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## Reversible Cl/Cl<sup>-</sup> redox in a spinel Mn<sub>3</sub>O<sub>4</sub> electrode†

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A unique prospect of using halides as charge carriers is the possibility of the halides undergoing anodic redox behaviors when serving as charge carriers for the charge-neutrality compensation of electrodes. However, the anodic conversion of halides to neutral halogen species has often been irreversible at room temperature due to the emergence of diatomic halogen gaseous products. Here, we report that chloride ions can be reversibly converted to near-neutral atomic chlorine species in the Mn<sub>3</sub>O<sub>4</sub> electrode at room temperature in a highly concentrated chloride-based aqueous electrolyte. Notably, the Zn<sup>2+</sup> cations inserted in the first discharge and trapped in the Mn<sub>3</sub>O<sub>4</sub> structure create an environment to stabilize the converted chlorine atoms within the structure. Characterization results suggest that the Cl/Cl<sup>-</sup> redox is responsible for the observed large capacity, as the oxidation state of Mn barely changes upon charging. Computation results corroborate that the converted chlorine species exist as polychloride monoanions, e.g., [Cl<sub>3</sub>]<sup>-</sup> and [Cl<sub>5</sub>]<sup>-</sup>, inside the Zn<sup>2+</sup>-trapped Mn<sub>3</sub>O<sub>4</sub>, and the presence of polychloride species is confirmed experimentally. Our results point to the halogen plating inside electrode lattices as a new charge-storage mechanism.

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## Introduction

As the world continues to shift away from fossil fuels toward renewable energy sources, there is an ever-growing demand for energy-storage solutions that are safe, low-cost, and use abundant and environmentally benign material resources.<sup>1–3</sup> Unfortunately, the current Li-ion batteries are lacking in each of these considerations.<sup>4,5</sup> Thus, immense efforts have been devoted to other more sustainable battery systems, e.g., Na-ion,<sup>6,7</sup> K-ion,<sup>8,9</sup> and Zn-ion batteries.<sup>10–12</sup> Beyond these systems that operate *via* the reversible (de)insertion of cation charge carriers in electrode hosts, more recently, systems that use anions as the ion charge carriers have begun to attract significant interest.<sup>13,14</sup> These so-called anion-shuttle batteries, including dual-ion batteries<sup>15</sup>

and anion rocking-chair batteries,<sup>16,17</sup> are attractive due to their potentially high energy densities and low costs, as well as resource availability.

A unique feature of using anionic charge carriers is the possibility of the anions undergoing anodic reactions to form neutral species, which can be deemed as plating of non-metals. Redox of Cl<sup>-</sup>, for example, has been studied and utilized in batteries since the 19th century.<sup>18</sup> However, the Cl<sub>2</sub>/Cl<sup>-</sup> redox process generally suffers from poor reversibility due to loss of gaseous Cl<sub>2</sub>.<sup>19–25</sup> Recently, Dai *et al.* demonstrated Cl<sub>2</sub>||alkali metal batteries that operate *via* the reversible Cl<sub>2</sub>/Cl<sup>-</sup> redox at carbon-based electrodes.<sup>26,27</sup> The effective trapping of Cl<sub>2</sub> as the charge product at the electrode hosts was deemed essential in affording the reversibility of these systems. Wang *et al.* showed high reversibility of the Cl<sub>2</sub>/Cl<sup>-</sup> redox couple in an aqueous NaCl electrolyte by storing the as-produced Cl<sub>2</sub> in nonaqueous, water-immiscible phases such as CCl<sub>4</sub>.<sup>28</sup> Other approaches for overcoming the loss of gaseous Cl<sub>2</sub> include the formation of interhalogen species with higher boiling points, e.g., BrCl and ICl, or operating the electrode below the boiling point of Cl<sub>2</sub> liquid.<sup>29–33</sup>

Another approach for avoiding the escape of gaseous Cl<sub>2</sub>, which has yet to be explored, would be to “plate” neutral Cl atoms inside a host material. Such a mechanism would require a host material to effectively anchor the plated Cl atoms, where the strong binding between the inserted Cl and the host inhibits the formation of the Cl–Cl diatomic bond. Our group recently

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reported on the reversible anodic charge-storage behaviors of a spinel  $\text{Mn}_3\text{O}_4$  electrode after trapping  $\text{Zn}^{2+}$  cations in the first discharge in a concentrated  $\text{ZnCl}_2$ -based electrolyte.<sup>34</sup> After  $\text{Zn}^{2+}$  is trapped, the as-formed  $\text{Zn}_{0.25}\text{Mn}_3\text{O}_4$  electrode exhibited a specific charge capacity of over  $200 \text{ mA h g}^{-1}$  with an average operating potential above  $1.6 \text{ V vs. Zn}^{2+}/\text{Zn}$ . Herein, we report that the large capacity observed in the charging process is not due to the oxidation of Mn-ions of  $\text{Mn}_3\text{O}_4$ , where the oxidation state of Mn remains nearly unchanged during cycling, but from a conversion from chloride to partially charged polychloride species stored in the distorted lattice of the  $\text{Mn}_3\text{O}_4$  cathode.

## Results and discussion

### Electrochemical performance of the $\text{Mn}_3\text{O}_4$ electrode

The electrochemical performance of the  $\text{Mn}_3\text{O}_4$  (space group,  $I4_1/amd$ , PDF # 24-0734, Fig. S1†)<sup>34,35</sup> electrode was first evaluated using a concentrated aqueous water-in-salt electrolyte (WiSE) of  $20 \text{ M ZnCl}_2 + 5 \text{ M NH}_4\text{Cl}$ . As reported before, when cycled in a two-electrode cell with Zn metal as the counter and reference electrode, the  $\text{Mn}_3\text{O}_4$  electrode demonstrates a relatively small first discharge capacity of  $128 \text{ mA h g}^{-1}$  at a potential of  $\sim 0.6 \text{ V}$  (vs.  $\text{Zn}^{2+}/\text{Zn}$  and hereafter) and a current rate of  $50 \text{ mA g}^{-1}$  (Fig. 1a).<sup>34</sup> The subsequent charging process results in a substantially larger capacity of  $218 \text{ mA h g}^{-1}$  at an average potential of  $1.66 \text{ V}$  (the potential at half the capacity). This exceedingly large hysteresis in the first cycle suggests that the initial insertion of  $\text{Zn}^{2+}$  cations is largely irreversible and that the oxidative insertion of anions was deemed responsible for most of the charging capacity. The large potential hysteresis disappears after the first cycle, and the second discharge delivers a capacity of  $226 \text{ mA h g}^{-1}$  at a slightly smaller potential

than the charging process, thereby indicating the excellent reversibility of the anion-hosting reaction. A self-discharge test was performed after the first cycle to assess the stability and reversibility of the charged electrode. After idling the charged electrode for 12 hours, the electrode delivered a Coulombic efficiency of 94.3%, suggesting the good stability and reversibility of the charge products in the electrode (Fig. S2†). Note that the first charge capacity with  $\text{Zn}^{2+}$  trapped is much larger than the case when we charged the  $\text{Mn}_3\text{O}_4$  cathode directly with a capacity of  $84 \text{ mA h g}^{-1}$  (Fig. 1b and S3†). To further evaluate the effect of the initial  $\text{Zn}^{2+}$ -trapping process, we cycled the  $\text{Mn}_3\text{O}_4$  electrode against an activated carbon counter electrode with another high-concentration chloride-based aqueous electrolyte of  $15 \text{ M}$  tetraethylammonium chloride (TEACl) (Fig. S4†). The initial discharge capacity was only  $\sim 13 \text{ mA h g}^{-1}$ , indicating that the bulky tetraethylammonium cation was not inserted into  $\text{Mn}_3\text{O}_4$  to any meaningful extent. The subsequent charge capacity was  $\sim 64 \text{ mA h g}^{-1}$ , which is closer to when we charged the pristine  $\text{Mn}_3\text{O}_4$  electrode first in the  $20 \text{ M ZnCl}_2 + 5 \text{ M NH}_4\text{Cl}$  WiSE. This significant capacity difference suggests that the initial trapping of  $\text{Zn}^{2+}$  cations transforms the  $\text{Mn}_3\text{O}_4$  structure in such a way that it facilitates the anodic process of anion storage. The question is: Can the trapped  $\text{Zn}^{2+}$  ions promote the storage of other anions?

We also investigated the redox behaviors of the  $\text{Mn}_3\text{O}_4$  electrode in common aqueous Zn-ion electrolytes of  $2 \text{ M ZnSO}_4$  and  $2 \text{ M Zn}(\text{ClO}_4)_2$ . In both electrolytes, the  $\text{Mn}_3\text{O}_4$  electrode also exhibits a low-potential plateau around  $0.4 \text{ V}$  in the first discharge. However, the  $\text{Mn}_3\text{O}_4$  electrode showed two apparent charge plateaus in these electrolytes, with the first plateau at potentials well below  $1.66 \text{ V}$ , the potential in the chloride-based WiSE (Fig. 1c and d). This two-plateau behavior is commonly observed for manganese oxide cathodes in mildly acidic aqueous electrolytes and is often attributed to  $\text{H}^+$  and  $\text{Zn}^{2+}$  coinsertion<sup>36,37</sup> or a combination of  $\text{Zn}^{2+}$  (de)insertion and  $\text{MnO}_x/\text{Mn}^{2+}$  dissolution/deposition reactions.<sup>38</sup> The distinctly different redox behaviors of the  $\text{Mn}_3\text{O}_4$  electrode in the chloride-based electrolyte and the non-chloride electrolytes are also displayed in the cyclic voltammetry (CV) curves, where  $\text{Mn}_3\text{O}_4$  exhibits two distinct pairs of redox peaks in the  $2 \text{ M ZnSO}_4$  in contrast to one pair in the chloride WiSE (Fig. S5†). We conducted inductively coupled plasma optical emission spectroscopy (ICP-OES) after the second discharge, where the dissolved concentration of Mn in the  $\text{ZnSO}_4$  electrolyte corresponds to 3.6 times the observed discharge capacity. However, in the  $\text{ZnCl}_2$  WiSE electrolyte, the dissolution of Mn could only account for 4.3% of the observed discharge capacity. The results suggest that the operation of  $\text{Mn}_3\text{O}_4$  in dilute electrolytes such as  $2 \text{ M ZnSO}_4$  occurs by the dissolution of Mn-ions and deposition of manganese oxides, where the Zn-trapping and the associated promoted anion storage are irrelevant.

### Characterization of the operation of the $\text{Mn}_3\text{O}_4$ electrode in the $\text{ZnCl}_2$ -based WiSE electrode

*Ex situ* X-ray diffraction (XRD) results indicate significant amorphization of the  $\text{Mn}_3\text{O}_4$  structure after the initial  $\text{Zn}^{2+}$

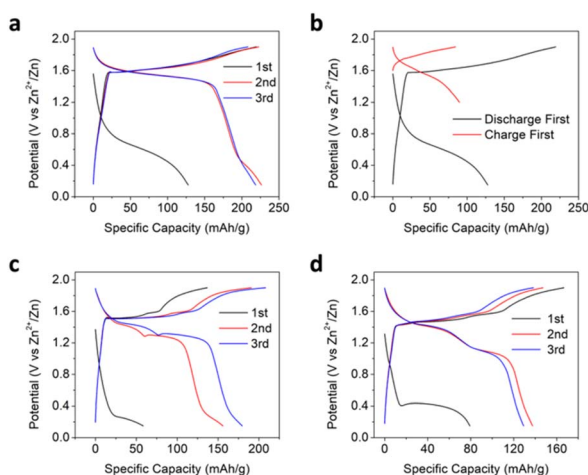


Fig. 1 (a) Galvanostatic charge–discharge (GCD) potential profiles of the  $\text{Mn}_3\text{O}_4$  electrode in the  $20 \text{ M ZnCl}_2 + 5 \text{ M NH}_4\text{Cl}$  WiSE. (b) Comparison of the first cycle GCD profiles of the  $\text{Mn}_3\text{O}_4$  electrode in the WiSE when it is discharged first to a lower cutoff potential of  $0.2 \text{ V}$  and when it is charged first with the lower cutoff potential raised to  $1.2 \text{ V}$  to eliminate  $\text{Zn}^{2+}$  insertion. GCD profiles of the  $\text{Mn}_3\text{O}_4$  electrode in common aqueous Zn-ion electrolytes of (c),  $2 \text{ M ZnSO}_4$  and (d),  $2 \text{ M Zn}(\text{ClO}_4)_2$ .



insertion (Fig. S6†). This loss in the long-range order could explain how the relatively large  $\text{Cl}^-/\text{Cl}$  anions/atoms are able to be lodged within the compact structure after the following charge. The energy dispersive X-ray spectroscopy (EDS) elemental mapping associated with TEM confirms the  $\text{Zn}^{2+}$  insertion inside the structure of  $\text{Mn}_3\text{O}_4$  after the initial discharge (Fig. 2a). Interestingly, the Zn content appears to be particularly enriched towards the surface of the  $\text{Mn}_3\text{O}_4$  particles. Indeed, the high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images indicate that the surface of the  $\text{Mn}_3\text{O}_4$  particle is furnished with  $\text{Zn}^{2+}$  cations rather than  $\text{O}^{2-}$  anions after discharging (Fig. 2b). Elemental mapping obtained after the subsequent charging process shows a uniform increase in Cl content, thereby indicating the insertion of  $\text{Cl}^-/\text{Cl}$  anions/atoms (Fig. 2c). Of note, the Zn content is significantly more concentrated at the  $\text{Mn}_3\text{O}_4$  surface after the charging process, as shown by the EDS mapping and the associated line scanning profile, which indicates that the inserted  $\text{Zn}^{2+}$  cations become trapped towards the surface of the particle (Fig. 2c and S7†) and the trapped  $\text{Zn}^{2+}$  cations are not static during cycling.

To reveal the charge storage mechanism of the  $\text{Mn}_3\text{O}_4$  electrode in the chloride-based WiSE, we examined the Mn oxidation state at different state of charge (SoC) using *ex situ* synchrotron-based X-ray absorption spectroscopy (XAS).<sup>39–41</sup> The Mn K-edge X-ray absorption near-edge structure (XANES) studies showed slight changes in the edge positions from the pristine, to the discharged, and charged samples (Fig. 3a and S8†). From fully discharged to fully charged in the first cycle, the valence state of Mn was calculated to increase by +0.09 (from  $\text{Mn}^{2.83+}$  to  $\text{Mn}^{2.92+}$ ). In theory, such an oxidation state change would result in a small specific capacity of only  $31.6 \text{ mA h g}^{-1}$ . However, we obtained a much larger specific capacity of  $218 \text{ mA h g}^{-1}$  for the first charge of the  $\text{Mn}_3\text{O}_4$  electrode (Fig. 1a). These very subtle changes in the oxidation state of Mn were corroborated by X-ray photoelectron spectroscopy (XPS), where the calculated oxidation states of Mn in the spectra of the pristine and charged electrodes were +2.63 and +2.75, respectively (Fig. 3b). Moreover, there were no obvious differences in the soft XAS (sXAS) spectra of Mn between the pristine, discharged, and charged samples (Fig. 3c), further indicating the

lack of significant Mn redox involved in the charge storage mechanism of the  $\text{Mn}_3\text{O}_4$  electrode in the chloride WiSE. This absence of the Mn redox in the (dis)charge processes of the  $\text{Mn}_3\text{O}_4$  electrode supports the possibility of  $\text{Cl}/\text{Cl}^-$  redox as being the major contributor to the observed capacity because only  $\text{Cl}^-$  and water can be oxidized in the charging process other than Mn, where  $\text{Cl}^-$  should be oxidized before water due to its lower redox potential at such a high concentration.

### Effect of $\text{Zn}^{2+}$ -trapping on $\text{Cl}/\text{Cl}^-$ plating/stripping and the generation of polychloride anions

To gain a theoretical understanding of how the initial  $\text{Zn}^{2+}$ -trapping process facilitates the subsequent  $\text{Cl}^-/\text{Cl}$  hosting and redox reaction, we conducted density functional theory (DFT) calculations to investigate the behavior of Cl insertion in  $\text{Mn}_3\text{O}_4$  before and after Zn trapping. Fig. 4a and b exhibit the configurations with Zn inserted into the octahedral (Oh) site (denoted as ZnOh) and the tetrahedral (Td) site (denoted as ZnTd) of  $\text{Mn}_3\text{O}_4$ , respectively. We found that the Td site is slightly more energetically favorable by 0.12 eV than the Oh site for Zn. During geometry optimization, the Mn atoms adjacent to Zn spontaneously move from the Td sites to Oh sites, leading to the formation of a layer of Td-site vacancies, resulting in a characteristic of spinel-to-layered structure transformation. This structural transformation results in a deformation of the crystal structure, accompanied by a volume expansion of approximately 4%. The calculated insertion energy of Zn into  $\text{Mn}_3\text{O}_4$  is  $-1.0 \text{ eV}$  (Table S1†), suggesting the stability of the structure after the initial Zn-trapping process.

Subsequently, we studied the behavior of Cl insertion in  $\text{Mn}_3\text{O}_4$  following the initial Zn-trapping process. Interestingly, upon comparing the energetics of various potential Cl intercalation sites, the computation results suggest the formation of polychloride monoanions within the structures. Specifically, within the ZnOh model, the inserted Cl atoms form trichloride  $[\text{Cl}_3]^-$  anions, while within the ZnTd model, they formed T-shaped pentachloride  $[\text{Cl}_5]^-$  anions (Fig. 4d, e, and S9†).<sup>42–47</sup> This unique finding sheds light on a new mechanism of Cl storage. The presence of these polychloride species helps explain the stability of “plated” chlorine species within the

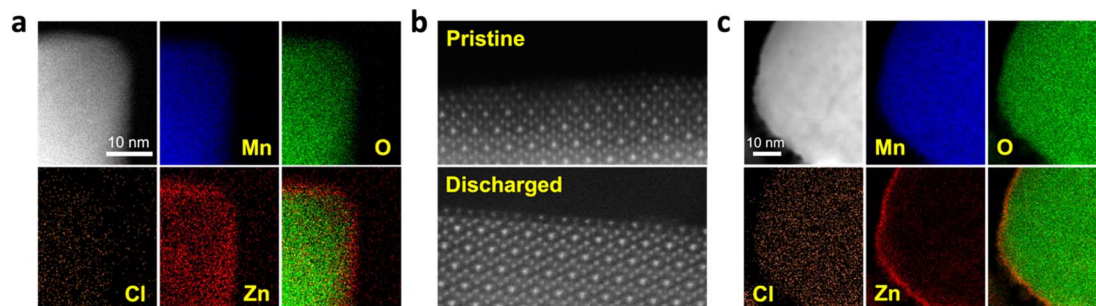


Fig. 2 (a) An HAADF-STEM image of the  $\text{Mn}_3\text{O}_4$  electrode and associated EDS elemental mappings of the Mn, O, Cl, and Zn contents after the first discharge. (b) HAADF-STEM images of the near-surface region of the  $\text{Mn}_3\text{O}_4$  before and after the first discharge, where the surface of the  $\text{Mn}_3\text{O}_4$  is furnished with Zn-ions after the first discharge. (c) HAADF-STEM image of the  $\text{Mn}_3\text{O}_4$  electrode and associated elemental mappings of the Mn, O, Cl, and Zn contents after the first charge.





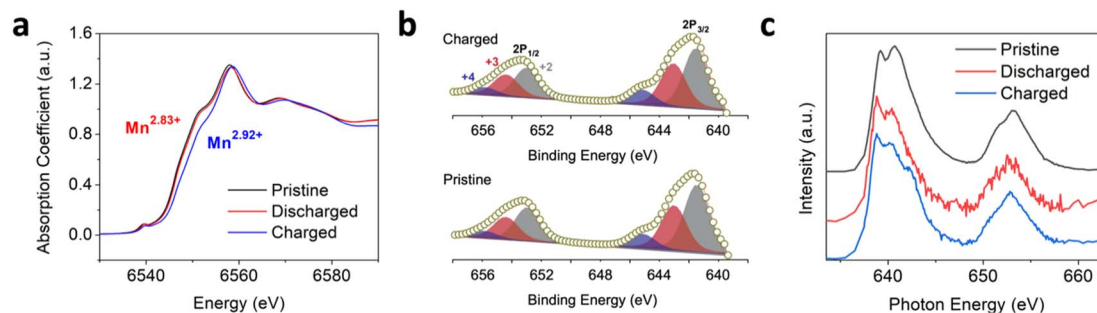


Fig. 3 (a) Normalized XANES of the Mn K-edge spectra of the pristine  $\text{Mn}_3\text{O}_4$  electrode and the  $\text{Mn}_3\text{O}_4$  electrode after the initial discharge and charge. The calculated oxidation state changes from +2.83 to +2.92 from the fully discharged to the fully charged state of the  $\text{Mn}_3\text{O}_4$  electrode in the first cycle. (b) XPS spectra of the charged (upper) and pristine (lower)  $\text{Mn}_3\text{O}_4$  electrode with Mn  $2p_{3/2}$  and Mn  $2p_{1/2}$  profiles. (c) Mn L-edge sXAS spectra of the pristine, discharged, and charged  $\text{Mn}_3\text{O}_4$  electrodes.

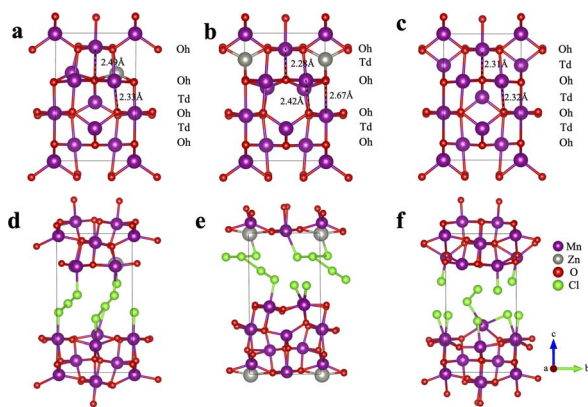


Fig. 4 (a) The optimized structure of Zn trapped in the octahedral site in  $\text{Mn}_3\text{O}_4$  (denoted as ZnOh). (b) The optimized structure of Zn trapped in the tetrahedral site in  $\text{Mn}_3\text{O}_4$  (denoted as ZnTd). (c) The structure of pristine  $\text{Mn}_3\text{O}_4$ . (d–f) Optimized structures upon Cl insertion into ZnOh, ZnTd, and pristine  $\text{Mn}_3\text{O}_4$ , respectively. The stoichiometry is  $\text{Zn}_{0.25}\text{Mn}_3\text{O}_4\text{Cl}_{1.75}$  for the Zn-trapped models and  $\text{Mn}_3\text{O}_4\text{Cl}_{1.75}$  for the pristine  $\text{Mn}_3\text{O}_4$  model.

crystal structure at room temperature. Notably, the oxidation of chloride into polychlorides has been demonstrated to be thermodynamically favorable in highly concentrated acidic chloride.<sup>47</sup> In our work, the WiSE electrolyte used is both highly acidic and features a high chloride concentration, making the oxidation of chloride into polychloride anions feasible. In contrast, for the pristine  $\text{Mn}_3\text{O}_4$  structure without Zn-trapping, only a small amount of dichlorides ( $\text{Cl}_2$ ) was formed after the insertion of Cl atoms (Fig. S9c†). This finding provides an explanation for the considerably lower capacity observed in the pristine  $\text{Mn}_3\text{O}_4$  electrode (Fig. 1b) in comparison to the Zn-trapped electrode. Furthermore, all three crystal structures experience significant volume expansion exceeding 40% upon Cl insertion. This substantial volume expansion may contribute to the observed amorphization suggested by the *ex situ* XRD patterns after cycling the electrode (Fig. S6†).

In order to assess the impact of the initial Zn-trapping on the Cl insertion process, we calculated the Cl insertion energy. Remarkably, the Cl insertion energies for the Zn-trapped

models were found to be much lower compared to the pristine  $\text{Mn}_3\text{O}_4$  model (1.9, 2.0, and 4.0 eV for the ZnOh, ZnTd, and  $\text{Mn}_3\text{O}_4$  models, respectively). This observation indicates that the initial Zn-trapping process plays a crucial role in facilitating the oxidation of  $\text{Cl}^-$  ions and the formation/insertion of polychloride ions, thus resulting in an enhancement in Cl storage capacity.

In addition, the hosting of these polychloride anions may explain the slight oxidation of Mn observed in the XAS and XPS spectra of the charged electrode. While the majority of the observed capacity can be attributed to the redox of the inserted  $\text{Cl}^-$  species, a slight oxidation of Mn occurs to accommodate the negatively charged polychloride monoanions (Fig. 3a–c). This observation of slight oxidation in Mn aligns with the findings from the Bader charge analysis,<sup>48</sup> where a slight increase in the Bader charge of Mn is observed after Cl insertion (Table S2†). Moreover, the COHP (crystal orbital Hamilton population) analysis<sup>49</sup> reveals the contribution of antibonding states near the Fermi level to the Mn–Cl bonds in the ZnOh and ZnTd models in contrast to the pristine  $\text{Mn}_3\text{O}_4$  model. This demonstrates that the chemical bonding between Mn and Cl is weaker in the Zn-trapped models, suggesting a facile extraction of  $\text{Cl}^-$  species after  $\text{Zn}^{2+}$ -trapping (Fig. S11†).

To confirm the formation and hosting of the polychloride monoanions predicted by the calculations, we conducted ultraviolet-visible (UV-vis) spectroscopy on the electrolyte after the charging process. Surprisingly, there was no noticeable difference between the spectra of the 20 M  $\text{ZnCl}_2$  + 5 M  $\text{NH}_4\text{Cl}$  WiSE before and after charging the  $\text{Mn}_3\text{O}_4$  electrode. This may be due to the strong binding between the polychloride monoanions and the host structure, considering the excellent self-discharge performance. Another explanation is that any diffused-out polychloride would have reacted with the Zn metal counter electrode before being detected by the UV-vis measurement of the electrolyte.<sup>50</sup> To address the issue, we conducted the UV-vis on another highly concentrated chloride-based aqueous electrolyte of 15 M TEACl before and after charging the  $\text{Mn}_3\text{O}_4$  electrode with an activated carbon free-standing film as the counter electrode (Fig. 5a). After charging, a broad peak appeared at  $\sim 270$  nm by the electrolyte, which is very likely indicative of the  $[\text{Cl}_3]^-$  anion.<sup>51,52</sup> To further



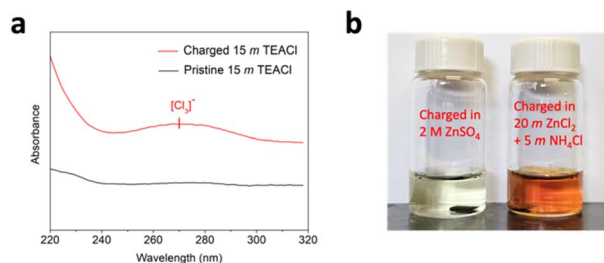


Fig. 5 (a) UV-vis spectra of the pristine 15 M TEACl electrolyte and the 15 M TEACl electrolyte after the  $\text{Mn}_3\text{O}_4$  electrode was charged in this electrolyte. (b) The 0.5 M KI solutions after immersing the  $\text{Zn}^{2+}$ -trapped  $\text{Mn}_3\text{O}_4$  electrode after charging in the 2 M  $\text{ZnSO}_4$  electrolyte (left) and after charging in the 20 M  $\text{ZnCl}_2$  + 5 M  $\text{NH}_4\text{Cl}$  WiSE (right).

confirm the existence of the polychloride monoanions formed with the  $\text{Mn}_3\text{O}_4$  structure after charging in the 20 M  $\text{ZnCl}_2$  + 5 M  $\text{NH}_4\text{Cl}$  WiSE, we immersed the fully charged  $\text{Mn}_3\text{O}_4$  electrode in an aqueous solution of 0.5 M KI. It was observed that the color of the KI solution quickly turned brownish, thereby indicating the presence of the polychloride monoanions as the charge products with the  $\text{Mn}_3\text{O}_4$  host (Fig. 5b). In stark contrast, when the  $\text{Mn}_3\text{O}_4$  electrode charged in the 2 M  $\text{ZnSO}_4$  electrolyte was immersed in the KI solution, the color of the solution did not change.

## Conclusions

In summary, we have demonstrated and characterized a new charge storage mechanism of reversible  $\text{Cl}/\text{Cl}^-$  “plating/stripping” at a spinel  $\text{Mn}_3\text{O}_4$  electrode in a high-concentration chloride-based aqueous electrolyte. The initial irreversible insertion of  $\text{Zn}^{2+}$  cations transforms the  $\text{Mn}_3\text{O}_4$  structure in such a way that it helps facilitate the subsequent reversible  $\text{Cl}/\text{Cl}^-$  redox reactions. The  $\text{Mn}_3\text{O}_4$  host acts as a “semi-catalyst” that allows the oxidation of  $\text{Cl}^-$  to  $\text{Cl}$  but not to  $\text{Cl}_2$  gas. Characterization by EDS, XAS, and XPS spectroscopies confirms that Mn redox is not responsible for most of the observed capacity. Instead, computation and experimental results suggest that the oxidized  $\text{Cl}^-$  anions preferentially form polychloride monoanions when hosted within the  $\text{Zn}^{2+}$ -trapped  $\text{Mn}_3\text{O}_4$ . Our results present a new strategy to use semi-catalysts as electrode materials that can effectively facilitate reversible  $\text{Cl}/\text{Cl}^-$  “plating/stripping” reactions at room temperature.

## Experimental

### Chemicals and materials

Nanoscale hausmannite  $\text{Mn}_3\text{O}_4$  powder was synthesized by a room-temperature precipitation method.<sup>34,35</sup> To begin, 1.126 g of  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (Alfa Aesar) was dissolved into 150 mL of deionized (DI) water. The aqueous  $\text{MnSO}_4$  solution was then titrated with 29%  $\text{NH}_4\text{OH}$  solution *via* dropwise additions under magnetic stirring until it reached a pH of 11. Once the solution was at pH 11, it was left to react under magnetic stirring for 1 h before being stored overnight at room temperature.

The brown precipitate was then washed with DI water and centrifuged until a pH of 7 was obtained. Lastly, the precipitate was dried at 80 °C overnight to obtain the final  $\text{Mn}_3\text{O}_4$  powder.

For the preparation of the 20 M  $\text{ZnCl}_2$  + 5 M  $\text{NH}_4\text{Cl}$  WiSE, anhydrous zinc chloride (metals basis, 99.95%) was purchased from Thermo Scientific. Ammonium chloride (ACS, 99.5%) and the water (HPLC grade) were purchased from Alfa Aesar.

### Electrochemical measurements

Electrochemical tests were done using Swagelok cells. The  $\text{Mn}_3\text{O}_4$  working electrodes were composed of 70 wt% active mass, 20 wt% KetjenBlack, and 10 wt% polyvinylidene fluoride binder coated on carbon fiber paper current collectors. The typical active mass loading was  $\sim 2 \text{ mg cm}^{-2}$ . The  $\text{Mn}_3\text{O}_4$  free-standing film electrodes used for obtaining the *ex situ* XRD patterns, self-discharge experiments, and the KI solution immersion tests were composed of 70 wt% active mass, 20 wt% KetjenBlack, and 10 wt% polytetrafluoroethylene (PTFE) binder. GCD measurements were obtained using a LANDT Battery Test System CT3002A, and CV tests were conducted with a VMP-3 multi-channel workstation.

### Materials characterization

XRD patterns were obtained using a Rigaku Ultima IV diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at a scan rate of  $1^\circ$  per minute. TEM data were recorded on an aberration-corrected (scanning) transmission electron microscope operated at 300 keV with a cold field-emission source (JEM-ARM300F Grand ARM). The energy dispersive X-ray spectroscopic (EDS) data were taken with dual 100 mm<sup>2</sup> silicon drift detectors (SDD). Hard XAS was performed at the Advanced Photon Source 10-BM in transmission mode. XAS data was processed using Athena for pre-edge background subtraction and normalization. The Mn oxidation state was determined with XANES edge position at a normalized absorbance of 0.5 and linearly interpolated with  $\text{Mn}_3\text{O}_4$  and  $\text{Mn}_2\text{O}_3$  standards as +2.67 (6544.8 eV) and +3 (6548.7 eV) oxidation states, respectively. sXAS at Mn L-edge was performed using total electron yield (TEY) mode at beamline 7.3.1 of Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory (LBNL).

For XPS, a Physical Electronics Quantera II Hybrid was used for the analysis. The system energy scale was calibrated to  $\text{Cu } 2p_{3/2}$  at 932.6 eV and  $\text{Au } 4f$  at 84.0 eV. The base pressure of the system was  $3 \times 10^{-7}$  Pa. The XPS experiments were measured on as-loaded samples at room temperature. XPS was performed using monochromatized  $\text{Al K}\alpha$  radiation ( $h\nu = 1486.6 \text{ eV}$ , at 50 watts and 100  $\mu\text{m}$  beam diameter). The electron analyzer pass energy was set to 69 eV, with an emission angle of  $45^\circ$ . The specimens were neutralized using a combination of an electron flood gun set to 0.6 eV at 20  $\mu\text{A}$  and an ion flood gun set to 0.1 kV. The XPS data were charge corrected to the C 1s aliphatic carbon binding energy at 284.8 eV. The XPS spectra were analyzed by fitting using CasaXPS software.

UV-vis spectroscopy analyses of the electrolytes were performed using a UV-vis-NIR spectrophotometer (PerkinElmer Lambda 750).



## Theoretical calculations

DFT calculations were performed *via* the Vienna *ab initio* simulation package (VASP).<sup>53</sup> The ion–electron interaction was depicted with the projector augmented wave (PAW) method. The electron exchange correlation was described by the Perdew, Burke, and Ernzerhof (PBE) functional with generalized gradient approximation (GGA).<sup>54</sup> The cutoff energy of the plane-wave basis set was set to 450 eV. The Brillouin zone was sampled by  $(3 \times 3 \times 2)$   $\Gamma$ -centered *k*-point mesh. The valence electrons of Mn, Zn, O, and Cl are  $3d^54s^2$ ,  $3d^{10}4s^2$ ,  $2s^2sp^4$ , and  $3s^23p^5$ , respectively. The convergence threshold for structural optimization and electronic energy was set to be 0.01 eV  $\text{\AA}^{-1}$  in force and  $1 \times 10^{-5}$  eV, respectively. The unit cell and atomic position were allowed to relax along with structure optimization. Spin polarization was considered in all computations. The DFT + U method was employed as the correction to simulate the strongly correlated materials, including transition metals.<sup>55</sup> The values of U and J for Mn were set to be 4.5 and 0.5 eV, respectively.<sup>56,57</sup>

In this work, the crystal structures were visualized using VESTA.<sup>58</sup> The atomic net charge was generated with code developed by Henkelman's group *via* the Bader charge analysis.<sup>48</sup> The crystal orbital Hamilton population (COHP) analysis was obtained using LOBSTER to analyze the chemical bond.<sup>49</sup>

The insertion energy of Zn ( $\Delta E_{Zi}$ ) and the insertion energy of Cl ( $\Delta E_{Ci}$ ) were calculated by the following equations:

$$\Delta E_{Zi} = E(\text{Bulk} + \text{Zn}) - E(\text{Bulk}) - E(\text{Zn}) \quad (1)$$

$$\Delta E_{Ci} = E(\text{Bulk} + n \times \text{Cl}) - E(\text{Bulk}) - n \times 0.5E(\text{Cl}_2) \quad (2)$$

where  $E(\text{Bulk} + \text{Zn})$  is the total energy of the  $\text{Mn}_3\text{O}_4$  unit cell with interstitial Zn atom and  $E(\text{Bulk})$  and  $E(\text{Bulk} + n \times \text{Cl})$  represent the total energy of a  $\text{Mn}_3\text{O}_4$  unit cell with or without interstitial Zn atom and that contain *n* interstitial Cl atoms, respectively.  $E(\text{Zn})$  and  $E(\text{H}_2)$  represent the energy of a Zn atom and one  $\text{H}_2$  molecule in a vacuum, respectively.

According to previous studies, the magnetic ordering of the  $\text{Mn}_3\text{O}_4$  unit cell was set to be  $(\uparrow\uparrow\downarrow\downarrow\uparrow\uparrow)$ .<sup>59</sup>

## Data availability

Additional characterization and computation results are provided in the ESI.†

## Author contributions

S. K. Sandstrom: investigation, formal analysis, visualization, data curation, writing – original draft. Q. Li: investigation, formal analysis, visualization, data curation. M. Lyons: investigation, formal analysis, data curation. C.-W. Chang: investigation, formal analysis, data curation. R. Zhang: investigation, formal analysis, data curation. Y. Sui: investigation, formal analysis, data curation. H. Jiang: investigation. M. Yu: investigation. D. Hoang: investigation. W. F. Stickle: investigation, formal analysis, data curation. H. L. Xin: funding acquisition, writing – review and editing, supervision. Z. Feng: funding acquisition, writing – review and editing, supervision. D. Jiang:

funding acquisition, writing – review and editing, supervision. X. Ji: conceptualization, funding acquisition, writing – review and editing, supervision.

## Conflicts of interest

There are no conflicts to declare.

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