Instability of Polyvinylidene Fluoride-Based Polymeric Binder in Lithium-Ion Cells: Final Report

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Instability of Polyvinylidene Fluoride-Based Polymeric Binder in Lithium-Ion Cells: Final Report

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Abstract

Thermal instabilities were identified in SONY-type lithium-ion cells and correlated with interactions of cell constituents and reaction products. Three temperature regions of interaction were identified and associated with the state of charge (degree of Li intercalation) of the cell. Anodes were shown to undergo exothermic reactions as low as 100°C involving the solid electrolyte interface (SEI) layer and the LiPF₆ salt in the electrolyte (EC:PC:DEC/IM LiPF₆). These reactions could account for the thermal runaway observed in these cells beginning at 100°C. Exothermic reactions were also observed in the 200°C to 300°C region between the intercalated lithium anodes, the LiPF₆ salt, and the PVDF. These reactions were followed by a high-temperature reaction region, 300°C to 400°C, also involving the PVDF binder and the intercalated lithium anodes. The solvent was not directly involved in these reactions but served as a moderator and transport medium. Cathode exothermic reactions with the PVDF binder were observed above 200°C and increased with the state of charge (decreasing Li content). The stability of the PVDF binder as a function of electrochemical cycling was studied using FTIR. The infrared spectra from the extracts of both electrodes indicate that PVDF is chemically modified by exposure to the lithium cell electrolyte (as well as electrochemical cycling) in conjunction with NMP extraction. Preconditioning of PVDF to dehydrohalogenation, which may be occurring by reaction with LiPF₆, makes the PVDF susceptible to attack by a range of nucleophiles.
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Acknowledgments

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Acronyms

DEC      diethyl carbonate
DMF      dimethyl formamide
DSC      differential scanning calorimetry
EC       ethylene carbonate
FTIR     Fourier transform infrared
LiPF$_6$ lithium hexafluorophosphate
NMP      n-methyl pyrrolidinone
PC       propylene carbonate
Pt       platinum
PVDF     polyvinylidene fluoride
SEI      solid electrolyte interface
1. Cell Characteristics

1.1 Introduction

Lithium-ion batteries (organic liquid electrolyte) have an advanced battery chemistry that exhibits superior performance characteristics to virtually all other rechargeable battery systems. Consequently, this system is experiencing unparalleled growth and growth potential. Lithium polymer batteries (gelled electrolyte) are currently under development, and it is expected that this system, once developed, will exhibit performance characteristics superior to those of lithium-ion battery systems. In order to ensure continued availability of these superior systems, the safety and reliability of these systems must be ensured. Toward this end, the interaction of the system components must be considered. Reports of decomposition of the polyvinylidene fluoride (PVDF) binder component at the cathode as well as highly exothermic reactions leading to loss of battery integrity raise questions about the fundamental compatibility of these polymers with typical cell materials. The stability of optimum cell structures needs to be confirmed, and the fundamental material interactions need to be characterized. The conditions leading to catastrophic instability and design/material changes need to be identified, thereby ensuring acceptable battery reliability and performance.

Fluorinated polymers, for example, PVDF, are being used in both lithium-ion and lithium polymer batteries. In lithium-ion batteries, PVDF-based polymers are used as a binder and/or gel matrix in cathode and anode electrodes. The monomeric structure of the PVDF is given below.

\[-(\text{CH}_2-\text{CF}_2)\_x-\]

It is known that these polymers can undergo highly exothermic decomposition reactions (a dehydrodefluorination type reaction). In these battery systems, lithium hexafluorophosphate (LiPF\(_6\)) is used as the salt. This salt can be easily decomposed to form free fluoride. The question of the reactivity and stability characteristics of PVDF in the presence of this salt and its decomposition products are not well understood. In the presence of the solvents typically used in these batteries, the exothermic nature of the reactions can lead to thermal runaway. The state of charge of the cell also greatly affects the thermal stability of the cell. Cells in the fully charged state exhibit lower thermal runaway temperatures and greater reactivity.\(^2\)

1.2 Cell Structure

In this work, cell materials corresponding to those used in the commercial SONY US18650 lithium-ion cell were investigated for thermal and chemical stability under charge/discharge conditions. The “as received” electrodes were initially received as sheets of current collector (aluminum for the cathode and copper for the anode) with coatings of active material on one or both sides. The SONY-type cells consist of Li\(_{x}\)Co\(_{1-x}\)O\(_2\) as the active cathode material and Li\(_x\)C\(_6\) (MCMB 2528 carbon) as the active anode material. Sheets of anode material of 70 \(\mu\)m thickness (9.4 mg/cm\(^2\)) were prepared on 25 \(\mu\)m copper foil, while the two-sided cathode material of 140 \(\mu\)m total thickness (18.9 mg/cm\(^2\) per side) was prepared on 20 \(\mu\)m aluminum foil. KS-6 graphite (5 wt\%) was added to the cathode oxide to increase conductivity. The anode films were prepared with 10 wt\% PVDF as the binder, using N-methyl pyrrolidinone (NMP) as a solvent during the coating process while the cathode films were prepared with 5 wt\% PVDF. The electrolyte (EM Industries, Inc.) consisted of ethylene carbonate (EC): propylene carbonate (PC): diethyl carbonate (DEC) (1:1.2 by weight) with 1.0 M LiPF\(_6\) as the salt. The electrode reactions are:

\[
\text{Cathode: } \text{Li}_{1.2}\text{CoO}_2 \xrightarrow{\text{charge}} \text{Li}_{1.2-y}\text{CoO}_2 + y\text{Li}^+ + ye \\
\text{Anode: } 6\text{C} + y\text{Li}^+ + ye \xrightarrow{\text{discharge}} \text{Li}_y\text{C}_6
\]

Overall \(\text{Li}_{1.2}\text{CoO}_2 + 6\text{C} \xrightarrow{} \text{Li}_y\text{C}_6 + \text{Li}_{1.2-y}\text{CoO}_2\)

The range of stability of the Li\(_x\)Co\(_2\) crystal structure limits the charged state of the cathode to about \(x = 0.5\) for the lithium, giving a nominal composition of Li\(_{0.5}\)Co\(_2\) for the fully charged cathode.\(^3,4\) The potential of the fully charged cathode referenced to Li/Li\(^+\) is 4.1 V while that in the discharged state (Li\(_{1.2}\)Co\(_2\)) is 3.0 V. The corresponding potential of the fully charged anode (Li\(_x\)C\(_6\)) is 0.0 V and 3.0 V in the discharge state (Li\(_{0.5}\)C\(_6\)).
2. Experiment

2.1 Experimental Plan

This research activity is divided into two major efforts. First, the thermal stability of the electrode components was investigated using differential scanning calorimetry (DSC). Calorimetric techniques have been shown to be very useful in the characterization of these types of cells. The cell components were characterized singly and in various combinations. Particular attention was given to interactions with the EC:PC:DEC solvent and the EC:PC:DEC/LiPF₆ electrolyte. The solid components were measured individually, both in a dry state and in the presence of the solvent/electrolyte. The “as received” electrode sheet material was also measured with and without the presence of the solvent/electrolyte to check for any processing effects. Next, the electrodes were individually cycled and placed in a state of known charge (known Li content). The state of charge is known to significantly affect the thermal activity of the cell. It is important to understand how the anode and cathode contribute individually to the thermal activity of the cell under varying states of charge and which cell components are participating in these thermal reactions. The electrodes were cycled in a half-cell apparatus, removed, rinsed with DEC to remove the electrolyte, and then vacuum dried. These rinsed and dried electrodes were then measured in the dry state, followed by measurement in the presence of the solvent, and finally measurement in the presence of the solvent/salt electrolyte. All measurements were performed in sealed DSC pans from ambient temperature up to 400°C. The stability of the PVDF in these cycled electrodes was also determined by dissolving the PVDF from the films and measuring shifts in the Fourier transform infrared (FTIR) spectra.

The second portion of the research investigated the stability of the PVDF in the presence of negatively charged nucleophilic species. Dimethyl formamide (DMF) was chosen as a solvent because it readily dissolves the PVDF, allowing standard electrolysis techniques to be used. DMF is also known to form negatively charged species by electrochemical cycling of PVDF/DMF/LiPF₆ solutions. Similar species may exist in Li-ion cells during normal cycling conditions. If so, changes in the PVDF structure could lead to premature degradation of the binder and loss of film adhesion. It has been reported that the PVDF can undergo a dehydrofluorination reaction when exposed to negatively charged species. FTIR analysis of the cycled solutions identified the forms of PVDF that are present and the changes resulting from the electrochemical cycling process.

2.2 Experimental Apparatus

DSC was performed using a DSC 2920 (TA Instruments, New Castle, Delaware). Samples were loaded under dry, room air atmosphere and sealed in aluminum sample pans to prevent liquid/vapor loss at high temperatures. Measurements were made of the cycled electrodes that consisted of three small (0.125 in dia) discs punched out from the larger T-cell disc and sealed in the DSC pans either with or without liquid solvent/electrolyte. These small sample discs were loaded with the metallic current collector facing down so that the Li intercalated coatings did not touch the aluminum pans, which could have resulted in alloying. This arrangement required that the coating on one side of the double-sided cathodes be removed prior to taking these measurements. The mass normalized data were calculated based on the total mass of the measured sample, including active material, electrolyte, and any metal current collector backing for the electrodes. Every effort was made to control the amount of electrolyte/solvent liquid in each sealed pan, but the small quantities involved made exact control impossible, resulting in variations in the relative amount of the liquid and subsequent variations in the relative electrolyte/solvent thermal signature.

Electrodes were cycled using a “T-cell” apparatus as shown in Figure 2-1. Discs of the electrode material (0.5 in diameter) were cut from the electrode sheets and held by spring tension in the T-cell. Lithium foil was used as the working and reference electrodes. The cells were cycled using an Arbin battery test system (Arbin Corp., College Station, Texas). Electrodes were cycled repeatedly (at least five times) at low current rate (0.4 mA/cm²) to allow for irreversible lithium uptake in the “as manufactured” films. Only electrodes exhibiting near 100% charge/discharge coulombic efficiency were used for further analysis.
Figure 2-1. T-cell apparatus for cycling electrodes.

Lithium levels were set by direct coulombic measurement using the coulombic baseline between maximum charge/discharge potentials as the reference for each electrode.

FTIR analysis of the PVDF in the cycled electrodes was performed by dissolving the PVDF from the electrodes in n-methyl/pyrrolidinone (NMP). The electrodes were first rinsed in DEC and vacuum dried to remove the salt containing electrolyte. A fixed amount of this NMP solution was placed on salt plates and allowed to evaporate overnight under vacuum conditions. FTIR analysis performed on these films in transmission mode confirmed that the PVDF is the monomeric species as opposed to the common copolymer.

Cyclic voltammetry of the PVDF/DMF-1 M LiPF₆ solutions was performed in a standard three-electrode electrochemical cell at room temperature. The counter and the working electrodes were separated by a medium porosity glass frit to reduce mixing of the electrolysis products generated at the working and counter electrodes. DMF was chosen as the solvent for this study because it is capable of dissolving PVDF. PVDF was dissolved in the DMF-1M LiPF₆ solution at 5 wt%. The working electrode [which is a Platinum (Pt) gauze] immersed in the above solution was biased, with respect to Pt reference, at different voltages and held at those voltages for ~30 minutes to reveal any visible color change in the solution. The results are described in Section 3, Results.
3. Results

3.1 Thermal Stability/Component Interactions

3.1.1 Single Components

DSC scans of the individual components were performed on LiCoO$_2$, cathode graphite, anode carbon (MCMB 2528), PVDF, LiPF$_6$, and EC:PC:DEC/1.0 M LiPF$_6$ electrolyte. The LiCoO$_2$, graphite and carbon showed no thermal activity over the measured temperature range. The PVDF exhibited an endotherm peaking near 175°C followed by an exothermic reaction in the 350°C to 400°C range. Figure 3-1 shows the DSC scan data for this measurement. This endotherm is probably a melt transition of the polymeric structure. A reheat scan of the sample showed a reduced amplitude 175°C endotherm but did not show the higher temperature reactions. Partial decomposition of the PVDF may have occurred, but detailed analysis of reactant products was not performed. Figure 3-2 shows the data for the LiPF$_6$, which showed a small endotherm near 200°C and a major endothermic decomposition at 285°C. Repeat scans showed no thermal reaction, indicating irreversible decomposition of the salt. DSC scan data of the electrolyte and the solvent are shown in Figure 3-3. The electrolyte and solvent decomposition/boiling is characterized by endotherms between 200°C and 300°C. This endothermic signature was seen in all the nonreactive component/electrolyte mixtures. Except for a small high-temperature exothermic reaction for the PVDF, all of the single component measurements showed endothermic behavior or no thermal reactions.

3.1.2 Binary Mixtures

Binary combinations of the cell components were also measured. Mixtures of PVDF with graphite and with LiCoO$_2$ showed no thermal interactions other than the previously observed PVDF endotherm. Mixtures of PVDF with the solvent (EC:PC:DEC)

![Figure 3-1. DSC scan of PVDF powder.](image-url)
and with the electrolyte (EC:PC:DEC/LiPF₆) showed a lowered endotherm temperature for the PVDF (85°C to 105°C) as indicated in Figure 3-4. Allowing the liquid to evaporate and remeasuring the PVDF showed that the PVDF endotherm recovered to its original value, indicating that no irreversible changes occurred in the PVDF. Mixtures of PVDF and LiPF₆ powders were also measured. Figure 3-5 shows the DSC scan of this mixture as well as the individual components for comparison. The data show a sharper decomposition reaction for the LiPF₆ but no discrete thermal interactions. The data also show the possibility of a slight, broad exothermic reaction above 275°C, the LiPF₆ decomposition temperature. Although later measurements showed the importance of the LiPF₆ in the liquid electrolyte in terms of thermal interactions, the solid powders did not show any appreciable thermal activity.

Although the lithium in the Li-ion cells is present as an ionic species, lithium may occur in the metallic state at the anode under overcharging conditions and result in highly exothermic interactions. Characterizations were made of the interaction between metallic lithium foil and PVDF as well as with the electrolyte to identify these possible interactions in the cycled electrodes. All samples were placed in Mo pans and then sealed in the aluminum DSC pans to prevent alloying between the Li and aluminum. Figure 3-6 shows the DSC data for Li/PVDF mixture. Reference data are also shown for the pure PVDF and Li metal. The figure shows that the Li metal underwent a melt transition at about 185°C, but no interactions occurred between the Li and the PVDF at lower temperatures or even when the Li foil melted. However, the data did reveal greater exothermic reactions of the PVDF in its normal decomposition range above 350°C. The interactions between the Li metal and the EC:PC:DEC solvent as well as the EC:PC:DEC/LiPF₆ electrolyte are shown in Figure 3-7. In this case, significant exothermic interactions occurred at and above the Li melt temperature in the range of 185°C to 275°C. These signature data were used to identify possible metallic Li interactions in the cycled electrodes.
Figure 3-3. DSC scan of EC:PC:DEC/1.0M LiPF₆ electrolyte.

Figure 3-4. DSC scan of PVDF with solvent and PVDF with solvent/salt electrolyte.
3. Results

Figure 3-5. DSC scan of PVDF/LiPF$_6$ mixture with single component PVDF and LiPF$_6$ reference data.

Figure 3-6. DSC scans of Li metal with PVDF including data for single component Li metal and PVDF for comparison.
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3. Results

3.1.3 “As Received” Electrodes

Uncycled electrode materials were measured in the “as received” dry state, in the presence of solvent and in the presence of solvent/salt electrolyte. The anode active film consisted of the MCMB 2528 carbon and the PVDF binder while the active cathode film consisted of LiCoO₂, graphite and PVDF. Figures 3-8 and 3-9 show the DSC scans for the anodes and the cathodes, respectively. The dry “as received” samples showed the PVDF 175°C endotherm as seen for the PVDF starting powder with weak exothermic decomposition reactions above 350°C. The addition of the solvent and the electrolyte lowered the PVDF endotherm as seen for the PVDF starting powders. The characteristic solvent/electrolyte decomposition endotherms were seen in the 200°C to 300°C region. Thus, the “as received” electrodes exhibit only the combined thermal signatures of the individual starting components and show no interactions or processing effects.

3.1.4 Cycled Electrodes

The anodes and cathodes were cycled at 0.4 mA/cm² between potentials corresponding to known stability limits and composition of the active materials. The electrodes were cycled at least five times until a stable and reproducible charge/discharge curve was obtained. Figure 3-10 shows a typical charge/discharge curve for the cathode material. The potential limit of the fully charged cathode (Li₁₀.₅CoO₂) is 4.1 V while that in the discharged state (Li₁₀.₅CoO₂) is 3.0 V. Figure 3-11 shows the discharge/charge curve for the anode material, varying from 0.0 V in the charged state (Li₁₀.₅CoO₂) to 3.0 V in the discharged state (Li₁₀.₅CoO₂). The anode material shows an initial irreversible Li uptake resulting from formation of a passivating solid electrolyte interface (SEI) layer. Tables 3-1 and 3-2 list the coulombic charge/discharge values for the cathode and anode, respectively. Intermediate states of charge were obtained by direct coulombic measurement using these base coulombic values as reference. After five conditioning charge/discharge cycles, the anode Li levels were set at 0.0, 0.1, 0.3, 0.5, 0.7, 0.9, and 1.0, and the cathodes were set at 0.5, 0.75, and 1.0.
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Figure 3-8. DSC scans of uncycled “as received” anodes dry, with solvent and with electrolyte.

Figure 3-9. DSC scans of uncycled “as received” cathodes dry, with solvent and with electrolyte.
Figure 3-10. Cathode charge/discharge profile.

Figure 3-11. Anode charge/discharge profile.
3. Results

Table 3-1. Charge/Discharge Data for Cathode

<table>
<thead>
<tr>
<th>Cell</th>
<th>Active Weight: 0.0232 g</th>
<th>LiCoO₂ Discharge Capacity (Li in)</th>
<th>Maximum Voltage (Li out)</th>
<th>End Voltage (Li in)</th>
<th>Coulomb Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.53E-03 109.00 2.34E-03 100.82 4.10E+00 3.00E+00 9.25E-01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2.50E-03 107.90 2.46E-03 105.91 4.10E+00 3.00E+00 9.82E-01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.41E-03 103.91 2.38E-03 102.74 4.10E+00 3.00E+00 9.89E-01</td>
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<tr>
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<td>2.26E-03 97.39 2.24E-03 96.66 4.10E+00 3.00E+00 9.92E-01</td>
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Table 3-2. Charge/Discharge Data for Anode

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<tr>
<th>Cell: 16</th>
<th>Active Weight: 0.0123 g</th>
<th>Carbon Discharge Capacity (Li in)</th>
<th>Maximum Voltage (Li out)</th>
<th>End Voltage (Li in)</th>
<th>Coulomb Efficiency</th>
</tr>
</thead>
<tbody>
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<td>5.05E-03 410.30 5.60E-03 455.41 3.62E+00 3.00E+00 1.11E+00</td>
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<td>3</td>
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<td>4</td>
<td>3.40E-03 276.07 3.48E-03 283.16 3.00E+00 3.00E+00 1.03E+00</td>
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<td>275.86</td>
<td>283.10</td>
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</table>

3.1.4.1 Cycled Cathodes

The cycled cathode electrodes were removed from the T-cell, rinsed and dried as previously described and measured in the DSC. Figure 3-12 shows weak exothermic reactions increasing with decreasing Li content over a temperature range of 250°C to 350°C. The addition of the EC:PC:DEC solvent resulted in significantly increased exothermic reactions for the cathodes with 0.75 and 0.5 Li levels. The exotherms increased in magnitude and occurred at lower temperatures with the decreasing Li levels. However, the fully discharged (x = 1.0) cathode showed only the characteristic solvent endotherm (Figure 3-13). The cycled cathodes in the presence of the EC:PC:DEC/LiPF₆ electrolyte showed similar behavior (Figure 3-14). The effects of solvent and electrolyte addition to the cycled cathodes are shown more clearly for each Li level in Figure 3-15 (x = 1.0), Figure 3-16 (x = 0.75), and Figure 3-17 (x = 0.5). These figures show that the fully discharged (x = 1.0) cathodes showed no thermal activity over the entire temperature range independent of solvent/electrolyte exposure. The cathodes with reduced Li level showed significantly enhanced exothermic reactions in the presence of the EC:PC:DEC solvent, independent of the presence of the LiPF₆ salt.

We believe that the removal of the Li from the LiCoO₂ crystal structure, which results in an increase in the oxidation potential of the active material, results in enhanced solvent decomposition at the crystal/solvent interface, possibly including interaction with the PVDF polymer. Thus, the cathode contribution to thermal instability in the cell only occurs after the cell has already reached high temperatures (≥200°C) and is not of concern for discharged cells.
Figure 3-12. DSC scans of cycled cathode electrode after rinsing and drying to remove electrolyte.

Figure 3-13. DSC scans of cycled cathode electrode: rinsed and dried, added solvent.
Figure 3-14. DSC scans of cycled cathode electrode: rinsed and dried, added electrolyte.

Figure 3-15. DSC scans of cathodes with Li level of 1.0 rinsed and dried, with solvent and with electrolyte.
Figure 3-16.  DSC scans of cathodes with Li level of 0.75 rinsed and dried, with solvent and with electrolyte.

Figure 3-17.  DSC scans of cathodes with Li level of 0.5 rinsed and dried, with solvent and with electrolyte.
3.1.4.2 Cycled Anodes

The cycled anodes were removed from the T-cell, rinsed and dried as described earlier, and measured in the DSC in the same manner as for the cathodes. Figure 3-18 shows the DSC data up to 400°C for each Li level. Exothermic reactions were seen in the 250°C to 400°C range for Li levels of 0.5 or greater. However, little or no thermal activity was seen for the 0.0 to 0.3 Li levels. The exotherms increased in magnitude with increasing Li content of 0.5 or greater, starting with a peak near 370°C and shifting to lower temperatures for the two highest Li levels. This activity suggests that the intercalated carbon is reacting directly with the PVDF. This behavior is distinct from the Li meta/UPVDF reaction where only a very broad, nondiscrete reaction took place above the melt temperature of the Li metal. No thermal activity was seen for any of the anodes at temperatures below 250°C.

The effect of adding EC:PC:DEC solvent to the anodes is shown in Figure 3-19. No thermal activity was seen below 300°C for any Li level, other than the characteristic solvent endotherms. Above 300°C, exothermic reactions occurred only for Li levels of 0.5 or greater, increasing with the Li content, as was seen for the rinsed and dried anodes. However, the exotherms were now broader with a peak around 375°C. This behavior was qualitatively similar to that seen in the rinsed and dried anodes, indicating that the solvent is not contributing significantly to this reaction.

The effect of adding the EC:PC:DEC/LiPF6 electrolyte is shown in Figure 3-20. The thermal reactions are now much more complex. Significant exothermic reactions occurred in the low-temperature regime below 200°C, with double exotherms centered around 100°C and 150°C. The magnitudes of the lower temperature peaks were not correlated with the Li levels. Repeat measurements showed similarly high peaks for Li levels of 0.1 and 0.7. The magnitude of the higher temperature peak was inversely related to the magnitude of the lower temperature peak. If the lower temperature peak was high, the higher temperature peak was low, and vice versa. This relationship suggests that the reaction is limited by a fixed...
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Figure 3-19. DSC scans of cycled anodes at increasing Li levels: rinsed and dried, added solvent.

Figure 3-20. DSC scans of cycled anodes at increasing Li levels: rinsed and dried, added electrolyte.
quantity reactant. Other work has attributed these reactions to an electrolyte/SEI layer interaction.\textsuperscript{5,6} We believe that this interpretation is correct because no reactions are observed for the "as received" anodes. However, a more accurate interpretation is that the LiPF\textsubscript{6} in the electrolyte reacts with the SEI layer and does not directly involve the solvent. This SEI/LiPF\textsubscript{6} reaction can contribute significantly to the thermal runaway behavior of the cell. The thermal release beginning near or below 100°C can drive the cell temperature higher, whereas further reactions in the intermediate-temperature regime, 200°C to 300°C, and the high-temperature regime, 300°C to 400°C, can further maintain the increasing cell temperature.

Increased exothermic activity was also seen in the 200°C to 300°C intermediate-temperature regime. An exothermic reaction was superimposed on the solvent endotherms, increasing with an increasing Li level and centered on 275°C. Because this behavior was not seen with the addition of solvent only, the LiPF\textsubscript{6} is again indicated as being involved in an exothermic reaction, probably involving the PVDF and possibly the solvent as a transport medium.

Exothermic reactions in the 300°C to 400°C high-temperature regime were very similar to those seen for the solvent-only runs. Peaks near 375°C were seen only for the high Li level materials. This indicates that the LiPF\textsubscript{6} salt was not involved in these high-temperature reactions. Thus, these reactions were primarily Li/PVDF interactions.

The role of PVDF in these reactions was clarified in a set of measurements where the cycled anode films (x = 1.0) were first removed using NMP. The PVDF dissolved in the NMP while the carbon, active material remained as solid particles. The solid particles were removed by filtration and rinsed with DME to remove the NMP. Electrolyte was added to the particles, and the mixture was measured in the DSC like the earlier anode materials. Figure 3-21 shows data for this measurement. Low-temperature exotherms were seen in the 100°C to 150°C range as measured previously. However, no exothermic activity was observed in the mid-temperature or high-temperature regime. The only thermal activity was the solvent endotherms. Repeat measurements showed the same behavior. These measurements confirm that the low-temperature reactions are LiPF\textsubscript{6}/SEI layer interactions and do not involve PVDF, whereas the PVDF is essential to the higher temperature reactions.

![Graph](image)

**Figure 3-21.** DSC scan of active carbon material from cycled anodes (x = 1.0) with no PVDF.
3.1.5 Overcharged Anodes

Li$_x$C$_6$ anodes that were fully charged to the $x = 1.0$ state occasionally showed a large single exotherm near 125°C (Figure 3-22). Anodes that exhibited this behavior may have metallic Li deposited in the anode material. The small carbon particles coated with metallic Li may exhibit enhanced reactivity at lower temperatures due to the large surface area. Fully charged/overcharged Li-ion cells have shown low thermal runaway temperatures near 100°C. Investigation of this behavior involved purposefully charging anodes over a narrow Li range (0.95 to 1.10) that would, it was hoped, transition into an overcharged condition that would generate these metallic Li particles. Measurements of Li content are based on measured coulombic charge transfer, which can vary from charge to charge. Thus, our measurements may not accurately represent the actual Li level but should show relative trends with increasing Li content. Figure 3-23 shows the DSC data for the overcharged anodes after the rinse and dry procedure described previously. As seen in our earlier measurements, the Li interacts exothermically with the PVDF over the 300°C to 400°C range with increasing magnitude as the Li level increases. The $x = 1.1$ Li level showed a dramatic increase in magnitude. The effect of solvent addition is shown in Figure 3-24. The thermal signatures here are the same as those for the rinsed and dried samples except for the characteristic solvent endotherms. Again, this shows that the solvent does not contribute to the thermal activity in this temperature range. The effect of electrolyte addition is shown in Figure 3-25. An increasing exotherm superimposed on the solvent endotherms was observed with an increasing Li level in the intermediate temperature range (200°C to 300°C), as seen previously. The exotherms in the high-temperature range were still seen but with reduced magnitude. This behavior suggests that the PVDF has been partially reacted at the lower temperatures and does not contribute as fully to the high-temperature reactions. No enhanced thermal exotherms were seen in the low-temperature range (70°C to 200°C), indicating that we did not deposit the metallic Li particles as hoped. Further investigation is needed to determine the conditions and Li levels that reproducibly result in increased exothermic reactions. These results are important to the understanding of thermal runaway in Li-ion cells.
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Figure 3-23. DSC scans of rinsed and dried anodes for near fully charged state.

Figure 3-24. DSC scans of rinsed and dried anodes with electrolyte for near fully charged state.
3.2 Electrochemical Measurements

As described in the experimental section, fresh electrolyte solutions of DMF containing 1M LiPF₆ and 5 wt% PVDF were prepared for the electrolysis measurements. Platinum gauze was used as the working electrode and gold foil was used as the counter electrode. A Pt wire was used as the reference electrode. Table 3-3 gives the voltages at which the solution was electrolyzed. The voltages are measured as V versus Pt reference, and to express them against Li⁺/Li, add 3.0 V to the voltages. For example, –2.75 V versus Pt is 0.25 V versus Li⁺/Li.

3.3 FTIR Analysis of Anode/ Cathode Films

Thermal analysis of cell electrodes can reveal the magnitude and range of cell component interactions and degradation. However, non-thermal and low-thermal events can occur that still result in changes in the cell components that may impact the cell performance and lifetime. FTIR analysis can be used to characterize and monitor the fundamental structure of cell components at a level that is unobservable by DSC techniques. We used FTIR to monitor the stability of the PVDF binder in the cycled anodes and cathodes under various exposure conditions. The PVDF was removed as described earlier and coated onto salt crystal substrates for analysis.

3.3.1 PVDF

PVDF can exist in several crystal phases, two of which are termed Phase I (orthorhombic) and Phase II (monoclinic). The phases are chemically identical but vary in their C-C-C angles and the orientations of the vinyl fluoride units with respect to each other. Granular PVDF (the powdered, “as-received” form) is present as the Phase II, or monoclinic PVDF. When this PVDF is recrystallized by casting, for example, dissolution in NMP followed by evaporation of the solvent on a substrate, Phase I (orthorhombic) PVDF is formed. The infrared spectra of the two forms are similar (Figure 3-26), with band clusters in the same regions of the infrared spectrum. However, because of differences in symmetry, the shapes of the band clusters are different for Phase I and II PVDF, and infrared bands peaking near 764, 797, 976, 1150,
Table 3-3. Electrochemical Electrolysis of PVDF/DMF-1M LiPF$_6$

<table>
<thead>
<tr>
<th>Applied Voltage (V vs. Pt)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.5</td>
<td>Did not notice visible changes</td>
</tr>
<tr>
<td>-2.75</td>
<td>Did not notice visible changes</td>
</tr>
<tr>
<td>-3.0</td>
<td>Solution turned color and a possible faint black residue on working electrode mesh</td>
</tr>
<tr>
<td>-3.25</td>
<td>The solution turned dark brown within couple of minutes and a definite black fluffy residue on working electrode mesh</td>
</tr>
</tbody>
</table>

and 1384 cm$^{-1}$ are present in the spectrum of monoclinic PVDF but not in the spectrum of orthorhombic PVDF. In order to identify chemical changes in PVDF from their infrared spectra, it is necessary to compare the spectra of exposed PVDF to that of unexposed PVDF in the same crystal form.

3.3.2 FTIR Analysis of PVDF from Cycled Anodes and Cathodes

PVDF was extracted from both carbon anodes and LiCoO$_2$ cathodes. Sonication using fixed volumes of NMP was generally necessary to complete the dissolution of electrochemically cycled electrodes. Aliquots of NMP containing material extracted from the electrodes were placed onto salt windows and spread to obtain liquid films of similar diameters. Then, the NMP was evaporated, in vacuum, leaving a film (casting) of solid material. Transmission infrared spectra were obtained by placing the salt windows into the macroscopic beam of a FTIR spectrometer. Spectra were obtained of castings from virgin “as received” electrodes, electrodes exposed to the EC:PC:DEC solvent, and electrodes exposed to EC:PC:DEC/LiPF$_6$ electrolyte.

The spectra of cast PVDF in Figures 3-26 and 3-27 show that NMP does not react directly with PVDF. Whereas the crystal form of PVDF is changed by the dissolution and casting procedure, the infrared bands in the spectrum associated with PVDF are caused by vibrational modes of PVDF. There is no evidence of residual NMP in this spectrum of cast PVDF as shown in Figure 3-27.

![Figure 3-26. FTIR spectra of “as-received,” granular PVDF and PVDF cast from NMP.](image-url)
Infrared spectra of the castings from carbon anodes are shown in Figure 3-28. The material extracted from the “as received” electrode, which had exposure neither to cell operating conditions nor even to the cell solvents and electrolyte, shows distinctive, dominant PVDF bands with a broad band peaking near 1650 cm\(^{-1}\) that may be caused by residual water vapor or NMP remaining after bake-out. Unaltered PVDF appears to compose the majority of the extract. The infrared spectrum (not shown) of the casting from the extract of a carbon anode exposed to the cell solvent (EC:PC:DEC) is essentially the same as that of the “as received” spectrum. However, when the anode is exposed to the complete cell electrolyte (EC:PC:DEC plus LiPF\(_6\)), the infrared spectrum of the electrode’s extract is significantly different. A strong carbonyl band centered at 1650 cm\(^{-1}\) forms, a P-F band, caused by residual LiPF\(_6\) in the electrolyte, is present, and bands corresponding to PVDF are of such low intensity as to be barely recognizable. The infrared spectrum of the extract from an anode electrochemically cycled in a lithium cell shows even less evidence for the presence of PVDF. The “cycled cell” spectrum also includes a carbonyl band, bands caused by Li\(_2\)CO\(_3\), which routinely forms on the anode during electrochemical cycling, and a P-F band, which is presumably caused by residual LiPF\(_6\). The effect of varying Li level on the spectra is shown in Figure 3-29. The Li\(_2\)CO\(_3\) bands are strongest for the higher Li levels. Although the Li\(_2\)CO\(_3\) is an SEI layer product resulting from reactions at the anode during cycling, removing the intercalated Li apparently also reduces the Li\(_2\)CO\(_3\).

Figure 3-30 shows the infrared spectra from castings of the extracts from LiCoO\(_2\) cathodes. A pattern similar to that found in the infrared spectra from the anode castings is present in this set of spectra. The infrared spectrum of the extract from the “as received” cathode shows distinctive and dominant PVDF bands, but these bands are missing from the infrared spectra of extracts from cathodes exposed to the electrolyte and from those cycled electrochemically. As with the spectra from the anodes, a carbonyl band appears in these spectra. Residual LiPF\(_6\) is evidenced by a P-F band in the spectrum from the uncycled cathode exposed to electrolyte. LiPF\(_6\) was apparently successfully separated from the extract of the cycled cathode because the P-F band in its spectrum is low in intensity. The infrared spectrum (not shown) of the extract from a cathode exposed only to solvent (EC:PC:DEC) shows distinctive PVDF bands plus band structure from another material in the 1000 to 1200 cm\(^{-1}\) region. The presence of the non-PVDF bands indicates that some reaction has occurred in the uncycled cathode material due to solvent exposure but did not involve any significant PVDF degradation.
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Figure 3-28. FTIR spectra of NMP extracts from carbon anodes.

Figure 3-29. FTIR spectra of NMP extracts from carbon anodes with increasing Li levels.
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Figure 3-30. FTIR spectra of NMP extracts from LiCoO₂ cathodes.

The infrared spectra from the extracts of both electrodes indicate that PVDF is chemically modified by exposure to the lithium cell electrolyte (as well as electrochemical cycling) in conjunction with NMP extraction. If the P-F and Li₂CO₃ bands are ignored, the infrared spectra from the extracts of both anodes and cathodes that were electrochemically cycled or exposed to electrolyte resemble the spectrum of polyvinyl pyrrolidone, a polymer with pyrrolidone side groups, whose backbone is that of a vinyl polymer.

Polyvinyl pyrrolidone is not present in any of the cell constituents; therefore, it must be a reaction product. We postulate that NMP reacts with unsaturated carbon linkages in PVDF to form a polymer similar to polyvinyl pyrrolidone. We know, however, that this reaction does not occur (Figures 3-29 and 3-31) when NMP dissolves PVDF granules or when NMP extracts PVDF from “as-received” anodes and cathodes or even from anodes exposed to the cell solvent (EC:PC:DEC). Apparently, the requisite unsaturation is not present in the PVDF chain in the “as-received” PVDF or PVDF in contact with only the EC:PC:DEC solvent.

When LiPF₆ is present, this unsaturated carbon bond reaction appears to occur, and it appears to go more to completion when the electrodes are subjected to electrochemical cycling. The formation of unsaturated carbon-carbon bonds in halogenated hydrocarbons occurs by dehydrohalogenation, the elimination of hydrogen and a halogen from adjacent carbon atoms. This reaction is mediated by mildly basic lithium salts in polar aprotic solvents and proceeds as follows in PVDF:

\[
\text{C} - \text{C} \xrightarrow{\text{Li}^+} \text{C} = \text{C} \\
\text{H} \quad \text{F}
\]

It is not clear that stable, unsaturated carbon-carbon bonds are formed by this reaction in the conditions of lithium cell operation. But, at the least, the electrolyte appears to pre-condition the PVDF to react with NMP, perhaps by formation of an adduct with LiPF₆. Although the reaction with NMP is not of direct concern, this reaction is an indicator of possible similar reactions in the operating cell where even more active chemical species may be present.

Additional evidence for the role of lithium salts in the aging of PVDF is suggested by Figure 3-31. Exposure to the EC:PC:DEC solvent alone does not seem to result in extensive chemical modification of the PVDF in the carbon anode. The infrared spectrum of its extract shows an NMP-like carbonyl band, but characteristic PVDF bands are still dominant in the spectrum. On the other hand, the PVDF bands in the spectrum of the extract from the LiCoO₂ cathode are of relatively low intensity. While the reaction of
PVDF with NMP does not appear to proceed as strongly as when LiPF₆ is present, clearly some reaction with PVDF is proceeding more strongly in the presence of LiCoO₂ versus carbon.

### 3.3.3 FTIR Analysis of PVDF/DMF/LiPF₆ Electrolysis Products

Pud et al. presented evidence for the electrochemical modification of fluorocarbon polyolefin polymers by nucleophiles derived from DMF. In their experiments, a solution of 0.1M tetrabutyl ammonium perchlorate in DMF was electrolyzed and then contacted with fluorine-containing polyolefin films. When subjected to this procedure, PVDF-containing films turned brown, suggesting that they had been chemically modified. This modification of the PVDF was suggested to be the result of attack on the PVDF by nucleophiles formed from the addition of an electron to DMF during its electrolysis. The nucleophile was believed to be the electron adduct of DMF, \([\text{OHCN}(\text{CH}_3)_2]^+\) or a cleavage product, \((\text{CH}_3)_2\text{N}^+\).

Figure 3-32 shows the infrared spectra of 1M LiPF₆/DMF solutions before and after electrolysis. DMF is a good solvent for PVDF and was thus used for the electrolyses because PVDF is insoluble in EC:PC:DEC. Band assignments for DMF are taken from Chalapathi and Ramiah. Individual spectra were scaled in intensity with respect to the 1255 cm⁻¹ band, a mode involving (N-CH₃) bonds, which are not believed to be strongly affected by expected chemical reactions. Except for what are believed to be solvent-electrolyte interactions, the spectrum of the solution before the electrolysis is essentially a superposition of DMF and LiPF₆ spectra. The solvent-electrolyte interactions result in a lowering of the frequency of the (C = O) stretching mode of DMF from 1685 cm⁻¹ to 1656 cm⁻¹ and a broadening of the 833 cm⁻¹ (P-F) mode from LiPF₆. The spectra of the electrolyzed solutions are little changed from the spectrum obtained before electrolysis, indicating that extensive cleavage of the DMF is unlikely. The most significant differences between the spectra of the LiPF₆/DMF solutions before and after electrolysis are a (further) broadening of carbonyl (C = O) and P-F related bands (1656 and 833 cm⁻¹) and a change in shape of the feature at 655 to 670 cm⁻¹, which includes contributions from P-F and carbonyl (O = C – N) related modes. These differences are...
most likely caused by increased solvent-electrolyte interactions, which may be caused by reduction of the DMF by formation of its electron adduct.

Solutions containing 5 wt% PVDF in 1M LiPF₆/DMF were also electrolyzed. After electrolysis, the PVDF was rinsed in DEC solvent to remove DMF and LiPF₆ and then centrifuged. In the centrifugate, there was a bottom layer of relatively light-colored (white) solid material and an upper layer of darker colored (brown) solid material. These two layers were removed from the centrifugate, placed on salt windows, dried at 70°C, and analyzed by FTIR using a microscope attachment.

Figure 3-33 shows infrared spectra of “as-received,” granular (monoclinic) PVDF and of the white material recovered, after the electrolysis and rinsing described previously, from the lower portion of the centrifugate. The white material is predominantly monoclinic PVDF, with some residual LiPF₆, as indicated by the band peaking near 840 cm⁻¹. The major differences between the spectra of the PVDF in the white material and the original PVDF are the development of a band at 940 cm⁻¹ associated with CCH groups and of a band at 1277 cm⁻¹ associated with C-F modes. One of the nucleophilic reactions possible with fluorocarbons is dehydrohalogenation (removal of HF) to form carbon-carbon double bonds. In addition to the nucleophilic DMF electron adduct, lithium compounds are known to initiate dehydrohalogenation. However, the infrared spectra show no evidence of the formation of carbon-carbon double bonds. If dehydrohalogenation is occurring, it must be coupled to rehalogenation, with a potential for redistribution of the hydrogens and fluorines on the vinyl fluoride polymer backbone (CH₂-CF₂)n. Rehalogenation might be mediated by the presence of fluorine atoms in PF₆⁻ groups from the LiPF₆ electrolyte. The redistribution of carbon-fluorine bonds could lead to lesser (CHF-CHF) or greater (CF₂-CF₂) local concentrations of fluorine atoms within the backbone. Such changes in fluorine atom distribution could affect local symmetries and result in the observed changes in the infrared spectra. Sites with relatively high concentrations of fluorine are more susceptible to direct electrochemical reactions.

Figure 3-34 shows infrared spectra of cast (orthorombic) PVDF and of the brown material recovered from the upper portion of the centrifugate. Except for a band at 837 cm⁻¹, which we believe to be due to LiPF₆ residues, the band pattern in the spectrum of the brown material generally corresponds to the cast form of PVDF. The differences between the spectra of the brown material and the cast form of PVDF parallel the differences (Figure 3-34) between the spectra of the white material and the granular form of PVDF: development of bands believed to be due to CCH modes (941 cm⁻¹) and C-F modes (1262 cm⁻¹). A mode peaking near 1650 cm⁻¹ in the spectrum of
Figure 3-33. Infrared spectra of granular PVDF and the white material recovered from the electrolysis solution.

Figure 3-34. Infrared spectra of cast PVDF and the brown material recovered from the electrolysis solution.
the brown material would be interpreted as due to C = O (an indication of oxidation of PVDF), except that bands in the O-H stretching region (3000 to 3700 cm⁻¹) suggest that it is due to OH bending motions of water in the sample. Note that the CCH (941 cm⁻¹) and C-F (1262 cm⁻¹) bands are relatively more developed in the spectrum of the brown material than those in the spectrum of the white material. Overall, the region from 1100 to 1300 cm⁻¹ in the spectrum of the brown material, which is dominated by modes involving C-F stretching vibrations, shows greater changes relative to the spectrum of cast PVDF than does the same region in the spectrum of the white material (Figure 3-34) versus that of granular PVDF. The electrolysis has modified the brown material to a greater extent than the white material. The nature of the modification, however, appears to be the same for both materials: rearrangement or redistribution of the bonds involving fluorine atoms. The brown color of the material in the upper centrifugate may be because of intense visible absorption by conjugated double bonds. If present, these double bonds must comprise less than a few percent of the carbon-carbon bonds because there is no evidence for them in the infrared spectra.

These experiments provide evidence for dehydrohalogenation and rehalogenation of the PVDF backbone during electrolysis in LiPF₆/DMF. The infrared spectra indicate that these reactions lead to rearrangement and/or redistribution of carbon-fluorine and, concomitantly, carbon-hydrogen bonds. The redistribution of carbon-fluorine bonds might affect the susceptibility of PVDF to direct electrolysis.
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4. Summary

The stability of Li-ion cathodes and anodes has been shown to be a complex function of constituent interactions and exposure conditions. Thermal analysis of the anodes and cathodes in these cells has shown that there are three regions of thermal activity. In the low-temperature regime (70°C to 200°C), cycled anodes showed an exothermic SEI layer reaction that did not involve the PVDF binder. The magnitude of the exotherms did not correlate with the Li level. These reactions only occurred with the presence of LiPF₆ in the electrolyte and did not directly involve the EC:PC:DEC solvent. Fully charged anodes on occasion showed large exotherms in this range and are believed to result from the presence of deposited Li metal particles. The conditions that consistently resulted in this behavior could not be reproduced even when the anodes were purposely overcharged.

In the intermediate temperature regime (200°C to 300°C), the cycled anodes underwent an exothermic reaction (275°C) superimposed on the solvent endotherms, increasing in magnitude with increasing Li level. The reaction again only occurred with the presence of the LiPF₆ in the electrolyte and did not occur for the pure solvent. This reaction is believed to be a Li/PVDF interaction not directly involving the solvent. Removal of the PVDF from the cycled films eliminated the reaction and confirmed that the PVDF is a main reactant.

In the high temperature regime (300°C to 400°C), the cycled anodes showed increasing exotherms with increasing Li level only for Li levels 0.5 or greater. Those anodes with Li levels below 0.5 showed little or no thermal activity under any exposure conditions. These reactions occurred for the rinsed and dried films as well as in the presence of solvent or electrolyte. Removal of the PVDF from the films eliminated the exotherms. These results suggest that Li/PVDF is the most probable interaction occurring in this temperature range.

The cycled cathodes showed much less thermal activity than was seen for the anodes. Exothermic reactions only occurred in the 250°C to 350°C range and only for the non-discharged states (Li < 1.0). The fully charged (Li = 1.0) cathodes showed no thermal activity over the entire 70°C to 400°C temperature range under any exposure conditions. The addition of solvent to the cathode films greatly enhanced the exothermic reactions, but no additional reactions were seen for the addition of the LiPF₆ salt. We believe that the removal of the Li from the LiCoO₂ crystal structure results in an increase in the oxidation potential of the structure, which results in enhanced solvent decomposition possibly including PVDF degradation.

Thermal runaway in these Li-ion cells is thus first affected by the anodes around 100°C involving the SEI layer reactions. Fully charged/overcharged cells may exhibit increased reactivity in this temperature range if elemental Li particles have formed. Once the cell temperature reaches the 200°C range, the charged cathode contributes to the accelerating thermal reaction. Further exothermic reactions from the charged anodes reacting with the PVDF contribute to this runaway once these higher temperatures are reached.

The stability of the PVDF binder is called into question even under benign exposure to EC:PC:DEC/LiPF₆ electrolyte. The infrared spectra from the extracts of both electrodes indicate that PVDF is chemically modified by exposure to the lithium cell electrolyte (as well as electrochemical cycling) in conjunction with NMP extraction. Preconditioning of PVDF to dehydrohalogenation, which may be occurring by reaction with LiPF₆, makes the PVDF susceptible to attack by a range of nucleophiles. Nucleophiles may be present as impurities (for example, water, ammonia) or they may be formed electrochemically during cell cycling. The electrochemical formation of nucleophiles provides a constant supply of species capable of reacting with and degrading preconditioned PVDF.
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5. References


5. References

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