



## Research article

## Properties of Mg/graphite and Mg/graphene as cathode electrode on primary cell battery

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## ABSTRACT

Since graphene was first isolated in 2004, it has become an attractive material on electrochemical energy storage devices. The purpose of this study is to compare Mg/graphite and Mg/graphene electrodes to commercial primary battery cathodes. This research is an experimental laboratory research. Graphene was synthesized with Hummer's method modified. Electrodes cathode of primary battery (Mg/graphite and Mg/graphene) were prepared using impregnation method. Graphene and electrodes cathode were analyzed with X-Ray Diffraction (XRD), Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX) and conductivity, respectively. The XRD data of graphene show that there is a weak and sharp peak on  $2\theta = 26,5^\circ$ , indicating graphene is formed. The peaks shape of  $2\theta = 35^\circ$  are totally different for Mg/graphite and Mg/graphene. At Mg/graphite, the sharp and narrow peak appears on  $2\theta = 35^\circ$ . It means Mg is well deposited on graphite. Interestingly, Mg/graphene has narrow and weak peak on  $2\theta = 35^\circ$ , indicating the Mg was deposited on graphene and properties of Mg has been changed by graphene. This data is also well confirmed by EDX data. Mg atoms exist on graphene (1.47 wt%) (EDX data). SEM images of Mg/graphite and Mg/graphene are significantly different, probably support material effect. The properties of Mg/graphite and Mg/graphene comparing to commercial primary battery cathode were evaluated using conductivity. The conductivity of Mg/graphene (1080  $\mu\text{S}/\text{cm}$ ) is highest among Mg/graphite (90  $\mu\text{S}/\text{cm}$ ) and commercial battery cathode (10  $\mu\text{S}/\text{cm}$ ). All of data show that the Mg/graphene is potentially used as a primary battery cathode.

## 1. Introduction

Batteries are electrochemical devices that convert chemical energy into electrical energy during the process of exchanging electrons between the anode and cathode [1]. Ideal batteries have specific energy [2], high power density [3], good life cycle [4], resistance to interference [5] and low cost [6]. The main components of the primary battery are carbon on the anode and carbon metal alloy at the cathode [1]. That is, the quality and cost of producing primary batteries is determined by their constituent materials (cathodes, anodes, and electrolyte pastes) [7]. Therefore,

we need an alternative new material that can be used to produce primary batteries in large quantities [8].

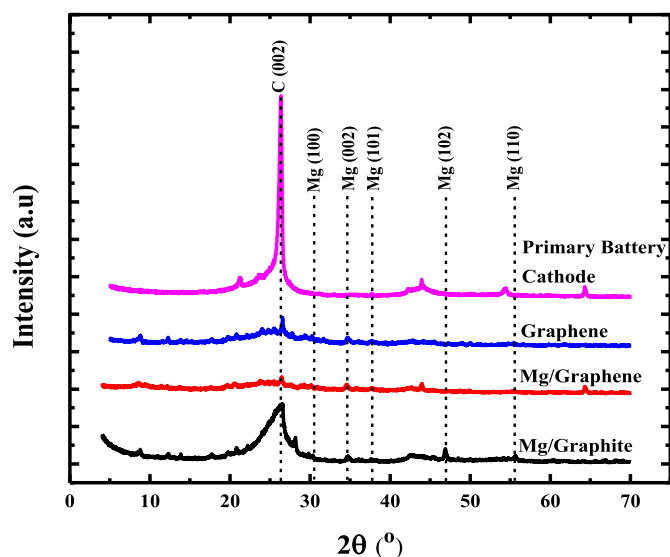
Graphene has become an interesting material to study specifically for electrochemical energy storage devices [9]. Graphene is a carbon monolayer layered with 2D lattice [10]. Features of graphene: carbon 2D [11],  $\text{sp}^2$  [12], very high strength [13], the surface area of  $2600 \text{ m}^2\text{g}^{-1}$  [14], electrical conductivity ( $1250 \text{ Scm}^{-1}$ ) [15] and thermal conductivity ( $4840\text{--}5300 \text{ Wm}^{-1}\text{K}^{-1}$ ) [16,17]. Graphene can be considered to be an energy storage material for Li and Na ions in battery ions, for example Li/Graphene has a specific capacity ( $744 \text{ mAhg}^{-1}$ ) and Li/Graphite ( $372 \text{ mAhg}^{-1}$ ) [18].

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**Figure 1.** XRD patterns of Mg/graphite, Mg/graphene, graphene and primary battery cathode.

The main problem with development battery is that the price of lithium is very expensive and becomes waste after usage, the density and energy capacity of primary batteries is still low [19] weak interactions between electrodes and transport of electrons [20] and loss of electrical contact at long usage times [21]. The solution to overcoming this problem is to use graphene. The important concept in this study are i) increasing energy storage capacity can be done by graphene; ii) The specific energy and energy capacity of the battery can be increased by graphene [22].

Previous research has been carried out by Kucinskis (2013) which uses graphene on primary battery cathodes [18]. The results obtained from this study are battery cathode materials when mixed with the addition of graphene will increase the conductivity of the

electrons and therefore the ability of the battery cathode to deliver will be better. Addition of Pt metal will increase cathode activity and the addition of metals can increase the quality of interaction electronically from graphene [21]. Modification of carbon materials especially with the use of magnesium has been proposed [23] and could be used as a supporting material as an electrode in the primary battery cell.

## 2. Experimental

### 2.1. Materials

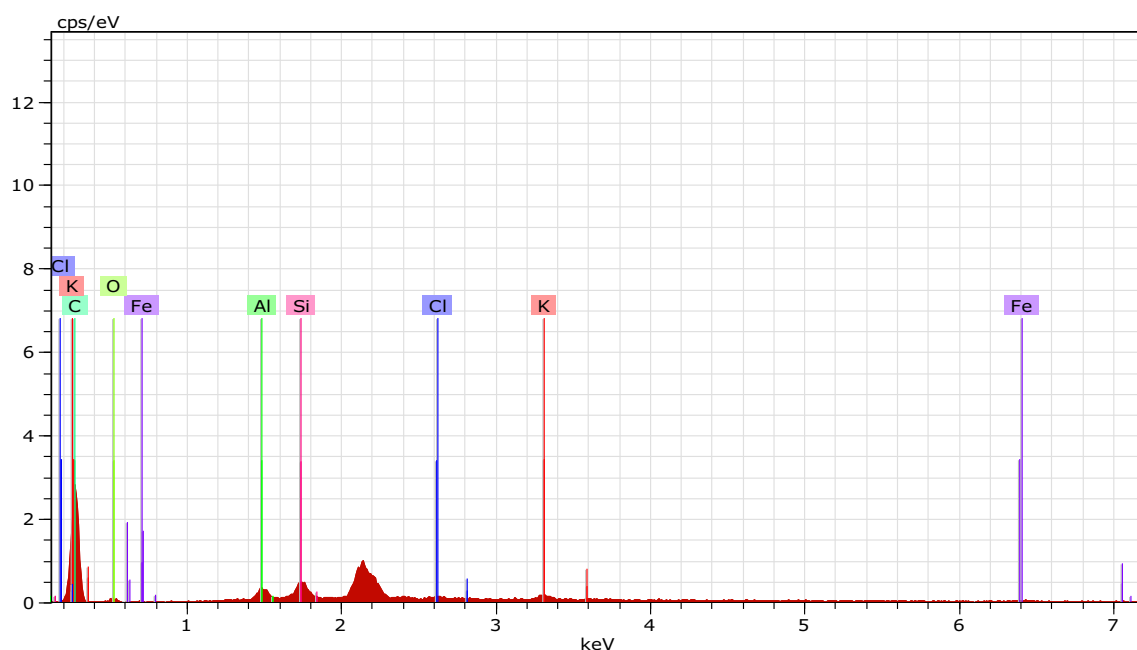
Graphite commercial powder (carbon 98wt%, ash wt15%), sulfuric acid ( $H_2SO_4$ , 98 wt%), potassium permanganate ( $KMnO_4$ , 99.5 wt%), hydrogen peroxide ( $H_2O_2$ , 30 wt%) and ammonia ( $NH_3$ , 25 wt%) were purchased from Sigma-Aldrich (Singapore). Sodium Nitrate ( $NaNO_3$ , 99 wt%), magnesium chloride ( $MgCl_2$ , 99 wt%), magnesium powder (Mg, 99 wt%) were purchased from Merck (Singapore). All the chemical reagents as approved without any further purification.

### 2.2. Synthesis of graphene

Briefly, 0.2 g of graphite was added with 0.2 g  $NaNO_3$  and 15 ml  $H_2SO_4$ , were stirred together for 2 h in an ice bath condition. Next, 1 g of  $KMnO_4$  was slowly added into the solution and stirred for 24 h to generate graphite solution. Finally, 20 ml of  $H_2SO_4$  5% and 1 mL  $H_2O_2$  30%, stirred for 1 h, respectively. The solution was centrifuged at 6500 rpm for 20 min and ultrasonication for 5 h, then allowed to cool and produce a solution graphene oxide. The graphene oxide solution was to be shared into two parts, the first solution was dried with an oven at 100 °C to result in the graphene oxide powder. The other solution was added with a 5 mg magnesium powder and stirred for 72 h, filtered and dried at 100 °C to produce graphene powder.

### 2.3. Preparation of Mg/graphite and Mg/graphene

$MgCl_2$ /graphite 1:1 by weighing 1 g of  $MgCl_2$  and graphite, each added 200 ml ethanol absolute and stirred for 1 h. Then the  $MgCl_2$ /



**Figure 2.** EDX spectra of Mg/graphite.

**Table 1.** Comparison of Elements of graphene, graphite/graphene, Mg/graphite and Mg/graphite (EDX Data).

Element	Graphene	Mg/Graphite	Mg/Graphene	Primary Battery Cathode
C	48.84	81.96	47.05	97
O	32.88	3.81	39.34	
Na	0.30		0.18	
Mg	0.91		1.47	
Al	5.59	1.52	5.27	0.5
Si	6.95	4.17	4.80	0.8
S	0.60			1.1
Cl	0.36	0.69	1.41	
K	1.79	2.83	0.24	
Ca	0.89			
Ti	0.26			
Fe	0.65	5.02	0.25	0.6

ethanol and graphite/ethanol solution were mixed and stirred again for 2 h. The solution was filtered and dried at  $T = 100\text{ }^{\circ}\text{C}$ . The similar way was done on the variation of Mg/graphene.

### 3. Results and discussion

#### 3.1. Analysis of XRD

In this research, there are some reasons, Mg was used in this research. Those are Mg has the similar period with Li; the capacity storage electron of Mg is highest among the others metal; Mg is more less reactive compare to Li, graphene may be hope increasing activity of Mg; deposit of Mg is largest than Li and price of Mg is cheaper than Li.

In order to prove that Mg was deposited on graphite and graphene, XRD was used to analyze them. Figure 1 shows the XRD patterns of primary battery cathode, graphene, Mg/graphite and Mg/graphene. Primary battery uses graphite as cathode. Graphite exhibited a basal

reflection (002) sharp peak at  $2\theta = 26.5^{\circ}$  corresponding to d spacing of  $3.370\text{ \AA}$  which is compatible with the literature data (JCPDS 75–2078). This data is similar to commercial primary battery cathode. It means the cathode of primary battery contains majority of graphite. In the XRD pattern of graphene obtained via the improved Hummers' method. Graphene has a broad peak centered at  $2\theta = 26.52^{\circ}$  corresponding to d spacing of  $3.35\text{ \AA}$  which might be attributed to very thin graphene layers. This data closes to Hassan (2014) reported [24].

Mg/graphite shown broad and sharp peak corresponds to Mg (100) on position  $2\theta = 35^{\circ}$ . It means probably Mg exists on graphite. Surprisingly, the narrow and weak peak appear on  $2\theta = 35^{\circ}$  for Mg/graphene, indicating Mg atoms were well deposited on graphene. Therefore, the properties of Mg may be changed by graphene. In addition, the size of Mg particles on graphene seemly is not similar compare to Mg particles of graphite. Thereby, we may modify properties of Mg with surface interaction between metal block-s (Mg) and  $\pi$ -bond of graphene (probably s- $\pi$  bonding).

#### 3.2. Analysis of SEM-EDX

SEM-EDX used in order to more prove that Mg atoms are well deposited on graphite and graphene. Figure 2 and Table 1 show the EDX and weight composition data of Mg/graphite.

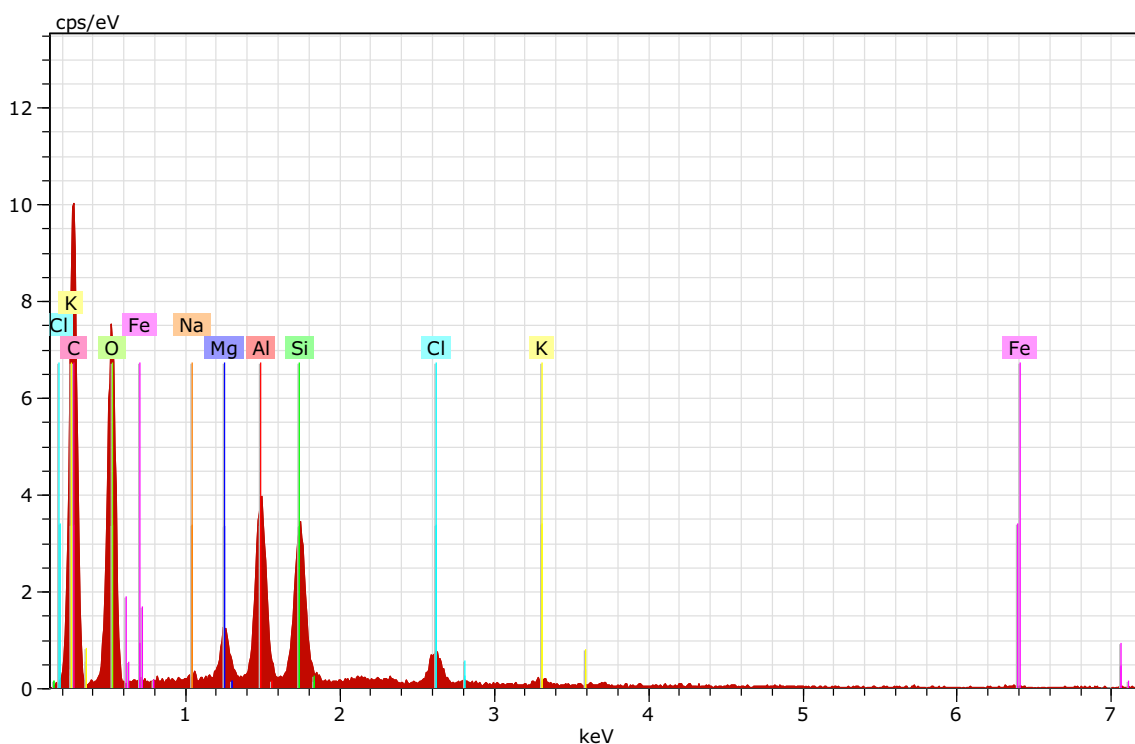
EDX data confirms that Mg atom is not appear on graphite. That is also consistent with weight percent data of Mg is absence on Mg/graphite (Table 1).

Interestingly, Mg atoms are deposited on graphene (1.47 wt%) (Table 1). This data is supported also with EDX data (Figure 3.).

Figure 3 clearly show that Mg atoms exist on graphene. In addition, graphene and commercial cathode also were confirmed with EDX measurement. Those data may be seen in Figures.4 and 5.

Graphene content majority is C (48.8 wt%) (Figure.4). The cathode battery has much more carbon weight percent (97 wt%) compare to graphene. It means carbon dominate on cathode battery.

The morphology of Graphene, Mg/Graphite, Mg/Graphene and Primary Battery Cathode may be seen in Figure 6. Graphene has wrinkled

**Figure 3.** EDX spectra of Mg/graphene.

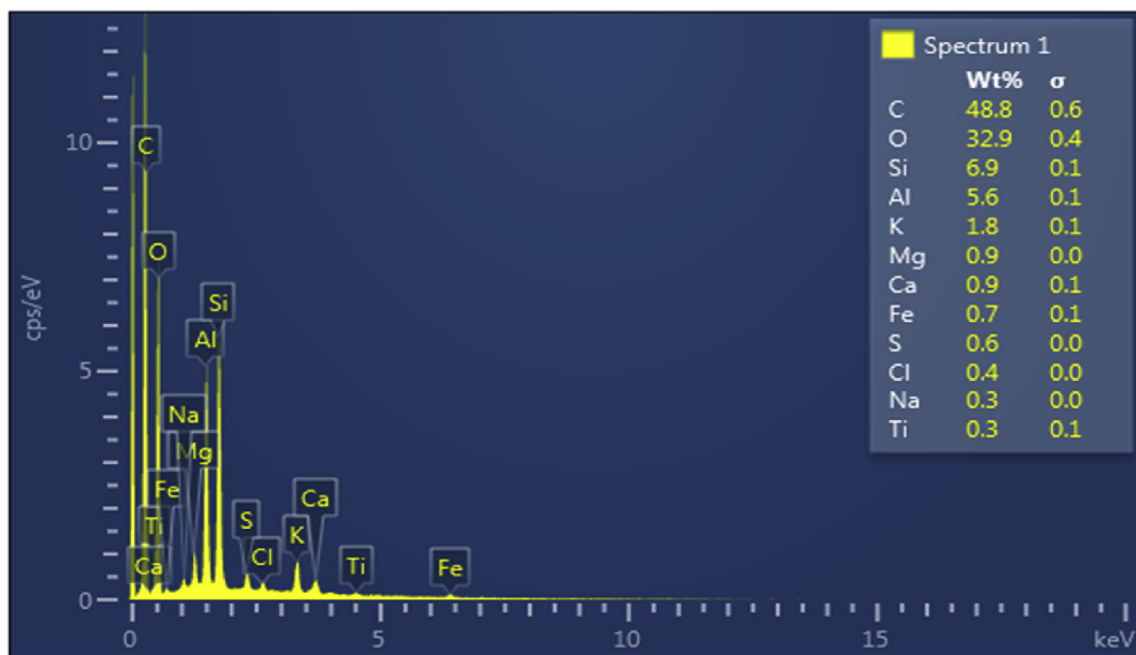


Figure 4. EDX spectra of graphene.

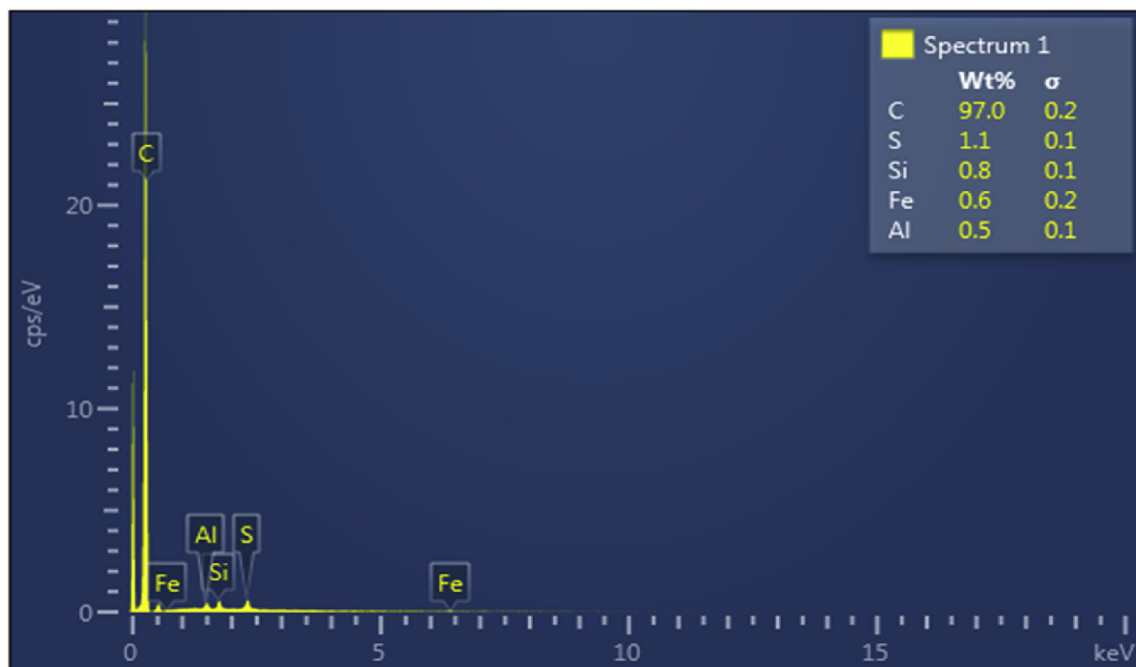


Figure 5. EDX spectra of primary battery cathode.

surfaces and thin sheets (Figure 6a.). In Mg/graphite (Figure 6b.) appears small white spots on graphite surfaces, indicating Mg atoms exist on it. Mg atoms seemly are deposited on graphene. It may be seen that many white spots on graphene surfaces (Figure 6c). The distinguish morphology shapes appear on cathode battery surface. It means absolutely cathode battery is not graphene (Figure 6d.).

### 3.3. Analysis of electrical conductivity

Analysis of electrical conductivity of graphene, Mg/graphite, Mg/graphene and commercial primary battery cathode were evaluated by

using AC780-Conductivity Meter i-SOLV at room temperature, respectively. All of electrical conductivity is shown in Table 2.

Table 2 shows that the electrical conductivity of Mg/graphene is highest and the lowest is battery cathode. Pristine graphene has electrical conductivity higher than battery cathode. That is caused battery cathode contains graphite. The electrical conductivity of graphite is low because stacking graphene occur on graphite. That is why electrons cannot move freely due to dense density on graphite surface. The other reason is gap between valence band and conductance band of graphite is still broad. Surprisingly, electrical conductivity of graphene is significantly higher than graphite. It proves electrons move fast on graphene surface. It occurs because high  $\pi$ - $\pi$  stacking are absence on graphene. Those data are

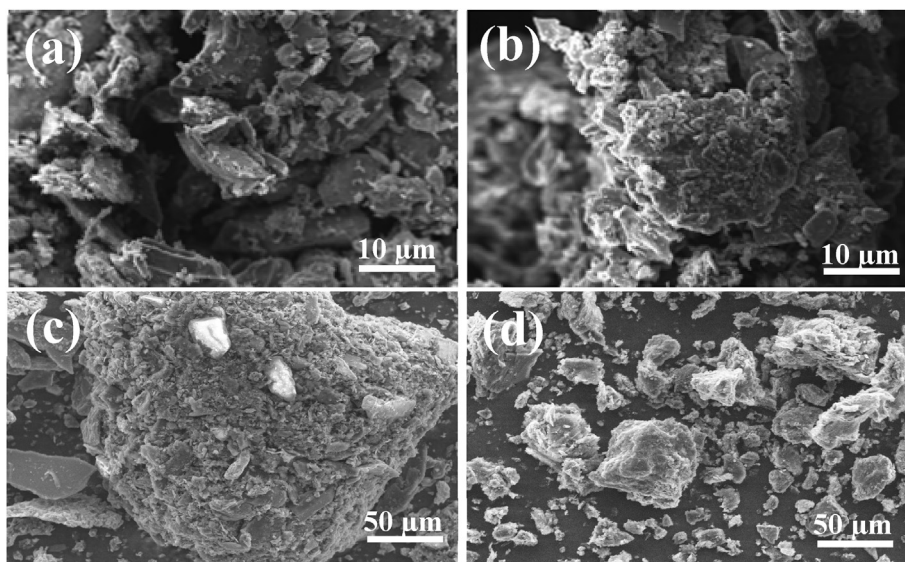


Figure 6. SEM images of Mg/Graphite (a), Mg/Graphene (b), Graphene (c) and Primary Battery Cathode (d) with magnification 1000x.

Table 2. Electrical conductivity.

Sample	Measurement of Conductivity ( $\mu\text{S}/\text{cm}$ )
Commercial Primary Battery Cathode	10
Graphene	170
Mg/Graphite	90
Mg/Graphene	1080

consistent while Mg deposited on graphene and graphite, respectively. The conductivity of Mg/graphene is significantly higher than Mg/graphite. It means graphene as well as supporting material may be expected to increase conductivity of Mg. That is possible because chemical interaction between Mg and graphene (probably  $\pi$ -s).

#### 4. Conclusions

Preparation of electrodes on primary battery cathodes by conducting graphite synthesis into graphene by the Hummer's method using magnesium reducing agent. And continued with the impregnation method to deposit metal in graphite and graphene. Modification of the primary battery cathode gets good results. Mg/graphene can be used as an alternative primary battery cathode because of its higher conductivity (1080  $\mu\text{S}/\text{cm}$ ) compared to the primary battery cathode (10  $\mu\text{S}/\text{cm}$ ).

#### Declarations

##### Author contribution statement

Crystina Simanjuntak, Rikson Siburian: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Harlem Marpaung, Tamrin: Analyzed and interpreted the data.

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##### Competing interest statement

The authors declare no conflict of interest.

##### Additional information

No additional information is available for this paper.

##### References

- [1] D. Linden, T.B. Reddy, *Handbook of Batteries*, McGraw-Hill, 2002.
- [2] J.B. Hou, Y.Y. Shao, M.W. Ellis, R.B. Moore, B.L. Yi, Graphene based electrochemical energy conversion and storage, *Phys. Chem.* 13 (2011) 15384–15402.
- [3] M.J. Allen, V.C. Tung, R.B. Kaner, Honeycomb carbon: a review of graphene, *Chem. Rev.* 110 (2010) 132–145.
- [4] Y. Si, E.T. Samulski, Synthesis of soluble graphene nanosheets, *Nano Lett.* 8 (2008) 1679–1682.
- [5] G.J. May, A. Davidson, B. Monahov, Lead batteries for utility energy storage: a review, *J Energy Storage* 15 (2017) 145–147.
- [6] K. Liu, Y. Liu, D. Lin, A. Pei, Y. Cui, Materials for lithium-ion battery safety, *Sci. Adv.* 4 (2018).
- [7] R. Raccichini, A. Varzi, S. Passerini, B. Scrosati, The role of graphene for electrochemical energy storage, *Nat. Mater.* 14 (2010) 271–279.
- [8] M. Supeno, C. Simanjuntak, R. Siburian, Facile and benign method to produce large scale graphene nano sheets, *Iranian J* (2019).
- [9] E.P. Randviir, D.A.C. Brownson, C.E. Banks, A decade of graphene research: production, applications and outlook, *Biochem. Pharmacol.* 17 (2014) 426–432.
- [10] A. Bianco, H.M. Cheng, T. Enoki, Y. Gogotsi, R.H. Hurt, N. Koratkar, T. Kyotani, M. Monthieux, C.R. Park, J.M.D. Tascon, All in the graphene family—a recommended nomenclature for two dimensional carbon materials, *Carbon* 65 (2013) 1–6.
- [11] U.K. Sur, Graphene: a rising star on the horizon of material science, *Int J Electrochemistry* (2012) 1–12.
- [12] C. Lee, X. Wei, J.W. Kysar, J. Hone, Measurement of the elastic properties and intrinsic strength of monolayer graphene, *Science* 321 (2008) 385–388.
- [13] A.A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, C.N. Lau, Superior thermal conductivity of single-layer graphene, *Nano Lett.* 8 (2008) 902–907.
- [14] M.D. Stoller, S.Y. Park, J. An. Zhu, R.S. Ruoff, Graphene based ultracapacitors, *Nano Lett.* 8 (2008) 3498–3502.
- [15] B. Seger, V.P. Kamat, Electrocatalytically active graphene – platinum nanocomposites. Role of 2 – D carbon support in PEM fuel cells, *J. Phys. Chem. C* 19 (2009) 7990–7995.
- [16] S. Thinius, M.M. Islam, P. Heitjans, T. Bredow, Theoretical study of Li migration in Lithium – graphite intercalation compounds with dispersion-corrected DFT methods, *J. Phys. Chem. C* (2014).
- [17] Y.S. Choi, C. Yeo, S.J. Kim, J.Y. Lee, Y. Kim, K.R. Cho, S. Ju, B.H. Hong, S.Y. Park, Multifunctional reduced graphene oxide-CVD graphene core-shell fibers, *Nanoscale* 11 (2019) 12637–12642.
- [18] K. Persson, Y. Hinuma, Y.S. Meng, A. Van Der Ven, G. Ceder, Thermodynamic and kinetic properties of the Li-graphite system from first-principles calculations, *Phys. Rev. B Condens. Matter Mater. Phys.* 82 (2010) 1–9.

- [19] G. Kucinskis, G. Bajars, J. Kleperis, Graphene in lithium ion battery cathode materials :A review, *J. Power Sources* 240 (2018) 66–79.
- [20] R. Sibirian, T. Kondo, J. Nakamura, Size control to a sub-nanometer scale in platinum catalysts on graphene, *J. Phys. Chem. C* 117 (2013) 3635–3645.
- [21] R. Sibirian, J. Nakamura, Formation process of Pt subnano-clusters on graphene nanosheets, *J. Phys. Chem. C* 116 (2012) 22947–22953.
- [22] S. on Tung, S.L. Fisher, N.A. Kotov, L.T. Thompson, Nanoporous aramid nanofiber separators for nonaqueous redox flow batteries, *Int. J. Electrochem. Sci* 14 (2019) 4185–4194.
- [23] L. Malyala, S. Thatipamula, V. Rani Jentti, Magnesium-Graphene Composite Coated on SS Mesh as Cathode Material for Rechargeable Magnesium Ion Battery, *Trans Indian Inst Met*, 2019.
- [24] M. Hassan, K.R. Reddy, E. Haque, S.N. Faisal, S. Ghasemi, A.I. Minett, V.G. Gomes, Hierarchical assembly of graphene/polyaniline nanostructures to synthesize free-standing supercapacitor electrode, *Compos. Sci. Technol.* 98 (2014) 1–8.