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Current Opinion in Electrochemistry

Review Article

Electromembrane processes for waste valorization: Energy recovery and storage

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Abstract

This article reviews the most recent advances on the contribution of electromembrane-based technologies to waste valorisation through their implementation in the sustainable recovery and storage of energy from waste streams. Two driving forces are considered, salinity and pH gradients. Recent advances and challenges in ion exchange membranes (IEMs) and bipolar membranes (BPMs) are presented. Reverse electrodialysis (RED) and reverse bipolar membrane electrodialysis (RBMED) are evaluated as primary batteries to harvest energy from salty streams. The potential of combining RED/ED and RBMED/BMED as sustainable secondary batteries is also presented. Overall, it is concluded that increasing the membrane performance is a key aspect to rise the maturity of the proposed technologies along with their adaptation to the different characteristics of current and future waste streams potentially available for energy recovery and storage.

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Current Opinion in Electrochemistry 2024, **45**:101477

This review comes from a themed issue on **Environmental Electrochemistry (2024)**

Edited by **Javier Llanos López** and **Ignasi Sirés**

For a complete overview see the Issue and the Editorial

Available online 7 March 2024

https://doi.org/10.1016/j.coelec.2024.101477

Keywords

Energy storage, Flow battery, Bipolar membranes, Valorization, Sustainability, Electrodialysis.

Introduction to electrodialysis processes for energy recovery and storage

In meeting the growing global energy demand while keeping emissions at bay, electromembrane technologies are recently regarded as key suppliers of continuous renewable electricity from unconventional energy sources. Reverse electrodialysis (RED) and reverse bipolar membrane electrodialysis (RBMED) are the leading technologies for converting the energy from salinity (SGE) and pH (pHGE) gradients into useful electricity. The use of low-cost electrolytes like alkali and acid solutions has made closed-loop electrodialysis (RED-ED) and closed-loop bipolar membrane electrodialysis (RBMED-BMED) rechargeable batteries a more preferred choice over conventional redox flow batteries (RFBs) for energy storage.

This scenario has also opened new possibilities for saline waste streams in energy production. The focus of this review is on the recent progress made in electromembrane-based technologies and their implementation in novel applications for energy recovery and storage, with a special emphasis on significant findings and challenges on the use of waste streams.

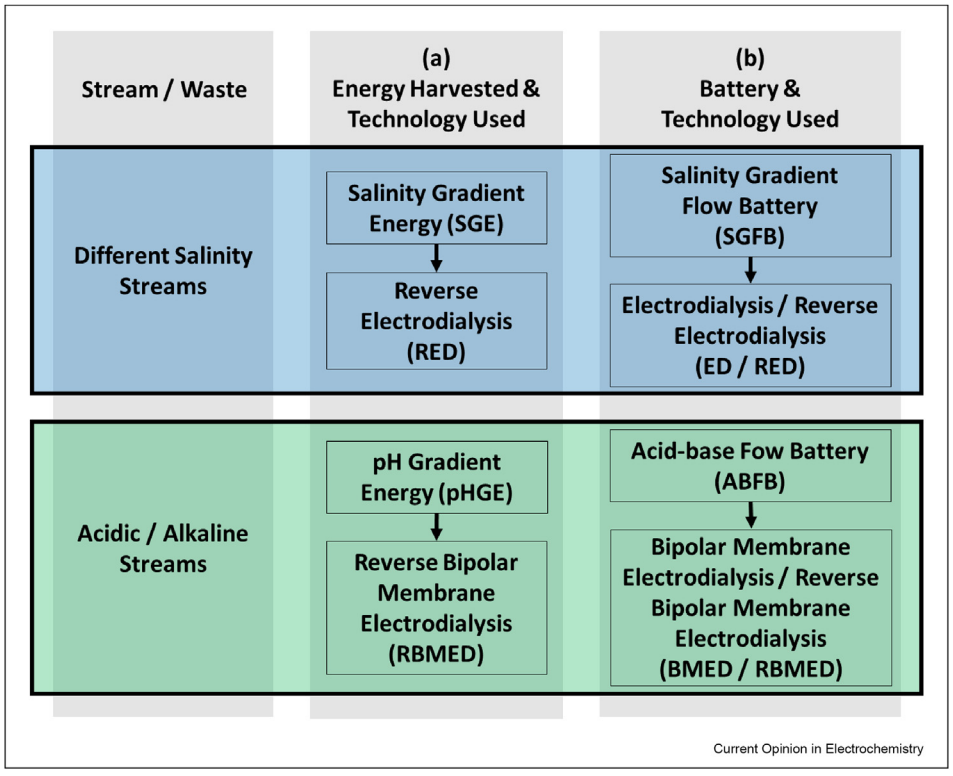
RED and RBMED work the opposite to ED and BMED, respectively. In RED, two streams with different salinity are mixed in a controlled way to recover SGE and produce an electrical current. Whereas in RBMED, two streams with different pH, typically an acidic and an alkaline solution, are controlled neutralized allowing the harvesting of pHGE.

Additionally, ED processes can be combined to achieve sustainable energy storage (secondary batteries). The combination of ED and RED stages using different salinity streams provides the so call salinity gradient flow battery (SGFB), while the combination of BMED and RBMED applied to different pH solutions is the key of the acid-base flow battery (ABFB) concept.

Therefore, as seen in Figure 1, electromembrane based technologies could act as: a) energy recovery devices (primary batteries), and b) flow batteries (FBs) to store and recover energy from solutions (secondary batteries).

SGE-RED harvesting from wastewaters has gained attention in the last decade increasing the maturity of the technology [1,2]. However, pHGE recovery is still at

Figure 1



Electromembrane based technologies: **a)** primary batteries by harvesting energy from waste streams, **b)** secondary (flow) batteries that store and recover energy from solutions.

a lower technological readiness level (TRL) although attracting attention in recent years [3].

Both the SGFB and the ABFB have been presented as safe and sustainable energy storage devices that could overcome the limitations of other batteries such as the toxicity of the chemical materials, intensive use of critical raw materials, pollution or high costs. Unlike other alternatives, the rated power and the total energy capacity are decoupled, in both systems [4]. The rated power is related to the stack size, number and size of the membranes implemented, while the total energy capacity depends on the volumes of the solutions, providing enormous flexibility and versatility to be integrated in multiple applications and scales.

Electromembranes for energy recovery and storage

Ion-exchange membranes (IEMs) and bipolar membranes (BPMs) are key components of the primary and secondary batteries based on salinity or pH gradients.

Ion-exchange Membranes (IEMs) determine the overall output energy produced in RED processes for energy harvesting. Important modifications over conventional ED membranes have been tackled to assure the needs of SGE-RED processes. On the one hand, RED processes operate at ambient temperature and atmospheric pressure, conditions at which the thermal stability and the mechanical strength of IEMs are not crucial. Besides, water dissociation in the RED cell is negligible, thereby solutions pH is expected to be stable and close to neutrality. On the other hand, it is crucial to decrease the RED cell electrical resistance and increase the membrane permselectivity over the conventional ED IEM to attain the goals of high energy efficiency and power density (PD) in RED. Conventional ED IEMs developed by companies such as Asahi Glass, Fujifilm, Fumatech, Tokuyama, RALEX or Dupont cannot meet the RED threshold level for the gross PD generated [5]. The use of perfluorinated or partially fluorinated materials such as Nafion in cation exchange membranes (CEMs) benchmark membranes impairs the ion conductivity and their life cycle environmental sustainability [6]. As a result, non-perfluorinated materials have attracted attention for IEMs fabrication. Two strategies stand out in recent years:

- *Developing new bare and blended polymeric IEMs.* Poly(vinyl alcohol) (PVA) based IEMs have been tested in several studies reaching PD in the range of 0.4 W m^{-2} to 1.82 W m^{-2}. The use of sulfonated polyetheretherketone (SPEEK) and

poly(epichlorohydrin) (PECH) as CEM and anion exchange membranes (AEM) has been reported to achieve a gross PD of 1.3 W m^{-2} [7,8].

- *Modification of conventional IEMs.* Polypyrrole (PPy)/chitosan composites have been used to modify commercial CEM membranes (Fujifilm) achieving a 40% increase of the PD compared to commercial CEM [9]. Cationic functional groups, e.g. 1-methyl-imidazolium (IMD) or tetramethylammonium (TMA), have been added to conventional poly(arylene ether sulfone) (PAES) achieving 1.2 W m^{-2}. Inorganic nanomaterials have been also used to modify CEMs through physical blending, sol–gel, or infiltration methods. Novel nanocomposite CEMs synthesized through oxidized multiwalled carbon nanotubes blended with poly (2,6-dimethyl-1,4-phenylene oxide) (SPPO) improved the highest gross PD by 0.48 W m^{-2}. In another work the maximum PD of 1.3 W m^{-2} was obtained using functionalized iron (III) oxide (F_2O_3–SO_4^{2-}) and SPPO composites as CEM. No nanocomposite AEMs have been reported so far [10].

Bipolar membranes (BPMs) are composed of anion and cation exchange layers (AEL and CEL), with an interfacial layer in between. Such membranes can operate in forward bias (water formation) and reverse bias (water dissociation). Thanks to the generated pH gradient across the BPM, the ABFB has the potential to obtain an energy density more than 3 times higher compared to the SGFB [11]. Nevertheless, BPMs have historically been designed for acid/base production and therefore, current commercial BPMs are not optimized for energy harvesting or ABFB applications. To be feasible on a larger scale, BPMs should assure stable performance in both reverse and forward bias, especially with low water dissociation potential in reverse bias and low voltage drop during forward bias. Al-Dhubhani et al. [12] compared the performance of five commercial BPMs under both biases and observed different behaviours that were explained by the different selectivities of the AEL and the CEL towards H^+ and OH^- among the commercial BPMs evaluated. An increase of the BPMs asymmetry, that is, the thickness ratio between the AEL and CEL, decreases the overall membrane resistance and it can also be beneficial to balance the asymmetrical co-ion fluxes through layers. Currently the main bottlenecks of the BPMs are related to: i) the AEL chemical stability, which can suffer in highly alkaline conditions (pH > 11); ii) the stability at high current density, as BPMs need to withstand high currents also under forward bias; and iii) the imperfect permselectivity [12].

Currently, bipolar membranes are limited to 500–1000 A m^{-2} in the charging phase. Typically, current densities in the range of 100–300 A m^{-2} are selected for BMED in battery applications. Although higher current densities could be employed, using lower current densities improves the electrical performance in terms of reducing the specific energy consumption (SEC, kWh kg^{-1} of product) of the charge, and increasing the round-trip efficiency (RTE) of the battery (charge and discharge).

The performance of BPMs under forward bias is still almost unexplored in the literature [12]. At present, the current density employed in the discharge phase is limited to 30 A m^{-2} [13,14] to avoid delamination of the BPM, occurring when water accumulates in the interlayer. These limitations make that, although BPMs have been used for decades in acid/based production, their application in energy conversion technologies is still far from the industrial scale [15]. Table 1 summarizes the state of the art and target values of the more relevant properties of BPM in energy recovery and storage applications.

Valorization of waste streams through salinity gradient energy recovery and storage

SGE, which can potentially be harnessed from the combination of two solutions with different salinity, is

Table 1

State of the art and target values of the more relevant properties of BPM in energy recovery and storage applications (adapted from Ref. [11]).

Property	State of the art	Desired
Mechanical stability at high current density – Reverse bias (BMED)	500–1000 A m^{-2}	>1000 A m^{-2}
Mechanical stability at high current density – Forward bias (RBMED)	<30 A m^{-2} (could be increased for short operating times)	>100 A m^{-2}
Thermal stability	Stable in 20–40 °C	>60 °C
Chemical stability	AEL suffers from highly alkaline conditions (pH > 11)	Long-term stability at high pH
Ion selectivity	High selectivity up to 1.0 M product concentration	>1.0 M product concentration
Price [16]	273 € m^{-2}	109 € m^{-2}, as for IEMs

estimated by the calculation of the Gibbs free energy of mixing (ΔG_{mix}). Increasing the salinity differences generate greater theoretical ΔG_{mix} [17], e.g. seawater—river water (0.6 mol L^{-1} and 0.0015 mol L^{-1} respectively), seawater desalination brine—wastewater (1.2 mol L^{-1} — 0.01 mol L^{-1}), engineered solutions (4.0 mol L^{-1} — 0.02 mol L^{-1}), and hypersaline brines—river water (5.3 mol L^{-1} — 0.0015 mol L^{-1}) reach ΔG_{mix} of 0.76, 1.53, 6.71 and 10.5 kWh m^{-3} of low concentrated solution (LCS). The output is the energy recovered, thus, the main results reported are power densities and specific energy. These results are not only dependent on solutions, but also on the module size. End concentrations are not typically reported, but as in other open loop systems, the final concentration would be determined by the residence time of the solutions in the stack.

Besides the relevance of IEMs, other components play an important role in RED efficiency. Efforts are oriented towards finer spacers than those in ED, contributing to decrease the ionic resistance of water streams, although at the expense of suffering enhanced fouling and pressure drop. The use of non-electroconductive spacers generates a shadow effect, which lowers the active membrane area and increases the ohmic resistance. Studies showed that the shadow effect could be responsible of reductions over 40% of the RED process efficiency [10]. Ruthenium, iridium coated in titanium and graphite are common electrodes used with a recyclable electrolyte solution, the iron based redox couple (Fe^{2+}/Fe^{3+}) or $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ being the most reported in the literature [18]. RED works seek the maximization of both PD and specific energy recovery; therefore, research has been carried out to evaluate different couples of waste streams, module sizes and operating conditions.

The first pilot-scale RED plant was built and operated in Italy under the REAPower project www.reapower.eu, with 125 cell pairs and 50 m^2 of total membrane area, registering 65 W (PD of 1.3 W m^{-2}) [19]. Since then, several attempts to upscale RED technology have been reported; however, the PD of large-scale RED systems is still constrained within 0.38—2.7 W m^{-2} of cell pair [20].

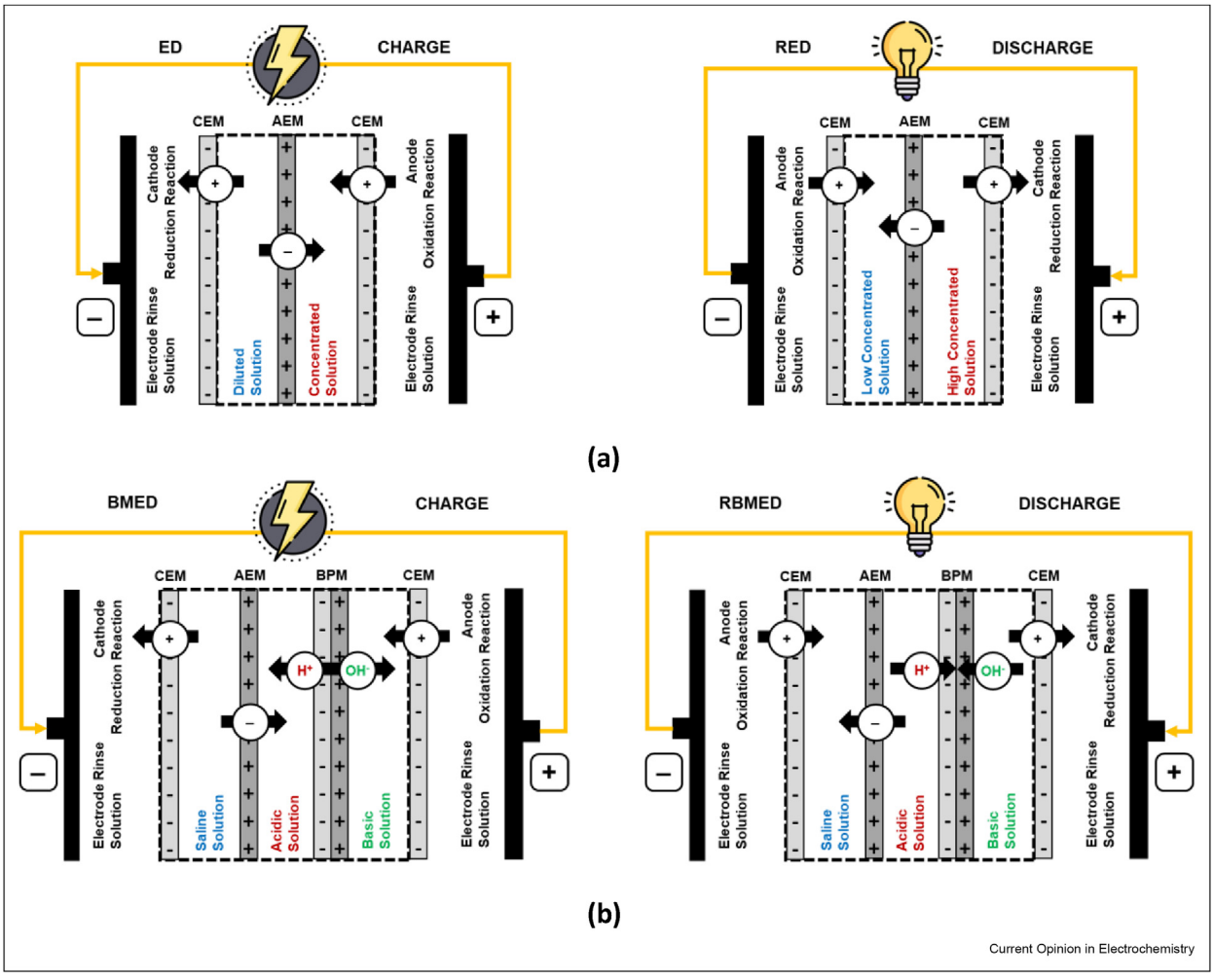
The advances in SGE-RED provide a new tool for the valorization of saline waste streams. The evaluation of the technology using seawaters with different salinity and the effluent of a wastewater treatment plant predicted values for SGE harvesting between 7 and 60 Wh m^{-3} of reclaimed water, the upper value being for the Mediterranean Sea water [21]. Tristan et al. evaluated the recovery of SGE by means of RED in seawater reverse osmosis (SWRO) desalination plants worldwide using the waste brine as high concentrated solution (HCS) [22] concluding that net specific energy values in the range of 0.08—0.15 kWh per m^{-3} of RO brines and net PD of 2.0—3.7 W m^{-2} could be obtained. Cipollina and coworkers [23], operating with 5 mol L^{-1} NaCl concentrated solutions as those found in bitterns from saltworks, reported PD of 5.0, 2.2 and 3.4 W m^{-2} in experiments performed using commercial membrane stacks provided by Fujifilm, Fumatech and Suez, respectively. Recently, produced waters (PW), generated in oil and gas production, have been identified as suitable HCS solutions for SGE recovery due to their high salinity (up to 270 g L^{-1}) and huge global production (41 million m^3 day^{-1}) [24—26]. A maximum PD of 2.5 W m^{-2} was observed during 25 days of long-run continuous operation using real PW as HCS (equivalent NaCl concentration of 50.3 g L^{-1}) and an artificial solution of 0.7 g L^{-1} NaCl as LCS [25]. Gaber et al. reported the generation of 0.94 W m^{-2} when operating with 150 and 3 g L^{-1} NaCl solutions as HCS and LCS, respectively, pointing out that the SGE generated could potentially satisfy the energy requirements for treating oilfield PW [24].

Working with real water and wastewaters, which contain natural organic matter and divalent ions, may induce fouling phenomena and reduce electromembranes performance. Membrane fouling mitigation strategies include periodic feedwater switching, chemical cleaning, UV lamps or even membrane modification with good results reported in literature [20,25,27] that support the viability of the technology in real scenarios.

Few studies have evaluated the economic feasibility of SGE-RED. At present, the levelized cost of energy (LCoE) falls in the range 0.2—0.5 USD kWh^{-1}, which is not yet competitive with other well stablished renewable energy sources such as wind or solar photovoltaic (0.1—0.15 USD kWh^{-1}) [20]. However, one of the latest contributions indicates that the LCoE of SGE-RED could be reduced to 0.1 USD kWh^{-1} achieving an energy efficiency of 40% [28].

Additionally, the combination of ED and RED has been proposed as an alternative for energy storage, especially if surplus power from intermittent renewable energies is available [17,29—32]. An ED/RED energy storage system (Figure 2a), also named SGFB or concentration battery, relies on the energy transformation into chemical potential by ED during the charging period and then, the conversion of the chemical potential energy stored in the form of a concentration difference, in electricity through RED during the discharge use. Both phases can be carried out in the same device in a closed-loop system where the main target is the maximization of the RTE, i.e., the maximization of the ratio between the energy recovered in the discharge phase and the applied energy in the charging phase. Kingsbury et al. [30] made the first attempt to demonstrate the SGFB

Figure 2



Working principles of: **a)** SGFB, ED as charging phase and RED as discharging phase; and **b)** ABFB, BMED as charging phase and RBMED as discharging phase.

device operation on a commercially available RED stack. However, RTE not higher than 21−34% were obtained due to water osmosis. Later, van Egmond et al. [31], identified four processes that dissipated the available free energy while cycling the SGFB: a) the resistance of the IEM and water to transport ions, with an ohmic component and the presence of boundary layers that limit mass transport; b) non-perfect selectivity of IEMs, which lowers the Nernst potential; c) water transportation, and d) co-ion transportation, that both change the salt concentration. Recently, an "ion-plus SGFB" has been proposed where the addition of supporting ions in low concentrations (0.1 M) to both the HC and LC solutions would significantly decrease the internal electric resistance withing the SGFB cell and facilitate the transformation of Gibbs free energy in the discharging cycles while decreasing the current consumption in the charging cycles, as well as accelerate the ion transfer without sacrificing the SG. This strategy reduced the electrical resistance between 62.4 and 90.7% and doubled the PD [32].

Valorization of waste streams through pH gradient energy recovery and storage

It is calculated that the global annual waste acids generation is equivalent to 100 million tons of concentrated H_2SO_4. The neutralization energy of a strong acid and a strong base is around −79.9 kJ mol^{-1}. If such global quantities of waste acid and base are utilized as acidic and alkaline electrolytes in an electroneutralization energy (ENE) cell, an estimate of the energy that could be harvested is around 44 TWh [33]. Despite the availability of large volumes of acidic and alkaline wastewaters generated in various industrial processes such as chemical production, electroplating, dyeing, and papermaking, pHGE recovery is so far a little-known

research topic [14,33]. Because both RBMED and ABFB are in an early stage of development, research on both technologies has been restricted to using synthetic solutions based on NaCl, HCl and NaOH.

To date, studies have aimed applications in ABFB, rather than simply harvesting the pHGE contained in wastewaters [34]. ABFB have been proposed as an improvement of SGFB due to their potential to achieve higher energy and power densities [35]. In ABFB charging and discharging cycles are performed in the same device, working in a closed-loop (Figure 2b). Several strategies are being proposed to pursue the objective of increasing the RTE, such as applying low current densities (100−300 A m^{-2}) to reduce the energy consumption of the charge phase, and increasing the current density in the discharge phase up to the maximum admissible to avoid BPM delamination (<30 A m^{-2}).

The stability of an ABFB working in BMED/RBMED cycles using NaOH and HCl model solutions at laboratory scale was demonstrated, reaching a high energy density of 2.9 Wh L^{-1} and a PD up to 3.7 W m^{-2}. However, unwanted transport of protons and hydroxyl ions caused energy dissipation, leading to low coulombic efficiencies between 13 and 27% [35]. Xia et al. [36] used a 20-triplet stack and 1 mol L^{-1} NaOH and HCl solutions, reporting a PD of ≈15 W m^{-2} excluding electrode losses.

Zaffora et al. [13] reported results of PD of ≈17 W m^{-2} for the discharge phase working in single pass mode with 1 mol L^{-1} NaOH and HCl solutions, estimating an energy density of 10.3 Wh L^{-1} of acid for the complete discharge. After testing the performance of five different commercial membranes, Al-Dhubhani et al. [12] reached a RTE of 65% using current densities of 60 A m^{-2} during discharge and 240 A m^{-2} during charge. As previously stated, understanding the behavior of BPMs under forward and reverse bias in multi-ion solutions results essential [37] for ABFB to be competitive with other commercial flow batteries, such as vanadium redox flow batteries (VRFB) [13,15].

Currently, a successful example of ABFB demonstration has been reported in Pantelleria (Italy). A pilot plant of 1.0 kW rated power was designed, installed, and operated, to provide the local power plant with additional energy storage, useful to meet the high energy demand in summer months [4,37,38]. Environmental and economic assessments revealed the outstanding potential of ABFB systems when compared to VRFB [38]. The net levelized cost of storage (LCoS) was 3.07 € kWh^{-1} for ABFB in contrast to 6.05 € kWh^{-1} for VRFB.

It may be envisioned that the pHGE will have broad applications in various fields, including the development of energy-efficient energy devices, industrial acid and alkali wastewater treatment, or electrochemical synthesis, but at the current stage, pHGE-assisted devices suffer from several bottlenecks including complicated assembly processes due to the employment of acid−base asymmetric electrolytes; relatively poor stability and durability due to the inevitable ion leakage/crossover and continuous consumption of acid and base; high internal electrical resistance of the device due to the use of a BPM or multiple ion-exchange membranes/compartments; the relatively high cost of using a BPM; and limited options of electrode reactions to pair a device due to the scarcity of pH-sensitive reactions [33].

Conclusions

This work reports the most recent advances on the state of the art of SGE and pHGE recovery as well as their respective application to energy storage using salinity or pH gradient flow batteries.

The strength of SGE-RED for energy recovery relies on the maturity of the technology and the advanced development of tailored RED membranes, while improvements are still required in other elements of the stack such as spacers. Nevertheless, the increasing generation of waste streams in the water industry together with the need for a continuous supply of renewable energy are a real challenge for the growth of SGE-RED. Despite its greater thermodynamic potential, the RBMED shows at the current state a weaker position as competitor for energy recovery, harmed by the more complex BPM requirements for energy recovery applications.

ABFBs present several strengths for energy storage over SGFBs, showing potential to achieve higher energy capacities. Both are safer and more sustainable than other batteries and have great flexibility and versatility due to the decoupling of rated power (stack) and total energy capacity (solution volumes).

Overall, the main weakness of electromembrane processes for energy recovery and storage lies in the need to advance in the development of electromembranes designed for energy applications, particularly in BPM intended for ABFB systems.

CRediT authorship contribution statement

Marta Herrero-Gonzalez: Conceptualization, Methodology, Investigation, Writing - Original Draft Preparation, Visualization. **Inmaculada Ortiz:** Supervision, Funding acquisition. **Raquel Ibañez:** Conceptualization, Resources, Writing - Review & Editing, Supervision, Funding acquisition. **Ane Urtiaga:** Supervision, Funding acquisition, Writing - Review & Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

Grant TED2021-129874B-I00 funded by MCIN/AEI/ 10.13039/501100011033 and by the European Union NextGenerationEU/PRTR.
Grant PID2020-115409RB-I00 funded by MCIN/AEI/ 10.13039/501100011033 and by ERDF A way of making Europe.
Grant PDC2021-120786-I00 funded by MCIN/AEI/ 10.13039/501100011033 and by the European Union NextGenerationEU/PRTR.
M. Herrero-Gonzalez research was developed under the Margaritas Salas postdoctoral grant funded by the Ministry of Universities (Spanish Government) and the European Union—Next Generation EU.

Abbreviations

ABFB	acid-base flow battery
AEL	anion exchange layer
AEM	anion exchange membrane
BMED	bipolar membrane electrodialysis
BPM	bipolar membrane
CEL	cation exchange layer
CEM	cation exchange membrane
ED	electrodialysis
HCS	high concentrated solution
IEM	ion-exchange membrane
LCoE	levelized cost of energy
LCS	low concentrated solution
PD	Power density
pHGE	pH gradient energy
PW	produced waters
RBMED	reverse bipolar membrane electrodialysis
RED	reverse electrodialysis
RTE	round-trip efficiency
SGE	salinity gradient energy
SGFB	salinity gradient flow battery
SWRO	seawater reverse osmosis
VRFB	vanadium redox flow batteries
ΔG_{mix}	Gibbs free energy of mixing

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