In Situ NMR Studies of Lithium Ion Batteries

by Nicole M. Trease, Thomas K.-J. Köster, and Clare P. Grey

Nuclear Magnetic Resonance (NMR) is a useful tool to probe the structural changes that occur in electrode materials on electrochemical cycling.[1] Most NMR studies of materials for lithium ion batteries have been performed *ex situ*: the battery is cycled to a specific state of charge, taken apart to extract a sample, and then NMR of this sample is performed. This has been an extremely successful approach because it allows fast magic angle spinning (MAS) methods to be used along with other modern NMR methods, providing considerable insight into the different structural processes that can occur and on the mobility of the various species. However, the approach does not capture short-lived metastable or reactive phases, which may react further before an *ex situ* NMR spectrum can be acquired. Furthermore, the wish to be able to quickly monitor the different local structural changes as a function of current and potential, to complement *in situ* X-ray powder diffraction measurements, or to investigate the electronic structure, to complement *in situ* X-ray absorption experiments, has motivated studies in this area. *In situ* NMR has now been implemented by a number of groups and despite a number of challenges provides a non-invasive means to study electrochemically induced structural changes, as briefly reviewed for ^{7}Li *in situ* NMR studies of lithium ion batteries (LIBs).

Extracting Information from Lithium NMR Spectra

A major challenge in *in situ* NMR spectroscopy of a LIB is to separate the resonances from the different components. Most lithium NMR experiments have been performed with [7]Li rather than [6]Li since the former is a more sensitive nucleus, although with enrichment [6]Li experiments should also be possible. Resonances from lithium in diamagnetic environments such as the electrolyte and lithium ions in the SEI (surface electrolyte interphase) appear at approximately ± 10 ppm. In contrast, the resonances from Li environments in paramagnetic phases can be shifted by as much as –500 to + 3000 ppm as a result of the (hyperfine) interaction with the unpaired electrons of the paramagnets. Metallic lithium is shifted to approximately 250 ppm, by a shift mechanism called the Knight shift, which is now caused by the interaction of the nuclear spins with the unpaired electrons located at the Fermi level of the conduction band. To date, most *in situ* NMR studies have been run as half-cells utilizing Li metal as one of the electrodes. This is convenient because the [7]Li shift of metallic lithium appears in a shift range, which is distinct from those of many other materials that have been investigated to date. [7]Li is a quadrupolar nucleus with spin I = 3/2. Although, it has only a small quadrupole moment, the [7]Li resonances can still be broadened by the quadrupolar interaction, but this can yield information on the local structure around a given nucleus. The sharper central transition, involving the -1/2 to +1/2 Zeeman levels is the easiest transition to detect for non-integer spin quadrupolar nuclei. The -3/2 to -1/2 and +1/2 to +3/2 satellite transitions are also observable for [7]Li and appear at ± $\nu_q/2$ from the central transition resonance, where ν_q is the quadrupole frequency, a function of the quadrupolar coupling constant. Both the shift positions of ^{7}Li NMR signals and quadrupolar parameters have been used to extract information on the structural changes that occur in LIBs during the electrochemical processes.

In Situ NMR Studies of Carbon

Since graphitic carbon is the most common anode material in commercial Li-ion batteries, with a capacity of 372 mAh/g, it seems appropriate that the first ^{7}Li *in situ* NMR studies were carried out on these electrodes. The first ^{7}Li *in situ* NMR experiments were performed on carbon-based materials by Gerald et al. in Argonne National Laboratory, using a home-built "near electrode imager" probe, where cylindrical batteries were studied and a solid copper rod was used as both the current collector and part of the NMR detector circuit. To overcome difficulties in fabricating symmetric electrodes to fit around the rod, they later modified the design, to study flat batteries with a "battery imager" NMR probe, where a solid copper disk was used instead of a rod.[2-3] This methodology made use of a non-standard NMR "Toroid" coil. In addition to spectroscopy measurements, this coil also allowed imaging experiments to be performed, since the response for a sample in the coil is not uniform and depends on the distance from the center of the coil. Thus, the concentration of species as function of the distance from the current collector could be monitored as a function of the reaction time and state of charge. The difficulties (albeit not insurmountable) and/or disadvantages of this design are the poor signal-to-noise obtained to date and the difficulty of combining this design with a standard LIB.

A simpler approach was taken by groups in Orléans and Amiens (Letellier, Chevallier, Morcrette, Tarascon, and coworkers) who used Bellcore-type plastic batteries[5] that could be placed directly into a conventional static NMR probe (Fig. 1). No specially designed probe was required. The method was employed to probe structural changes in graphitic[6-8] and amorphous carbon[8-10] electrodes. As lithium is intercalated into graphitic carbon, different staged compounds of graphite are formed until the fully lithiated stage 1 compound is formed at LiC_6. Distinct ^{7}Li NMR peaks are seen for the different stages. Due to the metallic nature of LiC_x, the [7]Li resonances are affected by a Knight shift, and with each stage (increased Li content) the peaks shift to higher frequency: ^{7}Li NMR resonances appear at 2, 6.8, 12.2, 45, and 42.6 ppm for stage 4' (LiC_{36}), stage 3' (LiC_{27}), stage 2' (LiC_{18}), stage 2 (LiC_{12}), and stage 1 (LiC_6), respectively. The lithium environments in each of the LiC_x phase are associated with a characteristic quadrupolar coupling constant and their satellite transitions are observable. The Knight shifts for stage 1 and stage 2 are similar and difficult to distinguish based on shift alone, but these structures can be distinguished from each other based on the quadrupolar coupling, as they have different ν_q values of 22.6 kHz and 17 kHz, respectively. The *in situ* NMR spectra of a graphitic carbon are shown in Fig. 2.

In contrast, in the ^{7}Li *in situ* NMR of disordered carbons, distinct crystalline LiC_x peaks are no longer seen, only a quasi-metallic (Knight shifted) Li_xC_6 peak appears, which shifts gradually to higher frequency (out to 104 ppm) as more lithium is inserted into the carbon. On lithium removal the peak shifts back to 0 ppm. The larger Knight shift of the fully lithiated material, in comparison to that seen for LiC_6, indicates that the lithium in the disordered carbon has become more metallic. This is consistent with the higher lithium content of this material, which contains 1.5 times more lithium than does the LiC_6 stage 1 compound.

Lithium Metal

Lithium metal, by definition, must have the highest capacity of all lithium based anode materials and will also give the highest cell voltage. However, safety issues due to dendrite and moss formation on the anode, which can cause short-circuits, have prevented
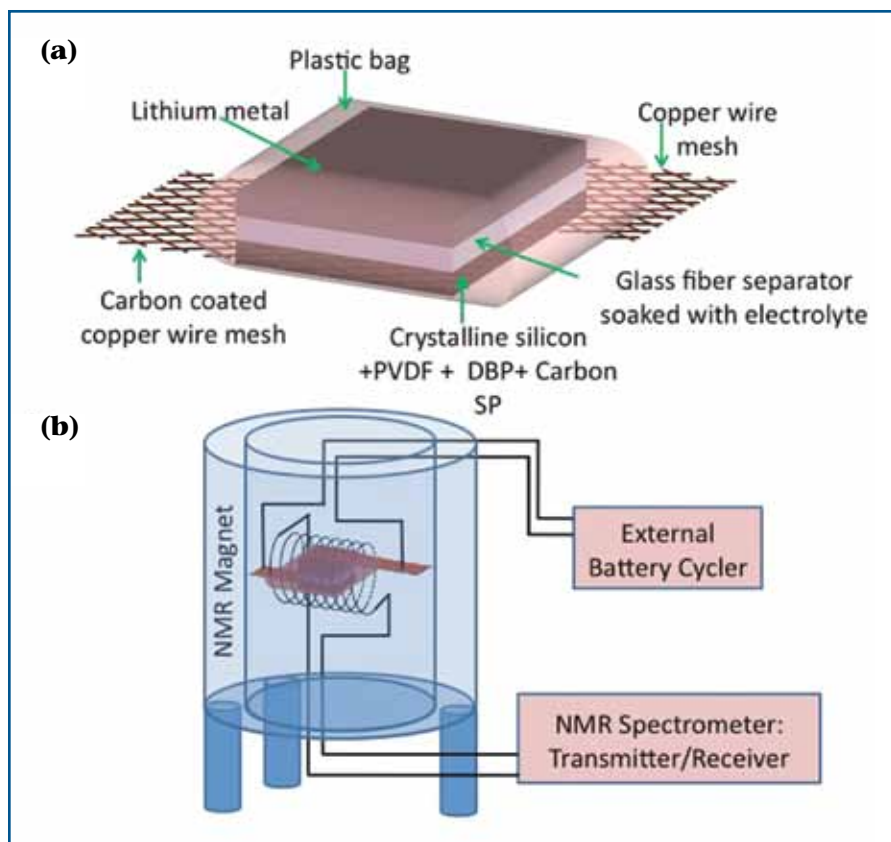
Fig. 1. In situ *NMR set up using Bellcore-type plastic batteries. (a) Schematic of plastic bag cell battery. (b) Set up of bag cell in NMR magnet. (Reprinted with permission from Ref. 4. Copyright 2009 American Chemical Society.)*

its widespread use in commercial rechargeable batteries. Dendrite formation and subsequent growth are dependant on numerous factors including the electrolyte salt and solvent, the rate at which the battery is cycled, the temperature and the pressure on the cell. *In situ* NMR provides a simple means to study the conditions under which dendrites form and to monitor their growth. Bhattacharyya et al. found that upon multiple cycles a second ^{7}Li metal peak appeared, shifted slightly from the original metallic peak, which is assigned to the formation of mossy or dendritic lithium.[11] This shift was attributed to bulk magnetic susceptibility (BMS) effects caused by the temperature independent paramagnetism of the lithium metal. This results in an orientation dependence between the metal anode strip and the direction of the static magnetic field: when the lithium metal strip was placed horizontal in the NMR coil, a ^{7}Li peak appeared at 250 ppm, while when it was vertical in the coil, this peak shifted to 270 ppm, as shown in Fig. 3. The shift was thought to arise from the fact that the dendritic or mossy lithium grows perpendicular to the surface of the electrode.

The key to using this method to investigate dendrite formation is the extent that the radio frequency (rf) field, used to excite the Li spins, can penetrate into the lithium metal (the "skin depth"). The skin depth depends on the type of metal (i.e., its resistivity and permeability) and also the Larmor frequency. Only the spins in the 1st 15 µm can be excited at 77 MHz, the number dropping as the field strength of the magnet increases. Since the dendrites are an order of magnitude thinner, the spins in the lithium dendrites can be observed, while those at >15 µm from the surface of the lithium metal anode cannot. A simple way to study dendrite growth is to use a symmetric lithium metal bag cell, i.e., a cell comprising two lithium electrodes. The mass of lithium metal is now constant, assuming side reactions are negligible, and any increasing in the intensity of the metal peak is then due to the formation of Li microstructure formation. ^{7}Li *in situ* NMR provides a quantitative and non-destructive means to study lithium microstructure (dendrites, moss, etc.) formation, which is not necessarily true for techniques such as optical and scanning electron microscopies. Utilizing this approach Bhattacharyya, et al., investigated the effects of different organic and ionic liquid electrolytes on dendrite formation in symmetric lithium bag cell batteries.[11] They compared the rate and current at which dendrites formed from different electrolytes. In Fig. 4 is the NMR and electrochemical data for a symmetric Li metal bag cell with an ionic-liquid electrolyte (C_2mimBF_4 + $LiBF_4$) and a vinylene carbonate (VC) additive, which has been shown to be a poor electrolyte for preventing dendrite formation, once the VC has been consumed. They cycled the bag cell for multiple charge-discharge cycles at a 0.5 mA cm^{-2} current rate. It is clear from the shifted Li metal peak in Fig. 4a2, and the increase in Li metal signal I_{expt} (Fig. 4d) that dendrites formed quickly (after 220 mins) at relatively low current rates. Dendrites are seen by NMR before they become apparent in the electrochemistry.

In situ NMR Studies of Silicon

Silicon represents a promising anode material for lithium ion batteries, as it offers very high specific capacities of about 3600 mAh/g. Although several companies have announced batteries containing this material, the large volume change in silicon upon lithiation, which leads to mechanical stress and particle rupture, and concerns associated with the formation of a stable SEI, have to date prevented a commercialization of this material. Attempts to solve this problem include the use of silicon nano particles, the use of suitable binders and additives, and the limitation of the voltages over which the anode is charged and discharged.[12,13] Many studies have been carried out to better understand the chemical processes that underlie the discharging/charging processes in silicon based anodes.[14-18] Starting with crystalline silicon, the Si-Si bonds are broken by insertion of lithium ions, resulting, in the initial discharge, in the formation of an amorphous phase Li$_x$Si. At very low voltages (<50 mV), a metastable phase Li$_{15}$Si$_4$ crystallizes. Upon charging, lithium ions are removed from the lithiated phase and Si-Si bonds are newly formed, resulting in completely amorphous silicon at full charge. As the electrochemical cycling of silicon involves a number of amorphous phases, the use of classical X-ray diffraction techniques to study these reactions is strongly limited. Instead, NMR is an ideal technique for the study of silicon based anodes and both *in* and *ex situ* studies have been performed.[4,18]

^{7}Li shifts in lithiated silicon and crystalline lithium silicides depend strongly on the coordination of the lithium ions. Whereas lithium ions near isolated Si anions (i.e., nearby Si anions that are not bonded to other Si ions/atoms) appear in the ^{7}Li NMR spectra at shifts of about 6 ppm, lithium ions near small silicon clusters and Si-Si dumbbells produce signals at larger shifts of up to 19 ppm. In an *in situ* NMR study of a Li/Si battery, Key et al. showed that during the initial discharge, the carbon in the Si/C composite electrode first reacts with the lithium. This is followed by the formation of small silicon clusters
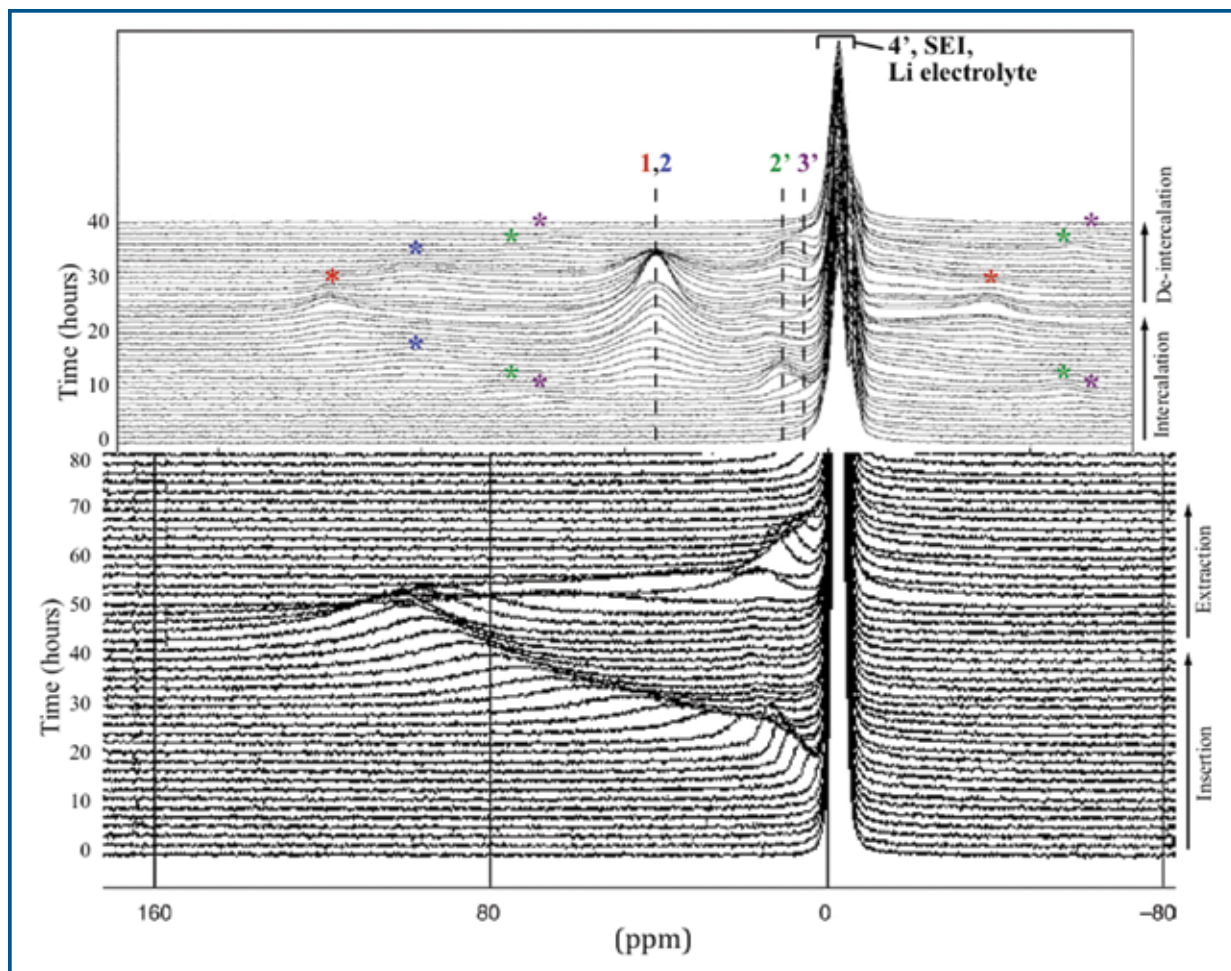
FIG. 2. *⁷Li in situ NMR of (top) graphitic carbon and (bottom) disordered carbon for the first cycle. The batteries were cycled with a C/20 (intercalate 1 lithium in LiC₆ in 20 h) rate, yielding cycling times of 40 h for graphite and 60 h for the disordered carbon. The initial spectra are at the bottom of each spectra; lithium is inserted/ intercalated moving up the spectra and then removed, until the lithium has been removed in the top spectra. The Li$_x$C phases and the Li electrolyte/SEI regions are marked. The * indicates the satellite transitions of the different staged compounds. (Reprinted from Ref. 8, with permission from Elsevier, Copyright 2006.)*

below 300 mV (broad peak at 8-20 ppm, Fig. 5). This continuing process is accompanied by further breakage of the silicon network and the occurrence of isolated silicon atoms (0-8 ppm). These results are in good agreement with *ex situ* NMR results. However at deep discharge (voltages below 100 mV, but more pronounced below 30 mV) the *in situ* experiment revealed a process that was not obvious from the *ex situ* experiments. A new signal appeared at -10 ppm, which occurs at about the same time as the reflections from the crystalline Li₁₅Si₄ phase are seen in the X-ray diffraction patterns. From the deviation between the chemical shifts of the new phase in the battery (-10 ppm) and Li₁₅Si₄ prepared by solid state reaction (ball-milling) (6 ppm) it can be concluded that Li₁₅Si₄ is not a line-phase but can accommodate small lithium non-stoichiometries in its structure. The overlithiated Li₁₅Si₄ formed at the end of the discharge easily reacts with the electrolyte, so it was not observed in the *ex situ* experiments; during the time between battery disassembling and
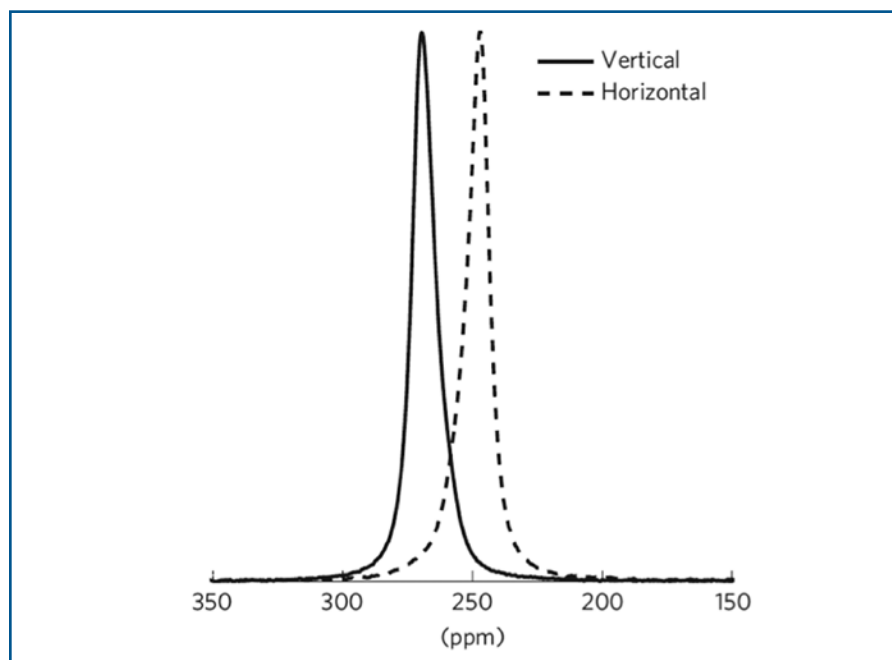
FIG. 3. *⁷Li NMR resonance of lithium metal at two different orientations with respect to the magnetic field, B₀. When the Li metal strip is placed vertically in the NMR coil (perpendicular to B₀) a peak is seen at 250 ppm, this peak shifts to 270 ppm, when the strip is horizontal in the NMR coil (parallel to B₀). (Reprinted from Ref. 11, with permission, copyright 2010.)*

the NMR experiment the overlithiated $Li_{15}Si_4$ had completely reacted. This reaction can explain the fast increase of open circuit voltage (OCV) to about 0.2 V after the battery has been discharged to 0 V. *In situ* NMR shows that during this "self-charge" (clearly a self-discharge process in a full cell) process, the -10 ppm resonance disappears. In an attempt to resolve the inconsistencies between *ex situ* and *in situ* data, batteries were discharged to 0 V and disassembled immediately before the *ex situ* NMR experiment. In this case, it was possible to observe the signal with the negative chemical shift in the *ex situ* NMR experiment. However, the example clearly shows that care must be taken in interpreting *ex situ* experiments, since it will never be clear whether any reactive or metastable phases may have already reacted.

Conclusions: Prospects and Challenges

The method is a relatively straightforward approach for following the changes that occur to the lithium ions/atoms in a lithium ion battery, as long as the relevant NMR signals are reasonably sharp and they do not overlap with the signals from other components in the cell. Resolution will be a concern in many systems, although methods for separating different signals, based on, for example, relaxation times or possibly double resonance NMR experiments (which select specific types of species), may help to resolve the signals from different environments. Magnetic susceptibility effects, which can be largely ignored in MAS are not negligible, particularly for paramagnetic materials, and they can complicate spectral assignment. Magnetic resonance imaging (MRI) may help with this problem as it may be possible to locate wherein the cell the different shifted components originate from.[19] Further analysis of the sources of the BMS and optimization of cell design/orientation may help minimize this problem. Despite the challenges, there are many systems that will be amenable to the methodology. Increased utilization of the *in situ* methodology by more NMR groups will help speed up the process of finding practical solutions to overcome some of the challenges and hurdles and will broaden the type of systems that can be investigated. In addition to the study of the electrode materials, as described above, applications to the study of electrode-electrolyte interfaces, to investigate capacitive and pseudocapacitive phenomena can be readily envisaged. Similarly, monitoring changes in electrolyte concentrations and speciation, Li metal
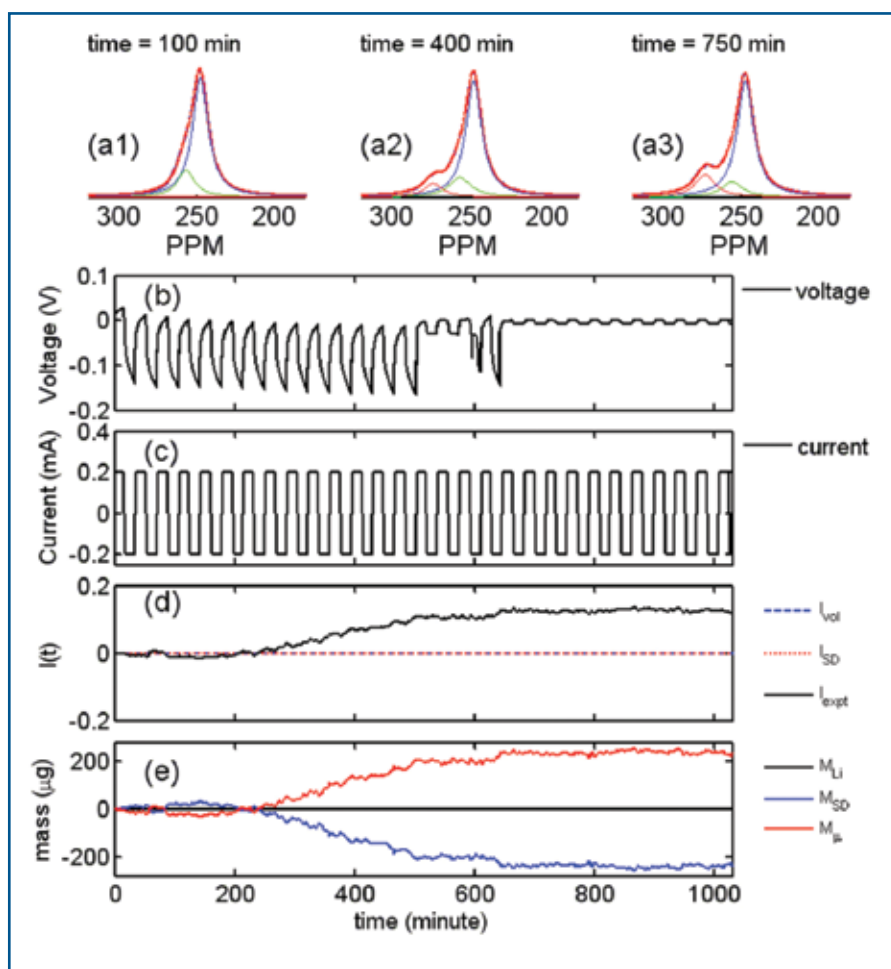

Fig. 4. *^7Li in situ NMR for a symmetric Li metal bag cell. (a1-a3) NMR spectra at different time intervals showing the growth of dendritic peaks. Electrochemical data for galvonostatic cycling are shown in (b) voltage and (c) current versus time. (d) Change in the experimental intensity, I_{exp}, of the lithium metal peak. (e) Change in the mass of the lithium microstructure, calculated from (d). (Reprinted from Ref. 11, with permission, copyright 2010.)*

and/or SEI formation, all represent very straightforward experiments where the *in situ* approach should yield valuable information.

Acknowledgments

About the Authors

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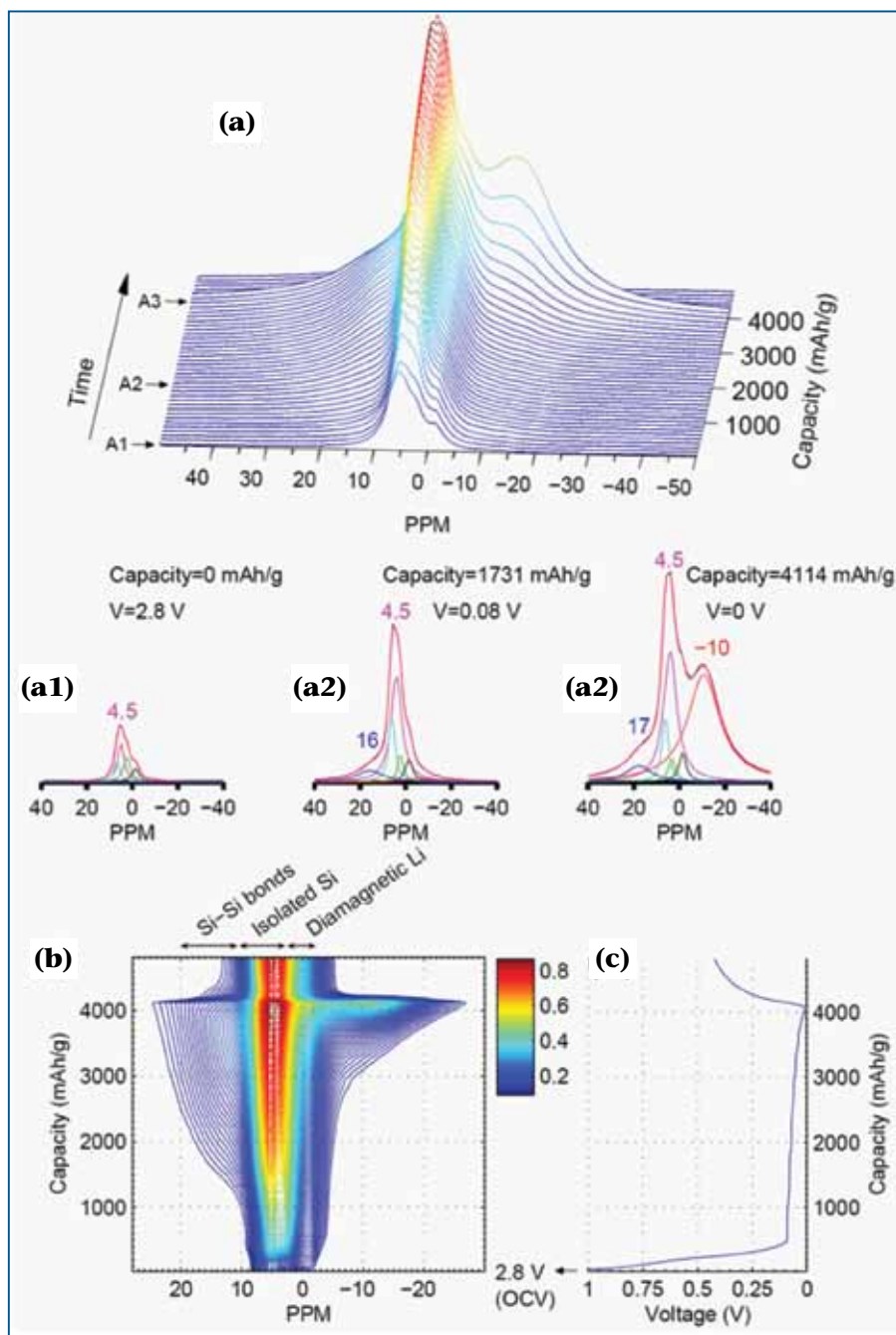
Fig. 5. *Stacked (a) and contour (b) plots of ^7Li in situ NMR spectra of a Li/Si battery during the first discharge and beginning of the first charge with corresponding electrochemical curve (c). a1-a3 show deconvoluted spectra at particular voltages. (Reprinted with permission from Ref. 4, copyright 2009, American Chemical Society.)*