SEPARATOR ELECTRICAL RESISTANCE: HOW LOW CAN YOU GO?

R. Waterhouse, C. La, E. Hostetler, C. Rogers, J. Kim, and R.W. Pekala
ENTEK International LLC
USA

S. Gerts, M. Ulrich, A. Brown, D. Walker, and D. Merritt
ENTEK International LTD
UK

September 15, 2016
OUTLINE

- What is resistance?
  - Electronic vs. Ionic

- How can we influence it?
  - Separator design and modeling

- How do we measure it?
  - Equipment
  - Test procedures

- How low can we go?

- What is the impact on battery performance?
**WHAT IS RESISTANCE?**

- Resistance is the property of a material that impedes the flow of current in the presence of a voltage gradient: \( I = \frac{V}{R} \)

  - **Current (I):** movement of charge
    - Electrons: \( e^- \)
    - Ions: \( Na^+ \) and \( Cl^- \) (seawater), \( H^+ \) and \( SO_4^{2-} \) (lead-acid battery)

  - **Voltage gradient (V):** results from a difference in electrical potential (voltage) between two points separated in space.
    - Residential: 230V, 50 Hz (gap varies with device), electrons
    - Spark plug: 50,000V across 1mm gap, corona discharge
    - Lead-acid battery: 2V across 0.5-2.0mm, ions (mostly H+)
Separator resistance is a function of the resistivity of the electrolyte (acid) plus the design, pore structure, and composition of the separator.

Resistance of electrolyte within a porous structure (Ω):

\[ R = \frac{\rho L \tau^2}{P A} \]

Where \( \rho \) = resistivity of the electrolyte, \( f \) (wt%, temperature)
\( L \) = thickness of the separator (design)
\( \tau \) = tortuosity of the pore path (structure)
\( P \) = porosity filled with acid (structure and composition)
\( A \) = area of the separator through which ions flow
ACID RESISTIVITY VS. CONCENTRATION AND TEMPERATURE

Acid resistivity is a strong function of both concentration and temperature. Both must be carefully controlled to get accurate results.

Operating range for lead-acid battery
SEPARATOR MORPHOLOGY
The morphology of a PE/SiO$_2$ separator is heterogeneous:
- Hydrophilic silica aggregates of different sizes
- Hydrophobic polyethylene fibrils
- Differences in structure between surface (polymer-rich) and bulk (silica-rich)
- Porosity and pore interconnectivity depend upon formulation and process conditions
- Broad range of pore sizes and shapes
- Not all pore volume is easily filled with electrolyte
  - Total pore volume ≠ acid accessible pore volume
UHMWPE fibrils

Silica Aggregates
POROSITY

Cumulative Intrusion vs Pore Diameter

- Z
- Y
- LR
- XLR
- STD 2.6

Increased Porosity

All separators are 0.15 mm backweb.
TORTUOSITY

Tortuosity > 1 when ion path length is greater than backweb thickness
HOW CAN WE MEASURE TORTUOSITY?

- Diffusion through a membrane separating two compartments:

\[
\ln \left( \frac{C_0 - 2C_d(t)}{C_0} \right) = -\frac{2A}{VR_d} \times t
\]

- Slope of the left-hand-side vs. time can be used to calculate the diffusional resistance
  - \(C_0\): initial concentration in the feed compartment
  - \(C_d(t)\): concentration of KCl in the diffusate compartment at time \(t\)
  - \(A\): Separator area exposed to the solutions
  - \(V\): volume of solution in one compartment
  - \(R_d\): Diffusional resistance of separator

- Diffusional resistance is related to tortuosity:

\[
R_d = \frac{t \times \tau^2}{D \times \varepsilon}
\]

- \(t\): separator thickness
- \(\tau\): tortuosity
- \(D\): Diffusivity
- \(\varepsilon\): porosity
Volume of liquid in the feed and diffusate compartments is the same.

Separator samples were boiled in DI water for 10 minutes, and equilibrate at room temperature (~ 22°C)
- Three 3” diameter disks were cut from each separator
- Conductivity of the solution in the diffusate compartment was measured with time for 1 hour.
- Diffusivity was assumed to be 1.90x10⁻⁵ cm²/s
- Stokes-Einstein radius of K⁺ and Cl⁻ ~ 1.3Å and 1.2Å

TORTUOSITY/DIFFUSIONAL RESISTANCE VS. FORMULATION

![Graph showing tortuosity and normalized diffusional resistance against formulation types.](image)

- Tortuosity
- Normalized Diffusional Resistance

**Formulation Types:**
- STD 2.3
- STD 2.6
- LR
The shift toward larger pore size seen on the LR separator brings about the decrease in tortuosity and increase in porosity.
Lower tortuosity and higher porosity contribute to the lower electrical resistivity of the LR separator.
The Palico system measures separator resistance by sensing the voltage drop between two pairs of sensing electrodes in response to current pulses delivered by electrodes at opposite ends of the bath. The difference in voltage drop, with and without a separator in the ionic current path, is used to calculate resistance.
LIMITATIONS OF PALICO TEST MEASUREMENTS

- Current density and temperature
  - Palico separator ER test: \( \frac{100\text{ma}}{32.3\text{cm}^2} = 3.1 \text{ ma/cm}^2 \) 27 °C
  - Hioki Battery HiTester: \( \frac{150\text{ma}}{2200\text{cm}^2} = 0.068 \text{ ma/cm}^2 \) 20-25 °C
  - Cold crank test: \( \frac{680000\text{ma}}{2200\text{cm}^2} = 309 \text{ ma/cm}^2 \) -18 °C

- Low leakage current is required to accurately measure separator resistance
  - Barrier resistance > 9 ohm
  - Multiple piece separator stacks give artificially low values

- Soak ER vs BCI test method
  - Time and temperature
Electrical resistance of a PE/SiO₂ separator is traditionally measured using the Palico Low Resistance Measuring System:

- **R_{SES}**: the areal resistance of the Separator-Electrolyte System (SES)
- **R_{Palico}**: The resistance value in milliohms measured by the Palico instrument times the area of the aperture (32.3 cm²)
- **R_{E}**: The areal resistance of the electrolyte that would occupy the same volume as the SES

\[ R_{SES} = R_{Palico} + R_{Electrolyte} \]
With knowledge of acid and separator resistivities, one can calculate overall resistance for the separator-electrolyte system (SES) with different separator profiles by using a parallel-series circuit model.

\[
\frac{1}{R'_T} = \frac{1}{R'_{\text{major}}} + \frac{1}{R'_{\text{bw}}} + \frac{1}{R'_{\text{minor}}}
\]
## ER CONSIDERATIONS

<table>
<thead>
<tr>
<th>162 x 0.80 x 0.25 GE</th>
<th>STD 2.6</th>
<th>LR</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palico ER (mΩ cm²)</td>
<td>92</td>
<td>55</td>
<td>-40.2%</td>
</tr>
<tr>
<td>Electrolyte (mΩ cm²)</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Sep-Elect-System (mΩ cm²)</td>
<td>192</td>
<td>155</td>
<td>-19.3%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>162 x 0.80 x 0.15 GE</th>
<th>STD 2.6</th>
<th>LR</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palico ER (mΩ cm²)</td>
<td>62</td>
<td>38</td>
<td>-38.7%</td>
</tr>
<tr>
<td>Electrolyte (mΩ cm²)</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Sep-Elect-System (mΩ cm²)</td>
<td>162</td>
<td>138</td>
<td>-14.8%</td>
</tr>
</tbody>
</table>

* Electrolyte resistance = 1250 mohm-cm x 0.08 cm = 100 mΩ cm²
R[SES] VS BW THICKNESS

Advanced Development approach
Assume each cell has 6 positive and 6 negative plates

- 5” x 6” electrodes (194 cm²)
- 161 x 1.0 x 0.15 mm separator; STD 2.3; 210 mohm cm² at -18°C
- Cell resistance from SES = 210 mohm cm² / (11 x 194 cm²) = 0.1 mohm
- Battery resistance attributable to separator system = 6 x 0.1 mohm = 0.6 mohm

CCA: 600 amps x 0.0006 ohm = 0.36 Volts

If STD 2.3 is changed to LR separator, voltage drop = 0.23 volts
If separator is removed and acid only between plates, voltage drop = 0.21 volts
Electrolyte resistance varies strongly as a function of temperature while the resistance of the metallic components is nearly constant.

A linear regression of battery resistance versus electrolyte resistivity gives the electronic resistance as the y-intercept as resistivity goes to zero.

Reference: James Klang, BCI 121st Convention, Las Vegas, May 3-6 2009
Electronic resistance is much greater than ionic at room temperature.

Ionic resistance becomes significant at low temperature.

Reference: James Klang, BCI 121st Convention, Las Vegas, May 3-6 2009
SUMMARY

- ER, the resistance to ion flow through the separator, is one of the most important characteristics of the separator, especially for high rate uses such as SLI and start-stop vehicle applications.

- Separator ER is a function of design, composition, and pore structure.

- ER is a difficult measurement to make and requires attention to detail.

- ENTEK has developed a simple, but effective, model for ER that is predictive for different geometries and can be included in battery level models used by our customers.

- The separator contributes approximately 5% of the battery resistance at room temperature and 10-15% at low (-18°C) temperature.