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Flexible and free-standing SiO_x/CNT composite films for high capacity and durable lithium ion batteries

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Abstract

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Keywords

free-standing, SiO_x/CNT, composite films, high, flexible, capacity, batteries, durable, lithium, ion

Disciplines

Engineering | Physical Sciences and Mathematics

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Flexible and free-standing SiO_x/CNT composite films for high capacity and durable lithium ion batteries

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Keywords: Silicon oxide, Carbon nanotube, Lithium ion storage, Flexible, Free-standing

Abstract

Flexible and free-standing electrode materials are prerequisite and key components for next-generation flexible energy storage and conversion devices. However, it is still a challenge to fabricate these materials from a continuous, straightforward, and facile method. Herein, we report a flexible composite film with silicon oxides decorated on few-walled carbon nanotubes, which can be continuously fabricated and directly drawn from the hot zone of the reactor. The composite film can be readily used for electrochemical lithium ion storage with high and reversible specific capacity, good rate capability, and excellent cycling performance. These exceptional characteristics make it very promising for flexible energy storage and other emerging applications.

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1. Introduction

Recently, there has been a significantly increased amount of effort devoted to wearable electronics or other flexible devices, including smart textiles, glasses, watches, or even artificial skin. In order to achieve the advances in these state-of-the-art devices, the bottleneck lies with the next-generation energy storage devices, which require higher gravimetric/volumetric energy densities, faster charge-discharge capability, and higher flexibility than conventional lithium ion batteries. In such a device, the electrode materials, which should be high-capacity, flexible, durable, and low-cost, are the key components to control the overall performance [1].

For instance, numerous investigations have been conducted based on various conductive materials (e.g. carbon nanotubes/nanofibers, graphene, or textiles) to build flexible electrodes [2-6]. Among these materials, carbon nanotubes (CNTs) are attractive due to their diversified structures, excellent electrical conductivity (especially compared to chemically derived graphene or other amorphous carbons), outstanding flexibility, high strength, good chemical stability, and low cost [7]. Despite these desirable characteristics, the intrinsically low lithium storage capacity of pristine CNTs makes it very difficult to meet the high energy requirements of future batteries or other energy storage devices [8]. Consequently, it is necessary to introduce additional active components (e.g. Sn, Sb, Si, or their oxides) with much higher Li ion storage capacity [9-12]. Extensive effort has been exerted on combining these high capacity materials with different forms of carbon materials, such as direct blending [2,13], vapor/liquid phase deposition [3,11,14,15], or thermal pyrolysis of the mixed precursors [16]. Despite improved Li-storage performance, the obtained materials usually exist in powder forms and require further treatment (e.g. cast-coating on metal foil), making it not elastic to use these materials for flexible applications/devices. Some studies have integrated active species with two or three-dimensional carbon assemblies [2-3], yet the obtained materials are often limited to a relatively low yield, leading to unsatisfactory economic viability.

For an ideal flexible electrode, an interconnected network is necessary for achieving high flexibility and good electrical conductivity. In addition, it should be easy to composite with high capacity species, in order to obtain higher energy densities for devices. [For example, Philip et al. successfully prepared flexible electrode materials by combining active materials Si particles and highly conductive CNTs sheets into a network. Zhang et al. reported a flexible electrode material with excellent performance on the basis of nanocarbons to form a 3D hierarchical structure. Gopukumar et al. synthesized flexible electrode materials by combining active Sb₂S₃ with CNTs \[17-19\].](#) Moreover, it should be capable of being produced on a large scale at

relatively low cost for the practical applications. Nevertheless, up to now, it is still very challenging to achieve these advantages simultaneously.

Herein, we report a highly flexible, free-standing, and continuous composite film electrode for high capacity alkaline ion storage applications, which can be uninterruptedly fabricated by a simple one-step method. For the film electrode, amorphous silicon oxide (SiO_x) thin layers (2-6 nm thick) and particles are decorated/embedded on the surfaces of highly graphitized and few-walled CNTs, which form a very effective network for electron transport. These unique structural characteristics result in outstanding performance for lithium ion battery (LIB) applications, including a high reversible capacity (1600 mAh g^{-1}) at 30 mA g^{-1} , excellent rate capability of 441 mAh g^{-1} at 2 A g^{-1} , and good cyclability up to 1155 mAh g^{-1} @ $100 \text{ mA g}^{-1}/100$ cycles or 400 mAh g^{-1} @ $3 \text{ A g}^{-1}/500$ cycles. All these excellent characteristics of this material, together with the high flexibility, simple synthesis process, and low cost, demonstrate its great potential for high-energy/power and smart energy storage applications.

2. Experimental

2.1. Preparation of SiO_x/CNT films

Assisted by water densification, we obtained a scroll of SiO_x/CNT films directly from a vertical floating catalyst chemical vapor deposition system. Tetraethyl orthosilicate ($\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$, TEOS, AR, Tianjin Guangfu Fine Chemical Research Institute) and ethanol ($\text{C}_2\text{H}_5\text{OH}$, GR, Tianjin Jiangtian Chemical Technology Co. Ltd) were used as the precursors for SiO_x and CNTs, respectively. Firstly, TEOS was dissolved in ethanol in weight percentages of 1, 4, and 8 wt.%. Subsequently, ferrocene ($\text{C}_{10}\text{H}_{10}\text{Fe}$, 1.9 wt.%, AR, Tianjin Guangfu Fine Chemical Research Institute) and thiophene ($\text{C}_4\text{H}_4\text{S}$, 1.0 wt.%, AR, Tianjin Guangfu Fine Chemical Research Institute) were added into the solution as the catalyst and the promoter, respectively. Then, the solution was stirred for 0.5 h to form a homogeneous precursor solution.

In the meantime, a vertical tube furnace was firstly purged with argon and then hydrogen at a flow rate of 800 sccm. Then, the furnace was heated and maintained at 1150°C , and the precursor solution was injected into the quartz tube at a rate of 6 ml h^{-1} . The resultant film in the hot zone of the furnace travelled downstream to the bottom of the quartz tube and was then drawn onto a spindle to form a continuous SiO_x/CNT film. Here, a series of analogue materials (pristine CNT film or SiO_x/CNT films with different SiO_x content) were prepared through the same methods by tuning the amount of TEOS in the precursor solutions (denoted as $\text{SiO}_x/\text{CNTs-A}\%$ ($A = 1, 4, \text{ and } 8$), where A was the TEOS content in the precursor). The thus-formed film

can be unwound from the spindle and pressed into a condensed thin film for subsequent characterizations and electrochemical assessments.

2.2. Characterization

X-ray diffraction (XRD) measurements of the SiO_x/CNT films were carried out on a RIGAKU D/Max 2500V diffractometer using Cu K α radiation ($\lambda = 0.15406$ nm), operating at 40 kV and 40 mA, to identify the crystal phase. The chemical state of the materials was analyzed using X-ray photoelectron spectroscopy (XPS, ESCALab 250). Raman microscopy was conducted to investigate the structure on a Renishaw LabRAM HR 800. Thermogravimetric analysis was performed on a NETZSCH, STA 499C at a heating rate of 10 °C min⁻¹ up to 1000 °C in air to determine the content of SiO_x. The morphology and microstructure of the materials were characterized by field-emission scanning electron microscopy (FE-SEM, JEOL, JSM-6700F) and transmission electron microscopy (TEM, FEI, Tecnai G2F20).

2.3. Electrochemical Testing

The obtained free-standing SiO_x/CNT films were directly used as the anode in a battery without using any conductive additives, binders, or current collectors. The films were punched into disc electrodes (diameter of 12 mm) and assembled in CR-2032 coin cells in an Ar-filled glove box (Microuna, China). [The initial thickness of the composite film used as electrode material is about 10 \$\mu\$ m, corresponding to an areal density of about 0.09 mg cm⁻².](#)

The electrolyte used in the cells was 1 mol L⁻¹ LiPF₆ dissolved in a mixture of ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 by volume), and porous polypropylene film (Celgard) was used as the separator. Lithium foil was used as the counter electrode, and the working electrode loadings were about 2 mg cm⁻². Galvanostatic charge-discharge tests were performed in the range of 0.01 to 3 V on a battery tester (Neware, CT 3008W). Cyclic voltammetry (CV) experiments were conducted on an electrochemical workstation (CHI 660D) at a scan rate of 0.1 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) studies were performed using 5 mV AC amplitude over 100 kHz-0.01 Hz on an identical electrochemical work station. [The full-cell was assembled using the asprepared SiO_x/CNTs electrode as an anode, commercial LiCoO₂ \(LCO\) as a cathode, and LiPF₆ solution as the electrolyte. The electrochemical tests were carried out between 3.0 and 4.3 V for the complete anode-limited full-cells with respect to the mass of the anode \(P/N ratio of the full cell is about 5.0\).](#)

3. Results and Discussion

3.1. Material Synthesis and Characterization

Fig. 1. Illustration of the flexibility and morphology of the SiO_x/CNT composite film. a) Schematic illustration of the synthesis of the SiO_x/CNT film from a vertical furnace; b) optical image of SiO_x/CNT film on a spindle; c) a flat film removed from the spindle; and d) optical images of the film under various deformations.

Continuous and free-standing SiO_x/CNT hybrid films were prepared by the modified floating catalyst chemical vapor deposition (CVD) method in a vertical tube furnace (Fig. 1a and S1a in the Supporting Information) [7]. Ferrocene, thiophene, and tetraethyl orthosilicate (TEOS) were used as catalyst, promoter, and silicon oxide precursor, respectively, and were dissolved in ethanol, which acted as the carbon precursor for CNTs. The precursor solution was then directly injected into the furnace tube under hydrogen atmosphere. Decomposition of the precursors occurred instantly once they reached the hot zone of the furnace, as evidenced by the formation of a smoke-like aerogel (Fig. S1b). The aerogel travelled downstream with the carrier gas flow, turned into a black, semi-transparent, sock-like soft tube (Fig. S1c), and was finally wound on a rotating spindle to form a continuous film (Fig. 1b and S1d). Thus, the composite films

prepared using this method in principle have no limitations on length, as long as the precursor solution is constantly fed into the furnace. The dimensions (length and width) of the as-prepared films can be adjusted by simply varying the winding time and mechanical traction (e.g. the movement of the spindle position and rotation speed). As shown in Fig. S1e, we present an optical image of the composite film with a size of 10.3×16.1 cm, ~15 mg. As a typical sample of the film continuously spun for half an hour, it was produced from 3 ml of the precursor solution. It should be pointed out that as long as the precursor is continuously supplied, our system is able to spin the thin films continuously. On this basis, about 30-40 mg of the film (~10 μm thick) can be produced every hour, which suggests that the facile method is of great versatility and potential for scaling-up production.

The as-prepared SiO_x/CNT composite film is paper-like and free-standing, and it shows excellent mechanical flexibility and structural integrity (Fig. 1c). It can withstand extreme deformation, such as being repeatedly folded, rolled, bent, twisted, or even made into a complex origami, without fracturing or suffering from any structural failures (Fig. 1d), indicating good suitability for applications in flexible devices. In order to clarify the relationship between the silicon precursor content (TEOS, which determines the content of silicon oxide in the product) and the mechanical properties of the composite films, we obtained a stress-strain plot to describe the tensile properties of the SiO_x/CNTs films (Fig. S2). Here, it should be pointed out that we have fixed the sample size of 0.5×1.5×0.01 cm to ensure the same testing condition. Interestingly, we found that with the increasing TEOS concentration, the tensile strength and corresponding strain behavior underwent a gradual change. Specifically, at a low TEOS content (i.e. SiO_x/CNTs-1% and 4%), the maximum stress of the samples was basically at the same level (~1 MPa), while the strain of SiO_x/CNTs-1% (49.6%) was larger than that of SiO_x/CNTs-4% (40.2%). When the concentration of TEOS was increased to 8%, the SiO_x/CNTs-8% still showed a maximum stress of 0.428 MPa. Even though, the strain of resultant films at breakage was still over 30%, which is obviously better than for other fiber or powder lithium-ion battery anode materials [7, 20], suggesting that our films are robust enough as self-standing and flexible electrodes. In addition, we further obtained the cross-sectional information of the samples through SEM observation (Fig. S2d, e), which showed the thickness of the samples was 12 μm, basically in the same order of magnitude as the value measured in Fig. S2a (~ 10 μm). The enlarged section of the red box in Fig. S2e showed dense distribution of CNTs and granular substances.

The microstructure of the SiO_x/CNT films was observed by SEM. Parallel thin strings can be observed in most sections of the SiO_x/CNT composite films, with some particles dispersing

between these strings (Fig. 2a, S3, and S4). Under higher magnifications, these strings are found to be around 20-40 nm in diameter, and have a core-sheath structure with thin CNTs (bundles) inside the silicon oxide surface sheath, indicating a successful in-situ and nanoscale composition of CNTs and SiO_x in this floating catalyst CVD procedure (Fig. 2b and S1). In addition, the pristine CNT film possesses a similar structure with better oriented CNT strings and much fewer particles between these strings (Fig. S5), which is similar to previous reports [7].

Fig. 2. Structural characterizations of the SiO_x/CNT composite films. a, b) SEM images of $\text{SiO}_x/\text{CNTs-8\%}$ at different magnifications; c) TEM image of $\text{SiO}_x/\text{CNTs-8\%}$ at low magnification; d) high resolution TEM image of the bare CNT section on $\text{SiO}_x/\text{CNTs-8\%}$; e, f, g, h) high resolution TEM images of the SiO_x coated CNT sections on $\text{SiO}_x/\text{CNTs-8\%}$; i) high resolution TEM images of the Fe particles on $\text{SiO}_x/\text{CNTs-8\%}$; j) XRD patterns of the pristine CNTs and SiO_x/CNT films; and k) Raman spectra of the samples, with enlargement of the spectra in the low shift region (inset). The scale bars in f, g, and h are all 5 nm.

Under TEM, it can be found that the composite strings are generally orientated with small particles located between them (Fig. 2c, S6, and S7), in accordance with the SEM observations. To reveal more structural information on this material, we then observed the bare CNTs (pink box), the SiO_x particles (yellow box) and the SiO_x coated CNTs (cyan box) in different sections of the composite film, as shown in Figure 2d under high resolution. As shown in Fig. 2e, the SiO_x species between the CNTs are generally amorphous without distinct crystal features. The bare CNTs show a typical graphitic structure with an interlayer spacing of ~0.34 nm (Fig. 2f), indicating that the incorporation of SiO_x species does not affect the formation of graphitic CNTs. A single CNT has an outer diameter of ~5-8 nm and inner diameter of ~4-5 nm (Fig. 2f and S6e, f). These CNTs are smooth on the surface, which is very similar to the surfaces of pristine CNT films (Fig. S8), meaning that the excellent characteristics (e.g. high electronic conductivity and excellent mechanical properties) of pristine CNTs could be inherited by the SiO_x/CNT composite film.

Moreover, the sections of SiO_x coated CNTs show a more complex structure (Fig. 2g, h). In these sections, the CNTs are generally the same as the aforementioned bare ones, as shown by their similar inner diameters and clearly graphitized walls, which are consistent with the bare sections. On the outside of the CNTs, the SiO_x coatings can be found to have a thickness of 2-6 nm, and these SiO_x coatings do not possess a well-defined crystalline structure, similar to the SiO_x species in between the CNTs (Fig. 2e). Beneath these SiO_x coatings, fine particles (~2-4 nm) also can be seen. The high resolution TEM images (Fig. 2i) of these particles show clear fringes with a spacing of ~0.2 nm, which is consistent with the (110) crystal plane of residual Fe catalysts (PDF:06-0696). They tend to coexist with the silicon oxide, possibly due to the better wettability of the oxygen-rich surface of the silicon oxides [21].

More structural information on the materials was obtained by X-ray diffraction (XRD) and Raman spectroscopy (Fig. 2j, k). As illustrated, the XRD patterns of the composite films show broad peaks at ~15-25° and better-defined ones at ~43°. The former peaks can be assigned to the poorly crystalline SiO_x, which almost overlap the signals from graphitic CNTs [22-23]. [The sharp diffraction peak of the CNTs films at about 25° becomes wider upon the introduction of silicon oxide in the materials.](#) The latter ones can be attributed to the (101) planes of the CNTs. As the SiO_x content is increased, the broad peaks (15-25°) also shift towards lower 2θ degrees, indicating a conversion from a more graphite-like characteristic to a more SiO_x-like characteristic of these materials. The Raman spectra of the materials show two prominent peaks centered at 1328 cm⁻¹ (D band) and 1584 cm⁻¹ (G band), which can be attributed to the disordered carbons on the edges or other defect sides of the graphitic structures, and the sp²

carbons in the well graphitized regions, respectively [24]. Remarkably, all the samples possess high peak intensity ratio I_G/I_D (1.45-1.88), indicating large crystalline graphitic domains in these materials, which is in agreement with the TEM observations of the CNT sections with highly graphitic structures [25]. Apart from these typical graphite characteristics, weak peaks can also be found in the region of 135 to 165 cm^{-1} (inset of Fig. 2k), which indicates the presence of single-walled CNTs in the material [26]. Based on these structural characterizations, it can be confirmed that a co-axial structure with amorphous SiO_x located outside the highly graphitized CNTs has been achieved in the materials, which is highly desirable for free-standing and flexible film electrodes and has rarely been achieved in previous studies [27-28].

Fig. 3. Elemental analysis of the SiO_x/CNT composite films. a) XPS survey scan of SiO_x/CNTs -8% and the contents of the elements (inset table); b) high resolution $\text{Si}2p$ spectrum of SiO_x/CNTs -8%; c) high resolution $\text{C}1s$ spectrum of SiO_x/CNTs -8%; d) EDS analysis of the elements of SiO_x/CNTs -8%; e-i) TEM image of SiO_x/CNTs -8% and the corresponding elemental mappings of various elements.

The chemical compositions of the materials were then studied by X-ray photoelectron spectroscopy (XPS). The survey scans of the SiO_x/CNT composite films show the existence of C, Si, O, S, and Fe in the material, and their contents are listed in the inset table (Fig. 3a and S9). It is notable that the ratio of O to Si in SiO_x/CNTs-8% is ~1.64, in between the stoichiometric ratios for SiO and SiO₂, indicating its complex nature. The detailed chemical states of Si and C were then probed by high-resolution XPS (Fig. 3b, c, and S9). The Si2p spectrum can be deconvoluted into three peaks at ~101.9, 103.6, and 104.3 eV, corresponding to Si²⁺, Si³⁺, and Si⁴⁺ species, respectively [29]. Accordingly, the x value in this specific SiO_x/CNTs-8% material can thus be calculated to be ~1.64, assuming that all these species bind with oxygen atoms. This agrees well with the O/Si ratio obtained from the XPS survey scan (~1.64) and the extra oxygen may come from the oxygen bonded with carbon in CNTs to form oxygen-containing functional groups. Accordingly, the SiO_x content in the SiO_x/CNTs-8% material can be determined to be ~62.6 wt.%, which is also in good agreement with the thermogravimetric analysis results (see the detailed discussions shown in Fig. S9 and S10). In addition, no signal of Si⁰ has been detected, indicating the absence of any elemental silicon in the materials, even though they were synthesized under high temperatures in H₂ atmosphere. On the other hand, the C1s spectra can be deconvoluted into several peaks, as shown in Fig. 3c, which can be assigned to sp² C (-C=C-), sp³ C (-C-C-), and various oxygen-containing functional groups (-C-OH, -C=O, -COOH), respectively [30-31], which are similar to the ones in the SiO_x/CNTs-1% and 4% samples, and the pristine CNT films (Figures S9 and S11). Interestingly, a small peak can be found at ~283.7 eV in the high resolution C1s spectra of all the SiO_x/CNTs samples, which takes up to ~0.8-1.8% of the total carbon atoms. This can be assigned to Si-C bonds in the material, which indicates the possible existence of doped carbon atoms in SiO_x, given that there are no carbides in the material, as shown in the XRD patterns [33].

To verify this and to further track the elemental distributions of the materials, we then conducted X-ray energy-dispersive spectroscopy (EDS) and elemental mapping of the materials from TEM characterization on a typical SiO_x coated CNT region. From the EDS spectrum, C, O, Fe, Si, and S elements have been detected, consistent with the XPS survey scan results (Fig. 3d). From the corresponding elemental mappings (Fig. 3e-i), intensive Si and O signals are found all over the material, due to the SiO_x coatings on the surface of the material. A weak Fe signal can also be seen, which is more concentrated inside the material than outside. Interestingly, carbon species can be found all over the material, rather than merely in the central CNT regions. This further corroborates the doped carbon atoms in the SiO_x and is in accordance

with the XPS results (Fig. 3c and S9). Based on the above structural and compositional investigations of the materials, it is reasonable to deduce that the composite fibers have a co-axial and sheath structure, with graphitized CNTs inside and amorphous SiO_x outside. This unique structure can be beneficial from several aspects: the SiO_x can act as high capacity active species for Li ion storage; the CNTs beneath it can function as conductive cores for efficient electron transport as well as strengthening the phase for high mechanical properties (e.g. flexibility and strength). These characteristics would be very attractive to providing high conductivity, capacity, flexibility, and stability for the material.

3.2 Lithium Ion Storage Performance of SiO_x/CNT Films

Fig. 4. Electrochemical lithium ion storage performance of the SiO_x/CNT composite films. a-d) galvanostatic charge-discharge profiles of the SiO_x/CNT composite films and the pristine CNT film; e) cycling performances of the SiO_x/CNT composite films and the pristine CNT film for 100 cycles at 100 mA g^{-1} f).

The resultant SiO_x/CNT composite films are free-standing, with good conductivity and superior flexibility. Therefore, they can be directly applied as electrodes for electrochemical lithium storage without using any conductive additives (e.g. carbon black), binders, or metal foil current collectors. As a result, these SiO_x/CNT composite films as well as the pristine CNT films were assembled into coin cells with a Li foil counter electrode to assess their electrochemical performances.

When galvanostatically tested between 0.01 and 3.0 V at a rate of 100 mA g⁻¹, samples with different SiO_x contents have charge-discharge profiles with similar shapes (Fig. 4a-d). Obvious difference between the first and subsequent charge cycles can be observed. In the initial charge curves (i.e. the lithiation process) of all the materials, there is a distinct plateau at 0.75-0.85 V, corresponding to the irreversible decomposition of the electrolyte and the formation of the solid electrolyte interphase (SEI) film, which contributes to most of the irreversible capacity in the first cycle compared to the subsequent cycles. This has often been observed on other CNT-based materials and is generally recognized to cause capacity loss in the first cycle [34].

It is interesting to find that, compared to all the SiO_x containing materials, the pristine CNT film possesses the highest initial capacity, up to 1600 mAh g⁻¹, although this is followed by a huge irreversible capacity loss of up to 1200 mAh g⁻¹ compared to the following cycles (Fig. 4d), which might be caused by the large surface area arising from the individual CNTs inside the pristine CNT film and has been observed in previous reports [35-36].

On the other hand, for the SiO_x/CNT composite films, with increased SiO_x, the charge-discharge behavior gradually becomes different from CNT-like character (i.e. the first charge capacity gradually decreases, simultaneously yielding a much smaller irreversible capacity (Fig. 4a-c), which is more favorable for practical applications. This is possibly due to their smaller surface area contributed by the high contents of the SiO_x active species. According to the nitrogen adsorption desorption results (Fig. S12), the calculated specific surface area of the composite films is approximately 20% smaller than that of the pristine CNTs film. Besides, with the increase of the SiO_x content in the material, the specific surface area of composite films also shows a decreasing trend. After the SEI formation in the first cycle, the aforementioned plateau disappears, and the charge and discharge behavior of the materials becomes stable. The cycling performance of the SiO_x/CNT composite films was then assessed at the rate of 100 mA g⁻¹ (Fig. 4e). For the pristine CNT film, even though it showed the highest initial capacity, its capacity quickly decreased in the first few cycles, which gradually declined during the remaining test to 303 mAh g⁻¹ after 100 cycles. In comparison, the materials containing different amount of SiO_x species gave distinctively better performance in terms of their higher capacities.

Specifically, when the SiO_x content was increased from 0 in the pristine CNT film to 62.6 wt.% in the SiO_x/CNTs-8% sample, the materials' capacity changed from slowly descending to quickly ascending as the cycling tests proceeded. Among them, the SiO_x/CNTs-8% shows the highest capacity: after the initial capacity rises for the first 45 cycles, its capacity remains fairly stable, and reaches ~1240 mAh g⁻¹ after 100 cycles. The increase of capacity during prolonged cycling is in agreement with the gradually decreasing electrochemical impedance of the materials (Fig. S13) [37]. We can see that the coulomb efficiency of all materials increases gradually with the increase of cycle number and finally stabilizes to 100%, which also reflects that the structure of materials will gradually become stable. Here, based on the TGA results mentioned above, the content of CNTs in each composite film is 73.0, 50.8 and 18.9 wt.% for SiO_x/CNTs-1, 4, 8%, respectively. According to the capacity of the pristine CNTs film, it can be calculated that the capacity contribution of CNTs to the three kinds of composite film is 62.39, 40.32 and 5.08 wt.%, respectively.

Fig. 5 SEM images of SiO_x/CNTs-8% at various magnifications after different cycles. a-c, e-g); cross-sectional image of the SiO_x/CNTs-8% after d) 200cycles and h) 500cycles.

From the above SEM, we can clearly see that although the SiO_x particles are still tightly attached on the wall of CNTs after being cycled at high current density (Fig. 5a-c, e-g), a volume expansion can still be seen from the cross-sectional image of the samples in Fig. 5d (15 μm) and h (16 μm), which is larger than the initial value of 12 μm before the cycling. In addition, the inset in Fig. 5a and e are the optical photos of the electrode material after 200/500 cycles, respectively. It can be seen that the material has not undergone any deformation in the lateral direction, indicating its excellent structural stability.

To better understand the initial capacity increase at the beginning of the cycling, we further investigated the morphology evolution during the charging-discharging process (Fig. 6).

Initially, the film possesses a fairly dense surface with SiO_x/CNT composite strings closely stacked on each other with SiO_x particles filling the spaces between the composite strings (Fig. 5a, b). After 200 cycles (Fig. 6c, d), the SiO_x particles are still attached on the surfaces of these strings, which implies to some extent the stability of our material. In the case when the composite film was cycling for 500 times, the overall morphology has not changed much (Fig. 6e, f). When the cycle numbers up to 1000, the SiO_x particles on the CNTs become loose and presents certain expansion effect on volume, which is greatly beneficial for ion diffusion obviously. This also means that in the cycling process, much more SiO_x are gradually activated as additional active materials, resulting in overall performance increase in specific capacity. In Fig. 6i, we clearly demonstrate the structural changes of the electrode materials during electrochemical charge and discharge. During the process of intercalation and deintercalation of lithium ions, the particles on the CNTs are gradually loosened and activated. Based on these observations, it is reasonable to deduce that the large volume variation of the SiO_x species during repeated cycling would possibly make the SiO_x/CNT composite film gradually loose and porous, which facilitates the wetting of the interior surfaces of the film by the electrolyte. As a result, an increasing amount of SiO_x can be involved in the electrochemical lithiation/delithiation process as the cycling goes on, resulting in increased capacity during the initial cycles. To gain the insight into the electrochemical processes in the materials, we conducted cyclic voltammetry (CV) testing at a scanning rate of 0.1 mV s^{-1} between 0.01 and 3 V (Fig. S14a, b). In the first cathodic scan, a distinct and broad reduction peak at around 0.6 V can be observed, which is caused by the formation of SEI films and is well consistent with the plateau in the first charge profiles of the materials (Fig. 4a-c). Moreover, there is also a pair of distinct peaks at around 1.6 and 2.6 V in the first CV loop (Fig. S13b), which may be ascribed to the reactions between SiO_x and Li. The weak peak at around 0.3 V mainly corresponds to the reduction of SiO_x [35]. In the reduction process, beside the formation of elemental silicon, Li_2O , $\text{Li}_2\text{Si}_2\text{O}_5$ and Li_4SiO_4 , among which $\text{Li}_2\text{Si}_2\text{O}_5$ are active to lithium. The dominant cathodic peak nearly 0 V corresponds to the alloying processes of the reduced silicon and pyrolyzed carbon. The broad anodic peaks at 0.1-1.6 V correspond to the dealloying processes of C and Si alloys, while the anodic peak at around 2.6 V is attributed to the lithium extraction process from $\text{Li}_2\text{Si}_2\text{O}_5$. In the remaining cycles, the CV curves almost overlap, and the above-mentioned irreversible peaks disappear, demonstrating highly reversible electrochemical behavior that is in agreement with the galvanostatic charge-discharge results.

Due to the excellent conductivity of the CNTs, our materials also possess high capacities at

higher, the capacity of all the materials generally decreased. At relatively low rates (30 to 200 mA g^{-1}), the charge-discharge profiles of the $\text{SiO}_x/\text{CNTs-8\%}$ sample almost overlapped, indicating its good rate performance and stable electrochemical behavior (Fig. 7a). As the SiO_x content gradually decreased, the profiles generally split from each other (Fig. S15). In particular, the 1% and 4% samples exhibited severe attenuation, and the corresponding capacity is less than 300 mAh g^{-1} , indicating their inferior rate capabilities in comparison with the $\text{SiO}_x/\text{CNTs-8\%}$. At the highest rate of 2 A g^{-1} , the $\text{SiO}_x/\text{CNTs-8\%}$ still delivers a moderate capacity of 441 mAh g^{-1} , which is much superior to the other SiO_x -based materials [38-39] and can be reasonably attributed to the intimate contact between the even sheath provided by the outer SiO_x and the inner CNTs that provide sufficient electronic conductivity for fast electrochemical reactions (Fig. 7b). In contrast, the $\text{SiO}_x/\text{CNTs-1\%}$ and 4% samples give lower capacities at all rates, due to the lower SiO_x content. In addition, when the testing rate is returned to 30 mA g^{-1} , the capacities can be restored, indicating the good structural stability of our SiO_x/CNT materials, even after rapid charge and discharge cycling.

Fig. 6. SEM images of $\text{SiO}_x/\text{CNTs-8\%}$ sample at various magnifications after different cycles. a-b) 0 cycle; c-d) 200 cycles; e-f) 500 times and g-h) 1000 cycles; i) schematic diagram of material change during cycling.

In order to further evaluate the potential of our materials for high rate applications, we then tested the SiO_x/CNTs-8% sample at a high current density of 3 A g⁻¹ for comparison (Fig. 7c). Similar to the results at 100 mA g⁻¹, the SiO_x/CNTs-8% sample displays a gradually increasing capacity, which stabilizes at a high value of 400 mAh g⁻¹ up to 500 cycles. In contrast, the pristine CNT film shows relatively stable but much lower capacity, less than 100 mAh g⁻¹. The flexible and free-standing SiO_x/CNT composite films possess not only high capacities but also excellent rate and cycling performances, which can be reasonably attributed to the unique and favorable structural/compositional characteristic of the materials. The few-walled and highly graphitized CNTs in the SiO_x/CNT composites can form a conductive network for efficient electron transport, contributing to the excellent rate performance of the materials. Furthermore, the SiO_x can act as the high capacity active component, resulting in high capacity for Li ion storage. The small thickness of the SiO_x on the CNTs (2-6 nm) further guarantees a relatively low volume expansion during the charge-discharge process, which results in good cycling performance of the material.

Fig. 7. Rate capabilities of the SiO_x/CNT composite films: a) galvanostatic charge-discharge profiles of the SiO_x/CNTs-8% composite film at various rates; b) charge capacities of the samples at various testing rates; c) cycling performance of the SiO_x/CNTs-8% and pristine CNTs films at 3 A g⁻¹ for 500 cycles, as well as their corresponding coulombic efficiencies.

To evaluate the practical viability commercial value of the SiO_x/CNTs anode for LiBs, we have also tested its electrochemical performance in full LIBs with LCO as the cathode and its electrochemical performance is showed in Fig. S16. Fig. S16a depicts the typical galvanostatic charge/discharge curves of the as-prepared $\text{LiCoO}_2//\text{SiO}_x/\text{CNTs-8\%}$ pouch cell. The resultant full cell does not have an obvious voltage plateau. Based on the mass of $\text{SiO}_x/\text{CNTs-8\%}$ anode, the reversible capacity is about 680 mAh g^{-1} in the first cycle. In Fig. S15b, it shows that the electrode still delivers a reversible capacity of 407 mA h g^{-1} after 50 cycles at 500 mA g^{-1} , with the capacity retention of 33.9%.

Based on the above analysis, the initial capacity increase of the composite films capacity, especially for $\text{SiO}_x/\text{CNTs-8\%}$ can be reasonably attributed to several aspects. In the initial several cycles, a large amount of Li ions were inserted into the carbon layers or adsorbed by the nanopores to form the SEI, which may block the further Li ion and electrolyte transportation inside the electrode material, thus resulting in the low initial capacity. During the subsequent cycles, the interlayer spacing of CNTs becomes more expanded, which is favorable for the deintercalation of Li ions. Meanwhile, with the electrolyte more thoroughly infiltrating into the electrode, a larger amount of active silica oxide species could be involved in the electrochemical Li ion storage to give an increased capacity [40-41]. The small surface area caused by the agglomeration of the silicon oxide particles inside the material, however, also indicates that such gradual wetting process could be fairly slow.

4. Conclusion

In summary, a continuous, flexible, and free-standing SiO_x/CNT composite film has been fabricated by a facile and one-step CVD method. In this material, a thin layer of SiO_x active material ($\sim 2\text{-}6 \text{ nm}$ in thickness) and SiO_x nanoparticles are located on the surfaces of highly graphitized and few-walled carbon nanotubes, which form a highly efficient network for rapid electron transport. These unique structural/compositional characteristics have endowed this material with outstanding performance in electrochemical Li ion storage, with a high and reversible specific capacity (1240 mAh g^{-1} @ 100 mA g^{-1}), very good rate performance (441 mAh g^{-1} @ 2 A g^{-1}), and excellent cycling stability (400 mAh g^{-1} @ $3 \text{ A g}^{-1}/500 \text{ cycles}$). The advantage and feasibility of the material can be further enhanced, especially when considering the simplicity, facile preparation, flexibility, and low cost of the material as well as the synthesis approach.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at (will be filled in by the editorial staff)

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