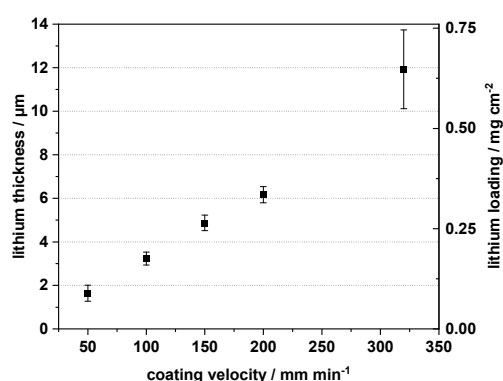


### 1. Temporary substrates – lithium on nickel foil

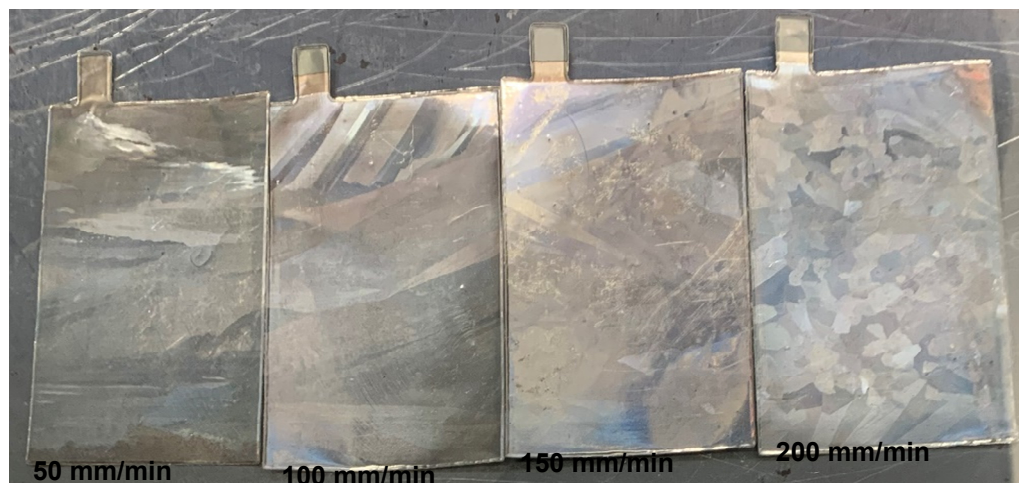
The temporary substrates were produced using a roll-to-roll equipment. Typically, for battery application the substrate foils are as thin as possible to reduce weight and volume of the electrodes. Very often copper and nickel foils  $<10\text{ }\mu\text{m}$  are used in the lithium melt deposition process. However, these ultra-thin foils show low mechanical stability. During the direct contact pre-lithiation process the temporary substrates are handled a lot. Firstly, they are lithium coated. Then they are punch cut or laser cut to the needed dimension, before they are stacked together for the pre-lithiation pressing. Finally, the temporary substrates have to be removed from the stack. All these handling steps, no matter if done manually or automated, require high mechanical stability. Therefore,  $25\text{ }\mu\text{m}$  Ni foils (hpul-cas) were used [1]. These rather thick foils are mechanically stable but flexible enough for roll-to-roll processing.

Figure S1 shows the lithium loading of the temporary nickel substrates produced by lithium melt deposition. The lithium loading depends strongly on the coating speed. Higher speed leads to higher lithium loading. There is some variation within each sample batch due to the quite simple tool used for coating. These variations in the lithium loading on the temporary substrates can influence the achieved grade of pre-lithiation of the graphite material, because typically, all the lithium from the temporary substrate is transferred to the graphite. More lithium on the temporary substrate therefore leads directly to higher grades of pre-lithiation.



**Figure S1.** Lithium loadings of temporary substrates coated by lithium melt deposition process with different coating velocities.

Figure S2 shows photographs of temporary nickel substrates with different lithium loadings. Different coating speeds lead not only to different lithium loadings. In addition, the cooling and therefore the solidification process is different, which leads to different lithium grain sizes. So far, no influence of the grain size on the pre-lithiation process was observed.

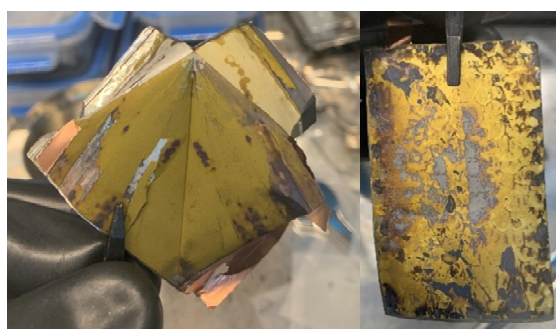


**Figure S2.** Temporary substrates processed by different coating velocities via lithium melt deposition showing different grain structures (from left to right: 50, 100, 150, 200 mm min<sup>-1</sup>) [2,3].

## 2. Complete lithium transfer from temporary substrate to the graphite electrode

It is important to transfer the lithium from the temporary substrate to the graphite electrode completely. After the direct contact pre-lithiation process the temporary substrate has to be removed. If lithium residues are still on the nickel foil, it would stick to the graphite surface and eventually delaminate parts of the graphite during separation. In addition, the grade of pre-lithiation is adjusted by the amount of lithium on the temporary substrate. If not all lithium is transferred, the gained grade of pre-lithiation can be too low.

Figure S3 shows electrodes without sufficient lithium transfer. Left-over lithium on the temporary substrate sticks to the graphite surface. Pulling apart the temporary substrate leads either to graphite delamination or tears up the electrode. Longer pressing time could improve the lithium transfer.



(a)

(b)

**Figure S3.** Temporary substrate and pre-lithiated graphite electrode still sticking together after pressing due to incomplete lithium transfer (a), pre-lithiated graphite electrode with >50 % pre-lithiation (b).

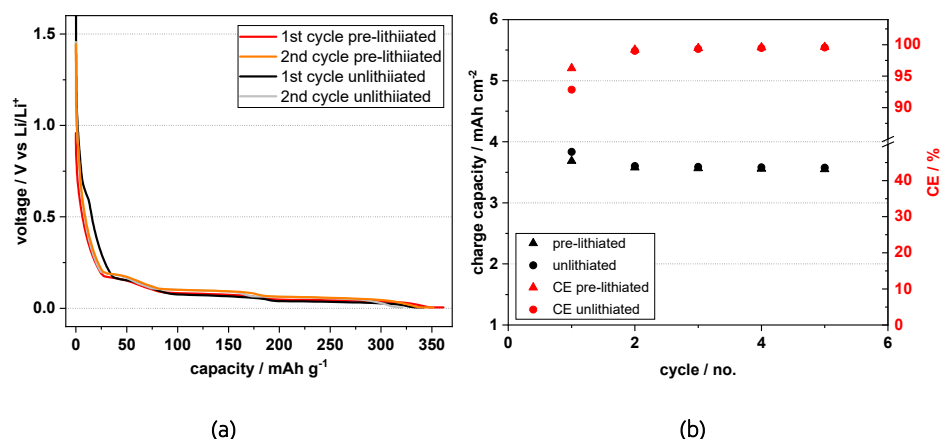
## 3. Pre-lithiated graphite electrodes in half cells

After pre-lithiation the graphite electrodes were tested in coin sized half cells with lithium metal as counter electrode.

Figure S4 (a) shows the voltage profiles of unlithiated and pre-lithiated graphite electrodes for the first two cycles. In the unlithiated cell the first cycle shows a slightly different profile which is not visible in the second cycle and which is also not visible in all cycles of pre-lithiated electrodes. This is due to SEI formation, which takes place during the first contact of lithium and electrolyte with the graphite material. In case of the pre-lithiated graphite, the SEI formation is already done before cycling since lithium and electrolyte are already in the graphite electrode after cell assembly. Therefore, pre-lithiated electrodes do not show this potential change.

Figure S4 (b) shows the charge capacities of unlithiated and pre-lithiated graphite electrodes during the first 5 cycles. A capacity difference can only be observed in the first cycle. Both electrodes show capacities higher than the theoretical capacity of  $3.45 \text{ mAh cm}^{-2}$ . In these experiments, lithium is not limited. The lithium metal counter electrode provides way more lithium than could be possibly used. So in every cycle, the amount of lithium is used which is necessary to completely fill the graphite electrode. In addition, some lithium is consumed by the SEI formation. Both effects together lead to a measured capacity higher than the theoretical capacity of the electrode. After the SEI is formed completely, the measured capacity is the theoretical capacity.

Here, the pre-lithiated electrode shows a lower capacity compared to the unlithiated electrode. For the unlithiated electrode the measured capacity results from filling the electrode plus SEI formation. In case of the pre-lithiated electrode a part of the graphite is already filled with lithium. Therefore, the measured capacity is lowered.



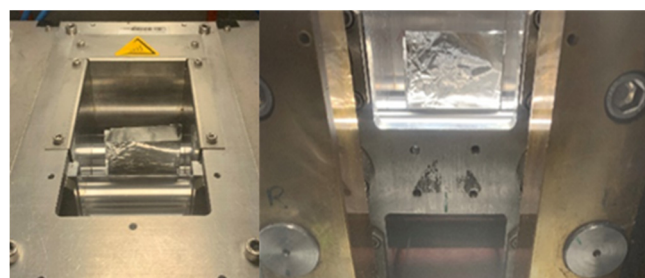
**Figure S4.** Voltage profile of first and second cycle of unlithiated and pre-lithiated electrodes (a); Charge capacity from unlithiated and pre-lithiated graphite electrodes during the first 5 cycles in half cells (b).

#### 4. Dynamic direct contact pre-lithiation

For a potential scale up of the process an attempt to use a homemade calendar was done. The calendar was placed inside an argon glovebox. The stack of temporary substrate and graphite electrode as well as Mylar foils was put into the calendar nip at minimum nip size ( $\sim 200 \mu\text{m}$ ) which means maximum pressing force (estimated to  $20 \text{ MPa}$ ). The calendar was heated up to  $120^\circ\text{C}$ .

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The sample stack was fed into the calender nip repeatedly for several times (Figure S5). Subsequently the stack was detached and evaluated electrochemically. The observed color change of the graphite indicated only a small amount of lithium transferred to the graphite after the first passage. The degree of goldish graphite surface increased with every passage and was comparable to the results of the static experiments. It was shown that a pre-lithiation can be achieved by this approach. Nevertheless, it was only possible to reproduce the results from the static experiments by passing the samples through the calender for several times since the maximum temperature as well as the line load of the used calender were too low.



(a)

(b)

**Figure S5.** Dynamic pre-lithiation using a heated calender nip to apply temperature and pressure. The contact time can be tuned by the roll velocity; sample stack in calender nip (a), sample stack after roll pressing in calender nip (b).

## References

- [1] Theodor Stuth, Verfahren zur Herstellung von Nickelband 2010.
- [2] S. Kaskel, H. Althues, B. Schumm, N. Dresel, K. Schönherr, Method for producing a substrate, which is coated with an alkali metal by means of a promoter layer, and a coated substrate 2018.
- [3] K. Schönherr, B. Schumm, F. Hippauf, R. Lissy, H. Althues, C. Leyens, S. Kaskel, Chemical Engineering Journal Advances 2022, 9, 100218.