

面向实用化硅基负极电解液及界面设计的思考

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摘 要: 高比能电池技术是实现国家“双碳”目标的重要支撑, 其中硅基负极以其超高克容量被认为是下一代高比能锂离子电池负极材料的首选。由于硅基负极在循环过程中体积形变严重, 导致硅材料的破裂及粉化严重、电解液在硅基材料表面形成的固态电解质膜不稳定, 进而导致电池循环膨胀严重、电池循环寿命缩短等问题, 使得该电池体系的实用化受到挑战。同时, 人们对实际工况下硅基负极的界面演化和失效机制等关键科学问题尚缺乏深入认识。本文从硅基负极的衰减机理出发, 评述了从材料结构到电解液设计的研究进展, 提出在面向实用化过程中, 电解液设计需要进一步明晰硅负极的衰减机理、构建新型表征方法、构筑新分子结构以提升硅负极的界面稳定性等几个方面, 推动匹配硅基高比能电池电解液和电池体系的实际应用。

关键词: 硅基负极; 电解液; 循环寿命; 衰减机理

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新能源技术的创新与颠覆性突破, 是推动我国能源革命和保障“双碳目标”国家战略实现的重要支撑。2020 年 9 月, 中国明确提出力争 2030 年前二氧化碳排放达到峰值, 努力争取 2060 年前实现碳中和目标(“双碳目标”)。自上世纪 90 年代开始, 凭借其优异的能量密度和循环寿命, 锂离子电池在全球电化学电源市场中逐渐占据了主导地位。但是, 近年来基于传统石墨负极的锂离子电池能量密度已经接近上限~250 W·h/kg, 无法满足长续航新能源汽车及电动飞机等应用场景的需求。因此, 如何进一步提升锂离子电池的能量密度(如>400 W·h/kg), 一直是学术界和产业界的研究热点。

硅(Si)的理论比容量是石墨的 10 倍(硅 4200 mA·h/g), 是行业公认的下一代高比能锂离子电池负极材料的首选^[1-2]。当采用“高硅”负极(负极材料中硅含量, 即质量分数大于 50%)配合高镍三元正极时, 全电池的能量密度可大幅提升至 400 W·h/kg 以上。但是, Si 在脱嵌锂过程中存在巨大体积变化(300%以上)、材料结构破坏及粉化、电极-电解液界

面不稳定、电池产气等问题, 使硅基负极电池的循环寿命面临巨大挑战。近年来, 围绕硅基负极的相关研究^[3]可以概括为 2 个主题:

1) Si 结构设计与复合: 当 Si 的粒径降低到临界尺寸~150 nm 以下, Si 可以适应较大的应力变化而不发生开裂和粉化。自中国中科院物理所在 1997 年首次提出纳米 Si 作为锂电池负极以来, 国内外的材料工作者主要通过结构设计来提高 Si 的循环稳定性, 包括设计纳米线、中空、多孔、核壳等结构^[4-8]。虽然纳米化对缓解 Si 的体积膨胀非常有效, 但由于纳米材料的比表面积非常高, 纳米 Si 负极在实用过程中存在的首周库伦效率低、压实密度低、成本高等问题。

为了解决这些问题, 将 Si 限域到石墨碳层之间制成“硅碳”复合材料, 可以明显改善其循环稳定性。其原理在于石墨层可以缓冲 Si 的体积膨胀, 同时避免部分 Si 与电解液接触形成高阻抗界面。目前, 低硅含量的硅碳负极(Si 的质量分数约为 5%)已进入产业化阶段, Tesla、ATL、贝特瑞、杉杉、兰溪致德、

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天目先导等公司都布局了该材料的生产及应用。具有更高硅含量(Si 含量>20%, 克容量>1200 mA·h/g)的超高比容量负极一直是前沿研究热点, 目前韩国蔚山科学技术院(UNIST)^[9]、中国科学院物理所^[10]、化学所^[11]、天津大学^[12]、北京卫蓝、美国 Sila Nano、Group 14 等学术机构和科技公司都开展了相关研究并取得显著进展。如韩国蔚山科学技术院(UNIST)的 Jaephil Cho 教授课题组^[9]利用气相沉积技术在碳层之间沉积了亚纳米级别的 Si 颗粒, 获得了比容量在 500~1000 mA·h/g 的硅碳负极材料, 构建的 110 A·h 方形电池在 2875 圈循环后容量保持率为 91%以上。此外, 针对纯硅负极的研究也取得了很大进展, 主要集中在高弹粘结剂^[13–15]的开发以及构建弹性导电网络^[16]等方面。

但对于高硅/纯硅负极来说, 无论是结构设计还是石墨限域等手段都无法完全缓解 Si 体积膨胀带来的固体电解质界面膜(SEI)破裂及材料的粉化。因此, 通过电解液调控, 在 Si 表面形成高离子电导和稳定的 SEI 成为了硅基负极的另一研究热点。

2) 电解液调控界面: 目前匹配硅基负极的电解液主要有 2 大类: 碳酸酯基和醚基。

碳酸酯基电解液: 具有较强的抗氧化能力, 可适配三元、钴酸锂等高电压正极, 同时还可以在石墨表面形成良好的 SEI, 因此, 碳酸酯基电解液在锂离子电池中应用最为广泛。对于硅基负极来说, 氟代碳酸乙烯酯(FEC)^[17–18]被认为是当下最有效的电解液组分, 其可以在 Si 表面构建富含 LiF 和弹性聚合物的稳定 SEI, 高硅负极需要使用大量 FEC 来防止由于其耗竭导致的容量跳水。但受限于 FEC 的热稳定性差, 电池的高温循环寿命短和高温存储产气严重等问题一直被广泛诟病^[19–20], 基于 FEC 的碳酸酯电解液在高硅负极电池里的应用面临极大挑战。

醚基电解液: 抗还原能力强, 可降低 SEI 界面的反应活性, 在硅基负极中获得了广泛研究。美国西北太平洋国家实验室的 Jiguang Zhang 和 Wu Xu 研究员等率先提出了局域高浓电解液概念^[21], 利用含 FEC 的醚基局部高浓电解液在硅碳负极表面构建了稳定的 SEI^[22], 克容量达到 1000 mA·h/g 以上, 300 圈循环后容量保持率 73.4%。厦门大学郑建明教授团队^[23]将 FEC 添加到醚基电解液中, 可以在硅碳负极上形成柔韧的 SEI, 比容量可达 900 mA·h/g, 循环寿命接近 500 圈。浙江大学范修林教授和美国马里兰大学 Chunsheng Wang 教授^[24]发现, 四氢呋喃/2-甲基四氢呋喃组成的醚基电解液可以在纯硅

负极表面形成高模量的 LiF-有机双层 SEI 结构, 可以将纯硅负极的容量稳定在 2400 mA·h/g 以上且稳定循环 200 圈。此外, 美国马里兰大学的 Chunsheng Wang 教授课题组还设计了具有新分子结构的离子液体^[25]和基于砷类^[26]的高电压电解液, 可以在稳定硅负极的基础上匹配高电压三元正极。以上工作表明, 通过电解液的设计和优化改善高硅/纯硅负极的界面稳定性, 从而提升硅基负极的循环寿命是可行的。

但从电池的实际工况看, 电解液研究依然面临很大挑战: 采用 FEC 基碳酸酯电解液的硅负极循环性能不够理想, 尤其是 FEC 高温稳定性差、产气等问题很难解决; 醚基电解液尽管可以明显提高硅基负极的循环稳定性, 但其抗氧化性差, 尤其在适配高电压正极和高温环境时, 如何解决其氧化分解和高温产气是此类电解液走向实用化必须面对和解决挑战。因此, 从底层机理到实用化等方面分析, 针对硅基负极电解液的设计和开发有以下几点需要特别关注:

1) 硅碳材料的衰减机理: 电极材料在特定化学场(电解液+电化学反应产物)和循环应力(结构形变+重复充放电)下工作时, 力学和化学失效模式相互促进, 这种耦合作用非常类似于广泛存在于金属材料中的“应力腐蚀开裂”。因此, 厘清和解耦这 2 种失效机制有助于电极和电解液的正向设计;

2) 新的表征和研究方法: 开发新的基于力学-化学学科交叉的研究方法, 建立微观尺度原位-非原位结合手段^[27]研究不同化学场下的电极及界面的裂纹扩展和结构演化, 进而揭示应力腐蚀失效机制的影响因素及演变规律;

3) 实际工况和器件对新电解液材料评估的重要性: 在高载量正负极、贫电解液、大容量电池、高低温滥用等工况条件下, 对电池循环和产气进行实际评估, 在此基础上解析界面演化和电池衰减机理;

4) 硅碳负极的电解液设计需要同时考虑硅和石墨的兼容性: 由于石墨和硅对电解液的要求不一致, 因此设计过程中需要平衡不同溶剂、添加剂对二者的兼容性;

5) 新型添加剂、溶剂分子的开发: 设计新分子替代 FEC, 解决高温产气问题是很有意义的一个方向。新分子的设计应满足: 具备良好的抗氧化性, 可以适配高电压正极, 同时也需对电解液中的痕量水稳定, 并在高温下具有良好的化学稳定性。

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Electrolyte and Interfacial Design for Practical Silicon-Based Anodes

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High-energy Lithium-based battery technology is a crucial support for achieving the national "dual-carbon" goals. In the technology, silicon (Si)-based anodes are considered as one of the most promising choices for next-generation high-energy Li-ion batteries (LIBs) due to their ultra-high specific capacity, which is 10 times greater than that of graphite (*i.e.*, silicon 4200 mA·h/g).

When a "Si-majority" anode (mass fraction of silicon greater than 50% in the anode) works with a high-nickel $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ ($x+y+z=1$, $x \geq 0.6$) cathode, the cell-level energy density can increase to over 400 Wh/kg. However, silicon usually experiences significant volume changes (*i.e.*, over 300%) during lithiation and delithiation, leading to structural degradation, pulverization, unstable electrode-electrolyte interfaces, and gas generation, which pose substantial challenges to the cycling life of silicon-based anode batteries. Also, there is still a lack of clarifying key scientific issues such as interfacial evolution and failure mechanisms under practical conditions. Recent research on silicon-based anodes can be summarized as two main directions.

1) Structure design and composites: Since nano-sized Si as an anode for LIBs was proposed, most of studies focus on the design of various nanostructured Si materials to improve their cycling stability, such as nanowires, hollow, porous, and core-shell Si anodes. However, nano-sized Si anodes suffer from a low initial Coulombic efficiency, a low packing density, and a high cost. To address these issues, Si-graphite composite materials are invented to buffer the volume expansion of Si *via* embedding those into graphite layers, thus improving the cycling stability and become a recent hot topic.

2) Electrolyte engineering: For Si-majority or pure-Si anodes, neither structural design nor graphite confinement can fully alleviate the issues caused by volume expansion, such as the cracking of the solid electrolyte interphase (SEI) and pulverization. Another strategy based on electrolyte engineering is thus proposed to form stable SEI with high ionic conductivity and favorable mechanical properties on the Si surface. Carbonate-based electrolytes, known for their strong oxidation resistance, are highly compatible with high-voltage cathodes (>4 V vs. Li/Li^+). For Si-based anodes, fluorinated ethylene carbonate (FEC) is considered as the most effective electrolyte component. However, FEC suffers from its poor thermal stability, leading to poor high-temperature cycling life and serious gassing at high temperatures. Ether-based electrolytes, featuring their strong reductive resistance, are extensively studied for Si-based anodes. For instance, some studies report that the rationally designed ether-based electrolytes can enable a high specific capacity of ~ 2400 mA·h/g with stable cycling for over 200 cycles. These findings demonstrate that the interface stability of Si-majority/pure-Si anodes can be improved through electrolyte design and optimization, thus enhancing their cycling life.

From the perspective of actual battery operating conditions, a research on electrolytes still faces some challenges. For silicon anodes with FEC-based carbonate electrolytes, the cycling performance is less than ideal, particularly due to the poor high-temperature stability of FEC and the issues of gas generation, which remain difficult to resolve. Ether-based electrolytes can improve the cycling stability of silicon-based anodes, and exhibit a poor oxidation resistance. This poses challenges such as oxidative decomposition and high-temperature gas generation, especially when paired with high-voltage cathodes and operating in high-temperature environments. It is thus essential for the practical application of such electrolytes to overcome these issues. An analysis spanning from fundamental mechanisms to practical implementation identifies the key points for the design and development of electrolytes tailored for silicon-based anodes:

Summary and prospects This review represents the research progress on Si-based anodes from material structure to electrolyte design, and highlights the need to clarify the degradation mechanisms of Si-based anodes, develop novel characterization methods, and design new molecular structures to improve interfacial stability. Some efforts in future research should be directed towards the following aspects, *i.e.*, 1) further elucidating the degradation mechanisms of Si-based anodes from the chemomechanical viewpoint. The Si-based anodes work under cyclic stress and chemical corrosion, which are highly intertwined. This coupling effect is highly analogous to the "stress corrosion cracking" well known in metals. Clarifying and decoupling these two failure mechanisms can guide the design of both electrodes and electrolytes, 2) developing novel interdisciplinary characterization and research methods. These methods should employ both in-situ and ex-situ techniques in microscale to investigate crack propagation and structural evolution of electrodes and interfaces under various chemical environments, 3) evaluating novel electrolytes under realistic conditions. It is essential to assess the performance of batteries, including cycling and gas generation, under realistic conditions such as high-loading electrodes, lean electrolytes, large-format cells and extreme temperatures to analyze the battery degradation mechanisms, 4) electrolyte design for Si-C anodes must consider the compatibility of both Si and Graphite. Since the requirements for electrolytes differ between graphite and silicon, a design needs to balance the compatibility of different solvents and additives with the both materials, and 5) developing novel additives and solvent molecules. Designing new molecules to replace FEC and address the gassing issue at high temperatures is quite meaningful for practical applications. The design of these molecules should ensure superior oxidation resistance, compatibility with high-voltage cathodes, stability with trace amounts of water in the electrolyte, and good chemical stability at high temperatures.

Keywords silicon-based anodes; electrolyte; cycle life; degradation mechanism