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Low Cost SiO_x-Graphite and Olivine Materials

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Project ID: es_19_zaghid

Overview

Timeline

- Start date: March 2006
- End date: February 2010
- 70% completed

Barriers

- Low energy
- Poor cycle/calendar life

Budget

- Total Project Funding
  - DOE: $992K
- FY09 funding $365K
- FY08 funding $250K

Partners

- V. Battaglia, V. Srinivasan (LBNL)
- J. Goodenough (U. Texas)
- P. Rotch (SNL)
- C. Julien-A Mauger (U. Paris 6)

Outline

PURPOSE OF WORK

- **Synthesize and evaluate manganese phosphate cathode material.**
- **Replace graphite anode with an alternative material that meets the requirement for low cost and high energy.**
- **Continue development of binders for the cathode and alternative anode to understand and improve the properties of the SEI layer.**

BARRIERS

- **Low energy and poor cycle/calendar life**

APPROACH

- **Develop an appropriate method to synthesize $LiMnPO_4$ (HT, S-State, Molten).**
- **Fabricate electrode coatings based on low-cost SiO_x-graphite and olivine.**
- **Evaluate SiO_x-graphite with different binders (PVDF, SBR, PEG, PVA and polyglycidol).**

Approach

- **HQ efforts in the BATT program to investigate and improve SEI layers on alternative anodes include several tasks:**
  - **prepare laminate anode films and powders, and supply them to investigators in Topic 3a involved with SEI analysis using different techniques.**
  - **utilize *in-situ* impedance measurements, *ex –situ* and *in-situ* SEM to investigate the SEI layer on the anode.**
  - **study the effect of additives on the SEI layer**

- **Continue effort to identify benefits of WSB (SBR, PEG, PVA and polyglycidol) compared to PVDF in new anode and cathode materials**

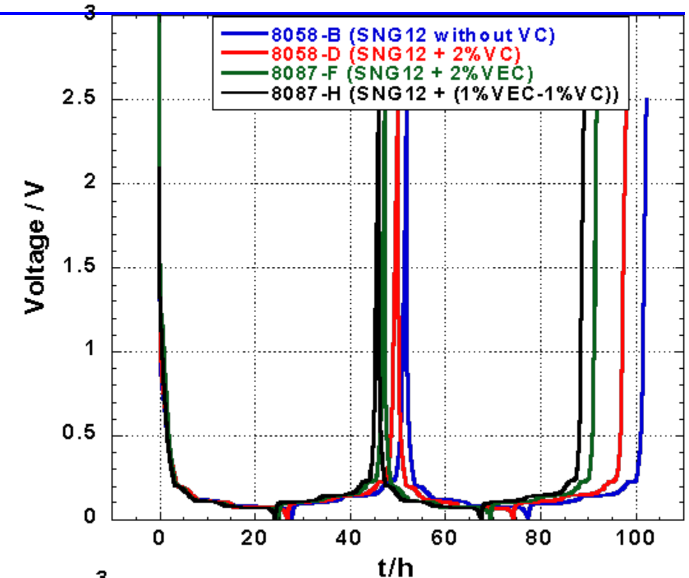
- **Investigate performance of alternative high-capacity anode and Mn-based olivine materials in laboratory cells**
  - **prepare laminate cathode films and powders and supply them to BATT investigators for evaluation**

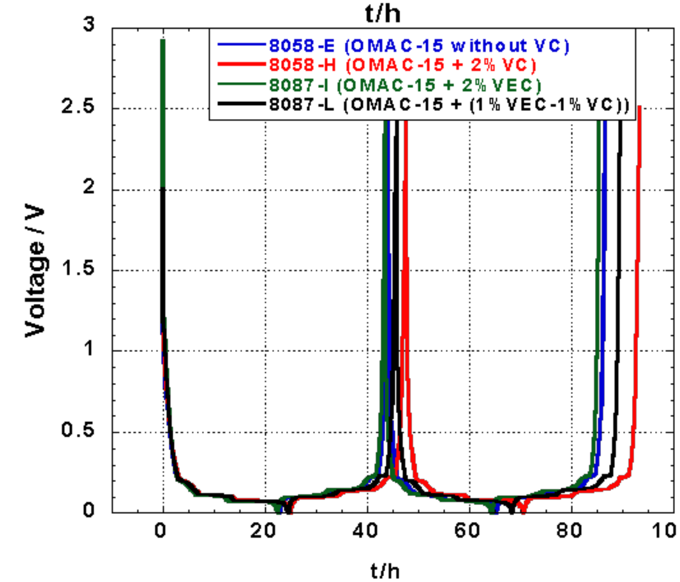
Li/graphite cell, Electrolyte with Additives

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

Graphite	SNG12		OMAC15	
Additives	1st CE (%)	Qrev (mAh/g)	1st CE (%)	Qrev (mAh/g)
No	85	369	93	358
2%VC	86	366	92	355
2%VEC	93	345	92	321
1%VC + 1%VEC	93	336	87	352

- SNG12 was sensitive to electrolyte additives compared to OMAC; 1st CE improved to 93% when VEC is added compared to 85% without additive.
- The reversible capacity of both graphites was reduced with additives in the electrolyte.





SiO_x Alternative Anodes for Li-Ion Cells

Silicon →

- ✓ High capacity (4000 mAh/g)
- ✓ Low cost material
- o High volume expansion

↓

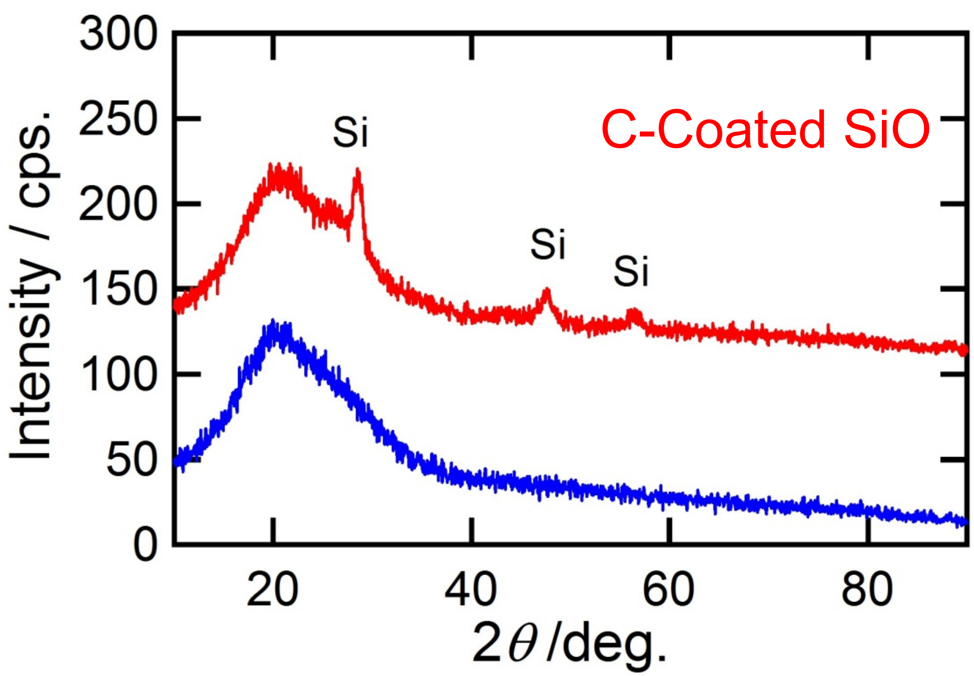
Silicon oxide →

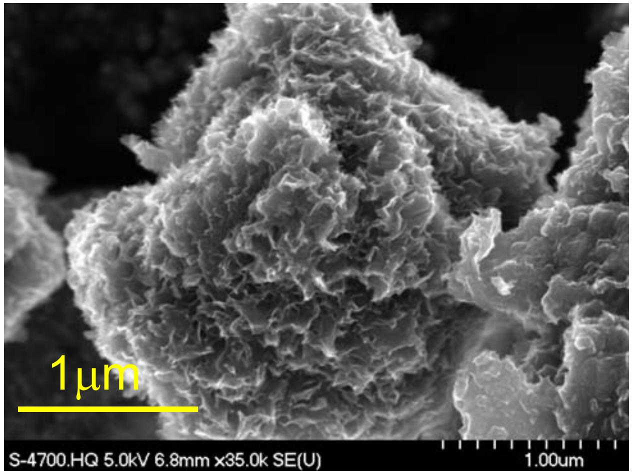
- ✓ Smaller volume change than Si
- ✓ High capacity (1338 mAh/g)
- o Low conductivity
- o Low 1st coulomic efficiency

↓

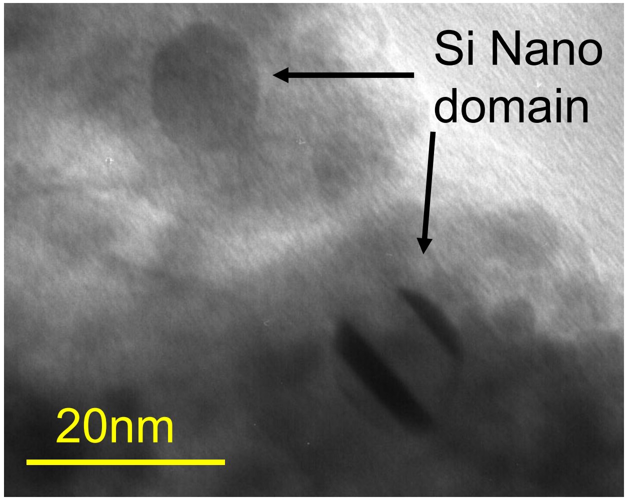
Carbon coating | Mixed with graphite

SiO$_x$ Characteristics





Surface Morphology



Cross-Section

- XRD of SiO showed mainly amorphous structure
    - Surface of SiO covered with fiber-like carbon
- Nano-domains observed in SiO:Si/SiO_2 particles

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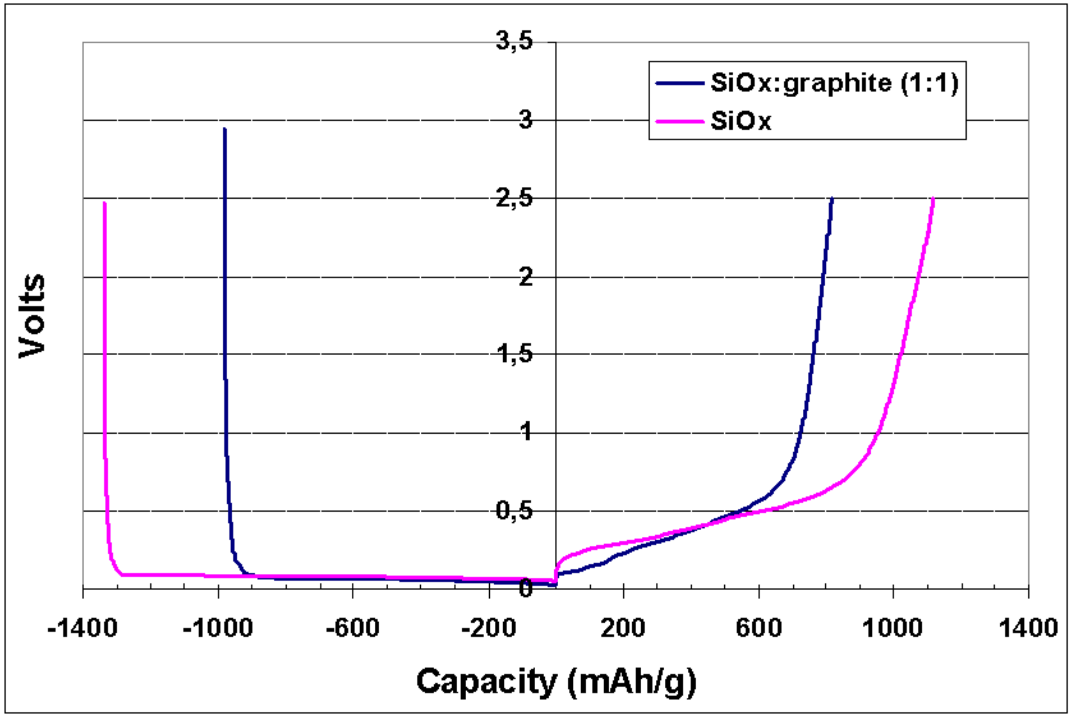
Li/Electrolyte/SiO_x

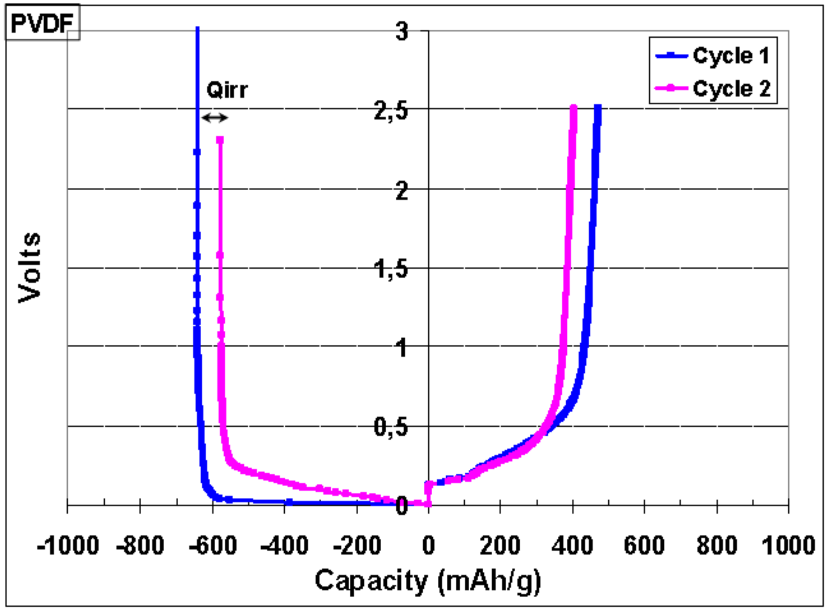
Binder:WSB
Discharge/Charge: C/24
1M $LiPF_6$-EC-DEC

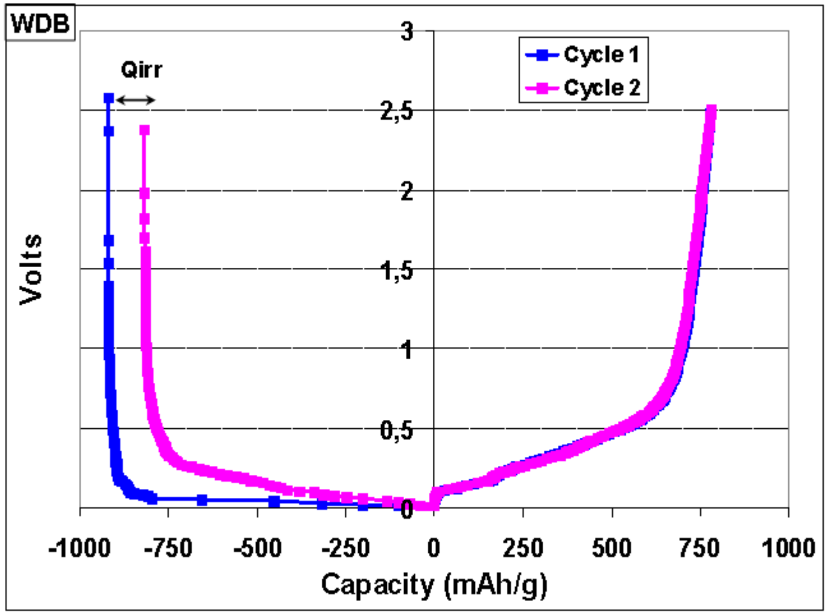


- **Reversible capacity higher with SiO_x than graphite anode**
- **Comparable coulombic efficiency with SiO_x mixed with graphite**

	Disch. Cap. (mAh/g)	Chg. Cap. (mAh/g)	Ah. Eff. (%)
SiO_x	1338	1118	84
SiO_x:Gr(1:1)	980	816	83

Li/Electrolyte/SiO_x-graphite (1:1)



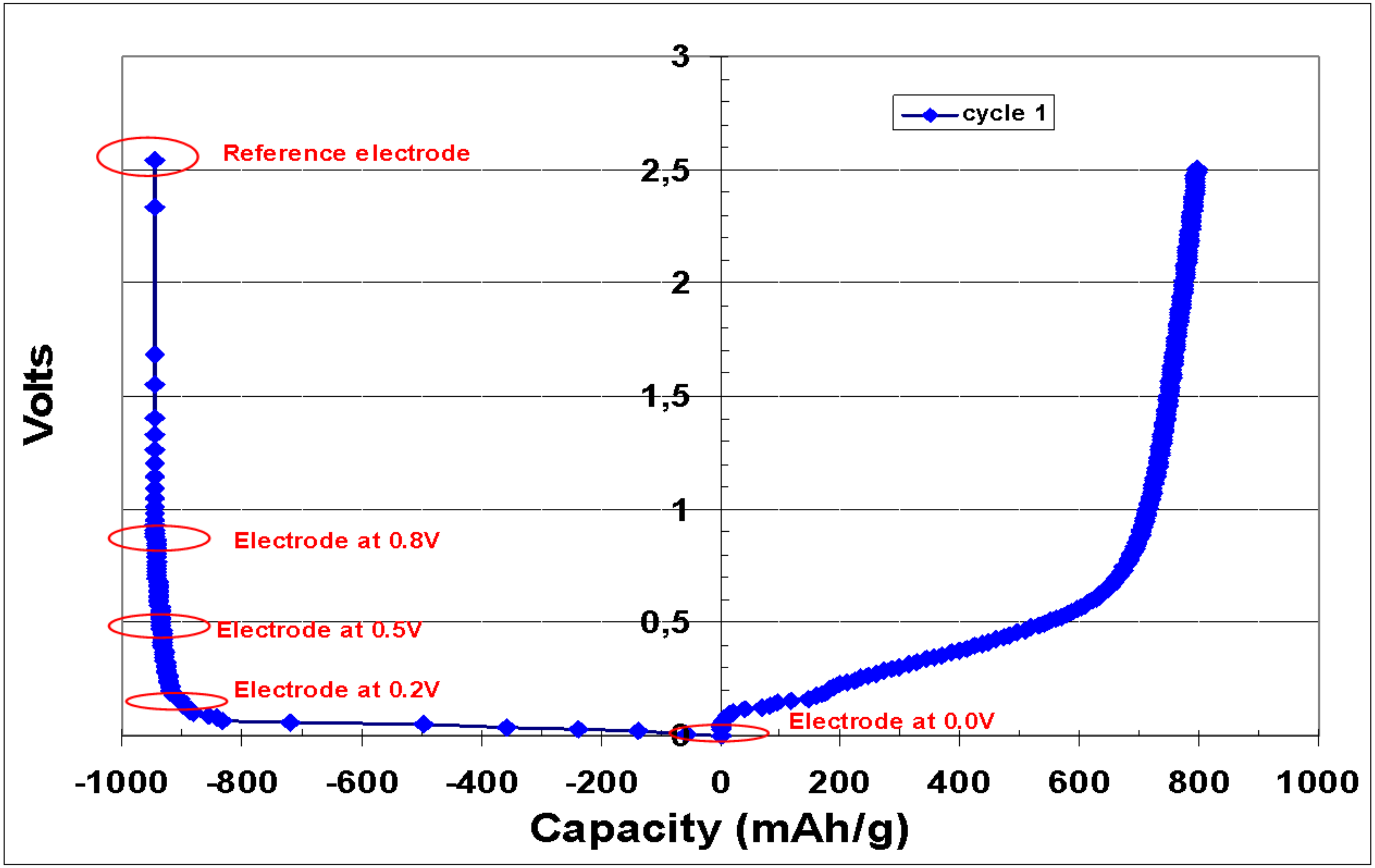


Discharge/Charge: C/24
1M $LiPF_6$-EC-DEC

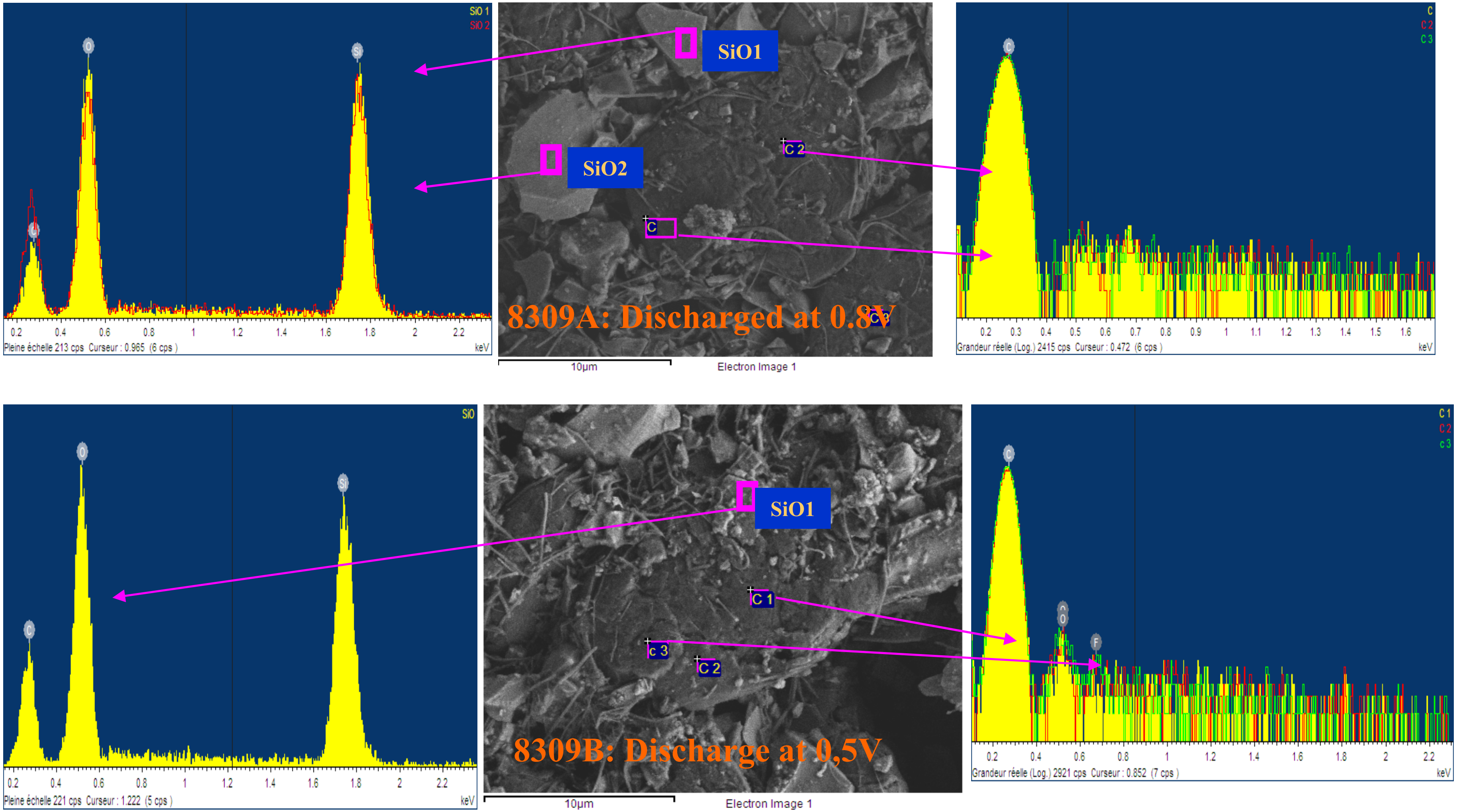
- **The electrodes with WSB binder have better performance than those with PVDF.**
- **Low reversible capacity and CE with PVDF-containing electrode.**

	Disch. Cap. 1st / 2nd	Chg. Cap. 1st / 2nd	Ah. Eff. 1st / 2nd
PVDF	642 / 541	472 / 394	74 / 73
WSB	919 / 817	778 / 778	85 / 95

SiOx-Graphite for samples for Ex-Situ SEM

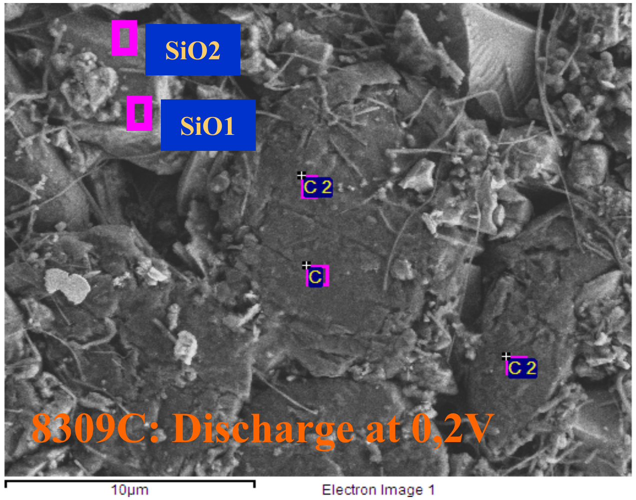


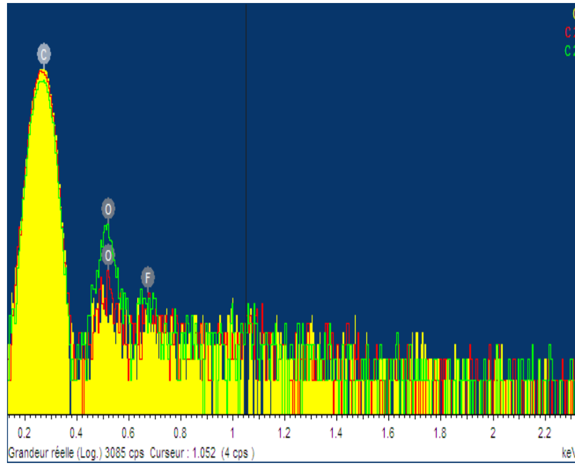
Local Chemical Analysis: Discharge at 0.8 and 0.5V

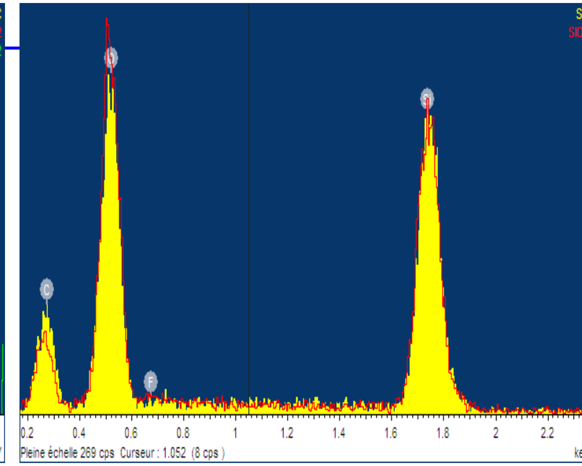


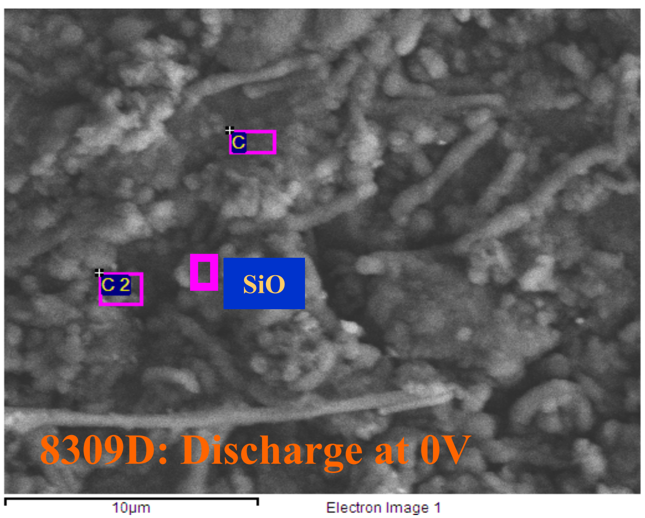
- O and F was not detected at the surface of graphite or SiO, C peak was detected at the SiO surface (0.8V).
- Start detecting some O and F was at different locations on the surface of graphite (0.5V)

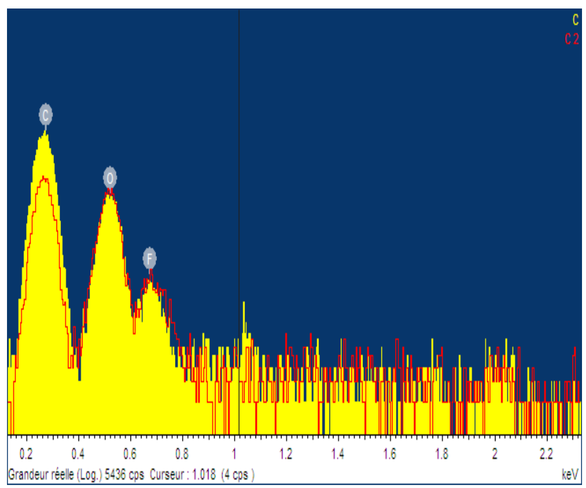
Local Chemical Analysis: Discharge at 0.2 and 0.0V

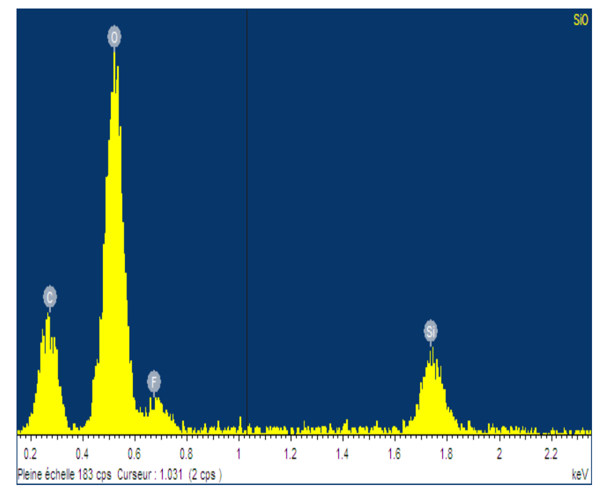






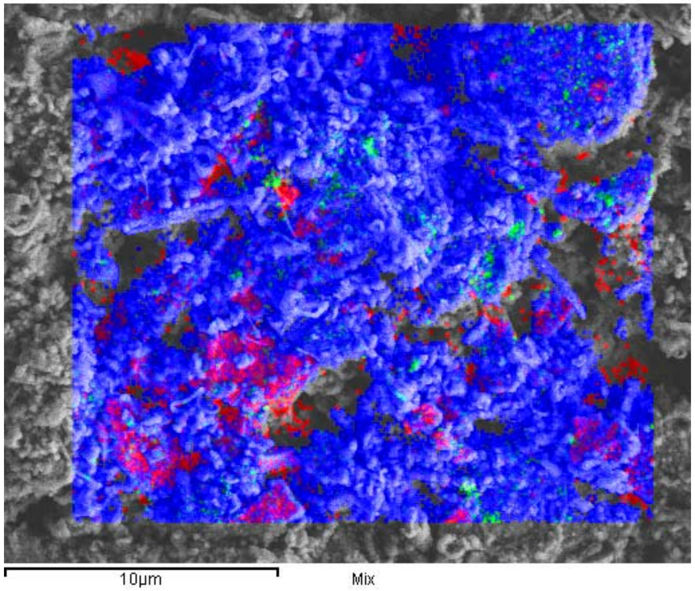


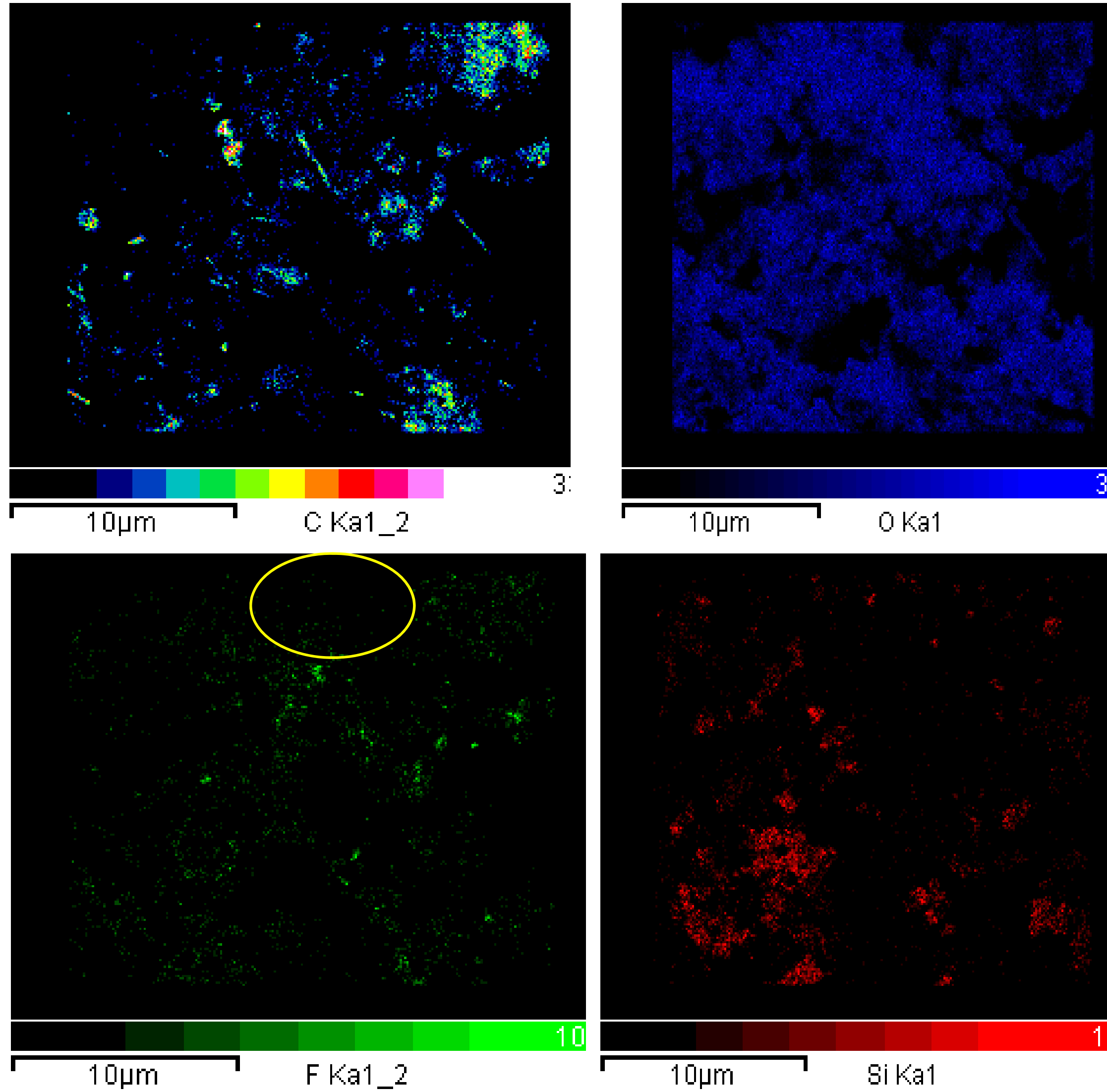




- Some O and F was found at different locations on the surface of graphite (0.2V)
- Strong peaks for O and F observed, confirming a thicker SEI layer for both C and SiO was present C peak was detected at the SiO surface (0,0V).

Local Chemical Mapping: discharge at 0 V (1.5 cycles); (8309-F)

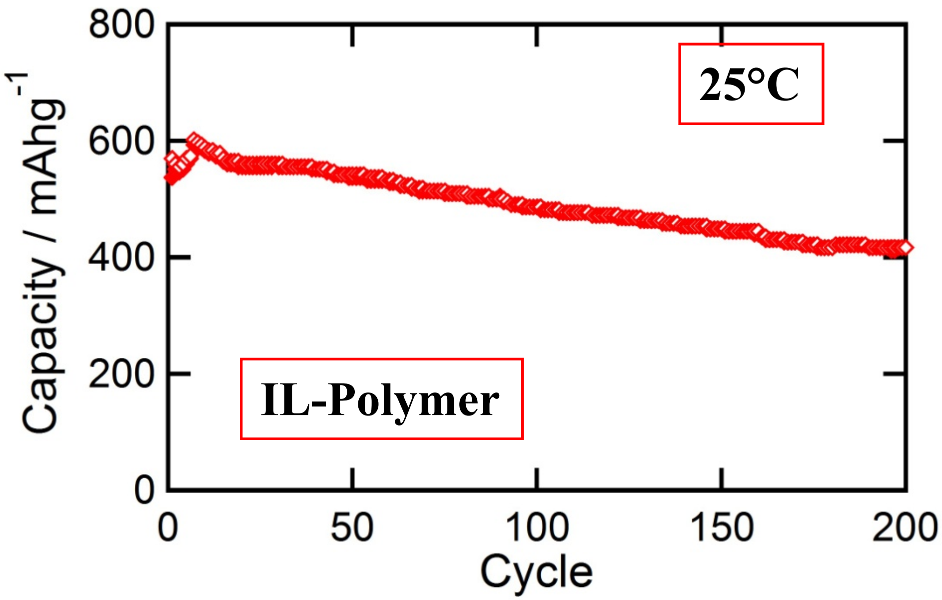


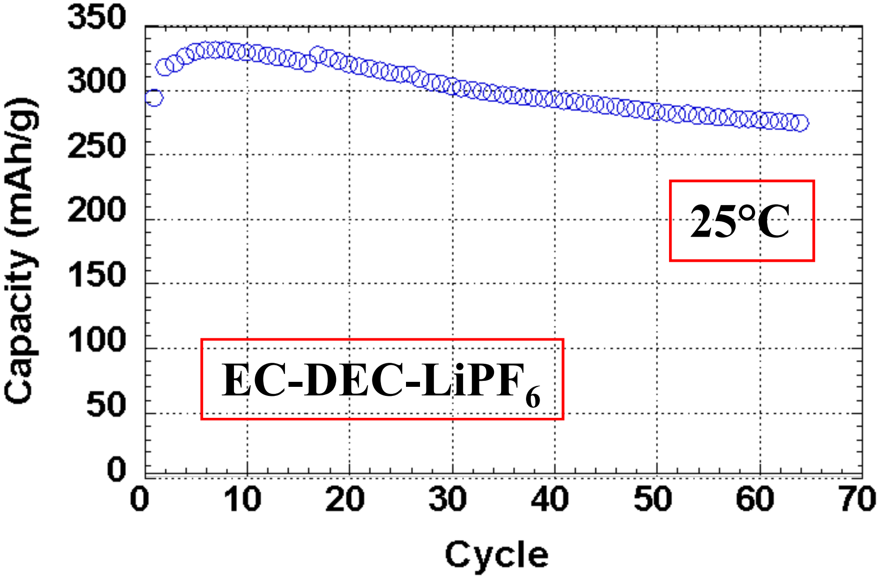


Local chemical mapping shows that F was non-uniformly dispersed

Cycling: SiO_x/Graphite in Ionic Liquid and EC-DEC

Disch - Ch: C/4





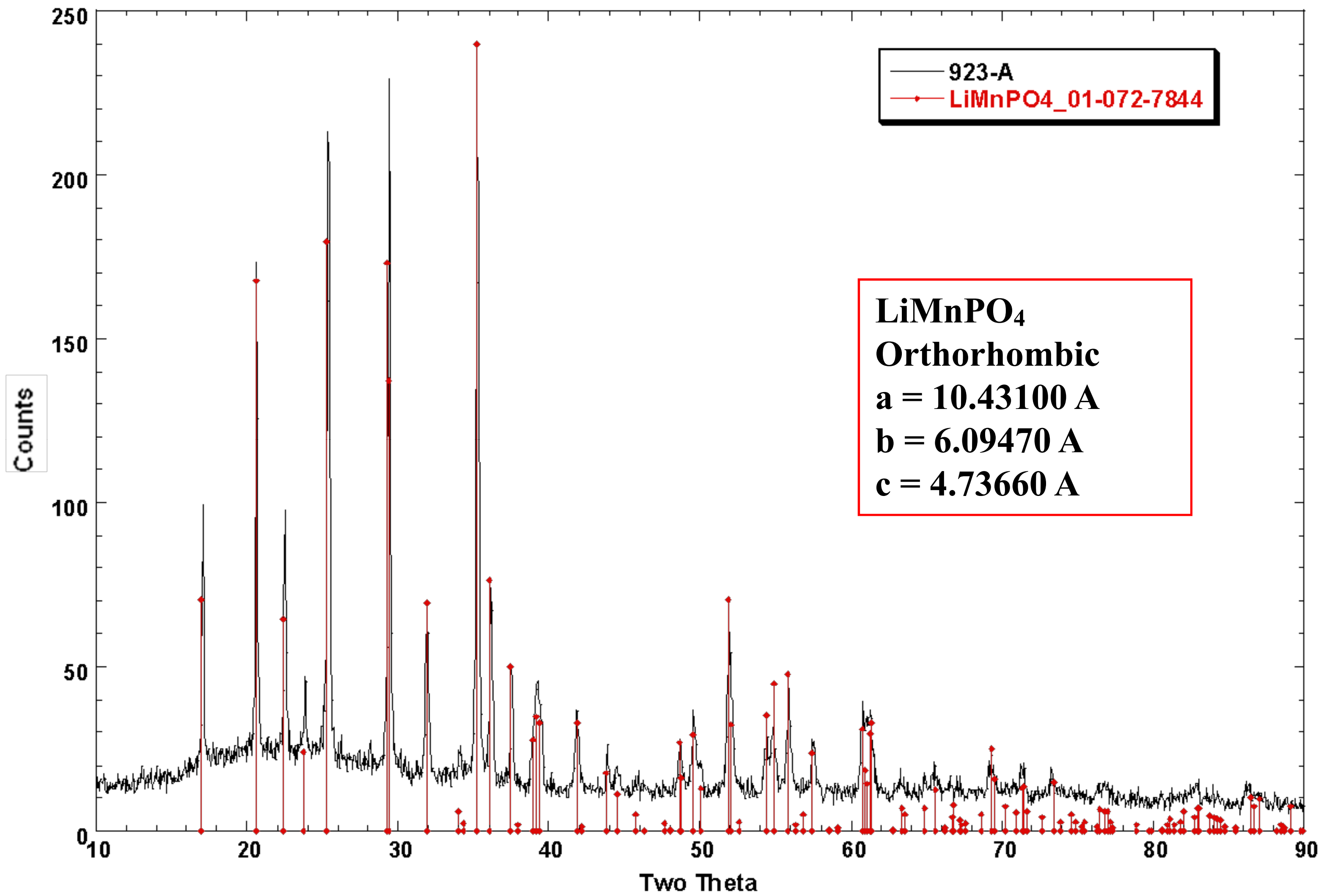
- **With polymer-IL(LiFSI), SiO_x-Gr maintain 70% initial capacity**
- **After 200 cycles, 400 mAh/g still exceeds graphite capacity**

- **With EC-DEC-$LiPF_6$, SiO_x-Gr shows only 335 mAh/g achieved.**
- **The reversible capacity is low at C/4, < graphite capacity.**

$LiMnPO_4$ Cathode Preparation

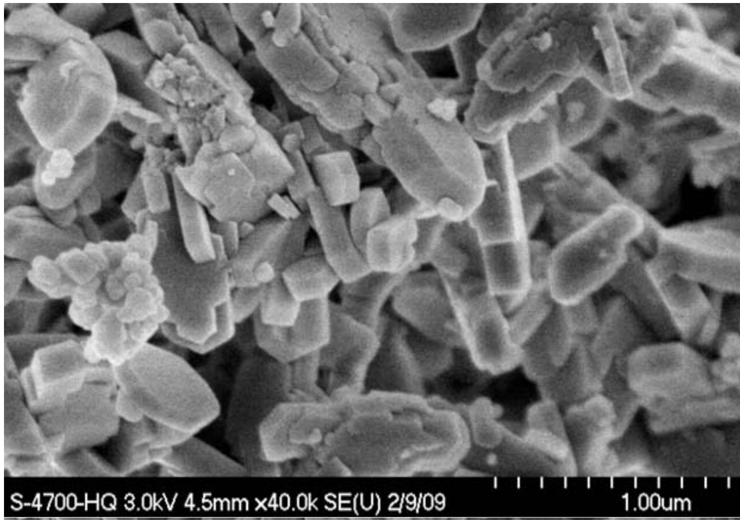
- $LiMnPO_4$ material synthesis techniques:
  - Microwave, Molten State and Polyol
  - Hydrothermal process
    - Carbon coated: ~ 2%
- Electrode:
  - Li $MnPO_4$ (from hydrothermal synthesis)
  - Composition: 5% VGCF, 10% carbon black, 10% PVDF

XRD of $LiMnPO_4$

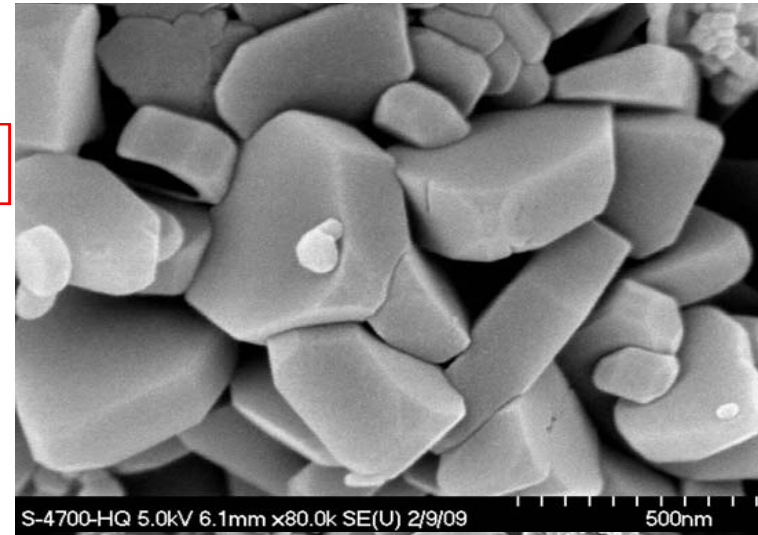


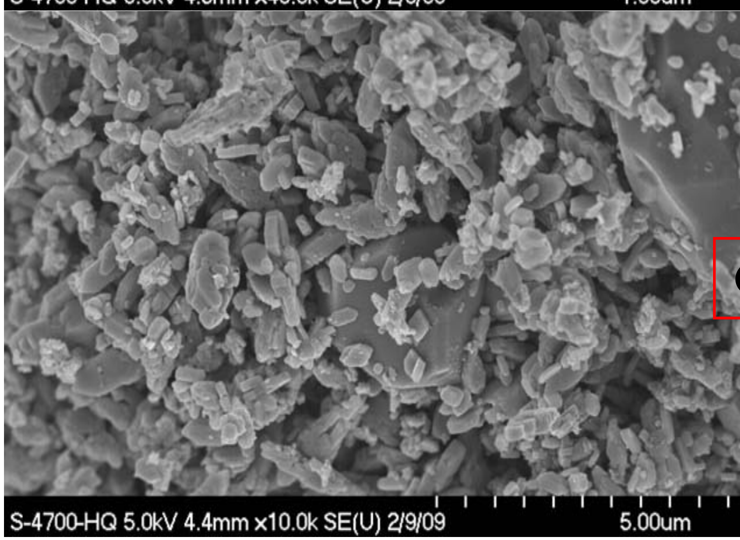
$LiMnPO_4$
Orthorhombic
a = 10.43100 A
b = 6.09470 A
c = 4.73660 A

SEM Images: $LiMnPO_4$ (923A)

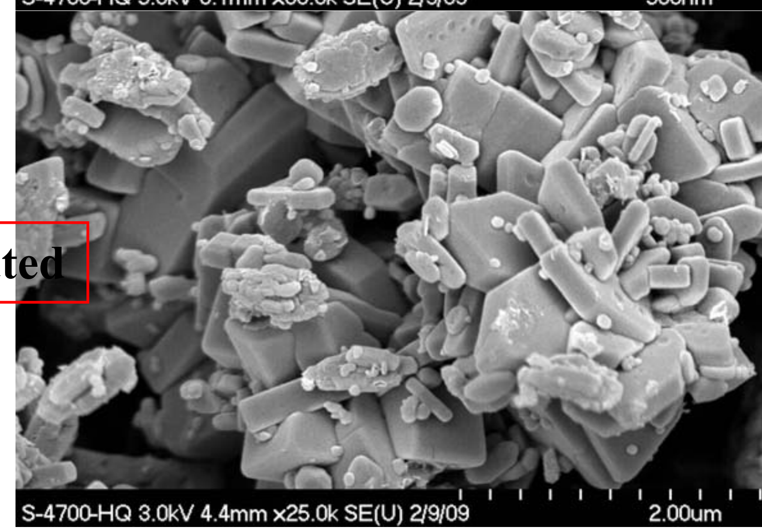


Uncoated





Carbon coated



- Powder particles are formed by grain agglomerates
- Most grains <1 µm but small fraction ~100 nm
- Grains are slightly plate-like.

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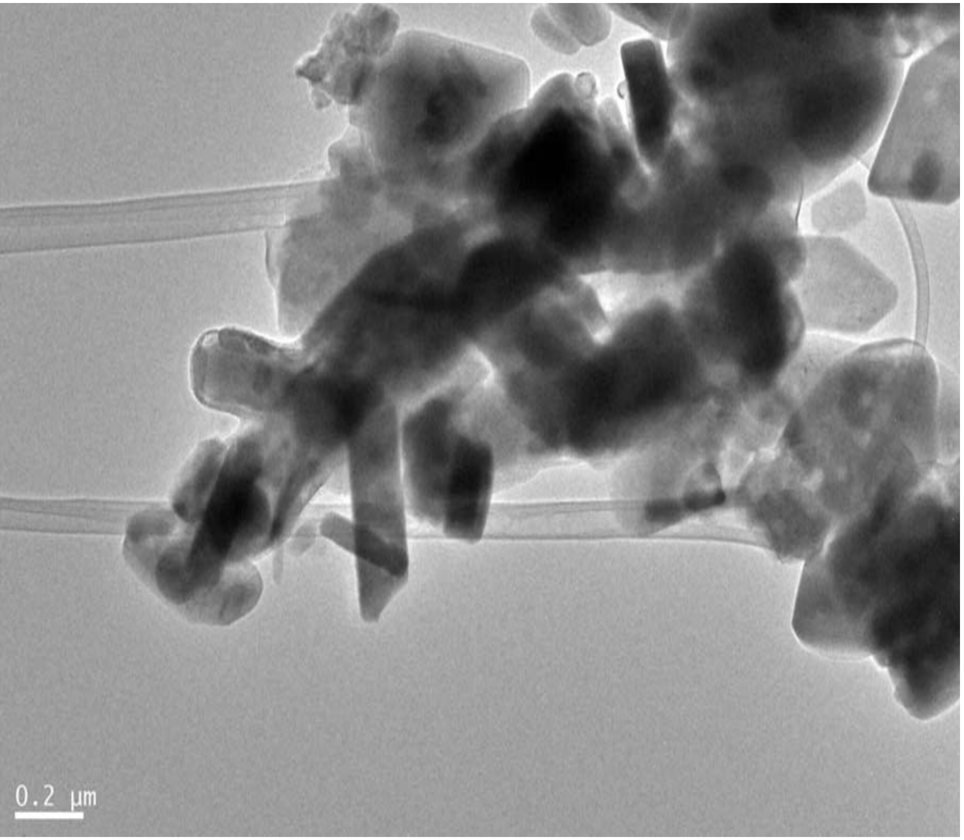
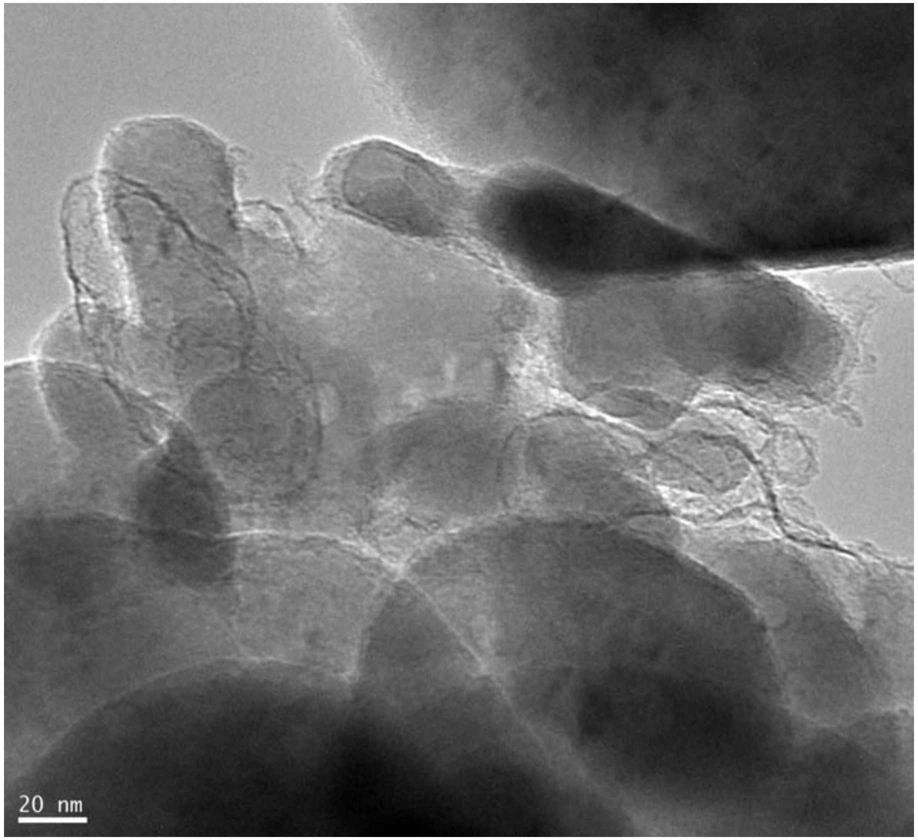
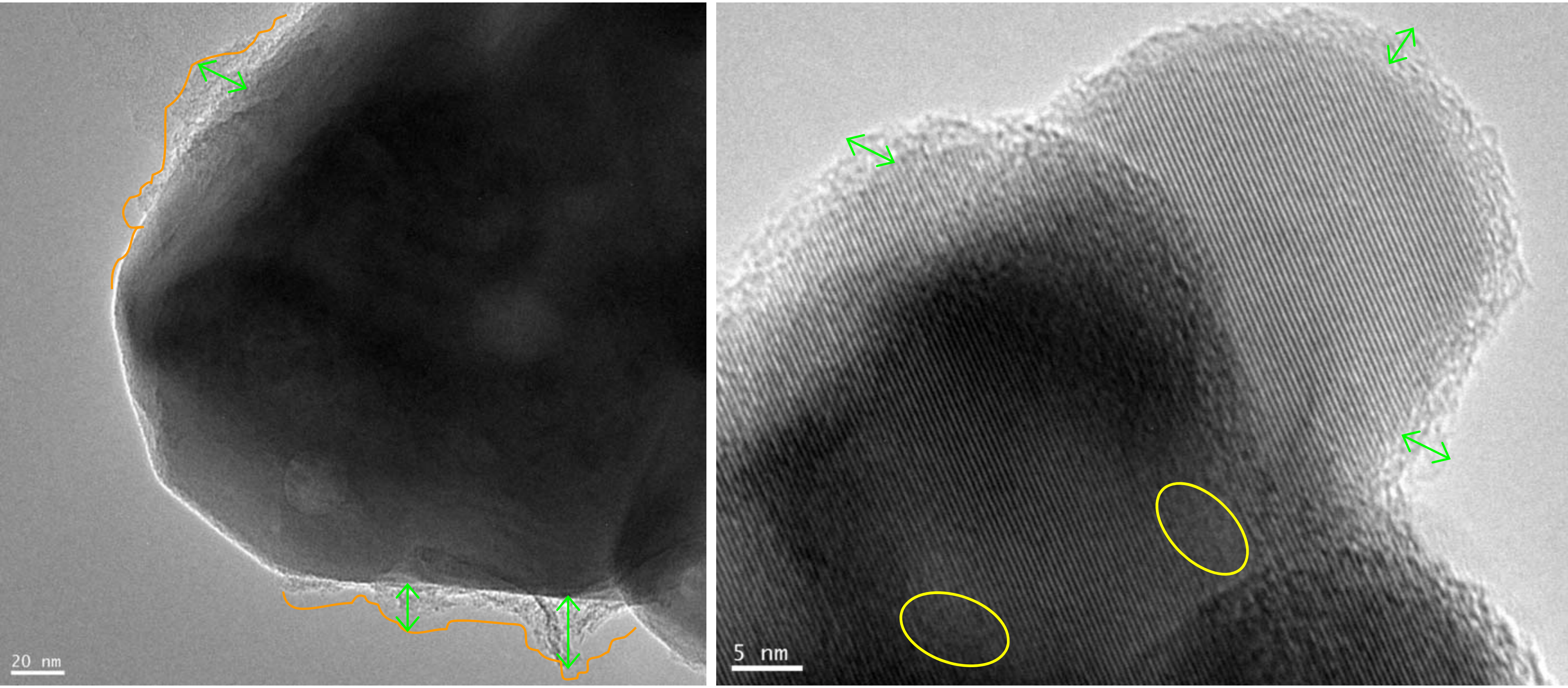
TEM Images: $LiMnPO_4$/C (923AC)





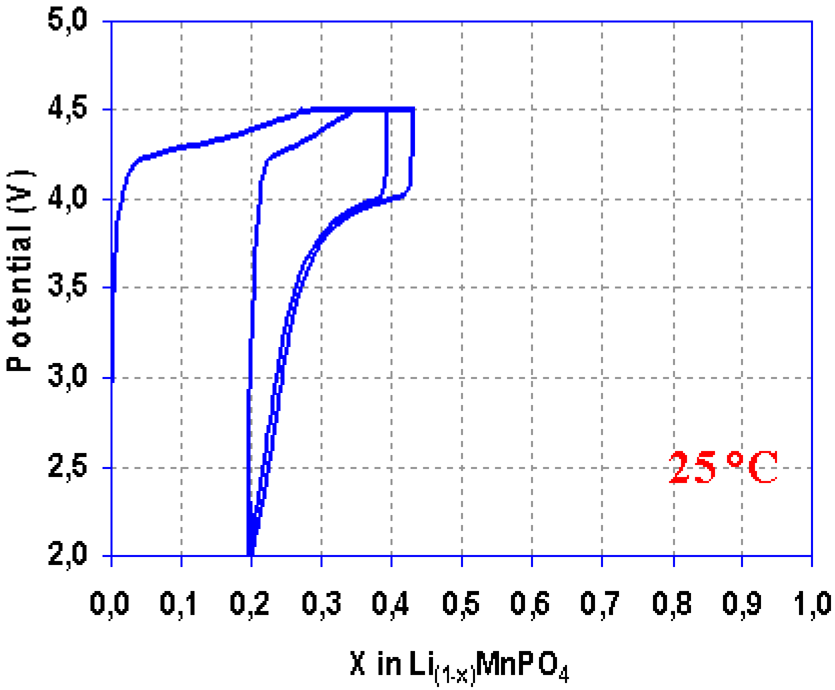
- Grain sizes vary from less than 100 nm to greater than 500 nm.
- Small grains located at grain boundaries .

TEM Images: $LiMnPO_4$/C (923AC)



- Lattice images and defects in the grain
- Carbon-coated layer is ~3 nm
- Non-uniform coating of carbon due low catalyst effect of Mn.

$LiMnPO_4$ Cathode Material



	Cap. (CC) mAh/g	Cap. (+ Floating) mAh/g	Eff. (%)
Charge1	46.0	66.6	
Disch1	33.4		50.0
Charge2	25	39.6	
Disch2	39		98.5

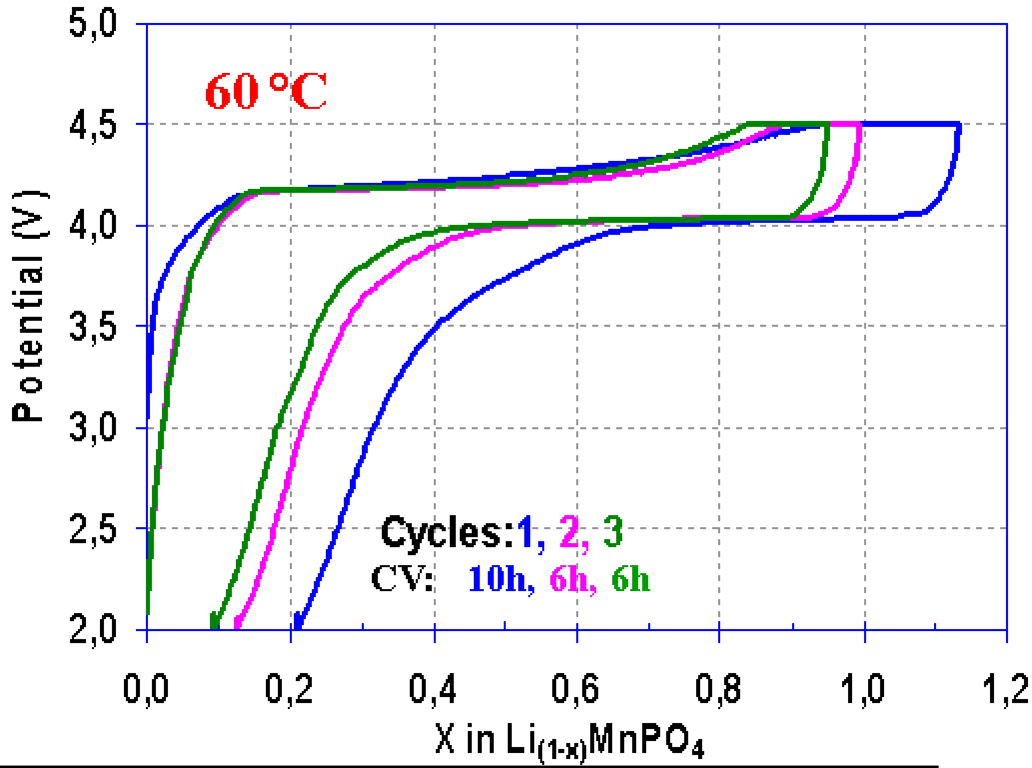
Rate:C/24
Floating: 10 h
Temperature: 25°C
1M $LiPF_6$-EC-DEC

-The first charge at 4.5 V gives a capacity of 46.6 mAh/g, and 66.6 mAh/g after 10 h float on charge.
-The second cycle gives 39 mAh/g reversible capacity, with high coulombic efficiency of 98.5%.
- Only 33% Li is reversibly intercalated at 25°C.

$LiMnPO_4$ Cathode Material

	Cap. (CC) mAh/g	Cap. (+ Floating) mAh/g	Eff. (%)
Charge1	158	188	
Disch1	156		89
Charge2	150	168	
Disch2	147		86
Charge3	142	160	
Disch3	145		91

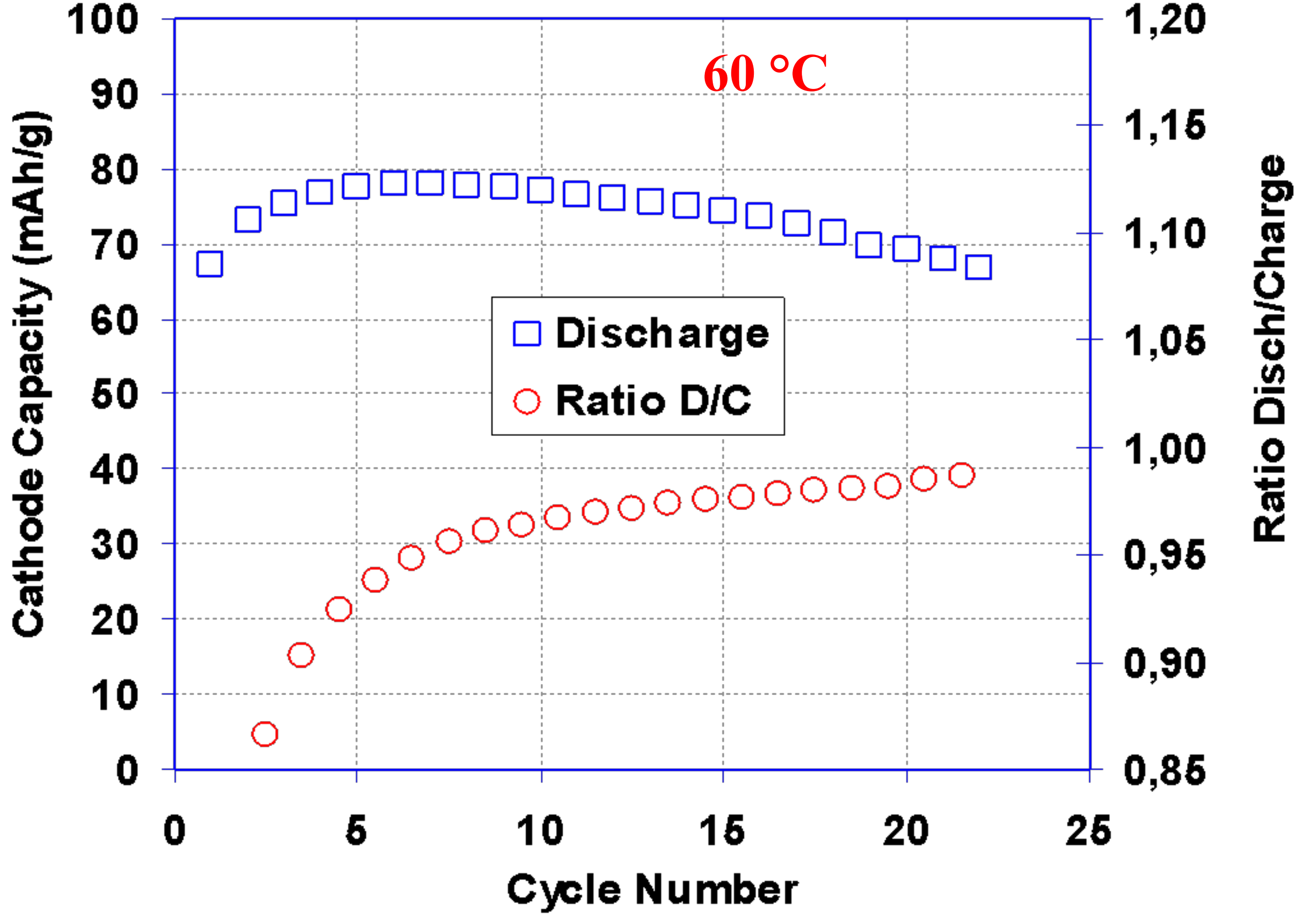
Rate:C/24
Temperature: 60°C
1M $LiPF_6$-EC-DEC



- The first charge at 4.5V gives a high capacity of 159 mAh/g, and 188mAh/g after 10 h float.
- The reversible capacity in the 3rd cycle was 145 mAh/g
- Better performance at 60°C related to improvement in the ionic conductivity.

$LiMnPO_4$ Cathode Material

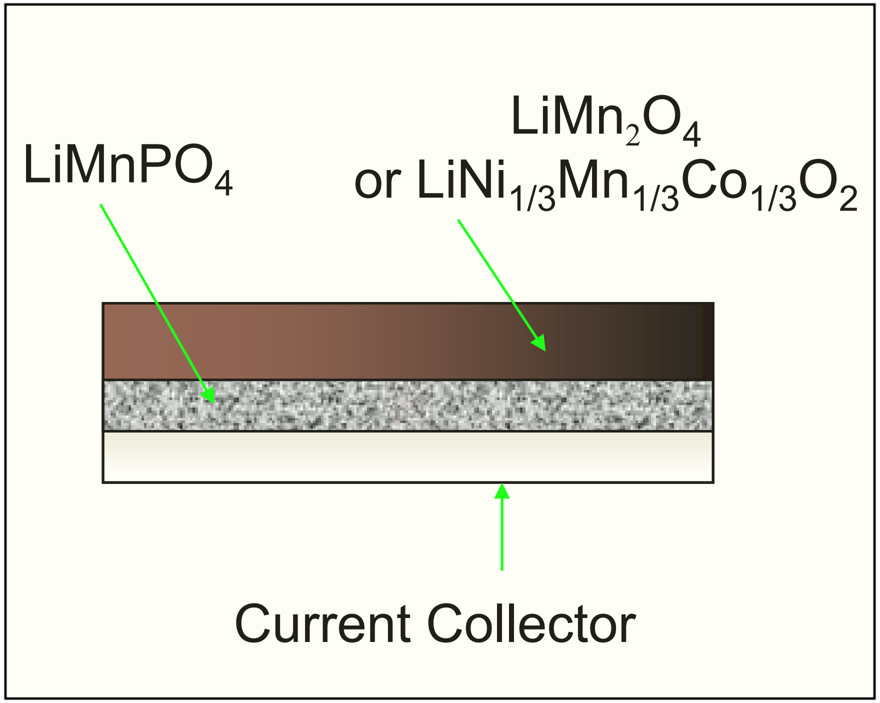
Disch:1C
Charge: C/4 + float
Temperature: 60°C
1M $LiPF_6$-EC-DEC



- Some capacity fading was observed, float charge at 60°C accelerates capacity loss.
- About 80 mAh/g can be extracted at C/4 at 60°C.

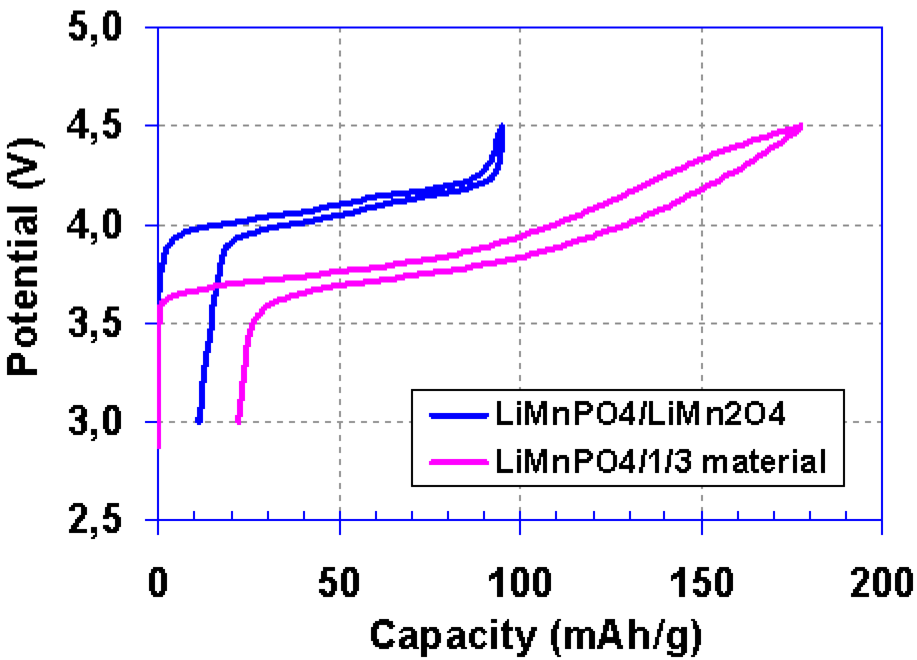
Dual Materials and Multilayer Electrodes

- **Low-cost mixed powders:**
  - **$LiMnPO_4$-$LiMn_2O_4$ (20%/80%)**
- **Multiyear electrodes:**
  - **$LiMnPO_4$ –$LiCo_{1/3}Mn_{1/3}Ni_{1/3}O_2$**
    - **Overcharge protection**
    - **Improved stability from decreased oxygen generation**

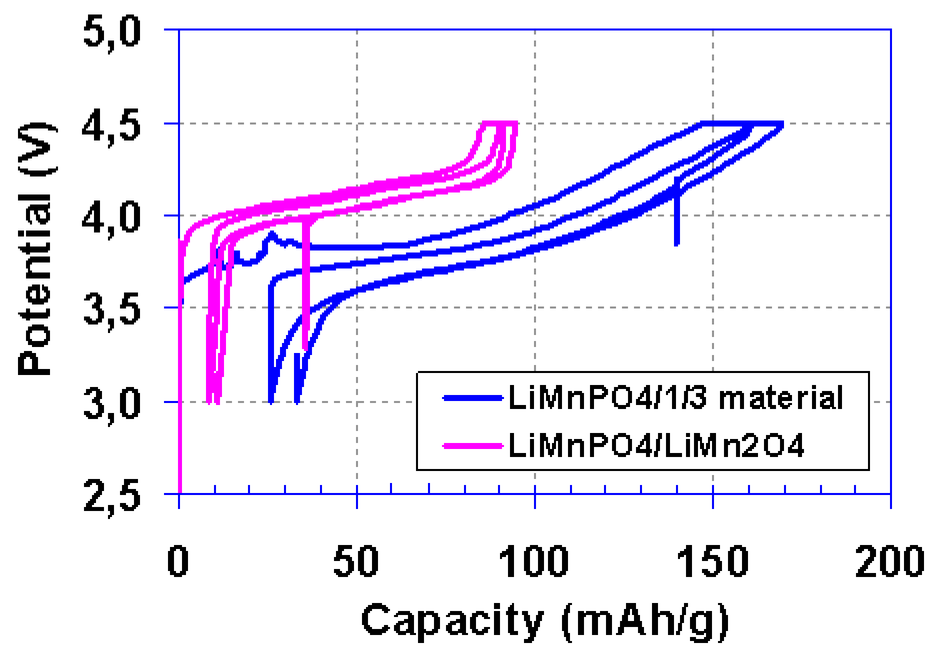


Dual Materials and Multilayer Electrodes - Evaluation

Blended cathode: 20/80



Multilayer electrodes

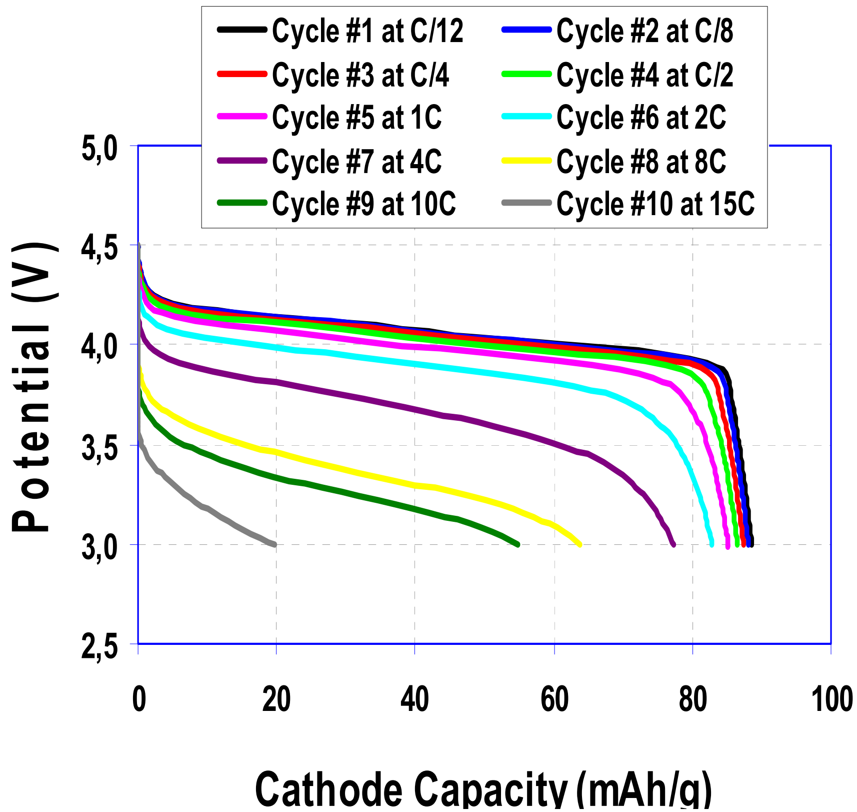


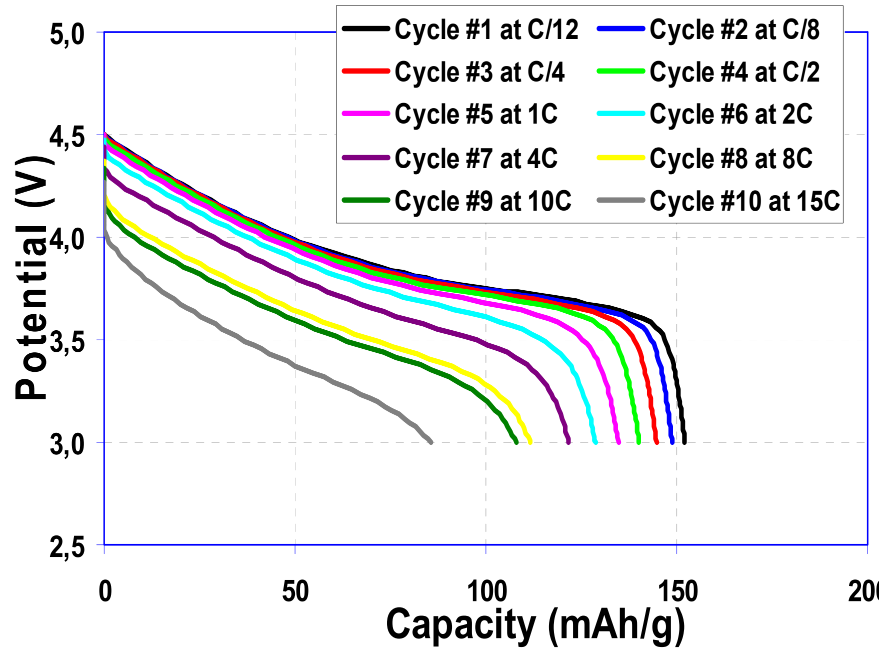
Blended $LiMnPO_4/LiCo_{1/3}Mn_{1/3}Ni_{1/3}O_2$ has higher irreversible capacity than blended $LiMnPO_4/LiMn_2O_4$ cathode

Multilayer $LiMnPO_4/LiCo_{1/3}Mn_{1/3}Ni_{1/3}O_2$ has higher irreversible capacity than multilayer $LiMnPO_4/\ LiMn_2O_4$ cathode

Dual Materials Electrodes - Evaluation

$LiMnPO_4/LiMn_2O_4$ **Blended cathode: 20/80** $LiMnPO_4$/ 1/3 material





Blended $LiMnPO_4/LiCo_{1/3}Mn_{1/3}Ni_{1/3}O_2$ has higher rate capability than blended $LiMnPO_4/LiMn_2O_4$ cathode

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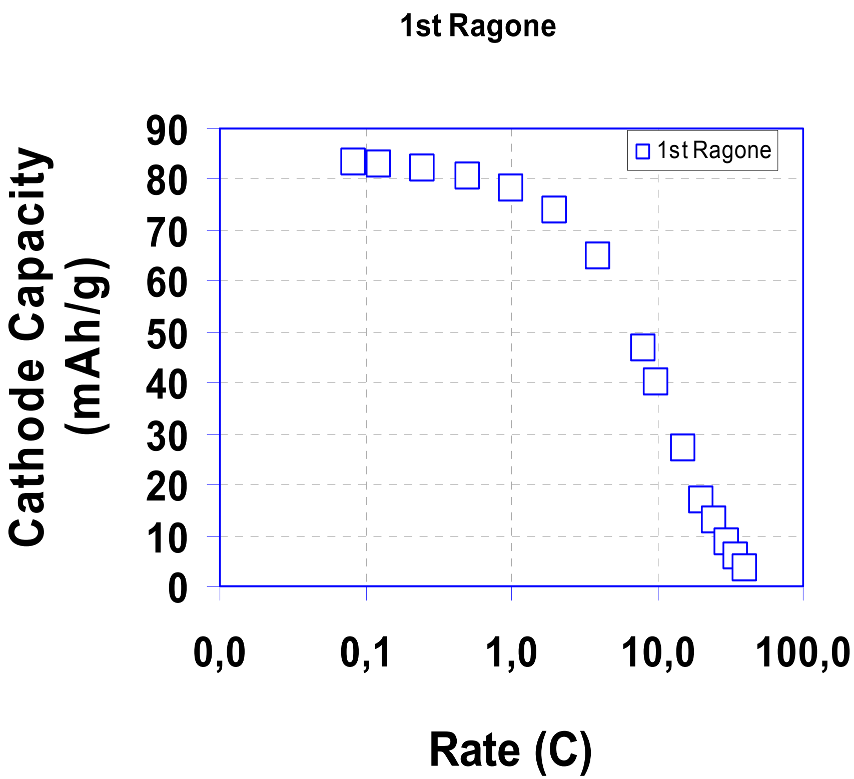
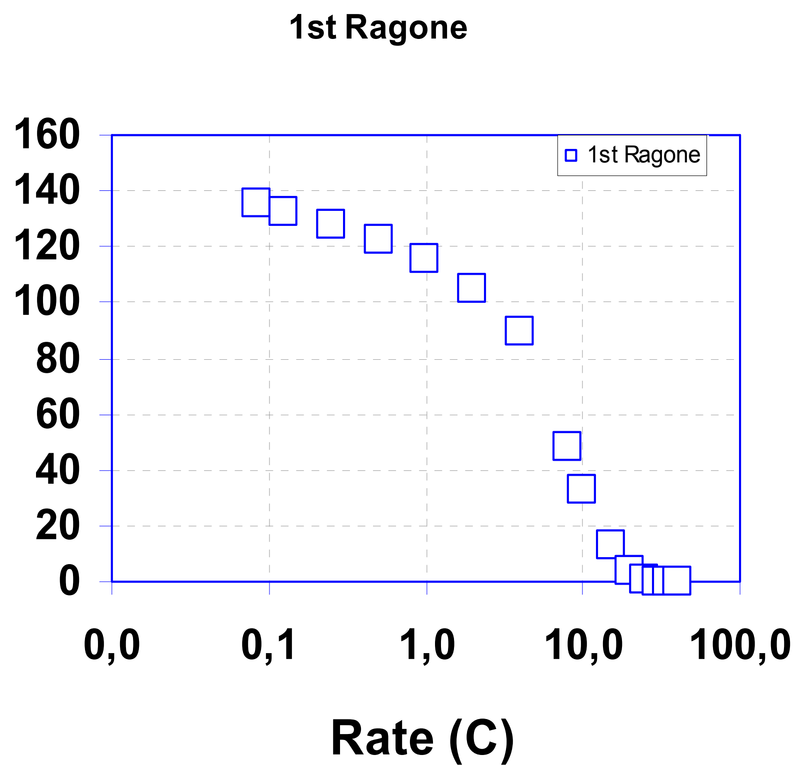
Multilayer Electrodes - Evaluation

$LiMnPO_4/LiMn_2O_4$

$LiMnPO_4$/ 1/3 material





$LiMnPO_4/LiCo_{1/3}Mn_{1/3}Ni_{1/3}O_2$ has higher capacity and rate capability than the multilayer $LiMnPO_4/LiMn_2O_4$ cathode
The rate capability of the electrodes is comparable

Conclusion

- **SNG12 was more strongly influenced by additives than OMAC:**
  - **1st CE improved to 93% when VEC is present, compared to 85% without additive.**
  - **The reversible capacity of both graphites decreased with additives in the electrolyte.**

- **The cells showed good thermal performance from the ARC test (Sandia Lab.)**

- **High reversible capacity, with 84% 1st CE, was obtained with SiO_x anode by using WSB:**
  - **1118 mAh/g for pure SiO_x**
  - **816 mAh/g for SiO_x mixed with graphite.**

- **The SEI layer on the mixed SiO_x:graphite (1:1) anode was studied by ex-situ SEM.**
  - **The breakdown of SiO_x particles initiated at 0.5 V during discharge, which results in capacity fade.**

- **Different synthesis routes of $LiMnPO_4$ were explored, and the hydrothermal method**
- **yielded the following results**
  - **67 mAh/g at 25°C for the 1st charge, but only 33% of Li was reversibly extracted.**
  - **Better performance was obtained at 60°C due to higher ionic conductivity, and 85% Li was reversibly extracted.**

- **Overcharge protection was improved with dual-chemistry and multilayer cathode materials.**

Activities for the Next Fiscal Year

- **Continue evaluation of mixed graphite-SiO_x as an alternative anode**
- **Examine the performance of other olivines, like $LiMnPO_4$ with different synthesis method, as cathodes in Li-Ion cells**
- **Conduct in situ SEM studies of olivines obtained by molten-state synthesis**
- **Evaluate wet-milling technique to reduce particle size of $LiMnPO_4$**
- **Investigate dual oxide-olivine as a powder mixture or in multilayer structures in cathodes**
- **Complete high-rate performance and cycling with WSB alternatives anodes**
- **Investigate techniques to improve the conductivity of olivines such as $LiMnP_{1-x}V_xO_4$**
- **Evaluate dual oxide-olivine as mixed powders or multilayer structures in cathodes**
- **Continue supplying laminated electrode structures and powders to investigators in the BATT program**
- **Screen $LiMPO_4$ cathodes and SiO/graphite anodes by fabricating and testing 18650 cells and provide cells to investigators in the BATT program for evaluation.**