Hydro Québec

Institut de recherche

Low-Cost Graphite and Olivine-Based Materials for Li-Ion Batteries

K. Zaghib

Hydro-Québec (IREQ), 1800 Lionel-Boulet
Varennes, QC, Canada, J3X 1S1

BATT Review Meeting

This presentation does not contain any proprietary or confidential information"

Collaboration BATT :
V. Battaglia
S. Venkat
J. Goodenough

February 25 – 28, 2008

Collaboration:
C. Julien (U Paris 6)
S. Chiaki (Showa Denko)
M. Gauthier (Phostech)

Outline

- **PURPOSE OF WORK**
  - Identify suitable graphite materials for anodes that meet the requirement for low cost and long cycle life.
  - Fabricate half cells (Li/graphite) and Li-ion (graphite/olivine) cells by optimizing parameters:
  - Li-graphite anode half cells and Li-ion cells by using:
    - PVDF vs. WSB
    - Olivine
- **BARRIERS**
  - Low energy and poor cycle/calendar life
- **APPROACH**
  - Fabricate electrode coatings based on low-cost graphite and olivine.
  - Evaluate MCMB graphite, which has demonstrated a stable SEI layer, as baseline anode material.
  - Optimize anode coating processes with new carbons that have different physical characteristics by identifying the suitable coating parameters that must be used.

Summary of Reviewers' Comments from BATT Merit Review

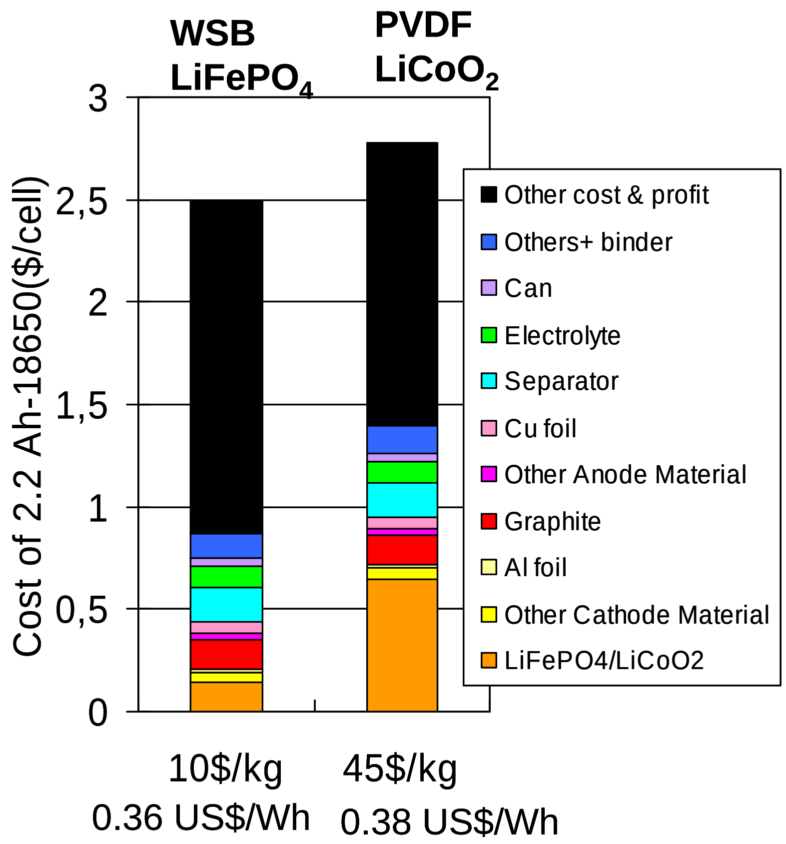
- Develop WSB , laminate Li ion cell with high rate capacity.
- Assess the cost and performance of the SOA LiFePO4, gel electrolyte and WSB and plan to improve over existing technology.
- De-emphasize gel work and emphasize range of binders (elastomers) available.
- Work on WSB should be supported

Response to BATT Merit Review Comments

- HQ developed WSB processing technology for cathodes and anodes that are very promising compared to PVDF binder

- Li-ion cells with graphite and olivine electrodes with WSB and gel electrolyte were successfully cycled (400 cycles Li/LFP at 60 °C)

- WSB will be evaluated with olivine and alternative graphite materials in Li-ion cells



Approach

- Meaningful analysis of SEI layers on graphite electrodes in the BATT program involves HQ efforts to:
  - prepare laminates anode films and powders, and supply them to investigators in topic 3a involved with SEI analysis using different techniques.
  - utilize in-situ impedance measurements to investigate the SEI layer on the anode
- Continue effort to identify benefits of WSB compared to PVDF in the anode
- Investigate performance of alternative anode materials in cells with the olivine cathode
  - prepare laminate cathode films and powders and supply them to BATT investigators for evaluation

Graphite Anodes for Li-Ion Cells

MCMB graphite

1. A good and stable SEI
2. Spherical shape
3. High cost

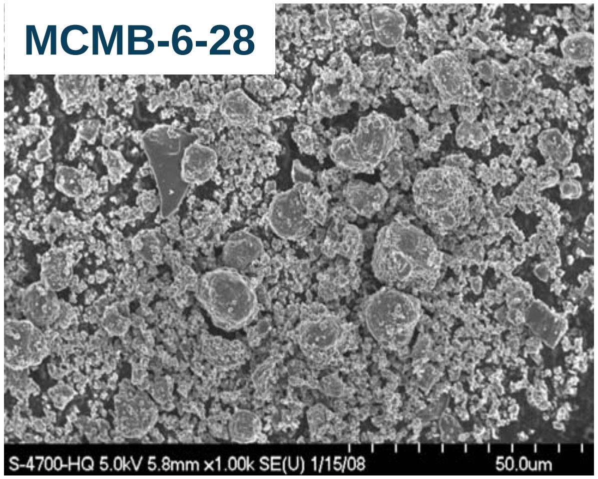
Osaka gas company stopped production

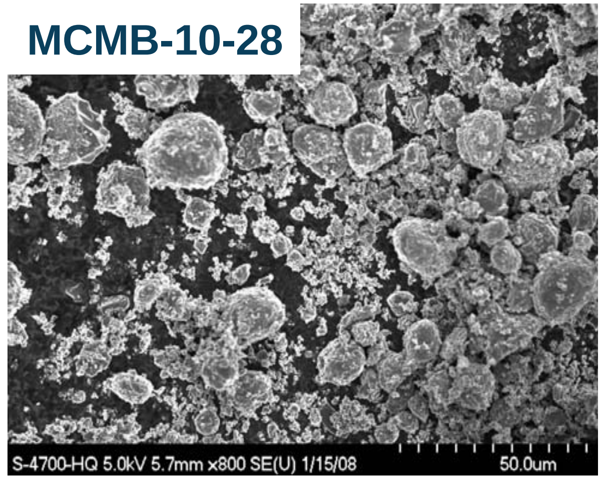
An alternative graphite is needed

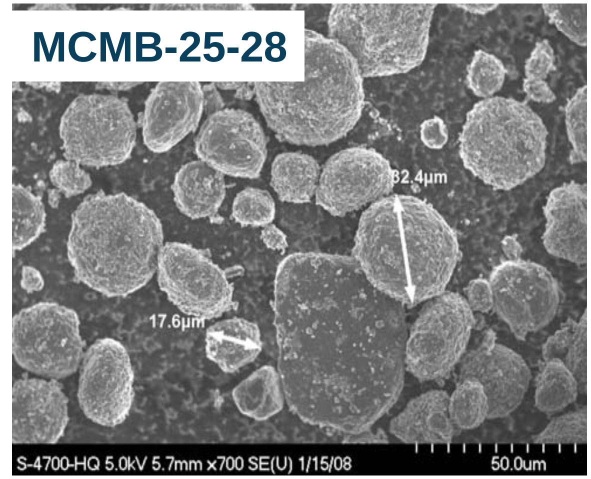
- OMAC, Osaka Gas Company
- SNG12, HQ

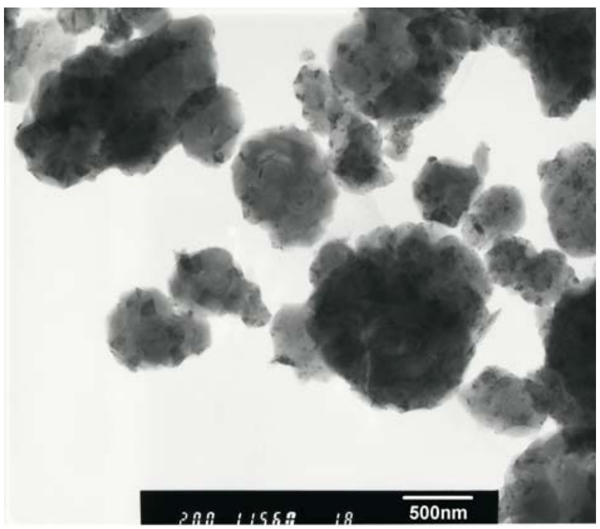
Pilot Coating with PVDF and WSB
Coating with and without carbon additive (AB, VGCF)

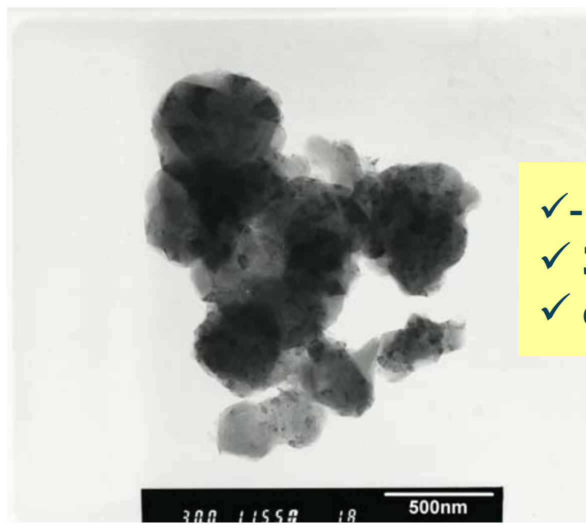
MCMB Characteristics





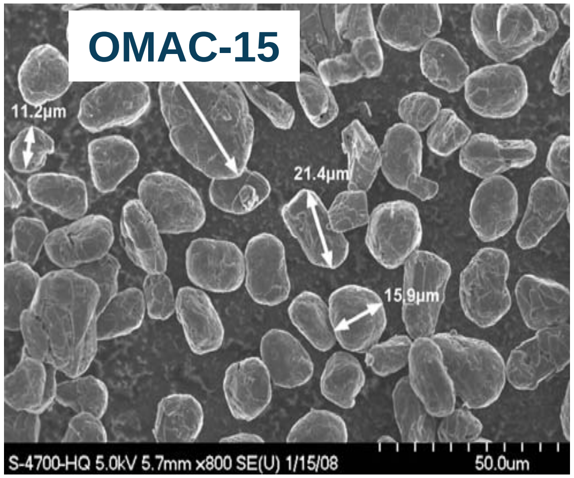


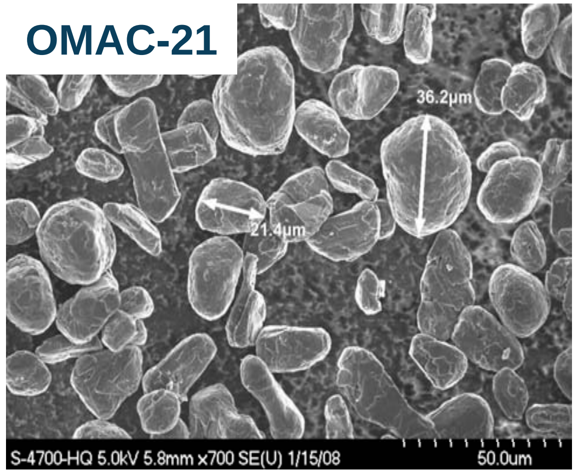


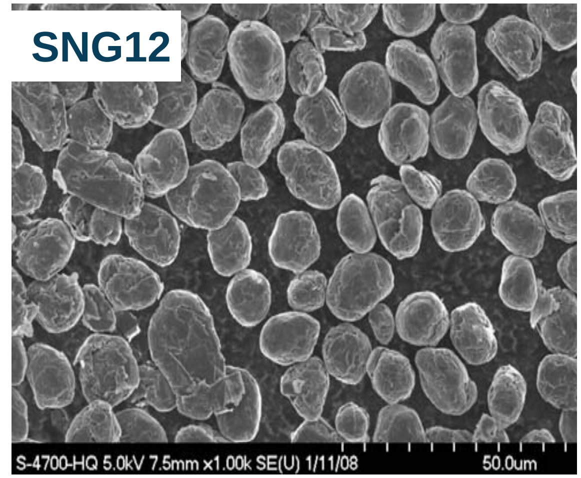


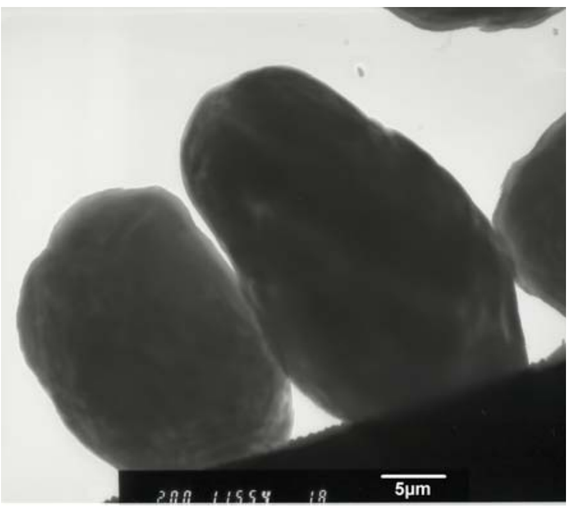
✓- MCMB has spherical shape
✓ 3D is suitable for efficient
✓ coating and high-rate applications

Alternative graphites

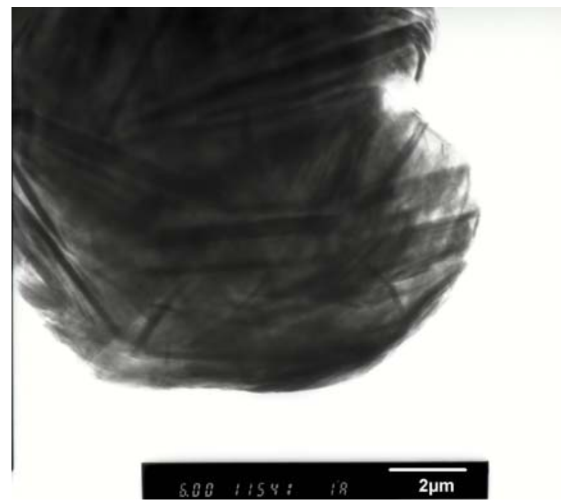




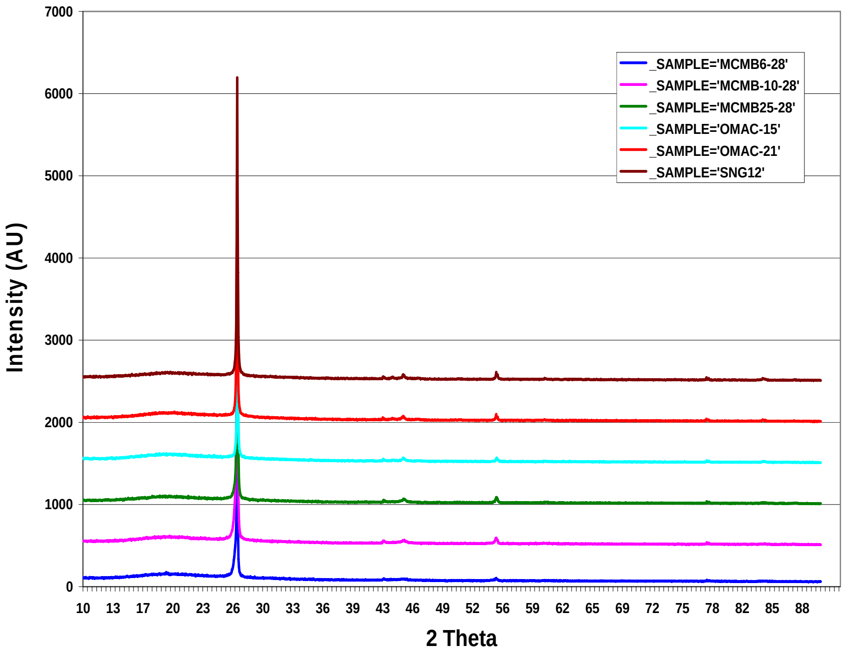


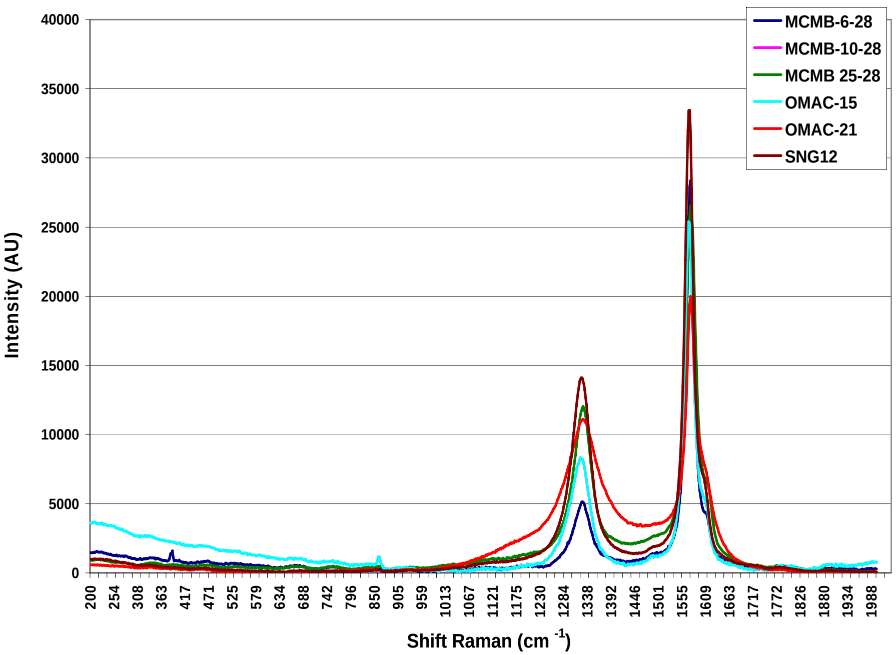


- ✓ **Alternative graphites have similar 3D shape as MCMB**



Graphite Analysis by XRD and Raman Spectroscopy



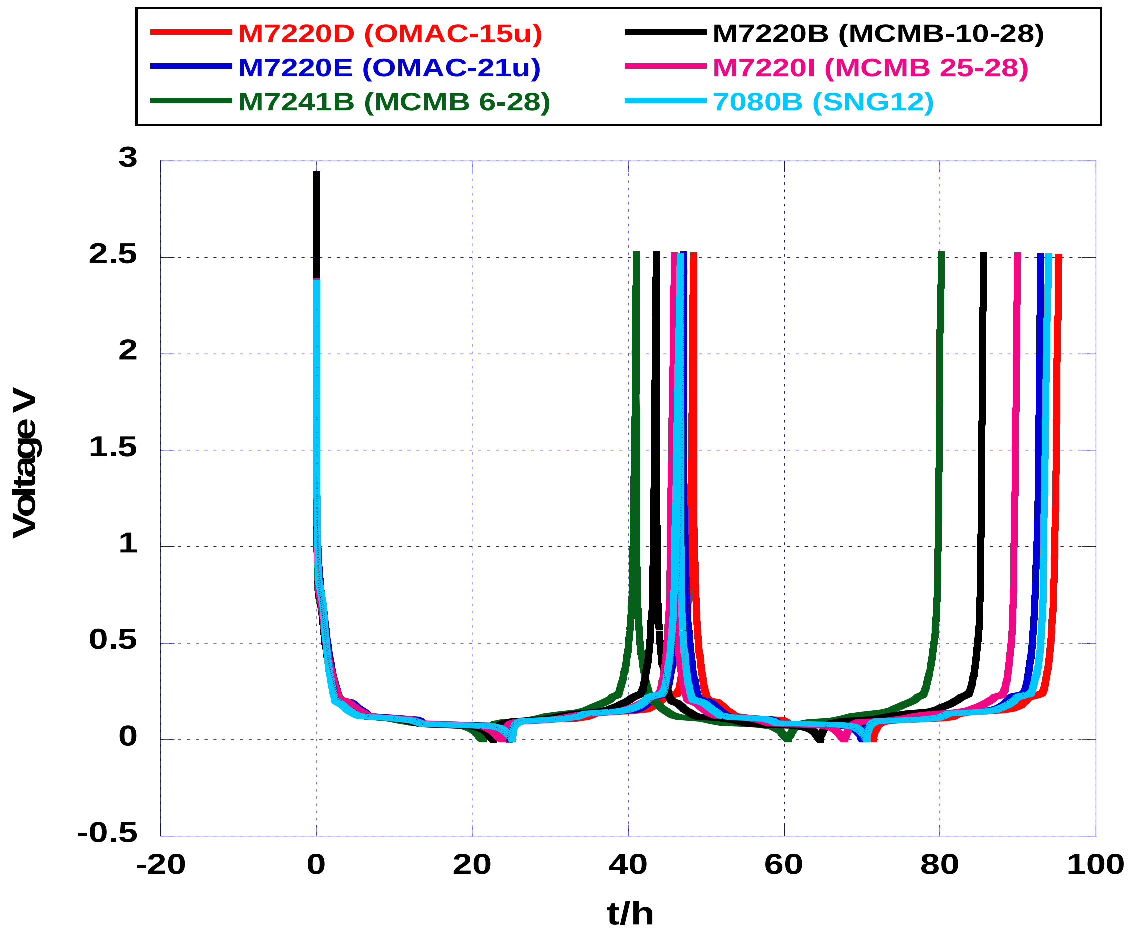


✓ **These carbons are highly graphitized with d002 = 0.335 nm**
✓ **MCMB6-28 has the lowest ratio D/G and OMAC-21 has the highest ratio**

Li/Electrolyte/Graphite (PVDF)

Discharge/Charge: C/24
1M $LiPF_6$-EC-DEC

Sample	1st CE (%)	2nd CE (%)	Rev. Cap (mAh/g)
MCMB-6-28	92	100	295.3
MCMB-10-28	92	100	326.9
MCMB-25-28	92	100	334.0
OMAC-15	96	100	364.9
OMAC-21	93	100	356
SNG12	86	97	370

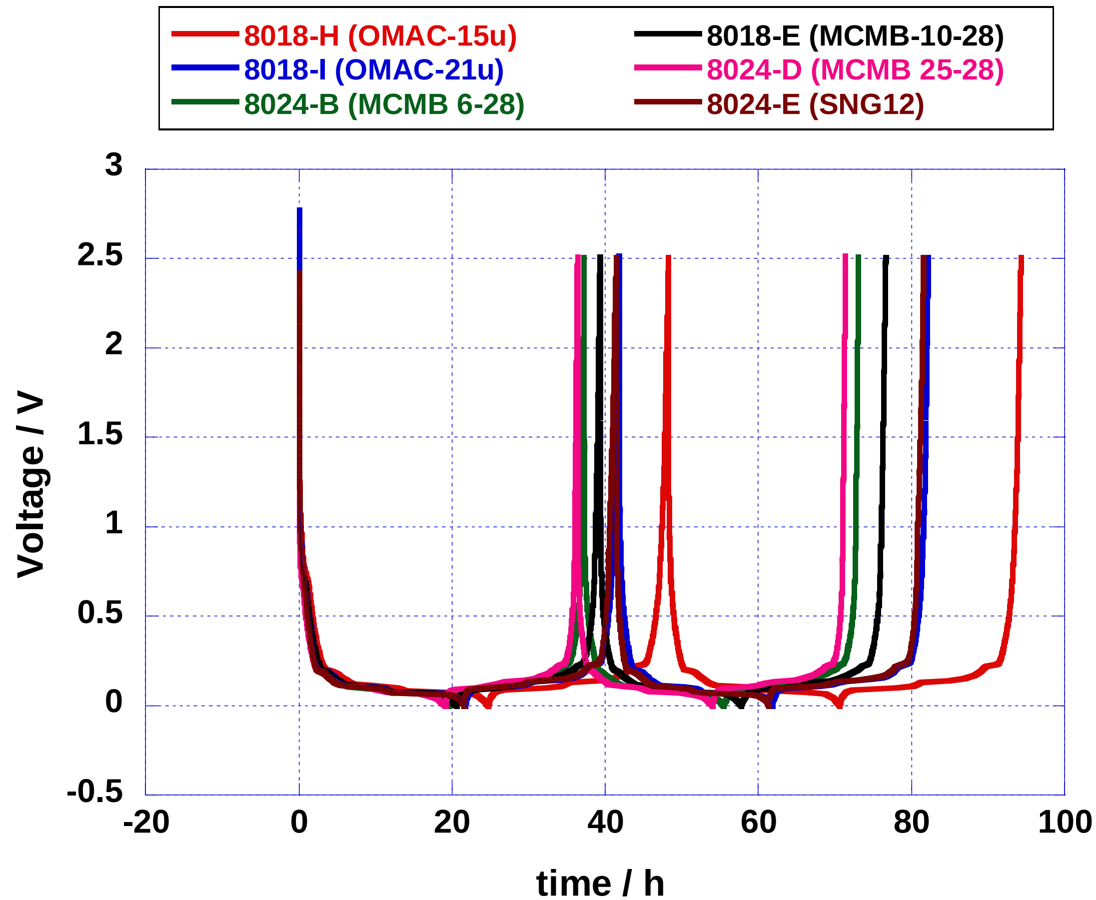


✓ OMAC has the highest 1CE and SNG12 has the lowest 1CE
✓ Highest reversible capacity was found with SNG12

Li/Electrolyte/Graphite (WSB)

Discharge/Charge: C/24
1M $LiPF_6$-EC-DEC

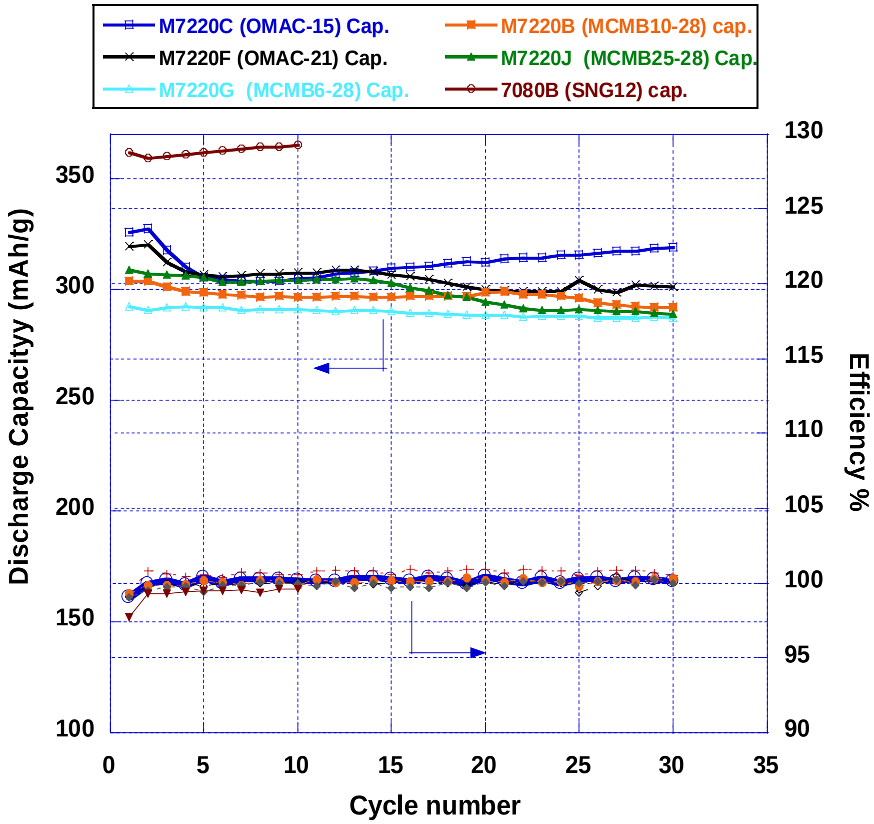
Sample	1st CE (%)	2nd CE (%)	Rev. Cap (mAh/g)
MCMB-6-28	90	97	285.8
MCMB-10-28	91	100	297.1
MCMB-25-28	90	98	268.2
OMAC-15	95	100	351.7
OMAC-21	92	100	304.0
SNG12	92	100	315.0

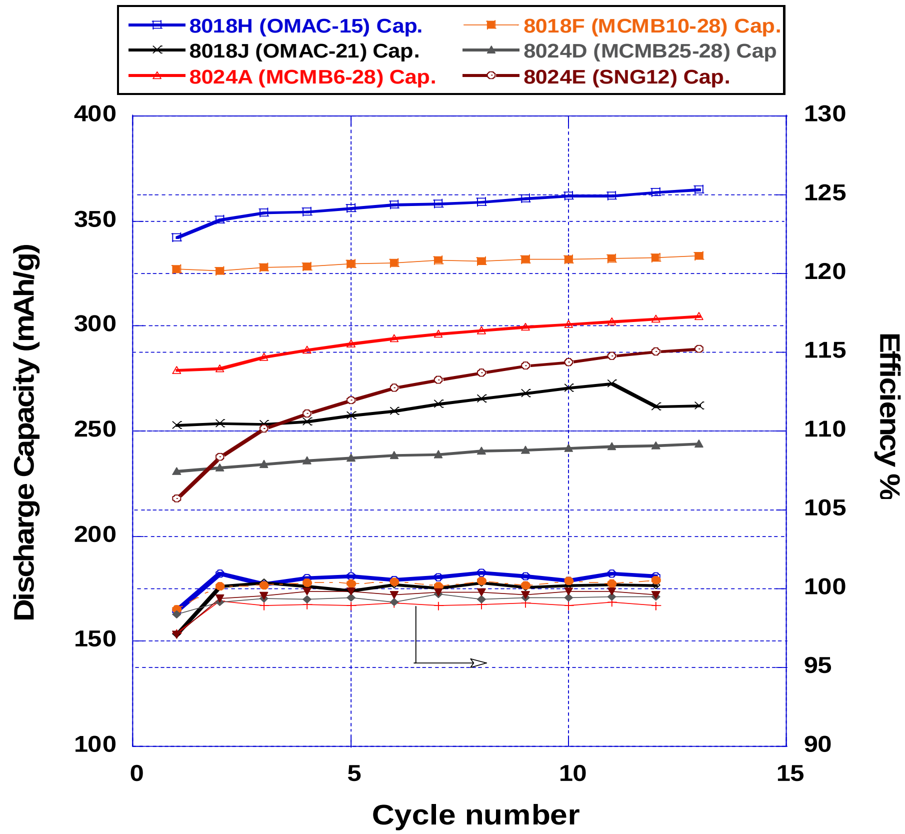


- ✓ OMAC-15 shows the highest 1CE and reversible capacity
- ✓ Increasing reversible capacity observed in the following order:

MCMB25-10< MCMB6-28< MCMB10-28< OMAC-2< SNG12 < OMAC21

Li/Electrolyte/Graphite, Cycling





Discharge:C/4
Charge: 1C
1M $LiPF_6$-EC-DEC

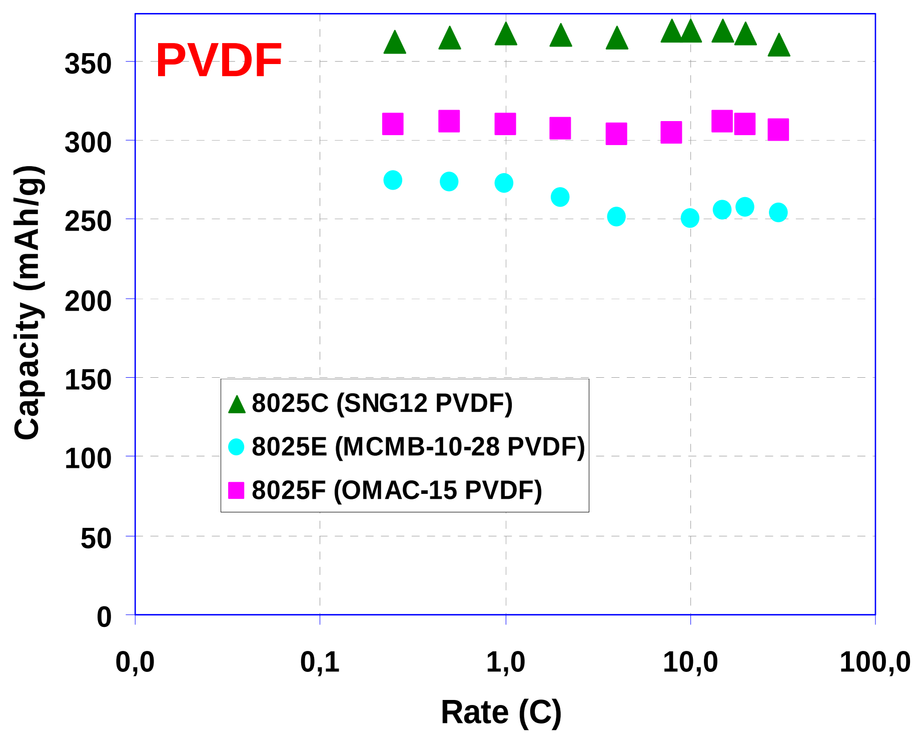
- ✓ MCMB has stable capacity with cycle life
- ✓ OMAC-15 has a capacity that increases with cycling
- ✓ CE of different carbons are comparable and stable with cycle life
- ✓ Large differences in capacities are observed with WSB

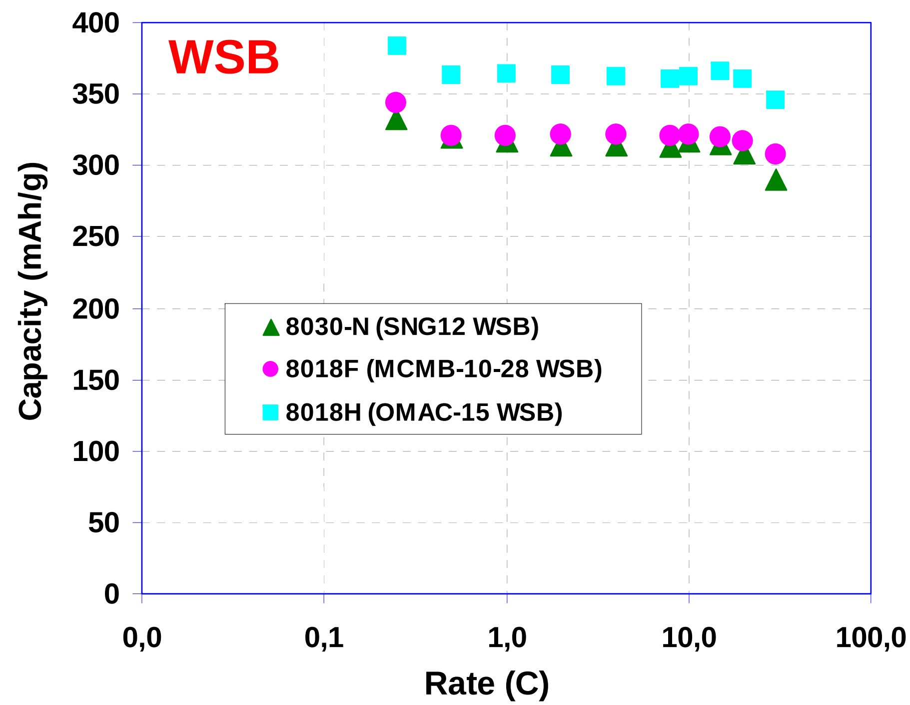
Hydro Québec

Institut de recherche

Li/Electrolyte/Graphite, Ragone

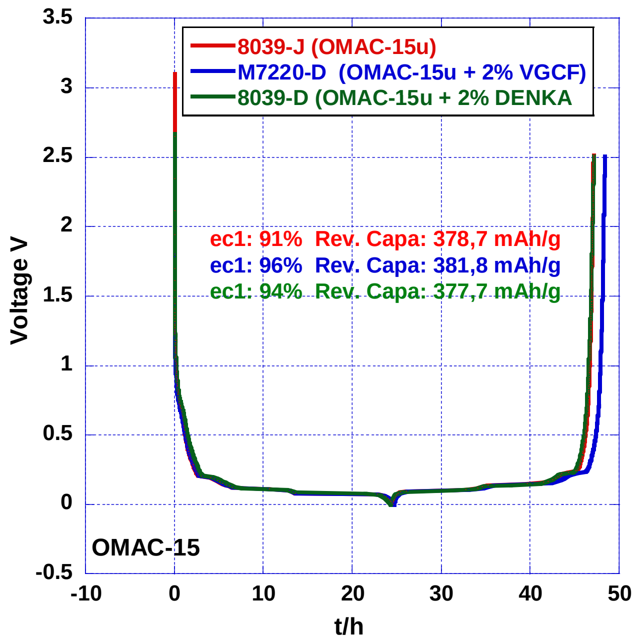
LiFePO4/1M LiPF6-EC-DEC/Graphite:
Discharge:C/4 and Charge: # rates

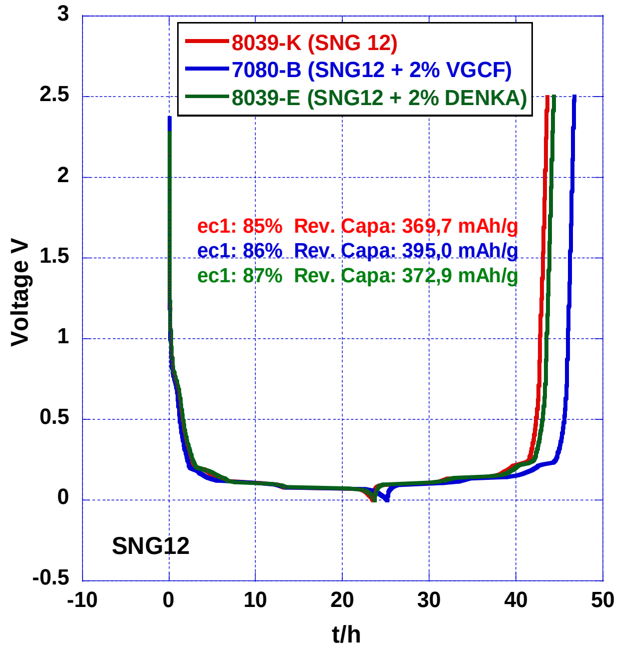


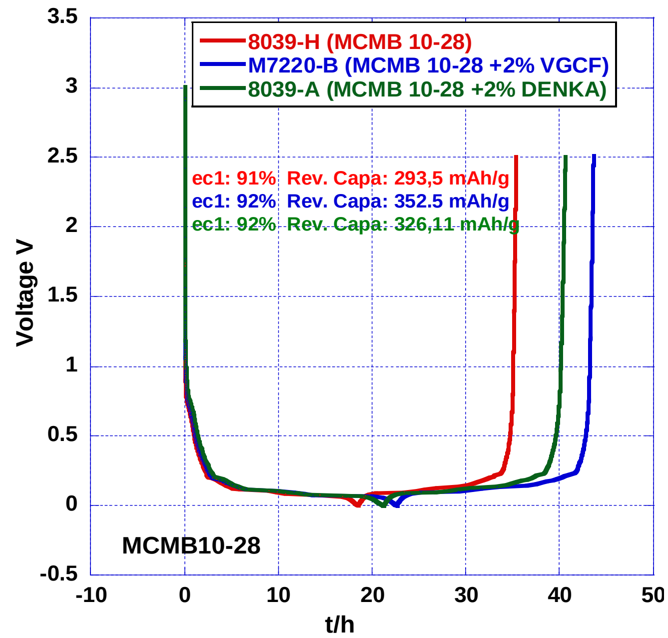


- ✓ **SNG12 exhibited the best rate capability with PDVF and comparable to MCMB when WSB is used.**
- ✓ **OMAC exhibited the best rate capability with WSB**

Effect of carbon additive





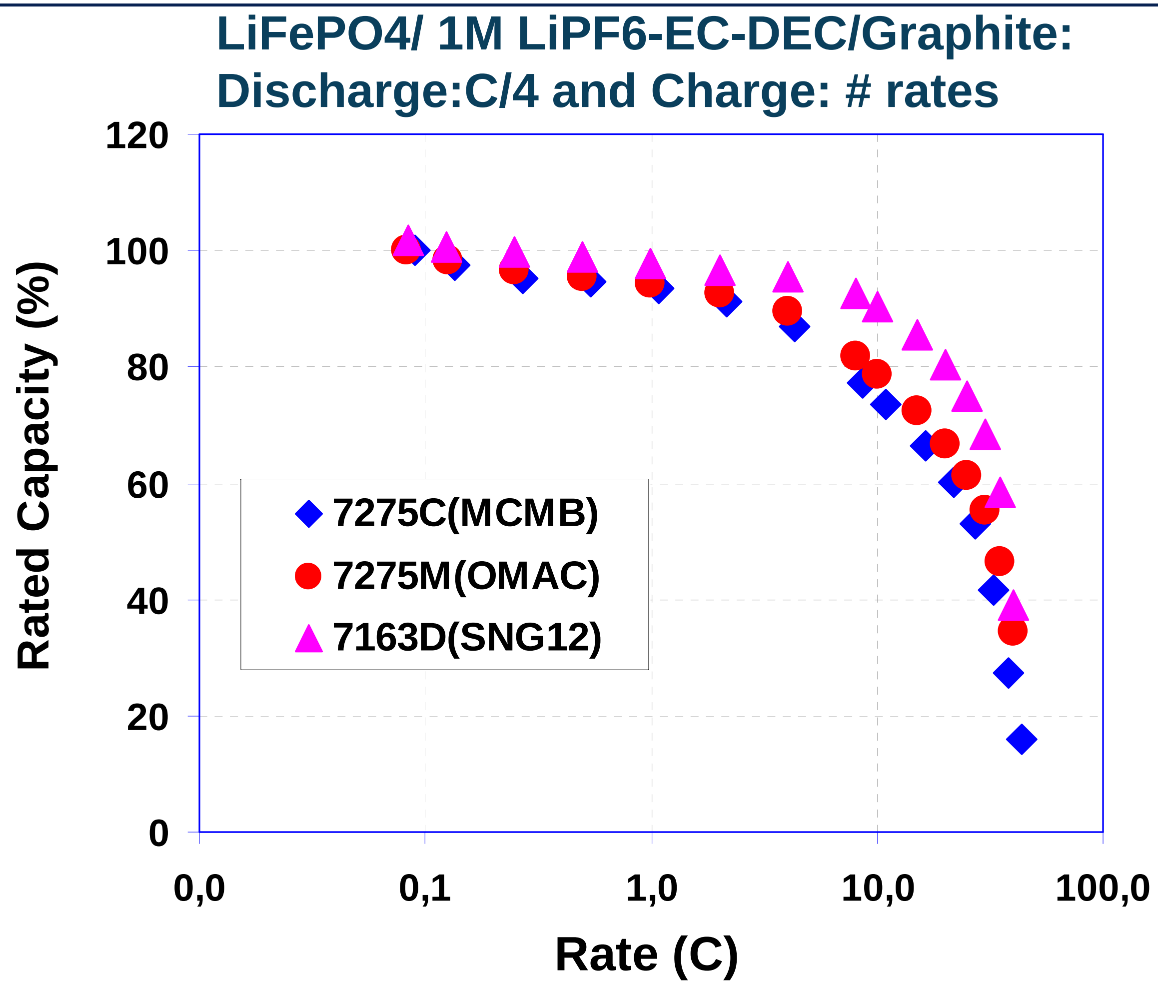


✓2 % VGCF increases the 1CE and reversible capacity by creating a best network conductivity of electrode

Hydro Québec

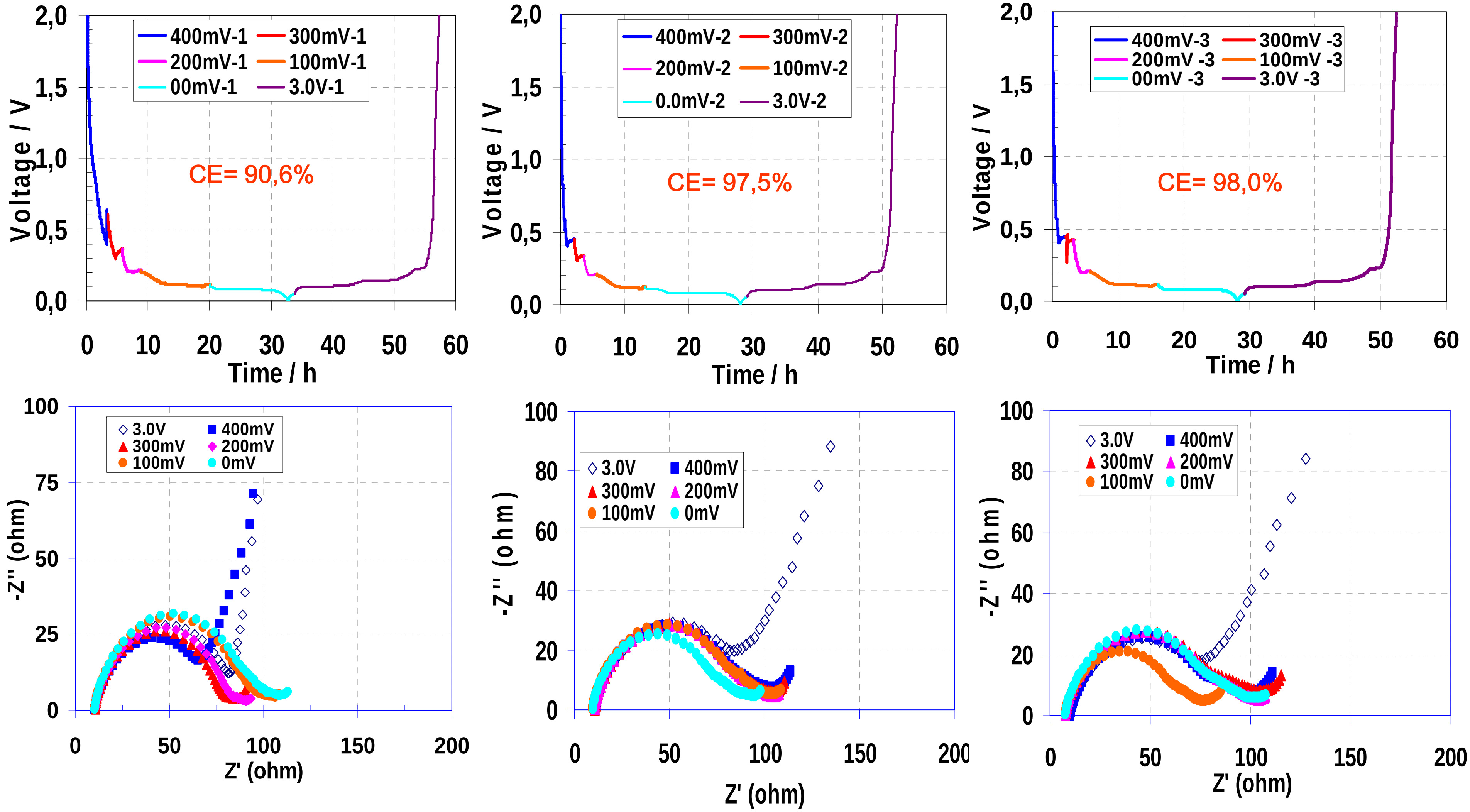
Institut de recherche

Li-ion Cells with PVDF, ragone



- ✓ **OMAC and MCMB have similar rate capabilities**
- ✓ **SNG12 exhibited the best rate capability**

Graphite/EC-DEC-1MLiPF$_6$/Li (C/24) Test

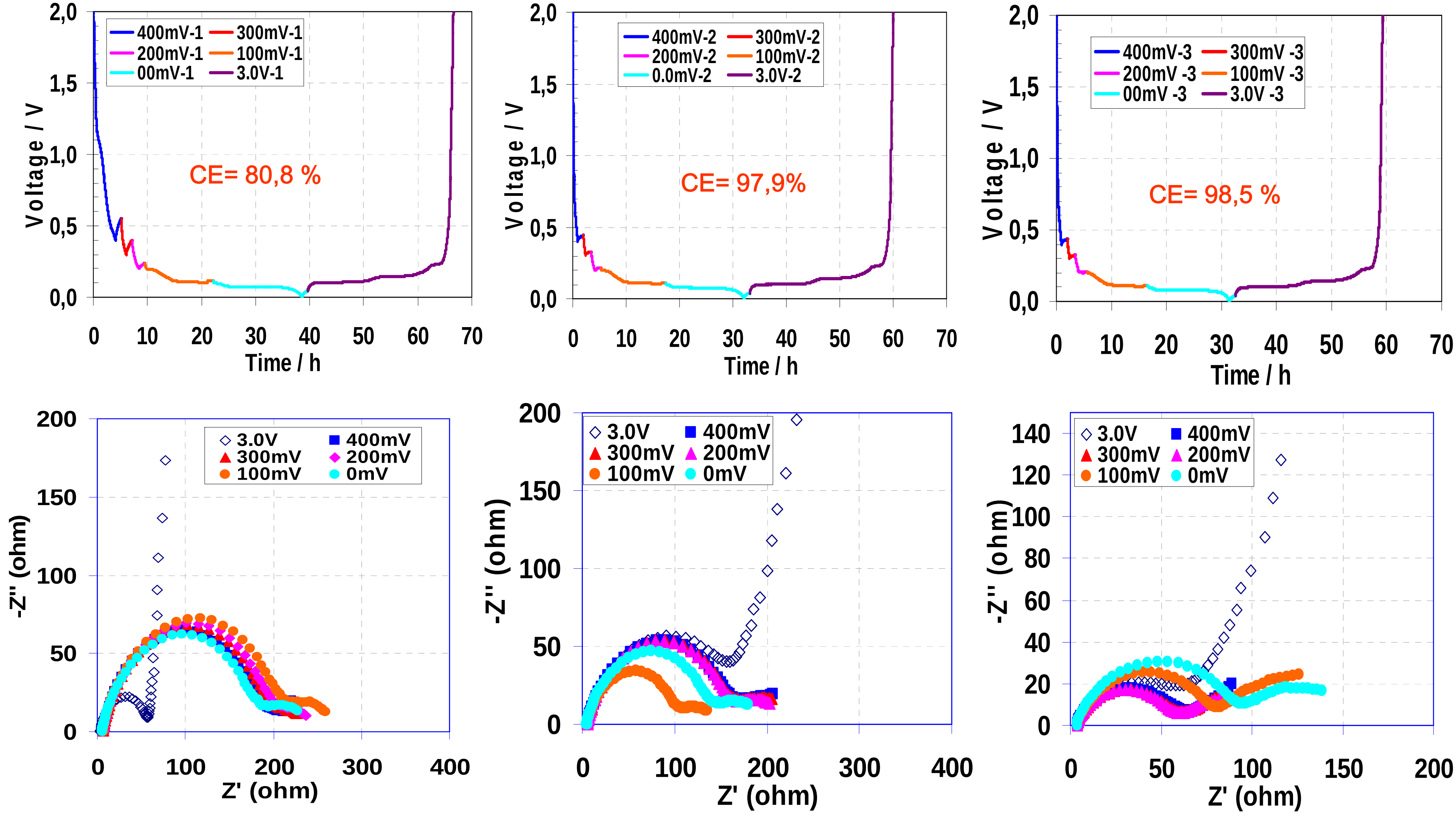


✓ **Interface resistance stabilizes during the first few cycles with the standard electrolyte**

Hydro Québec

Institut de recherche

Graphite/EMI(FSI)+0,7MLiFSI/Li (C/24) Test



- ✓ 1st cycle CE is lower than with conventional electrolyte
- ✓ Interface resistance is higher than with EC-DEC

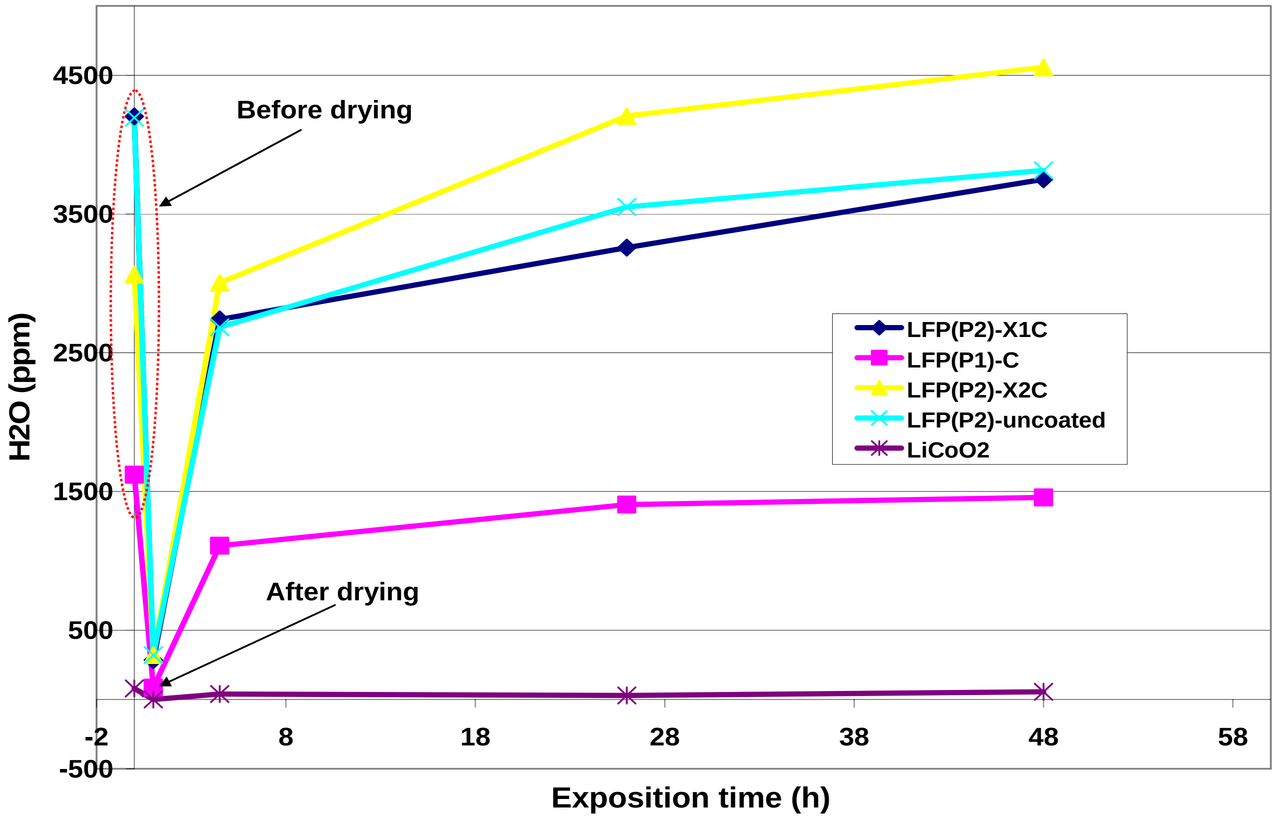
Hydro Québec

itut de recherche

Reaction of $LiFePO_4$ powder and H_2O

Dry at 120°C
In vacuum

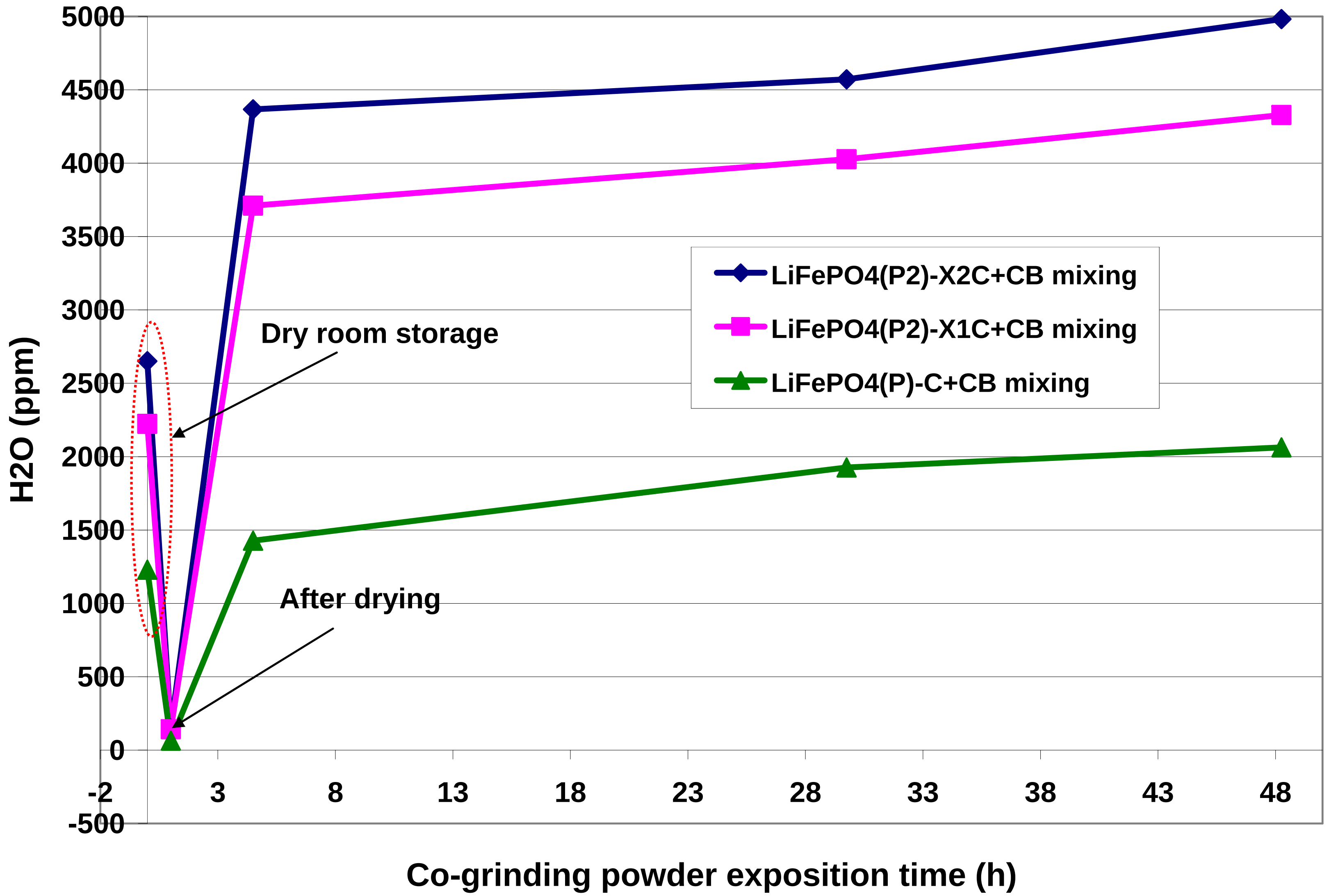
25 °C, 50 % humidly



- ✓ $LiFePO_4$ absorb significant amount of water in a few seconds
- ✓ $LiFePO_4$ from hydrothermal process absorb more water than from solid-state process
- ✓ Both uncoated and carbon-coated $LiFePO_4$ absorb water
- ✓ Water content depends on % carbon in powder

Hy Québec

Reaction of Co-grinding Carbon with C-$LiFePO_4$ powder and H_2O

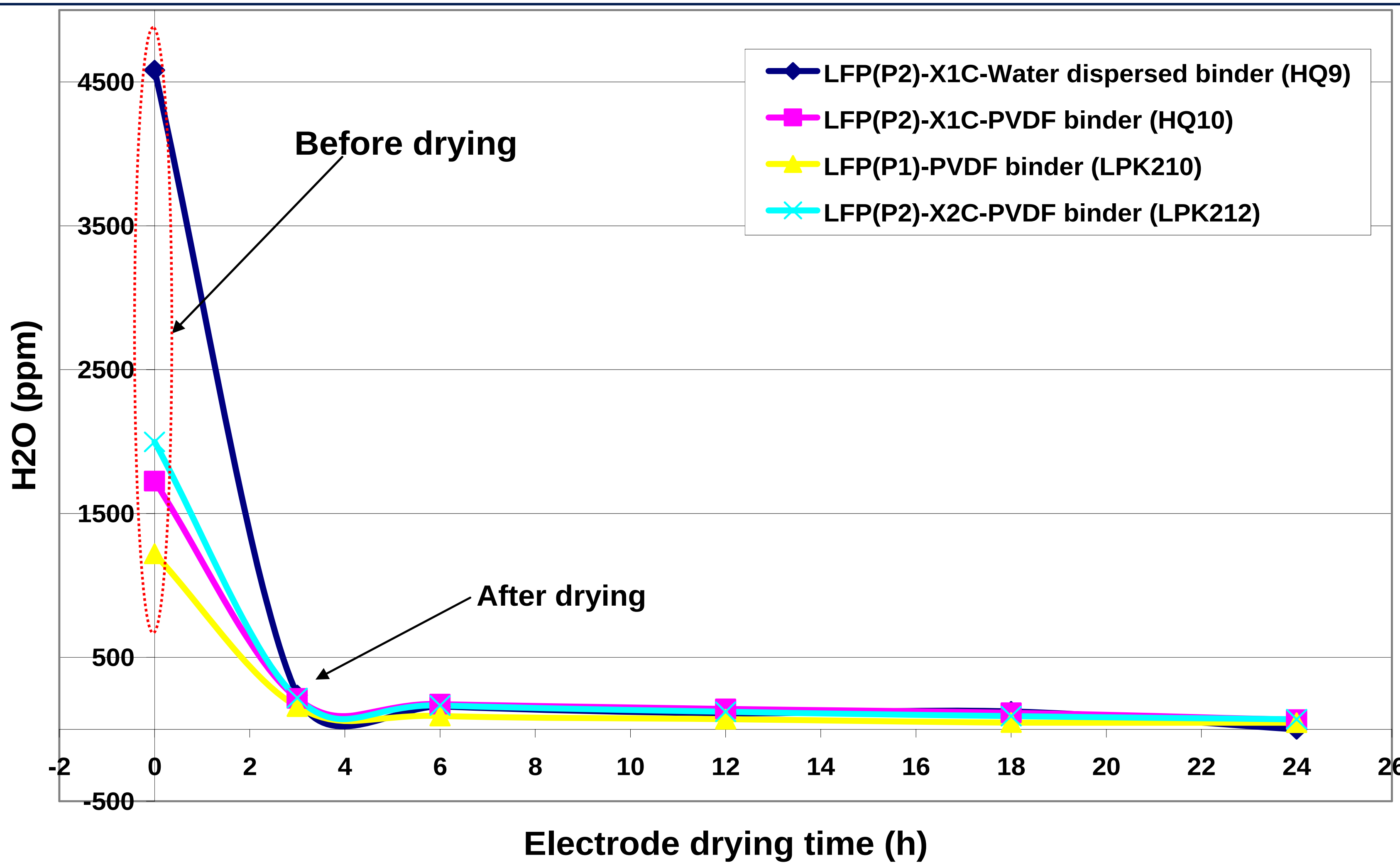


✓ **Water content decreases (< 100 ppm) after drying**

Hydro Québec

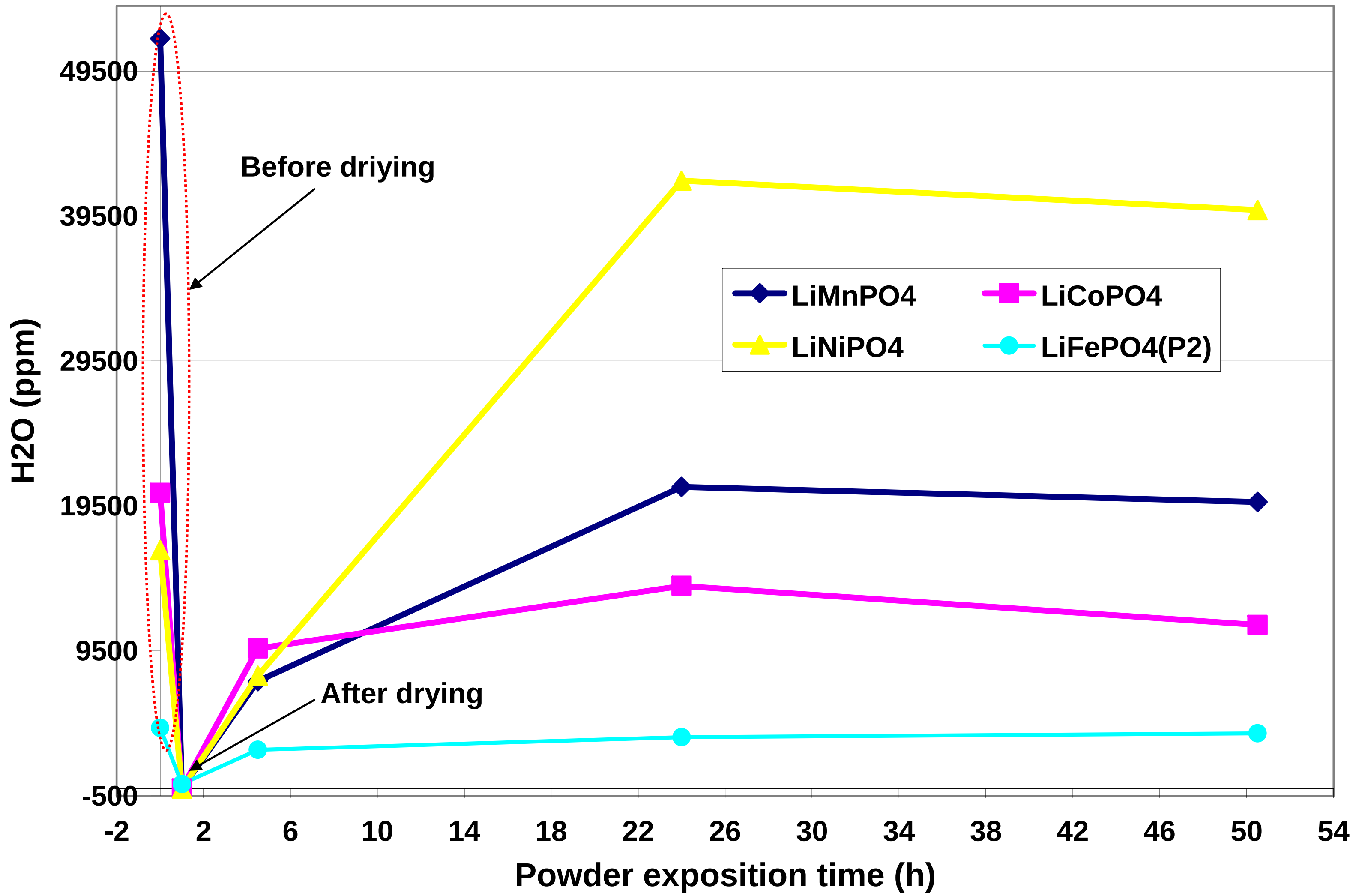
Institut de recherche

Reaction of C-$LiFePO_4$ based electrode with H_2O



- ✓ **Dry electrode has less than100 ppm of H_2O after 18 h**
- ✓ **Electrode from solid state C-$LiFePO_4$ and PVDF has lowest water content**

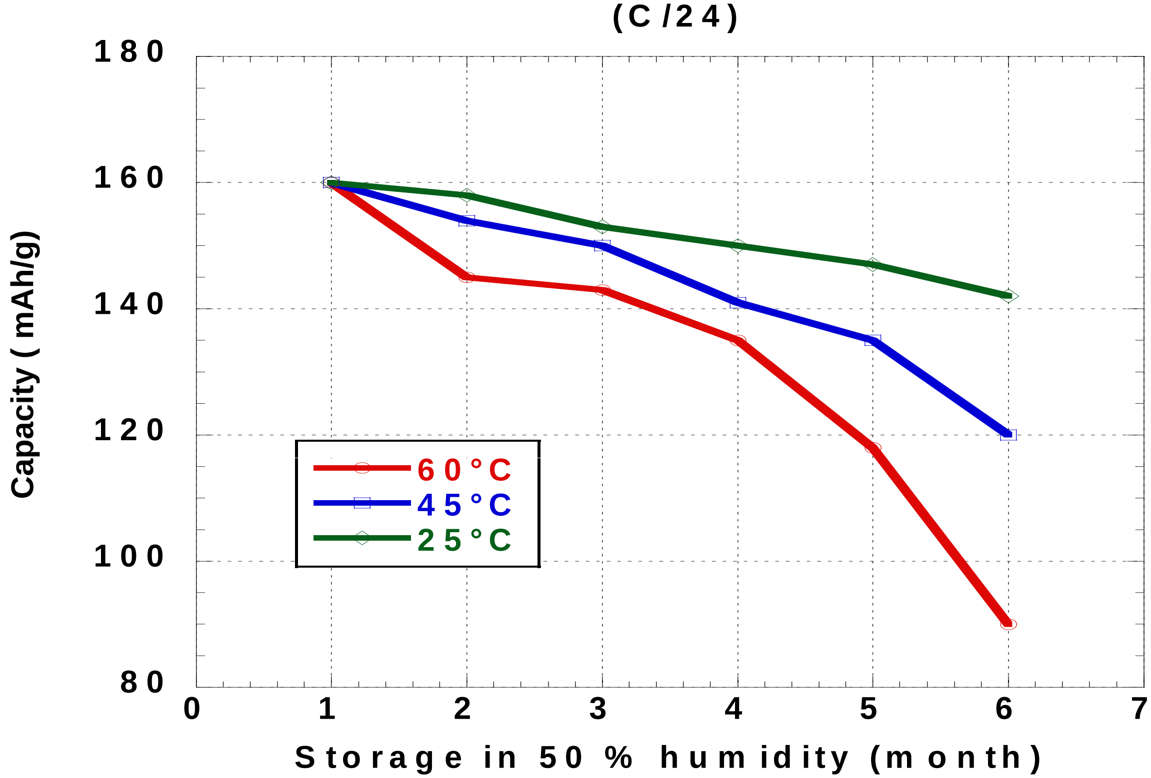
Reaction of $LiMPO_4$ (M=Fe, Mn, Ni, Co) powders with H_2O



✓ **H_2O absorption in $LiMPO_4$ decreased after 24 hr in the following order: $LiFePO_4$ < $LiCoPO_4$< $LiMnPO_4$<$LiNiPO_4$**

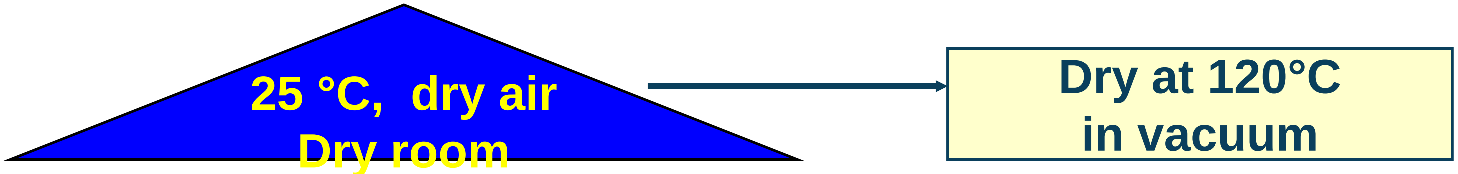
Electrode Storage with different Temperature (humidity)

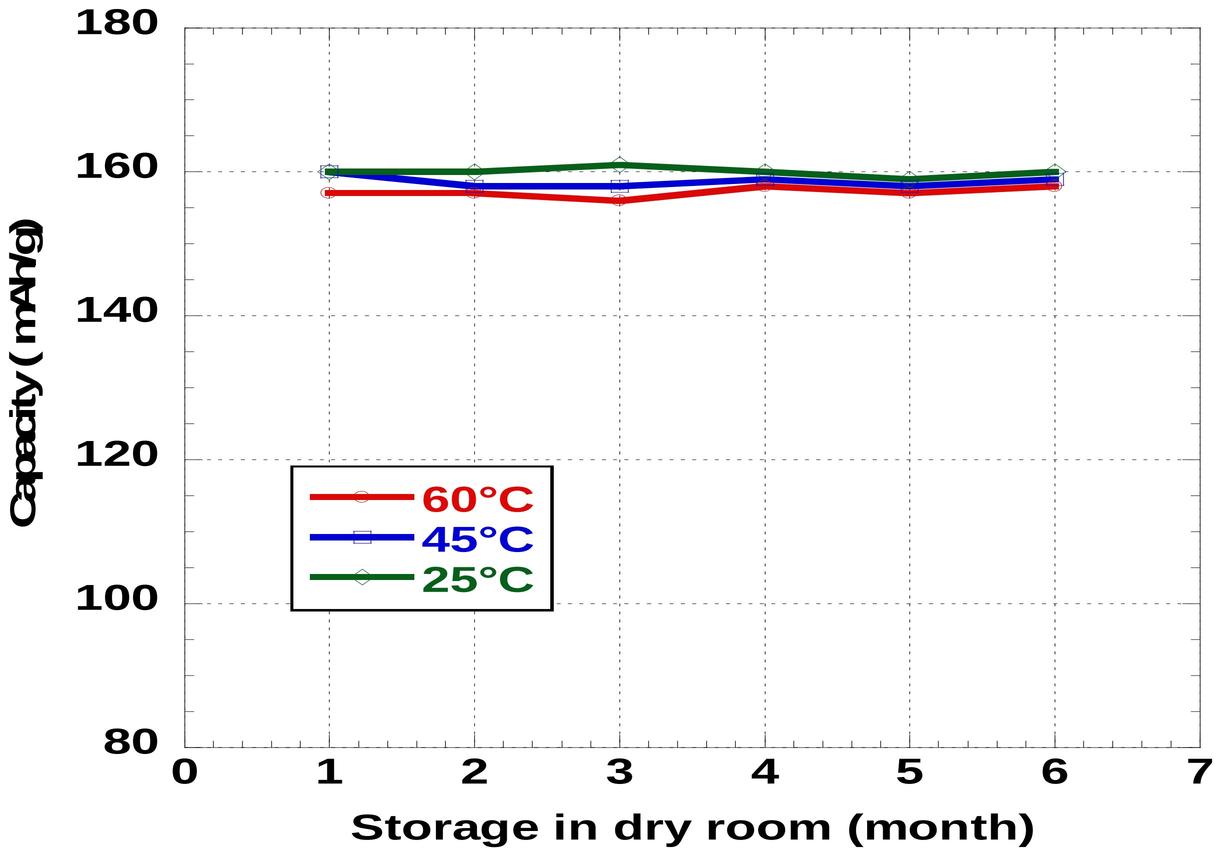
25 °C, 50 % humidly → Dry at 120°C in vacuum



✓Capacity decrease with when the time storage increasing
✓Capacity fade is higher when the temperature increasing

Electrode Storage with different Temperature (dry air)





✓Capacity constant with when the time storage increasing
✓No Capacity fade when the temperature increasing

Conclusion

- **OMAC-15 and SNG12 are suitable alternatives graphites in anodes fabricated with PVDF or WSB:**
  - **Comparable first cycle current efficiency was obtained with graphite fabricated with WSB or PVDF indicating WSB is a suitable substitute for PVDF**
  - **Li-ion cells with SNG12 anode and LiFePO4 cathode showed higher rate capability than comparable cells with MCMB and OMAC.**

- **In-situ impedance spectroscopy is a good tool to study the SEI layer (R_f, C_f vs. voltage and cycle number).**

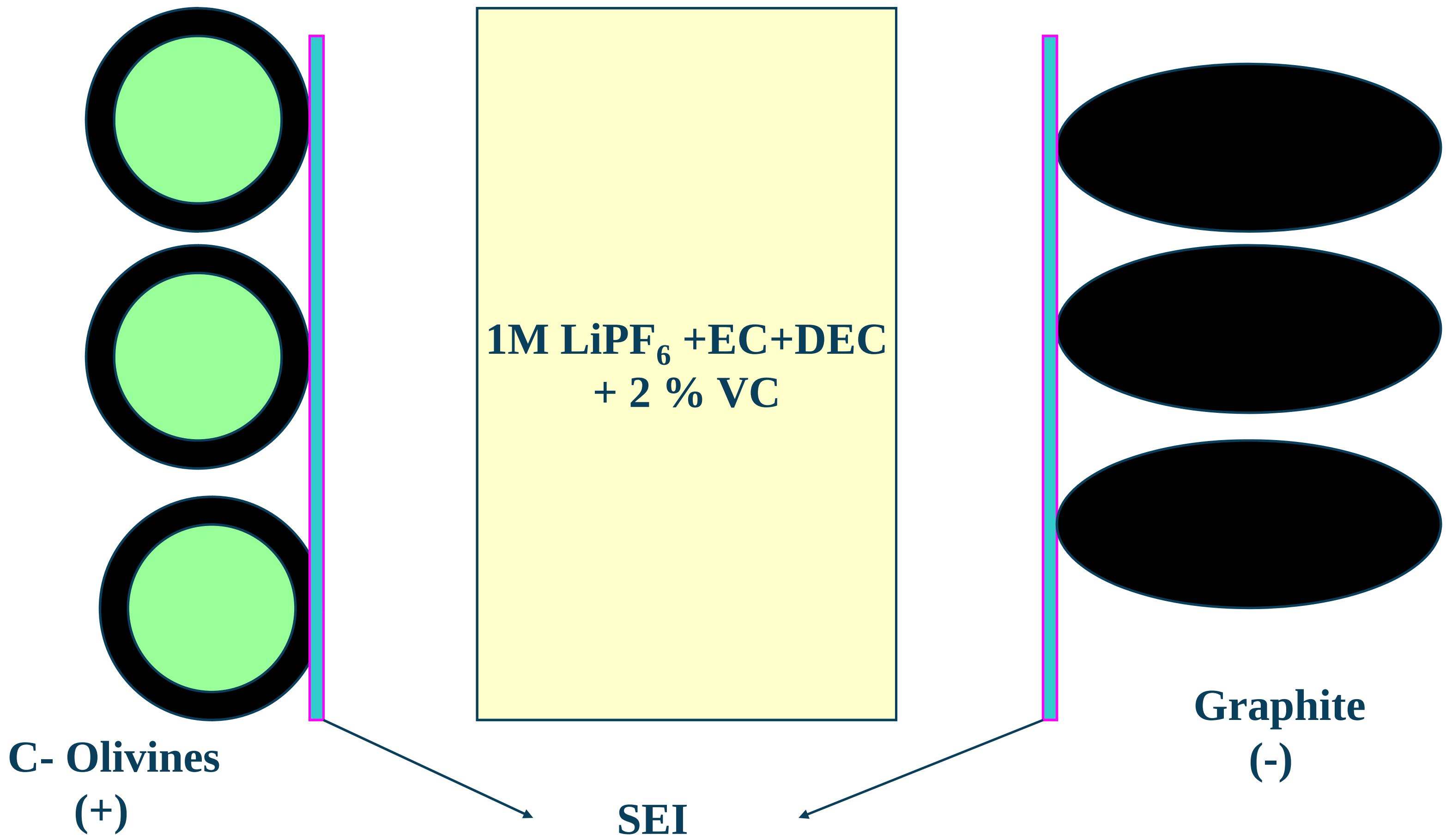
- **High rate performance was obtained with SNG12 anode and $LiFePO_4$ cathode material.**
  - **Significant water absorption by olivine compounds is observed, but is reduced by appropriate drying and storage.**

- **Water content is determinant factor on the performance of olivines.**

Activities for the Next Fiscal Year

- Analyze the physicochemical properties of the SEI layer on graphite and olivines in standard electrolyte (VC) and HQ ionic liquid
- In-situ impedance spectroscopy will be used in studies with graphite (MCMB, SNG12 , OMAC15 and OMAC12 (new)
- Complete high rate performance and cycling with WSB anodes and olivines
- Evaluate mixed graphite-SiO as an alternative anode
- Examine the performance of other olivines, like $LiMnPO_4$ as cathodes in Li-Ion cells
- Investigate dual oxide-olivine as a powder mixture or in multilayer structures in cathodes
- Continue delivering laminated electrode structures and powders to investigators in the BATT program
- HQ will built a new dry room (40 X 60 feet) and facilities for a18650 R&D assembly line at IREQ that will be available for the BATT program.

VC based standard electrolyte for SEI



VC based standard electrolyte will made simultaneously stable SEI on graphite anode and carbon coated olivines