



硅基负极材料空心结构构筑与储锂性能

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摘要 硅基负极材料具有比容量高和嵌锂电势低等优点, 已成为提高锂离子电池能量密度的关键材料之一, 但在循环过程中巨大的体积变化严重影响了电池的循环稳定性. 通过构筑具有特殊微纳结构的硅基负极可以有效缓解体积变化. 本文将硅基空心结构分为四大类: 空心球/笼、蛋黄-蛋壳结构、空心纳米管以及其他特殊空心结构, 从构筑硅基空心结构的必要性出发, 对具有空心结构的单质硅基负极材料的合成方法及储锂性能进行了综述. 最后, 对硅基空心结构负极材料研究当前存在的问题及未来发展方向进行了讨论与展望.

关键词 硅基负极材料, 空心结构, 锂离子电池, 能量储存, 体积膨胀

近年来, 随着国家对新能源汽车的大力支持, 清洁无污染的电动汽车销量实现了井喷式的增长. 2022年, 我国新能源汽车销量达688.7万辆. 尽管如此, 人们对新能源汽车仍存在“里程焦虑”. 国家发展和改革委员会发布的《产业结构调整指导目录(2024年本)》明确提出: 轻工产业要发展锂离子电池用硅碳负极材料等关键材料; 新能源汽车关键零部件中, 电池负极材料比容量高于500 mAh g⁻¹, 循环2000次后不低于初始放电容量的80%. 而目前商业化锂离子电池多以石墨为负极, 理论比容量仅为372 mAh g⁻¹, 远达不到上述要求. 因此, 发展高容量、长寿命、高安全的锂离子电池体系及电极材料已成为学术界和工业界关注的热点^[1~3].

在众多的负极材料中, 硅基负极材料因其地壳储量丰富、理论比容量高(4200 mAh g⁻¹)、氧化还原电位合适(0.2~0.4 V vs. Li/Li⁺)及成本低等优势, 被认为是最有前景的下一代锂离子电池负极材料之一^[4~7]. 自锂离子电池诞生以来, 研究者在硅基负极材料领域积

极探索, 取得了一系列的突破性成果. 1995年, Wilson等人^[8]通过化学气相沉积法(chemical vapor deposition, CVD)合成了硅含量为11%的硅碳复合负极材料, 材料的比容量高达600 mAh g⁻¹. 1999年, 中国科学院物理研究所陈立泉团队^[9]制备了Si纳米颗粒/炭黑复合材料, 其可逆容量高达1700 mAh g⁻¹. 2005年, 斯坦福大学崔屹团队^[10]制备了生长在金属集流体上的Si纳米线电极, 进一步提升其循环性能, 并持续致力于硅负极产业化进程. 现如今, 包括单质Si、SiO_x在内的各类商业化硅基负极蓬勃发展, 包括贝特瑞、Ampricus、Group 14、天目先导、杉杉等企业均已布局.

然而, 硅负极的电子电导率较低. 另外, 在脱嵌锂过程中会发生剧烈的体积变化(300%~400%)导致活性材料粉化、极片破裂进而容易失去电接触. 除此之外, 剧烈的体积变化导致固体电解质界面(solid electrolyte interphase, SEI)膜无限制生长、库仑效率低、活性物质脱离集流体等问题^[5,10~13]. 为了解决以上问题, 目前

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已发展的解决策略包括: 表面包覆或改性优化SEI膜的稳定性; 设计新型功能黏结剂改善极片的机械与黏合性能; 优化电解液配方以提升硅基负极循环稳定性和库仑效率. 硅基负极的结构优化是一种更为广泛的改性策略, 通过在材料中预留足够的体积膨胀空间, 可以改善材料在循环过程中的结构稳定性, 有效提升硅基负极材料的电化学性能^[14~16]. 相比于体相硅, 具有纳米结构的硅负极能更有效地释放循环过程体积膨胀带来的应力, 有效缓解电极材料的粉化, 提升循环稳定性^[17~21]. 2007年, 南开大学陈军团队^[22]采用溶剂热法合成了鸟巢状Si纳米空心球, 并将该硅基空心材料应用于锂离子电池负极. 2009年, Park等人^[23]以阳极氧化铝为模板制备出Si纳米管. 2012年, 崔屹团队^[24]发现, 与实心结构相比, 具有空心结构的硅基负极材料可以为体积膨胀提供足够的缓冲空间, 缓解扩散诱发应力. 通过建立空心Si纳米球锂化过程中扩散应力的有限元模型, 他们发现在相同体积下, 空心Si球的最大拉应力比实心Si球低得多, 这也意味着空心纳米结构的硅负极更不容易被破坏. 在这些工作的启发下, 近年来, 采用空心结构构筑策略缓解硅基负极材料在嵌锂/脱锂循环过程中的体积变化已取得较大进展. 基于此, 本文对单质硅基空心结构的构筑进行了系统的总结, 将硅基空心结构大致分为四大类(图1): 空心球/笼^[24~31]、蛋黄-壳结构^[32~40]、纳米管^[23,41~44]和其他特殊空心结构^[45~48], 并对其储锂性能进行了详细的比较. 最后, 我们对锂离子电池硅基空心结构负极材料研究领域当前存在的问题进行了讨论, 并对这类材料将来的发展方向进行了

展望.

单质硅具有 4200 mAh g^{-1} 的超高理论比容量, 且在除锂金属外的所有负极材料中, 体积容量也最高^[6,49~51]. 然而, 单质硅的电子电导率较低($\sim 10^{-3} \text{ S cm}^{-1}$), 循环过程中伴随的巨大体积变化易造成材料的粉化, 这都使得单质硅基负极材料在锂离子电池中的应用大大受限. 减小硅颗粒尺寸、构筑空心结构可以有效缓解硅的体积膨胀, 将硅与导电材料复合可以有效改善其导电性能. 表1列举了近年报道的典型单质硅基空心材料.

1 空心球/笼结构

单质硅基空心球/笼的合成方法相对简单, 通常可采用选择性刻蚀法、模板法、克肯达尔效应等方法合成. 根据空心球外壳的层数, 可以将空心球结构分为单层空心球结构、双层空心球结构和多层空心球结构. 空心球/笼具有一定的体积变化缓冲能力与较好的结构稳定性. 将Si纳米颗粒封装在其中, 能够有效提高硅基负极材料的循环性能. 外层的空心球/笼在一定程度上阻挡了电解液进入球壳内部与Si纳米颗粒直接接触, 可以提高硅基负极的首次库仑效率与在循环过程中的库仑效率. 需注意的, 这种空心结构也会牺牲硅负极的体积容量和振实密度, 因此需要综合考量空腔的整体占比.

克肯达尔效应(Kirkendall effect)是制备空心结构的一种经典途径, 其基本原理是两种材料的扩散速率不同, 使得材料界面处形成孔洞. 同济大学包志豪团队^[25]报道了一种在熔融盐中铝热还原 $\text{SiO}_2@\text{C}$ 球形成多孔空心硅球的方法(图2(a)). 在还原过程中, Si/O元素向外扩散的速度快于Al元素向内扩散的速度, 于是在界面处形成空腔. 被还原的Si在碳层内/外表面形核并生长, 最终形成多孔空心硅球. 该多孔空心硅球具有容量高、循环寿命长、倍率性能优异的特点. 在 1 A g^{-1} 的电流密度下, 多孔硅空心球在循环200圈后的比容量为 1774 mAh g^{-1} ; 在 8 A g^{-1} 的电流密度下, 循环600圈后容量稳定在 797 mAh g^{-1} . 清华大学邱新平团队^[73]报道了一种内部具有连通结构的空心纳米硅材料. 采用CVD法, 通过控制煅烧温度和通气时间, 合成了具有不同壳层厚度的空心纳米硅. 随着硅壳层厚度增加, 样品的首次库仑效率提高, 但容量保持率下降. 循环后中空结构及硅壳层厚度均未观察到明显变化, 且颗粒表面SEI膜厚度无明显增加. 传统的单层包覆策略在面对硅基负极材料巨大的体积膨胀效应时, 难以达到实际应

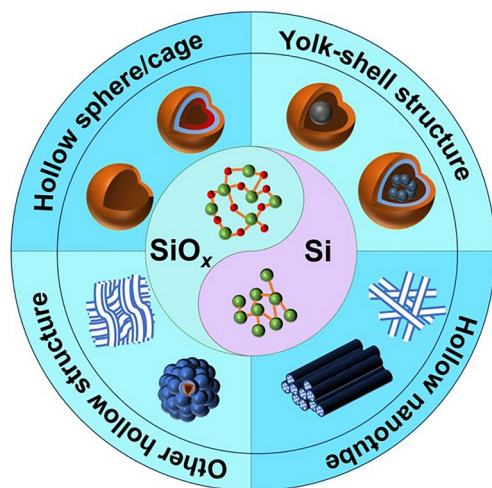


图1 (网络版彩色)硅基空心结构材料的主要类别
Figure 1 (Color online) Main types of Si-based hollow structures

表 1 典型单质硅基空心材料归纳

Table 1 Summary of typical hollow silicon-based anode materials

材料名称	结构类型	循环性能	文献
Si	空心球	1 A g^{-1} , 1774 mAh g^{-1} , 200圈	[25]
m-Si HC	空心球	4.2 A g^{-1} , 850 mAh g^{-1} , 800圈	[26]
SiNDs@DSHC	双层空心球	1 A g^{-1} , 750 mAh g^{-1} , 2000圈	[52]
Si/SiO _x -DSHSs	双层空心球	10 C , 360 mAh g^{-1} , 1000圈	[53]
Si/Cr ₂ O ₃ /C	多层空心球	500 mA g^{-1} , 716 mAh g^{-1} , 300圈	[54]
H-SiNS/C	多层空心球	2 A g^{-1} , $\sim 1040 \text{ mAh g}^{-1}$, 500圈	[55]
NC@Si-20	空心笼	100 mA g^{-1} , 1015 mAh g^{-1} , 100圈	[56]
Si@void@C	蛋黄-蛋壳结构	1 C , $\sim 1500 \text{ mAh g}^{-1}$, 1000圈	[35]
YS Si@50mC	蛋黄-蛋壳结构	420 mA g^{-1} , 1000 mAh g^{-1} , 400圈	[57]
SiNPs@C	蛋黄-蛋壳结构	250 mA g^{-1} , $\sim 570 \text{ mAh g}^{-1}$, 100圈	[58]
nano-Si@C	蛋黄-蛋壳结构	2.1 A g^{-1} , 1756 mAh g^{-1} , 1000圈	[59]
HCC-M-Si/CNF	蛋黄-蛋壳结构	2 A g^{-1} , 1000 mAh g^{-1} , 1000圈	[60]
Si@Void@C	蛋黄-蛋壳结构	2 A g^{-1} , 73.5%, 1000圈	[61]
Si@TiO ₂	蛋黄-蛋壳结构	2.1 A g^{-1} , 990 mAh g^{-1} , 1500圈	[62]
YS-Si/C	蛋黄-蛋壳结构	40 A g^{-1} , 220 mAh g^{-1} , 1200圈	[63]
SCMSC	蛋黄-蛋壳结构	0.166 A g^{-1} , 1330 mAh g^{-1} , 100圈	[64]
Multi-Si-Void@SiO ₂	蛋黄-蛋壳结构	1.2 A g^{-1} , 1440 mAh g^{-1} , 500圈	[65]
Si@Void@NGS	蛋黄-蛋壳结构	1 A g^{-1} , 1775 mAh g^{-1} , 750圈	[37]
DWSiNT	空心管结构	12 C , $\sim 600 \text{ mAh g}^{-1}$, 6000圈	[41]
Si/Ge nanotubes	空心管结构	200 mA g^{-1} , 590 mAh g^{-1} , 100圈	[66]
Si-Cu nanotubes	空心管结构	20 A g^{-1} , 780 mAh g^{-1} , 1000圈	[67]
SHC/NCF	空心管结构	0.5 A g^{-1} , 2000 mAh g^{-1} , 1200圈	[68]
Si@NiCNTs@NHCF	空心管结构	1 A g^{-1} , 1072 mAh g^{-1} , 1000圈	[69]
Si	石榴状结构	0.5 C , 1160 mAh g^{-1} , 1000圈	[70]
NL-Si@C	空心管网络	100 mA g^{-1} , $1422.5 \text{ mAh g}^{-1}$, 50圈	[71]
Si@IHCFS	分级核壳结构	0.2 A g^{-1} , 903 mAh g^{-1} , 100圈	[72]

用所要求的结构稳定性。Lu等人^[27]通过无模板法和镁热还原法制备了空心硅球，再以钛酸丁酯和葡萄糖包覆空心硅球，进而得到了具有高结构稳定性的Si@-TiO₂@C负极材料。这种新型的双层包覆-空心结构策略能有效改善单质硅的导电性并缓解其体积膨胀效应。

相较于单空心层球，双层空心球的壳层上具有更丰富的孔结构，该孔结构在协同缓冲硅体积膨胀的同时也可以诱导电解质向空心球的中空空腔扩散，改善电解质与单质硅的接触。双层中空结构可以缩短锂离子的固相扩散距离，优化硅基负极材料的储锂性能。硬模板法是一种常见的双层空心结构合成方法。首先，在硬模板上包覆/沉积一层目标材料，再依次将牺牲层与目标材料在核壳结构表面进行二次包覆，最终去除掉

硬模板和牺牲层，得到目标结构。西北大学王慧团队^[52]使用镁热还原和硬模板法制备了封装有硅纳米点的双层空心碳球(图2(b))。具有高介孔率的双层中空碳可以作为容器限制硅纳米点，缓解硅的体积膨胀，提高材料的结构稳定性。在 0.3 A g^{-1} 电流密度下，循环400圈后材料的容量仍高达 1350 mAh g^{-1} ；在 1 A g^{-1} 电流密度下，循环2000圈后材料的容量为 750 mAh g^{-1} 。类似地，郭少军团队^[53]等采用聚多巴胺衍生的氮掺杂碳复合中空Si/SiO₂纳米球，设计合成了Si/SiO_x@void@氮掺杂碳双层中空结构(Si/SiO_x-DSHSs)。

多层空心结构不仅可以为单质硅提供足够的自由空间缓冲体积变化，而且可以缩短锂离子的扩散路径，有利于提升材料的循环稳定性和倍率性能。武汉理工

大学周亮团队^[54]设计了一种独特的多层空心结构三组分复合负极材料($\text{Si}/\text{Cr}_2\text{O}_3/\text{C}$)(图3)。在该结构中, Si纳米颗粒被限域在碳包覆的 Cr_2O_3 多层空心球中。得益于 $\text{Cr}_2\text{O}_3/\text{C}$ 基体的体积变化缓冲能力与优异的结构稳定

性, 该 $\text{Si}/\text{Cr}_2\text{O}_3/\text{C}$ 复合负极材料展现出高的可逆容量(在 100 mA g^{-1} 的电流密度下, 比容量为 1351 mAh g^{-1})和稳定的循环性能(在 500 mA g^{-1} 的电流密度下, 循环300次后比容量保持在 716 mAh g^{-1})。

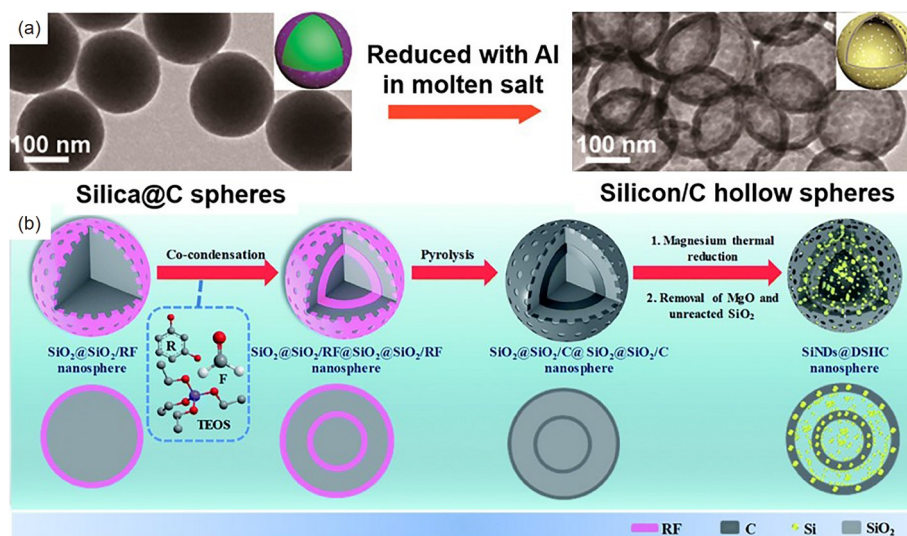


图2 (网络版彩色)典型单质硅空心球/笼负极示意图。(a) 熔融盐铝热还原制备多孔空心硅球示意图^[25], Copyright © 2018, American Chemical Society. (b) SiNDs@DSHC纳米球的合成示意图^[52], Copyright © 2020, The Royal Society of Chemistry

Figure 2 (Color online) Schematic illustration for typical silicon-based hollow sphere/cage anode materials. (a) Schematic illustration for the synthesis of hollow porous silicon spheres through molten salt reduction^[25], Copyright © 2018, American Chemical Society. (b) Schematic illustrations for the synthesis of SiNDs@DSHC nanospheres^[52], Copyright © 2020, The Royal Society of Chemistry

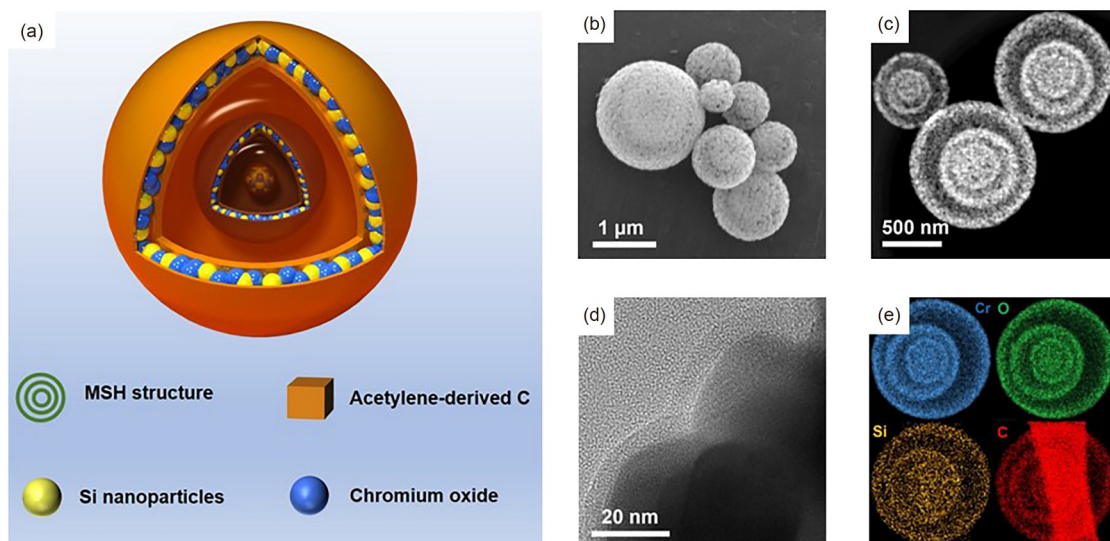


图3 (网络版彩色)典型单质硅基多层空心结构负极示意图^[54]。(a) $\text{Si}/\text{Cr}_2\text{O}_3/\text{C}$ 复合材料的结构示意图; $\text{Si}/\text{Cr}_2\text{O}_3/\text{C}$ MSHs的扫描电子显微镜照片(b)、透射电子显微镜照片(c, d)和元素分布图(e)

Figure 3 (Color online) Schematic illustration for typical silicon-based multi-shell hollow structured anode materials^[54]. (a) Schematic illustration of the $\text{Si}/\text{Cr}_2\text{O}_3/\text{C}$ composite; scanning electron microscope (SEM) (b), transmission electron microscope (TEM) (c, d), and elemental mappings (e) of $\text{Si}/\text{Cr}_2\text{O}_3/\text{C}$

纳米笼包覆Si纳米颗粒不仅可以避免Si纳米颗粒因体积膨胀而导致的粉化,而且可以促进载流子(锂离子和电子)的迁移。Yu等人^[56]以ZIF-90作为牺牲模板,以COF_{TB-BBTH}为氮掺杂碳纳米笼的前驱体,负载高容量的Si纳米颗粒。刻蚀后的ZIF-90为材料提供了自由空间,以适应Si纳米颗粒的体积变化。多孔N掺杂碳可以提高电子电导。负载Si纳米颗粒后的纳米微胶囊具有优异的电化学性能,在100 mA g⁻¹的电流密度下循环100次后,其放电比容量为1015 mAh g⁻¹。

2 蛋黄-蛋壳结构

蛋黄-蛋壳结构是硅基空心结构中最具有代表性的结构之一。蛋黄-蛋壳结构在嵌锂和脱锂过程中具有多重优势:首先,在循环过程中,由于壳与核之间具有一定的空间,可以减少硅体积膨胀对材料造成的影响;其次,由于碳壳将电解液隔绝在了材料表面,使得SEI膜能够在蛋黄-蛋壳结构表面均匀生长而不受硅体积膨胀的影响,有利于提高材料的库仑效率和循环寿命。

在大部分硅基蛋黄-蛋壳结构中,硅基材料分布在蛋黄部分,而碳或其他高导电性材料则分布在蛋壳层。

为进一步增强单质Si与外部导电壳层之间的接触,澳大利亚格里菲斯大学赵惠军团队^[38]提出一种独特的蛋黄-蛋壳结构硅基负极材料,他们通过在蛋黄-蛋壳结构内部原位生长碳纳米管,增强了Si纳米颗粒与导电蛋壳之间的接触,构筑了高速的导电桥梁,提高了材料整体的导电性。

崔屹课题组^[35]采用硬模板法设计了一种单质硅基蛋黄-蛋壳结构负极材料(Si@void@C, 图4)。以纳米硅颗粒为蛋黄、无定形碳为蛋壳,每个硅颗粒附着在碳壳的一侧,另一侧为80~100 nm的空腔。该空腔可以允许硅纳米颗粒在锂化时膨胀而不破坏碳外壳,并且确保SEI膜只在碳壳表面生长。这种Si@void@C蛋黄-蛋壳结构实现了高容量(在0.1 C倍率下的放电容量为2800 mAh g⁻¹)、长循环寿命(1000次循环,容量保持率为74%)和高库仑效率(99.84%)。

与具有完整碳壳的蛋黄-蛋壳结构相比,具有开放孔道的介孔碳壳层可以有效促进Li⁺的扩散,保证活性硅颗粒与电解液的充分接触,从而优化倍率性能。赵东元课题组^[57]设计了一种具有蛋黄-蛋壳结构的硅碳复合材料(图5(a, b))。通过非原位表征清晰地观察到沿着

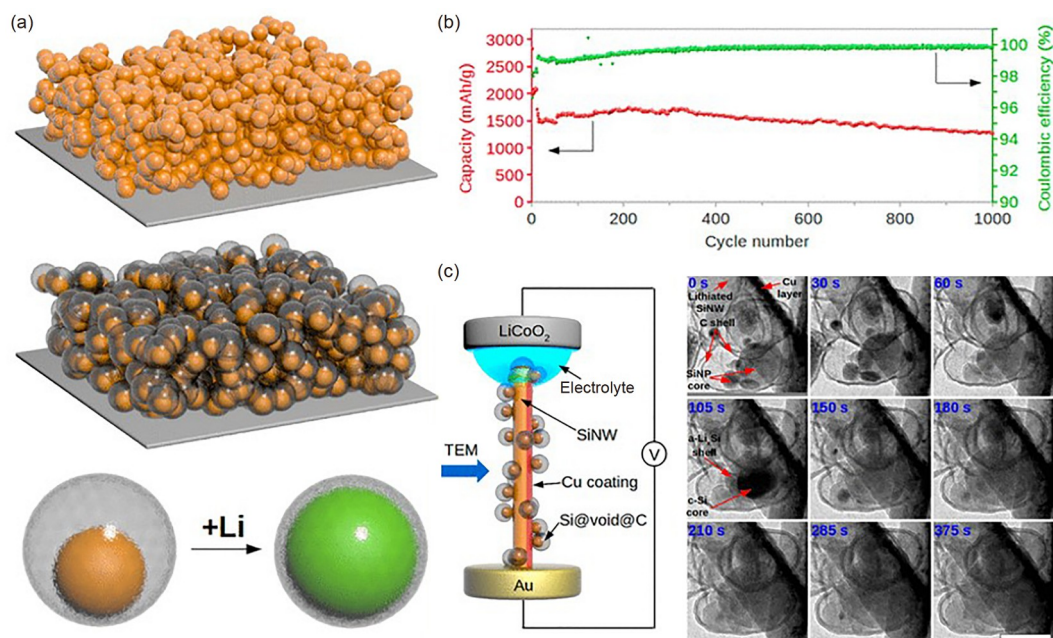


图4 (网络版彩色)典型硬模板法制备所得单质硅基蛋黄-蛋壳结构负极示意图^[35]。(a) 常规硅纳米颗粒电极、新型Si@void@C电极和单个Si@void@C颗粒示意图; (b) Si@void@C的循环性能; (c) 电化学锂化过程中Si@void@C膨胀的原位透射电子显微镜照片。Copyright © 2012, American Chemical Society

Figure 4 (Color online) Schematic illustration for typical silicon-based yolk-shell anode materials prepared by the hard templating method^[35]. (a) Schematic structure of conventional Si nanoparticle electrode, novel Si@void@C electrode, and Si@void@C particles; (b) cycling performance of Si@void@C; (c) *in-situ* TEM characterization of Si@void@C expansion during electrochemical lithiation. Copyright © 2012, American Chemical Society

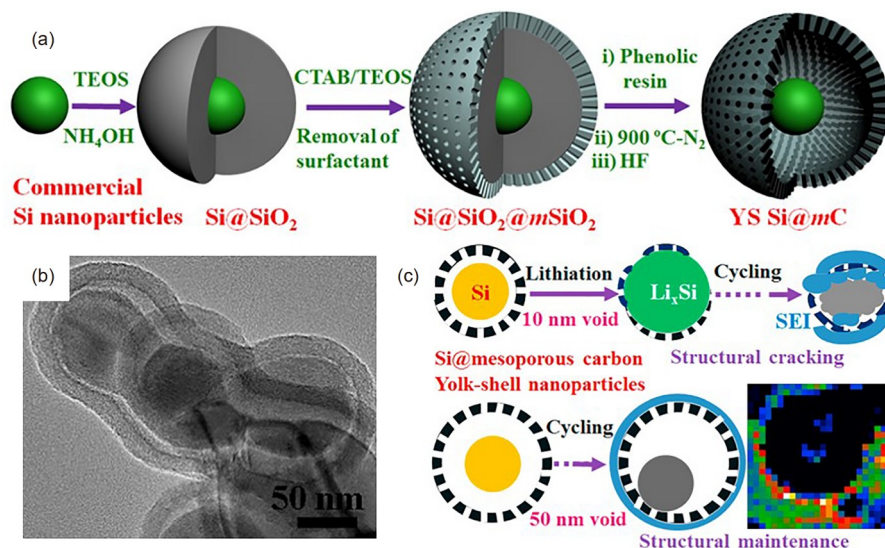


图5 (网络版彩色)典型软模板法制备所得单质硅基蛋黄-蛋壳结构负极示意图^[57]。(a) 介孔碳包覆商业硅蛋黄-蛋壳纳米颗粒合成示意图;(b) 介孔碳包覆商业硅YS Si@10 mC的透射电子显微镜照片;(c) YS Si@10mC和YS Si@50 mC的结构稳定性。Copyright © 2015, Elsevier B.V.

Figure 5 (Color online) Schematic illustration for typical silicon-based yolk-shell anode materials prepared by the soft templating method^[57]. (a) Schematic illustration of the synthesis of mesoporous carbon-encapsulated commercial silicon yolk-shell NPs; (b) TEM image of YS Si@10 mC; (c) schematic illustration of the structural stability of YS Si@10 mC and YS Si@50 mC during cycling. Copyright © 2015, Elsevier B.V.

介孔碳壳层形成的致密且均匀的SEI膜(图5(c))。这种具有介孔碳层的蛋黄-蛋壳复合材料具有优异的循环稳定性(循环400圈,容量保持率为78.6%)和优异的倍率性能(在 8.4 A g^{-1} 的高电流密度下,容量保持率为62.3%)。然而,硬模板法制备蛋黄-蛋壳结构通常需要用到氢氟酸等腐蚀性强、毒性大的试剂,更环保的蚀刻工艺亟待开发。

与硬模板法不同,软模板以表面活性剂在溶液中形成的胶束、囊泡、乳液作为模板,诱导中空结构的形成。去除软模板所需的条件较为温和,可以避免在去除模板时对结构造成破坏^[17]。郭居晨团队^[58]以烷基修饰的硅纳米颗粒为硅源($\text{C}_{12}\text{H}_{25}\text{-SiNPs}$)、十六烷基三甲基溴化铵为表面活性剂、间苯二酚与甲醛聚合产物为碳源,制备了SiNPs@C蛋黄-蛋壳复合材料。该材料在0.1 C倍率下具有 900 mAh g^{-1} 左右的比容量。自模板法不需要在合成过程中引入额外的模板,能更有效地避免模板脱除过程对产物造成的结构破坏。王丹课题组^[63]通过一种简单可控的湿化学方法将硅纳米颗粒封装在ZIF(zeolitic imidazolate frameworks)中,经过进一步的高温碳化合成了系列蛋黄-蛋壳Si/C负极材料。其中,碳壳内外两侧均生长有碳纳米管的蛋黄-蛋壳结构Si/C负极,在 0.1 A g^{-1} 的电流密度下具有高达 2200 mAh g^{-1} 的比容量和出色的循环稳定性。

3 纳米管结构

具有一维纳米管结构的单质硅具有高轴径比,可以缩短载流子的输运距离,减小充放电过程中的轴向体积膨胀,从而避免材料粉化。除此之外,对硅纳米管进行适当的包覆后可诱导单质硅在锂化时向内进行体积膨胀,并诱导SEI膜在包覆层外表面形成。崔屹团队^[41]设计了一种具有双层结构的单质硅基纳米硅负极(DWSiNT),其内壁为具有电化学活性的单质硅,外壁为可以限制硅体积膨胀的 SiO_x (图6(a))。在锂化过程中,锂离子可穿过外壁与内层活性硅发生反应,由于外壁的限制,内层硅只能向内部中空空间膨胀(图6(b))。此复合负极在1 C倍率下具有 1300 mAh g^{-1} 左右的比容量、优异的循环稳定性和出色的倍率性能(图6(c))。

楼雄文团队^[66]通过熔融盐电化学还原法合成了晶态Si/Ge合金纳米管。通过改变电化学还原过程中的过电位,可以实现从纳米管到空心颗粒的调控。南京大学的余林蔚和徐骏课题组^[67]通过 H_2 退火处理,将非晶态 $\alpha\text{-Si}$ 包覆的氧化铜纳米线转化为了中空Si-Cu合金纳米管。得益于Si-Cu合金纳米管独特的一维管状结构和高导电性,该材料在 0.84 A g^{-1} 的电流密度下具有高达 2160 mAh g^{-1} 的比容量、优异的循环稳定性和倍率性

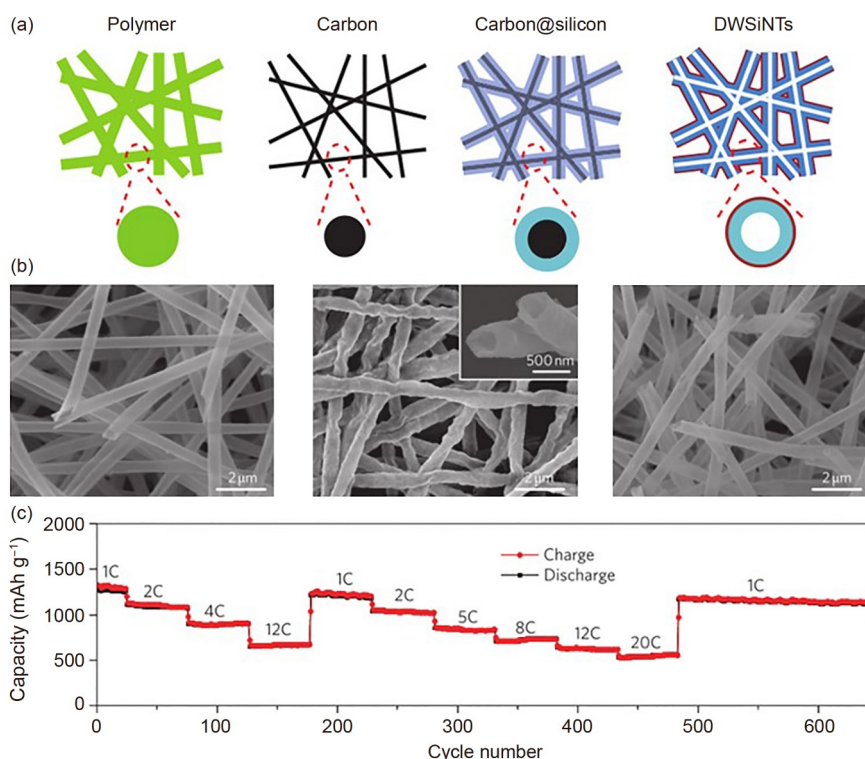


图6 (网络版彩色)典型单质硅基纳米管结构负极示意图^[41]。(a) DWSiNTs的合成流程示意图; (b) DWSiNTs、循环2000圈后含SEI膜和不含SEI膜DWSiNTs的扫描电子显微镜照片; (c) DWSiNTs的倍率性能。Copyright © 2012, Springer Nature Ltd.

Figure 6 (Color online) Schematic illustration for typical silicon-based nanotube anode materials^[41]. (a) Schematic illustration of the fabrication process for DWSiNTs; (b) SEM images of DWSiNTs, DWSiNTs after 2000 cycles with SEI, and DWSiNTs after 2000 cycles without SEI; (c) rate performance of DWSiNTs. Copyright © 2012, Springer Nature Ltd.

能。王慧团队^[68]通过静电纺丝将Si/C空心纳米球组装成项链状一维纳米纤维。该项链状复合负极材料在 200 mA g^{-1} 的电流密度下具有高达 2160 mAh g^{-1} 的可逆容量。刘全兵团队^[69]以Ni纳米颗粒为催化剂,在负载有硅纳米颗粒的氮掺杂空心碳纳米纤维中原位生长碳纳米管,制备了一种Si@Ni-CNTs@NHCF复合负极材料。该复合负极材料在 1 A g^{-1} 的电流密度下循环1000圈后仍具有 1072 mAh g^{-1} 的比容量。邱新平团队^[74]设计了一种同轴空心纳米电缆状硅碳复合材料。聚焦离子束扫描电子显微镜结果表明,硅在锂化/脱锂化过程中倾向于向内膨胀/向外收缩,证明中空结构化可以有效抑制硅负极表面SEI膜的过度生长。该硅基同轴空心纳米电缆在 0.6 A g^{-1} 的电流密度下循环500圈后仍具有 1150 mAh g^{-1} 的高比容量。需要指出的是,纳米管结构的堆积密度较低,会牺牲硅基负极的体积能量密度。因此,我们需要探索具有高堆积密度硅基纳米管的构筑策略。

4 其他特殊空心结构

从化学合成与结构调控的角度来看,如何将具有单一功能的硅基空心模块集成为具有分级有序结构、不同功能导向的特殊空心结构硅基负极十分关键。崔屹课题组^[70]设计了一种新型的石榴状结构硅碳负极微球(图7(a))。该微球以蛋黄-蛋壳结构Si@C纳米球为基本构筑单元。蛋黄-蛋壳结构Si@C纳米球内部的空腔可以容纳单质硅的体积膨胀;外部碳层可以作为电解质阻挡层,将SEI膜的生长限制在材料的外表面;由纳米球组装而成的微米球有利于电极涂覆过程。该石榴状结构硅碳负极材料具有较好的循环性能(1000次循环后容量保持率为97%),在 0.4 A g^{-1} 的电流密度下具有 1780 mAh g^{-1} 的稳定比容量。

潘安强课题组^[71]设计了一种项链状氮掺杂介孔碳包覆硅(图7(c, d))。在单个结构单元中,硅纳米颗粒被封装在氮掺杂介孔碳壳中,形成蛋黄-蛋壳结构;蛋黄-蛋

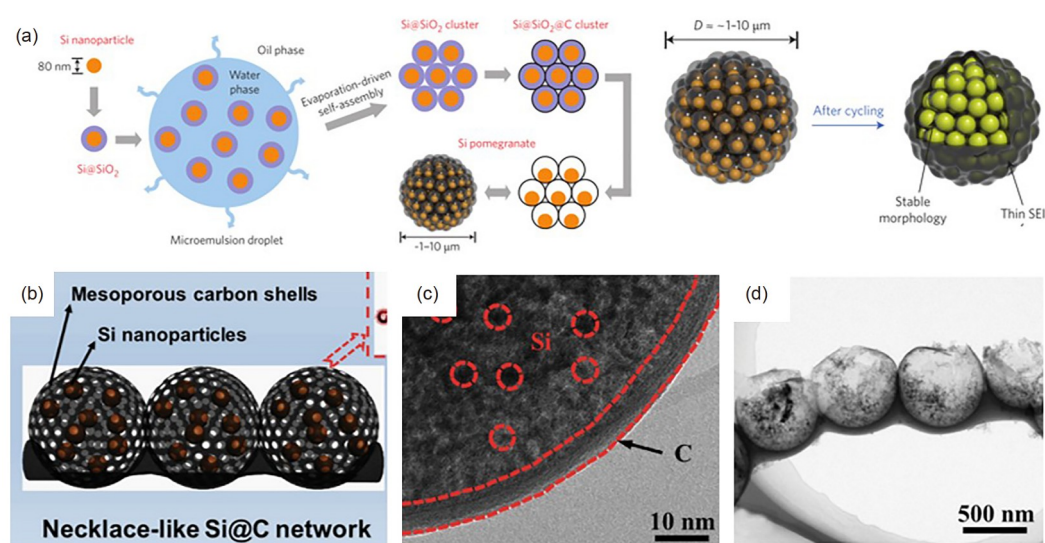


图7 (网络版彩色)典型单质硅基特殊空心结构负极示意图。(a)石榴状硅碳负极材料的合成示意图与循环过程中SEI膜的形成示意图^[70], Copyright © 2014, Springer Nature Ltd. (b)项链状Si@C网络的结构示意图^[71]; (c)项链状Si@C网络的透射电子显微镜照片^[71]; (d)项链状C网络的透射电子显微镜照片^[71]

Figure 7 (Color online) Schematic illustration for typical other hollow structured silicon-based anode materials. (a) Schematic illustration of the synthesis process and formation of SEI during cycling for pomegranate-like silicon anodes^[70], Copyright © 2014, Springer Nature Ltd. (b) Schematic illustration of the necklace-like Si@C network^[71]; (c) high magnification TEM image of the necklace-like Si@C network^[71]; (d) low magnification TEM image of the necklace-like carbon shell after removing the Si nanoparticles^[71]

壳结构纳米球相互连接形成项链状纳米纤维。该结构具有诸多优势: 首先, 蛋黄-蛋壳结构内部的空腔为单质硅嵌锂过程的体积膨胀预留了空间。其次, 碳壳层避免了单质硅与电解液的直接接触, 有利于形成稳定的SEI膜。再次, 项链状纳米纤维网络结构为载流子的快速传输提供了连续的通道, 同时也可有效避免Si@C蛋黄-蛋壳纳米球的团聚。该项链状复合负极在 100 mA g^{-1} 的电流密度下具有 $1422.5 \text{ mAh g}^{-1}$ 的高容量, 循环50圈的容量保持率为72.5%。

受蜂巢与蛛网结构的启发, 李宝华团队^[72]基于同轴静电纺丝技术, 将硅纳米颗粒封装在相互连接的中空碳纤维中, 制备了具有分级核壳结构的硅/碳复合材料。在该分级结构中, 硅纳米颗粒被封装在蜂窝状碳骨架中, 进一步被互相连接的蛛网状碳网络包裹。一方面, 中空纤维可以容纳Si纳米颗粒的体积膨胀并为锂离子提供快速的扩散通道; 另一方面, 相互连接的蛛网状碳网络有效提高了材料的导电性, 并在一定程度上阻隔了电解液与Si纳米颗粒的直接接触。这一分级结构硅碳负极材料在 0.2 A g^{-1} 电流密度下循环100圈后, 容量为 903 mAh g^{-1} , 容量保持率为89%。

5 总结与展望

硅基负极材料具有比容量高和嵌锂电位合适的优点, 是下一代锂离子电池负极材料的首选。本文对具有空心结构单质硅基负极材料的构筑及其储锂性能进行了系统的综述, 对锂离子电池用硅基空心结构负极材料研究领域当前存在的问题进行了讨论, 并对这类材料将来的发展方向进行了展望。

(1) 目前, 硅基中空结构的制备大多需要经过繁琐的合成步骤, 有的还涉及有毒试剂的使用以及特殊的实验装置, 这显著增加了其生产成本, 阻碍了其大规模应用。因此, 开发新型、简单、易规模化的硅基中空结构合成策略非常必要。

(2) 空心结构虽然能有效缓解硅基负极材料的体积效应, 改善其循环性能, 但同时也会牺牲硅基负极材料的体积容量和振实密度, 成为制约其大规模商业应用的瓶颈。因此, 优化硅基中空结构的空腔大小, 充分利用其空腔是实现其实际应用的关键。

(3) 考虑到硅基负极材料导电性低的问题, 将硅基空心结构与高导电碳复合是进一步提升硅基负极材料储锂性能的有效策略。但引入过量的碳又会降低硅基负极的比容量, 从而使其失去了作为高容量负极材料

的竞争性。因此,在合成中空硅碳复合材料时也需要找到含碳量和改性效果之间的平衡点,即如何利用更低的碳含量来实现更有效的性能提升。

(4) 硅基负极材料的首次库仑效率通常较低,在硅基负极材料中引入空心结构会增加材料的比表面积,导致其首次库仑效率进一步降低,因此,为硅基空心结构负极材料量身打造专属的预锂化策略至关重要。

最近, Group14公司通过化学气相沉积在多孔碳中沉积含量可控的单质硅,并为单质硅预留体积膨胀的空间,获得了兼具高容量、长循环、低体积膨胀的硅碳复合负极材料。我们有理由相信,随着简单有效的新合成方法的不断开发与科研工作者的不懈努力,硅基空心结构负极材料有望在下一代高能量密度锂离子电池中得到实际应用。

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Summary for “硅基负极材料空心结构构筑与储锂性能”

The construction and lithium storage performance of silicon-based hollow structured anode materials

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With the rapid developments of consumer electronics, electric vehicles, and stationary energy storage, there is an urgent need to develop new-generation lithium-ion batteries (LIBs) with higher energy density, longer cycle life, and better safety. Elemental silicon (Si) has been considered as one of the most promising anode materials for the next-generation LIBs, due to its high theoretical capacity (4200 mAh g^{-1}), rich abundance, easy synthesis, and environmental friendliness. However, the Si-based anode materials suffer from low intrinsic electrical conductivity and large volume variation (300%–400%) during lithiation/de-lithiation processes. The large volume fluctuation would lead to pulverization of Si particles, detachment of the Si particles from the current collector (electrode disintegration), and repeated formation and rupture of solid electrolyte interphase (SEI) films, eventually resulting in severe capacity fading. With unique merits such as high specific surface area, abundant active sites, full electrode/electrolyte contact, short charge (especially lithium ion) transfer paths, and volume buffering effect, hollow nanostructures are promising anode materials for LIBs. When compared to the solid counterpart, the hollow structures are able to provide adequate empty space for the volume expansion of Si, leading to significantly enhanced cycling stability.

In this review, we summarize the recent advances of Si-based hollow structured anode materials for lithium storage. The Si-based hollow structured anode materials can be generally categorized into four families: (i) Si-based hollow spheres/cages, especially double-shelled and multi-shelled hollow spheres; (ii) Si-based yolk-shell structures, especially that with a nanostructured Si yolk and a highly conductive carbon shell; (iii) one-dimensional Si-based nanotubes; and (iv) other Si-based intricate hollow structures, including pomegranate-like structure, necklace-like structure, honeycomb structure. The synthesis methods, electrochemical performances, as well as their structural merits and demerits have been discussed in detail.

Finally, the future perspectives on silicon-based hollow structured anode materials for LIBs have been discussed. (i) Both conventional and newly emerging methodologies for synthesizing Si-based hollow structures suffer from cumbersome synthesis processes. In this regard, more simple and scalable methods should be developed for constructing Si-based hollow micro/nanostructures. (ii) Optimizing the cavity size is of key importance for the practical application of Si-based hollow structures. Introducing too much cavity in the material would sacrifice the tap density and volumetric capacity, which is detrimental to the energy density of LIBs. (iii) Considering the low conductivity of Si-based materials, it is essential to composite the Si with highly conductive materials such as carbon. However, introducing too much carbon in the composite may compromise the capacity of the silicon-based anode materials due to the low lithium storage capacity of carbon. (iv) The initial Coulombic efficiency of Si-based materials is relatively low, and the introduction of hollow cavity would increase the surface area and thus further lower the initial Coulombic efficiency. Thus, it is essential to develop unique pre-lithiation technologies for the Si-based hollow structures. With the development of new synthetic methods and unceasing endeavor from the scientists, we strongly believe that the Si-based hollow structures would finally find real applications in next-generation LIBs.

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