SPECIAL TOPIC: Graphene Oxides towards Practical Applications

A high-volumetric-capacity bismuth nanosheet/graphene electrode for potassium ion batteries

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ABSTRACT Potassium ion batteries (PIBs) with high-volumetric energy densities are promising for next-generation low-cost energy storage devices. Metallic bismuth (Bi) with a structure similar to graphite, is a promising anode material for PIBs due to its high theoretical volumetric capacity (3763 mA h cm⁻³) and relatively low working potential (−2.93 V vs. standard hydrogen electrode). However, it experiences severe capacity decay caused by a huge volume expansion of Bi when alloying with potassium. This study reports a flexible and free-standing Bi nanosheet (BiNS)/reduced graphene oxide composite membrane with designed porosity close to the expansion ratio of BiNS after charging. The controlled pore structure improves the electron and ion transport during cycling, and strengthens the structural stability of the electrode during potassiation and depotassiation, leading to excellent electrochemical performance for potassium-ion storage. In particular, it delivers a high reversible volumetric capacity of 451 mA h cm⁻³ at the current density of 0.5 A g⁻¹, which is much higher than the previously reported commercial graphite material.

Keywords: potassium ion batteries, high volumetric energy density, bismuth nanosheet, controlled pore structure, graphite

INTRODUCTION

Recently, energy storage devices with high volumetric energy density and low cost have become more and more important for commercial applications [1–5]. Potassium ion battery (PIB), a newly developed energy storage system, is a promising candidate due to the low standard electrochemical potential of K⁺/K (−2.93 V vs. standard hydrogen electrode SHE) and the abundance of potassium resource in the earth's crust [6–13]. Graphite is a

commercialized anode material for batteries, showing a limited theoretical volumetric capacity of about 627.7 mA h cm⁻³ [14]. To improve the volumetric energy density of PIBs, many anode materials with high theoretical volumetric capacity and low charge-discharge platforms are explored, including antimony (Sb), bismuth (Bi), tin oxide (SnO₂), and phosphorus (P) [9,15–18]. Among them, Bi is an outstanding candidate for PIBs because of its high theoretical volumetric capacity of 3763 mA h cm⁻³ and relatively low working potential [19–22]. However, Bi endures a large volume expansion of ~411% during the charge and discharge processes, resulting in severe capacity decay. In addition, the large size of K⁺ (1.38 Å) could hinder the ion transport [15,17,23]. In the previous studies, constructing porous structures is a common strategy to inhibit the volume expansion, which provides extra space to accommodate the expansion [20,21,24]. However, the volumetric capacity of electrodes is also sacrificed to the range of 100–300 mA h cm⁻³ [1]. Therefore, a proper structural design of electrodes is crucial for achieving high volumetric energy density of the batteries.

Two-dimensional (2D) materials are promising for energy storage application due to their large interlayer spacing for the insertion/extraction of ion and large specific surface providing active sites for ion storage. Besides, used as the anode material for Li/Na ion batteries, bismuth nanosheets (BiNSs) have shown excellent structural stability due to the small lateral expansion during charge-discharge processes [25]. In this study, BiNS/reduced graphene oxide (rGO) composite membrane electrodes for PIBs with high volumetric energy density and electrochemical stability have been fabricated.

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Gas expansion and mechanical compression were combined to engineer the pore structure of the BiNS/rGO membrane (denoted as BiNS/rGO-30). The fabricated membranes are free-standing, flexible, highly conductive and with a porosity close to the expansion ratio of BiNS after charging. This membrane structure improves the electron and ion transport during cycling, and consolidates the structural stability of the electrode during the potassiation and depotassiation processes. The PIB with BiNS/rGO-30 as an anode exhibits a reversible specific capacity of 272 mA h g^{-1} after 90 cycles at 0.5 A g^{-1} and retains a capacity of $\sim 100 \text{ mA h g}^{-1}$ at 10 A g^{-1} . Moreover, the BiNS/rGO-30 electrode shows a high reversible volumetric capacity of 451 mA h cm^{-3} after 90 cycles at 0.5 A g^{-1} and a high reversible volumetric capacity of 197 mA h cm^{-3} after 700 cycles at 5 A g^{-1} because of the relatively dense structure design. For comparison, the BiNS/rGO electrode without mechanical compression (denoted as BiNS-rGO-P) only delivers a reversible volumetric capacity of 112 mA h cm^{-3} at 0.5 A g^{-1} .

EXPERIMENTAL SECTION

Materials preparation

All solvents and chemicals were of analytical grade and used without further purification. GO was synthesized with natural graphite flakes by an improved method [26].

Exfoliation of metallic BiNSs

In a typical process, 1 g Bi powder (7440-69-9, Macklin) was suspended in 100 mL of *N*-methyl-2-pyrrolidone (NMP, 872-50-4, Macklin) followed by probe sonication (VCX500, Sonics) for 12 h in a reflux device. The power output of the cell disruptor was set at 650 W. The product obtained was centrifuged at 1000 rpm for 15 min to obtain a supernatant. The supernatant was further centrifuged under 7000 rpm for 15 min to obtain the sediment. The obtained sediment was re-dispersed in a certain amount of NMP under an ultrasonic process for 0.5 h and the solution obtained was calibrated for use.

Synthesis of flexible BiNS/rGO membranes

Typically, the as-prepared thin BiNSs were mixed uniformly with GO at a mass ratio of 4:1 to form a dispersion. The composite membrane was prepared after vacuum filtration. The obtained composite membrane was chemically reduced by hydrazine hydrate at 65°C for 5 h. After that, flexible BiNS/rGO membrane was obtained. To prepare a BiNS membrane, the as-prepared

thin BiNS solution was directly vacuum filtrated. The mass loading of BiNSs was about 5.4 mg cm^{-2} . To investigate the electrochemical performance of the BiNS/rGO membranes with different areal loading of active material, BiNSs with areal loadings of 8.1 and 10.8 mg cm^{-2} were prepared by using the same experimental procedure. Besides, the BiNS/rGO membranes with the composition of BiNSs and GO at the mass ratios of 7:3 and 6:4 were prepared to investigate the effect of GO content on the electrochemical performance of the prepared electrode. The prepared BiNS/rGO membranes were set between two sheets of weighing paper and compressed under roller press with a certain rolling clearance (20 or $30 \mu\text{m}$) to engineer their pore structures.

Structure and morphology characterization

The structures of the obtained samples were characterized by X-ray powder diffraction (XRD, MDTC-EQ-M21-01) and Raman spectroscopy (HORIBA LabRAM HR800). Filed-emission scanning electron microscopy (FESEM, MDTC-EQ-M18-01), transmission electron microscopy (TEM, JEOL, Tokyo, Japan) and high-resolution TEM (HRTEM) were used to characterize the morphologies of the samples. The X-ray photoelectron spectroscopy (XPS) measurements (PHI5000 VersaProbeII) were performed to analyze the chemical states of the obtained samples.

Electrochemical measurements

The free-standing BiNS/rGO (or BiNS) membranes were directly used as the working electrode to assemble 2032 coin cells with K metal as counter and reference electrodes. The electrolyte consisted of 1 mol L^{-1} KPF₆ in dimethoxyethane (DME). Glass fiber (Whatman) was used as a separator film. The cells were assembled in an argon-filled glove box where both moisture and oxygen levels were kept below 0.1 ppm. The galvanostatic charge-discharge tests were conducted at a voltage range of 0.1–1.5 V. The specific capacity was calculated on the basis of the active BiNS (or Bi) materials. Cyclic voltammogram (CV) measurements were conducted at a scan rate of 0.2 mV s^{-1} on an electrochemical workstation (VMP-300, Bio-Logic). Electrochemical impedance spectroscopy (EIS) measurements were performed on the same electrochemical workstation in the frequency range from 100 kHz to 0.01 Hz.

RESULTS AND DISCUSSION

According to the previous reports [22,27], a three-step electrochemical reaction process occurs during the potassiation of Bi (Fig. S1), with the final potassiation pro-

duct of $K_3\text{Bi}$ retaining the 2D layer feature based on the arrangement of Bi atoms [27]. Besides, the distance between the adjacent Bi atoms in $K_3\text{Bi}$ expands by 277% along the z -axis and expands by 135% along the x -axis or y -axis during alloying (Fig. S2). Such a drastic expansion along the z -axis would greatly deteriorate the performance of Bi-based electrodes for batteries [28].

Exfoliation of bulk Bi into thin BiNSs and reassembling them into a controlled porous structure could possibly tackle the volume expansion. Bi powder was subjected to ultrasonication to fabricate BiNSs. FESEM and TEM images reveal that the granular-shaped Bi powder with particle size of about tens of micrometer (Fig. S3) was exfoliated into BiNSs with a lamellar shape and small size ($\sim 1\ \mu\text{m}$) (Fig. 1a and b). According to the atomic force microscopy (AFM) result, the thickness of BiNS is about 4 nm (Fig. S4). The HRTEM characterization (Fig. 1c) shows the clear lattice fringe of the dominating (012) crystal plane of Bi with a d -spacing of 0.322 nm, which demonstrates that the rhombohedral phase of Bi with a space group of $R3m$ is not changed after exfoliation. The crystallographic structure and phase purity of the pristine Bi powder and BiNS were investigated. The XRD results in Fig. 1d show that the pristine Bi sample exhibits a standard diffraction pattern of Bi, while the BiNS shows diffraction peaks at the same position but broadened. The dominating peak of (012) is broadened, which indicates

the decrease of the thickness of Bi crystals and proves the successful exfoliation [1,29]. The broad baseline between 15° and 30° in the spectrum of the exfoliated sample is ascribed to the amorphous silica from the XRD sample holder that we used in this experiment. No extra peaks appear in the XRD pattern of the exfoliated product, indicating that no observable side reaction was triggered during the probe sonication. Fig. 1e shows the Raman spectra of the pristine Bi powder and BiNS. It can be seen that the Raman characteristic peaks (E_g , A_g^1) of Bi are also widened after probe sonication, which further proves the decrease of the thickness of Bi crystals [1,29]. Fig. 1f shows the XPS results of the pristine Bi powder and BiNS. Compared with the pristine Bi powder, no other signal is detected in the exfoliated BiNS, indicating its high quality.

The obtained BiNS dispersion was directly filtrated to form a membrane. However, the pure BiNS membrane was unable to be freestanding and showed limited flexibility. To address these issues, GO was introduced to reinforce the membrane. The GO was mixed with the BiNS dispersion and further filtrated to form a membrane (Fig. 2). Because of the high processability and mechanical properties of GO, a freestanding filtrated membrane can be fabricated [30–32]. To improve the conductivity of the as-prepared membrane and engineer its pore structure, BiNS/GO membrane was reduced by hydrazine

Figure 1 FESEM (a) and TEM (b) images of the exfoliated BiNS. The granular-shaped Bi powder was exfoliated into BiNS with a lamellar shape and small size. (c) HRTEM image of the exfoliated BiNS. After exfoliation, the lattice fringe of the dominating (012) crystal plane of Bi can be seen clearly in BiNS, indicating the rhombohedral phase of Bi with a space group of $R3m$ is not changed. (d) XRD patterns of the pristine Bi powder and the exfoliated BiNS. The dominating peak of (012) is broadened after exfoliation, indicating the decrease of the thickness of Bi crystals. (e) Raman patterns of the pristine Bi powder and the exfoliated BiNS. Raman characteristic peaks (E_g , A_g^1) of Bi are widened after exfoliation, which proves the decrease of the thickness of Bi crystals. (f) XPS spectra of the pristine Bi powders and the exfoliated BiNS. Compared with the pristine Bi powders, no other signal is detected in the exfoliated BiNS, indicating the exfoliated BiNS with high quality.

Figure 2 Schematic illustration of the fabrication of the relatively dense BiNS/rGO membrane. A porous BiNS/rGO membrane was prepared after the BiNS/GO membrane was transferred into a hydrazine hydrate atmosphere under 65°C to reduce GO chemically into rGO. After further compression of the obtained BiNS/rGO membrane under roller press, a relatively dense BiNS/rGO membrane was obtained.

hydrate under 65°C to obtain BiNS/rGO membrane. Importantly, a large amount of gases were generated during reduction, and the dense membrane was expanded into a porous structure (Fig. 3a). The thickness of the as-prepared porous BiNS/rGO membrane (denoted as BiNS-/rGO-P) is about 120 μm and the porosity is about 93.2%. The elemental mappings of bismuth and carbon reveal a uniform distribution of Bi in the rGO matrix (Fig. S5a–d). After further compression of the BiNS/rGO-P membrane under roller press with a rolling clearance of 30 μm , a relatively dense BiNS/rGO membrane (denoted as BiNS/rGO-30) with much reduced porosity of 68.7% was obtained (Fig. 3b). The thickness of the BiNS/rGO-30 membrane is about 26 μm . It is worth noting that the porosity of the membrane approximates to the expansion ratio of the BiNS after charging. Compared with the BiNS membrane, the as-prepared BiNS/rGO-30 membrane is freestanding and bendable, and exhibits significantly improved mechanical properties (Fig. 2). To verify the superiority of the structure of the BiNS/rGO-30 membrane for potassium ion storage, a BiNS/rGO membrane with much denser structure was prepared by compressing the BiNS/rGO-P membrane under roller press with a rolling clearance of 20 μm (denoted as BiNS/rGO-20). The thickness of BiNS/rGO-20 membrane is about 10 μm and the porosity of the BiNS/rGO-20 membrane is about 18.57 % (Fig. S6).

The BiNS/rGO-P membranes were further characterized by XRD and Raman techniques. Fig. S7a shows the XRD pattern of the BiNS/rGO-P membrane. Similar diffraction peaks to that of BiNS were observed, indicating no side reaction during the vacuum filtration and reduction. Fig. S7b shows the Raman spectrum of the BiNS/rGO-P membrane. Besides the widened peaks of Bi, the prepared BiNS/rGO-P membrane shows two broad

Figure 3 FESEM images of the BiNS/rGO-P membrane (a) and BiNS/rGO-30 membrane (b). The BiNS/rGO-P membrane has a porous structure with thickness of about 120 μm . After compression, the BiNS/rGO-30 membrane has a relatively dense structure with thickness of about 26 μm . (The porosity of membrane was calculated based on the following formula: $P=(1-\rho_0/\rho)\times 100\%$, where P is the porosity of membrane, ρ_0 is the density of membrane, and ρ is the density of raw material.)

peaks at about 1580 cm^{-1} (G-band) and 1350 cm^{-1} (D-band), corresponding to the E_{2g2} graphitic mode and the defect-induced mode, respectively [33,34]. The intensity ratio of I_D/I_G in Raman spectrum that reflects the defective nature of the rGO is about 1.22, indicating the successful reduction of GO [33,35]. The XRD pattern of the BiNS/rGO-30 membrane was also characterized. It exhibits similar diffraction patterns to BiNS/rGO-P, indicating no side effects occurred during the compression process (Fig. S8).

The basic potassium storage performance of the freestanding BiNS/rGO-30 membrane was tested by using BiNS/rGO-30 as an anode electrode. Fig. 4a shows the CV curves of BiNS/rGO-30 as anode for PIBs in the voltage range of 0.1–1.5 V. During the first potassiation, a broad cathodic peak appears at about 0.24 V due to the potassiation of Bi and the formation of a solid-electrolyte interface (SEI) [21,36]. After the first cycle, three distinct couples of redox peaks appear at 1.16/0.92, 0.65/0.41, and 0.59/0.32 V, corresponding to the reversible transforma-

Figure 4 (a) CVs of BiNS/rGO-30 electrode between 0.1 and 1.5 V in PIBs at a potential sweep rate of 0.2 mV s⁻¹. The CV curves almost overlap after the first cycle, indicating good capacity retention of the BiNS/rGO-30 electrode. (b) Voltage profiles of the BiNS/rGO-30 electrode in PIBs at a current density of 0.5 A g⁻¹. The ICE of BiNS/rGO-30 is 70.5%. (c) Cycling performance of the BiNS/rGO-30 and BiNS electrodes in PIBs at a current density of 0.5 A g⁻¹. (d) Rate capability of the BiNS/rGO-30 and BiNS electrodes in PIBs. (e) EIS of the BiNS/rGO-30 electrode and BiNS electrode after the 4th discharge and the 20th discharge.

tion between Bi and KBi₂, KBi₂ and K₃Bi₂, K₃Bi₂ and K₃Bi, respectively [19,27]. The CV curves almost overlap after the first cycle, indicating high capacity retention of the BiNS/rGO-30 electrode. Fig. 4b shows the charge-discharge profiles of the BiNS/rGO-30 electrode at a current density of 0.5 A g⁻¹ for PIBs. The initial discharge and charge capacities of BiNS/rGO-30 are 525 and 370 mA h g⁻¹, respectively, showing a 70.5% initial Coulombic efficiency (ICE). After the first cycle, the BiNS/rGO-30 electrode shows three distinct discharge plateaus

at ca. 0.87, 0.38, and 0.29 V, which are consistent with the results from the CV test. The plateaus at 0.87, 0.38 and 0.29 V in the discharge process are caused by the transformation from Bi to KBi₂, KBi₂ to K₃Bi₂ and K₃Bi₂ to K₃Bi, respectively [27]. For comparison, the charge-discharge profiles of BiNSs at a current density of 0.5 A g⁻¹ were also investigated (Fig. S9). The initial discharge and charge capacities are 369.4 and 204.2 mA h g⁻¹, respectively, corresponding to an ICE of 55.3%. These results are comparable to those of previously reported Bi-based

anode for PIBs (~50%), but much lower than that of the BiNS/rGO-30 membrane electrode [21,24,36]. Compared with the conventional highly porous nanostructured Bi-based electrodes for PIBs, the higher ICE of the BiNS/rGO-30 electrode resulted from the formation of less SEI on the relatively dense membrane electrode [21,24,36]. Compared with the pure BiNS electrode, the higher ICE of the BiNS/rGO-30 electrode resulted from its excellent structural stability that can avoid the destruction of SEI during cycling [37]. Due to a certain amount of potassium ions are sacrificed in the SEI formation process, the second discharge capacity of the BiNS/rGO-30 electrode is decreased to $342.5 \text{ mA h g}^{-1}$, which is lower than the initial discharge capacity.

Fig. 4c shows the cycling performances of BiNS/rGO-30 and BiNS at a current density of 0.5 A g^{-1} for PIBs. The cycle performance of the BiNS electrode is stable with the CE approaching 98%, indicating that the volume expansion phenomenon was relieved to some degree due to the thin structure of the exfoliated BiNS. However, the reversible capacity of the BiNS electrode after 90 cycles is only 104 mA h g^{-1} due to its limited structural stability. In comparison, the reversible capacity of the BiNS/rGO-30 electrode after 90 cycles is 272 mA h g^{-1} , corresponding to 70.6% of the theoretical capacity of Bi (385 mA h g^{-1}). This indicates the structural instability caused by volume expansion of Bi was effectively relieved. To obtain further evidence of the improved electrochemical performance of BiNS/rGO-30 for PIBs, the rate capabilities of both BiNS/rGO-30 and BiNS electrodes were investigated (Fig. 4d). The BiNS/rGO-30 electrode delivered reversible capacities of 338, 320, 290, 228 and 100 mA h g^{-1} when cycled at 0.5, 1, 2, 5 and 10 A g^{-1} , respectively. When the current density was tuned back to 0.5 A g^{-1} , the reversible capacity could be recovered up to 220 mA h g^{-1} , showing an excellent stability of the electrode. In comparison, the capacity of the BiNS electrode as low as 30 mA h g^{-1} was delivered at 2 A g^{-1} , and nearly no capacity was delivered when cycling at 5 and 10 A g^{-1} . The electrochemical performance of the bare rGO membrane was also studied (Fig. S10). Compared with BiNS, the capacity of the bare rGO membrane can be ignored, because only a capacity of 12 mA h g^{-1} is released after 2 cycles.

To reveal the structural stability of the BiNS/rGO-30 electrode, the structure of the BiNS/rGO-30 electrode was examined after electrochemical cycles (Fig. S11). After extended cycling, the thickness of the BiNS/rGO-30 electrode is about $28.1 \mu\text{m}$, which has little change compared with the thickness before cycling. This indicates that the BiNS/rGO-30 membrane can effectively inhibit

the expansion phenomenon of Bi material when potassiation/depotassiation reactions occur. Besides, it can be seen that the original textural properties in terms of shape, size, and structural integrity can be well retained after cycling, showing high structural stability of the BiNS/rGO-30 electrode. These results indicate that the BiNS/rGO-30 membrane with good flexibility and porosity close to that of expansion volume of the BiNS after charging can effectively tackle the expansion issue and alleviate the structural instability during the electrochemical cycling [1,24].

We further tested EIS of the electrodes to investigate the transfer phenomena of electrons and ions. As shown in Fig. 4e, the charge-transfer (R_{ct}) resistance of the BiNS/rGO-30 electrode after 4 cycles is much smaller than that of the BiNS electrode, indicating a better dynamic process of the BiNS/rGO-30 electrode. After 20 cycles, nearly no resistance change occurred in the BiNS/rGO-30 electrode, indicating an excellent structural stability of the BiNS/rGO-30 electrode. Compared with the BiNS/rGO-30 electrode, though the resistance of the BiNS electrode somewhat increased after 20 cycles, it still showed much higher resistance than BiNS/rGO-30. The small resistance of the BiNS/rGO-30 sample is due to the conductive network provided by rGO, which can efficiently facilitate the electron transfer and the porosity of the BiNS/rGO-30 membrane can facilitate the potassium transfer [38]. It is worth noting that the increase of the rGO content shows a decrease of electrode performance due to the limit of the electrolyte infiltration (see detailed discussion in Fig. S12).

The electrochemical performance of the BiNS/rGO-P electrode (Fig. S13) and BiNS/rGO-20 electrode (Fig. S14) were also studied. The BiNS/rGO-P electrode shows initial discharge and charge capacities of 533 and 416 mA h g^{-1} , respectively (Fig. S13a). And, a reversible capacity of 312 mA h g^{-1} is maintained after 100 cycles (Fig. S13b), which is approximately equal to that of the BiNS/rGO-30 electrode. This phenomenon indicates that the compression process of the BiNS/rGO-P membrane under roller press with a rolling clearance of $30 \mu\text{m}$ has little negative effect on the electrochemical performance of the electrode. However, the BiNS/rGO-20 electrode shows a very low initial discharge and charge capacities of 19 and 40 mA h g^{-1} , respectively (Fig. S14a). After several cycles, the BiNS/rGO-20 electrode reaches its highest reversible capacity of 145 mA h g^{-1} . The activation phenomenon of the BiNS/rGO-20 electrode is caused by its dense structure that limits the contact between the electrode material and electrolyte. The initial activation

process of the BiNS/rGO-20 electrode was also verified by the CV tests (Fig. S14b). After 80 cycles, the reversible capacity of the BiNS/rGO-20 electrode gradually decrease to 33 mA h g^{-1} , which is much lower than that of BiNS/rGO-30 electrode and BiNS/rGO-P electrode. To reveal the reason of the inferior electrochemical performance of the BiNS/rGO-20 electrode, the EIS of the BiNS/rGO-20 electrode after 4 cycles and 20 cycles were investigated (Fig. S15). The R_{ct} of the BiNS/rGO-20 electrode after 4 cycles is much higher than that of BiNS/rGO-30, indicating the inferior dynamic process of the BiNS/rGO-20 electrode. And after 20 cycles, the R_{ct} resistance of the BiNS/rGO-20 electrode increases a lot, indicating the poor structural stability of the BiNS/rGO-20 electrode during potassiation and depotassiation processes.

We investigated the volumetric capacity of the as-obtained BiNS/rGO-30 electrode for PIBs. The BiNS/rGO-30 after compression exhibits a relative uniform structure with a thickness of about $26 \mu\text{m}$ and a density of 2.59 g cm^{-3} (see Fig. 3b). Fig. 5a shows the volumetric capacity of BiNS/rGO-30 at a current density of 0.5 A g^{-1} for PIBs. A high volumetric capacity of about 451 mA h cm^{-3} (based on the whole electrode) is maintained after 90 cycles. For the BiNS/rGO-P electrode, the reversible volumetric capacity for K-ion storage is only 112 mA h cm^{-3} at 0.5 A g^{-1} . Fig. 5b further reveals the volumetric capacity of the BiNS/rGO-30 electrode at a high charge-discharge rate for long cycling. The BiNS/rGO-30 electrode was first activated at a small current density of 0.5 A g^{-1} for 10 cycles and then cycled at 5 A g^{-1} . Even after 700 cycles, the BiNS/rGO-30 electrode still exhibited a high volumetric capacity of 197 mA h cm^{-3} with CE nearly 100%. Though the volumetric capacity of K-ion storage of the BiNS/rGO-30 electrode is still far from the theoretical volumetric ca-

capacity of Bi, the volumetric capacity of the BiNS/rGO-30 electrode is still unprecedented, which is much higher than that of previously reported graphite anode for PIBs (less than 300 mA h cm^{-3}) (calculated from reported results, please see detailed discussion in Fig. S16) [14,39]. The galvanostatic intermittent titration technique was used to measure the K^+ diffusivity coefficient in BiNS/rGO-30 (Fig. S17). According to Fick's second law: $D_K = 4 / \pi \tau (m_B V_M / M_B S)^2 (\Delta E_s / \Delta E_t)^2$, where D_K ($\text{cm}^2 \text{ s}^{-1}$) is the diffusion coefficient, m_B (g) is the total mass loading of the active material, V_M ($\text{cm}^3 \text{ mol}^{-1}$) is the molar volume, M_B (g mol^{-1}) is the molecular weight, S (cm^2) is the sum of the surface area of the electrode, τ is the current pulse time, ΔE_s is the variations in the steady-state voltage and ΔE_t is the total variation in the cell voltage taking place during the constant pulse, the calculated diffusivity coefficient of K^+ in BiNS/rGO-30 during charge and discharge process is from 9.47×10^{-7} to $9.22 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$.

It is known that a high areal loading of active material is important for the practical application of electrode. However, the areal loading of Bi in most Bi-based electrodes for PIBs are no more than 3 mg cm^{-2} due to their porous structures. Therefore, we also investigated the cycling performance of the BiNS/rGO-30 electrode at a current density of 0.5 A g^{-1} with increased areal loading of BiNS material (Fig. S18). When the areal loading of BiNS content increased to 8.1 and 10.8 mg cm^{-2} , a reversible capacity of 270 and 137 mA h g^{-1} were maintained after 30 cycles, respectively. The capacity of the BiNS/rGO-30 electrode decreased when the areal loading of active material increased due to the lower utilization of active material in the electrodes with higher areal loading of active materials [40]. To further improve the application potential of the BiNS/rGO-30 electrode, the transfer ability of potassium ions in thick BiNS/rGO-30 electrode

Figure 5 (a) Volumetric capacity of the BiNS/rGO-30 electrode in PIBs at a current density of 0.5 A g^{-1} . (b) The volumetric capacity of the BiNS/rGO-30 electrode in PIBs for 700 cycles at a current density of 5 A g^{-1} .

should be further improved.

CONCLUSIONS

In summary, we fabricated a flexible BiNS/rGO-30 membrane with controlled pore structure. The flexible BiNS/rGO-30 electrode exhibits excellent electrochemical performance for potassium storage. It delivers a reversible capacity of 272 mA h g^{-1} after 90 cycles with little capacity loss at 0.5 A g^{-1} . Even being cycled at 10 A g^{-1} , the BiNS/rGO-30 electrode still delivers a reversible capacity of 100 mA h g^{-1} . It is worth noting that, the prepared BiNS/rGO-30 electrode delivers a high reversible volumetric capacity of 451 mA h cm^{-3} at the current density of 0.5 A g^{-1} . The high performance of the BiNS/rGO-30 electrode is attributed to the BiNS/rGO-30 network with controlled pore structure which can effectively tackle the expansion and alleviate the structural failure of electrode during electrochemical cycling, and facilitate the transfer of potassium ions and electrons.

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Supplementary information Supporting data are available in the online version of the paper.

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一种用于钾离子电池的高体积容量铋纳米片/石墨烯复合物电极

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摘要 具有高体积能量密度的钾离子电池有望成为下一代的低成本储能设备。金属铋具有较高的理论容量($3763 \text{ mA h cm}^{-3}$)和相对较低的工作电位(-2.93 V vs. SHE), 是一种很有前途的钾离子电池负极材料。但铋在与钾的合金化过程中, 会产生大的体积膨胀, 导致电极容量严重衰减。本文报道了一种柔性、自支撑的铋纳米片/石墨烯复合物电极膜, 该电极膜具有优化的孔隙率, 可满足电极循环过程中的体积膨胀。此外, 该电极中优化的孔隙结构改善了循环过程中的电子和离子输运, 并提高了电极在钾化和去钾化过程中的结构稳定性, 使其具有良好的电化学储钾性能。特别是, 在电流密度为 0.5 A g^{-1} 的情况下, 该电极的体积容量可以达到 451 mA h cm^{-3} , 明显优于之前报道的商用石墨材料。