Novel Polyimide Battery Separator Imbibed with Room-Temperature Ionic Liquids

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Multifunctional Energy Storage to Improve Efficiency

Enable hybrid electric propulsion for commercial aircraft by coupling load-bearing structure with energy storage

Challenges

- Producing a structure capable of bearing weight and resisting forces associated with flight

Risks

- Current Li-Ion battery technology utilizes flammable components

Goals

- Develop a separator/electrolyte system which possesses sufficient ionic conductivity with non-flammability

Hybrid electric aircraft with multifunctional storage could reduce emissions by 80% and fuel consumption by 60%
Polyolefin Separators used in Li-Ion Batteries

- Polyethylene and polypropylene are among the most flammable polymers
- Limited number of electrolytes wet the polyolefins

<table>
<thead>
<tr>
<th>Separator/Properties</th>
<th>Celgard 2730</th>
<th>Celgard 2400</th>
<th>Celgard 2325</th>
<th>Asahi Hipore</th>
<th>Tonen Setela</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Structure</strong></td>
<td>Single Layer</td>
<td>Single Layer</td>
<td>Trilayer</td>
<td>Single Layer</td>
<td>Single Layer</td>
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<tr>
<td><strong>Composition</strong></td>
<td>PE</td>
<td>PP</td>
<td>PP/PE/PP</td>
<td>PE</td>
<td>PE</td>
</tr>
<tr>
<td><strong>Thickness (μm)</strong></td>
<td>20</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td><strong>Porosity (%)</strong></td>
<td>43</td>
<td>40</td>
<td>42</td>
<td>40</td>
<td>41</td>
</tr>
<tr>
<td><strong>Melt Temp. (°C)</strong></td>
<td>135</td>
<td>165</td>
<td>135/165</td>
<td>138</td>
<td>137</td>
</tr>
</tbody>
</table>
Electrolytes Currently Used in Li-Ion Batteries

- Current Li-ion technology uses combinations of carbonates as the electrolyte
- The ionic conductivity of polyolefin separators imbibed with carbonates is $\sim 10^{-2} - 10^{-3}$ S/cm
- However, the carbonates are highly flammable
Separator Requirements for Li-Ion Batteries

Separator Requirements

• Electronic insulator
• Minimal electrolyte resistance
• Mechanical and dimensional stability
• Sufficient mechanical strength to allow manufacture
• Chemical resistance to degradation by electrolyte
• Readily wetted by electrolyte
• Porosity of at least 40%
• Uniform in thickness
• Thermal stability
• Shut-off temperature

Photo courtesy Cnet.com
Comparison of Commercial Separator and PI Aerogel

Celgard® PE Separator

Polyimide Aerogel
What are Aerogels?

Aerogels are a class of porous solids which exhibit many extreme properties which originate from a nanoporous skeletal architecture.

- Highly porous solids made by drying a wet gel without shrinking
- Pore sizes extremely small (typically 10-40 nm)—makes for very good insulation
- 2-4 times better insulator than fiberglass under ambient pressure, 10-15 times better in light vacuum
- Invented in 1930's by Prof. Samuel Kistler
Development of Polyimide Aerogels

- Over 50 combinations of diamines and dianhydrides in the polymer backbone have been characterized
- Multiple cross-linkers have been investigated
- Properties dependent on backbone chemistry

Typical properties
- High porosity (>85%)
- Pore size 10-40 nm
- Open-cell fibrillar architecture
- High thermal stability
- Char-forming, non-flammable
- Tunable hydrophobicity
- Tunable mechanical properties
- Can be cast into flexible thin films
General Polyimide Reaction Scheme

4,4'-oxydianiline (ODA)

2,2'-dimethylbenezidine (DMBZ)

2,2'-bis(4-[4-aminophenoxy]phenyl)propane (BAPP)

3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA)

3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA)

1,3,5-tris(4-aminophenoxy)benzene (TAB)

Pyromellitic dianhydride
Down Selection to ODA-BPDA-N3300A

- Many polyimide backbone chemistries were synthesized and characterized
- Several factors were considered in down selection: film forming, mechanical strength, porosity
- ODA-BPDA-N3300A formed thin, mechanically robust films, with porosities of 93%
Higher Ionic Conductivities for Films that have not been Dried

1. Dissolve monomers in solution
2. Polyamic acid intermediate forms
3. Chemical imidization at room temperature
4. Addition of cross-linker
5. Cast gel into film
6. Supercritical CO$_2$ extraction

With 1-methyl-1-propylpyrrolidinium TFSI, conductivity is half when film is dried first.
Physical Characteristics of ODA-BPDA-N3300A PI

Graph 1:
- Pore diameter (log), nm
- Pore volume, cm$^3$/g
- Weight loss, %

- 10 wt%, n = 30
- Temperature, °C
- Weight loss, %

Graph 2:
- Temperature, °C
- ODA-BPDA-TAB
- ODA-BPDA-N3300A

Chemical structure:
- a, b, c
Properties of Ionic Liquids

- Room temperature ionic liquids (RTILs) consist of an asymmetric organic cation and a bulky anion with delocalized charge.
- RTILs are nonvolatile and nonflammable.
- Wide range of viscosities.
- Highly polar.
- Tunable miscibility.
- Highly thermally stable – imidazolium cation stable above 300 °C.
- Most RTILs do not wet polyolefins.

1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

Courtesy U.S. Department of Energy
Screening Study of RT Ionic Liquids

1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

1-ethyl-3-methylimidazolium tetaborate

1,3-diethylimidazolium bis(trifluoromethylsulfonyl)imide

1-methyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide

1-allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

1-(2-methoxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

diethylmethy lammonium trifluoromethanesulfonate

butyltrimethylammonium bis(trifluoromethylsulfonyl)imide

N,N-diethyl-N-methyl-N-(2-methoxyethyl) ammonium bis(trifluoromethylsulfonyl)imide

1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide

1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide
Viscosity Influenced but Did not Determine Conductivity

- All ILs use TFSI as the anion, except one which uses $\text{BF}_4^-$
- Viscosity has an effect on conductivity, but not the only important factor
- Several ILs showed electrochemical instabilities or compatibility issues with anode/cathode
Down Selection to Three ILs

- The ammonium compounds eroded the current collectors
- 2-methoxyethyl imidizolium and 1-allyl imidizolium are unstable electrochemically
- 1-ethyl-3-ethyl imidizolium BF$_4^-$ yellowed and degraded in the presence of the carbon cathode
- The propyl imidizolium possessed a low conductivity

- The 2 pyrrolidinium compounds displayed the highest degree of electrochemical stability
- EMIM TFSI showed the highest conductivity of the stable compounds
- The diethylimidizolium compound was more expensive and less conductive than EMIM TFSI
The porosity of the separator had a large influence on the ionic conductivity.
ODA-BPDA-N3300A produced the highest porosity samples.
Viscosity influenced conductivity when the porosity was the same.
PI/EMIM TFSI Gel Separator Cycled for 14 Hours

- EMIM TFSI is stable in the presence of the aluminum cathode and copper anode – no visible discoloration or reaction
PI/EMIM Gel Separator is Nonflammable Under Direct Contact with Flame
Conclusions and Future Work

• A separator based on a porous polyimide gel imbibed with an ionic liquid has been demonstrated

• Ionic conductivity increased as a function of increasing porosity and decreasing ionic conductivity

• The separator was stable in the presence of the copper anode or aluminum cathode over 14 hours cycling

• The separator was not flammable under direct exposure to flame
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Empirical modeling produces response surfaces

Variables

- \( X_1 = \) Total % Polymer (7\%, 8.5\%, 10\%)
- \( X_2 = n\)-Value (20, 30, 40)
- \( X_3 = \) Mole % Diamine (0\%, 25\%, 50\%)

Multiple Linear Regression Analysis

\[
Response = C + C_2 X_1 + C_3 X_2 + C_4 X_3 + C_5 X_1^2 + C_6 X_2^2 + C_7 X_3^2 + C_8 X_1 X_2 + C_9 X_1 X_3 + C_{10} X_2 X_3
\]

Analysis of Variation (ANOVA Table)

- Backward Stepwise Regression Analysis
- Statistically insignificant terms are removed from model sequentially until only significant terms remain \((p < 0.1)\)
Typical Battery Configurations

(a) button cell; (b) stack lead-acid; (c) spiral wound cylindrical lithium-ion; (d) spiral wound prismatic lithium-ion

P. Arora, Z. Zhang; Chem. Rev. 2004, 104, 4419-4462