

# Dual-Use of Seawater Batteries for Energy Storage and Water Desalination

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Seawater batteries are unique energy storage systems for sustainable renewable energy storage by directly utilizing seawater as a source for converting electrical energy and chemical energy. This technology is a sustainable and cost-effective alternative to lithium-ion batteries, benefitting from seawater-abundant sodium as the charge-transfer ions. Research has significantly improved and revised the performance of this type of battery over the last few years. However, fundamental limitations of the technology remain to be overcome in future studies to make this method even more viable. Disadvantages include degradation of the anode materials or limited membrane stability in aqueous saltwater resulting in low electrochemical performance and low Coulombic efficiency. The use of seawater batteries exceeds the application for energy storage. The electrochemical immobilization of ions intrinsic to the operation of seawater batteries is also an effective mechanism for direct seawater desalination. The high charge/discharge efficiency and energy recovery make seawater batteries an attractive water remediation technology. Here, the seawater battery components and the parameters used to evaluate their energy storage and water desalination performances are reviewed. Approaches to overcoming stability issues and low voltage efficiency are also introduced. Finally, an overview of potential applications, particularly in desalination technology, is provided.

## 1. Introduction

The global shift toward sustainability has intensified the development of new materials and technologies, constant improvement, and creative redesign.<sup>[1,2]</sup> The large-scale implementation

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of renewable, green energy goes hand-in-hand with the digitalization of our power distribution grid and the rigorous use of energy storage technologies.<sup>[3]</sup> Electrochemical energy storage (EES) plays a crucial role in this context, from enabling mobile computing and communication to large-scale intermittent power storage.<sup>[4]</sup> The so-far best-researched lithium-ion batteries are known for their comparably high energy density, long shelf life, and high energy efficiency.<sup>[5]</sup> Accordingly, they have become an essential power source for consumer electronics, portable devices, and electric vehicles. However, lithium-ion batteries mainly face two issues. First, lithium is a limited resource on our planet, which induces a future hard limitation to lithium-ion battery technology proliferation.<sup>[6]</sup> This shortage has increased the global quest to explore alternative lithium sources, such as hydrothermal water, seawater, and mining water.<sup>[7–9]</sup> Second, lithium-ion batteries' high cost and safety issues make it hard to meet the continuously increasing demand for electronic devices, both portable electronic

devices and large-scale stationary devices.<sup>[5,10]</sup> The high cost comes from the limited availability and exceeding the demand for lithium, nickel, and cobalt (in addition to price fluctuations due to fluctuating trade markets).<sup>[11]</sup> The safety concern arises from the toxicity of cobalt and the flammable organic electrolytes. Interesting energy storage systems beyond lithium attract attention and have been explored in past years.<sup>[12,13]</sup>

Over the last years, several alternatives to lithium-ion batteries have been researched. In particular, the pure focus is placed on naturally occurring alkali metal ions such as sodium and potassium, which offers the possibility of low-cost energy storage systems.<sup>[14–16]</sup> Simultaneously, multivalent charge carriers such as  $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Al^{3+}$ , and others are investigated, which theoretically transfer more than one electron, thus offering the possibility of a higher specific capacity and a higher energy density.<sup>[17–20]</sup> Especially sodium-ion batteries have received particular attention since 2011, as sodium is one of the most abundant elements on earth, offering the potential for low-cost energy storage systems.<sup>[21–24]</sup> Sodium is abundant in seawater and can be easily extracted from it. Another advantage is that Na-ion batteries do not require cobalt, which is still needed in Li-ion batteries. Most of the cobalt used today to make Li-ion batteries is mined in socially and environmentally challenged regions.<sup>[25,26]</sup> Thus, developing a promising

post-lithium energy storage technology with all its changes and optimizations represents an approach to the UN's Sustainable Development Goals (SDGs) claims. For example, direct contributions can be made to the areas outlined in the SDGs, which include the following indicators and measures: sustainable water management, sustainable consumption, production and development of communities, climate change mitigation, sustainable use of the oceans and terrestrial ecosystems, and affordable and clean energy. Sodium-ion-based and other beyond-lithium technologies can capitalize on know-how and materials available from decades of lithium-ion battery research and development.<sup>[27]</sup> In contrast, the Na-ion battery technology is still under development.<sup>[28,29]</sup> Researchers are working to increase its lifespan, shorten its charging time, and make batteries that deliver many watts of power.

Besides energy storage, sustainable water use is another vital part of sustainable development in the 21st century. According to the United Nations, ≈3 billion people currently have limited access to safe drinking water.<sup>[30]</sup> Two out of three humans will face water-stressed situations worldwide by 2050.<sup>[31]</sup> The oceans account for about 97% of the Earth's water, which has the great potential to be the drinking, agricultural, and industrial water resources. This particularly applies to the emerging global hydrogen economy, where seawater is an abundant source of water used for hydrogen production.<sup>[32]</sup> So far, various desalination technologies have been explored, which could be divided into thermal methods (i.e., multieffect distillation,<sup>[33]</sup> multistage flash distillation<sup>[34]</sup>), membrane-based processes (such as reverse osmosis<sup>[35]</sup>), and electrochemical methods (like electro-dialysis,<sup>[36]</sup> capacitive deionization,<sup>[37]</sup> desalination batteries,<sup>[9,38]</sup> desalination fuel cells<sup>[39,40]</sup>), according to the mechanism. Reverse osmosis is dominant in desalination with an energy consumption of 3–5 kWh m<sup>-3</sup>, which consumes more than 70% of the energy of the whole seawater desalination plants.<sup>[41,42]</sup> More energy-efficient technologies are required for large-scale seawater desalination.

A derivative of the rechargeable sodium-ion battery (NIB) is the rechargeable seawater battery, which could carry out simultaneous energy storage and desalination due to its unique configuration. Seawater, covering about two-thirds of our planet and a sodium concentration of around 470 mM, is a quasi-abundant resource of sodium ions.<sup>[43]</sup> The first commercial primary seawater batteries, which means cells that cannot be recharged, were developed in 1943.<sup>[44]</sup> The research field was re-energized with a focus on secondary (rechargeable) seawater batteries in 2014.<sup>[45,46]</sup> Aqueous rechargeable sodium-ion batteries are a promising and environmentally friendly way to store electrochemical energy by circulating seawater as a low-cost electrolyte; they eliminate many of the safety problems of organic electrolytes.<sup>[18]</sup>

A typical rechargeable seawater battery contains an organic electrolyte side and an aqueous electrolyte side, separated by the solid sodium diffusion membrane.<sup>[43]</sup> The organic parts resemble the typical NIB with elemental sodium as an anode. If the seawater battery is contacted with seawater, the catholyte's free and abundant sodium ions can migrate into the anode compartment during the charging process. They are ultimately stored as elemental sodium metal. At the cathode side, the oxygen evolution reaction

(OER,  $4\text{OH}^- \leftrightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$   $E = 0.77\text{ V vs SHE}$ ) produces a theoretical cell voltage of 3.48 V.<sup>[45]</sup> The sodium ions are rereleased and transferred to the seawater during the subsequent discharge, and the dissolved oxygen is reduced (oxygen reduction reaction, ORR).

Since the rechargeable seawater batteries entered the market in 2014,<sup>[47]</sup> most works have optimized the performance, including the anode and cathode materials, anolyte and catholyte, and cell architecture.<sup>[45]</sup> However, there is a lack of systematic review that analyzes the relationship between the components of rechargeable seawater batteries, their application in desalination systems, and their performance. This may correlate with a separation between the energy storage and electrochemical water desalination communities; in our view, both communities are strongly linked and situated within the critical water/energy research nexus. The realization that batteries are electrochemical ion management/ion storage devices is a key to unlocking unseen synergy between the battery and desalination communities.<sup>[48]</sup> Dual functionality may help to address, at the same time, storing intermittently available renewable energy and providing clean, potable water to residential areas and agriculture. A growing amount of desalinated water will also significantly advance the large-scale production of green hydrogen.

We provide a review to meet the need for crossing disciplines and application areas along with sustainable electrochemical application and exemplify the synergy and dual-use application for the intriguing system of seawater batteries. This review introduces the component and properties of rechargeable seawater batteries and explores the possible reason for the demerits. Subsequently, we summarized the adopted approaches to overcome these drawbacks, including the materials design, cell-structure adjustment, and parameters optimization. Additionally, the applications of rechargeable seawater batteries are presented. Finally, the challenges faced by rechargeable seawater batteries and prospects for their further development are discussed.

## 2. Rechargeable Seawater Batteries

Conventional seawater batteries enable the storage of electrochemical energy by combining a sodiation/desodiation anode and an electrolysis cathode. This concept mandates an open-cell architecture to be able to constantly supply fresh seawater as the catholyte during the charge–discharge process. Based on the evaluation and continuous improvement of the cell parts, the electrochemical performance such as the stability, power, voltage efficiency, Coulombic efficiency, and other parameters of the resulting cell is then evaluated and reflects the current state of the art.

### 2.1. Rechargeable Seawater Battery Design and Components

To combine the individual components of a seawater battery into a functioning and efficient cell, it is necessary first to optimize and examine all the individual elements. The essential components of the seawater battery are electrode materials

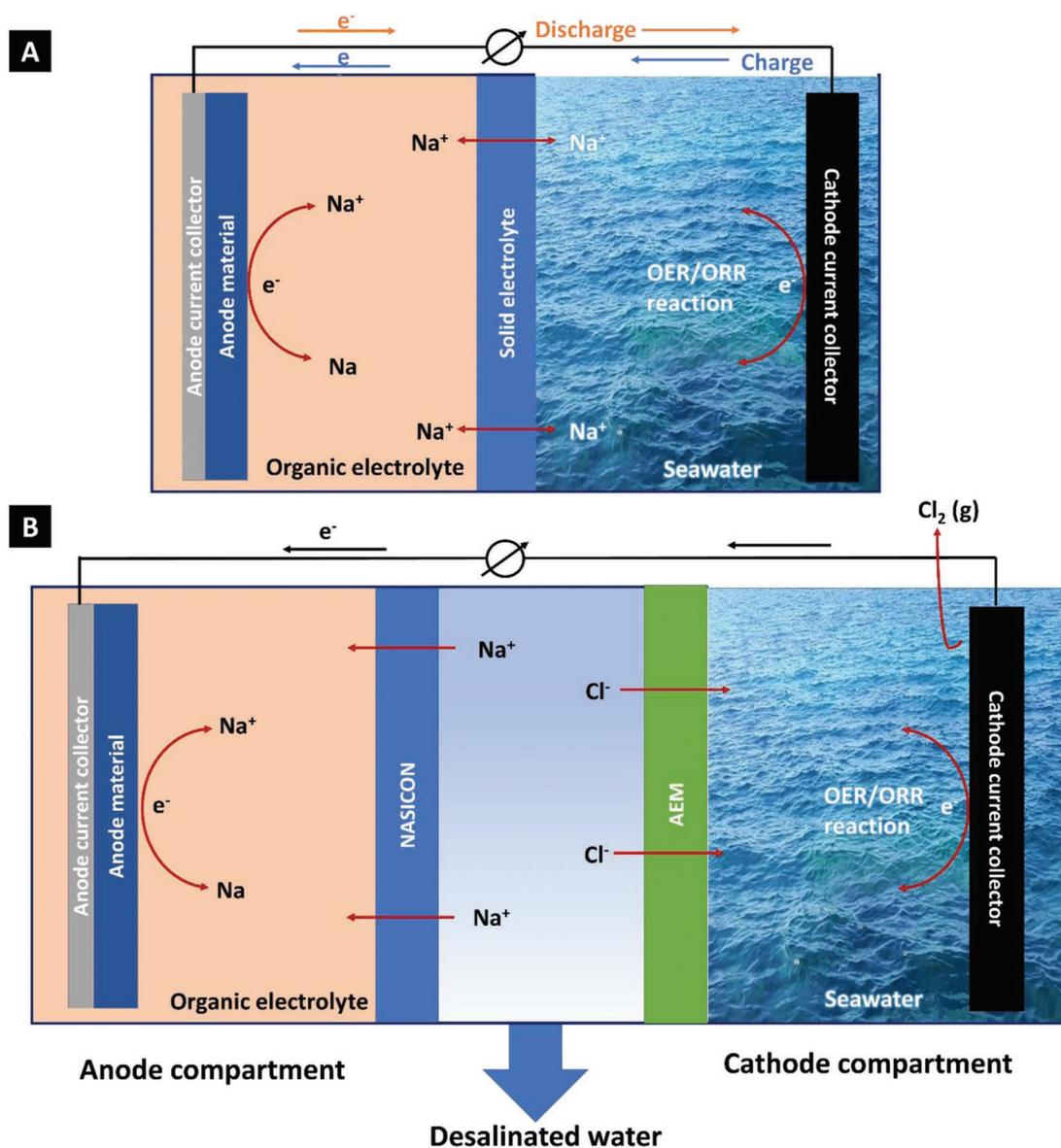
(cathode and anode), electrolyte (anolyte, catholyte), current collector, ceramic solid electrolyte, electrocatalyst, and the general cell type. The following sections explain the requirements for the individual components, what needs to be considered and optimized, and the current research state.

### 2.1.1. Anode

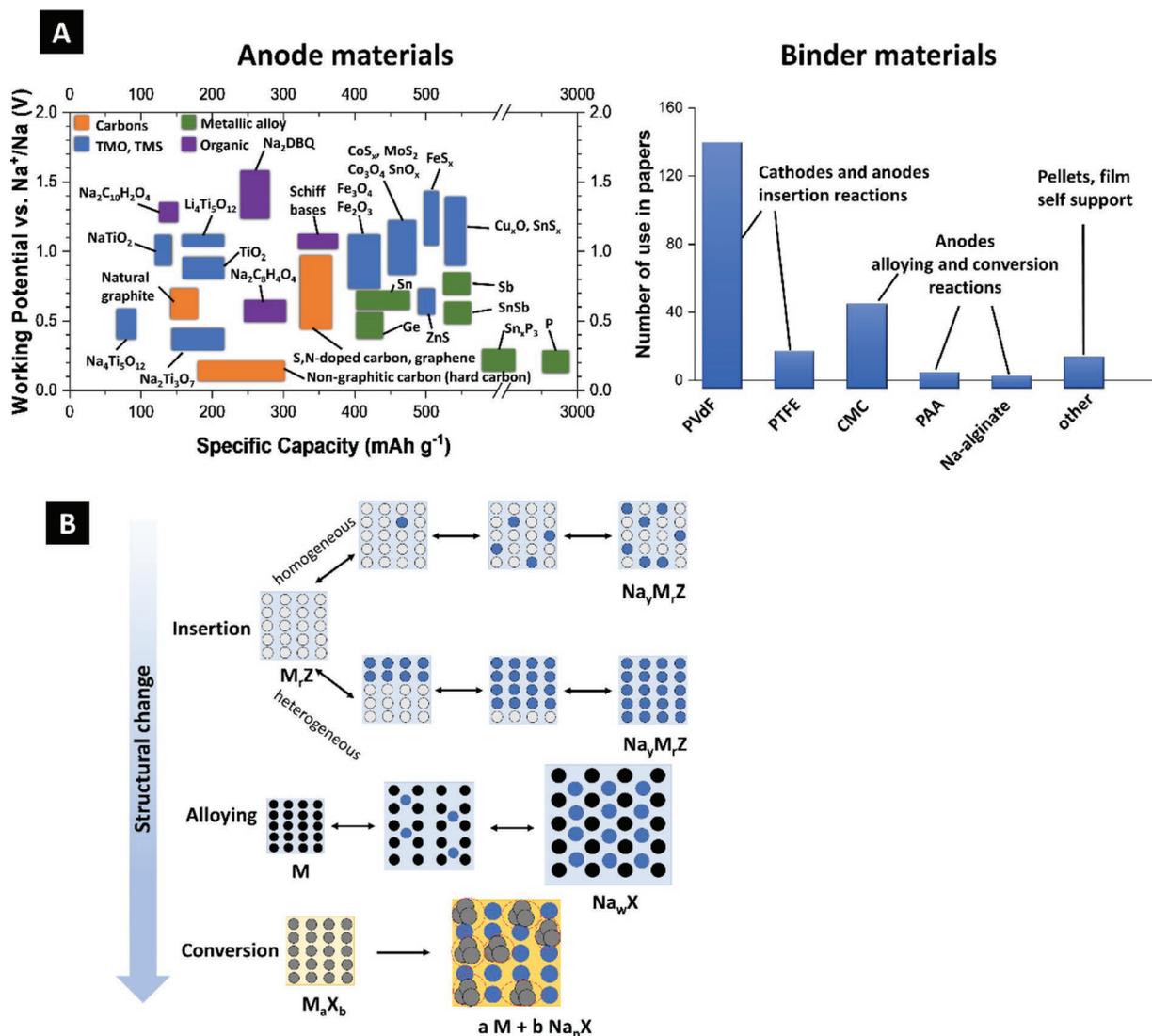
A seawater battery basically consists of an anode in an organic electrolyte and a seawater cathode with a current collector. This design allows its use both as an energy storage system and for water desalination (Figure 1). A high-performance seawater battery needs an optimized anode compartment, including electrolyte and electrode material.<sup>[43,49–51]</sup> The cell's anode in the past consisted of an organic electrolyte and an electrode material used as a negative electrode. In addition to the ability to uptake

ions reversibly, anode materials and the associated anode compartments must fulfill several criteria. Apart from avoiding side reactions leading to cell swelling and failure, the anode material must combine good conductivity, a suitable electrochemical stability window at a low voltage range, and low cost and toxicity.<sup>[52]</sup> Elemental sodium is highly abundant and frequently used as an electrode material, with a very high theoretical capacity of 1166 mAh g<sup>-1</sup>.<sup>[43,53–56]</sup> However, uncontrolled growth of sodium dendrites hinders safe battery operation, ruptures separators, and shortens the device lifetime while still exhibiting low Coulombic efficiency and battery performance.<sup>[57–61]</sup> Finally, light metals or alloy materials such as magnesium or aluminum promise access to a high theoretical specific capacity (Mg: 2200 mAh g<sup>-1</sup>, Al: 2980 mAh g<sup>-1</sup>) and can be considered as possible electrodes as well.<sup>[62,63]</sup>

The wealth of materials developed initially for high-performance electrodes of sodium-ion batteries can be capitalized on.



**Figure 1.** The operation principle of seawater battery A) for energy storage and B) for water desalination.



**Figure 2.** Overview of anode materials for sodium-ion batteries. A) Representation of the theoretical capacities of different anode materials and respective binder use in sodium-ion batteries. Adapted with permission.<sup>[214]</sup> Copyright 2017, Royal Society of Chemistry. B) Schematic representation of varying reaction mechanisms observed in electrode materials. Adapted with permission.<sup>[214]</sup> Copyright 2009, Royal Society of Chemistry. Abbreviation: PTFE = polytetrafluoroethylene, PVdF = polyvinylidene difluoride; CMC = carboxymethyl cellulose, PAA = polyacrylic acid, Na<sub>2</sub>DBQ = disodium salt of 2,5-dihydroxy-1,4-benzoquinone.

Figure 2 schematically presents different reaction mechanisms of electrode materials and the expected theoretical capacities of these materials in sodium-ion batteries. Different types of anode materials interact with sodium in specific ways, including intercalation or conversion and alloying reactions. A commonly used intercalation material such as hard carbons can be adopted from its use in NIBs.<sup>[51,64–68]</sup> Other cation intercalation materials are TiO<sub>2</sub>, Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, or Na<sub>7</sub>Ti<sub>3</sub>O<sub>7</sub>, the associated theoretical capacities of 335,<sup>[69]</sup> 175,<sup>[70]</sup> and 177 mAh g<sup>-1</sup>,<sup>[71]</sup> respectively. Nevertheless, these values are moderate compared to large charge transfer capacities associated with processes such as alloying and conversion reactions.

Alloying materials form Na-rich intermetallic compounds through alloying reactions and promise high-capacity materials due to their specific reaction mechanism.<sup>[72]</sup> However, these materials have a significant volume expansion during

sodiation and desodiation, potentially leading to capacity fading.<sup>[73,74]</sup> The strong forces can break the electrode and damage the electrode material. Some approaches are already known to prevent this rapid loss of capacity. For example, the volume change can be buffered, and composites can maintain the conductive path in the electrode with carbon or other layer-like structures. Successful applications in seawater batteries include Sn–C<sup>[75]</sup> in an ionic liquid electrolyte or red phosphorous.<sup>[49]</sup>

Conversion-type materials accomplish reversible charge storage via a phase transformation.<sup>[76]</sup> The solid-state reactions result in new compounds with new properties. Conversion materials also exhibit a relatively large voltage hysteresis, providing low energy efficiency during charge/discharge cycling.<sup>[77,78]</sup> Conversion materials also suffer from a significant volume change during cycling.<sup>[79]</sup> As already reported material in a seawater

battery,  $\text{Sb}_2\text{S}_3$  is a model material with a multistep conversion and alloying charge storage process.<sup>[80]</sup> In a seawater full-cell, the synthesized antimony sulfide nanoparticle aggregates provided a specific capacity of 470–485 mAh g<sup>-1</sup> at a discharge voltage of about 1.9 V after 50–70 charging and discharging cycles (corresponding Coulombic efficiency: 83–88%).<sup>[81]</sup> By contrast, the initial discharge capacity was relatively low.<sup>[81]</sup>

Comparing the specific capacities by using alloying or conversion-based materials in contrast to intercalation anode materials, one obtains values about 4–5 times as high. Typical carbon materials in seawater batteries provide a capacity of about 100–200 mAh g<sup>-1</sup>, which is much smaller than alternative systems, such as red phosphorus (900 mAh g<sup>-1</sup>; **Table 1**).<sup>[49]</sup>

### 2.1.2. Cathode

The unique design of seawater batteries and the underlying electrochemical processes make it impossible to use common battery electrode materials found in sodium-ion batteries. Also, the wettability of the cathode current collector and seawater catholyte must be considered to improve the battery performance (voltage efficiency).<sup>[82]</sup> Since an electrocatalytic process is used, the cathode employs only seawater and a current collector. Referring to standard seawater data, the amount of salt in one liter of water reaches about 35 g.<sup>[83]</sup> In addition to the main component of sodium chloride, many other cations and anions are found in standard seawater, such as magnesium, calcium, potassium, sulfates, bicarbonates, and fluorides (**Figure 3A**).<sup>[83]</sup> The composition of seawater varies from place to place, depth to depth, and time to time, depending on the respective climate, conditions, and environment. Since there is no typical solid electrode in this system, a current collector is still required at this point. Electrons released from the anode part during deintercalation/dealloying are carried away via the current collector. The current collector also carries the cathode reactions (oxygen evolution reactions and oxygen reduction reactions) and is required for the associated charge transport. Compared to organic batteries with solid cathodes, the current collector requires special properties like the stability in saltwater, which is indispensable for their use in seawater batteries.<sup>[53,84]</sup> Besides high electronic conductivity and electrochemical and mechanical stability, other criteria such as large surface area, uniformly distributed transport area, and a low mass are also considered.

Copper and aluminum foils are typical current collectors in alkali metal batteries. Depending on the potential, it can be decided which current collector can be used without forming alloys and other byproducts by also considering the cost-effectiveness. Since these metals are usually not stable in the presence of NaCl and after application of a potential, carbon-based collectors are the most common in seawater batteries.<sup>[45]</sup> A seawater battery current collector offers sites for the cathode reactions and ensures the charge transport. This mandates a large interface surface area, good electrochemical stability, and high electrical conductivity. An attractive current collector material should also be cost-effective and, ideally, based on an environmentally friendly material. These requirements are, in large parts, met by carbon-based current collectors. Carbons

are abundantly available and offer high corrosion resistance in seawater, predestined for use in the former primary seawater batteries with the ORR and HER (hydrogen evolution reaction).<sup>[85,86]</sup> Yet, the limited mechanical stability of carbon provides a limitation to its application.<sup>[47]</sup>

There are different carbon materials explored on the cathode side.<sup>[45]</sup> Carbon felts, which did not exhibit the previously explored weaknesses of carbon current collectors, showed mechanical stability, high flexibility, and conductivity.<sup>[64,84]</sup> **Figure 3B–D** shows scanning electron images of carbons commonly used as cathodes. Senthilkumar et al. investigated the cathode side porous carbon with defects and oxygen functional obtained from bio-organic waste (grapefruit peels).<sup>[87]</sup> The resulting materials provided efficient OER/ORR activities, a discharge capacity of 191–196 mAh g<sup>-1</sup>, and 96–98% Coulombic efficiency over 100 cycles of the full-cell.

Zhang et al. used an electrolytic carbon sponge with an open design and a highly interconnected and macroporous framework.<sup>[84]</sup> The bifunctional electrocatalytic OER and ORR activities yielded a low charge–discharge voltage gap, high voltage efficiency, high-power density, and long-term cycling stability.<sup>[84]</sup> In another work by Park et al., activated carbon cloth was used as a current collector on the cathode side and compared to the performance of a low surface area carbon felt.<sup>[64]</sup> In addition to the OER/ORR electrolytic activity, the carbon cloth electrode provides electrical double-layer formation. The hybrid electrochemical process improved the voltage/energy efficiency (86%) and power performance (16 mA cm<sup>-2</sup>) of high surface area carbon cloth as the current collector for seawater batteries.<sup>[64]</sup>

### 2.1.3. Ceramic Membranes

A sodium-ion-conducting membrane separates the anode and cathode compartments of seawater batteries. Such membrane materials are commonly employed as solid electrolytes in solid-state batteries.<sup>[88]</sup> The stability of the membrane against different types of liquid electrolytes has to be preserved to guarantee stability in organic and aqueous solutions. Essential for the application in an electrochemical system is applying a high current and stability in a relatively wide electrochemical potential window for the highest possible capacity without degrading parts of the cell.<sup>[89,90]</sup> In general, the solid electrolytes in seawater batteries also need to provide high sodium-ion conductivity, robust mechanical property, and ultralow porosity to avoid the penetration of electrolytes.

There are three main types of solid electrolytes that have the possibility of selective Na ion transport: ceramics, polymers, and inorganic composite.<sup>[91–94]</sup> Given the mechanical stability and effective separation of the organic/aqueous sides, inorganic compounds and ceramic membranes are commonly used as solid electrolytes in seawater batteries. The most often used membrane materials are the inorganic  $\beta''\text{-Al}_2\text{O}_3$  or sodium superionic conductor (NASICON) because of the high ion mobility and chemical stability.<sup>[54,88]</sup> A general issue of ceramic membranes is their mechanical brittleness, which imposes specific considerations onto seawater battery design and scalability.

$\beta''\text{-Al}_2\text{O}_3$  is a layered fast ionic conductor closely related to the widely studied class of  $\beta\text{-Al}_2\text{O}_3$  (**Figure 4A**). It consists of

**Table 1.** Comparison and summary of different parameters seawater battery in the state-of-the-art literature. CC: current collector.

| Anode  | Cathode/cathode current collector  | Solid electrolyte  | Liquid electrolyte  | Mechanism | Cell setup   | Capacity  | Coulombic efficiency/voltage efficiency | Refs. |
|--|--|--|---|-----------|--|---|---|-------|
| Prepatterned Cu/Al current collector (anode-free)          | Seawater carbon felt   | NASICON (Na <sub>3</sub> Zr <sub>2</sub> Si <sub>2</sub> PO <sub>12</sub> )  | 1 M NaOTf in DME  | –         | 2465-type coin cells                               | n.a.  | 98%                                     | [127] |
| Sodium with nickel mesh                                    | Seawater Ag foil   | NASICON (Na <sub>3</sub> Zr <sub>2</sub> Si <sub>2</sub> PO <sub>12</sub> )  | 1 M NaCF <sub>3</sub> SO <sub>3</sub> in TEGDME   | OER/ORR   | Seawater test cells (421Energy Co., Ltd)           | n.a.  | 98.6-98.7%<br>90.3%                     | [111] |
| Hard carbon:Super-P carbon black:PvDF 8:1:1                | Seawater carbon paper  | 1 mm thick β'-Al <sub>2</sub> O <sub>3</sub><br>3 mm thick NASICON (Na <sub>3</sub> Zr <sub>2</sub> Si <sub>2</sub> PO <sub>12</sub> ) | 1 M NaCF <sub>3</sub> SO <sub>3</sub> in TEGDME   | OER/ORR   | Seawater cell in water was from (421Energy Co Ltd) | ≈10 mAh g <sup>-1</sup><br>≈120 mAh g <sup>-1</sup> at 0.05 mA cm <sup>-2</sup>       | 91%                                     | [88]  |
| Activated carbon fiber coated with Na metal                | Simulated seawater carbon felt Pt wire Ag/AgCl Ref                               | PE separator NASICON (Na <sub>3</sub> Zr <sub>2</sub> Si <sub>2</sub> PO <sub>12</sub> )   | 1 M NaCF <sub>3</sub> SO <sub>3</sub> in TEGDME   | OER/ORR   | Coin cells   | 20 mAh g <sup>-1</sup><br>0.6 mA<br>(0.3 mA cm <sup>-2</sup> )                        | n.a.                                    | [194] |
| Na metal attached to Ni taps                               | Air cathode S-rGO-CNT-Co powder coating with PVdF on carbon felt electrocatalyst | NASICON (Na <sub>3</sub> Zr <sub>2</sub> Si <sub>2</sub> PO <sub>12</sub> )<br>PE separator  | 1 M NaCF <sub>3</sub> SO <sub>3</sub> in TEGDME   | OER/ORR   | Pouch cells  | n.a.  | n.a.                                    | [112] |
| Hard carbon:Super-P carbon black:PvDF 8:1:1<br>On Cu foil  | Ti mesh carbon Carbon paper  | 0.8 mm-thick NASICON (Na <sub>3</sub> Zr <sub>2</sub> Si <sub>2</sub> PO <sub>12</sub> )   | 1 M NaCF <sub>3</sub> SO <sub>3</sub> in TEGDME   | OER/ORR   | –  | 296 mAh g <sup>-1</sup><br>0.025 mA cm <sup>-2</sup>                                  | 98%                                     | [129] |
| Na metal on stainless-steel CC                             | Seawater   | NASICON membrane   | 1 M NaCF <sub>3</sub> SO <sub>3</sub> in TEGDME   | –         | Seawater battery coin cells                        | 37 mAh g <sup>-1</sup><br>0.5 mA cm <sup>-2</sup>                                     | Na-BP-DME<br>99.5% over<br>10 cycles    | [52]  |
| Al, Mg, and Zn   | NiHCF crystals:carbon black:PvDF 7:2:1 on carbon cloth                           | –  | Seawater  | –         | Two electrode cells                                | 57 mAh g <sup>-1</sup><br>At 1 A g <sup>-1</sup>                                      | n.a.                                    | [55]  |
| Na foil and Na/carbon composite on PAN-based carbon cloths | Seawater carbon felt   | NASICON (Na <sub>3</sub> Zr <sub>2</sub> Si <sub>2</sub> PO <sub>12</sub> )  | 1 M NaCF <sub>3</sub> SO <sub>3</sub> in TEGDME   | –         | Coin cell seawater battery                         | 40 mAh g <sup>-1</sup><br>At 1 mA   | 98%                                     | [218] |
| Na metal or hard carbon Ni tap CC                          | Seawater Ti mesh and a sheet of carbon paper                                     | 0.8 mm thick NASICON (Na <sub>3</sub> Zr <sub>2</sub> Si <sub>2</sub> PO <sub>12</sub> )   | 1 M NaCF <sub>3</sub> SO <sub>3</sub> in TEGDME   | OER/ORR   | –  | 190 mAh g <sup>-1</sup><br>hard carbon<br>0.05 mA cm <sup>-2</sup>                    | ~96–98%                                 | [87]  |
| Using Na metal   | Seawater heat-treated carbon felt  | PE Hong-type NASICON (Na <sub>1+x</sub> Zr <sub>2</sub> Si <sub>x</sub> P <sub>3-x</sub> O <sub>12</sub> , x = 2)                      | 1 M NaCF <sub>3</sub> SO <sub>3</sub> in TEGDME   | OER/ORR   | 2465-coin-cell seawater battery                    | n.a.  | n.a.                                    | [56]  |
| Pristine or graphene-coated Cu                             | Seawater carbon felt   | 1 mm thick NASICON (Na <sub>1+x</sub> Zr <sub>2</sub> Si <sub>x</sub> P <sub>3-x</sub> O <sub>12</sub> , x = 2)                        | 1 M NaOTf-DME   | –         | Modified 2465-type coin cell flow cell             | n.a.  | 95%                                     | [219] |
| Sn-C:Super-P carbon black:PvDF 8:1:1                       | Seawater carbon paper  | NASICON (Na <sub>3</sub> Zr <sub>2</sub> Si <sub>2</sub> PO <sub>12</sub> )  | 1 M solution of NaClO <sub>4</sub> in EC/DEC<br>And sodium bis(trifluoromethanesulfonyl) imide (NaTFSI) and N-butyl-N-methyl-pyrrolidiniumbis(trifluoromethanesulfonyl) imide (Pyr14TFSI) | –         | n.a.   | ~325 mAh g <sup>-1</sup> Sn<br>312 mAh g <sup>-1</sup> Sn<br>0.05 mA cm <sup>-2</sup> | 55% 1 <sup>st</sup> cycle<br>91%        | [75]  |
| Sodium metal/carbon cloth composite                        | Pyridinic-N catalyst, in a carbon cloth CC                                       | 1 mm thick NASICON (Na <sub>3</sub> Zr <sub>2</sub> Si <sub>2</sub> PO <sub>12</sub> )   | 1 M NaCF <sub>3</sub> SO <sub>3</sub> in DME  | OER/ORR   | Coin cell anode Seawater flow battery tester       | n.a.  | n.a.                                    | [169] |

**Table 1.** Continued.

| Anode   | Cathode/cathode current collector   | Solid electrolyte  | Liquid electrolyte  | Mechanism | Cell setup                               | Capacity   | Coulombic efficiency/voltage efficiency                                    | Refs. |
|---|---|--|---|-----------|--|--|--|-------|
| Na metal or hard carbon:carbon black:Super-P:PvDF 8: 1:1 Ni taps CC | CMO nanoparticles: carbon black Super-P:PvDF 8:1:1 Air-electrode CMO catalyst   | NASICON ( $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_3\text{O}_{12}$ , $x = 2$ )               | 1 M $\text{NaCF}_3\text{SO}_3$ in TEGDME  | OER/ORR   | Pouch cell seawater                      | 190 mAh $\text{g}^{-1}$ hard carbon<br>0.01 mA $\text{cm}^{-2}$                  | >96% energy efficiency<br>85%  | [68]  |
| Na metal foil   | Carbon felt catalyst and CC   | 0.8 mm thick NASICON ( $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_3\text{O}_{12}$ , $x = 2$ )  | 1 M $\text{NaCF}_3\text{SO}_3$ in TEGDME  | OER/ORR   | Coin cell                                | n.a.   | n.a.   | [54]  |
| Hard carbon:Super-P carbon black:PvDF 8:1:1                         | Seawater carbon paper   | NASICON ( $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ )                                      | 1 M $\text{NaClO}_4$ in EC/PC<br>1 M $\text{NaCF}_3\text{SO}_3$ in TEGDME   |           | Flowing-seawater cell                    | 118 mAh $\text{g}^{-1}$<br>125 mAh $\text{g}^{-1}$<br>0.05 mA $\text{cm}^{-2}$ . | n.a.   | [67]  |
| Na metal at Ni mesh   | 90 wt% PNC-electrocatalyst:PvDF 9:1 carbon felt CC  | 0.8 mm thick NASICON ( $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ )                         | 1 M $\text{NaCF}_3\text{SO}_3$ in TEGDME  | OER/ORR   | Pouch cell of seawater batteries         | n.a.   | n.a.   | [166] |
| Sodium metal or hard carbon   | P2-type $\text{Na}_{0.5}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ layered electrocatalyst:SP-carbon:PvDF 8:1:1 carbon felt CC | Celgard NASICON  | 1 M $\text{NaCF}_3\text{SO}_3$ in TEGDME  | OER/ORR   | Coin cell Flow cell tester               | 183 mA h $\text{g}^{-1}$ at 0.1 mA   | 85% Coulombic efficiency<br>80% voltage efficiency                         | [66]  |
| Hard carbon: SuperC45: CMC 8:1:1 On Cu foil                         | Seawater Carbon felt  | NASICON ( $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ )                                      | 0.1 M $\text{NaFSI}$ –0.6 M $\text{Pyr}_{13}\text{FSI}$ –0.3 M $\text{Pyr}_{13}\text{TFSI}$ and 0.1 M $\text{NaFSI}$ –0.6 M $\text{Pyr}_{13}\text{FSI}$ –0.3 M $\text{Pyr}_{13}\text{TFSI}$ with 5 wt% EC<br>1 M $\text{NaCF}_3\text{SO}_3$ in TEGDME | OER/ORR   | Coin cell                                | 290 mA h $\text{g}^{-1}$ hard carbon<br>1.0 C (= 300 mA $\text{g}^{-1}$ )        | ILE-EC 98% energy efficiency (80.5%)<br>76.3% for the LE                   | [124] |
| Sodium or hard carbon:SuperP:PvDF 8:1:1 Ni mesh                     | Seawater NiHCF:SuperP:PvDF 8:1:1  | 0.8 mm thick NASICON   | 1 M $\text{NaCF}_3\text{SO}_3$ in TEGDME  | OER/ORR   | Pouch cell                               | 56 mA h $\text{g}^{-1}$<br>20 mA h $\text{g}^{-1}$                               | 95% to 98%   | [65]  |
| Sodium anode Hard carbon Ti mesh                                    | Seawater activated carbon cloth (ACC) and carbon felt (CF; PAN-based, CNF)  | PE 1 mm thick NASICON ( $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_3\text{O}_{12}$ , $x = 2$ ) | 1 M $\text{NaCF}_3\text{SO}_3$ in TEGDME  | OER/ORR   | Coin cell                                | 16.2 mA $\text{cm}^{-2}$   | energy efficiency of 78% ACC-seawater battery<br>CF-seawater battery (60%) | [64]  |
| Na metal or a-Sb <sub>2</sub> S <sub>3</sub> electrode              | Natural seawater air electrode  | 0.8 mm thick NASICON ( $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_3\text{O}_{12}$ , $x = 2$ )  | 1 M $\text{NaClO}_4$ dissolved in a mixture of EC/DEC (1:1) with 5 wt% FEC  | OER/ORR   | Seawater flow cells (421Energy Co., Ltd) | 470–485 mA h $\text{g}^{-1}$<br>0.05 mA $\text{cm}^{-2}$                         | 83–88%   | [81]  |
| Red phosphorus: SuperP:polyacrylic acid 7:1:2 Al foil CC Or Na      | Natural seawater carbon felt  | NASICON ( $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ )                                      | 1 M $\text{NaClO}_4$ in EC:DEC + 5%FEC  | OER/ORR   | Coin cell                                | 900 mA h $\text{g}^{-1}$ composite<br>200 mA $\text{g}^{-1}$ composite           | >92%   | [49]  |
| Na metal Stainless steel  | Natural seawater Activated carbon cloth (ACC-5092-20, Kynol)  | PE NASICON ( $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ )                                   | 1 M $\text{NaCF}_3\text{SO}_3$ in TEGDME  | OER/ORR   | Coin cell                                | n.a.   | n.a.   | [53]  |

Table 1. Continued.

| Anode  | Cathode/cathode current collector | Solid electrolyte   | Liquid electrolyte                  | Mechanism | Cell setup   | Capacity  | Coulombic efficiency/voltage efficiency | Refs. |
|--|-----------------------------------|---|-------------------------------------|-----------|--|---|---|-------|
| Liquid anodes (Na-BPs, Na-PYRs, and Na-BP-PYRs) and the red phosphorus Semiliquid anodes (P/C@Na-BP-PYRs and the P/C@LE) | 0.47 m NaCl carbon fabric         | NASICON (Na <sub>3</sub> Zr <sub>2</sub> Si <sub>2</sub> PO <sub>12</sub> ) | LE: 1 m NaPF <sub>6</sub> in DEGDME | OER/ORR   | 2465-type seawater coin cells seawater flow cell testers | 7.5 mAh cm <sup>-2</sup><br>0.5 mA cm <sup>-2</sup> | n.a.                                    | [124] |

alumina blocks arranged in a spinel structure in between which the mobile sodium cations are postured in conductor planes.<sup>[95]</sup>  $\beta'$ -Al<sub>2</sub>O<sub>3</sub> is characterized by a higher proportion of sodium ions than other compounds in this class, which can be explained by the structural arrangement of the conduction planes, which comprises a network of sodium ions in the stoichiometric compound.

Kim et al. compared  $\beta'$ -Al<sub>2</sub>O<sub>3</sub> with a type of NASICON in a rechargeable seawater battery using a hard carbon anode and seawater as the catholyte.<sup>[88]</sup> It has been shown that protonated H<sub>3</sub>O<sup>+</sup> species in  $\beta'$ -Al<sub>2</sub>O<sub>3</sub> are allowed to pass through the conduction band into the anode compartment of the seawater battery, which in the end leads to not

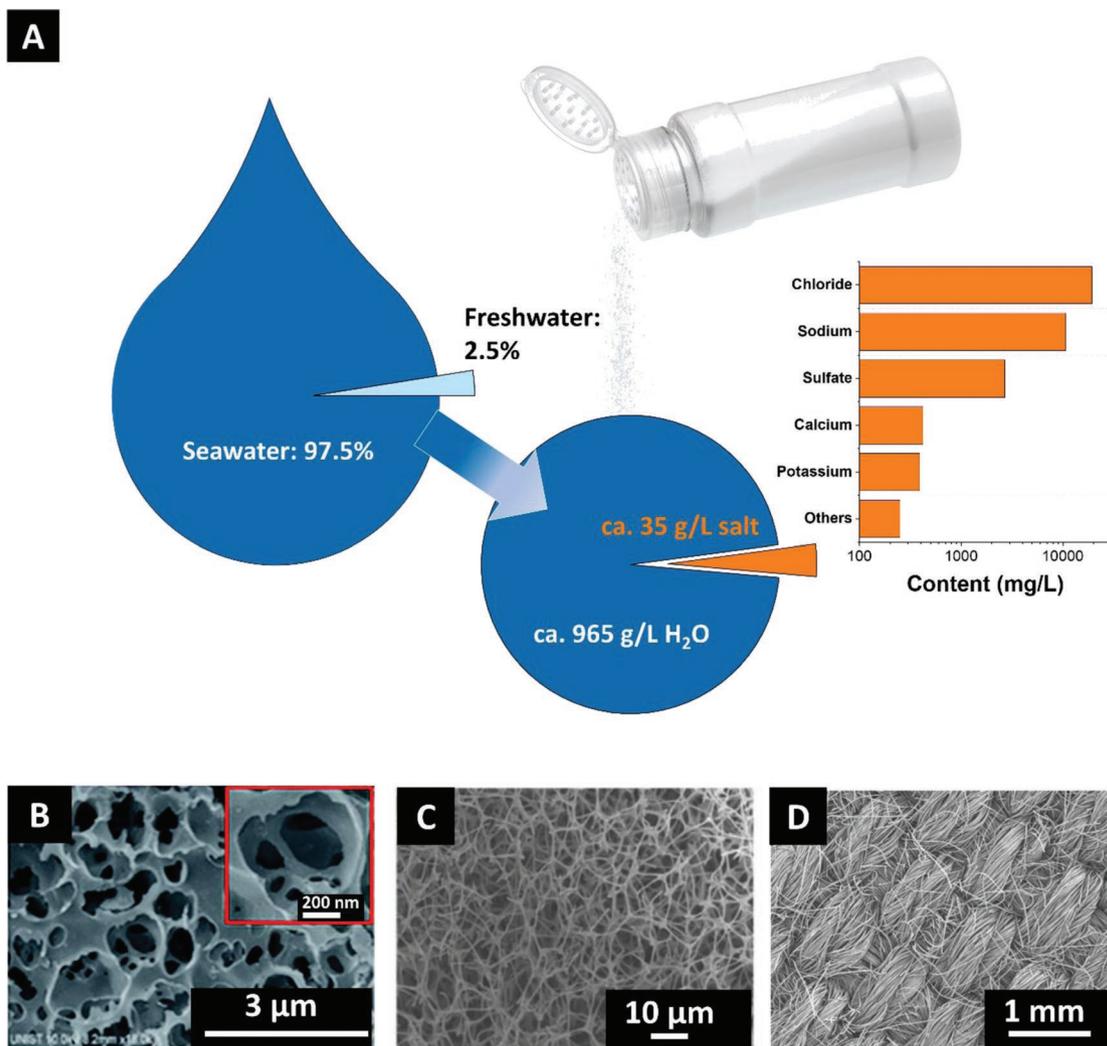
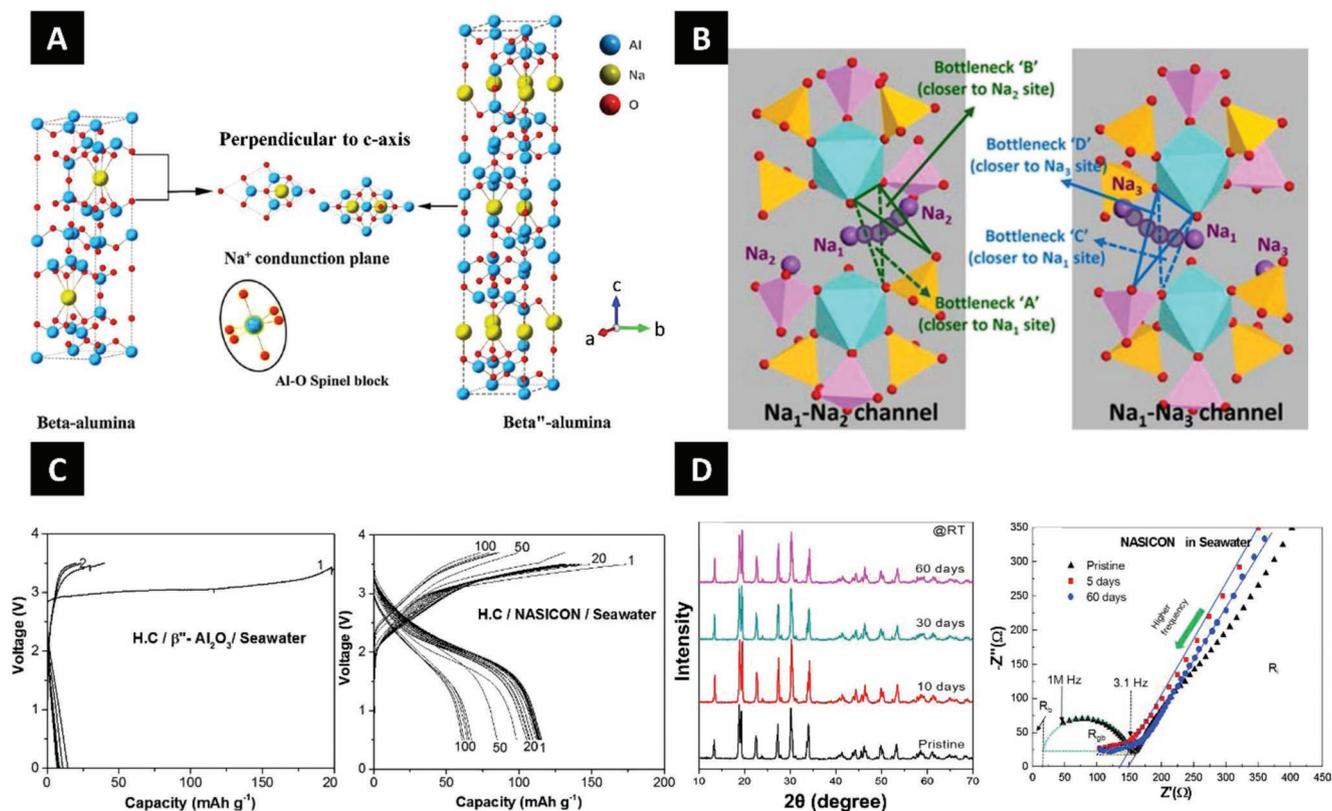


Figure 3. A) Main components and distribution of different ions in natural seawater. Scanning electron images of carbonaceous materials used as cathode current collector in seawater battery B) carbon felt, Reproduced with permission.<sup>[87]</sup> Copyright 2018, Elsevier, and C) carbon sponge. Reproduced with permission.<sup>[84]</sup> Copyright 2019, Elsevier, and D) carbon cloth. Reproduced with permission.<sup>[64]</sup> Copyright 2019, Elsevier.



**Figure 4.** A) The structure of  $\beta$ - $\text{Al}_2\text{O}_3$  and  $\beta''$ - $\text{Al}_2\text{O}_3$ . Reproduced with permission.<sup>[217]</sup> Copyright 2020, Elsevier. B) The structure of  $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ . Reproduced with permission.<sup>[217]</sup> Copyright 2016, American Chemical Society. C) The performance of rechargeable seawater batteries with  $\beta''$ - $\text{Al}_2\text{O}_3$  (left) and NASICON (right) as the solid membrane. Reproduced with permission.<sup>[88]</sup> Copyright 2016, Elsevier. D) Structural changes of  $\beta''$ - $\text{Al}_2\text{O}_3$  and NASICON membranes during stability testing. Reproduced with permission.<sup>[88]</sup> Copyright 2016, Elsevier.

satisfactory matched performance. NASICON-structured materials are desirable because they exhibit high structural stability and fast ionic conductivity ( $10^{-3} \text{ S cm}^{-1}$ ) because of their suitable tunnel size for sodium-ion migration in a 3D framework (Figure 4B).

In general, there are mainly two different NASICON types found for seawater batteries. The Hong-type NASICON ( $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ) offers the advantage compared to the von Alpen-type ( $\text{Na}_{1+x}\text{Zr}_{2-x/3}\text{Si}_x\text{P}_{3-x}\text{O}_{12-x/3}$ ) NASICON that it can be produced at lower temperatures ( $1250^\circ\text{C}$ ), even compared to  $\beta$ - $\text{Al}_2\text{O}_3$  ( $\geq 1600^\circ\text{C}$   $\beta$ - $\text{Al}_2\text{O}_3$ ,  $\geq 1300^\circ\text{C}$  Alpen-type NASICON), and still achieves very high densification.<sup>[96,97]</sup> In some works, the density ( $\leq 78\%$ ) of the synthesized NASICON membranes only insufficiently prevents water from penetrating the membrane. For this reason, the remaining open pore channels are filled with epoxy resin.<sup>[90,98]</sup> A recent report by Go et al. reported that a vA-NASICON ( $\text{Na}_{3.1}\text{Zr}_{1.55}\text{Si}_{2.3}\text{P}_{0.7}\text{O}_{11}$ ) has even better and more suitable properties compared to the Hong-type NASICON.<sup>[99]</sup> Due to the changed composition and the microstructure, higher ionic conductivity and a lower grain boundary resistance can be obtained. In addition to the higher bend strength, an improved voltage efficiency and higher power output for use in a seawater battery could be demonstrated in this way.<sup>[99]</sup>

NASICON structures are known for their use as materials in sodium-ion batteries, both as electrode material and solid

electrolytes. Goodenough and Hing discovered this electrode material and showed the formula  $\text{Na MMA}(\text{XO}_4)$ , where M and MA represent metals and X are silicon, phosphorus, or sulfur.<sup>[100,101]</sup> Due to the diverse use and the different structure of NASICON structures, a unique and targeted design is possible. Their open framework allows them to intercalate up to four sodium ions, making them a promising electrode material in sodium-ion batteries.<sup>[102]</sup> With their fast ionic diffusion, relatively high structural facile production/synthesis, stability in different solvents, and rich structural diversity, they are also attractive for seawater batteries. The catholyte, seawater, provides an ample supply of sodium ions to be transported across the NASICON membrane. Corrosion is inevitable even for NASICON, which provides much higher stability than  $\beta''$ - $\text{Al}_2\text{O}_3$  membranes (Figure 4C,D).

In the work of Kim et al., NASICON membranes were immersed in seawater for several days.<sup>[88]</sup> A slight change in the crystalline structure was observed due to changes in intensity ratios in the subsequent X-ray analysis, which was also reported in other publications.<sup>[103,104]</sup> A proposed mechanism can be attributed to a topotactic ion exchange between  $\text{Na}^+$  and  $\text{H}_3\text{O}^+$  ions at the surface of the NASICON grains.<sup>[103,104]</sup> Many factors influence this behavior, such as the applied current density, which at high rates ( $2 \text{ mA cm}^{-2}$ ) causes structural degradation with irreversible phase deformation and  $\text{Na}^+$  extraction.<sup>[54]</sup> However, further detailed investigations need to be carried out

in the future to better understand this process (and membrane degeneration in general).

#### 2.1.4. Liquid Electrolyte

Besides the solid electrolyte (membrane), a thorough selection of the liquid electrolyte is of defining importance. In sodium-ion batteries, an inorganic conductive salt dissolved in organic solvents is mainly used to guarantee ionic conductivity between the electrodes. The key points that apply here, such as a wide electrochemical stability window, thermal stability, or a low electronic conductivity, can only address the needs of the seawater battery to a minimal extent. However, this type of electrolyte shows relatively low stability at low potentials, so the Coulombic efficiency is generally low in the first cycles. The solid electrolyte interphase (SEI), the protective cover layer at the electrode surface, is also formed due to electrolyte decomposition.<sup>[105]</sup> The ideal liquid electrolyte would combine high ion mobility, high electrochemical stability, low cost, natural abundance, and low environmental impact.

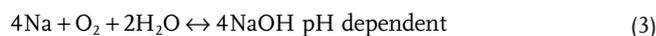
The electrolyte stability and SEI formation are essential in seawater batteries' operation and stability. The SEI is a passivating and isolating boundary layer that, ideally, protects the active material from direct contact with the electrolyte.<sup>[105]</sup> The SEI prevents continuous and degradative reactions between the electrolyte and the electrode material depending on the applied potential and type of electrode material.<sup>[106]</sup> The SEI is formed during the first cycle because of the (initial) instability stability of organic electrolytes at low potentials.<sup>[107]</sup> Applying organic electrolytes leads to forming a solid and dense SEI at the anode and protects the electrolyte from further decomposition.<sup>[108]</sup> An ideal SEI should have a low electronic but high alkali-ion conductivity, an appropriate thickness, good flexibility, and uniform morphology.<sup>[109,110]</sup> If this layer is too thick, the cell's capacity will decrease. However, especially in the early stage of seawater battery research, an electrolyte adapted from the NIB was often used in the anode compartment; that was later revised and replaced because its properties could not lead to high performance in seawater batteries.

An organic electrolyte that has been one of the most successful in seawater batteries is a 1 M sodium trifluoromethanesulfonate (NaCF<sub>3</sub>SO<sub>3</sub>) solution in tetraethylene glycol dimethyl ether (TEGDME)<sup>[53,64,111,112]</sup> since the SEI layer seems beneficial with the TEGDME-based electrolyte.<sup>[67]</sup> A disadvantage for the anode section is the occurrence of side reactions with resulting gas evolution in this compartment during cycling. This causes a swelling of this cell section; therefore, the battery cell cannot run for a long time and in stable conditions but rather breaks down relatively quickly.<sup>[113]</sup> It is not an easy task to solve this problem due to the high reactivity of the commonly used metallic sodium anode. Thereby, achieving long performance stability remains a tall challenge. Lee et al. developed an alternative system using sodium-biphenyl-dimethoxyethane (Na-BP-DME) as a redox-active.<sup>[52]</sup> This approach allows the chemical and electrochemical stability of the anode side to be optimized, which ultimately represents a decisive advantage for practical applications. Compared with the conventional, nonaqueous

liquid electrolyte (NaTf-TEGDME), the Na-BP-DME anolyte showed enhanced chemical and electrochemical stability with better cycling stability and cost-effectiveness.

#### 2.1.5. Electrocatalyst: Oxygen Evolution Reaction and Oxygen Reduction Reaction

Charging and discharging a seawater battery combines the concurrence of sodium-ion reactions (much common to NIBs) at the anode and an electrocatalytic reaction involving seawater at the cathode/catholyte side.<sup>[68,114]</sup> Due to the usually very open-structured design of the cathode in the seawater battery, this part is continuously exposed to the renewed inflow of oxygen from the environment. The battery cell takes advantage of this and uses this abundant gas directly to discharge as electricity. Due to the excess of (dissolved) oxygen, it actively participates in the redox reaction of the seawater catholyte, which leads to the well-known OER/ORR shown in Equations (1)–(3)



The facile reduction of oxygen dissolved in seawater carries the ORR process. During discharging, the stored chemical energy is converted to electricity, and charge-compensation is accomplished by transferring sodium ions from the anode compartment across the membrane (back) into the seawater. This two-electron reduction pathway process ( $\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{HO}_2^- + \text{OH}^-$ ) is kinetically advantageous but will cause a lower theoretical cell voltage of seawater batteries from 3.48 to 2.9 V with the pH of seawater at 8. This can be avoided by using the selective four-electron reduction pathway ( $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$ ) electrocatalysts, which lead to a thermodynamically favored process (pH = 8) with more charge carriers.<sup>[45]</sup> This reaction plays a crucial role in the process, strongly linked to the resulting cell performance. An electrocatalyst can be used as a critical component to enhance the reaction kinetics, and the cathode current collector can be carefully chosen.

To develop an optimal catalyst for this complex system, the following criteria must be fulfilled: 1) high catalytic activity, 2) high pore volume with a large specific surface area, balancing ion transport, and electrode kinetics, 3) high density of accessible, active sites with a homogenous distribution to enable a low OER and high ORR potential, 4) (electro)chemical and mechanical stability to enable device longevity, 5) high and volumetric activity, and 6) cost-efficiency associated with available resources.<sup>[45]</sup> Electrocatalysts used in seawater batteries can be divided into nonprecious metal oxide-based electrocatalysts (Co<sub>x</sub>Mn<sub>3-x</sub>O<sub>4</sub>,<sup>[68]</sup> Co<sub>3</sub>V<sub>2</sub>O<sub>8</sub> <sup>[115]</sup>), carbon-based electrocatalysts (mostly doped carbon black, nanotubes, porous carbon, graphene, and nanofibers),<sup>[116–119]</sup> and hybrid or composite electrocatalysts (graphene–carbon nanotube–cobalt hybrid)<sup>[112]</sup> as an alternative to the usual precious-metal-based electrocatalysts (iridium oxide, ruthenium oxide, and Pt/C). Catalysts such as

iridium oxide and ruthenium oxide are well-known for providing an attractive OER performance.<sup>[120,121]</sup> Most commonly, Pt/C catalysts are being used as an accelerator for the ORR.<sup>[113]</sup> However, using such noble metal catalysts does not align with the cost sensitivity intrinsic to large-scale applications.<sup>[122]</sup>

### 2.1.6. Cell Design

Since operation with only one electrode compartment is not energy-efficient, operation in the aqueous medium for the anode and cathode sides is not promising. One of the reasons for this is that most high-capacity materials are not stable in aqueous media, and the potential window is limited to the stable range of water (1.2 V). The main seawater battery design can be divided into an organic anode compartment and a seawater cathode compartment. Larger systems are also being designed and successfully used for applications beyond energy storage. These systems are mostly built as dual-use systems; while water is desalinated during the charging process, the charge is stored during subsequent discharging. Therefore, at least one additional compartment is responsible for the desalination, besides the sodium collection compartment and another compartment. This extra compartment, which consists of the seawater and a current collector, is used in this additional application in the work of Bae et al. as a carbon capture compartment.<sup>[123]</sup> In this hybrid system, silver was used to form AgCl particles during the charging of the system and the resulting oxidation on the Ag electrode. For this purpose, Na-ions are brought into the anode compartment in the same step as already done in the well-known seawater battery. In addition, the water is desalinated. In the subsequent discharge process, the Na metal in the Na-compartment is oxidized to ions and made available to the carbon capture side. At the same time, the ORR takes place, generating electrical energy. The presence of Ca<sup>2+</sup> in the seawater and the relaxed OH<sup>-</sup> leads to the formation of CaCO<sub>3</sub> from the CO<sub>2</sub> gas.<sup>[123]</sup>

Seawater battery design also capitalizes on established concepts and components from other energy storage segments (lithium-ion and sodium-ion batteries). So far, a modified coin cell, shown in **Figure 5A**, has been used in most cases, mostly with a direct connection to a flow-type cell tester. The pouch cell is also being used more and more. Recently, new optimization attempts have emerged that employ a rectangular cell produces an improved charge–discharge performance (comparison illustrated in **Figure 5B**). With improved conductivity and efficiency in stacking, this cell should show enhanced competitive performance with other already published commercial battery systems.<sup>[124]</sup>

## 2.2. Criteria Evaluating the Performance of Seawater Battery

The individual parts of the seawater battery are combined in a complex structure and are fully functional, which optimally results in an environmentally friendly battery cell with good performance. The following sections outline the criteria for seawater battery performance. An illustrative graph is given in **Figure 6** showing the actual performance of the seawater battery as well as the future design goals considering different key points

### 2.2.1. Capacity

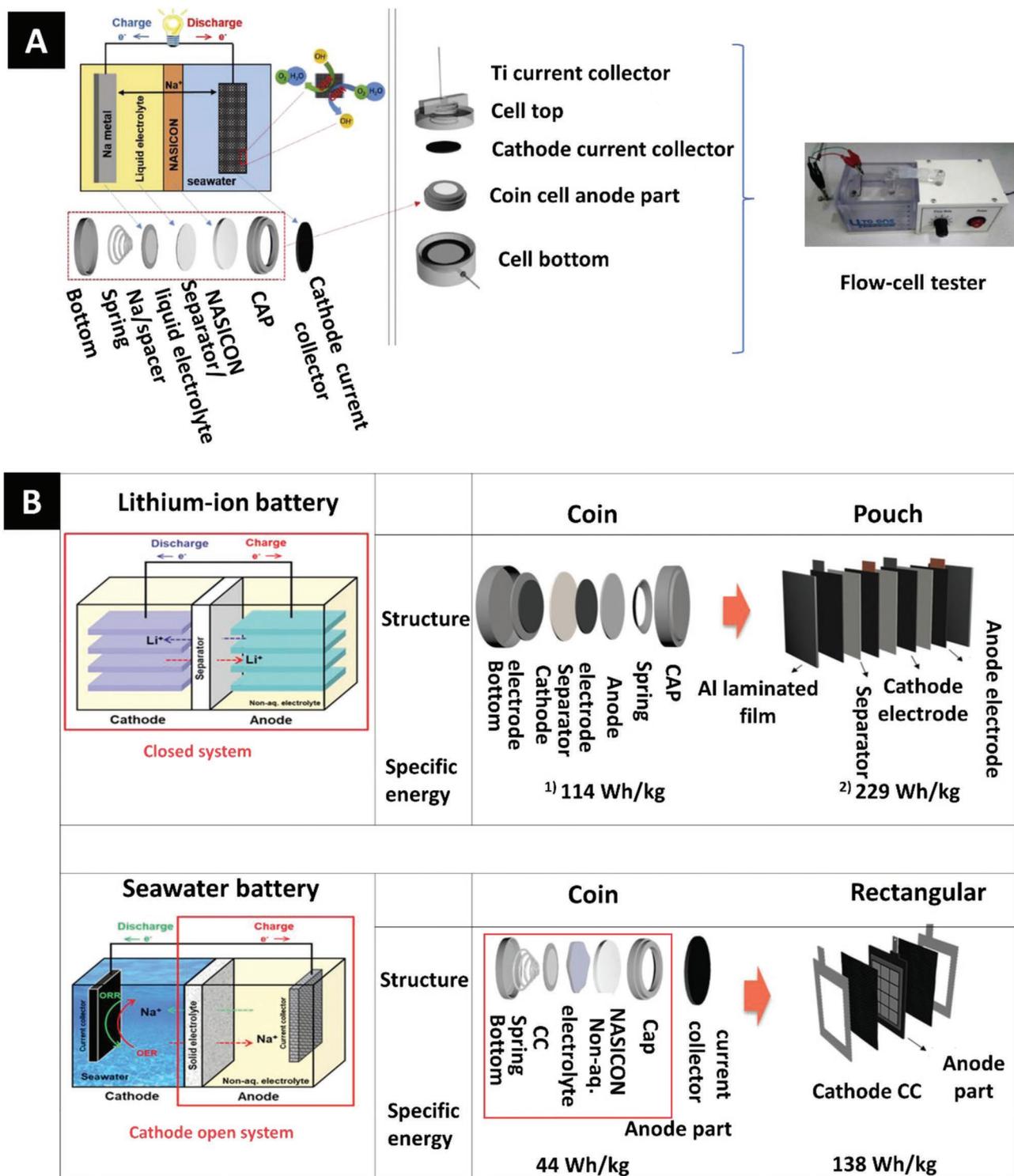
The capacity describes the charge storage capacity of an electrochemical energy storage device. The capacity indicates the amount of electrical charge  $Q$  that a battery can supply or store. Capacity is usually expressed in ampere-hours (Ah), and it is commonly normalized to mass (Ah g<sup>-1</sup>) or volume (Ah cm<sup>-3</sup>), thus forming the basis for the battery field naturalized nomenclature of mAh g<sup>-1</sup>. This index is applied to describe the performance of alkaline metal batteries, as well as likewise for seawater batteries. The capacity also depends on the type/amount of active material, discharge current, discharge voltage, and temperature<sup>[125]</sup> and can be used to calculate how long a given current or how long a specific current, or how much current can be extracted over a specific time. The limit of electrochemical charge storage is the theoretical capacity of a material given by Faraday's law of electrolysis.<sup>[126]</sup> The theoretical capacity cannot be reached in practical applications due to polarization effects or losses due to side reactions or material defects. The overall capacity of the cell can only be as good as the weakest component of a battery. Hence, anode and cathode must provide the same capacity, resulting in a balanced and perfectly composed interaction. While a high capacity is desired, other criteria and parameters are also critical. Typical values of the capacities, which are reached in the state-of-the-art seawater batteries, range from 10 mAh g<sup>-1</sup> ( $\beta'$ -Al<sub>2</sub>O<sub>3</sub> membrane and hard carbon anode<sup>[88]</sup>) to 900 mAh g<sup>-1</sup> (NASICON membrane and red phosphorus anode<sup>[49]</sup>), depending on the used electrode material, based on the reaction mechanism and the applied current.

### 2.2.2. Efficiency

Efficiency is a critical evaluation criterion that describes a particular system's performance, especially for electrochemical systems. Three parameters (Coulombic efficiency, energy efficiency, and voltage efficiency) are typically used in this context.

The Coulombic efficiency (CE) is the ratio of the amount of charge ( $Q$ ) flowing through the cell during discharging and charging and will be expressed as a percentage. Optimally, the standard potential of the cell at the start of charging should correspond to the lower end-of-charge voltage at the subsequent discharge. The Coulombic efficiency is based on losses such as SEI formation and aging effects. Past works show a Coulombic efficiency in the range of 76–98%,<sup>[51,111,127]</sup> whereas commercial lithium-ion batteries typically show values above 99%.

Two more efficiency values are to be considered. First, the voltage efficiency (VE) represents the voltage ratio between charging and discharging, considering the internal resistance and different polarizations. Second, the energy efficiency (EE) is a derivative of the Coulombic efficiency and the voltage efficiency ( $EE = CE \times VE$ ).<sup>[128]</sup> Several conditions, such as the temperature, electrolyte conductivity, specific current, and the selection of the membrane/separator, influence the values of the efficiencies. In general, the efficiency of the seawater battery can be evaluated with all these three factors. Commonly, the Coulomb efficiency is taken as a comparative value to determine the capacity loss cycle by cycle, which is an essential parameter for predicting the remaining battery life.

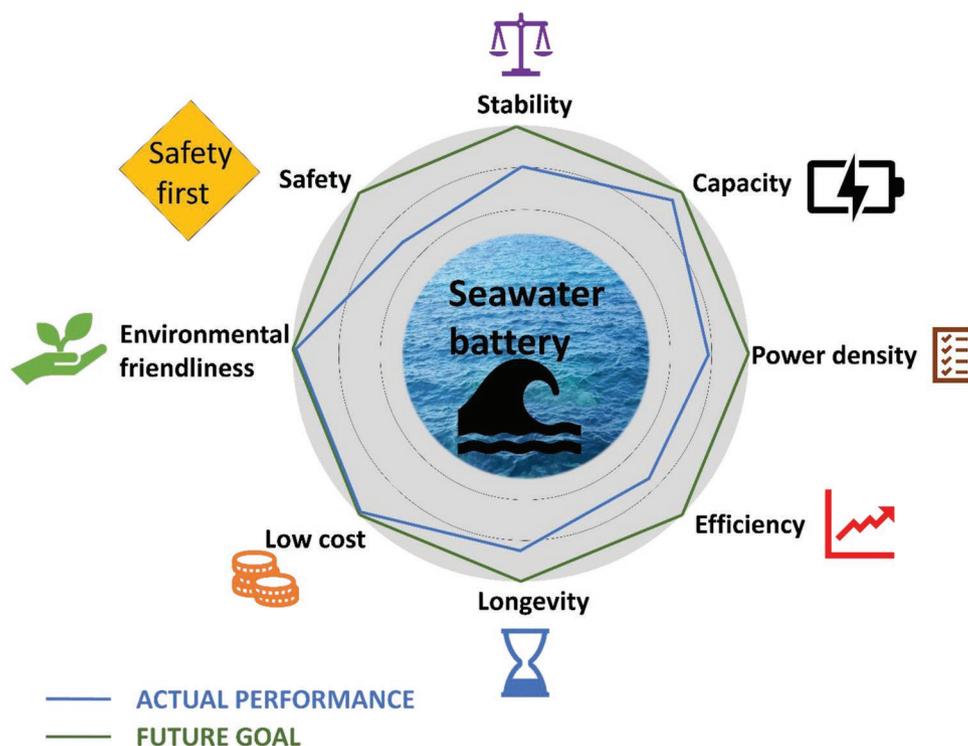


**Figure 5.** State-of-the-art seawater battery cell set up. A) Schematic diagram of the seawater battery (top) and the integrated cell components of the coin-type cell (bottom) and assembled coin-type cell with flow-cell tester adapted and modified with permission from.<sup>[82]</sup> Copyright 2018, Elsevier Note: (1) PD2450 rechargeable Li-ion battery, Routejade. (2) LG325134115 Li-ion polymer battery, LG chem. B) Scheme of the operating mechanism of a lithium-ion battery compared to a seawater battery and the corresponding unit cell adapted and modified with permission from.<sup>[124]</sup> Copyright 2020, John Wiley and Sons. CC = current collector.

### 2.2.3. Stability and Performance Longevity

In addition to the efficiency and capacity, which mainly characterize the instantaneous consumption of a state, the cell's

lifetime and stability are critical parameters for evaluating seawater batteries. In addition to all the other factors involved in the aging of battery cells and several side reactions, the stability of the solid electrolyte in the aqueous medium (NaCl solution)



**Figure 6.** Parameters of designing a good performing seawater battery.

is a limiting factor. The cycle numbers typically reported for seawater batteries are 20–100 cycles<sup>[52,55,56,87,129]</sup> with satisfying capacity retention. Therefore, the aim is to reduce these limiting factors as far as possible to create batteries that are as long-lasting and stable as possible.

#### 2.2.4. Safety and Environmental Friendliness

Seawater batteries present a particular issue as many device types employ both metallic sodium and water. A dangerous and unsafe action can also happen, for example, by forming Na dendrites, which can then cause a short circuit in the cell and trigger a simple ignition of the battery.<sup>[113]</sup>

An equally important aspect is the environmental friendliness of seawater batteries. There is the environmental hazard of some materials used as electrodes or even organic electrolytes. As common in the battery industry, polyvinylidene fluoride (PVdF) with *N*-methyl pyrrolidone (NMP) as its respective solvent is often used to prepare the electrode coating.<sup>[55,130–132]</sup> The environmental concerns of NMP are aggravated by health concerns, such as cancerogeneity and the cause of respiratory difficulties, and excessive mortality mandate to explore safer and greener alternatives.<sup>[133]</sup> As electrolytes are often adopted from the NIB community, the safety risks also apply to seawater batteries. So, the physical hazards associated with conventional  $\text{NaClO}_4$  and carbonate-based electrolytes are well documented.<sup>[134,135]</sup> Sometimes, this can result in elevated temperature, large combustion enthalpy, and high flammability.<sup>[135]</sup>

It is also necessary to consider recycling after the cell has reached the end of its battery life. So far, no work proposes or

applies the recycling of seawater battery components. While the metallic components may be straightforward to recycle and repurpose, issues arise with ceramic ion-exchange membranes. However, the ceramic membranes may well be the most cost-intensive component; therefore, their recyclability may be highly desirable.

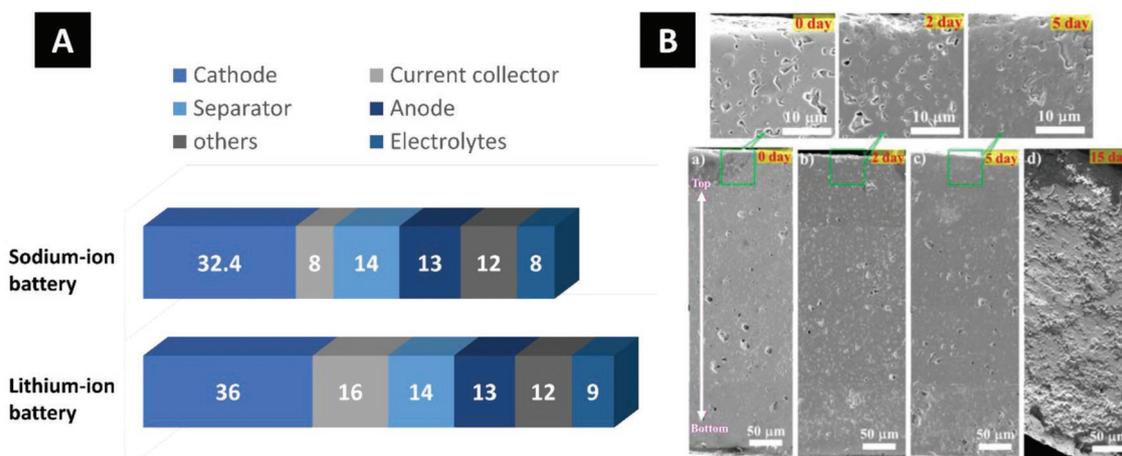
#### 2.3. Limitations and Advantages of Present-Day Seawater Batteries

Due to the growing electrification and increased demand for renewable energy storage systems, exploring alternatives and substitutes to existing primary power sources is necessary. These include, among other things, that the lithium-ion batteries must consider increased prices due to the exhausted resources of Li and the concerns about geopolitical and environmental aspects. Additionally, the typical metal-ions batteries, like lithium-ion and sodium-ion batteries, the cathode accounts for 30% to 35% of the total costs (**Figure 7A**).<sup>[49]</sup>

Using natural seawater as the catholyte is highly cost attractive, abundantly available, and rich in sodium ions. Seawater can be circulated along the aqueous components to mitigate possible heat-buildup in large-scale modules.<sup>[43]</sup> So far, it is not common in the seawater battery community to present the material's rate stability, and only a few works provide such data.<sup>[51]</sup>

##### 2.3.1. Issues at the Anode

On the anode side, if this is not an elementary anode, there are often simply degradation problems compared to those in



**Figure 7.** A) Comparison of cost contribution of each component for lithium- and sodium-ion battery system in percent. Reproduced with permission.<sup>[49]</sup> Copyright 2014, John Wiley and Sons. B) Scanning electron images of the polished surfaces of the Hong-type NASICON ceramic samples immersed in seawater at 80 °C for 0 d, 2 d, 5 d, and 15 d. Reproduced with permission.<sup>[45]</sup> Copyright 2017, American Chemical Society.

a NIB.<sup>[136]</sup> One problem is the proper selection of the binder. Many systems have been adopted directly from the lithium-ion battery community without considering a seawater battery's unique (electro)chemical setting. The choice of the binder significantly influences the battery life, costs, and the avoidance of toxic organic solvents.<sup>[137]</sup> PVdF is a standard binder in lithium-ion batteries. Due to the low number of functional groups, it has the advantage of low reactivity, good adhesion properties, and electrochemical stability.<sup>[138]</sup> Still, PVdF binder can also cause system instability as other side reactions may occur. For example, using fluorinated binders leads to reductions that influence the cell reaction and reduce the capacity and performance of the cell.<sup>[139]</sup> Sodium in the presence of the PVdF binder may also destabilize the cell.<sup>[140]</sup> The decomposition of PVdF weakens the electrode, so individual particles may become detached and act as insulators. This results in lower efficiency and high capacitance loss.<sup>[141,142]</sup> The formation of SEI also has a significant influence on the cell's performance. PVdF, for example, has a significantly lower cycle performance as it continuously reduces carbonate solvents, resulting in a (too) thick or unstable SEI layer.<sup>[143]</sup>

A further problem known from sodium-ion batteries relates to using elemental sodium as an electrode. During electrochemical cycling, dendrites can occur, and uncontrolled growth of tree-like Na dendrites hinders safe battery operation and shortens lifetime while still exhibiting low Coulombic efficiency.<sup>[57–61]</sup> Therefore, limiting or avoiding the growth of sodium dendrites is crucial. The future of seawater battery electrode materials may well be with anode systems that do not require binders or elemental sodium, such as the redox-mediated red-phosphorous semiliquid anode system.<sup>[144]</sup>

### 2.3.2. Stability of the Membrane and Cathode in Saltwater

The selective sodium permeable membrane's stability is highly important for seawater batteries. Like the rarely used  $\beta'$ - $\text{Al}_2\text{O}_3$  membrane, NASICON also shows signs of aging after a certain period (Figure 7B), whereby different stresses build up inside the NASICON ceramic during the structural

degradation process and increased compressive stress can be observed. Likewise, investigations by Jung et al. have described the local compaction of NaCl at the surface, which can be related to a reaction of the chloride ions with the sodium species from the NASICON structure.<sup>[145]</sup> These exposed sodium sites get occupied by  $\text{H}_3\text{O}^+$  ions in a subsequent reaction, which leads to volume changes and intense precipitation of NaCl.

Comparing the energy densities of different energy storage systems, the seawater battery with an energy density of mostly  $<150 \text{ Wh kg}^{-1}$ <sup>[65]</sup> has been relatively moderate. In comparison, considering a commercial lithium-ion battery, a conventional battery can deliver up to four times the energy density ( $250\text{--}590 \text{ Wh kg}^{-1}$ ).<sup>[6,146]</sup> The reasons are complex but can be due to the low capacity, achieved mainly by limitations in the anode and cathode selection and the low working voltage. At least one compartment must continuously be operated in the aqueous medium. However, optimizing the cathode materials remains challenging since they have to be stable in the aqueous medium and resistant to side reactions concerning the OER and ORR.

Despite this knowledge and further studies on undesired side-reactions in OER/ORR on the cathode side, there is still a lack of a more profound understanding of performance failure, especially performance degradation. From the transfer from fuel cells, it could be assumed that the primary carbon material used as a cathode current collector can be oxidized by a corrosion reaction and thus rendered unusable/less efficient.<sup>[147–154]</sup> Another issue is scaling via the possible precipitation of  $\text{CaCO}_3$  in primary seawater batteries.<sup>[155,156]</sup> This process may occur during the cell discharging via the ORR process in seawater.<sup>[53]</sup>

Activated carbon can be an environmentally friendly and (electro)chemically stable choice for the current collector at the cathode side. Past works show that it provides an increased voltage gap (0.6 to 1.42 V) and limited energy efficiency (64–83%).<sup>[53]</sup> The gradual increase in overvoltage and the recovery of voltage efficiency after replacement of the cathode suggests that the cathode is the leading cause of cell performance degradation and that there may be several degradation processes.<sup>[53]</sup> On the one hand, oxidation of the carbon

current collector surface probably occurs, leading to a gradual build-up of the impedance. On the other hand, structural damage to the cathode occurs after a critical running time of the cell.

## 2.4. Approaches to Improve Present-Day Seawater Battery Technology

### 2.4.1. Voltage Efficiency: Enhancing the Kinetics of ORR/OER

**Increasing Concentration of Dissolved Oxygen:** Since seawater batteries use seawater as catholyte, fresh reactants (water and oxygen) must be continuously supplied to the cathode current collector during cell operation.<sup>[45]</sup> If this is not the case, few to no reactants will be available, reactions will be slower and weaker, and the cell efficiency will be low. The concentration of dissolved oxygen in the catholyte can be increased to counteract this limiting factor by flowing seawater continuously through the cell compartment. Han et al. have compared the values of efficiency and overpotential with and without a continuous electrolyte flow. Without flowing the seawater, the charge and discharge voltage of the cell is slowly saturated with a voltage gap of 1.1 V between charging and discharging. By contrast, when the seawater is flowing, that difference decreases to 0.7 V. Thus, it also appears essential to have a continuous flow of seawater catholyte. This may partly be due to the facilitated diffusion of the reaction to the cathode current collector, resulting in reduced concentration polarization during the charge and discharge cycle.

**Synthesis of a New Catalytical Electrode with High Catalytical Activity:** To increase the efficiency, one can use a suitable bifunctional oxygen evolution reaction/oxygen reduction reaction electrocatalyst at the cathode. This approach could effectively reduce the side reactions (like other reactions of Cl<sub>2</sub> with the water) to OER/ORR at high overvoltages.<sup>[68]</sup> These side reactions depend on the applied current, the pH, and the local Cl<sup>-</sup> concentration at the air cathode.<sup>[68]</sup> The large overpotentials that often occur in the charge and discharge cycles result from slow OER and ORR reaction kinetics. This yields a significant difference between the discharging and charging voltage profiles; the low voltage efficiency is accompanied by a low energy storage ability and insufficient cycling stability.<sup>[157–159]</sup>

These problems can be (partially) overcome with effective electrocatalyst systems, which allow the reaction to proceed faster. Mainly elements taken from general catalyst research, such as Pt, Ru, Pd, Au, and Ir, are used. Due to their comparatively high costs and scarce availability, they have not yet established themselves in large-scale industrial use.<sup>[147–154,157,159–161]</sup> Many studies have explored nonprecious metal oxides or heteroatom(s)-incorporated carbonaceous materials. Mixed spinel-type transition metal oxides based on Ni, Co, and/or Mn are promising. For example, Abirami et al. used cobalt manganese oxide with a spinel structure (Co<sub>x</sub>Mn<sub>3-x</sub>O<sub>4</sub>, CMO) as a seawater battery electrocatalyst without noble elements.<sup>[68]</sup> This catalyst accelerated the cathode reactions (OER/ORR) because of the large specific surface area with many electrocatalytically active sites by reducing the voltage gap and enhancing the voltage efficiency to a value of 85%.<sup>[68]</sup>

Further approaches are proposed to eliminate the efficiency problems by synthesizing completely new catalytic electrodes with high catalytic activity. For example, Liu et al. showed Mg-ion-based seawater batteries.<sup>[162]</sup> The porous heterostructure of the synthesized CoP/Co<sub>2</sub>P provided a large specific surface area, abundant active interfaces, and enhanced active sites with accelerated charge transfer.<sup>[162]</sup> This enabled a high hydrogen evolution reaction activity, enhanced performance with good efficiency, and promising stability for Mg seawater batteries.<sup>[162]</sup>

Shin et al. proposed a new electrocatalyst that optimizes the kinetic of the seawater cathode OER/ORR process.<sup>[115]</sup> Co<sub>3</sub>V<sub>2</sub>O<sub>8</sub> with large active sites enabled an increased voltage efficiency of ≈76% by lowering the charge voltage from 3.88 to 3.76 V and increasing the discharge voltage from 2.80 to 2.87 V (compared to a cell without catalyst).<sup>[115]</sup> The resulting seawater battery provided promising cycling stability with voltage gaps of ≈0.95 V.<sup>[115]</sup>

**Modifying the Carbon Current Collector at the Cathode Side:** Side effects of carbon corrosion and scaling via CaCO<sub>3</sub> plague the cathode during the charging process. Preventing irreversible carbon corrosion at the cathode enables a higher voltage efficiency and better cycling stability.<sup>[53]</sup> This can be accomplished by using more corrosion-resistive carbons and catalyst materials.<sup>[163,164]</sup> For example, Tao et al. reported that inducing various defects and the resulting shift of charge in the subsequent electrochemical characterization makes it possible to increase the activity for electrocatalytic reactions (ORR, OER, and HER).<sup>[165]</sup>

The carbon current collector can also be modified by heteroatom doping. This can be explored to improve electrocatalytic activity. For example, Jeoung et al. fabricated PNCs (high surface area, nitrogen-doped carbon) and efficiently adjusted the porosity of PNCs by varying the transformation conditions.<sup>[166]</sup> The mesoporosity was crucial for controlling the electrocatalytic activity and the seawater battery performance. This distinct improvement made it possible also to obtain improved electrochemical properties (stable voltage gaps of <0.53 V at 0.01 mA cm<sup>-2</sup> over 20 cycles),<sup>[166]</sup> thus highlighting the use of PNCs as a promising metal-free catalyst in the seawater battery.

Another effective method to improve the efficiency from several points of view was proposed by Suh et al., who used hydrophilic carbon electrodes on the one hand and a 3D hybrid (S-rGO-CNT-Co).<sup>[112]</sup> The uniform distribution of Co/CoO<sub>x</sub> nanoparticles on the porous 3D graphene creates many active sites, resulting in good cycling stability and rate properties. The additional CNTs, with their high conductivity and stability, prevent rapid cell degradation due to electrode decomposition.

**Hybridizing Catalytic Reaction:** The optimized performance can also be enabled by hybridizing the catalytic reaction with other electrochemical processes or using other electrochemical processes as a substitute. No less attractive and effective is an approach in which the catalytic reaction is combined with another electrochemical process. Park et al. combined ion electrosorption via the formation of an electrical double-layer with the OER/ORR electrolytic activities in activated carbon cloth seawater batteries.<sup>[64]</sup> This lowered the voltage gap to 0.49 V, increased the voltage efficiency to 86%, and yielded increased power performance.<sup>[64]</sup> Kim et al. introduced a silver foil as a chloride ion capturing.<sup>[111]</sup> Silver's reversible Ag/AgCl reaction

with the  $\text{Cl}^-$  ions released from the seawater catholyte at 2.93 V versus  $\text{Na}^+/\text{Na}$  (in the charge and discharge cycle, respectively) bypasses the typical OER/ORR reaction. This process significantly reduced the voltage gap and increased the voltage efficiency to about 90%.<sup>[111]</sup>

#### 2.4.2. Stability

**Eliminating Side Reactions:** The problem of side reactions with a particular binder system and sodium is known from present-day NIB research and occurs in seawater batteries.<sup>[67]</sup> As a promising binder, sodium alginate is very stable, environmentally friendly, and supports the formation of a stable SEI.<sup>[167]</sup> The carboxymethyl cellulose binder, for example, is an environmentally friendly and green material. It is soluble in water, which allows the processing of aqueous pastes. However, due to the solubility in water, only an application in the anode compartment is possible since the electrode on the seawater side would dissolve otherwise. It is mainly used in anodes that have a high capacity.<sup>[137]</sup>

Using elemental sodium as electrode material leads to a high capacity. Still, the cell voltage is limited by the (electro)chemical stability window of water.<sup>[129,168]</sup> Some approaches to overcome this problem have been proposed in past works. For example, Tu et al. proposed a method with enhanced ORR/OER activities of seawater batteries using a cathode made from nitrogen-doped carbon cloth.<sup>[169]</sup> Abirami et al. presented work that used next to the CMO cathode catalyst also a hard carbon electrode as a sodium-free anode; their cell provided a discharge capacity of around  $190 \text{ mAh g}^{-1}_{\text{hard carbon}}$  with an average voltage of about 2.7 V during 100 cycles (corresponding with an energy efficiency of 74–79%).<sup>[68]</sup> Kim et al. proposed a hard carbon anode separated by a ceramic membrane from a carbon paper as a current collector for the seawater cathode side.<sup>[88]</sup> The discharge capacity of the resulting seawater battery was  $120 \text{ mAh g}^{-1}$  after the first cycle, with a resulting Coulombic efficiency of 91% after 20 cycles.<sup>[88]</sup>

Many attempts have been made to counteract the rapid and uncontrolled growth of the Na dendrites. For example, approaches from Li-ion battery chemistry have been adopted, such as adjusting the charge/discharge rate at the current collector, increasing surface tension to suppress the dendrite formation mechanically, or modifying the electrolyte concentration.<sup>[14,61,84,170–177]</sup> Other works explored using a  $\text{NaPF}_6$ /glyme electrolyte, an artificial  $\text{Al}_2\text{O}_3$  SEI layer, various inorganic electrolytes, or sodiated carbon as a nucleation layer.<sup>[178–186]</sup> Using a low current density may further delay dendrite formation and increase the critical nucleation radius.<sup>[171,187–189]</sup> Kim et al. proposed controlling the growth of sodium dendrites rather than avoiding their occurrence altogether.<sup>[189]</sup> Thereby, enhanced performance stability resulted from a low number of sodium dendrite cores formed on the homogenous surface of a graphene-coated copper current collector.<sup>[189]</sup>

**Optimizing of the Anode Compartment:** The liquid electrolyte is of critical importance at the anode because it reduces the interfacial resistance between the anode and the ceramic membrane (which serves as the solid electrolyte); this is important to enabling stable cell performance and efficiency.<sup>[111]</sup> An electrolyte adopted from the NIB was often used in the anode compartment. Still, some studies showed that an ethylene carbonate/propylene

carbonate(EC/PC) electrolyte could not provide sufficient cycling stability.<sup>[49,67,124]</sup> For example, Kim et al. showed for the EC/PC-based electrolyte the formation of a poorly conductive, thick SEI layer and the degradation of the PVdF.<sup>[67]</sup> Successful and high-performance electrolytes based on TEGDME have been developed, which show good cycle performance over 100 cycles and are successfully used in almost every present-day seawater battery.

The areal/absolute capacity of some anode electrode materials can be increased by employing a semisolid anolyte, which includes two redox mediators.<sup>[190]</sup> One of these mentioned anolytes would be, for example, sodium biphenyl, which has been successfully used in combination with a semiliquid negative electrode of red phosphorus for the realization of metal-free Na-seawater batteries. Remarkably, using the semiliquid electrode as a static anode, high area capacities of about  $11 \text{ mAh cm}^{-2}$  in Na half cells and  $15 \text{ mAh cm}^{-2}$  in Na seawater cells could be achieved at room temperature.<sup>[144]</sup> For sodium metal batteries, sodium biphenyl is an attractive and cost-efficient anolyte system, which prevents hydrogen evolution and suppresses sodium dendrite growth, thus increasing the capacity and providing performance stability.<sup>[191]</sup> Ionic liquids (ILs) may be a future choice for high-performance seawater batteries. For example, NaFSI salt in two ionic liquids ( $\text{Pyr}_{13}\text{FSI}$  and  $\text{Pyr}_{13}\text{TFSI}$ ) showed a very high (electro)chemical and thermal stability in combination with the well-known low vapor pressure of IL.<sup>[51]</sup> This was accomplished despite the small amount (5 mass%) of organic solvent (EC) added to facilitate and enable the formation of a stable SEI on the hard carbon anode. In contrast to the typical liquid electrolytes (i.e., organic solvents), ILs show a lower cell polarization resulting in higher energy efficiency.<sup>[51]</sup> Kim et al. used this electrode and anolyte to obtain a capacity of  $290 \text{ mAh g}^{-1}_{\text{hard carbon}}$  with a Coulombic efficiency of 98% during 600 charge/discharge cycles at rates up to 5.0C, and associated energy efficiency up to 80%.<sup>[51]</sup>

## 3. Dual-Use Application: Seawater Batteries for Energy Storage and Desalination

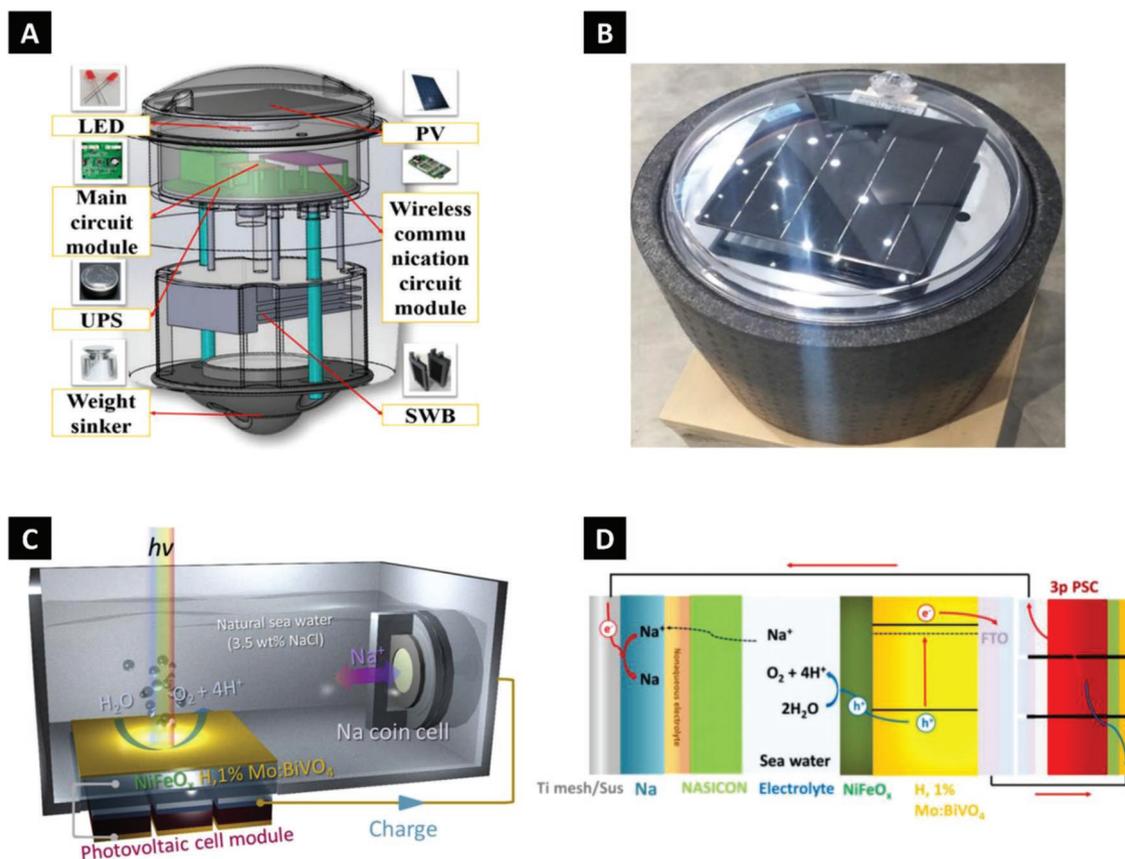
### 3.1. Energy Storage

#### 3.1.1. Wearable Devices

Marine wearable devices like life jackets and wetsuits are usually equipped with lights to illuminate and locate drowning persons. Since the seawater battery utilizes the seawater as the catholyte, it is very suitable for marine wearable devices' power supply. Cho et al. put forward a novel design for marine life jackets.<sup>[192]</sup> It takes advantage of the properties of seawater batteries that generate electricity once the cathode current collector contacts the seawater. Therefore, when people fall into the water wearing the life jacket, the batteries will be activated and charge the in-built global positioning system.<sup>[43]</sup>

#### 3.1.2. Marine Fundamental Facilities

Marine primary public facilities on the ocean, such as light buoys and water-quality monitoring stations, are commonly



**Figure 8.** A) The conceptual diagram and B) optical photograph of seawater battery-based wireless buoy system. Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>[192]</sup> Copyright 2021, the Author(s), Published by IEEE. C) Scheme image of unassisted solar-charging rechargeable seawater battery with NiFeO<sub>x</sub>/BiVO<sub>4</sub> PE combined with PSC or c-Si PVs and D) the mechanism image of it with three pieces of PSC as the example. Reproduced with permission.<sup>[193]</sup> Copyright 2019, Elsevier.

powered by solar batteries assigned with energy storage systems like lithium-ion batteries or lead-acid batteries. Once these batteries have some leakage, the toxic component in the batteries will be released into the sea. Therefore, power with a long lifespan, low cost, and low/no environmental pollution are required. Recently, Kim et al. designed a wireless marine buoy system based on rechargeable seawater batteries.<sup>[124]</sup> The system comprised seawater batteries (energy storage), light-emitting diodes light, the main circuit module, an uninterruptible power supply, a wireless communication circuit module, and photovoltaic batteries (self-powered energy resource), as shown in **Figure 8A,B**. The state-of-charge (SOC) is monitored by Coulomb counting, and variance measurements detect the state-of-health. Through wireless communication, the position of marine buoys and the SOC information of the batteries can be obtained on a mobile phone.

### 3.1.3. Large-Scale Energy Storage

Apart from the small devices, rechargeable seawater batteries are also expected to serve as the energy storage systems for the solar, wind, or tidal power station installed near the ocean. Recently, Kim et al. designed a combined photoelectrode (PE)– photovoltaic (PV) device to accomplish the solar energy-driven rechargeable seawater batteries.<sup>[193]</sup> In the cell, NiFeO<sub>x</sub>/H, 1% Mo:BiVO<sub>4</sub>, and

a series-connection of crystalline silicon solar cells or lead halide perovskite solar cells were applied as the cathode, and the other components were adopted from conventional rechargeable seawater batteries (**Figure 8C**). Oxygen and hydrogen are obtained during the charging process on the cathode side, while on the anode side, the sodium ions precipitate as metallic sodium, as shown in **Figure 8D**. This setup provides an avenue to apply rechargeable seawater batteries independently as marine facilities' power supply without extra power.

## 3.2. Desalination and Water Purification

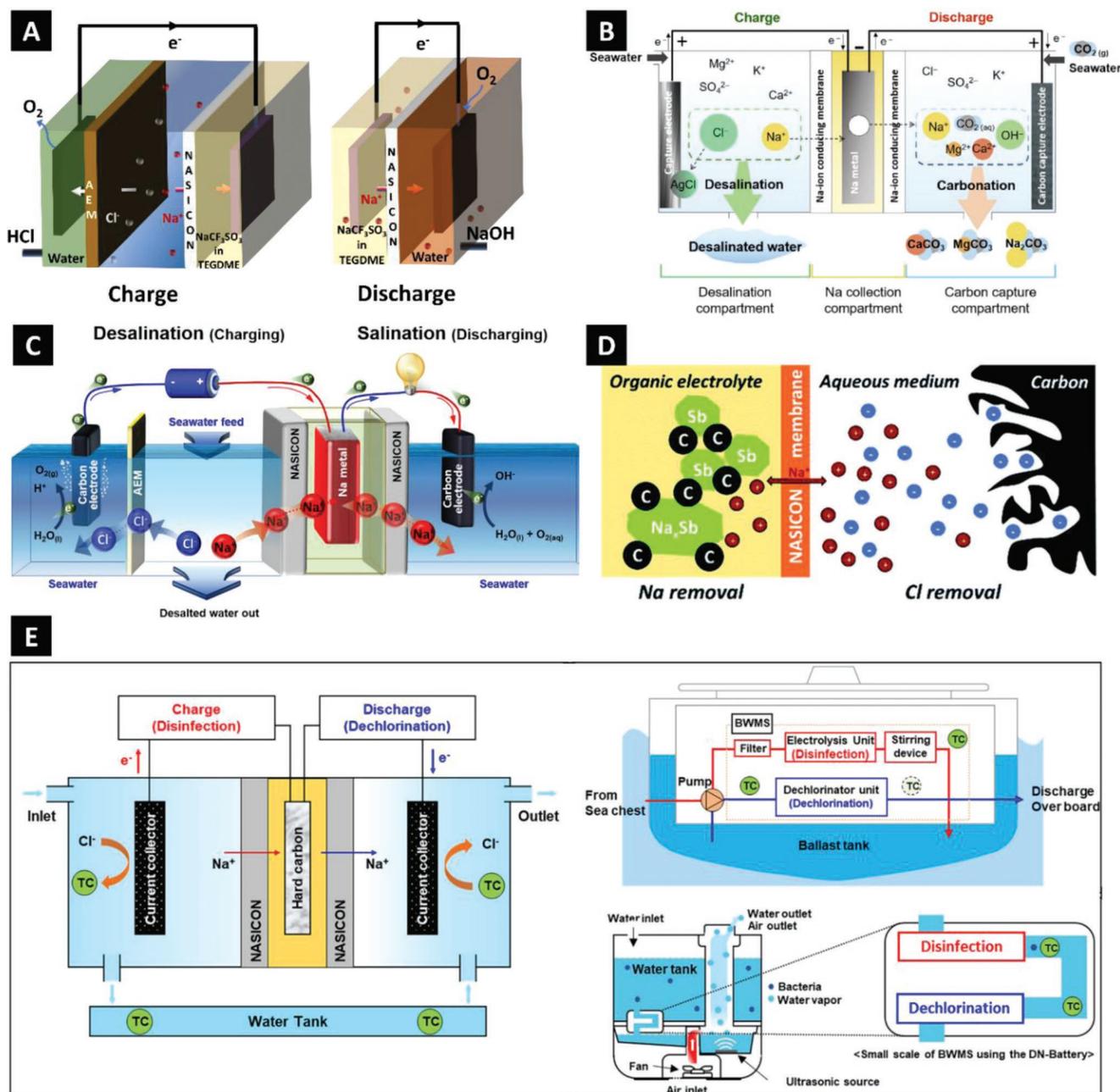
### 3.2.1. Cell Configurations and Performance Metrics

Due to the unique structure, containing both aqueous (seawater) electrolyte and organic electrolyte, it is easy to implement simultaneous water desalination and energy storage if the system of rechargeable seawater batteries is modified.

In 2018, Zhang et al. proposed a rechargeable seawater battery desalination system.<sup>[132]</sup> Unlike conventional seawater batteries, the system used still water as the catholyte and seawater as the feed water. Oxygen evolution reactions occur at the cathode part during the charging process, producing protons; sodium ions insert into the hard carbon anode. To keep the charge balance, Cl<sup>-</sup> and Na<sup>+</sup> in the seawater (middle channel)

will migrate through the anion exchange membrane (AEM) and the NASICON membrane, respectively. Thereby, HCl and desalinated water are produced during the charging process, and during the discharging process, the sodium anode is regenerated, and NaOH is formed (Figure 9A). Due to the high resistance partially caused by the AEM, there is a high overpotential for OER, resulting in the competition between OER and chloride evolution reactions ( $2\text{Cl}^- - 2\text{e}^- \rightarrow \text{Cl}_2$ ,  $E^0 = -1.36$  V vs

SHE). Thereby, the partial migrated  $\text{Cl}^-$  could also be removed by CER.<sup>[194]</sup> After 10 cycles, the total ion concentration decreases from 34.9 to 31.9 g L<sup>-1</sup>, with an average Coulombic efficiency of 92% and an energy efficiency of 76%. The relatively low-efficiency values could be due to the irreversible intercalation of  $\text{Na}^+$  in the hard carbon<sup>[132]</sup> or the energy dissipation caused by sluggish ORR and OER reaction kinetics and the high resistance of the cell.<sup>[194]</sup>

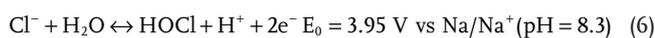
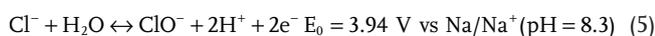
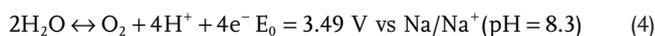


**Figure 9.** Schemes of different device technologies. A) Rechargeable seawater batteries desalination system with charging and discharging process, redesigned according to Figure 1 of ref. [132]. B) hybrid of desalination and carbon capture system based on rechargeable seawater batteries. Reproduced with permission.<sup>[123]</sup> Copyright 2019, Elsevier. C) Compartmentalized rechargeable seawater batteries desalination system. Reproduced with permission.<sup>[194]</sup> Copyright 2020, Elsevier. D) Desalination mechanism in bioelectrolyte desalination cell. Reproduced with permission.<sup>[90]</sup> Copyright 2021, Royal Society of Chemistry. The schematic diagram E) of disinfection–dechlorination battery (left side), conventional electrochlorination and dechlorination of ballast water (right upper corner), and the disinfection–dechlorination battery used in a humidifier (right bottom corner). Reproduced with permission.<sup>[195]</sup> Copyright 2021, American Chemical Society.

Following works modified the basic rechargeable seawater desalination system mentioned before to optimize the system or add more functionalities. For instance, Bae et al. combined the seawater battery system with a CO<sub>2</sub> capture system (Figure 9B).<sup>[123]</sup> This system contains the desalination compartment and the carbon dioxide capture compartment. Silver was used as a Cl<sup>-</sup> capture electrode instead of an OER catalytic electrode to compose the desalination parts with NASICON and Na metal, unlike the typical seawater battery system. This effectively reduces the overpotential and improves the voltage efficiency during the charging time caused by the sluggish kinetics of OER.<sup>[45]</sup> After the desalination process (system charging), the system is discharged with Na metal and porous carbon paper as the electrodes, where OH<sup>-</sup> is generated and CO<sub>2</sub> is captured by the metal hydroxides, like NaOH, Mg(OH)<sub>2</sub>, and Ca(OH)<sub>2</sub>. Consequently, CaCO<sub>3</sub> or MgCO<sub>3</sub> are simultaneously generated as a by-product.

Arnold et al. used carbon cloth as the alternative to OER, for its low price compared to Ag (Figure 9D).<sup>[90]</sup> With antimony/C as the anode, the initial capacity of the cell was 714 mAh g<sup>-1</sup> and the average desalination capacity was 294 mg<sub>Na</sub> g<sup>-1</sup><sub>Sb</sub> with a charge efficiency of around 74%. In 2020, Kim et al. improved the previous architecture of seawater batteries.<sup>[194]</sup> The cell contains independent desalination and salination parts (Figure 9C). This avoids disassembling cells between the charging and discharging process, which reduces the energy losses and enables a higher nominal cell potential of 3.46 V (pH 8.4) and a theoretical energy density of 4010 kWh kg<sup>-1</sup>. After galvanostatic charging for 20 mAh, 77% of the salts are removed from the seawater.

Apart from desalinating water, rechargeable seawater batteries also can disinfect the water if a higher voltage is applied. Recently, Park et al. proposed a disinfection-dechlorination battery with a NASICON ceramic membrane, depicted on the left part of Figure 9E.<sup>[195]</sup> During the charging process, the Na<sup>+</sup> moves through the NASICON membrane and deposits on the anode; Cl<sup>-</sup> or OH<sup>-</sup> partake at a redox reaction at the cathode (Equations (4)–(7)). The produced HOCl, ClO<sup>-</sup>, and Cl<sub>2</sub> could kill microbes in the water. The residual chloride base product will be oxidized into Cl<sup>-</sup> during the discharging process. After charging the cell for 3 h, the reduction rate of microorganism, *Escherichia coli* (MG1655), reaches 100%, while 8 h is required to 100% remove another microorganism, *Enterococcus aquimarinus* (DSM17690). This new system avoids the extra dechlorination process of standard disinfection technologies based on chloride disinfectant.<sup>[196]</sup> However, the competitive OER reactions would reduce the energy efficiency of this system, which may be addressed by applying selective catalysts for chloride evolution reactions.<sup>[197]</sup> In addition, the authors also put forward two typical applications; one is in the ballast water treatment, and the other is to disinfect microorganisms in humidifiers, which are illustrated in the upper right corner and bottom right corner of Figure 9E



### 3.2.2. Desalination Performance and Energy Consumption

Seawater batteries provide a high desalination capacity compared to other electrochemical desalination technologies. This beneficial performance results from the extended voltage window and the possibility of using materials with higher capacity as anodes, such as Na metal (theoretical capacity, 1165 mAh g<sup>-1</sup>),<sup>[47]</sup> red phosphorus (theoretical capacity, 2596 mAh g<sup>-1</sup>).<sup>[124]</sup> Therefore, seawater batteries could remove 70–80% of salts from seawater, among which Na<sup>+</sup> and Cl<sup>-</sup> dominate due to the selectivity of the NASICON membrane (Table 2).

Limited by the water-splitting voltage window, a relatively low voltage (generally <1.2 V) is applied in other electrochemical technologies, such as capacitive deionization,<sup>[37]</sup> and desalination batteries.<sup>[198]</sup> Consequently, materials with suitable potential range but relatively low capacity like carbon (5–30 mg<sub>NaCl</sub> g<sup>-1</sup><sub>electrode</sub>), some intercalation materials (50–100 mg g<sup>-1</sup>), and some conversion materials (100–150 mg g<sup>-1</sup>), are employed as the electrode, as shown in Table 2. Compared with the salt rejection rates of current seawater desalination technologies, such as reverse osmosis (RO) (≥99%),<sup>[199]</sup> multiple-effect distillation (MED) (almost 100%),<sup>[200]</sup> seawater batteries technology is not suitable to produce potable water, which requires the total dissolved solid lower than 500 mg L<sup>-1</sup>,<sup>[199]</sup> independently from the seawater. This is because seawater battery desalination generally removes sodium ions due to the selectivity of the NASICON membrane. However, it adapts desalinating the water with the salinity from low to hypersaline. Thereby, this technology could combine with some filtration technologies playing the role of pretreatment and the 2nd pass treatment to desalinate seawater; this technology could also replace some units or be added additionally in the current seawater desalination plants to reduce the energy consumption.

The energy consumption of seawater batteries must also be considered when assessing its application potential. The energy consumption of seawater batteries desalination depends on the amount of removed salt. The removal of 9% of all salt ions corresponded with an energy consumption of 4.7 kWh m<sup>-3</sup>.<sup>[132]</sup> The energy consumption increased to 53.9 kWh m<sup>-3</sup> when the salt removal increased to ≈75%.<sup>[201]</sup> Table 3 shows the energy consumption of some industrial plants with various desalination technologies. As can be seen, the energy consumption of RO is ≈3–5 kWh m<sup>-3</sup>,<sup>[202]</sup> varying from the operation parameters, which is less than that of MED (5–58 kWh m<sup>-3</sup>)<sup>[203]</sup> and electrodialysis (ED; 3–20 kWh m<sup>-3</sup>). These industrial plants also employ energy recovery devices to reduce the total energy consumption. Considering the energy recovery of seawater batteries desalination technologies (i.e., discharging process), the energy consumption could reduce to around 5 kWh m<sup>-3</sup> with the energy recovery reaching 90% by declining the voltage gap during the cycling.<sup>[131]</sup>

Recently, Ligaray et al. used reverse osmosis models to evaluate the energy consumption of a new system where a seawater battery is applied to be the energy recovery component or the substitute of the first RO in the conventional RO design with the energy recovery devices after the first filtration for the energy recovery of 50% (Figure 10A).<sup>[201]</sup> Their modeling assumed the Coulombic efficiency of seawater batteries to be 100%. Consequently, compared with the standard RO system

**Table 2.** Desalination performance of seawater-battery-based system, carbon materials, and Faradaic materials used for desalination.

|                               | Electrodes  | Feedwater salinity [mg L <sup>-1</sup> ] | Feedwater volume [mL] | Desalination                                      | Desalination capacity [mg g <sup>-1</sup> ] | Charge efficiency [%]                                | Energy consumption      | Refs. |
|-------------------------------|---|--|-----------------------|---|---|--|-------------------------|-------|
| Seawater-battery based system | Sodium metal//carbon felt                         | 33 460                                   | 3.4                   | 77%   | –   | ≈70% for Cl <sup>-</sup><br>≈80% for Na <sup>+</sup> | 37 kT ion <sup>-1</sup> | [194] |
|                               | Sodium metal//silver foil                         | 34 000                                   | –                     | 97% for Na <sup>+</sup><br>9% for Cl <sup>-</sup> | –   | –  | –                       | [123] |
|                               | Hard carbon//Pt/C                                 | 34 910                                   | 10                    | 9% after<br>10 cycles                             | –   | –  | 4.7 Wh L <sup>-1</sup>  | [132] |
|                               | Antimony/C//carbon cloth                          | 35 100                                   | –                     | –   | 294   | 74   | 16 kT ion <sup>-1</sup> | [90]  |
|                               | Sodium metal coated on carbon cloth//carbon cloth | 12 182.5                                 | 3.4                   | 73%   | –   | –  | –                       | [220] |
| Carbon materials              | Carbon cloth//carbon cloth                        | 58 400                                   | –                     | –   | 30  | ≈90  | 20 kT ion <sup>-1</sup> | [221] |
|                               | Activated carbon// activated carbon               | 292.5                                    | –                     | –   | 13  | 86   | –                       | [222] |
|                               | Activated carbon//activated carbon                | 35 100                                   | –                     | –   | 12  | 63   | –                       | [223] |

|                    | Electrodes  | Feed water salinity[mg L <sup>-1</sup> ] | Volume of the feed water [mL] | Desalination            | Desalination capacity [mg g <sup>-1</sup> ] | Charge efficiency [%] | Energy consumption      | Refs. |
|--------------------|---|--|-------------------------------|-------------------------|---|-----------------------|-------------------------|-------|
| Faradaic materials | Na <sub>0.44</sub> MnO <sub>2</sub> //BiOCl                 | 760                                      | 50                            | –                       | 69  | 97.7                  | –                       | [224] |
|                    | Na <sub>2-x</sub> Mn <sub>5</sub> O <sub>10</sub> //Ag/AgCl | 34 800                                   | ≈0.3                          | 25%                     | –   | –                     | 0.3 Wh L <sup>-1</sup>  | [38]  |
|                    | VS <sub>2</sub> -CNT//carbon cloth                          | 35 100                                   | –                             | –                       | 15  | >85                   | 29 kT ion <sup>-1</sup> | [225] |
|                    | NaNiHCF//NaFeHCF  | 34 465                                   | 0.6                           | 40% for Na <sup>+</sup> | 60  | –                     | 0.3 Wh L <sup>-1</sup>  | [226] |
|                    | Iodide// activated carbon                                   | 35 100                                   | –                             | –                       | 69  | 64                    | 1.6 Wh L <sup>-1</sup>  | [204] |
|                    | Bi/C// activated carbon                                     | 1000                                     | 50                            | –                       | 113   | –                     | –                       | [227] |

for seawater desalination, which contains the ultrafiltration (UF), RO, and brackish water reverse osmosis (BWRO), using seawater batteries as the additional energy storage devices could save about 104 kWh m<sup>-3</sup> energy by reducing the salt concentration from 61 200 mg L<sup>-1</sup> to less than 20 000 mg L<sup>-1</sup>. Applying seawater batteries instead of the first RO step (UF-SWB system, UF + SWB + BWRO), the seawater batteries could save 49–50 kWh m<sup>-3</sup>; utilizing nanofiltration (NF) + seawater batteries (NF-SWB system, UF + NF + SWB + BWRO) together as the alternative of first RO, the seawater batteries can save 24 kWh m<sup>-3</sup> and 1.1 kWh m<sup>-3</sup> pump energy could be reduced. The net specific energy consumption (SEC) of the UF-SWB

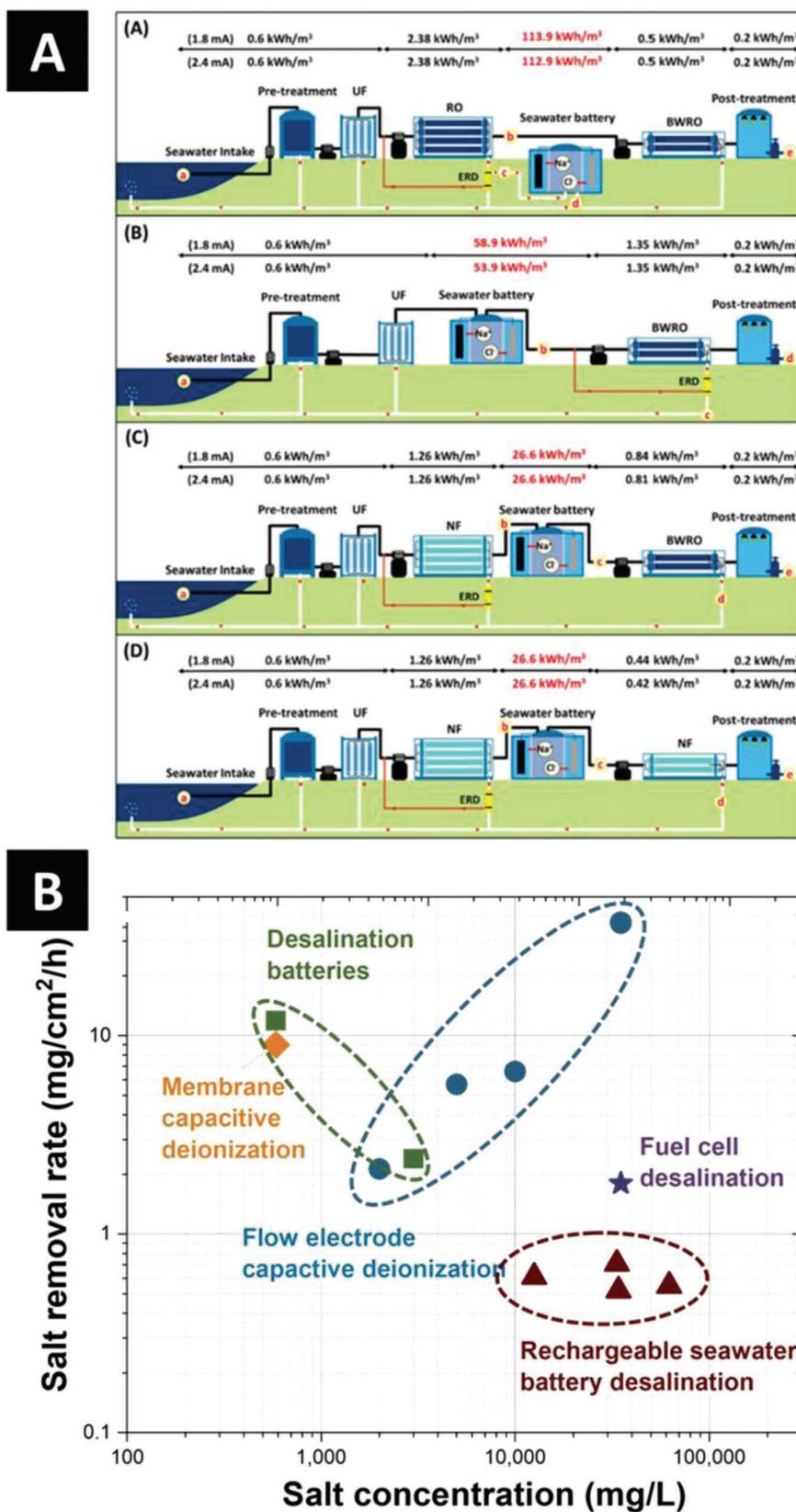
system and NF-SWB system are 1.35 and 2.1 kWh m<sup>-3</sup>, respectively; these values are below what is needed for the net SEC of a standard 2nd-pass-RO system (2.8 kWh m<sup>-3</sup>).

The energy consumption of the seawater battery system is relatively high compared with desalination batteries based on the intercalation materials<sup>[38]</sup> or redox electrolytes<sup>[204]</sup> (Table 2); this could be due to the high overpotential of the seawater battery system and the high resistance of NASICON membrane.<sup>[43]</sup> Another potential issue of the seawater battery system is the relatively low desalination rate (generally < 1 mg cm<sup>-2</sup> h<sup>-1</sup>), compared with other electrochemical technologies, for instance, flow electrode capacitive deionization (2–40 mg cm<sup>-2</sup> h<sup>-1</sup>)<sup>[205–211]</sup>

**Table 3.** Comparison the performance of current industrial desalination technologies and seawater batteries.

|                                  | TDS <sup>a)</sup> of feed water [mg L <sup>-1</sup> ] | TDS of product water [mg L <sup>-1</sup> ] | Water recovery [%] | Specific energy consumption [kWh m <sup>-3</sup> ] | Scale   | Refs. |
|----------------------------------|---|--|--------------------|--|---|-------|
| Reverse osmosis                  | 40 070  | 183  | 46                 | 4.8  | Industrial application<br>16 800 m <sup>3</sup> day <sup>-1</sup> | [228] |
|                                  | 35 000  | 174–214                                    | 30–50              | 1.89–2.04  | Modeling  | [229] |
| Electrodialysis                  | 35 000  | <500                                       | 50–60              | 16.21  | Pilot test<br>30 m <sup>3</sup> day <sup>-1</sup>                 | [230] |
|                                  | 35 000  | 450  | 41                 | 6.6  | Laboratory-scale experiments                                      | [231] |
| Multieffect distillation         | –   | –  | –                  | <5   | Industrial application<br>(10 000 t day <sup>-1</sup> )           | [200] |
| Seawater batteries <sup>b)</sup> | 33 700  | <200                                       | –                  | 1.35   | Modeling  | [201] |

<sup>a)</sup>TDS the abbreviation of total dissolved solid; <sup>b)</sup>The results are modeled by RO analysis software where seawater batteries replace RO in the typical RO system.



**Figure 10.** A) Proposed designs for rechargeable seawater battery desalination with various feed water. Reproduced with permission.<sup>[201]</sup> Copyright 2020, Elsevier. B) Average salt removal rate of different electrochemical desalination technologies. Data adapted from refs. [40,194,201,205–210,212].

and desalination batteries ( $1\text{--}10\text{ mg cm}^{-2}\text{ h}^{-1}$ ),<sup>[204,212]</sup> as shown in Figure 10B. This could be due to the relatively low ion diffusion rate of the NASICON membrane<sup>[94]</sup> and the sluggish kinetics rate of ORR and OER.<sup>[45]</sup> However, it should note that the salt removal rate also has a strong relationship with the operation parameters, like the voltage, current, and concentration of the feed water.<sup>[213]</sup>

#### 4. Conclusions

Since expanding the rechargeable battery industry is indispensable when considering the growing demand for portable electronic devices and sizeable stationary energy storage systems, the seawater battery offers a promising alternative. So far, mainly used lithium-ion battery technology cannot be used as the sole power due to the exploitation of raw materials, the resulting prices increase, and other concerns about geopolitical and environmental aspects. Therefore, the seawater battery, which uses a very environmentally friendly and resource-saving raw material, namely natural seawater, as an almost inexhaustible ion source, provides the possibility of more environmentally friendly energy storage.

Simultaneously energy storage and desalination encourage seawater desalination batteries to be a good choice for replacing some seawater reverse osmosis components. Additionally, attributed to the high selectivity of the NASICON membrane, using seawater batteries to desalinate the water also means extracting sodium ions from seawater. In addition, using other ion-selective membranes would enable elemental harvesting within the context of lithium extraction. Alternatively, nonselective membranes would boost the performance in seawater because cations beyond sodium would be removed. Finally, the advantages of seawater batteries provide a perspective toward sustainable, environmentally friendly, performance-oriented, and cost-efficient applications at the energy/water nexus.

Seawater battery development has yet to overcome technological challenges. A shortened lifetime, prevented safe battery operation, low Coulombic/energy efficiency, and low stability result from the partial instability of the individual cell components such as the solid electrolyte membrane or the anode electrode, as well as side reactions and nonoptimized cell components. Extending seawater batteries for desalination from the laboratory scale to pilot plants also requires optimized system design and benchmarking in real-water applications. The low desalination rate and high voltage gap are significant obstacles. However, these challenges can be addressed by advances in materials science, battery chemistry, and process engineering. In addition, the successful use and application of present-day seawater batteries make us optimistic about the more widespread application of this technology and the positive impact on sustainable devices at the energy/water research nexus.

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#### Conflict of Interest

The authors declare no conflict of interest.

#### Keywords

desalination, energy storage, ion removal, seawater batteries, sodium-ion batteries

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