Separator Effect on Zinc Electrodeposition Behavior and Its Implication for Zinc Battery Lifetime

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ABSTRACT: Uncontrolled zinc electrodeposition is an obstacle to long-cycling zinc batteries. Much has been researched on regulating zinc electrodeposition, but rarely are the studies performed in the presence of a separator, as in practical cells. Here, we show that the microstructure of separators determines the electrodeposition behavior of zinc. Porous separators direct zinc to deposit into their pores and leave “dead zinc” upon stripping. In contrast, a nonporous separator prevents zinc penetration. Such a difference between the two types of separators is distinguished only if caution is taken to preserve the attachment of the separator to the zinc-deposited substrate during the entire electrodeposition–morphological observation process. Failure to adopt such a practice could lead to misinformed conclusions. Our work reveals the mere use of porous separators as a universal yet overlooked challenge for metal anode-based rechargeable batteries. Countermeasures to prevent direct exposure of the metal growth front to a porous structure are suggested.

KEYWORDS: aqueous battery, zinc battery, porous separator, nonporous separator, zinc deposition, zinc stripping

Lithium-ion batteries have dominated power sources for portable devices and electric vehicles; however, its applications in large-scale storage are under debate mainly due to safety and cost concerns. To this end, researchers have explored alternative energy storage systems that use Earth abundant elements and may offer better safety features. Aqueous zinc batteries (AZBs) featuring water-based electrolytes and the high-capacity zinc anode (820 mAh g\(^{-1}\)) are competitive for large-scale storage owing to their intrinsic safety and perceived low cost. The rechargeability of AZBs is limited by zinc anode issues such as uncontrolled deposition morphologies, which have long plagued alkaline zinc–air and zinc–nickel batteries and remain problematic for recent near-neutral zinc batteries. Zinc is known to electrodeposit into mossy, flakelike, boulderlike, and dendritic structures which could pierce through separators and short-circuit cells. Therefore, various strategies such as substrate design, zinc surface modification, and electrolyte optimization have been developed to regulate zinc deposition morphologies and extend the cycle life for AZBs.

Studies for evaluating the effectiveness of dendrite mitigation strategies fall into two main categories: those in the absence of a separator and those in the presence of separators. Studies performed in the absence of a separator mimic electrowinning studies where zinc is plated without physical interruption. Cross-sectional observation of plated zinc morphologies in this configuration is the standard practice to probe the effect of varying plating conditions. The more relevant configuration for batteries, however, involves a porous separator placed immediately on the zinc-plating substrate. Observation of plated zinc in the latter studies typically includes plating zinc in the presence of the separator, peeling off the separator, washing, and (for cross-sectional observations) cutting the substrate and then observing the deposits. The additional peeling step could, as shown later, damage the plated zinc and lead to inaccurate observation, but the impact of the peeling has received limited attention. The effect of a separator on zinc plating is therefore not conclusively understood.

Recent studies to scrutinize the effect of porous separators on metal electrodeposition painted a complicated picture. Lithium was found to deposit beneath porous separators only when the pore size is smaller than the nucleate size of lithium (e.g., from 0.5 \( \mu \)m to more than 10 \( \mu \)m\(^{-1}\)). Otherwise, lithium deposits fill into separator pores and...
penetrate the separator as the plating proceeds. If the current density goes beyond the diffusion limit of Li+ in the electrolyte, lithium forms dendrites and penetrates separators regardless of the pore size of the separators. A few similar studies have been dedicated to zinc electrodeposition. An in situ visualization study by Yu fit et al. revealed that zinc deposits within the pores of a porous polypropylene separator and reaches the other side of the 100-μm-thick separator within 160 s under intentionally high local current densities. Such a rapid penetration was ascribed to the altered potential distribution and mass transport limit inside the separator pores. Phase-field simulation by Viswanathan et al. predicted the effect of zinc dendrite suppression on the porosity of porous separators. However, this simulation did not consider the potential redistribution and mass transport limit, leading to the formation of dendrites. It remains unclear how zinc electrodeposition responds to the presence of a separator under practical cell operation conditions.

In this work, we studied zinc plating/stripping in the presence of a series of porous and nonporous separators. Extra attention was paid to preserving the zinc-plated electrode and the separator as a whole throughout cell disassembly and characterization processes. An Ar-ion broad beam polisher was used to expose sample cross sections without introducing artifacts and distortions. We found that commercial separators made of polypropylene and glass fiber regulate zinc into directional growth along their porous structures. This pore-filling behavior is only observable when the separator is preserved on the zinc-deposited substrate. No trace of such filling could be observed on the substrate if the separator is removed from the substrate after deposition. A nonporous separator made of cross-linked poly(dimethylsiloxane-ethylene glycol polymeric) (PDMS-PEO), in contrast, confines zinc deposition beneath the separator. The impact of the two distinct deposition modes on electrode efficiency and cycle life were studied, and strategies to overcome direct exposure of the zinc growth front to a porous structure were proposed.

Three separators are used in this study. Glass fiber separator is chosen as the most widely used in AZBs studies. Polypropylene separator (Celgard 3501) is chosen to represent polyolefin-based separators which are widely used in lithium-ion batteries. We also chose a PDMS-PEO membrane to represent nonporous separators. The synthesis and characterizations of PDMS-PEO can be found in the Supporting Information (Figures S1–S4). SEM images of the surface (Figure 1a) and cross-section (Figure 1b,c) of a PDMS-PEO separator show no visible pores even under high magnification. The vertical scratches in Figure 1c were generated during the argon-ion beam milling process. The glass fiber separator is composed of cross-stacking fibers, forming a highly porous structure with a large pore size of several microns (Figure 1d–f). The polypropylene separator has small pores (64 nm on average) vertically connected toward the surface (Figure 1g–i). The contact angle measurements (Figure S5) reveal glass fiber separator has the best wettability toward electrolyte with a smaller contact angle (33°) than PDMS-PEO (72°) and polypropylene separator (78°). Such differences in microstructure and wettability of different separators affect electrolyte uptake, resulting in different ionic conductivities of 1 M Zn(OTf)2 aqueous electrolyte in the three separators. The results are shown in Figure 1j, and measurement details can be found in Table S1. Owing to its high porosity and good wettability, the glass fiber separator shows a very high electrolyte uptake of ~670%, resulting in its conductivity approaching that of bulk electrolyte. The polypropylene separator has about a sixth (~120%) of the electrolyte uptake as that of the glass fiber separator, and the electrolyte conductivity is lowered by a factor of 6. The PDMS-PEO separator shows a similar electrolyte uptake (~117%) as that of the polypropylene separator but a higher ionic conductivity, probably due to the PEO chain motion which facilitates ion transport.

To explore zinc electrodeposition behavior in the presence of separators, asymmetric cells with a configuration of zinc/separatormetallic were assembled in coin cells and tested with 1 M Zn(OTf)2 aqueous electrolyte. Zinc was deposited onto the stainless steel foil under a moderate current density of 0.5 mA cm−2. This current density is set to be smaller than the estimated limiting current density in different separator systems (Table S2) to avoid any electrolyte diffusion limit. A practically relevant areal capacity of 5 mAh cm−2 was set for all morphological studies unless noted otherwise. All cells were disassembled right after the electrochemical experiment to avoid possible morphological changes of zinc upon soaking in the electrolyte. After removing the zinc foil carefully, the separator—stainless steel stack was preserved as a whole piece and polished with an Ar-ion beam polisher to
expose the cross-section. For polypropylene and PDMS-PEO separators, a cryo polishing mode was used where the sample stage was cooled with liquid nitrogen to avoid heat damage of the polymers.

When PDMS-PEO was used as the separator, the voltage profile of the asymmetric cell shows a minor dip at the beginning of deposition due to metal nucleation (Figure S6a). A flat plateau was then observed, indicating the whole deposition process is within the Zn\(^{2+}\) diffusion limit of the electrolyte.\(^{30}\) The cross-sectional SEM image in Figure S6b shows that a uniform layer formed beneath the separator. The energy-dispersive X-ray spectroscopy (EDS) results in Figure 2a confirm the top layer as the O-containing PDMS-PEO and the bottom layer is zinc. The absence of O and F in the zinc layer indicates no appreciable amount of ZnO formation within the deposit, further supported by X-ray diffraction (XRD) (Figure S7). A closer look at the deposit (Figure S6c) reveals that zinc metal grains are closely packed in forming a dense layer that intimately attaches to the PDMS-PEO separator. Therefore, the PDMS-PEO separator enables a uniform zinc deposition underneath the separator layer, as illustrated in Figure 2b.

Figure 2. EDS mapping of the cross-section SEM images of separator–stainless steel stacks after zinc plating. Backscattered electrons SEM image, elemental mapping, and schematic representations of sample cross sections with (a,b) PDMS-PEO, (c,d) glass fiber, (e,f) polypropylene separator, and (g,h) without separators.

Figure 3. Cross-sectional characterizations of separator–stainless steel stacks after zinc plating/stripping at a current density of 0.5 mA cm\(^{-2}\). Backscattered electrons SEM image, elemental mapping, and schematic representations of sample cross sections with (a,b) PDMS-PEO, (c,d) glass fiber, and (e,f) polypropylene separator.
Zinc deposition with porous separators forms distinctively different structures. When a glass fiber separator was used, the voltage profile shows a decreasing overpotential (Figure S6d). Cross-sectional observation reveals that the bottom part of the fiber network is partially filled with relatively dense solids (Figure S6e,f), which turns out to be zinc as revealed by EDS (Figure 2c). Both O and Si, which signify the presence of glass fiber, intersperse the zinc deposit. This pore-filling behavior is illustrated in Figure 2d. Figure 2e shows the scenario when the polypropylene separator is used. The cell shorted at \( \sim 2.6 \text{ mAh cm}^{-2} \) during the deposition (Figure S6g). Cross-sectional SEM images (Figure S6h,i) reveal that the vertical channels of the polypropylene separator, especially those close to the substrate were solidly filled, forming fine fiberlike structures. EDS mapping (Figure 2e) confirms the fine fibers are zinc that grows along the vertical channels (Figure 2f). The signals of ZnO observed in EDS (Figure 2e) and XRD measurement (Figure S7) result from oxidation of nanosized zinc deposits in electrolyte due to their large surface area. Such phenomena were not observed in the case of PDMS-PEO and glass fiber separator as the deposits are micron-sized.

The zinc deposition behavior indirectly impacts its stripping behavior. Electrochemical stripping of deposited zinc was performed for all of the three zinc/separator/stainless steel asymmetric cells following electrodeposition, and the fully “recharged” cells were again subjected to morphological observation. The compact zinc layer formed in the cell with the PDMS-PEO separator was completely stripped away, leaving the PDMS-PEO separator, indicated by O element mapping, intimately attached to the substrate (Figure 3a,b). Only a thin layer containing Zn and O was left between the substrate and the separator, which is attributed to corrosion products (e.g., ZnO) responsible for the nonunity Coulombic efficiency (CE) of 92% (Figure S8a). The zinc/glass fiber/stainless steel cell shows blocks of zinc trapped inside the glass fiber network, indicated by Si and Zn in Figure 3c, after stripping and understandably a reduced CE of 80% (Figure S8b). The zinc/polypropylene/stainless steel cell also shows the trapping of zinc inside the separator as indicated by O and Zn mapping, this time as fine fibers (Figure 3e and Figure S9), and an even lower CE of 59% (Figure S8c). The incomplete stripping of the pore-filling zinc within the glass fiber and polypropylene separators can be attributed to the tortuous and porous nature of the deposits. Upon stripping, the thinning of the deposits with higher aspect ratio leads to partial detachment of the deposit from the substrate, as illustrated in Figure 3d,f. The detachment is more severe for the cell with the polypropylene separator due to the finer zinc deposits. The trapped “dead zinc” leads to loss of active material and may promote further zinc penetration through the separator in the next cycle.

The preceding observations are all made under an unoptimized electrolyte—current—substrate combination where, in the absence of a separator, zinc plates into “dendrites” (Figure 2g,h). A natural question would be does the deposit-into-separator mode still apply if the combination of conditions is optimized? We have therefore increased the plating current density for the zinc/glass fiber/stainless steel cell by 100 times to 50 mA cm\(^{-2}\) (Figure S10a); recent studies found that both high current densities\(^{25}\) and large current pulses\(^{30}\) favor dense and uniform zinc deposition. A glass fiber separator was chosen because the system showed the highest limiting current density (Table S2), allowing the high-current zinc deposition process to remain within the diffusion limit of the electrolyte. Much more uniform and denser zinc deposits were obtained (Figure 4a) compared with those formed at a low current density (Figure 2c). Still, the deposits overwhelmingly filled into the separator pores (Figure 4b). Stripping of this dense zinc again resulted in trapped zinc (Figure 4c−f) and a CE of 79% (Figure S10b), which was not an improvement over the low-current cell. This control experiment indicates that even under otherwise optimized electrodeposition conditions, a porous separator will cause zinc to plate into undesirable morphologies.

Zinc electrodeposition and its morphological observation can now be summarized as follows. In a separator-free scenario (Figure 5a), zinc electrodeposits in two modes, one under unoptimized conditions where directional and pointed zinc structures (“dendrites”) form (Figure 5b), the other under optimized conditions (e.g., high current) where uniform plating occurs (Figure 5c). Most previous reports assumed both electrodeposition modes to stay true when a separator is placed on the substrate (Figure 5d,e,g), and any short-circuiting under unoptimized conditions were conveniently attributed to dendrites piercing through the separator (Figure 5e)\(^{7,14,15}\). These assumptions were seemingly supported by morphological observations which were performed with the separators peeled off (Figure 5f,h). However, our study finds that porous separators alter zinc deposition behavior and direct zinc to fill into their pores and form deposits with high aspect ratios regardless of whether the deposition conditions are optimized (Figure S1j,l). Such deposition behavior could have been overlooked in previous studies because any zinc filled into separator pores was removed when the separators were peeled off. We ran a control cell with a polypropylene separator following the same electrochemical experiment procedure but peeled off the separator after cell disassembly (Figure 5k,m). The separator is tainted by some dark matter (Figure S11a), which is the filled zinc deposits observed in Figure 2e. Figure
In summary, we have demonstrated the separator effect on the electrodeposition of zinc in liquid electrolytes. We have first established a characterization protocol that emphasizes the preservation of the separator–substrate stack, a practice often overlooked but crucial to revealing the separator effect. We then studied zinc electrodeposition in the presence of porous and nonporous separators under practically relevant test conditions. Porous separators made of glass fiber and polypropylene prompted deposited zinc to fill into the separator pores during plating, risking short-circuiting, and left behind “dead zinc” upon stripping. In contrast, a nonporous PDMS-PEO separator confined zinc deposition beneath the separator and avoided the formation of dead zinc. These results emphasize that, in addition to manipulating the intrinsic zinc deposition morphology (e.g., via liquid electrolyte optimization, substrate design, etc.), the microstructure of the separator is an indispensable factor to consider in developing efficient zinc batteries. We may need to revisit strategies deemed effective in combatting zinc dendrite once this separator effect is identified. While this study focuses on zinc, the separator effect on metal electrodeposition behavior appears universal and could be applicable to other metal battery systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.1c03792.

Synthesis and characterization of PDMS-PEO separator; XRD and additional SEM images of the samples; and voltage profiles of asymmetric cells (PDF)

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S11b shows the morphology of the deposited zinc remaining on the substrate. The platelike morphology, albeit somewhat depressed, resembles that of freely deposited zinc shown in Figure 2g. Therefore, a proper evaluation of the separator effect on zinc electrodeposition behavior would require observation with the separator–substrate stack preserved. Lastly, zinc deposits under the separator into a dense and uniform morphology with a PDMS-PEO separator, even under unoptimized conditions (Figure S5n,o).

Given the universality of the separator effect regardless of the electrodeposition conditions, any strategy to address zinc electrode cyclability must also address the separator effect. In retrospect, many reported methods to combat “zinc dendrites” did, albeit unintentionally, also combat the separator effect. For example, 3D hosts confine zinc deposition within the hosts, thus negating any impact of separator structure.7 Zinc surface coatings or artificial interfaces function similarly to nonporous separators as in forcing zinc to deposit underneath.19,22,23,26,47,48 Gel polymer electrolytes such as those based on gelatin,27,28 poly(vinyl alcohol),19,50 and polyacrylonitrile19,51 are sometimes referred to as separators anyways, and the polymer structures in these electrolytes could resemble that of PDMS-PEO, depending on composition. Water-in-salt electrolytes might address the separator e

Figure 5. Schematic representations of zinc electrodeposition behaviors. (a–c) Zinc plating process in the absence of a separator. (d–h) When a porous separator is present, the presumed zinc deposition behaviors. (i–m) Pore-filling zinc deposition behavior under practical conditions, which is only observable when the separator–zinc-deposited substrate stack is preserved (j, l), not after the separator removal (k, m). (n, o) Zinc deposition beneath a nonporous separator. Dashed circles in parts f, h, k, and m mark the observation area.
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REFERENCES


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