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Communication

Resolving Fast Relative Kinetics in Inorganic Solid-State Synthesis

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ABSTRACT: Solid-state syntheses are generally regarded as being slow, limited by transport, and, as such, are often only stopped to check the products after many hours at high temperature. Here, using a custom-designed reactor to rapidly initiate solid-state syntheses, we are able to capture the earliest stages of a reaction using *in situ* X-ray scattering. For the reaction of TiO_2 and Li_2CO_3 to form spinel lithium titanate ($Li_4Ti_5O_{12}$)—an anode material for fast-charging applications—we capture two distinct kinetic regimes, including fast initial kinetics in the first seconds−minutes of the reaction that account for significant product formation. We use an Avrami model to compare the reaction at high temperatures (700−750 °C), which results in the rapid formation of $Li_4Ti_5O_{12}$ within minutes, and lower temperatures (482 °C), consistent with conditions that might be chosen based on "Tamman's rule", a common heuristic. Our analysis reveals characteristic Avrami slopes (i.e., dimensionalities) for each step in the chemical transformation. We anticipate that the fast initial reaction kinetics found here are likely to be common in the synthesis of other materials used in battery electrodes, solid-state electrolytes, ion-conductive membranes, etc. where ion transport is a prerequisite for functionality.

Solid-state synthesis of crystalline inorganic materials has long been accepted as being intrinsically slow, requiring heating at high temperatures for long periods to compensate for the limiting rate of diffusion in solids.[1,2] Reaction mixtures of metal oxides, carbonates, etc. are often heated in a furnace at temperatures that are high enough for diffusion to occur and only cooled and checked for products, byproducts, and impurities after hours, days, or weeks. Here the reaction temperature may be initially selected based on the experience of the researcher or guided by heuristics such as "Tamman's rule",[3] which estimates the temperature at which a reaction will proceed based on the melting temperatures of the precursors.[4] Reaction conditions are subsequently iterated and optimized, which can be time-consuming and inefficient.

While syntheses in the laboratory are blind to the transformations that occur behind the closed furnace door, *in situ* synchrotron-based powder diffraction experiments are increasingly being used to gain mechanistic insight into solid-state reactions.[5−8] Based on the expectation that the reactions are slow, occurring over hours−days, these *in situ* synchrotron experiments typically use a variable-temperature measurement strategy, wherein the temperature of the reaction mixture is progressively increased.[9,10] This has proven useful in estimating the onset temperature for reactions, identifying reaction intermediates, and inferring key steps in the reaction.[7,11]

Recently, studies have suggested that some solid-state reactions may occur much faster once initiated, for example, once a threshold temperature for the reaction is surpassed.[7,12−14] Indeed, in an investigation of transport-limited ion-exchange reactions, we see the evidence of fast reactions in the first minutes of the reaction,[13] time scales that are more typically associated with rapid gas−solid reactions.[15,16] Synchrotron-based powder diffraction measurements using area detectors allow data collection for quantitative phase and structural analysis with sub-second time resolutions to capture rapid transformations.[17] However, a critical technical challenge that prevents us from resolving fast reactions is being able to initiate solid-state reactions on time scales that are fast relative to the reaction kinetics. If initiation is slow relative to the reaction rate, then we see a distribution of states; intermediates and inflection points may not be resolved. With most solid-state reactions requiring heating of the reaction mixture at high temperatures, rapid reaction initiation requires rapid heating capabilities.[15]

Here we enable *in situ* X-ray scattering studies of fast solid-state reaction kinetics within a custom-designed reactor furnace that rapidly initiates solid-state reactions by shifting the sample into a pre-heated hot zone.[18] We apply this to probe the early reaction kinetics in a model reaction, the reaction of TiO_2 and Li_2CO_3 to form spinel lithium titanate ($Li_4Ti_5O_{12}$)—an anode material for fast-charging applications.[19−21] We evaluate the kinetics of the reaction at temperatures at which $Li_4Ti_5O_{12}$ is known to form and a temperature that is consistent with Tamman's rule.[3,4] These experiments reveal fast early kinetics, in the seconds time regime, which may be more common in solid-state reactions than previously appreciated.

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$Li_4Ti_5O_{12}$ has potential as an anode for fast-charging batteries.[21,22] Its performance depends on the material's particle size and crystallinity which, in turn, depend on the synthesis parameters and protocols.[23,24] Previous, variable-temperature *in situ* studies of the solid-state synthesis of $Li_4Ti_5O_{12}$ showed that an intermediate Li_2TiO_3 phase forms starting at >500 °C, which reacts further to form the $Li_4Ti_5O_{12}$ product at >650 °C, with lower reaction onset temperatures observed for precursors with smaller particle size.[20]

$$TiO_2 + Li_2CO_3 \rightarrow Li_2TiO_3 + CO_2 \quad (1)$$

$$3TiO_2 + 2Li_2TiO_3 \rightarrow Li_4Ti_5O_{12} \quad (2)$$

$$TiO_2\ (\text{anatase}) \rightarrow TiO_2\ (\text{rutile}) \quad (3)$$

Stoichiometric quantities of reagents were mixed and formed into pellets to optimize contact between particles before loading them into the capillary.[13] Capillary-loaded reaction mixtures were assembled within the reactor, and fast-time-resolved X-ray diffraction data were collected at beamline 11-ID-B of the Advanced Photon Source at Argonne National Laboratory (λ = 0.2116 Å) following actuation of the reaction mixture into the hot zone. Data were collected with exposures increasing from 1 to 30 s, matching the data density to the reaction kinetics.

The time-resolved *in situ* diffraction data (Figure 1) were acquired following the rapid initiation of the reaction upon heating to temperatures known to yield spinel $Li_4Ti_5O_{12}$ (700, 725, and 750 °C). During the first 10 s, as the reaction heats, the diffraction peaks shift to lower angles, reflecting the thermal expansion of the reagents, which includes anatase TiO_2 with a minor rutile TiO_2 impurity. Peaks associated with reagent Li_2CO_3 and anatase TiO_2 lose intensity, in tandem with the appearance and growth of peaks from the monoclinic ($C2/c$) Li_2TiO_3 intermediate. Beyond 30 s, peaks associated with Li_2CO_3 can no longer be distinguished, peaks associated with TiO_2 anatase continue to lose intensity, and Li_2TiO_3 is consumed as the spinel $Li_4Ti_5O_{12}$ product appears. The proportion of rutile phase TiO_2 increases throughout. After 10 min, the system is a three-phase mixture of rutile TiO_2, the Li_2TiO_3 intermediate, and the $Li_4Ti_5O_{12}$ product.

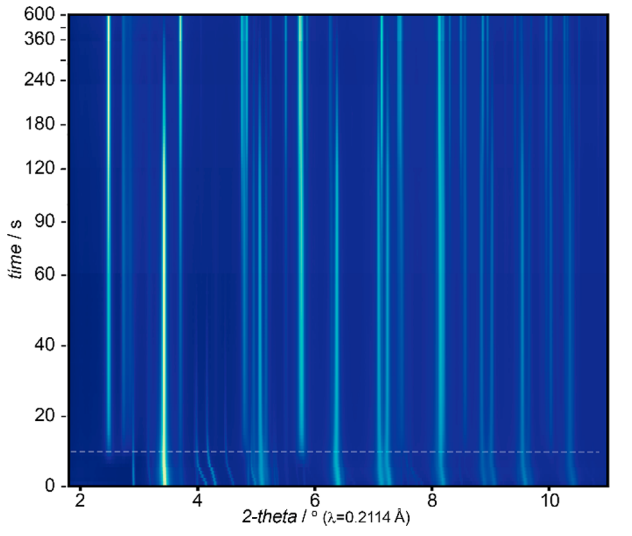

Figure 1. *In situ* X-ray diffraction data collected on the reaction between Li_2CO_3 and anatase TiO_2 at 700 °C. The reaction is initiated by rapid heating in under 10 s.

Quantitative analysis of the phase distribution throughout the reaction (Figure 2) reveals several distinct kinetic regimes.

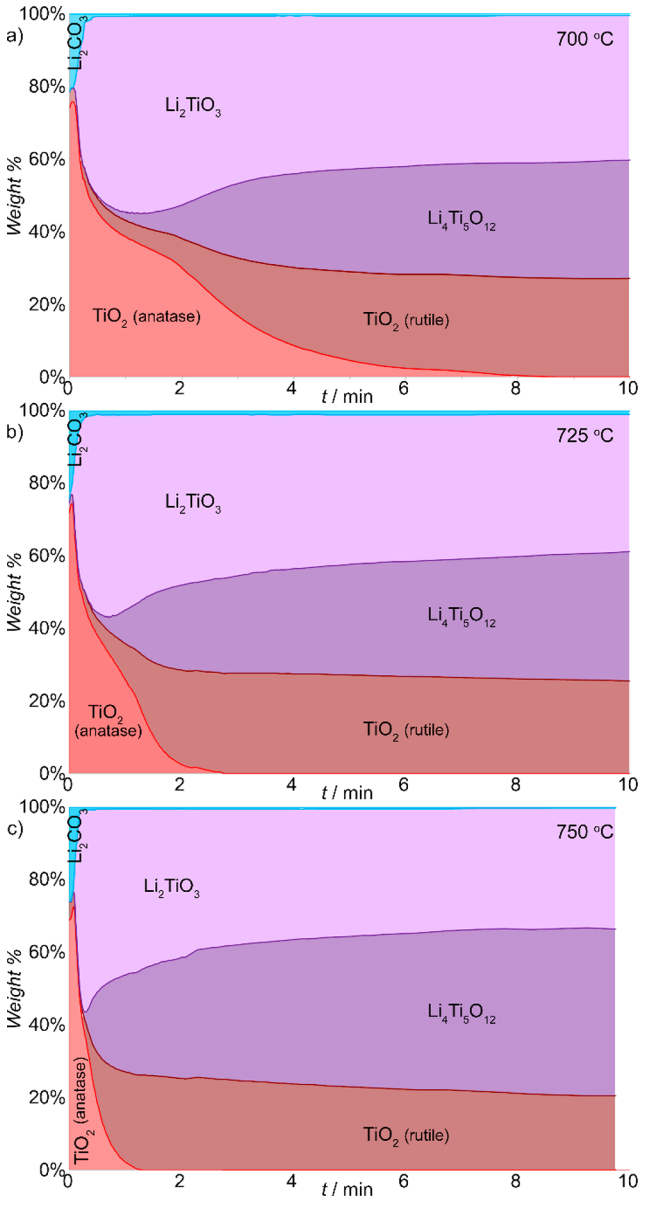

Figure 2. Phase distribution from Rietveld analysis of the $Li_4Ti_5O_{12}$ synthesis reactions at (a) 700 °C, (b) 725 °C, and (c) 750 °C.

The first step of the reaction of TiO_2 and Li_2CO_3 is initially fast and then slows as the Li_2CO_3 is consumed. The second step of the reaction and the formation of $Li_4Ti_5O_{12}$ follow an S-curve, initially slow, accelerating after ~1.5−3 min together with the conversion of anatase to rutile, and then slowing as anatase is eliminated.

The maximum quantity of Li_2TiO_3 observed during the reaction, ~52 wt%, exceeds the quantity expected for complete conversion to Li_2TiO_3 (48 wt%) without formation of $Li_4Ti_5O_{12}$. This suggests that this phase deviates from the nominal stoichiometry and is likely TiO_2-rich/Li-deficient (i.e., $Li_{2-x}TiO_{3-x}$). This initial kinetic intermediate product is richer

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in Li^+ than the final product, reacting with the remaining TiO_2 to form the $Li_4Ti_5O_{12}$ product.

The formation of $Li_4Ti_5O_{12}$ is faster in the presence of anatase TiO_2 and slows once only rutile remains. This correlation of anatase to the rate of $Li_4Ti_5O_{12}$ formation may be linked to a lower energy penalty to restructuring of anatase, a metastable polymorph, relative to rutile—the thermodynamic phase.

Further time-resolved *in situ* data evaluated the initial kinetics of the same reaction at a lower temperature, representative of that which may be chosen based on Tamman's rule (Figure 3). While Tamman's conjecture was

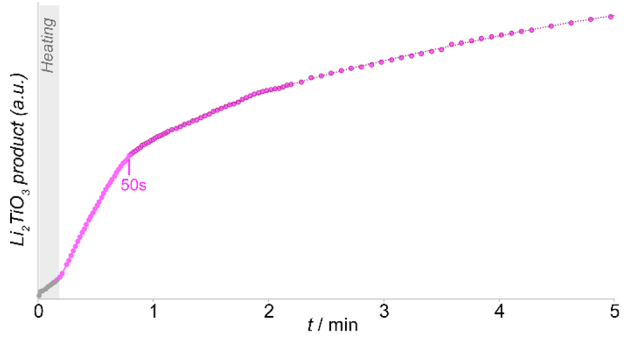

Figure 3. Two distinct kinetic regimes are observed in the formation of Li_2TiO_3 through reaction of TiO_2 and Li_2CO_3 at 482 °C, a temperature selected based on Tamman's rule.

proposed in the context of alloy formation,[3] it is often used as a rule-of-thumb to select an initial temperature for the syntheses of inorganic oxides. Selecting a temperature that is some fraction of the reagent melting point is thought to allow "sufficient" mobility and diffusion for the reaction to proceed. Specifically, the reaction was evaluated at 482 °C, two-thirds of the melting temperature (in °C) of Li_2CO_3, the lowest-melting reagent. The significant formation of Li_2TiO_3, the initial reaction product, at this temperature supports the validity of Tamman's conjecture for this system. This is despite the temperature being lower than the onset for Li_2TiO_3 formation seen in previous variable-temperature studies.[20] The $Li_4Ti_5O_{12}$ product is not observed in the time frame studied.

Quantitative phase analysis shows that even at this low temperature, the kinetics of the reaction are complex, with multiple kinetic regimes observed (Figure 3). Following initiation of the reaction at 482 °C, there is rapid formation of Li_2TiO_3 in the first ~50 s, after which the rate of Li_2TiO_3 formation drops suddenly. The reaction rate in the fast initial kinetic regime is 4 times the rate observed in the subsequent kinetic regime.

The relative kinetics observed for the reaction of TiO_2 and Li_2CO_3 at all temperatures were compared using an Avrami analysis (Figure 4),[25] based on the fraction of the initial Li_2TiO_3 product. The Avrami equation describes isothermal phase transformations based on nucleation and growth, although it has been applied to reactions in solids and other wide-ranging phenomena.[26−28] In the classic application of the Avrami model, the slope of the ln−ln plot is related to the dimensionality of the growth, while the *y*-intercept is related to the rate constant. The slopes of the Avrami curves are positive as Li_2TiO_3 forms and become negative when Li_2TiO_3 is subsequently consumed to produce $Li_4Ti_5O_{12}$.

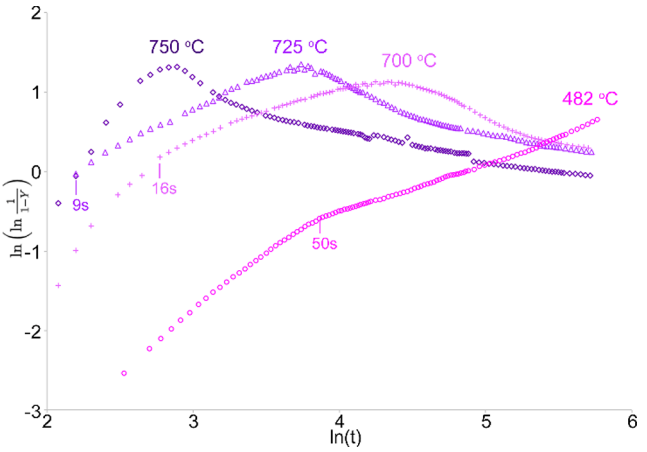

Figure 4. Application of an Avrami model to the formation/volume fraction of the initial Li_2TiO_3 product suggests that there are distinct kinetic regimes of the reaction where the transformation occurs with different dimensionality.

For all temperatures, a series of similar Avrami slopes are observed, suggesting that there are characteristic dimensionalities for each transformation. We identify two distinct slopes during the formation of Li_2TiO_3: a well-defined transition from high to low slope implies a change in mechanism from a higher to a lower dimensional transformation. The inflection point associated with this transition is most clearly defined for the slowest reaction (50 s at 482 °C) and occurs earlier at higher temperatures, where it becomes more difficult to distinguish. The non-integer values of the slopes of ~1.4 (high slope) and ~0.5 (low slope) are not straightforwardly interpretable in the context of dimensionality of the transformation. The transition between slopes may reflect features of the reaction architecture,[13] how the microstructure develops during the reaction, or a change in stoichiometry of the $Li_{2-x}TiO_{3-x}$ product. As Li_2TiO_3 and TiO_2 are consumed to form $Li_4Ti_5O_{12}$, there are also distinct common negative slopes: an initially high slope transitions to a lower slope. The similarities of the Avrami curves for reaction temperatures above and below the melting point of Li_2CO_3 suggest that melting of this reagent does not play a significant role in the reaction mechanism and kinetics.

This study identifies fast kinetics that occur in the earliest stages of a solid-state reaction, even at moderate temperatures, with the fast kinetic regime seen in the first minute accounting for a substantial fraction of the product formed. The specific reaction studied here leads to the formation of a phase of interest as an electrode material, an application for which ion mobility is a prerequisite. We propose that the high ion mobility of the product allows for fast ion diffusion and, hence, faster reaction kinetics. We anticipate that the fast reaction kinetics seen here may be common to the synthesis of other materials whose applications require that the structure accommodate transport of ions and non-stoichiometries, including other electrode materials,[13,14] solid-state electrolytes,[18] and ion-conductive membranes.

Capturing these earliest stages of fast reactions is enabled only by using the custom-designed heating reactor to initiate the reaction. These early stages are formative and set the course for the eventual product and phase selectivity. Previous *in situ* studies were not undertaken in a way that would allow the fast kinetics to be identified. Without this rapid initiation,

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in situ reaction studies miss the earliest kinetic regime and the transitions between different kinetic regimes.

The faster pace of the earliest part of the reaction holds promise for designing more efficient reactions. If we can identify the factors that trigger the transition between fast and slow kinetic regimes, we may have the opportunity to design reactions to extend the fast kinetic regime or eliminate the transition to the slower regime entirely. This may allow us to decouple key synthesis conditions such as time and temperature from outcomes that impact performance, such as ion-migration, sintering, and particle growth.[29] More generally, identifying and understanding fast initial reaction kinetics is important to defining accessible phase space, to evaluating what limits the progress of some reactions, to resolving transient metastable phase intermediates that may be consumed if allowed to react longer, and to optimizing the efficiency of reactions. Importantly, the accurate boundaries on the sufficient conditions for synthesis, with respect to time and temperature, are important for data-driven design of synthesis[4] and, ultimately, for predictive materials synthesis.[30]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c10916.

Details of the experiment and reactor performance (PDF)

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Notes

The authors declare no competing financial interest.

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