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# Porous Si@C Composite Anode Material Prepared Using Dopamine as a Carbon Source for High-Performance Lithium-Ion Batteries

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Porous silicon-carbon (Si@C) composites as anode materials for Li-ion batteries are considered to be the most effective material for solving the problem of poor cycling performance of conventional silicon anode materials. However, the preparation process is complex and there are still some defects and shortcomings from the carbon source that limit its further application. Herein, we demonstrate a method through the self-polymerization of dopamine to produce Si@C composite anode materials with core-shell structures. The preparation process is simple, and the raw materials are environmentally friendly and do not cause pollution. The experimental results show that the material has good cycling stability, rate capability and an initial Coulombic efficiency of 87.7%. This provides a new idea for the application of Si@C composite anode materials.

Keywords: Li-ion battery, Porous Si, Carbon coating, electrochemical properties.

# **1. INTRODUCTION**

With the rapid development of electric vehicles, there is an increasing demand for low-cost Liion batteries with high energy, high power density, and long cycling stability,. Traditional graphite anode materials cannot meet the industrialization demand[1-3]. Because of its high specific capacity ( $4200mAhg^{-1}$ ) and low lithium intercalation potential (0.4V vs Li+/Li), Si is considered to be an anode material with the greatest potential to replace graphite[4,5]. However, as a negative material, Si usually faces two problems that hinder its commercial application:1) as a semiconductor, its conductivity is only  $6.7 \times 10-7Sm^{-1}[6]$ , and 2) in the process of charging and discharging Li-ion batteries, Li-ion insertion and removal will cause serious volume expansion (>400%)[7]. Intense volume changes lead to serious electrode powdering, and an unstable solid electrolyte interface (SEI) is formed in repeated charge-discharge cycles, which leads to a rapid decline in the specific capacity. To solve these two problems, various solutions have been proposed. The most effective way is to coat the Si surface with a carbon coating. Silicon-carbon composites with a core-shell structure are considered to be able to significantly alleviate the volume expansion of Si during Li-ion charging and discharging. At the same time, the conductivity of the Si anode can be effectively improved by coating with a carbon layer. Cui et al.[8] reported a nano-Si@C composite material with a pomegranate structure. Experiments show that pomegranate-structured materials can provide enough free space for the expansion and contraction of Si during the cycling of Li-ion batteries. A carbon coating can effectively avoid direct contact between the Si and the electrolyte, while also helping the formation of a stable SEI[9]. Li et al.[10] prepared SiO@C as an anode for Li-ion batteries using pitch as the pyrolysis carbon source. The material has a specific capacity of 680mAhg<sup>-1</sup> for 100 cycles. The initial Coulombic efficiency is 84.5%. Deng et al.[11] used alkali lignin(al) or alkali lignin-derived azo polymer (al-azo-no2) as a carbon precursor and prepared carbon-coated silicon nanoparticles with a size of 50nm. The results show that a carbon coating can greatly improve the conductivity and cycling stability of Si anodes. However, the carbon coating preparation methods are mainly sol-gel, high-temperature ball milling and others[12,13]. These methods often have harsh experimental conditions and complicated processes. In addition, most of the organic carbon sources used in the pyrolysis and carbonization process release a large number of toxic gases at high temperatures, causing serious environmental pollution. Therefore, the further application of Si@C composite anodes is limited.

The fabrication of porous electrodes is another effective way to improve the cycling stability of Si anodes. A study[14] showed that porous Si anodes could reserve space for the volume expansion of Si during the charging and discharging process, thus alleviating the volume strain. At the same time, the special porous structure could provide a special channel for Li<sup>+</sup> transport, accelerate the transmission speed of Li-ion and improve its electrochemical performance. Huang et al.[15] prepared a Si@C-GR ternary composite anode with a porous structure by a hydrothermal synthesis. The material has a high specific capacity, excellent cycling performance, and a high rate performance.

Herein, we propose the use of dopamine (DA) as the pyrolysis carbon source to prepare Si@C composites with porous structures by pyrolysis at elevated temperatures using the self-polymerization of dopamine under alkaline conditions. DA was chosen as a pyrolysis carbon source mainly for the following three reasons[16-18] 1) DA has an amino group and catechol group, both of which can firmly adhere to the surface of any organic or inorganic substance after self-polymerization<sup>[16]</sup>. The process of operation is simple. As long as DA is dissolved in a weak alkaline solution (pH=8-8.5), it will self-polymerize under aerobic conditions to form a tight polydopamine (PDA) package and cover the surface of the material. 2) The coated carbon layer with a porous structure formed by pyrolysis and carbonization of PDA at high temperature has good conductivity, which improves the poor conductivity of the silicon anode, improves the effective channel for conduction of Li-ion and accelerates the diffusion speed of Li-ion[16,17]. 3) Compared with other organic carbon sources, the functional groups of PDA only contain N, H, and O. After carbonization at high temperature, no toxic gases will be generated, which beneficial for protecting the environmental. Compared with traditional silicon anodes, the Si@C anode prepared by dopamine as a pyrolysis carbon source has an initial Coulombic efficiency of 87%, a capacity of 420mAhg<sup>-1</sup> after 200 cycles at 1000mAg<sup>-1</sup>, and good rate

performance. It can effectively improve the comprehensive electrochemical performance of Si anodes, and hopefully, be used to realize the commercialization of high-performance Si anodes.

# 2. EXPERIMENTAL

## 2.1 Electrode preparation

# 2.1.1 In-situ Polymerization of Si@PDA Precursors

Nanosilicon (0.5g Ningbo Jinlei Nanomaterials Technology Co., Ltd.),and 0.25g, 0.5g, 0.75g, 1g poly4-(2-methylamino) benzene-1,2-bisphenol (dopamine) were added to a 250ml aqueous solution. Then 0.173g Tris were added after ultrasonic cleaning for 30 minutes and magnetic stirring for 8h. Deionized water was used to produce an even mixture. A silicon@poly 4-(2-methylamino) benzene-1,2-bisphenol (Si@PDA) precursor was obtained by vacuum filtration three times and drying in a vacuum drying chamber at 80°C for 24h.

## 2.1.2 Preparation of Si@C by High Temperature Carbonization Precursor

The prepared Si@PDA precursor was placed in a tubular furnace, and then the coated siliconcarbon composites (Si@C) were prepared by raising the temperature of the precursor to 700, 800 and 900°C for 2h at 5°C/min. In the process of high-temperature carbonization, high purity N<sub>2</sub> is introduced as a protective gas to prevent oxidation of Si@PDA at high temperature. The specific synthesis process is shown in Fig.1.



Figure 1. Schematic illustration showing the synthesis process of the Si@C nanocomposite with a carbon coating

#### 2.2 Materials characterization

The phase purity of the Si@C composite materials was characterized by X-ray diffraction (Ultima IV, Japan) with Cu K $\alpha$  radiation in a 2 $\theta$  range of 10°–80°. The Fourier transform infrared spectroscopy (FTIR) spectra of the samples were obtained by using Nicolet IS 10(IS50FT-LR., USA) in a range of 400–4500cm<sup>-1</sup>. Surface areas and pore sizes were obtained from Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) results by using a surface analyzer (ASAP2460, USA). The morphology of the Si@C composite materials was characterized using a scanning electron microscopy (SEM, S4800, Hitachi, Japan). Raman spectra were recorded on a spectrograph micro-Raman system (LabRam HR Evolution, France)

#### 2.3 Electrochemical performance tests

Using sodium alginate as a binder, graphite, and acetylene black as a conductive agent, the Si@C active material, conductive agent and binder were mixed in a certain proportion and evenly coated on a copper foil with a 60-micron preparation device. The prepared electrodes were dried for 24h in a vacuum drying chamber at 80°C. The copper foil was stamped into sheets with a 12mm diameter puncher and weighed. LiPF6, EC (vinyl carbonate), and DEC (diethyl carbonate), DMC (dimethyl carbonate) were mixed in proportion as an electrolyte, A Celgard 2400 was uesd as a diaphragm and a lithium sheet as the opposite electrode. A button battery was assembled by putting the electrode material into a vacuum glove box and testing at room temperature after 24h. The voltage range of the anode charge/discharge was 0.01-1.5V. The current density of the first four cycles was 100mAg<sup>-1</sup>, and was 1000mAg<sup>-1</sup> for the subsequent long-term cycling. A PARSTAT4000 electrochemical workstation was used to test the AC impedance of the experimental battery. The frequency range was from 0.01Hz to 100kHz, the AC amplitude was 0.01V, and the ambient temperature was 25°C.

# **3. RESULTS AND DISCUSSION**



3.1 Structure and properties of the materials



Figure 2. TG and DSC analysis of a)PDA and b)Si@PDA

The Si@C composite anode material was prepared by the carbonization of 0.5g dopamine coated Si@PDA. The TG and DSC results of PDA and Si@PDA at 5°C/min are shown in Fig.2. It can be seen from Fig.2a) that when the temperature rises to about 180°C, PDA begins to pyrolyze and carbonize, and there is an endothermic peak on DSC curve[18]. This is basically the same as the temperature of the first endothermic peak of PDA in reference. At this time, the carbonization rate of pyrolysis is slow and the weight loss of PDA is low. With increasing temperature, the weight loss of PDA increases rapidly. When the temperature reaches approximately 800°C, the PDA is basically completely weightless, which means that the PDA has been carbonized completely at approximately 800°C, and the weight loss of PDA does not change when the temperature continues to rise. Fig.2b) shows the weight loss curve of Si@PDA, which is also the starting point of pyrolysis and carbonization at 180°C and the completion of carbonization and pyrolysis at 800°C. At this time, the generated material is a Si@C composite anode material.

To verify that the precursor of PDA was successfully coated on the Si surface, the infrared spectra of the precursor Si@PDA and the Si@C obtained after heat treatment at different temperatures were measured with 0.5g dopamine-coated Si@C material, as shown in Fig.3. From the figure, it can be seen that the samples have obvious absorption peaks at 3503cm<sup>-1</sup>, 3361cm<sup>-1</sup>, 2458cm<sup>-1</sup>, 1618cm<sup>-1</sup>, 1490cm<sup>-1</sup> and 1288cm<sup>-1</sup>, which are consistent with the characteristic peaks of PDA<sup>[19]</sup>. At 3053cm<sup>-1</sup>, the phenolic hydroxyl group in the PDA structure corresponds to the characteristic stretching vibration absorption peak of the N-H bond in the amino group at 3361cm<sup>-1</sup>, the obvious absorption peaks at 1618cm<sup>-1</sup> and 1490cm<sup>-1</sup> correspond to the resonance peak of C=C in a benzene ring and the bending vibration peak of N-H, and the absorption peak at 1100cm<sup>-1</sup> corresponds to the shear vibration peak of N-H. The above characteristic peaks are consistent with those of PDA, indicating that polydopamine is successfully coated on the Si surface[20].Compared with the infrared spectrum of Si in reference, the peak value of Si@C is enhanced, and the peak at 1618cm<sup>-1</sup> is split into two peaks[21]. This result shows that there is a strong bond between silicon and carbon of C coating. The strong bond between carbon and silicon will improve the cycle stability, stable SEI and the coulomb efficiency in charge discharge cycle[22].After heat treatment at 700 and 800°C, most of the absorption peaks in PDA

disappear, and only the phenolic hydroxyl absorption peaks at 3361cm<sup>-1</sup> widen with increasing heat treatment temperature. This is because the high temperature destroys chemical bonds with elements such as carbon, oxygen, nitrogen, and hydrogen. PDA decomposes after a long-term heat treatment above 700°C, but the heat treatment is not complete. There is a weak characteristic absorption peak of the stretching vibration of the N-H bond at 3503cm<sup>-1</sup>. When the heat treatment temperature is 800°C, the carbonization is complete and there is no residual PDA. As the heat treatment temperature continues to rise to 900°C, the high heat treatment temperature makes the material inactive, so there is no obvious characteristic peak.



Figure 3. FT-IR spectra of Si@PDA at different heat-treatment temperatures



Figure 4. XPS of Si@PDA and Si@C

XPS tests were carried out on Si@PDA and Si@C materials before and after high-temperature pyrolysis and carbonization at 800°C, as shown in Fig.4. It can be seen from the figure that the N1 peak exists in Si@PDA, which indirectly indicates the successful coating of PDA, In contrast only the Si peak and C peak exist in the XPS of Si@C, indicating that the coating effect of Si@C material is relatively good after high-temperature pyrolysis, due to the absence of other miscellaneous peaks.

An XRD diffraction analysis of the Si@C composites prepared by pyrolysis of different PDA coatings was carried out. The results are shown in Fig5. It can be seen from the figure that the XRD spectra of different coatings are similar. The peaks of the (111), (220), (311), (400) and (331) planes of single crystal Si are visible at 28.70°, 47.50°, 56.30°, 69.3° and 78°, and all the peaks can correspond to the X-ray diffraction peaks of Si (JCPDS No.77-2111). The corresponding positions of the main peaks are the same, indicating that the carbon coating does not change the crystal structure of Si. However, with an increase in the coating amount, the main peak (111) gradually shifts to a small anglea according to the Prague formula:

 $n\lambda = 2dsin\theta \tag{1}$ 

It can be seen that the angle of theta decreases and the value of D increases with the increase in the amount of PDA coating. It shows that C-coating can change the surface spacing of (111)[23], This indicates that the interlayer spacing of silicon particles increases with the increase in the amount of PDA coating, which is more conducive for the diffusion of lithium ions in silicon anode materials<sup>[24]</sup>. There is a diffraction package near 24 degrees, which corresponds to the formation of pyrolytic charcoal after pyrolysis and carbonization. However, there is no peak for pyrolytic carbon, indicating that the C coating exists in the form of amorphous carbon[25].



Figure 5. XRD spectrum of silicon-carbon composites prepared with different quantities of carbon coating

To further determine the structure of the C coating, Raman spectroscopy was used to detect Si@C materials with different C coating amounts, as shown in Fig.6. When the amount of PDA coating is 0.25g, it can be seen from the figure that there are no obvious peaks for amorphous carbon (D-band) and graphitized carbon (G-band). This shows that when the amount of PDA is too small, the carbon layer cannot be coated on the surface of Si. With increasing PDA content, the peaks at 1335cm<sup>-</sup> <sup>1</sup> and 1610cm<sup>-1</sup> correspond to the peaks of amorphous carbon (D-band) and graphitized carbon (Gband), respectively. These values represent the vibrations of the carbon atom in the electronic configuration of SP<sup>2</sup> and the disordered carbon atom in the structure of SP3[26]. The strength ratio (ID/IG) of the D-band and G-band reflects the graphitization degree of carbon. The higher the ID/IG value, the smaller the degree of graphitization[27]. It can be seen from the figure that with an increase in the amount of coating, the ID/IG value has no obvious change, and is at approximately 1.1, indicating that the graphitization degree of the carbon proportion in the Si@C anode material is relatively low. The coating carbon is amorphous carbon. This is because the complex network structure of the phenol monomer unit in dopamine is difficult to graphitize during the carbonization process, and the amorphous carbon structure is conducive to the transport of Li-ion[11]. At the same time, the results of the Raman spectrum show that the Si@C material is successfully produced.

The morphology and microstructure of the Si@C samples were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Fig.7, the original Si and the prepared Si@C samples have similar particle sizes, with an average particle size of 4-6 microns. After coating with carbon, the surface of the Si@C particles becomes smoother, which is in contrast to the rough surface of the original Si particles (Fig. 7a) – 3d)). TEM further confirmed the uniformity of the carbon coating. It can be seen from Fig.7e) and f) that Si@C particles are uniformly distributed with a diameter of 400-500nm, which is consistent with the scanning results. The Si surface is uniformly coated with a carbon layer, and the thickness is approximately 100nm.



Figure 6. Raman spectra of silicon-carbon composites prepared with different quantities of carbon coating



**Figure 7.** Effect of coating amount on the structure and morphology of Si@C a) SEM images of Si b)c) SEM images of Si@C, and e)-f) TEM images of Si@C

To verify the successful preparation of the porous structure, nitrogen adsorption and desorption tests were carried out on the polymer PDA, precursor Si@PDA, C and Si@C composites heat-treated at 800°C(Fig.8). It can be seen from Fig.8a) and b) that the nitrogen adsorption capacities of PDA and Si@PDA are low. However, the C after high temperature carbonization shows a hysteresis loop with steep condensation steps in the range of relative pressure  $P/P_0 = 0.80-0.98$ , which is a typical feature of disordered porous materials[28]. After being treated at 800°C, the nitrogen adsorption capacity of the samples increases dramatically. At low relative pressure, the N<sub>2</sub> adsorption capacity of both samples

increases rapidly and then changes slightly at medium relative pressure. Finally, the N<sub>2</sub> adsorption capacity of the samples increases rapidly. There is no contact point between the adsorption and desorption branches at the lower P/P<sub>0</sub>, which may be due to the existence of micropores in the composite, whose size is almost the same as the adsorbate. Adsorbate condensation occurs at high relative pressure. The above characteristics can be judged to belong to type I adsorption isotherm[29], which indicates that there are a large number of micropores (<2nm) in the material. The micropores in the carbon layer mainly come from the high-temperature decomposition of PDA during heat treatment. The specific surface area of carbon obtained by PDA pyrolysis at 800°C is  $16.72m^2g^{-1}$  and that of the Si@C sample is  $72.63m^2g^{-1}$ . The PDA without pyrolysis is compact and porous with a specific surface area of only  $10.3m^2g^{-1}$  and  $50.99m^2g^{-1}$  for the silicon matrix composites coated with PDA as the pyrolysis carbon source.





Figure 8. N<sub>2</sub> adsorption/desorption isotherms of the a) PDA and its pyrolyzed carbon, b) Si@PDA and Si@C composite

#### 3.2 Electrochemical performance tests

To evaluate the electrochemical performance of the as prepared Si@C, the charge-discharge curves of different carbon-coated samples are shown in Fig.9. When the coating content is 0.5g, the Si@C composite has the highest first charge-discharge specific capacity and Coulombic efficiency, with a value up to 88.7%. This is mainly because when the PDA coating amount is 0.5g, a carbon layer with a suitable thickness can be obtained along with the complete coating of the silicon surface. The amorphous carbon layer increases the transmission channel for Li-ion, promotes the electrode reaction process and improves the Coulombic efficiency. When the coating amount of PDA reaches 0.25g, the carbon layer is too thin or incomplete because the coating amount is too low. It is impossible to completely suppress the irreversible breaking of negative material during charging and discharging. As a result, the capacity decreases sharply. For the first time, Coulomb efficiency is only 73.2%. When the coating amount increases to 0.75g and 1g, the distance and resistance of Li-ion diffusion increase with increasing coating amount and thickness, which is not conducive to the transport of Li-ion. With increasing coating amount, the irreversible capacity and Coulombic efficiency of Li-ion decrease.



Figure 9. First charge-discharge curve of Si@C composite anode material prepared by different quantities of PDA coating

Electrochemical cycling tests of Si@C composite anode materials prepared with different PDA coatings were carried out, as shown in Fig.10. It can be seen from the figure that there is an activation stage in the initial stage of Li-ion detachment/embedding in the Si@C composite anode material. Compared with the silicon anode material without a carbon coating, the PDA-coated pyrolysis carbonization can effectively improve its reversible specific capacity, and different amounts of coating have a large impact on its electrochemical performance. The first reversible specific capacity of PDA is 0.5g. Si@C has the highest first reversible specific capacity with a value of approximately 1048mAhg<sup>-1</sup>. An excessive or insufficient coating can reduce the reversible specific capacity of Si@C due to the incomplete or thin carbon coating when the coating amount is too small. In the process of Li-ion charging and discharging, the coating cannot fully play a role. As the volume of silicon expands, it is destroyed, which affects the specific capacity of the material and leads to the continuous decline of the cycling performance of the material. When the amount of carbon coating is large, a large carbon coating thickness is formed on the surface of silicon particles, which increases the diffusion distance of Li-ion, increases the diffusion resistance, and is not conducive to the diffusion of lithium ions, thus reducing the reversible specific capacity. When the coating amount is 0.5g, the silicon surface can obtain the most complete and suitable carbon coating. The amorphous carbon layer structure increases the diffusion channel, promotes the electrode reaction process, and has a good inhibition effect on the volume expansion of silicon. Therefore, it has the highest reversible specific capacity and stable cycling.



Figure 10. Cycling properties of the Si@C composite anode material prepared by different quantities of PDA coating

We further compare PDA as Si@C with other similar carbon sources in the literature, and the results are shown in Table 1. The results show that the Si@C composite anode material prepared with PDA as carbon source has higher capacity and cycle stability than other materials reported in reference at high current density. It also proves that PDA can be used as carbon source of Si anode material, and Si @ C material is a promising anode material for Li-ion battery.

**Table 1**. The comparison of various anode materials for Li-ion batteries.

Carbon source	Capacity(Cycle number) (mAhg <sup>-1</sup> )	Current Density (mAhg <sup>-1</sup> )	Reference
PDA	450(200)	1000	This work
PAN	652 (50)	100	[30]
PVDF	1290(30)	50	[31]
pitch	261.66 (150)	1600	[32]

The increased performance of Si@C prepared by different PDA coatings was tested, as shown in Fig.11. It can be seen from the figure that coating amorphous carbon on the silicon surface can improve the performance ratio of the negative silicon material. The amount of coating has a great influence on the performance. When the coating amount is low, the performance ratio cannot be improved because the carbon layer is too thin or incomplete. When the coating amount is too high, the diffusion resistance of Li-ion increases, and the ratio performance decreases. When the coating amount is 0.5g, Si@C has the best rate performance.



Figure 11. Ratio properties of the Si@C composite anode material prepared by different quantities of PDA coating



Figure 12. Impedance of the Si@C composite anodes prepared by different amounts of PDA coating

To further verify its conductivity, we tested the rate performance of the Si@C composite anode materials with different coating amounts after 50 cycles. As shown in Fig.12. All impedance maps are composed of semicircles in the high-frequency area, and semicircles and slashes in the low-frequency area[30]. The semicircle in the high frequency area is related to the contact impedance and the

impedance of the boundary film. The semicircle in the intermediate frequency region is related to the charge transfer impedance. The slant in the low frequency region is related to the diffusion process of Li-ion in the solid material[33]. Compared with the impedance of Si@C and Si, it can be found that a small amount of coating cannot significantly improve the conductivity of Si. After 50 cycles, it has a large semicircle in the high-frequency area. When the amount of coating reaches more than 0.5g, the composite has a small semicircle, and the slope of the low-frequency area is also steep. It is clear that the C coating can enhance the conductivity of the negative Si material and reduce the charge transfer resistance. At the same time, it is in a good state toward ion transport. However, with an increase in the amount of C coating, the conductivity of C does not change further.

Compared with the uncoated Si powder, the coated Si carbon powder composite has excellent electrochemical properties. The main reasons are as follows:1) Compared with the uncoated Si material, the coated Si@C composite material has a more stable structure[34,35]. The surface coated carbon can improve the volume expansion of the negative material and effectively extend the cycling performance of the negative material. 2) The carbon layer of the coated Si@C composite has a microporous structure, which can not only effectively buffer the volume expansion of silicon in the process of charging and discharging but also provide a channel for the transport of Li-ion[36,37]. The transmission speed of Li-ion is increased. 3) The carbon layer coating that is on the Si@C composite can effectively improve the poor conductivity of Si as a negative material[38], and improve its electrochemical impedance and rate performance.

## 4. CONCLUSIONS

In conclusion, the electrochemically stable Si@C composite anode material can be prepared by a simple self-polymerization using dopamine as the carbon source and coating at 800°C. The porous Si@C composite anode material with a core-shell structure can greatly improve the conductivity and cycling stability of the Si anode material. At a current density of 1000mAg<sup>-1</sup>, the capacity is 450mAgh<sup>-1</sup> and the initial Coulombic efficiency is 87.7%. These excellent properties ensure that the Si@C composite anode material can be applied as sustainable electrode materials in Li-ion batteries.

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