Organic and Inorganic Solid Electrolytes for Li-ion Batteries

Runqing Ou, Nader Hagh, Farid Badway and Ganesh Skandan, *NEI Corporation – Somerset, NJ*

Collaborates: (1) Kazuki Ishida, and Patrick T. Mather, *Syracuse University - Syracuse, NY*

(2) Ganesan Nagasubramanian *Sandia National Laboratories - Albuquerque, NM*

Acknowledgement: U. S. Department of Energy , Office of Electricity Delivery & Energy Reliability, Dr. Imre Gyuk

Abstract: The use of a solid polymer electrolyte instead of the conventional liquid or gel electrolyte can drastically improve the safety aspects of a Li-ion battery. However, existing PEO-based solid electrolytes do not meet the functional performance requirements. At low temperatures, the conductivity is poor due to the presence of crystalline PEO segments, which restrict the lithium ion mobility. This limits the useful operating temperature of Li-ion polymer batteries to between 70°C and 100°C, which excludes the use of solid polymer based batteries in room temperature commercial applications. A novel nanocomposite organic/inorganic hybrid material has been identified as a potential solid polymer electrolyte system that can exhibit high Li-ion conductivity at room temperature and below, along with good mechanical properties. The presence of inorganic moieties in the material inhibits the crystallization of PEO chains, which leads to increased low temperature ionic conductivity as well as increased lithium transference number. In addition, inorganic sulfide-based solid electrolyte was successfully synthesized, characterized and assembled in a Li-ion cell using the LCO cathode. The Galvanostatic cycling results of the cell showed a comparable performance to the conventional liquid-based LCO battery.

Background & Objectives

- Lithium ion batteries widely used in consumer applications Solvent leakage and flammability of conventional liquid electrolytes
- Current solid state electrolytes suffer from low ionic conductivity, inferior rate capability, and interfacial instability
- Objective of the program is to develop solid state organic and inorganic electrolyte that has enhanced ionic conductivity

I. Organic Solid Electrolyte

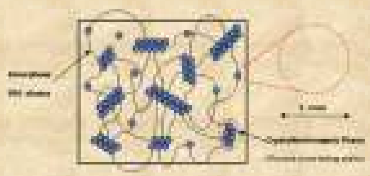

Figure 1: Schematic microstructure of organic solid electrolyte

- PEO based polymer electrolyte has poor room ionic conductivity due to crystallinity
- The current program develops a PEO based hybrid copolymer that disrupts crystallization and at the same time provides mechanical integrity

Synthesized Co-polymer

Table 1: Two series of copolymers synthesized: M series (sample id ending in M) and H series (sample id ending in H)

Sample	inorg/PEG (feed)	inorg/PEG (actual)	Di-isocyanate	M_n (kg/mol)	PDI (M_w/M_n)	PEG wt%
P_2PEG1K_1M	1/0.5	1/0.41	MDI	20.6	1.28	22.8
P_1PEG1K_1M	1/1	1/0.87	MDI	44.6	1.04	36.5
P_1PEG1K_2M	1/2	1/1.81	MDI	33.1	1.17	50.8
P_1PEG1K_3M	1/3	1/2.80	MDI	25.7	1.10	56.7
P_1PEG1K_4M	1/4	1/4.59	MDI	23.3	1.07	65.5
P_1PEG1K_5M	1/5	1/4.47	MDI	35.0	1.34	65.6
P_1PEG1K_8M	1/8	1/8.13	MDI	25.1	1.36	70.9
$P_1PEG1K_{10}M$	1/10	1/9.64	MDI	22.3	1.09	72.2
$P_1PEG1K_{16}M$	1/16	1/15.67	MDI	31.3	1.10	75.0
P_1PEG1K_5H	1/5	1/5.7	HDI	55.4	1.08	70.4
P_1PEG1K_8H	1/8	1/8.6	HDI	89.1	1.06	73.6

Membrane Fabrication

- Solution casting
- Lithium salt:$LiCF_3SO_3$
- Solvent: DMF
- Polymer/salt ratio: 5/1, 5/2, 5/3

Fabricated membrane

DSC of Polymer/Li Salt Complex

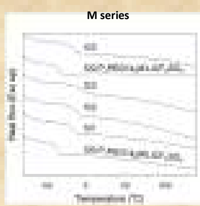

Figure 2: M series copolymer and copolymer/Li ion complex are amorphous.

Figure 3: H series copolymer is partially crystalline. Copolymer/Li ion complex is amorphous.

Ionic Conductivity

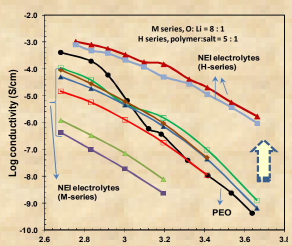

Figure 4: H series copolymer/Li complex has significantly improved conductivity over PEO and M series. For M series, conductivity increases with higher PEG content.

Voltage Stability

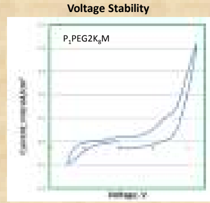

Table 2: Li^+ transference number

Sample	Li transference number T^+	
	At 40°C	At 80°C
PEO	0.26	0.31
P_1PEG1k_4M	0.42	0.46
P_1PEG1k_5M	0.48	0.50

Hybrid copolymers have significantly improved lithium transference numbers over PEO

Figure 5: Voltage stability and Li transference number for synthesized polymer.

Conclusions on Organic Solid Electrolyte

- Introduction of inorganic segments into PEO chains disrupts crystallization of PEO and results in a hybrid copolymer/Li ion complex that is amorphous.
- The H series of hybrid copolymer/Li ion complex has significantly improved conductivity over PEO and M series.
- Room temperature conductivity still needs to be improved for practical applications.

II. Inorganic Solid Electrolyte

Figure 6: Temperature dependence of conductivity in electrolytes. High conductivity of sulfide systems (e.g. Li_2S-P_2S_5-GeS_2)

Highlights :

- Larger ionic radii (170-180pm in S^{-2})
- Conductivity through mobile ion sublattice
- Presence of highly polarizable ions & anions (normally higher than oxide systems)
- Existing in the form of partially/fully sulfide

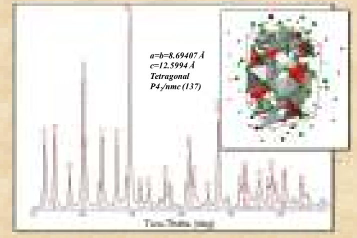

Figure 7: Calculated XRD pattern of ternary system (Li_2S-P_2S_5-GeS_2)

Synthesized Electrolyte

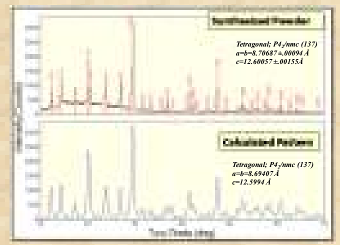

Figure 8: Comparison between the synthesized and calculated XRD patterns. Good match between calculated and synthesized electrolyte (crystal structure and lattice parameters)

Cell Performance

Solid State Battery

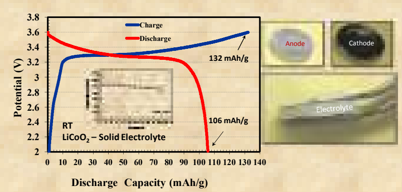

Figure 9: Actual battery pellet and first cycle voltage profile of the solid state battery. Capacity of cell containing solid electrolyte approaching that with liquid electrolyte at RT (T=25°C).

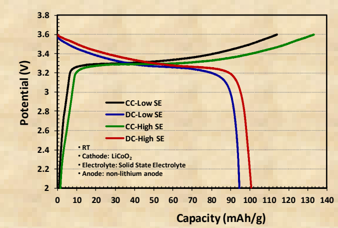

Figure 10: Effect of solid electrolyte content on electrochemical performance.

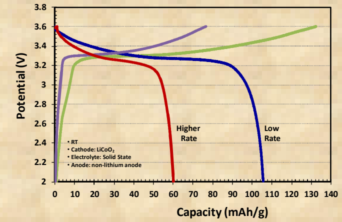

Figure 11: Effect of rate on electrochemical performance of solid state battery.

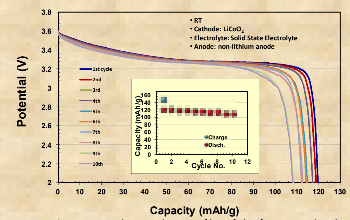

Figure 12: Discharge voltage profiles of the first ten cycles. (Inset: Corresponding capacity vs. cycle no.) representing the reversibility in all solid state battery.

Summary & Conclusions

- Successful synthesis and scale-up of the solid electrolyte
- Demonstrated the effect of electrolyte content, rate, and electrolyte content on the cell performance
- RT reversible cycling of the all solid state cell
- Comparable performance to liquid-based electrolyte however with much higher safety

Future Work

- Exploring the new cathode chemistries with higher capacity and higher voltage
- Improving the rate capability of the solid state battery at RT
- Low and high temperature performance testing of the solid state battery

For more information please contact:

Dr. Runqing Ou or Dr. Nader Hagh

NEI Corporation

400 Apgar Drive, Unit E

Somerset, NJ 08823

Tel: 732.868.3141

Fax: 732.868.3143

www.neicorporation.com