

基于金属有机框架的超级电容器电极材料的最新进展

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摘要

超级电容器(SC)在储能领域被普遍认为是一种很有前途的电化学装置。电极材料作为超级电容器的组成部分之一,对储能器件的电化学性能起着至关重要的作用。因此,寻找或合成新的电极材料至关重要。金属有机骨架(Metal-Organic Frameworks, MOFs)材料作为金属有机材料(Metal-Organic Materials, MOM)中一类重要的新型材料,由于其功能多样性、固有的多孔性、大的比表面积、可调的孔隙度和简单的合成方法,在SCs中得到了广泛的研究。在这篇综述中,讨论了由金属-有机框架材料衍生的不同类型的纳米/微米混合结构作为超级电容器应用的电极材料的性能。

关键词

金属有机骨架, 电极材料, 衍生物, 超级电容器, 能量转换

Recent Advances in Electrode Materials for Supercapacitors Based on Metal-Organic Frameworks

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Abstract

Supercapacitor (SC) is widely regarded as a promising electrochemical device in the field of energy storage. As one of the components of supercapacitors, the electrode material plays an impor-

tant role in the electrochemical performance of energy storage devices. Therefore, it is very important to find or synthesize new electrode materials. Metal-Organic Framework (MOF) is important new material in Metal-Organic Materials (MOMs). Due to its functional diversity, inherent porosity, large specific surface area, adjustable porosity and simple synthesis method, it has been widely studied in SCs. In this review, we discuss the performance of different types of nano/micro composite structures derived from metal-organic frameworks as electrode materials for supercapacitor applications.

Keywords

Metal-Organic Framework Material, Electrode Materials, Derivative, Supercapacitor, Energy Conversion

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1. 引言

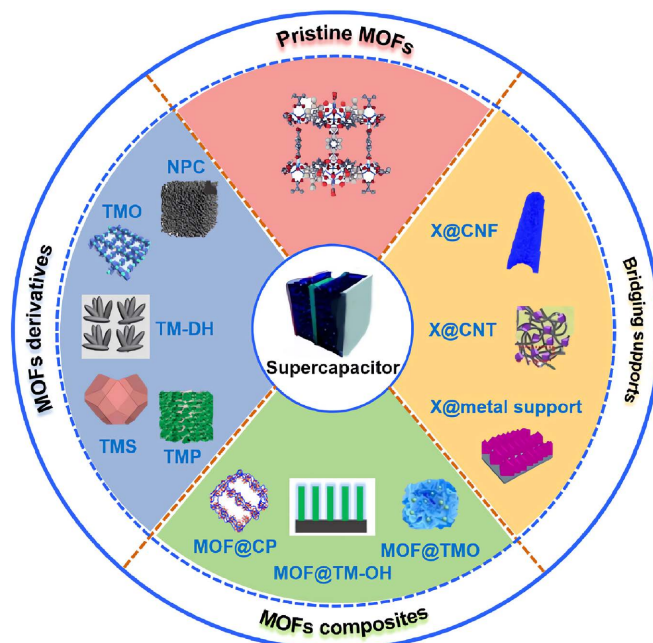


Figure 1. Illustration of the different MOFs and MOF-derived electrode materials for supercapacitors

图 1. 不同 MOF 及 MOF 衍生的超级电容器电极材料示意图

在世界能源中,越来越多的可再生能源(如太阳能、风能、潮汐能等)受到了更多的重视,占据着越来越重要的地位。然而,随着科技的发展和人类生活水平的提高,我们面临着日益严重的环境和资源问题,包括温室效应、光污染、资源短缺等。可再生能源资源的有限性和化石燃料消耗带来的污染极大地促进了对清洁绿色可持续能源的需求[1]。为了解决这个问题,大量的研究人员积极参与开发能量高效的转换和存储设备,如锂离子(Li-ion)电池、电容器和燃料电池[2] [3] [4] [5]。在这些清洁能源存储设备中,超级

电容器因其具有循环寿命长、功率密度高、工作范围宽、充放电速度快、储能能力强等优点而备受关注[6] [7] [8] [9] [10]。虽然超级电容器可以存储大量的电荷,可以用于提供比可充电电池更高的功率等级,但它比电池和其他燃料电池具有更低的能量密度[11]。因此,在不降低功率密度的前提下提高能量密度是超级电容器研发的主要目标。因为目前材料由于比表面积(SSA)和孔隙率不足而提供低的功率密度和充电周期[12] [13]。

尽管使用碳材料作为电极在一定程度上克服了这些缺点,但它们仍然缺乏高电容和能量密度[14]。此外,为了满足它们的性能,Yaghi等人[15]于1995年提出了一类新的多孔材料,称为金属-有机框架或有机-无机杂化框架,通过在金属节点和有机配体之间发展配位键得到的一类材料。各种类型的金属离子和有机配体的使用导致了MOF结构的多样性。迄今为止,已经发现了超过20,000种不同组成的MOFs[16]。金属有机骨架材料通常是孔径小于2 nm的微孔结构。它们具有高结晶度和更可调的组成,这使得它们比其他缺乏选择性和吸收限制的多孔结构(如活性炭和沸石)更有效[16] [17] [18]。我们详细总结了原始MOFs、MOFs衍生物和MOFs复合材料用于超级电容器的电化学性能分析,主要内容如图1所示。并总结了近年来该领域的重要成果,对该领域的主要挑战进行展望。

电化学超级电容器,又称超级电容器,根据不同的储能机制可以分为三种类型:分别为双电层电容(EDLC),赝电容和混合超级电容器(HSC)[19] [20]。在EDLC机制中,基于非法拉第氧化还原反应,在电极和电解质的边界表面形成双电层;而在赝电容机制中,活性物质发生法拉第氧化还原反应[21]。

已有文献表明,电极材料是影响SCs电化学性能的重要因素之一。EDLCs通常采用具有高表面积和适当孔隙率的碳基材料,如碳纳米管(CNT)、石墨烯和活性炭(AC),而过渡金属氧化物(MO)、过渡金属氢氧化物和导电聚合物通常用作法拉第赝电容器的电极材料[22] [23] [24]。不同于EDLCs和赝电容器,HSCs由电容型电极和电池型电极组成[25] [26] [27]。

利用两种不同的反应机理(非法拉第氧化还原反应和法拉第氧化还原反应)同时实现高的比能量和比功率。此外,根据活性物质的不同,超级电容器还可以分为对称超级电容器和非对称超级电容器。对称超级电容器具有相同的正负极活性物质,而非对称超级电容器(ASC)具有不同的正负极活性物质。与对称超级电容器相比,由电池型电极和电容型电极组装的ASCs不仅拓宽了工作电压,也大大提高了比电容和能量密度[28]。

在三类超级电容器中,开发先进的电极材料是获得高电化学性能的关键。MOF材料由于具有多孔性、多功能性、突出的比表面积、可调控的功能性、多样的结构和可控的化学组成,被普遍认为是下一代储能器件的有前途的材料[28] [29] [30] [31]。在气体存储/分离、污染物吸附、药物缓释、选择性催化等领域得到了广泛的应用[6] [32] [33] [34]。

MOF除了具有高比表面积、多孔性、多重氧化还原活性、化学和机械稳定性以及晶体结构多样外,还含有丰富的电荷存储活性位点。尽管上述优点有助于提高电化学性能,但大多数原始MOF在充放电过程中的低电导率和低化学/结构稳定性仍然限制了其在超级电容器中的应用。

2. 用于SCs的MOF电极材料

2.1. 原始MOF用于SC

由于其独特的性质,如可调的孔径、有序的晶体结构和极大的比表面积,MOF被广泛用于催化、药物输送、气体存储/分离和储能装置等领域[35] [36]。另一方面,MOF在储能领域的应用已经成为众多研究的焦点。由于其高度有序的结构和丰富的氧化还原金属中心,MOF最近被广泛用作超级电容器的电极材料[37] [38]。迄今为止,原始的M-MOF (M = Zn, Co, Mn, Fe, Ni)在几何形貌和结构上没有任何功能化,由于其原料丰富、廉价易得而被广泛研究。其中,沸石咪唑骨架材料(ZIFs)作为一类重要的MOF,由金

属离子和有机配体咪唑盐构筑而成,受到研究者的青睐。ZIFs 应用于 SCs 中最典型的材料是 ZIF-8 和 ZIF-67。ZIF-8 由锌离子和 N-甲基咪唑组成,具有良好的热稳定性,易于合成和近似的孔隙率,而 ZIF-67 由钴离子和 N-甲基咪唑构建[39]。Zhang 等人[40]报道了通过一步溶剂热法制备的 NiCo-MOF,与其他 NiCo-MOF 和 Ni/Co-MOF 相比,表现出最佳的电化学性能。由于其独特的三维球形树莓状结构,NiCo-MOF-3 显示出有效的内阻和电子转移电阻,以改善电能存储,在 1A/g 时表现出优异的质量比电容 639.8 F/g [41]。Nguyen 等人[42]报道了通过电泳沉积法制备 $\text{Ni}_3(\text{HITP})_2$,该 MOF 具有非常好的循环稳定性(如图 2 所示)。

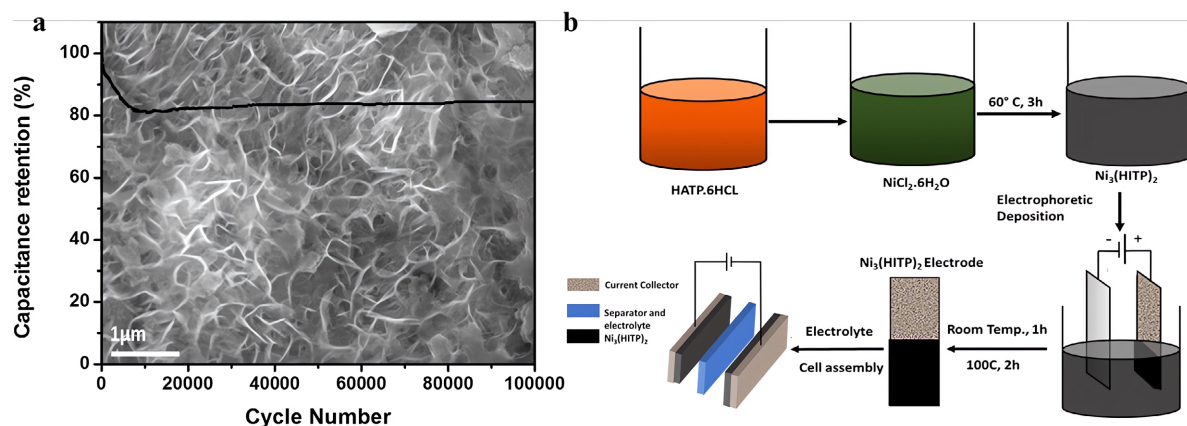


Figure 2. (a) The excellent cyclic stability of $\text{Ni}_3(\text{HITP})_2$; (b) Schematic illustration of preparation and EPD of $\text{Ni}_3(\text{HITP})_2$ supercapacitors [42]

图 2. (a) $\text{Ni}_3(\text{HITP})_2$ 优异的循环稳定性; (b) $\text{Ni}_3(\text{HITP})_2$ 超级电容器的制备及 EPD 示意图[42]

此外, Ma 等人[43]以 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 、4-氨基-1,2,4-三氮唑(atrz)和 1,3-苯二甲酸(1,3-BDC)为原料合成了另一种纯 MOF,称为 Cu_4 簇基三维 MOF (Cu-atrz-BDC)。在三电极体系中, Cu-atrz-BDC 作为电极材料在 1 A/g 的电流密度下表现出 5525 F/g 的超高比电容, 1000 次循环后仍保持 886 F/g 的高比电容保持率。此外,以 Cu-atrz-BDC 为正极、rGO 为负极的自组装非对称超级电容器也表现出了良好的倍率性能、循环稳定性、低内阻、快速电荷传输等优异性能。还有一些其他的原始 MOF 应用于 SCs,包括多孔晶体结构的新型纳米海绵状原始 Zr-MOF、UiO-66 和 Ce-MOF-808 等[44] [45] [46]。总的来说,原始的 MOF 很可能凭借其天然的优点成为电极材料的有前途的候选者。考虑到环境友好性、原料的丰富性和过程的复杂性,进一步探索具有良好导电性、形貌和粒径分布的原始 MOF。

2.2. MOF 衍生材料用于 SC

与原始 MOF 相比, MOF 衍生材料因其化学成分可控、形态独特、孔道丰富、孔隙度好等优点,在燃料电池、超级电容器等储能器件中具有广阔的应用前景[47] [48] [49]。

当这些 MOF 衍生物用作电极时,它们可以提供出色的电化学性能,如良好的电容、循环稳定性和增强的电导率[50]。近几十年来,相关研究人员在这一领域做了大量的工作。例如, MOF 衍生的多孔碳具有新颖的形貌和特定的分级多孔结构,有利于提高电化学性能。Wang 报道了两种 ZIF-8 衍生的多孔碳多面体(ZDPC)和电池状的 MoS_2 -ZIF 复合材料[51]。多孔碳多面体具有连续的 3D 多孔网络结构,具有极高的比表面积和可控的孔径分布 MoS_2 -ZIF 复合材料显示出具有开放框架的三维(3D)纳米结构(如图 3 所示) [51]。当它们用作电容器的电极时,该混合系统表现出较大的能量密度和 $20,000 \text{ Wkg}^{-1}$ 的高功率密度。作者认为该材料在能量、功率和循环寿命方面显示了当前混合超级电容器的最佳性能[51]。

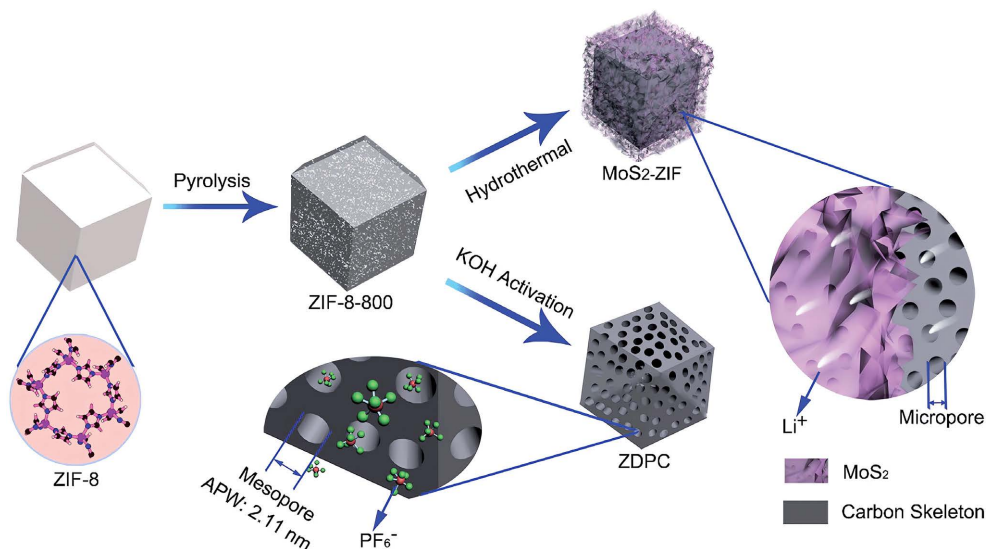


Figure 3. Schematic of the synthesis of the 3D MoS₂-ZIF composite and ZIF-8 derived porous carbon (ZDPC) [51]

图 3. 3D MoS₂-ZIF 复合材料和 ZIF-8 衍生多孔碳(ZDPC)的合成示意图[51]

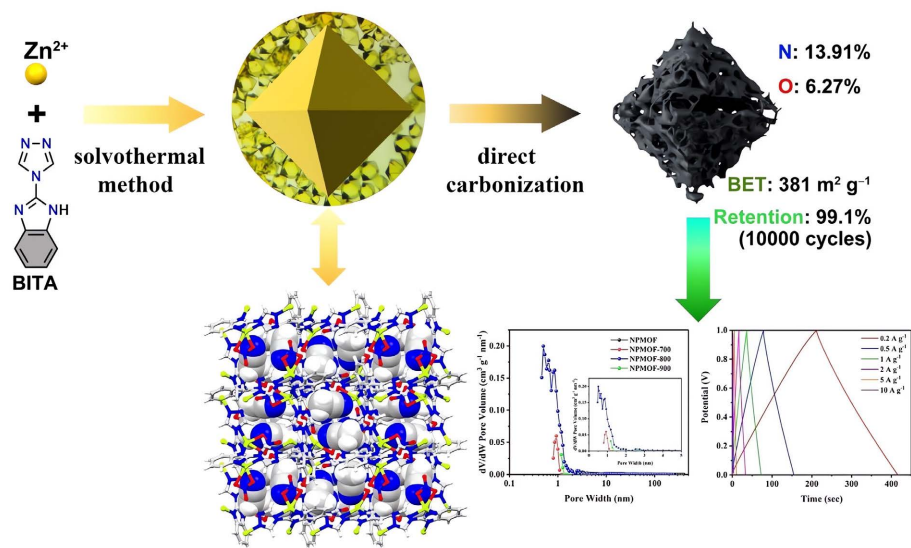


Figure 4. Schematic illustration for the preparation of MOF-derived porous carbons and single crystal structure of NPMOF [54]

图 4. MOF 衍生多孔碳的制备示意图及 NPMOF 的单晶结构[54]

为了进一步提高材料的热稳定性和热容量,通常采用多原子掺杂策略和化学活化,其中杂原子掺杂(N、S、B、P)在 MOF 应用中尤为重要[52]。其中,在特定条件下煅烧 MOF 在多孔碳中进行氮掺杂是其应用于电极材料的主要途径之一,且已有研究证明氮源来自于 N₂ 气氛或有机配体[53]。例如,Gu 等人[54]通过直接碳化纳米多孔 Zn-MOF 制备了氮和氧原子共掺杂的 NPC,其中有机配体含有丰富的氮元素(如图 4 所示)。在此过程中,通过调整热解温度,制备了一系列高 N/O 含量的 NPMOF 衍生多孔碳。由于 NPMOF-800 的有效表面积、孔径分布和杂原子掺杂,它们在三电极体系中表现出更好的电化学性能、良好的离子扩散和电荷转移行为。计算得到 NPMOF-800 的比电容可达 220 F/g,具有极高的比表面积归一化电容(57.7 mF/cm²),这可归因于其超高的杂原子含量(N: 13.91%, O: 6.27%)和超微孔特性。用作电极时,

它显示出优异的能量和功率密度, 良好的倍率性能, 在 10,000 次充放电循环后电容保持率为 99.1%。这些显著的优点归因于杂原子(N 和 O)的存在增强了赝电容和润湿性。

过渡金属氧化物在储能方面具有热容量高、化学稳定性好、尺寸和带型可控等特点[55] [56]。MOF 为各种形貌的金属氧化物提供了模板, 具有较大的比表面积和较好的循环稳定性[57] [58]。例如, Song 等人[59]通过将相应的 Cu-MOF 浸泡在 NaOH 溶液中, 制备了由纳米颗粒、纳米线和纳米片组成的具有 3D 海胆状和棒状超结构的两种新型 CuO。Tian 等人[60]制备了多孔中空四面体 Co_3O_4 作为锂离子电池负极材料选用双壁四面体 MOF 作为前驱体, 制备中空 Co_3O_4 。得益于高度多孔的中空结构, 所得材料表现出较大的储锂容量、优异的倍率性能和循环稳定性。

2.3. MOF 复合材料用于 SCs

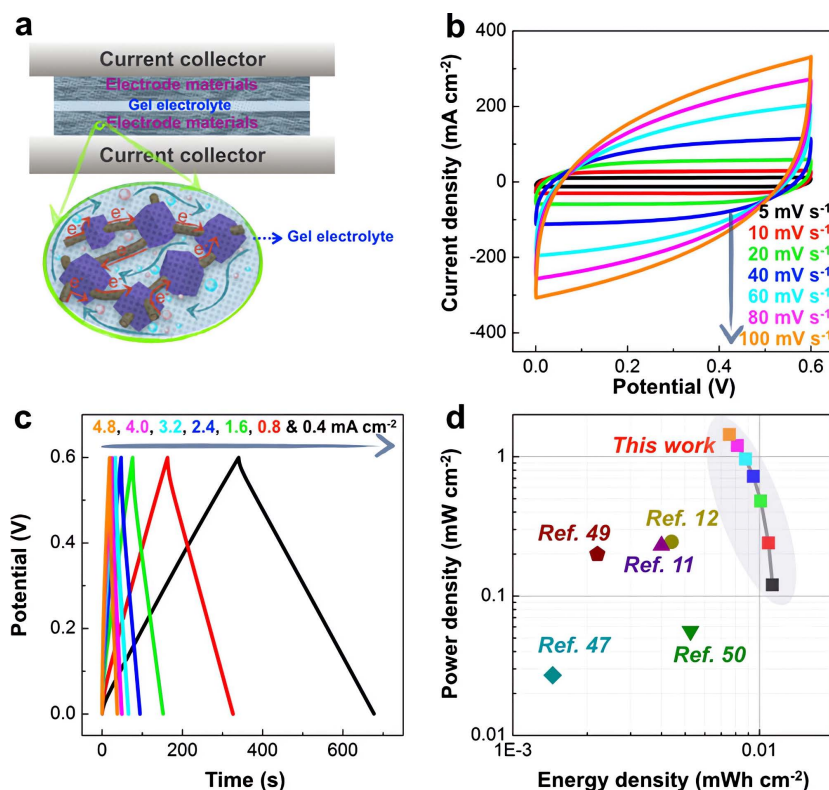


Figure 5. (a) Schematic representation of a flexible supercapacitor device based on ZIF-PPy-2 electrodes and gel electrolyte; (b) CV curves at various scan rates; (c) GCD curves at various current densities, and (d) Corresponding Ragone plots and comparisons of ZIF-PPy-2 flexible supercapacitor

图 5. (a) 基于 ZIF-PPy-2 电极和凝胶电解质的柔性超级电容器器件的示意图; (b) 不同扫描速率下的 CV 曲线; (c) 不同电流密度下的 GCD 曲线; (d) 相应的 Ragone 图和 ZIF-PPy-2 柔性超级电容器的比较

与电池相比, 较低的能量密度和较差的导电性阻碍了储能器件的进一步发展。为了解决这一问题, 人们采取了许多措施, 如探索具有优异导电性的新型 MOF, 制备其衍生物(过渡金属氧化物、过渡金属硫化物等), 合成 MOF 复合材料等。上述方法可以为 MOF 复合电极在长期循环过程中提供结构稳定性和高导电性[61]。MOF 复合材料作为一种新型功能材料, 目前发展迅速。由于它们的协同作用, 已被应用于气体吸附、分离、电化学发光、光电化学生物传感器、高效液相色谱、催化、气体传感、药物传递等领域, 甚至扩展到燃料电池和电催化等领域[62] [63] [64] [65]。

一般来说, 不同 MOF 与导电聚合物结合后, 其电化学性能各不相同。在最近的研究中, Ferhi 等人[66]

通过溶剂热法成功合成了缺陷型 MOF-808@聚苯胺复合材料用于高电容保持率的超级电容器电极。作者声称,这是首个使用缺陷的 d-MOF 来制备杂化材料 d-MOF-808@PANI,其中 d-MOF-808 和 PANI 的摩尔比不同(15:1, 30:1, 60:1)。在这种情况下,通过 d-MOF-808 活化、超声处理、真空干燥等步骤制备了缺陷 MOF-808@聚苯胺复合材料。活化后的 d-MOF-808@PANI (60:1)电极表现出比纯 d-MOF-808 和纯 PANI 电极更优异的电化学性能,在 10,000 次循环后电容保持率为 99.7%。一个可能的原因是有缺陷的结构可以减少 MOF 的堵塞。Wang 等人[67]还发表了一篇关于分级多孔 PANI/MIL-101 纳米复合材料的文章。在恒流充电和放电测试中,所得 PANI/MIL-101 在 1 A/g 下表现出 1197 F/g (即 957.6 C/g)的优异高电容。组装的柔性固态超级电容器还显示出良好的比电容、功率密度和良好的循环稳定性(在 10,000 次循环中 81%的电容保持率)。徐等人[68]通过加热处理合成了三维网络 MOF@PPy 复合材料,其中 PPy 作为 MOF 颗粒原位生长的支撑。在三电极测试中,该复合材料表现出 597.6 F/g 的高比电容和 2.33 F/cm² 的高面积电容。而且 ZIF-PPy-2 在 0~0.6 V 之间表现出稳定的性能。在柔性超级电容器器件中具有 225.8 mF/cm² 的高面积比电容(如图 5 所示)。

3. 总结与展望

为了满足对高性能能量储存和转换设备的巨大需求,电极材料的进展至关重要。MOF 可以通过简单的后处理(通常包括热解)转化为相当稳定的材料。这些新结构在许多应用中成为理想材料,并且经常优于传统结构。然而,MOF 基电极材料的应用存在一定的局限性。例如,原始 MOF 的低导电性是一个严重的缺陷。此外,MOF 衍生材料具有更好的稳定性,但不再具有任何规则孔隙率,MOF 基复合材料仍然存在原 MOF 的化学稳定性差的问题。本文的前几部分重点介绍了超级电容器材料的一些研究和开发报道。这些研究有着十分重要的作用,为后续继续探究超级电容器高性能材料奠定了基础。

未来还需要继续探究,以提高功率和超级电容器的能量密度。虽然在这一领域取得了很大进展,但前方仍有重大困难。首先,现有的 MOF 大多电导率低,这对实际应用来说是一个很大的缺点。因此制备新的具有更高导电性的 MOF 是解决超级电容器电极材料的最佳途径。第二,探究 MOF 衍生材料的更简单的制备方法。MOF 衍生材料不仅能保留本体 MOF 的性质不变,还能表现出更高的电化学性能。是储能材料不错的选择之一。因此,探索更简单环保的合成方法至关重要。第三,MOF 基复合材料保留了本体 MOF 的优点,其他组分可能提供优异的导电性能或与 MOF 结合形成互通的网络结构有利于电子传递和离子传输。由于这种协同效应,复合材料比任何单一组分都能表现出更强的电化学行为。因此对于复合材料的探究我们不能停止脚步。在未来,由于对各种新型高导电性原始 MOF 的理解仍然很少,因此需要大量的工作来阐明其导电机理。随着合成方法的进步和规模化,越来越多具有优异电化学性能的 MOF 衍生物和 MOF 复合材料将迅速发展成为一种具有广泛能源和环境应用价值的新型、经济、可持续的电极材料。

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