Temperature Dependence of Dendritic Lithium Electrodeposition: A Mechanistic Study of the Role of Transport Limitations within the SEI

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Temperature Dependence of Dendritic Lithium Electrodeposition: A Mechanistic Study of the Role of Transport Limitations within the SEI

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The accelerated failure of rechargeable Li-metal batteries due to dendritic Li electrodeposition particularly during charging at low temperatures is not well-understood. In this work, we investigate the effect of temperature on the initiation of Li dendrites during galvanostatic lithium electrodeposition. Using electrochemical measurements coupled with optical microscopy, we show that the dendrite onset time increases monotonically with temperature in the range 5 °C–35 °C. This observation is explained by incorporating temperature effects into an analytical transport model for Li dendrite initiation [J. Electrochem. Soc. (2018)], which considers solid state Li+ diffusion through a gradually thickening solid electrolyte interphase (SEI) layer. We conclude that sluggish Li+ transport at lower temperatures accelerates the depletion of Li+ at the Li-SEI interface, and this effect causes earlier initiation of dendrites at lower temperatures. Electrochemical impedance spectroscopy measurements of the temperature-dependent transport properties of the SEI, as well as plating efficiency measurements, are used to support the model.

Meeting the demand for high-energy density “beyond Li-ion” batteries remains a challenge due to the rapid capacity fade and safety concerns of secondary Li-metal anodes. The key bottleneck in adopting rechargeable Li-metal anodes is the uneven or dendritic morphology evolution during battery charging. A comprehensive understanding of the dendrite initiation process is still lacking. Whereas a number of studies have attributed the initiation of dendrites to non-uniformities in the solid electrolyte interphase (SEI), our recent work suggests the critical role of Li+ transport through a uniform but gradually thickening SEI. Specifically, we have shown that a model incorporating Li+ transport limitations in the SEI explains the influence of important factors on the dendrite initiation time. These factors include the Li plating current density, SEI thickness, and the application of pulsed currents.

Low temperature charging shortens the cycle life of Li-ion and Li-metal batteries. Li-ion batteries experience detrimental Li plating when charged at low temperatures. The similarity of these two systems (i.e., the presence of an SEI) and their issues with respect to sub-ambient temperature charging suggests an analogous transport limitation is at work.

The transport of Li+ through the SEI is critical in determining the kinetics and stability of Li-metal in electrochemical systems. Effects of temperature on Li battery performance and surface film growth were reported by Dey in the 1970’s. Churikov studied the role of temperature on charge-transfer kinetics at a Li electrode limited by transport processes within the SEI using pulse voltammetry, as well as photoemission spectroscopy. Heims et al. reported the energetics of SEI formation on intercalation electrodes during charging by using temperature-dependent electrochemical impedance spectroscopy (EIS). Despite intensive research activity characterizing and modeling the SEI, the precise mechanism of Li+ transport within the SEI is presently not well-understood.

Hess recently extended studies of the non-linearity in the SEI overpotential to a wide temperature range for several alkali metal anodes, and found that conduction mechanisms through SEI exhibit distinct temperature dependencies. Shi et al. performed experimental and DFT simulation studies to investigate the hopping of Li+ within the SEI, enabling the prediction of Li+ diffusion coefficients and the Li+ concentration evolution. Benitez and Seminario carried out molecular dynamics simulations of Li+ diffusional transport in the SEI in the temperature range 250–400 K.

In relation to mechanisms of Li surface morphology evolution and dendrite formation, Mogi et al. studied the effect of temperature on SEI and Li deposition morphology using AFM. While they found that the SEI became uniform and Li dendrites were suppressed at elevated temperatures, the uniform surface film formed at high temperatures did not prevent dendrite growth when plating was carried out at room temperature. Ota et al. also studied the correlation between Li surface film formation and plating morphology at various temperatures. Using diffusion-reaction modeling, Akolkar predicted a critical temperature below which uncontrolled Li dendrite propagation occurs. This prediction was a consequence of increased mass transport resistance at low temperature and decreased reaction resistance provided by a thinner SEI. Love et al. performed experimental studies of dendrite initiation times at ambient and sub-ambient temperatures and observed an increase in the propensity for Li dendrites at low temperatures, which was in qualitative agreement with the Akolkar model.

Hao et al. proposed that Li dendrites are initiated by two possible mechanisms: (i) Li+ depletion at the Li-SEI interface, and (ii) non-uniformity of the SEI, causing non-uniform local deposition rates. Recently, Mistry et al. presented a model of electrolyte confinement to explain Li dendrite initiation beyond the Sand criteria. Sano et al. reported the effects of temperature on Li electrodeposition in an ionic liquid electrolyte.

To explain the effect of temperature on the dendrite initiation time, a mechanistic model that incorporates Li+ diffusion through a dynamic SEI layer is needed. Herein, we provide electrochemical measurements of the dendrite onset time as a function of temperature. Chronopotentiometry and optical imaging are used to quantify the time at which Li dendrites initiate. This initiation occurs at a temporal maximum in the surface overpotential—a unique electrochemical signature that corresponds with and thus helps easily identify the first morphological appearance of Li dendrites.

Electrochemical impedance spectroscopy (EIS) is used to measure the growth of the SEI before and during Li electrodeposition over a range of temperatures. The continuous growth of the SEI leading to the depletion of Li+ at the Li-SEI interface during electrodeposition, and the eventual onset of Li dendritic growth is considered. The diffusional transport of Li+ through the SEI is shown to be the
Critical temperature-dependent process that explains the early initiation of Li dendrites at subambient temperatures.

Experimental

Cell materials and construction.—Li ribbon (99.9%, Sigma-Aldrich) with 0.38 mm thickness was used to prepare the working (WE), counter (CE), and reference (RE) electrodes. The electrode surfaces were polished with 400 grit sanding sheets. Discs were cut from the Li ribbon using a 0.5° diameter punch. Chemical-resistant compression tee fittings for 0.5° OD plastic tubing were used to construct the electrochemical cells (McMaster Carr). Stainless steel rod 0.5° in diameter was inserted into the compression fittings, sealing the Li WE and CE in place (Fig. 1). The projected area of the exposed Li WE and CE was 0.672 cm². A length of 18-gauge copper wire, which was used to contact the RE, was guided through the PTFE stopper inserted into the top of the tee fitting. The tip of the wedge-shaped Li RE exposed to electrolyte was cleaved prior to each experiment. Battery grade 1.0 M LiPF6 solution in 1:1 (v/v) EC/DMC electrolyte (MilliporeSigma) was dispensed into the cell by pipet. The total electrolyte volume in the cell was ∼3 ml.

Methods

Cells were prepared within an Ar-purged glovebox (MBraun). Moisture inside the glovebox was maintained below 5 ppm. A water circulating bath located outside the glovebox pumped chilled or heated water through tubing into a jacketed beaker, controlling the temperature of the electrolyte within the glovebox prior to cell fabrication. After fabrication, the cells were removed from the glove box for electrochemical characterization. During characterization, the temperature of the sealed cells was maintained by immersion in sand at controlled temperatures. The sand was either heated using a hot plate or cooled using refrigeration.

Chronopotentiometry and electrochemical impedance spectroscopy (EIS) experiments were performed using a VersaSTAT 4 potentiostat/galvanostat with built-in frequency response analyzer (Ametek). Chronopotentiometry was performed at an applied current density (i). Here, i refers to the applied current normalized to the exposed geometric surface area of the WE. For simplicity and consistency, we used the sign convention that cathodic (plating) current densities and overpotentials are positive quantities. The EIS experiments and analysis were performed using the methods described in our previous publication. In brief, galvanostatic EIS was performed with a direct current of 0 A and the RMS amplitude was 45 μA cm⁻². The frequency range used was 100 kHz to 1 Hz. The ohmic resistance Rₑ, determined at the high frequency limit, was used to subtract the iR drop in the liquid electrolyte. The surface resistance Rₛ was determined from the diameter of a circle fit to the Nyquist impedance plot.

The faradaic efficiency of plating was measured via anodic stripping coulometry. A 0.127 mm thick Cu foil (99.9%, Alfa Aesar) was used as substrate for galvanostatic Li plating and subsequent anodic stripping coulometry. Prior to Li plating, the Cu foil was cleaned in 2 M H₂SO₄ for 10 min, then rinsed with acetone and deionized water (Millipore). Li plating onto and stripping from the Cu foil were performed in the cell described above. The Cu substrate was used in place of the polished Li foil WE for plating efficiency studies. The electrolyte, RE, and CE were otherwise used in the same manner as above.

Results and discussion

In this section, we first describe experimental investigations of the temperature effects on Li dendrite initiation using chronopotentiometry, EIS, and plating efficiency studies. Next, we present a mechanistic model to explain the temperature effects invoking Li⁺ transport through the SEI.

Chronopotentiometry.—The Li dendrite onset time (t_onset) as a function of temperature was investigated under galvanostatic Li electrodeposition. Chronopotentiometry and optical imaging were used to study the initiation and growth of Li dendrites under controlled temperature. After soaking the freshly polished Li WE and CE in liquid electrolyte [1.0 M LiPF₆ solution in 1:1 (v/v) EC/DMC] for t soak = 30 min, galvanostatic plating was performed at an applied average current density i = 1 mA cm⁻² in the tee cell (Fig. 1). As reported in our prior work, the first appearance of Li dendrites (at t = t_onset) coincided with temporal maximum in surface overpotential, η = V - iRₑ (Fig. 2). In the present work too, similar behavior was observed at a variety of temperatures: η increased during an initial SEI growth phase, reached a local maximum at t = t_onset, and then decreased during the period of dendrite growth. A moderate increase in the temperature of the cell was found to increase t_onset. For instance, at 8 °C the measured t_onset was 30 s, while at 34 °C t_onset was 240 s. Thus, increasing the temperature of Li deposition by 26 °C resulted in an eight-fold increase in the plating time at which the first dendrite appeared. The increase in temperature also lowered the initial (t = 0) surface overpotential, and broadened the peak in the surface overpotential (at t = t_onset). Interestingly, the difference in η between t = t_onset and t = 0 was roughly constant (∼290 mV) and independent of temperature.

The dependence of t_onset on temperature at i = 1 mA cm⁻² is shown over the range from 5 to 35 °C (Fig. 3). A monotonic increase in dendrite onset time was observed over the range of temperatures studied. This temperature dependence within the range studied does not suggest the presence of a distinct critical temperature below which dendrites are initiated. On the contrary, while Li dendrites were found to initiate at all temperatures, lower temperatures favored an earlier onset (shorter t_onset) of Li dendrites. This effect of temperature on dendrite initiation will be discussed within the context of Li⁺ transport through the SEI layer in the following sections.

![Figure 1. Photograph (left) and schematic (right) of the tee cell setup used for Li electrodeposition studies.](image-url)
of the WE in contact
as:

and thus the SEI thickness\(^{26,51}\)
0splate.

\(R\) depends on \(R\) at a variety of temperatures is
remained relatively constant during the temperature
a fraction of the applied current is consumed
is plotted as a function of
\(vs\)
\(R\))
reached a local maximum. The plating current
\(t\)
reached a

,\(e\)
As a result, as is the case
parabolic growth is typical for surface
transport limitations of the reacting (e.g., \(Li^+\))
\(Li\) species.\(^{52}\)

Mathematically, \(R_s\) depends on \(t_{\text{soak}}\) as:

\[ R_s = (A \cdot t_{\text{soak}})^\alpha + B \]  \[1\]

In Eq. 1, \(A\) and \(B\) are constants. The data in Fig. 4b when fitted to
Eq. 1 provided values of the parameter \(\alpha\), which was 0.5 at 22 °C
and 31 °C, but 0.2 at 12 °C. The mechanistic origin of the temperature-dependence of \(\alpha\) particularly at low temperatures is
 presently unknown.

Nyquist plots immediately prior to plating (\(t_{\text{soak}} = 30\) min,
\(t_{\text{plate}} = 0\) s) are shown for 12, 22, and 31 °C in Fig. 5. The electrolyte
resistance \(R_s\) was found to be a weak function of temperature, while
the surface resistance \(R_s\) was observed to be strongly dependent on temperature. The weak temperature-dependence of \(R_s\), a liquid-
phase property that remains constant during plating, further
strengthens the conclusion that liquid-phase transport limitations are
not critical in Li dendrite initiation, as was shown in our previous
work.\(^{21}\) The solid-state property \(R_s\) depends on the SEI conductivity \(\kappa\) and the SEI thickness \(L\) as:

\[ R_s = \frac{L}{\kappa} \]  \[2\]

The quantitative temperature-dependence of \(\kappa\) in the temperature
range of interest is not known to us. While the theoretical
temperature-dependence was given by Peled,\(^{26}\) we do not have
access to the parameters needed to calculate \(\kappa\). Thus, at the present
time, quantitative determination of \(L\) at a variety of temperatures is
not feasible. We estimate \(L\) after \(t_{\text{soak}}\) to be between 3–8 nm based on
\(\kappa = 10^{-9} \text{ S cm}^{-1}\) for \(Li_2CO_3\) at room temperature.\(^{54}\)

In order to confirm that \(\kappa\) is indeed the relevant temperature-
dependent property, EIS measurements were performed on a Li WE
immersed in liquid electrolyte while the cell temperature was varied.
In this experiment, the Li WE in the cell was allowed to soak for
22 h until \(R_s\) reached an approximately constant value at 35 ± 3 °C.
The temperature of the cell was then decreased to 15 °C until
equilibrium was reached, and EIS was performed again (Fig. 6). The
figure shows that the value of \(R_s\) dropped measurably when the
temperature was increased from 15 °C to 35 °C; however, returning
the temperature to 15 °C produced nearly the same value of \(R_s\) as
was measured at 15 °C before the temperature increase. That is, \(R_s\)
was roughly the same before (1) and after (3) the temperature
increase (2) shown in Fig. 6. Such reversibility implies that the SEI
thickness \(L\) remained relatively constant during the temperature
changes, and that \(R_s\) changed due to temperature-effects on \(\kappa\). A
rough estimate of the energy barrier for the conduction of \(Li^+\) ions
was obtained from the slope of the In (1/\(R_s\)) vs T\(^{-1}\) curve. The
energy barrier was calculated to be 0.4 eV, which is comparable to
the energetics of an ion hopping transport mechanism reported by
Churkov,\(^{20}\) albeit for a different electrolyte composition. This
suggests that transport of \(Li^+\) ions through the SEI is a temperature-
dependent process, and thus it is a factor that must be accounted for in
understanding temperature effects on Li dendrite initiation.

In Fig. 7, the surface resistance \(R_s\) is plotted as a function of plating time (\(t_{\text{plate}}\)) during galvanostatic Li electrodeposition at an
applied current density \(i = 1\) mA cm\(^{-2}\). Three temperatures (12, 22,
and 31 °C) were evaluated. During the initial phase of Li plating, i.e.,
prior to reaching \(t_{\text{onset}}\), a fraction of the applied current is consumed
by the formation of additional SEI while the rest of the current
results in Li plating. A more quantitative study of these competing
processes is conducted in the next section. In Fig. 7, the slope of
the \(R_s\) vs \(t_{\text{plate}}\) curve must be proportional to the SEI growth rate and
inversely proportional to \(\kappa\) in accordance with Eq. 2. This slope is
observed to decrease with increasing temperature. Indeed, the
general shape of the \(R_s\) vs \(t_{\text{plate}}\) curve (Fig. 7) is similar to that of
the surface overpotential (\(\eta_s\)) time trend seen during galvanostatic Li
electrodeposition (Fig. 2). This is expected because \(\eta_s\) predominantly
represents the \(Li^+\) transport resistance through the SEI.\(^{26,52}\) While
the general form of the time evolution of \(R_s\) and \(\eta_s\) are similar, it
must be noted that the SEI is not strictly an ohmic resistor.\(^{29}\) This is

![Figure 2. Time-evolution of the surface overpotential during temperature-controlled galvanostatic Li electrodeposition at 1 mA cm\(^{-2}\) in 1 M LiPF\(_6\) 1:1 EC/DMC. The temperatures were 8 °C (blue), 18 °C (black), and 34 °C (red). The Li foil electrode was soaked in the electrolyte for \(t_{\text{soak}} = 30\) min before plating. A photograph (inset) of the Li metal surface at the dendrite onset time (\(t_{\text{onset}} = 114\) s), when dendrites were first observed and the surface overpotential \(\eta_s\) reached a local maximum. The plating current density was 1 mA cm\(^{-2}\) and the temperature was 24 ± 1.0 °C.](image)

![Figure 3. Dendrite onset time (\(t_{\text{onset}}\)) as a function of plating temperature. The values of \(t_{\text{onset}}\) were determined from the times at which \(\eta_s\) reached a local maximum during chronopotentiometry at current density 1 mA cm\(^{-2}\). The Li foil electrode was soaked in the electrolyte for \(t_{\text{soak}} = 30\) min before plating.](image)
evident from comparing the surface resistance \( R_s \) at \( t_{\text{plate}} = 15 \) s and at 22 °C to the surface overpotential \( \eta_s = 245 \) mV under similar conditions. The surface overpotential (measured at 1 mA cm\(^{-2}\)) corresponds to an area normalized surface resistance \( \eta_s/i \) of 245 \( \Omega \) cm\(^2\), which is significantly lower than that provided by EIS.

It should be noted that while the change in \( R_s \) due to temperature was explained by changes in \( \kappa \), the change in \( R_s \) during plating is not due to a transient change in \( \kappa \). This was shown previously by current interrupt experiments.\(^{21}\) The rise in \( R_s \) and \( \eta_s \) during plating is explained neither by concentration effects nor by conductivity effects. These changes due to SEI growth are irreversible and stable until dendrites pierce the SEI.

**Lithium plating efficiency.**—Coulometric measurements during Li plating and its subsequent anodic stripping were used to study the effect of temperature on the Li plating efficiency. Li was plated on a Cu substrate in a two-step process. First, an average current density of 2 mA cm\(^{-2}\) was applied for 5 s to facilitate high nucleation density Li plating on Cu leading to uniform substrate coverage by Li. Next, a current density of 1 mA cm\(^{-2}\) was applied for 120 s. The Li deposited on the Cu substrate was immediately stripped by applying an anodic potential of +0.5 V vs Li/Li\(^+\) RE (Fig. 8a). The charge corresponding to Li stripping \( (Q_{\text{strip}}) \) was compared to the total charge passed during plating \( (Q_{\text{plate}}) \), thus yielding the plating efficiency \( \varepsilon \):

\[
\varepsilon = \frac{Q_{\text{strip}}}{Q_{\text{plate}}}
\]

The experiments were repeated 3 times each at 20 ± 1.0 °C and at 30.5 ± 1.0 °C. As shown in Fig. 8b, the Li plating efficiency was not found to be a strong function of temperature. The average \( \varepsilon \) at 20 °C was 44%, while at 30.5 °C \( \varepsilon \) was 48%. The fraction of the charge that contributed to SEI growth during plating was \((1 - \varepsilon)\) and was related to the SEI growth rate as follows:

\[
\dot{L} = (1 - \varepsilon)\Gamma i
\]
In Eq. 4, $\Gamma$ is a constant which incorporates the physicochemical properties of the SEI such as density and molecular weight. Since $\varepsilon$ is not a strong function of temperature (Fig. 8b), Eq. 4 implies that the SEI growth rate $L$ at a fixed applied current density $i$ is also relatively independent of temperature. This conclusion will be used in the model development in the following section.

**Model incorporating Li$^+$ transport through the SEI**—In this section, we propose a model for explaining the temperature effects on Li dendrite initiation reported in Figs. 2 and 3. As a basis for the model development, we use the framework outlined in our previous publication. Briefly, the model we have proposed earlier considers the diffusional transport of Li$^+$ through a temporally evolving SEI layer. Whereas a typical SEI formed in EC/DMC with LiPF$_6$ salt has a complex bilayer structure with an outer organic layer and an inner compact layer composed of inorganic Li compounds, the present model assumes for simplicity a single uniform layer composed of Li$_2$CO$_3$. The SEI layer grows in thickness on the Li surface during soaking as well as during Li electrodeposition (Fig. 9). The SEI growth that occurs during the time period $t_{\text{soak}}$ (prior to commencement of Li plating) forms the initial SEI thickness $L_0$. During Li electrodeposition, the SEI grows at a roughly constant rate $L$ proportional to $(1 - \varepsilon)$ as in Eq. 4. The steady growth of the SEI layer manifests in experiments as a steady increase in the surface resistance $R_e$ seen in EIS data, and a steady increase in the surface overpotential $\eta$ seen in chronopotentiometry. To model transport of Li$^+$ ions across the SEI, we neglect electric field induced migrational transport ($q_i < 1$) and assume the development of a linear Li$^+$ concentration profile within the SEI that drives diffusional transport. At pseudo steady-state, the Li$^+$ diffusional flux is proportional to the applied current density $i$. Under galvanostatic conditions, this provides the Li$^+$ concentration at the Li-SEI interface ($C_e$):

$$C_e = C_0 - \frac{IL}{nfD_{\text{SEI}}}$$

In Eq. 5, $C_0$ is the constant Li$^+$ concentration in the SEI at the SEI-electrolyte interface (Fig. 9), and $D_{\text{SEI}}$ is the solid-state Li$^+$ diffusion coefficient in the SEI. As the Li plating progresses, the SEI layer thickness $L$ increases causing the gradual depletion of Li$^+$ at the Li-SEI interface. Eventually, as the plating time reaches $t_{\text{onset}}$, $C_e$ approaches 0 and, as demonstrated previously, this depletion is responsible for the initiation of Li dendrites. Assuming that $L$ increases linearly with time ($L = L_0 + L_{\text{plate}}$), the critical time $t_{\text{onset}}$ at which $C_e$ approaches 0 leading to onset of dendrites is:

$$t_{\text{onset}} = \frac{1}{L} \left( \frac{nF D_{\text{SEI}} C_0}{i} - L_0 \right)$$

Equation 6 provides insights into the effect of temperature on $t_{\text{onset}}$. First, as described above (Eq. 4 and related discussion), the SEI growth rate $L$ at a fixed applied current density $i$ is not a strong function of temperature. Furthermore, the initial thickness $L_0$ (which depends on $t_{\text{soak}}$) should increase with temperature because of faster transport through the SEI at elevated temperatures; however, per Eq. 6, this effect would lead to a decrease in $t_{\text{onset}}$ at higher temperatures, which is inconsistent with the experimental data in Figs. 2 and 3. Thus, temperature-dependencies of $L$ and $L_0$ do not explain the temperature-dependence of $t_{\text{onset}}$. Now, we examine the lumped parameters $D_{\text{SEI}}C_0$ comprising the diffusion coefficient ($D_{\text{SEI}}$) and the maximum concentration of mobile Li$^+$ species in the SEI ($C_0$). Although the precise temperature-dependence of $D_{\text{SEI}}C_0$ is not known, both parameters $D_{\text{SEI}}$ and $C_0$ are expected to increase with temperature, causing an increase in $t_{\text{onset}}$ per Eq. 6. Therefore, one or both of these parameters is responsible for the
At low temperatures, fewer SEI are formed due to lower $L$ at the Li-SEI interface. Low temperatures, the bulk concentration of Li and the concentration gradient is steeper due to lower $L$.

During Li electrodeposition, the SEI continued to grow in temperature-dependence of onset reaching the critical condition (strong in $F$).

Faster dendrite initiation time $\tau_{\text{onset}}$ at lower temperatures is explained by the increased resistance associated with Li diffusional transport.

The strong influence of temperature on $\tau_{\text{onset}}$. At low temperatures, fewer defects are present in the SEI (lower value of $C_0$) and solid-state diffusivity ($D_{\text{SEI}}$) is lowered too.$^{56,40,41}$ This causes lower $\tau_{\text{onset}}$ and thus an earlier onset of Li dendrite growth. At higher temperatures, a greater number of defects ($C_0$) and an elevated diffusion coefficient ($D_{\text{SEI}}$) permits the SEI to grow to a greater thickness $L$ before reaching the critical condition $C_2 \leq 0$ for dendrite initiation. Consequently, at elevated temperatures, Li dendrite initiation is delayed. Thus, our model qualitatively explains the observed temperature-dependence of $\tau_{\text{onset}}$ based on changes in Li$^+$ transport ($D_{\text{SEI}}C_0$) through the SEI.

**Conclusions**

The temperature-dependence of Li dendrite initiation during galvanostatic electrodeposition was investigated using experiments and modeling. The following main conclusions can be drawn from this work:

- (i) Li dendrite initiation time ($t = \tau_{\text{onset}}$) during galvanostatic Li electrodeposition was found to increase monotonically with an increase in temperature from 5 °C to 35 °C.
- (ii) During Li electrodeposition, the SEI continued to grow in thickness (for $t < \tau_{\text{onset}}$), as evidenced by an increase in surface overpotential and surface resistance, until the onset of dendritic growth.
- (iii) Temperature affects the solid state ionic conductivity ($\kappa$) of the SEI.
- (iv) The Li plating efficiency, and thus the SEI growth rate during galvanostatic electrodeposition, was shown not to be a strong function of temperature.
- (v) The temperature-dependence of the Li dendrite initiation time was explained within the framework of a previously-developed transfer model. The bulk concentration $C_0$ and diffusion coefficient $D_{\text{SEI}}$ of Li$^+$ within the SEI are suggested to be the temperature-dependent parameters responsible for the effect of temperature on $\tau_{\text{onset}}$ per Eq. 6.

The sluggish transport of Li$^+$ through the SEI imposes a major limitation during low-temperature charging of Li-metal batteries. The sluggish transport leads to faster depletion of Li$^+$ at the Li-SEI interface, triggering earlier initiation of Li dendrites at lower temperatures. Our work implies that while Li dendrite initiation during battery charging may be inevitable even at low current densities, avoiding low temperatures thereby facilitating faster Li$^+$ transport is critically essential in delaying dendrites. Other strategies such as artificial SEI layers, including materials with Li$^+$ transference numbers approaching unity, or solid electrolytes that do not continue to evolve in thickness, may hold the promise to preventing altogether the formation of Li dendrites.

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