Multifunctional Electrolyte Additive for Alkaline Electrolytes in Zinc Batteries

Akash Kota[1], Alex Karpinski[2], and Emily Dickens[1]
[1]Octet Scientific Inc., 7100 Euclid Avenue, Cleveland, OH, USA, 44103
[2]EaglePicher Technologies, 2000 S County Trail, East Greenwich, RI, USA, 02818
Contact Author Email: akash.kota@octetsci.com

Abstract

Rechargeable alkaline Zn metal batteries are emerging as promising candidates for stationary energy storage systems due to the intrinsic safety of aqueous electrolytes and appealing advantages of Zn metal anodes. However, the practical applications of Zn metal batteries are limited because of the poor reversibility of the zinc anode caused by the unstable electrolyte-anode interface. In this work we demonstrate the use of benzyltrimethylammonium hydroxide (BTMAH) as an electrolyte additive for high concentration alkaline electrolytes to suppress the Zn dendrites. The efficacy of BTMAH at different concentrations in aqueous electrolytes containing 8 M potassium hydroxide (KOH) and 0.1-0.2 M zinc oxide (ZnO) is investigated using electrochemical methods. It has been observed that BTMAH at 2% concentration is an effective electrolyte additive for suppressing dendritic growth during Zn electrodeposition.

Keywords

Zinc metal batteries; dendrite suppression; electrolyte additive; zinc electrodeposition; aqueous electrolyte

Introduction

Energy storage systems based on rechargeable zinc electrodes are potential candidates to fulfill the need for stationary and high discharge rate applications. Owing to its unique merits, including high theoretical capacity of 820 mAh/g, nontoxicity, easy availability, and low processing cost, zinc has been widely used as anode material in many alkaline batteries such as Zn-MnO_2, Zn-Ag_2O, Zn-NiO, and Zn-air batteries. In a zinc metal battery typically, zinc powder is used as the active material in anode and concentrated alkaline solutions are used as electrolyte. However, the practical applications of Zn metal batteries are limited because of the poor reversibility of the zinc anode caused by the unstable electrolyte-anode interface. Zn metal is thermodynamically unstable in aqueous electrolytes. During the charging, deposition of zinc-active material is a non-homogeneous process which results in uneven electric field distribution on the electrode/electrolyte interface. The uneven distribution of zinc on the electrode surface provokes dendritic diffusion-controlled deposition, which promotes zinc corrosion. In addition, zinc dendrites can easily detach from the electrode surface and lowers the zinc consumption rate. Dendrite growth may also cause a short-circuit over time. These detrimental processes will result in the loss of capacity retention and cycle life of battery in the long term.

To improve the stability of zinc anode, it is significantly important to suppress the dendrite growth. In the past, some functional materials including nano-$CaCO_3$, polyvinylidene fluoride (PVDF), and montmorillonite [1-3] have been reported as coatings on a Zn anode to regulate uniform Zn^{2+} flux, thus suppressing the dendrite growth. However, the traditional protective layers not only increase the interfacial resistance but are also easily pulverized during continuous cycling. As an alternative, in this work we demonstrate the use of benzyltrimethylammonium hydroxide (BTMAH) [2] as an electrolyte additive for high concentration alkaline electrolytes to suppress the Zn dendrites. The efficacy of BTMAH at different concentrations in aqueous electrolytes containing 8 M potassium hydroxide (KOH) and 0.1-0.2 M zinc oxide (ZnO) is investigated using different electrochemical methods such as chronoamperometry, potentiodynamic polarization, and electrochemical impedance spectroscopy.

Experimental

Materials: Aqueous electrolytes containing 8 M potassium hydroxide (KOH, Thermo Scientific) and 0.2 M zinc oxide (ZnO, Alfa Aesar) are used to perform Zn electrodeposition. Benzyltrimethylammonium hydroxide (BTMAH, TCI) is used as an electrolyte additive. The structure of BTMAH is shown in Figure 1.

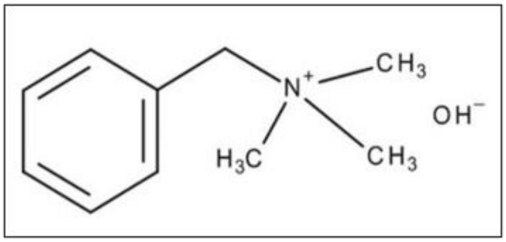


Figure 1. Molecular structure of BTMAH additive.

All electrolytes are prepared using analytical-grade reagents and deionized (DI) water.

Prior to testing, all the electrolytes are sparged using industrial grade nitrogen for 45 mins.

Methods: Zinc dendrite growth tests are performed using an electrochemical cell in a three-electrode configuration. The base electrolyte has 8 M KOH and 0.2 M ZnO. Experiments are performed either in the absence of BTMAH or in the presence of 0.1-2% BTMAH. A 1 mm diameter Zn wire (99.95% purity, Thermo Scientific), coated with AquaMend underwater repair epoxy is used as the working electrode (WE) for dendrite growth and polarization tests. Prior to each experiment the tip of epoxy coated zinc wire WEs are sanded with 1000 grit sandpaper, then polished with 5 µm alumina slurry (Aztron Technologies) on a terry cloth polishing pad (Grainger). A Hg/HgO electrode filled with 4.24 M KOH is used as the reference electrode (RE, $E_{Hg/HgO} = +0.098$ V vs SHE). A 0.5 mm diameter platinum wire (Sigma-Aldrich) is used as the counter electrode. A USB digital microscope camera is used to capture the images of electrodeposited zinc on the glassy carbon electrode. All electrochemical measurements are performed with BioLogic SP-300 potentiostat at room temperature.

Effect of BTMAH During Zinc Electrodeposition

To characterize the effect of BTMAH on zinc dendrite suppression, chronoamperometry tests are performed. Zinc electrodeposition is initiated by applying a constant potential (-1.6 V vs Hg/HgO (4.24 M KOH)) to the zinc wire WE. Two electrolytes are investigated: an additive-free control electrolyte, and electrolyte containing 2% BTMAH. The chronoamperometry curves are shown in Figure 2.

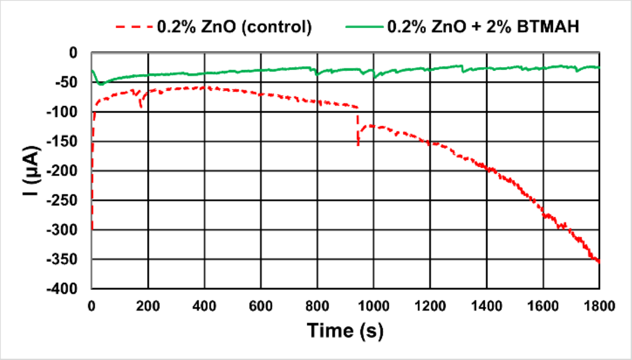
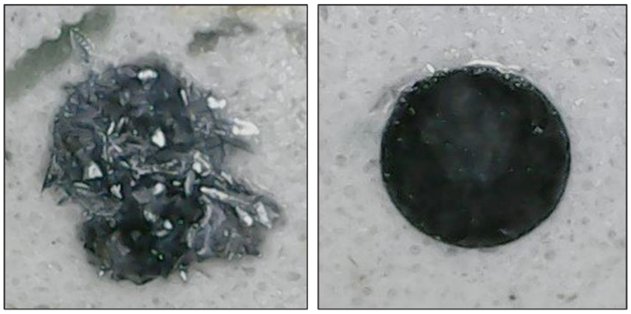


Figure 2. Chronoamperometry curves during zinc electrodeposition at -1.6 V vs Hg/HgO with and without BTMAH additive.

After 1800 seconds of zinc deposition at -1.6 V, digital microscopy confirms needle-like dendrites (Figure 3(a)) on the zinc wire electrode when using the 'no additive' control electrolyte. In the presence of BTMAH additive in the electrolyte, zinc dendrite formation is completely suppressed (Figure (3(b)).



(a) (b)

Figure 3. Microscopic image of zinc wire WE which shows **(a)** needle-like dendrites when using the base electrolyte, and **(b)** complete suppression of zinc dendrites when using 2% BTMAH additive in the base electrolyte.

The chronoamperometry curves in Figure 2 represent the evolution of the electroactive surface as dendrites grow on the WE. In the additive-free case ('red' curve), a substantial increase in the surface area due to dendrites is noted. However, in the presence of BTMAH ('green' curve), after 1000 seconds the current reaches at a time-invariant values of ~25 µA corresponding to a current density of ~3.125 $\mathrm{mA/cm^2}$. The time-invariant current implies no evolution of surface area and thus no dendrite formation in the presence of BTMAH, which is consistent with the digital microscopy data shown in Figure 3(b). Therefore, it can be concluded that BTMAH suppresses dendrites formation when the WE undergo zinc electrodeposition near its diffusion limit. These results indicate that by preventing the evolution of electroactive surface BTMAH additive can inhibit zinc electrochemical corrosion, which can be verified from polarization tests.

Effect of BTMAH on the Polarization Behavior of Zinc

To obtain the polarization curves, potentiodynamic Tafel scans are performed. The control electrolyte has 8 M KOH and 0.1 M ZnO. Experiments are performed on four electrolytes: an additive free control electrolyte, and electrolyte containing 0.1%, 1% and 2% BTMAH additive. The polarization behaviors of zinc in the alkaline electrolyte with and without BTMAH additive is shown in Figure 4. The corrosion inhibition efficiency of BTMAH additive is given as

$$\eta_p = \frac{\mathrm{i_{corr}} - \mathrm{i'_{corr}}}{\mathrm{i_{corr}}}, \qquad (1)$$

where, $\mathrm{i_{corr}}$ and $\mathrm{i'_{corr}}$ are the corrosion current densities of zinc with and without BTMAH additive in the electrolyte.

Table 1. Electrochemical corrosion parameters of zinc in 8 M KOH solution in the absence and in the presence of BTMAH at different concentrations.

Additives	**Control**	**0.1% BTMAH**	**1% BTMAH**	**2% BTMAH**
E_{corr} (V)	-1.428	-1.392	-1.389	-1.393
i_{corr} (μA/cm^2)	2081	238	239	219
η_p (%)	-	88.6	88.5	89.5
ΔE_{corr} (mV)	-	36	39	35

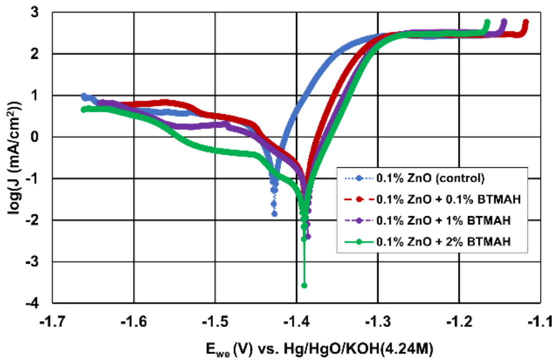


Figure 4. Tafel plot from potentiodynamic polarization curves of zinc in 8 M KOH solution with and without BTMAH additive obtained at a scan rate of 1mV/s.

The electrochemical corrosion parameters obtained from Figure 4 are listed in Table 1.

As shown in Figure 4 and summarized in Table 1, the control electrolyte (8 M KOH + 0.1% ZnO) has an $\mathrm{E_{corr}}$ of -1.428 V vs Hg/HgO/KOH (4.24 M). Compared with the corrosion potential of zinc in the control electrolyte, the corrosion potential becomes more positive in the presence of BTMAH additive. From Table 1, it can be observed that the presence of BTMAH additive at different concentrations in the electrolyte lead to an anodic shift of the corrosion potential with respect to the control electrolyte. This confirms that BTMAH additive can inhibit zinc electrochemical corrosion mainly by suppressing the anodic reaction, namely zinc dendrite suppression.

Effect of BTMAH on the Ionic Conductivity of the Electrolyte

Electrochemical impedance spectroscopy (EIS) tests are performed to study the effect of BTMAH concentration on the ionic conductivity of the electrolyte. The ionic conductivity is obtained for the control electrolyte (8 M KOH + 0.1% ZnO) and electrolyte containing 2% BTMAH additive. To perform the EIS experiment, electrolyte under test is loaded into a CR2032 coin cell with stainless steel (SS) electrodes [5]. The area of SS electrodes is 2.85 cm^2. A 25 μm thick polypropylene (PP) sheet is used as the separator. The coin cell components are assembled in the following order: SS electrode, 100 μl electrolyte, separator, and SS electrode. The prepared coin cell is connected to a BioLogic SP-300 potentiostat and EIS data is obtained in the frequency range of 0.1 Hz to 1 MHz at an applied alternating current (AC) potential of 10 mV. The EIS plot of electrolyte with 2% BTMAH is shown in Figure 5. The real (Z'_{real}) and imaginary $\left(Z''_{img}\right)$ impedances are plotted on the x and y axes, respectively. The x-intercept on the plot is taken as the electrolyte resistance (R_{ele}) from which the ionic conductivity (σ)is calculated as

$$\sigma = \frac{t}{R_{ele} \times A}, \qquad (2)$$

where, t is the thickness of the separator and A is the area of the SS electrode.

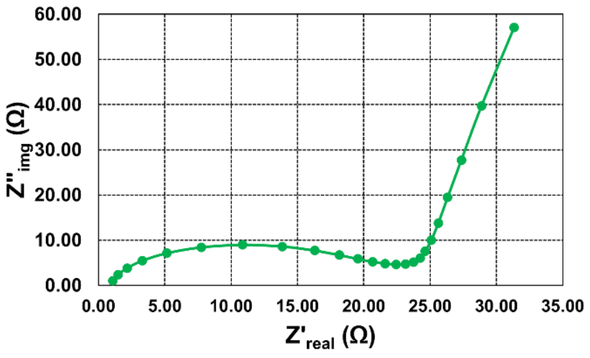


Figure 5. EIS plot of electrolyte with 2% BTMAH additive.

From Figure 5, it can be observed that the resistance of the electrolyte containing 2% BTMAH additive is found out to be 1.08 Ω. Using (2) the ionic conductivity can be calculated as 8.12×10^{-4}(S/cm). Similarly, the electrolyte resistance and ionic conductivity of the control electrolyte can be calculated as 0.42 Ω and 2.09×10^{-3}(S/cm), respectively. The effect of 2% BTMAH additive on the ionic conductivity of the electrolyte is shown in Figure 6.

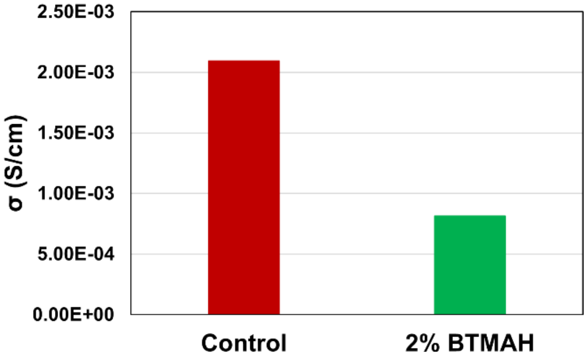


Figure 6. Plot comparing the ionic conductivities of the control electrolyte and the electrolyte containing 2% BTMAH additive.

From Figure 6 it can be observed that the ionic conductivity value of the electrolyte with 2% BTMAH additive is an order magnitude low compared with that of the control electrolyte. The decrease in the ionic conductivity suggests that BTMAH additive can suppress the dendrites by slowing down the kinetics of Zn^{+2} ions in the electrolyte during the electrodeposition process.

Conclusion

In this work, we demonstrate the use of BTMAH as an electrolyte additive in aqueous electrolytes containing 8 M KOH and 0.1-0.2 M ZnO. From the chronoamperometry tests it can be concluded that during zinc electrodeposition complete suppression of dendrites is noticed in electrolytes containing 2% BTMAH. The potentiodynamic polarization tests reveal that the electrochemical corrosion inhibition efficiency of BTMAH additive remains approximately the same at 89% within the concentration range of 0.1-2%. EIS tests reveal that the ionic conductivity of the electrolyte with 2% BTMAH is lower than that of the control electrolyte by an order magnitude. This behavior suggests that the BTMAH additive can regulate the Zn^{+2} ions by slowing down the Zn^{+2} kinetics to enable smooth plating of zinc during electrodeposition process.

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