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Perspectives in Magnetic Resonance

In situ and operando magnetic resonance imaging of electrochemical cells: A perspective

Mohaddese Mohammadi, Alexej Jerschow *

Department of Chemistry, New York University, 100 Washington Square East, New York, NY 10003, USA

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ABSTRACT

Nuclear Magnetic Resonance (NMR) spectroscopy and Magnetic Resonance Imaging (MRI) of electrochemical devices have become powerful tools for the *in situ* investigation of electrochemical processes. The techniques often take advantage of NMR's nondestructive/noninvasive properties, its sensitivity to frequency shifts, internal interactions, and transport processes, as well as its ability to measure liquid phases and disordered materials. Here, we provide a perspective on recent work on *in situ* MRI of electrochemical devices, batteries and relevant model systems, and discuss their applications and promises in assessing device performance, and electrochemical processes in cells.

1. Introduction

Nuclear Magnetic Resonance (NMR) spectroscopy has become a powerful technique for analyzing properties of electrochemical cell components and related materials. A more recent development is the use of *in situ* implementations, wherein a device is analyzed during operation or under realistic or simulated operating conditions (*operando*). NMR has earned its place alongside other *in situ*/*operando* methodology, such as for example, synchrotron-based scanning transmission X-ray microscopy (STXM) [1], X-ray micro-diffraction [2], energy dispersive X-ray diffraction (EDXRD) [3], X-ray diffraction in combination with other spectroscopic methods such as transmission electron microscopy (TEM) [4,5], operando neutron diffraction [6], operando video microscopy [7], and Raman spectroscopy [8].

Several excellent review articles have provided accounts of *in situ* NMR spectroscopy and magnetic resonance imaging (MRI) methodology [9,10]. The field of *in situ* or *operando* MRI is relatively young and is still much under development. In this article, we aim to provide a succinct review of and perspective on the most recent work in this area. The majority of *in situ* MRI work has been devoted to the study of electrolytes, and ion distributions, followed by the investigation of electrode materials. Until recently, such work was confined to the study of cells specifically made for study. An "inside-out" MRI technique has demonstrated measurements in commercial cell designs, which further underscored some of the yet untapped potential of NMR spectroscopy and MRI in this area [11–13]

In the following, we discuss some general considerations necessary for studying samples with conductive components, provide a brief overview of studies of both liquid and solid electrolytes, discuss dendrite localization, and provide a perspective on the inside-out MRI approach.

2. The presence of conductors in the tuned circuit

For an electrochemical system to represent the expected performance, the existence of sizable conducting electrode and current collectors is a necessity [14]. The presence of highly conducting materials (e.g. electrodes, current collectors, and to a lesser degree of electrolyte) in the probe circuit makes an *in situ* NMR and MRI implementation quite an atypical, and potentially challenging NMR or MRI experiment. The resulting distortions and limitations, however, have been shown to be controllable and manageable and could be reduced by certain experimental precautions [15,16]. Bhattacharyya et al. [15] explored the orientation of lithium bulk metal inside the magnet and its effect on lithium metal chemical shifts. The radio frequency (rf) skin effect itself, determining the depth of field penetration into a conductor, leads to both strong signal distortions, but does provide important diagnostic value by identifying structures on the basis of penetration depth. For example, the rf skin effect was used to highlight areas with a large amount of porous lithium microstructures, which rf can penetrate well [15–17].

* Corresponding author.
E-mail address: alexej.jerschow@nyu.edu (A. Jerschow).

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The conductive compartments of an electrochemical cell affect the MRI experiment in several ways: the most important effect is the appearance of eddy currents, which change the rf field significantly in the vicinity of the conductors as well as within them. These currents also can have a long-range effect, and even alter the circuit tuning conditions. It has been found that the best arrangement of conductive plates in the probe circuit is one that minimizes the surface area perpendicular to the incoming rf field [9,17–19]. Because the boundary conditions are such that the perpendicular component of B_1 has to be zero at the surface of a good conductor, it is important to avoid such situations. A maximal penetration of the conductor surface layers is insured by this parallel arrangement as shown in Fig. 1. Typically, the resonance frequency of the tuned circuit is also lowest in the parallel arrangement. Tuning conditions could also change during the experiment, for example, in response to magnetic susceptibility changes. An automatic tuning and matching device has been developed, which can help to improve reproducibility and optimal detection in such cases [19]. The device could also be used for interleaving the acquisition of electrolyte and electrodes, when frequent retuning is necessary [19].

The penetration length of rf into a conductive surface is characterized by the well-known skin effect expression, [20,21]

$$\delta = \sqrt{\frac{\rho}{\pi \mu_0 \mu_r \nu_0}}, \tag{1}$$

where δ is the radio frequency skin depth, ρ is the resistivity of the conductor, μ_0 is the vacuum permeability, μ_r is the relative permeability of the conductor, and ν_0 is the Larmor frequency. This expression would be exact for a conductive plane of infinite dimensions and represents a good approximation for finite surfaces of dimensions exceeding the skin depth by a factor larger than ~10 as well.

As shown in Fig. 2, the depth-dependence of the rf field itself could be used for localization via flip-angle dependent or nutation experiments. Applications could involve the accurate quantification of surface porosity, but also could allow for subsurface signal selection or particle size determination [21]. Furthermore, pulses could be especially designed to maximally excite or suppress signals from bulk metal [22], which provides additional image editing capabilities.

In addition to rf field attenuation, phase shifts are also observed upon the penetration of rf into a conducting surface. For accurate quantification, it is important to take these into account on the basis of the NMR reciprocity principle [23], and a recipe for this approach was described recently in the context of NMR in conductive media [24].

The orientation dependence as well as perturbations from both B_0 and B_1 fields were examined in further detail by Serša et al. [25], where the combined effects of rf penetration and susceptibility-induced frequency shifts were analyzed as a function of orientation. Eddy current effects were analyzed also by Vashaee et al. [26]. By using single-point acquisition strategies (e.g. SPRITE), in order to obtain purely phase-encoded images, the rf-induced eddy currents could be isolated from image misregistration artifacts [12].

As a result of the mentioned studies, the effect of sample orientation, and rf penetration are now well understood, and an accurate quantification of signals and minimization of associated artifacts can often be achieved.

3. Liquid electrolyte studies

The electrolyte is the easiest component to observe from within cells due to the high concentration, narrow line widths, and relatively long signal lifetimes. A good electrolyte should enable fast charge transport, withstand extreme conditions, and should be stable under potential. MRI studies have been done mainly to determine the distribution of electrolyte and ion concentration, and to measure the mobility of charge carriers.

Klett et al. investigated the ability to measure Li-ion concentrations using ^{7}Li 1D MRI across a symmetric Li-cell as a function of applied potential. From these measurements, the authors were able to determine the ion diffusivities based on an electrochemical transport model [27]. Krachkovskiy et al. measured partially and temporally resolved Li-ion concentration profiles with 1D imaging and determined mobilities with slice-selective NMR diffusion

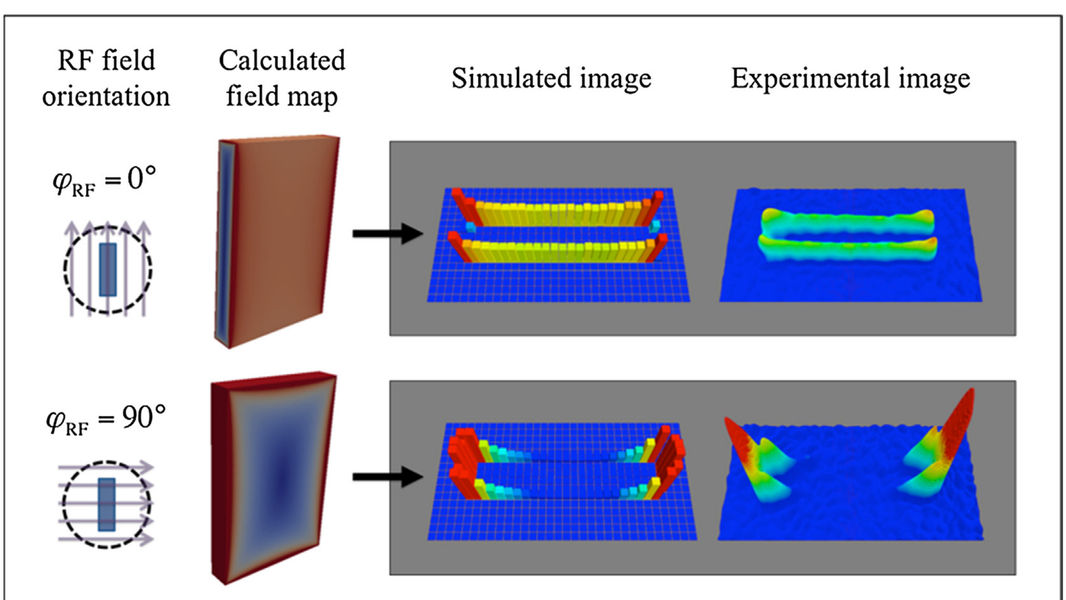

Fig. 1. Orientation-dependence of rf penetration into metal sheet. The maximum penetration of the RF field happens when the metal strip is parallel to the RF filed orientation. Adopted from "Visualizing skin effects in conductors with MRI: Li MRI experiments and calculations" by Ilott et al., 2014, *Journal of Magnetic Resonance*, 245, p. 143–149. Copyright 2014 by Elsevier Inc. Reprinted with permission.

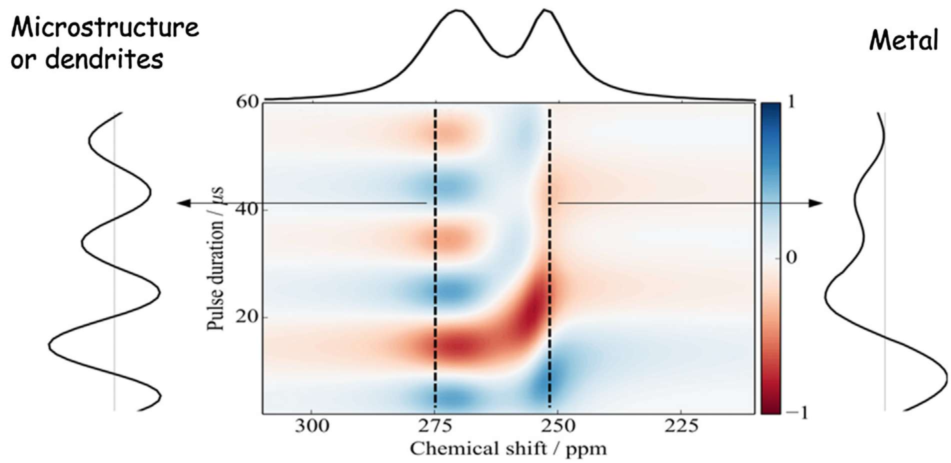

Fig. 2. ^{7}Li nutation experiment on a sample containing ^{7}Li plate and lithium dendrites. Adopted from Super-resolution Surface Microscopy of Conductors using Magnetic Resonance" by A.J. Ilott and A. Jerschow, 2017, *Scientific Reports*, 7, p. 5425. Copyright 2017 by Creative Commons. Reprinted with permission.

measurements [28]. These studies aim to provide measures of ion mobilities, and in particular the ionic transference numbers, which are difficult to obtain from electrochemical measurements alone.

In a study by Klamor et al. [29], the lithium concentrations were also profiled using1D MRI in a cell made of Li-metal and a nano-Si-graphite composite electrode. The authors explored the Li^+ concentration profile during the first cycle and related the Li^+ accumulation near the anode electrode surface to the formation of a solid electrolyte interphase (SEI). This approach represented an effort to provide quantitative spatial information on SEI properties using MRI. The main challenge remains that the SEI thickness is very small (tens of nanometers) [30], while MRI resolution is typically upwards of ~50 μm [17] Even the overall amount of SEI material is difficult to sense directly with MRI/NMR, and most studies aim to provide indirect measures. Recent DNP studies could help in this regard [31].

Sethurajan et al. [32] used MRI in combination with inverse modeling based on a Planck-Nernst model of the mass-transport problem to determine ionic diffusion coefficients, and transference numbers in electrolyte solutions. This approach was suggested as an alternative to pulsed field gradient (PFG) diffusion measurements. Krachkovskiy et al. [33] demonstrated a combination of MRI and PFG-NMR diffusion measurements under steady-state conditions in a cell of Li-metal against graphite in order to determine both ion distribution and diffusivities. In combination with the mass transport equation, one could then also obtain the transference numbers. In an extension of this work, Bazak et al. [34] have included pure-phase encoding MRI implementations to accurately measure concentration gradients. In temperature dependent studies, this work revealed evidence for salt precipitation, which could point to sources of capacity fade mechanisms in lithium-ion batteries. While the majority of this work was performed using ^{1}H MRI, other nuclei have been used as well. In particular, for example, ^{19}F 1D MRI has also been performed to determine the 1D concentration profile of the anions. The local electroneutrality condition was used to establish correspondence between Li^+ cation concentrations and $TSFI^-$ or PF_6^- anions [32]. Most of the studies allowed monitoring the concentration profile changes near the electrolyte surface [27–30,32]; Typically, the analysis of these results agreed well with a Maxwell-Stefan treatment in a one solvent and one salt system [35].

Relaxation image contrast has been used to monitor ion dissolution processes by MRI (utilizing rapid imaging with refocused echoes – RARE) [36]. In this work, Cu^{2+} ion distributions were followed in solution upon dissolution from the metal. In other work by Britton et al., the effect of the eddy currents on Zn ion dissolution processes have been quantified by observing the ^{1}H T_1 and T_2 relaxation maps [18].

4. Solid electrolyte studies

Solid electrolytes are currently under consideration for their potential to afford higher energy capacity, and enable the development of safer batteries by avoiding the use of flammable electrolytes. Romanenko et al. [37] have introduced the use of single-point imaging variants (SPRITE) to avoid distortions in imaging solid and liquid components of cells. Using this approach, the Li transfer into a matrix of organic ionic plastic crystals (OIPCs) was investigated [38]. Partial liquefaction behavior was observed as a function of lithium transfer.

Recently, Chien et al. [39] have used ^{7}Li MRI to examine the Li distribution and homogeneity in the solid electrolyte $Li_{10}GeP_2S_{12}$ within symmetric $Li/Li_{10}GeP_2S_{12}/Li$ cells (Fig. 3). This study revealed Li depletion from the electrode - electrolyte interfaces and increased heterogeneity of Li distribution upon electrochemical cycling. These effects were also measured in the presence of an electrode coating, which could represent a strategy for preventing lithium loss from the electrode. Significant changes in behavior were seen upon applying the coating.

In another work on detecting the spatial and temporal ionic concentration gradient in solid electrolyte, Chandrashekar et al. [40] studied the concentration-dependent diffusion in polymer electrolytes for lithium-ion batteries and determined the concentration-dependent diffusion of ions in a polymer electrolyte.

The MRI investigation of solid electrolytes has received less attention than the one of liquid electrolytes, mostly due to the increased difficulty of measuring these, as a result of broad resonance lines, associated larger required magnetic field gradients, and generally lower signal intensities. Nonetheless, emerging work has already demonstrated the utility of MRI for diagnosing important factors that determine the functionality of these materials and their interfaces.

5. Lithium dendrite localization and studies of conductors/electrodes

Repeated cycling of Li-ion cells, and, in particular, cells with Li-metal anodes can lead to deposits of irregular microstructure. Often these deposits appear in the form of ‘dendrites’ of lengths

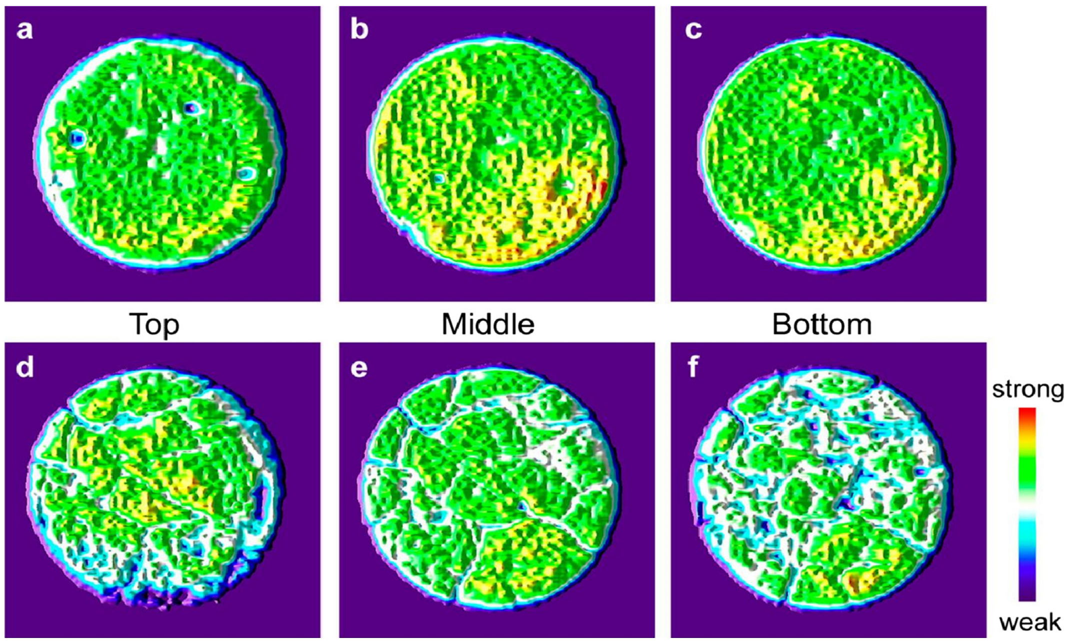

Fig. 3. 2D cross sections of 3D ^{7}Li magnetic resonance image of a symmetric $Li/Li_{10}GeP_2S_{12}/Li$ cell. Top row (a-c), 2D cross section of the electrolyte, $Li_{10}GeP_2S_{12}/Li$ at the start of electrochemical cycling. Bottom row (d-f) 2D images of the electrolyte after 3 days of cycling. Reprinted with permission from "Li Distribution Heterogeneity in Solid Electrolyte $Li_{10}GeP_2S_{12}$ upon Electrochemical Cycling Probed by 7Li MRI" by P.-H. Chien, X. Feng, M. Tang, J.T. Rosenberg, S. O'Neill, J. Zheng, S.C. Grant, Y.-Y. Hu, 2018, J. Phys. Chem. Lett. 9, p. 1990–1998. Copyright 2018 American Chemical Society.

of $\sim$10 μm and a diameter of $\sim$1 μm [15,41]. Ultimately, such structures may lead to capacity loss, and failure of a cell (including short circuits).

Gerald et al. observed Li dendrite growth on the surface of the hard carbon electrode under *in situ* conditions in a toroid cavity as well as in a coin-cell geometry [42]. An MRI-type implementation was demonstrated in this work, by using the rf field variations for localization in a toroid cavity. It is challenging, however, to obtain precise localization and quantification in such a geometry.

Chandrashekar et al. [17] first demonstrated phase-encoded 2D imaging, as well as 3D chemical shift imaging, which allowed to more precisely locate the positions of dendrite growth as well as quantify their overall amounts. The skin effect played a crucial role in the quantification of dendrites. Since the signal from bulk Li metal provided a constant background signal (because the rf penetration level is constant), it could be used as a reference signal through which the level of dendrite formation could be determined [15,17]

While dendrites are formed from metallic Li, they exhibit a characteristic frequency range, which is determined by the magnetic susceptibility difference between metal and electrolyte, and also by the morphology of the structures. The characteristic frequency shifts of dendrites were determined by Chang et al. [43], and these were also visualized in 3D Chemical Shift Imaging (CSI). Notably, short dendrites are easily distinguished from longer ones [44]. Fig. 4 shows a combination of electrolyte/Li-metal electrode imaging as a function of charge time and current density, performed in order to study the dendrite growth mechanisms. A series of CSI images was performed on both the electrolyte and the metal. In this work, it was possible to clearly delineate the onset of dendrite growth and to fit the results to a theoretical dendrite growth model (based on Sand's time) [43].

It was further demonstrated, that one could image dendrites indirectly, by imaging the space around them with a fast ^{1}H MRI method and taking a negative image [45]. The negative image reflects the space taken up by the dendrites, but also the space perturbed by the magnetic susceptibility differences between the metallic and electrolyte volumes. These susceptibility differences lead to a relatively large signal loss in the areas around the dendrites due to destructive interference, which provides a very strong image contrast enhancement in the negative image (up to 20-fold). In this work, a time-series of 3D images could be obtained to follow the changes in morphology over time (Fig. 5). Because the method does not rely on the ability to measure lithium or dendrites directly, the approach would be usable for electrodes and dendrites of materials other than lithium.

Tang et al. [46] have demonstrated measurements of lithiation fronts within electrodes using a selective saturation technique. In order to provide the very strong magnetic field gradients for localization within solid domains, these experiments were performed in the stray field of the magnet. This approach provided a resolution of 15 μm in 1D imaging [47].

A longstanding desire is to be able to characterize processes happening at the electrode-electrolyte interface. In particular, the nature of the solid electrolyte interphase (SEI) determines both the stability, integrity, and the performance of cells to a large degree. The paucity of NMR/MRI studies of the SEI layer is due to the fact that it is very thin (tens of nm) and consequently the obtainable signal is very weak. It is hence also unrealistic to assume that MRI would enable the visualization or localization of this layer. In a recent study, however, the layer properties were analyzed indirectly by monitoring the ^{6}Li and ^{7}Li isotope ratios in both the metal and the liquid phases over long periods of time, following the immersion of an enriched ^{6}Li plate in an electrolyte with natural abundance isotope ratios. Using a model that took into account the skin effect, diffusion in both the metal and liquid phases, the permeability of the layer, as well as the SEI growth rate, it was possible to study the exchange kinetics between the phases and derive therefrom the permeability and size properties of the SEI [48].

Electrode regions have been investigated with MRI in supercapacitor assemblies. Supercapacitors are electrochemical systems that are capable of rapidly storing energy at the solid/liquid interface in microporous electrodes (often made from carbon). Although

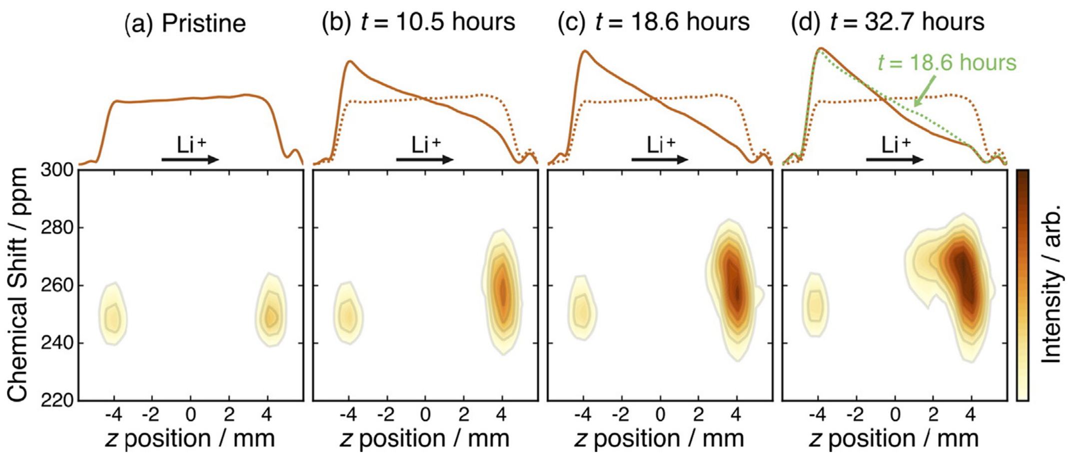

Fig. 4. The appearance and growth of lithium microstructure is obvious in the CSI series of the electrochemical system utilizing the chemical shift difference between bulk Li metal and its microstructure. Adopted from "Correlating Microstructural Lithium Metal Growth with Electrolyte Salt Depletion in Lithium Batteries Using ^{7}Li MRI", by H.J. Chang et al., 2015, Journal of American Chemical Society. 137, p. 15209–15216. Copyright by 2015 American Chemical Society. Reprinted with permission.

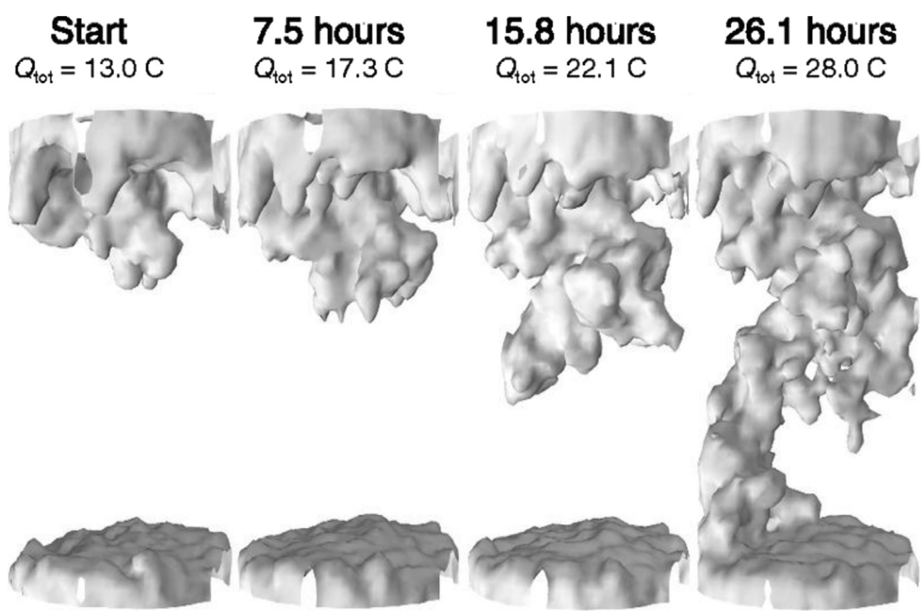

Fig. 5. 3D reconstruction of lithium dendrite microstructure growing inside a symmetric Li metal cell. Adopted from "Real-time 3D imaging of microstructure growth in battery cells using indirect MRI" by A.J. Ilott, M. Mohammadi, H.J. Chang, C.P. Grey, A. Jerschow, 2016, *Proceedings of Science of United States of America*, 113, p. 10779–10784. Copyright (2016) National Academy of Sciences. Reprinted with permission.

they are suitable for many applications that are in need of short and high power pulses [49], their energy density is significantly limited in comparison with lithium ion batteries [50]. Hence, much of the research in the area of supercapacitors is devoted to increasing their energy density without scarifying their power [50]. MRI enabled the determination of both cation and anion distributions within the supercapacitor electrodes across the charge cycle using both ^{1}H and ^{11}B MRI [51]. This information is helpful for the determination of practical capacity of the device, in relationship to its theoretical one.

EPR spectroscopy and imaging have been applied as well *in situ/operando*. Wandt et al. [52] studied Li plating with EPR with different electrolytes in $LiFePO_4$ cells. Niemöller et al. [53] showed that metallic lithium species could be mapped with μm resolution, which could be useful for determining points of failure. Plating and stripping, as well as, the formation of reversible $(O_2)^{n-}$ species have been measured with EPR spectroscopy and imaging by Sathiya et al. [54]. However, one difficulty of using EPR is the small penetration of microwaves into conductive areas and the potentially large distortions of microwave propagation.

6. Fully assembled commercial-style cells

A long-standing pain point in the battery industry is the lack of detailed diagnostic techniques for fully assembled cells in a commercial design. These cells typically have a conductive enclosure (for example, often a polymer-lined aluminum pouch), and electrode layers are either stacked or rolled such that there is very little spacing between the electrodes. All these factors make it nearly impossible to access the internal volume with rf irradiation in order to excite and detect signals from within. A possible solution could be a very low-field NMR implementation, in order to increase the skin depth, but this approach would also come with significant sensitivity losses. An alternative solution was recently developed, whereby rather than accessing the inside volume, MRI was used to map the volume surrounding a cell [11]. Cells were placed in a holder containing compartments filled with doped water for detection. Fast magnetic field mapping sequences were then used to map the magnetic field in these compartments, which were in close proximity of the cell. As a result, one could measure the small and spatially varying magnetic field changes surrounding a cell. These changes were linked to the variations of the magnetic susceptibility of cell materials. It is known that many cell components exhibit strong changes of magnetic susceptibility [55–59], depending on the amount of lithiation, and thus there is a strong link between the magnetic susceptibility and the state of charge (SOC) of a cell. As a result, magnetic field mapping around cells allowed the direct, fast, and nondestructive measurement of SOC distributions. Fig. 6 shows results from measurements of the changes in overall and localized state of charge across the charge cycle. The SOC is a quantity that is difficult to assess otherwise in a single-point measurement. In addition, the localized monitoring of SOC provides helpful diagnostics of cells.

This approach, henceforth termed inside-out MRI (ioMRI), was used to determine the ability of the technique to detect certain cell failures. It was shown that magnetic field maps created with ioMRI exhibited characteristic changes due to defects, and allowed some degree of cell classification.

In an extension of this method, electrical current distributions could be assessed within cells using the ioMRI approach. In a recent study [13], hotspots in current distribution were identified, the linearity of current distribution analyzed, symmetries between charge states were investigated, and changes in the current-induced magnetic fields were observed upon cell damage.

Many commercial cells can contain moderately magnetic components (such as Ni-plated wire or tabs). These can produce very strong image distortions. In recent work, it was demonstrated that such distortions could be minimized by the use of single point imaging variants. In particular the SPRITE (Single-Point Ramped Imaging with T_1 enhancement) approach was implemented, and shown to highlight magnetic susceptibility changes in pristine and damaged cells, including iPhone battereis [12].

The ioMRI measurements are fast, and could be applied in a high throughput manner. Furthermore, they could be in principle be implemented with a small footprint and low-field instrumentation. Such an approach would enable their use in quality control or battery diagnostics on an industrial scale.

7. Perspective & conclusion

The development of advanced battery materials and battery designs is challenged by the difficulty of detecting electrochemical processes *in situ*. NMR spectroscopy has provided many clues for material transformations at different stages of a charge cycle in a cell. By offering location-resolved measurements, MRI has

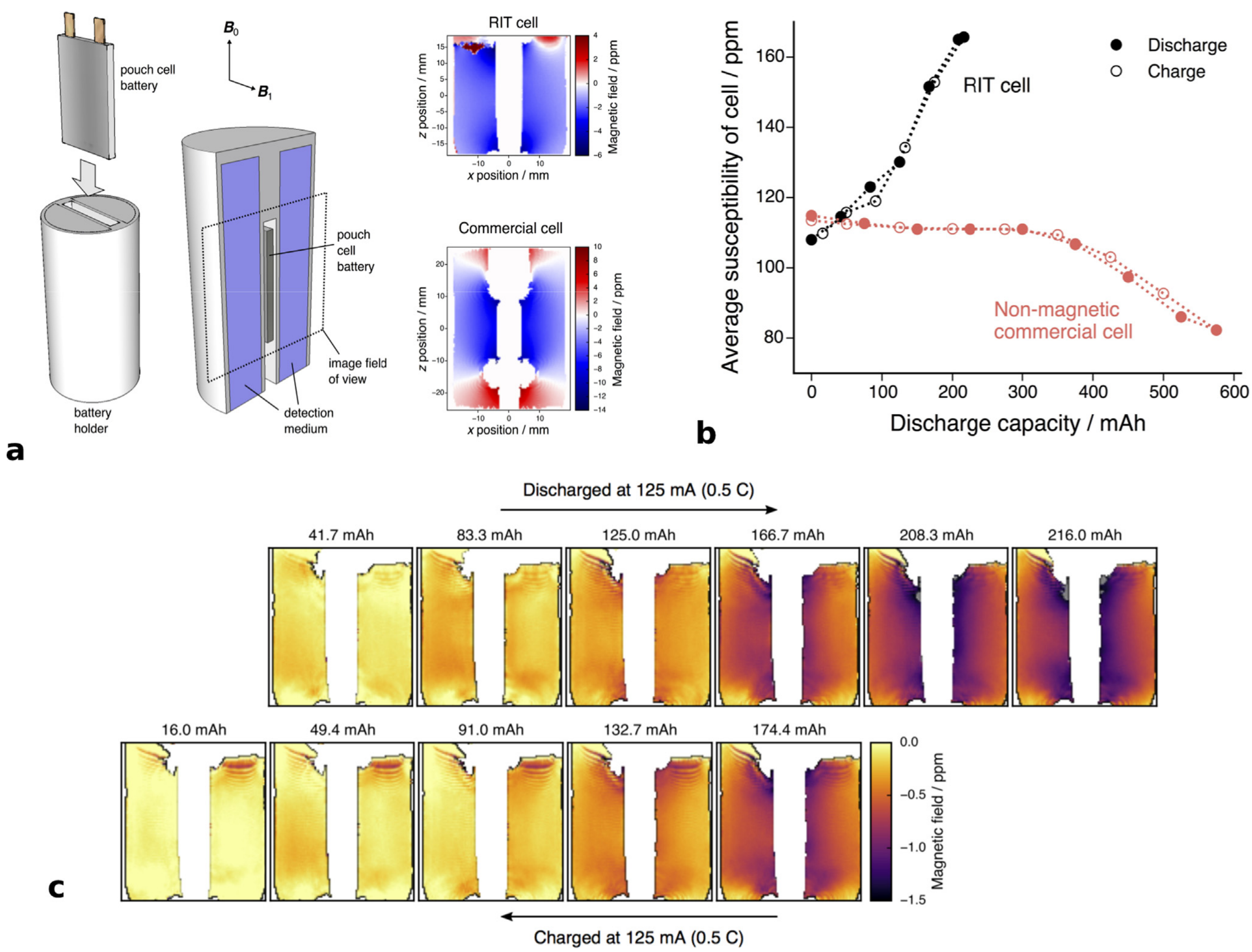

Fig. 6. Inside-out MRI of commercial batteries. (a) Experimental setup. (b) Average volume susceptibility changes for two different commercial cells. (c) The magnetic field map of the water container around the cell as the cell is being discharged. Reprinted from "Rechargeable lithium-ion cell state of charge and defect detection by *in situ* inside-out magnetic resonance imaging" by A.J. Ilott, M. Mohammadi, C.M. Schauerman, M.J. Ganter, A. Jerschow, 2018, *Nature Communication*. 9:1776. Copyright by 2018 American Chemical Society. Reprinted with permission.

provided the ability to sample heterogeneities and the spatial distribution of active materials. In particular, it has become possible to determine electrolyte and ion concentrations in devices, collect information on stages of dendrite formation, determine ion mobilities and transference numbers, and study interfacial properties.

While magnetic resonance approaches offer only comparatively coarse resolution (μm range), their particular qualities stem from their noninvasiveness, their applicability to disordered materials, liquid phases, and their ability to measure transport processes such as diffusion and flow.

Recently, a technique has been developed, which allows the measurement of commercial cell designs, which could bring the technology to industrial scale and use and perform true *in situ*/*operando* measurements on commercial cells. Distributtions of state of charge and current are currently the targets of opportunity for such measurements.

In conclusion, NMR and MRI can provide much needed detailed information about cell component behavior, failure modes, and charge storage processes. This information is crucial for understanding fundamental electrochemical processes and for desigining better electrochemical cells with higher energy storage and safety.

This research area is currently very active and one can expect much diagnostic power to be yet unlocked in the near future. Particular areas of activity include efforts to speed up measurements, increase sensitivity, expand to include studies of different isotopes, and widen the scope of true *in situ*/*operando* implementations.

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