

How Electrolytes Influence Battery Safety

by E. Peter Roth and Christopher J. Orendorff

Lithium batteries use organic electrolytes because of the wide operating voltage. For lithium ion rechargeable batteries, these electrolytes are almost universally based on combinations of linear and cyclic alkyl carbonates. These electrolytes make possible the use of Li as the anodic active component and results in the high power and energy densities characteristic of the Li-ion chemistries. However, these organic electrolytes have high volatility and flammability that pose a serious safety issue for their use in the consumer and transportation markets. If exposed to extreme conditions of elevated voltage and temperature, these electrolytes can react with the active electrode materials to release significant heat and gas.

The formulation of electrolytes is developed to meet performance criteria such as conductivity, temperature range (high and low), and voltage range stability. There are many studies that correlate relationship between performance criteria to selection of solvent species, solvent ratios, electrolyte salts, and additives. The choice of electrolyte can also have a significant impact on the safety, thermal stability, and abuse tolerance of the cell. Some materials that have superior performance properties, such as LiAsF₆, cannot be used because of high toxicity.¹ Some solvent species, such as propylene carbonate (PC), are limited in concentration because they cause disruption of the anode graphite grains. However, there are few studies that correlate the influence of electrolyte on the cell response during an abuse event.

For example, gas generation in Li-ion cells under abuse conditions has an effect on safety because gas production, if generated at sufficient pressure, will vent flammable solvent vapor into the surrounding environment. The resulting fuel-air mixture can be quite explosive and only requires an ignition source to ignite the vapors. The heat generation of the reactive cell components is often sufficient to self-ignite this mixture as shown in Fig. 1 for a Li-ion cell undergoing runaway and venting into an air-containing enclosure. In higher voltage modules and packs, there are often sparks that are generated during an abuse condition which can ignite these vapors.

Accelerating Rate Calorimetry (ARC) has been used as a sensitive analytical tool to determine the self-generated heat and gas evolution from cells and electrolytes from room temperature up through a full thermal runaway (up to 450°C). Special high-pressure fixtures are required to contain the vented gases and allow adiabatic temperature control of 18650 size cells.² Figure 2a shows an ARC thermal runaway profile of an 18650 cell showing this heat and gas volume

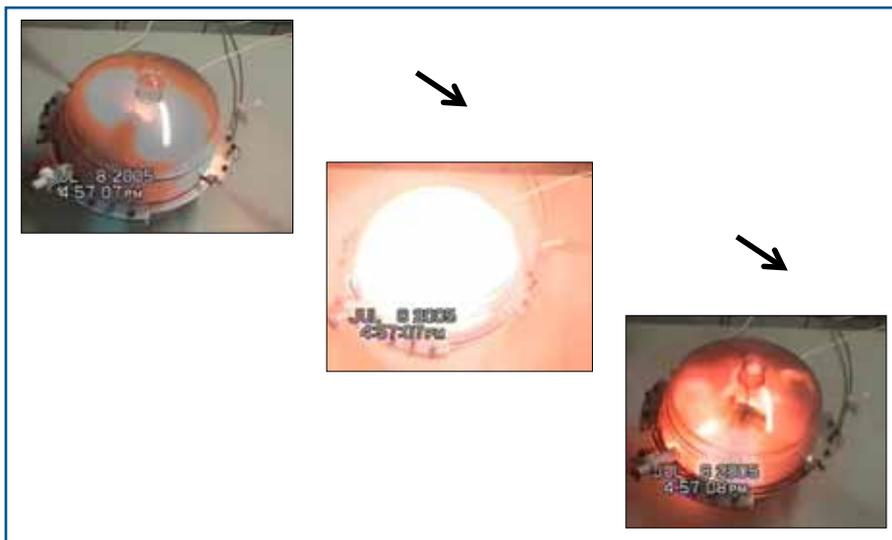
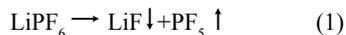


FIG. 1. Three sequential images of an ignition of vent gases in air for a Li-ion cell during thermal runaway.

generation over time while Fig. 2b shows the self-heating rate and gas generation as a function of temperature. Thermal runaway begins at 240°C. The alkyl carbonate-based electrolytes, which make up almost all of the Li-ion electrolytes, have been shown to breakdown at temperatures starting around 150–200°C. Venting may occur at lower temperatures strictly due to increased vapor pressure (as low as 130°C), but high rate gas generation usually accompanies (or immediately follows) the thermal runaway peak (commonly 250°C–350°C). It is the high-rate gas evolution during the thermal runaway peak that is of most concern for safety.

Gas generation results from the decomposition of the organic solvents which has been shown to result from catalytic reaction of the solvents with the electrolyte salt and its decomposition products. LiPF₆ is known to decompose as shown:



PF₅ is a strong Lewis acid which can result in ring opening of the EC cyclic carbonate and also attack the carbonyl oxygen atoms of the linear carbonates because of the higher electron density in those bonds. Reaction of the PF₅ with trace water in the electrolyte produces HF which can also lead to further solvent decomposition and gas generation. Solvent decomposition produces a number of different gas species including CO₂, CH₄, C₂H₄, C₂H₅F, and other subsequent reaction products. The details of electrolyte decomposition can be complex due to the possible variations in salt and electrolyte mixtures that are used in Li ion cells and reactions with the electrode materials.

The effect of LiPF₆ salt on the gas generation was investigated using ARC measurements on various electrolyte mixtures. As shown in Fig. 3a, electrolyte solvents consisting of EC/EMC (3:7) were prepared with increasing molarities of the LiPF₆ salt. The moles of generated gas (at STP) were calculated from the pressure profiles during the ARC run and normalized to the number of moles of the solvent (EC+EMC). The effect of the salt became clearly noticeable at 0.6 M, showing a sudden increase in gas generation at 200°C. Increasing salt molarity to 1.2 M lowered the onset decomposition temperature to 160°C and with full decomposition by 200°C. Increasing the salt molarity to 1.8 M did not result in any further change in the gas generation profile. This explains why the temperature of 160°C has been often associated with onset of gas generation in a wide variety of Li ion cells, resulting in venting and onset of cell disassembly.

Identification of the gas species produced during these reactions was obtained from GC/MS. CO₂ was responsible for the largest contribution to the gas volume, as shown in Fig. 3b, with other minor species including H₂, CH₄, C₂H₄, C₂H₆, and C₂H₅F. Increasing salt molarity did not significantly affect the ratio of gas species generated (although there was increasing gas volume).

The significance of these results is that the decomposition vent gases from Li ion cells undergoing thermal runaway are not inherently combustible, consisting largely of CO₂, which of itself would reduce

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flammability of the gas mixture. The main effect on safety is that the large and sudden generation of gas causes the cell to vent and release gas and the flammable electrolyte solvent vapor, possibly generating an explosive fuel-air mixture. Ignition of these vapors can then result in damage and rupture of the other cells as well as ignition of other materials in the battery. In the worst case outcome, this can result in a cascading failure of cells in the battery leading to a much larger release of energy.

Gas generation will result whenever the cell reaches the solvent decomposition temperature, whether from internal or external sources. Even the safest cathode and anode chemistries will not prevent this release of flammable vapors. The volume of gas released from a cell in full thermal runaway is more than can be contained by any standard cell fixture, either pouch or laser-welded can. Many cell designs purposely allow gases to be released through a designed vent. Measurements of the gas released from cells during thermal runaway using several different cathode materials have shown that the volumes of gas released at the end of the thermal runaway peak (typically 350°C) were all nearly equal (normalizing for cell capacities). Figure 4 shows that the gas generated from cell thermal runaway alone is about 1200 ml/Ah for five different cathode chemistries. Thus, the volume of electrolyte used in cell construction is a main factor in predicting gas generation volume and vent response.

The energy released by electrolyte combustion is several times larger than the electrical energy stored in a battery.⁹ However, the amount of oxygen released by even some of the most reactive cathodes is not nearly sufficient to cause complete combustion of the cell electrolyte. For example, $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$ only gives enough oxygen to react with 5-15% of the electrolyte. Thus, the largest source of oxidizable material is the vented solvents, which, if burned in air, have an energy release several times that of the cell-contained reaction enthalpies of the electrode materials.

Electrolyte Flammability

Flammability of the vented electrolyte is a significant unresolved safety issue for Li-ion batteries. The flammability of the mixture of vented solvents, decomposition gases, and air is a complicated, dynamic function of temperature, pressure, and solvent properties such as vapor pressure, heat of vaporization, and heat of combustion.^{10,11} The flammability of this mixture depends on the ratio of fuel and air, which can vary significantly around the venting cell, especially with turbulent mixing that can occur from a rapidly venting cell. Rapid cell venting can displace air immediately around the cell, which leads to an oxygen starved

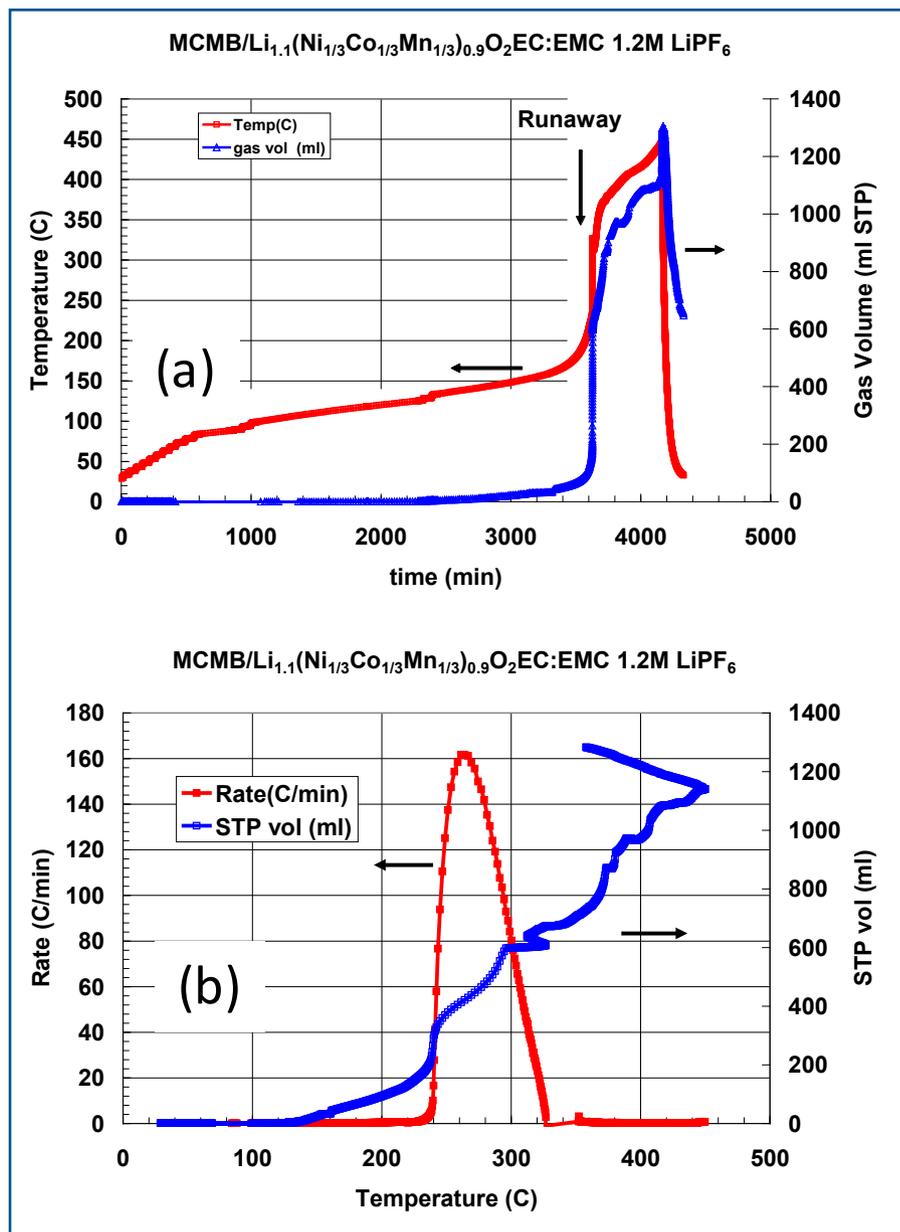


FIG. 2. (a) ARC thermal runaway profile as a function of time for an 18650 cell showing heat and gas generation; (b) ARC thermal runaway profile showing self-heating rate and gas generation as a function of temperature.

mixture that will not ignite. A highly diluted mixture of fuel to air may occur sufficiently far away from the venting cell, and this lean solvent-air mixture also will not ignite. However, there will be regions around the cell where the fuel-air mixture is in the flammability range and will combust if an ignition source is present.

Mitigation of this flammability issue can be achieved by either the use of flame retardant additives in the standard electrolytes or by the use of an inherently non-flammable electrolyte.

Flame Retardant Additives

Many flame retardant additives were originally developed for solid material flammability reduction and have limited

applicability to liquid electrolyte cells. Two mechanisms have been suggested to explain the effect of a flame retardant additive:¹²

- a physical char-forming process, which builds-up an isolating layer between the condensed and gas phases to retard the combustion process, and
- chemical radical-scavenging process, which terminates the radical chain reactions responsible for the combustion reaction in the gas phase.

For organic liquid electrolyte cells, the main flammability mechanism of concern is the radical chain reaction in the vapor. There are four main categories of flame retardant additives that have been reported in the literature: phosphates, phosphazenes, phosphides, and ethers. Two additives

that have been extensively evaluated are phosphorous-containing and halogen-containing compounds. In the vapor phase, the common mechanism is that phosphorous or fluorine radicals, which are provided by the decomposition of the additive, react with hydrogen radicals that are part of the flame's chain-reaction mechanism.¹³ Numerous flame retardant additives have been tested in most of the standard Li-ion electrolytes with mixed results.¹³⁻²⁰

Often, the amount of additive required to achieve non-flammability significantly reduces cell performance. Furthermore, some of the additives are not stable with the active electrode materials, especially against reduction at the anode. Use of flame retardant additives then requires additional additives to stabilize the anode. The long-term effect of these additives on the cell lifetime and performance is not known.

One of the major difficulties in evaluating the effectiveness of the flame retardant is a meaningful test that simulates the environment of a venting Li-ion cell. Most tests are based on open flame or burning wick type configurations. These tests are useful for evaluating the relative performance of different additives but do not adequately recreate the conditions of a vented cell that produces solvent vapor at elevated temperature and pressure. Flammability needs to be determined with full cells under controlled thermal conditions with multiple ignition sources to test for different fuel/air ratios.¹⁰ Several claimed non-flammable electrolytes using fire retardant additives have been shown to result in burning gas mixtures from real-world venting cells.²¹

Non-flammable Electrolytes

Several electrolytes have been developed and evaluated that may significantly reduce flammability that are not part of the alkyl carbonate family. These materials must also not significantly degrade the performance of the cells over their operating ranges. Often, mixtures of these electrolytes with the standard alkyl carbonates must be used to maintain cell performance.

One group of materials that have been investigated are Ionic Liquids (ILs).^{22,23} ILs are non-volatile, non-flammable, highly conductive, environmentally compatible, and can safely operate in a wide temperature range. This unique combination of favorable properties makes ILs very appealing materials as stable and safe electrolyte in lithium batteries.

Batteries filled with such a type of electrolytes do not contain any volatile components and therefore, they are not flammable. Room temperature ionic liquids (RTILs) are characterized by negligible vapor pressure, which makes them non-flammable. In addition, they show a broad electrochemical stability window, generally >4 V, which is necessary for the application in lithium-ion batteries with high-energy cathodes. Continued development is required for these electrolytes to meet performance and cost requirements but the improvement in safety may justify some non-optimal cell properties.

Hydrofluoroethers (HFEs) are another class of materials that have been proposed as non-flammable electrolyte solvents for lithium-ion cells. HFEs are attractive candidates for lithium-ion electrolyte co-solvents because they have either very high or no flash-point, are aprotic, and are low viscosity solvents. Linear HFEs such as methylperfluorobutylether (MFE) and ethylperfluorobutylether (EFE) were first proposed as co-solvents for lithium-ion cells by Arai *et al.* in 2002.^{24,25} However, the linear HFEs showed a significant negative impact on electrolyte conductivity and cell performance.^{24,25} More recently, Naoi *et al.*

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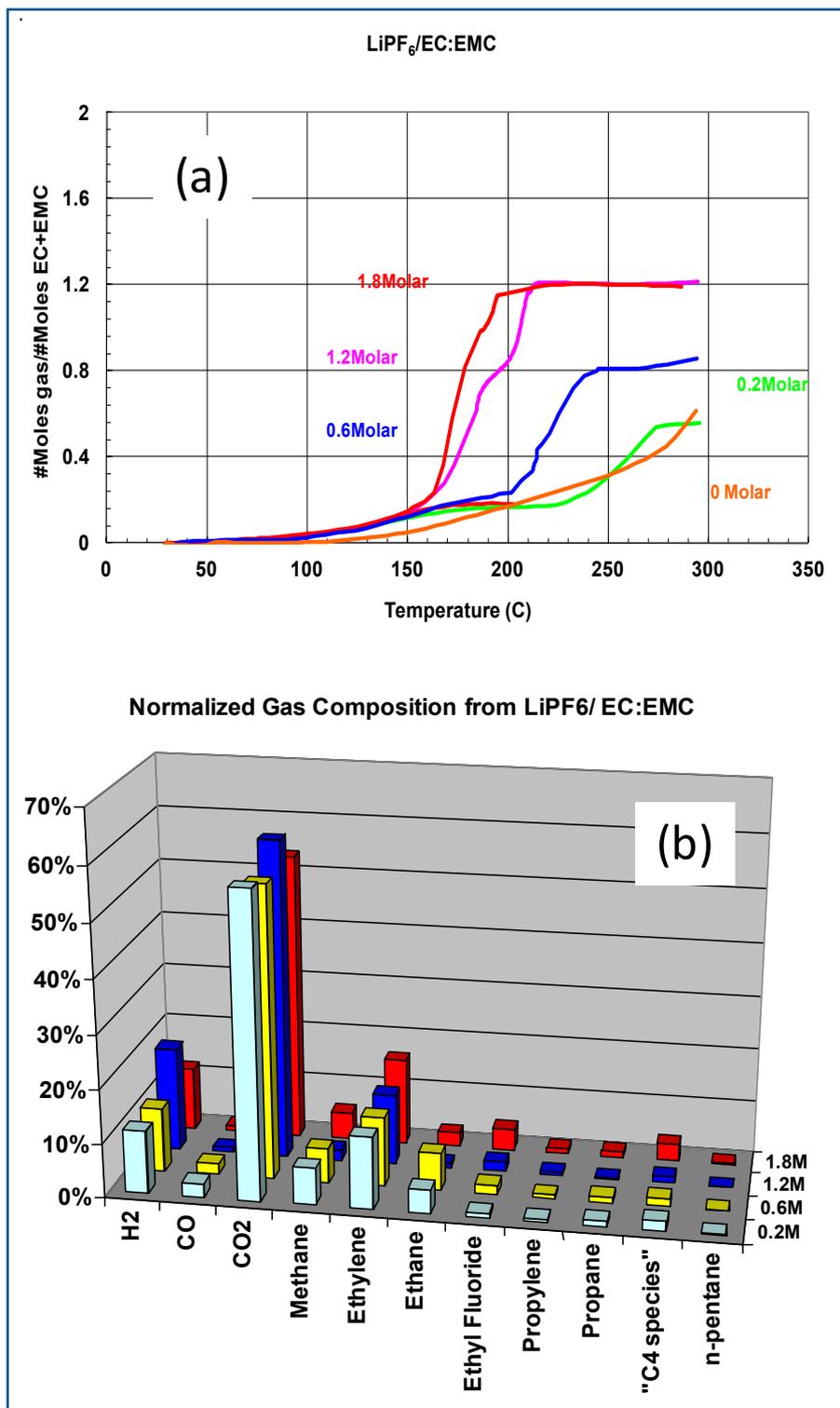


FIG. 3. (a) Gas generation profiles for EC/EMC electrolyte showing the effect of increasing salt molarity; (b) gas species from ARC runs of EC/EMC electrolyte with increasing LiPF₆.

reported the use of branched HFEs as a means to maintaining the non-flammable properties of the HFE in the carbonate solvent mixtures without as large of a trade-off in conductivity or performance.^{26,27} This work is focused on the characterization of electrolyte mixtures of carbonate solvents and two branched HFEs: 2-trifluoromethyl-3-methoxyperfluoropentane (TMMP) and 2-trifluoro-2-fluoro-3-difluoropropoxy-3-difluoro-4-fluoro-5-trifluoropentane (TPTP). Results from this work show good electrochemical performance with the HFE-containing electrolytes in 2032 coin cells but do not describe the ignition or flammability behavior of these HFE-containing electrolyte in great detail.^{26,27}

Nagasubramanian *et al.* continued the characterization of HFE-containing electrolytes in 18650 cells and flammability measurements of the branched HFE-based electrolytes with sulfonimide salts, lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) and lithium bis(pentafluoroethylsulfonyl)imide (BETI) salts.²⁸ Results show good voltage stability (> 5 V vs. Li/Li⁺) of the HFE-containing electrolyte (1M LiBETI in EC:DEC:TPTP (5:45:50)) and conductivities between 1-2 mS/cm at 25°C. Performance evaluation shows a ~10% decrease in discharge capacity in 18650 cells at a C/5 discharge rate for cells with NMC cathode and 1M LiBETI in EC:DEC:TPTP compared to 1.2 M LiPF₆ in EC/EMC (3:7). Figure 5 shows gas decomposition products of the HFE-containing electrolyte

compared to the carbonate electrolytes. Gas decomposition products of the HFE-containing electrolyte were compared to the carbonate electrolytes and results show a ~40 to 60% reduction in total gas decomposition product generated using the HFE electrolyte. Moreover, the onset temperature of gas generation is increased by using the sulfonimide salts compared to PF₆⁻, suggesting an improvement in the stability of the cell at elevated temperature.²⁸

This work also developed techniques to evaluate the flammability of these HFE electrolytes under conditions that mimic a venting cell using a spark ignition source.²⁸ Results from these experiments show no ignition of any HFE-containing electrolytes (at 50% HFE) and ignition of the EC/EMC (3:7) and EC/DEC (5:95) electrolytes measured. While the mechanism is not described in this report, it is likely due to radical scavenging process where the H[•] radicals produced react with the HFE to produce HF and inhibits flame propagation.¹⁰ These studies on a limited number of measurements for HFEs demonstrate the potential for formulating a truly non-flammable electrolyte for lithium ion cells.

Summary

Electrolytes have been shown to be a major source of poor safety response of Li ion cells. The physical hazards associated with conventional LiPF₆ and carbonate-based electrolytes are well documented and include high volume gas decomposition products at elevated temperature, large combustion enthalpy and flammability of solvent vapor. However, the physical and health hazards of the decompositions products can be often overlooked. Electrolyte additives proposed to reduce gas generation and mitigate flammability have not gained much traction, in general, because of the trade-off in cell performance. To maintain cell performance, quantities of additives are generally introduced in fractions <10% which significantly decreases the efficacy of the additive. New additives need to be developed in order to strike the balance between improving abuse tolerance and maintaining performance. Perhaps a more direct strategy is to develop a completely new class of electrolytes for Li ion based on thermally stable lithium salts and non-flammable, high vapor pressure solvents, albeit a challenge. Salts including the lithium sulfonimides and solvent systems including ionic liquids and fluorinated ethers offer some promise as new classes of Li ion electrolyte beyond convention with improved abuse tolerance.

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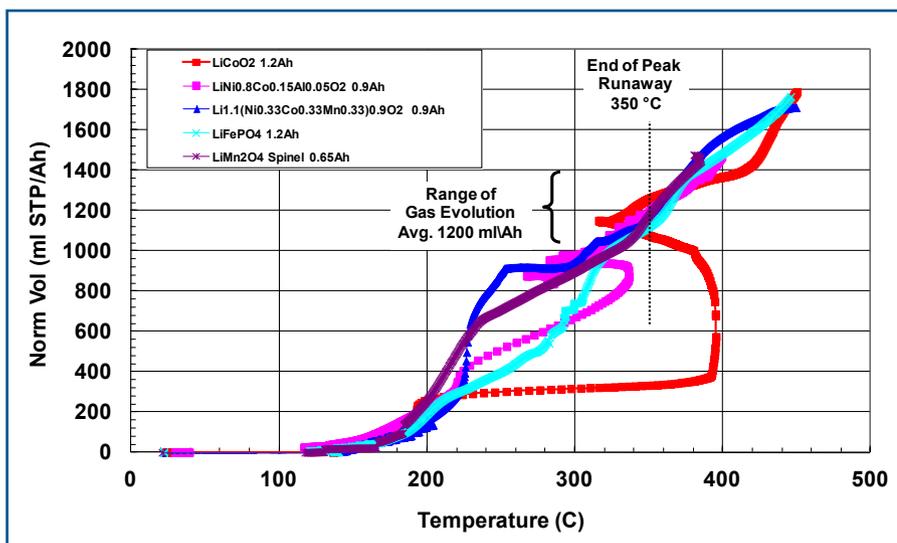


Fig. 4. Normalized ARC gas generation profiles from 18650 cells of several cathode chemistries showing equal gas volumes per Ah generated at end of thermal runaway.

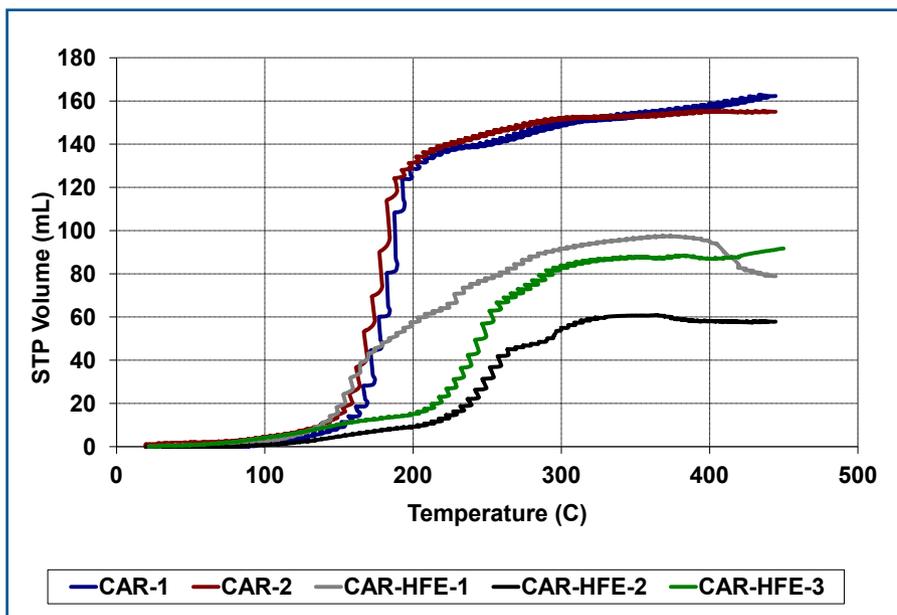


Fig. 5. STP gas volume (mL) of carbonate electrolytes 1.2 M LiPF₆ in EC/EMC (3:7) (CAR-1), 1.0 M LiPF₆ in EC/EMC (3:7) (CAR-2), and HFE-containing electrolytes 1.0 M LiPF₆ in EC/DEC/TPTP (5:45:50) (CAR-HFE-1), 1.0 M LiBETI in EC/DEC/TPTP (5:45:50) (CAR-HFE-2), and 1.0 M LiTFSI in EC/DEC/TPTP (5:45:50) (CAR-HFE-3). (From Ref. 28). Reprinted with permission from Elsevier.

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