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Degradation Mechanisms in Cylindrical Li-Ion Batteries During Cell Cycling

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Battery Power 2017

Dallas, May 17th

1: CIC energiGUNE energy cooperative research centre
2: IK4 IKERLAN Research Alliance

2017

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1. **CIC Energigune**
2. **Motivation**
3. **Cell Characteristics**
   Ageing Conditions
4. **Ageing and Post-test Analysis**

Where are we...?

Vitoria-Gasteiz, capital of the Basque Country

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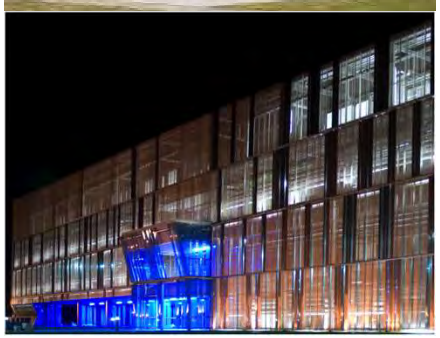

CIC energi GUNE energy cooperative research centre

Opening Date: Sept 2011

About 80 researchers

Electrochemical & Thermal Energy Storage

From Fundamental to Industrial Research

❑ Infrastructure:

- ✓ Synthesis laboratories (solid state and organic chemistry)
- ✓ Characterization laboratory (ICP-AES, TGA/DSC, FTIR, UV-vis…)
- ✓ Platforms (solid state NMR, XRD, EM…)
- ✓ Testing laboratory (potentiostats, Maccor, climatic chamber)
- ✓ Dry room (prototyping)
- ✓ Computational studies group

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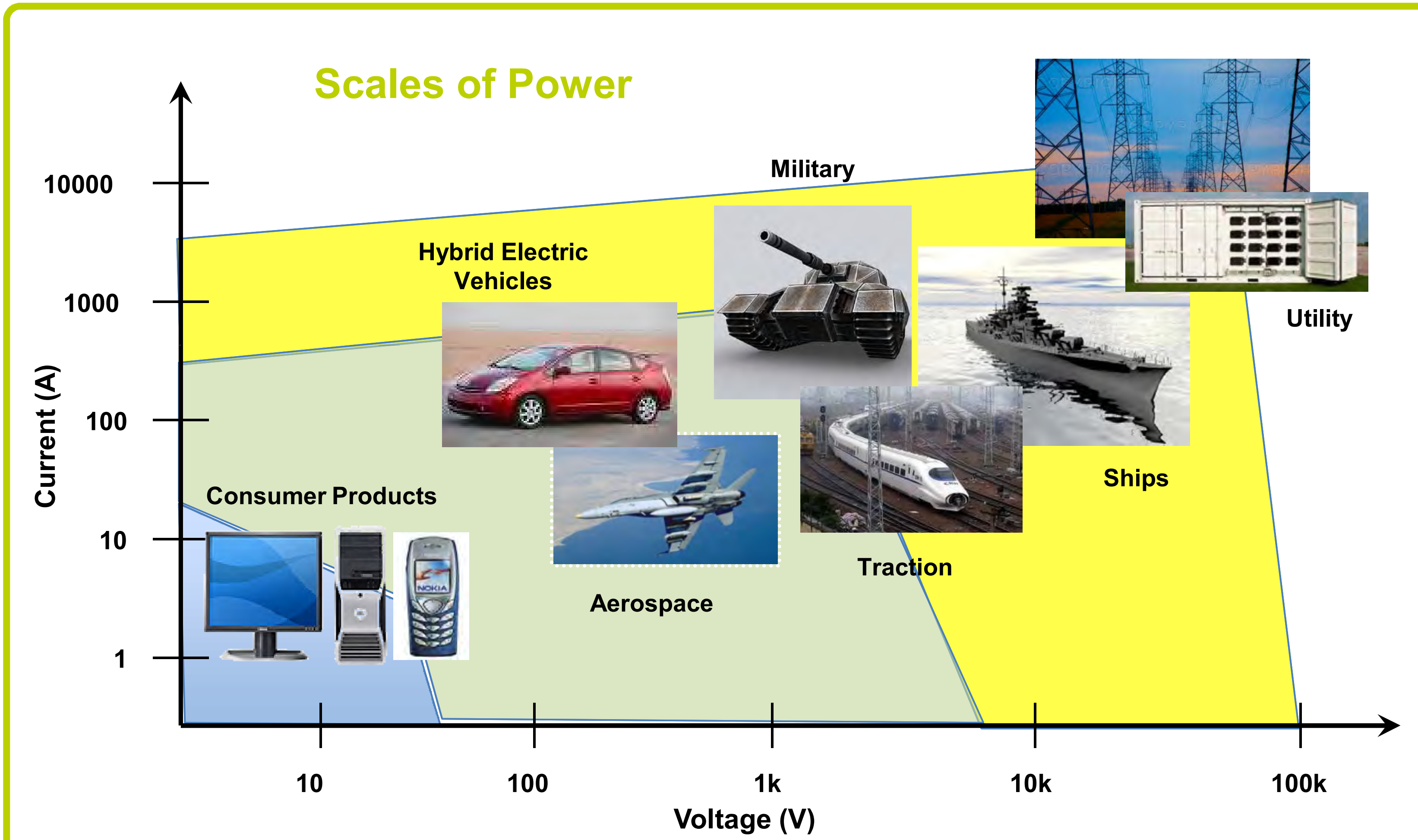
Battery Market Evolution…
…driven by Application Needs

Broad Range of Applications with various Energy Requirements



Li-ion Batteries: a High Concentration of Energy in a Small Casing...

From Portable Electronics:

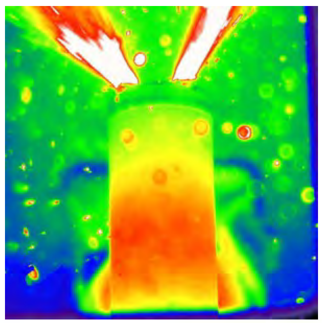
Performance** and **Ageing** will **differ** based on the type of **device, application,** and **technology.

To Transportation Applications:

Motivation

What is the Driving Force for Post-test Analysis?

- Better understanding the reasons behind battery failure
- What are the main degradation mechanisms occurring during ageing?
- How can we use this knowledge to improve cell manufacturing?
- Determination of the condition of use for an extended life

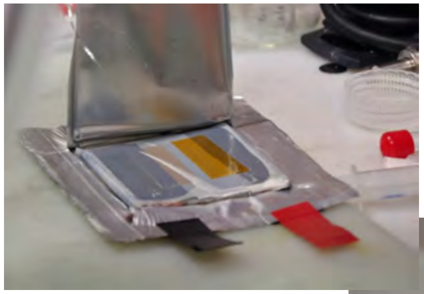


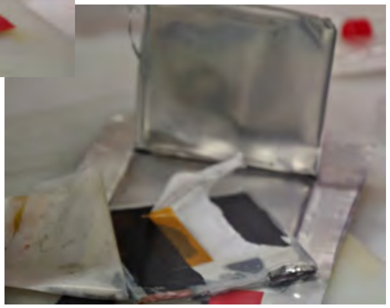
Battery Post-test Analysis

Critical Steps for Efficient Analysis

Ageing Conditions before cell opening :

- Calendar vs. Cycling
- States Of Charge, Depths Of Discharge, C-rates
- Cycling Environment (temperature, humidity, etc.)





Steps for post-test analysis* :

1º) Observe the aged cell

2º) Open the discharged cell

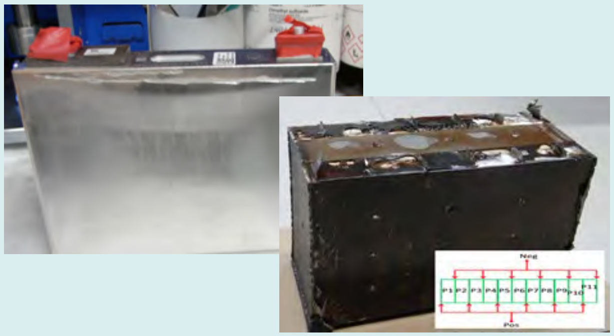
3º) Analyze the various components

* T. Waldmann et al. J. Electrochem. Soc. 2016, 163, A2149

Our Capabilities

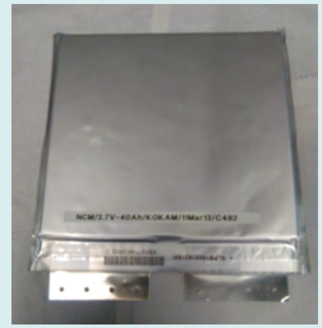
Which Type of Cells Can We Open?

Prismatic Device



Batteries: 40 Ah, ~3.7 V
Supercaps: 132 F, 24V

Pouch Cell

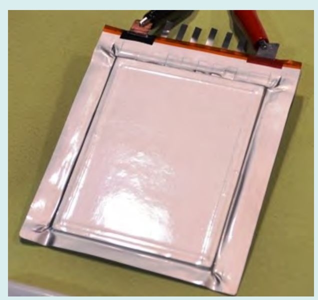


Batteries: 40 Ah, 4.2 V
Supercaps: 480 - 3000 F, 2.7V

Cylindrical Device

Batteries 2.3 Ah, 3.3 V
Supercaps 1-3000 F, 2.7V

Solid State Battery



300 mAh, 3.75 V

Coin Cell

< 1 mAh, 2.3 – 3.7 V

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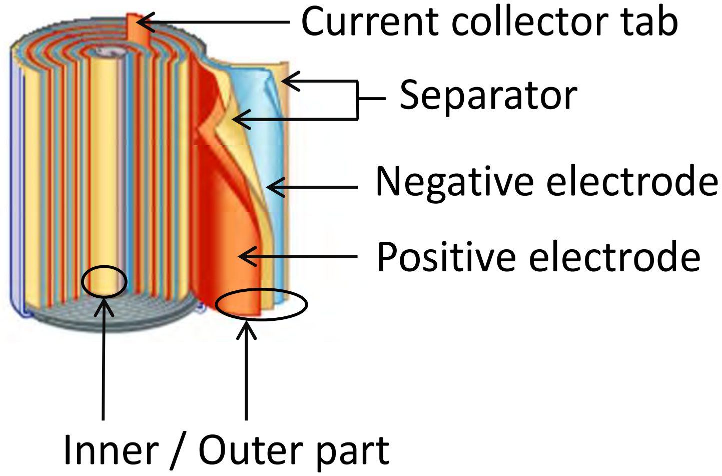
Cell Characteristics and Ageing Conditions

Li-ion Battery for High Energy Density

Selected system:

- $LiFePO_4$ / Graphite chemistry
- 2.3 Ah nominal capacity
- 26650 cylindrical cell



Cycling Ageing:

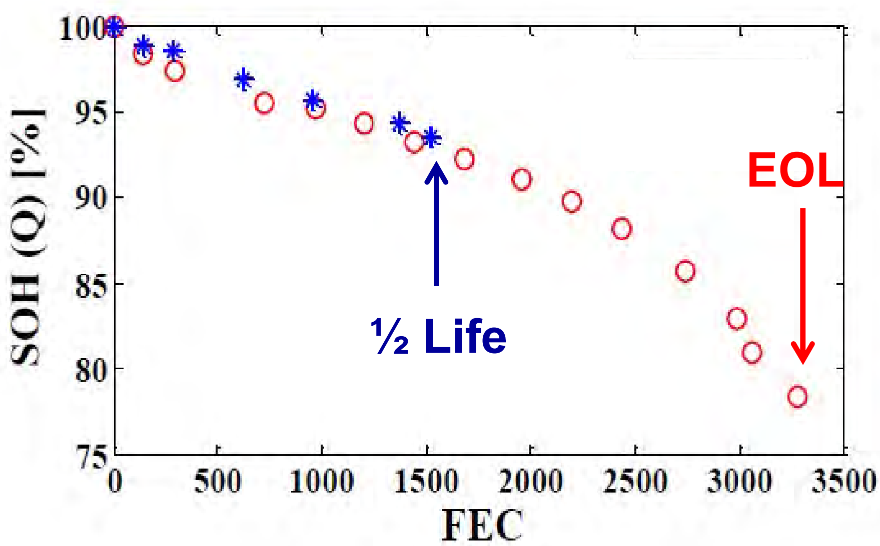
- 1 C → 2.3 A / cycle
- 30ºC in a climatic chamber
- 100 % DOD

→ **Impact of Large Cycling Amplitude on Cell Performances**

Post-test Analysis

Selection of Cells to Be Opened

- **Pristine Battery**
  as received from the manufacturer, discharged
- **Beginning of Life (BOL)**
  after conditioning and internal procedure for first check-ups
- **Half Life (½ Life)**
  aged for 1521 FEC, 93% SOC
- **End of Life (EOL)**
  aged for 3276 FEC, 79.5% SOC



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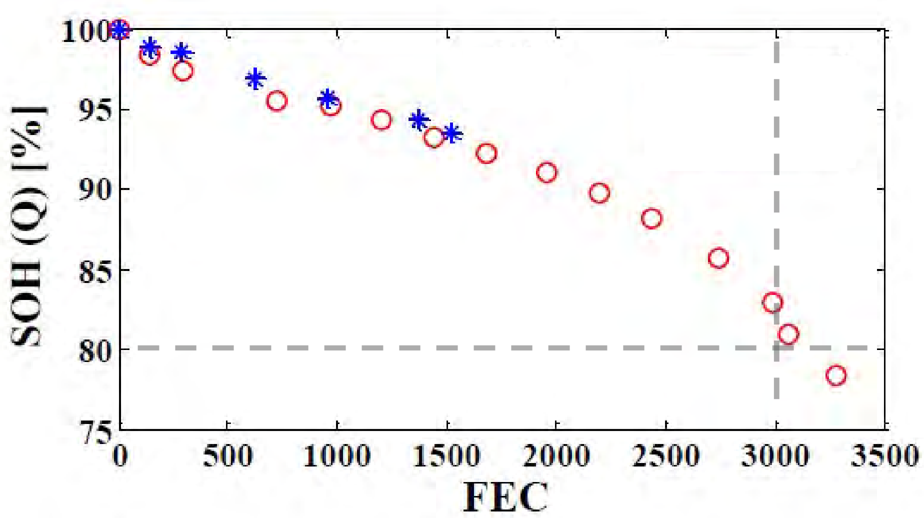
Cycling at 100% Depth of Discharge

Change in State of Health



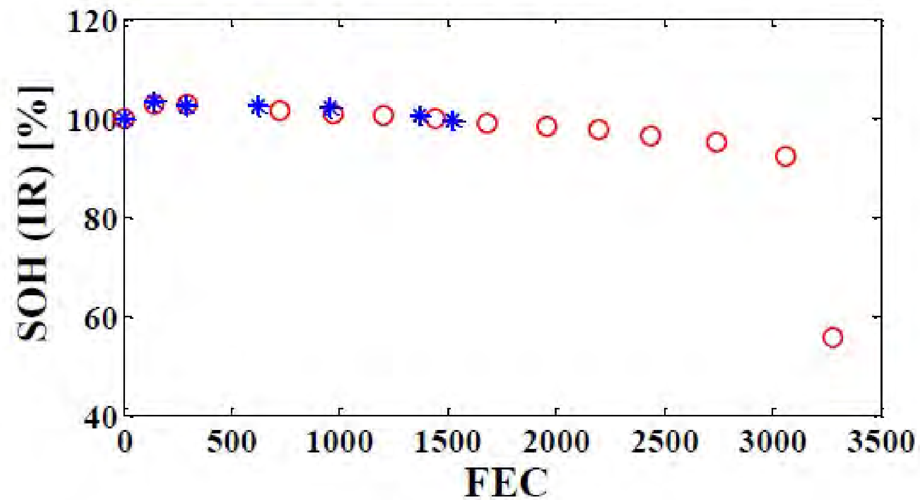
Capacity evolution:

- End of Life after 3000 cycles
- Linear fading < 2500 cycles
- More severe capacity loss afterwards

Internal Resistance:

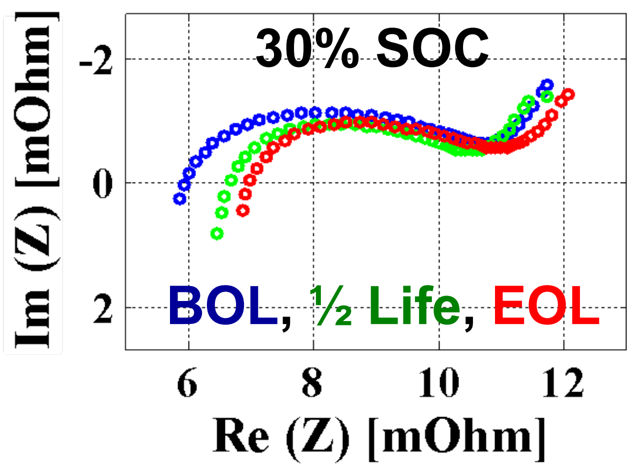
- Stable internal resistance
- Sharp decrease at EOL

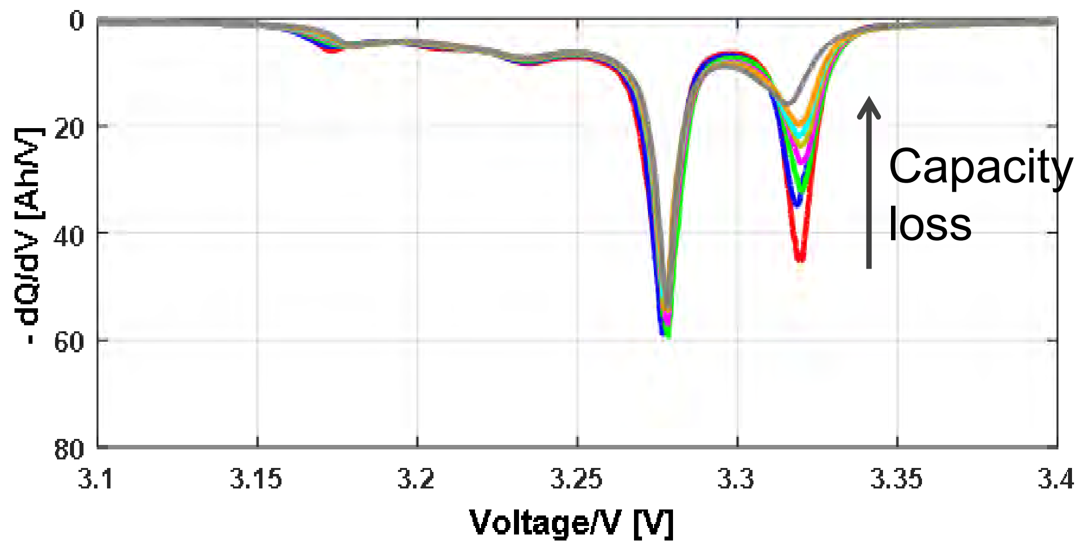
→ Change in degradation mechanism over cycling

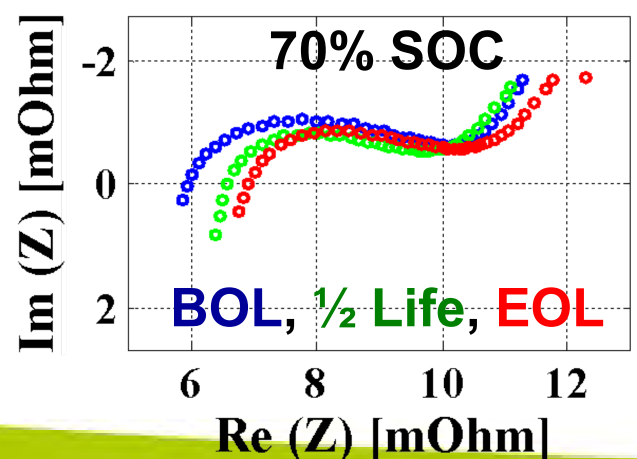


Cycling at 100% Depth of Discharge

Cell Degradation: 1st Hints







- **SOC:** no effect on cell resistance
- **Cycling:** increase of electrolyte resistance
  → Possible growth of SEI layer
- **Cycling:** Fading of anodic capacity
  → Possible degradation of graphite

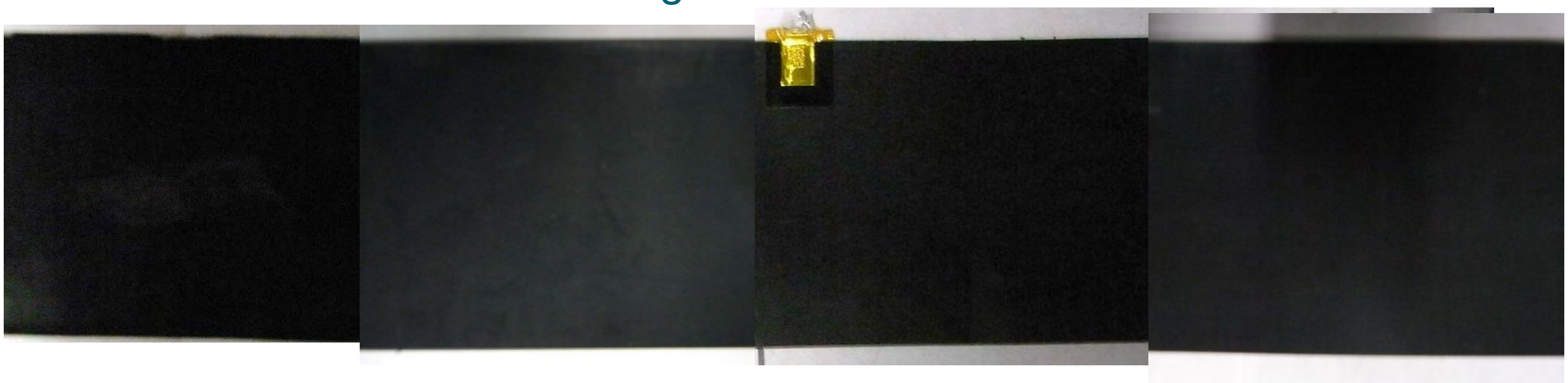
Opening of the Selected Cells

Visual Observations

Pristine **BOL** **½ Life** **EOL**

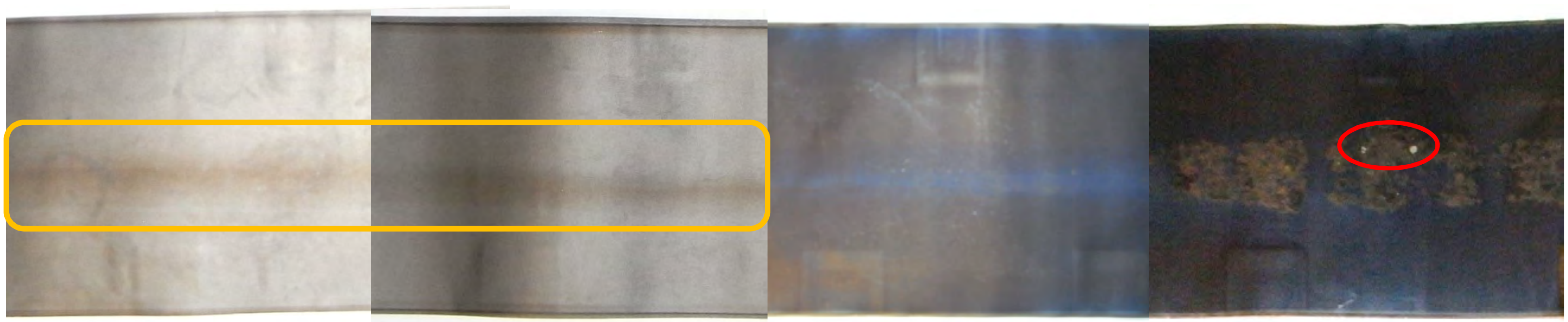
- **LFP cathode:** No visual degradation observed

Positive



- **Graphite anode:**

Negative



Golden coloration observed in center (discharged state)

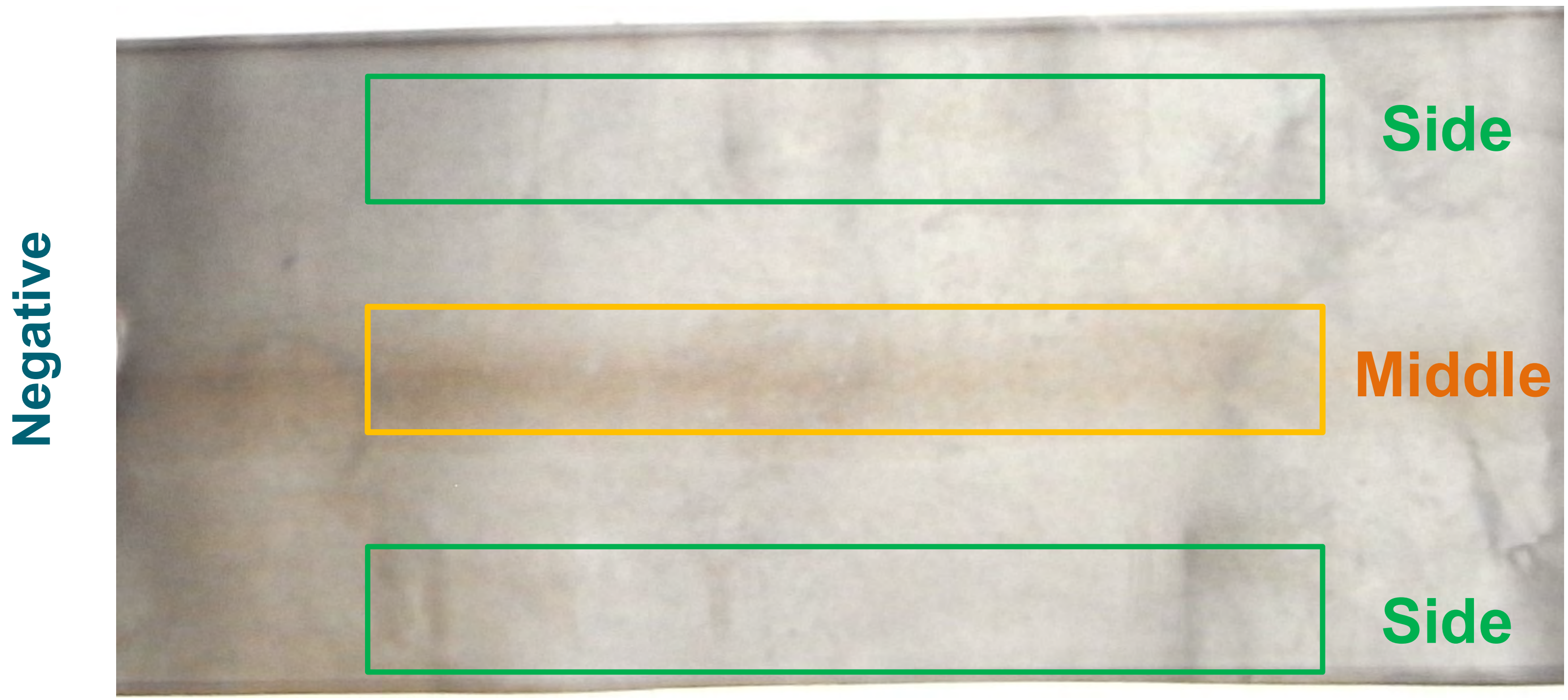
Change in coloration

Presence of plated metallic Li ?

Post-test Analysis

Mapping of Anode Electrode

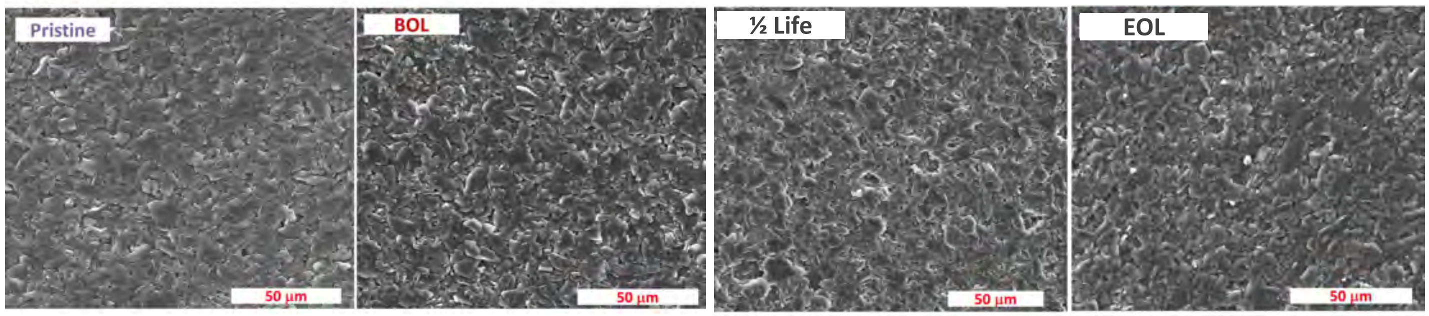
- **Graphite anode:**



Microstructural Analysis

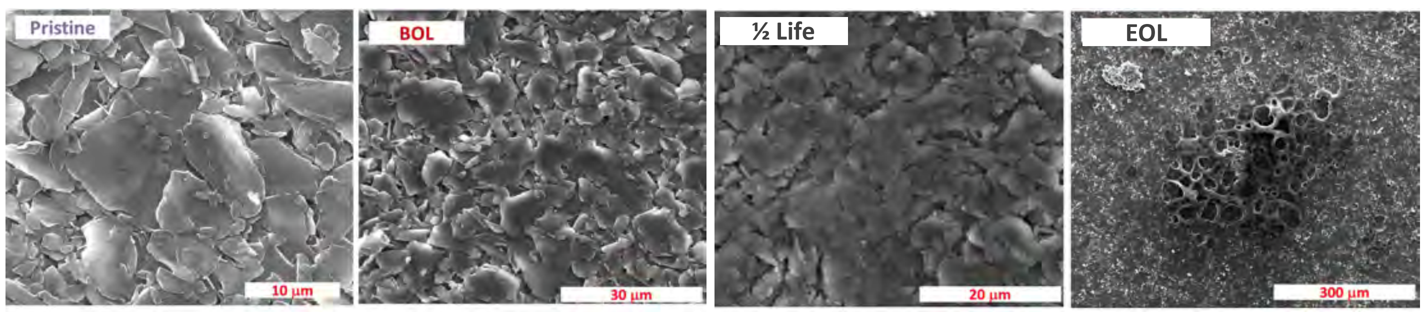
Graphite Anode: Summary

Side



- Formation of stable SEI layer

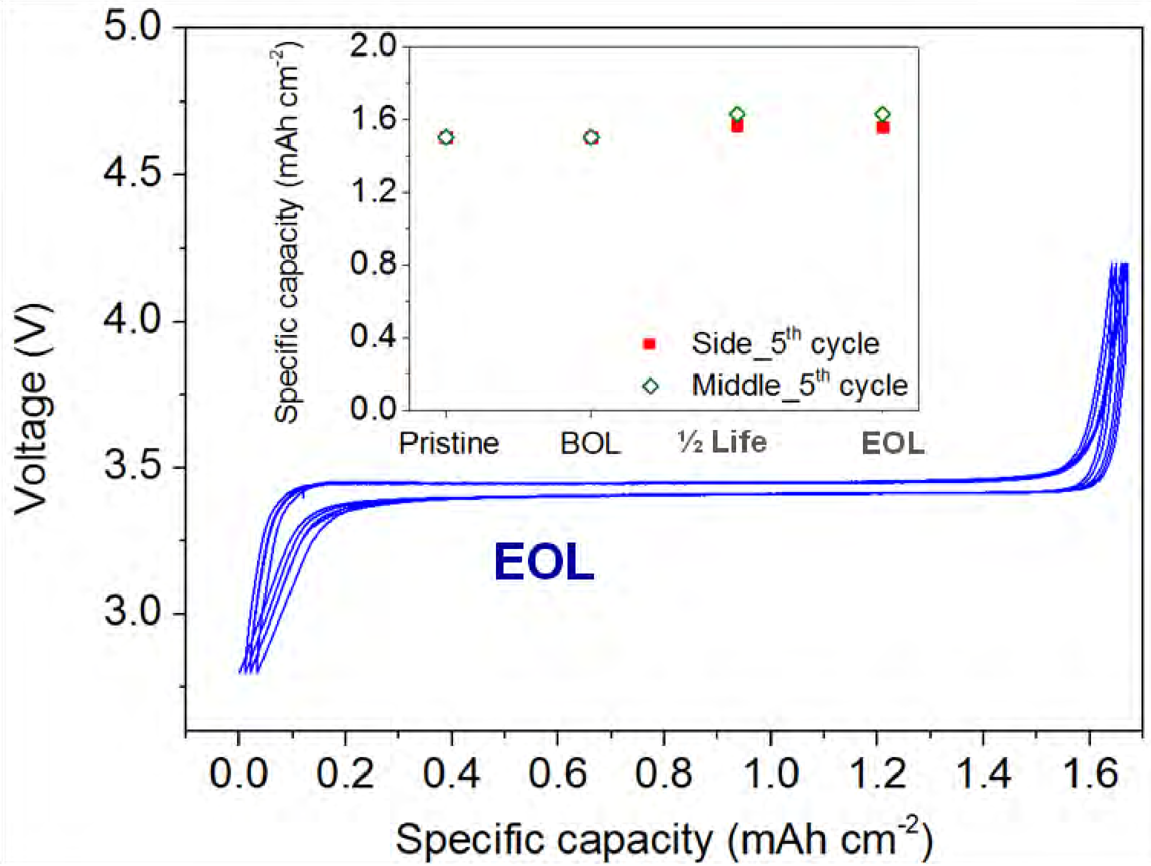
Middle



- SEI layer growth due to further electrolyte decomposition
- Potential gas formation due to degradation of SEI layer

Electrochemical Characterization

$LiFePO_4$ cathode vs. Li metal

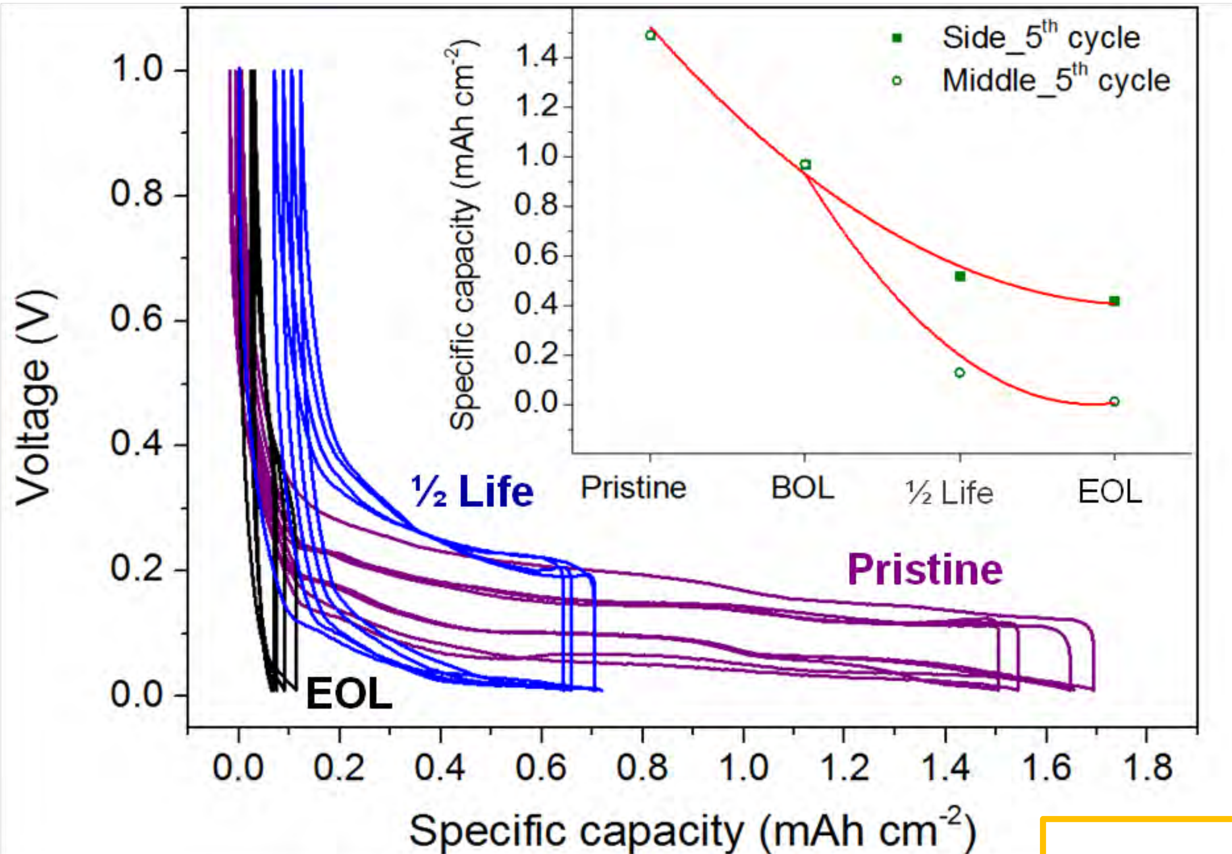


- **Upon ageing:**
  No loss of capacity
  No additional polarization

→ No degradation of LFP cathode

Electrochemical Characterization

Graphite anode vs. Li metal



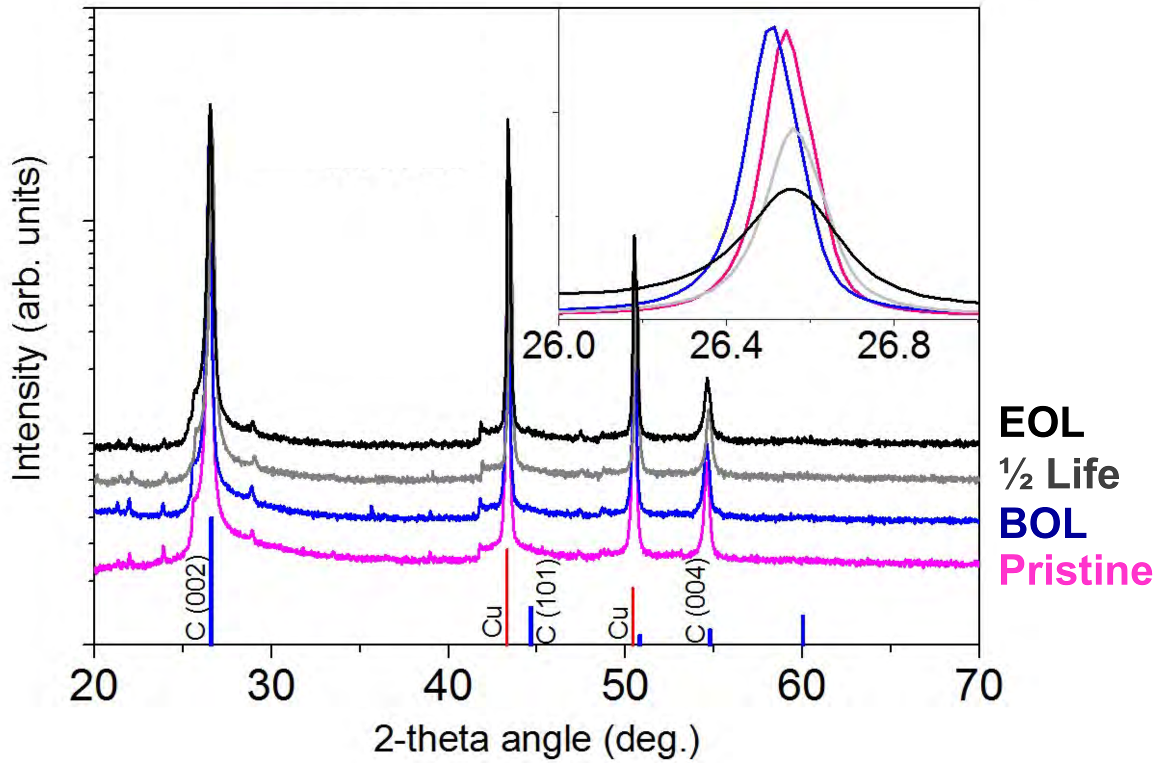
- **Upon ageing:**
  Loss of capacity
  Cell polarization

- **Increased degradation in the middle:**
  Side: 60% loss
  Middle: 95% loss

→ Degraded SEI layer on Graphite Surface Prevents Li^+ Insertion into Graphite

Structural Analysis

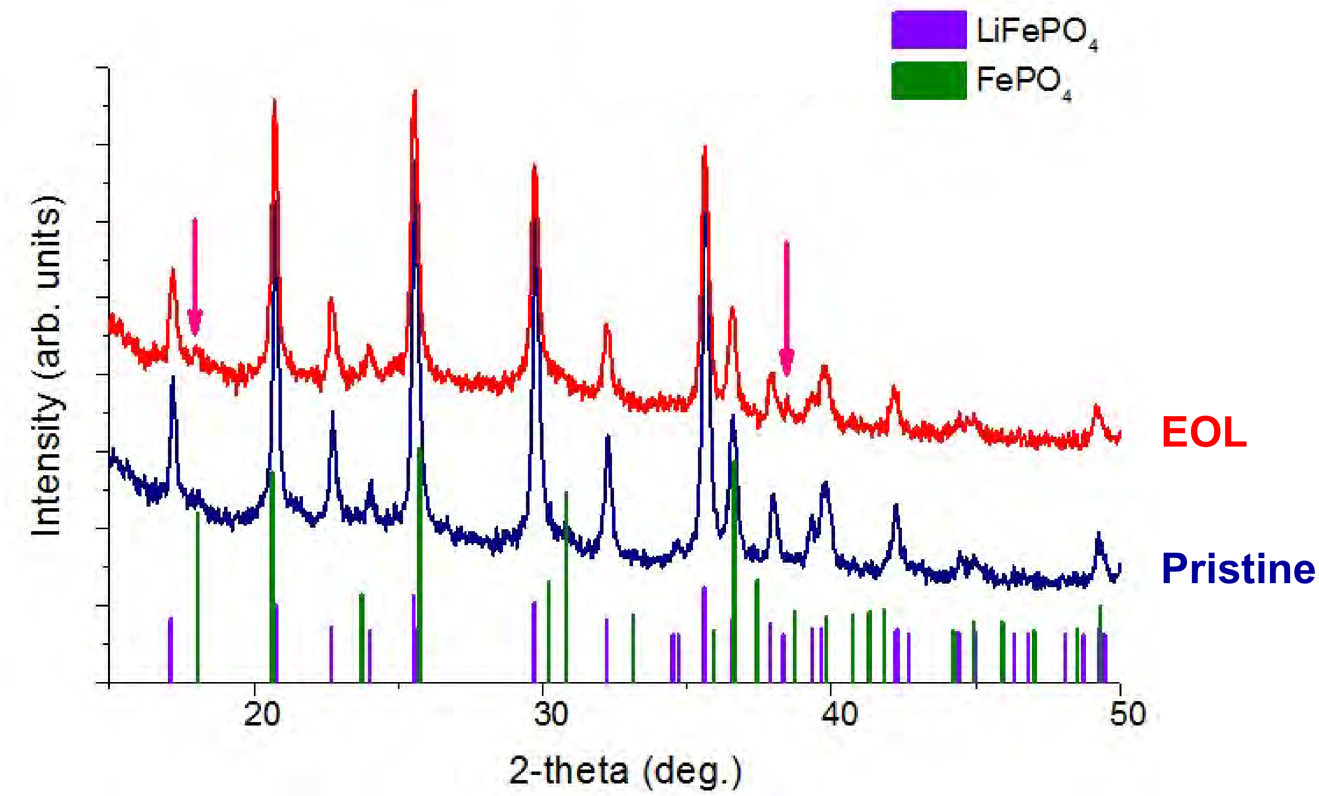
Graphite Anode



- No difference between side and middle of electrode
- No shift of (002) peak → **No Li^+ getting trapped upon ageing**
- Peak intensity reduction → **Growth of amorphous layer on top of graphite surface**

Structural Analysis

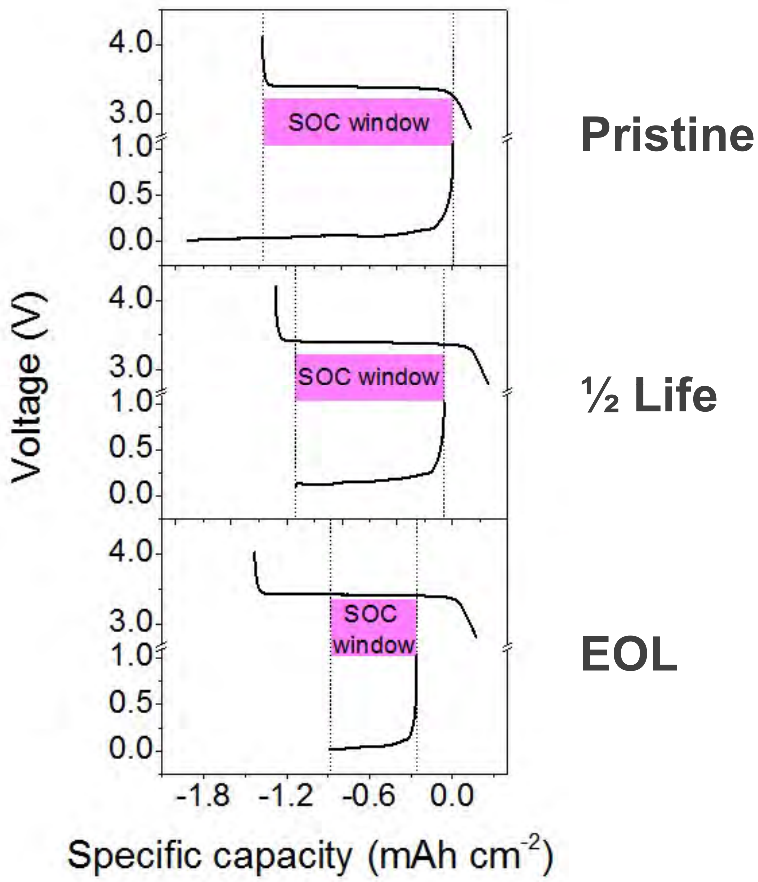
$LiFePO_4$ Cathode



- No structural changes observed upon ageing
- EOL: Presence of some $FePO_4$ after cell discharge
  → **some Li^+ loss, to be related to Li plating at graphite surface**

Evolution of SOC Window

In Particular for the Middle of Cell



- Growth and degradation of SEI layer at graphite electrode
- Li^+ loss due to electrolyte decomposition and Li plating

→ Diminution of available capacity within the voltage limits

Degradation Mechanisms during Cycling

Cylindrical cell $LiFePO_4$ / Graphite 2.3 Ah

- Ageing performed at 30ºC, 1C, 100% DOD
- $LiFePO_4$ electrode: no degradation observed
  → Excellent material
- Graphite electrode appeared inhomogeneous after initial discharge
- Decomposition of electrolyte on graphite surface to form SEI
  → Linear cell capacity fading
- Degradation of SEI layer on graphite surface
  → Accelerates cell degradation due to inactivity of graphite
  → Reduction of operating voltage window

Post-test Analysis Required to Understand Battery Failure!

Thank you for your attention!

For more on our research....

- Cycling Ageing:

  E. Sarasketa-Zabala et al., J. Phys. Chem. C, 2015, 119, 896.

  Understanding Lithium Inventory Loss and Sudden Performance Fade in Cylindrical Cells during Cycling with Deep Discharge Steps

- Calendar Ageing:

  A. Iturrondobeitia et al., J. Phys. Chem. C, 2017, under revision.

  Post-Mortem Analysis of Calendar Aged 16 Ah NMC/Graphite Pouch Cells for EV Application

  B. P. Matadi et al., J. Electrochem. Soc., 2017, 164, A1089

  Effects of Biphenyl Polymerization on Lithium Deposition in Commercial Graphite/NMC Lithium-Ion Pouch-Cells during Calendar Aging at High Temperature

- Review:

  T. Waldmann et al., J. Electrochem. Soc. 2016 , 163, 10, A2149-A2164

  Review—Post-Mortem Analysis of Aged Lithium-Ion Batteries: Disassembly Methodology and Physico-Chemical Analysis Techniques


COMING SOON
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2nd – 5th July 2017 Vitoria-Gasteiz, Spain
The 3rd International Forum on Progress and Trends in Battery and Capacitor Technologies


XXXVIII GE-RSEQ
XIX EIB
XXXVIII Reunión del Grupo de Electroquímica de la Real Sociedad Española de Química
XIX Encontro Ibérico de Electroquímica
5th – 7th July 2017 Vitoria-Gasteiz, Spain

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