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Na-seawater battery technology integration with renewable energies: The case study of Sardinia Island

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ABSTRACT

Europe has committed to net zero carbon dioxide emissions by 2050 to boost the clean energy transition. Renewable electricity will be the key energy medium for decarbonization and a huge increase in renewable energy sources (RES) exploitation is expected. Due to RES stochastic character, an extensive energy storage integration in the energy system is needed to avoid the mismatch between generation and demand profiles.

Reactive metals are promising energy carriers and storage media characterized by high volumetric energy densities and circularity, due to ease of storage and transportation, material availability and low cost. Among them, sodium is a largely available element since it can be extracted from seawater and exploited through the innovative sodium-seawater battery (SWB). Sodium cations are transferred from SWB's open cathode to the anode side during charging. Upon discharge, Na metal is oxidized to Na^+ ions, which are discarded in seawater.

This study assesses the impact of SWB technology focusing on Sardinia Island as a case study. For short-term application, SWB integration to wave energy converters allows a potential reduction of greater than 85% of generated power fluctuations, largely improving the quality of power injected into the grid. Regarding the long-term scenario, SWBs implementation in the energy system allows coverage of the Sardinia annual energy demand thanks to the integration of ~340,000 cubic meter of Na metal, corresponding to a 12-m height Na reservoir under 4 soccer fields. SWB application to Sardinia also produces CO_2 sequestration while covering ~29% of desalinated water requirements for the Sardinian population.

1. Introduction

Currently, the mandate to reduce carbon dioxide emissions and pollutants is promoting the utilization of "zero-emissions" stocks, such as renewable energy sources (RES) [1]. The implementation of RES is crucial to achieve the EU long-term strategy of net-zero carbon by 2050 [2]. To mitigate the uncertainty and intermittency of RES, energy storage systems (ESS) will play a fundamental role in the imminent future [3]. Owing to essential features such as high scalability, flexibility, efficiency and fast response, ESS are identified as the most effective solution to deliver sustainable, economic and secure electricity supplies [4]. ESS can be classified according to the type of converted energy [5]. Five main categories of ESS can be distinguished, namely: chemical energy storage (hydrogen, biofuels, etc.); electrochemical energy storage (batteries and fuel cells); electrical energy storage (supercapacitors); mechanical energy storage (i.e., flywheels, pumped hydro, and compressed air energy storage) and thermal energy storage.

Energy storage is typically characterized by four different time scales ranging from short-term (seconds up to minutes), intra-day (hours), mid-term (days/weeks), to long-term (month to a year or more). Fig. 1 illustrates the power and time ranges related to specific energy storage technologies [6]. Electrochemical and electrical ESS are used for short- and mid-term applications (intraday/weekly storage time) for grid support (e.g., power smoothing, frequency, and voltage support, etc.) and spinning power reserve. Pumped hydro storage and compressed air storage are also suitable for intra-day applications, while hydrogen is

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suitable for extended timeframes (weekly, monthly and possibly seasonal storage), even if the economic convenience of open batteries is demonstrated in previous studies [7]. Fig. 1 highlights reactive metals, such as Na, Mg and Al, can also be used as energy storage media and energy carriers to cover mid- and long-term storage since they have higher volumetric energy densities than hydrogen [8]. Among the most abundant reactive metals, Na can be accumulated and reused via purely electrochemical paths, granting high round trip efficiencies (RTEs).

Currently, Li-ion batteries (LIBs) dominate the electrochemical storage technologies market share because of their high energy density, efficiency and flexibility [9,10]. However, the forecasted market size increase, both for large-scale stationary and transport applications, requires strategies to resolve key issues such as the availability and cost of critical materials (primarily cobalt, nickel, and lithium), safety and environmental risks related to the thermal runaway phenomenon as well as the mandatory recyclability requirements planned by the European Commission [11]. According to an IEA study [12], the 2040 material demand for lithium, cobalt, and nickel for use in electric vehicle LIB cathodes will exceed today's production volume by up to 8 times.

Owing to their similar chemistries, Na-ion batteries (SIBs), have attracted increasing interest as the most suitable technology to replace LIBs in the short-/mid-terms [13]. The low cost, large abundance (∼2.6% of the earth's crust vs 0.0017 wt% of lithium [14]), low geopolitical supply risks and suitable electrochemical potential ($E^0 = -2.71$ V vs. the standard hydrogen electrode, SHE) of sodium has elevated Na-based batteries to the summit in the post-LIBs technologies race. In this context, sodium-seawater battery (SWB) employing seawater as highly abundant sodium-containing cathode material is a promising candidate [15] for application to the marine environment.

Unlike LIBs and SIBs, SWBs consist of an open-structured positive electrode (cathode) enabling infinite supply of Na^+ cations from seawater, which are transferred to the negative electrode (anode) during charging [13]. Moreover, seawater is an eco-friendly, safe, natural and widely abundant renewable resource covering nearly 70% of the earth's surface [16]. Therefore, in the view of the expected increase of offshore renewable energy generation (in particular, wind and wave energy), SWBs represent one of the most suitable technology for enhancing the energy transition to a net zero carbon society by 2050 [17,18]. SWBs play a crucial role in improving environmental and social welfares, since they provide ancillary features such as CO_2 capture and desalination [19]. The discharging product (i.e., sodium hydroxide, NaOH) spontaneously reacts with CO_2 forming sodium carbonate (Na_2CO_3) [20]. Furthermore, the balancing Cl^- anions evolve to chlorine during charge by means of catalysts. Such a gas can be stored and used in the chemical industry, providing an economic revenue that allows the reduction of SWB-related capital and maintenance costs.

Several research activities have been performed over the last years to develop highly-efficient and stable rechargeable SWBs [18,21–27], especially with regards to the SWB anolyte environmental and safety issues. An ideal anolyte for SWBs should possess non-volatility, low flammability, electrochemical stability, non-toxicity and affordability [28]. However, no studies related to the impact of the benefits introduced by SWB integration to a wide geographical area are present in the literature to date.

Herein, the SWB technology considered employs sodium-biphenyl (Na-BP) as the anolyte [15,25]. Both the anolyte (Na-BP) and the catholyte (seawater) flow through the battery cells, each in its own compartment (i.e., negative and positive, respectively), as in a conventional redox flow battery, constituting an open battery design. Similar configurations employing NaBP in a closed anode and seawater in an open cathode and their potential applications have been investigated in Refs. [29,30]. A key aspect of Na-BP-based SWBs lies in the possibility to externally store metallic sodium. This allows extension of the storage timeframe by increasing the Na metal external reservoir, enabling hourly to monthly and seasonal energy storage with only one device and thus decreasing the investment costs.

This work aims at demonstrating the applicability of SWB to meet the European energy requirements, to arise the interest of the public and private sectors into the further development needed to bring the laboratory scale cells so far developed into commercial applications. To this aim, SWBs are investigated both for short-term application, i.e., coupled to wave energy converters (WECs) with the purpose of operating a power smoothing effect towards the grid, and for long-term application with reference to the case study of Sardinia Island. Sardinia has a wide availability of renewable energy sources (i.e., solar, wind and wave energy as common to most islands), but an outdated energy infrastructure requiring refurbishment, and no methane distribution network. Hence, investing in a complete energy transition in Sardinia would also create a precedent for enabling the same transition throughout the Italian peninsula and beyond. Due to its high energy potential, Sardinia

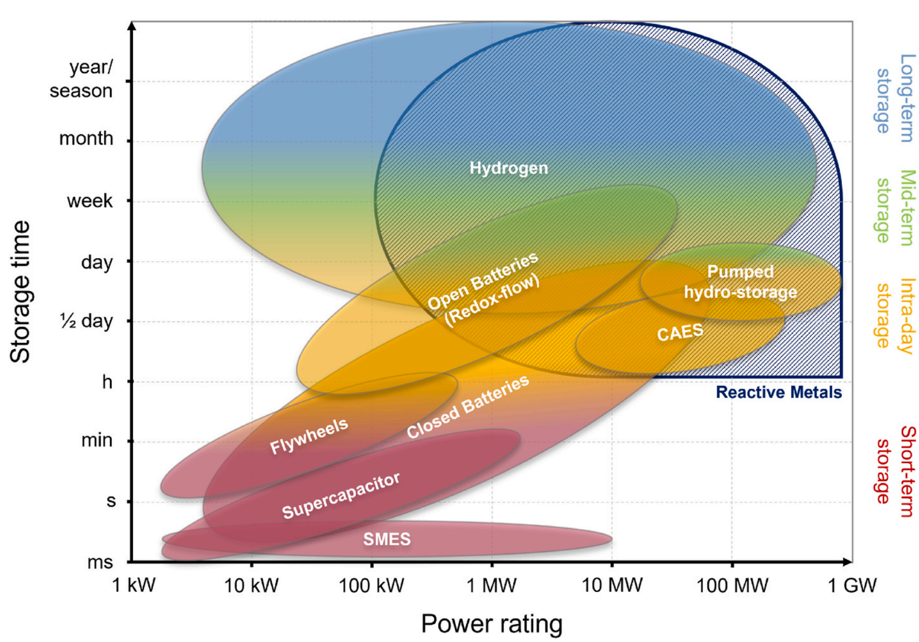

Fig. 1. Suitability of different ESS technologies for grid-scale applications (CAES: Compressed Air Energy Storage; SMES: Superconducting Magnetic Energy Storage).

is an exemplar to demonstrate the effectiveness of renewable sources in satisfying the entire energy demand to replace the use of fossil fuels.

For short-term applications, SWB integration with WECs, together with the implemented power management strategy, allows a reduction of produced power fluctuations of greater than 85%, largely increasing the quality of the power injected into the grid.

With reference to the long-term scenario, integrating SWBs in a fully decarbonized power generation system allows coverage of the Sardinia annual energy demand by storing only 12 m of Na metal in an area equivalent to 4 soccer fields (105 m × 68 m each). Moreover, the application of SWBs in Sardinia would reduce current Italian CO_2 emissions by 17%, while producing ~29% of desalinated water necessary for sanitary use of Sardinian inhabitants.

2. Fundamentals of Na-seawater technology

Sodium-based battery systems have recently attracted increasing research interest due to the abundant resources of the raw materials employed [31]. This has led to the introduction of a new rechargeable battery chemistry, which makes use of seawater and sodium related compounds as the positive and negative electrodes, respectively [21,23,24,32].

The use of seawater as electrolyte in energy applications was first proposed in the 1940s in a primary battery [33]. Upon charge, Na^+ ions are reduced (eq. (1)) in the anodic compartment, which needs to be closed, (i.e., isolated from seawater via a solid electrolyte layer enabling the flow of Na^+ ions only) while several oxidation reactions can take place at the positive electrode, such as the oxidation of hydroxide anions (OH^-) resulting in the oxygen evolution reaction (OER) (eq. (2)) and that of chloride ions (Cl^-) resulting in the formation of chlorine (eq. (3)).

$$\text{Anode: } Na^+ \text{ (aq)} + e^- + \text{Host} \rightarrow \text{Na-Host (s)} \tag{1}$$

$$\text{Cathode: } 4\ OH^- \text{ (aq)} \rightarrow O_2 \text{ (g)} + 2H_2O \text{ (l)} + 4e^- \tag{2}$$

$$2\ Cl^- \text{ (aq)} \rightarrow Cl_2 \text{ (g)} + 2e^- \tag{3}$$

Depending on the processing conditions, ClO^- anions can also be generated.

In the closed-anodic compartment a non-aqueous electrolyte enables faster sodium ion transport [34], which can deposit as Na metal on a current collector or bind to an appropriate host. Recently, the use of biphenyl in the SWB anolyte has emerged as an ideal candidate for the realization of cost-efficient and long-term stable large-scale electrochemical energy storage devices. Acting like a redox mediator, i.e., spontaneously forming Na-BP with Na^+ ions coming from the seawater and electrons, it contributes to the reversible sodium storage. The Na-BP complex can be accumulated outside the cell as in a conventional Redox-Flow Battery (RFB) cell, or further reduced to Na metal inside the anodic compartment of the cell or outside of the cell as depicted in the simplified scheme of Fig. 2.

During discharge, the oxidation of sodium metal at the anode releases sodium ions (eq. (4)) back into seawater, while at the positive electrode the oxygen reduction reaction (ORR) takes place (eq. (5)) resulting in the formation of NaOH (eq. (6)).

$$\text{Anode: Na (s)} \rightarrow Na^+ \text{ (aq)} + e^- \tag{4}$$

$$\text{Cathode: } 2H_2O \text{ (l)} + O_2 \text{ (g)} + 4e^- \rightarrow 4\ OH^- \text{ (aq)} \tag{5}$$

$$\text{Overall: } 4Na \text{ (s)} + 2H_2O \text{ (l)} + O_2 \text{ (g)} \rightarrow 4\ NaOH \text{ (aq)} \tag{6}$$

This latter compound can be used for CO_2-trapping, according to the overall reaction (eq. (7)):

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \tag{7}$$

The sodium carbonate, which can be easily produced bubbling air into the NaOH solution, can be stored for further use as CO_2 source in Power-to-Gas and Power-to-Fuels processes or simply released into the environment due to its inert and non-toxic nature.

By employing seawater as the positive electrode active material, the energy storage capacity of SWBs is only limited by the amount of Na metal (or Na-BP) stored in or outside the system. Additionally, seawater can act as an infinite supply of Na ion, avoiding the need of costly and/or critical metal ions, but also enabling the realization of anode-less cells [34].

The positive and negative cell compartments are separated by a solid electrolyte avoiding the direct contact of Na metal (or Na-BP) with water while ensuring Na^+ ion transport between the two electrode compartments. Thus, the solid electrolyte must possess: (i) high ionic conductivity at moderate temperatures (4–25 °C), (ii) high Na^+ selectivity, (iii) high chemical stability against both seawater and nonaqueous electrolytes, (iv) suitable electrochemical stability window and (v) high mechanical strength. These features are satisfied by $Na_{1+x}Zr_2P_{3-x}\ Si_xO_{12}$ (NASICON, Na Super Ion CONductor) solid electrolyte [27].

SWB cells employing BP have demonstrated high energy efficiency, exceeding 80%, which is higher than lead-acid batteries and vanadium redox flow batteries [13]. Due to such a high energy efficiency, efforts to industrialize this rechargeable chemistry are ongoing in Korea [35] and Italy ("Stoccaggio di energia con Batterie ad Acqua di Mare", SBAM

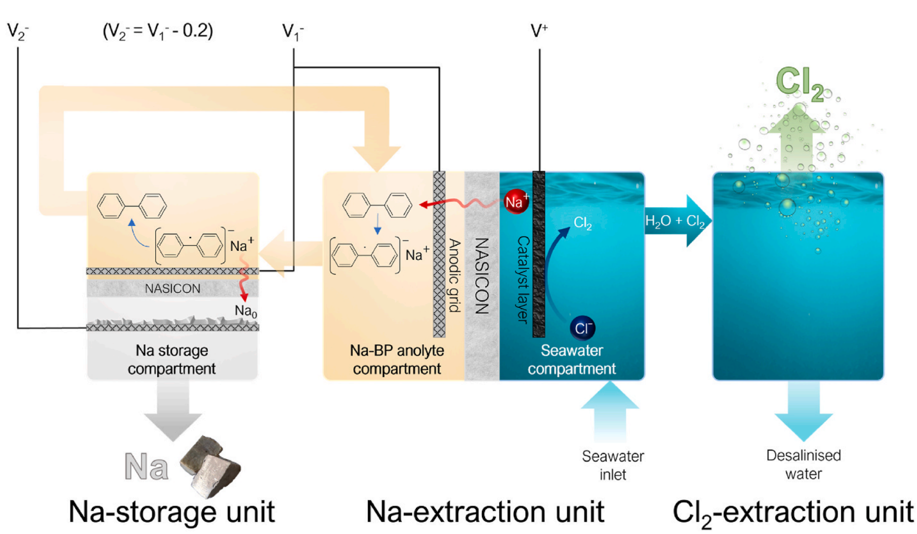

Fig. 2. Schematic overview of the Na-seawater system employing Na-BP (sodium-biphenyl) as anolyte and including two additional tanks for sodium metal storage and chlorine recovery.

project) to a lesser extent. Besides their use as large-scale, stationary, rechargeable batteries, these cells can be used to produce sodium metal from seawater via the extraction of sodium produced at the negative electrode. Ideally, these cells could be combined with offshore wind turbines, but also other renewable energy harvesting plants, such as photovoltaics, wave, tide, etc. Further, the SWB system could be appropriate for powering marine transportation.

An important by-product of the sodium metal production (i.e., the charging phase) via seawater cells is chlorine (Cl_2 in eq. (3)). This is a precious reactant heavily used by the chemical industry, which commercializes many chlorine-containing compounds, including polyvinyl chloride (PVC), but also metal chlorides (aluminum, magnesium, titanium, zirconium, among others) used as catalysts or precursors for producing the pure elements. Finally, a further potential use of sodium production via seawater cells is desalination, by a modification of the system as recently reported [16].

3. Na-seawater integration strategies and methodologies

The fluctuating and intermittent behavior of RES negatively affects the power grid stability and reliability, requiring energy storage systems that enhance the power quality. In view of the massive penetration of offshore renewable power plants, SWBs are one of the most suitable storage systems, because they can store energy over *i)* short timeframes (i.e., up to day/night cycle) as redox flow batteries, storing the energy in the anolyte as Na-BP, as well as for *ii)* long timeframes (i.e., up to seasonal/annual storage), storing the energy as metallic sodium within or even outside the system (Fig. 2).

This versatility enables substantial capital cost savings while providing a milestone for long-term energy storage. Importantly, metallic sodium has a higher energy density (i.e., 5.4 kWh L^{-1}) than liquefied hydrogen (2.3 kWh L^{-1}), as well as a simpler storage infrastructure.

a) Short-term energy storage: study of power smoothing effect on renewable energy generation

In the short-term timeframe, ESSs perform multiple attractive functions to power grid operation and load balancing, such as: *i)* helping in meeting peak electrical load demands, *ii)* providing time varying energy management, *iii)* alleviating the intermittence of renewable source power generation, *iv)* improving grid power quality/reliability [9,36]. To assess the benefits of SWB integration to offshore RES in terms of power quality injected into the grid, a specific application is investigated. A dynamic model consisting of an SWB coupled to WEC is developed in MATLAB/Simulink environment to evaluate the power smoothing effect of SWB towards the WEC generated power profile. Two Oscillating Wave Surge Converters (OWSC) are considered as WEC technology, with a rated power of 250 kW each [37]. Moving from real data gathered from a specific location, a statistical analysis is performed over the annual generated power profile [37]. This results in five different representative days selected to perform the simulations. Such days cover a wide range of annual occurrences related to the studied site, as depicted in Fig. 3, showing the probability density of the power ramp determined over the daily generation profile. Power ramp is defined as the difference between two consecutive power values with a time step of 1s.

Fig. 4 shows the schematic view of the implemented model in Simulink environment. Specifically, the power ramp over 1s time step of the wave power profile is calculated in the yellow section. This is used as input for the control section (green). Power exchanges between the SWB and the grid are assessed in the power management section (orange). Moreover, the SWB characteristics (i.e., state of charge and maximum dis-/charge powers) are used as input for the control section, where the power shares are defined considering the current state of the devices (i.e., WEC, SWB, grid, etc.). In the right side of the figure, SWB and grid sections are highlighted in green and red, respectively.

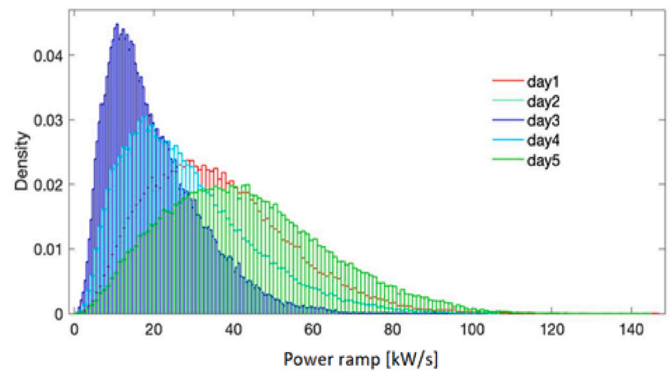

Fig. 3. *Probability density function for the selected days* [37].

Aimed at performing power smoothing at the point of common coupling (PCC) with the grid, a simultaneous perturbation stochastic approximation (SPSA)-based data-driven control strategy was developed by the authors according to previous studies [37–39]. Details relative to the SPSA control algorithm are provided in Supplementary Material.

Concerning the SWB subsystem, real charge and discharge voltages vs. State of Charge (SoC) at fixed current density (0.28 mA/cm^2) are used in the model according to Ref. [25]. Fig. 5 shows the voltage trends during charge and discharge processes respectively.

Such voltage trends are implemented in two look-up tables to emulate the real behavior of the SWB in reference to the current SoC. The input power required/provided to the battery and computed in the control section is divided by the instantaneous SWB voltage to obtain the current I_{bat}. The current is used to instantaneously determined the SoC as follows (eq. (8)):

$$\begin{cases} SoC_t = SoC_{t-1} + \int \frac{I_{bat}}{Q\eta} dt & \text{charge} \\ SoC_t = SoC_{t-1} - \int \frac{\eta I_{bat}}{Q} dt & \text{discharge} \end{cases} \tag{8}$$

where I_{bat} has a negative or positive sign during the charging/discharging process, respectively, and η is the SWB RTE, considered equal to 0.75 as cautionary hypothesis in consideration of values indicated in the literature [31].

The initial SoC is fixed at 1 (corresponding to a fully charged battery) at the beginning of the simulations. Since the considered SWB uses Na-BP solution as anolyte, its design is configured as an open flow battery. This allows the independent determination of the power and capacity of the battery according to the specifications of the studied application. According to the WECs total rated power (500 kW), the SWB is sized at 50 kW and 100 kWh as dis-/charge powers and capacity, respectively.

b) Long-term energy storage: renewable energy generation and energy storage demand assessment for Sardinia Island

Focusing on the EU carbon neutrality target by 2050 [40], Sardinia represents an interesting case study due to its wide accessibility to renewable energy sources. Although recent studies have considered the possibility of connecting the island to the methane distribution network [41], the high costs for the installation of new distribution plants as well as the need to reduce carbon dioxide emissions represent major hurdles. To demonstrate the effectiveness of renewable sources in satisfying the entire primary energy demand, avoiding the use of fossil fuels, wind and solar energy availability in Sardinia is presented. First, the monthly energy profile of the local availability of the sources is determined on the basis of hourly generation data by the European Network of Transmission System Operators for Electricity (ENTSO-E) aggregated by

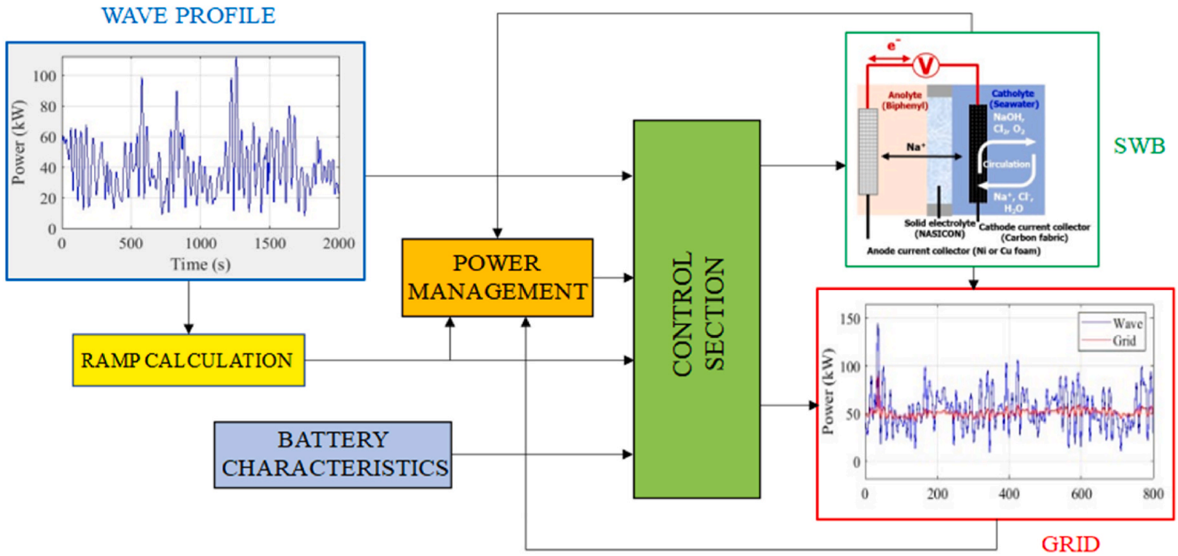

Fig. 4. The schematic layout of the implemented Simulink model consisting of a wave energy converter (WEC) integrating seawater battery (SWB) for WEC power smoothing.

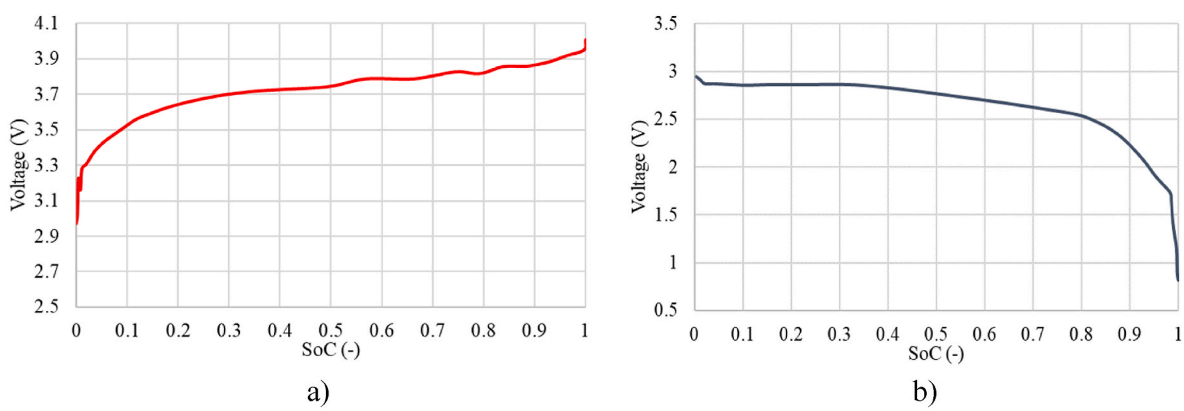

Fig. 5. Seawater battery voltage trends vs. SoC during a) charging and b) discharging processes at constant current density (0.28 mA cm^{-2}). The experimental data are extracted from Ref. [25].

source [42]. Specifically, wind and solar generation data relative to the "BZN|IT-Sardinia" area from 01/01/2015 to 30/09/2020 were considered. Data were grouped per month and the mean monthly trends of wind and solar produced energy are assessed (Fig. S1 in Supplementary Material) in reference to the overall period indicated above. Based on these data, the monthly variation trend with respect to the corresponding average value is determined for each source, as indicated in Fig. S2 reported in Supplementary Material.

Based on data presented in Fig. S1, annual generation values were determined resulting in a wind to solar ratio of ~2.4.

The same procedure was applied to the electric load profile, starting from the hourly demand records published by ENTSO-E [43] for the same area over the same period. The monthly fluctuation of the electricity demand is depicted in Fig. S2 with respect to the average value on a yearly basis. The seasonal variation of wind and solar production is only partially compensated, due to the different shares in the generation mix, resulting in the need for long-term energy storage. This is further increased by the monthly fluctuation of the electricity demand, which increases during summer whilst wind energy generation strongly decreases.

Finally, energy demand and energy generation mix were assumed for Sardinia Island in the fully decarbonized scenario in 2050. Energy demand was assumed equal to the Sardinia total primary energy consumption registered in 2019 (i.e., ~23.5 TWh) [41]. Moreover, it was assumed that primary energy needs will be fulfilled through renewable electricity, with up to 90% being provided by wind and solar sources [44].

Under these assumptions and the fluctuation trends depicted in Fig. S2, the monthly profiles of wind and solar generation as well as the electricity demand were assessed in 2050 considering the wind to solar generation capacity of 2.4 (on a yearly basis) will be maintained. All the obtained profiles are illustrated in Fig. 6.

Lastly, the required capacity for seasonal storage can be determined considering the trend of surplus/lack (Fig. 6) computed as the difference between solar and wind overall generation and the electricity demand, assuming that the remaining 10% of the primary energy needs will be satisfied by other sources (e.g., biomass, hydropower) [44]. As for seasonal energy storage, the application of SWBs is considered. Although their RTE is reported to exceed 80% [31], a conservative value of 75% is used for the model.

4. Results

a) Short-term energy storage

The smoothing effect applied to the WEC power profile by means of

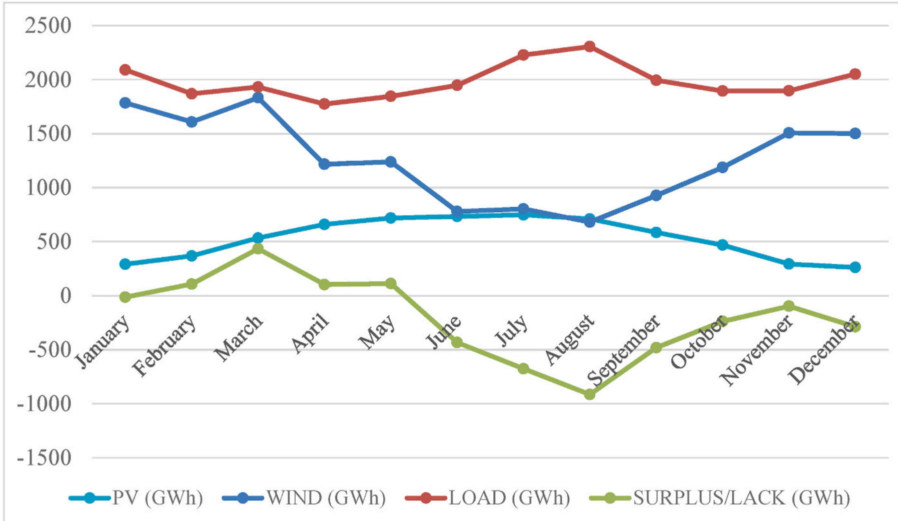

Fig. 6. Monthly profiles of wind/solar generation and electricity estimated demand by 2050.

SWB is depicted in Fig. 7 for a portion of Day 5. The power fluctuation at the PCC with the grid (red line) is hugely reduced with respect to the power generated by the WEC (blue line).

Specifically, such a reduction is quantified in Fig. 8 and Table 1 on the basis of the resulting profile of the power ramp parameter, being the difference between two consecutive power values with a time step of 1s. Fig. 8 illustrates the cumulative distribution function (CDF) of power ramp profiles assessed at both PCC and WEC terminals for all the selected scenarios defined in Section 3 (i.e., days 1–5). Notably, the power ramp towards the grid is substantially reduced with respect to the generated one due to the SWB integration to WEC. Moreover, evaluations for both the grid and the WEC power ramps, listed in Table 1, are computed in reference to the 80% CDF threshold.

Considering the reduction in terms of the grid power ramp registered at 80% CDF, the benefits introduced by the SWB, and the power management strategy allow an 85.6% reduction of power ramp for all investigated scenarios. This contributes to compliance with the regulations for the power injection to the grid as well as maximizing renewable energy generation without the need for any power curtailments.

b) Long-term energy storage

Under the methodology and assumptions stated in Section 3, a storage capacity of ~1.86 TWh was assessed on a yearly basis considering the surplus/lack profile in Fig. 6. Consequently, the impact of SWB technology on the Sardinia territory was evaluated in terms of the required energy carrier volume.

Considering the Na volumetric energy density of 5.4 kWh L^{-1}, the storage volume of Na metal which can be accumulated outside the SWBs is 344,444 m^3. This corresponds to a 12 m-thick layer of Na stored under 4 soccer fields (105 m × 68 m each), which is substantially lower than the storage volume needed if hydrogen is exploited as storage medium. Specifically, if compressed hydrogen at 700 bar is considered, due to a significantly lower RTE, the seasonal storage capacity increases up to 2.24 TWh, with a growth factor of 1.20. This result corresponds to 29% RTE considering systems including alkaline water electrolyzer and PEM fuel cell stacks, with a hydrogen storage pressure of 700 bar. Specifically, charging efficiency was assessed at 57.4% considering 67% electrolyzer efficiency [45], compression energy and 95% AC/DC converter efficiency. Regarding the discharging phase, 53.2% and 95% were considered as the maximum PEM fuel cell [46] and DC/AC converter efficiency values, respectively, resulting in 50.5% discharging efficiency.

Moreover, the storage medium volumetric energy density lowers from 5.4 kWh L^{-1} to 1.4 kWh L^{-1} resulting in a second growth factor of 3.86. Globally, both factors produce an increase in the storage volume of

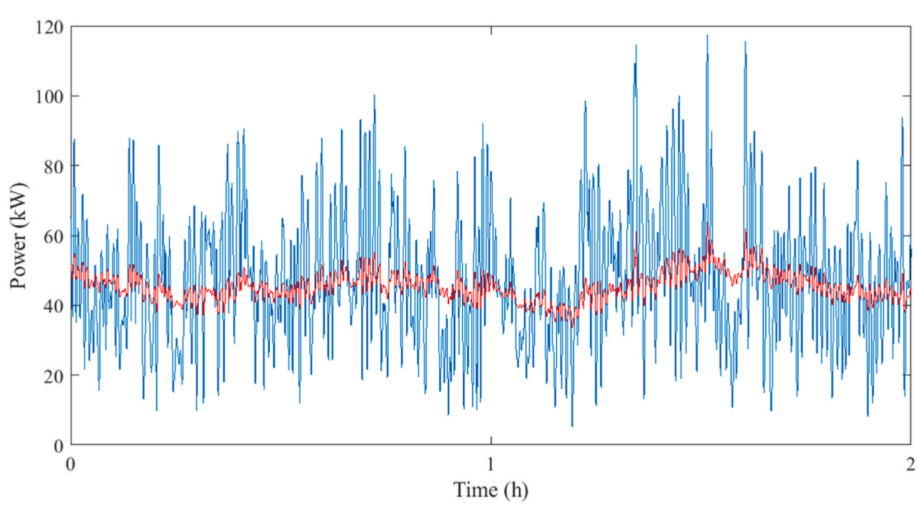

Fig. 7. Example of SWB power smoothing effect on power sent to the grid (red line) with respect to the power generation profile (blue line) for a portion of Day 5.

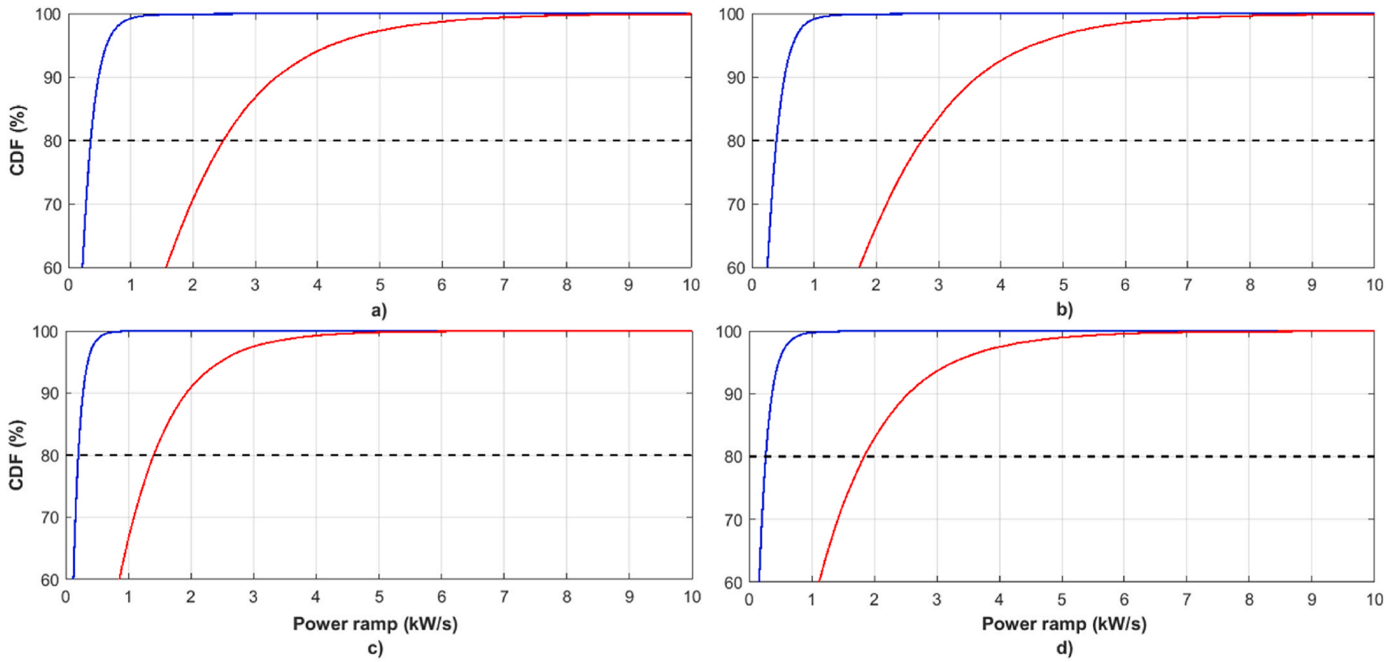

Fig. 8. Cumulative distribution function (CDF) of the power at the PCC with the grid (blue line) with respect to the generated power (red line) for: (a) Day 1, (b) Day 2 and Day 5, (c) Day 3 and (d) Day 4. Black dotted line represents the fixed CDF value for the power ramps evaluation.

Table 1
Power ramp values at the PCC with the grid and from the wave energy converter (WEC) for the selected days at 80% CDF.

	WEC Power Ramp (W s^{-1})	PCC Power Ramp (W s^{-1})
Day 1	2488	359
Day 2/Day 5	2732	394
Day 3	1404	202
Day 4	1839	266

4.63 times up to 1.6 mil m^3 if compressed H2@700 bar is used as storage medium, corresponding to the area of 19 soccer fields with the same height.

As detailed in Section 2, SWB provides ancillary functions that can positively affect the environment, i.e., NaOH formation at the cathode during the discharge phase, which can be further employed for CO_2 trapping from the atmosphere and desalinated water production at the same electrode during the charge process.

First, the amount of CO_2 trapped from the atmosphere in the sodium carbonate form, as expressed by eq. (7), was assessed resulting from the implementation in the Sardinia Island of 1.86 TWh capacity (E_{stored}) of Na metal storage and rechargeable SWBs for Na production and conversion for power generation. Considering 92% as discharge efficiency (η), metal Na volumetric energy density $ED_{Na,metal}$ (5.4 kWh L^{-1}), density ρ_{Na} (968 kg m^{-3}) and molar weight PM_{Na} (22.99 kg $kmol^{-1}$), the number of moles of produced NaOH (mol_{NaOH}) over the year was determined according to eq. (9), resulting in 15,764,048 kmol.

$$mol_{NaOH} = \frac{E_{stored}}{\eta \frac{ED_{Na,metal}}{\rho_{Na}} PM_{Na}} \text{ x } 10^6 \tag{9}$$

Considering a CO_2 capture efficiency of 20% at pH 9 ($\xi_{CO_2|pH=9}$) as indicated in Ref. [26], since each mole of CO_2 (PM_{CO_2} equal to 44.01 kg $kmol^{-1}$) reacts with 2 mol of NaOH according to eq. (7); the trapped CO_2 ($CO_{2,tr}$) resulted in 69,378 tons per year (eq. (10)).

$$CO_{2,tr} = \xi_{CO_2|pH=9} \frac{\left(\frac{mol_{NaOH}}{2}\right) PM_{CO_2}}{1000} \tag{10}$$

With reference to the installed storage capacity, it can be concluded that utilization of sodium as storage medium through the SWB technology has a positive environmental impact leading to a CO_2 reduction factor of −37.3 g_{CO2} per kWh of storage capacity. Considering the current Italian average CO_2 emission factor (i.e., 213.4 g_{CO2} per kWh in 2020), as reported in Ref. [47], the absorbed CO_2 by SWBs permits a reduction of ~17%.

Second, the potential production of desalinated water was determined for the implementation of 1.86 TWh storage capacity and compared with the drink and sanitary water requirements of the Sardinian population. The number of Na moles produced over the year was determined considering the volumetric energy density, density, and molar weight, as indicated above (eq. (9)). According to eq. (1) and assuming a charge efficiency of 82% (η_{ch}), the number of reacted NaCl moles was calculated. Subsequently, the mass in kg of dissociated NaCl (W_{NaCl}) was determined (eq. (11)) and considering the average NaCl concentration in seawater (C_{NaCl}, 27.123 kg_{NaCl} m^{-3}), the volume of treated seawater (TSW) resulted in ~37 million m^3 on a yearly basis (eq. (12)).

$$W_{NaCl} = \frac{E_{stored} \text{ x } 10^6}{ED_{Na,metal}} \frac{\rho_{Na}}{PM_{Na}} \frac{PM_{NaCl}}{\eta_{ch}} \tag{11}$$

$$TSW = \frac{W_{NaCl}}{C_{NaCl}} \tag{12}$$

Considering a population of 1.58 million of inhabitants in 2022 [48] and a specific consumption of 220 L per capita per day [49], the amount of desalinated water corresponds to ~29% of the Sardinian water requirements for sanitary uses.

With reference to desalination performance, ~80% salt removal can be achieved, in relation to the NaCl content in seawater. Moreover, according to the above procedure, the energy request for the charging phase results in ~50 kWh per m^3 of treated seawater. Considering that 82% of this amount of energy can be reused for discharging, following the procedure indicated in Ref. [26], the specific energy consumption (SEC) which can be accounted for desalination resulted in 9.76 kWh per m^3 of treated seawater according to eq. (13). This amount also includes 0.76 kWh m_w^{-3} due to additional treatments, i.e., intake (0.19 kWh m_w^{-3})

and pre-treatment (0.39 kWh m_w^{-3}) of seawater, and distribution of the produced clean water (0.18 kWh m_w^{-3}).

$$SEC = 50 * (1 - \eta_{ch}) + 0.76 \quad (13)$$

In summary, desalination can be provided by SWBs as an ancillary function with similar performance to the reverse osmosis process (i.e., 3.6 kWh m_w^{-3} at 100% salt removal).

5. Conclusions

This paper investigates the application of SWB for the short- and long-term energy storage system of Sardinia Island, taking advantage of the battery configuration enabling sodium storage as the Na-BP complex in the anolyte (RFB configuration) as well as outside the battery as metallic Na.

The results of the modeling demonstrate the effectiveness of SWB-based energy storage combined with the abundant renewable sources of Sardinia, enabling the full decarbonization of the energy system on the island.

Moreover, SWBs desalination and CO_2 capture functionalities is an exemplar of clean energy transition implementation that can be extended to other islands and coastal areas.

The integration of WECs with SWB-based energy storage promises a significant reduction in power fluctuations at the terminals of WECs (producing an extremely fluctuating power profile). The power ramp reduction, calculated as the difference between two consecutive power values with a timestep of 1 s, resulted in 85% reduction in power fluctuations.

Regarding long-term (seasonal) storage, Na metal offers higher volumetric densities (about 4 times) than compressed hydrogen at 700 bar. For the case of Sardinia, the Na storage volume needed is only a 12-m high reservoir extending under 4 soccer fields (105 m × 68 m each). The production of such an amount of Na is accompanied with about 37 million m^3 per year of desalinised water, corresponding to ~29% of water necessary for sanitary use of Sardinian inhabitants. Finally, the NaOH generated during the conversion of Na metal into electricity enables the sequestration of >69,000 tons of CO_2 per year, with a resulting carbon capture factor of 37.3 g_{CO2} per stored kWh.

The development of SWB technology, currently at the lab-scale, is fully aligned to the Net-Zero Industry Act regulation proposal, recently published by the European Commission, specifically concerning energy storage technologies [50]. Moreover, it fully complies with the requirements of the Critical Raw Material Act, which will be adopted by the European Commission in 2023 [51], since the active species used in the charge/discharge processes is sodium extracted from seawater and no raw critical materials are required for the components of the SWB storage system.

CRediT authorship contribution statement

Linda Barelli: Conceptualization, Methodology, Formal analysis, Investigation, Resources, Data curation, Supervision, Project administration, Funding acquisition, Writing – review & editing. **Dario Pelosi:** Methodology, Formal analysis, Investigation, Data curation, Writing – review & editing. **Gianni Bidini:** Writing – review & editing. **Graziano Di Donato:** Visualization, Writing – review & editing. **Maria Assunta Navarra:** Project administration, Funding acquisition, Writing – review & editing. **Stefano Passerini:** Conceptualization, Supervision, Funding acquisition, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Linda Barelli, Maria Assunta Navarra reports financial support was provided by MITE. Linda Barelli reports financial support was provided by Horizon Europe.

Data availability

Data will be made available on request.

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Nomenclature list

BP	Biphenyl
CDF –	Cumulative density function
ESS	Energy storage system
LIB	Li-ion battery
NASICON –	Na super-ionic conductor
OER	Oxygen evolution reaction
ORR	Oxygen reduction reaction
PCC –	Point of common coupling
RES	Renewable energy sources
RFB	Redox flow battery
RTE	Round trip efficiency
SEC –	Specific energy consumption
SIB	Sodium-ion battery
SPSA –	Simultaneous perturbation stochastic approximation
SWB	Seawater battery
WEC	Wave energy converter

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.rser.2023.113701.

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