Lithium-ion batteries (LIBs) have been widely used in portable electronic devices and as power sources for mobile machines such as electric vehicles, hybrid electric vehicles, e-bikes, e-scooters, and electric wheelchairs. To ensure the sustainability and endurance of these devices, it is necessary to understand battery degradation (in both capacity and power) due to daily use. LIBs are charged and discharged by Li insertion without chemical reactions, and the degradation of electrode materials is consequently small. LIBs are therefore widely considered to be excellent batteries, with long cycle lives. However, capacity fading occurs when LIBs are used outside moderate temperature ranges, at high current, with high voltage storage, etc. The capacity balance between positive and negative electrodes is lost (called “slippage”) because of charge and discharge operations with low accuracy controllers or parasitic reactions during operation. Slippage causes gradual capacity fading, because cell capacity is determined by the capacity balance between the positive and negative electrodes.

Previous studies have reported how and when slippage induces capacity fading, but not how slippage occurs and what it is exactly. To fully understand capacity fading and slippage, nondestructive measurements are needed, because capacity fading due to slippage will only be properly observed if the cell internal conditions are fully maintained.

To examine the state inside the battery without destroying it, we developed an in situ $^7$Li solid-state nuclear magnetic resonance (NMR) measurement method, using full-cell test equipment consisting of actual positive and negative electrodes. Using this method, we studied Li insertion/extraction in carbon with charge/discharge operations, Li dendrite growth during overcharges, and the properties of dendritic Li after being formed. The study investigated the change in NMR peak intensity of the Li stored in the cycle test, to elucidate capacity fading and slippage in terms of the amount of Li storage at the selected state of charge (SOC) at 100, 80, and 60%. The test full-cell consisted of a LiCoO$_2$ (LCO) positive electrode, a carbon negative electrode (one graphite (Gr) and hard carbon (HC))—and a 25-μm propylene separator. Organic liquid electrolyte—80 μL, 1 M LiPF$_6$, EC/EMC (30:70 vol. %) with 3 wt% of vinylene carbonate (VC)—was then injected into the cells, and they were sealed by heat pressuring. The 4.5 mAh designed LCO/Gr cells were operated between 4.2 V and 3 V; the 3.5 mAh designed LCO/HC cells were maintained between 4.2 V and 2.5 V. The cells were charge-discharge cycled with two different charge currents (0.5 C and 1.0 C) at two different temperatures (10 and 25°C), using a Toyo System Co. battery cycler. The cell capacity was estimated after every 100 cycles with a charge rate of 0.2 C at 25°C, and an NMR measurement was then performed. The cycle operation conditions and cell assignment are summarized in Table I.

The capacity fading of lithium ion batteries (LIBs) is investigated, using in situ $^7$Li solid-state nuclear magnetic resonance (NMR). LIB cells consisting of graphite or hard carbon and LiCoO$_2$ are used and cycled under two different temperatures (10 and 25°C) and charge current rates (0.5 and 1 C). The cell capacity and the amount of Li stored in carbon are measured with a battery cycler and in situ $^7$Li solid-state NMRs before the beginning of the test and after every 100 test cycles. The in situ $^7$Li solid state NMRs provide sufficient information throughout the cycle tests to characterize all test conditions. The cell capacities are analyzed in terms of the $^7$Li NMR peak intensity, attributed to Li stored in carbon. This intensity shows affine proportionality with the cell capacity for every evaluation, with an additive constant that decreases with the increase in cell capacity fading. This may be related to the loss of Li storage caused by voltage “slippage.”

Experimental

Cell preparation.—Laminated cells with an outer size of 20 × 30 mm were carefully assembled in an Ar-filled glove box, using a 115-μm Al-coated laminated film. Each cell was composed of a 3 mAh/cm$^2$ capacity one-side coated LCO positive electrode, a 3.2 mAh/cm$^2$ capacity one-side coated carbon negative electrode—graphite (Gr) and hard carbon (HC)—and a 25-μm propylene separator. Organic liquid electrolyte—80 μL, 1 M LiPF$_6$, EC/EMC (30:70 vol. %) with 3 wt% of vinylene carbonate (VC)—was then injected into the cells, and they were sealed by heat pressuring. The 4.5 mAh designed LCO/Gr cells were operated between 4.2 V and 3 V; the 3.5 mAh designed LCO/HC cells were maintained between 4.2 V and 2.5 V. The cells were charge-discharge cycled with two different charge currents (0.5 C and 1.0 C) at two different temperatures (10 and 25°C), using a Toyo System Co. battery cycler. The cell capacity was estimated after every 100 cycles with a charge rate of 0.2 C at 25°C, and an NMR measurement was then performed. The cycle operation conditions and cell assignment are summarized in Table I.

In situ solid state $^7$Li NMR measurements.—The in situ solid-state $^7$Li NMR spectra were recorded using a 7 T superconducting magnet and a home-built NMR spectrometer with a design that fully exploits the functionalities of a field-programmable gate-array. The NMR probe featured a genuine flattened solenoid coil tuned at the $^7$Li Larmor frequency (116.41 MHz), to make sufficient space for the cell, while still receiving an adequate signal. The cell was placed in the coil, and its plane face was directed perpendicular to the magnetic field. The used NMR settings are: single pulse sequence, 6 μs pulse length, 1 s pulse delay, 90° spin flip, 1000 scans, and chemical shifts referenced to a saturated aqueous LiCl solution. A spectral width of 200 kHz was used, which was sufficient to observe all Li components. The zero- and first-order phases were adjusted for a spectrum range of −800 to 800 ppm.

Results and Discussion

Capacity fading and $^7$Li NMR spectra.—Figure 1 shows the cycle test results for (a) the LCO/Gr cells and (b) the LCO/HC cells, under
the referred 0.5 C and 1 C charge current rates, at 10 and 25 °C. Two charge current conditions and temperatures were used to examine the influence of these factors on capacity fading, because high rate charges at low temperatures accelerate capacity fading. The cell capacity faded quickly under the low-temperature condition (10 °C) for both the Gr and HC cells, with a higher voltage drop effect being observed at 10 °C than at 25 °C. This trend was especially noticeable in the Gr cell, mainly because of the poor diffusivity of the intercalation process in graphite, when compared to that of the insertion process in hard carbon. Higher charge currents resulted in faster capacity fading, for both Gr and HC cells at 25 °C. Owing to the current effect and poor diffusivity, the Gr cell was not well cycled at 10 °C with 1 C. The capacity of the HC cells evaluated at 25 °C and at every 100 cycles decreased monotonically as the number of cycles increased; the Gr cells, however, recovered their capacity after low-current operation (0.2 C) at 25 °C. The degradation behaviors found in this study using the small pouch cells replicate well the estimated performance of commercial 18650 cells.9

Figure 2 shows the spectra measured after every 100 cycles for the (a) LCO/Gr cell (Gr3) and (b) LCO/HC cell (HC3), cycled at 0.5 C charge and 1.0 C discharge, at 25 °C. All spectra are plotted with the same intensity offset.

![Figure 1](image1.png)  
**Figure 1.** Cell capacity vs. cycle number, for (a) LCO/Gr cells and (b) LCO/HC cells, at 1 C discharge (plus one 0.2 C discharge at every 100 cycles).

![Figure 2](image2.png)  
**Figure 2.** In situ solid-state $^7$Li NMR spectra at every 100 cycles, for the (a) LCO/Gr cell (Gr3) and (b) LCO/HC cell (HC3), cycled at 0.5 C charge and 1.0 C discharge, at 25 °C. All spectra are plotted with the same intensity offset.

The cell capacity was plotted with the same intensity offset. NMR peaks corresponding to the Li stored in carbon were clearly measured throughout the cycle test. For the LCO/Gr cell, the peak attributed to Li stored in graphite (GIC: graphite intercalation compound) for 100% SOC appeared at about 40 ppm throughout the cycle test, but the peak intensity decreased slightly with cycle number (Fig. 2a).13–15 For the LCO/HC cell, the Li inserted in HC appeared at around 20 ppm, with a small shoulder peak (Fig. 2b).16–19 The peak of Li in the LCO cathode appears at around 0 ppm. The intensity varies with SOC, but the peak is much smaller than the peak for Li in the electrolyte or stored in the anode. The influence of the Li amount in the LCO cathode was thus negligible.

As shown in Fig. 2, the reproducibility of the NMR spectrum seems to be sufficient to estimate the amount of Li stored in carbon from evaluation of the peak ($P_{in}$) intensity. A previous report had already described the relation between cell capacity and the change in $P_{in}$, the peak of Li stored in carbon, at the same chemical shift.11 The cell capacity (usable capacity: $Qu$) can thus be expressed by

$$Qu = a \cdot P_{in} + b$$  \[1\]

where $a$ is a proportionality constant, and $b$ is a fraction of capacity not related with $P_{in}$ (which was confirmed to exist, because the analyzed peak was only responding to the higher stage structure such as LiC$_6$, and LiC$_{12}$ for Gr).
Analysis of the NMR peak vs. capacity fading relation.—The change of cell capacity ($Q_u$) was analyzed using equation [1] for the cycle test at 25°C. The cells were fully charged (100% of SOC) with 0.2 C and CCCV (at 4.2 V) mode at the beginning of life (BOL) and later on at every 100 cycles. The in situ $^7$Li NMR measurements were made at multiples of 20% of SOC (100, 80 and 60%), adjusted with the same capacity discharge (0.8 mAh) at a 0.2 C rate. The capacity gap between successive NMR measurements was therefore the same. The cell capacities ($Q_u$) as a function of the NMR peak intensities ($P_{\text{in}}$) are shown in Fig. 3 for (a) LCO/Gr cell (Gr3) and (b) LCO/HC cell (HC3) for 0.5 C charge, and (c) LCO/Gr cell (Gr4) and (d) LCO/HC cell (HC4) for 1 C charge at 25°C. The $Q_u$ plots show a clear proportional behavior with $P_{\text{in}}$ for a number of cycles up to 300 cycles (except for the Gr4 cell), while the value of $P_{\text{in}}$ at 100% SOC changes for successive 100 cycle groups. A drop in $P_{\text{in}}$ (100% SOC) with decreasing cell capacity would be expected. The observed increasing behavior in $P_{\text{in}}$ may suggest that there was a mechanism for capacity fading through unused remaining Li stored in carbon. The estimated parameters $a$ and $b$ in equation [1] are summarized in Table II. The proportionality constant $a$ for the Gr cells was found to be approximately 0.45, while for the HC cells a value of approximately 0.35 was obtained. The difference between these values is probably due to the sensitivity divergence of the peak corresponding to the Li stored in carbon. The fact that the proportionality constant $a$ showed similar values in both cases suggests that the cell capacities were influenced by similar mechanisms of Li storage. Parameter $b$ (the cell capacity where the NMR peak disappears) decreased with the cycle number, both in the Gr and HC cell cases. These results indicate that the cell capacity also fades with a decrease in the amount of Li stored in a lower voltage region of carbon Li insertion state (such as LiC$_6$, or LiC$_{12}$ in graphite).

![Figure 3. Cell capacity ($Q_u$) vs. $P_{\text{in}}$, for the (a) LCO/Gr cell (Gr3) and (b) LCO/HC cell (HC3) at 0.5 C charge, (c) LCO/Gr cell (Gr4) and (d) LCO/HC cell (HC4) at 1 C charge. Temperature: 25°C.](image)

| Table II. Linear regression parameters obtained at 25°C. |
| --- | --- | --- | --- | --- |
| cycle | Gr3 | Gr4 | HC3 | HC4 |
| BOL | 0.45 | 2.05 | 0.47 | 2.13 | 0.37 | 1.33 | 0.36 | 1.3 |
| 100 | 0.49 | 0.85 | 0.53 | 1.51 | 0.34 | 0.74 | 0.43 | 0.3 |
| 200 | 0.50 | 1.17 | 0.52 | 1.21 | 0.31 | 0.35 | 0.39 | 0.08 |
| 300 | 0.48 | 1.27 | 0.84 | 1.53 | 0.42 | 0.22 | 0.48 | 0.02 |
Figure 4 shows a plot of the cell capacity $Q_u$ versus $P_{in}$ for the cycle tests performed at 10°C. The evaluation was stably carried out up to 200 cycles, except in the case of the Gr2 cell, which was accidentally terminated after 100 cycles. These cells showed a behavior similar to the one of the cells cycled at 25°C. The capacity fading behavior was more distinct than the one obtained at 25°C. Lowering the temperature seems to reinforce this behavior, because of an increase in resistivity. Table III summarizes the estimated parameters for the cycle tests performed at 10°C. The proportionality constant $a$ for the Gr1 cell was approximately 0.45, the same value obtained for the Gr cells examined at 25°C. The proportionality constant $a$ for the HC2 cell had also a value similar to the one for the HC cells at 25°C, while the HC1 cell showed a proportionality constant $a$ slightly lower than those values. Parameter $b$ for these cells roughly decreased with the cycle number (or capacity fading), as had happened with those found in the cells tested at 25°C.

**Discussion of the NMR peak vs. capacity fading relation.**—Figure 5 shows the cell capacities $Q_u$ (at SOC 100%) as functions of parameter $b$ for both (a) 25°C and (b) 10°C cases. The cell capacities are proportional to $b$, as was expected from the previous discussion. The capacities of both Gr and HC cells showed similar proportional behaviors, even though the slope in the 25°C case (the proportionality constant in Fig. 5a is 1.2) was a little steeper than the one of the 10°C case (the proportionality constant in Fig. 5b is 0.87). While, the $P_{in}$ (at 100% SOC) did not always show good proportionality with $Q_u$ as seen in Fig. 3 and 4. These results suggest that cell capacity can be roughly predicted by parameter $b$ and, therefore, that capacity fading is related to a change in parameter $b$. Parameter $b$ is thought to be the expression of a physical lost capacity, related to Li stored in the same structure observed by in situ $^7$Li NMR with SOCs ranging between 60 and 100%. This region of SOC corresponds to a low region of
Figure 5. Cell capacity (Qu) vs. b, for (a) cycle at 25°C and (b) cycle at 10°C.

Figure 6. Schematic illustration of “slippage”, and the b parameter change, for graphite and hard carbon.

the voltage between the carbon negative electrode and the Li metal, usually below a few hundred millivolts. The HC cell showed smaller values of b, because the HC had a smaller capacity in this voltage region than graphite. This may lead to the faster degradation of HC cells than Gr cells as seen in Fig. 1.

Figure 6 shows a schematic diagram of the capacity fading and the change in parameter b associated with “slippage.” As the cycle test proceeded, the capacity balance between the negative and positive electrodes was lost, because of parasitic reactions (for example) occurring at one side of electrode, leading to the voltage shift (“slippage”)—shift from “BOL” to “cycled” in Fig. 6. The question was whether (i) the cell was charged but not discharged or (ii) the cell was not charged when “slippage” occurred. The change of parameter b indicated that, when “slippage” occurred, the negative electrode was not charged enough, leading to a decrease in the NMR peak intensity P_{in}.

Conclusions

The capacity fading effect was investigated using in situ {\textsuperscript{7}}Li solid-state NMR during a cycle test. The obtained results can be summarized as follows:

1. The LIB capacity fading can be examined in a non-destructive and continuous manner, using in situ {\textsuperscript{7}}Li solid-state NMR. The in situ {\textsuperscript{7}}Li solid-state NMR measurements reveal the precise behavior of Li responsible for the capacity fading mechanism during the cycle test.
2. The capacity fading caused by “slippage” can be explained by examining the behavior of the NMR peak intensity as a function of the cell capacity. This study also showed the state of the negative electrode when “slippage” occurred.
3. This study found that the NMR peak intensity can be used as an indicator, reflecting cell capacity throughout the cycle test.

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