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Olivines for HEV and PHEV Applications

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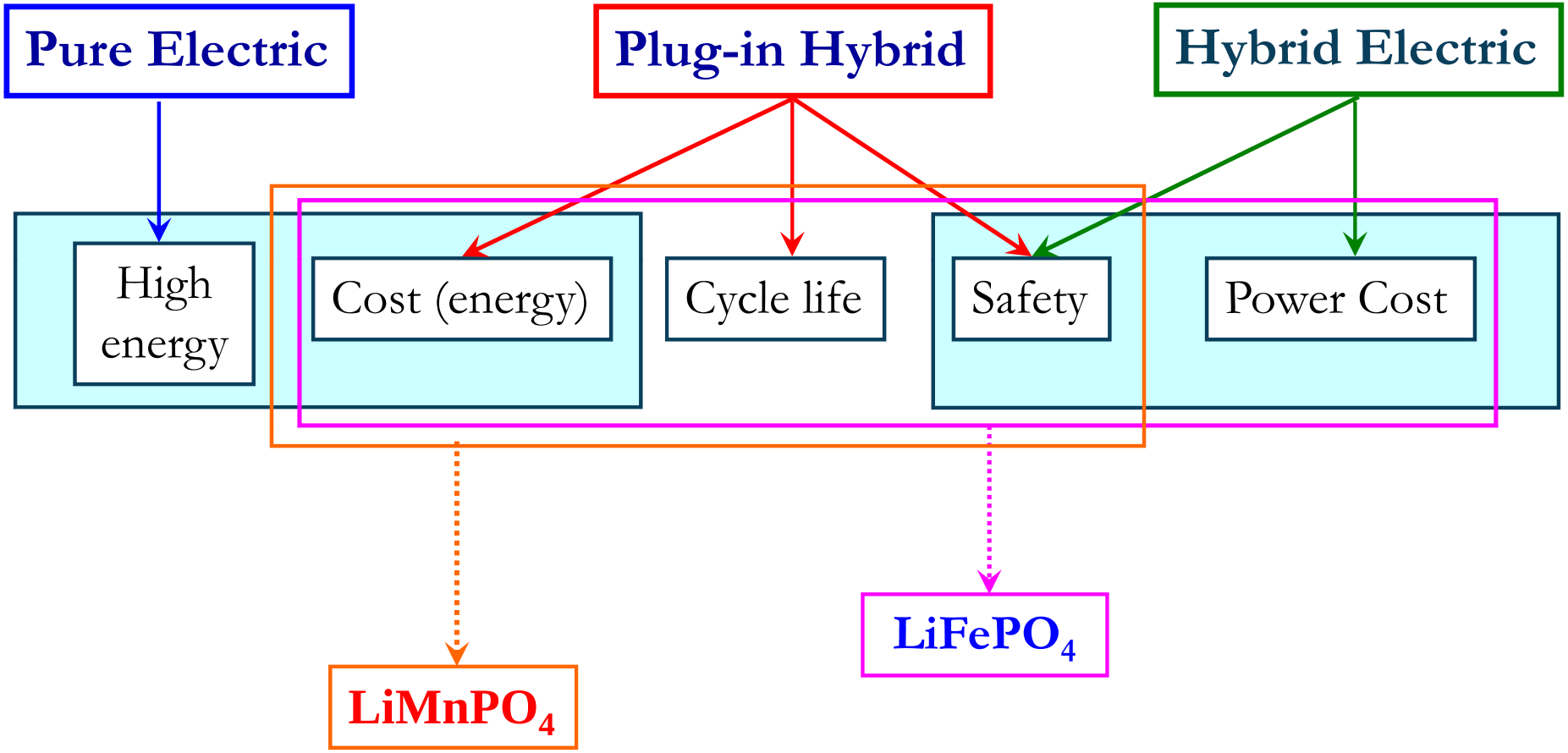
PHEV2007 Conference

November 1-2, 2007, Winnipeg, Alberta

Outline

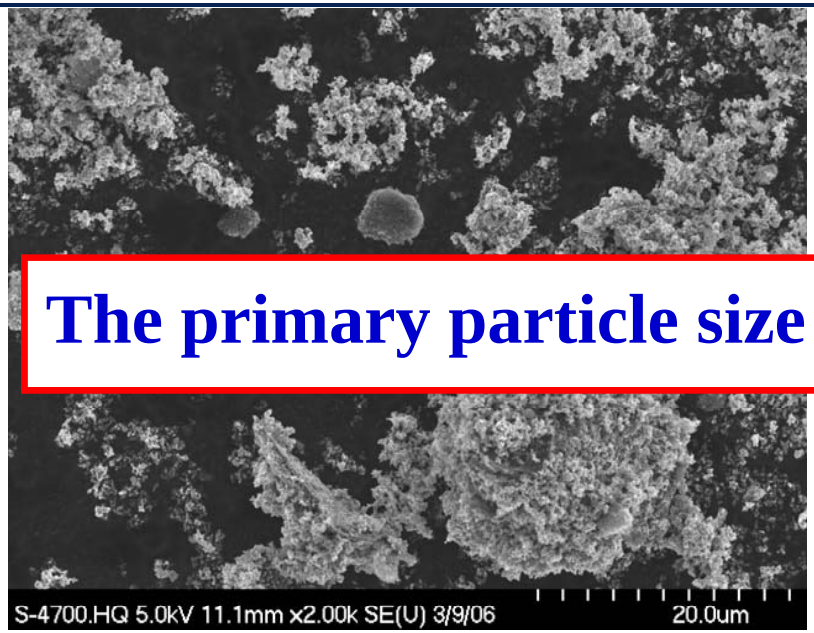
- Li-Ion system and technology choice
- Experimental part
- $LiFePO_4$ characterization with std electrolyte
- $LiFePO_4$ performance with gel polymer
- $LiFePO_4$ performance with ionic liquid
- Summary

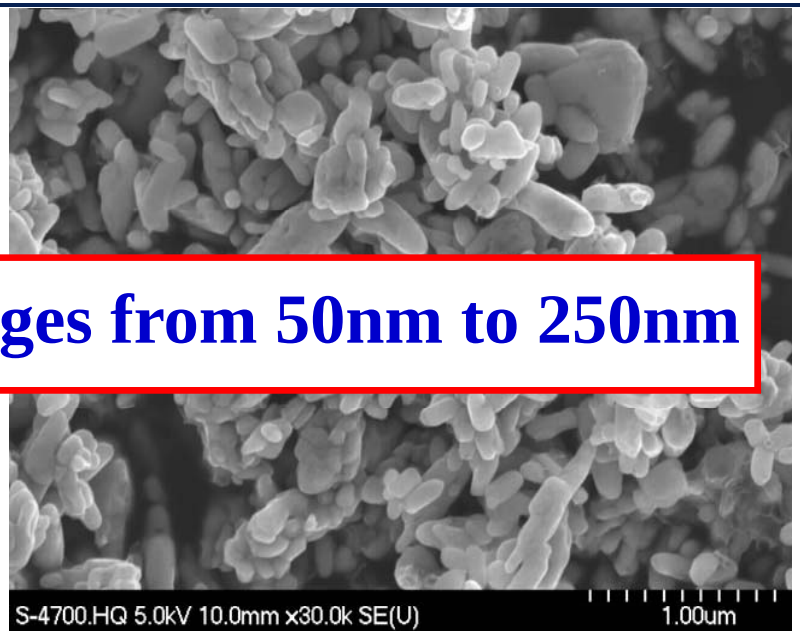
Technology choice



The barriers to commercialization of PHEVs are: batteries life , safety and cost.

Experimental

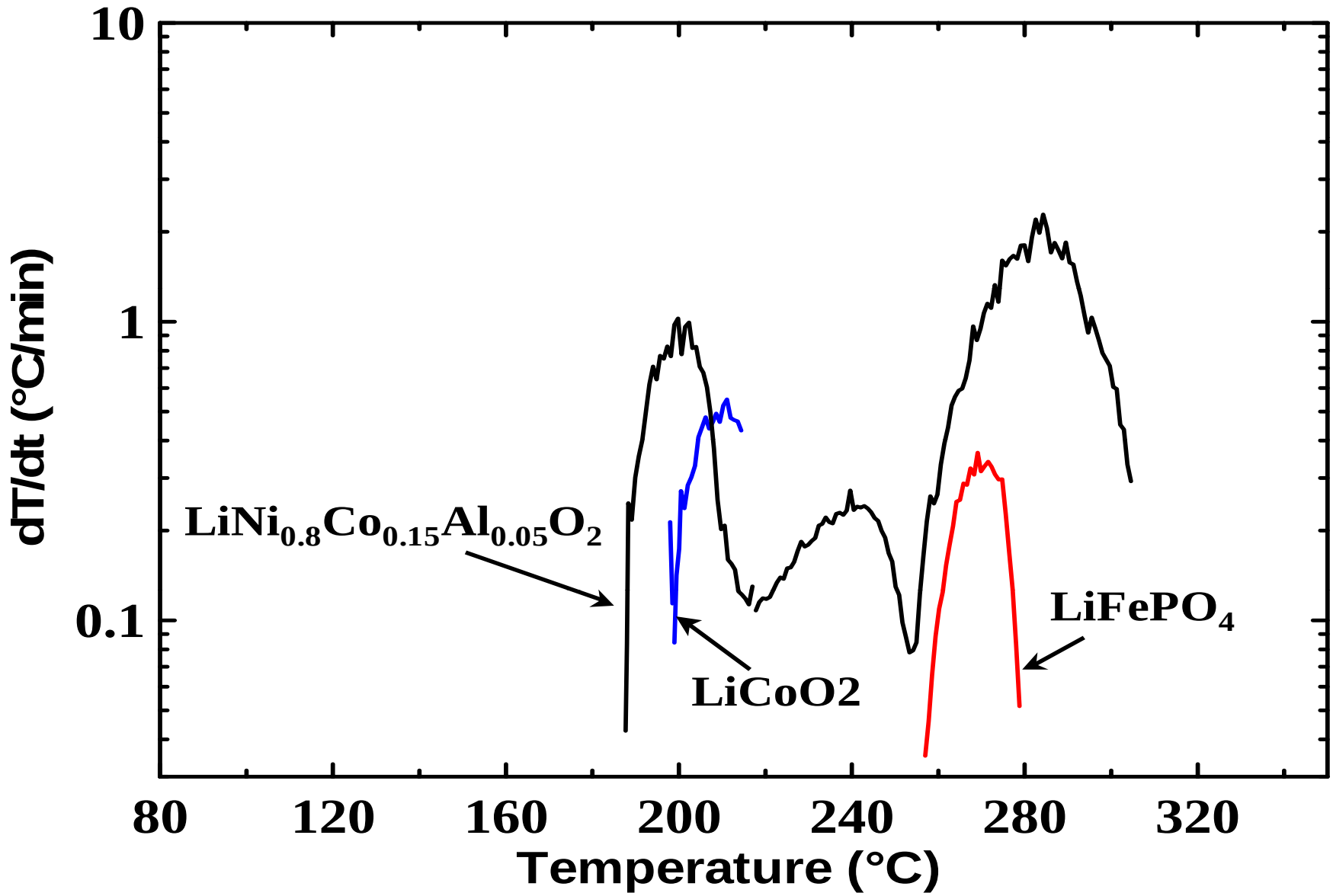




The primary particle size ranges from 50nm to 250nm

- **Laminated cell with 4cm^2 active surface area.**
- **Counter and reference electrodes: Li metal for half cell**
- **Electrolyte: 1M $LiPF_6$ in EC/DEC = 3/7**
- **Rate capability (Charge – 0.25C, Discharge – 0.1C to 40C)**
- **IL: *N*-Methyl-*N*-propyl-pyrrolidinium bis(fluorosulfonyl) imide (Py13[FSI]), EMI(FSI), Salts: LiFSI or $LiPF_6$**

ARC test on cathode materials



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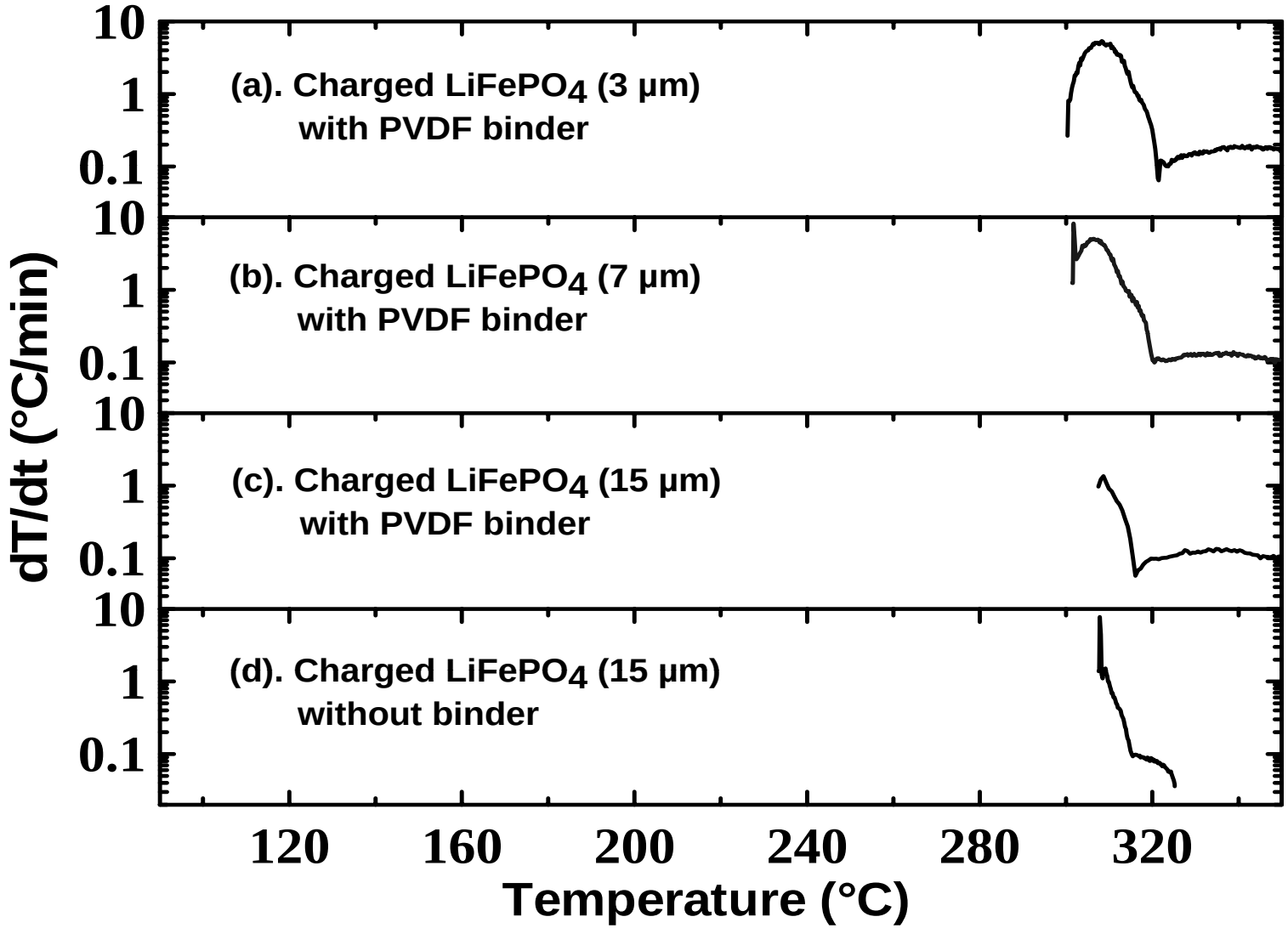
$LiFePO_4$: particle size effect on safety



No particle size effect on the safety of $LiFePO_4$

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Test data from Junwei Jiang and Jeff Dahn, $LiFePO_4$ from Hydro-Québec

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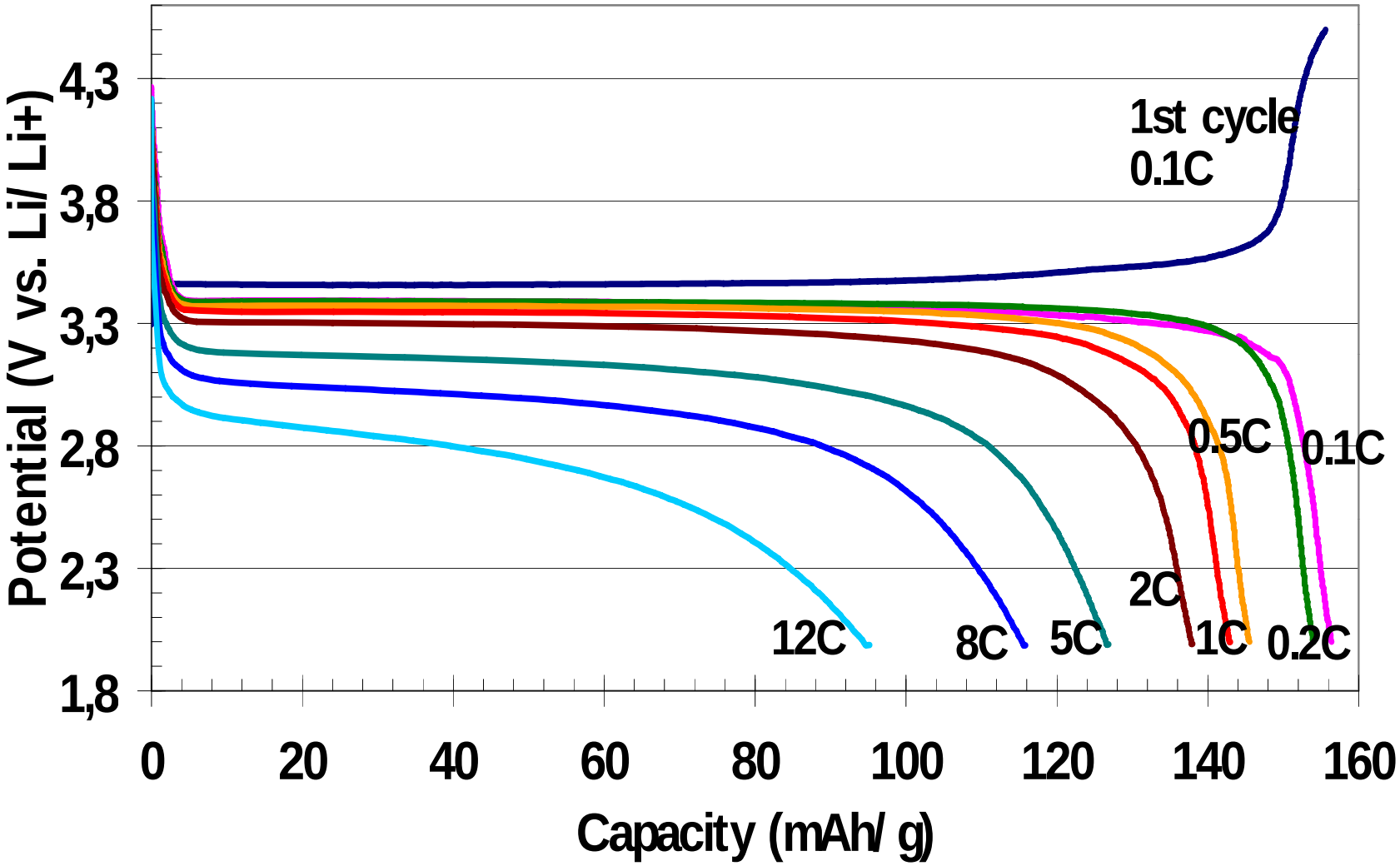
$LiFePO_4$: Rate Capability

25°C



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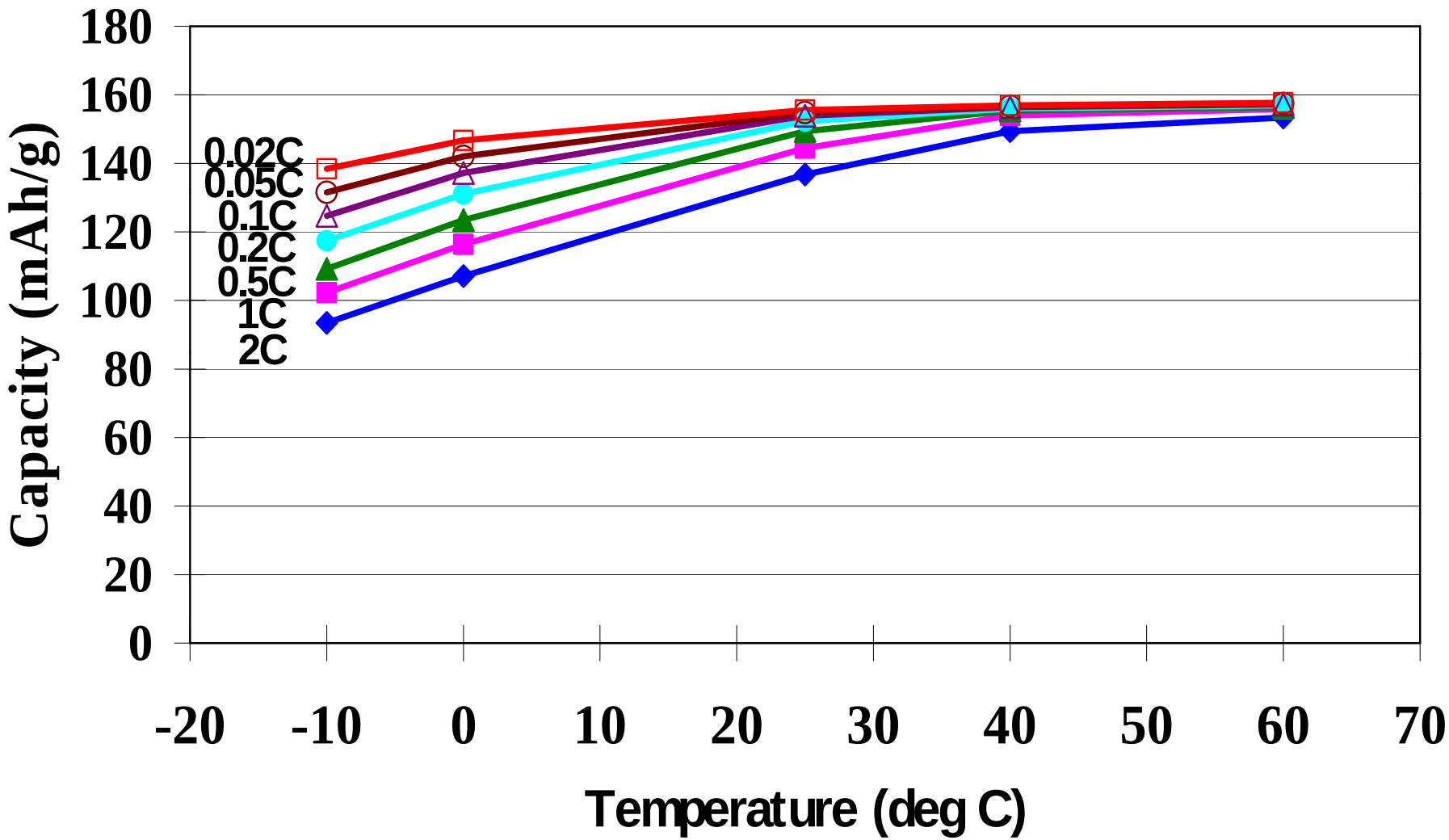
$LiFePO_4$: Temperature Effect



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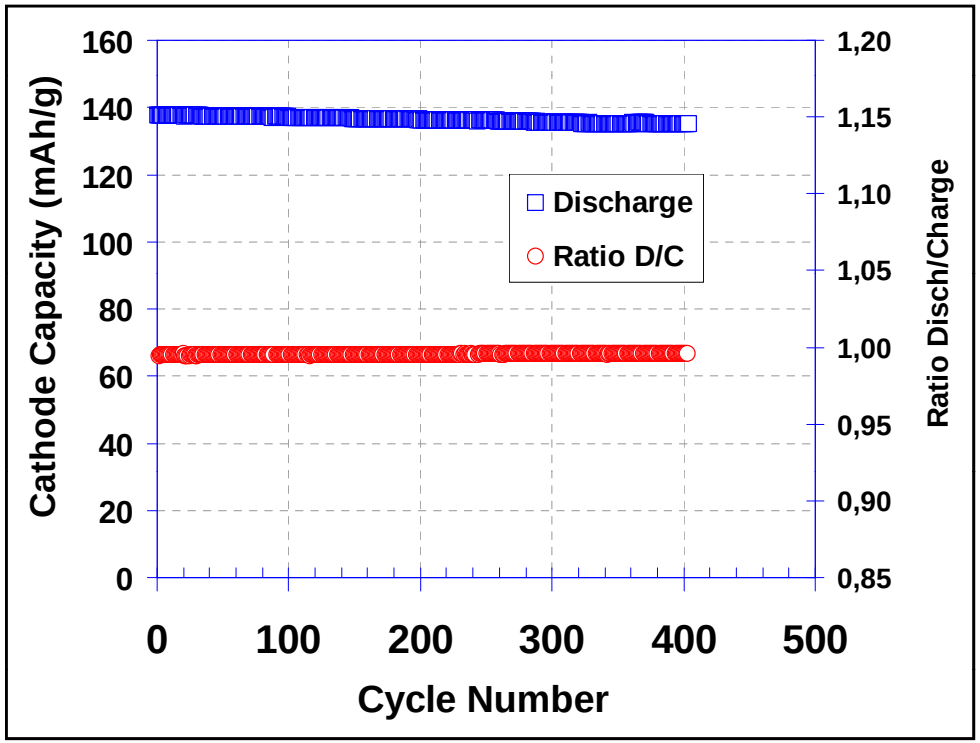
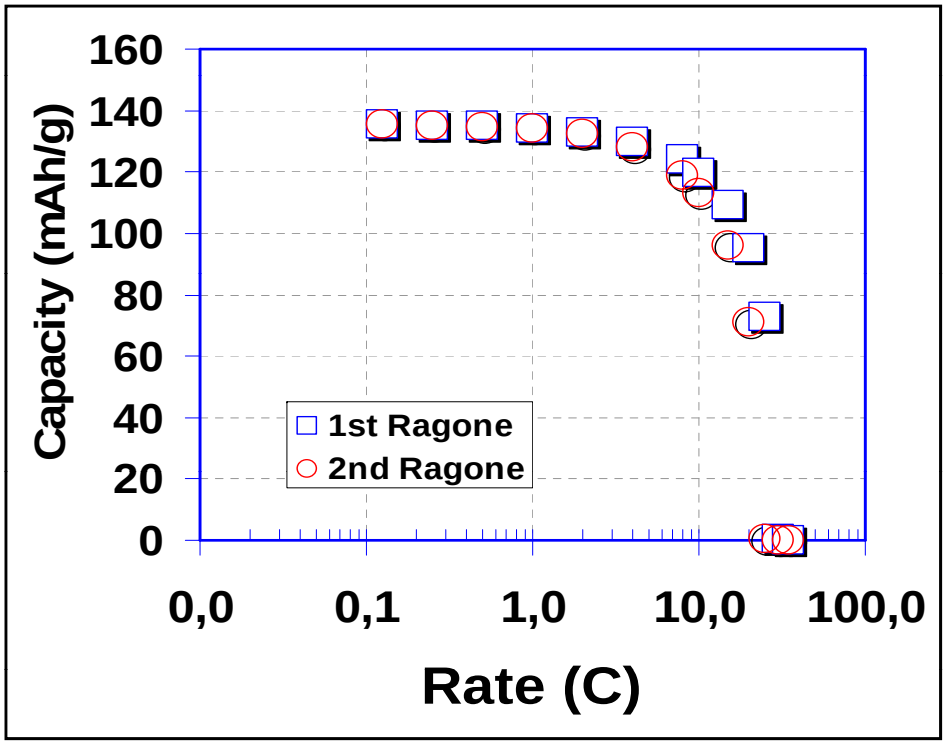
$LiFePO_4$: 60°C cycling

T= 60°C, Ch: C/4, Disc: 1C



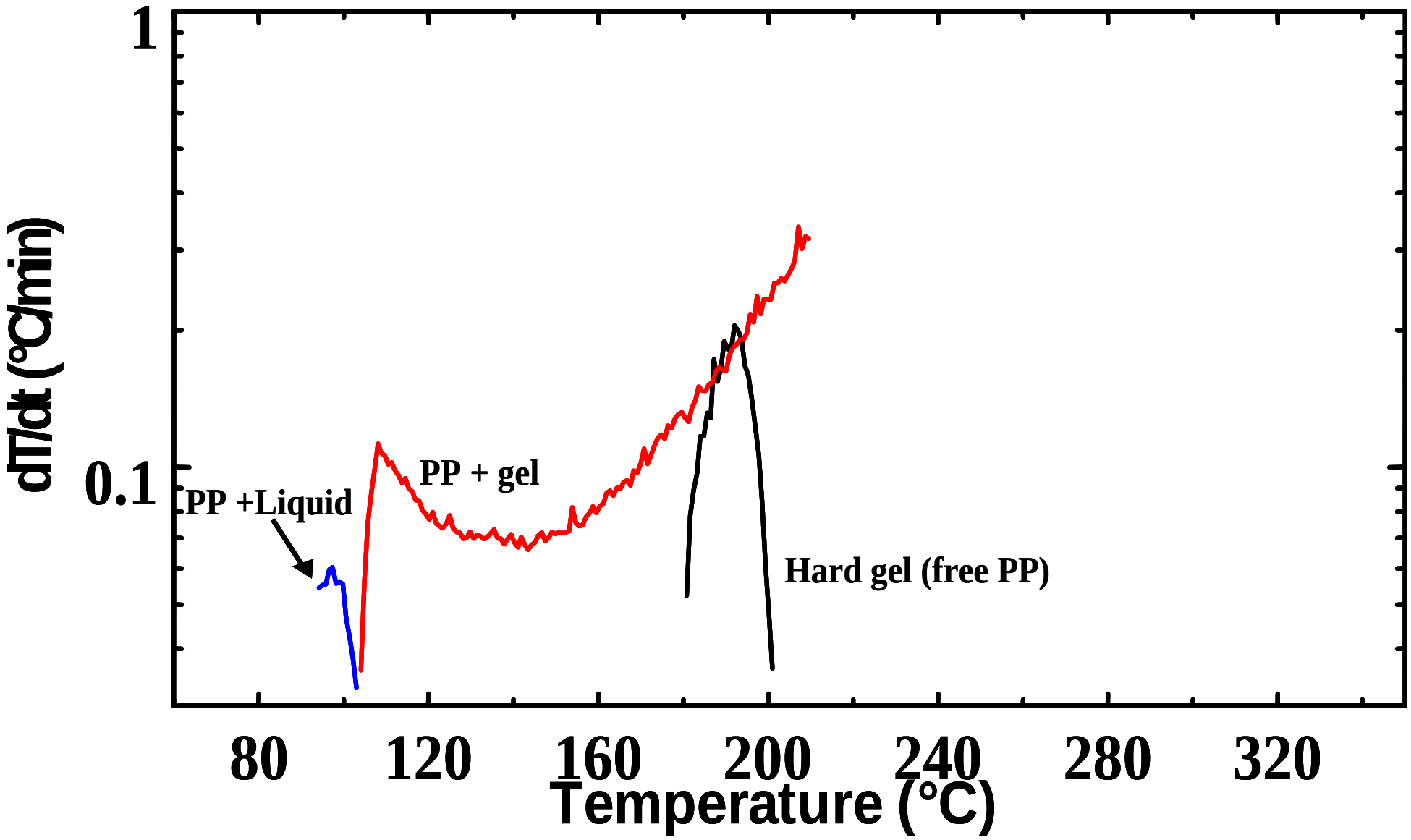
T= 60°C, Ch: C/4, Disc: # C



-After 400 cycles, Q=98.2% of the rated capacity.
-The coulombic efficiency remains constant during cycling at 99.6%.
-The capacity decreased only by 0.004% /cycle.

At 10C: 120 mAh/g
At 25C: still delivers 73 mAh/g

ARC Test : gel vs. liquid electrolyte



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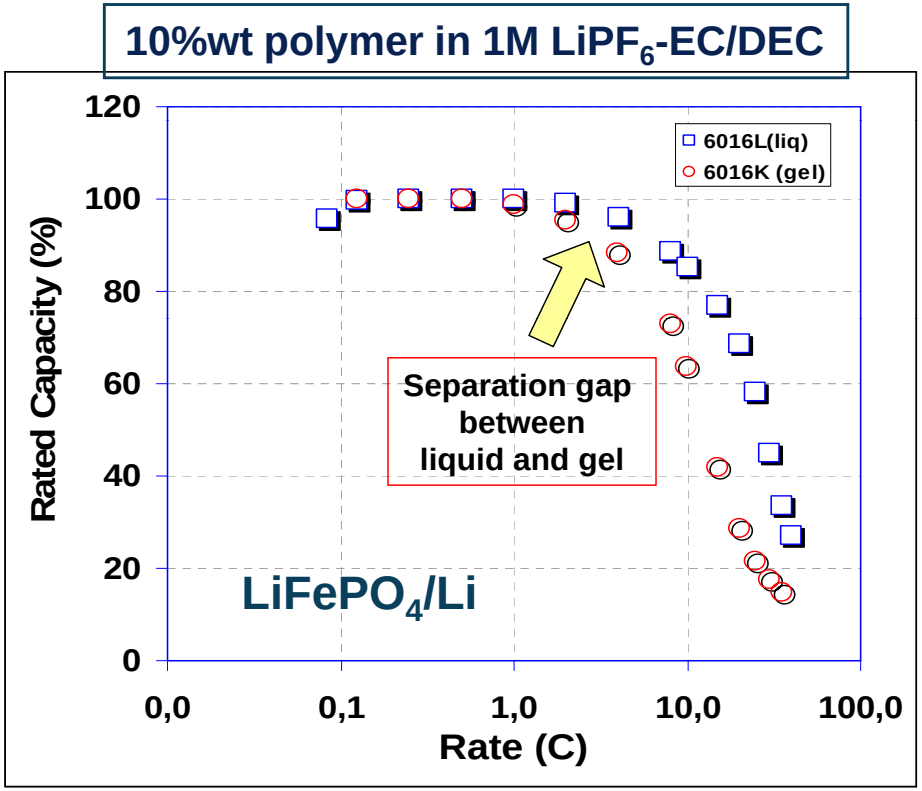
Gel Electrolyte

- No free liquid in the cell
- Cross linking reaction takes place only by heating at 60°C or even at 25°C(20h).
- Cell assembling process is similar with that of liquid electrolyte cell.
- Resulting stable chemical gel even at higher temperature.



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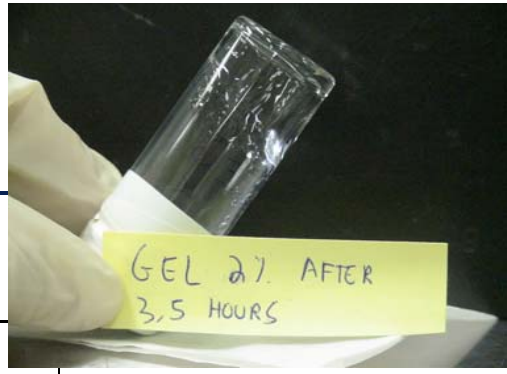
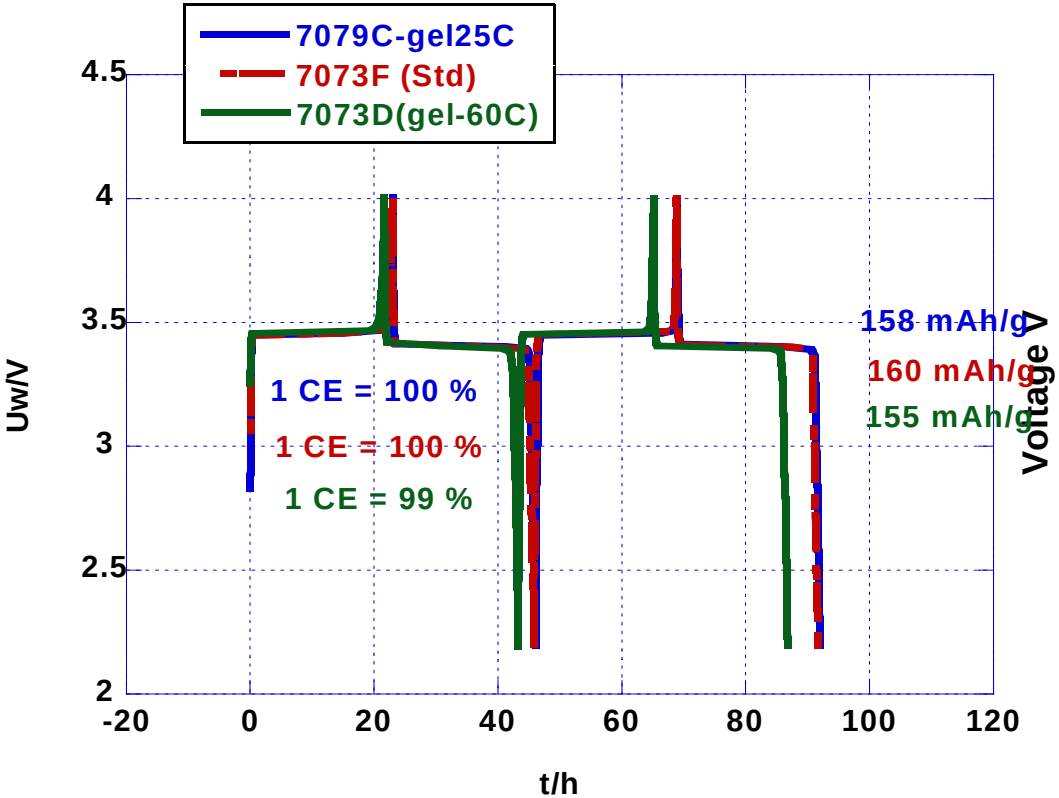
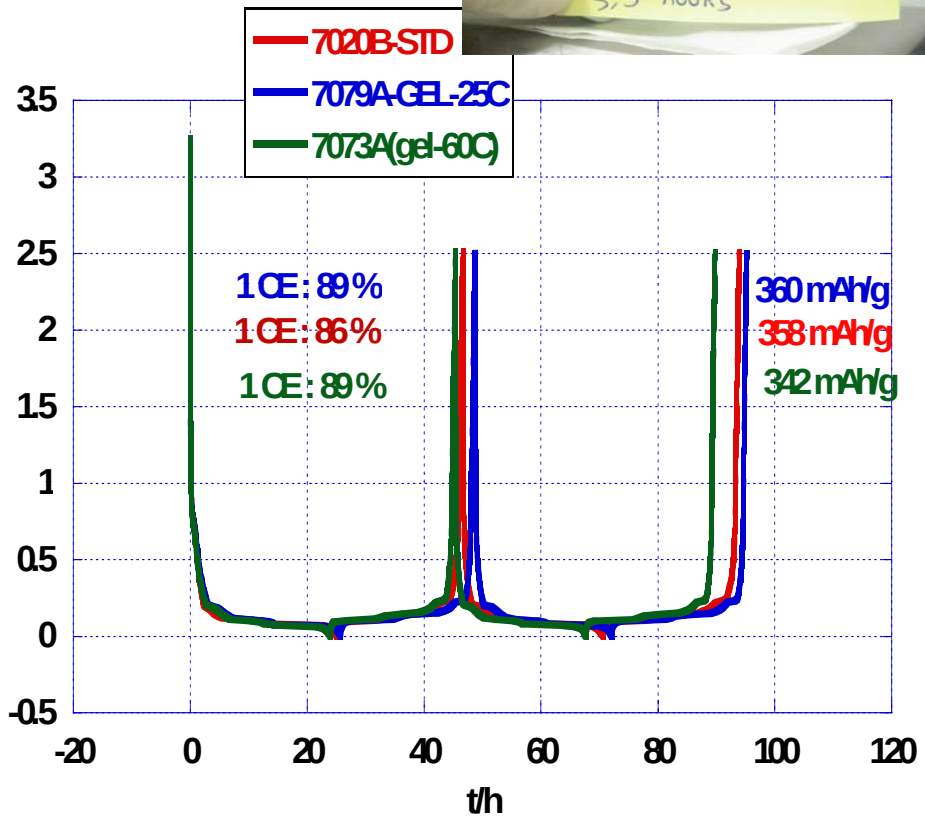
$LiFePO_4$: New gel electrolyte



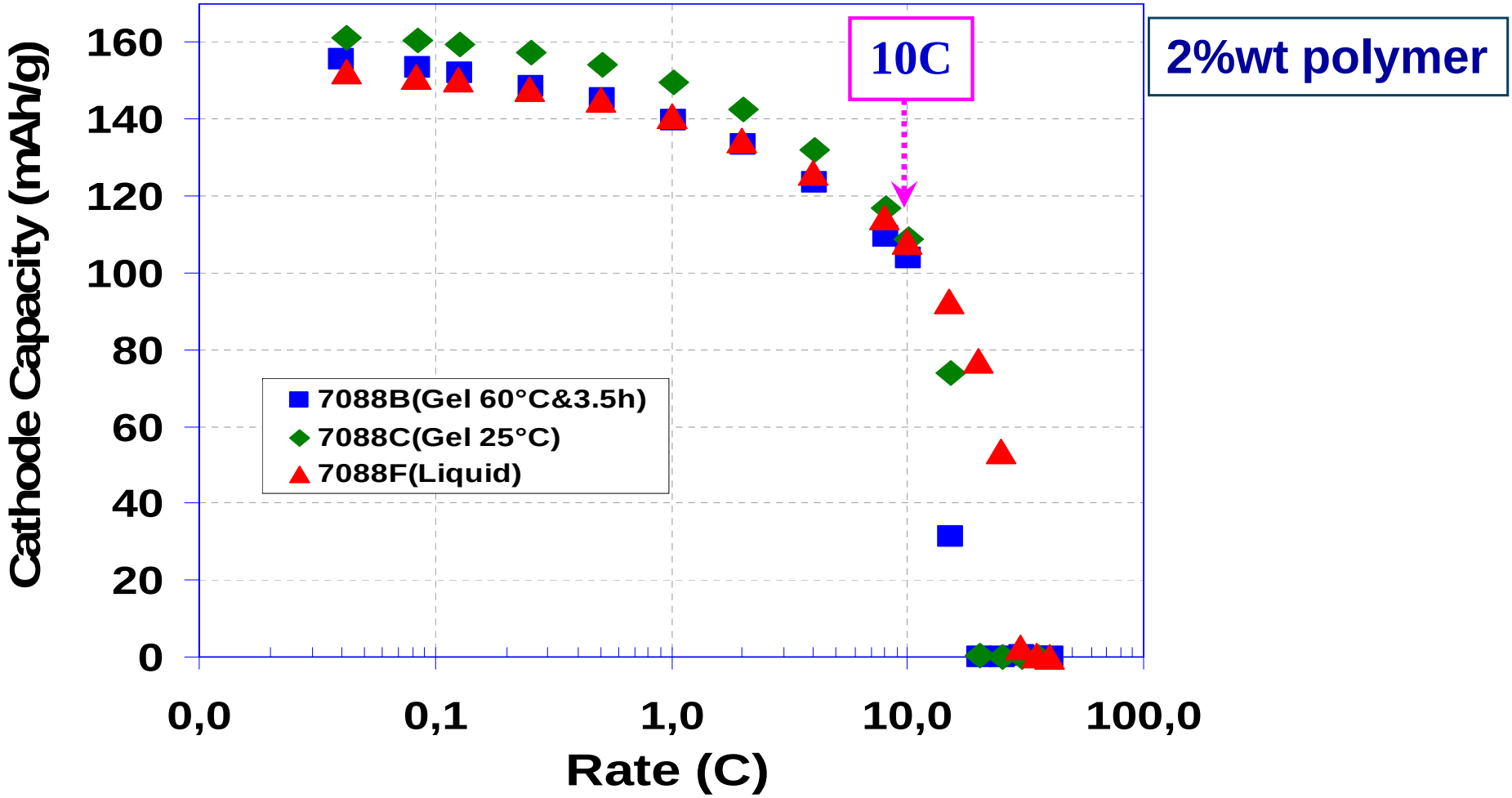
2%wt polymer





- High first coulombic efficiency, with the gel polymer.
- Gel formed at 60°C gives lower reversible capacity.
- Gel formed at 25°C shows the a comparable performance as standard electrolyte.

$LiFePO_4$: New gel electrolyte

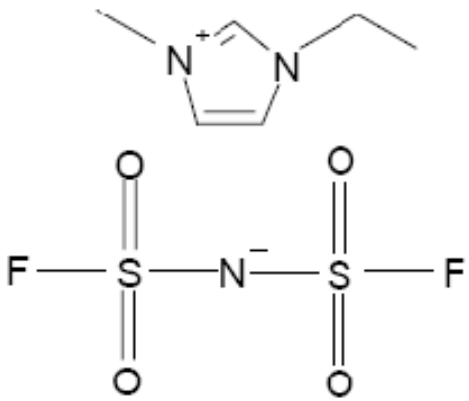


- At low rates, gel polymer perform as well as liquid electrolyte.
- Liquid and gel (formed) at 25°C cells have comparable performance up to 15C discharge rate.

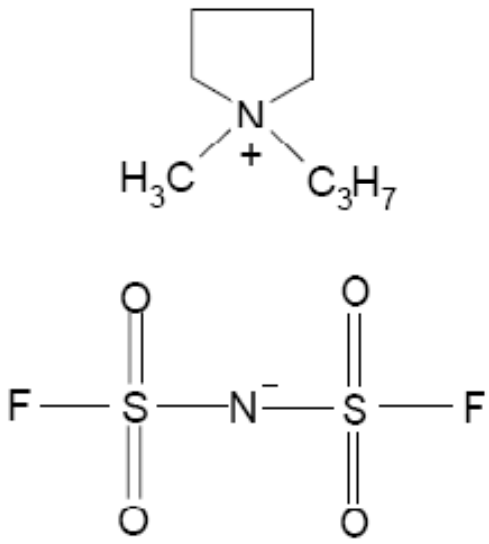
Room Temperature Ionic Liquid (RTIL)

- No vapor pressure & Good electrochemical stability
- Solvent for many salts and polymers
- Good resistance to oxidation > 5V vs. Li°
- Cost still high, some problem on passivation layer (SEI)
- Combination with Polymer:

  Shape flexibility & Decrease of IL content

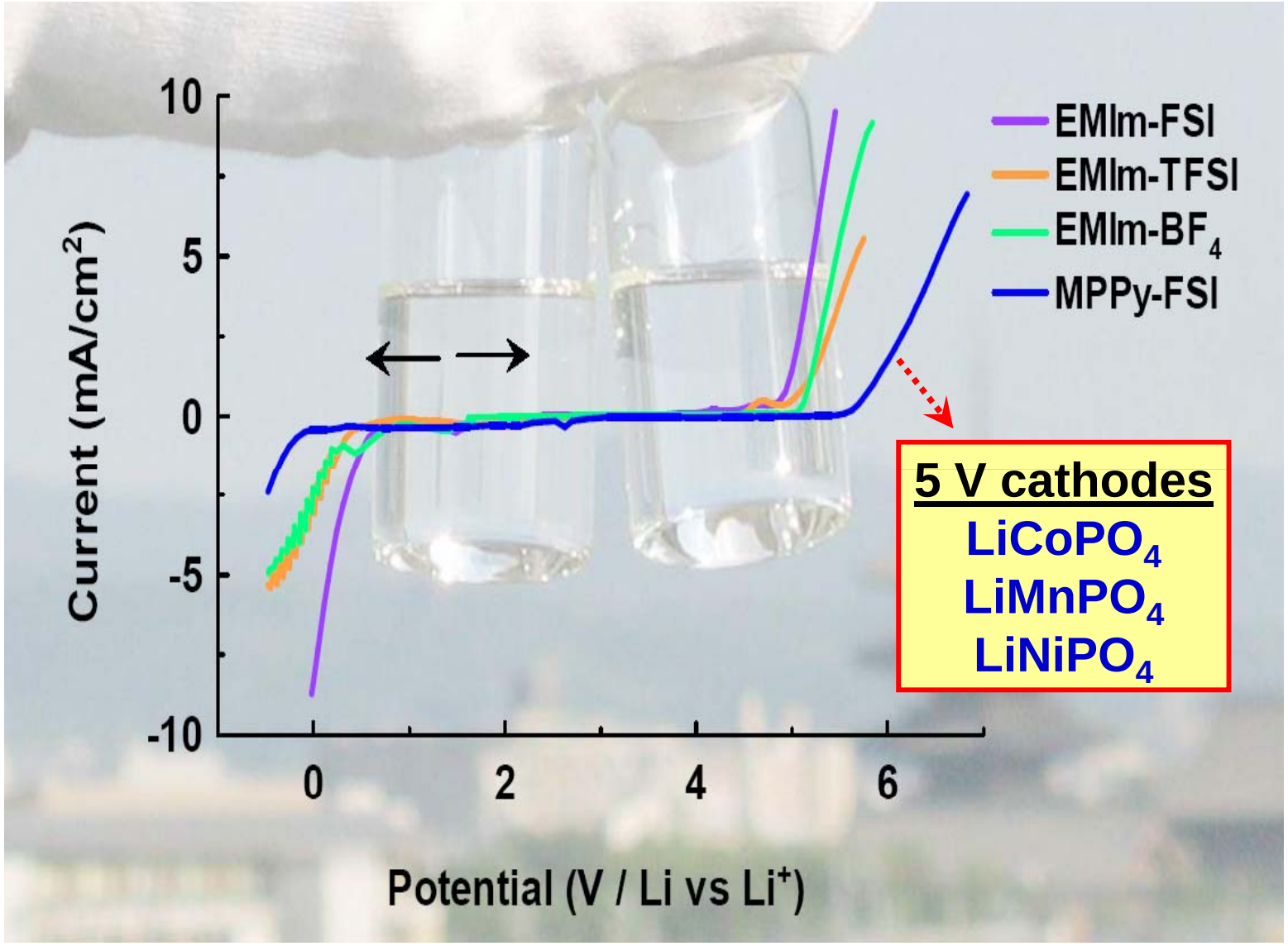


(a) EMI-FSI

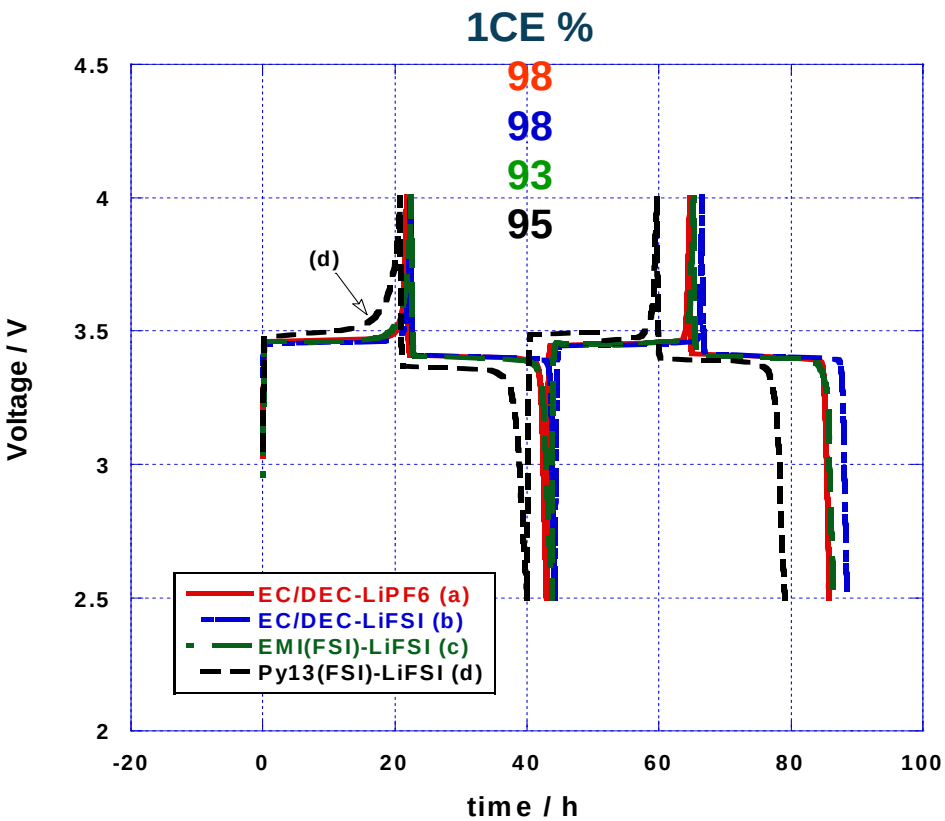


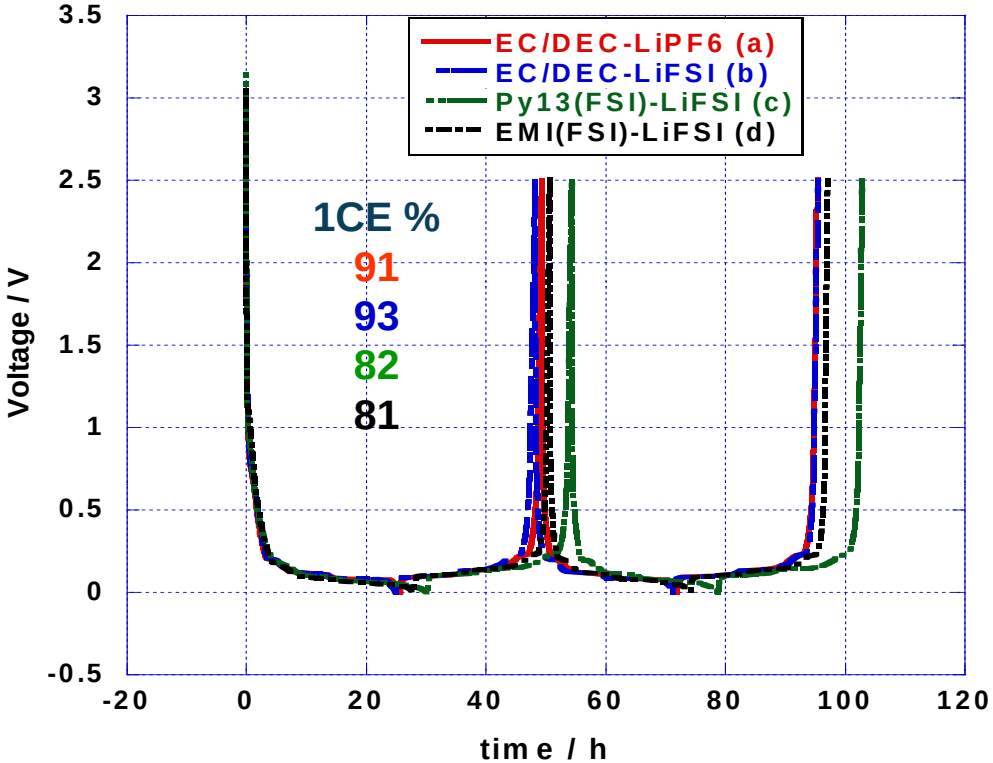
(d) Py13-FSI

ILs stability



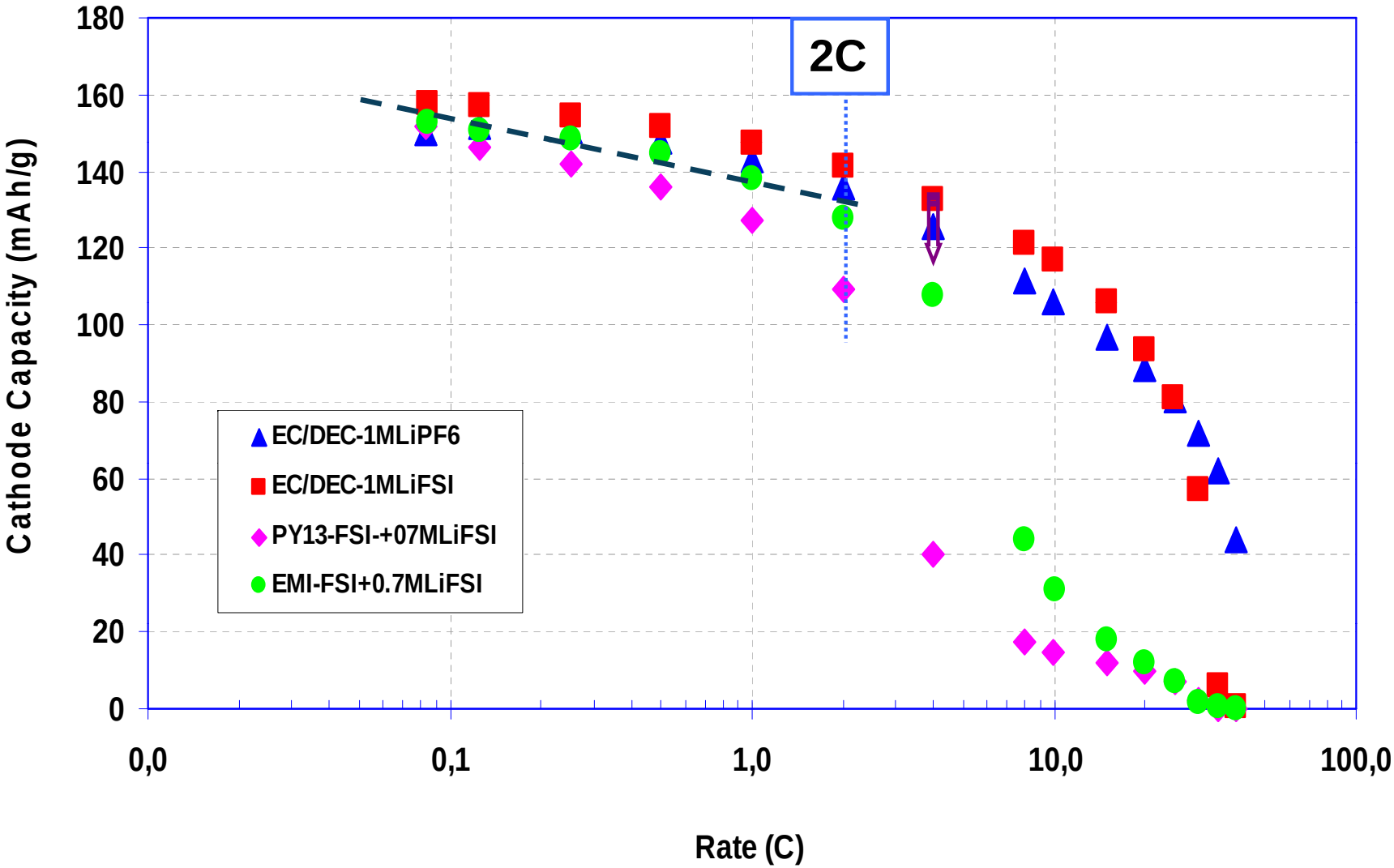
Ionic liquid & LiFSI





- FSI-ionic liquid is well adapted for $LiFePO_4$ cathode and graphite anode.
- ICL is higher when ionic liquid is used as electrolyte.
- Reversible capacity with ionic liquid is comparable to liquid electrolyte.

Ionic liquid & LiFSI ($LiFePO_4$/Li)



- LiFSI salt shows very promising data 115 mAh/g at 10C rate.
- Ionic liquid shows acceptable performance until 2C rate.

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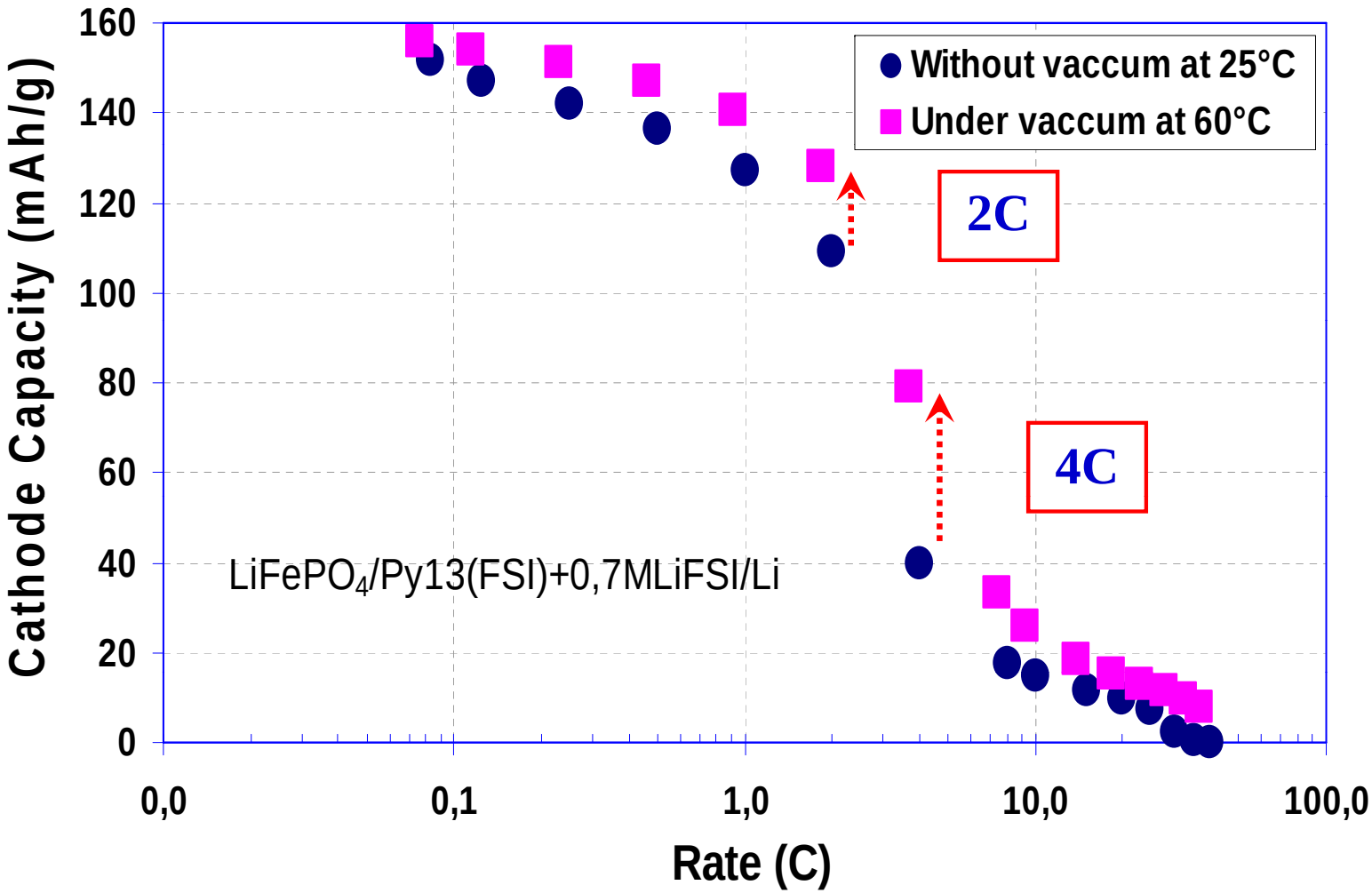
Vacuum & temperature effect on the IL



Vacuum and temperature have improved the cell performance

Summary

- $LiFePO_4$ material shows promising result on cycling and power with nano-particles (50-250nm) even at 60°C.
- At -10°C, 138mAh/g can be obtained from LiFePO4 cells at discharge rate of 0.02C. However, improvement in the high rate capacity at low temperature is still needed (only about 90mAh/g at 2C at -10°C).
- $LiFePO_4$ has demonstrated good performance with the gel and with IL (intermediate rates).
- Safety must be the first priority with large Li-ion batteries for transportation application; then the configurations:
  - graphite/Gel polymer/ $LiFePO_4$ and
  - graphite/Py13(FSI)-LiFSI/ $LiFePO_4$

  may be considered as potential choice for capacity and safety battery.
- Lithium-ion $LiFePO_4$ is considered the most commercially viable chemistry for PHEVs – due to the potential for power densities and acceptable energy and safety.
- Further improvements are needed before a larger market penetration of HEVs and PHEVs can take place.