

A New Rechargeable Seawater Desalination Battery System

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The exploitation and utilization of seawater resources has become a significant research topic nowadays. In this communication, we report a rechargeable desalination battery system for the first time. This design can integrate the electrochemical battery, seawater desalination, and acid-alkali production in one system. The basic working principle of the designed system was illustrated, and further proved by the results of the experiments. Furthermore, future research directions and outlooks of this system are proposed. This conceptual work provides a promising technology for utilization of natural seawater resources.

Energy and resources are the foundation of life and production. With the growth of the world population and the development of the global economy, the requirements of energy and resources are escalating greatly. Moreover, the growing environmental concerns associated with the traditional energy and resources utilization technologies are getting more and more attention all over the world. In view of these situations, the research and development of renewable, sustainable, green energy and resources utilization technologies have been the greatest challenge facing our humankind in the twenty-first century.^[1–5]

It is well known that ocean covers nearly three-quarters of the earth's surface. Ocean is a huge treasure house of various energy and resources. Several types of renewable ocean energy, such as wave energy, tidal energy, marine current energy, ocean thermal energy and salinity gradient energy, etc., have been researched and exploited in many coastal countries and regions.^[6–10] Furthermore, nearly 97% of water on earth is accumulated in ocean, that is seawater, which is saline (3.0–5.0% dissolved salts) in nature.^[11] Consequently, seawater desalination has become an important, promising and sustainable approach to address the serious global freshwater scarcity challenge, and has been heavily investigated.^[12–22] In addition, seawater contains large amounts of valuable minerals. Almost all the elements in the periodic table can be found in seawater,

although many elements are present in very low concentration.^[23] Minerals have been mined from seawater since ancient times. Common salt (NaCl) was apparently first systematically extracted from seawater some time prior to 2200 B.C. Many minerals can be produced as by-products during the seawater extraction process, although most elements have not been commercially extracted directly from seawater itself on any notable scale.^[24–28] Overall, it is very important for the sustainable development of our humankind to exploit and use the energy and resources in ocean.

Recently, a novel energy conversion and storage system, rechargeable seawater battery, using natural seawater as an abundant supply of active materials (sodium ion and dissolved O₂ in seawater), has been developed.^[29–31] That is a new technology for utilization of seawater resources. Herein, we propose, for the first time, a rechargeable seawater desalination battery system, which integrates the electrochemical battery, seawater desalination, and acid-alkali production in one system. The working principle will be illustrated, and further proved by the results of experiment. Finally, future research directions and outlooks of this system will be prospected.

Figure 1 shows a schematic illustration of the designed seawater desalination battery system and schematic diagram of charge and discharge processes. As shown in Figure 1, this system consists of two parts, which are charging and discharging, respectively. The charging part is composed of anode (hard carbon electrode in organic electrolyte), natural seawater, and cathode (Pt/C electrocatalyst in DI water). A NASICON ceramic electrolyte (Na₃Zr₂Si₂PO₁₂) separates the anode from the seawater, and an anion exchange membrane (AEM) separates the seawater from the cathode. The discharging part includes anode (hard carbon electrode in organic electrolyte) and cathode (Pt/C electrocatalyst in DI water) separated by a NASICON ceramic electrolyte.

During the charging process, the Na⁺ ions in the seawater are extracted and transported into the anode side through the NASICON separator, and then stored in the hard carbon, while Cl⁻ ions in the seawater are extracted and transported into the cathode side through the AEM, followed by combining with H⁺ ions, produced in electrochemical oxygen evolution reaction (OER) process: 2H₂O → O₂ + 4H⁺ + 4e⁻, to form HCl acid.

When discharging, Na⁺ ions stored in the hard carbon transfer to the cathode side through the NASICON separator, followed by combining with OH⁻ ions, produced in electrochemical oxygen reduction reaction (ORR) process: O₂ + 2H₂O + 4e⁻ → 4OH⁻, to form NaOH alkali.

The anode side in this design works like a reservoir and carrier for Na⁺ ions and electrons. During charging process, the Na⁺ ions are extracted from seawater and stored together with

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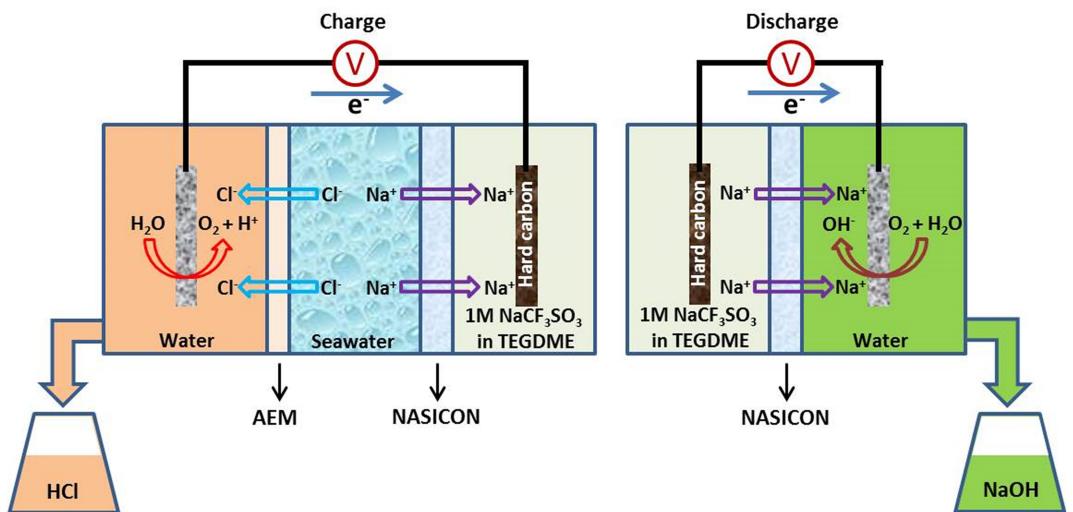


Figure 1. Schematic illustration of the designed seawater desalination battery system and schematic diagram of charge and discharge processes.

the electrons in the anode side. When discharging, the Na⁺ ions and electrons are delivered to form NaOH. Based on the above principle, this design can integrate the electrochemical battery, seawater desalination, and acid-alkali production in one system.

The designed seawater desalination battery system uses DI water as cathode electrolyte both in the charging and discharging processes. Due to the high resistivity of the DI water, the first charging started from a high voltage, and the first discharging started from a negative voltage, as shown in Figure S4. From the second cycle, the desalination battery system was cycled with a capacity-limited charging (200 mAh g⁻¹) and a voltage cut-off discharging (0.5 V) at a current density of 10 mA g⁻¹ (based on the mass of hard carbon anode material). Figure 2a illustrates the typical charge-discharge profiles of the desalination battery system. In the charge profiles, there appears a slope in the voltage range from starting to ~3.9 V, which can be associated with the adsorption behavior of Na⁺ ions on the surface, edges and the defected sites of hard carbon.^[32] Then, a plateau appears during the following charging process. This may be attributed to the intercalation of Na⁺ ions between the graphene layers in hard carbon.^[33] In the discharge profiles, the voltage drops from starting to ~3.0 V with a plateau observed. This may be attributed to the desorption of Na⁺ ions from the surface, edges and the defected sites of hard carbon. The plateau region can be assigned to the de-intercalation of Na⁺ ions from the graphene layers. Then, the voltage decreases gradually down to the deep discharge cut-off voltage of 0.5 V, in correspondence to the further de-intercalation behavior of Na⁺ ions from hard carbon. Figure 2b shows the charge-discharge capacity and corresponding coulombic efficiency versus cycle number of the desalination battery system. As can be seen, after charging 200 mAh g⁻¹, the battery can deliver an average discharge specific capacity of 182.9 mAh g⁻¹ with an average coulombic efficiency of 91.5% and an average energy efficiency of 75.8% during the first 10 cycles. The capacity loss may be

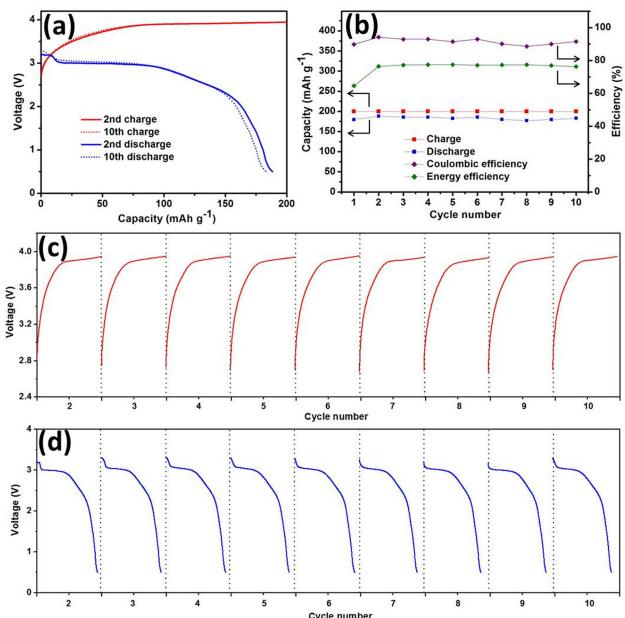


Figure 2. (a) Typical charge-discharge profiles; (b) Charge-discharge cycling performance; (c) 2nd to 10th charge profiles; and (d) 2nd to 10th discharge profiles of the seawater desalination battery system at a current density of 10 mA g⁻¹.

attributed to the partial irreversible intercalation of Na⁺ ions into the hard carbon. Figure 2c and 2d display the charge and discharge profiles of the 2nd to 10th cycles, separately. The consistency of the charge and discharge profiles indicates the good rechargeability and cycling stability of the designed seawater desalination battery system. It should be noted that the OER and ORR potentials change theoretically along with the change of pH value of the electrolyte. However, the charge-discharge profiles exhibit good consistency without obvious shift from 2nd to 10th cycles. We think that the charge-discharge profiles are not only affected by the OER and ORR processes, but also affected by some other factors, such as side reactions

at cathode electrodes and the electrocatalytic activities of the Pt/C used in this work. The future further detail research work will continue to explain the mechanism of this system.

Figure 3a displays the cycle number-profiled pH change of the cathode product after charging. It can be clearly seen that

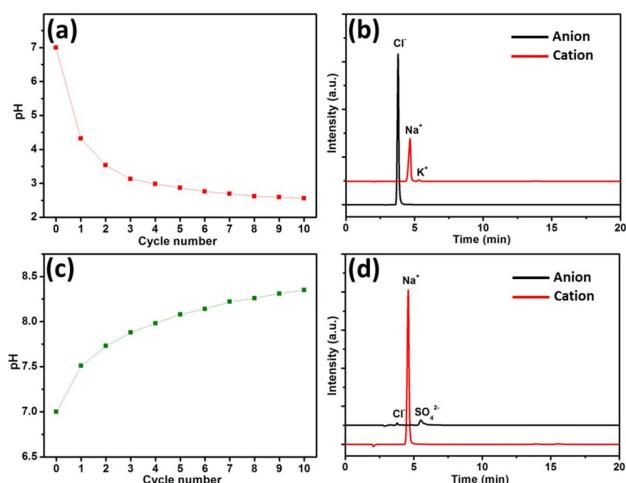


Figure 3. (a) Cycle number-profiled pH change, and (b) Anion and cation ion chromatography spectra of the acid product. (c) Cycle number-profiled pH change, and (d) Cation and anion ion chromatography spectra of the alkali product.

the pH value decreases with the increase of cycle number, confirming that H⁺ ions were produced from OER during charging process. After the 10th charging, the pH value decreased to 2.56. Ion chromatography (IC) was performed to analyze the ion species and their concentrations in the acid product. Figure 3b shows the anion and cation IC spectra of the acid product after the 10th charging. The concentrations of each ion species are listed in Table S1. The anions in the acid product are mainly Cl⁻ ions and a small amount of SO₄²⁻ ions. In addition, some cations such as Na⁺, K⁺, Mg²⁺ and Ca²⁺ ions were also detected in the acid product. The Cl⁻ ions account for 91.06% of the total ion concentration in acid product, which is in accordance with the ion selection rate (90~95%) of the AEM used in this work. For the cathode product after discharging, as shown in Figure 3c, the pH value increases with the cycle number, demonstrating that OH⁻ ions were produced from ORR during discharging process. After the 10th discharging, the pH value increased to 8.35. Figure 3d shows the anion and cation IC spectra of the alkali product after the 10th discharging. The cations in the alkali product are mainly Na⁺ ions and a small amount of K⁺, Ca²⁺ and Mg²⁺ ions. Besides, a few anions such as Cl⁻ and SO₄²⁻ ions were also detected in the alkali product. The impurity ions may come from the residual seawater on the surface of the coin-cell type anode switched between charging and discharging. The Na⁺ ions account for 99.79% of the total ion concentration in alkali product. Considering the charge balance of the acid and alkali products, [H⁺] and [OH⁻] were calculated to be 7.51 mM and 6.89 mM, respectively. However, [H⁺] and [OH⁻] calculated according to the pH values are 2.75 mM and 0.002 mM,

respectively. The discrepancies might be attributed to the side reactions during OER and ORR processes. When charging, carbon oxidation and chlorine evolution reaction (CER) might be inevitably occur accompany with the OER at cathode side. When discharging, most dissolved O₂ in water might be reduced to H₂O₂ through a two-electron process rather than through a four-electron process to OH⁻. The Faradic efficiency for H⁺ and OH⁻ production were calculated to be 30.6% and 0.02%. The further detail analysis of the cathode electrode reactions will be proceeded in future.

The comparison of ion concentration in pristine seawater and after 10th charging is shown in Table 1. After 10th charging,

Table 1. Ion concentration comparison between the pristine seawater and the seawater after 10th charging.

Sample	Ion concentration [mg/L]	
	Pristine seawater	After 10 th charge
Na ⁺	10,166	9,072
Mg ²⁺	1,229	1,171
K ⁺	395	369
Ca ²⁺	450	429
Cl ⁻	19,916	18,176
SO ₄ ²⁻	2,754	2,681
total	34,910	3,1898

the concentration of each ion species in the seawater decreased. Among them, the concentration of Na⁺ and Cl⁻ ions, two most concentrated ions in seawater, decreased more obviously. The concentration of Na⁺ ions decreased by 10.76% (corresponding to 911.7 mg/g hard carbon per cycle), while the concentration of Cl⁻ ions decreased by 8.74%. The total ion concentration decreased by 8.63% after 10th charging. The energy consumption for 8.63% salt removal can be calculated to be 4.69 Wh/L. These results demonstrate the desalination of seawater during the charging process.

These results of the experiment well prove the working principle, and fully confirm the feasibility of the proposed rechargeable seawater desalination battery system. Compared to other reported desalination batteries and electrodialysis systems, this design has an advantage of combining the seawater desalination with a high voltage electrochemical battery using the hybrid electrolytes structure.^[34–36] Looking forward to the future, we think that breakthroughs in several critical technologies are needed to develop this seawater desalination battery system. First, the battery system configurations should be improved. In this work, the charging and discharging cells are independent. The anode part must be switched between charging and discharging cells, making the operation process complicated. It is better to combine the charging and discharging cells together, so that the charging and discharging processes can be carried out continuously. Second, cheap and efficient electrocatalysts for OER/ORR processes need to be exploited. In this work, a noble-metal-based electrocatalyst, Pt/C, was used for OER/ORR during charging/discharging processes, raising the costs of the system. It is necessary to develop cheap and efficient non-precious metals or metal-free alternatives as OER/ORR electrocatalysts to

reduce the costs of the system. Third, novel anode materials need to be developed. Hard carbon was used as Na^+ ions storage material in this work. However, hard carbon has a low Na^+ ions capacity and high irreversible capacity. It is necessary to develop novel Na^+ ions storage materials with high capacity, low irreversible capacity, and high stability to improve the performance of the system. Fourth, Na super-ionic conductor (NASICON) ceramic electrolyte and anion exchange membrane (AEM) are important components in this system. It is significant to further exploit better NASICON ceramic electrolyte with higher Na ionic conductivity and better AEM with higher selectivity to develop this seawater desalination battery system. Finally, for future actual application, the stability of long-term running of this seawater desalination battery system is highly required. In this work, 10 cycles were conducted to prove the concept of the designed system. It is necessary to investigate the long-term cycling performance in the future work. However, this conceptual work provides a promising technology for utilization of natural seawater resources.

In summary, we propose a rechargeable seawater desalination battery system, which can integrate the electrochemical battery, seawater desalination, and acid-alkali production in one system. The working principle of the designed system was illustrated, and further proved by the results of the experiment. The charging and discharging profiles indicated the good rechargeability and cycling stability of the designed desalination battery system. The pH value of acid product decreased, while the pH value of alkali product increased with the increase of cycle number. The total ion concentration of the seawater decreased, demonstrating the desalination of seawater during the charging process. Looking forward to the future, the system configurations, electrocatalysts for OER/ORR, Na^+ ions storage materials, as well as the NASICON ceramic electrolyte and anion exchange membrane, need to be improved to develop this rechargeable seawater desalination battery system.

Experimental Section

To prepare hard carbon anode electrode, a mixture of hard carbon, super P acetylene black (AC) and poly(vinylidene)fluoride (PVDF) binder at a weight ratio of 80:10:10 in *N*-methylpyrrolidone (NMP) solvent was pasted on a Cu foil (99.9%), followed by drying at 80 °C for 10 h in a vacuum oven. The loading amount of hard carbon is ~3 mg cm⁻².

The coin-cell type anode part was assembled in a glove box under Ar atmosphere (O_2 and H_2O of <1 ppm). Figure S1 shows a schematic illustration of the coin-cell type anode part. A Cu foil ($\varnothing=16$ mm) coated with hard carbon (6 mg) was used as anode electrode. The organic electrolyte was 1 M NaCF_3SO_3 (Sigma Aldrich) dissolved in tetraethyleneglycol dimethylether (TEGDME, Sigma Aldrich). A polyethylene separator was put between the hard carbon electrode and the NASICON ($\text{Na}_2\text{Zr}_2\text{Si}_2\text{PO}_{12}$, a Na super ionic conductor with diameter of 16 mm and thickness of 1 mm) to prevent them direct contact. The coin-cell type anode part needed an “activation” process before it was used in the desalination battery system. The “activation” process is described in Figure S3.

Cathode electrode was prepared by coating a slurry (80 wt% Pt/C (20 wt%, Alfa Aesar), 10 wt% Super P acetylene black (AC), and

10 wt% poly(vinylidene)fluoride (PVDF) binder in *N*-methyl-2-pyrrolidone (NMP) solvent) onto a heated carbon felt (HCF) round disc ($\varnothing=16$ mm) with the catalyst loading amount of 5 mg, followed by drying at 80 °C in an oven. The cathode electrode was attached to a Ti mesh and immersed into the DI water (produces from water purification system) during charge and discharge processes.

For charging, the coin-cell type anode part was fixed to the charge cell, and the anion exchange membrane (AEM, Beijing Tingrun Membrane Technology Development Co., Ltd.) was fixed between two latex shims to separate the seawater from DI water, as shown in Figure S2. 10 mL natural seawater and 50 mL DI water were used for charging. When discharging, the charged coin-cell type anode part was taken out from the charge cell and fixed to the discharge cell. 50 mL DI water was filled into the discharge cell. The charge and discharge processes were operated under static condition. The battery performances were tested using a battery cycler (WBCS3000, WonAtech) at room temperature.

The pH of the acid and alkali were measured by pH meter (Thermo Scientific Orion Star A216). The anions and cations in the acid, alkali and seawater were quantitatively analyzed by ion chromatography (ICS-3000 for anions, ICS-1600 for cations, Dionex).

The seawater used in the charging process is natural seawater from Ilsan beach (Ulsan, Republic of Korea, GPS: 35.497005, 129.430996). The natural seawater was filtrated by using filter paper (Glass filter funnels-Buchner 500 mL, SciLab) to remove the floating particles before using it for the test.

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Conflict of Interest

The authors declare no conflict of interest.

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