Next generation Lithium Ion and Beyond lithium Ion

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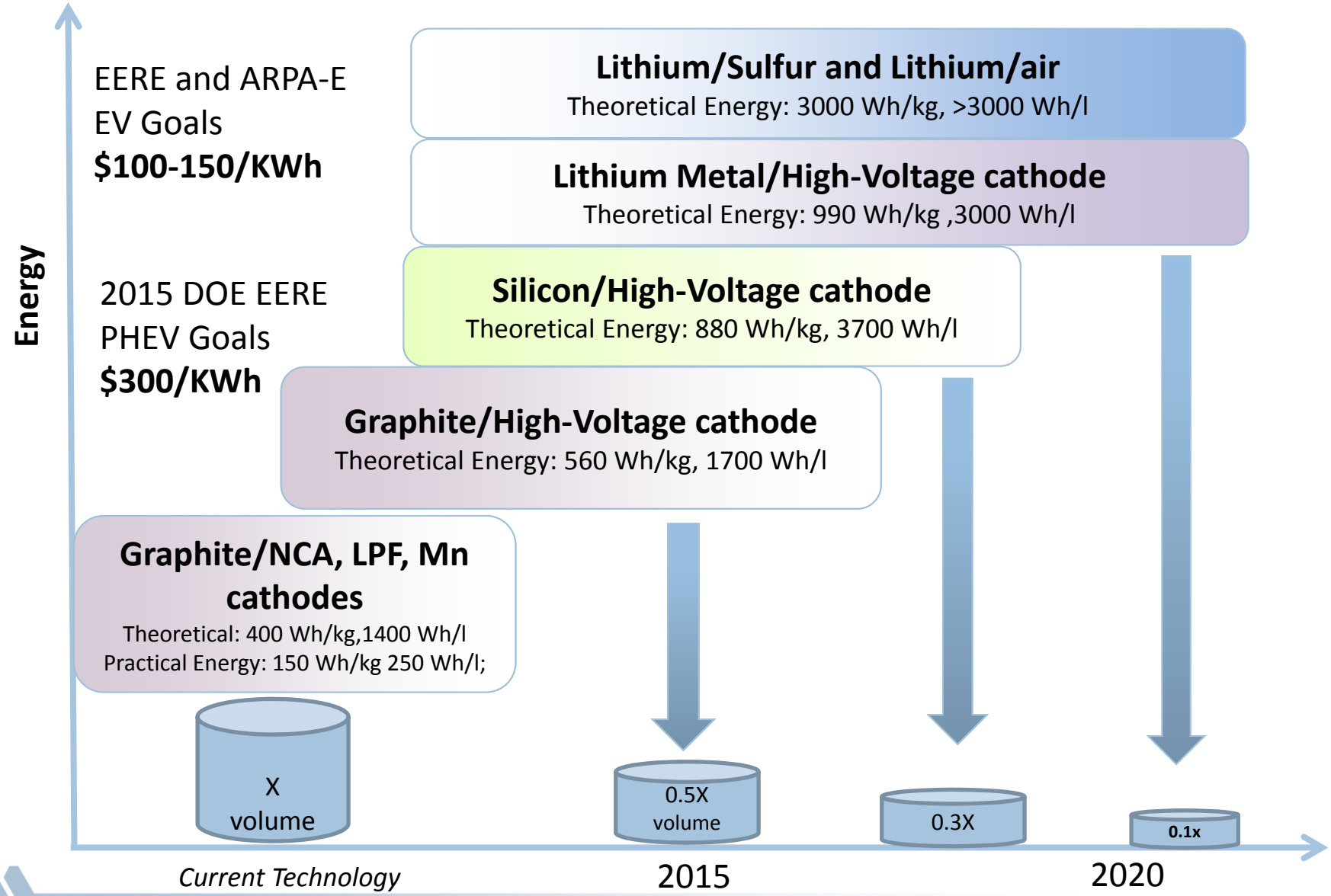
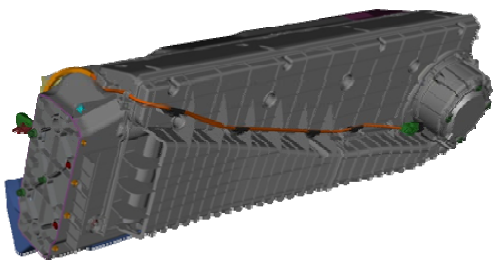
US DOE Energy Storage R&D Roadmap for 2015 and Beyond



Battery Technology Energy Evolution

EV Battery

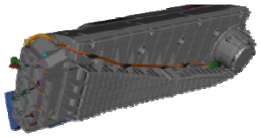
- 23kWh
- 500lbs
- 125 liters



1st Gen

EV Battery

- 23kWh
- 250lbs
- 75 liters



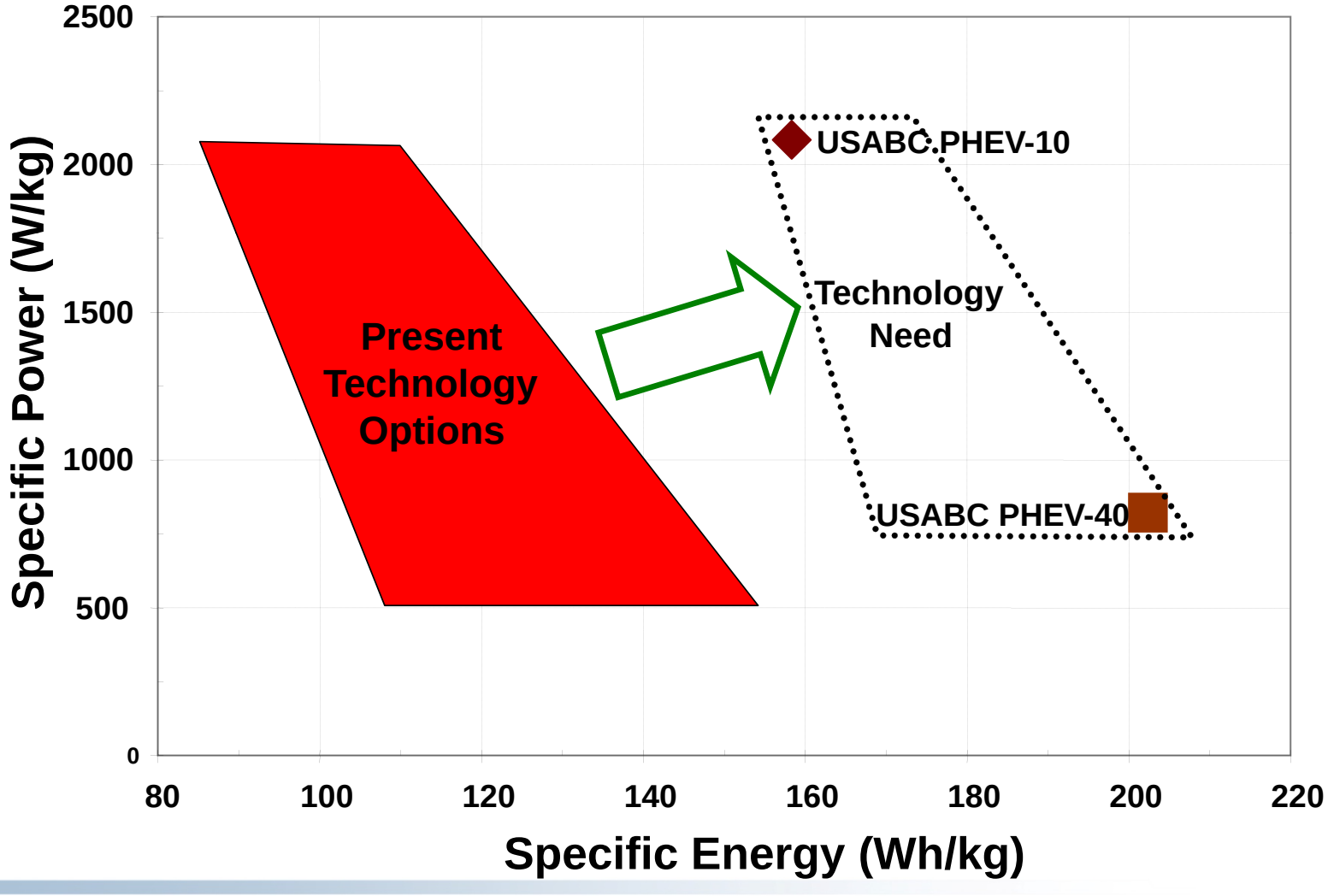
Future

Goal

Fuel Tank

- 23kWh
- 125lbs
- 60 liters

High Energy Battery Systems are Needed to Reduce Vehicle Cost



Next Generation lithium ion batteries

>250-400 mAh/g
3X current cathode
3.5 – 5.0 volt

Non flammable & high Voltage Electrolyte

> 1000 mAh/g
3X current anode
0 – 0.5 volt

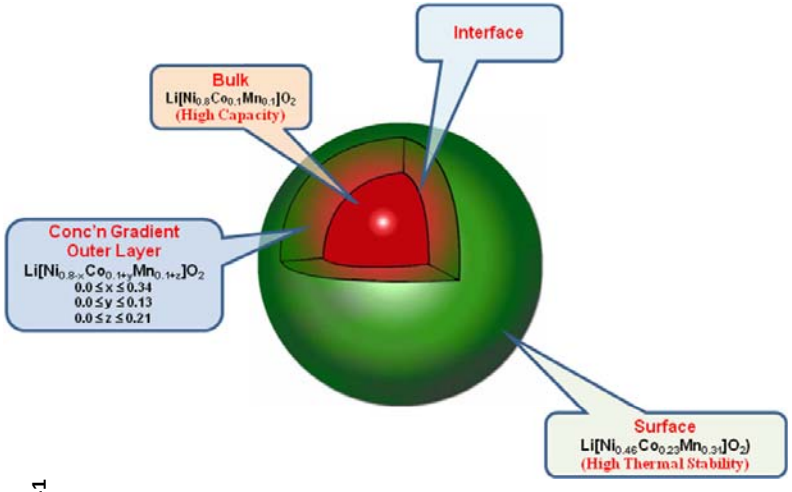
Next Generation anode

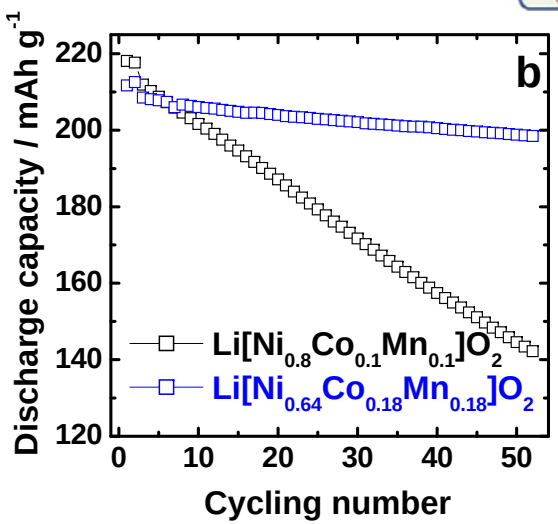
Next Generation electrolyte

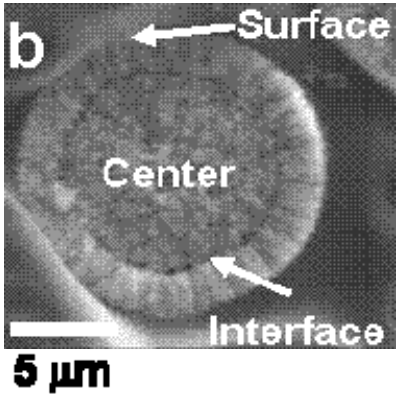
Next Generation Cathode

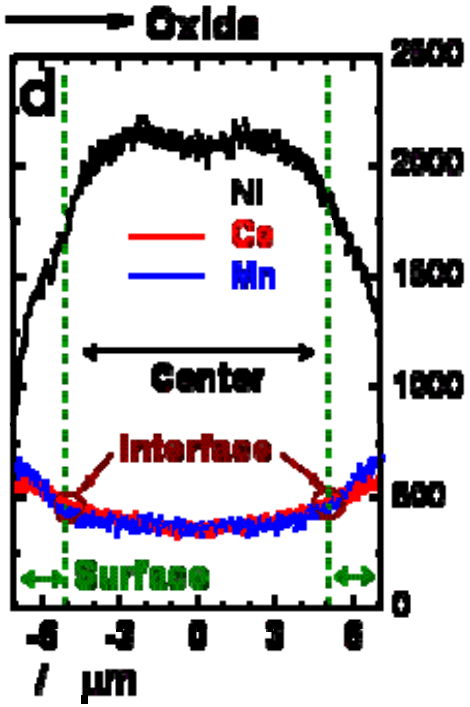
Electrode interface stabilization

Novel High Energy Gradient Concentration Cathode Material (260wh/kg)





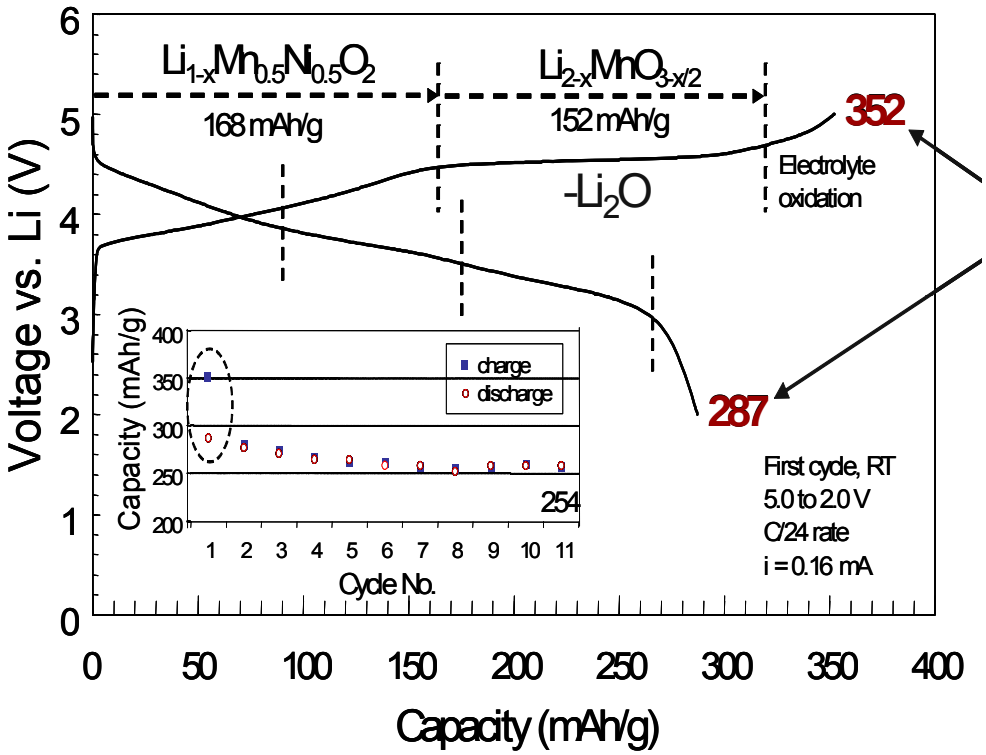




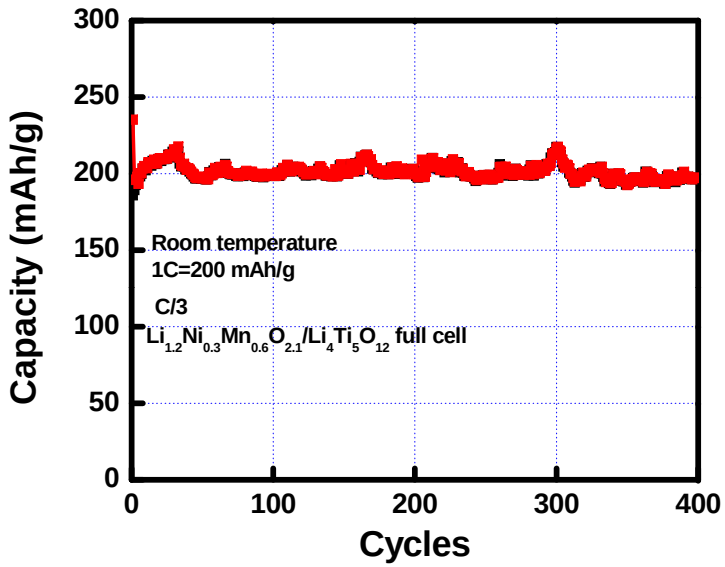
K. Amine et al

Nature mat., Vol 8, pp324, April 2009

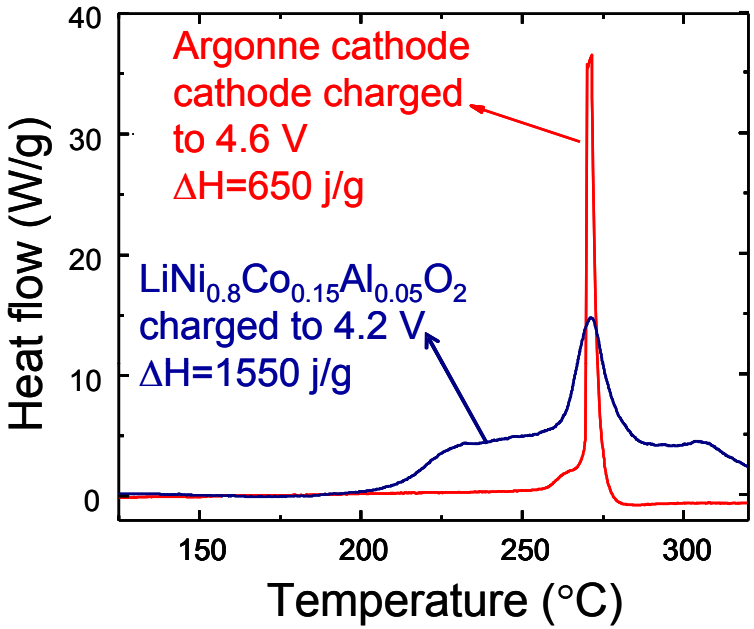
ANL's High Energy composite electrode [$xLi_2MnO_3 \bullet yLiMn_{0.5}Ni_{0.5}O_2$] (300wh/kg)



ANL High Energy Composite Electrode $xLi_2MnO_3 \bullet yLiMn_{0.5}Ni_{0.5}O_2$ for PHEV-40 & EVs

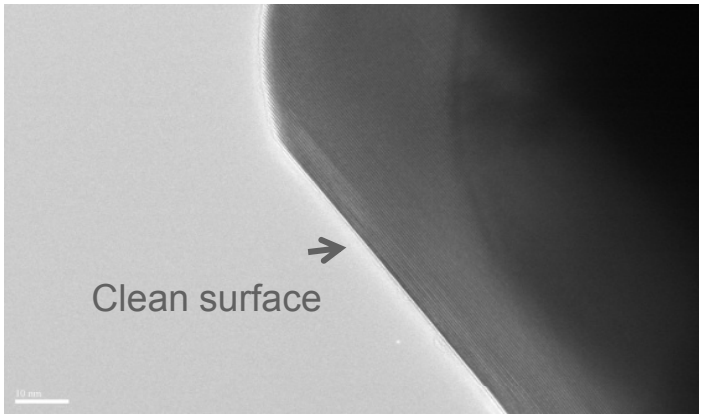


Cycling performance

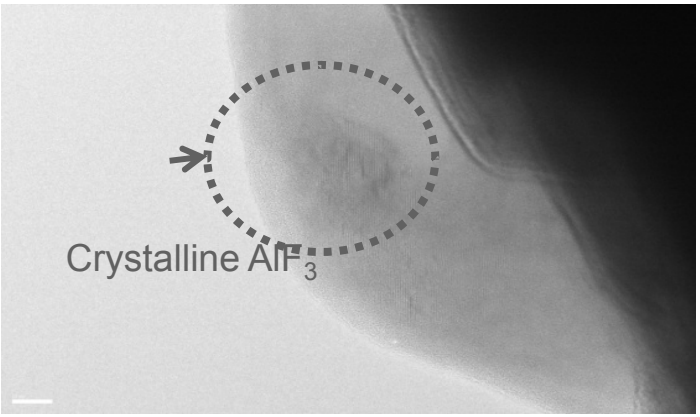


Differential Scanning Calorimetry test

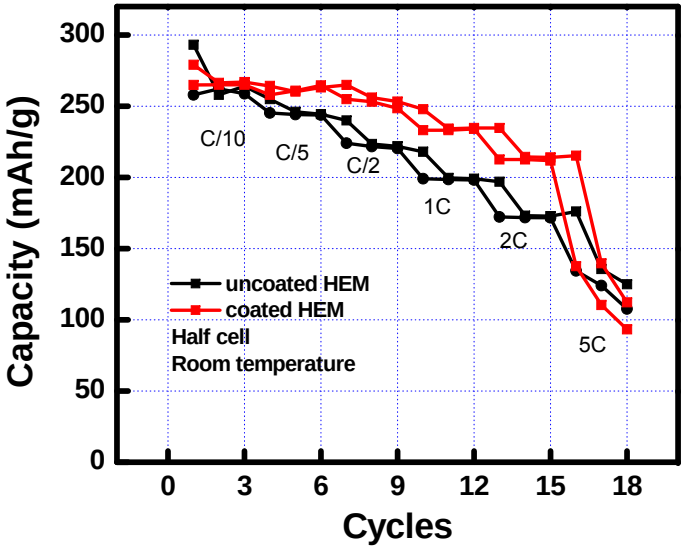
Effect of AlF_3-Coating on Rate and Cycle Life of high energy composite cathode at 55°C

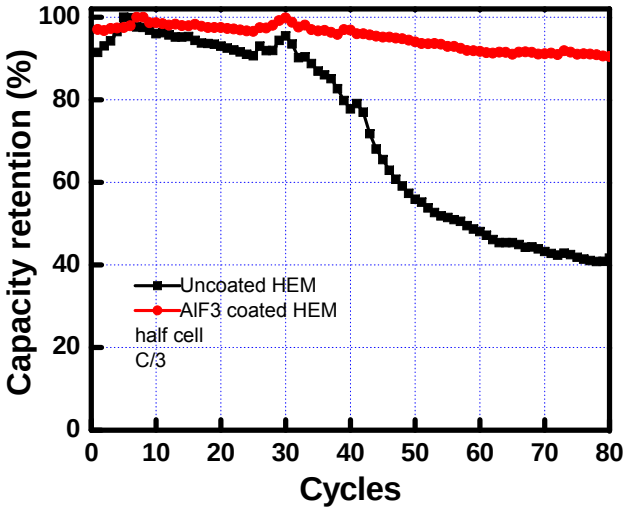


None **coated**

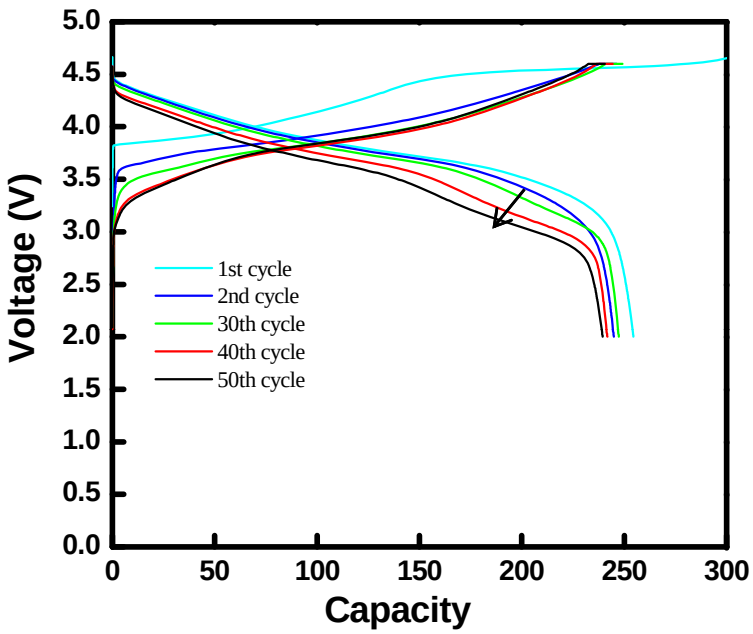


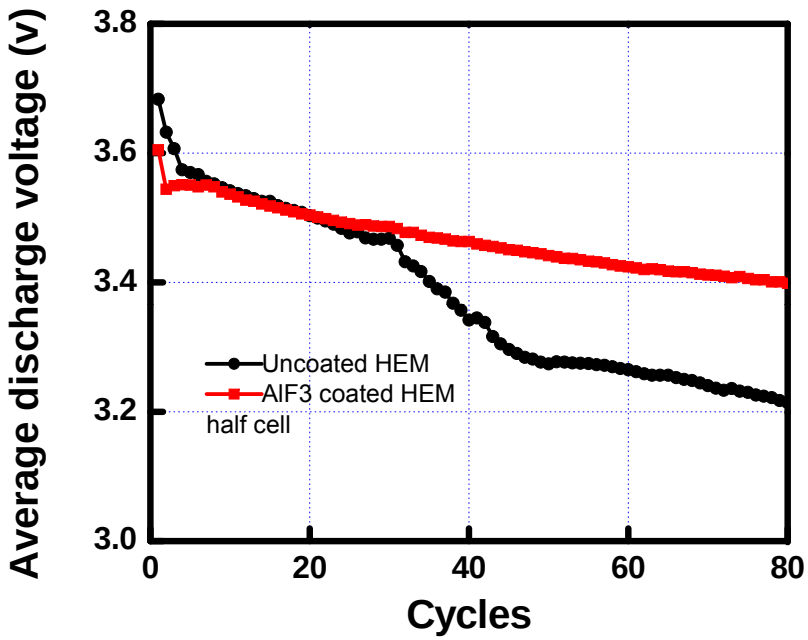
AlF_3 **coated**





Effect of AlF_3 coating on mitigating voltage drop of HEC material



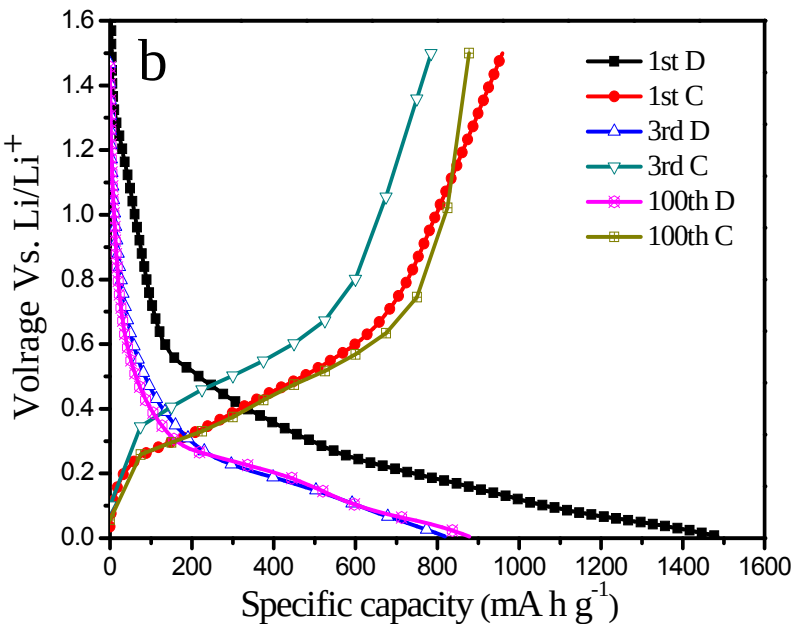


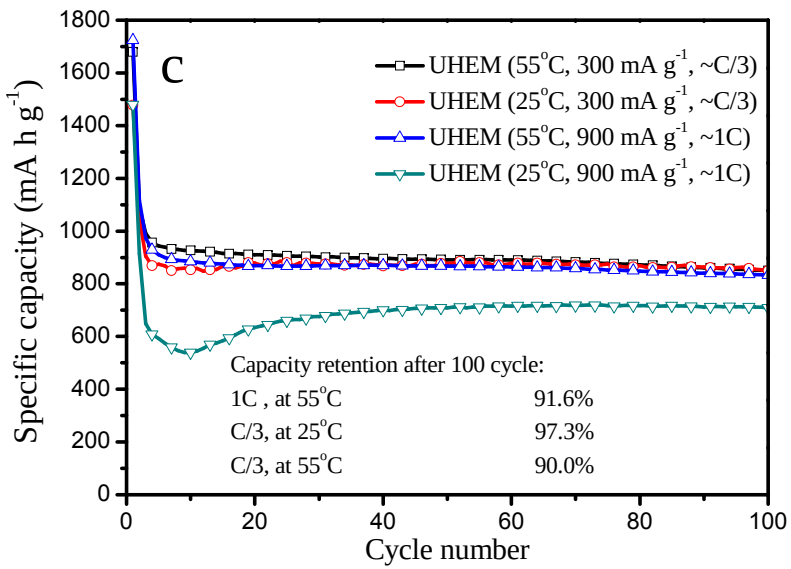
HEC material suffers from voltage drop at low State of Charge

AlF3 coating on HEM shows reduced voltage drop during cycling

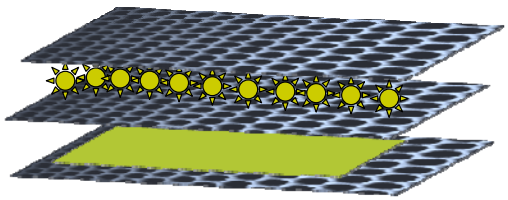
MO-$Sn_xCo_yC_z$ composite anode (MO=SiO, SiO_2, SnO_2, MoO_3)

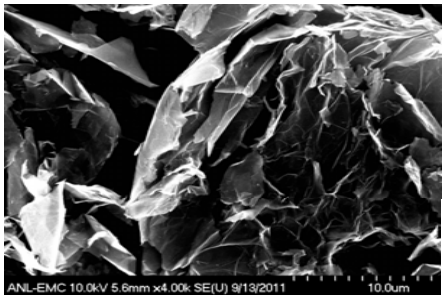
- MO-$Sn_xCo_yC_z$ (MO=SiO, SiO_2, SnO_2, MoO_3, GeO_2) anode materials were selected for investigation as high energy anode based on the following criteria:
  - $Sn_xCo_yC_z$ alloys are known to provide a capacity of 400-500mAh/g for hundreds of cycles.
  - SiO anodes are known to provide more than 1000 mAh/g with poor cyleability.



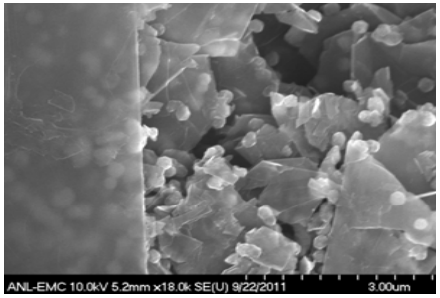


High Energy Si-graphene based Anodes

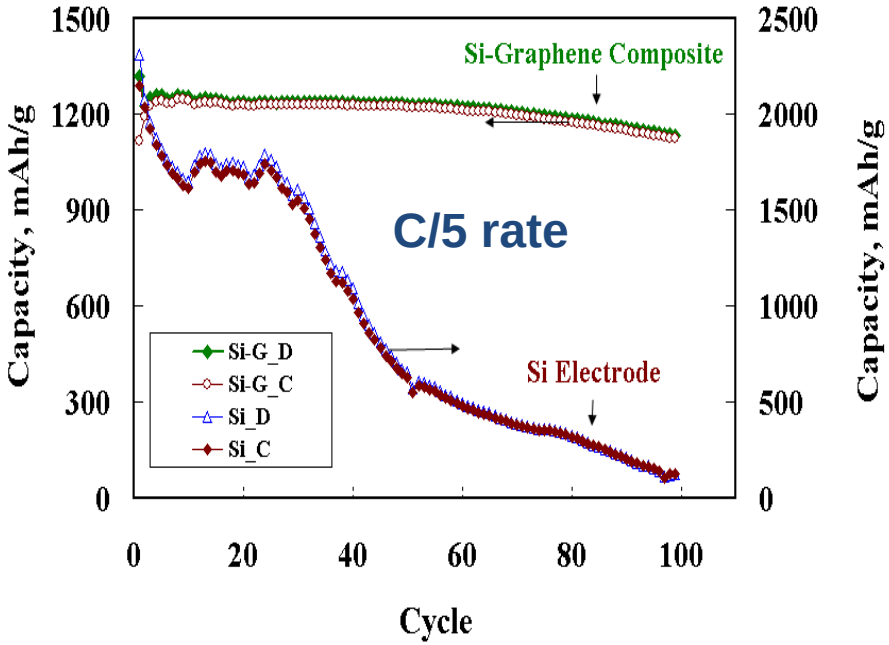


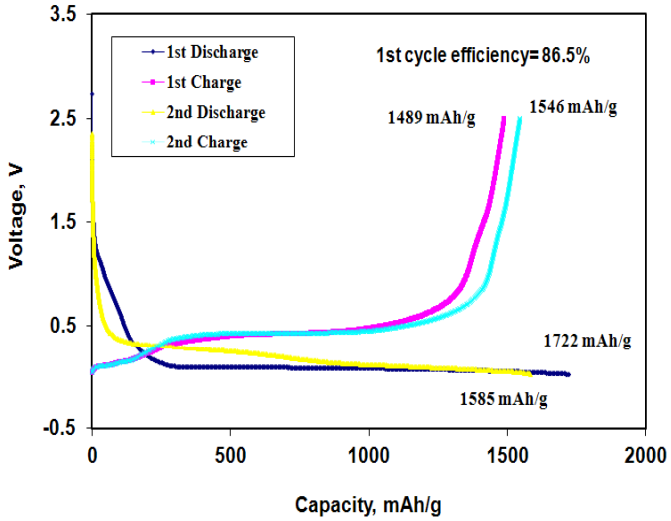


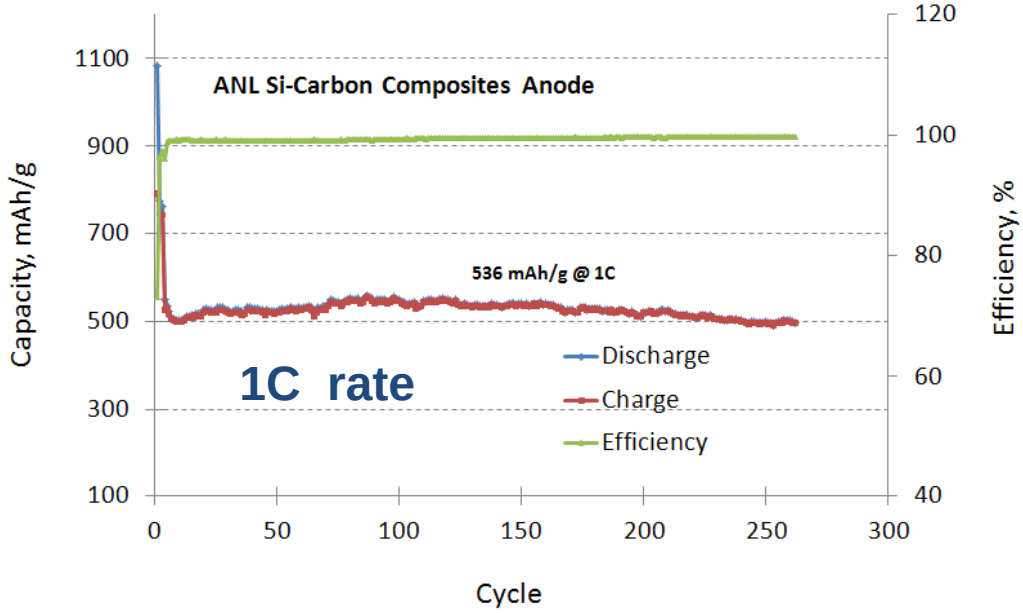
Graphene



Si-Graphene





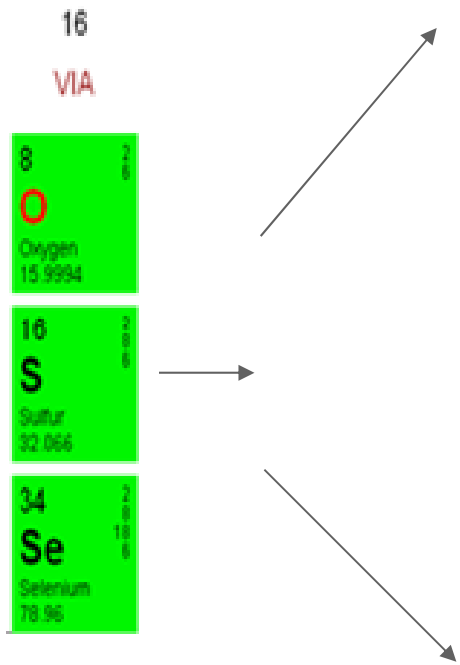


Beyond Lithium Ion

- Li-ion technology will initiate the path to electrification.

- Beyond Li-ion research Li-O and Li-S precipitation electrochemistry; these systems are significantly higher risk, but could result in improving our ability to store energy safely and inexpensively.

Li batteries with VIA group



Lithium air :

- ✓ 3351 $mAhg^{-1}$ based on Li_2O (with Li_2O_2 the capacity become : 1675 $mAhg^{-1}$.
- ✓ Polarization more than 1.5V between the charge and the discharge.
- ✓ Electrolyte decomposition.
- ✓ Poor cycleability and catalyst degradation.

Lithium sulfur :

✓1675 $mAhg^{-1}$ based on Li_2S.
✓Low tap density of sulfur ~2.07g/cc "volumetric capacity 3467Ah/l" .
✓Insulator character of sulfur (10^{-30}) S/cm, need more carbon additive (low active loading, low capacity at the electrode level)
✓Can't be cycle over 3.6V due to the formation of soluble polysulfide "redox shuttle effect".
✓Low voltage output ~1.8V. Energy density: 6240 Wh/l
✓Low melting point ~ 115ºC safety?

Lithium selenium :

✓675 $mAhg^{-1}$ based on Li_2Se.
✓High tap density of selenium ~4.8g/cc "volumetric capacity 3240 Ah/l".
✓Good conductor character of selenium *(10^{-6}-10^{-7}) S/cm*, limited use of carbon additive (high active loading, high capacity at the electrode level)
✓Can be cycle till 4.6V without the formation of soluble polysulfide "redox shuttle effect".
✓High voltage output ~2.5V. Energy density: 8100 Wh/l (30% more than S)
✓High melting point 220ºC "safer".

Se and SeS_2 price & toxicity

Se :

60$/kg for 99.99 purity. (Co: $45~55/kg)

✓50mg/day is recommended by doctor as a supplement.

http://www.wisegeek.com/what-is-a-selenium-toxicity.htm

SeS_2 :

commercially called selenium disulfide is sold as an antifungal agent in shampoos for the treatment of dandruff and seborrheic dermatitis associated in the scalp with *Malassezia* genus fungi. At the 2.5% strength, selenium disulfide is also used on the body to treat tinea versicolor, a type of fungal skin infection caused by a different species of *Malassezia*.

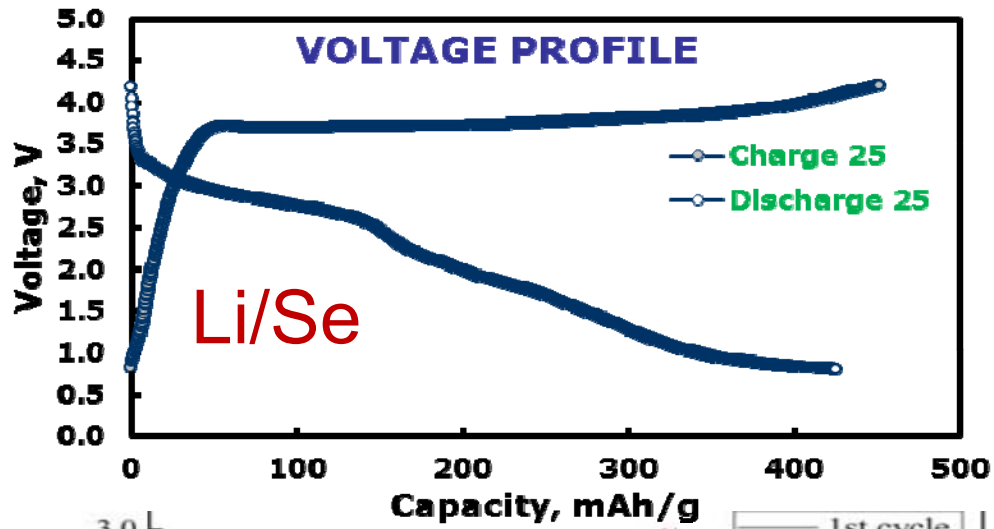
* We are not going to use H_2 or any H_2 sources that can lead to the formation of H_2Se.

Selenium Powder 99.99 China USD/KG				
Date	Low	High	Avg.	Change
Current pricing available to subscribers				
24 Apr 09	63.0	70.3	66.66	.05
17 Apr 09	63.0	70.3	66.61	.01
03 Apr 09	62.9	70.3	66.60	-.01
27 Mar 09	63.0	70.3	66.61	.08
20 Mar 09	62.9	70.2	66.53	0
06 Mar 09	62.9	70.2	66.53	0
27 Feb 09	62.9	70.2	66.53	-2.99
13 Feb 09	65.9	73.2	69.52	0
06 Feb 09	65.9	73.2	69.52	2.94
19 Dec 08	62.9	70.2	66.58	4.77
Source - Reuters / Shanghai Nonferrous Metals Prices include VAT				

Selenium Sulfide 2.5% Anti-Dandruff Shampoo, 40 Oz (18.5$)

Capacity & energy : Li/Se vs Li/S

Li/Se voltage out-put is more than 2.5V could be 2.7V if we improve the intrinsic conductivity. Electrode composition: 84% active 16% inactive (binder10% and carbon 6%)



Li/S voltage out-put is near 1.8V. (50%active and 50% inactive)

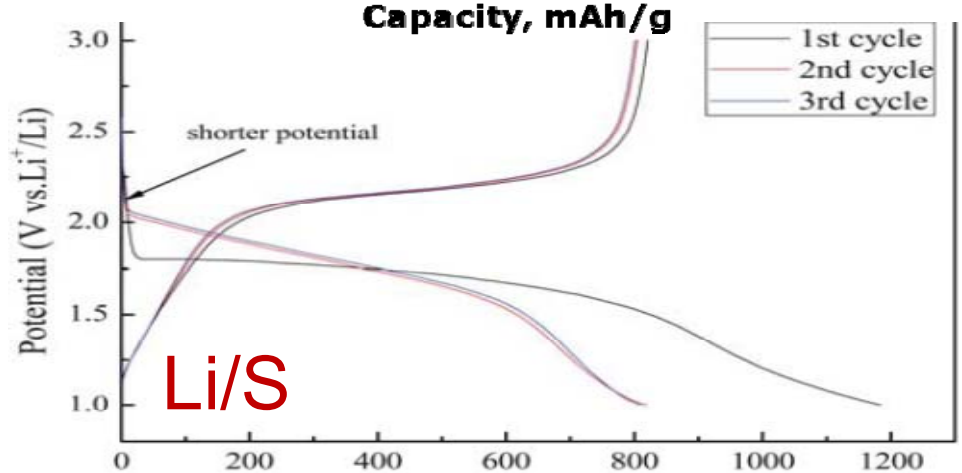


Fig. 1. Li/Se and Li/S voltage profile.

Overcharge and redox shuttle effect

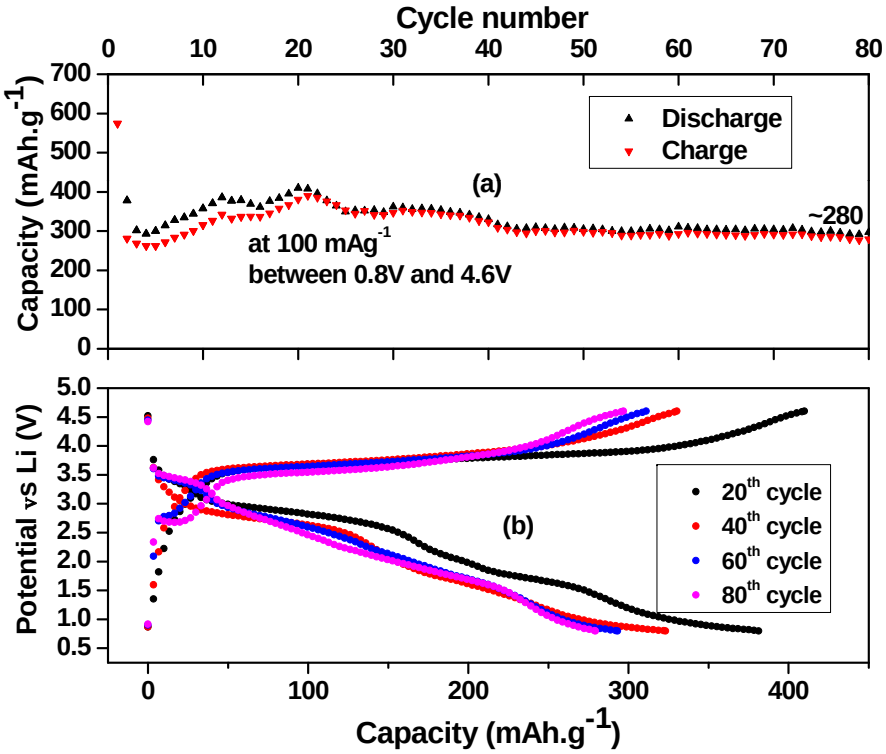


Fig. 2. Li/Se charging to 4.6V (84%active material).

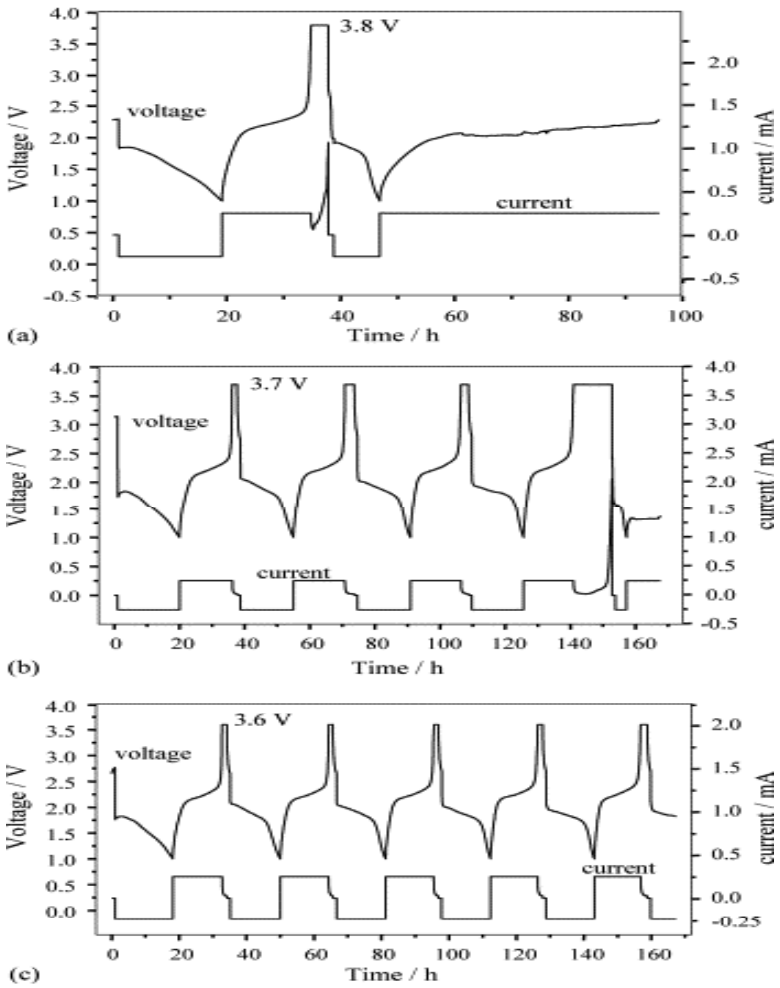


Fig. 3. Li/S overcharge to 3.6, 3.7 and 3.8V.

Opportunity of enabling Sulfur system trough coupling with Se: Li/Se_xS_y

- ✓ Improve the sustainability of the system:

Selenium-sulfur system is a rich phase diagram Se_5S, Se_5S_2, Se_5S_4, SeS, Se_3S_5, SeS_2, SeS_7. These materials offer a capacity between 675 and 1550 $mAhg^{-1}$.

Table 1: Theoretical capacity of few selenium-sulfur composites.

Material	Theoretical capacity ($mAhg^{-1}$)
Se	**675**
Se_5S	842
Se_5S_2	961
Se_5S_4	1119
SeS	1175
Se_3S_5	1300
SeS_2 (commercially available)	**1342**
SeS_7	1550
S	1675

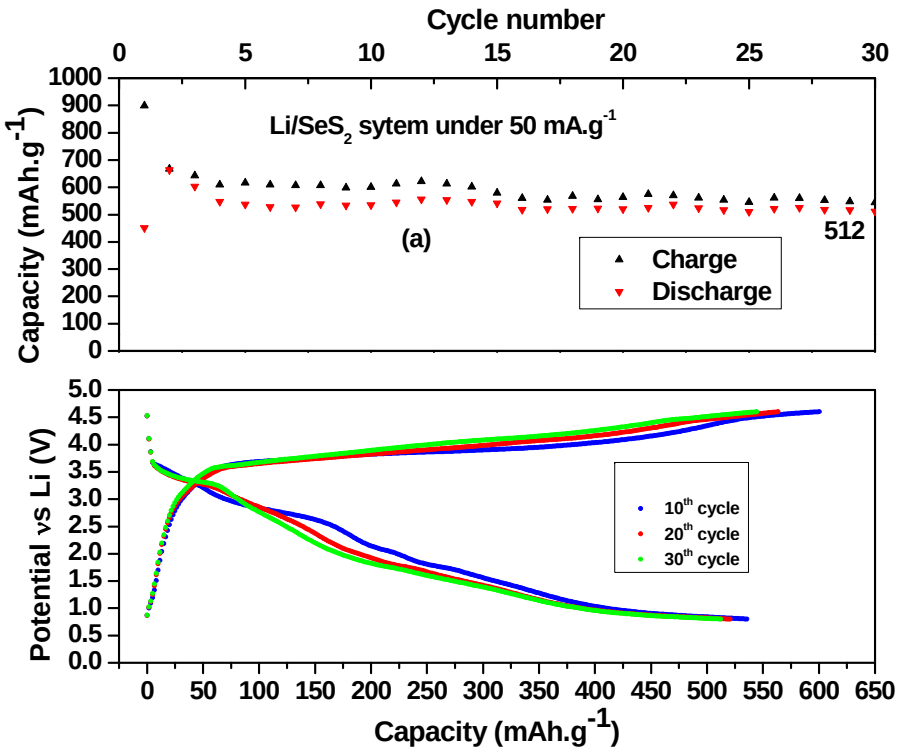
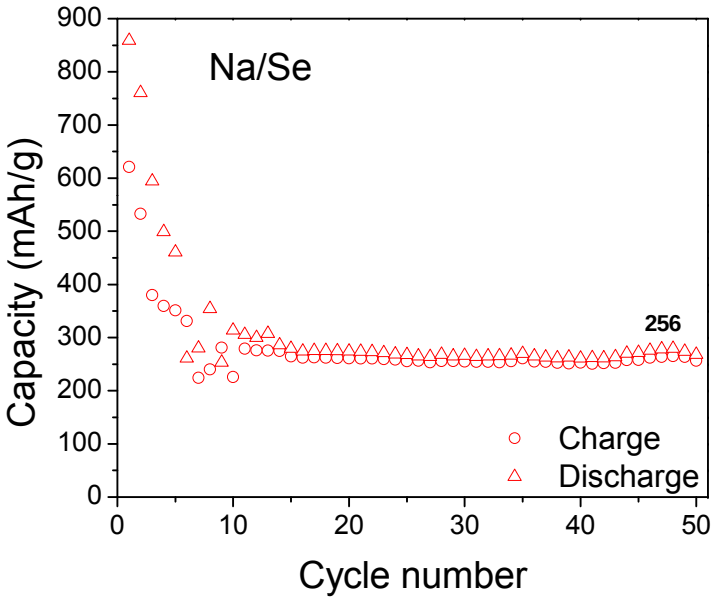
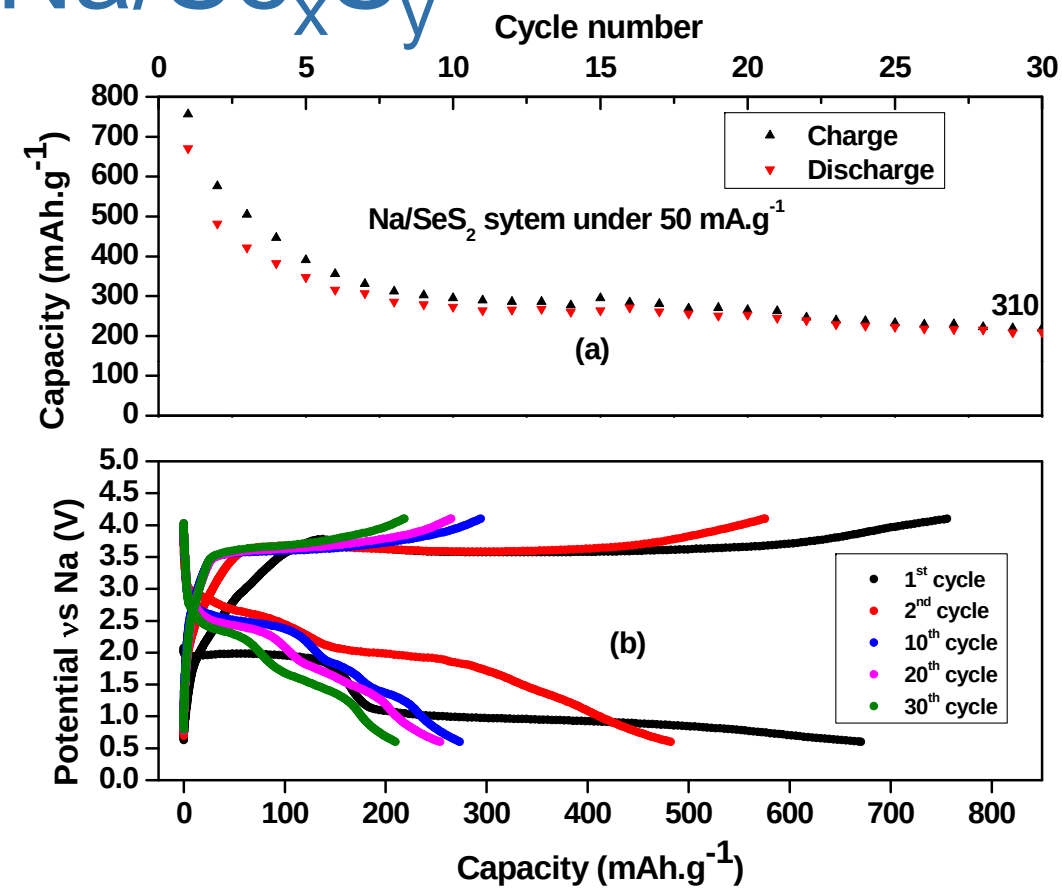


Fig. 4. (a) Cycle performance and (b) voltage profile of Li/SeS_2 system under 50 $mA.g^{-1}$ current rate between 0.8V and 4.6V.

SeS_2 delivers 30% more capacity than Se.

Room temperature Na/Se and Na/Se_xS_y





Cycle performance and voltage profile of Na/SeS_2 system under 50 $mA.g^{-1}$ current rate between 0.6V and 4.0V.

Conclusions

- ✓ To enable future electrification of vehicles, there is a need of developing very high energy battery systems: next generation lithium ion
  - ✓ Gradient concentration material
  - ✓ Composite Layered Oxide
  - ✓ Si composite
- ✓ New SexSy has the potential of being enabled since conductivity and redox shuttle may be overcame!
- ✓ Electrolyte is a key to enabling lithium air system