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Xanthan Gum as a Carbon Source for Preparation of Carbon-Silicon/Graphite Composite as Anode Materials for Lithium Ion Batteries

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Silicon anode materials have advantage of very high theoretical specific capacity (4200 mA h g^{-1}), and low intercalation lithium potential, but disadvantage of huge volume expansion. In this paper, xanthan gum (XG) and glucose (GLU) as carbon sources, and niobium pentoxide and a dispersant are added to modify the nano-silicon to prepare a series of carbon-silicon composite. The carbon-silicon composite are ground with graphite to obtain the carbon-silicon/graphite composite anode material Si@XG-G. XRD tests show that these composite materials have strong characteristic diffraction peaks of graphite and silicon, and there are no peaks of amorphous carbon. The first discharge and charge specific capacity of Si@XG-G is 414 mA h g^{-1} and 259 mA h g^{-1}, respectively, with a coulombic efficiency of 62.5 %. The first discharge and charge specific capacity of Si@XG/NO-G modified by adding niobium pentoxide (NO) was 448 mA h g^{-1}, and 285 mA h g^{-1}, with a coulombic efficiency of 63.6 %. When mixing the carbon-silicon composite that is doped by niobium pentoxide with graphite to prepare the carbon-silicon/graphite composite anode material, the first charge and discharge specific capacity as well as the coulombic efficiency of the composite anode materials are significantly improved. In addition, when modified by polyvinylpyrrolidone (PVP) again, the first discharge specific capacity and charge specific capacity of Si@XG/NO/PVP-G is 671 mA h g^{-1} and 489 mA h g^{-1}, respectively, with a coulombic efficiency of 72.9%. Obviously, the active material Si@XG/NO/PVP-G has a further improved specific capacity and coulombic efficiency.

Keywords: Carbon-silicon composite, Silicon/graphite composite, Xanthan gum, Niobium pentoxide,

1. INTRODUCTION

As a green and sustainable energy source, lithium-ion batteries have captured much attention for high energy density, long cycle life, light weight, no memory effect, clean and environmentally friendly, and are widely used in all kinds of power tools such as tablet computers, smart phones, drones, and electric cars.[1-3] However, the current performance of lithium-ion batteries is not good enough to meet the ever-growing demand for more long-life and more robust batteries. The energy density of lithium-ion batteries is expected to reach 350 Wh kg^{-1} in the year 2020, therefore, exploring novel materials to boost the performance of lithium-ion batteries is very meaningful.

In light of the high performance of cathode materials and the limited theoretical capacity of graphite-based carbon anode materials (372 mA h g^{-1}), the effective strategy to improve the energy density is using excellent anode materials with high specific capacity.[4-6] By decreasing the whole weight of the battery, the high energy density will be achieved. Under this circumstance, the development of novel high-performance anode materials has become a current research hotspot.[7-9]

Silicon is of great interest and very important in contemporary industry for the benign semiconductor properties. In energy storage field, silicon has a specific capacity of 4200 mA h g^{-1}, which is ten times more than that of graphite-based carbon anode materials.[10, 11] Silicon has low reaction activity with electrolytes and low production costs. As a result, the research of silicon as anode electrode material to pursue high-energy-density lithium-ion batteries has attracted much attention. However, silicon anode will generate a huge volume expansion up to 300% during lithium insertion/extraction process, easily cracking the silicon material and decreasing the cycle performance and rate performance sharply. Considering the problem of poor rate performance and huge volume expansion, researchers have proposed many solutions from various aspects, such as using nano-silicon materials instead of pure silicon materials, improving binders, developing new electrolytes, and compounding with non-silicon materials. Among of these methods, modified silicon by carbon is proven to be more effective.[12, 13]

Silicon and carbon are both IVA main group elements, and the chemical properties are somewhat different. When fused together as silicon-carbon composite anode materials, the two elements complement each other. The advantages of silicon-carbon composite materials are including: (1) silicon is a semiconductor material. When silicon is coupled with carbon to fabricate composite materials, the electronic conductivity of the silicon will be increased greatly. (2) As carbon materials, graphite has the characteristics of good cycle performance and low capacity. Silicon has a high capacity, but it has the disadvantages of severe volume expansion and inadequate cycle stability. Therefore, when silicon and graphite were composited, a higher theoretical specific capacity than graphite will be obtained. At the same time, the expansion rate of the battery material will be reduced. The structural stability as well as the cycle stability will also be strengthened greatly. (3) The excellent flexibility and mechanical strength of carbon materials can buffer the volume expansion effect of silicon, increase resistance to mechanical stress, and improve the cycling performance of silicon. The sources of carbon materials, including traditional graphite carbon, amorphous carbon, new carbon nanotubes, as well as biomass carbon materials, are very abundant and cost-effective, and all of them have their own characteristics.[7, 8, 14-18]

In order to improve the cyclic stability and limit the volume expansion of silicon, the carbon thin layer is coated on nano-silicon powder. With the thickness of the carbon layer increasing, the capacity may decrease, and its structural stability is strengthened. There are various types of amorphous carbon layers, such as glucose, pitch, methane, and acetylene. Lin et al [8] prepared a composite material by coating carbon nanotubes on silicon nanoparticles. For carbon nanotube array could transfer electron quickly, the conductivity of the silicon-coated carbon nanotube material is greatly enhanced. Because silicon is surrounded by mechanically tough carbon nanotubes, silicon can expand or contract in the voids of the carbon nanotubes. It was found that after 50 cycles, the capacity retention still reached 75%, which is showing good cycle performance and rate performance. Tao et al [12] used Ag as a catalyst and polysilicon powder as a raw material to prepare silicon/carbon composite anode material, with a specific capacity of 3850 mA h g^{-1} at a constant current of 0.4 A g^{-1}. After 60 cycles, it was found that the specific capacity still remained 1645 mA h g^{-1}, with the coulombic efficiency of 75 %. It is revealed that 3D porous silicon structure can effectively alleviate the volume expansion effect of the battery material, and avoid direct contact between the silicon surface and the electrolyte, which is improving the conductivity and cycle stability.

Obviously, the carbon source is a key inspect to achieve good performance of the silicon carbon materials. The xanthan gum is a macromolecular polymer with cohesiveness, good water solubility, thermal stable and cheap. Herein, xanthan gum and glucose were used as carbon sources to modify nano-silicon to prepare carbon-silicon composite. In order to enhance the performance, niobium pentoxide and polyvinylpyrrolidone or polyethylene glycol were also introduced to modify these carbon-silicon composite. After that, these composites were mixed with graphite to produce carbon-silicon/graphite composite anode material. The electrochemistry of carbon-silicon/graphite composite anode materials was investigated in detail.

2. EXPERIMENTAL PROCESS

2.1 Preparation of carbon-silicon/graphite composite

In a stainless steel cup, 50 ml of distilled water, 1 g of nano silicon powder, 0.625 g of xanthan gum (XG), and 2.5 g of glucose were added slowly in sequence at a speed of 500 r/min. When all the materials were added and stirred very evenly, the mixture was dried over and ground to the powder state. Then the powder was put into a tube furnace under a nitrogen atmosphere, heated at 500 ºC for 4 h, and naturally cooled to room temperature. The sintered material was ground again and passed through a 200-mesh standard sieve, and washed with dilute hydrochloric acid to remove sodium ions. After dried again, the material was denoted as Si@XG.

Niobium pentoxide (Nb_2O_5), polyethylene glycol (PEG), and polyvinylpyrrolidone (PVP) were also used here to modify the original silicon nanoparticles to produce novel carbon-silicon composite. The synthesis process was the same as mentioned above, in which the additives were used separately or in combination, and the mass of the additive was 10% of the mass of the nano-silicon powder. The carbon-silicon composite were denoted as Si@XG/NO, Si@XG/NO/PEG, and Si@XG/NO/PVP, respectively. At last, 6.0 g of graphite and 1.0 g of the carbon-silicon composite as prepared above, were mixed and ground mechanically to obtain carbon-silicon/graphite composite anode materials, which were named as Si@XG-G, Si@XG/NO-G, Si@XG/NO/PEG-G, Si@XG/NO/PVP-G, respectively.

2.2 Electrochemical performance test

Carbon-silicon/graphite composite, super-P conductive carbon black, and binder polyvinylidene fluoride (PVDF) were mixed at a mass ratio of 8: 1: 1 in N-methyl-2-pyrrolidone (NMP) and stirred with a magnetic stirrer for 5-6 h to form an even slurry. Then the slurry was coated on copper foil to form a thick film about 200 μm, and dried in a vacuum drying box at 120 ºC for 24 h. After rolled, the coated copper foil was cut into a 16 mm diameter wafer and weighed as a positive electrode. A 2032 button battery was assembled in a vacuum glove box, coupled with a lithium metal sheet as a counter electrode. The battery was sealed with a sealing machine and left to stand for 7-8 h.

The Shenzhen Xinweier CT-3008W high-precision battery test system was used to charge and discharge the assembled 2032 button battery. At room temperature, the parameters were set as follows: Firstly, set aside for 5 minutes and discharge to 0.05 V at constant current (0.1 mA), then set aside for 5 minutes, continue to charge to 1.5 V at constant current (0.1 mA), then charge at constant voltage (1.5 V), cycle discharge and charge 5 times. Then it is changed the charge and discharge current to 0.2 mA, 0.3 mA, 0.4 mA, 0.5 mA, and performed the test for 5 times. Finally, it was charged and discharged for 50 cycles at 0.3 mA. In this way, electrochemical parameters such as charge specific capacity, discharge specific capacity, first coulombic efficiency, and cycle stability of different carbon-silicon/graphite composite were obtained.

2.3 Material characterization

Particle size analysis of the material was obtained by using a Malvern Mastersizer 3000 particle size laser diffraction analyzer. Microscopic morphology of the material was obtained by scanning electron microscope (SEM, FEI / Quanta 250) testing. Powder X-ray diffraction (D8 ADVANCE, Bruker) radiated by Cu target was used to identify the crystalline phase of the synthetic material. The scanning range was from 10º to 80º with a step size of 0.02º.

3. RESULTS AND DISCUSSION

X-ray diffraction technology is an important method to characterize the crystal phase structure of materials. As can be seen in Figure 1, the strongest peak of the four carbon-silicon/graphite composites Si@XG-G, Si@XG/NO-G, Si@XG/NO/PEG-G, and Si@XG/NO/PVP-G is all around 26º, which coincide with the diffraction peak position of graphite. At the same time, the four materials have weak diffraction peaks around 28º, which is consistent with the position of the diffraction peaks of nano-silicon. It is clearly shown that the internal structure of the silicon and graphite in the four silicon-carbon composites are not changed. The amount of added niobium pentoxide or polyvinylpyrrolidone is particularly small, so the corresponding characteristic diffraction peaks of them in the XRD diffraction pattern are hardly observed. Due to the porosity and high conductivity of the carbon material, the carbon-silicon composite modification treatment can buffer the volume expansion of silicon and enhance the conductivity of electrons and lithium ions, thereby improving the cycling performance of silicon.[16, 18] In the process of modification, the addition of niobium pentoxide and polyvinylpyrrolidone is to make some small holes appear in the carbon layer, so that the silicon can expand and contract more freely.

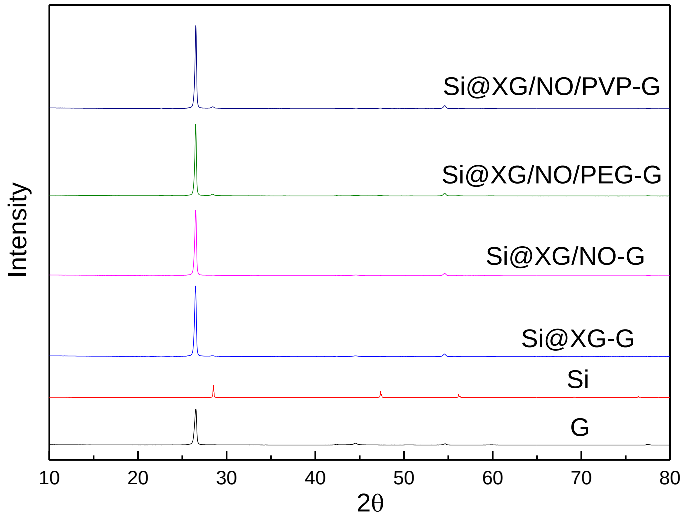

Figure 1. XRD patterns of four carbon-silicon/graphite composites, nano-silicon, and graphite

The SEM images of two carbon-silicon/graphite composites, Si@XG-G and Si@XG/NO/PVP-G, were shown in Figure 2. From the figure, it can be seen clearly that there are two kinds of materials with significantly different particle sizes. One type has a larger particle size, that is about 40-50 µm, and the other type has a smaller particle size, which is about 10-20 µm. The graphite used in this article is a commercially product and the particle size is very tightly controlled, and D50 is about 16 µm. Therefore, larger particles in carbon-silicon/graphite composites should be carbon-silicon composite. The shape of each particle is relatively clear, and there is no dramatical particles agglomeration. In the case of Si@XG-G, in which there is no niobium pentoxide and polyvinylpyrrolidone, it can be clearly observed that the silicon nanoparticles are not completely covered by the carbon, and the surface of the particles is not very uniform. Comparing the images before and after the addition of niobium pentoxide and polyvinylpyrrolidone modifier, the particle surface is more uneven after the modifier is added, has more irregularities, and is with more carbon. In another article, gelatin is deposited on the surface of SiO_2 nanospheres during spray drying to form the microspheres. After the magnesiothermic reduction, gelatin is carbonized and deposited in-situ on the surface of nanospheres and porous silicon nanospheres wrapped with a carbon layer are derived. The thickness of carbon and the porosity of obtained Si/C composite nanospheres can be modified by tuning the content of gelatin in the suspension. Two desired purposes, i.e. downsizing of Si particles and in-situ carbon coating of the nanoparticles have been achieved by this preparation.[19]

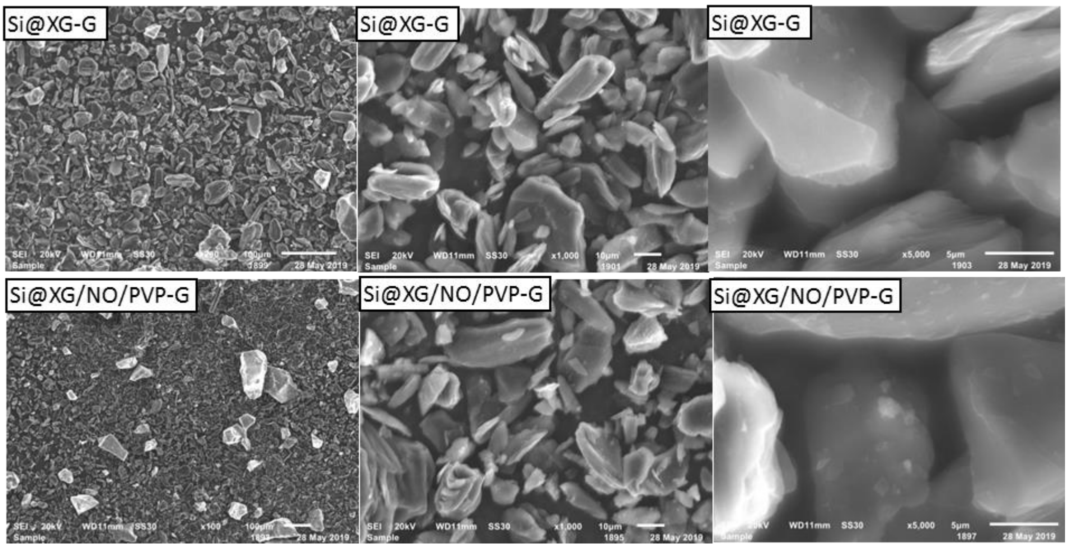

Figure 2. SEM images of Si@XG-G and Si@XG/NO/PVP-G

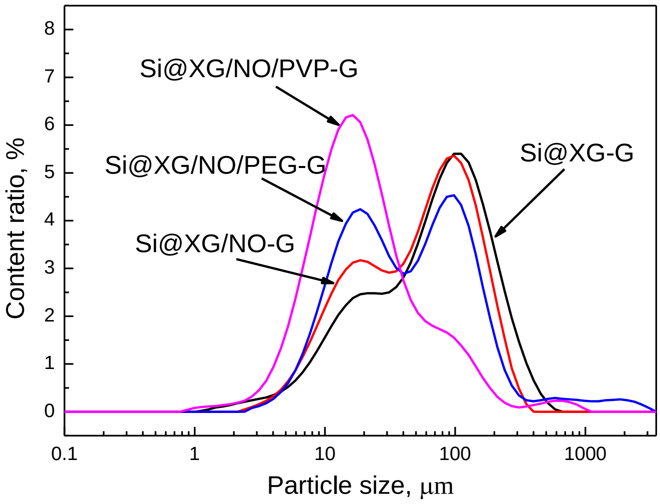

Figure 3. Particle size distribution of four carbon-silicon/graphite composite

In order to investigate the particle size distribution of Si@XG-G, Si@XG/NO-G, Si@XG/NO/PEG-G and Si@XG/NO/PVP-G, the particle size tests of these materials were performed, and the data were shown in Figure 3 and Table 1. As can be seen from Figure 3, the particle size of the four carbon-silicon/graphite composites all display bimodal distribution, with two peaks appearing at about 20 μm and 100 μm, respectively. The highest peak of Si@XG-G appears at about 100 μm, and the highest peaks of Si@XG/NO/PVP-G with NO and PVP additives appear at about 20 μm, which is in consistent with the analysis results of the previous scanning electron microscope. This maybe result in the high hardness of the sintered nano-silicon with xanthan gum and glucose as carbon source. This phenomenon is also found in the material preparation process, and it is difficult to grind and sieve for Si@XG-G. After adding niobium pentoxide and polyethylene glycol or polyvinylpyrrolidone, the hardness of the prepared carbon-silicon/graphite composites reduced, and the materials grind and pass through sieve easily. It is shown that niobium pentoxide and polymer additives are not only beneficial to the dispersion of nano-silicon, but also for the difference between the heat capacity and pyrolysis temperature and speed of the carbon source during the sintering process to the formation of the carbon layer on the surface of the nano-silicon. In this process, internal uneven stress is generated, which leads to a loose structure of the carbon layer. As shown in Table 1, the D50 of the four carbon-silicon/graphite composites Si@XG-G, Si@XG/NO-G, Si@XG/NO/PEG-G, and Si@XG/NO/PVP-G are 76.9 μm, 15.2 μm, 3.67 μm, and 3.10 μm, respectively. Li Xiaoge et al. [20] prepared TiO_2/C/Si composite by simple hydrothermal method. The permanent material embodies the excellent mass specific capacity of silicon and the excellent electrical conductivity of carbon. The role of replacing TiO_2 is to suppress the huge volume effect of Si.

Table 1. Particle size distribution of four carbon-silicon/graphite composites

Samples	D10 (μm)	D50 (μm)	D90 (μm)	D[4, 3] (μm)
Si@XG-G	12.7	76.9	223.0	101
Si@XG/NO-G	4.06	15.02	20	44.17
Si@XG/NO/PEG-G	2.30	3.67	5.31	22.45
Si@XG/NO/PVP-G	2.98	3.10	4.44	11.55

Table 2. First discharge and charge specific capacities of four carbon-silicon/graphite composites

Samples	The first discharge capacity (mA h g^{-1})	The first charge capacity (mA h g^{-1})	The first coulombic efficiency(%)
Si@XG-G	414	259	62.5
Si@XG/NO-G	448	285	63.6
Si@XG/NO/PEG-G	514	371	68.5
Si@XG/NO/PVP-G	671	489	72.9

As shown in Table 2, with the addition of niobium pentoxide and polymer dispersant, the first charge and discharge specific capacities of the three carbon-silicon/graphite composites are increased significantly. After the addition of niobium pentoxide, the first charge-discharge specific capacity is increased from 259 mA h g^{-1} and 414 mA h g^{-1} to 285 mA h g^{-1} and 448 mA h g^{-1}, with the increase rates of 10% and 8%, respectively. The first coulombic efficiency is also increased from 62.5% to 63.6%, with an increase of 1.1%. During the high temperature sintering process, adding niobium pentoxide that mixed with xanthan gum and glucose as carbon source, the difference in heat capacity and decomposition temperature of different materials decrease the density of the carbon layer in pyrolysis process, which is relatively loose for Si@XG/NO-G, Si@XG/NO/PEG-G, and Si@XG/NO/PVP-G. The porosity and high conductivity of the carbon material provides enough space for the volume change of nano-silicon during charge and discharge, and is conducive to the transport of the electrons as well as lithium ions. The first coulombic efficiency of Si@XG/NO/PVP-G added with polyvinylpyrrolidone reaches 72.9%, probably due to the reduced the surface tension of water after adding polyvinylpyrrolidone, which is beneficial to the uniform dispersion of nano-silicon.

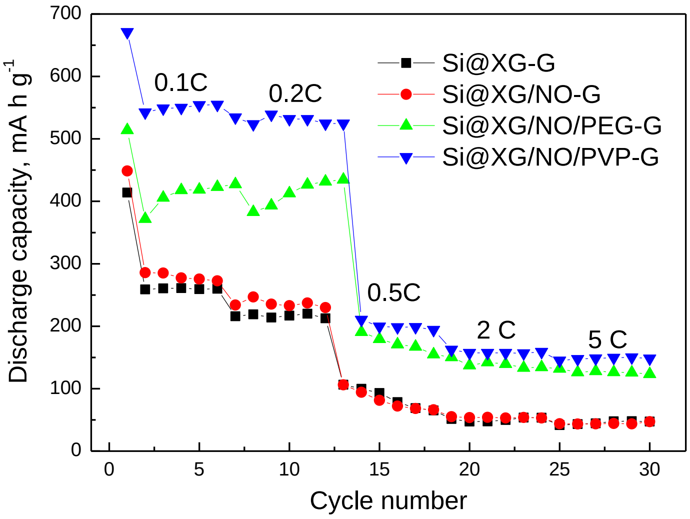

Figure 5. Discharge capacity curves of four carbon-silicon/graphite composites at different current densities

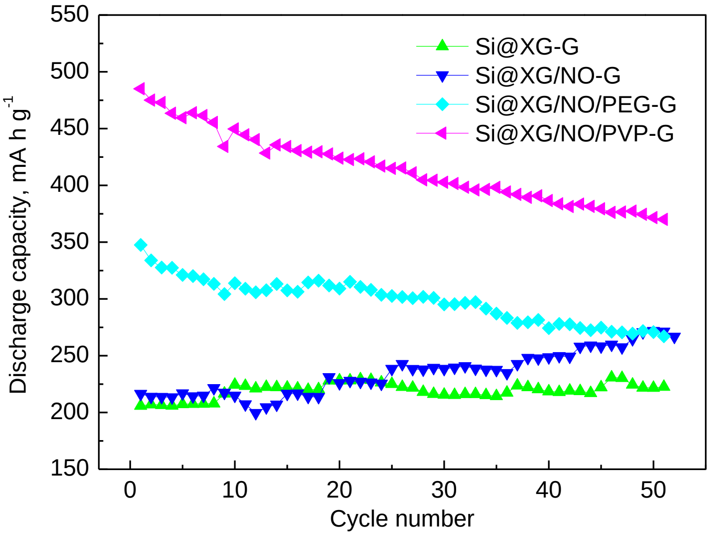

Figure 6. Curves of the specific discharge capacity of four carbon-silicon/graphite composites circulated for 50 times at a current of 0.3 mA

The discharge specific capacity curves of four carbon-silicon/graphite composites under different current densities were shown in Figure 5. The discharge specific capacities of Si@XG/NO/PVP-G at current of 0.1 mA, 0.2 mA, 0.3 mA, 0.4 mA, 0.5 mA are 554 mA h g^{-1}, 531 mA h g^{-1}, 198 mA h g^{-1}, 157 mA h g^{-1} and 148 mA h g^{-1}, respectively, which are significantly higher than Si@XG-G's discharge specific capacities at current densities of 0.1 mA, 0.2 mA, 0.3 mA, 0.4 mA, 0.5 mA of 260 mA h g^{-1}, 216 mA h g^{-1}, 93 mA h g^{-1}, 49 mA h g^{-1}, and 47 mA h g^{-1}, respectively. Especially under the large current of 0.5 mA, the specific discharge capacity of Si@XG/NO/PVP-G can still reach 148 mA h g^{-1}, about 26.7% of the specific capacity at 0.1 mA, exceeding the performance of Si@XG-G with a specific capacity of 47 mAh g^{-1} and a retention of 18.1%. This may be due to the addition of niobium pentoxide and polyvinylpyrrolidone, which is conducive to the dispersion of nano-silicon and anisotropic decomposition of carbon source, and can effectively reduce the particle size and compactness of carbon, thereby shorting the Li ion diffusion path. Zhu Jia et al. [21] prepared nano-silicon and germanium by high-speed ball milling to prepare particles with a diameter of about 150 nm by regulating the introduction of germanium, and prepared silicon alloy materials after etching with hydrofluoric acid. The material's first discharge capacity is 3200.8 mA h g^{-1}, and the first coulomb efficiency can reach 94.1%.

Table 3. Comparison of electrochemical performance for various silicon-carbon composite anodes

Sample	**Current density (mA g^{-1})**	**Reversible specific capacity**	**Reference**
Si/C composite nanospheres	200	240 mA h g^{-1} after 300 cycles	19
Si/C microspheres	50	281 mA h g^{-1} after 50 cycles	22
Si/SiO_2@C composite	50	218 mA h g^{-1} after 50 cycles	23
Silicon/carbon composite	100	515 mA h g^{-1} after 100 cycles	24
Silicon/graphite composite	300	375 mA h g^{-1} after 50 cycles	This work

Figure 6 is the discharge specific capacity curves of these four carbon-silicon/graphite composites circulated for 50 times under the current of 0.3mA. For Si@XG-G, the initial discharge specific capacity is 205 mA h g^{-1}, while after 50 cycles, the discharge specific capacity increases to 221 mA h g^{-1}, the capacity retention rate is 107.8%, with a slowly increased capacity. This may be related to the uneven dispersion of nano-silicon and the slow release of charge and discharge capacity. Capacity retention of the three other carbon-silicon/graphite composites, Si@XG/NO-G, Si@XG/NO/PEG-G and Si@XG/NO/PVP-G with the addition of niobium pentoxide and polymer dispersant are 125.5%, 77.8% and 76.5%, respectively. The carbon-silicon/graphite composites modified by niobium pentoxide and a polymer dispersant have a significantly improved specific discharge capacity, while the cycle performance is significantly reduced. This may be due to the addition of niobium pentoxide and polymer dispersant, which causes the coated carbon layer on the surface of the nano-silicon to be loose, and the structure is easily broken during repeated charge and discharge processes. Moreover, the cycling performance of Si@ XG/NO/PVP-G in this work is also comparable to those of reported Si/C anodes (Table 3), which has shown a competitive electrochemical performance.

4. CONCLUSION

Xanthan gum (XG) and glucose (GLU) were used as composite carbon sources, and niobium pentoxide and a polymer dispersant were added to modify the nano-silicon, to prepare carbon-silicon composite. Then, the carbon-silicon composites were ground with graphite to obtain four novel carbon-silicon/graphite composite anode materials. XRD test showed that the four composite anode materials have strong characteristic diffraction peaks of graphite and silicon, and there are no heterogeneous peaks of amorphous carbon. The particle size of carbon-silicon/graphite composites modified by niobium pentoxide and polyethylene glycol or polyvinylpyrrolidone is small (18-24 μm), which may be due to the heat capacity and pyrolysis of additives and carbon source during the sintering process of the material. The difference in temperature and speed causes internal non-uniform stress to the carbon layer formed on the surface of the nano-silicon, resulting in a loose carbon layer structure and easy grinding and crushing. Niobium pentoxide and polymer additives can improve the charge-discharge specific capacity and initial coulombic efficiency of the material, and the cycle performance of the carbon-silicon/graphite composites becomes a competitive electrochemical performance.

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