

Study of Graphene as a Negative Additive for Valve-Regulated Lead-Acid Batteries Working under High-Rate Partial-State-Of-Charge Conditions

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To extend the applications of graphene and improve the cyclic life of valve-regulated lead acid (VRLA) batteries applied in hybrid electric vehicles, graphene has been added to negative active materials of the VRLA batteries. The influence of graphene on the negative electrodes of valve-regulated lead-acid batteries during high-rate partial-state-of-charge cycling has been investigated by galvanostatic charge/discharge tests, scanning electron microscopy, X-ray diffraction and cyclic voltammetry. Results suggest that the addition of graphene in negative materials can diminish the charge cut-off voltage, boost the discharge cut-off voltage and improve the cyclic life of the VRLA batteries in high-rate partial-state-of-charge cycling. The superior electrochemical performance could be ascribed to the inhibition effect of graphene on the growth of lead sulfate. Therefore, graphene can be a promising negative additive for VRLA batteries.

Keywords: Graphene; Cycle life; Valve-regulated lead-acid batteries; Negative active material; High-rate partial-state-of-charge

1. INTRODUCTION

Over the last few years, valve-regulated lead acid (VRLA) batteries have been extensively applied in various energy storage devices, electric vehicles (EV) and hybrid electric vehicles (HEV) due to their simple structure, high safety and low cost [1-3]. VRLA batteries in HEV applications are often charged and discharged with high currents for a short period. As VRLA batteries could be charged only while the HEV are braking, they are usually operated at 50%-53% state of charge (SoC)

[4]. Therefore, VRLA batteries are operated in high-rate partial-state-of-charge (HRPSoC) conditions. In the operating conditions, the charge acceptance of the negative plates is limited, PbSO_4 particles are formed during the discharge process, and cannot be converted to Pb completely in the subsequent charge process, which leaves a portion of PbSO_4 in the negative active materials and results in the accumulation of PbSO_4 in the negative plates. As a result, the cyclic life of VRLA batteries is shortened [5].

Tremendous efforts have been made to solve these intractable problems. One promising strategy is to prepare the ultrabattery, which contains a PbO_2 positive plate and a negative plate comprised of two parts: half is a conventional lead plate and the other half is a carbon plate. In the ultrabattery design, the carbon plate could share the high charge and discharge currents under HRPSoC cycling, which diminishes the current density of the Pb plate and restrains the growth of PbSO_4 effectively [6-8]. Another approach involves the addition of additives to the negative activated materials of VRLA batteries. In the previous literature, several additives, such as graphite, carbon black, barium sulfate, activated carbon, poly-aspartic acid, etcetera, have been employed as inhibitors of PbSO_4 recrystallization [9-18]. For instance, K. Nakamura et al. have testified that carbon black could limit the sulfation of the negative plates during HRPSoC cycling [9]. D. Pavlov et al. have established that barium sulfate and electrochemically activated carbons would act as a nucleation agent for the formation of PbSO_4 crystal and maintain its uniform distribution [14]. In general, those auxiliary materials, especially carbon-based materials could restrain the progressively accumulation of PbSO_4 in the negative plates during HRPSoC cycling effectively. However, as promising additives for VRLA batteries, it is highly desired to explore other types of carbon-based materials that are suitable for the inhibition of PbSO_4 recrystallization in HRPSoC cycling.

Recently, graphene has attracted extensive attention due to its porous texture, good electric conductivity and high specific surface area [19, 20]. Various graphene-based composites have been prepared in lithium-ion batteries and supercapacitors with superior electrochemical properties [21-25], which enlightens us to explore graphene as a possible negative additive for VRLA batteries.

In this work, to extend the applications of graphene and solve the PbSO_4 recrystallization issues, we have therefore fabricated graphene and investigated the influence of graphene on the negative electrodes of VRLA batteries during HRPSoC operations. When used in HRPSoC cycling, the negative electrodes added with the graphene additive exhibit superior cycle life as compared to that without adding graphene. The improved electrochemical properties could be expected for the inhibition effect of graphene on the sulfation of the negative electrodes.

2. EXPERIMENTAL

2.1 Materials preparation

Graphene was synthesized by a modified Hummer's method [25]. 6 g of graphite was initially added to a mixture of 150 mL of 98 wt.% H_2SO_4 solution and 16.7 mL of 85 wt.% H_3PO_4 solution in an ice-water bath. Subsequently, 18 g of KMnO_4 was added gradually under continuously stirring.

After being continuously reacted at 35 ± 1 °C for 2 h, the mixture was added into 460 mL of distilled water and stirred for another 2 h. Then the resulting mixture was poured into 1500 mL of 1.8 wt.% H_2O_2 solution and stirred for 24 h at room temperature. After being washed with 1500 mL of 5 wt.% HCl solution for three times, the resultant graphene oxide was centrifuged and dried at 40 °C for 72 h. Finally, graphene was obtained after graphene oxide being put into a muffle oven preheated to 815 °C for 45 s.

2.2 Preparation of negative plates

The negative plate of VRLA batteries (denoted as Pb2) was prepared with lead oxide powder, humic acids, barium sulfate and graphene. The degree of oxidation of lead oxide powder was 76%. The contents of humic acids, barium sulfate and graphene were 0.3 wt.%, 1 wt.% and 0.5 wt.% respectively. The electrode without the graphene additive (denoted as Pb1) was served as a reference. All the negative plates were formed under the same conditions: in H_2SO_4 aqueous solution (1.05 g cm^{-3}) for 18 h, and the formation process was completed with twice higher quantity of electricity than the theoretical capacity of the negative plates.

2.3 Electrochemical measurements

The influence of graphene on the cycle life of VRLA batteries under HRPSoC conditions was investigated by using 1.5 Ah cells with one negative plate and two positive plates per cell. The thickness of the positive plates was 2.5 mm and the thickness of the negative plates was 2 mm. The electrolyte was H_2SO_4 aqueous solution (1.347 g cm^{-3}). The cycle life in HRPSoC conditions was tested by using Neware Battery Testing System. Firstly, the tested batteries were discharged to 50% SoC at 1 C. Subsequently, the batteries were subjected to the following cycling: charge at 2 C rate for 60 s, rest for 60 s, discharge at 2 C rate for 60 s, rest for 60 s. The cell voltage was measured at the end of each charge and (or) discharge process, and the test process was stopped when the cell voltage increased to 2.83 V or when the cell voltage fell down to 1.75 V.

Cyclic voltammetry measurements (CV) were performed on an electrochemical workstation (CHI 750D) at a scanning rate of 5 mV s^{-1} . The scanning range was -1.3 V to -0.7 V. The as-prepared Pb1 (or Pb2) negative plate was used as the working electrode, commercial PbO_2 positive plates were used as the counter electrodes, $\text{Hg/Hg}_2\text{SO}_4$ electrode was used as the reference electrode. The electrolyte was H_2SO_4 aqueous solution (1.347 g cm^{-3}).

2.4 Physical characterizations

The morphologies of the as-prepared graphene and negative plates were characterized by scanning electron microscopy (SEM, Hitachi S4700). The crystalline structure of the as-prepared graphene and the negative plates were identified with a D/max- γ B X-ray diffractometer (Cu Ka radiation ($\lambda=1.54178$), step size= 0.02° , $10^\circ < 2\theta < 90^\circ$).

3. RESULTS AND DISCUSSION

The phase identification of graphite (G), graphene oxide (GO) and graphene (RGO) were determined by X-ray powder diffraction (XRD), with the results shown in Fig. 1. The XRD pattern of G showed a strong diffraction peak at $\sim 26^\circ$, which corresponded to the (002) planes of graphite. In contrast, The XRD pattern of GO showed a main diffraction peak at $\sim 10.5^\circ$, and the peak at 26° disappeared, indicating that the graphite had been oxidized to GO successfully. For the XRD pattern of graphene, only a weak diffraction peak at $\sim 23^\circ$ was distinguishable, suggesting the highly amorphous nature of graphene. And the results indicated that GO had been reduced to graphene through thermal reduction [25].

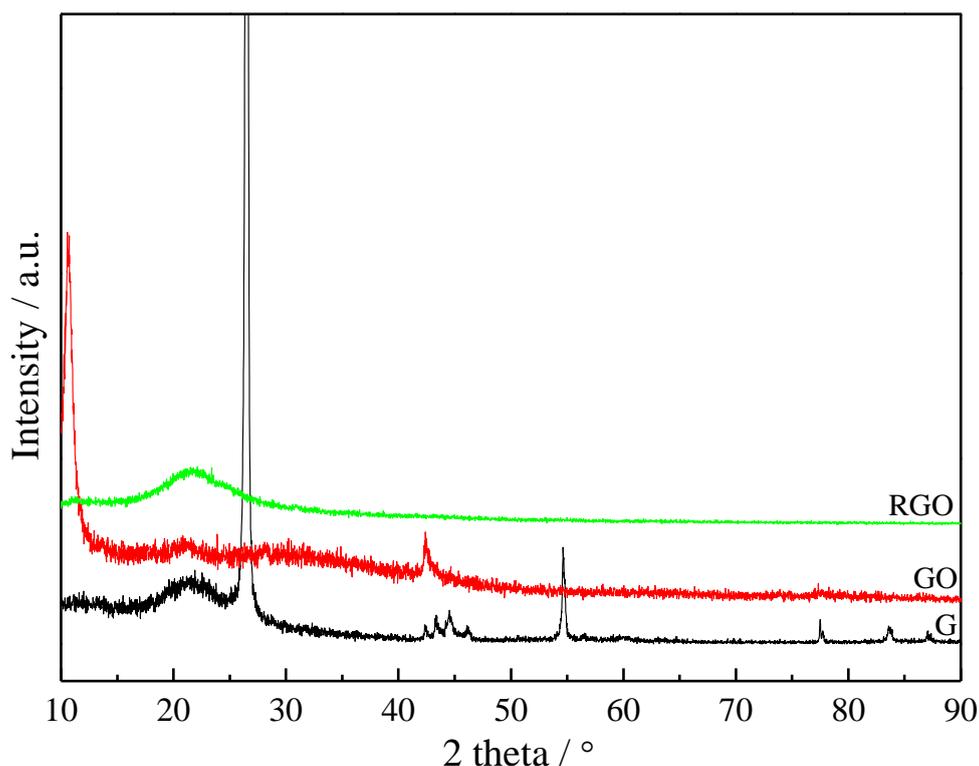


Figure 1. X-ray diffraction patterns for graphite, graphene oxide and graphene.

The morphology of the as-prepared graphene was depicted in Fig. 2a. The SEM image in Fig. 2a displayed a flexible porous structure of the graphene, which was favorable for the decoration of graphene with PbSO_4 particles. The porous structure of graphene may facilitate the uniform distribution of PbSO_4 particles during HRPSoC cycling. The influence of graphene on morphologies of the negative plates after formation was displayed in Fig. 2 b and c. Fig. 2b showed the porous spongy structure of the Pb1 electrode without adding graphene. It could be observed from Fig. 2c that the surface of the Pb2 electrode after formation featured a less regular structure with several graphene particles, and the lead active materials displayed dendritic structures, which may affect the HRPSoC cycling performance of the electrodes.

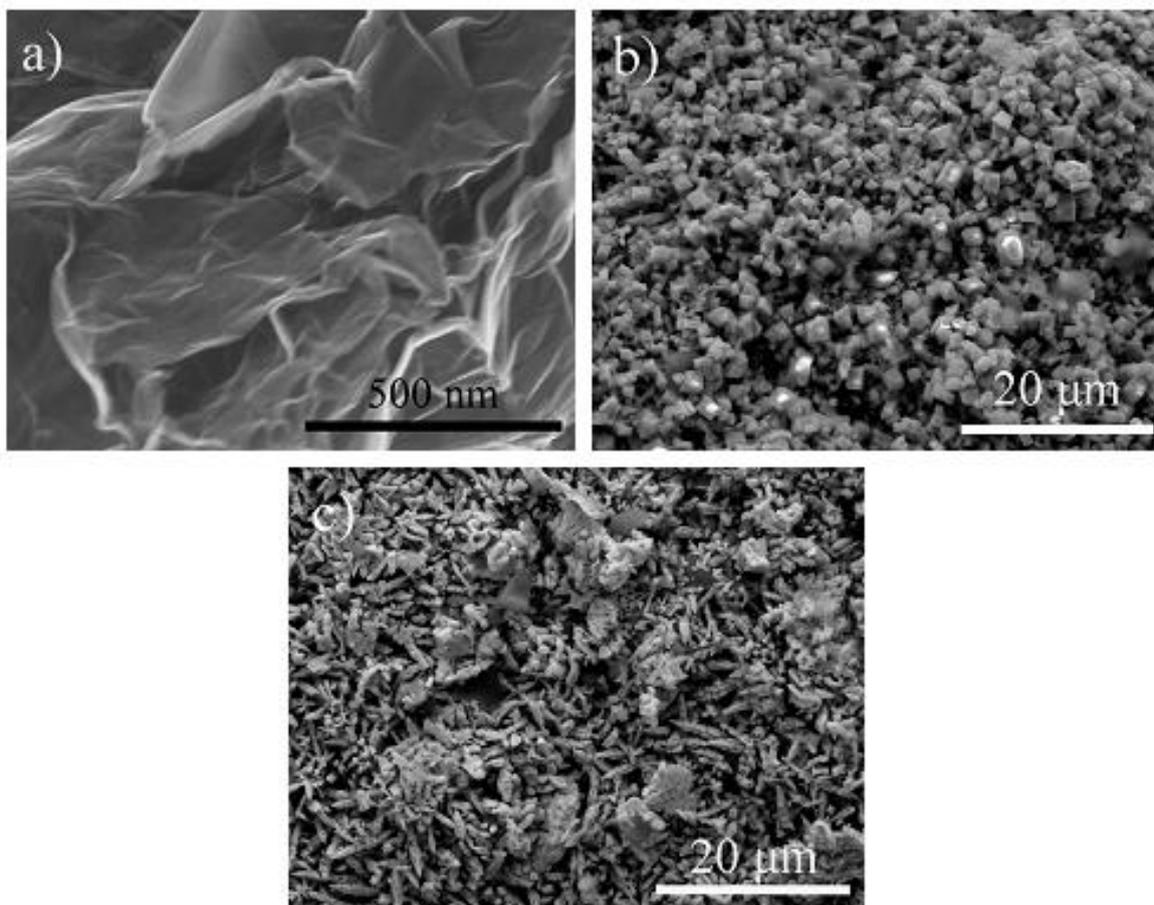


Figure 2. SEM images of (a) graphene, (b) the Pb1 electrode after formation, (c) the Pb2 electrode after formation.

The effect of graphene on the cycle life of VRLA batteries under HRPSoC conditions was shown in Fig. 3. It could be observed from Fig. 3c and Fig. 3d that the addition of graphene in the negative electrodes of VRLA batteries had a significant influence on the charge/discharge cut-off voltages and cyclic life of VRLA batteries. The charge cut-off voltage of both the Pb1 and Pb2 batteries increased rapidly in the initial stage of cycling life tests, which subsequently decreased gradually as the cycling number increased. As the charge and discharge electric quantity of the batteries was equivalent in each single cycle according to the HRPSoC charge/discharge test mode, the charge acceptance would play a crucial role in determining the discharge cut-off voltage of the batteries [27]. The batteries with superior charge acceptance can be charged more effectively, resulting in higher discharge cut-off voltage at the end of the discharge process. It was obviously observed from Fig. 3c and d that the addition of graphene in negative plates of VRLA batteries significantly decreased the charge cut-off voltage and boosted the discharge cut-off voltage in HRPSoC cycling, which indicated that the Pb2 negative plate added with the graphene additive exhibited a superior charge acceptance. As a result, although the cyclic life of the Pb1 battery was less than 2000 HRPSoC cycles, the cyclic life of the Pb2 battery could be extended to ~13000 cycles under the same conditions, which was long than [5, 15, 16, 21, 26] or comparable with [13, 14, 27] other negative electrodes added with

different additives. Therefore, graphene could be applied as a promising negative additive for VRLA batteries. The foregoing results obtained suggested that the addition of graphene in negative electrodes of lead-acid batteries played a crucial role in improving the HRPSoC cycling performance of VRLA batteries, due to that the addition of graphene in negative electrodes could promote the electron transfer, accelerate the charge process, retard the growth and deactivation of $PbSO_4$ and improve the utilization of active materials.

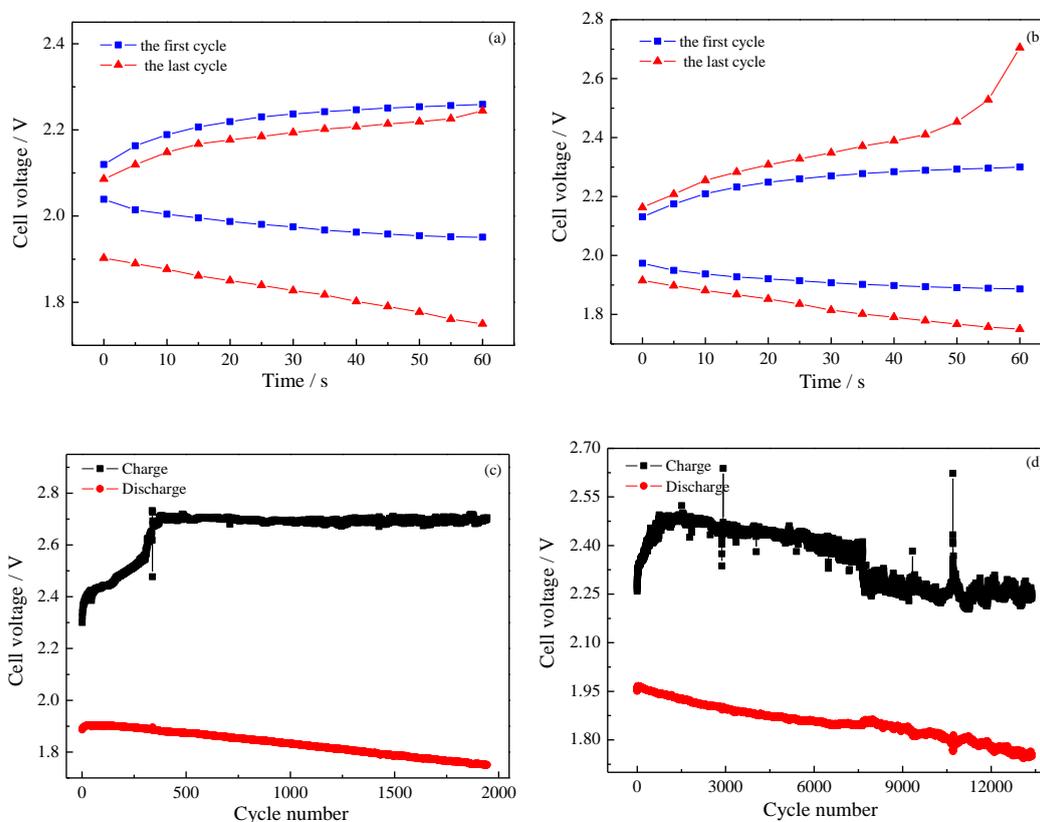


Figure 3. The different cycles' charge/discharge curves of (a) the Pb2 electrode, (b) the Pb1 electrode, (c) charge/discharge cut-off voltage of the Pb1 battery during HRPSoC cycling, (d) charge/discharge cut-off voltage of the Pb2 battery during HRPSoC cycling.

To better understand the influence of graphene on the negative plates of VRLA batteries during HRPSoC cycling, the surface morphology of the Pb1 and Pb2 negative plates were investigated after the termination of the HRPSoC cycle tests. The principal component was primarily $PbSO_4$ as the negative electrodes were in discharge state. As observed from Fig. 4, the Pb1 negative plate without adding graphene consisted of some relative smooth and big $PbSO_4$ particles. By adding graphene, the Pb2 negative plate, however, constructed with some relative loose and small $PbSO_4$ particles. The results obtained suggested that the addition of graphene in negative active materials could limit the sulfation of negative plates, due to that the porosity of graphene could supply plenty acid reservoirs in the interior of negative plates, which brought active sites for the migration of $PbSO_4$ during discharge process [7].

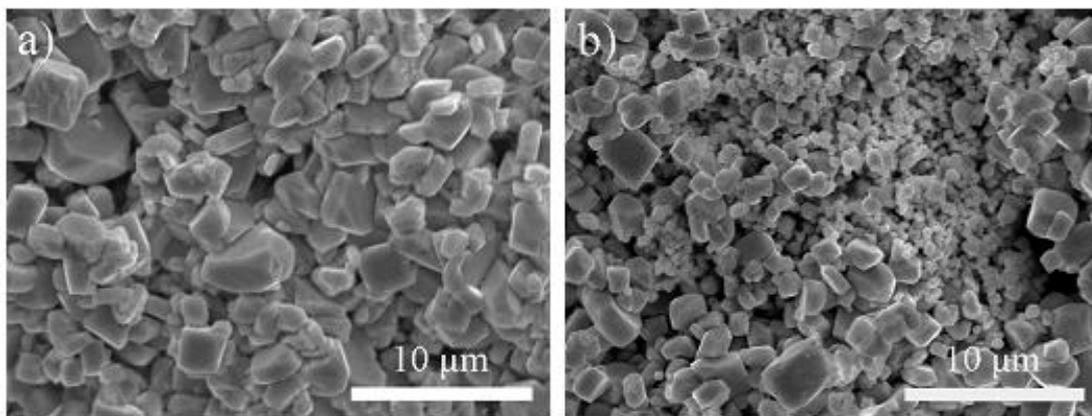


Figure 4. SEM images of negative plates after the termination of the cycle test: (a) the Pb1 plate, (b) the Pb2 plate.

The chemical compositions of the Pb1 and Pb2 negative active materials were further characterized by XRD after capacity recovery charging, with the results shown in Fig. 5. Both Pb and PbSO₄ diffraction peaks were observed in XRD patterns of the two negative active materials, which suggested that the SoC of the batteries was insufficient to convert all the PbSO₄ to Pb. Nevertheless, the intensity of the diffraction peaks for Pb and PbSO₄ were rather different between the two negative active materials. Compared to the Pb1 plate, the intensity of the Pb diffraction peaks of the Pb2 plate was greatly increased, while the intensity of the PbSO₄ diffraction peaks was significantly decreased. The phenomenon suggested that the addition of graphene in the negative active materials was highly beneficial for the conversion of PbSO₄ to Pb in the charge process. Therefore, the sulfation of the negative plates added with graphene was inhibited, and the cycling performance of the VRLA batteries had been significantly improved.

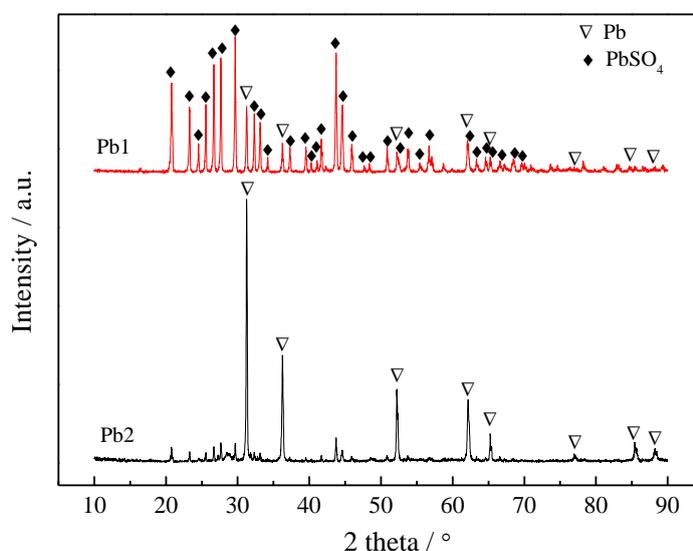


Figure 5. XRD patterns of the Pb1 and Pb2 negative active materials after capacity recovery charging.

The effect of graphene on the negative electrodes of VRLA batteries was further examined by cyclic voltammetry (CV), with the results shown in Fig. 6. Fig. 6a presented the CV curves of the Pb1 and Pb2 electrodes after formation. In the cathodic polarization process, a peak between -1.3 V and -1.1 V was observed, which was attributed to the reaction process of Pb^{2+} ions reduction to Pb. Turning to the subsequent anodic polarization process, the peak between -0.95 V and -0.8 V was observed, which was related to the oxidization process of Pb to PbSO_4 [5, 13, 14]. It was also observed from Fig. 6a that the CV curves of the Pb1 and Pb2 electrodes were almost overlapped. The results suggested that the influence of graphene on the negative electrodes of VRLA batteries was relative weak after formation. This may due to that the active material of the Pb1 plate was primarily spongy lead after formation, which exhibited good electronic conductivity and electrochemical performance as well. However, as observed from Fig. 6b, the charge current of the Pb2 electrode was much higher than the Pb1 electrode after 1500 cycles, which indicated that the negative electrode added with graphene exhibited superior reversibility as compared to the Pb1 electrode during the HRPSoC cycling. The phenomenon was due to that the spongy structure of Pb in the negative plate without adding graphene was gradually converted to irreversible lead sulfate, eventually decreasing the reversibility of the electrode during HRPSoC cycling, while recrystallization of PbSO_4 was inhibited in the negative active material added with graphene under HRPSoC conditions.

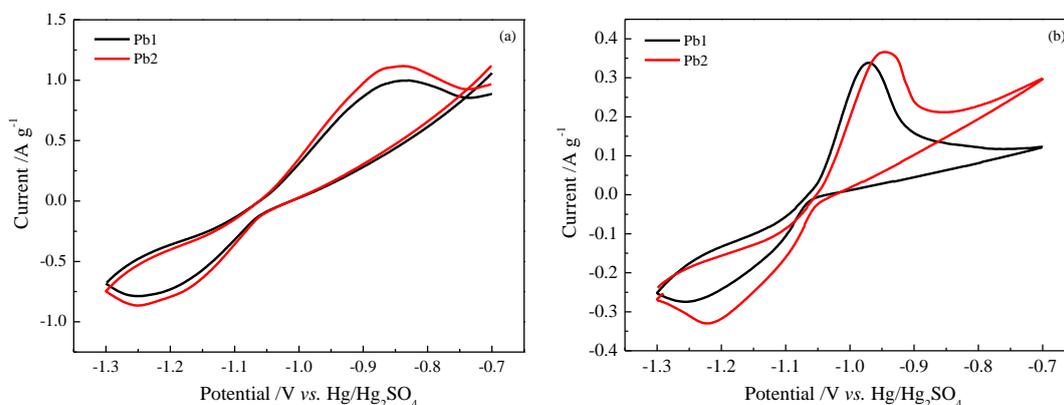


Figure 6. Cyclic voltammetry curves of the Pb1 and Pb2 electrodes (a) after formation, (b) after 1500 HRPSoC cycles.

As mentioned above, the addition of graphene into negative plates of VRLA batteries could not only decrease the polarization of the electrodes, but also limit the sulfation of the negative plates during HRPSoC cycling, resulting in prolonged cycling life. During the discharge process, for the electrodes without adding graphene, the electrochemically Pb would be oxidized to Pb^{2+} , and PbSO_4 particles would be aggregated on the surface of the pristine PbSO_4 . For the electrodes added with the graphene, PbSO_4 particles would be precipitated on the surface of both PbSO_4 and graphene, favoring the dispersion of PbSO_4 particles [5, 27]. Turning to the subsequent charge process, PbSO_4 would be dissolved and mostly reduced to Pb for the plates added with graphene due to that graphene could promote the electron transfer and accelerate the charge process. In contrast, a certain amount of the

aggregated PbSO₄ particles could not be reduced to Pb in the plates without adding the graphene additive, leading to the accumulation of lead sulfate. The recrystallization process would yield big PbSO₄ particles which were hard to dissolve, and eventually leading to sulfation of the negative electrodes.

4. CONCLUSIONS

In summary, graphene had been prepared and investigated as a negative additive for VRLA batteries. The influence of graphene on the negative plates of VRLA batteries was investigated by SEM, XRD, HRPSoC charge/discharge tests and cyclic voltammetry measurements. Results showed that the addition of graphene in the negative active materials could decrease the charge cut-off voltage and increase the discharge cut-off voltage in HRPSoC cycling, and the cycle life was greatly improved as compared to the electrodes without adding graphene. The significant improvement of electrochemical performance was due to that the addition of graphene in the negative plates was highly beneficial for the conversion of PbSO₄ to Pb in the charge process and the inhibition of PbSO₄ recrystallization during cycling.

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