



反向电渗析热机发生单元研究进展

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摘要 反向电渗析热机技术通过“热能-化学势能”和“化学势能-电能”两个转化过程完成电力生产, 是一种新型的低位余热利用技术. 热机由发生单元及反向电渗析电池单元构成, 分别对应上述两个转化过程. 其中, 发生单元对系统性能有显著影响, 故本文从提升发生单元效率和系统性能出发, 系统地综述了发生单元工质和发生方法的研究进展. 通过探究溶剂和溶质特性对发生单元及系统性能的影响机理, 凝练出工质筛选原则: 反向电渗析热机适合于低汽化潜热、低沸点、高活度系数和高电导率的工质. 调研发现, 现有发生方法主要有蒸馏法、膜蒸馏法和热分解法, 其中蒸馏法为最常见的发生方法. 3种发生方法的效率较低, 不可逆损失大, 未来研究可聚焦于系统最优浓度梯度的构建以及发生单元与发电单元的参数匹配. 此外, 反向电渗析热机技术除了设计用于回收低位工业余热, 亦可用于回收太阳能和地热能等中低品位可再生能源, 促进新能源的高效利用. 同时, 热机工作时伴随有电极反应, 表明采用反向电渗析热机进行发电的同时, 亦可进行污水处理、有机物降解、制氢及废酸、废碱中和处理.

关键词 反向电渗析, 热机, 余热利用, 工质筛选, 发生方法

能源是社会发展的核心动力. 工业革命后, 伴随人类社会的飞速发展, 能源需求量与日俱增. 据统计, 自1800~2018年, 人类一次能源消耗增长27倍, 2018年一次能源消耗量达到15万TW h^[1]. 飞速发展的另一面是化石能源的枯竭与日益严峻的环境问题, 若要维持人类社会的可持续发展, 势必进行能源革命.

能源革命通常有两条路线: 一是提高现有能源利用技术的效率; 二是发展太阳能、地热能 and 潮汐能等新能源利用技术. 余热是工业生产过程中以热能形式排放至空气中的能量, 该部分热量虽无法被既有工业系统利用, 但其温度高于环境温度, 仍可通过其他手段回收其中的有效能. 据统计, 每年工业生产约消耗

28000 TW h能量, 其中约9400 TW h的热量以余热的形式排入环境, 占总耗能量的1/3^[2], 余热的高效利用可以显著提高现有能源利用技术效率. 全球范围内, 太阳能和地热能储量丰富, 分别约为1550和8200 MW, 且使用过程中无污染物排放^[3]. 发展和使用新能源可缓解能源危机, 改善环境污染问题, 助力实现“碳达峰”和“碳中和”.

现有余热利用技术与新能源利用技术多适用于中高品位的热源, 鲜有技术适用于低品位热源. 在余热利用领域, 如图1所示^[4], 有机朗肯循环和卡琳娜循环等技术适用于温度为150°C以上的热源, 随热源温度的降低, 系统效率显著下降. 在新能源利用方面, 如太阳能利用

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和地热利用,亦缺乏150℃以下热源利用技术^[5].事实上,低品位余热约占余热总量的63%^[6],相较于中高品位余热更具有利用价值.因此,发展低品位热能利用技术尤为重要.反向电渗析热机技术(reverse electrodialysis heat engine, REDHE)适用于低品位余热,且焓效率远高于其他余热利用方式^[4],如图1所示.

REDHE技术由Loeb^[7]于1979年提出,系统由反向电渗析(reverse electrodialysis, RED)发电单元和发生单元构成. RED技术由Pattle^[8]于1954年提出, RED电池利用离子交换膜两侧浓度差,在内电路形成定向离子流,通过电极系统将离子流转化为电子流对外输出.发生单元由余热驱动,通过蒸馏或膜分离等发生技术将热能转换为溶液间化学势能,在离子交换膜两侧构建浓度差.

研究表明,发生单元约占整个系统焓损失的60%~70%^[9,10],对系统性能有显著的影响,但现有综述多侧重于RED电池单元性能^[11],仅有少量文章总结发生单元工作原理和性能^[12]. 本文将重点综述发生单元研究进展:首先介绍REDHE发生单元和电池单元性能参数及评价指标,其次阐述发生单元工质以及新型工质的筛选原则,之后总结发生单元的常见工艺循环以及REDHE除发电外的其他应用.

1 REDHE工作原理

REDHE可视为广义卡诺热机,系统工作于驱动热

源(高温热源)和环境热源(低温热源)之间,通过发生过程和反向电渗析过程将热能转化为电能并对外输出.系统由发生单元和RED电池单元两部分组成(图2).发生单元由低品位热能驱动,通过分离溶液中的溶剂和溶质得到稀溶液(dilute solution, DS)和浓溶液(concentrated solution, CS),发生后的溶液进入RED电池单元. RED电池单元通过反向电渗析发电过程将溶液间化学势能转换为电能对外输出,完成发电过程的溶液进入发生单元中,至此完成一个完整的工作循环.

当发生单元耗能为 Q_h 时,电池单元产生电能 E ,则REDHE整机效率为

$$\eta_{\text{gross}} = \frac{E}{Q_h} \quad (1)$$

1.1 发生单元工作原理

发生单元以余热为驱动力,分离溶液中的溶剂和溶质,其分离方法主要有溶剂分离法和溶质分离法两大类.溶剂分离法包括蒸发分离、液液萃取分离、吸收分离和共沸混合物分离.溶质分离法包括热分解盐分离和盐沉淀分离. REDHE系统主要采用蒸发分离法、膜分离法和热分解盐分离法,其余方法多处于探索阶段.

以蒸发分离为例,当采用卡诺热机进行溶液热分离时,热机输出功为 ΔG_{mix} .当溶剂受热蒸发后,剩余溶液浓度升高形成浓溶液,完成发生过程.分离单位体积

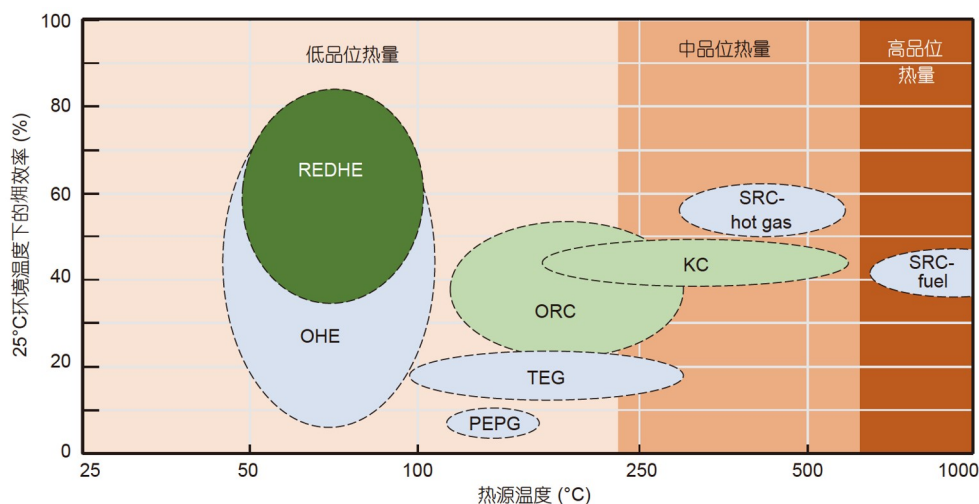


图1 不同余热利用技术的温区和效率^[4]. SRC-fuel: 燃料蒸汽朗肯循环; SRC-hot gas: 蒸汽朗肯循环; KC: 卡琳娜循环; ORC: 有机朗肯循环; TEG: 温差发电; PEPG: 废热驱动压差发电; REDHE: 反向电渗析热机; OHE: 压力延迟渗透热机

Figure 1 Temperature range and efficiency of different waste heat recovery technologies^[4]. SRC-fuel: Steam Rankine Cycle directly fuelled by fuels; SRC-hot gas: Steam Rankine Cycle; KC: Kalina Cycle; ORC: Organic Rankine Cycle; TEG: Thermoelectric generation; PEPG: Piezoelectric power generation with waste heat; REDHE: Reverse electrodialysis heat engine; OHE: Osmotic heat engine

溶剂所需理论最小分离热为^[13]

$$q_{\min} = \frac{-Q_{\min}}{V_d} = \frac{-\Delta G_{\min}}{V_d} \frac{T_h}{T_h - T_a} = \frac{-\Delta G_{\min}}{V_d \eta_c}, \quad (2)$$

式中, $Q_{\min}$ 为高温热源最小输出热量, V_d 为发生溶剂体积, T_h 为高温热源温度, T_a 为低温热源温度, η_c 为卡诺效率。

由式(2)可知, 理论分离过程与溶剂性能无关。但对于实际分离过程, 分离效率受溶剂性能影响, 实际分离过程效率为^[13]

$$\eta_{\text{sep}} = \frac{\Delta G_{\min}}{Q_h} = \frac{Q_{\min}}{Q_h} \left(1 - \frac{T_a}{T_h}\right) = \eta_c \frac{Q_{\min}}{Q_h} = \eta_c \eta_s, \quad (3)$$

式中, η_s 为实际过程热力学完善度。

1.2 RED电池单元工作原理

RED电池单元主要由离子交换膜、电解质和电极液及其腔室构成(图3)。工作时, 稀溶液和浓溶液分别进入稀溶液腔室和浓溶液腔室, 在离子交换膜两侧形成

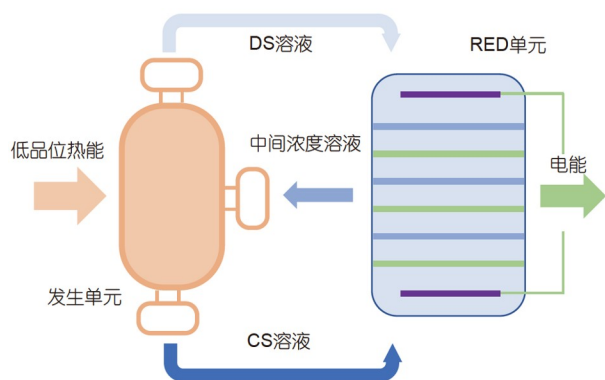


图2 REDHE系统结构图

Figure 2 System description of the REDHE

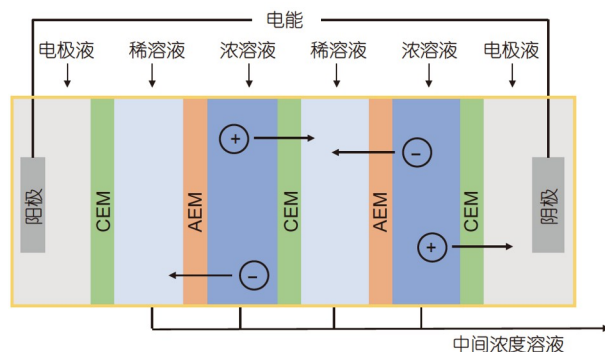


图3 RED单元工作原理图

Figure 3 Schematic diagram of the RED unit

浓度梯度。离子交换膜由阳离子交换膜(cationic exchange membrane, CEM)和阴离子交换膜(anionic exchange membrane, AEM)组成, CEM和AEM在电池内部交替排列形成若干溶液腔室。溶液中的离子在化学势能的作用下定向通过离子交换膜, 在溶液腔室内形成定向离子流并在膜两侧形成阴阳离子浓度差, 产生膜电势。在膜电势的作用下, 在电极液腔室内的电极发生氧化还原反应, 将定向离子流转换为电子流, 完成发电过程。

1.2.1 溶液化学势能

RED电池单元发电能量来自不同浓度溶液间化学势能差, 即吉布斯自由能差。在恒温恒压条件下, 混合浓溶液CS和稀溶液DS所得理论非膨胀功可用吉布斯自由能表示^[14]:

$$\Delta G_{\min} = G_b - (G_{\text{CS}} + G_{\text{DS}}), \quad (4)$$

式中, b 为中间浓度溶液(brackish), G 为溶液吉布斯自由能。

1.2.2 理论电压

理想情况下, 电池开路电压由离子交换膜和溶液浓度共同决定:

$$\text{OCV} = N_{\text{IEM}} (\alpha_{\text{CEM}} + \alpha_{\text{AEM}}) \frac{RT}{F} \left(\frac{\gamma_{\text{CS}} C_{\text{CS}}}{\gamma_{\text{DS}} C_{\text{DS}}} \right), \quad (5)$$

式中, α_{CEM} 和 α_{AEM} 为阳离子交换膜和阴离子交换膜选择性系数, N_{IEM} 为离子交换膜对数量, F 为法拉第常数, γ 为膜侧溶液活度系数, C 为膜侧溶液浓度。

1.2.3 电池内阻

RED电池单元内阻由欧姆电阻和非欧姆电阻构成, 欧姆电阻由离子交换膜电阻、溶液腔室电阻和电极腔室电阻构成。非欧姆电阻的产生主要是因为浓度极化现象和扩散边界层效应(diffusion boundary layer, DBL)。

计算欧姆电阻时, 可认为电极腔室电阻为恒定值, 且当膜对数足够多时可以忽略电极腔室电阻^[4]。欧姆电阻计算式如下:

$$R_{\text{ohmic}} = N_{\text{IEM}} \left(R_{\text{AEM}} + R_{\text{CEM}} + \frac{\delta_c}{\kappa_c} + \frac{\delta_d}{\kappa_d} \right) + R_{\text{el}}, \quad (6)$$

式中, R 为面电阻, δ 为溶液腔厚度, κ 为溶液电导率, R_{el} 为电极室电阻。

2 工质选取

对于卡诺循环, 工质的选取并不对系统的效率产

生影响,系统效率仅由高低温热源的温度决定.但对于实际循环,由于循环的非理想性,工质的选取极大地影响系统的效率以及系统内各部件的性能.为提升REDHE性能,需对工质类型进行筛选.同时,虽然本文仅对发生单元研究进展进行综述,但REDHE作为一个系统,电池单元的性能也会对整机性能产生影响.因此,工质选取亦需考虑工质对RED单元性能的影响.

RED单元的核心部件为离子交换膜.对于离子交换膜,一方面,目前商用离子交换膜对溶质通用性较高,可广泛适用于各类阴阳离子^[15];另一方面,离子交换膜对溶剂挑选较为苛刻,通常只适用于水,对有机溶剂的耐受性较差.当采用有机溶剂时,离子交换膜会出现溶胀甚至完全溶解的现象,但这并不意味着有机溶剂不可作为REDHE工质,亦有少量定制的离子交换膜适用于有机溶剂^[16].鉴于此,本节不仅论析各种电解质水溶液,亦论析电解质有机溶液对发生单元效率和系统性能的影响.

为提升发生单元耗能与低品位热能利用能力,通常选用低汽化潜热和沸点温度的工质.由式(3)可知,随着工质汽化潜热的升高,发生过程耗能增加,系统效率下降.当采用高沸点工质水为溶剂、浓溶液为饱和溶液时,系统的理论效率仅为2%^[17].与此同时,为了提高REDHE整机性能,工质的选取还需兼顾RED电池单元性能.如式(5)与(6)所示,工质活度系数与电导率影响电池单元开路电压和内阻.相同浓度下,工质活度系数越高,则电导率越高,系统开路电压越高,内阻损耗越小.由图4可知,不同盐溶液的最大功率密度差异巨大,两种溶液最大功率密度可相差近8倍^[4],选取合适的

盐溶液可显著提升电池单元功率.因此,工质的选取应综合考虑发生单元性能和RED电池单元性能.举例来说,乙醇的汽化潜热约为水的一半,以乙醇为工质时,可大大降低发生单元耗能.但乙醇会抑制电解质电离,降低溶液电导率和活度系数,进而影响发电单元效率.综合考虑发生单元和RED电池单元的需求,REDHE系统工质应具备如下特点:(1)发生单元适用低汽化潜热与低沸点工质;(2)电池单元适用高活度系数和高电导率工质;(3)工质的筛选需综合考虑发生单元能耗与电池单元内阻损失.

2.1 溶剂选取

溶剂的选取主要取决于发生单元.由于REDHE技术主要利用低品位余热,且发生单元需通过分离溶剂来使溶液再生,故应选取低沸点和低汽化潜热的溶剂.沸点低则发生温度低,进而提高系统利用低品位余热的能力.汽化潜热低,则发生单元耗能小.目前绝大多数研究以水为溶剂(表1),少量研究采用水、乙醇和甲醇等混合溶剂.Carati等人^[18]发现,系统效率随溶剂沸点的升高而升高,这是由于随着溶剂沸点的升高,热机需由更高温度的热源驱动.随着驱动热源温度的升高,系统性能得到提升.徐士鸣等人^[19]以水和乙醇为溶剂研究了电解质电导率,结果表明,电解质溶液的电导率随浓度、温度的升高而增加,而且溶液浓度越高,温度对其电导率的影响越大.吴曦等人^[20]研究了锂盐在甲醇、乙醇和三氟乙醇中的电导率,结果表明,当溶质相同时,乙醇体系电导率最大,异丙醇体系最小.

水的汽化潜热大,致使系统耗能较高.采用有机溶剂可显著提高系统效率,但现阶段多数离子交换膜并不适用于有机溶液.

2.2 溶质选取

早期RED电池单元主要利用河流入海口处海水和淡水的浓度差发电,故关于溶质的研究主要集中在氯化钠(NaCl),如表1所示.Zhu等人^[25]研究了溶液浓度和种类对RED电池单元性能的影响.结果表明,当NaCl溶液浓度从0.6 mol/L增大至3.6 mol/L时,功率随之增大;当浓度继续增大时,由于膜的选择透过能力有限,能量输出不再随浓度显著变化.虽然提升盐浓度可以增大电池功率,但过高的盐浓度会降低离子交换膜的选择透过性.Daniilidis等人^[23]的研究也得到了相同结论,即当溶液浓度过高时,离子交换膜选择透过性减弱,RED

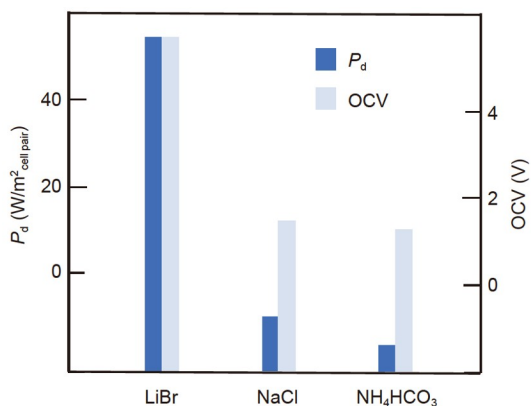


图4 不同盐溶液最大功率密度(P_d)和开路电压(OCV)
Figure 4 Maximum power density (P_d) and open circle voltage (OCV) of different salt solutions

表1 REDHE工质特性研究

Table 1 Study on the REDHE working fluid properties

文献	溶剂	盐
[18]	水	NaCl、NaOH、ZnCl ₂
[19]	水、乙醇	KI、LiCl、LiBr
[20]	乙醇、异丙醇、 三氟乙醇	LiCl、LiI、LiBr
[21]	水	NH ₄ HCO ₃
[22]	水	NH ₄ HCO ₃
[23]	水	NaCl
[24]	水	NH ₄ HCO ₃
[25]	水	NaCl
[26]	水	NaCl、Mg ²⁺
[27]	水	NH ₄ HCO ₃
[28]	水	NaCl、Ca ²⁺ 、Mg ²⁺ 、SO ₄ ²⁻
[4]	水	LiBr、NH ₄ HCO ₃ 、NaCl等
[29]	水	LiCl
[30]	水	NaCl
[31]	水	NaCl、K ⁺ 、Mg ²⁺ 、Ca ²⁺ 、SO ₄ ²⁻
[32]	水	NaCl、NH ₄ Cl、CsCl等
[33]	水	NaHCO ₃ 、Na ₂ CO ₃ 、NH ₄ Cl、NaCl
[34]	水	KAc、CsAc、LiCl
[35]	水	NaCl、Ca ²⁺ 、Mg ²⁺ 、SO ₄ ²⁻
[36]	水	NaCl、LiCl、NaAc、KAc、NH ₄ Br
[37]	甲醇、乙二醇、 三氟乙醇	NaAc

电池性能下降。

开式RED电池单元多以海水为工质,溶液中含有Mg²⁺、Ca²⁺和SO₄²⁻等杂质离子,影响电池性能;闭式系统也会由于溶质或溶剂纯度不够而受杂质离子的影响。杂质离子的出现会增加离子交换膜的电阻,降低离子交换膜的选择透过性。Avci等人^[26]研究了Mg²⁺对电池堆性能的影响。引入Mg²⁺后,NaCl电池堆开路电压从1.70 V下降至0.72 V。对电池进出口离子的色谱分析表明,MgCl₂溶液在0~30%范围内存在上坡输运迹象。电化学阻抗谱分析表明,Mg²⁺浓度强烈影响阳离子交换膜电阻,纯MgCl₂溶液膜阻高于纯NaCl溶液膜阻的10倍。Fontananova等人^[28]研究发现,Mg²⁺会增加阴离子交换膜的电阻。Guo等人^[31]研究了Ca²⁺、Mg²⁺、SO₄²⁻和K⁺对电池性能的影响,当注入上述杂质离子后,NaCl电池堆开路电压下降、内阻增加、最大功率密度下降。

随着REDHE研究的深入,近年来越来越多的研究聚焦于其他高性能盐上,包括低发生温度的盐溶液和高发电功率的盐溶液。碳酸氢铵(NH₄HCO₃)在37°C开始分解,在60°C完全分解,可利用超低品位余热(<80°C)。Huang等人^[24]研究了0.5~2 mol/L浓度范围内NH₄HCO₃的节点位,为NH₄HCO₃的应用提供了数据支撑。Cusick等人^[21]以NH₄HCO₃为工质,进行了发电能力测试,在微生物RED电池堆中得到了5.6 W/m²的发电功率。Hatzell和Logan^[22]分析了NH₄HCO₃热分解产生的CO₂和NH₃气体对系统的影响。研究发现,较短的溶液通道可以降低浓度极化,增加输出功率密度。虽然碳酸氢铵盐热分解温度低,发生温度低,但其发电功率较低。

研究者还对其他无机盐性能进行了测量和评价。Micari等人^[32]通过实验研究了纯盐和等摩尔二元混合盐的性能,以开路电压、电池电阻和矫正电流密度为参数,评价盐溶液性能。结果表明,NH₄Cl在实验浓度范围内综合性能最高,而LiCl功率密度最高。在某些情况下,二元混合物电池电阻低于各纯盐电池电阻,最大功率密度高于纯盐最大功率密度。Giacalone等人^[34]分析了若干新型溶液(NaCl溶液除外)的热力学性质及电池堆性能。他们通过Pitzer模型,计算了醋酸钾和醋酸铯在20~90°C范围的热力学参数,并通过理论模型计算了不同闭式单级和闭式多级RED发生单元的性能。结果表明,醋酸钾、醋酸铯和氯化锂溶液最有应用前景。Tamburini等人^[4]模拟分析了不同盐溶液最大功率密度和3种原型机性能。结果表明,单价锂离子盐溶液(LiBr、LiCl)功率密度最高(图4)。Luo等人^[33]研究发现,NaCl和NaHCO₃混合工质性能优于NaCl溶液性能。吴德兵等人^[36]研究了单价电解质水溶液对电池性能的影响。结果表明,KAc开路电压大于LiBr,但由于其溶液电阻值高,故最大输出功率低。

REDHE主要采用闭式循环,相比于开式循环,工质成分相对可控,目前溶质的选取仍处于探索阶段,需要考虑其对功率密度、电导率和活度的综合影响。

3 发生单元

由于工质的特性存在差异,发生单元需采用不同的发生方法,发生方法主要包括热分离法和热分解法。热分离法又可进一步分为蒸馏发生法和膜蒸馏发生法。在3种发生方法中,发生单元均由热能驱动,将热能转换为盐溶液间的化学势能。现阶段关于REDHE系统发生单元的研究较少,研究主要集中在探究不同进液速

率、进液浓度和操作温度对RED电池性能的影响,仅有少量研究集中在发生单元性能上(表2)。

不同的发生方法与不同的工艺循环均可归纳为图5所示的黑盒模型,可将发生过程分为能量传递与转化过程和质量传递过程。能量传递与转化过程可等效为电化学热机做功过程,即热机从高温热源吸热,并向低温热源放热,同时将部分热量转化为发生溶液间的化学势能。传质过程可分为溶剂发生过程(热分离法)和溶质发生过程(热分解法):对于溶剂发生过程,浓溶液中溶剂受热蒸发,并进入稀溶液中,使浓溶液浓度升高而稀溶液浓度降低;对于溶质发生过程,溶质受热分解,并从稀溶液中迁移至浓溶液中,使浓溶液浓度升高而稀溶液浓度降低。

3.1 蒸馏发生法

蒸馏法是目前最成熟的分离技术,并发展出多级蒸馏、多效蒸馏和连续变温蒸馏等分离方法。蒸馏法利用不同组分间沸点差异分离溶质和溶剂。蒸馏法及基于蒸馏原理的其他方法虽然技术成熟,但耗能较高且分离效果较差。多效蒸馏技术虽然可以在一定程度上提高分离效率,但设备尺寸大,维护成本高^[56]。Papa-

表2 REDHE发生单元研究^{a)}

Table 2 Study on REDHE regeneration units

文献	研究内容	发生温度(°C)	工质
[38]	不同发生方法理论效率	<100	—
[39]	热分解	60	NH ₄ HCO ₃ -H ₂ O
[40,41]	热分解	<90	NH ₄ HCO ₃ -H ₂ O
[42]	热分解	—	NH ₄ HCO ₃ -H ₂ O
[43]	热分解	—	NH ₄ HCO ₃ -H ₂ O
[44]	热分解	—	NH ₄ HCO ₃ -H ₂ O
[45,46]	膜蒸馏	—	NaCl-H ₂ O
[47]	膜蒸馏	40~80	NaCl-H ₂ O
[48]	膜蒸馏	40	NaCl-H ₂ O
[49]	膜蒸馏	80	NaCl-H ₂ O
[10,50,51]	多效蒸馏	65	NaCl-H ₂ O
[52]	多效蒸馏	100	NaCl-H ₂ O
[53]	多效蒸馏	—	NaCl-H ₂ O
[9]	多效蒸馏	100	NaCl-H ₂ O
[54]	多效蒸馏	100	NaCl/KAc-H ₂ O
[55]	多效蒸馏	100	NaCl/KAc-H ₂ O

a) “—”表示原文中未出现发生温度数据

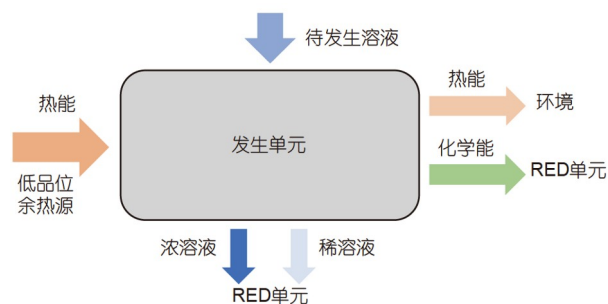


图5 发生单元原理图

Figure 5 Schematic diagram of regeneration units

petrou等人^[55]对REDHE进行了经济学分析和环境影响评估,评价参数包括MED(multi-effect distillation)效数、系统尺寸及盐溶液特性等。结果表明,采用多效蒸馏的REDHE只有在大功率机组时才具有经济性。

Bevacqua等人^[39]以热分解盐NH₄HCO₃为工质,研究了REDHD能量转换潜力。系统只考虑RED电池堆和溶液发生器,发生器采用汽提塔建模。在最优条件下,系统最大功率密度可达9 W/m²,最大焓效率可达22%。Giacalone等人^[40]第一次在实验层面上提出了热分解盐REDHE性能提升策略,即采用热集成和多柱布置的发生单元更加高效。Hu等人^[51]研究了系统结构参数和运行工况对系统性能的影响,发现当采用六效闪蒸分离器,热源温度为80°C,冷却水温度为20°C时,系统最大能量转换效率可达0.76%。结果还表明,提高热源温度和盐浓度增加分离塔效数可以提高系统性能。他们还对REDHE系统进行了焓分析^[10],研究发现,预热器、冷凝器和RED电池是主要焓损失来源,三者贡献总焓损失的59.8%。此外,提高热源温度不利于系统性能提升,但增加溶液浓度和闪蒸塔级数可提高系统效率。值得注意的是,提高驱动热源温度所造成的热机效率的下降并不违背卡诺定理:由于发生过程的温度保持不变,热源温度升高时,高温热源向热机传热过程的焓损失增加,进而造成系统性能下降。Ortega-Delgado等人^[9]对REDHE中各个部件进行焓分析,结果表明,分离塔是焓损失的主要来源,占总焓损失的70%。Ortega-Delgado等人^[54]以氯化钠和醋酸钾(NaCl和KAc)为工质,使用数值分析方法预测了闭式热机热效率,研究提升系统性能的方法。结果显示,在相同工况下KAc性能优于NaCl;当采用12级闪蒸、高性能膜和KAc工质时,系统最大焓效率可达43%。Palenzuela等人^[52]研究了多效REDHE性能,结果表明,随着RED电池稀溶液浓度的降低和浓

溶液浓度的升高, 相同发电功率下系统所需驱动热能减小. Brogioli等人^[57]探究了采用蒸馏法重建浓度梯度时的最高效率问题, 发现系统效率随溶液沸点的升高而提升.

3.2 膜蒸馏发生法

膜蒸馏发生法主要利用膜两侧气体分压不同来分离溶液. 由于利用膜的亲水性和疏水性来分离溶液, 其操作温度低, 特别适用于利用工业余热等低品位热能. 如图6所示, 高温待分离溶液(以NaCl溶液为例)和分离后的低温溶液分别从膜左右两侧流过. 由于膜的疏水性, 溶液并不能直接通过膜. 膜左侧溶液温度高于右侧溶液温度, 故膜左侧表面水蒸气分压 P_H 大于膜右侧表面水蒸气分压 P_L . 水蒸气从膜左侧迁移至右侧. 由于水蒸气的迁移, 膜左侧界面压力持续下降, 低于膜左侧溶液饱和蒸汽压. 左侧溶液持续蒸发, 蒸发出的水蒸气持续迁移至右侧, 完成水分离^[58]. 虽然膜蒸馏发生技术的分离温度低, 符合REDHE利用低品位热能的要求, 但是膜制备成本较高, 技术尚待完善. Micari等人^[49]对膜分离REDHE进行了可行性分析, 研究考虑溶液浓度、流速和设备尺寸等因素. 结果表明, 此循环最高效率为2.8%, 远小于相同温度下17%的卡诺热机效率. Mercer等人^[48]采用膜分离REDHE技术从人体尿液中回收电能, 结果表明, 当反应进程到一半时, 约有80%的能量被回收利用. La Cerva等人^[45]采用计算流体动力学(computational fluid dynamics, CFD)模拟研究了间隔器对膜分离单元的影响. 结果表明, 间隔器会降低最高传热系数. Long等人^[47]对膜分离REDHD性能进行了研究, 该热机最低可以40℃热源为驱动热源. 结果表明, 增加系统初始充注浓度可以提升系统效率; 当热机在20~60℃之间运行时, 最大效率可达1.15%.

3.3 热分解法

热分解法又称为溶质提取法, 与热分离法不同的是, 热分解法通过分离溶质来重构浓度梯度, 实现热能至化学势能的转化. 热分解法多以 NH_4HCO_3 为溶质, 运行原理如图7所示. 待发生稀溶液由RED电池单元进入发生器, 其中溶质 NH_4HCO_3 受热分解产生气体 NH_3 与 CO_2 , 完成稀溶液再生过程. 待发生浓溶液由RED电池单元进入吸收器吸收 NH_3 与 CO_2 , 浓度升高, 完成浓溶液再生过程.

为探究采用 NH_4HCO_3 为工质的RED电池的可行

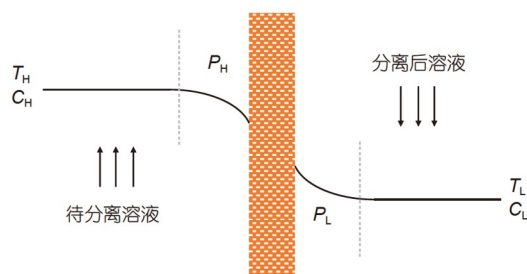


图6 膜蒸馏分离法原理图

Figure 6 Schematic diagram of the membrane distillation separation

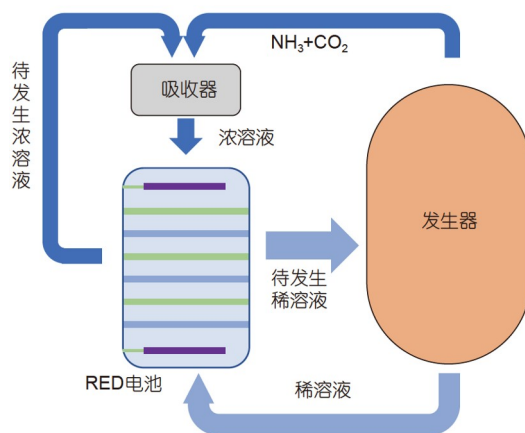


图7 热分解法原理图

Figure 7 Schematic diagram of the thermolytic method

性, 罗希等人^[59]研究了以 NH_4HCO_3 为工质的RED电池工作特性, 证明了 NH_4HCO_3 可作为REDHE的工质. 他们还研究了电池堆的最大能量转换效率^[42], 在最优工况下, RED电池最大离子利用率和效率分别为88%和31%. Bevacqua等人^[39]采用气体塔分解 NH_4HCO_3 , 实现浓差重构过程, 在最优工况下系统发电量可达9 W/m². Giacalone等人^[41]模拟了RED单元进液速度、进液浓度以及发生单元汽提塔级数对系统性能的影响, 在最优工况下, 系统焓效率可达8.5%. 上述研究均采用分体法研究整机性能, 即分别研究发生单元与RED单元性能. Giacalone等人^[40]第一次在实验层面上研究了热分解热机整体性能, 该系统可利用90℃热源进行电力生产, 能够稳定运行55 h.

当REDHE采用 NH_4HCO_3 为工质时, 系统发生温度低, 可有效利用低品位余热. 但 NH_3 与 CO_2 的吸收过程为放热过程, 需额外增加冷却系统促进吸收^[39], 这在一定程度上增加了系统的复杂性. 其次, 当吸收不充分时, 气体随浓溶液进入RED单元^[22], 影响电池性能.

4 结论与展望

反向电渗析热机技术最大的特点是利用低品位余热(温度低于150°C)进行发电,以实现能量的高效利用.伴随着工业生产,全世界每年约向环境中排放9400 TW h的余热,其中约有63%的余热为低品位余热.如果采用REDHE回收这部分热量,取热机效率为2%,每年可以从低品位的余热中回收118.4 TW h的电能.

目前针对该技术的研究主要集中在电池单元上,特别是研发高效、低成本的商业离子交换膜.但当采用REDHE技术回收低品位余热时,发生单元熵损失约占系统熵损失的60%~70%,极大地影响着系统的性能,而工质的性能和发生方法的选择极大地影响着发生单元的效率.

由于商用离子交换膜性能的限制,热机主要采用水作为溶剂.水的沸点和汽化潜热高,导致发生单元耗能高,低品位热能利用能力低. RED技术最早用于回收海洋中的蓝色能源,故溶质多为NaCl,但NaCl溶液发电性能较差,最大发电功率密度仅为LiBr的1/8.筛选工质时,需兼顾溶液热力学特性(沸点与汽化潜热)、电化学特性(电导率)和对系统元件的匹配性.

REDHE技术主要用于回收低品位热能,理论上所

有低温分离技术均适用于发生单元.主流发生方法为热分离法(蒸馏分离和膜蒸馏分离)和热分解法,但目前对发生单元热力学优化较少,发生单元不可逆损失大.同时,关于发生技术和发电技术耦合的研究较少.更值得注意的是,REDHE所需分离技术与传统分离技术有显著区别,前者的目标在于构建电池单元所需最优浓度,而非追求理想情况下组分完全分离.

鉴于此,未来研究应关注4点.(1)高性能盐的应用:REDHE采用闭式循环,为工质的选择提供更多可能性,可采用如LiBr在内的高性能盐.(2)有机溶剂的应用和配套离子交换膜研制:相较于水,有机溶剂通常具有低汽化潜热和低沸点温度的特性,可降低发生单元耗能,提升低品位热量利用能力.但有机溶剂的使用需要配套适用于有机溶剂的离子交换膜.(3)发生单元优化,提高发生单元热力学完善度.(4)最优浓度梯度构建:探究发生单元与电池单元匹配特性.

反向电渗析热机技术的驱动热源温度可低至40°C,表明该项技术可用于地热能和太阳能等低品位热能的回收,然而目前未有研究关注该领域.另外,REDHE技术的发电过程伴随着电极反应,表明采用REDHE进行发电的同时,亦可进行污水处理、有机物降解、制氢及废酸、废碱中和处理.

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Summary for “反向电渗析热机发生单元研究进展”

Progress on the regeneration unit of a reverse electrodialysis heat engine

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The reverse electrodialysis heat engine (REDHE) has emerged as a promising technique in the waste heat harvest field due to its ability to convert very low-grade waste heat (below 100°C) into power. A REDHE consists of a regeneration unit and a reverse electrodialysis (RED) cell unit, which are in charge of heat to the salinity gradient energy-conversion process and salinity gradient to the power conversion process, respectively. Despite the fact that a regeneration unit accounts for 60% to 70% of the energy destruction of the overall system, most of the research conducted on RED units has barely reviewed the regeneration units. Therefore, the evaluation of regeneration units is necessary. This work provides a review of the research progress made on regeneration units.

In this paper, a systematic review of the operating fluids and regeneration methods employed in a regeneration unit is provided. Also, the effects of solvent and solute characteristics on the performance of a regeneration unit and the overall system and the working fluid selection principle are investigated. Additionally, the disadvantages of the methods employed in existing and future development directions are analyzed. Finally, other applications of the heat engine (apart from power production) are presented.

Since the RED technology has been primarily used to recover blue energy, its operating fluid is the NaCl aqueous solution. However, the NaCl solution is not suitable for the REDHE technology. Specifically, it is not suitable for the regeneration process of a regeneration unit because the latent heat of water vaporization is huge, which leads to huge energy consumption in the regeneration module. Also, the power generation performance of the NaCl solution is poor, and the maximum power density is only 1/8 of that of the LiBr solution, resulting in the low efficiency of the overall system.

Since the REDHE technology is used to recover low-grade heat energy, its regeneration unit adopts a low-temperature separation technology. The main regeneration methods used are distillation separation and membrane distillation separation. The distillation separation technology is the most mature, but it consumes more energy and has a high maintenance cost. On the other hand, the regeneration temperature of the membrane distillation technology is low, but the required technology is difficult to apply, and the cost of the membrane is high. It should be noted that the biggest difference between the REDHE and traditional separation technologies is that the former aims to build an optimal concentration gradient for the battery cells, rather than to perform the complete separation of components. For example, the seawater desalination process assumes that the separated water is pure water. For an RED cell, if the diluted solution is pure water, the battery performance will decline rapidly due to the decrease in the solution conductivity. Currently, more research work has been conducted on various separation technologies and less on the coupling of regeneration technology with power generation technology. Future research should focus on the coupling of the thermal separation module with the power generation module.

Although the objective of the REDHE technology is to utilize the industrial waste heat, the heat-source temperature can be very low (down to 40°C), which means that the technology can also be used for low-grade heat recovery such as geothermal and solar energy. At the same time, although the technical efficiency of the REDHE is low, its power generation process is accompanied by electrode reaction and temperature change. This means that during power generation, the REDHE can also be used for sewage treatment, organic matter degradation as well as waste acid and alkali recovery.

reverse electrodialysis, heat engine, waste heat recovery, working fluids selection, regeneration methods

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