Neutron Imaging of Lithium Batteries

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Abstract:

Advanced batteries are critical to achieving net zero and are proposed within decarbonisation strategies for transport and grid scale applications, alongside their ubiquitous application in consumer devices. Immense progress has been made in lithium battery technology in recent years, but significant challenges remain and new development strategies are required to improve performance, to fully exploit power density capacities, to utilise sustainable resources and to lower production costs. Suitable characterisation techniques are crucial for understanding *inter alia* three-dimensional diffusion processes, formation of passivation layers or dendrites which can lead to drastic capacity reduction and potentially to hazardous short circuiting. Studies of such phenomena typically utilise 2D or 3D imaging techniques, providing locally resolved information. 3D X-ray imaging is a widely used standard method, while time-lapse (4D) tomography is increasingly required for understanding the processes and transformations in an operational battery. Neutron imaging overcomes some of the limitations of X-ray tomography for battery studies. Notably, the high visibility of neutrons for light Z-elements, in particular hydrogen and lithium, enables the direct observation of lithium diffusion, electrolyte consumption and gas formation in lithium batteries. Neutron imaging as a non-destructive analytical tool has been steadily growing in many disciplines as a result of improvements to neutron detectors and imaging facilities providing increasingly higher spatial and temporal resolutions. Further, ongoing developments of diffraction imaging for mapping structure and microstructure properties of battery components make the use of neutrons increasingly attractive. Here we provide an overview of neutron imaging techniques, generally outlining advances and limitations for studies on batteries, and we review imaging studies of lithium batteries. We conclude with an outlook of method developments in the field and discuss their potential and significance for future battery research.

Introduction

Batteries have achieved a ubiquitous place in modern society, primarily through their application in consumer electronics. Advanced batteries will play a growing role in our lives and are a cornerstone of plans to achieve net zero, with ambitious aims to decarbonise transport and grid-scale energy storage. The primary constituent materials of Li-ion batteries (LIB) were discovered in the 1970s and 1980s and were commercialised in the 1990s – however the maturation of the technology and the subsequent commoditisation of these batteries has been a protracted, and indeed ongoing, process. Alongside the portfolio of batteries generally recognised as Li-ion, there is a growing interest in the development of revolutionary Li-ion and post Li-ion technologies; in the near term these includes low-cobalt cathodes and organic electrodes such as Li-S, Li-Si or Li-air[1]. Limited resources and sporadic distributions of Li ore deposits stimulate the development of alternative charge carriers such as Na[2] or K[3] which are

in the focus of current research to compete with Li-ions technology. However, challenges remain with regard to structural transitions during cycling, and associated structural instabilities resulting in lower capacity retention and a lower operational voltage. Batteries based on multivalent metals such as Mg, Ca, Al or Zn have potential for future large-scale energy storage based on the high abundance of the constituent materials in the Earth's crust[4]. However, Na-/K-ions and multivalent ion alternatives alongside solid state chemistries are currently at lower technology readiness levels. The diverse portfolio of possible applications for energy storage, which spans stationary and mobile applications from micro-Watt to mega-Watt scales, mandates a diverse collection of battery technologies which variously balance key performance indicators spanning energy and power density, cost, lifetime, safety and recyclability.

In order to achieve the deployment of advanced battery technologies over short time scales, it is essential to accelerate their research and development. The development of new characterisation tools is central to this goal, and the advances in *in situ* and *operando* monitoring capabilities with coupled modelling and simulation provides a compelling opportunity to support the acceleration of these technologies.

Over the past decades, the development of imaging techniques has provided a unique insight into heterogeneous morphologies of battery electrode materials, alongside an improved understanding of device architectures. Magnetic resonance imaging (MRI) is sensitive to the nuclear magnetic resonance active nuclei, such as ^1H, ^7Li or ^{23}Na[5–7], and is able to provide quantitative information on chemical reactions[8–10], on transport processes in batteries[11], and on microstructure development such as Li or Na dendrite formation[12,13]. MRI provides a moderate spatial resolution of ≥ 10 µm and a small penetration depth into most metals of ≤ 10 µm. Electron microscopy (EM) offers significantly higher spatial resolutions from the nanometre range of scanning electron microscopes (SEM) and transmission electron microscopes (TEM) to the sub-Å resolution for scanning transmission electron microscopes (STEM) for thin samples <300 nm[14,15]. A myriad of EM techniques and modalities enable a range of *in-situ/operando* studies of solid electrolyte interphase (SEI) layers and dendrite formation[16,17], liquid electrolytes in Li-S[18] and Li-Si[19] batteries, alongside other battery chemistries such as Zn[20]. X-ray imaging offers spatial and temporal resolutions ranging from sub-second failure events[21,22] to long term durability studies[23], and from nanoscopic particle analysis[24] to testing of macroscopic devices[25]. Critically, X-ray tools have the penetrative power and tomographic capability to visualise processes of functional materials and working devices such as cylindrical and pouch[21,26–29] cells. X-ray imaging applications cover a vast range of battery materials and chemistries. Alongside conventional absorption imaging, spectroscopic X-ray fluorescence computed tomography (XRF-CT) methods reveal the distribution of the constituent elements which can be correlated to results from other techniques such as transmission X-ray microscopy (TXM) and X-ray Diffraction (XRD)[24].

Neutron imaging (NI) shares some important characteristics with X-rays, and provides valuable, alternative contrast mechanisms. Whilst X-rays are predominantly sensitive to electron density, neutrons are sensitive to nuclear density. Consequently, though some elements (e.g. lithium) are largely 'invisible' to X-rays, they can be readily visualised using neutrons. Similarly, high-Z materials in construction or current collection components in operating devices can overly attenuate an incident X-ray beam, leading to extended exposure times or low signal to noise ratios. Moreover, the isotopic sensitivity offered by neutron techniques enables enormous image contrast adaptability and dynamic investigations of materials evolution. NI therefore provides a helpful correlative tool to unravel the role of the myriad materials characteristic of operating battery devices.

The complementarity between neutrons and X-rays has been exploited for many decades, it is only more recently that substantial improvements in neutron flux and neutron detection have made NI (and indeed, tomography) a routine tool in the arsenal of scientific characterisation techniques. Within the fuel cell literature, the application of neutron radiography (NR) to visualise water is relatively widespread, however the application of NI to battery investigations is somewhat more nascent.

In this perspective, we reflect on recent developments in NI characterisation, which include significant progress in spatio-temporal resolution, and review its increasing role within battery research. With the growing portfolio of advanced batteries under development, and with a diverse material set spanning the periodic table, we identify a timely opportunity to explore the benefits and limitations of NI within the landscape of correlative imaging, diffraction and spectroscopy tools. We use X-ray imaging as the point of reference for NI due to the above-mentioned similarities and complementarity of the two probes.

Neutron radiography and tomography

Neutrons are chargeless particles and interact mainly with nuclei in contrast to X-ray probes which interact strongly with the charge of the electron shells of atoms. Therefore, neutron beam attenuation does not depend on the atomic number, while for X-rays the high-Z elements are stronger absorbers than low Z elements. The smaller size of the nucleus compared to the electron shell is the reason why neutrons are absorbed only weakly by many common materials. Hence, imaging with neutrons allows for the penetration of thick layers of metals, while providing high sensitivity to some light elements even if these are embedded in a closed metallic environment. **Figure 1A** illustrates the mass attenuation coefficients of neutrons of the elements compared to 100 keV X-rays. Neutron interactions vary randomly across the periodic table and may differ drastically for isotopes of the same element.

In the following we refer to radiography as the process of producing a radiogram or 2D projection of an object, and we refer to tomography (N-CT) as the process of producing a 3D real-space presentation from which cross-sectional slices can be extracted. We use the higher-level term neutron imaging (NI) to refer to NR and N-CT, as well as to spatially-resolved diffraction.

Conventional neutron attenuation radiography is based on the transmission of a collimated beam of thermal (wavelengths: ca. 1.0-2.5 Å) or cold neutrons (>2.5 Å) through a sample and the recording of the attenuated beam by a position-sensitive detector[30,31]. The transmitted intensity obeys Lambert-Beer's law stating that for a given neutron energy the ratio of the transmitted and the incident intensity is an exponential function of thickness multiplied by the attenuation coefficient of the sample.

For tomographic imaging the sample is rotated in the beam stepwise around a fixed (mostly vertical) axis allowing for acquisition of a projection image at each rotation angle using a position sensitive detector. The recorded set of angular projections is subjected to filtering and flat-field correction operations, and is then used for tomographic reconstruction. In this way, the entire volume of a sample can be unravelled in 3D by reconstructing the attenuation coefficient for each voxel of a sample from the collected projections by using mathematical algorithms such as filtered back projection or noise-suppressing iterative algorithms [30,32]. The spatial resolution of NI typically ranges between 5 and 200 microns, but can range up to millimetres for diffraction imaging.

Attenuation coefficients vary with neutron wavelength which needs to be taken into account when interpreting greyscales and attenuation levels in terms of materials compositions.

141 Moreover, crystal monochromators and time-of-flight methods are used for wavelength-
142 selection at reactor sources and accelerator-based pulsed spallation sources, respectively. By
143 distinguishing neutron wavelengths details of the two most important attenuation mechanisms
144 in neutron imaging can be exploited: neutron absorption and neutron (Bragg) diffraction[33]. For
145 Bragg edge imaging every camera pixel measures a spectrum rather than a greyvalue. Bragg
146 edges are sudden jumps in the neutron transmission due to neutrons being removed by Bragg
147 diffraction. By analysing positions, widths and heights of Bragg edges one can map structure
148 properties and crystallographic phases in 2D and 3D, albeit with coarse spatial resolutions of a
149 few hundred microns. Furthermore, isotopes and elements can be mapped using neutron
150 resonances at pulsed sources[34]. These transmission methods are complemented by spatially-
151 resolved neutron diffraction with a pencil beam and by recording the scattered neutrons; this
152 method provides rather coarse, (mm^3-sized spatial resolution[35]) but nonetheless exquisite
153 information about structural and microstructural details in each voxel, such as internal strains
154 and grain orientation. It is worth noting that further advanced NI methods are being
155 developed[31,36], but have not yet been used for battery studies. Phase contrast imaging exploits
156 refraction of neutrons at interfaces, to enhance contrast between features that are
157 indistinguishable via attenuation. Dark-field imaging[37] is capable of characterising nano- and
158 microstructure properties such as pore sizes and particle shapes with a spatial resolution of a
159 few hundred microns. Imaging with polarized neutrons[38] usually exploits the neutron
160 interaction with magnetic moments in materials, and can potentially be used to distinguish
161 incoherent hydrogen scattering from other interaction types.

162 **Advantages/limitations of neutrons for Li-ion batteries**

163 The feature sizes of the battery components such as electrodes, separators and solid electrolytes
164 are in the micrometre range. Further, the dynamics of Li ion diffusion processes during battery
165 operation are to be monitored in the time range of minutes. These boundary conditions have
166 initiated a tremendous improvement of both spatial and time resolutions of NI in recent years,
167 see **Figure 1B**. The additional demand for non-invasive *in situ* and *operando* investigations
168 became an important catalyst for the extension to 4D (3D spatial and time) imaging
169 capabilities. This allowed for dynamic volumetric studies of the distribution and movement of
170 light elements such as lithium and hydrogen in material components and in complete devices
171 that are used for energy conversion and storage, such as fuel cells and batteries.

172 Li batteries are suitable objects for NI because neutrons have a high visibility for Li ion charge
173 carriers and hydrogen-containing electrolytes which is required to visualise migration of Li
174 ions and subsequently to identify areas of reduced activity that are responsible for capacity
175 decline. During dis-/charge, a dynamic 3D measurement of the change in Li concentration can
176 be performed by measuring the change of neutron attenuation coefficients in corresponding
177 areas of the battery volume. Moreover, as mentioned above, neutrons interact with the nuclei
178 of atoms and are therefore sensitive to isotopes rather than elements, e.g. of lithium or
179 hydrogen, which allows for the application of isotopic labelling. Compared to highly
180 attenuating ^1H and ^6Li, the neutron beam attenuation for ^2H (D) and ^7Li is relatively low. This
181 can be used to enhance the visibility of hydrogen or lithium in particular battery components,
182 and not in others. Thus, Li exchange processes inside batteries can be followed by using e.g.
183 ^6Li on the anode side and ^7Li or ^{nat}Li on the electrolyte or cathode side, to provide important
184 information about the dynamic properties of the lithium diffusion during battery dis-/charging.

185 Neutrons and X-rays effectively complement each other in many cases, with regard to visibility
186 of and access to material features, components and physical properties. Nevertheless, neutrons
187 fluxes are low and, by nature of the weak interaction, neutrons are more difficult to detect,

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188 leading to comparatively low counts in image camera pixels and/or to much longer exposure
189 times for the same greyvalues. The achievable spatial and temporal resolutions are limited and
190 images are much more affected by low signal-to-noise compared to X-ray CT studies. This is
191 why broad-band ("white") neutron beams are employed without energy-discrimination where
192 possible, even though some information is averaged out (e.g. Bragg edges) and even if white-
193 beam imaging introduces additional difficulties with the analysis of the neutron images. For
194 high-absorption elements such as Li, for example, the measured attenuation coefficients
195 depend strongly on the wavelength band used, and beam hardening artifacts necessitate extra
196 corrections of the neutron images. It is furthermore worth noting that, as a downside of the
197 abovementioned high sensitivity for hydrogen, parasitic scattering of neutrons into the camera
198 screen produces scattering artifacts and hampers quantification of the material properties,

199 Neutrons produce no radiation damage in battery devices while beam damage in X–ray
200 synchrotron applications is sometimes problematic. On the other side, neutron-induced sample
201 activation cannot be avoided and may pose logistical challenges if battery cells are to be studied
202 by other methods immediately following the neutron analysis. However, the activation is
203 usually short-lived and decays in a matter of days.

Neutron imaging on Li batteries – a review of recent work

205 Whilst the advantages of NI over X-rays for lithium transport studies are often emphasised, the
206 volume of applications of NR and N-CT on LIBs is remarkably small, most likely related to
207 the over-powering absorption of lithium and related problems with opaque neutron images,
208 moderate spatial resolution, sample activation and lack of neutron source strength for time-
209 lapse studies. There are three main lines of investigations: lithium diffusion; electrolyte
210 consumption with associated gas evolution; and filling of cells with electrolyte. A small
211 number of studies were concerned with the evolution of structure and microstructures during
212 dis-/charging and lithium de-/intercalation by neutron diffraction and Bragg edge imaging.
213 Beyond that, N-CT was used to confirm post-mortem the absence of exterior lithium salt
214 depositions on a Boeing 787 'Dreamliner' lithium battery, supporting the assumption of an
215 internal short[39].

216 NI experiments on Li-ion electrodes and battery cells date back to the 1990s, with the first
217 lithium diffusion studies by Kamata et al.[40] using NR to visualise the Li-ion movement between
218 two spinel-type $Li_{1.33}Ti_{1.67}O_4$ electrodes, prepared with the less absorbing ^7Li isotope and with
219 a natural $^7Li/^6Li$ mixture used as cathode and anode, respectively. Likewise Takai et al.[41,42]
220 measured lithium diffusion coefficients in $Li_{1.33}Ti_{1.67}O_4$ and $La_{2/3-x}Li_{3x}TiO_3$ using different
221 lithium isotope concentrations, see **Figure 2A**. The first investigations on lithium distributions
222 in primary and secondary commercial battery cells for charged and discharged states under
223 different dis-/charge conditions were performed by Kamata et al.[43].

224 The development of digital NI camera systems, using charged coupled devices (CCD), CMOS
225 sensors or microchannel plates (MCP) enabled tomographic scans and *in-situ* NR and N-CT
226 analyses during cycling of lithium cells. Kardjilov et al.[44] produced an N-CT scan of a lithium-
227 iodine battery cell of a pacemaker device providing lithium distributions before and after
228 cycling, shown in **Figure 2B**. Further, Song et al.[45] showed that time-resolved NR can
229 contribute to studies of the dynamic redistribution processes related to dendrite growth from
230 lithium plating and stripping, which can cause short circuits in lithium metal batteries. In the
231 study they used a ^7Li-anode|separator|$LiMn_2O_4$-cathode ensemble with a thick cathode
232 configuration to study the dendrite formation. The large dendrites were clearly visible with the
233 available spatial resolution of the NI system (**Figure 2C**). The cell was charged several times
234 and finally discharged whereby *in operando* radiographs were taken and N-CT data were

collected at the end of each cycle step. The N-CT data clearly showed the separator and the natural lithium cathode particles below the separator. Due to its lower neutron cross section the ^{7}Li anode appears transparent. The results demonstrated the growth of dendrites at each charge step and loss of dendritic structure following discharge. Beside the low attenuating ^{7}Li isotope, high absorbing ^{6}Li helps to improve the visibility of fine changes in Li concentrations in small electrode samples such as demonstrated by Wang et al.[46] who studied the Li distribution during ^{6}Li intercalation in highly oriented pyrolytic graphite (HOPG). With time resolved NR they found a highly non-uniform Li distribution during the lithiation process with spots of large Li concentrations.

Tomographic NI has historically been limited by long collection times in the range of hours. NR on the other hand allows for *in situ* or *operando* analysis of lithium transport in parallel aligned electrode configurations, for which path integrals along the neutron trajectory are meaningful and with collection times in the range of seconds. High spatial resolution is required to achieve reasonable data on thin tailored electrodes that enable high dis-/charge currents with short Li ion paths between electrodes of commercial Li-ion cells. Siegel et al.[47,48] performed high resolution (20 µm) NR to investigate lithium transport in LiFePO$_4$/graphite pouch cells with electrode thicknesses between 40 and 100 µm. The setup enabled the detection of dynamic lithium concentrations, spatially resolved across the electrodes at different state of charge (SoC), and allowed the authors to follow the electrode swelling/thickness changes during lithium de-/intercalation. A sub-pixel resolution method revealed an irreversible electrode expansion as result of high C-rate charging and non-uniform lithium staging. Other studies have used thick electrode configurations to circumvent the coarse resolution of NI: Owejan et al.[49] took advantage of a 300 µm thick graphite composite electrode to quantify the lithium intercalation and to study capacity loss in relation to trapped lithium. Zhou et al.[50] utilised a 700 µm thick lithium-metal electrode sandwiched between two bulky graphite electrodes to demonstrate a gradually change of neutron transmission. Nie et al.[51,52] applied NR on sintered Li$_{4+y}$Ti$_5$O$_{12}$/LiCoO$_2$ full cells with electrodes up to, and thicker than, 600 µm in a coin cell configuration. By cycling with different current densities more lithium was transported at lower currents resulting in higher capacity, and Li ion de-/intercalation occurred only close to the separator for high C-rates such as shown in **Figure 2D**. The same study showed that electrode tortuosity had only a small influence at low C-rates.

N-CT is the preferred technique to unravel lithium diffusion inside spiral-wound battery cell designs, however, additional challenges have to be met to characterise such batteries due to the high neutron-attenuating elements in the active electrode materials such as Ni, Mn or Co in addition to Li. CT reconstructions of large LIBs using polychromatic neutrons show significant reconstruction artifacts such as beam hardening as demonstrated by several authors[53–56]. Such artifacts can be either prevented by using a monochromatic neutron beam[55], which however increases exposure times severely, or by applying a beam hardening correction during CT reconstruction. Generally, the low neutron transmission through cells and the related low counting statistics often limits investigations to *ex situ* studies.

Zhang et al.[57] demonstrated that N-CT is well suited to study the 3D lithium distributions in the de-/lithiation SoC of <1 mm thick V$_2$O$_5$ cathodes of commercial coin cells. The charged and discharged cells displayed different Li distributions, with a higher non-uniformity observed for the higher C-rate cycled electrodes. Further, Nanda et al.[58] visualised the variation of the discharge products across the bulk of the electrode in 3D to support a kinetically coupled diffusion based transport model for lithium-air batteries.

Banhart et al.[31] exploited the complementary imaging contrast for neutrons and X-rays for a lithium-iodine battery cell (**Figure 2B**). *In operando* X-ray and NR was used by Sun et al.[59] to

283 study the lithium alloying of Si-particles, demonstrating the particle evolution during the first
284 discharge, by taking advantage of increasing transmission for X-rays and decreasing
285 transmission for neutrons. Longer exposure times for high resolution N-CT often reduces the
286 applicability of the complementary imaging techniques to post-mortem studies as shown by
287 Sun et al.[60] in their investigation of structural changes in cycled lithium-oxygen batteries.
288 Nonetheless, the work by LaManna et al.[61,62] provided further evidence for the useful
289 complementarity of X-ray and N-CT for the inspection of commercial LIBs, where *inter alia*
290 neutrons identify the lithium containing components and the electrolyte, and X-rays highlight
291 metallic components such as the electrode current collectors and cabling in a battery cell.

292 The successful combination of both tomographic techniques on commercial lithium batteries
293 was demonstrated by Ziesche et al.[63] using *in operando* X-ray and *in situ* N-CT on commercial
294 CR2 Li/MnO$_2$ cells. The X-ray CT data revealed structural changes, such as electrode cracking,
295 particle movement and volume expansion due to lithium intercalation in the MnO$_2$ cathode
296 shown in **Figure 3A**. Conversely, N-CT tracked the electrochemistry such as the lithium
297 removal from the lithium-metal anode, the electrolyte consumption and inactive regions where
298 electrolyte and/or lithium are fully consumed such as shown in **Figure 3B**. In combination with
299 a novel virtual unrolling tool, both techniques revealed subtle changes through and along the
300 electrodes which are normally 'obscured' in the spirally wound electrode structure. **Figure 3C**
301 demonstrates the unrolling method used to follow the lithium transport, electrode movement
302 and expansion of multilayer sections of the measured N-CT datasets at different SoC. Further,
303 Ziesche et al.[64,65] demonstrates first 4D (3D spatial and 1D time resolved) N-CT experiments
304 on commercial Li/SOCl$_2$ battery cells with complementary X-ray CT in a two part study using
305 different NI instruments. With appropriate CT scanning strategies for neutrons[66], such as the
306 golden-ratio[67] scheme, the authors provide a quantitative correlation between the lithium that
307 is removed from the lithium-metal anode with the discharge current and the electrolyte
308 consumption. **Figure 3D** illustrates the pristine and the discharged SoC of an ER14505M cell
309 scanned with an on-the-fly scanning strategy and a post-mortem X-ray CT which displays the
310 anode and cathode current collectors that are less visible with neutrons. The complementary
311 X-ray CT helped do identify *inter alia* the LiCl protection layer on the anode surface and the
312 nickel current collector meshes inside both electrodes, which are invisible to neutrons because
313 these parts exhibited similar attenuation coefficients to the surrounding components.

314 NI is well suited to study electrolyte consumption and resulting gas evolution from electrolyte
315 decay, as well as formation of the solid electrolyte interphase (SEI) in lithium cells. This is due
316 to the high sensitivity of neutrons for hydrogen. A number of NR studies describe an
317 irreversible consumption of excess electrolyte during the first cell charge accompanied by gas
318 evolution. Lanz et al.[68] utilised NR to study the gas evolution and the resulting displacements
319 in commercial prismatic Li-ion cells during the first charge-discharge step, concluding that
320 most of the gas formation happened in the first charge period. Goers et al.[69] used NR to compare
321 different PVDF-based gel-type electrolytes by their percentage levels of evolved gas on the
322 graphite electrode. **Figure 4A** presents four of the *in situ* radiographs taken during the first
323 charge step with an EC:PC 2:3 1M LiClO$_4$ electrolyte mixture. The increased production of
324 bubbles and channels indicated gas evolution which correlated well with the electrochemical
325 data. Furthermore, the process of gas formation in high voltage Li-ion pouch cells was
326 investigated qualitatively and quantitatively by Michalak et al.[70,71] and Starke et al.[72]. The gas
327 evolution was based on oxidation and reduction of electrolyte solvents separated for anode and
328 cathode. The use of NR alongside differential electrochemical mass spectroscopy (DEMS) or
329 Prompt Gamma Activation Analysis (PGAA) allowed the gas species to be determined: C$_2$H$_4$
330 and H$_2$ formed on the graphite anode, and CO$_2$ formed on the cathode. *In situ* and *operando*

NR mapped regions of high activity following the charging process (**Figure 4B)** and helped to correlate the data with the electrochemical processes.

The filling and forming of lithium battery cells with electrolyte is a time-consuming process and one of the major cost drivers in cell manufacturing. A homogeneous electrolyte distribution/wetting of the electrode stacks is critical for the cell performance. NI provides a platform to analyse the filling and wetting processes time resolved and non-destructively. Wedanz et al.[73] studied the isotropic wetting process of electrode stacks of hard case prismatic cells from the outer cell regions towards the cell centres, observing that the wetting speed was reduced closer to the cell centre, and that filling in vacuum can reduce the wetting time by half. Habedank et al. [74] studied the wetting process on three different multilayer pouch cells with different engineered electrodes during *in situ* NR. The different degrees of wetting of the different electrodes with 30 % and 40 % porosity and laser structured electrodes is shown in **Figure 4C**. After 15 minutes the electrodes showed varying degrees of wetting, with a better cell wetting observed for the cell with higher porosity and a significant reduction of wetting time achieved for the laser structured electrodes, thus indicating potential to reduce manufacturing time and costs.

The radiography and tomography studies surveyed above are basically materials attenuation measurements, using polychromatic beams and neutron imaging cameras set-up in transmission mode. Instead, neutron diffraction imaging analyses the neutrons that are Bragg scattered by the sample. Different diffraction imaging techniques provide information from crystalline materials on structure transformations, phase compositions and microstructure properties. Spatial resolutions are modest compared to corresponding X-ray methods, in the range of mm^3 for pencil-beam scans, analysing the Bragg scattered beam, and hundreds of microns for Bragg edge imaging, analysing the transmitted beam.

Neutron diffraction is well suited to study the structure evolution of cathode and anode materials, e.g. observe the inhomogeneities of the Li phase distributions in a battery cell volume. Senyshyn et al.[54,55] utilised a neutron diffraction N-CT approach to study the evolution of the crystal structures versus SoC and to elucidate the Li-distribution in 18650 LIB. They concluded that the determination of Li concentrations by polychromatic N-CT is compromised by beam hardening artifacts resulting in pronounced attenuation gradients from the radial outer to the inner cell direction. The use of monochromatic N-CT and laterally resolved neutron diffraction proved a more promising approach, and resulted in a more homogeneous Li distributions. Senyshyn et al.[75] used spatially-resolved neutron diffraction, as a quasi-3D imaging technique, with a gauge volume of 2 x 2 x 20 mm^3 to create Li-concentration maps in the graphite anode of a charged 18650 cell by translating and rotating the cell as illustrated in **Figure 5A**.

Bragg edge transmission of materials used in LIBs was demonstrated by Butler et al.[56,76] who studied the stepwise evolution of the LiC_6 Bragg edge during dis-/charging in the graphite electrodes of prismatic cells with $LiCoO_2$ (LCO) as cathode material. Kino et al.[77,78] reported the use of 3D Bragg edge radiography (2D spatially and energy resolved) for studying crystallographic transitions in the cathodes and anodes of 18650 LIBs at different SoC. Later Kamiyama et al.[79] utilised the same technique to study the variation of the lithiated graphite structures in a LIB pouch cell. These studies captured the crystallographic phase transitions during dis-/charging of LIBs by a radiographic approach which yielded thickness-integrated information through the LIB as shown in **Figure 5B**. The first successful use of 4D Bragg edge tomography (3D spatially and energy resolved) on ultra-thick directional ice templated graphite electrodes for LIB cells was reported by Ziesche et al.[80]. From a set of energy separated radiographic projections in time-of-flight mode, 4D energy resolved tomographs were

379 reconstructed for an energy range that included the (hkl) Bragg edges for graphite (002), LiC_{12}
380 (002) and a fully lithiated LiC_6 phase (001). By fitting the Bragg edges on a voxel level, 3D
381 phase maps were obtained showing the phase fractions locally resolved such as shown for an
382 electrode at ca. 33 % SoC as horizontal and vertical orthogonal slices in **Figure 5C**. The spatial
383 resolution of Bragg edge imaging is currently limited to >100 μm, given the camera pixel sizes
384 of state-of-the art neutron detectors for time-of-flight experiments.

Perspectives

386 The examples presented in this article demonstrate the significant progress regarding spatial
387 and temporal resolution in NI achieved in the last several years. The further development of
388 the detector technology shows a potential for substantial improvements which would be a great
389 benefit for the majority of applications where the spatial and temporal resolution do need to be
390 traded off against each other for N-CT.

391 For instance the upgrade of the most commonly used imaging detector system by the utilization
392 of optical magnification and thin scintillator screens allow a spatial resolution better than 5
393 μm[81]. A small pixel size and high beam collimation require a high neutron flux in order to keep
394 exposure times short for *in operando* investigations. For this reason, imaging facility upgrades
395 were started at high-flux, steady state neutron sources, including the research reactors at the
396 Institut Laue-Langevin (ILL, France) and at NIST (USA). The future instrument NeXT at ILL
397 will provide very intense neutron beams for high resolution and high-speed applications[81,82]. A
398 good source strength is required to resolve the electrode features in the range of a few microns
399 and *in operando* on, for example, a stack of pouch cells in through-plane geometry. While the
400 inspection of sub-micrometre-size features, such as hollow needle-like Li dendrites[83], will
401 remain beyond the capabilities of neutron imaging for the foreseeable future, larger dendritic
402 microstructures[45] or moss like arrangements[84], with feature sizes from tens of micrometres to
403 the millimetre range can be examined.

404 Isotope substitution opens opportunities for contrast variation and noise reduction. Utilising Li
405 isotopes as contrast agents makes NI a unique technique for dynamic studies of the Li diffusion
406 and intercalation in rechargeable Li cells. A systematic respective substitution of ^6Li and ^7Li
407 can be exploited to map their distributions *in operando* investigations of real cells in cycling
408 mode. A corresponding approach can be employed for investigating the dynamics in liquid
409 electrolytes by replacing hydrogen by deuterium, also for improved visibility of Li and H
410 containing liquid electrolytes.

411 Besides attenuation imaging, different contrast mechanisms are now utilised in advanced
412 imaging setups. Energy-resolved NI using time of flight techniques are under development
413 with the promise of new and unprecedented possibilities. Currently available time of flight
414 detector technologies are still limited with regard to pixel and sensor sizes as well count rate
415 capabilities. Moreover, energy-resolving methods are more significantly reliant on high
416 neutron fluxes which will be available on the forthcoming ODIN instrument at the European
417 Spallation Source (ESS, Sweden)[85] and on the future VENUS and CUPID beamlines at the
418 Spallation Neutron Source (SNS, USA). Current work on the medium-flux IMAT beamline
419 (ISIS, UK) (see **Figure 5C**)[80], using capabilities that are also available at RADEN (MLF, J-
420 Parc, Japan), demonstrated that the new sources will enable 3D diffraction mapping of different
421 Li stages, e.g. LiC_6 and LiC_{12}, potentially in time-lapse mode and with much improved spatial
422 resolution. Such energy-selective multi-spectral imaging[86] will also help improving data
423 quantification and reducing image artifacts, including beam-hardening and scattering
424 distortions of the transmission signal. Direct mapping of the diffraction signals, as
425 demonstrated in **Figure 5A** will be possible with much smaller gauge volumes on the next

426 generation strain scanners at pulsed neutron sources. Further, use of neutrons in the thermal,
427 epithermal and fast neutron energy regimes will benefit studies of large battery types with
428 thicknesses of several centimetres, and potentially allow 2D or 3D mapping of elements and
429 isotopes via neutron resonance analysis using time-of-flight methods[34].

430 Progress in hardware is accompanied by developments of advanced image processing tools.
431 The implementation of regularised iterative and of neural network-based reconstruction
432 algorithms, as well as deep learning inspired analysis methods will help to deal with some of
433 the drawbacks encountered in NI, such as high-noise and under-sampled data sets, and thus
434 will help to reduce collection times and improve resolution. This is particularly important for
435 noise-affected multi-spectral imaging. Furthermore, future studies on lithium batteries will
436 endeavour to use neutron and X-rays simultaneously on the same beamline, as the two radiation
437 types are well suited for combinations of imaging/imaging and imaging/diffraction modes on
438 the same samples.

439 Besides the previously-mentioned advantages of neutron imaging for Li battery studies,
440 alternative chemistries can be probed albeit with much reduced image contrast for carriers in
441 Na-, K-ion and multivalent metal batteries. If neutron attenuation cross sections are similar to
442 the bulk components of the battery, the case for neutron imaging is much harder to make and
443 high-resolution X-ray CT will be more suitable for the majority of systems. However, for Bragg
444 edge transmission imaging and spatially-resolved neutron diffraction, strong absorption is
445 rather unwanted and thus diffraction studies will be worth considering for these battery types,
446 to study local microstructure variations and phase transitions inside batteries during cycling.

447 **Conclusions and Outlook**

448 In this article, we have reviewed the development of neutron techniques, and identified key
449 examples of their application to battery science and engineering from the extant literature. The
450 projected improvements to the suite of neutron techniques, largely enabled by hardware
451 optimisation, has been presented. Finally, in this section, we conclude with a perspective on
452 how these tools can be effectively applied to contemporary challenges in battery research.

453 Firstly, we envisage that the improved accessibility of NI beam-lines will facilitate their more
454 widespread adoption; akin to the rapid development and proliferation of X-ray techniques over
455 the past decade, we expect neutron techniques to grow in significance driven by the unique
456 contrast mechanisms offered. With improving spatial resolution, the increasing ability to
457 reconcile electrode behaviour with morphological characteristics will provide insight into the
458 role of micro-scale heterogeneities in determining macroscopic performance, whilst the
459 improvements in temporal resolution will facilitate routine studies of dynamic cell level
460 phenomena, including *in situ* and *operando* experiments. The current direction of technical
461 advances will support an overall shift from radiographic to tomographic measurements.
462 Generally, we anticipate that the increased throughput offered by developments in both source
463 and detector technology will substantially improve the accessibility of the techniques.

464 As a non-destructive tool, the extension of 3D NI into the fourth dimension, to evaluate
465 material and device changes over time, and in response to a range of environmental conditions,
466 will also follow the precedents from X-ray imaging. The alternative contrast mechanism
467 provides sensitivity to important elemental species, which naturally include metallic Li (and
468 other alkali metals), but also sensitivity to gas generation and liquid electrolyte movement. At
469 the electrode level, key challenges such as dendrite growth will (continue to) be informed by
470 NI, which may be particularly beneficial in solid state batteries, where the presence of high and
471 low-Z materials (in the form of e.g. ceramic electrolytes, and metallic Li respectively) can be

472 more readily resolved than with X-ray tools. In tandem with carefully selected isotopic
473 labelling, there is a compelling opportunity to examine the re-distribution of active species
474 within an electrode or device. At the cell level, key engineering challenges will also be
475 addressed, for example relating to gas generation during dis-/charging, or electrolyte drying
476 effects in long term operation. Whilst neutron tools remain much slower than equivalent
477 resolution X-ray imaging, the trajectory for improvements might also see the application of
478 neutron tools for characterisation of high speed events such as thermal runaway. Finally, the
479 introduction of novel techniques, such as Bragg edge imaging provide an opportunity to
480 reconcile crystallographic and microstructural information, which can be used to track
481 operation and degradation effects, and identify heterogeneities.

482 Clearly, neutron techniques are not without limitations. The spatial and temporal resolutions
483 have improved substantially in recent years, but are characteristically lower than for X-ray
484 tools. Moreover, the inherent requirement for a neutron source limits the application to large
485 scale facilities whereas, by contrast, laboratory X-ray generators are commonplace. However,
486 the unique sensitivities and contrast mechanisms of NI techniques offer some compelling
487 benefits and, consequently, NI will become more widely adopted within the pantheon of
488 correlative battery characterisation tools.

Author Contributions

496 R.F.Z. and P.R.S. conceived the study. R.F.Z. All authors wrote, reviewed and revised the
497 manuscript.

Declaration of Interests

499 The authors declare no competing interests.

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Figure 1: (**A**) Mass attenuation coefficients for thermal neutrons (25 meV) and X-rays (100 keV). Attenuation is a combined process of absorption and scattering. The interaction of X-rays with the electron cloud gives rise to a near-monotonic increase of the attenuation coefficient, while the nuclear interaction of neutrons is not a regular function of the atomic number and also differs for isotopes of the same element. (**B**) Spatial and time resolution development of NI for Li battery research over the last 20 years. The exposure times are given for a radiography (2D) or single projection of a computer tomography (3D) for corresponding spatial resolutions.

Figure 2: (**A**) NR study on standard samples with varying ^{7}Li contents and on diffusion couples of $Li_{1.33}Ti_{1.67}O_4$ (top) and corresponding digitised intensity spectra (bottom) from Takai et al.[41]. (**B**) X-ray (top left) and neutron (top right) radiographs of a lithium-iodine cell after discharging and rendered lithium distribution from an N-CT scan (bottom). Courtesy of Banhart et al.[31]; (**C**) N-CT of dynamic dendrite growth by Song et al.[45] indicating the dendrite evolution in a ^{7}Li/LiMn$_2$O$_4$ electrochemical half-cell at several stages of charge and the disappearance after discharge with transparent ^{7}Li-anode. The colour bar represents an increased neutron absorption from 0 to 1. (**D**) Time-lapse NR of thick sintered $Li_{4+y}Ti_5O_{12}$/LiCoO$_2$ electrodes discharged at C/20 (blue), C/10 (orange), C/5 (grey) and C/2.5 (purple), with the discharge profiles on the left and corresponding radiographs on the right (Nie et al.[52]). Red pixels indicate regions of lower lithium concentrations in the $Li_{4+y}Ti_5O_{12}$ electrode; blue pixels indicate lithium accumulation in the LiCoO$_2$ electrode.

Figure 3: 3D reconstructed orthogonal slices of *in operando* X-ray CT (**A**) and N-CT (**B**) of a CR2 Li/MnO$_2$ cell during discharging over a 4.5 Ω and a 4.7 Ω resistor. (**C**) shows cut-outs of the virtual unrolled multilayer sections at different SoC displaying the greyvalue changes, volume expansion of the MnO$_2$ electrode and electrode movement, as a result of the lithium migration (by Ziesche et al.[63]). (**D**) Lithium mass transport from the lithium metal anode to the liquid thionyl chloride cathode of a Li/SOCl$_2$ ER14505M cell discharged with 100 mA as orthogonal slices from 4D N-CT and post-mortem X-ray CT data, alongside with the quantified lithium anode depletion (by Ziesche et al.[65]).

Figure 4: (**A**) Normalised radiographs visualise the gas evolution (from left to right) in a graphite/LiMn$_2$O$_4$ cell with EC:PC 2:3 1M LiClO$_4$ electrolyte mixture during the first charge (by Goers et al.[69]). (**B**) Radiographs of LiFePO$_4$/graphite (a) – (d) at different SoC and cell potentials normalised to the initial radiograph (by Starke et al.[72]). The electrolyte displacement by evolved gas is visible as large bright areas where the intensity correlates to the gas amount. (**C**) *In situ* NR of the electrolyte wetting of multilayer pouch cells with different porosity and laser structured electrodes (from Habedank et al.[74]). A higher electrode porosity indicates faster cell wetting whereby laser structured electrodes show a significant increase of cell wetting after filling with electrolyte.

Figure 5: (**A**) Lithium concentration (x) of Li_xC_6 across horizontal and vertical orthogonal slices of a charged 18650 Li-ion cell by spatially-resolved neutron powder diffraction from Senyshyn et al.[75]. (**B**) 2D mapping of the fractions of (002) graphite and their lithiated stages at different capacities of a multilayer LiFePO$_4$/graphite pouch cell studied by Kamiyama et al.[79]. (**C**) maps of Bragg edge heights of graphite, LiC_{12} and LiC_6 phases for horizontal and vertical orthogonal slices of a directional ice templated graphite electrode at about 33 % SoC, reconstructed by Ziesche et al.[80]. The slices indicate inhomogeneous phase distributions and highest lithiation degree observed close to the lithium-metal counter electrode.