

Co-intercalation reaction for graphite in sodium ion batteries: Revival or revolution?

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ABSTRACT

Reversible intercalation of guest ions in graphite laid the foundation of modern battery technology, exemplified by the successful launch of Li-ion batteries (LIBs) 35 years ago. With sodium's natural abundance and low cost, sodium ion batteries (SIBs) are increasingly regarded an appealing contender for large-scale energy storage. However, the conventional intercalation chemistry that unlocks graphite anodes in LIBs is ineffective in SIBs. This obstacle is recently overcome by a co-intercalation chemistry involving the insertion of solvated ions, which rejuvenated graphite as a viable anode for SIBs by offering ultrafast reaction kinetics, excellent rate capability and long cycle life. Nonetheless, the incorporation of solvent molecules induces substantial challenges, including pronounced volume change, elevated redox potential, and limited Na storage capacities. Despite extensive efforts to accommodate these issues, the practical implementation of graphite anodes in SIBs remain elusive. In this Perspective, we briefly overview the principles and key advances in graphite co-intercalation chemistry, highlight the overlooked challenges, and propose potential directions for achieving regulated co-intercalation for practical graphite-based SIBs.

1. Introduction

The chemical similarity between sodium and lithium, combined with the natural abundance and low cost of sodium, position sodium ion batteries (SIBs) as a strong contender among post-lithium battery technologies for large-scale energy storage applications. To accelerate the commercialization of SIBs, early attempts to directly transfer commercial graphite anodes from LIBs into SIBs were unsuccessful, due to graphite's extremely low Na-storage capacity ($< 10 \text{ mAh g}^{-1}$) in conventional intercalation chemistry [1]. A breakthrough co-intercalation chemistry was reported in 2014, which involves the insertion of Na ions together with ether solvent molecules into graphite galleries. [2] This discovery renewed interest in developing graphite anodes in SIBs by providing capacities of $\sim 100 \text{ mAh g}^{-1}$ and cyclic life beyond 1,000 cycles. More importantly, the co-intercalation chemistry enables ultrafast charging (*i.e.*, $\sim 100 \text{ mAh g}^{-1}$ at 30 A g^{-1}) [3] and low-temperature capability (*i.e.*, 99.9% capacity retention after 750 cycles at $-30 \text{ }^\circ\text{C}$) [4], which are inaccessible in conventional intercalation chemistry of graphite anodes in Li-ion batteries (LIBs). Over the past decade, substantial progresses are made in unveiling and advancing the unique Na-

based co-intercalation chemistry in graphite. Although several reviews [5,6] have summarized the recent advancement, critical challenges hindering the practical implementation of graphite anodes in fast-charging SIBs remains unaddressed, necessitating a focused perspective to illustrate the future directions.

2. Opportunities and challenges of co-intercalation chemistry in graphite

Graphite has been the standard anode material for LIBs since 1990s via a conventional intercalation chemistry. In typical, the solvated Li ions in electrolyte solutions are desolvated and bare Li ions are subsequently inserted, yielding a binary graphite-intercalation-compound (*b*-GIC). In the co-intercalation reaction, solvated Na-ion species ($[\text{Na}^+(\text{solvent})_x]$) insert into graphite galleries simultaneously to generate ternary GIC (*t*-GIC) phases. The solvent co-insertion weakens the otherwise detrimental local Na^+ -graphene interaction [7,8], endowing graphite with decent Na storage capacities. Because of the incomplete desolvation of coordinated Na^+ , the desolvation energy barriers is reduced, thus enabling significantly enhanced reaction kinetics.

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However, this mechanism also evokes critical drawbacks: elevated redox potential (>0.6 V vs. Na/Na⁺), pronounced volume change ($\sim 250\%$), and limited capacities ($\sim 110\text{mAh g}^{-1}$) [9]. These features contrast significantly with these in LIBs, which operate at ~ 0.15 V vs. Li/Li⁺ [10], $\sim 10\%$ volume expansion [11], and a theoretical capacity of 372mAh g^{-1} . Practical application of graphite anodes in SIBs is unlikely until these issues can be effectively addressed.

2.1. Exceeding electrolyte

Durable co-intercalation typically requires flooding electrolytes, which can dramatically reduce the energy density by $\sim 84\%$ compared to commercial rechargeable batteries using lean electrolyte [12]. Studies that adopt lean electrolyte parameters for graphite anodes in SIBs are rarely reported. One major reason is the lack of consensus on the exact stoichiometry of $[\text{Na}^+(\text{solvent})_x]\text{C}_y$ product and the required amount of extra solvent in electrolytes. Reported values of x (0–11) and y (16–26) vary widely among studies [2,9,13]. On base of the fully sodiated phases ($x = 1$ or 2 in $[\text{Na}^+(\text{solvent})_x]\text{C}_y$ stoichiometries), the influence of the electrolyte amount and the intercalant composition on energy densities is plotted in Fig. 1. When x increases from 1 to 2, the energy density is predicted to drop by 16–20%. Even in the ideal case where all solvents in the electrolyte solutions are coordinated with Na-ion to intercalate into graphite galleries and the anode to cathode capacity (N/P) ratio is 1.2, there is a 11% reduction in energy density. Under more realistic scenarios, such as 50% additional solvent molecules in electrolyte solution, the baseline energy density of 160 Wh kg^{-1} SIB (value of the first-generation SIB provided by Contemporary Amperex Technology Co., Limited) using 3 g Ah^{-1} electrolyte will also be reduced to 73%. The energy density decline is substantial, demanding a fundamental trade-off between fast-charging and energy density.

2.2. High redox potential

The co-intercalation reaction of graphite is thermodynamically favorable, allowing appreciable change of Gibbs free energy and elevating working potentials of graphite. The elevated redox potential of graphite anode lowers the practical energy density of Na-ion full cells. The working potential of graphite anode is strongly dictated by electrolyte formulations, including solvent species and concentration. For linear ethers solvents, shorter chain length gives lower redox potentials as evidenced by a steady potential reduction of 180 mV from pentaethylene glycol to 1,2-dimethoxyethane (DME). [12] The contribution of concentration increment to redox potential is relatively limited, reducing 40 mV when the NaPF₆-DME electrolyte concentration increases from 1 M to 2 M. [12] Increasing operation temperature also promotes the reduction of redox potentials. For example, graphite achieved working potentials of 0.56 V and 0.4 V vs. Na/Na⁺ at 25 °C in 2 M NaPF₆ DME [12] and 1 M NaPF₆ DME/DMM (1:2 vol%, DMM: dimethoxymethane) [14] electrolytes. At a higher test temperature of 60 °C, the working potentials were reduced to 0.43 and 0.32 V vs. Na/Na⁺, respectively. Further lowering the working potential below 0.2 V vs. Na/Na⁺ is highly desirable to increase the overall voltage output and energy density of SIBs.

2.3. Large volume change

Large volume change can cause electrode swelling, mechanical failure, and battery safety risks. Upon full co-intercalation in SIBs, graphite particles can expand up to $\sim 278\%$ [9] and electrode by $\sim 190\%$ [15], which are far beyond acceptable limit for practical application. While introducing internal voids is a useful strategy for managing the extreme volume expanding electrode materials like silicon,

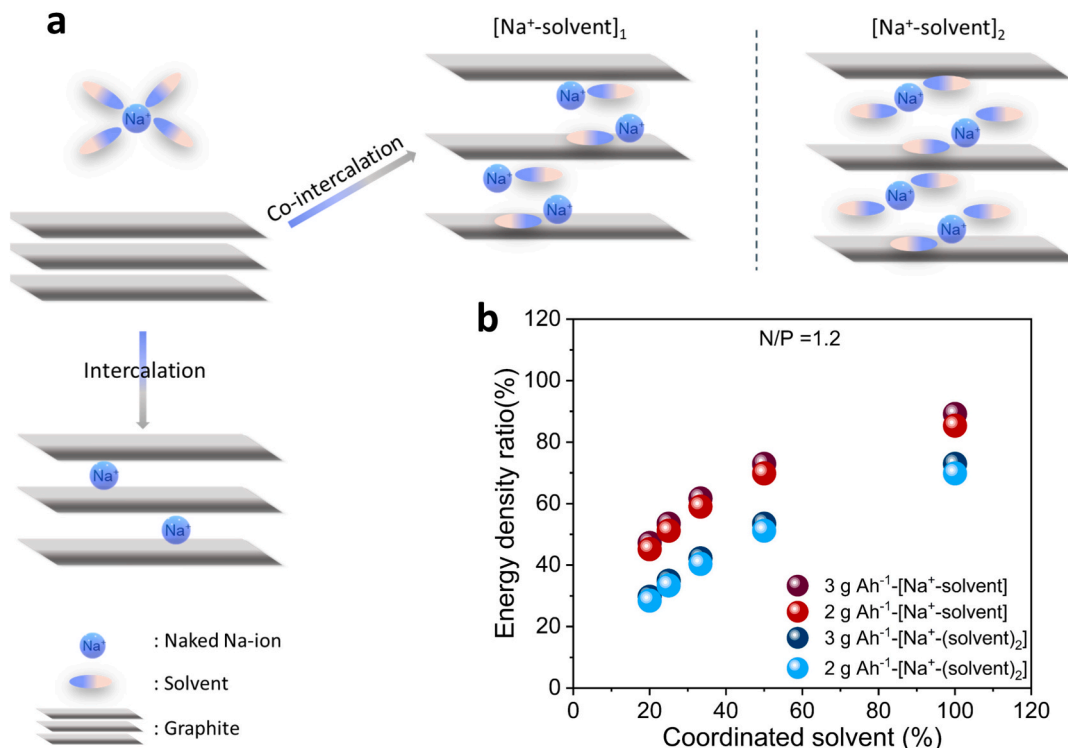


Fig. 1. (a) Schematic of intercalation and co-intercalation chemistry in graphite with different co-intercalants' stoichiometries, (b) Projected energy density ratio based on the variation of electrolyte amount and co-intercalants' stoichiometry. A base SIB (the first-generation SIB provided by Contemporary Amperex Technology Co., Limited) with a 160 Wh kg^{-1} energy density using lean electrolyte either 2 or 3 g Ah^{-1} assumed. Energy density ratio is the ratio between energy density of graphite-based SIB and the base SIB. Coordinated solvent ratio between the number of solvents coordinating Na-ion in graphite and the total number of solvents in pristine electrolyte. Ratio of areal anode capacity to areal cathode capacity (N/P ratio) is assumed for both base and graphite-based SIBs. Representative electrolyte 1 M NaPF₆ in DEGDME is used for estimation. For simplicity, influence of graphite's working potential on energy density is not considered.

this approach is not viable for graphite. The limited capacity of graphite anodes would be further reduced if non-active voids are accommodated, thus severely compromising the energy density of SIBs. The large volume change stems from co-intercalating solvent molecules. To this end, electrolyte solutions have been tailored under the motivation of reducing volume changes. Representatives are 1 M NaOTf in DEGDME/EN (10:1 vol%, NaOTf: sodium trifluoromethanesulfinate, DEGDME: 1-methoxy-2-(2-methoxyethoxy)ethane, EN: ethylenediamine) [16] and 0.5 M NaPF₆ in THF/DEGDME (95:5 vol%, THF: tetrahydrofuran) [17], reducing electrode expansion upon initial sodiation to 100–120% from the ~200% in linear ether only electrolytes. Binders with high Young's modulus like sodium carboxymethyl cellulose were reported to constrain the expansion of graphite flakes [16]. A more constructive strategy is to transfer the large pores or voids generated during coin-tercalation to accommodate Na metal deposition for high-capacity composite anodes. [18].

2.4. Limited capacity

In ether-based electrolyte solutions, graphite anodes exhibit reversible capacities of ~110mAh g⁻¹, which is much lower than Na metal and alloy-type anodes. To improve the Na-ion storage capacity in graphite, expanded graphite with increased interlayer spacing of 4.1–4.4 Å were synthesized to deliver capacities of 200–800mAh g⁻¹ [19–21]. However, the exceptionally high capacities are contributed by the kinetically slow intercalation reaction and pore filling reaction, instead of ultrafast co-intercalation. In addition, such expanded graphite with large surface area, numerous defects and oxygenated functional groups suffers low Coulombic efficiencies, considerable electrolyte consumption, and low tap density. Increasing the reversible capacity of graphite anodes to a competitive level without sacrificing the fast reaction kinetics remains a challenge.

3. The path forward

High energy density and low cost remain the central objectives in developing next-generation battery technologies. To date, the most effective strategy for enhancing the energy density of graphite-based SIBs relies on lowering the redox potential through destabilizing the GICs. This is primarily achieved by reducing volume of co-intercalating solvents [14] and introducing weakly solvating solvents [17]. Given the limited capacity of co-intercalated graphite, one promising route is hybridizing graphite with alloy-type anodes such as phosphorous (2596mAh g⁻¹ and ~0.4 V vs. Na/Na⁺) and Sn (847mAh g⁻¹ and ~0.2 V vs. Na/Na⁺) [22]. Such hybridization can simultaneously increase capacity, lower average working potential, and alleviate the heavy reliance on excess electrolyte. Nevertheless, the large volume changes (>300%) and sluggish kinetics of alloying materials necessitate careful control of their content and microstructures to preserve the intrinsic stability and high-power capability of graphite. A second direction is to fully exploit the ultrafast kinetics enabled by co-intercalation chemistry, targeting application regimes where energy density is not prioritized over the power density. In this context, graphite-based SIBs are particularly attractive for ultra-high-power applications, such as kinetic energy recovery systems in electric vehicles and grid frequency regulation. Beyond practical applications, insights from graphite-based co-intercalation chemistry have broader implications. They provide valuable guidance for extending graphite's host capability to multivalent metal ions, like Mg-ion [23] and Ca-ion [24], as well as non-graphitic

electrodes, such as layered transitional metal sulfide cathodes in SIBs [25].

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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