



# Hydrofluoroether electrolytes for lithium-ion batteries: Reduced gas decomposition and nonflammable

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## ABSTRACT

The optimum combination of high energy density at the desired power sets lithium-ion battery technology apart from the other well known secondary battery chemistries. However, this is besieged by thermal instability of the electrolyte. This “Achilles heel” still remains a significant safety issue and unless this propensity is improved the promise of widespread adoption of Li-ion batteries for Transportation application may not be realized. With this in mind we launched a systematic study to evaluate fluoro solvents that are known to be nonflammable, for thermal and electrochemical performances. We investigated hydro-fluoro-ethers (HFE) (1) 2-trifluoromethyl-3-methoxyperfluoropentane {TMMP} and (2) 2-trifluoro-2-fluoro-3-difluoropropoxy-3-difluoro-4-fluoro-5-trifluoropentane {TTPP} in Sandia-built cells. Thermal properties under near abuse conditions that exist in thermal runaway environment and the electrochemical characteristics for these electrolytes were measured. In the thermal ramp (TR) measurement, EC:DEC:TTPP-1 M LiBETI (or TFSI or LiPF<sub>6</sub>) electrolytes exhibited no ignition/fire. Similar behavior was observed for the EC:DEC:TMMP-1 M LiBETI. Further, in ARC studies the HFE electrolytes generated less gas by 50% compared to the EC:EMC-1.2 M LiPF<sub>6</sub> {CAR-1} electrolyte. Although in all cases the HFEs generated less gas, the onset of gas generation appears to depend on the salt. For the LiBETI and TFSI containing HFEs the onset is pushed out by ~80 °C and for the LiPF<sub>6</sub> the onset is comparable to that of the CAR-1. The solution ionic conductivity of these HFE electrolytes was lower (4–5 times) than that of the CAR-1 electrolyte however, the electrochemical performance was comparable. For example, full cells in 2032 type coin cells containing LiMn<sub>0.33</sub>Ni<sub>0.33</sub>Co<sub>0.33</sub>O<sub>2</sub> cathode and carbon anode showed around 5 mA h capacity and the computed specific capacity was ~154 mA h for all the electrolytes. In half-cells against lithium the cathode and anode gave specific capacity on the order of 170 mA h and 340 mA h respectively. These electrolytes when tested in 18,650 cells containing the above cathode and anode also showed comparable capacity. Further, the voltage stability window was not compromised by the HFEs. ARC measurements on 18,650 full cells showed less gas generation for the HFE electrolytes compared to CAR-1 electrolyte.

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## 1. Introduction

Early consumer electronics products with lithium-ion batteries suffered from publicized safety incidents including those resulting in battery fires. While infrequent, the flammability issues associated with lithium-ion battery electrolytes are significant concerns that do not exist for other, aqueous-based rechargeable energy storage systems (NiMH, NiCd, lead-acid). The scale and potential consequence of lithium-ion cell fires will magnify as these technologies are deployed in larger scale systems (>1 kWh) for the transportation (hybrid and electric vehicles) and stationary utility storage markets.

In addition to flammability, broader issues related to thermal stability of lithium-ion electrolytes including combustion energy and catalytic decomposition to gas byproducts can also impact performance, lifetime, safety, and ultimately cost of these systems and may prevent their widespread adoption for high energy systems. Over the years the burgeoning research and development efforts have led to the identification of the loci of the thermal stability issues in the cells and continued development of advanced materials with potential to mitigate the thermal instability. However, the thermal instability problems remain as elusive as ever. A number of approaches, including adding fire retardants [1,2] or fluoro compounds [3–6] to the electrolyte to mitigate or eliminate the pervasive susceptibility to fire, have been investigated. These additives improved the thermal stability of the cells (only marginally) but not enough for use in mobile applications. Recent preliminary investigations indicate that the new HFEs have the potential as non-flammable additives [7,8]. Naoi et al. have recently shown that the

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**Table 1**  
Electrolytes studied in this work.

Electrolyte	Denoted as
1. EC:EMC(3:7 wt%)-1.2 M LiPF <sub>6</sub>	<sup>a</sup> CAR-1 or standard
2. EC:EMC(3:7 wt%)-1.0 M LiPF <sub>6</sub>	CAR-2
3. EC:DEC(5:95 wt%)-1.0 M LiPF <sub>6</sub>	CAR-3
4. EC:DEC:TPTP(5:45:50 vol.%) -1 M LiPF <sub>6</sub>	CAR-HFE-1
5. EC:DEC:TPTP(5:45:50 vol.%) -1 M LiBETI	CAR-HFE-2
6. EC:DEC:TPTP(5:45:50 vol.%) -1 M LiTFSI	CAR-HRE-3
7. EC:DEC:TMMP(5:45:50 vol.%) -1 M LiBETI	CAR-HFE-4

<sup>a</sup> CAR denotes carbonate.

TMMP and TPTP HFEs are nonflammable while at the same time exhibiting a stable electrochemical behavior.

## 2. Experimental

These HFEs are not continuously miscible with the common battery non-aqueous electrolytes—in other words they have miscibility gaps. Naoi et al. have mapped out the miscibility regions in the form of a phase diagram and for our studies we have used only those compositions where the solvents form a homogeneous blend.

### 2.1. Electrolytes

The chemicals TMMP and TPTP were obtained from 3 M, St. Paul, MN, US. Other battery grade chemicals such as Ethylene Carbonate (EC), Ethyl Methyl Carbonate (EMC), Diethyl Carbonate (DEC) were purchased from Kishida Chemical Co. Ltd., Japan. Salts LiPF<sub>6</sub>, and LiBETI, LiTFSI were purchased respectively from Hoshimoto, Japan and 3 M, US. All the chemicals were used as received except that the solvents were tested for water content using a Karl Fischer Moisture Analyzer. The water content was found to be on the order of 5 ppm. A number of different electrolyte formulations were investigated in this study. These are given below in Table 1.

These electrolytes were prepared in an Argon filled glove box. Conductivity of the electrolytes were measured with a Z-plot software on a Solatron SI-1287 potentiostat equipped with a Solatron 1260 Frequency analyzer and controlled with a HP Z600 computer.

### 2.2. Conductivity measurement

For electrolyte conductivity measurements a commercial 2-electrode cell (platinized Pt electrodes with a cell constant  $k=1$ ) which is fitted into a fixture that allowed measurement of conductivity at different temperatures was used. Before measuring conductivity of the electrolytes the conductivity of a KCl standard solution was measured to verify if the cell constant is same as reported by the vendor. The measured conductivity of the KCl standard at 25 °C was identical to that certified by the National Institute of Standard and Technology for that concentration of the KCl solution.

### 2.3. Electrode materials

The cathode material LMNC (LiMn<sub>0.33</sub>Ni<sub>0.33</sub>Co<sub>0.33</sub>O<sub>2</sub>) was purchased from 3 M, USA and the carbon was obtained from Conoco Phillips, USA. These materials were baked out at 110 °C overnight in vacuum. Using our in-house capability we coated our own electrodes. A description of the in-house capability, typical electrode formulations and preparation were published elsewhere [9]. In this work we prepared Conoco Phillips (CP) carbon anode and LMNC cathode. The compositions of the anode and cathode are:

Anode: PVDF:SAB carbon:CP (6:2:92 wt%) and  
Cathode: PVDF:SAB carbon:cathode (5:5:90 wt%).

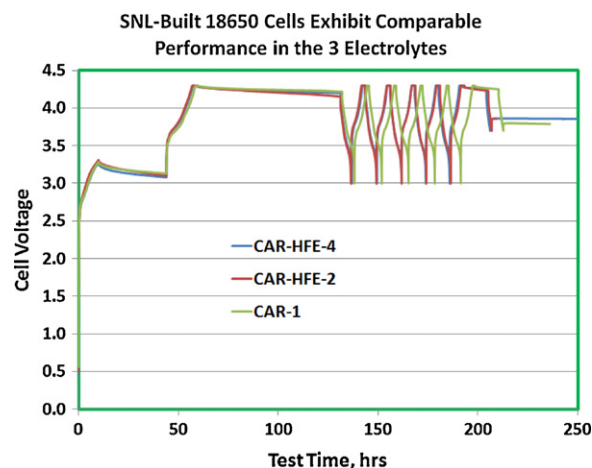


Fig. 1. Cell formation. Voltage vs. time.

### 2.4. Coin cells

Electrodes were punched out from large electrodes for 2032 size coin cell studies. Initially, the anode and the cathode were evaluated for capacity in half cells to check for reproducibility and finally these were evaluated in full cells. The cells were tested in a Maccor tester Model# Series 4000. Typically, the coin cells were charged at a 100  $\mu$ A current to 4.3 V and discharged at a 200  $\mu$ A current to 3 V at temperature. We also fabricated 18,650 cells and tested for performance (see below for details).

### 2.5. Cells

The Li-ion cells are fabricated discharged. Before they can be used they will have to be charged and before that because of the need to form SEI layer on carbon the cells have to undergo “formation”. Fig. 1 shows the formation for three electrolytes containing LMNC cathode and CP anode. The voltage time plots are very nearly equal for the three electrolytes. The cell voltage is raised very slowly to 4.3 V (this is the charge cut-off voltage as determined by the cathode) from the OCV which is  $\sim$ 0.2 V with a rest step in between. Once the charge cut-off voltage is reached the cell is allowed to relax for 72 h before cycling to obtain cell capacity. Fig. 7 (see Section 3) shows discharge capacity as a function of cycle# for the three electrolytes.

### 2.6. Thermal characterization of electrolytes and 18,650 cells

Accelerating rate calorimetry (ARC) was used to characterize the thermal stability of these electrolytes and 18,650 cells containing these electrolyte formulations. In addition, the ARC is equipped to measure total gas pressure from electrolyte vapor pressure and decomposition products (from which volume can be calculated) for electrolyte and cell samples while maintaining a completely adiabatic environment. For electrolyte samples, 0.5 g of electrolyte was placed in a titanium sample bomb in an Argon glove box. The ARC was heated in 5 °C steps from 25 to 400 °C. It is important to note that for these electrolyte samples, the sample size was small enough so that no exotherm was measured for these measurements. However, the intent of these ARC measurements was to determine the onset temperature of gas formation (vapor pressure and decomposition) and total gas volume.

For 18,650 cell measurements, cells at 100% SOC (4.3 V) were placed in stainless steel fixtures designed with a relatively small total volume (<25 mL) that are pressure tight to >3000 psi. These fixtures allow for the retention of the gas generated during the

### Comparison of conductivity at different temperatures for several electrolytes

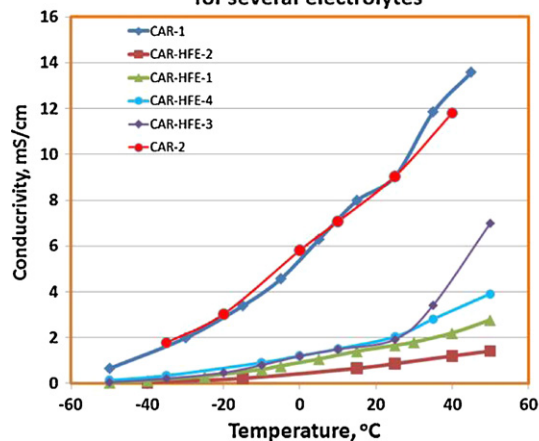


Fig. 2. Conductivity for different electrolytes.

experiment after a cell vent while keeping the system adiabatic. 18,650 cell samples were heated from 25 to 450 °C in 5 °C steps until the algorithm measures an exothermic reaction (referred to as an exotherm) from the sample (threshold  $0.02\text{ }^{\circ}\text{C min}^{-1}$ ) at which point the calorimeter follows the heat generated by the sample up to the end point (set to 450 °C). All ARC measurements were performed using a Columbia Scientific Instruments (CSI) Accelerating Rate Calorimeter.

### 2.7. Flammability measurements

5 mL of electrolyte is sealed in an 18,650 can with complete cell header (includes the rupture disk). The cell is heated until the vapor pressure causes the sealed can to vent. The vented solvent is sprayed directed into a spark ignition source positioned  $\sim 3$  cm above the sample can. The time it takes for the samples to ignite and the total burn time are recorded as measures of solvent flammability.

## 3. Results and discussion

### 3.1. HFE electrolyte conductivity

Fig. 2 shows the plot of conductivity for a number of electrolytes for temperatures in the range  $-50$  to  $50\text{ }^{\circ}\text{C}$ . The conductivity of CAR-1 and CAR-2 electrolytes at room temperature are about 4–5 times higher than that of the HFE containing electrolytes and the conductivities begin to converge with decreasing temperature. While the conductivity of the HFE electrolytes is significantly less than the conventional carbonate electrolytes, it is important to note that the HFE systems have conductivities that are significantly higher than other non-flammable electrolyte systems that have been proposed recently [10,11]. Moreover, it has been shown that these solvent systems have been used in graphite/LiCoO<sub>2</sub> and show little difference is cell capacity and better rate performance (12 C discharge rate with 80% capacity retention) than the carbonate based systems [7,8].

### 3.2. HFE electrolyte voltage stability

The electrochemical stability window was measured between two gold (Au) wires at a  $20\text{ mVs}^{-1}$  scan rate. The voltage was scanned 3 V on each side of the OCV (open circuit voltage) of the cell. Fig. 3 shows the electrochemical stability window for CAR-1 and CAR-HFE-2 electrolytes at two different temperatures.

### Cyclic voltammetric traces for different electrolytes at two temperatures. Au was used as electrodes.

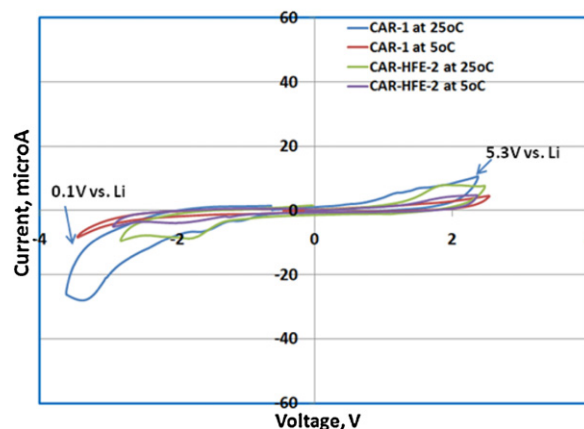


Fig. 3. Electrochemical stability window for CAR-1 and CAR-HFE-2 electrolytes at different temperatures.

After the measurement the voltage of the Au was recorded against Li and the calculated peak voltages against Li are also shown in the figure. Similar electrochemical stability window was obtained for the other electrolytes. The voltage window for this electrolyte is comparable to that observed for the conventional battery electrolytes by others [12,13]. The voltage values shown against Li are only approximate and could be off by less than a 100 mV.

### 3.3. HFE electrolyte gas decomposition

Fig. 4 shows gas volume (calculated at STP) as a function of temperature for 0.5 g samples of electrolytes with and without HFEs. It is important to note that thermal stability referred to in these data are measured by the volume of gas generated during electrolyte thermal decomposition and the onset temperature of gas generation. In a DSC measurement, the thermal stability is often quantified by the total heat flow and the onset temperature for exothermic decomposition. For all electrolytes, the gas volume increases at a relatively low rate ( $0.1\text{ mL }^{\circ}\text{C}^{-1}$ ) from room temperature up to  $140\text{ }^{\circ}\text{C}$ ; due to an increase in the solvent vapor pressure with temperature. CAR-1 and CAR-2 electrolytes (with LiPF<sub>6</sub>) undergo a steep increase in gas volume generation ( $3.5\text{ mL }^{\circ}\text{C}^{-1}$ ) at  $\sim 150\text{ }^{\circ}\text{C}$  and reach a maximum gas volume of 155 mL at  $300\text{ }^{\circ}\text{C}$  for a 0.5 g sample. CAR-HFE-2 and CAR-HFE-3 electrolytes with LiBETI and LiTFSI salts continue the low rate gas volume increase from sol-

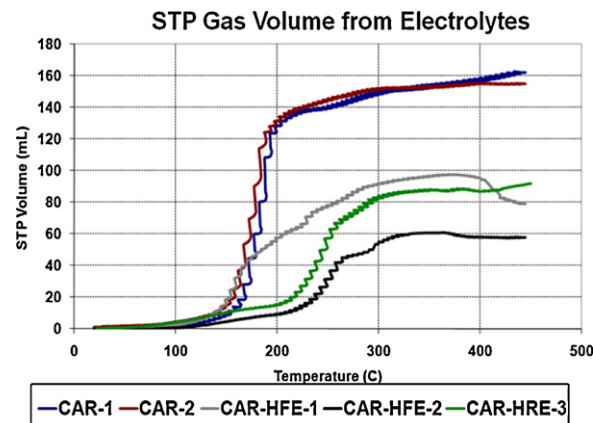


Fig. 4. STP total gas volume as a function of temperature for several electrolytes.

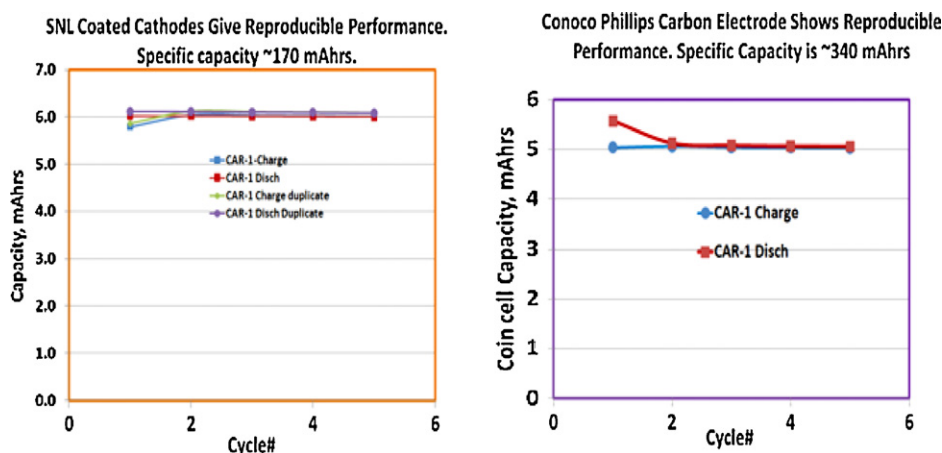


Fig. 5. Capacity vs. cycle# for LMNC cathode and CP anode in coin cell against Li.

vent vapor pressure to 220 °C. The gas volume increases at a rate of 0.75–1.0 mL °C<sup>-1</sup> and reaches a maximum at ~300 °C of between 55 and 80 mL (STP volume); a 40–60% reduction in total gas decomposition product compared to conventional CAR-1 and CAR-2 systems. As a control sample, CAR-HFE-1 electrolyte (LiPF<sub>6</sub> in HFE containing solvent) shows a steep gas generation onset temperature of ~150 °C which is comparable to the LiPF<sub>6</sub>/carbonate systems. However, CAR-HFE-1 degrades to give 90 mL of total gas volume at 300 °C; consistent with the other HFE electrolyte formulations. This suggests that the onset of electrolyte degradation in these samples is governed by the salt stability (LiPF<sub>6</sub> vs. LiBETI or LiTFSI) and the total gas decomposition product is dictated by the amount of carbonate solvent in the electrolyte. Results show the potential for these LiBETI or LiTFSI/HFE electrolytes to be more thermally stable with respect to decomposition to form large gas volumes in lithium-ion cells.

### 3.4. High temperature spray flammability

Traditional experiments to test bulk liquid flammability (wick testing, ignition testing, etc.) do not accurately represent the flammability hazard associated with organic electrolytes in lithium-ion cells when the cells vent or rupture (due to the degradation of cell components, typically at temperatures >100 °C). In this case, vented electrolyte is released from a cell under high pressure (>200 psi) as an aerosol spray. To determine the flammability of this electrolyte aerosol spray, a high temperature spray flammability test was developed that is relevant for lithium-ion systems. As described in Section 2, 5 mL of electrolyte is sealed in an 18,650 cell and heated until the vapor pressure increases, ruptures the burst disk in the 18,650 header and the can vents. The cell vent is directed vertically into a primary ignition source to determine vented solvent flammability. Flammability test results are quantified using several parameters including whether or not the sample ignites, delay time between venting and ignition, and time it takes for the flame to self extinguish (total burn time).

Table 2 summarizes the spray flammability results for five samples of the different electrolyte formulations including CAR-1, CAR-3, CAR-HFE-1, CAR-HFE-2 and CAR-HFE-3. While this is a relatively small data set, it is important to note that the results are binary; the HFE formulations (50% HFE) do not ignite or burn while the all carbonate solvent systems ignite and burn. Among the carbonate systems, the 70% linear carbonate (CAR-1) electrolyte takes longer to ignite and burns for only 6 s, while CAR-3 with 95% linear carbonate ignites <1 s after the vent and burns for several seconds. This observation suggests that if the linear

carbonate concentration is reduced {say for example to 40–50%} the electrolyte may be thermally stable. However, earlier study by Naoi et al. [7] indicates that EC:DEC (50:50 vol.%)–1 M LiBETI is flammable. It clearly shows electrolytes containing carbonate solvents only are flammable. Multiple tests were performed to check for reproducibility. Photo 1 shows CAR-1 and CAR-HFE-1 samples immediately after the electrolyte vents.

### 3.5. Coin cell electrochemical performance

Electrodes were coated as mentioned above. The carbon anode and the cathode were individually tested against Li in coin cells (2032 size) containing the standard electrolyte at 25 °C. Fig. 5 shows plots of capacity vs. cycle# culled from the charge/discharge data for the cathode and anode. The charge and discharge capacities values are virtually identical (except for the 1st cycle) to one another which indicate that there is complete freedom from side reactions and that the electrodes perform reproducibly. The capacity values were utilized to coat matched anode and cathode electrodes for building 18,650 cells. Following the ½-cell tests the electrodes were tested in full cells.

Cell voltage vs. discharge capacity plots for full cells are shown in Fig. 6 for CAR-1, CAR-HFE-2 and CAR-HFE-4. Each curve is average of 5 discharge cycles each. The capacities are very nearly equal for the 3 electrolytes which suggest that the lower conductivity of the HFE electrolytes did not diminish their electrochemical performance significantly compared to the standard.

### 3.6. Cell electrochemical performance

18,650 cells were built, as described above, with CP anode and LNMN cathode electrodes containing different electrolyte formulations. Fig. 7 shows the discharge capacity of cells containing CAR-1, CAR-HFE-2 and CAR-HFE-4 electrolytes obtained in the formation

Table 2  
High temperature spray flammability of electrolytes.

Electrolyte solvent	Ignition	$\Delta t$ (vent-ignition)	Burn time (s)
CAR-1	Yes	5	6
CAR-3	Yes	<1	36
CAR-HFE-1	No	NA	NA
CAR-HFE-2	No	NA	NA
CAR-HFE-2	No	NA	NA
CAR-HFE-2	No	NA	NA
CAR-HFE-3	No	NA	NA
CAR-HFE-3	No	NA	NA
CAR-HFE-3	No	NA	NA





Photo 1. Shows that CAR-1 on the left is flammable and CAR-HFE-1 on the right is nonflammable.

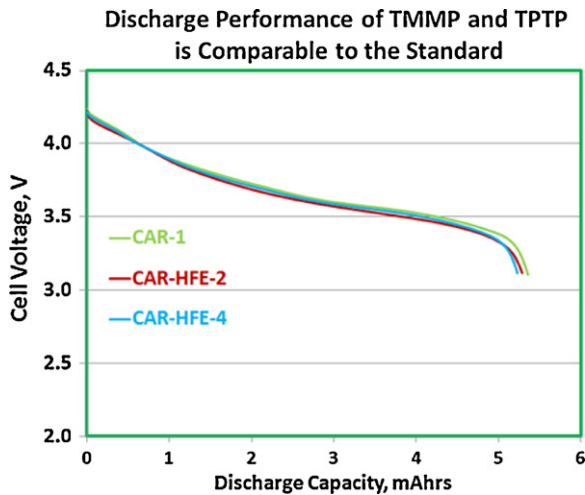


Fig. 6. Discharge curves for the LMNC cathode in full cells.

cycle. Results show only slightly decreased capacity ( $\sim 10\%$ ) for the HFE cells compared to the CAR-cell. Again this suggests that the diminished ambient temperature conductivity of the HFE electrolytes compared to CAR-1 did not affect the discharge capacity significantly. While there are typically trade-offs in one performance metric for another, it must be noted that in this case, the trade-off in cell capacity for reduced gas generation and flammability is relatively small. Moreover, for this small number of cycles there is no degradation in capacity over time; however, many more cycles will have to be completed to determine the long term stability of these electrolyte systems.

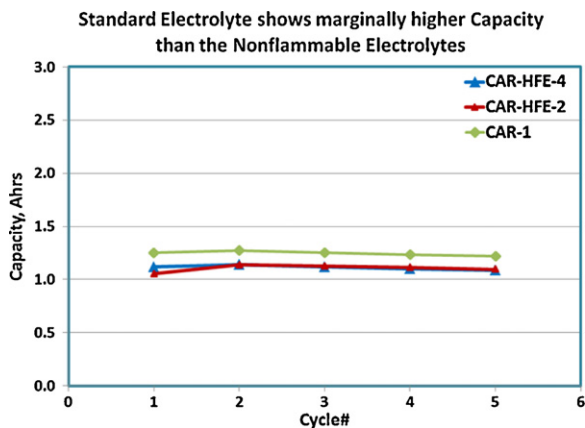


Fig. 7. Discharge capacity vs. cycle# for 18,650 cells with different electrolytes.

### 3.7. Gas generation in 18,650 cells

Fig. 4 shows gas generation profiles using ARC for 0.5 g samples of different electrolyte compositions. ARC can also be used to measure gas generation profiles of 18,650 cells during thermal runaway to determine if the materials-level improvements in gas generation translate to full cell improvements [14,15]. Fig. 8 shows ARC gas volume profiles for LNMC 18,650 cells with HFE and carbonate electrolytes. In the ARC experiment, cells are heated in  $5^\circ\text{C}$  steps until an exothermic reaction ( $0.02\text{ C min}^{-1}$  threshold) is measured. At that point, the ARC simply follows the heat generated by the cell sample and plotted as a temperature increase (Fig. 8). Once the cells vent, gas pressure is measured in the cell holder and STP volume is calculated using the measured pressure and sample temperature. At the onset of thermal runaway ( $220^\circ\text{C}$ ), STP volume of the baseline CAR-1 cells increase to 700–800 mL, while the HFE cells increase to  $\sim 300\text{ mL}$ . At the end of the cell runaway ( $320^\circ\text{C}$  for HFE cells and  $340^\circ\text{C}$  for EC:EMC cells), the cells initially cool without any increase in gas volume, then continue to generate gas as the cell temperature begins to increase. At  $400^\circ\text{C}$ , the total gas volume of the HFE cells ( $\sim 1100\text{ mL}$ ) is less than half that of the EC:EMC cells ( $\sim 2300\text{ mL}$ ).

These gas generation data indicate a significant improvement in the total gas decomposition volume using HFE electrolytes in 18,650 cells. Reduced gas generation represents a dramatic improvement in overall cell safety including potential exposure to inhalation hazards, reduction in pressure build up/rupture hazard in closed or sealed battery system designs, and mitigates the potential for a fire hazard. Additional work to analyze the composition of gas decomposition products and a complete thermal characteri-

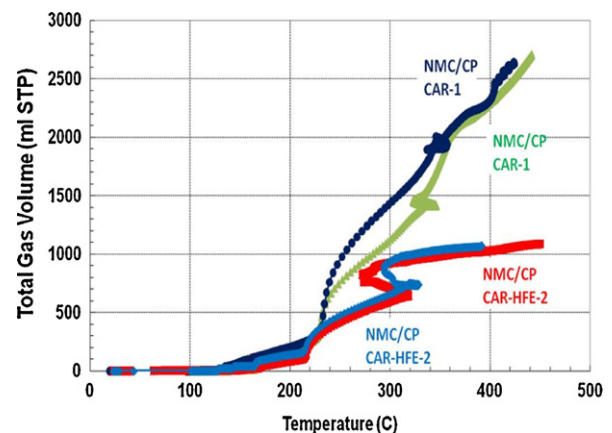


Fig. 8. STP gas volume as a function of temperature measured for 18,650 cells by accelerating rate calorimetry (ARC).

zation of HFE cells is currently underway and will be reported at a later date.

#### 4. Conclusions

We investigated different electrolyte formulations with and without the HEFs for conductivity, thermal and electrochemical properties. The conductivity is higher for the CAR-1 electrolyte than for the HFEs. However, lower conductivity does not affect significantly the electrochemical performance of the HFE electrolytes. The HFE electrolytes are thermally more stable than the CAR-1. Not only the HEF electrolytes generate less gas (~50%) but also the onset of gas generation is pushed out to a higher temperature especially for the LiBETI and LiTFSI. Reduced gas generation may be related to the reduced amount of carbonates in the electrolytes. HEFs do not seem to compromise the electrochemical stability window. These electrolytes were evaluated in cells built at Sandia. The performances of the HEF and CAR electrolytes are comparable in coin cells as well as in 18,650 cells. The volume of gas generated from full cells is less for the HFEs compared to the standard. This is a significant advancement which represents a dramatic improvement in overall cell safety including potential exposure to inhalation hazards, reduction in pressure build up/rupture hazard in closed or sealed battery system designs, and mitigates the potential for a fire hazard.

We believe that these results are significant and a first step in the right direction toward building a thermally stable Li-ion cell for the Transportation application. Other relevant criteria including long cycle life, low and high temperature performance are being addressed currently and the data will be published in the future. Finally, the thermal results have particular relevance to pouch cells, since they are more sensitive to the effects of gas formation.

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