The Development of Silicon Nanocomposite Materials for Li-Ion Secondary Batteries

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Abstract: With the rapid progress and wide application of Li-ion batteries, commercial graphite anode can not satisfy the increasing demand for higher capacities. Like other anode materials with higher capacities, silicon materials as anodes remain serious problems for their large volume variations and poor cyclabilities during cycling. One of key problem is how to stabilize the performances of Si anode materials. Various influencing factors of volume variation of silicon anode materials have been reviewed, which consist of discharging voltage, amorphous or crystalline type, tube or pore microstructure, interlayer adhesion, buffering and protective layer materials and conductive agents. Another hot issue is on the preparation methods for silicon anode materials with high performance. It covers not only the technics of high purity silicon materials, including the predominant Siemens process of electronic-grade silicon, but also the techniques of silicon film anodes, which consists of butyl-capped silicon precursor, the template methods of nanostructure, magnetron sputtering, ball-milling. From the screening of existing silicon anode materials in the literatures, the preparation methods for promising Si anode materials and their prospects have been offered.

Keywords: Li-ion secondary batteries, silicon nanocomposite materials, anode, large volume variations, electrochemical performances.

1. INCREASING DEMANDS FOR HIGHER CAPACITY ANODE CANDIDATES OF LITHIUM-ION SECONDARY BATTERIES

1.1. The Widespread Availability of Lithium-Ion Secondary Batteries

In the early applied accumulator field, there have been various batteries, such as lead-acid batteries, nickel cadmium batteries, nickel metal hydride battery. Since 1980s, the lithium secondary batteries using Li metal as the anode material have been into market.

However, due to the Li dendrite formation on the anode surface, lithium metal anode are found unsafe. Therefore, Carbon materials as anodes are used widely to commercial batteries, instead of Li metal [1].

The anode materials and cathodes of Li-ion batteries allow lithium insertion or deinsertion between the anodes and the counterpart cathodes. As shown in Fig. (**1**), when charged, electrons flow from the cathode to the anode, meanwhile positive Li ions from the anode to cathode; and contrariwise during discharged.

Carbon-intercalation materials [2] possess high mechanical stability and better capacity retention. They can form Li_xC_6, such as petroleum coke carbon and graphite; the latter can deliver a theoretical capacity 372 mAh/g due to inserting double of the lithium. Therefore, the majorities of commercial carbon anode materials are graphite or modified graphite materials at present.
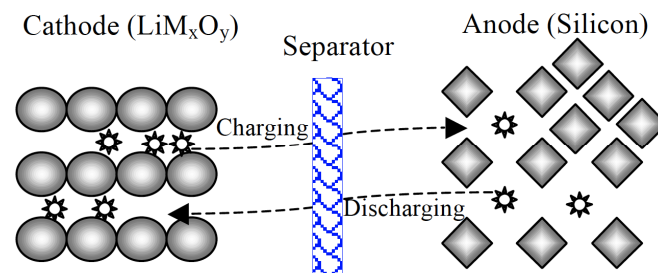

Fig. (1). Schematic of Li-ion secondary battery containing Silicon (anode) and lithium metal oxide (cathode) during charging or discharging processes.

As new scientific and technological products, the Li-ion secondary batteries have superior performance, such as high capacity, high discharge rate, stable discharge platform, non-memory effect, so they can accomplish the scheduled tasks successfully. First of all, the Li-ion batteries have been widely applied to various portable fields, such as mobile phones, MP3 (which stands for Motion Picture Experts Group-Layer3), personal computers, etc. Moreover, vehicle batteries have been exploited, such as the 50 electric automobile of MGL (Mengguli New Energy Technology Co., Ltd.) exhibition in the Beijing Olympics of 2008. Besides, in energy storage areas, they can assist or replace the electric network to absorb more uncertainty and non-stable electrical energy, so as to make use of wind power and

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photovoltaic energy, and make the electrical energy stored regularly. In addition, using the Li-ion secondary batteries systems as the standby power of trains might be a good choice, because they are more powerful and lighter than the lead-acid batteries.

1.2. Requirements for the Anode Candidates with Higher Capacities

Despite of many merits of carbon anode materials and lithium titanate, low capacity is a problem too severely to fit for the ever-increasing energy demands of modern devices in more and more areas, especially the vehicle batteries. Seeking new materials for smaller, lighter, and longer-lasting batteries is a hot focus of the battery research.

Some intermetallics metals [3-11], such as Sn, Si, Al, Bi, Pb, In, whose lithium-base alloys can deliver a high capacity anodic materials, especially Si and Sn can be inserted by maximum Li due to formation of Li-rich alloys, i.e., $Li_{4.4}Si$ and $Li_{4.4}Sn$, which can have high volume specific capacity (theoretical value 7254 mAh/cm^3, i.e., 990 mAh/g) and high weigh volume specific capacity (theoretical value 4200 mAh/g), respectively. Therefore, Si has been regarded as the subsequently promising anode materials [12, 13].

However, the present intermetallic materials mentioned above can not be used as commercial anode currently due to the unsafety issues and instability performance. The related major influencing factor is the large volume expansions or contraction upon lithiation or delithiation. Their volume expansion can be over 300%, while graphite is merely 6-10% and possesses higher mechanical stability. Moreover, the present intermetallic materials are liable to fracture [14, 15], which results in electrical contact with the remainder of the electrode, and increases the possibility of chemical attack by corrosive agents around the surface fracture areas. There are still questions to be overcome before silicon anode materials can be used commercially.

2. STABILIZING FACTORS OF SILICON COMPOSITE MATERIALS DURING CYCLING

Presently, silicon composite materials as anode may bring various problems during discharging or charging processes, such as volume variation, a very large first-cycle irreversible capacity, irreversible capacities, and capacity fading.

It is necessary to study the effect factors on silicon composite materials, including structure and composition, especially the huge volume variation. So, scientists and engineers can work out solutions to build-up a commercial silicon composite material system very soon.

2.1. Proper Charging/Discharging Programs Can Cause Minor Destruction

According to the model analog of theoretical research [14], there are greatly different between horizontal and vertical dimensions when silicon anode is deeply discharged. The dimensions variations in horizontal directions often increase by about 2 times. While the average increment rates in vertical directions increase rapidly with the further deep-discharging. There are no significant variations in the vertical at 0.5V, and suddenly increases by 3 times at 0.3V

of discharging; furthermore, raises to 7 times at 0.2V; in the end, it reaches 12.6 times at about 0.1V.

Due to the large volume variations of silicon anode materials, especially their larger variations in the vertical dimension, the film may be brittle to fall off partially and results in bad conductivity and loss of specific capacity.

Therefore, the suitable programmed charging/discharging processes for controlling the volume variations are necessary.

2.2. Amorphous Silicon Thin Films may have Homogeneous Volume Variations

Monocrystalline silicon and polycrystalline silicon can not present good electrochemical properties when used in Li-ion secondary batteries, even though they are the main materials of the semiconductor industry and photovoltaic fields.

In crystalline materials, new intermetallic phases are formed on lithium insertion. It's the transformation between crystalline type and amorphous type. This leads to inhomogeneous volume expansions in the two-phase regions, which can cause cracking and pulverization of the material. As a result, some of the particles may lose electrical contact with the electrode, and capacity is lost.

As for amorphous silicon materials, they may show a relatively uniform of volume variations. Therefore, amorphous silicon materials receive less destructive, due to their anisotropy characteristics [34].

It seems that amorphous silicon and amorphous silicon-containing alloys can exhibit much improved cycling performance. In amorphous alloys, including amorphous alloys of Si and Sn, the expansion on lithium insertion is homogeneous. And their submicron-thickness films expand and contract reversibly without further pulverization.

Besides the crystal forms, the film thickness also has a strong effect on the electrochemical performance. Some research [35] shows that film thickness also has an effect on structural variations that occur during the lithiation of a-Si films. Only in more than 3 microns thickness of silicon film, can crystal phase form $Li_{15}Si_4$ be definitely generated during cycling at the deep discharge voltage of 30mV.

As the silicon film thickness increases greatly, the vertical size variations might cause unexpected issues including fractures, pulverization or peeling. Thus, low conductivities and bad electrochemical performances may occur.

2.3. Porous Structures Can Buffer the Volume Variations

Porous structures including macroporosity, mesoporosity, microporosity, are listed in Table **1** [15, 16, 24, 38-47]. Microporous structures which size are below 2 nanometers, play an role of helping lithium-ion intercalation or deintercalation, while macroporous structures which size are above 50 nanometers, help the electrolyte storage as reservoir. Mesoporous structures which size are between 2 and 50 nanometers, also play a role of both of micropous and macroporous structures. In addition, porous materials can provide a large rate of volume for buffering the huge volume

Table 1.   Nanostructures of Si Composite Anode Materials and their Capacities

Structures Strategies	Structures and Component Characteristic	Capacity
mesoporous	Mesoporous Si@Carbon Core-Shell Nanowires [39]	3163 ~ 80 cycles
	encapsulated Si with mesoporous TiO_2 layer [38]	2000→900~5 cycles
	Mesoporous Si-TiO_2 [40]	1400 ~ 50 cycles
macroporous	Three-dimensionally ordered macroporous Ni–Sn [41]	455 ~ 30 cycles
nanoporous	nanoporous nanofibrous Si [42]	746 ~ 30 cycles
Nanowires	Crystalline-Amorphous Core-Shell Silicon Nanowires [43]	1000 ~ 100 cycles
	Mesoporous Si@Carbon Core-Shell Nanowires [39]	3163 ~ 80 cycles
	Silicon nanowire (HF-$AgNO_3$ etching) [24]	1000 ~ 30 cycles
	Carbon-Silicon Core-Shell Nanowires [44]	2000 ~
	silicon nanowires [15]	3500~20 (C/5)
nanofiber	Carbon-fiber-silicon-nanocomposites [45]	700 ~
	carbon-silicon composite nanofiber [46]	1240 ~ 20 cycles(0.1C)
nanotube	Nanoscale Si coating on pore-walls of SnO_2 nanotube [16]	1800-1600~90 cycles
	Si DC MWCNTs nanocomposite [47]	733 ~ 20 cycles

variation of silicon materials, so as to give a good electrochemical performance.

Nanostructure materials can promisingly minimize the expansion of lithiation and stabilize the electrochemical properties, while inappropriate nanostructures resulted in worse electrochemical properties [36-38]. Furthermore, compared with silicon nanowires, silicon nanotubes possess large surface area, large buffer capacity and better stability.

To buffer the silicon materials, other buffering materials are brought around the silicon sites. These materials have less or no expansions and contractions, e.g., carbon materials, titanium dioxide, copper materials, etc. And, they can be in various structures, such as fibers, nanowires, nanobelts, nanotubes, porous structures, etc. [16, 38-47].

2.4. High Interlayer Adhesions May Prevent the Si Active Substance from Peeling

Substrate pretreatments, including etching, corona treatment of the substrate, roughness, etc., are effective methods for increasing the attachment of silicon to substrate, enhancing the adhesion and improving conductivity properties, especially under the huge volume variation caused by the discharging or charging of silicon materials [48].

Magnetron sputtering is a preparation method as well as a pretreatment method, which enhances the adhesion between substrate and film of material through the plasma sputtering, and improves the adhesion between the particles of the film through the plasma deposition. So it possesses excellent adhesive films, compared with other deposition methods including CVD (chemical vapor deposition), evaporation techniques.

2.5. The Stable Protective Layer Can Avoid Further Useless Corrosion

Solid electrolyte interface (SEI) layer is usually formed when electrolyte decomposes on the anode surface during the first electrochemical cycles. The electrolyte does not

further decompose on graphite surface, so graphite materials have better capacity retention [49].

The SEI of silicon-containing material is different from that of graphite. The silicon sites begin fracture during cycling, caused by the large expansions and contractions, upon Li insertion and deinsertion. The SEI layer forms and disintegrates continuously, so more and more new SEI layers form on aged layers. In the end, a thick layer inhibits Li diffusion in the active materials, and especially reduces the battery capacity greatly [34, 48].

In order to keep it stable, some electrolyte should be used. Vinylene carbonate can be used in minimizing the SEI thickness of metal-based anodes, which can form a stable thickness SEI layer [50]. In addition, some outer surfaces are formed with the mixture of various oxide and/or carbon, so as to protect the silicon materials.

2.6. The Conductive Agents Doped May Improve the Electrical Properties

Due to a low conductivity of silicon materials, it is unfit for discharging at high rate instantaneously. To improve the conductivity, some conductive agents are often used, including acetylene black, carbon black, polyaniline, carbon nanotubes [18, 47, 55, 73]. Moreover, aluminum and tin are good candidates, which provide good electrical conductivity as well as high specific capacity, for their being active anode materials.
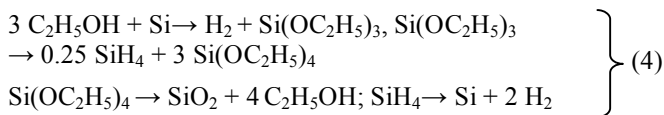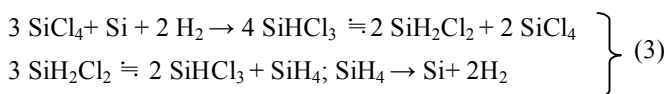
3. VARIOUS PREPARATION METHODS FOR THE SI COMPOSITE ANODE MATERIALS

3.1. Preparation Techniques for Silicon Materials

Silicon element in the earth shell is abundant, widely available, and inexpensive. However, the pure silicon materials are expensive for their high cost and complex process.

There have been some key methods for preparation of silicon with different purity. Metallurgical-grade silicon, whose purity is about 98.5%, is usually prepared by reducing

silica sand or quart with coke for metallurgy (shown in Reaction 1). Electronic-grade silicon as one of important semiconductor materials, whose purity is above 99.9999999% (9N), is achieved by the modified Siemens Method, which is of high cost and low productivity (shown in Reaction 2) containing a series of process: hydrochlorination of metallurgical-grade silicon, fractional distillation of trichlorosilane, hydrogen reduction. Solar grade silicon as the major solar cell materials whose purity is around 99.9999% (6N), is produced by silane decomposition method by Union Carbide Corporation (shown in Reaction 3) and National Laboratorys in USA (shown in Reaction 4) or other method hydrochloric treatment of silicate method by Kawasaki Steel and Flat glass company in Japan, etc. These reactions are shown below:

$$SiO_2 + C \rightarrow Si + CO_2 \tag{1}$$

$$3\ HCl + Si \rightarrow SiHCl_3 + H_2\ ;\ SiHCl_3 + H_2 \rightarrow 3\ HCl + Si \tag{2}$$

$$\left.\begin{array}{l} 3\ SiCl_4 + Si + 2\ H_2 \rightarrow 4\ SiHCl_3 \rightleftharpoons 2\ SiH_2Cl_2 + 2\ SiCl_4 \\[6pt] 3\ SiH_2Cl_2 \rightleftharpoons 2\ SiHCl_3 + SiH_4;\ SiH_4 \rightarrow Si + 2H_2 \end{array}\right\} \tag{3}$$

$$\left.\begin{array}{l} 3\ C_2H_5OH + Si \rightarrow H_2 + Si(OC_2H_5)_3,\ Si(OC_2H_5)_3 \\[2pt] \rightarrow 0.25\ SiH_4 + 3\ Si(OC_2H_5)_4 \\[6pt] Si(OC_2H_5)_4 \rightarrow SiO_2 + 4\ C_2H_5OH;\ SiH_4 \rightarrow Si + 2\ H_2 \end{array}\right\} \tag{4}$$

Amorphous silicon can be produced by reduction of silicon tetrahalogen or silicon dioxide with active metal or carbon, respectively. Furthermore, polycrystalline silicon can be obtained by annealing and heat processing of amorphous silicon, besides the modified Siemens Method.

As an important Si precursor, butyl-capped Si solutions are prepared by reduction of $SiCl_4$ with sodium naphthalene at 400°C for 9 h (mix with butyl-lithium in stirring overnight subsequently, remove the solvent and naphthalene by rotary evaporator under vacuum at 120°C respectively, and partition NaCl from LiCl using excess n-hexane and water). The final product, a pale-yellow viscous gel is given in the end [16-20]. The reaction process is as follows.
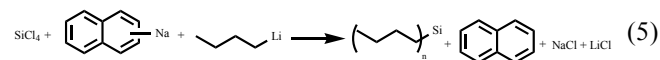
3.2. Preparation Techniques for Various Nanostructure Silicon Anode Materials

Various methods [16-19,21-32,39] including sacrificing template method, sol-gel method, template etching, chemical vapor deposition, sputtering, etc, are listed in Table **2**. Pore structure of mesoporous materials, macroporous materials, nanoporous materials, as well as fibers, nanowires, nanotubes and other structures can be obtained by the methods mentioned above.

Templates methods including hard or soft templates are important methods for preparation of various Silicon nanostructure materials. Silicon porous nano-materials, e.g., hollow 0 D nanoparticle or porous 3 D nanoparticle, can be obtained by Si precursor with silica nanoparticle as template [17]. Silicon nanowire or Silicon nanotube can be prepared by Si precursor with SBA-15 or Al_2O_3 membrane template, respectively [16-19, 39]. Moreover, B-dope monocrystalline silicon can be allowed to produce mesoporous silicon nanowires by etching of appropriate concentration of mixture of $AgNO_3$ and HF for 3-4 h at 25-50°C [26]. In addition, solvothermal preparation method can provide silicon nanocrystals or nanotubes throught the action of SiO [33].

Silicon film can be obtained by chemical vapor deposition, thermal evaporation, magnetron sputtering, which can produce the film of Si, Al, Sn, etc. [32]. The magnetron sputtering [21-23] of co-deposition can provide composite of two kinds of materials, such as Si-Al. Ball-milling [29-31] is also an important method for provide composite materials, such as Si-C, $Si_xCo_{0.3}Cu_{0.3}Cr_{0.6}Al_{0.2}$/modified graphite sphere composties, etc., through blending and doping various elements in the Silicon materials.

Table 2.   Preparation Methods of Si Composite Materials and their Capacities

Methods Strategies	Structures and Component Characteristic	Capacity
combinatorial sputtering	Si-Al-Sn films [21] Si-Al thin film [22,23]	1500 ~ 50 cycles 2258~10,1500~350 (0.5C)
Catalytic etching (HF-AgNO₃, etc.)	Silicon nanowire array films [24] silicon nanowire p-n junction diode arrays [25] Single Crystalline Mesoporous Silicon Nanowires [26] photoluminescent silicon nanoparticles [27] silicon nanowire of controlled diameter, length, density [28]	1000~30 cycles
ball milling	Ti-Si and Ti-Si-Al alloy [29] Si/carbon coating [30] $Si_xCo_{0.3}Cu_{0.3}Cr_{0.6}Al_{0.2}$/modified graphite sphere [31]	500~40 cycles 620~100 cycles 1700~40 cycles
Pulse electrodeposition	Sn film [32]	679 ~
Templates methods	Nanoscale Si coating on pore-walls of SnO₂ nanotube [16] Three-Dimensional Porous Silicon Particles [17] Silicon Nanotube [18] Sn₀.₉Si₀.₁/Carbon Core-Shell Nanoparticles [19] Mesoporous Si@Carbon Core-Shell Nanowires [39]	1800→1600~90 cycles 2800~100 cycles 3247~200 cycles 964~ (0.3 C) 3163~ 80 cycles

4. THE PROSPECTS OF HIGH CAPACITY Si COMPOSITE ANODE MATERIALS

4.1. The Characteristics of High Capacity Si Composite Anode Materials

As shown in Tables **3** and **4**, there are many kinds of silicon-free and silicon-containing composite materials, with various structures, components, and preparation methods, as anodes candidates of Li-ion secondary batteries. For example, meso-porous nanowires of silicon/carbon, mesoporous titanium dioxide-coated silicon, mesoporous polyaniline-titanium dioxide composite, macroporous nickel-tin, mesoporous silica-titania, silicon nanowires, carbon-silicon core-shell nanowires, carbon fiber/silica composite, tin oxide nanofibers tube-silicon/tin, silicon/single-walled carbon nanotube.

However, the anode materials with high capacity of over 1000 mAh/g, good cycle performance of over 100 times, are listed as followed:

(1) Amorphous silicon or silicon/aluminum film of micron-size prepared by magnetron sputtering of co-deposition can provide about 2000 mAh/g of specific capacities [22, 34].

(2) Amorphous silicon nanowires prepared by CVD of silane can possess 2000 mAh/g of specific capacities during 2000 cycles [43].

(3) Butyl-capped Si nanotubes as well as the mesoporous Si/carbon core-shell nanowires/nanofiber prepared by template methods can supply 2000- 3247 mAh/g of specific capacities during 80-200 cycles [18, 39, 46].

Table 3. The Capacity Properties of Si-Free Anode Materials

Sn-Free Anode Materials		Sn-Base Anode Materials	
natural graphite spheres [2]	200 ~	SnO$_2$ nanoparticles/3D macroporous C [57]	278
graphite-spheres/pyrolytic carbon [2]	320~15	Sn/C [58]	500~200
CNT/carbon layer [51]	572~100	SnO$_2$/C coaxial nanotubes [59]	542~200
TiO$_2$ Anode Materials		crystalline SnO$_2$ nanoparticles(11nm) [60]	1303~30
		SnO$_2$ nanoparticles/CMK mesoporous C [61]	1347→576
nanometer-sized rutile TiO$_2$ [52]	160~50	Li-Cu-SnO$_2$ [62]	1185.5~100
mesoporous TiO$_2$ nanotubes [53]	162~100	Sn film [32]	679
mesoporous TiO$_2$:RuO$_2$ (nano) [54]	214~20	ordered macroporous Ni-Sn [41]	455~30
Mesoporous polyaniline/anatase TiO$_2$ [55]	140~70	heteroatoms/tin nanoparticles [63]	544 or 413
Others		Cu$_6$Sn$_5$ alloy powders [64]	313~20
		Tin dispersed in an oxide matrix [65]	343 or 611
iron tungstate [8]	653→320	Sn-Co-C composite [4]	486~40
Aluminum(0.1-1um thickness) [10]	800→420	La-Co-Sn alloys [5]	500~40
needle-like Co$_3$O$_4$ nanotube [11]	950~30	Sn-encapsulated α- C hollow spheres [66]	468
Co$_3$O$_4$ nanowires/polymer layer/Li [56]			

Table 4. The Capacity Properties of Si-Containing Anode Materials

C-Free & Si-Base Anode Materials	mAh/g~Cycles	Si-C Anode Mateirals	mAh/g~Cycles
Si-Al thin film [22,23]	2400,1500~350	Mesoporous Si@C Core-Shell Nanowires [39]	3163~80
Nano-Si/pore-wall-SnO$_2$ nanotube [16]	1800→1600~90	Si@SiO$_x$-C Nanocomposite [69]	2000
encapsulated Si/mesoporous TiO$_2$ [38]	2000→900~5	Carbon-Silicon Core-Shell Nanowires [44]	620~100
Ti-Si and Ti-Si-Al alloy [29]	500~40 cycles	SiO and Li/ball milling + carbon coating [30]	700, 900
Mesoporous Si-TiO$_2$ [40]	1400~50 cycles	lithiated silicon-carbon based composites [70,71]	700
Si-Al-Sn films [21]	1500~50 cycles	Carbon-fiber-silicon-nanocomposites [45]	733~20
Si$_x$Co$_{0.3}$Cu$_{0.3}$Cr$_{0.6}$Al$_{0.2}$/graphitespher [31]	1700~40 cycles	Si DC MWCNTs nanocomposite [47]	1800→800~30
carbon-coated SiB [6]	550 ~ 10 cycles	Core double-shell Si@SiO$_2$@C [72]	1240~20
Si-CeMg$_{12}$ composites [7]	550 ~ 30 cycles	carbon-silicon composite nanofiber [46]	733~20
nanosized silicon-nickel-graphite [9]	900 ~ 60 cycles	Si/graphite/MWCNT composite [73]	970~40
nanosheets (Ni$_3$Si, Ni$_{31}$Si$_{12}$) [67]	540	Carbon/silicon (nano-composite) [74, 75]	568-1240
mesoporous Si/ZrO$_2$ nano-film [68]		Si/C composite [76-81]	~1000
Si Anode Mateirals			
Amorphous Si film(2 um thickness) [34]	1180→1159~300	nanoporous nanofibrous Si [42]	746 ~ 30
A thin film silicon(150nm thickness) [82]	2200~200cycles(1C)	Si nanowires [15,83]	3500~20 (C/5)
Cryst.-Amor. Core-Shell Si Nanowires [43]	1000~100 cycles(2C)	A nanosized silicon thin film [84]	

From the high capacity anode materials mentioned above, the highest capacity anode materials are Si nanotubes prepared by template methods, while their too high cost to be applied to commercial process. Amorphous silicon nano-wires also have high capacity while their low tap densities remain a problem. As for the amorphous silicon/aluminum film, thickened Si/Al film anode materials have been prepared by magnetron sputtering, which has 2000 mAh/g of average capacity at rate of 1.1 mA/mg over 140 cycles.

4.2. The Prospects for Silicon Composite Anode Materials of Li-Ion Secondary Batteries

Sub-micron material for anode materials will be paid attention to, because both nanostructure materials and micron materials are problematic: the former has high activity but instability, while the latter has high stability but low activity. Therefore, sub-micron material might balance between the active and stability.

Series of preparation skills could be adopted. Gradient buffer material [85] can be help to minimize the destruction of the buffer layer around silicon, because it is not easy for one layer materials to sufficiently buffer the huge volume variation caused instantly by silicon sites. Also, amorphous silicon composite materials with multi-layer films should be considered for their anisotropic properties. In addition, UV/X-ray curing methods and imprinting technology [86] can give excellent adhesive power and tailor-made microstructures, which could be considered for its more efficient.

With the further mechanics research of Li-ion secondary batteries [87-93] and the lithium-sulphur batteries [94, 95], the Si-containing anode materials with higher performances will be well-designed and developed in low-cost way.

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