Developing High Capacity, Long Life anodes

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DOE merit review

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Project ID # ES20_ AA

Overview

Timeline

- Start - October 1st, 2009.
- Finish – September 2013
- 100% complete

Barriers

- Safety of the battery.
- Power density of the battery.
- Cycle & calendar life span of the battery.

Budget

- Total project funding: 1112K
  - FY12: 212K
  - FY11: 300K
  - FY10: 300K
  - FY09: 300K

Partners

- Z. Fang (University of Utah).
- Y. Ren, M. Balasubramanian, Advanced Photon Source, (APS/ANL).
- Z. Fang (University of Utah).
- Dennis E. Brown (Northern Illinois University).
- FMC, Northwestern University,

Objectives

- ❑ Develop new advanced high energy anode materials with long life and improved Safety for PHEV and EV applications.

- ❑ Develop a low cost synthesis methods to prepare high energy anodes

- ❑ Full structural and electrochemical characterizations of the prepared anode materials.

- ❑ Demonstrate the applicability of these anodes in half and full cells systems.

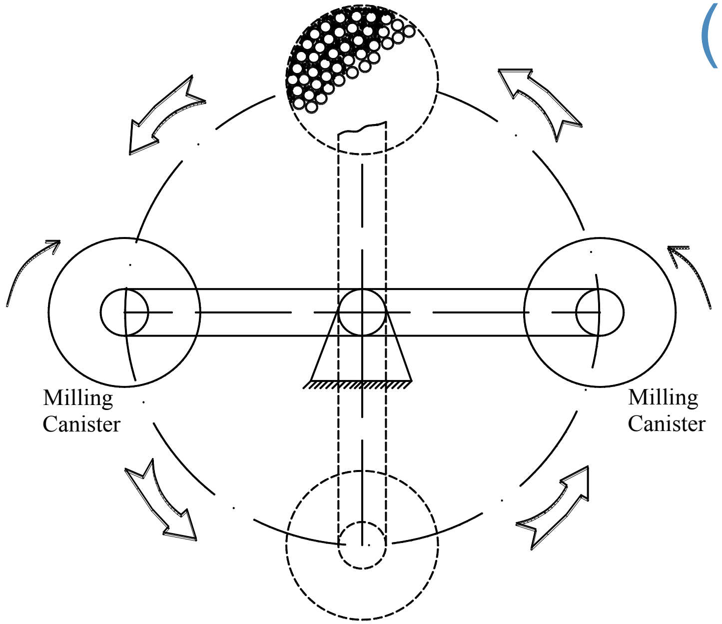
Approaches

- $MO\text{-}Sn_xCo_yC_z$ ($MO=SiO$, SiO_2, SnO_2, MoO_3, GeO_2) anode materials were selected for investigation as high energy anode based on the following criteria:
  - $Sn_xCo_yC_z$ alloys are known to provide a capacity of 400-500mAh/g for hundreds of cycles.
  - MO anodes are known to provide more than 1000 mAh/g with poor cyleability.
  - The formation of $Sn_xCo_yC_z$ and MO composite could lead to the increase in the capacity, reduce the amount of cobalt in the material and improve the cyleablity as $Sn_xCo_yC_z$ play the role of buffers against the volume expansion of MO.
  - This anode system is more safer than the graphite and possess low potentials in the range of 0.3-0.75V (expect high voltage cells when combined with high cathodes)
  - This anode system could offer higher practical capacity and higher 1^{st} cycle charge discharge efficiency
  - This anode system offers high packing density (up to 3 g/cc), much higher than graphite (1.1g/cc) (expect higher volumetric density)

Milestones FY 12 : High capacity and Long Life Anodes

- Some of the composite anode were prepared by mechanically alloying using metal (Co, Sn) carbon and oxides (MO). (*Completed)*
- Comparative studies between MO-$Sn_xCo_yC_z$ (MO=SiO, SiO_2, SnO_2, MoO_3, GeO_2) based on their electrochemical properties and their cost. (*Completed)*
- Investigation of their structural rearrangement during the intercalation or de-intercalation of lithium. *(Completed)*
- Selection of a candidate for further electrochemical characterization: full cells study. *(Completed)*

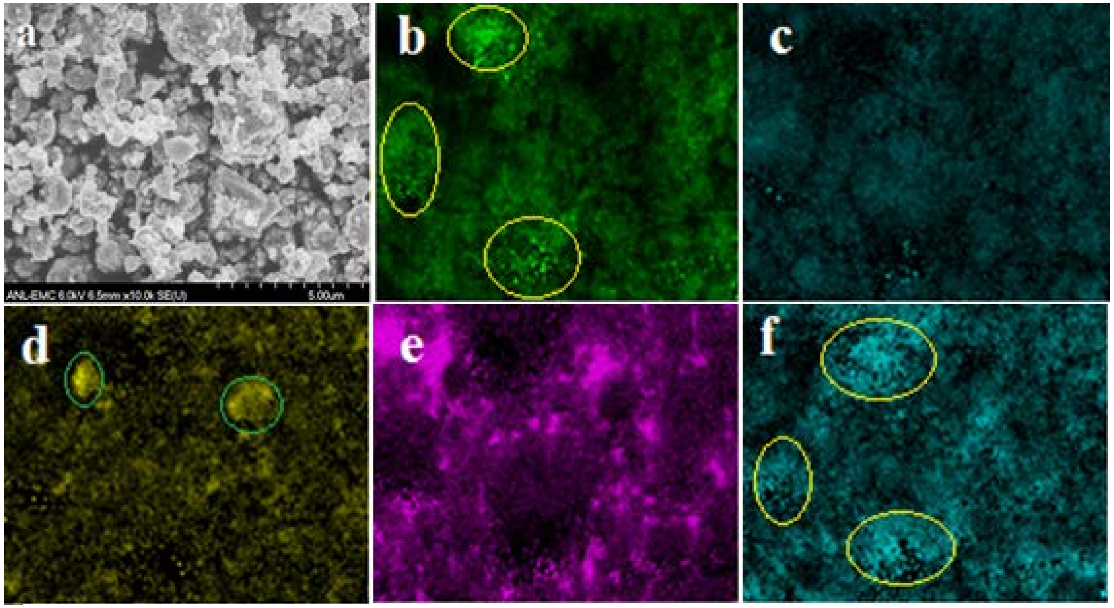
Scheme for ultra-high energy ball milling machine (UHEM)



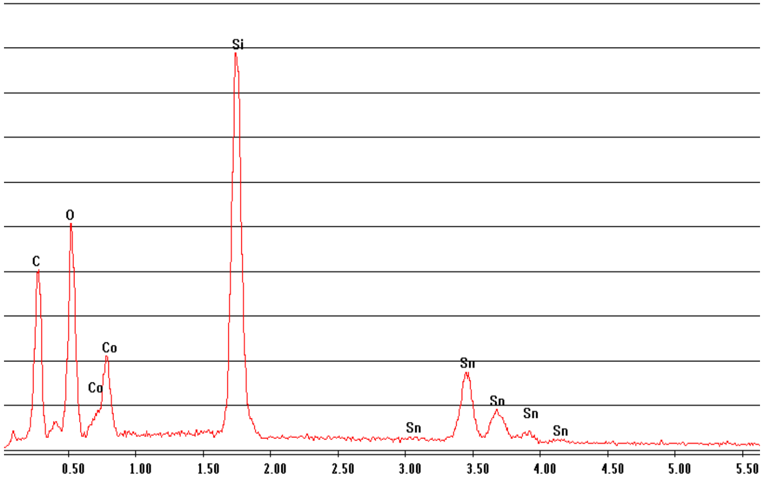
SPEX mill machine

- Custom-made planetary mill method (rotation in 2 directions) that creates a very high centrifugal field, confining the particles firmly in the interstices of the ball mass. (~250 gr of the material can be prepared in 1 shot).
- Traditional ball mills, adopt stirred mills or vibration mills. However, these mills exhibit a limitation regarding to the “dead zone”.
- We take SiO-SnCoC composite as an example to compare two kinds of mill machine.

SEM Mapping

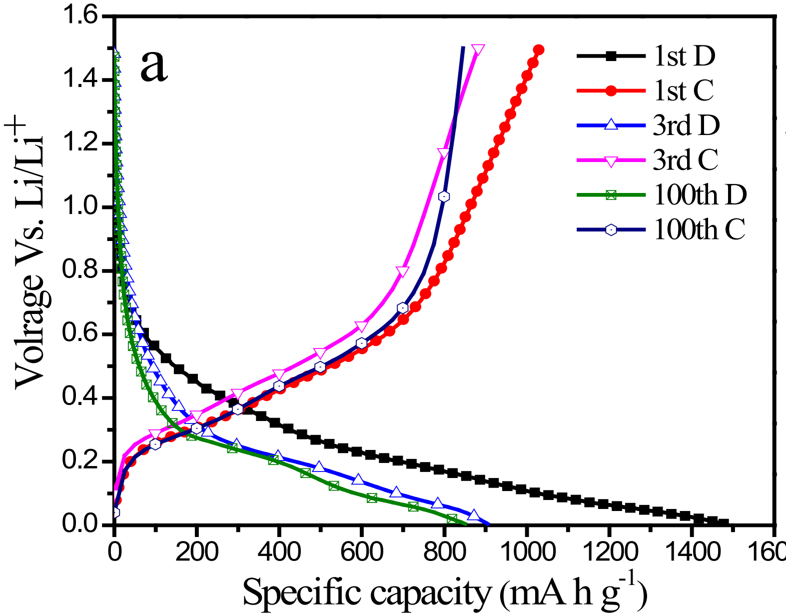


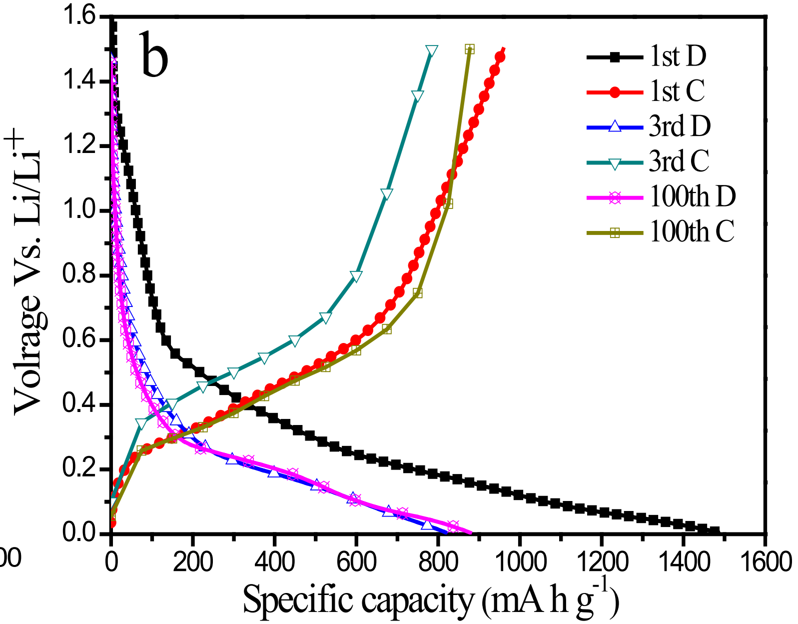
(a) SEM images and EDX elemental mapping of
(b) Si,
(c) O,
(d) Co,
(e) C,
(f) Sn



- Si (b) and Sn (f) exhibit similar distribution, especially in the yellow-circled areas.
- Perhaps Sn and Si formed a new alloy after high energy ball milling (UHEM).

Voltage profile of 50 wt% SiO–50 wt% $Sn_{30}Co_{30}C_{40}$

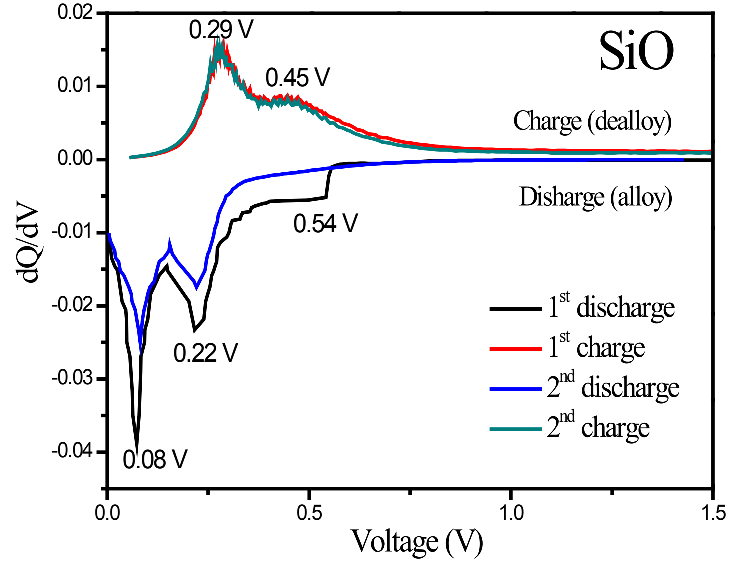


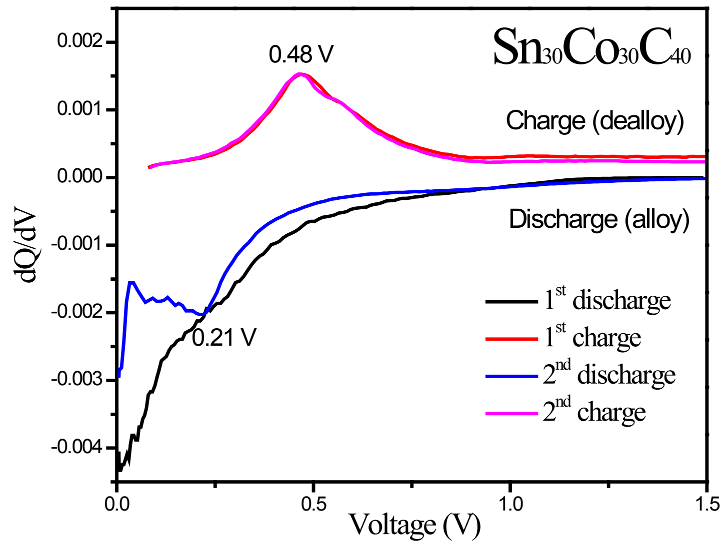


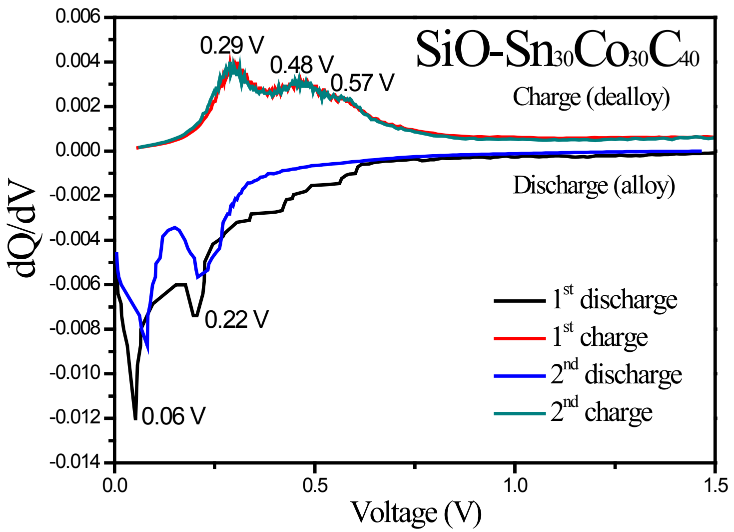
Charge-discharge curves of cells with UHEM anode cycled at rates of (a) 300 mA g^{-1} (~C/3) and (b) 900 mA g^{-1} (~1C)

- A Voltage ~ 0.3V higher than the graphite was observed.
- 1st cycle charge discharge effeciecy~65%.

dQ/dV plot of 50 wt% SiO–50 wt% $Sn_{30}Co_{30}C_{40}$

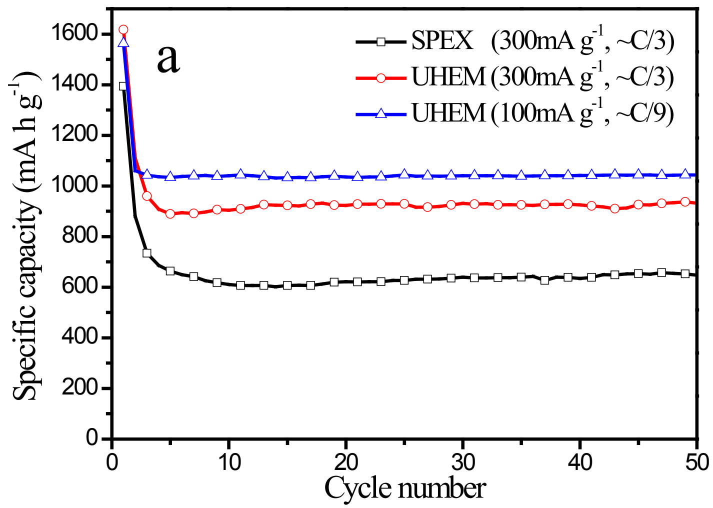


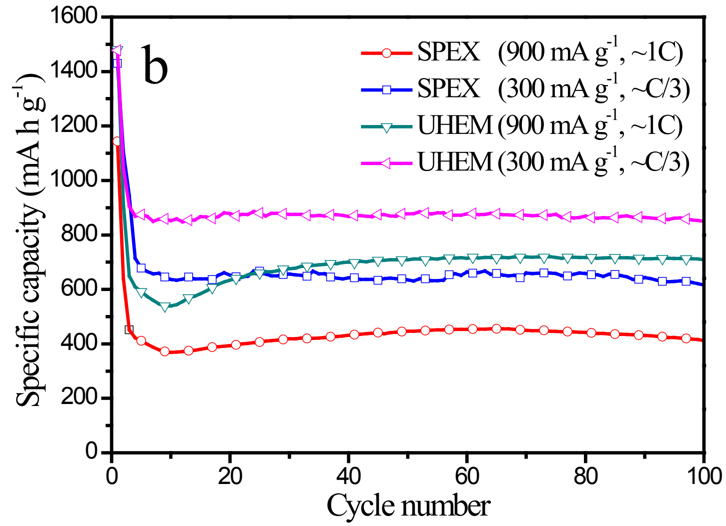


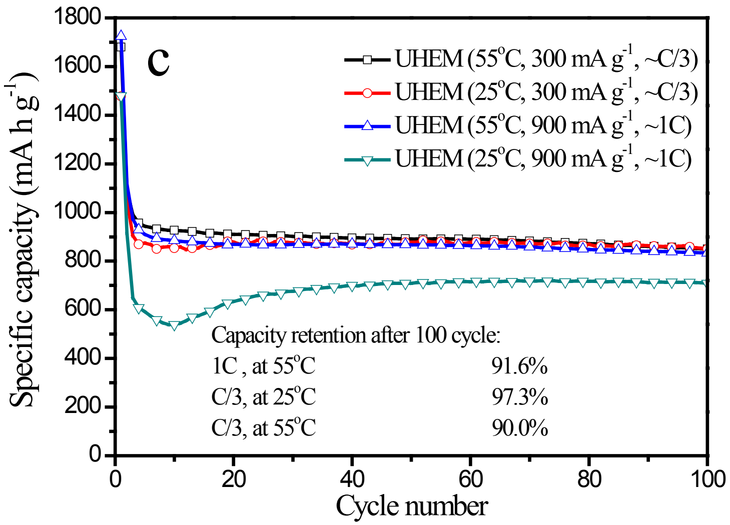


- For SiO-SnCoC, an SEI layer appeared to form at 0.6 V to 0.3 during the first cycle discharge.
- During the charge, the 0.29 V peak correspond to delithiation of Li_xSi alloy of SiO.
- The peak at 0.57 V might be related to the delithiation of Si-Sn alloy.

Cycle performance of 50 wt% SiO–50 wt% $Sn_{30}Co_{30}C_{40}$





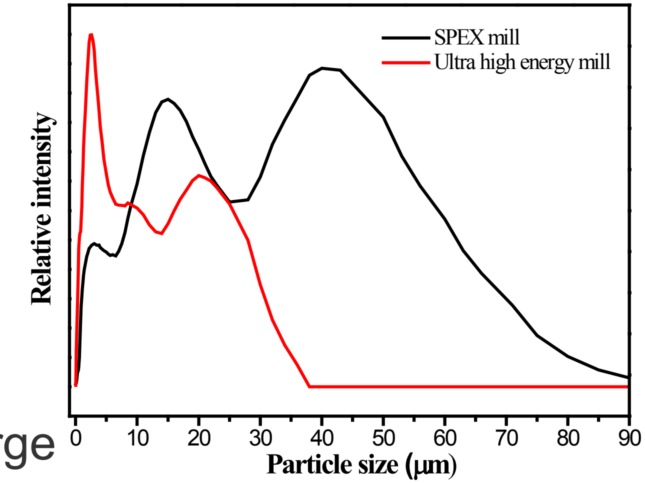


- UHEM anode delivers a specific capacity of 900 mA h g^{-1} at the rate of 300 mA g^{-1}, much higher than that (~600 mA h g^{-1}) of the SPEX anode at the same current.
- UHEM anode exhibits excellent rate capability, over 700 mA h g^{-1} at high rate 1C (900 mA g^{-1}) over 100 cycles.
- UHEM anode shows good thermal stability and excellent cycle life.

Question : why 300 mAh/g difference between Spex and UHEM milling samples?

1- Particle size :

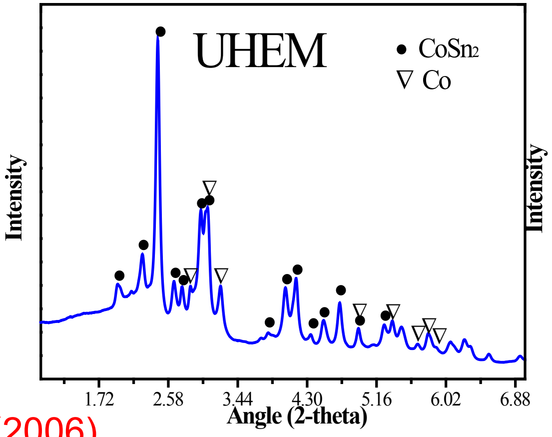
OAC	BET surface area (m^2/g)	Particle size distribution
UHEM	7.521	50% particle size < ~2.5µm
SPEX	4.733	50% particle size < ~13 µm

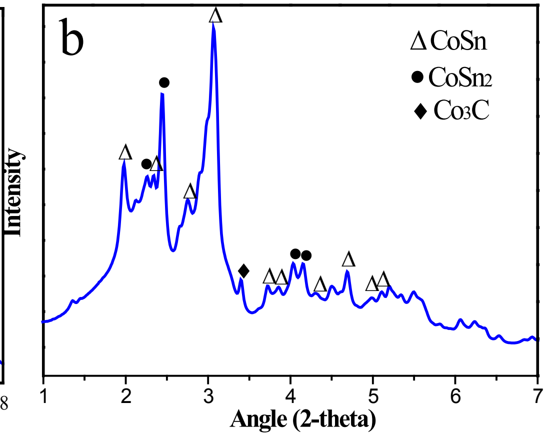


- Nanomaterials can decrease the (SEI) resistance and lead to higher specific capacities at high charge/discharge rates.

2- Materials structure :

UHEM sample which shows higher amount of $CoSn_2$ (it is known that $CoSn_2$ delivers more capacity than CoSn).



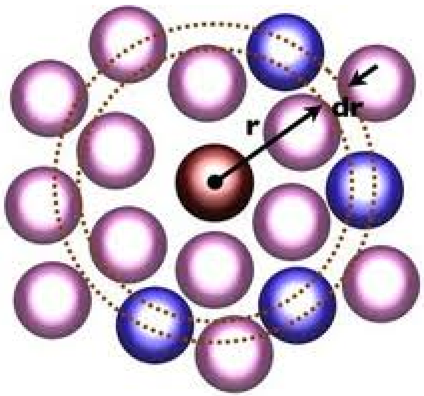


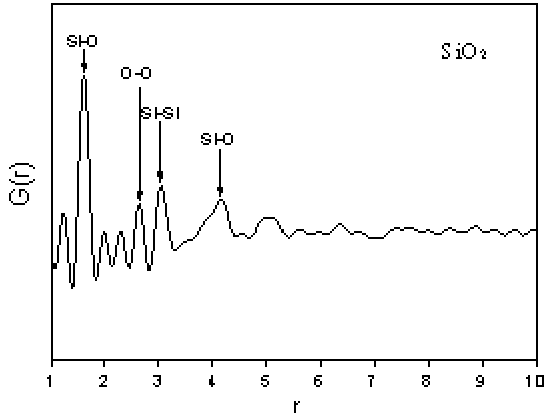
(*) J.J. Zhang et al., *JES*, **153** () A1466-A1471 (2006)

3-Short-range order structure :Pair distribution function

The *G*(*r*) gives the probability of finding an atom at a given distance *r* from another atom and can be considered as a bond length distribution.

XRD patterns only contain information about the long-range average structure.

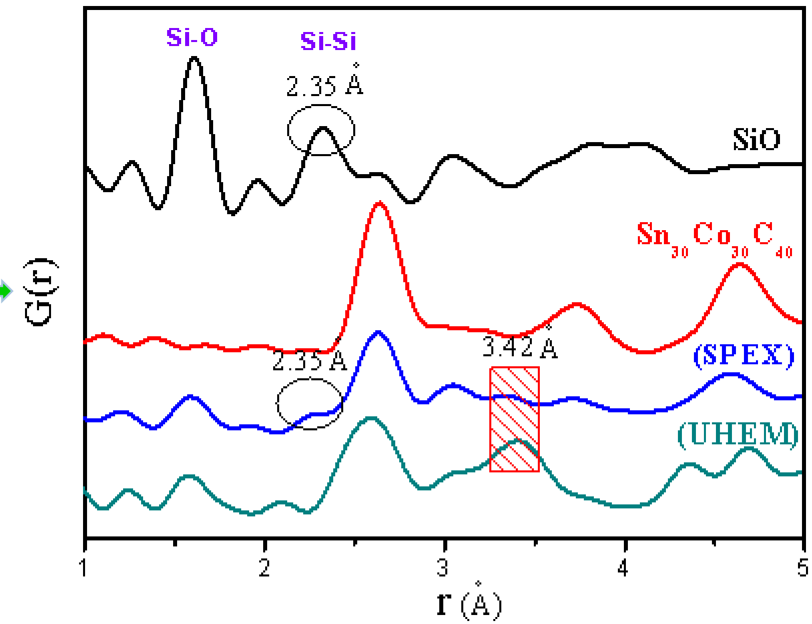




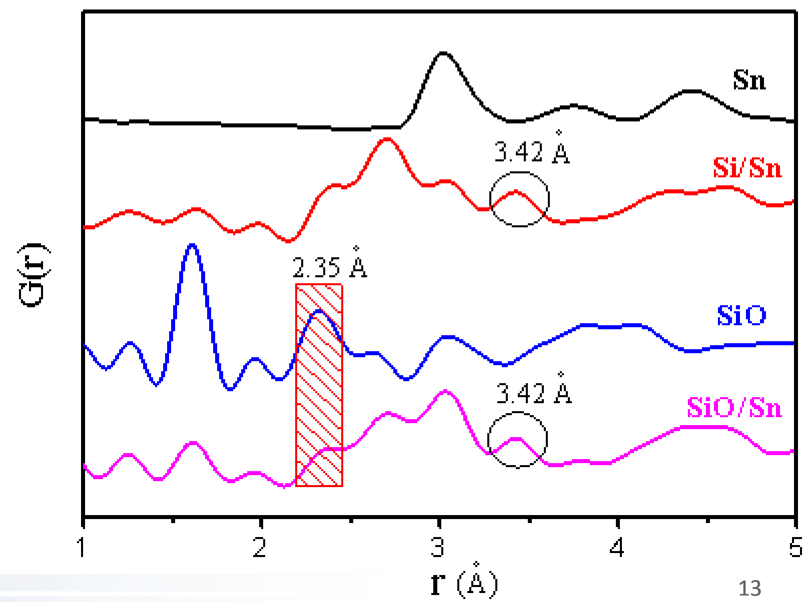
PDF analysis has been successfully used to investigate short-range order in lithium-ion battery electrode materials.

PDF study of 50 wt% SiO–50 wt% $Sn_{30}Co_{30}C_{40}$

- 2.35 Å peak of SPEX-milled anode is present and weak.
- 2.35 Å peak of UHEM anode diminished completely.
- 3.42 Å peak of UHEM anode is stronger.
- 3.42 Å peak didn't exist in (SiO, Sn, Si or $Sn_{30}Co_{30}C_{40}$,).

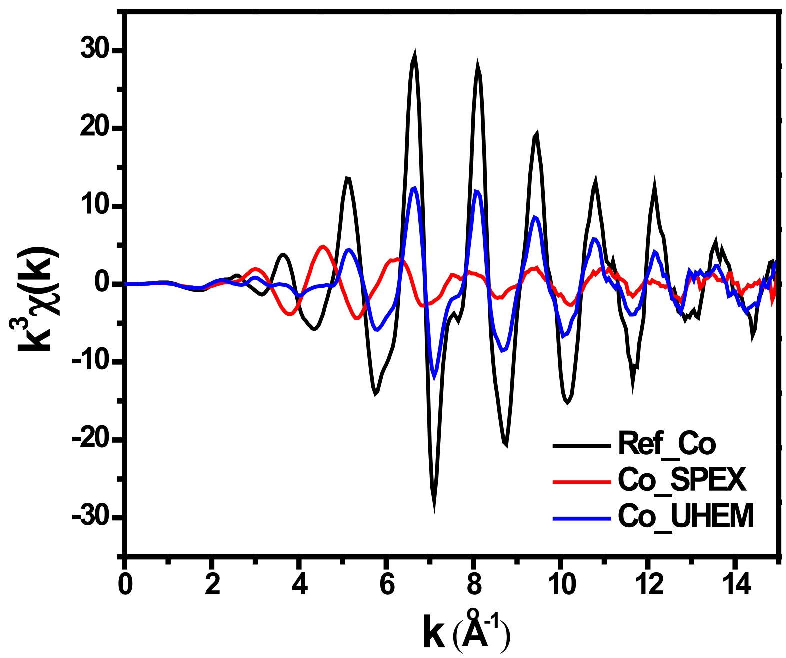


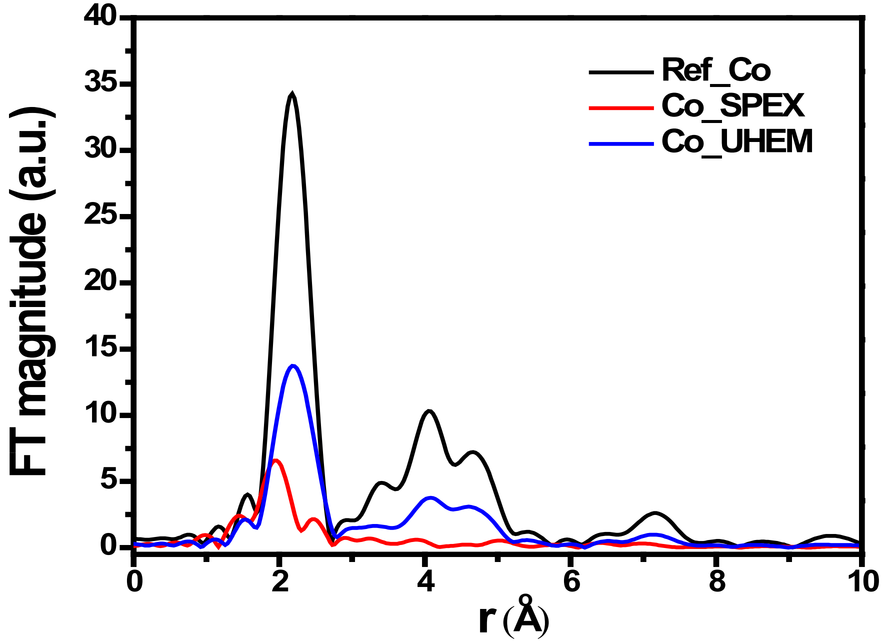
- 3.42 Å peak is attributed to the Si-Sn bond of Si-Sn amorphous alloy.
- The intensity of the Si-Si peak at 2.35 Å decreased with the emergence of the 3.42 Å peak. So large amount of Si-Sn alloy formed in UHEM, SiO/Sn and Si/Sn.
- For example $Si_{0.66}Sn_{0.34}$ prepared by sputtering method showed approximate 3000 mAh/g capacity (*).



(*) L. Y. Beaulieu et al., *JES*, **150** (2) A149-A156 (2003).

EXAFS : Cobalt edge



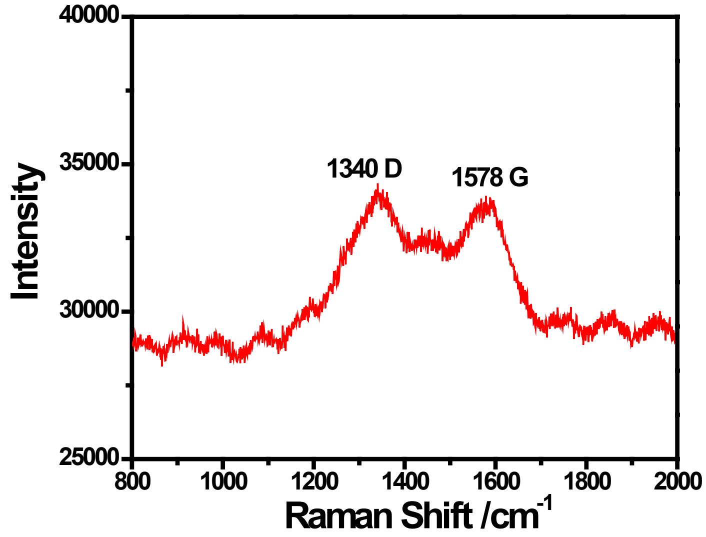


- Cobalt in both the SPEX and UHEM milled sample is largely metallic and no oxidized cobalt compound .
- ~ 40% of the Co atoms in the UHEM sample is present as metallic cobalt.
- Co alloys exist in SPEX sample.

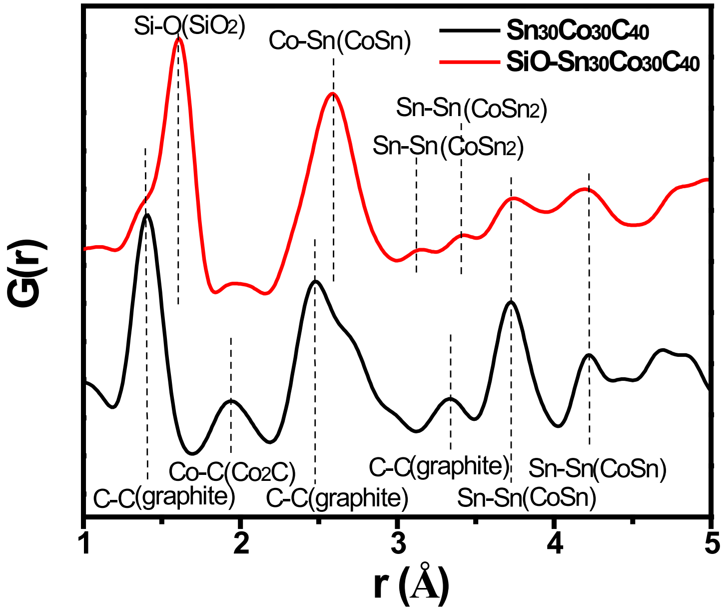
(*) B. Liu et al. *New anode material based on SiO-$Sn_{30}Co_{30}C_{40}$ for lithium batteries Chemistry of Materials 24(24), 4653 (2012).*

Nature of carbon in the material

- Two Raman scattering peaks at 1578 and 1340 cm^{-1} are assigned as G and D band, respectively.
- These peaks are due to intrinsic phenyl ring stretch (G band) and disordered band (D) in graphite.

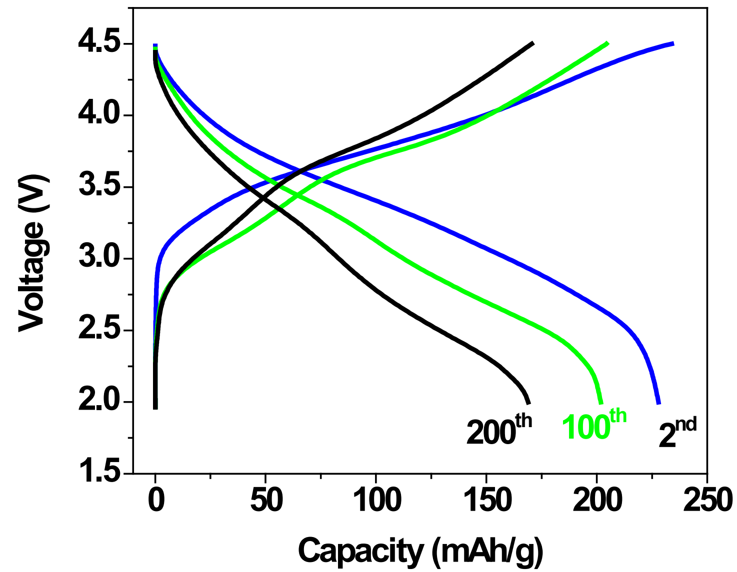


- Neutron PDF shows that the carbon is in the graphitic form with the presence of Co_2C alloy.



Full cell

Li_2MnO_3- $LiMO_2$ (M: Mn, Ni, and Co) : Cathode

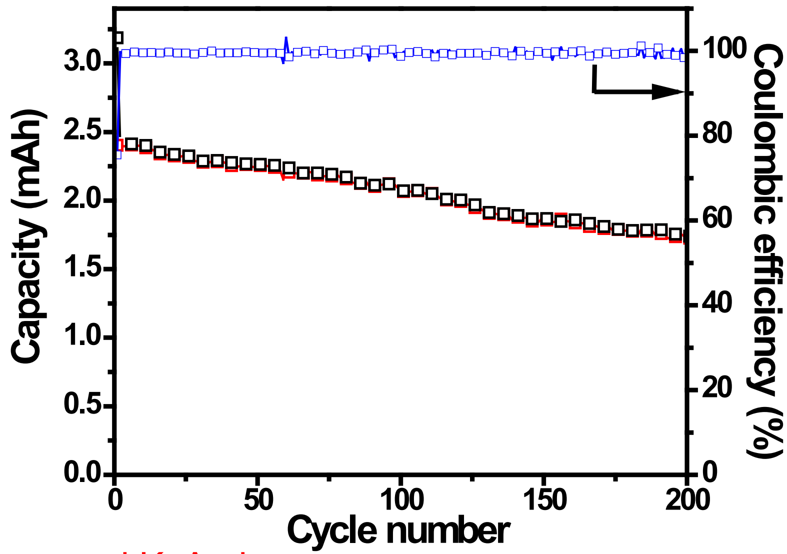


Cathode : $Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$ (Argonne cathode)

loading 7.7mg/cm²

Anode: 50wt%SiO-50wt%$Sn_{30}Co_{30}C_{40}$

loading 1.5mg/cm²



Voltage window: 2-4.5 V

Good cycle life in 200 cycles with 72% capacity retention

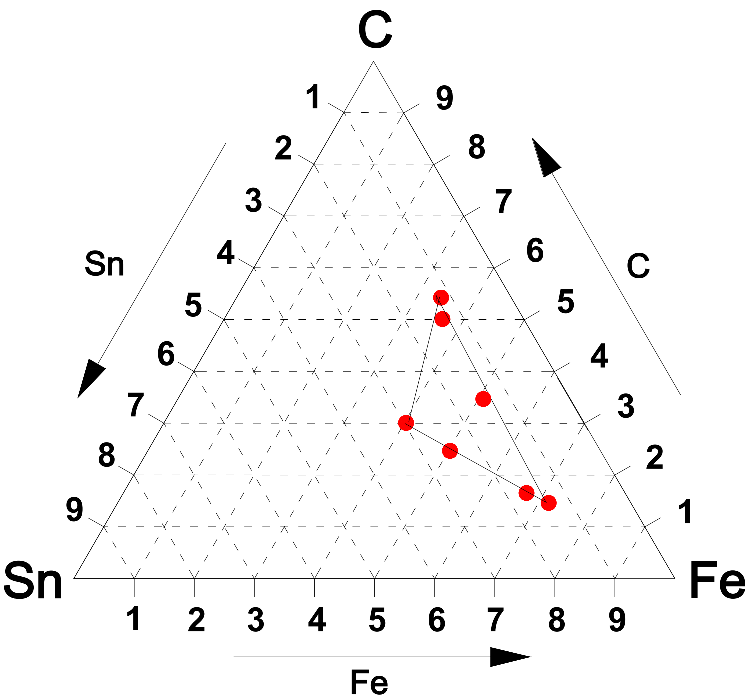
B. Liu, A. Abouimrane, Y. Ren, D. Wang, M. Subramanian, Z. Zak Fang and K. Amine

Chemistry of Materials 24(24), 4653 (2012).

50wt% SiO – 50 wt% $Sn_xFe_yC_z$

6 compositions are prepared :

Sample #	50 wt.% SiO-50 wt.% $Sn_xFe_yC_z$				Particle size (µm)	Capacity (mAh/g, 3rd cycle)	capacity (mAh/g, 100th cycle)
	SiO (wt. %)	Sn (at.%)	Fe	C			
1	50	16.7	50	33.3	9.08	695	397
2	50	12.5	37.5	50	8.62	644	472
3	50	11.1	33.3	55.6	9.20	620	538
4	50	25	50	25	7.79	706	333
5	50	16.7	66.6	16.7	8.99	646	511
6	50	14.3	71.4	14.3	10.27	578	440

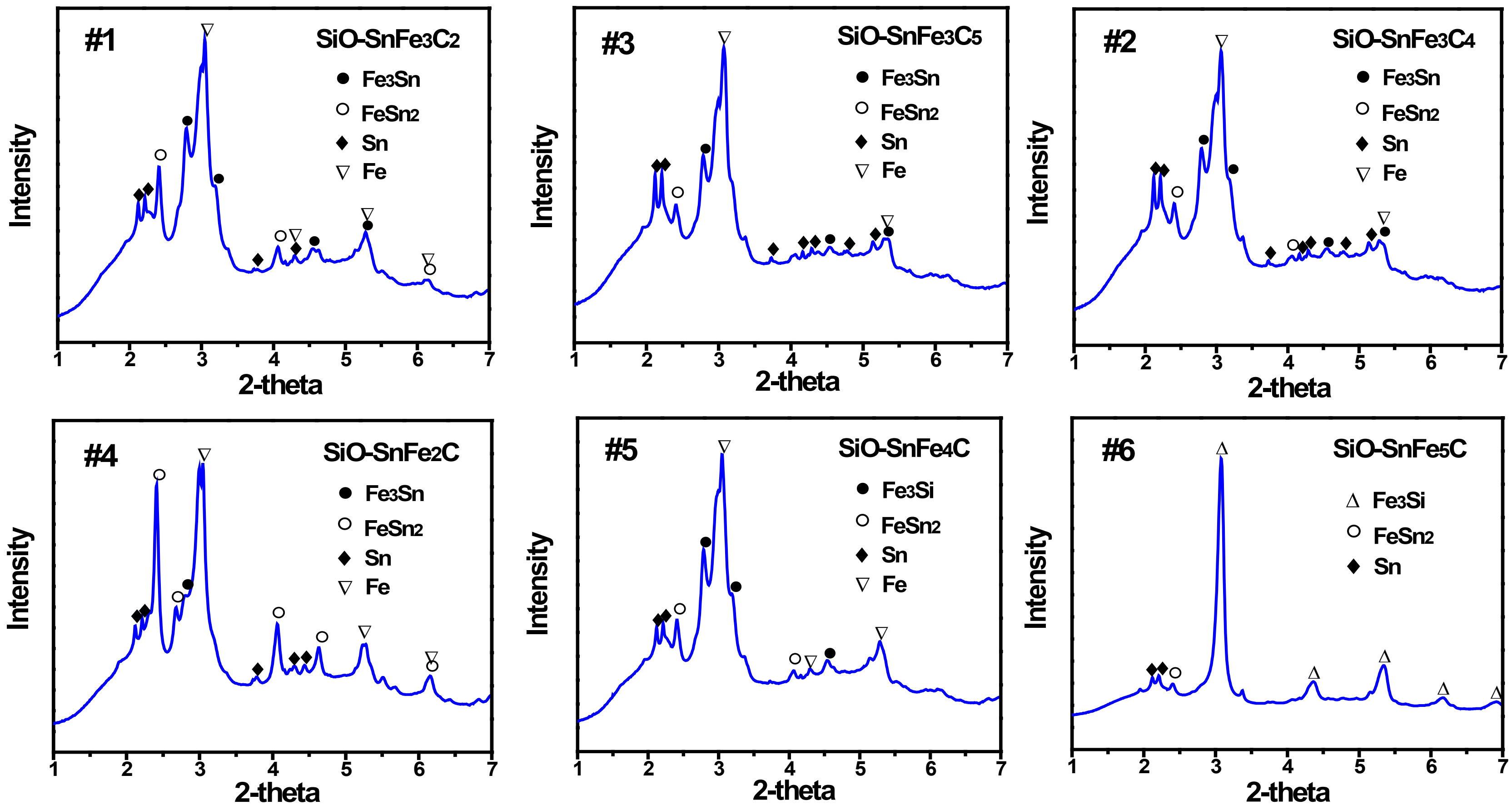


The as-milled samples can be divided into two groups:

(I) carbon rich

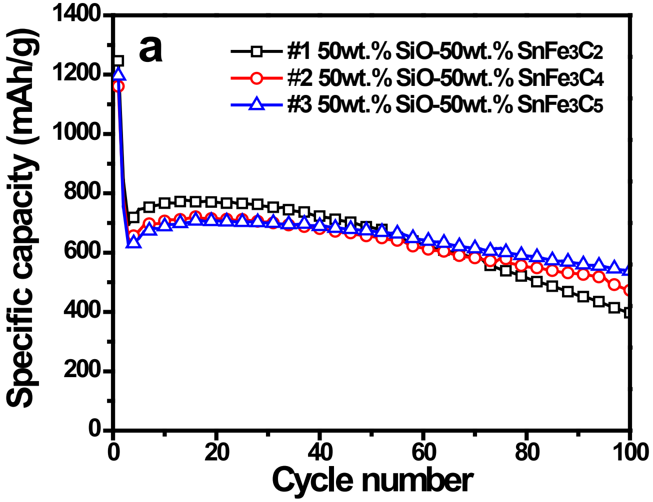
(I) iron rich.

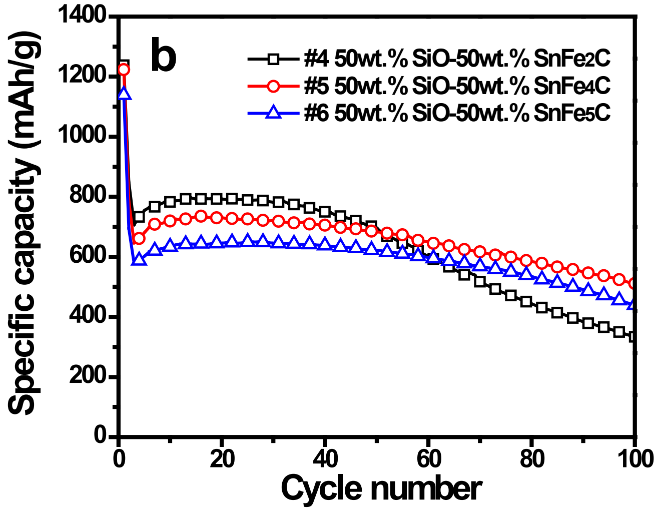
XRD



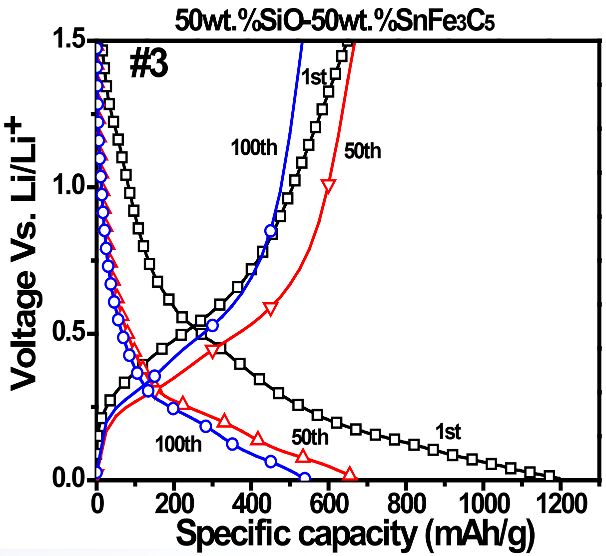
- XRD patterns for Group I scarcely changed with the increasing amount of carbon.
- The increase in the amount of iron in Group II leads to the formation of Fe_3Si in sample #6.

50wt% SiO – 50 wt% $Sn_xFe_yC_z$

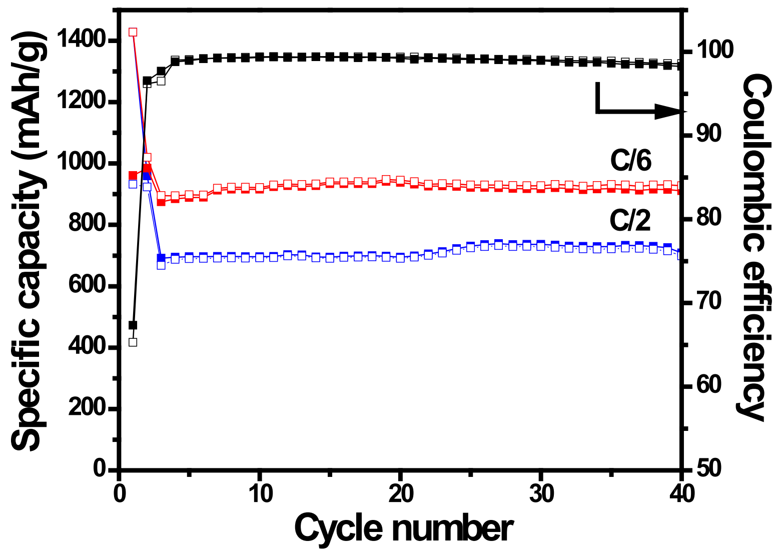


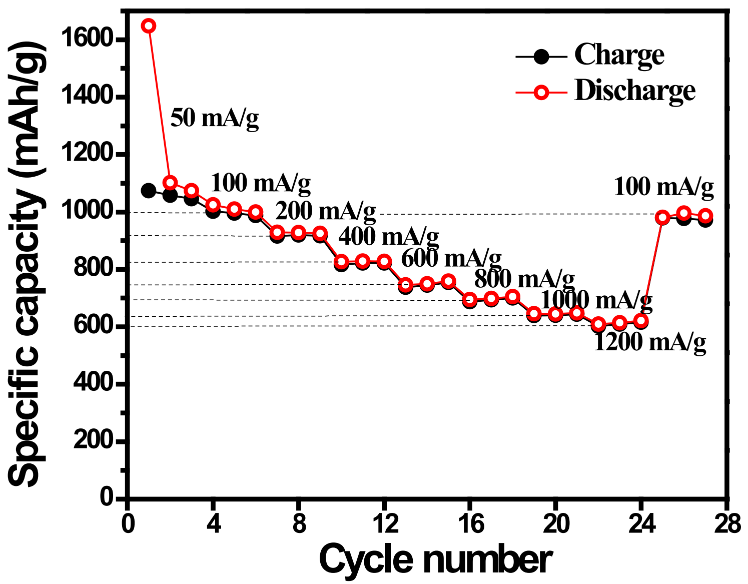


- Group I, the samples have higher carbon content resulted in better capacity retention in subsequent cycles.
- Group II, the best electrochemical performance (high capacity and better cycling) is exhibited by the sample #5 anode.



50wt% SiO – 50 wt% $Sn_{30}Fe_{30}C_{40}$





- It provide high capacity and good rate capability.
- But it is fading after 40 cycles.

B. Liu, A. Abouimrane, D. Brown, X. Zhang, Y. Ren, Z. Z. Fang, and K. Amine *Journal of Materials Chemistry A, 1(13), 4376 (2013).*

Summary

- $MO-Sn_xCo_yC_z$ (MO = SiO, SiO_2, SnO_2, MoO_2, GeO_2) system was prepared by mechanically alloying using SPEX ball milling.
- $MO-Sn_xCo_yC_z$ system where (MO = SiO, SiO_2, SnO_2) are the most competitive system in term of cost.
- 50wt% SiO - 50wt% $Sn_{30}Co_{30}C_{40}$ system shows promising properties in terms of cost, tap density, capacity, cycleability and 1st cycle charge discharge efficiency.
- To improve the electrochemical performance, ultra high energy ball milling was employed to obtain nanoparticles and new phase alloys.
- Full cell configuration was tested with $Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$ cathode material.
- $SiO-Sn_xFe_yC_z$ materials were prepared and tested as anodes.
- $SiO-Sn_xFe_yC_z$ materials exhibit moderate cycling performance with high capacity and good rate ability.