

·综述·

凝胶聚合物电解质及其在印刷超级电容器上的应用

王桂林 文 韬*

(华南理工大学前沿软物质学院 广东省功能与智能杂化材料与器件重点实验室 广州 510640)

摘要: 印刷超级电容器(PSC)因其可规模化制造和柔性集成特性,在柔性电子与新型储能系统中展现出广阔应用前景。凝胶聚合物电解质(GPE)作为其中关键功能层,对器件的性能与稳定性具有决定性影响。本文系统综述了近年来GPE在PSC中的研究进展,重点围绕聚合物体系类型、溶剂体系以及制备方法进行分类梳理,综合分析其对离子传输行为、电极/电解质界面特性及器件电化学性能的影响机制。在此基础上,进一步总结了不同GPE体系在印刷适配性、循环稳定性及柔性可靠性方面的优势与局限。当前研究表明,GPE在实现高离子电导率、良好机械性能与印刷工艺兼容性之间仍面临挑战,界面阻抗控制、环境适应性及规模化制造一致性仍是制约PSC性能提升和实际应用的关键问题。未来研究需从材料结构设计、作用机制解析及印刷工艺协同优化等方面入手,发展多功能与环境友好型的GPE体系,以推动PSC向高性能化、柔性化和系统集成化方向发展。本文的综述与分析可为GPE的合理设计及其在印刷储能器件中的应用提供实验参考及研究思路。

关键词: 凝胶聚合物电解质; 超级电容器; 印刷

Research Progress of Gel Polymer Electrolyte in Printed Supercapacitors

WANG Gui-lin, WEN Tao*

(School of Emergent Soft Matter, Guangdong Provincial Key Laboratory of Functional and Intelligent Hybrid Materials and Devices, South China University of Technology, Guangzhou 510640)

Abstract: Printed supercapacitors (PSC) have attracted increasing attention in flexible electronics and emerging energy storage systems owing to their scalability and compatibility with flexible integration. As a key functional layer, the gel polymer electrolyte (GPE) plays a decisive role in determining the performance and stability of PSC. This review systematically summarizes the recent research progress on GPE in PSC, with a particular focus on their classification based on polymer systems, solvent systems, and fabrication methods. The influence of the GPE on the ion transport behavior, electrode/electrolyte interfacial characteristics, and electrochemical performance of PSC was comprehensively analyzed. On this basis, the advantages and limitations of different GPE systems in terms of printability, cycling stability and mechanical reliability are further discussed. Current studies indicate that achieving a balance among high ionic conductivity, mechanical integrity and printing compatibility remains challenging, while interfacial resistance control, environmental adaptability and manufacturing consistency continue to limit the performance improvement and practical application of PSC. Future research should focus on material structural design, mechanistic understanding, and synergistic optimization of printing processes, aiming to develop multifunctional and environmentally friendly GPE systems to promote PSC toward high performance, flexibility, and system-level integration. This review provides experimental references and

2026-01-04 收稿, 2026-02-06 录用, 2026-04-14 网络出版

* 通信联系人: 文韬, E-mail: twen@scut.edu.cn

doi: 10.14028/j.cnki.1003-3726.2026.26.002

research insights for the rational design of GPE and their application in printed energy storage devices.

Keywords: Gel polymer electrolyte; Supercapacitor; Printing

引用: 王桂林, 文韬. 凝胶聚合物电解质及其在印刷超级电容器上的应用. 高分子通报, 2026, 39(5), 703–719.

Citation: Wang, G. L.; Wen, T. Research progress of gel polymer electrolyte in printed supercapacitors. *Polym. Bull.* (in Chinese), 2026, 39(5), 703–719.

随着全球能源需求的持续增长与便携式电子设备的快速发展, 开发高效、可靠且环境适应性强的新型储能器件已成为研究前沿^[1,2]。超级电容器(SC)凭借其高功率密度、长循环寿命和优异倍率性能, 在储能技术中占据重要地位。SC主要通过电极表面快速可逆的离子吸附/脱附(双电层电容)或表面氧化还原反应(赝电容)存储能量^[3]。

然而, 传统SC多为刚性块状结构, 体积和形状固定, 难以满足现代电子设备日益增长的柔性化、微型化、可穿戴及形状定制化需求。以金属箔为集流体、液态电解质封装于刚硬外壳内的传统结构笨重、缺乏形变能力, 且存在电解质泄漏、封装工艺复杂、难以与曲面设备集成等问题。印刷技术(如丝网印刷^[4–6]、喷墨打印^[7–10]、3D打印^[11–14]等)作为一种高效增材制造方法, 能够以低成本、高通量方式在各种基底上精确图案化沉积活性材料, 直接制备轻薄、柔性甚至可拉伸的储能器件, 推动了SC在智能标签、电子皮肤、可穿戴医疗监测等领域的应用。

在实现高性能印刷超级电容器(PSC)的诸多关键材料中, 电解质的选择至关重要。传统液态电解质虽离子电导率高, 但与印刷工艺兼容性差, 在柔性器件中易泄漏挥发, 带来安全隐患和性能衰减^[15]。因此, 开发兼具高离子导电性和机械稳定性的固态电解质成为必然选择。凝胶聚合物电解质(GPE)由聚合物网络锁定液态电解质构成, 既保留了接近液态电解质的高离子电导率, 又兼具固态电解质的防泄漏、高安全性及良好的成膜特性。此外, GPE前驱体溶液具有良好且可调的流变特性, 能完美适配各类印刷工艺, 实现电解质精确均匀涂布, 并与印刷电极形成紧密的界面接触, 为器件电化学性能和机械稳定性提供结构基础。

近年来, GPE在PSC中的应用研究取得了显著进展^[16–20]。本文系统综述了不同种类GPE的特点和制备方法, 以及其在PSC领域的应用进展。

1 GPE 的分类

GPE以聚合物凝胶作为结构骨架, 通过物理或化学交联构建起具有特定流变性质的三维网络, 通过掺杂酸、碱或离子盐实现质子或离子传导。其核心组分是作为结构骨架的聚合物基质, 如聚乙烯醇(PVA)、聚环氧乙烷(PEO)、聚偏氟乙烯(PVDF)和聚丙烯酸(PAA)等, 它们直接影响了电解质的机械性能、电化学稳定性及离子迁移行为。

1.1 PVA基凝胶电解质

PVA基GPE不仅具有易于加工、易于成膜和价格低廉等特点, 还兼具优异柔韧性、高离子电导率和安全性, 尤其适用于构建柔性SC^[21]。

PVA富含羟基, 易于形成氢键网络, 是自修复水凝胶最常用的载体之一^[22]。Chen等^[23]报道了一种室温下快速自修复的PVA基双网络水凝胶(图1)。这种水凝胶在室温下无需外部刺激就能表现出极快的自修复能力(10 s内恢复初始强度且延展性达100%)。但是, PVA基水凝胶通常含有大量水分, 在低温下极易结冰进而影响电化学性能和柔韧性。为此, 研究者们提出了一些解决策略。例如, Wu等^[24]采用盐溶液替代策略, 制备了一种兼具高韧性与抗冻性能的离子导电水凝胶。该方法将冷冻的PVA水凝胶前驱体浸泡于醋酸钾(KAc)溶液中, 利用KAc对PVA的盐析效应, 使所得水凝胶在 $-60\text{ }^{\circ}\text{C}$ 下仍能保持 $1.2\text{ S}\cdot\text{m}^{-1}$ 的高离子电导率。Rong等^[25]采用水/乙醇混合溶剂策略, 使PVA水凝胶在 $-40\text{ }^{\circ}\text{C}$ 下也能保持稳定的柔韧性和触变敏感性。

1.2 PEO基凝胶电解质

PEO基GPE由PEO与锂盐等增塑剂构成, 制备简单、安全性高, 是替代传统液体电解质的潜在选择^[26]。然而, PEO室温下结晶度较高, 导致其GPE离子电导率偏低、机械强度较差, 限制了其实际应用^[27]。

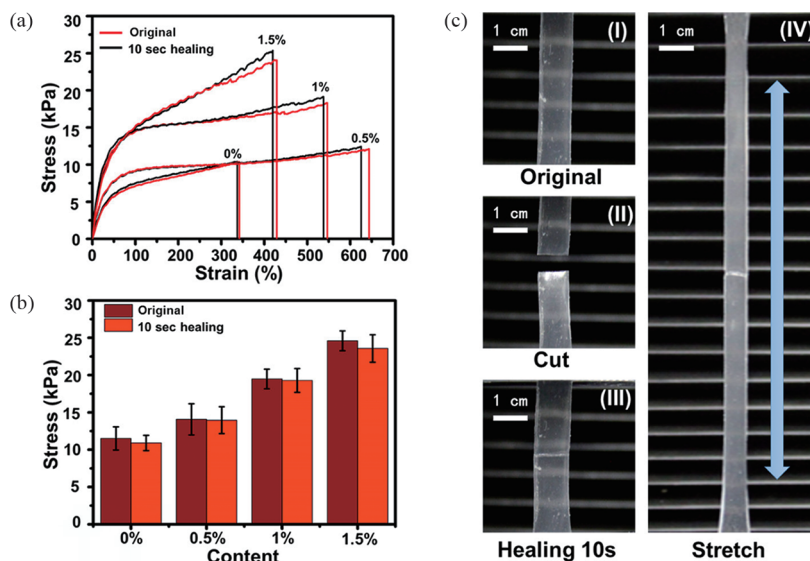


图1 PVA基水凝胶的拉伸和自修复测试以及自修复过程的照片^[23]。(a)原始PVA水凝胶和含不同琼脂含量(0.5 wt%、1.0 wt% 和 1.5 wt%)的琼脂/PVA DN水凝胶的拉伸应力-应变曲线,以及修复后的PVA水凝胶和琼脂/PVA DN水凝胶的曲线;(b)含不同琼脂含量(0.5 wt%、1.0 wt% 和 1.5 wt%)的PVA水凝胶和琼脂/PVA DN水凝胶的原始应力和修复后应力的直方图;(c)含1 wt%琼脂的条状琼脂/PVA DN水凝胶(I);水凝胶被切成两段(II);水凝胶在室温下接触10 s后可自动修复(III);修复后的水凝胶被拉伸(IV) (2018 American Chemical Society 版权许可)

Figure 1 Tensile and self-healing tests of PVA-based hydrogels and photographs of the self-healing process. (a) Tensile stress-strain curves of original PVA hydrogel and agarose/PVA DN hydrogel with different contents of agarose (0.5 wt%, 1.0 wt%, and 1.5 wt%), and the curves of healed PVA hydrogel and agarose/PVA DN hydrogel; (b) Original stress and healed stress histogram of PVA hydrogel and agarose/PVA DN hydrogel with different contents of agarose (0.5 wt%, 1.0 wt%, and 1.5 wt%); (c) Strip-shaped agarose/PVA DN hydrogel with 1 wt% of agarose (I); the hydrogel is cut into two pieces (II); the hydrogel can heal automatically after contacting for 10 s at room temperature (III); and the healed hydrogel is stretched (IV) (Reprinted with permission from Ref. [23]; Copyright (2018) American Chemical Society)

通过向PEO中加入无机填料是一种改善策略。例如, Groce等^[28]将纳米级陶瓷粉末作为PEO的固体增塑剂,通过动力学抑制结晶的方法,可提升室温电导率至 $10^{-5} \text{ S} \cdot \text{cm}^{-1}$ 。Zheng等^[29]采用纳米金属氧化物簇与PEO复合制备GPE,其在 $-20 \sim 100^\circ\text{C}$ 表现出优异质子电导率,并使得SC在极端环境下实现长期稳定工作(图2)。

1.3 PVDF基凝胶电解质

PVDF的 β 晶因其强极性而具备高介电常数。该特性有利于锂盐的解离并增强与电解质的亲和性。此外, PVDF自身具备优异的机械强度与宽电化学窗口。但是,由于PVDF具有较高的本征结晶度,研究者更倾向于使用结晶度更低、液体电解质浸润性更好的聚偏氟乙烯-六氟丙烯(PVDF-HFP)共聚物^[30~32]。常规的PVDF-HFP共聚物制备及表征流程如图3所示。

Hu等^[33]利用静电纺丝和浸泡法制备了一种具有高离子电导率、耐高温性和阻燃性的PVDF-

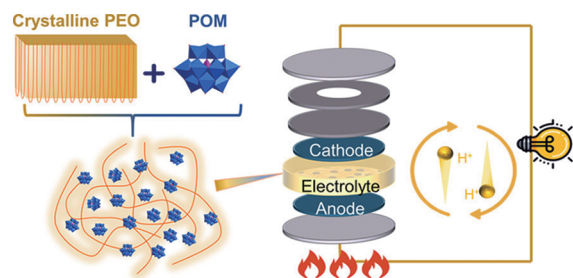


图2 PEO与纳米级的金属氧化物簇复合材料在极端环境下应用的示意图^[29] (2021 American Chemical Society 版权许可)

Figure 2 Schematic illustration of the application of PEO composites with nanoscale metal oxide clusters under extreme environments (Reprinted with permission from Ref. [29]; Copyright (2021) American Chemical Society)

HFP/明胶(GN)GPE。PVDF-HFP的静电纺丝网络及其对液体电解质的亲和力显著提升了GPE的离子传输能力。Bai等^[34]通过向PVDF-HFP中加入N掺杂碳量子点(N-CQDs)和 TiO_2 ,制备的器件具有较大的比电容($102 \text{ F} \cdot \text{g}^{-1}$)、优异的循环性

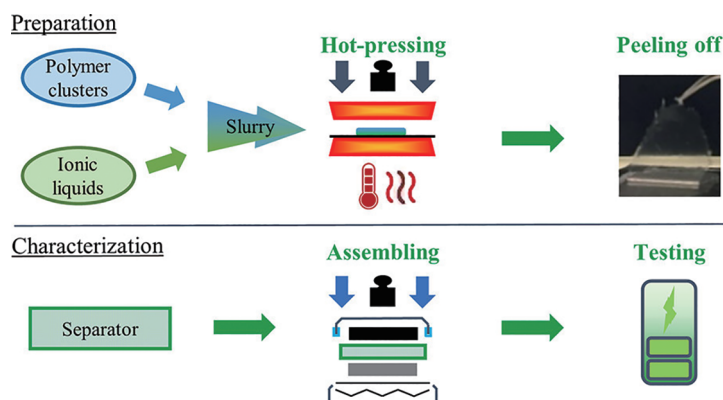


图3 PVDF-HFP共聚物基凝胶电解质的制备工艺流程^[35] (2018 American Chemical Society 版权许可)

Figure 3 Process flow diagram for the preparation of PVDF-HFP copolymer-based gel electrolyte (Reprinted with permission from Ref. [35]; Copyright (2018) American Chemical Society)

能(2×10^4 次循环后,容量保持85%)和倍率性能($40 \text{ A} \cdot \text{g}^{-1}$ 下,电容保持105%)。

1.4 PAA基凝胶电解质

PAA基GPE保水性好、离子电导率高,并兼具优异机械性能与自修复潜力^[36,37]。Hu等^[38]采用逐层沉积法,将电化学活性纳米复合材料依次构筑于PAA水凝胶电解质两侧,制备的一体化SC可承受高达60%的压缩应变与150%的拉伸应变(图4)。Guo等^[39]报道了一种铁离子交联的超分子PAA水凝胶电解质,其中离子键和氢键赋予 KCl-Fe^{3+} /PAA水凝胶电解质良好的自修复能力。同时,该水凝胶电解质保持了良好的机械性能和优异的电导率($0.09 \text{ S} \cdot \text{cm}^{-1}$)。

1.5 其他

除上述聚合物外,聚丙烯酸甲酯(PMMA)^[40,41]、聚丙烯腈(PAN)^[42,43]等也可以作为GPE基质。此外,随着“可持续发展”观念的增强,“天然高分子基GPE”如纤维素^[44,45]、壳聚糖^[46-48]、海藻酸盐^[49-51]和卡拉胶^[52]等也受到更多关注。

Li等^[53]以甲基纤维素为前驱体,硝酸铁和硼酸为双模板剂、活化剂及掺杂源,通过双模板辅助法制备了氮硼双掺杂多孔碳纳米片(NBC),并以细菌纤维素为基质制备了全纤维素基准固态SC。该NBC电极在酸性电解质中 $0.5 \text{ A} \cdot \text{g}^{-1}$ 电流密度下比电容达 $572 \text{ F} \cdot \text{g}^{-1}$ 。其所组装的BCC- NaClO_4 准固态SC电压窗口为2.3 V,能量密度可

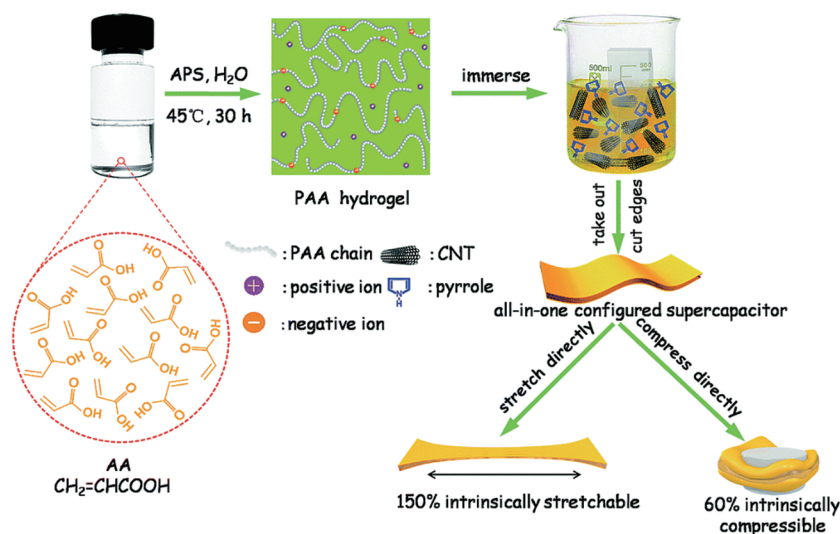


图4 PAA基水凝胶电解质的合成及一体化SC的制备^[38] (2018 The Royal Society of Chemistry 版权许可)

Figure 4 Synthesis of PAA-based hydrogel electrolyte and fabrication of integrated supercapacitors (Reprinted with permission from Ref. [38]; Copyright (2018) The Royal Society of Chemistry)

达 $43 \text{ W} \cdot \text{h} \cdot \text{kg}^{-1}$, 器件兼具高能量密度、优异倍率性能和长循环稳定性, 为可持续、高效储能器件的设计提供了低成本方案。

Zeng 等^[54] 另辟蹊径, 发展了一种完全由海带制备的全固态 SC。研究人员以海带为碳源和生物模板, 通过碳化和 KOH 活化得到了具有三维分级多孔结构的高比表面积 ($4425 \text{ m}^2 \cdot \text{g}^{-1}$) 活性炭电极材料; 同时从海带中提取出海藻酸钠, 并分别将其用作离子导电的黏结剂、隔膜和 GPE, 构建了对称型全固态 SC。该器件表现出优异的电化学性能, 电极比电容高达 $277 \text{ F} \cdot \text{g}^{-1}$ ($88.2 \text{ F} \cdot \text{cm}^{-3}$), 且循环稳定性良好 (循环 1×10^4 次后电容保持率达 97%)。该工作提供了一种全生物质来源、环境友好且具有生物相容性的器件构建策略, 尤其适用于高安全性要求的可穿戴电子设备和植入式医疗器件, 为发展高性能、低成本、高安全的固态储能系统提供了新思路。

2 不同溶剂体系对 GPE 的影响

根据溶剂体系的不同, GPE 可分为 3 类: 水系、有机系和离子液体。在 GPE 的基质以及离子盐等相同时, 溶剂体系的不同也会导致 GPE 的物化性质及电化学性能具有显著区别 (表 1)。

2.1 水系

水系 GPE 的优势在于安全、环境友好且成本低廉, 兼具优异的柔性与界面相容性^[55]。但是, 水系电解质存在着较窄的电化学窗口^[56], 同时在极端条件下易发生失水或相变。

针对上述问题, 研究者们通过结构设计和配方调控等方式进行优化。例如, Choi 等^[57] 以 PVA 为基质, H_2SO_4 为电解质, 去离子水为溶剂, 设计成非对称型 SC, 可实现 1.8 V 的最大电压, 并提供高能量密度 ($19.7 \text{ W} \cdot \text{h} \cdot \text{kg}^{-1}$) 和功率密度 ($6.8 \text{ kW} \cdot \text{g}^{-1}$)。而 Wang 等^[58] 则对电解质本身进行优化, 以 PVA、LiCl 和蒸馏水制备了 GPE。由于 LiCl 电解液为中性, 溶剂化作用能够有效抑制电极的化学溶解和不可逆的氧化反应以增大电压窗口 (图 5)。

在整体应用层面, 水系 GPE 在 PSC 中的应用主要受限于水分的高挥发性及其对环境条件的敏感性。在印刷过程中, 水系 GPE 对体系黏度窗口及干燥速率的调控要求较高。同时, 长期循环或开放环境条件下, 水分蒸发或电解质干涸现象易发生, 从而削弱器件的电化学稳定性及柔性器件的运行可靠性。因此, 在选择水系 GPE 作为电解质材料时, 有必要从整体应用角度综合评估其使用特性。

表 1 基于不同溶剂的 GPE 性能统计

Table 1 Statistical analysis of GPE performance based on different solvents

电解质	温度范围 (°C)	自放电率	电导率 ($\text{S} \cdot \text{cm}^{-1}$)	工作电压 (V)	环境友好性
水凝胶	窄	较高	高	1.5 V 左右	高
有机凝胶	较宽	中等	较高	可达 4 V	中
离子凝胶	宽	低	较高	可达 6 V	低

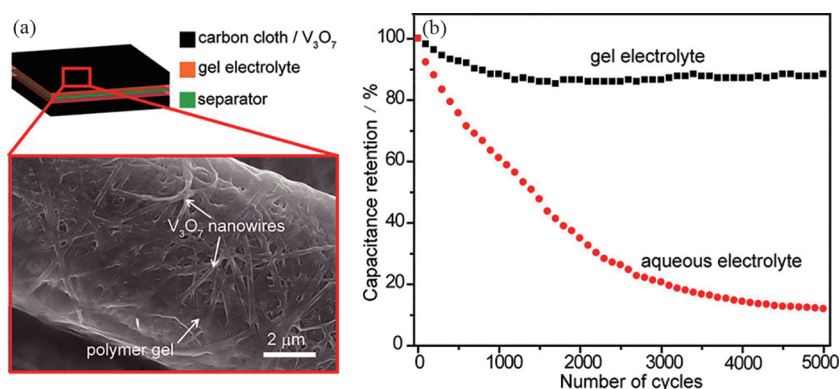


图 5 (a) 聚合物电解质与氧化钒纳米线微观结构示意图; (b) 水系电解液和水系 GPE 循环性能对比^[58] (2012 American Chemical Society 版权许可)

Figure 5 (a) Schematic diagram of the microstructure of polymer electrolyte and vanadium oxide nanowires; (b) Comparison of cycling performance between aqueous electrolyte and aqueous GPE (Reprinted with permission from Ref. [58]; Copyright (2012) American Chemical Society)

2.2 有机系

尽管水系GPE的电化学窗口在研究者的努力下已有较大提升,但通常是以牺牲机械性能或者低成本效益为代价。采用有机溶液为溶剂依旧是实现器件高能量密度的最常用途径。例如, Schroeder等^[59]以甲基丙烯酸酯为基质,异丁烯酸甲酯为溶剂,锂盐为电解质制备的有机凝胶,将工作电压提高到4 V,实现了能量密度的显著提升。

但是,有机系GPE的离子电导率普遍较低,在实际应用中其离子电导率亟待提升^[60]。加入无机填料是一种有效途径。例如, Jain等^[61]将气相纳米SiO₂加入PVDF-HFP-PC-Mg(ClO₄)₂有机凝胶中,使GPE在室温下具有 $5.4 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ 的电导率。Łatoszynska等^[62]则采用不同策略,以PC和DMF作为有机溶剂,通过用磷酸酯代替酸, GPE工作电压窗口提高到1.3 V,同时离子电导率在20 °C下可达 $3.1 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ (图6)。

相比水系体系,有机系GPE通常具有更宽的电化学稳定窗口,但其较低的挥发控制性和潜在的溶剂泄漏问题在印刷成膜及长期弯折循环过程中对界面稳定性和器件安全性提出了更高要求,限制了其在柔性印刷器件中的进一步应用。

2.3 离子液体系

离子液体是指在室温或接近室温下完全由阴离子和阳离子构成的液态有机盐^[63]。离子液体可以赋予GPE高离子电导率、宽电化学窗口、不挥发特性及高热稳定性,同时保留了聚合物自身的机械强度和柔性。

Lee等^[64]采用PVA/EC/KI聚合物基体,引入4种离子液体,通过溶液浇铸-干燥法制备出离子液体基GPE,并组装为全固态对称SC。其中,基于1-乙基-3-甲基咪唑四氟硼酸盐(EMIBF₄)的电解质性能最为优越,在 $0.5 \text{ A} \cdot \text{g}^{-1}$ 电流密度下表现出 $160.6 \text{ F} \cdot \text{g}^{-1}$ 的比电容和 $180.67 \text{ Wh} \cdot \text{kg}^{-1}$ 的能量密度(图7)。Pandey等^[65]研究了一种含有室温离子液体(RTIL)的GPE。将镁盐 $\text{Mg}(\text{CF}_3\text{SO}_3)_2$ 与离子液体1-乙基-3-甲基咪唑三氟甲磺酸盐(EMITf)混合后,利用PVDF-HFP固定,制备了具有优异机械强度的自支撑、半透明和柔性薄膜电解质,其最大室温电导率可达 $4.8 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ 。离子液体基GPE因其低挥发性和优异的热稳定性在长期循环和器件安全性方面具有优势,但其高黏度特性增加了印刷流变调控难度,同时较高成本和潜在的环境与工艺兼容性问题,仍制约其在大面积、低成本印刷超级电容器中的应用。

3 GPE的制备方法

除了所用的聚合物基质和溶剂, GPE的性能也依赖于电解质材料本身的制备方法和成型工艺^[66,67]。制备工艺会直接影响聚合物的微观结构、电解液吸附分布和电极-电解质界面接触状态等^[68]。

3.1 溶液浇铸法

溶液浇铸法作为一种经典且简便的制备方法被广泛用于GPE的制备中。制备过程通常是将聚合物、电解质盐和增塑剂/溶剂共溶于易挥发的有

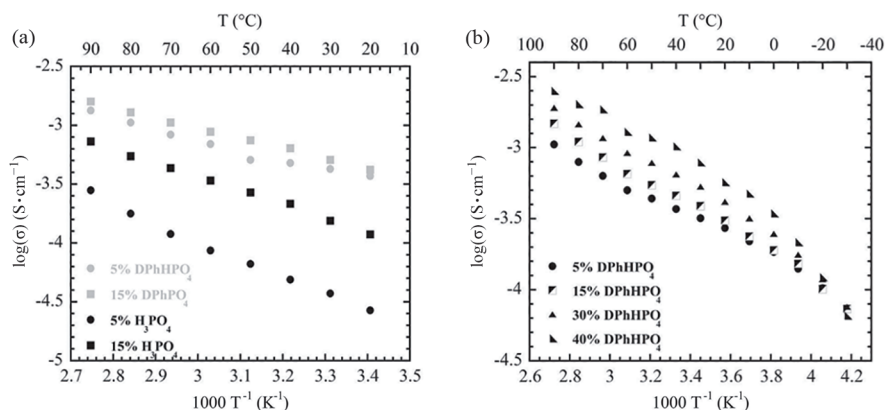


图6 含有不同浓度的质子供体基有机系GPE电导率与温度的关系:(a) H_3PO_4 和 DPhHPO_4 的比较;(b)不同浓度的 DPhHPO_4 ^[62] (2015 Elsevier 版权许可)

Figure 6 Relationship between the electrical conductivity and temperature of the organic system GPE containing different concentrations of proton donor groups: (a) Comparison of H_3PO_4 and DPhHPO_4 ; (b) Different concentrations of DPhHPO_4 (Reprinted with permission from Ref. [62]; Copyright (2015) Elsevier)

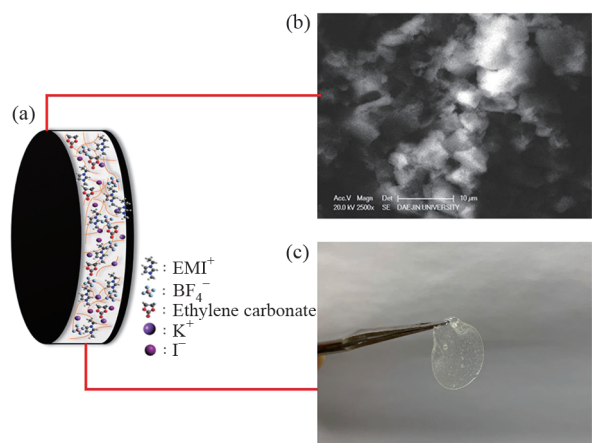


图7 (a)器件示意图;(b)基于AC电极的SEM图像;(c) EMIBF₄基GPE的照片^[64] (2021 Elsevier 版权许可)

Figure 7 (a) Schematic diagram of the device; (b) SEM image of the AC electrode-based; (c) Photograph of the EMIBF₄-based GPE (Reprinted with permission from Ref. [64]; Copyright (2021) Elsevier)

机溶剂中,通过浇铸成膜并蒸发溶剂,直接获得自支撑且柔性的GPE薄膜^[69,70]。

Tripathi等^[71]采用溶液浇铸法制备GPE薄膜,将PVDF-HFP溶于丙酮后,与增塑剂EC、PC及四乙基四氟硼酸铵(TEABF₄)混合,得到均匀的黏稠溶液。作者通过调节EC/PC/TEABF₄的比例和浓度,显著提升了该GPE的电导率和稳定性。Luo等^[72]同样以PVDF-HFP作为基质,将其与聚碳酸丙烯酯(PPC)混合溶于*N,N*-二甲基甲酰胺(NMF)后,掺入不同比例的陶瓷颗粒制得前驱体溶液;经溶液浇铸、溶剂挥发得到均匀的GPE薄膜。所得GPE薄膜表现出高离子电导率和5.2 V的宽电化学窗口。Chelfouh^[73]报道了一种由苹果果胶制成的新型可持续水凝胶电解质材料。通过使用简单的溶液浇铸方法,通过果胶凝胶化形成了一种基于生物的水凝胶。所得的水凝胶由水、锌和/或硫酸锂盐以及生物基聚合物等环境无害的化合物制

成。这种水凝胶电解质表现出与水溶液电解质(约 $5 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$)相似的环境离子电导率(图8)。

然而,溶液浇铸法在薄膜厚度精确控制和微尺度图形化方面存在一定局限,其成膜过程依赖溶剂缓慢挥发,难以与高分辨率印刷工艺直接匹配,在PSC中更适用于结构相对简单或后处理型电解质层的构筑。

3.2 相转化法

相转化法是一种通过相分离来构筑多孔结构的方法。一种典型的途径是让聚合物溶液在凝固浴中发生溶剂与非溶剂的交换,使聚合物从均相溶液中凝固而出,形成具有独特微孔结构的骨架^[74]。例如,Balakrishnan等^[75]提出利用相转化法,将PVDF/PMMA共混溶液刮涂于玻璃板上后,置于非溶剂浴中,体系发生溶剂交换形成均匀的微孔膜(图9)。作者通过调节PMMA的比例,微孔膜可实现电解质吸收率达413%,同时室温离子电导率达 $5.2 \text{ mS} \cdot \text{cm}^{-1}$ 。

相转化法有利于构筑连续的多孔离子传输网络以提升离子电导率,但其孔结构对溶剂交换条件高度敏感,均一性和重复性控制难度较大。研究人员重点可通过精细调控相转化动力学或引入印刷限定结构,实现性能与一致性的平衡。

3.3 紫外光固化法

紫外光固化法一般是将含有光引发剂的可聚合液态前驱体(包含单体、电解质盐和溶剂)直接涂覆于基底或电极表面,在紫外光照射下迅速引发原位聚合形成GPE薄膜。这一过程避免了如溶液浇铸法中出现的大量溶剂挥发,同时实现了界面的紧密贴合^[76]。

Li等^[77]将PEO基GPE的前驱体溶液涂敷于聚四氟乙烯(PTFE)板上,利用365 nm的紫外光照射10 s快速制得GPE薄膜。该薄膜在室温下表现出 $3.3 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ 的离子电导率。Lufrano等^[78]

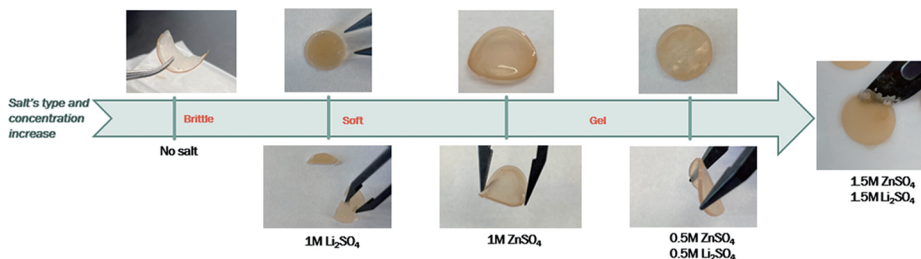


图8 使用溶液浇铸法制备的凝胶膜随盐浓度变化的演变^[73] (2022 American Chemical Society 版权许可)

Figure 8 The evolution of the gel film prepared by the solution casting method as the salt concentration changes (Reprinted with permission from Ref. [73]; Copyright (2022) American Chemical Society)

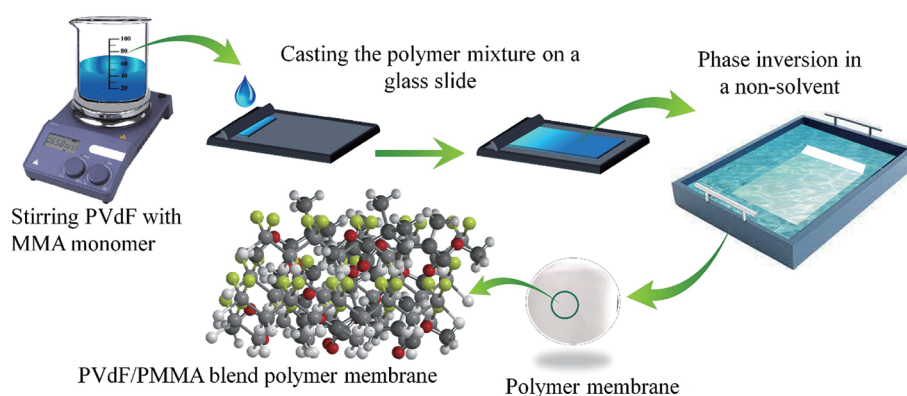


图9 相转化法制备GPE的示意图^[75] (2023 Elsevier 版权许可)

Figure 9 Schematic diagram of the preparation of GPE by phase inversion method (Reprinted with permission from Ref. [75]; Copyright (2023) Elsevier)

通过类似的方法,将前驱体溶液浇铸在2块玻璃板之间,随后以254 nm的紫外光照射10 min,制备了一种基于PEO和有机改性纳米黏土的纳米复合GPE薄膜(图10)。与溶液浇铸或相转化等方法相比,成膜速度更快,溶剂损失更少。

紫外光固化法优势在于可实现电解质的快速成膜和原位交联,具有良好的印刷兼容性和界面结合优势,但其性能受光引发体系和固化条件制约。若想要进一步拓展其在高性能PSC中的应用窗口,引发剂体系和固化策略的优化是重点途径。

3.4 静电纺丝法

静电纺丝法是一种通过高压静电场直接制备微纳米纤维膜的技术。该方法将聚合物溶液或熔体在电场力作用下拉伸、固化成直径极细且相互交联的三维无纺布纤维骨架。经液态电解质充分浸润后,该多孔网络结构能快速吸附并锁定大量

电解液,形成兼具高孔隙率、大比表面积和优异离子传输能力的GPE膜^[79-81]。

Li等^[82]采用静电纺丝技术,将预先制备好的PVDF/PEO混合溶液倒入针管注射泵后,通过高压驱动,在真空环境中进行静电纺丝制膜。制备的纳米纤维膜电解质在PVDF/PEO的重量比为1:5时,室温离子电导率为 $4.8 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$,电化学稳定窗口可达4.8 V。Shen等^[83]利用同样方法,结合吸附增塑剂制备了一种新型单离子导电GPE,在室温下具有 $2.8 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$ 的离子电导率(图11)。他们进一步对增塑机理进行了研究,发现增塑剂的高介电常数和配位能力促进了 Li^+ 的电离,从而提升了整体的离子电导率。

静电纺丝法优势在于能够构筑高比表面积的纳米纤维网络以促进离子传输。但是,其工艺复杂且难以与常规印刷流程直接集成。一种良好的兼容策略是可考虑将其作为功能增强层与印刷工

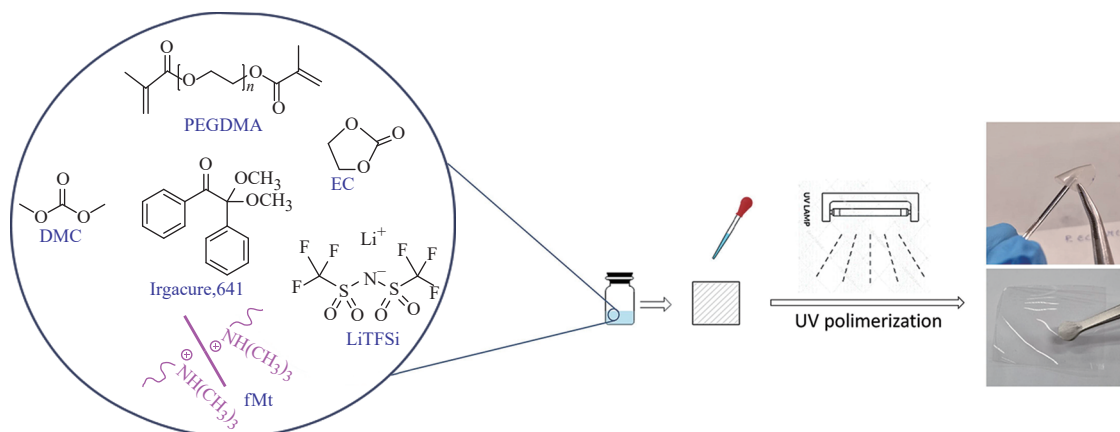


图10 紫外光固化法制备GPE膜的示意图^[78] (2023 Elsevier 版权许可)

Figure 10 Schematic diagram of the preparation of GPE film by ultraviolet light curing method (Reprinted with permission from Ref. [78]; Copyright (2023) Elsevier)

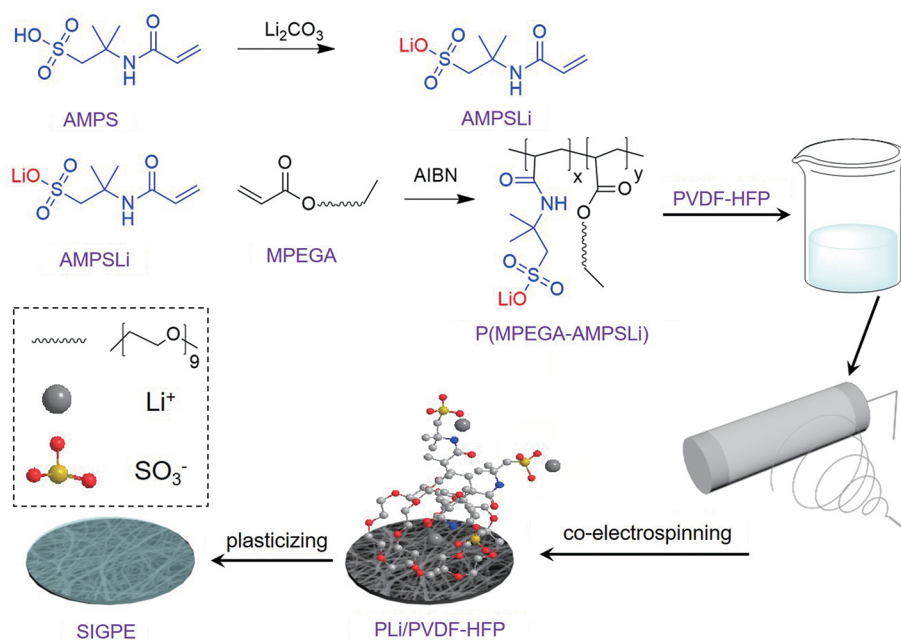


图 11 静电纺丝法制备纳米纤维膜的示意图^[83] (2020 Elsevier 版权许可)

Figure 11 Schematic diagram of the preparation of nanofiber membranes by electrospinning (Reprinted with permission from Ref. [83]; Copyright (2020) Elsevier)

艺协同使用, 以发挥其制备的GPE的结构优势。

4 GPE在PSC中的应用

PSC因具备柔性化、低成本和可规模化制备等优势, 在便携式电子设备、柔性储能器件等领域展现出广阔应用前景。结合具有黏度可调、易于涂覆等准固态特性的GPE, 显著提升了PSC的应用潜力。

4.1 SC的全印刷及柔性化制造

全印刷SC依托丝网印刷^[84-86]、喷墨印刷^[87,88]、3D打印^[89-91]等增材制造技术逐层构筑功能层, 兼具低成本、高效率、高设计灵活性和高集成度等优势。同时, 柔性化制造已成为满足现代电子设备发展需求的必然方向^[92-96]。将全印刷与柔性化制造相结合, 其核心在于通过一体化、可定制的增材工艺流程, 直接制备出能够耐受反复形变、贴合异形表面的高性能储能器件, 从而为下一代柔性电子设备提供关键支撑。

Areir等^[97]通过使用3D打印技术开发了一种兼具柔性和稳定性的双电层SC。他们将集流体、活性炭电极和PVA/ H_3PO_4 凝胶电解质逐层沉积, 在硅胶橡胶基底上全印刷制备了双电层SC。该器件具有优异的柔性, 在弯曲条件下进行 $50 \text{ mV} \cdot \text{s}^{-1}$ CV循环测试, 初始电容保持率可达58%。Liu等^[12]利用直接挤出打印的方式, 以GO/PANi-

PEDOT: PSS和石墨烯-PEDOT: PSS分别作为正负极材料、PVA/ H_3PO_4 作为GPE制备了柔性微型SC, 在 $5 \text{ mV} \cdot \text{s}^{-1}$ 下具有 $153.6 \text{ mF} \cdot \text{cm}^{-2}$ 的面电容, 并且可将电压窗口扩展到1.2 V。Lu等^[98]通过简单方法合成了非晶态 $\text{FeOOH}/\text{MnO}_2$ 复合物, 结合中性的PVA/LiCl电解质, 采用全丝网印刷的方法制备了高柔性的SC(图12)。该PSC在 $0.5 \text{ A} \cdot \text{g}^{-1}$ 的电流密度下表现出 $350.2 \text{ F} \cdot \text{g}^{-1}$ 的高比电容。

4.2 电极/电解质界面优化

对比传统分体式叠层“三明治”结构(SLSS)^[99], PSC通常采用原位印刷或聚合的方式

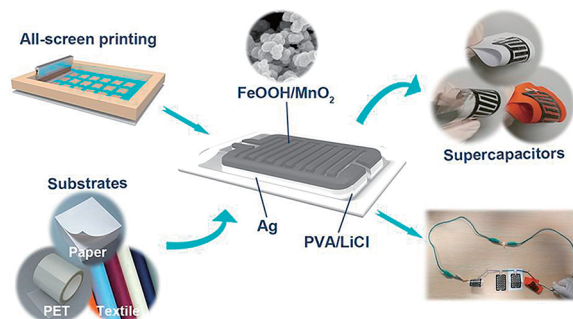


图 12 在不同基底上全丝网印刷制备印刷SC的示意图^[98] (2017 Elsevier 版权许可)

Figure 12 Schematic diagram of fabricating printed supercapacitors by full silk screen printing on different substrates (Reprinted with permission from Ref. [98]; Copyright (2017) Elsevier)

制备GPE层,消除了传统的SLSS中先制造再组装的繁杂工序。同时,PSC原位增材制造的方法配合黏度可调的GPE可以实现界面孔隙的无缝集成,显著降低界面阻抗,实现电化学性能的整体提升。

针对SC在机械操作过程中易发生电极与电解质界面的滑移和分层问题^[100],研究者们利用印刷技术结合GPE的特性,开发出了一系列具有一体化结构的SC。例如,Mo等^[100]制备了一种全聚合物、高弹性且非层状的SC。这种结构来源于原位印刷在丝素蛋白水凝胶膜上的聚吡咯电极层。该薄膜具有丰富的氢键和共价键,可以实现与电极界面的紧密连接,同时具有弹性和自愈能力。器件自愈率接近95.8%,同时提供 $0.37 \text{ F} \cdot \text{cm}^{-2}$ 的面电容和 $0.082 \text{ mW} \cdot \text{h} \cdot \text{cm}^{-3}$ 的体积能量密度(图13)。Qin等^[101]合成了一种基于氧化还原介导的物理交联双网络GPE,其中氢键和离子配位等作用赋予GPE优异的强度、韧性和自愈能力。他们以此GPE为印刷浆料,结合原位聚合的聚苯胺电极形成一体化结构,显著降低了界面电

阻,同时实现了极高的电容($271.6 \text{ mF} \cdot \text{cm}^{-2}$)和能量密度($98.1 \mu\text{Wh} \cdot \text{cm}^{-2}$)。Ma等^[102]也基于PVA/ H_2SO_4 水凝胶电解质中PVA链的动态氢键实现了电极/电解质界面自修复SC的制备,所得PVA水凝胶表现出快速自愈能力、优异机械性能(拉伸至238%后的应力为0.29 MPa)和高离子电导率($57.8 \text{ mS} \cdot \text{cm}^{-1}$)。

界面问题是影响PSC电化学性能优劣的主要因素之一。除文中已讨论的界面调控手段外,进一步优化印刷超级电容器中GPE与电极之间的界面接触仍可从材料设计与工艺改进两方面入手。在材料设计层面,可通过在GPE中引入功能性填料(如 SiO_2 、纤维素等),在提升凝胶力学强度的同时增强其对电极表面的贴合能力,从而改善界面接触状态。在工艺层面,可通过对电极表面进行等离子体处理或构建多孔结构,提高电极表面能和有效接触面积,以增强界面相容性并降低界面阻抗。此外,引入界面偶联剂或功能添加剂亦是一种有效策略,例如在电极浆料或GPE前驱体中加入具有双官能团的硅烷偶联剂,在电极与电解

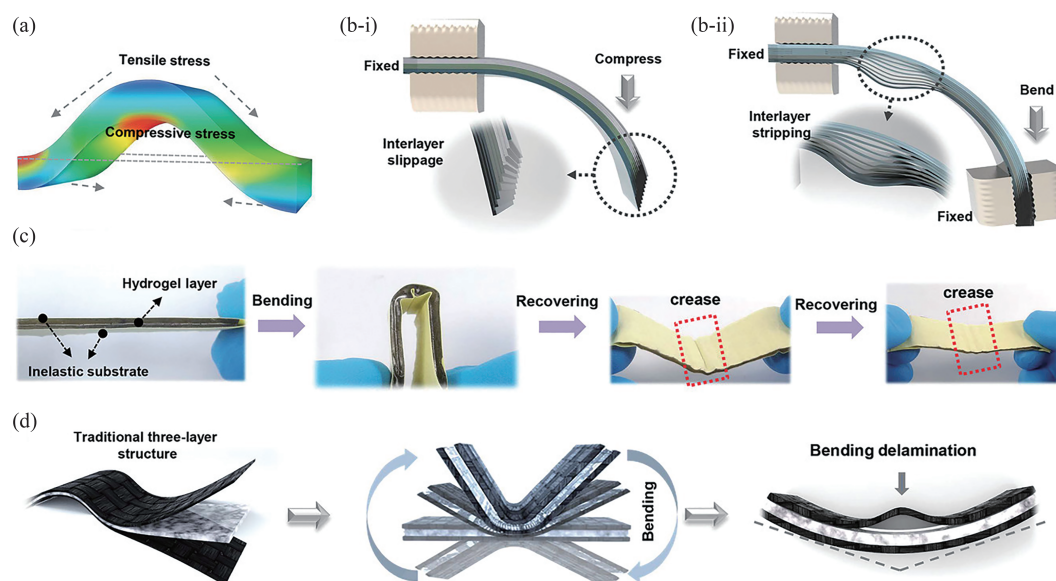


图13 传统叠层三明治结构和基于GPE在弯曲折叠下的不同表现情况^[100]。(a)设备在弯曲变形下的应力分布模型;(b)多层结构设备在单端固定弯曲(i)和双端固定弯曲下(ii)的示意图;(c)传统三层结构设备在弯曲变形时具有非弹性电极基底的示意图;(d)传统三层结构在反复弯曲变形下的示意图(2021 John Wiley and Sons 版权许可)

Figure 13 Comparison of the traditional laminated sandwich structure and the different performance of the structure based on GPE under bending and folding conditions. (a) Stress distribution model of a device under bending deformation; (b) Schematic illustration of the multilayered structure device under various bending deformations of one end fixed bending (i) and two-end fixed bending (ii); (c) Schematic illustration of the traditional three-layer structural device with inelastic electrode substrate upon bending deformation; (d) Schematic illustration of the traditional three-layer structure under repeated bending deformation (Reprinted with permission from Ref. [100]; Copyright (2021) John Wiley and Sons)

质之间形成化学桥接,从而进一步稳定界面结构并促进离子传输。

4.3 多功能与集成化系统

PSC的核心优势在于可以通过印刷技术实现低成本、大规模和定制化制备,从而与其他同样通过印刷或焊接制备的电子元件(如传感器、晶体管、显示器件等)实现无缝集成^[92~94,96,103~105],构建多功能与集成化系统。

Jost等^[106]为解决柔性储能器件无法直接与日常织物相媲美的特性(如触感和厚度),制备了一种能源纺织织物。该织物以碳纤维、活性炭墨水和PVA/H₃PO₄为双电层SC的主要组件,兼具柔性、可拉伸的物理特性和优异的电化学性能。这种全碳纺织SC在相同测试条件下与传统SC电容相当,在器件被拉伸和弯曲至180°时也能保持良好的机械性能和电化学稳定性。Hu等^[107]考虑到可印刷性、离子电导率和泄漏等问题,选择了PVA基GPE进行墨水直写打印。该GPE具有剪切稀化流变行为且无自凝胶化,满足印刷要求。针对二维平面叉指结构SC的空间浪费严重和能量密度不足等缺陷,Hu系统研究了基于三维结构的混合印刷策

略,并与二维平面结构的优缺点对比(图14)。三维结构可以使得SC在同一单位面积内与更多的电子设备实现紧凑集成。例如,他们展示了全印刷的ZnO微型紫外线传感器,其紧凑程度远超现有的SC-紫外线系统。

Li等^[108]采用全喷墨打印技术,在硅片和Kapton等多种基底上大规模制造石墨烯基微型PSC,并可简单调节其几何形状和厚度。他们在无需任何额外封装或保护的条件下,通过将超过100个微型PSC进行串并联集成,获得了输出电压达12 V的阵列。该阵列在超过8个月的测试中仍能保持性能稳定。该研究表明,全印刷技术为未来电子设备的紧凑型片上电源提供了一种前景广阔的解决方案。Jiang等^[109]结合喷涂打印与化学沉积技术,开发出一种高度紧凑的自充电电源单元。该单元将摩擦纳米发电机(TENG)与MXene基PSC集成于柔性可穿戴的采集-存储模块中,能够收集并存储人体日常活动产生的随机能量,从而延长设备的工作时间。其中,基于PVA/H₃PO₄的PSC在10000次循环后电容保持率高达95%,集成TENG的最大输出功率也高达7.8 $\mu\text{W}\cdot\text{cm}^{-2}$ 。

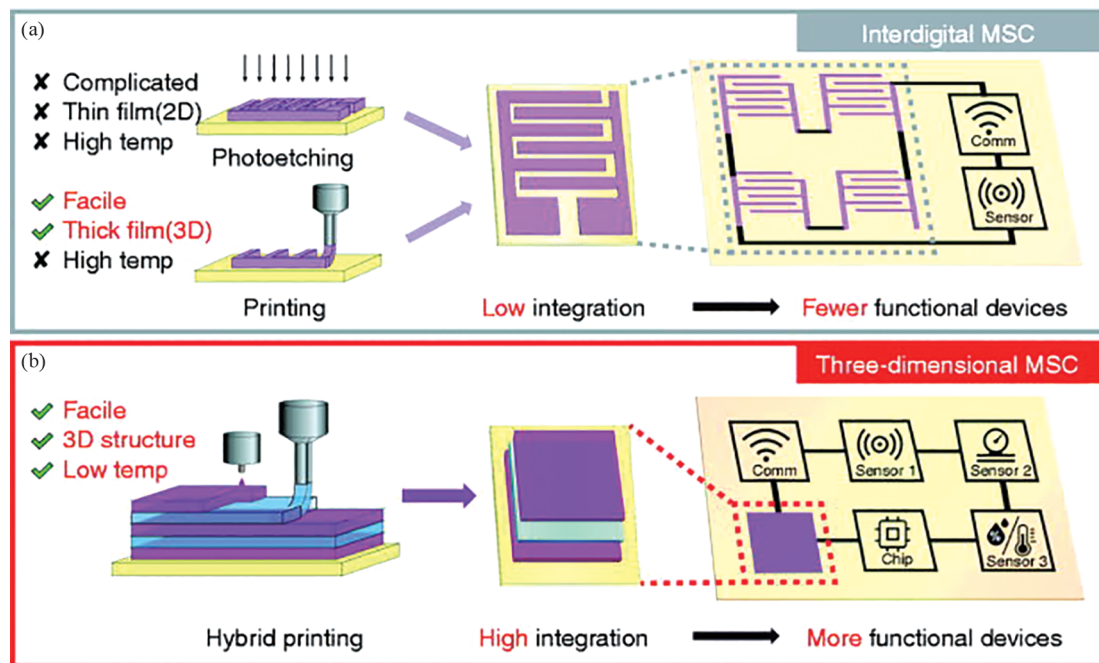


图14 三维和二维结构印刷SC与印刷电子器件集成对比示意图^[107]。(a)不同制造方法得到的指状MSC的示意图及应用中的低集成问题;(b)混合制造方法得到的具有3D框架的MSC的示意图及高集成优势(2021 AIP Publishing 版权许可)

Figure 14 Schematic diagram comparing the integration of three-dimensional and two-dimensional structure printed supercapacitors with printed electronic devices. (a) Illustration of the interdigital MSCs from different fabrication methods and low-integration problems in applications; (b) Illustration of the MSCs with the 3D framework from the hybrid fabrication method and high-integration advantages (Reprinted with permission from Ref. [107]; Copyright (2021) AIP Publishing)

5 总结与展望

综上所述, GPE 作为 PSC 的关键功能层, 其聚合物骨架结构、溶剂体系及微观相态分布共同决定离子传输行为、电极/电解质界面特性以及器件在高倍率和多次形变条件下的电化学稳定性。已有研究表明, 官能团—离子配位作用、溶剂诱导的链段运动能力以及多孔或纤维网络结构, 是影响离子电导率、等效串联电阻和循环寿命的主要因素, 凸显了需要从多尺度层面理解 GPE 作用机制的必要性。

尽管 GPE 在 PSC 中的应用取得了显著进展, 该领域仍面临关键的材料与工程挑战。在材料性能方面, 高离子电导率与力学完整性之间的协同优化仍是核心问题。尤其在低填料含量、低溶剂比例或极端弯折等条件下, 离子迁移通道易受破坏, 从而制约器件的倍率性能与长期稳定性。同时, 现有 GPE 体系在环境适应性方面仍存在不足, 如水系 GPE 在高湿或低温条件下性能波动明显, 而有机或离子液体体系则受限于成本与印刷安全性, 二者均影响其规模化应用。

在制备与工艺层面, 印刷适配性仍是 GPE 实现实际应用的关键瓶颈。未来研究需系统厘清 GPE 流变特性、固化行为与印刷分辨率之间的内在关系, 通过调控聚合物分子量分布、交联密度及溶剂挥发动力学, 实现高均一性成膜和稳定的电极—电解质界面构筑。同时, 发展低温、一步式或原位固化等先进工艺, 有助于降低制造能耗并提升器件一致性与集成度。

在面向未来应用时, 结合可降解、生物基聚合物构建环境友好型 GPE 体系, 并引入自修复、响应型或多功能复合结构, 将为 PSC 在柔性电子、可穿戴设备及物联网系统中的长期稳定运行提供新的发展路径。总体而言, 通过材料设计、作用机制解析与印刷工艺的协同优化, GPE 有望在推动 PSC 向高性能化、柔性化及系统集成化方向发展发挥关键支撑作用。

参考文献

- 1 Dissanayake, K.; Kularatna-Abeywardana, D. A review of supercapacitors: materials, technology, challenges, and renewable energy applications. *J. Energy Storage*, **2024**, 96, 112563.
- 2 Bao, L. H.; Li, X. D. Towards textile energy storage from cotton T-shirts. *Adv. Mater.*, **2012**, 24(24), 3246–3252.
- 3 Park, H. W.; Roh, K. C. Recent advances in and perspectives on pseudocapacitive materials for Supercapacitors—a review. *J. Power Sources*, **2023**, 557, 232558.
- 4 Liu, L.; Lu, Q.; Yang, S. L.; Guo, J.; Tian, Q. Y.; Yao, W. J.; Guo, Z. H.; Roy, V. A. L.; Wu, W. All-printed solid-state microsupercapacitors derived from self-template synthesis of Ag@PPy nanocomposites. *Adv. Mater. Technol.*, **2018**, 3(1), 1700206.
- 5 Wang, Y.; Shi, Y. M.; Zhao, C. X.; Wong, J. I.; Sun, X. W.; Yang, H. Y. Printed all-solid flexible microsupercapacitors: towards the general route for high energy storage devices. *Nanotechnology*, **2014**, 25(9), 094010.
- 6 Brooke, R.; Edberg, J.; Say, M. G.; Sawatdee, A.; Grimoldi, A.; Åhlin, J.; Gustafsson, G.; Berggren, M.; Engquist, I. Supercapacitors on demand: all-printed energy storage devices with adaptable design. *Flex. Print. Electron.*, **2019**, 4(1), 015006.
- 7 Singh, M.; Haverinen, H. M.; Dhagat, P.; Jabbour, G. E. Inkjet printing: process and its applications. *Adv. Mater.*, **2010**, 22(6), 673–685.
- 8 Choi, K. H.; Yoo, J.; Lee, C. K.; Lee, S. Y. All-inkjet-printed, solid-state flexible supercapacitors on paper. *Energy Environ. Sci.*, **2016**, 9(9), 2812–2821.
- 9 Sollami Delekta, S.; Smith, A. D.; Li, J. T.; Östling, M. Inkjet printed highly transparent and flexible graphene micro-supercapacitors. *Nanoscale*, **2017**, 9(21), 6998–7005.
- 10 Lin, Y. J.; Gao, Y.; Fan, Z. Y. Printable fabrication of nanocoral-structured electrodes for high-performance flexible and planar supercapacitor with artistic design. *Adv. Mater.*, **2017**, 29(43), 1701736.
- 11 Gao, T. T.; Zhou, Z.; Yu, J. Y.; Zhao, J.; Wang, G. L.; Cao, D. X.; Ding, B.; Li, Y. J. 3D printing of tunable energy storage devices with both high areal and volumetric energy densities. *Adv. Energy Mater.*, **2019**, 9(8), 1802578.
- 12 Liu, Y. Q.; Zhang, B. B.; Xu, Q.; Hou, Y. Y.; Seyedin, S.; Qin, S.; Wallace, G. G.; Beirne, S.; Razal, J. M.; Chen, J. Development of graphene oxide/polyaniline inks for high performance flexible microsupercapacitors via extrusion printing. *Adv. Funct. Mater.*, **2018**, 28(21), 1706592.
- 13 Zhou, Y. L.; Li, J.; Fu, H. Y.; Li, N.; Chai, S. M.; Duan, T. F.; Xu, L. J.; Wang, Z. J.; Xu, J. X. Additive-free $\text{Ti}_3\text{C}_2\text{T}_x$ MXene/carbon nanotube aqueous inks enable energy density enriched 3D-printed flexible micro-supercapacitors for modular self-powered systems. *Carbon Energy*, **2025**, 7(4), e698.

- 14 Orangi, J.; Hamade, F.; Davis, V. A.; Beidaghi, M. 3D printing of additive-free 2D $\text{Ti}_3\text{C}_2\text{T}_x$ (MXene) ink for fabrication of micro-supercapacitors with ultra-high energy densities. *ACS Nano*, **2020**, 14(1), 640–650.
- 15 Yang, P. H.; Mai, W. J. Flexible solid-state electrochemical supercapacitors. *Nano Energy*, **2014**, 8, 274–290.
- 16 Bertana, V.; Scordo, G.; Camilli, E.; Ge, L. M.; Zaccagnini, P.; Lamberti, A.; Marasso, S. L.; Scaltrito, L. 3D printed supercapacitor exploiting PEDOT-based resin and polymer gel electrolyte. *Polymers*, **2023**, 15(12), 2657.
- 17 Meng, J.; Tan, Z. J.; Zong, W.; Fan, W.; Chen, Y.; Zhang, C.; Li, L.; Liu, T. X. 3D-printed ultrahigh-conductivity polymer gel electrodes with high mass loading for thickness-independent zinc-ion hybrid micro-supercapacitors. *Adv. Funct. Mater.*, **2026**, 36(1), e10541.
- 18 Behzadi Pour, G.; Nazarpour Fard, H.; Fekri Aval, L. A comparison of the electrical properties of gel polymer electrolyte-based supercapacitors: a review of advances in electrolyte materials. *Gels*, **2024**, 10(12), 803.
- 19 Liu, D. N.; Wang, Z. Y.; Qian, Q. L.; Wang, J. Z.; Ren, J. B.; Chen, H. H.; Xing, W.; Zhou, N. J. Customizable supercapacitors via 3D printed gel electrolyte. *Adv. Funct. Mater.*, **2023**, 33(20), 2214301.
- 20 González-Gil, R. M.; Borràs, M.; Chbani, A.; Abitbol, T.; Fall, A.; Aulin, C.; Aucher, C.; Martínez-Crespiera, S. Sustainable and printable nanocellulose-based ionogels as gel polymer electrolytes for supercapacitors. *Nanomaterials*, **2022**, 12(2), 273.
- 21 Dai, H. L.; Zhang, G. X.; Rawach, D.; Fu, C. Y.; Wang, C.; Liu, X. H.; Dubois, M.; Lai, C.; Sun, S. H. Polymer gel electrolytes for flexible supercapacitors: recent progress, challenges, and perspectives. *Energy Storage Mater.*, **2021**, 34, 320–355.
- 22 Chan, C. Y.; Wang, Z. Q.; Jia, H.; Ng, P. F.; Chow, L.; Fei, B. Recent advances of hydrogel electrolytes in flexible energy storage devices. *J. Mater. Chem. A*, **2021**, 9(4), 2043–2069.
- 23 Chen, W. P.; Hao, D. Z.; Hao, W. J.; Guo, X. L.; Jiang, L. Hydrogel with ultrafast self-healing property both in air and underwater. *ACS Appl. Mater. Interfaces*, **2018**, 10(1), 1258–1265.
- 24 Wu, S. W.; Wang, T. W.; Du, Y. J.; Yao, B. W.; Duan, S. D.; Yan, Y. C.; Hua, M. T.; Alsaied, Y.; Zhu, X. Y.; He, X. M. Tough, anti-freezing and conductive ionic hydrogels. *NPG Asia Mater.*, **2022**, 14, 65.
- 25 Rong, Q. F.; Lei, W. W.; Huang, J.; Liu, M. J. Low temperature tolerant organohydrogel electrolytes for flexible solid-state supercapacitors. *Adv. Energy Mater.*, **2018**, 8(31), 1801967.
- 26 Ratner, M. A.; Shriver, D. F. Ion transport in solvent-free polymers. *Chem. Rev.*, **1988**, 88(1), 109–124.
- 27 Lu, Q. W.; Fang, J. H.; Yang, J.; Yan, G. W.; Liu, S. S.; Wang, J. L. A novel solid composite polymer electrolyte based on poly(ethylene oxide) segmented polysulfone copolymers for rechargeable lithium batteries. *J. Membr. Sci.*, **2013**, 425, 105–112.
- 28 Croce, F.; Appetecchi, G. B.; Persi, L.; Scrosati, B. Nanocomposite polymer electrolytes for lithium batteries. *Nature*, **1998**, 394(6692), 456–458.
- 29 Zheng, Z.; Li, M.; Zhou, Q. J.; Cai, L. K.; Yin, J. F.; Cao, Y. J.; Yin, P. C. Polyoxometalate-poly(ethylene oxide) nanocomposites for flexible anhydrous solid-state proton conductors. *ACS Appl. Nano Mater.*, **2021**, 4(1), 811–819.
- 30 Liu, W.; Zhang, X. K.; Wu, F.; Xiang, Y. A study on PVDF-HFP gel polymer electrolyte for lithium-ion batteries. *IOP Conf. Ser. Mater. Sci. Eng.*, **2017**, 213(1), 012036.
- 31 Jia, H.; Onishi, H.; von Aspern, N.; Rodehorst, U.; Rudolf, K.; Billmann, B.; Wagner, R.; Winter, M.; Cekic-Laskovic, I. A propylene carbonate based gel polymer electrolyte for extended cycle life and improved safety performance of lithium ion batteries. *J. Power Sources*, **2018**, 397, 343–351.
- 32 Singh, S. K.; Dutta, D.; Singh, R. K. Enhanced structural and cycling stability of Li_2CuO_2 coated $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ cathode with flexible ionic liquid-based gel polymer electrolyte for lithium polymer batteries. *Electrochim. Acta*, **2020**, 343, 136122.
- 33 Hu, X. Y.; Liu, K. L.; Zhang, S. J.; Shao, G. S.; Silva, S. R. P.; Zhang, P. A functional gel polymer electrolyte based on PVDF-HFP/gelatin toward dendrite-free lithium metal batteries. *Nano Res.*, **2024**, 17(4), 2790–2799.
- 34 Bai, Y. G.; Yang, C.; Yuan, B. H.; Li, H. J.; Chen, W. M.; Yin, H. S.; Zhao, B.; Shen, F.; Han, X. G. A UV cross-linked gel polymer electrolyte enabling high-rate and high voltage window for quasi-solid-state supercapacitors. *J. Energy Chem.*, **2023**, 76, 41–50.
- 35 Caimi, S.; Wu, H.; Morbidelli, M. PVdF-HFP and ionic-liquid-based, freestanding thin separator for lithium-ion batteries. *ACS Appl. Energy Mater.*, **2018**, 1(10), 5224–5232.
- 36 Liao, H. Y.; Zhou, F. L.; Zhang, Z. Z.; Yang, J. A self-healable and mechanical toughness flexible supercapacitor based on polyacrylic acid hydrogel electrolyte. *Chem. Eng. J.*, **2019**, 357, 428–434.
- 37 Ahn, B. K.; Lee, D. W.; Israelachvili, J. N.; Waite, J. H.

- Surface-initiated self-healing of polymers in aqueous media. *Nat. Mater.*, **2014**, 13(9), 867–872.
- 38 Hu, M. M.; Wang, J. Q.; Liu, J.; Zhang, J. H.; Ma, X.; Huang, Y. An intrinsically compressible and stretchable all-in-one configured supercapacitor. *Chem. Commun.*, **2018**, 54(48), 6200–6203.
- 39 Guo, Y. Z.; Zhou, X.; Tang, Q. Q.; Bao, H.; Wang, G. C.; Saha, P. A self-healable and easily recyclable supramolecular hydrogel electrolyte for flexible supercapacitors. *J. Mater. Chem. A*, **2016**, 4(22), 8769–8776.
- 40 Tsai, C. H.; Lu, C. Y.; Chen, M. C.; Huang, T. W.; Wu, C. C.; Chung, Y. W. Efficient gel-state dye-sensitized solar cells adopting polymer gel electrolyte based on poly(methyl methacrylate). *Org. Electron.*, **2013**, 14(11), 3131–3137.
- 41 Xu, J. J.; Ye, H. Polymer gel electrolytes based on oligomeric polyether/cross-linked PMMA blends prepared *via in situ* polymerization. *Electrochem. Commun.*, **2005**, 7(8), 829–835.
- 42 Zhou, X. Y.; Zhou, Y. F.; Yu, L.; Qi, L. H.; Oh, K. S.; Hu, P.; Lee, S. Y.; Chen, C. J. Gel polymer electrolytes for rechargeable batteries toward wide-temperature applications. *Chem. Soc. Rev.*, **2024**, 53(10), 5291–5337.
- 43 Kuo, P. L.; Wu, C. A.; Lu, C. Y.; Tsao, C. H.; Hsu, C. H.; Hou, S. S. High performance of transferring lithium ion for polyacrylonitrile-interpenetrating crosslinked polyoxyethylene network as gel polymer electrolyte. *ACS Appl. Mater. Interfaces*, **2014**, 6(5), 3156–3162.
- 44 Liu, W.; Zhang, S. Y.; Liu, K.; Yang, H. B.; Lin, Q. Y.; Xu, T.; Song, X. P.; Du, H. S.; Bai, L.; Yao, S. Q.; Si, C. L. Sustainable preparation of lignocellulosic nanofibrils and cellulose nanopaper from poplar sawdust. *J. Clean. Prod.*, **2023**, 384, 135582.
- 45 Xu, L.; Meng, T. T.; Zheng, X. Y.; Li, T. Y.; Brozena, A. H.; Mao, Y. M.; Zhang, Q.; Clifford, B. C.; Rao, J. C.; Hu, L. B. Nanocellulose-carboxymethylcellulose electrolyte for stable, high-rate zinc-ion batteries. *Adv. Funct. Mater.*, **2023**, 33(27), 2302098.
- 46 Abdul Khalil, H. P. S.; Saurabh, C. K.; A S, A.; Nurul Fazita, M. R.; Syakir, M. I.; Davoudpour, Y.; Rafatullah, M.; Abdullah, C. K.; M Haafiz, M. K.; Dungani, R. A review on chitosan-cellulose blends and nanocellulose reinforced chitosan biocomposites: properties and their applications. *Carbohydr. Polym.*, **2016**, 150, 216–226.
- 47 Suginta, W.; Khunkaewla, P.; Schulte, A. Electrochemical biosensor applications of polysaccharides chitin and chitosan. *Chem. Rev.*, **2013**, 113(7), 5458–5479.
- 48 Fu, L.; Wang, A. W.; Lyu, F. C.; Lai, G. S.; Yu, J. H.; Lin, C. T.; Liu, Z.; Yu, A. M.; Su, W. T. A solid-state electrochemical sensing platform based on a supramolecular hydrogel. *Sens. Actuat. B Chem.*, **2018**, 262, 326–333.
- 49 Lee, K. Y.; Mooney, D. J. Alginate: properties and biomedical applications. *Prog. Polym. Sci.*, **2012**, 37(1), 106–126.
- 50 Shang, W. S.; Zhu, J. H.; Liu, Y.; Kang, L. T.; Liu, S. Y.; Huang, B. K.; Song, J. S.; Li, X. M.; Jiang, F. Y.; Du, W.; Gao, Y. F.; Luo, H. J. Establishing high-performance quasi-solid Zn/I₂ batteries with alginate-based hydrogel electrolytes. *ACS Appl. Mater. Interfaces*, **2021**, 13(21), 24756–24764.
- 51 Wang, J. W.; Huang, Y.; Liu, B. B.; Li, Z. X.; Zhang, J. Y.; Yang, G. S.; Hiralal, P.; Jin, S. Y.; Zhou, H. Flexible and anti-freezing zinc-ion batteries using a guar-gum/sodium-alginate/ethylene-glycol hydrogel electrolyte. *Energy Storage Mater.*, **2021**, 41, 599–605.
- 52 Shao, Y. Y.; Zhao, J.; Hu, W. G.; Xia, Z.; Luo, J. R.; Zhou, Y. J.; Zhang, L.; Yang, X. Z.; Ma, N.; Yang, D. Z.; Shi, Q. W.; Sun, J. Y.; Zhang, L.; Hui, J. S.; Shao, Y. L. Regulating interfacial ion migration via wool keratin mediated biogel electrolyte toward robust flexible Zn-ion batteries (small 10/2022). *Small*, **2022**, 18(10), 2270046.
- 53 Li, K. X.; Li, P.; Sun, Z. N.; Shi, J.; Huang, M. H.; Chen, J. W.; Liu, S.; Shi, Z. C.; Wang, H. L. All-cellulose-based quasi-solid-state supercapacitor with nitrogen and boron dual-doped carbon electrodes exhibiting high energy density and excellent cyclic stability. *Green Energy Environ.*, **2023**, 8(4), 1091–1101.
- 54 Zeng, J.; Wei, L.; Guo, X. Bio-inspired high-performance solid-state supercapacitors with the electrolyte, separator, binder and electrodes entirely from kelp. *J. Mater. Chem. A*, **2017**, 5(48), 25282–25292.
- 55 Lu, X. H.; Yu, M. H.; Wang, G. M.; Tong, Y. X.; Li, Y. Flexible solid-state supercapacitors: design, fabrication and applications. *Energy Environ. Sci.*, **2014**, 7(7), 2160–2181.
- 56 Fic, K.; Lota, G.; Meller, M.; Frackowiak, E. Novel insight into neutral medium as electrolyte for high-voltage supercapacitors. *Energy Environ. Sci.*, **2012**, 5(2), 5842–5850.
- 57 Choi, B. G.; Chang, S. J.; Kang, H. W.; Park, C. P.; Kim, H. J.; Hong, W. H.; Lee, S.; Huh, Y. S. High performance of a solid-state flexible asymmetric supercapacitor based on graphene films. *Nanoscale*, **2012**, 4(16), 4983–4988.
- 58 Wang, G. M.; Lu, X. H.; Ling, Y. C.; Zhai, T.; Wang, H. Y.; Tong, Y. X.; Li, Y. LiCl/PVA gel electrolyte stabilizes vanadium oxide nanowire electrodes for

- pseudocapacitors. *ACS Nano*, **2012**, 6(11), 10296–10302.
- 59 Schroeder, M.; Isken, P.; Winter, M.; Passerini, S.; Lex-Balducci, A.; Balducci, A. An investigation on the use of a methacrylate-based gel polymer electrolyte in high power devices. *J. Electrochem. Soc.*, **2013**, 160(10), A1753–A1758.
- 60 Wang, G. P.; Zhang, L.; Zhang, J. J. A review of electrode materials for electrochemical supercapacitors. *Chem. Soc. Rev.*, **2012**, 41(2), 797–828.
- 61 Jain, A.; Tripathi, S. K. Experimental studies on high-performance supercapacitor based on nanogel polymer electrolyte with treated activated charcoal. *Ionics*, **2013**, 19(3), 549–557.
- 62 Łatoszyńska, A. A.; Żukowska, G. Z.; Rutkowska, I. A.; Taberna, P. L.; Simon, P.; Kulesza, P. J.; Wieczorek, W. Non-aqueous gel polymer electrolyte with phosphoric acid ester and its application for quasi solid-state supercapacitors. *J. Power Sources*, **2015**, 274, 1147–1154.
- 63 Rogers, R. D.; Voth, G. A. Ionic liquids. *Acc. Chem. Res.*, **2007**, 40(11), 1077–1078.
- 64 Lee, K. S.; Jeong, H. T. Development and optimization of ionic liquid based gel polymer electrolyte for all solid-state supercapacitor. *J. Energy Storage*, **2021**, 42, 103001.
- 65 Pandey, G. P.; Hashmi, S. A. Experimental investigations of an ionic-liquid-based, magnesium ion conducting, polymer gel electrolyte. *J. Power Sources*, **2009**, 187(2), 627–634.
- 66 Ahmed, M. S.; Islam, M.; Raut, B.; Yun, S. A.; Kim, H. Y.; Nam, K. W. A comprehensive review of functional gel polymer electrolytes and applications in lithium-ion battery. *Gels*, **2024**, 10(9), 563.
- 67 Ren, W. H.; Ding, C. F.; Fu, X. W.; Huang, Y. Advanced gel polymer electrolytes for safe and durable lithium metal batteries: challenges, strategies, and perspectives. *Energy Storage Mater.*, **2021**, 34, 515–535.
- 68 Xue, W. W.; Ahangaran, F.; Wang, H.; Theato, P.; Cheng, Y. J. Gel polymer electrolytes for lithium batteries: Advantages, challenges, and perspectives. *Macromol. Rapid Commun.*, **2025**, 46(23), 2500207.
- 69 Song, D. K.; Liao, J. L.; Huang, S. D.; Yuan, W. J.; Li, C. H.; He, J. H. A rigid-flexible gel polymer electrolytes with long cycle life and dendrite-free in lithium metal batteries. *J. Energy Storage*, **2024**, 75, 109591.
- 70 Shokrieh, A.; Lu, R. C.; Zhang, B. B.; Sharma, B. P.; Wei, Z. X. A buffering PVDF-HFP-based gel polymer electrolyte for stable and flexible lithium batteries. *Nanoscale*, **2024**, 16(38), 17954–17963.
- 71 Tripathi, M.; Bobade, S. M.; Kumar, A. Preparation of polyvinylidene fluoride-co-hexafluoropropylene-based polymer gel electrolyte and its performance evaluation for application in EDLCs. *Bull. Mater. Sci.*, **2019**, 42(1), 27.
- 72 Luo, K. L.; Yi, L. G.; Chen, X. Y.; Yang, L.; Zou, C. F.; Tao, X. Y.; Li, H.; Wu, T. J.; Wang, X. Y. PVDF-HFP-modified gel polymer electrolyte for the stable cycling lithium metal batteries. *J. Electroanal. Chem.*, **2021**, 895, 115462.
- 73 Chelfouh, N.; Coquil, G.; Rousselot, S.; Foran, G.; Briqueler, E.; Shoghi, F.; Caradant, L.; Dollé, M. Apple pectin-based hydrogel electrolyte for energy storage applications. *ACS Sustainable Chem. Eng.*, **2022**, 10(48), 15802–15812.
- 74 Li, G. C.; Li, Z. H.; Zhang, P.; Zhang, H. P.; Wu, Y. P. Research on a gel polymer electrolyte for Li-ion batteries. *Pure Appl. Chem.*, **2008**, 80(11), 2553–2563.
- 75 Balakrishnan, N. T. M.; Das, A.; Joyner, J. D.; Jabeen Fatima, M. J.; Raphael, L. R.; Pullanchiyodan, A.; Raghavan, P. Quest for high-performance gel polymer electrolyte by enhancing the miscibility of the bi-polymer blend for lithium-ion batteries: performance evaluation in extreme temperatures. *Mater. Today Chem.*, **2023**, 29, 101407.
- 76 Zeng, Y. J.; Yang, J.; Shen, X.; Li, R. Y.; Chen, Z. Q.; Huang, X.; Zhang, P.; Zhao, J. B. New UV-initiated lithiated-interpenetrating network gel-polymer electrolytes for lithium-metal batteries. *J. Power Sources*, **2022**, 541, 231681.
- 77 Li, W. Y.; Pang, Y.; Liu, J. Y.; Liu, G. H.; Wang, Y. G.; Xia, Y. Y. A PEO-based gel polymer electrolyte for lithium ion batteries. *RSC Adv.*, **2017**, 7(38), 23494–23501.
- 78 Lufano, E.; Coppola, L.; Nicotera, I.; Simari, C. UV-cured gel polymer electrolytes based on poly (ethylene glycol) and organo-modified nanoclays for lithium ions batteries. *Appl. Clay Sci.*, **2023**, 246, 107163.
- 79 Liu, W.; Liu, N.; Sun, J.; Hsu, P. C.; Li, Y. Z.; Lee, H. W.; Cui, Y. Ionic conductivity enhancement of polymer electrolytes with ceramic nanowire fillers. *Nano Lett.*, **2015**, 15(4), 2740–2745.
- 80 Nikodimos, Y.; Su, W. N.; Shitaw, K. N.; Jiang, S. K.; Abrra, L. H.; Weret, M. A.; Merso, S. K.; Hagos, T. M.; Huang, C. J.; Lakshmanan, K.; Huang, W. H.; Chang, C. Y.; Lin, J. M.; Wu, S. H.; Yang, C. C.; Hwang, B. J. Multifunctional electrospun PVDF-HFP gel polymer electrolyte membrane suppresses dendrite growth in anode-free Li metal battery. *Energy Storage Mater.*, **2023**, 61, 102861.
- 81 Tan, H. W.; Jia, S. J. Electrospun polyacrylonitrile/polyvinylidene fluoride/boehmite separator and

- gel polymer electrolyte polyethylene oxide/polyvinylidene fluoride-hexafluoropropylene/lithium bis(trifluoromethanesulfonyl)imide/boehmite composite separator are used for fast charging. *Macromol. Mater. Eng.*, **2023**, 308(10), 2300071.
- 82 Li, W. L.; Wu, Y. H.; Wang, J. W.; Huang, D.; Chen, L. Z.; Yang, G. Hybrid gel polymer electrolyte fabricated by electrospinning technology for polymer lithium-ion battery. *Eur. Polym. J.*, **2015**, 67, 365–372.
 - 83 Shen, X.; Hua, H. M.; Li, H.; Li, R. Y.; Hu, T. X.; Wu, D. Z.; Zhang, P.; Zhao, J. B. Synthesis and molecular dynamic simulation of a novel single ion conducting gel polymer electrolyte for lithium-ion batteries. *Polymer*, **2020**, 201, 122568.
 - 84 Torvinen, K.; Lehtimäki, S.; Keränen, J. T.; Sievänen, J.; Vartiainen, J.; Hellén, E.; Lupo, D.; Tuukkanen, S. Pigment-cellulose nanofibril composite and its application as a separator-substrate in printed supercapacitors. *Electron. Mater. Lett.*, **2015**, 11(6), 1040–1047.
 - 85 Shi, X. Y.; Pei, S. F.; Zhou, F.; Ren, W. C.; Cheng, H. M.; Wu, Z. S.; Bao, X. H. Ultrahigh-voltage integrated micro-supercapacitors with designable shapes and superior flexibility. *Energy Environ. Sci.*, **2019**, 12(5), 1534–1541.
 - 86 Sun, H.; Xie, S. L.; Li, Y. M.; Jiang, Y. S.; Sun, X. M.; Wang, B. J.; Peng, H. S. Large-area supercapacitor textiles with novel hierarchical conducting structures. *Adv. Mater.*, **2016**, 28(38), 8431–8438.
 - 87 Say, M. G.; Brooke, R.; Edberg, J.; Grimoldi, A.; Belaineh, D.; Engquist, I.; Berggren, M. Spray-coated paper supercapacitors. *npj Flex. Electron.*, **2020**, 4, 14.
 - 88 Wang, X. Y.; Lu, Q. Q.; Chen, C.; Han, M.; Wang, Q. R.; Li, H. X.; Niu, Z. Q.; Chen, J. A consecutive spray printing strategy to construct and integrate diverse supercapacitors on various substrates. *ACS Appl. Mater. Interfaces*, **2017**, 9(34), 28612–28619.
 - 89 Tanwailaisiri, A.; Xu, Y. M.; Harrison, D.; Fyson, J.; Arier, M. A study of metal free supercapacitors using 3D printing. *Int. J. Precis. Eng. Manuf.*, **2018**, 19(7), 1071–1079.
 - 90 Tanwailaisiri, A.; Xu, Y. M.; Zhang, R. R.; Harrison, D.; Fyson, J.; Areir, M. Design and fabrication of modular supercapacitors using 3D printing. *J. Energy Storage*, **2018**, 16, 1–7.
 - 91 Aeby, X.; Poulin, A.; Siqueira, G.; Hausmann, M. K.; Nyström, G. Fully 3D printed and disposable paper supercapacitors. *Adv. Mater.*, **2021**, 33(26), e2101328.
 - 92 Khan, Y.; Thielens, A.; Muin, S.; Ting, J.; Baumbauer, C.; Arias, A. C. A new frontier of printed electronics: flexible hybrid electronics. *Adv. Mater.*, **2020**, 32(15), 1905279.
 - 93 Yue, C. Z.; Wang, J. Y.; Wang, Z. Q.; Kong, B. Y.; Wang, G. Y. Flexible printed electronics and their applications in food quality monitoring and intelligent food packaging: Recent advances. *Food Control*, **2023**, 154, 109983.
 - 94 Hyun, W. J.; Secor, E. B.; Hersam, M. C.; Frisbie, C. D.; Francis, L. F. High-resolution patterning of graphene by screen printing with a silicon stencil for highly flexible printed electronics. *Adv. Mater.*, **2015**, 27(1), 109–115.
 - 95 Berggren, M.; Nilsson, D.; Robinson, N. D. Organic materials for printed electronics. *Nat. Mater.*, **2007**, 6(1), 3–5.
 - 96 Hübner, A. C.; Schmidt, G. C.; Kempa, H.; Reuter, K.; Hambsch, M.; Bellmann, M. Three-dimensional integrated circuit using printed electronics. *Org. Electron.*, **2011**, 12(3), 419–423.
 - 97 Areir, M.; Xu, Y. M.; Harrison, D.; Fyson, J. 3D printing of highly flexible supercapacitor designed for wearable energy storage. *Mater. Sci. Eng. B*, **2017**, 226, 29–38.
 - 98 Lu, Q.; Liu, L.; Yang, S. L.; Liu, J.; Tian, Q. Y.; Yao, W. J.; Xue, Q. W.; Li, M. X.; Wu, W. Facile synthesis of amorphous FeOOH/MnO₂ composites as screen-printed electrode materials for all-printed solid-state flexible supercapacitors. *J. Power Sources*, **2017**, 361, 31–38.
 - 99 González, A.; Goikolea, E.; Barrena, J. A.; Mysyk, R. Review on supercapacitors: technologies and materials. *Renew. Sustain. Energy Rev.*, **2016**, 58, 1189–1206.
 - 100 Mo, F. N.; Li, Q.; Liang, G. J.; Zhao, Y. W.; Wang, D. H.; Huang, Y.; Wei, J.; Zhi, C. Y. A self-healing crease-free supramolecular all-polymer supercapacitor. *Adv. Sci.*, **2021**, 8(12), 2100072.
 - 101 Qin, G.; Wu, C. F.; Song, X. Y.; He, W. J.; Yang, J.; Yu, X.; Chen, Q. Multifunctional enhanced energy density integrated supercapacitor based on self-healing redox-mediated gel polymer electrolyte. *Fuel*, **2024**, 357, 130033.
 - 102 Ma, W. B.; Zhu, K. H.; Ye, S. F.; Wang, Y.; Guo, L.; Tao, X. Y.; Guo, L. T.; Fan, H. L.; Liu, Z. S.; Zhu, Y. B.; Wei, X. Y. A self-healing hydrogel electrolyte towards all-in-one flexible supercapacitors. *J. Mater. Sci. Mater. Electron.*, **2021**, 32(15), 20445–20460.
 - 103 Kamysny, A.; Magdassi, S. Conductive nanomaterials for printed electronics. *Small*, **2014**, 10(17), 3515–3535.
 - 104 Wu, W. Inorganic nanomaterials for printed electronics: a review. *Nanoscale*, **2017**, 9(22), 7342–7372.
 - 105 Perelaer, J.; Smith, P. J.; Mager, D.; Soltman, D.; Volkman, S. K.; Subramanian, V.; Korvink, J. G.; Schubert, U. S. Printed electronics: the challenges involved in printing devices, interconnects, and contacts

- based on inorganic materials. *J. Mater. Chem.*, **2010**, 20(39), 8446–8453.
- 106 Jost, K.; Stenger, D.; Perez, C. R.; McDonough, J. K.; Lian, K.; Gogotsi, Y.; Dion, G. Knitted and screen printed carbon-fiber supercapacitors for applications in wearable electronics. *Energy Environ. Sci.*, **2013**, 6(9), 2698–2705.
- 107 Hu, J. Z.; Luo, J.; Xu, Z. H.; Xie, K. Y.; Yu, H. R.; Wang, H. M.; Shen, C.; Qi, L. H.; Wei, B. Q. Hybrid printed three-dimensionally integrated micro-supercapacitors for compact on-chip application. *Appl. Phys. Rev.*, **2021**, 8, 011401.
- 108 Li, J. T.; Sollami Delekta, S.; Zhang, P. P.; Yang, S.; Lohe, M. R.; Zhuang, X. D.; Feng, X. L.; Östling, M. Scalable fabrication and integration of graphene microsupercapacitors through full inkjet printing. *ACS Nano*, **2017**, 11(8), 8249–8256.
- 109 Jiang, Q.; Wu, C. S.; Wang, Z. J.; Wang, A. C.; He, J. H.; Wang, Z. L.; Alshareef, H. N. MXene electrochemical microsupercapacitor integrated with triboelectric nanogenerator as a wearable self-charging power unit. *Nano Energy*, **2018**, 45, 266–272.