Current trends in materials development for Li-ion batteries

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Li-ion Technology: where are we today

Although tremendous progress has been made over the last couple of decades state-of-the-art lithium-ion batteries still lack:

1. **Safety**
   - **thermal abuse tolerance**
2. **Energy**
   - **Cell Capacity has been increased to over 3 Ahrs in 18650 cells but the operating cell voltage remains low (for a PHEV application)**
3. **Power**
   - **Significant advancement has been made but lacks low temperature power performance**
4. **Life (15 years)**
   - **Remains a long shot**
5. **Operating temperature (-55 to 80°C)**
   - **Performance outside of -20 to 55°C range needs improvement and**
6. **Low cost**
   - **This also remains a long term goal**

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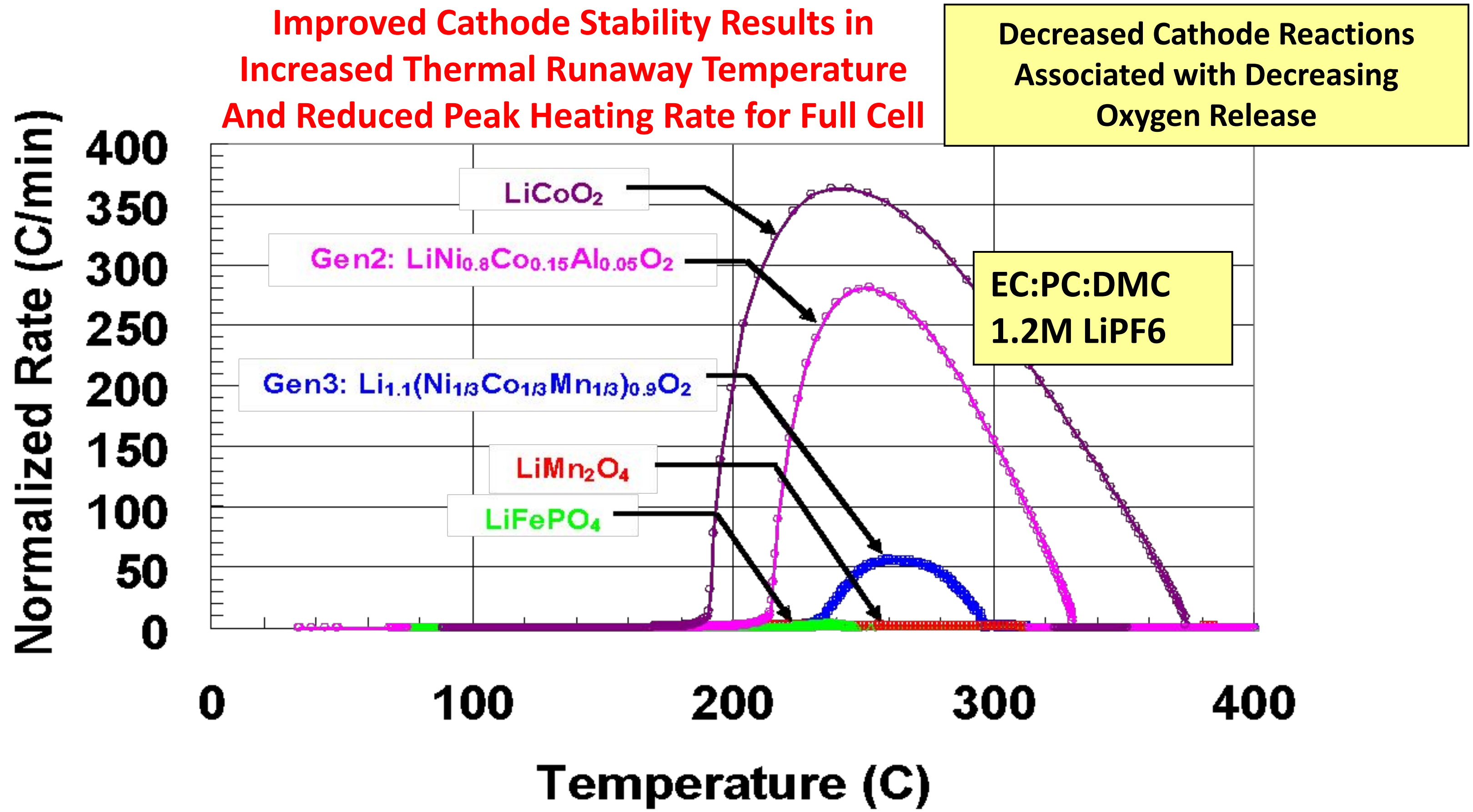
Sources of Thermal Instability

The three main battery components (anode, cathode, electrolyte etc) all jointly contribute to thermal instability. Additionally, the cell voltage exasperates the thermal instability problems. In the next VU graph thermal runaway cathode comparison is given.

Thermal Runaway Cathode Comparisons



Courtesy of Dr. Roth (Sandia)

Potential path forward to overcoming the constraints

- Replacement of carbon materials with Nano-particulate metal, semi-metal, intermetallic or conversion based anodes to increase capacity (both specific and volumetric)
- Exploitation of high potential materials (>4.5 V) to increase energy and power
- High-capacity composite cathode structures with (layered) /high-power (spinel) components
- Electrode surface protection – coating
- Non-flammable electrolytes

Anode Materials

1. Sony successfully used metal composite anode, showed higher capacity
   - Intermetallic compounds may hold the key for a safe anode
2. Transition metal sulfides (CoS, NiS and FeS) using conversion reaction for use as anode materials. These metal sulfides upon incorporation of Li are expected to form metal and Li_2S nano-composites (this is a reversible reaction). These materials show very high capacity on the order of 600 mAhr/g

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Sony's hybrid lithium-ion rechargeable battery

Sony developed a tin-based amorphous anode material where the lithium ion storage capacity per volume ratio has been increased by 50%, which increases the overall battery capacity by 30%. Taken from http://www.sony.net/SonyInfo/News/Press/200502/05-006E/index.html

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Nexelion Anode Composition

Table 2. Weight % of elements in the Nexelion anode.

Element	Weight %
Carbon	35.86
Tin	27.3
Cobalt	16
Titanium	2.42

- Weight ratio taken from ARL-TN-0257, June 2006 report
- Sony reports a weight ratio of carbon to metal as 1. The measured ratio by ARL is 0.8
- The % weight of the elements shown on the left doesn't include the polymer.

Comparison of Battery Performance

Item	Conventional Battery (14430G6)	Nexelion (14430W1)
Anode material	Graphite (Carbon)	Tin based Amorphous material
Cathode material	Lithium Cobalt oxide	Multi-stage composite cathode (Mixture of cobalt, manganese, nickel oxides and Lithium Cobalt oxide)
Electrolyte	Hybrid electrolyte	Newly developed hybrid eletrolyte
Size	Diameter 14mm x Height 43mm	Diameter 14mm x Height 43mm
Capacity(0.2CmA)Size	700mAh, 2.6Wh	900mAh, 3.1Wh diameter
Standard charging voltage	4.2V - 3V	4.2V - 2.5V
Energy Density	395Wh/l, 144 Wh/kg	478Wh/l, 158 Wh/kg
Weight	18 g	20 g

14430 is cylindrical with 14 mm dia. and 43 mm high

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Problems with the $LiCoO_2$ Cathode

- Only 50% of the Li content can be taken out before the structure collapses
  - Lower capacity
- Less thermally stable because of oxygen loss at elevated temperatures
  - Unsafe
- Expensive and toxic
  - Not affordable and not environmentally friendly
- Low voltage for PHEV application

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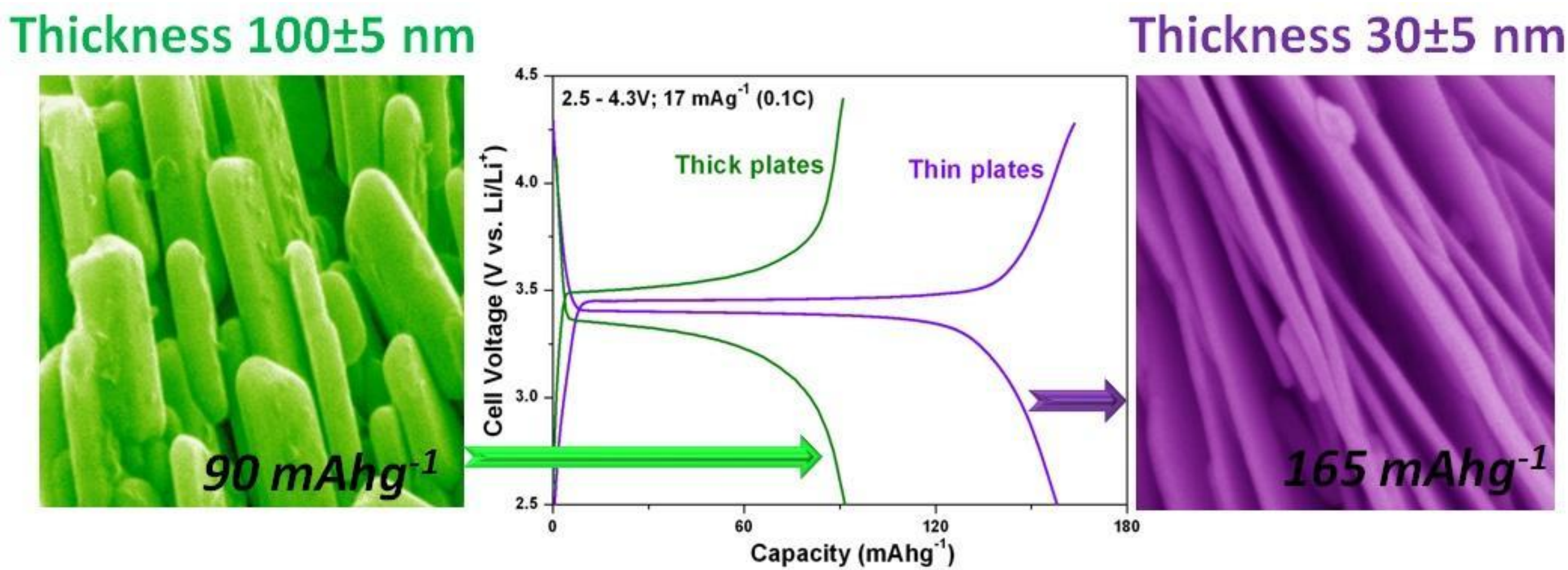
Ways to Improving Cathode Performance

- Increasing Energy Density
  - Investigate high voltage cathodes that can deliver all the Li in the structure
  - Will improve energy density
- Thin nano-plate materials seem to offer more energy at higher rate
  - 30 nm $LiFePO_4$ nano-plates performed better than thick material
- Meso porous $LiMn_2O_4$ is another material where there is reduced manganese dissolution
- Coating of cathodes with either ionically or electronically conductive material
  - AlF_3 coating on oxide materials is shown to improve performance

Thin Nano-plates show higher capacity and rate than Thick nano-plates



Comparison of $LiFePO_4$ nanoplates with thick plates [Saravanan et al. *J. Mater. Chem.*, 19 (2009) 605].

AlF_3 Coated Electrodes

1. The surface coating of electrodes seem to improve capacity retention and performance over the uncoated samples
2. For example $LiMn_2O_4$ showed only 3.4% capacity loss at 55°C after 50 cycles compared to ~18% decay without the coating (*Russian Journal of Electrochemistry, 2009, Vol. 45, No. 7, pp. 762–764)*
3. $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ also showed higher capacity retention and better thermal stability with coating than without (Journal of Power Sources 179 (2008) 347–350)

Potential Cathode Materials

1. Olivine based phosphates systems ($LiMPO_4$ where M = Mn, Ni) that can deliver more Li as compared to the conventional material $LiCoO_2$
2. Only very few groups have synthesized $LiMnPO_4$ successfully and this system has a potential around 4.3 V
3. $LiNiPO_4$ has a potential around 5.5V. It is believed that Li^+ diffusion coefficient is quite high in nickel phosphate in the range 10^{-5} m^2/s at around room temperature. It should have high thermal stability because the oxygen is covalently bound in the structure
4. Novel approaches for synthesis of nanostructured olivines are required to enhance both ionic and electronic conductivity.
5. $LiMn_2O_4$ may be another potential candidate material if the Mn dissolution can be suppressed
   - Mesoporous oxide with coating may stabilize Mn oxide

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Electrolyte (solvent + salt)

The state-of-the-art electrolytes for Li-ion cells contain a blend of organic carbonate solvents and $LiPF_6$ as salt. But these electrolytes suffer from several potential frailties including:

1. Flammability of solvents (Flash point < than 39^{o}C)
2. Reaction of $LiPF_6$ with the other materials in the electrolyte and with impurities such as water
3. Instability at high temperatures
4. No one mixture of the solvents has been shown to work well at both low and high temperatures and
5. The electrolytes appear to be reactive with the surfaces of standard cathodes and to be unstable at high voltages

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New Solvents

- New fluoro solvents are being investigated as nonflammable solvents
  - Solvent with a F to H ratio >4 appears to have improved thermal properties
  - In the wick test the electrolyte containing the fluoro solvent didn't catch fire.
- Fluoro solvents in conjunction with cyclic carbonates should exhibit improved thermal properties
  - Low temperature performance may suffer
    - Fluoro-EC may be an alternative

Salts

While the anions of the salts are unique and promise to improve many performance characteristics of the existing Li-ion cells there is no systematic understanding of how the salt's stability depends on the anion stability of the salt. Instead of trying several Li salts for stability by brute force, Fusaji etal have computed from the HOMO (Highest Occupied Molecular Orbital) theory the oxidation energy for some of the anions (J. Power Sources 90, 27(2000)) to scientifically understand the oxidative stability of the anion of the salt.

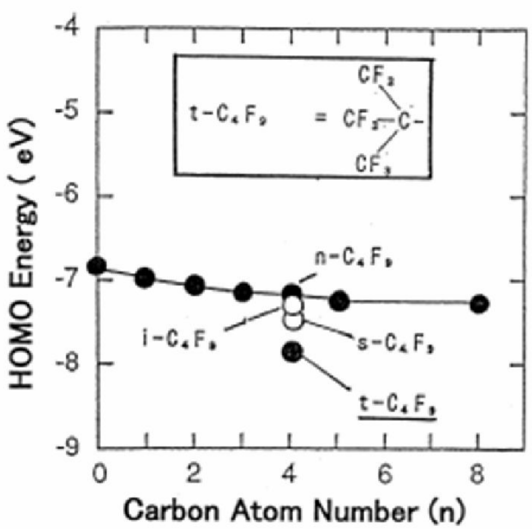

Figure 3. Anion HOMO Energy vs. Number of Carbon Atoms

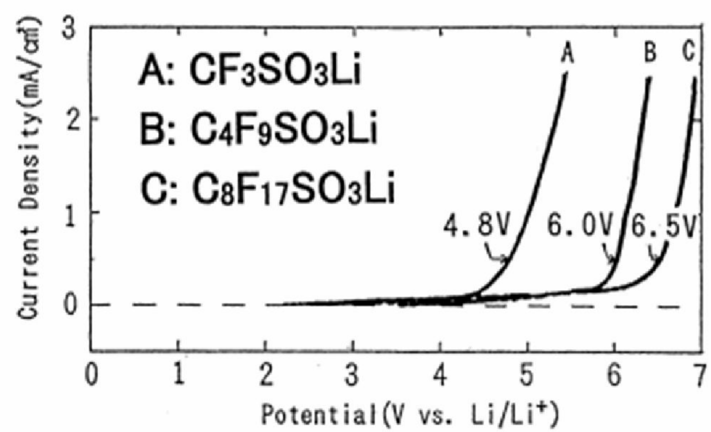

Figure 4. Potential Window of Electrolytes

Summary

- Need to investigate non-carbon or carbon doped with intermetallic compounds for improving cell performance
- Olivine based or stabilized $LiMn_2O_4$ type cathodes need to be investigated
- Fluoro solvents in conjunction may exhibit better thermal properties