

Supplementary Information to

Novel Insights into Aqueous Zn-MnO₂ Batteries: A Simple and Robust Approach to Refute Zn²⁺ Intercalation Mechanism

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SI1 Characterizations:

SI1.1 Electrochemical characterization:

Electrochemical impedance spectroscopy (EIS) tests were conducted using an Autolab Potentiostat/Galvanostat. It was performed to assess the conductivity of the entire battery system and AEM membrane, with a signal amplitude of 10 mV in a frequency range of 1 MHz to 1 Hz. The galvanostatic cycling tests of Zn-Zn symmetric cells and Zn-MnO₂ full cells were executed on a Neware battery tester at room temperature. All galvanostatic cycling was performed in a voltage range of 0.9–1.9 V (vs Zn/Zn²⁺) except section 2.5 where the voltage range was 1–2.15 V. The charging protocol was constant current at the areal current of 0.7 mA/cm² until the areal capacity of 0.7mAh/cm². The discharge protocol was constant current with the same areal current.

SI1.2 Morphological and structural characterization:

The morphology of the electrodes during various states of charge and discharge of the battery was analyzed using FE-SEM (S-4160, Hitachi-Japan). An elemental mapping line profile analysis for the cross-section of the cathode was conducted using the same device equipped with an EDX module.

Additionally, high-resolution XRD analysis was conducted using a Rigaku Ultima IV (Japan) multipurpose X-ray diffractometer to examine the structural characteristics of the electrodes.

The composition of the electrolytes was determined through Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, SPECTRO ARCOS SPECTRO Analytical Instruments GmbH-Germany).

SI2: Two Supplementary Tests for Assessing the Performance of the Ionsep:

To fully ensure the proper functionality of the Ionsep, in addition to the symmetric cell test discussed in the main paper, two additional tests were designed and conducted:

First System: In this initial system, which served as our primary test, an Ionsep membrane was placed in the center of the setup. On one side of the system, a 1 M Zn(Ac)₂ salt was added to an aqueous electrolyte, while on the other side, a 1 M MnSO₄ salt was poured. The system

remained in this state for two weeks. Following this, ICP tests were conducted on both sides' electrolytes (after dilution of samples), yielding the following reported ion concentration ratios in the respective electrolytes:

Table S1 ICP test system (without current)

| Electrolytes | Zn (ppm) | Mn (ppm) |
|--------------|----------|----------|
| 1 | 102 | <1 |
| 2 | <1 | 88 |

results for the first externally applied

As inferred by the ICP results, after a duration of two weeks, approximately one percent (or even less) of the cations have appeared on the opposite sides. Some portion of this quantity may be attributed to measurement accuracy, impurities, and other factors. Nevertheless, with the suspicion that the existence of an external field and the stimulation of ions could potentially result in the passage of cations through the membrane, another experiment was devised and executed.

Second System: In this experiment, we delved into investigating the impact of introducing an external electric field and establishing intra-membrane electric current flow. Following the guidelines outlined in Section SI2, utilizing the membrane, we enclosed a complete battery with a segregated electrolyte system. On the anode side of the battery, a 0.5 M ZnSO₄ electrolyte was introduced, while on the cathode side, a 0.5 M MnSO₄ electrolyte was incorporated.

After preparing the system, it was subjected to 30 charge and discharge cycles. The cycling was performed according to the protocol mentioned in section SI2. Following the completion of the charge and discharge cycles (one sample after charge and the other after discharge), the catholyte was tested using ICP to determine the concentrations of Zn²⁺ and Mn²⁺. The results are shown in the table below:

Table S2 test results for the second system (with externally applied current)

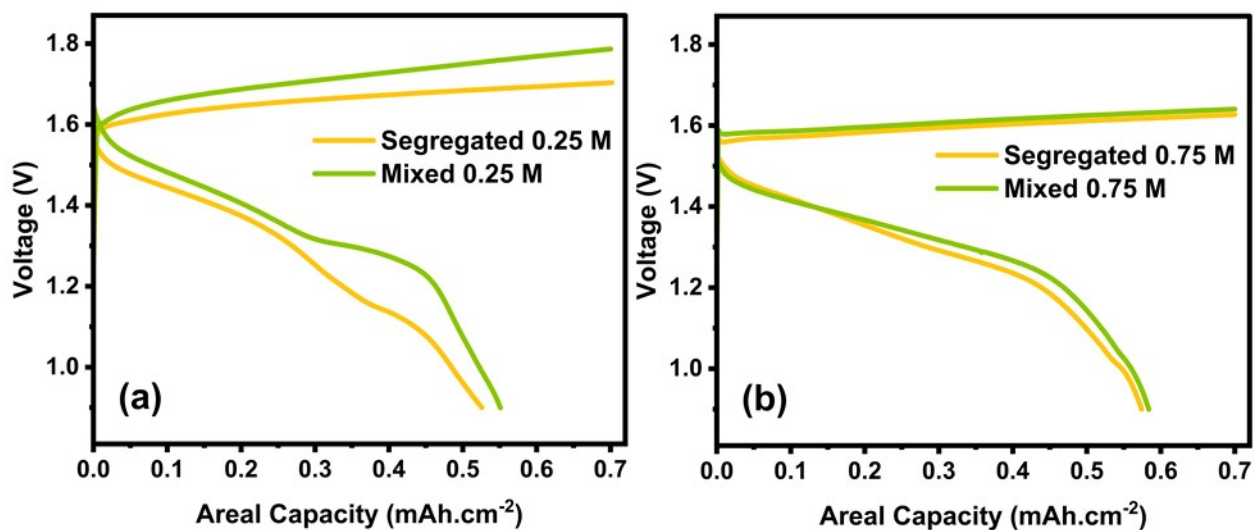
| State \ Elements | Zn (ppm) | Mn (ppm) |
|------------------|----------|----------|
| After Dchg | <1 | 91 |
| After Chg | <1 | 76 |

These results indicate a negligible passage (~1%) of Zn^{2+} and Mn^{2+} through the Ionsep confirming the effectiveness of the membrane in preventing the penetration of cations even under conditions of applied electric field and current. Furthermore, the reduction in the Mn element content at the end of the charging cycle is indicative of the oxidation of Mn^{2+} on the cathode.

SI3: The Impact of Segregating the Anolyte and Catholyte within 0.25 M and 0.75 M Acetate-based Electrolytes

Upon observing a minor variation in the initial discharge cycle between the mixed and segregated systems in the 0.5 M acetate electrolyte, we decided to duplicate this trial using lower and higher salt concentrations. Considering the favorable impact of 0.5 M acetate ions in contrast to 0.5 M sulfate ions on the alignment of the two graphs, we hypothesized that, elevating the salt concentrations would reduce these minor distinctions even more, rendering them less discernible. The outcomes are illustrated in **Fig S1**:

Fig S1. 1st Cycle GCD test results of mixed and segregated a) 0.25 M b) 0.75 M acetate-based electrolyte



In high concentrations of acetate salts, the difference between the graphs in segregated and mixed systems approaches zero. Upon closer examination of the data, it becomes evident that the columbic efficiency of the initial cycle experiences a slight increase with rising acetate ion concentration. Moreover, at a concentration of 0.25 M, the columbic efficiency of the mixed system surpasses that of the segregated system, likely attributed to the higher acetate concentration in the mixed system. This variance in columbic efficiency between mixed and segregated systems diminishes as salt concentration escalates from 0.25 M to 0.75 M, eventually converging towards zero.

Another noteworthy point in this regard pertains to the difference in the discharge curves of cycles 2 and 3 between the segregated and mixed systems in the 0.5 M acetate-based electrolyte, as shown in Fig. 9 of the main manuscript.

The reason for this difference might lie in the variance in acetate ion concentration between the two systems. As mentioned in the 'The Impact of Segregating the Anolyte and the Catholyte in Acetate-based Electrolytes' section of the manuscript, the acetate ion concentration in the segregated system is half of that in the mixed system. Furthermore, as demonstrated above, by increasing the concentration of acetate salts to 0.75 M, these differences between the segregated and mixed states diminish. In general, acetate ions facilitate the alignment of the graphs for the segregated and mixed states. The difference observed in Fig. 9 appears to be related to the activation process of the electrodes. As referenced in the main manuscript (Refs. 82, 83, 90, and 91), acetate ions exhibit strong and effective interactions with MnO₂ molecules. Therefore, increasing the acetate concentration can enhance the electrode-electrolyte interaction relative to lower acetate concentrations, resulting in faster electrode activation at higher acetate concentrations. Consequently, the second and third cycles in the mixed system which has higher acetate concentration approach a steady state more quickly and show fewer differences between them.