Best Practices for Zinc Metal Batteries

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Rechargeable aqueous zinc metal batteries represent a promising solution to the storage of renewable energy on the gigawatt scale. For a standardized set of protocols for their electrochemical performance measurements, we highlight the current common issues and recommend practices for future studies.

For low levelized energy costs (LECs) and sustainability, rechargeable batteries must embrace abundant materials, long cycle life, and ideally high energy density. Of growing interest is the aqueous zinc metal battery (ZMB), in which the zinc metal anode (ZMA) gets a layer added, i.e., plating, during charging and then has that layer taken away, i.e., stripping, when the battery discharges.[1,2,3] ZMBs can be competitive only if a long cycle life is secured, which in turn depends on the reversibility of the electrodes. This Comment pertains to the protocols for the evaluation of ZMBs, aiming to complement the good experimental practices that have been discussed previously in the literature.[4,5]

Fig. 1 Schematic summarizing a comprehensive approach to evaluate ZMBs, focusing on reversibility and stability as key factors.

Zinc Metal Anode

On the anode side, deposition of Zn with an irregular morphology can result in battery shorting and failure. Even when non-uniform deposits known as Zn dendrites are absent, soft short-circuit (SS) can lead to the illusion of "super-stability" in symmetric zinc cell testing, as recently highlighted by Zhi *et al.*[6] An SS features co-existing direct electron transfer and interfacial reaction while a hard short is overwhelmingly about electron transfer. The charge transfer resistance (R_{CT}) and activation energy (E_a) can be indicators of SS.[6]

A significant challenge of ZMBs is the hydrogen evolution reaction (HER) between Zn metal and the aqueous electrolytes. This reaction leads to the corrosion of pristine Zn metal, a phenomenon that persists during the battery's charge, discharge, and periods of rest. HER shortens both the cycle life and calendar life of ZMBs. The community evaluates ZMA's reversibility by measuring the plating/stripping Coulombic efficiency (CE) in galvanostatic cycling. It is worth noting that a high current density can "mask" the negative impacts of HER.[7] Therefore, a low current density, *e.g.*, 0.2 or 0.5 mA cm-2 is recommended. Conversely, high current densities are necessary to examine morphological stability because Zn dendrites tend to form under such conditions. However, here, a large areal capacity is needed to reveal the impact of the potential formation of dendrites.

It matters how the CE is measured. A conventional practice involves stripping all Zn metal plated onto the current collector to calculate the CE for each cycle. However, the CE of such tests can be a function of cycle number. Therefore, we recommend the reservoir CE test, pioneered by Aurbach and coworkers.[8] In a reservoir test, a specific amount of Zn is pre-plated onto the current collector as the "reservoir", from which a portion (10 to 50%) is stripped and plated repeatedly for 10 to 100 cycles. Subsequently, the remaining Zn capacity is determined by stripping to a higher upper cutoff potential, *e.g.*, 0.5 V. Alternatively, a thin zinc foil can serve as the reservoir. In addition, a full cell's cycle life can disclose the CE of the ZMA if the cathode's capacity remains stable and the initial N/P (anode/cathode capacity) ratio exceeds one. Noticeable fading of the measured cathode capacity occurs only when the effective N/P ratio falls below one.[9] In such a full cell, the cathode areal capacity needs to surpass 2 mAh cm-2, as highlighted recently on the importance of a practically relevant cathode active mass.[10]

Assessing the extent of HER can reveal the ZMA's reversibility, which can be conducted via *ex situ* gas chromatography (GC) or online electrochemical mass spectroscopy (OEMS).[11] The morphological changes of the cycled ZMA indicate its reversibility, particularly when evaluating a high utilization degree of ZMA with a large areal capacity. This can be investigated by *in situ* optical microscopy[7] and cryo-EM.

Additionally, forming a solid-electrolyte interphase (SEI) holds the promise to passivate the ZMA from HER. To this end, electrochemical quartz crystal microbalance (EQCM) can offer real-time insights into SEI formation and side reactions. However, conducting EQCM measurements in concentrated electrolytes presents challenges.

Cathode Materials

Interests in cathode materials for ZMBs predated the studies on the anode and electrolytes.[1] It was expected that Zn^{2+} ions would serve exclusively as the charge carrier within the host structures, while now it is recognized that many early studies inadvertently involved protons as co-carriers or even the primary carriers. The hosting of protons dominates the electrodes' behaviors at high rates and lower potentials.[12] It is advisable to evaluate the presence of Zn^{2+} intercalation and the Zn^{2+}/H^+ ratio using established characterization techniques. Proton co-intercalation is problematic for long-term cycling because it generates OH^- via water dissociation, which results in deposition of layered zinc double hydroxides on the cathode (and anode) surfaces.[13] Monitoring the pH value near the electrode becomes important to understand the mechanisms that govern the operation of these electrodes.[14]

The capacity fading of the cathode - in particular, metal oxides such as MnO_2 and V_2O_5 - is often due to the dissolution of active mass in mildly acidic electrolytes, which is a function of time. It is common that a high current rate such as 1 A g-1 is employed for cycling, which equates to a 5 C rate if the electrode's nominal capacity is 200 mAh g-1. While such high-rate cycling can demonstrate the extent of reversibility for ion storage within a short time frame, it does not probe the degradation of the cathode due to dissolution. Therefore, it is recommended that low current rates are employed (0.2 – 2C) and the days of cycling are marked, which better reflects the cycle life. Low rates also reveal issues with proton co-intercalation, which might be overshadowed at high current rates.[15]

When cycling MnO_2 as the ZMB cathode, it is a common practice to introduce Mn^{2+} into the electrolytes. However, the presence of Mn^{2+} may complicate the capacity sources of the electrode as Mn^{2+} can be oxidized and deposited as additional MnO_2 during battery charge. In addition, as most studies used flooded cells, Mn^{2+} from the electrolyte becomes an unlimited source of active mass. Therefore, when Mn^{2+} is added to the electrolyte, lean electrolytes that solvate a limited amount of Mn^{2+} ions can be helpful. Furthermore, the electrodeposition of MnO_2 releases protons to the electrolyte, where there may exist a correlation between the pH value near the electrode and the capacity.

It has been debated what ions serve as the *de facto* charge carriers for the operation of polymorphs of MnO_2 as the cathode, which may be Zn^{2+}, Mn^{2+}, and protons. It is critical to identify the charge carriers at different state of charge. For such studies, EQCM can provide critical information, in concert with physical characterization techniques (XRD, NMR, etc), to probe the nature of the intercalated cation.[16]

A critical consideration in cathode research lies in the choice of electrolytes. Unlike the research on ZMA that aims to establish the correlation between the electrolyte properties and the CE of ZMA, cathode research has often relied on common electrolytes such as $ZnSO_4$. It is recommended that the cathode studies use reported electrolytes that have demonstrated high CE values of the ZMA for anode-cathode compatibility.

Finally, the discovery of new cathode materials is imperative to enable high areal capacities that approach or exceed 4 mAh cm-2, ideally without proton co-intercalation.[17] Such high capacities mean that thick electrodes are needed, creating many other challenges. These include sluggish mass transport especially if Zn^{2+} (de)intercalation dominates, high voltage polarization, contact loss with current collectors, and crack formation during cycling. We recommend that the community focus on providing new cathodes capable of practical areal capacity that can be fully charged quickly. These may well involve organic materials. Engineering efforts should be directed to fabricate cathode materials as thick and dense films, where dry processing of free-standing electrodes may hold significant relevance.

Full Cells

ZMB full cells represent an engineering challenge. In particular, if the cathode active mass dissolves or becomes stripped into the electrolyte at a certain state of charge, testing cells may need to use a lean electrolyte because the cell performance can be a function of the electrolyte volume, which is well known in Li-S battery research. However, a challenge that the aqueous battery community faces is the lack of commercial thin separators to enable “lean electrolyte” conditions. In addition, the properties of a separator can profoundly affect the performance of electrodes and full cells. It is recommended that the community identifies a standard separator and adopts a standard volume of the electrolyte - while putting priority on the development of improved separator materials.

Finally, we note a new avenue of research in rechargeable aqueous zinc metal batteries that departs from Zn-ion intercalation chemistry at the cathode and instead exploits electrodeposition and stripping as the charge storage mechanism for metal oxide cathodes.[18] While these offer many exciting new opportunities and challenges, many of the considerations mentioned can apply to these systems.

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Competing interests

The authors declare no competing interests.