



BIG-MAP



D8.8 – First European platform open to researchers/industries outside of the consortium where batteries can be tested following the tests protocols defined in the BIG-MAP

VERSION

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NATURE	Websites, patents filing, etc.
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ABSTRACT

The establishment and diffusion of cycling protocols for the battery community aims to tackle the difficulties in comparing and reproducing scientific results. This deliverable describes the efforts to disseminate the best practices for battery cell assembly and testing procedures.

Battery assembly procedure

Aside from following the BIG-MAP set of protocols, the attention was directed towards the assembly procedure to achieve reproducibility of electrochemical results in coin cells. Aiming for some partners to conduct an optimal assembly protocol and coin cell tests, each applying its internal protocol for further performance comparison. To ensure that any differences would arise specifically from the assembly step only, industrial LNO and Gr electrodes of very high homogeneity and from the same batch were shared among partners for this specific application. The separator (Celgard 2500) and coin cell type (CR 2032) were similar for all partners. The primary study aspects were the volume of electrolytes and the internal pressure of the cell, the latter indirectly controlled by the components' stack height. The initial results are presented in Figure 1.

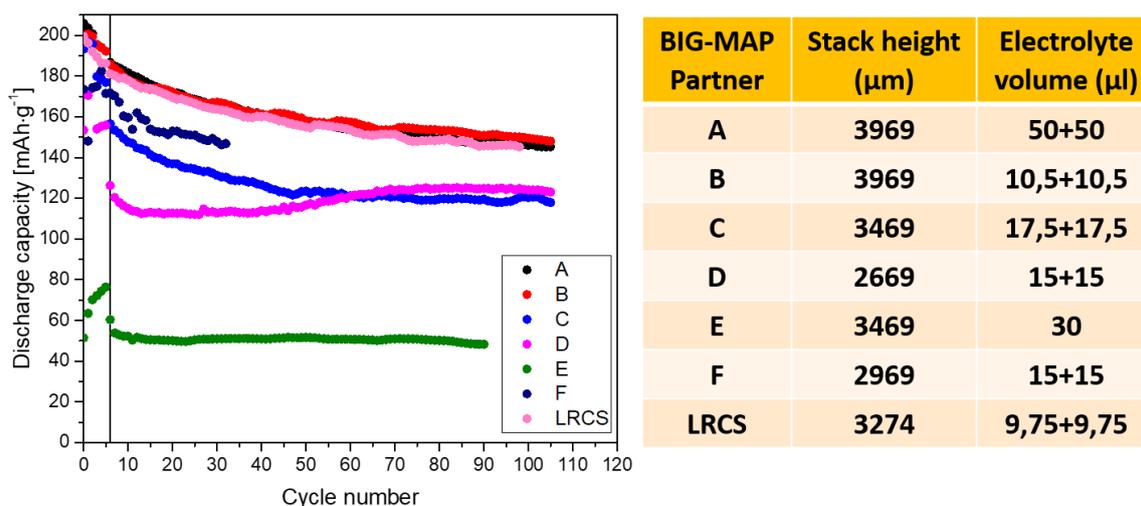


Figure Error! No text of specified style in document.. Discharge capacity vs. cycle number curves from LNO vs. Gr cells cycled between 2.5 V at $25^{\circ}\text{C} \pm 1^{\circ}\text{C}$. According to the protocol, 6 h of OCV is followed by three formation cycles (CCCV C/10, $i_{\text{cutoff}} < C/20$, D/10), three cycles at moderate current (CCCV C/3, $i_{\text{cutoff}} < C/20$, D/2); 100 aging cycles (CCCV 1C, $i_{\text{cutoff}} < C/20$, 1D). The table shows the partner codes and the cell stack height, the volume of electrolytes used, and how the electrolyte is added.

The results highlighted the impact of the assembly procedure on the cell performance, resulting in poor reproducibility. Analyzing the top performant cells (A, B, and LRCS), a relation of electrolyte volume and stack height with the performance was not evident, considering that non-studied aspects (e.g., crimping machine) could also have influenced the capacity and its retention. The basis was the one from LRCS (CNRS) with less electrolyte volume and lower stack height than the other top-performing assemblies. The procedure follows the model in Figure 2, in which one stainless steel spacer is placed between each electrode and the closest case. The predominant action among the partners with the electrolyte addition in two times (half over the negative electrode, and the other



half over the separator) instead of usual one time electrolyte addition, was adopted to improve wettability and minimize excess electrolyte flowing to empty spaces of the coin cell.

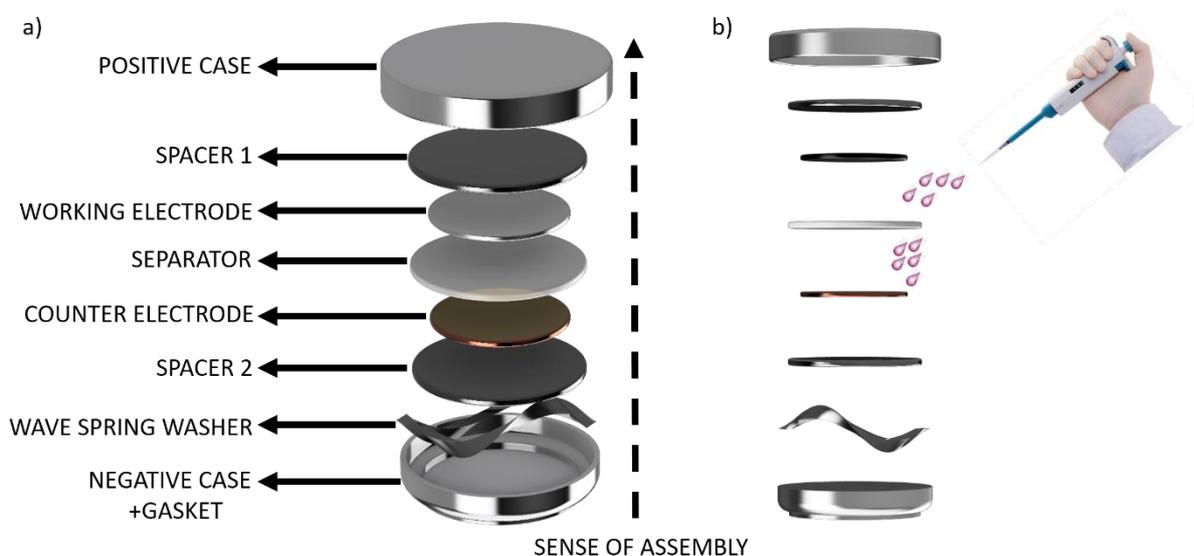


Figure 2. a) Coin cell components and the sense of assembly (from negative case to positive case). b) Coin cell components and electrolyte addition two times over the separator and the counter electrode.

The electrolyte volume in this work was also standardized as a function of the sum of the open porous volumes from the separator and the electrodes, labeled minimal volume:

$$\text{Minimal volume} = (\text{area} \times \text{thickness} \times \text{porosity})_{\text{cathode}} + (\text{area} \times \text{thickness} \times \text{porosity})_{\text{anode}} + (\text{area} \times \text{thickness} \times \text{porosity})_{\text{separator}}$$

The minimal volume is the minimum amount of electrolyte necessary to completely wet the separator and electrodes, allowing Li^+ ions to transport during charge/discharge and complete activity of the whole amount of the electrode. An insufficient amount of electrolyte compromises those parameters. On the other side, uncontrolled excess of electrolyte wastes material, dopes the cell, and can lead to leaks during the crimping procedure. Leaked electrolyte crystallizes and compromises cell sealing. However, a controlled excess is demanded because this cell configuration has a non-negligible empty volume. For that, a choice of a volume between four and six times the minimal volume is indicated. A table to rapidly calculate this volume was made (Figure 3).



	Current collector thickness [μm]	Total electrode thickness Current collector + coating [μm]	Coating porosity (%)	Electrode diameter [mm]
Cathode	15	37	43	13
Anode	10	35	30	13
	Separator thickness [μm]	Porosity [%]	Separator diameter [mm]	
Separator	25	55	16.5	
	Volume [μL]			
Added electrolyte amount	20.8			
Minimum porosity to fill [μL]	5.191228569			
Ratio - Used electrolyte / Total porosity (advised = 4-6)	4.006758655			
Comment	Target met - Suitable electrolyte amount			

Figure 3. A table calculates the suitable amount of electrolytes based on the area, thickness, and porosity of the electrodes and the separator.

The control of the internal contact between the coin cell components was done indirectly using spacers due to practicality. Reference for the control is the ratio (stack height)/(size of the sealed cell internally empty), both measurements including the thicknesses of the positive and negative cases. A ratio below one indicates that some components might not be in direct contact with each other, which prevents the cell from cycling. A ratio higher than one is possible due to spring deformation. Nevertheless, excess pressure due to a thick stack can compromise cell sealing or electrodes and separator integrities. Finally, one spacer on each side is recommended for pressure homogeneity. A series of tests conducted with coated NMC811/Gr coin cells with different combinations of spacer thicknesses resulted in a recommended ratio between 1.03 and 1.28 (Figure 4).

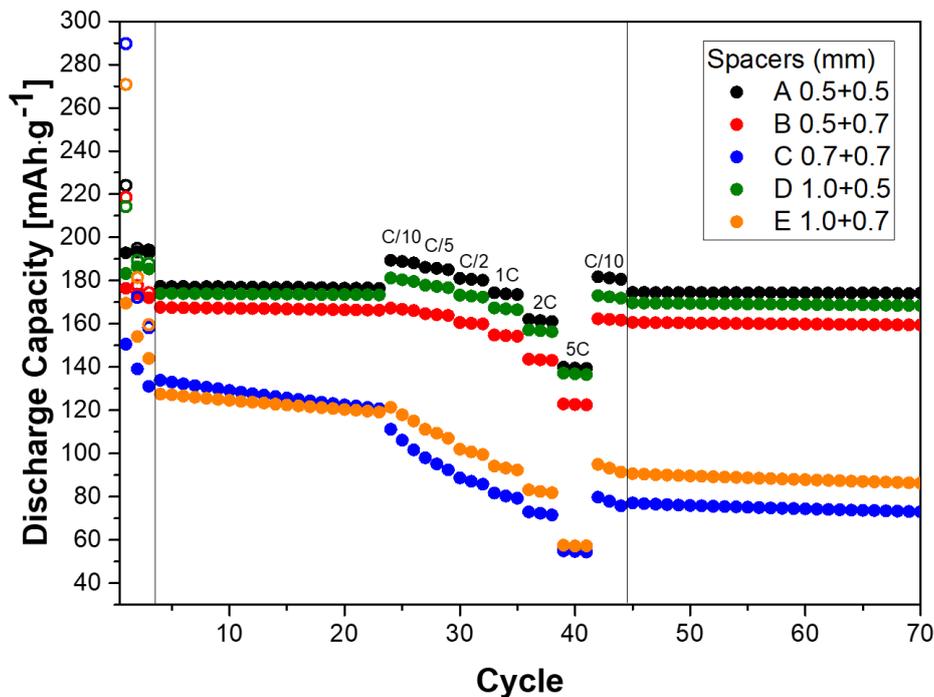


Figure 4. The discharge capacity vs. cycle number for the coated NMC811/Gr cells with different stack heights was obtained by varying the number and thickness of spacers. The unfilled circles represent formation cycle charge capacities. The cells were cycled between 2.5 V and 4.2 V at 25°C ± 1°C with Celgard 2500 separators and LP57 + 2% VC electrolyte.



A table was developed for each coin cell assembly to control the cell pressure using the stack height. It includes each component's thickness and can be varied as a function of the number and type of spacers added (Figure 5).

	Coin cell component	Used quantity	Single component height [μm]	
Chemistry	Anode (Current collector + coating) [μm]	1	32	
	Separator thin film [μm]	1	25	
	Separator Whatman	0	400	
	Li	0	380	
	Cathode (Current collector + coating) [μm]	1	38	
Cell components	Conical spring min [μm] max [μm]	1	1400	1620
	Stainless steel spacer [μm]	2	500	
	Wave spring [μm]	0	1200	
Cases	Positive case bottom thickness [μm]	1	248	
	Negative can with gasket flat bottom thickness [μm]	1	262	
	Negative can with gasket hilly bottom thickness [μm]	0	274	
	Total empty 2032 coin cell height [μm]	///	3100	
	Total sealed 2032 coin cell height [μm]	///	2913	
	Total thickness min spring [μm]			
	3005		3225	
	Stack height / Sealed cell height		1.03	
	Comment		1.11	
			Target met - Stack height is OK	

Figure 5. The table is used to verify if the stack height of the cell components is proper. The cell's parameters that use two spacers of 0.5 mm are shown.

Another factor to improve the reproducibility of the cycling results focuses on the ratio between the total capacities of the negative and the positive electrodes (ratio N/P). In cases where the working potential of the negative electrode approaches 0 V vs. Li^+/Li , this ratio should be > 1 to minimize the formation of Li metal concurrent to or posterior to the Li^+ ion intercalation. This ratio is even more relevant if the cycling conditions lead to high overpotentials, such as low temperature or elevated current densities. In addition, eventual electrode misalignment can locally cause $\text{N/P} < 1$ and thus lead to non-uniformity of reactions in different electrode points (at the same depth). To minimize risks, BIG-MAP adopted 14 and 15 mm for positive and negative electrode diameters. This practice, however, requires restriction of the negative electrode's surface that exceeds the positive electrode's surface, called overhang. once it is electrochemically active (being included in the N/P calculation) and will participate in the intercalation reactions differently from the greater part of the electrode in which anode and cathode superpose. To consolidate all the good practices converging to better reproducibility of coin cells, in 2021, a formation was conducted in LRCS to BIG-MAP partners (Figure 6). It included theoretical and practical activities of coin cell formation in a glove box, electrode manufacturing in a roll-to-roll pilot coater, and electrochemical cycling. In the sequence, the partners were invited to assemble and cycle coin cells in their facilities following the formation. The results ensured the improvement in the reproducibility of the results in coin cell electrochemistry (Figure 7).



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Figure 6. Partners involved in the training hosted at LRCS.

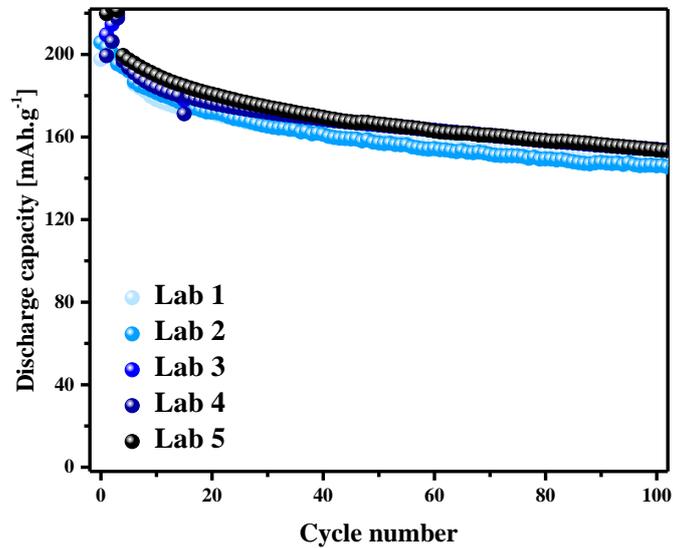


Figure 7. Cells cycled under the same conditions as in the initial round of experiments, presented in Figure 1.