material $\text{Li}_{1.1}\text{Ni}_{0.235}\text{Mn}_{0.735}\text{Cr}_{0.03}\text{O}_{2.3}$ with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coating," *Ceramics International*, vol. 43, no. 12, pp. 8800–8808, 2017.
- [2] Y. Liu, S. Zheng, H. Wan, A. Dou, D. Chu, and M. Su, "Synthesis and electrochemical properties of cation-disordered Li-Ni-Ti-O compounds as cathode material for lithium ion batteries," *Journal of Alloys and Compounds*, vol. 728, pp. 659–668, 2017.

- [3] M. Su, H. Wan, Y. Liu et al., "Multi-layered carbon coated Si-based composite as anode for lithium-ion batteries," *Powder Technology*, vol. 323, pp. 294–300, 2018.
- [4] W. Xiao, Z. Wang, Y. Zhang et al., "Enhanced performance of P(VDF-HFP)-based composite polymer electrolytes doped with organic-inorganic hybrid particles PMMA-ZrO₂ for lithium ion batteries," *Journal of Power Sources*, vol. 382, pp. 128–134, 2018.
- [5] L. Wu, S. Shi, X. Zhang et al., "Room-temperature pre-reduction of spinning solution for the synthesis of Na₃V₂(PO₄)₃/C nanofibers as high-performance cathode materials for Na-ion batteries," *Electrochimica Acta*, vol. 274, pp. 233–241, 2018.
- [6] L. Wu, Y. Hu, X. Zhang, J. Liu, X. Zhu, and S. Zhong, "Synthesis of carbon-coated Na₂MnPO₄F hollow spheres as a potential cathode material for Na-ion batteries," *Journal of Power Sources*, vol. 374, pp. 40–47, 2018.
- [7] J. Wang, Z. Liu, G. Yan et al., "Improving the electrochemical performance of lithium vanadium fluorophosphate cathode material: focus on interfacial stability," *Journal of Power Sources*, vol. 329, pp. 553–557, 2016.
- [8] L. Wu, S. Shi, X. Zhang et al., "Novel synthesis of LiCoPO₄-Li₃V₂(PO₄)₃ composite cathode material for Li-ion batteries," *Materials Letters*, vol. 152, pp. 228–231, 2015.
- [9] I. Lahiri and W. Choi, "Carbon nanostructures in lithium ion batteries: past, present, and future," *Critical Reviews in Solid State and Materials Sciences*, vol. 38, no. 2, pp. 128–166, 2013.
- [10] X. Zuo, J. Zhu, P. Müller-Buschbaum, and Y. J. Cheng, "Silicon based lithium-ion battery anodes: a chronicle perspective review," *Nano Energy*, vol. 31, pp. 113–143, 2017.
- [11] J. R. Szczech and S. Jin, "Nanostructured silicon for high capacity lithium battery anodes," *Energy Environmental Science*, vol. 4, no. 1, pp. 56–72, 2011.
- [12] W. J. Zhang, "Lithium insertion/extraction mechanism in alloy anodes for lithium-ion batteries," *Journal of Power Sources*, vol. 196, no. 3, pp. 877–885, 2011.
- [13] H. Tian, X. Tan, F. Xin, C. Wang, and W. Han, "Micro-sized nano-porous Si/C anodes for lithium ion batteries," *Nano Energy*, vol. 11, pp. 490–499, 2015.
- [14] H.-C. Tao, L.-Z. Fan, and X. Qu, "Facile synthesis of ordered porous Si@C nanorods as anode materials for Li-ion batteries," *Electrochimica Acta*, vol. 71, pp. 194–200, 2012.
- [15] H. Usui, N. Uchida, and H. Sakaguchi, "Influence of order in stepwise electroless deposition on anode properties of thick-film electrodes consisting of Si particles coated with Ni and Cu," *Journal of Power Sources*, vol. 196, no. 23, pp. 10244–10248, 2011.
- [16] M. Gauthier, J. Danet, B. Lestriez, L. Roué, D. Guyomard, and P. Moreau, "Nanoscale compositional changes during first delithiation of Si negative electrodes," *Journal of Power Sources*, vol. 227, pp. 237–242, 2013.
- [17] W. Liao, D. Chen, Y. Zhang, and J. Zhao, "Binder-free TiO₂ nanowires-C/Si/C 3D network composite as high performance anode for lithium ion battery," *Materials Letters*, vol. 209, pp. 547–550, 2017.
- [18] X. Zhuang, Y. Zhang, L. He et al., "Scalable synthesis of nano-Si embedded in porous C and its enhanced performance as anode of Li-ion batteries," *Electrochimica Acta*, vol. 249, pp. 166–172, 2017.
- [19] B. Gattu, R. Epur, P. H. Jampani, R. Kuruba, M. K. Datta, and P. N. Kumta, "Silicon-carbon core-shell hollow nanotubular configuration high-performance lithium-ion anodes," *Journal of Physical Chemistry C*, vol. 121, no. 18, pp. 9662–9671, 2017.
- [20] I. Kovalenko, B. Zdyrko, A. Magasinski et al., "A major constituent of brown algae for use in high-capacity Li-ion batteries," *Science*, vol. 334, no. 6052, pp. 75–79, 2011.
- [21] W. Wang and S. Yang, "Enhanced overall electrochemical performance of silicon/carbon anode for lithium-ion batteries using fluoroethylene carbonate as an electrolyte additive," *Journal of Alloys and Compounds*, vol. 695, pp. 3249–3255, 2017.
- [22] B. P. N. Nguyen, S. Chazelle, M. Cerebelaud, W. Porcher, and B. Lestriez, "Manufacturing of industry-relevant silicon negative composite electrodes for lithium ion-cells," *Journal of Power Sources*, vol. 262, pp. 112–122, 2014.
- [23] Y. Zhou, H. Guo, Z. Wang, X. Li, R. Zhou, and W. Peng, "Improved electrochemical performance of Si/C material based on the interface stability," *Journal of Alloys and Compounds*, vol. 725, pp. 1304–1312, 2017.
- [24] M. Li, J. Gu, X. Feng, H. He, and C. Zeng, "Amorphous-silicon@silicon oxide/chromium/carbon as an anode for lithium-ion batteries with excellent cyclic stability," *Electrochimica Acta*, vol. 164, pp. 163–170, 2015.
- [25] W. Liu, Y. Zhang, J. Xu, L. Xu, J. du, and N. Li, "Facile synthesis of hollow mesoporous silica microspheres via surface sol-gel process on functional polymeric microsphere template," *Journal of Nanoscience and Nanotechnology*, vol. 16, no. 12, pp. 12644–12650, 2016.
- [26] W. Xiao, C. Miao, X. Yan, and P. Mei, "Novel silicon-oxygen-carbon composite with excellent cycling steady performance as anode for lithium-ion batteries," *Ionics*, vol. 21, no. 8, pp. 2149–2153, 2015.
- [27] S. Xun, X. Song, M. E. Grass et al., "Improved initial performance of Si nanoparticles by surface oxide reduction for lithium-ion battery application," *Electrochemical and Solid-State Letters*, vol. 14, no. 5, pp. A61–A63, 2011.
- [28] Y. Yao, M. T. McDowell, I. Ryu et al., "Interconnected silicon hollow nanospheres for lithium-ion battery anodes with long cycle life," *Nano Letters*, vol. 11, no. 7, pp. 2949–2954, 2011.
- [29] X. Zhou, J. J. Tang, J. Yang, J. Xie, and L. L. Ma, "Silicon@carbon hollow core-shell heterostructures novel anode materials for lithium ion batteries," *Electrochimica Acta*, vol. 87, pp. 663–668, 2013.
- [30] Y.-S. Hu, R. Demir-Cakan, M.-M. Titirici et al., "Superior storage performance of a Si@SiO_x/C nanocomposite as anode material for lithium-ion batteries," *Angewandte Chemie International Edition*, vol. 47, no. 9, pp. 1645–1649, 2008.
- [31] Y. Yang, Z. Wang, G. Yan et al., "Pitch carbon and LiF co-modified Si-based anode material for lithium ion batteries," *Ceramics International*, vol. 43, no. 12, pp. 8590–8595, 2017.
- [32] C. Fang, Y. Deng, Y. Xie, J. Su, and G. Chen, "Improving the electrochemical performance of Si nanoparticle anode material by synergistic strategies of polydopamine and graphene oxide coatings," *Journal of Physical Chemistry C*, vol. 119, no. 4, pp. 1720–1728, 2015.



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