nature portfolio

Peer Review File

Diffusion-Like Overpotentials from Non-Diffusion Mechanisms in Battery Particles

Corresponding Author: Professor Stephen Kang

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The manuscript suggests that for smaller cathode particles in porous electrodes, the square-root behavior of overpotentials over time is not always caused by chemical diffusion in the electrode. Instead, it can arise from the way transfer equations work for porous electrodes, as illustrated in Figure 4. This explanation is reasonable, and I find the observations intriguing.

However, transmission-line effects (TLEs) in porous and fractal electrodes, which lead to $1/\sqrt{}$frequency scaling, are well known, as the authors themselves note on page 3. Surface roughness with a broad distribution of time constants also yields constant-phase elements that can be mistaken for Warburg impedance. Similarly, charge hopping and interfacial charge propagation in mixed ionic-electronic conductors can produce the same scaling. The authors acknowledge the multiplicity of such effects (see page 12) and note that they have been observed repeatedly in prior studies. Taht's correct. Square-root-over-time behavior of overpotentials has also been reported for capacitive charging/discharging RC networks, surface-limited adsorption/desorption, and many other systems. I recently read a paper on TLEs explaining solid-state diffusion and Warburg-like behavior:
https://pubs.rsc.org/en/content/articlehtml/2024/cp/d4cp00975d
This topic is fairly well established and widely reported in porous, fractal, and polymer electrolytes. While the authors suggest that TLEs are insufficiently known to researchers studying intercalation electrodes, the fact remains that TLEs are a common phenomenon. Therefore, this alone is not sufficient grounds for publication in a high-impact journal such as Nature.

The results are robust, the explanations are sound, and there may be practical implications, but the phenomena described are not novel enough to make a significant splash. I believe this is a good paper, but it would be better suited for publication in a more specialized journal. My recommendation is to reject this ms.

Minor point:
I am not sure why the discretization in Section S7.3 is discussed in such detail; it appears trivial.

Reviewer #2

(Remarks to the Author)
This manuscript provides new insights into the origin of overpotential battery electrodes. The scientific question addressed is highly significant, and the experimental design and analysis are both reasonable and rigorous. However, several issues require clarification or further revision. With additional discussion and clearer presentation, this work has the potential to become a highly influential and groundbreaking contribution:
1.The wording throughout the manuscript needs to be more precise. The title and parts of the discussion may give readers the impression that solid-state diffusion is “unimportant.” It is recommended that the authors clearly define the scope and boundaries of the study in the conclusions.
2.While the experimental design is sound, further explanation is needed regarding how other variables were excluded. In addition, the manuscript lacks discussion on the universality of the proposed mechanism. The authors should consider whether this mechanism is also important in other material systems, which would help define the broader impact of this work.
3.For readers without a background in modeling, the particle-level transmission line model may appear complex. Although the authors have provided some explanation, further simplification or more intuitive presentation of the key concepts is recommended.
4.The porous particle model effectively explains the experimental observations, but the authors are encouraged to elaborate on how the model parameters correspond quantitatively to the actual particle structure.

5.The manuscript would benefit from improvements in presentation and detail, which could enhance its readability and overall clarity.
6.In real batteries, neither solid-state diffusion nor liquid-phase diffusion can be entirely neglected. The authors should discuss how these two diffusion processes interact in practice, under what conditions one may dominate the other, and how the experimental design avoids their influence to enable the intended observations.
7.It is recommended that the circuit model on page 6 be presented as a standalone figure rather than embedded directly in the main text, as this would improve clarity and readability.
8.The manuscript proposes an innovative mechanism in which porosity within agglomerate particles induces diffusion-like behavior through a transmission-line effect. However, the model does not quantitatively link electrolyte penetration to specific pore structural parameters such as pore size distribution or connectivity. It is recommended to add simulations that vary pore-structure parameters and evaluate their influence on the correlation between the Warburg coefficient and charge-transfer resistance, or to incorporate direct structural evidence (for example, via Nano-CT).
9.Although the EIS and GITT results exhibit consistent qualitative trends with the model, the manuscript lacks quantitative error analyses such as standard deviations of experimental data points or goodness-of-fit metrics (for example, R^2).
10.The current study focuses solely on NMC111 electrodes and does not examine whether the proposed diffusion-like mechanism applies to other electrode materials, such as Ni-rich NMC or lithium iron phosphate, or to different particle morphologies, such as single-crystal or nanoscale particles. It is recommended to include in the Discussion a preliminary assessment of its potential generality across other systems or to outline directions for future extensions.
11.It is recommended to expand the conclusions with more explicit guidance for battery design, such as how particle-scale porosity could inform charging strategy optimization to mitigate pseudo-diffusion polarization, or practical pathways for reducing electrolyte resistance.

Reviewer #3

(Remarks to the Author)
Tranpsort behaviour in porous particle electrode is an important and common problem in battery and suprcapacitor field. The auhtors notice that the time-dependent voltage response and low-frequency
impedance behavior in porous electrodes changes with electrolyte salt concentration. This is in contradict with normal understanding that solid diffusion is the rate determing step. They find a clear dependence between the electrode's low-frequency impedance and charge-transfer resistance, which is notmally independent. They purpose that chemical capacitance can explain electrochemical features in this case, which is previously ragraded as solid diffusion. Furthermore, they purpose that the charge transfer resistances could also include transmission line effect from particle porosity. I feel that the experimental results and analysis are reasonable. Since the finding is a general issue, it will attract broad interest and remind the researchers to review previsous data in many cases.For that reason, I feel this manuscript could be accepted if the following points could be calrified further:
1) Normally, capacitor, Rct and diffusion have different temperature dependence behaviours. Could authors give the experession of the temperature dependence to reconfirm the analysis in this manuscript?
2) In nonaqueous batteries and supercapacitor, when shall the researcher consider such chemical capacitor behabviour? For the rate-determing step，what difference will be impact on the RDS from two type behaviors?
3) Under high rate situation, surface control will become more significant, please comment on the relationship of this finding.
4) In conclusion part or other parts, please summary the condition and boundary when the diffusion-like rate distribution become significant.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
I am the original Reviewer 1 for this manuscript. I would like to apologize to the authors for understating the novelty of the study. I acknowledge that the work does introduce new and important elements, and I agree that what the authors define as Novelty 1 (intraparticle porosity) and Novelty 2 (TLE vs. diffusion) represent meaningful and impactful contributions.
My concern is that, while these aspects are technically sound and valuable, neither their novelty nor their broader implications rise to the level of a Nature journal publication. In my view, they are more specialized, technical advances that would be of greatest interest to a focused community of researchers in the field, rather than to a broad audience of energy scientists.
This is not a judgment on the quality or rigor of the work, nor on its importance within the specialist community. Rather, it reflects the scope and generality expected for publication in a journal such as Nature. As the overall methodological framework appears well established, I view this contribution as an important refinement and extension of existing approaches, rather than a breakthrough study of the type typically featured in such a venue.
I thank the authors for clearly articulating the innovations in the manuscript. However, this does not alter my overall recommendation. There are many excellent specialized journals that would be well suited for this work, where it is likely to be well received, widely read, and appropriately cited.
Should the manuscript be transferred, I would be happy to provide a strong and supportive review for its submission to another journal.

Reviewer #2

(Remarks to the Author)

Reviewer #3

(Remarks to the Author)
Reponses and revision are satisifed for publication

Reviewer #1 (Remarks to the Author):

The manuscript suggests that for smaller cathode particles in porous electrodes, the square-root behavior of overpotentials over time is not always caused by chemical diffusion in the electrode. Instead, it can arise from the way transfer equations work for porous electrodes, as illustrated in Figure 4. This explanation is reasonable, and I find the observations intriguing.

However, transmission-line effects (TLEs) in porous and fractal electrodes, which lead to 1/√frequency scaling, are well known, as the authors themselves note on page 3. Surface roughness with a broad distribution of time constants also yields constant-phase elements that can be mistaken for Warburg impedance. Similarly, charge hopping and interfacial charge propagation in mixed ionic-electronic conductors can produce the same scaling. The authors acknowledge the multiplicity of such effects (see page 12) and note that they have been observed repeatedly in prior studies. Taht's correct. Square-root-over-time behavior of overpotentials has also been reported for capacitive charging/discharging RC networks, surface-limited adsorption/desorption, and many other systems. I recently read a paper on TLEs explaining solid-state diffusion and Warburg-like behavior:
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This topic is fairly well established and widely reported in porous, fractal, and polymer electrolytes. While the authors suggest that TLEs are insufficiently known to researchers studying intercalation electrodes, the fact remains that TLEs are a common phenomenon. Therefore, this alone is not sufficient grounds for publication in a high-impact journal such as Nature.

The results are robust, the explanations are sound, and there may be practical implications, but the phenomena described are not novel enough to make a significant splash. I believe this is a good paper, but it would be better suited for publication in a more specialized journal. My recommendation is to reject this ms.

We appreciate the reviewer for supporting the technical soundness of our manuscript. It is also understandable that, to someone very familiar with transmission line effects (TLEs), the core principle behind the appearance of an apparent Warburg component is not a new concept, as we had disclosed in the original manuscript. However, the novelty of our work is not in the TLE itself.

At the phenomenological level, the unprecedented observation is that the so-called "charge transfer resistance" and "Warburg impedance" are strongly correlated, *even after eliminating electrode TLE*. This particle-level phenomenon is not predicted by existing battery models. The underlying novelty we uncover based on this phenomenon is the following:

Novelty #1 The recognition of the TLE at a particle level (*not* electrode level), originating from electrolyte-penetrated particle porosity. We show that this effect is much stronger than what could be expected from surface roughness or a particle size distribution. This effect has not been reported in battery agglomerate particles.

Novelty #2 The finding that this TLE dominates over diffusion-controlled signals. It is highly disputed in the literature whether diffusion-controlled signals dominate, because the existence of TLE at the particle level is not recognized (i.e. observation of a Warburg component at the particle level is considered a signature of diffusion control).

Furthermore, we emphasize the **far-reaching impact** of our work, independent from novelty. Our findings prompt a reanalysis of decades of electroanalytical measurements reported in the literature.

Below, we detail these three points.

- ## Novelty #1

We demonstrate that the primary contributor to the observed TLE is electrolyte-penetrated particle porosity, rather than electrode-scale porosity or size distributions. Electrode-scale TLE has been previously studied and reported in the literature, but the particle-level TLE has not been investigated in those studies. We isolate the particle level TLE from the electrode-scale TLE, showing how the diffusion-like overpotentials are produced at the particle level and how it is controlled more by particle porosity than solid-state diffusion.

Conventionally, the TLE expected and analyzed from the porosity in porous electrodes is from the transmission line along the thickness coordinate. This view is also evident from the article suggested by the reviewer [Bumberger, Nenning, and Fleig, *PCCP* **26** 15068 (2024).], where it is stated that "the incremental resistance of ion transport through the electrolyte-filled pores" is "along the thickness coordinate." However, we observe TLEs even after minimizing this electrode-scale TLE. Our reported measurements are from extremely thin and lean-loaded electrodes, thin enough to accommodate only 1-2 particles in the thickness direction (active material loading <1 mg/cm^2). From the view of standard transmission-line models used for porous electrodes, the electrodes used in our experiment correspond to cases where TLEs are *not expected* from porosity (transmission lines may still be nested in the model, but those represent ambipolar transport in the solid-state, as noted in the same PCCP paper as well).

The primary source of the TLE we report is the electrolyte-penetrating porosity of the particle. This mechanism is generally omitted in electrochemical models in favor of solid-state diffusion or geometrical size distributions.

To add experimental support to this finding, we added a new set of experiments, where we examine the Warburg vs R_{CT} correlation using dense monolithic particles in place of agglomerate particles. We find that the Warburg vs R_{CT} correlation is non-existent (correlation coefficient = 0.12) for these dense monolithic particles, supporting our idea that the main source of TLE is related to the porosity of the agglomerate particles. At the same time, the Warburg coefficient is not independent of electrolyte concentration, suggesting that the Warburg coefficient is still not solely determined by solid-state diffusion. That is, other contributions such as size distributions or surface roughness cannot be excluded; their effect is simply much weaker than the TLE from particle porosity in agglomerates.

Related revisions

- We add data from measurements on monolithic particles:

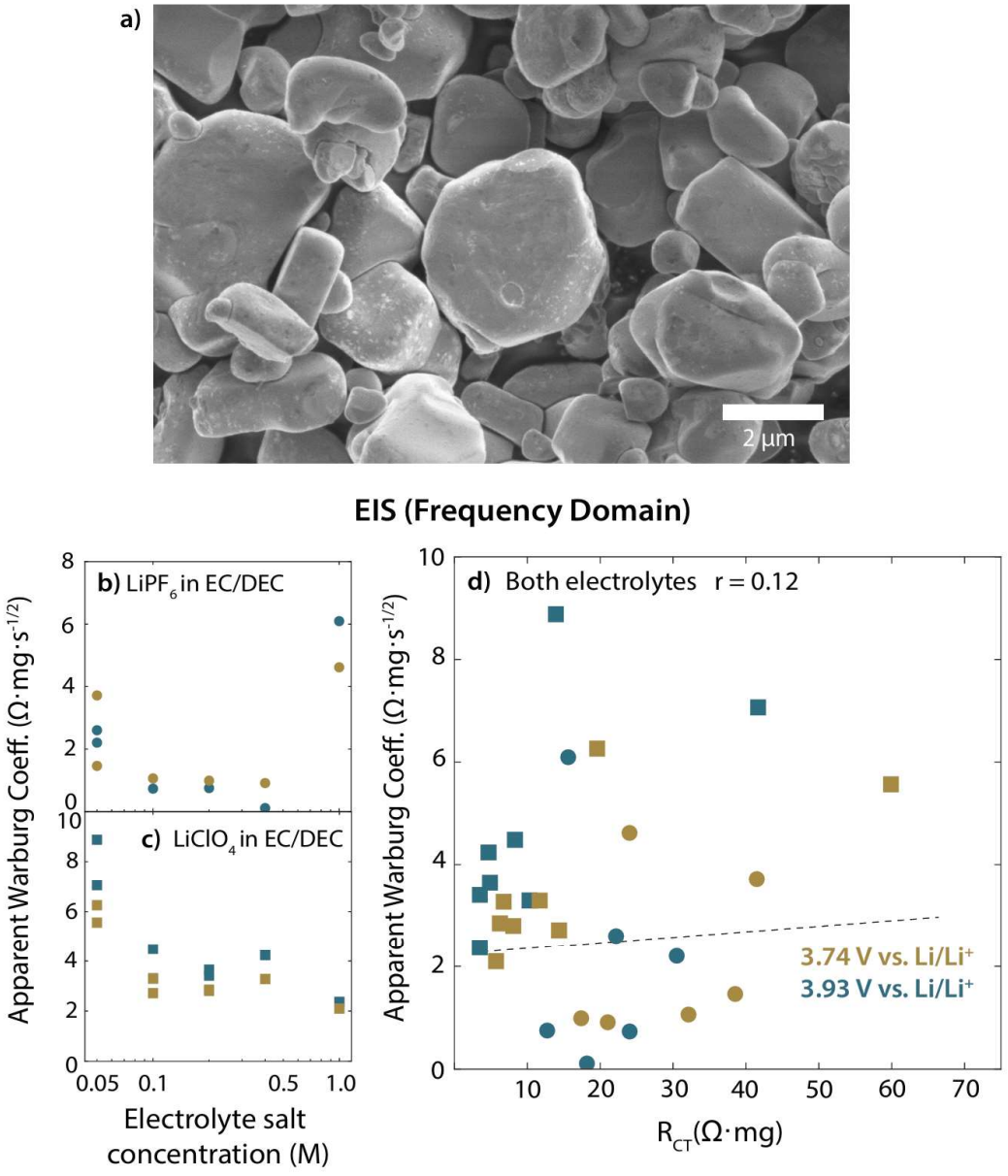


Figure S10: EIS investigation of thin electrodes made with single crystalline $Li_xNi_{0.83}Mn_{0.05}Co_{0.12}O_2$ particles. a) SEM image of the particles showing a non-porous morphology b) Apparent Warburg coefficients extracted from EIS measurements vs. $LiPF_6$ salt concentration in the electrolyte. c) Apparent Warburg coefficients extracted from EIS measurements vs. $LiClO_4$ salt concentration in the electrolyte. d) A lack of correlation between the apparent Warburg coefficients and R_{CT}. The material was obtained from BASF.

- We have revised the title of our manuscript to emphasize the novelty of our findings. Our new title reads: "*Diffusion-like Overpotentials from Non-Diffusion Mechanisms in Battery Particles*." We specify "battery particles" instead of broadly referring to "battery electrodes."

- In the main text, we add the following discussion to the end of the section "*Electrolyte Penetration Causes Diffusion-like Rate Distribution*": "*To experimentally support the idea that particle porosity is the primary factor responsible for the strong correlation between A_w and R_{CT}, we apply the EIS measurement method to dense monolithic (single crystalline) particles. The results (Fig. S10) show a correlation coefficient of 0.12, indicating no correlation between A_w and R_{CT}."*

- We have also added the suggested reference as an example of how electrode-scale TLE has been discussed in the literature: [Bumberger, Nenning, and Fleig, *PCCP* **26** 15068 (2024).]

- We revise the abstract to emphasize that we are reporting particle-level TLEs rather than electrode-scale TLEs:

  […] We generalize this phenomenon with a model that illustrates how particle chemical capacitance could have a distribution of response times that resembles diffusion, even without any diffusion processes involved. This model highlights that diverse mechanisms can produce diffusion-like electrochemistry, emphasizing the need to identify specific physical origins rather than assume solid-state diffusion a priori.. In the case of agglomerate particles, we find electrolyte-penetrating pores as the primary feature responsible. Thus, it is necessary to use a particle-level transmission-line approach to interpret experimental measurements and correctly extract diffusion coefficients and charge-transfer resistances. The impact of porosity on particle kinetics leads to underexplored routes for material optimization.

• Novelty #2

We demonstrate that the intra-particle TLE from particle porosity dominates over solid-state-diffusion signals, contradicting a common notion in the battery field that observing a Warburg-like feature (or square-root-time behavior of overpotentials) at the particle level is evidence for diffusion control. Although the TLE itself is a fairly well-established concept, widely reported in various systems, it has not been considered as an effect strong enough to dominate over the TLE behavior of ambipolar solid-state diffusion, especially at the particle level.

An explanation has been missing in the literature how to reconcile two seemingly contradictory observations: recent microscopic kinetics studies in the literature (refs 2, 34-36) show evidence of interface-controlled kinetics, but at the same time those systems

electrochemically produce overpotentials that look like diffusion. We fill this missing explanation with our finding about particle-level TLE.

Related revisions

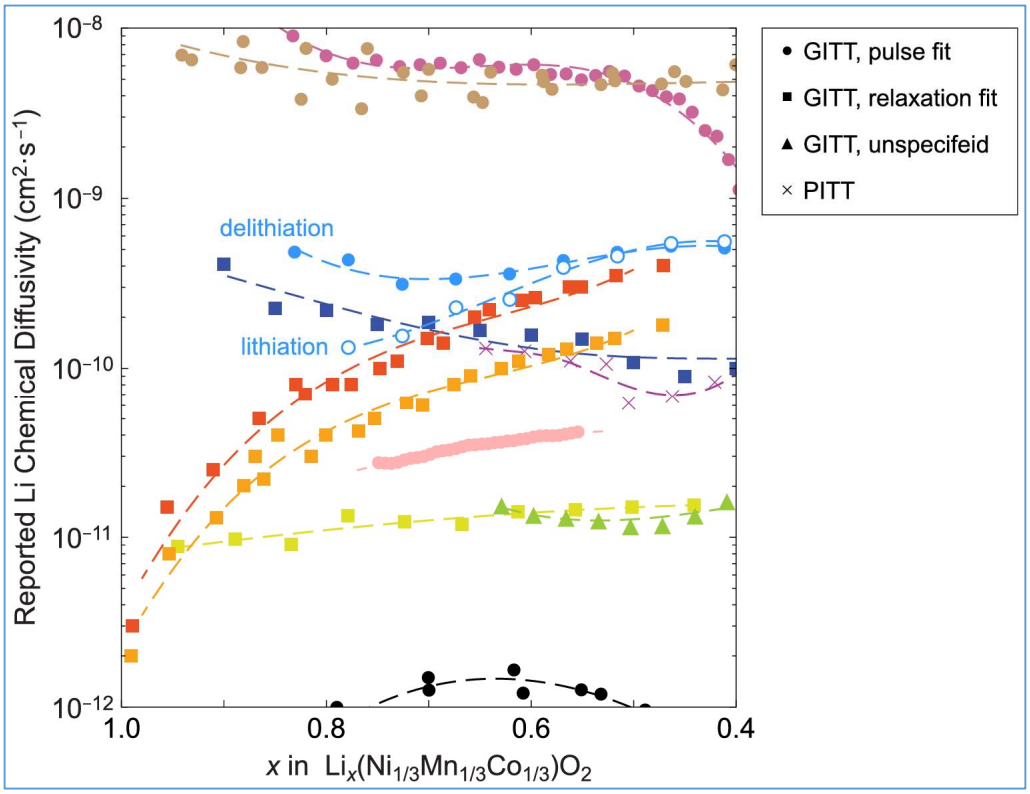
We emphasize this novelty point in the revised manuscript, in section "Implication for Particle Kinetics in Battery Electrodes":

- *Despite such evidence, the various perceived signatures of diffusion observed in electrochemistry have made it difficult for the research community to integrate surface-controlled phenomena into their models. For example, if a cell voltage changes as $\sqrt{t}$ upon current application, researchers tend to interpret that observation as evidence of diffusion control (especially if observed in a few-particle or single particle system). With our demonstration that diffusion-like overpotentials are not necessarily indicative of diffusion, it becomes easier to reconcile the recent evidence for surface-controlled kinetics with macroscopically measured electrochemical data.*

Far-Reaching Impact

Apart from the novelty of our study, we emphasize the importance of reporting our findings in a broad-readership journal by considering the sheer volume of instances that interpret TLE-produced overpotentials as diffusion-dominated without verification or justification. In the Li battery literature accumulated over decades, it has become a standard practice to directly convert sqrt(t) overpotentials or sqrt(1/freq) impedances to diffusion coefficients using diffusion equations. Just a quick search for such instances in the field of Li-ion batteries reveals over a hundred counts (we have attached our search result to the Appendix of this letter). An exhaustive search would result in hundreds (if not thousands) of cases. Considering that this is a de facto standard practice in the field, we emphasize that it is absolutely critical to deliver our message as broadly as possible to the research community.

The consequence of this electroanalytical practice can be appreciated by compiling the chemical diffusivity of a relatively stable compound, NMC111 (this compilation is copied from [Kang et al., *JECS* **168** 120504 (2021).], which is cited in the manuscript):



It is evident from this compilation that the standard electroanalytical practice in the battery field has led to massive inconsistencies in reported data. Note how the magnitude in reported chemical diffusivities span over 4 orders of magnitude. Furthermore, the Li composition dependency is different between each report. We argue that reminding researchers that a diffusion-looking signal may not solely be from diffusion is the first step of amending this unfortunate status of the battery literature.

Minor point:
I am not sure why the discretization in Section S7.3 is discussed in such detail; it appears trivial.

We would like to gently remind the reviewer that the battery community consists of researchers from an extremely wide range of disciplines. We find that it is often needed to explain concepts that might seem trivial to experts in the area. We believe this is one of the reasons why Reviewers #2 and #3 have made a few recommendations to make the manuscript's TLE explanation more accessible to a broader audience.

It is for this broader audience that we explain the TLE in detail in the manuscript. We acknowledge that this elaboration has a risk of masking the true novelty we are trying to deliver, but for a certain audience this elaboration makes our report more accessible. We have tried to improve this balance in the revised manuscript.

Regarding the discretization section in the SI, we have put the actual discretization into a sub-sub section to make it easier for uninterested readers to skip. The reason why the discretization is shown in detail is to clarify exactly how salt polarization and diffusion is (intentionally) removed from the model (rather than to explain the discretization itself).

Related revisions

- Electrolyte and solid phase discretization has been moved to a sub-sub section, making it more explicit that they are details targeted for specific readers.

Reviewer #2 (Remarks to the Author):

This manuscript provides new insights into the origin of overpotential battery electrodes. The scientific question addressed is highly significant, and the experimental design and analysis are both reasonable and rigorous. However, several issues require clarification or further revision. With additional discussion and clearer presentation, this work has the potential to become a highly influential and groundbreaking contribution:

We appreciate the reviewer for highlighting the significance and potential impact of our work, and for providing valuable feedback to improve the presentation. We have taken the opportunity to improve our manuscript, as detailed below.

1.The wording throughout the manuscript needs to be more precise. The title and parts of the discussion may give readers the impression that solid-state diffusion is "unimportant." It is recommended that the authors clearly define the scope and boundaries of the study in the conclusions.

We have come to the realization that the original title might misread as solid-state diffusion having no contribution whatsoever to the Warburg-like overpotentials observed in general. Even in our experimental system, our argument is that the Warburg-like component is not "solely" determined by solid-state diffusion. These issues are amended in the revised manuscript, as listed below.

Also, we have added discussion explaining how the two pathways (penetrated-electrolyte pathway and solid-state diffusion pathway) work in parallel. This helps the reader understand that diffusion should still be considered.

Related revisions

- We have revised the title of our manuscript to prevent it from misleading readers. Our new title reads: "*Diffusion-like Overpotentials from Non-Diffusion Mechanisms in Battery Particles*."

- We refine our wordings on how we conclude our study (In the conclusions section):

  Employing a porous particle model, we demonstrate that a distribution of times in accessing chemical capacitance (i.e. a transmission line effect) can explain additional contributions to electrochemical features typically attributed solely to solid diffusion.

- We revise the abstract to make sure the message is to comprehensively consider our newly proposed mechanism, rather than to entirely disregard solid-state diffusion:

[…] This model highlights that diverse mechanisms can produce diffusion-like electrochemistry, emphasizing the need to identify specific physical origins rather than assume solid-state diffusion a priori.

- We added a paragraph explaining the parallel nature of the two mechanisms (at the end of section "Generalization of Diffusion: Rate Distribution of Capacitance"):

  Specifically in electrolyte-penetrating particles, electrolyte-mediated pathways dominate if the solid-state diffusion time (proportional to length squared) exceeds the reaction time via the electrolyte transmission line; i.e., in Fig. 5b, pathways with capacitances that appear at higher frequencies would be the favored pathway. Then, as porosity becomes small and non-uniform, we could generally expect a mixed contribution from both penetrated-electrolyte pathways and solid-state diffusion.

2.While the experimental design is sound, further explanation is needed regarding how other variables were excluded. In addition, the manuscript lacks discussion on the universality of the proposed mechanism. The authors should consider whether this mechanism is also important in other material systems, which would help define the broader impact of this work.

First, regarding how we isolated particle porosity as the primary variable controlling the correlation we report, we have added a new experiment to further support our argument. Specifically, we examine the Warburg vs R_{CT} correlation using dense monolithic particles in place of agglomerate particles. Since the primary material variable that we propose is particle-level porosity, according to our argument this experiment with dense monolithic particles should not exhibit any meaningful correlation between the Warburg coefficient and R_{CT}.

Indeed, we find that the Warburg vs R_{CT} correlation is non-existent (correlation coefficient = 0.12) for these dense monolithic particles. At the same time, the Warburg coefficient is not independent of electrolyte concentration, suggesting that the Warburg coefficient is still not solely determined by solid-state diffusion. That is, other contributions such as size distributions or surface roughness cannot be excluded; their effect is simply much weaker than the transmission-line effect from particle porosity in agglomerates. The newly added data and text is summarized in the Related revisions list below.

Second, regarding the universality of the mechanism, our conclusion is that any agglomerate particle that has porosity permitting electrolyte penetration would, in principle, be impacted by contributions from this transmission-line effect. Two newly added experiments in our manuscript further support this argument. One is the above-mentioned experiment with dense monolithic particles, helping to further establish that particle porosity is the primary variable behind the correlation we report. Next is an EIS investigation on agglomerate particles of a different composition (NMC622 rather than NMC111) produced by a different manufacturer (Umicore). We find a strong correlation

between the Warburg coefficient and R_{CT}, identical to that observed with NMC 111 (Toda) particles. This data and text are also summarized in the Related revision section below.

Combining these new experiments with the newly added investigation on porosity dependency (see our reply to comment #8), we make a stronger emphasis on the universality of this particle-level mechanism that produces diffusion-like overpotentials.

Furthermore, a newly added porosity-variation study also supports the universality; this data is discussed in Comment #8.

Third, the competition aspect between this effect and solid-state diffusion must be considered to identify relative contributions of each mechanism. We have added a note on this aspect, helping the reader understand that the two mechanisms compete in parallel.

Related revisions

- In the main text, we add the following discussion to the end of the section "Electrolyte Penetration Causes Diffusion-like Rate Distribution":

  This analysis pointing out electrolyte penetration as the primary cause for diffusion-like behavior leads to two predictions: i) the strong A_w - R_{CT} correlation would diminish in dense particles that do not permit electrolyte penetration; ii) if particles permit electrolyte penetration, we expect a similar A_w - R_{CT} correlation from particles of different composition or production. We confirm both predictions experimentally. First, dense monolithic (single crystalline) particles show a correlation coefficient of only 0.12 (Fig. S10), indicating no correlation. Next, porous agglomerate particles of a different composition ($Li_xNi_{0.6}Mn_{0.2}Co_{0.2}O_2$) produced by a different manufacturer (Umicore) show a correlation coefficient of 0.96 (within one test condition; Fig. S17), indicating a strong correlation. Overall, these confirmation experiments support the idea that particle porosity is the primary factor responsible for the strong A_w - R_{CT} correlation, and that this effect could be universal for porous particles.

- At the end of the "Generalization of Diffusion: Rate Distribution of Capacitance" section we add:

  Specifically in electrolyte-penetrating particles, electrolyte-mediated pathways dominate if the solid-state diffusion time (proportional to length squared) exceeds the reaction time via the electrolyte transmission line; i.e., in Fig. 5b, pathways with capacitances that appear at higher frequencies would be the favored pathway. Then, as porosity becomes small and non-uniform, we could generally expect a mixed contribution from both penetrated-electrolyte pathways and solid-state diffusion.

- We add data from measurements on monolithic particles:

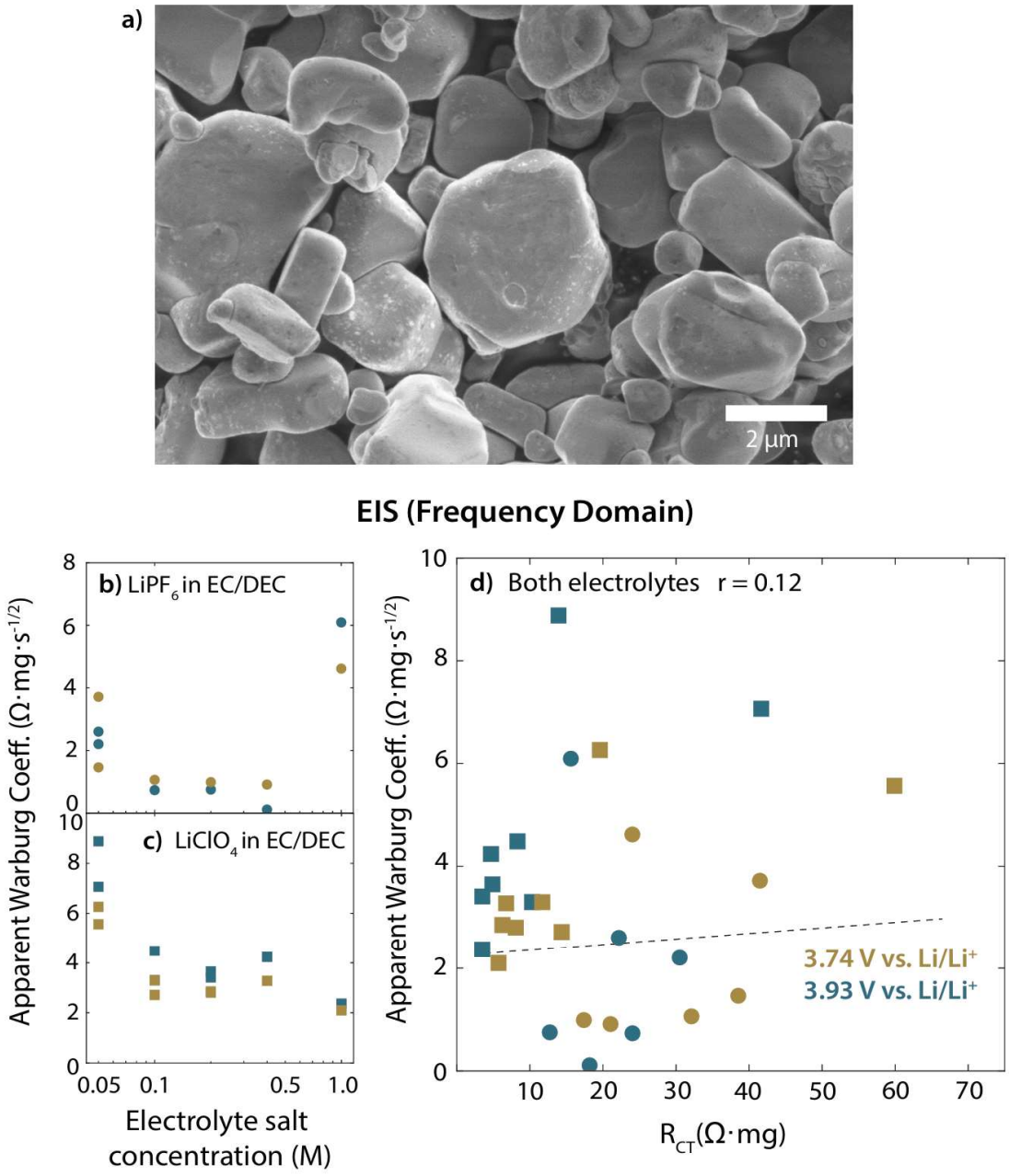


Figure S10: EIS investigation of thin electrodes made with single crystalline $Li_xNi_{0.83}Mn_{0.05}Co_{0.12}O_2$ particles. a) SEM image of the particles showing a non-porous morphology b) Apparent Warburg coefficients extracted from EIS measurements vs. $LiPF_6$ salt concentration in the electrolyte. c) Apparent Warburg coefficients extracted from EIS measurements vs. $LiClO_4$ salt concentration in the electrolyte. d) A lack of correlation between the apparent Warburg coefficients and R_{CT}. The material was obtained from BASF.

- We add Warburg vs R_{CT} data from NMC622 agglomerate particles:

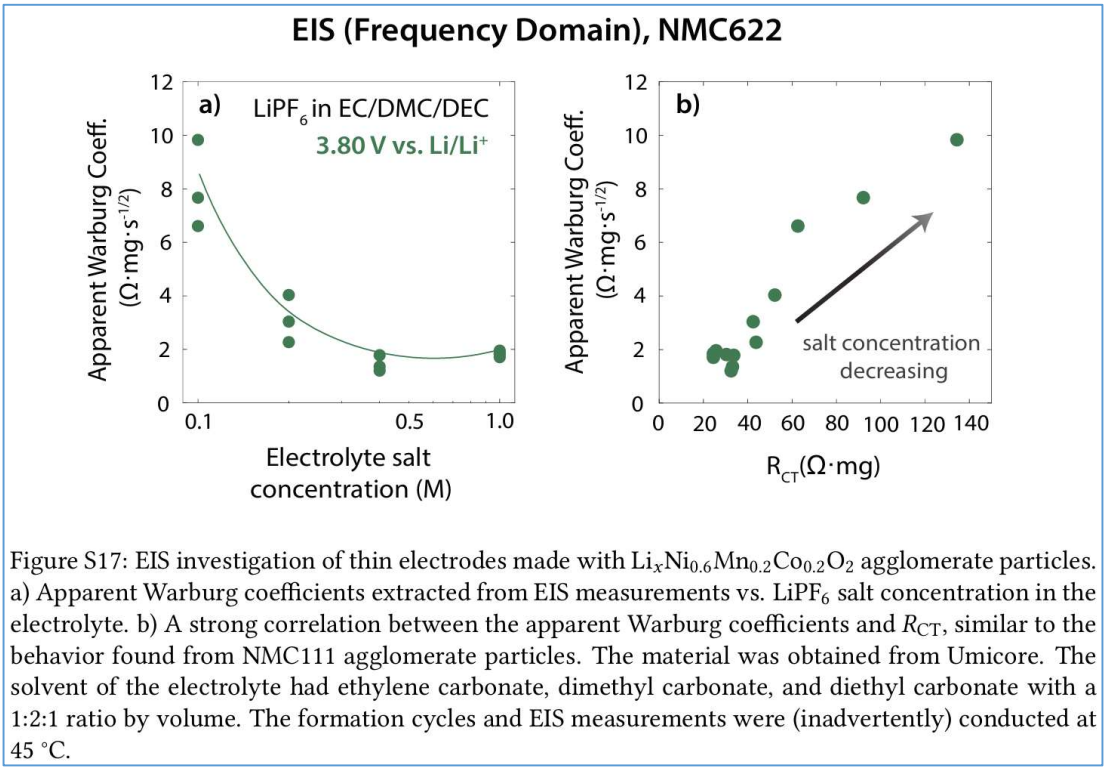


Figure S17: EIS investigation of thin electrodes made with $Li_xNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ agglomerate particles. a) Apparent Warburg coefficients extracted from EIS measurements vs. $LiPF_6$ salt concentration in the electrolyte. b) A strong correlation between the apparent Warburg coefficients and R_{CT}, similar to the behavior found from NMC111 agglomerate particles. The material was obtained from Umicore. The solvent of the electrolyte had ethylene carbonate, dimethyl carbonate, and diethyl carbonate with a 1:2:1 ratio by volume. The formation cycles and EIS measurements were (inadvertently) conducted at 45 °C.

3.For readers without a background in modeling, the particle-level transmission line model may appear complex. Although the authors have provided some explanation, further simplification or more intuitive presentation of the key concepts is recommended.

We thank the reviewer for reminding us of this important aspect of broad readability. To make it easier for readers without a background in modeling, we have broken down the original transmission line model presentation into two parts. In the first part, we discuss the higher-level picture, pointing out key features of the model. For non-modeling people, reading just this part should be sufficient to follow the story. In the following paragraph, we discuss a little bit more detail explaining the circuit components presented in Fig.4. This paragraph could be skipped for readers only looking for a high-level discussion, but at the same time it is the minimum information required for someone interested in the model to picture what is being calculated. We believe this new structure makes the manuscript more approachable to a broader readership.

Also, in the parts where we discuss the transmission line effect in relation to particle morphology, we revised the writing to be more readable to a person without modeling background.

For the rate-distribution discussion, we add some descriptions explaining what the corresponding physical picture is.

Related revisions

- In the section "Electrolyte Penetration Causes Diffusion-like Rate Distribution," we add this higher-level discussion:

  The key features we implement in this model are: 1) charge-transfer reactions are not limited to just the outer surface of the agglomerate, but are also allowed in the interior of the particle via electrolyte-penetrating porosity; 2) those electrochemically active sites placed in the interior of the particle require larger overvoltages than outer surface sites because of the resistance caused by the small-volume path of penetrated electrolyte; 3) diffusion effects are intentionally excluded. This setting serves the purpose of isolating the porous morphology effect and test whether the porous morphology alone is sufficient to cause diffusion-like kinetics.

- In the following paragraph, we keep the details:

  These key model features are implemented via the following parameters. Intrinsic charge-transfer resistance (ρ_{CT}) is assigned to all active sites. The "intrinsic" designation distinguishes it from the macroscopic electrode property R_{CT} extracted from experiments. Chemical capacitance (C_{ch}) accounts for the chemical charge storage in the bulk of the particle. To store or withdraw charges from the chemical capacitance via charge-transfer reactions, the active sites are connected both ionically (Li^+ conduction through the electrolyte, denoted by ρ_{ion}) and electronically (e^- conduction through the bulk solid, denoted by ρ_e). A capacitor (C_{dl}) value is added to the parallel circuit to account for double-layer capacitance from inactive components. Notably, we intentionally exclude contributions from solid diffusion (solid diffusivity is effectively set to infinity within each discretized shell, but non-existent between shells) and liquid salt diffusion (transference number of Li^+ ions is set to unity so that no salt concentration gradients occur in the porous particle). The detailed derivation of model equations and their mapping to circuit elements are provided in the SI. This porous particle model is mathematically consistent with literature models considering both electrode[31,32] and particle scales[33], but here we intentionally isolated non-solid diffusion components for clarity.

- In the particle TLE discussion, we now write:

  The result demonstrates that not just ρ_{CT}, but the transmission line resistances dominated by ρ_{ion} contribute significantly to R_{CT}. Note that varying ρ_{ion} has an effect similar to varying the morphology of the particle (such as tortuosity of the particle pores), affecting the accessibility of reaction sites, particularly ones deeper inside the particle. Therefore, the macroscopic R_{CT} feature is not solely controlled

by charge-transfer resistance in a porous particle and is instead a feature dependent on the particle pore structure as well.

- In the section "Generalization of Diffusion: Rate Distribution of Capacitance," we now write:

  We compare the charging time distribution between the porous and dense particle models (Fig. 5b). When a step voltage is applied, each of the chemical capacitors undergo charging at their respective time scales until equilibrium is reached. In the porous particle model, capacitance in the particle interior is accessed via reactions through the penetrated electrolyte (Fig. 5c). In the dense particle model, capacitance in the particle interior is accessed by Li diffusing between the particle surface and interior (Fig.5d). The time needed for each chemical capacitor to reach 90% of the equilibrium voltage was used to quantify the timescale of the capacitors. These times were converted to angular frequency (in mHz) to find the frequency-domain distributions shown in Fig. 5b.

4.The porous particle model effectively explains the experimental observations, but the authors are encouraged to elaborate on how the model parameters correspond quantitatively to the actual particle structure.

In the revised manuscript, we add nano-CT data investigating the particle porosity and profile. Nano-CT yields 0.5% porosity, which is the value we have used as a baseline for the porous particle model. However, we would like to ensure we disclose the limitations of this approach. First, as we note in the added discussion related to the nano-CT data, the resolution of nano-CT is about 50 nm but our evidence suggests that electrolyte penetration happens for pore sizes smaller than this resolution limit. Second is the fact that, although direct quantification of electrolyte penetration is most appropriate, we are not aware of such a method (such a method is under development by some of the authors of this manuscript). This direct quantification is important if we further consider that particle porosity changes upon cycling (it is a function of state-of-charge). Although this SOC dependency has been reported in the literature (and cited in our manuscript; ref. 29), quantification is not possible at this moment.

To overcome this difficulty, we resort to two strategies. One, we establish that the quantitative porosity is not critical for producing the diffusion-like overpotentials via transmission line effects. Two, we also establish that the radial distribution of porosity is also not critical for producing this effect. Both points are addressed via simulations, by identifying how the macroscopically extracted parameters scale with porosity and tortuosity. We discuss these points in more detail in response to comment #8. These conclusions are also supported by the newly added experiments on dense particles (Fig. S10) and NMC622 particles (Fig. S17).

Related revisions:
See responses to comment #8.

5.The manuscript would benefit from improvements in presentation and detail, which could enhance its readability and overall clarity.

Regarding the transmission line model presentation, please see our response to comment #3, where we have restructured the discussion to make the presentation more approachable.

We have also simplified the phenomenological equivalent circuit model used to analyze impedance data, presented in Fig.2. In fact, we had already used this simplified model for extraction (as any added complexity has minimal sensitivity with respect to data), but the original submission presented a version that had unnecessary components included in it. The extracted values remain unaffected regardless of how the data is analyzed.

We have also overhauled the figure captions to provide a more descriptive explanation for readers.

Related revisions:
See responses to comments #3 and #7.

- Caption of Fig. 4:

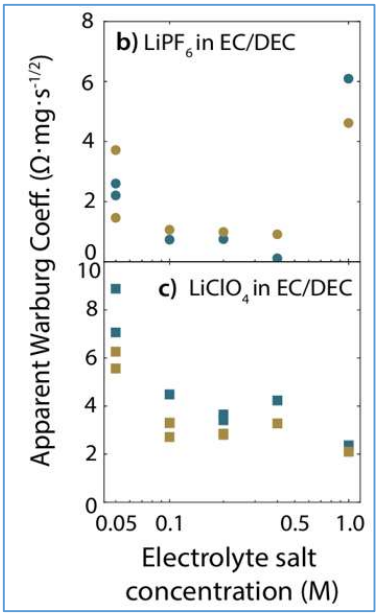
Fig. 4. Electrolyte-penetrated agglomerate model shows diffusive behavior without diffusion. a) Schematic of an NMC agglomerate with electrolyte penetration. **b)** Overlay of the circuit onto a slice of the agglomerate particle. **c)** Equivalent circuit of the model, with multiple slices corresponding to different radial positions of the agglomerate particle. **d-f)** Simulated impedance data while varying ρ_{CT} and ρ_{ion} to emulate electrolyte salt concentration changes. The Nyquist plot (**d**) shows a Warburg-like feature despite the model not having any diffusion processes. The apparent Warburg coefficient shows strong correlations with both salt concentration (e) and R_{CT} (f). **g-i)** Simulated impedance data while varying ρ_{ion} and fixing ρ_{CT} at 2.57x10^{-3} Ohm-m^2. ρ_{ion} shows a strong correlation with both R_{CT} (h) and the apparent Warburg coefficient (i). Investigated ρ_{ion} values correspond to different electrolyte salt concentrations (marker labels). The porosity of the particle is set to 0.5%.

6.In real batteries, neither solid-state diffusion nor liquid-phase diffusion can be entirely neglected. The authors should discuss how these two diffusion processes interact in practice, under what conditions one may dominate the other, and how the experimental design avoids their influence to enable the intended observations.

First, we address liquid-phase diffusion. The liquid-phase diffusion process relevant in batteries is that of salt. For example, in thick electrodes, a non-unity transference number in the liquid electrolyte causes salt depletion and accumulation at the lithiating and delithiating electrode, respectively. At the electrode scale, this process is important as soon as the electrode thickness and loading level become significant relative to the electrolyte diffusion capability. This electrode-scale relevance is somewhat independent from the particle-level kinetics (note that salt diffusivity is many orders of magnitude larger than the Li diffusivity in active materials). In our study, our key finding is a phenomenon from particle-level kinetics, which is also somewhat independent from the electrode-scale salt polarization. To make sure these two different phenomena are isolated, we

specifically design our electrodes to have extremely lean loading levels (<1mg/cm^2). This loading level, combined with the electroanalytical protocols, ensures that liquid-phase salt diffusion does not contribute to the signals we study. Whether this design is working or not can be confirmed from our experimental procedure. The longest continuous bias applied in our study is during GITT measurements. In this protocol, all current pulses are applied in both current directions, from which a slope is extracted (Eq.3 in the main text; details are reported in Ref. [J. Electrochem. Soc. 168, 120503 (2021)]). Since salt polarization effects are asymmetrically larger for depletion and accumulation, if salt polarization has an impact it should impact the symmetry of our pulse experiments. However, all experiments produce symmetrical results (otherwise, we would have very large error bars on the GITT data points). Therefore, liquid-phase diffusion could be considered excluded from our experiments.

Next, we address the concurrent contributions of solid-state diffusion when reactions can occur within porous particles due to electrolyte penetration. In this case, we do not introduce any intentional design elements to experimentally exclude contributions from solid state diffusion. We rather use the conventional assumption as the starting point of our assumption: that solid-state diffusion controls the low-frequency Warburg component (equivalently, the sqrt(t) behavior in the time domain). Our investigation provides evidence to reject this assumption (the correlation of the Warburg coefficient with both the electrolyte salt concentration and R_{CT}). As the reviewer correctly points out, this observation does not entirely rule out contributions from solid-state diffusion; it simply tells us that solid-diffusion is not the solely dominant process as assumed in the literature. While it is difficult to experimentally exclude contributions from solid-state diffusion, it is possible to minimize contributions from electrolyte penetration by using dense particles as the active material. This newly added data (Fig. S10) shows that solid-diffusion is still not the solely dominant process controlling the Warburg coefficient. Here, we reproduce Figs. S10b-c showing this result:



As discussed in the manuscript, this result indicates that the low-frequency rate distribution (for accessing the chemical capacitance portions of the particle) has additional contributors other than electrolyte penetration. Another way to put it is that solid-state diffusion is not rate-limiting enough to be the sole dominant source. Again, we emphasize that this is not equivalent to entirely excluding contributions from solid-state diffusion; it suggests that we should at least consider mixed-controlled regimes rather than a solely diffusion-controlled regime.

To summarize, liquid-phase diffusion of salt is more relevant at the electrode scale due to the much larger diffusion coefficient than that of Li in solids (a few orders of magnitude). Solid-phase Li chemical diffusion is more relevant at the particle scale, but our findings suggest that it should not be assumed as the sole limiting process in accessing chemical capacity. The liquid-phase diffusion contributions can be excluded via experimental design; solid-phase diffusion will work in parallel with our suggested mechanism enabled by electrolyte penetration.

Related revisions:

- In the revised manuscript, we explicitly note that lean loading and thin electrodes exclude the influence of liquid-phase diffusion:

  We eliminate the impact of electrode-scale electrolyte transport by using thin, lightly loaded electrodes (<40 \mum thickness, active material <1 mg/cm2).

  Meanwhile, electrode-scale transmission-line effects are considered insignificant since we designed our experiment using thin electrodes with low material loading (<1.0 mg/cm^2).

- We also elaborate on the implication from our dense particle study, explaining that it excludes diffusion as the sole limiting process (rather than making its contribution entirely irrelevant):

  Meanwhile, we find that the Warburg coefficient is still not independent of the electrolyte salt concentration, as seen in Figs. S10b-c. This observation indicates that, as in the agglomerate particles, the Warburg coefficient is not solely controlled by the solid-state diffusion of Li in these dense particles. The implication is that we still have sources that contribute to the rate distribution for accessing chemical capacity, but particle porosity is no longer the dominant source of that. This finding supports the idea presented in Fig. 5b: that a Warburg-like behavior is not an exclusive indicator of diffusion.

- At the end of the “Generalization of Diffusion: Rate Distribution of Capacitance” section we add:

  Specifically in electrolyte-penetrating particles, electrolyte-mediated pathways dominate if the solid-state diffusion time (proportional to length squared) exceeds the reaction time via the electrolyte transmission line; i.e., in Fig. 5b, pathways with

capacitances that appear at higher frequencies would be the favored pathway. Then, as porosity becomes small and non-uniform, we could generally expect a mixed contribution from both penetrated-electrolyte pathways and solid-state diffusion.

7.It is recommended that the circuit model on page 6 be presented as a standalone figure rather than embedded directly in the main text, as this would improve clarity and readability.

We agree that such a presentation makes the manuscript easier to read. We also note that, in the initial submission, another high frequency component was included in the equivalent circuit. We have removed that component altogether in the revised manuscript since it is unnecessary in analyzing the 3E cell data we measure, where the anode component is excluded. This change does not impact the extracted data but makes the manuscript more straightforward to understand for readers.

Related revisions:

- In the revised manuscript, we present the phenomenological equivalent circuit as a standalone figure, as recommended by the reviewer:

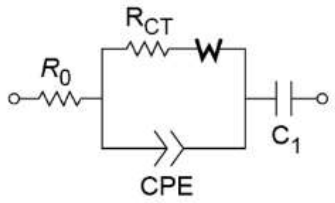


Fig. 2. Phenomenological equivalent circuit model used to analyze impedance data. The circuit is intended to extract a Warburg coefficient similar to what would be determined by commonly practiced analysis methods.

8.The manuscript proposes an innovative mechanism in which porosity within agglomerate particles induces diffusion-like behavior through a transmission-line effect. However, the model does not quantitatively link electrolyte penetration to specific pore structural parameters such as pore size distribution or connectivity. It is recommended to add simulations that vary pore-structure parameters and evaluate their influence on the correlation between the Warburg coefficient and charge-transfer resistance, or to incorporate direct structural evidence (for example, via Nano-CT).

We take both suggestions by the reviewer to enrich the discussion on particle pore structure.

First, we have added nano-CT data, characterizing the porosity of the un-delithiated agglomerate particle at a ≈ 50 nm resolution. As a result, we quantify the nano-CT porosity as 0.5%, which is the base porosity we use in the simulations for the main model demonstration. We note that caution should be taken in understanding the context of this value. On one hand, the nano-CT measurement has a resolution limit of around 50 nm,

meaning that any porosity at small scale (e.g. mesoporosity) would not be captured with this technique. The data from He pycnometry measures 100% of the crystallographic density, whereas the majority of the pores are seen as closed pores in the nano-CT data. That means, those pores simply appear as closed pores because of the limited nano-CT resolution. On the other hand, our nano-CT data is on un-delithiated particles, whereas it has been reported that agglomerate particles have SOC-dependent porosity. Furthermore, existence of porosity does not guarantee electrolyte penetration into those pores. Based on these technical limitations on quantifying electrolyte penetration, we conclude that using simulation is more rewarding for evaluating the influence of pore structure.

Next, based on the limitations of quantifying porosity, we use simulations to evaluate the impact of pore structures. Here, we cite the data and discussion incorporated in the revised manuscript.

Related revisions:

- We discuss the impact of pore structures in the newly added discussion while referring to the newly added data (Fig.S13):\

  Here, we address the question on how particle porosity profiles affect low-frequency impedances.

  First, consider uniform changes in porosity. Since the low-frequency impedance resembles the behavior of diffusion, an easy way to anticipate the impact of porosity is to consider how porosity would change the effective diffusivity in a diffusion-controlled system. As known from effective medium theory, the effective diffusivity of a medium scales with ε/τ (porosity divided by tortuosity). Then, the Warburg coefficient would scale with $\mathrm{sqrt}\{\varepsilon/\tau\}$ in such a system. In the porous particle case where the Warburg coefficient is controlled by the transmission-line effect from the electrolyte-penetrated pores, the apparent Warburg coefficient still behaves similarly as in a diffusion-controlled system; i.e. the apparent Warburg coefficient scales with $\mathrm{sqrt}\{\varepsilon/\tau\}$.

  Next, consider the impact of non-uniform porosity. Here, it is useful to recognize which time scale controls the determination of the Warburg coefficient. In an EIS analysis where the scaling behavior of Z vs. $f^{-1/2}$ is relied on to extract a Warburg coefficient, it is typically the higher frequency part of the low-frequency region that controls the parameter determination. For example, if one observes a finite-length behavior but still relies on the Z vs. $f^{-1/2}$ scaling, that is equivalent to extracting the Warburg coefficient from the -45 degree region on a Nyquist plot. Such a region would occur at frequencies higher than the region where impedance starts to resemble that of a pure capacitor. Similarly in a time-domain analysis like GITT, it is the shorter time scales showing a $\mathrm{sqrt}\{t\}$ behavior that is typically used to extract a Warburg coefficient. Overall, we see that the shorter time scales (higher frequencies) of the diffusion-like behavior controls the determination of the

Warburg coefficient in these techniques. Then, when the porosity is non-uniform inside a particle, it would naturally be the porosity near the surface that controls the extracted Warburg coefficient.

We confirm this porosity-scaling argument with model simulations. We allow particle porosity to vary over the radial direction of the particle, as plotted in Fig. S13a. Here, the volume-weighted-average porosity is kept identical between three cases. Next, apparent Warburg coefficients are extracted using GITT simulations (the uniform porosity case in Fig. S13a is identical to that shown in Fig. S12). By scaling the apparent Warburg coefficients with sqrt{ε/τ} = $\varepsilon^{0.75}$ (we are assuming $\tau = \varepsilon^{-0.5}$) using the porosity of the surface of the particle, it is seen the curves collapse upon each other, as shown in Fig. S13b. R_{CT} also shows similar scaling behavior, seen in the correlation plot in Fig. S13c.

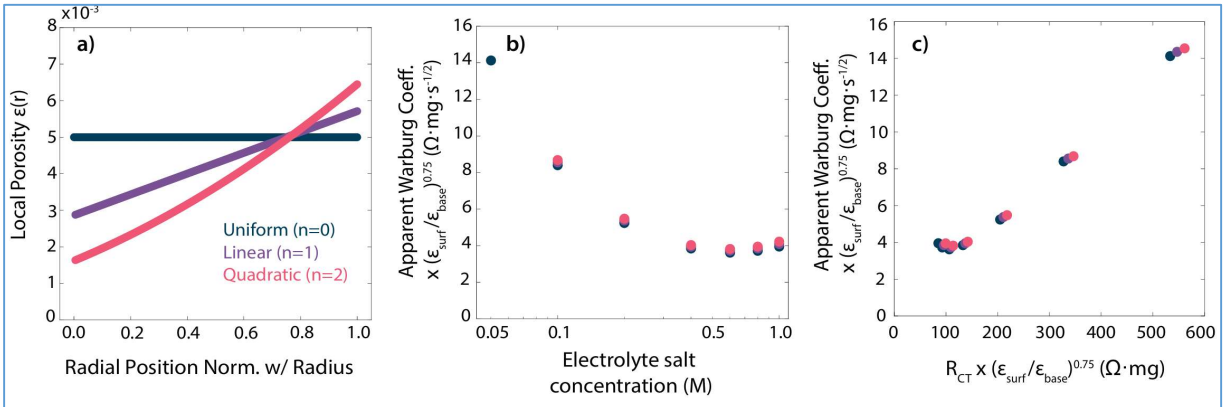


Figure S13: Scaling behavior of the Warburg coefficient in a particle with non-uniform porosity. a) Three different porosity profiles considered in the model. b) Apparent Warburg coefficients normalized with $\varepsilon^{0.75}$ of the surface showing similar dependencies on the salt concentration. Note that tortuosity is simultaneously scaling via $\tau = \varepsilon^{-0.5}$. c) The Warburg vs R_{CT} correlation, showing that the macroscopically determined R_{CT} also scales with $\varepsilon^{0.75}$. ε_{base} refers to the volume-weighted-average porosity, while ε_{surf} is the porosity at the outer surface of the particle.

Other Related revisions:

We add nano-CT data:

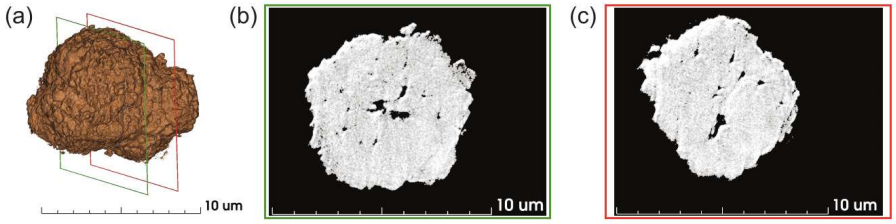


Figure S16: A nano-computed tomography image of a representative NMC111 agglomerate particle **(a)** 3D reconstruction of a NMC111 agglomerate particle. **(b)** A cross section image corresponding to the green frame in (a). **(c)** A cross section image corresponding to the red frame in (a).

9.Although the EIS and GITT results exhibit consistent qualitative trends with the model, the manuscript lacks quantitative error analyses such as standard deviations of experimental data points or goodness-of-fit metrics (for example, R^2).

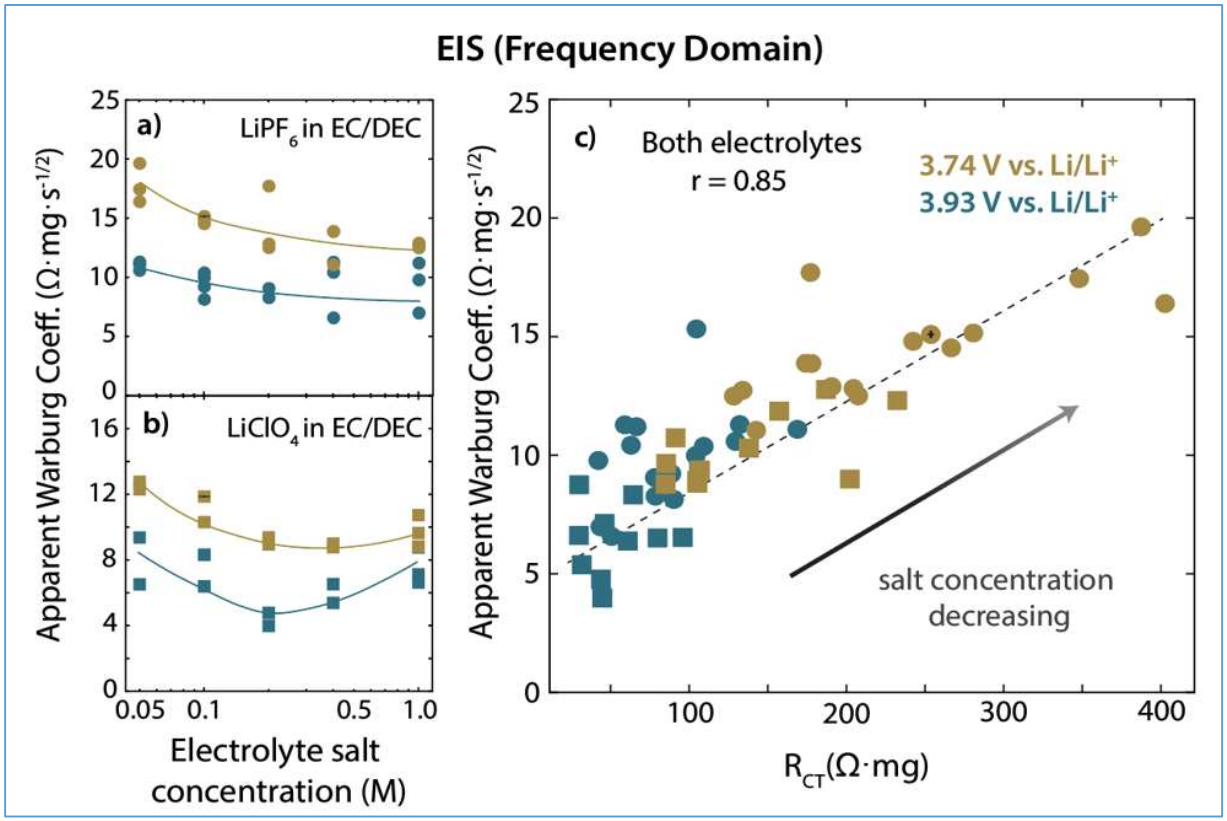
We apologize for not clarifying this point in the previous manuscript.

For the EIS data points plotted in the manuscript, the 95% confidence intervals of the evaluated parameter (estimated from the fitting process) is smaller than the marker size. We note this information in the revised manuscript.

For the GITT data points plotted in the manuscript, we calculate the 95% confidence intervals of the data points and note it on some of the data points. Specifically, we choose data points with confidence interval sizes close to the median value of the overall distribution, so that the selected points can represent the general size of the error bar (putting error bars on all data points proved to obscure the visibility of the plot).

Related revisions:

- We add representative error bars to the data markers (barely visible in EIS):



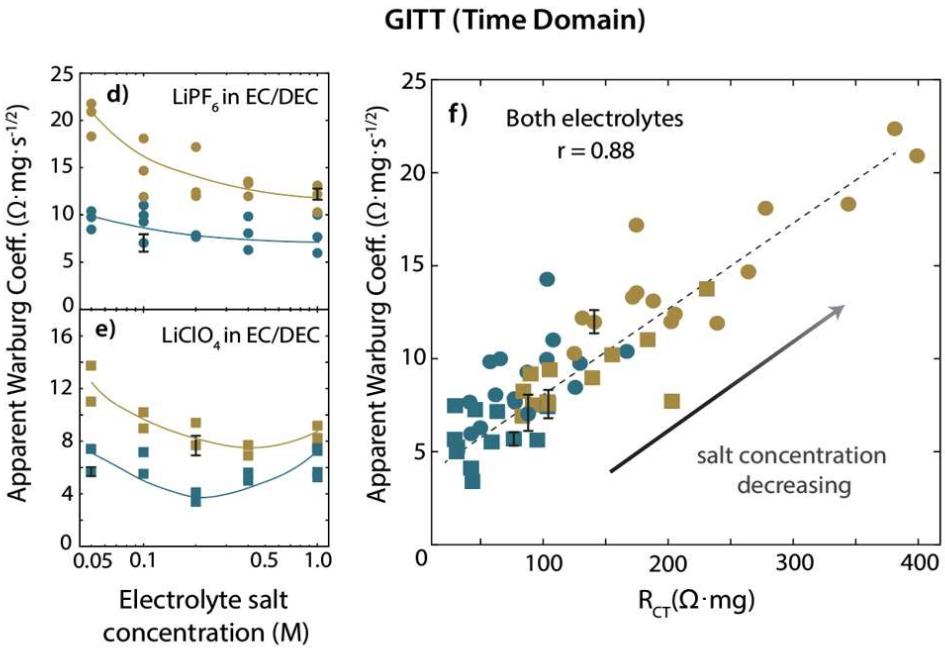


Fig. 3. GITT and EIS results from varying electrolyte concentration. a-b) Extracted Warburg coefficient from EIS measurements vs. $LiPF_6$ (**a**) and $LiClO_4$ (**b**) salt concentration in the electrolyte. Trend lines are guides to the eye. **c)** Correlation between the Warburg coefficients and R_{CT} (both from EIS). **d-e)** Extracted Warburg coefficient from GITT measurements vs. $LiPF_6$ (**d**) and $LiClO_4$ (**e**) salt concentration in the electrolyte. For the GITT sequence, six different 3-minute pulses (τ = 3 min) were used: 0.04C, -0.04C, 0.06C, -0.06C, 0.08C, and -0.08C (1C defined as 278 mA/g), each followed by 3 hours of relaxation. **f)** Correlation between the Warburg coefficients and R_{CT} (both from GITT). Each of the R_{CT} and Warburg coefficient pairs were extracted using the same sample. Error bars represent the 95% confidence intervals from fitting (shown on markers that have intervals close to the median of the data set).

10.The current study focuses solely on NMC111 electrodes and does not examine whether the proposed diffusion-like mechanism applies to other electrode materials, such as Ni-rich NMC or lithium iron phosphate, or to different particle morphologies, such as single-crystal or nanoscale particles. It is recommended to include in the Discussion a preliminary assessment of its potential generality across other systems or to outline directions for future extensions.

We thank the reviewer for encouraging to follow up with these further investigations. In our revised manuscript, we have added results from NMC622 agglomerates. Furthermore, we have investigated monolithic single crystalline particles (dense particles) of high Ni content. Based on these results, we highlight that particle porosity is the primary factor controlling the phenomenon, rather than material composition. To further support this point, our revised manuscript includes simulations showing how porosity and tortuosity scales the parameters affected by the transmission-line configuration.

Related revisions:
See the revision notes for comments #2 and #8.

11.It is recommended to expand the conclusions with more explicit guidance for battery design, such as how particle-scale porosity could inform charging strategy optimization to mitigate pseudo-diffusion polarization, or practical pathways for reducing electrolyte resistance.

We thank the reviewer for reminding us to connect our study back to practical aspects of particle development and production. We added a paragraph addressing this subject.

Related revisions:

- In the "Implication for Particle Kinetics in Battery Electrodes" section, we add:

  From a particle morphology perspective, our study shows why agglomerate particles seemingly "too big" for favorable kinetics may still provide reasonable rate capability. If a particle permits electrolyte penetration, then it would appear as if "diffusion" in the particle is faster than a fully dense particle. While producing dense particles is generally preferred in practice for its advantage in energy density, our study shows that a minimal amount of porosity (e.g. mesoporosity) might be required to maintain a suitable rate capability.

Reviewer #3 (Remarks to the Author):

Tranpsort behaviour in porous particle electrode is an important and common problem in battery and suprcapacitor field. The auhtors notice that the time-dependent voltage response and low-frequency impedance behavior in porous electrodes changes with electrolyte salt concentration. This is in contradict with normal understanding that solid diffusion is the rate determing step. They find a clear dependence between the electrode's low-frequency impedance and charge-transfer resistance, which is notmally independent. They purpose that chemical capacitance can explain electrochemical features in this case, which is previously ragraded as solid diffusion. Furthermore, they purpose that the charge transfer resistances could also include transmission line effect from particle porosity. I feel that the experimental results and analysis are reasonable. Since the finding is a general issue, it will attract broad interest and remind the researchers to review previsous data in many cases.For that reason, I feel this manuscript could be accepted if the following points could be calrified further:

We thank the reviewer for putting the far-reaching impact of our findings in perspective. In answering the clarification points raised by the reviewer, we put back in some discussion that we had originally removed in favor of brevity. We realize that these points help readers put our findings into perspective, and thank the reviewer for making the suggestions.

1) Normally, capacitor, Rct and diffusion have different temperature dependence behaviours. Could authors give the experession of the temperature dependence to reconfirm the analysis in this manuscript?

In principle, temperature dependency indeed provides a good opportunity to distinguish between different mechanisms, and we thank the reviewer for bringing up this question. Each process under consideration has physically different temperature-dependent components.

The temperature dependency of solid-state chemical diffusivity combines many contributions, but generally the largest contribution is expected from the formation energy of the dominant mobile defect and then the migration enthalpy barrier related to those mobile defects. In an extremely simplified picture where the Warburg coefficient is solely controlled by solid-state diffusion, and also under the assumption that solid-state diffusion follows an Arrhenius-type temperature dependency, the activation energy of the Warburg coefficient would be one half of that from solid chemical diffusivity. While we proceed with caution in comparing experiments of a complicated system with a simplified picture, literature reports do suggest that the temperature dependency of Warburg coefficients are difficult to explain with just solid-state diffusion. Activation energies of the Warburg coefficient of NMC622 agglomerate particles have been reported in [Gunther et al., *JECS* **172** 030525 (2025).], importantly by utilizing thin electrodes to exclude electrode-scale transport effects. In this study, a SOC-independent value of about 0.13 eV (one half of the value reported for diffusivity) is reported at practical Li compositions (Li fraction below 80% and above 30%). It would be easier to reconcile this SOC-independency if the

temperature dependency primarily comes from mechanisms that are *not* related to solid-state diffusion (e.g. electrolyte-related mechanisms). That is because the components contributing to solid-state diffusion are all expected to vary if the Li composition is changed from 30 to 80%. Meanwhile, the electrolyte concentration used for this measurement by Gunther et al. is 0.25 M. In the literature, temperature dependent conductivity of a 0.4 M $LiPF_6$ electrolyte is reported in [Valoen & Reimers, *JECS* **152** A882 (2005).], where an activation energy of about 0.11 eV can be calculated, similar to the activation energy of the Warburg coefficient reported by Gunther et al. While we shall not jump to conclusions based on this one comparison, the point is to demonstrate feasibility. On the other hand, the reported temperature dependency of the Warburg-derived diffusivity by Gunther et al. is quite different than what has been observed with dense bulk samples reported in [Kang et al., *JECS* **168** 120503 (2021).]. Overall, our analysis of the Warburg coefficient provides an explanation for the temperature dependent Warburg coefficient reported in the literature that is difficult to reconcile solely with a solid-state diffusion mechanism.

Related revisions

- We add the following discussion to the "Implication for Particle Kinetics in Battery Electrodes" section:

  Thermal activation energies of apparent diffusivity might find a feasible explanation if electrolyte penetration is considered. For example, activation energies independent of Li composition has been reported in $Li_xNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ ($x<0.8$, agglomerate particles) from GITT measurements on thin electrodes that isolate particle-level kinetics.[37] While it appears difficult to reconcile why the activation energy would be independent of Li composition if it is governed by solid-state diffusion, we note that the reported activation energy is about 0.13 eV in terms of a Warburg coefficient (one half of the value expressed in terms of apparent diffusivity). A similar value of 0.11 eV has been reported from electrolyte conduction,[38] implying that the diffusion-like behavior from agglomerate particles might be better explained by considering electrolyte penetration.

2) In nonaqueous batteries and supercapacitor, when shall the researcher consider such chemical capacitor behabviour? For the rate-determing step，what difference will be impact on the RDS from two type behaviors?

The diffusion-like overpotential mechanism we report could show up from a variety of sources. In fact, it is quite general so that both chemical or non-chemical capacitances can produce the effect if there is a mechanism that provides a transmission line configuration. The scenario we uncover in our manuscript is when the source mechanism comes from the porosity of the particle itself. Although it is difficult to predict all scenarios where one should expect a similar behavior, a good rule of thumb for batteries and similar electrodes would be to look out for diffusion-like overpotentials whenever porosity (both mesoporous and microporous scales) exists in the system, and when that porosity provides "shortcuts" to the solid-state diffusion-mediated kinetic process. If those short cuts provide a transmission-line configuration, then the effect appears as if it is from

diffusion. If we apply this principle to the case of agglomerate particles, the electrolyte penetrating the porosity in agglomerate particles provide a “shortcut” for reacting the chemical capacitance in the interior of the particles. The porosity provides a transmission-line configuration and produces diffusion-like overpotentials. In the revised manuscript, we add a discussion about this point to help readers understand their own electrodes.

The second part of the question, as we understand, is how a more traditional Warburg originating from diffusion vs an alternative mechanism originating from porosity-related TLE influence the RDS of battery kinetics. One way to consider this question is from a diagnostic point of view. That is, given an observation or measurement of a Warburg-like feature, what conclusion can we make if it is controlled by one vs the other. If the chemical capacitance distribution in frequency primarily originates from solid-state diffusion, then one could imagine the series process to be a surface reaction followed by a diffusion process. The rates of these two shall be compared to determine the RDS. In the other case, one would need to identify the source of TLE. Assume it’s the electrolyte transport effect. Then, the rate of this process shall be compared with the surface reaction rate. In the example shown in the text, the rate of the charge transfer process is still slower than the TLE-producing mechanism, so the RDS does not necessarily change from the fact that we have TLEs. To summarize this thought process, this effect does not necessarily produce an RDS. But if this TLE is not considered, one could reach a wrong conclusion in diagnosing the RDS.

Related revisions

- The overall discussion emphasizing the importance to consider TLE when diagnosing the RDS is given in the first paragraph of the section “Implication for Particle Kinetics in Battery Electrodes”:

  In intercalation battery electrodes, the kinetic rate limitation at the particle level traditionally favors a diffusion-limiting interpretation.[9] However, as size scales down, kinetics become increasingly limited by surface processes rather than bulk processes.[11] In other words, as particles become optimized for performance, as has now been accomplished for a variety of active material chemistries, it is natural to tend toward surface-limited kinetics. Indeed, recent studies report evidence for surface-controlled phenomena in a variety of systems, as seen from inter-particle heterogeneity dominating over intra-particle heterogeneity.[2,34-36] Despite such evidence, the various perceived signatures of diffusion observed in electrochemistry have made it difficult for the research community to integrate surface-controlled phenomena into their models. For example, if a cell voltage changes as $\sqrt{t}$ upon current application, researchers tend to interpret that observation as evidence of diffusion control (especially if observed in a few-particle or single particle system). With our demonstration that diffusion-like overpotentials are not necessarily indicative of diffusion, it becomes easier to reconcile the recent evidence for surface-controlled kinetics with macroscopically measured electrochemical data.

- This consideration of RDS is relevant for considering the morphology design of particles. We highlight this point, how the TLE from electrolyte penetration could make the RDS somewhat unaffected by particle size:

  From a particle morphology perspective, our study shows why agglomerate particles seemingly "too big" for favorable kinetics may still provide reasonable rate capability. If a particle permits electrolyte penetration, then it would appear as if "diffusion" in the particle is faster than a fully dense particle. While producing dense particles is generally preferred in practice for its advantage in energy density, our study shows that a minimal amount of porosity (e.g. mesoporosity) might be required to maintain a suitable rate capability.

3) Under high rate situation, surface control will become more significant, please comment on the relationship of this finding.

As the reviewer points out, one implication of our finding is that, to improve the rate capability of agglomerate particles, the focal point should expand beyond the bulk-oriented approach and look into engineering particle porosity/tortuosity and enhance charge transfer kinetics. This point relates to the previous question about diagnosing the rate-determining step, because understanding the transmission line effect at multiple length scales is crucial in correctly identifying the component to improve for higher rate capability. One of the areas that we anticipate to become important is the characterization of electrolyte penetration. Currently, electrolyte penetration into particles is evaluated somewhat indirectly. Developing more quantitative methods should prove rewarding in finding pathways to improve the rate capability of agglomerate particles.

Related revisions

- We conclude the manuscript by making this additional comment:

  Developing methods to quantify electrolyte penetration in particles could be rewarding for better engineering particle-level kinetics.

4) In conclusion part or other parts, please summary the condition and boundary when the diffusion-like rate distribution become significant.

We concur that it is important to help readers understand when to expect this diffusion-like behavior. As we further clarify in our revised manuscript, particle porosity and electrolyte penetration are the primary factors that cause this effect. We add a paragraph discussing how the evidence collectively points to this direction, leading to conclude that we could expect this effect whenever there is electrolyte penetration through particle pores.

Related revisions

- In the main text, we add the following discussion to the end of the section "Electrolyte Penetration Causes Diffusion-like Rate Distribution":

  "*This analysis pointing out electrolyte penetration as the primary cause for diffusion-like behavior leads to two predictions: i) the strong A_w - R_{CT} correlation would diminish in dense particles that do not permit electrolyte penetration; ii) if particles permit electrolyte penetration, we expect a similar A_w - R_{CT} correlation from particles of different composition or production. We confirm both predictions experimentally. First, dense monolithic (single crystalline) particles show a correlation coefficient of only 0.12 (Fig. S10), indicating no correlation. Next, porous agglomerate particles of a different composition ($Li_xNi_{0.6}Mn_{0.2}Co_{0.2}O_2$) produced by a different manufacturer (Umicore) show a correlation coefficient of 0.96 (within one test condition; Fig. S17), indicating a strong correlation. Overall, these confirmation experiments support the idea that particle porosity is the primary factor responsible for the strong A_w - R_{CT} correlation, and that this effect could be universal for porous particles.*"

Appendix: Literature Survey of Cases Directly Converting Warburg Measurements to Solid-State Diffusivity

*Note: This compilation is meant to illustrate the wide-reaching impact of our findings through a quick search. The list only shows a small glimpse of a large literature body and we the intention was not to make an exhaustive compilation. We have not reviewed the validity of the individual references listed below. It is rather a simple case count to show the wide-spread practice of converting Warburg measurements to solid-state diffusivity, either through time-domain or frequency-domain methods.

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The reviewers did not have additional comments to address.

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