High Voltage Electrolytes for Li-ion Batteries

Kang Xu, Jan L. Allen, T. Richard Jow
U.S. Army Research Laboratory
19 May 2009

Project ID: **esp_20_jow**

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Start: Sep 2008
- End: Sep 2011
- 20 % complete

Budget

- Total project funding
  - DOE $600K
- Funding received in FY08
  - $200K (DOE)
- Funding for FY09 and FY10
  - $400K (DOE)

Barriers

- State-of-the-art $LiPF_6$/ Carbonate Solvents electrolytes decompose at voltages of about 4.2 V.
- Electrolytes containing sulfone based solvents are stable anodically up to 5.8 V but lack of SEI formation capability at the anode.
- Sulfone based solvents are viscous.

Partners

- Argonne National Laboratory
- Saft Batteries
- University of Maryland

Objectives

- **Develop high voltage electrolytes that enable the operation of Li-ion batteries with high voltage cathode at higher voltages for enhanced energy density for plug-in hybrid electric vehicles**

Milestones

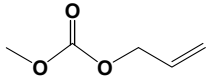
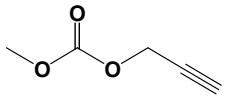
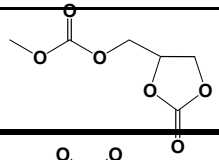
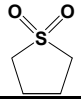
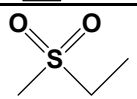
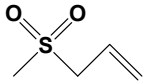
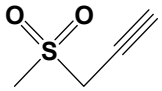
- **Sep 2009: Synthesize sulfone based solvents with and without unsaturated bonds and evaluate their electrochemical properties**
- **Sep 2010: Test, evaluate and formulate electrolytes containing the synthesized sulfone based solvents**
- **Sep 2011: Select promising formulations for further performance evaluation and demonstration in cells of 18650 or larger sizes**

Approach

- Explore asymmetric sulfone with different functional groups for lower melting points and low viscosity
- Explore sulfone solvents with functional group containing un-saturated bonds as additives
- Explore non-sulfone based additives in combination with sulfone solvents for improved performance

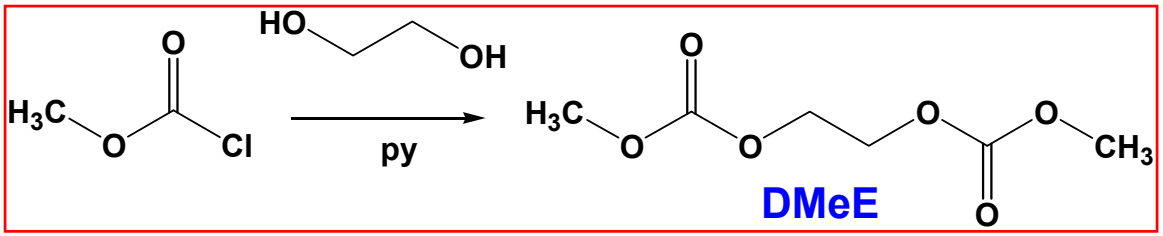
Technical Accomplishments

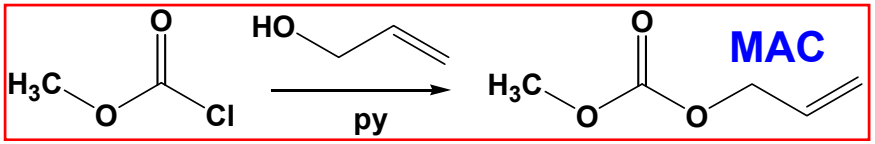
- **Synthesized sulfone solvents with new structures are listed below.**

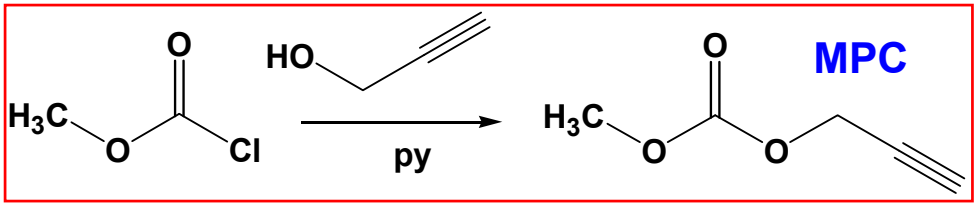
Solvent	Structure	Melting Point (oC)	Boiling Point (oC)	LUMO* (eV)	HOMO* (eV)	Reduction Potential (vs. Li+/Li)	Oxidation Potential (vs. Li+/Li)
MAC		<-50	130	1.15/0.97	10.43/10.30	0.83	5.56
MPC			150	1.11/0.94	10.98/10.75	0.83	6.20
LLC		80		0.87/0.72	12.95/12.89	1.33±0.11	7.85±0.04
SL		35		0.87/0.65	11.55/11.58	1.34±0.02	6.23±0.03
EMS		36.5		0.90/0.72	11.87/11.66	1.26±0.02	6.32±0.03
MAS				0.91/0.66	10.73/10.76	1.31	5.65
MPS				0.99/0.73	11.25/10.99	1.24	6.21

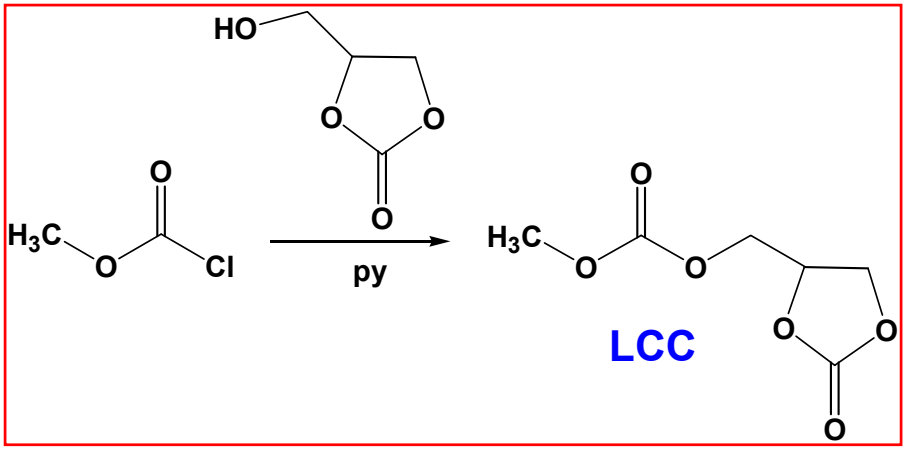
*** LUMO and HOMO computational work performed by Prof. J. Klauda at UMD**

Synthetic Routes: Carbonates

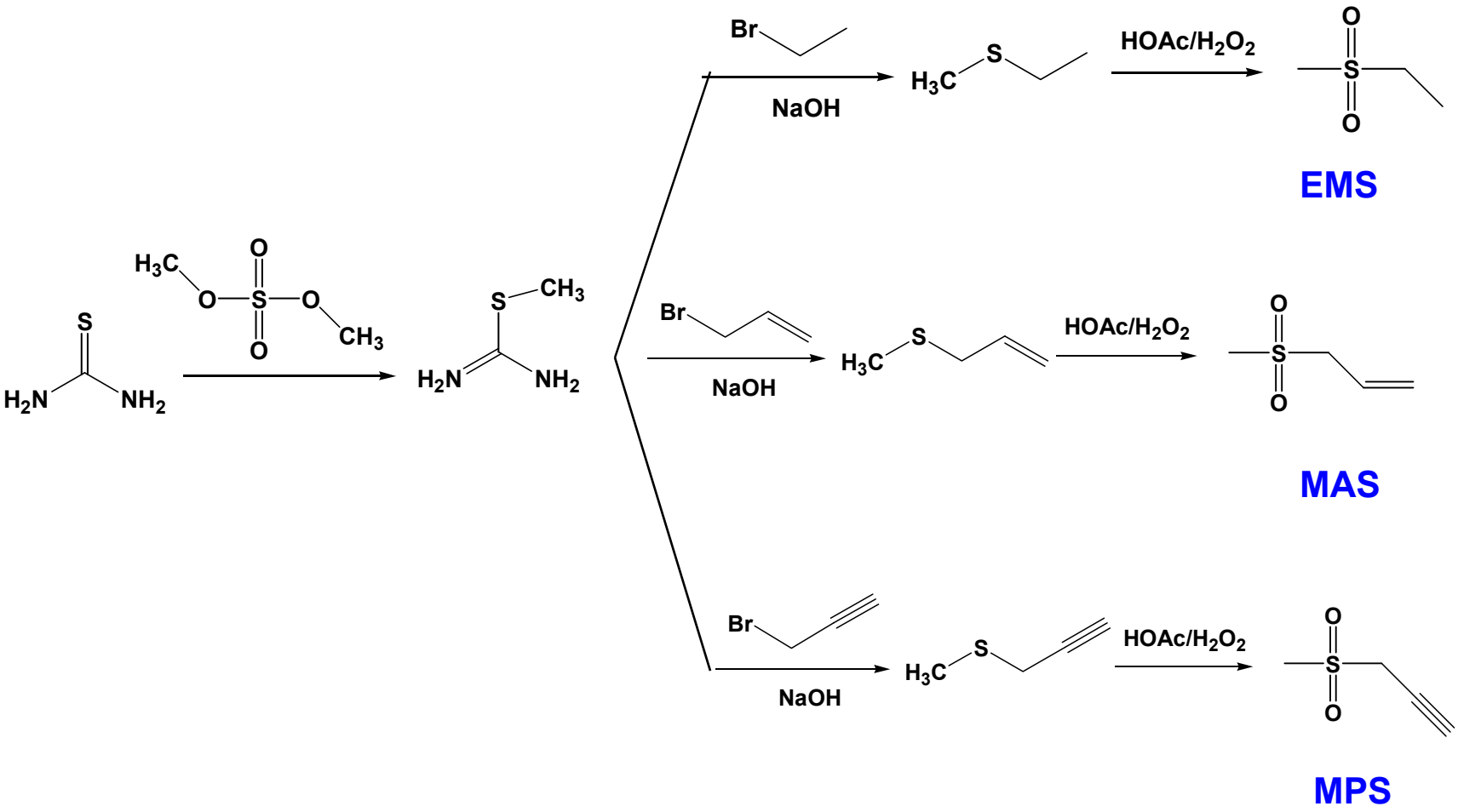






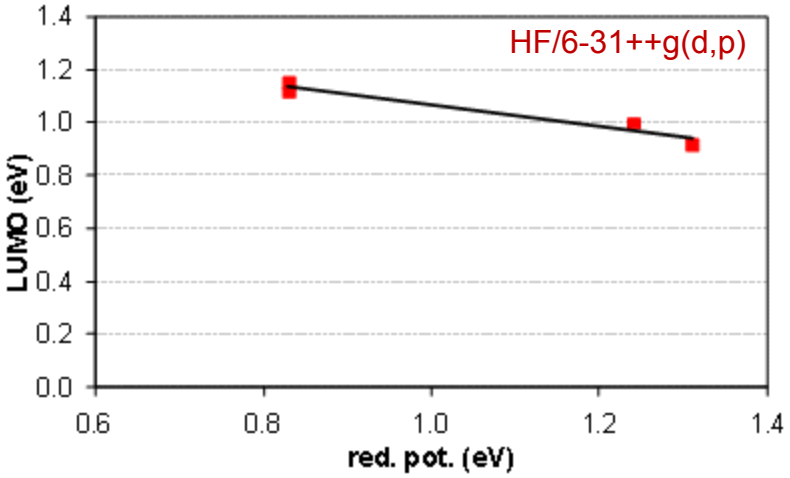


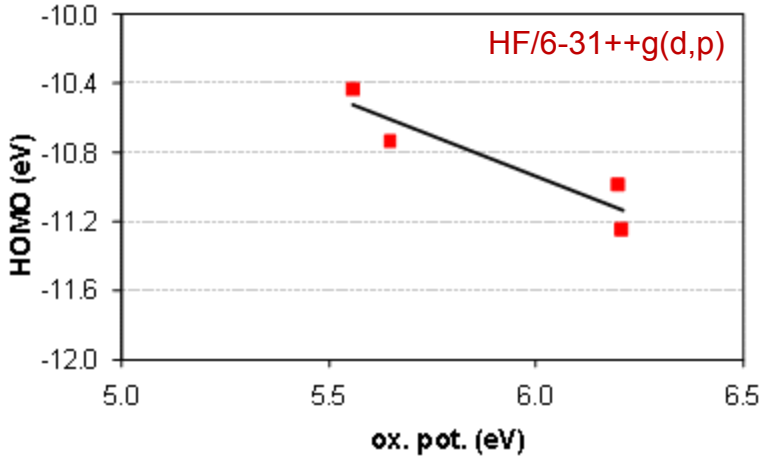
Synthetic Routes: Sulfones



HOMO/LUMO Calculations
(Prof. J. Klauda, UMD)

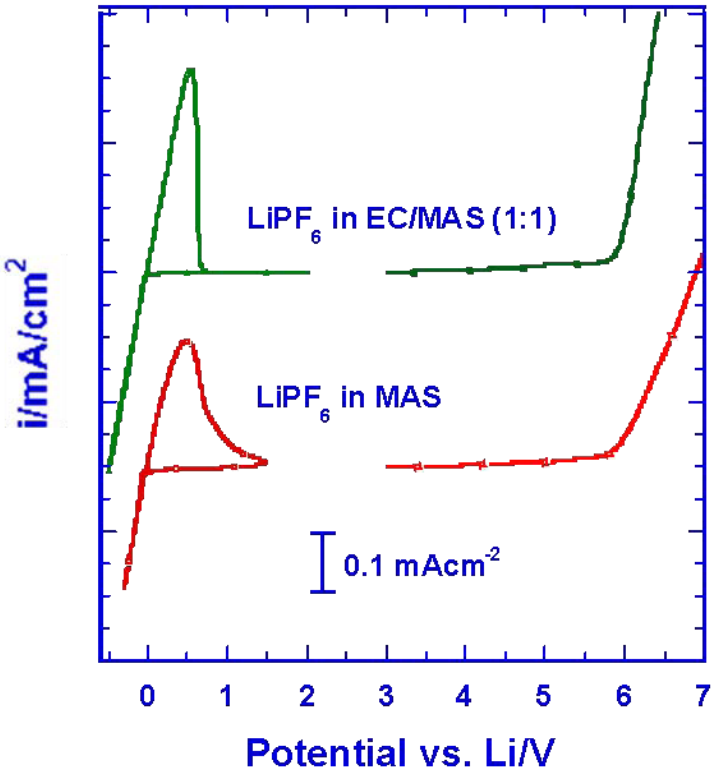
- **The QM method used for these HOMO/LUMO calculations**
- **The correlation coefficients between LUMO/reduction or HOMO/oxidative potentials are -0.968 and -0.919 for HF/6-31++g(d,p), respectively (-0.994 and -0.748 for MP2/aug-cc-pVDZ) for the additives (not EC).**





Preliminary Electrochemical Characterizations

- Three electrode configuration
- Pt as working
- Li as counter and reference
- ~ 6 V oxidation limit
- Need further test on cathode surfaces



Future Work

- Continue the syntheses of the sulfones with new functional groups and the electrochemical and physicochemical characterizations of $LiPF_6$ in these solvents
- Evaluate $LiPF_6$ in conventional carbonate solvents with and without VC additives in cells containing high voltage cathodes such as $LiNi_{1.5}Mn_{0.5}O_2$, $Li_{1+x}Ni_{0.33}Mn_{0.33}Co_{0.33}O_2$, and $LiCoPO_4$ as baselines.
- Evaluate $LiPF_6$ in sulfone solvents and their combination with other solvents in cells containing high voltage cathodes and compare with the results from the baseline.

Summary

- The high voltage electrolytes development has been focused on the development of anodically more stable sulfone based than currently used carbonate based solvent systems.
- Sulfone with different functional groups will be explored and synthesized as improved solvents and additives for Li-ion batteries.
- The formulated electrolytes containing developed sulfone based solvents in combination with other solvents will be evaluated with the high voltage cathodes in Li-ion cells.