



液流电池的热管理研究进展

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摘要: 液流电池作为一种长时储能技术, 具有安全性高、寿命长、容量和功率相互独立、易回收利用等优势, 在国内外得到广泛的关注和应用。在其充放电过程中若不对系统温度进行干预, 则很容易突破正常运行的温度区间, 严重影响电池效率并易发生故障。本文系统梳理了液流电池的产热及散热机理, 同时, 从加快散热以及抑制产热两个方面综述了目前的热管理方法。最后与锂离子电池的热管理进行对比, 希望为后续的科研及产业发展提供参考。

关键词: 液流电池; 热管理; 产热机理; 冷却系统

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引言

近年来, 为了实现低碳发展, 对风能和光能等清洁能源需求的不断增长。新能源发电随季节和天气变化而不稳定, 在发电、输电和用电三个环节都存在借助储能系统实现持续稳定供电的需求。目前已经开发出的大规模储能技术有抽水蓄能、飞轮、压缩空气、超导和电化学储能^[1-5]。其中, 电化学储能是将可再生能源转化为化学能储存, 相较于抽水和压缩空气不局限于地理环境, 具有广阔的发展前景。液流

电池作为长时储能技术由于安全性好、设计灵活和使用寿命长, 被认为是大规模储能最有前途的技术之一^[6]。

液流电池的概念最早是由 Thaller^[7]于 1974 年提出。该电池本身并不参与电化学反应, 只为活性电解质提供反应场所。因而液流电池的容量由电解液的浓度和体积决定, 功率由电池和电堆决定, 这使其设计灵活, 大规模应用更有优势。自 20 世纪 70 年代来, 研究者们探索了多种液流电池, 根据其正负极电解质活性物质的氧化还原电对种类不同, 典型的液流电池

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包括全钒液流电池、铁铬液流电池、铅酸液流电池、锌基液流电池以及有机液流电池等, 其中全钒液流电池是最接近产业化和规模化的一种。尽管液流电池种类繁多, 但系统结构和组成基本相似, 主要包括正负极储罐、电堆、泵、管路和控制系统等。电解液从储罐出发通过泵在电堆中进行循环流动, 并在电极表面上发生氧化还原反应, 质子交换膜将正负极隔开以免串电, 双极板用来收集和传导电流。以全钒液流电池为例, 详见图1。目前关于液流电池的综合评述多聚焦于材料研发进展、电池/电堆的结构设计优化以及系统模型的仿真分析, 而对热分析及热管理方面的探讨则相对较少。本文将从产热及散热机理、热管理、与锂离子电池热管理进行对比三个方面介绍, 希望对液流电池的热管理提供见解, 为后续科研工作和产业发展提供参考。

1 液流电池热管理的重要性

液流电池(RFB)在工作中会产生大量的热, 如果不能及时有效散热, 会导致电池温度升高, 从而影响电池性能和安全。电化学反应情况、离子导电性、离子跨膜运行的速率以及电解液的黏度等都与运行过程中的温度密切相关^[8-14]。具体来说, 升高温度可以

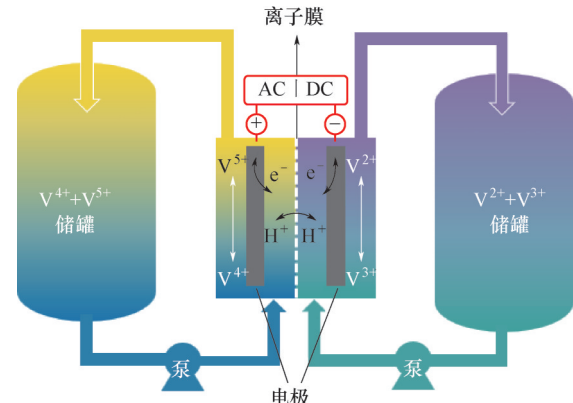


图1 全钒液流电池工作原理示意图

Figure 1 Schematic diagram of the working principle of vanadium redox flow battery

提高反应速率常数, 促进电化学反应中的反应动力学。同时, 高温也会使电解液黏度降低, 从而提高钒离子从主体到电极表面上的传输效率, 降低浓度极化电势。但当温度超出一定范围时, 会有致命的影响。以全钒液流电池(VRFB)为例, 它的正常运行温度范围是0~40℃。随着温度的升高, 负极上的析氢反应会显著增强, 造成库仑效率的降低^[9](图2)。同时钒离子通过离子膜的扩散能力增强, 使得容量衰减情况加剧。此外, 电解液中的钒活性离子在温度异常时不稳定易析出沉淀^[15], 当2 mol/L VO_2^+ + 3 mol/L H_2SO_4 的电解液在40℃下放置2 d后, 其中的 VO_2^+ 转化成

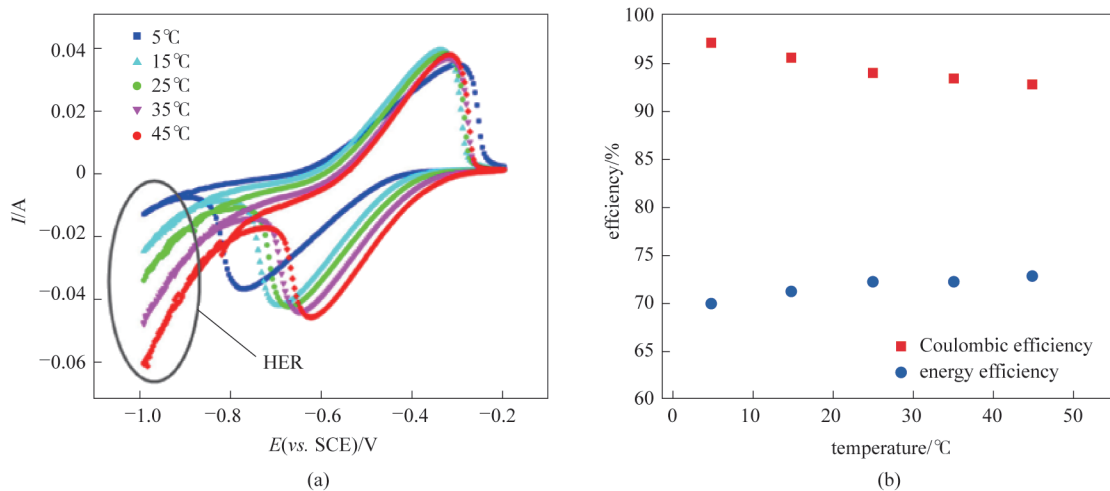


图2 负极HT-CF(热处理碳毡)在不同温度下的循环伏安曲线, 扫描速率2 mV/s (a); HT-CF在100 mA/cm²、不同温度下的库仑效率和能量效率 (b)^[9]

Figure 2 Cyclic voltammety of negative side HT-CF at different temperatures, with a scan rate of 2 mV/s (a); Coulombic efficiency and energy efficiency of HT-CF at 100 mA/cm² and different temperatures (b)^[9]

V_2O_5 沉淀; 而在 15°C 下放置 7 d 后, 电解液中的 V^{2+} 会产生沉淀^[16-17]。这种产生的沉淀会堵塞流道, 覆盖碳毡和离子膜, 导致泵功率损失增加, 发生电池故障^[9, 18]。

Trovò 等^[19-21]模拟了工业规模 VRFB 电堆 (9 kW) 的温度变化, 发现在 667 mA/cm^2 的电流密度下连续放电 8 h 后, 电解液温度超过 50°C (图 3), 所以需要加入冷却系统。在 GB/T 32509—2016《全钒液流电池通用技术条件》中规定了工作温度在 $0\sim 40^\circ\text{C}$ 之间, GB/T 41986—2022《全钒液流电池设计导则》中也说明了电池的设计应根据环境温度、工作温度和实际需要配置热管理系统。此外, 温度持续过高也会加速电池内部电极、质子膜等材料的老化, 从而缩短电池的使用寿命。所以, 温度热管理对维护液流电池的稳定运行具有重要意义。

1.1 VRFB 的热模型及传热机理

为了保障液流电池运行的稳定安全, 需要建立热模型来对电解液的温度进行预测和控制, 进一步指导电池优化控制, 这也是热管理系统的重要部分之一。Tang 等^[22]基于能量守恒建立了以传热为主的动态模型, 该模型基于 $2.5\text{ kW}/15\text{ kWh}$ 电堆模块, 研究在不同环境温度和操作条件下储罐以及电堆中电解液的温度变化情况, 但模型没有考虑化学反应产生的可逆热。随后他们将自放电反应和分流产热考虑到模型中, 研究其对电堆温度和效率的影响^[23, 24]。Wei 等^[25]

考虑了水力摩擦产热并建模研究了电堆内部流动模式对电解质温度的影响, 结果表明, 在低流速下, 电池系统中存在显著的温度梯度, 而在相对高的流速下, 电解质温度趋于相同。Yan 等^[26]讨论了电池设计、环境温度和电解质流速在不同应用中对 VRFB 热行为的影响。Zhang 等^[27]描述了操作温度对 VRFB 性能的影响。他们的工作表明, VRFB 的库仑效率和容量随着操作温度的升高而降低, 并且有必要建立热管理模型, 以确保最佳的热运行条件, 从而实现可靠高效的运行。随后 Zhang 等^[28]利用有限元法在模型中考虑了流动分布情况。此外, Chen 等^[29]建立了由八个电堆组成的 VRFB (250 kW) 系统的热模型, 模型与测试验证效果较好 (图 4)。模型研究了传输延时、环境温度和储罐输送方式等对电堆模块温度的影响, 研究发现不同电堆中电解液的温度非常接近, 且正负极储罐温度相同, 储罐温度整体上比电堆高 0.5°C 。

在全钒液流电池运行过程中产生热量的因素包括电化学反应、过电位、水力摩擦、交叉反应和分流, 其中电化学反应和过电位产热相对于另外三种占比较大。Ren 等^[30]用五个单电池建立了电化学-热耦合模型来预测热行为, 其中考虑了欧姆电阻随温度和电荷状态的变化情况。若流体流量恒定, 则液体产生的摩擦生热功率即可视为恒定值 46 W 。图 5 展示了 5 个单电池在不同电流密度下一次充放电中电化学反应热、过电位热、分流电流热以及交叉副反应热的情况。图 5(a)前半部分是充电的吸热过程, 后半部分是放电

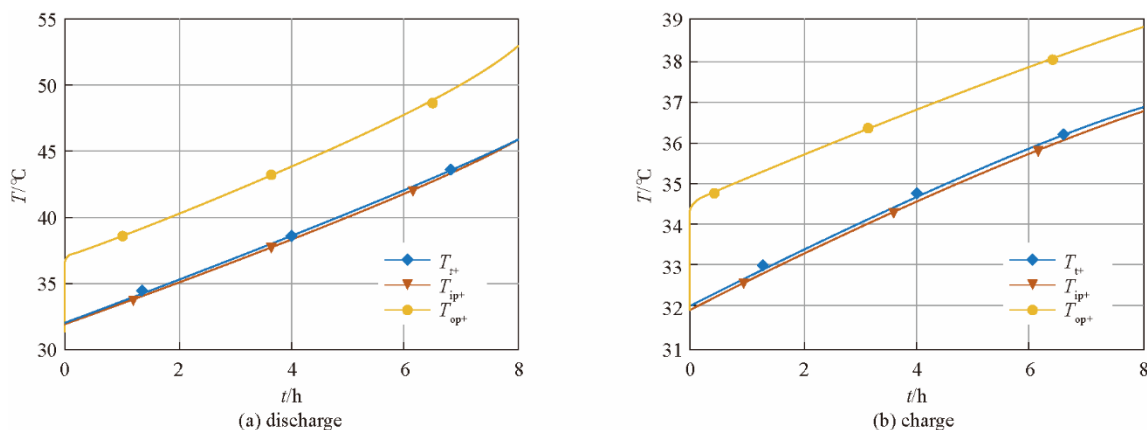


图3 模拟大电流 (400 A) 8 h 充放电情况下正极电解液温度情况 (ip—电堆入口; op—管路出口; t—储罐)^[21]

Figure 3 Positive electrolyte temperature under high current (400 A) 8 h (ip—stack inlet; op—pipeline outlet; t—tank)^[21]

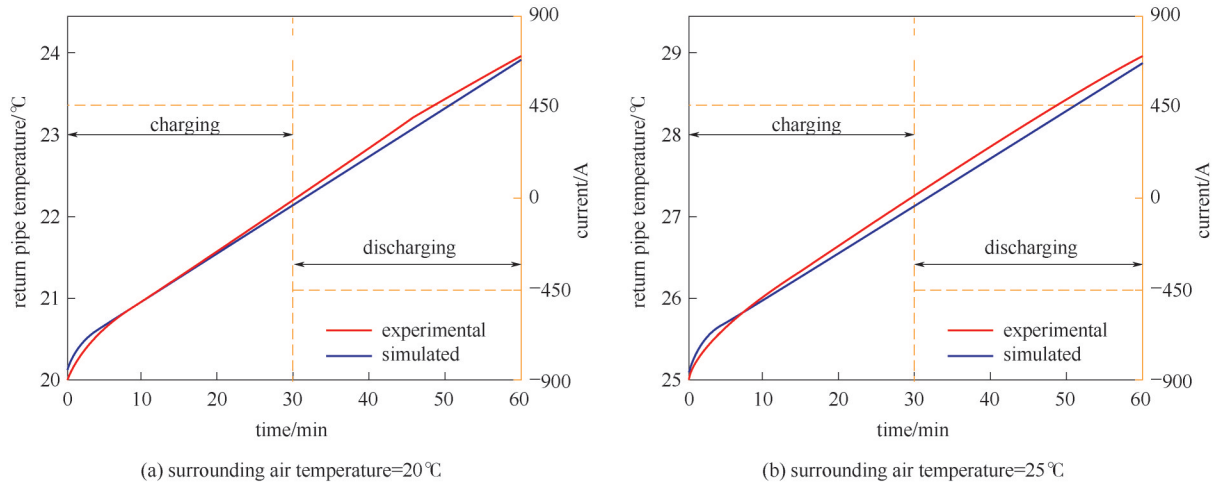


图4 20°C(a)和25°C(b)的环境温度下, VRFB模块在充放电循环过程中的温升^[29]

Figure 4 Temperature rise of practical VRFB module during charge-discharge cycling at surrounding temperatures of 20°C (a) and 25°C (b)^[29]

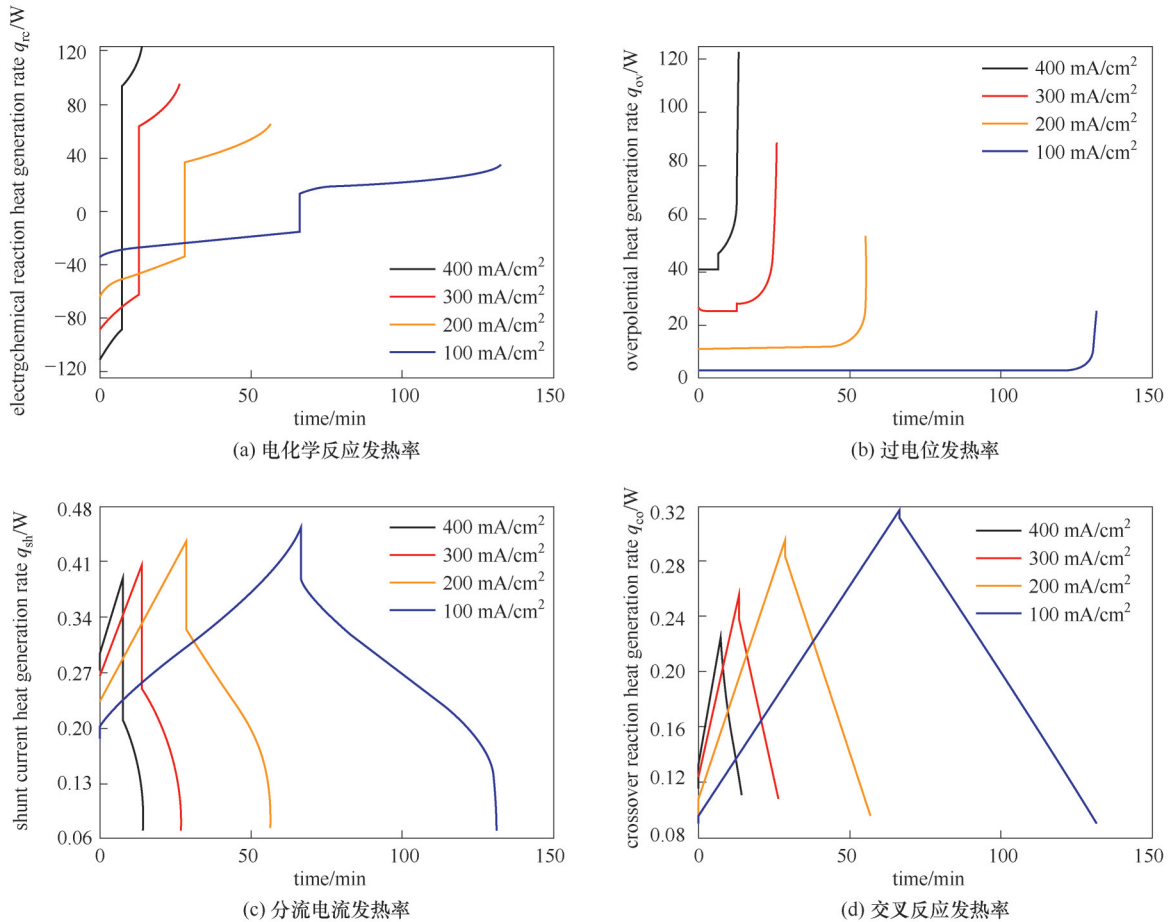


图5 在不同电流密度、环境温度为25°C的条件下, VRFB在第10次充放电循环中的电化学反应发热率(a)、过电位发热率(b)、分流电流发热率(c)和交叉反应发热率(d)^[30]

Figure 5 The heat generation rate of electrochemical reaction(a), overpotential(b), shunt current(c) and crossover reaction(d) in the 10th charge-discharge cycle for the VRFBs at different current densities, ambient temperature is 25°C^[30]

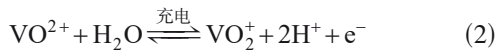
放热过程; 对于过电位产热[图 5(b)], 放电过程的发热率明显高于充电过程, 且随着电流密度的增加, 最大发热率可以从二十多瓦增大到百瓦。相比之下, 交叉反应产热和分流产热[图 5(c)、(d)]只占到两者的百分之一左右。

VRFB 电极表面上发生的电化学反应如下

负极



正极



电化学反应可逆熵热可由热力学基本公式推导, 已知 $\Delta_r G_m = -zEF$, 得到

$$\left[\frac{\partial(-zEF)}{\partial T} \right]_p = -\Delta_r S_m \quad (3)$$

$$\Delta_r S_m = zF \left(\frac{\partial E}{\partial T} \right)_p \quad (4)$$

式中, $\Delta_r G_m$ 为摩尔反应 Gibbs 自由能; z 为反应中的计量系数; E 为反应电动势; F 为法拉第常数; T 为反应的温度; P 为反应的压力; $\Delta_r S_m$ 为摩尔反应熵。

所以在等温情况下, 可逆反应的热效应为

$$Q_m = T\Delta_r S_m = zFT \left(\frac{\partial E}{\partial T} \right)_p \quad (5)$$

式中, Q_m 是单位摩尔反应热, 在液流电池充电时电流为正值, 放电时电流为负值。所以这部分可逆反应热体现为: 充电过程吸热, 放电过程放热。

$$Q_r = \frac{IT\Delta S}{zF} = IT \left(\frac{\partial E}{\partial T} \right) \quad (6)$$

式中, Q_r 为反应热; I 为电流。由 Nernst 方程可以得到 (活度系数的乘积可以近似看作 1) [31]

$$E = E^\ominus + \frac{KT}{zF} \ln \left[\left(\frac{c_{\text{VO}_2^+} c_{\text{V}^{2+}} c_{\text{H}^+}^2}{c_{\text{VO}^{2+}} c_{\text{V}^{3+}}} \right) \left(\frac{r_{\text{VO}_2^+} r_{\text{V}^{2+}} r_{\text{H}^+}^2}{r_{\text{VO}^{2+}} r_{\text{V}^{3+}}} \right) \right] \quad (7)$$

$$E^\ominus = -\frac{\Delta G^\ominus}{zF} = -\frac{\Delta H_r^\ominus - T\Delta S_r^\ominus}{zF} \quad (8)$$

式中, c 为反应浓度; r 为离子的反应活度因子; K 为气体常数。将 $E^\ominus$ 代入 Nernst 公式中, 并对 E 求偏导并代入可逆熵热公式得

$$Q_r = IT \frac{dE}{dT} = \frac{IT}{zF} \left[\Delta_r S^\ominus + K \ln \left(\frac{c_{\text{VO}_2^+} c_{\text{V}^{2+}} c_{\text{H}^+}^2}{c_{\text{VO}^{2+}} c_{\text{V}^{3+}}} \right) \right] \quad (9)$$

式中, $\Delta_r S^\ominus$ 是反应的标准摩尔熵变。过电势损失产热 η 分为三部分, 分别是欧姆极化、活化极化和浓差极化产生的过电势, 即

$$\eta = \eta_{\text{act}} + \eta_{\text{con}} + IR \quad (10)$$

式中, η_{act} 为活化过电势; η_{con} 为浓差过电势; I 为电流; R 为电阻。电化学反应动力学决定了活化过电势 ($\eta_{\text{act}+/}$), 由 Butler-Volmer 方程推导可得

$$j_{\pm} = j_{0_{\pm}} \left[e^{\frac{\alpha_{\pm} F \eta_{\text{act}_{\pm}}}{KT}} - e^{\frac{-(1-\alpha_{\pm}) F \eta_{\text{act}_{\pm}}}{KT}} \right] \quad (11)$$

式中, $\alpha_{\pm}$ 为正负极传递系数; $j_{\pm}$ 为电流密度; $j_{0_{\pm}}$ 为交换电流密度; 其中电流密度和交换电流密度由式 (12) 计算

$$j_{+} = j_{-} = F k_{0_{+}} c_{\text{VO}_2^+}^{(1-\alpha_{+})} c_{\text{VO}^{2+}}^{\alpha_{+}} j_{0_{-}} = F k_{0_{-}} c_{\text{V}^{3+}}^{(1-\alpha_{-})} c_{\text{V}^{2+}}^{\alpha_{-}} \quad (12)$$

式中, $k_{0_{+}}$ 和 $k_{0_{-}}$ 分别为正、负极反应速率常数。

浓差过电势由式 (13) 计算

$$\eta_{\text{con}_{\pm}} = \frac{KT}{zF} \ln \left(1 - \frac{j_{\pm}}{zF k_m c^{\pm}} \right) \quad (13)$$

式中, $c^{\pm}$ 为充放电时正负极的反应浓度; k_m 为正负极表面传质系数[32], 按式 (14) 计算

$$k_m = 1.6 \times 10^{-4} u^{0.4} \quad (14)$$

式中, u 为流动速度。综上, 总过电势生热 Q_a 为

$$Q_a = I\eta \quad (15)$$

散热项主要有储罐散热、电堆散热和管路散热, 由于在这 3 部分中都是流体流动, 所以每个部分都存在热传导和热对流。采用传统的散热计算公式即可。以储罐散热为例, 包括: ①热流体在流动过程中把热量传给储罐壁面的对流传热; ②通过储罐壁面的热传导; ③储罐壁面与冷流体的对流传热。

储罐的综合传热系数 K

$$K = \frac{1}{\frac{d_i}{\alpha_o d_o} + \frac{b d_i}{\lambda d_m} + \frac{1}{\alpha_i}} \quad (16)$$

式中, d_i 为储罐内直径; d_o 为储罐外直径; d_m 为储罐内外的平均直径; b 为壁厚; α_i 为储罐内的对

流传热系数; α_o 为储罐外的对流传热系数; λ 为储罐材料的导热系数。所以对于储罐的传热 Q_t , 可以按式 (17) 计算

$$Q_t = KA(T - t) \quad (17)$$

式中, A 为储罐传热面积; T 为环境温度; t 为储罐温度。

2 液流电池热管理技术

相对于锂离子电池, 液流电池作为水系电池, 由热失控导致安全风险较低, 但它的监测控制系统并不简单, 除了对健康状态进行监测和估算外, 更侧重于对电化学反应过程调节, 以保证运行寿命和运行性能。所以为了确保 VRFB 系统在合适的温度范围内运行, 需要高效的热管理系统^[33]。

2.1 液流电池的散热技术

Bhattacharjee 等^[34]通过动态优化流速对电堆温度进行管理, 并通过了 1 kW/6 kWh 的实验验证。储罐通常由聚丙烯 (PP)、聚四氟乙烯 (PTFE) 或聚氯乙烯 (PVC) 组成, 都具有较低的导热性, Tang 等^[22]提出在液流电池储罐相同的体积下增大表面积来提高传热, 但表面积的增加也是有限的。由于大部分热是在电堆中产生的, 乐山伟力得能源有限公司等^[35]提出一种相变材料 (PCM) 包裹 VRFB 电堆的结构, 通过 PCM 吸收 VRFB 堆产生的热量来控制温度, 但包裹体积小则散热有限, 体积大则占地面积更大; 为了改善通过管道的热传递, 可以在正极半电池的出口和正极罐的入口之间连接一个钛金属管式热交换器, 钛

金属管具有高导热性, 其表面还覆盖有耐腐蚀的 TiO_2 层, 可以保护其免受硫酸的侵蚀。

目前, 电化学储能系统的热管理技术路线主要分为空气冷却、液体冷却、热管冷却和相变冷却四种, 市场上液流电池储能热管理的主流技术路线是空气冷却和液体冷却^[36]。这些散热方式的选择取决于电池的规模、设计、运行条件以及成本效益^[37-40]。

2.1.1 空气冷却 空气冷却即风冷, 是以空气为介质, 以热传导和热对流的方式将系统内部的热量带走, 从而实现系统的冷却。风冷按驱动方式分为自然风冷和强制风冷, 自然风冷利用自然风压、空气温差、空气密度差等自然条件实现对电池的冷却效果。图 6 展示了自然对流和强制对流的空气冷却示意图。自然风冷的对流传热系数远低于强制风冷, 所以很难将电池产生的热量完全散掉。对于电池的低倍率充放电情况, 可以将系统温度控制在一定温度范围内, 但系统电流密度的增强就很容易使温度超出限制区间。因此, 尽管自然风冷具有简单、轻巧和低成本的优势, 但是适用范围极小, 现在已经很少受到研究^[41]。强制风冷是通过风机或风扇产生的强制气流将热量带走, 此时强制气流的传热系数大大提高。与液体冷却方式相比, 风冷具有结构简单、易维护、成本低等优点, 但需要消耗一定的电能, 且散热效率、散热速度和温度的均匀性较差, 通常适用于小型或中等规模的电池系统^[42]。Park 等^[43]研究了几种电池布局和传热流体类型对锂离子电池的冷却性能, 研究也证实空气冷却是小尺寸电池综合设计中最合适的选择。大连融科^[44]设计了一种风冷热交换器 (图 7), 用环境空气或冷却器冷却电解质, 在

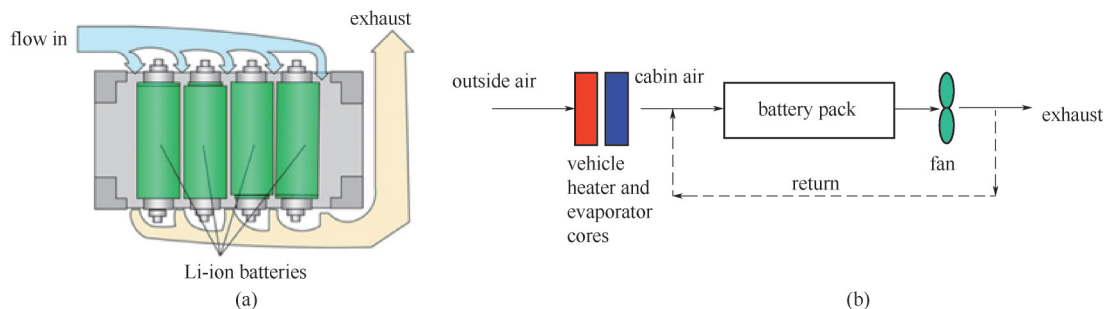
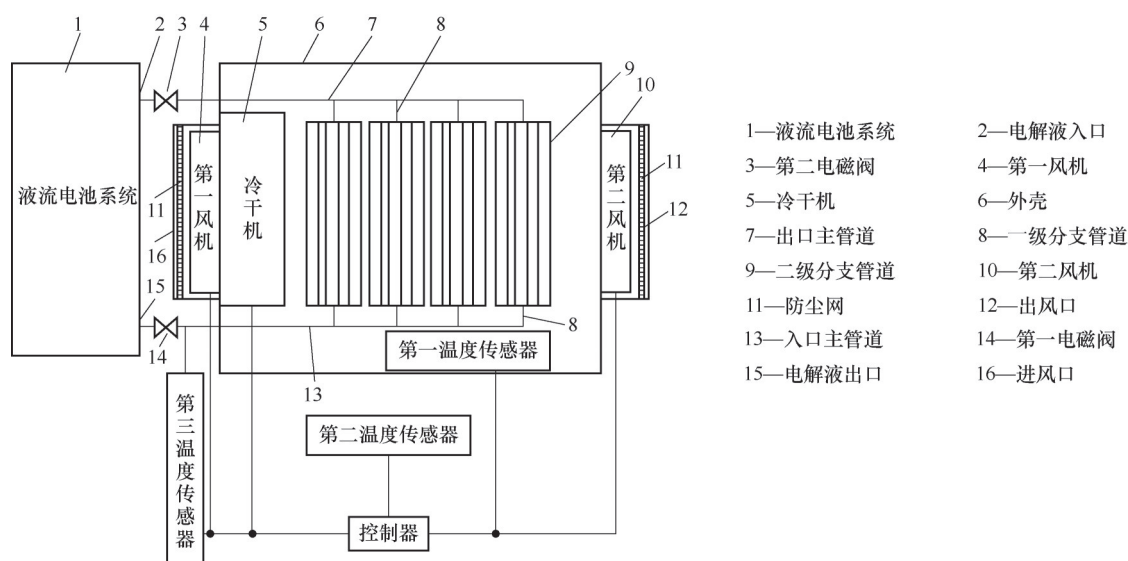


图 6 自然对流(a)^[45]和强制对流(b)^[46]空气冷却示意图

Figure 6 Schematic diagram of natural convection air cooling(a)^[45] and forced-air cooling(b)^[46]

图7 VRFBs 热处理及控制装置^[44]Figure 7 Heat treatment and control device for VRFBs^[44]

一次充放电循环后，它可以将正极侧的电解质温度从48.3℃冷却到43.3℃。

2.1.2 液体冷却 液体冷却（液冷）是以冷却液为介质，利用较高的比热和换热系数进行散热。液冷系统可以提供更高的散热效率和更好的温度控制效果，但系统复杂度和成本也相对较高，适用于大型电池系统。常用的冷却剂有水、乙二醇水溶液、纯乙二醇、空调制冷剂和硅油等^[47]。由于液流电池电解液中的电荷易顺着冷却液流至整个系统，危险性较高，所以冷却介质的选择也很重要。但对于液流电池最常见的是应用耐腐蚀且不导电的换热器，内部材料一般同电解液储罐相同，采用PVC或PP，或者应用钛金属管式换热器，将其内表面覆盖上有耐腐蚀性能的

TiO₂层^[48], 保护换热器免受硫酸的侵蚀。Wei等^[49]模拟研究了强制冷却策略的管壳式换热器的冷却效果, 模型包括风冷和液冷。结果表明, 冷却剂的流速对电解液温度有显著影响。相比之下, 电解液的流速对传热的影响有限。因为即使在电解液流速较小时, 在做曲线流动时也会出现湍流, 同时, 电解液与换热器的接触面积很大, 此时, 电解液的流速不会对传热造成太大影响。但冷却剂沿换热器内直管流动, 且与换热器的接触面积小, 因此增加冷却剂的流速可以显著改善传热效果(图8)。

2.2 抑制产热的策略

全钒液流电池作为最有前景的可再生能源存储技

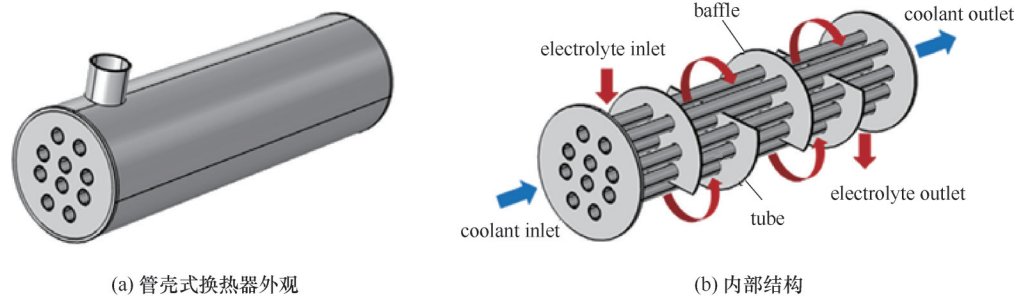


图8 管壳式换热器外观(a)和内部结构(b)^[49]

Figure 8 appearance(a) and internal(b) structure of shell and tube heat exchanger^[49]

术之一, 在运行期间的过度发热问题极大地影响了系统的效率和稳定性。以上综合了从系统散热角度上通过加速热传递的方式来进行温度控制的方法。此外, 也可以在抑制产热角度从源头上为VRFB热管理系统提供可行方案。

2.2.1 电堆核心部件的改进 VRFB电堆是由十几个或几十个单电池叠加串联而成的, 单电池作为电堆的基本单元, 核心部件包括双极板、电极、离子交换膜、集流体和端板等。在产热研究中, 过电势产热和电化学反应产热占到系统的大部分。电极作为全钒液流电池的核心部件之一, 为氧化还原点提供活性位点, 催化钒离子进行氧化还原反应, 它的材料活性会影响活化过电势, 而它的电阻将影响充放电过程中的欧姆过电势, 进而对系统的过电势产热造成影响。在电极材料中, 石墨毡(碳毡)因其机械性能良好、耐腐蚀、表面积大和导电性能好等优点, 成为市场的主要应用^[50]。Sun等^[51]将石墨毡在98%的硫酸中煮沸5 h, 电池内阻降为 $2.5 \Omega \cdot \text{cm}^2$, 能量效率最高可达到91%。He等^[52]在 NH_3 氛围中 900°C 热处理石墨毡, 改性后的电极性能也有一定的提高, 电池的循环稳定性也明显增强。Li等^[53]利用同步电沉积法将铋纳米颗粒沉积到石墨毡的表面, 其电池过电势显著降低, 电池性能大幅提升(图9)。

此外, 设计双极板材料、优化双极板结构、提高

电解液在流道及多孔电极中的均匀程度, 可缓解浓差极化、欧姆极化及局部过热问题^[54]。为了降低电极与双极板上的接触电阻, 众多学者提出了电极-双极板一体化结构。Qian等^[55]采用热塑性酚醛树脂、炭黑、石墨粉制备导电黏结层(ACL), 并将其涂覆于柔性石墨板的表面, 然后在 150°C 下将石墨毡电极与ACL热黏结得到电极-双极板一体化结构。Jing等^[56]采用电沉积的方法, 将三维氧化还原石墨烯多孔凝胶材料电沉积在柔性石墨板的表面, 制备了一体化结构。与传统的电极-双极板结构相比, 一体化结构质量轻、接触电阻更低。但是目前仍处于初期研究阶段, 需从材料选型、结构以及制备工艺等方面出发, 提升一体化结构的批量可行性和经济性。

2.2.2 电解液的优化 之所以要对VRFB系统进行热管理, 是因为其工作温度区间窄。若能从源头拓宽电解液在充放电过程中的温度区间, 则可以促进电化学反应速率, 提高离子传输效率, 从而降低浓差电势, 提高电池性能。同时, 也可以减少对温度控制系统的依赖。

目前, 针对热稳定性差的难题, 主要有电解液中加添加剂和更换更优性能的电解质两种思路。添加剂的类型包括两类: 有机添加剂和无机添加剂^[57]。有机添加剂含有官能团 $-\text{SH}$ 、 $-\text{COOH}$ 、 $-\text{COH}$ 、

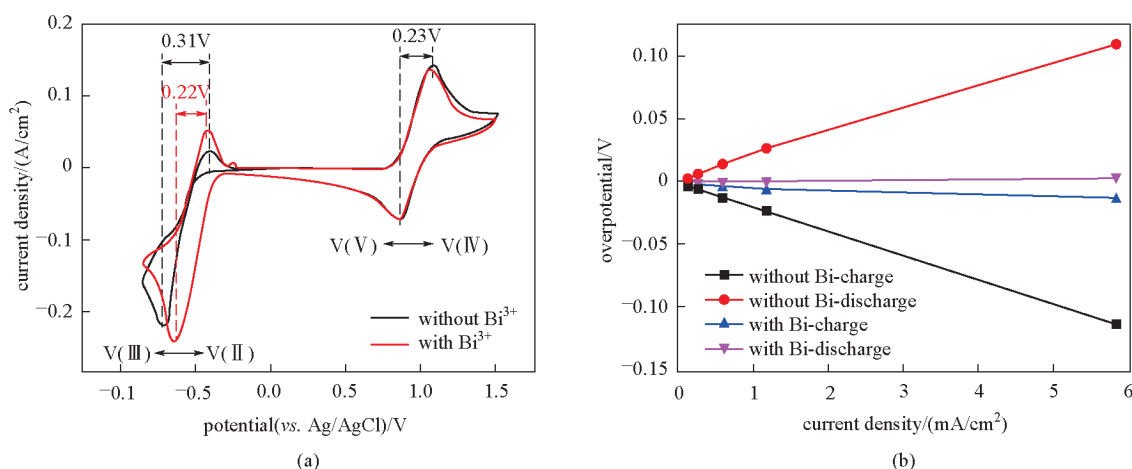


图9 使用玻碳电极为工作电极, 添加或不添加 0.01mol/L BiCl_3 的循环伏安曲线(a); 原玻碳电极和涂有Bi的玻碳电极为工作电极, 过电位随电流密度的变化(b)^[53]

Figure 9 Cyclic voltammetry with or without 0.01mol/L BiCl_3 using glassy carbon(a); Overpotential as a function of current density with pristine glassy carbon and Bi-coated glassy carbon as working electrodes(b)^[53]

—OH、—NH₂等, 可以吸附在钒离子成核的表面, 抑制晶体生长, 从而延长高浓度电解液的稳定时间^[58-60]。然而, 有研究表明具有可还原基团的有机添加剂在正极电解液中会被VO₂⁺缓慢氧化, 导致VO₂⁺被还原为VO²⁺, 降低了电池的容量, 不利于VRFB电解质的长期稳定性^[61]。无机添加剂主要包括磷酸盐、硫酸盐、氯化物等。Kim等^[62]提出利用盐酸作为支持电解质, 发现此时电解液中钒浓度可达2.3 mol/L, 并且可以在更宽的温度区间(0~50℃)稳定运行。然而, 由于诸多限制目前依旧以硫酸作为支持电解质, 例如氯离子的析出及不可忽略的成本问题等。

3 液流电池系统温度控制装置

南京林源电力在电堆的正负极管路之间利用珀尔帖效应来控制电堆正负极电解液流入管和流出管的温度^[63]。湖北中钒储能设计了一种全钒液流电池电解液的温控装置, 如图10所示^[64]。图中左半部分是壳体, 右边是电池电堆, 壳体上半部分通过冷却板(7)和冷却管(8)起冷却作用, 下半部分通过电加热板(12)起加热作用。广东三水工业大学研究院研究了一种全钒液流电池管理系统, 包括电解液温度控制装置和中央控制装置, 特点在于中央控制装置能够

依据用户需求和内部或外部指令来驱动电解液温度控制装置对正负极电解液进行单边交替换热^[65]。北京和瑞储能提出将系统采用间接换热的方式, 将加热/冷却单元、换热单元、泵输送单元、控制单元集成撬装装置, 对整个系统进行温度控制。液流电池流量大时, 经过换热器的流阻随之增大, 通过增加换热器尺寸会解决这一问题, 但成本也会增加^[66]。针对这一问题, 巨安储能提出了一种增加一条与换热器并联流体支路的方法, 通过调节支路阀门来调节进入换热器的流量, 经过一条支路冷却的电解液与第二支路的电解液汇合后流入电堆, 如图11所示^[67]。

4 液流电池与锂离子电池在热管理方面的区别

液流电池和锂离子电池在主要构成部件上基本相同, 电池主要由正极、负极、隔膜、电解液、集流体等部分组成, 但整体结构、工作方式的不同导致两者在传热和热管理需求上有所不同。

4.1 产热

锂离子电池在正常工作状态下, 热量的来源是可逆的熵变热和不可逆的极化热及焦耳热, 这些热量包括电化学反应、极化效应和欧姆效应^[68-72]。而液流电

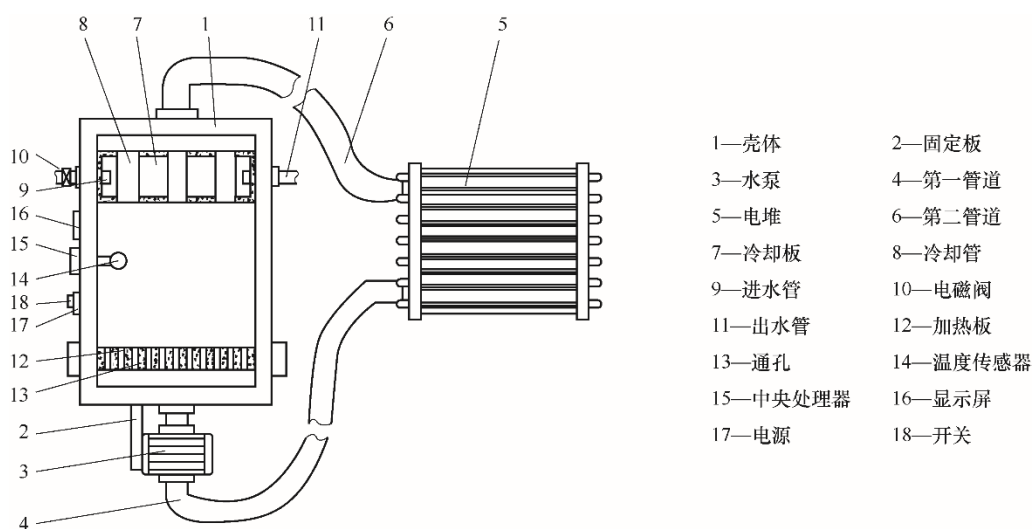


图10 全钒液流电池电解液温控装置^[64]

Figure. 10 Electrolyte temperature control device for vanadium redox flow battery^[64]

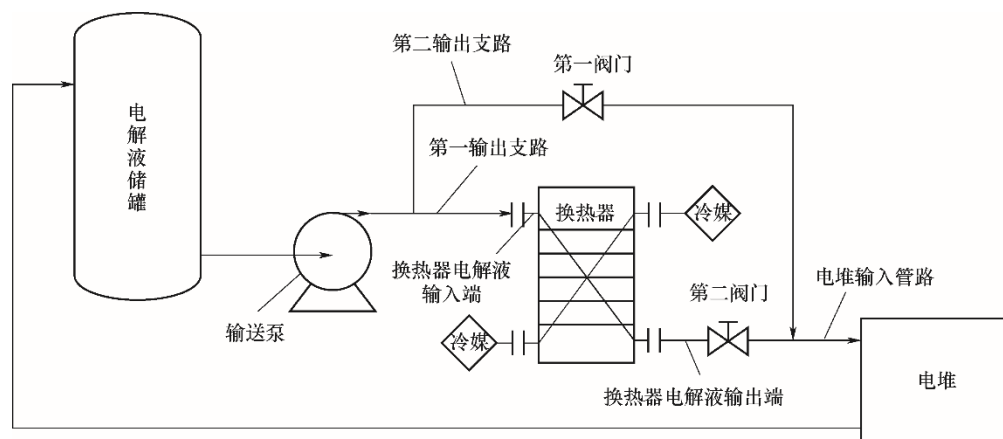


图11 液流电池的热管理方法、储能系统和控制器^[67]

Figure 11 Thermal management methods, energy storage systems and controllers for redox flow batteries^[67]

池的产热主要来自于电解液在电堆中的电化学反应、极化效应和欧姆效应。液流电池的电解液在外部储罐中存储, 通过泵输送至电池堆发生反应。

4.2 散热

锂离子电池的热传递包括电池内部的热传导、电池内部电解质的热对流、电池外表面与空气的对流换热^[73]。而液流电池的散热主要由电解液储罐承担, 所以与液流电池相比, 锂离子电池的电解液流动散热几乎可以忽略。

4.3 热管理复杂性

尽管液流电池是水系电解液, 和锂电池相比热安全性较高。但液流电池的管理系统可能更为复杂, 因为它除了像锂离子电池对电池监测和荷电状态估算等, 还需要对整个系统, 包括储罐、电堆和管路里的温度、压力、流量进行控制和调节, 来保证电池性能和寿命^[74]。此外, 与液流电池相比, 锂离子电池的发展时间足够长^[75-80], 在热管理控制方面技术较为成熟, 而液流电池温度控制系统方案有待进一步完善。锂离子电池的热控制问题是重点也是难点, 它的热管理技术分为内部热管理和外部热管理。内部热管理技术即从材料层面上对其进行改性升级, 主要包括正负极材料、电解液和隔膜。但是受开发工艺的限制, 在材料上的解决前景不易。因此目前应用更多的还是外

部冷却技术, 且倾向于多种冷却技术相互耦合进行热管理^[41]。而液流电池的热管理系统中则是以液冷技术中的换热器控温前景较好。

5 结语

与当前主流的锂电池储能相比, 液流电池由于采用水系电解液, 安全性大大提高, 而且具有容量和功率相互独立的特性, 因此成为长时储能的有力选择之一。但由于其较窄的工作温度区间, 考虑到温度波动对电池充放电效率、容量衰减等的影响, 以及储能设施所处气候条件、储能时长的差异性, 对其进行控温及热量的平衡和优化成为电池管理系统的重点内容。在热管理上, 液流电池更倾向于在电堆与电解液储罐连接的管路上, 加入耐腐蚀材质的管壳式换热器。建议未来可以将工厂实际运行情况与VRFB系统传热模型结合起来, 共同实现在多层面上的风险缓解及运营维护。

液流电池产热机理与锂离子电池的基本相似, 但是液流电池具有泵送系统、储液装置及管路形成的循环系统, 在散热途径方面有所区别, 而且与液流电池接触的电堆以及配套设备和管路都采用导热性能较差的非导电材质, 散热更加困难, 因此其热管理需要依据自身特性优化操作参数, 例如冷却剂流量的快慢既可影响电堆反应效率, 也能影响产热以及散热速率。液流电池的储能容量和功率相互独立, 该特性也是其

热管理应该注意和考虑的环节。由于温度升高也可提高系统效率, 所以未来也应该通过一定的办法提高VO₂⁺的高温稳定性, 以及减少膜在高温下的交叉和水迁移。

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Heat Management of Redox Flow Batteries and Its Progress

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Highlights

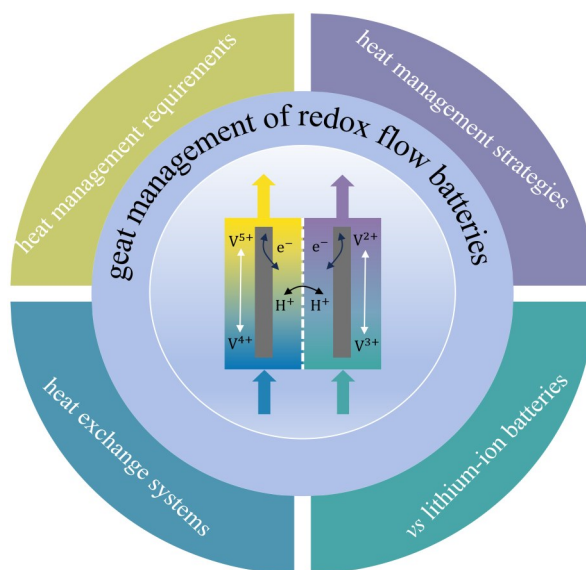
Highlighted the critical role of heat management in redox flow batteries for long-term energy storage.

Analyzed heat generation mechanisms and thermal models of vanadium redox flow batteries.

Reviewed air cooling and liquid cooling techniques for heat management.

Compared heat management of redox flow batteries with lithium-ion batteries.

Graphical Abstract



Abstract: Energy is the cornerstone of human society's survival and development, with the continuous consumption of large amounts of fossil energy, resulting in excessive carbon dioxide emissions, gradually triggering the greenhouse effect and rapid changes in the world's climate. In 2020, China has clearly set the goals of "carbon peak" by 2030 and "carbon neutrality" by 2060, and renewable energy is considered to be the key to achieving this goal. However, wind, solar and other renewable energy generation is discontinuous, unstable and uncontrollable, and large-scale integration into the power grid will bring serious impact on the safe and stable operation of the power grid. Energy storage technology through the storage and release of energy, can effectively inhibit large-scale renewable energy power generation access to the grid brought about by the volatility, and effectively promote the balance of power generation and load in the operation of the power system, to improve the security of grid operation, economy and flexibility.

Therefore, the development of large-scale energy storage technology has become the key to solving the energy problem, as well as the technical basis for the further and promotion of renewable energy technologies. In fact, energy storage technology can be applied to a variety of occasions, throughout the power system of power generation, transmission, distribution and use of electricity in all major aspects. According to the needs of different applications, people have developed a variety of energy storage technologies. Common energy storage technology to physical energy storage and chemical energy storage, of which, physical energy storage mainly includes pumped storage, compressed air energy storage, flywheel energy storage, superconducting energy storage and so on. Chemical energy storage mainly includes lithium-ion batteries, redox flow batteries, sodium sulfur batteries and lead-acid energy storage. Among them, pumped storage and compressed air energy storage have the outstanding advantages of mature technology, good economy, long life cycle and large energy storage capacity, but due to geographic limitations, their application has received great constraints; lithium-ion batteries have high energy density and good cycling performance, but the economy of the life cycle is low, and there are certain safety hazards; redox flow batteries are safe and reliable, the economy of life cycle is good, the environment is low load, and they are the most suitable for the scale of lead-acid energy storage. Flow battery is one of the most suitable technology solutions for large-scale energy storage with safety,

reliability, good life-cycle economy and low environmental load.

As a long-term energy storage technology with the advantages of high safety, independent capacity and power, and high residual value, redox flow battery has gained wide attention and application at home and abroad. After decades of development, great progress has been made in the mechanism of the battery, key materials, and electric stack design. However, the narrow operating temperature has also become a serious obstacle limiting its application, and the various heat transfer behaviours under different operating conditions cause complex thermal problems. If the system temperature is not intervened, the efficiency and stability of the battery will be greatly affected. This paper firstly describes the importance of thermal management of vanadium redox flow batteries. In general, the temperature at which all-vanadium redox flow batteries can work safely for a long period of time is limited to 10–40 °C, and the electrolyte is prone to problems such as precipitation and clogging when the temperature is either too high or too low, which will affect the performance and lifetime of the batteries. Therefore, the article firstly describes the heat generation and dissipation mechanism of vanadium redox flow battery, and the researcher establishes a thermal model according to different focuses, and analyses the behaviours and percentage of heat generation. The heat generated during the operation of vanadium redox flow batteries comes from electrochemical reactions, overpotential, hydraulic friction, crossover reactions, and shunt current. Among them, the heat generated by electrochemical reactions and overpotential accounts for a relatively large proportion. If the operating temperature of redox flow batteries is controlled, thermal management techniques need to be reviewed. The article reviews existing thermal management techniques in terms of both external heat transfer and internal heat generation. External thermal management mainly elaborated on air cooling technology and liquid cooling technology. At present, in vanadium redox flow batteries system management, it is more effective to add heat exchangers between stacks and the tanks. Then, the current temperature control devices are also elaborated, and a brief comparison made between the thermal management technologies of vanadium redox flow batteries and lithium-ion batteries. Finally, it is hoped that the actual data can be combined with the model to facilitate the operation, monitoring, and optimization of the temperature control system. In this paper, we have conducted an exhaustive literature research and summary on this topic to provide a comprehensive overview of the thermal management of redox flow batteries and its progress, which we hope will be helpful to the readers and practitioners in the field.

Keywords: redox flow batteries; heat management; heat generation mechanism; cooling system