High-Precision Coulometry Studies of the Impact of Temperature and Time on SEI Formation in Li-Ion Cells

L. D. Ellis,1 J. P. Allen,1 I. G. Hill,2 and J. R. Dahn1,2,∗

1Department of Chemistry, Dalhousie University, Halifax, B3H 4R2, Canada
2Department of Physics and Atmospheric Science, Dalhousie University, Halifax, B3H 3J5, Canada

Electrolyte reacts at the surfaces of charging electrodes during the first cycle of a Li-ion cell (formation). This creates the initial solid electrolyte interphases (SEIs), which passivate the electrodes against further reactions with the electrolyte. The quality of the SEIs improve over time as a cell matures. The coulombic efficiencies (CEs) of fresh cells (measured by high-precision coulometry, (HPC)) stabilize after a certain period of time (up to 600 hours), after which different cell chemistries can then be ranked for their quality. The purpose of this work is to accelerate the maturation of SEIs during the first cycle, allowing for stabilized CE measurements to be taken after less time. The effects of formation cycle temperature, voltage and duration on subsequent CE are explored. Undergoing formation at 60 °C accelerates the maturation of cells. XPS analysis suggests that organic SEI species are replaced by inorganic SEI species on a cell matures. These results give insight into the mechanisms of cell maturity. Application of the formation protocol described in this work may decrease the time needed for HPC experiments.

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The first cycle of a lithium-ion cell is when the initial solid electrolyte interphases (SEIs) form from the decomposition of electrolyte at the surfaces of the charging electrodes. If an SEI is ionically conductive and electronically insulating, it passivates the electrode against further reactions with the electrolyte. SEI quality is related to both the SEI thickness1–4 and the SEI chemistry.5–7 The SEI layers formed in the first cycle are not completely passivating but become more and more passivating over time. Over the past years, the Dahn lab has cycled thousands of new Li-ion cells on its ultra high precision chargers (UHPCs), used to evaluate cell chemistries and rank them in order of coulombic efficiency.8–13 In every case, the CE of a fresh cell increases toward the ideal value of 1.0000. . . during testing but may allow for more accurate comparisons between them.

Ideally in a search for the optimum electrolyte chemistry for a particular cell type, a number of cells differing only in electrolyte composition should undergo formation under the same conditions and be mounted for UHPC testing after the same time interval after formation. This is the way experiments are carried out in our laboratory where we are fortunate to be able to fill pouch cells with electrolyte and perform the formation steps ourselves. Even with this degree of control it is important to consider methods to speed the maturation of the SEI layers to shorten UHPC testing time and improve throughput of UHPC testing systems. Therefore, the purpose of this work was to design a first cycle (formation) protocol that would yield the most passivating SEI and the most stable CE in the shortest amount of time.

Cells from different manufacturers, which may have seen vastly different formation and storage conditions before UHPC testing, also need to be considered. Now that UHPC testing systems are relatively common,20–22 device manufacturers need to bring cells from different manufacturers to a common state, if possible, prior to UHPC testing. Finding a way to maximize or more importantly, standardize, the maturity of the SEI layers in purchased cells before UHPC testing may allow for more accurate comparisons between them.

The effects of formation conditions on SEI quality and cell performance have been studied several times over the years. The authors of this paper have witnessed many different procedures adopted by many companies ranging from slow formation at or near ambient temperature to rapid formation at elevated temperature. This alone suggests the effect of formation temperature on the quality of the SEI is debateable. Several studies using Li/graphite half-cells with LiPF6 electrolyte have found that the quality of the SEI is best when it is formed at low temperature (20 °C).23,24 but a similar study using LiClO4 electrolyte found that the SEI is best when formed at higher temperatures (60 °C).25 Studies using full cells with LiPF6 have also shown that higher temperatures (45 °C) yield the most passivating SEIs.26,27 These reports suggest that electrolyte salt, temperature, and the presence of the positive electrode may have an effect on the cell performance and negative electrode SEI quality.

In this work, the effect of cell formation conditions (duration, temperature, and cell voltage) on subsequent CE is investigated, to find preferred conditions for forming a mature SEI that rapidly leads to stable CE. The mechanism by which cells mature is discussed. The effect of cell formation conditions on SEI thickness and chemistry is observed with XPS.

Experimental

Electrolyte preparation.—Electrolyte was prepared in an Ar-filled glove box to ensure minimal exposure to moisture and oxygen. 1.2 M electrolyte solutions were prepared by dissolving LiPF6 (BASF, 99.9%, water content <14 ppm) in a 3:7 weight ratio of ethylene carbonate: ethyl methyl carbonate (EC-EMC) solvent (BASF, water content < 20 ppm). The salt was weighed on an analytical balance and transferred to a Nalgene vial. The amount of solvent needed to make a 1.2 M solution was added to the vial using a pipette (Rainin lite XLS). The following additives were used in this study: vinylene carbonate (VC, BASF, 99.97%), prop-1-ene-1,3-sultone (PES, Lianhuachung Medicinal Chemistry Co., Ltd., China, 98.20%), 1,3,2-dioxathiolan-2,2-oxide (DTD, Suzhou Yacoo Chemical Reagent Co., > 98%), tri(trimethylsilyl) phosphite (TSTP, TCI, 95%), and ,5,2,4-dioxadithiane-2,2,4,4-tetraoxa (MMD5, Guangzhou Tinci Co. Ltd, 98.70%). Ternary blends of these additives were used in some cases. Henceforth “PES21” refers to a ternary blend of 2% wt PES, 1% wt DTD and 1% wt TSTP. Similarly, “PES22” refers to a blend of 2% wt PES, 2% wt DTD and 2% wt TSTP. “VC21” refers to a blend of 2% wt VC, 1% wt MMD5 and 1% wt TSTP. Lithium-ion pouch cell construction.—Machine-made lithium-ion pouch cells were obtained sealed, without electrolyte, from LiFun Technologies (Xinma Industry Zone, Golden Dragon Road, Tianyuan District, Zhuzhou City, Hunan Province, PRC, 412000). The negative
Table I. Cell chemistries and upper voltage limits of cells used in this study. In all cases the electrolyte was 1.2 M LiPF6 and the solvent was 3:7 wt EC:EMC except in test #5 where the solvent was just EMC. HV indicates an undisclosed, proprietary “high voltage” coating. The prefix “SC” for “SC-NMC532” signifies that the NMC material consisted of single-crystals, not the usual agglomerated particles.

| cell # | electrolyte additive | NMC - coating | Graphite | Cycling voltages |
|-------|----------------------|---------------|----------|------------------|
| 1     | 2% VC                | 622-Al2O3     | Natural  | 4.1, 4.2, 4.3 V  |
| 2     | 2% VC                | 622-HV        | Natural  | 4.4 V            |
| 3     | 5% FEC (in EMC)      | 622-HV        | Natural  | 4.2 V            |
| 4     | PES211               | 622-Al2O3     | Natural  | 4.2 V            |
| 5     | PES211               | 622-HV        | Natural  | 4.2 V            |
| 6     | PES211               | SC-NMC532     | Artificial | 4.2 V         |
| 7     | PES222               | 622-Al2O3     | Natural  | 4.1, 4.2 V       |
| 8     | PES222               | 622-HV        | Natural  | 4.2, 4.4 V       |
| 9     | 2% FEC + 1% DTD      | SC-NMC532     | Artificial | 4.2 V         |
| 10    | VC211                | 622-Al2O3     | Natural  | 4.2 V            |

electrode of these cells was 96% graphite, 2% carbon black (conductive diluent) and 2% sodium carboxymethylcellulose/styrene butadiene rubber (binder). Some cell types contained natural graphite and others contained artificial graphite. The positive electrode was 96% Li[Ni0.5Mn0.2Co0.3]O2 (where x, y, and z are the ratios of Ni, Mn, and Co, respectively abbreviated to NMCxyz), 2% carbon black and 2% polyvinylidene fluoride binder. Several types of coated and uncoated NMCs were used in this study: Al2O3-coated NMC622 (henceforth abbreviated 622A), proprietary “high voltage” (HV)–coated NMC622 (henceforth abbreviated to NMC622-HV), SC-NMC532, and single crystal NMC532 (henceforth abbreviated SC-NMC532). The NMC622 grades were obtained from Umicore (Korea) and the SC-NMC532 is described in the paper by Li et al. The ratio of negative/positive electrode capacity allowed for cell voltages of 4.5 V to be reached without lithium plating, with a capacity of 250 mAh. The combinations of cell types, electrolyte additives and upper voltage limits used in this work are listed in Table I. Prior to filling with electrolyte, the cells were opened and dried under vacuum for 14 hours at 100 °C, to remove residual moisture. The cells were then transferred to an Ar-filled glove box, without exposure to air. 0.9 g of electrolyte was added to each dried cell. This amount was in slight excess of the volume required for adequate electrode wetting. The aluminium-laminate cell casings were sealed at a temperature of 170 °C, under a gauge pressure of ~90 kPa, using a vacuum heat sealer (Model MSK-115A from MTI Corp).

**Lithium-ion pouch cell formation.—** After filling with electrolyte, the cells were held at 1.5 V for 24 hours. This allowed time for the electrolyte to permeate the electrodes. The voltage of 1.5 V was applied to prevent oxidation of the copper current collector, which occurs above 3.2 V vs Li/Li+. Prior to cell formation, the cells were clamped inside polyethylene holders, using rubber blocks and metal shims to sandwich the cells tightly. The rubber blocks were made from 5/8” medium-hard rubber (McMaster Carr, part number 5508T45). The pressure exerted on the cell by this type of clamping method is approximately 5–10 psi. A photo of the clamping method has been provided in a previous paper from our group. The importance of clamping cells during formation and cycling has also been discussed in a paper from our group. If pouch cells are not clamped, gas evolution, if it occurs, can decrease the stack pressure between the electrodes. This can cause inhomogeneous lithiation of the negative electrode, which can lead to lithium plating.

Cells were then transferred to temperature-controlled boxes and charged using a Maccor 4000 series test system. Cells underwent their first charge in one of three ways: a) C/20 charge to 4.2 V, hold at 4.2 V for 1 hour at 40 °C (henceforth called “standard formation”), b) the same procedure at 60 °C, or c) the same procedure at 60 °C, with a 15 hour long hold at 4.2 V (henceforth called the “preferred formation”). All cells were subsequently discharged at C/20 to 3.8 V, equilibrated at this voltage for 1 hour, then degassed. Degassing was done in an Ar-filled glove box, where the cell casings were cut open to release the gas. The cells were then resealed under ~90 kPa gauge pressure.

**Quantification of gas using archimedes’ method.—** Changes in cell volume due to gas evolution were measured using Archimedes’ method. In this method, cells are weighed while suspended from a fine wire and submerged under a fluid. According to Archimedes’ principle, if the mass of the cell remains constant, the change in cell volume is proportional to the difference in the submerged weight before and after testing. Measurements were made at room temperature, by weighing cells suspended from a fine wire attached to the underhook of an analytical balance (Shimadzu, AUY200D), while the cells were submerged under de-ionized water (18.2 MΩ/cm, Thermo Scientific Barnstead NANOpure Water Purification System).

**Electrochemical impedance spectroscopy (EIS).—** EIS measurements were conducted on cells after formation. EIS measurements were performed at 10.0 ± 0.1 °C, using a potentiostat (BioLogic VMP3) to induce a 10 mV bias, at frequencies ranging from 100 kHz to 10 mHz. Rct was taken to be the diameter of the mid-frequency semicircle in the Nyquist plot.

**Ultra-high precision coulometry (UHPC) cycling.—** After formation, cells were cycled using a UHPC system, designed and built at Dalhousie University, described in several publications. Prior to UHPC cycling the cells were clamped inside polyethylene holders, using rubber blocks and metal shims to sandwich the cells tightly. Cells were cycled once before being charged to 4.2 V. Some cells were held at 4.2 V for 15 or 30 hours before open circuit voltage storage. All cells, regardless of formation temperature, were stored at 60.0 ± 0.1 °C.

**Automated storage.—** After formation some cells were tested on an automated storage system, which was designed and built at Dalhousie University. Prior to storage testing, the cells were clamped inside polyethylene holders, using rubber blocks and metal shims to sandwich the cells tightly. Cells were cycled once before being charged to 4.2 V. Some cells were held at 4.2 V for 15 or 30 hours before open circuit voltage storage. All cells, regardless of formation temperature, were stored at 60.0 ± 0.1 °C.

**X-Ray photoelectron spectroscopy (XPS).—** After formation, certain cells were transferred to an Ar-filled glove box. The electrodes were removed, and rinsed several times with EMC, to remove LiPF6 and EC. Removal of these species is essential for the underlying SEI components to be observed by XPS. Removal of EC and LiPF6 is also important for maintaining low pressures in the XPS system. Rinsing with EMC is not expected to dissolve any SEI components, as EMC is the major component of the electrolyte in which the SEI was formed. Once the rinsed samples were dried, they were mounted onto a molybdenum sample holder, using double-sided, ultra-high vacuum-compatible copper tape. The sample holder was transferred into the XPS system, without exposure to air, using a specially designed air-tight apparatus that could be evacuated to low pressures. Electrodes were left under ultra-high vacuum overnight to allow for off-gassing of any remaining volatile components. The samples were then transferred to the analysis chamber of the XPS, which has a base pressure of 1 × 10⁻¹⁰ mbar and was maintained below 2 × 10⁻⁹ mbar during the experiments. Analysis was performed with a SPECS spectrometer equipped with a Phoibos 150 hemispherical analyzer, using unmonochromatized Mg Kα radiation and a pass energy of 20 eV. Preliminary and final survey scans were compared to ensure that no photochemical degradation was induced during analysis. Data analysis was done using CasaXPS software (v. 2.3.18). Charge correction was done by fitting the adventitious carbon peak, and shifting the x-axis down such that this peak fell at 285.0 eV. XPS spectra were fit with a non-linear Shirley-type background. This background was subtracted from the signal to allow for qualitative comparison.
of atomic concentrations between samples using relative peak areas. Peaks were fit with a mixed Gaussian (30%)/Lorentzian (70%) line shape.

Results and Discussion

The standard formation protocol (described fully in the Experimental section) was as follows: at 40°C, charge at a rate of C/20 to the upper voltage, hold one hour to equilibrate at this voltage, discharge at C/20 to 3.8 V (∼50% state of charge, SOC) and hold one hour at that voltage to equilibrate. Several modifications to this protocol were made to see what conditions affected the subsequent CE the most. NMC622-Al2O3/natural graphite cells balanced to 4.5 V and the most common electrolyte (1.2 M LiPF6 in 3:7 wt EC:EMC, with 2% wt VC) were chosen as a vehicle for the initial tests. Some of these cells were stored for various lengths of time, at different voltages, at 40, 60 or 80°C. Other cells were rapidly cycled 10 times after formation. The greatest improvement to subsequent CE during the first 10 UHPC cycles was observed when cells were held at 60°C for longer periods of time. To be sure that this trend was not unique to the cell type and electrolyte used, 10 other cell chemistries, listed in Table I, were formed either with a) the 40°C standard formation protocol, b) 60°C standard formation, or c) a 60°C modified formation protocol in which the one-hour upper voltage hold was extended to 15 hours. This third formation protocol will henceforth be referred to as the preferred formation protocol.

After formation, the cells were cycled on the UHPC using the same standard protocol: C/20 charge/discharge, between 2.8 V and the upper voltage, at 40°C. Figure 1a shows CE vs cycle number for cells with 2% VC and 622A positive electrodes, formed with the three different protocols. When the cells were formed at 40°C, the CE was initially low, and increased until it plateaued after ~15 cycles. When the cells were formed at 60°C, the initial CE was higher. When the cells were formed at 60°C with the preferred formation protocol, the initial CE was higher still. If the test continued beyond 20 cycles, it is likely that the CE for all three tests would have converged to the same value. The UHPC cycling data for 11 other cell chemistries and voltage limits is shown in Figure 1b. For ease of viewing (and for the mathematical model described later), coulombic inefficiency (CIE), is plotted vs. the inverse of the square root of time. The data plotted in this way makes a straight line after the first few cycles. Low CIE in the first three cycles—particularly for the cells that underwent the 15-hour hold at high voltage—is because of capacity gain from the “overhang” region of the negative electrode. The overhang is a narrow region of extra negative electrode that protrudes from the jelly roll, designed to prevent the possibility of having positive electrode with no negative electrode opposite. Over time during a high voltage hold, lithium will fill this overhang region. Lithium slowly leaves the overhang if the cell is subsequently cycled, leading to an apparent increase in capacity. Figure 1b shows that, as a general rule, the CIE of cells that underwent formation at 40°C (black) is higher than the CIE of the cells that underwent formation at 60°C (red), which is higher than the CIE of cells that underwent a 15-hour hold at the top of charge during 60°C formation. Near the end of the 20 cycles, the CIEs converge on a representative value for a particular cell chemistry.

If the preferred formation protocol enabled accelerated UHPC measurements to rank cell chemistries in the same way as slower UHPC measurements, then this project would be deemed a success. Figure 2 and Table II show the CIE of cells formed with the optimized protocol (60°C, with a 15-hour hold), at cycles 10 and 20, vs. the CIE of the same cells formed with the standard protocol (40°C). The points in Figure 2 indicate the average CIE of duplicate cells, and the lines passing through the dots indicate the difference between pair cells. The points are numbered from left to right, they rank in order of lowest to highest CIE at cycle 20 after standard formation. From bottom to top, the order of the red points is the rank of the cells that underwent the preferred formation, at the 10th cycle. The order of the
blue points from bottom to top is the rank of the cells that underwent the optimized formation at the 20th cycle. The ranks obtained after the two formation protocols (by reading the graph left-right and down-up) are not identical, but they are very similar. The same well-established conclusions can be made 10 cycles after the preferred protocol (rank the points left to right): i) cells with single crystal NMC532 positive electrodes and natural graphite negative electrodes; ii) cells with the ternary additive blend PES211 outperform cells with 2% VC; iii) within cells of the same chemistry, the CIE increases with increasing cycling voltage; iv) in cells with PES211, the Al2O3-coated positive electrodes outperform those with the proprietary “high voltage” coating. These results suggest that a UHPC experiment, to rank new cells with different chemistries, can be shortened to 10 cycles, if the preferred formation protocol were used.

Figure 2 shows that after 20 cycles, most cells formed with the preferred formation will always be better than the others’. It begs the question: Did the preferred formation protocol mature the cells (the CIEs will converge at a later point), or did the preferred formation improve the cell chemistry (the CIE of cells that underwent the preferred formation will always be better than the others’)? It appears that the former is the case, since Figure 1 shows that the CIEs of the cells converge over time. However, it was important to ensure that the preferred protocol had no lasting or detrimental effects on the cells, especially since prolonged storage at high SOC and elevated temperature can cause gas evolution, impedance growth and capacity loss. Figure 3 shows that the volume change after formation and UHPC cycling, Rct after formation, and the capacity fade from long-term cycling are all the same, within experimental error, for cells with 2% VC and 622A positive electrodes, cycled to 4.2 V. This shows that the additional 15 hours of storage at 4.2 V and 60°C did not have a detrimental or lasting positive impact on cell performance.

### Table II. Cell chemistries from Figure 2 ranked by order of CIE after standard formation.

| Label (40°C Rank) | CIE/10^{-3} (40°C, 20 cycles) | CIE/10^{-3} (60°C, 20 cycles) | Additive | Positive electrode | upper voltage |
|-------------------|-------------------------------|-------------------------------|----------|-------------------|---------------|
| 1                 | 0.74 ± 0.04                   | 0.76 ± 0.02                   | PES211   | SC532             | 4.2 V         |
| 2                 | 1.059 ± 0.005                 | 0.92 ± 0.01                   | 2%FEC 1%DTD | SC532             | 4.2 V         |
| 3                 | 1.1 ± 0.1                     | 0.94 ± 0.02                   | PES211   | 622A              | 4.1 V         |
| 4                 | 1.22 ± 0.08                   | 1.13 ± 0.01                   | PES222   | 622A              | 4.2 V         |
| 5                 | 1.22 ± 0.02                   | 1.085 ± 0.009                 | PES222   | 622HV             | 4.2 V         |
| 6                 | 1.29 ± 0.08                   | 1.07 ± 0.06                   | PES211   | 2% VC             | 622A          |
| 7                 | 1.324 ± 0.006                 | 1.34 ± 0.04                   | PES211   | 622A              | 4.2 V         |
| 8                 | 1.431 ± 0.008                 | 1.12 ± 0.03                   | PES211   | 2% VC             | 622A          |
| 9                 | 1.453 ± 0.006                 | 1.2 ± 0.01                    | VC211    | 622A              | 4.2 V         |
| 10                | 1.547 ± 0.004                 | 1.31 ± 0.01                   | PES211   | 622HV             | 4.2 V         |
| 11                | 1.555 ± 0.005                 | 1.34 ± 0.04                   | PES211   | 2% VC             | 622A          |
| 12                | 1.577 ± 0.005                 | 1.42 ± 0.03                   | 5% FEC   | 622A              | 4.2 V         |
| 13                | 1.82 ± 0.04                   | 1.594 ± 0.006                 | PES222   | 622HV             | 4.4 V         |
| 14                | 2.2 ± 0.05                    | 2.00 ± 0.01                   | 2% VC    | 622HV             | 4.4 V         |

### Modelling cell maturity vs. time.
—CIE has sometimes been modeled as inversely proportional to the degree of passivation, x, at a time, t, and proportional to a SEI passivation growth constant, k:  

\[ \frac{dx}{dt} = \frac{k}{x} \propto CIE \]  

The degree of passivation, x, and the CIE at a time, t₁, can be found by integration and substitution:

\[ \left[ \frac{2kt}{k} \right]_{0}^{t₁} = \int_{a}^{b} \frac{dx}{x} \propto CIE \]

\[ x₁ = \sqrt{2k} t₁ \]

If the temperature of the cell is fixed at 60°C from t = 0 until t = t₁ and is then changed from 60°C to 40°C, at a time, t₂, the expression for the CIE changes for the time period between t₁ and t₂,

\[ \frac{dx}{dt} = \frac{\sqrt{2k}}{2\sqrt{t₁}} \propto CIE \]
Figure 3. a) volume change after formation and after 20 UHPC cycles, b) $R_{ct}$ after formation, and c) capacity vs. cycle number after UHPC testing for cells with 2% VC and 622A positive electrodes, cycled to 4.2 V, at a rate of C/3 and at 40°C.

to reflect the change in passivation constant, $k$:

$$\frac{x_2^2}{2} = [k_{40°C} t]_{t_1}^{t_2}$$  \[5\]

$$\frac{x_2^2}{2} - \frac{x_1^2}{2} = k_{40°C} (t_2 - t_1)$$  \[6\]

Equation 3 is used to substitute for $x_1^2/2$ to get:

$$\frac{x_2^2}{2} = k_{60°C} t_1 = k_{40°C} (t_2 - t_1)$$  \[7\]

$$x_2 = \sqrt{2(k_{40°C}(t_2 - t_1) + \frac{k_{60°C}}{k_{40°C}}t_1)}$$  \[8\]

$$\frac{dx_2}{dt} = \frac{\sqrt{k_{40°C}}}{\sqrt{2(t_2 - t_1 + \frac{k_{60°C}}{k_{40°C}}t_1)}} \propto CIE.$$  \[9\]

Equations 4 and 9 are shown graphically in Figure 4a. Equation 4 is used to model the SEI maturity of cells that were formed and cycled at 40°C. Equation 9 is used to model the SEI of cells that were formed at 60°C (for a duration of $t_1$) and subsequently cycled at 40°C. Equations 4 and 9 were fit to the data in Figure 1 using a least squares fitting routine, to determine the $k$ values at 40 and 60°C. For the cells with 2% VC and 622A positive electrodes, cycled to 4.2 V, $k_{60°C}$ was found to be about nine times $k_{40°C}$ (0.0069 ± 0.0004). This suggests that the SEIs matures nine times faster at 40°C than it does at 40°C for this cell chemistry (the ratio of $k_{60°C}/k_{40°C}$ varied between six and ten for the other cell chemistries). CE vs cycle number for these cells, calculated using the $k$ values from the fit, is shown in Figure 4. The calculated CE bears a good resemblance to the measured CE, which suggests that this model is a decent approximation for cell maturity.

Probing the mechanism of cell maturity.—The model described above was previously used to model negative electrode SEI maturity as a function of time at different temperatures. However, the improvement in CIE from the preferred protocol is not strongly related to reduced discharge capacity, $Q_d$, fade (a hallmark of good negative electrode passivation). Figure 5 shows that the capacity fade is not very different when the cells are formed with the different formation protocols. To easily compare the contribution of fade to the CIE, the fade in Figure 5b is plotted as fractional fade per cycle. CIE is the sum of the fractional fade ($Q_d$ lost in a cycle) and the fractional charge-end point capacity slippage (slipC, due to oxidation of species at the positive electrode):

$$CIE = \frac{\text{fade}}{Q_d} + \frac{\text{slipC}}{Q_d}$$  \[10\]

The improvement in CIE is more strongly related to reduced charge end point capacity slippage, as shown by Figure 6. This is observed again in Figure 7, which shows that increasing the temperature and the time spent at high voltage during formation reduces the amount of self-discharge during open-circuit voltage (OCV) storage at 60°C. Evidently the preferred formation protocol reduces parasitic redox reactions at the positive electrode, more than at the negative electrode. This may explain why early studies on Li/graphite half-cells found that low temperature resulted in better passivation, while later studies on graphite/positive electrode full-cells found the opposite, that high temperature formation resulted in better passivation.
Figure 5. A) discharge capacity vs. cycle number for cells with 2% VC and 622A positive electrodes, B) fractional capacity fade vs inverse square root of time (time increases right to left) for all the cell types listed in Table I.

The cause of reduced charge end point capacity slippage and voltage drop after the preferred formation could be due either to a) the increased time spent at 60°C (in accordance with the model suggested in the previous section), or b) the increased time spent at high voltage, during which the positive electrode oxidizes and removes some soluble species that are generated from the reduction of electrolyte and negative electrode SEI formation. In either case, the effect is possibly due to the presence of lithium alkoxides, formed from the reduction of linear alkyl carbonates at insufficiently passivated negative electrodes. Lithium alkoxides are known to oxidize at the positive electrode, causing voltage drop and charge end point capacity slippage.38

Figure 6. A) charge end point capacity slippage per cycle vs. cycle number for cells with 2% VC and 622A positive electrodes, B) fractional charge end point capacity slippage vs inverse square root of time (time increases right to left) for all the cell types listed in Table I.
To see whether temperature or voltage had the greatest impact on the initial CIE and charge end point capacity slippage, cells with 2% VC and 622A positive electrodes were formed at either 40°C or 60°C, with the 15-hour voltage hold done at a variety of voltages in the first charge. The CIE and fractional charge end point capacity slippages of these cells during subsequent UHPC cycling are shown in Figure 8. The cells with the lowest initial CIE and charge end point capacity slippage are those that that underwent formation at 60°C, among which there is little difference between those that were held at different voltages. This suggests that the benefit of the preferred formation protocol is due to the increased length of time spent at 60°C, not the increased exposure to high voltage. This result is in agreement with the mathematical model for SEI maturity described above.

To see what effects the preferred formation had on the positive and negative SEIs, and to better understand what “a mature SEI” means in a physical sense—be it a thickened SEI layer, or a SEI of a certain chemistry—XPS was done on electrodes from cells after standard formation at 40°C, 60°C, or after the optimized formation. The XPS spectra of these electrodes (from cells with 2% VC and 622A positive electrodes) are shown in Figure 9. The XPS spectra of the positive electrodes were virtually identical, indicating that the SEI composition of the positive electrodes were very similar, regardless of the protocol used during formation. The thickness of the positive electrode SEI, inferred from the area of the NMC lattice oxygen peak, at 529 eV, is virtually the same for all three positive electrodes. This result agrees with previous work, done with cyclic voltammetry and electrochemical quartz microbalance, which showed that oxidation of electrolyte does not cause the precipitation of oxidized species on the positive electrode.

The XPS spectra of the negative electrodes also show no compelling evidence for a thickened SEI on more mature electrodes, judging from the area of the lithiated graphite, LiC₆, peak at 283 eV. The area of this peak is approximately the same in all cases, indicating that the overlying SEI is approximately the same thickness. The most significant difference between the three negative electrodes is the relative amount of LiF. This suggests that the SEI ages not by growing thicker, but by becoming more inorganic over time, as others have observed. It is proposed that LiPF₆ from the electrolyte reacts with carbonates (or hemi-carbonates, RCO₃Li) in the SEI, to form LiF by Equations 11 or 12:

\[
2\text{RCO}_3\text{Li} + \text{LiPF}_6 \rightarrow 2\text{LiF} + 2\text{RF} + \text{LiPO}_2\text{F}_2 + 2\text{CO}_2 \tag{11}
\]

\[
\text{RCO}_3\text{Li} + \text{LiPF}_6 \rightarrow 2\text{LiF} + \text{RF} + \text{POF}_3 + \text{CO}_2 \tag{12}
\]

The evolution of LiPO₂F₂ may be a contributing factor to the maturity of cells, since many recent reports have shown that LiPO₂F₂ is a beneficial electrolyte additive. Despite the solubility only up to 1.6 w%, very small amounts of LiPO₂F₂ have been shown to significantly improve charge end point capacity slippage and voltage drop during storage in lithium-ion cells. It has been suggested by Leroy et al. that evolution of LiF could occur from the reaction of acidic species with carbonates in the SEI, according to

![Figure 8](https://example.com/figure8.png)

*Figure 8.* a) CIE, b) fractional charge end point capacity slippage per cycle, and c) fractional fade per cycle plotted versus the inverse square root of time (time increases right to left) for cells that underwent formation at 40°C (blue) or 60°C (red), with 15-hour voltage holds done at various points during the first charge cycle.
The initial purpose of this work was to create a formation protocol that would allow for shorter UHPC experiments, by accelerating the maturity of new cells. This was achieved by forming cells at 60°C, instead of 40°C, and by prolonging the duration of the formation cycle by 15 hours. The preferred formation protocol gave neither short-term damage, nor permanent advantage to the cells formed with the standard formation protocol. It was found that the preferred protocol benefited the cells predominantly by reducing the initial rate of charge end point capacity slippage. This is likely because incomplete passivation causes lithium alkoxides to be evolved, which are subsequently oxidized at the positive electrode, causing reversible self-discharge. The optimized formation protocol did not lead to thickening of the SEI on either electrode, but more inorganic species were observed in the SEI of the negative electrodes that spent longer at 60°C. This suggests that LiPF$_6$ reacts with carbonates in the SEI to create a more inorganic SEI over time (perhaps with the evolution of LiPO$_2$F$_2$, a beneficial electrolyte additive). It is possible that this change in SEI chemistry is correlated with the improved CE of cells that underwent the preferred formation protocol.

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Figure 9. XPS spectra of positive and negative electrodes taken from cells with 2% VC after standard formation at 40°C or 60°C, or after the preferred formation at 60°C, which included a 15-hour hold at 4.2 V.

Equation 13:

$$\text{RCO}_{x}\text{Li} + 2\text{HF} \rightarrow \text{LiF} + \text{RF} + \text{H}_2\text{O} + \text{CO}_2$$  \[13\]

Acidic species can be formed by the reaction of LiPF$_6$ with moisture impurities. Acidic species can also be evolved from the oxidation of electrolyte species or H$_2$ at the positive electrode, which may explain why some have observed increased amounts of LiF on graphite in the SEI of the negative electrodes that spent longer at 60°C, in-