THERMAL STABILITY STUDIES OF LI-ION CELL NEGATIVE ELECTRODE MATERIALS:

GRAPHITE, MCMB, HARD-CARBON AND InSb

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Introduction

A Li-ion cell typically consists of a carbon-based negative electrode (NE); a porous polymer membrane separator (polypropylene and/or polyethylene); and a lithiated transition metal oxide (LiM_xO_y, M=Co, Ni, and/or Mn) positive electrode (PE). Electrodes are made by casting slurries of PE or NE-materials, PVDF-binder and carbon-black onto metal current collectors. Mixtures of Li-salts and organic solvents provide an electrolyte medium for lithium ions to shuttle between the PE and NE. Upon cycling, passivation layers (SEI-layer) form over the surface of NE and PE-materials. Studies agree that this SEI-layer on the carbon-based NE consists of Li_2O, LiOH, Li_2CO_3, $LiCO_2$-R and LiF or LiCl, depending on whether $LiPF_6$ or $LiClO_4$ salt is used. This SEI-layer prevents excessive electrolyte reaction with the NE and thus improves cell cycle-life [1].

Under thermally abusive conditions, however, this SEI-layer breaks down near 100°C, electrolyte thermal decomposition and reaction with NE occur, then electrolyte and its decomposition products react with PE-material, and finally a strong exothermic reaction occurs between lithiated carbon and PVDF-binder. A major part of the total heat generation in the carbon-based NEs is due to the reaction of Li_xC_6 and PVDF [2].

To improve lithiation capacity of NE-materials for Li-ion batteries, researchers are investigating the application of modified/doped carbons, and the inter-metallic alloys such as Li_xAl, Li_xSi and Li_xSn. For the alloy systems, the added benefit could be of improved safety. This is related to metallic-nature and higher lithiation potential (0.5 V) of these materials vs Li-metal, it is expected that these alloys will offer a higher thermal stability than most carbons that have a lithiation potential (0.1 V) closer to that of Li-metal. These alloys are known to have poor cycling performance, because of their dramatic volume expansion due to lithium insertion and extraction [3]. However, it is believed that cycle-life may be improved if fine particles of the active alloy are dispersed in a matrix of inactive alloy systems that could provide structural support to composite electrode and prevent volume expansion of the active material upon cycling. An example of such alloy systems is InSb, which was studied by the battery group at the Argonne National Laboratory (ANL) as potential candidate for NE-material in Li-ion cells.

Here, we have investigated the thermal behavior of NE-materials consisting of soft and hard carbons, carbon mixtures and InSb. Differential Scanning Calorimetry (DSC) and Accelerating Rate Calorimetry (ARC) are used for thermal analysis. The onset-of-chemical-reaction (OSCR) temperatures and total heat generation (THG) values are reported and compared. Other parameters studied include the effects that the types of binder and content have on the thermal stability of NEs lithiated to various stages.

Experimental

Electrode Preparation- NEs of synthetic graphite (SFG-44, Lonza Co., Switzerland), mesocarbon microbeads (MCMB-2528, Osaka Gas Co. Japan), lignin-based HC (Motorola, USA), mixtures of HC:SFG-44 (50:50 wt%) and SFG-44:MCMB (50:50 wt%) as well as InSb were prepared. The sample electrodes were made by casting mixtures of carbon (92 wt%) and PVDF (8 wt%), dissolved in N-methyl-pyrolidone, onto copper foil.

The effect of a mixed binder formulation was evaluated on NEs made of SFG-44:MCMB. The binder mixture consisted of phenol-formaldehyde (PF) mixed with PVDF in a range of relative mass ratios (8.0:0.0, 3.0:5.0, or 1.5:6.5 wt%, respectively). The NEs of SFG-44:MCMB with PVDF (8 wt%) binder are noted as "NE-SMP8", and the NE of SFG-44:MCMB with mixed binders PVDF:PF (3.0:5.0 wt %) are noted as "NE-SMP3". The InSb-based NEs contained 4-wt%

PVDF and 1-wt% carbon-black. The battery group from Argonne National Laboratory (ANL, Michael Thackeray and co-workers) provided the InSb material. XRD results indicate that SFG-44 is a highly graphitic carbon, the MCMB is less graphitic than the SFG-44, and the HC has very little degree of graphitization [4].

Electrochemical activation- NEs (dia.=12.5 mm) were fitted into Teflon-Swagelok T-cells with Li-metal counter and reference electrodes, a Celgard-2300 separator and electrolyte (1M $LiPF_6$ in EC:DEC:DMC 40:30:30 v/o). T-cell assembly was carried out in a He-filled dry box. A Bitrode (Model LeN 4800) battery tester was used for electrochemical conditioning of the samples, which were discharged/charged for 5-cycles using 0.25 mA current, between 0.005 and 2.0 V. The last discharge step followed by tapering the current down to 0.025 mA, while voltage was kept as 0.005 V. The InSb samples were cycled 5-times between 1.2-0.45 V, using 0.5 mA.

Thermal Stability Studies (DSC)- Material thermal stability studies were carried out using a nitrogen-atmosphere controlled Simultaneous Thermal Analyzer (STA-Model 410, a DSC/TGA by Rheometric Scientific). The heating rate was 10°C/min, and the temperature ranged from 35 to 500°C. Prior to thermal analysis, all samples were washed in generous amount of DEC and then vacuum-dried at 65-70°C for 12-14 hours. For comparison proposes, we also studied thermal stability of samples in the presence of the same electrolyte noted above. These were to determine the role of PE and NE materials in the thermal behavior of full Li-ion cells under thermally abusive conditions.

Thermal Stability Studies (ARC): ARC measurements in the Heat-Wait-Search (HWS) mode were used to determine the thermal response, (temperature vs. time) and Self-Heat-Rates (SHR, °C/min), of NE-SMP8 or NE-SMP3 samples. These samples were recovered from fully charged 660-mAh Li-ion cell and then washed by following the same steps noted above. Cells consisting of Li_xCoO_2 as PE-material and the same electrolyte as noted above were cycled 5-times between 2.75-4.2 V. Detailed procedures for the ARC test and the importance calibration and sample-holder thermal mass are discussed elsewhere [4-6].

Results and Discussion

Electrochemical Properties of NEs: Figure 1a shows voltage vs. capacity profiles from the 5th-cycle of lithiated HC, HC:MCMB, HC:SFG-44, SFG-44, MCMB and SFG-44:MCMB samples. Soft carbon based samples (SFG-44, MCMB and SFG-44:MCMB) have two voltage-plateaus between 0.1 and 0.02 V, and there are a small differences among their voltage profiles. Note that

there is a distinct difference between voltage profiles of lithiated hard and soft carbon samples: no voltage plateau can be seen in the pure HC sample. Figure 1b illustrates how the voltage (Y-axis in log_{10}-scale) profile of the HC carbon flattens due to mixing with MCMB or SFG-44 carbons.

It is known that HCs can intercalate lithium at a faster rate than highly graphitic carbons. This is due to the porous structure of the material and the high number of short-range disordered graphene layers with edge-carbons [7]. Figure 1a shows that the HC in HC:MCMB or HC:SFG-44 samples is lithiated more rapidly initially, probably due to the high discharge rate selected for the experiment. As the intercalation potential drops and HC's non-graphitic sites are filled, lithium begins intercalating into the soft carbon component (SFG-44 or MCMB) and small graphitic sites in HC. Beyond the point where the HC potential crosses the potential of mixed samples (about 0.06V), the shape of the voltage plateau depends on the degree of graphitic carbon content in the mixed-samples. Note that the voltage plateaus in the HC:SFG-44 and HC:MCMB samples become closer to the voltage
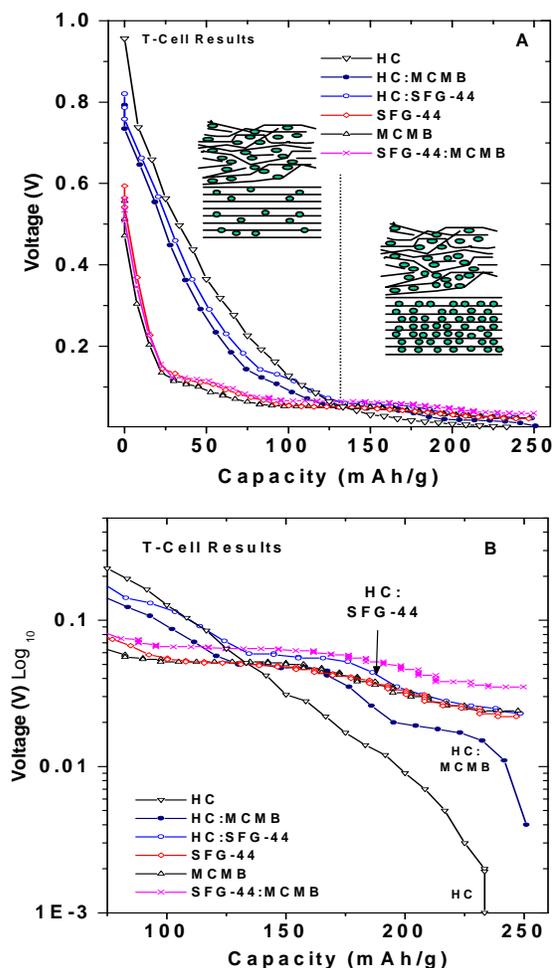

Figure 1. Discharge profiles of various carbons

plateaus of SFG-44 and MCMB, respectively. Such results suggest that it is possible that the addition of a certain percentage of soft carbon could prevent the HC voltage from decreasing below 0.06 V too rapidly where the lithiation limit is reached near 0.0 V.

Figure 2 shows voltage vs. capacity profiles of InSb, cycled 5-times using 0.5 mA discharge/charge current. Notice the strong capacity fading upon cycling. This fading is attributed to volume expansion of the material with continued cycling. Studies conducted by ANL shows marginally less capacity fading from the same material that we have tested in this work [6].
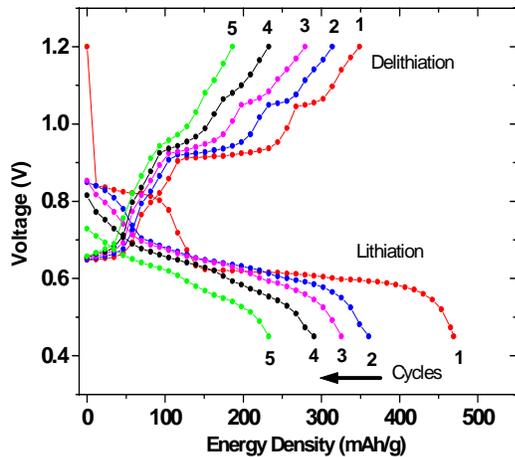

Figure 2. Dicharge profiles of InSb vs. Li-Metal

Thermal Analysis of Carbon-based NEs (DSC): Table 1 lists the samples evaluated and their lithiation capacity values, OSCR, heat generation, and maximum temperature rise. Figures 3 a-c show heat generation profiles of SFG-44, MCMB and HC samples lithiated to the capacity value given in the figure insets. Note that the total heat generation of all samples increases with increasing lithiation. The OSCR for the soft carbon samples do not change as significantly with degree of lithiation as it does for HC and HC:SFG-44. The differences in thermal behavior between the soft and hard carbons could be attributed to structural differences among these carbon samples and the physicochemical status of lithium in them. In the case of SFG-44 or MCMB, where there is only a fixed number of adsorption and/or lithiation sites possible, a discrete amount of thermal energy is needed in order for the Li-ions to be released from their sites and then react with PVDF-binder. On the other hand, the values of bonding energies of the lithium in HC's pores and/or carbon-edge sites are not clearly defined. We believe these are

possible reasons for the differences in thermal responses between the soft and the hard carbon samples. The heat generation of HC, with 0.0 lithium capacity (Figure 3c), is attributed to the reaction of irreversible lithium and PVDF. This heat generation is expected to increase with an increasing content of irreversible lithium in HC.

Table 1. Thermal behavior of Li-ion cell NE carbon materials lithiated to various stages

Sample	Capacity (mAh/g)	Heat Gener. (J/g)	OSCR (°C)	T max (°C)
8 wt% PVDF Binder				
SFG-44	50.00	482.0	----	----
	78.00	574.0	250	267, 380
	197.0	939.0	210	294
	336.0	1182.0	210	295
MCMB	44.00	410.0	275	323,425
	88.00	421.0	225	286,488
	194.0	782.0	215	292
	375.0	1044.0	220	300
HC	0.000	660.0	305	347-440
	165.0	760.0	275	345
	315.0	970.0	230	290
SFG-44: MCMB (SMP8)	0.0	47	471	489
	165	837	225	296, 424
	337	1062	230	295
SFG44: HC	0.0	411	347	411,474
	165	744	235	284
	311	995	210	282

Table 2. Thermal behavior of NE-materials as a function of binders: PF and Mixed PVDF:PF

Samples	Binder Content (wt%)	Cap. mAh/g	Heat Gener. (J/g)	OSCR (°C)	T amx (°C)
SFG-44: Binder (PF)	8.0	0.00	208	118	------
	8.0	159	220	122	------
	8.0	300	240	120	200
SFG- 44: MCMB PVDF:PF	1.5: 6.5	337	397	230	270
	3.0: 5.0	329	760	230	289
	8.0: 0.0	334	1062	230	305

Binder Effects on the Thermal Stability of NEs: Table 2 gives values of capacity, total heat generation, OSCR and maximum temperature rise for NE-material made with PF binder (8 wt%) and PVDF:PF binder mixtures. Figure 4 compares the total heat generation value, vs. lithiation capacities for the NE-materials (HC, SFG-44 and MCMB) made using 8 wt% PVDF with a NE-material of SFG-44 made with 8 wt% PF binder. Note that the heat generation of the sample, with pure PVDF binder increases with increasing lithiation; heat generation of the sample with PF binder is nearly independent of lithiation. The overall heat generation values from samples with pure PVDF binder are higher than the samples containing pure PF binder.
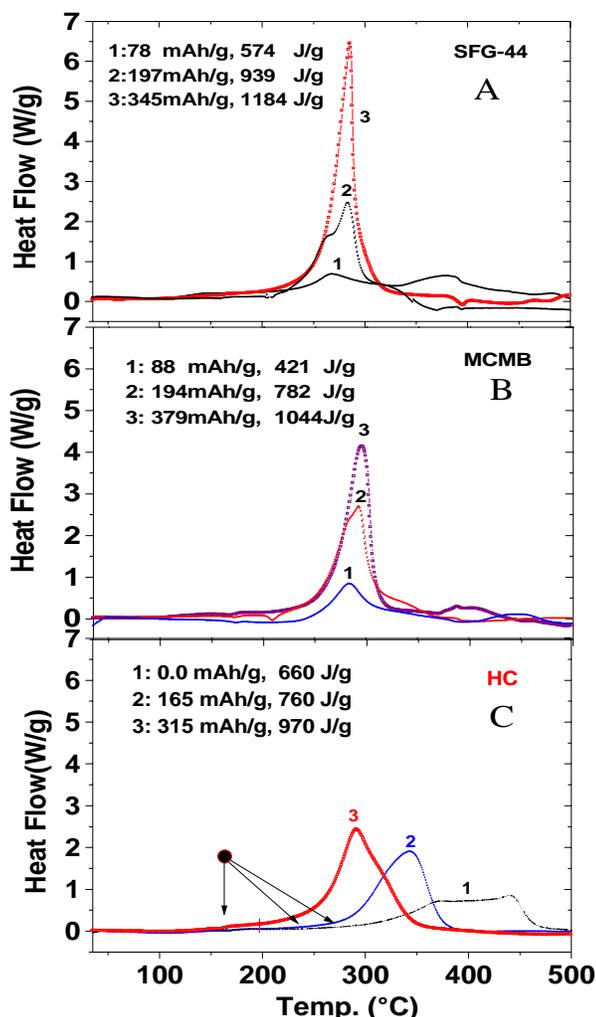

Figure 3. DSC scans of carbon-based NEs lithiated to various stages

Thermal Analysis of NE-Materials (ARC): Figure 5a and b show temperature vs. time and Self-Heat-Rate (SHR, °C/min) profiles for the lithiated SMP8 and SMP3

samples. The main OSCR for these NE samples starts near 170°C and 158°C respectively. Small self-heating reactions are evident in the range from ~90°C up to the OSCR temperatures for both samples. This is attributed to the presence of small amounts of electrolyte residue and/or ARC-heating step artifacts. These SHR data points, however, are below the ARC sensitivity limits (0.02°C/min). For further confirmation, ARC tests were conducted on "unwashed" lithiated SMP3 and SMP8 samples. The OSCRs started near 91°C and 96°C, respectively, with SHR of 0.03°C/min. There was no evidence of small SHR at temperatures below the OSCR. Thus, exothermic self-heating of the washed samples, at temperatures below the OSCR, were likely due to the presence of small electrolyte residue.

Quantitative comparison of ARC and DSC data is difficult because of the fundamental differences between the nature of experiments. However, both results agree that full/partial substitution of the PF binder for PVDF will increase the thermal stability of the carbon based NE-materials. Such conclusions were also noted by Pasquier *et al.* [8]. They showed that the substitution of 10 wt% PVDF with PVDF:HFP decreases the heat generation of fully lithiated MCMB-2528 by 23%.
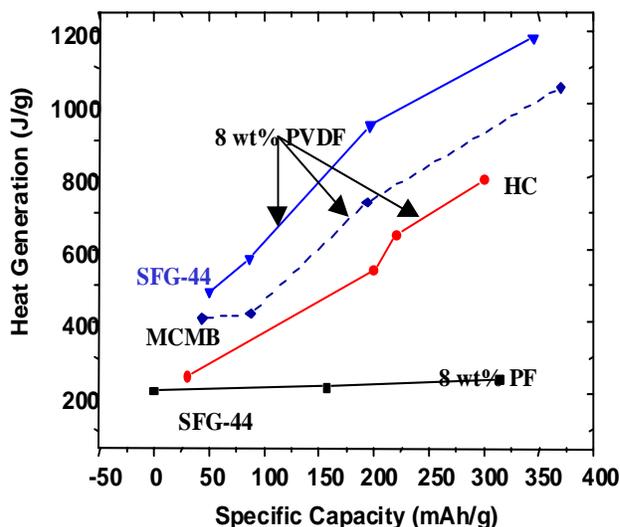

Figure 4. Total heat generation of NEs of various carbons, lithiated to various stages, with 8 wt% PVDF or PF binder.

Thermal Analysis of InSb-based NE (DSC): Table 3 lists energy density values and the corresponding OSCR and heat generation for the InSb-NE samples, washed in DMC and vacuum-dried at 70°C. Tests were conducted between 50-400°C. Results indicate that the OSCR in InSb starts between 100-120°C. The material has a mass loss of <1.5 wt% only, and yet it generates

considerable heat even as fresh powder or as a coated electrode. The overall results show that the heat generation increases with either increased cycling and/or lithiation. Increasing heat generation with cycling, normally does not occur in carbon based NEs, except in cases of repeated Li-plating with continued cycling. However, further work is needed in order to investigate the relation between the melting of In (155°C) and the sudden rise in heat generation.

Table 3. Data on thermal behavior for InSb: fresh powder, coated electrode and electrodes lithiated to various stages

Cell No.	Cells Cycled using 0.5mA			Cells Ch. or Dich. @C/50	
	1-st Disch. (mAh/g)	6-th Ch. (mAh/g)	6-th Disch. (mAh/g)	No electrolyte	
				OSCR (°C)	THG (J/G)
1	138.24	-----	-----	102	805
2	476.93	-----	-----	117	943
3	468.55		-----	118	1010
4	456.45	221[CH]	-----	105	1097
5	456.37	224[CH]	-----	115	966
6	466.08	-----	217[DC]	115	1109
7	475.35	-----	217[DC]	100	1193
Fresh Powder	-----	-----		118	288
Fresh Electrode	-----	-----		120	324

#1: The cell was discharged to 0.7V using 0.5mA (~C/10 Rtae)
[CH]: After 5-cycles the T-Cells were charged to 1.2 V at C/50
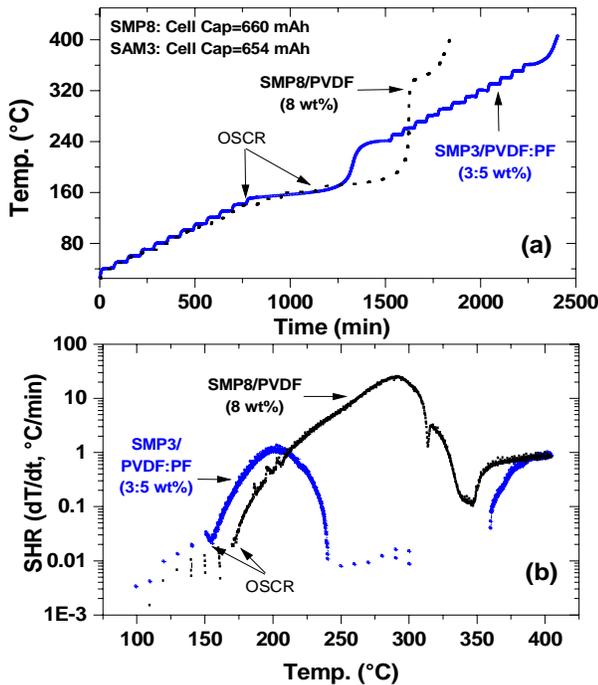[DC]: After 5-cycles the T-Cells were discharged to 0.45 V at C/50

Comparison of InSb with Graphite: One of the critical issues in thermal stability studies is that the thermal performance of individual components does not directly translate into cell safety. High safety limits required not only by selecting materials that offer high thermal stability but also that perform well when combined with each other in a full cell environment. In view of this, we compared the thermal stability of PE (Li_xCoO_2) and NE (graphite), recovered from fully charged commercial Li-ion cell with fully lithiated InSb prepared under half-cell conditions. Figure 6 shows the corresponding thermal profiles of samples tested in the presence of electrolyte.

Note that the major heat generation of graphite-NE occurs at a higher temperature range than that for the InSb-NE. Most importantly, the high heat generation range of InSb falls directly over the range where the heat generation of Li_xCoO_2 is at its maximum. From a safety standpoint, however, the use of InSb in a Li-ion cell, would tend to lower the onset temperature of thermal runaway because the thermal reactions of both PE and NE occur within same temperature range (150-260°C). Ideally, thermal reaction of the individual cell components should occur at a slow rate and at temperatures that are not superimposed on each other. This allows the generated heat to be dissipated rather than accumulated and prevents pushing the cell to a higher temperature that could lead to thermal runaway in a short time.
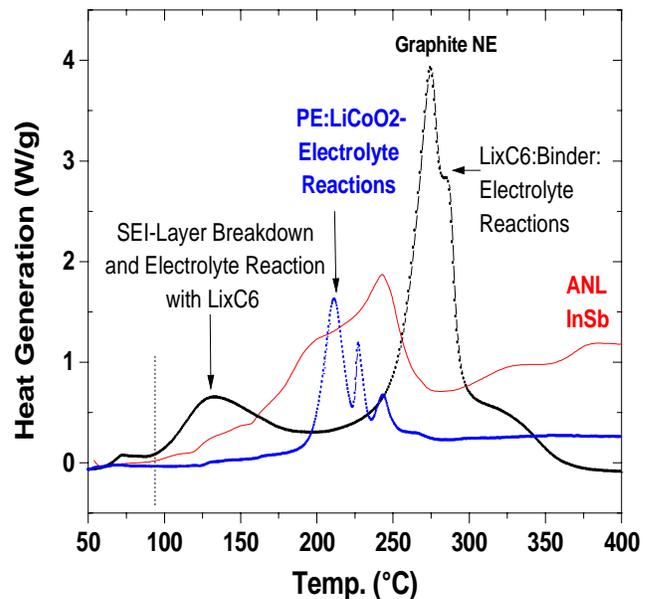

Figure 5. ARC test results for lithiated NE consisted of SFG44-MCMB (50:50 wt%) and PVDF (8 wt%) or mixture binder PVDF:PF (3.0:5.0 wt %)

Figure 6. Comparison of DSC scans of lithiated InSb-NE with PE and NE-materials recovered from fully charged commercial Li-ion cell.

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Conclusions

Negative electrodes (NE) for Li-ion cells are typically made by casting a mixture of carbon with polyvinylidene difluoride (PVDF) onto copper current collectors. DSC results (without electrolyte) indicate that the total exothermic heat generation of lithiated synthetic graphite (SFG-44), mesocarbon microbeads (MCMB), lignin-based hard carbon (HC) or mixtures of these materials increase with an increase in lithiation. This heat generation is attributed to the reaction of PVDF with Li_xC_6. The onset temperature for the thermal reaction of PVDF with SFG-44 or MCMB does not depend strongly on lithiation content. However, this onset temperature decreases significantly with increasing lithiation in HC electrodes. Differences between thermal stability of SFG-44 or MCMB vs. HC are attributed to structural differences among these materials.

The heat generation from the PVDF reaction with Li_xC_6 can be reduced by partial or complete substitution of PVDF with a phenol-formaldehyde (PF) based binder. NE's made with PF binder show comparable electrochemical performance in full Li-ion cells both in terms of delivered capacity and cycle-life. While these results are encouraging, additional studies are needed to evaluate the interactions of other cell components on the thermal performance of PF and its potential for use as a binder in practical cells.

Results indicate that the InSb material studied here exhibits exothermic reaction even as raw material or as freshly coated electrodes. Its heat generation increases with increasing lithiation, cycling, or addition of electrolyte. The overall heat generation rate of fully lithiated InSb is slower than the fully lithiated graphite. The InSb material could be suitable for Li-ion cells of very thin and large surface area, once it is demonstrated that it can provide a reasonable cycle-life and rate capability.

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