A Near-Neutral Chloride Electrolyte for Electrically Rechargeable Zinc-Air Batteries

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Near-neutral electrolytes based on zinc chloride and ammonium chloride are examined for rechargeable zinc-air battery application. The effects of pH value, salt concentration, and polyethylene glycol and thiourea additives are investigated and a chloride electrolyte is developed. The reversible zinc deposition and zinc stripping processes are studied by cyclic voltammetry with rotating-disc electrode technique. The zinc anode and air cathode behaviors in near-neutral chloride electrolyte are characterized by quasi steady-state polarization and impedance spectroscopy. Prototyped zinc-air battery with near-neutral chloride electrolytes can sustain more than 1000 hours and hundreds of discharge-charge cycles with minimized zinc dendrite formation and no carbonate formation problem, under discharge-charge capacity ranging from 20 to 120 mAh. The near-neutral chloride electrolyte provides a safer and more robust alternative to traditional alkaline electrolyte for rechargeable zinc-air batteries.

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Zinc-air batteries (ZABs) are efficient electrochemical energy storage devices with the advantages of high specific energy, safety and low cost. Primary ZABs batteries are commercially available to power hearing aids, railroad track circuits, warning lights and remote signals. These types of devices typically discharge at low rate over a long period of time. For broad applications and environmentally benignity, it is of great interest to upgrade the primary ZABs into electrically rechargeable ones. However, secondary ZABs batteries have not been commercialized due to some technical challenges.

Electrolyte carbonation is one of the technical hurdles of electrically rechargeable ZABs. The traditional alkaline electrolyte reacts with CO2 and results in the reduction of ionic conductivity. The precipitated carbonate particulates block the diffusion channels of air electrode. This problem can be avoided by employing non-alkaline electrolytes, where no reactions with CO2 occur. Another technical challenge comes from the zinc dendrite formation. During battery charging, zinc tends to grow on protruded surfaces and results in zinc dendrites after prolonged charging/discharging cycles. Zinc dendrites could penetrate through the separator and eventually lead to short circuit when it reaches the air cathode. Generally, two mechanisms of additive are commonly known: (i) ligating with metal species and forming complexes; or (ii) adsorbing on the electrode surface and inhibiting metal nucleation.

In this study, a near-neutral electrolyte was developed for electrically rechargeable zinc-air battery application. The effects of salt concentration, pH value and additives on zinc electrodeposition and stripping were studied in ZnCl2-based electrolyte baths by cyclic voltammetry and ZAB prototype tests. A suitable chloride-based near-neutral electrolyte suppressing zinc dendrite formation was developed for electrically rechargeable ZABs. The air cathode catalyst was commercial manganese oxide (MnO2) with conductive carbon materials due to its good oxygen reduction reaction (ORR) activity and low cost. The zinc anode and air cathode was characterized by quasi steady-state polarization curves and impedance spectroscopy. The near-neutral electrolyte was demonstrated to be a more technically viable alternative to traditional alkaline counterpart.

Experimental

Zinc chloride (ZnCl2, Sigma Aldrich, ACS >97%), ammonium chloride (NH4Cl, Alfa Aesar, min. 99.5%), polyethylene glycol (PEG, Mw = 8000, Aldrich), thiourea (Nacalai Tesque), NH4OH (Alfa Aesar), MnO2 (activated, Sigma Aldrich, >90%), carbon black (VC, Vulcan XC-72, Cabot), Nafion perfluorinated resin solution (5 wt%, Sigma Aldrich), carbon paper (GDL 10 BC, SGL Carbon), zinc sheet (Alfa Aesar, 99.9%) were used as-received. All aqueous solutions were prepared with ultrapure water (>18 MΩ cm) obtained from a Milli-Q plus system (Millipore).

Cyclic voltammetry (CV), linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) were conducted through a potentiostat/galvanostat (Autolab PGSTAT302N) in three-electrode configuration. The working electrode for CV was a platinum rotating disk electrode (3 mm in diameter) at a rotating rate of 400 rpm. The working electrodes for LSV and EIS were either zinc plate or air cathode, with working area of 0.5 cm². The counter electrode and reference electrode were platinum foil and Ag/AgCl (3 M KCl), respectively. The bare chloride bath consisted of 0.51 M ZnCl2 and 2.34 M NH4Cl. The potential sweeping rates for CV and LSV was 20 mV s⁻¹ and 5 mV s⁻¹, respectively.

The catalyst slurry consisted of 66 wt% MnO2, 22 wt% Vulcan XC-72 and 12 wt% Nafion. The slurry was roll-pressed on a SGL carbon paper and dried at 70 °C for 1 h to achieve a loading of 4.5 mg cm⁻². The working area of the air cathode and polished zinc sheet anode was 2 cm². A zinc air battery prototype was assembled by an acrylic cell fixture with the cell volume of 30 mL and the distance between anode and cathode of 30 mm. The electrolyte was ZnCl2-NH4Cl bath with or without additives and the pH value was adjusted by NH4OH. Battery testing and cycling experiments (Mac-cor 4300) were performed with the recurrent galvanic pulse method at 25 °C and under ambient air condition. Surface morphology of zinc anodes was observed by field emission scanning electron microscopy (SEM, JEOL JSM-6700F). Crystalline structure of zinc anodes and air cathodes were characterized by X-ray diffraction (XRD, Bruker D8 GADDS).

Results and Discussion

The hydrogen evolution reaction occurs near –1.15 V vs. Ag/AgCl in a 2.34 M NH4Cl solution (Figure 1). The Zn reduction occurs at


Electrodeposition processes.11 The Zn reduction potential is shifted −0.59 V are typical for overpotential-driven nucleation and growth electrodeposition processes.12 The Zn reduction potential is shifted cathodically to −1.05 V in a solution containing 0.51 M ZnCl₂ and a 2.34 M NH₄Cl (hereafter ZnCl₂-NH₄Cl). The cathodic shift of Zn deposition implies the inhibition of Zn²⁺ reduction by zinc-ammonia complexes such as [Zn(NH₃)₆]²⁺,12 which is thermodynamically stable in ZnCl₂-NH₄Cl solutions.13 As given in Figure 1, the peak position of the zinc stripping loop is significantly shifted to −0.82 V (cf. −0.66 V for bare ZnCl₂ bath), indicating that the zinc deposition and stripping processes are more reversible than those in the bare ZnCl₂ bath.

With increasing pH values, both the reduction potential of Zn²⁺ and peak positions of the zinc stripping loops shift to the negative direction, and the full width at half maximum (FWHM) of the zinc stripping loops are narrowed (Figure 2). These observations imply more sluggish reduction of zinc-ammonia complex but more facile zinc stripping processes are more reversible than those in the bare ZnCl₂ bath.

Reduction of [Zn(NH₃)₆]²⁺ requires higher activation energy than [Zn(NH₃)₄]²⁺, thus explaining the cathodic shift of zinc reduction potential with the increasing pH value. The pH values of all ZnCl₂-NH₄Cl baths were adjusted to be 6.0, unless explicitly stated.

The CVs show that zinc deposition and stripping processes are slightly affected by the addition of 1000 ppm PEG, as reflected from a zinc reduction potential shift from −1.041 V to −1.043 V and a mild depression of the zinc stripping loop (Figure 3). In contrast to PEG, the incorporation of 1000 ppm thiourea exhibits pronounced inhibition effect, where zinc deposition initiates at −1.071 V. Simultaneous addition of PEG and thiourea further shifts the Zn reduction potential to −1.092 V. Interestingly, the peak current of Zn stripping is reduced from 257 mA cm⁻² for the bare chloride bath to 85 mA cm⁻² in the same bath containing PEG and thiourea. These results demonstrate that PEG and thiourea, when used concurrently, are effective additives in inhibiting zinc deposition and stripping processes. Such an inhabitation effect would be beneficial for mitigating zinc dendrite formation in ZABs.

Figure 4 shows the impedance spectra of zinc anode and air cathode. Polarization resistance (Rₚ) is defined by the difference between the low-frequency intercept and high-frequency intercept of an impedance spectrum. The impedance spectrum of zinc anode is featured by a depressed impedance arc and a high-frequency inductive loop. Compared to Rₚ of 4.9 Ω cm² under OCP condition which was −1.00 V, Rₚ of zinc anode is decreased by 41% and 92% when polarized at 100 mV and 100 mV potential biases, respectively, implying that zinc deposition is a more sluggish process than zinc dissolution. Rₚ of air cathode are about one order of magnitude larger than those of zinc anode, cf. Figures 4d–4f to Figures 4a–4c. To better understand the reaction mechanisms of air cathode, all air-cathode impedance spectra were fitted with relevant equivalent circuits, as given in the insets of Figures 4d–4f. The cathodic polarized impedance spectrum is modeled by a resistor Rₚ, which models the lumped resistance, in series with a Voigt-type Rₚ/Q sub-circuit where Rₚ is the polarization resistance and Q is the constant phase element (CPE) describing the non-ideal capacitive feature of the electrochemical cell. The OCP and anodic polarized impedance spectra have a high-frequency depressed arc and a low-frequency impedance tail which is described by a CPE connected in series. The open impedance tail implies the infinite diffusion characteristic of the air cathode, possibly due to the sluggish oxygen transport in the chloride electrolyte. Rₚ of air cathode polarized at −0.3 V (cathodic bias of 550 mV) is 78.3 Ω cm², comparable with 69.0 Ω cm² that is under an anodic bias of 350 mV. The low-frequency diffusional impedance of air cathode under anodic bias implies that the oxygen evolution reaction is impeded by some reaction steps with large time constants, such as adsorption/dissociation of oxygen molecule and surface diffusion of oxygen ad-atoms.

Figure 5 shows the i–η responses and the Tafel plots of air cathode and zinc anode, respectively. Current responses at specific potentials
Figure 4. Impedance spectra of zinc anodes at OCP (a), $-0.9$ V (b) and $-1.1$ V (c) and of air cathodes at OCP (d), $-0.3$ V (e) and 0.6 V (f). Note that OCP of zinc anode and air cathode are $-1.10$ V and 0.25 V, respectively.

Figure 5. Quasi steady-state polarization curves of air cathode (a) and zinc anode (b). The Tafel plots of air cathode (c) and zinc anode (d).
The half-cell reactions of zinc anode and air cathode of ZAB in the near-neutral chloride electrolytes are:

\[
\text{Zinc anode : } \begin{align*}
\text{Zn} & \rightarrow \text{Zn}^{2+} + 2e^- \\
\text{Zn}^{2+} + 6\text{NH}_4\text{OH} & \leftrightarrow [\text{Zn}(\text{NH}_3)_6]^{2+} + 6\text{H}_2\text{O} \\
[\text{Zn}(\text{NH}_3)_6]^{2+} + 7\text{H}_2\text{O} & \leftrightarrow \text{ZnO} + 6\text{NH}_4\text{OH} + 2\text{H}^+ \\
\text{Overall : } \text{Zn} + \text{H}_2\text{O} & \rightarrow \text{ZnO} + 2\text{H}^+ + 2e^- \\
\text{Air cathode : } \text{O}_2 + 4\text{H}^+ + 4e^- & \rightarrow 2\text{H}_2\text{O}
\end{align*}
\]

Discharging:

\[
\text{Charging : } [\text{Zn}(\text{NH}_3)_6]^{2+} + 6\text{H}_2\text{O} + 2e^- \rightarrow \text{Zn} + 6\text{NH}_4\text{OH} \\
[\text{Zn}(\text{NH}_3)_6]^{2+} + 7\text{H}_2\text{O} \leftrightarrow \text{ZnO} + 6\text{NH}_4\text{OH} + 2\text{H}^+ \\
\text{Overall : } \text{ZnO} + 2\text{H}^+ + 2e^- \rightarrow \text{Zn} + \text{H}_2\text{O}
\]

When discharging, zinc releases electrons and coordinates with ammonia to form Zn-ammonia complex, which would be reversibly changed to ZnO, and O₂ was reduced to H₂O at the cathode. When charging, ZnO is dissolved to form Zn-ammonia complex, which is further reduced to metallic zinc. On the meanwhile, O₂ is evolved from H₂O at the cathode. Based on Eqs. 2–10, the full-cell reactions of ZAB in the near-neutral chloride electrolytes are:

\[
\text{Air cathode : } 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- \\
\text{Zinc anode : } \begin{align*}
\text{Zn} & \rightarrow \text{Zn}^{2+} + 2e^- \\
\text{Zn}^{2+} + 6\text{NH}_4\text{OH} & \leftrightarrow [\text{Zn}(\text{NH}_3)_6]^{2+} + 6\text{H}_2\text{O} \\
[\text{Zn}(\text{NH}_3)_6]^{2+} + 7\text{H}_2\text{O} & \leftrightarrow \text{ZnO} + 6\text{NH}_4\text{OH} + 2\text{H}^+ \\
\text{Overall : } \text{Zn} + \text{H}_2\text{O} & \rightarrow \text{ZnO} + 2\text{H}^+ + 2e^- \\
\text{Air cathode : } \text{O}_2 + 4\text{H}^+ + 4e^- & \rightarrow 2\text{H}_2\text{O}
\end{align*}
\]

The theoretical open circuit voltage (OCV) for ZABs in the chloride bath at pH of 6.0 is 1.638 V. Experimental OCV of 0.51 M ZnCl₂-2.34 M NH₄Cl was 1.42 V. The theoretical specific energy is 1353 Wh/kg based on Zn as anode active material and O₂ as cathode active material. The longevity of ZAB is, however, paralyzed when it is subjected to relatively large discharge-charge cycling capacity. At a rate of 5 mA, while the ZAB performs stably for 42 discharge-charge cycles (504 h equivalent) and 120 cycles (1440 h equivalent) under the 5 mA/20 mAh, it can sustain 91 cycles (1092 h equivalent), 100 cycles (1200 h equivalent) and 120 cycles (1440 h equivalent) under the 5 mA/20 mAh, 2 mA/8 mAh, and 1 mA/4 mAh, respectively. Under a rate of 10 mA discharging and 5 mA charging, the discharge-charge potential gap is 1.4 V and the discharge-charge efficiency is 36%. The ZABs can sustain 21, 15, 22 and 26 discharge-charge cycles when running at bare chloride bath, chloride bath with thiourea, chloride bath with PEG, and chloride bath with both thiourea and PEG, respectively. The degradation rate of the discharge-charge potential gap of ZAB with the ZnCl₂-NH₄Cl-PEG-thiourea electrolyte is 7%.

### Table II. Current densities under polarized conditions and the exchange current density of air cathode and zinc anode. The units of \( i \) and \( i_0 \) are mA cm⁻².

| Oxygen reduction reaction (cathodic) | Oxygen evolution reaction (anodic) | Zinc deposition (cathodic) | Zinc dissolution (anodic) |
|------------------------------------|-----------------------------------|---------------------------|--------------------------|
| \( i @ \eta = 100 \text{ mV} \)   | \( i_0 \)                           |                           |                          |
| -1.66                              | 1.42                               | -25.2                     | 71.7                     |
| -2.57                              | 1.93                               | -8.7                      | 32.1                     |

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Figure 6. Discharge-charge cycling tests of rechargeable Zn-air batteries with different salt concentrations without pH adjustment (a) and with or without PEG and/or thiourea additives (b). A complete cycle comprises a discharge process at 10 mA for 4 h and a charge process at 5 mA for 8 h. The unadjusted pH values of electrolytes in (a) are around 4.8. The pH values of electrolyte in (b) are adjusted to be 6.0. The battery tests are stopped at the charging stage.

15.3 mmol. As an example of discharge-charge capacity at 120 mAh, 2.2 mmol of Zn is dissolved/deposited on each discharging-charging cycle. This corresponds to the depth of discharge (DOD) of 14%. Figure 9 further demonstrates that the high-rate capability remains a technical challenge for ZAB with chloride electrolyte. Better bifunctional catalysts in near-neutral aqueous media than MnO₂-VC would increase the rate capability of ZABs.

Figure 10 shows the XRD patterns of zinc anode after 6 discharge-charge cycles and a 7th discharge process in the ZnCl₂-NH₄Cl electrolyte. The phases are Zn (JCPDS 04-0831), ZnCl₂ (JCPDS 16-0850) and Zn(NH₃)₂Cl₂ (JCPDS 24-1435). Figure 11 shows the zinc anodes after 6 discharge-charge cycles and a 7th discharge, where any soluble salts were removed by soaking the dismantled zinc anodes in large quantity of water. No reaction products were detected in the ZnCl₂-NH₄Cl electrolyte except the Zn. ZnO was detected in ZnCl₂-NH₄Cl-thiourea. Trace of ZnO appears on zinc anodes in ZnCl₂-NH₄Cl-PEG-thiourea. Based on the XRD results, it is proposed that the immediate ZAB discharging product is zinc-ammonia complex (Eq.3) while the final reaction product is ZnO (Eqs. 4 and 5).

Figure 12 shows the surface morphology of zinc deposits after 7 discharge-charge cycles where the battery test was stopped after the 7th charging stage. The zinc deposits from the ZnCl₂-NH₄Cl are porous and cloudy. The zinc deposits are relatively compact and granulated for ZnCl₂-NH₄Cl-PEG and consist of mixed granulates and cross-linked flakes for ZnCl₂-NH₄Cl-thiourea. It is interesting to note that compact and uniform ripple-like zinc deposits are formed in ZnCl₂-NH₄Cl-PEG-thiourea. Figure 13 shows the surface morphology of zinc anode after 4 discharge-charge cycles and a 5th discharge battery test. The discharged zinc anode in the bare ZnCl₂-NH₄Cl bath consists of flake-like structures on the zinc anode surface. The addition of PEG to the chloride bath significantly flattens the zinc anode surface, whereby the inset of Figure 13b shows zinc deposits composing of compact...
and fine granules grouped in hemispherical clusters in diameters of 80 to 150 nm. Ripple-like zinc deposits are observed in chloride baths with sole thiourea and PEG and thiourea.

PEG was known as inhibitor against hydrogen embrittlement during metal electrodeposition.15,16 Banik and Akolkar found the addition of PEG-200 (PEG, M.W. = 200) substantially lowered the $i_0$ but not the cathodic transfer coefficient ($\alpha_c$) of zinc deposition from zinc halide solutions.17 PEG-200 suppressed the activation-controlled zinc dendrite propagation by absorbing on the electrode surface and forming a passivation layer.17 In this study, PEG functions as a surface smoothing agent and prevents deleterious zinc dendrite formation during prolonged operation of rechargeable ZABs. The addition of 4–8 wt% of thiourea in acidic zinc electroplating bath reduced the corrosion rate in sea water by 30%.18 Thiourea would perform as an inhibition agent to increase the overpotential of zinc dissolution/deposition during the ZAB discharge-charge cycles, thus leading to fine structures of zinc deposits. In contrast, the zinc dendrite growth in alkaline electrolyte is so significant that it will penetrate to the air cathode and short the battery cell. Zinc deposits generated from alkaline zincate solutions were very rough and showed dendritic and heavy spongy morphologies.19,20 With the elimination of carbonate formation and zinc dendrite problems that are inherent to traditional alkaline electrolyte, the near-neutral chloride electrolyte casts light on the commercialization and realization of electrically rechargeable zinc-air batteries.
lense glycol and thiourea additives was developed for rechargeable zinc-air battery application. A chloride bath consisting of 0.51 M ZnCl₂, 2.34 M NH₄Cl, 1000 ppm PEG, 1000 ppm thiourea, and with the pH value of 6.0 showed satisfactory electrochemical and zinc air battery performance. The incorporation of PEG and thiourea additives posed inhibitory effects on zinc deposition from the chloride baths. The reaction kinetics of air cathode was almost one order-of-magnitude more sluggish than that of zinc anode, as reflected from the impedance spectroscopy and exchange current densities. For both zinc anode and air cathode in three-electrode configuration, the cathodic and anodic branches of the quasi steady-state polarization curves were asymmetric. Rechargeable zinc-air battery tests proved that this type of chloride electrolyte system can sustain more than 1000 h and hundreds of discharge-charge cycles, under discharge-charge capacity ranging from 20 to 120 mAh. No zinc dendrite formation was observed after prolonged zinc-air battery test.

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Conclusions

A class of near-neutral chloride baths containing zinc chloride (ZnCl₂) and ammonium chloride (NH₄Cl) in the presence of polyethy-