Seawater-based electrolyte for Zinc–air batteries

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**HIGHLIGHTS**

- Clarifying the influences of Cl\textsuperscript{-} anions on oxygen reduction and evolution reactions.
- Constructing successful seawater-based zinc–air battery prototypes.
- Evaluating feasibility of seawater-based electrolyte with various electrocatalysts.
- Demonstrating possible application occasions of batteries.

**GRAPHICAL ABSTRACT**

**ABSTRACT**

Aqueous zinc–air batteries (ZABs) are highly regarded as a promising electrochemical energy storage device owing to high energy density, low cost, and intrinsic safety. The employment of seawater to replace the currently used deionized water in electrolyte will bring great economic benefits and broaden the application occasions of ZABs. However, ZABs using seawater-based electrolyte remain uninvestigated without an applicable cathode electrocatalyst or a successful battery prototype. Herein, seawater-based electrolyte is successfully employed in ZABs with satisfactory performances. The influence of chloride anions on the cathode electrocatalytic reactivity and battery performance is systemically investigated. Both noble-metal-based and noble-metal-free electrocatalysts are applicable to the chloride-containing alkaline electrolyte. Further evaluation of ZABs with seawater-based electrolyte demonstrates comparable battery performances with the conventional electrolyte in terms of polarization, capacity, and rate performance. This study demonstrates a successful prototype of seawater-based ZABs and enlightens the utilization of natural resources for clean and sustainable energy storage.

Due to continuing consumption of fossil fuels and serious energy crisis, great efforts have been made to develop efficient energy storage technologies to utilize renewable energy sources (solar, wave, wind, etc.). Aqueous metal–air batteries such as zinc–air batteries (ZABs) are considered as promising alternatives, owing to low cost using naturally abundant active materials, intrinsic safety originated from aqueous electrolyte, and high theoretical energy density benefiting from infinite supply of cathodic oxygen \citep{1–3}. A typical ZAB mainly consists of a zinc anode and an air cathode packaged together with aqueous alkaline electrolyte, based on which electricity is reversibly released/stored via the cathodic oxygen reduction/evolution reactions (ORR/OER) and the anodic zinc dissolution/deposition processes \citep{3}. The most widely used ZAB electrolyte consists of high-purity deionized water (DI water) with dissolved alkalis and zinc salts, where the existence of impurity ions (especially halide anions) is considered to hinder the ORR/OER kinetics and ZAB performances. Therefore,
high-purity DI water has long been recognized as a key component for ZABs.

Generally, seawater is saline due to the existence of salts in the form of dissolved ions, where chloride (55.0%) and sodium (30.6%) ions account for the majority, together with minority cations and anions including SO\textsubscript{4}\textsuperscript{2−} (7.6%), Mg\textsuperscript{2+} (3.7%), Ca\textsuperscript{2+} (1.2%), K\textsuperscript{+} (1.1%), HCO\textsubscript{3}− (0.4%), etc. [4] Compared with DI water, seawater possesses advantages of natural abundance (~96.5% of the total water resource on earth) and low cost, showing great potential in replacing DI water in the fields of electrochemical energy storage [5–7]. Especially for ZABs, employment of seawater-based electrolyte will bring multiple economic and social advantages. It not only reduces the electrolyte and battery costs, but also alleviates the competition with the consumption of finite freshwater resource by human activity. More importantly, seawater-based electrolyte can greatly broaden the application occasions of ZABs in island, ocean, and coastal areas where usually suffer from shortage of freshwater but have sufficient seawater resource [5,8]. However, the exploitation of seawater as electrolyte in ZABs is rarely reported without a successful battery prototype [9–11].

The main challenges of seawater-based ZABs lie in the influences of the complex seawater component on the cathodic kinetics, which largely determines the energy efficiency of ZABs. Primarily, as the chief dissolved constituent in seawater, the chloride anions impede the cathodic reactions via multiple mechanisms, including the Cl\textsuperscript{−} adsorption behaviors on active sites during ORR, the competition of hypochlorite formation reaction with OER, and corrosion of electrocatalysts under working conditions [12–16]. The development of high-performance ORR/OER bifunctional electrocatalysts with chloride-resistant capability remains challenging. Several pioneer works exhibit that the Cl\textsuperscript{−} adsorption intensity of Pt is highly correlated with crystal structural sensitivity during ORR [12,17], and the activity of Fe–N\textsubscript{x}–C species is slightly suppressed by Cl\textsuperscript{−} due to its affinity to the Fe active sites [18]. Meanwhile, the insoluble particulates and microorganism in seawater also poison the electrodes and electrocatalysts by burying the active sites [9,19]. On the other hand, the interference of chloride anions is highly dependent on the pH of electrolyte. For instance, under alkaline conditions, high OH\textsuperscript{−} concentration can suppress Cl\textsuperscript{−} adsorption on electrocatalysts to some extent and benefit OER kinetics with advantages over chlorine evolution reactions to achieve a desired selectivity [15]. However, there has not been a systematic investigation on bifunctional oxygen electrocatalysts or ZAB prototypes using chloride-containing and seawater-based electrolytes, considering that the attempts of seawater-based ZABs are of great importance for utilization of natural resources for clean and sustainable energy storage.

Herein, seawater-based electrolyte is introduced into ZABs with applicable cathode electrocatalysts and a successfully constructed battery prototype. The influences of chloride anions on ORR/OER electrocatalytic reactivity as well as battery performance are investigated, revealing the scientific feasibility of ZABs under alkaline chloride-containing environment. Furthermore, the performance of the ZABs using seawater-based electrolyte is verified to be at the same level as those with the conventional electrolyte, while noble-metal-free electrocatalysts exhibit better compatibility. Furthermore, several seawater-based ZAB prototypes are presented to demonstrate future application occasions.

Generally, the concept design of seawater-based ZABs is composed of an air cathode comprising oxygen electrocatalysts, a reactive zinc anode, and a seawater-based electrolyte (Fig. 1). During discharging, a ZAB supplies electricity via liberating electrons at anode by converting Zn into Zn(OH)\textsubscript{2}\textsuperscript{−} ions while gaseous oxygen is reduced to OH\textsuperscript{−} at the three-phase reactive interface within air cathode via the O\textsubscript{2} process [3,20]. During charging, it stores electric energy via the OER process and zinc deposition at the cathode and anode, respectively. Despite of thermodynamic feasibility, seawater-based electrolyte causes several uncertainties on reaction kinetics. Therefore, understanding the influences of chloride anions on the ORR/OER electrocatalytic processes in air cathode becomes the prerequisite for developing seawater-based ZABs.

The electrocatalytic activity of ORR/OER bifunctional electrocatalysts in various chloride-containing electrolytes was evaluated. Previously, a series of highly active electrocatalysts have been proposed to enhance the inherently sluggish ORR/OER kinetics, including two broad categories, one is noble-metal-based alternatives such as Pt, Ir, and derived compounds; the other is noble-metal-free alternatives such as transition metal oxides/chalcogenides/hydroxides [21–23]. Therefore, we chose Pt/C–Ir/C and the composite of Co\textsubscript{3}O\textsubscript{4} and graphene (Co\textsubscript{3}O\textsubscript{4}/G) as the representatives of noble-metal-based and noble-metal-free electrocatalysts. Pt/C–Ir/C was prepared by mixing equal amounts of commercial Pt/C and Ir/C, whose morphology is shown in Fig. S1. Co\textsubscript{3}O\textsubscript{4}/G was prepared through a liquid-phase reaction system [24]. As shown in scanning electron microscope (SEM) and transmission electron microscope (TEM) images, Co\textsubscript{3}O\textsubscript{4} nanoparticles are in situ composited on graphene sheets (Fig. S2). For the X-ray diffraction (XRD) characterizations, the main peaks are indexed to the (111), (220), (311), (400), (422), (511), and (440) lattice planes of Co\textsubscript{3}O\textsubscript{4} (JCPDS card no. 42–1467), whereas the broad peak around 26° indicates the existence of graphene (Fig. S3) [25].

With the same electrocatalyst mass loading of 0.25 mg cm\textsuperscript{−2}, the electrocatalysts were tested in electrolytes designed as O\textsubscript{2}-saturated 0.10 M KOH dissolved in DI water accompanied with various concentrations of NaCl additive. In general, the half-wave potential (E\textsubscript{1/2}) vs. the reversible hydrogen electrode (RHE) is employed to evaluate the ORR activity, being defined as the potential to reach half of the limiting current density (herein defined as ~3.0 mA cm\textsuperscript{−2}). The potential to reach a current density of 10.0 mA cm\textsuperscript{−2} (E\textsubscript{10}) is used to evaluate the OER activity. ORR and OER linear sweep voltammetry (LSV) profiles with 95% iR-compensation of the Pt/C–Ir/C electrocatalyst in 0.10 M KOH + x M NaCl (x = 0, 0.2, 0.5, and 1) electrolytes are presented in Fig. 2a and b. With the NaCl concentration increased from 0 M to 1 M, the E\textsubscript{1/2} slightly decreased from 1.61 V to 1.58 V. Obviously, when compared with the conventional electrolyte (0 M NaCl), the introduction of NaCl within a certain amount gave rise to negligible impacts on the activity of Pt/C–Ir/C. As summarized in Fig. 2c, the bifunctional electrocatalytic performance can be evaluated by the potential gap (ΔE) between E\textsubscript{1/2} and E\textsubscript{10}, which revealed little difference in terms of NaCl concentration, with a variation degree of less than 40 mV.

The Co\textsubscript{3}O\textsubscript{4}/G electrocatalyst showed a similar yet slightly different tendency. As the NaCl concentration increased from 0 M to 1 M, the E\textsubscript{1/2} also stayed stable around 0.74 V but the E\textsubscript{10} slightly increased from

![Fig. 1. Schematic illustration of the cell design and operating mechanism of a rechargeable seawater-based zinc-air battery.](image-url)
1.62 V to 1.65 V, rendering a slightly increased $\Delta E$ (Fig. S4 and Fig. 2d). It is suggested that the competing effect of hypochlorite formation reactions with OER emerges as a detrimental side reaction [26,27]. This different chloride-resistant capability between Pt/C–Ir/C and Co3O4/G should originate from not only the intrinsic electrocatalytic property, but also the multiscale architecture of electrocatalysts which determine the exposure of active sites and mass/electron transfer [13,28–30]. However, in total both of the electrocatalysts can tolerate the chloride environment to demonstrate acceptable impact on activity, affording satisfactory feasibility of the seawater-based ZABs.

ZABs using alkaline electrolytes with various NaCl concentrations are further constructed with the same cathode electrocatalysts. It is worth noting that when compared with low-concentration and slow-diffusion dissolved oxygen in electrolyte, gaseous oxygen can be utilized more efficiently for ZABs and thus the mass transfer and interface issues become more significant. Fig. 3a compares the discharge/charge polarization curves of ZABs with the Pt/C–Ir/C electrocatalyst (hereinafter referred to as Pt/C–Ir/C ZABs) at a scan rate of 10 mV s$^{-1}$, using 6 M KOH $+ 0.2$ M Zn(Ac)$_2$ $+ x$ M NaCl ($x = 0, 0.2, 0.5$, and $1$) electrolytes. After introducing chloride, the discharge voltage of ZAB required for 10 mA cm$^{-2}$ was almost unchanged around 1.28 V, rendering negligible difference at a low current density. However, the voltage required for 100 mA cm$^{-2}$ became differentiated, which first increased and then decreased within the range of 0.99–1.03 V with an increasing NaCl concentration. It reached the maximum current for the 0.5 M NaCl electrolyte, with a maximum discharge power density ($P_{\text{max}}$) of 143.9 mW cm$^{-2}$. In comparison, the $P_{\text{max}}$ of the ZAB using the conventional electrolyte (158.9 vs. 155.6 mW cm$^{-2}$), indicating a superior stability and resistance of both two electrocatalysts in chloride-containing electrolytes (Fig. 3b). It is worth noting that the Pt/C–Ir/C ZABs and Co3O4/G ZABs achieve the highest $P_{\text{max}}$ using electrolytes with various NaCl concentrations, that 0.2 and 0.5 M, respectively. Although the $P_{\text{max}}$ corresponding to various NaCl concentrations are actually close, the slight difference might originate from inherent resistance of electrocatalysts to chloride anions [13]. In addition to the influences on electrocatalysts, the performance of ZABs using chloride-containing electrolyte can also be affected by various aspects including ionic conductivity, solubility of oxygen, and viscosity, thus the practical results are a balance of the multiple impacts [3,31,32].

As the concentration of Cl$^-$ in seawater is ~0.54 M, the 6 M KOH $+ 0.2$ M Zn(Ac)$_2$ $+ 0.5$ M NaCl electrolyte was investigated emphatically as the simulated seawater-based electrolyte. The corresponding long-term cycle performance of ZABs is directly compared with that of the conventional electrolyte. As shown in Fig. 3c, the Pt/C–Ir/C ZAB using conventional electrolyte delivered discharge and charge potentials of 1.13 and 2.02 V at 10.0 mA cm$^{-2}$ after the initial activation process, respectively. Both the discharge and charge overpotentials gradually increased, with a voltage gap increasing from 0.89 to 1.14 V upon 200 cycles. When it came to the simulated seawater-based electrolyte, a lower discharge voltage was observed as the cycle proceeded. For example, the discharge voltage corresponding to the simulated seawater-based electrolyte was only 0.92 V after 200 cycles, but that of the conventional electrolyte maintained at 1.02 V. It is understandable that the discharge voltage of ZABs is more sensitive to the ORR three-phase interface. The addition of NaCl into such a high concentration (6 M) KOH electrolyte increases the viscosity and hinders mass transfer, resulting in disadvantages during ORR [33].

Fig. 2. Electrocatalytic activity investigation of the electrocatalysts in chloride-containing electrolytes. (a) ORR and (b) OER LSV profiles of the Pt/C–Ir/C electrocatalysts in 0.1 M KOH $+ x$ M NaCl ($x = 0, 0.2, 0.5$, and $1$) electrolytes. (inset of a: optical photographs of various electrolytes). (c and d) Comparison of $E_{1/2}$, $E_1$, and corresponding bifunctional activities of the Pt/C–Ir/C or Co3O4/G electrocatalysts in various electrolytes.
By contrast, the Co₃O₄/G ZABs demonstrated more stable discharge/charge voltage gaps at 10 mA cm⁻², with a variation degree of only 30 mV upon 200 cycles for both conventional and simulated seawater-based electrolytes (Fig. S5). The performance difference between the two electrolytes was quite small, revealing stronger chloride-resistant capability of Co₃O₄/G over Pt/C–Ir/C. Such advantages benefit from not only the intrinsic activity but also the multiscale architecture of electrocatalysts [34]. The quantified average voltage gaps of Pt/C–Ir/C and Co₃O₄/G ZABs are further summarized in Fig. 3d and e, respectively, to give an intuitive comparison which suggests excellent feasibility of the seawater-based ZABs. Moreover, the morphologies of electrocatalysts after the above long-term cycling are investigated. The Pt/C–Ir/C electrocatalyst well maintained its pristine structure after cycling in either conventional or simulated seawater-based electrolyte, and similar phenomenon was observed for the Co₃O₄/G electrocatalyst (Figs. S6 and S7). Therefore, it is concluded that the corrosion effect on the electrocatalysts is slight.

When compared with the chloride-containing electrolyte, direct replacement of DI water with natural seawater in electrolytes is of more significance. In addition to chloride anions, insoluble particulates and microorganism covering on the electrode and electrocatalyst surface are detrimental, especially for the hydroxide precipitates (e.g., Mg(OH)₂) generated in alkaline seawater-based electrolyte (Fig. S8) [15]. The electrocatalytic activity of Pt/C–Ir/C and Co₃O₄/G electrocatalysts in seawater-based electrolyte was firstly evaluated. As shown in Fig. S9, ORR and OER LSV profiles with 95% iR-compensation of Pt/C–Ir/C show E₁/₂ of 0.86 V and E₁₀ of 1.63 V, both values are close to those in DI water-based electrolyte in Fig. 2a. A similar tendency was also observed for Co₃O₄/G (Fig. S10). Therefore, the interference effect of the seawater component on both two electrocatalysts is limited.

Furthermore, the ZABs using seawater-based electrolytes are tested to evaluate the technologic feasibility. Fig. 4a compares the polarization curves of the Pt/C–Ir/C and Co₃O₄/G ZABs using seawater-based and DI water-based (conventional) electrolytes. It was found that the discharge potentials of ZABs using seawater-based electrolyte were highly close to those using DI water-based electrolyte, no matter Pt/C–Ir/C or Co₃O₄/G electrocatalyst was used. The difference in P_max was also negligible, in particular, the P_max of Pt/C–Ir/C ZABs using seawater-based electrolyte (136.5 mW cm⁻²) was close to that using conventional electrolyte (135.9 mW cm⁻²), similarly for the Co₃O₄/G ZABs (156.4 vs. 157.5 mW cm⁻²).
Furthermore, the specific capacity of various ZABs was tested at a discharge current density of 25 mA cm$^{-2}$ and normalized to the mass of the zinc anode (Fig. 4b). The specific capacities of the Pt/C–Ir/C ZAB using seawater-based electrolyte (724 mAh g$_{Zn^{-1}}$) was slightly lower than that using DI water-based electrolyte (733 mAh g$_{Zn^{-1}}$), and similar phenomenon was observed for the Co$_3$O$_4$/G ZABs. It is promising that the employment of seawater-based electrolyte makes little impact on the battery performance, being at the same level as the DI water-based electrolyte. The slight performance differences between seawater-based and conventional electrolytes result from synergistic effect of multiple factors originated from seawater, for example, the blocking effects on active sites by chloride anions, the burying effects of active sites by insoluble components, the corrosion of electrocatalysts by chloride anions, and other side effects related to impurities [4,12,19]. From the perspective of electrocatalysts, their inherent resistance and structure characteristics also play a significant role.

Furthermore, rate tests at various current densities were performed (Fig. 4c and d). For the Pt/C–Ir/C ZABs, the discharge voltages corresponding to the DI water-based electrolyte were 1.23, 1.21, 1.14, and 1.05 V at 5.0, 10, 25, and 50 mA cm$^{-2}$, respectively, while those corresponding to the seawater-based electrolyte were only 1.21, 1.18, 1.10, and 1.00 V. Obviously, at a relative high current density, the seawater-based electrolyte endows the ZABs with a discharge voltage disadvantage. When the current density increased from 5.0 to 50 mA cm$^{-2}$, the discharge voltage difference also increased from 20 mV to 50 mV. By contrast, the discharge voltages of Co$_3$O$_4$/G ZABs using the seawater-based electrolyte were almost the same as those using the DI water-based electrolyte. At a current density of 50 mA cm$^{-2}$, the former remained a discharge voltage of 1.05 V which is even 20 mV higher than the latter. It demonstrates the potential of seawater-based ZABs in large current applications, especially for the noble-metal-free electrocatalyst [35].

To further exemplify the practical applications of seawater-based ZABs, besides the South China Sea, seawaters collected from other sea areas were utilized to prepare alkaline seawater-based electrolytes, including Bohai Sea, Yellow Sea, East China Sea, and South China Sea. (Fig. 5a). As compared in Fig. 5a, the specific capacities of Pt/C–Ir/C ZABs using seawater-based electrolytes based on various sea areas were relatively close, while the Yellow Sea and South China Sea electrolytes were superior. Meanwhile, the polarization curves of the above four ZABs showed minor different performances. The discharge voltage of the ZAB using the Bohai Sea electrolyte was obviously lower than other ZABs, accompanied with the lowest P$_{max}$ of 111 mW cm$^{-2}$. In total, the South China Sea electrolyte achieved the best ZAB performance. Such a performance variation may result from the differences of salinity, turbidity, and water quality in the sampling sites of the different sea areas. In addition, two as-assembled Pt/C–Ir/C ZABs using the South China Sea electrolyte can power a light emitting diode (LED) light for long time (Fig. 5c).

As freshwater becomes a more and more precious resource, ZABs using seawater-based electrolyte possess multiple advantages, including broader application occasions, reduced costs, and alleviated consumption of freshwater. Although the complex seawater component (e.g., chloride anions and insoluble matters) theoretically harms the electrocatalyst and electrode processes, remarkable battery performances were still achieved by our seawater-based ZABs, which delivered no disadvantages as compared to the ZABs using the conventional electrolyte.
based on DI water. Herein, the seawater-based ZAB worked as a model battery, which aimed to improve raw materials of electrolyte.

In summary, the employment of seawater-based electrolyte in ZABs are successfully realized. For the Pt/C-Îr/C and Coâ„„Oâ„„/G electrocatalysts, chloride anions within certain concentration have little influence on their ORR/OER reactivities and ZAB performances. Direct applications of seawater-based electrolyte in ZABs deliver satisfactory performance indexes that are at the same level as the conventional electrolyte. Meanwhile, Coâ„„Oâ„„/G shows certain advantages over Pt/C-Îr/C to render greater potential of noble-metal-free electrocatalysts. This study clarifies the scientific and technologic feasibility of seawater-based ZABS and inspires the usage of natural resources in future energy devices.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References


