

A Long-Overlooked Pitfall in Rechargeable Zinc–Air Batteries: Proper Electrode Balancing

Daniel Deckenbach and Jörg J. Schneider*

In times of an ever-increasing demand for portable energy storage systems, post-lithium-based battery systems are increasingly coming into the focus of current research. In this realm, zinc–air batteries can be considered a very promising candidate to expand the existing portfolio of lithium-based rechargeable battery systems due to their high theoretical energy density of 1086 Wh kg^{-1} . Despite a steady increase in research over the past 5 years, a breakthrough in realizing fully electrically rechargeable zinc–air batteries has yet to come. This perspective article highlights pitfalls that have probably hampered the development of rechargeable zinc–air batteries over years. This involves a fundamental evaluation of the zinc–air battery system, whereby fallacies of an alleged rechargeability are uncovered. Especially, the electrode balancing of the zinc anode as well as the interface between anode and electrolyte is focused herein. Known phenomena such as morphological changes are re-evaluated by taking the contrasting battery stresses from shallow discharge to a highly desirable deep discharge into account. Existing challenges are discussed and prospected based on current approaches aiming to shed new light on a fundamental understanding and an opening of new avenues for rechargeability in zinc–air batteries.

1. Setting the Scene of Rechargeability

Rechargeable batteries are experiencing an enormous upswing, as they offer tremendous possibilities for consumers as portable electronics take on an ever-increasing demand in our everyday life. Currently, rechargeable batteries are being pushed as an energy storage device for future private transport due to their emission-free operation, which makes the demand for rechargeable batteries literally explode. Without the development of the lithium-ion battery, which began its technological

advance at the end of the 1990s, the current electrification needs in nearly all sectors would be difficult to imagine, striving our daily life from miniaturized applications up to massive energy storage demands in transportation. With regards to zero-emission passenger transportation using battery powered vehicles, the advantage of the lithium-ion battery seems currently undisputed.

This steadily increasing demand for lithium-ion batteries currently raises the question of whether and how long the availability of raw materials can be guaranteed. Moreover, the constantly expanding range of applications for the lithium-ion technology means that the safety aspects to be fulfilled are becoming ever more stringent, which are known to be the weak spot of this system due to the high reactivity of lithium.^[1–4] Consequently, the lithium-ion battery is subjected to enormous performance pressure, because as a universal remedy it must meet the most diverse requirements.^[5]

Nevertheless, the lithium-ion battery is meanwhile used ubiquitously due to the current absence of suitable and technologically mature alternatives, which further exacerbates the raw material situation.^[5,6]

Due to the enormous application potential of the lithium-ion battery, other battery technologies (nickel–cadmium, nickel–metal hydride, lead-acid) that have been known for a long time are meanwhile pushed out of the market or represent only niche products known for just a specific application.^[7–9] This is true for the zinc–air battery too, which is mainly known to the consumer as a non-rechargeable battery for hearing aids. However, it has also been known as a battery and mobile charger for military applications, since it is heavy duty under the most adverse conditions, while allowing high energy density and maintaining high safety requirements.^[10–12]

Yet, already in the mid-1990s, zinc–air batteries were on the verge of their breakthrough as a rechargeable energy storage device that would usher in the complete electrification of Germany's postal fleet at that time.^[13] As a mechanically rechargeable battery system in a van fleet of 60 cars, the used zinc metal (Zn) anodes were removed as a full pack from the spent battery set and replaced by a fresh metal pack to recover the battery. With that, a usage of more than 320 km with an energy density of 200 Wh kg^{-1} had already been achieved under realistic conditions.^[13]

D. Deckenbach, J. J. Schneider
Fachbereich Chemie
Eduard-Zintl-Institut für Anorganische und Physikalische Chemie
Technische Universität Darmstadt
Alarich-Weiss-Straße 12, 64287 Darmstadt, Germany
E-mail: joerg.schneider@tu-darmstadt.de

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In retrospect, the performance data of the zinc–air battery was remarkable and superior to its immediate competitor at the time, the lead-acid battery, by far.^[13] Even in direct comparison with today's lithium-ion technology, the zinc–air battery can keep up in terms of energy density.^[14–16] Of course, an exclusion criterion for the market maturity of the zinc–air battery at that time was certainly a realization of suitable battery charging or exchange infrastructure, with more than 150 kg of material, which has to be exchanged and recycled per refueling step (Figure 1).^[13]

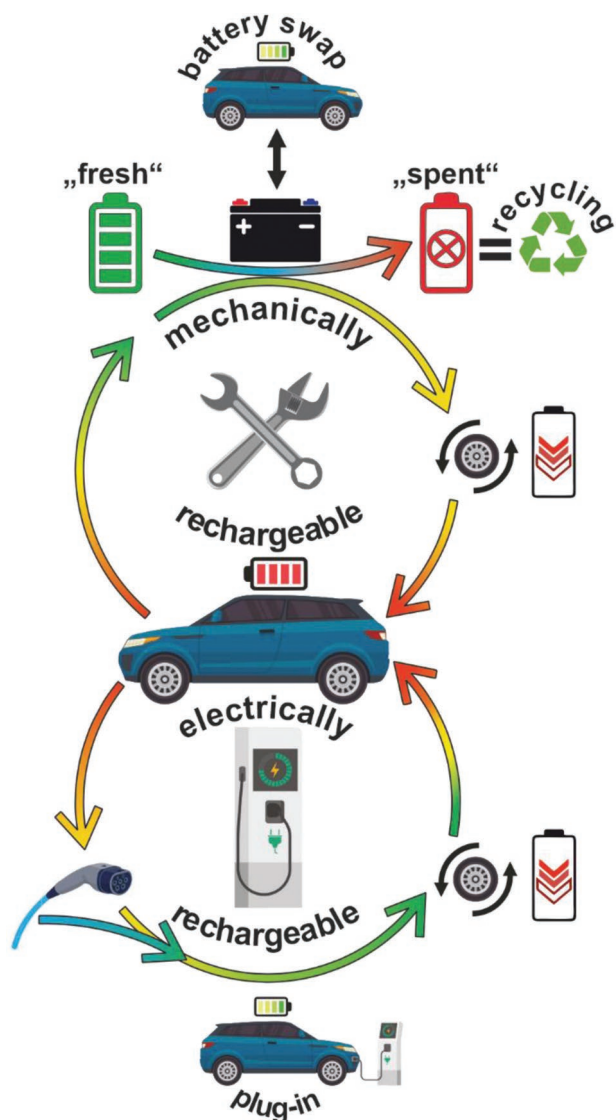


Figure 1. Schematic comparison of mechanical and electrical rechargeability illustrated by the example of an electric car. Whereas in the case of mechanical rechargeability, the battery must be removed after discharge in order to be refurbished at great expense, in the case of electrical rechargeability, the battery can be charged by means of electrical energy. The mechanically rechargeable battery is to be classified as defective after the complete discharge, while the electrically rechargeable battery retains its function as a battery for multiple cycles. A major disadvantage of the mechanically rechargeable battery and an important reason for its lack of market maturity was the need for a complete dismount of the spent battery which necessitates a full recycling of the depleted materials.

Ultimately, there is no way around achieving electrical rechargeability for the zinc–air battery once it should become a valuable alternative in the field of electrical energy storage. As a battery system, currently zinc–air technology is clearly at a disadvantage compared to the state-of-the-art lithium-ion battery standard due to its lower power output. However, the zinc–air battery is convincing in terms of active material balancing since the oxygen electrode is inexhaustible.^[17] Here, a common problem in current lithium-ion technology is the irreversible lithium loss during the first charge cycle, where 5–20% of the available lithium from the active cathode material is irreversibly consumed to form the anodic solid electrolyte interface.^[18–20] Usually, to compensate for the first-cycle lithium loss, the cathode is overbalanced with additional active material, but this inevitably leads to a reduction in the energy density of the entire battery due to the low capacity of cathode active material ($<200 \text{ mAh g}^{-1}$).^[18,21]

Currently, prelithiation techniques are used to circumvent this situation and to buffer the irreversible lithium losses while maintaining the energy density, but the proper balancing remains a delicate task, as a large excess can quickly lead to lithium plating, which must be avoided in any case.^[18,22,23] On the one hand, the zinc–air battery apparently circumvents the problem of counterbalancing the cathode active material by using an inexhaustible oxygen electrode. Due to a semi-open cell configuration, molecular oxygen is available unlimited.^[24] Thus, the cathode in zinc–air batteries is not affected by a material limitation and since the cathode active material is in a gaseous state, it does not contribute to the increase of the total mass but on the other hand increases the energy density of the whole battery. Due to unlimited oxygen supply at the oxygen electrode, the zinc reservoir on the anode side is regulating the energy taken from the cell, where the complete oxidation of the zinc anode terminates the battery operation. Although the oxygen electrode is inexhaustible, this does not imply that the zinc reservoir of the anode does not need to be regulated in a proper way. If a zinc–air battery is to be operated as an electrically rechargeable type, the balancing of the zinc anode is of paramount importance, whereby an excess of zinc, which can be understood as zinc metal uninvolved in the electrochemical reaction, has to be minimized under any circumstances. In this case, the depth of discharge (DoD), which is equal to the zinc utilization, must be maximized as far as possible while maintaining cyclability, as it will sensitively depress the specific energy in a delicate manner.

However, in the current literature, the vast majority of reported works continue to use excessive amounts of zinc as anodes to demonstrate the rechargeability of the zinc–air battery configuration studied.^[25–41] In this context, it was already mentioned in the 1990s during the development of mechanically rechargeable zinc–air batteries that this situation imposed by improper balancing should “not become an additional anchor the car or truck has to haul” besides the inevitably necessary. Consequently, this implies that metallic zinc present must be used completely for the electrochemical conversion.^[13] Nevertheless, the zinc reservoir of these oversized zinc anodes is only used to a small extent for the electrochemical conversion, which is referred to as shallow cycling. Currently, the widely used shallow cycling is not able to assess the rechargeability of the

battery system under complete zinc conversion. On the other hand, at low depths of discharge, when the turnover ratio of metal species is low, the anode failure criteria like passivation, corrosion, hydrogen evolution reaction, and dendrite formation are largely irrelevant, as the excess zinc overcompensates thus masking the real situation with respect to any true rechargeability.^[42] However, for any realistic rechargeability of a zinc–air battery, the cell must reach a point where no further discharge is possible and no more metallic zinc is available. From this point onward, it can be clearly demonstrated that further battery operation is only possible through the reversibility of the underlying fundamental reactions.

The attainment of rechargeability is the foremost goal to be achieved with a zinc–air battery, since only rechargeability ensures the sustainable use of all battery components. This then would represent a true economic usage of all resources in a technologically closed cycle. This fact clearly distinguishes the secondary electrically rechargeable zinc–air battery from its primary cell counterpart, as well as other designs, where the zinc anode side is just maximized to achieve a high battery life and where the excess of zinc has no functional use and thus represents no ecological and economical sustainability but rather a burden. Future developments should take this into account and devise resource-saving approaches in which the zinc species are truly cycled in a closed redox loop employing reversible oxidation and reduction processes instead of using an oversized zinc excess, which just masks this unsatisfactory situation. If this issue could be solved successfully it would allow for reducing the demand of zinc while aiming for much longer runtimes. Indeed, research into modification of the zinc anode in electrically rechargeable zinc-based battery systems has established its role in current research and is attracting considerable attention.^[43] To improve rechargeability further, the interface design at the metal anode should be given a special priority, where complete usage of zinc as well as the stabilization of zinc plating and stripping behavior during operation is of central importance. In addition to the zinc anode, the electrolyte has a significant influence on the interphase. However, the stability of the zinc in classical alkaline potassium hydroxide (KOH) electrolytes is distinctly limited and the electrolyte itself is not resistant to CO₂-containing air.^[44] This calls for an additional change of the electrolyte system, away from the widely used aqueous KOH since it undermines the concept of a rechargeable zinc–air battery by having no resistance to the intended operating conditions in ambient air. There are already promising candidates in the field of alternative electrolyte systems, such as zinc triflate or even zinc sulphate, which do not tend to form carbonate, but the development of a finely tuned overall system remains a challenge.^[44–46] Here, the mass transfer within the cell, especially at the interface anode/electrolyte/cathode should experience a stronger research focus, taking the battery operation under shortage of cell active materials into account.

In this perspective we will first focus on the elemental charging situation on the zinc anode side. Here we try to shine light on the importance of a proper understanding of the discharge processes occurring under low and high depth of discharge processes. This is followed by a critical discussion of issues related to aspects of reversibility on the electrode/electrolyte interface. Next, composition and electron household of

the electrolyte and how those affect rechargeability will be illustrated. Altogether, with this short perspective we try to focus on typical pitfalls which are eminent throughout the current literature and try to shed new light and a fresh look on currently overlooked aspects, which still bear enormous room for further improvements on achieving the overall goal of rechargeability in secondary zinc–air cells.

2. Assessing Rechargeability in Zinc–Air Battery

Looking at current reports in the field of rechargeable zinc–air batteries, one often finds cycling protocols over a multitude of hundreds of cycles and more. But such a large number of cycles imply directly, that it is a rechargeable zinc–air battery? On the contrary, one can theoretically achieve 100 discharge cycles if only 1% of the active material is consumed per cycle, even if the battery is not recharged. Of course, the number of cycles is a valuable measure for the quality of a battery, but the reason for rechargeability is solely founded on the reversibility of the individual anodic and cathodic partial reactions. The underlying fundamental reaction is the oxidation and reduction of zinc by means of oxygen from the environment. Due to the gaseous state and the inexhaustibility of oxygen, this rechargeability criterion must thus be approached by studies of the zinc anode behavior.^[47]

However, the clear verification of this reversibility criterion turns out to be problematic throughout the current literature since the assessment of rechargeability is often performed under conditions of shallow cycling (35 mWh cm⁻²_{geo}).^[17,48,49]

Indeed, shallow cycling makes the determination of rechargeability enormously difficult as illustrated in **Figure 2** schematically by the comparison of the cyclization of classical zinc metal anodes under a low depth of discharge as well as at high depth of discharge (see also Figure S2, Supporting Information, for real electrode images of the processes depicted in Figure 2).

Let us assume two zinc anodes of the same mass in an otherwise identical cell architecture within a zinc–air battery set up. Both batteries have an identical theoretical energy density **1**. One zinc anode with a thickness of 100 μm is operated up to a DoD of 1%, whereas the other 100 μm zinc anode is deep discharged up to a high DoD of 42%.

At low DoD, the zinc anode is only superficially oxidized, since, following the DoD, only 1 μm of the zinc anode is formally converted during discharge, which is why the morphology of the original electrode is largely preserved **2**. Due to the shallow depth of discharge, only a surface roughening of the anode is visible, which manifests itself in the formation of pores (Figures S3a–c and S7b, Supporting Information). The surface of the zinc anode is only slightly corroded and appears etched on a scale of a few micrometers (Figure S3d–f, Supporting Information). Thus, the low-DoD anode is still in a charged state after the discharge cycle due to an excess of metallic zinc present. A subsequent charge cycle does not lead to any further change in the bulk electrode morphology of the anode under low DoD, so that the zinc anode is almost pristine after a complete discharge–charge cycle **3**. In the charging process the previously generated pores are covered due to the

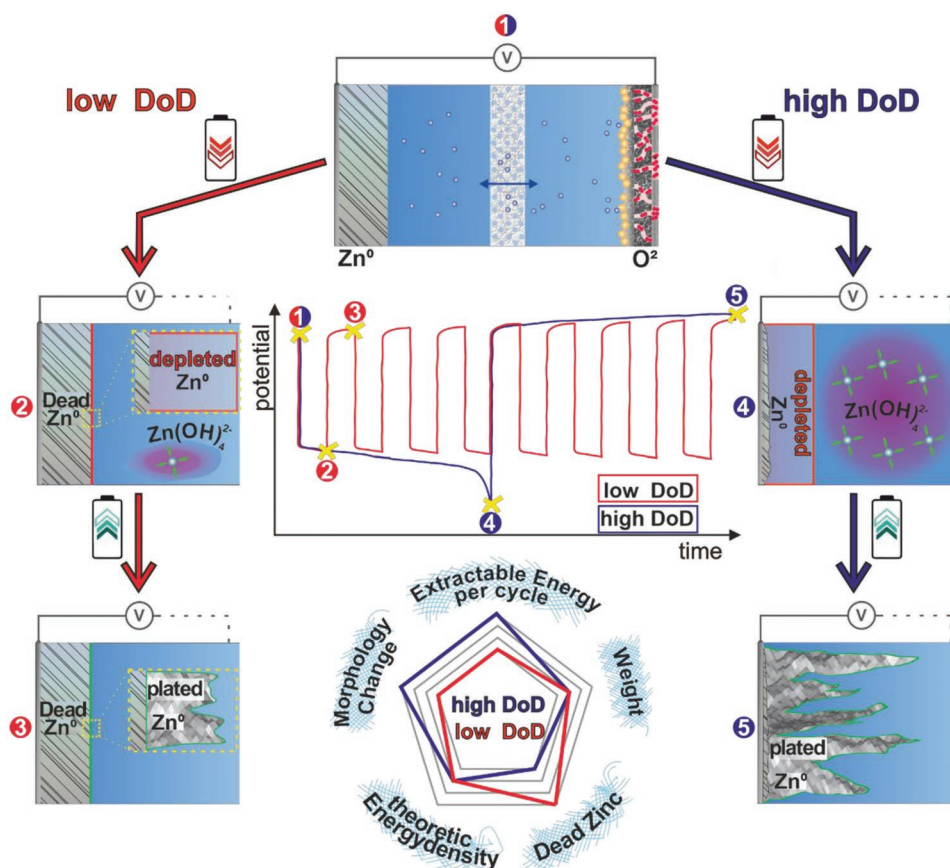


Figure 2. Schematic illustration of zinc metal anode behavior during battery operation under shallow and deep discharge. At low DoD, the zinc metal reacts only on the surface during discharge, a complete zinc conversion is not achieved, whereby the zinc anode shows only minor morphological changes and only the smallest amounts of zincate are formed in the electrolyte. In the potential–time diagram, cyclization at low DoD is characterized by a stable discharge plateau. In the following charge cycle, zinc plating again takes place only on the surface of the anode, whereby morphological integrity is maintained. Contrary to this, strong morphological changes of the zinc anode are to be expected in the discharge as well as in the charge cycle at desirable high DoD, which is accompanied by a strong zincate formation in the electrolyte.

zinc deposition and only slight irregularities can be observed on the surface with an axial elongation of less than 5 μm (Figures S4 and S7c, Supporting Information).

The presence of large quantities of metallic zinc even after a discharge cycle makes the determination of reversibility and thus rechargeability extremely difficult, since the formation of metallic zinc in the charging state is a benchmark for assessing reversibility, but not in this situation, where 99% of the state of charge is still available after the discharge cycle. In general, a decreasing discharge capacity as the number of battery cycles increases indicates a diminished reversibility. However, this drop of discharge capacity cannot be observed with the low-DoD anode, due to the zinc reservoir, which is considered inexhaustible under these conditions. Highly relevant at that point, is the fact that it cannot be determined whether the rechargeability is due to true reversibility or whether the zinc reservoir masks a possible limited rechargeability by continuously providing zinc from the reservoir electrode. Under shallow cycling conditions, it cannot be ruled out that the battery acts only as a primary zinc–air battery, as it cannot be determined exactly how much zinc is reduced. Thus, a stable cyclization protocol, as in shallow cycling, feigns a high degree of reversibility, which

is probably not existent to this extent. The widespread use of shallow cycling thus masks that the targeted recharge capability of current investigations is far from being achieved.

On the other hand, if the zinc anode is operated at a high DoD above 40%, the determination of rechargeability is not problematic, since the zinc anode suffers a discharge limitation. A further discharge of the zinc anode is thus impossible, as either the entire zinc reservoir is exhausted or electrochemically shielded by ZnO passivation. Thus, a charging cycle is inevitably required, which generates metallic zinc and ensures that zinc is available for a new discharge cycle. Based on the discharge capacity obtained, the reversibility and thus the true rechargeability can be determined unambiguously and precisely. This situation immediately raises the question why the majority of scientific studies on electrical rechargeability in zinc–air battery research are not conducted at high DoD? Might the zinc anode not be morphologically stable under these more realistic conditions? Indeed, an operation under full DoD conditions thus produces strong morphological changes in the zinc anode. This ranges from a significantly large mass loss in the discharge cycle, where the zinc species is bound in the electrolyte as zincate ($\text{Zn}(\text{OH})_4^{2-}$) ④, to an immense increase in

electrode roughness **5**. During the discharge of the high DoD anode where 42% of the total zinc mass is turned over, the morphology of the originally existing zinc anode inevitably changes and shrinkage due to massive zincate formation is observed. The zinc anode after deep discharge reveals an uneven contour line with thickness deviations of $\pm 50 \mu\text{m}$ resulting in an extremely roughened surface (Figures S5 and S7d, Supporting Information). Due to the severely changed morphology of the zinc anode at the end of the discharge, the subsequent charge cycle does not lead to a homogeneous distribution of the deposited zinc. Furthermore, the created unevenness promotes the tip effect during zinc plating, so that besides a clear anode shrinkage, a pronounced dendrite growth can be observed (Figures S6 and S7e, Supporting Information).

As a matter of fact, this instability of the zinc anode at high DoD has a clear effect on the cyclization, which can be observed in the corresponding potential–time diagrams. With increasing time, more and more zinc is oxidized and a passivating zinc oxide layer is built up, which restricts percolation paths creating this characteristic anodic overpotential (Figure S5c, Supporting Information). At low DoD, however, a stable discharge plateau is observed, indicating that the morphology of the zinc anode is unchanged from its initial state and a negligible amount of zinc oxide is formed (Figure S3a, Supporting Information).

Based on the potential–time diagram, it could be concluded that true rechargeability is only present at stable cycling. Does that indeed hold for a low DoD, certainly not! The zinc anode cycling at low DoD indeed shows a better cycling stability over a longer period of time. But at low DoD 40 discharge cycles compared to one high DoD discharge cycle are required to extract the same energy at the same current density. In this way, the low DoD anode avoids the degradation process by only allowing the battery to be used for a short time. Assuming a system-level specific energy of 450 Wh kg^{-1} ^[50] for a DoD of 42%, which is common for practical Zn–air cells, this implies that in the same cell system the reduction of the DoD to 1% to avoid anode degradation is reduced to a value of 10.7 Wh kg^{-1} . Tolerating such a low DoD precludes any practical application, since the specific energy is not competitive exhibiting an energy storage capacity less than 10% of conventional lithium-ion batteries (150 Wh kg^{-1}) or about one third of system-level lead-acid batteries ($30\text{--}50 \text{ Wh kg}^{-1}$).^[50,51]

This shortcoming poses severe consumer-related practical implications on the secondary zinc–air battery. As an example, for the typical usage of a cell phone with an average daily usage time of up to 4 h, the battery has to be charged eight or more times per day, when shallow cycling is applied with characteristic charging–discharging times of 30 min and less. And this despite the fact that there is more than enough zinc available to ensure a longer service life.^[52–61] Moreover, operating a zinc–air battery in low DoD mode also affects the cost per installed energy, which is a key driver in the development of rechargeable zinc–air batteries, as reducing the DoD does not reduce the mass of the zinc installed. Based on the cost of Electric Fuel Ltd.'s mechanically rechargeable zinc–air battery of $\$121 \text{ Wh}^{-1} \text{ kg}^{-1}$ (inflation adjusted),^[62] which provided a specific energy of 200 Wh kg^{-1} at a DoD of 80% (see Section 1), the potential costs for a high DoD of 42% and a low DoD of 1% are extrapolated.^[10] At a DoD of 42%, the costs increase to

$\$230 \text{ kWh}^{-1}$ and are thus in the order of magnitude of current lithium-ion technology, whereas the costs explode to an inconceivable $\$9680 \text{ kWh}^{-1}$ at a DoD of 1%.^[62]

Altogether, these circumstances do not vindicate operating a battery in low DoD mode to avoid anode degradation.

Obviously, the proportion of unused zinc in shallow cycling is enormously high, which is often justified with the good availability of the zinc metal and its low cost. However, most of the anode mass is inactive and must be carried along as dead-weight in any device. Consequently, the battery operation under shallow cycling cannot be regarded as a full-cell test, but rather represents half-cell conditions because the zinc anode can be seen as inexhaustible and redox chemistry occurs only at the interface region of the metal surface under low conversion efficiency. It becomes more and more clear that cyclization of zinc–air batteries under high DoD should be recommended to allow reliable statements about rechargeability.

3. Interface Engineering as Key to Improved Rechargeability

The morphological changes of the zinc anode in the course of the battery operation pose an immense problem toward a stable and thus reversible cyclization. The solid/liquid anode–electrolyte interface plays a crucial role here. A comparison of the cyclization under opposing conditions of low and high DoD is intended to highlight the importance of this interface on the rechargeability. The analysis is particularly based on the zinc oxide produced, which is an important influencing factor in the anode–electrolyte interface. Going further, we believe that the classical Zn/ZnO/KOH electrolyte interface represents a bottleneck toward rechargeability and currently prevents much-needed further investigations under real operating conditions for zinc–air batteries (Figure 3).

If the depth of discharge falls below a value of 1%, the surface of the zinc anode is only oxidized on the outer surface of the metal foil, so that the potentially formed ZnO layer is lower than the critical size for passivation of $2 \mu\text{m}$ ^[63] and the KOH electrolyte is able to transfer the small amount of the zinc species directly into solution. The corresponding zinc anode shows no indication of a ZnO layer formed after a single discharge at a low DoD of 1%. Explicit, the low DoD anode refreshes itself immediately and automatically, so that in the subsequent charge cycle the zinc can be deposited unhindered on a metallic, electrically conductive surface (Figure S3, Supporting Information).

As the depth of discharge increases, so does the thickness of the zinc oxide layer. At a high DoD of 42% the zinc anode is fully covered by a highly developed zinc oxide layer, which forms a massive passivating shell over large areas (Figure S5c,g, Supporting Information). In the particular case of a $100 \mu\text{m}$ zinc metal anode, at a DoD of 42% more than 0.5 mmol mL^{-1} of the zinc is formally transferred into the soluble zincate species, thus exceeding the solubility and promoting ZnO passivation. Considering a static electrolyte, the zincate species is subject to a concentration gradient with the maximum in the vicinity of the zinc anode, which further increases the local zincate concentration and thus extremely favors the zinc oxide formation.^[64]

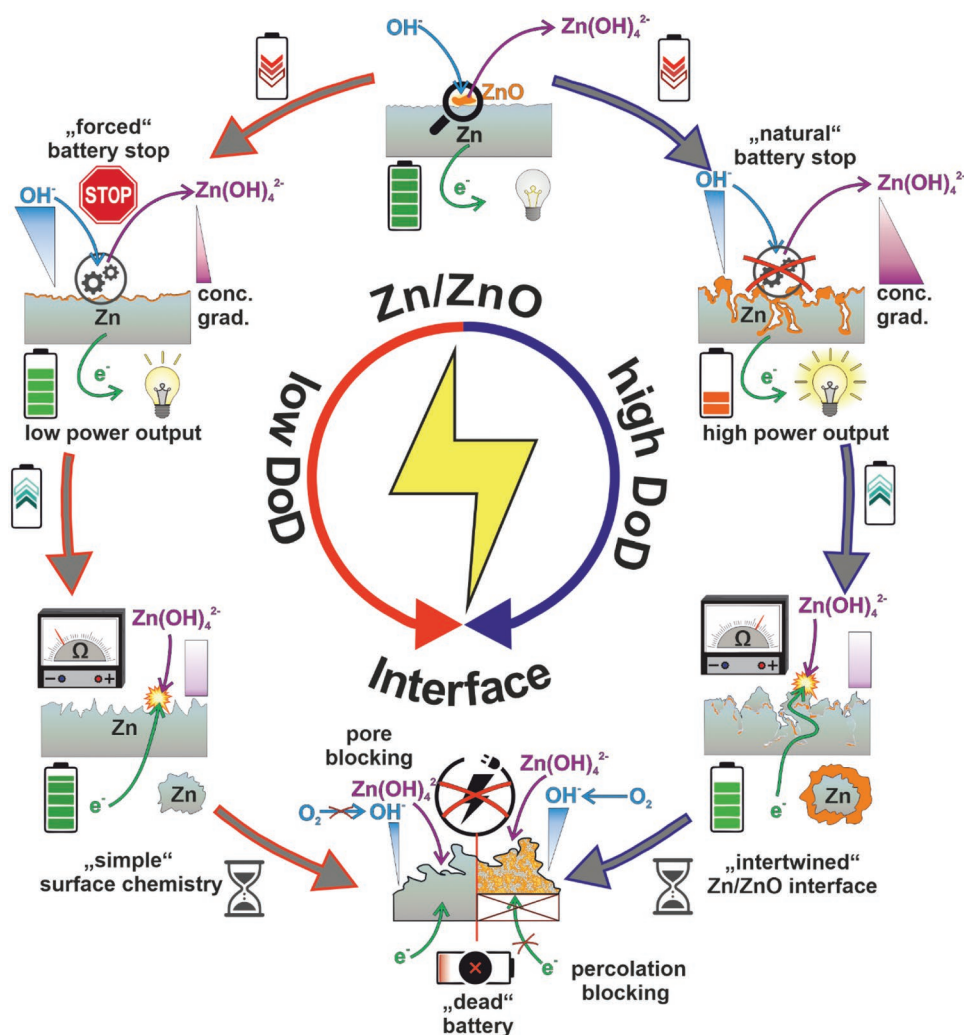


Figure 3. Graphical overview of the Zn/ZnO interface of a zinc anode at low DoD as well as at high DoD. Under shallow cyclization conditions, no distinct Zn/ZnO interface is to be expected (low DoD half cycle). The predefined cycling protocol stops the discharge, the energy drawn is comparatively low and the battery has lost little of its original state of charge and is still almost fully charged. At high DoD, a massive formation of a passivating ZnO layer can be observed which ultimately stops discharge naturally due to an intrinsic inhibition of the anode. The energy extracted clearly exceeds that of the anode at low DoD, so the state of charge of the battery has dropped drastically at high DoD. The charge cycle at low DoD does not lead to the formation of overpotentials. Ultimately only metallic zinc is present in the charged state, whereas at high DoD the overpotential increases because a Zn/ZnO interface remains intact after charging. This reduces the percolation pathways. Long-term cyclization leads to a morphologic change of the zinc anode even at low DoD, but this does not involve drastic restriction of electron conduction, as is the case with the formation of a complex Zn/ZnO interface at high DoD. With both low and high DoD, further cyclization is not possible. At low DoD, due to the longer service life, the carbonate formation blocks the oxygen diffusion through the gas diffusion electrode, whereas at high DoD, the Zn/ZnO interface significantly prevents further cyclization.

Within the discharge time, the alkaline electrolyte is now no longer able to remove this amount of zinc oxide from the electrode by means of zincate formation. The surface of the high DoD anode, right before the charge cycle is thus characterized by a significant Zn/ZnO interface (Figure S5b, Supporting Information). At this junction the zinc deposition in the charging step is diminished due to the reduced electrical conductivity of the present ZnO. Consequently, the zinc deposition during charging preferentially takes place on the electrically conducting metallic surfaces, which result in an inhomogeneous distribution of the zinc species (Figure S6a,b, Supporting Information). Due to the extensive thickness of the passivation of up to 50 μm , which arose by discharging a 100 μm zinc anode

up to a DoD of 42%, the critical size of passivation is clearly exceeded (Figure S6c, Supporting Information). As a result, not all the previously generated zinc oxide can be converted into metallic zinc in the reduction process during charging, since a large portion of the zinc is not electrically contacted due to the low electron conductivity of ZnO. Moreover, it cannot be ruled out that certain metallic zinc areas are encapsulated by zinc oxide, resulting in a formation of Zn/ZnO core-shell morphology as consequence.^[65,66] This means that individual areas are no longer accessible for the electrochemical processes and the Zn/ZnO interface becomes more fragmented and complex, which ultimately leads to a brittle, pulverized and thus destroyed zinc anode (Figure S6e, Supporting Information).

Inevitably, the formation of these Zn⁰/ZnO domains leads to a diminished utilization of the zinc reservoir. This leads to the conclusion, that the zinc anode consisting only of a simple metal sheet should not be used in the high DoD range without further ado, as the degradation processes do not permit any deep discharge.^[44]

The gradual degradation of the zinc anode can be detected by the formation of overpotentials that evolve due to reduction of the percolation pathways along the Zn/ZnO interface.

By contrast, a significantly lower overpotential occurs at low DoD, which allows a direct correlation to lower electrode degradation, primarily by preventing increased ZnO formation.^[63] The supposedly higher stability of the low DoD anode is not an indication of an increased rechargeability. Rather, the degradation mechanisms have too little influence at this low conversion rate of zinc oxide, so that they can be neglected for the most part.

Nevertheless, this behavior is once again not a solution toward the development of rechargeable zinc–air batteries but even covers up real problems of anode degradation that need to be solved. But it may give a clue, why the assumed reversible surface chemistry of the battery operation at low DoD is most often chosen to demonstrate the excellent activity of the bifunctional catalyst in a rechargeable zinc–air battery. In doing so, the aspect of rechargeability is insufficiently investigated.

In 2018, Parker et al. already defined a minimum standard of the depth of discharge of 20%, based on zinc, in order to achieve a technologically relevant threshold at all.^[47] Extensive disregard even of this moderate limit of rechargeability once again shows that current investigations are far from a breakthrough. Furthermore, this also shows that the further development of rechargeability of the zinc–air battery is currently to a large extent limited by the zinc anode and no longer by the bifunctional catalyst.

Despite these facts, there is light on the horizon. Currently there have been some new approaches introduced aiming at improving the rechargeability through innovative concepts to mitigate the degradation processes at the zinc anode. In this context, studies have gained importance in which the anode/electrolyte interface has been redesigned by developing ZnO/carbon composite anodes that show minor degradation phenomena compared to classical zinc anodes. A critical role in these models is played by the migration of zincate species away from the vicinity of the zinc anode into the electrolyte volume, whose prevention is a task of these anodes. The two most important types are just mentioned very briefly. On the one hand, physical retention by size exclusion is achieved by means of an anion-exchange ionomer, which at the same time ensures good hydroxyl ion diffusion. Thus, a controlled environment for reversible conversion of metallic zinc to zinc oxide and vice versa is created. On the other hand, highly porous ZnO/carbon composites are being developed, in which the embedding of ZnO into carbon (C) minimizes the diffusion of the zinc species and thus significantly improves the rechargeability. The carbon scaffold is not morphologically changed during cyclization and does not lead to the formation of a complex intertwined Zn/ZnO interface. This and similar work are currently the cornerstones which have advanced our fundamental understanding of rechargeability in zinc–air batteries.^[63,64,67,68]

4. Developments in Electrolyte Systems Promoting Rechargeability

The KOH alkaline electrolyte remains the medium of choice in the majority of current investigations up to date, despite its well-known triggering of carbonate formation by atmospheric CO₂ and the problematic effect this has on the lifetime of the battery. Furthermore, the KOH electrolyte is so aggressive that it corrodes the zinc anode and therefore prevents significant progress in developing rechargeable zinc–air batteries, since the corrosion of the zinc anode leads to an incessant removal of zinc into the electrolyte volume. This occurs directly after the battery assembly without a load being connected, so that an excess of zinc seems unpreventable to buffer the zinc corrosion while maintaining battery operation.^[44] For a better understanding, this process can be compared to a leak in the fuel line of a passenger car. While this comparison may be misleading in terms of the fact that there is no actual leakage. So there is no actual zinc removal from the semi-open battery system, but since the zinc plating efficiency in the KOH electrolyte is so low, zinc is ultimately irreversibly removed for further battery operation. Again, an oversized zinc anode masks problems associated with the low chemical resistance of zinc by having a sufficiently large metal reservoir to compensate this drawback. If alternatively, a limiting zinc anode is used, which does not include excess zinc, the combination of zinc and the KOH electrolyte becomes a substantial obstacle for the operation of a rechargeable battery. Rather, this massive impairment of rechargeability by the KOH electrolyte suggests the necessity of a change in research direction for the entire electrolyte system.

In this context, the recently introduced use of zinc triflate as a conductive salt can already be regarded as a game changer in zinc–air battery research.^[44,46] Both carbonate formation and zinc corrosion are completely eliminated by the zinc triflate electrolyte and, on top of that, the new electrolyte system enables an exceptionally high reversibility of the redox reaction. To this end, the zinc triflate electrolyte breaks new ground in this field by re-modeling the battery system using zinc peroxide chemistry.^[44] All this comes at a price, due to the now prevailing zinc peroxide chemistry that proceeds through a two electron (2e⁻/O₂) process, new requirements are placed on the catalyst at the cathode. The tediously optimized four electron oxygen electrocatalysts prove unsuitable due to the now important ZnO₂-chemistry present with this electrolyte.^[44] Consequently, two electron catalysts, which are being intensively researched for the production of hydrogen peroxide, are the sought after catalysts, now.^[44,69–73] However, the necessary turnaround by changing the battery chemistry is extremely rewarding and triggers a paradigm shift in research on secondary zinc–air batteries.

To illustrate the potential of the novel zinc triflate electrolyte in zinc–air batteries, a comparison of the zinc triflate electrolyte with the state-of-the-art alkaline KOH electrolyte is intriguing (Figure 4).

For this purpose, we investigated the rechargeability of zinc anodes in a discharge–charge–discharge sequence in a zinc–air cell. Here, the anode consists of a metallic zinc layer with a thickness of 1 μm (high DoD), respectively, 100 μm (low DoD) and is operated against a benchmark catalyst. The catalyst

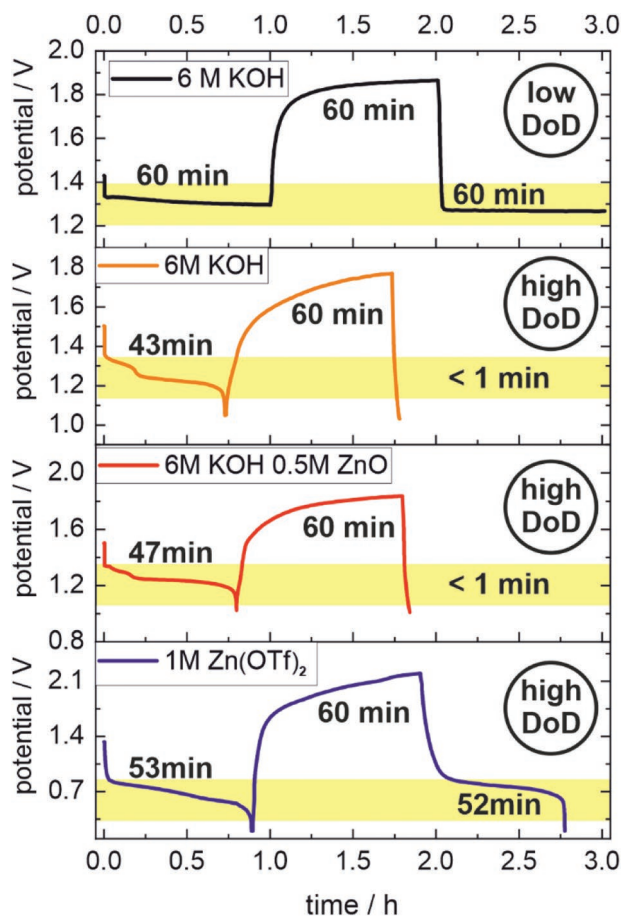


Figure 4. Discharge–charge–discharge sequence of zinc anodes in KOH and zinc triflate electrolyte systems in comparison. The benchmark Pt/C and Ir/C (in aqueous KOH electrolytes) and activated carbon (in aqueous Zn(OTf)₂ electrolyte) were used as catalyst in an otherwise identically cell design and experimental conditions.^[64] Whereas in the first discharge cycle a discharge capacity in all four investigated zinc anodes is observable, with the KOH electrolyte only at low DoD an discharge plateau is detectable in the second cycle. At high DoD no extractable capacity is identifiable with the KOH electrolyte at all, which indicates poor reversibility. Increasing the Zn²⁺ concentration in the KOH electrolyte by saturation with ZnO does not enhance the zinc plating efficiency. On the other hand, the zinc triflate electrolyte allows most complete reversibility even in the second discharge at high DoD, in that 86% of the input energy can be recovered again.

is composed of a physical mixture of platinum (Pt/C) and iridium (Ir/C) on a carbon support for the KOH electrolyte or activated carbon (see the Supporting Information) for the zinc triflate electrolyte. A different electrode thickness was chosen to keep both the current density and the discharge time constant in order to create comparable reaction conditions while still realizing different depths of discharge. Since Zn²⁺-ions are inevitably present in the zinc triflate electrolyte, which can influence the experiment, the rechargeability in ZnO-saturated KOH electrolyte was also considered to modulate a Zn²⁺-environment in the KOH electrolyte. The Zn reservoir is completely consumed in the case of the limiting anode at a high depth of discharge (DoD) of 100%, whereas a low depth of discharge of 1% is adjusted at the 100 μm zinc anode.

The widely used metallic zinc anode, which is operated in 6 M KOH electrolyte at low DoD, shows the well-known decent discharge and charge plateaus. According to the preset specifications, charging and discharging take place for 1 h each. Now, if a zinc anode is operated under the exact same conditions at high DoD, it can be seen that a significantly shorter discharge time of 43 min is obtained in the initial discharge, whereby a discharge time of 1 h was aimed at on the basis of the deposited zinc reservoir. This shows the parasitic zinc corrosion within the KOH electrolyte, which leads to the loss of active material reducing the discharge time considerably. As there was no zinc left on each electrode after the first discharge at high DoD, the difference in discharge time must be due to a reduced amount of zinc in both KOH-based systems. Therefore, the zinc must have been corroded by the KOH electrolyte and a part of the zinc has been dissolved of the electrode before the cell was put into operation. A further comparison of the high DoD anodes shows that the pure 6 M KOH electrolyte attacks the zinc most aggressively, whereas the saturation of the KOH electrolyte with ZnO weakens the etching of the zinc so that the zinc triflate electrolyte shows the highest compatibility with the zinc anode. So, in case of a typical KOH electrolyte less zinc was available for the discharge and the discharge time is consequently reduced.

Now, since all the zinc is oxidized at the limiting anode at high DoD in the discharge cycle, the reversibility clearly determines the rechargeability. As a discharge capacity can only be obtained in the second cycle if the reaction is reversible, then the ratio of charge to discharge time is a measure of reversibility. The second discharge cycle thus reveals the differences between low and high DoD mode and gives an unvarnished insight into reaction reversibility and rechargeability. While at low DoD a second discharge capacity in the KOH electrolyte is easily obtained, which is in the order of magnitude of the initial discharge, at high DoD no discharge capacity can be obtained in the 6 M KOH electrolyte despite a 1 h charge. On the one hand, this reveals the insufficient reversibility of the system based on KOH electrolyte and zinc anode, on the other hand it manifests the situation, that an excess of zinc feigns reversibility and thus masks the rechargeability. Even the addition of Zn²⁺ ions into the KOH electrolyte to increase the plating efficiency by enriching the electrolyte with ZnO until the zincate saturation concentration is reached, does not alter the reversibility behavior in the KOH electrolyte. In sharp contrast to this finding, the zinc triflate electrolyte shows that rechargeability and thus reversibility is feasible, with the discharge time of 53 min after a 1 h charge time, reflecting an 86% efficiency. This illustrates that the addition of Zn²⁺ species alone does not enable reversibility but instead indicates the specific role of the counterion in the conducting salt. Indeed, the zinc triflate electrolyte affects the solvation of zinc ions by its spatial expansion of the bulky CF₃SO₃⁻ anion, highlighting the special role of the solid/liquid interface between the electrode and the electrolyte. In case of the aqueous zinc triflate electrolyte, which can be understood as a solution of a zinc salt in water, forming a hexa-aquo [Zn(H₂O)₆]²⁺ species in the primary conductive sheath layer.^[44,74] The presence of the CF₃SO₃⁻ anion reduces the number of water molecules surrounding the Zn²⁺ cation, thus diminishing the solvation effect while facilitating Zn²⁺

transportation and charge transfer during charging.^[75] Hence, the use of the zinc triflate electrolyte increases the reversibility and the rechargeability of the zinc–air battery. An almost opposite scenario is evident for the zinc species found in the alkaline aqueous KOH electrolyte. In the discharged state, the zinc component is dissolved in the electrolyte as tetrahydroxozincate $[\text{Zn}(\text{OH})_4]^{2-}$ species. Following a model of Bockris, the reduction of the zincate proceeds stepwise during the charging process from $\text{Zn}(\text{OH})_4^{2-}$ via $\text{Zn}(\text{OH})_3^{1-}$, $\text{Zn}(\text{OH})_2^{1-}$, $\text{Zn}(\text{OH})$ to metallic zinc. According to Sharma and Reed, who suggested that both OH^- and H_2O serve as ligands for the zinc ion, $\text{Zn}(\text{OH})_2(\text{H}_2\text{O})_2$ as well as $\text{Zn}(\text{OH})_3(\text{H}_2\text{O})^-$ are feasible soluble zinc species in addition to the known $\text{Zn}(\text{OH})_4^{2-}$. As a result, the number of water molecules surrounding the zinc ion increases during charging, apparently causing an enhanced solvation effect that reduces reversibility and thus rechargeability.^[76,77]

Despite the immense upheaval in the entire battery system, the triflate electrolyte paves the way to rechargeability by significantly extending battery life, so neither carbonate formation nor aggressiveness or even detrimental effects toward the metallic zinc remains a problematic issue.^[44] Although the zinc triflate electrolyte has only recently been introduced into the field of rechargeable zinc–air batteries, zinc triflate is already widely used as an electrolyte in zinc-ion battery research.^[78–96] By using the zinc triflate electrolyte for zinc–air batteries, a change from OH^- ion conduction to Zn^{2+} ion conduction is carried out, as is the case with the zinc-ion battery. The combination of a zinc anode, a Zn^{2+} -containing electrolyte and a gas diffusion cathode can therefore be understood as a hybrid technology of zinc–air and zinc-ion battery, allowing to exploit the advantages of both battery systems. We believe, the hybrid derivative combines the long-life cyclability of a zinc-ion battery with the inexhaustible oxygen cathode of the zinc–air battery to form a rechargeable battery with high energy density.

Nevertheless, even the employment of mild electrolytes is not the keystone in the development of rechargeable zinc–air batteries, but raises at least as many questions as it solves existing problems. In the case of the zinc triflate electrolyte with peroxide chemistry, the deposition of zinc peroxide (ZnO_2) on the gas diffusion electrode is a critical issue. Although this ZnO_2 formation is to be reversibly dissolved during the charge process, the problem arises of how much zinc peroxide the gas diffusion electrode can hold until it is blocked. Besides, ZnO_2 is a strong oxidizing agent that can corrode the gas diffusion electrode and thus can cause cell failure. Also, on the part of the catalyst there are challenges to be encountered, first and foremost a deceleration of the reaction kinetics, which is highly detrimental to the formation of overpotentials for an aqueous battery system. If no suitable bifunctional catalysts are on hand to boost the reaction kinetics, the intensified hydrogen evolution leads to a steady drain on the electrolyte and carbon corrosion at higher charging potentials affects the vulnerable gas diffusion electrode, which seriously limit the battery life.^[97] Since the range of potentially suitable catalysts for the two-electron oxygen reduction reaction (ORR) is much more limited than for four-electron ORR, the selection of a catalyst tailored to the system is challenging to avoid cell dry out. The supposedly experimental straightforward solution of increasing the electrolyte volume is not recommended since this is followed by a

drastic reduction of the specific energy by increasing the total mass of the battery without any appreciable energy gain.

5. A View on Cell Design

Due to the inexhaustible open cathode, in which molecular oxygen, does not contribute to the total weight of the cell, metal–air batteries like the zinc–air battery, are a forward-looking technology for lightweight applications, especially in portable devices. As a result, cell design is a broad field of research that is subject to a constant optimization in order to adapt the battery system to a wide variety of external conditions. In this context, concepts of flexible batteries are increasingly studied, which includes the cell design of zinc–air batteries.^[98–104] Despite the manifold of zinc–air battery cell types, most of them share a similar shortcoming, the use of an excessive zinc anode, which can certainly be attributed to the previously discussed KOH-based electrolytes. Again this, severely limits further development.^[101–104] Many of these cell concepts, despite their different geometries, face similar challenges in optimizing the interface between the anode and the electrolyte. For a better comparison, the following consideration of the influence of cell design on the rechargeability in zinc–air batteries will focus on two very prominent cell setups, which dominate current research, the stack cell, and the coin cell. However, elaboration is by no means to be applied only to the stack and coin cell, but should rather be understood as a generally applicable guideline in the development of a wide variety of cell types, also including flexible and solid-state devices. (Figures 5 and 6). Both, flexible cell designs as well as solid-state electrolytes are of particular interest for zinc–air batteries. The incentive for the development of flexible battery systems for zinc–air batteries is evident, since the actual cathode material, oxygen, does not contribute to the total weight and can thus be understood as a lightweight energy storage device. Because of these lightweight properties, zinc–air batteries are a serious technology for portable energy storage, which can also be close to the body and should therefore adapt to the external contours, for example when in motion. In the current scientific discourse, a wide variety of potential flexible battery systems is apparent, ranging from simple setups to demonstrate battery operation at different bending angles to elaborate battery concepts with custom-developed fiber-shaped oxygen electrode architectures and zinc anodes tailored to them.

The design of the stack cell can be described in simple terms by lining up the individual cell elements with intermediate planar housing components, which provide both the electrolyte volume and sufficient mechanical stability so that the cell seals itself against leaking electrolyte during assembly by pressing and screwing the individual components together. Owing to this cell structure, only a small proportion of the active material, primarily the zinc anode, have access to the electrolyte and can therefore participate in the electrochemical process (Figure 5).

Again, this overdimensioning of the zinc anode makes it unrealistic to determine the specific capacity and even more so the energy density of the entire system. Since all the installed components contribute to the total mass of the battery, the inactive mass will unnecessarily skyrocket. Therefore, it is almost

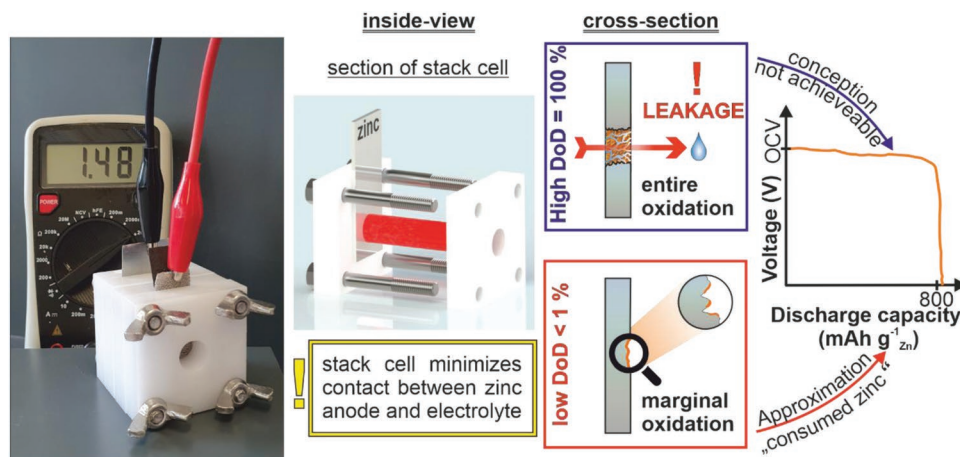


Figure 5. Photographic and schematic depiction of a zinc–air cell in the stack-cell type. The inside view of the cell shows the contact surface of the zinc anode, which is in physical contact with the electrolyte and is therefore referred to as electrochemically active area. The schematic comparison of the zinc anode at high and low depth of discharge reveals the disadvantages of the stack cell. A 100% DoD with full dissolution of the zinc anode is equivalent to a leakage of the cell and proves to be extremely unsuitable. At low DoD, it is only possible to determine the actual discharge capacity by referencing the consumed zinc, which represents only an approximation for determining the rechargeability.

essential that the entire zinc reservoir is able to come in contact with the electrolyte, thus maximizing the interface between the electrode and the electrolyte. This conceptual problem may require sufficient sealing within the stack cell to prevent unintentional electrolyte spillage.

Nevertheless, the operation of a stack cell poses further problems for current research on electrically rechargeable zinc–air batteries, which require a fundamental recap and revision of the cell design. Here, too, the type of cyclization plays a more decisive role in the development of the cell design again emphasizing a pronounced difference between low and high DoD.

At high DoD, the problem is as simple as it is fatal (Figure 5). If the DoD exceeds a threshold value of 40%, at which a porous zinc anode is obtained that shows a perforation in the order of several 100 μm , leakage is the inevitable consequence. This eliminates the simultaneous use of the zinc anode once as an active material, but also as a current collector to the greatest possible extent for deep discharging. For classic zinc metal anodes it is not guaranteed that the zinc is removed evenly over the complete cross-section thus preventing pitting corrosion by controlling the depth of discharge. The use of a current collector, as is common in many battery systems such as the lithium-ion battery, seems advisable, if a high depth of discharge is aimed for. Certainly, the external, non-zinc based, current collector can be understood as extra weight, which lowers

the specific energy and would increase the Zn-ion deposition barrier, so the zinc excess could just as well function as the current collector. But this would result in the sacrifice of deep discharge. Thus, the benefits of an external electrochemically stable current collector clearly outweigh the downside of introducing an additional dead weight.

Consequently, the present stack cell type cannot be used for realistically operated secondary zinc–air batteries. Certainly, the scenario of complete oxidation across the entire cross-section of the anode is not realistic due to the shielding and passivation properties of ZnO with typically used zinc foil anodes. However, the complete conversion of the accessible zinc must continue to be the ultimate goal of a rechargeable zinc–air battery. This requires a compelling revision of the present stack cell concept.

Numerous studies have calculated the specific discharge capacity on the basis of the so called “consumed zinc” instead of using the total mass of the installed zinc plate when using stack cell, as it is common practice in battery research.^[54,105–115] The discharge capacity in the “consumed zinc”-approximation is not determined by battery cyclization but by discharging the cell once. The capacity obtained can be taken from the discharge curve, which is shown schematically in Figure 5. Here, the voltage drop indicates the end of the discharge. However, this drop in the potential does not mean that the cell is already

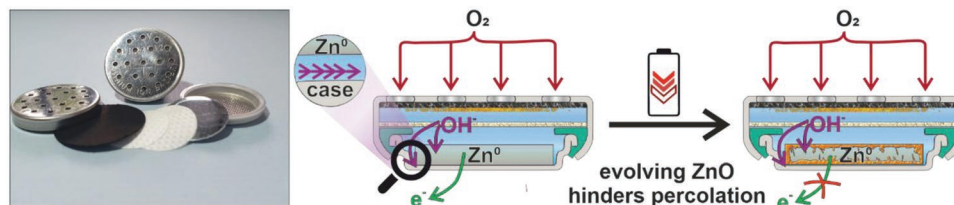


Figure 6. Graphic illustration of a zinc–air cell in coin cell configuration. The coin cell is advantageous over the stack cell because the compact design guarantees a high energy density by limiting the electrolyte volume. Also the coin cell case encloses the entire zinc reservoir in the cell and thus allows the electrochemical reaction access to the anode. The large contact area of the electrolyte with the zinc anode also has disadvantages, e.g., the coin cell architecture does not shield the zinc anode against oxidation.

completely discharged but that no more zinc is available for the electrochemical reaction. The formation of a passivating ZnO layer is the main reason for the termination of the battery operation (see Section 3), whilst further active zinc material is still present.

Based on the mass difference of the zinc anode before and after the single discharge, the specific discharge capacity for the “consumed zinc” is obtained. The determination of the mass of the consumed zinc is not clearly defined and holds pitfalls. On the one hand, the zinc oxide formed counts as consumed zinc, which in principle increases the total mass of the zinc plate. On the other hand, the amount of zincate generated, which is in solution and generally reduces the mass of the zinc plate, also counts as “consumed zinc.” To determine, the actual consumed zinc, i.e., zinc converted by the electrochemical reaction, the ZnO formation and the zincate conversion counteract each other in terms of mass. This makes it non-trivial to determine the exact amount of zinc consumed. Nevertheless, values in the order of magnitude of the theoretic capacity of zinc are exclusively obtained, suggesting that zinc has been completely converted. However, this is not the case. Rather, it merely indicates that the amount of zinc that has been electrochemically oxidized, was converted without electron-consuming side reactions, which is not surprising considering the low turnover. Since side reactions usually only come into play with increasing anode degradation at elevated DoD as we have shown before. The value of information for evaluating the rechargeability based on the “consumed zinc”-approximation is limited due to a tremendously unrealistic assumption. Correctly, this test is declared as a primary cell test, but many reported results suggest excellent battery performance without providing valid proof of it. Despite the discharge capacity is an important criterion for assessing the performance of a battery, currently too little attention is given to the discharge capacity curve over a large number of cycles in zinc–air battery research. However, it is this discharge capacity over time that allows a quick and valid assessment of the battery performance.

In order to assess the reversibility of processes taking place under real operating conditions, it is essential that the entire zinc reservoir is completely present inside the cell and is in contact with the electrolyte in ionic form and contacting the current collector electrically. From this point of view, the coin cell, which is also frequently used, represents an actual optimization, because here, the entire zinc reservoir is located in the cell and is in contact with the electrolyte.^[116–125] However, the coin cell setup also causes problems in the operation of the zinc–air battery and is not to be advocated without further ado. The schematic cross-section of a zinc–air battery in coin cell configuration illustrates the problem originating from the extensive contact between zinc anode and the electrolyte in such a configuration (Figure 6).

In a typical coin cell architecture, it is not possible to prevent a back side contact of the zinc anode facing the cell housing with the electrolyte. Therefore, zinc oxide also forms at the interface case/anode. Consequently, the electron flow is inhibited by the lack of sufficient percolation pathways and the cyclization is terminated although the zinc reservoir is not yet exhausted. Thus, it must be stated that the stack cell as well as the coin cell type, although used proves to be

extremely unsuitable for investigations of rechargeability, when zinc turnover is high and the respective zinc oxide formation is massive.

However, there are solutions that try to overcome these obstacles. So in the case of the coin cell, the infiltration of the electrolyte in-between all void spaces is prevented by introducing, i.e., a thin flexible layer made of PTFE to isolate the contact space between the stainless steel housing and the current collector.^[126,127] Nevertheless, this structure is not widely used, which is certainly due to the non-trivial arrangement and alignment of the individual layers. However, future research should take into account the uncontrolled oxidation of the zinc anode and take precautions to ensure that the current is supplied and distributed continuously during operation irrespective of the reactions taking place. However, not only passivation affects the cell design, which is predominantly found in alkaline aqueous electrolytes, but also the zinc plating, which is significantly more prevalent in mild Zn²⁺-containing electrolytes requires an adaptation of the cell design. Especially in zinc–air batteries, which feature a well-balanced zinc anode, one must take into account that the deposition of the zinc from the electrolyte also influences the zinc reservoir. This inevitably leads to the need for surface sealing of all metallic or electrically conductive components in contact with the electrolyte, so that the zinc deposition can be exclusively on the active material and not on other auxiliary components, i.e., current collector or contact aids (springs). Since the zinc reservoir in well-balanced zinc anodes is ideally designed for the intended use for instance in terms of energy storage capacity, codeposition of the zinc from the electrolyte leads to deviations and must be controlled and taken into consideration when calculating performance parameters.

Yet, the development of electrically rechargeable zinc batteries lacks a uniform and widely accepted prototypical cell system, which could serve as a standard on a laboratory scale, that would allow better comparability of research results while simultaneously circumventing the pitfalls of coin and stack cell. The Swagelok-cell, which has been approved for lithium-ion batteries as a standard test cell on a laboratory scale, offers a solid working basis for future cell development, as it fully integrates the zinc anode into the cell system and thus enables maximum contact with the electrolyte, while at the same time keeping the electrolyte volume low. Individual modifications of the Swagelok-derived cell as a prototype standard have recently been devised and show promising properties to further advance the development of electrically rechargeable zinc–air batteries.^[44,64]

6. A Promising New Twist: Sophisticated Anode Concepts on the Advance

Looking at the development of rechargeable zinc–air batteries, we have outlined before that simple zinc metal anodes show decisive disadvantages in the further development of high-performance zinc–air batteries. However, zinc metal anodes are still preferentially favored in current studies, which are difficult to comprehend due to the known anode degradation.

Why is the current zinc–air battery community still sticking to classic zinc anodes?

One possible explanation for this discrepancy becomes clear by comparing the zinc–air battery with the quite similar zinc-ion battery (ZIB), which has to overcome largely the same challenges on the anode side. However, and in contrast to the zinc–air battery a multitude of innovative anode concepts are already known for the zinc-ion battery and the development of sophisticated approaches to overcome anode degradation is a virulent field in research.^[43,128,129] Here, in the development of new anode concepts for ZIB, some basic principles can be identified which have the shared purpose of solving the major issues of zinc anodes, i.e., dendrite growth, corrosion, and hydrogen evolution reaction. These unique approaches not only focus on the anode but also consider the interface between electrode and electrolyte, therefore advanced electrolyte optimization is also progressing rapidly. Among other things, emphasis is placed on the redistribution of the electric field, the regulation of surface binding energy, or the weakening of the solvation effect (Table S1).

It is very likely that the reason for the advanced development stage of the zinc-ion battery is probably since the ZIB, in comparison to the zinc–air battery, is not operated with a highly corrosive electrolyte that attacks all zinc species present in the device, but rather relies on chemically mild Zn^{2+} electrolytes. Consequently, the development of elaborate new anode concepts for zinc–air batteries is severely limited by the alkaline KOH electrolyte, whereby a constant loss of active material had to be compensated by an oversized zinc reservoir. If alternatively, a limiting zinc anode with a reasonably designed zinc reservoir is used, anode degradation mechanisms must be strictly prevented, as these cause a reduction of active mass and

thus have a drastic negative impact on the energy density of the cell. For example, nanoscale metallic zinc materials are less suitable in KOH electrolytes as potential active material, since complete oxidation of active material occurs immediately after cell assembly, due to the small particle size and the aggressiveness of the KOH electrolyte. Here, the critical size of passivation is hypothesized to be $\approx 2 \mu\text{m}$.^[63] Not only metallic zinc, but also ZnO-based anodes are depleted by the electrolyte, which further restricts the variety of potential anode materials.

Considerable improvements could already be achieved through elaborate anode concepts, in which a zinc sponge anode achieved a depth of discharge of $>90\%$ in a primary cell test after a single discharge and a DoD of 40% with high rate cyclization, even though a KOH electrolyte was used.^[130] Nevertheless, the difference in DoD achieved between the single discharge and the cyclization tests indicates that passivation still remains a challenge in porous electrodes and reversibility is not yet satisfactory in KOH electrolyte. Consequently, purely metallic, porous zinc anodes do not solve the underlying problem in its entirety.

Since electrode passivation plays a subordinate role in the new Zn^{2+} electrolyte systems such as the zinc triflate electrolyte, as can be seen from the high zinc utilization ratio of up to 83.1%, the development of sophisticated anode concepts will experience a real upswing due to the use of these electrolyte systems.^[44]

However, these Zn^{2+} -containing electrolytes might require a revision of the zinc–air battery due to a complete change in the plating and stripping behavior during battery operation. Here classic zinc anodes suffer from a clear disadvantage (Figure 7).

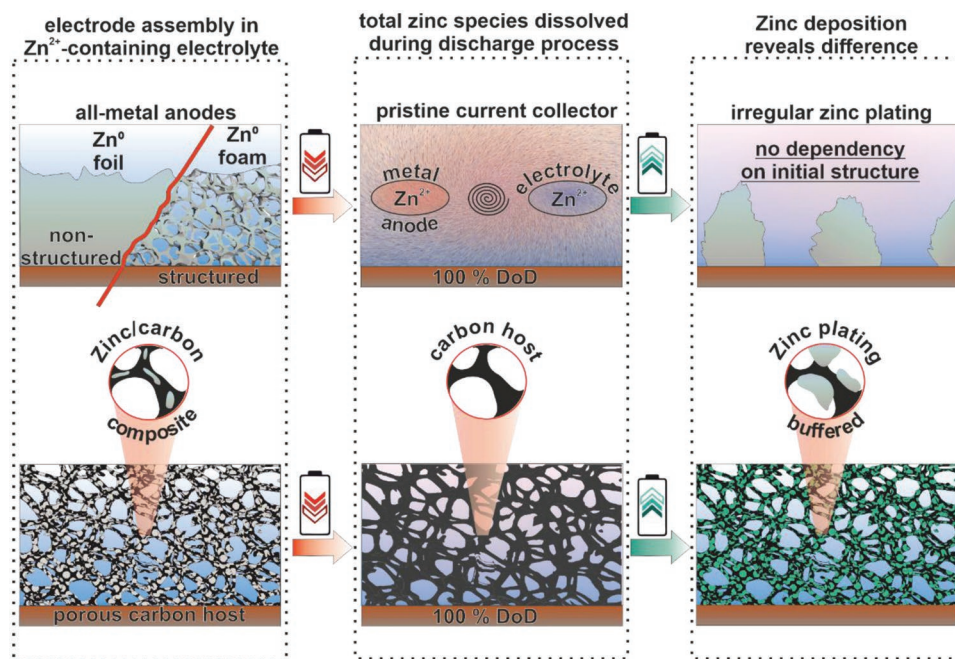


Figure 7. Schematic visualization of the behavior of zinc metal anodes in Zn^{2+} -based electrolyte systems such as $Zn(OTf)_2$ compared to the use of novel composite electrodes for rechargeable zinc–air batteries recommended herein. During the discharge, pure metallic zinc anodes are completely dissolved by the electrolyte at a targeted DoD of 100% regardless of the morphology used. Inhomogeneous zinc plating takes place in the charge cycle, again, regardless of the original shape of the anode. In order to buffer the strong volume change of the zinc metal anode, zinc/carbon composite electrodes could be increasingly used in the future. Here, zinc is homogeneously bonded to an electrically conductive framework structure, which is stable even during cyclization and does not change its shape macroscopically, thus enabling a controlled environment for reversible zinc plating and stripping.

For example, if a zinc plate anode in a zinc triflate electrolyte is deeply discharged within a zinc–air battery, the zinc plate is almost completely dissolved, which exposes the underlying current collector. A porous anode, such as a zinc sponge electrode, can probably increase the accessibility of zinc during discharge and thus increase the DoD. Nevertheless, the morphology of the pure metallic zinc anode is largely irrelevant, as it will at best be completely dissolved during the desired complete discharge. In the charging cycle, the metallic zinc is then deposited from the electrolyte solution on the surface of the current collector. Here, the deposition is not based on the original morphology of the zinc anode, but rather on the local conditions of the current collector. Thus, with a high zinc utilization ratio, the morphology of the zinc anode would only be decisive for the initial discharge and would ultimately have no far-reaching influence on the subsequent cyclability. As irregular zinc plating can ultimately lead to dendrites, which will penetrate the separator, a controlled deposition of the zinc species in solution is worthwhile (Figure 7).

Here, porous zinc–carbon composites can certainly be a reasonable consideration. When, the cell is discharged and the metallic zinc bonded on the carbon dissolves, the porous carbon scaffold will remain unaltered in its morphology. The porosity of the carbon scaffold allows good ionic accessibility of the zinc reservoir, while the electrically conductive backbone of the carbon framework guarantees electrical conduction. In the opposite charge cycle, the carbon framework enables homogeneous deposition of the zinc species. Certainly, the morphology of the freshly deposited zinc will differ from the original morphology of the zinc used.

However, this only leads to a change in volume at the microscopic scale. On the macroscopic electrode level, the carbon scaffold can buffer this change in volume, so that the separator is prevented from being pierced by zinc dendrites, as it would be the case with purely metallic zinc anodes (Figure 7).

In contrast to these advantages, there is a downside of each composite electrode independent of the respective battery system. Because every additive that is not involved in the electrochemical conversion reaction, which is in case of the zinc–air battery ultimately everything except of zinc, will raise the dead weight. Especially, if other auxiliary agents are introduced, such as a binder, which may be necessary to anchor both components and thus protects the composite electrode from mechanical stress. In the worst scenario, this can lead to a severe impairment of the gravimetric, but also the volumetric energy density. Apart from parameters that influence the energy density of the overall system, there are also concrete influences on the battery chemistry to be expected. Thus, the introduction of a supplementary component is considered to have a significant impact on the zinc plating and stripping behavior, which will not only have benefits, but also presumably favor the formation of overpotentials due to the elevated zinc deposition barrier. Therefore, in the development of composite electrodes, the benefits expected from composite electrode must clearly outweigh the disadvantages, and optimization should benefit either the depth of discharge or the cyclability, in the best case both of them simultaneously without lowering the specific energy.

The possibilities for developing new anode concepts seem to open new avenues, when following these ideas due to the low

restrictions imposed by the new electrolyte system and is therefore not only limited to zinc/carbon composites. More decisive is the overall concept of a porous, electrically conductive matrix which allows to host the homogeneously dispersed metallic zinc sites.

7. Conclusion

In the present work, we have shed light on the rechargeability of zinc–air batteries by considering the interface between the zinc anode and the electrolyte. A particular focus is placed on the proper electrode balancing of the zinc anode in the interplay of high and low DoD. Within this framework, a re-evaluation of the rechargeability is made when using classical zinc metal anodes, therefore the resulting challenges that arise for the Zn/ZnO interface, the electrolyte, and the cell design are critically assessed.

The commonly used combination of a zinc metal anode and an alkaline KOH electrolyte has proven to be extremely unsuitable for the further development of electrically rechargeable batteries. First and foremost, there is an insufficient reversibility of the zinc plating and stripping if the zinc anode is not in surplus. At a zinc surplus however, the zinc metal anode thus pretends to be rechargeable, which is simply not the case to this extent. The use of an excess of zinc is not an adequate solution to the problem of achieving rechargeability, as only a limited part of the existing zinc reservoir is available for the battery operation due to electrode passivation. Thus, the adaptation of the zinc reservoir to the operating conditions of the battery, the electrode balancing, turns out to be an important parameter. Apart from that, the alkaline KOH electrolyte requires an oversizing of the metallic zinc anode since the harsh electrolyte causes corrosion of the zinc and thus severely reduces the available active material. These contradictory conditions limit the reversibility and therefore the development of rechargeable zinc–air batteries in a delicate way.

A revision of the anode/electrolyte interface seems inevitable. In fact, Zn²⁺-containing electrolytes show promising properties which have the potential to outperform the KOH electrolyte. Especially the aqueous zinc triflate electrolyte impresses with its resilience against carbonate formation and its excellent chemical stability toward zinc while at the same time facilitating a high electrochemical reversibility. The development of mild, non-corrosive electrolytes is increasingly driving the advancement of sophisticated anode concepts, which require a reassessment of the anode/electrolyte interface. The well-established combination of an oversized zinc metal anode and the KOH electrolyte seems to be a dead end for achieving high performance and technological maturity in secondary zinc–air batteries. The time is now to switch gears toward true rechargeability of zinc–air batteries. The breakthrough of the secondary zinc–air battery as a serious alternative to the lithium-ion battery could thus be within reach.

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.

Keywords

metal anode, rechargeability, zinc, zinc oxide, zinc–air battery

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- [1] Y. Chen, Y. Kang, Y. Zhao, L. Wang, J. Liu, Y. Li, Z. Liang, X. He, X. Li, N. Tavajohi, B. Li, *J. Energy Chem.* **2021**, 59, 83.
- [2] X. Jiang, Y. Chen, H. Meng, W. Cao, C. Liu, Q. Huang, N. Naik, V. Murugadoss, M. Huang, Z. Guo, *Carbon* **2022**, 191, 448.
- [3] B. Liu, Y. Jia, C. Yuan, L. Wang, X. Gao, S. Yin, J. Xu, *Energy Storage Mater.* **2020**, 24, 85.
- [4] X. Hu, Z. Jiang, L. Yan, G. Yang, J. Xie, S. Liu, Q. Zhang, Y. Xiang, H. Min, X. Peng, *J. Power Sources* **2020**, 467, 228367.
- [5] F. Duffner, N. Kronemeyer, J. Tübke, J. Leker, M. Winter, R. Schmuch, *Nat. Energy* **2021**, 6, 123.
- [6] S. Kala, A. Mishra, *Mater Today Proc.* **2021**, 46, 1543.
- [7] J. Shin, J. W. Choi, *Adv. Energy Mater.* **2020**, 10, 2001386.
- [8] Y. Ahoutou, A. Ilinca, M. Issa, *Energies* **2022**, 15, 1579.
- [9] Y. Zhao, O. Pohl, A. I. Bhatt, G. E. Collis, P. J. Mahon, T. Rütther, A. F. Hollenkamp, *Sustainable Chem.* **2021**, 2, 167.
- [10] J. Goldstein, I. Brown, B. Koretz, *J. Power Sources* **1999**, 80, 171.
- [11] Y. Li, H. Dai, *Chem. Soc. Rev.* **2014**, 43, 5257.
- [12] K. Harting, U. Kunz, T. Turek, *Z. Phys. Chem.* **2012**, 226, 151.
- [13] M. L. Wald, *The New York Times*, July 11, **1993**, p. 9.
- [14] J. Wen, D. Zhao, C. Zhang, *Renewable Energy* **2020**, 162, 1629.
- [15] Y. Yang, W. Yuan, X. Zhang, Y. Ke, Z. Qiu, J. Luo, Y. Tang, C. Wang, Y. Yuan, Y. Huang, *Appl. Energy* **2020**, 276, 115464.
- [16] G. Zubi, R. Dufo-López, M. Carvalho, G. Pasaoglu, *Renewable Sustainable Energy Rev.* **2018**, 89, 292.
- [17] J. Zhang, Q. Zhou, Y. Tang, L. Zhang, Y. Li, *Chem. Sci.* **2019**, 10, 8924.
- [18] Y. Sun, H.-W. Lee, Z. W. Seh, N. Liu, J. Sun, Y. Li, Y. Cui, *Nat. Energy* **2016**, 1, 2058.
- [19] Z. Rao, J. Wu, B. He, W. Chen, H. Wang, Q. Fu, Y. Huang, *ACS Appl. Mater. Interfaces* **2021**, 13, 38194.
- [20] Y. Yu, Z. Yang, Y. Liu, J. Xie, *Carbon* **2022**, 196, 589.
- [21] F. Schipper, E. M. Erickson, C. Erk, J.-Y. Shin, F. F. Chesneau, D. Aurbach, *J. Electrochem. Soc.* **2017**, 164, A6220.
- [22] G. Gabrielli, M. Marinaro, M. Mancini, P. Axmann, M. Wohlfahrt-Mehrens, *J. Power Sources* **2017**, 351, 35.
- [23] Z. Huang, Z. Deng, Y. Zhong, M. Xu, S. Li, X. Liu, Y. Zhou, K. Huang, Y. Shen, Y. Huang, *Carbon Energy* **2022**, 4, 1107.
- [24] Z. Zhao, X. Fan, J. Ding, W. Hu, C. Zhong, J. Lu, *ACS Energy Lett.* **2019**, 4, 2259.
- [25] X. Chen, D. Chen, G. Li, P. Sha, J. Yu, L. Yu, L. Dong, *Electrochim. Acta* **2022**, 428, 140938.
- [26] Y. Li, K. Xu, Q. Zhang, Z. Zheng, S. Li, Q. Zhao, C. Li, C. Dong, Z. Mei, F. Pan, S. Dou, *J. Energy Chem.* **2022**, 66, 100.
- [27] W. Li, W. Chen, H. Zhang, Z. Zhang, *Chem. Eng. J.* **2022**, 435, 134900.
- [28] Y. Han, H. Duan, C. Zhou, H. Meng, Q. Jiang, B. Wang, W. Yan, R. Zhang, *Nano Lett.* **2022**, 22, 2497.
- [29] B. J. Park, H. Lee, J. Kim, H. S. Park, *J. Ind. Eng. Chem.* **2022**, 109, 413.
- [30] X. Zhang, S. Hu, S. Sun, X. Zhang, *ChemistrySelect* **2022**, 7, 202201503.
- [31] L. Sun, Y. Qin, L. Fu, Y. Di, K. Hu, H. Li, L. Li, W. Zhang, *J. Alloys Compd.* **2022**, 921, 166128.
- [32] L. Song, J. Zhang, S. Sarkar, C. Zhao, Z. Wang, C. Huang, L. Yan, Y. Zhao, *Chem. Eng. J.* **2022**, 433, 133686.
- [33] X. Bao, K. Xie, Z. Zhang, Z. Liu, H. Zhou, F. Luo, D. Zhou, H.-E. Wang, *Ionics* **2022**, 28, 1273.
- [34] U. Bhardwaj, A. Sharma, A. Mathur, A. Halder, H. S. Kushwaha, *Energy Storage* **2022**, 4, 293.
- [35] X. Chen, J. Pu, X. Hu, Y. Yao, Y. Dou, J. Jiang, W. Zhang, *Small* **2022**, 18, 2200578.
- [36] Y. He, Z. Xi, C. Xu, *Nanotechnology* **2022**, 33, 475401.
- [37] Q. Lu, X. Zou, Y. Bu, K. Liao, W. Zhou, Z. Shao, *Small* **2022**, 18, 2105604.
- [38] K.-L. Bao, J.-Y. Xu, N.-F. Yu, J.-B. Kuang, Z.-T. Yang, H. Chen, J.-L. Ye, Y.-P. Wu, *Energy Fuels* **2022**, 36, 6542.
- [39] S. Zhao, S. Ran, N. Shi, M. Liu, Y. Zeng, W. Sun, Z. Zhu, *Int. J. Hydrogen Energy* **2022**, 47, 30449.
- [40] T.-X. Tu, X. Zhou, P.-F. Zhang, L. Tan, Z.-F. Xu, M.-Q. Liu, W.-Y. Li, X.-M. Kang, Y.-J. Wu, J.-Z. Zheng, *ACS Sustainable Chem. Eng.* **2022**, 10, 8694.
- [41] P. Zhang, Y. Liu, S. Wang, L. Zhou, T. Liu, K. Sun, H. Cao, J. Jiang, X. Wu, B. Li, *Small* **2022**, 18, 2202725.
- [42] Z. Zhao, W. Yu, W. Shang, Y. He, Y. Ma, Z. Zhang, P. Tan, *J. Power Sources* **2022**, 543, 231844.
- [43] Y. Zhang, X. Zheng, N. Wang, W.-H. Lai, Y. Liu, S.-L. Chou, H.-K. Liu, S.-X. Dou, Y.-X. Wang, *Chem. Sci.* **2022**, 13, 14246.
- [44] W. Sun, F. Wang, B. Zhang, M. Zhang, V. Küpers, X. Ji, C. Theile, P. Bieker, K. Xu, C. Wang, M. Winter, *Science* **2021**, 371, 46.
- [45] Y. Huang, Q. Gu, Z. Guo, W. Liu, Z. Chang, Y. Liu, F. Kang, L. Dong, C. Xu, *Energy Storage Mater.* **2022**, 46, 243.
- [46] L. Cao, D. Li, T. Pollard, T. Deng, B. Zhang, C. Yang, L. Chen, J. Vatamanu, E. Hu, M. J. Hourwitz, L. Ma, M. Ding, Q. Li, S. Hou, K. Gaskell, J. T. Fourkas, X.-Q. Yang, K. Xu, O. Borodin, C. Wang, *Nat. Nanotechnol.* **2021**, 16, 902.
- [47] J. F. Parker, J. S. Ko, D. R. Rolison, J. W. Long, *Joule* **2018**, 2, 2519.
- [48] B. J. Hopkins, C. N. Chervin, J. F. Parker, J. W. Long, D. R. Rolison, *Adv. Energy Mater.* **2020**, 10, 2001287.
- [49] C. Li, L. Wang, J. Zhang, D. Zhang, J. Du, Y. Yao, G. Hong, *Energy Storage Mater.* **2022**, 44, 104.
- [50] B. J. Hopkins, C. N. Chervin, J. W. Long, D. R. Rolison, J. F. Parker, *ACS Energy Lett.* **2020**, 5, 3405.
- [51] G. J. May, A. Davidson, B. Monahov, *J. Energy Storage* **2018**, 15, 145.
- [52] J. Guo, N. Xu, Y. Wang, X. Wang, H. Huang, J. Qiao, *ACS Appl. Mater. Interfaces* **2020**, 12, 37164.
- [53] Z. Wang, J. Ang, J. Liu, X. Y. D. Ma, J. Kong, Y. Zhang, T. Yan, X. Lu, *Appl. Catal., B* **2020**, 263, 118344.
- [54] W. Peng, Y. Wang, X. Yang, L. Mao, J. Jin, S. Yang, K. Fu, G. Li, *Appl. Catal., B* **2020**, 268, 118437.
- [55] C. Chen, D. Cheng, S. Liu, Z. Wang, M. Hu, K. Zhou, *Energy Storage Mater.* **2020**, 24, 402.
- [56] X. He, Y. Tian, D. Deng, F. Chen, J. Wu, J. Qian, H. Li, L. Xu, *ACS Sustainable Chem. Eng.* **2021**, 9, 17007.
- [57] Y. Liang, Q. Gong, X. Sun, N. Xu, P. Gong, J. Qiao, *Electrochim. Acta* **2020**, 342, 136108.
- [58] M. Qian, M. Xu, M. Guo, T. T. Isimjan, E. Shoko, Z. Shi, X. Yang, *J. Power Sources* **2021**, 506, 230221.
- [59] Y. Kumar, E. Kibena-Pöldsepp, J. Kozlova, A. Kikas, M. Käärrik, J. Aruväli, V. Kisand, J. Leis, A. Tamm, K. Tammeveski, *ChemElectroChem* **2021**, 8, 2662.

- [60] I. Kone, Z. Ahmad, A. Xie, L. Kong, Y. Tang, Y. Sun, Y. Chen, X. Yang, P. Wan, *Energy Technol.* **2021**, *9*, 2001117.
- [61] Y. Xu, A. Sumboja, A. Groves, T. Ashton, Y. Zong, J. A. Darr, *RSC Adv.* **2020**, *10*, 41871.
- [62] S. B. Sherman, Z. P. Cano, M. Fowler, Z. Chen, *AIMS Energy* **2018**, *6*, 121.
- [63] Y. Yan, Y. Zhang, Y. Wu, Z. Wang, A. Mathur, H. Yang, P. Chen, S. Nair, N. Liu, *ACS Appl. Energy Mater.* **2018**, *1*, 6345.
- [64] D. Deckenbach, J. J. Schneider, *J. Power Sources* **2021**, *488*, 229393.
- [65] A. Nakata, H. Arai, H. Murayama, K. Fukuda, T. Yamane, T. Hirai, Y. Uchimoto, J.-I. Yamaki, Z. Ogumi, *APL Mater.* **2018**, *6*, 047703.
- [66] L. Ma, M. A. Schroeder, O. Borodin, T. P. Pollard, M. S. Ding, C. Wang, K. Xu, *Nat. Energy* **2020**, *5*, 743.
- [67] D. Stock, S. Dongmo, D. Damtew, M. Stumpp, A. Konovalova, D. Henkensmeier, D. Schlettwein, D. Schröder, *ACS Appl. Energy Mater.* **2018**, *1*, 5579.
- [68] D. Stock, S. Dongmo, K. Miyazaki, T. Abe, J. Janek, D. Schröder, *J. Power Sources* **2018**, *395*, 195.
- [69] Y. Ding, W. Zhou, L. Xie, S. Chen, J. Gao, F. Sun, G. Zhao, Y. Qin, *J. Mater. Chem. A* **2021**, *9*, 15948.
- [70] M. Wang, X. Dong, Z. Meng, Z. Hu, Y.-G. Lin, C.-K. Peng, H. Wang, C.-W. Pao, S. Ding, Y. Li, Q. Shao, X. Huang, *Angew. Chem., Int. Ed. Engl.* **2021**, *60*, 11190.
- [71] Z. Wu, T. Wang, J.-J. Zou, Y. Li, C. Zhang, *ACS Catal.* **2022**, *12*, 5911.
- [72] M. Dan, R. Zhong, S. Hu, H. Wu, Y. Zhou, Z.-Q. Liu, *Chem. Catal.* **2022**, *2*, 1919.
- [73] M. Warczak, M. Osial, W. Urbanska, M. Pisarek, W. Nogala, M. Opallo, *Electrochem. Commun.* **2022**, *136*, 107239.
- [74] I. Dueramae, M. Okhawilai, P. Kasemsiri, H. Uyama, *Sci. Rep.* **2021**, *11*, 13268.
- [75] N. Zhang, F. Cheng, Y. Liu, Q. Zhao, K. Lei, C. Chen, X. Liu, J. Chen, *J. Am. Chem. Soc.* **2016**, *138*, 12894.
- [76] A. R. Mainar, O. Leonet, M. Bengoechea, I. Boyano, I. de Meatza, A. Kvasha, A. Guerfi, J. A. Blázquez, *Int. J. Energy Res.* **2016**, *40*, 1032.
- [77] W.-J. Peng, Y.-Y. Wang, *J. Cent. South Univ. Technol.* **2007**, *14*, 37.
- [78] S. Huang, F. Wan, S. Bi, J. Zhu, Z. Niu, J. Chen, *Angew. Chem.* **2019**, *131*, 4357.
- [79] I. Dueramae, M. Okhawilai, P. Kasemsiri, H. Uyama, R. Kita, *Sci. Rep.* **2020**, *10*, 12587.
- [80] Y. Zhang, F. Wan, S. Huang, S. Wang, Z. Niu, J. Chen, *Nat. Commun.* **2020**, *11*, 2199.
- [81] P. Hu, T. Zhu, X. Wang, X. Zhou, X. Wei, X. Yao, W. Luo, C. Shi, K. A. Owusu, L. Zhou, L. Mai, *Nano Energy* **2019**, *58*, 492.
- [82] X. Liu, Q. Ma, J. Wang, Q. Han, C. Liu, *ACS Appl. Mater. Interfaces* **2022**, *14*, 10384.
- [83] W. Deng, Z. Zhou, Y. Li, M. Zhang, X. Yuan, J. Hu, Z. Li, C. Li, R. Li, *ACS Nano* **2020**, *14*, 15776.
- [84] R. Li, H. Zhang, Q. Zheng, X. Li, *J. Mater. Chem. A* **2020**, *8*, 5186.
- [85] S. Li, Y. Liu, X. Zhao, Q. Shen, W. Zhao, Q. Tan, N. Zhang, P. Li, L. Jiao, X. Qu, *Adv. Mater.* **2021**, *33*, 2007480.
- [86] D. Li, T. Lv, Z. Chen, Y. Yang, Y. Liu, J. Wan, Y. Qi, S. Cao, T. Chen, *Small Struct.* **2022**, *3*, 2200027.
- [87] W. Liu, P. Guo, T. Zhang, X. Ying, F. Zhou, X. Zhang, *J. Phys. Chem. C* **2022**, *126*, 1264.
- [88] W. Kao-ian, M. T. Nguyen, T. Yonezawa, R. Pornprasertsuk, J. Qin, S. Siwamogsatham, S. Kheawhom, *Mater. Today Energy* **2021**, *21*, 100738.
- [89] X. Jin, L. Song, C. Dai, H. Ma, Y. Xiao, X. Zhang, Y. Han, X. Li, J. Zhang, Y. Zhao, Z. Zhang, L. Duan, L. Qu, *Energy Storage Mater.* **2022**, *44*, 517.
- [90] Y. Du, X. Wang, Y. Zhang, H. Zhang, J. Man, K. Liu, J. Sun, *Chem. Eng. J.* **2022**, *434*, 134642.
- [91] Q. Zong, W. Du, C. Liu, H. Yang, Q. Zhang, Z. Zhou, M. Atif, M. Alsalihi, G. Cao, *Nano-Micro Lett.* **2021**, *13*, 116.
- [92] Q. Zhang, D. Lei, N. Liu, Z. Ren, J. Yin, P. Jia, W. Lu, Y. Gao, *Adv. Mater.* **2022**, *34*, 2205369.
- [93] X. Zhang, F. Xue, X. Sun, T. Hou, Z. Xu, Y. Na, Q. An, Z. Chen, S. Cai, C. Zheng, *Chem. Eng. J.* **2022**, *445*, 136714.
- [94] Y. Liu, C. L. Liu, Y. Gong, *Adv. Mater. Interfaces* **2022**, *9*, 2200641.
- [95] D. Liu, Z. Tang, L. Luo, W. Yang, Y. Liu, Z. Shen, X.-H. Fan, *ACS Appl. Mater. Interfaces* **2021**, *13*, 36320.
- [96] D. Wang, X. Guo, Z. Chen, Y. Zhao, Q. Li, C. Zhi, *ACS Appl. Mater. Interfaces* **2022**, *14*, 27287.
- [97] P. Pei, K. Wang, Z. Ma, *Appl. Energy* **2014**, *128*, 315.
- [98] M. Yang, X. Shu, W. Pan, J. Zhang, *Small* **2021**, *17*, 2006773.
- [99] P. Zhang, K. Wang, P. Pei, Y. Zuo, M. Wei, X. Liu, Y. Xiao, J. Xiong, *Mater. Today Chem.* **2021**, *21*, 100538.
- [100] T. Liu, J. Mou, Z. Wu, C. Lv, J. Huang, M. Liu, *Adv. Funct. Mater.* **2020**, *30*, 2003407.
- [101] Z. Li, H. Yang, H. Sun, S. Liang, G. Lu, Z. Liu, S. Kou, *ACS Sustainable Chem. Eng.* **2021**, *9*, 4498.
- [102] F. Qiang, J. Feng, H. Wang, J. Yu, J. Shi, M. Huang, Z. Shi, S. Liu, P. Li, L. Dong, *ACS Catal.* **2022**, *12*, 4002.
- [103] X. Yang, S. Li, D. Ye, J. Kuang, S. Guo, Y. Zou, X. Cai, *Adv. Mater. Technol.* **2022**, *7*, 2100673.
- [104] M. Fan, Y. Cheng, X. Peng, H. Zhang, J. Wu, H. Tang, B. Li, Y. Zong, *ACS Sustainable Chem. Eng.* **2022**, *10*, 7664.
- [105] D. Jiang, H. Wang, S. Wu, X. Sun, J. Li, *Small Methods* **2022**, *6*, 2101043.
- [106] W.-Z. Cheng, J.-L. Liang, H.-B. Yin, Y.-J. Wang, W.-F. Yan, J.-N. Zhang, *Rare Met.* **2020**, *39*, 815.
- [107] C. Xiao, J. Luo, M. Tan, Y. Xiao, B. Gao, Y. Zheng, B. Lin, *J. Power Sources* **2020**, *453*, 227900.
- [108] C.-X. Zhao, J.-N. Liu, B.-Q. Li, D. Ren, X. Chen, J. Yu, Q. Zhang, *Adv. Funct. Mater.* **2020**, *30*, 2003619.
- [109] S. Ramakrishnan, J. Balamurugan, M. Vinothkannan, A. R. Kim, S. Sengodan, D. J. Yoo, *Appl. Catal., B* **2020**, *279*, 119381.
- [110] Z. Xiao, C. Yang, S. Liu, W. Yan, F. Wang, X. Liu, T. Yang, X. Li, Y. Chen, *Sustainable Energy Fuels* **2021**, *5*, 5184.
- [111] J. Zhang, J. Wu, T. Guan, G. Zhang, S. Guan, J. Han, J. Wang, K. Li, Z. Liu, *ACS Sustainable Chem. Eng.* **2022**, *10*, 9303.
- [112] H. Pourfarzad, M. Shabani-Nooshabadi, M. R. Ganjali, *J. Power Sources* **2020**, *451*, 227768.
- [113] Z. Xiao, Y. Wu, S. Cao, W. Yan, B. Chen, T. Xing, Z. Li, X. Lu, Y. Chen, K. Wang, J. Jiang, *Chem. Eng. J.* **2021**, *413*, 127395.
- [114] M. Wang, Y. Long, H. Zhao, W. Zhang, L. Wang, R. Dong, H. Hou, H. Wang, X. Wang, *ChemSusChem* **2022**, *15*, 202201518.
- [115] B. Ji, J. Gou, Y. Zheng, X. Zhou, P. Kidkhunthod, Y. Wang, Q. Tang, Y. Tang, *Adv. Mater.* **2022**, *34*, 2202714.
- [116] M. M. Kumar, C. R. Raj, *ACS Appl. Mater. Interfaces* **2022**, *14*, 15176.
- [117] W. Niu, S. Pakhira, K. Marcus, Z. Li, J. L. Mendoza-Cortes, Y. Yang, *Adv. Energy Mater.* **2018**, *8*, 1800480.
- [118] T. V. Pham, Y. Li, W.-B. Luo, H.-P. Guo, X.-W. Gao, J.-Z. Wang, H.-K. Liu, *Global Challenges* **2019**, *3*, 1900027.
- [119] L. Su, L. Liu, Y. Wang, Y. Lu, X. Yan, *Chin. Chem. Lett.* **2020**, *31*, 2358.
- [120] S. Hyun, S. Shanmugam, *ACS Omega* **2018**, *3*, 8621.
- [121] S. J. Han, M. Ameen, M. F. R. Hanifah, A. Aqsha, M. R. Bilad, J. Jaafar, S. Kheawhom, *Catalysts* **2020**, *10*, 822.
- [122] J.-S. M. Lee, S. Sarawutanukul, M. Sawangphruk, S. Horike, *ACS Sustainable Chem. Eng.* **2019**, *7*, 4030.
- [123] P. Bonnicksen, J. R. Dahn, *J. Electrochem. Soc.* **2012**, *159*, A981.
- [124] Y. Wu, Y. Zhang, Y. Ma, J. D. Howe, H. Yang, P. Chen, S. Aluri, N. Liu, *Adv. Energy Mater.* **2018**, *8*, 1802470.
- [125] B. Li, J. Quan, A. Loh, J. Chai, Y. Chen, C. Tan, X. Ge, T. S. A. Hor, Z. Liu, H. Zhang, Y. Zong, *Nano Lett.* **2017**, *17*, 156.
- [126] S. Dongmo, D. Stock, J. J. Alexander Kreissl, M. Groß, S. Weixler, M. Hagen, K. Miyazaki, T. Abe, D. Schröder, *ACS Omega* **2020**, *5*, 626.

- [127] S. Dongmo, J. J. A. Kreissl, K. Miyazaki, T. Abe, T.-H. You, C.-C. Hu, D. Schröder, *Sci. Data* **2020**, *7*, 395.
- [128] W. He, S. Zuo, X. Xu, L. Zeng, L. Liu, W. Zhao, J. Liu, *Mater. Chem. Front.* **2021**, *5*, 2201.
- [129] J. Yang, B. Yin, Y. Sun, H. Pan, W. Sun, B. Jia, S. Zhang, T. Ma, *Nano-Micro Lett.* **2022**, *14*, 42.
- [130] J. F. Parker, C. N. Chervin, I. R. Pala, M. Machler, M. F. Burz, J. W. Long, D. R. Rolison, *Science* **2017**, *356*, 415.