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# Influence of High Loading on the Performance of Natural Graphite-Based Al Secondary Batteries

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Abstract: In recent years, novel Al secondary batteries with Al anodes, natural graphite cathodes, and ionic liquid electrolytes have received more attention. However, most research on Al secondary batteries used lower graphite loading (<8 mg/cm<sup>2</sup>), which will inhibit the batteries from commercialization in the future. Here, we prepared Al secondary batteries using Al anode, low-cost natural graphite cathode, and cheaper ionic liquid electrolyte. The effects of loading (7–12 mg/cm<sup>2</sup>) on performance were investigated. Based on our observations, graphite-based Al secondary batteries (GABs) using 10 mg/cm<sup>2</sup> graphite electrodes had better performance of 82 mAh/g and 6.5 Wh/L at a current density of 100 mA/g. Moreover, the 10 mg/cm<sup>2</sup> GABs showed a long life of 250 charge–discharge cycles with a high coulombic efficiency of 98% and excellent performance rate up to 1000 mA/g.

Keywords: Al secondary batteries; natural graphite; ionic liquid

# 1. Introduction

Considering the urgent issues of an energy crisis and global warming, clean and renewable energy such as solar and wind power has attracted more attention [1–3]. However, renewable energy depends on climate, so it is intermittent and difficult to provide enough electricity compared to traditional fossil fuel. Regarding this issue, it is necessary to develop large-scale energy storage secondary batteries to balance unstable power generated by renewable energy [2–4]. Among these secondary batteries, lead–acid and Li-ion batteries are widely applied to energy storage systems [2–10]. Concern about environmental pollution hinders lead–acid battery development in large-scale energy storage systems, although it is cheaper than other batteries [2,11]. On the other hand, high cost and unsafe Li-ion batteries, are also unsuitable for large-scale energy storage applications [1,4,12,13]. In view of novel batteries, Al secondary batteries can be a potential candidate because of their low cost (Al is abundant in the earth's crust), long life cycle, nonflammable electrolyte, and high theoretical capacity (2980 Ah/kg via three-electron Al<sup>3+</sup>/Al redox reaction) [1,2,4,8,12–15]. Table 1 shows a comparison of abovementioned batteries [1,2,4,8,12–19].

Recently, various cathodic materials have been applied in Al secondary batteries, such as transition metal oxides, sulfides, and carbon [1,2,4,8,12-16,20]. Chloroaluminate (AlCl<sub>4</sub><sup>-</sup>) can intercalate/deintercalate graphite during charge and discharge [2,8,12,14,15]. In addition, graphite-based Al secondary batteries (GABs) exhibit excellent stability, long life cycle, and high



operating voltage [2,8,12,14,15]. For instance, Lin et al. developed ultrafast rechargeable GABs using a graphitic-foam cathode, which showed a discharge voltage platform of ~2.0 V and a discharge capacity of ~60 mAh/g at a current density of 5000 mA/g [15]. Wu et al. claimed that the synthesized 3D graphitic foams used in GABs had a discharge capacity of ~60 mAh/g at a high current density of 12,000 mA/g and a long life cycle of ~4000 cycles [21]. Elia et al. reported that GABs using pyrolytic graphite cathodes exhibited discharge capacities of about 75, 62, 60, and 50 mAh/g at current densities of 25, 50, 75, and 100 mA/g, respectively [22]. Zafar et al. manufactured GABs using commercial ordered mesoporous carbon, namely CMK-3, as cathode. They found that these GABs displayed a discharge capacity of 33 mAh/g at a current density of 980 mA/g and a long life cycle of 36,000 cycles [12]. Wang et al. manufactured GABs using commercial kish graphite, and they found that the capacity and energy density of these GABs were 142 mAh/g and 65 Wh/kg, respectively [23]. Uemura et al. prepared GABs using graphene nanoplatelet [24]. They reported that the GABs had a long life cycle of 3000 cycles at 2000 mA/g. Chen et al. synthesized a trihigh tricontinuous graphene

a super long-term life of 250,000 cycles at 400 A/g [25]. With so many successful cases found in the literature, we reasonably anticipated that carbon-based materials could be effective cathodes for Al secondary batteries. However, the reported carbon-based cathodes involved complex, expensive synthesis processes and low graphite loading  $(4-8 \text{ mg/cm}^2)$ , which are difficult to commercialize [4,14,15,22,25]. To overcome the aforementioned problems, low-cost, high-stability, and commercially available natural graphite without complex synthesis processes could be a suitable cathode for GABs. Moreover, the reported GABs usually used a high-cost electrolyte based on 1-ethyl-3-methylimidazolium chloride (EMIC) [4,14,15], so we chose a relatively low-cost room-temperature ionic liquid electrolyte based on 1-butyl-3-methylimidazolium chloride (BMIC), which is about three times cheaper. Accordingly, natural graphite-based GABs using an  $AlCl_3/BMIC$  electrolyte could not only reduce cost, but also bring GABs from the lab scale to the pilot production line, even to commercialization for large-scale energy storage. In addition, another interesting question of how the graphite loading affects the electrochemical behavior of GABs has not been systematically investigated. In this study, we prepared higher graphite loading cathodes  $(7-12 \text{ mg/cm}^2)$  with an AlCl<sub>3</sub>/BMIC electrolyte for GABs. The effects of various natural graphite loading amounts on GAB performance were investigated.

film and applied it to GABs [24]. They claimed that the capacity of these GABs was 120 mAh/g with

Dropartias	Al Batteries	Pb-Acid Batteries	Li-Ion Batteries		
Properties			NCM	LiFePO <sub>4</sub>	LTO
Energy density (Wh/L)	45 to 91 [12,16]	50 to 90 [16,17]	150 to 300 [18,19]	90 to 247 [18,19]	200 [18]
Life cycle (times)	250 to 250,000 [2,12,25]	400 to 600 [17]	500 to 1000 [18,19]	1000 to 3600 [18,19]	15,000 [18]
Efficiency (%)	90 to 99.5% [2,4,12,25]	90% [16]		90%–95% [16]	
Discharging C-rate	10 to 4000 [1,2,4,12,15,25]	0.2 to 5 [19]	2 to 3 [18]	3 [18]	5 to 10 [18]
Safety [1,2,4,8,12–16]	High	High	Low	Medium	High
Operating temperature (°C)	20 to 150 [2]	-20 to 50 [19]	-20 to 45 [18,19]	-30 to 45 [18,19]	-30 to 55 [18,19]
Battery cost (USD/kWh)	-	150 [17]		>200 [17]	

Table 1. Comparison of Al batteries, Pb-acid batteries, and Li-ion batteries.

#### 2. Materials and Methods

#### 2.1. Preparation of Natural Graphite Electrodes

The natural graphite (LT Tech. Co., Ltd., New Taipei City, Taiwan) was mixed with polyvinylidene difluoride (PVDF) in methylpyrrolidone (NMP, Alfa Aesar, Lancashire, UK) under vigorous stirring at room temperature for 4 h to get a homogeneous slurry. The natural graphite slurry was coated on carbon papers to deposit graphite film and dried at 120 °C for 2 h to obtain the natural graphite electrode. The specific graphite loading was 7, 9, 10, and 12 mg/cm<sup>2</sup>.

## 2.2. Preparation of AlCl<sub>3</sub>/BMIC Electrolytes

GAB electrolyte was prepared by mixing BMIC (98%; Alfa Aesar, Lancashire, UK) and anhydrous AlCl<sub>3</sub> (99%; Alfa Aesar, Lancashire, UK) in an argon-filled glove box. Before mixing, BMIC was baked at 60 °C in a vacuum oven for 3 days to remove residual water. AlCl<sub>3</sub> and BMIC were mixed together with continuous stirring for 30 min. Finally, a light-yellow transparent liquid was obtained. The mole ratio of AlCl<sub>3</sub> to BMIC was 1.5. The water content of this electrolyte was analyzed to be ~300 ppm via a Karl Fischer coulometer (Metrohm 756 KF Coulometer, Herisau, Switzerland).

## 2.3. Fabrication of Pouch Cells

Pouch cells were also assembled in an argon-filled glove box using an as-prepared natural graphite electrode as the cathode, Al foil anode (50 mm, 99.9999%; Alfa Aesar, Lancashire, UK) as the anode, AlCl<sub>3</sub>/BMIC ionic liquid as the electrolyte, and 2 layers of Whatman glass fiber as the separator, which separated anode and cathode to prevent battery shorting (Figure 1).

#### 2.4. Characterizations

Raman spectra were obtained using a Thermo Scientific DXR Raman microscope (Waltham, MA, USA) equipped with a green light laser (532 nm). The top views of samples were investigated by a scanning electron microscope (SEM; Hitachi S4800, Tokyo, Japan). The X-ray diffraction (XRD) patterns of samples were measured by the D2 Phaser diffractometer (Brucker, Billerica, MA, USA) using Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å) and recorded in the 2-theta range from 20° to 40° and at a scan rate of 1°/min. The thickness of the films was analyzed via  $\alpha$ -Step (Force EZstep, New Taipei City, Taiwan).

#### 2.5. Electrochemical Performance Measurements

The galvanostatic charge–discharge measurements were analyzed via a Neware BTS-25V20A battery test system (Saint-Priest-en-Jarez, France) at constant current densities in the voltage range of 1.0 to 2.5 V at room temperature. Cyclic voltammetry (CV) measurements were performed using a Biologic VMP3 potentiostat (Seyssinet-Pariset, France).

Warburg impedance measurement was performed by applying 2.5 V in a frequency range of 0.01 to 100,000 Hz using a Biologic VMP3 potentiostat. Diffusion can be derived from Warburg impedance according to the following equation [14,26–28]:

$$Z = \sigma(\omega)^{-1/2} (1 - j)$$
(1)

where  $\omega$  is the frequency and  $\sigma$  is the Warburg coefficient. Based on the above equation, the Warburg coefficient can be written as [14,26–28]:

$$\sigma = \frac{RT}{n^2 F^2 A \sqrt{2}C \sqrt{D}} \tag{2}$$

where *D* is the diffusion coefficient of  $AlCl_4^-$  anions, *n* is the number of electrons involved, *A* is the surface area of the electrode, and *C* is the bulk concentration of the diffusing species (moles/cm<sup>3</sup>) [14,26–28].



Figure 1. Demonstration of graphite-based Al secondary battery (GAB) pouch cell fabrication.

#### 3. Results and Discussion

# 3.1. Properties of Electrolyte and Proposed Charging–Discharging Reactions

The ionic conductivity of AlCl3/BMIC electrolyte with a ratio of 1.5 was ~9.2 mS/cm at room temperature that is higher than that of other low-cost AlCl<sub>3</sub>/urea-based electrolyte systems [29]. The vibration of electrolyte was analyzed by Raman spectra (Figure 1a). In Figure 2a, both AlCl<sub>4</sub><sup>-</sup> (~350 cm<sup>-1</sup>) and Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> (~309 and ~430 cm<sup>-1</sup>) major anions were present in our electrolyte simultaneously due to Lewis acidic mixtures (fraction of AlCl<sub>3</sub> > 0.5) [2,15,29]. The AlCl<sub>4</sub><sup>-</sup> peak was assigned to the Al–Cl terminal stretching frequencies and two Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> peaks were assigned to Al–Cl vibrations [30]. On the other hand, we also found two tiny vibration peaks at 603 and 625 cm<sup>-1</sup>, which belonged to the imidazolium ring vibration of BMI<sup>+</sup> cations [31]. This result was confirmed to show the formation of AlCl<sub>3</sub>/BMIC electrolyte and no impurity vibration appeared. Therefore, we propose the GAB charging–discharging reactions in accordance with Lin et al. as shown in Figure 2b. The charging and discharging reactions can be expressed as follows [15]:

On anode:

$$4\text{Al}_2\text{Cl}_7^- + 3\text{e}^- \leftrightarrow \text{Al} + 7\text{Al}\text{Cl}_4^- \tag{3}$$

On cathode:

$$C_n + AlCl_4^- \leftrightarrow C_n[AlCl_4] + e^-$$
(4)

where n is the molar ratio of carbon atoms to intercalated anions in the graphite. During the charging reaction,  $AlCl_4^-$  anions intercalated into graphite and Al deposited on Al foil via  $Al_2Cl_7^-$  anions simultaneously (Equation (3)). Conversely,  $AlCl_4^-$  anions deintercalated from graphite combined with Al dissolution from Al foils to form  $Al_2Cl_7^-$  anions during the discharging reaction (Equation (4)) [15]. As shown in Figure 2c, we investigated the graphitic cathode reactions of GABs by CV measurement. We found oxidation peaks of 1.83 to 2.50 V (versus Al) and reduction peaks of 1.16 to 2.36 V (versus Al), which were attributed to intercalation and deintercalation of  $AlCl_4^-$ , respectively [2,8,15,24].



**Figure 2.** (a) AlCl<sub>3</sub>/[BMIm]Cl electrolyte Raman spectra; (b) schematics of the Al battery charging–discharging process; and (c) cyclic voltammetry (CV) curve at 1 mV/s.

#### 3.2. Effects of Graphite Loading on Electrochemical Performance

Figure 3a–d shows the GAB cycling performance in the initial 50 cycles for graphite loading of 7, 9, 10, and 12 mg/cm<sup>2</sup> at voltage ranges of 1.0–2.5 V. In addition, it can be seen that the capacity and efficiency of the first cycle for all batteries was unstable, but, after 10 cycles, the capacity was improved and stable. This might be attributed to the increased graphitic interlayer distance with repeated AlCl<sub>4</sub><sup>-</sup> intercalation/deintercalation at the initial cycles [4,10]. At a constant current density of 100 mA/g, all the GABs exhibited a high coulombic efficiency of 98.5%. The discharge capacity values of GABs were 105, 88, 82, and 60 mAh/g for 7, 9, 10, and 12 mg/cm<sup>2</sup> natural graphite electrode, respectively. The results show that the capacity strongly depended on graphite loading. Due to excess Al anodes, the loading of graphite cathode affected the capacity of GABs [8]. As shown in Table 2, we also found that the thickness of graphite electrode increased with increased loading of graphite electrode. The above results might be explained by the following considerations. Since no additional active carbon or co-catalyst was applied, different graphite loading led to different thicknesses of graphite electrodes, causing different diffusion coefficients and battery performance. The diffusion of  $AlCl_4^-$  anions in graphite electrode can be analyzed via a Warburg impedance measurement [14,26–28] from electrochemistry impedance spectra (EIS) curves (Figure 4a). The linear dependence of Z" on  $\omega^{-1/2}$  is shown in Figure 4b. We found that the value of slope increased with increased graphite loading. In other words, the diffusion coefficient of 12 mg/cm<sup>2</sup> graphite loading is lower than the  $9-10 \text{ mg/cm}^2$  graphite loading based on Equation (2) [14,26–28]. This is attributed to the reduced intercalated ability of AlCl<sub>4</sub><sup>-</sup> anions with increasing thickness of graphite electrode. Consequently, the capacity of GABs with higher graphite loading was reduced [14,26–28].



**Figure 3.** Cycling performance of Al batteries with loading of graphite electrode at a current density of 100 mA/g: (**a**) 7; (**b**) 9; (**c**) 10; and (**d**) 12 mg/cm<sup>2</sup>.



**Figure 4.** (a) Electrochemistry impedance spectra (EIS) curves with graphite loading; and (b) relationship between Z" and  $\omega^{-1/2}$  of the related EIS plots. The EIS measurement of the Al batteries was analyzed under charging at 2.5 V.

Loading (mg/cm <sup>2</sup> )	Thickness (µm)	Discharge Capacity (mAh/g)	Volume Energy Density (Wh/L)
7	89	105	5.8
9	120	88	6.2
10	130	82	6.5
12	142	60	5.3

**Table 2.** Thickness, discharge capacity, and calculated volume energy density of loading graphite electrode at a charge–discharge current density of 100 mA/g.

For commercialization purposes, the volume energy density of GABs is an important criterion. As can be seen in Table 2, the calculated volume energy density of GABs increased initially with ~10 mg/cm<sup>2</sup> loading of graphite electrode and then gradually decreased with increased loading of graphite electrode (loading ~12 mg/cm<sup>2</sup>). The volume energy density reduction of GABs with graphite loading over 10 mg/cm<sup>2</sup> could be attributed to a thicker graphite layer, which hindered the diffusion of AlCl<sub>4</sub><sup>-</sup> anions. Based on the above results, a suitable graphite loading of GABs was found to be 10 mg/cm<sup>2</sup>.

## 3.3. Characterizations and Electrochemical Performance of GABs with Graphite Loading of 10 $mg/cm^2$

Based on Section 3.2, it was shown that GABs with graphite loading of 10 mg/cm<sup>2</sup> had the highest volume energy density of 6.5 Wh/L. Therefore, a detailed electrochemical performance, including high-rate capability and long-term cycling stability, was examined. Figure 5 shows the charge–discharge capacities of the 10 mg/cm<sup>2</sup> GABs at various C-rates. As shown, reasonable discharge capacities of 82, 71, 51, 45, and 40 mAh/g were measured at current densities of 100, 300, 500, 700, and 1000 mA/g (namely, 1C, 3C, 5C, 7C, and 10C), respectively (data shown in Table 3). These results revealed that higher discharge capacities were obtained at current densities of  $\leq$ 3C (300 mA/g) and then decreased at higher current densities because of the slow diffusion rate of AlCl<sub>4</sub><sup>-</sup> anions through the graphitic layers [2,32]. Furthermore, when the current density returned to 1C (100 mA/g) after cycling at 10C (1000 mA/g), the capacity rebounded to 83 mAh/g, close to that in the first 20 cycles.



Figure 5. Cycling performance of 10 mg/cm<sup>2</sup> graphite electrode at different C-rates.

Charge–Discharge Current Density (mA/g)	Discharge Capacity (mAh/g)
100	82
300	71
500	51
700	45
1000	40

**Table 3.** Discharge capacity of 10 mg/cm<sup>2</sup> graphite electrode at various charge–discharge current densities.

Figure 6a shows the stability test of the 10 mg/cm<sup>2</sup> GABs using a constant current of 100 mA/g within the voltage range of 1.0–2.5 V for 250 cycles. The capacity still remained at 74.5 mAh/g with a coulombic efficiency of 98% after 250 cycles, which showed excellent stability. It is worth mentioning that the capacity was a little low initially but increased after 50 cycles because of other side reactions [33]. As shown in Figure 6b, the charge and discharge curves of 10 mg/cm<sup>2</sup> GABs recorded at the 10th, 50th, 100th, 150th, 200th, and 250th cycles were almost similar, indicating a highly reversible reaction. In addition, all curves have two obvious discharge voltage plateaus at 2.2 and 1.8 V, which is similar to the results of Wang et al. [14].



**Figure 6.** Electrochemical properties of the 10 mg/cm<sup>2</sup> graphite electrode at 100 mA/g: (**a**) long-term stability test; (**b**) discharge–charge curves at constant current of 100 mA/g (1C); (**c**) Raman spectra for pristine, fully charged, and discharged graphite electrodes.

In order to confirm the intercalation/deintercalation of  $AlCl_4^-$  anions into the natural graphite, Raman spectroscopy, XRD, and SEM were employed to analyze the pristine and fully charged/discharged natural graphite electrodes, respectively. Figure 6c shows the Raman spectra for the pristine, fully charged, and discharged graphite electrodes. For all plots, signals at ~1350 and ~1580 cm<sup>-1</sup> correspond to the D-band and G-band, which present the disordered graphitic structure and the crystallinity of graphite, respectively [8,34]. The  $I_D/I_G$  ratio of pristine graphite electrode was 0.039, which indicated good graphitization. The  $I_D/I_G$  ratio increased to 0.073 for the fully charged sample due to the intercalation of  $AlCl_4^-$  anions, causing disorder of the graphitic structure. On the

other hand, the  $I_D/I_G$  ratio returned to 0.043 for the discharged sample, which was similar to that of the pristine sample. The slight difference between pristine and discharged sample might be caused by the residual  $AlCl_4^-$  anions in the graphite structure at the discharged state [10]. According to the Raman spectra, the cathodic reaction of GABs was confirmed, as schematically illustrated in Figure 2b [15].

The pristine and postcycled natural graphite electrodes were also analyzed via XRD, and results are shown in Figure 7. For the XRD pattern of the pristine sample, there was only one diffraction peak at 26.5°, which corresponded to the (002) of the graphite. By contrast, this peak shifted to ~27° and broadened asymmetrically after 250 cycles due to highly strained graphite layers via  $AlCl_4^-$  intercalation, causing irreversible change of the graphite structure [2,15]. The SEM images of the pristine and postcycled natural graphite are shown in Figure 8a,b. The pristine natural graphite was spherical particles with an average size of ~12.7 µm. After cycling, the particle size increased irregularly, as shown in Figure 8b. This result is similar to the finding of Wei et al., who reported amorphous carbon–graphite composite cathode for GABs [34]. Based on the above results, although there were irreversible structure changes of the natural graphite structure after 250 cycles, the capacity and coulombic efficiency of GABs had no obvious decay. Thus, we believe that the low-cost and highly stable natural graphite is a good candidate for cathode materials for GABs.



Figure 7. X-ray diffraction patterns of pristine and post-cycled natural graphite electrodes.



Figure 8. SEM images of (a) pristine and (b) postcycled natural graphite.

# 4. Conclusions

In this study, we prepared AlCl<sub>3</sub>/BMIC ionic liquid-based GABs using a low-cost and commercial natural graphite cathode. The effects of graphite loading on performance were investigated. Results from battery measurement show that the GABs with graphite loading of 10 mg/cm<sup>2</sup> exhibited a discharge capacity of 82 mAh/g at a current density of 100 mA/g. Furthermore, they delivered the highest volume energy density of 6.5 Wh/L among the studied graphite loading (ranging from 7–12 mg/cm<sup>2</sup>). After 250 charge–discharge cycles at 100 mA/g, the capacity of GABs with graphite loading of 10 mg/cm<sup>2</sup> reached as high as 74.5 mAh/g. Because of the low-cost cathode, abundance of Al anode, and cheaper ionic liquid, GABs with high graphite loading show great potential for energy storage systems in the future.

Author Contributions: M.C.H. and C.-C.C. conceived and designed the experiments; S.-C.C., Y.-F.C., C.-Y.L., and Y.-L.L. prepared the graphite electrodes; M.-C.H., L.Y.W., and S.-C.C. performed the experiments; M.-C.H. and C.-H.Y. wrote the manuscript; C.-C.C., C.-C.Y., and W.-S.C. contributed regents/materials/analysis tools.

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## Nomenclature

Al	Aluminum	
AlCl <sub>3</sub>	Aluminum chloride	
AlCl <sub>4</sub> <sup>-</sup>	Chloroaluminate	
$Al_2Cl_7^-$	Dialuminum heptachloride	
mAh/g	Capacity	
mA/g	Charge–discharge rate	
mg/cm <sup>2</sup>	Graphite loading	
Wh/L	Energy density	
ω	Frequency	
σ	Warburg coefficient	
D	Diffusion coefficient	
п	Number of electrons involved	
Α	Surface area of the electrode	
С	Bulk concentration of diffusing species	
$\mathrm{cm}^{-1}$	Wavenumber	
C <sub>n</sub>	Molar ratio of carbon atoms	
V	Potential vs. Al	
I <sub>D</sub>	Intensity of D-band	
I <sub>G</sub>	Intensity of G-band	
mS/cm	Ionic conductivity	
Abbreviations		
EMIC	1-ethyl-3-methylimidazolium chloride	
BMIC	1-butyl-3-methylimidazolium chloride	
GABs	Graphite-based Al secondary batteries	
PVDF	Polyvinylidene difluoride	
NMP	Methylpyrrolidone	
SEM	Scanning electron microscope	
XRD	X-ray diffraction	
CV	Cyclic voltammetry	
EIS	Electrochemistry impedance spectra	
1C-10C	100 to 1000 mA/g	

## Superscripts

2	Square
-1	To the negative one

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