



Trace Degradation Analysis of Lithium-Ion Battery Components

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Rechargeable lithium-ion batteries (LIBs) are key components for portable electronics, medical devices, industrial equipment and automobiles. They are light weight, provide high energy density and recharge without memory effects. Much research has been spent on improving product safety, lifecycle and power output over a range of high and low temperatures, yet understanding fundamental processes and degradation mechanism in LIBs remains a challenge.

making contact and causing a short circuit.

During discharge, Li-ions migrate from the anode to the cathode. Electrons move in an external circuit in the same direction as the Li-ions. Current moves in the opposite direction. The discharging process is referred to as de-intercalation. During charging, an external electrical power source (i.e., house current) applies an over-voltage that forces the lithium ions to pass in the reverse direction. This process is referred to intercalation. During intercalation, Li-ions move

from an ordered Li metal cathode lattice and become embedded between graphene sheets in the anode.

The solid electrolyte interface (SEI) enables the LIB to operate in an efficient and reversible manner. The SEI film is composed of electrolyte reduction products that start forming on the surface of the anode during the initial battery charge. The SEI film functions as an ionic conductor that enables Li to migrate through the film during intercalation and de-intercalation over the life of the battery. At the same time, the film also serves as an inductively passive electronic insulator which prevents further electrolyte reduction products forming on the

anode, under typical operating conditions.

While capable of operating efficiently for years, LIB's can begin to fail prematurely when exposed to a-typical conditions such as elevated temperature, charge effects or the presence of trace contaminants. These effects can initiate irreversible cell degradation resulting in a loss in energy density, cycle life and safety.

The following are five exothermic degradation reactions that can occur between cell components:

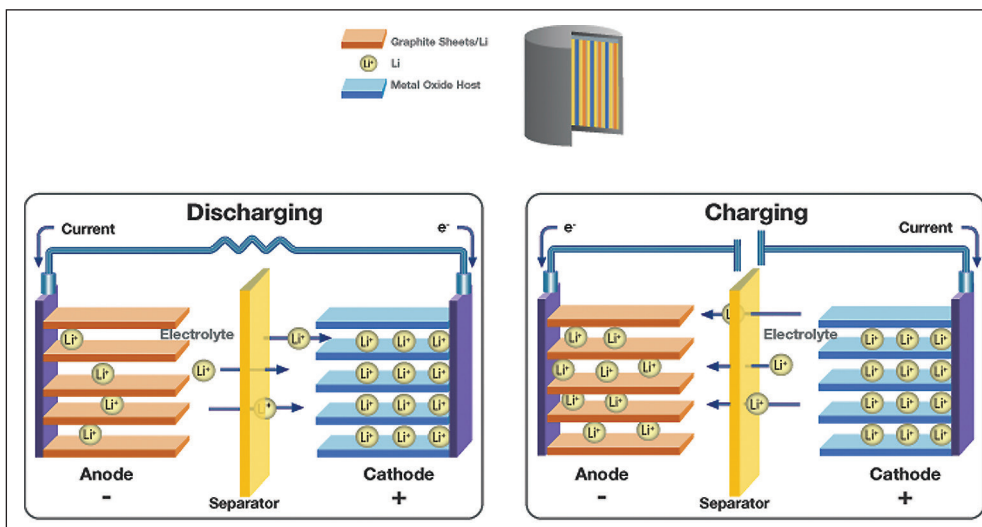


Figure 1: Depicted is the operation of a Li-ion battery during discharging and charging. Images: Thermo Fisher Scientific Inc.

To understand LIB degradation processes it's important to understand how they operate. Figure 1 depicts the operation of a LIB. The cell is composed of an anode, cathode, electrolyte and a separator. The anode is composed of carbon or graphite, the cathode of a lithium metal oxide and the electrolyte of a lithium-ion salt in a non-aqueous (aprotic) solvent. The separator is composed of a permeable membrane that enables the Li-ions to shuttle between the anode and cathode and keeps the two electrodes from

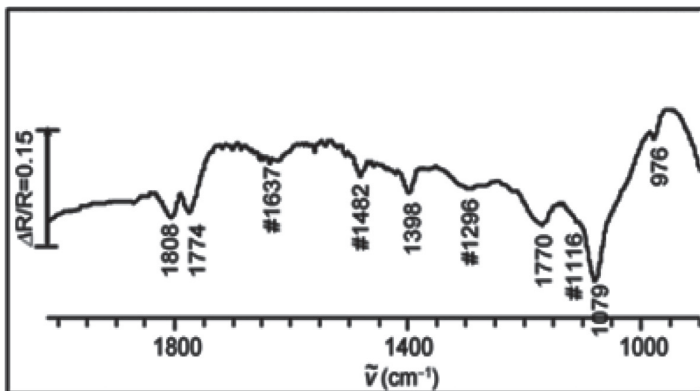


Figure 2: Shows results from the characterization of an SEI layer by FTIR spectroscopy. The SEI film formed on a thin-film graphite anode by cyclic voltammetry in 1M LiPF₆ in a 1:1 mixture of EC and DEC. The absorption bands at 1645 cm⁻¹ ($\nu_{C=O}$), 1,482 cm⁻¹ (δ_{CH}), 1,116 cm⁻¹ (ν_{C-O}) and 849 cm⁻¹ (δ_{OCO}) suggest the SEI film is composed mainly of alkyl lithium carbonates (ROCO₂Li). Analysis was performed on a Thermo Scientific Nicolet Nexux 870 FT-IR spectrometer (or equivalent Thermo Scientific Nicolet iIS 50R FT-IR spectrometer).

1. Chemical reduction of the electrolyte by the anode.
2. Thermal decomposition of the electrolyte.
3. Chemical oxidation of the electrolyte by the cathode.
4. Thermal decomposition by the cathode and anode.
5. Internal short circuit by charge effects.

ANODE

The SEI film that forms on the anode is composed of a mixture of inorganic and organic reduction products. These include lithium oxide, lithium fluoride and semicarbonates (e.g., lithium alkyl carbonates). Under typical conditions, such as room temperature and the absence of charge effects and contaminants, the SEI reaches a fixed film thickness and the LIB can operate reversibly for years.

CHEMICAL REDUCTION OF THE ELECTROLYTE BY THE ANODE

At elevated temperatures, alkyl carbonates on the SEI decompose into insoluble Li₂CO₃ that can increase the film thickness of the SEI layer, clogging the pores on the carbon surface, and limiting accessibility of lithium ions to the anode surface. Inhibiting intercalation leads to an increase in impedance, and eventually a loss in battery capacity, also referred to as capacity fade. Gases formed by the decomposition of the electrolyte increases the internal pressure in the cell and raises potential safety issues in a sensitive environments such as a cell phone.

There are two sources of battery capacity loss; calendar loss and cycling loss. Calendar loss results from the passage of time and is measured from the maximum state of charge. Cycling loss is due to charging and discharging the battery and depends on both the maximum state of charge and the depth of discharge. Capacity fade is measured as the percentage of total capacity range that is used during a cycle.

Extended storage of the LIB is another condition that results in an incremental increase in SEI film thickness and capacity fade.

INTERNAL SHORT CIRCUIT

Overcharging the LIB (greater than 4.2 V) can initiate the reduction of Li⁺ on the anode as lithium plates, resulting in irreversible capacity fade. The randomness of the metallic lithium embedded in the anode during intercalation results in the formation of dendrites. Over time the dendrites can accumulate and pierce the separator, causing a short circuit between the electrodes leading to a release of heat, a possible fire and/or explosion. This process is referred to as thermal runaway.

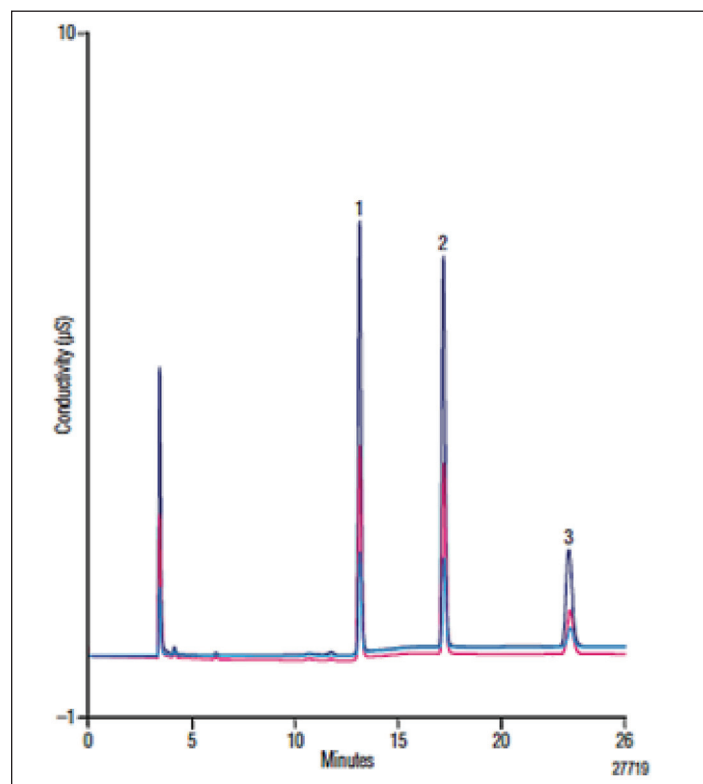


Figure 3: Shown is the analysis of a simulated mixture of three liquid electrolytes by ion chromatography. The chromatogram shows the separation of (Peak 2) Perchlorate, and (Peak 3) Hexafluorophosphate at concentrations of 5, 10 and 20 mg/L for each analyte. Analysis was performed using a Thermo Scientific Dionex IonPac AS20 (4 by 250 mm) column with its matching guard and suppressed conductivity. The eluent used was Potassium hydroxide (Gradient conditions—7 to 10 min 15 mM, t₀ to 13 min 15 to 80 mM, and held at 80 mM for 1 min). All three analytes were separated from each other with an analysis time of less than 25 min.

Over discharging (less than 2 V) can also result in capacity fade. The anode copper current collector—a less commonly referenced battery component used to facilitate electron transfer—can dissolve into the electrolyte when the LIB is discharged. However when charged, the copper ions can reduce on the anode as metallic copper in addition to the copper collector. Over time, metallic copper dendrites

can form and lead to a short circuit in the same manner as metallic lithium dendrites.

STRUCTURAL DISORDER OF THE ANODE

The anode is composed of materials that have a high surface area and provide large discharge and charge capacity. Cycling the lithium-ion battery at a high cycling rate and at high state of charge induces mechanical strain on the graphite lattice from a high concentration of lithium-ion packed between the graphene sheets. The mechanical strain caused by the insertion and de-insertion results in fissures and splits of the graphite particles making them less oriented as compared to the original graphite particles. A relative change in the orientation of the graphite particles affects the reversible capacity of the anode and results in capacity fade.

ELECTROLYTES

The majority of electrolytes used in LIBs are composed of a lithium hexafluorophosphate (LiPF_6) electrolyte in a solvent mixture of linear and cyclic carbonates (e.g., ethylene carbonate (EC) and dimethyl carbonate (DMC)). The combination of LiPF_6 and carbonates is selected because of their high conductivity and SEI forming ability. A mixture of carbonate solvents is needed to satisfy the requirement for high ionic conductivity—to dissolve and coordinate the lithium salt ions—and low viscosity—where the solvated ions occupy a small volume. As the two properties are mutually exclusive in a single carbonate solvent, the requirement is satisfied by mixing a high ionic conductivity solvent with a low viscosity solvent.

Electrolyte degradation mechanisms include hydrolysis, and thermal decomposition.

HYDROLYSIS

Water is a major concern in LIBs. At concentrations as low as 10 ppm, water begins catalyzing a host of degradation products that can affect the electrolyte, anode and cathode.

Under typical conditions the electrolyte LiPF_6 provides an ionic medium enabling Li^+ to shuttle between the electrodes during intercalation and de-intercalation. However LiPF_6 also participates in an equilibrium reaction with LiF and PF_5 .

Under typical conditions, the equilibrium lies far to the left. However in the presence of water, the equilibrium reaction starts shifting to the right to form LiF , an insoluble electronically insulating product. LiF forms on the surface of the anode resulting in an increase in SEI film thickness. As the SEI film thickens, it gives rise to an increase in impedance that can ultimately lead to capacity fade.

The hydrolysis of LiPF_6 also yields PF_5 , a strong Lewis acid that reacts with electron rich species, such as water. Phosphorus pentafluoride reacts with water to form hydrofluoric acid and phosphorus oxyfluoride. Phosphorus oxyfluoride can in turn react with a second equivalent of water to form an additional quantity of HF and the byproduct difluorohydroxy phosphoric acid.

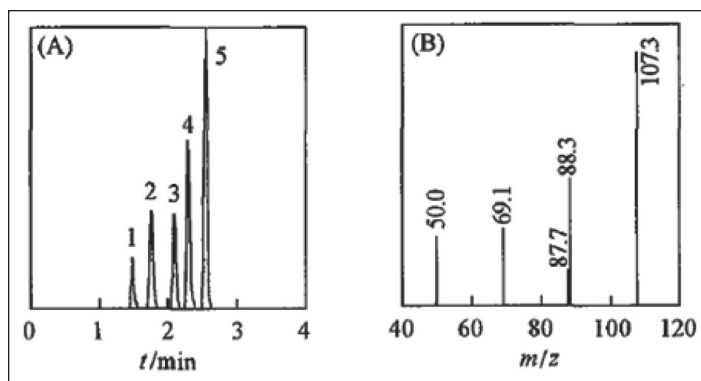


Figure 4: Shown is the characterization of PF_5 gas (a precursor in the preparation of LiPF_6 electrolyte) by gas chromatography and mass spectrometry. The mass spectrum of peak 5 in caption A was identified as PF_5 by a reference NIST mass spectrum. The PF_5 m/z fragmentation ions that correspond to PF_4^+ , PF_3^+ , PF_2^+ and PF^+ appear in caption B. Analysis was performed using a Thermo Scientific Finnigan Trace DSQ GC-MS (or equivalent Thermo Scientific ISQ LT GC-MS).

The presence of HF converts the rigid SEI film into a fragile one. In the case of the SEI layer that forms on the cathode, the carbonate solvent can diffuse onto the surface of cathode oxide over time causing the release of heat and a possible thermal runaway condition.

In addition to liquid electrolytes, solid electrolytes are also in commercial use. Solid polymer electrolytes (SPE) offer low environmental impact, aren't as toxic as their liquid counterparts, are relatively low cost and remove any risk of flammable electrolyte and carbonate mixtures leaking out of the battery.

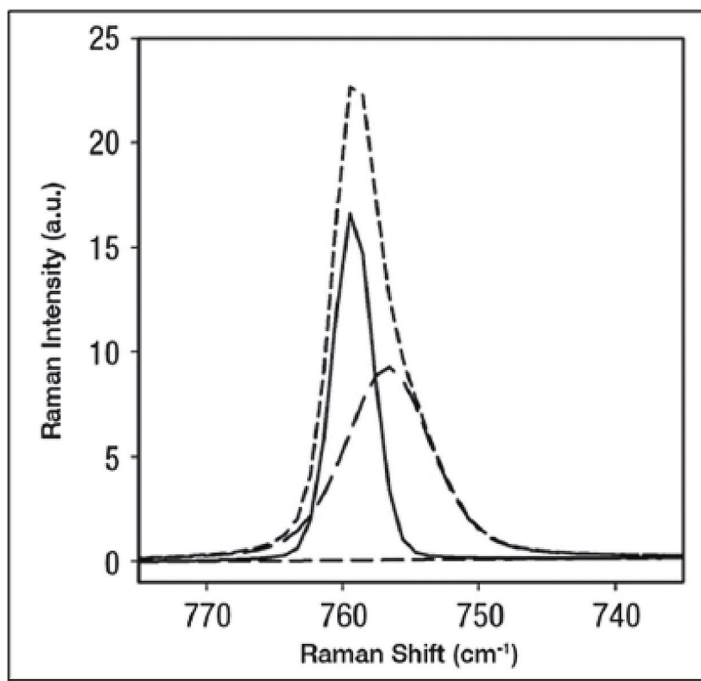


Figure 5: Shown is the deconvolution of the CF_3 band of the Raman spectra into bands for the free ions and ion pairs of lithium triflate in $\text{PEO-LiCF}_3\text{SO}_3$, where PEO is a poly(ethylene oxide)-based solid polymer electrolyte. Analysis was performed using a Thermo Scientific Nicolet XR Raman Spectrometer.

However there are two inherent disadvantages; low ionic conductivity and low lithium transference. The low ionic conductivity results from poor salt dissociation. SPE is reported to dissociate as ion pairs. The low lithium transference results from stronger interaction of the polymer matrix with lithium cation as compared to the anion.

Studies show immobilizing the anion with additives produces a relative increase in lithium transference and ionic conductivity. Results from the analysis of an anion receptor, lithium triflate (LiCF_3SO_3) attached to an SPE composite by Raman spectroscopy show the distribution of electrolyte components in the polymer in Figure 5.

THERMAL DEGRADATION OF THE ELECTROLYTE

Carbonate-based LIB, while effective at forming efficient SEI and providing power requirements, suffer from thermal decomposition. Decomposition of electrolyte salts and interactions between the salts and solvent start at as low as 70C. Significant decomposition occurs at higher temperatures. At 85C transesterification products, such as dimethyl-2,5-dioxahexane carboxylate (DMDOHC) are formed from EC reacting with DMC.

CATHODE

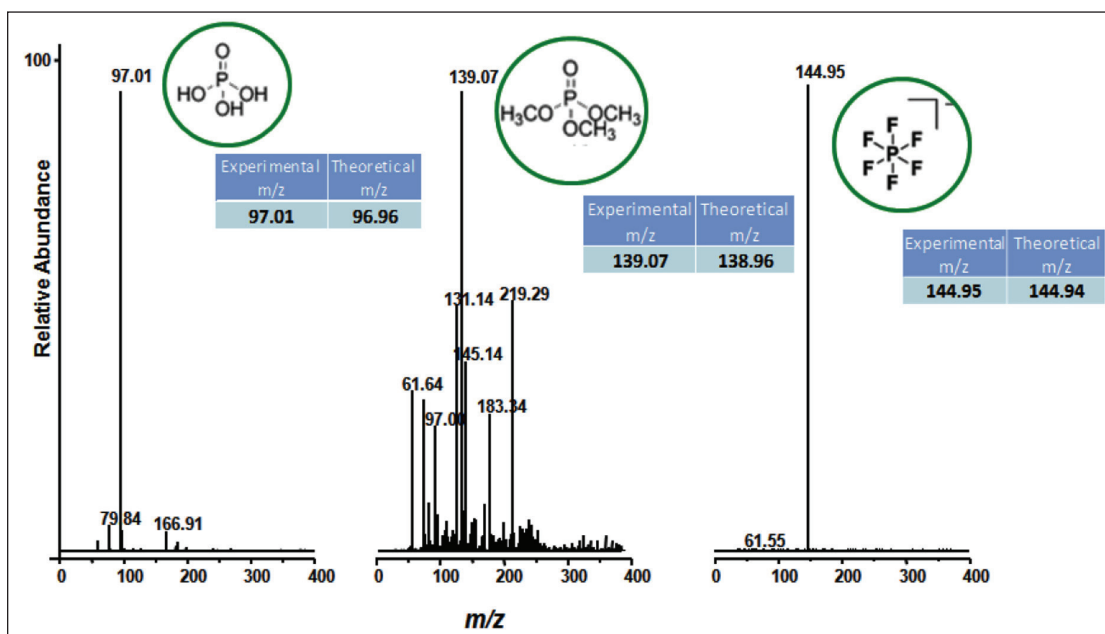


Figure 6: Shown are results of the aqueous extract from an anode following cycle aging by ion chromatography and single quadropole mass spectrometer. The three products, hexafluorophosphate, phosphoric acid, and phosphoric acid trimethyl ester were analyzed using an IonPac AS 11 Anion-Exchange Column (2 mm I.D.) using 5 to 50 mM with its matching guard and suppressed conductivity. Analysis was performed using a Thermo Scientific MSQ Plus Mass Spectrometer.

Two of the most commonly studied cathode materials are lithium cobalt oxide (LiCoO_2) and lithium manganese oxide (LiMn_2O_4). Lithium cobalt oxide is the most widely

used cathode material. LiMnO_4 is considered a suitable alternative because of its low cost and ease of preparation, but its relatively poor cycling and storage capabilities has prevented it from being considered as a commercial replacement.

Cathode degradation mechanisms include manganese dissolution, chemical oxidation of the electrolyte by the cathode and structural disorder of the cathode.

MANGANESE DISSOLUTION

The dissolution of manganese into the electrolyte is reported to occur as a result of hydrofluoric catalyzing the loss of metallic manganese through disproportionation of trivalent manganese, shown below;



Material loss of the spinel results in capacity fade. Thermal effects can also result in decrease in LIB performance. Temperatures as low as 50C initiate the deposition of the Mn^{2+} on the anode as metallic manganese—similar to lithium and copper plating), leading to an increase in impedance, a loss in battery capacity and potential thermal runaway. Cycling the LIB over the theoretical max and min voltage plateaus also results in severe capacity fade due to destruction of the crystal lattice from Jahn-Teller distortion,

which occurs when Mn^{4+} is reduced to Mn^{3+} during discharge.

ELECTROLYTE OXIDATION BY THE CATHODE

Storage of an over-charged LIB (greater than 3.6 V) initiates electrolyte oxidation by the cathode and induces formation of an SEI film on the cathode. As observed with the anode, excessive formation of the SEI on the cathode serves as an insulator resulting in capacity fade and can also lead to uneven current distribution.

Storage of an undercharged LIB (less than 2 V) results in the slow degradation of LiCoO_2 and LiMn_2O_4 cathodes, the release of oxygen and irreversible capacity loss.

CONCLUSION

The demand in Li-ion batteries for use in portable electronics, medical devices, industrial equipment and automobiles is projected to continue growing over the next several years. With the growing demand comes the expectation of improvements in battery performance and safety. These expected improvements include higher power output, mini-

	Measured Concentration	RSD (%)	Spec.
Major Element (% w/w)			
Al	1.4	1.8	1.1 – 1.5
Li	4.2	2.9	3.9 – 4.5
Mn	56	2.7	54 - 59
Impurity (mg/kg)			
Ca	171	1.0	<200
Cu	<1	-	<20
Fe	24	2.5	<70
K	388	3.5	<500
Mg	21	4.1	<100
Na	2340	2.5	<3000
Ni	<5	-	<100
S	2773	3.0	<5000
Si	45	2.2	<400
Zn	<2	-	<20

Figure 7: Shown are results from the determination of major elements and impurities in a cathode material using inductively coupled plasma optical emission spectroscopy (ICP-OES). All major elements (manganese, lithium and aluminum) fell within specifications. All impurities were also below the specification limits required in this sample type. Analysis was performed on a Thermo Scientific iCAP 7600 ICP-OES.

mal capacity loss and extended battery life over extremes in temperature, charging and storage conditions.

One of the most significant improvements to the performance of Li-ion batteries, the SEI layer, is also one of its key weaknesses. The SEI layer is composed of electrolyte—carbonate reduction products that serve both as an ionic conductor and electronic insulator between the electrolyte and the electrode, but as results show, it is prone to thermal degradation. Formation of the thin layer on the anode and cathode has been the subject of great interest as it determines many performance parameters of the battery. But as the layer is formed after the battery has been assembled it makes it difficult to analyze *in situ*, making *ex-situ* analysis the only practical alternative. As a result, there are still many unanswered questions regarding SEI formation, composition and decomposition.

Advances in battery technology will be required to meet

the growing demand for Li-ion batteries. To build high-performance batteries, a variety of instruments and technologies will be needed to effectively understand battery degradation processes for each batter component individually and how they interact together as a system.

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