REVIEW

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Membrane-based processes for sustainable power generation using water

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Water has always been crucial to combustion and hydroelectric processes, but it could become the source of power in membrane-based systems that capture energy from natural and waste waters. Two processes are emerging as sustainable methods for capturing energy from sea water: pressure-retarded osmosis and reverse electrodialysis. These processes can also capture energy from waste heat by generating artificial salinity gradients using synthetic solutions, such as thermolytic salts. A further source of energy comes from organic matter in waste waters, which can be harnessed using microbial fuel-cell technology, allowing both wastewater treatment and power production.

A remarkable amount of energy is available from the salinity difference between sea water and fresh water. In theory, up to 0.8 kilowatts per cubic metre could be extracted — equivalent to the energy generated from water falling over a dam more than 280 metres high[1,2]. The limiting factor in obtaining this energy is the supply of fresh water: about 2 terawatts (1 TW is equal to 1,000 gigawatts) is available globally from rivers flowing into the sea, of which perhaps 980 GW could be harnessed[3]. In addition, wastewater release into the ocean could provide another 18 GW of salinity-gradient power. Although 800 GW of power is currently obtained from hydroelectric processes globally, salinity-gradient energy remains a large and untapped resource. Capturing this energy will require the engineering and development of efficient energy-conversion technologies.

Several approaches to capture salinity-gradient energy are being developed, but the most promising are pressure-retarded osmosis (PRO)[4,5] and reverse electrodialysis (RED)[6,7]. Both are relatively close to commercialization, but their application is limited by cost and fouling of membranes, reducing the useful lifetimes of the membrane-packed modules that both systems use. PRO uses the flow of water — but not ions — through the membranes to produce pressurized water that generates electricity using mechanical turbines. RED uses membranes for ion — but not water — transport, and the electrical current generated is captured directly from the flow of ions. Capacitive systems, which are based on alternate charging (using salt water) and discharging (using fresh water) of materials, may also contain membranes[8–10], but are less advanced than either RED or PRO and are not covered in this Review. PRO and RED have been used mainly to capture natural salinity-gradient energy using sea water and river water[3], but the use of thermolytic solutions offers opportunities to capture the energy from waste heat using these systems[11–13].

Microbial fuel-cell (MFC) technologies can generate energy from organic matter in waste waters and biomass[14]. Microorganisms oxidize the organic matter and release electrons outside the cell, allowing the generation of an electrical current that can be used for producing electrical power, biofuels and valuable chemical products[15]. In the United States, as much as 3% of the electricity generated (15 GW) is used for wastewater treatment[16]. If that energy was no longer needed for treatment, three times that amount could be saved in primary energy (assuming a 33% efficient power plant), with further energy produced from the organic matter in the waste water. The same MFC technologies can also be applied to capture energy from biomass, a resource that could contribute more than 600 GW of renewable power[17]. MFCs can be combined with other processes, such as fermentation of complex organic matter into soluble organics[18,19], and a 'stack' of RED membranes to increase efficiency and to recover additional energy[20,21].

PRO, RED and MFCs are distinct from the more common methods of electricity generation, which are based on harvesting non-renewable materials from nature. These newer processes offer the opportunity to generate energy from abundant but largely unused resources; however, they are at various stages of transfer from the laboratory bench to practical application. We review these three water-based processes and the challenges for their widespread application.

Power production using PRO

PRO extracts salinity-gradient energy by using semipermeable membranes to allow the transport of water from a low-concentration solution (such as river, brackish or waste water) into a high-concentration draw solution (sea water)[3,22–25] (Fig. 1). Sea water can also be used as the low-concentration solution with brines produced from seawater desalination as the draw solution. In theory, the maximum extractable energy during the reversible mixing of a dilute stream with saline draw solutions is substantial, ranging from 0.75 kW-hours per cubic metre to 14.1 kWh per cubic metre of the low-concentration stream (Fig. 1). The actual energy extracted will always be lower because of inherent, irreversible energy losses.

The development of PRO has been hindered for many years by the lack of a membrane capable of allowing an adequate flow[22,23,26,27]. The bulky support layers of the reverse-osmosis membranes cause severe internal concentration polarization (ICP), which markedly reduces permeate-water flux and therefore power density[22,26,28–30]. Cellulose-acetate membranes specifically designed for forward osmosis have substantially reduced ICP effects, stimulating a resurgence in PRO research and development[22,23,31]. The power density has increased from less than 1 W m^{-2} to 2.7 W m^{-2} for river water and sea water, and, using a sea water reverse-osmosis brine[22,31,32], the power density reached 4–5.1 W m^{-2}. Thin-film composite polyamide membranes may allow 5.7–10 W m^{-2} to be achieved because of their higher intrinsic water permeabilities and lower ICP than cellulose-acetate membranes[5,30,33].

The main challenges for implementing PRO for the economical production of energy using natural waters are the development of

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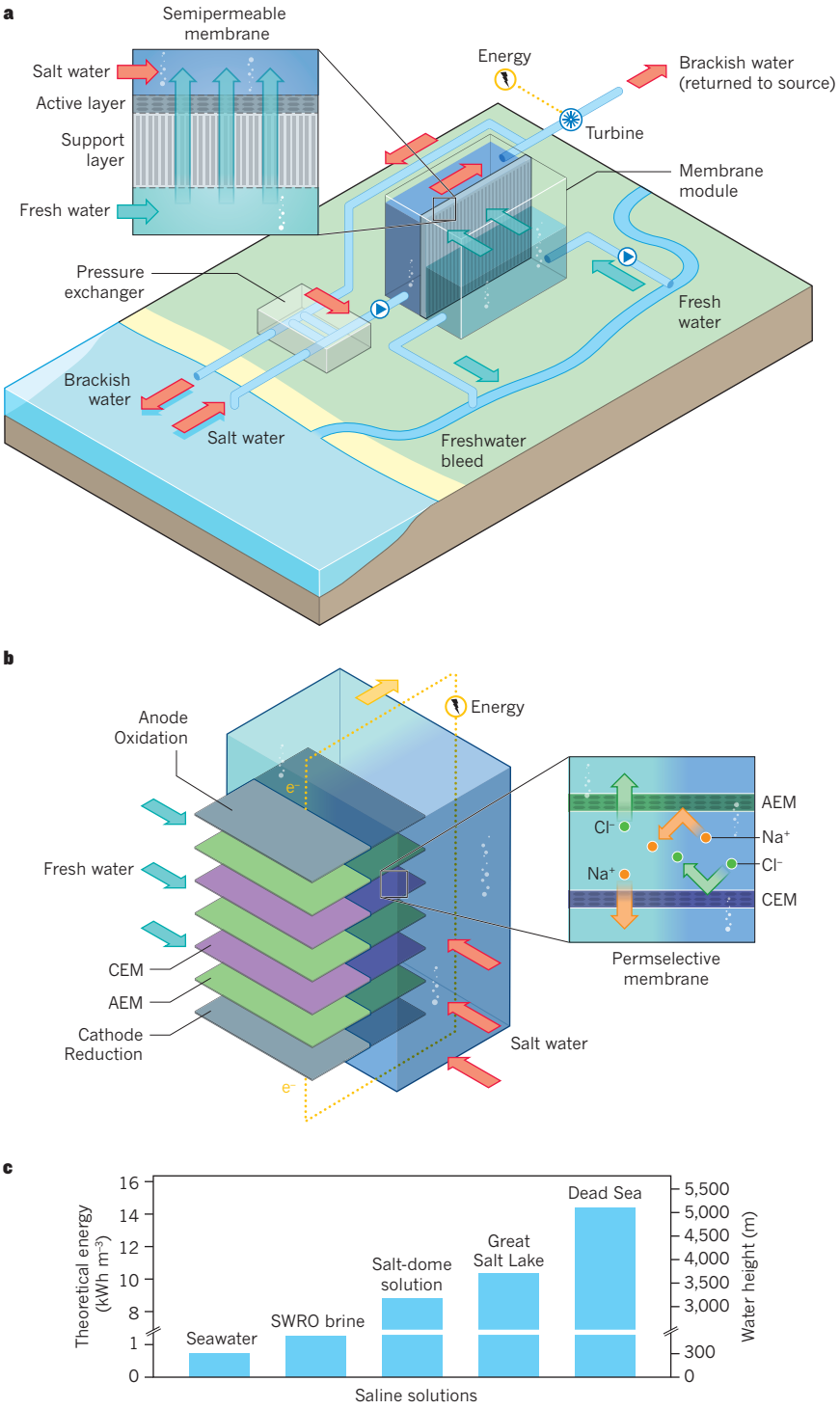

Figure 1 | Comparison of PRO and RED systems. **a**, In PRO, the low-concentration feed solution and high-concentration draw solution are separated by a semipermeable membrane through which, ideally, only water moves from low to high concentration, with ions selectively retained at the membrane active layer. As the two solutions flow in adjacent chambers, water is drawn into the saltwater side across the membrane, diluting the solution and increasing the volume flow rate of water. The resultant high-pressure solution is split into a flow that drives a turbine and a flow that returns to the pressure exchanger. The exchanger transfers pressure energy from a high-pressure fluid stream to a low-pressure fluid stream, thereby pressuring the saltwater feed. The diluted water returns to the source, and the turbine generates energy. **b**, In RED, the energy generated by the mixing of fresh (blue arrows) and salt water (red arrows) is captured using alternating cation-exchange membranes (CEMs) and anion-exchange membranes (AEMs), with low- and high-concentration solution flowing through each alternate channel. These permselective membranes transfer cations through the CEM and anions through the AEM from high- to low-concentration solutions. The difference in electrochemical potential as a result of the positive ions moving one way and the negative ions moving the other is turned into an electrical current at the electrodes, which can be used to generate energy. **c**, The maximum energy that is theoretically extractable from the reversible mixing of a dilute stream with saline solutions from five sources. The height needed to produce the same energy from falling water is also shown. The maximum theoretical energy per cubic metre of the dilute solution is about equal to the osmotic pressure of the respective saline solutions: 27 bar for typical sea water[81], 375 bar for the Great Salt Lake in Utah[82], 507 bar for the Dead Sea on the border of Israel and Jordan[82,83], seawater reverse-osmosis plant (SWRO) brine was assumed to be 54 bar (for 50% recovery) and 316 bar for salt-dome (subsurface geological structures) solution assumed to be 5 M sodium chloride[82] (calculated using OLI Stream Analyzer software).

low-cost and robust membranes that have minimal ICP and fouling and the potential environmental impacts caused by the disruption of the natural flow of water. In addition, feed and draw streams need to be extensively pretreated to prevent membrane fouling and deterioration in performance potential. A plant in Norway, used to pilot PRO as a method of generating power from natural salinity gradients, generated less than 1 W m^{-2} using commercial, asymmetrical cellulose-acetate membranes[23]. This is much lower than the target power density of 5 W m^{-2} needed to make PRO economically viable[23,27,34]. Pretreatment of river water and sea water can consume a considerable amount of energy (0.2–0.3 kWh m^{-3}) (ref. 35). In a PRO plant with a 50% overall efficiency, the actual extractable energy from the mixing of river water and sea water is 0.3–0.4 kWh m^{-3}, leaving about 0.1 kWh of useful energy that can be derived per cubic metre of river-water feed solution. This energy consumption indicates the need to develop fouling-resistant membranes with tailored surface properties and membrane modules with improved hydrodynamic mixing to mitigate fouling.

Electricity production using RED

The advantage of using a RED system for capturing energy is that electricity is generated directly from salinity gradients. Sea water and fresh water are introduced into arrays or stacks of membranes with alternating anion-exchange membranes and cation-exchange membranes, directly generating an electrochemical potential (Fig. 1). In theory, water can be split using about 10 membrane pairs because each pair generates around 0.1–0.2 V from typical river and sea water. But in

reality, the energy needed to overcome energy losses at the electrodes, or overpotential, means that at least 20 pairs are needed.

Alternatives to water splitting have been investigated to increase energy capture and improve safety. Water splitting releases oxygen and, from seawater, toxic chlorine gas from the anode, and potentially explosive hydrogen gas at the cathode that needs to be either used properly or vented. Iron-based oxidation–reduction (redox) couples could allow recycling of electrolyte solutions, avoiding the need to split water[36]. Ferrocyanide–ferricyanide has been used as a reversible redox couple, but it could potentially produce toxic hydrogen-cyanide gas at the electrodes. In addition, some leakage of these compounds into natural waters is inevitable because of the non-ideal permselectivity of ion-exchange membranes. The ferrous–ferric iron redox couple is also promising, but iron can precipitate on and within membranes and electrode surfaces, leading to fouling and a decrease in current. Although there are energy losses at the electrodes, when 50–100 membrane pairs are used to generate electrical power, these losses become an increasingly smaller percentage of the overall energy balance, and are therefore acceptable.

Substantial advances are being made to increase RED power densities and energy efficiencies through improvement of membrane materials, spacing and architecture. The highest power density for a RED stack with 50 cell pairs is 0.93 W m^{-2} total membrane area at about 3 V, neglecting electrode overpotentials and pumping losses (based on each type of ion-exchange membrane having a 0.5 m^2 total surface area, or 93 W m^{-2} based on the planar cross-sectional area between the electrodes)[37]. Pumping required roughly 25% of the total power produced[37]. A larger stack (with a total area of 19 m^2) generated a net power of 0.4 W m^{-2}, with an energy efficiency of 18%, although efficiency could have been increased to 30% with a lower net power density (0.35 W m^{-2}) (ref. 7). In 25-membrane-pair stacks, optimizing membrane materials and reducing the spacing between membranes increased power densities to 1.2–2.2 W m^{-2} (refs 38, 39). The use of ion-conductive spacers between the membranes[40] or introducing ridges and flow patterns into the membrane material to avoid using spacers[41] are promising methods for reducing the size of RED systems and increasing power generation. Power density is estimated to reach to 3.4–4 W m^{-2} for RED[3,39] and 7.7 W m^{-2} (4 kW m^{-3}) for PRO when river–seawater solutions are used[3]. For these estimated power densities, 9 W reactors with comparable power per area would produce 0.16 kW m^{-3} for RED, and 1.1 kW m^{-3} for PRO[3,38,42].

The main challenge for the commercialization of RED is the cost of ion-exchange membranes, but a global increase in demand could lower costs. Over the past decade, new materials, improved fabrication methods and increased production of reverse-osmosis membranes resulted in a decrease in the cost, which was a major factor in the increased use of reverse osmosis for water desalination[35].

Closed-loop PRO or RED using synthetic solutions

Open-loop PRO and RED use natural water or wastewater effluents that require extensive pretreatment and fouling-control measures, and they can have an environmental impact because of the withdrawal of natural water from ecosystems. Closed-loop systems use synthetic solutions, which avoid these problems and potentially produce much higher power densities. A closed-loop system that converts thermal energy to mechanical work or electricity — termed a heat engine[22,43] — is ideally suited to sustainable energy production (Fig. 2). In such a system, low- and high-concentration streams are used to generate energy by PRO or RED, and thermal energy is used to separate the resultant mixed stream into low- and high-concentration streams that are recycled back into the system. The heat engine can be economically viable if waste heat is used in the separation stage; this low-grade heat can come from industrial processes or power plants, or as geothermal energy from shallow wells[44].

Closed-loop systems use salt solutions that can be separated by low-grade heat. Of these thermolytic solutions, an ammonia–carbon-dioxide solution is particularly promising and is capable of generating high power densities of 250 W m^{-2} at 5 M concentrations (Fig. 2)[12,44]. Very soluble ammonium salts can create high osmotic pressures, are rejected

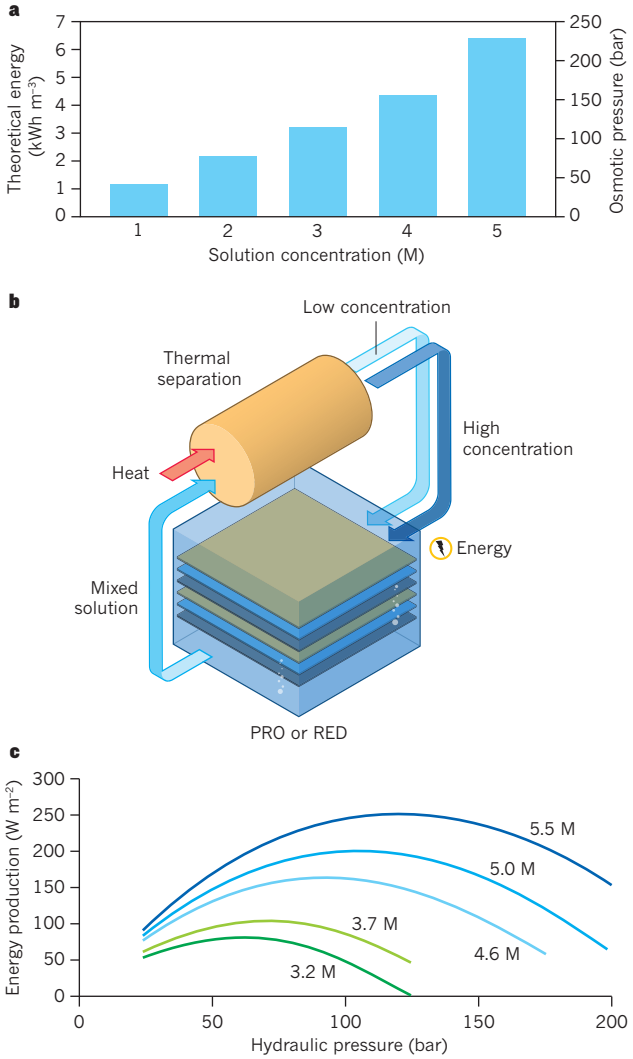

Figure 2 | A heat engine. **a**, The maximum energy theoretically extractable based on the reversible mixing of ammonia–carbon-dioxide solutions with water. The osmotic pressures of 1–5 M solutions show that there is high potential for energy generation compared with open-loop PRO systems that use sea water and river water. **b**, A closed-loop system in which synthetic low- and high-concentration solutions pass through a PRO or RED system to generate electrical power. Thermal energy is used to separate the mixed solution back into high- and low-concentration streams, which are then recycled back into the system. **c**, Theoretical membrane power densities achievable by the ammonia–carbon-dioxide osmotic heat engine for 3.2–5.5 M solutions at various applied hydraulic pressures. Maximum power density is achieved with a hydraulic pressure that is roughly 50% of the ammonia–carbon-dioxide solution osmotic pressure. Data used in parts **a** and **c** taken from McGinnis *et al.*[12].

well by semipermeable membranes and can be separated from water and recycled with low-grade heat by conventional distillation processes[12,45]. In theory, a large amount of energy can be extracted from the reversible mixing of a dilute stream with the ammonia–carbon-dioxide solution (Fig. 2). Using low-grade heat at 50 °C, the thermal energy needed to separate the diluted ammonia–carbon-dioxide solution into water (low-concentration stream), and ammonia and carbon dioxide (that reform the high-concentration stream) is 358 MJ m^{-3} (99 kWh m^{-3}) for a 1 M solution and 593 MJ m^{-3} (165 kWh m^{-3}) for a 2 M solution[12].

Highly soluble inorganic salts, such as sodium chloride, can also be used in closed-loop heat engines with separation processes that use low-grade heat. For example, membrane distillation uses a vapour pressure gradient created by the temperature difference across the membrane to transport water vapour through microporous hydrophobic membranes[46]. Thermal-energy requirements for membrane distillation

can range from 40 kWh m^{-3} to 650 kWh m^{-3}, depending on membrane properties, system design, heat source and operating temperature[47].

To successfully implement closed-loop systems that use synthetic solutions, several challenges need to be addressed. The main challenge for PRO is the development of membranes with sufficient mechanical strength to withstand the high hydraulic pressures that occur with very high salt concentrations (Fig. 2). For membrane distillation to be viable in these systems, efficient and low-cost membranes need to be developed.

Energy production from waste matter using MFCs

Waste water can be a substantial source of energy. In the United Kingdom, the energy content of waste waters ranges from 2.1 kWh m^{-3} for domestic to 4.7 kWh m^{-3} for mixed-use (commercial and domestic) water[48]. Typical wastewater treatment plants use high concentrations of bacteria supplied with oxygen, through aeration of the water, to remove the organic matter. The overall energy consumption in conventional plants with this treatment is roughly 0.6 kWh m^{-3} with about half of that used for aeration[16]. Some treatment plants have become energy neutral, mostly though the production of methane gas from solids captured or produced during treatment[16].

MFCs offer a unique approach to directly capture the energy in water, effectively turning a wastewater treatment plant into a power plant[49,50]. Exoelectrogenic bacteria release protons into the waste water and transfer electrons to electrically conductive, inert and high porosity anodes — such as carbon cloth, felt and graphite fibre brushes[50,51](Fig. 3). At the cathode, the electrons and protons combine with oxygen to form water, generating an overall maximum voltage of about 0.5 V, compared with a theoretical maximum of 1.1 V (ref. 52). In this process, oxygen is transferred passively from the air to the cathode, not through water aeration, providing substantial energy savings compared with conventional processes, even without including the energy that would have been needed for the production of power. For waste waters, power generation using MFCs is usually limited by low solution conductivity (1 mS cm^{-1}), organic-matter concentration, temperature, and microbial kinetics and rates of oxygen reduction under these conditions. Under optimal conditions with acetate as a fuel, and using very large cathodes relative to the projected area of the anode, power densities have reached 6.9 W m^{-2} (normalized to the cathode surface area)[53] and 1.55 kW per cubic metre of reactor volume (2.77 W m^{-2}) (ref. 54). That is considerably higher than that typically produced using actual waste waters (less than 0.3 W m^{-2}), although 1.24 W m^{-2} (0.41 W m^{-3} based on liquid volume) has been achieved using special carbon-nanotube-coated sponge anodes[55]. There have been few tests on reactors larger than tens of litres[56–58] and none of systems larger than one cubic metre. Power densities have remained relatively constant with increased reactor size when the area of the cathode per unit volume of the reactor is kept constant[57,59,60]. Low power densities and a lack of demonstrations of larger-scale systems have led to debate on whether MFC-based treatment plants can ever compete with more conventional wastewater treatment systems that are engineered to achieve a slight net power production[16].

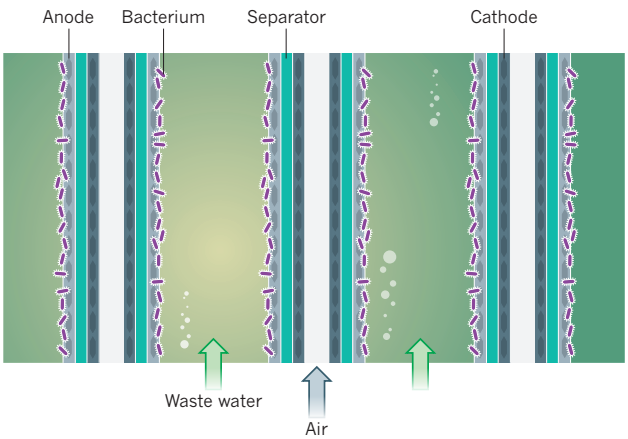

Figure 3 | An MFC stack. MFCs are arranged close together to reduce internal resistance and form compact reactors. Within the stack the electrodes consist of repeating units of an anode coated in a mat of bacteria, or biofilm, an insulating separator and a cathode. Waste water flows over the anodes and air over the cathodes. The individual anode and cathode are connected by a wire (not shown).

By modifying MFCs, they can also be used for chemical remediation and to produce hydrogen, methane and acetate. For example, thermodynamically favourable reactions can be generated at the cathode without oxygen by using electron acceptors such as ferrous iron[61]. Pollutants in waste waters, such as nitrates, copper, chromium and vanadium, can be precipitated or removed in MFC processes, saving energy that would otherwise be used in treatment[62–64]. Adding energy to the potential generated by the anode bacteria can increase the current densities, allowing otherwise non-spontaneous reactions. Adding voltage to that already produced by bacteria (typically –0.25 V or less) reduces that needed to produce hydrogen gas (–0.414 V), although more than this difference is added because of overpotentials[65,66]. Inorganic catalysts, enzymes or microorganisms can be used to reduce these overpotentials. Methane is produced by methanogenic microorganisms from acetate or hydrogen, and it can also be produced from electrical current using methanogens; however, this bioelectrochemical production requires additional voltage to be added to the cathode to overcome electrode overpotentials. Appreciable methane can be produced at cathode potentials more negative than –0.7 V using methanogens on a cathode[67], compared with the –0.24 V that is theoretically needed. Organic chemicals, such as acetate, can also be produced at the cathode directly from electrical currents, using microorganisms[67–69].

Cellulosic and algal biomass sources, among others, can be used in MFCs[18,70,71], but they must be made soluble first, and usually converted by fermentation into simple molecules that the exoelectrogenic bacteria can use — such as acetate, lactate, pyruvate, formate and ethanol. The generation of biofuels from cellulose through enzyme and fermentation processes is well under way, with ethanol and hydrogen as the main products. Bioelectrochemical systems can also be used to produce electricity and biofuels either from using these same sources of organic matter or using waste streams from biorefineries[72,73].

The main challenges for the implementation of MFCs for energy production are the cost and longevity of the electrodes, and achieving high current densities through the reduction of internal resistances by improved stack design. Anodes are relatively inexpensive and are stable over the long term, but the cathodes are not[59,60]. Although the use of precious metals in the cathode can be avoided by using activated carbon for oxygen reduction, the performance drops noticeably over time[74,75].

Hybrid technologies

Various combinations of technologies are being explored to create more synergistic approaches (Fig. 4). For example, a brine solution could be used as the high-concentration stream in RED or PRO, and sea water as the low-concentration stream[76] (Fig. 4a). Waste water can be used to dilute sea water, with a forward-osmosis membrane either placed inside a conventional bioreactor or used to extract water after wastewater treatment[77]. Because the energy demand of reverse-osmosis desalination decreases with decreasing feed-water salinity, using waste water to dilute seawater reduces the overall energy of sea water desalination.

Forward-osmosis membranes can also be used with various bioreactors, including MFCs. The salinity of waste water increases during treatment with a forward-osmosis membrane[78] as a result of the increased solution conductivity, reducing the internal resistance of the anode — and improving current densities. Placing the cathode in the draw solution eliminates solution resistance in the cathode chamber[79](Fig. 4b). The maximum power density from an MFC using a forward-osmosis membrane (called an osmotic MFC) was 15% higher with a 35 g l^{-1} sodium-chloride solution than from the MFC alone[79]. A substantial concentration

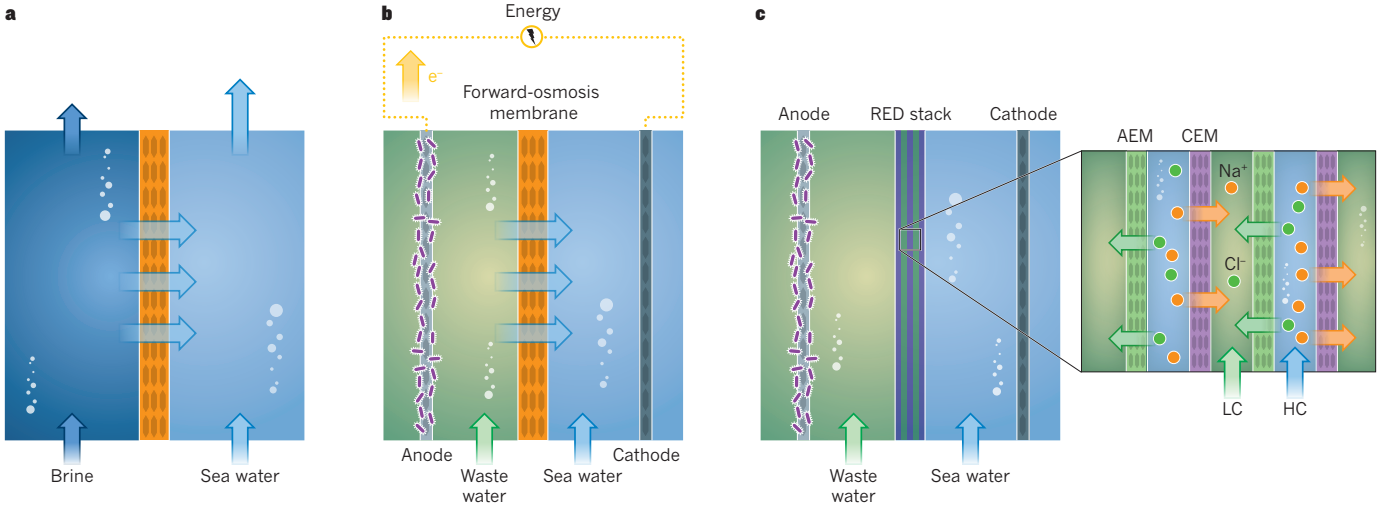

Figure 4 | Hybrid systems could allow further energy recovery. **a**, Power can be extracted from sea water in PRO or RED systems by using brine as the high-concentration (HC) stream. The two concentrations are separated by either a RED stack or a PRO membrane depending on the system. Either ions (in RED) or water (in PRO) moves from high to low concentration (LC) (see Fig. 1). In PRO, the volume leaving the system is lower for brine than it is for sea water as a result of water flow through the membrane. Once used, the water would be discharged into the sea. **b**, In a forward-osmosis MFC, waste water is used for desalination. Sea water acts as a draw solution, producing a less salty solution through a forward-osmosis membrane and generating a current. **c**, A RED stack built into an MFC increases the voltage and power production compared with an MFC alone. AEM, anion-exchange membrane; CEM, cation-exchange membrane.

of organics in the waste water because of water loss could allow the use of methane- and energy-producing anaerobic digestion, rather than energy-consuming aerobic systems, such as activated sludge. However, if the treated waste water has very high salinities, this could prohibit its discharge into certain environments or its further reuse.

Microbial RED cells are hybrid reactors that have a RED stack placed directly between the MFC electrodes[20,21] (Fig. 4c). When a five-membrane-pair RED stack was used in such a cell for electricity generation, the maximum voltage (1.3 V) and power density (4.3 W m^{-2}) were substantially increased compared with those obtained with the MFC alone (0.5 V, 0.7 W m^{-2}), with acetate as the fuel and sodium-chloride solutions pumped through the RED stack[21]. The use of ammonium bicarbonate in the RED stack further increased performance to 5.6 W m^{-2} with acetate fuel[13]. When domestic waste water was used with ammonium bicarbonate in the RED stack, the maximum power was about 2.8 W m^{-2}, which was nearly an order of magnitude higher than when waste water alone was used[13]. In addition, treatment of the soluble organics was completed within a few hours, which is much shorter than the time needed for domestic wastewater treatment using only the MFC.

Hydrogen gas can be produced in a modified MFC without any external power source by placing the RED stack between the electrodes[20,80]. The energy efficiency achieved from this, based on total energy in the acetate solution and ammonium-bicarbonate solutions entering and leaving the reactor, was 35% (ref. 80). This is lower than the 65% efficiency produced using sodium-chloride solutions with similar concentrations to sea water and river water[20], suggesting that the performance using thermolytic solutions such as ammonium bicarbonate could be increased through system optimization.

Hybrid systems are in an early stage of development, but so far combining technologies seems to be a promising way to overcome the limitations of individual systems. The main challenges, like those for individual systems, are the high cost of materials and achieving high power densities. Hybrid systems will also require co-localization of different energy sources, such as waste water and sea water, or waste water and heat.

Outlook and future directions

Although the advantages of capturing energy using PRO and RED from natural waters are known, relatively little attention has been given to waste heat, brines or waste waters. Conventional power plants provide abundant waste heat — a typical efficiency of 33% would generate 2 GW of waste heat for every 1 GW of electrical power. If we optimistically assume that PRO can recover 60% of the energy in a thermolytic solution such as ammonium bicarbonate, and that 25% of the waste heat from a power plant can be captured in this solution, then PRO could produce as much as 300 MW of additional power (to give an overall energy efficiency of 43%). RED processes may be able to capture only about half this energy, but they can be designed to make use of valuable products at the electrodes, such as using hydrogen as an energy carrier or oxygen for improving combustion efficiency. Energy recovery from brines could be used to improve energy efficiencies of desalination plants, especially in hot, arid environments, where additional low-grade heat could be captured and used in the systems. Although waste water and biomass offer opportunities to improve energy capture, for wastewater treatment, the main benefit may be the energy saved or even just an energy-neutral wastewater treatment process that could allow the adequate sanitation of water globally[16].

The energy-producing processes described in this Review depend on effective and inexpensive membranes that are uniquely tailored to specific solutions and their application. For example, PRO membranes must be optimized for water transport and ion selectivity, and either be resistant to fouling when using sea water and river water or able to remain stable and intact when using thermolytic solutions with high hydraulic pressures. In all applications, power densities need to be high and the cost of membranes very low for these processes to be competitive with other methods of energy production[3]. Tremendous improvements have been made to reverse-osmosis membranes during the past few decades, and membranes for processes driven by osmosis have begun to show substantial improvements, increasing the possible applications of PRO. The cost of ion-exchange membranes could be expected to fall with system advances, which would allow the application of RED[40,41]. For natural waters, a reduction in fouling and improvements to the fouling resistance of membranes are crucial to advancing applications. With these improvements, the energy available from salinity gradients, waste water and biomass could be effectively harnessed as renewable and environmentally sustainable sources of power. ■

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