

IMPROVING PERFORMANCE OF LEAD-ACID BATTERIES THROUGH CARBON LEAD HYBRID ELECTRODES

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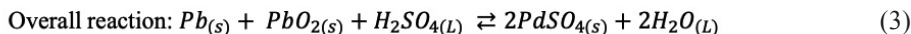
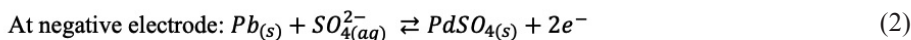
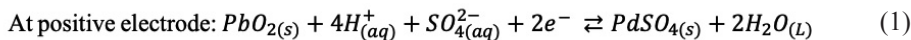
Abstract: This paper presents the study of the addition of carbon materials to negative electrodes to upgrade the performance of lead-acid batteries through avoiding sulfation and getting super capacitance effects due to their high specific surface area. Two kinds of carbon materials including carbon fibre paper and activated carbon cloth with high electrical conductivity and porosity are selected in the experiments. The required hydrophilicity of the carbon materials is pretreated and checked through the surface contact angle measurement before added. The surface morphology of carbon materials, negative electrodes are also observed using Scanning Electron Microscope. The results show that the performance of the carbon-added battery cells is improved. The initial capacity and specific energy of the tested battery cells with the carbon cloth addition are about 15% higher than those of battery cells without the carbon addition. Moreover, the lead sulphate crystal size formed on the negative electrode surfaces of the carbon added batteries are smaller than that on the negative electrode surfaces of the conventional batteries, revealing that carbon addition can improve the battery lifespan.

Keywords: Lead-acid battery, battery performance, carbon lead hybrid, carbon material.

Introduction

Lead-acid batteries are the most used battery in automobile, transportation and telecommunication industries. They basically consist of sponge lead plates (negative electrodes), separator (insulation material), lead dioxide plates (positive electrode), and

the electrolyte (sulfuric acid). The chemical reactions take place at anode and cathode during the charge/discharge processes as follows (Zimáková *et al.*, 2015) (note that the upper arrow represents the direction of the reaction during discharging and the lower arrow while charging):



With advanced technology, to provide the power capability and adequate service-life in advanced systems, lead-acid batteries should work as effectively as possible under high-rate, partial-state of charge/discharge (HRPSoC) conditions that quickly cause the accumulation of lead sulfate ($PbSO_4$) on the negative plates

which can't be converted successfully back to spongy lead during the charging process, leading to battery failure (Lam *et al.*, 2004). In recent years, many researchers are interested in improving performance and cycling life of lead-acid batteries in order to meet the demands of modern applications.

Many attempts have been carried out, and it is found that adding carbon to lead-acid electrodes during paste preparation in a variety of forms, including activated carbon, carbon black, graphite and carbon nanotubes, can enhance both performance and lifespan of the batteries. In particular, Shiomi *et al.* (1997) investigated the benefits of carbon added to the negative active material (NAM). They proposed that the advantages were caused by a conductive network of carbon particles formed on PbSO_4 crystals leading to the improvement of cycle life performance. Their opinion was later agreed by Ohmae *et al.* (Ohmae *et al.*, 2003). They also suggested that highly conductive carbon should be used to retard the sulfation process. Pavlov *et al.* (Pavlov *et al.*, 2009) discovered that the electrochemical reaction of lead ions occurs simultaneously on both surfaces of Pb and carbon particles during the cycling of cells. A parallel electrochemical mechanism was also proposed based on their experiments. Xiang's group (Xiang *et al.*, 2013) has pointed out that the roles of carbon additives to negative plates under HRPSoC duty can be summarized from three aspects: (i) increasing the porosity and active surface area of NAM due to formation of a new porous-skeleton builder; (ii) facilitating electrolyte diffusion from the surface to the inner of plates; (iii) sharing excess charge and discharge current with negative plates. Sugumaran *et al.* (2015) demonstrated that the incorporation of discrete carbon nanotubes (dCNT) was useful not only in negative plates but also in positive plates. Cycle life tests of the batteries increased more than 60% as the negative plates were accompanied by dCNT while it was significantly improved by 500% in the case of both electrodes added. The dCNT/ H_{ad} overcharge reaction mechanism was also proposed to explain their observation. A similar observation when adding carbon materials to anode and cathode electrodes was also reported by Lang *et al.* (2018). Furthermore, the impact of different types and concentrations of carbon materials have been studied as additives in lead-acid batteries. Cycle life under HRPSoC operation was enhanced as the optimized

content of graphite and black carbon was the same amount of 2wt.% (Boden *et al.*, 2010). In addition, the maximum cycle number was achieved at low concentration of graphite (near 1~1.5 wt.%) added to negative plates as observed by some other researchers (Bača *et al.*, 2011; Soria *et al.*, 2005). Blecuca *et al.* (2017) investigated the influences of different carbon materials on lead-acid batteries used for micro-hybrid vehicles. They reported that carbon materials with big particle size were able to improve cycle life and charge acceptance while carbon black with small particle size ($<1 \mu\text{m}$) may increase water consumption and fail to prolong cycle life. In addition, the effects of specific surface area (SSA) and morphology of different carbon materials added to the cathode electrode of lead-acid battery were explored by Hu *et al.* (2019). Carbon materials with larger SSA and smaller carbon particle size are beneficial for enhancing battery performance. The former can enlarge the electrochemical active surface of the active material while the latter is more effectively dispersed within the active materials. Besides, Yin *et al.* (2018) also demonstrated that high reversibility of the anode and low hydrogen evolution of lead-acid battery can be achieved by grafting lead on the anode C/Pd composite. They concluded that the main roles of C/Pd composite in the anode includes maintaining a solid anode structure with high specific surface area and enhancing charge acceptance. In their latter work (Yin *et al.*, 2019), the optimized composition of C/Pd was also obtained. The results showed that the cycle life of the battery cell with the addition of optimized C/Pd composite to the negative plate is about 11 times longer than that of the blank one under HRPSoC. Carbon material addition can be designed to provide super capacitance effects. Particularly, Lam *et al.* (Lam *et al.*, 2006; Lam *et al.*, 2007) have developed the ultra-battery with a conventional PbO_2 positive plate and a negative plate consisting of two parts: half of it is a sponge lead material and the other half is a carbon electrode. Their results showed that the performance of the ultra-battery increased by 50% and its cycle life is significantly improved

compared to the conventional lead-acid battery. The carbon electrode in the ultra-battery design acts as an asymmetric supercapacitor which is able to provide and rapidly absorb charge during HRPSOC operations. The application of the ultra-battery design for a fuel cell hybrid vehicle was then numerically investigated (Huang *et al.*, 2016). By applying a lithium battery and the ultra-battery as auxiliary power sources in the fuel cell hybrid vehicle module, the simulation results showed that the power output curves of the ultra-battery and lithium battery are extremely similar, while the cost of ultra-batteries is competitive with the lithium battery.

Carbon fiber papers or carbon clothes are currently the most common materials used to make gas diffusion layers (GDL) in fuel or biofuel cells (Zhang *et al.*, 2002; Liu *et al.*, 2009; Zhang *et al.*, 2017). In addition, it is also preferred for use in supercapacitors as electrodes (Shang *et al.*, 2017; Bavio *et al.*, 2017; Wang *et al.*, 2016; Li *et al.*, 2017) because they possess the advantages of good conductivity, porous form, high specific surface area, corrosion resistance, stability, and moderate cost. In the last two decades, the advantages of using carbon papers or carbon clothes instead of using metallic alloy in lithium-ion batteries have been discovered by many research groups (Su *et al.*, 2012; Isaev *et al.*, 2003; Arbizzani *et al.*, 2005; Arbizzani *et al.*, 2006). As carbon papers were used as a substrate-current collector, it enhanced not only constant capacity but also cycle life due to the flexible property of carbon materials which provides good contact with the cathode surface, offering electron pathways during lithiation/delithiation (Arbizzani *et al.*, 2005; Arbizzani *et al.*, 2006). When the microporous carbon paper was inserted between cathode and separator, it decreased the internal charge transfer resistance and captured the migrating polysulphides during electrochemical reactions.

From earlier studies, it is obvious that the addition of carbon materials can enhance the performance and prolong the cycle life of lead-acid batteries. However, mixing carbon powder with active electrode materials will

make manufacturing processes of lead-acid batteries more complex. Therefore, in this work, a simple approach without elaborate synthesis of composites and surface chemistry modification is studied for improving the capacity and cycle life of conventional lead-acid batteries. Highly porous and electrically conductive carbon materials under the form of fiber paper or cloth are prepared and directly added in parallel to the negative plates of an assembled 2 V lead-acid cell with two positive plates and three negative plates that are separated by absorbed glass-mat (AGM). The carbon interlayer is expected to provide the electrically conductive network on the negative electrode surface and the super capacitance effect which not only acts to limit the formation of hard sulfation inside the cell but also increases its charge acceptability. The ratio of the surface area of carbon sheets to negative plates is 1:2 or 1:1. The contact angle measurement, SEM, and chronopotentiometry are employed for the characterization of carbon materials, carbon lead hybrid electrodes and constant current discharge in this investigation.

Materials and Methods

Preparation and Characterization of the Added Carbon Materials

Carbon fiber papers and activated carbon clothes (produced by CeTech, Taiwan) with thicknesses of 0.60 mm and 0.65 mm were used in this study as shown in Figure 1(a) and (b), respectively. The specific surface area and porosity analysis for the prepared samples were characterized by N₂-adsorption/desorption isotherms at 77K (ASAP 2020, Micromeritics, USA). The pore volume and pore size were calculated according to the method of BJH (Barrett Johner Halenda). The characteristics of the carbon paper and activated carbon cloth are summarized in Table 1. The results show that the specific surface area and pore volume of the activated carbon cloth are larger than those of the carbon fiber paper. The estimated average pore size for the activated carbon cloth (115.036 Å) is also much greater than that of the carbon fiber paper (20.927 Å).

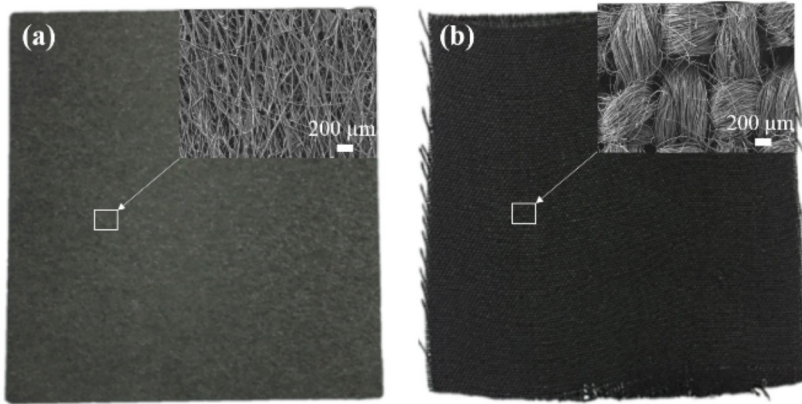


Figure 1: Carbon materials: (a) Carbon fiber paper and (b) Activated carbon cloth

Table 1: Specific characteristics of carbon materials used in this study

Carbon type	BET surface area (m ² /g)	Pore area (m ² /g)	Pore volume (cm ³ /g)	Average pore size (Å)
Carbon fiber paper	1.4773	1.2845	0.000672	20.927
Activated carbon cloth	1.6006	1.4695	0.004226	115.036

Preparation of the Negative and Positive Plates

In this study, the positive plates and negative plates mainly made of lead dioxide and sponge lead, respectively, were all produced by Taiwan KUNG LONG batteries industrial CO., LTD. The areal loadings of the negative plate, positive plate, and AGM separator are 1.06, 1.09, and 0.064 g cm⁻², respectively. The sizes of the negative and positive electrodes are 75 mm × 37 mm × 1.8 mm and 75 mm × 37 mm × 2.0 mm, (height × width × thickness), respectively. Absorbent Glass Mats (AGMs) with a size of 80 mm × 40 mm × 3.0 mm were used to separate the positive plates and negative plates. The electrolyte was H₂SO₄ with a density of 1.28 g/cm³ (Yang *et al.*, 2017) used during all tests. The real battery cell is presented in Figure 2.

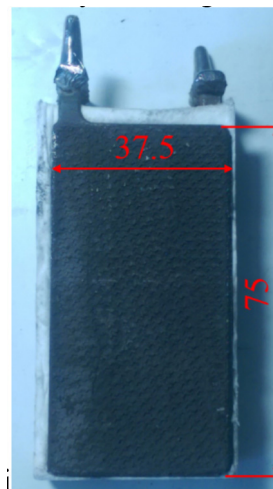


Figure 2: The actual battery cell used in this work

Design of the Tested Lead-Acid Cells

The influence of the addition of carbon fiber paper and activated carbon cloth to negative plates on battery performance was investigated in 2 V test cells. The schematic of the test cells is shown in Figure 3. In each 2 V test cell, three negative plates were assembled with two positive plates and AGM separators with a thickness of 3.0 mm. The prepared carbon papers or cloth were manually introduced to the cell. In particular, three negative plates electrically connected by bridge weld were interlaced with two positive plates electrically connected in the same manner. After that, Absorbent Glass Mat (AGM) and carbon fiber paper or cloth, prepared to the proper sizes, were inserted into the gap between the negative and positive plates, where the carbon fiber was contacted with the negative plates as shown in Figure 3. The ratio of the surface area of the carbon material to the negative plate was 1:2 or 1:1 (50% or 100%, defined as insertion ratio). The designed cell was placed inside a plastic container provided by the supplier (Taiwan KUNG LONG batteries industrial CO., LTD). Subsequently, the electrolyte (H_2SO_4) was introduced to the cell from the top. After that, the cell was sealed with a top cover and sealing glue to form a sealed lead-acid battery. The positive and negative terminals were exposed outside the top cover for charge and discharge processes. There was a safety valve on the cover designed to release any excess pressure if the battery is overcharged. As a result, the loss of H_2SO_4 in the sealed lead acid battery cell can be significantly diminished. For

comparison, a 2 V cell consisting of the same negative and positive plates without carbon sheet addition was also produced.

Capacity Test

For this test, fully charged battery cells were discharged to the final voltage of 1.6 V (cut-off voltage) at a constant current of 0.5 A. The cells were then charged for 12 h at a constant voltage of 2.5 V with a current limit of 0.25 A. These cells were subsequently cycled. All the tests are carried out at room temperature ($\sim 25^\circ C$). The capacity and specific energy of the tested battery cells were calculated from the following Eqs. (4) and (5).

$$C = I \times t \quad (4)$$

$$E_s = \frac{1}{m} \int_{t_0}^t U(t) \times I \times dt \quad (5)$$

where: C is the capacity (Ah); E_s is the specific energy (Wh/kg); I , $U(t)$, t , and m are the discharge current (A), discharge voltage, discharge time (h), and mass of battery cell (kg).

Results and Discussion

Carbon fiber paper and activated carbon cloth were required to have hydrophilic characteristics in order to make H_2SO_4 solution or water easily penetrate these layers. However, by using Optical Contact Angle Meter Model 100SB, the original carbon fiber papers and activated carbon cloth were hydrophobic with the surface contact angle of 129.99° and 124.60° , respectively, as

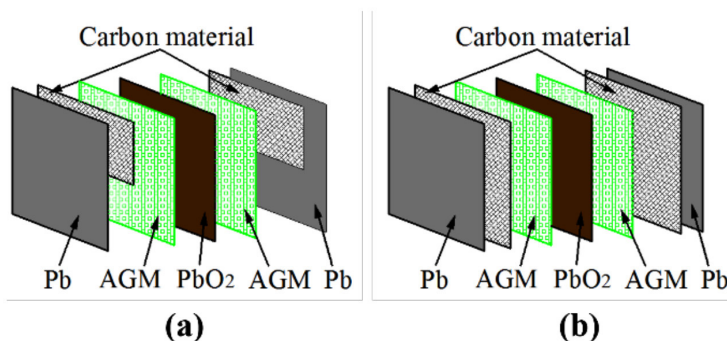


Figure 3: Schematic of the tested lead-acid cell: (a) 50%; (b) 100%

depicted in Figures 4(a) and (b). To form the hydrophilic functional group (COOH), they were immersed in the mixture of concentrated acids (H_2SO_4 : $\text{HNO}_3 = 3:1$) for 10 minutes with sonication to produce carboxylic acid group (COOH) (Zhang *et al.*, 2008). The contact angle measurement of the treated carbon materials was then observed. As shown in Figures 4(a1) and (b1), after modification, a droplet of contact angle measurement was immediately absorbed once it reached the carbon paper or carbon cloth surfaces. Water was evenly laid on the surfaces and it is defined as the contact angle 0° . In other words, the hydrophilicity of the modified carbon materials meets the requirement for this investigation.

Figure 5 shows the discharge curves of the batteries with and without adding carbon materials at a constant discharge current of 0.5 A. It is observed that the discharge time of the battery cells with carbon fiber paper or activated carbon cloth is longer than that without carbon addition, indicating that the performance of the carbon-inserted battery cells is improved. The initial capacity and specific energy of the tested battery cells were also calculated and presented in Table 2. With carbon insertion, the initial capacity and specific energy of the tested batteries increase. It is expected that the presence of the carbon pieces could have two main benefits. The first is increasing the charge acceptance during

charging, due to the super capacitance effect of the inserted carbon materials (Lam *et al.*, 2007; Huang *et al.*, 2016; Smith *et al.*, 2002). In other words, with carbon fiber addition, a super capacitor is formed based on one lead-dioxide positive plate and one carbon-based negative plate. As a result, during the charging process, a certain amount of charge will be electrostatically stored on the carbon plates and release this additional charge in the discharge process, improving the cell capacity. The second benefit is enhancing electron conductivity on the negative electrode surfaces due to a conductivity network formed by the carbon plates (Moseley *et al.*, 2006). During discharging, the partial transfer of electrons generated on the negative electrode surface can be implemented through the carbon plate, helping the sponge lead react with HSO_4^- to evenly form PdSO_4 on the negative surface. Conversely, in the charging process, the external electrons are partially transferred from the carbon plate to the negative plate, making a better dissolution of PdSO_4 . Accordingly, the reversibility of the charging and discharging processes is improved. The results also show that the larger an area of carbon materials was added, the better battery performance was achieved. This makes sense, because more charge will be stored on the larger carbon surface area. In general, a higher insertion ratio is also beneficial for both conductive network

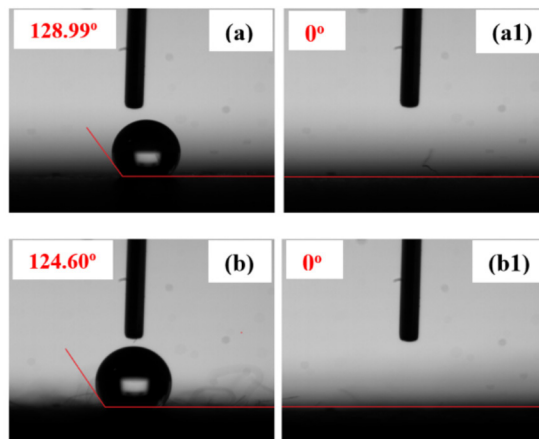


Figure 4: Contact angle measurement of carbon fiber paper: (a) before modification; (a1) after modification and of activated carbon cloth: (b) before modification; (b1) after modification

formation and supercapacitance effect, leading to better battery performance. The highest improvement of the specific energy of the tested battery cell with the insertion ratio of 1:1 of the activated carbon cloth is around 15% compared to the conventional battery cell. Furthermore, the addition of activated carbon cloth exhibits better initial capacity and specific energy than that of carbon fiber paper. This could be due to activated carbon cloth possessing higher flexibility and larger specific surface area (as presented in Table 1) compared with the carbon fiber paper. As a result, the first property will make better contact between the carbon cloth surface and negative electrode surface, which provide a

better conductive network for electrons transfer during chemical reactions while the second one will provide large gravimetric capacitance and hence energy storage density (Zhang *et al.*, 2013; Ji *et al.*, 2014). The reported improvement of lead-acid battery performance using different carbon materials as additives is summarized in Table 3. It can be seen that our lead-acid battery cell with carbon-lead hybrid negative electrodes exhibits a comparable initial capacity, as compared with the previously reported results in lead-acid battery researches, suggesting that the carbon fiber insertion to the negative electrodes can be used for improving the performance of conventional lead-acid batteries.

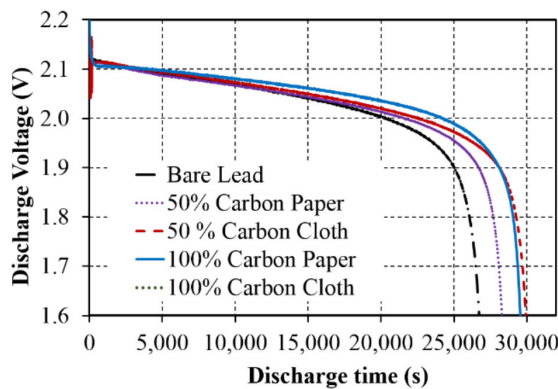


Figure 5: Discharge curves of the tested battery cells

Table 2: Initial capacity and specific energy

Tested Cell	Bare lead	50% carbon paper inserted	50% carbon cloth inserted	100% carbon paper inserted	100% carbon cloth inserted
Initial Capacity (Ah)	3.76 ±0.11	3.98 ±0.13	4.25 ±0.10	4.21 ±0.14	4.32 ±0.13
Specific energy Wh/kg	32.03±0.11	33.90 ±0.12	36.16 ±0.10	36.02 ±0.14	36.88 ±0.12
Improved capacity (%)	-	5.9	13.2	12.0	14.9
Improved specific energy (%)	-	5.8	12.9	12.5	15.1

Table 3: Reported improvement of lead-acid batteries using different carbon materials as additives

Discharge rate	Improved percentage of initial capacity (%)	Reference
0.05C	23.5	(Saravanan <i>et al.</i> , 2012)
0.5C	3.5	(Hong <i>et al.</i> , 2014)
0.5C	10.7	(Kumar <i>et al.</i> , 2014)
1C	26.7	(Zou <i>et al.</i> , 2014)
0.1C	5.5	(Saravanan <i>et al.</i> , 2015)
0.1C	19.9	(Lang <i>et al.</i> , 2018)
0.1C	14.9	(Yin <i>et al.</i> , 2019)
1.8C	11.5	(Hu <i>et al.</i> , 2019)
0.125C	14.9	This work

To observe the lead sulfate crystals on the negative electrodes after discharging, the negative electrodes were rinsed in several baths of deionized water and scanned using SEM (Hitachi model S-3400N). The SEM images of different negative electrode surfaces are shown in Figure 6. It can be observed that the size of the lead sulfate crystals on the carbon added negative electrode surfaces are smaller than those on the bare negative electrode surfaces. This is because the added carbon materials can facilitate the formation of small isolated PbSO_4 particles which are easy to dissolve and restrict PbSO_4 crystal growth (Shiomi *et al.*, 1997). The results indicate that the lifespan of battery cells with carbon materials inserted could be improved compared to the original battery cells since the larger lead sulfate crystals are harder and cannot be completely converted back to sponge lead during the charge process (Sugumaran *et al.*, 2015; Pavlov *et al.*, 2012; Murali *et al.*, 2017). In addition, the lead crystals formed on the negative electrode with carbon cloth addition have a smaller size than those formed on the negative electrode with carbon paper addition. This could be due to the higher flexibility of carbon cloth than carbon paper, which provides better contact between the carbon cloth and the negative electrode surface, leading to better electron conduction during the chemical reactions. This observation is consistent with the initial capacity results in which the better

capacity of the lead-acid batteries with added carbon cloth is achieved compared to the lead-acid batteries with added carbon fiber paper. The surface area and porosity measurements for the negative electrodes will be conducted in future work.

Conclusion

A simple method to boost the performance of lead-acid batteries has been proposed and experimentally studied in this work. The results show that the lead-acid batteries exhibit improved performance when carbon paper or carbon cloth is added to the negative electrode surfaces. The initial capacity of the battery with 100% carbon cloth insertion increases by 15% compared to the original lead-acid counterpart. Additionally, morphology analyses of negative electrode surfaces indicate that the cycle life of batteries with carbon lead hybrid electrodes could be prolonged. Further experiments are ongoing to demonstrate the newly designed battery works effectively under different working conditions, and will be published in the future.

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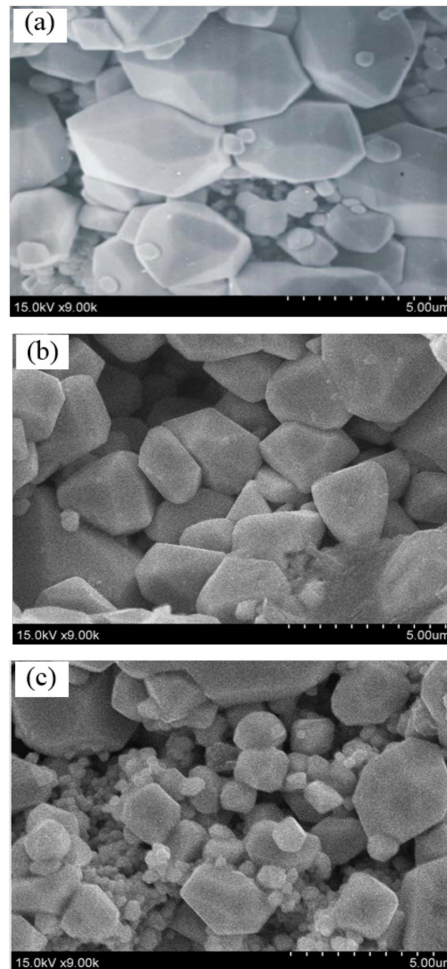


Figure 6: SEM images of negative electrode surface after discharge to 1.6 V: (a) without carbon material; (b) with carbon paper; (c) with carbon cloth

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