



Short communication

Highly improved voltage efficiency of seawater battery by use of chloride ion capturing electrode

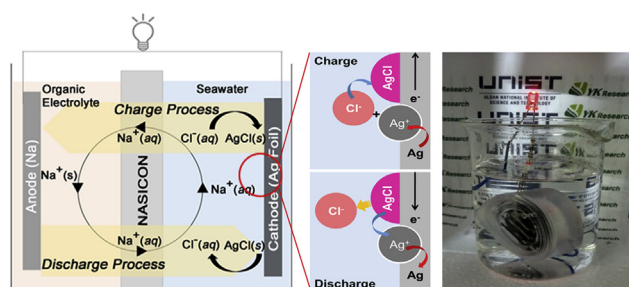
Kyoungho Kim¹, Soo Min Hwang¹, Jeong-Sun Park, Jinhyup Han, Junsoo Kim, Youngsik Kim*

School of Energy & Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), UNIST-gil 50, Ulsan 689-798, Republic of Korea

HIGHLIGHTS

- A seawater battery is fabricated using a chloride ion-capturing electrode.
- The chloride ion-capturing Ag leads to the reversible redox reaction.
- The Ag cathode results in excellent cycling performance of the battery.
- High Coulombic efficiency (98.7%) and voltage efficiency (90.3%) during 20 cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

Cost-effective and eco-friendly battery system with high energy density is highly desirable. Herein, we report a seawater battery with a high voltage efficiency, in which a chloride ion-capturing electrode (CICE) consisting of Ag foil is utilized as the cathode. The use of Ag as the cathode leads to a sharp decrease in the voltage gaps between charge and discharge curves, based on reversible redox reaction of Ag/AgCl (at -2.9 V vs. Na^+/Na) in a seawater catholyte during cycling. The Ag/AgCl reaction proves to be highly reversible during battery cycling. The battery employing the Ag electrode shows excellent cycling performance with a high Coulombic efficiency (98.6–98.7%) and a highly improved voltage efficiency (90.3% compared to 73% for carbonaceous cathode) during 20 cycles (total 500 h). These findings demonstrate that seawater batteries using a CICE could be used as next-generation batteries for large-scale stationary energy storage plants.

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1. Introduction

Global warming and the depletion of fossil fuels have forced us to seek renewable and sustainable energy and relevant technologies [1–3]. The development of cutting-edge electronic devices,

such as portable electronics, electric vehicles, and grid-scale stationary energy storage systems, has increased the importance of electrical energy generation and storage technologies.

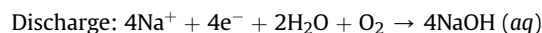
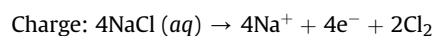
Recently, Na-air batteries have received attention due to their low-cost and more than three times higher theoretical energy density than that of existing lithium-ion batteries [4–8]. Na-air batteries are divided into two types according to their electrolytes: aqueous and non-aqueous. Non-aqueous batteries, whose reaction follows $\text{Na}(s) + \text{O}_2(g) \leftrightarrow \text{NaO}_2(s)$ and/or $\text{Na}(s) + 1/2\text{O}_2(g) \leftrightarrow 1/2\text{Na}_2\text{O}_2(s)$, can offer a large theoretical capacity. However,

* Corresponding author.

E-mail address: ykim@unist.ac.kr (Y. Kim).¹ These authors contributed equally to this work.

their cycle performance is limited due to their insoluble discharge products, such as NaO_2 or Na_2O_2 that can clog the gas diffusion layer electrode [5,8]. A gas tank is also required to provide pure O_2 and avoid contamination of the electrolyte and Na metal by H_2O and CO_2 from ambient air. In this regard, they are really Na- O_2 batteries. In aqueous Na-air batteries, the aqueous electrolyte participates in the redox reactions at the cathode as $\text{Na(s)} + 1/2\text{H}_2\text{O(l)} + 1/4\text{O}_2\text{(g)} \leftrightarrow \text{NaOH(aq)}$. The discharge product NaOH is soluble in the electrolyte, and there is no need for oxygen tanks. During the discharge process, however, as water is consumed, the concentration of metal hydroxides may reach their solubility limit, which consequently limits the specific capacity of the battery [8].

We have recently reported a novel type of eco-friendly 'seawater battery' system that utilizes circulating seawater (aqueous electrolyte containing approximately 0.46 M NaCl), one of the most abundant resources on the Earth, as the active material in an open-structured cathode [9–11]. The seawater battery is operated by redox reactions of Na^+ at the anode and evolution/reduction reactions of O_2 and Cl_2 gases at the cathode upon charge and discharge processes [9–11]. The redox processes can be described as follows:



The formation of gas species on the electrode yields a large polarization inside the cell, which results in a big voltage difference (~ 1.0 V) between charge and discharge curves [9–11]. This is the problem needed to be solved for the further development of the seawater battery as well as metal-air batteries. One of the common approaches for this challenge is to use electrocatalysts such as Pt/C, MnO_2 , or Co_3O_4 for oxygen evolution reaction/oxygen reduction reaction (OER/ORR) in the cathode compartment [12–15].

In this work, we employ a chloride ion capturing electrode (CICE) consisting of an Ag foil as the cathode in seawater batteries. Silver can reversibly react (capture/release) with Cl^- ions supplied from the seawater catholyte at 2.93 V vs. Na^+/Na upon the charge-discharge processes, and therefore, it can bypass the OER/ORR reaction route and significantly reduce the voltage gap. This is expected to improve the voltage efficiency. It has been reported that silver was used in a desalination system as the negative electrode to selectively remove Cl^- from seawater, based on redox reactions of Ag/AgCl, and this system demonstrated a total Coulombic efficiency of 80%, based on the amount of chlorides before and after the operation [16]. Our seawater batteries using CICE showed high voltage efficiency (90.3%) and Coulombic efficiency (98.6–98.7%) during 20 cycles, compared to previously reported metal-air batteries and seawater batteries using carbonaceous cathodes. The superior cell performance was attributed to the reversible redox reactions of Ag/AgCl at the cathode during cycling. These results suggest that the use of CICE should trigger practical applications of seawater batteries in large-scale stationary energy storage systems.

2. Results and discussion

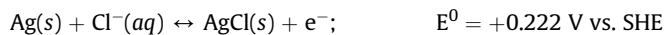
The battery used 1.0 M NaCF_3SO_3 /tetraethylene glycol dimethyl ether (TEGDME) as the anolyte, a sodium super ionic conductor (NASICON)-type solid electrolyte, a piece of Ag foil as the cathode, and seawater as the catholyte (Fig. 1a). The solid electrolyte was employed to (i) separate the cathodic compartment from the anodic to prevent mixing of the electrolytes and (ii) allow only the transport of sodium ions between seawater and the anode. The operating mechanism of seawater battery with the CICE can be described as follows. Upon charging, Na^+ diffuses from seawater to

the anode through the solid electrolyte, and Cl^- diffuses and reacts with the Ag cathode to form AgCl (top right in Fig. 1a). The reverse reaction occurs during discharging (bottom right in Fig. 1a). The overall and half-cell reactions in the battery during charge-discharge processes can be expressed as:

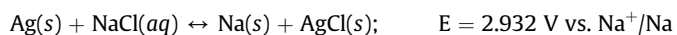
Anode reaction:



Cathode reaction:



Overall reaction:



where SHE stands for standard hydrogen electrode.

To verify this operating mechanism, we performed galvanostatic charge-discharge tests of seawater batteries with CICE and carbonaceous cathode at a current of 0.1 mA, and compared the cell performance. The galvanostatic first charge-discharge curves of the seawater battery using CICE at a current rate of 4.76 mA g^{-1} are shown in Fig. 2a, where ΔV denotes the voltage difference between charge and discharge curves. The CICE battery showed excellent performance with a ΔV of 291 mV. The charge voltage plateau and discharge voltage plateau were at 3.09 V and 2.80 V, respectively, which are close to the theoretical cell voltage (2.932 V). The charge and discharge overpotentials were thus measured to be 158 mV and 133 mV, respectively, reflecting the reversibility of the redox reaction of Ag/AgCl in the seawater battery system. In comparison, the seawater battery with carbonaceous cathode showed a large voltage difference ($\Delta V = 1.58$ V): the charge and discharge voltage plateaus were 4.07 V and 2.49 V, respectively, which were attributed mainly to large overpotentials for OER/ORR. The specific charge and discharge capacities of the CICE battery were 119.9 mAhg^{-1} and 118.3 mAhg^{-1} , respectively.

In order to investigate the phase, morphological, and compositional changes of the CICE during the charge and discharge processes, we analyzed the surface of Ag electrodes by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS). Fig. 2b exhibits the XRD patterns of the Ag electrode before and after the first charge and discharge cycle. The data after charging contains mostly cubic AgCl (space group: Fm3 m (225), JCPDS #31-1238) plus a smaller amount of cubic Ag (space group: Fm3 m (225), JCPDS #04-0783) from the foil itself. After discharging, the AgCl phase disappeared and only Ag remained. The formation/removal of AgCl phase by charge-discharge without any other phase implies the reversible redox reaction of Ag/AgCl on the CICE in the seawater battery.

Fig. 3a–e display the surface morphology and elemental composition of the CICE before and after the initial cycle. The surface of the pristine Ag foil (Fig. 3a) had certain parallel microscale scratches, which were thought to occur during the manufacturing and/or shipping as a roll. After the first charging (Fig. 3b), the surface was covered with round-shaped precipitate particles 1–7 μm in size. The precipitates were found to be AgCl from EDS elemental mapping (red box in Fig. 3b), which is in accord with the XRD result. After initial discharge, AgCl disappeared and the electrode surface was covered by irregularly sized and rectangular pure Ag particles (Fig. 3d and e). This roughened surface was the result of the reduction of AgCl precipitates into Ag and Cl^- , as well as the removal of Cl^- during discharging. This morphological change might be attributed partly to the oxidative etching of Ag surface by Cl^- and O_2 dissolved in the seawater during discharging [17]. It was

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