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Observation of memory effects associated with degradation of rechargeable lithium-ion cells using ultrafast surface-scan magnetic resonance imaging.

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ABSTRACT

Lithium-ion cells represent the most wide-spread power storage devices in portable electronics and electric vehicles. Cells can follow various degradation pathways that cause safety concerns associated with flammable components and high energy density. With the growing demand for batteries, new screening methods are becoming critical in avoiding catastrophic failures. A cell that has undergone a hazardous life cycle event (*e.g.*, overcharging) could be identified via magnetic field patterns associated with direct currents through the cell's electrodes. Accurate detection of these patterns has been impossible due to insufficient sensitivity of recent acquisition protocols. An operando magnetic resonance imaging (MRI) methodology, surface-scan MRI, has been developed to address this challenge. The magnetic field distribution produced by an operating Li-ion cell is measured in a thin solid-state detection medium layer placed in direct contact with the cell. A speedy purely phase-encoded two-dimensional acquisition is the key to accurate distortion-free visualization of rapid charge transfer processes. At rates of multiples of C, the method is highly sensitive to onset of degradative processes in cell's electrodes and to hazardous states preceding internal short-circuits. Surface-scan MRI is a non-destructive technique suitable for diagnostics of Li-ion and other types of cells. The method is compatible with both research and commercial cell designs. Degradation of active electrochemical materials in overcharged Li-ion cells can manifest through a hysteresis-like behaviour of local current-induced magnetic fields. Such novel "memory" effects can be potentially observed in a variety of hazardous scenarios including formation of dendrites, damage of electrodes and decomposition of electrolyte.

Introduction

Recent lithium-ion batteries (LiB) failures resulting in potentially catastrophic events and recalls of millions of portable devices highlight the importance of detailed Li-ion cell diagnostics. Battery malfunction can stem from mechanical deterioration, electrode degradation and violations of operational specifications, among other things.[1-10] Due to a combination of high energy densities and flammable components of LiBs, some of these scenarios can lead to thermal runaways. While it is important to predict a cell's propensity to lead to catastrophic events, it is equally important to be able to identify slow degradative processes resulting in premature ageing and loss of capacity (soft shorts). Although a wide range of diagnostic solutions has been developed,[11-13] addressing the safety concerns non-invasively, rapidly, and reliably remains a challenge. For instance, LiBs undergoing overcharging are at risk of internal shorts due to dendrite formation and lithium metal plating.[9,10] Identification of such cells can be difficult as the localized onset of electrode degradation may not manifest itself through the conventional state of health metrics, *e.g.*, state of charge (SoC), voltage, capacity, or electrochemical methods.

Magnetic resonance spectroscopy and imaging have been at the forefront of electrochemical material research in recent years.[14] Non-invasive MRI testing of commercial cells became possible with the development of an "inside-out" (io) MRI concept.[15-17] A magnetic field distribution formed outside of the cell's conductive casing is a sensitive marker of SoC, mechanical defects, and undesirable chemical alterations of electrode materials.

Information about the cell's health is also encoded in magnetic fields generated by direct currents (DC) inside electrodes.[17] Local variations in chemical composition, structure and morphology of the electrodes modulate local current densities and the overall pattern of the magnetic field. Thus, the detection of the DC-induced fields enables non-destructive diagnostics of hazardous states in commercial cells. The magnetic field can be mapped with a specialized detection medium device which eliminates the need for radio-frequency (RF) field penetration through the conductive materials of the cell.[15,17] An approach for measuring alternating current (AC) fields has also been proposed recently.[18]

Considering strong magnetism of the battery components, the choice of MRI pulse sequence becomes critical. Conventional MRI approaches[19] employing frequency encoding and slice selective pulsed field gradients are affected by the magnetic and conductive objects giving rise to severe image misregistration artifacts.[20,21] In this context, fully phase-

encoded Single Point Ramped Imaging with T_1 Enhancement (SPRITE) provides artifact-free visualization of magnetically heterogeneous systems and solids.[16,22]

Although volumetric io-MRI ensures a “bigger picture”, a lengthy 3D SPRITE acquisition is often not a realistic approach for wide-scale battery testing. On the other hand, a single slice through the 3D io-SPRITE image can be sufficient for detection of cell abnormalities. Herein, we propose a method, termed “surface-scan” MRI that quantifies the magnetic field distribution inside a thin layer of polymer material placed in contact with one side of the cell (Fig. 1a). As a result, reduced dimensionality acquisition becomes possible, thereby accelerating the scan. The surface-scan MRI is executed here with a 2D centric-scan SPRITE scheme. The measurement consumes only a few seconds and is therefore feasible for high-throughput and/or industrial battery screening applications. Centrically ordered *k*-space trajectories arranged as sectoral interleaves ensure optimal image intensity and isotropic resolution.[23] Importantly, since magnetic field perturbations are the strongest near the cell, the surface-scan configuration provides a sufficient sensitivity with just one MRI scan, *i.e*., avoiding signal averaging.

Results and discussion

A cell placed into the uniform external magnetic field creates a spatially dependent magnetic field perturbation ΔB. Io-MRI data analysis can be performed using independent terms attributable to static field perturbations B_{ST} (geometrical configurations of the cell, magnetic tabs, and terminals), quasi-static SoC-dependent components B_{SoC} (active electrode materials), and magnetic fields induced by DCs (B_{DC}) that also can be SoC dependent:

$$\Delta B(SoC,\, I) = B_{ST} + B_{SoC} + B_{DC} \qquad (1)$$

In theory, all terms of Eq.1 can be sensitive to mechanical integrity of the cell’s components. B_{SoC} characterizes the oxidation state of active electrode materials, and B_{DC} is sensitive to conductive properties of electrodes and the electrolyte. Specifically, B_{DC} variations can be indicative of local electrolyte degradation which affects the current density distribution.

To isolate contributions of interest, one may select a “reference” io-MRI image that is subtracted from other images measured at different states or under different operation modes. For instance, a fully charged cell (*SoC = 100%*) operating at a current *I* will produce a B_{DC} map calculated as:

$$B_{DC} = \Delta B(100\%, I) - \Delta B(100\%, 0), \quad (2)$$

where the map $\Delta B(100\%, I)$ and the reference image $\Delta B(100\%, 0)$ are measured independently. To examine the dependence of B_{DC} on SoC, a series of experiments at different SoCs is required.

$$B_{DC}(\mathrm{SoC}) = \Delta B(SoC, I) - \Delta B(SoC, 0) \quad (3)$$

A magnetic field map $\Delta B(100\%, 0)$, Fig. 1b, measured for a fully charged cell (Fig. 1c) in the rest state shows field perturbations ~ 30-70 ppm. The domains with the most intense ΔB's are attributed to magnetic terminals (bottom-left corner) and the Ni-plated extended tab (a dipolar pattern at the top-left corner). The field distortions induced by active electrode materials (B_{SoC}) are an order of magnitude lower (Fig. 1d, e). Gradual discharging of the cell led to an increase of the B_{SoC} term from 0 to ~10 ppm due to a decrease in cathode's susceptibility.

For an accurate measurement of the B_{DC} component, one should ensure that the B_{SoC} term does not change significantly during the duration of an MRI scan. In this context, a rapid measurement is a key aspect of the surface-scan MRI which allows visualization of charge transfer processes occurring at a rate of multiples of C. For instance, a 2D centric-scan SPRITE scheme employed here consumes only 3.5 s. At a current of 4 A, this duration results in a change of SoC ~ 0.36% (3.7 mA h). The same degree of B_{SoC} averaging in the original 3D SPRITE approach[16] would be achieved at a much lower current (~0.125 A). Note, the sensitivity of the B_{DC} measurement is proportional to the current magnitude (I). For an MRI scan duration T_S and an allowable SoC variation ΔSoC, the maximum current can be determined as $I = T_S^{-1}$ Q ΔSoC / 100, where Q is the cell capacity. Thus, the overall sensitivity per unit time of the B_{DC} measurement is proportional to $IT_S^{-1} \propto T_S^{-2}$.

We tested this approach using the "classic" Nokia's BL-5C cell. This cell is a representative commercial device known for its mechanical robustness due to a durable aluminium casing. This design ensured a degree of safety during high-current *operando* MRI tests. Due to its compact size, the cell also fits into the conventional microimaging probe (Bruker's Mini0.5) and can be scanned entirely. The demonstrated approach can be easily adapted for testing larger commercial cells using clinical or preclinical MRI scanners, or new low-field imaging hardware.

Maps of the B_{DC} field produced by a fully charged Nokia cell (SoC = 100%) operating at ±4 A are shown in Fig. 2a. The local B_{DC} field and the pixel-by-pixel average, $\langle B_{DC} \rangle$,

changed linearly with the applied current (Fig. S.1) and inverted with the current polarity, as expected based on the Biot–Savart law. Figure 2b shows histograms of the B_{DC} distribution for the fully charged cell operating at ±1, ±2 and ±4 A. Note, the cell operating at ±4 A generates local B_{DC} magnitudes approaching 12 ppm (≈ 1 Gs), Fig. 2a.

Electrochemical processes such as lithium dendrite formation and copper migration from the anode current collector occur in overcharged and over-discharged Li-ion cells, respectively.[4-10] These are well known hazardous states preceding internal shorts and thermal runaways. Therefore, the identification of cells that had a history of these states is critical for preventing catastrophic events. Here we demonstrate that B_{DC} fields generated by sufficiently high currents can reveal the history of Li-ion cell overcharging. For this, we introduce a new quantitative indicator of the cell degradation:

$$\Delta B_{DC} = B_{DC}(\text{SoC}) - B_{DC}(100\%), \quad (4)$$

ΔB_{DC} is a spatially resolved map of the B_{DC} field deviation from a standard pattern established at a SoC of 100%. A series of ΔB_{DC} maps measured for a wide range of SoCs can be part of a standard io-MRI data base of "healthy" cells. Pixel-by-pixel averages, $<\Delta B_{DC}>$, and the root-mean-square-deviations, RMSD, of ΔB_{DC} distributions can be additional quantitative metrics of the cell's health:

$$< \Delta B_{DC} > = \frac{\sum_1^N \Delta B_{DC}}{N}, \quad (5)$$

$$\text{RMSD} = \sqrt{\frac{\sum_1^N (\Delta B_{DC}(SoC) - < \Delta B_{DC} >)^2}{N}}, \quad (6)$$

where N is the number of pixels within the region of interest covering the detection medium.

Localized degradation of electrodes, electrolyte or a hazardous interface process can manifest as an intense sporadic B_{DC} field variation confined in an area of a few MRI pixels, *i.e.*, a statistically insignificant part of the MRI image. Thus, in such cases, the use of the average metrics (Eqs. 5 and 6) for cell diagnostics can be limited.

"Healthy" cells that did not have a history of overcharge showed a weak dependence of B_{DC} on SoC, with $<\Delta B_{DC}>$ around ~ - 0.25 ppm (Fig. 2c) and RMSDs in the range from 1.1 to 1.7 ppm at a discharge current of 4A. Near full discharge, SoC ≈ 6.9%, $<\Delta B_{DC}>$ sharply changed to ~ - 0.85 ppm, as apparent from an overall shift of the distribution, Fig. 2c. The latter is attributed to lithium depletion at the anode and is a known reversible effect.[17]

A ΔB_{DC} map of one "healthy" cell (Fig. 3a) shows a "noisy" pattern (Fig. 3b) characterized by a statistical distribution centred around zero, Fig. 3c (blue histogram). Overcharging the cell at 0.4 A to SoC of 158% led to a gradual formation of a markedly different pattern, Fig. 3d, with a broader ΔB_{DC} distribution, Fig. 3c (red histogram). Distinct ΔB_{DC} features are indicated with dashed circles. These locations are shown in Fig. 3a with respect to the examined surface of the cell. The overcharge pattern did not disappear after the cell was discharged to within the normal SoC range (< 100%). RMSDs of ΔB_{DC} distributions measured for the healthy cell are shown in Fig. 3e (blue squares). After overcharging, the cell had substantially wider ΔB_{DC} distributions even after it was discharged to SoC < 100%, Fig. 3e (red circles). In the context of io-MRI methodology, we will further refer to this effect as "overcharge hysteresis".

According to the Kirchhoff's First Law, alterations in conductive elements of an electric circuit should lead to a rebalancing of currents. When a damage to the active electrochemical materials of the cathode, anode, or electrolyte is produced locally by overcharging or other types of hazardous operational states, electric currents are rerouted inside the cell. The current rerouting is a consequence of local permanent changes in the materials' resistivities. Thus, the observed "hysteresis" of the magnetic field pattern can be seen as a "memory" effect associated with local current rerouting.

Another example of the overcharge hysteresis phenomenon is provided in Fig. 4. ΔB_{DC} images of a Nokia cell at SoC of 88% (before overcharging) and 178% (overcharged) are shown in Fig.4 a and b, respectively. Overcharge patterns started to appear at SoC ≈ 110%. Three domains with the most intense B_{DC} field deviations are indicated with dashed circles, and their corresponding locations with respect to the cell are shown in Fig. 4c. The ΔB_{DC}(SoC) plots established at these positions are shown in Fig. 4d, e and f. Note that the range of the ΔB_{DC} values of the "healthy" cell (blue squares) is distinctly different from that of the cell subjected to overcharging (red circles). In the positions 2 and 3, the B_{DC} fields dropped by ≈ 14 and 19 ppm, respectively, which indicates significantly reduced local current densities. These changes are likely to be associated with known cell failure mechanisms resulting from overcharging, *e.g.*, structural deterioration of the cathode, electrolyte oxidation, and an onset of dendrite formation.[3,9,10]

In summary, the magnetic field measurements provide clear evidence of a cell's history with respect to overcharging. Examination of multiple cells demonstrated that overcharge-induced components of ΔB_{DC} maps are local, sporadic and can be intense $\Delta B_{DC} \approx B_{DC}$. This

highlights the importance of spatial resolution in cell diagnostics and the benefits of SPRITE as a misregistration-free method.[16] It can be expected that parameters extracted from the magnetic field distributions will also prove to be diagnostic of a broader range of defect indicators for cells.

Surface-scan MRI can be suitable for non-destructive *in situ* studies of numerous effects associated with degradation of electrochemical cells. Hazardous operational conditions of immediate interest are “extreme” ambient temperatures (low and high), extreme charge/discharge rates, and different types of externally induced mechanical stresses. These measurements can also serve to support high-level multi-physics simulations of magnetic fields produced by realistic operating cells. Studies of heat distribution within cells can also be envisaged. Another plausible direction of this research is testing multiple cells at a time, and diagnostics of commercial battery packs.

Conclusions

Our findings provide a basis and a general approach for non-destructive detection of secondary Li-ion cells that undergo hazardous life cycle events alternating local current density, *e.g.*, overcharge, over-discharge, short circuit, and over-current. Importantly, surface-scan MRI was specifically developed and adapted for detection of this type of events irreversibly alternating active cell materials. Interrogation of current density distributions via monitoring associated magnetic fields revealed a hysteresis behaviour of such cells. The technique is not limited to Li-ion systems and can be applied to a broad range of energy storage devices. Testing an array of cells in a wide bore MRI system would result in a sub-second scan time per cell. Due to its time efficiency and an inexpensive design, we envisage the surface-scan MRI as a commercially viable battery diagnostic tool.

Methods

Nokia BL-5C cellular phone batteries (capacity, 1020 mA h; nominal voltage, 3.7 V) have dimensions $53 \times 34 \times 5$ mm^3. The capacities were verified by cycling the cells between 2.8 and 4.2 volts at 0.1 A. The protection circuit module was removed to prevent its interference with io-MRI tests. The cell testing, operation and SoC were controlled using a BTS-4008-5V6A-S1 battery testing system (NEWARE, Hong Kong, China).

The detection medium was prepared from a polymer (PVC) suspension Plastisol (The Golden Grub Lure Co, 'Soft formula'). A suspension was brought to ~100 ºC in a beaker ~100 mm diameter. After cooling to the room temperature, the suspension formed a layer of polymer. Its thickness was controlled by adjusting the initial volume of the suspension. The spin-lattice relaxation time constant (T_1) of the polymer is 70 ms. A rectangular 1 mm thick slice of the polymer was attached to a rigid cardboard liner facilitating the alignment of the detection medium and the cell in the RF probe.

MRI experiments were carried out using a Bruker *Avance* III spectrometer equipped with a 9.4 T vertical bore magnet (89 mm bore diameter), a Mini 0.5 S triaxial gradient system (0.45 T m^{-1}) and GREAT (1/40) gradient amplifiers. The ^{1}H MRI signal was detected with a birdcage resonator (34 mm inner diameter) at a frequency of 400.09 MHz. In the RF probe, the cell was aligned with the B_1 field to minimize RF field distortions, Fig. 1a.[23, 24] The centric-scan SPRITE pulse sequence was designed in the Bruker *ParaVision* 5.2 environment. The sequence consisted of repetitive excitation - acquisition in the presence of ramped gradient pulses. An elementary SPRITE block included gradient ramp (T_{GR}) and stabilization (T_{GS}) intervals 1 and 0.5 ms, respectively, followed by an RF pulse (P_α) 4 μs long (flip angle π/40), phase encoding period (T_P) varying from 114 to 170 μs and data sampling. Eight complex data points per excitation were acquired with a sampling period (*DW*) of 8 μs giving rise to eight phase-encoded images. The *k*-space data were sampled using an interleaved 2D acquisition in the plane parallel to the cell, Fig. 1a. Four centrically ordered trajectories were designed to form a 32 × 32 matrix on a Cartesian grid. Interleaves were separated with a recovery delay (T_0) of 0.4 s. The total measurement time was ≈ 3.5 s.

B_{DC} measurements were performed for a series of SoCs starting from the fully charged state. The detection discharge current (-4A) was switched on for 3.5 s during which an io-MRI scan was performed. Between SoCs, the cell was charged or discharged at 0.4 A. A reference map was acquired in the rest state (I = 0) at each SoC.

Image reconstruction and analysis were implemented in *MATLAB* (R2019b, The MathWorks, Inc.). Field-of-views (FOV) of the eight phase-encoded images were scaled using a chirp Z-transform algorithm.[25] io-MRI maps were calculated by pixel-by-pixel linear regression of the temporal phase $\varphi(T_P)$ evolution, Eq. 7, using a *MATLAB* function "polyfit".

$$\Delta B_0(R) = \gamma^{-1} \, d\varphi / dT_P \qquad (7)$$

Phase unwrapping was performed using a custom algorithm.

Author contributions

K. R. designed and planned the experiments in discussion with A. J. during KR's employment with New York University (Jerschow Lab) in 2019. K. R. prepared the samples, carried out MRI and electrochemical tests, processed the data, and drafted the manuscript. All authors contributed to the final version.

Conflicts of interest

There are no conflicts to declare.

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