Vehicle-to-grid (V2G) and Grid-to-vehicle (G2V) strategies are often cited as promising approaches to mitigate the intermittency of renewable energy on electric power grids. However, their impact on vehicle battery degradation have yet to be investigated in detail. Since battery degradation is path dependent, i.e. different usage schedules lead to different degradation mechanisms, it is essential to investigate batteries under realistic V2G and G2V scenarios. The aim of this work is to understand the effect of bidirectional charging on the degradation mechanisms of commercial Li-ion cells used in electric vehicles today. Results showed that an extra V2G step during cycle-aging accelerated capacity loss and degraded the kinetics at the negative electrode. Moreover, for all cycling duty cycles, the loss of active material at the negative electrode was higher than the loss of lithium inventory. This condition could trigger lithium plating and shorten cell lifetimes. In the calendar-aging experiments, state of charge was shown to be an important factor and interacted with temperature to accelerate the loss of active material at the positive electrode and the loss of lithium. It was also found that high state of charge values caused loss of active material at the negative electrode and kinetic limitations.

Based on projected electric vehicles (EV) penetration in the near future, EV batteries could provide significant energy storage for the electric power grid, by giving, Vehicle-to-grid (V2G), and taking, Grid-to-vehicle (G2V), energy when needed. This bidirectional charging could provide a wide range of ancillary services for the grid and supplement building power.

The use of EV battery capacity for grid storage has been heavily discussed and modeled in recent years, but few studies have tested the impact on the battery themselves. Although some modeling studies (e.g. ) predicted some potential benefits for the cells if intelligence was used to monitor the cells, the models that were used did not represent realistic battery degradation. Indeed, these models were capacity-based and did not consider intrinsic degradation mechanisms.

Battery degradation is well known to be path dependent and, under certain conditions, lead to accelerated capacity loss. In a previous work, it was shown that this second stage of degradation cannot be predicted from the evolution of the capacity nor the resistance with aging, but that it can be predicted from proper analysis of the voltage response of the cell using electrochemical potential spectroscopies.

This work is a follow up of our previous studies on the impact of bidirectional charging and calendar aging on the battery durability of commercial cells. Part 1 was devoted to the study of the cell-to-cell variations and to the emulation of the electrochemical behavior.

Part 2 was a capacity- and resistance-based analysis of the cycle- and calendar-aging experiments. In this work, the degradation mechanisms induced by cycle and calendar aging were investigated using incremental capacity analysis and the features of interest approach in order to quantify the different degradation modes, determine the path dependency of the degradation, and verify the capacity- and resistance-based forecast proposed in part 2.

Experimental

A batch of 100 Panasonic cylindrical 3350 mAh NCR 18650B was used in this work. Details on these cylindrical 18650-size graphite /LiNi$_x$Co$_{1-x}$Al$_2$O$_3$ (NCA) cells, as well as the cell-to-cell variation analysis, were presented in part 1 of this work. Out of the 100 cells, 36 were chosen for the cycle-aging experiment and 16 for the calendar-aging experiment. Overall, 52 cells were tested under 20 different conditions (3 cells per condition for the cycle-aging experiment and 2 cells per condition for the calendar-aging experiment). Details on the experimental testing procedure can be found in part 2 of this work.

Computer simulations were performed using the proprietary 'alawa toolbox that served as a user interface to facilitate the use of our mechanistic degradation model. Experimental post-mortem validation supporting our approach for the emulation of the impact of loss of lithium inventory (LLI) and loss of active material (LAM) degradation modes based on electrode matching changes were reported by other groups. The half-cell data necessary for this work was harvested from the disassembly of one of the 100 cells of the batch. More details on this procedure can be found in part 1 of this work.

The data for the positive and negative electrode half cells was used to build an emulated full cell that presented the exact same electrochemical characteristics than of the experimental cell. A thermodynamic cell-to-cell variation analysis proved that all the cells in this study could be matched by the emulated cell with an accuracy above 99%.

Results

Experimental results.—Figure 1 summarizes the cycle-aging experiment and displays the 12 different aging conditions. Each day was decomposed into four portions: starting at home (@Home), driving to work, staying at work (@Work), and driving home. The two driving portions were kept constant for all the duty cycles. The aging conditions were classified as a function of the duty cycles performed during the @Work and @Home portions of the day. For consistency purposes, the same notation and color code in the previous work were preserved. During the @Work and @Home portions of the day, the cells were subjected to either a discharge V2G operation before recharging and resting (DCR), charge then rest (CR), rest then the charge (RC) i.e. a delayed charge, or just rest (R, but only for the @Work section). As reported in a previous work, the cells experienced between 5% and 9% of capacity loss after 18 months of cycle aging with the maximum loss exhibited by the cells that experienced V2G twice a day and the minimum loss exhibited by the cells that charged twice a day without any participation in V2G. The differences also manifested themselves in the cell voltage response as elucidated by the C/55 incremental capacity (IC) curves in Figure 2. The top row of graphs (the blue curves) are the voltage responses of the cells that experienced a discharge during the @Work period. The left column are the incremental capacity curves from the cells that experienced a discharge during the @Home period.
Figure 1. Schematic summarizing the cycle-aging experiment with (a) the matrix of experiment, (b) the 12 different duty cycles, and (c) the resulting rate of capacity loss.

To visualize the IC curves under comparable circumstances, Figure 3 displays all 12 aging conditions after (a) 9 months of cycling, (b) 18 months of cycling, (c) 500 Ah exchanged, and (d) 900 Ah exchanged. Upon cycling, the most prominent differences in the IC curves were seen in the lowest voltage peak labeled G just below 3.4 V and in the inverted peak designated as the arch between 3.7 V and 3.9 V. Only the intensity values changes in the lowest voltage peak, while both the positions and intensities varied for the arch (insets in Figure 3). The same variations were observable when comparing the cell data evolution with exchanged capacity, Figures 3c and 3d, but the differences were less marked. These variations were identified as features of interest (FOI). The IC curve evolution was verified to be similar for all three cells tested under each condition.

Figure 2. Evolution of the C/35 incremental capacity curves with aging for the cycle-aging experiment (12 different aging conditions).
Figure 3. Evolution of the C/35 incremental capacity curves at comparable aging conditions: (a) 9 months of cycling, (b) 18 months of cycling, (c) 500 Ah exchanged, and (d) 900 Ah exchanged. The figure also highlights the selected FOI. FOI 1 is chosen as the area above 4 V. FOI 2 is the arch intensity. FOI 3 is the arch voltage. FOI 4 is the area under the low voltage peak.

Figure 4 presents the C/35 IC curves for the cells that underwent calendar aging. In this experiment, 8 pairs of temperature/state of charge (SOC) were tested from low temperature and low SOC to high temperature and high SOC. Testing conditions are summarized in Table 1. The capacity loss associated with the 66 weeks of calendar aging ranged from 1% (−27°C/99% SOC) to 13% (55°C/81.5% SOC). Calendar aging conditions also influenced the cell voltage response. As in the cycle-aging experiment, the differences between curves were most evident in changes to the lowest voltage peak G and the arch between 3.7 and 3.9 V. The high SOC cells (right column)
Table I. Calendar-aging experimental conditions.

| # Experiment | Temperature (°C) | SOC (%) | Capacity loss after 66 weeks (%) |
|--------------|------------------|---------|----------------------------------|
| 1            | −27              | 5       | 1.4%                             |
| 2            | −27              | 99      | 1.5%                             |
| 3            | 25               | 50      | 2.8%                             |
| 4            | 25               | 100     | 4.5%                             |
| 5            | 45               | 20      | 6.1%                             |
| 6            | 45               | 70      | 10.1%                            |
| 7            | 55               | 5       | 6.5%                             |
| 8            | 55               | 81.5    | 13.0%                            |

demonstrated much more variation in peak G and the overall shape (position and intensity) of the arch when compared to the low SOC cells (left column). Additionally, the IC curves for cells that experienced high temperature and high SOC (g) decreased in intensity in the region above 4 V more noticeably over time. The IC curve evolution was verified to be similar for both the cells tested under each condition.

Meticulous analysis of the IC curves for all 20 conditions was necessary to understand the differences produced by cycle aging (Figure 3) and calendar aging (Figure 4) and to ascertain the impact of the path dependence on the aging of the cells. Each path was defined as the conditions under which the cells were tested. The degradation caused by each path was characterized from the quantification of the different modes: LLI, LAM on the positive and negative electrode (PE and NE, respectively), and kinetic changes to each of the electrodes. The degradation modes were quantified by relating the experimental evolution of the FOIs to their theoretical evolution under each of different degradation modes. Based on the experimental data, the area under 4 V (FOI 1) was chosen as the first FOI, the arch intensity (FOI 2) and voltage (FOI 3) were selected as the second and third FOIs, and the area under peak G (FOI 4) was designated as the fourth and final FOI, Figure 3a. The difference in the FOIs was then plotted with respect to time for both the cycle-aging and the calendar-aging experiment and with respect to exchanged capacity for the cycle-aging experiment.

Figure 5 presents the evolution of the four FOIs for the 12 different cycle aging duty cycles as a function of equivalent months of driving (left column), capacity loss (center column), and exchanged capacity (right column). The evolution of FOI 1 showed that the area under 4 V was decreased under all duty cycles by 3 to 5%. When the FOI 1 evolution is plotted versus equivalent months of driving, as opposed to a function of the exchanged capacity, the distribution of differences was found to be tighter. This observation suggested that FOI 1 was influenced by time more than usage. The opposite can be inferred from the evolution of FOI 2 and FOI 4 since the distribution was much tighter if plotted against the exchanged capacity compared to equivalent months. Indeed, when plotted as a function of equivalent months of driving, there was a clear distinction between the cells that underwent V2G once a day (DCR- or DCR), V2G twice a day (DCR-DCR), and no V2G at all (no DCR).

The evolution of FOI 3 was the more complex with no apparent trend even as a function of capacity loss. The last two points for the cells that experienced V2G twice a day (DCR-DCR, blue curve and marker) were out of graphing range because the arch intensity increased to the point where the arch shape completely disappeared. As a result, its position could not be determined accurately.

Figure 6 presents the evolution of the 4 FOIs for the 8 different calendar aging duty cycles as a function of aging time in weeks (far left column), capacity loss (middle left column), temperature (middle right column), and SOC (far right column). Variations in FOI 1, Figures 6a–6d, at high temperature and high SOC were larger (more than 9%) than the FOI 1 variations in the cycle-aging experiment. The loss of area below 4 V was influenced by temperature, Figure 6c, but not by SOC, Figure 6d. The evolution of FOI 2, Figures 6e–6h, was dependent on the sample conditions. The intensity of the arch, Figure 6h, decreased for the cells tested at low SOCs (50% or less), but increased for the cells tested at high SOCs (70% or more). FOI 3, Figures 6i–6l, increased for all conditions and tightly correlated with capacity loss and temperature. Lastly, FOI 4, Figures 6m–6p, was found to follow the same trend as that of FOI 1 exhibiting an inverse correlation with all four conditions.

Figure 5. Evolution of the 4 FOIs: the area above 4 V (a–c), the arch intensity (d–f), the arch voltage (g–j), and peak G area (k–m) as a function of the equivalent months of driving time (left column), capacity loss (center column), and exchanged capacity (right column).
Simulations results.—From the analysis of Figure 5 and Figure 6, the selected FOIs evolved differently depending on the duty cycle illustrating the path dependency of the degradation. To understand the origin of these variations and to relate them to their degradation modes, the FOIs were tracked for each individual degradation mode using an emulated cell constructed from the half-cell dataset. The data from the full cells were matched to the half-cell dataset by determining the appropriate loading ratio and offset. The matching was discussed in our previous work. The correspondence between the experimental (circles) and the emulated data (thick line) is shown in Figure 7a. Different degradation modes changed the matching between the positive and the negative electrodes. A loss of lithium inventory shifted the SOC of the NE relative to the PE. A loss of active material decreased the capacity of the affected electrode compared to the other. Kinetic degradations effectively decreased the rate of charge/discharge of one electrode compared to the other. Knowing the individual signature of each electrode allowed all of these matching changes to be emulated. Thus, their impact on the full-cell capacity loss and voltage response was predicted. The impact of LAMPE and LAMNE on a delithiated PE, LAM on a lithiated PE, LAM on a delithiated NE, and LAM on lithiated NE, Figures 7a–7e, respectively. In addition, the impact of 10-fold changes in the electrode kinetics is presented in Figure 7f for the PE and Figure 7g for the NE. As explained in a previous paper, the model in the toolbox was using a hypothesis that assumed that degradation of electrode kinetics could be emulated by using the voltage response of the cell at a higher rate with an adjusted IR drop. For example, a C/10 cycle with a rate degradation factor (RDF) of 2 could be simulated from a C/5 cycle by cutting its ohmic resistance in half. It was also assumed that the overall electrode capacity remained constant. If capacity loss arose, it was taken into account as LAM. Finally, Figure 7h presents the capacity loss associated with LLI, LAM on a delithiated PE, LAM on a lithiated PE, LAM on a delithiated NE, and LAM on lithiated NE.

The evolution of the FOIs based on degradation table in Figure 7 are presented in Figure 8 for up to 10% degradation or 10-fold increase in the kinetic limitations. The impact of LAMPE and LAMNE were not discussed because they are a combination of the effect of LLI and the corresponding LAM. FOI 1, Figure 8a, was mostly sensitive to LAMPE and LAMNE. FOI 2, Figure 8b, was influenced mainly by the kinetics of the NE (RDFNE). FOI 3 was predicted to increase for some degradation modes (LLI, RDFNE, and RDFPE) and decrease in case of loss of active material (LAMPE and LAMNE).

Discussion

Degradation diagnosis.—From the comparison of the experimental (Figure 2 to Figure 5) and theoretical (Figure 7 and Figure 8) voltage and FOI variations, it was evident that the degradation of the cells was convoluted and was not explained by a single degradation mode. To understand the degradation mechanisms, it was necessary to investigate the different degradation modes one by one. It was critical to follow a strict procedure and verify the unique identifiability of all the different degradation modes. First, FOIs that were related to single degradation modes were evaluated. Subsequently, the FOIs that were related to several degradation modes were considered. If variations were verified as the simple addition of the modes, Figure 8 was applied for quantification. For FOIs with non-additive relationship, Figure 8 was not used, instead full simulations with all varying parameters were employed.

To start, the focus was set on the loss of active material at the positive electrode. From Figure 8, FOI 1 was inversely proportional to LAMPE, but a decrease of FOI 1 could also be associated with LAMNE and RDFPE. However, the voltage changes above 4 V associated with LAMNE and RDFPE (Figure 7) were different from what was seen in the experimental data. In addition, the actual evolution of FOI 4 was not indicative of RDFPE. Therefore, the decrease of FOI 1 must be associated with LAMPE. Based on Figure 5 and Figure 6, LAMPE can then be estimated between 3 and 6% for the cycle-aging experiment and between 0 and 10% for the calendar-aging experiment depending...
Figure 7. Degradation table for the selected battery with the IC curves associated with up to 10% of (a) LLI, (b) LAM_{dePE}, (c) LAM_{liPE}, (d) LAM_{deNE}, and (e) LAM_{INE}; the IC curves associated with up to 10x kinetic hindrance for (f) RDF_{PE}, and (g) RDF_{NE}; and the capacity loss (h) associated with (a)-(e).

Figure 8. Variation under theoretical single degradation modes of (a) FOI 1, (b) FOI 2, (c) FOI 3, and (d) FOI 4.
on the aging conditions. This estimation has not taken into account the increase of FOI 1 that might be possible if LLI and RDFNE were occurring at the same time.

Under our initial assumptions, RDFNE and RDFPE did not induce any capacity loss. Hence, the capacity loss was assumed to be caused only by LLI, LAM_{aPE}, and/or LAM_{dNE}. The analysis of FOI 1 in this study eliminated LAM_{dNE} as a factor in capacity loss. Hence, the capacity loss originated from LLI or LAM_{aPE} minus the initial offset. Indeed, both LLI and LAM_{aPE} influenced the data in a similar manner. Thus, it was reasonable to assert that only the more prominent of the two caused the capacity loss. In this study, based on Figure 2 to Figure 5, the estimation of the capacity loss that could be induced by LAM_{aPE} was in every case lower than the observed capacity loss. Therefore, the capacity loss was not induced by the loss of active material, but solely by LLI.

Figure 9 elucidates the quantification of LLI for the cycle-aging experiment as a function of time (a-b) and exchanged capacity (c-d). The quantification for the calendar-aging experiment is presented as well, Figures 9e–9f. Since the percentage of LLI was directly proportional to the capacity loss, the previous analysis of the capacity loss was applied to describe the dependence of LLI with time and exchanged capacity from a factor of 3 for the cells that charged twice a day and experienced no V2G to a factor of 9 for the cells that experienced a V2G step twice a day. The kinetic limitations appeared to be related to the exchanged capacity. Up to 500 Ah exchanged, Figure 10d, all cells have similar degradation. The distribution broadened at values higher than 500 Ah, Figure 10c, especially for the cells that experienced V2G twice a day.

The quantification for the calendar-aging experiment is presented in Figures 10e–10f. There was a clear distinction between the cells stored at low SOCs (< 50%) and the cells stored at high SOCs. Indeed, the kinetics of the cells at low SOC did not change; whereas, one of the cells stored at high SOC and high temperature degraded by a factor of 2.

An increase of FOI 2 on an IC curve corresponded to the disappearance of a peak on a differential voltage curve. The trend observed here was thus also identified on the DOE GEN2 baseline cell, though the change was more pronounced in the cycle-aging experiments.

With LLI and RDFNE quantified, FOI 1 was used to estimate LAM_{dPE} with more accuracy. Figure 11 displays the quantification of LAM_{dPE} for the cycle-aging experiment as a function of time (a-b) and exchanged capacity (c-d). LAM_{dPE} increased with time. The distribution of all cells that experienced cycle aging was compact between 4 and 6% loss after 18 months of equivalent driving, Figure 11a. No clear distinction was resolved between duty cycles, Figure 11b. On an exchanged capacity scale, Figures 11c and 11d, the cells that exchanged the most capacity (DCR-DCR) lost the least active material at the PE indicating LAM_{dPE} was associated with time and calendar aging. This conclusion was confirmed by the dependence of the LAM_{dPE} on both temperature and SOC in the calendar-aging experiment, Figures 11e–11f. The impact of temperature and SOC on LAM_{dPE} and LLI was similar. The loss of positive active material in NCA-type cells reported during calendar aging and cycling was proposed to be induced by the formation of a surface layer.

The next step was quantifying the last degradation mode, LAM_{dNE}. In theory, it could have been done and validated from the variations of FOI 3 and FOI 4, respectively (or inversely), but the method was proven unsatisfactory for this work because the hypothesis for the
Figure 10. Quantification of RDF_{NE} for the cycle-aging experiment (a) as a function of time, (b) after 18 months of equivalent driving, (c) vs. exchanged capacity, and (d) after 500 Ah exchanged. Quantification of RDF_{NE} for the calendar-aging experiment (e) vs. time and (f) vs. temperature and SOC after 66 weeks of aging.

The quantification of the effect of kinetic degradation was not valid. Although the hypothesis was sufficient for the changes in the intensity of FOI 2, it did not capture accurately the changes in FOI 3 and FOI 4 prohibiting the automated determination of LAM_{dNE}. The true impact of kinetic changes will be investigated in a follow-up work.

For the purposes of the analysis presented here, a manual estimation of LAM_{dNE} based on the calculated values of LLI, LAM_{PE}, and RDF_{NE} was used to find the best possible fit for all 20 duty cycles.

Figure 11. Quantification of LAM_{dPE} for the cycle-aging experiment (a) as a function of time, (b) after 18 months of equivalent driving, (c) vs. exchanged capacity, and (d) after 500 Ah exchanged. Quantification of LAM_{dPE} for the calendar-aging experiment (e) vs. time and (f) vs. temperature and SOC after 66 weeks of aging.
66 weeks. In this case in which the kinetics of the cell did not change, both the experimental and the simulated curves were in perfect agreement. This result demonstrated the benefits of the FOI approach. The approach automatically and correctly described the degradation of the cell. The same perfect agreement was confirmed for the other three conditions with no kinetic variations (calendar aging at SOCs ≤ 50%). Since the simulations were in good agreement before any adjustments for LAMNE, it was concluded that calendar aging at low SOCs did not induce any active material loss on the negative electrode. Figure 12 presents the experimental and the simulated IC curves for the 55°C/81.5% SOC experiment for the fresh cell and the cell aged 66 weeks with no LAMNE (solid red curve) and 6.5% LAMNE (solid blue curve). For this cell, the aging at high SOC induced some kinetic limitations (~ x2). It was observed that the simulation without any LAMNE did not fit the arch position (FOI 3) well. Therefore, under these conditions, it was concluded LAMNE did occur and needed to be taken into account to describe degradation accurately. Based on the arch position, the LAMNE value was estimated to be around 6.5% (solid blue curve). However, the changes in the area of FOI 4 could not be replicated because of inaccuracies in emulating kinetic changes, but the rest of the peaks were well modeled.

The comparison of the experimental and simulated IC curves was repeated all the cells that underwent calendar aging and the results of the quantification of LAMNE after 66 weeks of aging are presented as a function of temperature and SOC in Figure 13a. No loss was observed for cells aged at SOC ≤ 50%. For aging at higher SOCs, LAMNE was found to increase with temperature and SOC up to 6.5%.

Path dependence of the degradation.—Based on Figures 2, 3, 8, 9, and 10, there was little doubt that different duty cycles caused different degradation modes throughout the life of the batteries. Figure 9d shows that the cells that charged only once a day were more prone to LLI and consequently, degraded faster than the cells charged twice a day at equivalent duty cycle. Figure 9f shows that LLI was also influenced by temperature and SOC. Figures 10b and 10f proved that cycle aging induced significant kinetic hindrance. Whereas, kinetic hindrance was not an issue in the analysis of the calendar-aged cells. Figure 11b shows that all the cycle-aged cells lost between 4 and 6% of their positive electrode active material. This loss was exacerbated by temperature and SOC. Finally, Figure 13 suggested that no active material at the negative electrode was lost during calendar aging at low SOC even at high temperature. However, LAMNE did occur at high SOCs. This result was in contrast to published research. Hence, it was surmised that these losses of active material was specific to this batch of cells. An illustration of the path dependence is provided in Figure 14 in which the degradation quantification (LLI, LAMPE, LAMNE, and RDFNE) for 8 cells at 5% capacity loss is presented on a
The prognosis proposed in our previous work\cite{30} was optimistic because the ratio was greater than 1, perhaps closer to 2 for some cells. There was a silent degradation mode, LAMNE, and specifically the ratio LAMNE:LLI was estimated between 7 and 12% and LLI was estimated to lie between 20% and 40% of the total capacity loss. In this study, the most interesting silent degradation modes were quantified, this prognosis method was proposed based on the evolution of the capacity loss. Now that the silent degradation modes were quantified, this prognosis method was applicable. As part of the previous work,\cite{30} a forecast was proposed based on the evolution of the capacity loss. The prognosis method is tied to its ability to predict the point at which a silent degradation mode starts to contribute to capacity loss. In this study, the most interesting silent degradation mode was LAMNE and specifically the ratio LAMNE:LLI. Indeed, LAMNE should alone introduce capacity loss quite quickly via irreversible lithium plating once the excess relative capacity of graphite in the cell (loading ratio always > 1 at the beginning) is consumed.\cite{26,31,47} Lithium plating is prevented if LLI is occurring simultaneously because the loss of lithium inventory shifts the negative electrode toward a higher SOC.\cite{38} Figure 15a presents the evolution of the capacity loss for different ratios of LAMNE and LLI assuming 100% irreversible plating. For ratios below 1, LAMNE remains silent. For ratios above 1, LAMNE becomes prominent at some stage in the life of the cell. For ratios between 1 and 1.3, LAMNE begins to influence properties only after 20% overall capacity loss. Hence, its effect does not discourage its use in EVs, but is an issue for second use.\cite{48} Ratios above 1.6 drastically reduce the life of the battery and a second stage starts after 10% capacity loss. Based on this study, the LAMNE:LLI ratio for the calendar-aging experiment was under 1 and is expected to remain under 1 based on LLI and LAMNE individual prognosis. The prognosis proposed in a previous paper\cite{30} was therefore applicable. As for the cycle-aging study, the exact ratio cannot be calculated because LAMNE could not be quantified accurately. However, LAMNE was estimated between 7 and 12% and LLI was estimated to lie between 6 and 9% after 18 equivalent months of driving. It was likely that the ratio was greater than 1, perhaps closer to 2 for some cells. Therefore, the prognosis proposed in our previous work\cite{30} was optimistic and the cells will lose capacity more rapidly than originally predicted. This realization was consistent with a second stage of aging observed in these same commercial cells that was induced by degradation of the negative electrode with some change in the composition of the SEI layer.\cite{25,49} Figure 15b presents an example of the new prognosis considering a LAMNE:LLI ratio of 1.5 ± 0.2. Under this hypothesis, the cells that were subjected to V2G twice a day (DCR-DCR) could potentially reach 20% capacity loss in less than 4 years without even considering calendar aging and start the accelerated aging stage, in which plating occurs, after only 2 years of usage. Further testing is in progress to provide a better estimation of the LAMNE:LLI ratio.

The onset of the second stage during cycle aging could be prevented if the cell is subjected to conditions where LLI occurs but not LAMNE, thus reducing the LAMNE:LLI ratio. This is a case where V2G strategies could actually be beneficial for the durability of the cells without lowering the overall capacity loss. However, it necessitates a smart-grid algorithm imposing the correct conditions.\cite{22} The calendar-aging experiment showed that LAMNE occurred at higher SOCs. Therefore, a second stage to reduce the SOC of the cells prior to rest time ensures that the calendar-aging step induced LLI but no LAMNE and thus reduces the LAMNE:LLI ratio and increases cell lifetime. This reasoning was also true for G2V strategies that involved resting at lower SOCs. Since LAMNE is silent, there is no apparent difference in terms of capacity loss, but the start of the second stage of aging could be delayed if not suppressed by modifying standard rudimentary battery usage.

Conclusions

In this work, the modes causing the degradation of commercial graphite/NCA cells subjected to 20 different duty cycles, including cycle and calendar aging, were investigated. It was found that, in general, the cells did not degrade in the same way, and that the degradation was path dependent. Cycle aging, with or without an extra charge step to determine the effect of V2G strategies on battery life, resulted in greater loss of active material and more kinetic limitations on the negative electrode than calendar aging. Temperature induced additional loss of lithium inventory and loss of active material at the positive electrode. SOC, on top of catalyzing the temperature effect, caused kinetic limitations and loss of negative electrode material. Most noteworthy, the loss of active material at the negative electrode was faster than the loss of lithium inventory in the cycle-aging experiment. This finding was a clear sign that the cycled cells will enter a stage of advanced aging characterized by the onset of lithium plating. This result led to a revision of the lifetime prognosis for the usage of these cells for EV application. However, the manifestation of the second stage could be delayed or suppressed with intelligent control algorithms.

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