Developing High Capacity, Long Life anodes

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DOE merit review

May 14, 2012

Project ID ES020

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Overview

Timeline

- Start - October 1st, 2009.
- Finish – September 2014
- 70% complete

Barriers

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

Budget

- Total project funding: 1200K
  - FY12: 300K
  - FY11: 300K
  - FY10: 300K
  - FY09: 300K

Partners

- Z. Fang (University of Utah).
- Y. Ren, D. Dambournet, P. Chupas, K. Chapman, Advanced Photon Source, (APS/ANL).
- 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 high capacity and cycle life of these anodes in half and full cell 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 cycleablity since $Sn_xCo_yC_z$ can play a role of buffer against the MO volume expansion.
  - This anode system is more safer than the graphite and possess low potential in the range of 0.3-0.75V (expect high voltage cells when combined with high cathodes)
  - This anode system could offer high practical capacity and high 1st cycle charge discharge efficiency
  - This anode system offers high packing density (up to 3 g/cc), much higher than graphite (1.1g/cc) (expect high volumetric density)

Milestones FY 11 :
High capacity and long life anodes

- Prepare composite anode by mechanical alloying using metal (Co, Sn) carbon and oxides (MO). (*Completed)*

- Perform comparative studies between MO-$Sn_xCo_yC_z$ (MO=SiO, SiO_2, SnO_2, MoO_3, GeO_2) based on their electrochemical properties and cost. (*Completed)*

- Investigate structural rearrangement of these anode composite during the intercalation and de-intercalation of lithium. *(Completed)*

- Select promising candidates for further electrochemical characterization in full cell tests. *(On going)*

- Improve the 1st cycle charge discharge efficiency of promising anode. *(On going)*

Recent accomplishments and progress

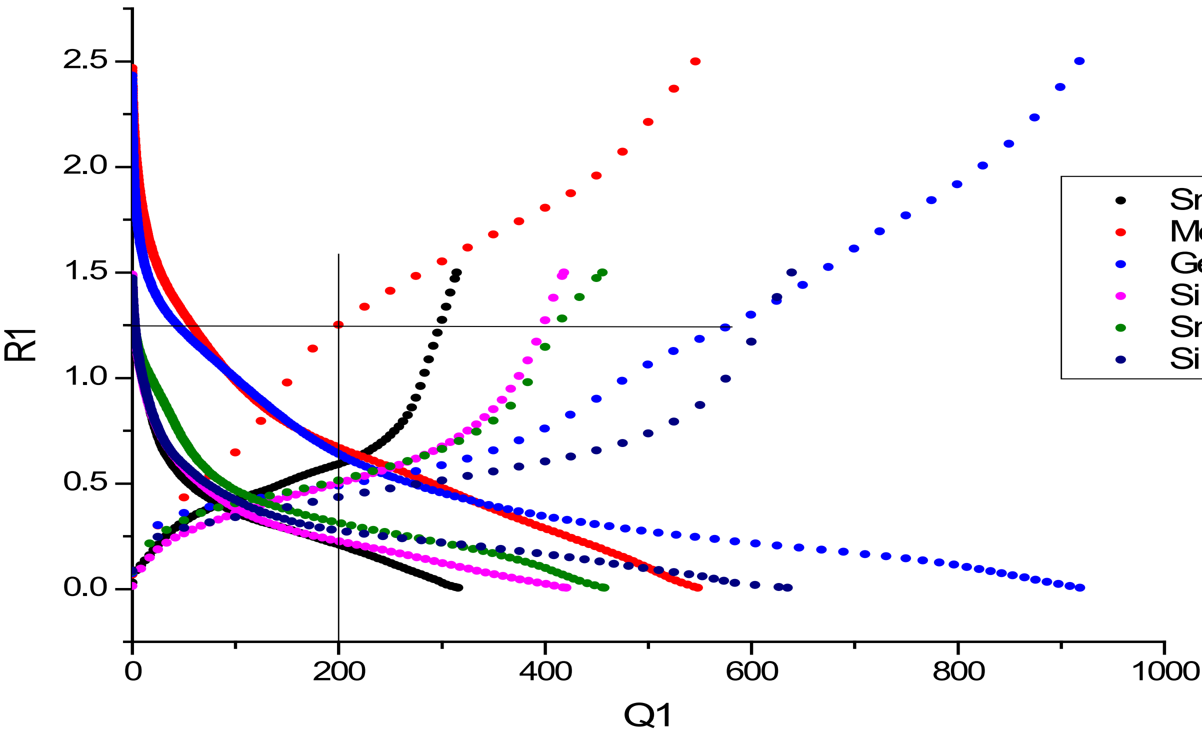
- Prepared successfully (50 wt% SiO – 50 wt% $Sn_{30}Co_{30}C_{40}$) composite using ultra-high energy ball milling equipment UHEM.
- Improved performance of (50 wt% SiO– 50 wt% $Sn_{30}Co_{30}C_{40}$) composite prepared by UHEM by 30% vs. traditional ball mills
- Demonstrated high capacity and long cycle life of (50 wt% SiO – 50 wt% $Sn_{30}Co_{30}C_{40}$) composite prepared by UHEM
- Determined the structure of the (50 wt% SiO – 50 wt% $Sn_{30}Co_{30}C_{40}$) composite prepared by UHEM using PDF
- Initiated a full cell study using $LiNi_{0.5}Mn_{0.5}O_4$ and 50 wt% SiO–50 wt% $Sn_{30}Co_{30}C_{40}$ composite prepared by UHEM

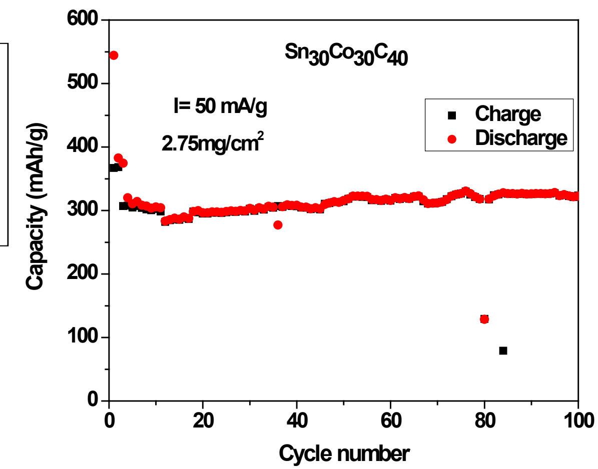
Densities of 50 wt% MO – 50 wt% $Sn_{30}Co_{30}C_{40}$ (MO= MoO_3, SnO_2, GeO_2, SiO_2, SiO)

Material 50 wt% MO – 50 wt% $Sn_{30}Co_{30}C_{40}$	Tap density g/cc	True density g/cc
MO = MoO_3	2.74	6.05
MO = SnO_2	3.02	7.13
MO = GeO_2	2.62	5.06
MO = SiO_2	1.43	3.58
MO = SiO	1.89	3.78

- Materials based on tin, molybdenum and germanium have the highest tap density.
- Materials based silicon and tin are the cheapest.

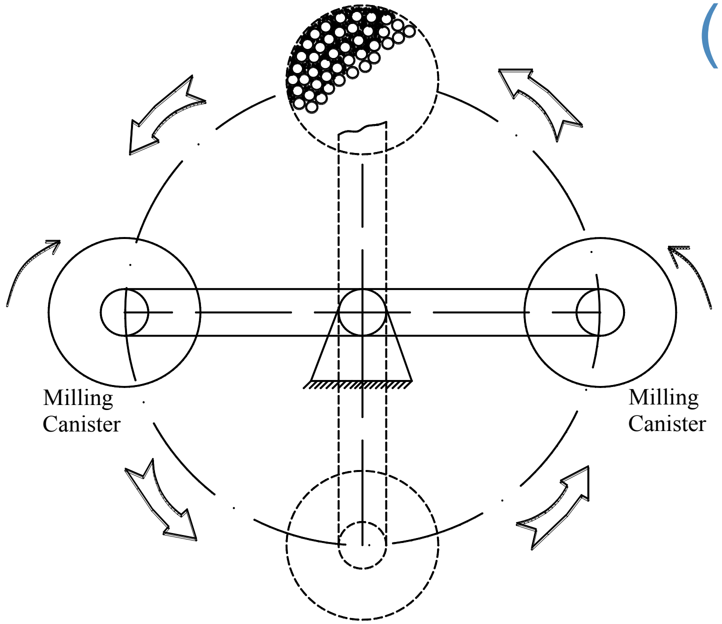
Voltage profile, capacity and cycleability of 50 wt% MO – 50 wt% $Sn_{30}Co_{30}C_{40}$ (MO=MoO_3, GeO_2, SnO_2 ,SiO_2,SiO) and $Sn_{30}Co_{30}C_{40}$





- SiO-$Sn_{30}Co_{30}C_{40}$ is the most promising in term of price, capacity, cycleability and voltage.
- SnCoC capacity varies with precursors (Co and Sn metals or $CoSn_2$ alloy, electrode loading)

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



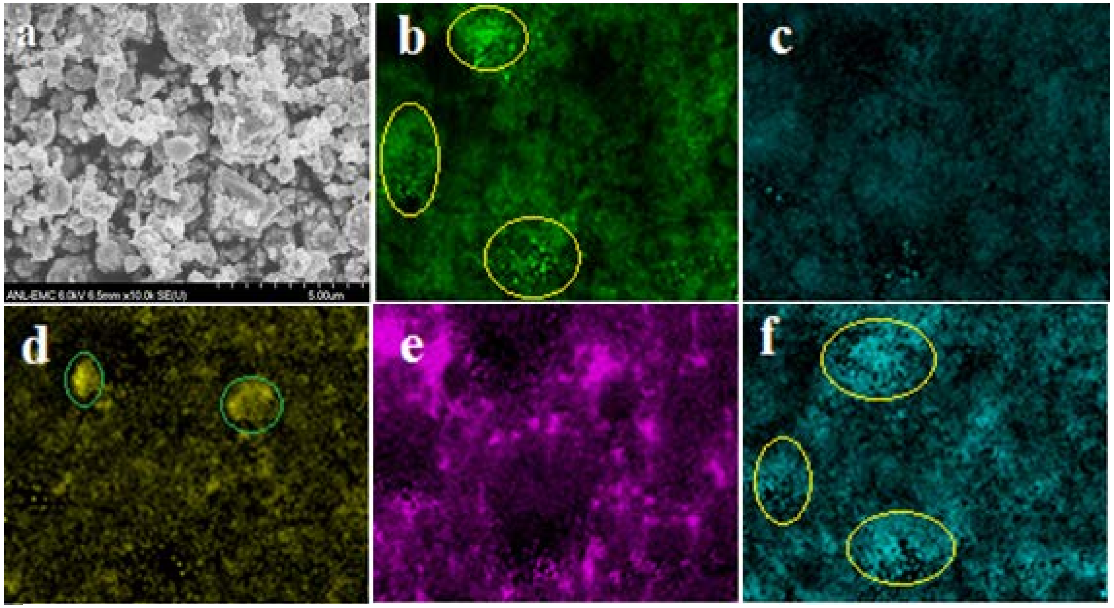
SPEX mill machine

- Custom-made planetary mill machine (rotation in 2 directions) that creates a very high centrifugal field, confining the particles firmly in the interstices of the ball mass was used. (~250 gr of the material can be prepared in 1 shot).

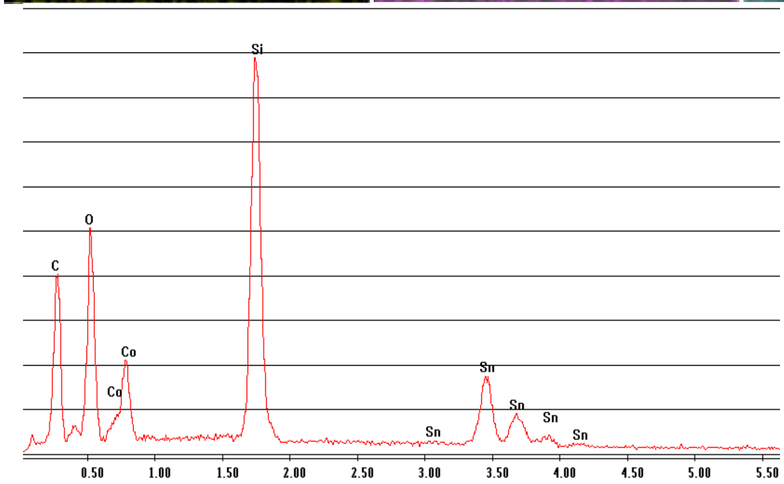
- Traditional ball mills, adopt stirred mills or vibration mills. Only few grams of material can be made

SiO-SnCoC composite was prepared using both techniques for comparison study

SEM Mapping

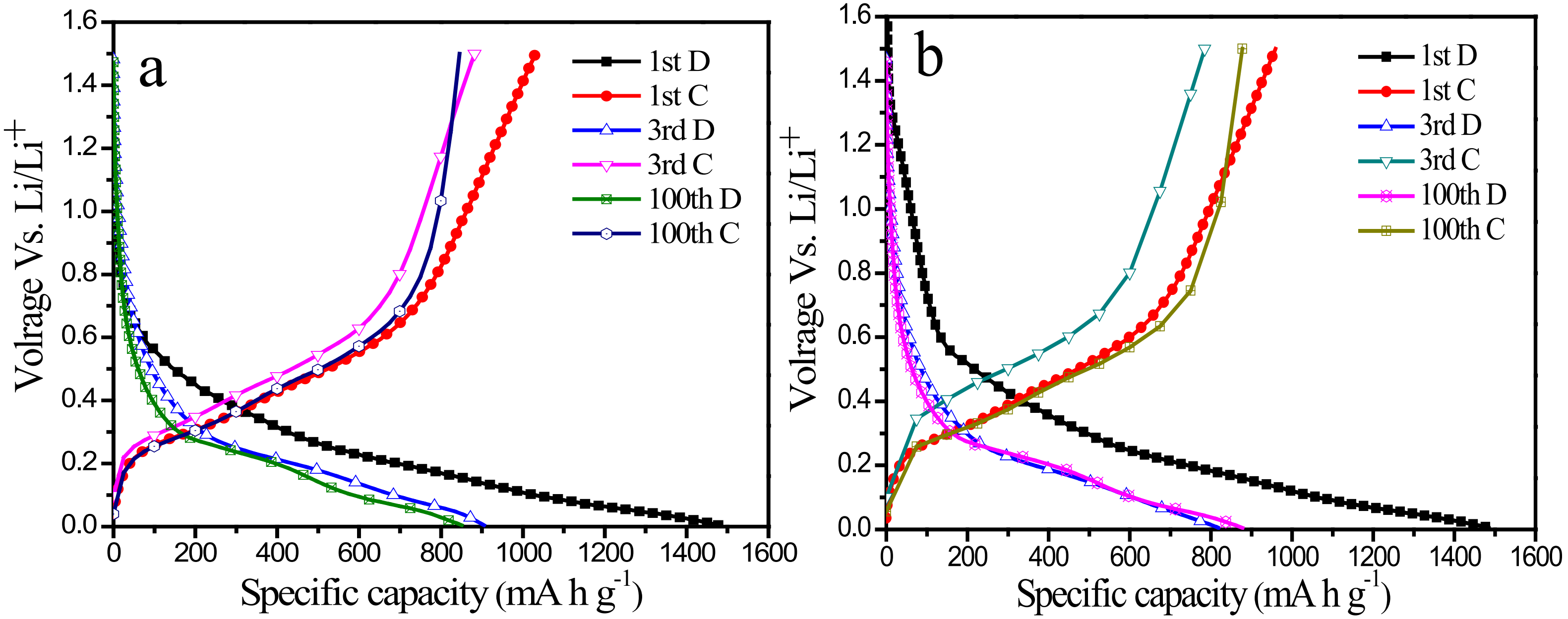


(a) SEM images and EDX elemental mapping of
(b) Si,
(c) O,
(d) Co,
(e) C,
(f) Sn



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

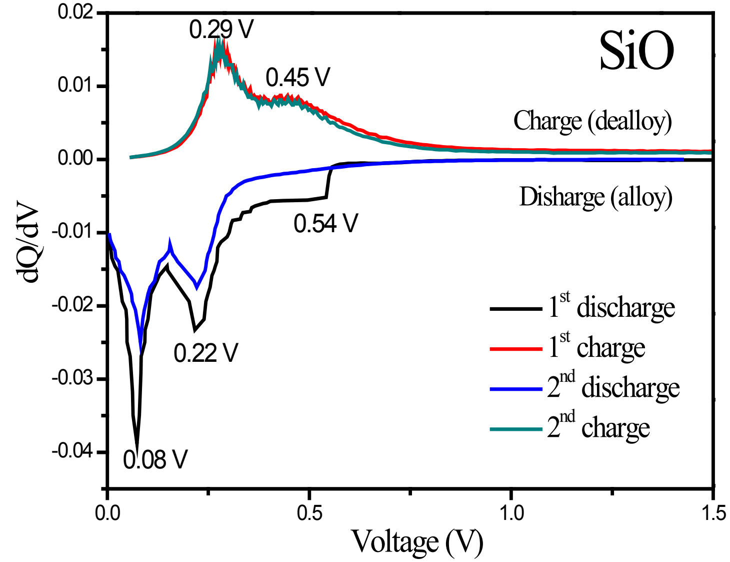
Voltage profile of 50 wt% SiO–50 wt% $Sn_{30}Co_{30}C_{40}$

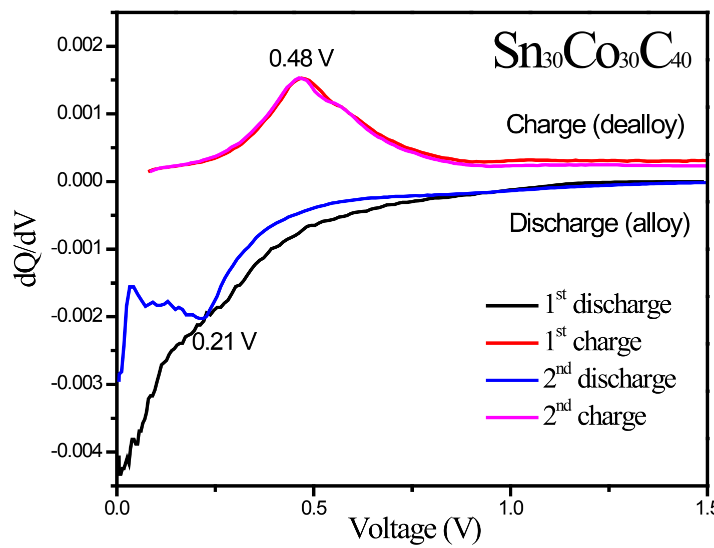


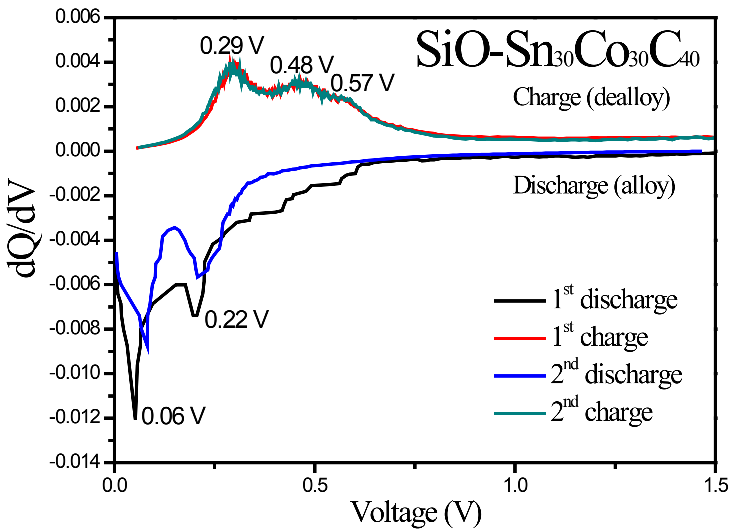
Charge-discharge curves of cells with UHEM anode cycled at rates of (a) 300 mA g^{-1} (~C/3) and (b) 900 mA g^{-1} (~1C)

- 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% $Sn_{30}Co_{30}C_{40}$

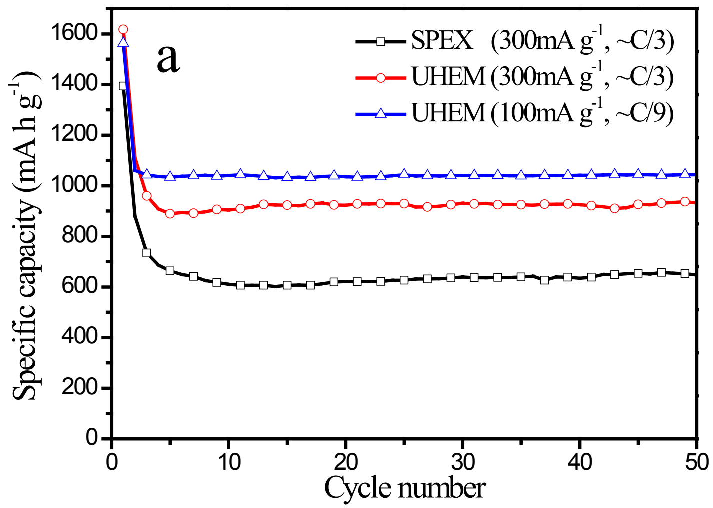


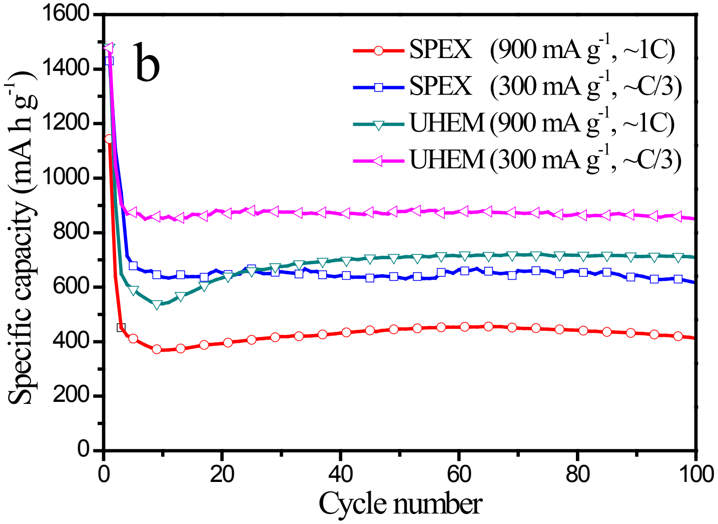


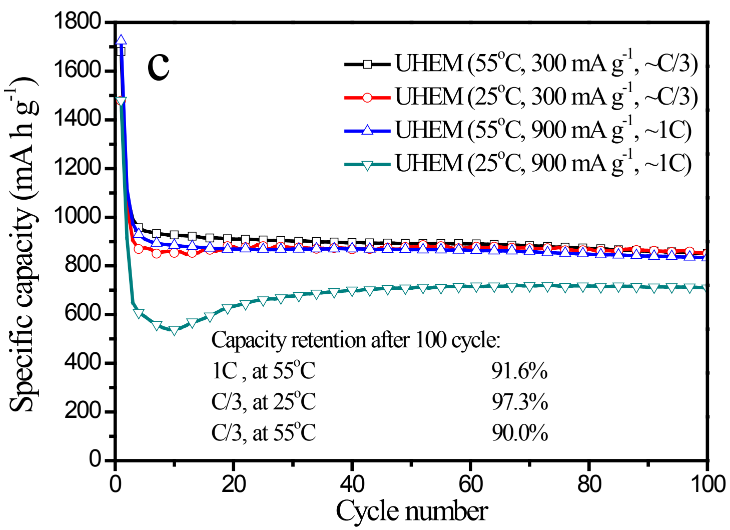


- For SiO-SnCoC, an SEI layer appeared to form at 0.6 V to 0.3 during the first cycle discharge.
- During the charge, the 0.29 V peak correspond to delithiation of Li_xSi alloy of SiO.
- The peak at 0.57 V might be related to the delithiation of Si-Sn alloy.

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







- Anode made by UHEM 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 anode made by SPEX at the same current.

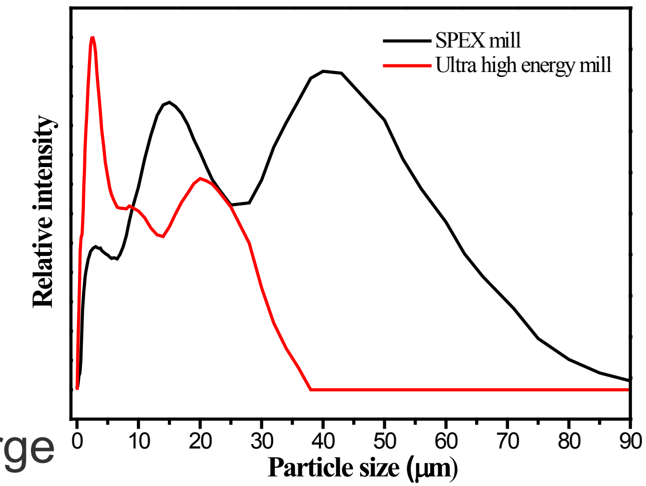
- Anode made by UHEM exhibits excellent rate capability, over 700 mA h g^{-1} at high rate 1C (900 mA g^{-1}).

- Anode made by UHEM shows good stability and excellent cycle life (no capacity fade after 100 cycles).

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

1- Particle size :

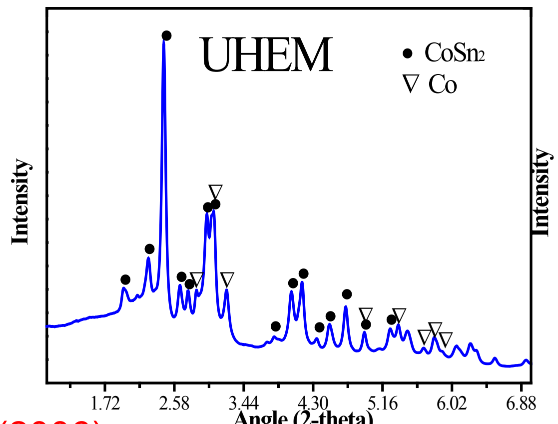
OAC	BET surface area (m²/g)	Particle size distribution
UHEM	7.521	50% particle size < ~2.5µm
SPEX	4.733	50% particle size < ~13 µm

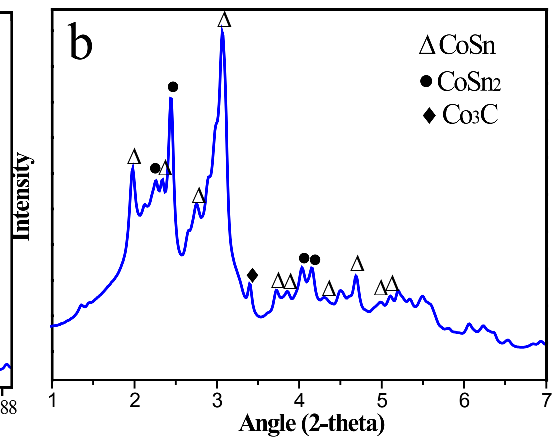


- Nanomaterials can decrease the (SEI) resistance and lead to higher specific capacities at high charge/discharge rates.

2- Materials structure :

sample made by UHEM shows high amount of $CoSn_2$ ($CoSn_2$ delivers more capacity than CoSn)*.



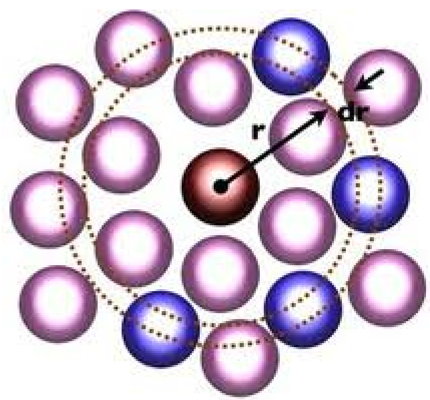


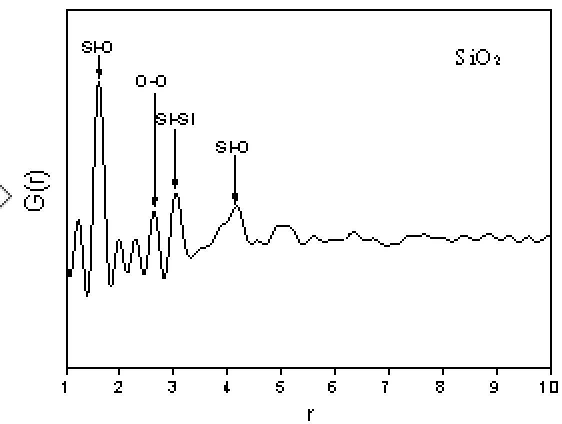
(*) J.J. Zhang et al., *JES*, **153** () A1466-A1471 (2006)

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.

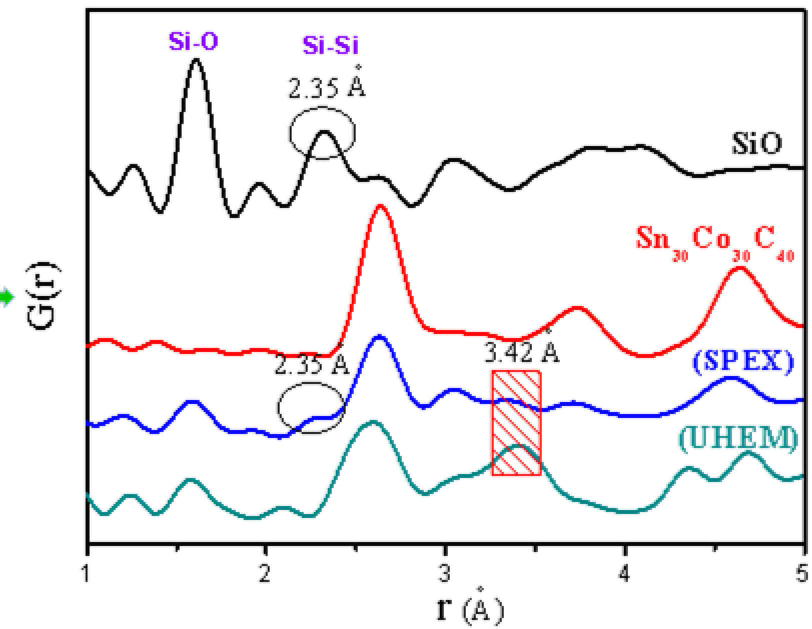




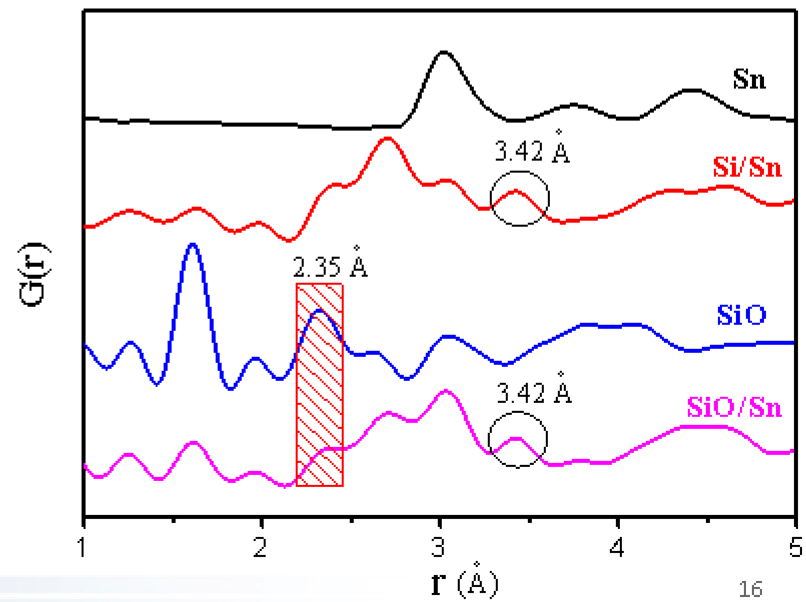
PDF analysis has been successfully used to investigate short-range order in lithium-ion battery electrode materials.

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 disappears.
- 3.42 Å peak of UHEM anode is strong.
- 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 is 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).

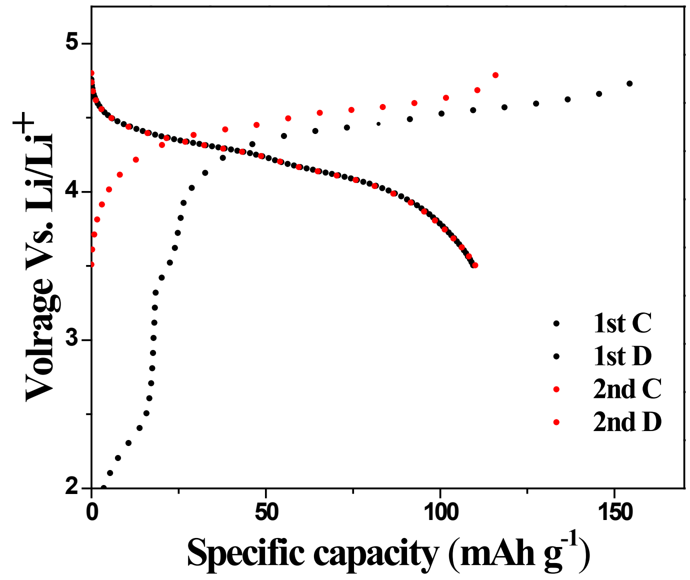
5V/SiO–50 wt% $Sn_{30}Co_{30}C_{40}$ Full cell

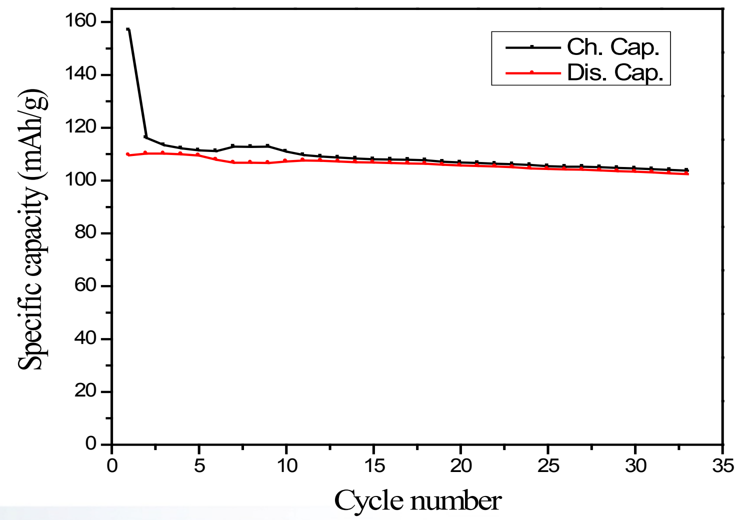
- The anode was first lithiated using lithium metal anode as we have 30% 1st cycle irreversibility. (rate is 45 mA/g)

- 4.3 V cell with $LiNi_{0.5}Mn_{0.5}O_4$.

- ~ 110 mAh/g in Full cell (capacity based on the cathode, cathode limited).

- Preliminary result shows good cycleability and good charge-discharge efficiency.





Summary

- MO-$Sn_xCo_yC_z$ (MO = SiO, SiO_2, SnO_2, MoO_2, GeO_2) systems were prepared by mechanical 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 1^{st} cycle charge discharge efficiency.

- Improved electrochemical performance can be achieved by ultra high energy ball milling to obtain nanoparticles and new phase alloys.

- PDF study demonstrated the formation of Si-Sn amorphous alloy, which is the main reason of the improvement of electrochemical performance.

Future Works

⇨ Investigate of MO-$Sn_xCo_yC_z$ (MO = SiO) system in full cell configuration.

⇨ Explore alternative to Co such as Fe in the composite

⇨ Surface characterization of lithiated anode materials by XPS

⇨ Investigate the pulse-discharge and charge performance of designed cell based on MO-$Sn_xCo_yC_z$ (MO = SiO, SiO_2, SnO_2, MoO_3, GeO_2) system anode through hybrid pulse power characterization (HPPC test).

⇨ Understand the causes of the first cycle charge discharge irreversibility and try to reduce it.

Collaborations

- FMC corporation
- PJ. Chupas, and Y. Ren Advanced Photon Sources, Argonne
- Z. Fang University of Utah.