Ref. Ares(2020)2856016 - 03/06/2020

D1.3

General framework of assessment and monitoring protocol

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 875629

D1.3	Work Package No.	1	Task/s No.	1.3
Work Package Title	WP 1. Requirements, specifications, and assessment protocol			
Linked Task/s Title	Task 1.3 General framework of assessment and monitoring protocol			
Status	Final	(Draft/Draft Final/Final)		
Dissemination level	PU-Public			
Due date deliverable	2020-05-31	Submission date	2020-06-02	
Deliverable version	General framework of assessment and monitoring protocol V 1.2			

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Document History

Version	Date	Comment
1.0	2020-05-31	
1.1	2020-06-02	

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List of abbreviations

Abbreviation	Description
CEI	Cathode electrolyte interface
HC	Hard Carbon
NVPF	Na3V2(PO4)2F3
RT	Room Temperature
SEI	Solid-Electrolyte Interphase
WP	Work Package

1. Executive Summary

The general framework of assessment and monitoring protocol is a task in the work package 1 that identifies requirements, specifications, and assessment protocol. This framework is required to establish a link between modules and packs that will be used for energy storage systems (ESS) in the Naima project. The assessment and monitoring protocols are built based on the prototype proposed in the previous task (T 1.2) that meat with the end-user's specifications for specific applications.
The general framework of assessment and monitoring protocol includes:

- Protocols to test and validate packages and modules
- Assessment of raw materials in half cells
- Assessment of raw materials in full cells
- Assessment of raw materials in different battery designs (coin cells and 18650 cell designs)

The application of this document is the responsibility of Naima project partners, which synthesize and assess raw materials and finished products. This document will be a fixed protocol to assess materials for all the Naima project partners which enables attaining similar comparable results upon following the same fixed protocols.

2. Introduction

To maintain reproducible results, unifying a standard protocol for all partners to follow is required. In the Naima project, some partners will be synthesizing anode materials (Bio-based hard carbons for negative electrodes) while others will be synthesizing cathode materials (polyanionic and lamellar oxide materials for positive electrodes). Accordingly, other partners will be using these manufactured raw materials to formulate electrodes and formulate cylindrical cells to form packs to meet with the end-user specifications.

Work package 2, which is led by the CEA, with partaking of IHE, CNRS, NIC, and Biokol are responsible for formulating Bio-based hard carbons for negative electrodes. These anode materials will be tested according to protocols that these work package participants find favourable. As part of their deliverables, physicochemical characterisation and electrochemical performance tests are defined. Thus, the electrochemical testing protocols presented here have been agreed between these partners. These test parameters are unified and are considered the standard testing and assessment protocol to be followed by all the Naima partners to evaluate the anode materials.

Work package 3, which is led by the CNRS, with the participation of Solvay and Umicore, is responsible for formulating polyanionic and lamellar oxide materials for positive electrodes. As part of their deliverables, physicochemical characterisation and electrochemical performance tests are defined. Thus, the electrochemical testing protocols presented here have been agreed between these partners. These test parameters are unified and are considered the standard testing and assessment protocol to be followed by all the Naima partners to assess the anode materials.

Finally, other work package leaders, such as Tiamat, will be using these raw materials to formulate cylindrical cells to be implemented in the prototypes proposed task 1.2. The three prototypes are as follows:

1. Prototype 1: High power density package and cells for EDF
2. Prototype 2: High power density package and cells for Gestamp
3. Prototype 3: High energy density package and cells for Goldline

The electrochemical testing protocols presented here have been proposed by the consortium based on the state of the art batteries they are using (high power density) and based on the provided scientific proposition delivered by partners working for the high energy density cells. In general, all three mentioned protocols formulate the general framework of assessment and monitoring protocol provided in this report for half cells, coin cells, and cylindrical cells.

3. Assessment and monitoring protocols for coin cells

In this section, a discussion of protocols defined for the tests of the positive and negative electrode materials in lab-scale coin cells (half and full cells) is provided. These protocols will be optimized accordingly to the new materials developed for the positive and negative electrodes in the framework of the WP2 and WP3, respectively.

Table 1 displays the recommendations for formulating coin cells with standard parameters that include each electrode's composition (anode and cathode), the casting technique, calendaring, and electrolyte used. This table permits partners to reproduce electrodes and coin cells with unified parameters. It is worth noting that at a laboratory scale, the electrode composition usually is different than that of the production. Nevertheless, to avoid any non-rhythmic results, the active mass materials for anodes and cathodes are fixed at more than 80 wt.%. The coin cells of CR2032 can permit the study of half cells (anodes or cathodes versus a sodium metal) or full cells (anodes versus cathodes). The electrolyte will be provided by Tiamat throughout the testing of these materials to minimize further the risk of having non-coherent results.

Table 1. Cell preparation parameters for the negative and positive electrode materials for coin cells

Cell preparation	To test the negative electrode materials	To test the positive electrode materials
Electrode composition	PVDF/NMP/SuperC65, > 80% active material	> 80% active material, Carbon SC45/PVDF 5130/NMP Loading of more than 6 mg per cm^2
Casting type	Doctor Blade	Doctor Blade
Current collector	Al	Al
Calendaring	Hydraulic press < 5 tons	Coating of 150 µm, Drying at 90°C, uniaxial pressing of 10 tons for 1 min (16 mm disks) Drying under vacuum: RT (2h) then 20°C (12h) and then 40°C (20h)
Cell type	Coin cell (CR2032)	Coin cell (CR2032)
Electrolyte	NAIMA Standard electrolyte from TIAMAT	NAIMA Standard electrolyte from TIAMAT

Table 2 presents the recommendations for electrochemical performance tests for negative and positive electrodes in coin cells. For negative electrodes, the SEI layer formation step is identified for half cells (negative electrodes versus sodium metal). The formation step is divided into two steps, as shown in the table. For the positive electrodes, half and full cell formation techniques are recommended, and prior to launching electrochemical experiments, a relaxation/impregnation time of 12 hours is recommended. Furthermore, the table displays the C-rate measurements, which are also known as the kinetic limitation tests for the anodes and the cathode materials. Finally, a standard room temperature, high and low temperatures parameters are identified to test the electrode materials. It is worth noting that modifying some parameters in these tests might be required after synthesizing these materials since they can behave differently.

Table 2. Electrochemical tests for negative and positive materials in coin cells

Electrochemical tests	Protocol to test the negative electrode materials	Protocol to test the positive electrode materials
Galvanostatic tests	<u>Formation step:</u> 1 cycle at C/10 2.5V – 0.01V (followed by constant voltage) <u>Cycling step (2 conditions):</u> (2.5V – 0.01V + Constant Voltage) 100 cycles at C/10 100 cycles at C	The cells are prepared and the testing protocol starts after electrolyte impregnation, +12hlet impregnated. <u>Half cells for all the prospected materials</u>: Cycling at C/10 up to 4.3 V vs. Na$^+$/Na and at D/10 down to 3.5 V (C rate defined as C/5/ion) <u>Full cells for the optimized compositions only</u>: 6 formation cycles at C/5 D/5 at RT, and then C/10 D/10
C-rate measurements	C/10 (10 cycles) – C/5 (10 cycles) - C/2 (10 cycles) - 1C (10 cycles) - 5C (10 cycles) - 10C (10 cycles) - C/10 (100 cycles) in a potential window of 0.01 V - 2.5 V	5 cycles at C/10, at C/5, at C/2, C and at 2C before coming back to C/10.
Room T°C on every sample	25°C	25°C
High T°C on best samples	60°C	60°C
Low T°C on best samples	-10°C	-10°C

4. Assessment and monitoring protocols for full cell prototypes

In this section, the assessment protocols for three different prototypes (mentioned earlier) are presented. The high-power density and the high energy density cell are based on two different technology of cathode materials. Accordingly, two different assessment protocols are proposed:

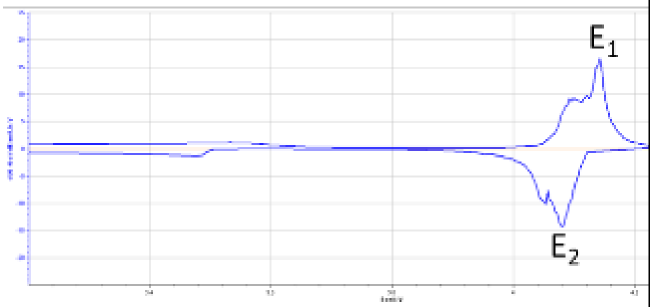
1- High power-density testing protocols (Polyanionic cathode vs. Hard Carbon)
2- High energy-density testing protocols (Lamellar oxide cathode vs. Hard Carbon).

It's worth noting that the same electrolyte will be used for both technologies.

4.1. Assessment and monitoring protocol for high power-density cells

Table 3 displays testing protocols for cylindrical full-cell designs, which include parameters identified from the state-of-the-art technology found at Tiamat. The table consists of electrochemical protocols to follow permitting SEI-CEI formulation, polarization tests, C-D rate tests (kinetic limitation tests), standard and fast cycling parameters, pulse tests, self-discharge tests, and calendar aging tests

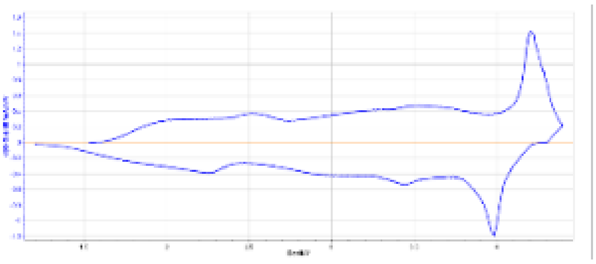
Table 3. Electrochemical tests for high power density cells designated for EDF and Gestamp

Test	Procedure	Measurement
Formulation of interphases (SEI and CEI)	*GCPL* Measurements - Charge to 4.25 V at a C/5 current rate - Discharge to 2.0 V at a D/5 current rate - Repeat for 5 cycles @25°C	- Reversible capacity = final (5th cycle) discharge capacity - Irreversible capacity = $(C_{Theoretical} – C_{Reversible})/ C_{Theoretical}$ - % Irreversible capacity = Irreversible capacity *100
Internal resistance	*PEIS* Measurements - 25°C - 3.6V (30% of SoC) - From 1Hz to 10kHz @20mV	Internal resistance corresponds to the curve intersection with the Re(Z)' axis
Cell kinetics and Coulombic Efficiency	*GCPL* Measurements Charging & discharging from 2 to 4.25 V @25°C ***Testing (symmetric current rates):*** C/2+D/2 1C+1D 2C+2D 3C+3D 4C+4D 5C+5D 10C + 10D and C/5D/5 (retention C/C_0) ***Testing (asymmetric current rates)*** C/2+1D C/2+3D C/2+4D C/2+5D C/2+10D 1C+D/2 3C+D/2 4C+D/2 5C+D/2 10C+D/2	***Testing (symmetric current rates):*** The drop of capacity as a function of current rate is more severe at high C/D rates ***Testing (asymmetric current rates):*** The drop of capacity as a function of current rate is more severe at high C rates than high D rates - Coulombic Efficiency = $C_{Discharge} / C_{Charge}$ * 100
Polarization	*GCPL* Measurements - dQ/dV vs. Ewe (V) of the formulation curves (C/5+D/5) - dQ/dV vs. Ewe (V) of the 1C+1D, 5C+5D curves - dQ/dV vs. Ewe (V) of the 1C+D/2, 5C+D/2 curves - dQ/dV vs. Ewe (V) of the C/2+1D, C/2+5D curves	Polarization is the difference between the charge and discharge peaks at the second stable cycle ($Polarization = E_1-E_2$) 
CC-CV	Charge @10C from 2 to 4.25 V CV for 8min @25C	Capacity recovered compared to the nominal capacity

Standard cycling	*PEIS* Measurements Before cycling using the same conditions of the internal resistance *GCPL* Measurements Charge discharge from 2 to 4.25V @25°C and 1C+1D for 2000 cycles	PEIS will display the evolution of the overall resistance (internal resistance and charge transfer resistance) Capacity loss upon cycling is expected (C/C_0 displays the $C_{Discharge}$/ $C_{Reversible}$)
Fast cycling	*PEIS* Measurements Before cycling using the same conditions of the internal resistance *GCPL* Measurements Charge discharge from 2 to 4.25V @25°C and 5C+5D for 1000 cycles	PEIS will display the evolution of the overall resistance (internal resistance and charge transfer resistance) Capacity loss upon cycling is expected (C/C_0 displays the $C_{Discharge}$/ $C_{Reversible}$)
Max pulse charge	*GCPL* Measurements • 2 to 4.25 V @25°C • Charge from 10C to 30C + 1D	Recovered capacity at each C rate Evolution of polarization at each C rate Coulombic Efficiency at each C rate
Max pulse discharge	*GCPL* Measurements • 2 to 4.25 V @25°C • Charge 1C and discharge from 10D to 30D	Recovered capacity at each C rate Evolution of polarization at each C rate Coulombic Efficiency at each C rate
Self-discharge	*GCPL* Measurements • Charge to 4.25V (1C) and store @25°C • Monitoring of the voltage evolution every day for 1 week • Discharge the cell (1D) @ 25°C to 2V	The voltage evolution upon storage The remaining capacity after storage of 1 week @25°C
Calendar aging	*1)* *PEIS* Measurements Before cycling using the same conditions of the internal resistance *2)* *GCPL* Measurements • 3 cycles from 2 to 4.25 V (1C @ 25°C) • Charging back to 3.6 V (11C @ 25°C) • Storing for 1 week Then repeat steps 1 (PEIS) and 2 (GCPL)	The recovered capacity should display a decrease with aging The resistance increases with aging

4.2. Assessment and monitoring protocol for high energy-density cells

Table 4. Electrochemical tests for high energy density cells designated for Goldline

Test	Procedure	Measurement
Formulation of interphases (SEI and CEI)	*GCPL* Measurements - Charge to 4.4 V at a C/10 current rate - Discharge to 1.2 V at a D/10 current rate - Repeat for 5 cycles @25°C	- Reversible capacity = final (5th cycle) discharge capacity - Irreversible capacity = $(C_{\text{Theoretical}} - C_{\text{Reversible}}) / C_{\text{Theoretical}}$ - % Irreversible capacity = Irreversible capacity *100
Internal resistance	*PEIS* Measurements - 25°C - 2.5V (30% of SoC) - From 1Hz to 10kHz @20mV	Internal resistance corresponds to the curve intersection with the Re(Z)' axis
Cell kinetics and Coulombic Efficiency	*GCPL* Measurements Charging & discharging from 1.2 to 4.4 V @25°C ***Testing (symmetric current rates):*** C/5+D/5 C/4+D/4 C/2+D/2 1C+1D 2C+2D 3C+3D and C/510+D/10 (retention C/C_0) ***Testing (asymmetric current rates)*** C/5+D/2 C/5+1D C/5+2D C/5+3D C/2+D/5 1C+D/5 2C+D/5 3C+D/5	***Testing (symmetric current rates):*** The drop of capacity as a function of current rate is more severe at high C/D rates (> 1C) ***Testing (asymmetric current rates):*** - Coulombic Efficiency = $C_{\text{Discharge}} / C_{\text{Charge}} * 100$
Polarization	*GCPL* Measurements - dQ/dV vs. Ewe (V) of the formulation curves (C/10+D/10) - dQ/dV vs. Ewe (V) of the C/5+D/5, 1C+1D curves - dQ/dV vs. Ewe (V) of the 1C+D/5, 3C+D/5 curves - dQ/dV vs. Ewe (V) of the C/5+1D, C/5+3D curves	Polarization is the difference between the charge and discharge peaks (principle peak) at the second stable cycle (Polarization = E_1-E_2) 
CC-CV	Charge @1C from 1.2 to 4.4 V CV for 8min @25C	Capacity recovered compared to the nominal capacity
Standard cycling	*PEIS* Measurements Before cycling, using the same conditions of the internal resistance *GCPL* Measurements	PEIS will display the evolution of the overall resistance (internal resistance and charge transfer resistance)

	Charge discharge from 1.2 to 4.4V @25°C and 1C+1D for 2000 cycles	Capacity loss upon cycling is expected (C/C_0 displays the $C_{Discharge}$/ $C_{Reversible}$)
Fast cycling	*PEIS* Measurements Before cycling using the same conditions of the internal resistance *GCPL* Measurements Charge discharge from 1.2 to 4.4 V @25°C and 5C+5D (or the highest attainable current rate) for 1000 cycles	PEIS will display the evolution of the overall resistance (internal resistance and charge transfer resistance) Capacity loss upon cycling is expected (C/C_0 displays the $C_{Discharge}$/ $C_{Reversible}$)
Max pulse charge	*GCPL* Measurements • 1.2 to 4.4 V @25°C • Charge from 3C to 10C + D/5	Recovered capacity at each C rate Evolution of polarization at each C rate Coulombic Efficiency at each C rate
Max pulse discharge	*GCPL* Measurements • 1.2 to 4.4 V @25°C • Charge C/5 and discharge from 3D to 10D	Recovered capacity at each C rate Evolution of polarization at each C rate Coulombic Efficiency at each C rate
Self-discharge	*GCPL* Measurements • Charge to 4.4 V (1C) and store @25°C • Monitoring of the voltage evolution every day for 1 week • Discharge the cell (D/5) @ 25°C to 1.2 V	The voltage evolution upon storage The remaining capacity after storage of 1 week @25°C
Calendar aging	*3)* *PEIS* Measurements Before cycling using the same conditions of the internal resistance *4)* *GCPL* Measurements • 3 cycles from 1.2 to 4.4 V (C/5 @ 25°C) • Charging back to 3.6 V (1C @ 25°C) • Storing for 1 week Then repeat steps 1 (PEIS) and 2 (GCPL)	The recovered capacity should display a decrease with aging The resistance increases with aging

Table 4 displays testing protocols for cylindrical full-cell designs, which include parameters identified by partners that synthesized lamellar oxide cathode materials. The table comprises electrochemical protocols to follow permitting SEI-CEI formulation, polarization tests, C-D rate tests (kinetic limitation tests), standard and fast cycling parameters, pulse tests, self-discharge tests, and calendar aging tests. The proposed test meets with the end-user specifications for Goldline for private households' application.

5. Conclusion

The **general framework of assessment and monitoring protocol** was proposed. This framework fixes standard parameters for electrode formulation for anode and cathode materials, fixes the electrochemical tests and protocols for **coin cells (half and full cells), and** fixes the electrochemical tests for **cylindrical-full cells** designated for prototype identified in task 1.2. The framework includes a set of parameters and measurements that ensures attaining comparable and similar results for all the partners working in the Naima project.