Low Cost Components: Screening of Advanced Battery Materials

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Outline

- Purpose of Work
- Address Previous Review Comments
- Barriers
- Approach
- Performance Measures and Accomplishments
  - Coated graphites and soft carbons from Hitachi Chemical
  - ConocoPhillips graphites (discussed in low temperature work)
  - Mitsubishi Power Graphite
  - $LiMnPO_4$ from HPL
- Technology Transfer
- Publications
- Plans for Next Fiscal Year
- Summary

Purpose of Work

- Identify and evaluate battery materials made by vendors from around the world that have the potential to offer low cost, long calendar life and better abuse tolerance. This past year's effort was focused on lower cost graphites.

Reviewer Comments from Aug. '06 Merit Review

- "Evaluate lower cost graphite"
  - Received and tested new graphite materials from Hitachi Chemical, Mitsubishi Chemical, and ConocoPhillips

Barriers

- Identify lithium-ion battery materials, with enhanced stability, that lower cell-level costs while simultaneously extending life and enhancing inherent abuse tolerance.
  - An overwhelming number of materials are being marketed by vendors. How to select and screen these materials within the effort allocated to this project?

Approach

- Consider materials that are commercially viable
  - Avoid materials based on rare elements, expensive precursors, or elaborate processing
- Many commercial materials were developed for high energy applications, not high power
  - Evaluate these materials for HEV use by testing their rate capability, HPPC impedance, and cycle life
  - Use laboratory scale cells
    - *Coin cell (1.6 cm^2)*
    - *SS planar test fixture (32 cm^2)*
    - *Pouch cells (25 to 50 cm^2)*
- Evaluate materials for use in the higher energy PHEV
- Recommend promising materials for further thermal abuse evaluation and consider for use in longer-term aging studies.

Advantages of New Carbon Anode Materials

SMG: surface modified graphite

- Hitachi Chemical is developing a surface modified Natural Graphite (NG) using a "fusing technology" to develop several new carbon anodes with high capacity, long life, and low cost
- Surface modifications are very homogeneous and have a thickness as low as 10 nm
- Material is tolerant to 30% PC and doesn't require the use of EC based electrolyte

SC: soft carbon

- Hitachi Chemical is developing a soft carbon as a replacement to the hard carbon used at the moment in HEV battery development, which is desired for cathodes that have flat voltage plateaus

MPG: Mitsubishi Power Graphite

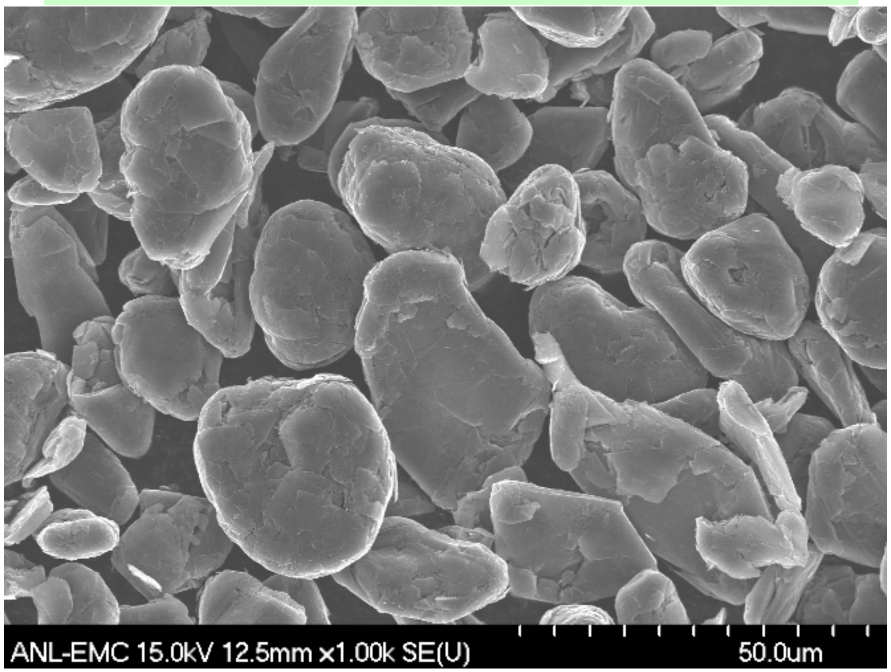
- Mitsubishi Chemical developed a surface modified graphite for high power Li-ion battery application (HEV)

Particle Shape Not Affected by Hitachi Modification

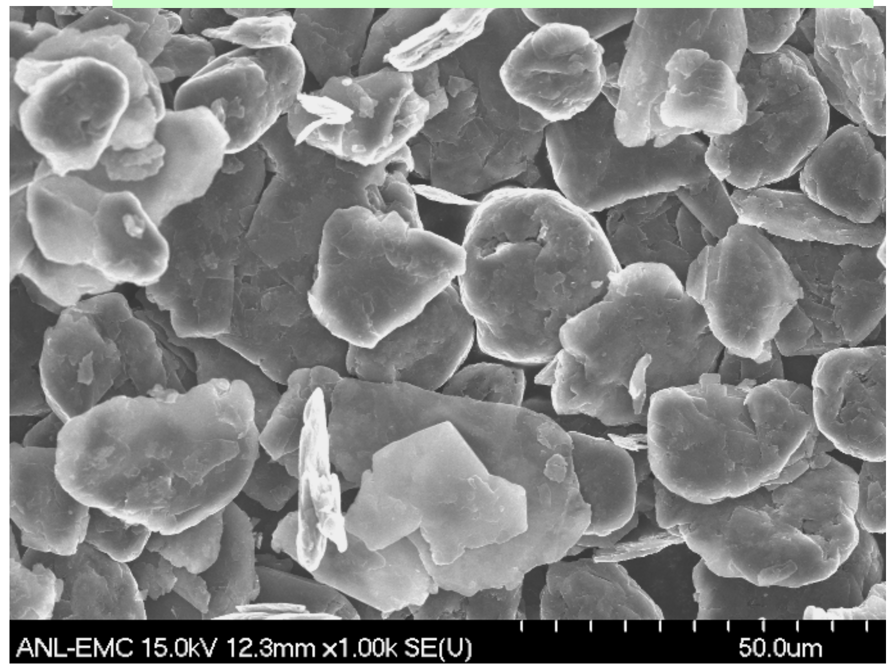
Natural graphite with round-edge shape

Surface modification decreased specific surface area from 5 m^2/g to 2 m^2/g

Untreated: SMG (Blank)-20
D_{50}:19.8 μm
S.A.: 5.0 m^2/g
Tap Density: 0.80 g/cm^3



Treated: SMG-NAL1-20C
D_{50}:23.4 μm
S.A.: 2.0 m^2/g
Tap Density: 0.87 g/cm^3

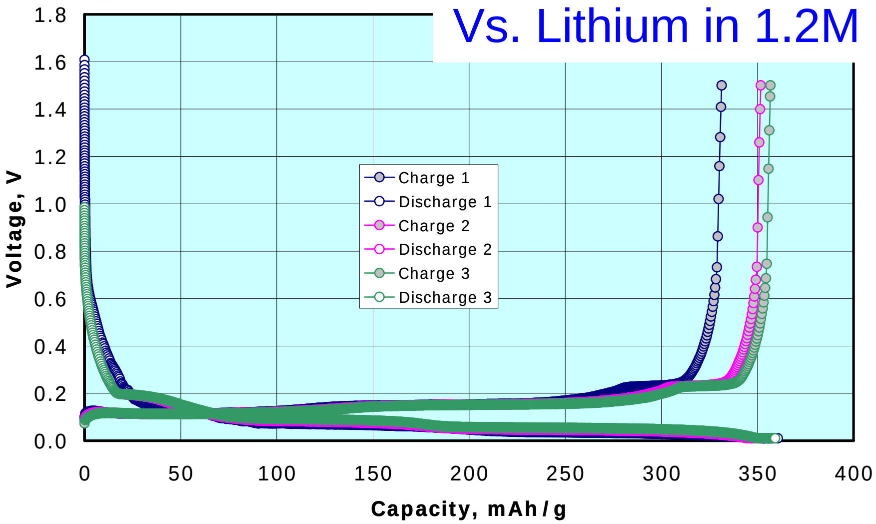


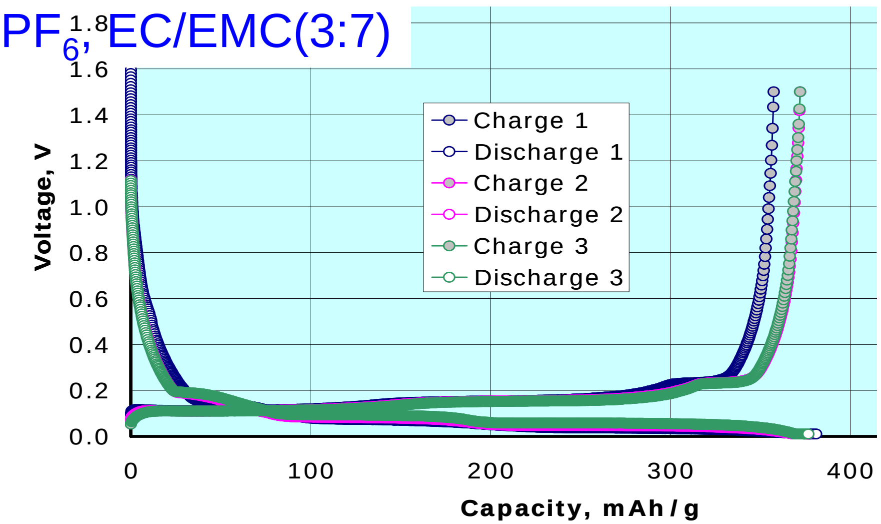
Modification has Small Effect on Graphite's Power

SMG (Blank)-20

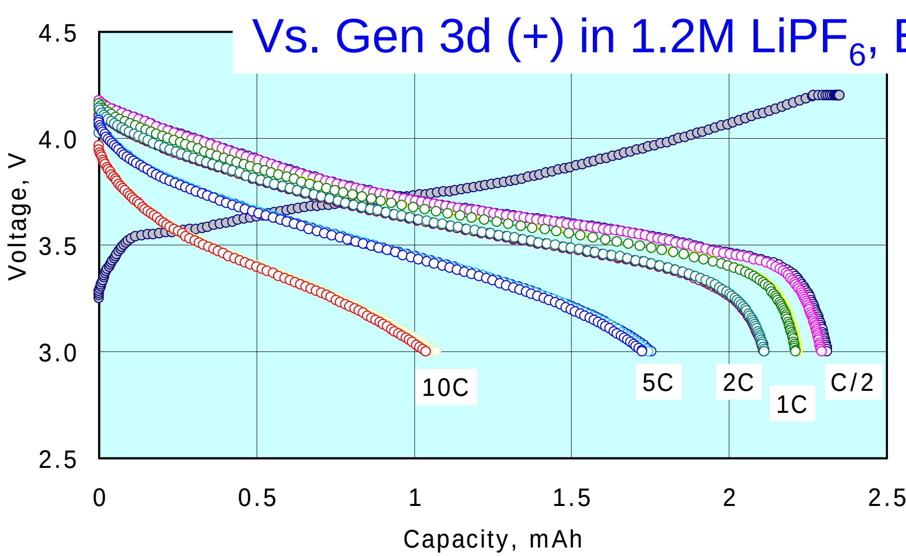
SMG-NAL1-20C

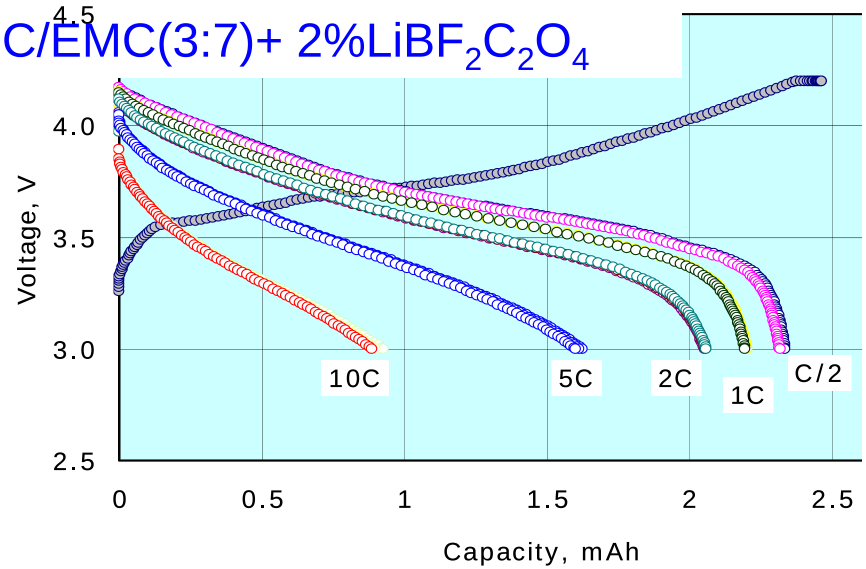
Vs. Lithium in 1.2M $LiPF_6$, EC/EMC(3:7)



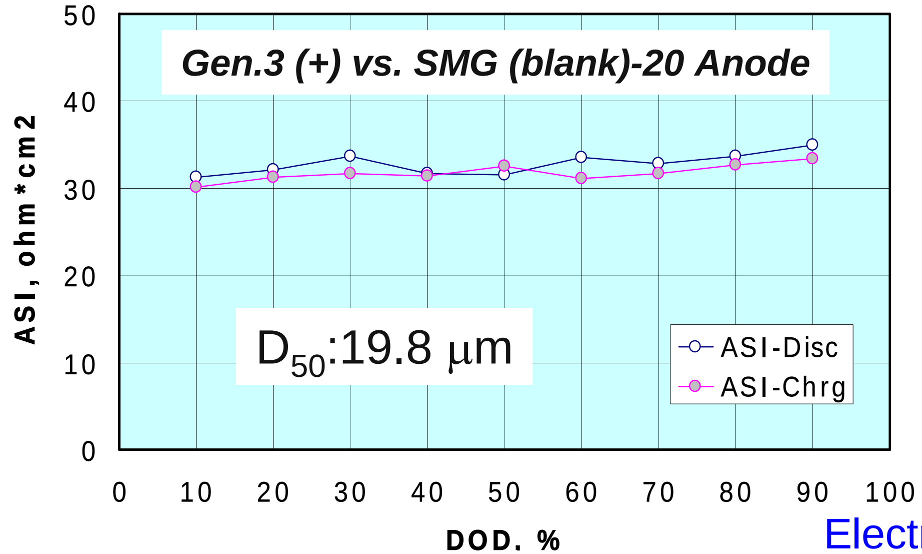


Vs. Gen 3d (+) in 1.2M $LiPF_6$, EC/EMC(3:7)+ 2%$LiBF_2C_2O_4$



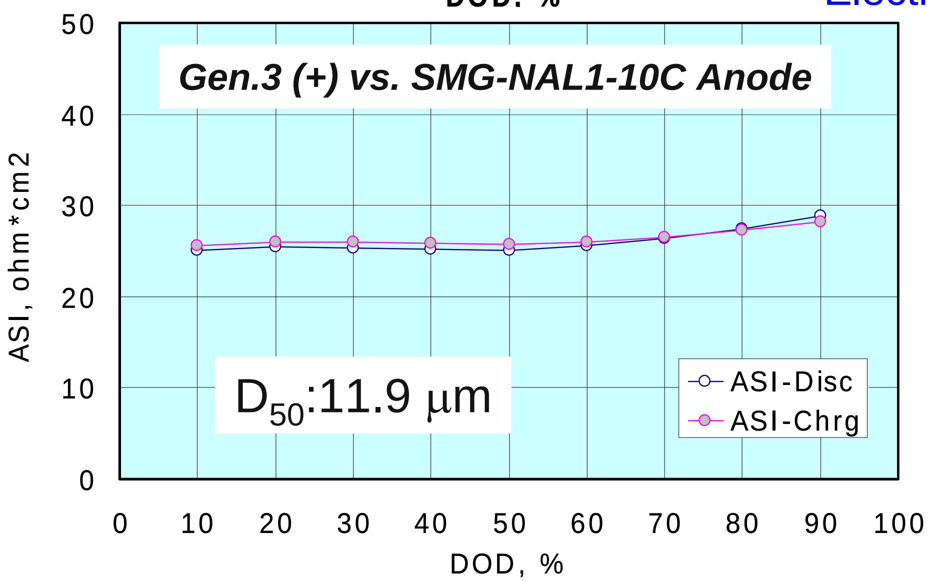


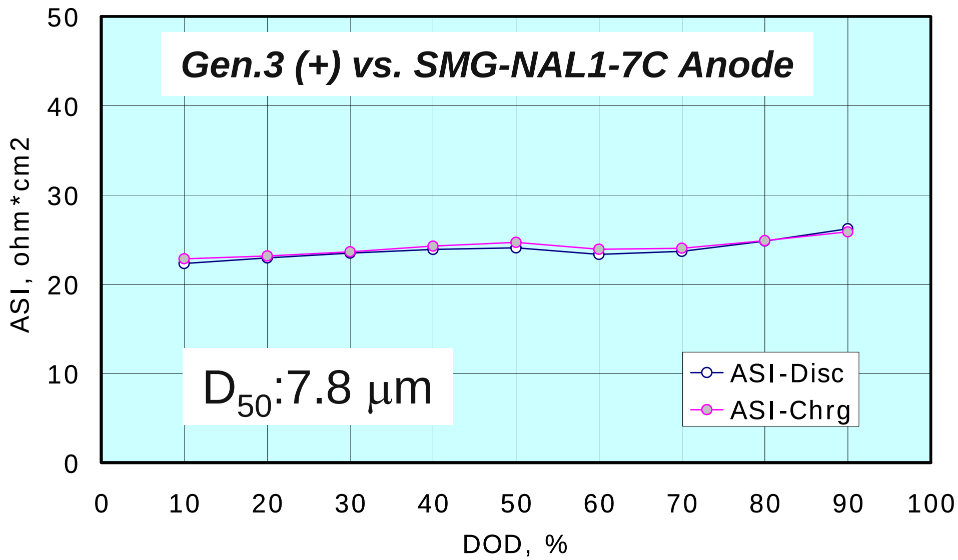
Low ASI of Hitachi SMG Anodes Enables Use In HEV



- HPPC ASI decreases as particle size decreases
- Abuse tolerance is next criteria

Electrolyte: 1.2M $LiPF_6$, EC/EMC(3:7)+ 2%$LiBF_2C_2O_4$



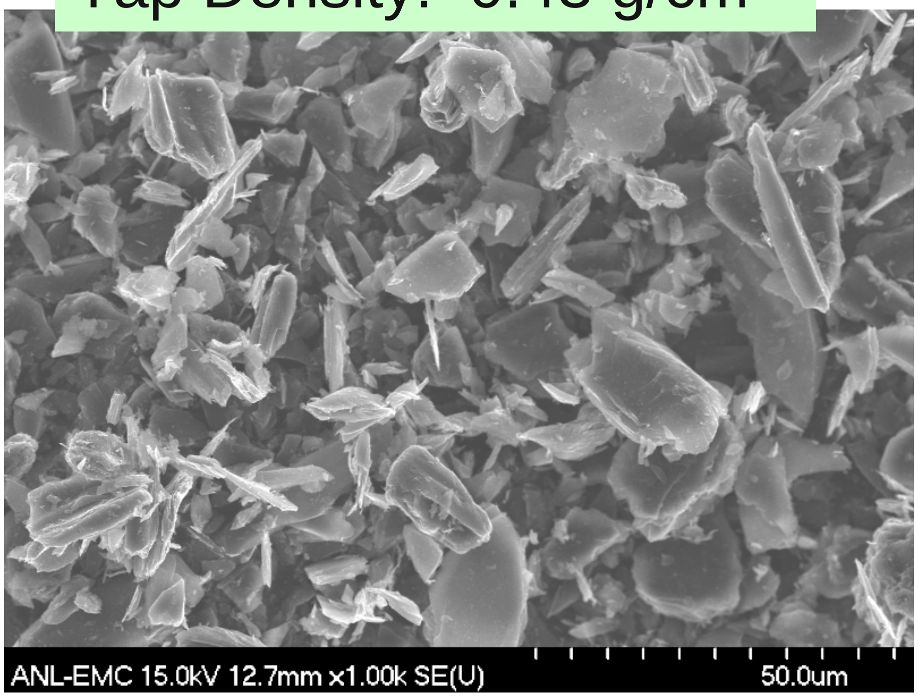


Particle Shape Not Affected by Hitachi Modification

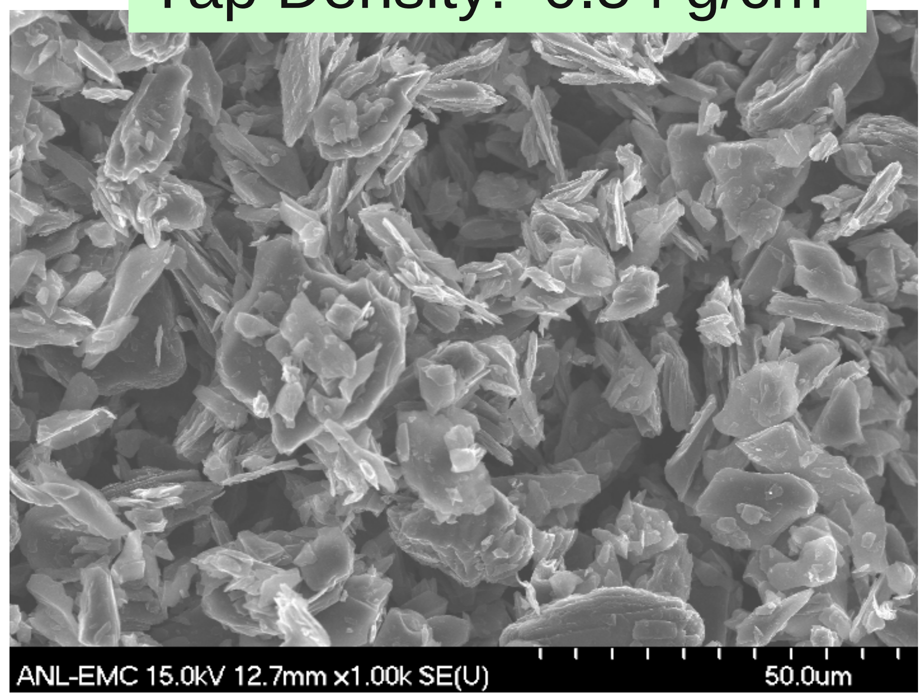
Soft Carbon (using specified coke as raw material)

After treatment, specific surface area decreased from 11.3 m^2/g to 2.4 m^2/g

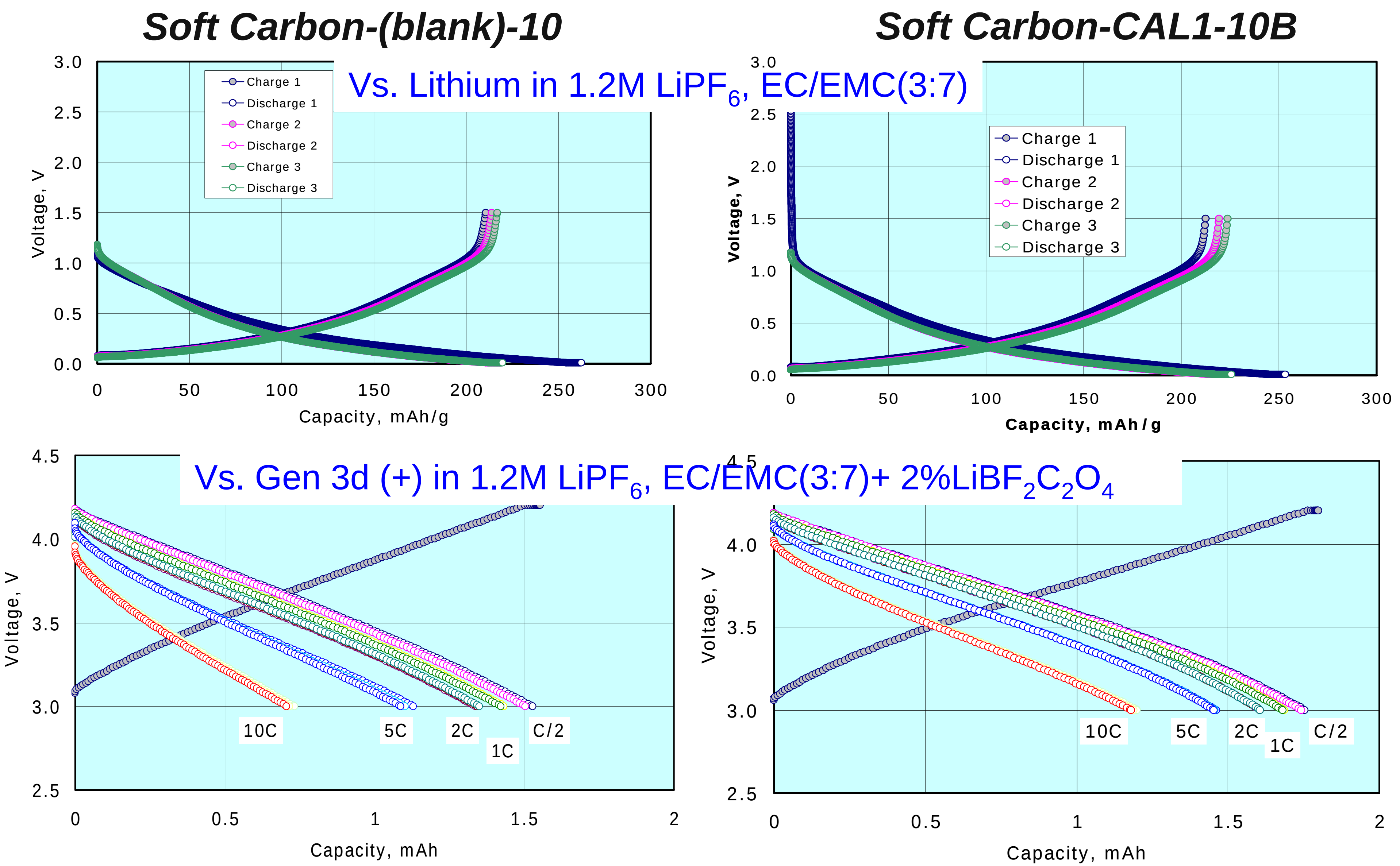
Untreated: SC-(Blank)-10
D_{50}:10.3 μm
S.A.: 11.3 m^2/g
Tap Density: 0.43 g/cm^3



Treated: SC-CAL1-10B
D_{50}:12.1 μm
S.A.: 2.4 m^2/g
Tap Density: 0.54 g/cm^3



Modification Improves Soft Carbon's Rate Capability

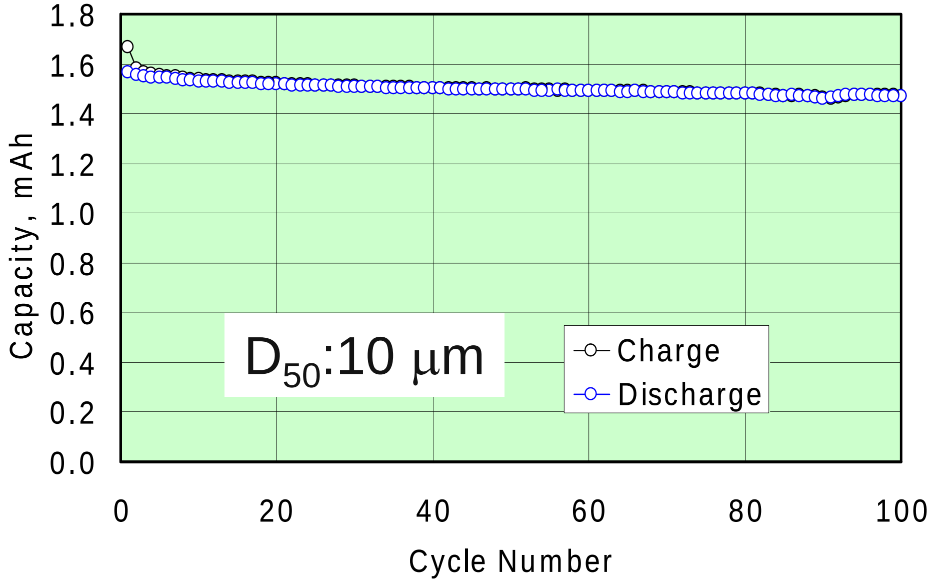


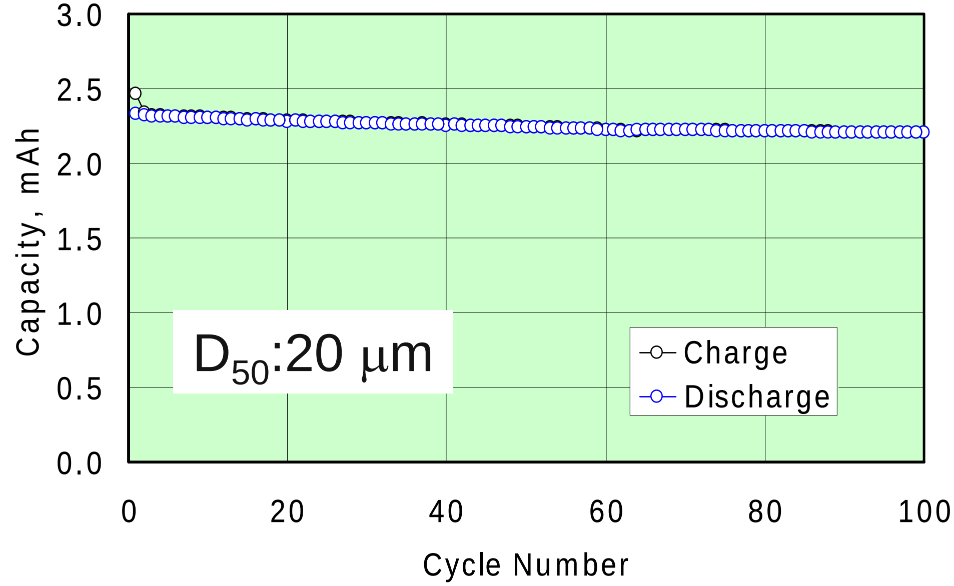
Good Cycle Performance of Hitachi Anodes at C/1 Rate

Soft Carbon

SMG Graphite

Vs. Gen 3d (+) in 1.2M $LiPF_6$, EC/EMC(3:7)+ 2%$LiBF_2C_2O_4$



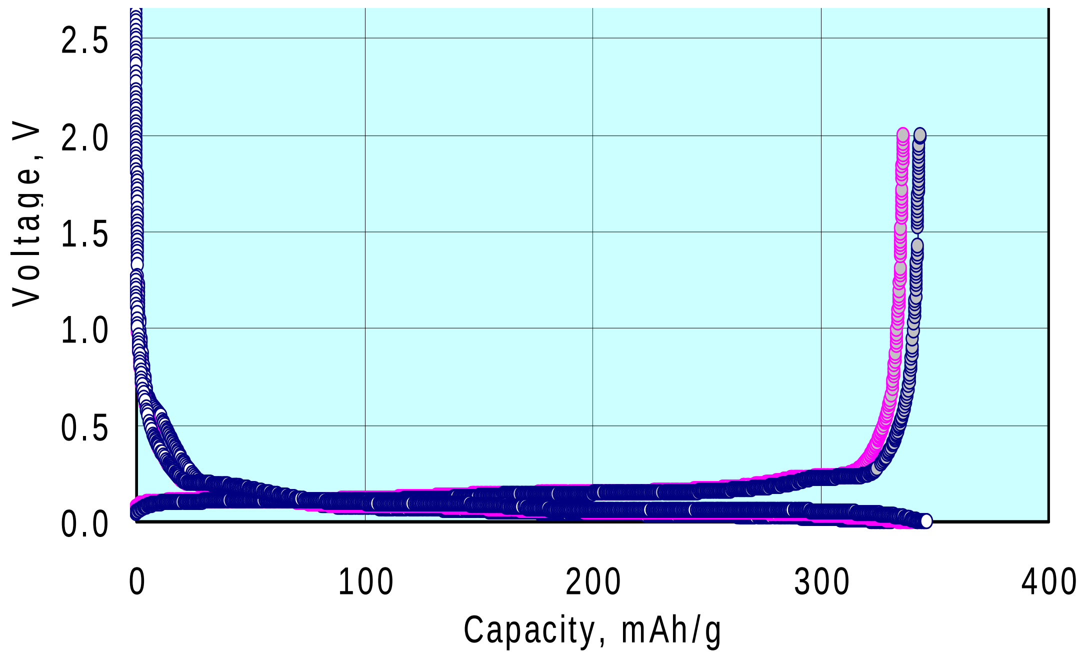


Mitsubishi Chemical's Graphite has Good Capacity

MPG: Mitsubishi Power Graphite

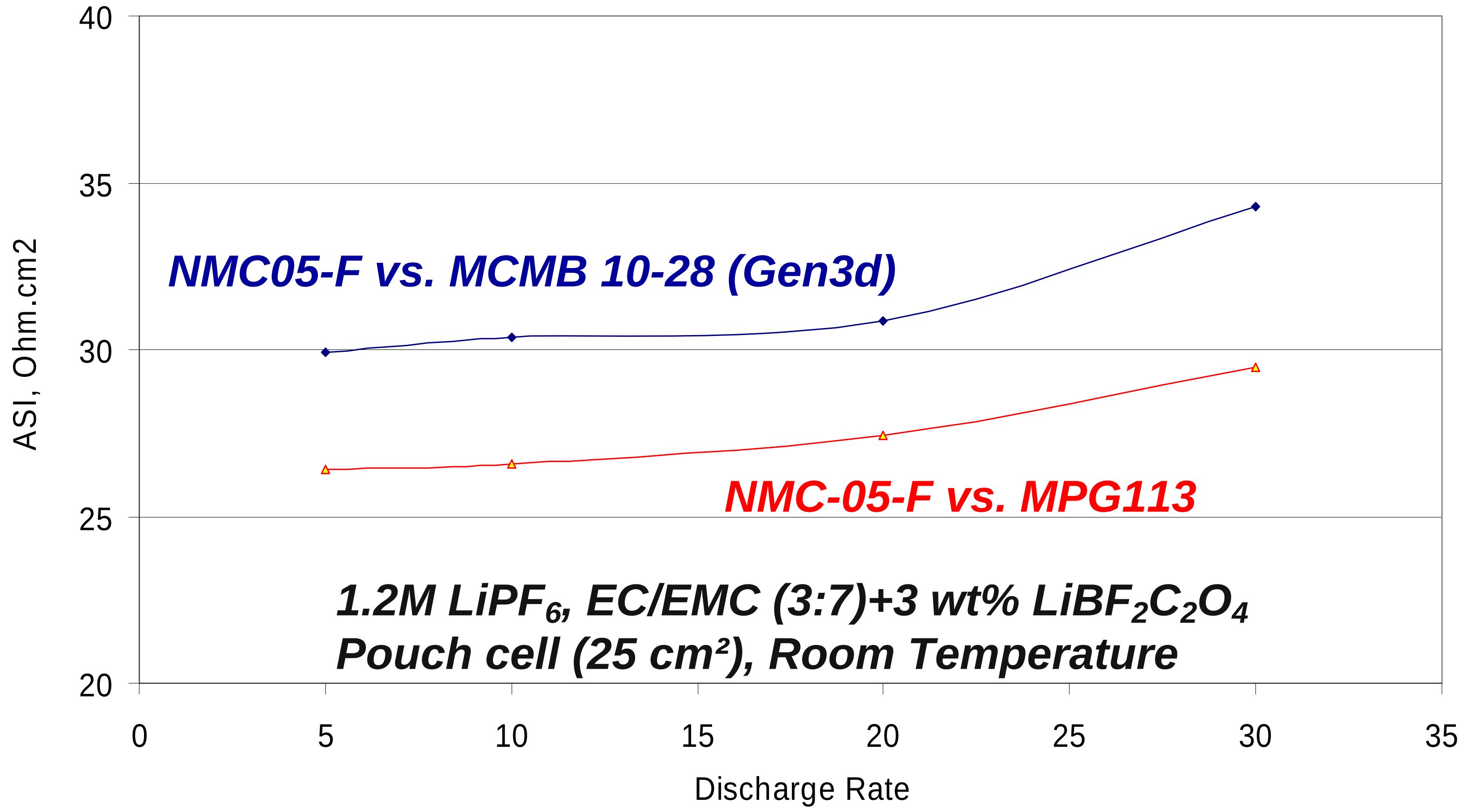
Sample	MPG 113 (synthetic)
Mean Particle Size	13.4 μm
Specific Surface Area	3.6 m^2/g
Tapping Density	1.07 g/cc

Capacity close to 350 mAh/g vs. Li



Mitsubishi Electrodes are Designed for High Power

Mitsubishi also made a cathode electrode, NMC-05-F, from $Li[Li_x(Ni_{1/3}Co_{1/3}Mn_{1/3})_{1-x}]O_2$



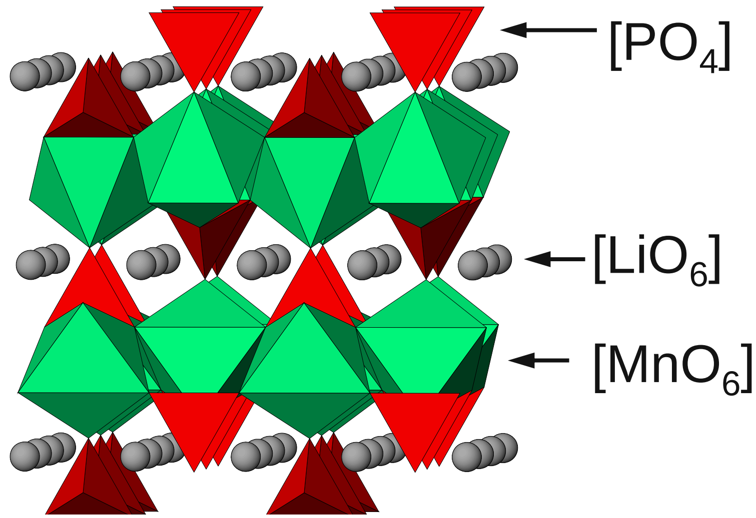
Olivine $LiMnPO_4$ as Cathode for Lithium Batteries

- $LiMnPO_4$ has a flat 4.2 V plateau, which is 600 mV higher than $LiFePO_4$, and a theoretical capacity of almost 178 mAh/g (possibility of reducing the number of cells and cost by taking advantage of high cell voltage)
- Mn^{2+} and Mn^{3+} are very stable and less oxidizing than Ni^{4+} in conventional 4 V $LiNi_{0.8}Co_{0.2}O_2$ oxide (potential for long calendar life and safety)

But!!!

- $LiMnPO_4$ has much lower electronic conductivity than $LiFePO_4$

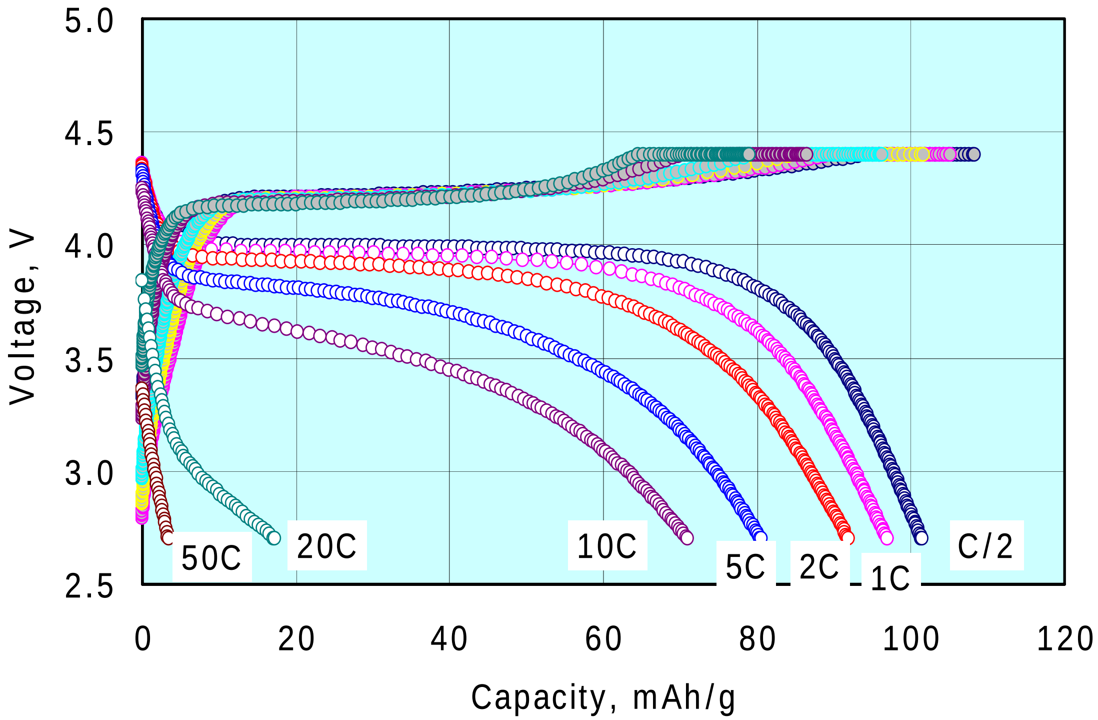
Olivine structure (orthorhombic)



HPL's $LiMnPO_4$ Cathode Shows Some Promise

Measurement	Data sheet
BET SSA	30 m^2/g
Average pore diameter	13.6 nm
Tap density	1.0 g/cm3

Vs. Lithium in 1.2M $LiPF_6$, EC/EMC(3:7)



$LiMnPO_4$ cathode has a 1st discharge capacity of 126 mAh/g vs. Li and coulombic efficiency of 83 %. More work is needed to increase the capacity.

Technology Transfer

- The nature of this work does not lend itself easily to publications or patents
- Results are made available to the DOE, USABC, and battery developers and suppliers at regular review meetings (depending on vendor agreement)

Publications (Technical Report)

- "Advanced Cathode Materials for High Power Applications", K. Amine, J. Liu, I. Belharouak, S. –H. Kang, I. Bloom, D. Vissers, and G. Henriksen, *J. of Power Sources*, Vol.146 Issues 1-2, (2005)111-115

- "Screening Report on Cell Materials for High-Power on Cell Materials for High-Power Li-Ion HEV Batteries", Technical Report No. ANL-03/16, by J. Liu, A. Kahaian, I. Belharouak, S. Kang, S. Oliver, G. Henriksen, and K. Amine (2003). *Available on-line at http://www.ipd.anl.gov/anlpubs/2003/04/46424.pdf*

Future Work

- Investigate materials from different suppliers for high power (HEV) and high energy (PHEV) application
  - Hitachi Chemical's latest batch of anode materials
  - $Li_4Ti_5O_{12}$ from Kyorix, Ishihara, and others
  - Nano-sized particles $LiFePO_4$ from Mitsui Eng. and others
- New protocol will be implemented for advanced materials evaluation that is beneficial to one or both high power HEVs or higher energy plug-in HEVs
- Continue to evaluate advanced cathode, anode, binder, and electrolyte systems as they become available from various sources

Summary

- Hitachi's surface modified natural graphite has good capacity and power capability. Full cell ASI at 10C pulse rate is less than 35 Ohm-cm^2, which meets the power requirement for HEV application
- The capacity of Hitachi's soft carbons is lower than graphite, but it has very good power capability. Full cell ASI at 10C pulse rate is less than 35 Ohm-cm^2, which meets the power requirement for HEV application
- MPG graphite from Mitsubishi Chemical has very good power capability and higher tap density. Their cathode material also has good power capability
- Manganese-based olivine from HPL is not yet ready for HEV use but advances in this area will be monitored
- ConocoPhillips' graphite materials also meet HEV power criteria
- The next step is to evaluate the thermal abuse response of these graphite and soft carbon materials

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