矿物复合材料及其能量存储与能源催化应用

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摘要 矿物复合材料是近些年来发展起来的材料科学分支学科, 是与地质学领域的矿物岩石学融合创新的交叉领域. 它既具有矿物所具备的特定功能和属性, 又包含复合材料的鲜明特征, 在生态环境、新能源、大健康等领域具有广阔应用前景, 并符合“碳达峰、碳中和”的战略需求. 随着人类对能源可持续性的探索, 与能源相关的材料已然成为材料研究领域的热点, 其中, 具有来源丰富、低成本的矿物复合材料在能源和催化领域日益受到重视. 欲实现矿物复合材料在能量存储和能源催化等领域的应用, 仍待取得更多突破并亟待进一步研究与探讨. 本文从矿物复合材料的概念和学科分支的形成出发, 首先梳理了矿物复合材料的发展历程, 初步定义了矿物复合材料的分类, 归纳了常见矿物复合材料中矿物组分在能量存储和能源催化应用中的作用; 介绍了矿物复合材料在能量存储领域的应用, 包括压电自发电、超级电容器、二次电池等; 总结了矿物复合材料在能源催化领域的应用, 涵盖了以光催化/电催化析氢反应、热释电催化和压电催化为主的应用. 最后, 对矿物复合材料未来可能面临的科学问题和发展方向作出了展望.

关键词 矿物复合材料, 能量存储材料, 能源催化, 超级电容器材料, 电池材料

矿物复合材料是指组成复合材料的多种组分中, 含有一种或多种矿物组分从而使材料具有新性能的多相固体材料^[1], 且以矿物材料为主要或重要组分的复合材料^[2]. 其中的矿物组分可以包括工业矿物与岩石, 不仅可以是以长石、石英、铝土矿等为代表的工业矿物原料, 也可以是包括天然矿物材料和人工矿物材料的工业矿物材料^[3], 如石墨、云母、沸石等, 还有以高岭土、膨润土为主的工业岩石原料和工业固体废物等.

随着科学技术发展和社会进步, 地球科学的矿物学与材料科学的复合材料学得以交叉融合创新发展. 矿物复合材料作为一类新型复合、融合与杂化材料逐渐被研究者提出并接受^[1~9]. 美国亚利桑那大学Cal-

vert^[4]认为, 纳米矿物材料具有很多有趣的特性, 但往往需要借助微妙的表面处理或通过渗透一个相来发挥其作用, 如层状硅酸盐矿物填充聚合物复合材料的力学性能随矿物含量的提升往往比球形纳米颗粒填充聚合物效果要好. 随后, 美国康奈尔大学Giannelis研究组^[5]、麻省理工学院Thomas研究组^[6]相继报道了蒙脱石矿物插层纳米结构及其力学性能和阻隔性能等有关研究. 例如, Giannelis研究组^[7]设计了一种以层状硅酸盐为无机增强体的材料, 利用高分子复合的制备方法将层状硅酸盐插入单体和聚合物的层与层之间, 并通过离子交换反应实现了烷基铵阳离子衍生硅酸盐与各种聚合物的相容性. 本研究组^[8]利用蒙脱石制备了层状

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硅酸盐纳米复合薄膜, 认为在聚酰亚胺基体中加入适量蒙脱土, 可同时提高室温和超低温下的强度、模量和延展性。随着科技的发展, 矿物复合材料逐渐步入材料科学研究领域, 由此得到的聚合物基层状硅酸盐纳米复合材料表现出了与传统黏土复合材料不同的硬度、强度和阻隔性能。后来, 随着人们对天然复合材料认知的深入和提升, 矿物复合材料也融入了天然材料的设计理念, 为矿物复合材料的设计开创了新的理念, 为矿物复合材料学科分支的形成、发展及应用奠定了良好基础。例如, 鲍鱼壳^[9]是一种碳酸钙和有机材料组成的天然复合材料, 其抗断裂性比纯矿物的单晶高5000倍。Stupp研究组^[10]使用pH诱导肽两亲物自组装来构造纳米结构的纤维状支架并诱导羟基磷灰石矿化, 使羟基磷灰石沿晶体学c轴与有机纤维平行生长, 得到的类骨骼状层次结构, 为矿物复合材料的医学应用^[11]奠定了基础。

现如今, 随着国际材料科学的发展及我国对新能源技术和生态环境保护的大力支持, 能量存储与能源催化材料已逐渐成为功能材料领域的研究热点。例如, 由天然矿物石墨衍生出的石墨烯复合材料^[12]和黏土矿物插层复合材料^[13]已经在储能、催化、光电、生物医药等领域大放异彩。由天然辉钼矿衍生出的二维MoS₂^[14]复合材料具有典型的半导体特性。Ajayan研究组^[15]从天然赤铁矿(α -Fe₂O₃)中分离得到一种新的二维材料赤铁矿烯, 将其负载于二氧化钛纳米管阵列时, 表现出优异的光化学能量转换效应, 以及继承天然矿物的过渡金属氧化物^[16]、硫化物复合材料的多价离子存储和电催化应用等^[17,18]。因此, 下一代矿物复合材料的形态、功能和应用很可能会随着人类对材料物理机制的挖掘而不断地丰富和增长(图1)。

矿物复合材料具有诸多优点: 首先, 矿物来自于大自然, “人与自然和谐相处”和“天人合一”等理念早已深入人心, 由此衍生而来的矿物复合材料符合我国生态文明建设和“碳中和”战略需求; 第二, 地球及行星系的矿产资源丰富, 对降低复合材料成本有明显优势; 第三, 资源综合利用与矿物复合材料还包括对矿产资源开采和选矿过程产生的大量尾矿及工业固废进行综合利用, 有利于实现变废为宝、践行“两山理论”(绿水青山就是金山银山), 创新“双碳技术”(碳达峰与碳中和)。目前, 关于新材料在能源相关应用方面的研究论文和综述较多, 但鲜有从地球资源矿物材料角度出发, 系统评述由天然矿物加工或改性用于能量存储和能源催化应用的复合材料。

本文将从以下几方面重点介绍矿物复合材料在能量存储和能源催化领域的应用: (1) 矿物复合材料的分类和作用; (2) 矿物复合材料在能量存储领域的应用研究进展, 包括压电自发电功能、超级电容器、二次电池等; (3) 矿物复合材料在能源催化领域的应用研究进展, 包括光催化/电催化析氢反应(hydrogen evolution reactions, HER)、热释电/压电催化等。

1 矿物复合材料的分类和矿物的作用

按照常见矿物复合材料的类型和矿物组分的种类与形态^[1], 矿物复合材料往往可分为层状插层矿物复合材料^[19](蒙脱石、高岭石、蛭石、累托石、云母等复合材料)、链状硅酸盐矿物复合材料^[20](凹凸棒石、海泡石、硅灰石等复合材料)、多孔矿物复合材料^[21](硅藻土、沸石和膨胀珍珠岩等复合材料)、石墨矿物复合材料(改性石墨和石墨烯复合材料)、矿物纤维复合材料^[22](玄武岩纤维、岩棉纤维、硅酸铝纤维、水镁石纤维、

图1 (网络版彩色)矿物复合功能材料的发展历程

Figure 1 (Color online) A brief development history of mineral functional composites

硅灰石纤维等复合材料)、尾矿复合材料^[23](粉煤灰、煤矸石、微硅粉、矿物聚合物和改性赤泥等复合材料)和其他矿物复合材料(碳酸钙、水镁石、重晶石等复合材料^[24])等.按照其应用领域,可以分为矿物复合能源存储材料、矿物复合生态环境材料、矿物复合生物医药大健康材料、矿物复合光电信息材料等.

根据矿物组分,可将矿物在矿物复合材料中的作用分为3种:(1)矿物功能单元:本身具有直接应用功能属性的矿物,如黄铁矿复合材料用于钠离子存储^[25],赤铁矿复合材料用于超级电容器^[26];辉钼矿复合材料用于HER^[27]等.(2)矿物结构单元:本身无直接功能属性,主要起分散性、负载性等结构性作用.如埃洛石复合材料用于光催化HER^[28],尾矿复合材料用于资源化综合利用^[29]等.(3)矿物辅助单元:不具备直接应用功能属性,但具有辅助功能属性的矿物.如电气石复合材料用于光催化抗菌应用^[30],电气石本身不是光学半导体,却能自身受激产生载流子用于光催化;石墨烯不具备发电功能,但可作为聚偏氟乙烯-六氟丙烯共聚物(PVDF-HFP)薄膜自储能发电的填料调控压电-介电耦合发电^[31]等.

2 矿物复合材料在能量存储领域的应用

2.1 用于能量存储自发电功能的矿物复合薄膜材料

随着科技的发展和水平的提高,人类对可穿戴柔性材料的需求不断上升. PVDF及其聚合物由于其特有的压电性和柔韧性,具有制备柔性可穿戴传感器/储能器的潜力.但PVDF压电聚合物压电系数较小,压电响应弱于传统无机压电材料,而制备PVDF/矿物压电材料^[32]则能较好地解决该问题.以石墨烯^[33]、云母^[34]、蒙脱石^[35]、埃洛石^[36]等为代表的矿物材料表面拥有丰富的官能团或电子云,有利于诱导PVDF类高分子形成电活性的 β 相或者为电荷移动提供路径,且上述材料成本较低,制备工艺简单,是合成复合压电储能器材的理想材料之一.例如,最新研究表明^[37],二维层状云母片内部富含 K^+ ,在外加电场下可以沿着电场定向移动,使最初绝缘的云母具有导电性,且通过调节外加电场的大小可进一步在云母器件中得到具有不同单/双开关窗口的电流-电压特性等阻变特性.又如,以石墨为原料制备的石墨烯是碳基矿物材料的一种,由于其独特的二维结构、大的比表面积、优异的机械强度、良好的化学亲和性等优点在聚合物复合材料领域备受关

注,且该材料还具有一定的电能储存和转化潜力,被证明可以提升PVDF基薄膜的压电性能^[38].

本课题组^[39]用4-叠氮基四氟苯甲酸(TFB)对rGO薄膜进行化学修饰,将介电常数 k 提高至158并将薄膜的电损耗保持在0.42(100 Hz)的低水平,实现了柔性发电与电容器的双重应用.该薄膜装置为运动能量的收集和运动产生的电输出提供了良好的性能保障.如果直接在压电聚合物PVDF-HFP中添加导电填料石墨烯或炭黑等碳材料^[31],当填料含量低于渗透阈值时,可以有效地将低频机械能转换为电能,在力撤去后产生的开路电压逐渐降低为0,呈现压电-介电耦合效应.当增加至超过渗透阈值时,导电填料呈现屏蔽效果,无法进行压电-介电耦合.该过程的电压输出强度主要取决于薄膜恢复过程中可用的极化电荷数量和能量增益.这类石墨烯/高分子压电和介电材料或将促进功能材料系统的发展,且该类复合材料还可应用在传感^[39]、活性分子控释^[40]、表面拉曼增强^[41]、光催化增强^[42]等领域(图2).

2.2 用于超级电容器的矿物复合材料

超级电容器是一种功率密度高和充电速度快的新能源器件^[43,44],常常被用作锂离子电池的替代品.其工作原理分为双电层电容机理和赝电容机理.如果在正负极和电解液之间的两个电荷界面层发生了静电吸脱附,则称为双电层电容机理;如果发生了高度可逆的氧化还原反应,且没有质量转移局限性,则称为赝电容机理^[45,46];如果能像电池一样发生快速深入的离子嵌入脱出,则称为插入式赝电容机理.

用于超级电容器的电极材料包括具有双电层电容的碳材料以及具有赝电容的金属氧化物和导电聚合物^[47].其中,金属氧化物中的一些具有赝电容行为的矿物引起人们的关注,它们往往具有制备简单、资源储量丰富等优点,如水钠锰矿(birnessite, MnO_2)、钴尖晶石(Co_3O_4)、赤铁矿(Fe_2O_3)、辉钼矿(MoS_2)等.水钠锰矿^[48]是由 $[MnO_6]$ 八面体单元沿着 c 轴方向无限共享形成的二维层状薄片.由于具有一定的导电性、合适的层间距(~ 0.7 nm)^[49,50]和稳定的层结构,水钠锰矿很容易被 Li^+ 、 Na^+ 、 K^+ 、 H^+ 、 Co^{2+} 等阳离子交换、插层、嵌入或脱出.最新研究表明,其电容电荷存储由层间阳离子插层控制^[51].同时,由于纳米限域层间结构水的存在,增加了嵌入阳离子和水钠锰矿主体之间的距离,导致相互作用降低,表现出电容性质,并引起了极小的结构变化(图3(a), (b)).因此,其在锂离子存储和超级电容

图2 (网络版彩色)基于石墨烯/PVDF-HFP薄膜的压电感应电荷发生器及其拓展应用^[32]. Copyright © 2020, John Wiley & Sons
 Figure 2 (Color online) Graphene/PVDF-HFP-based film piezoelectric-induced charge generator and its extended applications^[32]. Copyright © 2020, John Wiley & Sons

器方面具有很好的应用前景。为提升水钠锰矿的电容值并拓展其超级电容器应用, Zhang等人^[52]使用碳纤维作为还原剂制备了蜂窝状水钠锰矿型 MnO_2 @碳纤维复合电极材料(图3(c), (d)), 得到的核壳结构比电容在 100 mA g^{-1} 时达到 295.24 F g^{-1} , 并具有良好的倍率性能和循环稳定性, 即使在3000次循环后仍具有96.4%的比电容(图3(e), (f)). 制备的对称型 MnO_2 @碳纤维// MnO_2 @碳纤维超级电容器器件的最高能量密度达到 22.2 W h kg^{-1} , 功率密度为 400 W kg^{-1} . 此外, 作为代表性的尖晶石氧化物, Co_3O_4 被广泛用于二次电池^[53,54]、超级电容器^[55]和电催化^[56]等电化学应用中。其晶胞由8个面心立方单元构成, Co^{3+} 和 Co^{2+} 分别占据了8个四面体和16个八面体^[57], 其中四面体和八面体占据的原子分别呈现高自旋 $\text{Co}^{2+}(\text{e}^4 \text{t}_2^3)$ 和低自旋 $\text{Co}^{3+}(\text{t}_{2\text{g}}^6 \text{e}_\text{g}^0)$ 态(图3(g)).

本课题组^[58]将钴尖晶石负载在p型光催化材料g-

C_3N_4 上构成p-n结复合材料, 制备得到对称型 $\text{Co}_3\text{O}_4/\text{g-C}_3\text{N}_4$ @碳布// $\text{Co}_3\text{O}_4/\text{g-C}_3\text{N}_4$ @碳布超级电容器。其在 60 mA cm^{-2} 电流密度下经5000圈循环, 容量保持率可达83.3%。我们还研究了光辐照策略对 $\text{Co}_3\text{O}_4/\text{g-C}_3\text{N}_4$ 复合材料的电容影响(图3(h)~(j)). 结果表明, 光辐照后 $[\text{CoO}_6]$ 八面体中的电子自旋和配位态发生了显著变化, 其八面体结构扭曲提高了Co-O键的强度并提供足够的氧化还原活性位点, 大大提高了材料的电导率和电荷转移效率。因此, 在 26.6 mA cm^{-2} 的电流密度下, 制备的对称型超级电容器器件在模拟太阳光辐照后, 比电容增加了70.6%。同时, 在 6.4 kW kg^{-1} 的功率密度下, 光辐照将能量密度从7.5提高至 12.9 W h kg^{-1} (图3(j, k)).

2.3 用于二次电池的矿物复合材料

2.3.1 有色金属矿物复合材料

尽管锂离子电池在储能领域得到了广泛的应用,

图3 (网络版彩色)用于超级电容器的水钠锰矿型 MnO_2 复合材料(a-f)和钴尖晶石复合材料(g-k)。水钠锰矿的 $[\text{MnO}_6]$ 八面体结构单元(a)和用于离子存储的晶体结构示意图(b)^[50], Copyright © 2020, Royal Society of Chemistry. (c, d) 水钠锰矿/碳纤维纳米复合材料的扫描电子显微镜(SEM)照片。电化学储能机理(e)及其循环稳定性(f)^[52], Copyright © 2015, Elsevier. (g) 钴尖晶石的 $[\text{CoO}_6]$ 八面体结构单元堆积图^[54], Copyright © 2017, American Chemical Society. (h) 制备的钴尖晶石/ $\text{g-C}_3\text{N}_4$ 纳米复合材料的透射电子显微镜照片(TEM)。 (i) 钴尖晶石/ $\text{g-C}_3\text{N}_4$ @碳布基超级电容器器件示意图。器件的恒流充放电性能(内嵌图)(j)和循环稳定性及其超级电容器器件在光照中的恒流充放电结果(k)^[58], Copyright © 2020, John Wiley & Sons

Figure 3 (Color online) Birnessite MnO_2 composite (a–f) and cobalt spinel composite (g–k) for supercapacitors applications. $[\text{MnO}_6]$ octahedral structure unit (a) and crystal structure diagram for ion storage (b)^[50], Copyright © 2020, Royal Society of Chemistry. (c, d) SEM images of Birnessite MnO_2 /carbon fiber nanocomposites. Energy storage mechanism (e) and its electrochemical cyclic stability (f)^[52], Copyright © 2015, Elsevier. (g) Cobalt spinel structure with $[\text{CoO}_6]$ octahedral units^[54]. (h) TEM image of $\text{Co}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposites. Diagram of cobalt spinel/ $\text{g-C}_3\text{N}_4$ @carbon cloth supercapacitor device (i) and its galvanostatic charge-discharge performance (GCD) (inside image) and electrochemical cyclic stability (j). (k) The GCD results of the supercapacitor with photo-irradiation^[58], Copyright © 2020, John Wiley & Sons

然而锂的价格和安全性问题仍然是当今社会面临的巨大挑战。相应地, 由于硫和钠在地壳中储量丰富, 且为轻质元素, 因此, 钠离子电池和锂硫电池^[59–63]应运而生。天然矿物材料中的一些金属硫化物本身具有高的理论容量和低放电平台, 往往具有相当的储能性能, 主要是石墨和天然硫族化合物^[64], 如闪锌矿^[65]、辉锑矿(Sb_2S_3)和黄铁矿^[66]等。然而, 由于天然矿物的电导率较差, 常常需要设计矿物复合材料提高其离子迁移和结构稳定性。

Sb_2S_3 属斜方晶系 $Pnma$ (图4(a))^[67], 每mol可以容纳12 mol Na^+ , 显示出比 Sb_2O_3 更高的电导率和理论比容量(947 mAh g^{-1})^[68]。Sun研究组^[60]认为辉锑矿的储能失效机制起源于 Sb_2S_3 体积膨胀带来的Sb、S两相分离, 从而破坏了Li/Na-S可逆反应的稳定性。因此, 通过复合碳材料设计了具有双碳原子的Sb–C键结构, 结果表明

碳原子的引入不仅缓解了电极的体积膨胀, 还通过界面桥键形成了快速传输的离子通道。制备的辉锑矿@双碳结构复合材料($\text{M-Sb}_2\text{S}_3@\text{DC}$)在 5.0 A g^{-1} 时, 锂存储容量约为 674 mAh g^{-1} ; 用作钠离子电池负极时, 其倍率容量在 3.0 A g^{-1} 时可达 366 mAh g^{-1} , 远大于同电流密度下纯 Sb_2S_3 ($\text{M-Sb}_2\text{S}_3$)的容量。与镍铁普鲁士蓝类似物组装的全电池, 在 0.5 A g^{-1} 时第5圈可逆容量仍可达 330 mAh g^{-1} (图4(b)); 在 0.5 A g^{-1} 下经过30个循环后, 其容量可以保持在 237 mAh g^{-1} , 展示了辉锑矿复合材料作为钠离子全电池电极的优势(图4(c))。

在锂硫电池中^[63], S_8 还原为长链 Li_2S_x ($6 < x \leq 8$)并缓慢溶解于醚类电解液, 进而逐步还原为短链 Li_2S_x ($2 < x \leq 6$)和 Li_2S , 随着其在醚类电解液中溶解和迁移, 使活性物质获得电子并完成放电反应。然而, 硫及其还原产物 Li_2S_2 和 Li_2S 的绝缘性和多硫化物的溶解/扩散阻

图 4 (网络版彩色)分别用于钠离子电池负极和锂硫电池正极的辉锑矿(a~c)和黄铁矿(d~f)复合材料。(a) 辉锑矿的晶体结构^[59], Copyright © 2016, American Chemical Society. 辉锑矿复合材料用于钠离子存储的恒流放电性能(b)和用于全电池的循环性能(c)^[60], Copyright © 2020, John Wiley & Sons. (d) 黄铁矿的晶体结构^[61], Copyright © 2015, Royal Society of Chemistry. $\text{FeS}_2/\text{FeS}/\text{S}$ 复合材料的制备过程(e)和与CNT/S的容量对比(f)^[62], Copyright © 2019, John Wiley & Sons

Figure 4 (Color online) Stibnite composite (a–c) and pyrite composite (d–f) for sodium-ion batteries anode and lithium-sulfur batteries cathode, respectively. (a) Crystal structure of stibnite^[59], Copyright © 2016, American Chemical Society. The GCD performance of the as-prepared pyrite composite for Na^+ storage (b) and the cyclic performance of the full sodium-ion battery (c)^[60], Copyright © 2020, John Wiley & Sons. (d) Crystal structure of pyrite^[61], Copyright © 2015, Royal Society of Chemistry. The preparation of $\text{FeS}_2/\text{FeS}/\text{S}$ composite (e) and the comparison of capacity between $\text{FeS}_2/\text{FeS}/\text{S}$ composite and CNT/S composite (f)^[62], Copyright © 2019, John Wiley & Sons

碍了锂硫电池性能的发挥。为此, Li研究组^[62]使用连续球磨工艺合成了黄铁矿(FeS_2)/ FeS/S 复合材料, 在30次循环后的最大可逆容量可达 $1044.7 \text{ mAh g}^{-1}$, 峰值体积容量为 2131.1 Ah L^{-1} , 远高于碳纳米管复合材料的体积比容量(452 Ah L^{-1})(图4(d)~(f))。密度泛函理论计算结果证实了黄铁矿组分对高阶多硫化物的裂解反应具有很强的催化作用, 且复合物中的 FeS 纳米颗粒组分也可以被多硫化物部分氧化形成 FeS_2 , 从而在放电过程中实现快速还原反应。因此, 黄铁矿/ FeS/S 复合材料具有比CNT/S复合材料更好的充放电性能。

2.3.2 非金属矿物复合材料

埃洛石是一种具有中空管状结构且表面带有相反电荷的天然黏土矿物, 其化学成分为铝硅酸盐($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$), 因其具有广泛的可获得性、低成本和生物相容性而被广泛应用于药物控制释放系统、热力学增强材料和膜过滤等^[69]领域。此外, 由于埃洛石是天然的硅酸盐矿物, 还常常被用作制备硅负极的硅源^[70]。例如, Park研究组^[71]采用熔盐剥落和化学还原进行的一步处理工艺制备了高纯度5 nm厚的介孔硅纳米片, 而采用两步处理(即先剥落硅酸盐片, 再化学还原)则不

能达到这样的二维结构和尺寸。一步法制备的碳包覆硅纳米片负极在 1.0 A g^{-1} 时的可逆容量达 865 mAh g^{-1} , 经500次循环后容量保持率为92.3%。即使纳米片电极在200次循环后也只表现出42%的体积膨胀。

埃洛石复合材料用作二次电池往往可以有效改善电解质的锂离子导电性、隔膜的质子交换导电性及热力学稳定性。Liu研究组^[72]将天然埃洛石纳米管(HNT)直接用作锂硫电池的固态电解质填料, 通过调整HNT/聚环氧乙烷(PEO)质量比, 使锂硫电池可以在25和 100°C 下正常工作, 且离子电导率分别达到 1.11×10^{-4} 和 $2.14 \times 10^{-3} \text{ S cm}^{-1}$ 。埃洛石纳米管表面上相反的表面电荷将锂盐分离成锂离子, 锂离子吸附在带负电的二氧化硅表面上, LiTFSI中的 $(\text{NSO}_2\text{CF}_3)_2$ 则倾向于吸附在带正电的 $-\text{Al}-\text{OH}$ 官能团表面。同时, PEO上的环氧乙烷单元的孤对电子将与埃洛石纳米管外表面的锂离子相互作用, 使聚合物有序地与HNT交联(图5)。由于HNT、LiTFSI和PEO之间存在Lewis酸碱相互作用, 可以有效地将电解质离子排列到三维通道中并显著缩短锂离子的自由迁移距离, 有效抑制了PEO结晶并降低相转变温度。该策略为锂离子提供了快速传输通道, 并

图5 (网络版彩色)用于全固态锂硫电池电解质的埃洛石纳米管纳米复合材料^[72]. Copyright © 2017, Elsevier
Figure 5 (Color online) Halloysite nanotube composite electrolyte for all-solid-state lithium-sulfur batteries^[72]. Copyright © 2017, Elsevier

使固态电解质聚合物薄膜更加均匀, 且具有更好的机械强度. Sui研究组^[73]制备了可生物降解的醋酸纤维素/聚乳酸/HNT纳米纤维膜, 用作锂离子电池聚合物凝胶电解质. 他们认为HNT的加入显著抑制了聚合物的结晶行为, 并提高了聚合物纳米纤维膜的热稳定性. 制备的纳米复合纤维膜的聚合物凝胶电解质具有 $1.52 \times 10^{-3} \text{ S cm}^{-1}$ 的高离子电导率、合适的锂离子迁移数和良好的电化学稳定性. 此外, 使用该纤维膜制备的Li/GPE/LiCoO₂电池的初始放电容量、循环性能和倍率性能均优于商用Celgard@2500电池.

因此, 黏土类矿物在二次电池中常常用于制备隔膜和电解质材料, 所制备的黏土类矿物复合电解质/隔膜材料往往具有良好的锂离子迁移行为和热力学稳定性.

3 矿物复合材料在能源催化领域的应用

3.1 用于HER的矿物复合材料

随着人类对新能源的开发, 氢能作为一项非常有潜力的可再生能源被大力推崇. 由于传统的工业制氢对化石能源比较依赖以及对自然环境的污染, 如水煤气和烯烃裂解制氢都会不可避免地释放污染物, 因此电解水产氢^[74]被认为是一项绿色环保的制氢技术. 其阴极发生HER过程, 往往需要使用活性位点丰富、电导率高、循环稳定性好和热力学活性强的电催化剂. 尽管Pt基金属催化剂的催化活性很强, 但其高昂的价格和有限的地球储量往往难以实现商业化应用. 据报道,

从辉钼矿生产MoS₂电催化剂生产率的实验值可达 1.3 g h^{-1} ^[75], 价格仅为~10美元/m², 比商业Pt/C电催化剂的价格低约30倍. 因此, 开发价格低廉的矿物复合材料用于HER很有必要.

部分天然矿物本身具有一定的HER性能和电导率, 如辉钼矿、黄铁矿^[76-79]、石墨^[80]等, 地球储量丰富的其他化合物^[81]如水滑石类化合物、硫族化合物(CoS₂、NiS₂及其合金^[82])、硫盐也具有优异的电催化活性. 如果将它们加工制备成复合材料, 有利于暴露其电催化活性位点. 据报道, 使用FeS₂薄膜用于电催化HER, 在 $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ 中测试时, 10 mA cm^{-2} 时的过电位可以达到约260 mV^[83]. Hu研究组^[76]利用黄铁矿中的FeS₂颗粒和石墨烯制备了FeS₂-RGO复合膜(图6(a), (b)). 致密的FeS₂纳米粒子在短时间(≈12 ms)通过高达~2470 K的高温电流感应在RGO内原位形成并均匀分布. 与具有优异耐久性的可逆氢电极相比, 嵌入RGO之间的FeS₂纳米颗粒具有出色的HER电催化活性, 在139 mV的低过电位下可实现 10 mA cm^{-2} 的电流(图6(c), (d)). 通过第一性原理计算了H在S末端的(100)、(111)和(211)面上的吸附吉布斯自由能(ΔG), 发现FeS₂(100)表面在几何结构和吸附自由能方面都表现出了更好的HER活性(图6(e)).

为了激活惰性边缘位点并提升其电催化析氢性能, 进行复合材料的表面工程和界面工程常常必不可少. 本研究组^[77]使用了一种层层自组装策略, 将两种导电聚合物(聚苯胺(PANI)和聚吡咯(Ppy))分别与MoS₂复合, 通过第一性原理计算, 在PANI/MoS₂和Ppy/MoS₂中

图 6 (网络版彩色)用于HER的黄铁矿复合材料(a-e)和辉钼矿复合材料(f, g). (a) 黄铁矿原矿及其微颗粒形貌. (b) 制备的FeS₂/rGO复合薄膜. 微纳米结构黄铁矿的HER极化曲线(c)和塔菲尔斜率(d). (e) 计算的H在3种FeS₂晶面上的吸附构型和吸附能^[76], Copyright © 2017, John Wiley & Sons. 剥离后的辉钼矿MoS₂的形貌(f)及第一性原理计算结果(g)^[77], Copyright © 2021, American Chemical Society

Figure 6 (Color online) Pyrite composite (a-e) and molybdenum composite (f, g) for HER applications. (a) The morphology of pyrite ore and its microparticles. (b) The as-prepared FeS₂/rGO composite film. The HER polarization curves (c) and Tafel slopes of nano-/micro-structured FeS₂ (d). (e) The calculated configurations and adsorption energy of H adsorption on three different FeS₂ crystal planes^[76], Copyright © 2017, John Wiley & Sons. The morphology of molybdate MoS₂ nanosheets after exfoliation (f) and the related first principle calculation results (g)^[77], Copyright © 2021, American Chemical Society

S原子位置顶部的 ΔG 值显著降低至0.0512和0.074 eV, 且面内S原子可以被构建的界面激活, 并具有与Mo边缘活性位点相当甚至更高的HER活性(图6(f), (g)). 因此, 构建层层自组装的辉钼矿复合催化剂有利于实现催化剂界面结构的精细调节, 从而平衡活性位点的数量和电荷转移性质.

3.2 用于光催化产氢的矿物复合材料

自1972年被Fujishima和Honda^[84]报道以来, 光催化技术引起人们对太阳能光解水、光催化污染物降解、抗菌和光催化合成燃料等应用^[85]的研究兴趣. 基于光催化反应的原理, 设计光催化剂往往需要构造具有良好光吸收、电荷分离和催化反应活性的半导体或异质结. 层间以碳酸盐作为补偿阴离子或过渡金属离子的水滑石(layered double hydroxides, LDHs)材料, 曾被广泛用作碱催化反应或氧化还原反应的多相催化剂. 后

来, 它们的光催化性能逐渐被报道^[86,87]. 由于LDHs含有两种不同的金属, 且两种金属的比例可控, 因此, LDHs可作为提供“掺杂半导体”的理想光催化材料. 例如, 当较高价金属是钛或二价金属是镍时, 可以获得类似二氧化钛和氧化镍的材料^[88]. Zhang研究组^[89]利用共沉淀法合成了富含氧缺陷的M^{II}M^{III}-LDHs(M^{II} = Mg、Zn、Ni、Cu; M^{III} = Al、Cr)系列纳米片光催化剂, 其中, CuCr-LDHs纳米片光催化剂在可见光照射下(甚至波长>500 nm)表现出优异的水相光还原N₂活性. 第一性原理计算结果表明, 超薄LDHs纳米片中氧空位引起的[MO₆]八面体单元的畸变显著增加了N₂吸附, 而且促进了光生电荷从LDHs转移到N₂, 同时还充当了N₂和H₂O分别反应成NH₃和O₂的催化活性位点.

然而, 天然矿物材料中, 类似水滑石、赤铁矿^[90,91]的符合严格意义半导体属性的材料却很少. 改性黏土矿物的引入往往可以提高光催化剂的分散性和比表面

积,为催化反应提供活性物种负载位点.这些天然矿物^[92,93]包括埃洛石、海泡石、凹凸棒石、石墨、磷灰石、膨润土、硅藻土、蛭石、高岭土、石英砂、沸石、累托石、碳酸钙、电气石、重晶石等.例如, Ma等人^[94]在凹凸棒土(attapulgite, ATP)表面负载了均匀分布的 Ag_3PO_4 纳米粒子, Ag_3PO_4 的光催化活性和稳定性显著提高.此外, Ag_3PO_4 -ATP-Co催化剂的溶液在90 min内(包括60 min吸附时间)的酸性橙II降解率可达99%. ATP载体大大提高了催化剂稳定性,且光催化复合材料中的银含量从纯 Ag_3PO_4 中的77.3wt%降至复合材料中的18.8wt%,有效降低了污染处理成本.此外, Ag_3PO_4 也可以作为一种涂层负载于其他矿物载体上,以避免纳米颗粒在溶液中的团聚.

Lin等人^[95]通过在HNT上原位生长 $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$,制备了 $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}@\text{HNT}$ 复合材料(图7(a)),其最优光解水产氢速率高达 $25.67 \text{ mmol g}^{-1} \text{ h}^{-1}$,周转频率可达 5006 h^{-1} ,是纯 $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ 的7.03倍,表观量子效率达到32.29%(图7(b), (c)).在大幅提高光解水产氢性能的同时,其还展示出良好的储氢性能. Wang等人^[96]验证了CdS/黏土系列矿物(包括埃洛石、海泡石、坡铝石、蒙脱石)复合材料具有光催化降解刚果红性能,证实

HNT矿物组分的引入不仅能防止CdS的团聚,还能阻止CdS在光催化降解过程中的电化学腐蚀.

因此,构建矿物复合光催化材料可以显著提升半导体光催化反应活性,大大降低光催化剂的成本,同时为光催化材料的回收再利用提供有利条件,有利于光催化技术走向商业化应用.

3.3 用于压电催化和热释电催化的矿物复合材料

热释电材料可以将环境中的热能转化为电能并生成极化载流子.近年来,随着 LiTaO_3 、 BaTiO_3 ^[97]、 ZnO 、 BiFeO_3 ^[98]和 ZnSnO_3 等材料在温度变化条件下的热释电催化反应相继被报道,热释电催化和压电催化开始成为催化领域兴起的新方向.它们都依赖于催化剂对外场的极性.电气石属于 $R3m$ 空间群的三方晶系^[99],具有唯一的3次旋转对称轴,这种对称型使电气石晶体的顶部和底部始终具有不同的极性且具有热释电和压电特性(图8(a)).据报道,微米级电气石表面上存在约 106 V m^{-1} 的电场^[100]. Yin研究组^[101]通过简便的沉淀-水热法合成了 ZnO /电气石复合材料,与纯 ZnO 相比,该复合材料对亚甲基蓝(MB)的降解表现出显著增强的光催化活性,在连续5个光催化反应循环后,降解率仍

图7 (网络版彩色)用于光催化产氢的埃洛石复合材料.埃洛石@ $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ 光催化复合材料的制备(a)及其周转频率(TOF)(b)和表观量子产率(AQY)(c). Copyright © 2019, John Wiley & Sons

Figure 7 (Color online) Halloysites composite for photocatalytic H_2 production. The synthesis of halloysites@ $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ composite (a) and its turnover frequency (b) and apparent quantum yield (c). Copyright © 2019, John Wiley & Sons

图 8 (网络版彩色)用于热释电催化和压电催化的矿物复合材料。用于热释电催化的电气石^[100](a)、ZnO/电气石复合材料^[101](b)和Sillen-Aurivillius结构的 $\text{Bi}_4\text{Nb}_6\text{O}_{18}\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$)钙钛矿材料晶体结构(c)。Copyright © 2008, American Chemical Society; Copyright © 2019, Elsevier。负载Pt的 $\text{Bi}_4\text{Nb}_6\text{O}_{18}\text{X}$ 材料的形貌(d)及其光-压电协同催化应用^[102](e)。Copyright © 2020, John Wiley & Sons

Figure 8 (Color online) Mineral composite materials for pyroelectric catalysis and piezoelectric catalysis. Tourmaline^[100] (a) and ZnO/tourmaline composite materials^[101] (b) for pyroelectric catalysis, and crystal structure of Sillen-Aurivillius-structured $\text{Bi}_4\text{Nb}_6\text{O}_{18}\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) perovskite materials (c). Copyright © 2008, American Chemical Society; Copyright © 2019, Elsevier. The morphology of Pt-loaded $\text{Bi}_4\text{Nb}_6\text{O}_{18}\text{X}$ materials (d) and its applications for synergistic photo-piezoelectric catalysis^[102] (e). Copyright © 2020, John Wiley & Sons

能保持90.8%(图8(b))。他们认为电气石不仅可以提高ZnO纳米片的比表面积,以暴露更多催化活性位点的形式提升其热释电催化活性,而且可以诱导光生电子-空穴对的定向传输和分离,从而提高光催化活性。

由于压电体中非中心对称的晶体结构,在外部应力作用下会在晶格内部形成非零态的偶极矩,并在压电体两侧引起压电极化电荷产生压电电势^[102~104]。它们不仅能促进光生载流子在材料体相和表面的分离,也能调节界面处的能带弯曲和电荷迁移。Xu研究组^[105]利用超声波震动诱导 BaTiO_3 微米树状晶体和ZnO纳米纤维的压电电荷产生,在足够的电势下,水中应变的压电体触发水的氧化还原反应,产生氢气和氧气。 BaTiO_3 微米晶体在前50 min的氢气产率达到了 $1.25 \times 10^{-2} \text{ ppm s}^{-1}$ (ppm, parts per million)。ZnO纳米纤维的氢气产率在前40 min达到 $3.4 \times 10^{-3} \text{ ppm s}^{-1}$,且与氧气产率的比值符合2:1的化学计量比,验证了压电体的机械能向可再生能源的直接转化。Jia研究组^[106]报道了ZnO纳米棒对光和压电的能量捕获应用,该纳米棒在紫外光照射和振动的共同作用下,在100 min内对酸性橙7的分解率达到约80.8%,均高于光催化和压电催化各自的降解率。Hu等人^[102]报道了一种极性Sillen-Aurivillius结构的 $\text{Bi}_4\text{Nb}_6\text{O}_{18}\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$)钙钛矿材料用于压电催化产氢,该钙钛矿由单层 $[\text{NbO}_6]$ 八面体和 $(\text{Bi}_2\text{O}_2)_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$)

组成(图8(c)),通过压电响应力显微镜和扫描开尔文探针显微镜证实了它的压电性能。在光和超声的共同照射下, $\text{Bi}_4\text{Nb}_6\text{O}_{18}\text{X}$ 表现出优异的光催化氧还原反应(oxygen reduction reaction, ORR)产 H_2O_2 活性,超过了光和超声单独作用下产量的总和。 $\text{Bi}_4\text{Nb}_6\text{O}_{18}\text{Br}$ 的 $\cdot\text{O}_2^-$ 、 $\cdot\text{OH}$ 和 H_2O_2 产率分别达到98.7、33.2和 $792 \mu\text{mol g}^{-1} \text{ h}^{-1}$ 。在其表面负载助催化剂Pt后,光催化 H_2 的生产率提高了28.7倍(图8(d), (e))。这种显著增强的活性来自于能带弯曲、极化电场和催化反应活性位的富集,协同促进了电荷的有效分离。

综上所述,构建矿物复合热释电催化和压电催化材料的优势如下:其一,利用以电气石为代表的压电/热释电矿物材料的内建电场可以促进载流子分离,减少光生电子-空穴对的复合效率以增强光催化性能;其二,以矿物作为基底可以提高光催化剂的分散性,有利于克服纳米材料易于团聚的缺点;其三,能够有效降低光催化剂的成本,更有利于商业化应用。

4 总结与展望

本文综述了近年来矿物复合材料在能量存储和能源催化等方面的综合应用,首先梳理了矿物复合材料的发展历史,并按照矿物复合材料的分类与组成进行归纳,形成如下结论:(1) 对用于电化学能源存储和机

械能存储的矿物功能单元或辅助单元的改性、修饰或复合,可大大提高其储能密度和能量转换效率。如水钠锰矿复合材料用于超级电容器,石墨烯高分子复合材料用于压电-介电耦合的自发电等。(2) 对用于能源光催化、压电和热释电催化领域的矿物结构单元或辅助单元进行负载或复合,有利于提高光吸收、抑制光生载流子再复合和促进表面反应,提高催化反应活性。(3) 对用于能源电催化领域的矿物进行剥离并复合,有助于大大暴露其催化活性位点,降低HER过程所需的活化能等。

现今,矿物复合材料作为一个新的发展领域已初步形成,代表着对矿物功能性开发提高到新的水平。随着能源热点领域研究的不断发展,矿物复合材料领域的研究水平也在不断提高,已逐渐由早期的具有良好结构性能和热力学性能的矿物复合材料逐渐拓展为面向多功能、现代化的矿物功能复合材料,但是该领域在科学和产业化的道路上仍然面临着许多问题。如矿物复合材料的批量化制备、矿物复合材料的稳定性问题等。此外,矿物复合材料各组分的作用机理还不是很明确。例如,矿物复合电极材料中各组分配置如何优化,

如何设计均一和稳定的矿物复合光催化剂,如何提升矿物复合材料中矿物原料的纯度等一系列问题。基于以上问题,如下建议可供参考:(1) 利用第一性原理、模拟仿真等技术,拓展对矿物晶体构效关系的研究,明确原子掺杂、缺陷浓度调控、原子占位、化学键合、异质结构建等因素对矿物晶体或矿物复合材料性能的影响。(2) 发展现代原位表征技术,通过电化学原位XRD、X射线光电子能谱、X射线精细吸收谱、红外光谱、电化学石英晶体微天平仪器明确矿物电极材料在电化学过程中的机理与变化规律,明确矿物复合光电催化剂的反应决速步和中间产物对催化剂表面反应的影响。(3) 工业上应充分利用选矿手段如重选、浮选、磁选、生物选矿等工艺对天然矿物原料深加工,提高原有矿石的品位,保证样品的纯度和结晶度;针对矿物复合材料功能对天然矿物表面进行充分的改性,如表面电性、表面官能团富集度等。此外,需要充分结合物理化学表征手段和理论计算与分析仿真强化矿物复合材料作用机制,方可有利于指导未来新功能矿物复合材料的设计,从而获得价廉、绿色生态环保的矿物复合材料。

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Summary for “矿物复合材料及其能量存储与能源催化应用”

Mineral composite materials and their energy storage and energy catalysis applications

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Mineral composite material is a cross-field of mineralogy and composite material that has emerged in recent years. These materials have specific functional properties of minerals and the unique characteristics of composite materials. Energy-related materials are currently a research hotspot. However, a systematic review of energy storage and energy catalysis in composite materials from natural minerals is few. Mineral composite materials have the following advantages. (1) Minerals are natural composite materials conducive to ecological civilization construction. (2) Mineral resources are abundant on the Earth, which means pronounced cost reduction in composite materials. (3) Mineral-derived tailings wastes can be comprehensively turned into treasure. This study presents the advances in energy storage and catalysis applications of composite materials from a mineral composite perspective.

First, we discussed this discipline's evolution, the development process, and classified mineral composite materials. Second, we introduced the applications of mineral composites in the field of energy storage, such as piezoelectric self-power generation, supercapacitors, and secondary batteries. Finally, we summarized the applications of mineral composites in the domain of energy catalysis, including electrocatalysis, energy photocatalysis, and pyroelectric/piezoelectric catalysis.

The regulation of mineral functions or auxiliary units can significantly improve energy storage and catalytic activities. Specifically, the mineral loading/recombination strategy for photocatalytic applications helps inhibit the recombination of photo-generated carriers and enhance their light absorption. Stripping the mineral ore and forming a composite material for energy electrocatalysis are beneficial in exposing its active catalytic sites and reducing the activation energy required for hydrogen evolution reaction applications.

Mineral composite materials have evolved from mechanical functional mineral composite materials to multi-functional mineral composite materials. However, numerous problems remain on the path to scientific research and industrialization, such as batch preparation and mineral composites' stability. We conclude that strengthening the practical design of multi-functional mineral composites enables us to understand the mechanism of mineral composite materials by combining crystal structure design, physical and chemical characterizations, and theoretical calculation/simulation. Further, we presented future scientific challenges and development opportunities for mineral composite materials.

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