

Research Article

Group VI metallic pillars for assembly of expanded graphite anodes for high-capacity Na-ion batteries

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ABSTRACT

Despite the economic viability and promising potential of Na-ion batteries, their commercialization remains unrealized because of the limited intercalation of Na⁺ ions into graphite anodes due to the large ionic radius of Na and instability of Na⁺ ions on the interstitial sites, which result in a poor cell performance. Herein, we report a synthetic strategy for increasing the graphite interlayer distance along *c*-axis to facilitate the intercalation of Na⁺ ions by embedding Group VI W metallic pillars between the graphene layers. The strong electrostatic attraction between the positively charged W⁶⁺ ions and the negatively charged graphene oxide (GO) layers enables the assembly of the expanded graphite layers by W pillars (W-rGO) via a subsequent chemical reduction. The interlayer spacing of the reconstructed W-rGO increased to 11.1 Å, which is three-fold larger than that of graphite (3.34 Å). Consequently, the W-rGO anodes delivered an exceptionally high capacity of 678 mAh g⁻¹ for a Na-ion battery compared with that of a pristine rGO anode (240 mAh g⁻¹). Further, we elucidate the structural characteristics and electrochemical reaction mechanisms of the W-rGO anodes. This work presents a simple and effective strategy for developing high-performance carbon-based anode materials for the realization of Na-ion battery technology.

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1. Introduction

Energy storage devices have become the most essential equipment for a variety of small and large electrical appliances as they ensure long-term on-call wireless operation without external electricity supply [1–3]. Li-ion batteries, a technology that won the Nobel Prize, are considered an unreplaceable energy storage device owing to their wide applications in a range of devices such as smart devices, electric vehicles, and electrical energy storage systems [4–6]. Because of the increasing demand for Li-ion batteries, the substantial Li resources are quickly exhausting, giving rise to raw material supply issues since Li reserves are mainly located in South America, resulting in fluctuation in battery cost [7–9]. In this regard, Na-ion batteries have received considerable attention because of the low cost and abundance of Na resource

and the structural similarity of Na-ion batteries to existing Li-ion batteries [10–12]. In addition, the electrode fabrication and cell preparation technologies of Li-ion batteries can be directly applied to the Na-ion battery systems without overall modification.

Recent research on Na-ion batteries has been focused on finding suitable electrode material candidates. Conventional anode materials used in Li-ion batteries are unsuitable for Na-ion batteries because of (i) the larger ionic radius of Na⁺ (1.02 Å) than that of Li⁺ (0.76 Å), (ii) the instability of Na⁺ ions on the interstitial sites in the anode materials, and (iii) structural instability caused by repeated Na⁺ ion intercalation [13–15]. For instance, graphite has been explored as a commercial anode material owing to its decent available capacity of ~350 mAh/g and stable cycling properties in Li-ion cells; however, it delivers a poor capacity (<50 mAh/g) due to the sluggish intercalation and instability of Na⁺ ions on the binding sites in Na-ion cells [16,17]. To resolve this issue, non-graphitic hard carbon alternatives have been explored to further accept Na⁺ ion carriers into the enlarged space and numerous voids, which resulted in a high capacity of up to 300 mAh/g [18–20]. However, hard carbon anodes have the drawbacks of a high synthetic cost

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and structural instability related to short-range-ordered carbon stacking [21,22]. In addition, the low-voltage plateau of hard carbon anodes near 0 V unexpectedly leads to Na electroplating on hard carbons and detrimental dendrite formation, posing safety problems during fast charging [20,23].

To overcome the intrinsic limitations of conventional graphite anodes, much effort has been devoted to modifying the graphite structure by increasing the interlayer spacing along the axial direction instead of using non-graphitic hard carbons. Expanded graphite called reduced graphite oxide (rGO) can be prepared by the stacking of surface-functionalized graphene layers (i.e., surface functionalized with hydroxyl and carboxyl groups) [24–30]. The distance between the graphene layers can be increased from 3.4 Å (pristine graphite) to 4.3 Å by functionalizing with anionic groups, which facilitates the intercalation of large Na^+ ions [24,31]. However, the surface of graphite oxide (GO) sheets is negatively charged, which leads to repulsive interaction between the layers, thus hindering the long-range-ordered restacking of the sheets. Besides, anion pillar species between rGO sheets are highly reactive with the electrolyte component and thus tend to form byproducts such as sodium oxide (or hydroxide), which lead to substantial irreversible reaction [22,24,32]. To address this issue, an interesting concept of introducing trivalent Al^{3+} pillars has been recently suggested to facilitate the self-assembly of GO layers and consequently achieve an exceptionally expanded graphite interlayer of ~ 7 Å that delivered an outstanding specific capacity of 780 mAh/g [33]. Nevertheless, the large amount (~ 20 wt%) of Al pillars present in the expanded graphite hinder Na diffusion in the interlayers and reduce the gravimetric energy density. Therefore, a lower amount of suitable cation pillars that induce a strong attraction between the GO layers thereby facilitating their self-assembly should be introduced to stabilize the structure with a long-range order arrangement and further increase the axial interlayer spacing of the expanded graphite anodes to satisfy the requirement of high capacity of Na-ion cells.

In this work, we expanded the graphite structure by atomically inserting Group VI cation pillars between the graphene layers to improve the intercalation reaction kinetics of Na-ion batteries. We introduced hexavalent tungsten (W^{6+}) into a negatively charged GO flake solution for the self-assembly of the W^{6+} cations and GO flakes (Fig. 1). The hexavalent W pillars can effectively balance the negative repulsive interaction caused by the anion species and successfully promote the self-assembly of the graphene layers with a long-range order along the *c*-axis. The reconstructed graphite materials containing atomically dispersed W pillars (W-rGO) facilitate the insertion of Na^+ ions into the enlarged interlayer spaces and subsequently catalyze Na^+ ion diffusion between the interlayers. The high atomic number of the W pillars corresponding to large atomic radius can effectively support the graphite interlayer even at relatively smaller amounts compared with the trivalent Al^{3+} pillars since an excess amount of pillars would block the binding sites of Na^+ ions, subsequently hindering ion diffusion for cell operation. Thus, we determined the effect of the concentration of W pillars on the structure and interlayer distance of the reconstructed graphite materials. In addition, we evaluated the effect of the concentration of W pillars on the electrochemical performance of the reconstructed graphite anodes for Na-ion batteries. Our proposed synthetic strategy of modifying graphite structures by inserting Group IV atomic pillars provide guidance for designing potential carbon-based anode materials for next-generation alkali-ion batteries.

2. Experimental

2.1. Materials

Graphene oxide solution (conc. ~ 5 g/L) was purchased from Graphene Supermarket. Tungsten hexachloride (WCl_6 , $>99.9\%$, trace metal basis), hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 98.0%), sodium perchlorate (NaClO_4 , anhydrous, $\geq 98.0\%$), propylene carbonate (PC, anhydrous, 99.7%), 1-methyl-2-pyrrolidone (NMP, anhydrous, 99.5%), and poly(vinylidene fluoride) (PVDF, Mw $\sim 180,000$) were purchased from Sigma-Aldrich (Korea). Deionized (DI) water was obtained using a water purification system purchased from Millipore (Direct Q3). We used the PC solvent after removing moisture by dipping freshly activated molecular sieves (type 4 Å) into the solvent for two weeks. The other materials were used as received without further purification.

2.2. Preparation of W-rGO anode materials

The W-rGO anode materials were synthesized with four different W concentrations (0, 1, 5, 10 mM) by changing the amount of tungsten precursor added to the solution. Different amounts of WCl_6 were respectively dissolved in 30 ml of DI water to prepare a dispersed solution. Then, 30 ml of this solution was slowly poured into 10 ml of GO solution and stirred at room temperature for 1 h. Then, 10 ml of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ solution as a reducing agent was added to the mixed solution and stirred with a magnetic bar (280 rpm) at 100°C for 3 h to reduce the GO flakes and induce attractive interaction between GO and the W^{6+} ions. Finally, an aqueous solution containing black W-rGO was formed, and powder form of W-rGO was obtained after freeze-drying for 24 h.

2.3. Characterization

The crystalline and amorphous phases of the samples were identified by powder X-ray diffraction (XRD, MiniFlex600, Rigaku) analysis performed with $\text{Cu-K}\alpha$ ($\lambda = 1.54$ Å) radiation. The surface morphologies of the W-rGO materials were analyzed by scanning electron microscopy (SEM, JSM-7600F, JEOL). The W contents and thermal behaviors of the W-rGO samples were determined by thermogravimetric analysis (TGA, TG 209 F3) performed in the temperature range of 30 – 800°C at a heating rate of $10^\circ\text{C min}^{-1}$ in air. Raman spectroscopy (NRS-3100, JASCO) was performed with a 532 nm Nd:YAG laser to determine the vibrational modes of molecules. The crystal structures and surface atomic compositions were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific).

2.3.1. Electrochemical characterization

The W-rGO electrodes were fabricated on copper foil using a casting slurry consisting of 80 wt% active material, 10 wt% carbon (Super-P), and 10 wt% PVDF binder in NMP. The electrodes were then dried in vacuum at 75°C prior to cell assembly. Half-cells were assembled in an argon-purged glovebox with the prepared electrodes using Na metal foil as the counter electrode, 1 M NaClO_4 in PC as the electrolyte, and a glass microfiber filter (13 mm diameter, Whatman Co. Ltd.) as the separator. All potentials were referred to Na/Na^+ . The electrochemical experiments were performed at room temperature. A Bio-Logic VSP potentiostat was used for cyclic voltammetry (CV) experiments. Charge/discharge tests were conducted using a potentio-galvanostat (WBCS3000, WonATech, Korea) at a current density of 50 mA g^{-1} in the voltage range of 0.01 – $2.5 \text{ V vs. Na}/\text{Na}^+$.

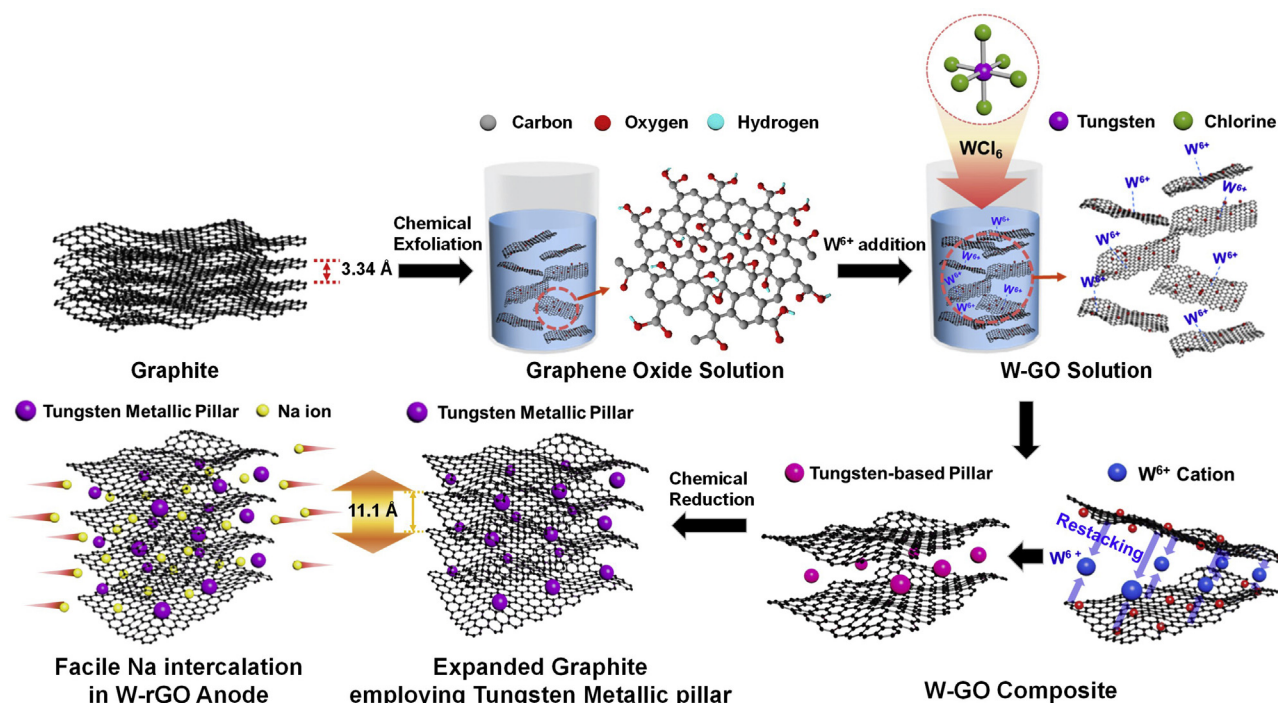


Fig. 1. Schematic illustration of the control of interlayer space and the synthesis of reconstructed graphite. Schematic of the synthesis process of reconstructed graphite anode materials for Na-ion batteries using W pillars. Negatively charged graphene oxide flakes are self-assembled with W^{6+} cations. After chemical reduction, interlayer expansion can be achieved by introducing atomically distributed W pillars between the graphite layers. (A colour version of this figure can be viewed online.)

2.3.2. Ex situ characterization

To determine the structural changes occurring during cycling, the *ex situ* characterization of the W-rGO electrodes was performed by XRD analysis, XPS, and Raman spectroscopy. The samples were prepared after galvanostatic charge and discharge in the voltage range of 0.01–2.5 V at a current density of 50 mA g⁻¹. Each cell was collected after the second discharge and second charge, respectively. The cycled cells were disassembled, and each electrode was retrieved using a tweezer. The collected electrodes were soaked in the electrolyte to remove residual salts from the electrodes. The entire sample preparation process was conducted in an argon-filled glove box.

3. Results and discussion

The synthesis of expanded graphite by the insertion of W pillars by mixing the WCl_6 precursor solution with a GO flake dispersion solution is schematically shown in Fig. 1. The positively charged W^{6+} ions strongly attract the negatively charged species on the surface of the dispersed GO sheets, thereby creating W^{6+} cation/GO composite layers along the *c*-axis. We chose the W^{6+} species among the various cation alternatives because the W^{6+} species with a high oxidation number can serve as robust internal bridges, enhancing the attractive interaction with the GO flakes. In addition, compared with other metal cations (e.g., Al^{3+}), the heavy and large W^{6+} cations can effectively increase the interlayer distance even at a low concentration (Fig. S1) [33]. This facilitates the long-range ordering (high crystallinity) and vertical arrangement of the GO sheets through self-stacking. The reconstructed W-rGO material was successfully obtained after the chemical reduction of the W-GO composite. We optimized the concentration of W in the precursor solution to determine the optimal synthetic conditions for preparing anodes to achieve the maximum performance for Na-ion cells. Samples with different W concentrations are denoted as

Wx-rGO, where $x = 0, 1, 5$, and 10 (W0-rGO, W1-rGO, W5-rGO, and W10-rGO) corresponding to the 0, 1, 5, and 10 mM WCl_6 concentration in the precursor solution added to the GO dispersion solution, respectively.

Fig. 2 shows the characterization results of the Wx-rGO samples. Fig. 2a shows the digital images of the mixture solution comprising rGO dispersion solution with different amounts of W pillars. W^{6+} ions strongly interact with the negatively charged functional groups on the GO sheets, thereby facilitating the assembly of GO layers to form GO composites containing W in its interlayer space. The hydrophilic repulsive interaction between the oxygen species on the GO sheets in the aqueous solution is effectively balanced by the W^{6+} cations (Fig. 2a). This observation supports our hypothesis that the W^{6+} species promote the self-assembly of the GO flakes by acting as internal bridges. Fig. 2b presents the SEM images of the Wx-rGO samples. As can be seen, there is no remarkable nucleation or segregation of W particles on the surface of the GO sheets; this indicates that W pillars are present inside the graphene layers. However, after the addition of W, the graphene layers noticeably wrinkled because of the strong attractive interaction between the W^{6+} ions and the negatively charged GO surface (Fig. S2).

The crystalline structure and lattice distance of the Wx-rGO materials were investigated by XRD analysis; the XRD spectra are shown in Fig. 2c. Based on Bragg's law ($2d\sin\theta = n\lambda$, where d is the interplanar spacing, θ is the scattering angle, λ is the wavelength, and n is a positive integer quantifying the reflection order), we estimated the lattice distance corresponding to the (002) plane of reconstructed graphite. For W0-rGO (pristine rGO), the peak at 24° implies an interlayer distance of 3.8 Å, which indicates the restacking of rGO layers along the *c*-axis. The peak in the range of 16°–30° is a characteristic peak of rGO arising primarily from the aggregation of GO sheets and multilayer alignment due to the reduction process [30,34]. An additional peak was observed at 8° in the XRD spectra of W1-rGO, W5-rGO, and W10-rGO corresponding

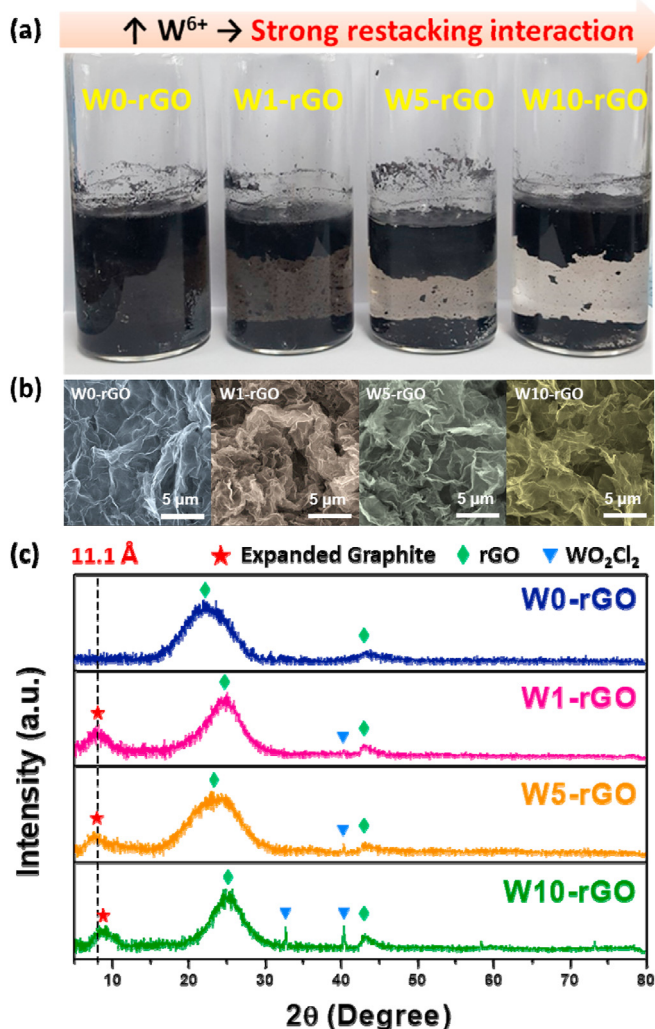


Fig. 2. Morphological features and crystallographic information of the reconstructed Wx-rGO materials. (a) W-embedded restacked Wx-rGO dispersion solutions after reduction. (b) SEM images and (c) XRD spectra of the reconstructed graphite materials (Wx-rGO) containing different amounts of W pillar species. (A colour version of this figure can be viewed online.)

to a large d-spacing of 11.1 Å, which indicates the increase in the interlayer spacing of graphene. The result implies that the W pillars between the graphene layers can significantly increase the interlayer spacing compared with that of conventional graphite (~3.4 Å) and rGO (~3.8 Å), thereby facilitating the intercalation of Na⁺ ions. Some additional sharp peaks appeared in the XRD spectra of W1-rGO, W5-rGO, and W10-rGO, which can be indexed to WO₂Cl₂ formed by the reduction of WCl₆ precursor [35,36]. The intensity of this peak increased with increasing concentration of WCl₆.

Further, we investigated the thermal behavior of Wx-rGOs and determined the weight fraction of W pillars by performing TGA in an air atmosphere; the results are presented in Fig. 3a. W0-rGO exhibited a significant weight loss of approximately 89% starting at 550 °C, which corresponds to the destruction of carbon skeleton (carbonyl groups/double bond) and its subsequent decomposition to CO or CO₂ gases [28]. In contrast, the decomposition temperatures of W1-rGO, W5-rGO, and W10-rGO increased to over 650 °C because of the strong binding of the W species with the functionalized anionic species attached to carbon, which prevented the decomposition of carbon to CO or CO₂ gases at lower temperatures.

The residual weight percentages of the Wx-rGO samples after decomposition increased with increasing W pillar content (10.18, 11.97, 18.42, and 18.21% for W0-rGO, W1-rGO, W5-rGO, W10-rGO, respectively). Interestingly, the residual weight percentages of W5-rGO and W10-rGO are almost the same, which implies that only a limited amount of W pillars can be incorporated in the interlayers. Considering that the XRD peaks of W10-rGO are sharper than those of W5-rGO, it can be concluded that the W pillar species are further segregated each other in the interlayer of W10-rGO and tend to be aggregated in the materials although they possess similar W amount.

The elemental composition and chemical states of the constituent elements of the Wx-rGO materials were analyzed by XPS; the results are shown in Fig. 3b–d and Fig. S3. The W 4f XPS profiles of W1-rGO, W5-rGO, and W10-rGO exhibit peaks corresponding to W 4f_{5/2} and W 4f_{7/2} orbitals, indicating the presence of WO_x components in these samples (Fig. 3b) [37]. In the Cl 2p XPS profiles, the peak corresponding to the chloride of WO₂Cl₂ increased with increasing W concentration (Fig. 3c). Besides, the C 1s XPS profiles of the samples do not exhibit peaks related to the residual oxygen groups at the basal plane or edge of GO, which indicate the sufficient reduction of W-GO without surface impurities (Fig. S4) [38]. Furthermore, the intensity of the peak at 532.4 eV in the O 1s region corresponding to the C–O bonds increased with increasing W content, and the O 1s XPS profile of W5-rGO exhibited an additional peak related to WO_x; this indicates a stronger binding between W and O instead of the segregation of W species in W5-rGO as indicated by the XRD results (Figs. 3d and 2c). Raman spectroscopy was performed to examine the chemical structures and molecular interactions in the Wx-rGO samples; the results are shown in Fig. 3e and f. No peaks were observed between 200 and 1000 cm^{−1} due to the negligible formation of crystalline tungsten oxide or chloride impurities (i.e., WO₃ or WCl₆) in the samples (Fig. 3e). In addition, the results indicate that the W species are intercalated in the interlayers and are not independently segregated on the rGO surface. Furthermore, the Raman spectra of the W-rGO samples exhibited typical D and G bands at 1350 and 1580 cm^{−1}, respectively (Fig. 3f). The intensity ratio of the D band to the G band (I_D/I_G) is generally used to evaluate the degree of crystallinity and structural defects in graphene materials. The W-rGO samples exhibited similar I_D/I_G ratios, which indicate that the degree of reduction of the GO sheets is not significantly affected by addition of W pillars. Thus, structural characterization revealed that the tailored assembly and synthesis of W-embedded rGOs with expanded interlayer spacings could be successfully achieved via the simple introduction of hexavalent pillar species into a graphene dispersion solution.

The electrochemical performance of the Wx-rGO materials was evaluated to determine the feasibility of using the reconstructed graphite materials as an anode for Na-ion batteries (Fig. 4). The discharge-charge profiles of the Na-ion cells employing the Wx-rGO (x = 0, 1, 5, 10) anodes measured in the potential range of 0.01–2.5 V (vs Na/Na⁺) at a current density of 50 mA g^{−1} are shown in Fig. 4a. Pristine rGO (W0-rGO) exhibited a 2nd discharge capacity of 240 mAh/g, which is consistent with the values reported in literature [24,39,40]. Notably, the incorporation of W pillars considerably increased the discharge capacity of the W pillar-embedded reconstructed graphite anodes by two- or three-fold than that of pristine rGO. In particular, W5-rGO delivered an outstanding capacity of 678 mAh g^{−1} compared with the W1-rGO (393 mAh g^{−1}) and W10-rGO (434 mAh g^{−1}) anodes. This indicates that the W pillars efficiently expanded the interlayer space of the reconstructed graphite anodes, thereby providing more Na storage sites and yielding a high-capacity host material. The theoretical capacity of graphite is 372 mAh/g for 1 Na⁺ per C₆; thus, the excess Na⁺ ions, that is, more than 2 Na⁺ per C₆ can be stored in the

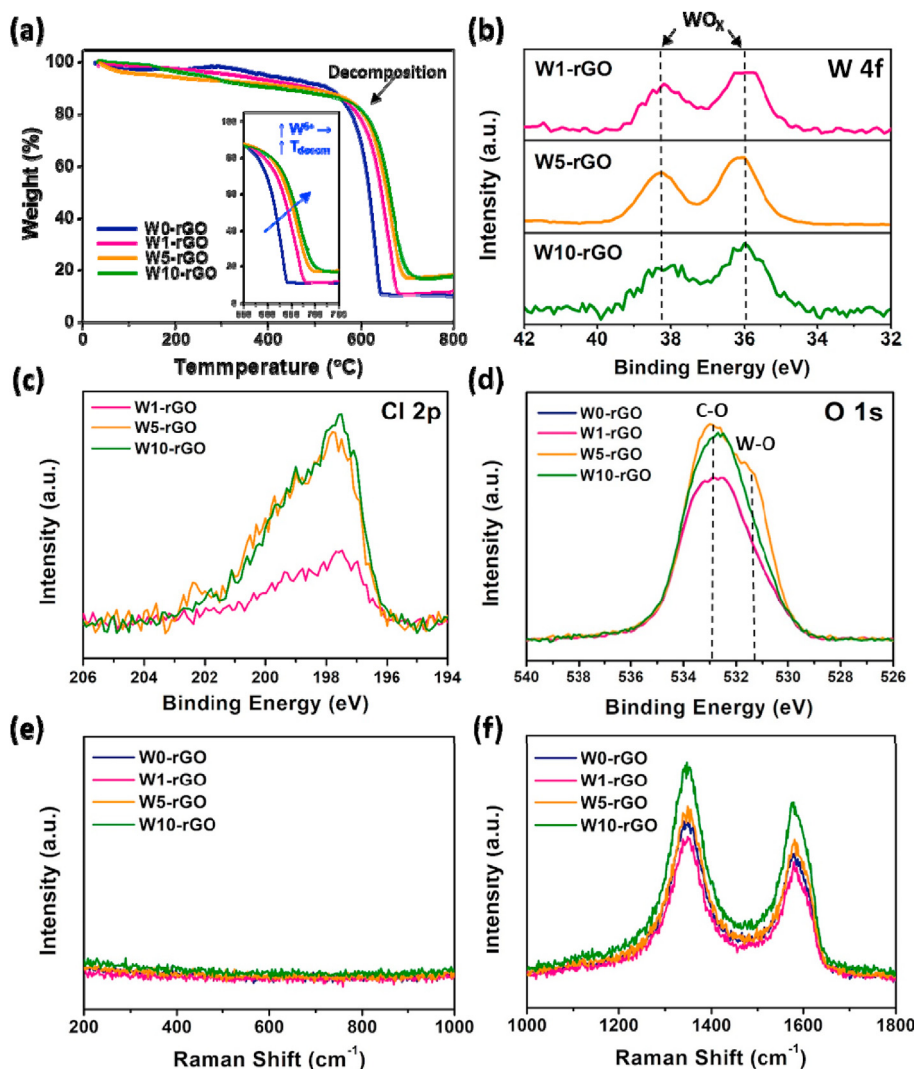


Fig. 3. Chemical composition and bonding properties of the synthesized W_x -rGO materials. (a) TGA curves of the reconstructed graphite materials (W_x -rGO) containing different amounts of W pillar species. (b) W 4f, (c) Cl 2p, and (d) O 1s XPS profiles of W_x -rGOs. Raman spectra of the reconstructed graphite materials (W_x -rGO) containing different amounts of W pillar species measured in the wavenumber range of (e) 200–1000 cm^{-1} and (f) 1000–1800 cm^{-1} . (A colour version of this figure can be viewed online.)

prolate space. Interestingly, W10-rGO delivered a lower capacity than that of W5-rGO despite having the highest W content. This suggests that an excess amount of pillar ions degrades the capacity of the cell because the inactive pillars densely occupy the interlayer space, blocking the diffusion sites of Na^+ ions. Therefore, an optimal concentration of W pillar species should be introduced to maximize the performance of Na-ion cells comprising the W_x -rGO anodes. Another interesting feature of the discharge-charge profiles of the Na-ion cells comprising W_x -rGO ($x \geq 1$) was the continuous sloping curve over the entire potential range without any plateau. This implies that the intercalation mechanism of the W_x -rGO anodes is closer to a one-phase reaction than to a two-phase reaction. In contrast, conventional graphite exhibited multiple plateaus at different voltages due to phase change (e.g., stage IV $\rightarrow$ stage I) [41,42]. Thus, the numerous Na-binding sites in the expanded interlayers facilitate homogenous Na intercalation into the structure without the migration of the heterogeneous phase boundary. Fig. 4b presents the cycling performances and the corresponding Coulombic efficiencies of the W0-rGO, W1-rGO, W5-rGO, and W10-rGO anodes for 100 cycles. W5-rGO exhibited a high reversible capacity of 271 mAh g^{-1} compared with that of rGO (124 mAh g^{-1})

and retained its high capacity even after 100 cycles with an average Coulombic efficiency of $>99\%$. Although all the samples exhibited capacity retention in the initial cycles, the retention rate gradually decreased over 100 cycles. W0-rGO, W1-rGO, W5-rGO, and W10-rGO exhibited considerably high irreversible capacities, which is attributed to the irreversible formation of a solid electrolyte interphase [43]. This can be resolved by adding sacrificial additives into the cathode or by reducing the fraction of oxygen in the W-rGO (Figs. S5a–d) [44,45]. High irreversible capacity issue should be addressed by introducing the possible solutions in the future work.

Further, the effect of W pillars on the electrochemical properties of the samples was determined by performing CV; the CV profiles of W0-rGO and W5-rGO at different scan rates are shown in Fig. 4c and d. Because of their homogeneous and one-phase reaction characteristics, the W-rGO samples exhibited a gradual decrease in current for the cathodic reaction and a wide peak for the anodic reaction without a distinct peak signal, which are typical features of the anode materials of Na-ion batteries [46–48]. The distorted rectangular shape of the CV curves implies Faradaic adsorption and desorption of Na^+ ions during the insertion and extraction of Na^+ ions in the cathodic and anodic processes, respectively [48]. Based

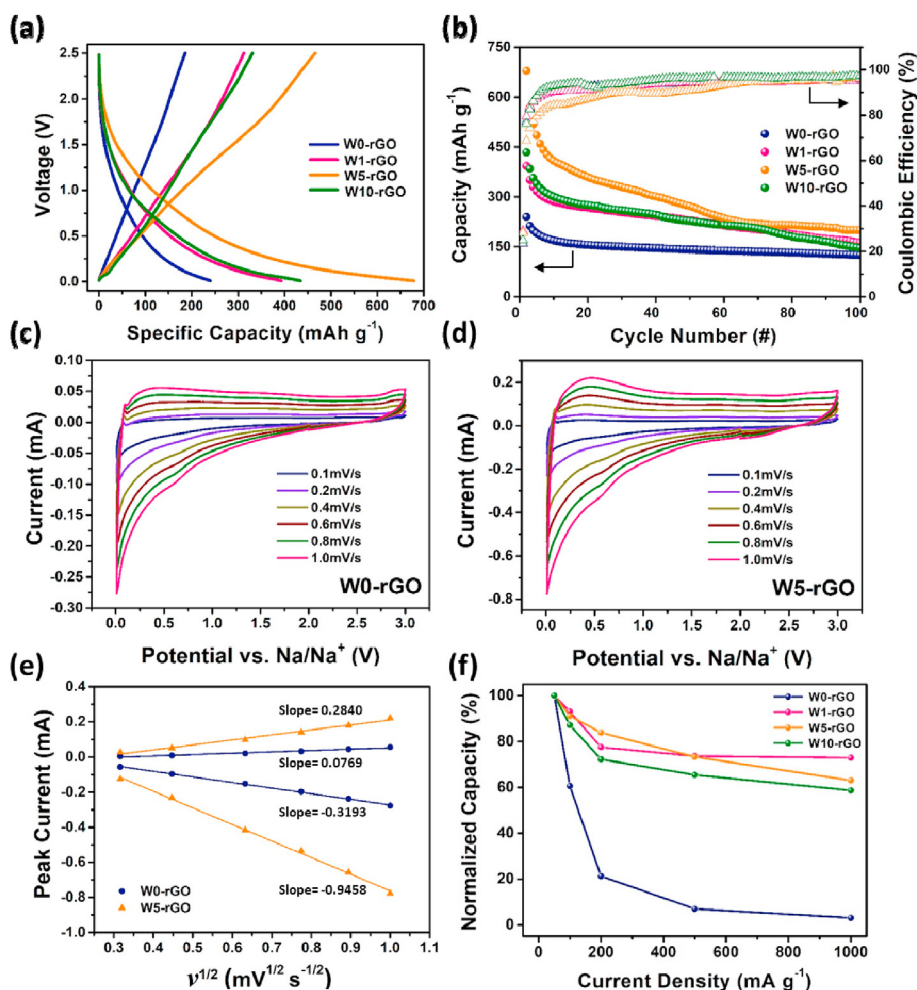


Fig. 4. Electrochemical performance of the cells comprising the Wx-rGO anode materials. (a) Second charge-discharge curves and (b) cycle performance of Na-ion cells with the reconstructed graphite anode materials (Wx-rGO) containing different amounts of W pillar species in the potential range of 0.01–2.5 V at a current density of 50 mA g⁻¹. CV curves of (c) W0-rGO and (d) W5-rGO at a scan rate of 0.1–1.0 mV/s (e) linear relationship between the cathodic and anodic peak currents (i_p) versus square root of scan rate ($v^{1/2}$). (f) Rate capability of Wx-rGOs containing different amounts of W pillars in Na-ion cells at current densities of 50, 100, 200, 500, and 1000 mA g⁻¹. (A colour version of this figure can be viewed online.)

on the CV results, we analyzed the diffusion kinetics of Na⁺ ions in the W0-rGO and W5-rGO samples and determined the Na⁺ ion transport ability in the electrode during charge and discharge by the Randles-Sevcik equation (1) [49–51]:

$$i_p = 2.69 \times 10^5 \times n^{1.5} S C D^{0.5} v^{0.5} \quad (1)$$

where i_p is the peak current (mA), n is the number of electron involved in the redox reaction, S is the electrode area, C is the molar concentration of Na ion in solid-state electrode, D is the diffusion coefficient, and v is the scan rate (mV s⁻¹), respectively. Therefore, the diffusion coefficients can be estimated by the slopes from the linear relationship between the cathodic and anodic peak currents and square root of the scan rate. By using the Randles-Sevcik equation, the slopes of the W0-rGO and W5-rGO obtained from the linear relationship between the peak currents and the scan rates in the anodic/cathodic CV curve are shown in Fig. 4e. Interestingly, the slopes of the W5-rGO corresponding to the sodiation(cathodic)/desodiation(anodic), respectively, showed 3 and 3.7 times higher values than those of the pristine rGO, which is attributed to the expansion of the interlayer space by the W pillars, thus facilitating more Na ion transport pathways during charge and

discharge process. The W-embedded reconstructed graphite exhibited improved charge transfer for Na⁺ intercalation reaction, and thus had a rapid Na⁺ ions diffusion during cycling due to the enlarged ion path and improved electron transport through the W pillar-embedded rGO anodes.

To confirm that the expanded interlayer of rGO by W pillars enable a fast Na⁺ intercalation reaction, we evaluated the rate capability of the reconstructed graphite anodes with increasing applied current densities. As shown in Fig. 4f, all the reconstructed graphite anodes incorporating W pillars exhibit improved kinetics even at a high current density of 1000 mA g⁻¹ compared with the pristine rGO (W0-rGO). The W pillars induce strong attractive interaction between the graphene sheets, producing a robust laminated layer structure. This unique structure can withstand the rapid migration of Na⁺ ions in the W-rGO at a high rate. While W5-rGO exhibited the highest rate capability until 500 mA g⁻¹, W1-rGO demonstrated a better rate capability than W5-rGO did at 1000 mA g⁻¹. This indicates that a smaller amount of pillar species in the interlayers is better for the fast migration of Na⁺ ions since it avoids the blockage of Na-binding sites.

The structural changes in W-embedded graphite electrodes at different electrochemical states were investigated by *ex situ* XRD

analysis; the results are presented in Fig. 5a. The pristine electrode was soaked in the electrolyte for 12 h before analysis for accurate comparison. The pristine, discharged, and charged electrodes exhibited broad peaks at 20° , which can be indexed to graphite. Discharged W-rGO exhibited a notable peak at 6.45° corresponding to a d-spacing of 13.7 Å. This interesting result demonstrates that the peak around 8° corresponding to the expanded layer (11.1 Å) of W-rGO is related to structural expansion up to 13.7 Å during discharge due to Na intercalation. After discharge and subsequent charge, the peak at 6.45° disappeared for the pristine electrode, indicating reversible sodiation and desodiation in the expanded layer of W-rGO. In addition, during the reversible Na^+ intercalation/extraction in the expanded layer (13.7 Å), it is possible that the solvated Na^+ ions in the electrolyte co-intercalated into/extracted from the expanded interlayer without de-solvation [42,52–54]. *Ex situ* Raman spectroscopy was performed to further examine the structural change of the reconstructed graphite upon Na^+ insertion and extraction (Fig. 5b). The pristine, discharged, and charged electrodes exhibited typical D and G bands at 1355 cm^{-1} and 1600 cm^{-1} , respectively, which indicate the absence of any significant damage to the carbon structure due to Na^+ ion intercalation. The I_D/I_G ratio decreased from 1.39 to 1.19 after discharge and recovered after charge (1.28). The D band arises from the vibration of the sp^3 -bonded carbon atoms attributed to the defects in the graphene structure, whereas the G band arises from the in-plane stretching vibration of sp^2 carbon atoms [55–57]. During discharging, the carbon ring structures are distorted by the Na^+ ions occupying the interstitial sites of graphene, resulting in a decrease in defects. After charging, the Na^+ ions are extracted from the interstitial sites of graphene and return to the initial structure with the defects, resulting in an increase in the I_D/I_G ratio. The recovery

of the I_D/I_G ratio related to the carbon defects suggests the reversible Na^+ ion insertion/deinsertion reaction of the W-rGO anodes in the Na-ion cells [58]. To confirm the surface composition and chemical state of the W-rGO electrode materials during cycling, *ex situ* XPS analysis was performed for the pristine, discharged, and charged W5-rGO electrodes; the Na 1s and W 4f XPS profiles are shown in Fig. 5c and d, respectively. The Na 1s XPS profiles of the pristine, discharged, and charged electrodes exhibited peaks at 1071.28 eV corresponding to the sodium species. The pristine electrode exhibited a negligible peak in the Na 1s region. The peak in the XPS profile of the discharged electrode was attributed to Na intercalation into the W5-rGO electrode. The charged electrode exhibited a lower peak intensity than that of the discharged electrode, indicating the reversible insertion and extraction of Na^+ ions in the W-rGO anode. Further, the W 4f XPS profile of the pristine W-rGO anode exhibited WO_{3-x} peaks and partial W metal peak [59]. After discharge, the WO_{3-x} peak disappeared and the W metal peak appeared at a lower binding energy. The W metal peak remained even after charge without the reformation of the WO_{3-x} phase, which implies that W metal becomes inactive pillars that do not significantly affect the capacity of Na-ion batteries.

4. Conclusions

In summary, we synthesized advanced expanded graphite anodes with fully expanded interlayer spacings by introducing Group VI metallic pillars between the layers. The introduction of positively charged, highly oxidative W^{6+} ions facilitates the self-assembly of the negatively charged GO sheets by balancing the repulsive forces even at a low concentration. The W pillars significantly increased the interlayer spacing of the expanded graphite materials to $\sim 11\text{ Å}$,

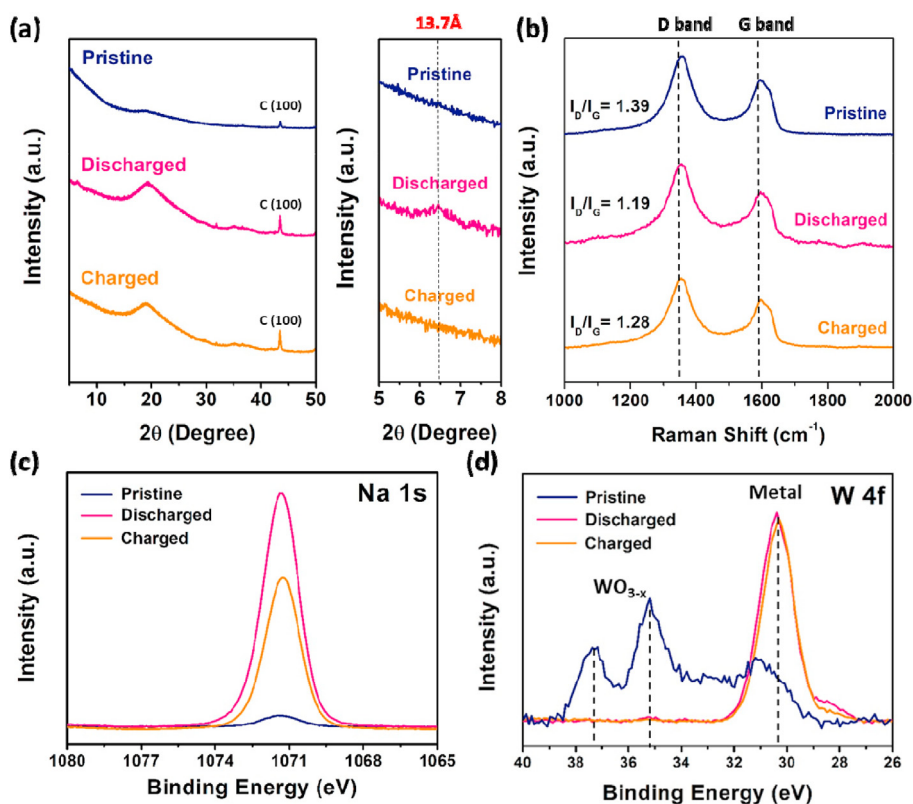


Fig. 5. *Ex situ* measurements of Wx-rGO electrodes. (a) *Ex situ* XRD spectra and (b) Raman spectra of pristine, discharged, and charged W5-rGO electrodes. *Ex situ* (c) Na 1s and (d) W 4f XPS profiles of pristine, discharged, and charged W5-rGO electrodes. (A colour version of this figure can be viewed online.)

thereby enabling the facile insertion and extraction of Na⁺ ions. The W-rGO anode delivered a high specific capacity of 678 mAh g⁻¹, which is approximately three times higher than that of the pristine rGO anode (240 mAh g⁻¹), and retained considerable capacity even after 100 cycles. Further, the W-rGO anodes in the Na-ion cells demonstrated improved diffusion kinetics, delivering a high capacity and an excellent rate capability. The W-rGO anodes sufficiently maintained their morphological and structural features during the substantial reversible Na intercalation. In addition, we demonstrated that the W species preferentially act as inactive pillars in the W-rGO anodes. The proposed strategy is a simple yet valuable synthetic route to producing expanded graphite anode materials by introducing metallic pillar ions, and can not only improve the performance of Na-ion batteries, but also serve as guidance for the development of promising carbon-based anode materials.

CRedit authorship contribution statement

You Jin Kim: Conceptualization, Methodology, Validation, Writing - original draft, preparation, Investigation, Data curation, Formal analysis, Visualization. **Seongji Pyo:** Methodology, Validation, Investigation, Data curation. **Suji Kim:** Methodology, Validation, Investigation, Data curation. **Won-Hee Ryu:** Conceptualization, Methodology, Supervision, Writing - review & editing, Project administration, Funding acquisition.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.carbon.2021.01.006>.

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