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ARTICLE

Transformation and migration in secondary zinc-air batteries studied by *in situ* synchrotron X-ray diffraction and X-ray tomography

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There are numerous challenges associated with developing secondary Zn-air batteries regarding e.g. power density and cycle life. Some of the challenges are related to morphological changes in the anode during cycling due to combined electrochemical and chemical processes involved in the reversible Zn – ZnO transformation. We present a unique *in situ* synchrotron X-ray diffraction study, where a combination of time and spatial resolution allows information about transformation and transport in a Zn/ZnO anode during discharge/charge operation. By tracking Zn and ZnO reflections during cycling of two Zn-air batteries we see that the conversion of these phases is accompanied by transport into the anode and the anode configuration does not return to its initial state after recharge due to ZnO migration to other parts of the battery. During charge Zn metal is deposited as microcrystalline material, changing the morphology and phase distribution in the anode. The XRD results were supported by qualitative *in situ* X-ray computed tomography that confirms depletion of ZnO and non-homogeneous distribution of Zn.

Introduction

With the increasing prevalence of intermittent renewable energy generation, the need for energy storage is becoming more important. Batteries are already being used towards this purpose and are anticipated in the future to contribute to an even larger degree¹. The two most common battery types for this purpose are Li-ion and lead-acid batteries because of their high capacity and low price, respectively. With the ever-increasing demand, a battery that provides high energy storage capacity at low cost is needed. The Zn-air battery is an ideal candidate, due to the low price of zinc metal² and the high theoretical specific energy (1300 Wh/kg). The specific energy obtained for current Zn-air batteries are reported between 350 and 500 Wh/kg^{1,3,4}. Zn-air batteries obtain these high capacities due to the open nature configuration of the cell, where the cathode (O₂) is outside the battery, leaving only an air electrode, electrolyte, separator and the active material to contribute to the weight.

During discharge oxygen is reduced at the cathode:

The hydroxide ions migrate toward the anode and create zincate ions in the electrochemical reaction with Zn according to the reaction:

Non-electrochemical precipitation of ZnO from zincate occurs according to:

Yielding the overall reaction (which is thereby a combination of an electrochemical and a chemical reaction):

Zn has a long history of being applied in batteries and the Zn-air battery has been well-established commercially since 1933, although only as a primary battery as electrical rechargeability is challenging⁵. In order for secondary Zn-air battery technology to reach large scale application in the market it needs to have high cycle stability. Consequently, to achieve long cycle-life a number of challenges need to be overcome:

1. Obtain highly stable, efficient and bi-functional catalysts.
2. Reduce reaction of alkaline electrolytes with CO₂, which leads to precipitation of K₂CO₃ in the pores and thereby choking of the air electrode.
3. Improve water management to reduce evaporation.
4. Hinder zinc dendrite formation.
5. Reduce self-corrosion and hydrogen formation of the anode.
6. Control and anticipate shape/morphology changes and redistribution of material in the anode during discharge/charge cycling.

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Shape changes in the negative electrode are caused by: 1) Chemical expansion occurring due to the reaction of Zn to ZnO, causing the anode to expand and contract during cycling. Chemical expansion is the reason why commercial primary Zn-air button cells have a headspace to accommodate volume expansion⁶. 2) Transport of Zn species happens because the conversion between Zn and ZnO occurs through dissolved zincate ions, enabling non-electrochemical deposition of ZnO. This could lead to redistribution inside the electrode or migration to e.g. the separator or positive electrode.

A secondary zinc-air cell would therefore experience not only expansion and contraction of the negative electrode but also morphology changes. Anodes need to be carefully designed and well understood to retain performance over many cycles. As shape changes and transport has a direct effect on the performance and reversibility of the Zn-air battery, this is an important parameter to investigate, and *in situ* studies are necessary in order to obtain detailed information in real time about the processes involved.

Zn-air batteries have been investigated with the aim of understanding the mechanism of both primary and secondary batteries. Schröder *et al.* has applied tomography to commercial ZA13 button cell primary batteries to verify simulation results and found that zinc oxide formation initially occurs close to the separator and that Zn particles closest to the current collector would oxidize last during discharge. Associated with the conversion of Zn to ZnO a structural expansion factor for the Zn electrode of 1.5 was found.⁷

In 2014 Arlt *et al.* developed a Zn-air battery design suitable for x-ray computed tomography and used it to investigate electrolyte redistribution during discharge. They observed that flooding of the pores in the air electrode contributed to end of life for the cell⁸. Franke-Lang *et al.* improved on the technique and demonstrated that modifying the density of the Zn-matrix in the anode to accommodate expansion could reduce the stress induced by the structural expansion. They also highlighted how parasitic reactions could result in gassing that would also deteriorate the anode⁹.

Nakata *et al.* investigated artificially grown zinc dendrites and their effect on cycle life. It was shown that the zinc dendrites can be completely dissolved using low oxidation currents. Later they used *in situ* X-ray diffraction (XRD) to investigate in-plane changes in the Zn electrode of a Zn/NiOOH battery and found that suppressing non-uniform Zn deposition would enhance cycle life.^{10,11}

Zn/MnO batteries with an ionic liquid electrolyte have been investigated by Abad *et al.* using synchrotron X-ray diffraction and XPS to study how Zn was converted to ZnO through a Zn(OH)₂ intermediate¹².

In the present study we investigate morphology changes in a Zn-air battery and redistribution through the anode using time- and spatially resolved synchrotron X-ray diffraction. The anode is a mixture of Zn, ZnO in a paste-electrode; addition of ZnO to the anode facilitates ZnO deposition as it provides additional nucleation sites⁶. The goal is to increase the understanding of the redistribution and transport in the paste

anode and through this to be able to increase the cycle life of the battery.

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Experimental

In situ battery cells

The capillary-based *in situ* battery cell used in these experiments consisted of two sizes of borosilicate capillaries (Hilgenberg GmbH) with an outer diameter (OD) of 3 mm and 2.4 mm and inner diameter (ID) of 2 mm and 1.6 mm, respectively. The anode and cathode were contained in two pieces of the smaller capillary, which were inserted in a piece of the larger capillary, using a glass fiber separator and held in place with UV-glue U3200 and U3600 Cyberbond. The anode current collector was a 1.8 mm Cu-wire, which were inserted in the bottom of the glass pieces and held in place by UV glue. The Cu-wire was polished on the top to provide a smooth surface. The anode paste was made using the recipe in reference 13: 49.3 wt. % Zn (Umicore BIA100), 21.1 wt. % ZnO (Umicore Pharma B) 28.2 wt. % electrolyte and 1.4 wt. % CMC (Cekol 30000P (CP Kelco), sodium carboxymethyl cellulose) gelling agent. The electrolyte was added to the powders immediately before use and the entire anode glass part was weighed to determine the capacity. The weight of the anode for the two batteries used (named Zn1 and Zn2) was 10 mg and 9.2 mg, respectively, which yields an initial capacity of 4.0 mA and 3.75 mA.

The cathode was made from NiCo₂O₄ and polytetrafluoroethylene (PTFE) with a 0.5 mm thick Ni wire inserted into as a current collector. The cathode was prepared from a powder mixture of 85 wt. % NiCo₂O₄ powder (Cerpotech) and 15 wt. % PTFE (Sigma Aldrich) powder. The mixture was dispersed in 300 wt. % of isopropanol and homogenized using a magnetic stirrer for 10 minutes. The resulting slurry was filled into the capillary to a height of at least 1 cm and the nickel (Ni) wire was inserted all the way through. The glass capillary with wet slurry and Ni wire was heated to 340 °C for one hour in a furnace. The procedure was adapted from Wittmaier *et al.*¹⁴. For XRD measurements at a synchrotron, the capillary cell was mounted in 3D printed PLA plastic frame, which holds the wires and contact clips (Figure 1a). The electrolyte was 6 M aqueous solution of KOH from pellets (Sigma Aldrich). The separator was made using 20 mm long 1 mm wide Whatman GF/A separator. The batteries were assembled immediately before being mounted at the beamline.

Figure 1a) The capillary cell mounted in the *in situ* XRD experiment, red arrow indicates the where the incoming interacts with the sample. b) Schematic illustration of the capillary Zn-air battery.

Figure 2: Cross section of a capillary cell anode that depicts the interaction volume with the beam designated as position 1-10 where 1 is closest to the separator. Position 10 is adjacent to the polished Cu wire.

Cells characterized by x-ray computed tomography (CT) were similar to the cells characterized by XRD, however, the anode and cathode current collector had a 63 μm diameter Cu wire attached by silver epoxy (Chemtronics) to allow for rotational freedom around the vertical axis of the cell. Similarly the Ni wire was glued to the side of the glass capillary to reduce the effect of torsion during rotation. The anode was contacted through the metal stage that held the sample. Evaporation of electrolyte was not observed to impact the electrolyte within the timeframe of the experiments.

Synchrotron X-ray diffraction

The *in situ* synchrotron X-ray diffraction experiments were performed at PETRA III, beamline P02.1. The X-ray beam was selected by a diamond 111 Laue crystal and a silicon 111 Laue crystal and collimated by slits. The wavelength was determined as 0.2072 $\text{\AA}$ using the diffraction pattern from a silicon standard (NIST). Diffraction data were collected using a PerkinElmer XRD1621 area detector (400 x 400 mm^2 , pixel size 200 x 200 μm^2).

Time and spatially resolved diffraction data were collected with an X-ray beam defined by slits: vertically 0.2 mm and horizontally of 1 mm. The beam exposes between 8-10 points along the anode in a consecutive manner (Figure 2). The anode contains very fine-grained ZnO particles, which gives smooth Debye-Scherrer rings, and zinc metal powder with a wide size distribution, containing approximately 16 wt. % crystallites 425 μm . This results in very grainy Debye-Scherrer rings with over-exposed diffraction spots in the detector images.

Calibration of the sample-detector distance, tilt parameters, beam center etc. (using a LaB_6 standard sample) as well as reduction of the obtained 2D diffraction patterns, were performed using the DAWN software^{15,16}. For data reduction a mask for the beam stop was used, as well as a threshold mask to eliminate over-exposed pixels from the large zinc crystallites. However, the presence of large zinc crystallites results in larger fluctuations in the integrated intensities for the zinc phase compared to the ZnO phase.

Data analysis: The presence of large Zn crystals, resulting in over-exposure of the detector, presents a challenge for the data analysis as the integrated intensity of diffraction peaks from the initial zinc crystallites do not necessarily quantitatively reflect the amount of crystalline material. For this reason, Rietveld or LeBail refinement of the diffraction data could not be used for extracting information about the relative and absolute amounts of the Zn and ZnO material present. Data analysis was performed using raw summation of selected diffraction peaks, subtracting a linear background determined at the ends of the integration interval and the diffraction patterns were normalized using background points. The synchrotron runs in top-up-mode, resulting in small fluctuations of the ring-current (ca 1%). The diffraction data were not corrected using the ring current due to the high stability of the ring current at the beamline.

For each position in the anode, see Figure 2, all the reflections from Zn and ZnO were identified and integrated between the selected boundaries as seen for sample two, position 2, in Figure S1. The method of peak integration is illustrated in Figure S2. The resulting integrated intensities can be seen in Figure S3 for each of the reflections. In the following analysis we mostly focus on Zn (102) and ZnO (002) in several positions in each sample, but as can be seen in the supporting information (SI) the intensity variations are similar for the other reflections. Position 1 contains the interface between anode and electrolyte and displays intensity variations with time which are similar to those for position 2. However, the diffracted intensities are lower than for the other positions due to smaller amount of material in the beam. Also, volume changes in the anode move the electrolyte/anode interface

resulting in significant intensity variations. The data from position 1 were not included in the analysis, but the time series can be found in Figure S4 and S5. Similarly, positions 6 and beyond are found in Figure S6 and S7 for sample Zn1 and Zn2 respectively. Notice that sample Zn2 only has 8 positions, as it is slightly shorter.

Figure 3: Electrochemical cycling data for two batteries with a) 4 h of discharge/charge time, with 10 min OCV in between cycles and b) 1 h and 15 min of discharge/charge time with 10 min OCV between cycles.

In situ Micro X-ray CT

In situ X-ray micro Computed Tomography, μ CT scans were conducted with an Xradia Versa XRM-410 instrument using a W reflection target. Scans were performed at a voltage of 140 kV, a power of 10 W, no filter, 4 x optical magnification, binning 4, an exposure time of 1 s and a total of 1451 projections over a 186° rotation, resulting in a pixel resolution of 4.5 μ m. The acquisition of one tomogram was set to take ca. 1 hour, and 20 tomograms were recorded successively without breaks in between during cycling of the capillary Zn-air battery. The recorded data were reconstructed using Feldkamp-Davis-Kress reconstruction algorithm with a beam hardening constant of 0.05 and a smooth filter constant of 0.5. The commercial software Avizo was used for visualizations.

Post-mortem XRD

Post mortem in-house XRD conducted on the cathode and separator. ZnO was found in the separator along with other unidentified crystalline compounds. Some of these compounds are likely from reaction between the KOH and the glass fiber separator. In very long cycle experiments, these effects are detrimental to the battery as it dilutes the electrolyte and introduces potential contamination of the electrodes. Whatman GF/A was chosen for these experiments as it is easy to work with, holds electrolyte well and because the experiments are relatively short. No ZnO was observed in the cathode.

Results and discussions

Two Zn-air battery cells were investigated; Zn1 with a full discharge/charge cycle and Zn2 which was cycled using partial, time limited charge/discharge cycles with Open Circuit Voltage, OCV measurements in between cycles. In Figure 3 the electrochemical cycling profile for each of the battery cells are seen. Each battery cell has an initial OCV around 1.4 V. Battery Zn1 was discharged for four hours and charged for four hours at 0.5 mA. The total mass of the Zn1 anode is 10.0 mg yielding a capacity of 4.1 mAh resulting in a C-rate of 1/8. After the discharge/charge cycle no more discharge capacity was observed as the cell immediately hits the lower voltage limit of 0.85 V. An additional charge capacity was found as the battery was charged for 2 hours before hitting the upper voltage limit of 2.2 V. Battery Zn2 was cycled by discharging and charging at 0.4 mA for 1 h and 15 minutes three times with lower voltage limit of 0.6 V and upper voltage limit of 2.4 V. The mass of this anode is 9.2 mg resulting in a capacity of 3.76 mAh and a C-rate of 1/9. The discharge potential decreases for each cycle, and from cycle three the discharge capacity decreases and the battery hits the low voltage limit. The charge plateau is constantly around 2 V.

XRD

Following the normalized intensities of a Zn and ZnO peak over time in each sample it is evident that significant changes are taking place both in phase distribution and morphology of the zinc metal crystallites. From the raw detector images in Figure 4 the grainy nature of the Debye-Scherrer rings from Zn is clearly seen due to the large zinc crystallites (Fig. 4a). When looking at a series of raw diffraction images (Video included in Supplementary Information) it was observed that diffraction spots disappear and appear rapidly in the Debye-Scherrer rings indicating that the orientation of the individual Zn crystals changes quickly during the experiment. Because the anode paste is viscous any movement can affect the arrangement of the particles in the paste. Perturbations could be from gas evolution from parasitic reactions or from the aggregated effect of the entire electrode undergoing shape change. The dynamic nature of the crystallite orientation makes it impossible to mask out the individual reflections from the larger Zn particles.

A dramatic change in the Debye-Scherrer rings of Zn is observed from the initial sample (Figure 4a) to the recharged battery (Figure 4b). The final Debye-Scherrer rings of Zn after almost 6 hours of recharge (Figure 4c) are smooth and well defined as opposed to the grainy rings from the initial zinc powder. This shows that Zn is re-deposited as small crystallites.

Figure 4: Cutout of detector images obtained during cycling of battery Zn1, position 2 (0.2 mm beneath the anode electrode interface) in the anode. a) Initial anode obtained during OCV. b) After 4 hours of discharge. c) After subsequent charging for 4 hours. d) A reference image to facilitate interpretation using highlighted Debye Scherrer-rings. Red: ZnO, Green: Overlapping reflection (Zn + ZnO) and Black: Zn.

Figure 5 shows the integrated intensities of the ZnO(002) and Zn(102) reflections as a function of time for position 2-5. In position 2, 0.2 mm below the anode electrolyte interface i.e. from the top part of the anode (Figure 5a) it is seen that despite the large particles, Zn is completely consumed within two hours of discharge while ZnO is deposited. In position 3, 0.4 mm below the interface (Figure 5b) Zn is consumed after almost 4 hours. Even further below the interface Zn is not entirely consumed during discharge (Figure 5c, d). The results show clearly that the degree of transformation ($\text{Zn} \rightarrow \text{ZnO}$) is larger close to the electrode/electrolyte interface and that the reaction is initiated at the interface and propagate through the anode towards the current collector.

A similar behavior is observed during charge. ZnO is fully consumed within 2-3 hours in position 2 while in position 5, 0.4 mm deeper into the anode, ZnO is consumed after 4 hours of charge. Again it is observed that the reaction is fastest close to the electrode/electrolyte interface displaying a high degree of conversion, while deeper into the anode conversion is delayed. However, as seen in Figure 6, which shows the sum of the integrated intensities for all positions, a considerable amount of ZnO is consumed during the first 4 hours of charging, amounting to 115% of the amount produced during discharge. As the initial discharge was 4 hours and the operating current was the same during charge and discharge, some of the ZnO initially present in the anode paste must be consumed during charge. From Figure 6 it can be seen that the main reason for the discrepancy is found in the first hour of discharge, where the formation rate of ZnO is slower than expected. As the Zn oxidation process proceeds via a zincate

anion, the delay may be caused by establishment of equilibrium and concentration gradients due to local pH variations. After the first hour of charge, the rate of ZnO formation during discharge is similar to the rate of ZnO consumption during charge, indicating a reversible Zn/ZnO conversion reaction.

The charge was continued for a total of 6 hours which resulted in a complete conversion of ZnO in the anode, Figure 6, showing that overall the charging process and oxygen evolution reaction is very efficient. However, a significant dependence of the conversion progress with position in the anode is observed. In the part of the anode closest to the separator (up to 0.8 mm into the anode) all ZnO is consumed within the first four hours, including the ZnO in the original paste. This shows that the conversion is very inhomogeneous, and that it is important to take into account the spatial variation in the conversion, when composing the anode mixtures. From Figure 5 it can also be seen that when ZnO is depleted the Zn signal levels off. However, close to the separator, e.g. in position 2, the amount of Zn continues to increase, although not at the same pace as when ZnO is present in the same layer. The fundamental mechanism of the Zn conversion that entails the soluble zincate ion is responsible for the migration. The electrolyte and remaining ZnO can both contribute to deposition of Zn in the electrolyte interface as when the concentration of the ion decreases. To enhance cycle life of an anode this should be taken into account.

Figure 5. Integrated intensities of the red Zn (102) and black ZnO (002) reflections from battery Zn1 over time in different positions in the anode starting a): 0.2 mm (position 2), b) 0.4 mm (position 3), c) 0.6 mm position (4) and d) 0.8 mm (position 5) below the anode electrolyte interface, the positions can be seen in Figure 2. The green line indicates the current in the battery.

A second *in situ* battery cell (Zn2) was investigated using three discharge/charge cycles with the current set to 0.4 mA and the

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discharge and charge time reduced to 1 hour and 15 min. Ideally, the deposition and consumption during one charge/discharge cycle should match. However, as seen from Figure 7 ZnO is still consumed over time, although there is clearly re-deposition of ZnO during discharge. Especially close to the electrolyte the ZnO deposition during discharge is smaller than ZnO consumption during discharge resulting in an overall downward slope. The amount of Zn is closer to following the expected saw tooth pattern (0.2 mm and 0.4 mm below the separator) and is increasing slightly in this depth toward the end of the experiment. This indicates that there is a redistribution of materials over time, where Zn is accumulated in the top of the anode and ZnO is absent. In position 5, Figure 5d, 1 mm below the separator, which is halfway to the Cu-current collector, there is a slight change in the amount of ZnO and almost no variation in the amount of Zn indicating that ZnO is moving into the separator or possibly into the cathode as suggested by Franke-Lang *et al.*⁸ If ZnO was deposited in the cathode it would obviously be undesirable. Redistribution of Zn and ZnO in the anode will severely limit how many cycles the anode can experience before it affects the performance of the cell, due to transport limitations or loss of nucleation sites and percolation. The solution could be to not utilize the full capacity of the anode and run asymmetrical currents or timescales during discharge and charge to avoid severe redistribution. The primary redistribution is removal of ZnO, which is controlled by the concentration of Zn(OH)_4^{2-} in the battery, and lower currents, i.e. slower conversion rates could increase the homogeneity by giving more time for the intermediate to diffuse.

Looking at the battery as a whole, Figure 6, the amount of Zn and ZnO should be inversely correlated, when the intensities of the Zn and ZnO reflections from all positions are added. As seen in Figure 6a this is the case for 4 h cycling data, while it for the 1 h and 15 min cycles, Figure 6b, is less clear. It is however clear that the intensity of the ZnO (002) reflection is decreasing in both instances and the Zn (102) signals increase even after the ZnO is entirely depleted in the anode. This means that ZnO migrates from elsewhere in the battery and before being converted to Zn.

Figure 6: Accumulated intensities for Zn (102) and ZnO (002) in a) battery Zn1 and b) Zn2 over the entire anode as a function of time.

Figure 7 Sample Zn2 integrated intensities of Zn (102) and ZnO (002) signal over time in different positions in the anode starting a): 0.2 mm, b) 0.4 mm, c) 0.6 mm and d) 0.8 mm below the anode electrolyte interface. The green line indicates the current in the battery.

Quasi *in situ* X-ray CT

Figure 8 depicts the electrochemical data for the *in situ* tomography cell. The cell has a normal OCV of around 1.4 V, but on discharge there is a high overpotential as the cell voltage is close to 0 V. The voltage displays noise throughout the experiment in the order of 0.1 V. The noise and overpotential is likely related to poor oxygen transport into the cathode or loss of hydrophobicity in the cathode.

In the tomographic cross sections displayed in Figure 9, the density is displayed in grey scale where the densest material appears white and lighter materials appear dark. We therefore interpret the brightest regions as Zn particles and as the Cu current collector below, darkest regions as electrolyte and the intermediate contrast regions as ZnO. The initial paste, Figure 9a, contains large and sometimes elongated Zn-particles, while ZnO is much finer particles that are too small to be resolved and are dispersed between the Zn particles in the slurry of ZnO and KOH. During discharge, Figure 9b and 9c, Zn is initially consumed in the top, leaving dark (electrolyte) areas in the top quarter of the anode. When the charging starts, Zn reappears in the interface with the electrolyte, although the particles are smaller and their boundary is less well defined as seen in Figure 9d. During the second discharge, seen in Figure 9e, the top of the anode dissolves to an even larger degree, leaving the anode hollow and dark. Unlike the end of the previous discharge, the top part of the anode is no longer filled with ZnO, which agrees with the findings of the XRD measurements. During the second charge the Zn is redeposited, again as a porous mass. In the final tomogram collected two hours into the second charge, Figure 9f, the top of the anode appears

darker indicating a low content of ZnO. The larger Zn particles in the anode are not fully converted and the bottom part contains dark areas that might be small air bubbles from when the cell was assembled.

Figure 8: Electrochemical cycling data for the tomography battery with the alternating background shading displaying the duration of each tomogram.

In the rest of the anode, the large Zn particles have mostly disappeared and the ones that remain have fuzzy outlines, meaning that the surface has been converted at some point in the experiment. This is consistent with the XRD, which indicates that Zn is redeposited as fine particles. Throughout the entirety of the experiment there is no discernable gas build-up in the anode from corrosion of the Zn. In the final tomogram Zn is building up as bright spots in the top of the anode. Measuring the number of pixels the final tomogram, Figure 9f, ZnO is depleted to a depth of 0.42 mm. This is consistent with the XRD experiments on Zn 1 which show that after 4 hours of discharge, Zn is entirely depleted, in the top of the anode.

Figure 9: Ortho slices displaying a cross-section of the anode a) before discharge b) the second cross-section obtained after 104 minutes c) after the first discharge d) after the first charge, e) after the second discharge and f) during the second charge.

Conclusions

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The conversion of Zn and ZnO during cycling of a zinc-air battery was investigated by spatially and time-resolved synchrotron X-ray diffraction and in-house X-ray tomography using an *in situ* capillary battery cell. The initial cathode consisted of a mixture of large-grained Zn and microcrystalline ZnO, which was added to facilitate nucleation of zinc oxide during discharge. By tracking the Zn (102) and ZnO (002) diffraction peaks over time for various positions along the anode it was possible to determine the redistribution of the active materials in the anode. It was shown that Zn and ZnO conversion initially happens in the top of the anode, i.e. closest to the cathode, and progresses downwards over time. Zn was initially present as large crystallites, but during charge it is redeposited as very fine microcrystalline material. Zinc oxide was totally consumed during the first charge in a large part of the anode closest to the electrode/electrolyte interface.

The results from the *in situ* diffraction experiment show that the phase distribution, composition, morphology and size distribution in the anode changes dramatically even after the first discharge/charge cycle. After several discharge/charge cycles the total amount of ZnO did not return to its original value, meaning that it is slowly removed from the anode and migrates to other parts in the battery. Using in-house post mortem XRD on cells after the *in situ* experiment it was shown that ZnO was present in the separator, but neither Zn nor ZnO was found in the cathode.

The observed anode materials redistribution during cycling was supported by in-house X-ray tomography on a similar capillary cell. It was seen that conversion primarily occurs closest to the electrolyte and by cycling zinc is becoming the prevalent phase in the top part of the anode.

Conflicts of interest

There are no conflicts to declare.

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Transformation and migration in secondary zinc-air batteries studied by in situ synchrotron X-ray diffraction and X-ray tomography

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Unique information about transformation and phase redistribution in a Zn-air battery anode was obtained using high energy synchrotron X-ray diffraction.