Develop & evaluate materials & additives that enhance thermal & overcharge abuse

Khalil Amine (PI)

Lu Zhang, John (Zhengcheng) Zhang, Zonghai Chen and Wenquan Lu

Argonne National Laboratory

May 9th, 2011

Project ID: ES035

Overview

Timeline

- Start: 10/01/2008
- End: 09/30/2014
- 35% completed

Budget

- Total project funding
  - DOE - $880K
  - Contractor - $ 0
- Funding received in FY09
  - $440K
- Funding received in FY10
  - DOE - $300K

Barriers

- Barriers addressed
  - Safety

Partners

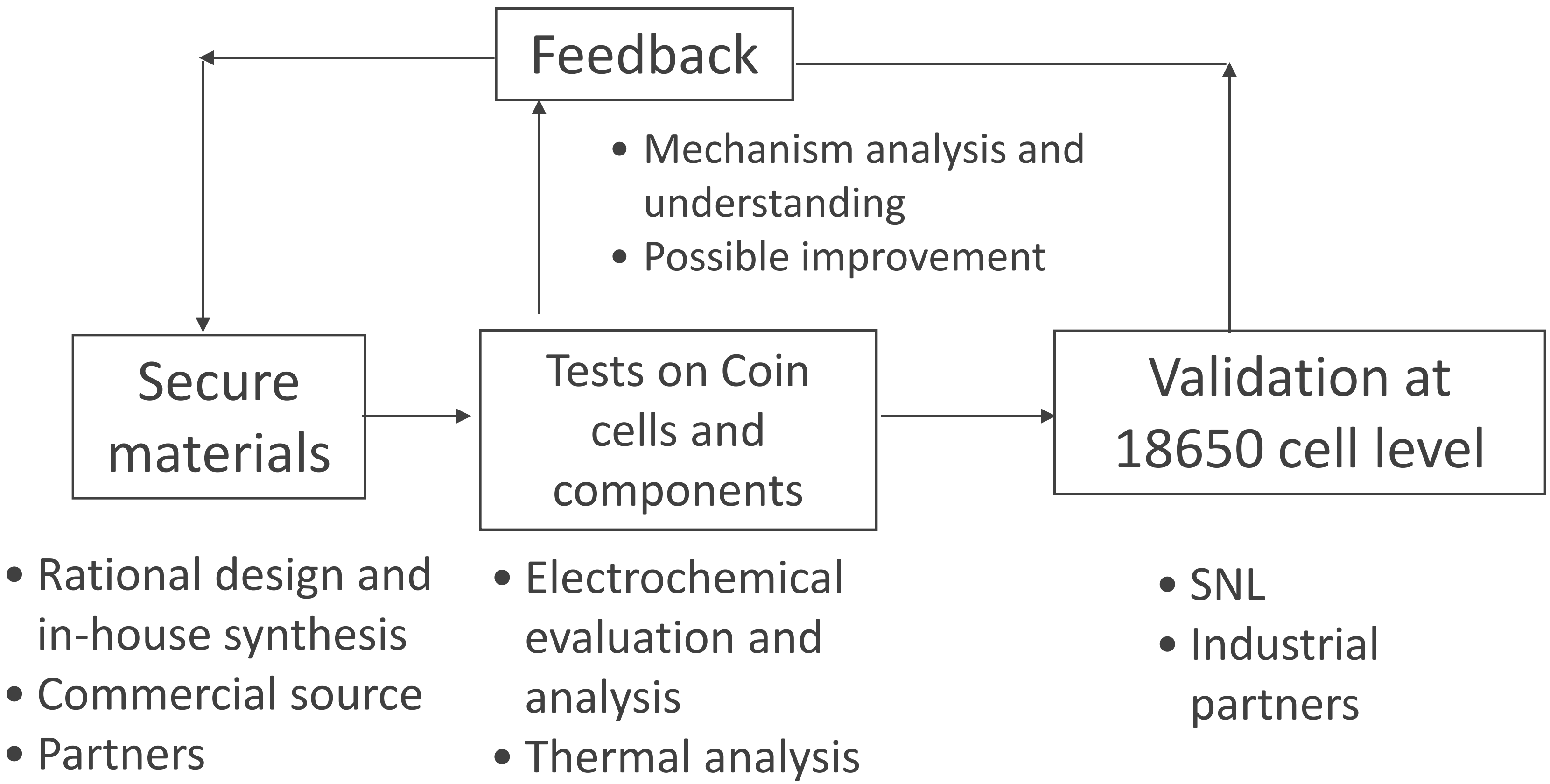
- Sandia National Laboratories
- EnerDel®
- Hitachi Chemicals
- ECPRO

Objectives of the work

- Identify the role of each cell material/components in the abuse characteristics of different cell chemistries.
- Identify and develop more stable cell materials that will lead to more inherently abuse tolerant cell chemistries.
- Secure sufficient quantities of these advanced materials (and electrodes) & supply them to SNL for validation of safety benefits in 18650 cells.

Approach

Current targets: a) redox shuttles for overcharge protection
b) additives for stable SEI on anode
c) understanding thermal behavior of lithium-ion cell system



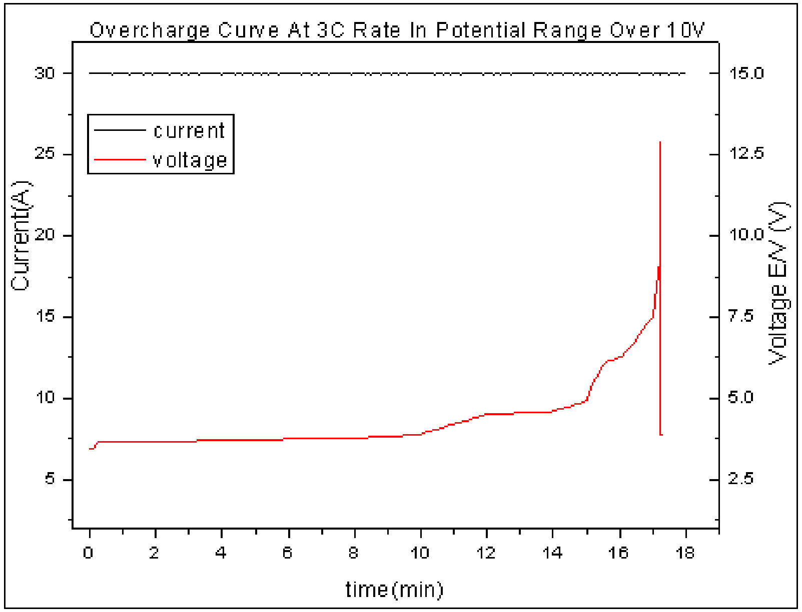
Recent Accomplishments and Progress

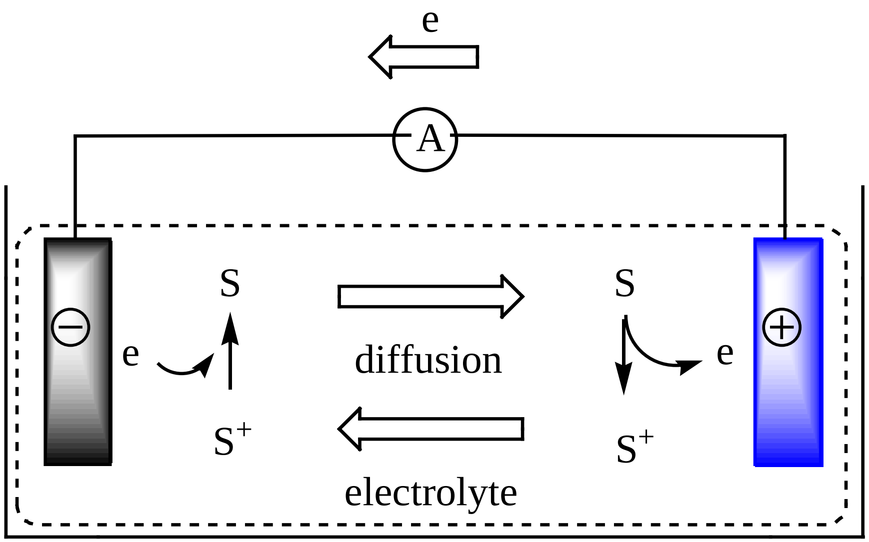
- **Electrolyte additive for stable SEI layer**
  - Novel electrolyte additives were identified to provide stable SEI on graphite and hence improve the safety of lithium ion cells.
  - Better capacity retention with the electrolyte additives.

- **Redox shuttles for overcharge protection**
  - Two new redox shuttles have been developed based on various design strategies;
  - **(1,4-Bis(2-methoxyethoxy)-2,5-di-*tert*-butyl-benzene** (ANL-2) redox shuttle shows excellent overcharge properties with little negative effect to the cell system;
  - Scale-up of this material is ongoing and kilogram scale up has been achieved with satisfactory electrochemical reproducibility.

In this presentation, only redox shuttle work will be presented, including the most promising redox shuttle that had been developed in ANL.

Safety Issues: Overcharge Abuse and redox shuttle





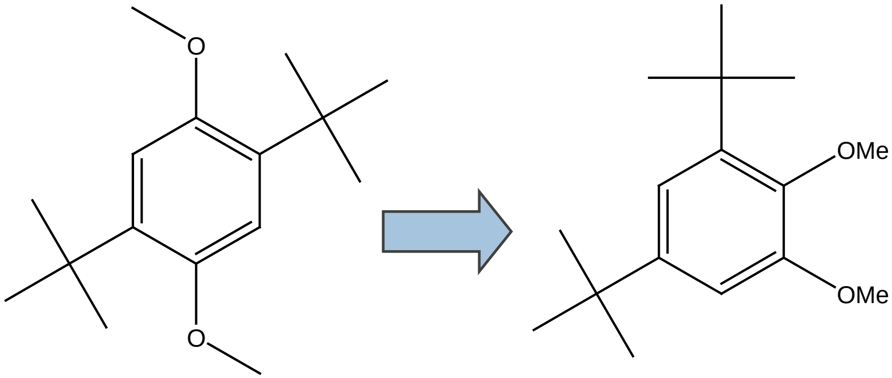
Overcharge is one common factor that could lead to serious safety issue in automotive applications.

Protections:

Electronic devices with specific chargers

Additives: redox shuttles that can be reversibly oxidized and reduced at specific potential slightly higher than the end-of-charge potential of positive electrode

2,5-ditertbutyl-1,4-dimethoxybenzene (DDB) redox shuttle and Its Limits



DDB: 3.92 V

ANL-1: ? V

One possible solution is to break down the symmetrical. chemical structural

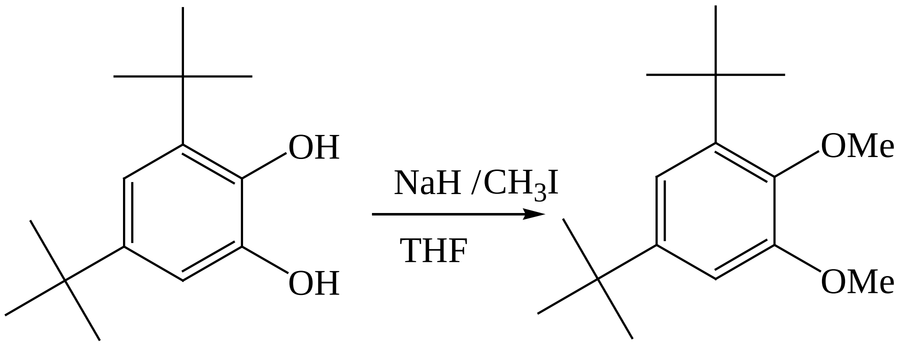
Advantage of DDB:
Suitable potential; Excellent stability;

Drawback of DDB:
Low solubility in conventional electrolyte and the concentration is dependant on lithium salt concentration (< 0. 08 M in Gen 2 electrolyte), requirement of specific formulated electrolyte (0.5 M LiBOB in PC:EC:DEC:DMC= 1:1:2:2 by volume), adding cost and complexity;

New designs:
Improve the compatibility of redox shuttles without weakening their stabilities and lowering potentials.

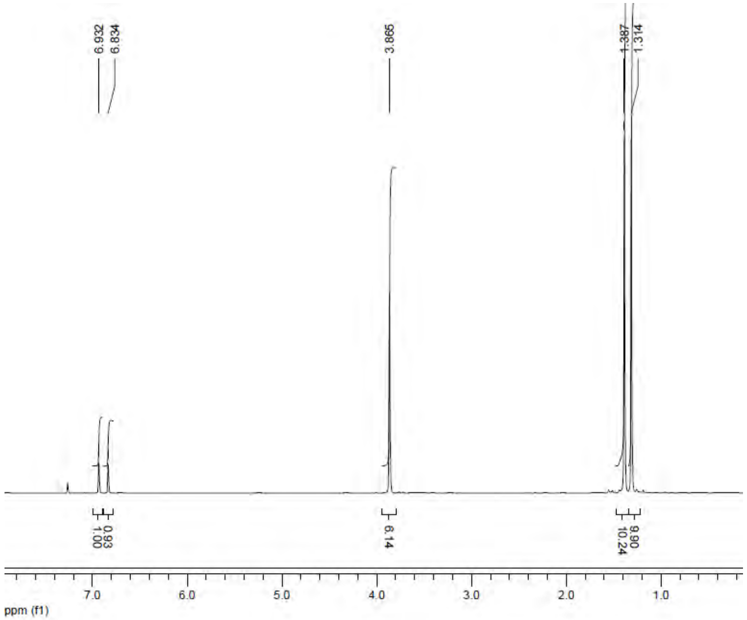
C. Buhrmester, J. Chen, J. Jiang, R.L. Wang, J.R. Dahn, J. Electrochem. Soc. 152 (2005) A2390.

Synthesis and chemical characterization of Catechol-like Version of DDB --- ANL-1

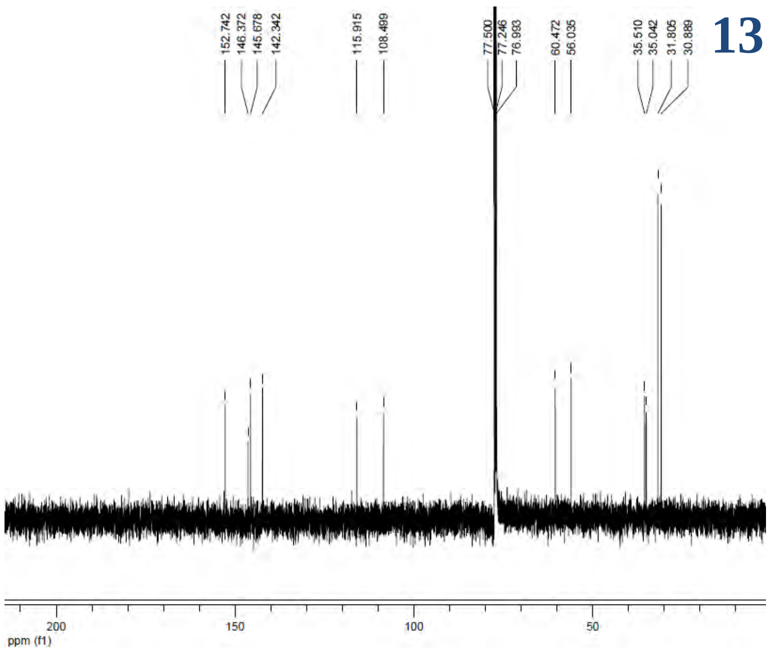


ANL-1, yield 71 %

1H NMR

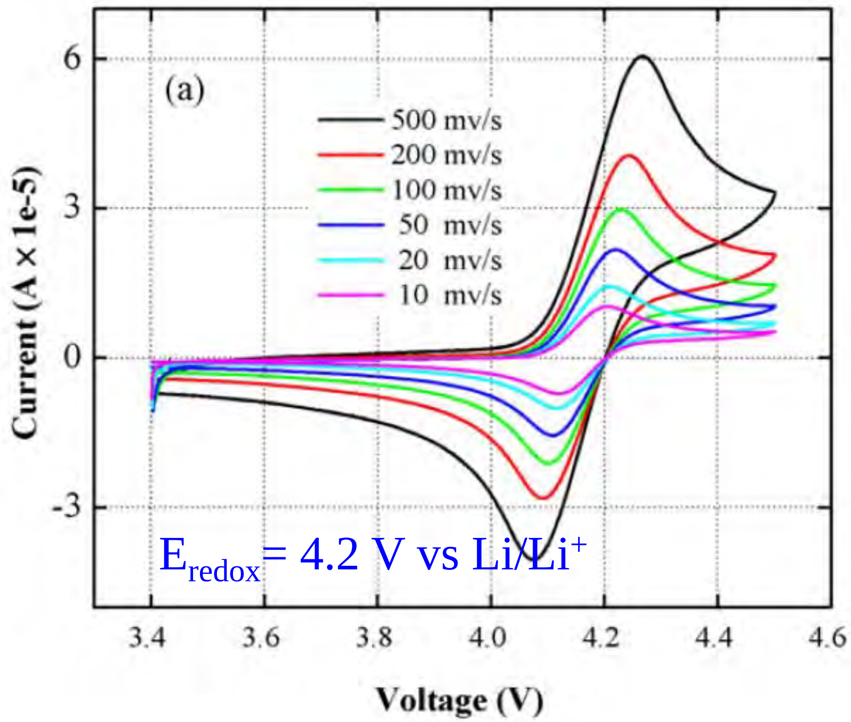


13 C NMR

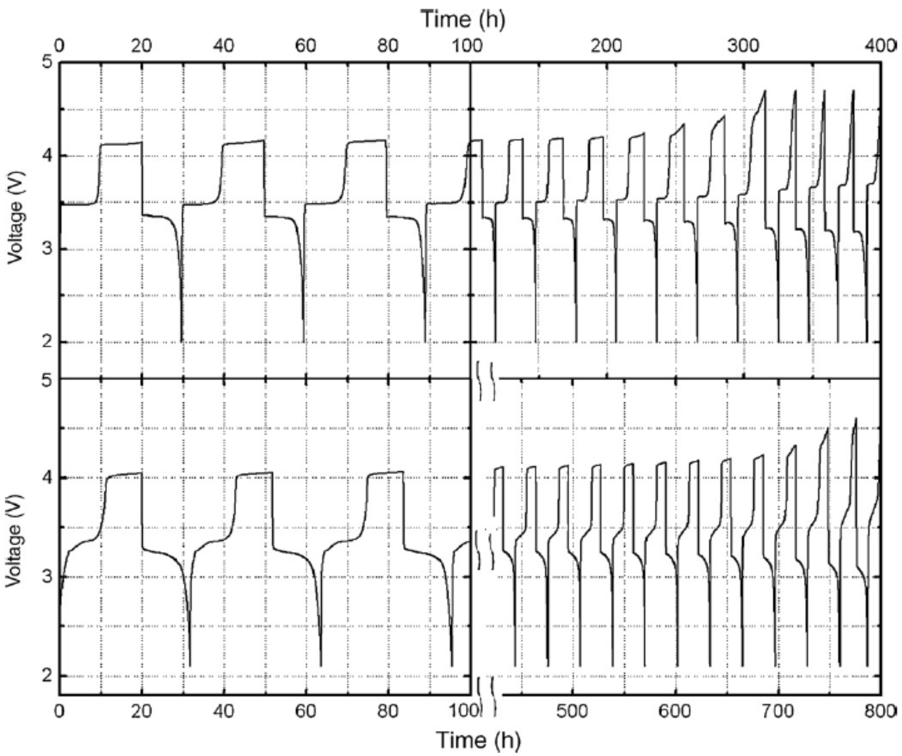


Both 1H and 13 C NMR confirm the structure of this shuttle additive

Electrochemical evaluation of ANL-1



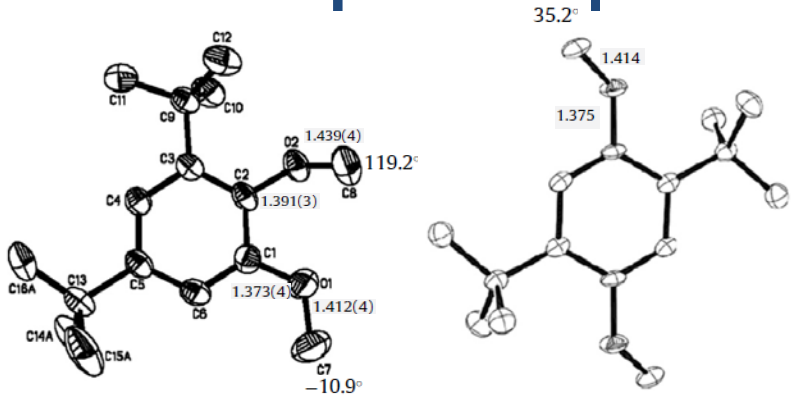
Cyclic voltammograms of ANL-1 (10 mM) in 1.2 M $LiPF_6$ in EC/EMC (3:7 by weight) 100mV/s.



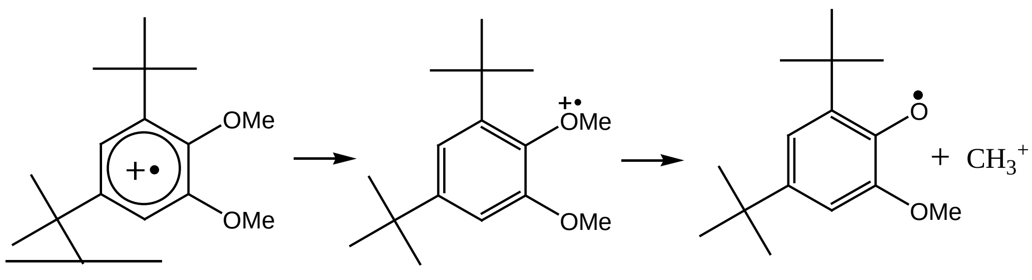
Voltage and capacity retention profiles of Li/$LiFePO_4$ cell containing 0.1 M ANL-1 in 1.2M LiPF6 in EC/EMC (3:7 by weight) during the course of 0-2300 h. Charging rate is C/10 and overcharge rate is 100%. More soluble but less stable than DDB.

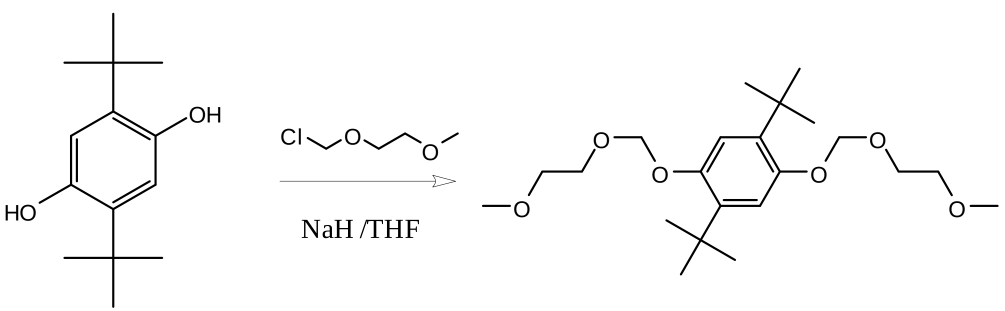
Cell based on ANL-1 shuttle additive shows limited overcharge stability

Possible decomposition path ways of ANL-1 and new strategy



ANL-1 DDB





For DDB, the methoxy bond is stronger than the one in ANL-1

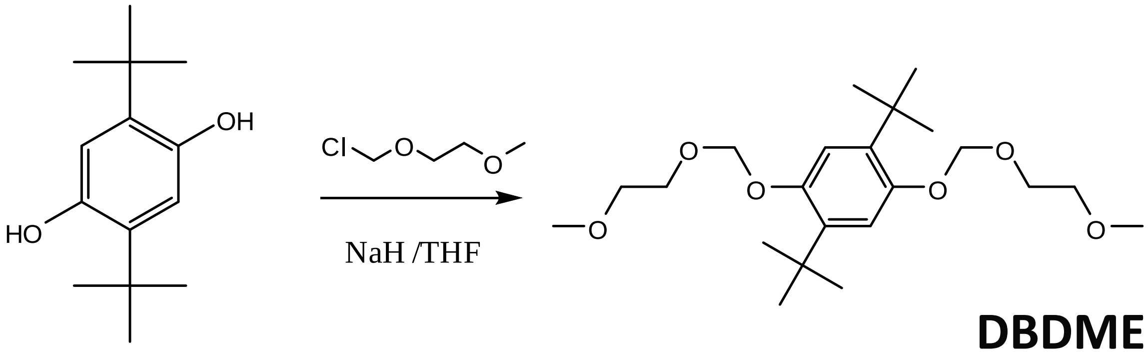
Decomposition path ways for radical cation:
polymerization on the benzene ring or the cleavage of the alkoxy bonds

Breaking down the symmetry of the chemical structure increased the solubility
but decreased the electrochemical stability.

Polyether groups substitution into the novel redox shuttles to improve the solubility;

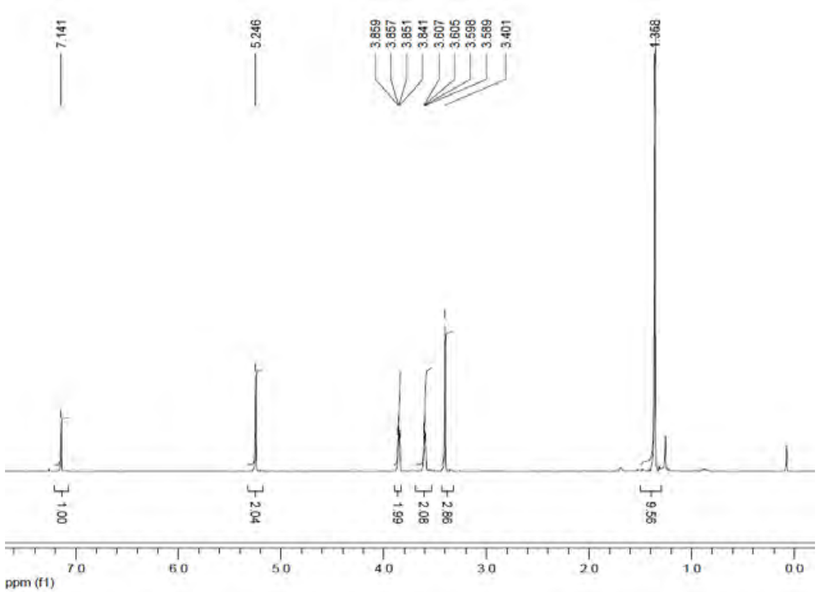
Advantages: keep the symmetric structure and thus keep the electrochemical properties

Synthesis and chemical characterization of DBDMEMB

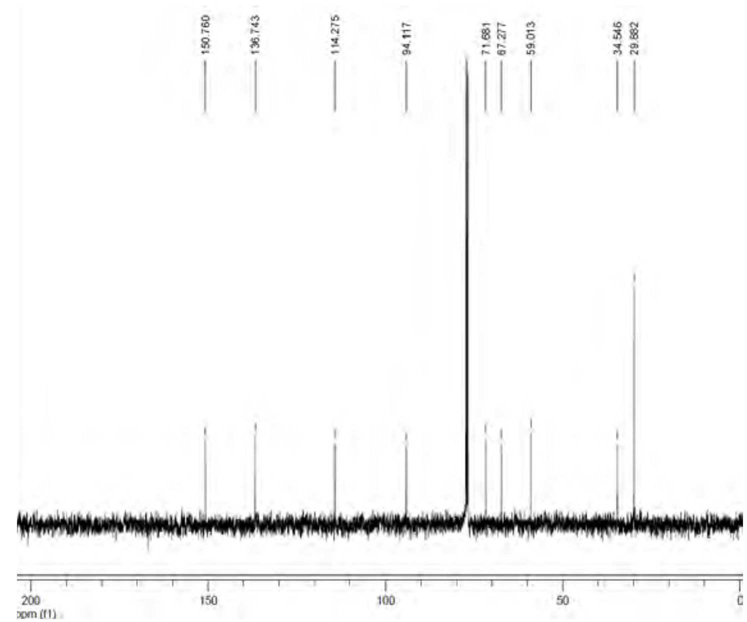


DBDMEMB, yield 75 %

1H NMR

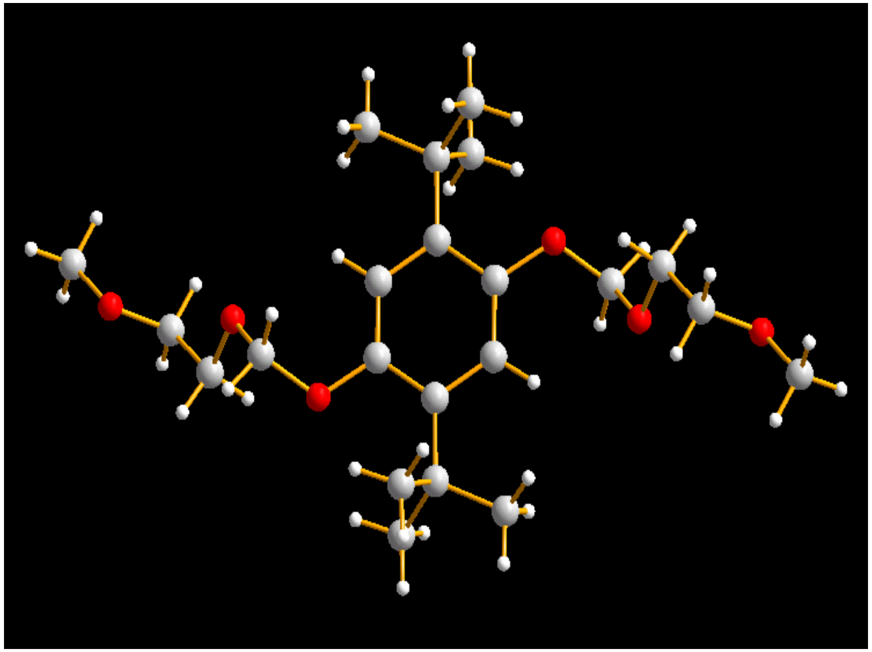


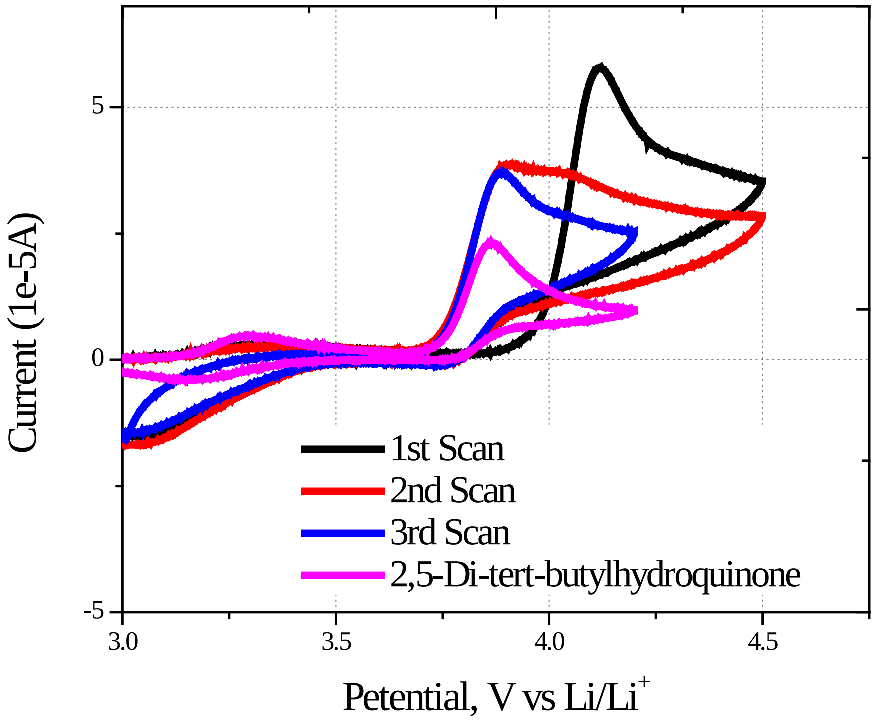
13 C NMR



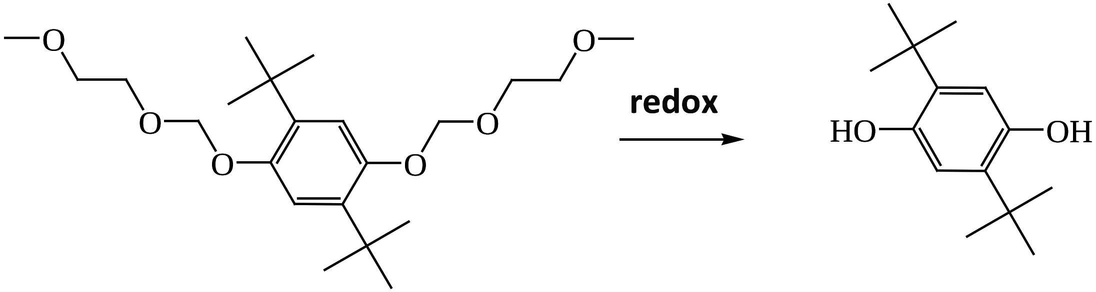
Both 1H and 13 C NMR confirm the structure of this shuttle additive

Single crystal and CV test of DBDMEMB



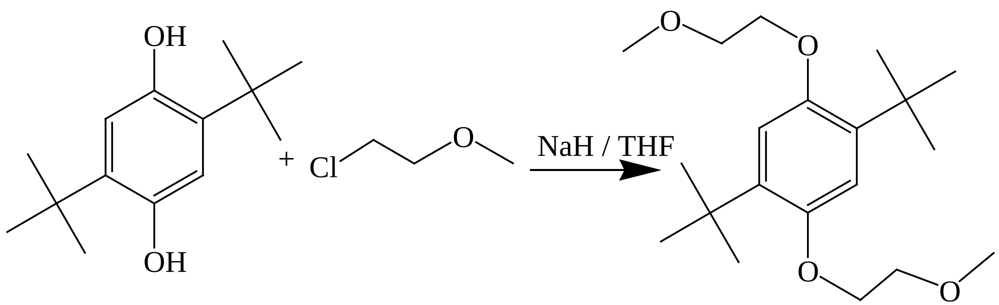


Cyclic voltammograms of DBDMEMB (10 mM) in 1.2 M $LiPF_6$ in EC/EMC (3:7 by weight) 100mV/s



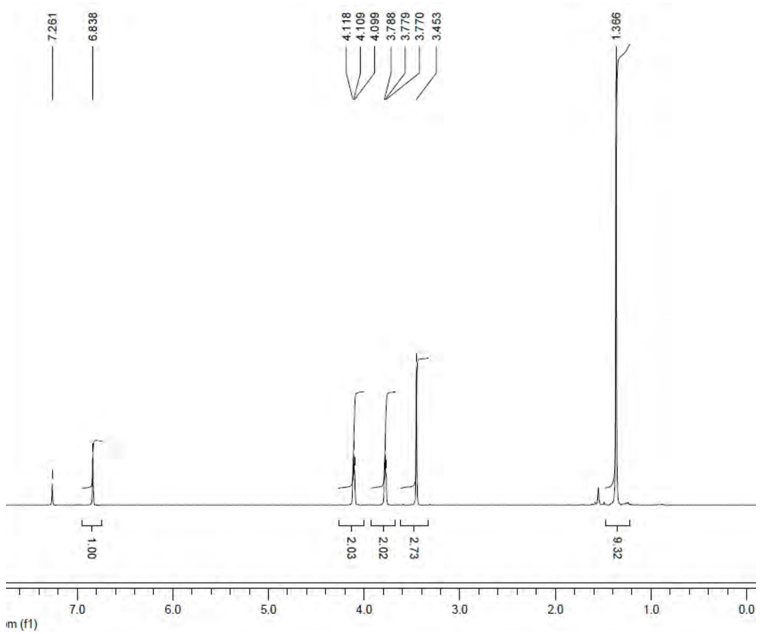
The O-C-O linkage is not electrochemically stable

Improve the electrochemical stability of the linkage:
ANL-2 (1,4-Bis(2-methoxyethoxy)-2,5-di-*tert*-butyl-benzene)

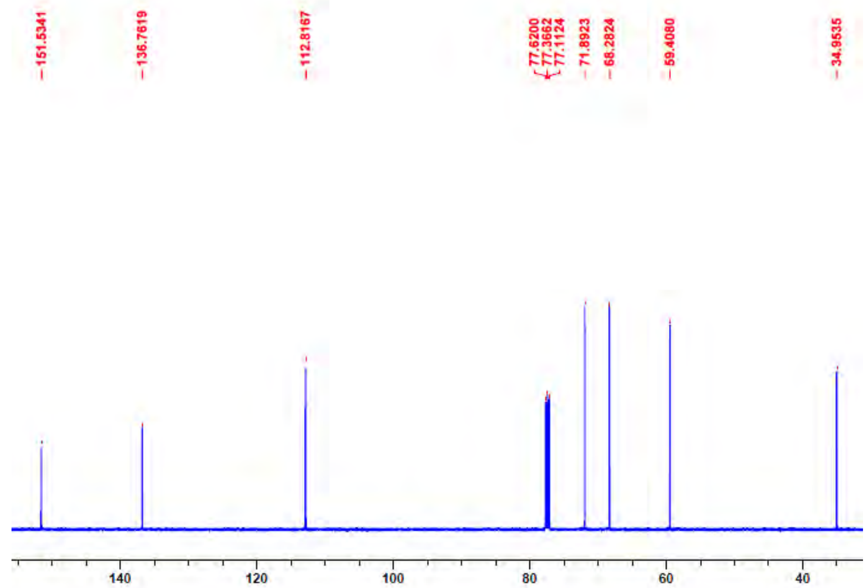


ANL-2, yield 70 %

1H NMR

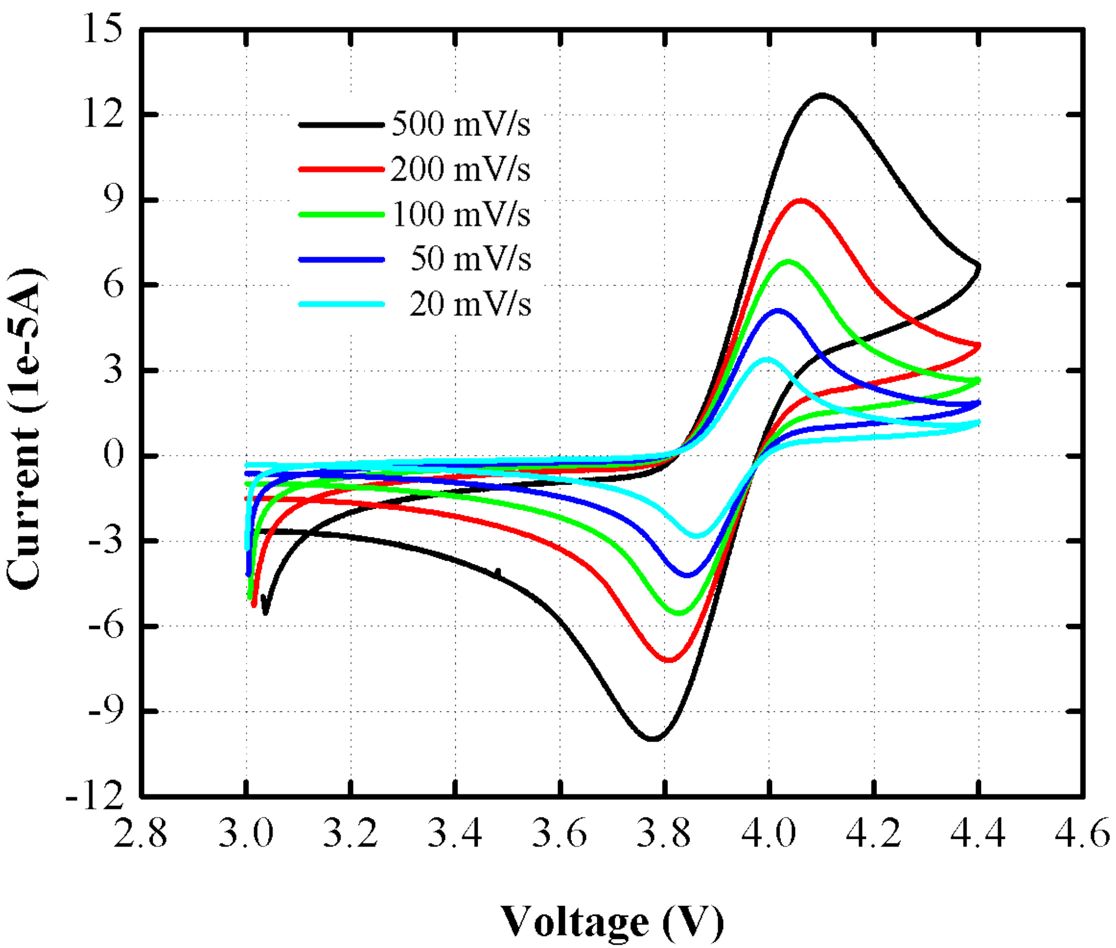


13 C NMR



Both 1H and 13 C NMR confirm the structure of this shuttle additive

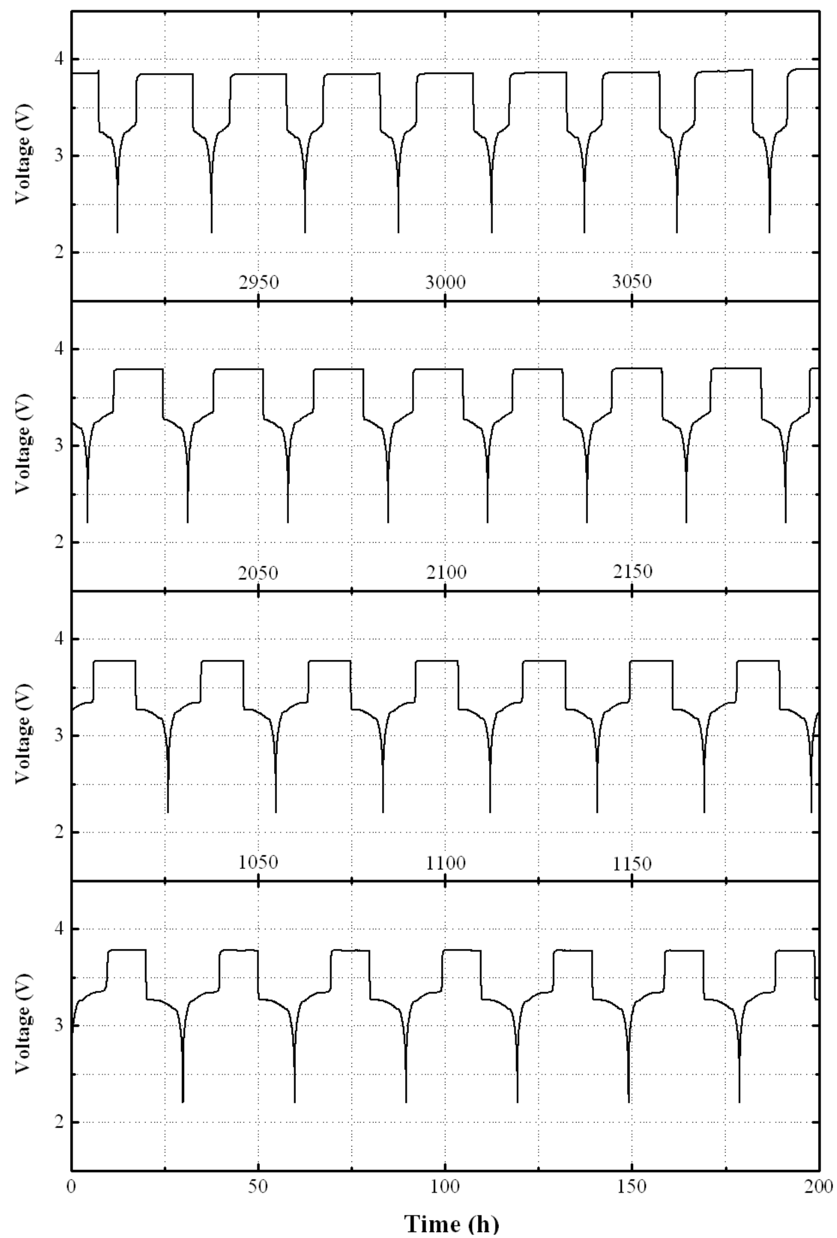
Cyclic voltammetry of ANL-2

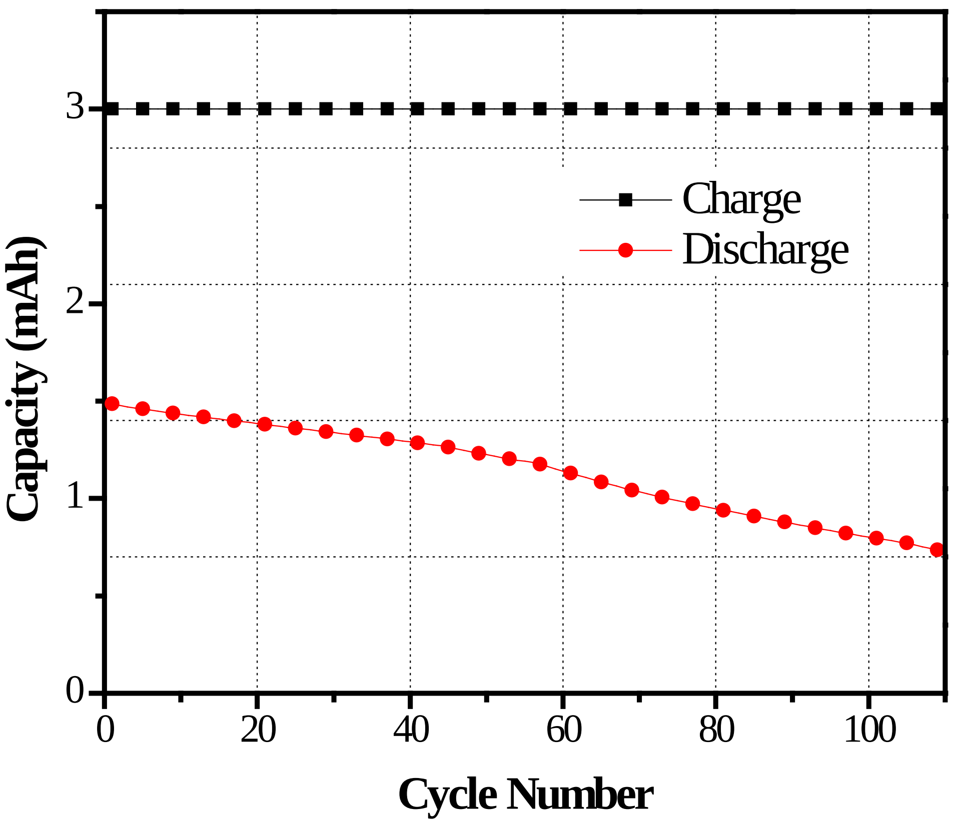


Increase the carbon number between the two oxygen atoms significantly improve the electrochemical stability, as a result ANL-2 exhibits perfectly reversible redox peaks at 3.9 V vs Li/Li^+

Cyclic voltammograms of ANL-2 (10 mM) in 1.2 M $LiPF_6$ in EC/EMC (3:7 by weight) 100mV/s.

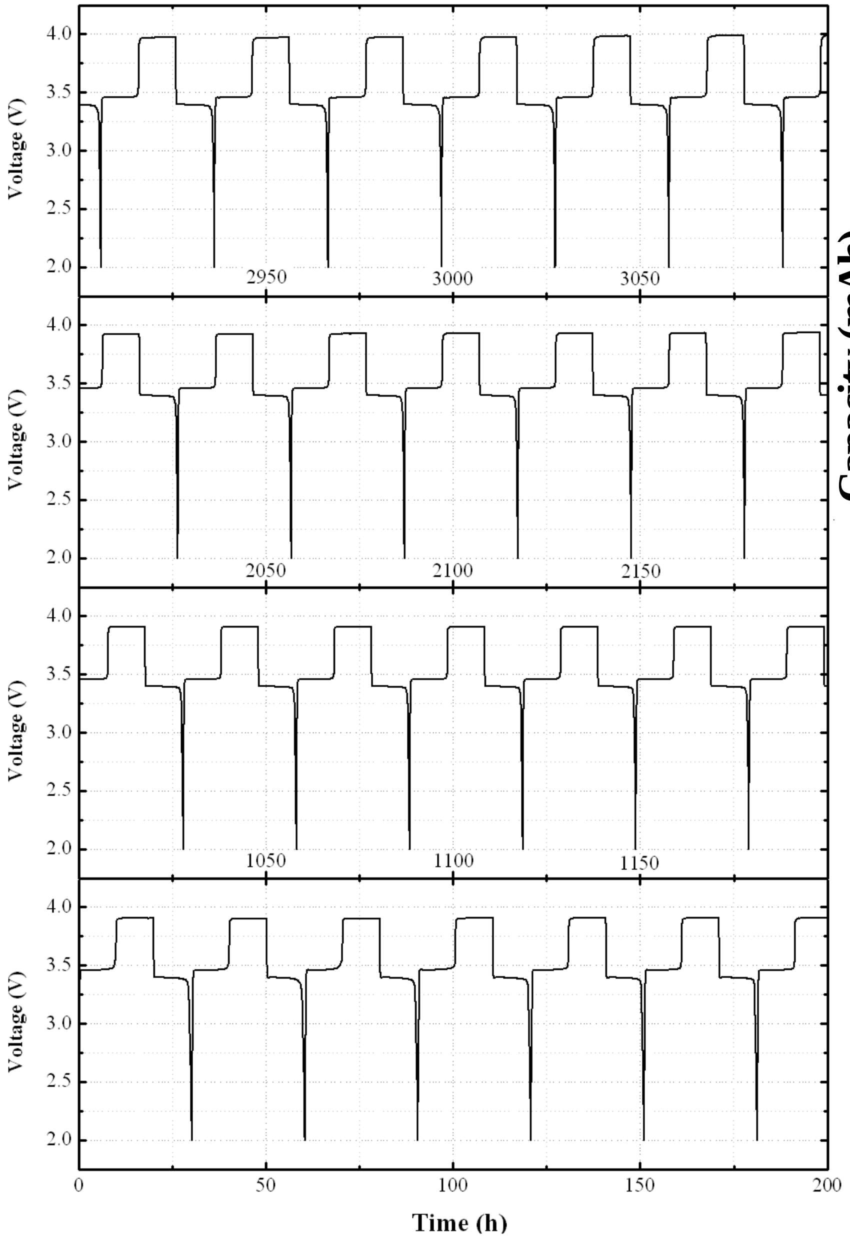
Cycling tests of ANL-2 --- MCMB/$LiFePO_4$

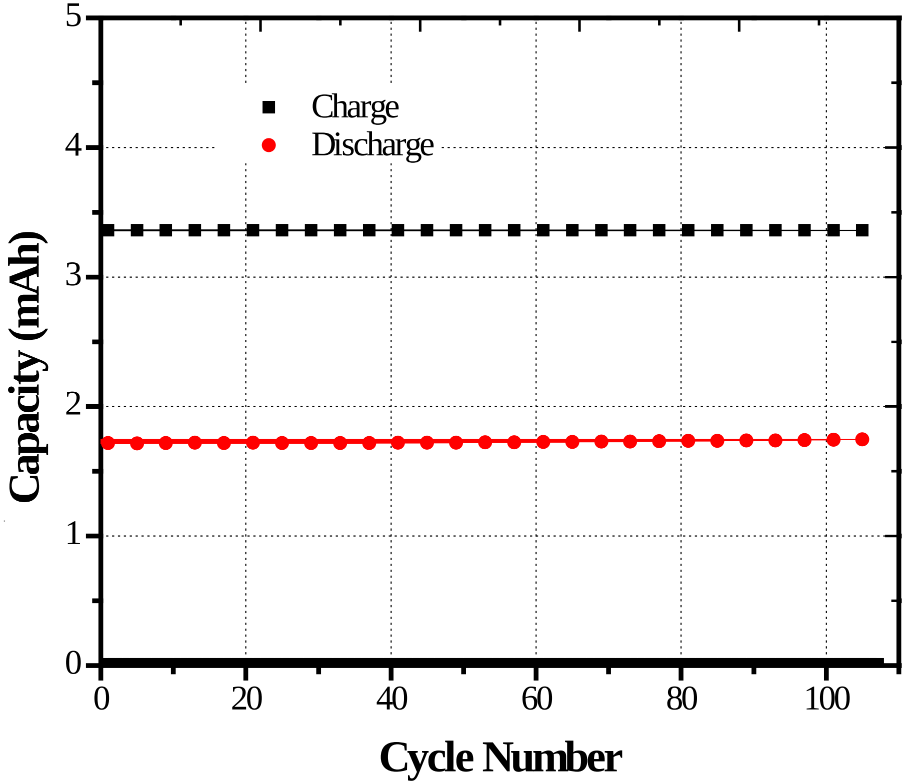




Voltage and capacity retention profiles of MCMB/LiFePO4 cell containing 0.1 M ANL-2 in 1.2M $LiPF_6$ in EC/EMC (3:7 by weight) during the course of 0-2300 h. Charging rate is C/10 and overcharge rate is 100%.

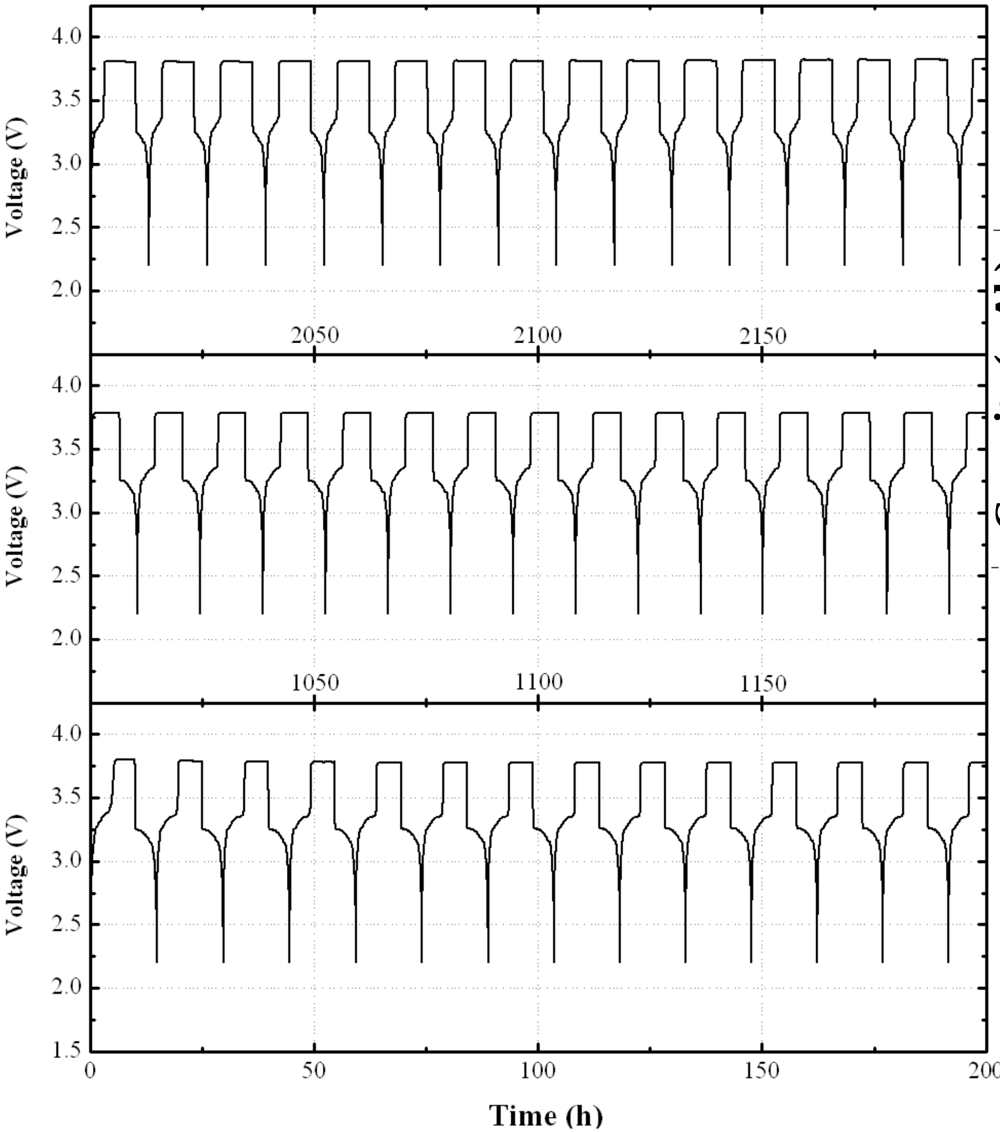
Cycling tests of ANL-2 --- Li/$LiFePO_4$

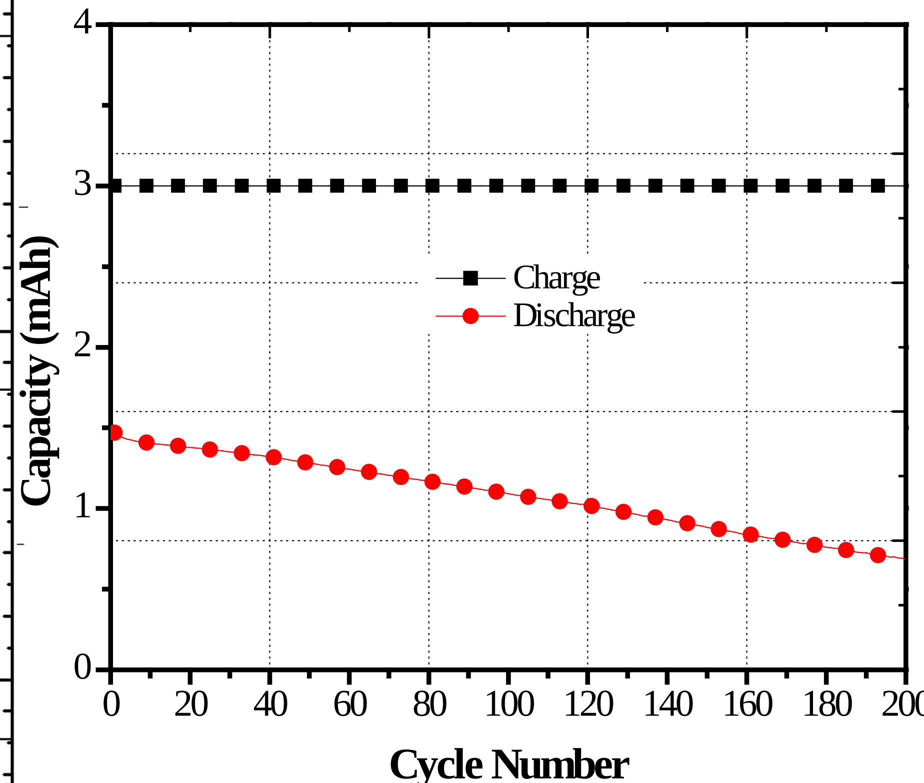




Voltage and capacity retention profiles of Li/$LiFePO_4$ cell containing 0.1 M ANL-2 in 1.2M $LiPF_6$ in EC/EMC (3:7 by weight) during the course of 0-2300 h. Charging rate is C/10 and overcharge rate is 100%.

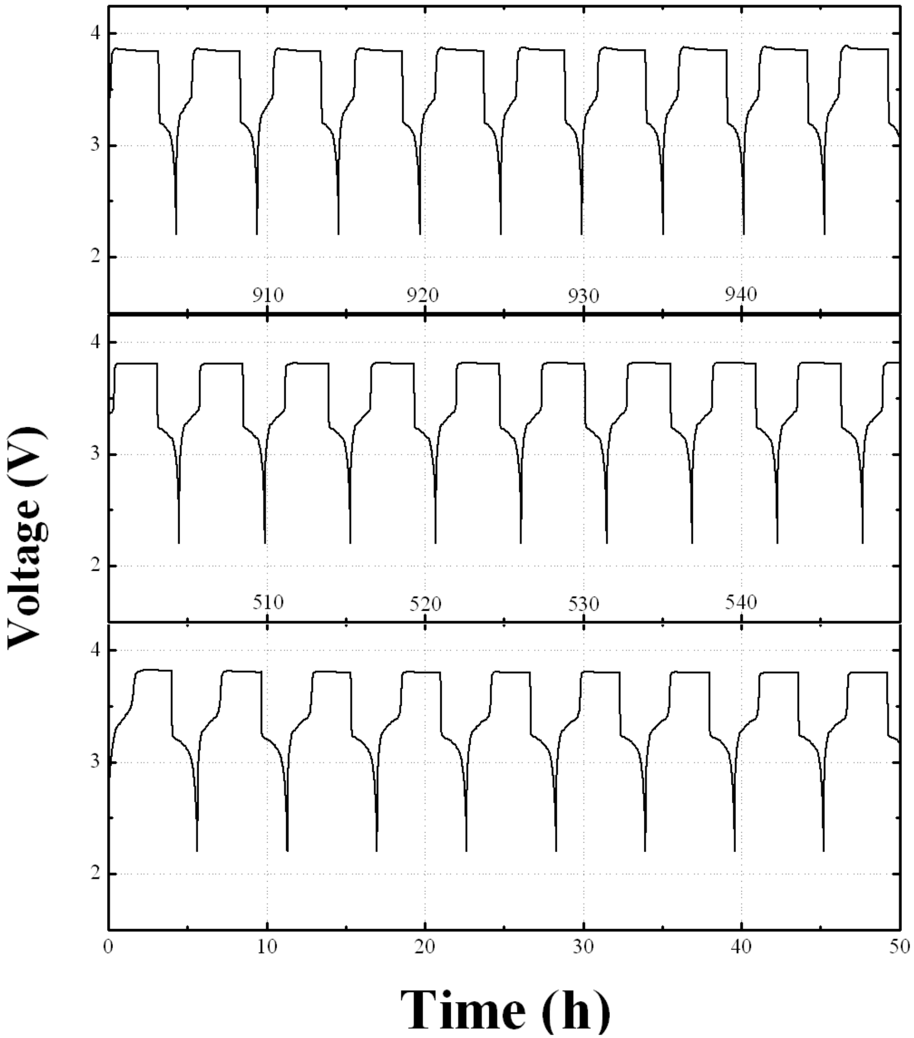
Fast cycling tests of ANL-2 --- MCMB/$LiFePO_4$ (C/5)

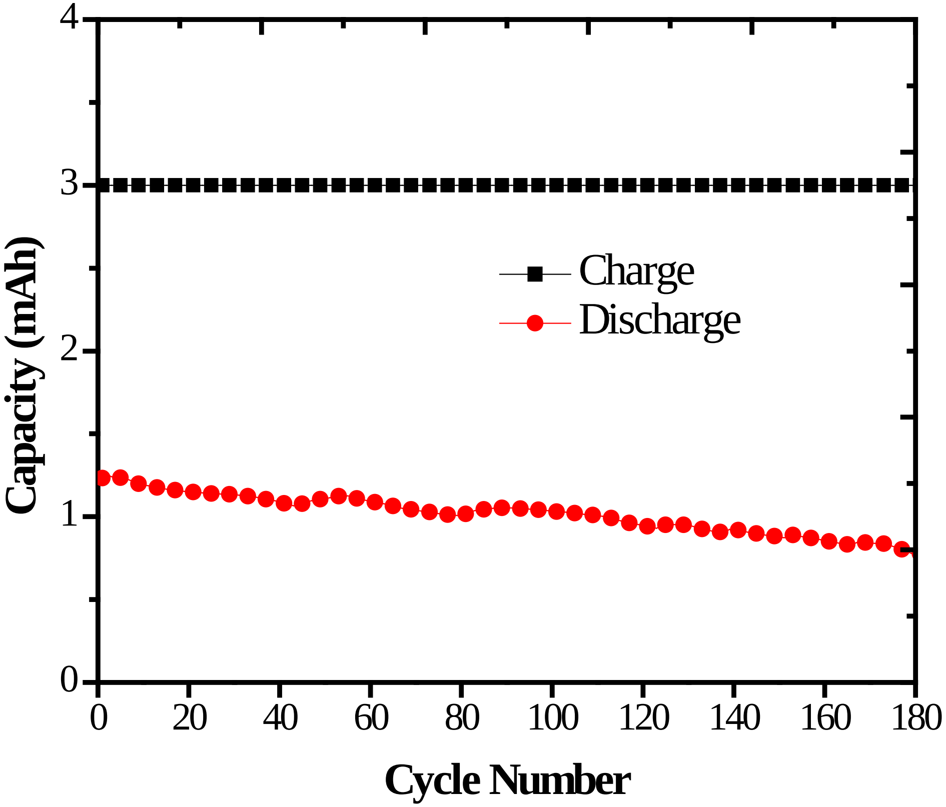




Voltage and capacity retention profiles of MCMB/$LiFePO_4$ cell containing 0.2 M ANL-2 in 1.2M $LiPF_6$ in EC/EMC (3:7 by weight) during the course of 0-1100 h. Charging rate is C/5 and overcharge rate is 100%.

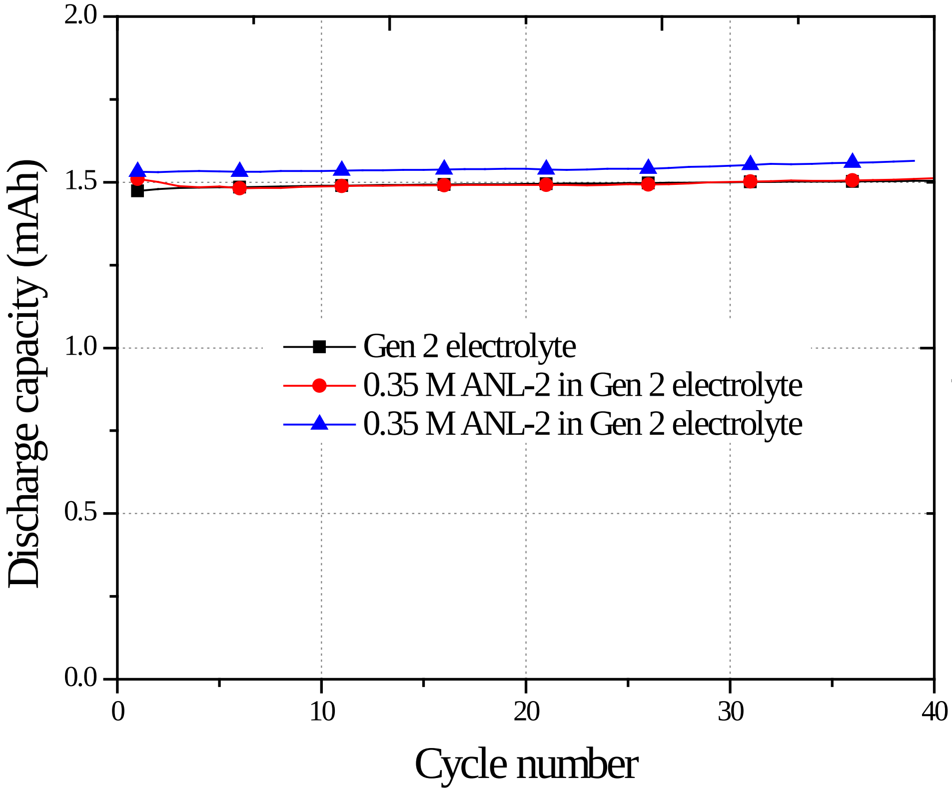
Fast cycling tests of ANL-2 --- MCMB/$LiFePO_4$ (C/2)

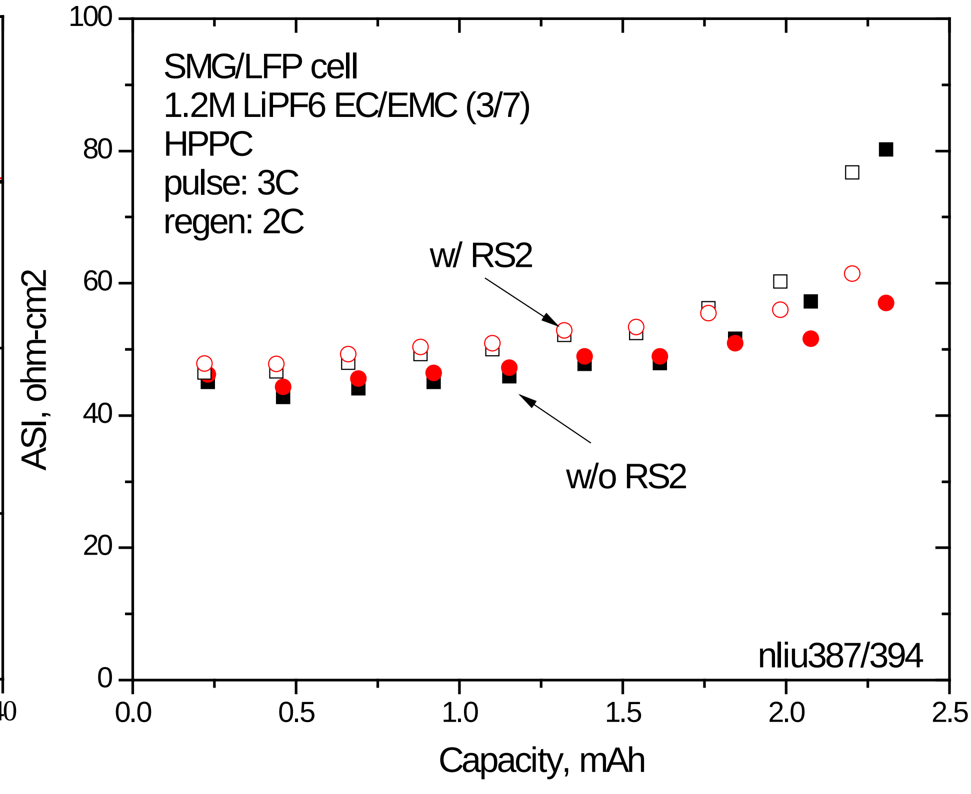




Voltage and capacity retention profiles of MCMB/$LiFePO_4$ cell containing 0.4 M ANL-2 in 1.2M $LiPF_6$ in EC/EMC (3:7 by weight) during the course of 0-1000 h. Charging rate is C/2 and overcharge rate is 100%.

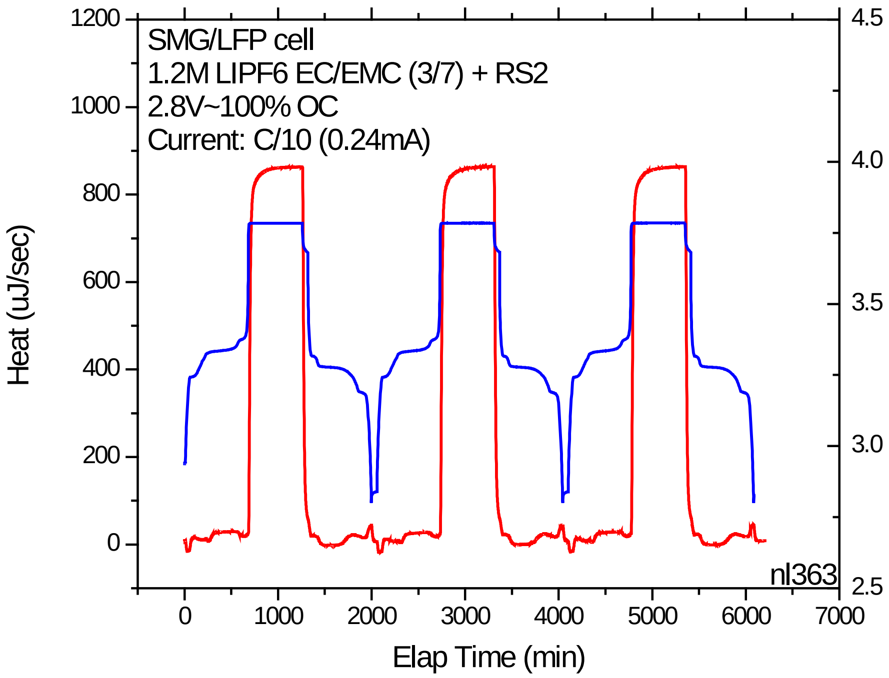
Normal cyclability and HPPC comparison with and without ANL-2

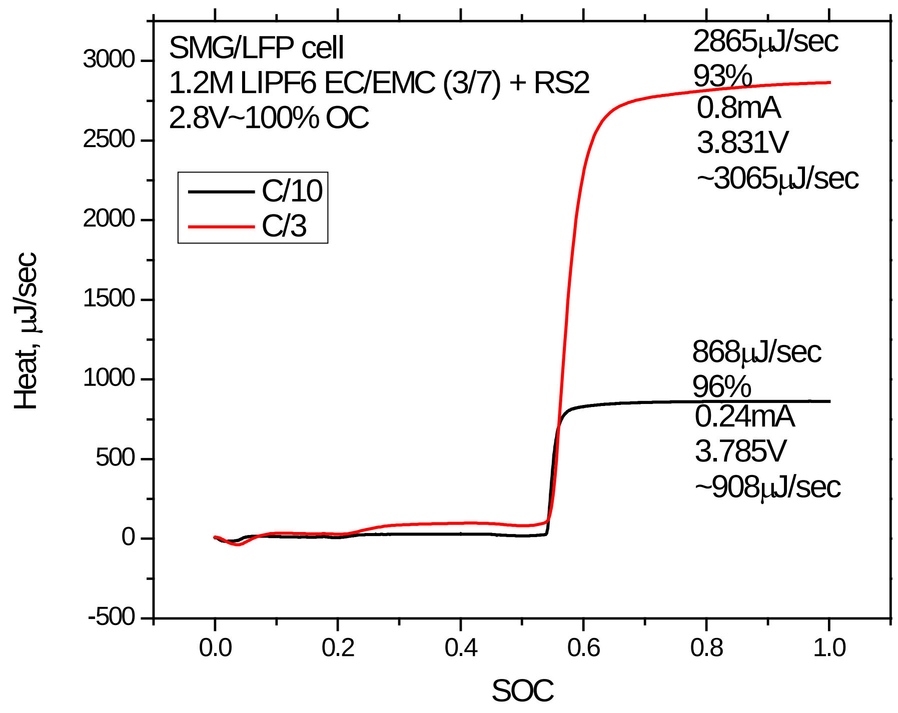




Capacity retention and HPPC profiles of MCMB/$LiFePO_4$ cells containing none or 0.35 M ANL-2 in 1.2M $LiPF_6$ in EC/EMC (3:7 by weight). Charging rate is C/3 and cut off voltage is 2.3 ~3.6 V. Pulse: 3C and regen :2C.

Heat flow during overcharge process





Heat generation was observed during overcharge process, and the estimate of electricity-to-heat conversion rate is over 93 percent, indicating the high efficiency of ANL-2 redox shuttle. Temperature control may be needed when ANL-2 is used in a battery system.

Collaborations

- **Partners**

  -Sandia National Laboratory: cell level verification of safety improvement using components identified at ANL.

  -EnerDel: overcharge abuse and nail penetration test of 18650 cells.

  -Hitachi Chemical: collaboration on the safety characteristics of carbon anodes and 18650 cell fabrication.

  -ECPRO: collaboration on 18650 cell fabrication using NCA based 18650 cells (Coated & non–coated NCA)

- **Technology transfer:**

  Collaboration with EnerDel, A123®, Emprex® & JCI® to validate ANL's redox shuttles.

  - overcharge protection

  - cell capacity balancing

Proposed Future work

- Systemically characterize ANL's new redox shuttles, and continue exploring new shuttle structures.

- Continue exploring electrolyte additives for improving thermal stability of batteries.

- Quantify the impact of $LiPF_6$ on the thermal stability of delithiated cathode and explore the possible safety mitigation techniques.

- Investigate the role of none flammable electrolyte & ionic liquid on the safety of lithium battery

- Investigate the role of electrode and particle coating on the safety of lithium batteries

Summary

- Novel redox shuttles have been developed using various organic synthesis strategy:
  - (a) ANL-1 shows improved solubility and weakened stability;
  - (b) Incorporation of ether chain group helped the solubility of redox shuttle, but dramatically affect the electrochemical stability;
  - (c) ANL-2 was developed based on an improved design with ether chain to achieve high solubility . This novel redox shuttle showed excellent electrochemical stability during overcharge test;
  - (d) Normal cycle tests confirm that addition of ANL-2 redox shuttle to lithium-ion cells does not negatively affect the cell performance;
  - (e) Heat generation was observed during overcharge process, and the estimate of electricity-to-heat conversion rate is over 93 percent.