Supplementary Information for

Dual Characteristics of Mn^{2+} Dissolution from Manganese Oxide Cathode Materials in Aqueous Zinc Batteries: Trade-offs between Active Material Loss and Double Capacity Contribution

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Table of Content

1. Measurements of Mn concentrations in electrolytes

As discussed in the main text, the quantitative analysis of reaction contributions in MnO_2 cathode materials first calls for the accurate measurement of Mn concentrations in electrolytes at different states. They can be obtained by in-situ UV-vis or ex-situ ICP-OES analysis, as detailed below.

1.1 In situ UV-vis measurements

UV-vis spectroscopy provides precise measurements of solution concentrations according to the Beer-Lambert law. The concentrations of Mn^{2+} can be measured directly by itself or with the help of chromogenic reagents (such as anthocyanidin). The calibration curve and its linear range are firstly determined. For in situ cell assembly, the MnO_2 cathode and Zn anode are placed on either side of the testing cell filled with the electrolyte, and the transmission light travels through the middle part for the continuously record of absorbance during charge-discharge.

1.2 Ex situ ICP-OES measurements

For ex situ analysis, the Mn concentrations in electrolytes at different states are measured from different cells. Therefore, close MnO_2 loadings on the cathodes should be maintained for the testing cells. Meanwhile, three or more pieces of separators are used. Galvanostatic charge-discharge would be carried out in two-electrode coin or Swagelok® cells and stopped at the destinated charge/discharge states for cell disassembly. The separators facing either the cathode or the anode would be sticked by active materials, so the center one(s) with only soaked cycled electrolyte are taken to immerse in deionized water and diluted to the measurable range of inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis. Since it is difficult to accurately measure the initial volume of the electrolyte on the separators, the Zn concentration is used as an internal reference to normalize the Mn concentrations. Specifically, the measured Mn/Zn ratio in each sample and the known Zn concentration in electrolytes are used to calculate the Mn concentrations.

It is noted that the Zn concentrations in electrolytes change at different states in Zn-MnO_2 cells, since the cathode is not a pure Zn^{2+} de/intercalation process. Nevertheless, this fluctuation can be only a minority of the overall Zn content in the original electrolyte by setting desired boundaries. For instance, the cells would contain 1 mg loading of MnO_2 on the cathode and 150 μL of 3 M $ZnSO_4$ electrolyte. Assuming full MnO_2/Mn^{2+} and Zn/Zn^{2+} reactions at the cathode and anode, respectively, the mole of both dissolved Mn and Zn are 1 mg ÷ 86.94 mAh g^{-1} (molecular weight of MnO_2) = 0.0115 mmol. The electrolyte contains a total of 150 μL × 3 M = 0.45 mmol of Zn. Therefore, the maximum Zn concentration change in the electrolyte is 0.0115/0.45 = 2.6%, which introduces a low deviation in the calculation of Mn concentration.

2. Calculation equations for the reaction contributions in MnO_2 cathode materials

With the obtained Mn concentrations at different states, the reaction contributions in the MnO_2 cathode materials can be calculated according to the equations listed in Table S1 as explained below.

Table S1 Calculations of each part contribution in the cathode in aqueous Zn-MnO_2 batteries.

Cathode metrics	Equations
m_2: mass of part 2 (g)	$m_2 = (conc_{dis.} - conc_{ch.}) \times V_{electrolyte} \times M_{MnO_2}$ (1)
m_3: mass of part 3 (g)	$m_3 = conc_{ch.} \times V_{electrolyte} \times M_{MnO_2}$ (2)
C_2: capacity delivered from part 2 (mAh)	$C_2 = m_2 \times (616\ mAh\ g^{-1})$ (3)
C_1: capacity delivered from part 1 (mAh)	$C_1 = C_{total} - C_2$ (4)
m_1: mass of part 1 (g)	$m_1 = \frac{C_1}{308\ mAh\ g^{-1}}$ (5)
m_4: mass of part 4 (g)	$m_4 = m_{total} - (m_1 + m_2 + m_3)$ (6)

Firstly, part 2 corresponds to the MnO_2/Mn^{2+} two-electron dissolution/deposition reaction, and its mass (m_2) is directly determined by the Mn concentration change between the charged and discharged state according to equation (1). Part 3 corresponds to the irreversible Mn^{2+} dissolution, and its mass (m_3) is obtained from the Mn concentration at the charged state according to equation (2). Here, $conc_{dis.}$ and $conc_{ch.}$ represent the Mn concentrations in electrolytes at the discharged and charged states, respectively; $V_{electrolyte}$ corresponds to the volume of electrolyte; M_{MnO_2} is the relative molecular mass of MnO_2 (86.94 g mol^{-1}).

Subsequently, since the theoretical capacity of the two-electron transfer reaction is 616 mAh g^{-1}, the capacity delivered from part 2 (C_2) is obtained from its mass according to the equation (3). The other reaction path to contribute capacity is from the one-electron reaction. Therefore, the capacity of part 1 (C_1) is obtained after subtracting the capacity of part 2 from total capacity (C_{total}), and mass of part 1 (m_1) is further calculated according to its theoretical capacity of 308 mAh g^{-1}, as shown in the equation (4) and (5). After subtracting the above mass of part 1-3 from the overall cathode material (m_{total}), the rest mass corresponds to part 4 (m_4) which is dead MnO_2, and it is calculated by the equation (6).

The above quantitative analysis is also summarized in Figure S1.

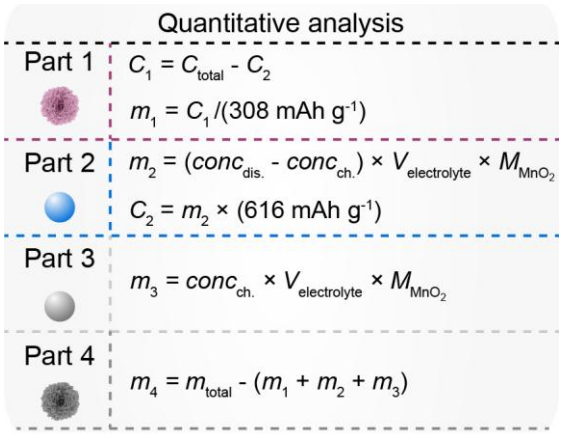

Figure S1. The quantitative analysis of each part in the cathode in aqueous Zn-MnO_2 batteries.