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Innovation and Creativity

The Carbon-Electrolyte Interface at High Cathodic Voltages

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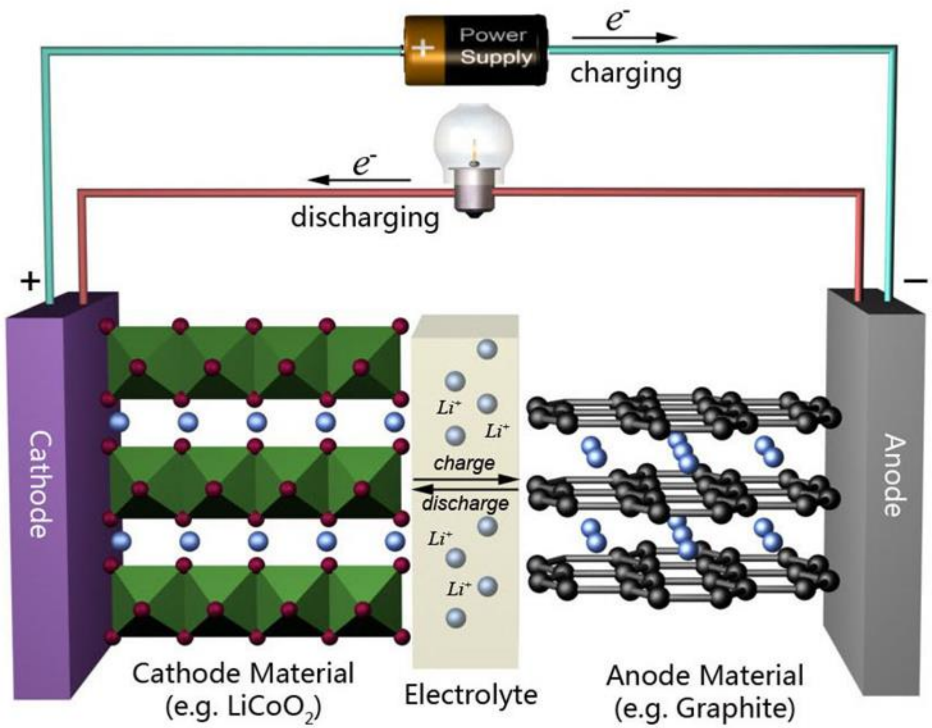
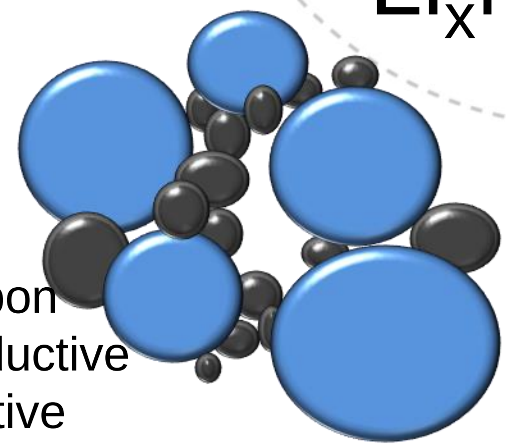
Outline

- Introduction
- Carbon materials, properties
- Results
  - Electrochemical characterization (galvanostatic cycling, cyclic voltammetry)
  - *In-situ* XRD
- Potential route for mitigation of structural damage
- Summary

Carbon conductive additives in Li-ion batteries



Li_xMO_y



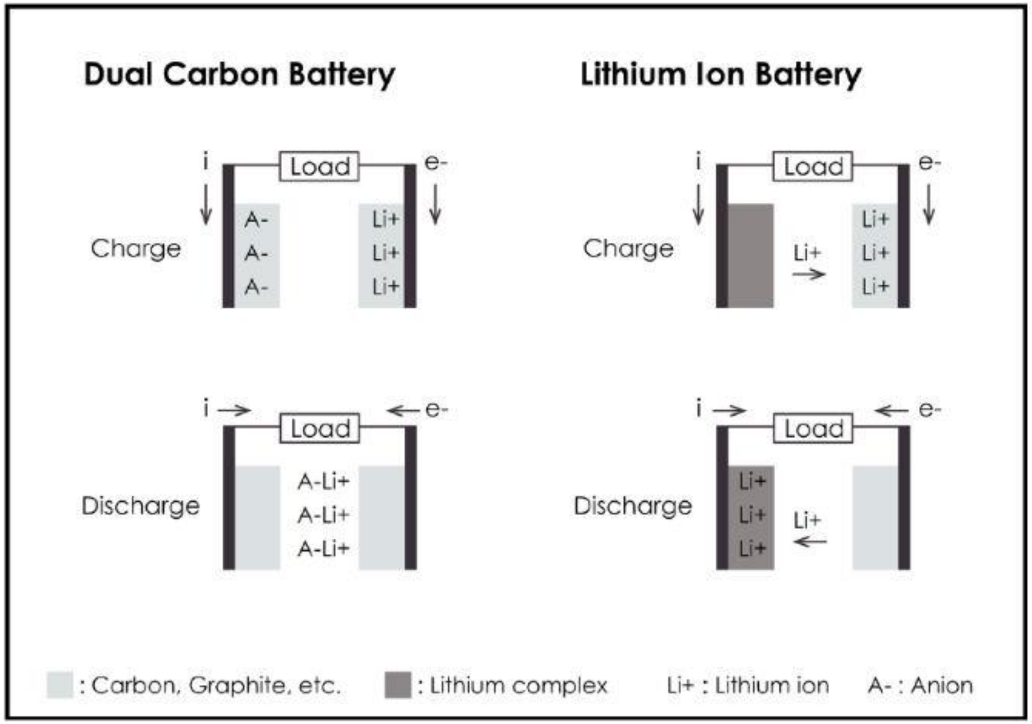
Carbon conductive additive

Positive electrode: $LiMO_2 \rightleftharpoons Li_{1-x}MO_2 + xLi^+ + xe^-$

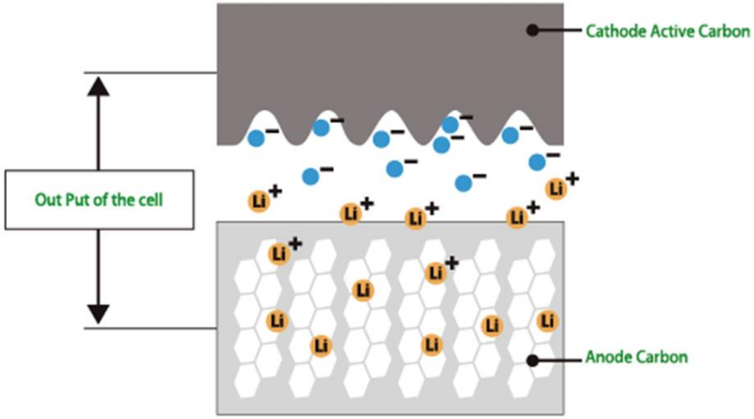
Negative electrode: $C_6 + xLi^+ + xe^- \rightleftharpoons Li_xC_6$

Total cell reaction: $LiMO_2 + C_6 \rightleftharpoons Li_{1-x}MO_2 + Li_xC_6$

Anion intercalation

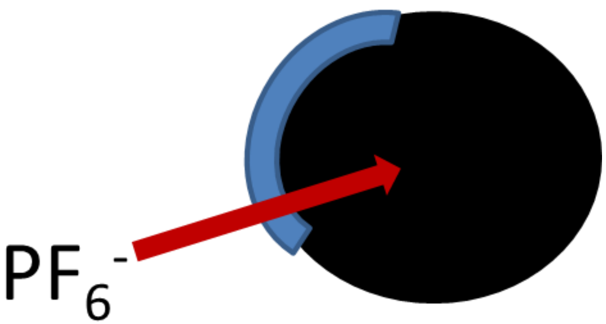


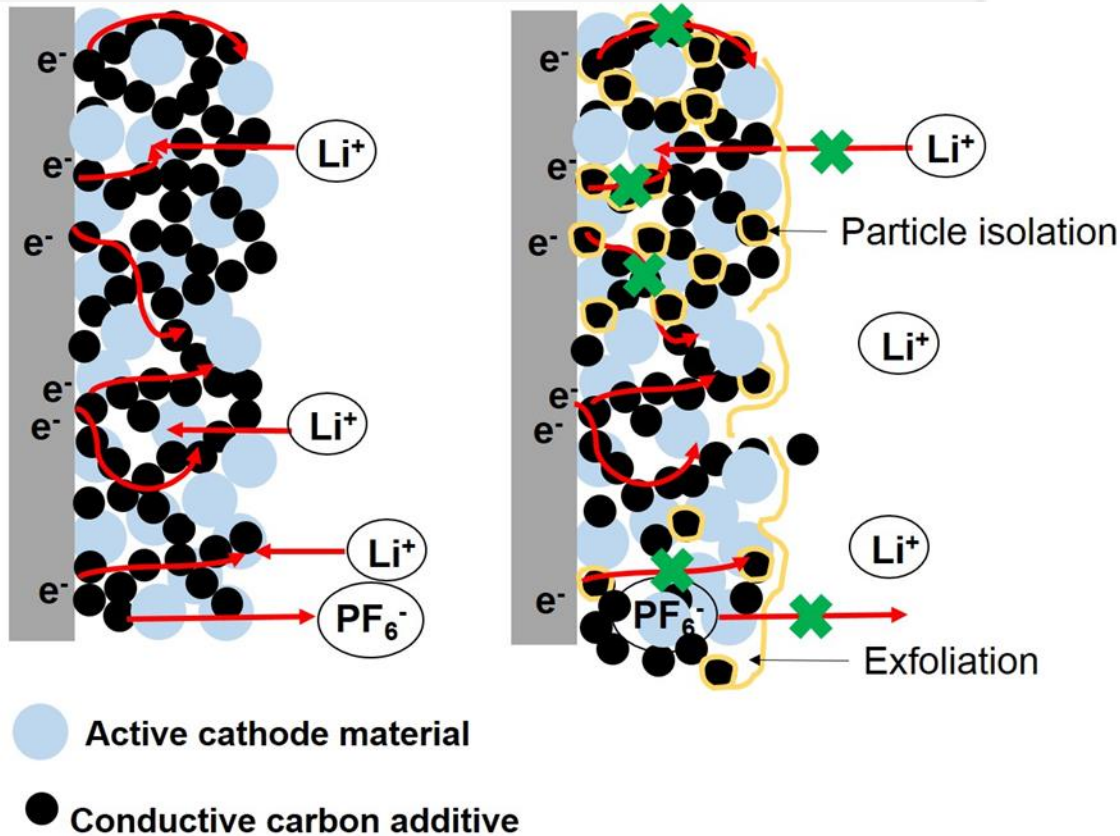
Li-ion hybrid capacitor



salts: $LiPF_6$, $LiBF_4$, LiF…

At high voltages: Electrolyte oxidation and anion intercalation





- Loss of conductive network, loss of contact to active material
- Structural/mechanical stability, loss of adherence to current collector

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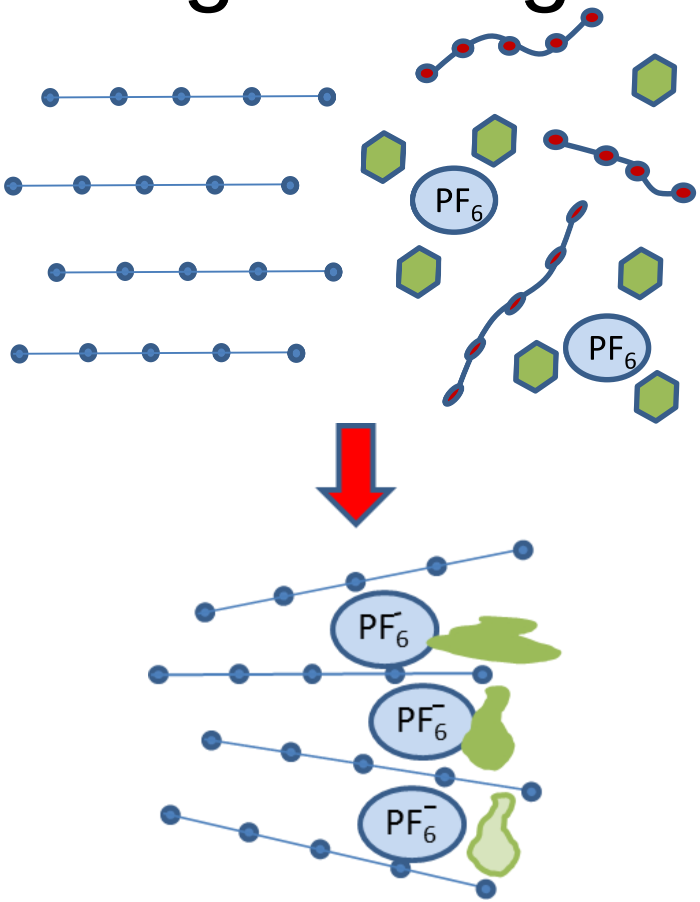
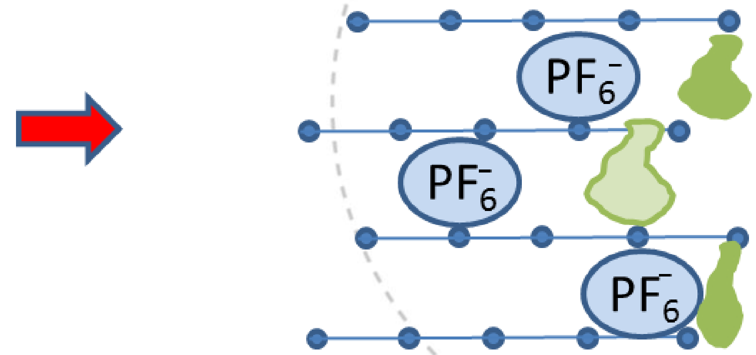
At high voltages





- Preferential oxidation of EC[1,2]
- No film, but decomposition products integrated in surface region[3]

[1]F. Joho, P. Novak, *Electrochim. Acta,* **45,** 3589-3599 (2000).
[2]L. Xing, and O. Borodin, *Phys. Chem. Chem. Phys.*, **14,** 12838-12843 (2012).
[3]Younesi *et al.*, *J. Electrochem. Soc.*, **162** (2015) A1289

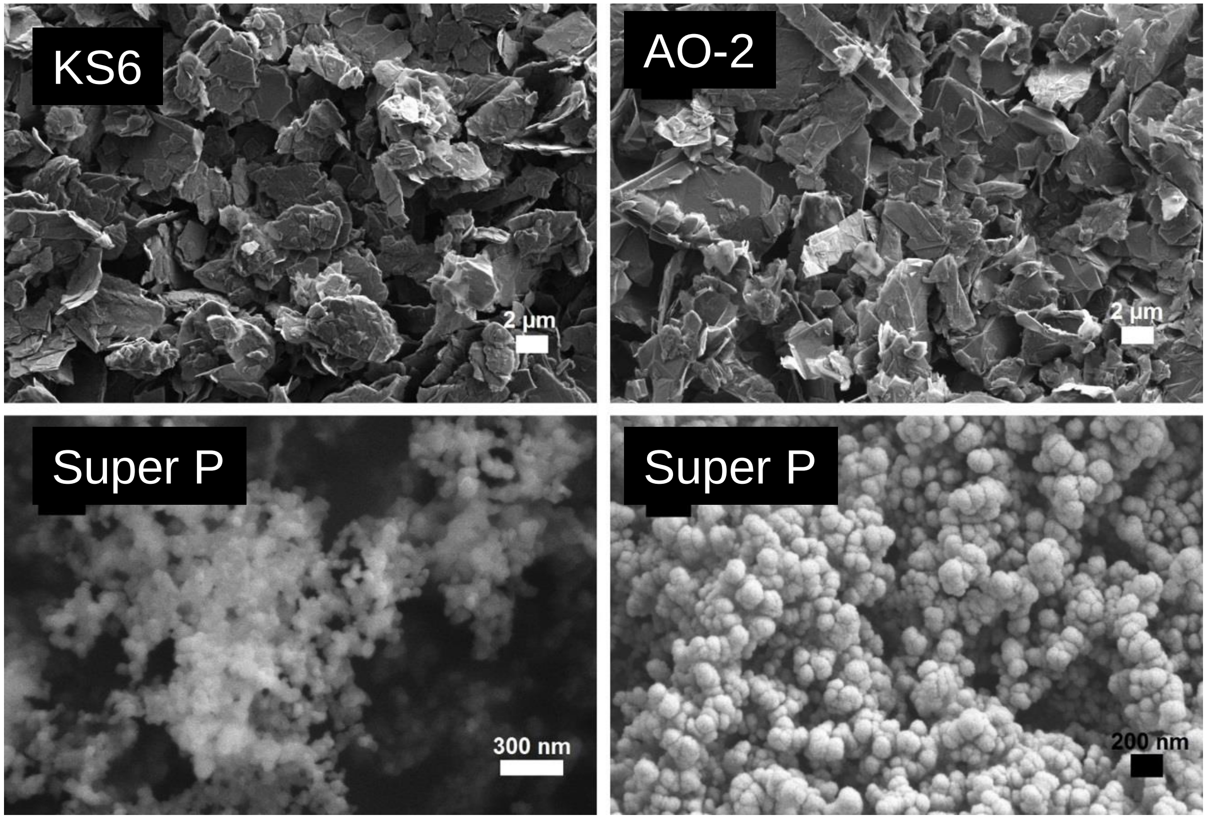
- Oxygen surface groups[4]

[4]Qi *et al.,*Phys. Chem. Chem. Phys., **16** (2014) 25306

- Exfoliation due to co-intercalation or mechanical stress of decomposition products[5]
- Exfoliation depends on crystallinity of carbon[6,7]

[5]J.A. Seel and J.R. Dahn, *J. of Electrochem. Soc.,* **147**(3), 892-898 (2000)
[6]W. Märkle *et al.,* *Electrochimica Acta,* **55,** 4964-4969 (2010).
[7]W. Märkle, *et al., Carbon,* **47,** 2727-2732 (2009).

Materials



KS6 graphite powder
Particle size ~ 3 µm, *IMERYS*

AO-2, multilayer graphene (graphitic) *Graphenesupermarket*
Particle size 0.15-3 µm

Super P Li, carbon black
Particle size ~ 40-60 nm
IMERYS

Gold coated cast of Super P Li

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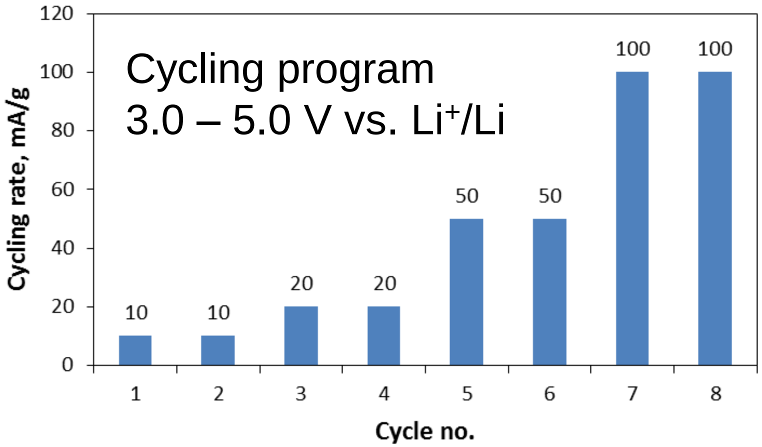
Material properies

	KS6 graphite	AO-2 'graphitic'	Super P Li (carbon black)
Particle size[1]	3 µm (d50)	0.15-3 µm	40-60 nm
Surface area (N_2 ads) [m^2/g]	22.4	57.8	64.9
Ratio [%] edge:basal:defect planes (N_2 ads)	30:53:17	92:4:4	29:50:21
d002 [Å]	3.357	3.357	3.532
L_c [Å]	649	539	30

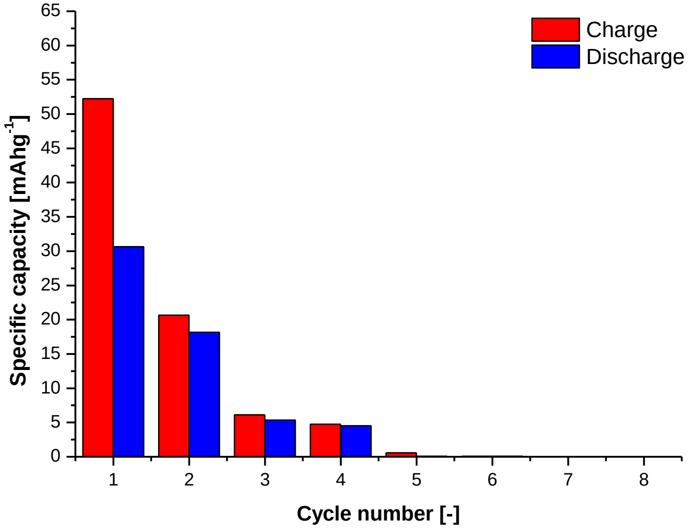
[1]From suppliers

Galvanostatic cycling

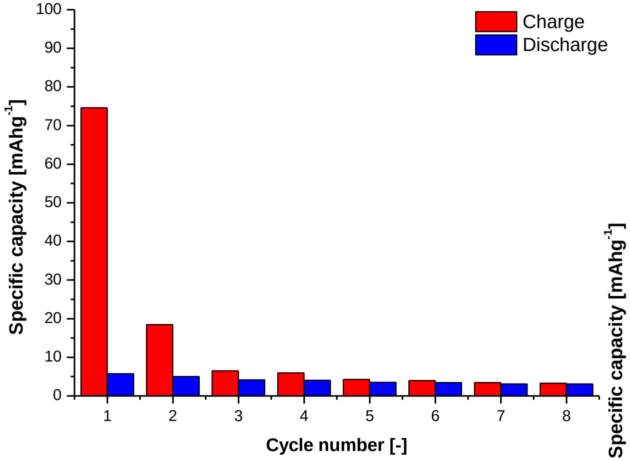
1 M LiPF6 3:7 EC:DMC



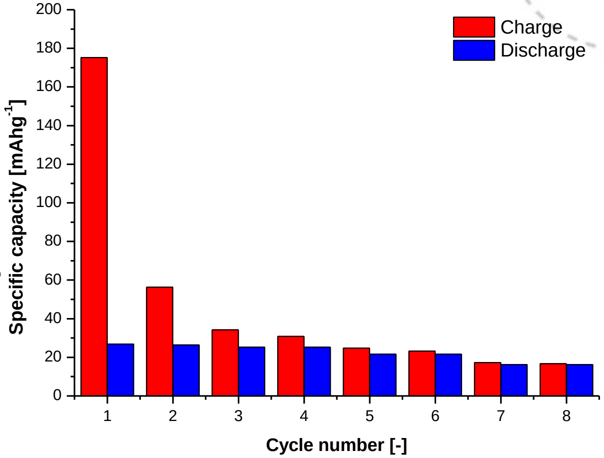
KS6 graphite



SuperP Li



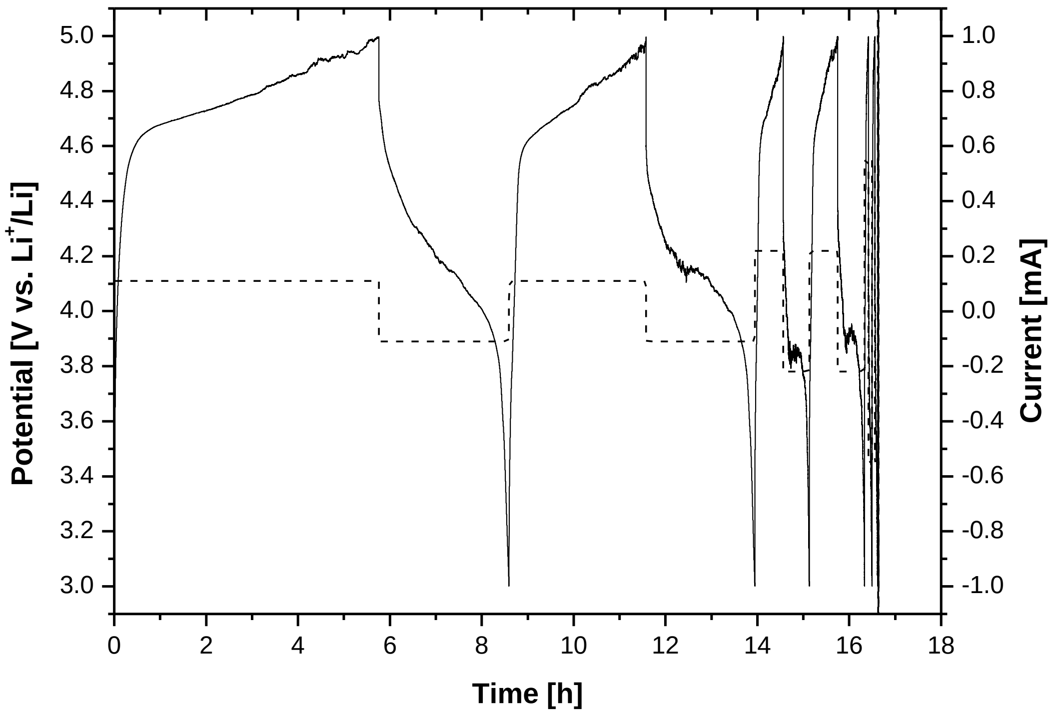
AO-2



High 1st cycle ICL for all materials
- Correlates to surface area of edge planes

Voltage profile during galvanostatic cycling

KS6 graphite



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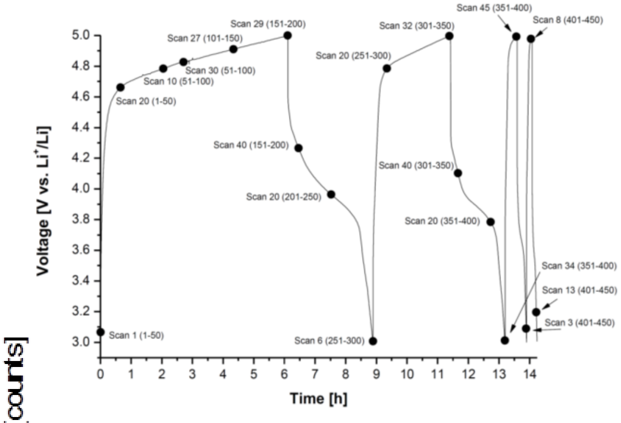
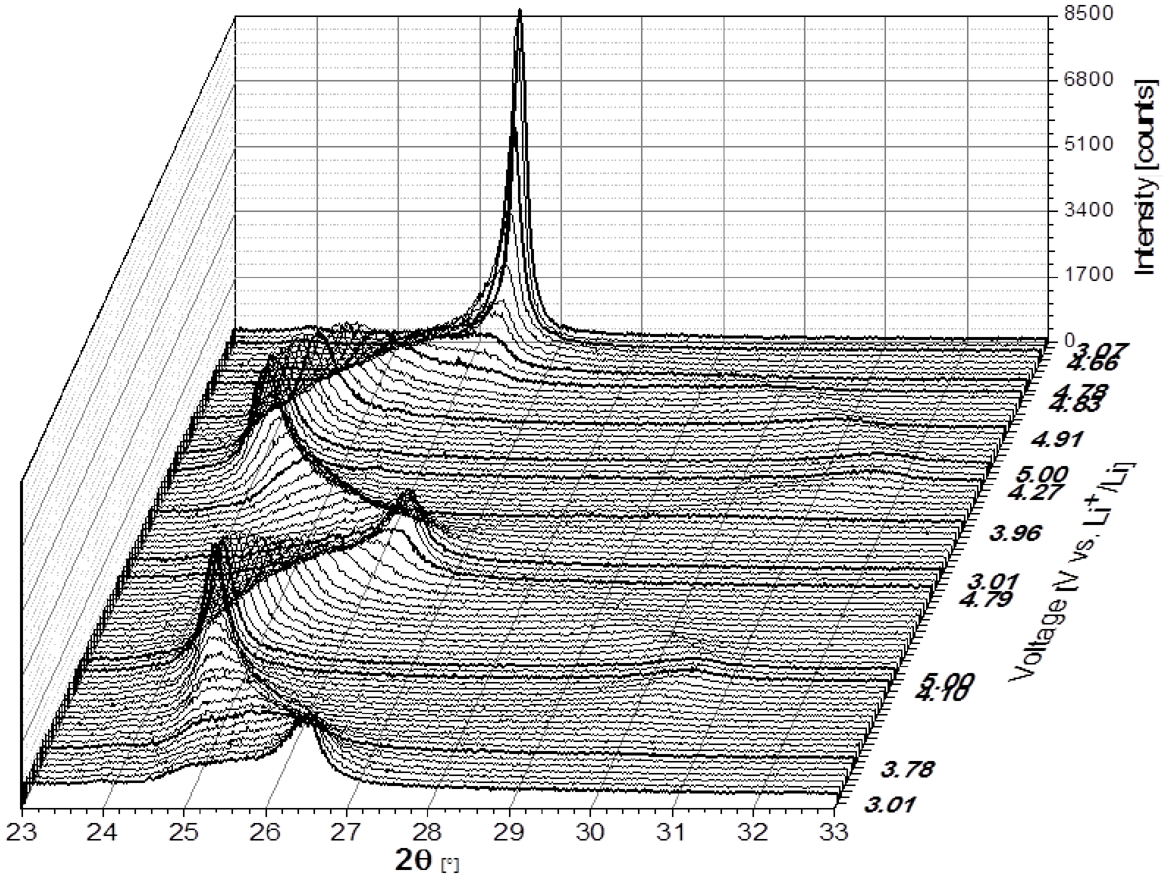
In-situ XRD, KS6 (graphite)



2x10mA/g
2x20 mA/g



9.6 % increase in *d002*

Staged intercalation, stage index between 3 and 4

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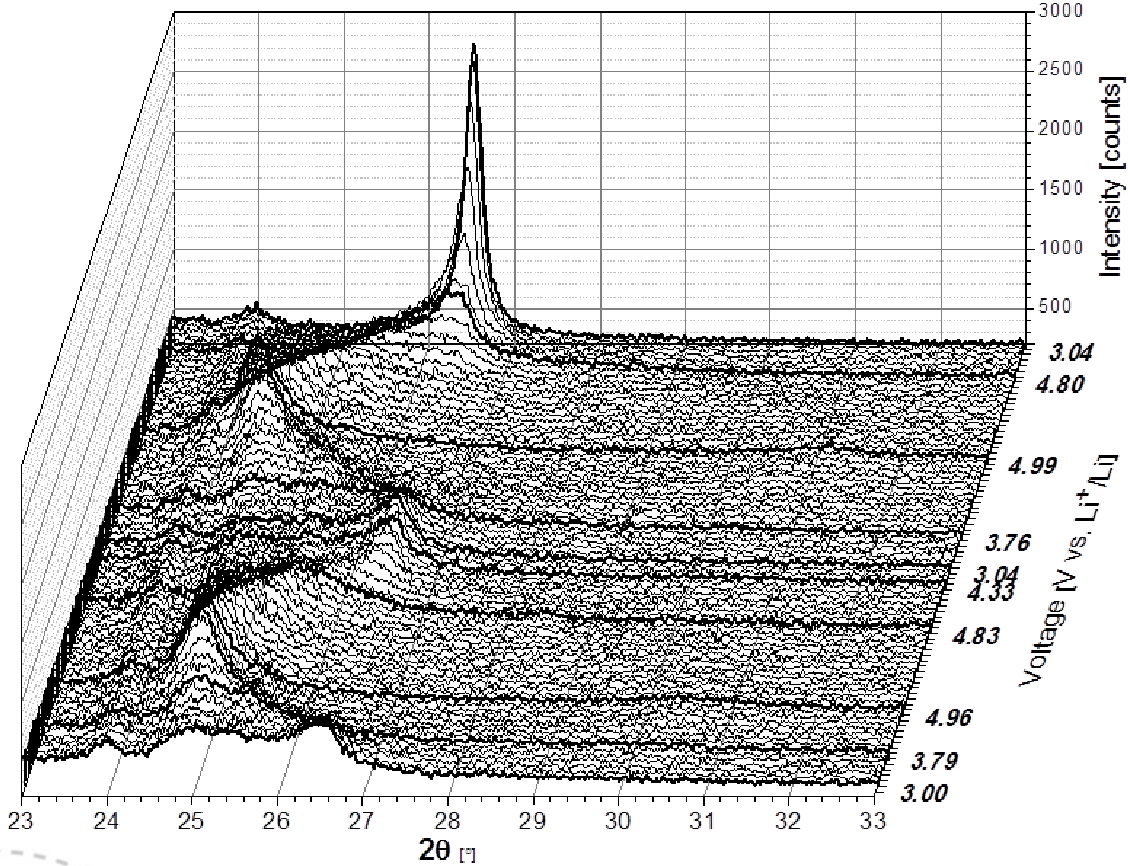
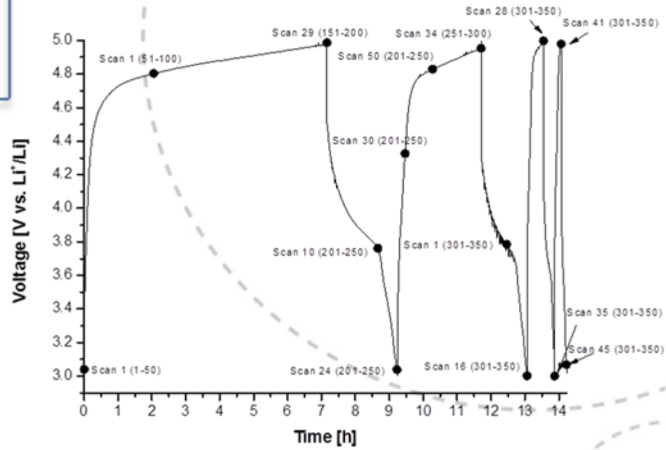
In-situ XRD, AO-2





2x10mA/g
2x20 mA/g

8.4 % increase in *d002*

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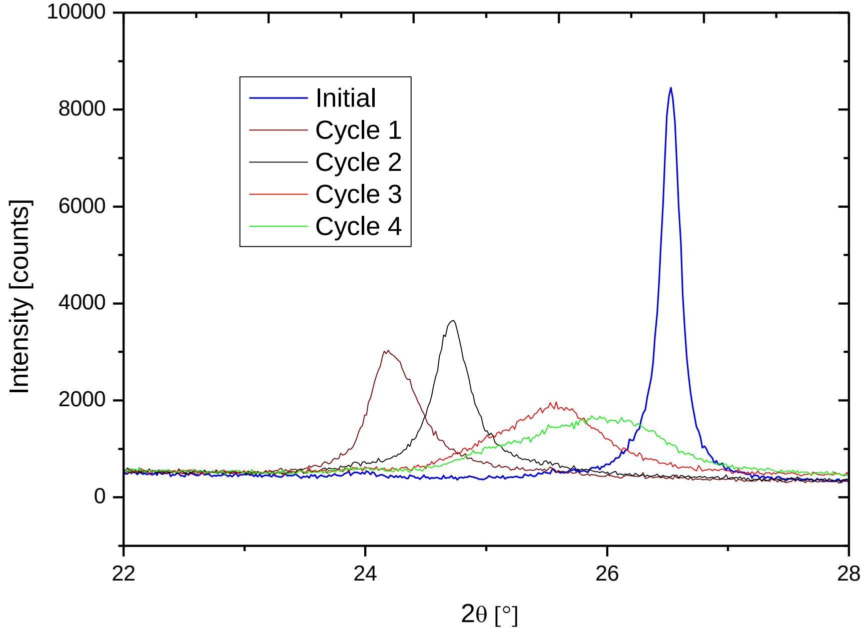
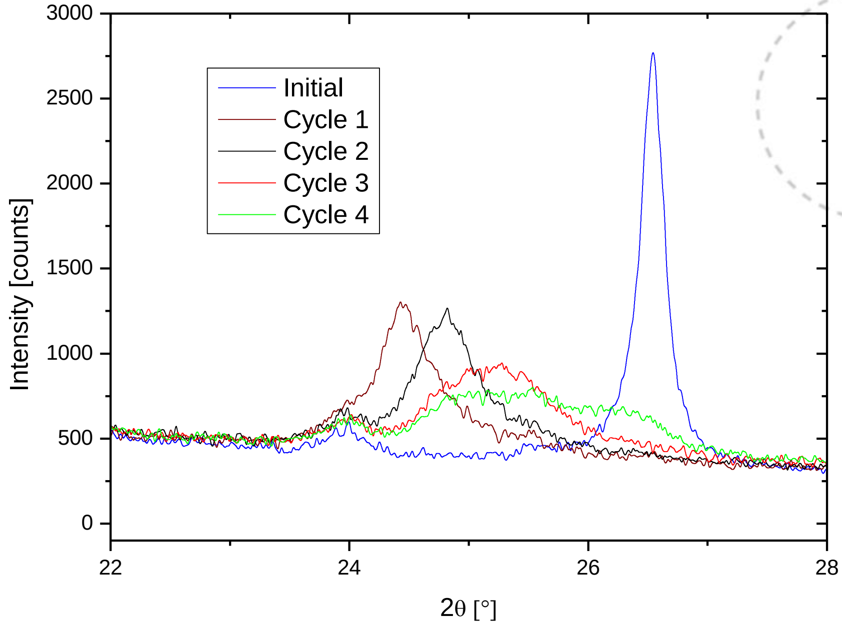
XRD patterns at 5V vs cycle

KS6



AO-2



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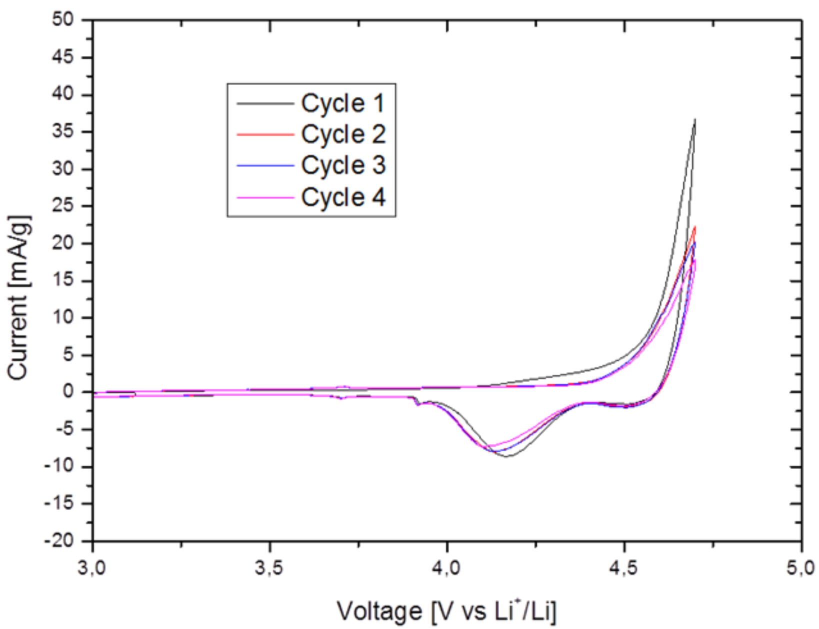
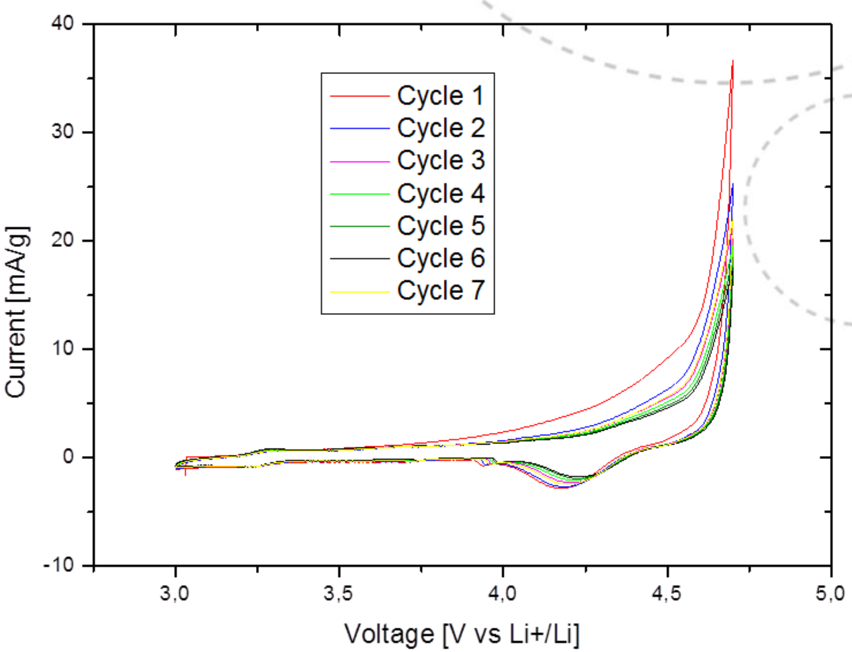
Cyclic voltammetry, cut-off voltage = 4.7 V 0.1 mV/s

KS6



AO-2



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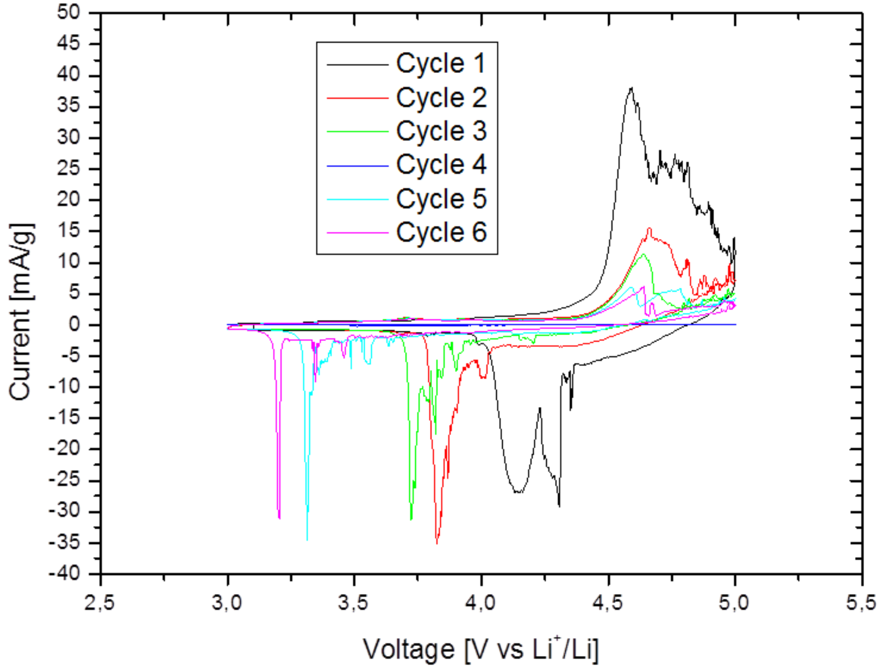
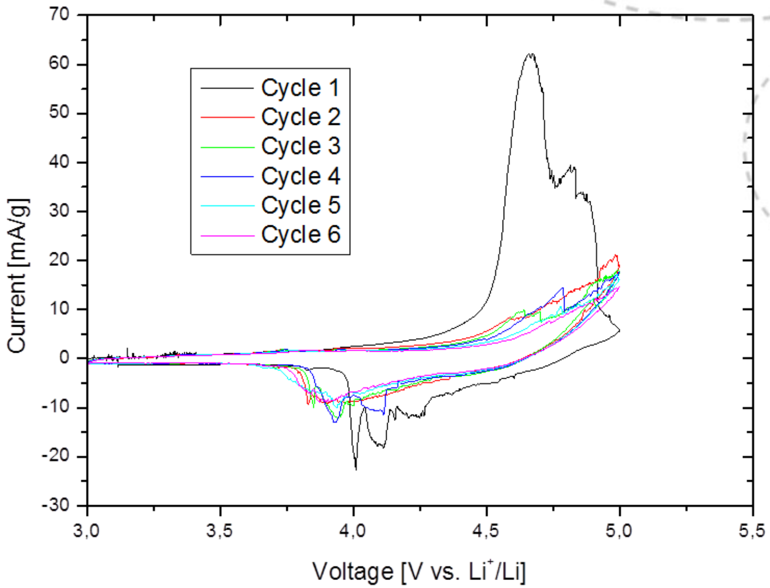
Cyclic voltammetry, cut-off voltage = 5 V

KS6



AO-2



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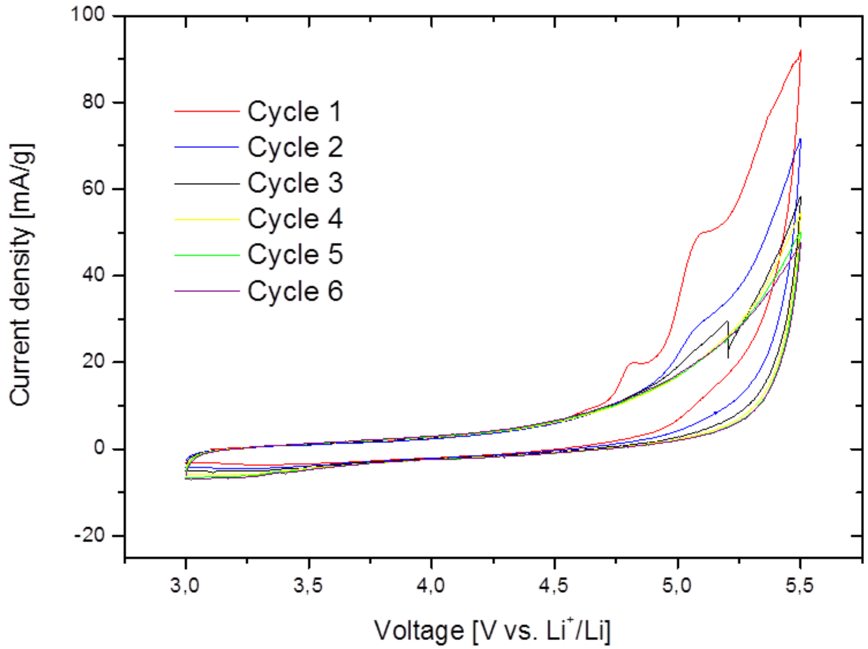
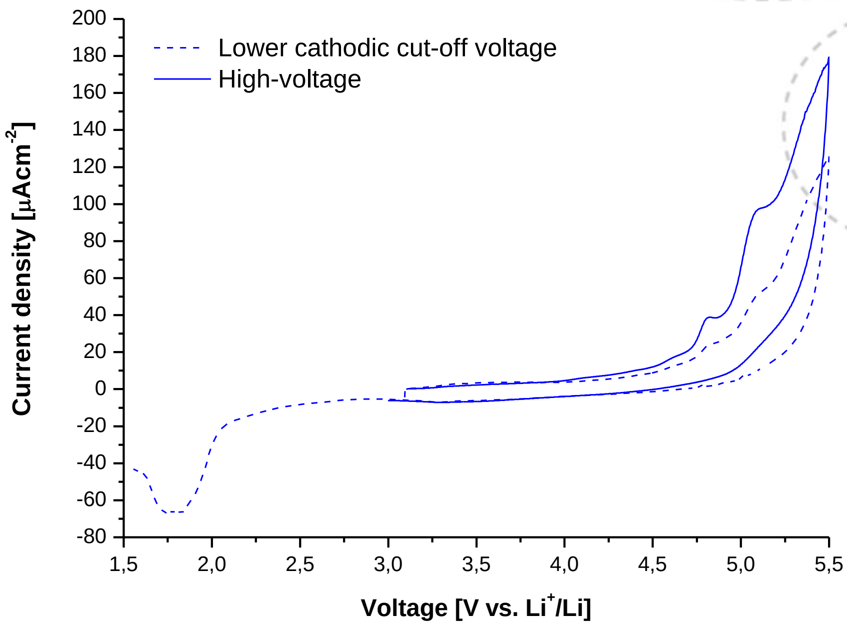
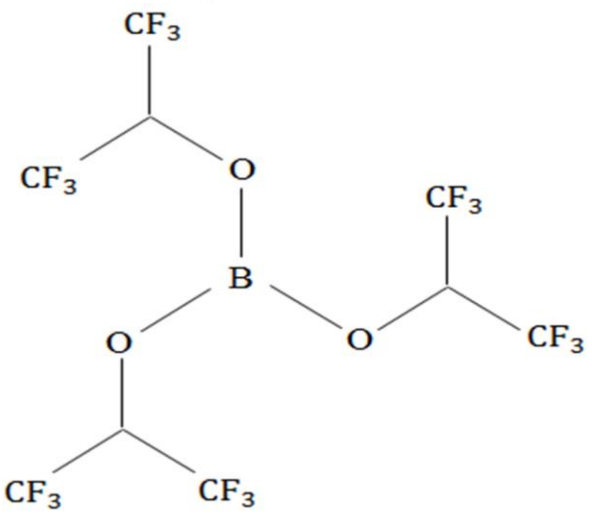
Cyclic voltammetry, Super P Li, cut-off voltage = 5.5 V



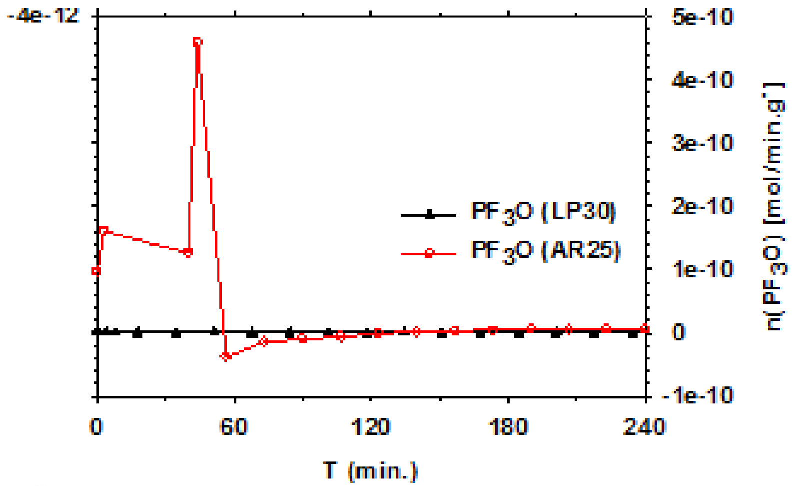


Addition of anion receptor, Tris (hexafluoroisopropyle) borate THFIPB (AR)

- Borate with fluorinated functional groups
- Reduced ion-pairing in electrolyte
- Improved SEI stability of graphite anode demonstrated



$$PF_6^- + THFIPB \rightarrow THFIPB - F^- + PF_5$$



Increased release of PF_5 and PF_3O observed[1]

[1]OEMS performed at PSI

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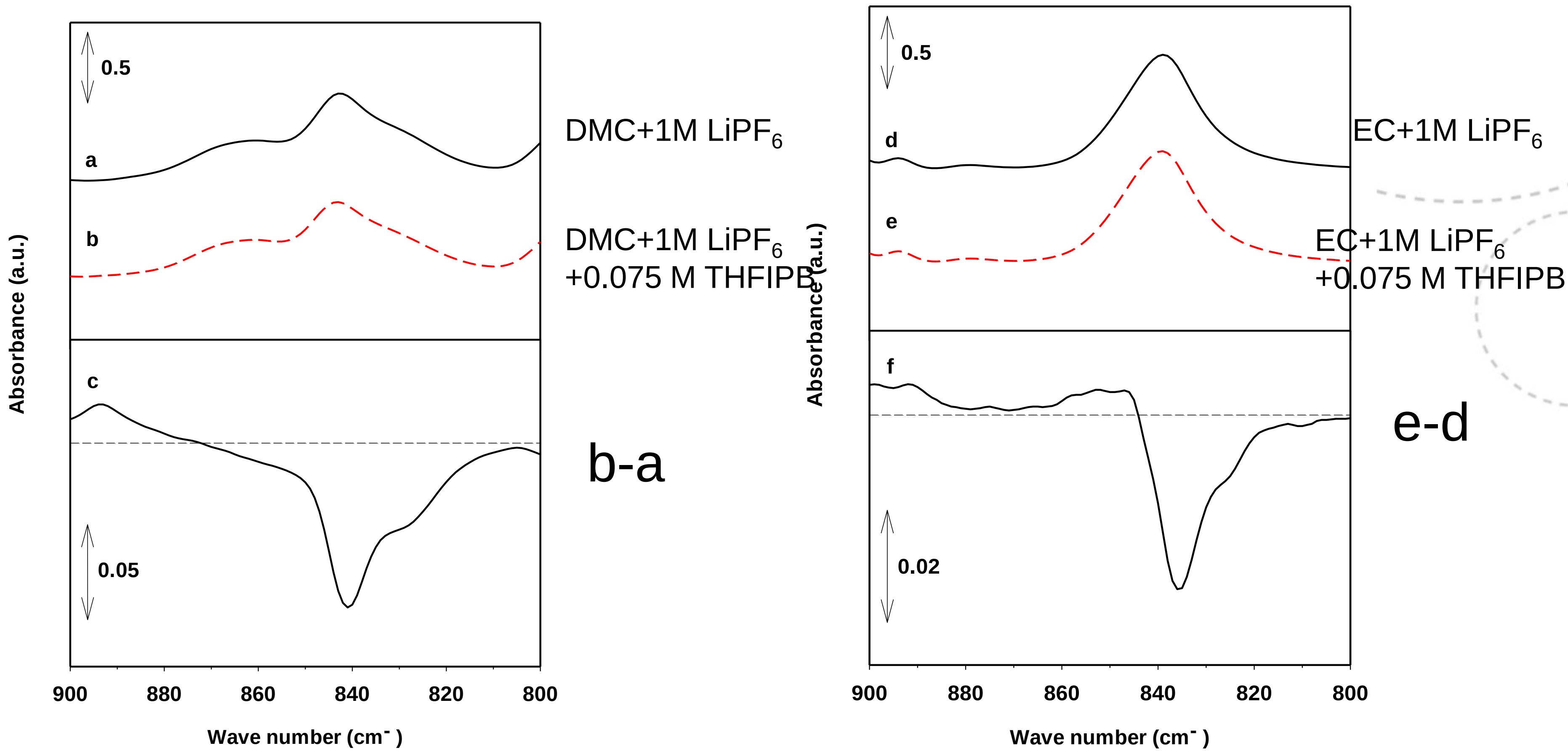
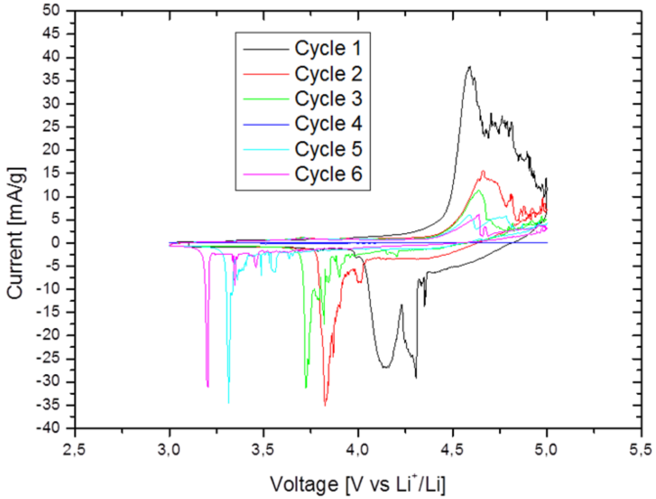
FTIR spectra of pure electrolyte



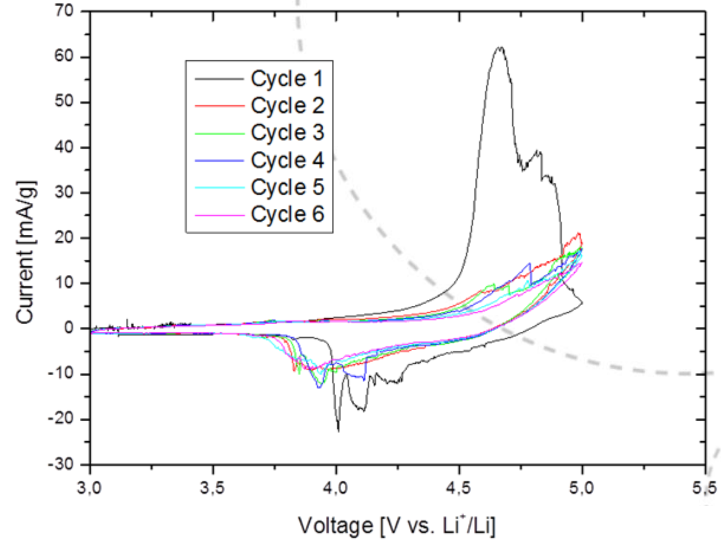
Experiments performed at PSI

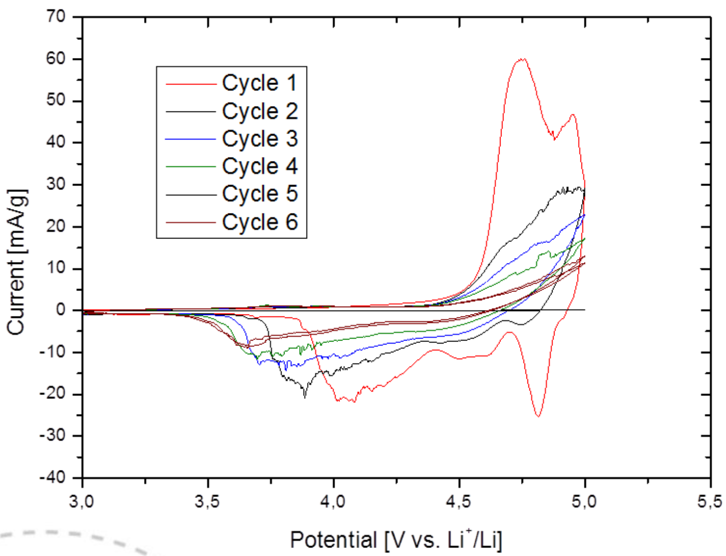
CV, KS6

CV, AO-2

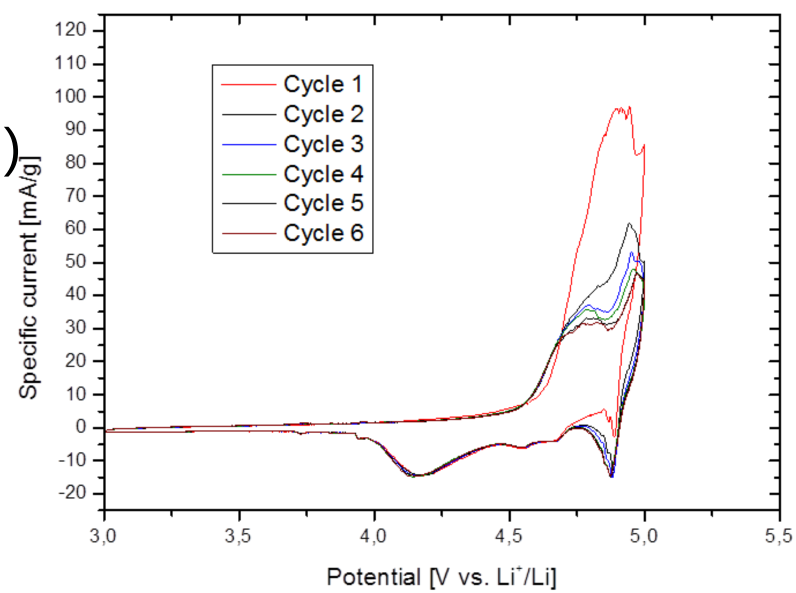


wo AR
(0.025 M)

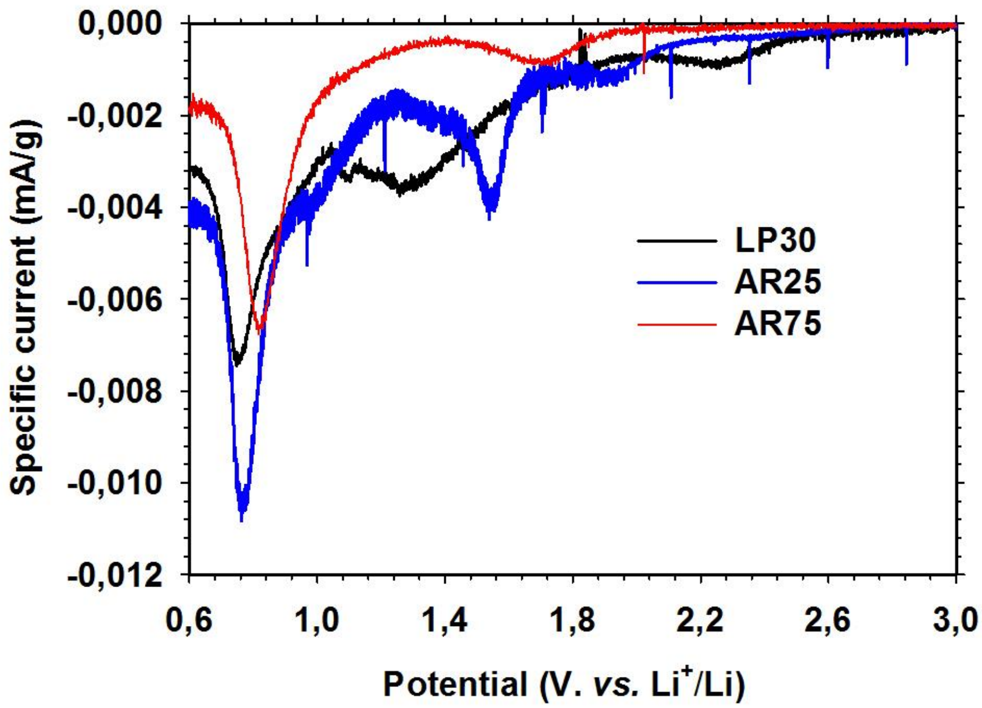




with AR
(0.025 M)



Cyclic voltammogram, cathodic, SLP30 graphite



AR25 = 0.025 M AR
AR75 = 0.075 M AR

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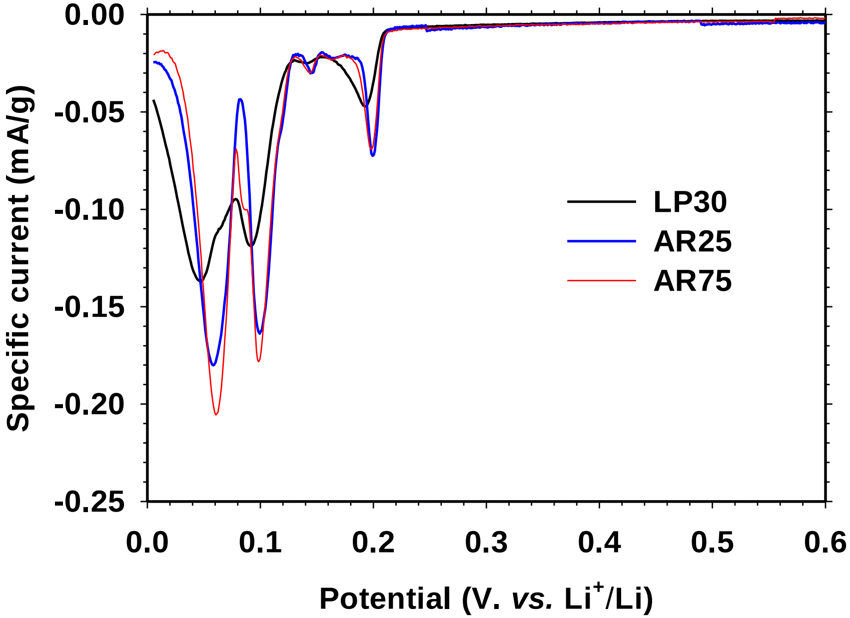
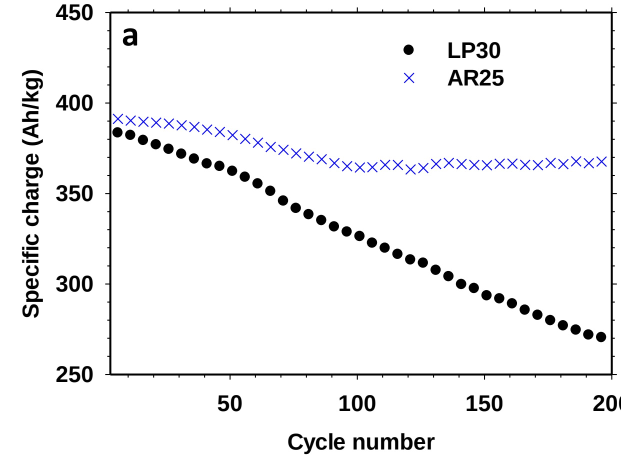
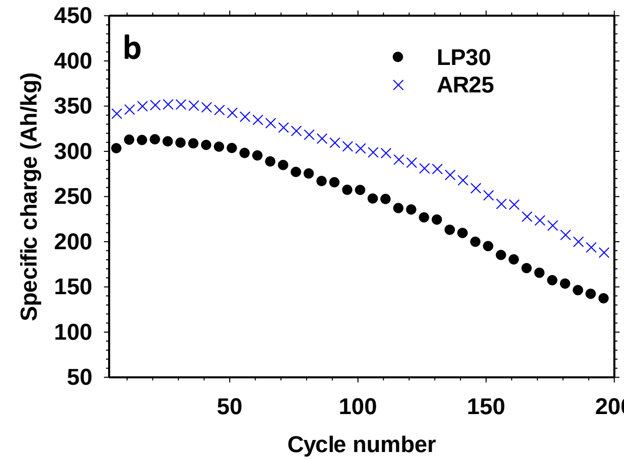
Effect of AR on graphite anode





200 cycles at 1 C, total charge (above), galvanostatic charge (below)



SUMMARY

- Anion intercalation occurs from around 4.6 V for graphitic materials
- Irreversible capacity loss correlates with edge plane surface area
- Growth of film from electrolyte decomposition products prevents anion intercalation
- Structural damage caused by anion intercalation is observed for graphitic materials (by in-situ XRD)
- Structural damage occurs during first cycle
- Chemical surface film formation, for example by addition of an anion receptor, possibly involving oxygen surface groups, may prevent structural damage.

Thank you for your attention!!

NTNU and PSI are acknowledged for the support

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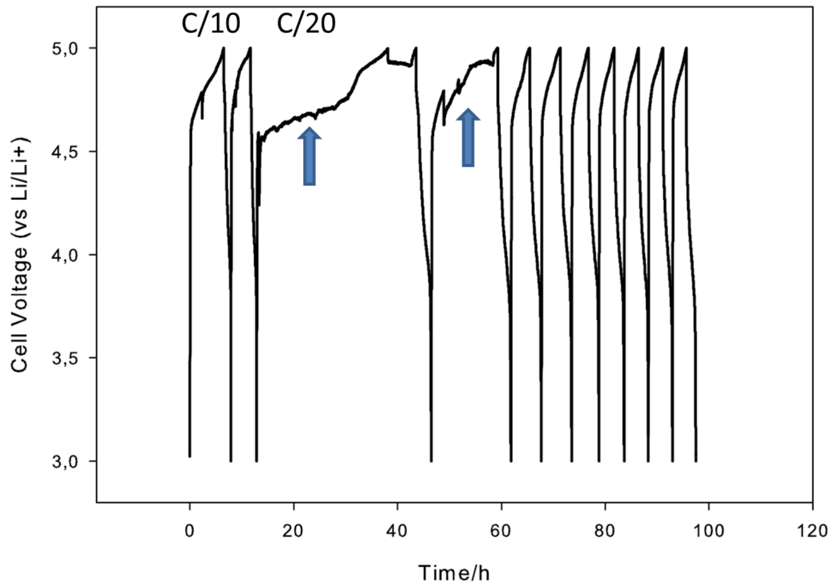
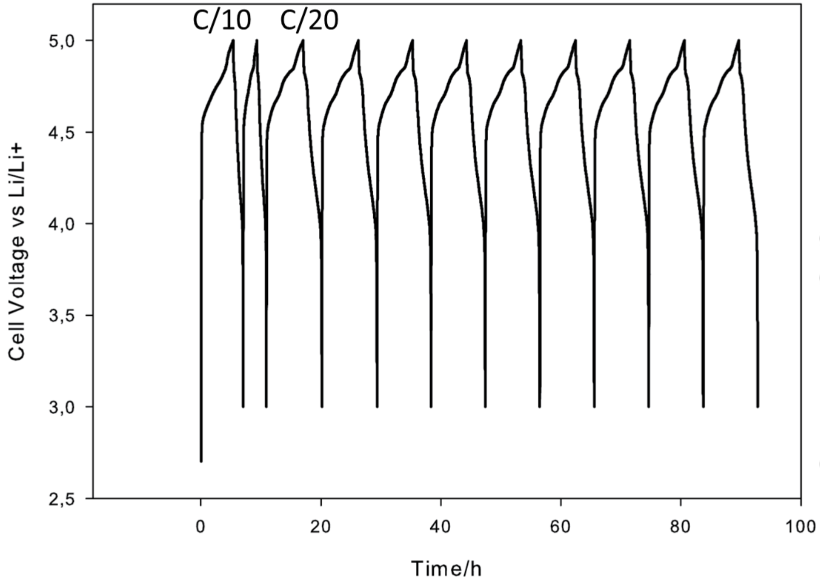
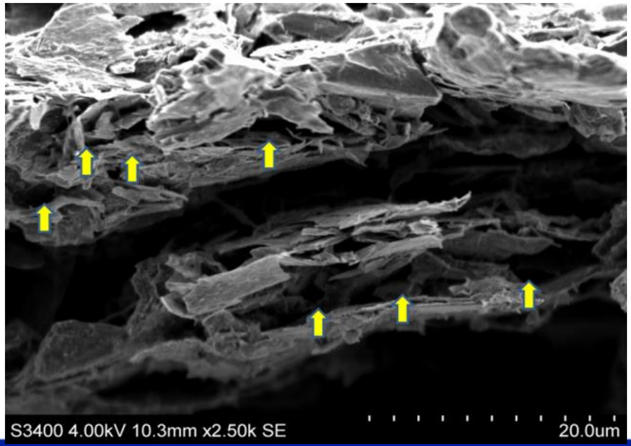
SFG44 in 1.2M $LiPF_6$-PC:DMC

wo AR (0.025 M)



with AR (0.025 M)





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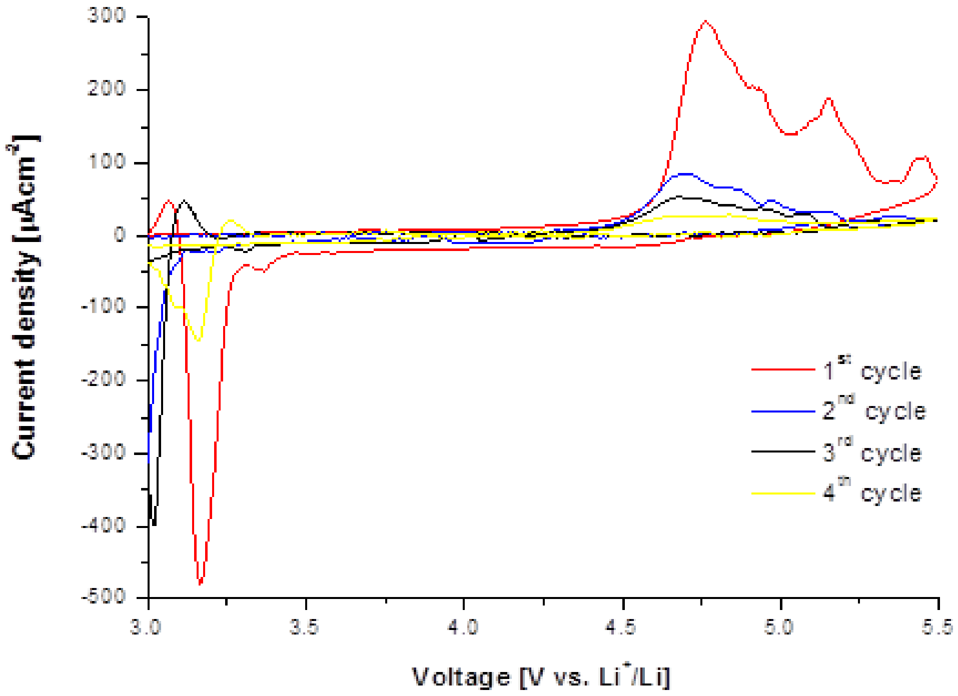
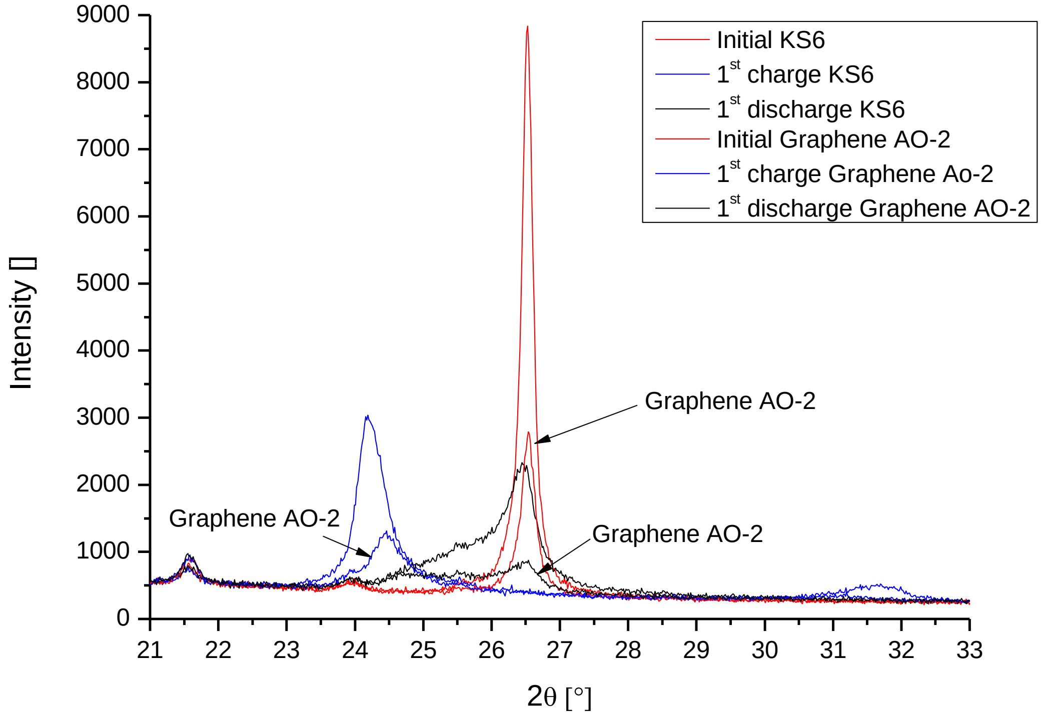
Cyclic voltammetry, KS6 and AO-2



Reduction of current upon multiple cycles

Shift in cathodic peak (de-intercalation peak) after cycling

1st charge/discharge



		d002 [Å]
KS6	initial	3.358
	1st charge	3.679
	1st discharge	3.365
Graphene AO-2	initial	3.357
	1st charge	3.639
	1st discharge	3.358

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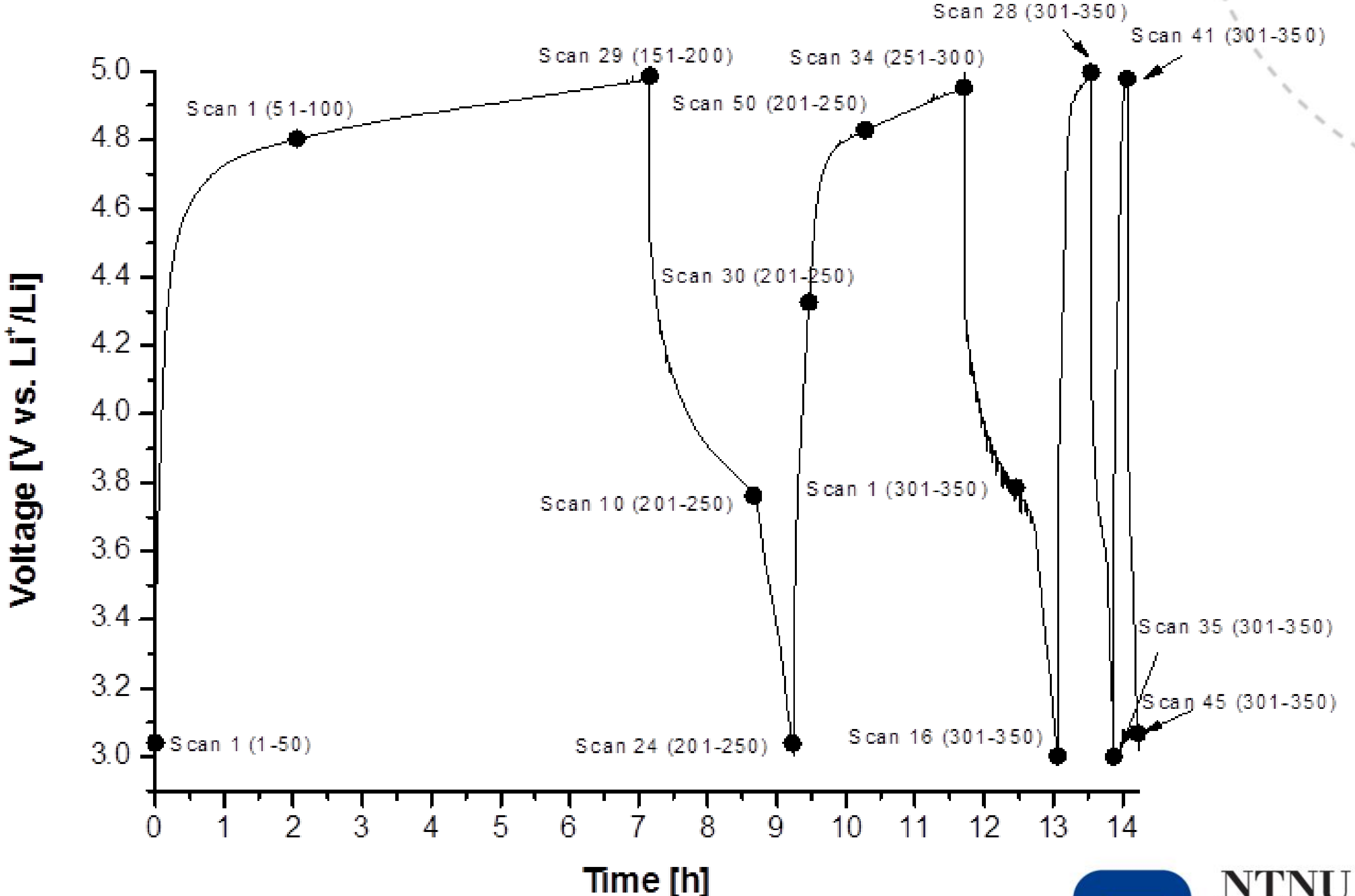
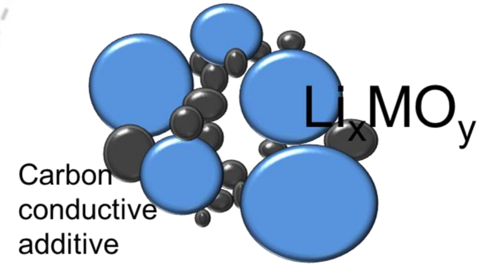
Galvanostatic cycling, AO-2 (multilayer graphene)

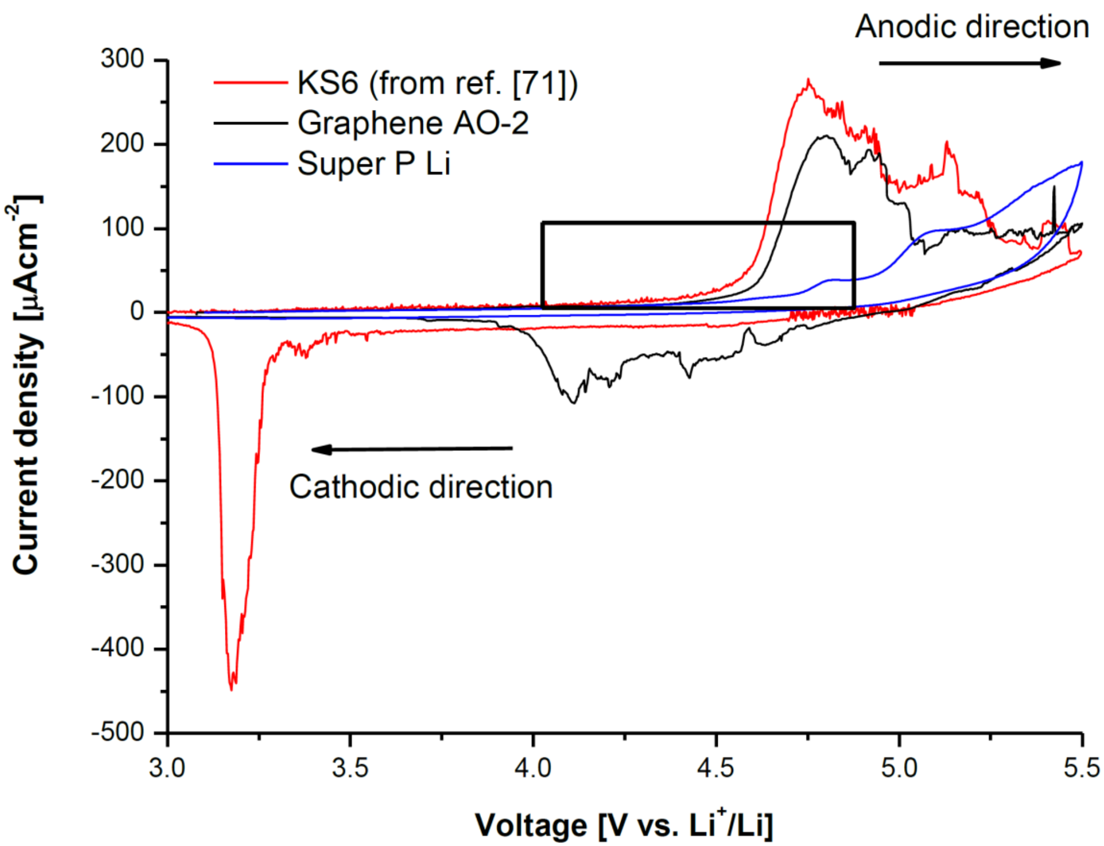


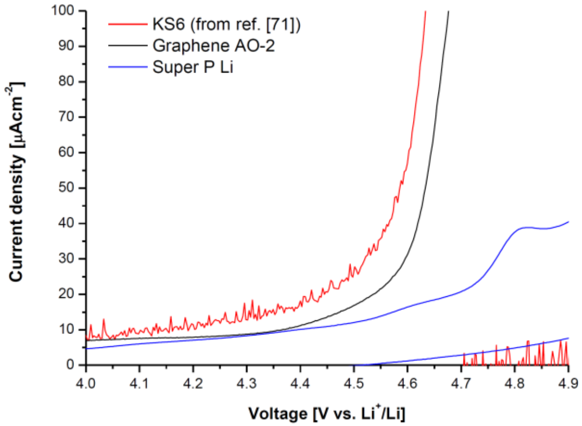
Carbon conductive additives



Cyclic voltammetry, 1M LiPF6 3:7 EMC:DMC

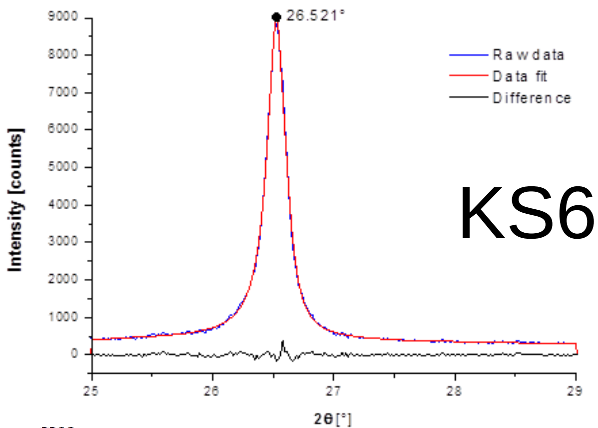
Potential range: 3.0 – 5.5 V vs. Li^+/Li, 0.1 mVs^{-1}

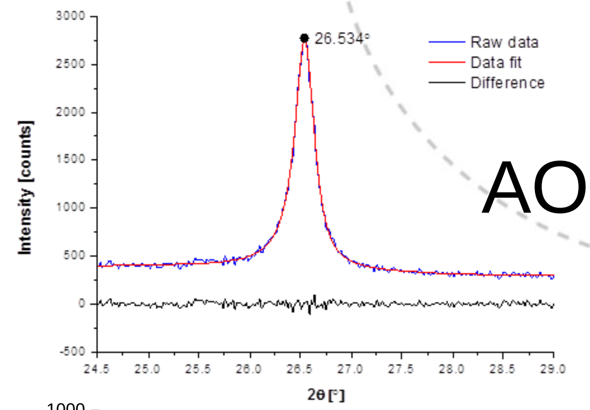




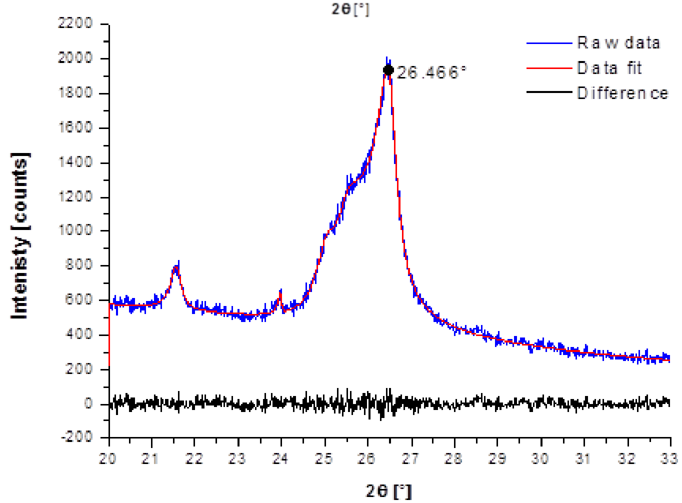
Comparison KS6 and AO-2

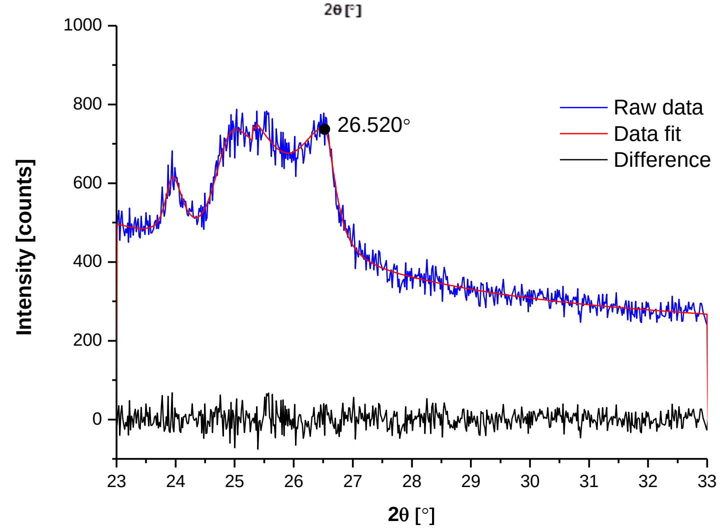
Initial





Final





Increase in d002 from initial to 4th discharge:	
KS6	0.20 %
Graphene AO-2	0.05 %

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