

面向长时储能的液流电池储能技术: 发展、挑战及未来展望

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摘要 随着可再生能源的快速发展, 新型电力系统对长时间储能技术的需求日益增加. 液流电池体系因其高安全性和长寿命的特点, 成为理想的长时储能设施选择. 液流电池系统由电池组、电解液和循环泵组成, 通过管路相互连接, 利用电解液中的氧化还原反应进行化学能与电能的相互转化, 从而实现能量的高效存储和释放. 本文综述了无机和有机液流电池体系的关键材料, 从电池组件、电解液和催化剂等方面优化电池性能的研究进展, 以及液流电池在材料成本、性能优化和抑制副反应等方面面临的挑战. 最后, 本文展望了液流电池在未来长时储能技术中的发展前景, 指出需要加大新材料和技术的开发, 推进高性能的电堆设计, 开展不同环境下运行模式的创新, 实现液流储能的高效利用.

关键词 能源脱碳, 长时储能, 液流电池, 关键材料

全球变暖和化石能源的消耗已经成为人类面临的严峻问题, 碳达峰碳中和也逐渐成为全球的共识. 许多国家也制定了相应的碳中和目标^[1], 大国之间碳中和目标的竞争以及能源与工业的革命必将深刻影响全球环境及社会经济的发展. 我国是能源大国, 能源脱碳是实现“双碳”目标的必然措施. 风能、太阳能等可再生能源在能源体系中的占比逐渐增加, 但可再生能源的波动性、间歇性与随机性将对稳定的电力供应提出挑战, 而储能技术可以作为能源媒介, 实现可再生能源为主体的新型电力系统的稳定调控. 根据中关村储能产业技术联盟的统计, 截至2023年底, 大型储能设施中抽水蓄能占比最大为59.4%, 但受地理条件的限制分布不均. 新型储能中锂离子电池占比97.3%, 作为大规模储能, 安全性受到挑战^[2]. 液流电池具有高安全、大容量、长寿命等特点, 且不受地理环境限制, 因此在大规模长

时储能领域有着非常好的应用前景^[3,4].

液流电池由美国航空航天局的Thaller在1974年提出^[5]. 典型的液流电池系统由电池组、电解液和循环泵组成, 并通过管道相互连接(图1(a)). 其中, 正负极电解液自储罐中由泵输送到电池组, 并分别在由隔膜隔开的2个腔室中发生电化学反应, 电解液在氧化还原过程中由化学能转化所储存的电能则由电池组的电极提取进而向外输送, 隔膜则确保了载流子的穿梭同时阻隔正负极电解液的渗透污染. 基于独特的结构, 液流电池的功率(由电极的有效面积和电堆中的电池数量决定)和容量(由电解液的氧化还原电对种类、浓度和体积决定)可单独进行设计, 模块化的结构也便于检修和更换故障部件, 进而使液流电池具有更长的使用寿命, 大大降低了维护成本^[6,7]. 液流电池可分为水系液流电池和非水系液流电池^[8]. 水系液流电池具有

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高安全性、高离子电导率和高溶解度等优势,但受到水电化学窗口较窄(<2 V)的限制^[9]。非水系液流电池拥有更广泛的电化学窗口,因此能够设计高电压、高能量密度的电池,但目前非水系体系的离子电导率低、成本较高且缺乏高性能的膜,其发展落后于水系液流电池^[9,10]。

自水系液流电池系统被提出以来,涌现了各种不同的材料作为氧化还原电对,如铁铬液流电池、锌溴液流电池、全铁液流电池和全钒液流电池等(表1),同时研究人员对电极材料^[11]、电池结构^[12]和隔膜^[13]等进行了一系列设计优化。液流电池根据氧化还原电对种类可分为无机体系液流电池和有机体系液流电池^[14](图1(b))。本文综述液流电池的技术发展现状和目前面临的诸多挑战,最后对其未来发展进行总结和展望。

1 无机液流电池

1.1 全钒液流电池

全钒液流电池(vanadium redox flow battery, VFB)被认为是最成熟的液流电池类型,于1985年由新南威尔士大学的M. Skyllas提出,已经进入了商业化阶段^[15],如2022年100 MW/400 MWh大连储能调峰电站于大连并网使用^[8]。VFB采用 $\text{VO}_2^+/\text{VO}^{2+}$ 与 $\text{V}^{2+}/\text{V}^{3+}$ 作为正负极氧化还原电对,有效克服了电解质渗透交叉带来的污染问题,效率高、功率大且析氢量少^[16]。研究者致力于优化电池的组件来进一步提高电池的性能并降低成本,包括提高电极的电催化活性^[17]、开发具有更高离子选择性和更低成本的多孔膜^[18,19]、流场设计^[20]等。

目前,全钒液流电池处于商业示范阶段,然而较低

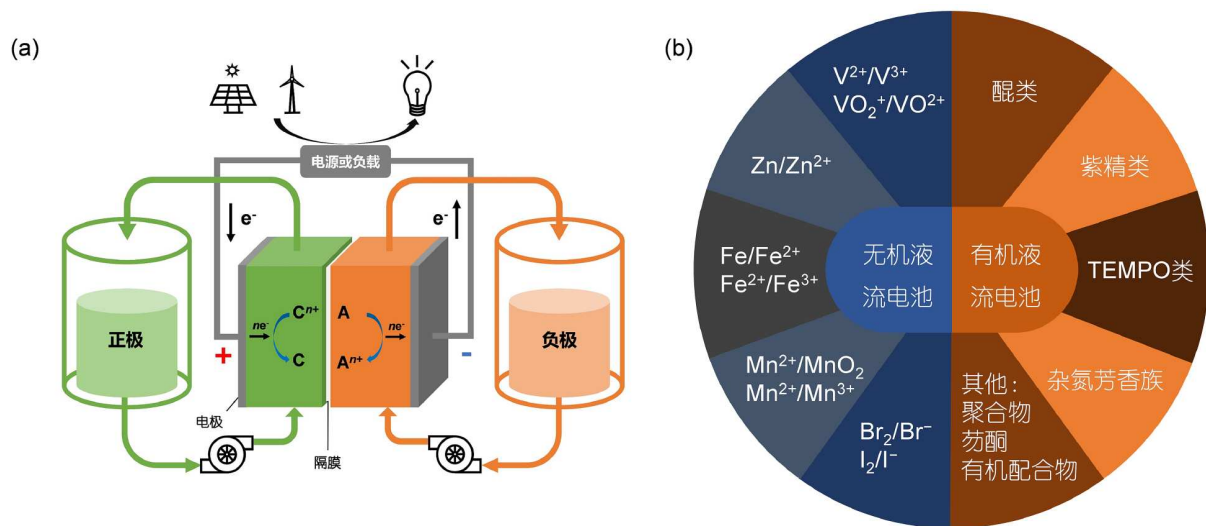


图1 (网络版彩色)液流电池结构与电解液材料示意图。(a)典型的液流电池结构;(b)用于液流电池的无机与有机氧化还原材料

Figure 1 (Color online) Schematic diagrams of the flow battery structure and electrolyte materials. (a) Typical structure of a flow battery; (b) inorganic and organic redox materials used in flow batteries

表1 不同液流电池体系优势与缺点对比

Table 1 Comparison of advantages and disadvantages of different flow battery systems

液流电池体系	优势	缺点
全钒液流电池	技术成熟、效率高、寿命长	电解液成本较高、能量密度低
锌溴液流电池	电解液成本低、能量密度高、放电电压高	枝晶和析氢副反应、 Br_2/Br^- 动力学缓慢、面容量有限
锌铁液流电池	电解液成本低	枝晶和析氢副反应、面容量有限、活性物质浓度偏低、水迁移问题
铁铬液流电池	电解液成本低、环境友好	析氢副反应、 $\text{Cr}^{3+/2+}$ 动力学缓慢、渗透交叉问题
全铁液流电池	电解液成本低	混合全铁液流电池存在枝晶和析氢副反应并且容量受负极面容量限制、商业化程度有限、全溶性全铁液流电池寿命不足
有机液流电池	潜在的成本优势、材料种类丰富、分子结构可调节	分子合成复杂、高浓度稳定性不足

的功率密度限制了其广泛应用,而功率密度较低的限制因素之一则是膜的离子电导率较低,离子选择性较差^[21].液流电池应用最广泛的膜是全氟磺化离子交换膜如Nafion膜,但Nafion膜的渗透交叉率高,导致电池的库仑效率低、容量衰减快,并且高昂的价格也限制了在全钒液流电池中的产业化.此外,新型膜的开发需要对离子电导率和膜选择性进行权衡^[22].为应对这一挑战,研究者开发了一系列离子交换膜和多孔膜应用于全钒液流电池.离子交换膜分为阴离子交换膜和阳离子交换膜,通过主链设计^[23,24]、侧链设计^[25-27]和纳米材料掺入^[25,28,29]等修饰可以提高离子交换膜的性能.如通过降冰片烯开环复分解聚合制备的新型侧链型两性离子交换膜,具有分子结构易修饰、聚合简单可控、膜化学稳定性高的优点,并且在芳香族主链和离子基团之间引入的疏水间隔基(烷基链-(CH₂)₆-)可以避免因两性离子基团增加而出现过量的水膨胀^[25].Zhang等人^[29]将改性Zr-MOFs作为填料引入非氟磺化聚醚醚酮基质构建的界面质子通道和内部质子通道,大大提高了杂化膜的电导率,采用优化膜的电池在200 mA cm⁻²下实现了79.6%的能量效率.相比于离子交换膜,多孔膜没有带电基团,因此具有更好的化学稳定性.相转化法是制造多孔膜最常用的方法^[22].Shi等人^[30]通过两步非溶剂相转化所制备的聚苯并咪唑(polybenzimidazole, PBI)具有独立控制的选择性表层和多孔支撑层,受益于薄而致密的表层和高度多孔的支撑层,该膜在提高选择性的同时提高了电导率,PBI膜组装的全钒液流电池在220 mA cm⁻²下表现出80%的能量效率.引入无机纳米材料、聚合物及其混合物分离层作为基底也是提高多孔膜性能的有效方法^[21,31,32].Dai等人^[21]在多孔聚醚醚酮/磺化聚醚醚酮共混物基底上引入超薄聚酰胺选择性层制备的超薄复合膜(thin-film composite membranes, TFCMs),打破了V/H选择性和质子电导率之间的权衡,具备高水合钒离子抵抗性和低质子抵抗性(图2(a)),电池在260 mA cm⁻²电流密度下的能量效率高于80%(图2(b)).

电极是液流电池的关键材料,其中碳基材料由于具有优异的稳定性而得到广泛应用^[33].研究人员尝试添加催化剂^[17,34,35]、引入官能团^[15,36,37]和创建多孔结构^[38]等措施改性电极以加快电极反应.目前大多数用作催化剂的材料是金属和金属氧化物,也有碳纳米材料被掺入电极研究.Jiang等人^[35]用UiO-66(Zr-MOF)纳米粒子对石墨毡进行改性,并通过高温碳化使其转化

为多孔纳米复合材料(ZrO₂@C),为钒氧化还原反应提供了大量的活性位点,改进后的全钒液流电池在200 mA cm⁻²下的能量效率达到75.2%.Xing等人^[17]将一种中空多孔碳球催化剂(hollow porous carbon sphere catalyst, NMPC-A)引入到全钒液流电池,这种催化剂能够原位负载于石墨毡上形成石墨电极,为催化钒氧化还原反应提供了大量活性位点;该电极组装的电池在200 mA cm⁻²下的能量效率达到82.7%,电池稳定循环1000次(图2(c)).引入电极的官能团有含氧官能团、含氮官能团和含磷官能团.Zhang等人^[15]通过简单的臭氧加速酸氧化方法对碳毡上的氧官能团进行定制,在碳纤维表面引入了丰富的氧官能团(羟基、羰基和羧基),增强了负极的氧化还原动力学;受益于增强的V²⁺/V³⁺动力学,电池在300 mA cm⁻²下的能量效率达到了72.8%.使用多孔电极则能够获得更高的电解液渗透率.Wu等人^[38]将ZnO层均匀分布在碳纤维上,然后在高温下进行碳热还原反应;伴随着Zn(g)和CO(g)蒸发的碳热还原反应,碳纤维形成了分级多孔网络结构,电极中碳纤维交叉形成的微米级孔隙有利于电解液渗透,而碳纤维表面的亚微米级和纳米级孔隙则促进钒离子扩散和氧化还原反应;这种多尺度电极的结构和表面特性极大地提高了电池的性能,在320 mA cm⁻²的电流密度下能量效率达到81.9%.

全钒液流电池流道的设计可以使电极内的电解液均匀分布,提高电极中电解液的浓度并降低浓差极化.全钒液流电池的流道结构常见的有蛇形流道、交叉流道、平行流道和螺旋流道^[39].Jiang等人^[40]采用Nafion 211膜权衡电压效率与库仑效率,制备了沉积铈纳米颗粒的多尺度石墨毡以提高电极活性,降低了电池的活化和欧姆损耗,并通过使用交叉流道提高了电池的电解液利用率,优化后的全钒液流电池在600 mA cm⁻²下能量效率超过80%.Pan等人^[41]将机器学习引入全钒液流电池的流道设计,提出了一种新颖的死区补偿流场(dead-zone-compensated flow field, DZCFF)设计(图2(d)),实验表明DZCFF在80%的能量效率下最大电流密度为205 mA cm⁻².

1.2 锌基液流电池

锌元素储量丰富,锌基液流电池具有能量密度高、低成本和高安全性等优势^[42].锌在氧化还原过程中进行一步两电子转移,并且电化学势较低,在酸性体系和中性体系中为-0.763 V vs SHE,在碱性体系中与羟基

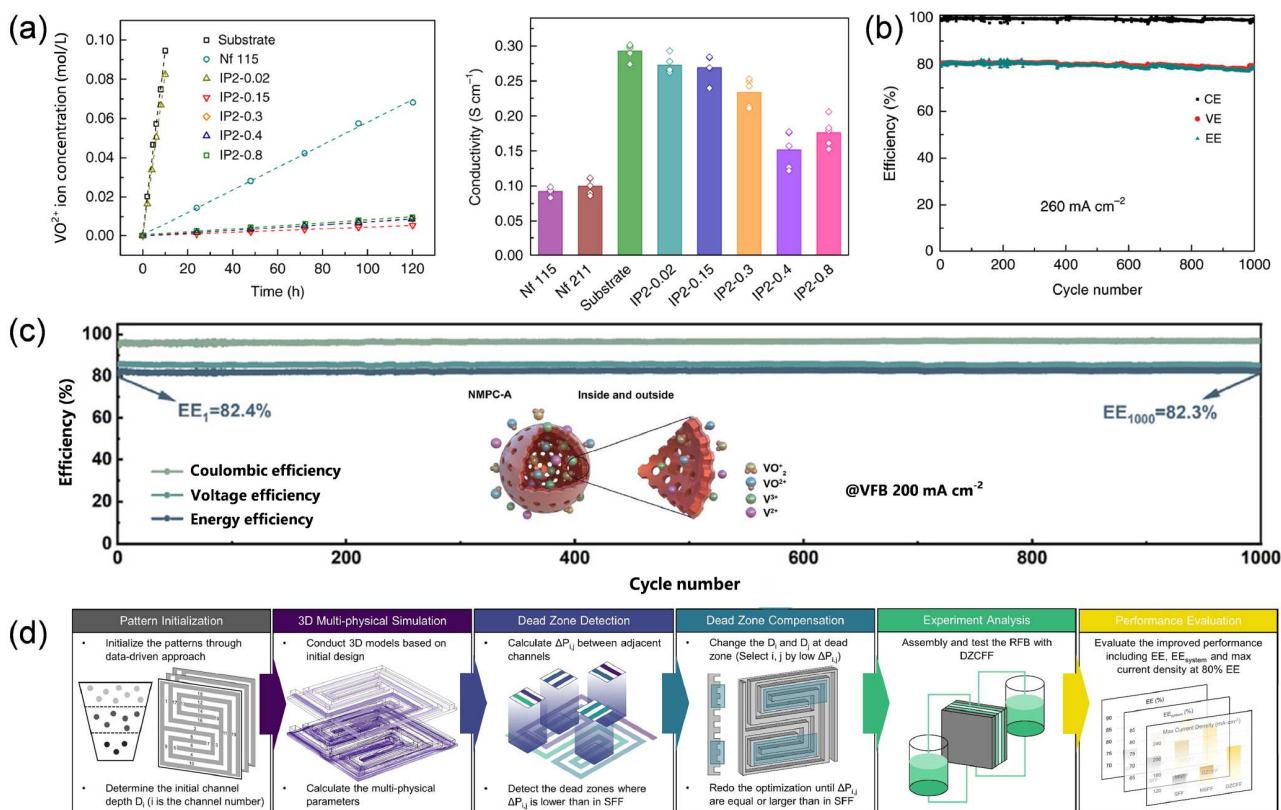


图 2 (网络版彩色)通过改进膜、催化剂和机器学习提升全钒液流电池的性能。(a) TFCM膜的低渗透率和高电导率(TFCM被称为IP2- x , 其中 x 代表均苯三甲酰肼TMC的浓度)^[21]; (b) 配备IP2-0.15的全钒液流电池在260 mA cm⁻²下的循环性能^[21]; (c) 使用NMPC-A@GF电极在200 mA cm⁻²下的全钒液流电池循环性能^[17]; (d) DZC设计方法的典型方法包括图案初始化、3D多物理仿真、死区检测、死区补偿、实验分析和性能评估^[41]

Figure 2 (Color online) Enhancing performance of all-vanadium redox flow batteries through improved membranes, catalysts and machine learning. (a) The low permeability and high electrical conductivity of TFCM membranes (TFCM is referred to as IP2- x , where x represents the concentration of TMC)^[21]; (b) cycle performance of VFBs equipped with IP2-0.15 at a current density of 260 mA cm⁻²^[21]; (c) cycle performance of the VFB using NMPC-A@GF electrodes at 200 mA cm⁻²^[17]; (d) the typical approaches for the DZC design method include pattern initialization, 3D multiphysical simulation, dead-zone detection, dead-zone compensation, experiment analysis, and performance evaluation^[41]

络合后能达到-1.216 V vs SHE. 基于此, 已经开发出锌溴液流电池、锌铁液流电池和锌锰液流电池等^[43].

1.2.1 对锌负极的研究

与液-液液流电池不同, 锌基液流电池(zinc-based flow battery, ZFB)属于混合液流电池, 负极在氧化还原过程中存在固液相变^[44]. ZFB在高容量和高电流密度下运行时, 锌枝晶的问题会导致电池的极化增大、可逆性变差, 因此当前针对锌基液流电池的研究主要集中在锌的均匀沉积问题上^[42], 包括添加剂^[45,46]、电极修饰^[47,48]和膜设计^[49,50].

添加剂是诱导锌均匀沉积的有效方法, 目前研究人员引入了铬、钨等金属离子和金属氧化物, 以及聚乙烯醇、聚乙二醇、烟酰胺等有机物作为添加剂^[51].

Bae等人^[52]将Cr³⁺作为添加剂引入锌溴液流电池中, 当锌离子沉积时, 铬离子在锌粒周围形成带正电的静电屏蔽层, 该正电屏蔽层排斥接近锌粒的锌离子并诱导锌离子移动到负极的相邻区域进而抑制锌枝晶的形成. Yang等人^[45]将烟酰胺(nicotinamide, NAM)作为中性ZnCl₂电解液的添加剂, 取代了Zn²⁺-6H₂O溶剂化层中的2个水分子进而重塑Zn²⁺的溶剂化结构, 并且NAM能够吸附在沉积的锌层上来诱导Zn²⁺向电极界面扩散从而避免不良的尖端效应, 因此锌在碳毡电极上能够实现高度可逆的沉积/溶解过程(图3(a)).

三维碳材料是锌基液流电池常用的负极集流体, 具有高比表面积、高电子电导率、高化学稳定性等优点^[53], 碳毡和石墨毡因导电性好、耐腐蚀性好、高孔

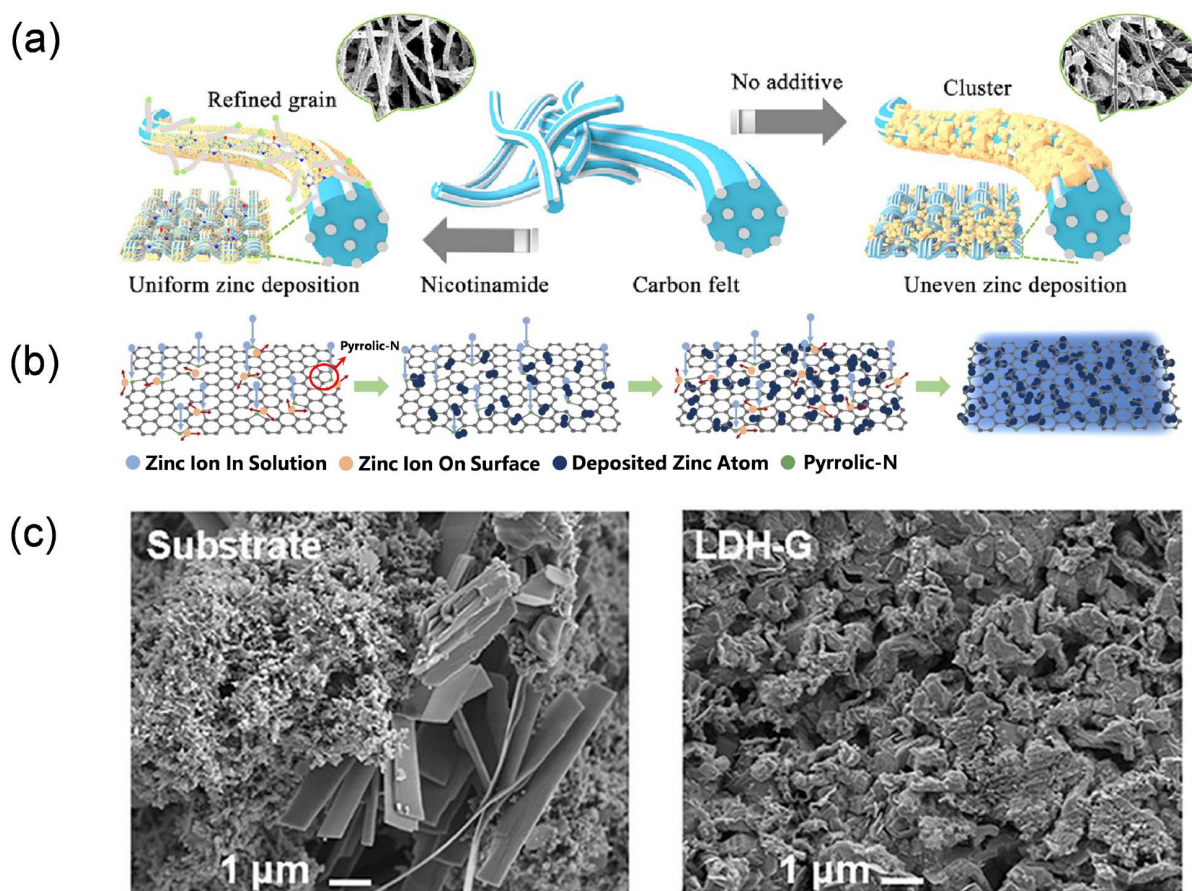


图 3 (网络版彩色)通过添加剂、优化电极和膜设计实现锌的均匀沉积。(a) ZnCl_2 和 ZnCl_2 -NAM电解质中Zn沉积过程的示意图^[45]。(b) 空心碳球内丰富的空间可缓解长期电池循环过程中的结构应力。N官能团增强了Zn的吸附,从而抑制了Zn在电极表面高活性位点的成核和生长,实现了均匀沉积^[56]。(c) 80 mA cm^{-2} 下用LDH-G和底物组装的AZIFBs在充电结束时Zn形貌的扫描电子显微镜图像^[49]

Figure 3 (Color online) Achieving uniform zinc deposition through additives, optimized electrodes and membrane design. (a) Schematic diagrams of the Zn deposition process in both ZnCl_2 and ZnCl_2 -NAM electrolytes^[45]. (b) The rich space within the hollow carbon spheres relieves structural stress during long-term battery cycling. The N functional groups enhance Zn adsorption, thus inhibiting the nucleation and growth of Zn at the highly active sites on the electrode surface and achieving uniform deposition^[56]. (c) Scanning electron microscope (SEM) images of the Zn morphology at the end of charging for the AZIFBs assembled with LDH-G and substrates at 80 mA cm^{-2} ^[49]

隙率和低成本等优势在碳材料中脱颖而出^[54]。碳毡中的碳纤维间隙较大,因此需要压缩来增加纤维自连接并更好地与电极基板接触^[55]。Saupsor等人^[54]使用碳毡和聚偏二氟乙烯制备了压缩复合材料,引入石墨烯以提高锌反应的电化学活性。与原始碳毡相比,压缩复合碳毡电极提供了更均匀的电场和更低的锌成核过电位,具有改良电极的锌铁液流电池在 10 mA cm^{-2} 电流密度下放电容量为 39.6 mAh cm^{-2} ,库仑效率达到96%。通过调节石墨毡电极的碳表面性质,可以改变锌的形貌和分布。Jiang等人^[53]采用第一性原理计算研究了锌在代表性碳表面上的吸附,包括原始表面石墨(0001)、单空位、双空位、环氧基、羰基和羟基,其中锌原子能够

锚定在单空位石墨毡中成为锌的成核位点,制备的具有高碳缺陷含量的石墨毡负极比原始电极有更均匀的锌分布。此外,具有3D结构的导电框架能使电流均匀分布,并形成相对均匀的锌沉积。Shi等人^[56]制备了具有高比表面积的空心氮掺杂碳球(hollow nitrogen-doped carbon spheres, HNCs),这些HNCs可以为锌沉积提供足够的内部空间,并且N官能团增强了锌在电极表面的吸附,抑制了锌在电极表面高活性位点的成核和生长,从而实现了锌的均匀沉积(图3(b))。

膜设计也是实现锌均匀沉积的有效措施。如层状双氢氧化物膜(layered double hydroxide membrane, LDH-G)具有高氢氧根离子电导率和离子选择性,无缺

陷的LDHs层可以作为缓冲层实现均匀的Zn沉积(图3(c)),从而有效提高电池的面容量,采用LDH-G组装的碱性锌铁电池在 260 mA cm^{-2} 下能够保持80%的能量效率,并稳定循环1200 h^[49]。Wu等人^[42]设计出了一种具有“图灵图案”的Turing-PBI,相比于平面PBI, Turing-PBI具有更高的阳离子选择性和更多的沉积空间,表面配位的铜离子(Cu^+ 、 Cu^{2+})与 $\text{Zn}(\text{OH})_4^{2-}$ 相互作用能够促使形成均匀致密的锌沉积,在 80 mA cm^{-2} 的高电流密度下, Turing-PBI组装的碱性锌铁液流电池稳定工作110个循环,并具有 160 mAh cm^{-2} 的超高面容量,能量效率达到90.10%。

1.2.2 对正极的研究

(1) 锌溴液流电池。溴拥有丰富的价态,能够进行可逆的多电子转移,锌溴液流电池具有高放电电压、高能量密度、低成本电解液等特点^[57,58]。然而, Br_2/Br^- 氧化还原电对较慢的动力学导致电池正极大极化较大^[59],同时由于多溴化物的高溶解度,其充电过程中形成的产物会产生渗透交叉进而导致循环稳定性的损失和库仑效率的降低^[60]。添加吸附剂以及溴络合剂是抑制溴渗透交叉的有效方法^[61]。Li等人^[62]引入一种新型溴络合剂1-乙基-2-甲基-溴化吡啶鎓(1-ethyl-2-methylpyridinium bromide, BCA)来抑制溴的渗透交叉,BCA表现出了很好的结合性能,并且电池能够在 60°C 的高温下稳定运行,在 40 mA cm^{-2} 下能量效率达到84%。此外,为了提高 Br_2/Br^- 氧化还原电对的活性,研究人员引入了具有高导电性、高比表面积的碳材料作为增强溴动力学的电催化剂^[63,64]。Pandiyar等人^[63]从余甘子叶生物质中提取了活性炭(activated carbon, AC)作为催化剂,羧基、羟基官能团的存在以及AC的多孔性质提供了更多的活性位点来参与 Br_2/Br^- 氧化还原反应,电池在 30 mA cm^{-2} 下表现出99%的库仑效率和82%的能量效率。除碳材料外,Tang等人^[65]将十六烷基三甲基溴化铵(hexadecyl trimethyl ammonium bromide, CTAB)插入 $\text{Ti}_3\text{C}_2\text{T}_x\text{MXene}$ 作为锌溴液流电池的电极,CTAB作为溴络合剂形成了稳固的溴配合物, $\text{Ti}_3\text{C}_2\text{T}_x\text{MXene}$ 则作为高活性载体(图4(a))。这种设计中,CTAB的固体络合效应可以有效抑制可溶性溴物种的扩散,同时很好地克服了固体络合物对反应动力学的不利影响,组装的电池在 80 mA cm^{-2} 下静置24 h仍有82.93%的容量保持率,表现出超低的自放电特性,在 180 mA cm^{-2} 的高电流密度下能够实现66.67%的电压效率和66.06%的能量效率。

(2) 锌铁液流电池。锌铁液流电池的电解液成本低^[66],研究人员开发了一系列修饰方法来提高锌铁液流电池的性能。Xie等人^[67]开发了一种负极以HAc/NaAc为介质、正极以 H_2SO_4 为介质的酸性锌铁液流电池,负极电解质中HAc/NaAc的存在可以将pH保持在2.0~6.0之间,在这个pH范围内Zn与 H^+ 的化学反应微不足道, H^+ 的电还原也被显著抑制,电池利用率接近90%,在50个循环后能量效率为71.1%。Kim等人^[68]将吡啶作为锌铁液流电池正极Fe(II)的络合配体,Fe(II)与吡啶强大的键合作用提高了Fe(II)/Fe(III)氧化还原过程中的反应动力学和电子转移,并且可以抑制Fe(III)水解和聚合发生的水铁矿沉淀,电池在100次循环后仅有2.9%的放电容量损失。Xie等人^[69]采用 FeCl_2 和 ZnBr_2 作为正负极氧化还原材料,温和的电池环境使其能够使用更低成本的多孔膜,同时还引入甘氨酸作为络合剂来抑制铁离子的水解和渗透交叉,电池在 40 mA cm^{-2} 下能量效率达到86.66%,稳定运行超过100个循环。Liu等人^[70]研究了电解液添加剂对碱性锌铁液流电池水迁移的影响,证明了水迁移的原因是浓度梯度、离子强度以及电场的协同作用;添加剂能够抑制水迁移,其中葡萄糖等有机添加剂会导致极化的增大,而无机添加剂如 Na_2SO_4 则对电池性能没有影响;使用 Na_2SO_4 作为负极添加剂的碱性锌铁液流电池在 80 mA cm^{-2} 下循环120次仍有99%的库仑效率和88%的电压效率。Gong等人^[71]提出了一种基于双膜三电解质设计的新型锌铁液流电池,每千瓦时的成本低于100美元且功率密度达到 676 mW cm^{-2} 。

(3) 其他锌基液流电池。碘基电对具有高溶解度,可进行多电子转移^[72]。然而,固体碘会对电极产生钝化,具体而言,碘的氧化还原反应涉及电化学反应 $2\text{I}^- \rightarrow \text{I}_2(\text{不溶}) + 2\text{e}^-$ 和化学反应 $\text{I}_2 + \text{I}^- \rightarrow \text{I}_3^-(\text{溶解})$,中间产物 I_2 溶解度很低并可能沉淀在电极上^[73],导致碘基液流电池极化较大,电流密度低($<100 \text{ mA cm}^{-2}$)^[74]。Xie等人^[75]摒弃了正极侧传统的储罐和泵,而是在高孔隙率($>90\%$)的碳毡中填充高浓度电解液作为正极,电解质中高度可溶的 I^- (7.5 mol/L KI)可以完全充电转化为固体 I_2 并覆盖在碳纤维上,实现了高比容量和利用率。最重要的是,3D碳毡的高孔隙率和表面积提供了足够的非导电固态 I_2 的沉积位点,确保了电池的低极化,而去掉正极电解液储罐可以抑制 O_2 氧化副反应和水迁移问题,此结构的电堆(200 W)可以在 80 mA cm^{-2} 下连续运行300个循环以上。通过加入 Br^- ^[76]、 $\beta\text{-CD}$ ^[73]和乙

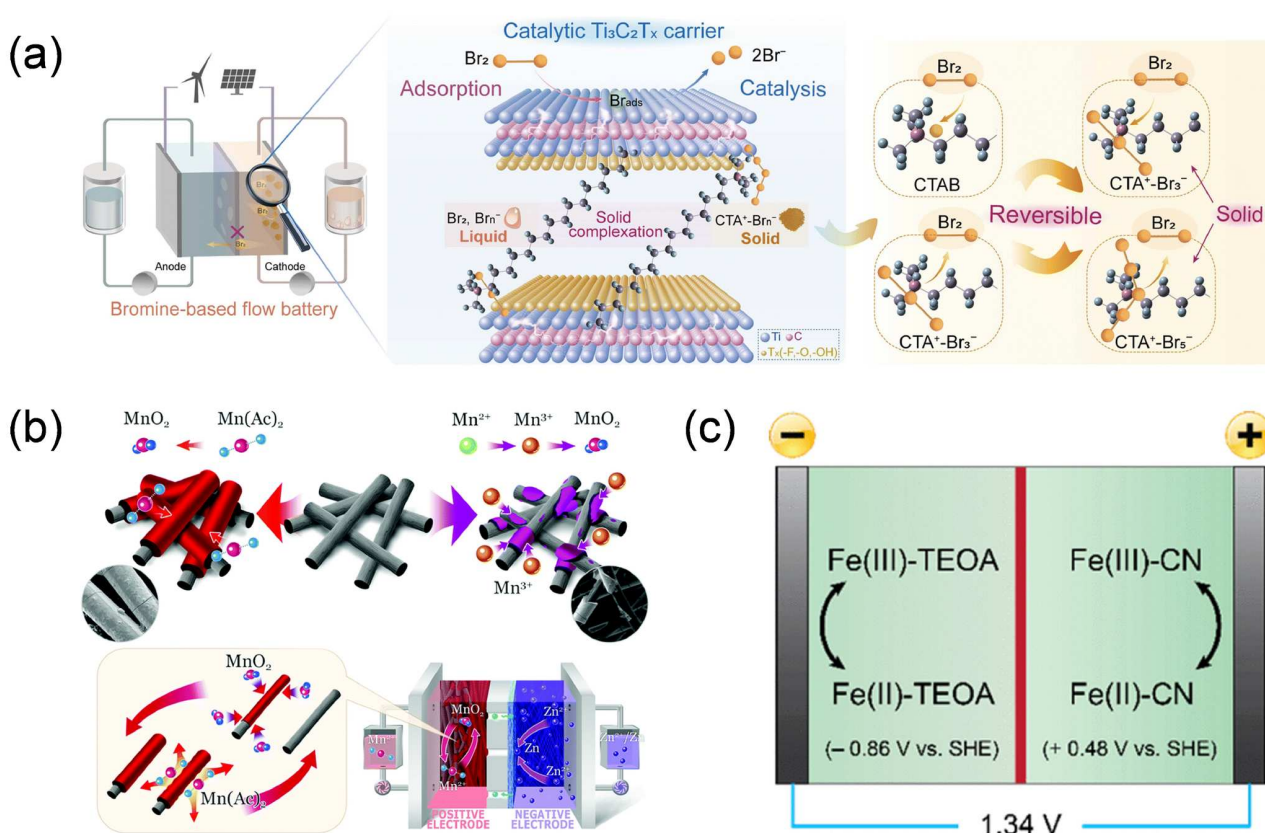


图4 (网络版彩色)其他锌基液流电池和全铁液流电池示意图。(a)插图显示 $\text{Ti}_3\text{C}_2\text{T}_x$ -CTAB修饰的电极具有高催化活性和优异的溴保留能力,适用于具有超低自放电和长寿命的溴基液流电池^[65];(b)一种在中性介质下基于 MnO_2 和可溶性 $\text{Mn}(\text{CH}_3\text{COO})_2$ 的液流电池^[82];(c)铁与三乙醇胺结合的全溶性全铁液流电池^[96]

Figure 4 (Color online) Schematic diagrams of other zinc-based flow batteries and all-iron flow batteries. (a) Illustration of the $\text{Ti}_3\text{C}_2\text{T}_x$ -CTAB decorated electrode with high catalytic activity and excellent bromine retention capacity for a Br-FB with ultralow self-discharge and a long lifespan^[65]; (b) a neutral-medium flow battery based on MnO_2 and soluble $\text{Mn}(\text{CH}_3\text{COO})_2$ ^[82]; (c) all-soluble all-iron RFB with iron and TEOA complexation^[96]

睛^[74,77]等添加剂可以稳定游离碘,进而抑制碘在电极上的沉淀。Shin等人^[73]利用(2-羟基)- β -环糊精((2-hydroxypropyl)- β -cyclodextrin, HP- β -CD)的主客体相互作用促进了 I_2 的水溶性,且不影响 I_2 向 I_3^- 的转换,有效解决了 I_2 沉淀的问题,加入HP- β -CD的电池稳定运行100个循环,库仑效率超过99%,利用率达到84%。Zhao等人^[74]向正极电解液添加7.5 vol%的共溶剂乙腈,通过削弱 I_2 和碳电极之间的相互作用,将速率常数提高一个数量级,应用于锌碘液流电池后,共溶剂将稳定充电的电流密度提高到 $80\sim 140 \text{ mA cm}^{-2}$,并在 100 mA cm^{-2} 下实现170次稳定循环。除锌碘体系外,碘也作为正极与其他负极材料联用。最近,Xie等人^[78]将 Br^- 引入到 I^- 溶液中,通过形成中间体 IBr 和 Br_2 避免了 HIO 的形成和歧化副反应的发生,减小了 I_2/IO_3^- 之间的电位差并实现了可逆的多电子转移,6 mol/L I^- 电解质实现超过

30 mol/L的电子转移, I^-/IO_3^- 正极的比容量超过 840 Ah L^{-1} ,以 Cd/Cd^{2+} 作为负极的电池表现出超过 1200 Wh L^{-1} 的高能量密度,120 mA cm^{-2} 电流密度下能量效率为72%。

锰在地壳中含量丰富,具有较高的氧化还原电位(1.23 V vs SHE)^[79,80],但 MnO_2 相变和 H_2O 插层结构的不稳定性会导致 MnO_2 的结构坍塌进而加剧容量衰减。Huang等人^[81]直接使用层状 MnO_2 作为电极材料避免了相变,同时将聚苯胺(polyaniline, PANI)插入到 MnO_2 中来强化层状结构,其层状 MnO_2 和中间层中PANI的纳米级尺寸能有效地促进电荷存储,因此电池能够在 280 mAh g^{-1} 的高容量下稳定循环200次。Xie等人^[82]通过实现 $\text{Mn}^{2+}/\text{MnO}_2$ 的溶解/沉积反应来避免结构坍塌问题(图4(b)),通过 Ac^- 的配位效应使 Mn^{2+} 可以直接以 MnO_2 的形式沉积在电极上,实现了 MnO_2 和可溶性 $\text{Mn}(\text{Ac})_2$

的高度可逆且稳定的二电子转移固液反应。由此设计的锌锰液流电池在 40 mA cm^{-2} 下循环超过400次, 能量效率达到78%。除锌锰体系外, 锰也作为正极与其他负极组合成液流电池如铜锰液流电池^[83]和硫锰液流电池^[84]等。

1.3 铁基液流电池

铁元素储量大、化学毒性低、成本低^[85]。铁基液流电池包括铁铬液流电池和全铁液流电池等。

铁铬液流电池是最早被研究的液流电池技术, 但 $\text{Cr}^{3+/2+}$ 的氧化还原行为涉及强烈的Jahn-Teller效应, 这是由于电子在高自旋 $\text{Cr}^{\text{II}}(\text{d}^4)$ 轨道中的不均匀占据使得电子态出现同时分裂和对称性降低的畸变, 这种现象导致了 $\text{Cr}^{3+/2+}$ 氧化还原电对缓慢的动力学, 同时 $\text{Cr}^{3+/2+}$ 在酸性条件下的低还原电位还会引起严重的析氢反应^[86,87]。研究者通过电解液^[86,87]、电极修饰^[88]、催化剂^[89,90]等对电池性能进行提升。Jang等人^[87]引入了一种强场氰化物配体 $[\text{Cr}(\text{CN})_6]^{4-}$ 来调节新型铁铬液流电池系统, 减轻了 $\text{Cr}^{3+/2+}$ 氧化还原电对的Jahn-Teller效应, 同时配合物的优先低自旋态促进了快速的氧化还原反应, 组装的铁铬液流电池稳定运行了500个循环, 具有 38.6 Wh L^{-1} 的高能量密度。Liu等人^[88]使用枝晶状TiN纳米棒阵列修饰了3D石墨毡复合电极, 增加了电极的比表面积并降低了接触电阻, 表面的氮、氧元素为 $\text{Cr}^{3+/2+}$ 提供了更多的吸附位点和活性位点; 使用该修饰的3D石墨毡电极的电池最大功率密度达到 427 mW cm^{-2} , 在 80 mA cm^{-2} 下库仑效率为93.0%, 电压效率为90.4%, 能量效率为84.1%。Ahn等人^[90]引入了嵌入铋纳米颗粒(Bi-C)的科琴黑(ketjenblack, KB)碳的双功能催化剂, 其中Bi的存在抑制了析氢反应, 而KB则提高了 $\text{Cr}^{3+/2+}$ 氧化还原反应的活性, 以Bi-C催化剂为负极的电池在 40 mA cm^{-2} 下具有86.54%的能量效率。

混合全铁液流电池正极为 $\text{Fe}^{2+}/\text{Fe}^{3+}$ 氧化还原电对, 负极则为 Fe^{2+}/Fe 氧化还原电对。混合全铁受到负极面容量的限制^[91], 并且随着时间的推移, 负极析氢和枝晶的问题会逐渐对电池产生负面影响^[92], 因此研究者通过有机配体与铁形成络合物调节铁的溶剂化结构来改善铁的沉积, 实现铁沉积/溶解过程的高度可逆性^[93,94]。Yang等人^[94]添加了N,N-二甲基乙酰胺(N,N-dimethylacetamide, DMAc)作为铁负极的添加剂, DMAc可以通过部分取代配位水分子来协同重塑 Fe^{2+} 溶剂化结构, 并通过重建氢键网络将自由水群体限制在 Fe^{2+} 溶剂化鞘层

之外, 在低于 -10°C 的条件下实现了平滑细粒的铁沉积和 Fe^{2+}/Fe 的高度可逆性, 组装的全铁液流电池运行超过103 h后仍保留95.59%的容量。

除了混合全铁液流电池以外, 全溶性全铁液流电池可以有效避免金属铁参与带来的析氢副反应等问题。全溶性全铁液流电池正负极为 $\text{Fe}^{3+}/\text{Fe}^{2+}$ -配合物的氧化还原过程, 通过有机配体与铁离子进行配位, 能够改变金属原子附近电子的部署进而影响氧化还原电位, 而进一步改进配体能够使得配合物更加稳定^[95,96]。如Gong等人^[96]通过结合铁-三乙醇胺 $[\text{Fe}(\text{TEOA})\text{OH}]^+$ / $[\text{Fe}(\text{TEOA})(\text{OH})]^{2+}$ 和铁-氰化物 $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ 提出了全溶性全铁液流电池(图4(c)), FeTEOA 氧化还原电位为 -0.86 V vs SHE , 组装的电池开路电压(1.34 V)高于现有的混合全铁液流电池(1.12 V), 放电功率密度超过 160 mW cm^{-2} 且稳定工作超过110个循环。Shin等人^[95]利用3-(N,N-双[2-羟乙基]氨基)-2-羟基丙磺酸(3-[bis (2-hydroxyethyl) amino]-2-hydroxypropanesulfonic acid, DIPSO)作为有机配体制备的 $\text{Fe}(\text{DIPSO})$ 具有 $-1.05 \text{ V vs Ag/AgCl}$ 的氧化还原电位, 表现出1.37 V的电池电压, 并且DIPSO能够与亚铁离子形成较强的结合力, 有助于提高配合物的稳定性, 防止亚铁离子被进一步还原。

2 有机液流电池

有机液流电池由于其灵活的分子调节和潜在的成本优势而得到了广泛关注^[97]。目前已经发展了一系列母核作为液流电池的氧化还原电对, 如醌、吩噻嗪、吩嗪、咯嗪、紫精、有机金属配合物等^[98]。然而, 未经过修饰的母核由于溶解度、电位、稳定性等问题无法满足直接用于氧化还原电对的要求, 因此需要对分子、电解液等进行改进。

2.1 醌类液流电池

醌类包括苯醌(benzoquinone, BQ)、萘醌(naphthoquinone, NQ)和蒽醌(anthraquinone, AQ), 是研究最广泛的有机分子种类, 醌类具有的2个羰基能够进行可逆的两电子转移反应^[99,100]。

苯醌在水中容易发生迈克尔加成导致不可逆的结构转变, 需要通过引入基团来减少苯醌未取代位置或通过空间位阻来抑制水的进攻^[101]。Hoover等人^[101]在苯醌上引入1个磺酸基和2个甲基, 设计了3,6-二羟基-2,4-二甲基苯磺酸, 磺酸基团有效提高了分子的溶解

度, 具有给电子效应的甲基在减少未取代位置的同时也抑制了水的亲核加成. Wang等人^[102]在萘醌分子上引入羟基和羧基, 合成了2-羟基-3-羧基-1,4-萘醌. 这种化合物具有 $-0.73\text{ V vs Ag/AgCl}$ 的低氧化还原电位, 并且在碱性溶液中展现出 1.2 mol/L 的高溶解度. 以2-羟基-3-羧基-1,4-萘醌作为负极材料的液流电池表现出 1.02 V 的电池电压, 并且在经过100次循环后, 容量保持率达到94.7%. 蒽醌(AQ)具有比苯醌和萘醌更大的共轭平面, 因此具有更高的稳定性、更多的结构修饰位点及快速的氧化还原动力学. Wu等人^[103]引入了2个甲基丁酸取代蒽醌, 这种通过水溶性基团杂原子与碳连接的侧链结构具有更优异的稳定性, 在 $\text{pH } 14$ 条件下容量衰减率 $<1\%$ /年. 此外, 可以通过引入基团调节分子的氧化还原电位, 如 $\text{N,N'-(9,10-蒽醌-2, 6-二基)-二-}\beta\text{-丙氨酸}$ 含有1个 N-烷基羧酸酯基团 , N 的给电子效应降低了分子的电位, 使得电池拥有 1.12 V 的开路电压^[104].

2.2 紫精类液流电池

紫精分子稳定性较好、反应动力学较快, 在中性条件下具有较高的溶解度^[105]. 紫精(methyl viologen, MV)只能进行 $\text{MV}^{2+/+}$ 电对的单电子转移, 因为紫精的电荷中性状态 MV^0 在水中的不溶性导致第2个电对 $\text{MV}^{+/0}$ 不能被利用, 对此可以通过亲水性基团取代紫精 N 原子上的甲基来增加 MV^0 的水溶性^[106,107]. 然而, 紫精分子的2个电子转移并非一步进行, 由于吡啶鎓的强吸电子效应, 邻近第1个电子转移的电位很高, 第1个吡啶鎓在电子转移后形成的还原态吡啶鎓具有给电子效应, 使得第2个电子转移的电位很低, 因此2个电子转移具有很大的电位差. 通过在2个吡啶鎓之间连接 π 共轭框架可以有效减小电位差并提供更好的稳定性^[108]. Hu等人^[109]在2个吡啶鎓之间引入1个旋转苯环, 即1,1'-双[3-(三甲基铵)丙基]-4,4'-(1,4-苯基)双吡啶四氯化物, 该分子在氧化态时共轭关闭使得2个吡啶鎓还原独立进行, 在还原态时共轭打开使得电荷有效离域, 提高了分子的稳定性. 除分子结构修饰外, Carrington等人^[110]证明了紫精还原态的电子转移和反应性由自由基态的分子内和分子间耦合控制. 具有宽单线态-三线态能隙(分子内电子耦合)、低归中反应和高二聚常数(分子间电子耦合)的分子, 其耐空气氧化性显著增强, 这与普遍认为的二聚会导致容量衰减的观点截然相反. 基于此, 他们提出了一种基于共轭核的凯库勒取代模式, 来促使分子形成闭壳电子的结构, 从而增强还原态分子的 π 二聚

(图5(a)).

2.3 TEMPO类液流电池

TEMPO在 pH 中性有机液流电池中能够实现快速的单电子氧化还原反应, 通过4位的取代基取代能够进一步提高氧化还原电位、增加溶解度^[111]. 然而, TEMPO分子会发生一系列副反应导致分子降解, 如TEMPO催化醇氧化导致分子失去氧化还原活性、TEMPO的环裂解以及TEMPO的歧化二聚化, 因此对TEMPO分子的设计应有效应对这些副反应^[112]. Fan等人^[113]将乙酰氨基和三甲基铵基团枝接在TEMPO上, 开发的4-[3-(三甲基铵)乙酰氨基]-2,2,6,6-四甲基哌啶-1-氧代氯化物有效避免了分子开环. TEMPO分子渗透污染较为普遍, Wang等人^[114]设计了一种双极性氧化还原活性有机分子1-(1-氧基-2,2,6,6-四甲基哌啶-4-基)-1'-(3-(三甲基铵)丙基)-4,4'-联吡啶三氯化物, 即使带电物质渗透过膜, 液流电池也可以通过极性反转再平衡策略恢复以避免永久退化. Lv等人^[115]系统研究了21种离子液体模拟(2,2,6,6-四甲基哌啶-1-基)氧基二聚体((2,2,6,6-tetramethylpiperidin-1-yl)oxyl dimers, i-TEMPOD), 通过强水配位环境实现了“盐包水”的状态, 提高了溶解度并抑制了分子的渗透交叉(图5(b)), 正极电解液具有 101 Ah L^{-1} 的体积容量, 其中性能最好的 N+TEMPOD 在 4 mol/L 电子浓度下稳定循环超过96天, 没有观察到容量衰减.

2.4 杂氮芳香族类液流电池

吩嗪衍生物能够实现双电子氧化还原反应, 氮原子周围较高的电子密度给予分子较低的氧化还原电位, 在碱性液流电池中负极的应用十分具有前景. 然而, 未经修饰的吩嗪溶解性很差, 在水溶液中几乎不溶, 通过分子修饰可以提高溶解度并进一步降低氧化还原电位. Hollas等人^[116]用磺酸基团和羟基取代吩嗪, 基于7,8-二羟基吩嗪-2-磺酸的电池具有很好的倍率性能并且在 1 mol/L NaOH 中的溶解度达到了 1 mol/L 以上, 0.1 mol/L 时在 50 mA cm^{-2} 下容量衰减率为 0.0079% /循环. Cui等人^[117]引入羟基将吩嗪氧化还原电位降低了 0.4 V , 并使得电池稳定循环9000次, 容量衰减率仅为 0.075% /循环. 吩嗪衍生物不同的取代位置导致分子不同的稳定性, 如2,7和1,8位氨基酸取代的吩嗪倾向于互变异构的失活, 而1,6位则具有更好的稳定性^[118]; 1、4、6和9位羟基取代的衍生物具有较好的稳定性, 而2、3、

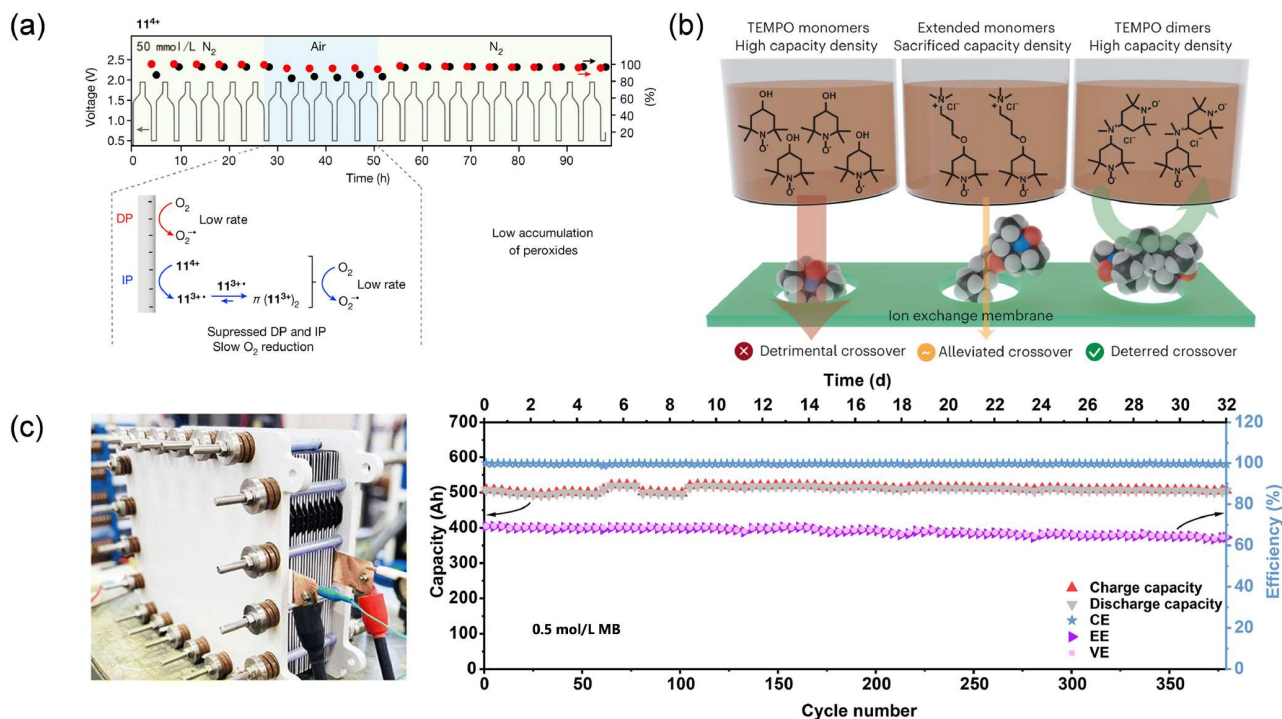


图5 (网络版彩色)碱性、中性和酸性条件下有机液流电池的代表性研究。(a) π -二聚化有效地降低了自由基单体即充当电子介体的物种的分数(间接途径)^[110];(b) 相较于HO-TEMPO和TMAP-TEMPO, N+TEMPOD有效抑制了渗透交叉且具有更高的容量^[115];(c) 0.5 mol/L MB/V液流电池电堆在50 mA cm⁻²下的循环^[123]

Figure 5 (Color online) Representative studies of organic flow batteries under alkaline, neutral and acidic conditions. (a) π -dimerization, which efficiently lowers the fraction of free radical monomeric species acting as electron mediators (indirect pathway)^[110]; (b) compared with HO-TEMPO and TMAP-TEMPO, N+TEMPOD effectively suppresses crossover and has a higher capacity^[115]; (c) life cycle of the 0.5 mol/L MB/V flow stack batteries at 50 mA cm⁻²^[123]

7和8位取代的衍生物则会产生不稳定的衍生物^[119]。

咯嗪衍生物灵感来自于天然黄素因子, 能够进行可逆两电子氧化还原反应。Lin等人^[120]引入羧基团使得咯嗪在pH 14条件下溶解度达到2 mol/L, 并在循环的每个周期保持99.95%的容量保持率。黄素单核核苷酸的钠盐也可用于碱性液流电池的负极, 电池在100个循环后容量保持率超过99%。通过添加助溶剂, 烟酰胺可以与黄素单核核苷酸的钠盐形成堆积复合物来进一步增加分子溶解度, 进而提高电池的能量密度^[121]。

吩噻嗪衍生物拥有较高的氧化还原电位, 并可分为噻嗪染料衍生物(I型)和N-取代吩噻嗪衍生物(II型)。原始的吩噻嗪不溶于水, 通过引入亲水性基团可以提高溶解度。Zhang等人^[122]将亚甲基蓝(methylene blue, MB)应用于液流电池正极, 和V(II)组成的液流电池在1.2 mol/L浓度下容量衰减率为0.025%/循环, 1.5 mol/L浓度下容量衰减率为0.074%/循环。MB具有优异的空气稳定性。Zhang等人^[123]组装的千瓦级液流电池在0.1

和0.5 mol/L浓度下都能保持长期的循环稳定性(图5(c))。Zhang等人^[124]还将吩噻嗪和吩恶嗪的3, 7位引入氨基以提高分子的氧化还原活性和电化学稳定性, 3,7-取代氨基作为氧化还原活性位点可以通过在酸性溶液中电子密度离域来稳定中间自由基, 防止亲核/亲电攻击; 采用设计的3,7-双-(2-羟乙基)(甲基)氨基吩噻嗪-5-溴化物为正极的液流电池运行18000个循环(62天), 容量衰减率为0.00029%/循环。

2.5 茚酮类液流电池

茚酮在水中还原时形成的自由基阴离子会不可避免地质子化并被还原为醇, 在水中的电化学可逆性较差。Feng等人^[125]引入羧基和磺酸基到茚酮, 得到的4-羧基-7-磺酸茚醇(4-carboxylic-7-sulfonate fluorenol, 4C7SFL-OH)能够进行可逆的加氢脱氢, 实现接近3 mol/L的电子浓度, 以4C7SFL-OH为负极的液流电池在100 mA cm⁻²下能够稳定循环超过700次。具有特定

pKa的茚酮衍生物的去质子化速率会显著影响电池的放电力学。Feng等人^[126]添加了 β -环糊精,利用 β -环糊精与茚酮之间良好的氢键作用改变了茚酮的去质子化速率,加速了醇氧化,含有 β -环糊精的茚酮液流电池表现出增强的倍率性能和高容量,以0.7 mol/L 4-羧基-9-氧代-9H-茚酮-2,7-二磺酸酯为负极的电池连续运行一年以上,平均容量衰减率为0.0235%/天。

2.6 金属配合物类液流电池

研究人员开发了金属配合物二茂铁衍生物应用于液流电池,并通过分子修饰使电位提高。Hu等人^[127]设计了水溶性(二茂铁基甲基)三甲基氯化铵((ferrocenylmethyl)trimethylammonium chloride, FcNCl)作为液流电池正极, FcNCl在铵基的作用下在2 mol/L NaCl溶液中溶解度达到了3 mol/L, 电位提升到了0.61 V vs NHE,与紫精配对的液流电池在60 mA cm⁻²下能够进行700次循环,每循环容量保持率超过99.99%。Ruan等人^[128]将三(2,2'-联吡啶)铁(tris(2,2'-bipyridyl)iron, [Fe(bipy)-3]^{3/2+})络合物应用于液流电池正极, [Fe(bipy)₃]^{3/2+}相对于标准氢电极的电压为1.03 V,在硫酸中溶解度达到0.7 mol/L,与紫精配对的液流电池每循环容量保持率达到99.96%。

3 总结与展望

液流电池作为长时储能领域的重要角色,其高安全和长寿命的特点能够在发展新能源和实现“双碳”目标的道路上发挥关键作用。尽管当前应用于液流电池的氧化还原活性材料种类繁多,但仍面临诸多挑战。

全钒液流电池是目前商业化最成熟的体系,但是全钒体系的能量密度较低,受钒矿储量限制,初始投资成本相对较高。因此,降低体系的成本是目前全钒体系需要在规模化解决的重要问题。同时,一系列不同类型

的具有潜在低成本新体系液流电池储能技术不断涌现,如电解液成本低廉的全铁、锌基、硫基和多电子转移电对等无机体系以及具有资源可持续潜力的有机活性电对体系。锌基液流电池具有低成本的优势,但仍然面临着枝晶和析氢的问题。尽管电池电压相对较高,但大多数锌基混合液流电池的电流密度仍然小于50 mA cm⁻²,对此可以引入添加剂、开发新的膜和三维负极集流体来抑制副反应。卤素、锰等正极材料已经应用于锌基液流电池,但仍面临较慢的氧化还原动力学、对电极的钝化和结构坍塌等挑战,引入添加剂并开发高性能电极材料能有效改善缓慢的动力学并实现可逆的固液反应。铁基液流电池发展出了铁铬液流电池、混合全铁液流电池和全溶全铁液流电池。铁铬液流电池受铬的电化学动力学差、稳定性差和膜渗透污染等问题的限制,通过修饰电极和引入催化剂能有效提升电池性能;有机配体的引入为全铁液流电池带来无限可能,开发稳定、高溶解度和高电位的有机-铁配合物至关重要。有机液流电池具有灵活的分子调节和潜在的成本优势,分子修饰和电解液调控等措施被用来提高分子溶解度、电化学性能和稳定性等,然而大部分有机液流电池仍处于实验室规模。许多有机材料的合成需要繁杂的步骤,甚至使用昂贵的催化剂,因此,需要开发具有更简易合成方法、更低成本的分子。

总之,为了满足新型电力系统对高安全、大规模电化学储能技术的重大需求,需加大新一代液流电池关键材料及技术的开发:开发低成本短流程的钒电解液制备技术和高性能离子传导膜以提升电池电堆功率密度,并在此基础上开展大功率电堆、模块和系统的设计;开发高稳定性的新体系电解液制备技术、长寿命和低成本电池电堆设计技术。此外,还需要针对不同应用场景和地理环境等因素开展运行模式创新,实现液流储能高效利用。

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Summary for “面向长时储能的液流电池储能技术: 发展、挑战及未来展望”

Flow battery for long duration energy storage: Development, challenges and prospects

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The seriousness of global warming and the consumption of fossil fuels has become increasingly evident, prompting countries to take active measures to address this challenge, including setting carbon neutrality goals to tackle severe environmental issues. Decarbonizing energy is an inevitable measure to achieve dual carbon goals, and renewable energy is a key strategy to achieve energy decarbonization. However, renewable energy generation, such as solar and wind energy, faces challenges like volatility and intermittency, and direct integration into the power grid is extremely risky. Therefore, the long-term energy storage technology is needed to regulate power to achieve the effectiveness of renewable energy utilization. Among various long-term energy storage technologies, flow batteries have garnered considerable attention due to their rare advantages such as large capacity, high safety, and long lifespan.

Flow battery technology consists of an electrochemical cell stack, electrolytes, and pumps, which are connected to each other through pipelines. The electrolyte is pumped into two chambers separated by the membrane for redox reactions, while the electrical energy is transported to the outside through the electrodes for power generation. The decoupling of flow battery energy and power makes it highly flexible and adjustable, and its modular design also greatly reduces maintenance costs. Since being first proposed in the 1970s, flow batteries have developed two systems: Inorganic and organic. The anolyte and catholyte of the inorganic system are inorganic materials, including all-vanadium flow batteries, zinc-based flow batteries, iron-based flow batteries, and halogen-based flow batteries, etc. Organic systems, on the other hand, have at least one side made of organic materials, including quinone flow batteries, viologen flow batteries, TEMPO flow batteries, and aza-aromatic flow batteries. Each system of flow batteries has its unique advantages, such as all-vanadium flow batteries with high power and high stability, zinc-based flow batteries with low cost and high energy density, and organic flow batteries with abundant molecular tunability and potential cost advantages. At present, technologies such as all-vanadium flow batteries, zinc-bromine flow batteries, and iron-chromium flow batteries have entered commercial application, and with the increase in demand for long-term energy storage facilities, their applications will be further expanded. Meanwhile, organic flow batteries are still at the laboratory scale and have not yet entered the stage of large-scale industrialization. This article reviews the cutting-edge research and commercial applications of various flow battery technologies in two fields: Inorganic and organic, analyzes the key issues faced by various flow battery technologies, and finally gives an overview of the long-term potential of flow battery technologies. Challenges and future developments in the energy storage field are proposed.

In short, flow battery technology, as a key player in the field of long-term energy storage, can not only become a reliable energy storage solution for the energy system but also promote the large-scale application of renewable energy, providing strong support for solving environmental problems and achieving dual carbon goals. Although it still faces some challenges, it is believed that flow battery technology will have broader prospects with breakthroughs in key issues.

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