ABSTRACT: The effects of both graphene nanoplatelets and reduced graphene oxide as additives to the negative active material in valve-regulated lead–acid batteries for electric bikes were investigated. Low-temperature performance, charge acceptance, cycle performance, and water loss were investigated. The test results show that the low-temperature performance, charge acceptance, and large-current discharge performance of the batteries with graphene additives were significantly improved compared to the control battery, and the cycle life under 100% depth of discharge condition was extended by more than 52% from 250 to 380 cycles. Meanwhile, the amount of water loss from the batteries with graphene changed only slightly compared with the control cells. The excellent performance of the batteries can be ascribed to the graphene promoting the negative-plate charge and discharge processes and suppressing the growth of lead sulfate crystals.

1. INTRODUCTION
Over the past decade, the number of lead–acid battery (LAB) applications has expanded and the market demand has also increased dramatically. Lead–acid batteries occupy more than a 60% market share of the secondary power supply. China is one of the world’s leaders in LAB production, accounting for 30% of the global LAB output. China’s large market demand comes from a substantial increase in the number of electric bikes (e-bikes). In 2017, the number of e-bikes in China reached 29.96 million and the social adoption rate of e-bikes was above 10%. At present, the main concern for consumers of e-bikes is the battery performance. As the number of cycles increases, more PbSO4 crystals irreversibly accumulate on the negative plate, and the very low conductivity of PbSO4 combined with the poor solubility of large crystals leads to a decrease of the effective active material of the negative electrode, which hinders the charge and discharge processes of the negative electrode. As a result, the battery capacity degrades prematurely, greatly reducing the battery cycle life.

In order to solve the problem of cycle life of VRLA batteries, many researchers have studied and found that adding a certain amount of carbon materials (activated carbon, carbon black, graphite, or carbon nanotubes) to the negative active material (NAM) of the batteries can boost...
the utilization of active substances, charge acceptance, high-current discharge performance, cycle performance, and low-temperature performance. Carbon materials are able to effectively prolong the cycle life of batteries by restraining the sulfation of the negative plates, but their effects are different depending on their types and specific surface area (SSA). Moseley concluded that carbon materials with a high SSA (1400 m² g⁻¹) are more favorable for extending battery cycle life of batteries than carbon materials with a lower SSA (less than 100 m² g⁻¹).

Moseley and others summarized the contributions of negative carbon additives to the battery performance: (i) diminishing the contact resistance between the NAMs and decreasing the polarization; (ii) enhancing the SSA and overall conductivity of NAMs; (iii) promoting uniform distribution of lead sulfite in the negative plate, reducing the active material pore size, and impeding the growth of PbSO₄ crystals; and (iv) absorbing excess charge as a capacitor and forming a conducting bridge between lead sulfite and carbon particles.

In recent years, graphene use in VRLA batteries has drawn extensive attention because of its outstanding properties such as its porous structure, good conductivity, and large SSA. Yeung et al. reported that the addition of 1.0 wt % graphene to the negative plate of hybrid electric vehicle (HEV) VRLA batteries resulted in a partial-state-of-charge (PSoC) cycle life improvement of 140%, average PbSO₄ crystal particle size reduction of about 25%, and reduced interfacial resistance. In addition, Li et al. noted that adding 0.9 wt % graphene nanosheets to the NAM as skeletons to construct a 3-D conductive framework in HEV batteries greatly enhanced the cycle life by more than 370% from 2842 to 10 527 cycles under high-rate PSoC (HRPSoC) conditions and increased the utilization of the NAM. Zhu et al. concluded that graphene as a negative material additive could reduce the charge cutoff voltage, increase the discharge cutoff voltage, and also greatly improve HRPSoC cycle life. However, all of these studies investigated graphene added to VRLA batteries for HEV applications. Hence, it could be quite advantageous to add graphene in the NAM to further improve the performance of VRLA batteries for e-bike duty.

In this work, we reported, for the first time, that graphene as a negative additive can significantly enhance the performance of e-bike motive power VRLA batteries. When used in the 100% depth-of-discharge (100% DoD) cycle, the cycle life of the batteries containing graphene was increased by more than 52% compared to that of the control batteries containing acetylene black. In addition, the low-temperature performance and the charge acceptance ratio of the batteries with graphene in the negative electrode were improved.

2. EXPERIMENTAL SECTION

2.1. Graphene Materials. In this experiment, reduced graphene oxide (RGO) was prepared and tested alongside graphene nanoplatelet materials provided by XG Sciences Inc. having three different SSAs as shown in Table 1: graphene 1 (G1), graphene 2 (G2), and graphene 3 (G3). The SSAs of G1, G2, G3, and RGO were 300, 467, 730, and 189 m² g⁻¹, respectively. RGO was prepared by Hummers’ oxidation-reduction reaction method. Table 1 lists the basic characteristics of four types of graphene additives used in this work. The conductivity of the four kinds of graphene is provided by the suppliers.

2.2. Preparation of VRLA Batteries. E-bike batteries were used in this study. The VRLA (48 V 20 A h) batteries consist of four 12 V modules (Figure 1). Each battery (module) (Figure 1b) has six cells, and each cell is composed of four positive plates, five negative plates, and absorptive glass mat separators. The negative plates were prepared using either graphene or acetylene black (for a regular control battery) additives. Manufacturing procedures included acid blending, grid casting, paste mixing, coating, plate curing, sectioning of positive and negative plates, assembling, cast-weld and into the case, over bridge welding and inspection and seal-capping, soldering the terminal and sealed glue filling, leakage test, acid (gel) filling, container formation, and finally matching for delivery. It is worth noting that the whole production process for the e-bike VRLA batteries with graphene was carried out using a battery manufacturing plant line located in the Shandong Branch of the Chilwee Company, which is the largest motive power e-bike VRLA battery producer in China. The graphene and acetylene black additive content in the NAM was 0.3 wt % (based upon the mass of leady oxide, where 3 kg of graphene or acetylene black is added to 1000 kg of leady oxide in every experiment). Other than the different types of graphene added, all conditions were exactly the same as that of a commercial manufacturing process of e-bike VRLA batteries.

2.3. Battery Tests Following the Standard E-Bike Test Profile in China. 2.3.1. Discharge Capacity (Room and Low Temperatures). 2.3.1.1. Two Hour Capacity Test. Fully charged batteries were put into a temperature box (25 ± 2 °C) for 12 h. When the temperature of batteries reached 25 ± 2 °C, the discharge capacity test was started. The batteries were discharged to 42 V under a constant current of 10 A and then charged and discharged for three cycles; the third discharge time was recorded.

2.3.1.2. Discharge Performance Test at a Low Temperature (−15 °C). Batteries fully charged at room temperature

Table 1. Types of VRLA Batteries Used in This Work

| type of batteries | negative plate additives | BET surface (m² g⁻¹) of additives | conductivity (S/m) of additives |
|------------------|--------------------------|----------------------------------|-------------------------------|
| control batteries | acetylene black          | 20                               | 2 × 10⁻¹                      |
| G1 batteries     | graphene 1               | 300                              | 4.3 × 10⁻¹                    |
| G2 batteries     | graphene 2               | 467                              | 4.6 × 10⁻¹                    |
| G3 batteries     | graphene 3               | 730                              | 5.5 × 10⁻¹                    |
| RGO batteries    | RGO                      | 189                              | 5.1 × 10⁻¹                    |
were put into a low-temperature box (−15 ± 1 °C) for 12 h. The batteries were then discharged to 42 V at a constant current of 10 A, and the discharge time was recorded.

2.3.1.3. Charge and Discharge Performance Test at a Low Temperature (−10 °C). The batteries were put into a low-temperature box (−10 ± 1 °C) for 12 h. The batteries were fully charged and then discharged to 42 V at a constant current of 10 A in the low-temperature box, and the process was repeated for five cycles. The fifth discharge time was recorded. It is worth noting that the batteries were fully charged and discharged at a low temperature of −10 °C during the whole measurement process.

2.3.2. Larger Current Discharge (1.8C). Fully charged batteries were stored under the condition of 25 ± 2 °C for 1−4 h. The batteries were then discharged to 42 V at a constant current of 36 A, and the discharge time was recorded.

2.3.3. Charge Acceptance. Fully charged batteries were discharged for 5 h (25 °C). The discharge current, \( I_0 \), is \( C/10 \) A, where \( C \) (Ah) is the largest capacity in 2 h capacity test. After being discharged, the batteries were immediately put into a low-temperature box (0 ± 1 °C) and held for 20−25 h. Then, the batteries were taken out and charged at a fixed voltage of 57.6 V for 10 min, recording the current, \( I_\text{ca} \). The charge acceptance ratio is \( I_\text{ca}/(C/10) \), where \( C \) is the rated capacity (2 h).

2.3.4. Cycle Life Test. Under the condition of 25 ± 5 °C, the fully charged batteries were discharged to 42 V at a constant current of 10 A (100% DoD). Then, the batteries were charged at 58.8 V with a constant current of 2.5 A. When the terminal voltage of batteries reached the charge limit voltage, they were charged at a constant voltage of 55.2 V until the charge current fell to \( \leq 0.5 \) A. Then, they were allowed to rest for 10 min, followed by charging at a constant voltage of 55.2 V for 4 h. Afterward, they were allowed to rest for 1 h before repeating the next charge and discharge cycle. The cycle life test was concluded when two consecutive discharge times of less than 96 min (at a constant current of 10 A) were recorded.

2.4. Physical Characterization. The morphology and structure of the graphene additives were characterized by scanning electron microscopy (SEM, FEI QUANTA 200F) and transmission electron microscopy (TEM, JEOL JEM-2100). The SSA and pore structure of the samples were characterized using N₂ adsorption−desorption characteristics measured with a Micromeritics ASAP 2020 instrument. The samples were degassed at 200 °C for 5 h before measuring under vacuum. Pore size distribution was based on the isotherms using the Barrett–Joyner–Halenda (BJH) model. Raman spectra of graphene additives were measured using a LabRAM HR Evolution instrument with an excitation wavelength of 473 nm (blue). The functional groups on the graphene additives were determined by Fourier transform infrared spectroscopy (FT-IR, Nicolet 5700).

3. RESULTS AND DISCUSSION

3.1. Characterization of the Four Graphene Samples. The variation in physical properties of different graphene materials, such as aggregation size/shape, particle size, Brunauer−Emmett−Teller (BET) surface area, and pore volume, can affect the performance of VRLA batteries. In order to draw conclusions about the effect of different-SSA graphene on the batteries, four kinds of graphene materials were characterized.

Nitrogen adsorption−desorption isotherms and BJH pore size distributions of the four graphene materials are shown in Figure 2. The nitrogen adsorption−desorption isotherms (Figure 2a) of G1, G2, G3, and RGO samples all show typical type-IV isotherms with an H4 hysteresis loop in the relative pressure range of \( P/P_0 = 0.40−0.90 \), indicating the typical mesoporous structure in all samples.\(^5\) The SSA and pore volume of the four samples were obtained by BET analysis. G3 possesses a large SSA of 730 m² g⁻¹ and a BJH desorption...
cumulative volume of pores of 1.032 cm$^3$ g$^{-1}$ between 1.7 and 300 nm width, whereas G1 and G2 show much smaller SSAs (300 and 467 m$^2$ g$^{-1}$, respectively) and BJH desorption cumulative volumes of pores (0.478 and 0.709 cm$^3$ g$^{-1}$, respectively). However, RGO had an SSA of 189 m$^2$ g$^{-1}$ and a BJH desorption cumulative volume of pores of 0.571 cm$^3$ g$^{-1}$. As shown in Figure 2b, all samples showed similar BJH pore size distributions and only one mesoporous peak. The pore sizes of G1, G2, and G3 are concentrated at 3–4 nm. As the SSA increases, the pore size moves toward the smaller 3 nm, whereas RGO had a smaller pore size of 2.5 nm, indicating that the four samples had a homogeneous mesoporous structure. A mesoporous structure can provide channels for the transmission of the acid electrolyte within the cell and be useful to enhance the charge acceptance capability of e-bike VRLA batteries in the deep cycle duty. The FT-IR spectra (Figure 2c) show the oxygen-containing functional groups of the four different graphene additives. The characteristic peaks in the spectra of G2, G3, and RGO around 3462 and 1098 cm$^{-1}$ are related to the O–H stretching and alkoxy C–O stretching vibrations, respectively. Additionally, the peak at 1652 cm$^{-1}$ is weakly associated with hydroxyl C–OH, and the peak at 1565 cm$^{-1}$ is strongly attributed to the –C=–C– vibration of the graphene lamellae. However, there is no obvious characteristic peak for G1 in the spectrum. This is probably because G2 and G3 need longer processing time, and this process is carried out in air, so there exist some oxygen-containing functional groups in the carbon layer.

Figure 3 shows the morphology and structure of four samples with different SSAs of graphene using a scanning electron microscope. Figure 3a shows that the G1 particle is a large number of flakes stacked into a micrometer-sized block. The particle size of G3 (Figure 3c) aggregation is significantly smaller than that of G2 (Figure 3b), and G3 is more evenly distributed than G2. Furthermore, the G1 particle size is obviously larger than those of the other two particles. With a longer processing time and an increase of the SSA, the particle size decreases. The image of RGO (Figure 3d) shows a typical wrinkled and corrugated laminar structure film. RGO thin films have some structural disorders rather than the ideal monolayer so that their effective SSA becomes smaller. The flexible porous structure of graphene facilitates the full contact between the electrolyte and the surface of the electrode material and promotes the uniform distribution of PbSO$_4$ particles during deep charge–discharge cycles.

The Raman spectra of graphene in Figure 4 consist of two typical Raman bands of carbons: the D band at 1336 cm$^{-1}$ is due to defects and disordered carbon and the G band at 1581 cm$^{-1}$ is used to characterize the structure of the sp$^2$-hybridized carbon atom. Comparing spectra in Figure 4a, 4b, and 4c, the defect-related D peak is increasingly higher. With the increase of processing time, the SSA and pore volume increased, so the defect degree of the samples is also increased. In Figure 4d, the D peak intensity of RGO is apparently higher than that of the other three patterns in that only a portion of sp$^2$-hybridized carbon atoms are reduced to sp$^2$-hybridized carbon atoms after redox, a lot of defects resulting in the degree of disorder of the RGO structure increases, accordingly the D peak is relatively high. In addition, a 2D peak appears at 2658 cm$^{-1}$ of the spectra, and the number of graphene layers can be distinguished by observing the intensity ratio of the 2D and the G band peaks in the samples. It is found in the figures that the intensity of the G band is much stronger than that of the 2D band peak, corresponding to multilayered graphene, which is confirmed by TEM observations.

The microscopic structure of four kinds of graphene is further studied by TEM and high-resolution TEM (HRTEM). Figure 5a–c further verifies that the particle sizes of G1, G2, and G3 decrease with increasing mechanical exfoliation processing time. As can be seen from Figure 5a, the particle size of G1 is the largest and structurally complete. The particle size of G2 (Figure 5b) is noticeably smaller than that of G1, but the agglomeration is rather serious. However, the particle size of G3 (Figure 5c) is smaller than that of G2, but the stacking is more serious and a great quantity of small particles disorderly stacked together. This characterization is consistent with the SEM observation. RGO (Figure 5d) displays a disordered, transparent, and wrinkled gauze shape, which indicates that the sheet is thinner. The HRTEM images (Figure 5a1–d1) show that the four graphene samples have multiple graphene sheets, which are consistent with the Raman spectra. The number of layers of graphene decreases with a longer processing time. In addition, the RGO film is large and complete with obvious folds and stack of partial sheets to form a multilayered structure. It implies that the graphene film prepared by the Hummers’ method is thinner than the graphene prepared by the processing method.

3.2. VRLA Battery Tests. After assembly, the batteries were tested for performance. Four types of graphene materials were used as negative electrode additives for VRLA batteries in a concentration of 0.3 wt %, and the batteries with acetylene black were used as control batteries. It is well-known that acetylene black has a SSA of about 20 m$^2$ g$^{-1}$ and a conductivity of around 2 × 10$^3$ S/m. Table 1 shows the types of VRLA batteries used in this work.

3.2.1. Discharge Capacity (Room and Low Temperatures). The discharge capacity and discharge time of VRLA batteries at room and low temperatures with different graphene materials are compared to those of the control batteries with acetylene black, as shown in Figure 6. Batteries were discharged to a 42 V cutoff voltage at a constant current of 10 A to measure the 2 h discharge capacity at room temperature; Figure 6a shows the discharge time for the third cycle. The actual discharge capacity of the batteries is calculated by multiplying the discharge...
current by the duration of the discharge. National standards stipulate that the actual capacity of qualified batteries is greater than the rated capacity; that is, the discharge time is over 120 min. It can be seen from the figure that the discharge times of the batteries with graphene are longer than those of the control batteries. Moreover, when G2 is added, the discharge capacity of batteries is the highest and the discharge time is 132 min, which is 4 min longer than that of the control batteries.

Compared with the control batteries, the discharge times of the batteries with graphene have an extension of 1−3%. Experimental results show that the discharge capacities of graphene-containing batteries are larger than those of the control batteries, which are attributed to the much larger SSA of graphene.

There are two kinds of low-temperature performance tests: one is the room-temperature charge and low-temperature discharge (−15 °C) and the other is low-temperature charge and low-temperature discharge (−10 °C). Low-temperature capacity performance of batteries is related to the working performance of the batteries in a low-temperature environment. If the discharge capacity of a battery at low temperatures is less than the standard (≥85 min), the battery will be less effective in winter conditions, especially in locations such as northern China. As a consequence, the state mileage performance at low temperatures is much worse than that at room temperature. Therefore, it is necessary to improve the low-temperature performance of the battery. Figure 6b indicates that the discharge times of the batteries with graphene are significantly higher than those of the control batteries at a low temperature of −15 °C (charged at room temperature). The discharge time of the G3 batteries is 5 min longer than that of the control batteries, and the discharge times of batteries with G1, G2, G3, and RGO are very similar. The discharge times for batteries with graphene additives after five cycles (charge and discharge) at a low temperature of −10 °C are shown in Figure 6c. The four batteries with graphene additives have the same discharge time. A significant improvement of 9% is observed in the discharge times of batteries with graphene when compared to control batteries, indicating that graphene additives have a better low-temperature performance, can be recharged faster, and have longer life in a low-temperature environment.

Comparing the discharge performance at room temperature and low temperature, it is clear that the capacity at a low temperature is reduced compared to that at room temperature. This is because of poor electrolyte fluidity, slow chemical
reaction, and an increase in battery internal resistance at low temperatures.

3.2.2. Larger Current Discharge (1.8C<sub>2</sub>). When the e-bike is started, the discharge current will exceed 1C discharge, which also affects the battery life. Accordingly, it is of great significance to study the large-current discharge performance of the battery. It is observed from Figure 6d that the discharge time of the batteries with graphene under 1.8C<sub>2</sub> (36 A) current is 29 min, representing an improvement in large-current discharge performance compared with the control batteries. When a large current is discharged, the capacity drops particularly rapidly because the reaction occurs only on the surface of the active materials on the plate. Moreover, the formation of lead sulfate particles on the surface of the negative plate hinders the contact of the internal active materials with the electrolyte. Consequently, lead–acid batteries can cope with short periods of large current discharge, but the capacity for continuous discharge under large current is poor.

3.2.3. Charge Acceptance. Charge acceptance is an important performance of VRLA batteries for e-bike applications. The high charge acceptance ratio ensures the normal use of the battery and prolongs the battery cycling life. Figure 7a shows that the charge acceptance ratio, I<sub>sa</sub>/I<sub>c</sub> (I<sub>c</sub> is the 2 h-rated current), value of G3 batteries is about 28.5% higher than that of the control batteries. A higher I<sub>sa</sub>/I<sub>c</sub> value indicates that the battery has better charge acceptance. The charge acceptance of batteries with graphene is higher than that of the control batteries. The results show that the charge acceptance of batteries with high-SSA graphene is greater than that of those with low-SSA graphene. Accordingly, the best charge acceptance performance comes from G3 with the highest SSA. A graphene material with a large SSA improves the electrochemical active area of NAM, which is beneficial to the dissolution of PbSO<sub>4</sub> and the reduction of Pb<sup>2+</sup> and the improvement of charge acceptance of batteries. The RGO has the smallest SSA; however, the charge acceptance of RGO batteries was only slightly lower than that of G3 batteries. This is probably because the RGO films have a unique flexible porous structure and the sheets are thin and complete, which facilitates the transport of hydrogen sulfate ions and electrolyte, promotes the even distribution of PbSO<sub>4</sub> particles, and improves the utilization rate of active mass.

3.3. Cycle Life in a 100% DoD Condition. Cycle life is one of the key battery performance parameters. Cycle life is defined as the number of complete charge–discharge cycles that an e-bike battery can perform before its capacity drops to below 80% of the nominal capacity (i.e., discharge time is 96 min). The cycle life of the batteries is required to be not less than 250 times, and those that do not meet this requirement are rated unqualified batteries. The effect of graphene with different SSAs on the cycle life of VRLA batteries under 100% DoD at C<sub>2</sub> discharge rate is shown in Figure 7b. The control batteries show a sharp decline in the discharge time within 250 cycles, which is a typical level of the state-of-the-art technologies for VRLA batteries of 12 V 20 A h on e-bike duty. This may be because the charge acceptance of the control batteries is poor, and the water loss is significant during the cycling, causing premature capacity loss and accelerating battery failure. However, the batteries with graphene in the negative plate achieved 380 cycles. Variation trends of the G1 and G2 batteries are basically the same. The G3 and RGO batteries generally display a similar superior cycling. In addition, the discharge time of G3 and RGO batteries remained stable within 300 cycles, but the discharge time dropped rapidly after 300 cycles, which may be due to electrolyte stratification. With increasing numbers of the battery cycles, the internal resistance of the batteries increases continuously during the discharge process because of the consumption of electrolytes and the decrease of active materials. Important to this is the
accumulation of lead sulfate crystals with poor conductivity on the negative plates during the discharge process. Furthermore, during the last 20 cycles, the batteries may be in the critical state of thermal runaway because of the excessive water loss of electrolyte.7

According to the above results, it is clear that the VRLA batteries with graphene can not only increase charge acceptance of the batteries but also suppress the sulfation of the negative plates during deep cycling.30 Moreover, the cycle life of the batteries with graphene improved by 52% compared to that of the control batteries under a 100% DoD condition. These results are attributed to graphene having better conductivity and larger SSA than acetylene black.

### 3.4. Water Loss Performance

The main reason for the failure of the long-life batteries is the loss of water, which is caused by gassing output. The electrolysis of water occurs during battery charging, and then the hydrogen evolution reaction occurs on the negative electrode. Carbon additives typically reduce the hydrogen overpotential, resulting in more gassing output. It is important to determine the influence of graphene additives on water loss.

At the end of charging, PbSO₄ is substantially reduced to Pb (reaction I). The excess charge current will decompose the water in the electrolyte, the oxygen gas generated at the positive plate (reaction II) is transported to the negative plate, and the oxygen recombination reaction occurs at the negative electrode (reaction III). However, if the charging current is too large, the oxygen recombination reaction at the negative plate will not keep up with the rate of oxygen evolution, and the gas will open the exhaust valve and cause water loss. On the other hand, hydrogen evolution (reaction IV) occurs on the negative plate of the battery. The positive plate cannot absorb hydrogen, and finally, it will also discharge the gas chamber and cause the loss of water. In the charging process, the positive and negative reactions are as follows:

- **On the negative electrode,**
  \[ \text{PbSO}_4 + 2e^- \rightarrow \text{Pb} + \text{SO}_4^{2-} \]  
- **On the positive electrode,**
  \[ \text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2e^- \]  
  \[ \text{Pb} + \frac{1}{2}\text{O}_2 + 2\text{H}^+ + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 + \text{H}_2\text{O} \]  
  \[ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \]

Figure 8 presents the amount of water loss during the cycling process. As the number of cycles increases, the battery water loss also increased. However, in batteries with graphene, the water loss was slightly increased compared with the control batteries. While the graphene may exacerbate the water loss during the late stage of the cycles, the results show that the amount of water lost by the batteries containing graphene is within a controllable range, with no significant differences from the control batteries. After 350 cycles, the water loss of the batteries reached 28.3–29 g. It is possible that the water loss of batteries increases the concentration of acid, accelerates the sulfation of the negative plate, reduces the batteries capacity, shortens the cycle life of batteries, and even causes the thermal runaway of batteries.38

**3.5. Mechanism of Adding Graphene on the Negative Plate.** On the basis of the above results, we proposed a possible mechanism for extending the battery life from 250 to 380 cycles after adding graphene. The battery for e-bikes is required to charge and discharge in deep cycle duty under a 100% DoD condition. Uneven lead sulfate crystals continuously accumulate on the negative plate, forming small PbSO₄ crystals with high solubility, whereas big lead sulfate crystals with lower solubility will be recrystallized into larger PbSO₄ crystals.39,40 It is well-known that acetylene black has a small spherical structure.
When acetylene black (Figure 9a) is added as a negative additive, a point-to-point contact forms between acetylene black particles and PbSO₄ particles. However, when graphene (Figure 9b) is added to the negative plate, PbSO₄ becomes smaller and results in a uniform distribution because of the formation of a surface-to-point contact between graphene and PbSO₄ particles. It is possible that graphene is a two-dimensional sheet structure that can form a continuous conductive network structure, which is helpful for forming small-sized and uniform distribution of lead sulfate crystals with high solubility and facilitating the diffusion of electrolyte from the surface to the interior of the plate.14,41 The contact area between graphene and lead sulfate particles (surface-to-point) is much larger than that of acetylene black and lead sulfate particles (point-to-point). Therefore, graphene additives can better restrict the growth of lead sulfate crystals on the negative plate and prolong the cycle life of the battery.

In the deep cycle duty, the electrochemical reaction process occurs not only on the lead surface of the NAM but also on the surface of graphene.81,42 This probably corresponds to the parallel mechanism12 on both Pb and graphene surfaces, which retards sulfation of the negative plates and prolongs the cycle life of the batteries. Figure 9c shows a schematic diagram of electron migration through the Pb and carbon interfaces in the negative plate. Figure 9. (a,b) Schematic diagram of acetylene black and graphene on the negative plate under a 100% DoD condition, respectively. (c) Schematic diagram of electron migration through the Pb and carbon interfaces in the negative plate.

When acetylene black (Figure 9a) is added as a negative additive, a point-to-point contact forms between acetylene black particles and PbSO₄ particles. However, when graphene (Figure 9b) is added to the negative plate, PbSO₄ becomes smaller and results in a uniform distribution because of the formation of a surface-to-point contact between graphene and PbSO₄ particles. It is possible that graphene is a two-dimensional sheet structure that can form a continuous conductive network structure, which is helpful for forming small-sized and uniform distribution of lead sulfate crystals with high solubility and facilitating the diffusion of electrolyte from the surface to the interior of the plate.14,41 The contact area between graphene and lead sulfate particles (surface-to-point) is much larger than that of acetylene black and lead sulfate particles (point-to-point). Therefore, graphene additives can better restrict the growth of lead sulfate crystals on the negative plate and prolong the cycle life of the battery.

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4. CONCLUSIONS

In summary, graphene nanoplatelets with different SSAs and RGO materials were employed as the negative additives of e-bike motive power VRLA batteries. The effects of graphene addition to the NAM of the batteries were investigated by large current discharge, charge acceptance, cycling performance, and water loss tests. The results show that the addition of graphene to the batteries can improve large-current discharge performance and increase low-temperature performance, promote charge acceptance, and lengthen 100% DoD cycle life by 52%, as compared to the control batteries with acetylene black additives. Moreover, the water loss problems of the batteries with graphene are in a controllable range. In addition, the batteries with the highest SSA of G3 and RGO exhibit the most stable cycle performance and a better charge acceptance stability, compared to the batteries with G2 and G1. These excellent properties were derived from G3 with a larger SSA and pore volume. A higher SSA enhances electrochemical active surface, suppresses the irreversible sulfation of the negative plate, and improves charge acceptance of the negative plate during charging and cycle performance. While the SSA of RGO film is small, the sheets are thin and complete and have abundant pore structure. The significant improvement in battery performances can be attributed to the addition of graphene on the negative plate to promote the reduction of PbSO₄ to Pb during charging and to resist the accumulation of lead sulfate during cycling. We wish to emphasize that this is the first report on improving battery performance in e-bikes by using graphene as an additive.

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: kvinodg@nccu.edu.
*E-mail: nanodai@gmail.com, gpdai@ncu.edu.cn, gdai@nccu.edu (G.-P.D.).

ORCID
Kizhanipuram Vinodgopal: 0000-0002-0741-6282
Gui-Ping Dai: 0000-0001-9208-9994

Notes
The authors declare no competing financial interest.

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■ REFERENCES

1. Liu, W.; Sang, J.; Chen, L.; Tian, J.; Zhang, H.; Palma, G. O. Life cycle assessment of lead-acid batteries used in electric bicycles in china. J. Cleaner Prod. 2015, 108, 1149–1156.
(41) Moseley, P. T.; Rand, D. A. J.; Peters, K. Enhancing the performance of lead-acid batteries with carbon—In pursuit of an understanding. *J. Power Sources* **2015**, *295*, 268−274.

(42) Pavlov, D.; Rogachev, T.; Nikolov, P.; Petkova, G. Mechanism of action of electrochemically active carbons on the processes that take place at the negative plates of lead-acid batteries. *J. Power Sources* **2009**, *191*, 58−75.