

功能煤基碳材料制备及电化学应用研究进展

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摘 要: 功能煤基碳材料具有来源广泛、价格低廉、结构易调控等优点, 被广泛用于电化学能量/物质转化与储存领域, 成为当前国际前沿研究热点之一。本文分析了无烟煤、烟煤、褐煤、煤沥青等代表性煤炭原料的结构特点与适用性, 系统评述了制备功能煤基碳材料的液相法、固相法、气相法、直接炭化法和偶合法等, 详细分析了各制备方法的优势与调控机制, 综述了功能煤基碳材料在燃料电池、电催化 CO_2 还原、超级电容器和锂/钠离子电池等领域的应用研究进展, 揭示了材料制备-结构调控-性能优化的内在关联性。在此基础上, 分析讨论了功能煤基碳材料面临的制备工艺优化、性能提升机制研究和产业化关键挑战等问题, 以期为高性能功能煤基碳材料的设计、合成和应用提供理论和技术支撑。

关键词: 煤炭; 功能煤基碳材料; 电化学能量/物质转化与储存; 结构调控; 构效关系; 煤炭清洁高效利用

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煤炭是地球上储量丰富、分布广泛的化石资源, 对世界各国的经济发展和社会进步起到极为重要的作用, 被誉为“工业的食粮”“黑色的金子”^[1-2]。煤炭的主要利用途径有直接燃烧发电和供热、煤气化、煤液化和煤焦化等^[3-4]。然而, 传统的煤炭利用方式带来的环境污染和气候变化问题日益严峻^[5-6]。因此, 亟须转变煤炭使用方式, 促进煤炭资源的绿色低碳利用。

研究表明, 煤是一种由短脂肪链和醚键连接芳香环、氢化芳香环及一些杂环组成的特殊高分子聚合物, 碳含量高。煤组成结构中存在短程有序、长程无序的微晶石墨结构^[7]。此外, 煤的微晶石墨结构随其煤化程度的提高而增大。煤中较多的石墨化结构使其可通过加工转化为各种功能煤基碳材料。因此, 煤炭不仅是一种化石燃料, 同时还是一种优良的碳材料前驱体。以煤为原料开发、制备功能煤基碳材料可转变传统煤炭利用方式, 实现煤炭的非燃料化利用, 提升煤炭利用价值, 延长煤炭产业链, 进而有助于推动煤炭资源的绿色低碳利用^[8]。

当前, 功能煤基碳材料成为国际上煤炭清洁高效利用的新趋势, 世界各国积极开展煤基碳材料领域的科学研究^[9-12], 以期将煤炭利用从传统的直接燃烧发电、供热和冶金等领域扩展到碳材料领域, 实现煤炭由能源属性向资源属性的转变。在全球能源结构转型的背景下, 中国相继出台《“十四五”能源领域科技创新规划》《2030年前碳达峰行动方案》等政策, 明确提出要加快煤炭清洁高效利用技术的研发与产业化, 推动煤炭由燃料向原料与材料并重转变。

功能煤基碳材料兼具原料丰富、成本低廉的核心优势与结构高度可调、性能优异(可媲美甚至超越商业碳材料)的突出特点, 使其在电化学能量/物质转化与存储领域展现出广阔的应用前景^[13-19]。功能煤基碳材料的原料多样性(如无烟煤、烟煤等)和全球广泛分布性, 为其大规模应用于电化学器件提供了坚实的经济基础。更重要的是, 其发展深入契合国家推动能源结构转型、实现煤炭清洁高效利用和碳中和的重大战略需求, 为传统煤炭产业开辟了高

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附加值、环境友好的新发展路径。

近年来, 科研人员在功能煤基碳材料领域取得重要研究进展。但是, 目前对这一快速发展领域系统性综述还很少, 特别是针对功能煤基碳材料结构设计合成和电化学性能优化之间的关联性尚未有全面梳理。为此, 本文深入总结功能煤基碳材料在电化学领域的最新研究进展, 揭示材料制备-结构调控-性能优化的内在关联。希望本综述可为新型电化学材料的开发提供理论参考和技术支撑, 继而推动先进催化和储能技术的创新发展。

1 煤炭原料结构特点与适用性

煤炭作为一种复杂且非均质的有机矿物, 其物理化学性质随煤化程度呈现出明显的梯度变化, 而这种物理化学性质上的差异会显著影响煤炭作为碳材料前驱体的加工方法与最终产物的结构组成和性能。为此, 重点剖析 4 种代表性煤炭原料——高阶无烟煤、中阶烟煤、低阶褐煤以及煤沥青的结构特点, 并阐述其在功能煤基碳材料制备中的适用性, 包括适宜的加工处理方法、目标材料类型及电化学应用。

1.1 无烟煤

无烟煤是煤化程度最高的煤种, 具有较高的固定碳含量(>90%)、较低的挥发分(<10%)。其分子结构主要由高度缩合、排列相对有序的稠环芳烃单元组成, H/C 原子比低, 杂原子含量低, 结构高度致密, 孔隙结构以微孔为主, 比表面积相对较小^[20]。无烟煤高度稳定和低反应活性的结构特点使其适用于通过液相法和固相法制备具有丰富微孔结构的功能煤基碳材料^[18,21], 材料微孔结构的空间限域效应可以牢固锚定活性位点, 提升材料电化学稳定性, 同时还可增加活性位点周围局域反应物浓度, 加快反应速率。因此, 富微孔无烟煤基碳材料在燃料电池和电催化 CO₂ 还原等领域表现出突出的电化学性能。另外, 直接炭化法可利用无烟煤固有的结构有序性特点, 制备出具有石墨化结构的碳材料, 该类材料具有导电性好、碳微晶层间距大、化学性质稳定等优点, 使其成为极具竞争力的锂/钠离子负极活性材料之一^[22-23]。无烟煤经高温炭化处理其内部会形成较大尺寸的石墨晶体, 通过液相氧化还原法处理该高石墨化结构的碳源可制备煤基石墨烯材料^[24-25]。煤基石墨烯材料具有比表面积大、电导率高、缺陷位点丰富等优点, 其在超级电容器领域被广泛应用^[26-27]。

1.2 烟煤

烟煤的煤化程度介于无烟煤和褐煤之间, 其固定碳含量(75%~90%)、挥发分(10%~40%)适中, 其分子结构中包含稠环芳香簇和较为丰富的脂肪族侧链、桥键以及含氧官能团^[28]。烟煤物理结构相对疏松, 含有原生孔隙, 兼具适中的反应活性和结构可塑性。烟煤因其适中的结构和反应活性, 具有较广的加工适用性。通过液相法或固相法将烟煤与活化剂混合, 在热处理过程中, 烟煤适中的挥发分和反应活性使其易于被活化剂蚀刻, 进而制备出具有大量介孔/大孔结构、高比表面积的多孔碳^[29-30]。此外, 烟煤适中的反应活性使其在高温条件下可与 CO₂、水蒸气、氨气等气体发生化学反应, 实现煤炭形貌结构与杂原子掺杂协同调控, 因此, 烟煤也适用于气相法制备多孔功能煤基碳材料^[31]。烟煤基多孔碳材料独特的结构特点使其在电化学反应中具有很高的传质/传荷效率, 其成为超级电容器电极的理想材料之一。另外, 烟煤适中的固定碳含量和挥发分使其在直接炭化过程中同时生成石墨微晶片层、缺陷和闭孔结构, 这种混合结构有利于锂/钠离子的传输和吸附。因此, 烟煤也被普遍用于锂/钠离子电池^[32-33]。

1.3 褐煤

褐煤煤化程度最低, 固定碳含量较低(60%~77%)、挥发分较高(>40%), 其富含大量的含氧官能团(羧基、羰基、甲氧基等)、脂肪族结构以及矿物质^[34-35]。褐煤分子结构疏松无序, 芳香度低, H/C 和 O/C 原子比较高。孔隙结构常含有较多的大孔。褐煤的高活性、高挥发分和高氧含量特点决定了其适合液相法加工处理路径^[36-37]。其丰富的含氧官能团和疏松结构使其极易与活化剂发生反应, 在相对温和的条件下即可制备出高杂原子掺杂量、大比表面积且具有层次化孔结构(微孔、介孔、大孔兼备)的多孔碳。褐煤基多孔碳丰富的孔结构有利于提升双电层电容, 同时大量的杂原子可提升赝电容, 因此, 该多孔碳材料适用作超级电容器的电极材料^[36-38]。

1.4 煤沥青

煤沥青是煤焦油蒸馏后的残留物, 并非原生煤, 但其是重要的煤基衍生原料。煤沥青主要由稠环芳烃及其衍生物组成, 分子量分布广, 具有固定碳含量高(>90%)、灰分低(<10%)、热塑性优良等优点, 其结构特点是芳香度高, 具有易石墨化的潜力^[39-40]。此外, 煤沥青可溶于 N,N-二甲基甲酰胺、四氢呋喃

等有机溶剂, 这为精准调控煤沥青基碳材料的形貌结构及化学组成提供了有利的加工处理条件^[41–43]。因而, 液相法是煤沥青核心加工路线。将煤沥青溶于纺丝液中, 通过静电纺丝工艺可制备高性能的碳纤维, 碳纤维因其具有导电性好、比表面积大, 且一维结构有利于离子和电子的传输等优点, 被广泛用作超级电容器和锂/钠离子电池的电极材料^[41–44]。通过液相法将煤沥青、活化剂和掺杂剂混合, 随后通过热处理可制备出煤沥青基杂原子掺杂碳纳米管材料, 碳纳米管材料局部缺陷对电子结构的调控作用以及其表面形态对原子排列和配位关系的调节使其表现出较高的催化活性, 目前煤沥青基碳纳米管材料在燃料电池领域表现出优异的电化学性能^[45]。另外, 液相法可通过使用不同类型活化剂或模版剂

构筑形貌结构迥异的煤沥青基多孔碳材料^[44]。煤沥青基多孔碳材料高度可调控的多孔结构、较好的石墨化程度和导电网络、表面化学性质可修饰性的结构特点, 使其在燃料电池、超级电容器、锂/钠离子电池等储能领域表现出优异的电化学性能^[46–49]。

煤炭原料的结构特性决定了其在煤基碳材料制备中的适用性分工(见表 1)。无烟煤结构致密、固定碳含量高, 适于制备燃料电池/电催化用富微孔碳、锂/钠离子电池石墨化碳及超级电容器石墨烯。烟煤结构活性均衡, 利于制备超级电容器多孔碳或含石墨微晶/缺陷的电池负极材料。褐煤活性高、氧含量高, 适于制备高表面积、杂原子掺杂的超级电容器多孔碳。煤沥青芳香度高、可溶/热塑性强, 是制备碳纤维、碳纳米管及多孔碳的关键原料。

表 1 煤炭原料的结构特点及适用性

Table 1 Structural characteristics and applicability of coal raw materials

Coal raw materials	Structural characteristics	Suitable processing methods	Typical products	Advantages	Suitable applications
Anthracite	High fixed carbon content, low volatile matter, dense structure	Liquid-phase method, solid-phase method	Rich microporous porous carbon	High stability, large specific surface area, microporous confinement	Fuel cells, electrocatalytic CO ₂ reduction
		Direct-carbonization method	High graphitized carbon	High conductivity, large interlayer spacing, stable properties	Lithium/sodium ion batteries
		Direct-carbonization method coupled with liquid-phase method	Graphene	Large specific surface area, high conductivity, rich defects	Supercapacitors
Bituminous coal	Moderate fixed carbon content and volatile matter, relatively loose structure	Liquid-phase method, solid-phase method	Porous carbon	Large number of pore structures, high specific surface area	Supercapacitors
		Direct-carbonization method	Rich graphite microcrystals/defective carbon materials	High conductivity, numerous defects, closed pore structure	Lithium/sodium ion batteries
Lignite	Low fixed carbon content, high volatile matter, abundant oxygen-containing functional groups, loose and disordered structure	Liquid-phase method	Porous carbon	High doping content of heteroatoms, large specific surface area, hierarchical pore structure	Supercapacitors
Coal tar pitch	High fixed carbon content, low ash content, high aromaticity, soluble in organic solvents	Liquid-phase method	Carbon fiber	Good conductivity, large specific surface area	Supercapacitors, lithium/sodium ion batteries
			Carbon nanotubes	Active sites with high electronic activity	Fuel cells
			Porous carbon	Highly adjustable porous structure	Supercapacitors, lithium/sodium ion batteries

2 功能煤基碳材料制备方法

煤炭原料本身比表面积小、孔结构少, 结构不规则, 且缺乏活性位点, 难以直接作为电极材料。因此, 需要采用合适的加工处理方法调控煤炭原料的形貌结构, 提升材料在电化学过程中的传质/传荷效率, 优化热力学/动力学, 进而制备出高活性的功能煤基碳材料。功能煤基碳材料的制备方法决定其形貌结构和化学组成, 而材料的形貌结构和化学组

成直接影响其电化学能量/物质转化与储存性能, 因此, 功能煤基碳材料的制备方法对其电化学性能至关重要。以下重点分析制备功能煤基碳材料常用的液相法、固相法、气相法、直接炭化法、耦合法等方法, 揭示制备方法对功能煤基碳材料结构和组成的调控机制。

2.1 液相法

液相法可分为一步液相法和两步液相法。一步

液相法是指将煤炭、活化剂、掺杂剂等按一定质量比例加入溶剂中,混合均匀后,在保护气氛中热处理混合物以制备功能煤基碳材料^[18]。两步液相法是指先将煤炭和活化剂按一定质量比例加入溶剂中,经混合浸渍、保护气氛热处理等过程制备出煤基多孔碳,随后将煤基多孔碳和掺杂剂按一定质量比例加入溶剂中,待浸渍一段时间后,在保护气氛中热处理,制得功能煤基碳材料^[50]。

2.1.1 一步液相法 一步液相法制备步骤简捷,可在活化剂造孔的同时,将掺杂剂杂原子原位限域于煤基前驱体孔道内,同步实现孔结构的构筑与杂原子的掺杂改性,协同优化功能煤基碳材料的组成与性能。KOH 是制备功能煤基碳材料最常用的化学活化剂,其在高温条件下可与煤炭中的碳原子发生化学反应,生成 K_2CO_3 、 K_2O 等,进而蚀刻煤炭,由此煤炭产生大量孔隙结构^[51-53]。双氰胺、三聚氰胺、尿素等小分子是常用的氮掺杂剂,其热分解产生的杂原子容易掺入煤炭原料的碳晶格中,形成氮掺杂结构^[54-56]。Liu 等^[18]利用 KOH 活化剂和双氰胺掺杂剂对无烟煤进行活化掺杂改性,以提升功能煤基碳材料的电催化 CO_2 还原性能(见图 1a)。研究发现,在固定双氰胺用量的条件下,煤基碳材料的比表面积和孔容均与 KOH 用量呈显著正相关。相对较低的 KOH 用量可使煤炭形成较小的微孔结构及较少的边缘缺陷,同时微孔结构单位孔体积内双氰胺热解产生的碳-氮含量较多,由于微孔结构孔体积小,孔内碳-氮含量高,微孔的孔壁则会对碳-氮组分产生挤压效应,由此碳-氮组分中的氮原子可以掺入微孔表层的石墨碳晶格之中,进而形成高活性的石墨氮位点。但是,较高的 KOH 用量使得材料形成较大的孔结构及丰富的边缘缺陷位点,较大的孔结构其单位孔体积内双氰胺热解产生的碳-氮含量偏低,孔结构的孔壁空间约束作用减弱,其难以对碳-氮组成产生挤压作用,这使得氮原子倾向于以吡啶氮和吡咯氮的形式锚定在大孔的边缘缺陷位上。另外,在固定 KOH 用量的条件下,增加双氰胺的用量虽可以增加煤基碳材料的石墨氮含量,较多的双氰胺会堵塞孔结构,致使材料的比表面积和孔容偏小。试验得出的最佳方案是煤炭、KOH、双氰胺的质量比例为 1:1:3,在该条件下制得的功能煤基碳材料的比表面积达 $545\text{ m}^2/\text{g}$,微孔比例达 69%,石墨氮含量达 43%。因为大量的氮原子插入煤载体石墨晶格中,材料石墨化程度降低,缺陷增大,这为 CO_2 的吸附和活化提供了充足的反应位点。因而,

该功能煤基碳材料在电催化 CO_2 还原制 CO 反应中实现了 95% 的选择性和 $2.3\text{ mA}/\text{cm}^2$ 的电流密度。Ren 等^[57]以低阶褐煤为原料、KOH 为活化剂、三聚氰胺为掺杂剂,采用一步液相法制备了氮掺杂多孔煤基碳材料,以提升材料的电容性能。他们发现褐煤、KOH、三聚氰胺的质量比例为 1:2:1 时制备条件性能最好,对应的功能煤基碳材料的比表面积高达 $1\,793\text{ m}^2/\text{g}$,且具有丰富的微孔、介孔结构及大量的氮杂原子。X 射线衍射光谱和拉曼光谱结果显示 KOH 的活化作用及三聚氰胺的掺杂效应使得材料无定型碳的比例高于其石墨碳的,由此说明材料具有丰富的缺陷位点,这可为电解液离子提供丰富的吸附位点。另外,丰富的孔结构可加快质量传输,大量的氮原子有助于离子吸附和电荷转移。因此,该煤基碳材料在超级电容器中的功率密度达到 $999.8\text{ W}/\text{kg}$,能量密度达到 $19.4(\text{W}\cdot\text{h})/\text{kg}$ 。

2.1.2 两步液相法 由于活化剂的存在,一步液相法难以实现金属物种负载,而只适用于制备非金属元素掺杂的功能煤基碳材料。而两步液相法将活化和掺杂过程分开,这使得金属物种也能高效地负载到煤载体上,扩展了功能煤基碳材料的应用范围,并提升了材料的电化学性能。Liu 等^[50]先将无烟煤和 KOH 加入溶液中,待混合均匀后,通过高温热处理制备出了具有丰富微孔结构的煤载体;随后他们将多孔煤载体、六水硝酸镍、2-甲基咪唑再次加入溶液中,待反应完成后,通过高温热处理制备出了镍/氮共掺杂煤基碳材料(图 1b)。KOH 活化减少了煤载体中的石墨微晶数量并增加了缺陷密度,从而为负载镍-氮位点提供了充足空间。另外,煤载体微孔结构的限域生长效应使得镍-氮活性位点可以均匀地锚定在微孔内,防止金属原子的过度团聚,从而提高催化剂的利用率。另外,富含微孔结构的无烟煤碳载体在强化镍-氮活性位点的电子传递与底物(CO_2)传输方面发挥了关键作用,显著提升了镍-氮位点处电子与底物的交互效率。一方面,载体丰富的微孔结构赋予了材料优异的 CO_2 吸附能力(CO_2 吸附量达 $56.3\text{ cm}^3/\text{g}$),可在电催化过程中富集并显著提高镍-氮活性位点周围的局域 CO_2 浓度,确保反应物的高效供给;另一方面,无烟煤自身致密的碳骨架结构,使载体具备优异的导电性,其电荷转移电阻低至 $1.2\,\Omega$,保障了电子能够从电极基底快速、高效地传输至镍-氮活性位点。这种由微孔结构实现的高效传质(保障 CO_2 局域浓度)与由高导电性碳骨架实现的高效传荷(保障电子快速传输)之间

的协同作用,有效强化了镍–氮位点处电子与底物 CO_2 的交互作用,使得 CO_2 分子能够在该活性位点上快速获得电子并高效还原。因此,该催化剂在电催化 CO_2 还原反应中展现出卓越的综合性能:实现了工业级电流密度(223.0 mA/cm^2)、高 CO 选择性(97%)以及优异的稳定性(120 h)。因此,具有丰富微孔结构的无烟煤载体通过提升活性位点周围底物浓度和优化电子传导路径,强化了镍–氮活性位点的电子/底物交互作用,进而实现优异的催化活性。Zhang 等^[58]以煤沥青为原料,采用先 KOH 活化、后钴–

氮活性物种负载的两步液相法制备了钴/氮共掺杂煤基碳材料,实现了氧还原和氧析出双功能催化。X 射线衍射光谱显示材料具有较宽的石墨碳(002)晶面和(101)晶面衍射峰,表明材料石墨化程度低,这一特征同时佐证了液相法有助于 KOH 对煤沥青高效活化,进而促进材料形成丰富的微孔和介孔结构,这种发达的多级孔结构可有效促进传质过程并暴露更多的活性位点。在电化学方面,该材料在氧还原反应中表现出优于商业铂碳的催化性能,同时,其在氧析出反应中也展现出良好的性能。

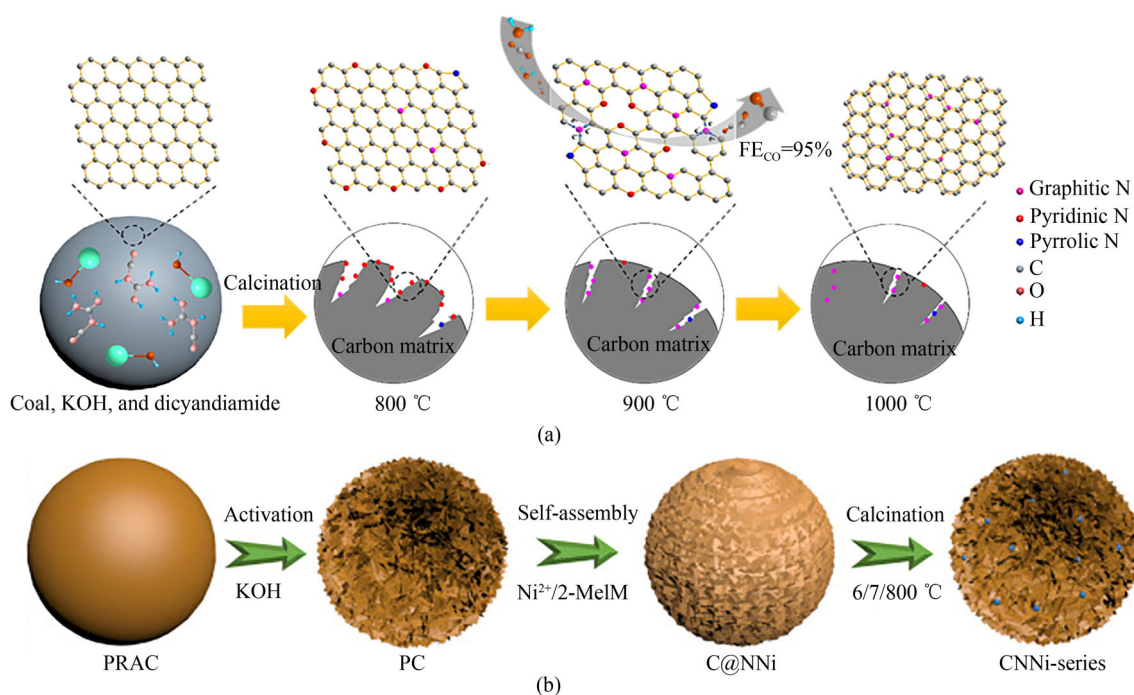


图1 液相法制备功能煤基碳材料 (a) 一步液相法制备氮掺杂煤基碳材料^[18]; (b) 两步液相法制备镍/氮共掺杂煤基碳材料^[50]
Fig. 1 Preparation of functional coal-based carbon materials by liquid-phase methods (a) Preparation of nitrogen-doped coal-based carbon materials by one-step liquid-phase method^[18]; (b) Preparation of nickel/nitrogen co-doped coal-based carbon materials by two-step liquid-phase method^[50]

由上可知,液相法的核心优势在于其灵活调控材料组成与孔结构的能力。一步液相法通过活化剂造孔与掺杂剂引入杂原子同步进行,实现高效改性。两步液相法则通过分离活化与掺杂步骤,有效解决了金属物种在强碱环境下的负载难题,实现了金属物种的精准锚定,拓展了材料的应用范围,该方法的典型产物结构特征显著:1) 高比表面积与丰富孔结构: KOH 活化作用赋予材料较高的比表面积及丰富孔结构,提供了充足的活性位点锚定空间,提高了传质效率;2) 低石墨化与高缺陷密度:材料石墨化程度相对较低、缺陷丰富,这增强了其对反应物(如 CO_2 、电解液离子)的吸附能力,有效提升了催化速率和储能容量;3) 可控杂原子掺杂:该方法不仅能在煤炭上高效负载多种

类型的非金属杂原子,更关键的是能够负载金属物种,并通过孔道限域实现其均匀分布。以上结构特征共同驱动了材料在多个领域展现出卓越的电化学性能。

然而,液相法也存在局限,如对溶剂的依赖、相对复杂的多步操作(尤其是两步液相法涉及多次浸渍和热处理)以及使用过的溶剂后处理问题。为了实现更简洁、低成本和绿色化的制备,固相法应运而生。该方法通过无溶剂混合与高温热处理策略,有望为功能煤基碳材料的规模化制备提供新思路。接下来将重点阐述固相法的工艺特征、结构调控机制及其性能优势。

2.2 固相法

相比于液相法,固相法不需要溶剂体系或液相反

应步骤, 仅需通过机械混合和高温处理即可制备功能煤基碳材料, 降低了工艺复杂度。固相法采用球磨、研磨等机械力化学方法将煤炭、活化剂、掺杂剂等充分混合, 随后通过在保护气氛中高温热处理制备出功能煤基碳材料^[59-60]。球磨或研磨过程能够利用机械力化学效应打破原料颗粒的团聚, 实现煤炭与其他试剂的充分混合, 进而提升功能煤基碳材料的结构均一性和性能稳定性^[61]。因而, 固相法以其工艺简便、掺杂活化效果好、产品性能稳定等优点, 成为制备功能煤基碳材料的重要选择。固相法也分为一步固相法和两步固相法: 一步固相法即将煤炭、活化剂和掺杂剂等一起混合, 随后通过热处理制备出功能煤基碳材料; 两步固相法即将活化过程和掺杂过程分开, 通过两次机械化学处理过程制备功能煤基碳材料。

2.2.1 一步固相法 一步固相法操作相对便捷,

可实现活化与掺杂原位同步反应, 避免杂原子局部聚集。Jiang 等^[62]利用球磨机将碳源无烟煤、活化剂草酸钾和氮源石墨氮化碳充分混合, 随后通过热处理制备出氮掺杂多孔碳材料。在机械力化学效应作用下, 草酸钾可以更充分地活化煤炭, 使得该材料呈非晶态结构, 具有极高的比表面积($1673 \text{ m}^2/\text{g}$)和丰富的微孔结构($0.77 \text{ cm}^3/\text{g}$), 同时石墨氮化碳分解形成的高活性吡啶氮和吡咯氮可高效地负载到孔结构内。具有高活性表面的孔结构可以传递更多的电解质, 缩短扩散路径, 并最大限度地减少扩散损失, 从而提升电化学反应动力学。该功能煤基碳材料在双碳锂离子电容器中表现出 $750 (\text{mA}\cdot\text{h})/\text{g}$ 的高比容量, 并在 800 次循环后保持 97% 的优异容量保持率。Fu 等^[63]利用煤炭、三聚氰胺和草酸钾通过一步固相法制备了氮/氧共掺杂煤基碳材料(见图 2a), 机械力

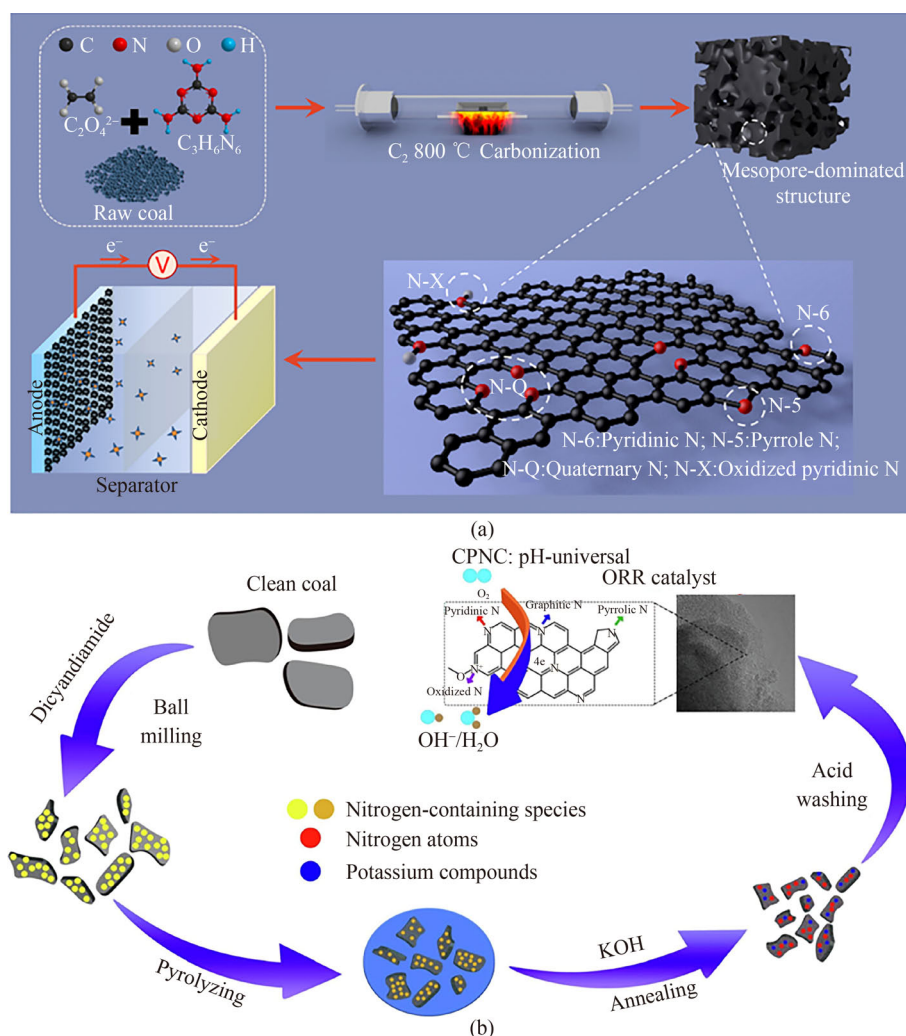


图 2 固相法制备功能煤基碳材料 (a) 一步固相法制备氮/氧共掺杂煤基碳材料^[63]; (b) 两步固相法制备氮掺杂多孔煤基碳材料^[21]

Fig. 2 Preparation of functional coal-based carbon materials by solid-phase methods (a) One-step solid-phase method for preparing nitrogen/oxygen co-doped coal-based carbon materials^[63]; (b) Two-step solid-phase method for preparing nitrogen-doped porous coal-based carbon materials^[21]

化学效应使得三聚氰胺和草酸钾可同时发挥活化剂和掺杂剂作用：三聚氰胺热解产生的 NH_3 气体可与碳骨架反应，创造微孔结构，同时其热解生成的含氮物种可嵌入碳骨架中，形成氮活性位点；草酸钾的充分活化使得材料形成较大孔径的介孔结构，同时其分解产生的含氧物种嵌入碳骨架并形成氧活性位点。该制备方法赋予煤炭高比表面积、大量的微孔/介孔结构及丰富的掺杂原子，使得该功能煤基碳材料在水系双电层电容器和锌离子混合超级电容器中均表现出优异的电化学性能。

2.2.2 两步固相法 相比于一步固相法，两步固相法将活化与掺杂过程分开，可独立调控煤基碳材料的孔隙率与掺杂浓度，继而可避免一步固相法中活化与掺杂的相互影响。Qi 等^[21]首先利用球磨法将无烟煤和双氰胺混合，通过低温热处理制备出氮掺杂煤基碳材料；随后他们通过研磨将得到的氮掺杂煤基碳材料与 KOH 混合，最后利用高温热处理制备出氮掺杂多孔煤基碳材料(见图 2b)。通过该方法，成功地将氮杂原子密封并限域在煤载体的碳层和骨架中，同时高效调节材料的形貌结构(大比表面积、丰富微孔结构、缺陷和边缘)，因而材料表现出典型的无定型碳结构特征。得益于大量的催化反应位点和发达的孔隙结构，该功能煤基碳材料首次实现了酸、碱、中性全 pH 范围内高效电催化氧化还原性能。Benoy 等^[64]以次烟煤为原料，利用先 NH_4Cl 活化掺杂、后 KOH 活化造孔的两步固相法制备了用于超级电容器的功能煤基碳材料。 NH_4Cl 和 KOH 的 2 次活化作用使得材料石墨微晶大量减少，由此表现出非晶特性。材料的比表面积达到 $1996 \text{ m}^2/\text{g}$ ，这一较大的表面积为氮杂原子提供了充足的锚定位点(氮含量 4.36%，质量分数)。该功能煤基碳材料分级多孔的有利结构，结合掺杂效应，确保了良好的电化学性能，其在超级电容器中最大能量密度达 $22.4 (\text{W}\cdot\text{h})/\text{kg}$ ，最大功率密度达 $17 \text{ kW}/\text{kg}$ 。

由上可知，固相法通过机械化学实现原料的均匀混合，结合高温热解制备功能煤基碳材料，其核心优势在于工艺简洁，并实现对功能煤基碳材料结构和表面化学的高效调控。相较于液相法，该方法无须溶剂参与，避免了复杂的浸渍与液相反应步骤，显著优化制备过程和降低制备成本；机械力作用可以打破原料聚集，提升组分分散均一性，这能实现更高效的活化掺杂。该方法典型产物结构特征包括：1) 超高比表面积和分级孔隙：机械力强化活化剂的造孔效果，赋予材料显著提升的比表面积和以微孔

结构为主导的分级孔结构，为离子/反应物传输提供高效通道；2) 非晶体主导的低石墨化结构：固相法更高效的活化过程大幅减少石墨微晶，形成非晶碳主导的无定型碳结构特征，丰度的缺陷位点能增强反应物的吸附；3) 高含量杂原子可控掺杂：机械混合促使掺杂剂与煤炭充分混合，实现氮、氧等杂原子的高效掺杂，形成了高活性位点。这些结构特征赋予材料优异的电化学储能与催化性能。

然而，固相法仍存在局限，如较强的机械力作用会破坏煤炭本征结构，难以对煤炭孔隙结构及表面性质进行精细调控。为进一步实现原子级精准掺杂与孔隙定向设计，气相法通过利用气体在煤炭表面的化学吸附与反应，为构筑高性能煤基碳材料提供了新策略。以下将系统讨论气相法的工艺机制与结构调控优势。

2.3 气相法

与液相法和固相法活化工艺不同，气相法是利用水蒸气、氧气、 CO_2 、氨气等气态活化剂在高温下处理煤炭原料，通过造孔、扩孔和疏孔等过程形成发达的空隙结构，同时将氧或氮杂原子掺入碳骨架中^[65–69]。气相法活化煤炭一般分为 2 个阶段。

①气体扩散阶段：反应气体首先吸附在煤炭表面，随后通过分子扩散向内部渗透。扩散速率受温度、孔径分布和气体分压影响，高温有助于气体分子深入煤炭内部。②反应–逸出阶段：气体与碳原子发生气化反应(如 $\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$, $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$)，生成的气体(如 CO 、 H_2)逆向扩散至表面脱附。

Zou 等^[31]分别利用纯 CO_2 气体、纯水蒸气以及由 CO_2 和水蒸气组成的混合气对准东煤进行活化处理(见图 3a)。他们发现在煤炭活化为多孔碳的过程中，主要发生无定型碳的蚀刻和石墨微晶的复合，纯 CO_2 气体主要沿煤炭表面蚀刻，纯水蒸气主要沿煤炭深度方向蚀刻，而混合气有利于煤炭表面和内部无定型碳的“同时”蚀刻。煤炭在 CO_2 和水蒸气的协同活化作用下形成多级孔结构，同时其还具有丰富的石墨微晶结构、长程有序的石墨网络及丰富的含氧官能团。因此，相比于单独由 CO_2 或水蒸气活化的煤炭碳材料，由 CO_2 和水蒸气混合气协同活化制备的材料具有更大的比表面积($556 \text{ m}^2/\text{g}$)、更多的孔隙结构及更高的杂原子含量(8.9%)，同时这也使其表现出更优异的电容性能。Li 等^[14]利用氨气处理烟煤制备氮掺杂多孔碳，以实现高效电催化 CO_2 还原(见图 3b)。氨气较强的蚀刻作用使其可以破坏石墨微晶、无定型碳及杂原子官能团，因而材料的石

墨化程度偏低, 缺陷位点丰富, 比表面积大($974\text{ m}^2/\text{g}$), 且具有大量的微孔和介孔结构。同时, 氨气在高温下分解产生的活性氮物种直接嵌入碳骨架中, 形成

了吡啶氮、石墨氮和吡咯氮活性位点。得益于发达孔隙结构与氮活性位点之间的协同效应, 该功能煤基碳材料表现出 92% 的高 CO 选择性。

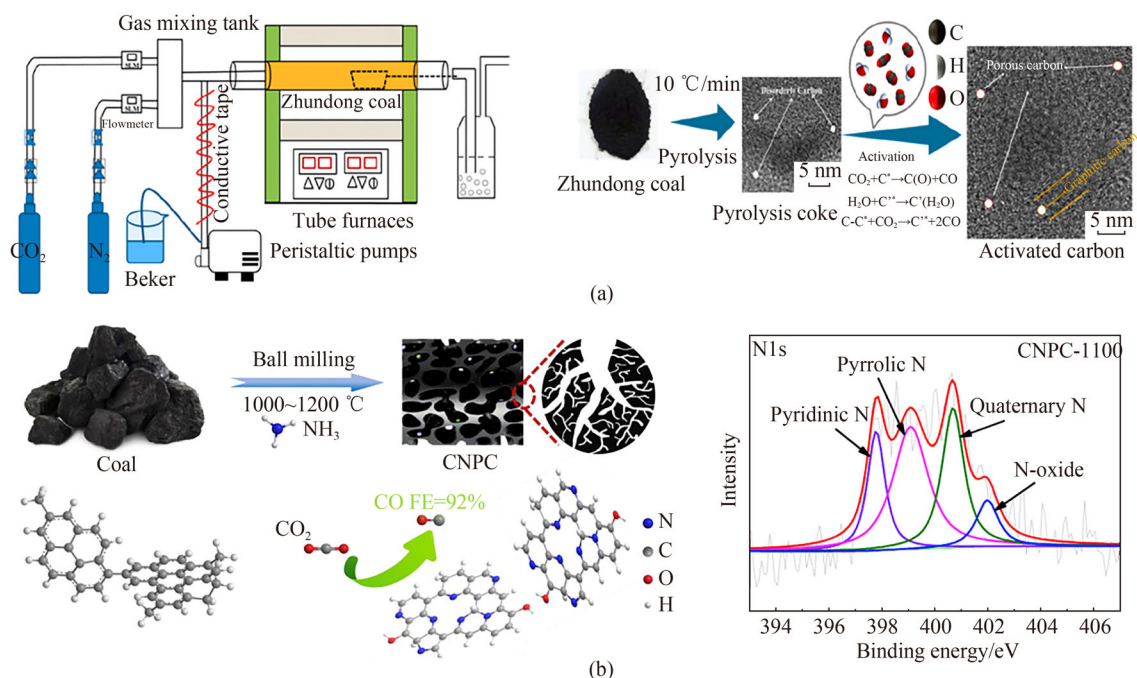


图 3 气相法制备功能煤基碳材料 (a) CO_2 和 H_2O 共活化准东煤^[31]; (b) 氨气活化烟煤制备氮掺杂多孔煤基碳材料^[14]
Fig. 3 Preparation of functional coal-based carbon materials by gas-phase methods (a) CO_2 and H_2O co-activation of Zhundong coal^[31]; (b) Preparation of nitrogen-doped porous coal-based carbon materials from ammonia-activated bituminous coal^[14]

由上可知, 气相法通过气态活化剂在高温下对煤炭进行原位蚀刻与掺杂, 其核心优势在于气体分子可深入渗透至煤炭内部, 实现孔隙和组成的空间精准调控。气体分子通过表面吸附-内部扩散-气化反应的级联过程, 实现精准可控造孔; 同时活化气体热解产生的杂原子可直接插入碳骨架, 实现杂原子原位掺杂。相较于固相法、液相法, 该方法无须机械混合和溶剂参与, 可避免本征结构的机械损伤以及 KOH 等强碱试剂的使用, 进而实现了绿色、高效制备功能煤基碳材料。该方法典型产物结构特征包括: 1) 分级孔结构精准构筑: 气体蚀刻同时作用于材料表面与内部碳组分, 形成微孔-介孔协同的分级孔结构, 这可显著提升材料的离子扩散效率与活性位点数量; 2) 有序-缺陷结构选择性可控合成: 利用不同类型气体可实现有序石墨化结构与无序无定型碳结构的选择性可控合成, 保持材料内部导电石墨网络以提升导电性, 同时增加材料表面缺陷位点以优化界面吸附; 3) 构型可控的杂原子表面掺杂: 气体分解产生的杂原子直接嵌入碳骨架, 形成表面富集型掺杂, 同时通过改变气体种类/处理温度精准调控杂原子掺杂类型/比例, 构筑高

效的反应界面。这些结构特征赋予材料优异的电化学性能。

然而, 气相法也存在局限, 如气体分压精密调控难度大, 制备工艺条件优化困难。另外, 强蚀刻易导致材料孔道结构坍塌或石墨微晶断裂, 降低机械稳定性。为此, 直接炭化法凭借相对简便的制备工艺条件及无气相腐蚀特性, 在保留煤炭本征结构的同时实现可控炭化, 成为平衡结构精度与工艺复杂性的新路径。以下将系统讨论直接炭化法制备功能煤基碳材料机制及其结构调控优势。

2.4 直接炭化法

相较于液相法、固相法和气相法, 直接炭化法无须使用活化剂或掺杂剂, 直接将煤炭在保护气氛中高温煅烧, 制备功能煤基碳材料^[70]。煤炭的天然多环芳烃结构在高温环境中易形成短程有序、长程无序的碳层结构, 其层间距较大, 这有利于锂/钠离子的嵌入/脱嵌, 是理想的锂/钠离子电池负极材料^[71-72]。

煅烧温度是直接炭化法的重要参数, 因此, 探究煅烧温度对煤基碳材料结构和性能的影响规律是优化材料性能的重点。Tian 等^[73]对烟煤进行不同温

度炭化处理(600~1600 °C), 研究煤炭化过程中化学、微晶和孔结构变化(见图4)。发现在第1阶段(1000 °C 以下), 煤炭的结构受碳骨架断裂和小分子物质释放的影响, 其石墨层间距增大和缺陷浓度增加, 并产生超微孔结构; 在第2阶段(1000~1600 °C), 由于碳层的定向排列及晶格的逐渐修复, 煤炭的石墨层间距和缺陷浓度逐渐减小。在 1000~1200 °C 炭化温度下制备的煤基碳材料表现出丰富的类石墨结构, 具有较大的层间距(3.78 ~ 3.82 Å)、较高的缺陷浓度、丰富的纳米微孔和闭孔结构。煤基碳材料大层间距的短程有序结构有利于离子和电子的高效转移, 同时其高缺陷浓度和微孔/闭孔结构可为离子提供更多的活性位点和迁移路径。因而, 该煤基碳材料在

锂/钠离子电池中均表现出优异的可逆容量和倍率性能。Li 等^[22]用低灰无烟煤作为钠离子电池负极材料前驱体, 在氩气气氛中将无烟煤置于不同温度下煅烧, 探究炭化温度对煤炭中无定型碳、石墨微晶等微观结构的影响规律, 并揭示微观结构对煤基碳材料储钠性能的作用机制。1200 °C 炭化材料具有丰富的短程有序石墨微晶片层及结构缺陷, 其中石墨微晶片层可以为钠离子的快速嵌入/脱出提供传输通道, 结构缺陷可为钠离子电池存储提供充足的活性位点。另外, 材料较小的比表面积可抑制固体电解质界面膜的形成, 这有利于提升初始库伦效率。独特的结构特点使得该材料在钠离子电池中表现出 222 (mA·h)/g 的可逆比容量。

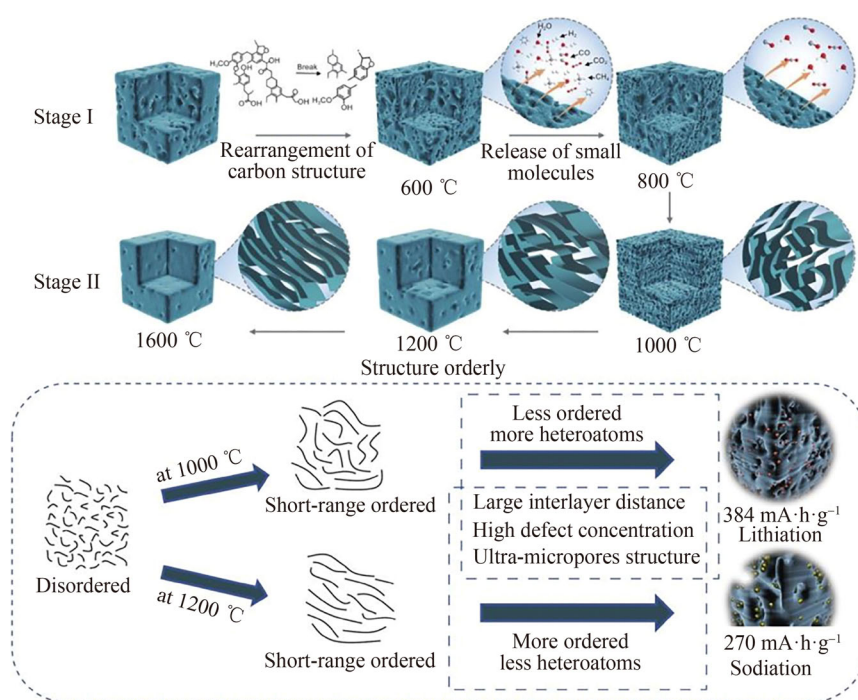


图4 直接炭化法制备功能煤基碳材料及炭化过程煤炭结构变化^[73]

Fig. 4 Direct-carbonization methods for preparing functional coal-based carbon materials and structural changes in coal during carbonization processes^[73]

由上可知, 直接炭化法通过在保护气氛中对煤炭高温热解, 直接制备功能煤基碳材料。该方法的核心优势在于无须使用活化剂或掺杂剂, 利用煤炭固有的多环芳烃结构制备具有独特电化学活性的碳材料, 尤其适用于锂/钠离子电池负极材料。该方法典型产物结构特征包括: 1)较高的缺陷浓度: 煤炭在炭化过程中结构演变产生纳米微孔和闭孔结构, 同时伴随产生高浓度的结构缺陷, 这可提供大量电化学活性位点, 提升材料的可逆容量和倍率性能; 2)较大的石墨层间距与局域有序性: 在优化的中温炭化区间, 材料形成短程有序的石墨微晶结构, 碳

层层间距增大, 这有效降低了锂/钠离子嵌入/脱出的扩散能垒, 促进了离子的快速传输; 3)闭孔结构与小比表面积: 煤炭挥发分的热解产物较多的闭孔结构, 同时, 相比于活化法, 直接炭化法制备的材料比表面积较小, 闭孔结构可为锂/钠离子提供储存位点, 而较小的比表面积有助于抑制固体电解质界面膜的形成, 进而有利于提升电池性能。

然而, 直接炭化法仍存在局限, 如其对材料微观结构的精准调控(如孔隙分布、缺陷类型与密度等)能力有限, 高度依赖前驱体煤种的结构特性和单一的温度调控参数, 难以同时优化高容量、高倍率、

长寿命等综合性能。为了突破这些限制,科研人员正积极发展耦合法,将两种或多种制备方法结合,以更精准地协同调控材料的形貌结构、表界面化学性质等,从而有望实现煤基碳材料电化学性能的跨越式提升。以下将系统讨论耦合法制备功能煤基碳材料机制及其结构调控优势。

2.5 耦合法

耦合法是将 2 种或多种方法耦合(如液相法-固相法、固相法-气相等),通过整合不同方法的优势,实现对功能煤基碳材料结构、组成及性能的多维度精准调控^[74-76]。耦合法的灵活性和可调性为开发高性能煤基功能材料提供了重要的研究思路。

Li 等^[77]使用液相-固相耦合法处理无烟煤,液相法引入的大量含氧官能团可以在固相法中为淀粉修饰剂提供有利的结合位点,促进无烟煤与淀粉发生化学交联。该交联前体可防止在炭化过程中碳微晶发生重排,进而形成具有较大层间距与丰富微孔和闭孔的伪石墨结构,得益于这种独特的结构特点,

该功能煤基碳材料在钠离子电池中实现了 332 (mA·h)/g 的高可逆比容量。Zou 等^[78]使用固相-气相耦合法处理准东煤,固相法引入的微量 K_2CO_3 可以在气相活化过程中辅助 CO_2 和水蒸气活化煤炭。 K_2CO_3 与煤炭反应产生的孔隙促进了气体活化剂的扩散和渗透,这使得煤炭形成了多级孔结构、丰富的石墨微晶、长程有序的石墨网络及大量的含 O/N 官能团(见图 5)。因而,该功能煤基碳材料实现了 277.7 F/g 的比电容,以及在对称超级电容器中表现出 209.9 W/kg 的能量密度和 10.5 (W·h)/kg 的功率密度。Zhao 等^[79]以煤沥青为原料,使用液相-气相-液相耦合法制备了镍/氮共掺杂泡沫碳材料,氨气蚀刻与镍-氮掺杂使得材料形成丰富的微孔结构(孔容: 0.41 cm^3/g)和大比表面积(922 m^2/g),进而材料表面缺陷丰富,石墨化程度较低,这利于增加三相界面接触面积和暴露活性位点。该材料在电催化 CO_2 还原过程中表现出 92.4% 的 CO 选择性和 71.6 mA/cm^2 的电流密度。

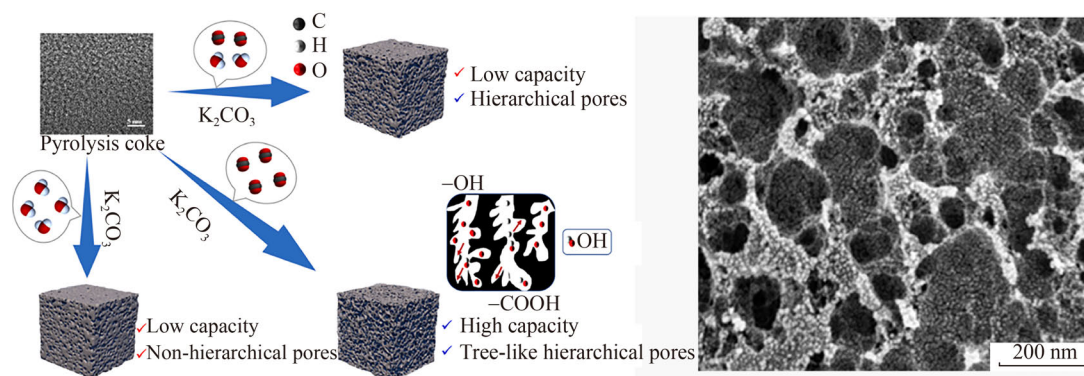


图 5 耦合法制备功能煤基碳材料^[78]

Fig. 5 Coupling methods for preparing functional coal-based carbon materials^[78]

由上可知,耦合法通过整合液相法、固相法、气相等不同方法的优势,精准调控煤基碳材料的形貌结构、化学组成及表面性质等结构参数,其核心优势在于多维度精准调控能力,这为开发不同电化学领域的高性能煤基碳材料提供了关键策略。该方法典型产物结构特征包括:1)大层间距与类石墨结构:耦合法可有效抑制炭化过程碳微晶的过度重排与石墨化,形成具有大层间距和适度无序性的类石墨结构,这可提供充裕的离子存储位点和更低的离子扩散能垒,从而提升电池的性能;2)多级孔道网络结构与高比表面积:耦合法能高效协同造孔,构筑发达的多级孔道网络及高比表面积,这可增加传质及电极/电解液界面接触面积,提升储能/催化效率;3)丰富表面缺陷与活

性杂原子:耦合过程中的液相或气相活化掺杂可创制大量的结构缺陷并精准掺杂活性原子,这些缺陷和杂原子可作为高效的反应位点,提升材料的本征催化活性和反应选择性。耦合法通过上述结构特征的协同作用,从离子/电子传输/储存和界面反应活性等维度优化煤基碳材料的电化学性能,使其在储能与催化领域表现出巨大潜力。但需注意的是,耦合法整合了多种制备方法,导致其工艺复杂度高,参数优化难度较大。

2.6 不同制备方法的比较与总结

功能煤基碳材料的制备方法对其形貌结构、化学组成及电化学性能具有决定性影响。通过对液相法、固相法、气相法、直接炭化法和耦合法的系统分析(见表 2),可明确各制备方法的优势与不足。

表 2 功能煤基碳材料制备方法的综合比较

Table 2 Comprehensive comparison of preparation methods for functional coal-based carbon materials

Preparation method	Advantages	Specific surface area and pore structure	Crystal structure	Surface properties	Suitable electrochemical applications	Deficiency
Liquid-phase method	Solvent assisted flexible pore control and metal/non-metal doping	High specific surface area (500–1700 m ² ·g ⁻¹), micropores	Low graphitization, high defect density	Controllable doping of heteroatoms (metal/non-metal)	Supercapacitors, electrocatalytic CO ₂ reduction	Dependent on solvents, complex processes, and difficult post-processing
Solid-phase method	Efficient activation and doping assisted by mechanochemistry	Ultra-high specific surface area (1600–2000 m ² ·g ⁻¹), micropores/mesopores	Amorphous carbon	High content of heteroatoms	Supercapacitors, fuel cells	Difficulty in precisely controlling pore structure and surface properties
Gas-phase method	<i>In situ</i> etching and doping of gaseous activators, precise control of pore structure	Medium specific surface area (500–1000 m ² ·g ⁻¹), hierarchical micropore and mesopore	Controllable construction of ordered-defect structures	Surface enriched heteroatom doping	Supercapacitors, electrocatalytic CO ₂ reduction	Difficulty in regulating gas partial pressure
Direct-carbonization method	No need for activators or dopants	Small specific surface area (<100 m ² ·g ⁻¹), closed pores and nanopores	Short range ordered graphite microcrystals, large interlayer spacing	Numerous defects	Lithium/sodium ion batteries	Restricted performance optimization
Coupling method	Collaboration of multiple methods	Wide range of specific surface area (30–900 m ² ·g ⁻¹), multi-level pore structure	Graphite-like structure, rich in defects	Highly active heteroatoms and defects	Batteries, supercapacitors, electrocatalysis	High process complexity and difficulty in parameter optimization

液相法通过溶剂辅助混合调控孔隙与掺杂，制得高比表面积、富含缺陷的材料，适用于电催化和超级电容器，但工艺复杂且溶剂难处理；固相法采用机械混合实现无溶剂化制备，产物为高比表面积、多孔且高掺杂的无定型碳，适合超级电容器和燃料电池，却存在结构破坏风险且调控能力受限；气相法利用气态活化剂高温蚀刻实现孔隙与表面掺杂的精准调控，无溶剂，无机械损伤，适用于超级电容器和电催化 CO₂ 还原，但对气体控制要求高且易致结构失稳；直接炭化法工艺简单，仅需高温热解即可获得具石墨微晶、大层间距及闭孔结构的材料，利于锂/钠离子存储与传输，专长于锂/钠离子电池应用，但结构调控能力弱；耦合法整合多种方法优势，协同优化微晶排列、孔道结构与杂原子掺杂，显著提升材料在储能与催化中的综合性能，是重要发展方向，但工艺复杂且参数优化难度大。

功能煤基碳材料的电化学性能受其结构参数(如比表面积、孔隙结构、石墨化程度)与表面化学特性(缺陷密度、掺杂原子类型与数量)的协同控制。不同的制备方法通过定向调控材料的这些关键参数，使得材料可以高效地应用于不同的电化学能量/物质转化与储存领域。基于此，下文将系统分析功能煤基碳材料的构效关系，聚焦其在燃料电池、电催化 CO₂ 还原、超级电容器、锂/钠离子电池等主流电化学领域的应用，

揭示材料制备-结构调控-性能优化的内在关联性。

3 功能煤基碳材料电化学应用

随着碳达峰、碳中和成为世界各国的共识，电化学能源/物质储存与转化技术快速发展，如燃料电池、电催化 CO₂ 还原、超级电容器、锂/钠离子电池等^[80–84]。这些电化学技术要实现高效快速的能源/物质储存与转化，需要电极材料具有快速传质/传荷能力及有利的反应热力学/动力学。功能煤基碳材料天然鲁棒性碳骨架和丰富的孔道结构使其可以高效地传输电荷、底物和电解液，进而可强化传质/传荷过程^[50]。此外，功能煤基碳材料通过杂原子掺杂(如氮、氧、镍等)可构建高活性的反应位点，优化反应热力学/动力学，继而可显著提升反应速率^[21]。另外，功能煤基碳材料原料丰富，价格低廉，更易于工业化推广^[6]。因此，功能煤基碳材料因其独特结构优势和丰富资源储备，在电化学领域展现出重要的应用价值。

3.1 燃料电池

燃料电池能够通过电化学反应将储存在燃料中的化学能直接转化为电能，不受卡诺循环限制，进而可实现较高的能量转化效率^[85]。因此，该技术被视为解决能源危机的有效方案之一。然而，燃料电池阴极侧发生的氧还原反应(ORR)动力学过程较为

迟缓,限制了燃料电池的功率/能量输出^[86]。尽管贵金属基材料(铂及其合金)在提升阴极催化反应动力学方面发挥重要作用,但它们的催化活性和稳定性仍不足,这成为制约燃料电池整体性能提升的关键瓶颈。因此,亟须开发高性能的 ORR 电催化材料。

功能煤基碳材料不仅具有天然鲁棒性碳骨架,同时其表界面还负载大量高活性位点,可显著提升燃料电池的活性和稳定性,进而使其成为替代贵金属基材料的理想选择。表 3 总结了近年来报道的关于功能煤基碳材料在燃料电池中的研究工作。

表 3 功能煤基碳材料在燃料电池领域的研究工作

Table 3 Research on functional coal-based carbon materials in field of fuel cells

Functional coal-based carbon material	Electrolyte	Onset potential/V	Half-wave potential/V	Limiting current density/(mA·cm ⁻²)	Reference
NS@C-900-10	0.1 mol/L KOH	0.97	0.82	5.9	[13]
	0.1 mol/L KOH	0.97	0.84	4.9	
CPNC-5-850	0.5 mol/L H ₂ SO ₄	0.80	0.64	4.6	[21]
	0.1 mol/L PBS	0.87	0.65	4.9	
ACTP5@Co,N-800	0.1 mol/L KOH	1.00	0.98	5.1	[58]
NCOH5-900	0.1 mol/L KOH	0.94	0.84	5.4	[87]
ANPC-2-900-6	0.1 mol/L KOH	0.96	0.85	4.8	[88]
Co/NSC	0.1 mol/L KOH	0.95	0.71	2.6	[89]
C-PT-C	0.1 mol/L KOH	0.81	0.6	2.5	[90]
AC-4	0.1 mol/L KOH	0.82	0.76	3.7	[91]
N,S-AC	0.1 mol/L KOH	1.00	0.79	6.3	[92]
	0.1 mol/L KOH	0.97	0.85	6.3	
N ₄ P ₄ C-900	0.5 mol/L H ₂ SO ₄	0.82	0.65	6.4	[93]
	0.1 mol/L PBS	0.87	0.67	7.1	
	0.1 mol/L KOH	1.00	0.84	5.7	
NCM-900	0.5 mol/L H ₂ SO ₄	0.81	0.69	5.5	[94]
	0.1 mol/L PBS	0.90	0.74	5.9	

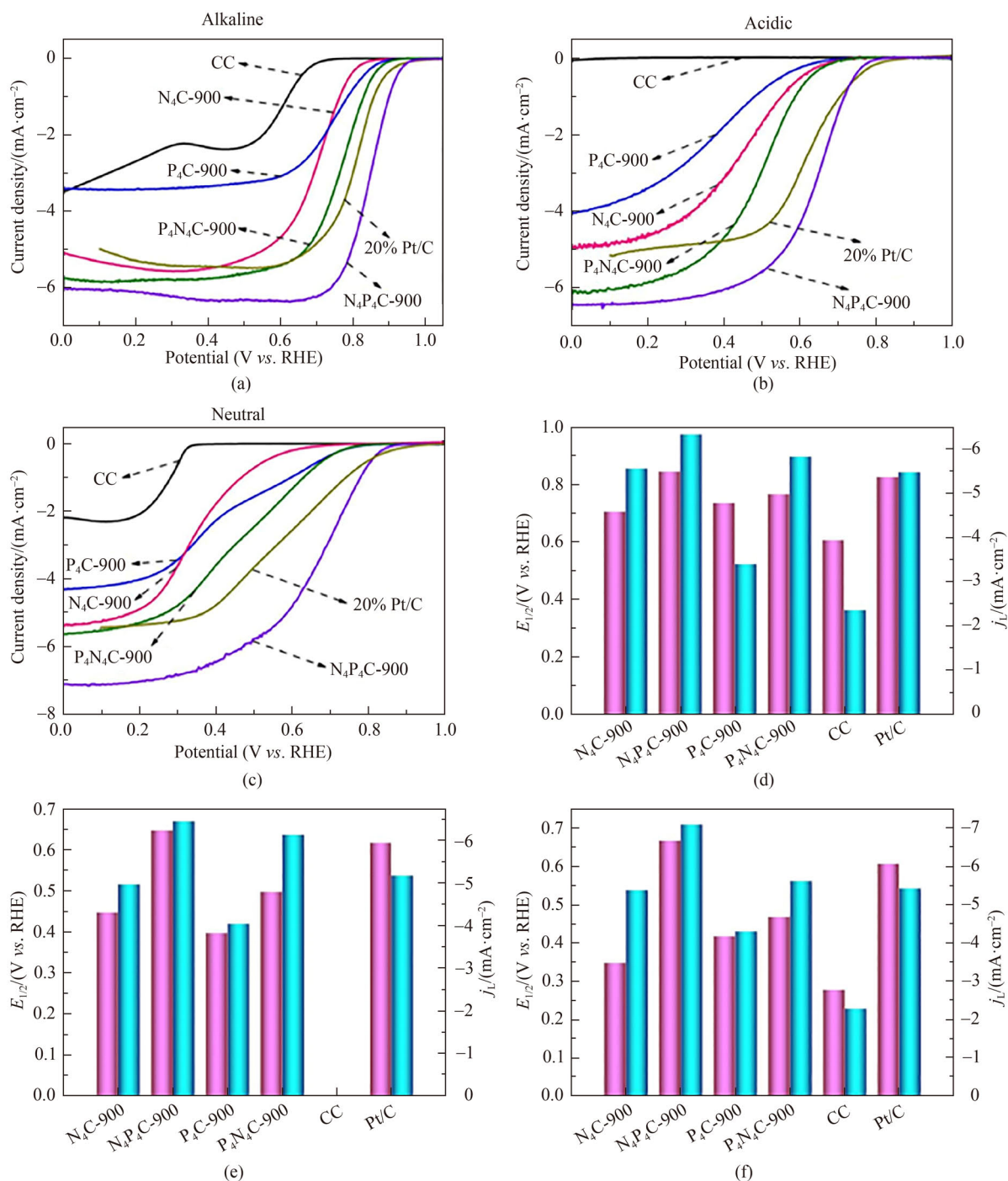
为了提升 ORR 电催化材料的性能, Qi 等^[93]以太西无烟煤为原料,通过耦合法制备了一种高活性的氮/磷共掺杂煤基碳材料。该煤基碳材料在碱性、酸性和中性电解液中均表现出比商业铂碳更优异的电化学性能(起始电位: 0.97、0.82 V 和 0.87 V; 极限电流密度: 6.3、6.4 mA/cm² 和 7.1 mA/cm²。见图 6)。该优异的电化学性能主要归因于 KOH 和磷酸的双重活化作用赋予材料大比表面积(807 m²/g)及以微孔为主的分级孔道结构,这不仅为氮、磷活性物种提供了充足的锚定位点,同时也显著提升了质量传输效率;另外,材料高含量氮、磷共掺杂引入的丰富缺陷和活性位点,促进了 O₂ 分子的吸附,显著降低了 ORR 热力学能垒。

由以上可知,功能煤基碳材料作为燃料电池阴极 ORR 的非贵金属催化剂,其性能极度依赖于制备方法对其形貌结构和化学组成的精准调控。研究表明,材料制备过程(如活化剂类型、掺杂元素种类和数量等)是结构组成调控的关键。例如,利用 KOH 和磷酸双重活化可实现高比表面积和以微孔为主的分级孔道结构,这不仅提供了丰富的杂原子锚定位点,更显著提升了反应过程中的质量传输效率。同时,氮、磷等杂原子的掺杂直接影响材料表面缺陷密度和电子结构,进而促进 O₂ 分子的吸附与活化,这种由制

备方法决定的结构组成(比表面积、孔结构、缺陷密度、掺杂原子种类与数量等)最终协同作用于催化性能。因此,优化制备工艺(如双重活化、杂原子共掺杂)来精细构筑具有独特结构特征的功能煤基碳材料,是提升材料 ORR 催化活性,并实现在碱性、酸性及中性电解液中超越商业铂碳性能的根本方法。

3.2 电催化 CO₂ 还原

现代工业的高速发展消耗了大量的化石能源,同时将大量的 CO₂ 排放到大气中。大气中高浓度的 CO₂ 已引起全球范围内的气候异常,严重威胁生态、环境与健康^[95]。因此,CO₂ 问题亟待解决。电催化 CO₂ 还原技术可利用可再生能源产生的清洁电能,在常温常压条件下将 CO₂ 转化为高附加值化学品或燃料,实现具有经济效益的碳转化与资源化利用,因而成为解决 CO₂ 问题的重要方法^[96-98]。然而,CO₂ 分子具有线性中心对称结构,其 C=O 键的解离能达 750 kJ/mol,这导致 CO₂ 分子难以被活化,进而致使电催化材料的催化活性和选择性偏低^[99]。因此,亟须开发高性能的 CO₂ 还原电催化材料。功能煤基碳材料具有丰富的孔结构和大量的高活性位点,孔结构与活性位点之间的协同效应可实现高效电催化 CO₂ 还原。表 4 总结了近年来功能煤基碳材料在电催化 CO₂ 还原领域的研究工作。

图6 功能煤基碳材料在全 pH 范围均表现出优异氧还原性能^[93]Fig. 6 Excellent ORR performance of functional coal-based carbon materials across the entire pH range^[93]表4 功能煤基碳材料在电催化 CO_2 还原领域的研究工作Table 4 Research on functional coal-based carbon materials in the field of electrocatalytic CO_2 reduction

Functional coal-based carbon material	Electrolyte	Product type	Current density/ $(\text{mA} \cdot \text{cm}^{-2})$	Faradaic efficiency/%	Reference
CNPC-1100	0.1 mol/L KHCO_3	CO	0.3	92	[14]
NPC-900	0.5 mol/L KHCO_3	CO	2.3	95	[18]
CNNi-700	1 mol/L KOH	CO	223.0	97	[50]
NH_3 -NINCF	0.1 mol/L KHCO_3	CO	71.6	90	[79]
WNCNs-1000	0.1 mol/L KHCO_3	CO	1.1	84	[100]
CF-120	0.1 mol/L KHCO_3	CO	18.0	65	[101]
V_0 - SnO_x /CF-40	0.1 mol/L KHCO_3	HCOOH	30.0	86	[102]
C/Cu/PTFE-0.05-R	1 mol/L KOH	C_2H_4	142.4	62	[103]

Liu 等^[50]以无烟煤为原料, 利用两步液相法制备了一种高活性的镍/氮共掺杂煤基碳材料, 该材料在电催化 CO_2 还原过程中表现出 223.0 mA/cm^2 的大电流密度和 97% 的高 CO 选择性(见图 7)。该材料具有突出电催化性能的原因是 KOH 的活化作用在材料表层创制大量的微孔结构及缺陷位点, 这不仅使材料具有较大的比表面积($1250 \text{ cm}^2/\text{g}$), 同时也使材料拥

有高的 CO_2 吸附量($56.3 \text{ cm}^3/\text{g}$), 微孔结构的空间限域效应可提高孔内镍-氮活性位点周围局域 CO_2 浓度, 这为材料实现高效 CO_2 还原提供了有利的微反应环境; 同时, 无烟煤载体内部致密的碳骨架结构具有较低的电荷转移电阻(1.2Ω), 这可为镍-氮位点快速供给电子。因此, 材料镍-氮活性位点处高效的电子/底物交互作用使其表现出突出的催化活性。

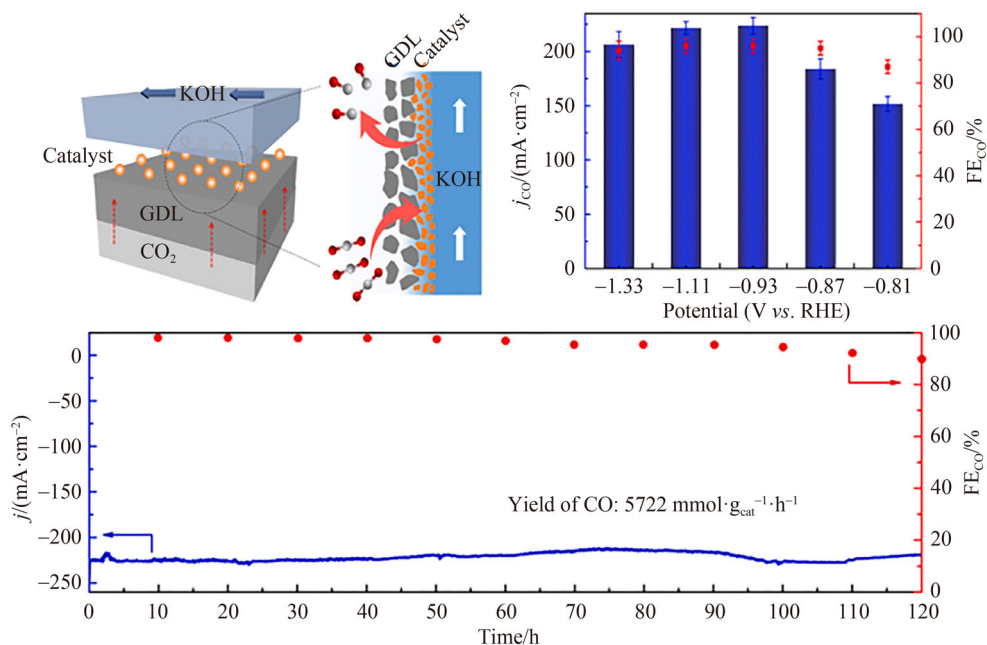


图 7 镍/氮共掺杂煤基碳材料高效电催化 CO_2 还原制 CO ^[50]

Fig. 7 Efficient electrocatalytic reduction of CO_2 to CO using nickel/nitrogen co-doped coal-based carbon materials^[50]

综上所述, 功能煤基碳材料在电催化 CO_2 还原领域中表现出优异的电化学性能, 这显著体现出了材料制备、结构调控与性能优化之间的紧密关联。其制备方法直接决定了材料的关键结构特征。例如, KOH 活化可创制丰富的微孔结构和缺陷位点, 这可增加材料的比表面积与提升其 CO_2 吸附能力; 镍、氮等活性组分的引入可构筑高活性的催化反应位点。这些特殊的结构特征协同提升材料的电化学性能。因此, 从材料制备入手, 通过精准调控材料形貌结构和化学组成, 协同优化底物局域浓度、电荷转移效率及活性位点催化能力, 使得功能煤基碳材料能够实现高产物选择性和电流密度, 这为实现高效电催化 CO_2 还原提供了创新研究思路。

3.3 超级电容器

超级电容器是一种新型的绿色储能装置, 因具有功率密度高、瞬时电流大、充放电速率快、循环寿命长等优点, 其在新能源、智能电网、电动汽车等领域被广泛应用^[104-107]。研究表明, 超级电容器的性能与电极材料的形貌结构和化学组成等参数密切相关^[108-110]。功能煤基碳材料拥有比表面积

大、孔径结构易调控、表面官能团丰富、导电性优异等特点, 这有助于提升超级电容器的双电层电容和赝电容性能。因此, 开发高性能功能煤基碳材料成为超级电容器领域重点研究内容。表 5 总结了近年来煤基碳材料在超级电容器领域的研究工作。

Liu 等^[116]利用液相法精准调控煤炭的形貌结构和化学组成, 制备了高性能的富微孔氮/氧共掺杂煤基碳材料。该材料表现出 371 F/g 的大比电容, 同时其在对称超级电容器中具有 625 W/kg 的高功率密度和 $40 (\text{W}\cdot\text{h})/\text{kg}$ 的高能量密度(见图 8)。该材料表现出优异储能性能的原因是制备过程中甲酸钾的活化作用与尿素的掺杂效应使得材料碳层间距增大, 并在碳骨架中引入大量的缺陷位点, 这有利于存储电解液离子, 进而有助于提升材料电容性能; 同时, 材料表面的 $\text{C}=\text{O}$ 官能团可以显著增加离子吸附量, $\text{C}-\text{O}$ 和 $\text{O}-\text{C}=\text{O}$ 官能团可作为氧化还原反应的位点, 吡咯氮能提升碳骨架的电化学活性, 四配位氮则可以提升电荷传输速率。得益于这些形貌结构和化学组成优势, 该煤基碳材料在超级电容器中表现出优异的储能性能。

表 5 功能煤基碳材料在超级电容器领域的研究工作

Table 5 Research on functional coal-based carbon materials in the field of supercapacitors

Functional coal-based carbon material	Electrolyte*	Specific capacitance/(F·g ⁻¹)	Power density/(W·kg ⁻¹)	Energy density/((W·h·kg ⁻¹))	Reference
SHC ₃	6M KOH	324	—	11	[15]
ANPC-1-800-0.25	6M KOH	346	—	20	[88]
NDHPC ₁₋₇₀₀₋₂	6M KOH	336	250	7	[111]
NHPC-60	6M KOH	219	510	28	[112]
CAC-3	6M KOH	219	501	11	[113]
HS-Et-PC	6M KOH	195	442	11	[114]
PC	6M KOH	317	296	23	[115]
NPC-1.5	6M KOH	371	625	40	[116]
AE	6M KOH	276	/	/	[117]
POCA800	6M KOH	174	125	8	[118]

*Note: All data in the table were obtained from tests conducted in 6 mol/L KOH electrolyte.

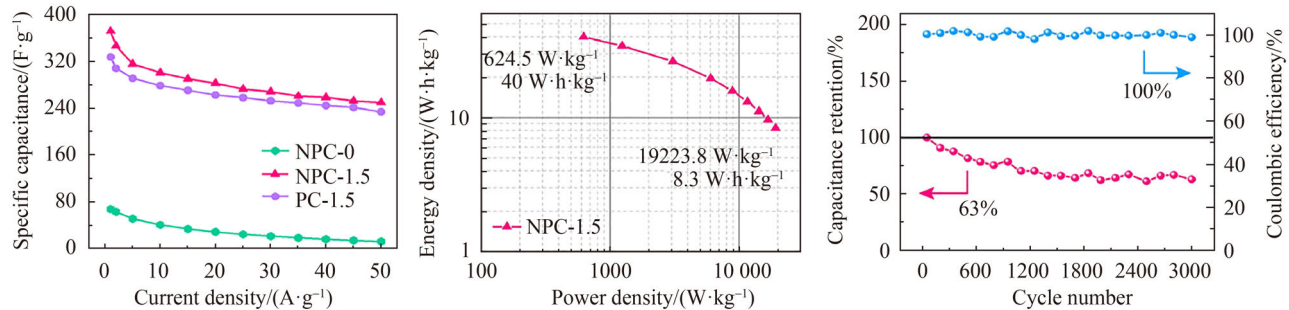


图 8 功能煤基碳材料在超级电容器中的比电容、能量密度、功率密度及稳定性^[116]

Fig. 8 Specific capacitance, energy density, power density, and stability of functional coal-based carbon materials in supercapacitors^[116]

综上所述，功能煤基碳材料在超级电容器中表现出优异的电化学性能，这得益于材料制备方法对其结构及组成的精准调控。上述研究表明，通过液相法制备工艺可高效调变煤基碳材料的关键结构参数，提升电解液离子的扩散速率和传质效率，实现高双电层电容；引入的大量氮、氧等杂原子不仅能改变碳骨架的电子云密度，还可以增加表界面电化学活性。制备方法对材料结构和组成的协同调控直接提升了材料电化学性能：实现了高比电容、功率密度和能量密度。因而，制备方法对材料形貌结构和化学组成的协同设计与精准调控，使得煤基碳材料在超级电容器中表现出优异的电化学性能。

3.4 锂离子电池

锂离子电池具有能量密度高、充放电平台稳定和循环寿命长等优点，在现代社会中发挥着重要作用^[119–122]。而且相比于传统电池技术，锂离子电池不含毒重金属镉或铅，对环境污染较低。作为锂离子电池的关键组成之一，负极材料对锂离子电池的电化学性能至关重要^[123–124]。功能煤基碳材料具有

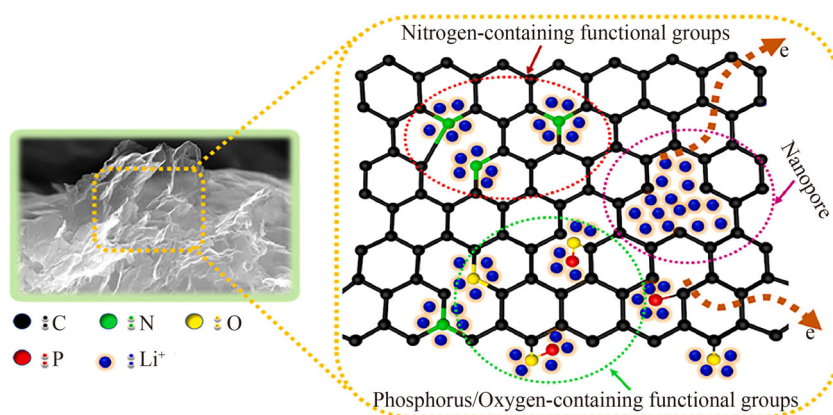
稳定的碳骨架和良好的导电性，能够有效嵌入和脱出锂离子，有助于提高电池的循环稳定性和倍率性能。因此，将功能煤基碳材料用作锂离子电池的负极材料，为锂离子电池的降本增效和绿色制造提供了新的可能。表 6 总结了近年来功能煤基碳材料在锂离子电池领域的研究工作。

Liang 等^[129]以无烟煤为原料，通过耦合法制备了一种氮/氧/磷三元掺杂煤基多孔碳材料。该材料在锂离子电池中表现出高可逆容量[1 079 (mA·h)/g]、长循环寿命(100 次循环后比电容保持率 100%)及良好的倍率性能[1 000.0 mA/g 时为 336 (mA·h)/g]。该材料具有优异锂电性能的原因是耦合法使得该材料通过交联碳纳米片构筑了三维多孔网络，这不仅形成了利于锂离子嵌入/脱出的类石墨结构，还为锂离子的传输和电子传导提供了便利的通道；另外，吡啶氮、吡咯氮和磷-氧官能团对锂离子具有很强的亲和力，这有助于提高材料的锂离子存储容量和倍率性能(见图 9)。因而，该煤基碳材料表现出突出的锂电性能。

表 6 功能煤基碳材料在锂离子电池领域的研究工作

Table 6 Research on functional coal-based carbon materials in the field of lithium-ion batteries

Functional coal-based carbon material	Electrolyte	Specific capacity/ ((mA·h)·g ⁻¹)	Capacity retention	Rate performance	Reference
DCG-6B	1.0 mol/L LiPF ₆	323	100% (500 cycles, 500.0 mA·g ⁻¹)	112 (mA·h)·g ⁻¹ (1 000.0 mA·g ⁻¹)	[125]
CGNs-50	1.0 mol/L LiPF ₆	726	88.1% (200 cycles, 100.0 mA·g ⁻¹)	255 (mA·h)·g ⁻¹ (1 000.0 mA·g ⁻¹)	[126]
A900	1.0 mol/L LiPF ₆	331	94.8% (1 000 cycles, 1 000.0 mA·g ⁻¹)	153 (mA·h)·g ⁻¹ (5 000.0 mA·g ⁻¹)	[127]
CBC-700	1.0 mol/L LiPF ₆	844	100% (500 cycles, 1 000.0 mA·g ⁻¹)	517 (mA·h)·g ⁻¹ (1 000.0 mA·g ⁻¹)	[128]
N/O/P-CCNs	1.0 mol/L LiPF ₆	1079	100% (100 cycles, 1 000.0 mA·g ⁻¹)	336 (mA·h)·g ⁻¹ (1 000.0 mA·g ⁻¹)	[129]
NPC-2	1.0 mol/L LiPF ₆	734	100% (500 cycles, 1 000.0 mA·g ⁻¹)	397 (mA·h)·g ⁻¹ (1 000.0 mA·g ⁻¹)	[130]
C-LIG	—	330	99% (80 cycles, 100.0 mA·g ⁻¹)	149 (mA·h)·g ⁻¹ (2 000.0 mA·g ⁻¹)	[131]
A-CSG-800	—	366	100% (15 000 cycles, 1 000.0 mA·g ⁻¹)	36.6 (mA·h)·g ⁻¹ (5 000.0 mA·g ⁻¹)	[132]
N-PCNS	—	727	100% (1 000 cycles, 5 000.0 mA·g ⁻¹)	344.6 (mA·h)·g ⁻¹ (5 000.0 mA·g ⁻¹)	[133]
PGC-900-10	1.0 mol/L LiPF ₆	386	90.7% (400 cycles, 100.0 mA·g ⁻¹)	325 (mA·h)·g ⁻¹ (1 600.0 mA·g ⁻¹)	[134]

图 9 氮/氧/磷三元掺杂煤基多孔碳材料储锂机理^[129]Fig. 9 Lithium storage mechanism of nitrogen/oxygen/phosphorus ternary doped coal-based porous carbon materials^[129]

由上可知, 功能煤基碳材料作为锂离子电池负极材料展现出优异的电化学性能, 其核心优势源于制备方法对材料结构组成的精准调控及带来的性能优化。研究表明, 通过特定的处理方法可有效调控煤基碳材料的微观结构: 一方面, 活化过程能抑制碳微晶生长、引入大量缺陷并显著增大碳层间距, 这促进了锂离子在碳层间的快速嵌入/脱出; 另一方面, 这些方法同时构建了发达的多孔网络结构, 不仅为离子传输提供了高效通道, 也为锂离子存储创造了充足空间。更重要的是, 元素掺杂策略可在碳骨架中引入具有强锂离子亲和力的官能团, 进而能进一步提升界面反应活性与电池容量。这种通过制备方法实现的多孔网络构筑、层间距优化和高活性杂原子掺杂的结构特点, 使得功能煤基碳材料能够在锂离子电池中实现高可逆容量、优异的循环稳定性和倍率性能。因此, 功能煤基碳材料的研发体现了“制备方法决定结构特征, 结构特征引领电化学性能”的内在关联性, 这为锂离子电池开发低成本、高性能的负极材料提供了新思路。

3.5 钠离子电池

钠离子电池是依靠钠离子在正极和负极之间移动来工作, 与锂离子电池工作原理相似。钠离子电池因其具有资源丰富和成本低廉等优势, 近年来被视为锂离子电池的重要补充或替代品^[135-138]。然而, 由于钠离子的半径较大, 商业石墨负极材料的层间距较小, 钠离子难以在石墨层中嵌入和脱出, 导致钠离子电池的性能较差^[139]。与石墨相比, 煤基碳材料具有更大的层间距和更多的孔结构, 能够有效地容纳较大的钠离子, 从而有助于提升钠离子电池的性能。表 7 总结了近年来功能煤基碳材料在钠离子电池领域的研究工作。

Liu 等^[141]采用固相-液相耦合法制备了具有丰富闭孔结构的煤基硬炭材料以提升钠离子电池性能。该材料在钠离子电池中表现出 326 (mA·h)/g 的高比容量, 以及 100 次循环后 87% 的高电容保持率。该材料具有突出钠电性能的原因是其具有丰富大孔容的闭孔结构(0.197 cm³/g)和较大的层间距(3.78 nm), 较大的闭孔结构可增加钠离子的储存位

点, 合适的层间距允许钠离子进入闭孔, 同时可防止溶剂分子进入闭孔, 进而可抑制孔内形成固体电解质界面膜(见图 10), 这一独特的结构特征使得材料的平台电容比例到达 70.3%, 而高的平台电容比

例不仅有助于提升倍率性能, 使材料在高电流密度下仍能保持较高的容量, 还可以增强循环稳定性, 减少充放电过程中的体积应变和结构坍塌。因而, 该功能煤基材料表现出优异的钠电性能。

表 7 功能煤基碳材料在钠离子电池领域的研究工作

Table 7 Research on functional coal-based carbon materials in the field of sodium-ion batteries

Functional coal-based carbon material	Electrolyte	Specific capacity/ ((mA·h)·g ⁻¹)	Capacity retention	Rate performance	Reference
NLC-260	1 mol/L NaPF ₆	294	80% (1 000 cycles, 500.0 mA·g ⁻¹)	30 (mA·h)·g ⁻¹ (1 000.0 mA·g ⁻¹)	[140]
BCPC-10	1 mol/L NaClO ₄	326	87% (100 cycles, 50.0 mA·g ⁻¹)	90 (mA·h)·g ⁻¹ (300.0 mA·g ⁻¹)	[141]
SOAS	1 mol/L NaPF ₆	260	9% (500 cycles, 1 000.0 mA·g ⁻¹)	240 (mA·h)·g ⁻¹ (100.0 mA·g ⁻¹)	[142]
CABC-P-2.5	/	290	90% (100 cycles, 0.2 C)	136 (mA·h)·g ⁻¹ (1 C)	[143]
P-HC	1 mol/L NaClO ₄	284	54% (500 cycles, 100.0 mA·g ⁻¹)	61 (mA·h)·g ⁻¹ (1 000.0 mA·g ⁻¹)	[144]
BCoal-SM-700	1 mol/L NaClO ₄	286	74% (1 000 cycles, 1 C)	97 (mA·h)·g ⁻¹ (5 C)	[145]
BPHC	1 mol/L NaClO ₄	200	100% (150 cycles, 100.0 mA·g ⁻¹)	58 (mA·h)·g ⁻¹ (1 000.0 mA·g ⁻¹)	[146]
ZT3WYM7	1 mol/L NaPF ₆	272	80% (1 300 cycles, 10 C)	229 (mA·h)·g ⁻¹ (10 C)	[147]
N-AC-1200	1 mol/L NaClO ₄	220	83% (500 cycles, 100.0 mA·g ⁻¹)	182 (mA·h)·g ⁻¹ (500.0 mA·g ⁻¹)	[148]
1-KMO	0.8 mol/L NaClO ₄	175	92% (1 000 cycles, 500.0 mA·g ⁻¹)	156 (mA·h)·g ⁻¹ (1 000.0 mA·g ⁻¹)	[149]

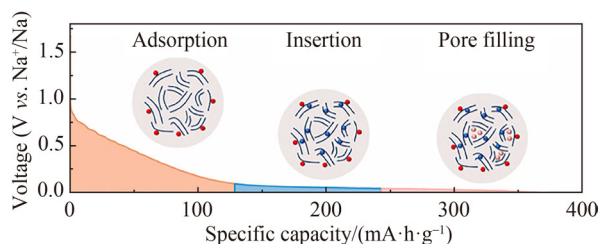


图 10 煤基碳材料的钠离子存储机制及比电容^[141]

Fig. 10 Sodium ion storage mechanism and specific capacitance of coal-based carbon materials^[141]

基于上述文献分析, 功能煤基碳材料在钠离子电池负极中的性能优化遵循“制备-结构-性能”协同机制。针对钠离子半径较大导致的动力学缓慢和商业石墨不适用等关键挑战, 科研人员通过优化制备方法调控材料结构参数: 增加层间距, 为钠离子高效传输提供通道; 构筑闭孔结构, 为钠离子大量储存提供空间, 同时阻隔电解液, 抑制固体电解质界面膜过度生长。因此, 通过制备方法定向调控材料的层间距、闭孔结构结构参数, 可使材料在钠离子电池中实现高效储能。

综上, 功能煤基碳材料的性能优化高度依赖于材料制备-结构调控-性能优化的内在关联性: 制备方法直接决定了材料的比表面积、孔结构、石墨化程度、缺陷密度、碳层间距和掺杂原子种类/含量等结构参数, 而这些结构参数协同影响传质/传荷效率、反应热力学/动力学和底物吸附强度/局域浓度等, 并最终使材料在各个应用领域实现优异的电化学性能。这种内在关联性体现出功能煤基碳材料作为低成本、高活性电化学材料的巨大潜力, 这为电

化学能量/物质转化与储存技术的发展提供了重要的研究思路。

4 结论与展望

通过高效便捷的制备方法开发高性能功能煤基碳材料用于电化学领域至关重要。高性能功能煤基碳材料与电化学能量/物质转化与储存技术的有机结合, 为实现煤炭清洁高效利用和碳中和提供了切实可行的发展方向。本文系统综述了功能煤基碳材料的制备方法与其在电化学能量/物质转化与储存技术的应用进展, 详细探究了材料结构与其电化学性能的内在关联性, 得出以下核心结论:

1) 制备方法决定性能: 功能煤基碳材料的电化学性能高度依赖所选制备方法对其关键结构参数的调控, 针对特定应用场景选择最优制备方法是提升材料电化学性能的关键。

2) 电化学性能突出: 得益于可调控的结构优势, 功能煤基碳材料在燃料电池、电催化 CO₂ 还原、超级电容器、锂/钠离子电池等应用中展现出优异性能, 应用前景广阔。

3) 绿色与经济性并重: 开发功能煤基碳材料是实现煤炭高附加值、非燃料化清洁利用的有效途径, 契合国家能源转型与碳中和战略, 同时为传统煤炭产业升级提供了新方向。

基于上述功能煤基碳材料制备及电化学应用的研究现状, 我们对功能煤基碳材料的未来研究方向提出展望:

1) 绿色低碳制备工艺创新: 发展环境友好、低能耗、低排放的新方法(如物理活化法、绿色化学工艺等), 减少强酸强碱试剂的依赖, 减少制备过程的碳排放。

2) 材料构效关系与性能提升机制的深入解析: 结合先进原位表征与理论计算, 深入揭示材料在工况条件下的结构演变规律与性能提升机制, 建立精确的“制备-结构-性能”构效关系, 指导高性能煤基碳材料理性设计。

3) 面向产业化的关键技术突破: 着力解决原料煤质差异、规模化制备工艺与装备、产品一致性与稳定性等产业化瓶颈, 推动高性能功能煤基碳材料的实际应用。

随着上述关键科学问题及工程技术的突破, 功能煤基碳材料有望在电化学能量/物质转化与储存领域起到极为重要的作用, 为实现“双碳”目标提供物质与技术支撑。

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Research Progress on Preparations and Electrochemical Applications of Functional Coal-Based Carbon Materials

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Extended Abstract

Coal is a fossil resource that is abundant and widely distributed, and it plays an extremely important role in the economic

development and social progress of different countries. However, conventional coal utilization methods (such as direct combustion for power generation and heating, and metallurgy) produce large amounts of CO₂, sulfides, and nitrides, seriously threatening ecology, environment, and human-being health. It is thus necessary to improve the utilization methods of coal and promote the green and low-carbon utilization of coal resource. Functional coal-based carbon materials exhibit a superior performance in the field of electrochemical energy/matter conversion and storage due to their unique physicochemical properties, such as high electrical conductivity, large specific surface area, controllable pore structure, and rich surface functional groups. This is of great significance for achieving high value-added utilization of coal and carbon neutrality. In recent years, researchers have made significant progress in the preparation of functional coal-based carbon materials and their electrochemical applications. However, there are a few systematic reviews summarizing this rapidly developing field, and the relationship between the structural design and synthesis of functional coal-based carbon materials and the optimization of their electrochemical properties has not been comprehensively studied yet. This review deeply analyzes the latest research progress on functional coal-based carbon materials in the field of electrochemistry. Firstly, the structural features and chemical element composition of the different coal raw materials are summarized, and the applicable processing methods are described *via* analyzing the structural characteristics and applicability of representative coal raw materials. Subsequently, the process flows of commonly used methods for preparing functional coal-based carbon materials (*i.e.*, liquid-phase, solid-phase, gas-phase, direct-carbonization, and coupling) are analyzed. The effect of preparation method on the macrogeometric structure, mesoscopic surface physicochemical properties, and microscopic active site electronic structure of coal is discussed, and the regulatory mechanisms of preparation methods on the structure and composition of functional coal-based carbon materials is revealed. Afterwards, an in-depth investigation on the applications of functional coal-based carbon materials in mainstream electrochemical fields such as fuel cells, electrocatalytic CO₂ reduction, supercapacitors, and lithium/sodium-ion batteries is represented. The intrinsic correlation among material preparation, structural regulation, and performance optimization is given *via* studying the impact of the structure and composition of functional coal-based carbon materials on their electrochemical performance. Finally, this review looks forward to the future development directions of functional coal-based carbon materials, proposes strategies for optimizing the preparation methods and for improving material performance, and points out the key challenges for the industrialization of functional coal-based carbon materials. This review can provide theoretical guidance and technical references for the designs and electrochemical applications of functional coal-based carbon materials, promoting the clean and efficient utilization of coal resource and the rapid development of electrochemical technologies.

The main methods for preparing functional coal-based carbon materials include liquid-phase, solid-phase, gas-phase, direct-carbonization, and coupling methods. The liquid-phase method involves mixing coal raw materials, activators, and dopants with solvents, followed by heat treatment to prepare porous coal-based carbon materials doped with heteroatoms. The advantage of this method is its ability to precisely modulate the materials' morphological structure and surface physicochemical properties, as well as to load highly active metal species onto the coal support. The solid-phase method utilizes mechanochemistry (such as ball mills, mortars, *etc.*) to mix coal raw materials, dopants, and activators, which can prepare functional coal-based carbon materials with large specific surface areas, high doping contents of heteroatoms, and uniform structures. The gas-phase method utilizes gases to synergistically regulate the morphology of coal and types and contents of doped atoms, enabling atomic-level modification of the coal surface. The direct-carbonization method converts coal into functional coal-based carbon materials with an large number of defects and closed pore structures through high-temperature carbonization, which is suitable for anode materials in lithium/sodium ion batteries. Coupling method integrates the advantages of different methods to achieve multidimensional and precise modulation of the structure, composition, and performance of the functional coal-based carbon materials.

Functional coal-based carbon materials have attracted widespread attention in electrochemical energy fields such as fuel cells, electrocatalytic CO₂ reduction, supercapacitors, and lithium/sodium-ion batteries due to their structural designability and cost advantages. For fuel cells, the functional coal-based carbon materials can significantly improve the efficiency and stability of fuel cells due to their better mass/charge transfer efficiency and stronger corrosion resistance, compared to commercial platinum carbon materials. In the field of electrocatalytic CO₂ reduction, functional coal-based carbon materials can enhance the local concentration of CO₂/intermediates around their active sites *via* leveraging the size effects of their geometric structures (*e.g.*, spatial confinement effect). In addition, the functional coal-based carbon materials can also optimize the adsorption strength and thermodynamic conversion energy barriers of CO₂/intermediates *via* regulating the local electron density of the active sites, thereby achieving a highly selective conversion of CO₂ into valuable chemicals such as CO and ethylene. In supercapacitors, the functional coal-based carbon materials with large specific surface areas, hierarchical porous structures, and rich surface functional groups can improve electrolyte transfer rates and provide sufficient adsorption sites for ions, thereby achieving high double-layer capacitance and pseudocapacitance. For lithium/sodium-ion batteries, the large interlayer spacing, rich defects and closed pore structures of functional coal-based carbon materials enable them to optimize the transfer and adsorption processes of lithium/sodium ions, thereby improving the storage capacity and rate performance of batteries.

The structural adjustability of functional coal-based carbon materials enables to adopt different preparation methods according to the actual application scenarios to obtain the suitable functional coal-based carbon materials, greatly promoting the development of electrochemical energy/matter conversion and storage technologies. Moreover, developing functional coal-based carbon materials can achieve the non-fuel utilization of coal and reduce environmental pollution generated during coal utilization, which is in line with the concept of green sustainable development. Also, the combination of functional coal-based carbon materials and electrochemical

technologies can extend the coal industry chain and enhance the added value of coal, thus promoting the transformation and upgrading of the coal industry.

Summary and Prospects Functional coal-based carbon materials demonstrate an enormous application potential in the field of electrochemical energy/matter conversion and storage due to their abundant raw materials, low cost, and adjustable structure. This review systematically summarizes the research progress on the preparation methods and electrochemical applications of functional coal-based carbon materials, and explores the intrinsic relationships between material structure and electrochemical performance. Based on the existing research status of the preparations and electrochemical applications of functional coal-based carbon materials, we propose some prospects for their future research directions, *i.e.*, 1) Simple and environmental-friendly physical activation methods need to be developed, such as supercritical CO₂-assisted activation and microwave carbonization, which achieve controllable pore structure construction through radical reactions and interfacial energy regulation. Low-energy technologies such as photothermal-driven carbonization and plasma pulse activation should be developed to utilize non-equilibrium thermodynamics to regulate the degree of graphitization and defect quantity of carbon layers, thereby reducing carbon emissions from the preparation process. In addition, machine learning can be also used to optimize preparation parameters (such as temperature field, pressure field, atmosphere composition, *etc.*) to achieve accurate prediction and targeted control of materials' morphology, structure, and chemical composition, 2) The structure–property relationship and performance improvement mechanism of materials need to be analyzed. In-situ characterization techniques (such as electrochemical-synchrotron radiation coupling technology and in-situ aberration-corrected electron microscopy) can analyze the material structure and composition during electrochemical processes, clarify the mechanisms of material performance degradation under complex conditions, and develop modification strategies. In addition, it is also necessary to develop kilowatt-scale industrial electrochemical devices suitable for functional coal-based carbon materials to promote the practical application of coal-based carbon materials and 3) Some precise coal quality analysis methods and standardized coal processing methods need to be established and the continuous, large-scale production equipment needs to be developed, thereby addressing the impact of coal raw materials on product structure and performance consistency. For instance, establishing a rapid analysis of coal quality (*i.e.*, combining near-infrared spectroscopy with Raman spectroscopy)-three-dimensional structural simulation (*i.e.*, Material Studio)-process parameter feedback system ensures that the structural parameters of coal raw materials from different production areas remain within a certain range. The design of a modular mobile doping-activation-pyrolysis integrated system is expected to enable the continuous conversion of coal raw materials into functional coal-based carbon materials, thus addressing the impact of conventional batch preparation process on the product performance. These technologies can contribute to the large-scale production and application of high-performance functional coal-based carbon materials.

Keywords coal; functional coal-based carbon material; electrochemical energy/matter conversion and storage; structural regulation; structure-activity relationship; clean and efficient utilization of coal