



Review article

Strategic comparison of membrane-assisted and membrane-less water electrolyzers and their potential application in direct seawater splitting (DSS)

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Abstract

Electrocatalytic splitting of water by means of renewable energy as the electricity supply is one of the most promising methods for storing green renewable energy as hydrogen. Although two-thirds of the earth's surface is covered with water, there is inadequacy of freshwater in most parts of the world. Hence, splitting seawater instead of freshwater could be a truly sustainable alternative. However, direct seawater splitting faces challenges because of the complex composition of seawater. The composition, and hence, the local chemistry of seawater may vary depending on its origin, and in most cases, tracking of the side reactions and standardizing and customizing the catalytic process will be an extra challenge. The corrosion of catalysts and competitive side reactions due to the presence of various inorganic and organic pollutants create challenges for developing stable electro-catalysts. Hence, seawater splitting generally involves a two-step process, i.e., purification of seawater using reverse osmosis and then subsequent fresh water splitting. However, this demands two separate chambers and larger space, and increases complexity of the reactor design. Recently, there have been efforts to directly split seawater without the reverse osmosis step. Herein, we represent the most recent innovative approaches to avoid the two-step process, and compare the potential application of membrane-assisted and membrane-less electrolyzers in direct seawater splitting (DSS). We particularly discuss the device engineering, and propose a novel electrolyzer design strategies for concentration gradient based membrane-less microfluidic electrolyzer.

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1. Introduction

The increasing global population and urbanization have augmented the utilization of carbon-based fuels and worsened the air quality [1,2]. Carbon dioxide level has been linearly

increasing globally to reach 418 ppm in January 2022. On the other hand, fossil fuel sources are depleting due to extensive utilization [3]. This has motivated researchers across the world to work on alternate carbon-neutral energy sources [4–9]. In this context, the storage of renewable energy is necessary for using on demand. Calorific value of hydrogen is very high compared to conventional fossil fuels like petrol. The by-product upon hydrogen combustion is water vapor unlike any harmful by-products released from partial or complete

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oxidation of fossil fuels [10,11]. Hence, electrocatalytic splitting of water using renewable energy as the electricity source is a very promising method for surplus renewable energy storage in the form of green hydrogen. Thus, hydrogen and oxygen production using the water splitting process has become an attractive research field [12–20].

Nevertheless, oxygen evolution reaction (OER) step is a bottleneck in splitting of water because it comprises four-electron-transfer [21]. There have been multiple efforts for improving the OER activity via introducing precious metal or transition metal oxide to electrocatalytic water oxidation [22–25]. Although there are many reports on electrocatalysis for improving OER and HER activities, research on this topic primarily focuses on utilizing pure water with alkaline electrolytes [26–30]. High level of water security threat is faced by four-fifths of the world's population [31,32]. As scarcity of potable, fresh water is a serious problem in most parts of the world, it is worth shifting the electrocatalytic water splitting research using seawater directly.

There are following advantages of using seawater (i) Seawater contributes around 96.5% to the world's total water. Thus it can be considered as sustainable resource. (ii) There are available renewable power-generation technologies in the coastal areas (for example wind, photovoltaics, and wave energy). Thus it is convenient to couple electrochemical seawater splitting process with any of these sustainable clean energy technologies. Therefore, these renewable energy or surplus of these energy can potentially be put in storage as “green” hydrogen [33,34]. (iii) Additionally, hydrogen fuel cell or combustion technologies can be attached to these sites which will allow the generation of freshwater upon the consumption of hydrogen gas that is produced from the seawater splitting

process. This will serve as fresh drinking water with essential minerals addition [35,36]. (iv) Pure water has poor ionic conductivity. Mostly, KOH or H_2SO_4 is required to add into the pure water system to increase its ionic conductivity [37,38]. Most electrodes undergo corrosion in highly acidic or basic media [39–41]. This results in great challenges in developing corrosion-resistant electrodes. Seawater consists around 0.6 M NaCl and provides a relatively better electrical conductivity (at 25 °C around 33.9 mS cm^{-1}) [38,42]. Moreover, seawater is a near neutral condition (pH about 8) [42]. The neutral pH has a low corrosion impact on catalytic electrodes. (v) In addition, seawater-splitting is thus expected to avoid the addition of alkaline or acidic species, this not only eliminates extra work but also reduces the cost associated with the chemicals [38].

However, there are many challenges associated with the use of seawater. (i) Understanding the precise mechanism of the overall process becomes slightly difficult compared to pure water due to its complex composition [43]. (ii) Oil spills, the presence of various organic and inorganic pollutants also bypasses the HER and OER. These pollutants are degraded during the water splitting event to impose a competitive pathway. The primary contaminant is Chloride ions (Cl^-) which imposes competition to the OER pathway [44,45] and gets oxidised to chlorine gas. (iii) A well-defined catalyst system for a given seawater source may require further standardization for another seawater source. For example, an established seawater splitting method for the Red Sea may further need standardisation for Arabian Sea. (iv) In near-neutral pH like seawater (pH ~ 8), the electrocatalytic efficiency of OER is considerably lesser than conventional acidic or alkaline media [46,47]. (v) Furthermore, a buffered

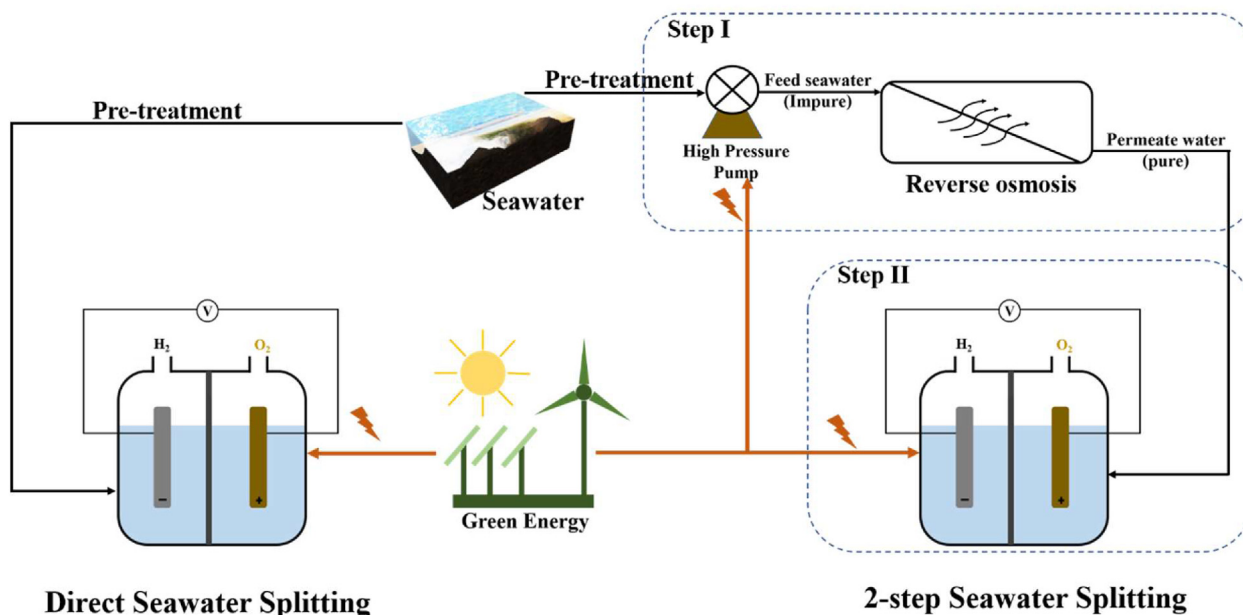


Fig. 1. Seawater can be split in two ways: (i) Direct Seawater splitting, where seawater is directly used as a feed into the electrolyzer without purification. (ii) Two-step seawater splitting, where reverse osmosis (RO) is used for the desalination of seawater in the first step; and then the electrolysis of water is executed subsequently with the obtained fresh water.

electrolytes are very often required for neutral media for a sustained electrocatalytic activity and catalyst robustness [48,49]. (vi) Though without any additives, in principle, seawater can be used in the electrolyzer, it cannot achieve desired efficiency. This is because ionic H^+ and OH^- are in miniscule concentration for effective ion transport. Buffer molecules also are not sufficiently capable of transporting the OH^- and H^+ formed at the cathode and anode, respectively [50]. This results in local pH differences which in turn changes the thermodynamics unfavourably of both HER and OER. This might also results in earth alkali metal hydroxide precipitation.

To avoid the challenges associated with seawater splitting, researchers have preferred to purify the seawater before using it in the electrolyzer (Fig. 1). The purification of seawater before splitting is mainly executed by reverse osmosis (RO) process at the high pressure. Thus, it involves a two-step process. In this case, seawater is first sent to a reverse osmosis chamber with applied high pressure to produce fresh water by separating the impurities, and in the subsequent step the resulted fresh water is used as the feed in the electrolyzer. However, this process requires two separate chambers and larger space compared to the direct seawater splitting.

In the case of direct seawater splitting, seawater is directly used as the feed into the electrolyzer without purifying the pollutants. This process is simple since only one reactor, i.e., electrolyzer is enough for carrying out the process. As this process does not require water purification unit, it results in a more compact design; thus system engineering challenges and space requirements are reduced.

Most recently, Hausmann et al. have concluded that direct seawater splitting does not have any considerable advantage compared to the two-step process of water-splitting where

water is purified in the first step [51]. They have suggested that two-step seawater splitting is more promising than the direct seawater splitting, because water purification cost of the first step is insignificant with respect to the cost associated with the second step, i.e., pure water electrolysis. However, larger space requirement, extra maintenance and engineering complexity remain as challenges. Thus, there is the need of technologies that will not only eliminate the extra step of pre-purification, but also avoid the drawbacks of direct seawater splitting due to pollutants.

There are a few review articles which discuss challenges and recent progress of electrocatalytic splitting of seawater. Liu et al. have discussed latest progresses in electrocatalysts research for splitting of seawater [52]. They have represented basic principles, issues and the recent development on HER and OER electrocatalysts for seawater electrolysis. In another report, Dresp et al. have described the opportunities and challenges of direct electrolytic seawater splitting [53]. They have concluded that chloride ion oxidation is the key challenges, hence, design of robust and selective electrodes are necessary for suppressing unwanted routes for contaminants interference; reverse osmosis prior to the seawater splitting would be useful considering less cost of RO process compared to water electrolysis. Tong et al. have discussed various important aspects in a recent review, for example, they stressed on the fact that suitable membrane is very crucial for fabricating an efficient electrolyzer for using seawater or impure water [54]. They have concluded that OER selectivity can be achieved if the system operates in strong alkaline conditions such as at high pH ~13. Of course, at this pH metal hydroxide precipitation formation will be another challenge. To address this issue, the strong buffer medium that can control the pH of 8–9 is necessary.

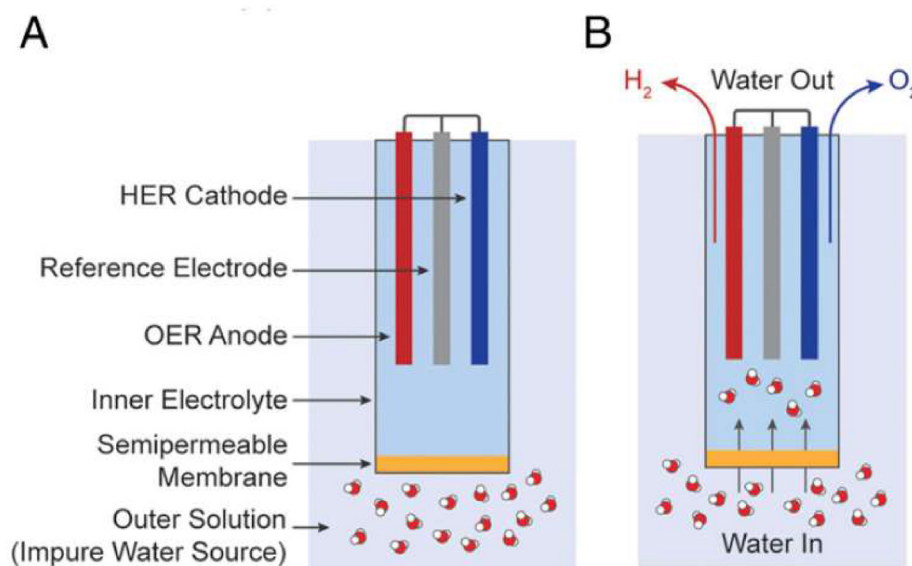


Fig. 2. Schematic representation of Forward Osmosis Water Splitting (FOWS) cell by Veroneau and Nocera [55] (A) Basic components of FOWS cell, and (B) Underlying working principle for forward osmosis water splitting cell. It shows the simultaneous H_2O influx due to FO and effective H_2O outflux via O_2 and H_2 production.

Although these review articles cover various important aspects, to the best of our knowledge, no literature discusses membranless microfluidic electrolyzer for seawater splitting; and its possibility and potential application of emerging single-step direct seawater splitting processes that overcomes pollutant related challenges while eliminates the reverse osmosis step and facilitates reduction of space requirements. In this review, we will discuss recent smart designs to combine two steps into a single reactor for using the naturally abundant seawater without the separate purification steps. We will also discuss fabrication methods, and propose a novel approach for single-step seawater splitting using concentration gradient based membranless microfluidic electrolyzer.

2. Membrane assisted water splitting: potential for direct seawater splitting (DSS)

2.1. Reactor design based on forward osmosis (FO)

Recently, Veroneau and Nocera have reported an interesting approach for direct water splitting without the purification step (Fig. 2) [55]. They have combined the two-step process in a unique way that has simplified electrochemical seawater splitting. The process consists of passive forward osmosis that facilitates persistent splitting of impure water including seawater with nominal efficiency loss.

In their approach, impure seawater is kept in the outer solution portion of the reactor. The inner solution contains the active electrolyte with higher concentration. These two solutions are separated by a semipermeable membrane (Fig. 2). Water flows from the outer impure solution to the more concentrated designed inner electrolyte due to the concentration gradient. When water is split into H_2 and O_2 gases, the concentration of inner electrolyte changes, i.e., the water

splitting process creates an effective outflux of H_2O . This again results in a concentration gradient with the outer solution of impure seawater. This outflux is balanced with an influx of H_2O delivered by forward osmosis through the semipermeable membrane.

To make a continuous process, the rates of influx and outflux are kept equal, this is how forward osmosis helps to extract purified H_2O from a polluted water source. Their strategy has been proven to be useful for conventional and stable electrodes at high current densities. The direct use of seawater in a compact electrolyzer will potentially simplify water purification processes and decrease auxiliary component expenses.

10 mL of 0.8 M NaPi (Pi = phosphate) was used as the inner electrolyte maintaining the pH at 7 using buffer solution, and cellulose acetate semipermeable membrane was used to separate the inner electrolyte from 0.6 M NaCl outer solution in the FOWS cell described by Veroneau and Nocera. At the applied current of 250 mA, 0.2 M concentration gradient was selected to process electrochemical water splitting. At this current, electrochemical water splitting resulted in a stable operating potential of ~ 2.80 V vs. standard hydrogen electrode (SHE) over a 48-h period.

Although the approach described by Veroneau and Nocera is unique and provides a novel approach to the direct seawater splitting, it has some drawback that may limit its practical application. For example, Logan et al. [56] have pointed out that (i) there is no separator between the electrodes in the system described by Veroneau and Nocera. This will result in mixing of the produced Oxygen and Hydrogen, inducing the risk of explosion. Moreover, separating the produced H_2 and O_2 gases will require another extra step. (ii) As forward osmosis and reverse osmosis membranes are not fully selective, therefore there is still chance that the chloride ions will

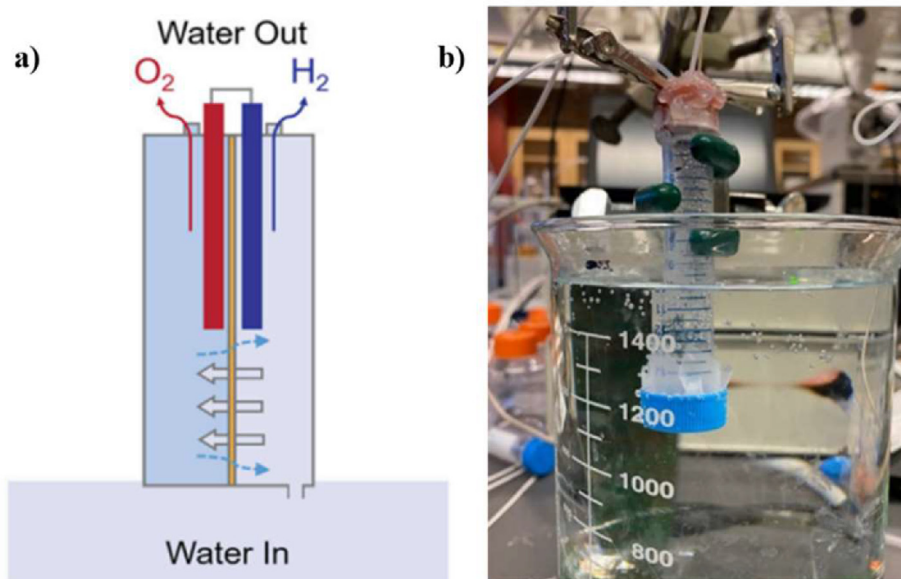


Fig. 3. (a) Schematic representation of a modified FOWS electrolyzer proposed by Logan et al. [56]. (b) Experimental set up of the FOWS cell by Veroneau and Nocera [55].

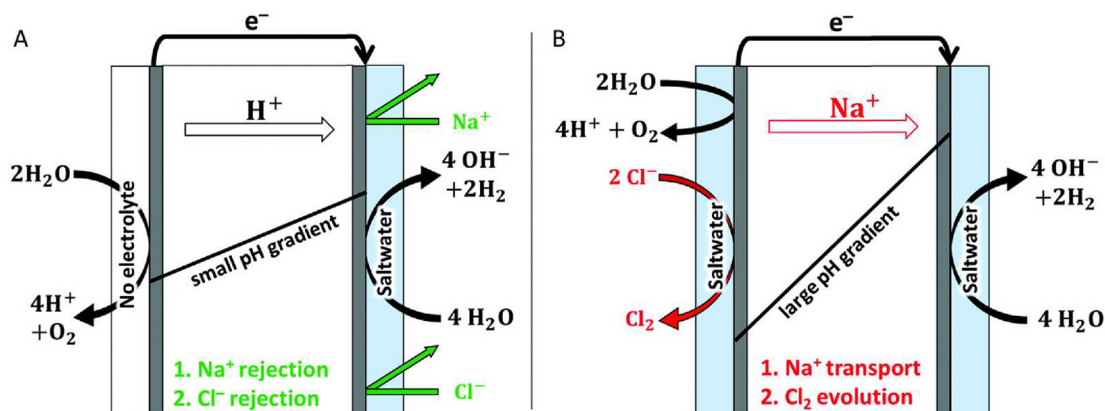


Fig. 4. (A) Anode and vapor-fed cathode with saltwater (B) both anode and cathode using saltwater. In the first design, only vapor is fed to the anode chamber and the PEM limits the transport of Cl^- from cathode to anode. Figure obtained from the reference [57].

travel through the forward osmosis membrane and be oxidized at the anode, resulting in products that can damage electrolyzer components (Cl_2 (lower pH) and hypochlorite (higher pH)). It was observed that 0.4 mmol of Cl^- was leaked into the inner electrolyte solution after 24 h [55].

(iii) A concentration gradient across the forward osmosis membrane may lead to a reverse solute flux and thus loss the phosphate buffer into the seawater which may impact

economic and environmental aspects. It was found that less than 3 molar % of the total phosphate (Pi) leached from the FOWS cell into the outer chamber after 48 h. This resulted in $\sim 4.7 \mu\text{mol h}^{-1}$ Pi leaching whereas water electrolysis rate was 2.3 mmol h^{-1} [55].

Logan et al. have proposed [56] using of a proton exchange membrane (PEM) in acidic electrolyte, or anion exchange membranes (AEMs) in alkaline electrolyte for avoiding the

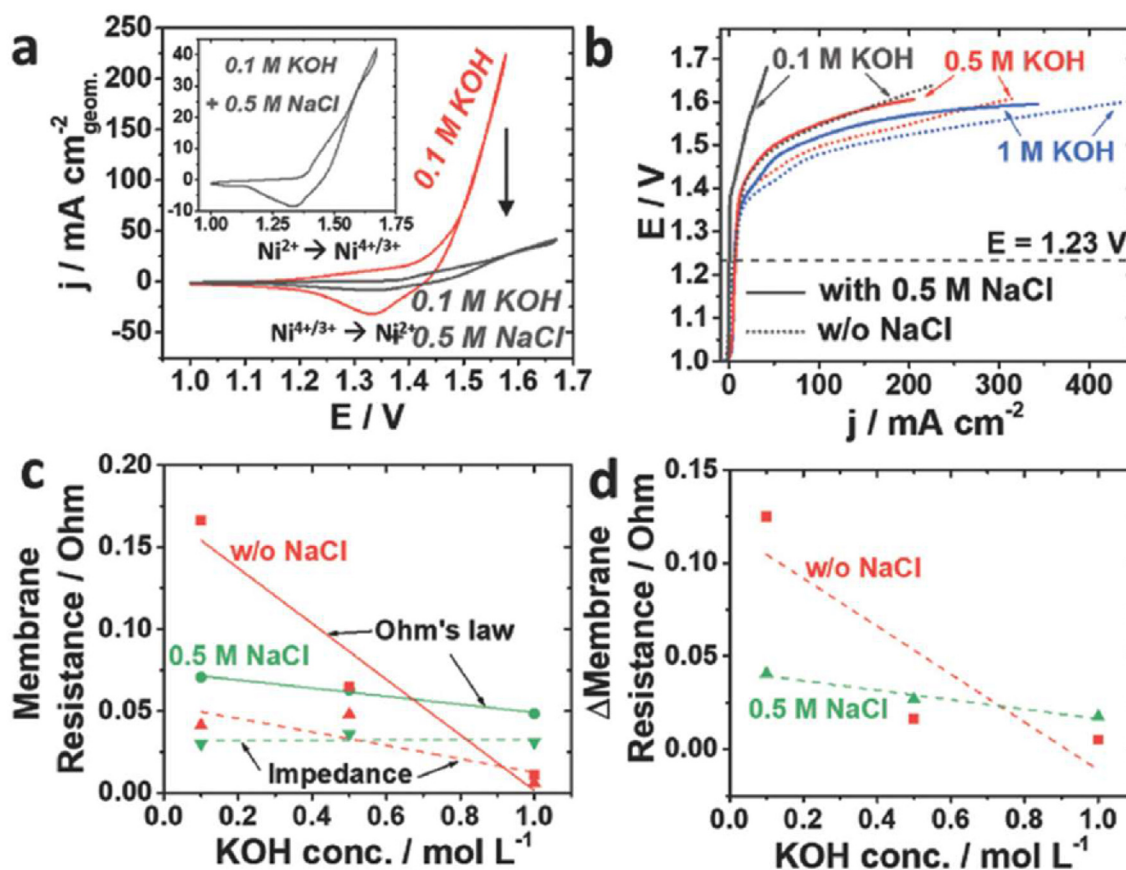


Fig. 5. Result obtained by Drespe et al. [58] a) Two-electrode cyclic voltammetry in presence and absence of 0.5 M NaCl. b) Polarization curves extracted from the cyclic voltammetry in different electrolyte concentrations (with and without NaCl). c) Membrane resistance in in different KOH concentrations with 0.5 M and without NaCl d) Capacitive resistance of the membrane at different KOH concentrations for NaCl free (w/o) and NaCl containing electrolytes.

Table 1
Comparison of PEM and AEM technology.

Electrolyzer type	Advantages	Disadvantages
PEM	Higher performance	High cost of components
	Higher voltage efficiencies	Acidic corrosive components
	Good partial load	Noble metal catalyst
	Rapid system response	Stack below Megawatt range
	Compact cell design	
AEM	Dynamic operation	
	Non-noble metal catalyst	Laboratory stage
	Noncorrosive electrolyte	Low current densities
	Compact cell design	Membrane degradation
	Low cost	Excessive catalyst loading
	Absence of leaking	
	High operating pressure	

mixing of H_2 and O_2 (Fig. 3) gases. They also discussed that the PEM or AEM have an extra advantage of production of H_2 gas at a high pressure which can potentially reduce the cost associated with the compression of H_2 gas. One needs to be cautious about the selection of the suitable ion exchange membrane. However, this design also has some shortcomings such as salt ion crossover due to Cl^- ion transportation into the anolyte via the membrane, and salt ions that should be retained in the anolyte can leak into the seawater catholyte; this can be avoided by using highly selective OER catalysts.

Although Logan et al. have proposed the use of PEM or AEM membranes to overcome the limitation of the FOWS by Veroneau and Nocera, we believe that the practical application potentials of such electrolyzers will be hampered. This is because the impurities present even after the forward osmosis process will affect costly membranes and reduce their lifetime; as the forward osmosis and reverse osmosis membranes are not fully selective. The best way to separate the oxygen and hydrogen gas, and increase the durability of the electrolyzer simultaneously will be possible if a microfluidic membrane-less device is used. The gases are separated by the advection (advection is the transport of a substance or quantity by bulk motion of fluid) and being membrane-less, this kind of electrolyzers bypasses the possibility of membranes being affected by the seawater impurity. This is discussed in more detail in the following sections.

2.1.1. Fabrication of FOWS cell

Veroneau and Nocera have used an inverted 15-mL centrifuge tube as the cell (Fig. 3b). The anode and cathode were made of Pt mesh electrodes, whereas Ag/AgCl electrode was used as a reference electrode. The conical end of the centrifuge tube was cut at the 2-mL mark. A hole (diameter = 1 cm) was bore through the dome of the cap of the centrifuge tube. A Buna-N O-ring (113, outer diameter = 0.75 in) was introduced through the cap in way so that it stayed underneath the threading. A cellulose flat sheet membrane was kept on the threaded end of the pre-cut centrifuge tube. The membrane was made leak proof using the screw cap (with O-ring). Two 4 cm Pt flag electrodes were introduced through a septum stopper; a 1-mL long polypropylene divider was

placed between the electrodes. The air inside the tube was replaced with inert gas before use. The FOWS cell was fabricated in the laboratory scale and the prototype cost is subject to its volume.

2.2. PEM and AEM based water splitting

Rossi et al. have developed a water electrolyzer configuration that used saline water as the catholyte feed by using a vapor-fed anode chamber (Fig. 4) [57]. The vapor-fed anode leverages the charge of the PEM and the direction of the electric field to limit the intrusion of competing ions into the anode. The PEM has the negative sulfonated moieties which helps to limit the diffusion of Cl^- to the anode by charge repulsion, while the electric field due to the electron transport diminishes the diffusion of sodium ions to the anode as it needs to be balanced by positive ions transported from anode (vapor) to cathode (saltwater), limiting the development of large pH gradients across the PEM.

In their design, required water for the OER at the anode is provided by the vapor-feed and by water diffusing from the saline water catholyte through the membrane. The unwanted transport of chloride ions from the catholyte to the anolyte is stopped by charge repulsion of the PEM, while sodium ion transport is minimized by charge transfer of protons from the anode through the PEM, enabling high current densities. However, long time performance and poor membrane stability due to the presence of Na^+ remains a challenge.

Dresp et al. have reported the first anion exchange membrane based electrolyzer operating in the seawater mimicking condition [58]. They have used highly crystalline NiFe-LDH (layered double hydroxide) as anode material.

They have found that higher KOH concentrations resulted higher performances (current density), but the relative stability was lowered proportionally in Fig. 5. When 0.5 M NaCl was added to the electrolyte to mimic the seawater condition, the current density was decreased. This was explained by a lower OH^- conductivity of the used AEM due to the presence of Cl^- ions.

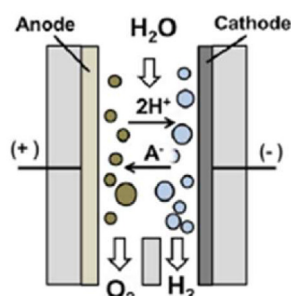
In a 100 h study, NaCl-free 0.1M KOH measurements performed stable after an activation time of 12 h, however, for all other electrolyte conditions the current density decreased per time. Dresp et al. concluded that SEM images and impedance investigations indicated a membrane-induced stability loss. They used Extended X-ray Absorption Fine Structure (EXAFS) technique to show that a major fraction of activity loss is related to chloride ions blocking the membrane, at least hindering the OH^- transport across the membrane.

For fresh water splitting, proton exchange membrane (PEM) is a matured technology, commercially available, and a better fit for its potential large-scale application. Its performance is stable and its life span can reach 8–10 years. Typical Discharge H_2 pressure (bar) for PEM is 30–80 bar, this facilitates direct use of produced hydrogen on PEM fuel cells for on-demand electricity regeneration. The structure of such an electrolyzer is very compact and the internal resistance is

small with a high current density up to 2.5 Acm^{-2} . Moreover, the hydrogen permeability of the PEM is low and the purity of produced hydrogen can reach up to 99.999%. In addition, without aqueous electrolytes, PEM electrolyzers can respond

quickly to the input power. Demonstrated rated power for PEM is 1.8–174 kW. However, chloride oxidation reaction competes with OER in acidic medium. This makes use of PEM for seawater splitting practically impossible.

Membraneless Flow-by electrodes



Membraneless Flow-through electrodes

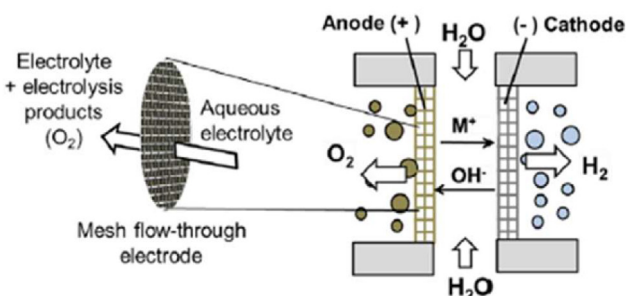


Fig. 6. Types of membrane-less electrolyzers. Figure adapted from the reference [62].

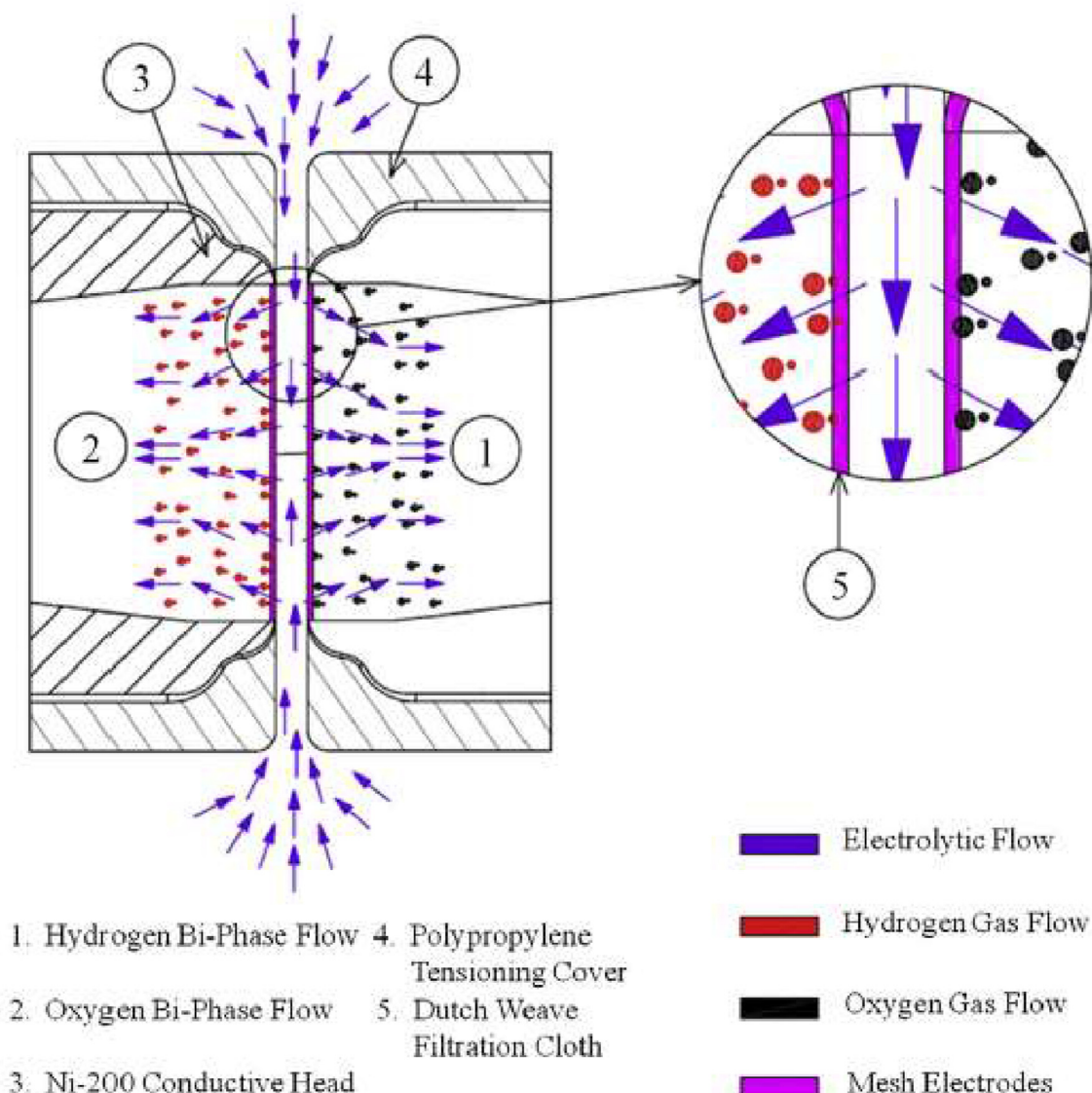


Fig. 7. Schematic representation of a flow-through membrane-less alkaline electrolyzer by Gillespie et al. [67].

On the other hand, Anion exchange membrane (AEM) electrolyzers are not as mature as PEM (it is in the R&D stage), however, AEM electrolyzers are lower in cost due to the use of cheaper electrode material unlike the noble metal for PEM [59–61]. AEM offers benefits of both PEM and alkaline electrolysis. However, the stability is much lower and this technology is not well-established for large-scale application. Conventional current density can reach up to 0.5 Acm^{-2} for AEM. Demonstrated rated power for AEM is 1.3–4.8 kW. The purity of produced hydrogen from AEM electrolyzers can reach up to 99.99%. Table 1 summarises the differences of PEM and AEM technologies (Table 1).

However, both PEM and AEM based water splitting technologies cannot use seawater directly as water feedstock. This is because the impurities present in seawater attacks the costly PEM and AEM membranes [33,53]. Hence, a membrane-less technology is expected to serve better for seawater splitting.

3. Membrane-less water splitting: potential for direct seawater splitting (DSS)

3.1. Membrane-less macro-electrolyzers

Highly acidic or alkaline environments are always needed for the water electrolysis. This is because pure water has very poor ionic conductivity. Transportation of OH^- and H^+ is not sufficient due to very low concentration. This will result in local pH differences which in turn will induce the unfavourable thermodynamics of the OER and HER. As discussed earlier, this might also cause earth alkali metal hydroxides precipitation. Moreover, for separating the H_2 and O_2 gas, PEM or AEM is required. The use of PEM or AEM has their own disadvantages. For example, these membranes are very costly resulting in high capital cost. These membranes can be affected by impurity, and its lifetime shortening will not only be

associated with higher cost but also result in extra maintenance. Moreover, besides membrane and catalysts, a single PEM cell requires, bipolar plates, gas diffusion layers, gaskets, ionomer, current collectors, etc. This increases fabrication processes and costs, and makes the device engineering complex.

Seawater has a near-neutral pH. At this pH, the PEM or AEM membranes will not be functional; moreover, the impurity present in seawater will damage the membranes, thus requiring extra seawater purification steps. However, the operation of water electrolysis in pH neutral conditions is desirable because (i) there are safety issues associated with strong alkaline or acidic electrolytes in the liquid form, which are unlikely in the case of neutral water electrolysis. (ii) A pH-neutral environment will allow using cheaper construction material and catalyst that usually undergo corrosion in the acidic or basic media. To serve this process, emerging methods of membrane-less electrolyzers are promising. As the membrane-less electrolyzers do not use any membrane which is otherwise susceptible to impurities, it has potential to be used for direct seawater splitting. pH of the electrolyte and nature of ions do not influence the ionic conduction through the liquid electrolyte. Hence, membrane-less electrolyzers can be utilised in any pH. Fig. 6 depicts the examples of membrane-less electrolyzers [62]. A membrane-less system will simplify the research strategy to concentrate only on selective electrode design. Various literatures are available with multiple strategies for obtaining high selectivity and stability of OER electrocatalysts in Cl^- -containing water. These includes use of the intrinsic OER selectivity criteria, formulating an inert Cl^- retarding layer, or decorating with an anion-rich surface [63–66]. Thus, if a selective electrocatalyst is used, direct seawater splitting can potentially be possible in a membrane-less electrolyzer.

Membrane-less electrolyzers can be mainly classified into two types: In Type I, the membrane-less electrolyzers usually

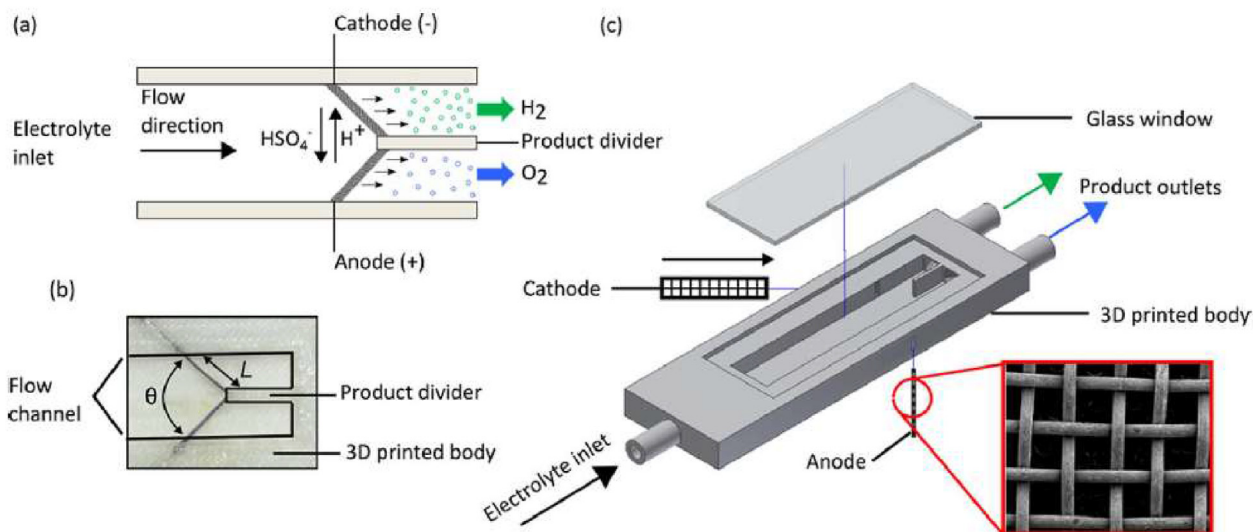


Fig. 8. A mesh flow-through membrane-less electrolyzer is depicted here [68]. (a) Basic working principle is shown in the 2D schematic. (b) Photograph of the two mesh electrodes which are placed at an angle θ , with electrode length L , and product divider. (c) 3D CAD rendering is shown with two electrodes. Inset shows SEM image of the mesh electrode.

depend on flow-induced product separation using advection (forced fluid flow). O_2 and H_2 are separated by advection before they can cross over to the opposite electrode. Here, H_2 and O_2 products flows separately via the downstream effluent channels with the aqueous electrolyte solution that flows parallel to the electrode surfaces. The architectures of this type of membrane-less electrolyzers are almost similar to the flow batteries and laminar flow fuel cells.

In the Type II electrolyzers, flow-through electrodes are used. In this case, electrodes are porous in nature and the flowing electrolyte passes through porous electrodes. Generally, two metallic mesh electrodes are placed in a face-to-face arrangement while electrolyte are passed across the electrode gap using pressure from an outer chamber. During this time, the flow diverges, carrying the oxygen and hydrogen away into separate effluent channels. The hydrogen and oxygen gases are generated on the surface of the pores of cathodes and anodes

respectively. When the electrolyte flow through the pores of electrodes, it carries the hydrogen and oxygen gas from the cathode and anode pores with its pressurized flow before the gases can mix.

Gillespie et al. have reported a flow-through membrane-less alkaline electrolyzer with a hydrogen purity of 99.83% (Fig. 7) [67]. Electrode gap determined the electrolyte velocity. Using mesh electrodes of 30 mm diameter, at an optimal electrode gap of ~ 2.5 mm, an electrolytic flow velocity of 0.075 – 0.1 m s^{-1} was achieved with a current density of 3500 mA cm^{-2} . Smaller optimal gap (~ 0.8 mm) allowed operating at greater velocities (>0.1 – 0.2 m s^{-1}).

A type II design based on mesh flow-through electrodes is reported by O'Neil et al. (Fig. 8) [68]. The design is simple and the electrodes are placed at an certain angle. These electrodes are separated by an insulating baffle, and it was 3D printed as a single, monolithic component. In fact,

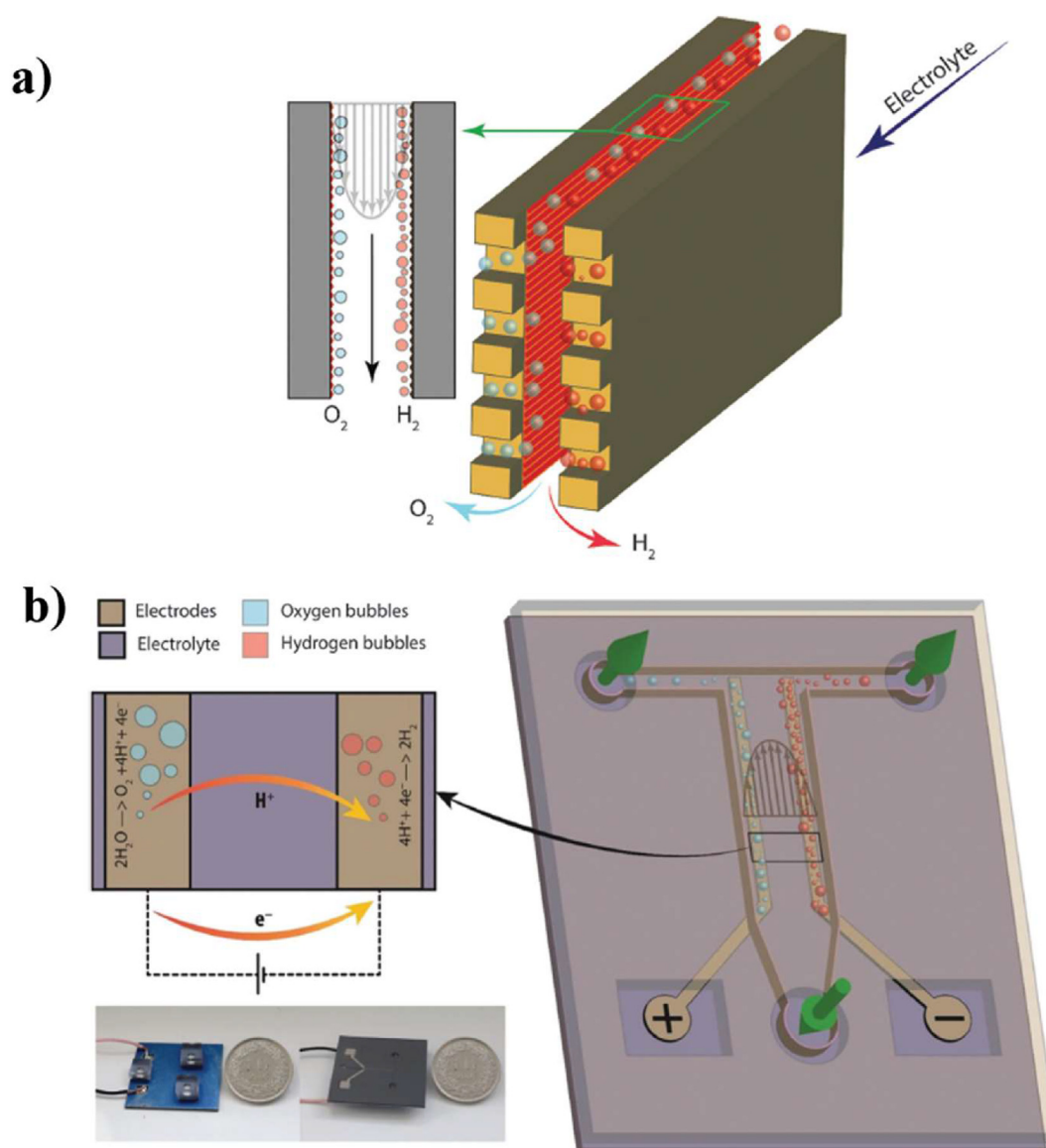


Fig. 9. Schematic diagram of the membrane-less microfluidic electrolysis by Hashemi et al. [71].

this configuration is suitable for in situ imaging of the crossover phenomenon.

Membrane-less electrolyzers has potential to be robust and has long operating lifetimes. Moreover, this type of electrolyzer is tolerant to contaminations with superior robustness in the extreme operating conditions that would usually damage a

membrane. Hence, these above-mentioned approaches can potentially be used for seawater.

3.1.1. Fabrication of membrane-less electrolyzers

The electrolyzer can be fabricated using a 3D printer. In the report by O'Neil et al. [68], the devices were fabricated by 3D

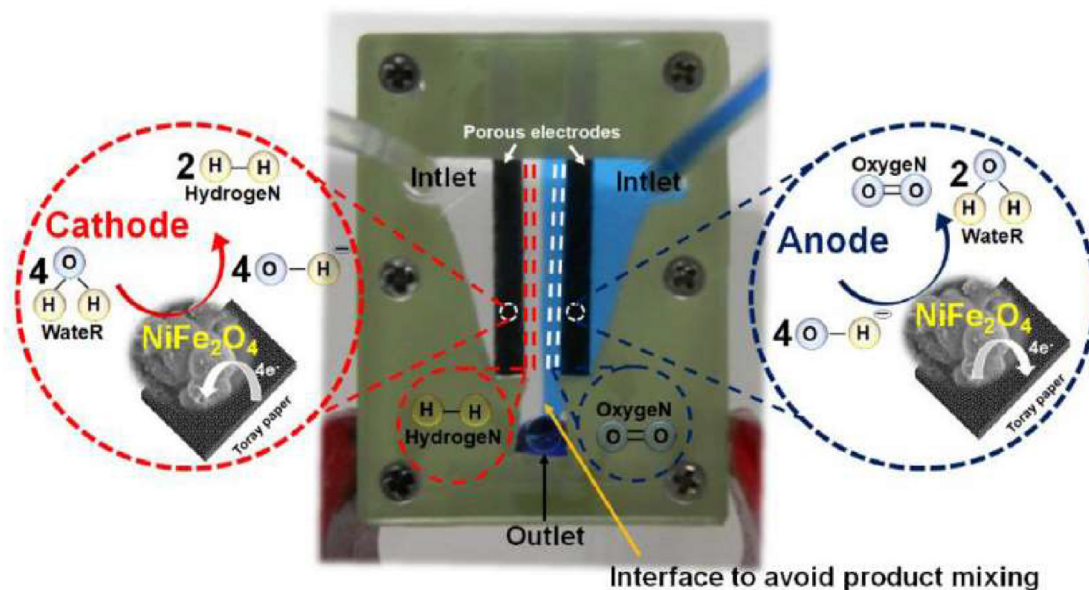


Fig. 10. Microfluidic water splitting system reported by Martínez-Lázaro et al. [72].

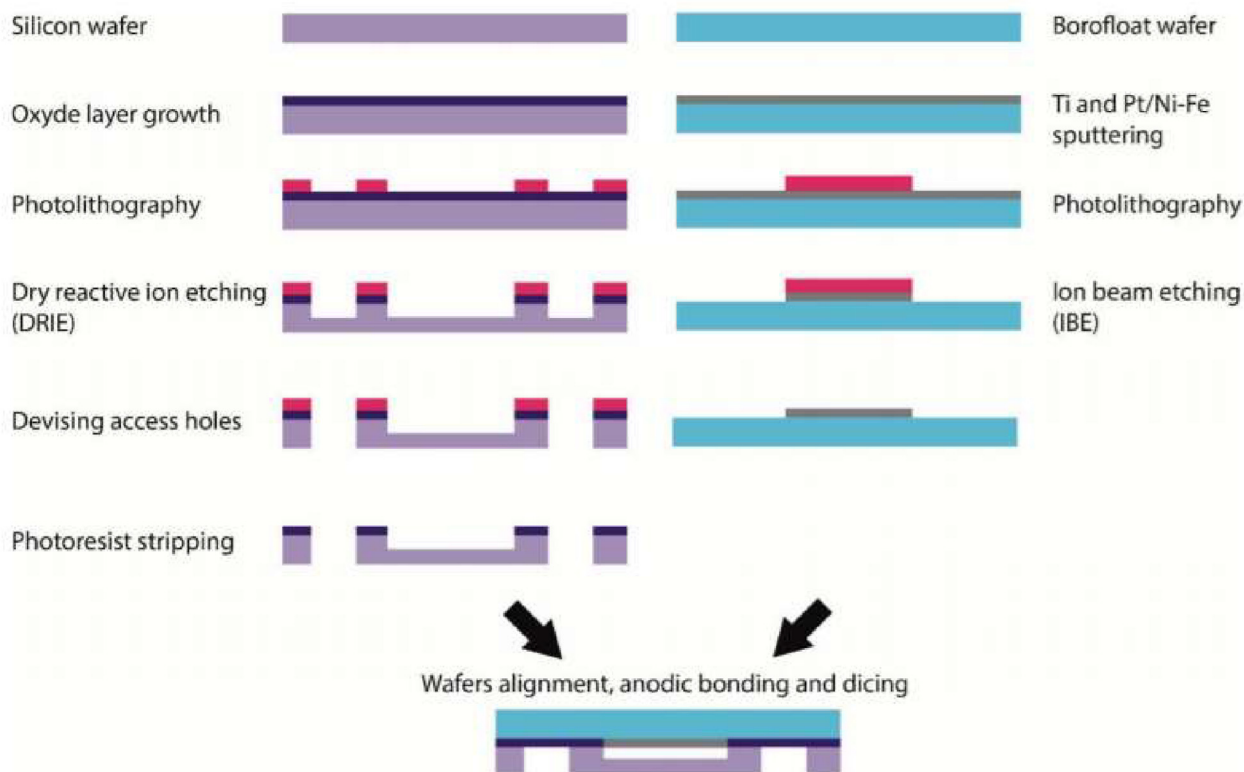


Fig. 11. Fabrication process of microfluidic membrane-less electrolyzer by Hashemi et al. [71].

printing using Polylactic Acid (PLA) filament for acidic and neutral electrolytes or Acrylonitrile Butadiene Styrene (ABS) filament for the alkaline electrolyte. Electrolyzer frames were made at a high resolution, with a 0.1 mm line height and 15% infill.

Initially, Pt particles were electrodeposited on Ti mesh electrodes in a K_2PtCl_4 (3 mM) and NaCl (0.5 M, pH = 3.15) solution to make the working electrode.

For assembling the membrane-less flow electrolyzers, two mesh electrodes were placed properly (Fig. 8 c inset) within the electrolyzer body and epoxying them overnight for the epoxy to completely set. A see-through glass window was sealed to the front flow cell by directly epoxying to the electrolyzer body. This aids visualizing the inner-workings of the membrane-less devices. The fluidic channel had a width, length and height of 1.3 cm, 7.0 cm and 0.5 cm respectively. A 1.0×0.1 cm gas divider was located downstream of the electrodes. The product channel cross-section was 0.5×0.6 cm.

3.2. Microfluidic membrane-less electrolyzers

Although membrane-less electrolyzers have many advantages, it has a few challenges as well. For example, at high operating current densities, membrane-less electrolyzer usually have lower voltage efficiency due to solution IR losses. The distance between two electrodes in membrane-less electrolyzers is much higher than that of Nafion membrane in PEM electrolyzer. Although the added electrolyte, i.e., concentrated H_2SO_4 and KOH electrolytes have a higher ionic conductivity than PEM or AEM, the effect of distance cannot be compensated. The larger distance result in higher ohmic resistance of solution (R_s) for ion transport. This results in a higher ohmic voltage loss. In this context, microfluidic membrane-less electrolyzers can be a promising alternative due to its very narrow electrode gaps (Fig. 9).

In this case, two parallel electrodes placed in such a manner that the distance between them is in micrometer scale, typically

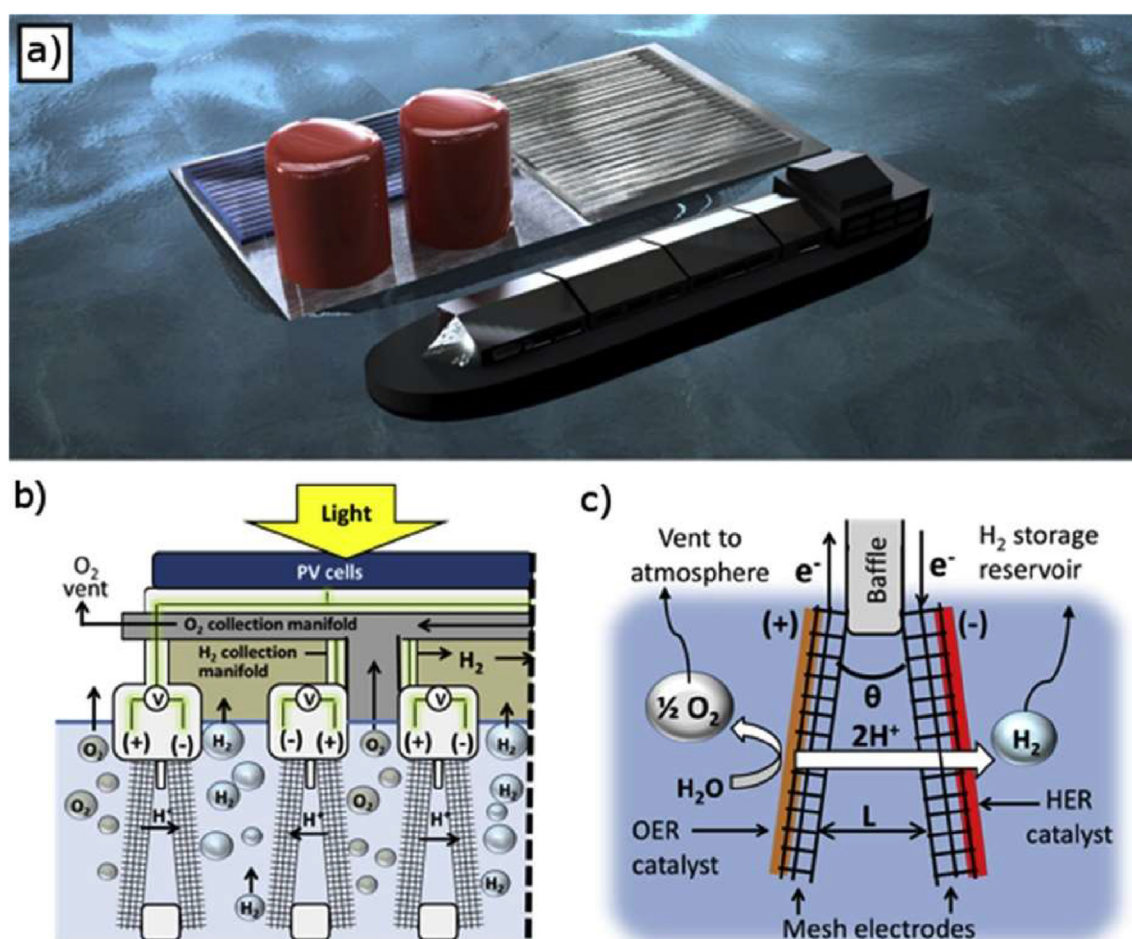


Fig. 12. (a) A schematic representation of a floating membrane-less PV-electrolyzer by Davis et al. [73] (b) A futuristic schematic of novel membrane-less electrode assemblies. The electrolyzers are assembled in parallel, and use electricity supplied by the PV panels to split water into H_2 and O_2 . (c) A close up schematic for buoyancy-based product separation in a membrane-less electrolyzer. The mesh electrodes are placed at an angle, and the electrocatalyst is deposited on the outward facing sides so that the product gas nucleation and growth is confined to this region only. The gas bubbles float directly upward for collection when they become sufficiently large enough to detach.

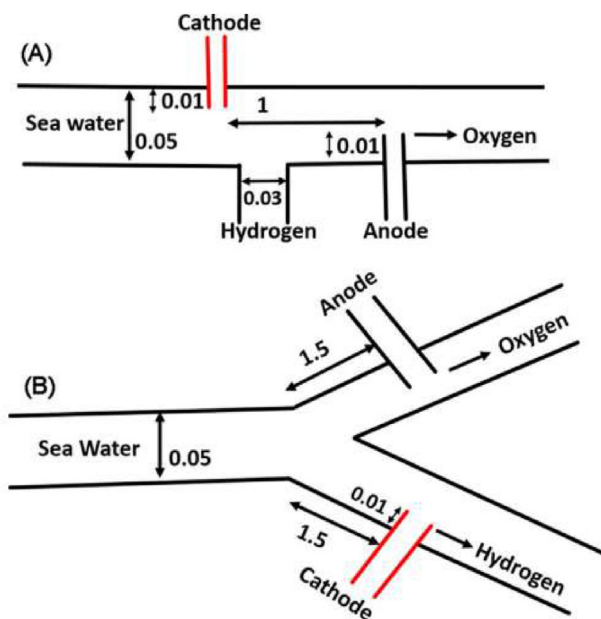


Fig. 13. (A) Schematic diagram of a straight-channel microfluidic electrolyzer with a separator (B) Schematic diagram of the Y-channel microfluidic electrolyzer with a separator. The electrodes were placed on the Y-arms (All dimensions are in cm). Figure is taken from the reference [74].

a hundred micrometers or so. The evolved gas moves with the electrolyte very close to the corresponding catalyst surface between the electrodes due to the Segré-Silberberg effect [69].

If we consider a dilute suspension of any particles (or bubbles) flow in a laminar flow in a tube, there is velocity difference of the fluid inside the tube. This velocity gradient exerts a net inertial lift force on the bubbles. Also, there is another counter force between the wall and those particles or bubbles. This helps the particles to stay in equilibrium. The particles equilibrates at a distance of $0.6R$ from the tube's centre. This phenomena is called as Segré-Silberberg effect. This depends on the velocity of the fluid. The viscous drag forces are responsible for driving particles along the flow streamlines, whereas the inertial forces are responsible for the lateral migration of particles across the flow streamlines. Non-rigid entities, such as bubbles and droplets, experience an additional lift force due to deformability which directs them

away from the wall. This results in further shifting the bubbles equilibrium position towards the centre. This can be overcome by increasing the velocity (i.e. flow rate) of the fluid. Thus, if bubbles are mixing, increase in flow rate will help separating the bubbles.

The gas streamers are collected in designated outlets. Although, this kind of device is very small in nature, this can be scaled up by multiplying the stacks of these planes horizontally [70]. In a method reported by Hashemi et al., the product gases (i.e. H_2 and O_2) are separated by controlling the delicate balance between fluid mechanic forces in the device (Fig. 9) [71]. Their devices achieved a current densities over 300 mA cm^{-2} with 42% power conversion efficiency, and 0.4% crossover of H_2 gas into the anode side. The method of Hashemi et al. has the capability of yielding non-flammable H_2 streams (due to very low crossover of gases), uninterruptedly and stably at all any pH. In another report, Martínez-Lázaro et al. have demonstrated a $NiFe_2O_4$ -based material for water splitting in a microfluidic device. They have achieved H_2 production rate of $2.5 \times 10^{-5} \text{ mg s}^{-1}$ for a 3D $NiFe_2O_4$ hollow-spheres (Fig. 10) [72].

As stated earlier, membrane instability due to impurity in seawater will be avoided if a membrane-less electrolyzer is used. The microfluidic system will reduce the ohmic loss and increase the efficiency of catalysts due to larger specific surface area of miniaturised systems. Thus, a microfluidic membrane-less electrode will facilitate research concentrating only on selective electro-catalyst. If an electro-catalyst can work in alkaline chloride-containing electrolytes (i.e., seawater) with an overpotential of less than 480 mV, it can achieve greater OER selectivity. Decoration of catalyst surface using anions also efficiently alleviates electrode corrosion. Hence, a microfluidic membrane-less electrolyzer that operates in alkaline medium below the overpotential of 480 mV with chloride retarding coating can potentially be applied for direct seawater electrolysis.

3.2.1. Fabrication of microfluidic membrane-less electrolyzers

Hashemi et al. have fabricated microfluidic membrane-less electrolyzers in the following procedure. They have used a

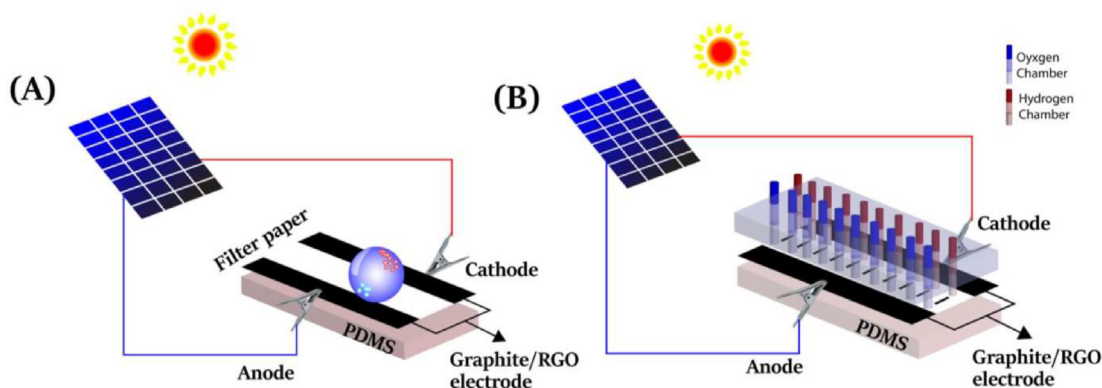


Fig. 14. Schematic diagram of (A) 'open' electrolyzer (B) Production and separation of hydrogen and oxygen in a 'close' electrolyzer [75].

Borofloat glass wafer for patterning the electrodes on it. Initially, a Titanium film of 10 nm is sputtered on top of the glass wafer for stimulating adhesion of Platinum (of 175 nm thickness), or Nickel–Iron top layer of 150 nm thickness (81% Ni, 19% Fe). Ion Beam Etching (IBE) and Photolithography are used for patterning the shape of electrodes on top of Platinum/Ni–Fe layer. The edge-to-edge distance of the electrodes are kept 105 μm , while each electrode is 1 cm long and 70 μm wide. Deep Reactive Ion Etching (DRIE) technique is employed for etching the microchannels in the photolithographically patterned silicon wafer. A 100 nm thick oxide layer is grown on the wafer using Low Pressure Chemical Vapor Deposition (LPCVD) to render it non-conductive before the photolithography step. The depth is observed to be 61 μm , as measured by a mechanical profilometer, with a main channel width of 275 μm . The T-junction branch has a width of 100 μm on each side. After this step, all the holes for the electric and fluidic access are devised by a diamond scribe.

Each wafer is patterned with four set of electrodes and fluidic networks. The two wafers are aligned together after plasma cleaning in a Back Side Aligner (BSA) tool and bonded using standard anodic bonding technique. The microchannel side-wall and the electrode's edge has a distance of 15 μm . Lastly, a dicing machine is used to separate the four devices on the bonded platform; and flexible bed for connections is provided by plasma bonding on top of fluidic ports with small Polydimethylsiloxane pieces. The fabrication procedure is described as a flow diagram in Fig. 11.

4. Recent advancement of membrane-less electrolyzers for seawater splitting

Davis et al. have reported an interesting design for membrane-less water electrolysis (Fig. 12) [73]. Their strategy is based on the use of buoyancy-driven separation of the produced hydrogen and oxygen bubbles that are produced on

mesh electrodes. They have reported the lowest percent H_2 cross-over to be 1%. In a floating PV-electrolysis module, a solar-to-hydrogen efficiency of 5.3% was achieved in 0.5 M H_2SO_4 . However, they found that significantly larger voltages are required to achieve the same electrolysis current density in the NaCl solution (simulated seawater) compared to the sulfuric acid solution [73]. For example, voltages of 2.44 V and 3.68 V are required to operate at a current density of 100 mA cm^{-2} in the 0.5 M H_2SO_4 and 0.6 M NaCl solutions, respectively. This increase in operating voltage of 1.24 V results in a decrease in the electrolysis efficiency from 50.4% (in 0.5 M H_2SO_4) to 33.4% (in 0.6 M NaCl).

In another report Rarotra et al. have used Y-shaped microfluidic electrolyzer in which the electrodes were positioned on the Y-arms (Fig. 13) [74]. They have run the electrolyzer with DC power, PV power using seawater, and found that the combination of PV cells with seawater produced the lowest volume of hydrogen because of the fluctuations in the solar illumination during the daytime. Although the study reported an interesting phenomena, detailed study on the basis of their activity, selectivity, and stability is required. In another recent report, Rarotra et al. have demonstrated micro-electrolyzers based on graphite/rGO coated paper electrode, for seawater electrolysis. The metal-free micro-electrolyzer facilitated the water-splitting at a much lower applied voltage with an efficiency of 1–2% [75] (Fig. 14).

Rarotra et al. have integrated their electrolyzers with a photovoltaic (PV) cell. The 'open' electrolyzer (OME) consists of a microchannel confined by a pair of graphite electrodes, which is drawn with the help of pencil tips. A sea water microdroplet has been dispensed at the junction of the electrodes while the PV cell is integrated to the electrodes to supply current. The microscale width of channel generates a high intensity electric field even at a lower potential, which facilitates the microdroplets to electrolyze into H_2 and O_2 near the cathode and anode. The rate of production of the gases

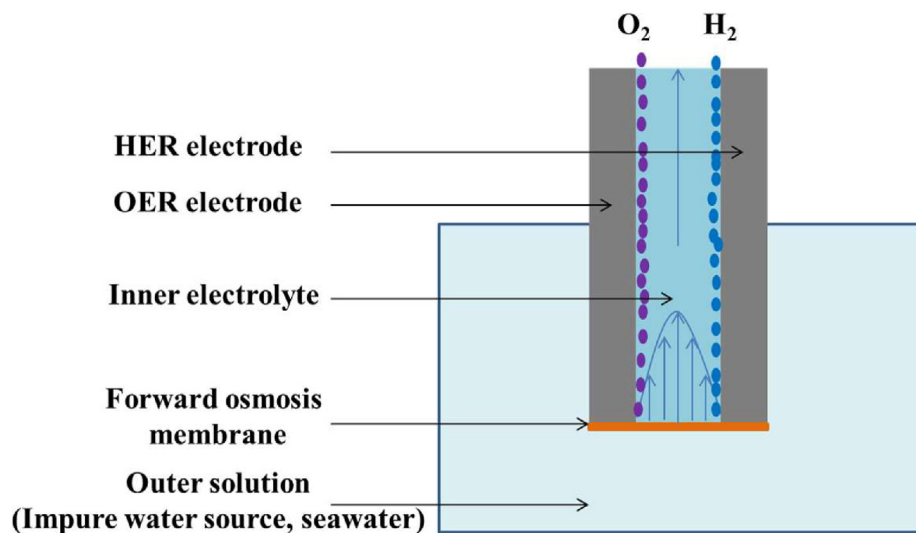


Fig. 15. A novel design for the forward osmosis based membrane-less microfluidic electrolyzer. A membrane-less microfluidic electrolyzer is directly connected with the seawater storage chamber via a low cost simple forward osmosis membrane for direct seawater splitting. The inner electrolyte concentration can be kept higher so that natural spontaneous water flow from seawater chamber to inner electrolysis chamber is possible.

increased with field intensity. In the ‘close’ electrolyzer (CME), the paper decorated with graphite electrodes is covered with a substrate embedded with polymeric micro-channels. The microcapillaries are placed closer to the anode and cathode for in situ separation of H_2 and O_2 . Rarotra et al. have observed that the water splitting starts at a potential of ~ 2.1 V. Water splitting kinetics and bubble generation is very low at lower potentials, ranging from ~ 1.23 V– 2.1 V. Thus, further improvement and stability study is required.

5. Concentration gradient based membrane-less microfluidic electrolyzer: a novel design

Combining the concept of a concentration cell (where two different concentrations can be used to create a concentration gradient for a spontaneous flow) with a membrane-less microfluidic device, a membrane-less microfluidic concentration cell can potentially utilise the seawater directly without separate reverse osmosis purification step. We propose a new electrolyzer design for this purpose in Fig. 15.

In this scenario, impure water (e.g., seawater) can be kept as an outer solution. A membrane-less microfluidic electrolyzer can be separated from the outer solution with a simple forward osmosis based semipermeable membrane. A higher concentrated electrolyte using fresh water is first used in the microfluidic electrolyzer. Due to the concentration gradient of the inner and outer solution, H_2O can move into the microfluidic electrolyzer through the forward osmosis membrane. Thus, costly PEM or AEM can be avoided in this design resulting in lower capital cost. When H_2O is split into H_2 and O_2 , an effective outflux of H_2O is generated. Thus, a spontaneous H_2O flow can occur from the outer solution to the microfluidic electrolyzer. The mixing of H_2 and O_2 does not happen due to laminar flow principle. This design not only will potentially avoid mixing of H_2 and O_2

but also protect the electrode from impurities present in the seawater.

We believe that the membrane-less electrolyzer design can be promising in the context of DSS as it has the potential to solve the problems currently prevailing in DSS, e.g., the addition of acid/base or expensive buffer species, membrane instability, the poor selectivity, activity, and cost of the electrode materials, the low gas separating efficiency but high complexity, as well as the additional by-products elimination.

This design has the following potential advantages compared to seawater splitting after desalination:

(i) High cost of the currently available electrolyzers arises from the expensive PEM or AEM membranes. Membrane-less electrolyzers will significantly reduce the cost. (ii) The seawater impurities affect the costly membranes. Being membrane-less, effect of seawater impurities is nullified. Moreover, use of direct seawater bypass the challenge of fresh water scarcity. (iii) Membrane-less electrolyzers can be used across all pH. This eliminates the addition of expensive buffer or other additives. This is beneficial in terms of environmental aspect. (iv) The research focus can be shifted entirely on the electrode design. This makes the research strategy less complicated. (v) The efficiency of such electrolyzers can be potentially increased by making the electrolyzers in micro-scale, thus eliminating the ohmic potential drop due to solution resistance. (vi) Short distance also bypass the use of highly acidic or basic for effective ion transport. Micro-scale transport is supported by the fluid advection. Bypassing the use of acid or base makes the process benign to environment. (vii) H_2 and O_2 mixing does not happen due to laminar flow in the micro-scale (viii) Space requirement is lower compared to desalination plant [76].

A comparative table are given below for all types of devices (Table 2).

Table 2
Comparison of various devices for seawater splitting.

Systems	Advantages	Disadvantages
Conventional 2-step process	i. Reverse osmosis removes impurities from seawater. Electrodes are at low risk of impurities.	i. Larger space requirement. ii. More auxiliary steps, system design and maintenance.
Forward osmosis electrolyzer	i. Direct use of seawater or other low-grade impure water. ii. Costly PEM or AEM is not required. iii. Less space requirement.	i. Mixing possibility of hydrogen and oxygen gas increases explosion risk. ii. Cl^- ions diffuse into the inner electrolyte. iii. Diffusion of buffer solution to the outer water.
Membrane-less electrolyzer	i. Costly PEM or AEM is not required. ii. Possibility of using direct seawater if selective OER electrode is used. iii. A pH-neutral water source can be used without acid or alkali addition. iv. Simplifies the research strategy to concentrate only on selective electrode design. v. Less space requirement.	i. Distance between two electrodes in membrane-less electrolyzers is much higher than that of Nafion membrane in PEM electrolyzers. At high operating current densities, membrane-less electrolyzers usually have lower voltage efficiency due to solution IR losses. ii. Multiple stacks required for large scale application.
Microfluidic membrane-less electrolyzers	i. Distance between two electrodes is small. Low solution IR loss. ii. Costly PEM or AEM is not required. iii. Possibility of using direct seawater if selective OER electrode is used.	i. Multiple stacks required for large scale application.

(continued on next page)

Table 2 (continued)

Systems	Advantages	Disadvantages
Concentration gradient based membrane-less microfluidic electrolyzer	iv. A pH-neutral water source can be used without acid or alkali addition. v. Simplifies the research strategy to concentrate only on selective electrode design. vi. Less space requirement.	
	i. Less risk of impurity-triggered electrode corrosions (as FO filters the impurities). ii. Direct use of seawater or other low-grade impure water. iii. Distance between two electrodes is small. Low solution IR loss. iv. Costly PEM or AEM is not required. v. Possibility of using direct seawater if selective OER electrode is used. vi. A pH-neutral water source can be used without acid or alkali addition. vii. Simplifies the research strategy to concentrate only on selective electrode design. viii. Less space requirement.	i. Forward osmosis membrane required.

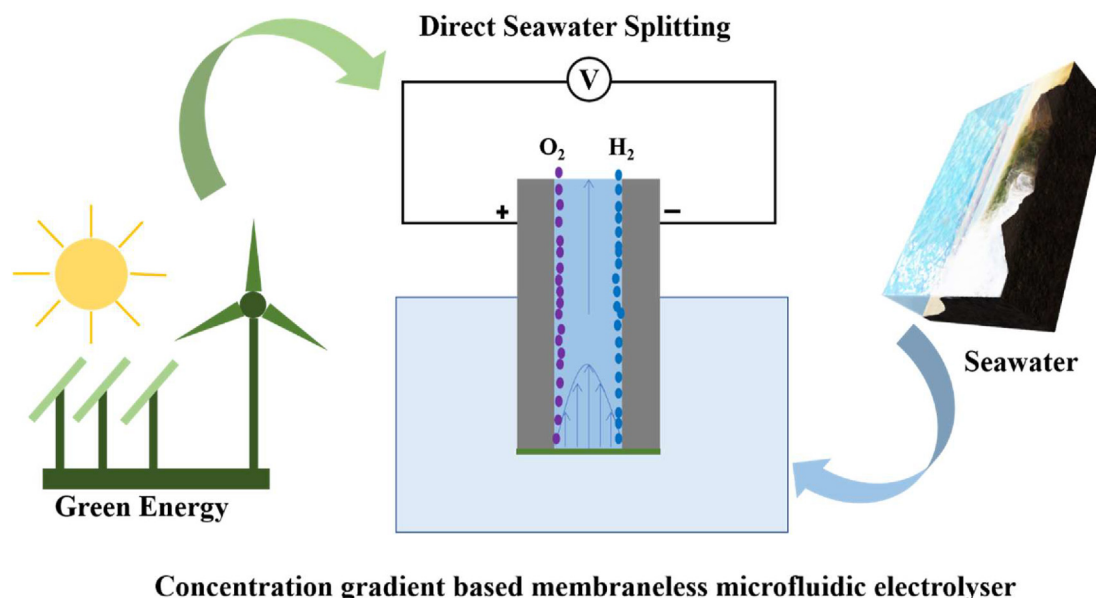


Fig. 16. A representation of direct splitting of seawater using green energy in a concentration gradient based membrane-less microfluidic electrolyzer.

6. Future perspective

The potential for microfluidics in electrochemical energy systems has been discussed in detail in a review by Modestino et al. [77]. There are a few reports among others on the successful demonstration of microfluidics [78–80].

Concentration gradient can in principle be applied to directly use the impure seawater as feed if a proper reactor design is apprehended (Fig. 16). Microsystems have some intrinsic advantages: (i) As the catalysis occurs on the electrode surface, increase in effective surface areas will result in augmented efficiency. For microsystems, specific surface area (i.e., surface area to volume ratio) is larger than that of the macro-systems with a similar volume. (ii) The short separation between electrodes will serve in lowering undesirable solution

Ohmic drops. (iii) Microsystem energy devices could enhance efficiency, energy density, and materials utilization in large scale if they are designed appropriately with microscale features to facilitate the transport of reactants, products and ionic charge carriers. (iv) Miniaturized flow-based electrochemical systems such as electrolyzers could be potentially implemented into electronic devices and achieve energy densities that exceed those of batteries. (v) Typical microelectrolyzers can support up to several Acm^{-2} current densities. In the light-absorber of photovoltaics, the current densities are in the order of 10 mA cm^{-2} . This implies that a relatively large photovoltaic device can be combined with miniaturized electrolyzers for optimum cost and performance. Hence, if microfluidic systems can be industrially translated into viable devices, it will serve better efficiencies.

7. Conclusions

If seawater could be directly split with renewable electricity without the reverse osmosis purification step, it would not only be a sustainable source but also help to avoid the larger space requirements and system engineering related auxiliary steps. Based on the discussion, it can be concluded that membrane-less electrolyzers can be used for seawater splitting. Because membrane is the part that is mostly affected by the pollutant present in the seawater. Being membrane-less, the system has the potential to get rid of high cost associated with the sensitive PEM or AEM membranes. Moreover, membrane-less electrolyzers will help researchers to focus on only OER selective electrode design, and thus will simplify the research strategy. We envisage that concentration gradients can potentially be utilised in a membrane-less microfluidic system. Based on this insight, a novel design is proposed in this article for potential application in seawater electrolysis. This will open up new strategic research for single-step direct seawater splitting (DSS).

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.

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