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Research Article

rGO and carbon black embedded positive electrode for lead-acid battery

R. J. Dissanayeka [1,2], W.G.K.S. Buddhika [1,3], K.K. Pipun Randika [1,3], M.K.T. Madushan [1,4], R.C.L De Silva [1], A.M.K.L. Abeykoon [*,1], and I.R.M Kottegoda [1]

1 Materials Technology Section, Industrial Technology Institute, Sri Lanka
2 Department of Physics, University of Sri Jayewardenepura, Sri Lanka.
3 Faculty of Technology, University Colombo, Sri Lanka
4 Faculty of Technology, University Sabaragamuwa, Sri Lanka

Abstract

Lead acid battery has long been recognized as a versatile cost-effective energy storage solution for applications, including automotive, renewable energy integration, and telecommunications. The present research aims to investigate the impact of specific additives such as carbon black and reduced graphene oxide on the positive electrode of lead oxide batteries. To assess the performance of lead oxide batteries, the electrode material is formulated by combining lead oxide, lead dioxide, and additives at appropriate ratios and characterized using XRD and SEM. The discharge capacity of each positive electrode is investigated using a two-electrode cell and results were compared with a similar commercial cell. When the rGO or carbon black ratio of the positive electrode is 0.4% (w/w), the respective discharge capacities of the battery were 276.4mAh and 243.68mAh which is well above the discharge capacity of a commercial battery under similar conditions. In addition, the respective voltage drops of the battery with each rGO and carbon black were 0.22V and 0.30 V which is significantly less than that of a similar commercial battery (1.07V). In addition, a stable capacity was observed in the rGO based battery during the charge-discharge cycling. These findings highlight the potential of rGO and carbon black as additives in improving the electrochemical performance of lead-acid batteries.

Keywords: Lead acid battery, positive electrode, rGO, carbon black.

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* Corresponding author: lahiru.kulanga@gmail.com

1. INTRODUCTION

A lead-acid battery is a type of rechargeable energy storage device invented by Gaston Planté in 1859, consisting of a spirally wound lead-acid battery system [1][2], which was later improved by C.A. Faure using a lead plate with lead oxide paste [3]. Over time, there have been continuous advancements in battery materials and manufacturing processes. The evolution of lead acid battery technology has been extensively discussed since then [4][5][6]. Lead-acid batteries are found in medium to large-scale energy storage devices including automobiles [7], telecommunication [8], UPS-uninterruptible power supplies [9], electric vehicles with low speed [10][11], and renewable energy system[12]. They offer a reversible charge-discharge process, resistance to harmful chemical reactions, and reliable performance at various temperatures. The affordability, reliability, and versatility combined with good performance and cycle life contribute to the popularity of lead acid batteries [13][14].

Despite the aforementioned attractive features of lead acid batteries, there are limitations, including relatively lower energy density and the requirement for periodic maintenance, such as electrolyte level detection and occasional topping up with distilled water [15]. These factors lower the optimal performance of lead-acid batteries and limit their application in certain high-energy storage scenarios. Lead-acid batteries also face challenges in terms of their performance, particularly related to the positive electrode which significantly impacts the battery capacity, cycle life, and overall efficiency [16]. Hence, the improvement of these factors is crucial for improving the performance and expanding the range of applications of lead-acid batteries. Therefore, exploring ways to improve the performance of the positive electrode through incorporating additives is of great importance. During the discharge and charge cycles, electrodes undergo chemical reactions with the electrolyte, leading to the conversion of chemical energy into electrical energy and vice versa [17]. The composition, structure, and characteristics of the positive electrode significantly impact the battery capacity, cycle life, charge acceptance, and overall performance.

An improvement of the positive electrode is essential for enhancing the efficiency and reliability of lead-acid batteries. Introducing additives to the positive electrode has shown potential in improving various electrochemical properties and overall battery performance [18]. Lead carbon batteries for future energy storage devices have been recently reviewed [19]. The introduction of additives such as reduced graphene oxide (rGO) [20] and carbon black (CB) [19][21] has demonstrated a remarkable performance to substantially augment the electrical conductivity and charge transfer characteristics within the electrode matrix, exhibiting considerable promise in enhancing battery performance. In the present research, we aim to investigate electrochemical modifications induced by the incorporation of rGO and CB in the positive electrode of lead acid batteries. The discharge capacity and charge-discharge cycle performance analysis are conducted to understand the overall electrochemical behavior of the lead acid battery.

2. EXPERIMENTAL

2.1 Preparation of Graphene Oxide (GO)

Graphene oxide was produced from natural graphite using a modified Hummers method [22][23]. 25g of graphite was mixed with 625 ml of 98% concentrated H_2SO_4 at a temperature of 0ºC and stirred for one hour. 75 g of $KMnO_4$ was gradually added to the mixture while stirring at the same low temperature. The temperature was then maintained at approximately 30ºC for 30 minutes. Slowly, 1125 g of ice was introduced into the mixture, and the temperature was raised to 98ºC for one hour. Afterward, 500ml of 30% H_2O_2 was added to the mixture until no further effervescence is observed. To separate the solids, the mixture was undergone centrifugation at 3000 rpm for 20 minutes. The resulting solid was then subjected to repeated washing with 5% HCl until no detectable sulfate is observed using $BaCl_2$. Subsequently, the solids are washed several times with distilled water and dried in a laboratory oven overnight at 60ºC to obtain graphite oxide (GO).

2.2 Preparation of Reduced Graphene Oxide (rGO)

rGO was prepared using a thermal method followed by Kottegoda *et. al.*(2015) [24]. The dry sheets of prepared graphene oxide (GO) were fragmented into smaller pieces and introduced into a beaker and placed in a forced convection oven. Argon gas was purged into the oven, and the temperature was raised to 250ºC to induce the thermal exfoliation of GO into reduced graphene oxide (rGO).

2.3 Positive electrode fabrication

The materials required for the preparation of positive electrode such as lead monoxide, lead dioxide, carbon black, or rGO were mixed thoroughly in appropriate proportions given in the Table 1. Distilled water was added and mixed further. Subsequently, the mixture was supplemented with several drops of a binder and remixed well. The resulting paste was applied on a cleaned grid of a commercial battery, ensuring it was well compressed onto the grid to form the electrode. Next, the electrode was allowed to dry in the air and then in an oven at 70˚C for one hour to obtain positive electrodes with each rGO and carbon black.

Table 1- Positive electrode paste composition.

Plate Number	PbO/g	PbO_2/g	rGO/g	Carbon Black/g	Water/ml	Binder /ml
01	14.425	4.5	0.075	-	2	3
02	14.425	4.5	-	0.075	2	3

2.4 Characterization

X-Ray Diffraction (XRD) analysis was carried out using Rigaku Ultima IV X-Ray diffractometer at CuK (λ= 1.54 Å) to examine the crystalline structure and composition of materials. Crystallographic information was obtained from the Inorganic Crystal Structure Database (ICSD). Scanning Electron Microscopic analysis (SEM) was carried out to observe the surface morphology of the samples using ZEISS EVO SEM. Positive electrode with carbon black, and rGO were analyzed using XRD and SEM.

2.5 Electrochemical analysis

The electrochemical performance of the Pb-acid battery was conducted using a two-electrode method. 25% H_2SO_4 solution was used as the electrolyte. The negative electrode was obtained from a commercial battery and used without any modification. A constant current of 100mA was applied to the electrodes using a potentiostat for charging 16 hours and discharging 2 hours. Subsequently, long-term charge-discharge cycling was executed in between 1.8V and 2.7V with a constant current of 100mA for 3 hours. For comparison, a positive electrode from a commercial battery was also charge-discharged at identical conditions.

3. RESULTS AND DISCUSSION

3.1 Scanning electron microscopy (SEM) Analysis

SEM images of samples comprising lead oxide, lead dioxide, and rGO or CB are shown in Figure 1. According to the SEM analysis, the lead oxide appears as aggregates of spherical shape particles while the lead dioxide possesses a flaky morphology [25]. By distinguishing particle sizes in SEM micrographs, smaller particles represent lead oxide, while larger particles can be attributed to lead dioxide. The SEM images do not reveal any observable particles of either rGO or CB, presumably due to shielding by lead oxide particles.

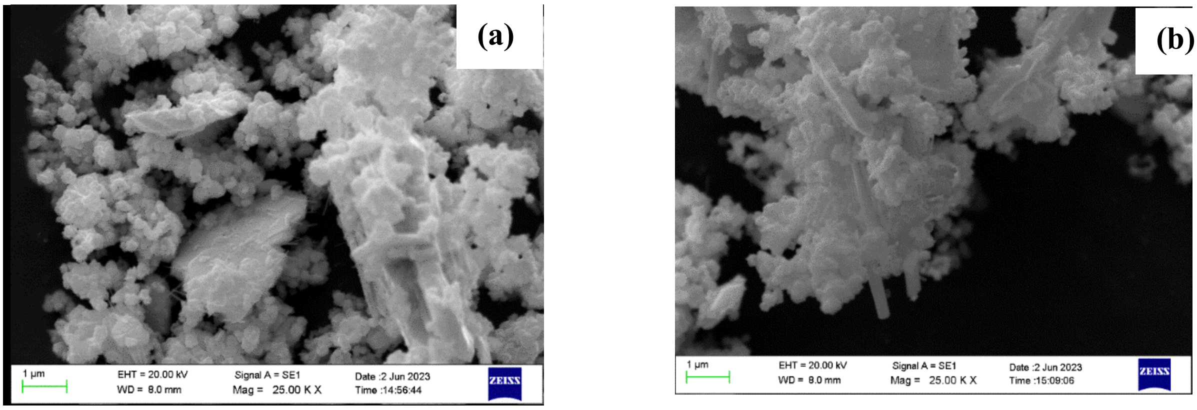

Figure 1: SEM images of positive plate with rGO (a) and Carbon black (b) as additives

3.2 X-Ray Diffraction (XRD) Analysis

Figure 2 shows XRD spectra of GO, rGO and carbon black which shows a sharp characteristic peak at about 11.9° for GO, and respective broader peaks at $2\theta = 26^\circ$ and $2\theta = 26.4^\circ$for rGO and carbon black [23] rGO has a single peak whereas CB has several miner peaks other than the main peak at $2\theta = 25.16^\circ$ which is attributable to some impurity phases.

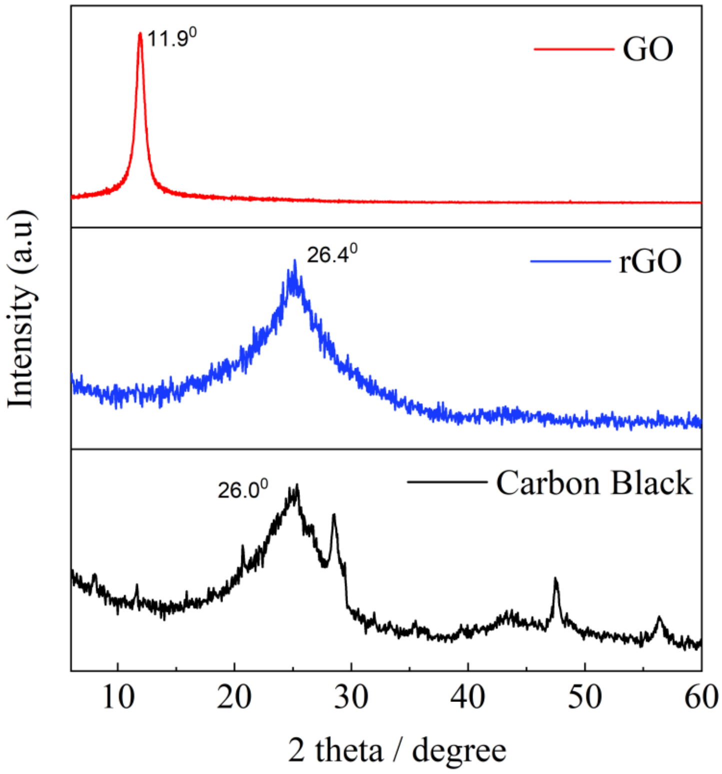

Figure 2: XRD spectra of GO, rGO and carbon black.

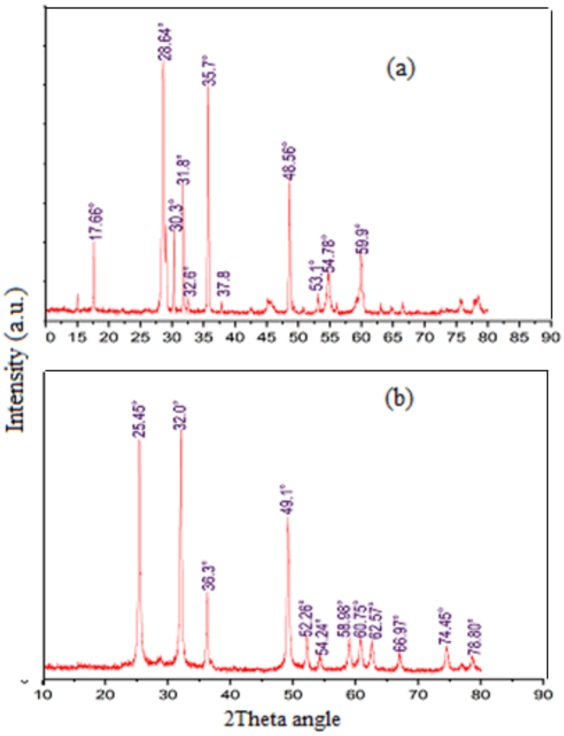

Figure 3: XRD spectra of lead oxide (a) and lead dioxide (b)

Figure 3 (a, b) shows XRD spectra of lead oxide and lead dioxide. The X-ray diffraction (XRD) pattern of the lead oxide reveals prominent peaks at 17.64°, 28.62°, 31.82°, 35.72° and 48.56° which correspond to the (001), (111), (020), (002) and (200) crystal planes of lead oxide, respectively [26][27] while lead dioxide shows prominent peaks at 25.45°, 32.0°, 36.3°, 49.1°, 52.26°, 58.98°, 62.57° and 66.9° assigned to the respective (110), (101), (200), (211), (220), (310), (301) and (202) planes of β-PbO2 [28][29].

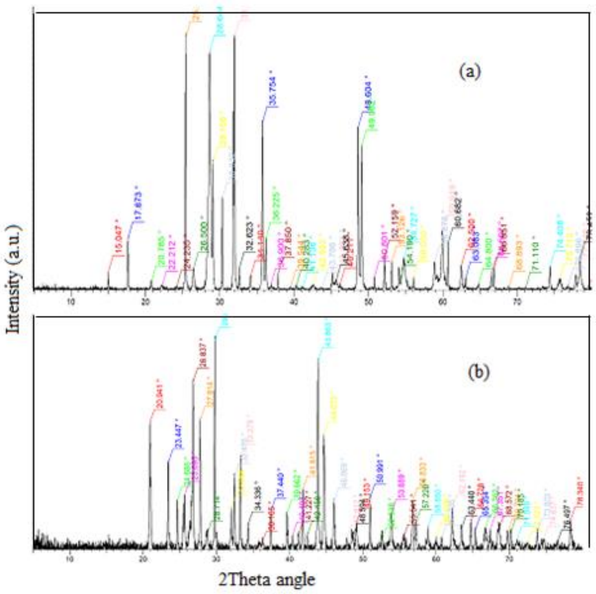

Figure 4: XRD spectra for positive electrode paste with (a) rGO and (b) carbon black as additives.

Figure 4 represents the XRD spectra of positive electrode composing lead oxide, lead dioxide, and rGO (a) or carbon black (b). A noticeable peak at 2ϴ=26° can be observed in Figure 4 for rGO, which is not present in Figure 3. This clearly indicates the presence of rGO in the positive electrode although could not clearly observed through SEM views.

3.3 Discharge capacity

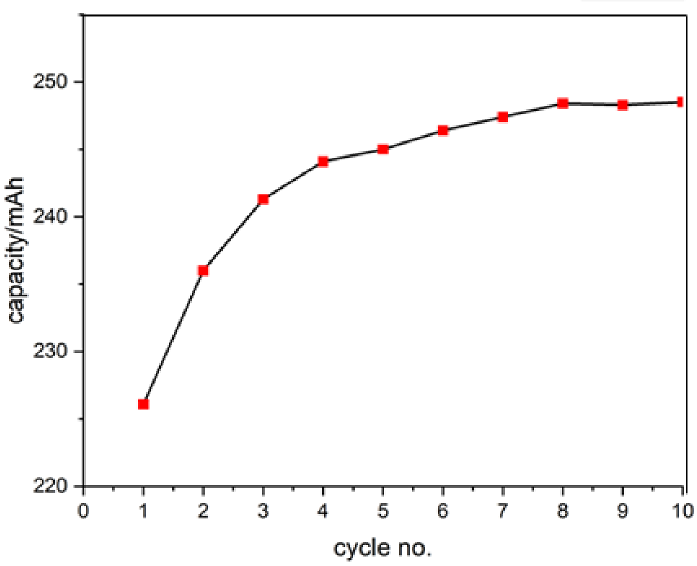

Figure 5: Discharge capacity behavior of the two-electrode cell with carbon black additive.

Figure 5 shows discharge capacities of the two-electrode cell, when carbon black is used as an additive in the positive electrode. Discharge capacity gradually increases over the first eight cycles, starting from 226.1 mAh and reaching a maximum of 248.5 mAh also showing some stability after 8th cycle. This indicates an initial formation period where the capacity of the electrode is improving. During the initial cycles, the electrode goes through an activation and formation process. The trend of increasing capacity suggests that the electrode formation process was effective, resulting in improved electrochemical performance. This involves the electrochemical reactions between the electrode materials and the electrolyte, leading to the formation of a stable and functional electrode-electrolyte interface [30]. As this interface develops and becomes more optimized, the electrode's capacity tends to stabilize. After the initial formation period, from Cycle 8 to Cycle 10, the capacity of the electrodes remains relatively stable, showing minor fluctuations but no significant increase or decrease. This stable performance indicates that the electrodes have reached a state of equilibrium, where the active materials are functioning optimally and providing consistent discharge capacities. The stability in capacity suggests that the electrodes are operating within their intended design parameters and are capable of delivering reliable performance. The average discharge capacity is 243.68mAh. Detail charged-discharged cycling is in progress.

Mechanism behind the good performance can be explained using properties of carbon black which is a very fine, porous material with a large surface area [31] holding more lead oxide particles leading to higher capacity. In addition, carbon black is a good conductor of electricity which forms a network of interconnected pathways within the electrode structure. Also helps distributing the charge more uniformly across the electrode [32]. This helps to ensure that the electrochemical reactions take place evenly throughout the battery. Further, carbon black bridges the gaps between the active material particles and provides an easier path for electrons to move through the electrode balancing charge distribution, promoting more uniform electrochemical reactions maximizing the electrode's capacity utilization.

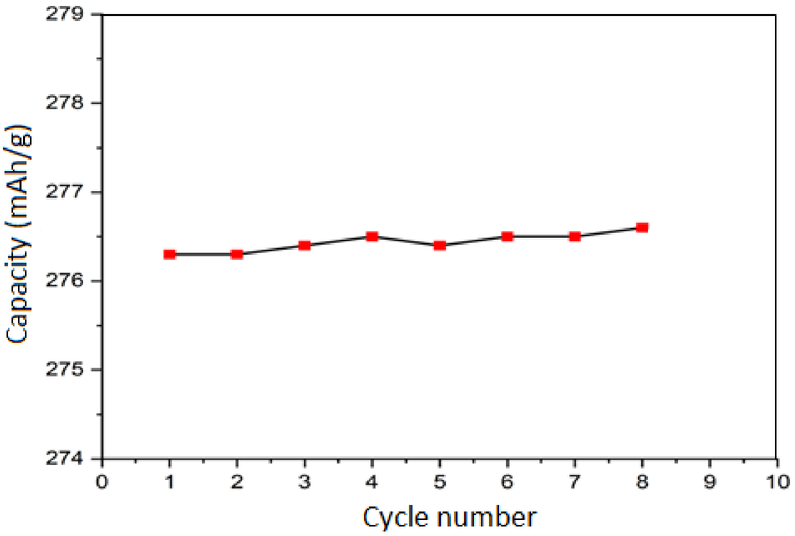

Figure 6: Discharge capacity behavior of the two electrode cell with rGO additive

Figure 6 shows discharge capacities of two cells when rGO is used as an additive in the positive electrode. It appears that the discharge capacities remain relatively consistent in the range of 276.1 to 276.6 mAh in oppose to the carbon black based cell. The consistent discharge capacities suggest that the graphene based additives such as rGO is contributing to the overall stability of the battery performance. Materials such as graphene or rGO are excellent conductor of electricity due to its unique atomic structure and high electron mobility which tends to improve the overall conductivity of the battery [33]. This increased conductivity facilitates faster and more efficient movement of ions and electrons within the battery, leading to improved discharge capacity. Moreover, due to its atomic structure, it possesses an exceptionally large surface area compared to its volume [34]. Graphene has high theoretical surface area nearly 2,629 m^2 /g [35] and being few layer, rGO may also have high surface area [24]. This large surface area provides ample space for electrochemical reactions to take place. In addition, when graphene is added to the electrode material, it can create a highly porous structure. The graphene sheets can stack on top of each other with gaps or voids between them, forming a network of interconnected channels. This porous structure increases the available surface area for electrochemical reactions and creates numerous active sites where reactions can occur. With more available surface area and active sites for electrochemical reactions, a greater number of ions can participate in the reaction, resulting in higher capacity output during the discharge [20]. The higher capacity observed for rGO compared to carbon black is attributable to these unique properties of graphene-based materials.

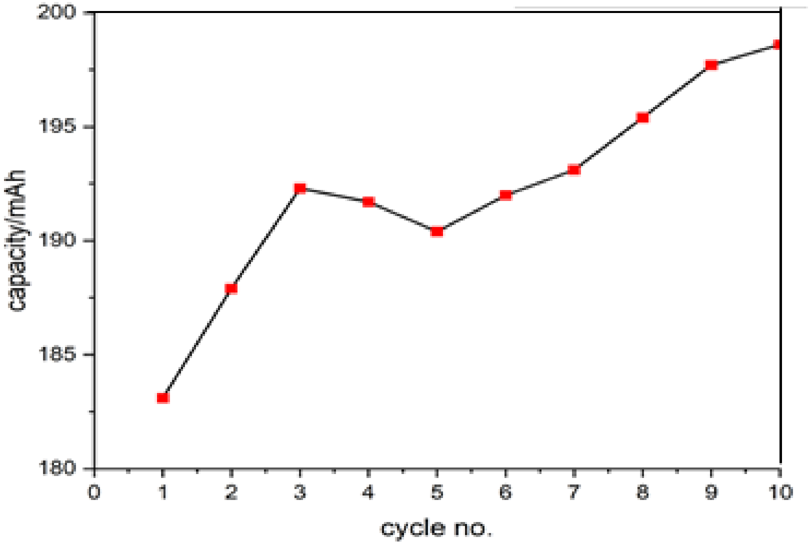

Figure 7: Discharge capacity behavior of the commercial two electrode cell

Figure 7 shows discharge capacities of the battery when commercial electrode is used as the positive electrode. The initial capacity in the first cycle is 183.1 mAh. In the early cycles from 1 to 3, there is a trend of increasing capacity from 183.1 mAh to 192.3 mAh, indicating a positive trend. Subsequently, the capacity stabilizes and shows minimal fluctuations. From 4th to 10th cycle, the capacity continued to increase up to 198.6 mAh. Unlike positive electrodes with carbon black and rGO, the commercial cell, continue to increase the capacity which might stabilize at a later stage. Further work is on the way to study detailed comparison performance which will be published separately.

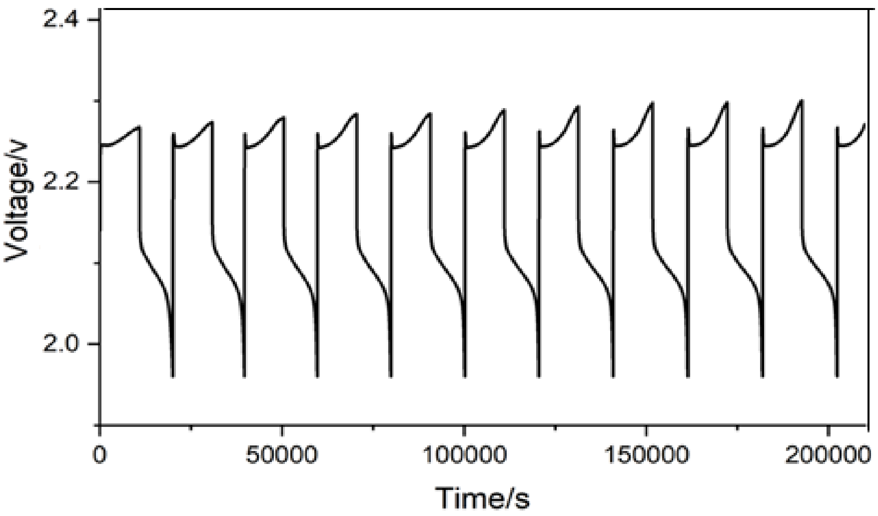

Figure 8: Charge-discharge cycle performance of the two-electrode cell with carbon black

3.4 Charge-discharge performance

Figure 8 shows charge-discharge cycle performance when carbon black is used as an additive in the positive electrode. At the end of the charging phase, the voltage reaches 2.26V, while during the subsequent 3-hour discharging period, the voltage decreases from 2.26V to 1.96V.

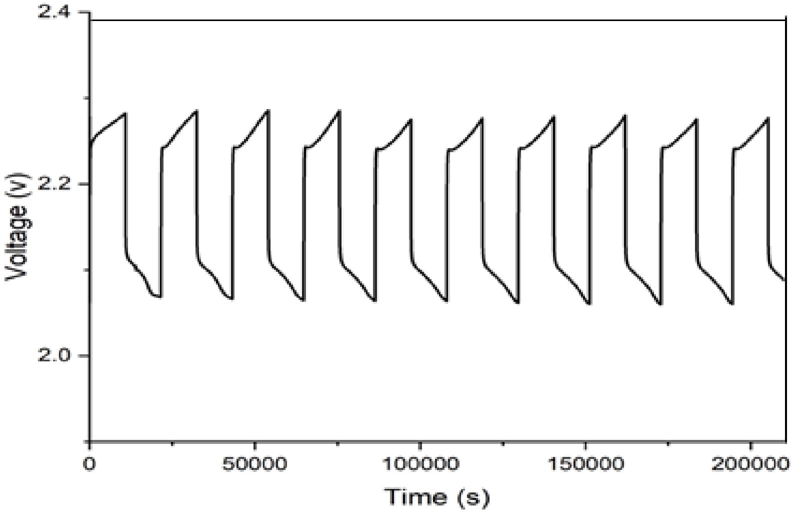

Figure 9: Charge-discharge cycle performance of the two-electrode cell with rGO additive

Figure 9 shows charge-discharge cycle performance of the cell when rGO is used as an additive in the positive electrode. At the end of the charging phase, the voltage reaches 2.28V, while during the subsequent 3-hour discharging period, the voltage decreases from

2.28V to 2.06V. When compared to voltage differences of rGO and carbon black based cells, rGO shows better charge- discharge cycling performance.

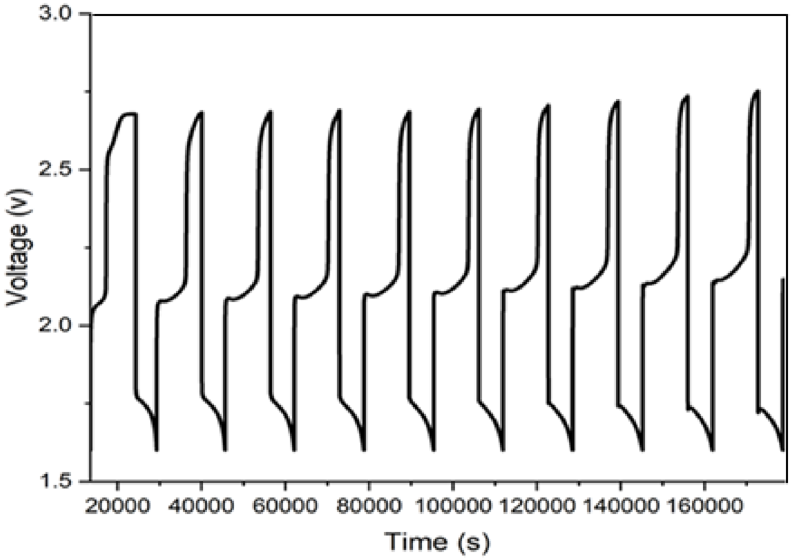

Figure 10: Charge discharge cycle performance when commercial cell is used as a positive electrode.

As shown in Figure 10, when a commercial cell is used as a positive electrode the voltage reaches up to 2.68V at the end of the charging phase while during the 3-hour discharging period, the voltage decreases from 2.68V to 1.61V. When comparing the voltage drops during the 3-hour discharging period, the cell with the carbon black additive had higher voltage drop of 0.30V compared to the cell with the rGO additive which had a voltage drop of 0.22V. In contrast, the commercial cell experienced the highest voltage drop of 1.07V, which means commercial lead acid cell demonstrated the biggest voltage lost compared to cells with rGO and carbon black additives.

4. CONCLUSION

The present study compared the electrochemical performances of two positive electrodes consisting of carbon black and rGO (graphene) as additives with that of commercial battery for lead acid battery. Positive electrodes were successfully prepared by mixing appropriate proportion of lead oxide, lead dioxide, carbon black or rGO which is verified using XRD. The positive electrode with carbon black and rGO respectively exhibits capacity of 33.15% and 51.12% higher than a similar commercial cell during first 10 cycles. This suggests that the incorporation of both rGO and carbon black as an additive enhances the energy storage potential of the positive electrode significantly. Among two additives, rGO exhibits the most significant, stable high capacity over corresponding cycles. Moreover, both rGO and carbon black based battery shows smaller voltage drops of 0.22V and 0.30V respectively which is very less compared to that of commercial battery (1.07V) showing a considerable enhancement in energy storage potential. Further work is needed to investigate long term stability and capacity achievement on prolonged charge-discharge cycling which intends to publish separately. The study provides valuable insights into the role of carbon-based additives in lead acid batteries, contributing to the development of more efficient and reliable energy storage systems.

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