CEN-CENELEC WS DEFACTO

Date: 2023-07

prCWA_XXXX-2:2023

Secretariat: UNE

Experiments and characterisation techniques for data required for modelling cells

CCMC will prepare and attach the official title page.

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European foreword

Results incorporated in this CWA received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 875247.

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Introduction

Modelling the material, cell and manufacturing process behaviour allows to accelerate cell development and the R&I process. The work can be done on an iterative exchange process for model development, validation and optimisation using two cell technologies for the automotive market: an industrial scale state of the art Layered Oxide $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ NMC622/Graphite cell (NMC622/G) and a competitive Nickel Rich Layered Oxide $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ NMC811/silicon-carbon composite prototype (NMC811/G-Si). Additionally, High-Voltage Spinel Oxide $LiNi_{0.5}Mn_{1.5}O_4$/silicon-carbon composite (LMNO/G-Si) can be studied to explore the versatility of the built models.

Modelling work requires input parameters and data for validation. Before starting the experimental work, it is necessary to define precisely the nature, the sensitivity requirements for input parameters and the appropriate experiment and characterisation techniques for a list of physical and chemical characteristics.

This CWA is based on some of the results of the European Union's Horizon 2020 research and innovation programme DEFACTO (funded under grant agreement No 875247).

1 Scope

This document specifies the most suitable experiment(s) needed for obtaining the data required for modelling the material, cell and manufacturing process for cells for the automotive market, based on physical and chemical characteristics of cells of NMC622/G, NMC811/G-Si, LMNO/G-Si chemistry types.

This document shall be read in conjunction with the document prCWA XXXX-1 Data required for modelling the material, cell and manufacturing process for cells for the automotive market.

2 Normative references

prCWA XXXX-1, *Data required for modelling the material, cell and manufacturing process for cells for the automotive market*

3 Acronyms and abbreviations

NMC	$LINI_XMN_YCO_ZO_2$ WITH $x + y + z = 1$
NMC622	$LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$
NMC811	$LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$
LMNO	$LiMn_{1.5}Ni_{0.5}O_4$
G	Graphite
Si	Silicon
PNM	Pore Network Model
P4D	Pseudo 4D
DEM	Discrete Elements Method
CFD	Computational Fluid Dynamics
LBM	Lattice Boltzmann Model

4 List of experiments

The experimental characterisation and cell prototyping activities allow to build, validate and optimise multiscale and multiphysics models which will improve the understanding of the mechanical and electrochemical processes occurring during cell manufacturing and performance: from the atomistic to the cell level, from the slurry mixing to the cell assembly and finishing steps. The following table list all the experiments which are needed to determine the model parameters defined in prCWA XXXX-1. A short description and the data type are also defined for each experiment.

Table 1 — List of experiments to determine data for modeling

Name	Code Name	Type	Description	Data type
Micro Computed Tomography	**µCT**	Imaging	Electrode structure determination	Picture
Ultrasonic acoustic wave	**Acoustic**	Process	Ultrasonic acoustic wave transportation through batteries to study the filling kinetics of the porous structures by electrolyte and detect possible defects	Float functional
Angle of repose	**Angle of repose**	Process	Rotating drum/heap measurement	Point
Accelerated Rate Calorimeter	**ARC**	Thermal	Netzsch ARC 254 for cylindrical cells & Netzsch MMC 274 Nexus for button cells	Float functional
Chronoamperometry	**Chronoamperometry**	Electrochemical	Determination of time dependancy of filling process	Float functional
Coating thickness	**Coating thickness**	Process	Wet thickness: ultrasonic absorption Dry thickness: beta gauge and micrometer caliper Ultrasonic Absorption and Beta Gauge: Thickness as a function of the loading in g/m^2; for the double-side coated anode it is only possible to determine the loading of both sides simultaneously. Each side individually is not possible	Point
Coating temperature during drying	**Coating_T_drying**	Process	Single point measurement by infrared sensor	Point
DFORM	**DFORM**	Mechanics	In-house test bed to measure the swelling pouch cell upon cycling	Float functional
Incremental capacity	**dQ/dV**	Electrochemical	The dQ/dV analysis takes a refined step to estimate the capacity displaced in each incremental change of voltage in the reaction	Float functional
Electrochemical Impedance Spectroscopy	**EIS**	Electrochemical	Electrochemical impedance spectroscopy to determine ionic resistances, charge transfer resistance, transport numbers, and post-mortem analysis, using coin cells (half, symetric or full) configurations	Float functional
Electrochemical characterization of the cells	**Electrochemical tests**	Electrochemical	C-rate and galvanostatic tests in coin cell and pouch cell at different temperatures	Float functional

Name	Code Name	Type	Description	Data type
Electrode adhesion strength	**Electrode adhesion strength**	Mechanics	Adhesive strength of the electrode determined with pull-off adhesive test or simple in-house designed method	Float functional
Electrode thickness	**Electrode thickness**	Process	Micrometer caliper	Point
Electrode thickness during calandering	**Electrode thickness calendering**	Process	Measurement by the gap between calander rolls	Point
Electrode thickness during drying	**Electrode thickness drying**	Process	Tabletop coater + heating + laser triangulation. Specific measurement for lab scale kinetics of thickness during drying for model development	Float functional
Electrolyte density	**Electrolyte density**	Process	Precision balance	Point
Electrochemical quartz crystal micro balance	**EQCM**	Electrochemical	Measurement of layer deposition and stripping during operation of electrode (ex : growth of SEI layer during formation). Balance swings in a certain frequency and shows changes in electrode weight through changes in frequency	Float functional
Focus Ion Beam - Scanning Electron Microscopy	**FIB-SEM**	Imaging	Images 2D & 3D of the electrode microstructure	Picture
Air convection and temperature during drying	**Flow_T_drying**	Process	Hand unit to measure air flow	Float functional
Galvanostatic Intermittent Titration Technique	**GITT**	Electrochemical	Determination of OCV and diffusion coefficients in coin cells configuration	Float functional
Laser diffraction	**Laser diffraction**	Process	Particle size distributions of powders	Float functional
Mercury intrusion	**Mercury intrusion**	Process	Pore size distribution	Float functional
Microcompression/ Nanoindentation	**Microcompression/ Nanoindentation**	Mechanics	Mechanical behavior of particles and electrodes	Float functional
Nuclear Magnetic Resonance	**NMR**	Chemistry	Lithium metal detection	Float functional
Pressure during electrolyte filling	**Pressure electrolyte**	Process	Pressure sensors during electrolyte filling	Float functional
Capilary pressure saturation	**p-s-curves**	Process	Measurement of saturation of porous system for given capillary pressure	Float functional
Pycnometry	**Pycnometry**	Process	Density measurement of solids	Point
Reference electrode	**Reference electrode**	Electrochemical	Measurement of each electrode potential	Float functional

Name	Code Name	Type	Description	Data type
Rheology for electrode	**Rheology electrode**	Process	Measurement of solvent and slurry	Float functional
Rheology for electrolyte	**Rheology electrolyte**	Process	Measure viscosity of electrolye	Float functional
Segmented cell	**Segmented cell**	Process	Determination of time dependency of filling process with better accuracy than chronoamperometry. Can also be used to determine inhomogeneities of porous system, current distribution etc.	Float functional
Scanning Electron Microscopy - Energy Dispersive X-ray spectrometry	**SEM-EDX**	Imaging	Image microstructure coupled with elemental analysis for material distribution in electrodes	Picture
Slurry density	**Slurry density**	Process	Precision balance; Coriolis mass flowmeter	Point
Solvent density	**Solvent density**	Process	Precision balance	Point
Transmission Electron Microscopy	**TEM**	Imaging	Image of crystal structure	Picture
Temperature of calendaring rolls	**T-calendering**	Thermal	The temperature of the rolls is measured externally with a hand-held equipment. It is also possible to measure and control the temperature of the flowing oil that is used to heat up the rolls.	Point
Tensiometer	**Tensiometer**	Process	Surface tension for solvent, electrode suspension	Point
Thermogravimetric analysis connected with gas chromatograph	**TGA-GC**	Process	TGA shows at which temperatures material decomposes into gas phase. Gas chromatograph is used to analyse evaporated species to determine which componed decomposes at which temperature.	Float functional
Estimation of separator tortuosity	**Tortuosity separator**	Process	Technique based on work of Landesfeind and uses two copper contacts in an electrolyte bath	Point
Xray Photoelectron Spectroscopy	**XPS**	Chemistry	Electrode surface analysis	Float functional
X-Ray Diffraction	**XRD**	Chemistry	Lithiation stage, identification of the phase	Float functional
Zeta potential	**Zeta potential**	Process	Electrostatic interactions between particles	Point

Annex A (informative)

Experiments for cells ageing mechanisms

The ageing of lithium batteries is caused by electrochemical and mechanical degradation processes, due to charging and discharging cycles as well as storage, and leads to a drop in battery capacity and power over time.

This Annex describes a process to force and characterise various ageing mechanisms in cells.

Table A.1 describes an experimental matrix of tests to be carried out on monolayer pouch cells to determine the limit conditions to induce ageing mechanisms in larger cells. The goal is to test several conditions and make deep analysis on small lab cells to limit the quantity of materials, limit thermal/mechanical heterogeneities, limit damages in case of thermal runaway and guarantee fast capacity decay in larger cells to allow saving time and resources. For some chemistries, such tests must confirm that ageing mechanism is not occurring.

The analysis to identify of ageing laws (1) Li plating, (2) Heterogeneities, (3) Expansion+SEI, (4) Dissolution+ CEI/SEI) both at monolayer and pouch cell level is described below. All these tests are performed on fresh cells with same chemistry and after a conventional formation step (by default, low C-rate (C/10 or below) on full DoD with CV step at end of charge until current equivalent to C/40 or lower, and at room temperature).

At least two cells per tests should be launched for reproducibility check. All the monolayer cells are instrumented with a third reference electrode in order to characterize the individual signature of each electrode.

Table A.1 — Experimental matrix for monolayer cells

	Ageing mechanism targeted	Conditions	Criteria	Goal	Sensitive chemistry
Test 01	Li plating	Increasing C-rate in charge 0.2C, 0.5C, 1C, 2C, 3C / constant C-rate for discharge 0.2D at 10 °C Then, decrease T° and repeat test	Repeat at lower temperatures until Uanode < 0V vs. Li at 3 different temperatures If limits are not reached on studied temperature range, repeat with increasing C-rates in charge	Determine min. charge current and max. temperature for Li plating Note: larger cells will have lower resistance (better C-rate performances) and lower heat dissipation (cell temperature > ambient controlled temperature) a need to apply more severe conditions for larger cells	All with graphite, graphite-Silicon, silicon anodes
Test 02 (only once Test 01 is completed)	Li plating	Direct condition determined from Test 01	Uanode < 0V vs. Li on several cycles, fast capacity decay	Validate that Li plating is induced directly, and that it is not resulting from previous cycling	All with graphite, graphite-Silicon, silicon anodes
Test 03	Dissolution, SEI or CEI growth	Charge at low C-rate (<=0.2C) then CV step at SOC 100% at 45°C with regular EIS	Potential evolution during CV SEI and/or CEI growth with increase of medium frequency resistance in EIS If no increase in EIS, repeat with increasing T°	Enhance cross contamination inducing SEI growth	High voltage cathode (Ni-rich, LNMO)
Test 04	Dissolution, SEI or CEI growth	Charge at low C-rate (<=0.2C) then OCV step at SOC100% 45°C with regular EIS	Potential evolution during CV SEI and/or CEI growth with increase of medium frequency resistance in EIS If no increase in EIS, repeat with increasing T°	Enhance cross contamination inducing SEI growth	High voltage cathode (Ni-rich, LNMO)

	Ageing mechanism targeted	Conditions	Criteria	Goal	Sensitive chemistry
Test 05	Electrode expansion, structural evolution of active material, SEI growth	Charge and discharge at low C-rate with 0-30%, 0-50%, 50-100%, 0-80%, then 0-100% DoD at 25 °C Repeat test at 45 °C	Check balancing and Umin/Umax for each electrode depending on T° and DoD SEI and/or CEI growth with increase of medium frequency resistance in EIS	Generate different irreversible microstructure and/or crystal structure evolution, control lithiation/delithiation depth	High voltage layered oxide (Ni-rich) Si-based anode
Test 06	Heterogeneities	Constant C-rate for charge 0.2C / Increasing C-rate in discharge 1D, 2D, 3D at 10 °C Then, decrease T° and repeat test	Repeat at lower temperatures until Umin < 0V vs. Li or Umax > Ulimit cathode If limits are not reached on studied temperature range, repeat with increasing C-rates in discharge	Determine max discharge rates and min T° to promote max heterogenities without inducing other mechanisms such as Li plating or material dissolution or SEI/CEI growth	All

Several combinations of C-rate in charge/C-rate in discharge/T° can be then applied on large cells to study long-term effect of ageing mechanims with a reduced number of tests.

To confirm the occurrence of the expected ageing mechanisms, some destructive physico-chemical analyses could be performed on the monolayer/large cells after test. Table A.2 details the ex-situ analyses proposed to demonstrate the occurrence of degradation mechanisms and quantify morphological, structural and/or chemical changes.

Table A.2 — Experiments to determine degradation mechanisms

Degradation mechanism/Cell chemistry	Gr/NMC622 cells		GrSi/ NMC811 cells	
	Gr	NMC622 cells	GrSi	NMC811
Expansion-Cracking	–	–	Surface morphology (SEM)	–
SEl/CEI formation	Surface morphology/comp. (SEM-EDX) Surface composition (XPS) Thickness (TEM)	Surface morphology/comp. (SEM-EDX) Surface composition (XPS) Thickness (TEM)	Surface morphology/comp. (SEM-EDX) Surface composition (XPS) Thickness (TEM)	Surface morphology/comp. (SEM-EDX) Surface composition (XPS) Thickness (TEM)
Li plating	Surface morphology (SEM) Oxidation degree, environment of Li (NMR)	–	Surface morphology (SEM) Oxidation degree, environment of Li (NMR)	–
Dissolution of TM	TM migration identification (XPS, EDX)	–	TM migration identification (XPS, EDX)	–
Heterogeneities	Surface morphology/comp. (SEM-EDX) Lithiation state (XRD)	Surface morphology/comp. (SEM-EDX) Lithiation state (XRD)	Surface morphology/comp. (SEM-EDX)	Surface morphology/comp. (SEM-EDX)
Reference cell/component	All	All	All	All

NOTE More information on degradation of batteries can be found in deliverables D6.3 and D6.4 of the project INVADE (Deliverables – Invade (h2020invade.eu)).