Sodium ion batteries (SIBs) have been revived as important alternative energy storage devices for large-scale energy storage, which requires SIBs to have a long cycling life and high power density. However, the scarcity of suitable anode materials hinders their application. Herein, we report a bismuth intercalated graphite (Bi@Graphite) anode material, which is substantially different from the previously reported metal@Graphene. In Bi@Graphite, the Bi nanoparticles between graphite interlayers enhance the capacity, while the graphite sheath provides a robust fast electronic connection for long cycling stability. The Bi@Graphite possesses a safe average storage potential of approximately 0.5 V vs. Na/Na⁺, delivers a capacity of ~160 mA h g⁻¹ at 1C (160 mA g⁻¹), exhibits outstanding cycling stability (ca. 90% capacity retention for 10,000 cycles at 20C), and can maintain 70% capacity at 300C (~110 mA h g⁻¹ at 48 A g⁻¹), which is equivalent to full charge/discharge in 12 s. Bi@Graphite demonstrates the highest rate-capability ever reported among all anodes for SIBs. Detailed characterization results indicate that the unique Bi nanoparticle-in-graphite structure and the fast kinetics of ether co-intercalation into graphite are responsible for these significant improvements, which could translate into SIBs with excellent power densities.

**Introduction**

The past decades have witnessed the rapid development of renewable energy sources, such as wind, tide, and solar energy. However, these energy sources are not continuously available. Large-scale electric energy storage battery systems are becoming extremely important to realize the smooth integration of these intermittent energies into the grid because of their flexibility, high energy conversion efficiency and simple maintenance. Sodium-ion batteries (SIBs) have aroused a great deal of interest recently, particularly for large-scale stationary energy storage applications, due to sodium being practically abundant and environmentally benign. The major criteria of stationary batteries for energy storage systems are a long cycle life, high rate capability, low cost, and high safety. The exploration of high-rate anodes with long cycling life is urgently needed. Herein, for the first time, we reported the fabrication of a bismuth intercalated graphite (Bi@Graphite) material through intercalation-conversion reactions. The as-prepared material exhibits the highest capacity retention at high rate (70% at 300C, equivalent to full charge/discharge in 12 s) and one of the longest cycling stabilities (ca. 90% capacity retention for 10,000 cycles at 20C) of all reported anodes for SIBs. The exceptional rate capability and cycling stability of the Bi@Graphite is attributed to the unique sandwich structure with Bi nanoparticles uniformly distributed within the conductive protecting graphite sheath. The Metal@Graphite with metal nanoparticles intercalated into graphite layers offers a new direction for the exploration of the next generation of electrode materials for rechargeable batteries.

**Broader context**

Sodium-ion batteries (SIBs) have aroused a great deal of interest recently, particularly for large-scale stationary energy storage applications, due to sodium being practically abundant and environmentally benign. The major criteria of stationary batteries for energy storage systems are a long cycle life, high rate capability, low cost, and high safety. Hence, an abundant, nontoxic, stable, and high-rate electrode material for SIBs needs to be developed to ensure large-scale and long-term applications, and to decrease battery management costs. Extensive research has been devoted to developing long cycling and high power density electrode materials. Significant performance advances have been achieved in cathodes. Cathode materials with NASICON, P₂, or O₃ structures exhibited long cycling stability as well as high rate capability. However, the advance in anode materials in terms of high rate capability and long cycling stability is still unsatisfactory. Intercalation anodes, for example the well-known LiC₆ in Li-ion batteries (LIBs), which belongs to the binary graphite intercalation compounds (GICs),
cannot be formed as effectively in SIBs, because of the crystalline mismatch between the graphite lattice and sodium ions.8 Until recently, Philipp et al. solved the unfavorable mismatch issue through the mechanism of sodium co-intercalation with ether solvents, forming ternary GICs.9 They demonstrated stable cycling for 1000 cycles. Unfortunately, the low capacity of \( \sim 110 \, \text{mA h g}^{-1} \) and density (\( \sim 2.25 \, \text{g cm}^{-3} \)) cause low gravimetric and volumetric energy densities. More recently, Kang et al.10 further revealed the excellent rate performance (50% capacity retention achieved at a high current density of 10 A g\(^{-1}\) with respect to capacity at a low current density of 1 A g\(^{-1}\)) of natural graphite in ether electrolytes, making graphite an ideal platform for developing high-rate anodes for SIBs. Unlike graphite, hard carbon can deliver higher capacity,11 however, the rate capability and cycle life are still not satisfactory.12 Moreover, the low sodium intercalation potential of hard carbon facilitates the detrimental sodium dendrite formation, especially at high rates, making hard carbon unsuitable as the anode material for large-scale energy storage batteries. On the other hand, theoretical calculation suggests that group IVA and VA metals such as Sn, Sb and Bi are capable of delivering high capacities by forming Na-rich alloys.13 Despite their high theoretical capacity, the practical application of these alloy-based anode materials for SIBs is still a huge challenge. One commonly recognized reason is the capacity decay caused by the aggregation (slower kinetics due to the loss of nanoscale diffusion distance) and pulverization (the loss of electrical contact) of the active materials, which is induced by severe volume variation during sodiation/desodiation. The strategies toward improving the cycle life of alloy-type anodes mainly focus on designing efficient nanostructures and introducing a conductive carbon host/substrate (e.g., carbon nanofibers and graphene), but only limited improvement in the reaction kinetics and cycle life has been achieved.14 Among the applied conductive carbon matrices, graphene has emerged as an attractive alternative to other carbon allotropes because of its fascinating electronic, thermal and mechanical properties, high specific surface areas, and easy availability from graphite.15 However, these methods usually consist of tedious oxidation–exfoliation of graphene, anchoring of a metal precursor onto graphene oxide (GO) and the reduction of GO and the metal precursor to get reduced graphene oxide (rGO) and metal particles, respectively.16 The obvious drawback of these strategies is that the procedure inevitably increases the environmental imperilment, augments the preparation cost, and adds complexity to the preparation processes.17 On the other hand, in such formed composites, graphene is loosely stacked with a much lower conductivity compared with graphite because of there being plenty of defects on the basal plane. The large metal/rGO surface normally leads to large irreversible capacity.13 Moreover, the large volume change of the metal alloy upon sodium ion insertion can only be accommodated to a limited degree, which offers only a modest improvement in cycling stability. It is highly desirable to take advantage of the above excellent properties of graphene while maintaining the close contact between the metal and graphene as well as the integrity of graphene and the graphite structure.

Herein, for the first time we report a method for the direct intercalation of metal nanoparticles (NPs) into graphite layers through the GIC route (Fig. 1). Bi was chosen as a model metal to demonstrate this idea because of its high theoretical gravimetric capacity of 385 mA h g\(^{-1}\), extremely high volumetric capacity (3765 mA h cm\(^{-3}\)) and favorable sodium alloy potential (0.5 V vs. Na\(^+\)/Na) to avoid dendrite formation. Novel sandwich-like Bi@Graphite was synthesized via an intercalation-transformation method. Details of the synthesis and mechanism are included in the ESI.† In such a system, Bi NPs are intercalated between the adjacent graphene layers and tightly immobilized, which can provide a buffer matrix for the volume change of Bi during the charge–discharge cycling, and effectively maintains the active surface and leaves stable and open channels for ion transport. Meanwhile, the low-defect graphene layers in graphite provide higher electrical conductivity and a structural scaffold to prevent the aggregation of Bi, enabling the Bi@Graphite to exhibit extremely fast charge–discharge capacity (70% capacity retention at 300°C with respect to 1°C) as well as excellent stability (90% capacity retention for over 10,000 cycles). Detailed characterizations show that the unique layered structure with Bi nanoparticles confined on the graphite layers plays the key role in the long cycling stability and the ultra-fast rate capability.

Results and discussion

The overall strategy for the synthesis of Bi@Graphite is schematically depicted in Fig. 1. A detailed description is given in the experimental section. Briefly, a KBI alloy was first synthesized by heating a mixture of K and Bi in a double quartz ampule at 550 °C. The X-ray diffraction (XRD) data of the heated K and Bi mixture (Fig. S1a, ESI†) indicate successful alloying of K and Bi, which is also supported by the greenish color of the alloy (K,Bi) after synthesis. Subsequently, the KBI alloy was mixed with highly crystallized graphite (Fig. S1b, ESI†) and Bi by hand milling using a mortar and pestle in a glove box, and then sealed under vacuum in a double ampule setup again and heated to 550 °C for intercalation. The XRD pattern of the as-synthesized KBI–GIC powders showed several peaks with d-spacings of 13.26, 6.62, and 4.42 Å (Fig. 2a), corresponding to the reflections of (001), (002), and (003), respectively. This suggests a stage-Ih-type structure, where the KBI alloy intercalates in between every two graphene layers (KBI\(_{0.8}\)C\(_{0}\)). The absence of the (002) reflection at 2θ = 26.6° of graphite suggests a complete intercalation of graphite by the KBI adducts.

The stoichiometry of this stage-Ih KBI–GIC is KBI\(_{0.8}\)C\(_{0}\) as previously determined by chemical analysis.18 For the next step, the as-prepared KBI–GIC was initially washed with ethanol to deintercalate K in KBI–GIC to form Bi@Graphite,19 and also to react with the unintercalated...
KBI alloy yielding Bi, which was evidenced by the emergence of strong Bi reflections in the XRD pattern (Bi + Bi@Graphite in Fig. 2a). These strong Bi reflections are from two different groups of Bi particles (Bi outside and Bi@Graphite). The Bi metal particles outside the graphite are then removed by washing with dilute nitric acid, while the Bi intercalated between graphite sheets in the Bi@Graphite was well-protected by the graphite layers from nitric acid, as demonstrated by Bi diffraction peaks in the XRD pattern of Bi@Graphite in Fig. 2a. The inside Bi NPs are well protected by the micro-sized graphite substrate with low surface area, and are expected to achieve higher reversible capacity, better rate performance and a long cycle life.

The XRD peaks of Bi in Bi@Graphite are much broader compared to the Bi peaks in the XRD patterns of Bi + Bi@Graphite or Bi. The broadening of these peaks suggested a significant reduction in the crystallite sizes of Bi after intercalation–deintercalation, and the crystallite sizes were estimated from the XRD data using the broadening analysis proposed by Balzar et al. and implemented in the TOPAS 4.2 package. A LaB₆ standard was used for the calibration of instrument broadening, and the subsequent refinement procedures were described elsewhere. The broadening analysis gave the crystallite sizes of 11 ± 1, 46 ± 3, and 193 ± 10 nm for the Bi phase in Bi@Graphite, Bi + Bi@Graphite, and Bi samples, respectively (Fig. S2, ESI†). This is expected for Bi@Graphite since all of the Bi nanoparticles are located between the graphite layers. During the deintercalation of K, the graphite layers blocked the possible aggregation of the Bi NPs, resulting in a much smaller crystallite size for Bi in the Bi@Graphite.

The graphite structure in the Bi@Graphite is characterized using Raman spectroscopy, which is a powerful tool for studying the structure of graphitic carbon materials. Usually, the Raman spectrum of a graphitic carbon material consists of the D-, G-, and 2D-bands of carbon. The D-band (1330–1340 cm⁻¹) is associated with the defect-activated breathing modes of six-membered carbon rings, and the G-band (1580–1600 cm⁻¹) is assigned to the E₂g phonons at the Brillouin zone center, while the 2D band corresponds to the second order of zone-boundary phonons. Specifically, the intensity ratio of D- to G-bands, I_D/I_G, reflects the defect density in graphene. It should be noted that our method is non-destructive to graphene sheets, as confirmed by the negligible increase of I_D/I_G from 0.072 for graphite to 0.094 for Bi@Graphite, which is in sharp contrast to the common value of 0.8–1.7 for GO and rGO. The major difference between the Raman spectra of graphite and Bi@Graphite is the 2D feature. The 2D peak in the bulk graphite consists of two components 2D1 and 2D2, typical for graphite or > 5 layer graphene. While the 2D peak of Bi@Graphite is much broader with respect to graphite, indicating the existence of few-layer graphene in the Bi@Graphite. Usually, after the deintercalation of intercalants, the graphite structure can be fully restored by the restacking of graphene sheets. The unusual phenomenon in the case of Bi@Graphite reflects that the remaining Bi NPs act as spacers located in between the graphene sheets that prevent the full re-stacking of the graphene sheets.

The structure and the morphology of the Bi@Graphite were further characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis. The SEM images of the Bi@Graphite show a typical platelet structure (Fig. 3a), similar to the precursor graphite (Fig. S5, ESI†), indicating that the flake morphology of the graphite has been well retained. Both the graphite and Bi@Graphite exhibit a very smooth and clean surface (Fig. S4, ESI†), and no Bi particles outside the graphite can be observed in the Bi@Graphite (Fig. S4a, ESI†). Instead, some particles can be seen under the superficial graphene sheets in the enlarged SEM images of Bi@Graphite. The existence of Bi in the Bi@Graphite is further verified by elemental mapping using energy-dispersive X-ray spectroscopy (EDS). As shown in Fig. 3b, the signal of Bi coincides with the carbon signal from graphite except the carbon tape (for SEM testing) in the top right corner. The low-magnification SEM image and EDS mapping further confirmed the uniform Bi distribution in all of the graphite particles on a large scale (Fig. S5, ESI†). Since no Bi NPs can be seen on the surface of Bi@Graphite, the Bi signal can only be attributed to the Bi inside graphite. The unique Bi-in-graphite structure in the Bi@Graphite has been further proved by TEM. It can be clearly seen that the dark spots, which are Bi NPs, locate between the graphene layers in graphite (Fig. 3c). The high-resolution TEM
HRTEM image (Fig. 3d) of the Bi@Graphite reveals two sets of lattice fringes: a spacing of 0.327 nm in the NPs corresponding to the (012) planes of Bi; and 0.335 nm for the graphite (002) planes at the periphery, respectively.

As expected, Bi NPs are well preserved in the Bi@Graphite, and tightly wrapped by graphene sheets in the graphite as schematically demonstrated in Fig. 1. This is the first report of the synthesis of a metal nanoparticle intercalated graphite composite for metal ion batteries. The electrochemical performance of the Bi@Graphite as an anode material for SIBs was firstly evaluated using galvanostatic charge/discharge cycling. The specific capacity (mA h g\(^{-1}\)) and the current density (mA g\(^{-1}\)) are calculated based on the total mass of the active material including both the Bi and graphite material. Fig. 4a shows the charge–discharge curves of the Bi@Graphite at 80 mA g\(^{-1}\) within the potential window of 1.8–0.01 V. The Bi@Graphite delivered a discharge capacity of ~220 mA h g\(^{-1}\) and a charge capacity of 164 mA h g\(^{-1}\) in the first cycle, corresponding to an initial Coulombic efficiency of 74.5%. The small amount of irreversible capacity is mainly attributed to the reduction of the surface functional groups of graphite with minor contribution from forming an isolated solid electrolyte interface (SEI). This initial Coulombic efficiency is higher than those of graphene based anodes, which typically give values below 50%.\(^{28}\)

The overlap of subsequent discharge/charge curves indicates the excellent reversibility of the Bi@Graphite electrode during sodiation/desodiation cycles. It should be noted that the capacity of Bi@Graphite is 45% more than that of the precursor graphite of ~110 mA h g\(^{-1}\) (Fig. S6a, ESI†), indicating that a higher energy density than that of graphite can be achieved using the Bi@Graphite electrodes. The capacity originating from the graphite and Bi was calculated from the galvanostatic charge/discharge curves in Fig. 4a by attributing the two 1:2 plateau capacity to Bi, which corresponds to the two-step alloying reaction of Bi as expressed below:\(^{29}\)

\[
\text{Bi} + \text{Na}^+ + e^- \leftrightarrow \text{NaBi} \quad (1)
\]

\[
\text{NaBi} + 2\text{Na}^+ + 2e^- \leftrightarrow \text{Na}_3\text{Bi} \quad (2)
\]

Accordingly, graphite and Bi contribute 54 and 106 mA h g\(^{-1}\) composite\(^{-1}\), respectively. Given the 30% Bi content in the Bi@Graphite determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), the specific capacity with respect to Bi is 353 mA h g\(^{-1}\), slightly higher than the capacity of pure Bi (~330 mA h g\(^{-1}\)) with micro-size after activation cycles (Fig. S7a, ESI†), indicating a better utilization of Bi in the case of Bi@Graphite electrodes. On the other hand, the specific capacity of graphite is only 77 mA h g\(^{-1}\), lower than the 110 mA h g\(^{-1}\) obtained from graphite electrodes (Fig. S6a, ESI†). The partial loss of capacity for the graphite is due to

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![Fig. 4](https://example.com/fig4.png)

*Fig. 4* (a) Galvanostatic charge/discharge curves of the as-synthesized Bi@Graphite composite at a constant current of 80 mA g\(^{-1}\) in the voltage window 0.01–1.8 V at room temperature (25 °C); (b) rate capability at different charge/discharge rates; (c) voltage–capacity curves at different rates (increased from 1C to 300C); (d) comparison of rate capability with the reported anodes for SIBs.\(^{10,30–38}\)
Bi NPs occupying spaces and spots where solvated sodium should be stored. It is also worth noting that the volumetric capacity was significantly increased by 88% from ~250 mA h cm\(^{-3}\) (co-intercalation capacity of graphite) to 470 mA h cm\(^{-3}\) for Bi@Graphite, which is beneficial for volumetric capacity-sensitive applications such as portable electronics and electrical vehicles.\textsuperscript{39}

The unique Bi-in-graphite structure in Bi@Graphite enables its capability to be discharged/charged at ultra-high rates. A rate of \(nC\) corresponds to a full charge/discharge in \(1/n\)h (according to the stable capacity of 160 mA h g\(^{-1}\) of Bi@Graphite, the rate of 1C indicates a discharge/charge current density of 160 mA g\(^{-1}\)). Fig. 4b presents the rate capability of the Bi@Graphite composite with the corresponding charge–discharge curves plotted in Fig. 4c. As can be observed, the Bi@Graphite electrode delivers a capacity of 155 mA h g\(^{-1}\) at 10C. At a 100C discharge/charge rate (36 s to total charge or discharge), more than 140 mA h g\(^{-1}\) can still be achieved. Even at a much higher rate of 300C (12 s to full charge or discharge), a capacity of 113 mA h g\(^{-1}\) (70% of the capacity at 1C) is obtained. Moreover, when the rate is finally returned to 2C after over 1000 cycles, a capacity of 156 mA h g\(^{-1}\) (98.7% of the initial 158 mA h g\(^{-1}\)) is recovered, implying the excellent tolerance for the rapid sodium ion insertion/extraction reactions as well as good stability of the Bi@Graphite electrode. To the best of our knowledge, the capacity retention of the Bi@Graphite at high rates is the highest ever reported for anodes in SIBs (Fig. 4d). In comparison, the Bi electrode can only retain 15.2% of its capacity when charged/discharged at 64C (Fig. S7b and c, ESI\textsuperscript{†}). The clear difference in capacity retention at high rates demonstrates that the high rate capability of the Bi@Graphite is closely related to its unique Bi-in-graphite structure.

To understand the mechanism for high rate capability of the Bi@Graphite, the rate performance of graphite and microsized pure Bi was also evaluated in the same electrolytes. As shown in Fig. S6b (ESI\textsuperscript{†}), at a high rate of 300C, the graphite electrode can retain 80 mA h g\(^{-1}\) (74.8% with respect to 107 mA h g\(^{-1}\) at 1C). The charge/discharge curves of the graphite electrode at different rates are shown in Fig. S6c (ESI\textsuperscript{†}), demonstrating the fast kinetics of the graphite. These results are in accordance with previous reports on fast co-intercalation of graphite by ether-solvated sodium ions.\textsuperscript{10} It is worth noting that the fast kinetics of co-intercalation into graphite can be clarified as follows. In the traditional carbonate electrolyte, SEI will be formed in the first discharge. The Li-ions intercalating into graphite have to dissociate the coordinated solvent first, and then transport through the SEI, transfer the charge, and finally intercalate into the graphite. The desolvation of Li-ions limits the reaction kinetics of electrochemical Li intercalation.\textsuperscript{10} Different from the Li-ion intercalation, the co-intercalation of Na-ions with ether solvent (in our case, Na-ions with DME molecules) eliminates the desolvation step, which greatly accelerates the reaction kinetics. On the other hand, the Bi anodes show much higher capacity (theoretical 385 mA h g\(^{-1}\)) but much worse rate capability (Fig. S7b, ESI\textsuperscript{†}) than graphite (Fig. S6b, ESI\textsuperscript{†}). To increase the graphite capacity without sacrificing the high rate performance, nano-sized Bi should be intercalated into the graphite layer as we synthesized in the Bi@Graphite, which also prevents Bi pulverization/aggregation and maintains a similar cycle life to the graphite. In addition, the uniform nanoscale (~10 nm) active material Bi affords a shorter Na\(^+\) transport pathway, enhancing the alloying reaction kinetics and the utilization of the active material upon discharge and charge. The Bi-in-graphite structure not only provides the excellent structural stability of the composite, but also provides continuous conductive paths between Bi NPs, and therefore reduces the particle to particle interfacial resistance.

The controlling step for the rate performance of the Bi@Graphite electrode was further investigated using cyclic voltammetry (CV) at different scan rates from 0.1 to 2 mVs\(^{-1}\) (Fig. 5a). In theory, the voltammetric response of an electrode-active material at various sweep rates can be summarized as follows:\textsuperscript{41}

\[ i = a v^b \]

in which the measured current (\(i\)) at a fixed potential obeys a power-law relationship with the potential sweep rate (\(v\)). For a redox reaction limited by semi-infinite diffusion, the peak current \(i\) follows a linear relationship with \(v^{0.5}\) (i.e., \(b = 0.5\)); for a capacitive process, it varies with \(v\) (i.e., \(b = 1\)).

As shown in Fig. 5a, there are 5 distinguishable cathodic (discharge, sodiation) and 3 anodic (charge, desodiation) peaks in the CV curves of Bi@Graphite, denoted as D1–D5 (discharge) and C1–C3 (charge), respectively. The two largest peaks in the CV curves are in good agreement with the two main plateaus in the discharge/charge curves. By carefully comparing the CV curves of the Bi@Graphite (Fig. 5a), graphite (Fig. 5b), and Bi (Fig. 5c), we can assign the D1, D2 and D4 peaks in Bi@Graphite to graphite, and D3 and D5 mainly to Bi, respectively. While the C1 and C2 peaks are the overlapping of graphite and Bi capacity, C3 can be attributed solely to graphite. Fig. 5d–f shows the \(b\)-value for each peak derived from linear fit of \(\log(i)\) vs. \(\log(v)\) plots at each peak potential (Fig. S8–S10, ESI\textsuperscript{†}). It can be seen that graphite-related processes have \(b\)-values approaching 1, indicating a fast capacitive-dominant characteristic; while the Bi-related processes have \(b\)-values close to 0.5, indicating a redox reaction (alloying for the case of Bi) behavior.\textsuperscript{29} Thus the whole capacity of the Bi@Graphite can be divided into two parts, fast capacitive capacity from the graphite sheath and diffusion-controlled alloying capacity from the Bi cores.

Since all the rate performances for Bi@Graphite, graphite and Bi were tested in a two-electrode Bi@Graphite||Na cell, the impact of the Na counter electrode on the voltage polarization of the cells was evaluated in a symmetrical Na||Na cell using the same electrolyte. As shown in Fig. S11a (ESI\textsuperscript{†}), the overpotential can be as high as ~300 mV when the current density reaches 30 mA cm\(^{-2}\) (corresponding to 300C in the Bi@Graphite||Na cell). Considering the symmetrical Na||Na cell structure, it is believed that ~150 mV out of the overall ~350 mV overpotential (Fig. 4c) in the Bi@Graphite||Na is from the electrolyte and Na metal side at 300C (similar current density as shown in Fig. S11b, ESI\textsuperscript{†}). Therefore, the rate performance will be further improved if an electrolyte with higher conductivity is employed and/or an ultra-high rate cathode is paired.

The rate performance of the Bi@Graphite has also been tested at different temperatures from −20 to 60 °C (Fig. S12, ESI\textsuperscript{†}). It is noted
Fig. 5  (a–c) CV curves at different sweep rates (0.1–2 mV s\(^{-1}\)) of the (a) Bi@Graphite composite, (b) graphite, and (c) Bi electrode; and (d–f) the corresponding \(b\)-value of different current peaks.

Fig. 6  (a) Cycling test at 20C after 20 cycles at 0.5C. (b) SEM image of the Bi@Graphite flakes on Cu foil after cycling and the corresponding C, Na, and Bi, elemental mapping images; (c and e) TEM and (d and f) HRTEM images of the Bi@Graphite after cycling.
that this material can work well within a wide temperature range. At low temperatures, the rate capability becomes lower due to the decreased ionic conductivity of the electrolyte as well as more sluggish ion diffusion inside the graphite. At high temperatures, the rate performance is slightly better than that at room temperature (25 °C) because of the increased ionic conductivity. By comparing the performance in the range of −20 to 60 °C, it can be concluded that at temperatures over 20 °C, the rate determining step is no longer the electrolyte conductivity but the ion transport inside the material. Another interesting phenomenon is the voltage shift of the graphite intercalation plateau. A graphite intercalation reaction is known to be exothermal, thus the lower the temperature, the more favourable the intercalation reaction, and the higher the intercalation potential. In our case, the voltage plateau of the graphite intercalation reaction at 20 °C locates between the two plateaus of Bi sodiation. Upon heating to 60 °C, it downshifted and merged with the lower Bi sodiation plateau. When cooled down below 0 °C, it upshifted and merged with the higher Bi sodiation plateau. This further confirms the prior assignation of the 0.57 V plateau to the co-intercalation of solvated Na⁺ into graphite.

The Bi@Graphite electrode also shows exceptional cycling stability; as shown in Fig. 6a and Fig. S13 (ESI†), the capacity retention is as high as ~90% for over 10 000 cycles at 20C and ~96% for over 600 cycles at 2C, respectively. It should be pointed out that the stable cycling is still on going without any decaying trend, and the cycling Coulombic efficiency is over 99.9%, higher than the typical values of ~98–99.5% for graphene-based materials. The safe average discharge voltage of approximately 0.5 V, outstanding rate capability, and excellent cycling stability makes Bi@Graphite a promising anode material for the next-generation of high energy low cost SIBs.

The morphology and the composition of the Bi@Graphite after cycling were characterized using SEM, TEM, and HRTEM techniques. Fig. 6b shows the morphology and elemental mapping of the Bi@Graphite after the 100th charge/discharge cycle. The original morphology of a flake-like shape is well preserved. Moreover, the surface is smooth without any cracks (Fig. S14, ESI†), demonstrating that the graphite is robust enough to accommodate the volume change of Bi NPs. As can be seen from the elemental mapping, the Bi element signal still overlaps the carbon element signal, similar to the elemental mapping results before cycling (Fig. S15, ESI†), indicating that Bi is still located in the graphite layers after cycling. The detailed TEM and HRTEM images in Fig. 6c-f also confirm that the Bi@Graphite core-sheath structure is retained. The Bi NP cores indicated by the lattice fringes of the Bi 012 planes (Fig. 6f) are well covered by the graphite sheath indicated by the graphite 002 planes (Fig. 6d). This structural characteristic effectively provides a highly conductive pathway and highly stable matrix for the inner Bi NPs.

Conclusions

In summary, uniform Bi NPs with a size of ~10 nm were successfully intercalated into the graphite layers by the co-intercalation of K and Bi and then depotassiation. Benefiting from the unique sandwich structure with Bi NPs uniformly distributed among the graphite layers in a conductive protecting graphite sheath, the Bi@Graphite composites provide an extremely high rate capability (70% capacity retention at 300C with respect to 1C) at room temperature, which is the highest capacity retention of an anode material for SIBs charged/discharged at such a rate (Fig. 4d). Besides, the Bi@Graphite composite electrode can maintain a reversible capacity of 142 mA h g⁻¹ at 20C after over 10 000 cycles with a capacity retention of ~90%. Considering the low cost of the raw materials, the Bi@Graphite is an ideal anode material for stationary SIBs. On the other hand, the reported method provides a new way to synthesize a metal–carbon composite in which both the advantages of the high capacity of the metal and the high conductivity of graphite can be fully utilized. It should also be noted that the chemistry of GICs is very rich. In addition to Bi@Graphite, this method can be further applied to the preparation of Metal@Graphite using IVA and VA metals such as Sn and Sb with higher capacities. The Metal@Graphite with metal nanoparticles intercalated into the graphite layers could open up a novel avenue for both the fundamental research and practical application of highly stable, high-rate, alloying-type anode materials for SIBs.

Conflicts of interest

The authors declare no competing financial interest.

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