**Operando** Electrochemical Kinetics in Particulate Porous Electrodes by Quantifying the Mesoscale Spatiotemporal Heterogeneities

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Electrochemical energy systems rely on particulate porous electrodes to store or convert energies. While the three-dimensional (3D) porous structures are introduced to maximize the interfacial area for better overall performance of the system, spatiotemporal heterogeneities arising from materials thermodynamics are localizing the charge transfer processes onto a limited portion of the available interfaces. Here, a simple but precise method is demonstrated to directly track and analyze the *operando* (i.e., local and working) interfaces on the mesoscale in a practical graphite porous electrode to obtain the true local current density, which turns out to be two orders of magnitude higher than the globally averaged current density adopted by existing studies. The results shed light on the long-standing discrepancies in kinetics parameters derived from electroanalytical measurements and from first principle predictions. Contradictory to prevailing beliefs, the electrochemical dynamics are not controlled by the solid-state diffusion process once the spatiotemporal reaction heterogeneities emerge.

1. Introduction

Electrochemical energy storage and conversion systems are critical for a sustainable future.[1] Lithium-ion batteries (LIBs) that offer the highest energy density have revolutionized electronic devices, portable power tools, and electric cars.[2–4] But their further advancements have been impaired by the random occurrences of elusive safety accidents,[5,6] which are believed to originate from microscopic heterogeneities in the particulate porous electrodes.[7] State-of-charge (SOC) heterogeneities have recently been identified in both the solid-solution[8–12] and phase-transforming electrodes,[13–20] as a direct result of nonuniform distribution of electrochemical reactions due to either the structures of the composite porous electrodes[8,21] or the thermodynamics of the active materials.[22,23] While the nanoscale heterogeneities in individual particles detected by synchrotron X-ray provide deep insights on the possible degradation mechanisms, the evolutions of the heterogeneities among hundreds of particles sitting in realistic surroundings are critical for the understanding of the true local electrochemical kinetics that dictate the real-time performance. Recent breakthroughs in a few synchrotron facilities have enabled in situ imaging of large number of particles in realistic battery electrodes.[18,19,24–27] However, achieving very high spatial and temporal resolutions at the same time is still very challenging. Yet more accessible testing platforms that can enable the economical and systematic verifications of new mathematical models to achieve the comprehensive understanding of dynamic heterogeneities in relevant electrochemical systems are critically needed.

The immediate consequence of the spatiotemporal heterogeneities is that the actual reacting interfacial area at any instant, i.e., area of the *operando* (local and working) electrochemical interface, is only a small portion of the total available interfacial area usually obtained from the Brunauer–Emmett–Teller (BET) method. Given that existing electroanalytical techniques[28,29] rely on the square-law scaling \( D_{Li} \sim [I(t)/S]^2 \) to extract the diffusion coefficient \( D_{Li} \) from the total current \( I(t) \) and the assumed constant total interfacial area \( S \), the electrochemical kinetics in systems with strong heterogeneities may have been misinterpreted due to the smaller *operando* interfacial area.

As one of the most widely used electrodes for both the nonaqueous[15,30] and aqueous[31] batteries, graphite electrodes are known to have strong reaction heterogeneities[13,15] reflected by its particle-by-particle reaction mechanism.[15,22] during the phase transformation between ordered stages[32] upon ion intercalation. Depending on the choices of electrode area, e.g., BET or geometric, the lithium-ion diffusion coefficient in graphite \( (D_{Li}) \) extracted by the classic electroanalytical methods varies by about 8 orders of magnitude in the literature.[13–41] Still, \( D_{Li} \) obtained for SOC ranges with phase transformation were always about 2 orders of magnitude lower than the average.[34,40] The discrepancy has long been doubted as the inaccuracy of the interfacial area,[42] but conclusive evidence is still missing. Similar orders-of-magnitude discrepancies also exist in other porous electrodes composed of phase-transforming[29] or solid-solution particles[43–45] missing satisfactory explanations.
discrepancies in the kinetic parameters directly affect the determination of the rate-limiting step, and thereafter the validity of traditional electroanalytical techniques and the effectiveness of the predicted rational design strategies.

Here, we use graphite as a model system to demonstrate the direct quantification of the true local currents densities for precision electrochemical kinetics. The unique color changing property during graphite lithiation allows us to develop economical operando platform with optical microscope (Figure S1, Supporting Information) to investigate the dynamics of the heterogeneities at high speed and at the mesoscale (imaging hundreds of particles simultaneously every two seconds). Our study reveals that the SOC heterogeneities are indeed the result of reaction heterogeneities, which lead to the localization of the reaction flux onto a limited number of particles in the electrode. Using the moving phase boundaries between different stages (phases) of lithiated graphite to approximate the operando electrochemical interfacial area, the true local current density was determined to be at least 2 orders of magnitude higher than the averaged current density over the adjusted BET surface area. The insights gathered from the interface area and the true local current density suggest that, once the heterogeneities emerge, the operando (i.e., local and working) electrochemical kinetics of the porous electrode is not diffusion limited. This study highlights the need of tracking the phase boundaries to resolve the long-standing huge discrepancies between experiments and theoretical predictions.

2. Results

2.1. Spatiotemporal Heterogeneities

We conducted three sets of potentiostatic intermittent titration technique (PITT) experiment with 10, 100, and 200 mV steps, respectively. Figure 1a–c demonstrates the color evolution in the thin graphite electrode with thickness of 5 µm (Figure S2, Supporting Information) during the 10 mV PITT experiment, with a threshold current of C/20. The entire lithiation process can be divided into three segments based on the colors of the lithiated graphite (Video S1 and Figure S3, Supporting Information). In segment (I) all empty particles (dark gray) reacted concurrently regardless of their morphology and size to become blue (Stage 3). At this point, the blue particles accommodated 23% of the total capacity supplied in the entire PITT discharge and brought down the cell voltage from 275 to 85 mV. Since, at this moment (t = 0 s shown in Figure 1a), all the particles were in Stage 3 (blue), the SOC associated with Stage 3 was determined to be the global SOC of the electrode, i.e., xB = 23%, slightly higher than the values adopted in earlier works.

In segment (II), a few blue particles began to turn red at the onset of the PITT voltage stepping from 85 to 75 mV. The localized red (Stage 2) regions always coexisted with the blue (Stage 3) regions within the same particle. The evolving boundaries between the red and blue regions clearly reveal the phase transformation process. Upon careful visual inspection, we observed that the Li+ ion flux prefers to go into particles with phase boundaries. The remaining blue (Stage 3) particles will begin receiving Li+ ion flux only after existing boundary-containing phase-transforming particles become completely red. The red particles then remain idle, waiting for all the other particles to reach the same stage. This process is consistent with not only the sequential reaction front in thick graphite electrode, but also the particle-by-particle reaction mechanism of LiFePO4 electrodes at low current densities. Similarly, we determine the SOC associated with Stage 2 (xB) to be 55%, which is the global SOC when all particles turned red. In segment (III), while the cell is still under the same voltage held at 75 mV, the red particles start a similar particle-by-particle phase transformation process to turn gold (Stage 1). The SOC associated with Stage 1 (xG) is calibrated to 100%. The phase transformation process from Stage 3 to Stage 1 is shown in Video S2 and Figure S4 of the Supporting Information. By converting the color into standard RGB map (Figure 1c), we were able to exclude the all-time inactive region and accurately quantify the areas covered by the three colors (Stages) in thousands of operando snapshots. The sequential reaction process is quantitatively reflected by the evolution curves of the area fractions for the colors, shown in Figure 1d.

2.2. Currents Carried by Individual Colors (Phases)

With the SOCs for each color determined above, i.e., xB = 23%, xG = 55%, xC = 100%, the area fraction evolution curves can be converted into capacity evolution curves (Figure S5, Supporting Information), by Q = xai(t)qAT. Here, i represents blue, red, and gold colors, Q is the area, and q is the areal capacity of the entire electrode, and AT is the total area of particles accounted in the image analysis. The capacity curves directly converted from experimental data were physically adjusted based on charge conservation, to exclude possible system and sampling errors. By further taking the first order time derivative of the capacity associated with each color (phase), the phase current can be obtained

\[ I_i(t) = \frac{dQ_i}{dt} = x_i q_A T \left( \frac{da_i}{dt} \right) \]  

Figure 1d of the derived phase currents suggests that the stable phases grow/diminish faster than the rate of charge addition (total current), which points toward the direction that the local kinetic rate reflected by the phase boundary propagation is much higher than the electrochemical reaction rate estimated by using the total current. Since Li+ ions insert into graphite particles through the edge planes, not the basal plane that reveal the colors, the area of the phase boundary, i.e., length of the phase boundary times the thickness of the particle, needs to be determined to quantify the true local current density for more accurate analysis of the kinetics. Figure S6 of the Supporting Information shows the area evolution and phase currents during 100 and 200 mV PITT experiments.

2.3. Operando Interfacial Current Densities

In principle, Li+ ions can intercalate into graphite particles from anywhere on the edge plane to form a shrinking-core type...
pattern, as observed in a 50 µm graphite disk and 400 µm graphite flake. For our graphite particles with a mean particle size of 8.13 µm (Figure S7, Supporting Information), however, ion intercalations appear to occur only on a limited portion of the particle perimeter. The phase boundary, originated from the edge, appears to straighten itself to form an intercalation wave propagating through the remaining body of the particle (Figure 2a). Since we only observe color change at the phase boundaries and not in the stable regions during Li⁺ ion intercalation, the net flux within any color is conserved. Therefore, the flux that leads to the movement of phase boundary is identical to the reaction flux at the particle edges. Based on this observation, we propose to use the mathematical product of the total length of the phase boundaries and the thickness of the graphite particles to evaluate the true \textit{operando} interfacial area within the porous electrodes (see the Experimental Section). With proper Boolean operations (see the Experimental Section; Figure S8, Supporting Information), the length of the phase boundaries can be determined (Figure S9, Supporting Information). As shown in Figure 2b, the total length of the blue-red

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**Figure 1.** Evolution of the ordered stages induced by Li⁺ ion intercalation during the voltage stepping from 85 to 75 mV versus Li/Li⁺. a) Snapshots of the entire viewing area under the optical microscope with the 50× objective, at four times: t = 0 s, 1000 s, 8000 s, and 14400 s. b) Magnified photos highlighting the coexistence of different stages intra- and inter particles. c) The converted RGB images showing the actual area fraction quantification by ImageJ. The observed blue, red, and gold colors were converted to standard blue, red, and green colors, respectively. d) The evolution curves of the colored areas during the voltage stepping, obtained from the direct image analysis along with the physically adjusted analytical curves (refer Section S8 of the Supporting Information for the fitting parameters). e) The derived phase currents based on the time-derivative of the physically adjusted area evolution curves. Scale bar: 10 µm.
($L_{BR}$) boundaries increased at the beginning of the voltage stepping from 85 to 75 mV, then decreased toward zero in a time span of 1250 s. While the total length of the red–gold boundaries ($L_{RG}$) slightly increased at the onset of voltage stepping, it remained relatively constant at a value close to zero. The trend is consistent with the decaying of the global total current. At the moment $L_{BR}$ decayed to nearly zero and stopped changing, a rapid increase in $L_{RG}$ was observed, corresponding to the onset of phase transformation from red (Stage 2) to gold (Stage 1), while the global total current was still decreasing, indicating a dramatic change of the true local (operando) interfacial current density. Similar to $L_{BR}$, $L_{RG}$ decayed after reaching its peak value but with a much slower rate in accordance with the slow decaying rate of the total current during the red-to-gold phase transition.

The growth periods of the three stable phases are mutually exclusive, suggesting that the entire global current at any time is carried only by one phase. Hence, by using the global current and the operando interfacial area calculated above, the operando interfacial current density, i.e., the truly working local current density, can be estimated. As shown in Figure 2c, the operando interfacial current densities are more than two orders of magnitude higher than the average current density calculated using the BET area ($9.424 \text{ m}^2 \text{ g}^{-1}$). This discrepancy questions the prevailing belief that the rate-limiting step of Li$^+$ ion intercalation in graphite is the bulk solid-state diffusion.

2.4. Physical Interpretation of the Evolving Phase Boundaries

As suggested above, the color change only occurs at the phase boundaries during lithiation, which implies that their movement should be equivalent to the net reaction flux. At the same time, multiple nucleation and growths can emerge within a single particle (Figure 2a), followed by impingements between the growing domains. The observation is consistent with the classic recrystallization process that can be analyzed by the Kolmogorov–Johnson–Mehl–Avrami (KJMA) theory$^{[49–53]}$. As shown in Figure 3a schematically, KJMA theory assumes that the ratio between the normalized actual incremental area of the new phase ($dA$) and the normalized “extended” incremental area ($dA_{\text{ext}}$) is always equal to the fraction of the untransformed area, $dA/dA_{\text{ext}} = (1 – f)$, where $f$ is the fraction of the transformed area, identical to $A$. The differential equation can be solved (see the complete derivation in Section S10, Supporting Information) to obtain the normalized transformed area as $A = f = 1 – \exp(-A_{\text{ext}})$, and further develop into the final Avrami kinetic equation by incorporating the growth rate and dimensions for the ideal $A_{\text{ext}}$. However, the challenge for electrochemical phase transformation in our graphite electrode...
is to quantify the evolution dynamics of the total length of the phase boundaries, instead of the area. The key question is how much of the phase boundary associated with the ideal “extended” incremental growth $dA_{\text{ext}}$, designated as $l_{\text{ext}}$, will lie in the transformed region that cannot be accounted for the total length of the actual phase boundary $l$, as shown in Figure 3a. Following the same strategy of KJMA, we propose that \( l/l_{\text{ext}} = (1-f) = \exp(-A_{\text{ext}}) \). Further considering the shape factor $S$, the dimension of growth $n$, and the growth velocity $k$, we obtained the final kinetic equation for phase boundary evolution as

\[
l = nS(kt)^{n-1} \exp\left[-\left(Skt\right)^n\right]
\]  

Equation (2)

Interestingly, Equation (2) is essentially the first-order time derivative of the classic KJMA equation.

As shown in Figures 3b,c, our Equation (2) fit the normalized length of phase boundary very well, especially for the boundary between the blue and red regions (Figure 3b). While for an ideal 2D growth problem, the dimension exponent $n$ should be 2, and the shape factor $S$ should be $\sqrt{\pi} \approx 1.77$ for an isotropic circular growth, as can be seen in Section S10 of the Supporting Information, here we relaxed the constraints during the fitting to keep the analysis general. As can be seen in Table 1, the fitted dimension exponent $n$’s are indeed close to 2, especially for the blue-red phase boundary for all three sets of the operando PITT experiments (Figure 4), which indicate that the new phase growth through plate-like graphite particles in our thin-layer porous electrode is indeed 2D. The fitted shape factor $S$ is close to but not equal to the value of $\sqrt{\pi}$, indicating that the growth is not ideally isotropic as a shrinking-core process.

The third parameter in Equation (2) also has clear physical meaning. It represents the rate of growth of the new phases, i.e., the propagation velocity of the phase boundary, which is a direct result of the net reaction flux and can be quantified from the operando experiments by using mass conservation.

\[
u(t) = \frac{\int m(t)V}{F}
\]  

Equation (3)
$u(t)$ is the effective 1D growth velocity of the new phase at time $t$. $j_{\text{int}}$ is the interfacial current density of the corresponding phase calculated by dividing the global current $I(t)$ with the operando interface area $A(t)$. $V_m$ is the molar volume of that particular phase of the lithiated graphite, and $F$ is the Faraday constant. Figure 3d schematically shows the growth of the new phase. The complete derivation can be found in Section S11 of the Supporting Information.

Equation (3) shows that the growth velocity can be directly estimated from the operando interfacial current density. Since the operando interfacial current densities are relatively stable for the major portion of the corresponding phase transformation segments, despite spikes at the beginning and/or the end, an averaged growth velocity $\langle u \rangle$ can be calculated (Figures 3e–f and 4e–h). Table 1 lists the fitting parameters obtained from Equation (2) for all three cases, along with the averaged growth velocities obtained by using operando interfacial current densities. It is noteworthy that Equation (2) returns the growth velocity $k$ with the units of $\text{s}^{-1}$. To find the actual growth velocity, we solved for Equation (2) with actual dimensions shown in Section S10 of the Supporting Information. Equation (2) that fits the transient total length of the phase boundary, and Equation (3) that derived from the ratio between the transient total current and the transient phase boundary, independently explain the same phenomena from different perspective, but surprisingly obtain almost the same growth (i.e., interface propagation) velocity in the units of $\text{nm s}^{-1}$. The self-consistent results not only validate our new model on the kinetics of the phase boundary evolution, but also indicate that the dynamic is controlled by the operando (i.e., local and working) electrochemical reaction flux, not solid-state diffusion.

### Table 1. Parameters used to fit the operando interface lengths with Equation (2) and the averaged growth velocity calculated from operando interfacial current densities.

|            | 10 mV | 100 mV | 200 mV |
|------------|-------|--------|--------|
| Blue–red   | $n$   | 1.75   | 1.90   | 1.98   |
|            | $S$   | 1.48   | 1.36   | 1.48   |
|            | $k_0$ (nm s$^{-1}$) | 13.4   | 11.6   | 15.8   |
|            | $k_{\text{exp}} = \alpha$ (nm s$^{-1}$) | 8.02   | 14.20  | 12.10  |
| Red–gold   | $n$   | 1.39   | 1.58   | 1.60   |
|            | $S$   | 1.41   | 1.52   | 1.43   |
|            | $k_0$ (nm s$^{-1}$) | 0.5    | 1.5    | 2.2    |
|            | $k_{\text{exp}} = \alpha$ (nm s$^{-1}$) | 0.33   | 1.62   | 1.24   |

Figure 4. Growth velocity from operando observations during phase transition induced by 100 and 200 mV steps. Replication of operando interface length with KJMA equation during a) blue–red transition and b) red–gold transition in 100 mV case, and c) blue–red transition and d) red–gold transition in 200 mV case. Average growth velocity estimated from operando interfacial current density during e) blue–red transition and f) red–gold transition in 100 mV case, and g) blue–red transition and h) red–gold transition in 200 mV case.
2.5. Determination of the Diffusion Coefficients

The direct correlation between the growth velocity and the operando interfacial current density revealed above raises the question whether the solid-state diffusion coefficient can still be reliably extracted from the standard PITT method originally established specifically for the evaluation of solid-state diffusion.[54] As can be seen in Figure 5a–c, the lack of straight lines (predicted by the classic Cottrell equation) suggests that the processes are likely not diffusion-limited. As our first attempt, we adopted the modified PITT (mPITT) model,[55,56] without the presumption of the rate-limiting step, to fit the operando interfacial current densities. Both the diffusion coefficient $D_{\text{Li}}$ and the electrochemical Biot number $B$, can be obtained by minimizing the least squares. Good agreements can be found for the solid solution processes (Figure 5a), but not for the blue–red phase transformation (Figure 5b). Interestingly, the mPITT model (Equation (S7a) in Section S12, Supporting Information) can fit the operando interfacial current density for the red–gold phase transformation in the $t \ll l^2/D_{\text{Li}}$ regime fairly well, especially in the PITT experiments with 10 and 200 mV steps. It is worth noting that, among all the recorded phase transformation processes, only the red to gold transformation was long enough to enter in the regime of $t \gg l^2/D_{\text{Li}}$, but cannot be fitted by the

![Figure 5](image)

Figure 5. Independent experiments to estimate the kinetic parameters. a) The fitting of representative operando interfacial current density during solid-solution processes in all the three sets of experiments with the modified PITT model to extract the Li$^+$ ion diffusion coefficient into graphite. The voltage mentioned in brackets are the voltage step during the corresponding PITT experiment. b) The operando interfacial current density during blue–red phase transformation in all the three sets of experiments. They could not be fitted with the modified PITT model owing to their highly nonmonotonic nature. c) The fitting of operando interfacial current density during red–gold phase transformation in all the three sets of experiments with the modified PITT model to extract the Li$^+$ ion diffusion coefficient into graphite. d) Extracted $D_{\text{Li}}$ and $B$ from the fitting the operando interfacial current densities in panel (a) and (c) with the mPITT model. The vertical dashed lines separate the entire region into diffusion-controlled, mixed control, and reaction-controlled regimes. e) Fitting of experimental EIS data with the specified equivalent circuit model composed of two RC circuits and a porous-bounded Warburg impedance. The blue and red semicircles are the individual contribution of the two RC circuits with the frequencies of the respective peaks being $\omega_{\text{SEI}}$ and $\omega_{\text{dl}}$. Here, $R_{\text{SEI}}$ and $R_{\text{CT}}$ are the charge-transfer resistances of the SEI and double layer, CPE$_{\text{SEI}}$ and CPE$_{\text{dl}}$ are the constant phase elements of SEI and double layer, and $Z_{\text{W}}$ is the porous-bounded Warburg impedance. f) Exchange current density estimated from the EIS using operando interface area and that from mPITT averaged over three sets of experiments along with its close agreement with the exchange current densities calculated from $D_{\text{Li}}$ and $B$ using mPITT model.
the rate-limiting step can give a rough estimate of the diffusion form within the SEI; and ii) the charges at the electrolyte of graphite particles, but beneath the solid electrolyte interphase that the charge transfer reaction occurs on the surface to the solid-state Li+ ion concentration, R is the gas constant, and T is the temperature. Again, the model becomes inapplicable in the “ideal” phase-transformation regimes due to $\partial U/\partial C$ being zero leaving $j_0$ impossible to identify. Nevertheless, the application of a modified PITT (mPITT) model without presumption of the rate-limiting step can give a rough estimate of the diffusion coefficients of Li+ ions into graphite. The Li+ ion diffusion coefficients, extracted from fitting the mPITT model on the operando interfacial current density during the solid-solution lithiation (Segment (I)), lies between $1.35 \times 10^{-10}$ and $3.27 \times 10^{-10}$ cm$^2$/s$^{-1}$, consistent with the reported values. The corresponding electrochemical Biator number (B) shown in Figure 5d suggest a diffusion-limited process. On the other hand, the diffusion coefficients for the red–gold phase transformation processes lying in the range of $1.98 \times 10^{-8}$–$1.31 \times 10^{-7}$ cm$^2$/s$^{-1}$ across the three sets of experiments, which are in very good agreements not only with the Cahn–Hilliard phase field simulation of a 50 µm graphite disk, but also the first principles calculations. Such a fast diffusion means a very low diffusion time constant, $\tau_0 = L^2/\bar{D}_{\text{Li}} = 1–8$ s where $L$ is the diffusion length, set to be one half of the dimension of basal plane, i.e., 4 µm for our case. Figure S10 of the Supporting Information shows consistent interpretation for the responses in other PITT voltage steps during solid-solution intercalation. Our results provide a straightforward evidence that once the spatiotemporal heterogeneities emerge, the process is no longer diffusion-limited, consistent with a recent scaling analysis.

2.6. Impedance Analysis for the Operando Exchange Current Densities

While the mPITT method itself allows the evaluation of $j_0$, independent electrochemical impedance spectroscopy (EIS) experiments were performed on the same operando cells to assess the interfacial reaction kinetics during Li+ ion intercalation. Figure 5e shows the Nyquist plot of a typical EIS spectra, which appears to have two partially merged semicircles followed by a Warburg tail. While the Warburg tail can be attributed to the solid diffusion in graphite particles, the two semicircles need careful examination of their physical basis. Based on the consensus that the charge transfer reaction occurs on the surface of graphite particles, but beneath the solid electrolyte interphase (SEI) layer, we hypothesize that i) the electrical double layer capacitance associated with the charge transfer will form within the SEI; and ii) the charges at the electrolyte|SEI interface and those at the SEI|graphite interface will form a double-plate capacitor filled with the SEI layer. To test the hypothesis, the EIS spectra were fitted with the equivalent circuit model shown in Figure 5e to obtain the two resistances ($R_{\text{SEI}} = 38.4$ Ω and $R_{\text{CT}} = 52.0$ Ω), which were then used to calculate the capacitances from the two characteristic frequencies ($\omega_{\text{SEI}} = 1266$ Hz and $\omega_{\text{CT}} = 146.5$ Hz) labeled in Figure 5e, via the general formula $\omega = (RC)^{-1}$. The calculated capacitances ($C_{\text{SEI}} = 20.5$ µF and $C_{\text{CT}} = 214$ µF) were then used to determine the associated dielectric constants via $C = \varepsilon_0 \varepsilon A_{\text{edge}}/d$, where $A_{\text{edge}} = 1.459$ cm$^2$ is the total area of the edge planes based on image analyses, $d$ is the thickness of the respective capacitors (assuming 10 nm for the SEI layer and 1 nm for the electrical double layer), $\varepsilon_0$ is the permittivity of vacuum, and $\varepsilon$ is the dielectric constant. The resulting dielectric constants (161.2 and 167.5) are surprisingly very close to each other, but much higher than the dielectric constants for liquid electrolyte (<90) we used in the operando cells yet consistent with the reported values for the solid electrolyte interphase and those at the SEI | edge. This quantitative physical confirmation validates our hypothesis on the microstructure of the equivalent circuit model. All the parameters obtained from the fittings of the equivalent circuit model at 10–100% SOCs are displayed in Table S3 in Section S13 of the Supporting Information.

The charge-transfer resistance ($R_{\text{CT}}$) thus obtained were used to calculate both the exchange current density via $j_0 = RT/(F R_{\text{CT}} A_{\text{int}})$ as shown in Figure 5f, and the reaction time constant $\tau_0 = Q/j_0 A_{\text{int}} = (Q F R_{\text{CT}})/(RT)$. Here, $A_{\text{int}}$ is again the operando interfacial area, $Q$ is the total charge transferred to the electrode, $R$ is the gas constant, and $F$ is the Faraday constant. These values of $j_0$ are in good agreement with those obtained from mPITT fitting at selected SOCs. The reaction time constant $\tau_0$ calculated from the maximum capacity of the electrode lies between 488 and 680 s for the three sets of experiments. These maximum possible values of $\tau_0$ is almost half of the blue-red transition time (1000–1250 s), and 7–20 times lower than the red–gold transition time (5000–13 000 s). While this comparison between time constants seems to suggest that the process is not limited by reaction, it is the actual operando interfacial current density, not the exchange current density or the exchange reaction rate that plays the role in the actual process, which was also pointed out by Fraggedakis et al.

3. Discussion

From analyzing the dynamics of phase boundary evolution by using Equation (2) and evaluating the true local exchange current density by using the physics-based equivalent circuit model, our results clearly suggest that the electrochemical lithiation process of particulate graphite electrode is not diffusion-limited. Therefore, classic electroanalytical methods based on the diffusion-limited assumption are not appropriate for determining the diffusion coefficient, even if the true local current density can be accurately determined. This is particularly important for phase-transformation electrodes, for which the classic methods require the term $\partial U/\partial C$ that becomes zero at the phase-transformation voltage plateau, making other physical quantities impossible to identify. This is also the reason...
that the Warburg fittings from our physics-based EIS analysis cannot be used to determine the diffusion coefficient, as the $dU/dC$ term is again required for the Huggins equation to convert the Warburg factor. From a deeper perspective, the original derivation of now the widely used Warburg impedance appears to be modeling the transients from a single particle with precise operand current density.

Regarding the rate-limiting step of electrochemical processes in particular phase transformation electrodes, our results reject the simple yet convenient terms of diffusion-limited or reaction-limited. It should rather be designated as phase-transformation controlled for two reasons at two different scales. First, at the single particle scale, the reaction rate is controlled externally by electrochemical driving force. Therefore, whether the entire process is diffusion-limited or reaction-limited is extrinsic. Unless the local current density for the single particle can be exclusively and precisely determined and controlled, determining the rate-limiting step and the kinetic parameters would remain very challenging. Second, at the mesoscale with at least hundreds of particles, while one can precisely determine and control the total current, the self-adapted local driving force would allow different numbers of particles to share the total current, leading to unexpected operand current density. As can be seen in Figure S5, the operand interfacial current densities from 200 mV PITT experiments are surprisingly and significantly lower than those from 10 and 100 mV PITT experiments, which are the exact results of the higher driving force (200 vs 10 and 10 mV) promoted more phase transforming particles with longer total phase boundaries. This observation is consistent with a recent study on thick graphite electrodes using X-ray diffraction computed tomography (XRD-CT), in which the phase transformation from stage 2 (red) to stage 1 (gold) requires higher local overpotentials to initiate and move the reaction front. It is the phase transformation dynamics that controls how many particles and how much interfacial area will be activated for working, and it is still the phase transformation dynamics that controls the evolution of phase boundaries within each particle. Therefore, it should be recognized that the phase-transformation controlled mechanisms at both scales induce the spatiotemporal heterogeneities and limit the overall performance of the electrode.

Our results also raise a fundamental question: whether the electrochemical response from electrode under small excitations (e.g., low total current) can be considered from quasi- or near-equilibrium physical processes. It is apparent now that the electrochemical responses of the electrode (total current and terminal voltage) are collective behaviors of far-from-equilibrium dynamics contributed only from a small portion of the electrodes. The insights from this study stress the necessity of careful examination of the local electrochemical activities.

The accuracy of our image analysis is largely dependent on the color segmentation process, as described in the Experimental Section. The color segmentation process is susceptible to human error, and careful multipoint calibrations must be implemented. We also performed a necessary sensitivity analysis on the choices of thresholding criteria extracted from the benchmark images (Figure S8, Supporting Information). The results suggest only minor variations in the extracted areas (Figure S13, Supporting Information), which must be further verified by charge conservation (Figure S5, Supporting Information). Due to the brightness changes of different colors under the visible light microscope, it is necessary to exclude some very small particles that can only be clearly revealed when they are gold. The application of a black mask on all the digital images ensures the consistency for all cases. Despite being an area approximation method, the systematic calibration and validation ensure the fidelity of our method to be a simple yet effective way to study the dynamic heterogeneities in thin electrodes. It is noteworthy that the characterization of in-plane spatiotemporal heterogeneities should only be performed on thin electrodes (<5 μm), such that dynamic heterogeneities along the thickness direction as reflected by the reaction front between two colors will not be accommodated.

Our method, with an ability to clearly identify particles as small as ~2 μm and phase boundaries (color interfaces) as thin as ~0.1 μm, is not limited to the PITT experiment. Revealing the mesoscale spatiotemporal heterogeneities under other types of electrochemical excitations (e.g., galvanostatic cycling, cyclic voltammetry, etc.) will lead to critical refinements to existing understandings of the electrochemical kinetics and rate-limiting steps. For electrode materials without this unique visible color-changing property, our setup may be combined with other imaging techniques such as Raman spectroscopy and XRD-CT to achieve more accurate heterogeneity maps with enriched physical information, which can be further analyzed following our methods to obtain the operand interfacial kinetics.

4. Conclusion

By exploiting the colorimetric behavior of lithiated graphite, we have demonstrated a direct, simple, yet precision method to monitor and quantify the spatiotemporal heterogeneities in particulate porous electrodes. The true local current density, i.e., the operand interfacial current density by our definition, obtained from direct image analysis is ~100 times higher than the BET-average current density. Although all the particles in the porous electrodes are electrochemically active and eventually get fully intercalated with the Li⁺ ions, at any time instant, only a limited number of particles and limited portion of the total available area receive the ionic flux. Given the significant changes of the actual reacting interfacial areas, using a constant “adjust BET area”, i.e., a constant faction of the total BET area may only be limited to certain stages of the entire electrochemical processes. Our operand monitoring clearly revealed that once a successful nucleation event occurs and phase boundaries start to form in a randomly chosen particle, it is preferred for further intercalation irrespective of its shape and size. Since the Li⁺ intercalation into graphite particles is not diffusion-limited, smaller particles do not necessarily provide a substantial
improvement in the high-rate performance. However, reducing particle size may help eliminate the reaction heterogeneities by altering the nucleation barrier for solid-state phase transformation in individual particles, such that the concurrent reaction pathway becomes thermodynamically favorable.

5. Experimental Section

Thin Electrode Preparation: Graphite flakes (7–10 μm, 99%, Alfa-Aesar), PVdF binder (>99.5%, MTI Corp.), and conductive acetylene black powder (35–40 nm, MTI Corp.) were mixed in the ratio 88:10:2 and dissolved in 1-methyl-2-pyrrolidone (NMP, 99.5%, Sigma-Aldrich) to form a homogeneous slurry. To ensure the best imaging quality, the slurry was coated onto separator film by the doctor-blade method. The electrodes were punched out and were kept under vacuum at 70 °C to remove the NMP.

To form a homogeneous slurry, a particular phase as shown in Figure S8 of the Supporting Information. To ensure the best imaging quality, the slurry was coated onto separator film by the doctor-blade method. The electrodes were punched out and were kept under vacuum at 70 °C to remove the NMP.

Operando Setup and Experiments: A half-cell using the thin graphite electrode, a Li anode, a glass-fiber separator, and 1 m LiPF 6 in EC:DMC (50:50 wt%) in a standard 2032 coin cell with a 2 mm hole on the top, was assembled in an Ar-filled glovebox. A 5 × 5 mm glass window was attached using epoxy to seal the cell and view the graphite flakes under the optical microscope. The coin cell was placed on a stage of the Olympus BX53M microscope under objective 50x for operando observation. The cell was cycled at C/4 current five times between cut-off voltages 1.5 V and 0.4 mV, to form a stable SEI. A three PITT discharge experiments were then performed from 245 to 0.1 mV, varying the voltage steps and C/20 threshold current: 1), with 10 mV, 2) 100 mV, and 3) 200 mV step sizes, while capturing the time frames every 10 s. All the acquired digital photos were processed using ImageJ to quantify the colored regions. The detailed description of the procedures is mentioned below. See Sections S3–S9 of the Supporting Information for more details.

An EIS was conducted at intervals of 10% SOC from 10% to 100% SOCs. The cells were discharged at 0.1 C current to the relevant SOC and relaxed for 2 h to reach equilibrium before taking the EIS measurements. All the EIS measurements were taken at 10 mV amplitude in the frequency range 1 MHz–1 Hz. The obtained Nyquist plots were fitted using the equivalent circuit model, shown in Figure S5a.

Color Thresholds for Area Quantification: The built-in Hue-Saturation-Brightness threshold method of ImageJ was used to identify the blue, red, and gold colors in the photos captured in the operando PITT experiment. ImageJ autoselects the brightness to accommodate all the nonblack regions/graphite flakes. Due to the difference in the brightness of blue, red, and gold colors, some smaller particles (<2 μm), which were not clearly visible when they were blue or red, got illuminated upon turning into gold color. This illumination caused the autoselect feature of ImageJ to select more area when the particles entered Segment I (or Stage 1). The maximum difference in the selected area across all the images was <10%, but still resulted in slight inconsistency while calculating the area fraction of different phases. To avoid this inconsistency, the same sampling region was defined based on the images at 55% SOC while converting the surrounding areas black (i.e., excluding voids, in which there could be small blue and red particles that are not clearly visible). Note that at 100% SOC, all active particles should appear bright gold. The unreacted regions (in the saturation range between 0 and 40) were selected and converted into black. The final black mask was applied to all the images. Within the sampling regions, a fixed range of hue was used to select similar colored regions (red: 0–24, gold: 24–44, and blue: 44–255) while maintaining the same range of saturation (40–255) and brightness. The criteria were selected based on the low current discharge (C/72) when all the particles are in a particular phase as shown in Figure S8 of the Supporting Information. The above criteria were applied to all the digital images with the help of an ImageJ script. A variation of ±10% in the selected thresholds results in a deviation of only ±0–5% in the selected areas of blue, red, and gold as shown in Figure S13 of the Supporting Information.

Charge Conservation Calibration: The area evolution curve in Figure 1c was investigated to understand how the stable phases change, which is responsible for the surface reaction, by applying the charge conservation within the electrode. ∑qiА(t) = qiА(t), where i represents blue, red, and gold, qi is the areal capacity of the i-th color and can be calculated from the SOC of the i-th color (estimated above) and the theoretical areal capacity of the material (qi). qi = xixiA А, is the area covered by i-th color, qi is the areal capacity of the electrode, and А is the total surface area of particles in the electrode. The above equation can, then be transformed into ∑xixiAА(t) = xixiА(t) where x is the area fraction of the i-th color, and x is the global SOC of the electrode. For known area fractions of stable phases, a phase-transforming material should inherently follow this equation. Since a 100 × 100 μm window was only observed under the optical microscope, the validity of the above equation for the observed region confirms that the analysis can be confidently extrapolated to the entire electrode (Section S5, Supporting Information).

Curve Validation and Physical Adjustment: The capacity carried by each stage during the PITT discharge was calculated using Qi = qiА(t) = xixiА(t), as explained in the main text. The equation is valid because the intercalation process satisfies the equation ∑xixiА(t) = xixiА(t) during the entire PITT (Section S5, Supporting Information). The individual capacity contribution follows the same trend as the area fraction evolution curve in Figure 1c. They were individually represented by analytical expressions, for instance, Stage 3 by an exponential curve, Stage 2 by a 6th order polynomial equation and Stage 1 by a logistic S-shaped curve. A detailed description with fitting parameters is provided in Section S5 of the Supporting Information. The phase currents were calculated by taking a 1st order time derivative of the obtained analytical expressions (Equation (1)).

Small noises were observed while estimating the length of interface using ImageJ (Figure 2a) due to errors arising in the pixel-by-pixel measurement. This noise was removed by applying a quadratic regression method in MATLAB, enabling to obtain smooth interfacial current densities.

Determination of the Effective Interfacial Area: For a shape with two colors, ImageJ can be used to find the perimeter covered by each color, and the outer perimeter of the shape, which together can be solved for the length of the interface. In this case, particles existed in three different states at a time. To calculate the length of the interface, for instance, the blue–red interface, it was relied on the fact that the phase transformation in graphite can only occur in one order: Stage 3 to Stage 1. All the green regions were converted in the transformed RGB images, to the standard red color, thus eliminating all red–gold interfaces. This enabled to find the length of the blue–red interface using the above methodology from the following equation, lbr = (lblue + lred − lparticle)/2. Similarly, the length of the red–gold interface was calculated by converting all the blue regions to the standard red and applying following equation, lrg = (lred + lgold − lparticles)/2 where lbr and lrg are the lengths of blue–red and red–gold interfaces respectively, lblue, lred, and lparticle are the perimeters of the blue, red, and gold regions in the corresponding transformed images, and lparticle is the outer perimeter of all the particles within the viewing frame.

Considering disk-shaped flakes with an average diameter 8 μm and thickness 0.5 μm, ~5 μm thick electrode constituted ~10% particles with ten layers stacked over each other. On making a statistical assumption that all layers were similar, the active area was calculated by multiplying the total length of phase boundaries with the electrode thickness.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.
Acknowledgements

P.B. acknowledges the support from a National Science Foundation grant (Award No. 2044932), and the startup support from Washington University in St. Louis. The materials characterization experiments were supported in part by IMSE (Institute of Materials Science and Engineering) and by a grant from InCEES (International Center for Energy, Environment and Sustainability) at Washington University in Saint Louis.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

P.B. conceived and supervised the study. S.A. and P.B. designed the experiments. S.A. performed the experiments, carried out the analysis. S.A. wrote and revised the manuscript.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Code Availability

The ImageJ scripts for direct image analysis and MATLAB code for model calculation are available from the corresponding author upon reasonable request.

Keywords

electroanalytical techniques, growth theory, impedance diagnosis, intercalation dynamics, optical microscopy

Received: October 22, 2020
Revised: January 17, 2021
Published online: February 12, 2021

[1] S. Chu, Y. Cui, N. Liu, Nat. Mater. 2016, 16, 16.
[2] J. M. Tarascon, M. Armand, Nature 2001, 414, 359.
[3] J. B. Goodenough, Y. Kim, Chem. Mater. 2010, 22, 587.
[4] J. W. Choi, D. Aubarch, Nat. Rev. Mater. 2016, 1, 16013.
[5] N. Williard, W. He, C. Hendricks, M. Pecht, Energies 2013, 6, 4682.
[6] X. Liu, D. Ren, H. Hsu, X. Feng, G. L. Xu, M. Zhuang, H. Gao, L. Lu, X. Han, Z. Chu, J. Li, X. He, K. Amine, M. Ouyang, Joule 2018, 2, 2047.
[7] S. J. Harris, P. Lu, J. Phys. Chem. 2013, 117, 6481.
[8] C. Tian, Y. Xu, D. Nordlund, F. Lin, J. Liu, Z. Sun, Y. Liu, M. Doeff, Joule 2018, 2, 464.
[9] W. E. Gent, Y. Li, S. Ahn, J. Lim, Y. Liu, A. M. Wise, C. B. Gopal, D. N. Mueller, R. Davis, J. N. Weker, J.-H. Park, S. Doo, W. C. Chueh, Adv. Mater. 2016, 28, 6631.
[10] S. Fang, M. Yan, R. J. Hamers, J. Power Sources 2017, 352, 18.
[11] T. Nakamura, T. Watanabe, Y. Kimura, K. Amezawa, K. Nitta, H. Tanida, K. Ohara, Y. Uchimoto, Z. Ogumi, J. Phys. Chem. C 2017, 121, 21118.
[41] P. Maire, H. Kaiser, W. Scheifele, P. Novák, J. Electroanal. Chem. 2010, 644, 127.
[42] K. Persson, Y. Hinuma, Y. S. Meng, A. Van Der Ven, G. Ceder, Phys. Rev. B: Condens. Matter Mater. Phys. 2010, 82, 125416.
[43] S. Yang, X. Wang, X. Yang, Y. Bai, Z. Liu, H. Shu, Q. Wei, Electrochim. Acta 2012, 66, 88.
[44] R. Amin, Y. M. Chiang, J. Electrochem. Soc. 2016, 163, A1512.
[45] A. Verma, K. Smith, S. Santhanagopalan, D. Abraham, K. P. Yao, P. P. Mukherjee, J. Electrochem. Soc. 2017, 164, A3380.
[46] P. Maire, A. Evans, H. Kaiser, W. Scheifele, P. Novák, J. Electrochem. Soc. 2008, 155, A862.
[47] Y. Guo, R. B. Smith, Z. Yu, D. K. Efetov, L. Wang, P. Kim, M. Z. Bazant, L. E. Brus, J. Phys. Chem. Lett. 2016, 7, 2151.
[48] D. Fraggedakis, N. Nadkarni, T. Gao, T. Zhou, Y. Zhang, Y. Han, R. M. Stephens, Y. Shao-Horn, M. Z. Bazant, Energy Environ. Sci. 2020, 13, 2142.
[49] M. Avrami, J. Chem. Phys. 1939, 7, 1103.
[50] M. Avrami, J. Chem. Phys. 1940, 8, 212.
[51] A. N. Shiryaev, Selected Works of A. N. Kolmogorov (Volume II Probability Theory and Mathematical Statistics), Springer, Dordrecht, Netherlands 1992, p. 188.
[52] M. E. Hyde, R. G. Compton, J. Electroanal. Chem. 2003, 549, 1.
[53] P. Bai, G. Tian, Electrochim. Acta 2013, 89, 644.
[54] C. J. Wen, R. A. Huggins, Mater. Res. Bull. 1980, 15, 1225.
[55] J. Li, X. Xiao, F. Yang, M. W. Verbrugge, Y. T. Cheng, J. Phys. Chem. C 2012, 116, 1472.
[56] P. C. Tsai, B. Wen, M. Wolfman, M. J. Choe, M. S. Pan, L. Su, K. Thornton, J. Cabana, Y. M. Chiang, Energy Environ. Sci. 2018, 11, 860.
[57] K. Xu, Chem. Res. 2004, 104, 4303.
[58] F. Single, B. Horstmann, A. Latz, J. Phys. Chem. C 2019, 123, 27327.
[59] A. Arya, A. L. Sharma, J. Mater. Sci. Mater. Electron. 2018, 29, 17903.
[60] C. Ho, I. D. Raistrick, R. A. Huggins, J. Electrochem. Soc. 1980, 127, 343.
[61] N. Takami, A. Satoh, M. Hara, T. Ohsaki, J. Electrochem. Soc. 1995, 142, 371.
[62] E. Flores, P. Novák, E. J. Berg, Front. Energy Res. 2018, 6, 1.