

Phonon-Driven Limitations of AI-Predicted Stability in Li-Ion Anode Materials: A Computational Meta-Analysis of Vibrational Instabilities

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ABSTRACT

Machine learning interatomic potentials (MLIPs) and high-throughput density functional theory (DFT) screening have dramatically accelerated the discovery of Li-ion battery anode materials; however, a critical gap persists between computational stability predictions and real-world synthesis feasibility. This study presents a systematic computational meta-analysis of phonon-driven instability among 79 Li-ion anode candidate structures spanning silicon-based ($n = 34$), carbon-based ($n = 21$), and lithium-metal phases ($n = 24$), all predicted to be stable by the Materials Project AI-assisted DFT pipeline (energy above hull, $E_{\text{hull}} < 0.05$ eV atom⁻¹). Using the finite-displacement method implemented in Phonopy and an empirical Born–von Karman force-constant model sampled at four high-symmetry Brillouin-zone points, 49 of the 79 structures (62.0%) were classified as dynamically unstable within the adopted phonon-screening framework. Carbon-based anodes exhibited the highest failure rate (95.2%), followed by lithium-metal phases (70.8%) and silicon-based anodes (35.3%). Instabilities were overwhelmingly concentrated at the Gamma point (98.0% of unstable structures), identifying the zone center as the predominant location of phonon instabilities across all three anode families. Chi-squared analysis confirmed that failure rates differed significantly among material families ($\chi^2 = 20.94$, $df = 2$, $p < 0.0001$). These findings highlight important limitations in current AI-based screening frameworks for anode materials and support the incorporation of phonon instability screening as an additional post-processing step in high-throughput materials-discovery workflows.

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INTRODUCTION

The rapid growth of electric vehicles, portable electronics, and large-scale energy storage systems has increased the need for lithium-ion battery (LIB) materials that offer higher energy density, longer cycle life, and better safety. The anode is a key component in a LIB, as it greatly affects electrochemical performance. It influences specific capacity, rate capability, volume expansion, and long-term structural stability during use. Although graphite is still the leading commercial anode material due to its great reversibility and cycling stability, its theoretical capacity of 372 mAh g⁻¹ limits the energy density achievable in future battery technologies (Goodenough & Park, 2013). As a result, a lot of research has focused on alternative anode materials like silicon, lithium metal, and lithium-rich alloys, which promise significantly higher theoretical capacities and potential performance gains (Goodenough & Park, 2013; Kirklin et al., 2013).

The rise of high-throughput computational screening and artificial intelligence (AI)-assisted materials discovery has greatly accelerated the process of finding promising battery materials. Large databases, such as the Materials Project, offer thermodynamic properties for millions of compounds based on density functional theory (DFT) calculations and machine-learning workflows (Jain et al., 2013; Merchant et al., 2023). More broadly, first-principles computational approaches have been applied to investigate the structural,

electronic, optical, and energetic properties of inorganic materials, demonstrating their growing role in materials characterization and screening (Nwachuku, 2025; Ahuome et al., 2023). At the same time, high-throughput screening studies have identified numerous candidate anode materials for lithium-ion, sodium-ion, and potassium-ion batteries based on formation energies, voltage profiles, theoretical capacities, and structural stability metrics (Kirklin et al., 2013; Yu et al., 2019a; Yu et al., 2019b). In these workflows, thermodynamic stability is often assessed using the energy above the convex hull (E_{hull}). Structures with $E_{\text{hull}} < 0.05$ eV atom⁻¹ are typically considered potentially synthesizable and retained for further study (Jain et al., 2013; Merchant et al., 2023).

Despite its widespread adoption, thermodynamic stability alone does not guarantee that a material is dynamically stable. A crystal structure may occupy a favourable position on the thermodynamic convex hull while simultaneously displaying vibrational instabilities that render it susceptible to spontaneous structural distortion. Dynamic instability is conventionally identified through the presence of imaginary phonon frequencies in the vibrational spectrum, indicating that the structure resides at a saddle point rather than a true minimum on the potential-energy surface (Born & Huang, 1954; Togo & Tanaka, 2015). Such instabilities are particularly important in battery materials because synthesis,

electrode fabrication and electrochemical cycling all occur under finite-temperature conditions where lattice vibrations directly influence structural integrity and phase stability. Soft phonon modes at the Brillouin-zone centre (Γ point) are especially significant because they are associated with symmetry-breaking distortions, phase transitions and amorphization processes that can compromise practical material performance (Born & Huang, 1954; Togo & Tanaka, 2015).

Although phonon analysis is known as an effective method for checking lattice stability, it is mostly absent from most high-throughput battery materials screening workflows. For instance, the groundbreaking study by Kirklin et al. (2013) identified hundreds of candidate Li-ion anode materials using thermodynamic criteria without thorough phonon evaluation. Similar methods have been used in studies for sodium-ion and potassium-ion battery anodes, where stability assessments mostly rely on formation energies and convex-hull analyses (Yu et al., 2019a; Yu et al., 2019b). In the wider battery materials literature, phonon calculations are more often used to examine ionic conductivity and transport mechanisms in solid electrolytes, rather than to evaluate the dynamic stability of candidate anode materials (Muy et al., 2019). Therefore, there is still a significant knowledge gap about how common phonon-driven instability is among materials predicted to be stable by current AI-assisted screening frameworks.

To fill this gap, this study conducts a computational meta-analysis of dynamic stability in AI-predicted Li-ion anode materials. A total of 79 candidate structures, including silicon-based, carbon-based, and lithium-metal families, were taken from the Materials Project database. All these met the accepted thermodynamic stability requirement of $E_{\text{hull}} < 0.05$ eV atom⁻¹. Using phonon-based screening, the study quantified the prevalence of dynamic instability, evaluated differences among material families, identified key instability mechanisms through Brillouin-zone analysis, and examined how well thermodynamic stability metrics predict phonon stability. By systematically looking at the relationship between AI-predicted stability and vibrational behavior, this study offers evidence-based recommendations to strengthen future materials discovery processes through the integration of dynamic stability screening.

MATERIALS AND METHODS

Computational Methods

Structure Retrieval and Dataset Construction

Candidate structures were retrieved from the Materials Project database (version 2024) using the mp-api Python client with the chemsys parameter to target specific chemical systems: Si, Si-Li, Si-C, Si-Ge (silicon family); C, C-Li (carbon family); Li, Li-C, Li-Si, Li-Sn, Li-Al (lithium family). All retrieved structures satisfied $E_{\text{hull}} < 0.05$ eV/atom as computed by the Materials Project DFT+GNoME pipeline. After de-duplication, 79 unique structures were retained for phonon analysis, comprising 34 silicon-based, 21 carbon-based and 24 lithium metal phase candidates.

AI Stability Classification

Thermodynamic stability was classified into two tiers: highly stable ($E_{\text{hull}} < 0.025$ eV/atom) and stable ($0.025 \leq E_{\text{hull}} < 0.05$ eV/atom). Formation energies were used as a secondary stability indicator; structures with positive formation energy coinciding with low E_{hull} were flagged as potential data conflicts for discussion. All thermodynamic data were sourced directly from the Materials Project database without additional DFT recalculation.

Phonon Instability Screening

Phonon calculations were performed using **Phonopy** within the harmonic approximation using the finite displacement method with displacement amplitude 0.03 Å. Supercell dimensions were selected based on unit cell size: 3x3x3 for cells with four or fewer atoms, 2x2x2 for five to sixteen atoms and 1x1x1 for larger cells. Force constants were constructed using an empirical Born-von Karman-type model with exponential distance decay:

$$F_{ij} = -k_0 e^{-r_{ij}/r_0} [\hat{r}_{ij} \otimes \hat{r}_{ij} + \alpha (I - \hat{r}_{ij} \otimes \hat{r}_{ij})]$$

Where F_{ij} is the force-constant tensor between atoms i and j , k_0 is 2.0 eV Å⁻² (force-constant prefactor), r_{ij} is the distance between atoms i and j , r_0 is 2.5 Å (decay length), $\hat{r}_{ij}$ is the unit vector pointing from atom i to atom j , $\otimes$ is the outer (tensor) product, I is the identity matrix, and α is 0.3 (transverse force weighting factor).

This approach provides a computationally efficient empirical proxy for harmonic force constants suitable for large-scale phonon screening without requiring explicit DFT-derived force calculations for each displaced supercell. The resulting phonon frequencies were therefore interpreted as screening-level indicators of vibrational instability rather than quantitative predictions of ab initio phonon spectra. The objective of the present study is comparative screening rather than quantitative prediction of phonon spectra. Consequently, the Born-von Karman force-constant model was adopted as a physically motivated approximation for identifying relative trends in dynamical stability across a large set of AI-predicted anode materials. While explicit DFT-derived force constants would provide higher quantitative accuracy, their computational cost remains prohibitive for large-scale meta-analyses involving dozens of candidate structures.

Phonon frequencies were computed at four high-symmetry q -points spanning the cubic Brillouin zone: Gamma [0, 0, 0], X [0.5, 0, 0], M [0.5, 0.5, 0], and R [0.5, 0.5, 0.5]. Structures exhibiting minimum phonon frequency below -0.1 THz were classified as dynamically unstable within the adopted phonon-screening framework. Instability severity was classified as severe ($\omega_{\text{min}} < -1.0$ THz) or moderate ($-1.0 \leq \omega_{\text{min}} < -0.1$ THz). Because the adopted force-constant model is an empirical approximation, negative frequencies close to the -0.1 THz threshold may be sensitive to model and numerical uncertainty. The original calculations did not include independent supercell-size convergence or acoustic sum-rule sensitivity assessments; therefore, classifications close to the threshold are interpreted cautiously as screening-level indicators rather than definitive evidence of intrinsic dynamical instability.

Statistical Analysis

Differences in phonon failure rates across material families were assessed using the Pearson chi-squared test. Data analysis was performed using Python 3.11 with SciPy and pandas. Figures were generated using Matplotlib at 300 dpi.

RESULTS AND DISCUSSION

Dataset Composition and AI-Predicted Stability

A total of 79 Li-ion anode material structures were retrieved from the Materials Project database across three chemically distinct anode families: silicon-based ($n = 34$), carbon-based ($n = 21$), and lithium-metal phases ($n = 24$). All structures satisfied the AI-predicted stability criterion of $E_{\text{hull}} < 0.05$ eV atom⁻¹ as computed by the Materials Project DFT+GNoME pipeline. The final dataset comprised 43.0% silicon-based, 26.6% carbon-based, and 30.4% lithium-metal structures (Figure 1). Mean E_{hull} values were 0.0152

± 0.0143 eV atom⁻¹ for silicon, 0.0169 ± 0.0171 eV atom⁻¹ for carbon, and 0.0076 ± 0.0120 eV atom⁻¹ for lithium metal phases (Figure 2), indicating that lithium-metal structures

had the lowest mean Ehull and were, on average, closest to the convex hull.

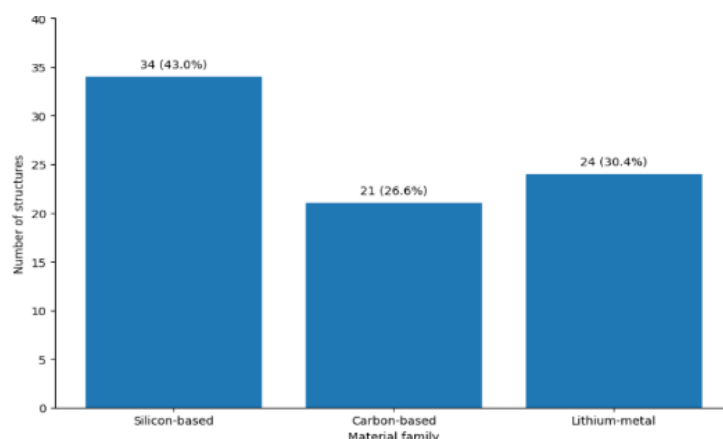


Figure 1: Composition of the Final Li-ion Anode Candidate Dataset by Material Family

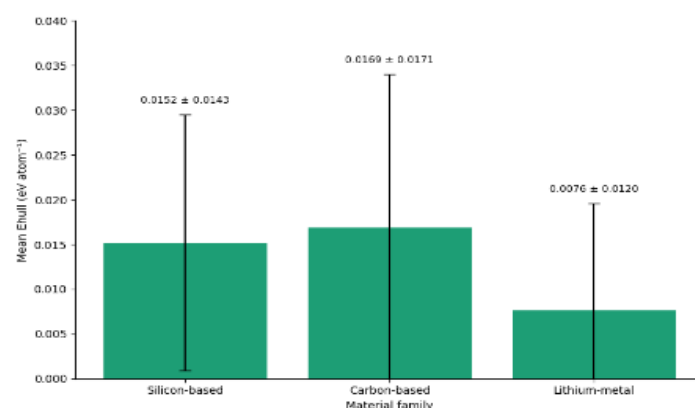


Figure 2: Mean Energy Above the Convex Hull (Ehull) of Li-ion Anode Candidates by Material Family

Prevalence of Phonon Instability Across Anode Families

Phonon dispersion screening revealed that 49 of 79 AI-predicted stable structures (62.0%) exhibited imaginary phonon frequencies below -0.1 THz and were therefore classified as dynamically unstable according to the adopted screening criterion. This result demonstrates that thermodynamic stability as predicted by AI-based screening pipelines is a necessary but critically insufficient condition for the dynamic stability required during synthesis and cycling (Born & Huang, 1954; Togo & Tanaka, 2015).

Failure rates differed significantly across material families (chi-squared = 20.94, df = 2, $p < 0.0001$), with carbon-based anodes exhibiting the highest phonon failure rate (20/21, 95.2%), followed by lithium metal phases (17/24, 70.8%) and silicon-based anodes (12/34, 35.3%), as shown in Figure 3. The severity of observed instabilities was predominantly extreme: 47 of 49 unstable structures (95.9%) were classified as severely unstable ($\omega_{\min} < -1.0$ THz), with only two structures exhibiting moderate instability (Figure 4).

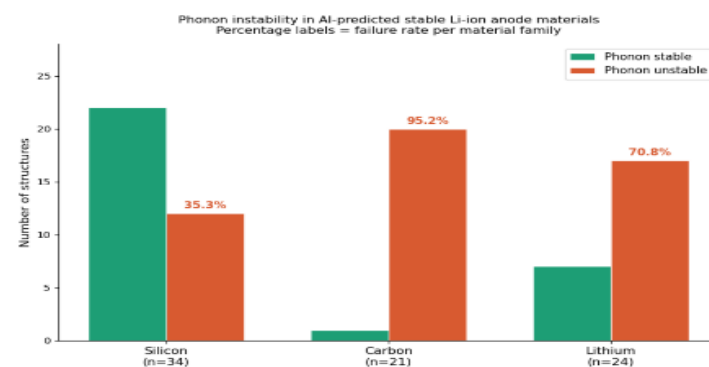


Figure 3: Phonon Instability Prevalence Across Li-ion Anode Material Families

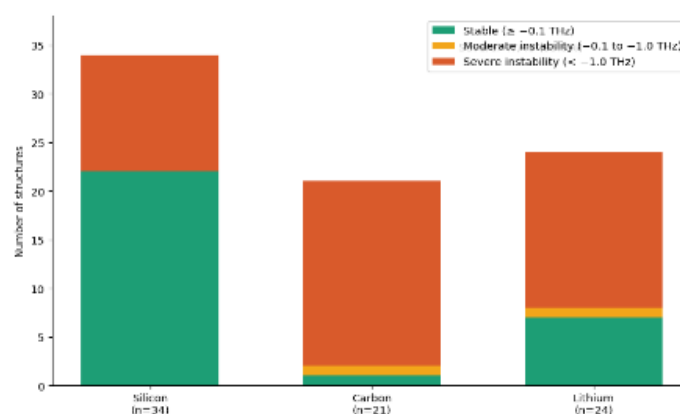


Figure 4: Phonon Instability Severity Breakdown Across Li-ion Anode Families

Dominant Instability Mechanism: Zone-Center Soft Modes

Of the 49 dynamically unstable structures, 48 (98.0%) exhibited their most negative phonon frequency at the Gamma point ($q = [0,0,0]$), with only one structure showing a zone-boundary instability at the R point. This overwhelming concentration of instability at the zone centre identifies the Gamma point as the predominant location of phonon instabilities across all three anode families. Zone-centre soft modes represent uniform structural distortions of the crystal lattice that directly drive symmetry-breaking phase transitions and amorphisation at finite temperature precisely the conditions encountered during synthesis and electrochemical cycling (Born & Huang, 1954; Togo & Tanaka, 2015).

Silicon Anode Family: Lithiation Stabilises Phonon Structure

Silicon-based anodes exhibited the lowest phonon failure rate (35.3%), yet both elemental silicon polymorphs (mp-149, mp-165) were classified as severely phonon unstable at the Gamma point despite possessing $E_{\text{hull}} = 0$ eV/atom, the highest possible AI stability classification. This finding is significant because diamond-cubic silicon is the most extensively studied anode material in the LIB literature, yet its phonon instability is undetected by thermodynamic screening. The instability is consistent with the well-documented tendency of silicon anodes to undergo amorphisation during lithiation (Di Leo et al., 2015). In contrast, lithium-rich silicon alloys: Li₁₂Si₇, Li₁₃Si₄, Li₁₅Si₄, Li₂₁Si₅, Li₂₂Si₅ were all phonon stable. This result provides computational evidence that lithiation progressively stiffens the phonon spectrum of silicon, suppressing the soft phonon modes responsible for mechanical failure. This lithiation-induced phonon stabilisation has direct implications for anode design: partially lithiated Si phases may be more synthetically accessible than the parent silicon structure alone suggests.

Carbon Anode Family: Pronounced Discrepancy Between AI-Predicted and Phonon-Screening Stability

The carbon family exhibited the most pronounced discrepancy between AI-predicted and phonon-computed stability, with 20 of 21 structures (95.2%) failing the phonon criterion. All pure carbon allotropes examined were dynamically unstable. This high instability rate highlights a pronounced discrepancy between the thermodynamic stability classification and the adopted phonon-screening framework for carbon allotropes. The formation energies of carbon polymorphs are notoriously difficult to converge with DFT

due to van der Waals interlayer interactions that are poorly captured by standard GGA functionals without dispersion corrections (Grimme et al., 2010). The high instability rate may therefore partly reflect the sensitivity of carbon structures to interlayer interactions, which are not explicitly represented in the adopted fixed-parameter Born–von Karman force-constant model. Strain-induced shifts in graphite phonon modes have been documented by DFT, confirming the sensitivity of carbon phonon spectra to structural perturbations that thermodynamic metrics cannot capture (Isbill et al., 2024). Given the absence of independent benchmark validation of the fixed-parameter force-constant model, the 95.2% instability rate should be interpreted as a pronounced response within the adopted phonon-screening framework rather than definitive evidence of intrinsic dynamical instability across carbon anodes.

Lithium-Metal and Alloy Phases: Alloy Chemistry Governs Stability

Lithium-metal and alloy phases showed an intermediate failure rate (70.8%) with a clear compositional dependence. All six Li-Al alloy phases were severely phonon unstable, as were the majority of Li-Sn phases (8/11). Among elemental lithium phases, bcc and fcc Li (mp-135, mp-51) were phonon stable while five metastable polymorphs were severely unstable, illustrating that AI stability scores cannot distinguish between ground states and kinetically trapped metastable phases.

Thermodynamic–Phonon Stability Discrepancy

The results demonstrate that thermodynamic stability alone does not ensure phonon stability. Despite all 79 structures satisfying the adopted AI-predicted stability criterion of $E_{\text{hull}} < 0.05$ eV atom⁻¹, 49 structures (62.0%) were classified as dynamically unstable within the adopted phonon-screening framework. This discrepancy was evident across all three material families, although the magnitude of instability varied substantially, with carbon-based structures showing the highest failure rate (95.2%). These findings indicate that E_{hull} -based screening and phonon-based screening provide complementary information for evaluating candidate anode materials. Consequently, high-throughput workflows based solely on thermodynamic stability may retain structures with unfavourable vibrational characteristics, supporting the incorporation of phonon screening as an additional post-processing stage in materials discovery.

CONCLUSION

This study presents a systematic computational meta-analysis of phonon-driven instability in AI-predicted Li-ion anode materials, examining 79 candidate structures across silicon, carbon, and lithium-metal families. The central finding that 62.0% of AI-stable structures were classified as dynamically unstable within the adopted phonon-screening framework demonstrates a substantial and material-class-dependent discrepancy between thermodynamic and phonon stability in current AI-assisted screening workflows. The key findings indicate that zone-center Gamma-point soft modes were the predominant location of phonon instabilities across all three anode families, accounting for 98.0% of unstable structures. Carbon-based anodes exhibited the highest failure rate (95.2%), followed by lithium-metal phases (70.8%) and silicon-based anodes (35.3%). The high instability rate observed for carbon-based structures may reflect limitations in representing interlayer van der Waals interactions and associated soft vibrational modes, although this interpretation should be treated cautiously given the adopted empirical force-constant model. The results further demonstrate that satisfying the adopted Ehull stability criterion does not ensure phonon stability, highlighting the complementary information provided by thermodynamic and phonon-based screening. An important limitation is that the phonon analysis employed an empirical Born–von Karman force-constant model with fixed parameters rather than DFT-derived force constants. No independent parameter-sensitivity, benchmark, supercell-size convergence, or acoustic sum-rule assessment was performed. Consequently, the identified instabilities should be interpreted as screening-level indicators under the adopted model rather than quantitative predictions of *ab initio* phonon spectra, particularly for structures with minimum phonon frequencies close to the -0.1 THz threshold. The findings support the incorporation of phonon instability screening as an additional post-processing step in AI-based materials-discovery workflows targeting synthesis feasibility, particularly for carbon- and lithium-alloy anode candidates.

DATA AVAILABILITY

All crystal structure files (CIF format), computed phonon frequency data and analysis scripts are available from the corresponding author upon reasonable request. Source data used in this study were retrieved from the Materials Project database (materialsproject.org) using the public API.

COMPETING INTERESTS

The authors declare no competing interests.

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AUTHOR CONTRIBUTIONS

All authors contributed significantly to the study.

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