PHYSICAL VAPOR DEPOSITION OF METALLIC LITHIUM LAYERS AND LITHIATED SILICON LAYERS FOR HIGH-PERFORMANCE ANODES

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PURPOSE & CONCEPT

Energy storage efficiency plays a key role to use continuous and intensive regenerative energy resources and to replace traditional energy sources based on fossil fuels. Substituting conventional graphite anodes with materials based on Si and metallic Li are attractive alternatives in rechargeable Li-ion batteries, owing to their extremely high capacities beyond 3600 mAh/g. Despite their advantages, numerous issues remain to be addressed:

- **Silicon swelling:** Expansion during lithiation resulting in capacity fade [1]
- **Charged Si Reactivity**: Silicide anions acting reducing and have high reactivity with the electrolyte, resulting in charge compensation locally by reduction of the solvents [2]
- **Dendrite growth** on the anode causes severe safety concerns by potential short circuits [3]
- **Solid electrolyte interphase (SEI) layer**: consuming Li and electrolyte [4]

In order to overcome the drawbacks, we use a bottom-up approach based on PVD process to synthesize a porous anode. This porous morphology offers the possibility to decrease the current density during cycling without having to accept low charging times. The method is focused on two optional routes:

- pure Li route: lithium thin films with porous morphology are deposited in a special manner by applying prior to the coating process an adequate plasma pre-treatment of the substrate surface [5].
- Li-Si route: prelithiated Si layers with varying composition will be deposited [6].

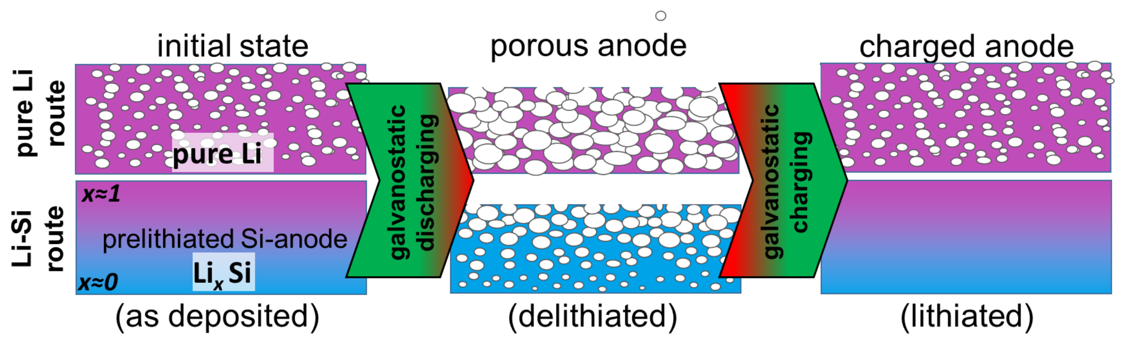

Fig. 1: (left) Scheme of the formation of pure Li thin film (purple) with interspersed pores and Li-Si layers after deposition
(middle) Li extraction while discharging leads to generation and/or magnification of pores
(right) After Li reinjection while charging, the optimized initial morphology will be restored thus capacity fade is minimized

COATING PREPARATION

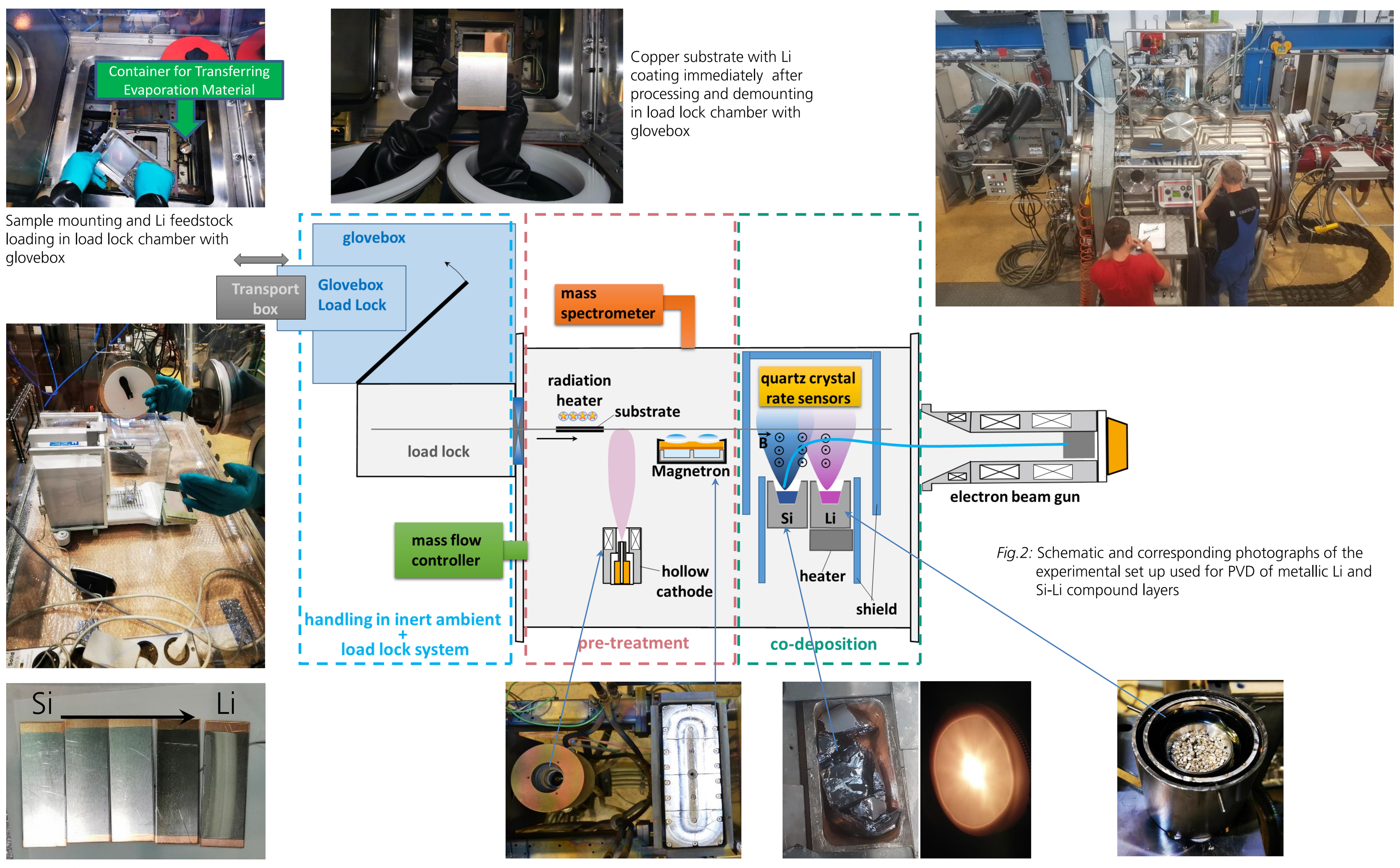

Fig. 2: Schematic and corresponding photographs of the experimental set up used for PVD of metallic Li and Si-Li compound layers

- The coatings were prepared using high vacuum tool VERSA with a glovebox at the lock chamber. This allows to prepare and to post-process the sensitive materials in a separate external Ar glovebox (O_2, H_2O < 0.1 ppm) and to transfer them directly to the vacuum system without any air contact.
- Within the load lock, the evaporation material, e.g. Li granules 99+%, can be transferred via the transport carrier through a special container with a release mechanism into the evaporation crucible.
- A resistance heater installed at crucible is used as the evaporation device for Li. Si coatings were prepared using electron beam physical vapor deposition (EB-PVD) at beam power of 5-15 kW. Si was evaporated from water cooled copper crucible filled with Si (5N) nuggets.
- A large distance of approx. 300 mm between the vapor source and the coating level was deliberately selected, on the one hand to minimize the effective process heat due to thermal radiation. On the other hand, to be able to mix lithium and silicon in a targeted manner during co-evaporation.
- The deposition process can be either static, where the substrate in the form of a metal plate with a maximum dimension of 200 mm x 120 mm is positioned in the vapor stream for a defined time. In addition, a dynamic coating process is possible, in which the substrate is moved through the vapor stream at a constant speed of 1 - 100 mm/s and thus a continuous coating process can be simulated, as it would occur in a roll-to-roll process. The substrate temperature can be adjusted in the range of 20 - 400 °C by means of a rear side radiation heater and thus their influence on the coating properties can be investigated. Prior to the coating process, the substrate surface can be cleaned in situ by a sputter etch process under the impact of a hollow cathode arc generated argon plasma [7].
- Initial evaporation experiments with lithium show that the coating rate can be controlled in a very controlled and reproducible manner via the evaporation temperature (Fig. 3). The resulting heat flux density to the substrate at maximum applied deposition rate is as low as 50 mW/cm².

RESULTS & COATING PROPERTIES

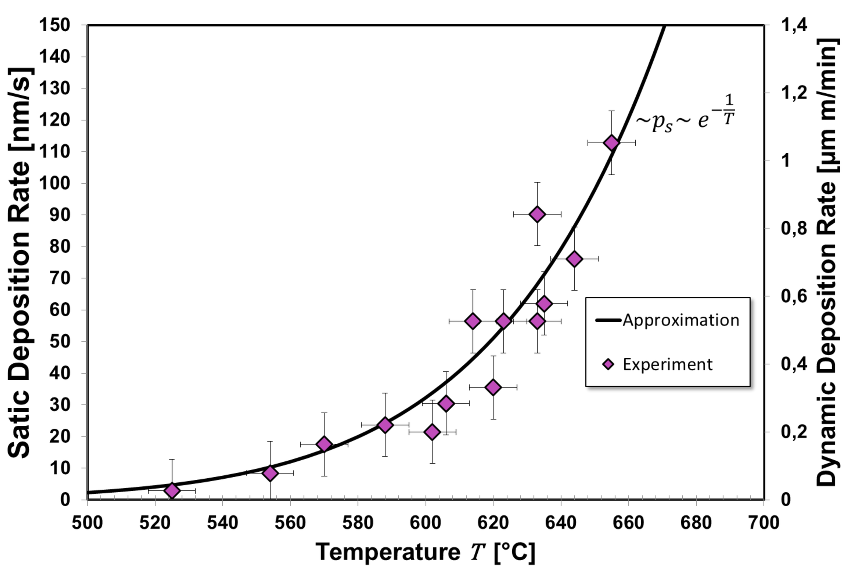

Fig. 3: Measured static deposition rate during Li coating (left ordinate) and determined dynamic deposition rate (right ordinate). The black solid curve represents data, determined from saturation vapor pressure of lithium and geometric conditions of coating facility

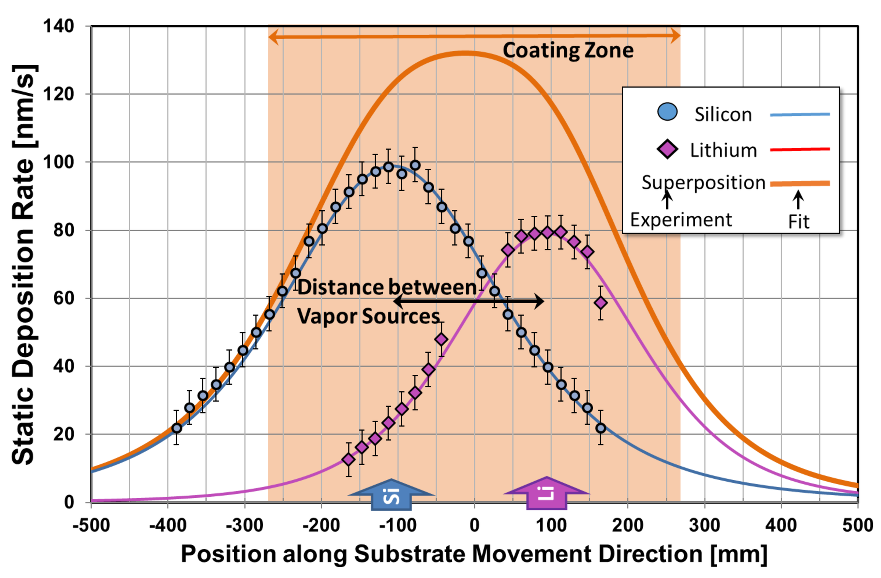

Fig. 4: Measured lateral distribution of static deposition rate for silicon (blue circles) and lithium (purple diamonds) together with fits and superposition of it

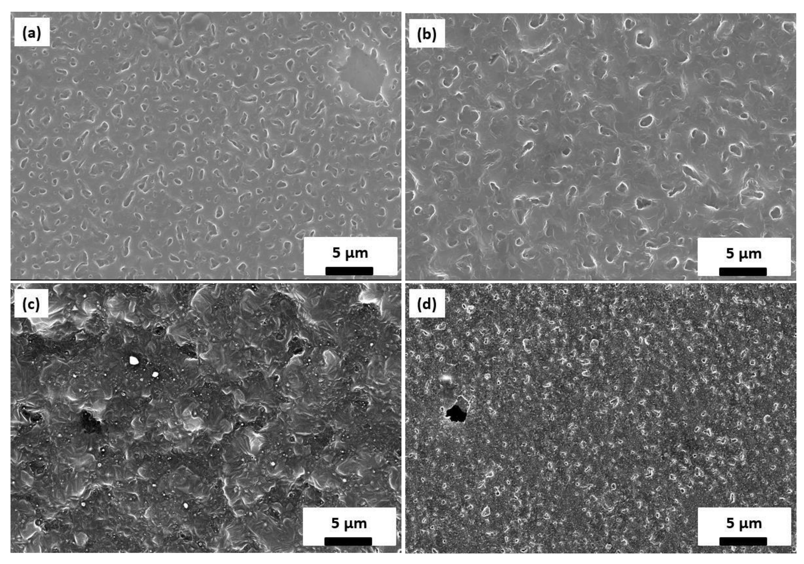

Fig. 5: SEM micrographs of as deposited pure Li layer surfaces fabricated according to IP [5] showing pores with various size (a,b) and comparative examples fabricated outside the suitable parameter range and showing an almost compact morphology (c,d)

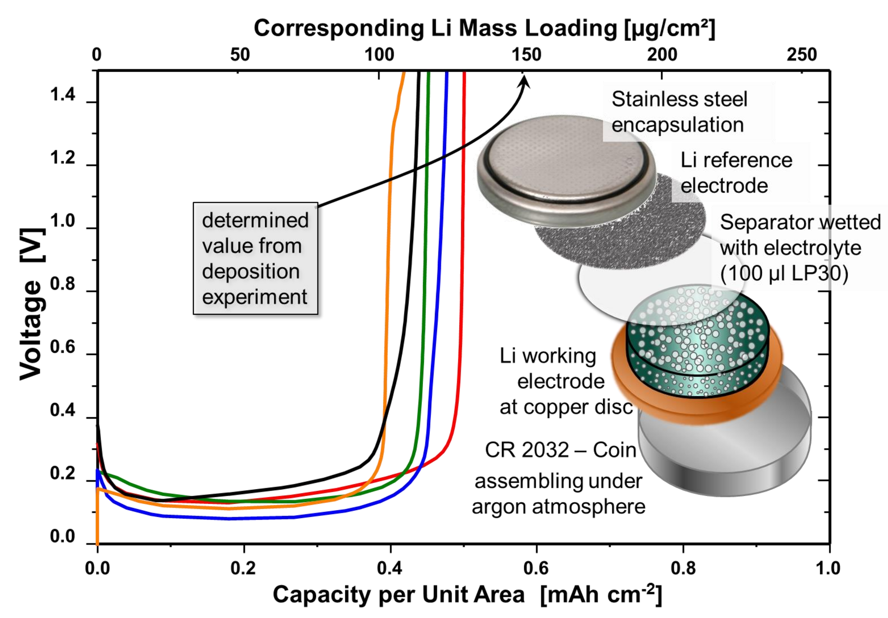

Fig. 6: Capacity vs. voltage measurements at several equivalent samples with porous Li layer (cf. to Fig. 5b). The upper abscissa axis was calculated from lithium theoretical specific capacity (3860 mA/g_{Li}). This concludes up to 85% of the Li coating is electrochemical active.

PROPOSED CONCEPT FOR PRODUCTION

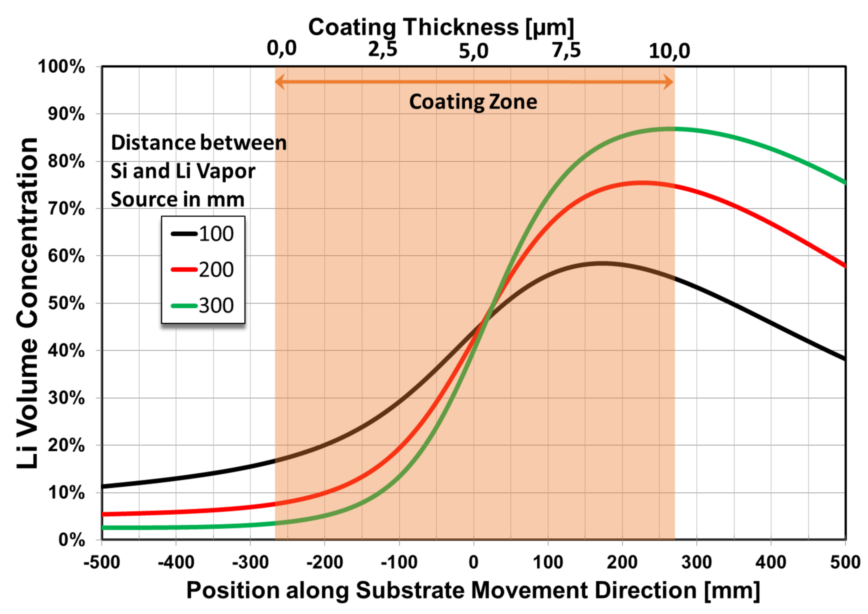

Fig. 7: For a static deposition calculated Li content in terms of substrate position for 3 distances of vapor sources (cf. to Fig. 4). For a dynamic deposition within the coating zone of 10 µm tick layer , the curves correspond to the dependency on the layer growth thickness (upper abscissa axis).

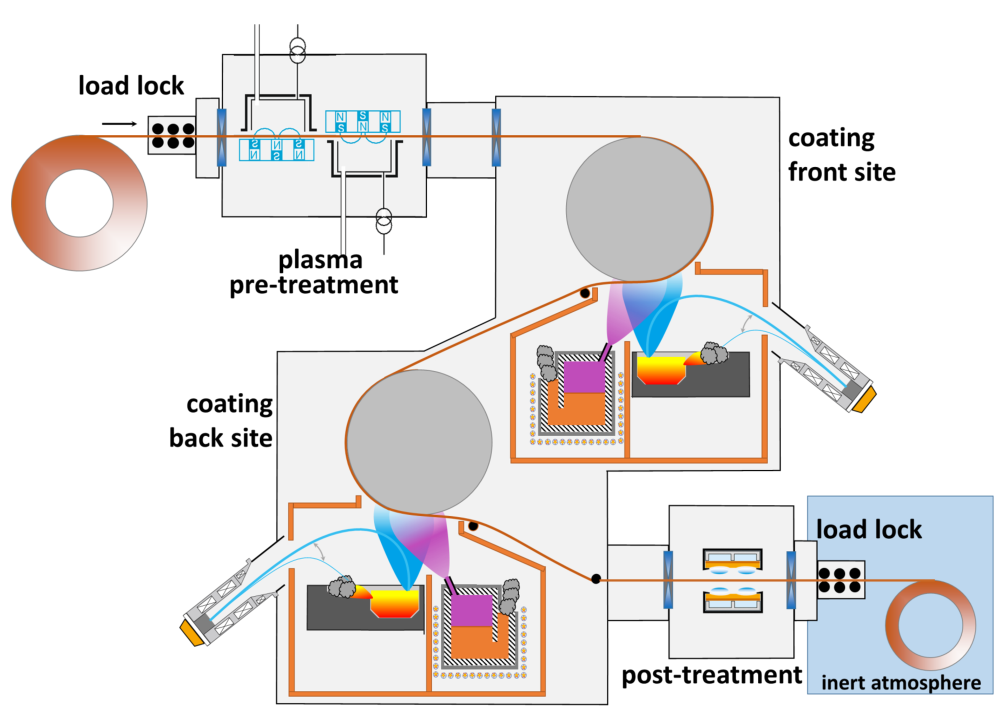

Fig. 8: Schematic design of an idea for a production plant with two Si-Li evaporation stations for double-sided coating of thin metal strips and subsequent post-treatment

- The reachable upscaling potential for continuous roll-to-roll coating of thin metal strips was estimated based on experimental data. Perspectively, a static deposition rate of 1.2 µm/s for Li and of 1.5 µm/s for Si and moreover a corresponding dynamic deposition rate of 26 µm·m/min for compound layers by superposing of vapor streams seem to be feasible.
- For dynamic deposition process, the composition will be varied with layer thickness. The concentration profile depends on the design of interpenetrating vapor streams, e.g. the distance between vapor sources for Li and Si (Fig. 7).
- A concept for production plant for a continuous double-sided processing was derived assuming a strip width of 1000 mm, a strip speed of 44 mm/s and an aimed layer thickness of 10 µm (Fig. 8).
- With designed process line an annual production throughput capacity of 0.8 million m² is feasible.

CONCLUSIONS & OUTLOOK

- An experimental setup for vacuum processing of reactive materials has been assembled
- Metallic Li thin films and Li_xSi-compound layers have been fabricated by applying an innovative approach via vacuum processing with capability for upscaling to high throughput production
- The feasibility to obtain porous Li layers with high electrochemical performance was demonstrated
- Results are greatly encouraging but offer also space for optimization, especially for the Li_xSi-system
- Further investigations regarding pore size distribution and its influence on electrochemical performance are necessary in order to further improve the cycle stability
- Fraunhofer FEP is open for any cooperation to transfer the results into high-performance products

REFERENCES

[1] Koerver et al., *Energy Environ. Sci.*, (2018)11, 2142-2158
[2] Han et al., *ACS Appl. Mater. Interfaces,* (2019) 11, 33, 29780-29790
[3] Liu, *J. Phys.: Conf. Ser.* 2152 (2022) 012060
[4] Oumellal et al., *J. Mater. Chem.*, 2011,21, 6201-6208
[5] Saager, Decker, Tenbusch, „Verfahren zur Herstellung einer porösen Lithiumschicht“, Aktenzeichen DE 10 2022 104 935.3, Anmeldetag: 02.03.2022
[6] Uxa et al., *J. Electrochem. Soc.* 167 (2020), 130522.
[7] Heinß et al., "Sputter Etching", FEP Technology Flyer (2021) G03

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