Joule

Article

Solid-state batteries enabled by ultra-highfrequency self-heating

Graphical abstract



Highlights

- Ultra-high-frequency self-heating enables fast cold starts of solid-state batteries
- Battery warms to optimal temperature in under 1 min using voltage pulse
- Heating method improves energy output without modifying battery structure
- Scalable thermal strategy reduces energy loss in large battery packs

Authors

Buyi Zhang, Divya Chalise, Yuqiang Zeng, ..., Sumanjeet Kaur, Chris Dames, Ravi Prasher

Correspondence

rsprasher@lbl.gov

In brief

Solid-state batteries are attracting attention for their high energy density and safety but struggle to perform at room temperature due to sluggish ion transport and poor interface contact. This study demonstrates a rapid, non-invasive selfheating method using ultra-highfrequency voltage pulses, enabling full battery performance within 1 min. The approach improves energy output and is scalable for electric vehicles and energy storage systems.



Joule



Article Solid-state batteries enabled by ultra-high-frequency self-heating

Buyi Zhang,^{1,2} Divya Chalise,^{1,2} Yuqiang Zeng,^{2,3} Fengyu Shen,² Michael Tucker,² Sumanjeet Kaur,² Chris Dames,¹ and Ravi Prasher^{1,2,4,*}

¹Department of Mechanical Engineering, University of California, Berkeley, Berkeley, CA 94720, USA

²Energy Technology Area, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

³School of Microelectronics, Southern University of Science and Technology, Shenzhen 518055, China

⁴Lead contact

*Correspondence: rsprasher@lbl.gov https://doi.org/10.1016/j.joule.2025.101973

CONTEXT & SCALE Solid-state batteries (SSBs) promise improved safety and higher energy density over today's lithium-ion batteries (LIBs), but their poor performance at room temperature has limited widespread use. We demonstrate a fast, non-invasive self-heating method that warms SSBs to optimal operating temperature in under a minute using ultra-high-frequency electrical pulses. This approach requires no structural changes, adds minimal energy cost, and is scalable to commercial battery packs. It opens new opportunities to reduce the range anxiety of electric vehicles and provides reliable cold starting. By introducing a more suitable thermal strategy than those conventionally used in liquid-electrolyte batteries, this work may shift how SSBs are managed, potentially accelerating their adoption in next-generation energy storage and transportation systems.

SUMMARY

Solid-state batteries (SSBs) are promising next-generation batteries due to their high energy density and enhanced thermal stability and safety. However, their sluggish kinetics and transport at room temperature result in high internal impedance and critically reduce the attainable discharge energy density. Taking advantage of their strong temperature-dependent ionic conductivity, here we introduce ultra-high-frequency (greater than 10^5 Hz) self-heating (UHFSH) of SSBs, which can rapidly warm up the batteries from room temperature to operating temperature (~65°C) in less than a minute. As proof of concept, UHFSH experiments were conducted on symmetric solid-state cells with lithium aluminum germanium phosphate electrolyte in different configurations. Using an experimentally validated model, pack-level simulations predict fast heating (50 K/min) and minimized heating energy consumption (less than 4%). Without any modification of the materials or structure of the batteries, our non-intrusive self-heating strategy potentially enables SSBs to discharge more than 2-fold energy in 25°C ambient.

INTRODUCTION

Over the past decades, lithium-ion batteries (LIBs) have been widely used as energy storage devices in mobile electronics and electric vehicles (EVs).¹ However, traditional LIBs using a liquid electrolyte still suffer from relatively lower energy density and significant safety problems because of the flammable nature of the electrolyte. Solid-state batteries (SSBs) stand out as one of the most promising next-generation battery technologies to overcome these issues. By using a lithium-metal anode, SSBs can potentially offer gravimetric and volumetric energy densities that are 40% and 70% higher than those of LIBs, respectively.² Moreover, benefiting from their inherent mechanical rigidity and high cationic transference number, inorganic solid electro-

lytes (ISEs) can potentially improve the fast-charging performance and degradation of batteries.³ Additionally, replacing the organic liquid electrolyte with a non-flammable solid-state electrolyte (SSE) can enhance the thermal stability window and address safety concerns.^{3–5} SSBs with ISEs have shown superior cycling performance up to 100° C,⁶ whereas LIBs suffer from accelerated side reactions and degradation at higher temperatures (~60°C).^{7,8} However, for many SSEs, except for a few sulfide electrolytes, at room temperature (RT), the lithium-ion transport kinetics in the electrolyte/electrodes and at the interfaces^{9,10} is very sluggish. Sluggish kinetics at RT indicate markedly lower ionic conductivity, leading to several challenges, including a significant reduction in the attainable practical energy density and power density of SSBs and limited discharge

CellPress



capability above 0.1C at RT. This limitation poses a practical challenge, as it may prevent an EV from starting reliably due to the risk of under-voltage. Although some SSBs can deliver sufficient power at RT, their theoretical energy densities remain inherently limited because of low electrode loading and thick electrolytes.¹¹

To decrease the large internal resistance of SSBs, various heating strategies have been proposed as a mild temperature rise of 50°C can result in an increase in the ionic conductivity of the SSE by orders of magnitude.^{9,12–14} For example, the ionic conductivity of solid polymer electrolytes (SPEs) increases by 1–2 orders of magnitude.^{9,15} For ISEs such as lithium lanthanum zirconium oxide (LLZO) and lithium aluminum germanium phosphate (LAGP), it can increase to as much as 5 times as activation energy exceeds 0.3 eV,^{13,16,17} reaching levels comparable to those of liquid electrolytes at RT (10⁻¹–10⁻² S cm^{-S}).² Furthermore, with the same temperature increase, the interfacial resistance between the electrodes and solid electrolytes decreases by an order of magnitude due to improved wetting and contact.¹⁴ Therefore, in lab environments, additional heating environments such as a temperature chamber and oven are usually used to achieve excellent cycling performance of SSBs.¹¹ However, external heating strategies such as convective heating are not practical in actual applications such as an EV for many reasons such as the very slow temperature ramp rate due to the high thermal mass of the battery packs and bulkiness of designing a convective heating system itself. Recently, cell-level heating strategies have been developed to circumvent this problem by embedding a thin heater in the cell itself for both LIBs at very low temperatures and SSBs at RT.^{15,18,19} Wang et al. proposed to embed nickel foil heaters inside the battery to achieve a heating rate of 1°C/s,¹⁸ and likewise, Ye et al. integrated a thin nickel film in the current-collector layers with a polyimide substrate.¹⁵ However, these approaches are intrusive, raising safety concerns, and require additional materials and processing in the existing battery manufacturing chain,²⁰ which has been refined by the industry over several decades.

Alternating current (AC) self-heating, on the other hand, is a non-intrusive method for heating batteries without inducing structural changes, depending on the applied frequency.²¹ AC heating has been successfully implemented in traditional LIBs to facilitate cold-temperature start-up. The temperature ramp rate of AC self-heating for LIBs is ~0.1°C/s,²¹ which is significantly faster than conventional external heating. However, this rate remains too low for practical applications, as it requires over 5 min to reach the ideal ionic conductivity necessary for battery discharge and vehicle start-up. From a practical standpoint, achieving a high temperature ramp rate is critical to ensure that the EV can start within a reasonable short time (around a minute), rather than requiring a prolonged waiting period for the battery to warm up to its optimal operating temperature.

In this paper, we apply the idea of AC heating to SSBs; however, the temperature ramp rate is nearly one order of magnitude higher than those reported for LIBs, i.e., close to 1°C/s, which enables discharge of the full capacity at a reasonable C-rate, making it practically viable to start the vehicle within a minute. This high-temperature ramp rate is achieved by insulation and ultra-high-frequency self-heating (UHFSH), where the frequency is in the MHz range as opposed to the kHz range explored for LIBs in the literature. Without an extra embedded heater or any modification of the internal structure of the cells, our method enables rapid and uniform heating, raising the cell temperature by 45°C within 1 min, thereby potentially increasing the discharge energy density 2-fold, from 50 to 150 Wh/kg. Additionally, with thermal insulation improved by the pack-level configuration, the heating energy consumption is only 3.5% of the overall battery energy.

RESULTS AND DISCUSSION

Overview of UHFSH

Figure 1A shows the energy discharge density for LIBs with a nickel manganese cobalt (NMC) and lithium iron phosphate (LFP) cathode and an SSB with a LFP cathode as a function of temperature. Both share the characteristic that when the temperature rises, all the kinetic and transport processes are accelerated. For commercial LIBs, at low temperature (<0°C), their internal impedances are large, leading to a low terminal voltage and reduced discharge capacity.²⁹ Their discharge energy density approaches the theoretical capacity when discharging at RT (~25°C) and may decrease slightly due to the occurrence of other side reactions at high temperature. However, for SSBs, their discharge energy density performance is continuously enhanced as the temperature increases beyond RT,¹⁵ also see Figure S1. There are a few differences between LIBs and SSBs, which make UHFSH easier and the heating time much shorter for SSBs. SSBs can have 20% less thermal mass per watt-hour (3 J/K/Wh) than LIBs (3.82 J/K/Wh; Table S1³⁰⁻³²). And SSEs, especially ISEs (LLZO and LAGP), have higher thermal conductivity (1.4 and 2.2 W m^{-a}K⁻¹) than liquid electrolytes (0.2 W m⁻ K⁻¹) and wet separators (cross-plane, 0.1-0.4 W m⁻ K⁻¹),^{31,33} which implies faster heating speed and smaller temperature gradient.

The mechanism behind UHFSH of SSBs with lithium anodes with AC is illustrated in Figure 1B. During charging (positive current), the lithium ions are moving from cathode material particles to the lithium anode through a solid electrolyte; and during discharging (negative current), they move in the reverse direction. At the electrode/electrolyte interface, both electrochemical reactions and the formation of an interfacial electrical double layer are occurring. The total current i is composed of the reaction (faradaic) current i_{rxn} and interfacial electrical double-layer current i_{inf}. For direct current (DC) signals and low-frequency excitations, the interfacial capacitance is large, resulting in no or a negligible interfacial current. Consequently, the total current is nearly equivalent to the reaction current. As the signal frequency increases (Figure 1C), the interfacial electrical double layers, which act like a capacitor, allow a more significant current to pass through at high frequencies (shown in Figure 1B). This effect can be understood in more detail by considering the timescale of electrochemical processes occurring in a solid-state electrochemical cell as outlined by Lu et al.³⁴ Notably, the timescale for the charge-transfer reaction is approximately 100 Hz, which is significantly lower than the MHz frequencies used for heating. At MHz frequencies, only the charge transfer across grain boundaries occurs, resulting in ohmic resistance and consequently ohmic heating within



Figure 1. An overview of the UHFSH method

(A) Discharge energy density as a function of temperature for LIBs (INR18650 MJ1 NMC, LFP-32700 LFP) and SSBs¹⁵ (polymer-based LFP|Li), with the solid line serving as a guide to the eye.

(B) Schematic of SSBs under certain VAC. The AC *i* through the cell splits into a capacitive component *i*_{inf} passing through the electric interfacial capacitance and a reactive component *i*_{con} driving electrode reactions.

(C) Effect of frequency on reaction current and heating rate; the reaction current decreased and the heating rate increased under a constant alternating voltage. (D) Temperature ramp rate (heating rate) comparison between external heating, $^{22-25}$ AC heating $^{26-28}$ (10¹-10³ Hz), and this work (10⁵-10⁶ Hz).

the electrolyte, which causes localized heating effects only in the electrolyte, in the absence of electrochemical reactions and any chemical changes to the SSBs. In addition, the reduced capacitive reactance at high frequency leads to the reduction of the total impedance magnitude, thereby increasing the total current at fixed magnitude of alternating voltage. As a result, the total heating rate increases with increasing frequency (Figure 1C). However, induction effects come into play when the frequency is too high (discussed later). We can determine the optimal frequency for the largest heat generation, leading to the largest temperature ramp rate, based on the electrochemical impedance data of SSBs. An additional constraint applied on UHFSH is the need to limit the voltage to the highest allowable voltage for a given chemistry, which is 4.35-2.35 V for an LiCoO₂/LiNi_xMn_yCo_{1-x-y}O₂|Li cell.

One major difference between our ultra-high-frequency technique and the prior literature on low-frequency³⁵ AC heating is that in low-frequency literature constant current was applied as opposed to constant voltage applied in our study. Since every battery chemistry has a maximum voltage limit,³⁶ in the constant current case, one can only increase the current till the maximum voltage is reached. This significantly limits the amount of heat that can be generated. In our method, we have applied constant voltage. Since $Q_{max} = V_{limit}^2/R$, *R* needs to be minimized. For AC current passing through a cell, minimum resistance/impedance is achieved at the highest frequencies. Therefore, going to ultra-high-frequency minimized R and maximized Q_{max} for a given voltage limit. Figure 1D summarizes our UHFSH results (discussed later) and provides a comparison with conventional external heating^{22,23,37,38} and AC heating^{19,26,27} for LIBs. UHFSH resulted in an increase in the heating rate by nearly one order of magnitude.

UHFSH experiments and modeling

As proof of concept, we conducted UHFSH experiments on a symmetric LAGP cell. These experiments were also used to validate our numerical model using electro-thermal co-simulation in COMSOL. The structure of the built single-laver SSB is shown in Figure 2A. The LAGP electrolyte (350 µm) is sandwiched by two lithium electrodes (100 μ m) and the copper current collectors (50 μ m). Electrical connections were made to the copper current collectors by spot welding 50-µm-diameter insulated copper wires. Metal tabs were connected with the other sides of the wires and served as the terminals for the pouch cell. A T-type thermocouple is placed at the center of the copper current collector, with Kapton tape (63.5 μ m) as the electrical insulation layer in between. The temperature signal from the thermocouple is denoted as T_{cc} . The environment temperature is denoted as T_{amb} . The cell is stacked with the thermal insulation materials (aerogel) to provide good thermal insulation. The full stack shown in Figure 2A is vacuum sealed inside a pouch and pressed under \sim 350 kPa. The high-frequency voltage source is provided by a function generator. An oscilloscope is connected to the cell terminals to record the cell voltage.

In a typical experiment, the solid-state cell shown in Figure 3A was first stabilized at RT for 10 min and then heated when ± 2 V sinusoidal excitation was generated from voltage source (Figure 3B). The voltage range was selected as an example and was approximately half the maximum stable potential of LAGP.³⁶ The overall voltage change (4 V in this case) must be

CellPress

Joule Article



Figure 2. The experimental setup and modeling of UHFSH on SSB (A) Experimental setup for UHFSH of LAGP symmetric cell. (B) Reduced equivalent circuit model of SSBs.

kept below the maximum stable voltage. We swept through frequencies of 0.5, 1, 2, 5, and 7 MHz to investigate the frequency dependence. For a single-layer-structured cell (Figure S2A), as the frequency increased from 0.5 to 7 MHz, the temperature rise (ΔT) after 2 min increased from 0.45°C to 0.8°C (Figure 3C). ΔT became stable around 0.85°C when the excitation frequency was beyond 2 MHz.

For stacked two-layer cells (Figure S2B), the thermal insulation conditions were better since the ratio of the surface area to volume was reduced. As a result, ΔT in 2 min at different signal frequencies was higher compared with that of the single-layer cell, as shown in Figure 3C. The maximum ΔT in 2 min was approximately 1°C. Moreover, the steady-state ΔT for the two-layer cell was higher than that for the single-layer cell, as shown in Figure 3D. As the size of the cell increases, we expect the surface area-to-volume ratio to decrease, which increases the overall heating rate and the rate of temperature rise, which is evident in module- and pack-level simulations discussed later.



Furthermore, we conducted electro-thermal co-simulation in COMSOL numerical simulation to model the heating behavior of solid-state cells using the UHFSH method. We built an equivalent circuit model for our symmetric cell. The lithium anode and electrode/electrolyte interface impedance were modeled as the charge-transfer resistance in series with a Warburg element and in parallel with electrical double-layer capacitance. The internal ohmic resistance mainly originates from the solid electrolyte. For the symmetric LAGP cells we constructed, the Warburg element was omitted as mass transport effect from the lithium diffusion in the lithium anode is negligible. In large-capacity cells, inductance of the layer may become important (discussed later); however, for these small single- and two-layer cells, they are negligible.

One simulated cross-section temperature distribution is shown in Figure S3. The thermal properties such as the heat capacity and thermal conductivity of the LAGP electrolyte, lithium foil, and other materials were measured using differential



(A) Images of the assembled single-layer symmetric LAGP pouch cell (12-mm diameter 100- μ m Li electrode, 23.3 mAh).

(B) Sinusoidal voltage wave used in experiments. Schematics of single-layer and two-layer cells are provided in Figure S2.

(C) Temperature rise $\Delta T = T_{cc} - T_{amb}$ (T_{cc} is measured at the cell current-collector center, as shown in Figure 2A; T_{amb} is the ambient temperature) in 2 min across AC-pulsed voltage frequencies from 0.5 to 7 MHz for a single-layer cell and stacked two-layer cell.

(D) Temperature evolution for the single-layer cell and stacked two-layer cell as a function of time under 5 MHz sinewave.



Joule Article

CellPress



Figure 4. The heating performance analysis on cell- and pack-level SSB

(A) Battery configurations for different capacities (small to large): single layer to pouch cell and module and pack level.

(B) Ultra-high-frequency heating power per electrode area as a function of frequency under ±1 V excitation at various uniform cell temperatures. The overall voltage change of 2 V is within the stable voltage of LCO|Li.

(C) An example of simulated temperature distribution of pack (62-kWh pack after 45.2 s \pm 1-V 0.2 MHz voltage heating, assuming 25-µm-thick electrolyte with ionic conductivity at 25°C as $\sigma_0 = 10^{-4}$ S/cm and heat transfer between battery surface and the environment h = 10 W/m²/K).

(D) Temperature evolution for 19-Wh pouch cell and 62-kWh pack with 25- and 50- μ m electrolyte thickness under ±1-V pulse at optimal frequency of 0.2 MHz shown in (B), assuming ionic conductivity at 25°C, $\sigma_0 = 10^{-4}$ S/cm, and heat transfer between battery surface and the environment h = 25 W/m²/K.

(E) Heating energy consumption of different SSB sizes and solid-electrolyte thickness, assuming temperature rise $\Delta T = 40^{\circ}$ C and heat transfer between battery surface and the environment $h = 10 \text{ W/m}^2/\text{K}$.

scanning calorimetry and the 3-omega method or were taken from the literature (Note S1). The heat generation is calculated from cell-impedance data and voltage using $P = V_{cell}^2 Z_{Re}/$ $|Z|^2$. V_{cell} is the cell terminal voltage, |Z| is the magnitude of the cell impedance, and Z_{Re} is the real part of the cell impedance. In the model, the only fitting parameter is the heat-transfer coefficient (h) between the thermal insulation surface and the ambient (Figure 2A). The estimated h values for the single-layer cell and double-layer cell are 25 and 20 W/(m^2K), respectively; see also Note S2 for detail. The simulated temperature evolutions of the pouch cells match well with the experimental data, as shown in Figures 3C and 3D. Moreover, to extend the generality of our technology and modeling, similar experiments and simulation were done for symmetric LLZO cells. Detailed setup and results can be found in Note S3 and are not repeated here.

The impact of UHFSH on solid-state cell state of health was also investigated. An NMC|Li₃YBrCl₅|Li-In halide full cell was fabricated and tested under UHFSH cycles. We applied the voltage with 7 MHz frequency, 0.72 V amplitude, and 3 V offset on the cell terminals. After 100 5-min on/off heating cycles, the decreased capacity due to heating was less than 1.4%. There was no significant capacity fade in the full cell after UHFSH; see Note S4.

We use the electro-thermal model to predict large-scale celllevel and pack-level performance of SSBs, as discussed in the next section.

Heating performance on cell and pack level

In this section, we use our validated electro-thermal co-simulation model to predict the performance of SSBs at the pouch and pack level to understand the impact of UHFSH on the commercial scale. Figure 4A shows the multilayer configurations of commercial batteries from the cell to pack level. In general, a cell is composed of many (30–50) stacks of layers for a pouch cell or a jelly roll in a cylindrical cell. Moreover, in EV applications, hundreds of cells are arranged in modules. They are connected in series or parallel to achieve the desired voltage and energy capacity. A whole battery pack could consist of several to tens of modules.

One of the biggest differences between the lab-scale singleand two-layer systems vs. a commercial-scale system is that the surface-to-volume ratio is much smaller for the commercial-scale systems. This smaller ratio greatly reduces the heat loss to the environment, thereby enabling a faster temperature rise. Another difference is that large multilayer cells have more inductance in the cell impedance.^{39–42} The inductance behavior (negative imaginary impedance) is trivial for small-capacity cells; however, it must be considered for large-capacity batteries because of their multilayer structure.

Effect of voltage frequency on heating power

Figure 4B shows the estimated heat generation per electrode area using our equivalent circuit model ($P = V^2 Z_{Re}/|Z|^2$; see Note S5) under volts AC (VAC) as a function of temperature

CellPress

and input frequency with a 400- μ m-thick electrolyte. Considering the full-cell LCO|Li voltage range (4.35–2.35 V), we are using ±1 V amplitude and a square wave form to maximize the heat generation. The heating power as a function of frequency is not monotonic, unlike the single-layer cell case. At low frequency, the large interface and charge-transport impedance dominate and lead to low heat generation. At the higher frequency, the electrical double layer behaves like a capacitor, resulting in shorting of the charge-transfer resistance. Therefore, the total impedance, both the imaginary and real parts, is reduced, resulting in a significant increase in heat generation. However, if the frequency is too high, the inductance becomes dominant, and the overall impedance increases, resulting in lower heat generation.

Effect of SSE on heating rate

Both the ionic conductivity and thickness of the SSE are very critical as they are part of the overall electrical impedance of the cell. The broader research and development (R&D) community and the industrial community are actively working on reducing the thickness of SSEs and increasing their ionic conductivity.^{11,43} We investigated the impact of UHFSH for a wide range of ionic conductivity and thickness of the electrolyte. Using the calculated heat generation from the last section, we started the simulation on a 19-Wh LCO|LAGP|Li pouch cell that consists of tens of layers (see Figure S4A and Note S6). We applied a ±1-V square wave signal with the optimal frequency 0.2 MHz (Figure 4B) to estimate the temperature rise. With a fixed 25-µm electrolyte thickness, the same as the separator thickness in LIBs, we show how the heating time would decline as the electrolyte ionic conductivity increases in Figures S4B and S4C. A contour plot of time to increase ΔT by 40°C as a function of electrolyte thickness and ionic conductivity is presented in Figure S4D. With smaller thickness and higher ionic conductivity, the required heating time decreases and becomes sub-minute.

To reproduce the thermal behavior in compact battery packs of EVs, besides the cell level, we built three different battery sizes: 5.2 kWh (module), 62 kWh (small pack, Figure 4C), and 104 kWh (large pack). Figure 4D shows that for a 25-µm-thick electrolyte, the battery (pack) temperature can increase to over 70°C in 1 min. The temperature rises at an optimal frequency in 2 min for a 62-kWh battery pack are 10°C higher than that of a 19-Wh single cell. The small surface-to-volume ratio of the pack enhanced the battery insulation and improved the heating rate.

Heating energy consumption

Figure 4E shows the percentage of heating energy consumption over the energy stored in the battery using our electrothermal model of SSBs for the whole pack size, with comparison to the module level. The variations across different solid-electrolyte thicknesses are also shown. In terms of raising the battery by 40° C up for 1-h operation with $h = 10 \text{ W/m}^2/\text{K}$, the energy required to heat a 104-kWh battery pack is only 3.4% of the total battery energy. Additionally, the reaction heat released during battery discharge is not included in the calculated energy consumption, which will further reduce the energy loss to maintain



the temperature during operation. Based on our study of UHFSH on SSBs so far, this fast-heating method could be further optimized in a practical SSB management system to achieve higher obtainable energy density, better cycling, and fast start-up performance.

Conclusions

In summary, we have successfully developed an ultrafast-heating method for SSBs using an ultra-high-frequency voltage pulse, which can enable SSBs to start from RT in minutes. In contrast to previous advances in battery materials and interfaces to commercialize SSBs, our method retains the original battery structure and leverages the small heat-energy consumption to achieve a large energy density increase. Considering the new challenges and opportunities for SSBs, their optimal operating temperature can be adjusted promptly via the UHFSH in a smart battery thermal management system.

METHODS

Electrochemical thermal simulation and verification

We used the equivalent circuit model and heat transfer module in COMSOL Multiphysics 5.6 for the simulation of SSB heating under different alternating voltage excitation and thermal conditions, see Note S7 for further details.

SSE LAGP preparation

The LAGP pellets were made from the commercially available sodium super ionic conductor (NASICON) Li_{1.5}Al_{0.5}Ge_{1.5}P₃O₁₂ powder (300–500 nm MSE Supplies). The powders were pressed in a 15-mm-diameter stainless steel die under 15,000 pound force for 10 min. Then, the pellets were sintered on alumina inside the furnace in air at 700°C for 10 h. In addition, the pellets were sputtered with 40-nm gold on both sides to enhance the interface contact with the lithium foil.

SSB with thermal insulation preparation

With the prepared electrolytes, 100-µm-thick lithium foil (MSE Supplies) was punched into 12-mm-diameter coins as the electrodes, and they were cleaned on both sides with a tweezer to remove the surface oxides or contaminants. Then, the cleaned lithium discs were pressed on both sides of the LAGP pellets. The structure was then sandwiched between two 50-µm-thick copper (McMaster-Carr) circles with 15-mm diameter. The 50-µm-diameter insulated copper wires were spot welded with the copper current collector at one end and with nickel tabs at the other end. We used the wires for better thermal insulation. Then, the nickel tabs served as the battery's terminal and were connected to alternating signals. A thermocouple was placed at the center of one copper circle, with the Kapton tape in between as the electrical insulator. The entire structure was sandwiched between the 3.2-mmthick aerogel blocks (Airloy x103) with 20-mm squared surface. The cell was finally sealed in a pouch-cell configuration (MTI Corporation) in an Ar-filled glove box (O₂ < 0.1 ppm and $H_2O < 0.1$ ppm). After cell assembly, the cell was annealed in a furnace at approximately 65°C for 7 h.

Joule Article

UHFSH experiments

The pouch cell was held with a lab-made pressure jig and load sensor and placed inside the test equity model TEC1 thermoelectric temperature chamber. The cell and environment temperature were recorded with T-type thermocouples (Omega Engineering) by a Pico TC-08 thermocouple data logger. The high-frequency alternating voltage wave was supplied by a RIGOL DG4062 function waveform generator. The cell terminal voltage was measured using an Agilent DSO3202A digital storage oscilloscope. The temperature rises and terminal voltages were documented under various high-frequency sine signals.

EIS

The electrochemical impedance spectroscopy (EIS) measurements were performed using a Biologic VMP3 multichannel potentiostat. The symmetric cells were rested for 15 min before tests and under 350 kPa during tests. A signal with 2-V amplitude was applied to the cell with a frequency ranging from 0.1 Hz to 7 MHz with 20 data points per decade of frequency. An equivalent circuit model⁴⁴ was used to fit the EIS results (see Note S5 and Figures S5 and S6). The parameters determined from the EIS analysis are summarized in Table S2.

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Ravi Prasher (rsprasher@ lbl.gov).

Materials availability

This study did not generate new unique materials.

Data and code availability

- Data that support the plots and other findings of this study and all original code have been deposited at Figshare at https://dx.doi.org/10. 6084/m9.figshare.28926884 and are publicly available as of the date of publication.
- Any additional information required to reanalyze the data reported in this paper is available from the lead contact Ravi Prasher (rsprasher@lbl. gov) upon reasonable request.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Yanbao Fu for the patience and support with the cell-assembly procedure and Dr. Kenneth Higa (LBNL) for the fixturing clamp setup to apply pressure. The authors acknowledge support from the Energy Efficiency and Renewable Energy, Vehicle Technologies Program, of the US Department of Energy under contract no. DEAC0205CH11231.

AUTHOR CONTRIBUTIONS

B.Z. and R.P. conceived the idea. B.Z. designed and conducted the electrochemical simulations and cell assembly and heating experiments. Y.Z., D.C., and M.T. discussed the results. F.S. fabricated the halide full cell. B.Z., C.D., S.K., and R.P. contributed to the writing of the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

CellPress

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.joule.2025.101973.

Received: September 10, 2024 Revised: March 25, 2025 Accepted: May 15, 2025

REFERENCES

- Schmuch, R., Wagner, R., Hörpel, G., Placke, T., and Winter, M. (2018). Performance and cost of materials for lithium-based rechargeable automotive batteries. Nat. Energy *3*, 267–278. https://doi.org/10.1038/ s41560-018-0107-2.
- Janek, J., and Zeier, W.G. (2016). A solid future for battery development. Nat. Energy 1, 1–4. https://doi.org/10.1038/nenergy.2016.141.
- Vishnugopi, B.S., Kazyak, E., Lewis, J.A., Nanda, J., McDowell, M.T., Dasgupta, N.P., and Mukherjee, P.P. (2021). Challenges and Opportunities for Fast Charging of Solid-State Lithium Metal Batteries. ACS Energy Lett. 6, 3734–3749. https://doi.org/10.1021/acsenergylett.1c01352.
- Albertus, P., Anandan, V., Ban, C., Balsara, N., Belharouak, I., Buettner-Garrett, J., Chen, Z., Daniel, C., Doeff, M., Dudney, N.J., et al. (2021). Challenges for and Pathways toward Li-Metal-Based All-Solid-State Batteries. ACS Energy Lett. 6, 1399–1404. https://doi.org/10.1021/acsenergylett. 1c00445.
- Bates, A.M., Preger, Y., Torres-Castro, L., Harrison, K.L., Harris, S.J., and Hewson, J. (2022). Are solid-state batteries safer than lithium-ion batteries? Joule 6, 742–755. https://doi.org/10.1016/j.joule.2022.02.007.
- Kato, Y., Hori, S., Saito, T., Suzuki, K., Hirayama, M., Mitsui, A., Yonemura, M., Iba, H., and Kanno, R. (2016). High-power all-solid-state batteries using sulfide superionic conductors. Nat. Energy *1*, 1–7. https://doi.org/10. 1038/nenergy.2016.30.
- Hao, M., Li, J., Park, S., Moura, S., and Dames, C. (2018). Efficient thermal management of Li-ion batteries with a passive interfacial thermal regulator based on a shape memory alloy. Nat. Energy 3, 899–906. https://doi.org/ 10.1038/s41560-018-0243-8.
- Pinson, M.B., and Bazant, M.Z. (2013). Theory of SEI Formation in Rechargeable Batteries: Capacity Fade, Accelerated Aging and Lifetime Prediction. J. Electrochem. Soc. *160*, A243–A250. https://doi.org/10. 1149/2.044302jes.
- Hoffman, Z.J., Shah, D.B., and Balsara, N.P. (2021). Temperature and concentration dependence of the ionic transport properties of poly (ethylene oxide) electrolytes. Solid State Ionics 370, 115751. https://doi. org/10.1016/j.ssi.2021.115751.
- Wan, J., Xie, J., Kong, X., Liu, Z., Liu, K., Shi, F., Pei, A., Chen, H., Chen, W., Chen, J., et al. (2019). Ultrathin, flexible, solid polymer composite electrolyte enabled with aligned nanoporous host for lithium batteries. Nat. Nanotechnol. 14, 705–711. https://doi.org/10.1038/s41565-019-0465-3.
- Wu, J., Yuan, L., Zhang, W., Li, Z., Xie, X., and Huang, Y. (2021). Reducing the thickness of solid-state electrolyte membranes for high-energy lithium batteries. Energy Environ. Sci. 14, 12–36. https://doi.org/10.1039/ DOEE02241A.
- Allen, J.L., Wolfenstine, J., Rangasamy, E., and Sakamoto, J. (2012). Effect of substitution (Ta, Al, Ga) on the conductivity of Li7La3Zr2O12. J. Power Sources 206, 315–319. https://doi.org/10.1016/j.jpowsour. 2012.01.131.
- Sastre, J., Priebe, A., Döbeli, M., Michler, J., Tiwari, A.N., and Romanyuk, Y.E. (2020). Lithium Garnet Li7La3Zr2O12 Electrolyte for All-Solid-State Batteries: Closing the Gap between Bulk and Thin Film Li-Ion Conductivities. Adv. Mater. Interfaces 7, 2000425. https://doi.org/10.1002/admi. 202000425.
- Sharafi, A., Meyer, H.M., Nanda, J., Wolfenstine, J., and Sakamoto, J. (2016). Characterizing the Li–Li7La3Zr2O12 interface stability and kinetics

CellPress

as a function of temperature and current density. J. Power Sources 302, 135–139. https://doi.org/10.1016/j.jpowsour.2015.10.053.

- Ye, Y., Huang, W., Xu, R., Xiao, X., Zhang, W., Chen, H., Wan, J., Liu, F., Lee, H.K., Xu, J., et al. (2022). Cold-Starting All-Solid-State Batteries from Room Temperature by Thermally Modulated Current Collector in Sub-Minute. Adv. Mater. 34, e2202848. https://doi.org/10.1002/adma. 202202848.
- Samson, A.J., Hofstetter, K., Bag, S., and Thangadurai, V. (2019). A bird'seye view of Li-stuffed garnet-type Li7 La3 Zr2 O12 ceramic electrolytes for advanced all-solid-state Li batteries. Energy Environ. Sci. 12, 2957–2975. https://doi.org/10.1039/C9EE01548E.
- Rohde, M., Cui, Y., Ziebert, C., and Seifert, H.J. (2020). Thermophysical Properties of Lithium Aluminum Germanium Phosphate with Different Compositions. Int. J. Thermophys. 41, 31. https://doi.org/10.1007/ s10765-020-2607-0.
- Wang, C.-Y., Zhang, G., Ge, S., Xu, T., Ji, Y., Yang, X.-G., and Leng, Y. (2016). Lithium-ion battery structure that self-heats at low temperatures. Nature 529, 515–518. https://doi.org/10.1038/nature16502.
- Ji, Y., and Wang, C.Y. (2013). Heating strategies for Li-ion batteries operated from subzero temperatures. Electrochim. Acta 107, 664–674. https:// doi.org/10.1016/j.electacta.2013.03.147.
- Zhang, B., Fan, B., Huang, Z., Higa, K., Battaglia, V.S., and Prasher, R.S. (2023). A Review of Dispersion Film Drying Research. J. Electrochem. Energy Convers. Storage 20, 030801. https://doi.org/10.1115/1.4055392.
- Hu, X., Zheng, Y., Howey, D.A., Perez, H., Foley, A., and Pecht, M. (2020). Battery warm-up methodologies at subzero temperatures for automotive applications: Recent advances and perspectives. Prog. Energy Combust. Sci. 77, 100806. https://doi.org/10.1016/j.pecs.2019.100806.
- Luo, Y., Lang, C., and Luo, B. (2016). Investigation into Heating System of Lithium-Ion Battery Pack in Low-Temperature Environment. J. S. China Univ. Technol. Nat. Sci. Ed. 44, 100–106. https://doi.org/10.3969/j.issn. 1000-565X.2016.09.015.
- Li, J., Wu, P., and Tian, H. (2014). Researches on heating low-temperature lithium-ion power battery in electric vehicles. In IEEE Conference and Expo Transportation Electrification Asia and the Pacific (ITEC Asia-Pacific), pp. 1–6. https://doi.org/10.1109/ITEC-AP.2014.6941276.
- Chen, M., and Li, J. (2021). Experimental study on heating performance of pure electric vehicle power battery under low temperature environment. Int. J. Heat Mass Transf. 172, 121191. https://doi.org/10.1016/j.ijheatmasstransfer.2021.121191.
- Wang, Y., Rao, Z., Liu, S., Li, X., Li, H., and Xiong, R. (2021). Evaluating the performance of liquid immersing preheating system for Lithium-ion battery pack. Appl. Therm. Eng. *190*, 116811. https://doi.org/10.1016/j.applthermaleng.2021.116811.
- Qin, Y., Du, J., Lu, L., Gao, M., Haase, F., Li, J., and Ouyang, M. (2020). A rapid lithium-ion battery heating method based on bidirectional pulsed current: Heating effect and impact on battery life. Appl. Energy 280, 115957. https://doi.org/10.1016/j.apenergy.2020.115957.
- Ruan, H., Jiang, J., Sun, B., Zhang, W., Gao, W., Wang, L.Y., and Ma, Z. (2016). A rapid low-temperature internal heating strategy with optimal frequency based on constant polarization voltage for lithium-ion batteries. Appl. Energy 177, 771–782. https://doi.org/10.1016/j.apenergy.2016. 05.151.
- 28. Li, Y., Gao, X., Qin, Y., Du, J., Guo, D., Feng, X., Lu, L., Han, X., and Ouyang, M. (2021). Drive circuitry of an electric vehicle enabling rapid heating of the battery pack at low temperatures. iScience 24, 101921. https://doi.org/10.1016/j.isci.2020.101921.
- Zhang, S.S., Xu, K., and Jow, T.R. (2003). The low temperature performance of Li-ion batteries. J. Power Sources *115*, 137–140. https://doi.org/10.1016/S0378-7753(02)00618-3.

 Villano, P., Carewska, M., and Passerini, S. (2003). Specific heat capacity of lithium polymer battery components. Thermochim. Acta 402, 219–224. https://doi.org/10.1016/S0040-6031(02)00612-3.

Joule Article

- Cheng, Z., Zahiri, B., Ji, X., Chen, C., Chalise, D., Braun, P.V., and Cahill, D. G. (2021). Good Solid-State Electrolytes Have Low, Glass-Like Thermal Conductivity. Small 17, e2101693. https://doi.org/10.1002/smll. 202101693.
- Morganti, M.V., Longo, S., Tirovic, M., Blaise, C.-Y., and Forostovsky, G. (2019). Multi-Scale, Electro-Thermal Model of NMC Battery Cell. IEEE Trans. Veh. Technol. *68*, 10594–10606. https://doi.org/10.1109/TVT. 2019.2943052.
- Zeng, Y., Chalise, D., Lubner, S.D., Kaur, S., and Prasher, R.S. (2021). A review of thermal physics and management inside lithium-ion batteries for high energy density and fast charging. Energy Storage Mater. 41, 264–288. https://doi.org/10.1016/j.ensm.2021.06.008.
- Lu, Y., Zhao, C.-Z., Huang, J.-Q., and Zhang, Q. (2022). The timescale identification decoupling complicated kinetic processes in lithium batteries. Joule 6, 1172–1198. https://doi.org/10.1016/j.joule.2022.05.005.
- Zhu, J., Sun, Z., Wei, X., Dai, H., and Gu, W. (2017). Experimental investigations of an AC pulse heating method for vehicular high power lithium-ion batteries at subzero temperatures. J. Power Sources 367, 145–157. https://doi.org/10.1016/j.jpowsour.2017.09.063.
- Zhu, Y., He, X., and Mo, Y. (2015). Origin of Outstanding Stability in the Lithium Solid Electrolyte Materials: Insights from Thermodynamic Analyses Based on First-Principles Calculations. ACS Appl. Mater. Interfaces 7, 23685–23693. https://doi.org/10.1021/acsami.5b07517.
- Zhu, T., Min, H., Yu, Y., Zhao, Z., Xu, T., Chen, Y., Li, X., and Zhang, C. (2017). An Optimized Energy Management Strategy for Preheating Vehicle-Mounted Li-ion Batteries at Subzero Temperatures. Energies *10*, 243. https://doi.org/10.3390/en10020243.
- Ye, X., Zhao, Y., and Quan, Z. (2018). Thermal management system of lithium-ion battery module based on micro heat pipe array. Int. J. Energy Res. 42, 648–655. https://doi.org/10.1002/er.3847.
- Schindler, S., and Danzer, M.A. (2017). Influence of cell design on impedance characteristics of cylindrical lithium-ion cells: A model-based assessment from electrode to cell level. J. Energy Storage 12, 157–166. https://doi.org/10.1016/j.est.2017.05.002.
- Meddings, N., Heinrich, M., Overney, F., Lee, J.-S., Ruiz, V., Napolitano, E., Seitz, S., Hinds, G., Raccichini, R., Gaberšček, M., et al. (2020). Application of electrochemical impedance spectroscopy to commercial Li-ion cells: A review. J. Power Sources *480*, 228742. https://doi.org/10.1016/j. jpowsour.2020.228742.
- Korth Pereira Ferraz, P., Schmidt, R., Kober, D., and Kowal, J. (2018). A high frequency model for predicting the behavior of lithium-ion batteries connected to fast switching power electronics. J. Energy Storage 18, 40–49. https://doi.org/10.1016/j.est.2018.04.024.
- Landinger, T.F., Schwarzberger, G., and Jossen, A. (2021). High frequency impedance characteristics of cylindrical lithium-ion cells: Physical-based modeling of cell state and cell design dependencies. J. Power Sources 488, 229463. https://doi.org/10.1016/j.jpowsour.2021.229463.
- Paolella, A., Liu, X., Daali, A., Xu, W., Hwang, I., Savoie, S., Girard, G., Nita, A.G., Perea, A., Demers, H., et al. (2021). Enabling High-Performance NA-SICON-Based Solid-State Lithium Metal Batteries Towards Practical Conditions. Adv. Funct. Mater. *31*, 2102765. https://doi.org/10.1002/adfm. 202102765.
- Choi, W., Shin, H.-C., Kim, J.M., Choi, J.-Y., and Yoon, W.-S. (2020). Modeling and Applications of Electrochemical Impedance Spectroscopy (EIS) for Lithium-ion Batteries. J. Electrochem. Sci. Technol. 11, 1–13. https://doi.org/10.33961/jecst.2019.00528.