Operando soft X-ray microscope study of rechargeable Zn–air battery anodes in deep eutectic solvent electrolyte

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Funding information
EPSRC “Access to Nanolithography” programme, Grant/Award Number: EP/K040324/1; Diamond Light Source, Grant/Award Number: SP14027

Zn–air batteries are very promising devices for energy storage at high energy density due to their intrinsic safety, environmental friendliness, and low cost, but still, there are key issues to be solved to get to the industrial scale. One of the unsolved problems is the poor cyclability of batteries based on aqueous solvents that urges to consider nonaqueous solvents. Among different possible options are deep eutectic solvents, which are cost-effective and technologically relatively easy to implement. The present investigation reports for the first time an operando scanning soft X-ray microscope analysis of the Zn behaviour in a choline–chloride/urea deep eutectic solvents electrolyte during the cathodic and anodic phase formation processes taking place in battery charge and discharge, providing a platform for in-depth space–time dependent investigations of the chemistry of crystallites evolving during potential cycling. These operando measurements have been enabled by the construction of a novel wet cell, improving the design and filling protocol of earlier generation cells developed by authors.

High-resolution soft X-ray microscope images were acquired in two modes: (a) dynamic mode at a fixed beam energy, allowing to follow morphology evolution under electrochemical control and (b) static mode for selected morphologies representative of characteristic Zn growth and dissolution steps.

1 | INTRODUCTION

The steady increase of electrical energy demand brings into the spotlight ethical, environmental, societal, and political concerns related to the usage of fossil fuels. Renewable sources could replace hydrocarbons, but sustainability imposes the integration with reliable and efficient energy storage facilities.[1,2] Electrochemistry is playing a key role in the quest for the definitive efficient energy storage device, and among diverse electrochemical storage concepts, Zn–air batteries exhibit storage potentialities ranging from low-power portable consumer electronics to automation, home, and grid applications.[3,4] Aqueous chemistries have been extensively investigated and have shown high potentialities for primary (nonrechargeable) devices, whereas serious drawbacks are delaying the full-scale development of secondary (electrically rechargeable) concepts. The use of nonaqueous electrolytes, such as deep eutectic solvents, is highly promising for electrically rechargeable systems.[5] In order to gain fundamental

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understanding on battery materials, in situ and operando methods—specifically synchrotron-based ones—are gaining momentum and are starting to be implemented on a broad basis. So far, their application has been essentially focussed on lithium-ion technologies, but a range of studies on chemistries relevant to zinc-air have recently started to appear, and appreciable selections have been reviewed in Bozzini et al and Bozzini and Goldoni.

The present paper reports the first operando soft X-ray microscope (SXM) study of cathodic and anodic processes of Zn electrochemical phase formation from a choline-chloride/urea deep eutectic solvent (DES) electrolyte. High-resolution SXM images have been acquired by scanning the photon energies across the Zn L-edge under electrochemical control during the electrodeposition and corrosion processes that, respectively, accompany the charge and discharge of the Zn-air battery. Our operando measurements employed a novel wet cell, improving the design and filling protocol of earlier generation cells developed by the same authors. In order to calibrate the electrochemical conditions, we have performed classical cyclic voltammetry (CV) measurements in the wet cell, showing clear under- and over-potential Zn electrodeposition and stripping. The DES reactivity within the operating potential range was confirmed to be negligible.

In this work, we have proved for the first time the possibility of mapping the distribution of Zn under operando conditions during electrodeposition in the soft X-ray range. Unstable growth features have been followed dynamically, and the local current density distribution can be correlated with the development of SXM images. These results provide fundamental information for the control of dendrite development, a process not only of general interest in electrometallurgy but also specifically exhibiting a notable impact on battery durability. Moreover, successful operation of our wet cells has provided useful information for the development of a fully microfluidic device.

2 | EXPERIMENTAL DETAILS

For this study, we have designed and employed electrochemical wet cells allowing to carry out operando phase formation studies under standard electrochemical control during soft X-ray transmission measurements. It is worth noting that in situ work with hard X-rays is relatively common but X-ray microscopy in transmission mode and in the soft X-ray range is quite challenging and the development of wet cells is still an open field of study. Figure 1a shows a diagram of the wet cell exhibiting a gold (Au) three-electrode configuration supported on a 100-nm thick Si₃N₄ window with area of 500 μm². The special electrode geometry prepared by lithography (Silson Ltd., England) allows keeping within the field of view of the microscope an area exhibiting a range of reaction rates correlating with position, thus imparting combinatorial capability to the cell. The cell consists of two Si₃N₄ membranes separated by 1-μm thick SU-8 epoxy patterned with inlet and outlet channels. The assembled
cell is sandwiched in a fixture—containing inlet and outlet ports for liquid injection—and sealed with silicon rubber gaskets for liquid injection. The injection procedure, performed with a syringe pump, was monitoring under a visible light microscope (Figure 1c). Figure 1b shows a set of images taken during the whole injection process, going from empty cell (left) to the filled one (right). The notable novelty of this wet cell with respect to those described in the literature, including previous work in our group, is that electrolyte injection can now be performed through a system of microtubes with precise pressure control, without need of applying a final seal to the mounted cell after completion of cell filling. This capability allows a significantly simplified handling protocol for the cell with far less risk of breaking the optical window and fulfils the fluid flow requirements from the cell side of the next-generation microfluidic version of the device.

In this experiment, the wet cell was filled with the Zn–DES electrolyte and vacuum-sealed prior to mounting on the modified sample stage and loading into the vacuum system.

Figure 2 gives an overall view of the experiment set-up at I08-SXM beamline. The SXM combines various techniques and has multimodal detection capabilities. The operating photon energy range is from 250 to 4,400 eV, generated by an undulator (Apple II type). The source can be optimised for linearly or circularly polarised radiation to exploit numerous novel studies. In imaging mode, a lateral resolution down to ~20 nm can be achieved depending on the imaging mode. At the time of present investigation, the facilities for simultaneously running high-resolution imaging and spectroscopy were still under development, and we performed a proof-of-principle study in which we carried out in situ dynamic imaging of growing and corroding Zn crystallites at fixed energies in the neighbourhood of the Zn L-edge, and we have demonstrated spectroscopy on homogeneous samples of the functionally key materials.

A schematic cartoon along with a photo of the SXM optics is also shown in Figure 2. The incoming monochromated X-ray beam is focussed by a Fresnel zone plate. A small pinhole, called order selecting aperture (OSA), eliminates undesired diffraction orders leaving only the first order to provide a nanoprobe. Sample raster scanning (fly mode) in the focal plane and transmitted X-ray beam intensities are directly measured using a photodiode connected to an amplifier for imaging and NEXAFS. The data acquisition protocol for NEXAFS at the Zn L-edge consisted in recording stacks of SXM images over the energy range of 1,010–1,080 eV with 0.5-eV steps in transmission mode. NEXAFS spectra were extracted from the stacks of images using the MANTiS software program (2nd Look Consulting, Hong Kong, China). MANTiS is also used for SXM images analysis and demonstration. The spectra are normalised using $I_0$ (incident beam without sample) and dark subtracted (average background signal without beam). SXM images are acquired by raster scanning the sample in steps (thus generating pixels) and recording intensity of the transmitted beam for a given exposure time (dwell time), varying

FIGURE 2 Scheme of soft X-ray transmission microscopy optics showing Fresnel zone plate and order selecting aperture (OSA) for focusing X-rays onto the sample and transmission beam to the detector. The image shows the wet-cell as it is loaded into the microscope chamber at I08 beamline with three-wire connection for operando measurements.
from 1 to 10 s of microseconds. The cell is equipped with three electrical connections to the electrodes that in turn connect via a feedthrough to a potentiostat (VersaSTAT) hosted outside the microscope chamber.

The DES chosen for this study as electrolyte is a 2/1 urea/choline chloride mixture. This DES is non-toxic, biodegradable, stable under ambient conditions (exposure to moist air), readily available, and low priced. The solvent was prepared by mixing urea and choline chloride at 80°C until a clear, viscous liquid was obtained. The Zn bath was formulated by simply adding 0.1M ZnSO₄ to the solvent that readily dissolves at room temperature under gentle stirring. Similar preparations have been described in the literature.[12,13] In order to calibrate the electrochemical conditions within the wet cell, we have performed classical CV measurements in conventional three-electrode electroanalytic cells, and we have compared them with the same measurements carried out in the wet cell. These measurements were performed in a wet cell that was not used for microspectroscopy, because of irreversible changes in the electrode conditions brought about by the imposed electrodeposition cycles. Electrochemical calibration experiments, carried out in a conventional three-electrode cell, employed the same materials used in the wet cell for SXM: The working electrode was polycrystalline Au, polished with diamond pastes down to 0.25 μm, sonicated in acetone, and cleaned in 65% HNO₃. The quasireference electrode (QRE) was an Au wire, as typically used in the literature,[14] cleaned in the same way as the working electrode. During preliminary electrochemical experiments, the stability of the Au QRE was systematically checking with prolonged Open Circuit Potential (OCP) measurements. The counter electrode was an Au wire of total area ~3 cm². Moreover, in order to refer the potentials to a well-defined electrochemical reference scale, we also measured the potential of the Au QRE against an Ag/AgCl quasistandard. The quasistandard was fabricated by growing an AgCl film on an Ag wire at 1 mA cm⁻² for 5 min in an aqueous 3M KCl solution. The Ag/AgCl electrode was simply immersed in the choline–chloride electrolyte. The potential of Au versus Ag/AgCl was very stable, and even though we always used an Au QRE for our measurements, we decided to report the potentials versus the Ag/AgCl standard.

3 | RESULTS AND DISCUSSIONS

In Figure 3, we report CV of the pure DES electrolyte and of the Zn–DES bath, in contact with an Au electrode. The panel (a) shows the results obtained with the wet cell and panel (b) the calibration experiments (see Section 2 for details). The CVs clearly show under-potential (peak D) and over-potential (peak E) Zn electrodeposition and stripping (peaks A–C) and fully conform to cognate literature.[15,16] The electrodeposition parts (formation of metallic Zn, battery charge) of the CVs are identical in the wet cell and in the calibration experiments. Regarding quantitative details, the relative intensities of the stripping peaks are influenced by mass transport, and this explains the differences observed with the two types of cell that can be accurately modelled with the numerical procedure described in Bozzini et al.[17,18] The separation between the over-potential deposition and under-potential deposition peaks, characteristic of the interaction of Zn atoms with the Au substrate, in DES is ~0.69 V, slightly higher than the values reported in classical work with aqueous solutions (e.g., Kolb[19]). The DES reactivity in the potential

![FIGURE 3](image_url)

**FIGURE 3** Cyclic voltammetries recorded (a) in the wet cell and (b) in a classical three-electrode cell with the deep eutectic solvent electrolyte and the Zn–deep eutectic solvent electrodeposition bath. The potential of the Au quasireference electrode has been calibrated with respect to an Ag/AgCl reference electrode.
range relevant to electrodeposition is negligible: In the cathodic range (feature F), it occurs at potentials far more cathodic than those at which Zn is electrodeposited and in the anodic range DES oxidises ~1 V after Zn dissolution is completed. The comparison of the panels in Figure 3 proves that the reaction conditions prevailing in our wet cell are perfectly under electrochemical control. The electroanalytical value of this result cannot be overemphasised, because this proves factually that in our thin-layer wet cell, the same precision of electrochemical control can be achieved as in dedicated voltammetry cells.

The SXM experimental protocol consists in recording sequences of absorption images either by scanning the beam energy and mapping static Zn features obtained after a defined growth interval (representing a steady-state condition of an electrodeposited Zn film) or by keeping the photon energy fixed and following the time evolution of the growing or dissolving Zn morphology (representing the dynamics of Zn electrodeposition or corrosion).

In a first experiment, Zn was grown at −1.0 V for 1,000 s (the inset of Figure 4 shows a typical current density time series corresponding to the application of −1.0 V), and then, stacks of SXM images were collected at the edge between the electrode and the electrolyte. During data acquisition, the Zn film was kept under cathodic protection conditions at −0.725 V in order to avoid dissolution due to galvanic coupling with the Au substrate.

A selection of representative results of the steady-state experiment carried out after electrodeposition at −1.0 V for 1,000 s is reported in Figure 5. A clear formation of dendrites can be noticed in the high-current density region of the working electrode (panel [c], ~2.5 mA cm\(^{-2}\); for an estimate of the local current density in this electrode configuration, see Bozzini et al\(^{[20]}\)). Growth of Zn dendrites was evident also in the low-current density (~0.5 mA cm\(^{-2}\)) regions of the electrode (panel [d], image corresponding to 0 min). Inspection of the NEXAFS pointwise spectra acquired in these conditions shows that a distribution of chemical states of Zn, depending on the electrodeposition conditions, is indeed encoded in the acquired data: Details on this point are beyond the scope of this paper that is meant to prove the feasibility of energy-dependent, dynamic SMX measurements during active Zn growth and corrosion under potential control. We can anticipate here that the chemical-state scenario prevailing at the Zn electrodeposited interface includes elemental Zn, Zn(II) from the solvated state in the bath, and an intermediate Zn oxidation state, possibility corresponding to the Zn(I) species that was postulated on the basis of phenomenological kinetics (see, e.g., Lacitignola et al\(^{[21]}\)). After the second growth step, the working electrode was left at open-circuit conditions, resulting in corrosion of Zn galvanically coupled to the Au substrate, while SXM images were subsequently collected (Figure 5d): The progressive dissolution of the pre-electrodeposited Zn dendrites can be clearly followed.

**FIGURE 4** Potentiostatic conditions used for operando Zn growth experiments
Two sets of dynamic growth experiments were then run, again at −1.0 V, in a pristine cell. In order to assess the time-dependent current distribution issues and the corresponding unstable growth phenomena, we compared low (~0.5 mA cm$^{-2}$) and intermediate (~1.2 mA cm$^{-2}$) c.d. regions. A selection of results is reported in Figures 6 and 7. In both figures, the formation, development, and branching of dendritic unstable outgrowth features can be clearly seen. Within the population of dendrites, a subpopulation is progressively selected, coherently with the mass-transport-controlled mechanism.$^{[22]}$ Cognate work on in situ dynamic imaging of Zn growth by hard X-ray transmission microscopy is known in the literatures.$^{[23,24]}$ The former reference investigated the structural and morphological impact of Bi additions in zincate electrolytes, with combined

**FIGURE 5** A selection of operando soft X-ray microscope images (photon energy of 1,025 eV) of Zn electrodeposited (−1.0 V, 1,000 s) in the deep eutectic solvent electrolyte. (a) Soft X-ray microscope overview image of the cell, showing the position of the electrodes. Pixel size = 10 μm; dwell time = 1 ms. (b) Magnified image of a typical high-current density region. Pixel size = 1 μm; dwell time = 1 ms. (c) Differential map shows dendrites formed in the high-current density region (~2.5 mA cm$^{-2}$). Pixel size = 250 nm; dwell time = 2 ms. The scale bar refers to the optical density. (d) Progressive corrosion of dendrites grown in the low-current density region (~0.5 mA cm$^{-2}$). Pixel size = 250 nm; dwell time = 15 ms. The scale bars for images (a), (b), and (d) are in arbitrary units.

**FIGURE 6** Operando time-evolved soft X-ray microscope images of Zn electrodeposited from a deep eutectic solvent electrolyte at −1.0 V, typical low-current density region (~0.5 mA cm$^{-2}$). (a) Optical micrograph of the cell at the end of the experiment. (b,c) Soft X-ray microscope images measured (photon energy of 1,035 eV) after 100 s (panel b) and 500 s (panel c) of electrodeposition. Pixel size = 250 nm; dwell time = 5 ms. The scale bar for images (b) and (c) is in arbitrary units.
microdiffraction work, whereas the latter concentrated on additive effects in DES electrolytes. Moreover, in situ hard X-ray methods have also been used to follow structural (diffraction) and chemical (PES) changes during cycling of Zn/MnO$_2$ batteries,$^{[25]}$ as well as the rearrangement of the anodic Zn particles (tomography).$^{[26]}$

Notwithstanding the thematic similarity, it is crucial to note the extreme methodological and experimental differences and consequently the completely different focus and types of results of these investigations with respect to our present contribution. Our research is focused on building an electrochemical platform for SXM with 20-nm lateral resolution, combined with NEXFAS, whereas the other works presented above are based on hard X-ray techniques, with a totally different type of lateral resolution and chemical sensitivity. Moreover, the instrumental requirements of the two approaches are deeply different: In fact, for hard X-ray work, there is no need of vacuum at the sample stage, and it is possible to use cells with comfortably thick layer of electrolyte. The two classes of studies can thus be regarded as methodologically orthogonal, although of course contributing, from

**FIGURE 7**  *Operando* time-evolved soft X-ray microscope images (photon energy of 1,025 eV) of Zn electrodeposited from a deep eutectic solvent electrolyte at $-1.0$ V, intermediate current density regions ($-1.2$ mA cm$^{-2}$). (a) Optical micrograph of the cell at the end of the experiment. (b) Representative sequence of soft X-ray microscope images recorded at the indicated times. Pixel size = 250 nm; dwell time = 1 ms. The scale bar for images in panel (b) is in arbitrary units.

**FIGURE 8** NEXAFS Zn L-edge spectra for Zn and ZnO thin films with 150-nm thickness and for a ZnSO$_4$ standard.
different perspectives, to the same type of materials-science problems. Specifically, the key innovation allowed by the approach herein presented will be the possibility of monitoring the growth of unstable electrodeposition features, such as dendrites with nanometre precision combined with the chemical and structural sensitivity of NEXAFS. This information is of utmost importance on the one hand to understand the chemical changes undergone by the Zn(II) liquid precursors to form flat or branched structures and, on the other hand, for the knowledge-based design of additives for dendrite suppression. We are currently working at the optimization of instrumental technicalities that will enable this type of analysis on a routine basis. As a first step in the spectroscopic direction, we have concentrated on the analysis of the chemical state of different Zn compounds, relevant to Zn, ZnO, and ZnSO₄. We acquired NEXAFS spectra with the same set-up of SXM microscope at I08-SXM beamline. Zn and ZnO thin films are deposited on Si₃N₄ membranes, and ZnSO₄ standard is cast on Si₃N₄ membranes as well from a powder sample dissolved in ethylene. The results of Zn L-edge NEXAFS spectra are plotted in Figure 8. The spectra show clearly distinguishable absorption features in the main, pre-, and post-edge regions, due to the excellent energy resolution in our data. NEXAFS is very well suited for the speciation of elements reacting in electrochemical systems, such as batteries, and will provide useful information about the electronic structure of the interested atom in the material and electronic interaction with its neighbour atoms.²⁷

4 | CONCLUSIONS

The present investigation has demonstrated for the first time the possibility of mapping by scanning soft X-ray transmission spectroscopic microscopy (SXM) under operando conditions a dynamic Zn anode with lateral resolution of a few tens of nanometre. Unstable growth features—of the kind typically giving rise to capacity fade and short circuiting of batteries, impairing their durability—have been followed dynamically with chemical sensitivity, thanks to the acquisition of groups of images at selected energies across the Zn L-edge. Moreover, the morphochemical changes of predeposited Zn, resulting from the application of discharge conditions, were imaged as a function of time. These results prove the feasibility of measurements able to disclose otherwise inaccessible fundamental information for the control of dendrite development and electrode shape change. Moreover, successful operation of our wet cells has provided useful information for improving the design and the filling procedure, in view of developing a fully microfluidic device. Future investigations will address the systematic chemical-state mapping of Zn as a function of applied potential, time, and electrode history, in order to achieve a full quantitative understanding of the behaviour of Zn electrodes in Zn–air batteries, in view of the development of knowledge-based chemical and electrical control strategies that will allow a quantum jump in the achievement of industrial-scale reliability of these energy-storage devices.

ACKNOWLEDGEMENTS

We thank B. Kaulich and T. Araki on beamline I08-SXM at the Diamond Light Source, Harwell Science And Innovation Campus, UK, for great support and instrument operation during our beamtime that was funded by Diamond Light Source (Grant SP14027). We would like to thank Carmen Sanchez Derojas, Matthew Shand, and Peter Anastasi from Silson Ltd., Warwickshire, England, for development and fabrication of the wet cells. M. K. thanks Richard Cousins for fabrication of Zn and ZnO thin films in the Nanofabrication Facility at the University of Bath, supported by the EPSRC “Access to Nanolithography” programme (Grant EP/K040324/1).

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