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Facile preparation of electrodes derived from graphene oxide@metal organic framework hybrid materials and their electrochemical property

Jin-Young Hong[1], Soo-Jin Park[2], Seok Kim[1,♠] and Sungwook Chung[1,♠]

[1]School of Chemical and Biochemical Engineering, Pusan National University, Busan 46241, Korea
[2]Department of Chemistry, Inha University, Incheon 22212, Korea

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♠Corresponding Author
E-mail: seokkim@pusan.ac.kr
sungwook.chung@pusan.ac.kr
Tel: +82-51-510-3874
+82-51-510-2397

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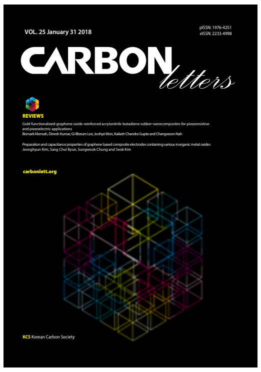

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Since the commercialization of lithium-ion batteries (LIBs) in 1990, they evolved to improve energy density [1]. To achieve this purpose, it is need to increase the available capacity of cathode, optimize manufacturing process of electrode material and increase the voltage limit. When estimating the performance improvement of LIB for xEV by 2020, the battery capacity will increase by more than 120 Ah, 1.4 times and the weight energy density will be doubled to 320 Wh kg^{-1} [2]. For these reasons, it is necessary to develop a silicon-carbon composite anode material [3], a cathode material having a nickel content of more than 80% and a multifunctional and high performance electrolyte [4].

However, there are limitations in improvements of capacity and energy density due to LIB principle by intercalation and de-intercalation of lithium ions [5]. Therefore, research and development of next-generation energy storage devices are essential for requirements of high performance and power equipment.

The lithium-sulfur (Li-S) batteries are one of the next-generation energy storage system and have 1675 $mAhg^{-1}$ of theoretical specific capacity and 2500 Wh kg^{-1} of energy density [6]. Due to these reasons, it is expected that Li-S batteries could achieve five times higher capacity than conventional LIBs. Furthermore, sulfur, which is eco-friendly and abundant material, as a cathode material, can lead to reduce cost for manufacturing the rechargeable batteries. However, it is not fully developed due to the irreversible loss of lithium polysulfide, which is an intermediate product generated in cycles, and it can lead to decrease in cycle life. Besides, sulfur as a cathode material, has a lower conductivity [7].

To improve these disadvantages of energy storage devices, many nano-structured carbon materials such as mesoporous carbon, carbon nanotubes and graphenes have been considered due to their superior electrochemical and structure properties [8-14]. Despite these efforts, it is difficult to commercialize Li-S batteries and there are several obstacles such as a still low sulfur utilization and short stable cycle life.

On the other hand, metal organic framework (MOF) is composed of metal ions and organic ligands with coordination and has a high specific surface area. There are many kinds of MOF because they can be obtained with various combination of chemicals [15]. For this reason, the structure of MOF can be controllable and applied to gas adsorption, catalysts and energy storage devices. MOF, which has a large surface area and enough space for the better charge transfer, could be expected to enhance the electroactivity of Li-S battery cathode. To our best knowledge, the influence of changing organic ligand of MOF on the electroactivity of sulfur-based electrodes was not fully investigated. In this study, to study effect of organic ligand of MOF on electrochemical properties, the composites were prepared by changing the chemical ligand structure.

Graphene oxide (GO) was prepared by Hummer's method using oxidants. One gram of graphite (Bay Carbon Co., USA) and 1.1 g of sodium nitrate (Junsei, Japan). After that, 5.1 g of potassium permanganate (Daejung, Korea) was added to the solution and stirred at 35°C for 2 h. And then, distilled water and hydrogen peroxide (Junsei) were added. The oxidized solution was filtered and rinsed using hydrochloric acid (Daejung). The rinsed yellow brown GO was washed again with ethanol and water several times, with centrifugation. After freeze

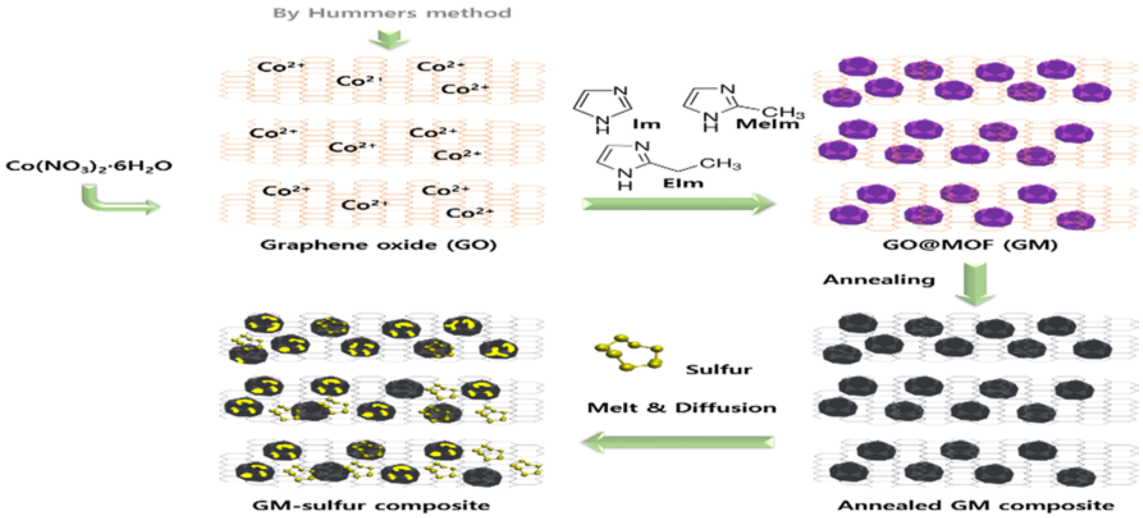

Fig. 1. The schematic diagram for a preparation process of the graphene/MOF-sulfur composites.

drying for 2 d, GO powder can be obtained.

First of all, 0.3 g of GO was dispersed in 100 mL of water and sonicated for 1 h. 1.35 g of cobalt nitrate hexahydrate (Sigma-Aldrich, USA) was dissolved in 9 mL of another water, and the solution was poured to sonicated GO solution and mixed for 30 min. 3.35 M of ligand solutions which were added different ligands such as imidazole (Sigma-Aldrich), 2-metyhlimidazole (Sigma-Aldrich) and 2-ethylimidazole (Sigma-Aldrich) were prepared and former solution poured to later ligand solution under vigorously stirred for 6 h at 35°C. The purple precipitates were collected by centrifugation, and washed with mixture of water and methanol at least three times. Finally, they were dried in freeze drying for 2 d. The samples were named according to added ligand; GMIm, GMMeIm and GMEIm.

The obtained GM composites were thermally treated at 800°C for 3 h under argon atmosphere using a raising rate of 5°C min^{-1}. These carbonized GM composites and elemental sulfur (Sigma-Aldrich) were mixed with carbon disulfide (Kanto chemical Co., Japan). The mixtures were also treated in quartz tube furnace at 160°C for 12 h under argon atmosphere. After above preparation process, the final GM-sulfur composites could be obtained.

The electrochemical properties of each GM-sulfur composite were estimated using CR-2016 type coin cell. The active material is composed of GM-sulfur composite, conductive material (Super-P; Alfa Aesar, USA) and polyvinylidene fluoride (Sigma-Aldrich). This mixture was dispersed in an N-methyl-2-pyrrolidione solvent (NMP, Junsei) and the prepared slurry was coated on aluminum foil. After drying, dried coated foil was used as a cathode. In glove box which control low humidity and dirt, assembling coin cell was conducted under argon atmosphere. Former prepared coated film as a cathode, polypropylene film as a separator, lithium metal as a anode and 1 M LiTFSI (Sigma-Aldrich) and 0.1 M $LiNO_3$ (Sigma-Aldrich) in mixed solvent of 1,2-dimethoxyethane (Junsei) and 1,3-dioxolane (Sigma-Aldrich) (1:1 volume ratio) as a electrolyte were used.

Electrochemical characterizations were conducted on WBCS-3000S battery tester (WonATech, Korea) and cyclic voltammetry (CV) test was performed in a voltage range of 1.5–3.0 V. The charge-discharge tests were estimated in the voltage window of 1.5–3.0 V with 100 mAg^{-1} of current density for 100 cycles.

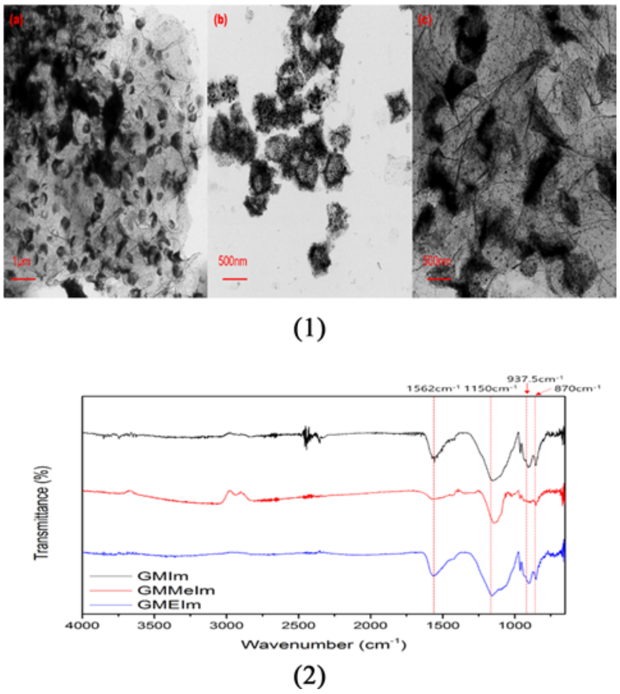

Fig. 2. (1) Structural characterizations of composites: FE-TEM image of (a) GMIm, (b) GMMeIm, (c) GMEIm, and (2) the FT-IR spectra of GM-sulfur composites

Fig. 1 illustrated the process for preparation of the GM-sulfur composite via solvothermal reaction at room temperature. The morphology of obtained composite through this process were characterized by field emission transmission electron microscopy (FE-TEM).

As shown in Fig. 2(1), porous ZIF particles and translucence graphene sheets were observed. The ZIFs are around 400–500

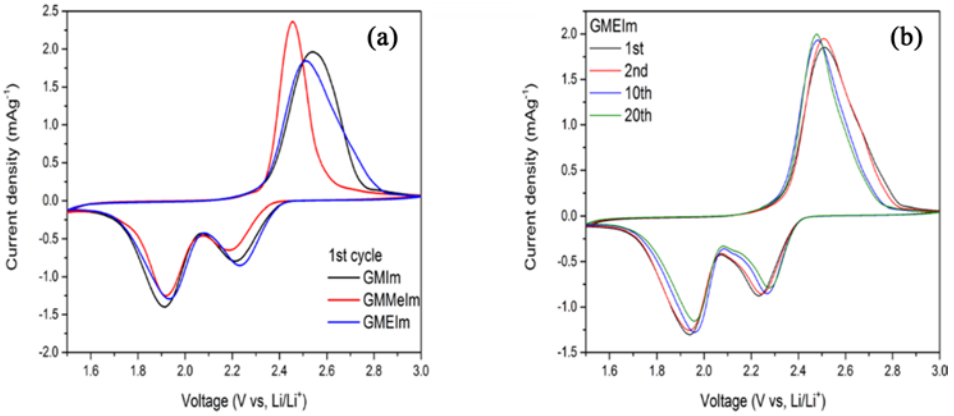

Fig. 3. The cyclic voltammogram of the composites: (a) the first cycle CV curves of samples which have a different ligand for MOF and (b) the CV curves of GMEIm for 20 cycles.

nm diameter. GMMeIm showed regular structure but the others were irregular or nearly amorphous especially in Fig. 2(1) (c). It seems that the structure had been changed due to interaction from the functional groups of ligands [16].

Fig. 2(2) showed the Fourier transform infrared (FT-IR) spectra of composite. The FT-IR spectra were analyzed over a wavenumber range of 4000–650 cm^{-1}. The peaks at 1562 cm^{-1} is assigned to N-H stretch bend in amines and amides and other peaks at 1150 cm^{-1} is assigned to C-N in amines. Further, the peaks at 937.5 cm^{-1} is ascribed to out-of-plane bend in aromatics and out-of-plane bend in alkanes peaks were at 870 cm^{-1}. The strong peaks were observed at around 750 cm^{-1} in case of GMEIme . The nitrogen-containing functional groups seemed to help alleviate dissolution of lithium polysulfide [17].

Fig. 3 showed the CV curves of as-prepared GM-sulfur composites at a scan rate of 0.2 mV s^{-1} between 1.5 and 3.0 V. Overall, there were two reduction peaks at 2.3 and 1.9 V correspond to the sulfur–lithium polysulfide–lithium sulfide two-steps reaction mechanism [10,12]. Besides, there was an oxidation peak at 2.6 V corresponding to lithium sulfide–ring sulfur oxidation process during electrochemical reacting process. Fig. 4b showed the CV curves of GMEIm for 20 cycles and nearly similar curves were observed. This suggested the good reversibility of charge and discharge cycles.

The effects of ligand structure to electrochemical properties were observed in Fig. 4. The initial profiles were shown in Fig. 4a and GMEIm has a 1583 mAhg^{-1} of initial specific capacity and 770 mAhg^{-1} of capacity after 100 cycles. Fig. 4b showed the cycling performance for 100 cycles at 100 mAg^{-1} of current density between 1.5 and 3.0 V and GMEIm also showed the better cycling performance than other ligand GM composites.

In summary, we have studied that hybrid material of GO blended with MOF as a sulfur immobilizer was successfully synthesized by solvothermal reaction. To study effect of organic ligand of MOF, the composites were prepared by changing the chemical ligand species. The prepared composites were investigated through morphological and electrochemical characterizations. Based on these electrochemical experiments, the composite prepared by using 2-ethylimidazole ligand showed the better electrochemical performance than the other samples. Specifically, GMEIm prepared with 2-ethylimidazole had an irregular particle morphology, rather showed the higher specific capacity and cycling performance. Despite the irregular structures, the better electrochemical properties (1583 mAhg^{-1} of initial capacity and 770 mAhg^{-1} after 100 cycles) could be from due to functional groups of ligands. Besides, the structure of ligands could affect on morphological structure and capacity properties. Our approach not only optimize the structure of MOF sulfur-contained electrodes but also offers a various synthesis route of GM composite electrode material for Li-S batteries.

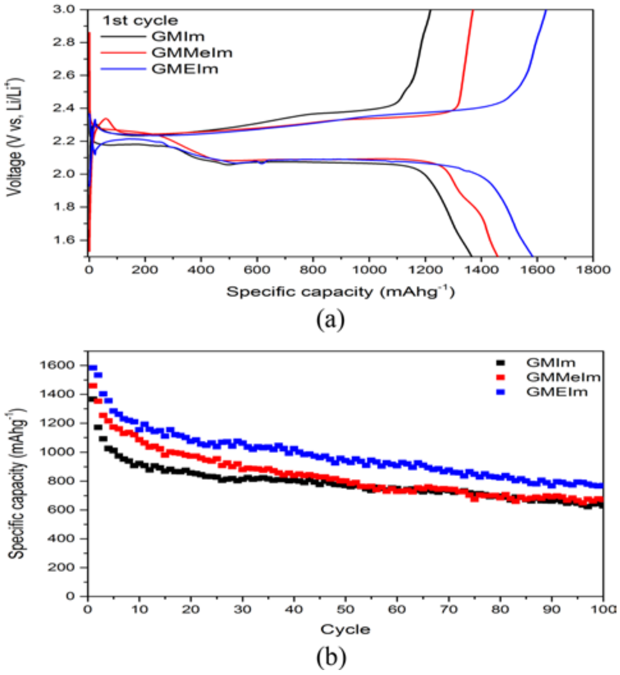

Fig. 4. (a) Charge-discharge profiles at first cycle of various composites at 100 mAg^{-1} of current density and (b) the specific capacity retention of the composites for 100 cycles at 100 mAg^{-1} of current density.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

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References

[1] Tarascon JM, Armand M. Issues and challenges facing rechargeable lithium batteries. Nature, **414**, 359 (2001). https://doi.org/10.1038/35104644.

[2] Croguennec L, Palacin MR. Recent achievements on inorganic electrode materials for lithium-ion batteries. J Am Chem Soc, **137**, 3140 (2015). https://doi.org/10.1021/ja507828x.

[3] Wen ZS, Yang J, Wang BF, Wang K, Liu Y. High capacity silicon/carbon composite anode materials for lithium ion batteries. Electrochem Commun, **5**, 165 (2003). https://doi.org/10.1016/S1388-2481(03)00009-2.

[4] Nitta N, Wu F, Lee JT, Yushin G. Li-ion battery materials: present and future. Mater Today, **18**, 252 (2015). https://doi.org/10.1016/j.mattod.2014.10.040.

[5] Salunkhe RR, Lee YH, Chang KH, Li JM, Simon P, Tang J, Torad NL, Hu CC, Yamauchi Y. Nanoarchitectured graphene-based supercapacitors for next-generation energy-storage applications. Chem Eur J, **20**, 13838 (2014). https://doi.org/10.1002/chem.201403649.

[6] Manthiram A, Fu Y, Su YS. Challenges and prospects of lithium–sulfur batteries. Acc Chem Res, **46**, 1125 (2013). https://doi.org/10.1021/ar300179v.

[7] Guo J, Xu Y, Wang C. Sulfur-impregnated disordered carbon nanotubes cathode for lithium–sulfur batteries. Nano Lett, **11**, 4288 (2011). https://doi.org/10.1021/nl202297p.

[8] Pang Q, Liang X, Kwok CY, Nazar LF. Review: the importance of chemical interactions between sulfur host materials and lithium polysulfides for advanced lithium-sulfur batteries. J Electrochem Soc, **162**, 4, A2567 (2015). https://doi.org/10.1149/2.0171514jes.

[9] Evers S, Nazar LF. New approaches for high energy density lithium–sulfur battery cathodes. Acc Chem Res, **46**, 5, 1135 (2013). https://doi.org/10.1021/ar3001348.

[10] Lee HY, Kim KY, Kim S. Electrochemical characterization of nano-structured graphene oxide/CNT electrodes containing sulfur for lithium rechargeable cells. J Nanosci Nanotechnol, **16**, 9186 (2016). https://doi.org/10.1166/jnn.2016.12888.

[11] Lee HY, Jung Y, Kim S. Conducting polymer coated graphene oxide electrode for rechargeable lithium-sulfur batteries. J Nanosci Nanotechnol, **16**, 2692 (2016). https://doi.org/10.1166/jnn.2016.11061.

[12] Kim KY, Jung Y, Kim S. Study on urea precursor effect on the electroactivities of nitrogen-doped graphene nanosheets electrodes for lithium cells. Carbon Lett, **19**, 40 (2016). https://doi.org/10.5714/CL.2016.19.040.

[13] Kim S, Sohn HJ, Hong SK, Park SJ. Preparation and electrochemical characterization of platinum and ruthenium catalysts deposited on fluorinated carbon supports. J Appl Electrochem, **39**, 1553 (2009). https://doi.org/10.1007/s10800-009-9837-y.

[14] Kim J, Kim S. Surface-modified reduced graphene oxide electrodes for capacitors by ionic liquids and their electrochemical properties. Appl Surf Sci, **295**, 31 (2014). https://doi.org/10.1016/j.apsusc.2013.12.156.

[15] Tang J, Salunkhe RR, Liu J, Torad NL, Imura M, Furukawa S, Yamauchi Y. Thermal conversion of core–shell metal–organic frameworks: a new method for selectively functionalized nanoporous hybrid carbon. J Am Chem Soc, **137**, 1572 (2015). https://doi.org/10.1021/ja511539a.

[16] Huang XC, Lin YY, Zhang JP, Chen XM. Ligand-directed strategy for zeolite-type metal–organic frameworks: zinc(II) imidazolates with unusual zeolitic topologies. Angew Chem, **118**, 1587 (2006). https://doi.org/10.1002/ange.200503778.

[17] Liu X, Wang C, Wu Q, Wang Z. Metal-organic framework-templated synthesis of magnetic nanoporous carbon as an efficient absorbent for enrichment of phenylurea herbicides. Anal Chim Acta, **870**, 67 (2015). https://doi.org/10.1016/j.aca.2015.02.036.