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## REVIEW

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## 1. Introduction

Worldwide, renewable power technologies such as solar, wind, and tidal are considered potential alternatives to thermal and nuclear power technologies for producing clean green electricity. Thermal power plants emit CO<sub>2</sub> gas, which is the cause of global warming,1-3 and nuclear power plants are based on highly radioactive materials that are highly hazardous to nature and all living organisms, including humans.4,5 Hence, most countries have already started to produce the maximum amount of electricity from renewable power technologies by reducing the number of thermal and nuclear power plants. However, renewable power technologies have the drawback of an intermittent electricity supply. This intermittent nature motivated us to deploy a suitable electrical energy storage system (ESS) that can store a large amount of electricity produced from renewable power technologies and transfer electricity on demand economically.<sup>3,6</sup> An electrochemical ESS, which can be chosen from among many ESSs, is a great solution for matching fluctuating electricity supply with demand. Generally, electrochemical ESSs can offer carbon-free electricity, low maintenance, high round-trip efficiency, a long cycle life, and flexible power and energy features.<sup>2,3,7-9</sup>

## Emergence of rechargeable seawater batteries

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New concepts or chemistry is an urgent requirement for rechargeable batteries to achieve a low-cost, userfriendly nature with adequate energy densities and high levels of safety. Rechargeable seawater batteries (SWBs) are a new electrochemical system for the storage of electrical energy that utilizes seawater, as an infinite resource, as a source of the Na<sup>+</sup> ion cathode. Seawater is a naturally available abundant renewable resource that covers nearly 70% of the Earth's surface. This review provides an essential comprehensive introduction to new rechargeable SWBs. First, we present details of seawater and then the history of primary SWBs and rechargeable SWBs, and the structure and chemistry of rechargeable SWBs. Next, we describe the research progress that has so far been made on various components of SWBs, such as cathode current collectors, electrocatalysts, solid electrolyte, anodes, and non-aqueous electrolyte, including the performance metrics reported in the literature. Moreover, some concepts of modified rechargeable SWB design for desalination and CO<sub>2</sub> reduction application are discussed. Lastly, we provide our future outlook on the development of rechargeable SWBs and emphasize the main practical issues with the hope of stimulating further research progress.

> At present, rechargeable Li-ion batteries (LIBs) are the most renowned electrochemical ESS owing to their characteristics of high-energy-density charge storage  $(250 \text{ kW h}^{-1})$  and cycle life,<sup>10</sup> and these characteristics make them superior in portable devices, electronics, electric vehicles, and grid energy storage applications.9,11,12 However, LIBs are very costly (~USD 250 per kW h) and have safety issues, which are the main factors hindering their scale-up, especially in the grid energy storage field. The high-cost concern is due to the use of expensive lithium and cobalt-based raw materials in LIBs for achieving the high-energy system. The element cobalt is not only expensive but also toxic and has limited availability, like lithium.13 The safety problem of LIBs arises from their operation in low-flashpoint flammable organic electrolytes.14 Most importantly, compared with energy density, batteries should provide low cost, sustainability, and safety for their wide application; this situation compelled researchers to seek an alternative rechargeable battery system for LIBs.

> It is recognized by battery experts that the use of earthabundant metals such as aluminum (Al), magnesium (Mg), sodium (Na), potassium (K), and calcium (Ca)-based materials in batteries<sup>15–21</sup> would significantly reduce their cost because, Al, Mg, Na, K, and Ca are more abundant and cheaper elements. Nonetheless, seawater is an infinite resource for the Na element, which is the fourth most abundant element due to its availability in the form of Na<sup>+</sup> ions in seawater.<sup>22–24</sup> The concentration of Na<sup>+</sup> ions in seawater is approximately 0.47 M;<sup>25</sup> thus, it can possibly act as an Na<sup>+</sup> ion source, like the cathodes used in rechargeable Na-ion batteries. With this motivation, recently, rechargeable seawater batteries (SWBs) have been

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developed that use seawater, as an unlimited resource, as a source of the Na<sup>+</sup> ion cathode for electrical energy storage. In this battery, an anode in a non-aqueous electrolyte is protected from the seawater cathode by an Na<sup>+</sup> ion-conductive solid electrolyte, which can block water molecules and ions other than Na<sup>+</sup> ions<sup>25-27</sup> (a detailed discussion regarding the cell structure and their electrochemical reactions will be provided in the subsequent section).

From our efforts, we hope that the utilization of abundant seawater and its free natural availability will enable its application in large-scale ESSs with eco-friendly and pricecompetitive features. Compared with LIBs, however, the research on rechargeable SWBs is still in an embryonic stage for commercialization. However, our general goal is to develop rechargeable SWBs with price competitiveness in terms of energy, power, cycle life, and compatibility in future ESS applications. Therefore, several investigations are active concerning electrolytes and electrode materials for the anode side, electrocatalysts and current collectors for the cathode side, and selective Na<sup>+</sup> ion-conductive membranes (*i.e.* a solid electrolyte). In this review article, we first provide details on seawater and then a comprehensive overview of conventional primary seawater batteries (SWBs) and their comparison with rechargeable SWBs based on design and working principles. Subsequently, we summarize the current state of the art of progress in rechargeable SWBs to understand research approaches and the various performance metrics reported in the literature. Following this, we discuss modified rechargeable SWBs for desalination and CO2 reduction applications. Lastly, we offer future perspectives on the development of rechargeable SWBs and highlight the main practical issues ahead. We hope that this review will motivate and attract many readers, graduate students, and young researchers to work in this new area and stimulate further research progress.

## 2. Seawater

Before discussing SWBs, we have to understand seawater and some of the properties that influence SWBs' performance. Water is the most abundant substance on Earth; nearly 71% of the Earth's surface is covered by water. More importantly, of the total available water, 97.5% is seawater, while the remainder is freshwater (2.5%).<sup>28,29</sup> Seawater exists in oceans. Naturally, this seawater is saline compared with freshwater due to the existence of salts in the form of dissolved ions (note: there are 35 grams of salt in 1 L of seawater). Table 1 shows the concentration of the major dissolved ions in standard seawater, where  $Na^+$  (10.7 g) and  $Cl^-$  (19.3 g) ions are the main dissolved ions, comprising 90% of all dissolved ions in seawater. Therefore, we can infer that Na<sup>+</sup> and Cl<sup>-</sup> ions are the main reason for the high saline nature of seawater. Many of these dissolved salt ions in seawater are supplied to seas/oceans by rivers. In brief, while flowing as river water on soil, the rainwater breaks rocks and brings salts and minerals in the form of dissolved ions into the ocean. Volcanic eruptions also provide some dissolved ions, mainly chlorine and sulphur dioxides, to the ocean.<sup>30</sup> However,

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Table 1	Compo	osition	of	standard	seawater <sup>2</sup>

Chemical ions	Percentage of total salt content (%)	Concentration (ppm) g kg <sup>-1</sup>		
Cl <sup>-</sup> (chloride)	55.0	19.345		
Na <sup>+</sup> (sodium)	30.6	10.752		
$SO_4^{2-}$ (sulfate)	7.6	2.701		
Mg <sup>2+</sup> (magnesium)	3.7	1.195		
Ca <sup>2+</sup> (calcium)	1.2	0.416		
K <sup>+</sup> (potassium)	1.1	0.390		
HCO <sup>3-</sup> (bicarbonate)	0.4	0.145		
Br <sup>-</sup> (bromide)	0.2	0.066		
$BO_3^{2-}$ (borate)	0.08	0.027		
Sr <sup>2+</sup> (strontium)	0.04	0.013		
F <sup>-</sup> (fluoride)	0.003	0.001		

it must be emphasized that the concentration of dissolved salt ions is not similar throughout the ocean; it differs from place to place, and is mainly controlled by the local weather (cold or hot), environment, and rainfall rate.

Moreover, the presence of dissolved salt ions in seawater supports a high ionic conductivity of approximately 50 mS cm<sup>-1</sup> (at 20 °C). Thus, seawater has been considered as an electrolyte for several applications, such as water electrolysis<sup>29,31,32</sup> and electrochemical cells (for example: supercapacitors and batteries).<sup>33-36</sup> However, the conductivity of seawater varies depending on temperature and salinity.<sup>37-39</sup> Generally, the pH of seawater is approximately 8.1, which shows that seawater is slightly more basic in nature than freshwater (pH = ~7). Likewise, seawater not only contains dissolved salt ions but also dissolved gases. O<sub>2</sub> and CO<sub>2</sub> are the main dissolved gases in seawater. These gases for seawater are provided by the atmosphere. However, the dissolved gas concentration depends on the solubility and salinity, temperature, and pressure of seawater.<sup>40</sup>

# 3. History: development of SWBs from primary (non-rechargeable) to secondary (rechargeable)

Fig. 1 shows a diagram of the development history of SWBs from a primary to a secondary system and their applications. In the past few years, SWBs have been the subject of renewed interest. Since the 1940s, seawater has been directly employed as an electrolyte in batteries (or electrochemical power cells); such batteries were later represented as SWBs. Mg (anode)-silver chloride (AgCl; cathode) batteries were the first developed commercial primary SWBs (from 1943), and they were originally particularly produced for military use (1943-45) and later for civilian applications (1945-52).41 For the same purpose, due to the high cost of the silver cathode, Mg-cuprous chloride (CuCl; cathode) batteries were produced in 1949.41 However, the high hygroscopic nature of CuCl and its poor chemical stability impelled the further development of a primary SWB system employing cheap and stable cathode materials, such as lead chloride (PbCl<sub>2</sub>),<sup>42</sup> mercurous chloride (Hg<sub>2</sub>Cl<sub>2</sub>),<sup>43</sup> cuprous



Fig. 1 Timeline of SWBs and their major developments from a primary to a secondary system.

iodide (CuI),<sup>44</sup> and cuprous oxide (Cu<sub>2</sub>O).<sup>45</sup> Since these classical batteries are primary systems, they cannot be recharged after the first discharge. Hereafter, it must be noted that classical SWBs are denoted as primary SWBs.

In the meantime, for deep-sea applications or long-term underwater operation, metal (anode)-seawater (cathode) batteries, including the Mg-seawater battery<sup>46</sup> and Al-seawater battery,<sup>47</sup> were developed as high-energy-density batteries during the 1990s, and their long-term operation in the deep sea was proven. These metal-seawater batteries can be operated via two modes: (i) oxygen-reduction reaction ( $O_2 + 2H_2O + 4e^- \rightarrow$ 4OH<sup>-</sup>)<sup>47</sup> on a cathode current collector with water (H<sub>2</sub>O) molecules through the utilization of dissolved oxygen  $(O_2)$  (DO) as a cathode oxidant in seawater and (ii) hydrogen evolution (2H<sub>2</sub>O +  $2e^- \rightarrow H_2$  +  $2OH^-$ )<sup>47</sup> through the consumption of water molecules as a cathode oxidant supplied by seawater. This kind of SWB also works on the principle of the primary concept. Along with Mg, Al,48-51 and its alloys, Zn50 was also examined as an anode in primary SWB systems. However, these tested metal anodes showed a high self-discharge rate and their performance was disturbed by electrode blockage owing to unwanted metal hydroxide formation  $(MA + nOH^- \rightarrow MA(OH)_2 + ne^-;$  where MA means metal anode).<sup>35,52,53</sup> Furthermore, the operating voltage of such batteries is very low (1 to 1.8 V) when using Mg, Mg alloys, Al, and Zn as the anode.54 As we know, the cell voltage is also one of the main dominating factors for the energy density of batteries. Therefore, in early 2006, the PolyPlus Battery Company designed a primary-type Li-SWB to improve cell voltage by using a protected lithium electrode as the anode. This technological Li-seawater battery with DO enabled an experimental cell voltage of 3 V ( $\nu s$ . Li/Li<sup>+</sup>), and with hydrogen evolution, this enabled an experimental cell voltage of 2.3 V (vs. Li/Li<sup>+</sup>).55,56

With the above primary SWBs, it is impractical to store electrical energy. Thus, in 2014, rechargeable SWB technology was proposed and patented by Y. Kim's research group; it uses seawater as the  $Na^+$  ion cathode for electrical energy storage. This rechargeable SWB has a promising future in a broad range of applications such as ESSs for tidal and wind power near coastal areas, an energy provider in the military, and other civilian applications. The main aim of this review article is to increase the prominence of rechargeable SWBs. In the following section, we will discuss the chemistry and structure of SWBs and their research, performance metrics, and so on.

## 4. Rechargeable SWB structure and chemistry

Generally, as shown in Fig. 2a, the proposed rechargeable SWB consists of an anode in a non-aqueous electrolyte, seawater with a cathode current collector, and a solid electrolyte (ceramic membrane) situated between the two electrodes and separating the non-aqueous (liquid) electrolyte and seawater.26,57 The rechargeable SWB has a cathode open-structured system; usually, seawater is exposed to ambient air.58 The anode stores Na<sup>+</sup> ions harvested from seawater by charging, so the anode plays a vital role in determining the rechargeable SWB energy. The ceramic solid electrolyte plays a role as an electrolyte and separator. Due to the excellent selectivity of the solid electrolyte, only Na<sup>+</sup> ions are transported to the anode during the charging process and they return from the anode to seawater during discharge. Other cations in seawater are blocked. Seawater is a supplier of Na<sup>+</sup> ions for anodic reactions during charging, and DO is an oxidant during discharging, so seawater acts as the sole active cathode material.25 The current collector offers



Fig. 2 (a) Schematic representation of the structure of rechargeable SWBs and their electrochemical process at the anode and cathode-side during the charge and discharge process. (b) Simulated Pourbaix diagram for seawater at 25 °C, where the chlorine system is constructed by assuming a total chlorine concentration ( $C_{T,Cl}$ ) of 0.54 m, with chloride ions (Cl<sup>-</sup>) as the only chlorine species, since a typical concentration of Cl<sup>-</sup> in seawater is  $\approx 0.54$  M. A H<sub>2</sub>O/O<sub>2</sub> system is built by considering an O<sub>2</sub> partial pressure ( $P_{O_2}$ ) of 0.206 atm and activity coefficients for all species are assumed to be 1. (c) Typical charge–discharge voltage profile of a rechargeable SWB using HC as the anode (HC|seawater). (b and c) Reproduced with permission.<sup>25</sup> Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

reaction sites for cathodic reactions and serves as the holder of the catalyst or active materials and paths for electrons.<sup>59,60</sup>

The electrical energy in the rechargeable SWB is stored at the anode side as Na metal by harvesting Na<sup>+</sup> ions from seawater *via* the oxygen evolution reaction (OER; reaction (1)) during the charging process. During the discharge process, easily reducible species of DO, which is present in seawater, are involved in the oxygen reduction reaction (ORR; reaction (1)) with the aid of water while the stored chemical energy is released as electricity with Na<sup>+</sup> ions transferred back from the anode into seawater (reaction (2)). The half-cell (anodic and cathodic) reactions are stated below:<sup>25</sup>

Cathode (in seawater at pH = 8):

$$4OH^{-} \leftrightarrow O_{2} + 2H_{2}O + 4e^{-} (ORR \leftrightarrow OER),$$
  

$$E = 0.77 \text{ V } \text{vs. SHE}$$
(1)

Anode (in a nonaqueous electrolyte):

$$4\mathrm{Na}^{+} + 4\mathrm{e}^{-} \leftrightarrow 4\mathrm{Na}, E = -2.71 \mathrm{V} \text{ vs. SHE}$$
(2)

The overall cell reaction in the rechargeable SWB during charge/discharge is expressed below:

Overall reaction:

$$4\text{Na} + \text{O}_2 + 2\text{H}_2\text{O} \leftrightarrow 4\text{NaOH}, E_{\text{cell}} = 3.48 \text{ vs. Na/Na}^+ \quad (3)$$

Therefore, the theoretical cell voltage of the rechargeable SWB is approximately 3.48 V ( $\nu s$ . Na/Na<sup>+</sup>) (eqn (3)).

As we know, the pH of standard seawater is approximately 8, so during the charging process of the SWB at this pH, according to the Pourbaix diagram (Fig. 2b), a hypochlorite (ClO<sup>-</sup>) formation reaction (HCFR; Cl<sup>-</sup> + OH<sup>-</sup>  $\leftrightarrow$  ClO<sup>-</sup> + H<sub>2</sub>O + 2e<sup>-</sup>; *E* = 1.24 V *vs.* SHE)<sup>61</sup> can also occur on the cathode current collector in addition to the OER (eqn (1)). Here, the HCFR has a kinetic advantage compared with the OER because the HCFR is a two-electron oxidation reaction and the OER process is based on a four-electron oxidation reaction. However, as shown in the Pourbaix diagram, the OER (0.77 V *vs.* SHE) is highly thermodynamically favored over the HCFR (1.24 V *vs.* SHE) in seawater

at pH 8. Hence, the OER is the most probable reaction on the cathode current collector of the rechargeable SWB during the charging process. In case, the charging process for the SWB appears over 3.95 V ( $\nu s$ . Na/Na<sup>+</sup>), that could belong to the HCFR (eqn (2)) process.<sup>25</sup>

During discharge, suppose the ORR occurs by a two-electron reduction pathway ( $O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-; E = 0.21 V$ vs. SHE (at pH = 8), in contrast to a four-electron reduction pathway  $(O_2 + 2H_2O + 4e^- \rightarrow 4OH^-; E = 0.77 \text{ V} \text{ vs. SHE}$  (at pH = 8)), the resultant theoretical cell voltage for this SWB will be 2.9 V (vs. Na/Na<sup>+</sup>). Anyway, this two-electron reduction pathway process can be avoided by using the selective four-electron reduction pathway electrocatalysts. On the other hand, it must be noted that when seawater does not have enough DO or using high current, the discharge process of the rechargeable SWB can occur through the hydrogen  $(H_2)$  evolution reaction  $(2H_2O +$  $2e^- \rightarrow H_2 + 2OH^-$ ; E = -0.47 V vs. SHE (at pH = 8)), and the theoretical cell voltage will be 2.2 V (vs. Na/Na<sup>+</sup>).<sup>25</sup> So, during discharge, it is essential to maintain the concentration of DO in seawater and the use of optimized low current, which is more favorable for the ORR. Fig. 2c displays the typical charge and discharge curves of a rechargeable SWB operated using hard carbon (HC) as the anode, respectively. The resultant charge and its reversible discharge profiles imply the sodiation and desodiation processes through the OER and ORR processes, respectively. The required Na<sup>+</sup> ions for sodiation in HC are harvested from seawater. However, it must be noted that the cell voltage depends on the potential of the anode and kinetics of the ORR process, and the voltage gap between the charge and discharge curves depends on the kinetics of both the OER and ORR processes (which will be discussed in the following sections).

## 5. Research progress on rechargeable SWBs

Some primary SWBs, such as Mg–AgCl, Mg–CuCl, and Al–AgCl batteries, have already been established efficiently and applied mainly in military- and navy-related areas. However,

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rechargeable SWBs are still in the early R&D stage and needs a solution for various issues before their commercialization (these will be discussed in the following sections). Therefore, for the practical application of rechargeable SWBs, structural design, engineering, and optimal materials are still required (*i.e.* the anode, nonaqueous electrolytes, cathode current collector, and electrocatalysts). Fig. 3 shows the record of research efforts, which have been moving toward the development of rechargeable SWBs for real-time applications. Each type of research progress is described in the following sections.

## 5.1. Cell design and engineering: from proof-of-concept to coin cells

As shown in Fig. 2a, the rechargeable SWB system employs multilayer electrolytes consisting of a non-aqueous electrolyte, a solid electrolyte, and an aqueous natural seawater catholyte. Due to these structural features, a new cell platform and testing environments are essential for testing rechargeable SWB systems. Initially, we hand-made a cell for the proof-of-concept of the rechargeable SWB<sup>26</sup> by considering critical cell components. Although it confirmed the possibility of the development of rechargeable SWBs, due to the liquid leakage problem, it was changed to a pouch-type rechargeable SWB design.<sup>60,62</sup> Nonetheless, the size of each cell is different for each researcher. Hence, the results are different and so it is quite hard to acquire consistent data for analysis. Therefore, it is imperative to construct a standard cell platform and its testing conditions considering the core components of rechargeable SWBs to obtain reliable and uniform data.25 Furthermore, we have developed a coin-type unit-cell (SWB2464) and prototype tester of the rechargeable SWB (Fig. 4a and b).58 Rechargeable SWBs

use natural seawater in an open-structured cathode; the cathode part must be in direct contact with seawater, but the anode part should be completely sealed to avoid contact with seawater. Therefore, the tester design is also essential for obtaining consistent electrochemical performance. The assembled SWB coin-cell combines with the carbon-based cathode current collector and can be loaded in the bolts/nutstype tester (Fig. 4a). The first prototype, the bolts/nuts-type tester, experienced the problem of seawater leakage between the bolts and nuts (Fig. 4a). To solve this problem through the engineering process, we developed a screw-type tester (Fig. 4b), and, eventually, a flow-cell tester was also developed over the past few years (Fig. 4c). Since rechargeable SWBs utilize seawater as a cathode material, it is crucial to provide fresh seawater to supply unlimited  $Na^+$  ions and oxygen (O<sub>2</sub>) to the reaction sites continuously. For this reason, the flow-cell was designed, and the seawater and oxygen could circulate continuously (Fig. 4c).

To investigate the seawater flow effect, seawater cells were tested using heat-treated carbon felt (HCF) as the cathode current collector in the flow ON and flow OFF modes.<sup>58</sup> Fig. 4d shows the charge/discharge voltage profiles in the flow ON and flow OFF modes at a current rate of 0.025 mA cm<sup>-2</sup> for 5 hours. In the flow OFF mode, a large voltage gap ( $\sim$ 1.1 V) was observed and the terminal charge/discharge voltages were  $\sim$ 3.9 V and  $\sim$ 2.8 V, respectively. On the other hand, in the flow ON mode, the cell showed fast saturation of the charge/discharge voltage; the charge/discharge terminal voltages were  $\sim$ 3.7 V and  $\sim$ 3.0 V, respectively ( $\Delta V = 0.7$  V). It should be noted that the seawater flow effect plays an essential role in enhancing the voltage efficiency of rechargeable SWBs. To check the DO content in seawater, we examined the flow ON and flow OFF modes in the



**Fig. 3** Various types of research progress involving developing high-performance rechargeable SWBs for commercial products for real-time applications. The SEM image shown for electrocatalysts was adopted with permission.<sup>57</sup> Copyright 2017, Royal Society of Chemistry. The images shown for applications were adopted with permission.<sup>25</sup> Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.



Fig. 4 (a) Prototype of a bolts and nuts type tester and (b) screw-type tester, where both types of testers are immersed in seawater for the electrochemical test. (c) Assembled coin-type cell and optimised flow-type tester. (d) Charge/discharge voltage profiles of the cell measured at a current rate of 0.025 mA cm<sup>-2</sup> for 5 h in the seawater flow ON and OFF modes (Na|seawater). (e) Discharge voltage profile of the cell measured at a current rate of 0.1 mA cm<sup>-2</sup> and the dissolved oxygen (DO) content in seawater catholyte in the flow ON and OFF modes. (c–e) Adopted with permission.<sup>58</sup> Copyright 2017, Elsevier.

discharging process at a current rate of 0.1 mA cm<sup>-2</sup> (Fig. 4e). It can be seen in Fig. 4e that the DO content and the discharging voltage were maintained at a certain level in the flow ON mode, but the DO content and discharging voltage sharply decreased to  $\sim$ 5.9 mg L<sup>-1</sup> and  $\sim$ 1.9 V, respectively, in the flow OFF mode. As described above, the discharge process of the SWB is based on the ORR, which consumes DO, showing that a sufficient oxygen supply has an important influence on the performance of rechargeable SWBs. From these results, we confirmed that it is important to supply adequate reactants (seawater and oxygen) to the reaction sites (the surface of the cathode current collector) through the seawater flow mode, and, consequently, the overpotential arising from the OER/ORR can be reduced. Based on these efforts, the potential of the SWB can be easily tested, and its results can be compared with those collected by other research groups.

## 5.2. Selective Na-ion-conducting solid electrolytes (membranes)

The selective Na-ion-conducting solid electrolyte is at the heart of constructing and demonstrating the rechargeable SWB concept, as shown in Fig. 2a. The solid electrolyte used in the SWB should have the features (Fig. 5a) of high (Na<sup>+</sup>) ionic conductivity at a low temperature, high ionic (Na<sup>+</sup>) selectivity (it should not allow any ions other than Na<sup>+</sup>), electrical insulation properties to separate the anode and cathode, high chemical stability against seawater and nonaqueous electrolytes, electrochemical stability while operating in a wide electrochemical window, and high mechanical/physical strength to separate the nonaqueous electrolyte and seawater physically. There are three kinds of solid electrolytes with the ability to conduct Na<sup>+</sup> ions: inorganic, polymer, and polymer–ceramic composite.<sup>63-66</sup> Among them, inorganic electrolyte has high density and high mechanical strength to separate the nonaqueous electrolyte and seawater physically compared with polymer-based electrolytes because polymer-based solid electrolytes generally have weak mechanical strength and relatively low density, which results in physical cell failure and/or chemical cell failure (a mixture of organic liquid electrolyte and seawater). However, all inorganic solid electrolytes still cannot be used for rechargeable SWB application.

The most well-known inorganic solid electrolytes are sulfide and oxide-based solid electrolytes (Fig. 5b and c). The sulfidebased solid electrolyte is a promising solid electrolyte for sodium batteries due to its ductile mechanical properties and high ionic conductivity (>1  $\times$  10<sup>-3</sup> S cm<sup>-1</sup> at room temperature (RT)) derived from the large ionic radius of sulfur and weaker electrostatic interaction with Na<sup>+</sup> ions. However, these sulfidebased solid electrolytes are unstable in humidity and air. Na<sub>3</sub>PS<sub>4</sub> and Na<sub>3</sub>SbS<sub>4</sub> are examples of sulfide-based solid electrolytes. 63,64,67,68 Na3PS4 can quickly react with water and oxygen, producing toxic H<sub>2</sub>S gas, while Na<sub>3</sub>SbS<sub>4</sub> also with water forms the Na<sub>3</sub>SbS<sub>4</sub>·xH<sub>2</sub>O phase, resulting in low ionic conductivity.<sup>69-71</sup> In contrast, oxide solid electrolytes are impermeable, white ceramics that have higher chemical stability and significant mechanical strength with high ionic conductivity. The representative examples of oxide solid electrolytes are βalumina NASICON (Na super conductor; and ion



Fig. 5 (a) Requirements of solid electrolytes for rechargeable SWBs. (b) Representative sulfide solid electrolytes and their general properties. (c) Representative oxide solid electrolytes and their general properties. (a) Adopted with permission.<sup>67</sup> Copyright 2018. Cell Press. (b)  $Na_3PS_4$  and  $Na_3SbS_4$  structures adopted with permission.<sup>68</sup> Copyright 2019, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (c)  $Na-\beta''$ -alumina structure adopted with permission.<sup>66</sup> Copyright 2017, Elsevier. (c) NASICON structure reproduced with permission.<sup>66</sup> Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

 $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ).<sup>63,64</sup> More information regarding betaalumina and NASICON can be obtained from the following subsections.

**5.2.1.** β-alumina solid (ceramic) electrolyte. The β-alumina electrolyte, produced from oxides and hydroxides of aluminum, sodium, and lithium, was discovered in 1967,72 and has two crystal structures,73,74 i.e., sodium-β-alumina (Na-β-Al<sub>2</sub>O<sub>3</sub>) and sodium- $\beta''$ -alumina (Na- $\beta''$ -Al<sub>2</sub>O<sub>3</sub>) (see Fig. 6a). Both have a layered crystal structure and sodium ions transferred through a two-dimensional (2D) sodium conduction plane. However, they have different compositions and crystal structures. Na-β- $Al_2O_3$  is  $Na_2O \cdot xAl_2O_3$  (x = 8-11) with a hexagonal structure. On the other hand, Na- $\beta''$ -Al<sub>2</sub>O<sub>3</sub> is Na<sub>2</sub>O·xAl<sub>2</sub>O<sub>3</sub> (x = 5-7) with a rhombohedral structure. The higher sodium content in the conduction plane of  $Na-\beta''-Al_2O_3$  yields higher ionic conductivity (~2  $\times$  10<sup>-3</sup> S cm<sup>-1</sup> at room temperature)<sup>75</sup> than  $\beta$ alumina. Therefore, Na-\u03b3"-Al2O3 was a successfully adopted solid electrolyte in electrochemical ESSs, particularly in sodium-sulfur (Na-S) batteries and sodium-metal chloride or ZEBRA (zero emission batteries research activity) batteries,73 where it separates the cathode and anode and acts as a fast Naion-conducting solid electrolyte. In this sense, we have used commercially available  $Na-\beta''-Al_2O_3$  to construct an SWB; however, this electrolyte is sensitive to water induced by the slow diffusion of  $H_3O^+$  ions into the Na- $\beta''$ -Al<sub>2</sub>O<sub>3</sub> phase. Therefore, an SWB with an  $Na-\beta''-Al_2O_3$  solid electrolyte and a poor cycle life (Fig. 6b) was observed with AlOOH phase formation. AlOOH formation was confirmed by comparing the XRD result of the Na- $\beta''$ -Al<sub>2</sub>O<sub>3</sub> solid electrolyte before and after cycling, as shown in Fig. 6c. With the AlOOH phase, the ionic conductivity of this electrolyte was dramatically decreased, inducing significant overpotential.76

**5.2.2. NASICON solid (ceramic) electrolyte.** The term NASICON (sodium (NA) SuperIonic CONductor) was proposed

by Hong and Goodenough in 1976.<sup>77,78</sup> The general formula of NASICON is  $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ , where  $0 \le x \le 3$ ,<sup>79</sup> which results from  $NaZr_2P_3O_{12}$  solid solution with the partial replacement of P by Si. The nominal composition for achieving better conductivity is  $Na_3Zr_2Si_2PO_{12}$  (at x = 2). NASICON generally forms in two phases (crystal structure), which are



rhombohedral and monoclinic (see in Fig. 7a),<sup>66</sup> and it is worth noting that this different phase formation depends on its composition and synthesis temperature.<sup>80</sup> However, both phases comprise three-dimensionally (3D) linked ZrO<sub>6</sub> octahedra sharing corners with SiO<sub>4</sub> and PO<sub>4</sub> tetrahedra and offer a 3D pathway for Na<sup>+</sup> transportation.

The procedures for NASICON synthesis are more convenient than those for  $\beta$ -alumina synthesis. So far, various synthesis methods (e.g., sol-gel, spark-plasma sintering, solid-state reaction, combustion, ion exchange, and hydrothermal reaction) have been used to fabricate NASICON; however, some only contribute to achieving a highly dense NASICON with the expected conductivity. Since 2014, Y. Kim's group has been involved in the fabrication of NASICON pellets via the solidstate reaction route, as mentioned in the steps in Fig. 7b. Now, two different NASICON shapes (viz. a circle and square, as shown in Fig. 7c and d) are commercially produced from 4TOONE Co. Ltd (http://www.4toone.com). The bulk density and ionic conductivity of this commercially available NASICON are >3.03 g cm<sup>-3</sup> (>93% of theoretical density value) and  $\sim 1 \times$ 10<sup>-3</sup> S cm<sup>-1</sup>, respectively.<sup>25</sup> Fig. 7e shows the backscattered electron image of a square shape NASICON pellet. There are 3 phases that exist in a NASICON pellet, i.e. NASICON, amorphous and ZrO2, where NASICON grains are attached to each other and the supports to transferred Na ions through the NASICON grains and their grain boundary.

With the feature of 3D Na<sup>+</sup> pathway conductivity, various NASICON applications have been recognized, such as ZEBRA batteries,  $CO_2$  sensors, and sodium batteries; therefore, we expect it to be a good candidate for building an SWB. However, for rechargeable SWB applications, NASICON should be stable

with seawater since it is exposed to seawater directly. In previous studies, NASICON was found to be unstable with water. However, the testing conditions of the studies were different from those of the rechargeable SWB, such as deionized (D.I.) water and high temperature. To evaluate rechargeable SWB applicability, a NASICON pellet was exposed to seawater for about two months and it was confirmed through SEM and XRD analysis (not shown here) that there was no significant surface degradation or phase changes,<sup>25</sup> respectively. Moreover, in the preliminary studies, the rechargeable SWB built with NASICON showed a stable cycle performance over 200 cycles, while NASICON retained its phase stability (Fig. 7f).<sup>76</sup> Later, we successfully cycled the rechargeable SWB for 600 cycles<sup>81</sup> as shown in Fig. 7g, which further confirms the potential of NASICON and its real-time applicability in rechargeable SWBs. Furthermore, it was more stable against a non-aqueous electrolyte (1 M NaCF<sub>3</sub>SO<sub>3</sub> in TEGDME (tetraethylene glycol dimethyl ether)) and a Na metal anode at the anode side of the rechargeable SWB cell.23 Therefore, NASI-CON is still the most appropriate solid electrolyte in rechargeable SWBs.

#### 5.3. Cathode compartment

As shown in Fig. 2a, the cathode compartment of the rechargeable SWB consists of a cathode current collector and seawater. The operation of the rechargeable SWB depends on the sluggish OER/ORR process; thus, the electrocatalyst was also used on the current collector as a critical component to enhance the reaction kinetics. Additionally, each component in the cathode part played a distinctive role. In the subsequent subsections, we have described the research progress of these



Fig. 7 (a) Schematic illustration of the rhombohedral and monoclinic structures of NASICON, where, in the monoclinic structure, three Na<sup>+</sup> interstitial sites (Na1, Na2 and Na3) are located between polyhedrons, featuring two Na<sup>+</sup> transfer channels (Na1–Na2 and Na1–Na3) and in the rhombohedral structure, two Na<sup>+</sup> interstitial sites (Na1 and Na2) are located between polyhedrons, which offer only one Na<sup>+</sup> transfer channel (Na1–Na2). (b) Solid-state reaction route of NASICON. (c) Square and (d) circle type NASICON pellets that are available commercially. (e) The backscattered electron image of a square shape NASICON pellet. (f) XRD patterns of the surface of the NASICON pellet before and after 100 cycles in a rechargeable SWB (HC|NASICON|seawater). (g) Charge–discharge curve of the rechargeable SWB (HC|NASICON|seawater). (a) Reproduced with permission.<sup>66</sup> Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (f) Adopted with permission.<sup>76</sup> Copyright 2017, Elsevier.

cathode components and their influences on the performance of rechargeable SWBs.

5.3.1. Current collector. The cathode current collector plays an essential role in determining the performance of a rechargeable SWB as it provides reaction sites for the cathode reactions (OER/ORR) as given in eqn (1) and electron paths. Hence, the cathode current collector for a rechargeable SWB should be selected based on the criteria of high electronic conductivity, large surface area, strong electrochemical and mechanical stability, uniformly distributed transport area, costefficiency, lightness of weight, and wide availability for commercial purposes. Metal (or its alloy) and carbon-based collectors are the most-used current collectors in various kinds of battery systems. However, it must be noted that employing current collectors varies from system to system based on electrochemical potentials and electrolyte mediums. According to previous reports, except for titanium and its alloys, other metal-based materials cannot be used in the medium of seawater as a cathode current collector due to their instability with seawater. The existence of chloride ions in seawater can easily destroy the oxide film on the surface of other metals and form a complex with metal ions, resulting in the corrosion of metals in seawater.82,83 Nonetheless, Ti-based current collectors are also not suitable for use in SWBs as they are not electrocatalytically active in nature toward the OER/ORR reactions.

On the other hand, carbon-based current collectors have been recognized for their high corrosion resistance in seawater and then utilized in primary SWB applications as cathode current collectors for ORR and HER activity.84,85 Based on these characteristics, carbon paper was first tested in a rechargeable SWB in the search for a suitable cathode current collector.<sup>26</sup> Unfortunately, due to its poor mechanical stability (easily broken), carbon felt<sup>86</sup> was later used. Carbon felt features mechanical stability and also offers high conductivity and flexibility. However, pristine carbon felt shows very poor wettability against seawater due to the presence of a hydrophobic surface, which mainly emanates from the existence of sizing agents in pristine carbon felt for mechanical reinforcement. Thus, before use in an SWB, pristine carbon felt was subjected to heat treatment at 500 °C for 2 or 3 h in ambient air to become hydrophilic.58 The contact angle results (not shown here, refer ref. 58) showed a difference in the hydrophobic nature of the pristine carbon felt, and the hydrophilic nature of heated carbon felt with seawater. The wettability of heated carbon felt is a result of the introduction of hydrophilic surface functional groups (i.e., C=O and C-O). Subsequently, the heated carbon felt relatively lowered the voltage gap ( $\Delta V \sim 1.4$  V) of the rechargeable SWB compared to pristine carbon felt ( $\Delta V \sim$ 1.6 V) (not shown here, refer ref. 58), which implies improved OER/ORR activity of heated carbon felt.

**5.3.2. Electrocatalysts.** The rechargeable SWB with the aforementioned carbon current collectors still shows a low voltage efficiency with a large voltage gap ( $\sim$ 1.0 V) between charge and discharge voltage curves due to the sluggish kinetics of the OER and ORR processes. In these circumstances, to diminish charge-discharge voltage gaps, it is desirable to employ electrocatalysts on the cathode current collector to

improve the OER and ORR activity. An electrocatalyst is a catalyst that enhances electrochemical reactions and can modify and increase the rate of chemical reactions without being consumed in the process. Generally, the available commercial electrocatalysts are mostly noble metal-based, such as Pt, Ru, and Ir. The IrO2- and RuO2-based electrocatalysts are considered the best electrocatalysts for the OER<sup>87</sup> and Pt/C for the ORR,<sup>88</sup> therefore making them inadequate for use as bifunctional catalysts in a rechargeable SWB. The high cost and scarcity of noble metals also hinder their widespread use in large-scale applications.89 For efficient bifunctional (OER/ORR) electrocatalytic activity, the electrocatalyst should possess the following features: (i) high active site density and uniform distribution for low OER and high ORR onset potential and high catalytic activity, (ii) a large surface area and a sufficiently porous structure for sufficient mass transfer pathways and enhanced electrode kinetics, (iii) a robust architecture for chemical and mechanical stability for high durability, (iv) high mass and volumetric activity, and finally (v) an abundant resource with a low cost. Therefore, we prepared and tested several bifunctional electrocatalysts in an SWB as substitutes to noble metals. Based on reports found in the literature, bifunctional electrocatalysts can be classified into three groups: nonprecious metal-based catalysts, carbon-based catalysts, and hybrid catalysts. This section will provide the research efforts that have been made on different electrocatalysts to obtain enhanced performance in rechargeable SWBs.

5.3.2.1. Non-precious metal oxide-based electrocatalysts. Nonprecious metal oxide-based electrocatalysts are a great alternative to noble metal-based electrocatalysts because of their earthabundance, acceptable price and easy preparation compared with a noble metal catalyst, which makes them more suitable for practical application.90,91 Besides, some great approaches have been proposed in recent studies to improve the catalytic activity of metal oxide-based electrocatalysts, including tuning their elemental composition and creating porous nanostructures to increase the density of active sites. Accordingly, Abirami et al. prepared highly porous cobalt-manganese oxide  $(Co_x Mn_{3-x}O_4)$  nanoparticles (see the TEM image in Fig. 8a) with a surface area of ~64.5  $m^2~g^{-1}$  by using  $Mn[Co(CN)_6]_2 \cdot nH_2O$  as a precursor and employed them as a bifunctional electrocatalyst in SWBs.92 The SWB cell containing the CMO exhibited a significantly reduced voltage gap ( $\Delta V \sim 0.53$  V) (Fig. 8b) with a voltage efficiency of  $\sim$ 85% compared to that of the cells containing Pt/C (~0.64 V) or Ir/C (~0.73 V), or without any catalyst ( $\sim$ 1.05 V) at a current density of 0.01 mA cm<sup>-2</sup>, as well as stable performance during 100 cycles. Shin et al. reported the synthesis of cobalt vanadate (Co3V2O8) nanoparticles as an electrocatalyst for SWB application.93 The Co3V2O8 improved the kinetics of the OER/ORR and exhibited a small voltage difference of 0.95 V at 0.1 mA cm<sup>-2</sup> during 20 cycles (total 400 h) with a voltage efficiency of 76%.

5.3.2.2. Carbon-based electrocatalysts. Carbon-based electrocatalysts are also known as metal-free electrocatalysts and because of their large surface area, various structures, and costeffectiveness are considered as alternatives to expensive noble metal-based catalysts. Therefore, carbon-based electrocatalysts



**Fig. 8** (a) TEM image of  $Co_xMn_{3-x}O_4$ . (b) Charge-discharge profile of a rechargeable SWB (Na|seawater) using  $Co_xMn_{3-x}O_4$  derived from Mn  $[Co(CN)_6]_2 \cdot nH_2O$  as a precursor where its performance is compared with that of a cathode current collector (carbon paper) and different electrocatalysts (*i.e.* Pt/C and Ir/C). (c) SEM image of porous carbon. (d) Charge-discharge profiles of a rechargeable SWB (Na|seawater) using porous carbon derived from grapefruit peel where its performance is compared with that of a cathode current collector (carbon paper) and various electrocatalysts. (e) TEM image of a S-rGO-CNT-Co catalyst. (f) Charge-discharge profiles of the rechargeable SWB cell using the S-rGO-CNT-Co catalyst where its performance is compared with that of a cathode current collector (carbon paper) and Pt/C. (g) SEM image of carbon sponge. (h) Charge-discharge profiles of the rechargeable SWB cell using the rechargeable SWB cell using the carbon sponge. (h) Charge-discharge profiles of the rechargeable SWB cell using the rechargeable SWB cell (Na|seawater) using 3D macroporous carbon sponge where its performance is compared with permission.<sup>50</sup> Copyright 2016, American Chemical Society. (c and d) Adopted with permission.<sup>57</sup> Copyright 2017, Royal Society of Chemistry. (e and f) Reproduced with permission.<sup>140</sup> Copyright 2017, Elsevier. (g and h) Reproduced with permission.<sup>152</sup> Copyright 2018, Elsevier.

are also one of the most examined electrocatalysts in metal–air battery systems which are operated based on the OER and ORR.<sup>94,95</sup> The widely studied carbon-based electrocatalysts include porous carbon, graphene, carbon black, nanotubes, and nanofibers that are usually doped with heteroatoms (S, N, O, P and B) and/or contain defective carbon atoms.<sup>95–98</sup> Therefore, to obtain a high performing OER and ORR, carbon catalysts require a careful and creative choice of carbon sources, doping sources, carbon precursor, template, and synthetic conditions.

Based on the above context, we fabricated porous carbon catalysts with high surface areas, defects, and self-doped oxygen functional groups which were prepared from an organic biowaste of grapefruit peel using hydrothermal carbonization combined with the chemical activation process.99 The rechargeable SWB with this porous carbon (see the SEM image in Fig. 8c) catalyst exhibited excellent cycling stability with a narrow voltage gap ( $\Delta V \sim 0.47$  V) during 100 cycles compared to other electrocatalysts, such as Pt/C ( $\sim 0.68$  V), IrO<sub>2</sub> ( $\sim 0.66$  V),  $MnO_2$  (~0.73 V), and Vulcan X72 (~0.80 V) (Fig. 8d). This grapefruit derived porous carbon can be an excellent/costefficient substitute for the expensive carbon materials of graphene and carbon nanotubes. Jeoung et al.86 prepared porous Ndoped carbon (PNC) by using thermolysis of a Zn-based metalorganic framework [Zn(FMA)(4-(phenylazo)pyridine)<sub>2</sub>(H<sub>2</sub>O)] in an inert atmosphere. The PNCs demonstrated in the rechargeable SWB featured low voltage gaps of <0.53 V at 0.01 mA cm<sup>-2</sup>. Similarly, Khan and his co-researchers<sup>100</sup> synthesized N-doped and N, S-doped carbon nanosphere (referred to as NCS and NSCS, respectively) electrocatalysts by using pyrolysis of polydopamine (PDA) nanospheres and studied their feasibility in a rechargeable SWB. The rechargeable SWB tested with NSCS showed a low voltage gap ( $\Delta V \sim 0.56$  V), round-trip efficiency (84%), and outstanding cycle stability up to 100 cycles.

5.3.2.3. Hybrid or composite electrocatalysts. Metal oxidebased catalysts show better bifunctional OER and ORR catalytic activity, but typically they face two main issues. One is poor electrical conductivity, and another is fast degradation of active sites by particle aggregation during redox reactions, which should be rectified for their practical use.<sup>91,94</sup> Therefore, to solve these issues, metal-based catalysts are mixed with carbon materials to make a composite. One-dimensional carbon nanotubes (CNTs) with the encapsulation of cobalt-based nanoparticles on a three-dimensional internetworked reduced graphene oxide (named as S-rGO-CNT-Co) were synthesized (see the TEM image in Fig. 8e) by using steam activation and microwave irradiation.59 The as-prepared material was used as a bifunctional electrocatalyst in the cathode current collector of an SWB cell. The cell showed a small voltage gap ( $\Delta V \sim 0.42$  V) compared to bare carbon paper ( $\sim$ 0.88 V) at a current density of  $0.01 \text{ mA cm}^{-2}$  (Fig. 8f).

*5.3.2.4. Current collector cum electrocatalyst.* All the above electrocatalysts were mostly prepared or used in the form of powder. Thus, to attach them on cathode current collectors of rechargeable SWBs, it is necessary to use inactive binders. However, binders are usually a form of insulating polymer and thus can hinder the ion and electron transport in the system, resulting in an influence on the overall performance of electrocatalysts, and also increase the production costs of the

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battery.<sup>101</sup> Therefore, Zhang and his co-researchers in our group prepared 3D macroporous carbon sponges (see the SEM image in Fig. 8g) and directly employed the sponges as a cathode current collector as well as a carbon-based electrocatalyst for the OER/ORR in a rechargeable SWB.<sup>102</sup> Interestingly, the tested SWB using a carbon sponge exhibited a small charge–discharge voltage gap ( $\Delta V \sim 0.46$  V) and high voltage efficiency (~83.2%) with long term cycling stability (100 cycles) (Fig. 8h).

5.3.3. SWB with non-OER/ORR cathode chemistry. Even after using an electrocatalyst on a cathode current collector, the voltage gap is still high due to the slow kinetic nature of the OER and ORR processes. Therefore, to achieve a smaller voltage gap, SWBs with other cathode chemistries (see Fig. 9a) such as (i) chloride (Cl<sup>-</sup>) capture/release reaction, (ii) intercalation/ deintercalation, and (iii) a combined intercalation/ deintercalation and OER/ORR process have also been reported elsewhere.<sup>103-105</sup> It is worth noting that the SWB was operated based on intercalation/deintercalation and chloride (Cl<sup>-</sup>) capture/release reactions where seawater acted as an electrolyte. Nonetheless, for intercalation/deintercalation combined with the OER/ORR processes, seawater acted as both an electrolyte and a cathode.

As we know, seawater contains more than enough  $Cl^-$  ions. Therefore, when using Ag as a cathode in an SWB,<sup>104</sup> the reversible redox reaction of Ag/AgCl (Ag (s) +  $Cl^-$  (aq)  $\leftrightarrow$  AgCl (s) at ~2.9 V vs. Na<sup>+</sup>/Na) can occur during the cell operation. This Ag/AgCl reaction delivers an enhanced electrochemical performance compared to the OER/ORR processes that occur on carbon felt (*i.e.* common cathode reaction in the rechargeable SWBs). The obtained voltage gap and voltage efficiency for the Ag electrode are 0.3 V and 90.3%, while they are 1.58 V and 73% for carbon felt (Fig. 9b). However, Ag is very expensive and not a practical/viable cathode for real-time application. Recently, Bi (bismuth),<sup>106</sup> BiOCl (oxychlorides),<sup>107</sup> polypyrrole,<sup>108</sup> and polysilsesquioxane<sup>109</sup> have also been considered as potential chloride storage materials; thus we hope that they could be our future alternative cathode for the expensive Ag.

On the other hand, nickel hexacyanoferrate (NiHCF) with intercalation/deintercalation characteristics was used as the cathode. The assembled SWB with NiHCF<sup>103</sup> showed a relatively small voltage gap between the charge–discharge curves with a typical discharge voltage of 3.4 V (Fig. 9c), owing to the highly reversible and fast Na-ion intercalation/deintercalation characteristics of NiCHF. However, in the above strategies, the voltage efficiency can be improved, but the energy is limited by the amount of cathode chemistry. Recently, to enhance the energy performance, Na<sub>0.5</sub>Co<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> (NCMO, P2-type layered oxide) was employed<sup>105</sup> as the cathode for Na-ion intercalation/ deintercalation and as the electrocatalyst for the OER and ORR processes. As we expected, NCMO showed a dual electrochemical process, *i.e.* intercalation/deintercalation and OER/ORR during the charge and discharge operations, as shown in



**Fig. 9** (a) Other cathode chemistries apart from the OER/ORR used for rechargeable SWBs. (b) Charge and discharge profiles of a rechargeable SWB using Ag as a cathode for chloride (Cl<sup>-</sup>) capture/release reaction and a comparison of its performance with that of a carbonaceous electrode. (c) First ten charge–discharge curves of a rechargeable SWB using a NiHCF cathode for Na-ion intercalation/deintercalation. (d) Charge–discharge profiles of NMCO and a comparison of its performance with that of carbon felt. NMCO offers Na ion intercalation/deintercalation and OER/ORR processes. (b) Adopted with permission.<sup>104</sup> Copyright 2016, Elsevier. (c) Adopted with permission.<sup>105</sup> Copyright 2018, Royal Society of Chemistry.

Fig. 9d, where the OER occurs followed by Na<sup>+</sup> intercalation and ORR occurs followed by Na<sup>+</sup> intercalation. This dual electrochemical process characteristic of NCMO was further confirmed via cyclic voltammetry analysis by the authors.<sup>105</sup> Because of NCMO, a reasonably reduced voltage gap (0.78 V) was attained for the assembled SWB (Na/seawater/NCMO@carbon felt). This obtained smaller voltage gap was much better than that of the carbon felt (1.06 V) and closer to that of Pt/C coated carbon felt which was used only for the OER/ORR processes. Anyway, NiHCF and NCMO are not the only limited materials for Na-ion intercalation/deintercalation and dual electrochemical process (intercalation/deintercalation and OER/ORR); however, still many materials are available that could also be studied at the cathode side of this SWB.  $Na_2Ni_{0.4}Co_{0.6}[Fe(CN)_6]$ (85 mA h  $g^{-1}$ ),<sup>110</sup> FeFe(CN)<sub>6</sub> (125 mA h  $g^{-1}$ )<sup>111</sup> and Na<sub>2</sub>Mn  $[Mn(CN)_6]$  (209 mA h g<sup>-1</sup>)<sup>112</sup> can be considered for the Na-ion intercalation/deintercalation process with high capacity.  $Na_{0.95}MnO_2$  (~42 mA h g<sup>-1</sup>),<sup>113</sup>  $NaMn_9O_{18}$  (45 mA h g<sup>-1</sup>),<sup>114</sup>  $Na_{0.44}Mn_{0.44}Ti_{0.56}O_2$  (76 mA h g<sup>-1</sup>)<sup>115</sup> and  $NaNi_{0.33}Mn_{0.33}$ - $Co_{0.33}O_2$  (120 mA h g<sup>-1</sup>)<sup>116</sup> can be used for a dual electrochemical process or only for the Na-ion intercalation/ deintercalation process.

#### 5.4. Anode compartment

The anode compartment comprises an anode and nonaqueous electrolyte. Both play a critical role together in the SWB. The anode has more responsibility for electrical energy storage by harvesting Na-ion from seawater, which can readily supply an unlimited number of Na ions while flowing through the rechargeable SWB. The non-aqueous electrolyte acts as an ionic transport medium between the anode and a solid electrolyte during the charging and discharging processes and it is generally also one of the main factors that influence the cycling performance by offering interfacial stability to the anode and voltage window stability. We have described in the subsequent subsections the research studies that have been carried out so far on the anode and non-aqueous electrolyte to develop rechargeable SWBs.

**5.4.1. Anodes.** The anode materials that are reported or considered for a sodium-ion battery can be used as an anode in rechargeable SWBs as well. There are several kinds of feasible anode materials available for sodium storage: sodium metal (Na) or harvested sodium from the seawater cathode, intercalation materials (hard carbon (HC), TiO<sub>2</sub>, Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>, *etc.*), alloying materials (Bi, Sn, SnSb, P, *etc.*), conversion materials (Fe<sub>2</sub>O<sub>3</sub>, MoS<sub>2</sub>, NiO, *etc.*), conversion-alloying materials (Sb<sub>2</sub>S<sub>3</sub>, SnS<sub>2</sub>, *etc.*) and organic materials (Na<sub>2</sub>C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>) (see Fig. 10).<sup>22,117-120</sup> The search for appropriate anodes for rechargeable SWBs is not an easy task; however, some of the materials have been reported to be useful as anodes in rechargeable SWBs, such as hard carbon,<sup>99</sup> antimony sulfide (Sb<sub>2</sub>S<sub>3</sub>),<sup>121</sup> tin/carbon (Sn/C),<sup>122</sup> and phosphorus/carbon (P/C).<sup>123</sup>

5.4.1.1. Sodium metal. When considering its low electrochemical potential and high capacity, sodium  $(E_{\text{Na}^+/\text{Na}} = -2.71 \text{ V})$  vs. SHE and 1166 mA h g<sup>-1</sup>)<sup>124</sup> could be an ideal anode material for rechargeable SWBs. The low electrochemical potential of Na



**Fig. 10** Average redox potential *versus* gravimetric capacity of various anode materials which can be used for Na ion storage in rechargeable SWBs.

can encourage the achievement of a high cell voltage (~3.48 V vs. Na/Na<sup>+</sup>) in rechargeable SWBs (see eqn (1)-(3)) and then this achieved high cell voltage along with the high capacity could furnish high energy density rechargeable SWBs (theoretically 4057 W h kg<sup>-1</sup> with respect to the Na anode). Taking full advantage of Na, we used Na as an anode in rechargeable SWBs in two different forms, individually, i.e. (i) Na harvested from seawater by charging<sup>124</sup> and (ii) Na metal (commercially available).26 However, because of the highly reactive nature of Na, during the charging process, electrodeposited Na shows a tendency towards dendrite formation and growth. Also, Na anodes typically suffer from unstable solid-electrolyte interphase (SEI) layers and large electrode dimensional changes upon repeated plating/stripping. Consequently, rechargeable SWBs face several problems: low cycling, low rate capability, and low coulombic efficiency.124,125

To enhance the lifespan of Na anodes, there are several approaches that have been developed<sup>126</sup> to prevent dendrite growth and form a uniform and stable SEI layer on Na anodes by using artificial SEI layers on Na metal, additives in the electrolyte, electrolytes with super concentrations, three dimensional (3D) current collectors, Na/carbon anodes, and nanoscale interfacial engineering. With this background, to build anodefree rechargeable SWBs, graphene-coated Cu (graphene/Cu) current collectors have been developed using a chemical vapour deposition method by D. H. Kim et al.127 Before their use in rechargeable SWBs, the graphene/Cu current collectors are subjected to a galvanostatic plating and stripping test using a symmetric (graphene/Cu|separator|Na anode) cell architecture. Graphene/Cu current collectors compared to Cu current collectors lower the nucleation overpotential (40 mV), stabilize plating/stripping (Fig. 11a), and stabilize coulombic efficiency even after 200 plating/stripping cycles (not shown here; see ref. 127). When using this graphene/Cu current collector in a rechargeable SWB, a stable voltage plateau is obtained with a more extended cycling profile compared to a Cu current



Fig. 11 Comparison of (a) cycling performance of graphene-covered Cu (red line) and pristine Cu (black line) current collectors at 0.32 mA cm<sup>-2</sup> for 1000 s in 1 M NaOTF/DME electrolyte. (b) Galvanostatic discharge–charge profiles of rechargeable SWB cells with graphene Cu (red line) and pristine Cu (black line) current collectors at 0.075 mA cm<sup>-2</sup>. SEM images of plated Na from seawater on (c) graphene covered Cu and (d) pristine Cu metal current collectors (0.675 mA h cm<sup>-2</sup> (0.075 mA cm<sup>-2</sup>) for ~9 h). (e) Comparison of cycling performance of a Na/C composite anode and bare Na anode at 3 mA cm<sup>-2</sup>. SEM images of the (f) Na/C composite anode and (g) bare Na anode after cycling (scale bars = 40  $\mu$ m). (h) Galvanostatic discharge–charge profiles of rechargeable SWB cells containing a Na/C composite anode and bare Na anode at different current densities from 0.5 to 3 mA. (a–d) Reproduced with permission.<sup>127</sup> Copyright 2018, Royal Society of Chemistry. (f–h) Reproduced with permission.<sup>125</sup> Copyright 2019, American Chemical Society.

collector (see Fig. 11b).<sup>127</sup> From the SEM image, it was distinguished that the plated Na metal on graphene/Cu current collectors of rechargeable SWBs have a large grain size, fewer nuclei, and a smooth surface (Fig. 11c), unlike a Cu current collector (Fig. 11d). Similarly, the feasibility of a Cu prepatterned Al current collector was examined by Jung et al. for metal-free rechargeable SWBs.128 From the symmetric cell test, it was found that Na prefers Cu surfaces for its deposition rather than Al within the current collector, and Na islands later merged to form a film-like aggregation. Therefore, the authors anticipated that this film-like aggregation could control the dendrite growth in rechargeable SWBs. As expected, a rechargeable SWB with a Cu pre-patterned Al current collector exhibited a significant increase of coulombic efficiency which was maintained at approximately 98% over 200 cycles, which is much better (four times) than a Cu collector rechargeable SWB.

On the other hand, Go *et al.*<sup>125</sup> prepared Na/carbon composite anodes by immersing 3D carbon cloth in melted Na (melt infusion strategy) for use in rechargeable SWBs. The resulting anodes exhibited a stable potential and a small

hysteresis beyond 80 h in the asymmetric cell test at 3 mA cm<sup>-2</sup>, but the bare Na anode showed unstable and fluctuating hysteresis even after 10 h under the same testing conditions (at 3 mA cm<sup>-2</sup>) (Fig. 11e). The Na/C anode showed an almost smooth surface (Fig. 11f) and the bare Na anode showed porous and uneven surfaces (Fig. 11g). It is suggested that the stable cycle performance for the Na/C anode came from its even and smooth surface. Consequently, the performance of the Na/C anode was checked in a rechargeable SWB. The high surface area feature of the Na/C anode decreased the local current density and resulted in a lower voltage gap even at a high current compared to the bare anode (see Fig. 11h).<sup>125</sup>

Anyway, the direct use of the Na anode in rechargeable SWBs could create a fire safety issue during operation, as it tends to react with water (seawater). To address this concern, it is essential to use an alternative anode to Na metal with high cycle stability, high reversibility, and low electrochemical potential.

5.4.1.2. Na intercalation hard carbon (HC). Among the carbonaceous anode materials, HC can be a leading anode for sodium storage in sodium-ion batteries due to their low average

operating potentials and relatively high reversible specific capacities. In the early 2000s, Stevens and Dahn first studied its Na storage ability. HC is also known to be non-graphitizable, and its structure typically contains small turbostratic (fewlayer-stacked graphite) nano-domains with nanovoids which exist in between these nano-domains. Hence, HC (commercial) was first studied as a metal-free anode in a rechargeable SWB battery. In Fig. 12a, (i) and (ii) show the normalized charge and discharge curves of a cathode half-cell (Na/seawater/carbon felt (cathode current collector)) and an anode half-cell (Na/HC) and (iii) displays a comparison of the measured and simulated charge and discharge curves of metal-free (or full cell) rechargeable SWBs (HC/seawater/carbon felt). More interestingly, it can be seen that the simulated and measured charge and discharge curves provide a similar result. Senthilkumar et al.99 tested a HC-based metal-free rechargeable SWB with a combination of a grapefruit peel derived porous carbon electrocatalyst under a capacity cut-off condition of 200 mA h  $g^{-1}$ upon charging, and a voltage cut-off condition of 0.5 V upon discharge (0.05 mA cm<sup>-2</sup>). Fig. 12b shows the improved performance of the HC-based rechargeable SWB after using a porous carbon electrocatalyst on a cathode current collector (carbon paper). Notably, the HC-based rechargeable SWB exhibits a discharge capacity of 191 mA h  $g^{-1}$  (at the 7th cycle), a voltage efficiency of 83-84% and an excellent life over 100 cycles (Fig. 12c). In the cycling result, it can be noted that the discharge capacity and coulombic efficiency were relatively low during the initial cycling of approximately four cycles because of the development of the solid electrolyte interface (SEI) layer on HC due to charging. However, after the 7th cycle, as seen in

Fig. 12c, a stable discharge capacity was noted. Besides, when a porous cobalt-manganese oxide  $(Co_x Mn_{3-x}O_4)$  was used on the cathode current collector of an HC-based rechargeable SWB,<sup>92</sup> the results showed an increased reversible discharge capacity (~190 mA h g<sup>-1</sup>), high energy efficiency (~74–79%), and stable cycle performance over 100 cycles. These results were obtained under the capacity cut-off condition of 200 mA h g<sup>-1</sup> upon charging and a voltage cut-off condition of 0.5 V upon discharge (0.01 mA cm<sup>-2</sup>).

5.4.1.3. Alloy-based materials ( $Sb_2S_3$ , Sn/C and P/C). HC exhibits a consistent discharge capacity with relatively small volume expansions during the electrochemical insertion/ extraction reaction with Na<sup>+</sup> ions harvested from seawater cathodes. However, HC still suffers from limited capacity utilization due to their intrinsic constraint ascribed to their structures which can lower the specific energy density of rechargeable SWB systems. As an alternative to HC, so far Sb<sub>2</sub>S<sub>3</sub>,<sup>121</sup> Sn/C<sup>122</sup> and P/C<sup>123</sup> were investigated as potential high capacity anodes for Na-ion storage in SWBs because they can store a large number of Na ions in the host structure with a relatively low operating potential (below 1.0 V).

The advantages of  $\text{Sb}_2\text{S}_3$  are its high theoretical capacity (946 mA h g<sup>-1</sup>) compared to Sb (660 mA h g<sup>-1</sup>) for Na insertion, as well as an expected improvement in mechanical stability due to smaller volume changes during charge and discharge from the sulfides. This high capacity feature comes from the combination of a conversion reaction ( $\text{Sb}_2\text{S}_3 + 6\text{Na}^+ + 6\text{e}^- \rightarrow 2\text{Sb} + 3\text{Na}_2\text{S}$ ) and an alloying reaction ( $2\text{Sb} + 6\text{Na}^+ + 6\text{e}^- \rightarrow 2\text{Na}_3\text{Sb}$ ).<sup>129,130</sup> For SWB's anode application, Hwang *et al.*<sup>121</sup> synthesized spherical nanoparticles of  $\text{Sb}_2\text{S}_3$  using a simple



**Fig. 12** (a) Measured and calculated charge-discharge voltage profiles of anode (Na|hard carbon) and cathode (Na|seawater) half and full cells (HC|seawater). (b) Charge-discharge voltage profiles of a rechargeable SWB full cell (HC|seawater) based on carbon paper and porous carbon@carbon paper and their obtained voltage gap. (c) Cycle performance of a rechargeable SWB full cell based on porous carbon@carbon paper at 0.05 mA cm<sup>-2</sup>. (d) Charge-discharge voltage profiles of a P/C composite anode using a rechargeable SWB full cell (P/C composite|seawater). (e) Capacity retention of the rechargeable SWB full cell (P/C composite|seawater) operated with the P/C composite anode. (a) Reproduced with permission.<sup>25</sup> Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b and c) Reproduced with permission.<sup>57</sup> Copyright 2018, Royal Society of Chemistry. (d and e) Reproduced with permission.<sup>123</sup> Copyright 2018, Royal Society of Chemistry.

solution process at room temperature. In the full cell rechargeable SWB, the results showed a specific capacity of 233 mA h  $g^{-1}$  in the first cycle which reached 485 mA h  $g^{-1}$  at the 70<sup>th</sup> cycle. These results were obtained under the testing conditions of capacity cut-off at 550 mA h  $g^{-1}$  during charging and a voltage cut-off with 0.4 V on discharge (current density was 0.05 mA cm<sup>-2</sup>).

The Sn-based anode has a theoretical capacity of 847 mA h  $g^{-1}$ , based on the full sodiation state of Na<sub>15</sub>Sn<sub>4</sub>.<sup>131</sup> The P-based anode has a theoretical capacity of 2596 mA h  $g^{-1}$ based on the formation of Na<sub>3</sub>P.<sup>131</sup> Both are known to be cheap and abundant materials. However, both greatly suffer from volume changes and poor electrical conductivity. Therefore, using carbon-conducting techniques such as carbon coating and/or formation of composites with a 2D or 3D carbon matrix are a very beneficial way to buffer the volume changes and create electric conducting pathways. Hence, J. K. Kim<sup>122</sup> and Y. Kim<sup>123</sup> prepared an Sn/C composite by carbonizing a SnO<sub>2</sub>/ carbon<sup>132</sup> compound and P/C composite by mixing P and carbon nanoparticles using a ball-milling method.<sup>123</sup> These carbon composites for Sn and P not only act as a conductive matrix but also as a buffer to control the volume changes. As a result, Sn/C anodes used in a full cell rechargeable SWB exhibit a discharge capacity of approximately 300 mA h  $g^{-1}$  (0.05 mA cm<sup>-2</sup>) over 30 cycles. Fig. 12d and e display the charge-discharge profile and the relative cycle performance of a full cell rechargeable SWB that used P/C as an anode. Interestingly, in the first cycle, a discharge capacity of  $\sim$ 700 mA h g<sup>-1</sup> with a coulombic efficiency of 70% was achieved and after a few cycles, over 950 mA h g<sup>-1</sup> was obtained with coulombic efficiencies of 90-96%, which was retained even after 80 cycles (see Fig. 12e). The low reversible capacity with low coulombic efficiency in the first cycle is due to the formation of an SEI layer in the P/C anode and the increase of capacity after a few cycles caused a gradual activation of the PC composite. The stable high reversible capacity implies the stability of the formed SEI layer on P/C and structural rearrangement of P/C within the first cycles.

It can be commonly seen with all the studied anode materials that during the first or first few cycles, a low discharge capacity with low coulombic efficiency was obtained which is attributed to SEI formation. The SEI layer is usually formed by the decomposition of electrolytes with the consumption of Na ions, thus leading to the low capacity during the first or first few cycles. However, rechargeable SWB systems are an open system that can supply unlimited Na ions from the seawater cathode. Hence, in the following cycles, it is possible to compensate for the Na ions consumed on the anode for SEI layer formation and thereby achieve better cycling stability.

5.4.2. Nonaqueous electrolytes. The ideal non-aqueous electrolyte for the rechargeable SWB anodes should have (i) high stability over the operating voltage (in the low and high voltage regions), (ii) should not hinder the Na-ion transfer kinetics and (iii) should not damage the structure of the anode materials or react with the anode. Therefore, it is essential to use an appropriate electrolyte for the respective anode materials. Mostly, all non-aqueous electrolytes used for sodium batteries can be employed for the anode of a rechargeable SWB, likely 1 M NaClO<sub>4</sub> in EC/PC (EC stands for ethylene carbonate and PC for propylene carbonate). However, in the comparative study, it was found that 1 M NaCF<sub>3</sub>SO<sub>3</sub> in a TEGDME (tetraethylene glycol dimethyl ether) electrolyte for hard carbon anodes in a rechargeable SWB exhibited a better capacity for reversibility (Fig. 13a) and cycling stability performance with a capacity retention of 90% over 100 cycles (Fig. 13b) compared to 1 M NaClO<sub>4</sub> in EC/PC.<sup>133</sup> It is found that 1 M NaClO<sub>4</sub> in an EC-PC electrolyte exhibits poor stability cycle performance from the 30<sup>th</sup> cycle. The reason is that 1 M NaCF<sub>3</sub>SO<sub>3</sub> in a TEGDME electrolyte supports the formation of a thin and stable SEI layer on hard carbon compared to 1 M NaClO<sub>4</sub> in EC-PC.<sup>133</sup>

Ionic liquid electrolytes are well known for their excellent electrochemical and thermal stability. The appropriateness of different ionic liquids as an electrolyte for Sn/C and hard carbon anodes in rechargeable SWBs has been studied by J. K. Kim<sup>122</sup> and Y. Kim,<sup>81</sup> respectively. NaTFSI/Pyr<sub>14</sub>TFSI (1 : 9) ionic liquid electrolyte with an Sn/C anode in a rechargeable SWB showed



Fig. 13 (a) Charge–discharge voltage profile and (b) cycling performance of rechargeable SWB cells (HC|seawater) with 1 M NaClO<sub>4</sub> in EC/PC and 1 M NaCF<sub>3</sub>SO<sub>3</sub> in TEGDME electrolytes at 0.05 mA cm<sup>-2</sup>. (c) Comparison of cycling performance of rechargeable SWB cells (HC|seawater) with NaFSI–Py<sub>13</sub>FSI–Py<sub>13</sub>TFSI electrolyte and 1 M NaCF<sub>3</sub>SO<sub>3</sub> in TEGDME electrolyte. Herein, Pyr<sub>13</sub>FSI stands for *N*-methyl-*N*-propylpyrrolidinium bis(fluorosulfonyl)imide; Pyr<sub>13</sub>TFSI stands for *N*-methyl-*N*-propylpyrrolidinium bis(fluorosulfonyl)imide; A and b) Reproduced with permission.<sup>133</sup> Copyright 2018, Royal Society of Chemistry. (c) Adopted with permission.<sup>81</sup> Copyright 2017, Elsevier.

stable cycle performance over 50 cycles.<sup>122</sup> Concurrently, 1 M NaClO<sub>4</sub> in EC/PC electrolyte lost its stability within 30 cycles. On the other hand, impressive reversible capacity, energy efficiency, and capacity retention were attained when the synthesized quaternary ionic liquid composed of Pyr<sub>13</sub>FSI (0.6 M ratio), Pyr<sub>13</sub>TFSI (0.3 M ratio), and NaFSI salt (0.1 M ratio) with 5 wt% EC additive as a liquid electrolyte was combined within a hard carbon anode in a rechargeable SWB.<sup>81</sup> As shown in Fig. 13c, this ionic liquid electrolyte allowed the hard carbon (derived from peanut shells) anode used in a rechargeable SWB to achieve a stable cyclability with a high energy efficiency of 80–85% over 300 cycles, but the same HC-based rechargeable SWB with 1 M NaCF<sub>3</sub>SO<sub>3</sub> (in TEGDME) electrolyte displayed an ambiguous decrease in energy efficiency after 150 cycles.

Using nonaqueous electrolyte and anode electrode materials separately in the anode side of the rechargeable SWBs could increase the total cost of the system. In this regard, we are attempting to utilize a sodium polycyclic aromatic hydrocarbon<sup>134</sup> based semi-liquid as an anode, for instance, sodium biphenyl.135,136 The merit of this kind of semiliquid anode is that it can behave as an electrolyte as well unlike conventional anodes (hard carbon, Sb<sub>2</sub>S<sub>3</sub>, Sn/C, P/C, etc.).<sup>22</sup> Consequently, we are expecting that the successful employment of sodium polycyclic aromatic hydrocarbon based semi-liquid as an anode will reduce the cost of rechargeable SWBs for their commercialization.

collected scientific and methodological knowledge. Development related to cell components such as Na-ion-conducting membranes, current collectors, anodes, electrolytes for an anode, electrocatalysts, and assembly/processing steps has been conducted accordingly. Our coin cell designs can be used only for lab purposes and cannot be used for real application. Therefore, the prismatic cell has been designed for practical application purposes through appropriate engineering. Fig. 14a displays the fabricated prismatic cells with and without cathode current collectors (i.e. carbon cloth). These prismatic cells are the thinnest and lightest so they can offer a smaller space utilization when being used in large scale application as well as have the potential for larger capacity and higher electrical energy storage. Square-type NASICON ceramics with 24 numbers (12 per side) are used in this prismatic cell. Fig. 14b shows the prototype module which is composed of 40 prismatic cells. Recently, assembling several prototype modules (composed of 2000 cells) in a rack as shown in Fig. 14c, we have reached 10 kW h. The obtained galvanostatic charge-discharge and power performance results of the unit cell and stacked cells (in parallel) are shown in Fig. 14d and e. From this result, it can be determined that when the number of cells in a stack increases, the voltage gap decreases (for tests of 5 hours) and power output increases.25

## 7. Application of rechargeable SWBs

## 6. Prismatic cell design and cell stack

We have developed coin cell platforms and flow-type cell testers over the past few years (see Section 5.1) through which we have Rechargeable SWBs can be operated as an open cathode system where the charge and discharge processes are completed in seawater as a cathode. Therefore, it is expected that these rechargeable SWBs are more suitable for the marine sector,



**Fig. 14** Schematic illustration of the development of rechargeable SWB prismatic cells for ESSs. (a) Anode part of the unit cell (Ver. 1) and complete unit cell (Ver. 2). (b) A module of rechargeable SWB that comprises 40 prismatic cells. (c) Arrangement of several modules in a rack that contains 2000 prismatic (rechargeable SWB) cells. (d) Charge–discharge voltage profiles of the unit cell, 3 cell stack and 5 cell stack rechargeable SWBs operated at a current of 30 mA. (e) Polarisation curves of the unit cell, 3 cell stack rechargeable SWBs plotted at a scan rate of 0.04 mA s<sup>-1</sup> per unit cell. (d and e) Adopted with permission.<sup>25</sup> Copyright 2019, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

offshore and seaside power sources, or energy storage applications. The possible applications of rechargeable SWBs are illustrated in Fig. 15. Our expected applications for rechargeable SWBs are described briefly as follows.

### 7.1. Life jackets

For life jacket applications, the battery should provide instant power necessary to activate mounted GPSs and light sources. Likely, the anode part of this rechargeable SWB is completely isolated from the cathode so when its cathode part comes into contact with seawater, it can start to provide instant power. Therefore, marine life jackets could use this type of SWB (in the charged state) to power a light source and operate a GPS attached to the jackets. The light and GPS can provide the positioning of a person who needs help in emergencies,<sup>11</sup> for example, during a shipwreck or when a boat capsizes.

### 7.2. Light buoys

The light buoy is a kind of object like a lighthouse which is also used in the sea/ocean as navigational equipment or warning points about obstructions for ships and boats. Present light buoys mostly use toxic, poor energy density, and heavy lead-acid batteries to power the mounted LED lights, GPS, and monitoring systems (used for monitoring water temperature, current/wind speed and direction, and water salinity). Compared to lead-acid batteries, rechargeable SWBs can provide a high energy density, eco-friendly, low weight, and



Fig. 15 Possible potential applications for the rechargeable SWBs. Power sources for life jackets, power buoys, automatic surface vehicles (example: sonar sensors for depth calibration), underwater vehicles (example: robots, drones and scooters). ESSs for wave/tidal energy and offshore energy islands that comprise solar panels and wind turbines.

maintenance-free option. Hence, it is possible to replace leadacid batteries with rechargeable SWBs.

## 7.3. Autonomous surface vehicles (ASVs)

ASVs are similar to floating equipment on seawater like a light buoy. They are used to evaluate the water depth and detect obstructions using ultrasonic signals for ships and boats. Most ASVs are deployed in ports and harbors. RSWBs can store the power from solar panels and provide a non-stop power supply to provide 24 hours of operation on the water surface.

## 7.4. Underwater robots, drones, and scooters

Underwater robots and drones are also called remotely operated vehicles (ROVs) which are used in the military and heavy industries like oil extraction companies. They are also used for oceanographic research to study marine life and their difficulties. Underwater scooters (UWSs) are used for tour purposes for viewing colorful fish and intricate reefs inside the oceans. However, all of these are operated by an electrical power supply of batteries, so these rechargeable SWBs can be a good candidate to be adopted as a power source in ROVs and UWSs.

### 7.5. Offshore and seaside energy storage

Nearly 50% of the world's population lives near the sea. Of the 17 largest cities in the world, 14 are located near coasts, and they consume the majority of electrical energy. The required electrical power transferred from a long distance increases costs and reduces energy efficiency. Recently, renewable energy technologies such as solar, wind, wave, and tidal-based energy generators have been deployed offshore and on the seaside to minimize energy transmission distances. However, a large-scale EES system is necessary to supply stable electrical energy and rechargeable SWBs can be a much better option for electrical energy storage in huge quantities. It is expected that the offshore and seaside deployment of rechargeable SWBs could be very easy as they operate in seawater as main battery components.

Herein it must be noted that the application of rechargeable SWBs is not limited only to applications shown in Fig. 15 but can also be extended to other applications.

## 8. Extended concept for rechargeable SWBs

Considering the unique features of rechargeable SWBs such as the cathode open structure for different possible cathode electrochemical processes and sodium harvesting (or removal) from seawater and their advanced cell design, it was expected that there is a great opportunity to extend their concept for seawater desalination,  $CO_2$  capture, photo-charging of SWBs,  $H_2$ production and seawater disinfection without losing their energy storage characteristics. Some of the reported proof-ofconcept studies for the extended rechargeable SWB concept are described below.

#### 8.1. Seawater battery (SWB)-desalination system

As can be observed above, during the charging process, the Na<sup>+</sup> ions move from seawater to the anode and the moved Na<sup>+</sup> ions are isolated by NASICON from seawater. Therefore, if we could modify the cathode side of a rechargeable SWB to (re)move chloride ions, we can expect the function of desalination to be achieved. Therefore, a rechargeable SWB can be modified into a SWB-desalination system, as shown in Fig. 16a. This proof-of-concept of the SWB-desalination system contains<sup>137</sup> four compartments which are charge cathode, desalination, anode, and discharge cathode parts. The desalination compartment is separated from the charge cathode compartment at the left side by an anion exchange membrane (AEM) and anode compartment at the right side by NASICON, respectively. NASICON is also used to separate the anode from the discharge cathode compartment.

Fig. 16b shows the charge and discharge capacity and the coulombic and energy efficiency of SWB desalination systems (from the  $2^{nd}$  cycle). During charging of the system, Na<sup>+</sup> ions move to the anode side, and simultaneously Cl<sup>-</sup> ions transfer to the charge cathode compartment and form HCl solution by electrochemical reaction with water. During discharging of the system, NaOH solution is formed in the discharge cathode compartment by the electrochemical reaction of Na<sup>+</sup> ions transported from the anode side with water and dissolved oxygen. After 10 individual charging cycles, the concentration of Na<sup>+</sup> and Cl<sup>-</sup> ions of seawater in the desalination compartment



Fig. 16 (a) Schematic diagram of the designed SWB-desalination system and its possible charge and discharge process. (b) Charge and discharge capacities and the corresponding coulombic efficiency of the SWB-desalination system for ten cycles at 10 mA g<sup>-1</sup>. The pH change with cycle number during charge (c) and discharge (d). (a–d) Reproduced with permission.<sup>137</sup> Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA.

Table 2Ion concentration of seawater before and after the 10thcharging. Reproduced with permission from ref. 137. Copyright 2018,Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

	Ion concentration (mg $L^{-1}$ )								
Sample	$Na^+$	Mg <sup>2+</sup>	$\mathbf{K}^+$	Ca <sup>2+</sup>	$Cl^-$	$\mathrm{SO_4}^{2-}$	Total		
Pristine seawater After the 10 <sup>th</sup> charge	10 166 9072	1229 1171	395 369	450 429	19 916 18 176	2754 2681	34 910 31 898		

decreased, as shown in Table 2. Moreover, the pH value of water in the charge cathode compartment increases due to the formation of  $H^+$  ions through the OER (Fig. 16c). On the other hand, with increasing discharge cycles, the pH value of water in the discharge cathode compartment rises due to the creation of  $OH^-$  ions *via* the ORR (Fig. 16d). Therefore, this proposed proofof-concept SWB-desalination system can not only store/deliver electricity and desalination, but can also produce an acidalkali solution.

## 8.2. Seawater battery-desalination carbon capture (SWB-DC) system

The SWB-DC system is also a modified system of rechargeable SWBs and operated in a very similar manner to the SWBdesalination system.<sup>138</sup> As shown in Fig. 17a, the SWB-DC system is comprised of three main sections: (i) desalination, (ii) anode, and (iii) discharge cathode (carbon-capture). NASI-CON separates the anode section from the desalination and discharge cathode sections. In this system, the charging process completes the desalination where Cl<sup>-</sup> ions and Na<sup>+</sup> ions from seawater are removed by Cl<sup>-</sup> capture using an Ag (foil) cathode and  $Na^+$  harvesting at the anode, respectively (eqn (4) and (5)). The discharge process completes the carbon-capture with the assistance of NaOH which forms during the ORR. This carbon capture process can occur through the reaction between NaOH and  $CO_2$  (eqn (6)) and a metal hydroxide (for instance,  $Ca(OH)_2$ ) or  $Mg(OH)_2$  and  $CO_2$  (eqn (7)) where  $Ca(OH)_2$  and  $Mg(OH)_2$  can be formed via a reaction between Ca<sup>2+</sup>, Mg<sup>2+</sup>, and NaOH in seawater (eqn (8)).138

During charge:

$$Na^+ + e^- \rightarrow Na$$
 (4)

$$Ag(s) + Cl^{-}(aq) \rightarrow AgCl(s) + e^{-}$$
(5)

During discharge:

$$2\text{NaOH} (\text{aq}) + \text{CO}_2 (\text{g}) \rightarrow \text{Na}_2\text{CO}_3 (\text{aq}) + \text{H}_2\text{O} (\text{l})$$
 (6)

$$\begin{array}{l} M(OH)_2 \mbox{(aq)} + 2CO_2 \mbox{(g)} \rightarrow MCO_3 \mbox{(aq)} + H_2O \mbox{(l)}; \\ M = Mg \mbox{ or } Ca \mbox{(7)} \end{array}$$

Metal hydroxide formation  $(\mbox{Ca}(\mbox{OH})_2\mbox{ and }\mbox{Mg}(\mbox{OH})_2)$  in seawater:

2NaOH (aq) + MCl<sub>2</sub> (aq) 
$$\rightarrow$$
 2NaCl (aq) + M(OH)<sub>2</sub> (aq);  
M = Mg or Ca (8)



Fig. 17 (a) Schematic illustration of the designed SWB-DC system and its charge and discharge process. (b) Change of  $CO_2$  concentration with time at 0.1 and 1 mA cm<sup>-2</sup>. (c) XRD patterns of the collected powders after the discharge process (0.1 mA cm<sup>-2</sup>) using distilled water and NaOH (aq) of various concentrations (0.01–1 M) for  $CO_2$  capture. The inset shows the powder obtained from the distilled water after the discharge process. (a–c) Reproduced with permission.<sup>138</sup> Copyright 2019, Elsevier.

Na<sup>+</sup> and Cl<sup>-</sup> ion concentrations in seawater changed with charging time at different current densities (0.1 to 0.5 mA cm<sup>-2</sup>) where the ion (Na<sup>+</sup> and Cl<sup>-</sup>) concentration decreased with time, and elevated current density encouraged the quick reduction of ion (Na<sup>+</sup> and Cl<sup>-</sup>) concentration with time (not shown; for details see ref. 138). As a result, there was a decrease of 3.3% Na<sup>+</sup> and 8.3%  $Cl^-$  at 0.1 mA cm<sup>-2</sup>, and 19.9%  $Na^+$  and 20.4%  $Cl^-$  at 1 mA cm<sup>-2</sup>.<sup>138</sup> Moreover, it was confirmed that the concentration of CO<sub>2</sub> decreased with charging time (see Fig. 17b). The XRD results, as shown in Fig. 17c, validate the reaction between NaOH and CO<sub>2</sub> and their product of sodium (bi)carbonates. CaCO<sub>3</sub> formation was also confirmed using XRD results (not shown; for details see ref. 138), which confirms the CO<sub>2</sub> reaction with Ca(OH)<sub>2</sub> where MgCO<sub>3</sub> was not formed because CaCO<sub>3</sub> formation is thermodynamically favored over MgCO<sub>3</sub> formation in seawater. This modified rechargeable SWB system provides a great way to carry out desalination and carbon-capture together using a single system.

## 9. Summary

The search for low-cost and environmentally friendly battery systems with reasonable energy and power density has revealed several new battery chemistries in recent decades. In this line, the development of rechargeable SWBs as a new battery system has attracted significant interest due to their ideal merits: (i) use of abundant seawater as a cathode, which can significantly reduce the cost of the system, and (ii) an open cathode structure, thus allowing a supply of fresh seawater for unlimited electrical energy storage in the form of Na<sup>+</sup> ion storage. Also, the flow of fresh seawater through the open cathode structure can diminish the heating problem of the battery system. More importantly, there are several possible applications identified for SWBs where they could act as a potential power provider or ESS. In this review, we introduced in detail the structure and chemistry of SWBs, ongoing academic research, and R&D progress to achieve high-performance rechargeable SWBs in terms of cathode current collectors, electrocatalysts, solid electrolytes, anodes, and non-aqueous electrolytes for the anode. In contrast, the relevant fundamental studies and technologies are still in their early stages; thus, rechargeable SWBs need further R&D before commercialization.

## Challenges and future directions

Through this review, we have identified several challenges that need to be studied and solved, both fundamentally and technically, for SWBs as listed below.

(i) Currently, the OER and ORR are reported as an expected cathodic reaction, but along with the OER, practical reactions like the HCFR or chlorine evolution reaction can perhaps occur when these SWBs are operated at high currents due to the sluggish kinetics of the OER process. To assess this consequence, an *in situ/ex situ* quantitative analysis will need to be conducted in future research.

(ii) There are several electrocatalysts which have been studied on cathode current collectors to elevate the OER/ORR process to reduce the voltage gap or improve the voltage efficiency of SWBs (see Section 5.3). While studying the feasibility of electrocatalysts in SWBs, it was noted that after a few cycles, voltage gaps had been increased. Unfortunately, the reason behind this was not identified. This voltage gap increases after some cycles and could have arisen from either instability of the anode/non-aqueous electrolyte or the degradation of the electrocatalyst or cathode current collector during the OER and ORR processes; thus a systematic investigation is required for verification. Carbon and carbon cloth are currently used as lowcost and stable cathode collectors in seawater cathodes but studies comparing their stability with other cathode current collectors are still lacking.

(iii) The pH of seawater near the cathode current collector does not need to be similar during the charge/discharge process and can change. This pH change could affect cell components or cell performance indirectly. For example, alkalization during the ORR process can encourage the formation or precipitation of insoluble salts of magnesium and calcium (Mg(OH)<sub>2</sub> and CaCO<sub>3</sub>/CaSO<sub>4</sub>) on the current collector, which will significantly disturb the operation of this battery system and output voltage. On the other hand, seawater not only contains several dissolved salt ions (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, *etc.*) but also microorganisms and algae. The microorganisms and algae can accumulate or grow naturally (*i.e.* biofouling), which can harm the overall battery system and reduce the life of the battery system. Hence, the influence of insoluble salt formations, and microorganism and algae accumulation on rechargeable SWB components can affect the performance and lifetime of battery systems, which will be examined through elaborate systematic studies.

(iv) The current SWB battery performs well only at low current densities due to high resistance associated with NASICON solid electrolytes, which results in low power performance. Consequently, ionic conductivity needs to be improved from  $\sim 1 \times 10^{-3}$  S cm<sup>-1</sup>, and the thickness must be reduced to attain rechargeable SWBs with reasonable power performance. Introducing foreign atoms by replacing Na or Zr or excess Na in NASICON could help to improve the conductivity. The electrochemical stability of NASICON against seawater and non-aqueous electrolytes has been tested for a small number of cycles, which is not enough to assess its potential; therefore, a long cycle performance study with testing for more than 1000 cycles with a duration of 6 months is highly desired. Similarly, NASICON acts a separator for the non-aqueous electrolytes and seawater so it must have enough mechanical stability to keep them always away from each other. In this sense, the mechanical stability of NASICON during cell fabrication and assembly must be studied. Particularly, the cost-effectiveness of NASICON must be confirmed for its mass production.

(v) To improve the life of the Na metal anode, developing the interface on the anode current collector and 3D Na metal anode is not sufficient for controlling dendrite growth. Creating a stable SEI layer on an Na anode is also one the most effective ways to control the dendrite growth. The ideal SEI layer should be electronically insulating but Na<sup>+</sup> ion conductive. However, the properties of an SEI layer is largely determined by electrolyte compositions (solvent, Na salt, and additive). Accordingly, the different strategies need to be combined at the same time to improve the Na metal performance in future research. The SEI layer formation mechanism, structure, composition, and SEI layer stability or failure mechanism must be elucidated using advantageous techniques, for instance, synchrotron radiationrelated techniques and synchrotron-based X-ray techniques.139 Most importantly, Na combusts when it comes into contact with water, so the safety of the Na anode used in the rechargeable SWB system must be confirmed through appropriate technical studies.

(vi) Hard carbon has been the most widely studied anode for SWBs and a stable capacity and coulombic efficiency over 300 cycles has been achieved when hard carbon is combined with NaFSI-Py13FSI-Py13TFSI electrolyte in an SWB. However, the achieved cycle stability is not enough for certain applications. Besides, unlimited Na<sup>+</sup> can be received from seawater for the anode to achieve high energy. Considering this, P/C, Sb<sub>2</sub>S<sub>3</sub> and Sn/C have been studied as high capacity anodes in rechargeable SWBs, but the cycle performance is not satisfactory. Further studies should work on improving the cycle performance of anodes by choosing suitable electrolytes, working on cutting up the voltage, and rational composition design and particle surface modification for high capacity anode materials. As an alternative to P/C, Sb<sub>2</sub>S<sub>3</sub>, and Sn/C, there are many choices of anode as shown in Fig. 10, and their feasibility must be studied in future research.

(vii) Expensive titanium frames are usually used as an electrical lead in SWB packs. In further studies, graphite frames will be designed and considered as an alternative to titanium.

We hope the proposed future research directions can further accelerate the research progress of rechargeable SWBs toward its commercialization.

## Conflicts of interest

There are no conflicts to declare.

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