锂离子电池负极材料力学行为研究进展

杨辉,曲建民

美国塔夫茨大学机械工程系,马萨诸塞州梅德福 02155,美国

摘要 可充电锂离子电池被广泛应用于便携式电子设备、电动汽车等领域。随着其应用领域的快速发展,迫切需要进一步提高其能量密度。本文综述对目前广泛研究的高能量密度负极材料(如硅、锗)在充/放电过程中力学行为的研究进展;基于最新实验手段及数值模拟方法,介绍负极材料由于电化学-力学耦合所造成的变形和破坏,并讨论相关技术在其他电池系统研究中的应用。

关键词 锂离子电池;负极材料;电化学-力学耦合

与传统的铅酸、镍镉可充电电池相比,锂离子电池具有能量密度高、设计灵活、绿色环保等显著优点,因而正成为目前最流行、最有应用前景和价值的电化学储能和能量转化设备,并被广泛应用于便携式电子设备、电动汽车等领域[1]。现阶段,已商业化的锂离子电池主要采用石墨作为负极材料。这种锂离子电池价格相对便宜,并具有很好的循环寿命。然而,受到石墨材料自身理论储锂容量极限的制约[2-3],基于石墨材料的锂离子电池很难满足来自新一代电子设备对于高能量密度电池的需求,因此人们对新的价格低廉、能量密度高、循环性能好的可替代负极材料做了深入研究,并开发出一系列高能量密度的锂离子二次电池体系[2-7]。

根据锂离子电池的工作原理,在充电过程中,锂离子在外加电场的驱动下从正(阴)极材料脱嵌后透过电解质迁移至负(阳)极材料内部;而在放电过程中,锂离子则从负极材料经电解质迁移至正极材料内部。因此,锂离子电池的能量密度主要取决于所采用电极材料所能容纳锂的能力[8]。研究表明,目前最常用的石墨材料在锂化之后生成物为LiC_6,导致其理论储锂容量极限仅为372 mA·h/g[2-3](图1[9])。相较于Li-C化合物,Li-M(Li_xM, M=Sn, Al, Ge, Si)合金拥有非常高的理论容量和储锂密度[2, 3, 9]。其中,硅(Si)作为锂离子电池的首要备选负极材料,储锂容量最高,在常温下锂化之后生成$Li_{15}Si_4$[10-11],使得相应的储锂容量比传统的石墨材料高1个数量级[2, 3, 12-13]。

由于高储锂容量电极材料的固有特性,在充电(放电)过程中,锂离子的嵌入(脱嵌)将会导致电极材料经受极大的体积变形和应力。例如,在完全充电之后,锡、锗、硅的体积膨胀分别为258%[14-16]、280%[17-18]和300%[11, 19]。在电池快速充放电过程中,由于锂的分布不均匀,此问题将更为严重,往往导致不同锂化程度区域变形不协调,致使裂纹产生、电极整体结构碎裂及电池寿命衰减[16, 19-29]。例如,在充/放电循环过程中高达300%的体积改变会引起硅薄膜的破裂(图2[20])。近年来,随着纳米技术的快速发展,基于纳米结构的电极材料被广泛用于锂离子电池研究[7, 30-33]。一方面,这些纳米结构有利于应变的松弛,在一定程度上能够缓解电极材料的破坏和电池寿命的衰退[34-35](图3[34]);另一方面,由于尺寸较小,纳米材料使锂离子更快地嵌入和脱嵌,促使电池功率的提高[6, 36]。这些纳米尺度电极材料的尺寸效应已在以前的研究中得到证实[28, 32, 37]。同时,不同形状的纳米电极也得到了广泛而深入的研究,例如纳米线[11, 34, 35, 38-40]、纳米管[41-43]、纳米颗粒[44-50]和纳米

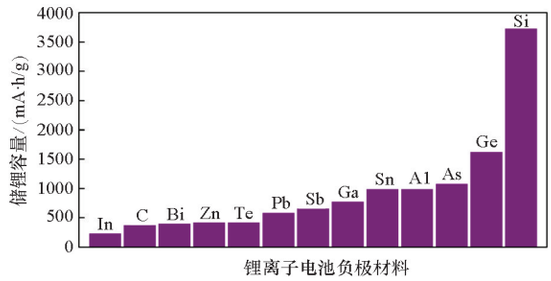

图1 可选锂离子电池负极材料的储锂容量

Fig. 1 Gravimetric capacities of different candidate anode materials

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作者简介:杨辉,博士后,研究方向为新兴能源材料力学,电子信箱:Hui.Yang@tufts.edu;曲建民(通信作者),教授,研究方向为理论和应用力学,电子信箱:Jianmin.Qu@tufts.edu

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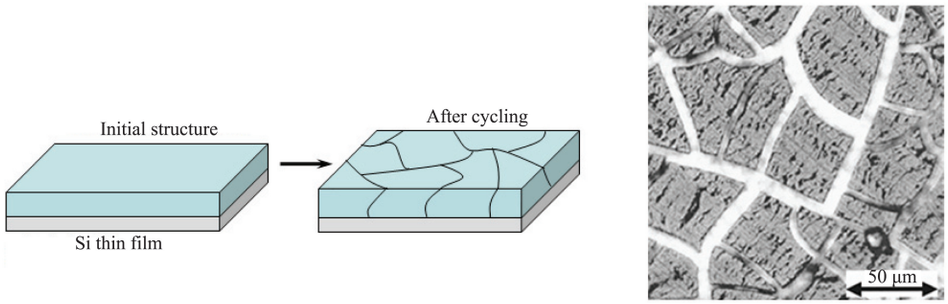
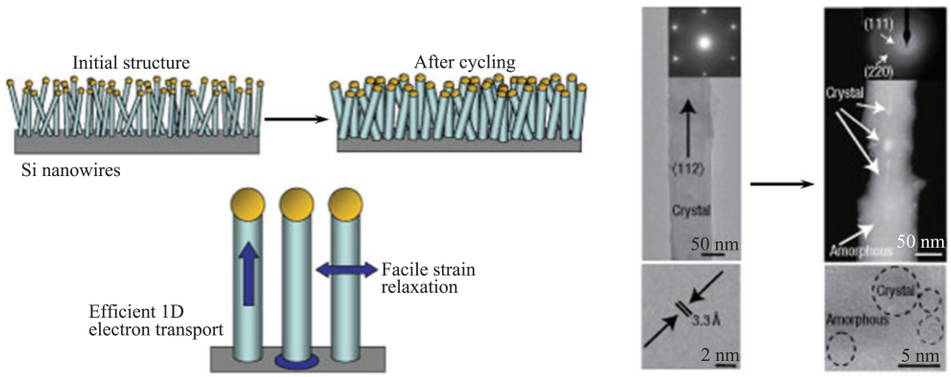


(a) 硅薄膜电极结构在充/放电循环过程中形态变化及破裂失效示意　　(b) 实验结果

图2　硅薄膜电极结构在充/放电循环过程中形态变化及破裂失效的示意和实验结果

Fig. 2　Schematic and experiment of morphological changes of Si thin films during electrochemical cycling



(a) 生长在集电器上的硅纳米线在充/放电循环过程中行为的示意　　(b) 实验结果

图3　生长在集电器上的硅纳米线在充/放电循环过程中行为的示意和实验结果

Fig. 3　Schematic and experiment of electrochemical cycling of Si nanowires (SiNWs) grown on the current collector

级薄膜[22, 51-52]等。为了提高电极的循环能力,基于不同纳米材料的特性,人们设计出各种复合材料电极结构,其中一种材料(如硅)用于提供电池容量,另一种材料(如石墨烯)则保证电极的导电性能和结构稳定性[53-60]。

最近研究表明,即使电极材料采用纳米结构,由充/放电引起的材料结构的衰退与破坏仍是锂离子电池发展的一大障碍。因此,对高容量电极材料在充/放电过程中的变形和破坏机理的认识,将成为设计和发展新一代超长寿命锂离子电池的关键。本文介绍目前广泛研究的高能量密度负极材料,例如硅、锗,在充/放电过程中力学行为研究进展,包括基于这些负极材料的实验表征、观测及跨尺度、多物理的数值模拟。

1　实验研究

1.1　透射电子显微镜实时研究

为了更好地研究纳米尺度电极材料在充/放电过程中的行为,Huang等[25, 61-63]设计了一种基于高倍透射电子显微镜的实时实验平台(*in-situ* TEM)。不同的纳米线或纳米颗粒和固态块状金属锂组装成开放型纳米电池单元,并被置于该实验平台进行观察。其中,纳米线或纳米颗粒为工作电极,固态块状金属锂为参照电极,金属锂表面的氧化锂层为固态电解质(图4[17, 19])。在外加电压驱动下,锂离子通过流入/出工作电极材料实现电极的充/放电循环过程。基于该实验平台,

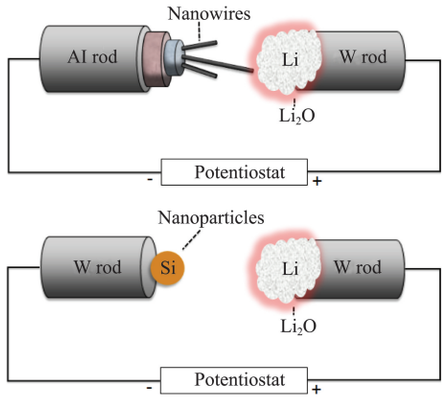


图4　在高倍透射电子显微镜的实时实验平台中,由不同纳米线或纳米颗粒和固态块状金属锂组装而成的开放型纳米电池单元

Fig. 4　Schematics of the *in-situ* nanobattery setup in a high-resolution transmission electron microscope, consisting of a single nanowire or nanoparticle as the working electrode, bulk Li as the counter electrode

对电极材料在充/放电过程中的变形、相变及裂纹的产生和扩展进行实时观察和记录[11, 17, 19, 40, 49, 50, 64-65]。该实验平台为认识电极材料的衰退机理提供了一个独特的研究手段。

基于该透射电子显微镜实时实验平台,发现晶体硅纳米结构的锂化过程是通过锂浓度突变的锂化界面(ACI)向结构内部的不断推进而实现的[63]。当未经充电的硅纳米线(图5(a)[63])部分锂化后(图5(b)[63]),厚度~1 nm[66]的锂化界面将纳米线分成2部分(图5(c)),纳米线的外层转变为已锂化的非晶体硅锂合金外壳(a-Li_xSi),内部为未经锂化的晶体硅核心(c-Si)。由于锂浓度在锂化界面上的突变,该锂化界面可以视为已锂化材料相和未经锂化材料相的相界。同时,晶体硅的锂化速率高度依赖于其晶体取向,不同晶体取向会导致锂化界面上不同的电化学反应速率[63]。因此,不同取向的晶体硅结构在锂嵌入后不仅会呈现出各向异性的变形[19, 26, 38],而且会导致依赖于晶体取向、尺寸的断裂模式[19, 27],如纳米线在充电之后,其横截面的变形、裂纹的起裂位置高度依赖于纳米线的取向[19, 27](图6)。图6中沿纳米线轴线方向的裂纹取向如图中红色箭头所示,插图部分为缓慢充电之后未破裂纳米线的俯视截面图[38],标尺长度为200 nm。此外,实验证明,锂的嵌入速率不仅取决于晶体取向,而且受充/放电过程中电极自身产生的应力影响,致使充电过程中迟滞效应的产生[47, 67]。

此外,锗(Ge)纳米线在充/放电循环过程中会产生可逆的纳米孔洞结构。由于锂在孔洞自由面上较高的扩散速度和应力在孔洞结构上的松弛效应,该电极材料拥有更高的充/放电速率及更好的结构稳定性[40]。同时,充电引起的锗纳米线横截面形状的变化,相较于硅纳米线,呈现出非常低的体积膨胀的各向异性[18, 29, 40]。对于锗纳米颗粒的研究证实,正是由于这种非常低的各向异性,锗纳米颗粒的电化学循环性能远远高于晶体硅纳米颗粒[17]。如图7(a_1)~(a_3)所示的初始直径为~160 nm晶体硅纳米颗粒,材料的各向异性使得未经锂化的核心部分呈现出由{110}[62-63]面组成的六边形形状(图7(a_1))。当其尺寸大于~150 nm[28]的临界值时,在第一次充电过程中就会破裂(图7(a_2)、(a_3))。然而,初始直径为~160 nm锗纳米颗粒(图7(b_1)~(b_3)),由于非常低的各向异性,未经锂化的核心部分几乎呈现出圆形(图7(b_1)、(b_2)),而且该颗粒能够在反复的充/放电过程中稳定地膨胀/收缩而不破裂(图7(b_3))。进一步的研究表明,初始直径为~540 nm非晶体硅纳米颗粒(图7(c_1)~(c_3)),由于其材料的各向同性及其分2阶段的锂化模式,拥有更好的结构稳定性和更大的断裂临界尺寸[49, 50, 68]。此外,研究证明,外力的施加也会影响电极结构的锂化模式。例如,当锗纳米线先弯曲后再充电时,由于受外加应力场的影响,受拉一侧的充电效率明显高于受压的一侧[18]。

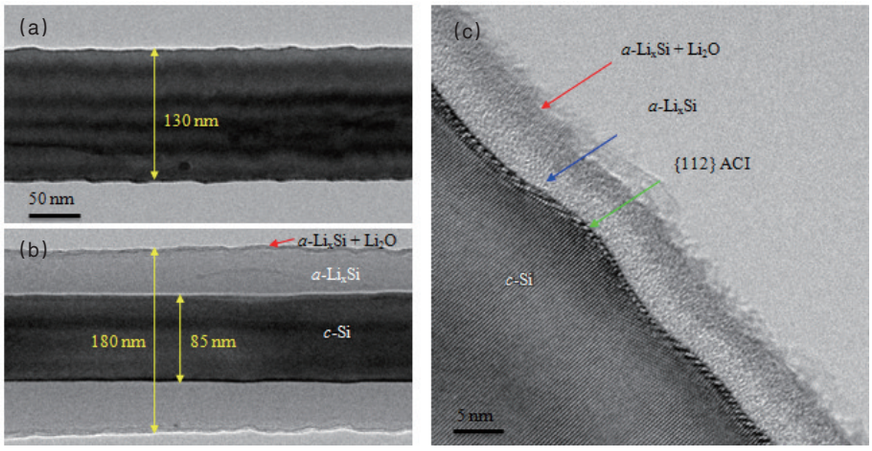
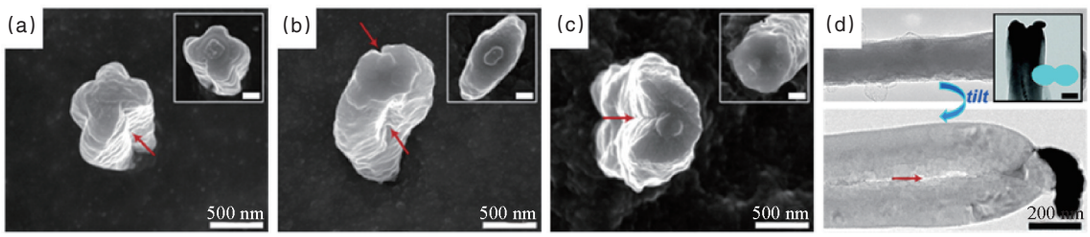


图5 高倍透射电子显微镜实时实验中观测到的〈112〉硅纳米线充电过程

Fig. 5 *In-situ* TEM experiment of lithiation of a 〈112〉 Si nanowire



(a) 纳米线<100> (b) 纳米线<110> (c) 纳米线<111> (d) 纳米线<112>

图6 不同晶体取向的硅纳米线在充电之后各向异性的变形和断裂模式

Fig. 6 Anisotropic swelling and fracture in lithiated SiNWs with four different axial orientations

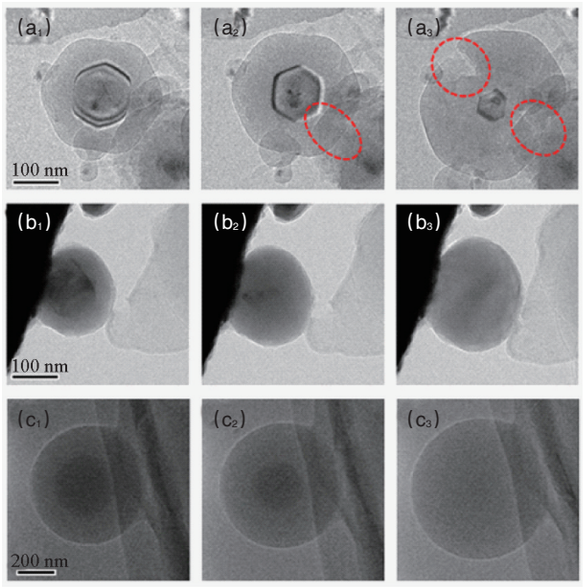


图7　由充电引起的晶体硅纳米颗粒的各向异性的体积膨胀和破裂,对比于晶体锗纳米颗粒和非晶体硅纳米颗粒的几乎各向同性的、稳定的体积变形

Fig. 7　Lithiation-induced anisotropic swelling and fracture in a *c*-SiNP versus the isotropic swelling without fracture in a *c*-GeNP and *a*-SiNP

基于透射电子显微镜实时实验平台,人们对其他高容量电极材料也做了广泛研究。研究表明,锂的嵌入使得原本具有高强机械性能的碳纳米管变得非常脆弱[43]。然而,层状结构的石墨烯在电化学循环过程中却具有非常稳定的性能[62, 64]。金属镓(Ga),有别于其他固态材料,在放电之后只会出现单一的孔洞[69]。同时,其常温下的液体状态使其具有很高的自愈合能力[70-71]。Wang等[16]通过对锡纳米颗粒在充/放电循环中的研究确定了其依赖于颗粒尺寸的破坏机理,即在充电过程中锂的嵌入使锡纳米颗粒熔合在一起,而放电过程中锂脱嵌时引起的高应力会导致较大的纳米颗粒破裂。此外,对不同复合材料电极结构的充/放电效率、结构稳定性也进行了深入研究,如壳-核空心结构、不同的镀层结构等[58, 72-77]。

1.2　其他实验方法研究

除透射电子显微镜之外,透射X光显微镜(TXM)[14-15, 78]、扫描式电子显微镜(SEM)[27, 29, 38, 60, 79]、原子力显微镜(AFM)[80-82]、纳米压痕[83-84]等材料观测和表征技术也被广泛应用于电极材料的研究中。

透射X光显微镜被用于追踪纳米颗粒在充/放电过程中孔洞、裂纹的产生和扩展[14, 78]。扫描式电子显微镜被用于不同晶体取向的硅纳米线横截面在充电之后的变形和破裂的研究[27, 38],如图6(a)~(c)所示,以及各种薄膜材料在电化学循环过程中形态的变化[22, 51, 52]。例如,基于SEM和TEM,Lee等[79]研究了充电过程中硅纳米线相互作用所引发的锂化动力学的改变,并发现纳米线的相互作用能够缓解应力集中,从而提高其抗破坏能力。原子力显微镜和纳米压痕技术被用于测量在不同锂化程度下的锂化产物的材料性质,例如杨氏模量、硬度以及断裂韧性。Hertzberg等[84]研究表明,多晶硅薄膜锂化产物的杨氏模量和硬度都随着锂化程度的升高而降低,其中杨氏模量从多晶硅的92 GPa降为$Li_{15}Si_4$的12 GPa,而硬度则从5 GPa转变为1.5 GPa。然而,Wang等[85]基于纳米压痕的研究显示,锂化前的非晶体硅的断裂韧性为$0.51\pm0.014\ \mathrm{MPa}\sqrt{m}$。随着锂化程度的升高,锂化产物的断裂韧性先降低后升高,并在Li:Si=0.31时取得最小值。当Li:Si=1.09时,相应的断裂韧性为$0.77\pm0.03\ \mathrm{MPa}\sqrt{m}$。而当锂硅的比例Li:Si超过1.5时,断裂模式从脆性断裂转变为韧性断裂。此外,基于曲率测量技术,Sethuraman等[86]研究了应力在硅薄膜材料充/放电过程中的演变,Pharr等[87]测量了硅薄膜锂化后的断裂能量随着锂浓度的变化关系。

2　数值模拟研究

在固态电极材料衰退的过程中,电化学反应和大变形力学问题的相互耦合起着决定性的作用。实验表明,在充/放电循环过程中,电极材料会经历一系列复杂的相变[88-90]。例如,在常温下,晶体硅锂化后会生成固态非晶体合金,而在高温条件下(~415°C)[88],则生成晶体态的锂化产物。在锂化界面的前沿,锂和电极材料进行电化学反应。该电化学反应的速率不仅依赖于电极材料的晶体取向,而且决定了锂化界面向前推进的速度[17, 19, 38, 47, 63]。在锂化界面的后面,锂浓度的梯度促使锂向着锂化界面不断扩散。锂化界面的移动性、锂的扩散性及锂化产物的机械性能都取决于锂的浓度。此外,锂化界面将电极结构分成已锂化部分和未锂化部分,进而致使不协调应力的产生[17, 63, 66]。这些锂化引起的应力,一方面使得高度锂化的电极材料部分通常经受大幅度的塑性变形[86];另一方面,能够延缓电化学的反应速率和降低锂的扩散性,导致锂化迟滞效应的产生[47, 67]。因此,从根本上认识电极材料在充/放电过程中的变形与锂的电化学反应和扩散的相互耦合作用,是对长寿命、抗失效电极进行稳健性设计的先决条件。

电极材料衰退过程的跨尺度、多学科特性对试图了解其电化学-力学过程的研究者提出了挑战。尽管通过高倍透射电子显微镜实验平台能够实时地观测电极材料在充/放电过程中的行为,然而关于纳米尺度的电化学反应过程的关键信息,如不同晶面的反应速率和反应模式,由于现阶段实验手段的局限性,依旧缺失。因此,大量的努力被用于电化学-力学数值模型的建立,进而更好地了解高能电池材料在工作过程中固有的电化学-力学耦合问题。

在原子尺度,第一性原理计算被广泛应用于计算高容量电极材料的晶格长度及锂在其中的结合能和迁移的能量势垒等[91-107]。同时,密度泛涵理论(DFT)计算也被用于模拟锂在电极材料中的嵌入和脱嵌机理,以及锂化后的各种合金相(Li_xM,M=Si,Ge,Sn等)的结构和相关的材料性质,例如杨氏

模量、泊松比等[108-111]。例如,Shenoy等[101]的DFT计算显示硅锂化后产物的弹性性质随锂浓度增加而不断降低,材料展现出弹性松弛效应。Zhao等[106]通过DFT计算研究了锂化过程中非晶体硅塑性应变机理。然而,由于对计算资源巨大的需求,基于第一性原理和密度泛涵理论的计算所能模拟的材料尺寸有局限性,所得的大部分结果仅仅适用于锂浓度比较低的情况。因此,为了对较大尺寸的电极材料进行更加深入的研究,发展了多种描述原子间相互作用的力场,并将其应用于电极材料的分子动力学模拟。其中之一是经典的分子动力学力场[112-113],另一类是反应力场(reactive force field, ReaxFF)。由于能够较为准确地描述电化学反应过程中的键序及化学键的断裂和形成,反应力场被广泛应用于揭示发生在电极材料中及电极和电解质界面上的电化学反应机理[114-121]。例如,基于石墨烯和碳纳米管反应力场的分子动力学模拟显示,裂纹尖端附近的应力梯度促使锂原子从裂纹远场迁移至裂纹尖端附近,从而引起锂在裂纹尖端附近的聚集[117-118];而锂的聚集会进一步导致裂纹尖端化学键强度的削弱,进而引起裂纹向前扩展。因此,带裂纹的石墨烯和碳纳米管在锂化过程中呈现出一种自我弱化的衰退机理。同时,Fan等[119]计算了不同锂化程度硅锂合金在不同加载情况下的屈服和断裂强度,发现随着锂浓度的增加,硅锂合金从共价玻璃态向金属玻璃态转变。此外,Cui等[112-113]开发了一个基于硅锂合金的第二近邻嵌入原子势(2NN MEAM),并计算了不同硅锂合金在单向拉伸情况下的屈服强度[112]。研究表明,随锂浓度的升高,非晶体硅锂合金的屈服强度从Li_1Si_1时的2.0 GPa降低到$Li_{15}Si_4$时的0.5 GPa。基于该原子势,Ding等[122]研究了非晶体硅锂合金的断裂行为,展现了随锂浓度的升高,非晶体硅锂合金由脆性断裂向韧性断裂转变的机理。

在长度尺度谱的另外一端,不同的连续介质层面的锂扩散-力学耦合模型被用于捕捉电极材料的结构、应力及应变状态在锂化过程中的演变[123-129]。在这些模型中,锂的嵌入被描述为锂原子在固态电极材料中的扩散,相应的基本物理过程包含由锂的扩散引起的电极材料成分和体积的改变。如果体积变化不能得到很好的容纳,应力将会在电极材料中产生。这些应力反过来会影响锂在电极材料中的扩散[125]。然而,这些模型都是基于单一相锂化的假设,即锂在电极中的分布呈现出连续和渐变的模式。根据这些模型的预测,固态电极材料的表层在充电过程中将经受周向方向的压应力,这与实验过程观察到的裂纹通常在电极材料表面产生的事实相违背[17, 27-28, 47]。

实验表明,晶体硅纳米线及纳米颗粒的锂化过程是通过原子级突变的锂化界面不断向前推进而实现的。该原子级突变的锂化界面将锂化过程中的电极结构分成2个不同的材料相,其中一个是几乎完全锂化的非晶体外层,另一个是尚未锂化的内部原始材料[17, 19, 28, 63]。基于此实验观察,不同的双重相锂化模型被用于描述硅材料在充电过程中的弹塑性大变形和应力的演化[130-136]。其中,Cui等[133]提出了一个基于有限变形和应力-扩散相互耦合的数学模型,并用于研究二元体系结构中界面化学反应和体扩散的相互影响。Huang等[134]建立了一个将锂化界面上的化学反应作为扩散问题考虑的模型。在这个模型中,一个随锂浓度变化而非线性改变的锂的扩散系数方程被用于实现实验中观测到的锂浓度突变的锂化界面。基于这个模型,Huang等研究了球形颗粒在锂化过程中应力的演变(图8[134]):位于颗粒表面附近的一点A,随着锂化界面不断的向内推进,其圆周方向的应力将经受由拉到压再到拉的转变。在该颗粒中,锂化界面将其分成已锂化的部分(灰色)和未经锂化的部分(白色)。在锂化的初始阶段,点A位于未经锂化的材料内部。锂化部分材料的向外膨胀导致了拉应力在点A处的产生,如图8(a)、(d)中的阶段a所示。当锂化界面扫过点A时,由于锂的嵌入所产生的锂化应变将受周围材料的限制,导致点A经受较高的压应力,如图8(b)、(d)中的阶段b所示。随着锂化界面的继续向前推进,在锂化界面附近产生的锂化应变将迫使已锂化的外层材料部分向外膨胀,致使点A的应力状态由压应力向拉应力转变,如图8(c)、(d)中的阶段c所示。这样,点A经受的高水平的拉应力将会导致裂纹在颗粒表面的产生,这与实验观察有着很好的吻合[17, 19, 27, 47]。Huang等[134]对单一相锂化和双重相锂化模型的比较更加证实:双重相锂化模式导致的表面周向拉应力能引起颗粒表面的破裂,而单一相锂化模式引起的表面周向压应力则与实验中观察到的裂纹通常在颗粒表面产生的事实相违背[17, 28, 47]。

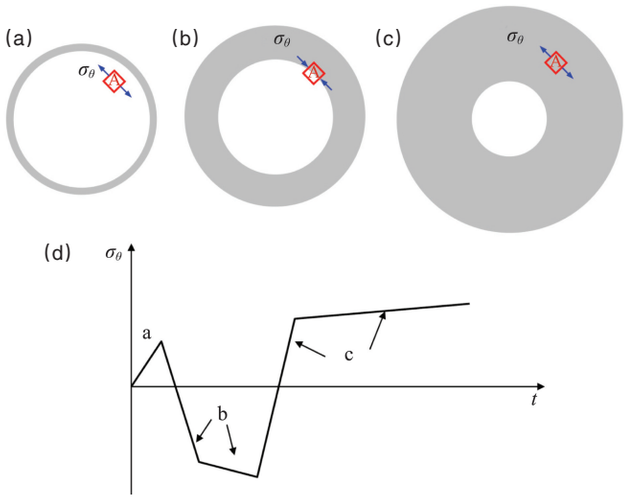


图8 球形颗粒圆周方向的应力σ_θ随着锂化界面向颗粒内部不断推进时的演变

Fig. 8 Illustration of the change of hoop stress σ_θ with the lithiation phase boundary moving toward the center of a spherical particle

基于透射电子显微镜实时实验平台观测,晶体硅的锂化过程具有以下重要特点:突变的锂化界面、依赖于晶体取向的膨胀及锂化引起的塑性大变形[19, 63]。在考虑这些特点后,Yang等[131, 135]建立了一个包含锂化界面上化学反应方向性的扩散-力学耦合有限元模型。基于该模型,Yang等模拟了不同取向的晶体硅纳米线的锂化过程(图9),并证实了锂化界面上化学反应的方向性决定了晶体硅纳米结构在锂化后各向异性的变形模式[131]。同时,应力分析表明,在锂化过程中,纳米线的表面将经受高水平的拉应力(图9)[135]。在锂化快速通道[17, 63](如{110}面)的交界处,应力集中将会导致表面裂纹的产生,而且由该模型预测出的裂纹起裂位置与实验能够很好地吻合[17, 19, 27]。此外,该模型还被用于研究其他高容量电极材料锂化过程中锂化动力学和应力的相互作用(图10)[137]。研究表明,锂化界面上化学反应的方向性将会导致〈111〉硅纳米线横截面上的锂化界面呈现出六边形形状(图10(a_1)),从而致使纳米线表面应力的集中(图10(a_2))及裂纹在该应力集中位置的发生[27]。然而,由于锗纳米线在锂化过程中锂化界面的弱方向性[17, 18, 29]和非晶体硅在锂化过程中锂化界面的无方向性,其锂化界面呈现圆形(图10(b_1)(晶体锗)、图10(c_1)(非晶体硅))。圆形的锂化界面能够有效缓解应力集中,使得相应的电极具有较高的抗破裂能力[17, 29, 49, 69](图10(b_2)、(c_2))。同时,有别于晶体硅和晶体锗,非晶体硅分2阶段的锂化模式使其在相同锂化程度下应力水平最低[49-50](图10(c_2)),因而具有更大的断裂临界尺寸和更高的结构稳定性[49, 69]。此外,锂化过程中在锂化界面附近产生的压应力将延缓锂化界面附近电化学反应的速率和降低锂的扩散性,导致锂化迟滞效应的产生[47, 67]。而且锂化界面上化学反应的方向性越明显,相应的迟滞效应就越大[137]。

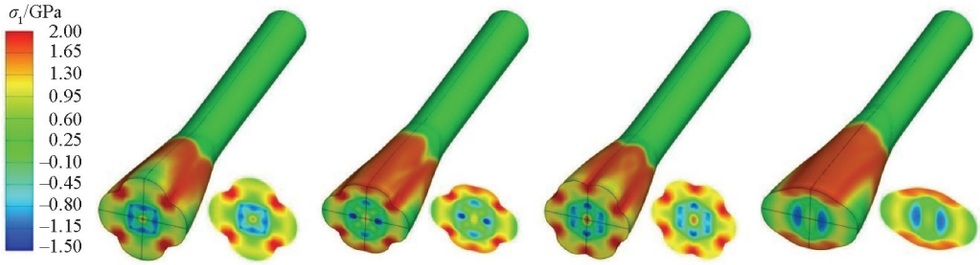


图9 最大主应力 σ_1 在部分锂化后的不同晶体硅纳米线中的分布

Fig. 9 Maximum principal Cauchy stress σ_1 distributions in the lithiated c-SiNWs

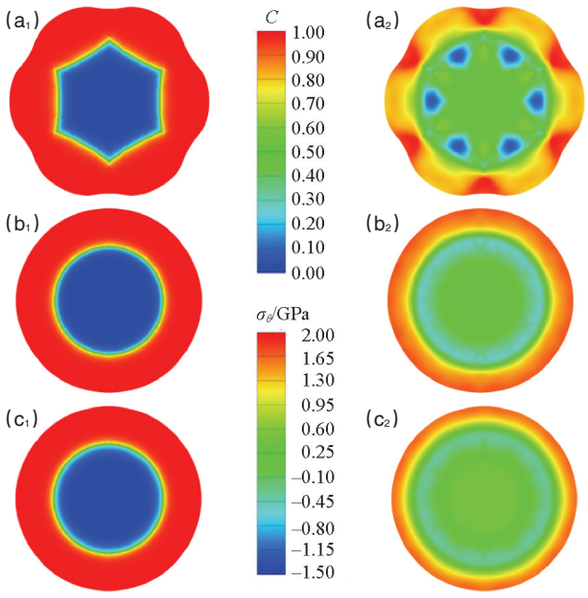


图10 锂浓度 c (a_1,b_1,c_1)和周向应力 σ_θ (a_2,b_2,c_2)在部分锂化后纳米线横截面上的分布

Fig. 10 Lithium (a_1, b_1, c_1) and hoop stress (a_2, b_2, c_2) distributions in the cross section of a partially lithiated nanowire

此外,基于双向耦合的扩散-弹塑性大变形有限元模型还被用于研究电极材料工作的环境因素(如来自外界的载荷、环境对其变形的约束等)对其充/放电的影响。其中,Gu等[18]模拟了弯曲的锗纳米线在充电过程中的表现,发现受拉应力影响一侧的锂化速率远高于受压应力影响的一侧,使得两侧锂化部分的不对称性,从而证实了外加力场对锂化动力学的影响。Xu等[138]研究证明,电极材料之间及电极材料与电池基底材料之间的相互作用也会影响锂化动力学,导致变形及应力在电极中的分布明显有别于独立电极的情况。

另外,相场法(phase field method)[139]由于在描述不同材料相之间界面的扩散和复杂微观结构演化方面所具有的优势,也被广泛应用于电极材料的研究中。例如,Chen等[140]建立了一个考虑弹塑性大变形的相场法模型,并用其模拟了晶体硅在充电过程中的相变、形状及应力的演变。Liu等[40]用相场法模拟了锗纳米线放电过程中多孔结构的产生和演变的过程。Liang等[70]用相场法模拟了镓纳米液滴放电过程中单一孔洞的产生和生长(图11[69])。图11中绿色代表Ga_xLi基底,白色区域为放电过程中产生的孔洞,红色代表界面区域。在放电过程中,孔洞在镓纳米颗粒与参照电极相接触的位置产生,并随着锂的脱嵌而不断生长。由于放电后的金属镓为液态,其表面能使得所产生的单一孔洞在三维空间呈现

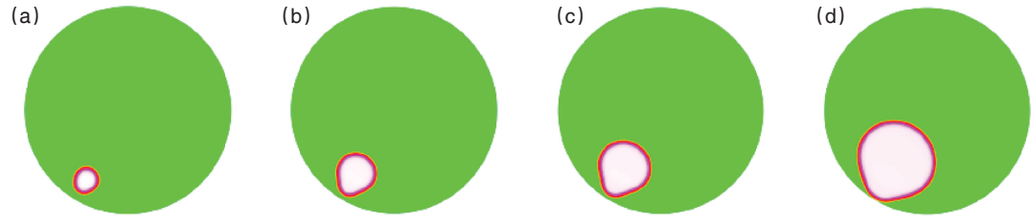


图11　镓纳米液滴放电过程中孔洞的产生和生长的相场法模拟

Fig. 11　Phase field modeling of void nucleation and growth during the delithiation of Ga nanodroplets

近似球状。此外,Klinsmann等[141]和Zuo等[142]分别用相场法研究了电极材料在电化学循环中的裂纹扩展问题。

3　结论与展望

由于近年来在锂离子电池研发方面的不懈努力,人们开发出了一系列可用于研究电极材料充/放电行为的实验方法,进行了相关数值模型,并在高容量电极材料充放电过程中的变形和破坏机理的认识上取得了突破性进展。基于这些新认识,设计出了多种新的电极结构去缓解电极材料在电化学循环过程中由体积不断膨胀/收缩引起的衰退和失效问题[60, 72, 143-148]。例如,双层硅-氧化硅纳米管在锂化之后只会向纳米管内部膨胀,从而保证了结构表面固态电解质界面的稳定性,使得由该双层纳米管构成的电极在经受6000次充/放电循环之后仍能保持85%的初始容量[143]。多层次的、孔状的电极结构通过有效缓解材料在充电过程中的向外膨胀使得电池具有更加稳定的循环性能[144]。这些新的设计使得基于高容量电极材料的锂电池(如硅-锂电池)在商业化层面取得长足的进步,并在可移动电子设备中得到初步应用。此外,依据对电化学-力学耦合问题的新的认识,Kim等[149]开发出了一套基于锂电池的机械俘能系统。

需指出的是,尽管本文仅对锂离子电池负极材料的研究作了初步的总结,但是所列实验和数值方法同样适用于正极材料的研究。研究表明,将负极材料的容量提高10倍仅能提高整个电池能量密度的47%,而正极材料的容量增加1倍就能导致整个电池能量密度57%的改变[8]。由此,基于这些负极材料的实验和数值方法,同样可以对新的正极材料展开研究和设计[150]。

此外,由于钠离子和锂离子具有较为相近的电化学性质,基于钠离子的电池系统(如钠-碳、钠-磷电池)近年来也吸引了广泛的关注[151]。由于钠丰富的储量和低廉的价格,钠离子电池作为对锂离子电池系统可选的补充和替代,将具有更为广阔的商业化应用前景,尤其在大型电网储能方面。因此,对锂离子负极材料的了解和认识同样可以应用于钠离子电池的开发。

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Advance in lithiation mechanics of anode materials in lithium ion battery

YANG Hui, QU Jianmin

Department of Mechanical Engineering, Tufts University, Medford, Massachusetts 02155, United States

Abstract Rechargeable lithium-ion batteries (LIBs), due to their high energy density and design flexibility, are the most prevailing and promising electrochemical energy storage and conversion devices, and are being widely used in portable electronics and electric vehicles. However, with their wide range applications, an urgent requirement is raised for the further improvement of their energy density. This paper presents an overview of recent advances in understanding the mechanical behavior of high capacity anode materials, i.e., silicon and germanium, in their charging/discharging cycling. Particular emphasis is placed on the state-of-the-art experimental and numerical studies of the deformation and failure of anode materials caused by the electrochemo-mechanical coupling. In addition, possible extension of current techniques to the research of other energy systems is discussed.

Keywords lithium-ion batteries; anode material; electrochemistry-mechanics coupling

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