



Data Article

Kinetical threshold limits in solid-state lithium batteries: Data on practical relevance of sand equation

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ABSTRACT

The here shown data support the article “The Sand Equation and its Enormous Practical Relevance for Solid-State Lithium Metal Batteries”. [1] In this data set, all cells include the poly (ethylene oxide)-based solid polymer electrolyte (PEO-based SPE). The behaviour in symmetric Li||Li cells are provided in a three-electrode cell setup, thus with the use of a reference electrode. Moreover, the Sand behaviour is reported for varied negative electrodes with the focus on polarization onset, defined as transition time. The data of the electrochemical response after the variation of additional parameter, *i.e.* SPE thicknesses, are shown, as well. The theoretical Sand equation is linked with practically obtained values also for varied Li salt concentration. Finally, the discharge behaviour is provided including further charge/discharge cycles with the use of $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NMC622) as active material for positive electrodes.

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Specifications Table

Subject	Chemistry
Specific subject area	Electrochemistry, Energy storage
Type of data	Figure, equation
How data were acquired	Constant current (galvanostatic) methods
Data format	Raw
Parameters for data collection	The parameter are Li salt concentrations, temperatures, currents, mass loadings, SPE thicknesses, electrode materials.
Description of data collection	The data is collected <i>via</i> monitoring the voltage values during constant current application in parameter varied cells. Polarizations, specific capacities and link to Sand equation are obtained on these relations.
Data source location	Institution: Helmholtz Institute Münster City/Town/Region: Münster Country: Germany
Data accessibility	With the article
Related research article	L. Stolz, G. Homann, M. Winter, J. Kasnatscheew, The Sand Equation and its Enormous Practical Relevance for Solid-State Lithium Metal Batteries. Materials Today. In Press: https://doi.org/10.1016/j.mattod.2020.11.025

Value of the Data

- The data link theoretical and practical relations with respect to kinetic aspects in solid-state lithium batteries
- The data can support the quantification and prediction of kinetic limits, which can be beneficial for R&D of solid-state batteries.
- Based on these data and relations, the limiting parameters can be properly determined prior application and used as a valuable pre-selection criterion for application

1. Data Description

This manuscript provides additional data on manuscript [1]. For more insights and information a three-electrode cell setup is provided in Fig. 1 using PEO₂₀LiTFSI-based electrolyte. In a

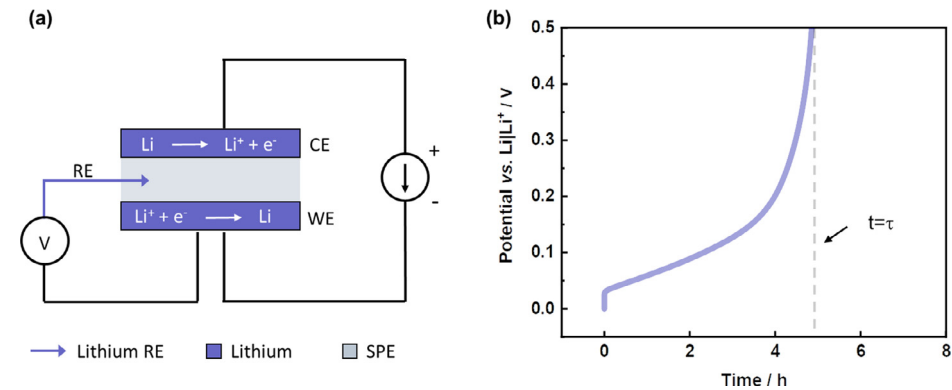


Fig. 1. (a) Three-electrode cell setup including a Li-based reference electrode (RE) to precisely monitor the potential of the Li-based working electrode (WE). The Li-based counter electrode (CE) serves as the source of active Li, thus as the source of the electrons required for the constant current measurement. (b) Constant current measurement of the three-electrode cell setup using a current density of $30 \mu\text{A cm}^{-2}$ for an EO:Li salt concentration of 20:1 of the PEO-based SPE.

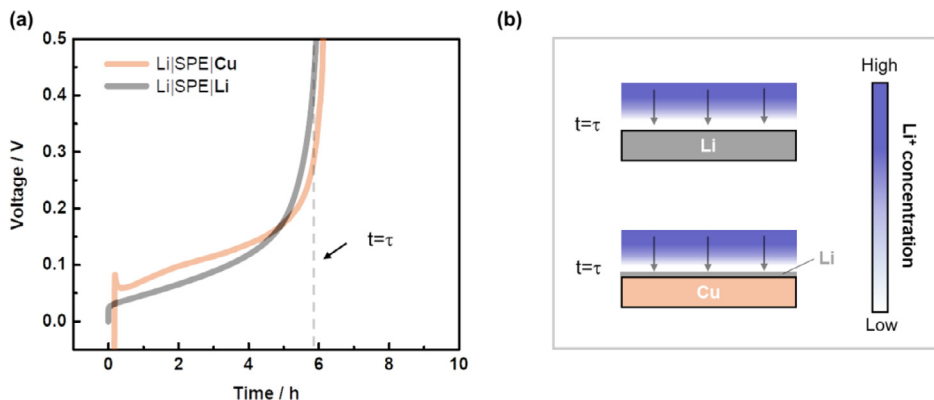


Fig. 2. (a) Galvanostatic charge of the Li|PEO₂₀LiTFSI|Li and Cu|PEO₂₀LiTFSI|Li cells with a plating current density of 30 $\mu\text{A cm}^{-2}$. As illustrated in (b) the similar transition time is independent of the negative electrode material.

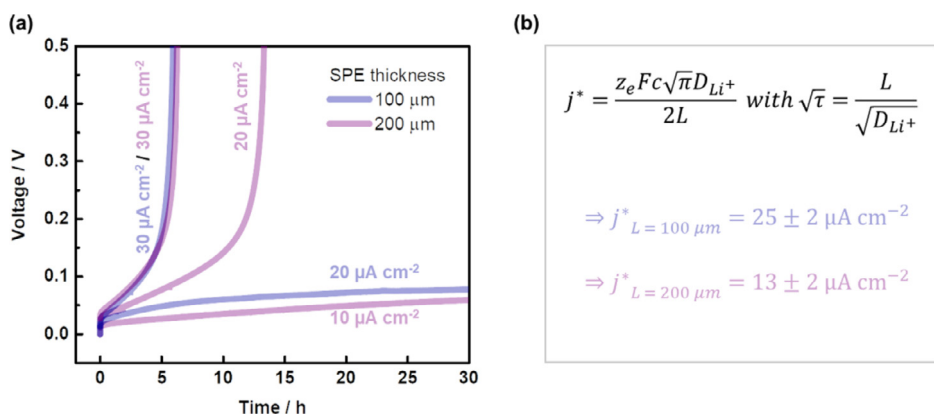


Fig. 3. (a) Galvanostatic charge of Li|PEO₂₀LiTFSI|Li cells with varied plating current densities and SPE thicknesses. (b) The related Sand equation mathematically predicting the threshold current densities for respective SPE thicknesses.

conventional two-electrode cell setup the voltage, *i.e.* potential difference of negative and positive electrode is measured. The reference electrode in a three-electrode cell setup can monitor the single potential of a selected electrode and provide more specific insights. In this cell setup, data of the electrode potential during lithium plating is precisely obtained and respective processes precisely attributed to the respective electrodes. In this experiment similar transition time is obtained as in a two electrode cell set-up and Sand behaviour still observed.

In Fig. 2 the Li-based negative electrode is substituted with Cu-based electrode using PEO₂₀LiTFSI-based electrolyte and Li-based positive electrode. During galvanostatic charge with 30 $\mu\text{A cm}^{-2}$ slight differences in voltage can be observed initially. Nevertheless, the polarization onset is at similar time.

In Fig. 3 the thickness of the PEO₂₀LiTFSI-based SPE is varied for varied current densities in a Li|SPE|Li symmetric cell setup. With increasing the SPE thickness the path of Li⁺ transport increases. Dependant on the thickness, different polarization onsets and threshold current densities are obtained. The obtained values and variation fit in the Sand equation shown in Fig. 3(b).

The curves of the Sand equation according Fig. 3(b) are depicted in Fig. 4 for varied Li salt concentrations using PEO-based SPE. For each Li salt concentration three practically obtained

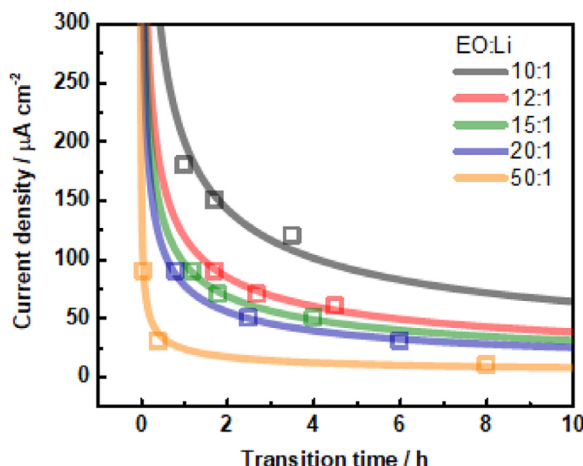


Fig. 4. The curve of the Sand relation for respective Li salt concentrations in Li|PEO_xLiTFSI|Li cells including the three experimentally obtained values for each curve.

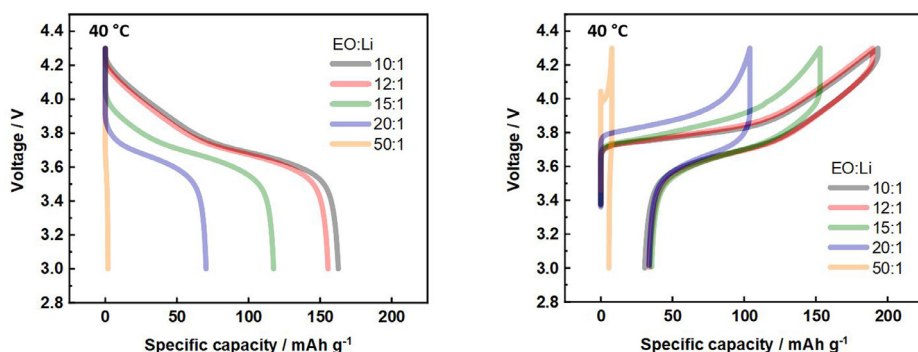


Fig. 5. (a) Voltage-capacity discharge curve of NMC622|SPE|Li cells after previous charge to 4.3 V using a specific current of 15 mA g^{-1} ($= 30 \text{ } \mu\text{A cm}^{-2}$ current density for Li plating process). The Li salt concentration is varied within the PEO-based SPE. (b) The entire charge/discharge voltage-capacity curve.

values are highlighted. The practical values (current density/transition time) are obtained from Li|SPE|Li symmetric cell setup for varied current densities and obtained transition time.

In Fig. 5(a) the discharge voltage-capacity curves are depicted after previous charge to 4.3 V in NMC622|SPE|Li cells with varied Li salt concentration of PEO-based SPE using a specific current of 15 mA g^{-1} , which corresponds to $30 \text{ } \mu\text{A cm}^{-2}$ current density for Li plating process. Higher specific discharge capacities are obtained for higher Li salt concentration in PEO-based SPE. In Fig. 5(b) the cyclic charge/discharge curve is depicted. With increasing Li salt concentration also the specific charge capacity increases, while the specific capacity loss remains similar, except for the Li salt concentration of 50:1 (EO:Li). Additionally, the voltage hysteresis and *IR*-drops are higher for lower Li salt concentration in the SPE.

Fig. 6 depicts the charge/discharge cycling behaviour of NMC622|PEO_xLiTFSI|Li cells within the voltage range of 4.3 – 3.0 V for varied Li salt concentrations at 40 °C. The activation polarization in the initial voltage curve of cycle no.1 above 25 mA g^{-1} disappears at cycle no.2.

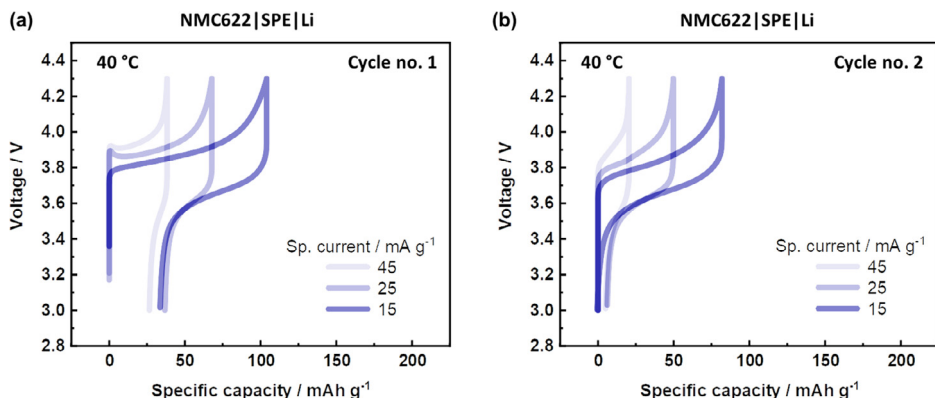


Fig. 6. Voltage-specific capacity profiles of charge/discharge cycles of NMC622||Li cells with PEO based SPE using a Li salt concentration of 20:1 (EO:Li) within a voltage range of 4.3–3.0 V and varied specific currents.

2. Experimental Design, Materials and Methods

a) Materials

Poly(ethylene oxide) (PEO, MW 300.000 Da), 1-methyl-2-pyrrolidinone (NMP, anhydrous, 99.5%) were purchased from Sigma-Aldrich, Germany. Lithium bis(trifluoromethanesulfonyl) imide (LiTFSI, 99.9%) and polyvinylidene difluoride (PVdF, Solef 5130) were purchased from Solvay, France. Super C65 carbon black was received from Imerys, France. Mylar foil (100 μm thickness) was purchased from DuPont, USA. The active materials $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NMC 622) were purchased from Targray, Canada. Lithium metal (Albemarle) was used as counter and reference electrode. Material storage and sample preparations was performed in a dryroom (dew point -65°C). PEO was dried under vacuum (10^{-7} mbar) at 45°C and LiTFSI at 110°C for 2 days before use. All other chemicals were used as received.

b) PEO-based SPE membrane preparation

PEO-based SPE polymer membranes were prepared by dry mixing PEO and LiTFSI with varied salt concentrations using a mortar. The obtained mixture was stored in a pouch bag under vacuum overnight (60°C). The resulting gum-like material was sandwiched between Mylar foil sheets and pressed at 100°C with an applied pressure of 15 bar for 10 min. The thickness of the resulting membrane in the range of $100 \pm 5 \mu\text{m}$ was controlled by the usage of a spacer.

c) Electrode preparation and cell assembly

NMC622 electrodes consisting of 91wt% NMC622, 4wt% Carbon Black and 5wt% PVdF were prepared by dissolving PVdF in NMP followed by the addition of carbon black and NMC622. The mixture was homogenized using a dissolver. The slurry was casted on aluminium foil using a doctor blade with a wet coating thickness of $50 \mu\text{m}$. The electrode sheets were dried at 80°C under vacuum for 3 h, punched into circular electrode and dried again at 120°C over night before use. The average active mass loading of NMC622 electrodes was $\approx 2 \text{ mg cm}^{-2}$. The cells were prepared in two electrode setup (coin cell) using a NMC622 based positive electrode,^[20] the PEO-based SPE as polymer membranes and lithium metal as negative electrode. The cells were assembled using the polymer membranes (12 mm diameter) inside rings of mylar foil (outer diameter: 16 mm, inner diameter: 12 mm) sandwiched between lithium metal (overall 16 mm diameter, due to the SPE, only 12 mm active diameter) and NMC622 electrodes (12 mm diameter) and/or between a further lithium metal in case of symmetrical cell configuration. Cells in three-electrode setup were prepared using lithium metal as counter electrode (CE) and reference electrode (RE).

d) Electrochemical measurements

All constant current cycling experiments were conducted on a Maccor Series 4000 battery cell test system at 40 °C in a climate chamber (Binder KB400). The used C-rates and corresponding specific currents are mentioned within the text and/or in the figure captions. All electrode potentials used in this work were measured vs. a lithium reference electrode in a three-electrode cell configuration (Swagelock®).

CRediT Author Statement

Lukas Stolz: Conceptualization; Writing - original draft; Methodology; Investigation. **Gerrit Homann:** Investigation; Writing - review & editing. **Martin Winter:** Conceptualization; Writing - review & editing. **Johannes Kasnatscheew:** Conceptualization; Writing - original draft; Methodology.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships which have or could be perceived to have influenced the work reported in this article.

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Supplementary Materials

Supplementary material associated with this article can be found in the online version at doi:[10.1016/j.dib.2020.106688](#).

Reference

- [1] L. Stolz, G. Homann, M. Winter, J. Kasnatscheew, The Sand Equation and Its Enormous Practical Relevance for Solid-State Lithium Metal Batteries Materials Today. 2020 In Press: <https://doi.org/10.1016/j.mattod.2020.11.025>.