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Perspective—Does the Sand Equation Reliably Predict the Onset of Morphological Evolution in Lithium Electrodeposition?

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For galvanostatic metal electrodeposition under diffusion-limited conditions, the Sand's equation provides the time at which the concentration of the cation being reduced reaches zero at the electrode-electrolyte interface. Such a condition causes amplification of the electrodeposit roughness and triggers dendritic growth during electrodeposition. In this perspective article, the question of whether the classical Sand equation reliably predicts the onset of morphological evolution in lithium electrodeposition is addressed and answered in the negative. A comparison of Sand's times (t_{Sand}) with experimentally observed lithium dendrite onset times reveals significant discrepancies over a wide range of Li electrodeposition current densities. Specifically, it is shown that morphology evolution in lithium electrodeposition from organic liquid electrolytes commences at time-scales that are at least 1–2 orders of magnitude lower than Sand's time. To explain this discrepancy, we present a modified Sand's approach in which transient multi-phase diffusion through the liquid electrolyte as well as through the solid-electrolyte-interphase (SEI) layer is considered. The proposed approach leads to increased accuracy in the prediction of the morphology onset time in lithium electrodeposition. We hope that this perspective helps researchers circumvent the erroneous application of the classical Sand's equation for lithium electrodeposition. We morphology evolution in lithium electrodeposition.

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List of Symbols		
Symbol	Description	Units
C	Concentration of cation	М
D	Diffusion coefficient	$cm^2 s^{-1}$
${\mathcal F}$	Faraday constant	$C \text{ mol}^{-1}$
i	Current density	mA cm ⁻²
iL	Limiting current density	mA cm ⁻²
L	SEI layer thickness	cm
m	Mass transfer coefficient	$\rm cm~s^{-1}$
n	Number of electrons	_
x	Position	cm
t	Time	s
δ	Stagnant zone in the liquid phase	cm
Subscript	Description	Units
S	Pertaining to the SEI "solid" phase	_
1	Pertaining to the electrolyte "liquid" phase	-
Superscript	Description	Units
0	Refers to initial or fixed value	-
e	Refers to value at the electrode surface $x = 0$	-

Lithium (Li) metal batteries possess higher energy density in comparison to state-of-the-art Li-ion batteries in part due to the higher theoretical capacity of a Li-metal anode compared to an intercalation anode.¹ However, development and adoption of re-chargeable Li-metal batteries has been hindered by numerous challenges. The most significant among these challenges is capacity loss and safety hazards due to growth of dendrites on the anode surface during charge-discharge cycling. In a recent review of "beyond Li-ion" battery chemistries, Whittingham identifies "a way of plating metals without the formation of dendrites or mossy metal" as a major challenge.²

The mechanism of dendrite formation in metal electrodeposition is complex. In electrodeposition of metals such as zinc and silver from aqueous electrolytes, it is known that roughness evolution and dendritic growth are favored as the deposition current density approaches the diffusion limit.^{3,4} Under such conditions, flat regions of the electrode surface experience concentration polarization but tips of surface asperities with micro-scale radii of curvature are locally released from diffusion control (due to 3D "spherical" diffusion) and begin to propagate rapidly under activation control. However, this conventional mechanistic picture is not readily extendible to Li electrodeposition from organic electrolytes for various reasons. First, when Li metal is brought into contact with an organic liquid electrolyte, a surface film called the solidelectrolyte-interphase (or "SEI") spontaneously forms on the Li electrode through a reaction between the Li metal and the salt and solvent components of the electrolyte.^{5–7} When electrodepositing Li metal, Li⁺ cations must be transported across the liquid electrolyte as well as across the SEI layer. This multi-phase transport of Li⁺ is presently not accounted for in models of dendritic Li electrodeposition.⁸ Second, it is known that the SEI layer comprises physical and chemical heterogeneities which cause non-uniform Li deposition and dissolution behavior.^{9,10} Finally, the morphological features of Li electrodeposits themselves are diverse and distinctive, ranging from "mossy" growth, "tip controlled" vs "base controlled" growth, whisker growth and fractal dendrites.^{11,12}

In addition to the growth behavior of dendrites, the early stage of morphology initiation is also of practical importance. A central question when studying dendrite initiation in electrodeposition is: at what time instant do dendrites first form? For electrodeposition of metals in aqueous electrolytes, the answer to this question is also rooted in considerations of transient diffusional transport. For galvanostatic electrodeposition, dendrites initiate when the concentration (of the cation being reduced) at the electrode-electrolyte interface approaches zero. At this point, localized deposition is favored at surface asperities due to rapid "spherical" diffusion which releases the asperity from diffusion control.^{3,13} Depletion of cation concentration at the interface occurs only gradually after galvanostatic electrodeposition is commenced. If the applied current density (i) is equal to or larger than the steady-state diffusion-limited current density $(i_{\rm I})$, then the cation concentration at the electrode surface \mathscr{C}_{I}^{e} has the following time dependence as obtained by Sand via solution of the unsteady-state diffusion problem in one-dimensional semiinfinite domain¹⁴:

$$\mathscr{C}_{l}^{e} = \mathscr{C}_{l}^{0} - \frac{2i}{n\mathcal{F}}\sqrt{\frac{t}{\mathscr{D}_{l}\pi}}$$
[1]

The gradual depletion of ionic species eventually leads to an instant when \mathscr{C}_l^e reaches zero. This is called the Sand's time (t_{Sand}) at which roughness amplification and dendrite formation begins:

$$t_{\text{Sand}} = \pi \mathscr{D}_l \left(\frac{n \mathcal{F} \mathscr{C}_l^0}{2i} \right)^2$$
[2]

The Sand's time is a widely used concept for characterizing dendrite initiation in a variety of electrodeposition systems.^{15,16} In relation to Li electrodeposition too, the concept of Sand's time (or associated cation concentration depletion at the electrode-electrolyte interface) has also been invoked. However, it is shown here, using a survey of the Li electrodeposition literature, that morphology evolution in Li electrodeposition in organic liquid electrolytes is not strongly correlated to the Sand's time. In vast majority of literature reports, evolution of Li electrodeposit morphology (dendritic morphology among other forms) is observed well before the Sand's time is reached. An extension of the classical Sand framework to Li

electrodeposition is proposed in which diffusional transport of Li^+ across a temporally-evolving SEI is incorporated in addition to its diffusion in the liquid electrolyte. Ramifications of the multi-phase transport of Li^+ to morphology onset in Li electrodeposition are discussed, and directions for future work are suggested.

Current Status

A schematic of concentration gradient development near the electrode-electrolyte interface during galvanostatic electrodeposition leading up to the Sand's time is shown in Fig. 1a. To assess its applicability to Li electrodeposition, we first conducted a comprehensive survey of the Li electrodeposition literature. Specifically, we targeted our study of literature pertaining to Li electrodeposition from organic liquid electrolytes where direct observation (via in situ or ex situ microscopy) or indirect evidence (from Li|Li symmetric cell failures) of Li dendrite formation was presented. A summary of our findings is outlined in Table I. Note here that the form of morphology, i.e., mossy vs dendritic, varied across the reports cited in Table I; however, commencement of morphological evolution was clear and unequivocal. Furthermore, we restricted our analysis to deposition current densities below 2 mA cm^{-2} because this "low" range of current densities is commonly employed in Li electrodeposition studies, and it represents deposition significantly below the liquid-phase diffusion limited current density. The observation of substantial morphological evolution even at such low electrodeposition rates in studies cited in Table I already suggests deviation of system behavior away from classical diffusion models of roughness and dendrite growth. To assess if onset of morphological evolution during Li electrodeposition conforms to the Sand's time (Eq. 2) or not, we computed the Sand's time for each of the studies reported in Table I. Note that \mathscr{C}_l^0 and *i* needed to calculate t_{Sand} are known, but \mathscr{D}_l is not. Thus, we assumed $\mathscr{D}_l = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, i.e., the lower bound of diffusivities of Li⁺ in organic liquid electrolytes yielding a lower bound of t_{Sand} .¹⁷ Furthermore, we assumed Li⁺ transference number of 0, which although not realistic, provides also a lower bound of t_{Sand} . It is clearly seen in Fig. 1b that time at which morphology evolution was experimentally observed (t_{obs} , Table I) is at least 1–2 orders of magnitude lower than the corresponding t_{Sand} value suggesting that morphological evolution is initiated much earlier than when t_{Sand} is reached. This observation is true over a variety of salts (LiPF₆, LiTFSI, LiClO₄), solvents (PC, EC:DMC, DOL:DME), and current densities $(0.01-2 \text{ mA cm}^{-2})$. In a related study not included in Table I,¹⁸ observations were shown to conform to t_{Sand} ; however, the authors of that study carefully distinguished between "mossy" growth and "dendritic" growth and applied the



Figure 1. (a) Concentration profile development during galvanostatic electrodeposition leading up to the Sand's time t_{Sand} at which the cation concentration at the electrode-electrolyte interface reaches zero. (b) Comparison of the Sand's time to experimentally observed dendrite onset times (from literature) reveals that dendritic morphology is observed in experiments well before the Sand's time is reached.

Table I. Literature summary including Li electrodeposition conditions (salt, solvent, i) and associated times at which dendritic morphology was observed, and a comparison to respective Sand's times
(Eq. 2). It is observed that morphology evolution commences in Li deposition well before t_{Sand} is reached.

References	Electrolyte (Salt, Solvent)	Current density <i>i</i>	Time at which morphology evolution was observed (t_{obs})	Corresponding Sand's time (t_{Sand}), Eq. 2 ^{a)}
Ding et al. ¹⁹	1 M LiPF ₆ PC	0.1 mA cm^{-2}	$3.6 \times 10^3 \mathrm{s}$	$7.31 \times 10^5 \mathrm{s}$
Maraschky and Akolkar ²⁰	1 M LiPF ₆ EC:DMC	0.1 mA cm^{-2}	$7.0 imes10^3~ m s$	$7.31 \times 10^5 \mathrm{s}$
		0.5 mA cm^{-2}	$6.5 imes 10^2 \mathrm{s}$	$2.92 \times 10^4 \mathrm{s}$
Crowther and West ²¹	1 M LiPF ₆ EC:EMC (3:7)	2 mA cm^{-2}	$1.8 imes10^2\mathrm{s}$	$1.83 \times 10^3 \mathrm{s}$
	1 M LiPF ₆ PC:DMC (1:3)	1 mA cm^{-2}	1600 s	$7.31 \times 10^{3} \mathrm{s}$
		0.5 mA cm^{-2}	3000 s	$2.92 \times 10^4 \mathrm{s}$
Lu et al. ²²	1 M LiTFSI PC	$10 \ \mu A \ cm^{-2}$	$1.4 imes10^5\mathrm{s}$	$7.31 \times 10^7 \mathrm{s}$
		$40 \ \mu A \ cm^{-2}$	$7.2 imes10^4\mathrm{s}$	$4.57 \times 10^{6} \mathrm{s}$
		$60 \ \mu A \ cm^{-2}$	$3.6 imes10^4\mathrm{s}$	$2.03 \times 10^6 \mathrm{s}$
Li et al. ²³	1 M LiTFSI DOL:DME (1:1)	2 mA cm^{-2}	$3.6 \times 10^2 \mathrm{s}$	$1.83 \times 10^3 \mathrm{s}$
Nishikawa et al. ²⁴	1 M LiClO ₄ PC	0.5 mA cm^{-2}	$1.8 imes10^3 ms$	$2.92 \times 10^4 \mathrm{s}$

a) To compute Sand's time at various current densities, we used $\mathscr{D}_l = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and Li⁺ transference number of 0, providing a lower bound on t_{Sand} . Despite this, t_{Sand} is 1–2 orders of magnitude higher than t_{obs} .



Figure 2. Transport equations and associated initial and boundary conditions representing multi-phase Li⁺ diffusion through the liquid electrolyte and across the SEI layer. Solution of this transport model provides a modified Sand's time ($t = t_{Sand}^{Li}$ when \mathscr{C}_s reaches 0 at x = 0) for predicting onset of morphology evolution during galvanostatic Li electrodeposition.

Sand's analysis only to the latter dendritic growth regime. Albeit this, morphological evolution before reaching t_{Sand} was evident in optical microscopy data even in this study.¹⁸

Future Needs and Prospects

As shown above, the classical t_{Sand} (Eq. 2) is not a very accurate predictor of morphology evolution in Li electrodeposition. This leads naturally to the questions: Can the Sand's approach be modified by incorporating the transport processes specific to Li electrodeposition, and could such an approach improve its reliability in predicting morphology evolution? Recognizing that the Lielectrolyte interface always comprises an SEI layer, we resorted to modeling of the Li⁺ transport simultaneously across two domains: (*i*) the stagnant liquid electrolyte (domain on the right side in Fig. 2); and (ii) the solid SEI layer (domain on the left side in Fig. 2). Analogous to the conventional Sand approach, diffusion was assumed to be the predominant mode of transport in both domains. The relevant transport equations, and associated initial and boundary conditions for galvanostatic Li electrodeposition are depicted in Fig. 2. This system of equations was solved using COMSOL® Multiphysics version 6.0. The following parameters were assumed: $\mathscr{C}_{l}^{0} = 10^{-3} \text{ mol cm}^{-3}; \mathscr{C}_{s}^{0} = 10^{-5} \text{ mol cm}^{-3}; \mathscr{D}_{l} = 10^{-6} \text{ cm}^{2} \text{ s}^{-1};$ $\mathscr{D}_{s} = 10^{-9} \text{ cm}^{2} \text{ s}^{-1}; m = 10^{-2} \text{ cm} \text{ s}^{-1}; \delta = 1 \text{ cm}.$ These parameters represent typical transport properties in the solid and liquid phases. For numerical simulations, a finite but very large domain size δ (liquid electrolyte) was used to mimic the semi-infinite domain assumption in the classical Sand model. As shown later, the concentration profile development is relatively unaffected by the choice of the value of δ as long it is large: $\delta \gg (\mathcal{D}_l t)^{\frac{1}{2}}$. The SEI thickness was assumed to be L = 10 nm but it was varied later on to characterize the effect of a gradually thickening SEI on Li⁺ concentration profile development. The value of the mass transfer coefficient m, i.e., the effective rate of mass transfer of Li⁺ ions across the SEI-liquid electrolyte interface, is not precisely known. However, choosing $m = 10^{-2} \text{ cm s}^{-1}$ ensures that mass transfer across this interface is fast (not rate limiting) in comparison to diffusional mass transport. Finally, Li electrodeposition at i = 0.5mA cm⁻² was assumed, where *i* is below the diffusion limited current density across the SEI (= $n\mathscr{F}\mathscr{D}_{s}\mathscr{C}_{s}^{0}L^{-1} = 1 \text{ mA cm}^{-2}$).

Figure 3a shows Li⁺ concentration profile development in the SEI layer (\mathscr{C}_s , blue) and across the liquid electrolyte (\mathscr{C}_l , red). It was assumed that the Li surface had an SEI layer of thickness L = 10 nm initially, i.e., when Li deposition commences. From Fig. 3a, it is observed that the Li⁺ concentration profile within the SEI layer

reaches steady-state very rapidly, i.e., within less than a second. This is expected because the diffusion time constant (L^2/\mathcal{D}_s) is merely 10^{-3} ³ s. From impedance spectroscopy, it is known that the SEI layer thickness increases with electrodeposition time; however, the measured SEI growth rate is in the vicinity of 0.016 nm s⁻ Thus, during a short time period of Li deposition [t = 2 s, Fig. 3a], any changes to the SEI layer thickness can be assumed to be negligibly small. From Fig. 3a, it is noteworthy that, despite noticeable Li⁺ concentration profile development across the SEI layer, that across the liquid electrolyte is practically absent. In Fig. 3a, only the profile at t = 2 s is shown for the liquid electrolyte (red). The length scale over which concentration gradient develops in the liquid is $(\mathcal{D}_l t)^{\frac{1}{2}}$. For t = 2 s, this length scale is 10^{-3} cm in the liquid electrolyte and thus small in comparison to the size of the stagnant liquid domain ($\delta = 1 \text{ cm}$), implying that concentration profile development in the liquid is not expected at such early stages of Li deposition. In conclusion, Fig. 3a establishes that: (i) Li^+ concentration reaches steady-state in the SEI layer nearly instantly; and (ii) For short times, the Li⁺ concentration at the Li-SEI interface does not approach zero for small current densities ($i < n \mathcal{F} \mathcal{D}_s \mathcal{C}_s^0 L^{-1}$).

As mentioned above, the SEI layer during deposition evolves in thickness from its initial value of 10 nm: L = 10 + (SEI growth rate)t. Taking SEI growth rate to be 0.016 nm s⁻¹ at i = 0.5 mA cm⁻², ²⁰ the SEI thickness reaches L = 15 nm at t = 313 s. The transport model in Fig. 2 was solved again for this thicker SEI, which provided the steady-state Li⁺ concentration profile across the SEI layer [Fig. 3b, blue]. In reality, a moving boundary simulation is needed to capture the transient concentration profile development together with a temporally-evolving SEI layer; however, because the diffusion time constant for the SEI domain is small (L^2/\mathcal{D}_s) is of the order of 10^{-3} s), steady-state is nearly instantly reached at any SEI thickness. At moderate times [t = 313 s, Fig. 3b], it is noted that the concentration of Li⁺ at the Li-SEI interface has decreased due to a greater transport resistance offered by a thickened SEI layer. Also, at moderate times (t = 313 s), boundary layer development in the liquid electrolyte is visible. Finally, when the SEI layer thickness reaches L = 19 nm at t = 563 s [Fig. 3c], the Li⁺ concentration \mathscr{C}_{s} at the Li-SEI interface (x = 0) reaches zero. This condition is analogous to the classical Sand's time, but incorporates the presence of solid-state diffusional transport of Li⁺ across the SEI layer. Hence, we call this time instant a modified Sand's time relevant to Li electrodeposition ($t_{\text{Sand}}^{\text{Li}}$). Note here that $t_{\text{Sand}}^{\text{Li}}$ (= 563 s) is reached when concentration profile development and Li⁺ depletion in the liquid electrolyte is relatively insignificant. Thus, $t_{\text{Sand}}^{\text{Li}} \ll t_{\text{Sand}} =$



Figure 3. Li^+ concentration profile development across the SEI layer (blue) and across the liquid electrolyte (red) at various stages of Li electrodeposition obtained from solution of the transport model in Fig. 2: (a) t = 2 s; (b) t = 313 s; and (c) $t_{Sand}^{Li} = 563$ s. In (c), the Li⁺ concentration at the Li-SEI interface C_s reaches zero while the Li⁺ depletion in the liquid electrolyte is still insignificant. This analysis emphasizes the transport resistance across the SEI, and provides a modified Sand's time applicable to Li electrodeposition. At $t = t_{Sand}^{Li}$, morphology evolution is triggered well before the classical Sand's time (t_{Sand} corresponding to Li⁺ depletion in the liquid electrolyte) is reached.

 2.92×10^4 s, i.e., the Li surface experiences severe Li⁺ depletion (a condition needed for morphology evolution) well before liquidphase transport limitations kick in. This explains why observed dendrite onset times in numerous studies [Fig. 1b] are orders of magnitude lower than the corresponding Sand's times calculated by applying Eq. 2.

The value of the modified Sand's time obtained ($t_{Sand}^{Li} = 563$ s for $i = 0.5 \text{ mA cm}^{-2}$ in Fig. 3 through numerical modeling is in agreement with the analytical expression for dendrite onset time $(\tau_{\text{onset}} = 625 \text{ s})$ provided by Maraschky and Akolkar.²⁰ This is not surprising since Ref. 20 also invokes transport across a temporallyevolving SEI layer. In Ref. 20, Maraschky and Akolkar employed optical microscopy, chronopotentiometry and impedance spectroscopy to demonstrate that dendrites initiate when the surface overpotential reaches a maximum value. This maxima in overpotential is due to gradual thickening of the SEI layer similar to that shown in Fig. 3. Furthermore, the modified Sand's time obtained here $(t_{\text{Sand}}^{\text{Li}} = 563 \text{ s})$ is generally consistent with experimental observations. From Table I, experimentally observed dendrite onset times for 0.5 mA cm^{-2} are in the 650–3000 s range. The slightly lower value of $t_{\text{Sand}}^{\text{Li}}$ may be due to the assumption of 100% coulombic efficiency of Li deposition. From Figs. 2 and 3, it is observed that the modified Sand's condition ($\mathscr{C}_s = 0$ at x = 0) depends on the Li deposition partial current density. If the Li deposition rate is increased, the Li⁺ concentration gradient across the SEI would be steeper leading to lowering of t_{Sand}^{Li} —this prediction is consistent with the experimental data trends seen in Fig. 1. Similarly, if coulombic efficiency is lower than 100%, then the Li deposition partial current density would be lower than the applied current *i*, thereby increasing t_{Sand}^{Li} . Values of model parameters such as $\mathscr{C}^0_s, \mathscr{D}_s$, the coulombic efficiency and the SEI growth rate are not precisely known, and their accurate determination would certainly aid in bringing the proposed theory in even better alignment with experiments over a wider range of current densities.

Conclusions

This perspective presents a comparative analysis of the classical Sand's time (Eq. 2) and experimentally observed onset times for morphology evolution in Li electrodeposition. The comparison reveals significant discrepancies between the two times over a wide range of Li deposition current densities leading to the conclusion that the classical Sand's time is not a reliable predictor for morphology evolution in Li deposition. To address the aforementioned discrepancy, we present here a modified approach to diffusional transport of Li⁺ by incorporating a temporally-evolving SEI layer in the transport model. This approach leads to a multi-phase diffusion-reaction framework more representative of electrodeposition at a Li-SEI interface, and it predicts a modified Sand's time (t_{Sand}^{Li}) that is in better alignment with experimental morphology development in Li deposition systems. Following key conclusions are noted:

- (a) Application of the Sand's time (t_{Sand} , Eq. 2) to Li electrodeposition for characterizing morphology evolution and dendrite formation may lead to erroneous results, and thus should be applied with caution or preferably avoided altogether.
- (b) The presence of the SEI layer on the Li surface, and the transport of Li⁺ across it should be accounted for in mechanistic studies of Li electrodeposition, especially those pertaining to Li dendrite initiation.
- (c) Significant gaps presently exists, both from an experimental and theoretical perspective, in studying Li dendrite initiation. Experimentally, early stages of Li dendrite initiation must be investigated using advanced in situ probes. Parameter values

corresponding to the SEI (\mathscr{C}^0_s , \mathscr{D}_s , coulombic efficiency of Li deposition, and the SEI growth rate) should be precisely measured. Contributions from migrational transport in the SEI layer should be investigated, and appropriate modifications to the model must be considered.

We hope that the present perspective will alert researchers on the pitfalls associated with applying the classical Sand's equation to morphology evolution in Li electrodeposition. Furthermore, we hope that our perspective stimulates discussion and research activity on understanding the complexities of multi-phase transport in this technologically-relevant system.

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