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Reproducible Production of Lithium-Ion Coin Cells

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Abstract: Due to the simple structure and the possibility of manual production, coin cells enable fast and, compared to larger cell formats, an inexpensive examination option in battery research. The comparability and traceability of coin cell structures in literature are only feasible to a limited extent due to the lack of a standard in manual production. Since the findings from the literature are barely building up on each other and have not been repeated, a full factorial Design of Experiments (DoE) was performed to investigate the significance of earlier findings in terms of their influence on the reproducibility of the performance. The parameters studied were the anode-to-cathode ratio, the amount of electrolyte, the spring type and the separator count. To quantify the reproducibility of coin cell assembly, the number of functional cells (here: successful formation followed by 30 cycles) and the empirical coefficient of variation for the performance parameters discharge capacity, internal resistance and coulombic efficiency were compared. The critical parameters found in prior literature have no statistically significant influence on reproducibility when focusing on the number of functional cells. Instead, other uninvestigated parameters seem to influence the system coin cell more. By further examining the parameter settings that produced the most functional cells (≥75% of 8 cells), guidance for constructing coin cells (type R2032) was suggested, and other potential influencing parameters are discussed for further study.

Keywords: coin cell; reproducibility; test cell production; Lithium-Ion; CR2032; Design of Experiments

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1. Introduction

Anyone who manually produces coin cells, which are still the most common cell format used in academic battery research, is initially faced with the problem of first producing functional coin cells and later coin cells with a performance that is as reproducible as possible. The higher the reproducibility of an experiment, the more valuable the study findings become. To achieve higher reproducibility, the term reproducibility needs to be clarified and quantified. In experimental research, reproducibility refers to the repeatability of results achieved by an experiment when replicated [1]. In [2], it was recently highlighted that more than 70% of researchers trying to replicate experiments from others are unable to reproduce the findings and more than half are unable to reproduce their own results. According to their survey, reasons such as insufficient reporting, pressure to publish, insufficient replication in the lab and low statistical power were the main reasons for lowering the reproducibility.

To reproduce, learn or build upon others' experiments, it is essential to eliminate as many unknown disturbance variables as possible by making each experiment traceable with a high level of detail in the reporting, referring to materials, tools and methods being utilized. Several studies [3–7] were conducted to increase reproducibility in full coin cells. Each approach tested multiple parameter settings to increase coin cell performance and reproducibility. These were:

- Electrode preparation (slurry mixture and coating) [5],
- Electrode washing (when reassembling cells) [4],

- Hollow punch vs. professional cutting tool (EL-Cut) [4],
- The anode-to-cathode ratio (N/P ratio) [5,6],
- Separator type [3],
- Vacuum pen vs. tweezers for assembly (trial and error) [3],
- Electrolyte volume [6],
- Wetting time [5], and
- Test protocol [5].

To quantify the influence of the mentioned parameters, each approach examined different quality parameters, which are listed below:

- Cycle performance and capacity retention [3,5,6],
- Charge and discharge curves [5,6],
- Coefficient of variation of electrochemical impedance spectroscopy [4],
- Coulombic efficiency (CE) [4,6],
- Modified hybrid pulse power characterization (HPPC) [6],
- Area-specific impedance [6], and
- Visual inspection of misaligned components after disassembly [3].

Table 1 presents the mentioned literature on the topic and their given data. It can be seen that the diameters and materials of the electrodes, the separator types and their thicknesses, the spacer thickness, the spring type, the tools being utilized, the amount of electrolyte and the assembly order is either varying or not given at all.

Despite many differences, quite a few similarities in the finding can be observed. Regarding the electrodes, an area ratio of the anode to the cathode (N/P ratio) of 1.12–1.15 seems beneficial to compensate for misalignment by the assembler [5,6,8]. The electrolyte volume should be at least three times the pore volume, up to 100 µL [4,6].

Coin cells in research are often equipped with a relatively thick Whatman separator (~260 µm) or a BMF (Polypropylene Blown Micro Fiber) separator compared to separators used in commercially available larger cells (~20 µm) [9–13]. Using one thick or multiple thinner separators reduces the risk of a short circuit due to misalignment within a coin cell and increases the number of functional cells [3]. In contrast, increasing the distance between electrodes leads to a higher inner ohmic resistance and more needed electrolyte. If the structural differences between coin cells (~3 mAh) and commercially available larger cell formats (18650: ~3600 mAh) drift apart too much, then the main findings of coin cell experiments can only be transferred poorly [14]. To balance the reproducibility and transferability, one or two Freudenberg separators will be used instead of a thick Whatman separator in this study.

Many findings about optimizing reproducibility have already been gained. Nevertheless, the level of detail in the reporting was too low to ensure the experiment's reproduction and results by others. In this study, the influence of the already examined parameters N/P ratio and the electrolyte volume, together with new parameters such as the spring type and the separator count, will be investigated with a DoE. This experimental design, paired with a hypothesis test and a Half Normal Probability Plot according to [15–18], allows an investigation of the significance of the chosen parameters on the reproducibility and a closer look at the interaction between the parameters. Preliminary to the DoE, the surfaces of punched coin cell components were visually inspected with a laser scanning microscope to propose an optimal orientation of components within the cell. Considering the individual findings from the literature presented, this paper assesses the reproducibility of coin cell assembly at first with the number of functioning cells (successful formation followed by 30 cycles) followed by the empirical coefficient of variation (ECV) of the discharge capacity, ohmic resistance and CE.

Table 1. Reproducible production of coin cells in the literature [7–10].

Title	Electrode Condition	Housing	Cathode	Separator	Anode	Electrolyte	Tools	Assembly Order
"Highly Reproducible Results in Graphite-Based Li-Ion Full Coin Cells"—[5]	• self-made with detailed instruction • cathode/anode: vacuum dried overnight (v.d.o.n.) at 80 °C—punched—(anode then calendared) —v.d.o.n. at 120 °C	coin cell (2032)	• NMC70 • ⦰12.7 mm	-	• graphite • ⦰1.5/ 1.5875 mm	• 70 µL • 1 M $LiPF_6$ • EC:EMC 30:70 wt.% +2.0 wt.% VC	• punching tool • tweezers	(1) housing (+) (2) cathode (3) separator (4) anode (5) 2 spacer (0.5 mm) (6) Spring (7) housing (−)
"Enabling High-Energy, High-Voltage Lithium-Ion Cells: Standardization of Coin-Cell Assembly, Electrochemical Testing, and Evaluation of Full Cells"—[6]	new electrodes	coin cell (2032)	• NMC532 • ⦰14.0/14.3 mm	• PP/PE/PP • ⦰16 mm × 25 µm	• graphite (surface modified) • ⦰14/14.3/ 15 mm	• 1.7–8.7 x pore volume, • 1.2 M $LiPF_6$ • EC:EMC 30:70 wt.% with and without 2% vinylene carbonate (VC)	tweezers	-
"A Guide to Full Coin Cell Making for Academic Researchers"—[3]	• new electrodes punched in the air • v.d.o.n. at 110 °C	coin cell (2032)	• NMC622 (Al_2O_3 coated) • ⦰12.6 mm	• 2 Celgard or • 1 BMF	• graphite • ⦰12.6 mm	• 42 mg (~42 µm) • 1 M $LiPF_6$) • EC:DEC 50:50 wt.% • $LiPO_2F_2$ added	vacuum pen	(1) housing (+) (2) cathode + 12 mg electrolyte (3) 2 Celgard + 20 mg or 1 BMF + 24 mg electrolyte (4) anode + 6 mg electrolyte (5) spacer (6) spring (7) housing (−)
"Reproducibility of Li-ion Cell Reassembling Processes and Their Influence on Coin Cell Aging"—[4]	• reassembled • mechanical removed second layer of active material	PAT-CELL by EL-CELL	• NMC111 • ⦰18 mm	• glass fiber, 260 µm • DL—Sep., 220 µm • PP/PE/PP, new/used; 25 µm	• graphite • ⦰18 mm	• ~100 µL • 1 M $LiPF_6$ • EC:EMC:DMC 30:30:40 wt.% • EC:EMC 30:70 wt.%	• hollow punch and EL-Cut • tweezers	-

2. Experimental

This section presents the utilized tools, active and inactive materials, and the formation and aging.

2.1. Tools

An EL-Cut from EL-CELL and a hollow punch, as shown in Figure 1, were tested for the electrode and separator cutting.

Figure 1. (**a**) EL-Cut from EL-CELL; (**b**) hollow punches in various diameters.

The electrolyte was applied with a plunger-operated pipette from Eppendorf. Ceramic tweezers were used to handle the electrodes and separator. Cell assembly was performed with a hydraulic crimp machine from TMAX within an argon-filled glove box (M. Braun Inertgas-Systeme—UNIlab Pro Glove Box). The formation and cyclic aging were performed with a battery testing system from Neware (BTS4000) in an oven at 30 °C (universal oven UF55 from Memmert). Visual inspections were performed with a laser-scanning microscope from KEYENCE (VK-X200 series).

2.2. Active Materials

While the anode diameter was 16 mm for each experiment, the cathode diameter switched between 14 and 16 mm according to the parameter setting. Lithium nickel manganese cobalt oxide (NMC111) was used as cathode material.

Detailed properties are listed in Table 2. The separator used was produced by Freudenberg (FS3002). It has a porosity of 56%, a thickness of 0.023 mm and is made of polyethylene and ceramic. The separator band material was punched with a hollow punch into disks of 16.5 mm. The electrolyte was purchased from Solvionic and consisted of 1M $LiPF_6$ in an EC:DMC solution (1:1 vol%).

2.3. Inactive Materials

Inactive materials are all items in a coin cell that are not involved in the electrochemical process. As shown in Figure 2a, those inactive components are the housing with its sealing (visualized as an orange ring on the '−' side), the spacers and the spring. Housings and spacers can be delivered in different sizes and materials. The most common size choice is the R2032 type, with a diameter of 20 mm and a height of 3.2 mm. The most common material choice for housings, springs and spacer is steel 316 or 304. A spring is placed within the housing to apply constant pressure to the anode–separator–cathode compound (ASC). The disk and wave springs (Figure 2b) are the common spring types used in coin cell experiments. To fill the space in a coin cell and homogenously spread the spring's pressure to the ASC, one or more spacers of different thicknesses (0.2, 0.5 and 1 mm) can be used. In all tests presented here, cell type R2032 has been used. Steel type 316 was used for all inactive components since there were no detectable differences from 304 in preliminary tests. Wave and disk springs, as well as a 1 mm spacer, were used for this study.

Table 2. Electrode properties.

Layer	Anode	Cathode
Coating	• single sided • graphite • uncalendared • thickness: 0.110 mm • porosity: 60.1%	• single sided • NMC111 • uncalendared • thickness: 0.109 mm • porosity: 51.4%
Substrate	• copper • thickness: 0.018 mm	• aluminum • thickness: 0.020 mm

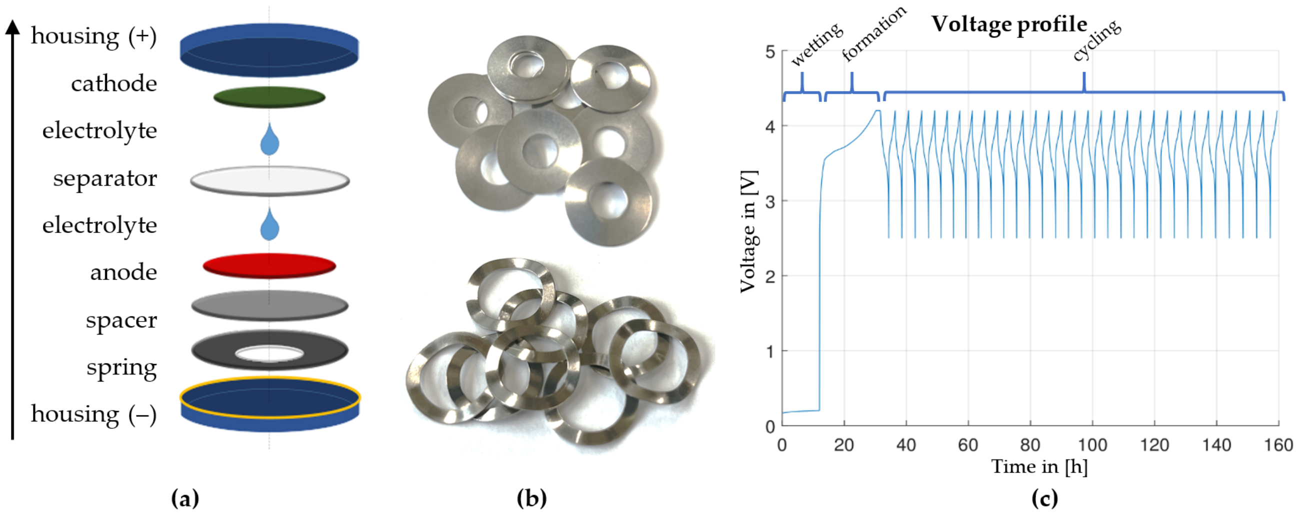


Figure 2. (**a**) Coin cell components; (**b**) spring types: wave springs (**top**) and disk springs (**bottom**); (**c**) voltage profile for wetting, formation and cyclic aging.

2.4. Wetting, Formation and Cyclic Aging

The assembled and sealed coin cells were placed in a temperature chamber at 30 °C. Connected to the battery tester, each cell started with a resting phase of 12 h to ensure the electrolyte reached all pores. Since this paper focuses on reproducibility instead of optimal performance, the formation was performed with one CCCV (CC—constant current; CV—constant voltage) charging cycle. For the CC phase, a rate of C/10 to 4.2 V and a stop current of C/50 were chosen for the CV phase. After a 10 s resting phase, the cyclic aging began. With a current of C/2, the coin cells were charged and discharged for 30 cycles between 2.5 and 4.2 V, as illustrated in Figure 2c.

3. Results

After specifying possible input variables which may have an impact on the reproducibility of coin cell experiments, a full factorial DoE is presented to identify the effects of certain factors, including the spring type, the amount of electrolyte, the N/P ratio and the separator count on the reproducibility of quality characteristics such as the number of functional cells, discharge capacity, CE and inner ohmic resistance. Based on the findings, an assembly method is proposed.

3.1. Input Variables on Reproducibility

Regarding the literature [3–7,19] and several preliminary tests, many parameters that could influence the reproducibility of coin cell performance were collected and categorized (Figure 3). These categories are the d, equipment, production and assembler and are presented in more detail in Sections 3.1.1–3.1.3.

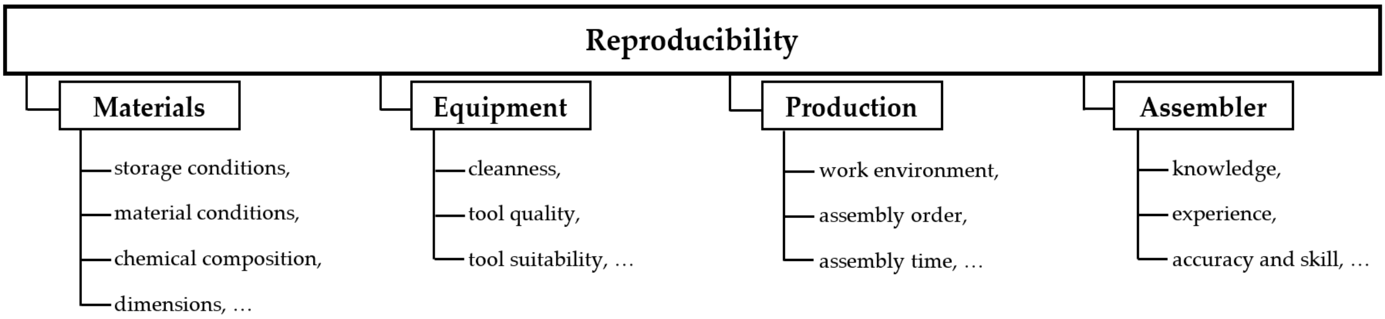


Figure 3. Input variables influencing the reproducibility.

3.1.1. Material Influence on Reproducibility

The material's influence has been examined the most in the presented literature. Influencing parameters are the storage and material condition, the chemical composition and the dimensions of the utilized components. Regarding the dimensions, ref. [7] mentioned that the pressure on the ASC has not been investigated for coin cells. The pressure can be adjusted with the thickness or number of spacers, the spring type, the housing, the applied pressure of the crimping device and the thicknesses of the ASC. To date, investigations of dimensions focused on the ACR instead [5,6]. By changing the diameter of the anode or the cathode, the alignment of the anode, the cathode and the separator can be influenced. A slight overhang of the anode to the cathode seems beneficial for performance and reproducibility [5].

The conditions of the electrodes and separator are crucial for the reproducibility of the cell since moisture or foreign particles in or on the electrodes and separator cause unwanted reactions leading, for example, to a reduced CE in the first cycles [20–23]. To minimize the amount of moisture, electrodes can be vacuumed in the glove box port, dried in an oven or stored in the glove box with an inert gas over an extended period.

Another material influence is the chemical conditions. These can change when electrodes, separators or the electrolyte get stored differently or when purchased from different manufacturers. Even one manufacturer can have minor differences within batches. Therefore, it is beneficial to purchase all materials for an experiment at once and store them the same way.

3.1.2. Equipment Influence on Reproducibility

The quality and suitability of the equipment and the conditions of the processed materials are closely connected. This section discusses the tool's suitability and quality.

The gloves of the glove box are often contaminated with various battery chemicals. To reduce the risk of contamination, fresh gloves over the glove box gloves are recommended. Since multiple layers of gloves impede the assembler's sensitivity, the tools utilized in the glove box should not be too small to handle. The conditions of the electrodes, separator and electrolyte can also be influenced by the researcher's tool selection or the tool quality. A reused pipette could impurify the electrolyte and reused tweezers could cross-contaminate anode and cathode materials. The influence of the cutting process was investigated in previous tests and is described in detail in Section 3.2. Assembling the coin cell materials, tweezers and/or a vacuum pen can be used according to [3] can be used. When using tweezers, the risk of short circuits can be avoided by using ceramic or plastic tweezers.

3.1.3. Production Influence on Reproducibility

This section discusses the work environment, the assembly order and time. When assembling coin cells, the assembler can start with the housing (−), as presented in Section 2.4, or the other way around. It is recommended to try both assembly directions before keeping the most convenient for the entire experiment. Since the electrolyte evaporates over time after application, keeping the duration for each assembly step the same and short is beneficial. To achieve a reproducible assembly, all tools and materials used should be arranged within reach of the assembler.

3.1.4. Assemblers' Influence on Reproducibility

The assembler's knowledge, experience and dexterity are crucial for reproducible coin cell production. Every person's dexterity is different. Especially when handling small and sensitive materials with several layers of gloves, every assembler achieves other process step times, tweezers or crimping pressures and accuracies in the material alignment. For this reason, it is highly recommended that each assembler gains experience by assembling multiple cells (e.g., ~50 coin cells) before main experiments and compares the results to other assemblers in the staff. Additionally, the assembler within one experiment should not be switched.

3.2. Impact of Cutting Tools

In most cases, the electrodes, the separators and even the spacers in a coin cell are punched into their disk shape. When a disk, such as a spacer, is punched out of a sheet, it is called a blank or slug. Due to the shearing process, the blank's geometrical changes occur, as illustrated in Figure 4a. While the face of the disk with the "roll-over" seems harmless, the burr of a spacer or the electrodes could be harmful to the ASC. In Table 3, the utilized spacers and punched anodes using an EL-Cut and a hollow punch were scanned and the maximum height of the scanned area was measured with a laser-scanning microscope. According to the maximum height, the tool choice or tool quality influences the edge quality and the orientation of the punched object. To ensure that the burr of an electrode does not pierce the separator or the burr of the spacer does not create irregularities in the pressure of the ASC, the punching burr must be either reduced, reworked or aligned outwards as recommended in Figure 4b (right).

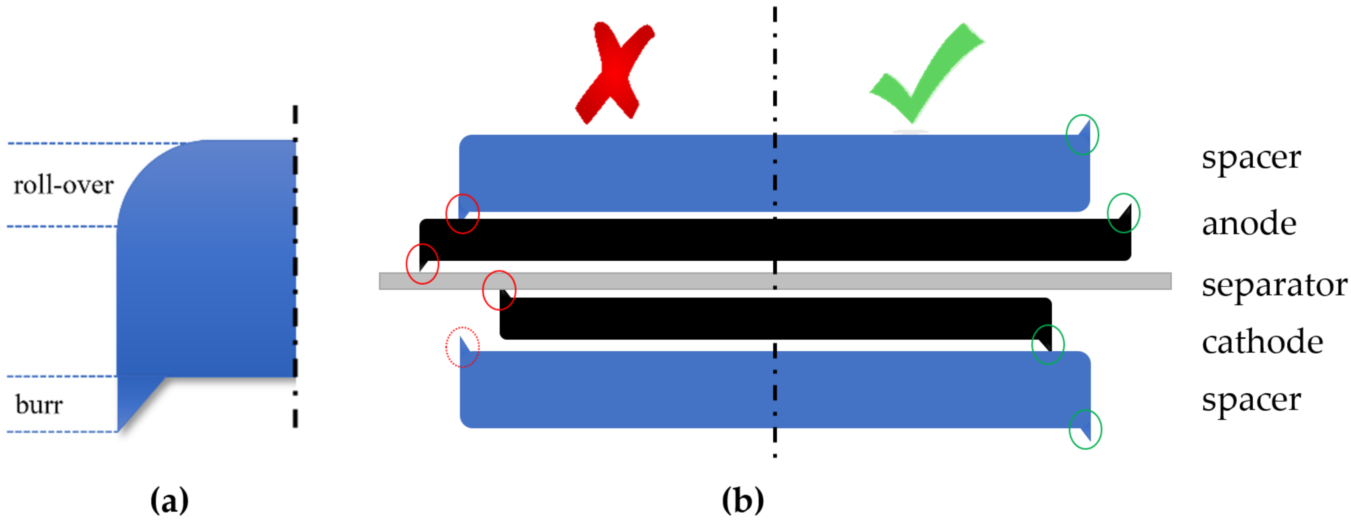
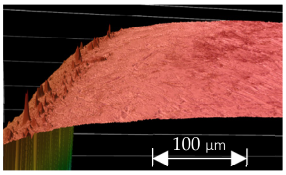
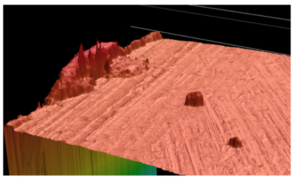
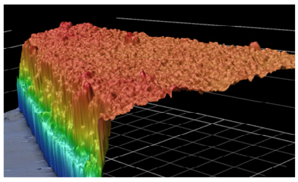
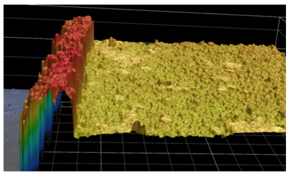
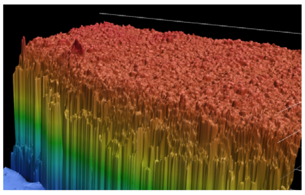
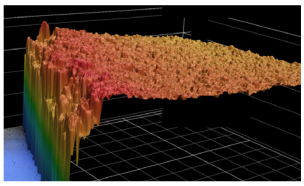


Figure 4. (**a**) Simplified geometrical shape of a punched disk; (**b**) alignment of punched coin cell materials (left: not suggested; right: suggested).

Table 3. Tool impact visualized with laser-scanning microscope (zoom: 20×).

Component	Tool	Orientation	3D-Scan	Height
spacer	punching machine	roll-over		23.18 µm
		burr		65.38 µm
anode	EL-Cut	roll-over		37.42 µm
		burr		85.43 µm
	hollow punch	roll-over		37.03 µm
		burr		68.66 µm

Regarding the processing time and handling, both tools are suitable for cutting electrodes but not for the separators. The more flexible a separator becomes, the more feasible the use of a hollow punch instead of the EL-Cut becomes. To raise the feasibility of the hollow punch and the edge quality of the separator, it can be suggested to use a polyoxymethylene (POM)-plate as a surface and the separator sheet can be placed between two sheets of regular paper. In Table 4, the suitability of the two tools, hollow punch and EL-Cut, are qualitatively evaluated in terms of edge quality, feasibility and reproducibility when used for separators and electrodes.

Table 4. Tool suitability for punching separators and electrodes.

		Separator				Electrodes			
Tool	**Criteria**	**Edge Quality**	**Feasibility**	**Reproducibility**	**Choice**	**Edge Quality**	**Feasibility**	**Reproducibility**	**Choice**
EL-Cut		◑	◔	◑	-	●	●	●	✓
Hollow punch		◕	●	◕	✓	◑	●	◑	(✓)

○ unfeasible; ◔ not suitable; ◑ slightly suitable; ◕ suitable; ● very suitable; ✓ recommendation.

3.3. Impact of Materials

As presented in Table 1, the material dimensions seem to impact coin cell production's reproducibility significantly. These are, for example, the diameter and thickness of the separator or the separator count, the N/P ratio and the amount of electrolyte. The difference in the diameters of a disk spring and a spacer is only 0.4 mm. If the spring and the spacer are slightly misaligned, the spacer and the ASC are tipping to one side during the crimp process, which leads to inhomogeneous applied spring pressure on the ASC or further misalignment within the ASC.

Since the wave spring always covers the spacer due to its construction, a DoE for the influence of materials is being performed, including the amount of electrolyte, the separator count and electrode ratio and the spring type to evaluate the material impact. With the selected 24-plan, the effects of the individual factors and possible interactions can be identified. The experimental design was performed once, with each factor combination performed eight times. For each of the mentioned factors, two states will be tested. Those states are disk (+) and wave spring (−) for the factor spring type, 1.3 (+) and 1.0 (−) for the N/P ratio, 100 µL (+) and three times pore volume (3 PV) (−) for the amount of electrolyte and two (+) and one (−) separator (Freudenberg FS3002) for the separator count. The measured quality features of the full factorial design are the number of functional cells and the median of the empirical coefficient of variation (ECV) of the discharge capacity, the CE and inner ohmic resistance of the functioning cells. In Table 5, all factor combination and their quality features are listed.

3.3.1. Functional Cells

The basic procedure for determining whether factors A to D and their combinations have a significant influence on the quality characteristic "functioning cells" in an experimental design that has been carried out once refutes the null hypothesis in a hypothesis test that the setting of the factors does not influence the number of functional cells [24]. For this, the relative frequencies of the effects can be shown in a Normal Probability Plot [16–18].

Table 5 gives an overview of the number of functional cells per series of the main test. The number of non-functional cells indicates whether a factor combination is prone to errors and, as a result, has insufficient reproducibility. Combinations in which at least six cells of eight ($y \geq 0.75$) completed formation successfully, followed by 30 cycles, are considered to be functional. These are marked in bold in Table 5.

Table 5. Full factorial design matrix for material impact on coin cell reproducibility.

Code	A	B	AB (A*B)	C	AC	BC	ABC	D	AD	BD	ABD	CD	ACD	BCD	ABCD	Spring	N/P Ratio	Electrolyte	Separator	Functional Cells	Empirical Coefficient of Variation (Median)		
																A	B	C	D		Discharge Capacity	Coulombic Efficiency	Internal Resistance
H1	—	—	+	—	+	+	—	—	+	+	—	+	—	—	+	wave	1.0	82.4 µL	1	5/8 (0.625)			
H2 *	**+**	**—**	**—**	**—**	**—**	**+**	**+**	**—**	**—**	**+**	**+**	**+**	**+**	**—**	**—**	**disk**	**1.0**	**82.4 µL**	**1**	**6/8**	0.3451	0.0348	0.5499
H3	—	+	—	—	+	—	+	—	+	—	+	+	—	+	—	wave	1.3	74.5 µL	1	1/8			
H4	+	+	+	—	—	—	—	—	—	—	—	+	+	+	+	disk	1.3	74.5 µL	1	2/8			
H5	—	—	+	+	—	—	+	—	+	+	—	—	+	+	—	wave	1.0	100 µL	1	3/8			
H6	**+**	**—**	**—**	**+**	**+**	**—**	**—**	**—**	**—**	**+**	**+**	**—**	**—**	**+**	**+**	**disk**	**1.0**	**100 µL**	**1**	**6/8**	0.0789	0.0172	0.2905
H7	**—**	**+**	**—**	**+**	**—**	**+**	**—**	**—**	**+**	**—**	**+**	**—**	**+**	**—**	**+**	**wave**	**1.3**	**100 µL**	**1**	**7/8**	0.1482	0.0034	0.0648
H8	+	+	+	+	+	+	+	—	—	—	—	—	—	—	—	disk	1.3	100 µL	1	2/8			
H9	—	—	+	—	+	+	—	+	—	—	+	—	+	+	—	wave	1.0	91.2 µL	2	5/8			
H10	+	—	—	—	—	+	+	+	+	—	—	—	—	+	+	disk	1.0	91.2 µL	2	4/8			
H11	—	+	—	—	+	—	+	+	—	+	—	—	+	—	+	wave	1.3	83.3 µL	2	5/8			
H12	+	+	+	—	—	—	—	+	+	+	+	—	—	—	—	disk	1.3	83.3 µL	2	5/8			
H13	**—**	**—**	**+**	**+**	**—**	**—**	**+**	**+**	**—**	**—**	**+**	**+**	**—**	**—**	**+**	**wave**	**1.0**	**100 µL**	**2**	**6/8**	0.1197	0.0050	0.1792
H14	+	—	—	+	+	—	—	+	+	—	—	+	+	—	—	disk	1.0	100 µL	2	5/8			
H15	—	+	—	+	—	+	—	+	—	+	—	+	—	+	—	wave	1.3	100 µL	2	4/8			
H16	**+**	**+**	**+**	**+**	**+**	**+**	**+**	**+**	**+**	**+**	**+**	**+**	**+**	**+**	**+**	**disk**	**1.3**	**100 µL**	**2**	**6/8**	0.1807	0.0063	0.4635

* Factor combinations in bold are considered "functional" with at least 6 out of 8 functioning cells.

Using the contrast method according to Equation (1), the effects and interactions on the quality feature—functional cell—are calculated. n stands for the test scope (here: 16) and y for the quotient of functional cells and manufactured cells (e.g., H1: $y_{H1} = 0.625$).

$$\sum = \frac{2}{n}\left(\sum_{i=1}^{n} y_{i+} - \sum_{i=1}^{n} y_{i-}\right) \tag{1}$$

The calculated effects are presented in Table 6.

Figure 5 shows the distribution of the effects in the Half Normal Probability Plot. The effects are normally distributed since they lie approximately on the red straight line. Effects very close to or on the red line are spurious effects and likely random with no statistically significant influence on the quality feature—functional cell—Effects close to the straight line cannot be assigned and are in the so-called gray area [24].

Based on the Normal Probability Plot, the following statements can be made:

- All effects lie approximately on a straight line and are therefore considered normal distributed;
- The effects of factors A, B, and D are spurious effects;
- The effect of factor C is in the gray area;
- The interactions of factors AB, AC, ABC and ACD are spurious effects;
- The interactions of factors BC, BD, CD, AD and ABCD are in the gray area;
- The strongest interactions are ABD and BCD.

Table 6. Effects of factors and interactions for functioning cells.

Factor	Mean (+)	Mean (−)	Effect
A	0.56	0.56	0.000
B	0.5	0.63	−0.125
AB	0.53	0.59	−0.063
C	0.61	0.52	0.094
AC	0.55	0.58	−0.031
BC	0.61	0.52	0.094
ABC	0.52	0.61	−0.094
D	0.63	0.5	0.125
AD	0.56	0.56	0.000
BD	0.63	0.5	0.125
ABD	0.66	0.47	0.188
CD	0.55	0.58	−0.031
ACD	0.61	0.52	0.094
BCD	0.48	0.64	−0.156
ABCD	0.64	0.48	0.156

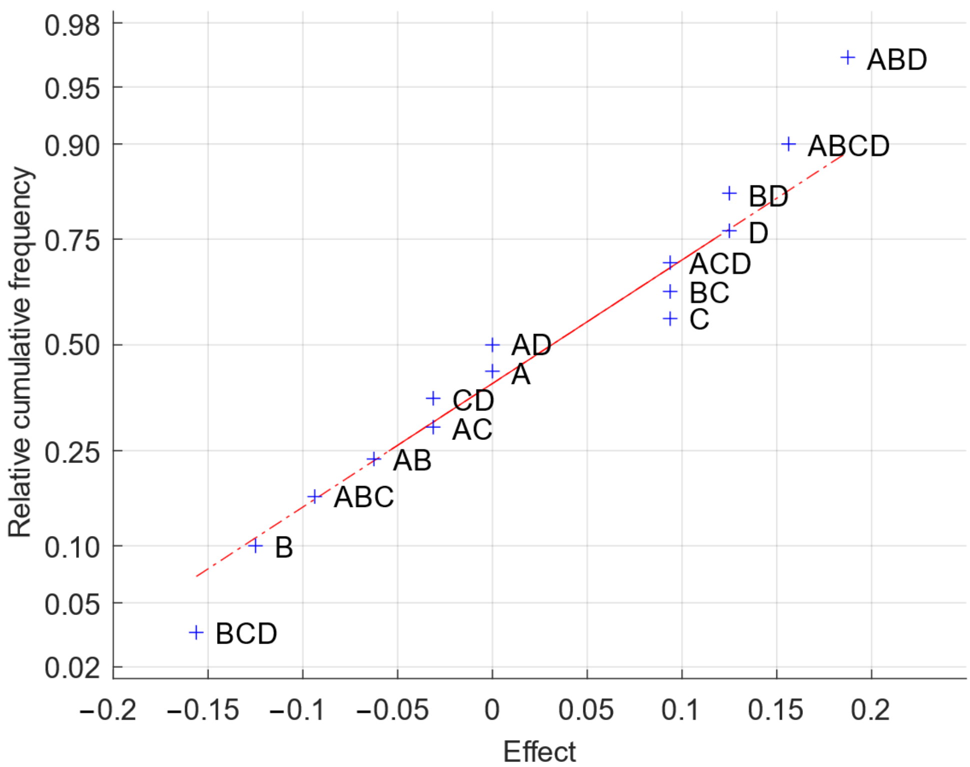


Figure 5. Calculated effects in Half Normal Probability Plot.

The random scatter of the effects is estimated to check the significance of individual effects. To do this, the effects lying on the straight line (A, C, AD, BC, ABD and BCD) are pooled and the variance $s_{\bar{d}}^2$ which results from the number of random effects (f) and the effects are calculated according to Equation (2) [16].

$$s_{\bar{d}}^2 = \frac{1}{f} \cdot \sum_{random\ effects} (effects)^2 \tag{2}$$

With a resulting $s_{\bar{d}}$ of 0.0943 and Student's t-distribution, confidence intervals for 95, 99 and 99.9% for two-sided confidence intervals can be determined. The effects of the factors and their interactions are shown in Figure 6. All effects are within the 95% confidence interval. Thus, no effect is considered statistically significant. The study of the statistical significance of the effects of the method, according to [25], gives the same result. Additionally, the possibility of eliminating factor A (only possible when the effect is 0) and a transformation of the 2^4- to a 2^3-factor design matrix leads to the same result of insignificance.

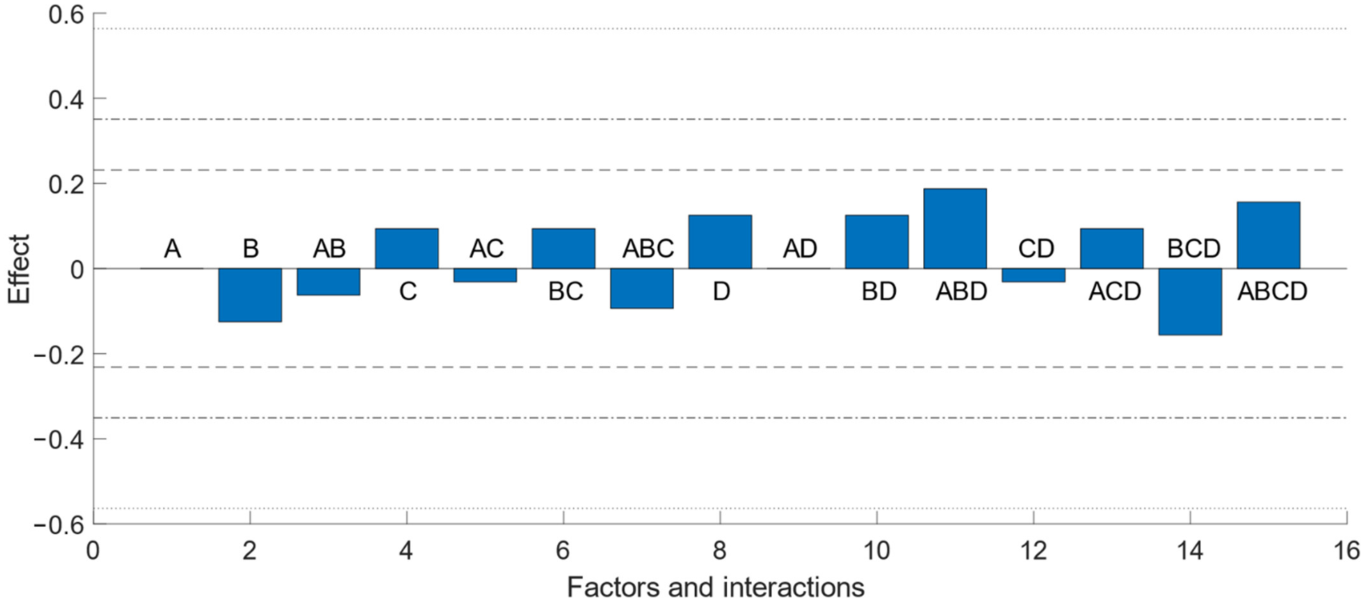


Figure 6. Effects of factors and their interactions within confidence intervals.

3.3.2. Performance Parameters

Due to the proven insignificance of the factors examined, the susceptibility to an error in most factor combinations is triggered by unknown disturbance variables. For that reason, only series that meet the criterion of functional cells by over 75% are considered below. These are the series of configurations H2, H6, H7, H13 and H16 (see Table 5). Cells that are not functional are discarded.

The empirical coefficient of variation $VarK$ was used as a measure for evaluating the reproducibility. It is defined by the quotient of the empirical standard deviation (s) and the arithmetic mean of the measurements X ($\overline{X}$) according to Equation (3).

$$VarK(X) = \frac{s}{\overline{X}} \tag{3}$$

For each combination found to be good, the median, the mean and the standard deviation of the ECV of each cycle from the first 30 cycles are determined. The lower the median, mean and standard deviation, the higher the reproducibility for a combination. The ECVs of the configurations H2, H6, H7, H13 and H16 for the discharge capacity for 30 cycles are shown in Figure 7 as an example. In Table 7, an overview of all ECVs is presented. Accordingly, the CE and the ohmic resistances in configuration H7 have the best reproducibility. The discharge capacity has the best reproducibility with configuration H6. Configuration H2 is the least reproducible.

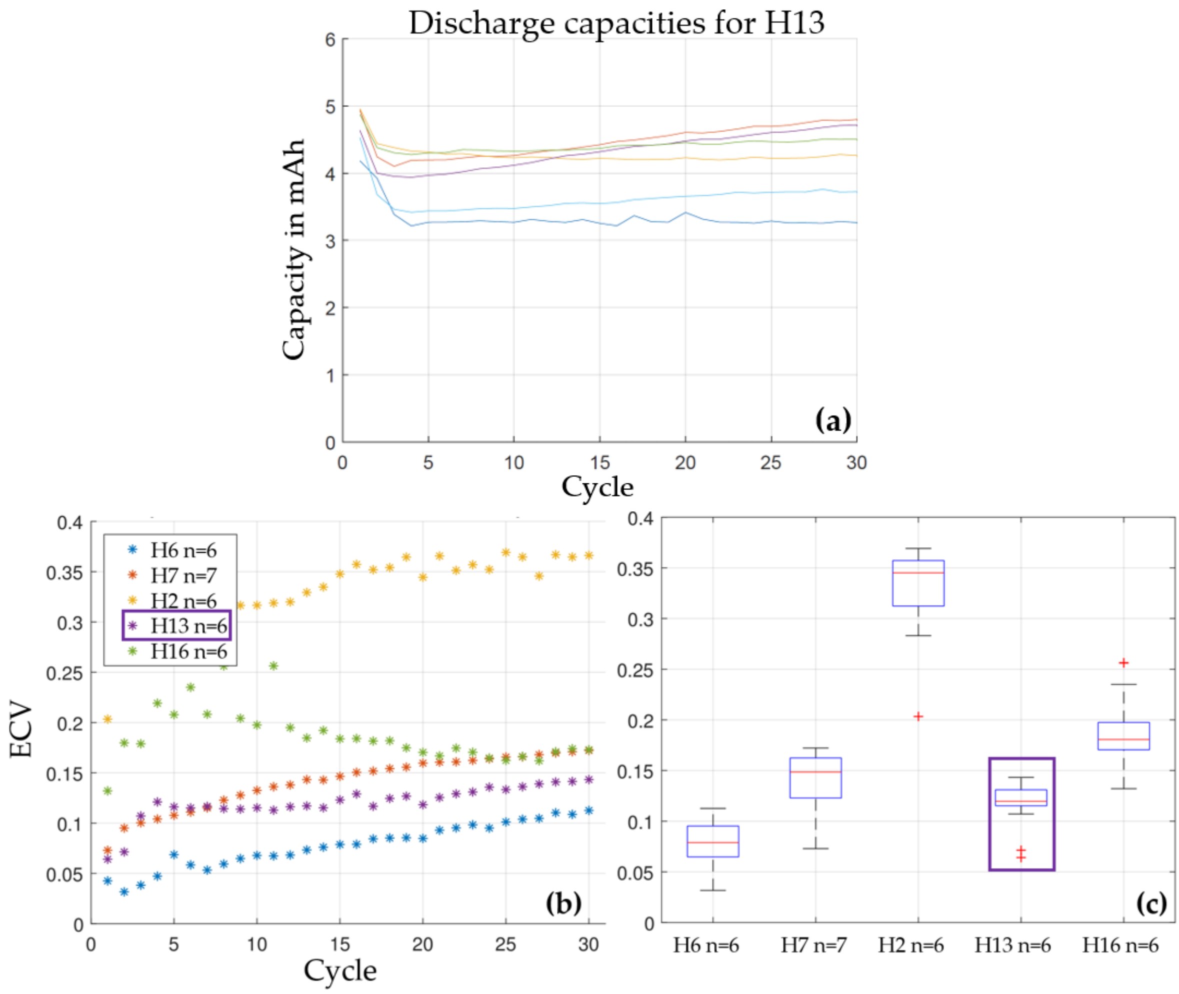


Figure 7. (**a**) Discharge capacities for factor combination H13; (**b**) empirical coefficient of variation (ECV) for the discharge capacity per cycle and for all cycles (**c**) in boxplots. (The purple line highlights the factor combination H13).

Table 7. Overview of median, mean and standard deviation for empirical coefficient of variation.

	H2	H6	H7	H13	H16
			Discharge Capacity		
median	0.3310	**0.0779** *	0.1409	0.1203	0.1870
mean	0.3451	**0.0789**	0.1482	0.1197	0.1807
sd	0.0367	0.0223	0.0266	**0.0174**	0.0273
			Coulombic Efficiency		
median	0.0580	0.0168	**0.0068**	0.0208	0.0120
mean	0.0348	0.0172	**0.0034**	0.0050	0.0063
sd	0.0713	**0.0134**	0.0137	0.0447	0.0161
			Internal Resistance		
median	0.5312	0.2611	**0.0778**	0.1384	0.4483
mean	0.5705	0.3252	**0.0504**	0.2194	0.4917
sd	0.0196	0.0601	**0.0183**	0.0266	0.0498

* The bold numbers represent the lowest value in a row.

3.4. Guidance for Coin Cell Assembly

The following guidance for coin cell construction strives for the highest possible reproducibility. On the one hand, the aim is to produce the highest possible number of functional cells and, on the other hand, it is to achieve the lowest possible spread of the performance parameters. To meet the demand to build up the production of products of high and constant quality, it is necessary to consider basic conditions—be it in complex industrial production processes or the context of manual production. A standard that approximates industrial principles should be striven for the selection and storage of materials for cell construction, for the handling of tools and the design of the workplace or the working environment. Therefore, the guidance includes these aspects and the cell structure itself.

(a) Materials: All materials—especially electrodes, separators and electrolytes—must be stored in a clean, closed environment. These materials should be kept away from the work environment to prevent contamination. Damage caused by accidents or other accidental mishaps on the part of third parties can thus be effectively avoided. This is more important the more sensitive the materials are. Incoming and outgoing warehouse inspections of the materials and monitoring of the storage parameters are standard industrial practices. They are of great importance for high-quality results in research and development. In case of doubt, materials whose quality cannot be verified are rejected. Otherwise, the quality of the manufactured cells cannot be guaranteed. Electrodes and separators sometimes vary greatly in their material thicknesses. In test series with different material thicknesses, it should be aimed for a similar overall thickness of the ESC and the spacers used so the compressive force of the disk spring on the ESC is the same. Greater material thicknesses in the separator and electrodes can be compensated for, for example, by using thinner spacers (typical spacer thicknesses: 0.2, 0.5, 1 mm) or even a different housing type (type R2032, R2025, etc.).
(b) Tools: All tools, such as tweezers, pipettes, punches or other electrode-cutting tools, should be checked for damage before cell assembly. For example, a broken cutting edge of a hollow punch can have a negative impact on the quality of the electrodes. To avoid short circuits, non-conductive tweezers should be used. Furthermore, the tools must be kept in a clean condition throughout the entire manufacturing process. This includes cleaning tools before and after use.
(c) Working environment: The working environment—both in a glove box and outside—must be kept clean and tidy at all times. This includes cleaning the work surfaces before and after cell construction and cleaning the glove box gloves or using a clean pair of gloves above. Impurities are disturbance variables that significantly worsen the quality of the results. It is advisable to define a classification system for tools and other objects and to ensure compliance with it. Ideally, each tool has an assigned place to which it is returned in a clean condition after use. In the glove box, the atmospheric parameters must be monitored regularly and kept constant. Since lithium is a highly reactive element, the recommended atmospheric parameters in an inert gas-filled glove box should be less than five ppm for H_2O and O_2 [14,26].
(d) Cell assembly: The coin cell is to be assembled beginning with the bottom of the housing (−) with the seal facing upwards (the assembly sequence is discussed in Section 2.4 in more detail). A plastic plate can serve as a work surface. The construction has to take place in a glove box. The individual materials are placed with tweezers or a vacuum pin. The electrolyte is applied with a pipette. Attention must be paid to accuracy. Each active material should be handled with a separate tool to prevent cross-contamination. After all the materials and components have been put together and the housing (+) has been put on, the cell must be crimped. Non-conductive tweezers should be used to turn the assembled, uncrimped cell so it can be crimped in standard crimping machines. When crimping, make sure that the pressure is always the same. In the case of manual crimping, 950 psi has been found suitable in preliminary tests. After assembly, the cells must be wiped clean of the electrolyte and carefully removed from the glove box. A visual inspection is recommended to identify damage due to misalignment in the crimping machine.
(e) Cell characterization: The cells are to be measured uniformly using a formation and cycling protocol. The atmospheric parameters must be kept as constant as possible during the measurement. 25–40 °C in a climate chamber is recommended for the wet-

ting and forming phase. Against the background of reproducibility, the temperature, the alignment and the time intervals between the work steps of the cells are particularly decisive. Aiming for the best performance, reference is made to the formation and measurement protocol from [6].

4. Conclusions

As part of this study, the construction of coin cells was examined for the reproducibility of various performance parameters. The most important quality feature for reproducibility was the number of functional cells produced within a series of eight cells with identical factor combinations. All cells in the DoE have been formed and cycled the same way, with current, voltage and capacity being recorded and then evaluated. The performance parameters of internal resistance, discharge capacity and coulombic efficiency have been determined. The statistical evaluation of the results shows that the factors spring type, the amount of electrolyte, number of separators and the anode-to-cathode ratio have no statistically significant effect on the number of functional cells. In this respect, differences are recognized as the result of statistically random events. Therefore, the parameters examined in this study are not the main factors affecting reproducibility. Subsequently, the position and scatter of the performance parameters of the functional cells have been examined, the series of which was at least 75% functional. The empirical coefficient of variation was used for comparison purposes. Although it lacks statistical significance, it is believed that the spring type does not affect reproducibility. The empirically determined best reproducibility was achieved with a configuration in which the diameter of the anode (16 mm) was slightly larger than that of the cathode (14 mm), 100 µL EC:DMC (1:1) was used as the electrolyte, one separator (instead of two) and a wave spring has been installed. Furthermore, visual inspection of the punched electrodes and spacers using a laser scanning microscope revealed that the punching process leaves a burr on the punched disk, which can lead to inhomogeneities or even short circuits when the burr faces the separator. The results of this study reveal that more investigations into reproducibility are needed. First, those parameters should be identified that have a significant impact on reproducibility. Until then, the results from coin cell experiments, as set up in this study, are only qualitative.

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