Precipitated iodine cathode enabled by trifluoromethanesulfonate oxidation for cathode/electrolyte mutualistic aqueous Zn–I batteries

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Article

Keywords:

Posted Date: July 27th, 2023

DOI: https://doi.org/10.21203/rs.3.rs-3164281/v1

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Abstract

Aqueous Zn – I batteries hold great potential for high-safety and sustainable energy storage. However, the iodide shuttling effect and the hydrogen evolution reaction that occur in the aqueous electrolyte remain the main obstacles for their further development. Herein, we present the design of a cathode/electrolyte mutualistic aqueous (CEMA) Zn – I battery based on the inherent oxidation ability of trifluoromethanesulfonate ([OTf]−) based aqueous electrolyte towards triiodide species. This results in the formation of iodine sediment particles assembled by fine iodine nanocrystals (approximately 10 nm). An iodine host cathode with high areal iodine loading was realized via a spontaneous absorption process that enriched redox-active iodine and iodide species from aqueous electrolyte onto nanoporous carbon based current collector. By tuning iodide redox process and suppressing competitive hydrogen evolution reaction, the assembled CEMA Zn – I batteries demonstrated a remarkable capacity retention of 76.9% over 1000 cycles, retaining a capacity ranging from 141 to 112 mAh g⁻¹ at a current density of 0.5 mA cm⁻². Moreover, they exhibited a notable rate capability, with a capacity retention of 74.6% when the current density was increased from 0.5 to 5.0 mA cm⁻², resulting in a capacity retention range of 130 to 97 mAh g⁻¹. This study demonstrates the feasibility of using the oxidation effect to repel redox-active species from the electrolyte to the cathode, paving a new avenue for high-performance aqueous Zn – I batteries.

Introduction

Aqueous Zn – ion batteries have gained considerable attention due to their unique advantages, including intrinsic safety, environmental benignity, and easy operation in air¹⁻³. Among various Zn – ion battery systems, such as Zn – halogen⁴,⁵, Zn – air⁶,⁷, Zn – S⁸,⁹, Zn – metal oxide batteries¹⁰,¹¹, the aqueous Zn – I battery employing a typical conversion-type redox chemistry of I₂/I⁻ couple is considered a promising candidate for scalable applications due to its high energy density and affordable costs¹²,¹³. However, the polyiodide shuttling effect during battery operation remains a significant obstacle to commercialization progress. To mitigate the polyiodide shuttling effect, extensive research efforts have been carried out, which mainly involve exploring various functional materials, such as nanoporous carbons, metal-containing compounds with catalytic activity, sieving membranes, and solid-state electrolytes¹⁴⁻²¹. These materials are able to absorb, electrostatically repel, and sieve iodide species, thereby improving the cycling ability, coulombic efficiency, and electrochemical kinetics. However, this approach inevitably drags the improvement of overall energy density. Additionally, hydrogen evolution reaction (HER) occurs in aqueous electrolyte when the battery voltage exceeds its critical potential²²⁻²⁵. The undesired HER in aqueous Zn-ion batteries, including Zn – I system, often leads to the drawbacks, including the formation of flammable H₂, battery swelling, and low charge storage efficiency²⁶⁻³¹. Therefore, it is crucial to have a comprehensive strategy to inhibit the polyiodide shuttling and the HER without sacrificing energy density. A promising solution would be to develop an aqueous electrolyte that spontaneously expels iodide
species, mitigates polyiodide diffusion, and suppresses the interactions of redox species/electrolyte. However, such consideration has rarely been addressed in previous studies of aqueous Zn–I batteries. Herein, we present a self-expelling strategy towards iodide species by harnessing the inherent oxidation effect of trifluoromethanesulfonate ([OTf]$^-$) in Zn[OTf]$_2$ aqueous electrolyte. Upon the addition of I$_3^{-}$ species in the Zn[OTf]$_2$ aqueous electrolyte, [OTf]$^-$ induced the formation of iodine sediment particles, leading to a mutualistic mixture of iodine sediment particles and aqueous electrolyte. Based on this mixture, we developed a cathode/electrolyte mutualistic (CEMA) aqueous Zn–I battery. During battery assembly, the iodine cathode and aqueous electrolyte were simultaneously formed through a facile in-situ filtering process, where the iodine and iodide species were retained by the carbon host cathode while the aqueous electrolyte further penetrated until reaching the metallic Zn anode. By tuning the I$_2$/I$^-$ ratios and I$_3^{-}$ concentrations, the iodide oxidation reaction was efficiently facilitated and the unwanted HER suppressed. The fabricated CEMA Zn–I batteries exhibited high rate performance, with a capacity retention ratio of 74.4% as the operation current density increased from 0.5 to 5.0 mA cm$^{-2}$. Long-term cycling tests revealed efficient control over the polyiodide shuttling effect, benefitting from the oxidation effects of [OTf]$^-$ on iodide species. The optimized pouch-type CEMA Zn–I batteries showed no distinct swelling after repeated galvanostatic charge/discharge tests, suggesting efficient inhibition of the HER. Our work provides proof-of-concept for the repelling effect of electrolyte on iodide species owing to its oxidation ability, promoting the development of advanced aqueous Zn–I batteries.

Results and discussion

**Oxidative effect of [OTf]$^-$ on iodide species.** The CEMA Zn–I battery was fabricated using a Zn anode, an aqueous electrolyte containing iodine sediment particles, and an iodine host cathode, as illustrated in Fig. 1a and detailed in the Methods section. Notably, the iodine sediment particles-containing aqueous electrolyte serves as a source of redox-active iodide species, as well as an aqueous electrolyte for constructing the Zn-I battery. The oxidation effect of [OTf]$^-$ on iodide species was experimentally demonstrated by adding [EMIm]I or NaI chemical reagents in 3 M Zn[OTf]$_2$ aqueous solutions, respectively. The transparent Zn[OTf]$_2$ aqueous solutions turned yellow immediately (Fig. 1b and S1a), confirming the occurrence of iodide oxidation. In contrast, no such color change was observed in the control experiment using a 3 M ZnCl$_2$ aqueous solution, even after adding the NaI reagent, indicating the absence of iodide oxidation reactions. These results suggest that the [OTf]$^-$ anions are responsible for the iodide oxidation reactions. To gain a comprehensive understanding of the oxidation behavior of [OTf]$^-$ on iodide species, we conducted additional theoretical calculations of molecular electrostatic potential (MESP) for Zn[OTf]$_2$. As shown in Fig. 1c, the result indicates that the −SO$_3$ moiety displays a significantly lower MESP of −19.34 kcal mol$^{-1}$ compared to that of the −CF$_3$ moiety (−15.14 kcal mol$^{-1}$). This disparity partially unveils the thermodynamic basis of the oxidation ability of [OTf]$^-$.
The oxidization product of iodide species by $[\text{OTf}]^-$ was characterized using ultraviolet-visible (UV-Vis) spectroscopy, as depicted in Fig. 1d. The presence of UV-Vis absorption peaks at 288 and 345 nm confirmed the formation of triiodide ($I_3^-$) anions, consistent with the Zn[I$_3$]$_2$ control sample. However, in the control experiment using NaI and [EMIm]I aqueous solutions, these UV-Vis absorption peaks were absent (Fig. 1d). Furthermore, the reductant product of $[\text{OTf}]^-$ by iodide ions was analyzed using Fourier transform infrared (FTIR) spectroscopy. The FTIR spectrum of the Zn[OTf]$_2$ aqueous solution after oxidation reaction showed locally emerging FTIR transmittance peaks at 960, 1055, and 1410 cm$^{-1}$, while other peaks remained consistent with the standard sample (Fig. 1e). The absence of these characteristic peaks in the FTIR spectrum of the standard Zn[I$_3$]$_2$ aqueous solution excludes the possibility of their origin in the formed triiodide product. These experimental results suggested a change in binding association within $[\text{OTf}]^-$. To track the structural evolution of $[\text{OTf}]^-$ during oxidation reactions, we further collected electron paramagnetic resonance (EPR) spectra of 3 M Zn[OTf]$_2$ aqueous solutions before and after adding iodide species. The consistency of EPR spectra before and after oxidation reactions (Fig. S2) indicated that no radical formation occurred during the oxidation process, suggesting a straightforward oxidation mechanism.

Oxidation effect of $[\text{OTf}]^-$ on triiodide species. In light of the oxidative effect of $[\text{OTf}]^-$ on iodide species, we conducted further studies to investigate its impact on triiodide species ($I_3^-$). In the first step, a Zn[I$_3$]$_2$ aqueous solution was prepared, which was subsequently injected into a 3 M Zn[OTf]$_2$ aqueous solution, as detailed in the Methods section. As soon as the prepared Zn[I$_3$]$_2$ aqueous solution was injected, iodine sediment particles formed instantly. Scanning electron microscopy (SEM) analysis of iodine sediment particles revealed the plate-shaped morphology with distinct sizes, as presented in Fig. 2a. Subsequent TEM and high-resolution TEM (HRTEM) observations showed a nanoporous structure assembled by tiny iodine nanocrystals with the size of approximately 10 nm (Fig. 2b, c). This is an unknown phenomenon in prior studies conducted on redox-active iodine electrodes$^{32-34}$. XRD analysis confirmed that the sediment particles were composed of iodine species, as demonstrated by the characteristic peaks at 24.5°, 28.7°, 44.4°, and 45.8° in Fig. 2d. Additional experiments on dissolution of the iodine sediment particles were carried out by dissolving them in a CCl$_4$ organic solvent. As a result, a purple solution was obtained after particle dissolution, which is comparable to I$_2$/CCl$_4$ solution, as shown in Fig. S3. Conversely, chemical reagents of ZnI$_2$ and Zn[OTf]$_2$ were found to be insoluble in the CCl$_4$ solvent (Fig. S3). Based on these experimental results, we conclude that $[\text{OTf}]^-$ also exerts an oxidative effect on triiodide species, generating more iodine products. The same peaks emerging in the FTIR spectra of Zn[OTf]$_2$ aqueous solutions after triiodide oxidation reactions suggest the underlying association change of $[\text{OTf}]^-$ (Fig. S4).

Surface passivation effect of $[\text{OTf}]^-$ on metallic Zn. The inherent reductive property of Zn metal necessitates an investigation of the surface passivation effect of $[\text{OTf}]^-$ on Zn metal anode. To accomplish this, Zn foil was immersed in a 3 M Zn[OTf]$_2$ aqueous solution to initiate the surface functionalization of Zn by $[\text{OTf}]^-$, as detailed in the Methods section. The surface passivated Zn foil was
analyzed using XRD, showing peak signals at 13.0°, 19.6°, and 22.5° (Fig. 3a). The emergence of these XRD signals in the soaked Zn foil compared to the pristine Zn foil and Zn[OTf]$_2$ suggests that the underlying surface functionalization reactions occurred during the immersion of metallic Zn in the Zn[OTf]$_2$ aqueous solution achieves the formation of an interfacial passivation layer. The surficial chemical compositions of both surface passivated and pristine Zn foils were performed using X-ray photoelectron spectroscopy (XPS). The deconvoluted F 1s XPS spectra exhibited a newly emerged peak at 689.03 eV, suggesting the existence of F species due to the surface functionalization of Zn metal, which is absent for the pristine Zn foil. The association environment of F in surface passivation layer differs from that in Zn[OTf]$_2$ as demonstrated by the shift in binding energy by 0.3 eV (Fig. 3b).

Additionally, S was also found to participate in the formation of the surface passivation layer on Zn foil, as demonstrated by the binding peaks at 169.45 and 171 eV in the deconvoluted S 2p XPS spectra (Fig. 3c). In contrast, these XPS signals were absent for the pristine Zn foil. Surface morphologies observed using SEM revealed a rougher Zn surface with deposited nanoplates (Fig. 3d – f). Overall, these results demonstrate the surface functionalization of Zn metal by [OTf]$^-$ anions, leading to the formation of a surface passivation layer containing F and S elements. The surface passivated Zn surface was further subjected to elemental analysis using energy dispersive X-ray (EDX) spectroscopy. Elemental mappings revealed the presence of F, S, and O elements in the interfacial layer, as shown in Fig. 3g and S5. It is noteworthy that the intensity of O element in the surface passivation layer was considerably higher than that in pristine Zn, as confirmed in Fig. S5. This indicates that intense oxidation reactions took place on the Zn foils. The emergence of elemental peaks for F and S elements in the surface passivation layer of Zn, compared with the pristine Zn foil, further suggests the involvement of F and S elements in the surface functionalization reactions of Zn mediated by [OTf]$^-$ anions. The FTIR analysis of Zn[OTf]$_2$ aqueous solution after the surface passivation of Zn foil showed no emerged peaks (Fig. S6). This suggests that the surface functionalization of Zn by [OTf]$^-$ only involves interfacial [OTf]$^-$, while the others maintain consistent ionic associations with the fresh sample.

**Promoting iodide redox and suppressing HER processes.** During battery operation, a competitive effect between the iodide redox and HER processes could possibly occur within the CEMA Zn – I batteries. This competitive process was investigated by analyzing the coulombic efficiency parameter during battery cycling. At a relatively high I$_2$/I$^-$ ratio, the HER processes could be efficiently suppressed, thereby promoting the iodide redox reactions (Fig. S8). We proposed that higher ratios of I$_2$/I$^-$ and lower concentrations of I$_3^-$ led to less retained/unoxidized iodide and triiodide species, which inhibited the ionizing effect between iodide/triiodide species and H$_2$O molecules, thereby suppressing the HER and facilitating the iodide redox process. After modifying the ratio of I$_2$/I$^-$, we have determined that a ratio of 1:1 for I$_2$/I$^-$ provides the optimal conditions for further electrochemical performance studies of CEMA Zn – I batteries. In addition, by increasing the concentration of I$_3^-$ and adjusting the charge cutoff voltages, we can modulate the charge-storage capacity while maintaining high coulombic efficiency. These findings suggest that careful control of the electrolyte composition and operating conditions can enhance the performance of CEMA Zn – I batteries.
Electrochemical studies of CEMA Zn–I batteries. The electrochemical performance of CEMA Zn–I batteries was systematically investigated at room temperature at various conditions. Firstly, we examined the cyclic voltammetry (CV) curves of CEMA Zn–I batteries with various I$_3^-$ concentrations and I$_2$/I$^-$ ratios and found that the discharge reaction of CEMA Zn–I batteries involved a two-step iodide redox process (I$_2$ → I$_3^-$ → I$^-$) as demonstrated by the bifurcate discharge peaks in the CV curves (Fig. S10)\textsuperscript{35}. The CV curves collected from 3–1/1 (i.e., an I$_2$ concentration of 3 M and an I$_2$/I$^-$ ratio of 1/1) CEMA Zn–I batteries with an iodide areal loading amount of 0.69 mg cm$^{-2}$ at 100 mV s$^{-1}$ exhibit a pair of redox peaks with a voltage hysteresis of 0.2 V, as illustrated in Fig. 4a. Moreover, the rate performance of 3–1/1 CEMA Zn–I batteries was evaluated at various current densities (0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 mA cm$^{-2}$), demonstrating a capacity retention ratio of 74.6\% (with the specific capacity attenuated from 130 to 97 mAh g$^{-1}$, or from 0.09 to 0.07 mAh cm$^{-2}$ in area) after a ten-fold increase in current densities, as shown in Fig. 4b. The voltage profiles of the CEMA Zn–I batteries at each current density exhibited a single voltage plateau, as indicated in Fig. 4c. Long-term cycling tests were conducted for the CEMA Zn–I batteries with various I$_3^-$ concentrations (1–1/1, 2–1/1, 10–1/1 corresponding to iodide areal loading amounts of 0.23, 0.46, 2.3 mg cm$^{-2}$, respectively) at different current densities. The 1–1/1 CEMA Zn–I batteries demonstrated stable cycling abilities, exhibiting a capacity retention ratio of 76.9\% (with the specific capacity attenuated from 141 to 112 mAh g$^{-1}$, or 0.03 to 0.02 mAh cm$^{-2}$ in area) over 1000 charge/discharge cycles at 0.5 mA cm$^{-2}$. When the I$_3^-$ concentration was increased from 1.0 to 2.0 M, the 2–1/1 CEMA Zn–I batteries delivered an initial specific capacity of 127 mAh g$^{-1}$ (or 0.06 mAh cm$^{-2}$ in area) and a capacity retention ratio of 65.7\% (83 mAh g$^{-1}$ or 0.04 mAh cm$^{-2}$ in area) after 1000 cycles at 0.5 mA g$^{-1}$ (Fig. 4d). Further increasing the I$_3^-$ concentrations to 10 M, the 10–1/1 CEMA Zn–I batteries delivered a specific capacity of 36 mAh g$^{-1}$ (or 0.05 mAh cm$^{-2}$ in area) at 5.0 mA cm$^{-2}$, as presented in Fig. 4e. These electrochemical results suggested that the CEMA Zn–I batteries could be cycled over 1000 times with a high coulombic efficiency approaching 100\%, by utilizing the oxidative ability of [OTf]$^-$ towards triiodide species to form insoluble iodine sediment particles. However, a critical concentration of I$_3^-$ exists, beyond which the redox reactions of largely loaded I$_3^-$ species are limited, thereby reducing the charge cutoff voltage and/or requiring greater current densities to suppress the unwanted HER. For example, compared to the 1–1/1 and 2–1/1 CEMA Zn–I batteries operated at 0.5 mA cm$^{-2}$ under a charge cutoff voltage of 1.4 V vs. Zn/Zn$^{2+}$, the 10–1/1 counterpart operated at 5.0 mA cm$^{-2}$ under a suppressed charge cutoff voltage of 1.27 V vs. Zn/Zn$^{2+}$ (Fig. S11), resulting in a relatively lower capacity of 105 mAh g$^{-1}$. Therefore, to achieve optimal capacity values, the concentration of triiodide species needs to be controlled while modulating the charge cutoff voltage and/or working current density.

The feasibility of the proposed CEMA Zn–I batteries was further evaluated under a more rigorous test setup using pouch-type batteries, showing the suppression of swelling due to the HER. A set of 4–1/1 CEMA Zn–I batteries was produced and powered a LED lamp, as demonstrated in Fig. 5a. During galvanostatic charge/discharge cycling tests, the pouch-type CEMA Zn–I batteries exhibited consistent
voltage profiles and a stable specific capacity of 96 mAh g\(^{-1}\) (or 0.10 mAh cm\(^{-2}\) in area) at 2.5 mA cm\(^{-2}\), with a high coulombic efficiency of 99.2%, as illustrated in Fig. 5b and c. Furthermore, the pouch-type batteries maintained their original thickness after cycling, without any observable swelling. The EIS of the pouch-type CEMA Zn – I batteries revealed a charge-transfer impedance of approximately 10 Ω, as depicted in Fig. 5d. These experimental findings indicate that the electrode/electrolyte mutualistic strategy is efficient in constructing aqueous Zn – I batteries, which exhibit retarded HER and iodide redox reaction-dominated charge storage during battery operation.

**Conclusions**

In this study, we demonstrate the oxidative effect of [OTf]\(^{-}\) on iodide and triiodide species and utilize this effect to fabricate a novel type of CEM mixture for CEMA Zn – I batteries. By exploiting the CEM mixture, we were able to produce an iodine host cathode and aqueous electrolyte through a facile in-situ filtration process. During battery operation, we explored the competitive effects of the iodide redox and the HER processes in terms of \(I_2/I^-\) ratio and \(I_3^-\) concentration. Severe ionization within the electrolyte would lower the critical potential for HER and facilitate its aggravation. However, by optimizing the \(I_2/I^-\) ratio and \(I_3^-\) concentration, we were able to achieve long-term cycling capability and high-rate performance with well-suppressed HER. Our findings suggest that the CEMA Zn – I batteries constructed based on the oxidation effects of [OTf]\(^{-}\) on iodide species represent a promising strategy for advancing long-cycling and low-cost aqueous Zn – I batteries.

**Declarations**

**Competing interests:**

The authors declare that there is no competing interest.

**References**


**Figures**
Figure 1

Schematic illustration of CEMA Zn−I batteries and characterizations of oxidation effects of [OTf]− on iodide species. (a) Schematic configuration of the CEMA Zn−I batteries. (b) Oxidation effects of [OTf]− on I− species. (c) Theoretical calculation of MESP for Zn[OTf]2. (d) UV-vis spectra of [EMIm][OTf]/Zn[OTf]2, NaI/Zn[OTf]2, I2, Zn[I3]2, [EMIm]I, and NaI aqueous solutions. (e) FTIR spectra of Zn[OTf]2, Zn[OTf]2/[EMIm]I, and Zn[I3]2 aqueous solutions.
Figure 2

Characterizations of the iodine sediment particles formed by the oxidation effect of [OTf]⁻. (a) SEM, (b) TEM, and (c) HRTEM images of iodine sediment particles. (d) XRD spectra of iodine sediment particles and commercial iodine powders.
Figure 3

**Characterizations of surface passivated Zn foil treated by [OTf]⁻.** (a) XRD spectra of surface passivated Zn foil, Zn[OTf]₂, and pristine Zn foil. (b, c) Deconvoluted XPS spectra at (b) F 1s and (c) S 2p regions of surface passivated Zn foil, Zn[OTf]₂, and pristine Zn foil. (d) Optical and (e, f) SEM images of surface passivated Zn foil. (g) EDX elemental mappings corresponding to the region in (f).
Figure 4

Electrochemical performance of the CEMA Zn–I batteries. (a) CV curves, (b) rate-performance, and (c) voltage profiles of the 3-1/1 CEMA Zn–I batteries. (d, e) Long-term cycling tests of the (d) 1-1/1, 2-1/1, and (e) 10-1/1 CEMA Zn–I batteries at (d) 0.5 and (e) 5.0 mA cm$^{-2}$, respectively.
**Figure 5**

**Electrochemical performance of pouch-type CEMA Zn–I batteries.** (a) Photographs of the as-fabricated pouch-type CEMA Zn–I batteries powering a LED lamp. (b) Cycling tests, (c) representative voltage profiles, and (d) EIS curve of the pouch-type CEMA Zn–I batteries.

**Supplementary Files**

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