3rd EFB + Heat Workshop Review

Bruges, 22-23rd May 2019

Bruges, at a Glance

- **Cosponsored by CENELEC and CBI**
  - Developed and orchestrated by Dr. Eckhard Karden
- **Attendees joining from:**
  - Academia (ex. Fraunhofer Institute, University of Aachen, etc.)
  - Battery Manufacturers (ex. Clarios, EPM, Fiamm, etc.)
  - Additive Suppliers (ex. Cabot, EnerG2, Hammond, etc.)
  - OEM (ex. Ford, PSA, etc)
  - Specification-Setting Committees (ex. CENELEC)
- **Workgroup Topics**
  A. Testing battery durability for start/stop microcycling
  B. Water loss and oxygen cycle in real-world EFB operation
  C. Measuring DCA and water loss in test cells ***[Highest Attendance in AM]***
  D. Test methods for battery durability in hot climate ***[Highest Attendance in PM]***
  E. Corrosion under PSoC microcycling conditions
  F. Measuring gas evolution directly

By The Numbers:

>88 = Number of Attendees

2 = Number of Days

6 = Number of Workshop Topics

6 = Hours of Plenary + Parallel Workshops

3 = Hours of Argonne Updates

11,675 = Max Miles Traveled by Attendee

A: Testing Durability for Start/Stop Microcycling

Moderator: Roberto Aliberti, Torsten Hildebrandt, and Christian Mondoloni

- **Negative lug thinning**
  - Not a real-world failure mechanism
  - A 2º effect of NAM sulfation which forces grid to sacrifice itself
- **Failure modes in different geographies**
  - Stratification/Sulfation/Undercharge
    - N. Europe, N. USA,
  - Cyclic Wear/PAM Degradation
    - Never dominant, but found everywhere to varying extents
  - Corrosion
    - S. Europe, S. USA, S. China
  - Noted that AM quality, not just geography, defines failure mode
- **Selecting Start/Stop batteries based on MHT results**
  - Low temp/mileage/S-S capacity: 640*C_n expected, +10-30% with no S/S
  - High temp/mileage/S-S capacity: 320-640*C_n expected, no increase with S/S off (change in failure mode to corrosion)
- **Request for standardized teardown procedure**

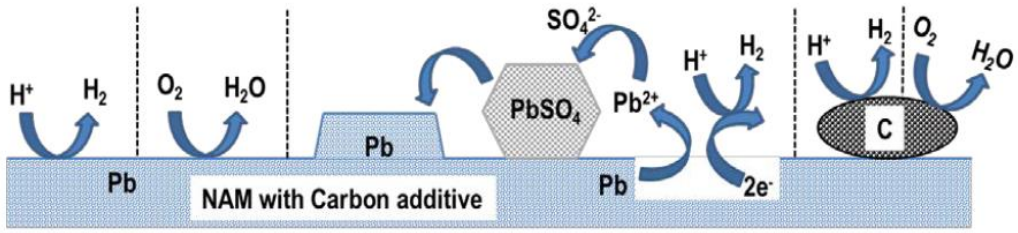
B: H_2O Loss / O_2 Cycle in Real-World EFB Operation

Moderators: Eberhard Meissner, Plamen Nikolov, Daisuke Hosaka

- **Continued Investigation of O_2 formation/reduction cycle in EFB**
  - Accepted as mechanism by which less water is lost than expected
    - Absorbs 1-2 mA/Ah in CC CHR, DCH, and RST
  - In high-temp EFB studies, O_2 bubble growth, diffusion, and solubility can be modelled to provide experimental evidence for the cycle
  - Seperator back web needs optimized for maximal O_2 availability
  - Temp. dependency test suggested, along with other evaluations
  - O_2 is detected at higher than stoichiometric amounts suggesting H_2 "leakage" limits recombination
  - Review of cycle in various battery designs (FLD, AGM) suggested

- **Parting Thought**
  - Can a battery be designed to maximize this oxygen cycle and lower water loss?

- ❑ Hydrogen evolution reaction on the surface of Pb;
- ❑ Hydrogen evolution reaction on the surface of Carbon;
- ❑ Oxygen reduction reaction on the surface of Pb – needs electrons; consumes additional current;
- ❑ Oxygen reduction reaction on the surface of C – needs electrons; consumes additional current;
- ❑ Oxidation of Pb with simultaneous formation H_2 gas and $PbSO_4$ – increase water loss;
- ❑ Subsequent reduction of the formed $PbSO_4$ back to Pb – needs electrons; consumes additional current and provokes NAM microstructure transformation



B: H_2O Loss / O_2 Cycle in Real-World EFB Operation

Moderators: Eberhard Meissner, Plamen Nikolov, Daisuke Hosaka

- **Experiments and models for NAM reactions during PSoC**
  - NAM non-homogeneity noted to create areas where self-DCH and gassing are possible
  - Fullsize-plate cell testing recommended to measure H_2/O_2/reference electrode potentials through microcycling
  - Effects of surface area increasing additives discussed
    - Increased surface area directly from additive (direct)
    - Increased Pb surface area brought about by additive (indirect)
  - Fast rate CV simulates PSoC and shows lower hydrogen evolution than steady-state overcharge situations

- **Why do EFB/EFB+C show similar H_2O consumption in microcycling?**
  - At 60 °C, over-voltages are biased for PAM gassing (O_2), PAM is often the same between EFB and EFB+C → *Gassing will be similar*
  - EFB produces more H_2 in urban, EFB+C produces more H_2 in highway cycling → *Gassing will be similar*

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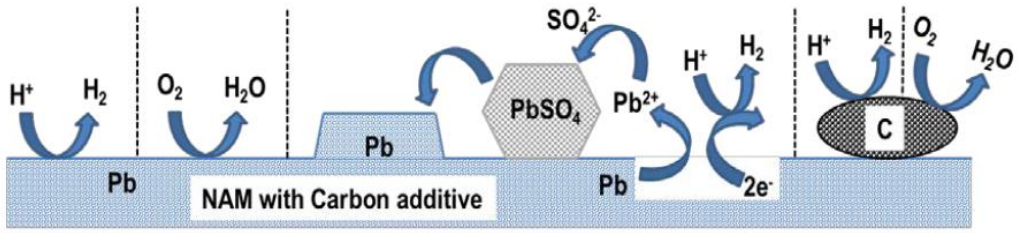
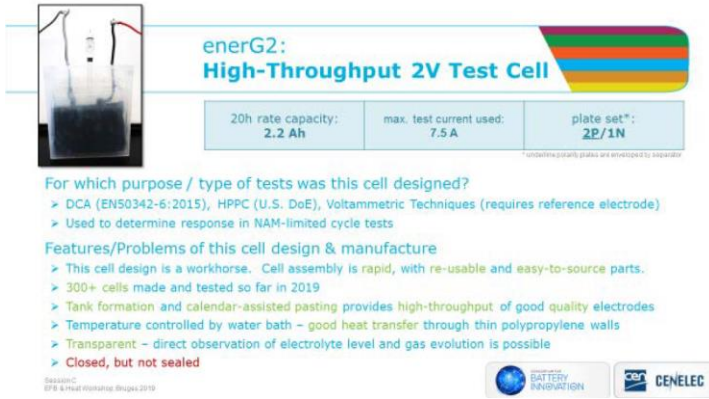


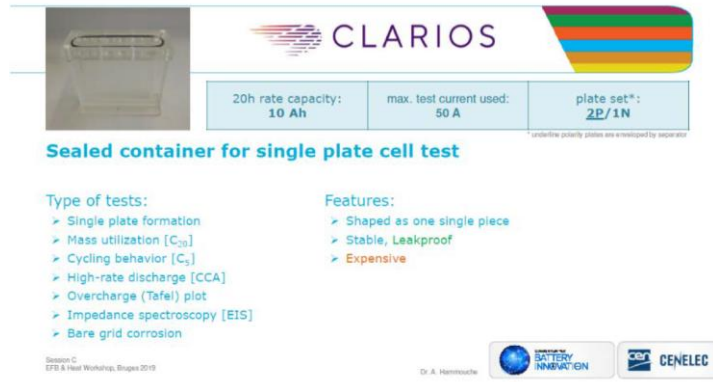
C: Measuring DCA and Water Loss in Test Cells

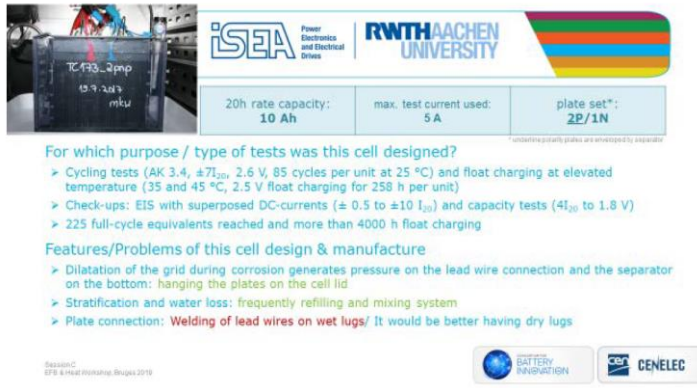
Moderators: Matt Raiford, Shane Christie, Adam Strong, Paul Everill, Sophia Matthies, Begum Bozkaya, Benjamin Hubner, Jesus Valenciano

- **Best practices for 2V cell manufacture**
  - Manual attracted much attention, but time not sufficient to red
  - New version distributed alongside workshop notes
  - Audio conferences planned to continue work on open items

- **Cell design for DCA measurements**
  - Frequently 2P/1N design to focus on NAM effects
  - Industrially MFR plates preferred for higher reproducibility
  - Connections are key, welding of wires to tabs recommended
  - Leak-free sealing vital for application-relevant observations
  - Void spaces in cells to be avoided:
    - Silica beads
    - Spacers
  - Heat uniformity during test is preferred
  - Acrylic instead of ABS for 3D cell printing







C: Measuring DCA and Water Loss in Test Cells

Moderators: Matt Raiford, Shane Christie, Adam Strong, Paul Everill, Sophia Matthies, Begum Bozkaya, Benjamin Hubner, Jesus Valenciano

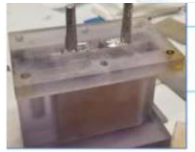
- **Running DCA tests in cells**
  - Cell quality is critically important
  - All participants sought to keep 2V design as close to 12V as possible
  - 2P/1N is sufficient, at least for comparative studies
  - DCA is best tested with field-relevant profiles (ex. 50342-6, Ford B)
  - PAM:NAM ratio AND AM:Electrolyte ratio are both critical
  - 2V cells correlate well to full-scale, but A/Ah magnitude is higher
  - Acid adjustment necessary to mimic 80% SoC if AM:E not balanced
  - DCA is limited by the NAM regardless of scale/geometry
  - DCA downscaling is instrument dependent but detailed in Appendix
- **Vapor-tight cell designs**
  - Rubber plugs > silicon around terminals
  - Pressurize cell (0.4 bar) to test for leaks
- **Water-consumption testing cell designs**
  - Water consumption is best measured from field-relevant protocols
  - New KLT at 75 °C is appropriate for water loss in PSoC testing (3-4w)
  - Use of eGas device will prove difficult on cell level; burette instead?

Fraunhofer ISC
New test cell for Lab scale

20h rate capacity:	max. test current used:	plate set*:
2.5 Ah	20 A	2P/1N

For which purpose / type of tests was this cell designed?
- Additive screening for negative and positive plates (such as carbon, silica, etc.)
- Applied tests: DCA (EN50342-6:2015), Run-in DCA (Test B, Ford), CA Test 2 (S 0101:2014), CCA (adapted from EN), Endurance Test 17.5 DoD (EN50342-6.2015), Charge Acceptance Test (VW 75073_2017)

Features/Problems of this cell design & manufacture
- Variable separators and spacers allow variable usage from 1N1P up to 3N2P
- Electrodes contacted via molten lead wire and soldered copper wire
- Dryout prevented by sealed lid coupled with degassing plug (vapour diffusion inhibited by flame retardant device)
- Usage of reversible hydrogen electrode (RHE) as reference for half-cell potential measurements
- Transparent lid
- Container formation, 36 h
- It should be optimized for tests at elevated temperatures



Black Diamond Structures:
Motorcycle-Scale 2V Cell

20h rate capacity:	max. test current used:	plate set*:
5.25 Ah	~40 A	3P/2N

For which purpose / type of tests was this cell designed?
- Additive screening
- EN 50342-6 DCA
- 17.5% DoD

Features/Problems of this cell design & manufacture
- PROS/CONS: Small size allows for high-throughput, plate ratio locked by defined case size, custom moulded contacts high-current stable, not good for water consumption, design is hard to "dump and refill" acid if protocol demands it
- PASTING: 1 kg PbO batch size, twisted-gate double-planetary mixer, hand-pasted, 32-36 h cure/dry protocol matching industrial partners, PAM plates are provided from a partner to remove variability from a second in-house built electrodes
- TERMINALS: Use "Hot-Pot2" hand-held smelters to melt pure Pb and Sn. Tabs are tin dipped, then plate stacks are manually pressed together and held upside down in a melted-Pb-filled, 3D-printed tab/post mould
- FORMATION: Case (polypropylene, polycarbonate) formed, 28h, 0.1C, 1.25 spgr acid (75 mL)
- QUALITY CONTROL: PbO free-Pb% and particle size, water purity to BS 4974 standards, acid <50ppm Fe, paste density/moisture content/crunch, paste weight per plate, dry plate weight

ArcActive:
Full-Size Automotive Cell

20h Rate Capacity:	Max Test Current Used:	Plate Set*:
60-80 Ah	750 A	6P/7N - 8P/9N

For which purpose / type of tests was this cell designed?
- Run-In DCA, CCA, DoD Cycling
- DCA [Ford Run-In (Test8), EN50342-6:2015], CCA [EN, SAE], DoD [17.5%, 50%]

Features/Problems of this cell design & manufacture
- Intent: Long-term / High Quality (~quantitative) / Sealed-cell Req Testing
- Case: ABS/ PolyCarb Lid (machined) / Epoxy Sealant (validate compatibility first!) / PolyCarb Spacers (if req'd)
- Construction: Tab-terminal strip + Cast Post (internally developed tooling) / Pocketed PE separators / *Mild* compression via spacers (subjective art)
- Terminals: DIN (cast) – necessary for high currents. Soldered Pb tab for voltage-connection (alligator clip) independent of current-lead connection
- Formation: In-Cell, multi-shot. 18-22 hrs.

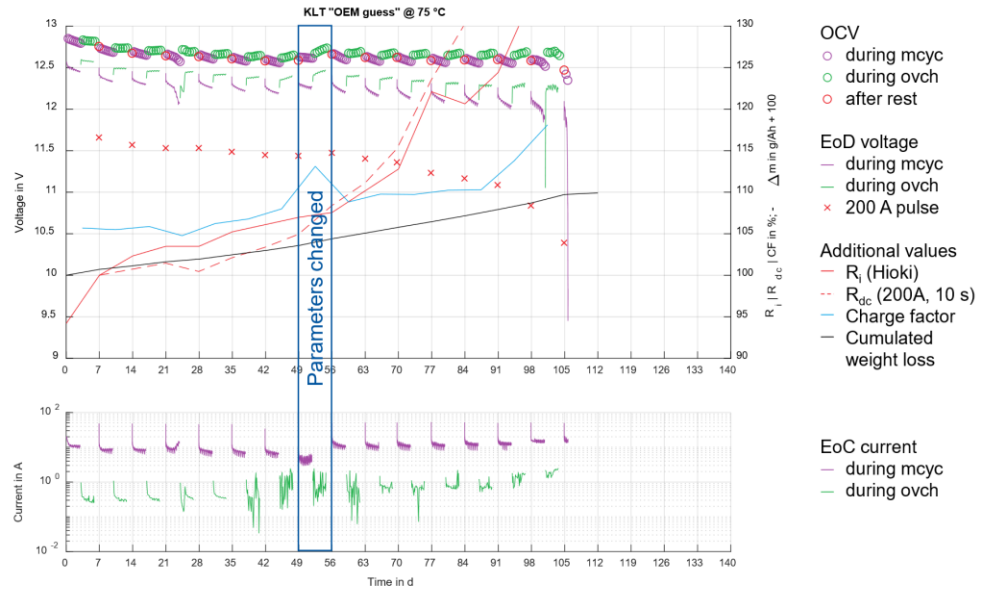
D: Test Methods for Durability in Hot Climates

Moderator: Eckhard Karden, Johnathan Wirth, Luca Brisotto

- **New Key Life Test (nKLT)**
  - Good traction, many companies are reviewing over Summer ’19
  - Additional test metrics added
  - Higher throughput version not chosen – less field relevant (less corrosion)
  - Target duration (weeks) not set, awaiting 2019 data
  - Excel sheet forwarded showing relevant KLT plot formatting
  - Expanding test for more grid types, AGM+C
  - Fleet testing required, unsure which geography (Vegas, China)

- **Li-Ion battery applicability to the nKLT**
  - Can 75 °C be tolerated?
  - Does the BMS protect or limit the battery during nKLT?
  - EPM (Bernd Engwicht)/Exide (Luca Brisotto)/Ford (Eckhard Karden) led conversation to find drop-in LiIon 12V battery and test via nKLT

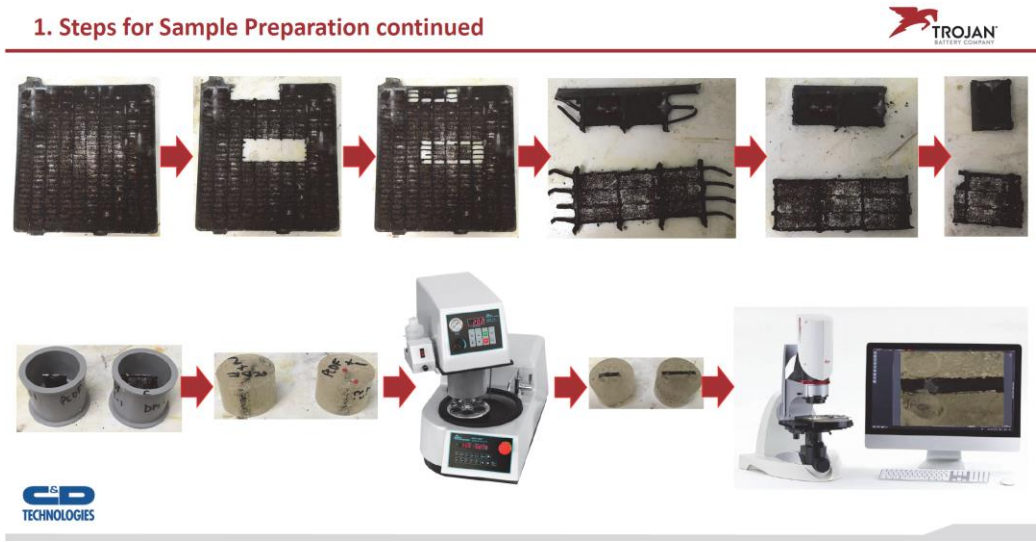
KLT „OEM guess“ @ 75 °C

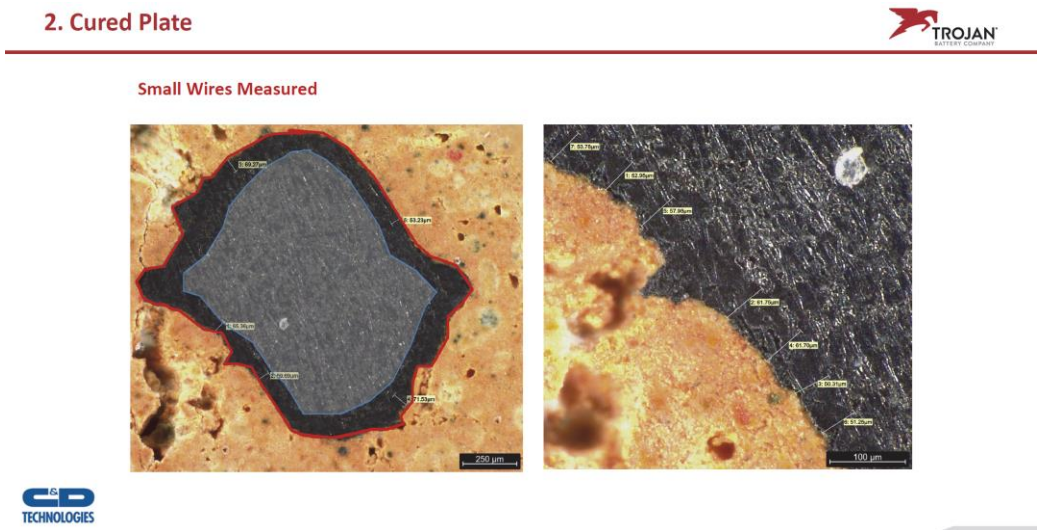


E: Corrosion Under PSoC Microcycling Conditions

Moderator: Jun Furukawa, Subhas Chalasani, Shawn Peng, Tim Fister

- **General discussion point**
  - Do microhybrid tests trigger the same corrosion processes as other tests, just to a different extent, or completely different processes?
- **Current corrosion measurements:**
  - Measurements taken from End-of-Life are too late
  - Results vary based on washing and sample preparation
  - Reference electrodes = higher PAM polarization speeds corrosion?
- **Proposed corrosion measurements:**
  - O_2/H_2 ratio measurement via eGas or similar device
    - Missing oxygen = corrosion
  - Additional teardowns/micrographs from start-of-life batteries
  - Gas measurements, IR cameras, EIS could assist measurements
- **Limitation: Field testing will look different from test cells**
  - Major caveat…





F: Measuring Gas Evolution Directly

Moderator: Heinz Rottmann

- **Validation testing of eGas device has been generally positive**

- **Findings/Optimizations ongoing:**
  - More moisture appears than expected at 60 °C
    - Leads to spikes in data recovery
    - Additional moisture trap could help
    - Need to determine if this truly affects conclusions
  - CO_2 content >5% has been observed in batteries/cells
    - Unclear if this is real or artifact, need more data
  - Vehicle tests present unexpected pressure differentials
    - May implement water or labyrinth chamber to mitigate
  - Sum of all gas measurements is over 100% (illogical)
    - Sensor calibration underway
  - Tubing material of construction in question
    - PVC = clear, helps with pH indicator; PTFE more durable
  - Optimal length/diameter of tubing
    - Shorter = more accuracy, longer = ease of use

Future Directions and Next Conference

- **Outstanding Follow Ups:**
  - Consider standardized teardown recommendation document
  - Continued updates to 2V Cell Building Recommendation Manual
  - Circulate 2V-modified EN-50342-6 DCA *[Done]*
  - Circulate nKLT data templates *[Done]*

- **EFB + Heat Workshops to continue per Dr. Karden**
  - Next location either Edinburgh or Sienna, TBD
  - Likely June 2020