BIFUNCTIONAL ELECTROLYTES FOR LITHIUM ION BATTERIES

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Project ID # es_41_srinivasan

Overview

Timeline

- Start Date: April 2009
- End Date: March 2013
- 0% complete

Budget

- Total project funding
  - **$ 798,000**
- Funding for FY09
  - **$ 199,665**

Barriers

- Barriers addressed
  - Abuse tolerance

Objectives

- **Development of bifunctional electrolytes will allow for species to perform dual action, i.e., support charge transport through the electrolyte and provide flame retardant properties and/or overcharge protection and thereby improve device safety.**

Approach

- **Impart electrolyte, i.e., solvent and salt, bifunctionality. Specifically, incorporate covalently linked groups to anions known to display high conductivity and stability with flame retardant and/or overcharge protection characteristics.**

Specific Approach

- Design, synthesis and physical, electro-chemical and interfacial characterization of judiciously functionalized single component Li salt anions containing phosphorous moieties known to impart materials with flame retardant properties. (Flame Retardant Ions, FRIONs).
- Further functionalization of the most promising bifunctional materials with suitable redox properties to serve as redox shuttles and thus protect batteries from overcharging. (Flame Retardant Overcharge Protecters, FROPs and Overcharge Protecting Ions, OPIONs).

Summary

- Judicious chemical functionalization affords means of imparting species with bi- and multi-functionality. Tactic expected to open new prospects for development of materials endowed with the required properties to meet DOE goals.

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Advanced Electrolyte and Electrolytes Additives

K. Amine and L. Curtiss

Argonne National Laboratory

May 21, 2009

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U.S. Department of Energy

UChicago Argonne LLC

Office of Science
U.S. DEPARTMENT OF ENERGY

A U.S. Department of Energy laboratory
managed by UChicago Argonne, LLC

Overview

Timeline

- Start – January 1, 2009
- Finish - September 30, 2009
- 10%

Barriers

- Barriers addressed
  - Cycle life
  - Calendar life
  - Abuse tolerance

Budget

- Total project funding
  - DOE share: $300K

Partners

- Interactions/ collaborations:

  Z. Zhang and Z. Lu
- Project leads:

  K. Amine & L. Curtis

Objectives of the work

- Develop an Advanced Quantum Model to predict functional additives that form stable Solid Electrolyte Interface (SEI) on carbon anode and cathodes.

- Expend the model to predict how additives interact with the surface of anode and cathode during the initial charging.

- Synthesize suitable additives predicted by model, characterize them and carry out extensive cycle and calendar life test.

Approach

- Search for new electrolytic additives that react in a preferential manner to prevent detrimental decomposition of other cell components.

- Quantum chemical screening of potential additive candidates for electrolytes.
  - Prediction of their oxidation and reduction potentials to find ones that will be operable over the desired potential window and form desirable coatings.
  - Prediction of decomposition pathways that lead to desirable coatings.

- Density functional studies of surface reactions on graphite surface to determine mechanisms for protective film formation from additives.

Quantum Chemical Prediction of Oxidation Potentials

- Full optimization of neutrals and ions at HF/6-31G(d) level of theory.
- Ionization potentials and electron affinities calculated using B3LYP/6-31+g(d) single point calculations (accuracy to within 0.2 to 0.3 eV of the experimental values).
- The PCM (Polarizable Continuum Model) was used to predict (ΔG)solv using the B3LYP/6-31+g(d) level of theory to obtain reduction potentials.
- Computational team was set up:
  - Offer to PD for mechanistic studies of surface reactions.
  - Staff member is starting on screening of electrolyte additive candidates for use in further developing and expending the model.

Thermodynamic Cycle Used to Calculate Oxidation Potentials

$$\begin{tikzcd}
A_g \arrow[r, "(\Delta G)_{gas}"] \arrow[d, "(\Delta G^{neut})_{solv}"'] & A^+_g + e^- \arrow[d, "(\Delta G^{pos})_{solv}"] \\
A_{solv} \arrow[r, "\Delta G"'] & A^+_{solv} + e^-
\end{tikzcd}$$

$$\Delta G = (\Delta G)_{gas} + (\Delta G^{pos})_{solv} - (\Delta G^{neut})_{solv}$$

Future Work

- Screen over 100 candidate materials for reduction potentials.
- For those candidate materials with required reduction potentials perform a further downselect based on those with optimal decomposition pathways.
- Initiate investigation of reactions on electrode surfaces of decomposition products.