3-D Imaging of separator pore structure and Li\textsuperscript{+} diffusion behavior

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1. Background

2. Method to measure diffusion rate of \( \text{Li}^+ \) within separator by \textit{PFG-NMR}

3. Direct observation of 3-D pore structure by \textit{FIB SEM}

4. Summary
1. **Background**

2. Method to measure diffusion rate of $\text{Li}^+$ within separator by *PFG-NMR*

3. Direct observation of 3-D pore structure by *FIB SEM*

4. **Summary**
Three kinds of separators used for LIB

SEM photo images of separators

One component dry process
Two components wet process
Three components wet process
Important roles of separators

Electronic insulation and ionic conduction

Shut down effect

[Diagram of battery components with labels for Charger, Discharge, Separator, Current collector, and electrolyte, showing the movement of electrons and ions.]

Graph showing the impedance of the separator as a function of temperature.
Outline

1. Background

2. Method to measure diffusion rate of Li⁺ within separator by **PFG-NMR**

3. Direct observation of 3-D pore structure by **FIB SEM**

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Principle of pulsed field gradient NMR (PFG-NMR)

Conventional NMR:
Excitation by electromagnetic pulse → detection

PFG-NMR: Excitation by electromagnetic pulse →
labeling of position by pulsed field gradient →
diffusion time → detection

After certain time
Migration from labeled position by self-diffusion

Static magnetic field

Intensity

Position

T0 T1 T2 T3 T4 T5
Principle of PFG-NMR

Diffusion coefficient by PFG-NMR: \( D \) in the following formula

\[
\ln\left(\frac{E}{E_0}\right) = -D \times (\gamma^2 \delta^2 g^2 (\Delta - \delta/3))
\]

- **E**: Peak intensity at each measurement
- **\( \gamma \)**: Gyromagnetic ratio of nuclear spin
- **\( \delta \)**: PFG exposure time
- **\( g \)**: PFG intensity
- **\( \Delta \)**: Diffusion time
- **\( E_0 \)**: Peak intensity without PFG

**Li transport no**: 0.46

- Li⁺: \(1.98 \times 10^{-10} \) m²/s
- TFSI⁻: \(2.33 \times 10^{-10} \) m²/s
- EC: \(3.79 \times 10^{-10} \) m²/s
- MEC: \(4.00 \times 10^{-10} \) m²/s

**Slope of diffusion plot \( \Rightarrow D \)**

Calculation of diffusion coefficient in direction of static magnetic field (vertical direction of test tube)
New method to measure ion diffusion coefficient within separator

**Electrolyte**
1M LiTFSI / EC-MEC (1:2 vol.%)

**Sample preparation**
Separator is impregnated with electrolyte, inserted in test tubes in three directions (X, Y, and Z axes) as shown at right.

**PFG-NMR measurement conditions**
Apparatus: ECA400 (JEOL)
Probe: GR probe (max. magnetic field gradient strength = 13 T/m)
\[ \Delta : 50 \text{ ms}, \; \delta : 0.3 \text{ ms (}^1\text{H,}^19\text{F)}, \; 0.5 \text{ ms (}^7\text{Li)}, \; \text{temp: } 30^\circ\text{C} \]

**Species detected**
- Cation: \(^7\text{Li}\)
- Anion: \(^{19}\text{F (CF}_3\text{SO}_2)_2\text{N}^-\)
- EC: \(^1\text{H}\)
- MEC: \(^1\text{H CH}_3\text{OCOC}_2\text{H}_5\)

Yoshino, A. et. al., The 51st Battery Symposium in Japan (2010), Nagoya, Japan
Ion diffusion coefficients within separator

<table>
<thead>
<tr>
<th></th>
<th>Li(^+) diffusion coefficient (m(^2) s(^{-1}))</th>
<th>Relative comparison</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk electrolyte solution</td>
<td>(2.36 \times 10^{-10})</td>
<td>1.0</td>
</tr>
<tr>
<td>X axis</td>
<td>(1.18 \times 10^{-10})</td>
<td>0.50</td>
</tr>
<tr>
<td>Y axis</td>
<td>(0.64 \times 10^{-10})</td>
<td>0.27</td>
</tr>
<tr>
<td>Z axis</td>
<td>(0.66 \times 10^{-10})</td>
<td>0.28</td>
</tr>
</tbody>
</table>
### Anisotropy of Li$^+$ diffusion coefficients within various separators

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_X$</td>
<td>$1.91 \times 10^{-10}$</td>
<td>$1.79 \times 10^{-10}$</td>
<td>$1.98 \times 10^{-10}$</td>
<td>$1.07 \times 10^{-10}$</td>
<td>$1.06 \times 10^{-10}$</td>
<td>$1.18 \times 10^{-10}$</td>
</tr>
<tr>
<td>$D_Y$</td>
<td>$0.73 \times 10^{-10}$</td>
<td>$0.78 \times 10^{-10}$</td>
<td>$0.81 \times 10^{-10}$</td>
<td>$0.50 \times 10^{-10}$</td>
<td>$0.65 \times 10^{-10}$</td>
<td>$0.64 \times 10^{-10}$</td>
</tr>
<tr>
<td>$D_Z$</td>
<td>$0.57 \times 10^{-10}$</td>
<td>$0.70 \times 10^{-10}$</td>
<td>$0.61 \times 10^{-10}$</td>
<td>$0.76 \times 10^{-10}$</td>
<td>$0.69 \times 10^{-10}$</td>
<td>$0.66 \times 10^{-10}$</td>
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To clarify this anisotropy, tried to take 3D photo images of pore of separators by FIB SEM.
Outline

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FIB-SEM measurements of separators

1. Take SEM photo
2. Sputter 10 nm
3. Take SEM photo
4. Sputter 10 nm
5. Repeat 200 times
2D and 3D SEM photo images of separator C

2D SEM photo images of separator C
(200 photo images)

3D SEM photo image of separator C
### 3D FIB-SEM images of pore of separator

#### X axis

![Image X axis]

#### Y axis

![Image Y axis]

#### Z axis

![Image Z axis]

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<td>2.36 \times 10^{-10}</td>
<td>1.0</td>
</tr>
<tr>
<td><strong>Separator</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X axis</td>
<td>1.98 \times 10^{-10}</td>
<td>0.84</td>
</tr>
<tr>
<td>Y axis</td>
<td>0.81 \times 10^{-10}</td>
<td>0.34</td>
</tr>
<tr>
<td>Z axis</td>
<td>0.61 \times 10^{-10}</td>
<td>0.26</td>
</tr>
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Anisotropy of Li\(^+\) diffusion coefficients
Animation of 3D pore structure of separator C

X axis
0.84

Y axis
0.34

Z axis
0.24
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Summary

• Ionic conductivity of separators is the most important performance

• It became possible to measure diffusion rate of Li⁺ within separators taken in X, Y, and Z axes by PFG-NMR

• There was a high correlation between diffusion coefficients ($D_X, D_Y, D_Z$) and the 3D pore structures of separator measured by FIB SEM

• This is a useful finding for separators and electrode design