

Solid-State Lithiation Reaction: What Is the Actual Lithiation Temperature?

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Supporting Information

Lithium-ion batteries (LIBs) have become an integral part of our lives. The exponential growth in the commercial success of LIBs has been reciprocated in the various research areas related to LIBs. In LIB research, several sub-research areas can be identified as electrode material development, electrolyte and separator development, cell optimization, battery system management, etc. For the development of cathode materials, the solid-state lithiation reaction is indispensable. The solid-state lithiation reaction consists of heating a metal ion precursor and lithium source (usually LiOH or Li_2CO_3) together at a high temperature under a controlled environment. Although the lithiation reaction seems to be a simple and straightforward experiment that consists of heating reactants under a controlled atmosphere for a certain length of time, cathode materials of LIBs are very sensitive to lithiation temperature. In the literature, however, one can find a wide range of optimum lithiation temperatures for the same types of reactants. Therefore, this aspect of cathode research needs to be critically reviewed.

In this Viewpoint, we will discuss, as a case study, the solid-state lithiation reaction of lithium nickel oxide (LNO), which is an eagerly anticipated cobalt-free, high-capacity cathode material for LIBs.¹ LNO precursor is typically synthesized as a hydroxide ($\text{Ni}(\text{OH})_2$) by the co-precipitation method.² The $\text{Ni}(\text{OH})_2$ precursor is then subjected to the lithiation reaction under a pure oxygen atmosphere. However, the reported lithiation reaction temperatures show a very wide variation for the syntheses of LNO. For example, there were 34 reports in the American Chemical Society (ACS) and Royal Society of Chemistry (RSC) journals in the past 5 years that reported the synthesis of LNO via solid-state lithiation reactions (Figure 1; see Supporting Information for the complete list of the research articles). Of these 34 reports, 22 synthesized $\text{Ni}(\text{OH})_2$ via co-precipitation, and 12 either did not report the origin of the Ni precursor or acquired $\text{Ni}(\text{OH})_2$ from vendors. In those 34 reports, the lithiation temperature of LNO varied from 550 to 750 °C. Even removing the outlier at 550 °C, the temperature ranges from 650 to 750 °C. The 100 °C difference may not seem to be a wide temperature range, but in our experience, LNO is very sensitive to lithiation temperature variation. Even a change of 25 °C can bring dramatic changes in its electrochemical characteristics, as will be discussed later. Moreover, when only $\text{Ni}(\text{OH})_2$ and LiOH as reactants are considered, the lithiation temperature ranges from 650 to 750 °C (Figures S1 and S2). We speculate that the

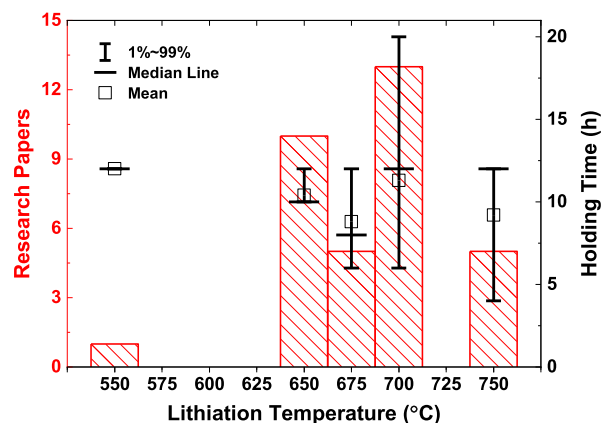


Figure 1. Histogram of LNO solid-state lithiation temperature and variation in the holding time reported in ACS and RSC journals in the past 5 years.

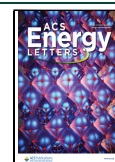
actual lithiation temperature in most reports may be similar, but the discrepancy arises from temperature measurements and reporting.

Before we present our own observations of LNO solid-state lithiation reaction conditions, we would like to further highlight the severity of the issue. In the current research environment, sometimes the engineering aspects of the experiments are ignored. Graduate students, if not guided properly, tend to believe the readings provided by the instruments without verifying the instrument's accuracy. In the case of the lithiation reaction, one of the most important parameters is the furnace temperature. Although the lithiation reaction seems to be a very simple experiment, underlying factors are not always apparent. The temperature displayed on the controller can vary widely compared to the actual temperature experienced by the samples. To give clear evidence, we tested three furnaces in our laboratory for temperature variations. The experimental setup is represented in the Scheme S1. All furnaces were subjected to different

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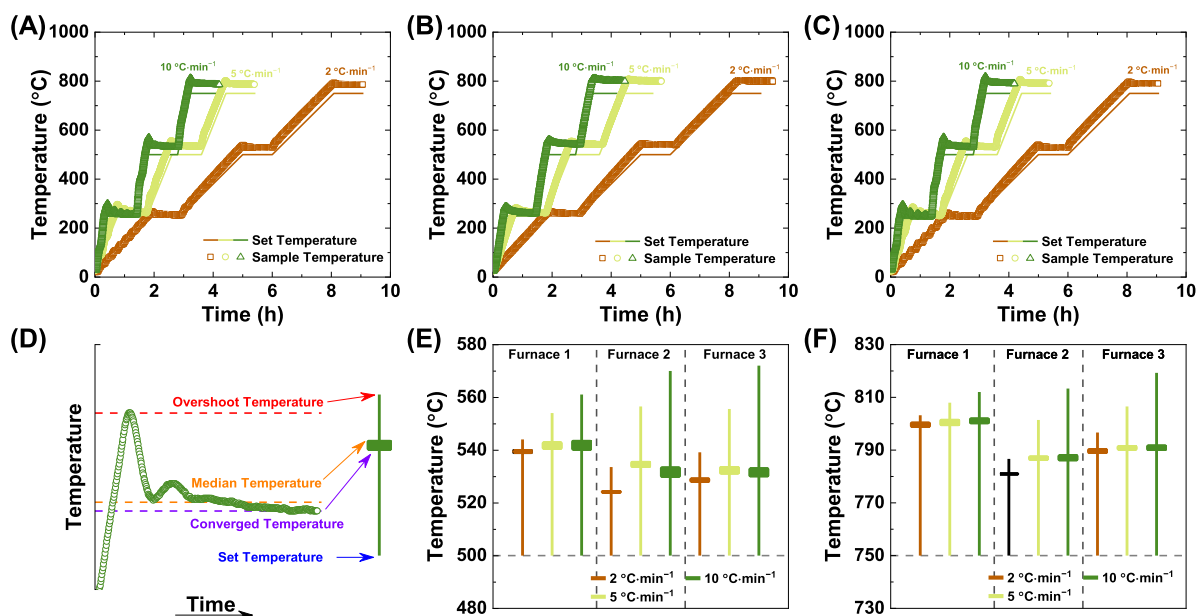


Figure 2. Set temperature and observed sample temperature profiles at different ramp rates in (A) Furnace 1, (B) Furnace 2, and (C) Furnace 3. (D) Illustration of features of candle-sticks used to elucidate temperature fluctuations in various furnaces at different ramp rates. Candle-stick plots of three different furnaces with holding temperatures set at (E) 500 °C and (F) 750 °C.

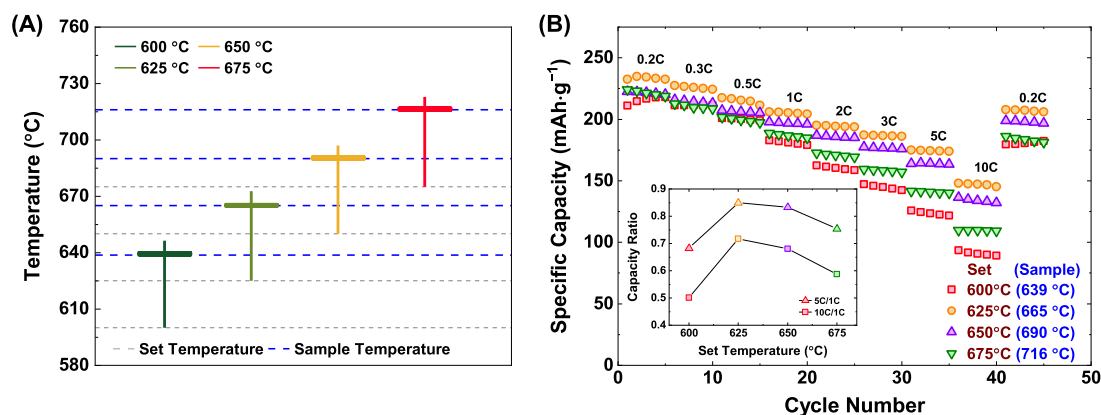


Figure 3. (A) Candle-stick plot of temperature fluctuations during LNO solid-state lithiation reaction at various holding temperatures (furnace set temperature). (B) Rate performance of LNO lithiated at holding temperatures ranging from 600 to 675 °C. The inset shows the 1C/1C and 1C/10C capacity ratios of various samples. 1C is equivalent to full battery charge/discharge in 1 h with a capacity of 200 mAh g⁻¹.

heating rates with temperature holding at various temperatures. An external thermocouple was placed in the tube with its tip right above the sample. The external thermocouple was inserted from the side with a custom-made cap. The insertion point was sealed with silicone rubber. Our experiments revealed a very high variation between the furnace set temperature and the actual sample temperature (Figure 2A–C). All furnaces experienced a temperature overshoot, which eventually decayed to a steady value (Figure 2D–F). However, even the steady values were also higher than the set temperature. Furthermore, the temperature overshoot and the time needed to reach a steady value showed a direct correlation with the ramping rate. Moreover, these variations were different for different furnaces. These observations seem well-established with clear results. However, the obvious and simple things (e.g., standard-based calibration of thermocouples) are usually ignored during experiments. Therefore, a reported temperature of 625 °C could have been 665 °C.

These variations depend on the furnace model, manufacturer, age, and condition of the furnace. Therefore, the temperature reported in the literature typically serves only as a broad initial estimate to reproduce the results. Each laboratory usually needs to optimize its own temperature to reproduce the results.

It could be argued that the variation of 50 °C is not a very high number for high-temperature reactions. Therefore, we prepared LNO with precise temperature control to highlight the magnitude of the situation. LNO was synthesized using the solid-state lithiation reaction from a mixture of Ni(OH)₂ prepared by co-precipitation and LiOH. The lithiation temperature ranged from 600 to 675 °C, with an increment of 25 °C. Two-step temperature profiles were used to minimize the temperature overshoot. A heating rate of 2 °C min⁻¹ and an intermediate hold at 500 °C for 30 min was used to minimize the temperature overshoot and temperature convergence time. As given in Figures 3A and S3, this

procedure was largely successful in attaining the desired results. A temperature overshoot of only 8–9 °C was observed, and it quickly subsided to steady values. However, sample temperatures, as measured by the thermocouple placed very close to the sample (within 1 cm), were higher than the set temperatures (Scheme S1). For example, the actual lithiation reaction temperature was 665 °C when the furnace temperature was set to 625 °C, indicating a difference of 40 °C.

The Ni(OH)₂ precursor used for all of the reactions was from the same batch to remove any factors that might influence the performance. The morphology of the LNO prepared at various temperatures was very similar (Figure S4). However, there was an increase in the crystallinity with the increase in temperature (Figures S5 and S6). The capacity and rate performance of LNO synthesized at various temperatures showed dramatic changes, despite their temperatures differing by only 25 °C (Figures 3B and S7). For the sake of simplicity, we will identify the LNO samples with their set temperatures. The specific capacity of LNO at a C-rate of 1C increased from 180 to 205 mAh g⁻¹ when the lithiation temperature was increased from 600 to 625 °C. This capacity decreased again to 196 mAh g⁻¹ when the temperature was increased to 650 °C and decreased to 186 mAh g⁻¹ with a further increase in temperature to 675 °C. The rate performance also showed a similar tendency (inset of Figure 3B). LNO synthesized at 625 °C showed the best capacity retention at a high C-rate. Any decrease or increase of temperature from 625 °C with an increment of 25 °C led to the deterioration of rate performance. The materials/electrochemical reasons for the variation in the performance of LNO at different temperatures are beyond the scope of current work. However, as observed, a temperature variation of 25 °C induces significant changes in the battery capacity and rate performance behavior of LNO.

At this temperature range, all furnaces showed a variation of ~40 °C in the steady temperature compared to the set temperature (temperature indicated on the furnace controller). All furnaces also experienced a temperature overshoot of 8–9 °C; however, it quickly subsided to a steady temperature due to the precautions taken to prevent this phenomenon. As LNO shows such dramatic changes in its battery behavior with a temperature variation of 25 °C during the lithiation reaction, the furnace temperature should not be reported as the lithiation reaction temperature without verification with additional temperature sensors. We believe that this discrepancy is one of the major reasons for the widespread reported optimum temperature for the lithiation of LNO and other battery materials.

Most, if not all, tube furnaces suffer from this variation of temperature because the thermocouple connected to the temperature controller is usually situated outside the tube for various technical reasons. Hence, it always read a temperature different than the conditions close to the samples. Furthermore, with aging, the difference between the furnace controller temperature and sample temperature varies due to thermocouple, insulation, and heater deterioration. Therefore, constant monitoring of the furnace is required to adjust temperature control parameters to minimize the temperature overshoots and fluctuations to obtain reproducible results with high-temperature uniformity. Therefore, we suggest researchers should always verify their sample temperature with an external thermocouple and report the precautions taken to ensure reproducible results. If temperature verification is not possible due to some technical or resource limitations, one

should report the lithiation temperature as the furnace controller temperature.

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■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acseenergylett.2c00804>.

List of chemicals and materials, experimental details, and characterization results, including Figures S1–S7 and Scheme S1 (PDF)

■ AUTHOR INFORMATION

Complete contact information is available at:

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Notes

Views expressed in this Viewpoint are those of the authors and not necessarily the views of the ACS.

The authors declare no competing financial interest.

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