Supporting the deployment of safe Li-ion stationary batteries for large-scale grid applications

Advanced sensors

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CEA

Düsseldorf, 10 March 2015
CEA in a few words

- Nuclear energy
- Defense programs
- Fundamental Research
- Technological Research for industry
- Micro-nanotechnologies for information and communication
- Embedded and Interactive Systems
- New technologies for energy and nanomaterials ~1400 p.

- 10 research centers
- 16 000 p.
- 4B€/yr budget

10 Mar 2015
STALLION–STABALID seminar, Düsseldorf
CEA-LITEN institute: New technologies for Energy

4 DIVISIONS

Solar/building/smart grids

Electromobility

Thermal/biomass/H₂

Nanomaterials
The sensors used

**Electrochemistry**
- Current
- Voltage
- Impedance

Determination of battery state by electrical measurements

Impact of battery state and electrical solicitation on temperature

**Temperature**

After discharge at 3C

**Acoustic emission**

Li-ion batteries generate sounds during their activity
- Thermal expansion
- Li insertion
- Gas evolution

**Deformation gauges**
The sensors used: deformation gauge

**Principle**

- Small resistive circuit made of several coils which extend under the influence of a local deformation of the structure on which it is closely attached.

\[
\text{Resistance } R = \rho \frac{L}{S} \\
\frac{\Delta R}{R} = K \frac{\Delta L}{L} = K \varepsilon
\]

- \( \rho \) = resistivity
- \( L \) = length
- \( S \) = cross-section
- \( \Delta R \) = resistance variation
- \( R \) = resistance of the gauge
- \( K \) = gauge factor
- \( \varepsilon \) = strain

- Gauge resistance proportional to the extension of the measuring point
- Measurement with Wheatstone bridge to increase precision: resolution \( 1 \, \mu m/m \)
- Use of rosette gauge to measure deformation in several directions
The sensors used: deformation gauge

Application to Li-ion batteries

- Electrochemical “breathing”
  - Depends on the nature of the active material
  - Amplitudes linked to the internal design (winding, mandrel)

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Positive</th>
<th>Negative</th>
<th>Global volume variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active material</td>
<td>Li$_x$Ni$_1/3$Co$_1/3$Mn$_1/3$O$_2$</td>
<td>Li$_x$FePO$_4$</td>
<td>Li$_x$C$_6$</td>
</tr>
<tr>
<td>Volume variation</td>
<td>-3.8%</td>
<td>-6.5%</td>
<td>+11</td>
</tr>
<tr>
<td>Technology</td>
<td></td>
<td>x</td>
<td></td>
</tr>
<tr>
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<td></td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

- Swelling due to the increase of the internal pressure (gas emission)
  - Dependent on the volume of gas (solvents, potential windows)
  - Continuous dilation expected during aging
The sensors used: acoustic emission

→ Types of phenomena that can be recorded:

- \(H_2\) Bubbles
- NiMH
- Cracking MH particules
- SEI formation

S. Didier-Laurent, and al., JPS, Vol179, 1, (2008), 412–416

Tests performed

» Different cell chemistries and designs
  
  Pouch, LTO/NCO  
  15 Ah
  
  Pouch, LTO/LFP  
  22 Ah
  
  Cylindrical, C/LFP  
  15 Ah

» Electrical tests *(not presented here)*
  
  » Optimisation of sensor attachment and position on the cell
  
  » Evaluation of SOC / SOH indication by sensors
  
» Safety tests in ARC
  
  » Thermal stability: overheating up to thermal runaway
  
  » Overcharge in adiabatic condition (worst case)
Thermal stability tests

- Performed in an Accelerated Rate Calorimeter (ARC)
- Overheating up to thermal runaway

**Thermal runaway protocol**

- Temperature (°C)
- Heat-Wait-Seek Mode
  - Observation: 20 min
  - $T^\circ$ step: 5°C
- Exothermic mode
  - Sensitivity: 0.020°C/min
  - Thermal runaway temperature
- Experiment stop
- Heating rate: 3.0°C/min
- Time (min)
Very strong deformation: signal saturation

Deformation begins around 45°C/ thermal runaway 90°C

→ signal different enough from normal operation to be used by BMS
Thermal stability tests / Deformation gauge

» Large deformation measured
   → Swelling of the pouch

» No explanation about the opposite behavior of J1 and J3 (yet symmetric)
   → Pouch deformation too random

Thermal runaway = 90°C
Thermal stability tests / Acoustic emission

→ ARC is highly a “polluted” environment: noise in terms of mechanical waves (ventilation/electromagnetic)

Cylindrical, C/LFP

1: Thermal runaway seeking
2: Beginning of Thermal runaway
3: Background AE
4: Triggering of ventilation
5: Background AE

→ Suppress ventilation noise
→ Post-treatment required
→ Blank test with aluminum tube
Thermal stability tests / Acoustic emission

» Removal of background noise from the ARC

Identification

Clustering

Cylindrical, C/LFP
Overcharge tests

» Initial standard charge @C/2

» Overcharge @1C with floating 2 x Vmax
  » Target 200% overcharge
  » Stop if temperature increase >10°C/min

» Tests done in ARC for thermal and safety aspect
  » ARC blast box as a container
  » Adiabatic calorimeter: worst case (no heat dissipation)
Overcharge tests / Deformation gauge

» Simultaneous increase of deformation and temperature

» Large deformation recorded on pouch cell

Pouch, LTO/NCO

Simultaneous increase of deformation and temperature
Large deformation recorded on pouch cell
Overcharge tests / Acoustic emission

» 120%: Start of AE

140%: Rise of AE

160%: High level energy AE

» 140%: High level energy AE

» Rise of EA at 4.1V (55°C) _140% overcharge

» 160% of overcharge: large high level energy

Predictive detection of degradation mechanism

Interest of acoustic emission to have BMS with overcharge detection

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Overcharge tests / Deformation gauge

- Earlier detection than with temperature sensor
- Signal saturation due to wide deformations
Overcharge tests / Acoustic emission

105%: Start of AE

113%: Rise of energy

117%: Large Rise of AE???

» Rise of EA at 5.6V (40°C)

» Predictive detection of degradation

Interest of acoustic emission to have BMS with overcharge detection
Overcharge tests / Acoustic emission

104%: Start of AE

- Rise of EA at 104% overcharge with no high level energy AE
- Cell showed electrolyte leakage

Plateau at 4.5V: Electrochemical behavior different from the prismatic C/LFP cell

Cylindrical, C/LFP
**Overcharge tests / Acoustic emission**

- **105%**: Start of AE
- **108%**: Rise of AE
  - 107%: Rise of acoustic hits at plateau of 4.7V
  - 113% (42°C): High energy ??
- **113%**: High level energy AE

- Strong signal measured after temperature decrease
- No opening of the cell
Conclusions: sensors for SOS indication

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<th>Thermal stability</th>
<th>Overcharge</th>
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<tbody>
<tr>
<td><strong>Acoustic emission sensors</strong></td>
<td>Early detection&lt;br&gt;Data treatment and calibration required</td>
<td>Early detection&lt;br&gt;Absolute energy as parameter</td>
</tr>
<tr>
<td><strong>Deformation gauges</strong></td>
<td>Large temperature variation alters measurement reliability</td>
<td>Strong signal&lt;br&gt;Simultaneous or before temperature rise</td>
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Thank you!
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