In situ methods for Li-ion battery research : a review of recent developments

Citation for published version (APA):

Harks, P. P. R. M. L., Mulder, F. M., & Notten, P. H. L. (2015). In situ methods for Li-ion battery research : a review of recent developments. *Journal of Power Sources*, 288, 92-105.
<https://doi.org/10.1016/j.jpowsour.2015.04.084>

DOI:

[10.1016/j.jpowsour.2015.04.084](https://doi.org/10.1016/j.jpowsour.2015.04.084)

Document status and date:

Published: 01/01/2015

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Review

In situ methods for Li-ion battery research: A review of recent developments

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H I G H L I G H T S

- All *in situ* techniques recently applied for Li-ion battery research are discussed.
- For every method the electrochemical cells for *in situ* research are described.
- Examples of exciting scientific results obtained through *in situ* research are given.

A R T I C L E I N F O

Article history:

Received 17 March 2015

Accepted 15 April 2015

Available online

Keywords:

In situ

In operando

Li-ion battery

Characterization methods

Review

A B S T R A C T

A considerable amount of research is being directed towards improving lithium-ion batteries in order to meet today's market demands. In particular *in situ* investigations of Li-ion batteries have proven extremely insightful, but require the electrochemical cell to be fully compatible with the conditions of the testing method and are therefore often challenging to execute. Advantageously, in the past few years significant progress has been made with new, more advanced, *in situ* techniques. Herein, a comprehensive overview of *in situ* methods for studying Li-ion batteries is given, with the emphasis on new developments and reported experimental highlights.

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1. Introduction

Society's increasing use of portable electronics, the need to balance the fluctuating output of renewable energy sources, and the rise of electric vehicles, put tremendous pressure on the further improvement of Li-ion batteries. As a result Li-ion batteries are studied extensively to optimize the existing technology and to discover new, more advanced, battery materials. In recent years a significant part of the investigations consisted of *in situ* studies.

While in a state of operation batteries are complicated systems in which a variety of chemical and physical processes take place, such as volume changes, phase transitions, side reactions, *etc.* *In situ*, and in particular *in operando* measurements, allow direct monitoring of these phenomena and thus offer the ability to

directly link these processes to the electrochemical response of the battery. The Latin expression "*in situ*" literally means "in position", and in battery research this refers to measurements that are performed on materials in their original position inside the device, *i.e.* without disassembling the battery. This allows characterization to take place under more realistic conditions, contrary to *ex situ* measurements. *Ex situ* measurements can furthermore be disturbed as a result of contamination during sample preparation and handling between battery use and characterization. *In operando* characterization represents a special case of *in situ* research, where the battery is in operation, *i.e.* is being (dis)charged during characterization, allowing measurements of non-equilibrated states that cannot be disclosed with *ex situ* characterization.

However, in order to conduct *in situ* experiments, batteries must be fully operational under the circumstances imposed by the diagnostic tool, which often demands specially designed devices and measurement setups, thereby hindering straightforward application of *in situ* techniques. Fortunately *in situ* methods to

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characterize Li-ion batteries recently experienced a rapid development, which is evident from the increasing amount of publications on this topic. All recent studies known to the authors, relevant to this topic, are listed in Table 1.

At present one review article which focusses on microscopic techniques [1], and a few brief overviews [2,3] of methods for *in situ* Li-ion battery research exist. In this review a comprehensive overview is given of recent *in situ* Li-ion battery research, in which techniques, cell design, as well as scientific results are described. The focus will be on recent developments and the challenges and requirements regarding the specially designed electrochemical cells.

2. X-ray techniques

2.1. X-ray diffraction

X-ray diffraction (XRD) is based on the scattering of X-rays by periodically spaced atoms in a crystal, producing a diffraction pattern that yields information about the crystallographic structure. In *in situ* battery research the method is used to monitor the structural evolution in an electrode as the (electro)chemical processes take place. For spatially resolved measurements energy dispersive XRD can be applied [4].

Table 1

In situ research on Li-ion batteries from 2009 onwards.

<i>In situ</i> technique	Investigated material
X-ray techniques	
X-ray diffraction	Ag ₂ VO ₂ PO ₄ [4] Ag ₂ VP ₂ O ₈ [107,108] C [13] CuF ₂ [109] Ge [110] LiFePO ₄ [5,111,112] Li ₂ FeSiO ₄ /C [8] Li[Li _{0.2} Ni _{0.2} Mn _{0.6} O] ₂ [6] Li _{1.2} Co _{0.1} Mn _{0.55} Ni _{0.15} O ₂ [113] LiCoPO ₄ [114] Li ₂ FeSiO ₄ [16] LiMn ₂ O ₄ [115] 0.5Li ₂ MnO ₃ ·0.5LiNi _{0.292} Co _{0.375} Mn _{0.333} O ₂ [116] LiNi _{0.5} Mn _{1.5} O ₄ [117,118] Li _x Mn _{1.5} Ni _{0.5} O ₄ [119,120] LiNi _{0.8} Co _{0.2} O ₂ [121] Li _{1.23} Ni _{0.09} Co _{0.12} Mn _{0.56} O ₂ [122] LiNi _{0.5} Mn _{1.5} O ₄ [123] Li ₂ RuO ₃ [124] K _{0.25} Mn ₂ O ₄ [125] Si [12,126] Sn [127] Sn–C [128] Sn ₃₀ Co ₃₀ C ₄₀ [129] Sn ₂₇ Cu ₃₁ C ₄₂ [7] TiO ₂ [130,131] V ₂ O ₅ [132] LiNi _{0.5} Mn _{1.5} O ₄ [133]
Coherent X-ray diffraction imaging	CuF ₂ [109] Ge [134] FeF ₃ [135] LiCoO ₂ [22,136,137] LiFePO ₄ [22,23,85,111] Li ₂ FeSiO ₄ [16,19]
X-ray absorption spectroscopy	Li _{1-x} Mn _{0.5} Fe _{0.5} PO ₄ [138] Li _{1.2} Mn _{0.525} Ni _{0.175} Co _{0.1} O ₂ [139] Li ₂ MnSiO ₄ [19] Li _{1.2} Ni _{0.15} Co _{0.1} Mn _{0.55} O ₂ [140] Li[Ni _{0.17} Li _{0.2} Co _{0.07} Mn _{0.56} O] ₂ [18] LiNi _{0.5} Mn _{1.5} O ₄ [123,141] Li ₂ RuO ₃ [124] Li ₃ V ₂ (PO ₄) ₃ /C [142] Mn ₃ O ₄ [15] RuO ₂ [21] TiO ₂ [131,143] V ₂ O ₅ [132]
Transmission X-ray microscopy	CuO [17] LiFePO ₄ [27] Sn [26,144] SnO [145] SnSb [144]
X-ray tomographic microscopy	Cu ₆ Sn ₅ [146] Li [147] Ge [30] Li _{1.2} Mn _{0.525} Ni _{0.175} Co _{0.1} O ₂ [139] Mn ₂ O ₄ [148] Si [149] Sn [29] SnO [28]
X-ray photoelectron spectroscopy	Li _x V ₂ O ₅ [150]
X-ray fluorescence	Sr ₂ MnO ₂ Cu _{3.5} S ₃ [151]
X-ray scattering	Reduction of LiPF ₆ electrolyte [152] SEI on graphene [153]
Scanning probe microscopy	
Atomic force microscopy	C [154] LiCoO ₂ [155] LiFePO ₄ [2,34] Si [31,156,157] Sn [158] Sn–Co–C [159] TiO ₂ [32,33] SEI on C [160] SEI on LiNi _{0.5} Mn _{1.5} O ₄ [161]
Scanning electrochemical microscopy ^a	C [162] LiFePO ₄ [163] MnO/Al ₂ O ₃ [52] Si [35,36,164,165] Sn [36]
Electron Microscopy	
Scanning electron microscopy	Li(Ni _{0.8} Co _{0.15} Al _{0.05})O ₂ [39] Si [37,166,167] SiO [166] SnO ₂ [38] lithium plating and stripping reactions [168–170]
Transmission electron microscopy ^b	CeO ₂ /graphene [171] Co ₃ O ₄ /graphene [172,173] CoS ₂ [174] Co ₉ S ₈ /Co-filled carbon nanotubes [175] CuO [176] FeF ₂ [177] Fe ₂ O ₃ /graphene [178] Ga [179] Ge [180] graphene [181] LiCl [182] LiFePO ₄ [50,183–185] LiMn ₂ O ₄ [186] Li ₂ O ₂ [187] LiV ₂ O ₄ [188] MnFe ₂ O ₄ /graphene [189] MoS ₂ [190] NiO/graphene [191] Si [47,53,192–197] Si/C [198,199] Si/graphene [200] Si/polymer [201] SiO ₂ /SiC [202] Sn [48,203] SnO ₂ [204–206] SnO ₂ /C [207] PbSe/graphene [208] TiO ₂ [209,210] Ti ₃ Sn/NiTi [211] RuO ₂ [212] ZnO [213] Zn ₄ Sb ₃ [214] all-solid-state nanobattery [54] all-solid-state thin film battery [57,59]
Optical techniques	
Raman spectroscopy	Au/SiO ₂ [66] C [64,65,67,215–217] LiCoO ₂ [61] LiFePO ₄ [63] Li ₂ MnO ₃ [62] Li ₄ Ti ₅ O ₁₂ [218] Si [68] V ₂ O ₅ [219] SEI on Li [220]
Fourier transform infrared spectroscopy	C [64,67,71,221] LiFePO ₄ [70] LiMn ₂ O ₄ [222] LiNi _{1/2} Mn _{3/2} O ₄ [222] Sn–Co [223] reduction/oxidation products of ionic liquids [69,224]
Optical microscopy	C [72,225–229] Li [230–233] Si [234]
Multi-beam optical stress sensor	C [235–237] Si [73,238–245] Sn [246]
Valence-differential absorption spectroscopy	manganese ferrocyanide [247]
Nonlinear coherent vibrational spectroscopy	SEI on Cu and Au [248]
Magnetic (resonance) techniques	
Nuclear magnetic resonance spectroscopy	C [249,250] Cu ₃ P [76] Li [82,83,251] LiCoO ₂ [79] Li _{1.08} Mn _{1.92} O ₄ [75,78] Si [252,253] liquid electrolytes [80,81]
Magnetic resonance imaging	Li [83] Li graphite [84] Li LiFePO ₄ [84] LiPF ₆ electrolytes [254]
Mössbauer spectroscopy	LiFe _{0.75} Mn _{0.25} PO ₄ [255] Li ₂ FeSiO ₄ /C [19] LiMn _y Fe _{1-y} PO ₄ /C [86] Sn/BPO ₄ [87] Sn ₂₇ Cu ₃₁ C ₄₂ [7] Sn ₃₀ Co ₃₀ C ₄₀ [129] Li [256]
Electron paramagnetic resonance spectroscopy	FeSb ₂ [257]
Electron magnetic measurements	
Neutron techniques	
Neutron diffraction	C [90] LiCoO ₂ [98] Li(Co _{0.16} Mn _{1.84})O ₄ [258] LiFePO ₄ [90,91,96] Li[Li _{0.2} Ni _{0.18} Mn _{0.53} Co _{0.1} O] ₂ [94] LiMn ₂ O ₄ [98,259,260] LiNi _{1/3} Mn _{1/3} Co _{1/3} O ₂ [94] LiNi _{0.5} Mn _{1.5} O ₄ /Li ₄ Ti ₅ O ₁₂ [261] Li ₄ Ti ₅ O ₁₂ [97,262] MoS ₂ [263] TiO ₂ /Li ₄ Ti ₅ O ₁₂ [264] commercial batteries [25,92,93,95,265–271]
Neutron reflectometry	Si [100,272] SEI on carbon [99] SEI on copper [273] SEI on LiMn _{1.5} Ni _{0.5} O ₄ [101] commercial batteries [106,274]
Neutron radiography	C [275,276] LiFePO ₄ pouch cell [277]
Neutron depth profiling	Sn [105,278] all-solid-state thin film battery [104]

^a This includes scanning ion conductance microscopy and electrochemical strain microscopy.

^b Only studies that have not been reviewed earlier [3,41,42] have been included in this table.

To conduct XRD measurements on an operating battery, an X-ray transparent window needs to be incorporated in the design in order to allow the X-rays to reach the electrode(s) under investigation. This can be done by using a battery with a very thin ($\sim 10\ \mu\text{m}$) current collector, without an additional casing [5]. This design does allow penetration of the incident X-ray beam, but this setup is also relatively vulnerable to air and moisture contamination. Therefore normally only a small part of the electrode is exposed by creating a hole in a much thicker protective casing or current collector, which in turn is sealed by an X-ray transparent material such as a Kapton foil [6] or Beryllium [7]. However Be, more particularly Be-oxide, is highly toxic and for the study of cathodes an additional protective layer is required to prevent corrosion of the beryllium at higher potentials. Recently conductive Kapton foil has also been employed as both the X-ray window and current collector [8]. Furthermore flexible [9], low-cost [10], battery designs for *in situ* XRD measurements are available, for which a proper pressure applied to the cell is essential to obtain reliable results [9,10]. Standard batteries, without modification, can be investigated by means of synchrotron-based high energy XRD [11–13]. As the high energy photons are able to fully penetrate the cell these measurements are conducted in the transmission mode in order to obtain 2D-diffraction patterns. This also means that the cathode and anode can be investigated simultaneously. A historical overview of *in situ* XRD cell designs can be found elsewhere [14].

An exemplary study of the added value that *in situ* measurements can have is the XRD study of Misra et al. [12] on the (de)lithiation mechanisms in Si nanowires. The measurements revealed the formation of the metastable crystalline $\text{Li}_{15}\text{Si}_4$ phase at low lithiation voltages. Previous *ex situ* studies showed that Si nanowires gradually lose their crystallinity during lithiation and become completely amorphous at the end of the cycle. The development of the transient $\text{Li}_{15}\text{Si}_4$ phase, which only can be disclosed through *in situ* characterization, reduces the cycle-life performance of Si-nanowire electrodes significantly. The authors show that by either limiting the cycles to a more positive cut-off voltage or adjusting the growth parameters of the nanowires, the formation of $\text{Li}_{15}\text{Si}_4$ during lithiation can be prevented, resulting in an improved capacity retention.

2.2. X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) is used to determine the local geometric and electronic structure of a material, associated with the redox reactions that take place in batteries. The absorption spectra feature two main regions, each of which disclose very specific information. The X-ray near-edge spectroscopic (XANES) part of the spectra provides information, among other things, about the oxidation state, while from the extended X-ray absorption fine structure (EXAFS) region information about the molecular structure can be obtained.

XAS cells for *in situ* measurements are very similar to the cells used for XRD research. However, XAS spectra are mostly obtained in the transmission mode, and the thick casing batteries therefore require two X-ray transparent windows at symmetric positions at the top and bottom of the cell [15,16]. To allow better penetration of the X-rays, carbon paper can be used as current collector instead of metal foils [17]. Standard pouch [18] and coffee bag [19] batteries can be employed without modification as the high energy photons that are applied for XAS are able to penetrate the entire battery stack. Furthermore the X-ray energy is tuned to the absorption edge of the element of interest and therefore absorption by other elements present in the battery components can be minimized [20].

Recently several noteworthy *in situ* XAS papers have been published. For example, Hu et al. [21] unraveled the origin of the

additional storage capacity found for nano-sized metal oxide conversion materials by using a combination of *in situ* XRD, EXAFS and XANES, together with *ex situ* NMR. Conversion materials, such as a metal oxide (M_xO_y), can reversibly react with lithium forming metal particles embedded in a metal oxide matrix, according to

The metal oxides, in this study RuO_2 , show more reversible capacity than estimated based on the reduction of the metal oxide to M^0 . The reason of this extra storage capacity is often thought to originate from the development of a so-called space-charge layer at the interface of the metal and lithium oxide particles. In this layer Li^+ ions can accumulate, charge compensated by electrons in the metal. However, the authors show that the additional storage capacity arises from the reversible reaction of LiOH with Li to form LiH and LiO_2 . The LiOH is formed from the reaction of Li and surface OH^- -groups naturally present on the RuO_2 nanoparticles. Although the formation of LiOH is considered to be mainly responsible for the additional storage capacity, the authors suggest that reversible SEI formation and simple Li adsorption on the Ru nanoparticles also may have minor contributions.

Yamamoto and co-workers [22] applied total-reflection fluorescence XAS to directly monitor the electronic structure at the electrode/electrolyte interface. This type of XAS can be used to perform surface sensitive measurements. The measurements showed that for a LiCoO_2 thin film electrode that exhibits gradual degradation upon electrochemical cycling, the Co-ions at the interface were reduced upon immersion in an organic electrolyte. Consequently, irreversible changes in the electronic structure at the interface were observed upon cycling. In contrast, in a LiFePO_4 thin film electrode with stable cycling performance, the electronic structure at the interface did not change and showed reversible cycling behavior. The stability of LiFePO_4 was attributed to the absence of a large potential drop across the space charge layer at the electrode surface. This study demonstrates a correlation between the stability of the electronic structure at the electrode/electrolyte interface and the cycling performance of Li-ion batteries.

To study the charge dynamics of battery electrodes, Liu et al. [23] used soft X-ray absorption spectroscopy (sXAS) to probe the oxidation state of metal ions in cathode materials during battery operation. Due to the short penetration depth of soft X-rays, the measurements require an ultra-high vacuum and are performed in the reflection mode. Detection holes were created across the current collector to expose some regions of the cathode material directly to the incident X-ray beam. During charging of LiFePO_4 (LFP) electrodes the iron atoms in the probed regions predominantly retained their $2+$ oxidation state and surprisingly even remained in this state when the battery was fully charged up to 4 V. Only after a relaxation period of 40 h under open-circuit condition a strong signal, corresponding to the charged state (Fe^{3+}), was observed. This indicates the existence of metastable phases that deviate from the well-known two-phase transformation that is expected to evolve in time. Indeed the exact (de)lithiation mechanism of LFP is still subject of debate [24,25]. Based on these results and additional *ex situ* measurements, the authors conclude that upon cycling the change in State-of-Charge (SoC) starts in the region adjacent to the current collector as indicated in Fig. 1. This contradicts the conventional consensus that the ionic conductivity is the rate-limiting process, which would cause the SoC changes to start at the cathode/electrolyte interface. Measurements were also conducted on $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NMC) where no large SoC gradients were observed. The authors designated the difference in behavior of the two cathode materials to a different (de)lithiation mechanism, i.e. two-phase transformation for LFP versus a solid-

Fig. 1. (a) Schematic representation of the charge distribution inside a LFP electrode as revealed by combined *in situ* and *ex situ* xXAS. The SoC distribution after charging (middle panel) equilibrates during open-circuit relaxation (bottom panel) at the same SoC. (b) Corresponding xXAS spectra. Reprinted by permission from Macmillan Publishers Ltd: Nature Communications ref. [23], copyright (2013).

solution mechanism for NMC, a difference in particle morphology and the difference in their respective ionic/electronic conductivity. The authors point out that due to the surface sensitivity of the applied method, local phenomena could be distinguished from the bulk behavior.

2.3. Transmission X-ray microscopy

With transmission X-ray microscopy (TXM), monochromatic X-rays are directed onto the sample under investigation and the radiation passing through is projected onto a CCD camera. In this way 2D images can be rendered of the internal electrode particle morphology.

As for many X-ray techniques, coin cells of which the covers of both sides are perforated and sealed with Kapton tapes to allow the X-ray beam to pass through can be used to facilitate this method [26].

Wang and colleagues [17] applied this method in combination with *in situ* XANES to map the chemical phase changes as well as the morphological development of CuO electrode particles during electrochemical cycling. In their subsequent study the same combination of techniques has been used to monitor the delithiation process of LiFePO₄ *in operando* [27].

2.4. X-ray tomographic microscopy

X-ray tomographic microscopy is an advanced form of TXM for which the *in situ* cell can be rotated through 180° to obtain a series

of 2D images. From these 2D images, 3D microstructure representations can then be reconstructed using a tomographic algorithm. Observations of the changes in attenuation coefficient are related to changes in composition and mass density, enabling visualization and quantification of the phase transitions of electrode particles.

To allow such 180° rotation without blocking the X-ray beam, cells devised for *in situ* measurements often have a cylindrical shape and are made from a highly X-ray transparent material. Examples are a polymeric Swagelok cell [28] and a Kapton capillary tube cell [29]. The X-rays are directed onto the working electrode from the side of the cell to limit the battery components in the path of the beam. A conventional pouch cell has also been used [30]. Due to its flat design the angular range that can be measured is limited to 140° but this is sufficient to reconstruct high quality 3D images. As in this configuration the current collector is in the pathway of the X-ray beam, it should be kept very thin, of the order of less than 2.5 μm.

Recently Ebner et al. [28] were the first to apply *in situ* X-ray tomography to investigate Li-ion batteries. In their study the morphological evolution as well as the change in chemical composition of individual SnO particles upon (de)lithiation were monitored. Three dimensional images could be rendered with a resolution of 2.0 μm. Fig. 2 shows the progress of the conversion reaction of SnO into Sn and LiO₂ according to Eq. (1), and the subsequent alloying of Li and Sn. The lithiation of the SnO particles leads to volume expansion and crack formation. Impressively, the authors were able to quantitatively link the electrochemically measured capacity losses to the observed electrically disconnected

Fig. 2. X-ray tomographic images of SnO particles during lithiation. (a) Vertical and (b) horizontal cross sections through a SnO particle during electrochemical reduction. Cross sections at 0 min are indicated by dashed white lines revealing the cutting planes. The white arrows point out crack locations. (c) Schematic representation of phase evolution and crack development of a SnO particle due to lithiation. (d) 3D rendering of sub-volume. Black arrows indicate fracture. Adapted from Ref. [28], with permission from AAAS.

particles. More recently this technique has also been used to investigate Sn [29] and Ge [30] electrodes upon cycling, achieving even nanometer scale visualization.

3. Scanning probe microscopy

3.1. Atomic force microscopy

Atomic force microscopy (AFM) is based on the deflection of a cantilever with a sharp tip to examine surfaces. By scanning the interphase between the electrode and the liquid electrolyte, a height distribution is obtained, and thus volume changes and/or SEI formation upon cycling can be visualized. Furthermore through AFM enabled nano-indentation [31], the mechanical properties of nanostructures during (de)lithiation can be measured. In most of the *in situ* AFM studies a passive probe is used, *i.e.* no electronic stimulus is supplied via the cantilever. Voltage-biased AFM [32,33], where the tip is acting as a current collector, allows studying the surface potential and topographic changes as a function of the applied voltage.

Obviously a critical feature of an *in situ* AFM design is the access of the cantilever into the battery. As an opening is necessary to facilitate the cantilever, measurements are often performed under inert atmosphere inside a glove-box to exclude contamination. The opening should be kept small and properly sealed since evaporation of the organic solvent will influence the measurements due to an increasing salt concentration of the electrolyte over time [34]. In order to scan the working electrode it should be sufficiently exposed and therefore the counter and reference electrodes are typically positioned to the sides of the working electrode. An elaborate discussion of the design guidelines for *in situ* AFM cells

can be found in Ref. [34].

3.2. Electrochemical strain microscopy

An adapted form of AFM has recently been developed to study the lithium motion on a nanometer scale. This technique, denoted electrochemical strain microscopy (ESM) [35], is based on the application of periodic high frequency voltage-bias between the cathode and anode. The resulting oscillatory surface displacement on top of the thin film battery can then locally be detected by the AFM tip. The amplitude of the surface displacement is directly related to the change in Li-ion concentration induced by the applied bias. Since with this technique the Li-ion transport is probed by measuring the strain and not by an electric current as is traditionally done, the obtained resolution is much higher due to the sensitivity of the AFM.

The method can be applied to all-solid-state thin film batteries where the top current collector is omitted allowing the conductive cantilever to directly scan the top-electrode and act as the current collector. All ESM measurements of Li-ion batteries so far have been conducted in ambient air.

3.3. Scanning ion conductance microscopy

Scanning ion conductance microscopy (SICM) offers the opportunity to directly measure ionic currents as well as the surface topography by the application of a nano-scale pipette that scans the electrode at the electrode/liquid electrolyte interface. The spatial resolution depends on the pipette tip geometry and is therefore practically limited to tens of nanometers. The current sensitivity can reach sub-pA levels.

A relatively simple setup is used for this method [36]. It consists of a petri dish to immerse an electrode in electrolyte and a pipette containing a lithium source that scans the interface while oscillating in the vertical direction. The apparatus is housed inside an argon glove-box.

4. Electron microscopy

4.1. Scanning electron microscopy

Scanning electron microscopy (SEM) is based on electrons to construct an image. An electron beam is focused on a sample and either the backscattered electrons or the secondary electrons emitted by the available atoms are detected. The technique offers a good spatial resolution to investigate morphological changes during battery operation, such as electrode volume expansion/shrinkage, electrode crack formation and delamination. Electron microscopes are often equipped with additional spectroscopy and diffraction tools that can give more detailed information. Force sensors and a piezo-actuators can be housed inside the SEM chamber to conduct mechanical experiments [37].

The monitoring ability is restricted to the outer surface and therefore the applied cells must have an open structure, where the electrode is directly exposed to the electron beam. Measurements require high vacuum and therefore *in situ* cells should be highly compatible with vacuum conditions. This can be achieved with batteries based on solid, polymer or low vapor pressure electrolytes, such as ionic liquids. To meet the requirements of having an open structure and vacuum compatibility an electrochemical cell can be employed that consists of a current collector mesh that is coated with electrode material in combination with an ionic electrolyte [38]. In this configuration the current collector does not obscure the electrode and the mesh allows permeation of the ionic liquid electrolyte to provide ionic contact. Another approach, applied by Miller et al. [39], is to assemble the battery inside the SEM chamber. Fig. 3 shows the actual setup. It consists of an electrode particle which is attached to a manipulator probe. The probe, also serving as electric lead, is used to bring the particle into contact with a droplet of ionic liquid electrolyte which covers the counter electrode.

Fig. 3. SEM image of the micro-scale battery setup as observed in the microscope. A probe is used to bring a single electrode particle into contact with an electrolyte droplet covering the counter electrode. The particle is etched with a focused ion beam for imaging purposes. Reprinted with permission from Ref. [39]. Copyright© 2013 WILEY-VCH.

4.2. Transmission electron microscopy

Unarguably the biggest recent breakthrough in the field of *in situ* techniques for battery research has been the development of *in situ* transmission electron microscopy (TEM). After the initial work of Huang et al. [40] in 2010 on the (de)lithiation of a single SnO_2 nanowire, many reports on nanostructured electrodes studied by *in situ* TEM followed. Several reviews on the subject are available [3,41–43].

With TEM electrons are detected that are transmitted through the sample of interest to construct an (atomic-scale) image, and therefore only ultra-thin samples *i.e.*, nano-batteries, can be investigated. In addition to the morphological changes that can be observed during battery operation, additional integrated techniques, such as electron diffraction and electron energy loss spectroscopy (EELS), can provide information about the local composition and structure.

TEM requires a high vacuum for its operation. Therefore liquid electrolyte batteries need to be sufficiently sealed to prevent electrolyte evaporation. This however requires extra material which adds to the thickness of the cell. To keep the cell as thin as possible and compatible with vacuum conditions, all-solid-state batteries or batteries containing ionic liquid electrolytes with an extremely low vapor pressure are applied. Fig. 4 shows the conventional setups for *in situ* TEM, the so called end-contact configuration where only a fraction of the nano-electrode under investigation is connected to either a solid- or ionic liquid electrolyte, which in turn is connected to a lithium source.

Amazing breakthroughs have taken place in the *in situ* TEM-monitoring of rechargeable batteries. However, many authors recognize the difference in configuration as well as testing methods, between the investigated nano-batteries and bulk-size batteries that are used in practice [41,42,44]. For instance, due to the required nano-sized configuration of the batteries, the contacts are very small and often non-optimized, inducing significant overpotentials during battery operation, which might influence their characteristics. Also, the currents involved in (de)lithiation processes of TEM batteries are often too small to be controlled in a galvanostatic mode, which hinders easy comparison with other

Fig. 4. Schematic representation of the open cell nano-battery setup, enabling *in situ* TEM. (a) Ionic liquid electrolyte (ILE) containing cell; a drop of the ILE is placed on the tip of a bulk cathode and long objects, such as nanowires, are used as anode. (b) Solid-state electrolyte cell; metallic Li acts as lithium source on which a naturally formed thin Li_2O layer serves as solid-state electrolyte. This configuration is suitable for small objects of interest, such as nanoparticles. Adapted from Ref. [3] with permission from The Royal Society of Chemistry.

battery research. Furthermore, the high energy electrons can induce crystallization or dissociation of materials [45]. Another concern is the use of vacuum compatible electrolytes. These electrolytes not necessarily influence the battery behavior as such, but do differ from the organic solvent-based electrolytes in conventional batteries. Lastly, during the TEM measurements the electrode typically only has a small part of its outer surface in contact with the electrolyte, whereas in a normal battery it would be entirely immersed in the electrolyte, the so called “flooding geometry”.

In response to these limitations some *in situ* TEM investigations have been deviating from the general setups described above. For instance, Zhong et al. [46] reported on a SnO_2 nanowire partially flooded in an ionic liquid for which very different lithiation behavior was found compared to a SnO_2 electrode in the conventional setup in an earlier study [40]. The flooded geometry exposed a new type of lithiation, in which oblique stripes were formed across the width of the nanowire, after which elongation and swelling of the wire occurred. Gu and co-workers [47] were able to conduct *in situ* TEM measurements on a silicon nanowire cell, containing a liquid electrolyte. To this end a design was used consisting of SiN membranes to contain the liquid. A similar design was used earlier for *in situ* electron diffraction measurements during electrochemical cycling of a thin film of Sn [48]. The configuration was kept thin enough to allow transmission of electrons for imaging. Because the silicon nanowire is fully immersed in the electrolyte, lithiation indeed proceeds by uniform swelling along the axial axis of the entire nanowire. This is different from the lithiation of a silicon nanowire connected at only one end to electrolyte, featured by a reaction front advancing in the axial direction [49].

With the configurations presented in the aforementioned studies, one is able to observe lithiation in a flooded geometry and potentially perform SEI analyses. However, due to the liquid electrolyte and the relatively thick membranes, these features are at the expense of spatial resolution and the ability to use the spectroscopy techniques available on electron microscopes. A type of spectroscopy that recently has been performed on a liquid cell is valence EELS, which probes the low energy regime, and can be employed in thicker liquid layers than is typically feasible with conventional EELS [50].

A good example of new insight *in situ* TEM can provide is the study of Liu et al. [51] on aluminum nanowires and their native oxide layers. It shows that upon cycling, prior to the metal core, the metal oxide layer (Al_2O_3) is lithiated first, turning into a Li-Al-O glass. The aluminum core pulverizes after delithiation but, remarkably, the nanowire as a whole maintains its mechanical integrity due to the Li-Al-O surface layer as shown in Fig. 5. Apparently the Li-Al-O glass acts as a SEI layer. It conducts Li -ions and mechanically confines pulverized particles, thereby preventing loss of active material. This finding clarifies some of the underlying principles of coating active battery materials with metal oxides such as Al_2O_3 , which is a well-known strategy to improve the overall battery performance [52,53].

Another interesting TEM study concerns the scaling limits of batteries. Ruzmetov and colleagues [54] investigated all-solid-state nano-batteries with a radial geometry, which were fabricated by subsequent (physical vapor) deposition of the various components onto Si nanowires. Based on their current–voltage characteristics the authors argue that the only 110 and 180 nm thick (LiPON) electrolyte layers were pin-hole free. However, the batteries suffered from severe self-discharge which, according to the study, is caused by the nano-scale dimensions of the electrolyte layer and the resulting onset of space-charge limited electronic conduction. The results show that in addition to the layer quality, other fundamental effects determine the scaling limits for nano-batteries.

Considering the early stage of development of *in situ* TEM for Li -ion batteries, an impressive amount of publications is already available. It therefore seems apparent that the method will continue to develop in the near future, also in terms of generating results that relate more to the world of real-life batteries. However, even in this stage a good consistency exists between the experimental data obtained by *in situ* TEM and other *ex situ* studies on bulk-type batteries [41].

4.3. Electron holography

In electron holography [55,56] the sample is exposed to an electron beam of which the phase will be modulated by the electrostatic potential and magnetic field across the samples. The signal coming from the sample and a reference signal are let to interfere with each other, which results in a hologram, *i.e.* an interference fringe pattern. The phase modulation extracted from the hologram is used to reconstruct the electrostatic and/or magnetic fields in the samples, *e.g.* the inner mean potential.

Yamamoto et al. [57] applied the relatively unknown technique of electron holography to map the electric potential distribution across the cathode/solid electrolyte interface during battery operation. The authors used a planar thin film all-solid-state battery of which the area of interest was thinned down by a focused ion beam to 60 nm for TEM observation. Fig. 6 shows a typical distribution of the measured potential together with the analyses of the lithium and electron distribution during charging. As can be seen, the profile has a linear voltage slope inside the cathode, a steep voltage drop across the interface and a more gradual slope in the solid electrolyte. The steep drop at the interface is consistent with the general consensus that voltage drops are mainly concentrated at the electrode/electrolyte interfaces. However the authors point out that the gradual slope of the potential distribution in the solid electrolyte is not easily accounted for. The length of about 1.5 μm is orders of magnitude bigger than the estimated Debye length, which is considered a measure of the thickness of the electrical double layer. The Debye length for this material, as calculated from the Gouy-Chapmann theory, only amounts to a few angstroms. It is furthermore remarkable that the obtained width of the space charge layer is of the same size of the entire electrolyte layer in conventional thin film batteries [58]. In a second paper using electron holography the anode side of the electrochemical cell has been investigated [59].

5. Optical techniques

5.1. Raman spectroscopy

Raman spectroscopy is based on the inelastic scattering of monochromatic light when it interacts with the sample. The shifts in wavelength or photon energy of the scattered light correspond to the vibrational modes of the system, which are characteristic for Raman-active molecules. Consequently, structural changes of electrodes during cycling can be determined. An extensive publication on *in situ* Raman spectroscopy in electrochemical research can be found elsewhere [60].

As an optical pathway needs to be created for laser light to reach the electrode, normally an opening in the *in situ* cell is provided in the outer casing behind which a piece of thin glass is applied. This creates a window for the laser light to go through. In order to reach the electrode, two configurations can be used [61]: The first configuration [62,63] makes use of a top current collector foil perforated near the casing opening, or is based on a current collector grid for which the mesh size is approximately an order of magnitude smaller than the laser beam diameter. The second

Fig. 5. EELS maps of an Al nanowire after three electrochemical cycles. (a) Zero loss image showing a pulverized nanowire, confined by a tube-like surface layer. (b–d) EELS maps of Li, Al, and O, respectively, revealing the nanoparticles are aluminum and the surface layer consists of Li, Al, and O. A three-window technique was used to obtain the energy-filtered maps. Adapted with permission from Ref. [51]. Copyright (2011) American Chemical Society.

option comprises of a current collector, a lithium foil and separator, which are all configured with a hole to expose the second electrode at the bottom of the electrochemical cell. However, as the separator has been perforated in the second configuration, the examined electrode area may not have an optimal ionic connection to the counter electrode [61]. Furthermore the first configuration allows the glass window to be close to the electrode under investigation. Therefore the amount of liquid electrolyte in the pathway of the laser light can be kept to a minimum to limit the undesired scattering of light by the electrolyte [64,65].

Fig. 6. Schematic representation of the formation of an electric double layer during battery charging. Distribution of lithium and electrons near the positive-electrode/electrolyte interface (top) and typical distribution of the measured potential distribution (bottom). Reprinted with permission from Ref. [57]. Copyright© 2010 WILEY-VCH.

Combining complementary *in situ* techniques on the same cell is a powerful approach to investigate Li-ion batteries. Hy et al. [66] studied the SEI formation and evolution on SiO_2 -coated Au nanoparticles during cycling, combining normal Raman spectroscopy with surface enhanced Raman spectroscopy to investigate the surface as well as the bulk of the electrode particles. A standard *in situ* Raman cell, as described above, can also be applied for surface enhanced measurements. Using the same strategy, combining Raman with a surface sensitive technique, Pérez-Villar and co-workers [64] combined Raman spectroscopy with Fourier transform infrared spectroscopy. A specially designed cell compatible with both techniques allowed measurements to be performed at the same location. The authors selected a window material (CaF_2) that is transparent to both types of light utilized for these techniques. Furthermore a microscope objective was applied, allowing the Raman signal to incident normal to the electrode and the infrared beam under a variable angle of incidence. Information could be obtained about the surface species involved in the interfacial reactions as well as the structural changes of the glassy carbon electrode induced by electrochemical cycling. In a follow-up study the same combination of techniques has been used to investigate a graphite electrode [67].

An interesting example of an *in situ* Raman study is the work on the effects of B and P dopants on the lithiation of crystalline Si. Long et al. [68] measured the intensity of the characteristic phonon mode corresponding to crystalline silicon as a function of the electrode potential vs a Li/Li^+ reference electrode. Since a decrease in the phonon mode intensity is indicative of the transition from crystalline to amorphous silicon, it corresponds to the onset of the

lithiation process. The B-doped Si showed an onset potential for the phonon decay at 0.68 V, whereas that of P-doped Si was found at 0.09 V. The authors concluded that, among other things, the different Fermi levels in B- and P-doped Si are responsible for the difference in onset voltage for the initial Li insertion.

5.2. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) is very similar to Raman spectroscopy, however, it is based on the absorption of infrared light rather than inelastic scattering. Due to the surface sensitivity of FTIR it is often applied to probe the interfacial reactions between a working electrode and the electrolyte in the reflective mode, but also to identify gas products that are formed, resulting from the reduction or oxidation of the electrolyte in the transmission mode.

A relatively large number of different battery setups for *in situ* FTIR research have been described [69–71]. Several window materials, that are transparent to infra-red light and allow the beam to reach the working electrode, have been applied. Examples are KBr [69], CaF_2 [70] and diamond [71]. Most experimental setups do not have a conventional half-cell, sandwich-like, structure but have a more open structure with the counter electrode positioned aside the working electrode. This configuration ensures good accessibility to the electrode of interest which is necessary as the infrared beam is incident at an angle to obtain maximum reflection intensity. Such a design furthermore allows the incorporation of a reference electrode. Fig. 7 shows a schematic representation of an *in situ* FTIR cell. Positioning the IR-window as close as possible to the working electrode is critical to limit the light absorption by the electrolyte between the window and electrode. However, it should be taken into consideration that as the liquid electrolyte film becomes too thin, the diffusion of electrolyte species to/from the electrode may become a limiting factor [71].

5.3. Optical microscopy

The resolution of optical microscopy is fundamentally restricted by the diffraction limit of visible light, which is not sufficient to monitor microstructural changes. However electrochemically induced macroscopic structural changes of electrodes and dendritic lithium formation can be investigated through (digital) optical microscopy. Since the color of lithiated graphite is a measure of its SoC [72], the (de)lithiation process of graphite can be studied with an optical microscope by tracking the color evolution.

This technique does not put many restrictions on the design of *in situ* cells and many different cells have therefore been described in the literature. The only requirement is the presence of a glass window that allows the exposure of the electrodes to visible light.

Fig. 7. Schematic representation of a representative *in-situ* FTIR cell. Reprinted with permission from Ref. [70]. Copyright© 2013 Elsevier B.V.

5.4. Multi-beam optical stress sensor

The multi-beam optical stress sensor technique (MOSS) is a method to determine the stress in thin films by measuring the change in substrate curvature. This is done by employing an array of parallel laser beams and measuring the relative change in the spacing between them as they are reflected from the substrate. The electrochemically induced stress/strain during battery operation in thin film electrodes can, in this way, be monitored.

A typical *in situ* MOSS cell has the characteristics of a flooded beaker cell, comprising of a lithium foil, acting as a counter electrode positioned at the bottom of the cell, covered by a separator immersed by the electrolyte and the substrate containing the thin film electrode material. The substrate on which the electrode layer has been deposited is placed in the electrochemical cell such that the electrode-side faces the separator. The incorporation of a glass window allows optical access to the back of the substrate. Unlike most battery setups no pressure is applied to this system [73]. The array of laser beams applied to measure the curvature are reflected at the back of the substrate. It is essential that the used substrates can deform elastically so that the induced stress in the thin film electrode is proportional to the measured substrate curvature. Barrier layers are deposited onto the substrate when necessary to isolate it from electrochemical reactions.

6. Magnetic resonance techniques

6.1. Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance spectroscopy (NMR) is based on the magnetic resonance properties of nuclear isotopes, which, depending on their nuclear spin and quadrupole moments, resonate at characteristic frequencies when placed in a strong static magnetic field. The nuclear magnetic resonance spectra are probed by additionally applying appropriate radio frequency (rf) magnetic field pulses at the resonance frequency. Slight variations in the observed resonance frequencies give detailed information about the local electronic environment around the nucleus. The local electronic environment of ^7Li (and ^6Li) can adequately be probed by NMR and, consequently, yields information about the Li environment and electrochemically induced structural changes of electrodes during or after cycling.

The metal parts normally present in a battery, such as casings, current collectors and metallic coatings in coffee-bag cells, shield the electrodes from the applied pulsed rf-fields. The batteries used for *in situ* measurements must therefore have as few metallic parts as possible. To this end Bellcore-type plastic cells have been successfully employed [74]. A common problem with plastic batteries is the lack of pressure across the cell. However, in this type of cell the components are laminated together through a process that involves heating under pressure and the addition of a binder, and they are therefore sufficiently coherent and stay attached. The cell furthermore comprises of a current collector mesh rather than a closed foil to limit the rf shielding effects [75]. Unlike batteries with a metal casing, plastic cells are permeable to air and relatively fragile. As an alternative a more robust cylindrical cell has been designed by Poli and colleagues [76].

^7Li NMR has shown to be an adequate technique to investigate anode materials. An elaborate overview has been provided by Blanc et al. [77]. However, recently researchers have shifted their interest to *in situ* NMR studies of cathode materials. This is quite challenging due to the signal broadening and peak shifting, which results from the paramagnetic nature of most cathode materials and the inability to use *in situ* magic angle spinning to overcome these limitations [78]. Detailed practical aspects associated with *in situ*

NMR measurements of cathode materials are discussed in detail for $\text{Li}_{1.08}\text{Mn}_{1.92}\text{O}_4$ [75,78]. Shimoda and co-workers [79] were able to observe the lithium extraction/insertion from/in LiCoO_2 by optimization of the cell components and increasing the magnetic field strength.

NMR is a quantitative method, but it yet remains challenging to obtain spatially resolved measurements. Recently, however, several *in situ* NMR studies have been conducted, measuring Li-ion concentration gradients [80,81] and monitoring lithium dendrite formation [82]. Klett et al. [80] employed a 10 mm cylindrical cell to study the concentration gradient build up in LiPF_6 electrolyte under current flowing conditions. The 1D lithium distribution could be obtained with a nominal resolution of 19 μm . From the measured data, the authors quantified the salt diffusivity and the Li^+ transport number on the basis of a physical mass transport model. Krachkovskiy and colleagues [81] applied 1D ^7Li NMR imaging in combination with slice-selective NMR to measure the Li^+ self-diffusion coefficients in liquid electrolytes.

Bhattacharyya et al. [82] were able to quantify the mass of moss/dendrite lithium microstructures formed during electrochemical cycling of a metallic Li electrode. Due to the skin effect, the applied rf-field penetrates the subsurface region only and the signal was therefore found to be proportional to the area of the metal electrode rather than its volume. This is, however, different for the microstructures formed upon cycling, which are totally penetrated by the magnetic field due to their limited size, resulting in a response which is directly proportional to their volume or mass. With the assumption that during cycling the total surface area of the bulk metal electrode was not changing significantly, the change in signal intensity was attributed to the amount of Li microstructures formed or stripped. Several different electrolytes were employed, resulting in different electrode behavior, which could be readily observed.

By applying NMR in the way discussed above, Chandrashekar et al. [83] measured the amount of deposited Li-microstructures during electrochemical cycling in a symmetric lithium cell. However, to determine the location of the lithium deposits, magnetic resonance imaging (MRI) was employed to obtain a three dimensional image. The obtained spatial resolution is of the order of hundreds of μm . Tang et al. [84] applied stray-field imaging, which makes use of a magnetic field with higher field gradients than that used for MRI to monitor the Li-ion transfer between the electrodes in Li-graphite and Li– LiFePO_4 half-cells, obtaining a 1D distribution with a resolution of 39 μm .

6.2. Mössbauer spectroscopy

Mössbauer spectroscopy (MS) is a nuclear hyperfine interaction method, which enables one to study the influence of the electronic environment on the nuclear hyperfine energy levels, and as such probes the structure of materials. The parameters probed are typically the Isomer Shift and Quadrupole Interaction that give information about the valence state and electronic configuration of the Mössbauer atom, as well as a magnetic hyperfine field (when present). In a typical experiment the intensity of the transmitted radiation is measured as a function of the Mössbauer source velocity. The specific requirements for a suitable gamma ray source limit the different isotopes that can be studied by this technique. Although theoretically several Isotopes relevant for Li-ion batteries can be investigated by MS, most research has been restricted to ^{57}Fe and ^{119}Sn Mössbauer experiments.

The gamma ray energies are generally higher than typical XRD X-ray energies. For that reason electrochemical cells for *in situ* MS research are very similar to *in situ* XRD and XAS setups since the gamma rays can penetrate the cells and window configurations. For

example, the specially designed cell by Leriche et al. [85] for *in operando* studies of Li-ion batteries using synchrotron radiation, has been applied for *in operando* MS experiments in combination with X-ray based techniques [86,87]. A simpler, yet similar, design [88] used for *in situ* MS measurements is a coin-type cell equipped with a Be window in the cell cap and case. The Be window is transparent to γ -rays and also acts as a current collector. When in contact with a cathode material a layer of Al is, however, required to prevent the Be window from oxidation [85].

7. Neutron-based techniques

7.1. Neutron diffraction

The technique of neutron diffraction is very similar to XRD. However, the technique can be used in addition to XRD, especially to study light elements such as lithium, as neutrons interact with the nucleus and its cross section rather than with the electrons surrounding the atom as is the case for X-rays [89]. Since the neutron cross section has similar but varying sizes for light and heavy isotopes throughout the periodic system, neutrons are sensitive to light elements (e.g. Li) next to heavier ones (e.g. Fe, Co), but can also be sensitive to the contrast between elements of almost the same mass (e.g. Ni and Mn).

Another difference is the weaker interaction of neutrons with matter and the resulting larger penetration depth. Consequently, a relatively high amount of electrode material is necessary for a proper measurement, which can be challenging for laboratory-scale batteries [90,91]. However, due to this large penetration depth of the neutrons, measurements can be performed on unmodified commercial cells and diffraction patterns of the anode and cathode can be obtained simultaneously [92]. These batteries, however, are not optimized for *in situ* neutron diffraction. For instance, the technique is very sensitive to the hydrogen present in the separators and liquid electrolytes of commercial cells, which unfortunately gives rise to large background signals from incoherently scattered neutrons [93–95]. The use of custom-made cells with low H-content components that mimic, for example, cylindrical 18650-type commercial batteries leads to a significant increase of the signal-to-noise ratio [89]. A common strategy to lower the H-content is the use of deuterated electrolytes and special fluorinated separators [89,96,97]. A remaining issue is however the presence of many cell components in the pathway of the neutron beam. This results in additional undesired Bragg reflections and increased background intensity [90]. Also the different electrochemical equilibrium phases that are generally present lead to overlapping spectra of anode and cathode. At this moment in time it remains challenging to obtain high-quality full pattern Rietveld refinements of *in situ* neutron diffraction data [91]. In an effort to resolve the aforementioned issues, several promising new battery cells for *in situ* neutron diffraction measurements have recently been proposed [90,91,94,96,98].

7.2. Neutron reflectometry

Neutron reflectometry or scattering involves directing a highly collimated beam of neutrons onto a surface and measuring the intensity of the reflected radiation as a function of angle or neutron wavelength. It is used to determine the scattering length density as a function of penetration depth which, in turn, is related to the atomic composition. This allows monitoring of thin film growth, such as SEI formation, and volumetric changes induced by battery operation.

Due to the large penetration depth of the neutrons, commercial cylindrical batteries and conventional coin cells can be used for *in*

situ reflectometry research. To prevent loss of intensity, isotopically enriched ^7Li electrodes can be applied, as ^6Li species are able to absorb neutrons [99]. To investigate thin films electrodes, custom-made electrochemical cells are used [100,101]. These cells allow the substrate, onto which the electrode of interest has been deposited, to be mounted. The substrate is the incoming medium for the neutrons.

7.3. Neutron depth profiling

With neutron depth profiling (NDP) one is able to probe the ^6Li isotope as a function of sample depth. The sample is bombarded with moderated thermal (low energy) neutrons of about 25 meV, which can be absorbed by ^6Li that has a high neutron absorption cross section, resulting in the emission of an alpha and triton particle, according to

The technique is considered non-destructive, since the amount of annihilated ^6Li atoms is negligible with respect to the total amount of Li atoms. Upon creation the alpha and triton particles have a well-defined energy. By measuring the energy loss of these particles when the detector is reached, the depth at which these were initially formed can be deduced. In order to obtain an accurate lithium depth profile the energy loss must only result from the interaction of the charged particles with the sample and not with gaseous species on the way to the detector. This implies that the measurements preferably must take place at sub-ambient pressures. As two different particles are emitted from the sample, two depth profiles can be obtained. The alpha particles with 2+ charge typically lose more energy while crossing the sample and can therefore be used to obtain a high resolution concentration profile of thin film batteries. The (1D) resolution can be as low as 72 nm for metal oxide cathodes [102]. To measure concentration profiles of bigger batteries the ^3H particles can alternatively be used.

Even though neutrons have a high penetration power, the created alpha and tritons particles are strongly absorbed by metal. Therefore, the thickness of the current collector of an *in situ* NDP cell must be kept as small as possible, and no metallic casing can be applied. The cell furthermore must be operational under vacuum conditions. However, in an exploratory study of Nagpure and co-workers [103] it has been shown that by the application of an inert helium atmosphere, measurements of (air-sensitive) materials are also possible at relatively high pressures.

Oudenhoven et al. [104] were the first to use *in situ* NDP to investigate Li-ion batteries. The study shows that NDP is a powerful method to probe the lithium concentration throughout a thin film battery. To achieve a better noise-to-signal ratio the measurements were conducted on a ^6Li enriched battery, as natural lithium consists of only 7.5% ^6Li . Recently Liu et al. [105] applied the technique to perform quantitative measurements on liquid electrolyte batteries. The used coin cell featured a Kapton window in the top casing to allow the ^3H particles to reach the detector. Because the study concerned the lithium concentration in a tin anode during battery operation the current collector could be omitted.

8. Outlook

The application of *in situ* methods to investigate battery materials plays an important role in the fundamental understanding of the operation of Li-ion batteries. Major developments have taken place in the recent years, most importantly the development of techniques that enable spatially resolved measurements such as *in situ* TEM and *in situ* X-ray tomography. The local probes enable

detailed insight at the single crystallite level which can be compared to the full battery overall characteristics.

Obviously, with several techniques still in the early development stage, there is significant room to improve the current *in situ* methods for Li-ion battery research. In particular techniques that are capable of providing information on the 3D morphology of electrodes as well as the chemical composition have shown to be extremely insightful [28,40,82,83] and further development is therefore expected. Furthermore, *in operando* measurements, probing the non-equilibrium states, require a high data collection rate, which is presently challenging for several *in situ* tools.

A crucial part of *in situ* research is the design of electrochemical setups that are compatible with the applied technique. Researchers should be mindful of the extent to which these custom-made cells relate to practical batteries and be cautious of artefacts. Obviously the combined use of multiple *in situ* techniques is very powerful and can give increased overall insights. For certain methods this can be achieved with relative ease due to the large similarities in design of their respective *in situ* cells. Examples of such combinations are: Raman and FTIR [64], XRD and XAS [21], XAS and MS [19], and neutron diffraction together with neutron scattering [106]. Given the recent progress it can be expected that *in situ* research will become increasingly important in the development of future generations of Li-ion batteries.

Acknowledgments

We kindly acknowledge S. Mitchell for his contributions to the manuscript. This work was supported by IWT Flanders (Belgium) under SBO project “SoS-Lion”, and ADEM, A green Deal in Energy Materials, of the Ministry of Economic Affairs of The Netherlands.

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