Developing High Capacity, Long Life anodes

K. Amine (P.I)

A. Abouimrane, D. Dambournet, and I. Belharouak,

Argonne National Laboratory

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Overview

Timeline

- Start - October 1st, 2009.
- Finish – September 2014
- 50% complete

Barriers

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

Budget

- Total project funding: 900K
  - FY11: 300K
  - FY10: 300K
  - FY09: 300K

Partners

- P. Chupas, K. Chapman, Y. Ren Advanced Photon Source, (APS/ANL).
- Z. Fang (University of Utah).
- 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-$Sn_xCo_yC_z$ (MO=SiO, SiO_2, SnO_2, MoO_2, 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) (except higher volumetric density)

Milestones FY 10 : 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_2, GeO_2) based on their electrochemical properties and their cost. (*Completed)*

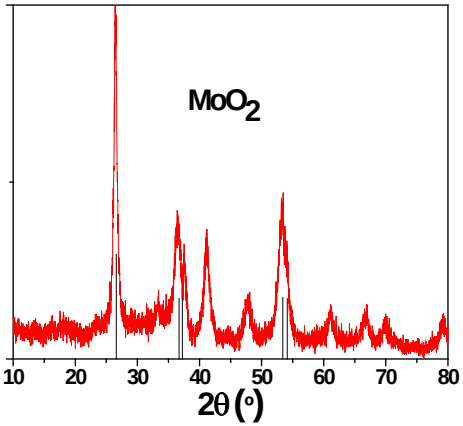
- Investigation of their structural rearrangement during the intercalation or de-intercalation of lithium. *(On going)*

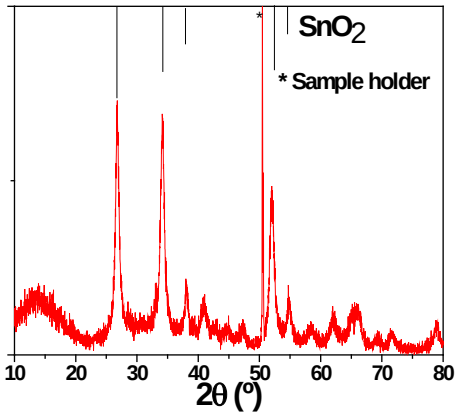
- Selection of a candidate for further electrochemical characterization: full cells study and HPPC tests. *(On going)*

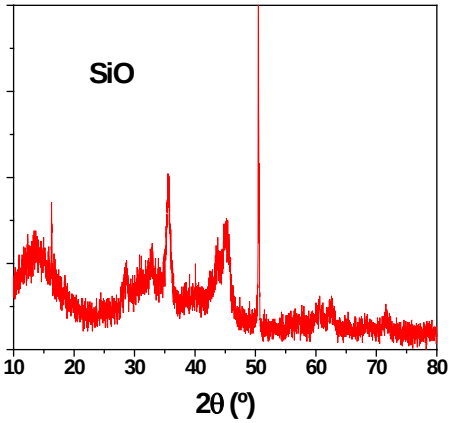
- Improvement of the 1st cycle charge discharge efficiency. *(On going)*

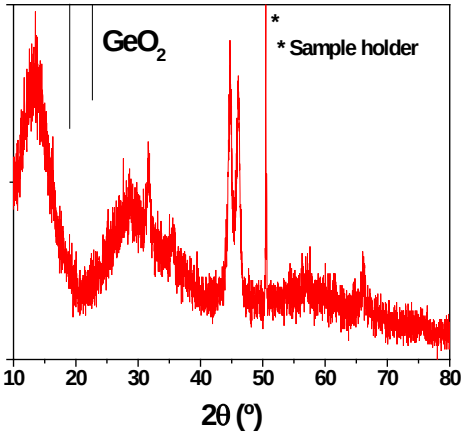
Preparation of 50 wt% MO – 50 wt% $Sn_{30}Co_{30}C_{40}$ (MO= MoO_3, SnO_2, GeO_2, SiO_2, SiO) materials

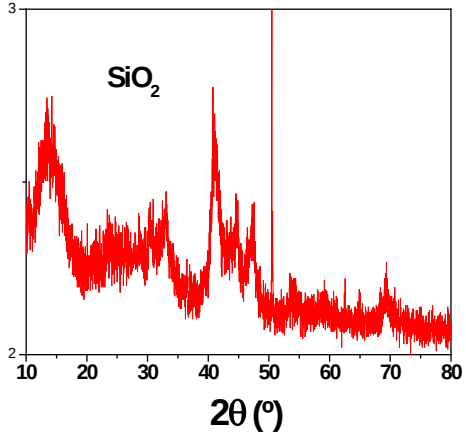
- All materialswere prepared using a high energy ball milling.











- XRD shows that the SnO_2 structure was conserved, MoO_3 was reduced to MoO_2 and no trace of GeO_2 is present confirming the composite structure.

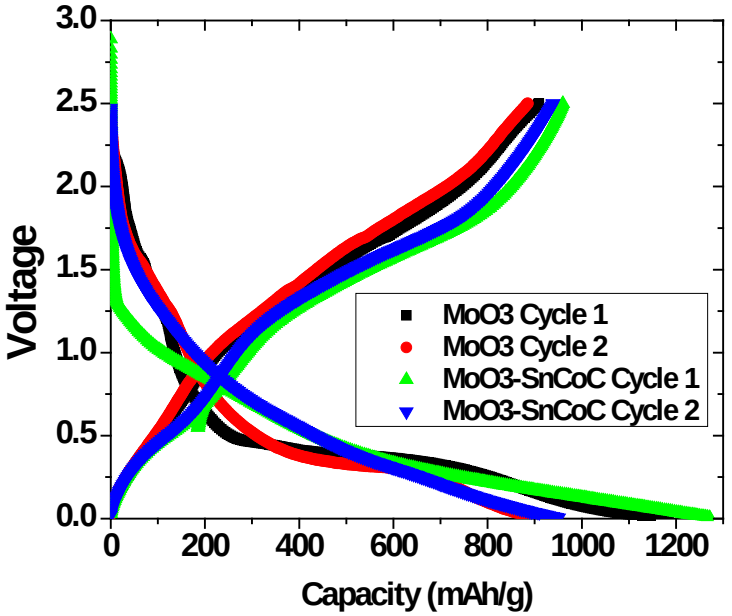
Densities of 50 wt% MO – 50 wt% $Sn_{30}Co_{30}C_{40}$ (MO= MoO_3, SnO_2, GeO_2, SiO_2, SiO)

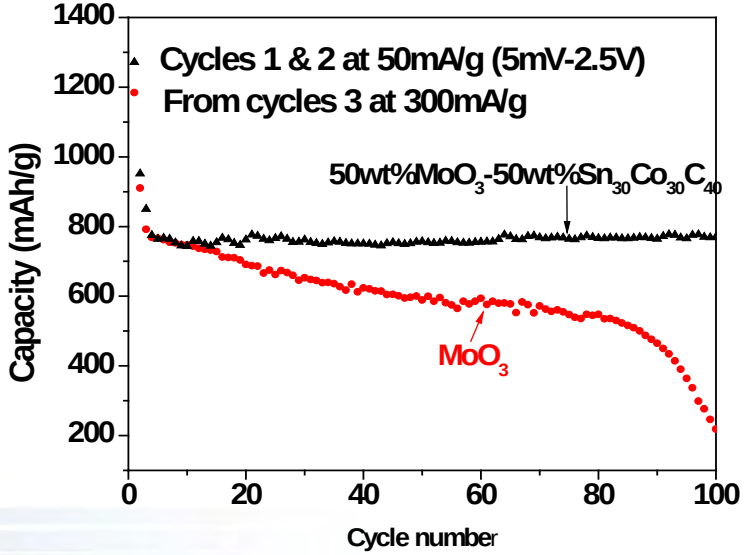
Material 50 wt% MO – 50 wt% $Sn_{30}Co_{30}C_{40}$	Tap density g/cc	True density g/cc
MO = MoO_3	2.74	6.05
MO = SnO_2	3.02	7.13
MO = GeO_2	2.62	5.06
MO = SiO_2	1.43	3.58
MO = SiO	1.89	3.78

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

Voltage profile and cycleability 50 wt% MO – 50 wt% $Sn_{30}Co_{30}C_{40}$ (MO= MoO_3)

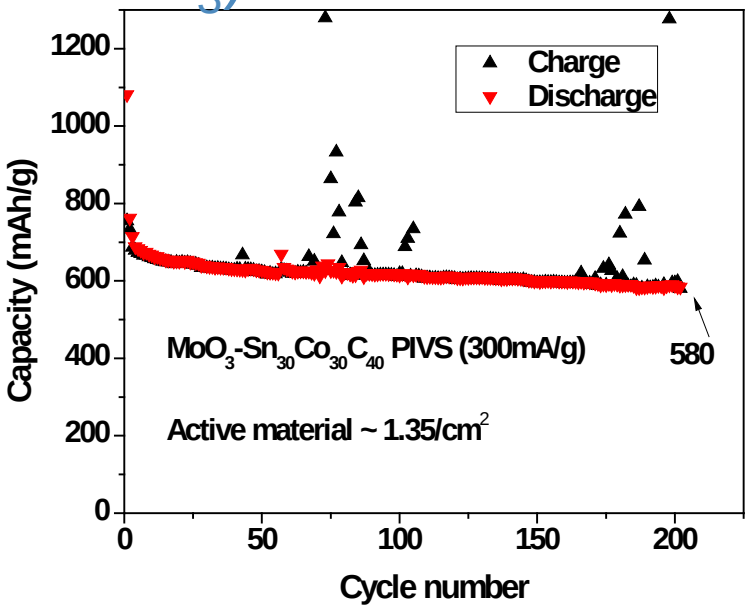
- The laminate is prepared by using 80% active material 10% Acetylene black and 10% Polyimide binder.
- Battery are cycled between 5mV and 2.5V.
- A Voltage ~ 0.6V higher than the graphite was observed. High Voltage means less Li- plating and better safety.
- The composite material cycles far much better than the MoO_3 oxide alone.

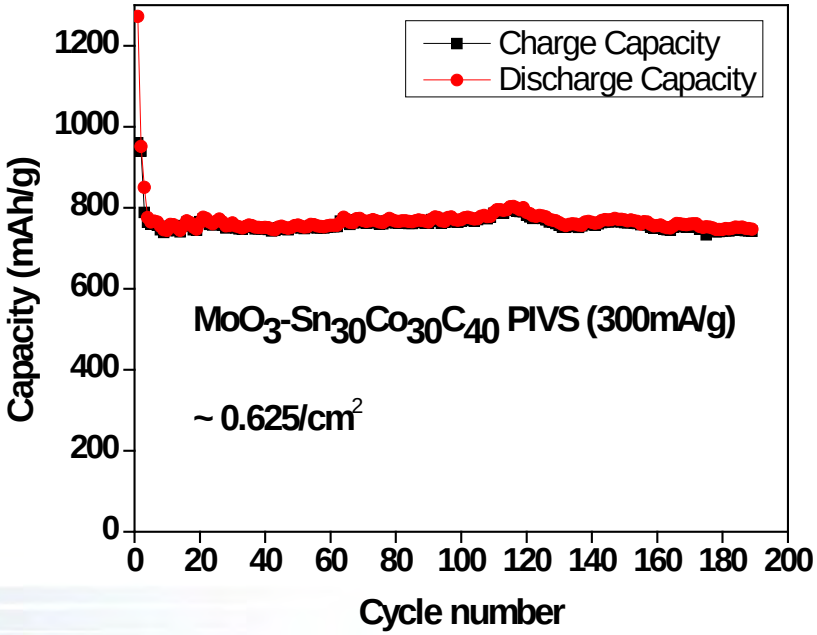




Cycleability and effect of loading on 50 wt% MO – 50 wt% $Sn_{30}Co_{30}C_{40}$ (MO= MoO_3)

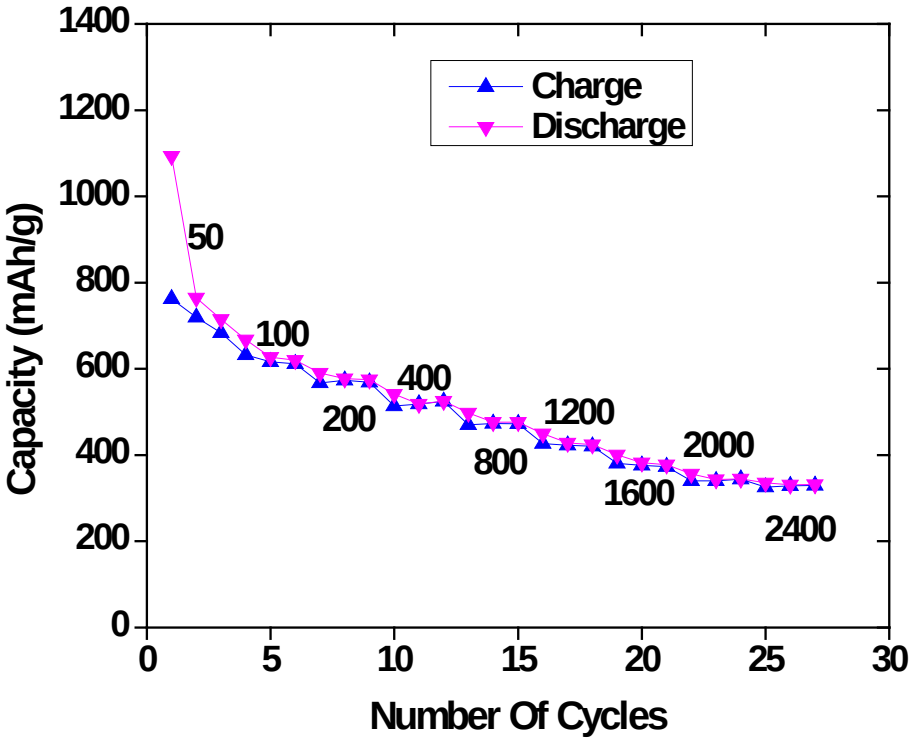
- A capacity near 580 mAh/g is delivered after 200 cycles under 300 mA/g current rate (over C/2 rate).
- 1st cycle effeciecy~70%.
- The capacity changes with the active material loading.
- With low active loading, a capacity of 800 mAh/g can be reached.





Rate capability of 50 wt% MO – 50 wt% $Sn_{30}Co_{30}C_{40}$ (MO= MoO_3)

Current (mA/g)	Capacity (mAh/g)
100	610
200	565
400	515
800	460
1200	415
1600	375
2000	335
2400	325

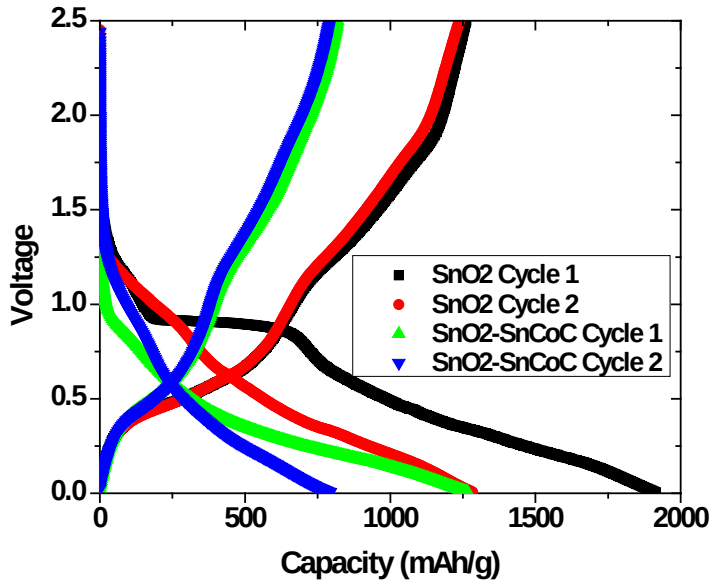


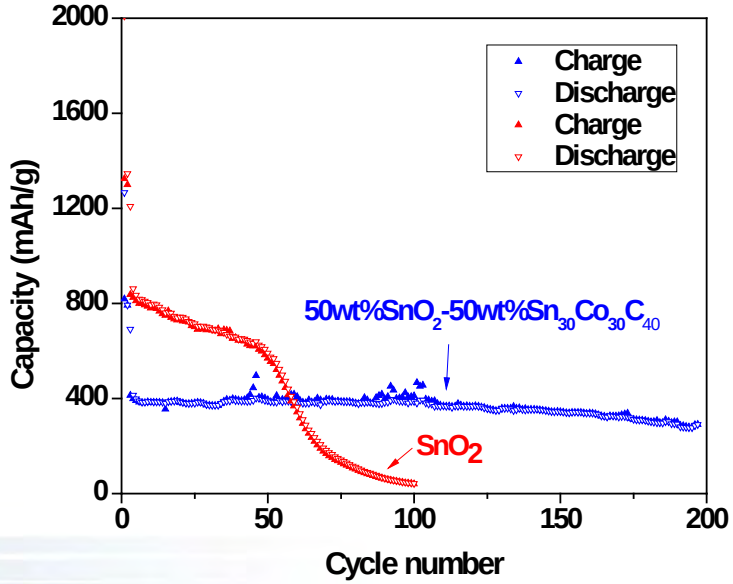
- Good cycling with high coulombic efficiency after the first cycle.

- 50 wt% MoO_3 – 50 wt% $Sn_{30}Co_{30}C_{40}$ anode showed superior rate capability, i.e. 325 mAh/g capacity under a 7~8C rate.

Voltage profile and cycleability of 50 wt% MO – 50 wt% $Sn_{30}Co_{30}C_{40}$ (MO= SnO_2)

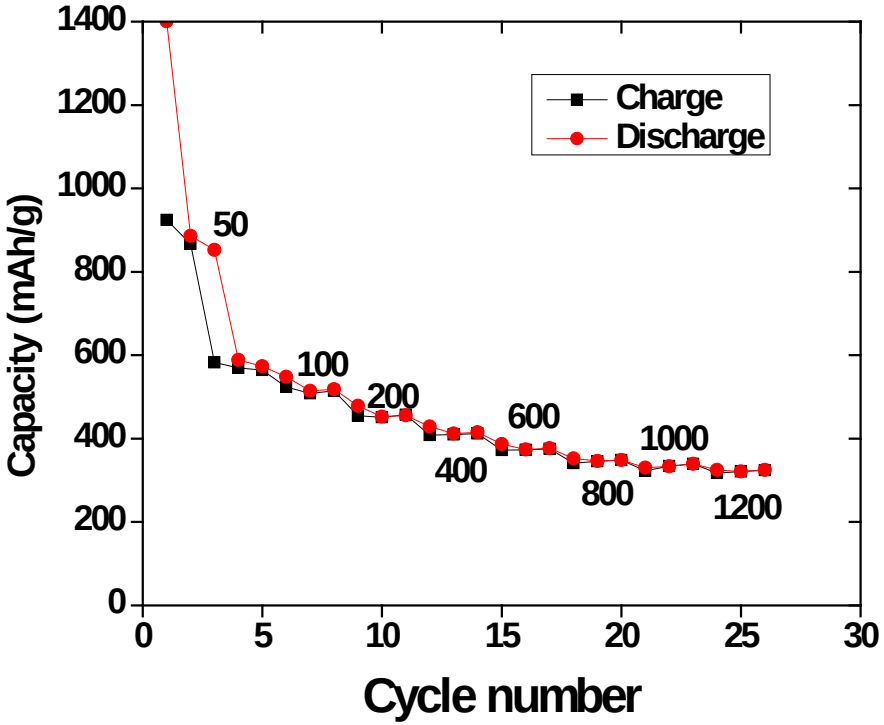
- **A Voltage ~ 0.75V, higher than the graphite that provide better safety and no lithium plating**
- **The composite shows a capacity of 400 mAh/g for more than 150 cycles with moderate capacity fade under 300mA/g current rate.**
- **1st cycle effeciecy~65%.**
- **The composite material cycles better than the SnO_2 oxide alone.**





Rate capability of 50 wt% MO – 50 wt% $Sn_{30}Co_{30}C_{40}$ (MO= SnO_2)

Current (mA/g)	Capacity (mAh/g)
100	510
200	455
400	410
600	371
800	342
1000	332
1200	316

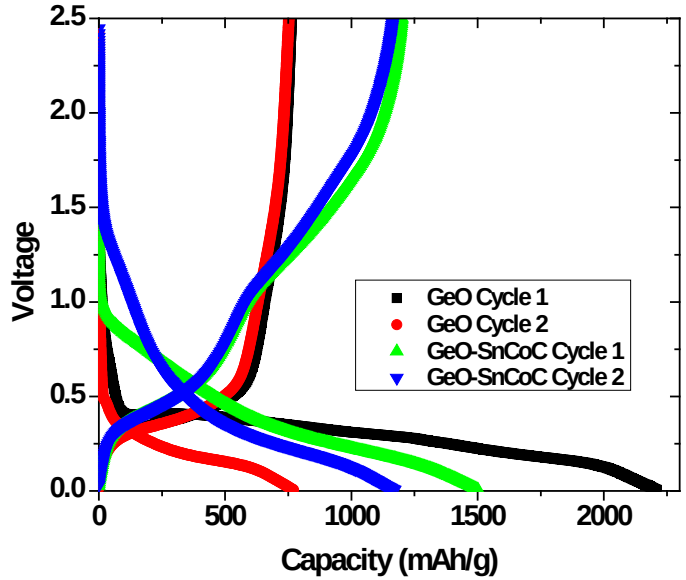


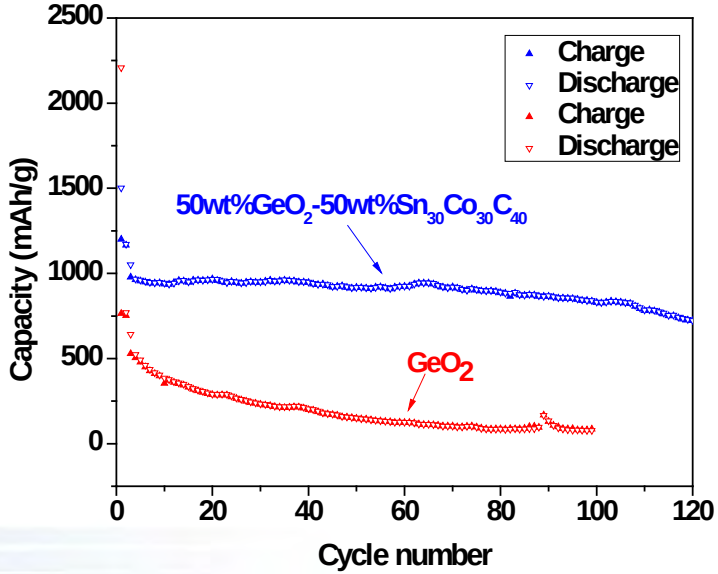
- **Good cycling with high coulombic efficiency (1st cycle irreversibility is about 65% due to the formation of Li_2O which is not active in the case of SnO_2-$Sn_{30}Co_{30}C_{40}$ composite).**

- **50 wt% SnO_2 – 50 wt% $Sn_{30}Co_{30}C_{40}$ anode showed superior rate capability, i.e. 316 mAh/g capacity under a 4C rate.**

Voltage profile and cycleability of 50 wt% MO – 50 wt% $Sn_{30}Co_{30}C_{40}$ (MO= GeO_2)

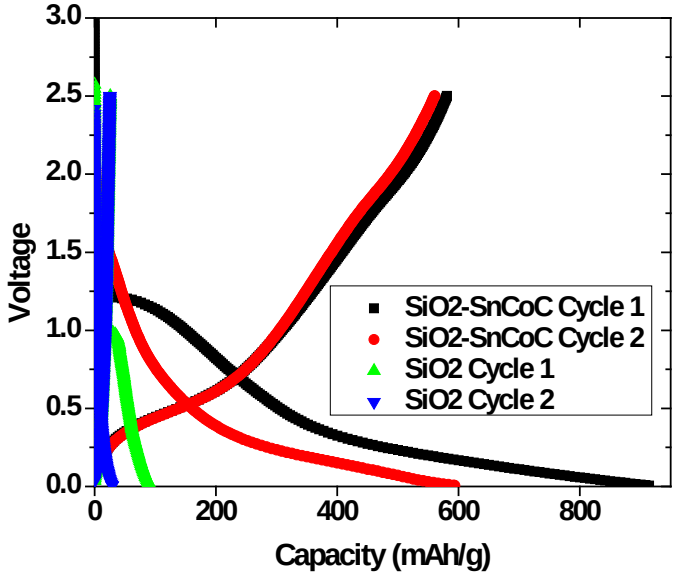
- A Voltage ~ 0.5V higher than the graphite was observed
- The composite shows a capacity of 800-1000 mAh/g for 100 cycles with moderate capacity fade under 300 mA/g current rate.
- 1st cycle charge discharge effeciecy~80%.
- The composite material cycles better than the GeO_2 oxide alone with much higher 1st cycle charge-discharge efficiency.

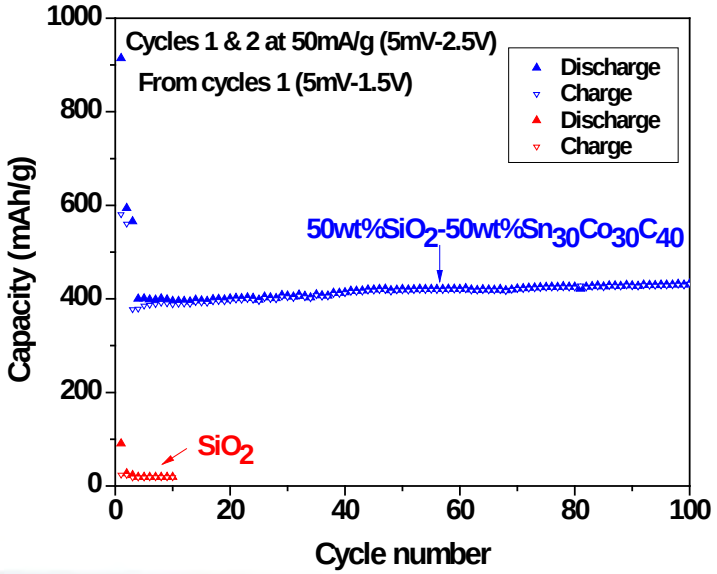




Voltage profile and cycleability of 50 wt% MO – 50 wt% $Sn_{30}Co_{30}C_{40}$ (MO= SiO_2)

- **A Voltage ~ 0.5V higher than the graphite with MO=SiO_2**
- **SiO_2 alone is not electrochemically active.**
- **The composite shows a capacity of 432 mAh/g for 100 cycles with outstanding charge discharge efficiency when it cycled between 5mV and 1.5V under 100 mA/g current using only a PVDF binder.**
- **1st cycle effeciency~64%.**



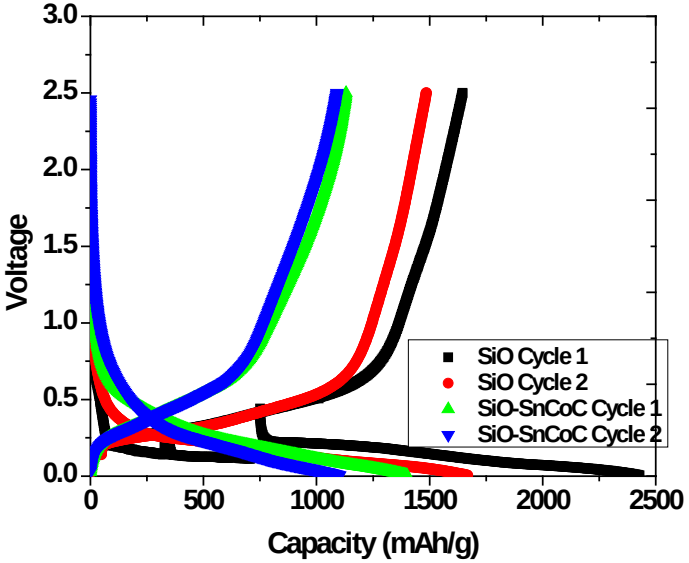


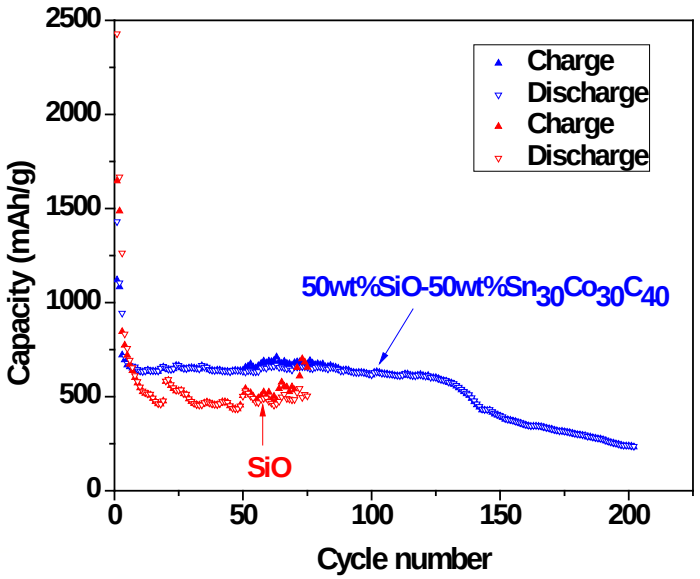
Voltage profile and cycleability of 50 wt% MO – 50 wt% $Sn_{30}Co_{30}C_{40}$ (MO= SiO)

- **A voltage ~0.5V higher than that of graphite.**

- **A capacity near 580 mAh/g is delivered after 130 cycles under 300 mA/g current rate between 5mv and 1.5V**

- **1st cycle charge-discharge effeciecy~79% is better than SiO alone (only 67%).**





Summary

- MO-$Sn_xCo_yC_z$ (MO = SiO, SiO_2, SnO_2, MoO_2, GeO_2) system was prepared by mechanically alloying using a high energy 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% SnO_2 - 50wt% $Sn_{30}Co_{30}C_{40}$ system provides the higher tap density but suffers from the first cycle irreversibility (near 65%).

- 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.

Future Works

⇨ Investigate of MO-$Sn_xCo_yC_z$ (MO = SiO, SiO_2, SnO_2, MoO_2, GeO_2) system in full cell configuration.

⇨ In-situ structural characterizations of MO-$Sn_xCo_yC_z$ (MO = SiO, SiO_2, SnO_2, MoO_2, GeO_2) system with APS (Dr. Ren).

⇨ Ex-situ PDF characterizations with APS (Dr. Chupas).

⇨ Surface characterization of lithiated anode materials by XPS with Utah University (Dr. Fang).

⇨ Investigate the pulse-discharge and charge performance of designed cell based on MO-$Sn_xCo_yC_z$ (MO = SiO, SiO_2, SnO_2, MoO_2, 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

A. Tressaud & A. Demourgues (ICMCB, Bordeaux, France)

FMC corporation

PJ. Chupas, and Y. Ren Advanced Photon Sources, Argonne

Z. Fang University of Utah.

Patents

Provisional application

- New Silicon-based anode material, A. Abouimrane, K. Amine, (IN-10-013).