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Abstract

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Keywords

derived, carbon, silicon, nanocomposites, life, cycle, long, batteries, ion, lithium, materials, anode, cheap, capacity, pitch, enhanced, tar, coal

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Nanocomposites of Silicon and Carbon Derived from Coal Tar Pitch: Cheap Anode Materials for Lithium-ion Batteries with Long Cycle Life and Enhanced Capacity

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ABSTRACT: From energy and environmental consideration, an industrial waste product, coal tar pitch (CTP), is used as the carbon source for Si/AC composite. We exploited a facile sintering method to largely scale up Si/amorphous carbon nanocomposite. The composites with 20 wt.% silicon with PVdF binder exhibited stable lithium storage ability for prolonged cycling. The composite anode delivered a capacity of 400.3 mAh g⁻¹ with a high capacity retention of 71.3 % after 1000 cycles. Various methods are used to investigate the reason for the outstanding cyclability. The results indicate that the silicon nanoparticles are wrapped by amorphous SiO_x and AC in Si/AC composite. This uniform structure is very favorable to lithium storage, the SiO_x and AC layers can supply sufficient conductivity and strong elasticity to suppress the stress resulting from the reaction of Si with Li during charge/discharge process.

Keywords: Si/C composite, amorphous carbon, coal tar pitch-based carbon, long-life lithium ion battery

1. Introduction

Rechargeable lithium-ion batteries (LIBs) are currently playing a critical role in energy storage technologies. Due to their overwhelming advantages, including high gravimetric and volumetric capacity, high rates of power, and low weight, LIBs have successfully been used in various portable electronic devices and mobile applications [1,2]. With the ever increasing power requirements for real-life applications and the concerning of the environment, it is necessary to improve the performance of the electrode materials in the same time to lower the costs, achieve large-scale production, and use industry waste materials as active materials [3,4].

Graphite is the conventional anode materials for commercial LIBs, in which every six carbon atoms can be intercalated with one lithium atom at maximum, with just over 10 % volume expansion. It shows high reversibility and stable capacity with prolonged cycling, but the reversible capacity has reached its theoretical limit ($\sim 372 \text{ mAh g}^{-1}$). Development of high capacity anodes to meet the demand is therefore imperative. Many materials with improved storage capacity have recently aroused great interest, such as silicon (3579 mAh g^{-1}) [5-7], and tin (994 mAh g^{-1}) [8-11]. silicon shows great advantages over the other candidates owing to its appealing features including exceptionally high theoretical capacity, lower voltage plateau, non-toxicity, low cost, and abundance, However, it generally suffers from enormous volume expansion (328 %) during the lithiation and de-lithiation processes, causing the cracking and pulverization of active materials, followed by disintegration of the electrode and eventually leading to rapid capacity fading. Large-volume change severely restricts practical applications [12-24]. In recent years, some

strategies devoted to nanostructured silicon can alleviate the volume expansion to some extent. These include chemical vapor deposition [15,16], the template method [17,18], and chemical reactions [19,20]. Nevertheless, the synthesis processes are complicated, expensive, and difficult to industrialize. The other effective tactic to overcome the volume changes is by means of an active/conductive matrix to form a composite [21-26]. Therefore, incorporating silicon to optimize carbon anode is a feasible and desirable solution to realize the high energy density needed for some practical applications [27]. The silicon content of the composite could significantly affect the overall properties of the electrode. If the composite were Si-rich, the electrode would definitely undergo large volume changes. It is evident that a Si-poor composite should go through less volume change and deliver better capacity retention to the electrodes [28]. Based on this principle, Si/C composite with a relatively low proportion of silicon is an excellent candidate to substitute for graphite anode in large-scale applications. Furthermore, from a commercial viewpoint, it is crucial to utilize a simple, green, and low-priced synthesis method, one that is also based on cheap and abundant raw materials. Coal tar pitch (CTP) as an industrial by-product, composed of cyclical hydrocarbons of various molecular weights and configurations. It has significant health hazards and environmental concerns. In China, the output of CTP was up to 8.7 million tons during the first four months of 2012 [29]. Recycling this low-cost waste into a promising active material for energy storage could be of great benefit to both the environmental issues and the energy challenges, and help to achieve green and sustainable energy development. Several previous works based on CTP have been devoted to its applications in LIBs and supercapacitors [30-32]. Previous works, however, only focused on activated carbon materials, which showed slightly lower capacity than the

already commercialized carbon. To date, there is still no report on using CTP as a cheap carbon precursor for Si/C composites. More recently, polymer binders attract wide attention, which have been shown can greatly influence the performance of Si-based composite electrodes. Compared with conventional poly(vinylidene fluoride)(PVdF), the polymers with carboxy groups, such as polyacrylic acid (PAA) and carboxymethyl cellulose(CMC), can react with hydroxyl functionalities on the both carbon and silicon surfaces to confine the active material to the binder, which is responsible for the improvement of the electrode.[33-34] Remarkable progress has been made recently, alginate sodium (AS), a new kind of bio-derived binder with higher content of carboxylic group, can result in a large number of possible binder-Si / binder-C bonds and eventually much better cycling performance.[35] Here, we present a facile sintering method to synthesize Si/amorphous carbon (AC) composite materials, which is easy to be scaled up. Certain amounts of silicon were introduced into AC derived from CTP. Furthermore, the binder effects have been revealed to determine lithium storage performances of the Si/AC.

2. Experimental

2.1 Material synthesis

The Si/AC composites were fabricated by pyrolyzing a mixture of silicon nanoparticles (50-100 nm; Nanostructured and Amorphous Materials Inc.) and coal tar pitch (CTP) (Bao Steel Ltd, China). To obtain an evenly dispersed Si/CTP mixture, the CTP was initially dissolved in N-methyl-2-pyrrolidone (NMP) (Sigma-Aldrich) under stirring for 1 h, and the Si nanoparticles were dispersed in NMP by ultrasonication for 30 min, before the silicon dispersion was added into the CTP solution. The blend was fully mixed by stirring for 5 h. The resultant solution was heated to 150 °C for

1 h in order to evaporate the NMP, which can be collected for reuse. The prepared mixture was sintered in a tube furnace at 850 °C for 5 h under flowing argon atmosphere. After the pyrolyzation, the composites (Si/AC), which consisted of silicon encapsulated by amorphous carbon (AC), were fabricated by naturally cooling the sample to room temperature under argon atmosphere. Two samples were fabricated with different weight ratios of Si to AC (estimated values were Si: C = 20: 80 and 50 : 50), which are denoted as 0.2 Si/AC and 0.5 Si/AC.

2.2 Structural characterization

The samples were characterized by field-emission scanning electron microscopy (FESEM; JEOL7500), transmission electron microscopy (TEM; JEOL JEM-2100F), and powder X-ray diffraction (XRD; GBC MMA) with Cu K α radiation. Raman spectra were collected by a 10 mW helium/neon laser at 632.8 nm excitation, which was filtered by a neutral density filter to reduce the laser intensity and a charge-coupled detector (CCD). Thermogravimetric analysis (TGA) was performed in air with the help of a SETARAM Thermogravimetric Analyzer (France). The X-ray photoelectron spectra (XPS) experiment was carried out using Al K α radiation and fixed analyser transmission mode. The pass energy was 60 eV for the survey spectra and 20 eV for specific elements.

2.3 Electrochemical Tests

The tests were conducted by assembling coin-type half cells in an argon-filled glove box. Lithium foil was employed as both reference and counter electrode. The working electrode consisted of 70 wt % active material (AC, bare Si, 0.2 Si/AC, and 0.5 Si/AC, respectively), 20 wt % black carbon, and 10 wt % polyvinylidene difluoride (PVdF). The electrolyte was 1.0 M LiPF₆ in a 1:1 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). Electrochemical cycling of electrodes was conducted at 200 mA g⁻¹ for galvanostatic measurements in the 10 mV to 1.2 V voltage window (vs. Li/Li⁺). Cyclic voltammetry was performed using a Biologic VMP-3 electrochemical workstation between 0.01-1.2 V at a scan rate of 0.1 mV s⁻¹.

3. Results and discussion

The composites proposed here has similar structure as the seeds (Si nanoparticles) in the pulp (AC) of kiwi fruit as shown in Figure 1. Two samples were fabricated with different weight ratios of Si to AC (estimated values of Si: C = 20: 80 and 50: 50), which are denoted as 0.2 Si/AC and 0.5 Si/AC. It is apparent that the addition of silicon to Si/C composite can effectively improve the capacity of the anode. On the other hand, when silicon nanoparticles are anchored to the carbon matrix, the carbon in the Si/C hybrid materials not only can modify the unstable solid electrolyte interphase (SEI) layer of Si into a robust and flexible one that can accommodate the mechanical strains induced by the volume changes [36], but also can effectively buffer the volume expansion and enhance the conductivity of Si, thus preventing the degradation of the electrode integrity [15,21,22]. Combining carbon with an appropriate amount of Si can eventually ensure higher capacity and stable performance over long cycling.

Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) were used to characterize the morphology of the obtained materials. Figure 2a presents a SEM image of 0.2 Si/AC at low magnification, showing that the silicon nanoparticles are uniformly dispersed into the amorphous carbon host. From the cross-sectional image (Figure 2b), it is obvious that the spheroidal nanosilicon particles are encapsulated in the carbon matrix. The TEM images clearly verify that the Si particles are surrounded by the AC matrix. The associated selected-area electron-diffraction (SAED) pattern (inset to Figure 2c) displays fine diffraction spots characteristic of Si, indicating the good crystallinity of the silicon. The high magnification TEM image (Figure 2d) illustrates the interface between the Si and the C; and an obvious amorphous layer exists in the interface, which could be deduced from the amorphous SiO_x. The inference is further confirmed by XPS and Raman results. (Figure 3a and b) The carbon is amorphous and in a layer about 5 nm in thickness. The lattice-resolved TEM images (Figure 2e and f) clearly show that the nanocrystalline Si

particle is coated by amorphous carbon. The measured interplanar distances in the two directions are approximately 0.31 nm and 0.19 nm, corresponding with the (111) and (220) planes, which is also supported by the X-ray diffraction (XRD) results (Figure 3a). The distortion in the lattice indicates that some nanocrystalline Si particles contain stacking faults and/or microtwins. The elemental mappings of silicon and carbon of 0.2 Si/AC and 0.5 Si/AC shown in Figure 3 in the Supporting information further corroborate the uniform embedding of the silicon in the amorphous carbon host and indicate that the silicon particles are distributed evenly throughout the AC bulk, which is ascribed to the favorable dispersion of silicon in the CTP solution.

Thermogravimetric analysis (TGA) was carried out in air to determine the silicon content in the Si/C hybrid composites. Figure 4a shows that the pure Si sample has increased in weight by 4 % due to the partial oxidation of Si under the air atmosphere; and about 2 % of AC is remained after 800 °C due to the impurity in coal tar pitch. Both the composites exhibit thermal stability below 450 °C, and rapid weight loss then occurs up to the temperature of 660 °C. Based on the mass loss percentage of the composite materials and the calibration curves, the Si content in the 0.2 Si/AC and 0.5 Si/AC composites was calculated to be approximately 16 % and 52 %, respectively. The XRD patterns of pure Si, AC, and the Si/AC composites are presented in Figure 4b. The XRD pattern of AC exhibits a broad weak diffraction peak between 20° and 30°, which shows that the carbon pyrolyzed from CTP is amorphous. The silicon nanoparticles are crystalline in structure, which is indicated by the (111), (220), (311), (400), and (331) diffraction peaks. In comparison with the pattern of the bare Si, the XRD spectra of the 0.2 Si/AC and 0.5 Si/AC composites yield fewer peaks with smaller intensity, implying that the silicon particles are mainly anchored in the AC framework. As mentioned before a thin SiO_x layer can be detected by HRTEM (Figure 2e), XPS and Raman (Figure 5), while no SiO_x peaks show up in the two samples, indicating that the amorphous property of SiO_x.

The components of the electrodes were further confirmed by X-ray photoelectron spectra (XPS). The spectra attributable to C1s, Si 2p_{3/2} and O1s were shown in Figure 5a, 5b and 5c, respectively. The spectrum of C1s revealed that the amorphous carbon from CTP represent the three possible bonds of graphite (C, ~284.4 eV), hydrocarbon(C-C, ~285.5 eV) and C=O (~287.5 eV), respectively [37]. The third peak shift to 288.91 eV and 288.30 eV in 0.5 Si/AC and 0.2 Si/AC, which is corresponding to the peak of C-O-Si [38]. The spectrum of Si 2p_{3/2} showed that two peaks can be attributed to the SiO and SiO_x/ C-O-Si, located at the binding energy of about 99.7 eV and ~103.5 eV [39-43]. It is obvious that the amount of Si⁰ is dominant in bare Si, which is decreasing as the amount of AC increases. The positions of binding energy for O1s are 532.4~532.9 eV and 531.4 eV for SiO_x and C-O-Si [38, 44]. In the O1s spectrum of bare Si, a peak of 103.0 indicates the electronic state of SiO_x. The corresponding peaks appear at 532.7 eV and 533.2 eV for 0.5 Si/AC and 0.2 Si/AC, which imply the peak may consist of overlapped peaks for SiO_x and C-O-Si. The amount of SiO_x for 0.5 Si/AC should be more than 0.2 Si/AC, thus leading to lower binding energy. The Raman spectrum (Figure 5d) of AC shows the typical G band and D band for carbon material, which is very sensitive to defects, disorders, edges and carbon grain size. The relative intensity (I_D/I_G) of D band and G band could index the disorder degree. The large I_D/I_G (1.16) and wide G band of AC indicate that the AC possesses a disordered structure, which is consistent with the XRD and TEM results. Adding Si into AC matrix can decrease the disorder degree of carbon frame, the corresponding ratio for 0.2 Si/AC and 0.5 Si/AC decline to 1.13 and 1.05. Compared with the bare Si, the band at ca. 515 cm⁻¹ shows a clear difference among those samples, the intensity of the band decreases with the increase of AC content, and an obvious blue shift can be observed. The differences are ascribed to the transverse optical mode, maybe result from a phonon confinement effect and/or a masking effect [36]; those indicate that the silicon nanoparticles are wrapped by amorphous SiO_x and AC. This structure is very favorable to lithium storage, which can supply sufficient conductivity and strong elasticity to withstand the deformation

stresses [45].

The charge-discharge curves of 0.2 Si/AC and 0.5 Si/AC with different binders are illustrated in Figure 6. For the 0.2 Si/AC anodes, all of electrodes show the capacity increase with the increase of cycle numbers. The first discharge has a short platform at around 0.65 V, which is the SEI formation potential on a Si/C surface due to the decomposition of electrolyte. The charge capacity slowly increases during the cycles, indicating that the silicon particles inside the carbon matrix are activated gradually. In the following cycles, the charge capacity tends to decrease slightly, which illustrates that the architecture of the hybrid Si/AC has begun to slowly collapse, inducing the Si particles to separate from the carbon matrix. The 0.2 Si/AC-PVdF shows obvious differences amongst the three electrodes, presenting sloping charge/discharge curves without any Li-Si alloying plateau and persistent capacity increase. It is probably due to the low amount of pure crystalline Si and the existence of amorphous SiO_x would activated gradually and AC play a main role in the PVdF binder. The CV curves and dQ / dV curves further prove this speculation by exhibiting obviously typical anodic and cathodic peaks for Si anode in lithium ion batteries [46]. Both the 0.2 Si/AC-AS and 0.2 Si/AC-CMC anodes show the typical voltage profiles, indicating the binders with carboxy groups would tend to form different SEI film and then the Si and SiO_x play a main role in the electrochemical performances. The similar conclusion can be drawn from the discharge/charge curves of the 0.5 Si/AC. Furthermore, the 0.2 Si/AC-PVdF shows the typical voltage profiles as well, which is ascribed to the high Si content (~50 wt.%) .

A slow scan cyclic voltammogram (CV) of the 0.2 Si/AC anode at 0.1 mV s⁻¹ is demonstrated in Figure 7a. A clearly irreversible peak at 0.61 V in the first cycle is ascribed to the formation of the interface between the Si/AC composite and the electrolyte, and this peak has disappeared in the following cycles, indicating the formation of a stable SEI film on the electrode surface with the aid of the AC matrix [47]. The characteristic peaks of Si anode in lithium ion batteries are exhibited during

the subsequent cycles. An obvious anodic peak near to 0 V is corresponding to the Li insertion in the AC matrix. A very slight peak observed at ~0.17 V represents Li de-intercalation from the AC matrix. The broad anodic peak at ~0.18 V is ascribed to the alloying of Li with silicon. The cathodic peaks at about 0.33 V and 0.51 V are associated with the de-alloying of Li from the Si/AC electrode. These observations from cyclic voltammetry are similar to those in previous reports [48-50]. The magnitudes of both the cathodic and the anodic peaks increase significantly with cycling, implying activation of more material to react with Li and an enhanced electronic kinetics process [51]. These electrode peaks show very stable repeatability in the subsequent 10 cycles, signifying that the composite anode has high reversible capacity and long cycle life. The dQ/dV curves (Figure 7b) are well consistent with the charge/discharge curves with a little bit voltage shift.

The cycling performances of 0.2 Si/AC and 0.5 Si/AC electrodes at various binders were presented at Figure 8. For 0.2 Si/AC electrode (Figure 7b), all cells underwent a capacity increment, indicating the silicon of the composites were activated gradually. The 0.2 Si/AC-AS, containing substantial $-\text{COOH}$ groups in AS binder, shows the highest capacity and the quickest capacity increase in initial cycles. The initial charge and discharge capacity is 815.7 and 1219.4 mAh g^{-1} respectively, corresponding to the coulombic efficiency of 66.9%. The charge capacity commenced to increase from the third cycles, which soared to 979 mAh g^{-1} at the 38th cycle, then declined to 529.8 mAh g^{-1} after 200 cycles. The 0.2 Si/AC-CMC electrode, with far fewer $-\text{COOH}$ groups in binder than AS, displays the similar performance with lower capacity. The initial coulombic efficiency of Si/AC-CMC is 57.1% with 633.3 mAh g^{-1} / 1108.2 mAh g^{-1} of charge and discharge capacity. The increase trend of charge capacity showed up from the 4th cycle, and arrived to the maximum of 782.9 at the 38th cycle. While it manifested faster capacity decline, only remaining 310.6 after 200 cycles. This demonstrates that binder-Si / binder-C bonds in CMC and AS, restricting the active material in the binders, efficiently prevented the fast capacity loss during initial cycles in Si based electrodes and

eventually much better cycling performance. While the cycling performance of 0.2 Si/AC–PVdF electrode is quite different, the capacity is much lower and increased slowly, indicating the silicon without forming Si-binder bond would contribute to the capacity little by little. The initial discharge and charge capacities are 1039.2 and 561.5 mAh g⁻¹, respectively. The discharge capacities increase from 561.5 mAh g⁻¹ to 663.9 mAh g⁻¹ during the 200 cycles. When the silicon content increased to 50% (Figure 8b), the 0.5 Si/AC anode with AS and CMC binder exhibit the similar trend compared with the 0.2 Si/AC-AS and 0.2 Si/AC–CMC electrode. The overall capacity is significantly improved due to higher silicon content. The initial capacities are 1507.1 mAh g⁻¹/2242.8 mAh g⁻¹ (67.1%) and 1345.3 mAh g⁻¹/1944.4 mAh g⁻¹ (69.2%) for 0.5 Si/AC-AS and 0.5 Si/AC–CMC, respectively. After 100 cycles, the charge capacity of them are as low as 885.1 mAh g⁻¹ and 555.2 mAh g⁻¹. The obvious differ is from 0.5 Si/AC-PVdF, which showed the lowest capacity and rapid capacity loss. The charge capacity fade from 1296.2 of mAh g⁻¹ of the first cycle to 292.1 mAh g⁻¹ of 100th cycle, which is mainly attributed to the PVdF binder undergo large volume changes and is largely deformed, inducing silicon separate from PVdF during their subsequent contraction. It is apparent the Si/AC composite anode would mainly embody the feature of AC for the anode with low silicon portion, therefore PVdF is more suitable for 0.2 Si/AC composite. For 0.5 Si/AC with high silicon portion, silicon would play key role for electrochemical performance, hence the 0.5 Si/AC with alginate sodium anode shows the best cycling properties. The charge-discharge curves of various electrodes is in agreement in the conclusion In brief, the 0.2 Si/AC-PVdF anode 0.5 Si/AC-AS anodes show the highest reversible capacity and performs over a long lifespan with the slightest capacity decay.

To highlight the superiority of 0.2 Si/AC anode, the prolonged cycling performances of the four electrodes are displayed in Figure 9. The capacity of pure AC with PVdF binder is about 310 mAh g⁻¹, with long cycle life even in a narrow voltage window (0.01~1.2 V). This means that the amorphous carbon derived from CTP by the direct sintering method has good Li storage capability. A rapid

capacity decline occurs in the bare silicon anode with alginate sodium binder, which is consistent with previously reported results with PVdF binder [52,53]. while it is out of accord with the excellent performance reported by I. Kovalenko et al.[35], which is probably ascribed to the different alginate sodium source and different amount of carboxy groups in the binder. Even though the first discharge capacity reached up to 2483.3 mAh g⁻¹, the reversible capacity was as low as 340 mAh g⁻¹ after 50 cycles. After introducing high-capacity silicon phase at 20 wt. % into AC to improve the capacity and cycling lifespan, the 0.2 Si/AC-PVdF anode endures prolonged cycling with higher reversible capacity, Its charge capacity increases to as high as 633.9 mAh g⁻¹ after 200 cycles. It is remarkable that the capacity remains 400.3 mAh g⁻¹ even after 1000 cycles. When the proportion of Si is enhanced to 50 %, the initial discharge and charge capacities of 0.5 Si/AC-AS are as high as 1345.3 and 1944.4 mAh g⁻¹, respectively, demonstrating that the amount of silicon can directly determine the overall capacity of Si/AC anode. Although the reversible capacity of the 0.5 Si/AC anode is much higher in the initial 60 cycles than for 0.2 Si/AC anode, this electrode undergoes rapidly capacity fading, only retaining 470 mAh g⁻¹ after 130 cycles. The capacity retentions of all the electrodes are shown in Figure 8b. The average coulombic efficiency of 0.2 Si/AC is as high as 99.7 % after 1000 cycles. It can be seen that the 0.2 Si/AC has the highest capacity retention, which is as high as 105.3 % over 350 cycles. After 1000 cycles, the capacity retention is still maintained at 71.3 %. In addition, Although the first cycle coulombic efficiency (CE) is a little bit low, which is ascribed to the formation of the SEI film and irreversible lithium insertion into the composite, the coulombic efficiency is above 99.5 % over the following 1000 cycles. The AC shows capacity retention of 100 % without capacity fading during 600 cycles, while for the pure silicon and the 0.5 Si/AC electrodes, the capacity retention is only 7 % and 34.2 % at the 130th cycle, respectively. Therefore, the silicon content embedded into the AC can hugely improve the total performance of the composite electrode. All the results confirm that the silicon is favorable to the enhancement of capacity, but harmful to the

cycling lifespan of the AC matrix anode. The amount of silicon plays a key role with respect to both of these aspects. The good Li-storage performance of 0.2 Si/AC can be attributed to its adequate silicon content and the effective buffering function of the AC matrix. The 0.2 Si/AC electrode can achieve a significantly improved reversible capacity without sacrificing its stable cycling performance.

The 0.2 Si/AC-PVdF anode was also subjected to higher current densities. As shown in the inset of Figure 10, the cell was cycled at current densities of 50, 100, 200, 500, and 1000 mA g⁻¹, and highly stable reversible capacities of 706.9, 635.6, 571.6, 492.9, and 436 mAh g⁻¹ were achieved, respectively. The capacity only decreased by 38 % when the rate was increased by 20 times, showing the excellent rate capability of this electrode. In addition, a rising capacity was observed, even when the current density was directly returned to 50 mA g⁻¹, which is consistent with the observed capacity increment in prolonged cycles, indicating that the silicon particles incorporated into the AC matrix undergo an inevitable activation process.

4. Conclusions

In summary, Si/AC composites were fabricated in large quantities by a facile sintering method. From environmental and energy considerations, an industrial waste product, coal tar pitch (CTP), was used as the carbon source of the composite. Certain amounts of silicon nanoparticles were encapsulated in the AC matrix. Various binders are utilized to study the effects of binder to the electrochemical properties of electrodes. Electrochemical measurements show that the 0.2 Si/AC composite with PVdF binder exhibits higher specific reversible capacity than pristine carbon materials, excellent cycling stability, and relatively good high rate capability. Moreover, the preparation process developed herein is simple, green, low-cost, and easy to scale up as well.

Therefore, coal tar pitch as a common industrial waste product provides a widely available and low-cost precursor to produce high-performance Si/C composite, supplying a practicality for the manufacture of lithium-ion batteries.

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Figure 1. Schematic illustration of the design of the materials with kiwi fruit as model.

Figure 2. SEM images of 0.2 Si/AC in (a) top view at low magnification and (b) cross-sectional view at high magnification. Low-(c) and high-(d) magnification TEM images of 0.2 Si/AC with the corresponding SAED pattern (inset of (d)). (e) and (f) High-resolution TEM images displaying details of silicon nanoparticle coated with AC.

Figure 3. SEM images and corresponding elemental mappings of carbon and silicon in (a) 0.2 Si/AC and (b) 0.5 Si/AC.

Figure 4. (a) Thermogravimetric Analysis (TGA) results and (b) XRD patterns of bare silicon, 0.2 Si/AC and 0.5 Si/AC.

Figure 5. XPS spectra of C1s (a), Si 2p_{3/2} (b), and O1s (c) and Raman spectrum (d) for bare Si, AC, 0.2 Si/AC and 0.5 Si/AC.

Figure 6. Charge/discharge curves of 0.2 Si/AC with AS binder (0.2 Si/AC-AS) (a), CMC binder (0.2 Si/AC-CMC) (b) and PVdF binder (0.2 Si/AC-PVdF) (c); 0.5 Si/AC with AS binder (0.5 Si/AC-AS) (d), CMC binder (0.5 Si/AC-CMC) (e) and PVdF binder (0.2 Si/AC- PVdF) (f).

Figure 7. (a) Cyclic voltammograms (b) Differential curves for selected cycles of 0.2 Si/AC-PVdF electrode in coin cell.

Figure 8. (a) Cycling performances of 0.2 Si/AC-AS, -CMC and -PVdF; and (b) Cycling performances of 0.5 Si/AC -AS, -CMC and -PVdF at 200 mA g⁻¹.

Figure 9. (a) Cycling performances of 0.2 Si/AC-PVdF with prolonged cycles at 200 mA g⁻¹. (b) Capacity retention of AC-PVdF, Si-AS, 0.2 Si/AC-PVdF, and 0.5 Si/AC-AS and Coulombic efficiency of 0.2 Si/AC-PVdF.

Figure 10. Rate capability profiles of 0.2 Si/AC-PVdF at different current densities

■ AC ■ Si

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figure 9.

Figure 10.