

高比能量锂离子电池硅基负极材料研究进展

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摘要: 硅的理论嵌锂比容量是石墨材料比容量的十倍以上, 脱锂电位低, 资源丰富, 倍率特性较好, 故高比能量的硅基材料成为了电动汽车、可再生能源储能系统等领域的研究热点。但由于其在脱嵌锂过程中巨大的体积膨胀效应会导致硅电极材料粉化和结构崩塌, 并且在电解液中硅表面重复形成的固相电解质层(SEI)使极化增大、库伦效率降低, 最终导致电化学性能的恶化。为了解决上述问题, 加快实现硅基电极的商业化应用, 本文系统总结了通过硅基材料的选择和结构设计来解决充放电过程中体积效应的工作, 并深入分析和讨论了具有代表性的硅基复合材料的制备方法、电化学性能和相应机理, 重点介绍了硅碳复合材料和 SiO_x ($0 < x \leq 2$) 基复合材料。最后对硅基负极材料存在的问题进行了分析, 并展望了其研究前景。

关键词: 硅基材料; 负极材料; 锂离子电池; 综述

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Silicon-based Anode Materials Applied in High Specific Energy Lithium-ion Batteries: a Review

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Abstract: Silicon has the highest theoretical lithium insertion specific capacity, more than ten times the theoretical specific capacity of graphite electrode material, and low delithiation potential, with abundant resources and good rate characteristics, high-energy-density lithium-ion battery silicon-based materials have become hot spots in application fields such as electric vehicles and renewable energy storage systems. However, it will cause powdering and structural collapse of the silicon electrode material due to its large volume expansion effect in the process of delithiation and lithium insertion. In addition, the solid electrolyte interface (SEI) layer on the surface of silicon is repeatedly formed in the electrolyte, which increases the polarization and reduces the coulomb efficiency, eventually leading to deterioration of electrochemical performance. In order to solve the above problems and realize the commercial application of silicon electrodes. This paper systematically summarizes the work to solve the volume effect in charge and discharge process through the selection and structural design of silicon-based materials, and deeply analyzes and discusses the preparation methods, electrochemical properties and corresponding mechanisms of representative silicon-based composite materials, focusing on silicon-carbon composites and SiO_x ($0 < x \leq 2$) based anode materials. Finally, the problems of silicon-based anode materials are analyzed and their prospects are prospected.

Key words: silicon-based material; anode materials; lithium-ion batteries; review

锂离子电池由于脱锂电位低,资源丰富,绿色环保,比能量较高、无记忆效应和工作电压高等优势,在手机、笔记本电脑及数码相机等电子产品领域得到了广泛应用。高比能量的锂离子电池从电子终端设备走向电动汽车和储能技术领域势在必行^[1-2]。常见的锂离子电池负极材料有软碳、硬碳、中间相碳微球(MCMB)、人造石墨、天然石墨、钛酸锂(LTO)和硅基材料等。目前,锂离子电池商用负极材料石墨的比容量已接近理论值(372 mAh/g),很难再有质的提升,LTO 虽然循环安全性较好,但是比容量太低(176 mAh/g),难以满足未来高比能量电池的发展需求。由几种负极材料的性能对比图(图 1)可见,要满足 2020 年高能量密度锂离子二次电池 300 Wh/kg 以上的需求,高容量低成本低电压平台的硅基材料是具有极大的潜力。

锂离子嵌入过程中形成硅锂合金 $\text{Li}_{22}\text{Si}_5$ 相,对应的理论容量是天然石墨的十多倍。同时,硅在地球上储量丰富,生产成本很低,且硅的电压平台为 0.3~0.5 V,在充电过程中不存在析锂隐患,大大提高了锂离子电池的安全使用性能。但其在充放电过程中,由于锂化和脱锂循环期间的高体积变化(200%~300%),造成颗粒粉碎和其表面的固相电解质层(SEI)重复形成,最终导致硅基负极材料容量的损耗和循环性能较差等问题^[3-4]。

针对硅基负极材料在嵌锂和脱锂中存在的问题,近些年研究者们通过对硅基材料的纳米化、复合化和核壳结构的改性设计,有效地提高了硅基材料的循环性能。本文主要深入分析和讨论硅基负极材料的储能及容量衰减机理,从硅碳复合材料和 SiO_x ($0 < x \leq 2$) 基复合材料两条主线出发详细总结了硅基电极材料的结构设计及改性研究的最新国内外进展,对未来的研究方向和应用前景作出了展望。

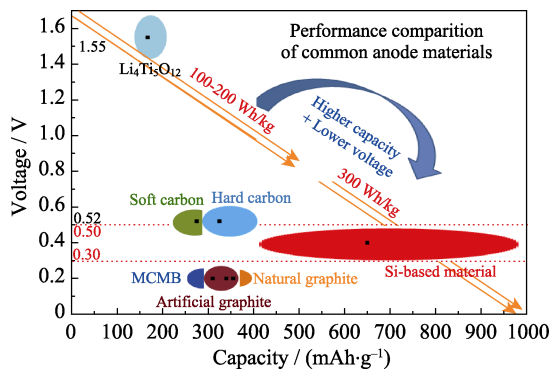


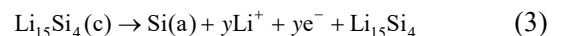
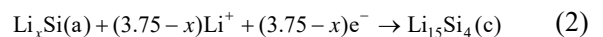
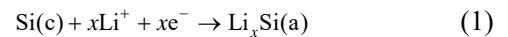
图 1 几种负极材料性能对比

Fig. 1 Performance comparison of common anode materials

1 硅的电化学机理

1.1 脱嵌锂机理

硅的脱嵌锂机理是通过与锂离子的合金化和去合金化进行的。实际电化学嵌锂是晶态硅与非晶亚稳态 Li_xSi 共存的过程^[5-7]。研究发现,在低充电电位 < 0.5 V (相对于 Li^+/Li) 时,硅锂合金化后最终形成相常见的是 $\text{Li}_{15}\text{Si}_4$, 对应的理论质量比容量为 3579 mAh/g^[8]。硅在常温下充放电过程如下式(1)~(3)所示:式(1)和(2)表示嵌锂过程;式(3)表示脱锂过程;式中 a 代表无定型, c 代表结晶态。



1.2 失效机制

硅在充放电过程中会发生巨大的体积膨胀效应,如图 2 晶胞示意图所示,理论上嵌锂生成 $\text{Li}_{22}\text{Si}_5$ 晶胞体积膨胀 300%左右^[9-12]。嵌锂过程中,电解质会发生分解并沉积在硅表面形成 SEI 膜^[13-15]。其失效机制如图 3 所示,由于脱嵌锂过程中硅体积的持续变化,暴露在电解液中新的硅表面 SEI 膜厚度持续增加,最终导致界面阻抗升高。研究表明,亚稳态硅锂合金及硅与电解液发生化学反应,造成锂离子的消耗,增加了锂离子的扩散距离,阻碍锂离子的顺利脱嵌,最终造成硅基负极材料容量的损耗^[16]。

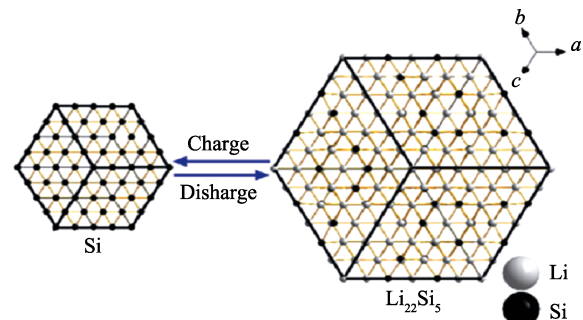


图 2 充电和放电期间硅体积膨胀示意图^[9]

Fig. 2 Illustration of Si volume expansion during charge and discharge^[9]

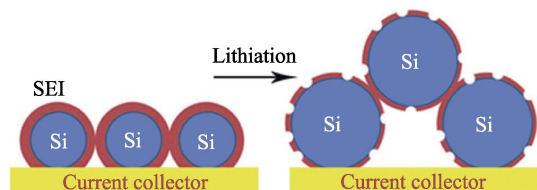


图 3 硅的失效机制示意图^[13]

Fig. 3 Schematic of the failure mechanism of silicon^[13]

2 硅基材料选择及设计

2.1 硅碳复合材料

2.1.1 低维化纳米硅碳复合材料

研究者倾向对硅颗粒纳米化处理,其具有较好的电化学循环性能。但当硅颗粒尺寸小于 100 nm 时,在充放电过程中大的比表面积会与电解液发生更多的接触,形成更多的 SEI 膜,且细小的纳米颗粒容易发生团聚而加快容量的衰减,故通常引入碳材料,设计出纳米硅管、薄膜等低维化的硅碳复合材料^[17-19]。Kim 等^[20]通过镁热还原法制备的 CNT@mp-Si 纳米多孔硅管的电极放电容量 300 次循环后为 1019 mAh/g,对应的库仑效率为 99.6%(见图 4)。可见硅纳米管较大的空间有效改善了体积膨胀,材料具有优异的循环性能。此外,二维化的硅薄膜能够很好地缓冲硅原子体积膨胀,减少机械应力的产生,进而提高硅基材料的循环稳定性^[21-24]。Tong 等^[24]通过磁溅射方法合成了非晶硅/碳(a-Si/C)多层薄膜,制备的微米级 a-Si/C 多层薄膜(1.1 mm)表现出良好的循环性能,超过 200 个周期容量为 1900 mAh/g。

2.1.2 三维化核壳硅碳复合材料

硅基材料的核壳结构是通过系列设计方法将硅与其它材料包覆起来而形成的特殊结构,多孔结构有利于锂离子快速传输,且能有效缓冲循环过程中的体积膨胀^[25-33]。多孔硅结构主要分为实心核壳结构和中空核壳结构两大类。

2.1.2.1 实心核壳硅碳材料

Cui Yi 团队^[25]设计了一种石榴状的纳米硅碳材料(图 5),首先实心纳米硅颗粒外层包覆了有膨胀空间的碳层,然后多个颗粒复合组装,在其表面再包覆一层碳层,最终形成微米级的实心核壳硅碳颗粒,且经过循环后颗粒表面形成稳定的 SEI 膜。其在 1000 次循环后保持 97%的容量,库仑效率达到 99.87%,比容量可达 1160 mAh/g。Xie 等^[26]设计出一种新型的实心蛋黄壳 Si@C@void@C 纳米复合颗粒(图 6)。与 Si@void@C 材料相比,所得的 Si@C@void@C 结构引入 Si@C 颗粒,而不是像蛋黄一样切断。这种额外的内部碳壳结构可以为 Si 核之间提供更好的电子传输和外部碳壳,具有更小的电荷转移阻抗。同时,内外碳壳共同作用,有效地完全覆盖实心 Si 颗粒,从而防止电极材料与电解质直接接触而发生不可逆反应。Si@C@void@C 的初始充电容量高达 1910 mAh/g,并在 50 个周期后保持 71%的容量。

2.1.2.2 中空核壳硅碳材料

虽然实心核壳结构能够改善硅材料的电化学性

能,但随着循环次数的增多,实心硅颗粒仍会面临体积膨胀问题,包覆表面的材料往往会产生裂纹从而丧失特有的结构功能。因此若活性硅材料本身具有一定的空隙结构,可以为充放电过程中的体积膨胀提供首要缓冲空间,从而进一步提高材料的循环性能^[27-29]。Bang 等^[27]利用 Ag 作为金属催化剂,在 HF 和 H₂O₂ 的混合液中诱导腐蚀微米硅颗粒,得到多孔硅颗粒(图 7),对其包碳处理后的核壳复合材料,首次比容量达到 2050 mAh/g,50 个周期后的容量保持率为 87%。Ge 等^[28-29]利用 Ag 作为金属催化剂处理得到具有多孔结构的纳米硅,再用 CVD 法制备得到多孔硅/碳复合材料,其在 0.5C 下,200 个周期后仍有 945 mAh/g 的可逆比容量。

Tian 等^[30]将大量低成本 Al-Si 合金铸锭通过酸蚀刻,球磨和碳化处理合成了由 20 nm 碳涂覆的二次 Si 组成的微米尺寸 Si/C 复合材料(图 8)。纳米多孔 Si/C 复合材料在电流密度为 50 mA/g 时,初始容

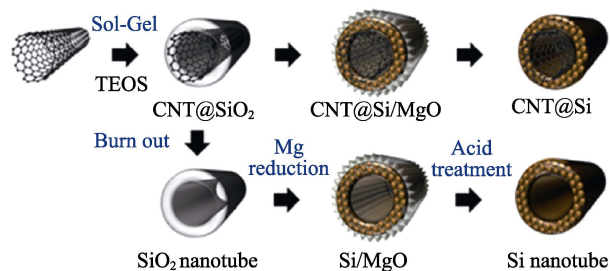


图 4 CNT@mp-Si 和中孔多孔 Si 纳米管的合成示意图^[20]
Fig. 4 The composite map of synthesis of CNT@mp-Si and meso-porous Si nanotube^[20]

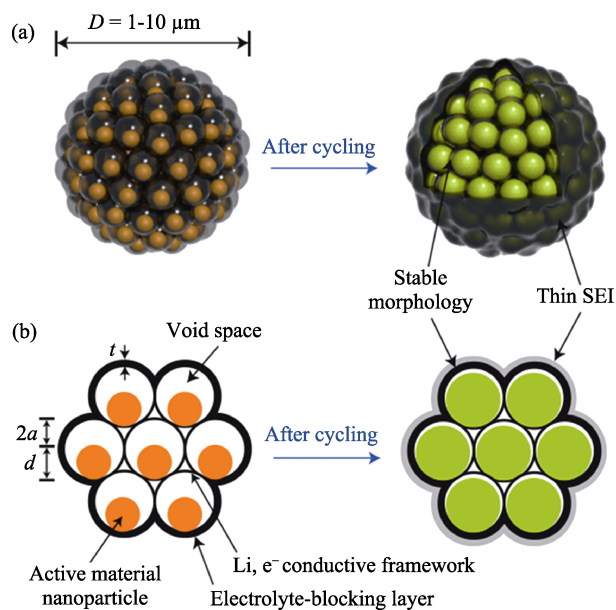


图 5 石榴状纳米硅碳材料设计示意图^[25]
Fig. 5 Schematic of the pomegranate-inspired design^[25]
(a) Three dimensional view and (b) simplified two-dimensional cross-section view

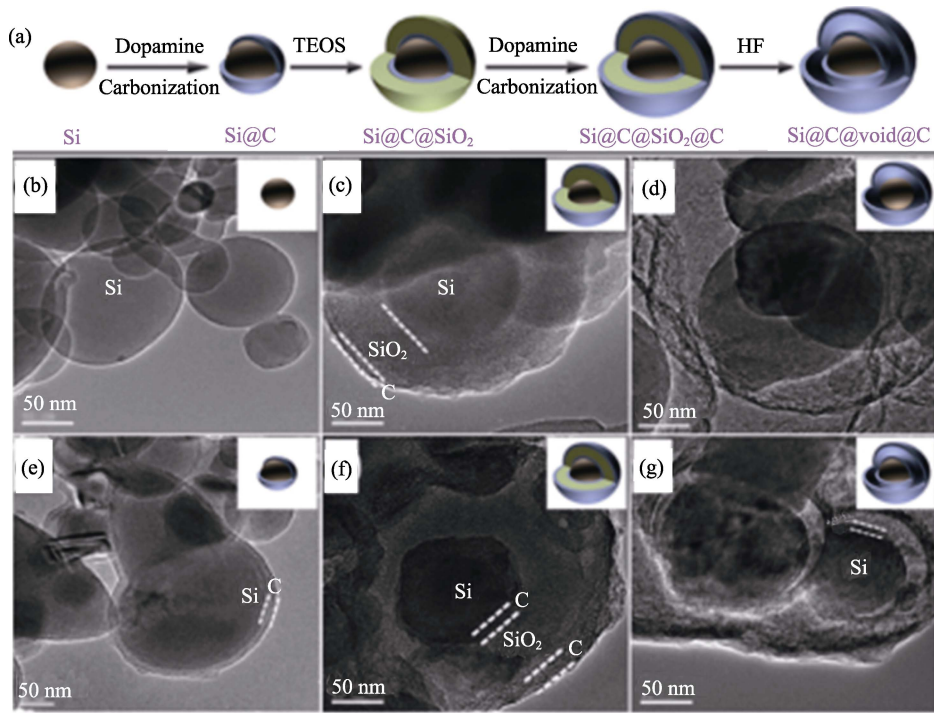


图 6 (a)新型实心核壳 Si@C@void@C 的形成过程示意图, (b)原料 Si、(c)Si@SiO₂@C、(d) Si@void@C、(e) Si@C、(f) Si@C@SiO₂@C 和(g) Si@C@void@C 的 TEM 照片^[26]
 Fig. 6 (a) Schematic diagram of the novel core-shell Si@C@void@C, TEM images of (b) raw Si, (c) Si@SiO₂@C, (d) Si@void@C, (e) Si@C, (f) Si@C@SiO₂@C, and (g) Si@C@void@C^[26]

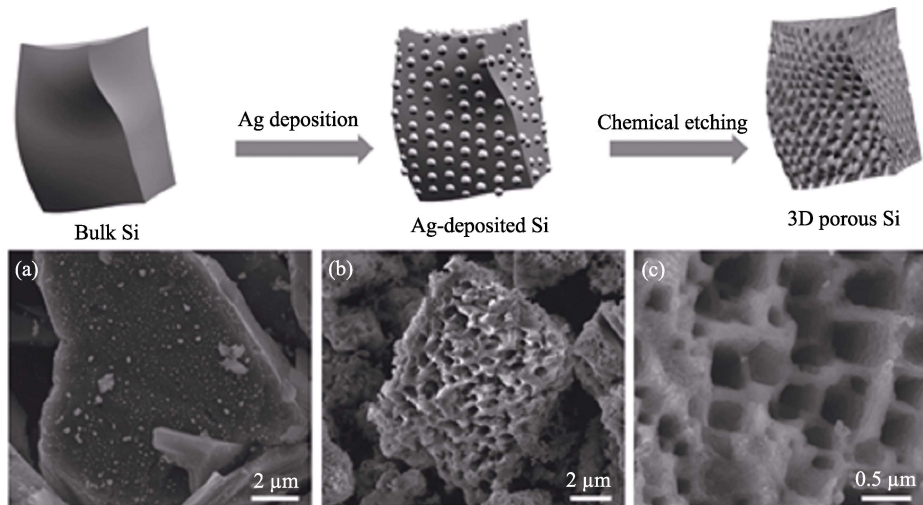


图 7 (a)硅表面沉积银颗粒和(b, c)金属诱导刻蚀硅的扫描电镜照片^[28]
 Fig. 7 Scanning diagrams of (a) Ag-deposited on Si and (b, c) metal induced etching Si^[28]

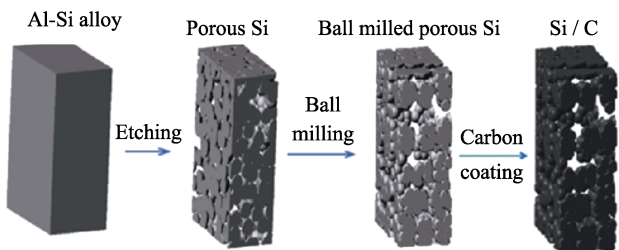


图 8 从 Al-Si 合金到 Si/C 复合材料的制备过程示意图^[30]
 Fig. 8 Schematic illustration of the preparation process from Al-Si alloy to the Si/C composite^[30]

量为 1182 mAh/g, 300 个循环后保持 86.8% 的容量。
 综上所述, 在硅材料不同维度化结构设计中, 碳是最常用来与硅基材料复合。碳与硅复合能够降低材料整体体积膨胀, 同时起到抑制活性物质颗粒团聚的作用, 此外碳的电导率较高, 与常规电解液相容性好, 复合材料一般具有良好的循环稳定性和优异的导电性^[34]。碳材料可分为传统和新型两类, 其中传统碳材料主要包括软碳、硬碳、中间相碳微球、人造石墨、天然石墨、炭黑等, 新型碳材料主

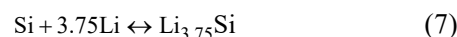
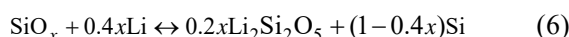
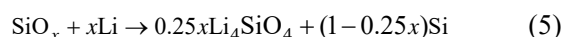
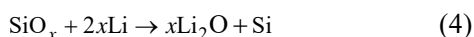
要有碳纳米管/线和石墨烯等。目前,新型碳材料在学术科研上被广泛关注,但相比新型碳材料的使用,传统热解碳材料的成本低,适于商业化应用推广。

本课题组从清洁能源生产和废料回收利用大背景下出发,采用光伏产业中金刚线切割的微米硅粉为原料,通过系列预处理,将硅粉纯度从2N(99%)提纯到5N(99.999%)左右,再利用高温热解碳制备的硅碳负极材料循环450次后仍有426 mAh/g以上的比容量,此工作对光伏产业金刚线切割废料的回收用于锂离子电池负极材料具有重要的指导意义。表1系统总结了几种典型碳与硅复合负极材料的情况。

2.2 SiO_x (0<x≤2)/碳复合材料

2.2.1 SiO_x材料的电化机理

SiO_x材料主要由Si与SiO₂或者Si和O₂在高温高真空下或惰性气氛下蒸镀制得(简称气相法)^[40-41],本课题组采用Si与SiO₂在高温高真空条件下电子束蒸镀得到SiO_x材料,开展了部分SiO_x负极材料结构改性的工作。SiO_x是一种结构相对复杂的非晶材料,ICM(Interface Clusters Mixture)模型认为, SiO_x是由纳米Si、团簇分布SiO₂及亚氧化硅界面构成,亚氧化界面区域占整体体积的比例介于20%到25%之间^[42-43]。SiO_x材料的电化机理与单质Si有所区别,首先SiO_x与锂离子反应形成纳米Si、Li₂O及锂硅酸盐,生成的Li₂O及锂硅酸盐主要抑制纳米Si颗粒发生团聚,起到缓冲体积膨胀的作用^[44-45]。如图9所示,Phillipe等^[46]通过硬质和软质XPS研究了硅纳米粒子和SiO₂层的界面机制,类似于不成比例的SiO_x纳米结构,有助于理解SEI膜形成机制。其中, SiO_x材料的充放电机理一般可表示如下:



2.2.2 SiO_x/碳复合材料改性

SiO_x循环稳定性较单质Si有所提高,但SiO_x材料在脱锂和嵌锂过程中仍然存在首次库伦效率较低和体积膨胀较大的劣势。目前,国内外研究者采用歧化反应、复合化、预锂化和多孔化等手段对SiO_x基负极材料进行改性研究,对提高材料的循环性能、首次库伦效率和倍率性能具有一定的改善效果。

2.2.2.1 歧化处理

利用SiO_x歧化反应改变材料内部的结构,提高循环性能。Park等^[47]研究表明通过1000℃、3h的歧化反应和6h的高能球磨处理,制备得到的nano-Si/SiO_x/graphite复合材料具有1516 mAh/g的初始放电容量,100个周期后容量保持率在70%以上,其循环性能明显优于未歧化热处理的milled-SiO/graphite材料。Morita等^[48]通过歧化反应和高温聚合反应制备得到纳米Si/SiO_x/C复合材料,研究发现歧化反应后,更多的纳米Si颗粒或团簇颗粒均匀分散在SiO_x基质中,其200个周期后的比容量仍有700 mAh/g,分析认为循环性能的提高归因于纳米Si团簇颗粒在硅的氧化物中的高度分散性。

2.2.2.2 预锂化处理

预锂化处理提高材料的首次库伦效率。Yang等^[49]研究发现在SiO/C复合材料中混合一定量的金属锂粉,通过机械球磨和化学还原法制备得到纳米硅基复合材料,其初始容量达到770 mAh/g,首次库伦效率达到81%。Seong等^[50]通过在SiO/C电极表面

表1 硅/碳锂离子电池负极材料的电化性能

Table 1 Electrochemical performance of some silicon/carbon composite anodes for lithium-ion batteries

Composite type	Si source	Carbon source	Electrochemical performance	Method	Ref.
Si/Porous-C	Nano-silicon powder	Pitch	723.8 mAh/g (1st) 600 mAh/g (100 mA/g, 100) ^a	Spray drying + High-temperature pyrolysis	[35]
Si@C@RGO	Silicon powder (80 nm)	Sucrose	1599 mAh/g (1st) 1517 mAh/g (100 mA/g, 100)	Spray drying + High-temperature pyrolysis	[36]
Si/C/G	Silicon powder (325 mesh)	Phenol-formaldehyde resin (PFR)	700 mAh/g (1st) 550 mAh/g (100 mA/g, 40)	High-temperature pyrolysis	[37]
Silicon-sponge	Si wafer (>20 μm)	Acetylene	790 mAh/g (1st) 726 mAh/g (100 mA/g, 300)	Electrochemical etching+ High-temperature pyrolysis	[38]
PS@C	Si powder (5 μm)	Propylene	1980 mAh/g (1st) 1287 mAh/g (100 mA/g, 100)	Chemical etching + CVD	[39]
Si/C	Al-Si alloy (2-10 μm)	Polyacrylonitrile (PAN)	952 mAh/g (1st) 826.3 mAh/g (200 mA/g, 300)	Chemical etching + High-temperature pyrolysis	[30]

Note: ^a- "723.8 mAh/g (1st), 600 mAh/g (100 mA/g, 100)" indicates that 1th cycle discharge capacity is 723.8 mAh/g; the discharge capacity is 600 mAh/g after 100 cycles at 100 mA/g

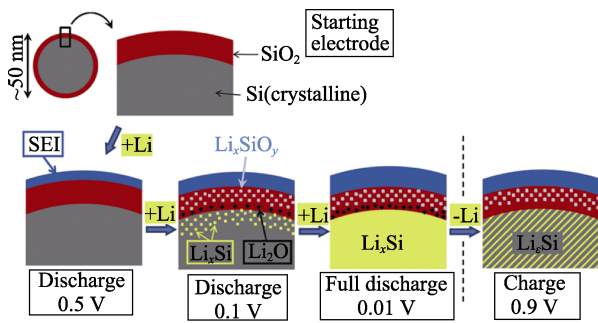


图 9 SiO_x 材料的基本电化学机理示意图^[46]

Fig. 9 Schematic diagram of the basic electrochemical mechanism of SiO_x -based materials^[46]

涂覆一层锂粉, 再放入电解液中浸泡进行预锂化强化处理, 使得 Li 与 SiO 形成 Li_4SiO_4 相, 其电极的首次库仑效率为 73%。Kim 等^[51]开发了一种可扩展卷绕的新型受控预锂化方法, 原始电极通过金属锂

箔的电路短路实现预锂化, 如图 10 所示, 同时可以监测两个电极之间的电压, 预锂化处理的 SiO_x/C 复合材料首次库仑效率高达 94.9%。

2.2.2.3 多孔化设计

复合材料的多孔化设计有利于锂离子在孔道中快速传输, 有助于提高电极材料的倍率性能^[52-56]。Yu 等^[53]对歧化处理的 SiO 材料, 用 NaOH 溶液腐蚀去除氧化硅基体中的部分纳米 Si 颗粒, 最终制得了多孔 Si/SiO_x 材料, 该材料循环 100 次后容量保持在 1242 mAh/g。Feng 等^[54]通过镁热还原法制备的多孔 $\text{SiO}_x/\text{Si}/\text{C}$ 复合材料(图 11)所示, 该材料可逆容量为 1250 mAh/g, 经过 100 次循环后容量保持率为 90.9%, 具有较好的倍率和循环性能。

此外, $\text{SiO}_x\text{-C}$ 复合材料受到多家日韩锂电企业及研究所的广泛研究和青睐^[57-58], 其中日本产业技

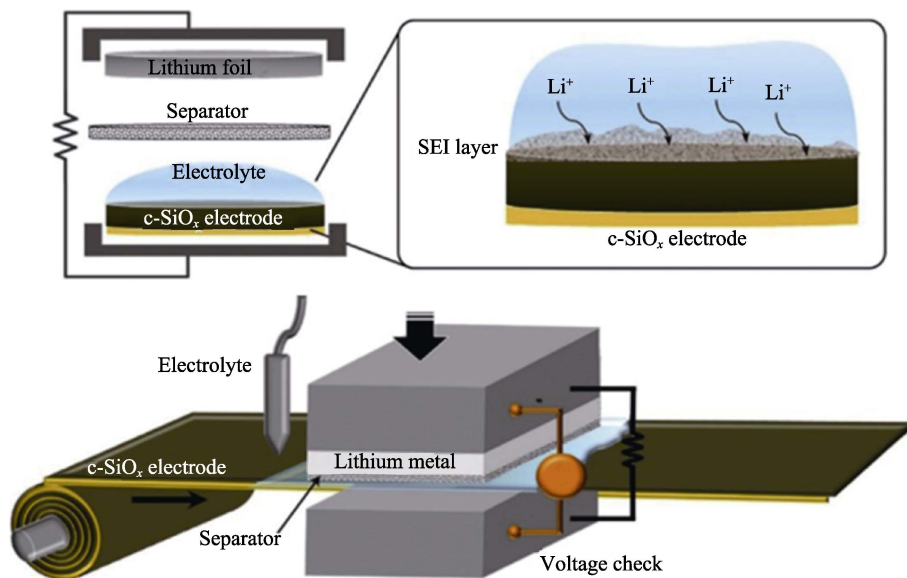


图 10 卷绕电池的金属箔电路短路预锂化处理的示意图^[50]

Fig. 10 Schematic diagram of short-circuit prelithiation treatment of metal foil circuit of batteries^[50]

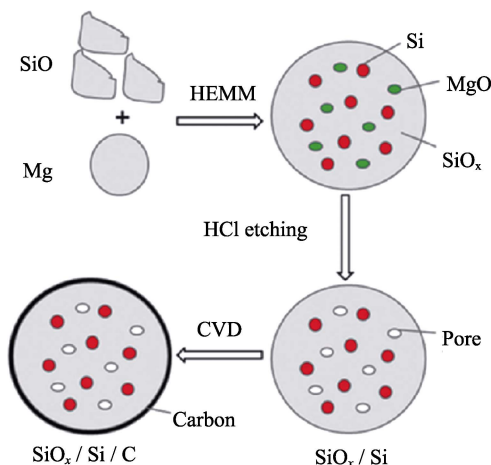


图 11 复合材料 $\text{SiO}_x/\text{Si}/\text{C}$ 的制备示意图^[54]

Fig. 11 Schematic diagram of preparation of the $\text{SiO}_x/\text{Si}/\text{C}$ ^[54]

术综合研究所将 SiO/C 复合负极材料与磷酸铁锂正极材料组装, 该全电池循环 600 个周期后, 容量保持率达到 90%, 且表现出优异的倍率性能^[58]。国内宁德时代新能源公司^[59]制备的中空结构 $\text{SiO}@\text{void}@\text{C}$ 复合材料(图 12)具有较优的电化学性能, 材料的可逆比容量高达 1305 mAh/g, 可稳定循环长达 500 圈, 容量保持率为 54%。

中国在“十三五”新能源汽车试点专项的共性关键技术类研究项目“高比能量锂离子电池技术”中提出: 到 2020 年, 电池单体能量密度 $\geq 300 \text{ Wh/kg}$ 。为此过去 20 年提出了多种技术解决手段, 目前商业化复合材料的可逆容量在 450 mAh/g 以下的碳包覆氧化亚硅、碳包覆纳米硅碳复合材料在循环性、倍

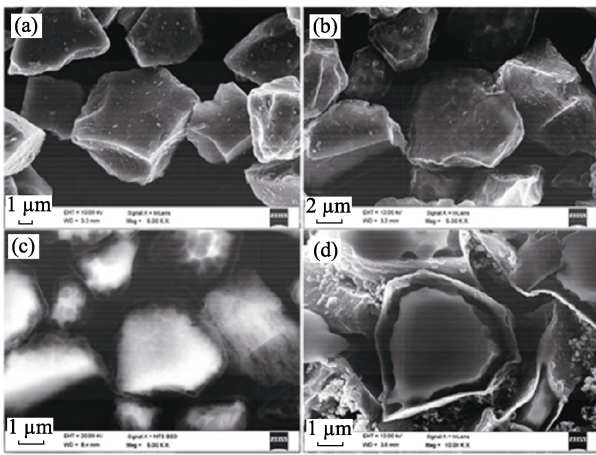


图 12 (a)初始 SiO@C 原料与中空 SiO@void@C 材料的表面((b)二次电子相, (c)背散射相)及(d)截面 SEM 照片^[59]
Fig. 12 SEM images of (a) initial SiO@C, surface ((b) secondary electron phase, (c) back scattered) and (d) cross-section of hollow SiO@void@C material^[59]

率特性方面基本能满足应用要求, 已开始小批量进入电动工具等市场。但 450 mAh/g 以上的硅基负极材料应用还有很多技术挑战。综上, 在硅基复合材料维度及结构设计时, 应更加着重于提高硅基负极材料选择和制备的性价比, 无需片面追求硅基负极复合材料的比容量, 当性价比较高的硅基复合材料的比容量能在 750 mAh/g 左右稳定循环 500 次以上, 即可有效提高电池的能量密度, 实现 2020 年 ≥ 300 Wh/kg 目标。

3 挑战和展望

未来高比容量硅基材料选择和结构设计的两个主要发展方向是硅碳复合材料和 SiO_x (0<x≤2)基复合材料, 但是二者在本质机理上都存在严重的体积效应。从几种典型硅基负极材料性能对比图(图 13)可知, 为了克服体积膨胀问题并加快商业化应用进程, 需要从以下几个方面解决:

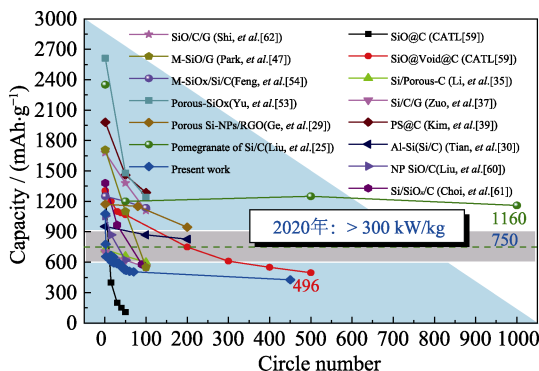


图 13 几种典型硅基负极材料性能对比^[25,30, 35-39,47,53-54,59-62]
Fig. 13 Performance comparisons of common Si-based anode materials^[25, 30, 35-39, 47, 53-54, 59-62]

1) 通过特殊制备方法得到具有特殊结构且性能非常优异的硅碳复合负极材料, 对科研发展具有重要的指导意义, 但是很多研究成果的制备流程冗长且成本较高, 很难短时间内实现产业化生产, 因此寻求成本更低、更易产业化生产的方法, 是高比能量硅基电极材料产业化亟需解决的问题。同时, 考虑到正负极材料的容量匹配问题, 硅基复合材料只要能稳定循环 500 个周期以上, 比容量还保持在 750 mAh/g 左右, 仍可有效提高锂离子电池的能量密度。

2) 相比 Si 材料, SiO_x 材料的体积膨胀效应更小, 是短期可实现商业化最有潜力的选择。有效地制备出循环性能和倍率性能更加优越的 SiO_x/C 复合材料仍将是日后研究的重点。同时需要进一步系统研究 SiO_x 材料的预锂化和电化学机理。

3) 硅基材料的导电性较差, 故在硅基材料中引入金属元素, 设计提高硅基材料的导电性和循环性能的硅/金属复合材料结构也将是今后一个研究热点。

参考文献:

- [1] GOODENOUGH J B, PARK K S. The Li-ion rechargeable battery: a perspective. *J. Am. Chem. Soc.*, 2013, **135**(4): 1167–1176.
- [2] TAN Y, XUE B. Research progress on lithium titanate as anode material in lithium-ion battery. *J. Inorg. Mater.*, 2018, **33**(5): 475–482.
- [3] LUO W, CHEN X, XIA Y, et al. Surface and interface engineering of silicon-based anode materials for lithium-ion batteries. *Adv. Energy Mater.*, 2017, **7**(24): 1701083–1–28.
- [4] XIAO Q Z, FAN Y, WANG X H, et al. A multilayer Si/CNT coaxial nano fiber LiB anode with a high areal capacity. *Energy Environ. Sci.*, 2014, **7**(2): 655–661.
- [5] HUANG S, FAN F, LI J, et al. Stress generation during lithiation of high-capacity electrode particles in lithium ion batteries. *Acta Mater.*, 2013, **61**(12): 4354–4364.
- [6] LI J, DAHN J R. An *in situ* X-ray diffraction study of the reaction of Li with crystalline Si. *J. Electrochem. Soc.*, 2007, **154**(3): A156–A161.
- [7] WANG F, WU L J, KEY B, et al. Electrochemical reaction of lithium with nanostructure silicon anodes: a study by *in-situ* synchrotron X-ray diffraction and electron energy-loss spectroscopy. *Adv. Energy Mater.*, 2013, **3**(10): 1324–1331.
- [8] OBROVAC M N, KRAUSE L J. Reversible cycling of crystalline silicon powder. *J. Electrochem. Soc.*, 2007, **154**(2): A103–A108.
- [9] DING N, XU J, YAO Y X, et al. Improvement of cyclability of Si as anode for Li-ion batteries. *J. Power Sources*, 2009, **192**(2): 644–651.
- [10] SETHURAMAN V A, CHON M J, SHIMSHAK M, et al. *In situ*, measurements of stress evolution in silicon thin films during electrochemical lithiation and delithiation. *J. Power Sources*, 2012, **195**(15): 5062–5066.
- [11] NADIMPALLI S P V, SETHURAMAN V A, BUCCI G, et al. On plastic deformation and fracture in Si films during electrochemical lithiation/delithiation cycling. *J. Electrochem. Soc.*, 2013, **160**(10): A1885–A1893.

- [12] GHASSEMI H, MING A, CHEN N, *et al.* *In situ* electrochemical lithiation/delithiation observation of individual amorphous Si nanorods. *ACS Nano*, 2011, **5**(10): 7805–7811.
- [13] LIANG B, LIU Y, XU Y. Silicon-based materials as high capacity anodes for next generation lithium ion batteries. *J. Power Sources*, 2014, **267**: 469–490.
- [14] WEN Z S, WANG K, XIE J Y. Interface formed on high capacity silicon anode for lithium ion batteries. *J. Inorg. Mater.*, 2007, **22**(3): 437–441.
- [15] CHAN C K, RUFFO R, HONG S, *et al.* Surface chemistry and morphology of the solid electrolyte interphase on silicon nanowire lithium-ion battery anodes. *J. Power Sources*, 2009, **189**(2): 1132–1140.
- [16] KEY B, BHATTACHARYYA R, MORCLETTE M, *et al.* Real-time NMR investigations of structural changes in silicon electrodes for lithium-ion batteries. *J. Am. Chem. Soc.*, 2009, **131**(26): 9239–9249.
- [17] JI H R, KIM J W, SUNG Y E, *et al.* Failure modes of silicon powder negative electrode in lithium secondary batteries. *Electrochem. Solid-State Lett.*, 2004, **7**(10): A306–A309.
- [18] HONG L, HUANG X, CHEN L, *et al.* The crystal structural evolution of nano-Si anode caused by lithium insertion and extraction at room temperature. *Solid State Ionics*, 2000, **135**(1): 181–191.
- [19] LIANG J W, LI X N, ZHU Y C, *et al.* Hydrothermal synthesis of nano-silicon from a silica sol and its use in lithium ion batteries. *Nano Res.*, 2015, **8**(5): 1497–1504.
- [20] KIM W S, CHOI J, HONG S H. Meso-porous silicon-coated carbon nanotube as an anode for lithium-ion battery. *Nano Lett.*, 2016, **9**(7): 2174–2181.
- [21] ZHOU Y N, XUE M Z, FU Z W. Nanostructured thin film electrodes for lithium storage and all-solid-state thin-film lithium batteries. *J. Power Sources*, 2013, **234**(21): 310–332.
- [22] DATTA M K, MARANCHI J, CHUNG S J, *et al.* Amorphous silicon-carbon based nano-scale thin film anode materials for lithium ion batteries. *Electrochim. Acta*, 2011, **56**(13): 4717–4723.
- [23] CHENG H, XIAO R, BIAN H, *et al.* Periodic porous silicon thin films with interconnected channels as durable anode materials for lithium ion batteries. *Mater. Chem. Phys.*, 2014, **144**(1/2): 25–30.
- [24] TONG Y, XU Z, LIU C, *et al.* Magnetic sputtered amorphous Si/C multilayer thin films as anode materials for lithium ion batteries. *J. Power Sources*, 2014, **247**(2): 78–83.
- [25] LIU N, LU Z, ZHAO J, *et al.* A pomegranate-inspired nanoscale design for large-volume-change lithium battery anodes. *Nat. Nanotechnol.*, 2014, **9**(3): 187–192.
- [26] XIE J, TONG L, SU L, *et al.* Core-shell yolk-shell Si@C@Void@C nanohybrids as advanced lithium ion battery anodes with good electronic conductivity and corrosion resistance. *J. Power Sources*, 2017, **342**: 529–536.
- [27] BANG B M, LEE J I, KIM H, *et al.* High-performance macro porous bulk silicon anodes synthesized by template-free chemical etching. *Adv. Energy Mater.*, 2012, **2**(7): 878–883.
- [28] GE M, LU Y, ERCIUS P, *et al.* Large-scale fabrication, 3D tomography, and lithium-ion battery application of porous silicon. *Nano Lett.*, 2014, **14**(1): 261–268.
- [29] GE M, RONG J, FANG X, *et al.* Scalable preparation of porous silicon nanoparticles and their application for lithium-ion battery anodes. *Nano Res.*, 2013, **6**: 174–181.
- [30] TIAN H, TAN X, XIN F, *et al.* Micro-sized nano-porous Si/C anodes for lithium ion batteries. *Nano Energy*, 2015, **11**: 490–499.
- [31] LIU N, WU H, MCDOWELL M T, *et al.* A yolk-shell design for stabilized and scalable Li-ion battery alloy anodes. *Nano Lett.*, 2012, **12**(6): 3315–3321.
- [32] KIM H, HAN B, CHOO J, *et al.* Three-dimensional porous silicon particles for use in high-performance lithium secondary batteries. *Angew. Chem. Int. Ed.*, 2008, **47**(52): 10151–10154.
- [33] JIANG H, ZHOU X, LIU G, *et al.* Free-standing Si/graphene paper using Si nanoparticles synthesized by acid-etching Al-Si alloy powder for high-stability Li-ion battery anodes. *Electrochim. Acta*, 2016, **188**: 777–784.
- [34] WRODNIGG G H, WRODNIGG T M, BESENHARD J O, *et al.* Propylene sulfite as film-forming electrolyte additive in lithium ion batteries. *Electrochem. Commun.*, 1999, **1**(3/4): 148–150.
- [35] LI M, HOU X, SHA Y, *et al.* Facile spray-drying/pyrolysis synthesis of core-shell structure graphite/silicon-porous carbon composite as a superior anode for Li-ion batteries. *J. Power Sources*, 2014, **248**(2): 721–728.
- [36] PAN Q, ZUO P, LOU S, *et al.* Micro-sized spherical silicon@carbon@graphene prepared by spray drying as anode material for lithium-ion batteries. *J. Alloys Compd.*, 2017, **723**: 434–440.
- [37] ZUO P, YIN G, MA Y, *et al.* Electrochemical stability of silicon/carbon composite anode for lithium ion batteries. *Electrochim. Acta*, 2007, **52**(15): 4878–4883.
- [38] LI X, GU M, HU S, *et al.* Mesoporous silicon sponge as an anti-pulverization structure for high-performance lithium-ion battery anodes. *Nature Commun.*, 2014, **5**(5): 4105–1–7.
- [39] KIM J S, HALIM M, BYUN D, *et al.* Amorphous carbon-coated prick-like silicon of micro and nano hybrid anode materials for lithium-ion batteries. *Solid State Ionics*, 2014, **260**: 36–42.
- [40] MIN K K, BO Y J, JIN S L, *et al.* Microstructures and electrochemical performances of nano-sized SiO_x (1.18 ≤ x ≤ 1.83) as an anode material for a lithium(Li)-ion battery. *J. Power Sources*, 2013, **244**: 115–121.
- [41] TAKEZAWA H, IWAMOTO K, ITO S, *et al.* Electrochemical behaviors of nonstoichiometric silicon suboxides (SiO_x) film prepared by reactive evaporation for lithium rechargeable batteries. *J. Power Sources*, 2013, **244**: 149–157.
- [42] SCHULMEISTER K, MADER W. TEM investigation on the structure of amorphous silicon monoxide. *J. Non-Cryst. Solids*, 2003, **320**(1): 143–150.
- [43] HOHL A, WIEDER T, AKEN P A V, *et al.* An interface clusters mixture model for the structure of amorphous silicon monoxide (SiO). *J. Non-Cryst. Solids*, 2003, **320**(1): 255–280.
- [44] LÜ P P, ZHAO H L, WANG J, *et al.* Facile preparation and electrochemical properties of amorphous SiO₂/C composite as anode material for lithium ion batteries. *J. Power Sources*, 2013, **237**(259): 291–294.
- [45] LIU X, ZHAO H L, JIE J Y, *et al.* SiO_x (0 < x ≤ 2) based anode materials for lithium-ion batteries. *Prog. Chem.*, 2015, **27**(4): 336–348.
- [46] PHILIPPE B, DEDRYVÈRE R, ALLOUCHE J, *et al.* Nanosilicon electrodes for lithium-ion batteries: interfacial mechanisms studied by hard and soft X-ray photoelectron spectroscopy. *Chem. Mater.*, 2017, **24**(24): 1107–1115.
- [47] PARK C M, CHOI W, HWA Y, *et al.* Characterizations and electrochemical behaviors of disproportionate SiO and its composite for rechargeable Li-ion batteries. *J. Mater. Chem.*, 2010, **20**(23): 4854–4860.
- [48] MORITA T, TAKAMI N. Nano Si cluster-SiO_x-C composite material as high-capacity anode material for rechargeable lithium batteries. *J. Electrochem. Soc.*, 2006, **153**(2): A425–A430.
- [49] YANG X L, ZHANG P C, WEN Z Y, *et al.* High performance silicon/carbon composite prepared by *in situ* carbon-thermal reduction for lithium ion batteries. *J. Alloys Compd.*, 2010, **496**(1): 403–406.
- [50] SEONG I W, KIM K T, YOON W Y, *et al.* Electrochemical be-

- havior of a lithium-pre-doped carbon-coated silicon monoxide anode cell. *J. Power Sources*, 2009, **189(1)**: 511–514.
- [51] KIM H J, CHOI S, LEE S J, *et al.* Controlled prelithiation of silicon monoxide for high performance lithium-ion rechargeable full cells. *Nano Lett.*, 2016, **16(1)**: 282–288.
- [52] XING A, ZHANG J, BAO Z, *et al.* A magnesiothermic reaction process for the scalable production of mesoporous silicon for rechargeable lithium batteries. *Chem. Commun.*, 2013, **49(60)**: 6743–6745.
- [53] YU B C, HWA Y, KIM J H, *et al.* A new approach to synthesis of porous SiO_x anode for Li-ion batteries via chemical etching of Si crystallites. *Electrochim. Acta*, 2014, **117(4)**: 426–430.
- [54] FENG X J, YANG J, LU Q W, *et al.* Facile approach to SiO_x/Si/C composite anode material from bulk SiO for lithium ion batteries. *Phys. Chem. Chem. Phys.*, 2013, **15(34)**: 14420–144206.
- [55] YANG T, XIAO L I, TIAN X D, *et al.* Preparation and electrochemical performance of Si@C/SiO_x as anode material for lithium-ion batteries. *J. Inorg. Mater.*, 2017, **32(7)**: 699–704.
- [56] LIU Y H, OKANO M, MUKAI T, *et al.* Improvement of thermal stability and safety of lithium ion battery using SiO anode material. *J. Power Sources*, 2016, **304**: 9–14.
- [57] MIYUKI T, OKUYAMA Y, SAKAMOTO T, *et al.* Characterization of heat treated SiO powder and development of a LiFePO₄/SiO lithium ion battery with high-rate capability and thermo stability. *Electrochemistry*, 2012, **80(6)**: 401–404.
- [58] MASAYUKI Y, KAZUTAKA U, ATSUSHI U. Performance of the “SiO”-carbon composite-negative electrodes for high-capacity lithium-ion batteries; prototype 14500 batteries. *J. Power Sources*, 2013, **225**: 221–225.
- [59] LIU X. Facile synthesis and electrochemical performance of hollow SiO@void@C composite as anode material for lithium-ion batteries. *Chin. Batt. Indust.*, 2017, **21(6)**: 3–9.
- [60] LIU W R, YEN Y C, WU H C, *et al.* Nano-porous SiO/carbon composite anode for lithium-ion batteries. *J. Appl. Electrochem.*, 2009, **39(9)**: 1643–1649.
- [61] CHOI I, MIN J L, OH S M, *et al.* Fading mechanisms of carbon-coated and disproportionated Si/SiO_x negative electrode (Si/SiO_x/C) in Li-ion secondary batteries: dynamics and component analysis by TEM. *Electrochim. Acta*, 2012, **85(1)**: 369–376.
- [62] SHI C C, YAN X L, ZHANG L L, *et al.* High-performance SiO/C/G composite anode for lithium ion batteries. *J. Inorg. Mater.*, 2013, **28(9)**: 943–948.