Ion-Sieving Carbon Nanoshells for Deeply Rechargeable Zn-Based Aqueous Batteries

Yutong Wu, Yamin Zhang, Yao Ma, Joshua D. Howe, Haochen Yang, Peng Chen, Sireesha Aluri, and Nian Liu

Energy storage technologies have the potential to change the energy infrastructure from relying heavily on fossil fuels to mostly using temporally intermittent renewable energy sources.[1] Lithium-ion batteries (LIBs), for instance, have been extremely successful in portable electronic devices.[2–4] In scaling up intermittent energy sources to be broadly utilized to power devices such as electric vehicles, the delicate balance between safety and performance has been a challenge due to the use of intrinsically flammable organic electrolyte materials. In addition to the high level of recent interest in all-solid-state LIBs,[5–8] an alternative is to develop battery technologies that use aqueous electrolytes which are intrinsically safe.[9–11]

Among candidate anode materials for aqueous batteries, Zn is the most active metal that is stable in water and also has one of the highest specific capacities. As an anode Zn has roughly three times the volumetric capacity (3854 mAh cm⁻³) compared to Li (2062 mAh cm⁻³).[12,13] When paired with an oxygen cathode, the theoretical volumetric energy density of a Zn-air battery (4400 Wh L⁻¹) approaches that of a Li-S battery (5200 Wh L⁻¹). Additional advantages of the Zn-air cell compared to the Li-S cell are that Zn is much more economical than Li[14–16] and the battery is safer due to absence of flammable organic liquid, making Zn-based batteries attractive candidates for electric vehicles and large-scale energy storage. There has been recent progress on rechargeable Zn anode materials in neutral or mildly acidic conditions that eliminate concerns of ZnO passivating the Zn surface.[17–19] In order for Zn-based aqueous batteries to have higher specific energy than state-of-the-art LIBs, however, an oxygen cathode must be used,[16] which favors alkaline electrolytes (e.g., KOH) to facilitate the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER). Although developing efficient ORR and OER electrocatalysts could lower the polarization and improve the round trip energy efficiency of Zn-air batteries, their reversibility is mainly limited by the Zn anode, which has received far less attention.[20–25]

A deeply rechargeable zinc anode in lean alkaline electrolyte (a cell utilizing the minimum amount of electrolyte) is a critical step toward zinc air battery that has not been achieved yet. A few attempts have been made before.[26–28] However, to the best of our knowledge, all of the electrochemical data in past reports were obtained in beaker cells (Figure 1) with ZnO saturated electrolyte or a low depth of discharge (DOD), which raises several problems: (1) the amount of electrolyte exceeds the amount of electrode materials by ≈1000 times, which lowers the overall energy density and covers the problem of...
electrolyte side reactions; (2) the open cell configuration covers the problem of gas evolution and cell swelling; (3) the electrolyte is usually saturated with ZnO to extend the cycle life. Yet, the capacity from the ZnO dissolved in the electrolyte is 250-folds of the active material used (assuming 10 mL of electrolyte and ZnO solubility of 0.256 mol L\(^{-1}\) measured by inductively coupled plasma), and the mass of dissolved ZnO is not counted when calculating the specific capacity. The true performance of the active material was not evaluated; (4) the utilization of Zn is usually low (<50%), which extends the cycle life, but lowers the overall energy density.

Testing under extremely harsh conditions (lean electrolyte, deep cycling, no ZnO in electrolyte) is not only necessary to evaluate the practicality of zinc anodes, but also places high demand on their performance. We test our battery material in coin cell which only uses 100 µL of electrolyte without any ZnO dissolved in the electrolyte from which the active material performance can be directly reflected in battery cycling. Also, we test to check if the active material can survive the harsh condition in the coin cell with problems such as electrolyte drying, gas evolution induced pressure build up, and loss of material contact. The testing condition is of 100% DOD and at 1C. A comparison of testing conditions between this work and most of the past reports is summarized in Table 1.

The typical electrochemical reactions of Zn anode in an alkaline electrolyte are shown in Equations (1)–(3). Rather than a solid-to-solid direct transition, Zn metal first electrochemically oxidizes to a soluble zincate ion, then precipitates to solid ZnO\(^{[29]}\)

\[
\text{Zn} (s) + 4\text{OH}^{-} (aq) \rightleftharpoons \text{Zn} (\text{OH})_{4}^{2-} (aq) + 2e^{-} \quad (1)
\]

\[
\text{Zn} (\text{OH})_{4}^{2-} (aq) \rightleftharpoons \text{ZnO} (s) + \text{H}_{2}\text{O} + 2\text{OH}^{-} (aq) \quad (2)
\]

Overall: Zn \( (s) + 2\text{OH}^{-} (aq) \rightleftharpoons \text{ZnO} (s) + \text{H}_{2}\text{O} + 2e^{-} \quad (3)
\]

Three major challenges currently exist for the rechargeable Zn anode for aqueous batteries as a result of the solid-solute-solid mechanism, the insulating nature of discharge product (ZnO), and the water stability window: (1) ZnO (the soluble and insulating discharge product) passivates the surface of unreacted Zn, which leads to low utilization of active material and a poor rechargeability (Figure 2A); (2) ZnO dissolution causes Zn deposition to happen in random locations, which leads to electrode morphology change and dendrite growth after continuous cycling. In a lean electrolyte configuration, the Zn dendrite can penetrate the separator to short-circuit the battery. (3) \( \text{H}_2 \) evolution on the Zn anode compromises Coulombic efficiency. Especially in a sealed cell with a limited amount of electrolyte (rather than the often-used beaker cell with saturated ZnO), \( \text{H}_2 \) evolution dries out the electrolyte, enhances internal pressure of the battery, and gas bubbles block the ionic pathway, which leads to a low Coulombic efficiency (~60%) and even sudden battery failure. The \( \text{H}_2 \) evolution reaction is shown in Equation (4)

\[
2\text{H}_2\text{O} + 2e^{-} \rightarrow \text{H}_2 + 2\text{OH}^{-} \quad (4)
\]

Bulk foil is the most commonly used Zn anode in aqueous batteries. Figure 2B shows the voltage profile of a Zn foil (0.25 mm thick) anode cycled with an excess-capacity NiOOH cathode in a 2032 coin cell. The current density is 2.55 mA cm\(^{-2}\) and the capacity is limited to 2.55 mAh cm\(^{-2}\) with voltage cut-offs of 2 V in charging and 1.4 V in discharging. The capacity decays quickly over cycling and completely diminishes after only seven cycles, suggesting that an irreversible and insulating ZnO layer quickly builds up during cycling. Such a passivation layer blocks the materials underneath this layer from further reaction. To confirm the surface passivation and morphology change, scanning electron microscopy (SEM) images of Zn foil before and after the test are shown in Figure 2C,D, respectively. Initially, the Zn foil has a flat surface (Figure 2C), but sub-micrometer particles appeared on the surface (Figure 2D) after cycling. 3D electrodes with micropores on the order of 50 µm have demonstrated promising performance,\(^{[30,31]}\) yet the feature size is still above the critical passivation size of ~2–3 µm (Figure S1, Supporting Information), so ZnO can build up and impair battery performance.

Starting with a nanomaterial with high-surface area could avoid the passivation layer problem. However, the dissolution

<table>
<thead>
<tr>
<th>Electrolyte volume</th>
<th>Harsh testing condition (this work)</th>
<th>Mild testing condition (most past reports)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 mL (limited OH(^{-}))</td>
<td>Saturated ZnO in electrolyte (extra capacity source)</td>
<td></td>
</tr>
<tr>
<td>Mass of ZnO in electrolyte</td>
<td>0 mg</td>
<td>208 mg(^{a})</td>
</tr>
<tr>
<td>Extra capacity from electrolyte</td>
<td>0 mAh</td>
<td>137 mAh (~250 times of active material)</td>
</tr>
<tr>
<td>Depth of discharge</td>
<td>100%</td>
<td>&lt;50%</td>
</tr>
</tbody>
</table>

\(^{a}\)Assuming 10 mL electrolyte. Zincate solubility (0.256 mol L\(^{-1}\)) determined by ICP.
problem is more severe. On the other hand, a nonporous coating could prevent ZnO dissolution but would also block the OH\(^-\) transport necessary for the zinc redox reaction to occur. Therefore, it has been a challenge to simultaneously solve the dilemmas of passivation and dissolution.\(^\[32-35\]\]

The concept of separating ions and molecules by size using selective membranes has been widely used in water purification, gas and fuel separation, and biomedical dialysis.\(^\[36,37\]\) A variety of materials such as graphene, graphene oxide, polymer, and metal carbide membranes with a controllable pore size and permeability have been demonstrated to have ion-sieving capabilities, in various applications.\(^\[38-42\]\) Applying the ion-sieving concept to Zn anode, to confine larger zincate ions and allow smaller hydroxide ions to permeate, is expected to prevent ZnO dissolution and electrode shape change.

In this work, we propose an optimized structure to solve Zn anodes’ passivation and dissolution problems simultaneously (Figure 2E). Specifically, the structure features (1) a sub-micrometer ZnO particle as the core, and (2) an ion-sieving carbon coating as the shell. First, unlike the bulk Zn foil which is several hundreds of micrometers thick, sub-micrometer level spherical particles will not have a passivation problem and will remain active in extended cycling. We choose to start from ≈100 nm ZnO nanoparticles (discharged state) rather than Zn nanoparticles (charged state) because on the synthesis and scalability aspect, compared to Zn, ZnO is much easier to make into...
nanostructures which serves as the starting material for this study. On the battery performance aspect, starting from Zn to ZnO will rupture the carbon shell due to volume expansion. It is of note that nanoparticles with even smaller diameter offer no further benefit to reversibility but have much more severe dissolution concerns. We deposit the carbon shell on these ZnO nanoparticles through carbonization of a uniform polydopamine coating. The ability of polydopamine coatings to form a uniform shell with controllable thickness has been confirmed before.[43–45] The two-step synthesis method we report here is simple and scalable, and the carbon shell thickness is controllable by simply adjusting the dopamine mass during synthesis; details of the synthesis can be found in the Supporting Information. Second, the pore size of the carbon nanoshell is tailored to allow hydroxide ions to pass through while blocking transport of zincate ions. During charging, the zincate intermediate is trapped inside the carbon shell and reacts with Zn within the shell, preventing deposition of Zn in another location. In contrast, theOH \(^-\) by-product can diffuse out freely through the micropores in the shell due to their smaller size. During discharging, the trapped Zn oxidizes to form ZnO with the participation of OH \(^-\) coming from outside the shell.

The uniform polydopamine shell is first coated onto ZnO nanoparticles by stirring the particles with dopamine hydrochloride in Tris buffer (pH 8.5) for 24 h at room temperature in the presence of air. After carbonization at 600 °C, ZnO@C nanoparticles are obtained. The SEM image of bare ZnO nanoparticles is shown in Figure 3A; the particles are of short rod-like shapes. SEM image shows a quasi-spherical morphology of ZnO@C (Figure 3B and Figure S3, Supporting Information), which indicates the coating is successful, and the particles are of slightly larger size than bare ZnO. The transmission electron microscopy (TEM) image in Figure 3C shows a single ZnO@C nanoparticle with an amorphous carbon shell coated uniformly on the surface and the thickness of the carbon shell is 20–30 nm. Notice that the coating thickness is tunable by simply changing the dopamine hydrochloride mass. TEM images of single coated particles with different coating thickness are shown in Figure S4 (Supporting Information). We choose 600 °C as the carbonization temperature because the ZnO core is reduced to Zn vapor and escape at above 680 °C, determined from the thermogravimetric analysis (TGA) results (Figure S5, Supporting Information). TEM results confirm partial ZnO loss inside the carbon shell at 700 °C (Figure S6, Supporting Information), and complete loss at 800 °C (Figure S7, Supporting Information). This phenomenon is also confirmed by the fact that 100 mg ZnO@polydopamine becomes ~20 mg after 800 °C carbonization, and ~70 mg after 600 °C treatment, respectively. Complete and self-supporting hollow carbon nanoshells can be obtained after etching away ZnO using HCl (Figure 3D). The carbon mass fraction in the ZnO@C nanoparticles is determined to be 41% by TGA in ambient air (Figure 3E). The X-ray diffraction (XRD) patterns in Figure 3F for both the bare ZnO and ZnO@C have the same peak positions, indicating the retention of ZnO hexagonal wurtzite crystalline structure after coating. No signature of crystallinity is observed for the carbon shell.

To investigate the nature of the zincate and hydroxide anion species, density functional theory (DFT) calculations are performed to study the structure and size of each species. Details of the DFT calculations are provided in the Supporting Information.[46–49] The sizes of hydroxide ion and zincate ion, without solvation shells, are simulated to be 2.42 and 6.09 Å, respectively (Figure 4A). We note that these “rigid molecule” sizes computed here are substantially smaller than the sizes of these ions under thermal motion, but that our calculations...
support the much smaller size of the hydroxide anion relative to the zincate anion species. An effective ion-sieving nanoshell should be uniform and have a pore size between the sizes of hydroxide and zincate ions. X-ray photoelectron spectroscopy (XPS) results confirm the uniformity of our carbon coating. As shown in Figure 4B, bare ZnO has strong Zn and O signals, while ZnO@C only has a C signal. A comparison between both samples’ high-resolution Zn spectra further confirms the complete coverage of carbon on ZnO in ZnO@C (Figure 4C). The Brunauer–Emmett–Teller (BET) method is used to analyze the pore size of carbon-coated ZnO (Figure 4D). The pore width is calculated from the adsorption/desorption isotherm to be around 5–8 Å (Figure 4E), between the sizes of hydroxide and zincate ions plus the solvation shell. We therefore expect hydroxide species to be more mobile and zincate species to be less mobile when diffusing through the nanoshell. In comparison, uncoated ZnO particles do not have pores in the same range. To directly verify the ability of the sample to prevent ZnO@C from dissolving into the alkaline electrolyte, both ZnO and ZnO@C powders are soaked in KOH (4 M) for 5 min, 1 d, and 10 d and the dissolved Zn(OH)\(^{2-}\) are quantified using inductively coupled plasma atomic emission spectroscopy (ICP-AES). As shown in Figure 4F, although Zn still dissolves into the electrolyte, the dissolved Zn(OH)\(^{2-}\) from bare ZnO is much lower and slower than that from ZnO@C, which confirms that the carbon nanoshell functions as a barrier to slow down the zincate escape.

To evaluate the electrochemical performance of ZnO@C nanoparticle anodes, we pair them with commercial Ni(OH)\(_2\) counter electrodes with largely excess areal capacity. 2032 coin-type batteries are used to limit the amount of electrolyte and mimic practical application conditions. A Ni(OH)\(_2\) counter electrode is used rather than an air electrode to evaluate our anode because Ni(OH)\(_2\) has simpler electrochemistry, fewer factors influencing its battery performance, and it is compatible with sealed coin cells. The cells are galvanostatically charged to the theoretical capacity (658.5 mAh g\(^{-1}\) ZnO) and fully discharged to 1.5 V at 1C rate and 100% DOD. An upper voltage cutoff of 2 V is set to avoid electrolyte decomposition. Figure 5A compares the specific capacity of ZnO@C anode with a bare ZnO anode at similar mass loading. Performance of Zn foil, which degrades quickly in only seven cycles due to severe ZnO passivation is also shown in the same plot. The bare ZnO anode lasts for 20 cycles before severe capacity degradation is evident, indicating the success of decreasing feature size in mitigating passivation. Without nanoshell encapsulation, zincate is able to dissolve and diffuse prior to redeposition, and electrode morphology changes over cycling. The ZnO@C anode outlasts the bare ZnO anode with \(\approx 1.6\) times longer life in terms of cycles, we attribute the increased performance to reduction in the mobility of zincate.

Noticeably, bare ZnO quickly decays to half of the initial energy storage capacity, while ZnO@C has a significantly slower decay and longer cycle life. Another set of cycling data shown in Figure S9 (Supporting Information) demonstrates similar battery performance. This supports our hypothesis that the carbon nanoshell has suitable pore sizes to reduce the transport of zincate ions while allowing the hydroxide ions to pass freely. The carbon shell also increases the conductivity of the anode material, which is helpful for preventing the formation
of a passivation layer, also with the help of the carbon nanoshell the overpotential for every single cycle of the battery with ZnO@C is lower than that of bare ZnO (Figures S10 and S11, Supporting Information). The nitrogen doping also facilitates the conductivity of the carbon layer and charge transfer at the interface.[50] Figure S12 (Supporting Information) shows the voltage versus specific capacity during the charging and discharging processes. The performances of the charging processes are similar, indicating a stable performance. Figure 5B–E shows the SEM images of both bare and coated ZnO anodes before cycling and after three cycles. Noticeably, the surface of bare ZnO anode has holes after cycling, labeled with yellow arrows in Figure 5C, which is a result of ZnO dissolution. In contrast, the ZnO@C anode maintained the electrode morphology, which confirms the ability of the carbon shell on ZnO@C to mitigate Zn anode dissolution and passivation. It is also confirmed from the TEM image in Figure S13 (Supporting Information) that after charging the active material is still confined in the nanoshell.

To compare the battery performance under harsh testing conditions reported in this work to the performance under mild testing conditions in most of the past reports, we test a ZnO@C pouch cell using electrolyte saturated with ZnO (Figure S15, Supporting Information), and the battery reaches 100 cycles with >90% efficiency under 100% DOD at 1C. Another ZnO@C pouch cell using electrolyte saturated with ZnO shows a performance of ~95% efficiency and 100% retention for 500 cycles (Figure S16, Supporting Information), but the battery is cycled at 12C. The comparison is clear evidence that a deeply rechargeable anode in lean electrolyte configuration is in demand and necessary to reflect the true performance of battery active material in Zn-based aqueous batteries while the drastically enhanced battery performance in most of the past reports is attributed to the ZnO saturated in the electrolyte and low utilization of active material.

In summary, we have simultaneously solved the dissolution and passivation problems of Zn anode materials by applying an ion-sieving carbon nanoshell coating onto ZnO nanoparticles which are well below the critical passivation thickness. The carbon nanoshell is uniform and complete. The micropores successfully slow down ZnO dissolution and limit zincate ion transport but allow hydroxide ions to pass freely, and the nanoshells’ rigidity prevents anode shape change and dendrite growth. The battery lifetime is greatly enhanced with the ZnO@C anode; the coated anode outperforms bare ZnO and Zn foil with ~1.6 and 6 times longer cycle life in a coin cell with harsh testing conditions, respectively. The synthesis is simple and scalable with a controllable nanoshell thickness. This work is expected to provide guidance to the future design of Zn anodes for high-energy rechargeable aqueous batteries, and other high-energy battery electrodes.

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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