Experimental Evaluation of PEFC Catalyst Layer Structure to Reduce Oxygen Transport Resistances

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Background and Purpose

Issues for PEFCs: High cost
→ Efficient use of Platinum is essential

O₂ transport resistance
Major performance loss
Especially at the Pt surface

Purpose
To evaluate oxygen transport resistances quantitatively
Formulation of oxygen transport resistance in CL

\[ R_{CL} = \frac{\delta_{CL}}{3D_{O_2}^{CL,\text{eff}}} + \frac{1}{\delta_{CL}k_{diss}yS_{ion}} + \frac{1}{\frac{1}{n_{ag}\delta_{CL}} \cdot 4\pi(r_{ag} + \delta_{p})y r_{ag} \cdot \frac{\delta_{p}}{D_{O_2}^P}} + \frac{1}{\delta_{CL}k_{Pt}yS_{Pt}} \]

Diffusion resistance in pores \( R_{pore} \)
Dissolution resistance into ionomer \( R_{diss} \)
Diffusion resistance in ionomer \( R_{\text{diff}} \)
Transport resistance at Pt surface \( R_{Pt} \)

\( D_{O_2}^{CL,\text{eff}} \): Diffusion coefficient in pores
\( k_{Pt} \): Oxygen transfer rate
\( k_{diss} \): Oxygen dissolution rate
\( \gamma \): The ratio of the oxygen concentration in the ionomer to that in the CL pores

\( R_{\text{diff}} \) is relatively small

(2) T. Hayashi, et al., 230th meeting (2016).
Formulation of oxygen transport resistance in CL

\[ R_{CL} = \frac{\delta_{CL}}{3D_{O_2}^{CL,eff}} + \frac{1}{\delta_{CL}k_{diss}\gamma S_{ion}} + \frac{1}{\delta_{CL}k_{Pt}\gamma S_{Pt}} \]  

Eq. (1)

- **Diffusion resistance in pores** \( R_{pore} \)
- **Dissolution resistance into ionomer** \( R_{diss} \)
- **Transport resistance at Pt surface** \( R_{Pt} \)

\( R_{pore} \): Proportional to thickness of the CL \( (\delta_{CL}) \)

\( R_{diss} \): Inversely proportional to the surface area of the ionomer \( (S_{ion}) \)

\( R_{Pt} \): Inversely proportional to the surface area of the Pt \( (S_{Pt}) \)

References:
Experimental Method

Fabrication method of CCM

1. Mixing materials
   - Pt/C (Ketjen black)
   - Ionomer (Nafion) etc. (I/C=0.8)
   - Mixing with ball mill

2. Applying and Drying
   - Catalyst ink
   - PTFE

3. Hot-pressing
   - 2MPa, 150°C (10min)

Measurement of IV curve and oxygen resistance

\[ R_{total} = C_{O_2, ch} \lim \frac{4F}{i} = R_{O_2}^{P, dep} + R_{O_2}^{P, ind} \]

\( O_2 1\% \)
Diffusion Resistance in Pores $R_{pore}$

**CLs with different thicknesses**

Pt/C 50wt%

- **Thin** CL thickness $\delta_{CL}$
- **Thick** CL thickness $\delta_{CL}$

**Multiplying Eq. (1) by $\delta_{CL}$**

\[
R_{pore} \cdot \delta_{CL} = \frac{1}{3D_{O2}^{CL, eff}} \delta_{CL}^2 + \frac{1}{S_{ion} k_{diss} \gamma} + \frac{1}{S_{Pt} k_{Pt} \gamma}
\]

From Eq. and the gradient

\[D_{O2}^{CL, eff} = 2.8 \times 10^{-7} \text{ m}^2/\text{s}\]

**Oxygen transport resistance [s/m]**

- $R_{O2}^{dep}$
- $R_{O2}^{ind}$

**CL thickness (δ_{CL})**

- 1.4μm
- 2.8μm
- 5.1μm
- 7.9μm

**Horizontal axis**

- Intercepts: $R_{pore} \cdot W_{carbon}$

**Diffusion resistance in pores $R_{pore} \cdot W_{carbon}$**

- $(R_{diss} + R_{Pt}) \cdot W_{carbon}$
Diffusion Resistance in Pores $R_pore$

CLs with different thicknesses

- PEM
- GDL
- Pt/C 30wt%
- Pt/C 70wt%

Different Pt density

$$R_{pore} \cdot \delta_{CL}$$

$$R_{diss} \cdot \delta_{CL}$$

$$R_{Pt} \cdot \delta_{CL}$$

$$R_{CL} \cdot \delta_{CL} = \frac{1}{3D_{O2}^{CL,eff}} \delta_{CL}^2 + \left( \frac{1}{S_{ion}k_{diss}\gamma} \right) + \left( \frac{1}{S_{Pt}k_{Pt}\gamma} \right)$$

Horizontal axis

$R_{O2,ind} \times W_{carbon}$ [s/m·g]

- 30%
- 50%
- 70%

Similar diffusion coefficient in pores

30%: $D_{O2}^{CL,eff} = 3.5 \times 10^{-7}$ m$^2$/s

50%: $D_{O2}^{CL,eff} = 2.8 \times 10^{-7}$ m$^2$/s

70%: $D_{O2}^{CL,eff} = 2.8 \times 10^{-7}$ m$^2$/s
CLs with different Pt surface areas

<table>
<thead>
<tr>
<th>Name</th>
<th>30%</th>
<th>50%</th>
<th>70%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt loading [mg/cm²]</td>
<td>0.10</td>
<td>0.22</td>
<td>0.48</td>
</tr>
<tr>
<td>A&lt;sub&gt;Pt&lt;/sub&gt; [m²·Pt/m²·CL]</td>
<td>101</td>
<td>148</td>
<td>250</td>
</tr>
<tr>
<td>CL thickness [μm]</td>
<td>5.4</td>
<td>5.5</td>
<td>4.9</td>
</tr>
<tr>
<td>R&lt;sub&gt;O_2ind&lt;/sub&gt; [s/m]</td>
<td>32.9</td>
<td>17.7</td>
<td>15.2</td>
</tr>
</tbody>
</table>

**Eq. (1)**

\[ R_{Pt} = \frac{1}{k_{Pt} \gamma} \cdot \frac{1}{A_{Pt}} + \left( \frac{1}{k_{diss} \gamma A_{ion}} + \frac{\delta_{CL}}{3D_{O_2}^{eff}} \right) \]

From Eq. and the gradient

\[ \rightarrow k_{Pt} = 3.6 \times 10^{-3} \text{ m/s} \]
Result of Model Analysis

\[ R_{CL} = \frac{\delta_{CL}}{3D_{CL,eff}^{O_2}} + \frac{1}{k_{diss} \gamma A_{ion}} + \frac{1}{k_{Pt} \gamma A_{Pt}} \]

- \( k_{Pt} = 3.6 \times 10^{-3} \) m/s
- \( D_{CL,eff}^{O_2} \): Varies by Pt density

- \( R_{pore} \): Relatively small
- \( R_{Pt} \): Dominant resistance

Low Pt loading:
- Large error especially at low Pt loading
- Small change due to Pt density

\( R_{Pt} \) and \( R_{pore} \) values for different Pt/C loadings:
- 2.5 μm: 30 wt%
- 4.9 μm: 50 wt%
- 8.9 μm: 70 wt%
- 1.4 μm: 30 wt%
- 2.8 μm: 50 wt%
- 5.1 μm: 70 wt%
- 7.9 μm: 30 wt%
- 1.8 μm: 50 wt%
- 2.4 μm: 70 wt%
- 4.7 μm: 30 wt%
- 7.1 μm: 50 wt%
Result of Model Analysis

\[
R_{CL} - \frac{\delta_{CL}}{3D_{O2}^{CL,eff}} = \frac{1}{k_{diss} \gamma A_{ion}} + \frac{1}{k_{Pt} \gamma A_{Pt}}
\]

- 30%: \( k_{Pt} = 6.2 \times 10^{-3} \text{ m/s} \)
- 50%: \( k_{Pt} = 6.2 \times 10^{-3} \text{ m/s} \)
- 70%: \( k_{Pt} = 3.2 \times 10^{-3} \text{ m/s} \)

\( k_{Pt} \) 70% differs from the others

Better estimation

- Problems
  - \( k_{Pt} \) decreases at higher Pt density
  - Ignoring \( R_{diss} \)
Examination of the Model

\[ R_{CL} = \frac{\delta_{CL}}{3D_{O2}} + \frac{1}{k_{diss} \gamma A_{ion}} + \frac{1}{k_{Pt} \gamma A_{Pt}} \]

**Diffusion resistance in pores** \( R_{pore} \)

**Dissolution resistance into ionomer** \( R_{diss} \)

**Transport resistance at Pt surface** \( R_{Pt} \)

Low Pt density

High Pt density

**Higher Pt density**

Change in \( k_{Pt} \)

Decreasing \( A_{ion} \)

Necessary to consider

Effects of Pt density on \( k_{Pt} \) and \( A_{ion} \)

• The oxygen transport resistance of various catalyst layers (CLs) was measured, and separated to resistance components, $R_{\text{pore}}$ and $R_{\text{Pt}}$.

• With the experimental values and the model, we determined the parameters related to the oxygen transport resistances. It is found that the transport resistance at Pt surface ($R_{\text{Pt}}$) is larger.

• The model results using the experimentally-determined parameters were consistent with the experimental results, except for low Pt loading CL.

• The oxygen transfer rates at Pt surface ($k_{Pt}$), estimated for each Pt density, are different especially at high Pt density. This indicates that it is necessary to consider the effects of Pt density on the transfer rate and the effective ionomer surface area ($A_{ion}$).

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