Rechargeable Dual-Ion Batteries with Graphite as a Cathode: Key Challenges and Opportunities

Journal Article

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Publication date:
2019-09-19

Permanent link:
https://doi.org/10.3929/ethz-b-000364990

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Originally published in:
Advanced Energy Materials 9(35), https://doi.org/10.1002/aenm.201901749
1. Introduction

The future progress in the utilization of intermittent renewable energy sources such as wind and solar will predominantly depend on the deployment of low-cost, TWh-level stationary energy storage systems. Moreover, there is a pressing need to stabilize the electric grid locally and globally. In this context, in addition to conventional storage means such as pumped hydroelectric storage (PSH), large stationary batteries are expected to play the major role. Generally, the economic feasibility of batteries for grid-scale electricity storage can be assessed by comparing the costs of stored energy (¢ kW h−1cycle−1) to those of PSH. To ensure their long-term sustainability, grid-scale battery technologies should have low-cost, easy-to-produce battery components, low CO2 footprints, and environmentally friendly. Additionally, there are numerous additional electrochemical battery performance characteristics that play an equally important role such as long-term cycling performance (cycle life), calendar life, Coulombic efficiency (measure for charge loss due to irreversible side reactions), energy efficiency, and the performance at different charge/discharge rates or at different temperatures. From this perspective, researchers constantly explore new anode and cathode materials for existing battery technologies as well as conceive new electrochemical energy storage concepts. In this context, the last two decades have seen a surge of reports on various low-cost anodes and cathodes for Li-ion and post-Li-ion batteries (Na-, K-, Ca-, Mg-, and Al-ion batteries). Moreover, new electrochemical concepts called graphite dual-ion batteries (GDIBs) have recently attracted significant attention. GDIBs show high potential for the use in grid-scale energy storage applications due to their low cost, relatively high energy densities of up to ≈200 Wh kg−1 and cyclic stability (thousands of cycles and potentially more). In this review, we provide an introduction to the basics of GDIBs. In particular, we discuss their operating mechanisms and cover the topic of energy density calculations. In addition, we highlight the importance of correct reporting of the performance metrics with respect to the energy density of GDIBs. Next, we discuss in detail factors governing the electrochemical performance of graphite cathodes in dual-ion batteries, such as graphite structure, morphology, and particle size. The factors that impact the voltage of electrochemical anion intercalation/deintercalation into graphite will be described as well. With respect to the practical application of the GDIBs, the current collector issues and volume changes of GDIBs will be discussed in the final sections.

2. Historical Aspects

Although GDIBs may appear to be newcomers in battery research, they have a long and tangible history. The concept of GDIBs was introduced in the patents of McCullough et al.1,2 in 1989. The experimental example consisted of two graphite electrodes acting as an anode and a cathode, and a 15 wt% solution of LiClO4 in propylene carbonate acting as an electrolyte. The oxidation and reduction of cathodic and anodic graphite electrodes occur with concomitant intercalation of Li+ cations and ClO4− anions, respectively. The latter process is known as the formation of donor-type (cationic) or acceptor-type (anionic) graphite intercalation compounds (GICs). Some years later, in the 1990s, the intercalation of various anions into graphite...
such as AlCl$_4^-$, BF$_4^-$, PF$_6^-$, CF$_3$SO$_3^-$, C$_6$H$_5$CO$_2^-$, and ClO$_4^-$ were studied in detail by Carlin et al. and Santhanam and Noel using various ionic liquids and organic solvent-based electrolytes, respectively. Those first publications have served as a basis for further exploration of this technology to be included for the estimation of cell-level charge storage capacity. The cell-level charge storage capacity-matched masses of the electrode active materials need to be estimated for the calculation of the cell-level theoretical energy density.

Cationic and anionic GICs had been known even earlier. For instance, in 1841, C. Schaffäutl synthesized H$_2$SO$_4$-GIC by reacting sulfuric acid with graphitic carbon. The first systematic studies of GICs were performed, however, only in the early 1930s, when Frezel et al. and Wellman et al. investigated in detail the mechanism of GIC formation (staging mechanism) using X-ray diffraction (XRD).

## 3. The Mechanism and Energy Density of GDIBs

### 3.1. Lithium, Sodium, and Potassium GDIBs

The working principle of GDIBs is depicted in Figure 1. GDIBs operate as an electrochemical energy storage system employing reversible intercalation of anion species into the graphite cathode upon charge (oxidation of the graphite network). Concurrently, intercalation, adsorption, alloying, or metal electroplating reactions might take place on the anode side of GDIBs. The examples of electrolytes used in GDIBs include ClO$_4^-$, bis(trifluoromethanesulfonyl)imide (TFSI$^-$), bis(fluorosulfonyl)imide (FSI$^-$), PF$_6^-$, and BF$_4^-$ anion-based salts of Li, Na, or K, dissolved in alkyl carbonates as solvents. Such polar solvents allow for high salt concentrations and a broad voltage window for operation. Contrary to a Li-ion battery (LIB) using graphite as an anode, GDIBs exploit the reversible oxidation of the graphite structure, that is, its cathodic functionality. Corresponding half-reactions for lithium GDIBs, wherein Li ions contribute to the anodic charge storage capacity during charging can be described as follows.

On the cathode:

$$xA^- + \text{Graphite} \leftrightarrow \text{Graphite}(A^-)_x + xe^- \quad (I)$$

On the anode:

$$1/6Li^+ + 1/6e^- + C \leftrightarrow Li_{1/6}C \quad (\text{intercalation}) \quad (II)$$

$$xLi^+ + xe^- + C(\text{hard carbon}) \leftrightarrow C(\text{hard carbon})Li_x \quad (\text{adsorption/insertion}) \quad (III)$$

$$4.4Li^+ + 4.4e^- + Sn \leftrightarrow SnLi_{4.4} \quad (\text{alloying}) \quad (IV)$$

$$Li^+ + e^- \leftrightarrow Li \quad (\text{electroplating}) \quad (V)$$

where $A^-$ is an anion (FSI$^-$, TFSI$^-$, PF$_6^-$, etc.).

The charging process stops when no cations or anions are left in the electrolyte, or when the graphite cathode or active material on the anode side reaches their highest charge storage capacity. Thereby, calculation of the cell-level theoretical energy density must account for the capacity-matched quantity of the electrolyte. In contrast, in rocking-chair-type LIBs, only the capacity-matched masses of the electrode active materials need to be included for the estimation of cell-level charge storage capacity. The cell-level charge storage capacity of GDIBs comprising alloying, intercalation, or adsorption/insertion reactions on the anode side of the battery can be calculated by the following equations (see details in the Supporting Information)

**Gravimetric $C_{cell}$**

$$C_sC_{cell}F(xM_d - M_c) = \frac{C_sF(xM_d - M_c) + C_cF(xM_d - M_c) + C_sC_p \times 10^3}{C_sF(xM_d - M_c) + C_cF(xM_d - M_c) + C_sC_c \times 10^3} \quad (1)$$

**Volumetric $C_{cell}$**

$$C_sC_{cell}F(xM_d - M_c) = \frac{C_sF(xM_d - M_c) + C_cF(xM_d - M_c) + C_sC_s \times 10^3}{C_sF(xM_d - M_c) + C_cF(xM_d - M_c) + C_sC_c \times 10^3} \quad (2)$$

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Maksym Kovalenko, born in 1982, grew up in Ukraine (Bukovina region). He studied chemistry at Chernivtsi National University and then continued his studies at the Johannes Kepler University Linz, Austria (Ph.D. in 2007 with Dr. Wolfgang Heiss; thesis topic: novel infrared-active colloidal nanocrystals). Subsequently, he joined the University of Chicago for postdoctoral training with Prof. Dmitri Talapin (research topic: inorganic ligand capping of colloidal nanocrystals), where he stayed until joining ETH Zurich in summer 2011. Since January 2017, Maksym Kovalenko has been an associate professor (with tenure) of functional inorganic materials at the Laboratory of Inorganic Chemistry. He jointed ETH Zurich in summer 2011 as a tenure-track assistant professor. The research activities of Maksym Kovalenko and his group focus on chemistry, physics, and applications of inorganic solid-state materials and nanostructures.
where $F = 26.8 \times 10^3$ mAh mol$^{-1}$ (Faraday constant), $M_d$ and $M_c$ are the molarities (mol L$^{-1}$) of the electrolyte in discharged ($M_d$) and charged ($M_c$) states, $\rho$ is the density of the electrolyte (g mL$^{-1}$), $x$ is the charge of the electroactive species in the electrolyte ($x = 1$ for systems comprising monovalent ions), $C_c$ is a specific gravimetric capacity of a graphite cathode (in mAh g$^{-1}$), and $C_a$ is a specific gravimetric capacity of the anode (in mAh g$^{-1}$).

The cell-level capacity of GDIBs, where a metal plating reaction takes place on the anode side of the battery, can be expressed as follows (see details in the Supporting Information)

$$C_{\text{cell}} = \frac{F x (M_d - M_c) C_c}{F x (M_d - M_c) + C_c \rho \times 10^3} \text{ (mAh g}^{-1})$$ (3)

$$C_{\text{cell}} = \frac{F x (M_d - M_c) C_c}{F x (M_d - M_c) + C_c \times 10^3} \text{ (mAh mL}^{-1})$$ (4)

To calculate the energy density of GDIBs, the $C_{\text{cell}}$ value should be multiplied by the average battery voltage $V_{\text{cell}}$. $E_{\text{cell}} = C_{\text{cell}} \cdot V_{\text{cell}}$. The latter can be determined by dividing the area under a discharge curve of the cell (voltage vs time curve) by the discharge time. We emphasize that $E_{\text{cell}}$ is an upper theoretical limit for an energy density. In accordance with assumptions of Winter and co-workers,$^{[28]}$ for estimation of practical energy density of GDIBs, $E_{\text{cell}}$ should be further reduced by $\approx 30$–45% due to the weight of current collectors, separators, and packaging.

As follows from Equations (1)–(4), the energy density of GDIBs is severely limited by the concentrations of the electrolytes. As an example, Figure 2a illustrates the impact of the electrolyte molarity on the overall energy density of the lithium GDIB battery (utilizing the electroplating reaction of lithium) using LiFSI in EC/DMC as an electrolyte. For simplicity, in Figure 2a, we assumed that an average voltage of the battery is constant (4.7 V) at all molarities. The primary conclusion is that the molarity of the electrolyte is the most useful variable, in addition to the capacity of the graphite, for improving the energy density of GDIBs because of the capacity-limiting effect of the electrolyte. Hence, to achieve an optimal energy density, not only must the highest capacity of the cathode ($C_c$) be harnessed, but a
concomitant increase in molarity must also be included. Using Equations (1)–(4) or similar expressions of gravimetric cell-level capacity reported by Dahn and Seel[7] as well as reported electrode capacities, battery voltages, and molarities of electrolytes, one can show that the cell-level energy densities of the state-of-the-art lithium, sodium, and potassium DIBs fall in the range of 22–207 Wh kg\(^{-1}\) (see the Supporting Information for details and Table 1).\[24,26,30,41–43,56,68–72\] We would like to emphasize that currently, no common methodology exists for reporting cell-level energy density for various GDIBs. Many reports focus exclusively on the specific capacity of individual electrodes without a realistic assessment of energy density limits. Wrong theoretical cell-level energy densities of DIBs are reported systematically and frequently, and are, unfortunately, often significantly overestimated due to the exclusion of the capacity-matched quantity of the electrolyte from the calculations.

### 3.2. Aluminum GDIBs

Similar to lithium, sodium, and potassium GDIBs, aluminum GDIBs exploit the reversible oxidation of the graphite network with intercalation of aluminum species between graphene layers. Concomitantly, on the anode side, reversible plating/stripping of aluminum takes place from chloroaluminate-based ionic liquids. The working principle of the aluminum GDIBs (Figure 3) can be represented by the following cathodic and anodic half reactions during charge.

**On the anode:** \(4\text{AlCl}_3^{−} + 3e^− \leftrightarrow 7\text{AlCl}_4^{−} + \text{Al}\)  \hspace{1cm} (VI)

**On the cathode:** \(xC^{+} + \text{AlCl}_4^{−} \leftrightarrow C_4(\text{AlCl}_4^{−}) + e^−\)  \hspace{1cm} (VII)

Chloroaluminate-based ionic liquids can be described as a mixture of \(\text{AlCl}_3\) and other \(\text{Cl}^{−}\) containing salts such as 1-ethyl-3-methylimidazolium chloride (EMIM), 1-butyl-3-methylimidazolium chloride (BMIM), and others. The mixture becomes liquid at room temperature (an ionic liquid) due to the acid-base reaction between \(\text{AlCl}_3\) (Lewis acid) and \(\text{Cl}^{−}\) (Lewis base) forming \(\text{AlCl}_4^{−}\) anions charge-balanced with, for instance, EMIM\(^{+}\) cation. The excess of \(\text{AlCl}_3\) over EMIMCl yields acidic ionic liquids containing \(\text{Al}_2\text{Cl}_7^{−}\). The electrodeposition of Al from chloride-based ionic liquids has been thoroughly studied in the past, leading to the consensus that only \(\text{Al}_2\text{Cl}_7^{−}\) (not \(\text{AlCl}_4^{−}\)) ions enable the electroplating of Al.[75–85] Aluminum, therefore, does not deposit from neutral or basic melts (excess of EMIMCl). Consequently, the amount of \(\text{Al}_2\text{Cl}_7^{−}\) ions, and hence the whole mass of the liquid phase, must match the capacity of the graphite. For each electrodeposited aluminum atom, three \(\text{AlCl}_4^{−}\) anions synchronously intercalate into the graphite. The charging process stops when there are only \(\text{AlCl}_4^{−}\) ions left, that is, the neutral melt forms (\(\text{AlCl}_3\):EMIMCl = 1), or when the maximum capacity of the graphitic cathode is reached. The highest molar ratio (\(r\)) of \(\text{AlCl}_3\):EMIMCl that still forms a usable ionic liquid is \(\approx 2:1\). Above this ratio, \(\text{AlCl}_3\) does not dissolve in the ionic liquid.

The performance of such a battery is not limited to EMIM-based ionic liquids: \(\text{AlCl}_3\)/urea/EMIMCl[86] \(\text{AlCl}_3\)/urea,[87] \(\text{AlCl}_3\)/Et\(_3\)NCl[88,89] or fully inorganic \(\text{AlCl}_3\)/NaCl[90] and \(\text{AlCl}_3\)/LiCl/KCl[91] melts have recently been presented as possible alternatives. We also note that starting with an aluminum anode is not a necessity. Any current collector supporting aluminum electrodeposition or coated with a minimally thin aluminum film as a seed layer is sufficient. We note that there is no unidirectional flow of \(\text{Al}^{3+}\) ions or any other Al species from one electrode to the other, for example, a “rocking-chair” principle of Li-ion batteries. For this reason, it is not correct to call this battery an “Al-ion battery.”

The actual operating mechanism is fundamentally different from the operating mechanism of metal-ion batteries: Al-species are depleted from the chloroaluminate-based ionic liquid during the charge process and are being taken up by both electrodes (Figure 3).

**Gravitometric:**

\[
\text{Gravitometric } C_{\text{cell}} = \frac{Fx(r-1)C_c}{Fx(r-1) + C_c(r \text{M}_{\text{AlCl}_3} + \text{M}_{\text{Cl}})} \quad (5)
\]

**Volumetric:**

\[
\text{Volumetric } C_{\text{cell}} = \frac{Fx(r-1)C_c \rho}{Fx(r-1) + C_c(r \text{M}_{\text{AlCl}_3} + \text{M}_{\text{Cl}})} \quad (6)
\]
Table 1. Comparison of performance metrics of lithium, sodium, and potassium GDIBs. The gravimetric energy density was calculated using expressions (1) and (3) for alloying/intercalation/adsorption/insertion and electroplating anodic reactions, respectively.

| Reference | Battery | Anode | Anode capacity [mAh g$^{-1}$] | Cathode | Cathode capacity [mAh g$^{-1}$] | Electrolyte/analyte capacity [mAh g$^{-1}$] | Cell capacity [mAh g$^{-1}$] | Anodic charge voltage | Cathodic discharge voltage [V] | Average discharge cell voltage [V] | Energy density [Wh kg$^{-1}$] |
|-----------|---------|-------|-------------------------------|---------|-------------------------------|---------------------------------|-------------------------------|-----------------------|-------------------------------|-------------------------------|-------------------------------|
| [68]      | KFSI/graphite (K plating) | KFSI | 844 | KFSI in EC/DMC | 21.27 | 17 | 0.4 V vs Na$^+$/Na | 4.4 vs Na$^+$/Na | 4.0 | 68 |
| [70]      | Pine needle derived carbon (PNC)/graphite | PNC | 200 | Graphite | 97 | 1 m NaPF$_6$ in EC/EMC | 21.27 | 17 | 0.4 V vs Na$^+$/Na | 4.4 vs Na$^+$/Na | 4.0 | 68 |
| [71]      | Carbon molecular sieve (CMS)/graphite | CMS | 200 | Graphite | 97 | 1 m NaPF$_6$ in EC/EMC | 21.27 | 17 | 0.4 V vs Na$^+$/Na | 4.4 vs Na$^+$/Na | 4.0 | 68 |
| [41]      | Sn/graphite | Sn | 226 | Graphite | 78 | 1 m NaPF$_6$ in EC/DMC/EMC | 21.27 | 16 | 0.2 V vs Na$^+$/Na | 4.2 vs Na$^+$/Na | 4.0 | 64 |
| [26]      | NaTFSI/graphite (Na plating) | Graphite | 40 | 0.3 m NaTFSI in Pyr14TFSI | 6 | 5 | 0 V vs Na$^+$/Na | 4.3 vs Na$^+$/Na | 4.3 | 22 |
| [72]      | NaPF$_6$/freestanding mesocarbon microbead film (FS-MCMB) (Na plating) | FS-MCMB | 84 | 1 m NaPF$_6$ in EC/DMC | 20 | 16 | 0 V vs Na$^+$/Na | 4.1 vs Na$^+$/Na | 4.1 | 66 |
| [42]      | Mesocarbon microbead/graphite | Mesocarbon microbead | 279 | Graphite | 61 | 1 m KPF$_6$ in EC/DMC/EMC | 21.27 | 15 | 0.3 V vs K$^+$/Kb | 4.7 vs K$^+$/K | 4.4 | 66 |
| [43]      | Sn/graphite | Sn | 452 | Graphite | 60 | 1 m KPF$_6$ in EC/DMC/EMC | 21.27 | 15 | 0.3 V vs K$^+$/K | 4.5 vs K$^+$/K | 4.2 | 63 |
| [56]      | Graphite/graphite | Graphite | 62 | 0.8 m KPF$_6$ in EC/DMC | 17.3 | 13 | 0.25 V vs K$^+$/K | 4.25 vs K$^+$/K | 4 | 52 |
| [24]      | Graphite/graphite | Graphite | 250 | Graphite | 45 | 0.3 m KTFSI in Pyr14TFSI | 6 | 5 | 0.25 V vs K$^+$/K | 4.75 vs K$^+$/K | 4.5 | 23 |
| [69]      | Soft carbon (SC)/graphite | SC | 160 | Graphite | 80 | 1 m NaPF$_6$ in EC/DMC | 20 | 15 | 0.5 V vs Na$^+$/Na | 4.1 vs Na$^+$/Na | 3.6 | 54 |
| [30]      | LiTFSI/graphite (Li plating) | Graphite | 80 | 3.4 m LiTFSI in DMC | 65 | 36 | 0 V vs Li$^+$/Li | 4.17 V vs Li$^+$/Li$^0$ | 4.34 | 156 |
| [30]      | LiTFSI/graphite (Li plating) | Graphite | 80 | 2.7 m LiTFSI in DMC | 52 | 32 | 0 V vs Li$^+$/Li | 4.36 V vs Li$^+$/Li$^0$ | 4.36 | 140 |
| [30]      | LiPF$_6$/graphite (Li plating) | Graphite | 90 | 3.5 m LiTFSI in DMC | 74 | 40 | 0 V vs Li$^+$/Li | 4.31 V vs Li$^+$/Li$^0$ | 4.31 | 172 |
| [30]      | LiPF$_6$/graphite (Li plating) | Graphite | 90 | 3.5 m LiTFSI in DMC | 67 | 38 | 0 V vs Li$^+$/Li | 4.26 V vs Li$^+$/Li$^0$ | 4.26 | 162 |

$^a$Voltage was taken from ref. [73]; $^b$Capacity and voltage were taken from ref. [74]; $^c$Average charge voltage. Abbreviations: EC = ethylene carbonate; DMC = dimethyl carbonate; EMC = ethyl methyl carbonate; DEC = diethyl carbonate; Pyr14TFSI = 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide; LiTFSI = lithium bis(trifluoromethanesulfonyl)imide; NaTFSI = sodium bis(trifluoromethanesulfonyl)imide; KTFSI = potassium(I) bis(trifluoromethanesulfonyl)imide; KFSI = potassium bis(fluorosulfonyl)imide.
where \( x = \frac{3}{4} \) (amount of electrons used to reduce 1 mol of the \( \text{AlCl}_2 \text{Cl}_7 \) ions). \( M_{\text{AlCl}_3} \) is the molar mass of \( \text{AlCl}_3 \) in g mol\(^{-1}\), \( M_{\text{XCl}} \) is the molar mass of \( \text{Cl}^- \) source (e.g., 1-ethyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium chloride, or \( \text{HCl} \) in the hypothetical simplest case) in g mol\(^{-1}\), \( r \) is the \( \text{AlCl}_3:X\text{Cl} \) molar ratio, and \( \rho \) is density of the chloroaluminate-based anolyte in g mL\(^{-1}\).

Figure 2b demonstrates the impact of acidity \( r \) on the overall energy density of aluminum GDIBs. In Figure 1b, we assumed the average battery voltage to be constant at 2 V for all theoretical curves. This value of the average discharge voltage is the highest reported value that was obtained experimentally at \( r = 1.3 \). As follows from Figure 2b, the parameter \( r \) is the most useful variable in addition to the cathodic capacity of the graphite for improving the energy density of GDIBs due to capacity-limiting effect of the anolyte. This effect can be illustrated by calculating the theoretical capacity of the ionic liquid \( C_{\text{an}} \) considering its whole mass (volume) as an anolyte as follows:

\[
\text{Gravimetric } C_{\text{an}} = \frac{Fx(r-1)}{rM_{\text{AlCl}_3} + M_{\text{XCl}}} \quad (\text{mAh g}^{-1})
\]

\[
\text{Volumetric } C_{\text{an}} = \frac{Fx(r-1)\rho}{rM_{\text{AlCl}_3} + M_{\text{XCl}}} \quad (\text{mAh mL}^{-1})
\]

The resulting gravimetric and volumetric capacities of \( \text{AlCl}_3:\text{EMIMCl} \) ionic liquids are 48 mAh g\(^{-1}\), 63 Ah L\(^{-1}\) and 19 mAh g\(^{-1}\), 24 Ah L\(^{-1}\) for \( r = 2 \) and \( r = 1.3 \), respectively. Hence, to achieve an optimal energy density, not only must the highest capacity of the cathode \( (C_{\text{C}}) \) be addressed, but a concomitant increase in \( r \) must also be included. As a reference point, we analyzed all available literature on aluminum GDIBs and identified that the highest experimental energy density of \( \approx 65 \text{ Wh kg}^{-1} \) was reported for an \( \text{AlCl}_3:\text{EMIMCl} \) anolyte with \( r = 2 \), a graphitic capacity of 142 mAh g\(^{-1}\), and a corresponding discharge voltage of 1.79 V (see Table 2). We note that most of reported data in the literature were obtained with \( r = 1.3 \). At this lower value of \( r \), the energy density does not exceed 30 Wh kg\(^{-1}\).

4. Graphite Materials Playground

The gravimetric capacities and average discharge voltages of various graphitic materials are summarized in Figure 4a. Overall, the voltage and capacities of graphite vary significantly upon altering the size of the anion, the nature and concentration of the electrolyte and graphite active materials, ranging within 3–5.0 V versus Li\(^+\)/Li and 66–150 mAh g\(^{-1}\). The highest capacity had been reported for highly crystalline graphite materials such as natural graphite and kish graphite flakes. The detailed analysis of the structural properties of the graphite in relation to its electrochemical performance will be discussed in the next section. In addition, the nature of the electrolyte solvent plays an essential role on the capacity of graphite cathode, which is attributed mainly to the ion solvation and solvent co-intercalation effects.\(^{[110-115]} \) For instance, it has been shown that electrochemical intercalation of \( \text{PF}_6^- \) anions into graphite from ethylene carbonate (EC) solvent is rather difficult leading to very small charge storage capacity of \( \approx 7 \text{ mAh g}^{-1} \).\(^{[113]} \) On the contrary, the addition of ethylmethyl carbonate (EMC) solvent revealed a significant increase in the graphite capacity of up to \( \approx 100 \text{ mAh g}^{-1} \). The explanation of this effect was that EMC solvent is a strong contender to EC in the formation of hydrogen bonding with \( \text{PF}_6^- \) anion. Consequently, the solvation of \( \text{PF}_6^- \) anions in EC solvent is affected by EMC. As a result, the configuration of \( \text{PF}_6^- \) anions solvated by the linear EMC molecules is more favorable for intercalation into graphite than the one based on \( \text{PF}_6^- \) anions solvated by the cyclic EC molecules. We note that in addition to the impact of the solvent, the molarity of the electrolyte and thereby its ionic conductivity are changing upon charge and discharge. The latter has also a direct impact on the rate capability of graphite and consequently, the power density of GDIBs.\(^{[116]} \)

In respect to the voltage, GDIBs comprising the smaller anions such as \( \text{PF}_6^- \) and \( \text{FSI}^- \) are generally characterized by the highest anion intercalation voltages of 4.5–5.0 V versus Li\(^+\)/Li.\(^{[68,112]} \) In contrast, the systems comprising the largest ions such as bis(pentafluoroethanesulfonyl) imide (BETI\(^+\)) demonstrate a relatively low intercalation voltage of \( \approx 4.3 \) V versus Li\(^+\)/Li.\(^{[14]} \) In addition to the intrinsic redox potential of graphite, there are a few other factors contributing toward the experimentally observed voltage of the anion intercalation. These are the energy needed to form separate anions from the electrolyte (anion desolvation energy; the smaller the anion, the higher this energy) and the energy required to intercalate anion into graphite lattice (intercalation energy of the anion; the larger the anion, the higher the energy). These two factors depend differently on the size of the anion. Specifically, to insert larger anions higher charging output is required to open up the interlayer spaces, thereby increasing intercalation voltage. On the other hand, larger anions have lower desolvation energy that would decrease the intercalation voltage. In recent paper of Placke and co-workers\(^{[14]} \) it had been demonstrated that desolvation energy can contribute more to the anion intercalation voltage than intercalation energy. One example is shown in Figure 4b, which compares voltage profiles of graphite using \( \text{PF}_6^- \), bis(trifluoromethanesulfonate) imide (TFSI\(^-\)), and BETI-based electrolytes (1 M LiPF\(_6\), 1 M LiTFSI, and 1 M LiBETI in...
Table 2. Comparison of performance metrics of various aluminum CDIBs. The gravimetric energy density of aluminum CDIBs was calculated using expression (6).

| Reference | Electrolyte | AlCl₃/EMIMCl (1.1:1 molar ratio) | AlCl₃/EMIMCl (1.5:1 molar ratio) | AlCl₃/EMIMCl (1.3:1 molar ratio) | AlCl₃/EMIMCl (1.1:1 molar ratio) | AlCl₃/EMIMCl (1.3:1 molar ratio) | AlCl₃/EMIMCl (1.5:1 molar ratio) | AlCl₃/EMIMCl (1.3:1 molar ratio) | AlCl₃/EMIMCl (1.1:1 molar ratio) |
|-----------|-------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| [35]      | Graphite    | 6.7 mAh g⁻¹ (66 mA g⁻¹)          | 2.9 mAh g⁻¹ (20 mA g⁻¹)          | 1.4 mAh g⁻¹ (14 mA g⁻¹)          | 0.7 mAh g⁻¹ (7 mA g⁻¹)           | 3 mAh g⁻¹ (30 mA g⁻¹)            | 1.5 mAh g⁻¹ (15 mA g⁻¹)         | 0.8 mAh g⁻¹ (8 mA g⁻¹)           | 0.4 mAh g⁻¹ (4 mA g⁻¹)           |
| [35]      | Carbon paper| 2.9 mAh g⁻¹ (20 mA g⁻¹)          | 1.4 mAh g⁻¹ (14 mA g⁻¹)          | 0.7 mAh g⁻¹ (7 mA g⁻¹)           | 3 mAh g⁻¹ (30 mA g⁻¹)            | 1.5 mAh g⁻¹ (15 mA g⁻¹)         | 0.8 mAh g⁻¹ (8 mA g⁻¹)           | 0.4 mAh g⁻¹ (4 mA g⁻¹)           | 0.2 mAh g⁻¹ (2 mA g⁻¹)           |
| [34]      | Graphene nanofibers | 1.4 mAh g⁻¹ (14 mA g⁻¹) | 0.7 mAh g⁻¹ (7 mA g⁻¹) | 3 mAh g⁻¹ (30 mA g⁻¹) | 1.5 mAh g⁻¹ (15 mA g⁻¹) | 0.8 mAh g⁻¹ (8 mA g⁻¹) | 0.4 mAh g⁻¹ (4 mA g⁻¹) | 0.2 mAh g⁻¹ (2 mA g⁻¹) |
| [32]      | Defect-free graphene aerogel | 0.7 mAh g⁻¹ (7 mA g⁻¹) | 3 mAh g⁻¹ (30 mA g⁻¹) | 1.5 mAh g⁻¹ (15 mA g⁻¹) | 0.8 mAh g⁻¹ (8 mA g⁻¹) | 0.4 mAh g⁻¹ (4 mA g⁻¹) | 0.2 mAh g⁻¹ (2 mA g⁻¹) |
| [39]      | Large-sized few-layer graphene | 3 mAh g⁻¹ (30 mA g⁻¹) | 1.5 mAh g⁻¹ (15 mA g⁻¹) | 0.8 mAh g⁻¹ (8 mA g⁻¹) | 0.4 mAh g⁻¹ (4 mA g⁻¹) | 0.2 mAh g⁻¹ (2 mA g⁻¹) | 0.1 mAh g⁻¹ (1 mA g⁻¹) |
| [96]      | Amorphous carbon-graphite composite | 1.5 mAh g⁻¹ (15 mA g⁻¹) | 0.8 mAh g⁻¹ (8 mA g⁻¹) | 0.4 mAh g⁻¹ (4 mA g⁻¹) | 0.2 mAh g⁻¹ (2 mA g⁻¹) | 0.1 mAh g⁻¹ (1 mA g⁻¹) | 0.05 mAh g⁻¹ (0.5 mA g⁻¹) |
| [102]     | Graphene paper | 0.4 mAh g⁻¹ (4 mA g⁻¹) | 0.2 mAh g⁻¹ (2 mA g⁻¹) | 0.1 mAh g⁻¹ (1 mA g⁻¹) | 0.05 mAh g⁻¹ (0.5 mA g⁻¹) | 0.02 mAh g⁻¹ (0.2 mA g⁻¹) | 0.01 mAh g⁻¹ (0.1 mA g⁻¹) | 0.005 mAh g⁻¹ (0.05 mA g⁻¹) |
| [96]      | Defect-free soft carbon | 0.4 mAh g⁻¹ (4 mA g⁻¹) | 0.2 mAh g⁻¹ (2 mA g⁻¹) | 0.1 mAh g⁻¹ (1 mA g⁻¹) | 0.05 mAh g⁻¹ (0.5 mA g⁻¹) | 0.02 mAh g⁻¹ (0.2 mA g⁻¹) | 0.01 mAh g⁻¹ (0.1 mA g⁻¹) | 0.005 mAh g⁻¹ (0.05 mA g⁻¹) | 0.002 mAh g⁻¹ (0.02 mA g⁻¹) |
ethyl methyl sulfone). Figure 4b indicates that the system based on small PF$_6^-$ anions has higher intercalation voltage than systems with larger TFSI$^-$ and BETI$^-$ anions. We note that in respect to the AlCl$_4^-$ anion intercalation from chloroaluminate ionic liquid, the voltage is defined primarily by the acidity of the ionic liquid (AlCl$_3$:EMIMCl molar ratio). As illustrated in Figure 4c, the higher the acidity of chloroaluminate ionic liquid is, the lower the voltage is. It is important to note that Wang et al.[103] had recently estimated the Al$^{3+}$/Al potential in chloroaluminate ionic liquid electrolytes (AlCl$_3$:EMIMCl) versus the standard hydrogen electrode (SHE), thus allowing a comparison of the Li and Na electrochemistry. Using specially constructed cells consisting of a β-alumina solid electrolyte and Na reference electrode, the Al$^{3+}$/Al redox reaction (electroplating/electrostripping) was determined to occur at ~0.7 V versus SHE and 2.3 V versus Li$^+$/Li. These results allow the estimation of the potential of AlCl$_4^-$ intercalation in graphitic materials versus Li$^+$/Li and compare them with the intercalation voltage of other anions. Another important aspect that needs to be mentioned is that the charging protocol has a profound effect on the gravimetric capacity of graphite. Specifically, in the recent publication of Wang et al.[75] about the electrochemical performance of graphite in aluminum GDIBs, the constant current–constant voltage (CCCV) charging protocol, which involves constant charging steps in the range of 1.9–2.1 V (terminated at a current drop of 90%), substantially improves the discharge capacity of graphite from 110 to 142 mAh g$^{-1}$. Notably, constant voltage (CV) steps at higher voltages of >2.1 V were detrimental because of side reactions that reduced the Coulombic efficiency. CV steps at lower voltages of <1.9 V were of limited effect. In addition to the CCCV charging protocol, the improvement of discharge capacity of graphite in aluminum GDIBs can be accomplished by lowering the temperature. Recently, Pan et al.[31] reported that the reversible discharge capacity of graphite could be enhanced at low temperatures (e.g., ~10 °C) rather than at room temperature for AlCl$_4^-$ anion intercalation (Figure 5a). The galvanostatic discharge (charge) curves of the aluminum GDIBs measured at room temperature exhibited only two characteristic plateaus at ~1.7 V (1.9 V) and 2.1 V (2.2 V) (Figure 5b, see Figure 5c for the CV curves). Contrarily, charge–discharge curves measured at ~10 °C showed an additional reversible plateau at upper discharge (charge) voltage of ~2.5 V (~2.6 V) (Figure 5b, see Figure 5d for the CV curves) that significantly improves both the average discharge voltage and capacity of the graphite in aluminum GDIBs.

5. Staging Mechanism and Voltage of Anion \ntercalation into Graphite

Complex anion species do not insert into graphite uniformly between graphene interlayers but in a unique periodic manner called the staging mechanism as depicted in Figure 6a. Gener-ally, such a mechanism results from the balance between the van der Waals forces of graphene–graphene layers and the ionic repulsion between and within the anion layers. Therefore, the anion intercalation proceeds into graphite through different
stages with a varying periodic repeat distance \( I_c \) (which is the distance between two neighboring anion intercalant layers), and a stage-independent intercalant gallery height \( d_i \) (i.e., the distance between two neighboring carbon layers with intercalant anions). A lower stage number (\( n \)) corresponds to an increase in intercalant concentration, so it also implies a higher charge storage capacity. Electrochemical intercalation of the anion into graphite, an increase in the intercalant gallery height \( d_i \), and the periodic repeat distance \( I_c \) with the stage number can be monitored by X-ray diffraction measurements through the decrease of the intensity of the (002) dominant peak and the appearance of two additional peaks, which correspond to the (00\( n+1 \)) and (00\( n+2 \)) planes. In a simplified form, the ratio between \( d \)-spacings values of (00\( n+1 \)) and (00\( n+2 \)) (\( d_{00n+1}/d_{00n+2} \)) reflect the stage number of the graphite intercalation compound.

\[
I_c = (n+1) \cdot d_{00n+1} = (n+2) \cdot d_{00n+2} = (n + m) \cdot d_{00n+m}, \text{ where } d_{00n+1}, \ d_{00n+2}, \text{ and } d_{00n+m} \text{ are the } d \text{-spacing values of (00}n+1\text{), (00}n+2\text{), and (00}n+m\text{) planes, accordingly.}
\]

Figure 6b shows an example of the XRD patterns obtained for the charging and discharging of a graphite cathode in the 5 m KFSI in EC/DMC electrolyte for the first two cycles. The splitting of the (002) peak of the graphitic structure during charging indicates the intercalation process. The appearance of two intense peaks corresponding to the (00\( n+1 \)) and (00\( n+2 \)) reflections also points to the intercalation of FSI\(^{-} \) anions into graphite. After being fully charged, the positions of the two strongest peaks (white dashed lines at 22.76° and 34.40° in 2θ units, 0.39 and 0.26 nm, respectively, in the \( d \)-spacing units) or \( d \)-spacing ratio (0.39/0.26 = 1.5) pointing to stage 1. At stage 1, as follows from computational results, graphite expands by ≈134% upon the FSI\(^{-} \) anion intercalation. \(^{68}\)

### 6. Structural, Morphological, and Size-Related Aspects of the Graphite

Analysis of the available literature shows that in recent years extensive efforts have concentrated on various types of synthetic and natural graphite or materials produced from graphite to maximize the cathodic charge-storage capacity and unravel the structure–electrochemical property relationship. In the following section, we describe the structural, morphological, and dimensional factors and their impact on the electrochemical performance of graphite as a cathode material in GDIBs in detail.

#### 6.1. Structure of the Graphite

The structure of the graphite can be described by two main characteristic parameters such as the degree of graphitization...
DG of natural graphites such as graphite flakes and vein graphite is close to 100%, contrary to, for instance, “amorphous graphite.” Actually, “amorphous graphite” is not structurally amorphous. The name “amorphous graphite” originates from the fact that the crystallinity of amorphous graphite powder is not visible by the naked eye or using optical microscopy. In fact, amorphous graphite is a microcrystalline form of graphite with granular morphology and the lowest DG among natural types of graphite.

DG of artificial graphites strictly depends on their synthesis. Synthetic graphite materials may have a strongly anisotropic structure approaching the properties of the graphite single crystals; the others (majority) may have a lower level of anisotropy. For example, graphite produced by the pyrolysis of methane and other gaseous hydrocarbons (pyrolytic graphite), pyrolysis of petroleum coke (synthetic graphite flakes), or carbon crystallization from molten steel during the steel manufacturing process (kish graphite) have the highest DG among artificial graphite materials. Notably, DG strictly determines the shape of the particle of the graphite material. The graphite material with high DG tends to form an anisotropic structure with well-defined flake-like particles.

The CP of graphite can be described as an ordering perfection of the atoms in the graphite that leads to the low level of...
defects (such as basal dislocations, nonbasal edge dislocations, prismatic screw dislocations, and prismatic edge dislocations), impurities, and structural disorder. Thus, these structural parameters can often represent the level of CP of the graphite. Specifically, a high level of CP corresponds to the smaller amount of the defects, the closest interplanar graphene–graphene distance to the ideal value of 0.3354 nm, and the large size of crystallites. The level of CP can be evaluated by XRD and Raman spectroscopy.\[120–122\] For instance, the average interplanar spacing distance between graphene layers in graphite crystallites (single graphite monocrystals) and their size can be calculated using XRD analysis. Concomitantly, Raman spectroscopy enables the estimation of the defectiveness of the graphite. The Raman spectrum of graphite usually shows a sharp peak at 1580 cm\(^{-1}\) (on the Raman shift scale), known as the G band (which corresponds to the in-plane symmetric C–C stretches), and an additional peak at 1350 cm\(^{-1}\), known as the D band, indicating the structural disorder of graphite such as stacking disorder, defects, etc.\[121,122\] Defectiveness increases significantly on the edges of the graphite crystallites. The ratio of the intensity of the D band to the intensity of the G band (I\(_D\)/I\(_G\) ratio) is often used for quantitative estimation of the level of defects in the graphite and is measured as an average amount of the defects present in the graphite basal plane and the graphite edge plane surfaces (see Figure 7). We note that a more precise approach for the estimation of the level of defects in the graphite requires deconvolution of the D band of the Raman spectra into four bands using Gaussian–Lorentzian fitting.\[124,125\]

In a recent example, the electrochemical performance of various types of graphite with different DG and CP has been assessed in rechargeable aluminum GDIBs (see Figure 8).\[75\] Figure 8a shows the charge-storage capacity of graphites using a typical low-acidity formulation of chloroaluminate ionic liquid (AlCl\(_3\)/EMIMCl; \(r = 1.3\)), wherein the tested materials exhibit drastic differences. As follows from Figure 8a–c, kish graphite flakes have the highest capacity values, the smallest interplanar \(d\)-spacing in their XRD patterns, and the lowest intensity of the D-band in the Raman spectra, which indicate the highest structural perfection (DG and CP). The potato-shaped graphite particles demonstrate much lower structural quality, which is associated with a high intensity of the Raman D-band. Amorphous carbon exhibits the lowest capacity and sloppy voltage profiles. The latter appear to be similar to the intercalation of Li\(^+\) ions into hard carbons, where the high charge-storage capacity is spread over a broad range of potentials.\[126,127\] In the context of the results mentioned above, it can be stated that the electrochemical behavior of the graphite cathode (capacity and voltage profile) with respect to the intercalation/deintercalation of the anions is much more sensitive to the quality of the graphite, even to the rather small difference in degree of graphitization, crystal perfection, or the origin/processing of graphite than in case of conventional intercalation of Li\(^+\) ions.

6.2. Morphology and Size of the Graphite

Apart from the structural aspects, the particle size of the graphite can also significantly influence its electrochemical performance. As indicated in the work of Kravchyk et al.\[96\] the electrochemical performance of large natural graphite flakes can be further improved by their processing into smaller GF, for instance, by sonication. As described by Kravchyk et al.,\[96\] sonication can preserve the GF and CP of the graphite, which contrasts with other mechanical top-down processes, such as ball-milling which partially amorphize the material. Importantly, as stated in that work, the use of small natural GF does not lead to the same result as with processed large GF, even though the size of both is the same/similar, again suggestive of the critical role played by the higher CP of the larger graphite flakes. Likely, this perfection also remains after they are broken into smaller sizes. As to the morphology of graphite particles, the interesting studies had been reported in the same work,\[96\] highlighting the fact...
that the flake shape of the graphite particles also plays an important role. The utmost comparison of the spherical (potato-like) graphite particles and graphite flakes revealed that potato-like graphite particles (used for LIBs) that have bent graphene layers (or sometimes closed edges) showed strongly reduced ability for intercalation of AlCl$_4^-$ anions (contrary to Li$^+$). Specifically, potato-shaped graphite particles exhibited a much lower capacity of 65 mAh g$^{-1}$ for AlCl$_4^-$ anions. In contrast, graphite flakes of large size (0.2–1 mm in lateral size) demonstrated a high capacity of 95 mAh g$^{-1}$ and a high energy efficiency of 90% at an average discharge voltage of $\approx 2$ V.$^{[75]}$ As stated by Kravchyk et al.$^{[96]}$ flake-like particles with clean and accessible edges are necessary for intercalation of large anions. Notably, intercalation of Li$^+$ and bulky anion into graphite shows a huge difference in terms of resulting volume expansion ($\approx 10\%$ for Li$^+$ (for so-called stage 1, i.e., formation of LiC$_6$) and 135–150% for anions, such as FSI$^-$, TFSI$^-$, AlCl$_4^-$, etc., even though the number of ions, in this case, is smaller). Thus, higher volume expansion of graphite during anion intercalation, contrary to Li$^+$, requires the use of such morphology of particles that would be able to accommodate such huge volumetric changes.

7. Current Collector Issues

In contrast to the conventional LIBs, where Al foil is considered an established cathodic current collector, the current collector on the positive side of GDIBs still needs to be developed. Common metals, such as Al and stainless steel, are easily oxidized at the high voltages of 4.5–5.25 V versus Li$^+$/Li employed during graphite cathode operation. The latter causes low Coulombic efficiency of GDIBs. Hence, oxidatively stable current collectors such as tungsten, molybdenum, and glassy carbon are employed in GDIBs. Interestingly, it has recently been proposed to use titanium nitride (TiN) as a compelling material for this purpose. As reported by Wang et al.$^{[103]}$ flexible current collectors were fabricated by a coating of TiN on stainless steel or flexible polyimide substrates by a low-cost, rapid, and scalable method, such as magnetron sputtering. The superior stability of TiN toward electrochemical oxidation enabled a higher Coulombic efficiency of $\approx 99.5\%$ to be achieved at currents of 1–10 A g$^{-1}$ for aluminum GDIBs. The aluminum GDIBs with TiN current collectors also exhibited a high power density of 4500 W kg$^{-1}$ at high graphite loading (10 mg cm$^{-2}$) and was stable for at least 500 cycles. We note that graphitic electrodes without a current collector have also been exploited as an alternative solution to solve the problem of current collector oxidation. For instance, Wang et al.$^{[32]}$ reported so-called freestanding natural graphite film. Figure 9 shows the schematics of the fabrication process of such graphite electrodes. The process includes graphite slurry preparation, slurry tape casting on the Cu foil, and a drying step following the etching of Cu foil by immersing the graphite/Cu electrodes into the iron chloride (FeCl$_3$) solution. Then, the formed graphite films were rinsed with deionized water to remove the residual FeCl$_3$ and then dried at 200 °C for 3 h. The average thickness of graphite films was in the range of 40–60 µm. For electrochemical measurements, the resulting graphite films were bonded to Ni.
bar current collectors by sandwiching conducting carbon tapes between the films and Ni bars to form the graphite cathode (see the photograph in Figure 9 (Step E)).

8. Discussion of Volume Changes in GDIBs

As follows from the mechanism of GDIBs, both graphite and the electrolyte undergo significant volume changes upon charge and discharge. Contrary to a rather small volume increase of graphite during intercalation of lithium ions of ≈10%, the volume of the graphite might expand up to 150% during intercalation of bulky anions.[68,128–131] The latter significantly impact the total volume change of the GDIBs on the cell level. Concomitantly, depending on the molarity or acidity of the electrolyte, its volume can change drastically. For instance, as indicated in Figure 10a,b, in the case of LiFSI in EC/DMC and AlCl₃:EMIMCl electrolytes, their volume might change by up to 50% or 30%, corresponding to depletion of 5 m LiFSI electrolyte solution or highly acidic chloroaluminate electrolyte (r = 2). The higher the molarity or acidity of the electrolyte is, the larger the volume change is. To demonstrate the practical importance of the volume variations in GDIBs during charge and discharge, we have calculated the volume changes of GDIBs composed of graphite cathode with areal capacity of 1 mAh cm⁻² and highly concentrated LiFSI (5.75 m LiFSI in EC/DMC) or chloroaluminate (AlCl₃:EMIMCl, r = 2) electrolytes. For simplicity, it has been assumed that the density of the graphite electrode equals 2.2 g cm⁻³. As shown in Figure 10c, 1 cm × 1 cm sized lithium GDIBs comprise a 48 µm thick electrolyte layer and 65 µm thick graphite electrode. After the charge, however, the thickness shrinks/expands to 30 µm and 111 µm for electrolyte and graphite, respectively. The latter corresponds to the overall 25% volume change upon a charge of lithium GDIBs. Similar results have been found for aluminum GDIBs comprising highly acidic chloroaluminate electrolyte (r = 2), with an ≈23% volume increase upon a charge.

9. Concluding Remarks

While significant progress was achieved in recent years in the development of GDIBs, much room remains for the improvement of gravimetric/volumetric energy densities as well as the development of commercially competitive prototypes with low capital cost. First, the proper engineering and optimization of a high mass loading graphite electrodes are necessary, which would enable the constraint of massive volume changes (of up to 150%) of the graphite particles without their disintegration from the current collector. In this context, the right balance needs to be found between porosity/tortuosity of pristine and charged electrodes to provide fast diffusion of the bulky anions within the electrolyte during the expansion of the graphite. In addition, new battery cell design and separator must be developed assuming substantial volume changes of electrolytes.
during charge and discharge. These factors are critical for securing the long cycling of GDIBs. Additionally, very little is known about the morphological and compositional evolution of active graphite materials during electrochemical cycling, and future studies should expand the use of in situ methods (X-ray tomography, Raman spectroscopy, transmission electron microscopy, small- and wide-angle X-ray scattering, etc.). In the context of impact of the electrolyte amount on the overall energy density of GDIBs, further research should be focused on finding the practical amount of the electrolyte needed for the operation of GDIBs. Most of the studies presented in the literature use a 2–10-fold excess of the electrolytes needed to match the cathodic graphite capacity. The latter is acceptable for research purposes but needs to be optimized in real battery applications. In this case, any problems with low Coulombic efficiency caused by oxidation of the electrolyte will have a profound effect on the electrochemical performance of GDIBs that is almost ignored in scientific publications. Finally, more work needs to be done with respect to the decrease in the redox potential of the Al plating/stripping in aluminum GDIBs, which is ≈1 V higher (≈−0.7 V vs SHE) than the redox potential of Al^3+/Al in aqueous solutions (−1.66 V vs SHE). Simple calculations show that a 1 V increase in the potential would allow increasing the energy density of aluminum GDIBs by up to 20% (to ≈100 Wh kg⁻¹). With these further developments, GDIBs might become mature energy storage technologies ready for the market.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

This research is part of the activities of SCCER HaE, which was financially supported by the Innosuisse – Swiss Innovation Agency.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

energy storage, graphite, graphite cathode, graphite dual-ion batteries

Received: May 31, 2019
Revised: July 3, 2019
Published online: August 7, 2019

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