Going beyond Intercalation Capacity of Aqueous Batteries by Exploiting Conversion Reactions of Mn and Zn electrodes for Energy-Dense Applications

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The recent trend in zinc (Zn) anode aqueous batteries has been to explore layered structures like manganese dioxides and vanadium oxides as Zn-ion intercalation hosts. These structures, although novel, face limitations like their layered counterparts in lithium (Li)-ion batteries, where the capacity is limited to the host’s intercalation capacity. In this paper, a new strategy is proposed in enabling new generation of energy dense aqueous-based batteries, where the conversion reactions of rock salt/spinel manganese oxides and carbon nanotube-nested nanosized Zn electrodes are exploited to extract significantly higher capacity compared to intercalation systems. Accessing the conversion reactions allows to achieve high capacities of 750 mAh g\(^{-1}\) (≈30 mAh cm\(^{-2}\)) from manganese oxide (MnO) and 810 mAh g\(^{-1}\) (≈30 mAh cm\(^{-2}\)) from nanoscale Zn anodes, respectively. The high areal capacities help to attain unprecedented energy densities of 210 Wh per kg-cell and 320 Wh per kg-total (398 Wh per kg-active) from aqueous MnO|CNT-Zn batteries, which allows an assessment of its viable use in a small-scale automobile.

1. Introduction

The current fossil-fuel-based global economy is seeing a societal push toward a greener source of power, where there is an urgent need to reverse the years of unregulated carbon emissions that have harmful effect on the environment and society.\(^{[1-4]}\) The two largest anthropogenic carbon emissions are from burning fossil fuels for electricity and transportation.\(^{[4]}\) The leading solutions to reduce these sources are by replacing traditional power plants with greener alternatives like solar, hydroelectric, and wind, and developing electric vehicles as a replacement for the internal combustion engines. Battery energy storage systems can make these solutions a reality by storing energy and delivering it upon demand. However, a number of criteria need to be satisfied like energy density, performance, safety, and cost.\(^{[5]}\) It is hard to find battery chemistries that can meet all criteria. The current battery storage landscape is dominated by lithium (Li)-ion chemistry, where the dominant mechanism is Li insertion into layered cathodes and anodes.\(^{[5]}\) Recently, there is a shift in strategy in the battery community, where conversion systems like lithium-sulfur and silicon anodes are being investigated and used for energy denser applications.\(^{[6-8]}\) However, lithium batteries face major drawbacks like high flammability, cost, and materials availability, which make it difficult to be used for a number of applications.\(^{[9]}\)

Aqueous-based batteries like multivalent zinc (Zn) ion batteries satisfy a number of the aforementioned criteria like low cost, high materials abundance, and low flammability, but their historic low energy density problems were plagued with high cost or lack of high capacity cathodes, and poor utilization of the Zn anodes.\(^{[10-15]}\) In recent years, Zn anode batteries have been reinvestigated from an intercalation standpoint.\(^{[16-21]}\) where researchers have tried layered or tunneled structures of manganese dioxide and vanadium oxide for intercalating Zn ions in acidic electrolyte achieving capacities of 285 and 300 mAh g\(^{-1}\) for the respective crystal structures.\(^{[22,23]}\) A number of papers have since investigated different polymorphs of manganese dioxide and stabilized vanadium oxide structures for Zn intercalation.\(^{[24]}\) These results have shown great promise of aqueous-based Zn anode structures. However, much like their Li-ion counterparts the capacity of the system has been limited to the host’s intercalation capacity of Zn ions. Also, the capacity utilization of Zn anodes in these systems has been low like in lithium batteries.

In this article, we propose a new strategy to achieve higher capacities of aqueous-based batteries by exploiting conversion reactions of rocksalt-structured manganese oxide (MnO) and Zn in alkaline electrolyte (Figure 1). Similar to Li conversion batteries, conversion reactions of MnO and Zn deliver very high capacities of ≈750 and 820 mAh g\(^{-1}\), respectively.
These high Coulombic capacities lead to high energy densities, which are comparable to Li-ion numbers. Conversion reactions have been tried in alkaline systems before; however, to lesser success. Parker et al. were able to discharge ≈728 mAh g⁻¹ in a single discharge with sponge Zn anodes for primary batteries; however, rechargeability was limited in this system, where the maximum rechargeable capacity obtained was ≈188 mAh g⁻¹.[25] The utilization of Zn anodes have been historically low because of dendrite formation, passivation, and shape change, which are primarily due to its dissolution–precipitation reactions in alkaline electrolyte that convert Zn to ZnO. This effect is exacerbated further when areal capacities have been higher than 1 mAh cm⁻².[26] Similarly, there have been very few conversion cathodes in alkaline Zn anode systems. Most commonly used cathodes have been proton insertion cathodes like nickel oxyhydroxide and nickel metal hydride.[27] MnO₂ has been known to show both, intercalation and conversion, reactions in alkaline electrolyte delivering 617 mAh g⁻¹.[28] However, conversion reactions are highly irreversible, so MnO₂ electrodes for over half a century had been limited to 10–20% of the intercalation capacity (308 mAh g⁻¹).[29] But recently, promising results were shown by Yadav et al., where the authors reported highly reversible conversion cathodes of layered MnO₂ electrodes.[29–33] Till now, to the author’s best knowledge, there have not been reports of highly reversible conversion cathodes and anodes in a battery at high specific and areal capacity because of the difficulty in controlling conversion reactions.

Herein, we report for the first time a new strategy in aqueous-based batteries, where we achieve 750 mAh g⁻¹ of MnO capacity and ≈810 mAh g⁻¹ of Zn capacity through conversion reactions aided by additives like bismuth oxide (Bi₂O₃) and copper (Cu) for the cathode and nanosized Zn powders (NanoZn) nested with carbon nanotubes (CNTs). The reversible capacity of these electrodes on continuous cycling is between 60% and 95% of their theoretical capacity depending on the percent loading of active material and the cycling rate of the cells. For the first time in literature, we show high areal capacities of ≈30 mAh cm⁻² for both cathode and anode, which is a breakthrough in the literature as areal capacities of ≈1–5 mAh cm⁻² are usually the norm. These high areal capacities show industrial applicability for these conversion electrodes. Ensuring that electrodes used in Zn-anode batteries have the capability to cycle at high areal capacities is very important as it is the only way that Zn-anode batteries can compete with Li-ion batteries. Li-ion batteries have a higher thermodynamic voltage advantage, which makes it possible to cycle electrodes at low areal capacities; however, for Zn-anode batteries to compete in terms of energy and cost, cathodes and anodes used in Zn-anode systems need to be cycled at much higher areal capacities. Through optical microscopy and UV-vis experiments, we show the dissolution–precipitation reaction of these conversion electrodes. Finally, we show full cell cycling of these electrodes together, and show a full battery connected in series as a demonstration in small-scale automobiles, which shows further promise of the use of this new battery for energy dense applications.
2. Results and Discussions

2.1. Enhancing Capacity Utilization of MnO Cathode and Characterization of its Conversion Reactions

MnO has a high theoretical capacity of ≈750 mAh g⁻¹. The closed rocksalt crystal structure of MnO blocks intercalation reactions during delivery of its capacity. To understand MnO's reactions, its cycling performance and corresponding reactions were first tested through cyclic voltammetry (CV) in a half-cell, where the counter electrode was nickel oxyhydroxide and the reference was Hg|HgO electrode. The CV of an electrode comprising of 50 wt% MnO and 50 wt% CNTs each is shown in Figure 2a at a scan rate of 0.1 mV s⁻¹. Two clear oxidation and reduction peaks were seen indicating that Mn²⁺ from MnO goes through two-stage process to oxidize to Mn⁴⁺ and reduce back to Mn²⁺. The peaks are very similar to a MnO₂ electrode going through its electroreduction and oxidation cycle.[29] However, the capacity obtained from an electrode containing MnO showed very poor capacity utilization as shown in Figure S1 in the Supporting Information. The maximum capacity it could deliver was 45 mAh g⁻¹, which is considerably lower than its theoretical. X-ray diffraction (XRD) of the cycled MnO electrode (Figure S2, Supporting Information) showed hausmannite (Mn₃O₄) and pyrochroite [Mn(OH)₂] as the dominant phases, which indicated that it is changing phases in alkaline electrolyte. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of a particle from the electrode (Figure S3a,b, Supporting Information) also confirmed the presence of Mn₃O₄, where the lattice was indexed to (004) and the particle showed an imperfect hexagonal-type shape. Electrochemical formation of inactive Mn₃O₄ is a known problem in MnO₂ electrodes, which also seemed to be the case in the MnO system.[32,34–36] The conversion reactions of MnO by itself would result in a capacity loss.

The formation of Mn₃O₄ partly showed that the electrode could be going through a dissolution–precipitation process. Bi₂O₃ and Cu were tried as additives to mitigate this problem as Bi₂O₃ is a known complexing agent for dissolved Mn ions and Cu can reduce the charge transfer resistance of the electrode.[29–36] These additives were added sequentially to understand the phase transformation of MnO. An electrode with 55 wt% MnO with Bi₂O₃ and CNTs was potentiodynamically cycled...
(CV) in the similar setup as aforementioned. The molar ratio of Bi$_2$O$_3$ to MnO was around 0.034 with the remaining being CNTs, which was 34 wt%. More details on electrode fabrication are in the Supporting Information. The CV curves in Figure 2a showed that addition of Bi$_2$O$_3$ increased the peak area of the oxidation and reduction reactions. This showed that addition of Bi$_2$O$_3$ had an effect on the dissolution–precipitation reactions as had been proven in literature. XRD of the electrode (Figure S2, Supporting Information) showed that Mn(OH)$_2$ was the dominant phase with the presence of some Mn$_3$O$_4$. This change in phases and crystal structure was significant as Bi$_2$O$_3$ deviated the pathway away from inactive Mn$_3$O$_4$. The TEM and HRTEM images in Figure S4a,b in the Supporting Information also showed the presence of the two phases on a particle captured in mid-transition state. Mapping results in Figure S4c in the Supporting Information showed the co-location of Bi with Mn and O, which probably indicated the presence of Bi within the crystal structure of Mn(OH)$_2$. The addition of Cu to the 55 wt% MnO electrode with Bi$_2$O$_3$ and CNTs showed dramatically better results as the peak area under the oxidation and reduction reactions considerably increased (Figure 2a). This suggested that charge transfer kinetics of MnO is very sluggish even with the presence of Bi$_2$O$_3$ and addition of Cu is necessary to improve it to extract more capacity out.

The problem of charge transfer resistance was further tested through galvanostatic or constant current cycling, where its effect would immediately be noticed. Also, galvanostatic experiments were done to gauge the cycling capability of the MnO electrodes in real world cycling conditions. The 55 wt% MnO with Bi$_2$O$_3$ electrode was cycled in a half-cell at C/4. The capacity retention of the electrode reached at maximum of 600 mAh g$^{-1}$ before plummeting to $\approx$100 mAh g$^{-1}$ as shown in Figure 2b. In terms of areal capacity this meant that the electrode reached a maximum of $\approx$25 and $\approx$5 mAh cm$^{-2}$ at the end of life. The Coulombic efficiency of these electrodes was $\approx$96%. The high areal capacity could be the cause of high charge transfer resistance in these electrodes as this meant more of the active material was present; however, these areal capacities are necessary for real world applicability. The effect of the high charge transfer resistance was clear on the cycling curves as shown in Figure 2c. The curves lost the flat plateau characteristics very early in cycle life. The addition of Cu to this electrode mix resulted in significant improvement in cycling characteristics. The capacity retention of the 55 wt% MnO with Bi$_2$O$_3$ and Cu improved significantly as shown in Figure 2d with a cycle life of 350, where the electrode delivered a maximum capacity of 750 mAh g$^{-1}$ before stabilizing near 600 mAh g$^{-1}$. The cycling curves for the 55 wt% MnO before and after the 200th cycle are shown in Figure S5 in the Supporting Information, where it can be seen that the curves are very stable and the capacity increase seen could be due to the efficient conversion reactions taking place over time. Also, it is important to note that the flat plateau curves are maintained very well even in later cycle life compared to the electrode with no Cu. The Coulombic efficiency of the cell was $\approx$99.5%. The effect of these additives was tested on an 80 wt% MnO electrode (Figure 2e) as well, which also showed significant improvement in capacity retention till 500 cycles. The areal capacity of 80 wt% MnO was lower compared to that of the 55 wt% MnO because the specific capacity of 80 wt% MnO was not able to reach high values because of increased resistivity resulting with increased wt% loadings in the electrode of the active material. It is the first time in literature that a combination of high cycle life, specificity, and areal capacity is reported for conversion MnO electrodes. The cycling curves of the 2 wt% MnO loadings in Figure 2f,g also showed greater stability and repeatability when Cu and Bi$_2$O$_3$ were both present. To ensure that the additives and CNTs were not contributing to the overall capacity of the electrode, they were also cycled individually between the same voltage limits against Hg/HgO reference, where it was noticed that these did not contribute to the overall capacity (Figure S6, Supporting Information). Potentiodynamic cycling of the additives is also shown in Figures S7 and S8 in the Supporting Information, where it can been seen that the additives are redox active and play a role in ensuring the high reversibility of MnO, which will be discussed later, but they do not contribute to the overall capacity of the electrode. Under constant current (galvanostatic) conditions, which are really indicative of battery cycling and capacity, these additives do not contribute as shown in Figure S6 in the Supporting Information.

Galvanostatic cycling showed that charge transfer resistance played a crucial role in stabilizing the cycling curves; however, to identify the point of formation of this resistance a galvanostatic intermittent titration (GITT)-type experiment was performed as shown in Figure 3a–h. The 55 wt% electrodes with Bi$_2$O$_3$, both with and without Cu, were cycled in a half-cell at C/20. In the 20 h charge and discharge, the curves were evenly split, where a constant current was applied for 10 min with 10 min of rest. This GITT experiment would show the onset of a charge transfer resistance via an ohmic drop during the successive current and rest steps. Impedance spectra were collected at each of these points to calculate the charge transfer resistance (Figure S9, Supporting Information). GITT experiments of the electrode with no Cu showed that exact point of charge transfer resistance increases ($R_{ct}$) as shown in Figure 3a–d. $R_{ct}$ dramatically increased in the first plateau as shown in Figure 3b,d, while the second plateau seemed to be relatively stable with not much of a difference in $R_{ct}$. This was indicative of a phase transformation, where the phase formed was highly resistive to electroreduction. The phase formed was most certainly Mn$_3$O$_4$ as was shown by the XRD of the 55 wt% MnO with Bi$_2$O$_3$ electrode that had undergone potentiodynamic cycling. Under constant current conditions, the rate of formation of Mn$_3$O$_4$ could be higher and thus, this could hinder the charge transfer kinetics of the MnO electrode. The stable $R_{ct}$ of the second discharge plateau was indicative of the stabilizing influence of Bi$_2$O$_3$. Bi$_2$O$_3$ is known to have a complexing effect on the dissolved Mn ions, but it could have a kinetic effect as well as it is known to reduce to Bi metal at the lower potentials versus Hg/HgO. The effect of the increased $R_{ct}$ was also seen on the charge step as shown in Figure 3a,c, where a build up of Mn$_3$O$_4$ resulted in eventual electrode failure.

For the MnO electrodes containing both Cu and Bi$_2$O$_3$, the $R_{ct}$ was higher in the first cycle compared to the MnO electrode containing only Bi$_2$O$_3$ (Figure 3f). The addition of additives to the electrode can increase the $R_{ct}$ as they are an extra part of the electrode component where charge can interact with it. This was also seen in the MnO electrode with only Bi$_2$O$_3$ in
Figure 3b, where the $R_{ct}$ increased in the second plateau region. Similarly, the $R_{ct}$ increased for the MnO electrode with Bi$_2$O$_3$ and Cu in the first plateau region, while it reached to the same value in the second plateau region compared to the electrode with no Cu. This indicated that Cu was affecting the first plateau of the discharge curve, which was seen more clearly in Figure 3h, where the $R_{ct}$ of the 2nd discharge cycle did not change much compared to that of the 1st discharge curve in Figure 3f. However, the comparison of the $R_{ct}$ of the 2nd discharge cycle of the electrode containing both additives and the electrode with only Bi$_2$O$_3$ was stark. These results decisively proved that Cu and Bi$_2$O$_3$ had a positive effect on the first and second discharge plateau of the MnO curve, respectively. A similar observation was also made for the charge process around the 15 h mark, where there was an increase in $R_{ct}$ for the Cu-containing electrode. This is related to the interaction with Cu ions with the formation of a layered MnO$_2$ (birnessite) phase, where it is getting intercalated in the interlayers. This will be discussed later in the article.

These GITT experiments showed that without Cu the charge transfer resistance of the electrodes increased considerably due to a phase formation of Mn$_3$O$_4$ during the first discharge plateau; however, with the addition of Cu the electrode was able to cycle stably. These experiments seemed to suggest that even spinel Mn$_3$O$_4$ could be made rechargeable by addition of Cu and Bi$_2$O$_3$. To test this theory, two cells were made, where one cell contained 55 wt% Mn$_3$O$_4$ with no additives and another contained 55 wt% Mn$_3$O$_4$ with Bi$_2$O$_3$ and Cu (Figure 3i,j). These cells were cycled at C/4 in a half-cell format. The cell with only Mn$_3$O$_4$ showed it could deliver capacity initially with two distinct plateaus similar to the ones seen in the MnO cells (Figure 3i). This confirmed that MnO converted to Mn$_3$O$_4$ without any additives; however, capacity was attainable out of commercially purchased Mn$_3$O$_4$ albeit initially. This could be due to the nanoparticle size of Mn$_3$O$_4$ that was purchased, but eventually this electrode also failed because the electrochemical formed Mn$_3$O$_4$ was highly resistive. The addition of Cu and Bi$_2$O$_3$, however, made the spinel Mn$_3$O$_4$ rechargeable like the rocksalt MnO as shown in Figure 3j. The CV curve of only Mn$_3$O$_4$ is shown in Figure S10 in the Supporting Information, where at 0.1 mV s$^{-1}$ the reduction and oxidation reactions are seen clearly. The addition of Bi$_2$O$_3$
and Cu ensures the reversibility and high capacity utilization of those reactions. It is also important to note that closed pack structures like MnO and Mn₃O₄ deliver high capacity through conversion reactions in alkaline electrolyte. There could be more materials behaving similarly.

The characterization of the 55 wt% MnO electrodes with Cu and Bi₂O₃ additives is shown in Figure 4. XRD, scanning electron microscopy (SEM), TEM and scanning transmission electron microscopy (STEM) were performed at regions 1, 2, and 3 as shown in Figure 4a. Regions 1 and 2 signified the first charge and discharge, respectively, while region 3 signified the fourth charge. XRD results in Figure 4b conclusively showed that at the charge state the MnO had transferred to layered birnessite (δ-MnO₂). The intensity of the layered (00c) peak between 11° and 13° increased from regions 1 to 3 indicating more distinct layers of birnessite formation. There was also a shift to the lower angle in region 3 of the layered peak indicating an expansion of the interlayer region. This interlayer region expansion indicated the presence of Cu²⁺ because of the potential region of the electrode in alkaline electrolyte. Cu is in 2⁺ oxidation state at high potentials of Hg/HgO in alkaline electrolyte. This is explained by its CV curves in Figure S8 in the Supporting Information. In the final oxidation step of Cu, it is present in its 2⁺ state (Cu⁴⁺), which is formed around the same potentials for birnessite formation as shown in Figure S8a in the Supporting Information. This supports the pathway for Cu²⁺ to intercalate within the layers of birnessite.

This also explained the presence of Cu(OH)₂ in the charged electrodes of regions 1 and 2. This process of Cu²⁺ intercalation into the layers of birnessite could explain the increase in Rₛ seen in Figure 3 during the charge process. Region 2 clearly showed the formation of dominant phase Mn(OH)₂ along with Mn₃O₄ and some peaks indexed to Cu₀.₅ Mn₂.₅O₄. The incorporation of Cu into the Mn₃O₄ could also lead to reducing charge transfer resistance. Metallic Bi was also detected in the XRD, which indicated that Bi₂O₃ was undergoing some reaction in alkaline electrolyte. The detailed reaction and pathway to Bi formation is described further in Note S1 in the Supporting Information.

SEM, TEM, HRTEM, and STEM images with mapping of regions 1, 2, and 3 are shown in Figure 4c–e and Figures S11–S14 in the Supporting Information. For the charged state, which are regions 1 and 3, the SEM images in Figure 4c and Figure S11 in the Supporting Information showed the formation of lamellar-like structure at the end of charge of the MnO electrodes. These lamellar structures are characteristic of layered birnessite structures. TEM images of regions 1 and 3 in Figure 4d and Figure S12 in the Supporting Information also showed structures characteristics of layered birnessites, where in region 1 (Figure S12, Supporting Information) the particle looked amorphous, while in region 3 (Figure 4d) the particle looked more crystalline to identify the lattice belonging to birnessite. STEM, X-ray mapping, and linescan mapping of regions 1 and 3 are shown in Figure 4e and Figures S13 and S14 in the Supporting Information, where it can be seen that Cu, Mn, and O are co-located with one another; thus, proving again that Cu is present within the interlayers of birnessite. SEM, TEM, and HRTEM images of region 2 in Figures S11 and S12 in the Supporting Information showed more crystalline particles forming at the end of discharge. The STEM mapping images of region 2 in Figure S16 in the Supporting Information also showed the elements co-located.

To get a more definitive proof of the dissolution–precipitation or conversion reactions of MnO in alkaline electrolyte, a special in-house cell was built to view the reactions under a microscope. The cell contained 55 wt% MnO with Bi₂O₃ and Cu as the cathode and an oversized capacity ZnO as counter electrode. A white fibrous paper was pressed onto the cathode to act as a background reference point for dissolution–precipitation reactions. The cell was cycled at C/10 for a single discharge and charge cycle to observe its respective reactions. The images of the start, mid-discharge, end of discharge, and end of charge were taken, which are shown in Figure 5a. It was very clear from the “start” and “mid-discharge” pictures of Figure 5a that dissolution–precipitation reactions are taking place for MnO as the white fibrous paper was visible. The end of discharge showed precipitation products over the white paper, while the end of charge showed a color transformation from black at the start to brown at the end of charge. This brown color was indicative of MnO₂ and layered birnessites have similar color. The white fibrous paper was no longer visible at the end of charge. The products that are seen in the images have already been characterized and discussed in the previous paragraphs; however, these images are the first conclusive proof of the conversion reactions of MnO.

The conversion reactions of MnO require the dissolution of Mn ions and eventual precipitation to form Mn(OH)₂ at the end of discharge and MnO₂ at the end of charge. Spectroelectrochemical in situ UV-vis experiments were performed to identify the Mn ion and the formation step of MnO₂ on charge. The experimental setup is shown in Figure S17 in the Supporting Information. A 55 wt% MnO with Cu and Bi₂O₃ was cycled potentiodynamically in the UV-vis setup in the similar way shown in Figure 2a. The electrode was first scanned in the positive direction to 0.5 V versus Hg/HgO for the charge step and then scanned to −1 V versus Hg/HgO for the discharge step. UV-vis spectra were recorded at a number of potentials, which are shown in Figure 5b–d. Figure 5b,c shows that Mn(III) was the dissolved ion present in the electrolyte during the initial charge and discharge process. Mn(III) in alkaline electrolyte usually exists as Mn(OH)₆³⁻ ions, which may also be the case here. During charge (Figure 5b) the intensity of Mn(III) increased, while during discharge (Figure 5c) the intensity decreased. The decrease in intensity of Mn(III) during discharge was because of reduction process to form Mn(II). Mn(II) exists in alkaline electrolyte as Mn(OH)₄²⁻ ions, which may then allude to a reaction process for reduction as follows

\[
\text{Mn(OH)}_6^{3-} + e^- \rightarrow \text{Mn(OH)}_4^{2-} \tag{1}
\]

\[
\text{Mn(OH)}_4^{2-} \rightarrow \text{Mn(OH)}_2 \tag{2}
\]

The increase in intensity of Mn(III) during charge was because of oxidation of Mn(II) to Mn(III) and eventually Mn(IV), which then points to the reverse of the reactions
Figure 4. a) Charge and discharge curves of a 55 wt% MnO electrode with Cu and Bi$_2$O$_3$ additives, which are stopped at different points for characterization. b) XRD of regions 1, 2, and 3 as pointed in (a). c) SEM image of region 3. d) HRTEM image of region 3. e) STEM and X-ray mapping of region 3.
pointed above. Figure 5d shows the conversion of Mn(III) to Mn(IV), i.e., formation of MnO₂ during charge. The intensity increase was very apparent in the region between \(-0.25\) and \(0.1\) V versus Hg/HgO indicating the formation of MnO₂ or birnessite (\(\approx 370\) nm).\(^{37,38}\) Cu\(^{2+}\) was also detected in the UV-vis (\(\approx 450\) nm) at the end of charge,\(^{39}\) which added another proof to Cu\(^{2+}\) intercalating in the layers of birnessite.

The new MnO electrode with Cu and Bi₂O₃ can cycle very stably and reliably at very high areal capacities of \(\approx 30\) mAh cm\(^{-2}\) and at high Coulombic efficiency through a conversion reaction mechanism. However, this conversion cathode requires another successful and reliable conversion anode of equally high areal capacity to provide an energy dense battery. Therefore, the next section proceeds with a novel method of increasing the capacity utilization of a Zn metallic anode.
2.2. Enhancing the Capacity Utilization of Conversion Zn Anodes

Zn is a conversion electrode, where it can deliver a capacity of 820 mAh g⁻¹ through a two-electron dissolution–precipitation reaction, which can be written as follows:

$$\text{Zn} + 4\text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-} + 2\text{e}^- \quad (3)$$

Traditionally, only a fraction of its theoretical capacity has been used because of problems like dendrite formation, shape change, and passivation. These problems are similar to metallic anodes in other battery systems, where a number of challenges exist to utilize a high fraction of its capacity. A high energy density battery also requires high capacity utilization from the anodes; therefore, increasing the energy density of Zn anodes is paramount.

A number of Zn electrodes were tested to try to utilize most of its capacity and test the best formulation. The detailed formulations are written in the Experimental Section and mentioned in Figure 6a. For brevity, the formulations will be mentioned by their wt% and Zn type. Umicore purchased zinc will just be called Zn, while nanosized Zn particles will be called “NanoZn.” These electrodes were tested in half-cell experiments and the electrodes were cycled at constant current at C/20 to extract maximum capacity. The cycle life of the different Zn electrodes is shown in Figure 6a. The worst performing electrodes were electrodes that comprised mostly of Zn with no additives in the mix. Powdered Zn electrodes like 85 Zn and 95 Zn had very poor capacity utilization. This was also the case with 100 Zn metallic sheet electrodes. The electrodes showed no sign of improvement by cycle 30. A notable improvement was observed when the Zn electrodes contained additives like Bi₂O₃ and Ca(OH)₂ in the mix. The Bi₂O₃ was used to reduce gassing and improve conductivity, while Ca(OH)₂ was used to keep the Zn localized near the electrode.\(^{[15,40]}\) The 80 Zn with the additives delivered a high capacity around 200 mAh g⁻¹. The improvement in performance of this electrode was considerable when CNTs were added to the mix as a conductive additive, where the capacity jumped from 200 to 550 mAh g⁻¹. This electrode achieved stable cycling at 450 mAh g⁻¹ after 30 cycles. The steady loss in capacity of this electrode was due to the loss of Zn from the electrode during the dissolution–precipitation reactions. To mitigate this loss,
zincate ions were formed in the electrolyte by dissolving zinc oxide in KOH to form 25% KOH with zincate. The addition of zincate ions in the electrolyte prevented loss of zinc ions from the electrode to give much better cycling stability as shown in Figure 6a. Conclusions were made from these experiments that Zn electrodes suffered from poor electrical conductivity during its dissolution–precipitation reactions to form ZnO and this could be considerably improved by the use of additives like CNTs, Bi2O3, and Ca(OH)2. However, the capacity utilization was still not reaching theoretical, which we postulated the reason to be the size of the Zn atoms which it ranged from 1 to 20 µm. These large particles would definitely play a role in reducing the capacity utilization of the anodes. Therefore, nanosized Zn particles averaging in particle sizes of 40–60 nm were tried as a replacement for the commercial Zn to achieve maximum utilization. Reducing the particle size of Zn resulted in greater capacity utilization, where the maximum capacity utilized reached near 810 mAh g−1. The cycling of this electrode also seemed to be stable as shown in Figure 6a. This phenomenal cycling performance was obtained also at high areal capacities of ≈30 mAh cm−2, which is the highest in metal Zn anode literature. Conversion reactions of NanoZn electrodes resulted in high areal and specific capacities.

The discharge curves of these different Zn anodes for cycles 5 and 16 are shown in Figure 6b,c. It was very clear that the electrodes containing CNTs and NanoZn had the better discharge characteristics, where the capacity and voltage characteristics had considerably improved compared to the other anodes. The two best performing electrodes had two well-defined voltage plateaus, while the other electrodes also showed two plateau characteristics but with longer second plateaus. The plateaus were related to the type of zincate ion formed during discharge, which will be explained later. Nevertheless, it was clear that utilizing nanosized Zn particles with CNTs resulted in better discharge characteristics. The NanoZn electrode was further tested in a full battery with nickel oxyhydroxide (Ni) as the cathode and cycled at C/5. The capacity retention and cycling curves of the Ni|NanoZn battery is shown in Figure 6d,e, where it was seen that the battery was able to deliver the 810 mAh g−1 of NanoZn anodes for 50 cycles (still cycling). The 50th cycle charge and discharge curve of the cell and NanoZn electrode is shown in Figure S15 in the Supporting Information. This was again cycled at high areal capacity of ≈30 mAh cm−2 to show the commercial applicability of these conversion anodes. The Coulombic efficiency of the anodes was around 99.2%.

The characterization of the different anodes was done to understand their cycling results. XRD of the 85 Zn, 95 Zn, and metallic Zn sheet showed a combination of Zn and ZnO phases present (Figure S18, Supporting Information); however, the intensity of ZnO peaks was considerably larger in the metallic Zn anodes. SEM images of these electrodes (Figure 7a and Figure S20a–c, Supporting Information) showed that large portions of the electrode were covered by thick white ZnO regions. These thick regions are generally called passivated ZnO in literature, which are unable to charge back to Zn.[38] In the powdered 85 Zn and 95 Zn images, a thick ZnO coating surrounding the Zn core could be seen indicating that eventually the electron path to Zn was prevented because of the resistivity of ZnO.[41] The metallic Zn sheets showed more rough edges that were deformed considerably during electrochemical cycling to create more passivated ZnO on the surface. Metallic Zn sheets unlike Li sheets are not very stable in alkaline electrolyte. The 80 Zn electrodes with CNTs and 80NanoZn electrodes showed much better performance compared to the other electrodes because of the starting structure of the electrode as shown in Figure 7b,c. The Zn particles were nested in CNT framework that provided enhanced conductivity compared to the electrodes without CNTs. The SEM images of the 80 Zn electrodes with CNTs at the end of charge and discharge are shown in Figure 7d–f, where it was seen that a Zn particle was caught in mid-transition state to form charged Zn and the ZnO formed at the end of discharge was more lose and fibrous-type rather than the thick passivated ZnO seen in the 85 Zn and 95 Zn electrodes. Similarly with the 80NanoZn electrodes, an SEM image of a charged state electrode is shown in Figure 7g with the corresponding X-ray maps showing that Zn was formed and localized on the electrode by Ca(OH)2. XRD at the end of charge and discharge of 80NanoZn electrodes showed efficient phase transformation between Zn and ZnO (Figure S19, Supporting Information). The change in particle size of Zn and formation of passivated and fibrous ZnO was a result of the dissolution precipitation reaction (conversion reactions) of Zn in alkaline electrolyte. The two plateaus seen in the discharge voltage curves of the 80NanoZn was due to the nature of electrolyte species present during discharge. This was captured by spectroelectrochemical in situ UV-vis setup, where a cell was cycled like the MnO electrode. The CV curve of the 80NanoZn electrode is shown in Figure 7h with the corresponding UV-vis spectra in Figure 7i,j. The green dots on the CV curve indicate the potentials where the spectra were taken. Two peaks are seen in the UV-vis spectra indicating that there are two types of zincate ions present in the electrolyte. The lower wavelength peak at ≈237 nm corresponds to Zn(OH)2·xH2O while the peak at ≈270 nm corresponds to Zn(OH)2·yH2O.[42] These ions become soluble in KOH during the Zn charging and discharging steps because of its conversion reaction nature. The intensity of the peaks increased and decreased during charging and discharging; however, a unique feature of the electrolyte was observed in the circled green region Figure 7h, where the two peaks merged during the start of discharge as shown in Figure 7j. This meant that the zincate ions polymerized[42] initially during discharge in the 80NanoZn electrodes to deliver its capacity. Further work is required to be done to understand the nature of zincate ions in the other Zn anodes, which will be the topic of another article.

Microscope experiments of the Zn anodes were also conducted to observe the dissolution–precipitation reactions and capture the behavior of different electrodes. These experiments were done on the 85 Zn, Zn metallic sheet, and 80NanoZn electrode. Figure 8a–c points to the different behavior of the Zn electrodes, where images from the start, end of discharge, and end of charge are shown, respectively. The 85 Zn electrode structure showed interconnected Zn particles at the start, which became blueish white and amorphous ghost white at the end of discharge. The amorphous ghost white region showed thicker appearance at the end of charge, while the blueish region became gray Zn. The thicker white region probably indicated the formation of passive ZnO on the electrodes, which are the cause of poor performance. The images captured for the Zn metallic sheet showed a stark transition from metallic
Figure 7. a) Cross-section SEM image of a cycled 85 Zn electrode showing passivated zinc. b) SEM image of a precycled 80 Zn anode containing CNTs showing that Zn particles are nested in CNT framework. c) SEM image of a precycled 80NanoZn electrode showing nanometer-sized Zn particles embedded in the CNT framework. d) Cross-section SEM image of a cycled 80 Zn electrode with CNTs on charge. e) SEM image of a cycled 80 Zn electrode with CNTs on discharge. f) SEM image of a precycled 80 NanoZn electrode showing nanometer-sized Zn particles embedded in the CNT framework. g) SEM image of a cycled 80 Zn electrode with CNTs on charge with corresponding maps showing Zn localized by Ca(OH)₂. h) CV curves of an 80NanoZn electrode with green dots indicating the points where the UV-vis spectra were taken. i) UV-vis spectra of an 80NanoZn electrode on charge. j) UV-vis spectra of an 80NanoZn electrode on discharge.
Figure 8. Microscope images of an in situ cell cycling. a) 85 Zn electrode. b) Metallic Zn sheet. c) 80NanoZn electrode. d) Schematic drawings summarizing the cycling characteristics of different Zn electrode formulations. e) Impedance spectra of 85 Zn, metallic Zn sheet, and 80NanoZn electrodes.
luster at the start to a disintegrated sheet at the end of charge. The breakdown of the electrode showed more mossy-type structures; however, poker-type Zn particles were also seen which could be indicative of early sites of dendrite formation. In contrast to these electrodes, the 80NanoZn electrode showed more uniform discharge and charge in the electrode structure. The ZnO formed more uniformly and charged back to Zn without forming passivated structures or dendritic structures. The CNT framework in the Zn anodes along with the nanosized Zn particles allowed for better performance during cycling. Impedance spectra of the 85 Zn, metallic Zn, and 80NanoZn electrodes were conducted at the end of discharge as shown in Figure 8e, where the charge transfer resistance for the NanoZn electrodes was 0.0268 ohm cm$^{-2}$ compared to 1.89 ohm cm$^{-2}$ of 85 Zn indicating that the ZnO formed from NanoZn electrodes had less resistance to charge back to Zn. The large resistance seen in the impedance spectra of the 85 Zn and metallic Zn is indicative of the nature of the traditional electrode design, where there is not a conductive pathway for the Zn to carry out its electrochemical reactions. Also, the formation of a passivated ZnO on the traditional Zn electrodes could act as a diffusion barrier for hydroxyl ions, which are required for the Zn to carry out its electrochemical reactions. The schematic of the different Zn anode cycling process is shown in Figure 8d, where the results are summarized of the different experiments to indicate the benefits of cycling a CNT nested NanoZn electrode.

2.3. Energy Dense MnO|CNT-NanoZn Conversion Battery

The culmination of the individual improvement of conversion-based MnO and NanoZn electrodes resulted in the fabrication of a full battery. The battery would undergo the conversion chemistry of both electrodes that had been discussed till now and this is summarized in Figure 9a. The cycling performance of a 55 wt% MnO electrode with Cu and Bi$_2$O$_3$ as additives with the 80NanoZn electrode is shown in Figure 9b, where the potential and the electrodes reference curves very stable at C/10. Very high areal capacities were used for the cathode and anode to deliver a high volumetric energy density of $\approx$210 Wh L$^{-1}$ (Figure 9c) taking into account the total thickness of both the electrodes. The electrodes need a formation procedure as they are cycled at high areal capacities and utilizations as seen in the initial cycling of Figure 9c, after which the electrodes are able to cycle very stably. This formation step is also seen in Figure 9f, where the initial Coulombic efficiency is low; however, after the formation is complete the Coulombic retention is $\approx$99.6%. This is the highest volumetric energy density reported for a conversion system after 44 cycles. Impedance and rate capability experiments were also performed to understand the electrochemical performance of this new system further. The new battery system showed low charge transfer resistance of 0.0122, 0.0144, and 0.0162 ohms cm$^{-2}$ for cycles 2, 3, and 4 as shown in Figure S21 in the Supporting Information. The rate capability of the cathode and the full MnO|CNT-NanoZn battery was also excellent as shown in Figure S22e in the Supporting Information, where it can be seen that this new battery chemistry is very stable and can be used for a wide range of applications. An 80 wt% MnO cathode with NanoZn electrode was also cycled as shown in Figure S23 in the Supporting Information, where it could be seen that a high wt% loading MnO could also cycle stably in this newly designed conversion system. Cycle life of the batteries currently shown are till around 50 cycles (still cycling at the time of this writing), but it is still an achievement for very high areal capacity electrodes because of the other challenges and complexities that arise when high mass areal loadings are used. We also cycled a battery at low areal capacity of 2.5 mAh cm$^{-2}$ as shown in Figure S24 in the Supporting Information, where it could be seen that obtaining high cycle life is not so much of a challenge at very low areal capacities. Also, as pointed out in the introduction section, for Zn-anode batteries to compete with Li-ion batteries on an energy and cost basis, the areal capacities of the electrodes need to be much higher than 10 mAh cm$^{-2}$.

We were also interested in testing the battery by connecting the electrodes in series. The Chem-E car team at CCNY currently uses an intercalation mechanism-based MnO$_2$|Zn battery to run their small-scale automobile. The car is called “Zincotron” because of the Zn anode chemistry used to run the automobile. The automobile requires $\approx$0.6 Ah to run; however, the intercalation-based MnO$_2$|Zn battery is oversized to 4 Ah to make sure the electrodes in the battery can last longer. This was done because we had discovered that the MnO$_2$ electrodes suffered breakdown in crystal structure when the utilization was high in the intercalation-based system. We designed a battery with the MnO|CNT-NanoZn conversion-based system, where the electrodes had a total capacity of 1.2 Ah based on 750 mAh g$^{-1}$ of the MnO cathode. As the total utilization of the conversion electrodes was possible, this meant that no extra addition of active materials was required or overbuilding the cell capacity. By utilizing the entire capacity of the electrodes in the conversion MnO|CNT-NanoZn battery, we could reduce the size and weight of the cell considerably as shown in Figure 9d.

Also, utilizing high conversion capacities directly relates to lowering the costs of the active materials used in the battery. The performance of the battery is shown in Figure 9e,f, where it can be seen that the electrodes are remarkably well balanced in the conversion system to deliver the complete capacity reversibly. The specific energy density of the battery when the total mass of the electrode is considered is $\approx$320 Wh kg$^{-1}$, which brings it to comparable numbers of Li-based chemistries but with the added benefit of safety and low cost.

3. Conclusions

For aqueous batteries to make a mark in the current energy storage landscape, a transformational improvement in capacity and energy is required. We proposed a new strategy based on conversion reactions that surpasses the intercalation capacity of current aqueous-based batteries. In this article, we specifically concentrated on Mn- and Zn-based aqueous batteries because of its tendency to undergo conversion reactions, and also, its added benefit of low cost and nonflammable characteristics. We proposed the MnO and Zn system because of its high theoretical capacity of 750 and 820 mAh g$^{-1}$, respectively. We found that the rechargeability of MnO was drastically improved
with the addition of Cu and Bi$_2$O$_3$ that played roles in reducing the charge transfer resistance of the electrode to cycle at high areal capacities, which is an important metric for commercial viability. Similarly, we found that the performance of the Zn anodes can be dramatically improved when the size of the Zn particles is reduced to nanometers and CNTs with Bi$_2$O$_3$ and Ca(OH)$_2$ are added to the electrode. The CNT framework kept the Zn nested inside and allowed for efficient electron transport and prevented passivation that also allowed the electrode to cycle at high areal capacities. A comparison of cycle life and areal capacity of intercalation-based systems and newly proposed conversion-based system is shown in Figure 10a.\textsuperscript{[43–50]} Also, a comparison of some of the best Zn anodes studied in literature in terms of areal capacity and cycle life is shown in Figure 10b, to illustrate that obtaining high cycle life is a challenge at high areal capacities.\textsuperscript{[51–56]} Finally, we showed the
applicability of this energy dense battery in a small-scale automobile, where it showed remarkable stability in cycling and capacity retention. The high volumetric and specific energy density of the battery opens up the new conversion-based aqueous batteries to many applications, where its use may have not been thought of before. Also, with the recent advent of high voltage (2.45–2.8 V) aqueous Zn-anode batteries (HiVAB) reported by Yadav et al.,\textsuperscript{[57]} highly energy dense cheap Mn-based Zn batteries with ultra-high areal capacities and voltage can be presented as a challenger to replace expensive and dangerous Li-ion batteries.

### Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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### Conflict of Interest
The authors declare no conflict of interest.

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aqueous chemistry, beyond intercalation, conversion battery, manganese oxide rocksalt, zinc anode

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[1] K. Keane, British Broadcasting Corporation. Calls to Speed Up Climate Change Action in Agriculture, https://www.bbc.com/news/uk-scotland-45617760?intlink_from_url=https://www.bbc.com/news/topics/cmj342mzw1t/climate-change&link_location=live-reporting-story (accessed: September 2018).
[2] B. Dunn, H. Kamath, J.-M. Tarascon, Science 2011, 334, 928.
[3] M. Armand, J. M. Tarascon, Nature 2008, 451, 652.
[4] Environmental Protection Agency, Sources of Greenhouse Gas Emissions, https://www.epa.gov/ghgemissions/sources-greenhouse-gas-emissions (accessed: September 2018).
[5] N. Nitta, F. Wu, J. T. Lee, G. Yushin, Mater. Today 2015, 18, 252.
[6] X. Fan, W. Sun, F. Meng, A. Xing, J. Liu, Green Energy Environ. 2018, 3, 2.
