Advances in Lithium Metal Anode-Based Rechargeable Batteries Utilizing Solid-State Electrolytes

National Research Council Canada
Automotive and Surface Transportation

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Outline

- About the NRC and The MET team
- Lithium Batteries Status and Prospects
- Li metal anode technical challenges
- Solid State Polymer Batteries
  - Application in Li/LFP
  - Application in Li-O₂
- Conclusions and perspectives
- Acknowledgments
About the NRC

Government of Canada's premier organization for R&D

- 4 R&D divisions and 12 portfolios
- 3,550 employees
- $909.3M budget
- 24 Locations across Canada (Industrial Research Assistance Program)
- Serves thousands of industrial and government clients annually
Materials for Energy Technologies Team

- R&D activities on **battery technologies**, **fuel cells**, **supercapacitors**, **electrolyzers**
- Clients from OGDs, OEMs, and SMEs from the entire supply chain
Lithium Batteries Status and Prospects

DOE Technology Roadmap and Targets

2020 DOE Targets
- Increase performance (energy, power, life)
- Reduce weight & volume
- Increase abuse tolerance
- Reduce cost (to $125/kWh for 100,000 units/year)

Advanced Materials Research Strategies
- High capacity cathodes
- Solid state electrolytes (high voltage)
- High capacity anodes (alloys, Li-metal)
- Research to enable lithium metal systems
Technical challenges associated with Li metal anodes

• Lithium dendrites growth
  - Mechanical reinforcement of the interface / solid-state electrolyte (inorganic or polymer)
  - New electrolytes/additives (optimal SEI composition, dendrite capping, chemical inhibition of dendrite initiation)

• Lithium metal interface stabilization / cycling efficiency
  - Optimal SEI layer
  - Prevention of side-reactions consuming the lithium (SEI cracking/repair cycle)

• Lithium anode volume change upon cycling
  - Chemical transformation anode: lithium metal is consumed/generated (rather than Li+ intercalation)
  - Cell design for stack pressure/volume compensation, (polymeric electrolytes compensate more than solid-state ceramic based)
Solid State Polymer Batteries
Application in Li/LFP Batteries

Project
- Funding: $800K
  - NRCan (Eco-EII program)
  - BlueSolutions
  - Vehicle propulsion Technology Program
- Duration: 4 years

Objective
- Development of high performance all-solid polymer electrolytes (SPE), with improved conductivity and performance at low temperature (LMP batteries operation temperature is 80°C) and improved safety related to the use of metallic lithium

Strategy
- Optimization of a generic SPE based on PEO/PVDF polymers
- Salts: mainly molten salts (room temperature ionic liquids), and alkali metal salts (LiTFSI, LiTF)
- A low-cost and solvent-free continuous process for manufacturing of robust thin solid polymer electrolytes
Solid State Polymer Batteries
Application in Li/LFP Batteries

Solvent-free continuous process to manufacture solid polymer electrolytes

- Solvent free continuous manufacturing process
- Easy integration with the cathode and/or lithium anode
- Allows for large-format cell production
- The process developed can be directly scaled-up to the process used by industry with minor modifications

Dry room
- Surface: 70 m²
- Dew point: -40 °F (20-60 ppm H₂O)
- Pilot-scale production of polymer-based electrolytes
- Pouch cell assembly

Width = 4 cm
Thickness > 10 µm

Width = 10-15 cm

Width = 20-35 cm
Solid State Polymer Batteries
Application in Li/LFP Batteries

ROOM TEMPERATURE IONIC LIQUIDS

- Salts or mixtures of salts (composed solely of ions)
- Liquids at room temperature (low symmetry of cations)
- Good solvents for lithium salts (enhance electrochemical conductivity)
- Very high thermal stability
- Non volatile (low vapor pressure)
- Non flammable (flame retardants)
- High electrochemical stability
- Large number of commercially available RTIL with different chemistries (cost decreasing, purity improving)

All ionic liquids selected are liquid at room temperature
- Relatively low viscosity
- Thermally stable at melt-processing temperature range 120-150°C
Solid State Polymer Batteries
Application in Li/LFP Batteries

N-IL DSC Analysis. Scan rate 20°C/min. N2 atm

- All SPE show comparable DSC profiles independently from the chemistry of RTIL
- Crystallinity of PEO, PVDF and LiTFSI inhibited when blended in the melt state and by the presence of RTIL salts
- Expected to promote ionic transport

P-IL TGA Analysis. Scan rate 20°C/min. N2 atm

- All SPE show similar TGA profiles independently from the chemistry of RTIL
- High thermally stability; weight loss at 300°C is < 2% mainly due to H2O absorbed during samples conditioning prior to the analysis
Solid State Polymer Batteries
Application in Li/LFP Batteries

- Overall ionic conductivity up to one order of magnitude higher at RT
- Ionic conductivity of reference SPE at 60°C is achieved at 40°C with some SPE with 15wt% N-IL (1-Ethyl-3-methylimidazolium)
- Ionic Conductivity of Phosphonium IL based polymer electrolytes is lower compared to N-IL
- Cations size is higher, reduced cations mobility, favours Li+ transfer during battery cycling

EIS on P-RTIL based SPE

- $E_a = 35 \text{ KJ/mol}$ for reference SPE
- $E_a = 21.7$ to $28.5 \text{ KJ/mol}$ for N based IL
- $E_a = 24.3$ to $27.7 \text{ KJ/mol}$ for P based IL

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$x = \text{IL/Li} = 0.5$

Reference SPE $x = 0$
Solid State Polymer Batteries
Application in Li/LFP Batteries

Non-crosslinked SPE

Crosslinked SPE

Crosslinked SPE + unstable N-IL1

Crosslinked SPE + stable N-IL3

SPE stability towards metallic lithium:
Accelerated Li stripping/plating cycling + EIS measurements (0.5 mA/cm²)
Solid State Polymer Batteries
Application in Li/LFP Batteries

Accelerated Li stripping/plating cycling (0.5 mA/cm²) + EIS measurements

- Slower Li dendrite formation kinetics
- > 300% improvement with PYR 14 IL compared to reference SPE
- > 450% improvement with P-RTIL

SPE stability towards metallic lithium:
Accelerated Li stripping/plating cycling + EIS measurements (0.5 mA/cm²)
• at 70 °C, P-RTIL based SPE shows improvement at high power (discharge at 2C)
• at 60 °C, both IL improve the capacity, P-RTIL outperform under faster charging conditions (C/2)
• at 50 °C, ref looses its capacity at C/2 while capacity is 80 mAh/g PYR14 IL and 120 mAh/g for P-RTIL
• at 40 °C, Only P-RTIL based SPE withstand a C/10 maintaining cell capacity around 140 mAh/g
Solid State Polymer Batteries
Application in Li-O₂ Batteries

**Project**
- Funding: $2M
  - NRCan (Eco-EII program)
  - Vehicle propulsion Technology Program
- Duration: 4 years

**Objectives:**
- Develop a polymer-based solid-state electrolyte
- Develop potential catalysts for the cathode and optimise deposition on non-carbon supports
- Design of the cathode-SPE integration layer
- Design and develop a realistic Li-O₂ prototype using a SPE-based technology
Solid State Polymer Batteries
Application in Li-O₂ Batteries

The Li-air technology

\[
\text{Anode: } \text{Li} \rightarrow \text{Li}^+ + e^- \\
\text{Cathode: } \text{O}_2 + 2e^- + 2\text{Li}^+ \rightarrow \text{Li}_2\text{O}_2
\]

- Huge theoretical energy density: 3500 Wh/kg
- Practical energy density target: 1000 Wh/kg
- Could enable 500 km range in a single charge for EVs
- Very challenging technology:
  - Air-cathode (design, stability, round-trip efficiency, kinetics, ...)
  - Electrolyte (physical and electrochemical stability, air-cathode integration, ...)
  - Anode (dendrite prevention, electrolyte interface stability, volume change, ...)
  - Manufacturability (scale-up, cell design, system integration, etc.)

A SPE can solve a number of the Li-O₂ challenges:
- No electrolyte evaporation
- Dendrite prevention
- Lithium metal interfacial stability
- Processability
Solid State Polymer Batteries
Application in Li-O\textsubscript{2} Batteries

SPE materials investigated
- PEO/PVDF based polymer
- LiTFSI or LiTf salts
- RTIL salts (Li\textsuperscript{+} conduction promoter, SEI stabilizer)
- CsTFSI (dendrite inhibitor)

- LiCF\textsubscript{3}SO\textsubscript{3} better than LiTFSI as a salt; more stable towards Li metal and shows better cell capacitance
- Triflate based polyelectrolytes show very low O\textsubscript{2} permeability compared to TFSI
- IL incorporation promote oxygen transmission through the electrolyte
- TFSI based IL are more hydrophobic that triflate based IL, might prevent or slow Li anode degradation
Solid State Polymer Batteries
Application in Li-O₂ Batteries

SPE with CsTFSI (dendrite inhibitor)

ionic conductivity up to one order of magnitude higher at RT
CsTFSI does not seem to contribute to the overall ionic conductivity (low concentration (0.1 mol%)
CsTFSI slows considerably lithium dendrite growth kinetics
Solid State Polymer Batteries
Application in Li-O₂ Batteries

SPE integration with the air cathode

- Compatibilization of a flat surface with a porous layer
  - Ionic junction
  - Keep O₂ percolation
- Optimization of the triple phase (e⁻ / Li⁺ / O₂)

SPE : PEO-PVDF-LiTFSI

Graph showing potential vs Li (V) vs capacity (mAh/g)
Solid State Polymer Batteries
Application in Li-O₂ Batteries

Multi-electrode pilot-scale prototype

- Design of a multi-electrode prototypes with integrated gas flow
- Design of pouch laminate mechanical sealing system
- Components scale-up (spray deposition on large surfaces, continuous melt-extrusion of the SPE and of the SPE integration layer)

Tools for concentric alignment-stacking of components of same or different sizes (Lithium+SPE or cathode+SPE integ. layer)

Example of alignment of the cathode with the SPE integration layer
Multi-electrode pilot-scale prototype

- Development of methodologies and specific tools for controlled components cutting and integration
- Prototype assembly and quality-control methodologies
Solid State Polymer Batteries
Application in Li-O2 Batteries

Multi-electrode prototype testing

- Prototype gets similar performances as lab-cells
- Slight issue of O₂ diffusion (Warburg behaviour at medium frequencies, 200 mV lower discharge voltage)
- Energy output not as high as expected: 250 Wh/kg and 180 Wh/L for the prototype
Solid State Polymer Batteries
Application in Li-O₂ Batteries

- Limited cyclability at 15% DOD shallow cycling
- Electrochemistry yet unstable
Conclusions and perspectives

- A solid-state polymer electrolyte has been successfully applied to the Li-O₂ electrochemistry, the first realistic pilot-scale (and scalable) Li-O₂ prototype, with multiple electrodes and gas flow channels has been demonstrated.

- The Li-O₂ technology still suffers from fundamental issues to be solved:
  - Cathode and electrolyte instability vs. Li₂O₂
  - Slow kinetics and low round-trip efficiency (large over-potential on recharge)

- All-solid polymer electrolytes are a viable alternative for a safe utilisation of lithium metallic anode, the chemistry of selected additives play a major role.

- RTIL show a great potential for Li/LFP batteries, with and improvement in low temperature performance, improved discharge capacity at high rate (higher power output) and a significant decrease in lithium dendrite growth kinetics.

- The RTIL chemistry choice is crucial to a stable SEI with metallic lithium.

- Replace PEO with polymers stable at higher voltage. High capacity cathode.
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Thank you

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