

碳材料改性 SiOC 负极在锂离子电池中的研究进展

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摘 要: SiOC 具有理论比容量高、机械柔性好、结构稳定和价格低等一系列优良性能, 被认为是极具潜力的锂离子电池负极材料之一。然而, SiOC 电导率低导致倍率性能和循环能力较差, 从而制约了其在锂离子电池领域的发展与应用。纳米碳材料具有高比表面积、高机械稳定性以及优异的导电性等特点, 与 SiOC 复合后作为负极材料可显著改善锂离子电池的电化学性能。本文综述了石墨、碳纳米管、石墨烯以及碳纳米纤维等与 SiOC 负极材料的复合工艺路线, 探讨了基于不同碳材料的改性设计思路, 以及电极微观结构与电化学性能之间的构效关系。最后, 指出了 SiOC/C 复合负极材料存在的主要问题和研究方向, 并展望了 SiOC 基负极材料的应用前景。

关键词: 硅氧碳; 碳材料; 负极; 电导率; 锂离子电池

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锂离子电池作为一种新型储能器件, 具有工作电压高、能量密度大、安全性高、环境友好等优点, 被认为是最有发展前景的化学电源。近年来, 电子产品、电动汽车和大型储能系统等的飞速发展, 对能量密度高、循环寿命长、安全性能优异的锂离子电池提出了更高要求^[1-2]。作为锂离子电池重要组成部分的负极材料, 需要具有优异的本征特性: 尽可能低的氧化还原电位并在锂可逆插入/脱嵌时保持稳定、电压范围内良好的电化学稳定性、较好的电导率、允许大量锂可逆插入/脱嵌、锂离子在主体结构中有较大的扩散系数等, 同时也要考虑负极材料较好的表面结构, 以利于吸附锂离子和形成良好的固态电极电解质界面(SEI)^[3-4]。

目前, 研究较多的锂离子电池负极材料主要分为石墨、钛酸锂和硅基 3 大类。石墨具有导电性能好、嵌锂电位低、脱嵌锂时体积变化小、首次 Coulomb 效率高、寿命长以及成本低等诸多优点, 作为锂离子电池的传统负极材料最先得到商业化应用, 但其较低的理论容量(372 mA·h/g)是制约高能量密度锂离子电池发展的主要因素^[5-6]。“零应变”的钛

酸锂(Li₄Ti₅O₁₂)负极材料由于其平稳的高电压放电平台(1.55 V)、充放电过程中结构稳定以及安全性高而被看作极具发展潜力的负极材料, 但低的理论容量(175 mA·h/g)和高的成本限制了它的实际应用^[7-9]。硅是目前已知理论容量最高的负极材料(4 200 mA·h/g), 但其在脱嵌锂过程中会产生大的体积膨胀(>300%), 使活性材料粉末化和集流体电接触失效, 并有新固相电解质层 SEI 重复生成。另外, 导电性差造成电极界面电阻大和电子传导速率低等问题, 从而影响循环性能与倍率性能^[10-12]。Si 颗粒与碳材料的复合被认为是稳定电极的有效策略。Si/C 复合材料通常通过包覆和表面修饰等方法制备获得, 碳不仅可为 Si 活性材料提供导电网络, 还可以作为应力缓冲基质来缓解 Si 颗粒脱嵌锂过程中产生的膨胀, 进而提高复合材料的电化学性能^[13-14]。Si/C 复合材料中的碳最早使用的是石墨和无定形碳, 后来随着技术的发展, 碳纳米管和石墨烯等因具有良好的导电性和机械柔韧性也被引入到 Si/C 材料中。与碳类材料相比, SiO_x 具有较高的比容量(1 965~4 200 mA·h/g)^[15], 与 Si 相比拥有良好的循环稳定性且在循环过程中

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体积变化较小(150%~200%)^[16],但其本征电导率低;此外,在首次嵌锂时, SiO_x 会和电解液中的 Li^+ 发生不可逆反应生成惰性相(Li_2O 、 Li_4SiO_4),加剧了不可逆容量,最终导致 SiO_x 负极材料首次Coulomb效率低,从而严重制约其高比能锂离子电池中的应用^[17–18]。因此,人们一直致力于开发具有高容量、优异循环稳定性和倍率性能的可替代负极材料。

自20世纪90年代初加拿大Dahn教授等^[19–23]提出将SiOC作为锂离子电池负极材料以来,由于其较高的理论容量(1350 mA·h/g)、较小的体积膨胀(7%)^[24]、优异的结构稳定性与热稳定性、制备工艺简单和成本低而受到越来越多的关注。良好的机械柔性是其他负极材料无法比拟的优势,通过静电纺丝法能制备出自支撑的SiOC负极材料,从而避免了粘结剂(电化学惰性的)、导电添加剂和集流体的使用,简化了锂离子电池的结构。然而,SiOC本身固有的低导电性造成倍率性能较差,并且在大电流密度下(>1 A/g)表现出快速的容量衰减,极大地限制了SiOC负极的性能^[25–26]。针对SiOC导电性低的问题,最简单、直接的方法就是通过使用富含苯基的聚合物前驱体使热解产物具有较高含量的自由碳相^[27],从而电导率得到提高。另外,通过引入二乙烯基苯(DVB)和聚乙烯醇(PVA)等乙烯基有机物,利用C=C双键与Si—H键发生硅氢化反应对聚硅氧烷进行改性,也可增加自由碳相的含量^[28–29]。但是,这些方法形成的自由碳相含量较少,对电导率的改善非常有限。

碳材料具有机械稳定性好、体积变化小和导电性优异等优点,常被用于改善各类材料的导电性^[30–31]。在与SiOC负极材料复合时,首先可以提升SiOC的导电性,加速 Li^+ 在脱嵌过程中的传输速率;其次可充当惰性缓冲层减小SiOC的体积效应^[32–34]。根据碳材料的不同,可以将其分为2大类:传统碳材料与纳米碳材料。传统碳材料包括石墨、活性炭和炭黑等;而纳米碳材料则指具有特殊结构或功能的新材料,如石墨烯、碳纳米管(CNTs)、碳纳米纤维(CNFs)等。其中,纳米碳材料由于具备超大的比表面积和多维导电网络,对提升SiOC负极的电化学性能具有更为显著的作用^[35]。

本文从SiOC的结构与电化学储锂机制出发,综述了SiOC与不同种类碳材料的复合工艺、结构设计,以及与电化学性能的关系,指出了SiOC负极材料今后研究的重点,并展望了其未来的发展方向。

1 SiOC的结构和储锂机理

SiOC是以含硅聚合物(聚硅氧烷、聚倍半硅氧烷)为原料,通过前驱体转化法高温热解(800~1200 °C)而成的无定形材料^[36],热解产物可表示为 $\text{SiO}_x\text{C}_{1-x/2}+m\text{C}_{\text{free}}$,式中 x 为O/Si摩尔比, m 为产物中C/Si摩尔比与 $(1-x/2)$ 之差^[37]。目前普遍认为SiOC的结构有2种模型,纳米结构模型^[38]和原子结构模型^[39],其中原子结构模型在表达其组成上更有优势。如图1所示,SiOC主要由SiOC四面体单元(硅原子同时与氧、碳原子结合,包括 SiOC_3 、 SiO_2C_2 、 SiO_3C 和 SiO_4)、自由碳相(类石墨烯碳)及纳米孔三部分组成,SiOC四面体分布在自由碳组成的网络结构中。通过优化含硅聚合物前驱体的组成、结构和热解条件,能够实现对SiOC材料的微观结构和组成的调控。

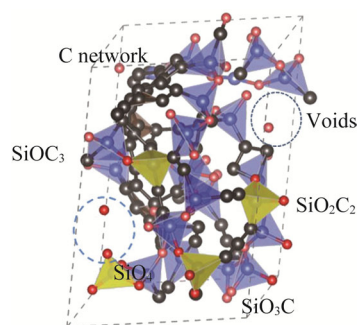


图1 SiOC的原子结构模型^[39]

Fig. 1 Atomic model of silicon oxycarbide (SiOC)^[39]

目前,研究者提出了许多关于SiOC负极材料的储 Li^+ 机理^[40–41]。Fukui等^[42–43]以苯基取代的聚硅氧烷 $(\text{Ph}_2\text{Si})_{0.85}(\text{PhSi})_{0.15}$ 和聚苯乙烯的混合物热解得到SiOC,通过 Li^7 核磁共振(NMR)分析,在SiOC中观测到了三处电化学嵌锂活性位点,即石墨烯的层间或边缘、无定形SiOC玻璃相及纳米孔,其中石墨烯层间或边缘被认为是主要的嵌锂单元。Wilson等^[19]通过分别热解二甲基聚硅氧烷和聚二甲基硅氧烷-聚甲基苯基硅氧烷前驱体得到SiOC,发现元素组成影响SiOC负极的储锂性能,其中游离碳的含量起决定性作用^[44]。而Liu等^[45]采用多官能团取代的聚硅氧烷和二乙烯基苯为前驱体热解得到SiOC,通过 Si^{29} NMR和X射线光电子能谱等研究发现,Li与SiOC玻璃相的合金化反应是可逆比容量的主要来源,且四面体单元中的 SiO_2C_2 、 SiO_3C 和 SiO_4 3种结构单元都可作为储锂位点,但 SiOC_3 结构单元仅对不可逆比容量有贡献并能转化为无电化学反应。

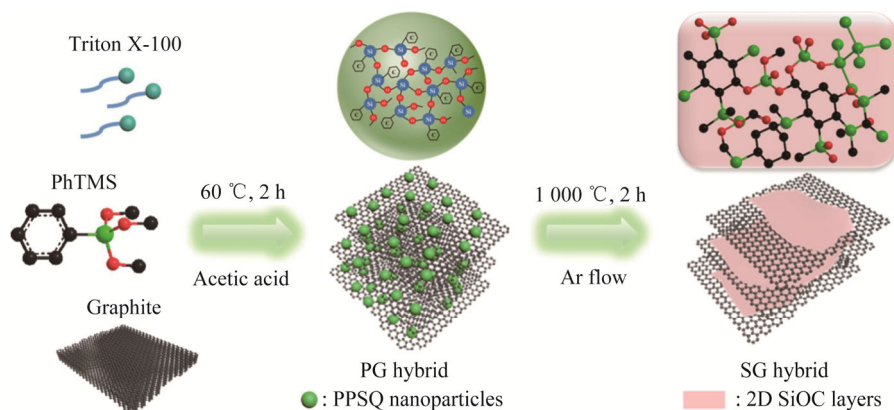
应活性的 SiC_4 结构单元。此外, 有研究认为^[46-47], SiOC 的网络结构和纳米孔结构可以有效缓冲 Li^+ 反复嵌入/脱出过程中的体积变化, 故具有更加优良的循环稳定性。但是, 由于 SiOC 的储锂机制较为复杂、活性位点较多, 且 SiOC 的结构组分对锂离子的存储行为具有影响, 至今对其储锂机理仍未达到共识。

2 SiOC/传统碳复合材料

2.1 SiOC/石墨复合材料

Wu 等^[48]以商业化的石墨和苯基三甲氧基硅烷 (PhTMS) 为原料, 通过热解法制备了 SiOC /石墨复合材料(图 2)。热解后, SiOC 纳米层嵌入到石墨层

间。石墨层增强了电子传导, 确保了结构的完整性; SiOC 层作为主要的储锂单元, 缩短了脱嵌锂距离, 故具有优异的倍率性能(在 2 A/g 下约为 $230 \text{ mA}\cdot\text{h/g}$)和循环性能(在 1000 次循环后放电容量为 $184 \text{ mA}\cdot\text{h/g}$, 容量保持率约为 80%)。而 Knozowski 等^[49]以乙烯基三乙氧基硅烷和石墨为原料, 利用了超声波辅助溶胶-凝胶法经热解制备了 SiOC /石墨复合材料。应用超声处理的新方法能防止石墨发生团聚, 使复合材料形成分布均匀且相互连接的导电网络。电化学测试结果表明复合材料具有稳定的容量(电流密度为 186 mA/g 时, 经 270 次循环后高达 $520 \text{ mA}\cdot\text{h/g}$)。



PhTMS is phenyltrimethoxysilane; PPSQ is polyphenylsilsesquioxane; PG is PPSQ-microspheres-loaded graphite; SG is SiOC-nanolayer-embedded graphite.

图 2 SiOC/石墨复合材料的制备流程^[48]

Fig. 2 Schematic illustration of the synthesis of SiOC/graphite composites^[48]

Konno 等^[50]将含乙烯基的环状有机硅化合物 $\{\text{CH}_3(\text{CH}=\text{CH}_2)\text{SiO}\}_n$ ($n=3\sim7$) 和含 $\text{Si}-\text{H}$ 键的链状有机硅化合物 $(\text{CH}_3)_3\text{SiO}\{\text{CH}_3(\text{H})\text{SiO}\}_m\text{Si}(\text{CH}_3)_3$ ($m\approx 20$) 混合, 通过浸渍将混合物吸附在石墨表面, 后经固化、热解制备 SiOC /石墨复合材料。当电流密度为 50 mA/g 时, 可获得 $650 \text{ mA}\cdot\text{h/g}$ 的容量; 由于第 1 次循环的插入容量较大, 初期效率较低 (60%~70%)。通过将工作电极与锂箔对电极短路一段时间, 几乎消除了第 1 次循环的不可逆容量。结果表明, 在复合材料中直接掺杂 Li^+ 是提高第 1 次循环效率的有效途径。

2.2 SiOC/其他传统碳复合材料

Kusrini 等^[51]将活性炭和硅油合成了 SiOC /活性炭复合材料, 研究发现活性炭内部微孔也可作为 Li^+ 的脱嵌提供活性位点, 有助于缩短锂离子的传输距离, 从而缩短充电时间。但是, 最高放电容量仅为 $223.3 \text{ mA}\cdot\text{h/g}$, 且 Li^+ 在脱嵌锂过程中会破坏无定形碳内部的缺陷, 从而使得首次 Coulomb 效率较低。Chen 等^[52]将苯基三乙氧基硅烷与沥青共混, 通过热

解获得了 SiOC/C 复合材料, 此电极具有低成本、高可扩展性、优异的结构稳定性等优点, 能有效避免在充放电过程中负极粉碎。电化学测试结果表明, 此复合材料具有优异的可逆容量(在 0.2 A/g 时, 为 $926.8 \text{ mA}\cdot\text{h/g}$), 长可循环性(在 1.0 A/g 下循环 600 次后容量保持率为 96.8%)和非凡的倍率性能(在 5 A/g 时为 $479.2 \text{ mA}\cdot\text{h/g}$)。

3 SiOC/纳米碳复合材料

3.1 SiOC/碳纳米管复合材料

碳纳米管是由层状结构石墨片卷成的无缝空心管, 相比于石墨颗粒, 碳纳米管/纳米纤维 (CNT/CNF) 得益于其高长径比的优势, 利用其导电性及网络结构可以构建连续的电子传递网络, 抑制颗粒团聚, 从而提高负极材料的电化学性能。Bhandavat 等^[53]将商业化的聚合物前驱体 1,3,5,7-四甲基-1,3,5,7-四乙烯基环四硅氧烷 (TTCS) 添加到具有 CNTs 的分散体中, 热解后产生壳/核结构的 SiOC/CNTs 复合材料。结果表明, 在 50、100、200、

400、800 mA/g 和 1 600 mA/g 的电流密度下各循环 5 次, 然后再返回 50 mA/g 时, SiOC/CNTs 复合材料的可逆容量为 750 mA·h/g, 几乎和初始循环的可逆容量持平。此后, Bhandavat 等^[32]通过真空抽滤 CNTs 得到碳纳米管纸(CNTs paper), 然后在其上滴涂 TTCS 直至浸透, 最后热解得到 SiOC/CNTs 复合纸电极。电化学测试显示 SiOC/CNTs 复合纸电极的可逆容量为 1 168 mA·h/g, 高放电容量可归因于碳纳米管上 SiOC 具有的丰富的介孔, 有利于锂离子富集在电极表面, 且碳纳米管纸的多孔网状结构孔隙开放相互连通有助于分子相互作用与功能化。该复合纸电极可用作锂离子电池的自支撑负极材料, 从而避免了粘结剂、导电添加剂和集流体的使用, 简化了锂离子电池的负极结构, 重量比传统负极减

轻了约 37%。

不同的是, Nara 等^[54]通过电沉积法将 SiOC 沉积在铜基底上, 也未使用粘结剂和导电添加剂。结果发现, 在 1 C 循环 2 000 次后获得了 1 045 mA·h/g 的放电容量。尽管放电容量较高, 但由于 SiOC 与 Cu 基底之间的结合强度较弱, 易导致在电沉积过程中 SiOC 从基底上脱落, 且不能获得较厚的 SiOC 复合膜。为了改善上述问题, Ahn 等^[55]在 SiOC 与 Cu 基底之间电泳沉积 CNTs 锚固层, 制备出 SiOC/CNTs 复合材料, 有效增加了 SiOC 与 Cu 基底之间的结合强度(如图 3 所示)。在 0.1 C 下循环 100 次后的可逆容量保持在 1 078 mA·h/g; 在 1 C 下, 容量保持率为 69.81%。此复合材料具有更好的电化学性能, 包括放电容量和倍率性能。

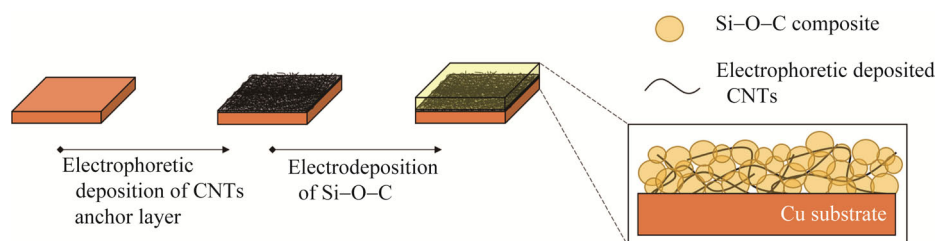


图 3 在 CNTs/Cu 衬底上沉积 SiOC 复合材料的示意图^[55]

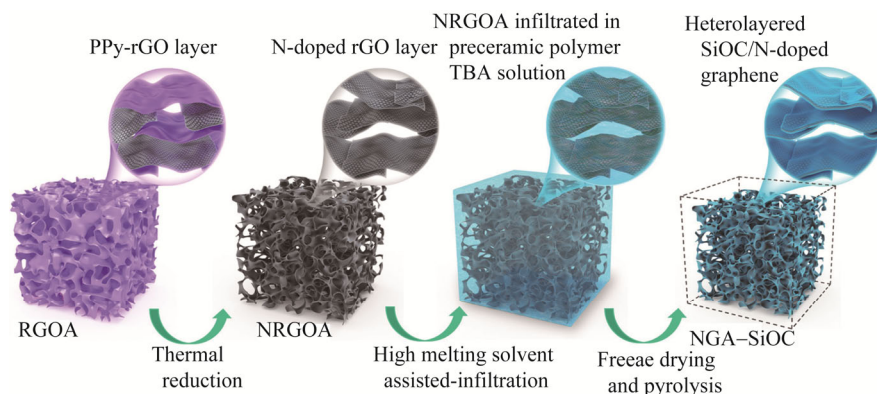
Fig. 3 Schematic illustration explaining SiOC composites deposition process on CNTs/Cu substrate^[55]

3.2 SiOC/石墨烯复合材料

石墨烯作为一种由碳原子排列成蜂窝结构的二维纳米材料因其优异的导电性、高比表面积和良好的柔韧性等特点, 广泛应用于储能领域^[30, 56]。Ji 等^[57]将氧化石墨烯(GO)分散到聚硅氧烷(PHMS 和 D₄Vi)前驱体中, 交联热解后得到 SiOC/GO 复合材料。当电流密度为 40 mA/g 时, SiOC/石墨烯复合材料的初始放电容量为 1 141 mA·h/g, 在 20 次循环后衰减为 357 mA·h/g。Ren 等^[58]通过将 TTCS 和 GO 物理混合制备了 SiOC/GO 复合材料, 在 50 mA/g 的电流密度下 90 次循环后仍可表现出 582 mA·h/g 的可逆容量。Kolathodi 等^[59]和 David 等^[60]分别将 TTCS 分散在氧化石墨烯悬浮液中, 后进行真空抽滤与热处理, 最后热解形成自支撑 SiOC/还原氧化石墨烯(rGO)复合材料。该复合材料结构由氧化石墨烯层组成, 层间有 SiOC。这种结构不仅保证了 SiOC 和 rGO 层之间的接触, 提供了体积变化所需的弹性空间, 促进了电极的高导电性, 从而提升了复合材料的电化学性能。后者制备的复合材料在电流密度为 100 mA/g 时, 放电容量为 702 mA·h/g; 当电流密度增加为 2.4 A/g 时, 容量仍保持在 543 mA·h/g, 具有良好的倍率性能和优异的长循环

稳定性, 在经过 1 020 次循环后其容量保持率为 94%。

为了解决石墨烯的团聚问题, Sang 等^[61]利用水热和冷冻干燥法先将 GO 制备三维石墨烯纳米片(3D-GNS), 然后将 3D-GNS 浸渍到聚硅氧烷前驱体(PSO)中制备出 SiOC/3D-GNS 复合材料。电化学测试显示, 在 100 mA/g 循环 100 次后, 可逆容量和容量保持率分别为 701 mA·h/g 和 84.8%; 而在 0.5 A/g 循环 200 次后, 可逆容量仍然保持在 586 mA·h/g。三维互连导电网络改善了复合材料的电导率, 缩短了 Li⁺的扩散路径, 使得 SiOC/3D-GNS 复合材料中的活性位点得到充分利用。Shao 等^[34]用聚吡咯(PPy)和 rGO 通过聚合还原工艺制备了还原氧化石墨烯气凝胶(RGOA), 接着在氮气下合成氮掺杂还原氧化石墨烯气凝胶(NRGOA)骨架, 最后将 NRGOA 骨架浸渍到硅氧烷前驱体(SILRES H62C)中得到 3D 氮掺杂石墨烯 SiOC 复合材料(SiOC/NGA), 如图 4 所示。结果发现, 在 1 480 mA/g 循环 1 000 次后, SiOC/NGA 复合材料的可逆容量保持在 352 mA·h/g, 容量保持率为 95%。三维石墨烯导电网络实现了离子和电子快速传输, 此外氮掺杂降低了氧含量, 进一步提高了材料的电子导电性。



RGOA is reduced graphene oxide aerogel; NRGOA is N-doped reduced graphene oxide aerogel; TBA is tert-butanol; NGA is N-doped graphene aerogel.

图 4 SiOC/NGA 复合材料的制备示意图^[34]

Fig. 4 Schematic illustration of the fabrication of SiOC/NGA composites^[34]

Sang 等^[62]首先静电纺丝得到 SiOC 纤维布, 交联热解后真空浸渍包覆氧化石墨烯, 最后热还原获得 SiOC/rGO 复合材料, 他们称之为 3D-GNS/SiOC_f(图 5)。SiOC 纤维布具有分级的多孔结构和粗糙的表面形貌, 有利于 Li⁺的嵌入和脱出, 而 rGO 包覆并连接 SiOC 纤维形成导电网络, 赋予复合材料高倍率和长循环的性能。此外, 石墨烯还可以进一步提高材料的机械性能, 因为它可以紧密地包裹在单根纤维上, 以保护它们免受灾难性的破坏。3D-GNS/SiOC_f的初始放电容量和 Coulomb 效率分别为 1 176 mA·h/g 和 78.5%, 且具有优异的循环稳定性, 在 0.5 A/g 循环 500 次后, 可逆容量为 686 mA·h/g, 同时也具有出色的倍率性能, 在 2.0 A/g 时, 放电容量为 330 mA·h/g。

Islam 等^[63]用两步法(第 1 步采用硅纳米颗粒作为模板, 在水热处理过程中, 部分硅颗粒与 rGO 形成 SiOC; 第 2 步采用高浓度的 HF 蚀刻形成多孔结构)在 rGO 上原位生长 SiOC 合成了 SiOC/rGO 复合材料。因此, 得到的 SiOC/rGO 复合材料具有很高的稳定性。该复合材料将 SiOC 的高 Li⁺亲和力与 rGO 的导电性和稳定性相结合。100 mA/g 循环 50 次后可逆容量保持在 507 mA·h/g, Coulomb 效率为 90.4%。

3.3 SiOC/碳纳米纤维复合材料

一维的碳纳米纤维具有碳材料的高导电性、稳定性和纳米纤维材料固有的特性^[64-65]。通常可利用静电纺丝法得到, 从而制备出二维柔性电极。Li 等^[66]通过交联、静电纺丝和热解法, 以 TTCS 和聚丙烯腈(PAN)为前驱体制备出 SiOC/CNFs 复合材料(图 10)。电化学测试表明, 当电流密度为 50 mA/g 时, SiOC/CNFs 的初始充放电容量分别为 1 150 和

839 mA·h/g, 在循环了 80 次后可逆容量仍保持在 669 mA·h/g。由于连续的 CNFs 网络, Li⁺可以容易地迁移并到达 SiOC/CNFs 的表面, 从而使得 SiOC/CNFs 复合材料具有高可逆容量和良好循环性能。与其不同的是, Li 等^[67]先用静电纺丝法制备聚丙烯腈纳米纤维(PNFs), 然后将 PNFs 置于 KH560 溶液中, 最后热解得到 SiOC/CNFs 复合材料。在 1 C 下, 可逆比容量为 715.8 mA·h/g; 当电流密度增加为 10 C 时, 循环 2000 次后仍具有 95.4%的容量保持率。此外, 即使在 20 C 下循环后, 当电流密度再降低到 1 C 时, 也可以立即恢复 702 mA·h/g 的容量, 说明该复合材料具有优异的倍率性能。

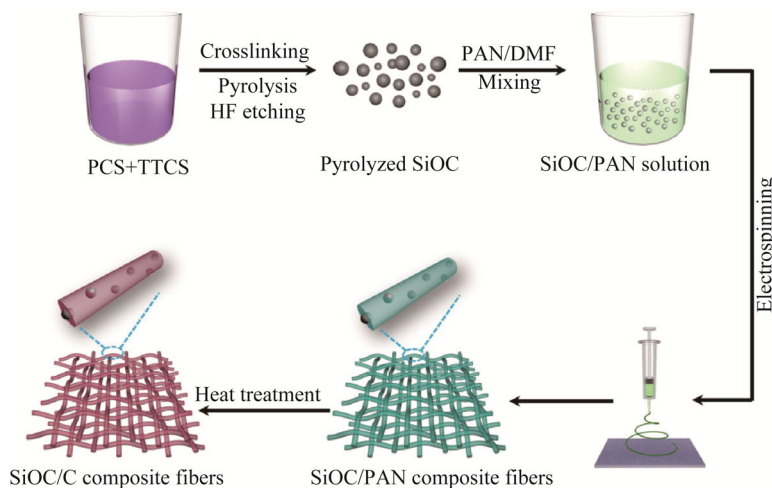
根据第一性原理计算, 由于缺陷位置的扩散势垒较低, 可以促进锂离子从空位扩散并穿过石墨烯片, 提供更多的活性位点。因此, 推动了氮掺杂石墨烯作为锂离子电池负极材料的研究^[68-69]。Ma 等^[70]先将聚碳硅烷(PCS)和 TTCS 通过交联、热解得到 SiOC 颗粒, 然后将 PAN 加入到含有 SiOC 的悬浮液中进行静电纺丝, 最后在氨气气氛下热解得到 SiOC/CNFs 复合材料(图 5)。此法使得 SiOC 颗粒紧密包裹 N 掺杂碳纤维中, 促进电子传递以及具有更快的反应动力学; 且氮掺杂碳纤维产生了更多的缺陷, 从而提高了电极的电导率、增加了电化学反应活性位点。因此, 使得 SiOC/CNFs 复合材料具有高达 73%的初始 Coulomb 效率, 且在 200 mA/g 循环 200 次后具有 595 mA·h/g 的可逆容量。Huang 等^[71]通过溶胶-凝胶法和热解法制备出 SiOC 颗粒, 然后将 SiOC 颗粒分散于氮掺杂碳纳米纤维溶液中, 通过静电纺丝和随后的热解将 Si—N 桥接引入混合 SiOC 单元中, 得到了 SiOC/CNFs 复合材料。此复合材料具有较高的可逆容量(100 次循环后, 在 0.1 A/g

时为 707 mA·h/g)、良好的倍率性能(1.6 A/g 时为 468 mA·h/g)和优异的循环稳定性(800 次循环后, 在 0.4 A/g 时为 570 mA·h/g)。

3.4 SiOC/生物质炭复合材料

生物质具有可再生、成本低、内在结构多样等优点, 将其作为前驱体制备电极材料可降低成本和提高锂离子电池的电化学性能^[72]。Xia 等^[73]以微藻作为生物模板和碳源、四乙氧基硅烷(TEOS)作为前驱体, 利用超临界 CO₂ 流体技术(SC-CO₂)合成多孔 SiOC/C 复合材料(如图 6 所示)。与传统的人工模板相比, 微藻资源丰富、可再生, 是一种很有前景的生物模板。同时, 具有高渗透、高扩散、高溶解能力的超临界 CO₂ 流体可以作为优良的溶剂, 保证前驱体的高效传质和均匀分散。电化学性能测试表明,

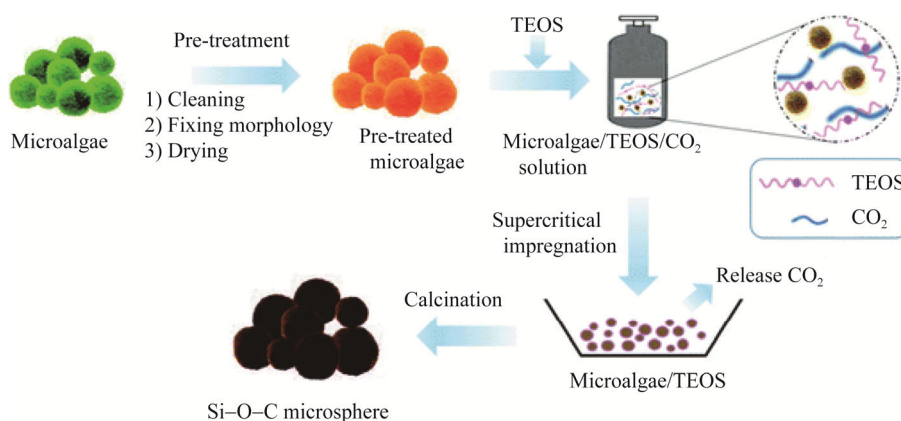
在 0.1 A/g 下循环 200 次后 SiOC/C 负极材料的可逆容量为 453.5 mA·h/g。这种结构可为 Li⁺ 存储提供更多活性位点, 同时有效地减缓充放电过程中的体积膨胀。随后, Xia 等^[74]又以玫瑰花粉为原料, 用同样的方法制备出了 SiOC/C 复合材料。电化学测试表明, SiOC/C 负极材料的初始容量为 1 031.6 mA·h/g, 且具有较好循环稳定性(在 0.1 A/g 的电流密度下, 经过 200 次循环后可逆容量为 351.3 mA·h/g)。生物质炭表面有大量孔隙, 有利于在电化学反应过程中电解质的快速渗透和 Li⁺ 的快速转移, 生物模板技术被认为是一种高效的策略, 可以制备尺寸均匀、形态多样、微观结构精细的各种功能材料。此课题组还利用竹子、棉花纤维、木棉纤维等多种生物材料作为生物模板和碳源合成电极材料^[75–76]。



PCS is polycarbosilanes; TTCS is tetravinylcyclotetrasiloxane; PAN is polyacrylonitrile; DMF is dimethylformamide.

图 5 SiOC/CNFs 的制备工艺示意图^[70]

Fig. 5 Schematic of the preparation process of SiOC/CNFs^[70]



TEOS is tetraethyl orthosilicate.

图 6 SiOC/C 的合成示意图^[73]

Fig. 6 Schematic illustration of the preparation process of SiOC/C^[73]

综上所述, SiOC 基复合材料的电化学性能与碳材料种类、制备工艺和复合设计等有关。碳材料的

选择对 SiOC/C 复合材料的电化学性能尤为重要。纳米碳有利于构筑导电网络, 且与 SiOC 复合后内

部存在较多微/介孔, 增强了电容效应, 电化学性能得到进一步提升, 故 SiOC/纳米碳复合材料的电化学性能优于 SiOC/传统碳复合材料。在 SiOC/纳米碳复合材料中, 碳纳米管高长径比的优势使得 SiOC/CNTs 负极材料具有较好的电化学性能(电流密度为 0.1 C 时, 循环 100 次后具有 1 078 mA·h/g 的高容量)^[55]。此外, 碳纳米管的一维结构也给 SiOC/纳米碳复合材料带来了工艺上的灵活性。用石墨烯制备的复合材料在 50 mA/g 的电流密度下循环 90 次后可表现出 582 mA·h/g 的容量^[58], 石墨烯因其自身结构更适合于设计和制备层状结构的 SiOC/C 复合

材料。通过静电纺丝得到的碳纳米纤维与 SiOC 的复合材料, 可直接作为自支撑电极, 且具有良好的循环性能以及在大电流密度下较高的容量, SiOC/CNFs 复合材料经大电流密度 1 372 mA/g 下循环 2 000 次后仍能保持 422.1 mA·h/g 的容量^[67]。生物质炭虽然可以得到更多的孔结构增加活性位点, 使复合材料具有较高的容量和稳定性(在 0.1 A/g 下循环 200 次后 SiOC/C 负极材料的可逆容量为 453.5 mA·h/g)^[74], 但工艺稳定性还有待于进一步完善。表 1 汇总了 SiOC/C 复合材料的典型结构与电化学性能。

表 1 SiOC/C 复合材料的电化学性能
Table 1 Electrochemical performances of SiOC/C composites

Composite	Carbon source	Reversible capacity (Cycle number), Current density	Capacity retention rate/%	First coulombic efficiency/%	Reference
SiOC/Carbon nanotubes	Multi-Walled carbon nanotubes	686.3 mA·h/g (40) at C/10	81.50	67.10	[53]
SiOC/Carbon nanotubes paper	Multi-Walled carbon nanotubes			46.20	[32]
SiOC/Carbon nanotubes	Multi-Walled carbon nanotubes	1 078.0 mA·h/g (100) at C/10		69.81	[55]
SiOC/Graphene	Graphite oxide	357.0 mA·h/g (20) at 40 mA/g	31.28		[57]
SiOC/Graphene	Graphite oxide	582 mA·h/g (90) at 50 mA/g	99.00	63.00	[58]
SiOC/3D-Graphene	Graphite oxide	701.0 mA·h/g (100) at 100 mA/g	84.80	65.70	[61]
SiOC/Graphene aerogel	Graphite oxide	352.0 mA·h/g (1 000) at 1480 mA/g	95.00		[34]
SiOC/Reduced graphene oxide	Graphite oxide	507.0 mA·h/g (50) at 100 mA/g			[63]
SiOC/Reduced graphene oxide paper	Graphite oxide	400.0 mA·h/g (30) at 50 mA/g	53.30		[59]
SiOC/Reduced graphene oxide paper	Graphite oxide	588 mA·h/g (1 020) at 100 mA/g			[60]
3D-Graphene/SiOC _r	Graphite oxide	686.0 mA·h/g (500) at 50 mA/g	99.00	78.50	[62]
SiOC/Carbon nanofibers	Polyacrylonitrile	669.0 mA·h/g (80) at 50 mA/g	79.70	72.90	[66]
SiOC/Carbon nanofibers	Polyacrylonitrile	422.1 mA·h/g (2 000) at 1 372 mA/g	95.40	71.40	[67]
SiOC/Carbon nanofibers	Polyacrylonitrile	595.0 mA·h/g (200) at 200 mA/g	83.90	73.00	[70]
SiOC/Carbon nanofibers	Polyacrylonitrile	707.0 mA·h/g (100) at 100 mA/g	47.70	68.20	[71]
SiOC/Graphite	Flake graphite	184.0 mA·h/g (1 000) at 2 A/g	80.00	71.50	[48]
Porous SiOC/C	Nannochloropsis	453.5 mA·h/g (200) at 100 mA/g	47.50	63.40	[73]
Porous SiOC/C	Rose pollen grains	351.3 mA·h/g (200) at 100 mA/g	34.10	63.70	[74]

4 结语与展望

SiOC 基负极材料是极具潜力的锂离子电池负极材料, 然而导电性差是 SiOC 负极难以实现商业化的最主要问题。SiOC/C 负极材料结合了碳材料的高电导率以及 SiOC 高容量、稳定性与机械柔性等优点, 通过碳材料的选择、制备工艺优化和复合结

构设计, 可使 SiOC/C 复合材料的电化学性能得到明显改善。其中, SiOC/纳米碳复合材料以更优异的电化学性能受到了众多研究人员的青睐。SiOC/C 负极材料目前存在的主要问题如下。

1) 纳米碳具有高比表面积和 van der Waals 力, 在复合材料的制备过程中易出现团聚现象, 在 SiOC 基体中分布不均匀, 从而导致纳米碳的负载有限,

无法形成连续网络,限制了复合材料的电化学性能。通过水热、冷冻干燥以及超声辅助法可在一定程度上减少团聚的发生。

2) SiOC 的粒径通常较大,导致活性位点的利用率较低。目前研究人员对氮掺杂碳进行的初步研究表明,利用产生的缺陷可获得更多的活性位点。但是,仍然需要探索其他掺杂元素的影响,以及通过多元复合进一步提升电化学性能的可行性。

3) SiOC 负极材料的储锂机理仍需进一步深入研究。利用原位表征技术观察储锂过程,分析脱嵌锂后微观结构的演变,在掌握储锂机理的基础上才能更有效地提高 SiOC 基负极材料的电化学性能。

提高锂离子电池的电化学性能和安全性是国内众多研究者们一直追求的目标。寻找易操作、成本低的材料制备工艺,设计合理的 SiOC 基负极材料的组成、结构对推动锂离子电池的发展和应用至关重要。克服上述问题必会使 SiOC 基负极材料在高性能锂离子电池,甚至锂硫电池、钠离子电池、钾离子电池^[72, 77–79]等领域得到广泛应用。

参考文献:

- [1] DUNN B, KAMAT C H, TARASCON J M. Electrical energy storage for the grid: A battery of choices[J]. *Science*, 2011, 334(6058): 928–935.
- [2] ISLAM M S, FISHER C A J. Lithium and sodium battery cathode materials: Computational insights into voltage, diffusion and nanostructural properties[J]. *Chem Soc Rev*, 2014, 43(1): 185–204.
- [3] CHENG H, SHAPTER J G, LI Y, et al. Recent progress of advanced anode materials of lithium-ion batteries[J]. *J Energy Chem*, 2021, 57(6): 451–468.
- [4] BALOGUN M S, QIU W, LUO Y, et al. A review of the development of full cell lithium-ion batteries: The impact of nanostructured anode materials[J]. *Nano Res*, 2016, 9(10): 2823–2851.
- [5] WANG X, CHEN J, DONG C, et al. Hard carbon derived from graphite anode by mechanochemistry and the enhanced lithium-ion storage performance[J]. *ChemElectroChem*, 2022, 9(5): 202101613.
- [6] LI S, WANG K, ZHANG G, et al. Fast charging anode materials for lithium-ion batteries: Current status and perspectives[J]. *Adv Funct Mater*, 2022, 32(23): 2200796.
- [7] SANDHYA C P, JOHN B, GOURI C. Lithium titanate as anode material for lithium-ion cells: A review[J]. *Ionics*, 2014, 20(5): 601–620.
- [8] WANG Q, ZHANG J, LOU Y, et al. Characteristic of gas evolution in lithium-ion batteries using an anode based on lithium titanate[J]. *Prog Chem*, 2014, 26(11): 1772–1780.
- [9] LIU R, MA G, LI H. Recent progress of lithium titanate as anode material for high performance lithium-ion batteries[J]. *Ferroelectrics*, 2021, 580(1): 172–194.
- [10] BITEW Z, TESEMMA M, BEYENE Y, et al. Nano-structured silicon and silicon based composites as anode materials for lithium ion batteries: recent progress and perspectives[J]. *Sustain Energy Fuels*, 2022, 6(4): 1014–1050.
- [11] MENG W J, HAN X Y, HOU Y L, et al. Defect-repaired reduced graphene oxide caging silicon nanoparticles for lithium-ion anodes with enhanced reversible capacity and cyclic performance[J]. *Electrochim Acta*, 2021, 382: 138271.
- [12] ZHANG Q, ZHANG F, ZHANG M, ET AL. A highly efficient silicone-modified polyamide acid binder for silicon-based anode in lithium-ion batteries[J]. *ACS Appl Energy Mater*, 2021, 4(7): 7209–7218.
- [13] FANG G, DENG X, ZOU J, et al. Amorphous/ordered dual carbon coated silicon nanoparticles as anode to enhance cycle performance in lithium ion batteries[J]. *Electrochim Acta*, 2019, 295: 498–506.
- [14] MI H, YANG X, LI Y, et al. A self-sacrifice template strategy to fabricate yolk-shell structured silicon@void@carbon composites for high-performance lithium-ion batteries[J]. *Chem Eng J*, 2018, 351: 103–109.
- [15] LIU Y, JING S X, LUO S H, et al. Non-volatile natural products in plant glandular trichomes: Chemistry, biological activities and biosynthesis[J]. *Nat Prod Rep*, 2019, 36(4): 626–665.
- [16] JIAO M, WANG Y, YE C, et al. High-capacity SiO_x (0≤x≤2) as promising anode materials for next-generation lithium-ion batteries[J]. *J Alloys Compd*, 2020, 842: 155774.
- [17] SONG J, GUO S, KOU L, et al. Controllable synthesis Honeycomb-like structure SiO_x/C composites as anode for high-performance lithium-ion batteries[J]. *Vacuum*, 2021, 186: 110044.
- [18] ZHANG J, HOU Z, ZHANG X, et al. Delicate construction of Si@SiO_x composite materials by microwave hydrothermal for lithium-ion battery anodes[J]. *Ionics*, 2020, 26: 69–74.
- [19] WILSON A M, XING W, ZANK G, et al. Pyrolysed pitch-polysilane blends for use as anode materials in lithium ion batteries II: The effect of oxygen[J]. *Solid State Ionics*, 1997, 100(3): 259–266.
- [20] WILSON A M, REIMERS J N, FULLER E W, et al. Lithium insertion in pyrolyzed siloxane polymers[J]. *Solid State Ionics*, 1994, 74(3): 249–254.
- [21] WILSON A M, ZANK G, EGUCHI K, et al. Pyrolysed silicon-containing polymers as high capacity anodes for lithium-ion batteries[J]. *J Power Sources*, 1997, 68(2): 195–200.
- [22] XING W, WILSON A M, ZANK G, et al. Pyrolysed pitch-polysilane blends for use as anode materials in lithium ion batteries[J]. *Solid State Ionics*, 1997, 93(3): 239–244.
- [23] XING W, WILSON A M, EGUCHI K, et al. Pyrolyzed polysiloxanes for use as anode materials in lithium-ion batteries[J]. *J Electrochem Soc*, 1997, 144(7): 2410–2416.
- [24] WANG J T, WANG Y, HUANG B, et al. Silicon supported on Stable SiOC skeleton in high-performance lithium-ion battery anode materials[J]. *Acta Phys-Chim Sin*, 2014, 30(2): 305–310.
- [25] FUKUI H, OHSUKA H, HINO T, et al. Polysilane/acenaphthylene blends toward Si–O–C composite anodes for rechargeable lithium-ion batteries[J]. *J Electrochem Soc*, 2011, 158(5): A550–A555.
- [26] HALIM M, HUDAYA C, KIM A Y, et al. Phenyl-rich silicone oil as a precursor for SiOC anode materials for long-cycle and high-rate lithium ion batteries[J]. *J Mater Chem A*, 2016, 4(7): 2651–2656.
- [27] LIAO N, ZHENG B, ZHOU H, et al. Effect of carbon content on the structure and electronic properties of silicon oxycarbide anodes for lithium-ion batteries: A first-principles study[J]. *J Mater Chem A*, 2015, 3(9): 5067–5071.
- [28] LIU G, KASPAR J, REINOLD L M, et al. Electrochemical

- performance of DVB-modified SiOC and SiCN polymer-derived negative electrodes for lithium-ion batteries[J]. *Electrochim Acta*, 2013, 106: 101–108.
- [29] LIU X, ZHENG M C, XIE K, et al. The relationship between the electrochemical performance and the composition of Si–O–C materials prepared from a phenyl-substituted polysiloxane utilizing various processing methods[J]. *Electrochim Acta*, 2012, 59: 304–309.
- [30] YAN M, QIN Y, WANG L, et al. Recent advances in biomass-derived carbon materials for sodium-ion energy storage devices[J]. *Nanomaterials*, 2022, 12(6): 930.
- [31] MOLAIYAN P, DOS REIS G S, KARUPPIAH D, et al. Recent progress in biomass-derived carbon materials for Li-ion and Na-ion batteries—A review[J]. *Batteries*, 2023, 9(2): 116.
- [32] BHANDAVAT R, COLOGNA M, SINGH G. Polymer-derived SiOC–CNT paper as lithium-ion battery anodes[J]. *Nanomater Energy*, 2012, 1(1): 57–61.
- [33] PAN J, PAN J, CHENG X, et al. Synthesis of hierarchical porous silicon oxycarbide ceramics from preceramic polymer and wood biomass composites[J]. *J Eur Ceram Soc*, 2014, 34(2): 249–256.
- [34] SHAO G, HANAOR D, WANG J, et al. Polymer-derived SiOC integrated with a graphene aerogel as a highly stable Li-ion battery anode[J]. *ACS Appl Mater Interfaces*, 2020, 12(41): 46045–46056.
- [35] LIU Z, YU Q, ZHAO Y, et al. Silicon oxides: a promising family of anode materials for lithium-ion batteries[J]. *Chem Soc Rev*, 2019, 48(1): 285–309.
- [36] BOIS L, MAQUET J, BABONNEAU F, et al. Structural characterization of sol–gel derived oxycarbide glasses. 2. Study of the thermal stability of the silicon oxycarbide phase[J]. *Chem Mater*, 1995, 7(5): 975–981.
- [37] CORRIU R, LECLERCQ D, MUTIN P, et al. Preparation and structure of silicon oxycarbide glasses derived from polysiloxane precursors[J]. *J Sol-Gel Sci Technol*, 1997, 8(1): 327–330.
- [38] SAHA A, RAJ R, WILLIAMSON D L, A Model for the nanodomains in polymer-derived SiCO[J]. *J Am Ceram*, 2006, 89(7): 2188–2195.
- [39] SUN H, ZHAO K, Atomistic origins of high capacity and high structural stability of polymer-derived SiOC anode materials[J]. *ACS Appl Mater Interfaces*, 2017, 9(40): 35001–35009.
- [40] FUKUI H, NAKATA N, DOKKO K, et al. Lithiation and delithiation of silicon oxycarbide single particles with a unique microstructure[J]. *ACS Appl Mater Interfaces*, 2011, 3(7): 2318–2322.
- [41] HAAKS M, KASPAR J, FRANZ A, et al. ⁷Li NMR studies of lithium ion dynamics in polymer-derived silicon oxycarbide ceramics[J]. *Solid State Ionics*, 2016, 287: 28–35.
- [42] FUKUI H, OHSUKA H, HINO T, et al. Preparation of microporous Si–O–C composite material and its lithium storage capability[J]. *Chem Lett*, 2009, 38(1): 86–87.
- [43] FUKUI H, OHSUKA H, HINO T, et al., A Si–O–C composite anode: high capability and proposed mechanism of lithium storage associated with microstructural characteristics[J]. *ACS Appl Mater Interfaces*, 2010, 2(4): 998–1008.
- [44] HALIM M, LIU G, ARDHI R, et al. Pseudocapacitive characteristics of low-carbon silicon oxycarbide for lithium-ion capacitors[J]. *ACS Appl Mater Interfaces*, 2017, 9(24): 20566–20576.
- [45] LIU X, ZHENG M C, XIE K, Mechanism of lithium storage in Si–O–C composite anodes[J]. *J Power Sources*, 2011, 196(24): 10667–10672.
- [46] ZHOU L, ZHANG K, HU Z, et al. Recent developments on and prospects for electrode materials with hierarchical structures for lithium-ion batteries[J]. *Adv Energy Mater*, 2018, 8(6): 1701415.
- [47] ZUO X, ZHU J, MULLER-BUSCHBAUM P, et al. Silicon based lithium-ion battery anodes: A chronicle perspective review[J]. *Nano Energy*, 2017, 31: 113–143.
- [48] WU Z, CHENG X, TIAN D, et al. SiOC nanolayers directly-embedded in graphite as stable anode for high-rate lithium ion batteries[J]. *Chem Eng J*, 2019, 375: 121997.
- [49] KNOZOWSKI D, GRACZYK-ZAJAC M, VRANKOVIC D, et al., New insights on lithium storage in silicon oxycarbide/carbon composites: Impact of microstructure on electrochemical properties[J]. *Composites, Part B*, 2021, 225: 109302.
- [50] KONNO H, MORISHITA T, WAN C, et al. Si–C–O glass-like compound/exfoliated graphite composites for negative electrode of lithium ion battery[J]. *Carbon*, 2007, 45(3): 477–483.
- [51] KUSRINI E, PRIYONO B, EGIEARA N C, et al. The effect of activated carbon and silicon oxycarbide as anode materials on lithium-ion battery[C]. *E3S Web Conf*, 2018, 67(4): 03027.
- [52] CHEN N, MA Z, LI H, et al. Asphalt-based carbon boosts the cyclability and rate capability of SiOC anode for high-performance lithium ion batteries[J]. *Ionics*, 2022, 28(9): 4177–4184.
- [53] BHANDAVAT R, SINGH G, Stable and efficient Li-ion battery anodes prepared from polymer-derived silicon oxycarbide-carbon nanotube shell/core composites[J]. *J Phys Chem C*, 2013, 117(23): 11899–11905.
- [54] NARA H, YOKOSHIMA T, MOMMA T, et al. Highly durable SiOC composite anode prepared by electrodeposition for lithium secondary batteries[J]. *Energ Environ Sci*, 2012, 5(4): 6500–6505.
- [55] AHN S, JEONG M, YOKOSHIMA T, et al. Electrophoretically deposited carbon nanotube anchor layer to improve areal capacity of Si–O–C composite anode for lithium secondary batteries[J]. *J Power Sources*, 2016, 336: 203–211.
- [56] MO R, TAN X, LI F, et al. Tin-graphene tubes as anodes for lithium-ion batteries with high volumetric and gravimetric energy densities[J]. *Nat Commun*, 2020, 11(1): 1374.
- [57] JI F, LI Y-L, FENG J M, et al. Electrochemical performance of graphene nanosheets and ceramic composites as anodes for lithium batteries[J]. *J Mater Chem*, 2009, 19(47): 9063–9067.
- [58] REN Y, YANG B, HUANG X, et al. Intercalated SiOC/graphene composites as anode material for Li-ion batteries[J]. *Solid State Ionics*, 2015, 278: 198–202.
- [59] KOLATHODI M S, DAVID L, ABASS M A, et al. Polysiloxane-functionalized graphene oxide paper: Pyrolysis and performance as a Li-ion battery and supercapacitor electrode[J]. *RSC Adv*, 2016, 6(78): 74323–74331.
- [60] DAVID L, BHANDAVAT R, BARRERA U, et al. Silicon oxycarbide glass-graphene composite paper electrode for long-cycle lithium-ion batteries[J]. *Nat Commun*, 2016, 7(1): 10998.
- [61] SANG Z, ZHAO Z, SU D, et al. SiOC nanolayer wrapped 3D interconnected graphene sponge as a high-performance anode for lithium ion batteries[J]. *J Mater Chem A*, 2018, 6(19): 9064–9073.
- [62] SANG Z, YAN X, WEN L, et al., A graphene-modified flexible SiOC ceramic cloth for high-performance lithium storage[J]. *Energy Storage Mater*, 2020, 25: 876–884.
- [63] ISLAM M S, KARIM M R, ISLAM S, et al. *In situ* generation of silicon oxycarbide phases on reduced graphene oxide for Li-ion battery anode[J]. *ChemistrySelect*, 2016, 1(20): 6429–6433.
- [64] ZHANG T W, SHEN B, YAO H-B, et al., Prawn shell derived chitin

- nanofiber membranes as advanced sustainable separators for Li/Na-ion batteries[J]. *Nano Lett*, 2017, 17(8): 4894–4901.
- [65] FRANCA E F, LEITE F L, CUNHA R A, et al. Designing an enzyme-based nanobiosensor using molecular modeling techniques[J]. *Phys Chem Chem Phys*, 2011, 13(19): 8894–8899.
- [66] LI Y, HU Y, LU Y, et al. One-dimensional SiOC/C composite nanofibers as binder-free anodes for lithium-ion batteries[J]. *J Power Sources*, 2014, 254: 33–38.
- [67] LI H, YAN X, MA Z, et al. Silicon oxycarbide-carbon hybrid nanofibers: A promising anode for ultralong-cycle lithium ion batteries with high rate capability[J]. *Ceram Int*, 2021, 47(5): 6867–6874.
- [68] XIE Q, BAO R, XIE C, et al. Core-shell N-doped active carbon fiber@graphene composites for aqueous symmetric supercapacitors with high-energy and high-power density[J]. *J Power Sources*, 2016, 317: 133–142.
- [69] LEE K H, OH J, SON J G, et al. Nitrogen-doped graphene nanosheets from bulk graphite using microwave irradiation[J]. *ACS Appl Mater Interfaces*, 2014, 6(9): 6361–6368.
- [70] MA M, WANG H, LI X, et al. Free-standing SiOC/nitrogen-doped carbon fibers with highly capacitive Li storage[J]. *J Eur Ceram Soc*, 2020, 40(15): 5238–5246.
- [71] HUANG X, CHRISTOPHER B, CHAI S, et al. Cowpea-like N-Doped silicon oxycarbide/carbon nanofibers as anodes for high-performance lithium-ion batteries[J]. *ACS Appl Energy Mater*, 2021, 4(2): 1677–1686.
- [72] AMARAL M M, MUJIB S B, SANTOS E A, et al. A sulfur host based on silicon oxycarbide for advanced lithium-sulfur batteries[J]. *J Energy Storage*, 2023, 72: 108388.
- [73] XIA Y, FANG R, XIAO Z, et al. Supercritical fluid assisted biotemplating synthesis of Si–O–C microspheres from microalgae for advanced Li-ion batteries[J]. *RSC Adv*, 2016, 6(74): 69764–69772.
- [74] XIA Y, CAI S, LU C, et al. Rose pollens as sustainable biotemplates for porous SiOC microellipsoids with enhanced lithium storage performance[J]. *J Alloys Compd*, 2020, 816: 152595.
- [75] TAO X, WANG J, LIU C, et al. Balancing surface adsorption and diffusion of lithium-polysulfides on nonconductive oxides for lithium-sulfur battery design[J]. *Nat Commun*, 2016, 7(1): 11203.
- [76] ZOU J, ZHU J, YANG Z, et al. A phototheranostic strategy to continuously deliver singlet oxygen in the dark and hypoxic tumor microenvironment[J]. *Angew Chem Int Edit*, 2020, 59(23): 8833–8838.
- [77] DEY S, SINGH G, WS₂ nanosheet loaded silicon-oxycarbide electrode for sodium and potassium batteries[J]. *Nanomaterials*, 2022, 12(23): 4185.
- [78] PARK J, KIM M, CHOI M, et al. Sb/C composite embedded in SiOC buffer matrix *via* dispersion property control for novel anode material in sodium-ion batteries[J]. *J Power Sources*, 2023, 568: 232908.
- [79] WEINBERGER M, SU P H, PETERLIK H, et al. Biphenyl-bridged organosilica as a precursor for mesoporous silicon oxycarbide and its application in lithium and sodium ion batteries[J]. *Nanomaterials*, 2019, 9(5): 754.

Research Progress on Carbon Materials Modified SiOC Anodes in Lithium-Ion Batteries

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Extended Abstract

Lithium-ion batteries are considered as the most promising chemical power source due to their high energy density, good safety, and environmental friendliness. As a key component of batteries, anode material plays an important role on the electrochemical performance. Graphite, Li₄Ti₅O₁₂ and Si-based materials have attracted much attention as anode materials in lithium-ion batteries. Among these materials, graphite has good conductivity, small volume change, high initial coulombic efficiency, and low cost. As a conventional anode material for lithium-ion batteries, graphite is first commercially applied. However, its low theoretical capacity is the main factor restricting the development of high energy density lithium-ion batteries. Li₄Ti₅O₁₂ anode material is considered to have a great development potential due to its stable structure during lithiation and delithiation processes and good safety. However, its low theoretical capacity and high cost restrict its practical application. Si has a high theoretical capacity, but it has a disadvantage of large volume expansion during lithiation and delithiation processes, resulting in the poor safety of batteries. The composite of Si and carbon materials is considered as an effective strategy for stabilizing electrodes.

SiOC is considered as one of the high potential anode materials for lithium-ion batteries due to its excellent properties such as high theoretical specific capacity, good mechanical flexibility and structural stability, and facile structure regulation. However, the low conductivity of SiOC leads to its poor rate performance and cycling ability, thus restricting its development and application in the field of lithium-ion batteries. The composition of SiOC materials can be controlled through optimizing the composition, structure, and pyrolysis conditions of polymer precursors. Carbon material has high specific surface area, high mechanical stability, and excellent electrical conductivity. Composite with SiOC anode materials, the conductivity of SiOC can be improved, accelerating the transfer rate of lithium ions during lithiation and delithiation processes. Carbon material can act as an inert layer to reduce the volume effect of SiOC. SiOC/C composites can improve the conductivity effectively, thereby significantly improving the electrochemical performance of lithium-ion batteries as anode materials.

For elucidating the structure of SiOC, this review analyzes the mechanism of lithium ions storage on SiOC anodes. To address

the poor conductivity of SiOC, the composite process of graphite, carbon nanotubes, graphene and carbon nanofibers with SiOC anode materials are reviewed. The design of modification based on different carbon materials and between the anode microstructure and electrochemical performance are discussed. The selection of carbon materials is particularly important for the electrochemical performance of SiOC/C composites. Nanocarbon is beneficial to constructing conductive networks, and after composite with SiOC, there are many micro-/meso-pores inside, which enhances the capacitance effect and further improves the electrochemical performance. Therefore, the electrochemical performance of SiOC/nanocarbon composite materials is better than that of SiOC/traditional carbon composite materials. The rate capability and cycling stability of SiOC-based lithium-ions batteries are improved.

Summary and prospects SiOC-based anode materials have a great potential for lithium-ion batteries, but the poor conductivity is the main problem that make it difficult to commercialize. The SiOC/C anode materials combine the high conductivity of carbon materials with some advantages of high capacity, stability, and mechanical flexibility of SiOC. Among them, SiOC/nanocarbon composite materials are developed due to their superior electrochemical performance. Although some progresses are achieved in the design of SiOC/C anode for the lithium-ion batteries, some challenges still remain in practical application. The main problems existing in SiOC/C anode materials are that the size of SiOC is larger, resulting in a lower utilization of active sites. The preliminary research conducted on nitrogen-doped carbon indicate that more active sites can be obtained *via* utilizing the defects. However, it is still necessary to explore the effect of other doping elements or through multi-component composites. To further enhance the feasibility of electrochemical performance, the lithium ions storage mechanism of SiOC anode materials still needs a further research. The detailed structure evolution of SiOC can be revealed during lithium ions storage process through some advanced *in-situ* characterization techniques. The lithium ions storage mechanisms can be further clarified, and, the electrochemical performance of SiOC-based anode materials can be improved more effectively. Improving the electrochemical performance and safety of lithium-ion batteries is a goal pursued by many researchers. Overcoming the above problems can lead to the widespread application of SiOC-based anode materials in high energy lithium-ion batteries, even in areas such as lithium sulfur batteries, sodium ion batteries, and potassium ion batteries.

Keywords silicon oxycarbide; carbon materials; anode; conductivity; lithium-ion battery