

Preparation and capacitance behaviors of cobalt oxide/graphene composites

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Abstract

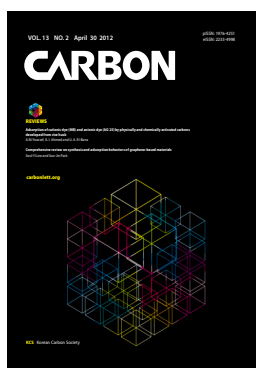
In this study, cobalt oxide (Co₃O₄)/graphene composites were synthesized through a simple chemical method at various calcination temperatures. We controlled the crystallinity, particle size and morphology of cobalt oxide on graphene materials by changing the annealing temperatures (200, 300, 400°C). The nanostructured Co₃O₄/graphene hybrid materials were studied to measure the electrochemical performance through cyclic voltammetry. The Co₃O₄/graphene sample obtained at 200°C showed the highest capacitance of 396 Fg⁻¹ at 5 mVs⁻¹. The morphological structures of composites were also examined by scanning electron microscopy and transmission electron microscopy (TEM). Annealing Co₃O₄/graphene samples in air at different temperatures significantly changed the morphology of the composites. The flower-like cobalt oxides with higher crystallinity and larger particle size were generated on graphene according to the increase of calcination temperature. A TEM analysis of the composites at 200°C revealed that nanoscale Co₃O₄ (~7 nm) particles were deposited on the surface of the graphene. The improved electrochemical performance was attributed to a combination effect of graphene and pseudocapacitive effect of Co₃O₄.

Key words: cobalt oxide graphene composites, calcination temperatures, electrochemical performance, pseudocapacitive effect

1. Introduction

Supercapacitors are energy storage devices that can supply extremely high but transient power output. They are being both utilized and considered for numerous power source applications, such as auxiliary power sources for hybrid electric vehicles and short term power sources for mobile electronic devices [1-3]. Recently, electrochemically active materials and metal oxides, such as Sn, Si, cobalt oxide (Co₃O₄), have attracted much attention as materials for supercapacitors. Among the metal oxides, Co₃O₄ has been reported as a priming electrode material for supercapacitors due to its excellent electrochemical performance [4-6]. However, a large specific volume change commonly occurs in the host matrix of these metals and metal oxides during the cycling process [7]. To solve this problem, graphitic carbons with high electric conductivity have been widely used as matrices for metals and metal oxides to improve their cycle performances [8-11]. Graphene, an integral part of graphite, has attracted tremendous attention since its discovery by Geim and co-workers in 2004 [12]. It is well known that metal oxides such as RuO₂, IrO₂, MnO₂, and NiOx can improve the electrochemical performance of carbon-based supercapacitors, as they can contribute pseudocapacitance to the total capacitance apart from the double-layer capacitance from the carbon materials [13].

In this work, we report a simple synthesis approach that involves the reduction of Cobalt (II) ions from salt solution and calcination in air to form Co₃O₄ nanoparticles on graphene materials. Through calcinations of different temperatures, we also searched for the optimal annealing temperature that can produce the most promising electrochemical performances.



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2. Experimental

Graphite oxide was synthesized from natural graphite (SP-1, Bay carbon) by a modified hummer's method. The graphite powder was added into a mixture of sulfuric acid, sodium nitrate, and potassium permanganate for the acid treatment. The oxidized and treated solution was filtered and washed with HCl (10%) and subjected to centrifugation (3600 rpm, 5 min) to remove residual graphite. To prepare Co_3O_4 /graphene composites, graphite oxide was added to an aqueous solution of cobalt nitrate hexahydrate (Dae Jung Chemical, Korea). The solution was sonicated and NaBH_4 solution was added dropwise to the above solution. The reaction mixture was heated at 90°C for 4 h. During this process, graphite oxide was reduced to graphene and cobalt (II) ions to cobalt nanoparticles simultaneously. The black powder precipitation was filtered, washed with distilled water and absolute alcohol several times, and dried in a vacuum oven. Finally, the samples were calcined in a muffle furnace at different temperatures for 2 h in air, and then cooled to room temperature. The resulting black powder was used for active materials and carbon black (Super-P, Alfa Aesar) and polyvinylidene fluoride (Aldrich) were mixed in a mass ratio of 85:15:5 in an *n*-methyl pyrrolidone solution. All electrochemical tests were done in a three-electrode system. Nickel foams coated with Co_3O_4 /graphene composites, a platinum foil and Ag/AgCl (3M KCl, 0.196 V vs SCE, Metrohm) served as counter and reference electrode. The measurements were carried out in 6M potassium hydroxide electrolytes. Electrochemical measurements were performed in an Iviumstat (Ivium Technologies, Netherlands).

3. Results and Discussion

The capacitance of the Co_3O_4 /graphene composites was compared to those of pristine graphene. The well-dispersed nanoscale Co_3O_4 particles on graphene not only effectively inhibited agglomeration of graphene, which resulted in a high double layer capacitance, but also increased the electrochemical active surface areas of the cobalt oxides. The capacitances of the composites that were calcinated at different temperatures are presented in Fig. 1. The capacitance of Co_3O_4 /graphene composites was enhanced by the deposition of cobalt oxides. In particular, a sample that was annealed at a low temperature, such as 200°C , had the highest capacitance. Fig. 1 shows the variation in the specific capacitance of the as-prepared samples as a function of scan rates. The specific capacitance decreased with the increase of scan rates from 5 to 100 mVs^{-1} . At a high scan rate (100 mVs^{-1}), diffusion of electrolyte ions was limited due to the time constraint and only the outer active surface was utilized for charge storage. The maximum specific capacitance of the composites (200°C) was 396 Fg^{-1} at 5 mVs^{-1} and 148 Fg^{-1} at 100 mVs^{-1} .

Fig. 2 shows the X-ray diffraction (XRD) patterns of Co_3O_4 /graphene obtained at different temperatures of 200, 300, and 400°C for 2 h in air. The crystallinity of the cobalt oxide appeared sharply according to the increase of calcination temperature. By analyzing the peak width of the XRD patterns using Scherrer's equation, particle sizes of the Co_3O_4 /gra-

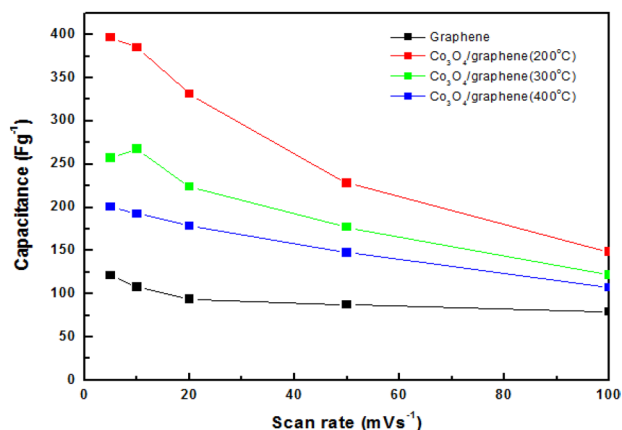


Fig. 1. Specific capacitance of graphene and cobalt oxide (Co_3O_4)/graphene samples at different scan rates from 5 to 100 mVs^{-1} .

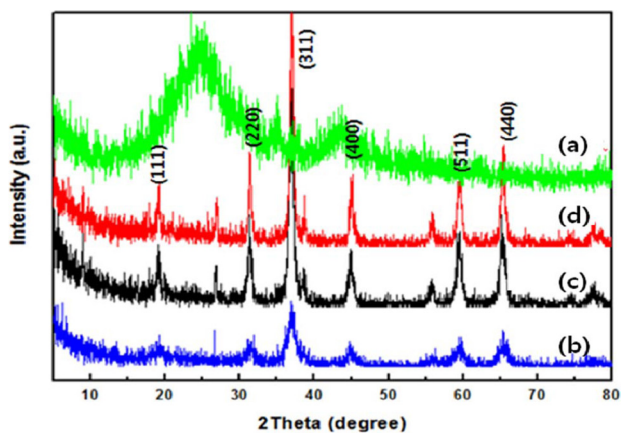


Fig. 2. X-ray diffraction patterns of (a) graphene and cobalt oxide (Co_3O_4)/graphene obtained at different annealing temperatures of (b) 200°C (c) 300°C , and (d) 400°C .

phene-200, Co_3O_4 /graphene-300, Co_3O_4 /graphene-400 were estimated to be 7.2, 10.3, 12.2 nm, respectively. The results indicated that the capacitances of the samples depended on the crystallinity and size of the particles. Generally graphene materials have a property that is stacked in a dry atmosphere [14]. Agglomeration of graphene sheets affects the initial capacitance because of a decrease in the active surface areas that include a double layer capacitance. Fig. 3 shows the transmission electron microscopy and scanning electron microscopy images of Co_3O_4 /graphene composites at different annealing temperatures. Annealing Co_3O_4 /graphene samples in air at different temperatures significantly changed the morphology of the composites (Figs. 3a-c). The surfaces of the composites were softened and were generated as a flower-like morphology depending on the increase of calcination temperatures. In addition, the Co_3O_4 particles with an average size of 7 nm were dispersed homogeneously on the surface of the graphene (200°C). A sample annealed at 200°C was found to be appropriate in terms of the capacitances. These structures had an enhanced specific surface area and electrolyte ion intercalation spots during an electrochemical reaction.

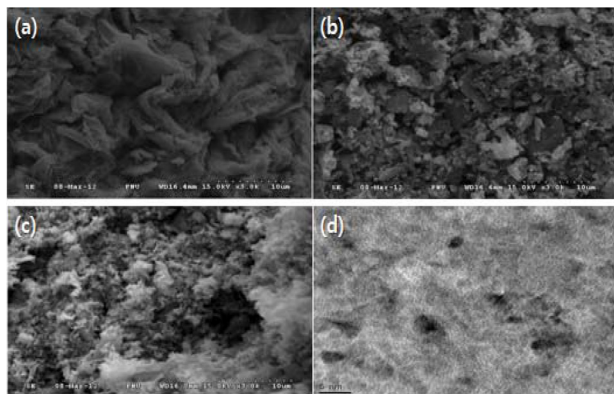


Fig. 3. Scanning electron microscopy images of cobalt oxide (Co_3O_4)/graphene obtained at different annealing temperatures in air (a) 200°C (b) 300°C (c) 400°C, and (d) transmission electron microscopy images of Co_3O_4 /graphene obtained at 200°C annealing.

4. Conclusions

In conclusion, Co_3O_4 /Graphene composites were prepared using a simple chemical approach using different calcination treatments. Co_3O_4 /graphene composites obtained by annealing at 200°C showed a high specific capacitance of 396 Fg^{-1} at 5 mVs^{-1} . The morphology and particle size of the cobalt oxide were tunable through the annealing process. The enhanced capacitance for the composite electrodes was related to the combination effect by the Co_3O_4 pseudo-capacitance and electrical double layer capacitance of the graphene. Co_3O_4 particles on the graphene provided electrochemical reaction sites and ion intercalation spots that were accessible to electrolytes ion.

Acknowledgments

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References

- [1] Sivakkumar SR, Nerkar Y, Pandolfo AG. Rate capability of graphite materials as negative electrodes in lithium-ion capacitors. *Electrochim Acta*, **55**, 3330 (2010). <http://dx.doi.org/10.1016/j.electacta.2010.01.059>.
- [2] Pandolfo AG, Wilson GJ, Huynh TD, Huynh TD, Hollenkamp AF. The influence of conductive additives and inter-particle voids in carbon EDLC electrodes. *Fuel cells*, **10**, 856 (2010). <http://dx.doi.org/10.1002/fuce.201000027>.
- [3] Yoo HM, Heo GY, Park SJ. Effect of crystallinity on the electrochemical properties of carbon black electrodes. *Carbon Lett*, **12**, 252 (2011). <http://dx.doi.org/10.5714/CL.2011.12.4.252>.
- [4] Liang YY, Schwab MG, Zhi LG, Mugnaioli E, Kolb U, Feng XL, Mullen K. Direct access to metal or metal oxide nanocrystals integrated with one-dimensional nanoporous carbons for electrochemical energy storage. *J Am Chem Soc*, **132**, 15030 (2010). <http://dx.doi.org/10.1021/ja106612d>.
- [5] Zhu T, Chen JS, Lou XW. Shape-controlled synthesis of porous Co_3O_4 nanostructures for application in supercapacitors. *J Mater Chem*, **20**, 7015 (2010). <http://dx.doi.org/10.1039/C0JM00867B>.
- [6] Chen SQ, Wang WJ. Microwave-assisted synthesis of a Co_3O_4 -graphene sheet-on-sheet nanocomposite as a superior anode material for li-ion batteries. *J Mater Chem*, **20**, 9735 (2010). <http://dx.doi.org/10.1039/C0JM01573C>.
- [7] Hu YS, Demir-Cakan R, Titirici MM, Muller JO, Schogl R, Antonietti M, Maier J. Ein $\text{Si}@\text{SiO}_x/\text{C}$ -nanokomposit als anodenmaterial für lithiumionenbatterien mit hoher speicherleistung. *Angew Chem*, **120**, 1669 (2008). <http://dx.doi.org/10.1002/ange.200704287>.
- [8] Wang GX, Ahn JH, Yao J, Bewlay S, Liu HK. Nanostructured Si-C composite anodes for lithium-ion batteries. *Electrochem Commun*, **6**, 689 (2004). <http://dx.doi.org/10.1016/j.elecom.2004.05.010>.
- [9] Yang SB, Song HH, Chen XH. Nanosized tin and tin oxides loaded expanded mesocarbon microbeads as negative electrode material for lithium-ion batteries. *J Power Sources*, **173**, 487 (2007). <http://dx.doi.org/10.1016/j.jpowsour.2007.08.009>.
- [10] Oh M, Kim S. Effect of dodecyl benzene sulfonic acid on the preparation of polyaniline/activated carbon composites by in situ emulsion polymerization. *Electrochim Acta*, **59**, 196 (2012). <http://dx.doi.org/10.1016/j.electacta.2011.10.058>.
- [11] Park DY, Lim YS, Kim MS. Performance of expanded graphite as anode materials for high power li-ion secondary batteries. *Carbon Lett*, **11**, 343 (2010).
- [12] Geim AK, Novoselov KS. The rise of graphene. *Nature Mater*, **6**, 183 (2007). <http://dx.doi.org/10.1038/nmat1849>.
- [13] Arico AS, Bruce P, Scrosati B, Tarascon JM. Nanostructured materials for advanced energy conversion and storage devices. *Nature Mater*, **4**, 366 (2005). <http://dx.doi.org/10.1038/nmat1368>.
- [14] Yang SW, Zhu ZW, Qiu L, Li D. Bioinspired effective prevention of restacking in multilayered graphene films: towards the next generation of high-performance supercapacitors. *Adv Mater*, **23**, 2833 (2011). <http://dx.doi.org/10.1002/adma.2011002>.