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¹ Synthesis of mesoporous reduced graphene oxide by Zn particles for ² electrodes of supercapacitor in ionic liquid electrolyte

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⁷ Introduction

8 Supercapacitors have attracted considerable attention recently
9 due to their high nouse density and long such life. They have ⁹ due to their high power density and long cycle life. They have $\frac{10}{10}$ higher energy densities than conventional canceliars and higher 10 higher energy densities than conventional capacitors and higher
11 nouvember densities than betteries and fuel sells which enables their ¹¹ power densities than batteries and fuel cells, which enables their $\frac{12}{2}$ prolication as the main or subsidiary power sources in electric 12 application as the main or subsidiary power sources in electric
 13 vehicles, however machines, and even portable devices $[1, 5]$ 13 vehicles, heavy machines, and even portable devices $[1-5]$. ¹⁴ Supercapacitors are categorized into electric double-layer capaci-
 $\frac{15}{2}$ and $\frac{15}{2}$ and negative procedure hand at their shares stepses 15 tors (EDLCs) and pseudocapacitors based on their charge storage 16 mochanism. An EDLC stores electric energy through a charge 16 mechanism. An EDLC stores electric energy through a charge
17 contration maintained by electrostatic forces in the interfacial 17 separation maintained by electrostatic forces in the interfacial
 18 double layer of an electrode material $[11]$. The electrodes of EDLCs 18 double layer of an electrode material [\[1\]](#page--1-0). The electrodes of EDLCs 19 are usually made of earbon based materials such as activated 19 are usually made of carbon-based materials such as activated 20 carbons carbon panotubes and graphenes which are generally 20 carbons, carbon nanotubes, and graphenes, which are generally 21 colocted, bocause of their high surface area and electrical 21 selected because of their high surface area and electrical 22 conductivity. Posudespacifiers at an anomy using reday restinger ²² conductivity. Pseudocapacitors store energy using redox reactions
²³ at the electrode surfaces of conducting motal oxides (such as PuO 23 at the electrode surfaces of conducting metal oxides (such as RuO₂, 1002 , 100304 , and V_2O_5) or conductive polymers [\[4](#page--1-0)–6]. The performance of a supercapacitor is determined largely by the ²⁵ performance of a supercapacitor is determined largely by the
²⁶ performance of a supercapacitor a performance provided a performance of the performance of the materials and 26 materials that constitute its electrode. Pseudocapacitors show
27 bigher capacitance than EDLCs but high material cost and low 27 higher capacitance than EDLCs, but high material cost and low
 28 electric conductivity limit their applications. The low energy electric conductivity limit their applications. The low energy

A B S T R A C T

Mesoporous reduced graphene oxide (m-rGO) was synthesized by mixing Zn and graphene oxide in acidic conditions followed by ultrasonication and was investigated as a supercapacitor electrode in a 1ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM-TFSI) electrolyte. m-rGO shows a specific capacitance of 104.3 F g^{-1} at 1 A g^{-1} and a decrease in capacitance of 3% after 5000 cycles. The high performance is attributed to the significant mesopores, facilitating mass transport of the electrolyte. Thus, we report the facile synthesis of m-rGO with enhanced capacitance and durability in an ionic liquid electrolyte that has great potential for electrochemical energy storage applications.

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> density of EDLCs can be overcome by increasing voltage limits,
which are determined by the stability of the electrolytes. Hence, 30 which are determined by the stability of the electrolytes. Hence, $\frac{30}{25}$ organic solvents or ionic liquids are widely used as electrolytes for ³¹
high-apergy density supercapacitors. Jonic liquids, bave wide high energy density supercapacitors. Ionic liquids have wide
electrochemical windows, high thermal and electrochemical 33 electrochemical windows, high thermal and electrochemical 33
etablity and moderate ionic conductivity [7, 10] and are therefore 34 stability, and moderate ionic conductivity $[7-10]$ $[7-10]$, and are therefore 34
regarded as ideal, electrolytes for supercapacitors. However 35 regarded as ideal electrolytes for supercapacitors. However, ³⁵
supercapacitors in ionia liquid electrolytes are hindered by the ³⁶ supercapacitors in ionic liquid electrolytes are hindered by the 36
slow diffusion of large jons into the narrow pores of the carbon slow diffusion of large ions into the narrow pores of the carbon-
based materials $[1112]$. For this reason, it is necessary to develop based materials [\[11,12\]](#page--1-0). For this reason, it is necessary to develop $\frac{38}{2}$
meconorous (2,50 nm) and macroporous (550 nm) materials to $\frac{39}{2}$ mesoporous $(2-50 \text{ nm})$ and macroporous $(>50 \text{ nm})$ materials to $\frac{39}{40}$ ⁴⁰ realize high performance supercapacitors. $\frac{40}{2}$

Graphene-based EDLC electrode materials have been widely $\frac{41}{4}$ studied because of their high surface area and conductivity. These $\frac{42}{13}$ are the most important properties for achieving high capacity and $\frac{43}{12}$
high power in supercapacitors, Chamical ovfoliation is the most high power in supercapacitors. Chemical exfoliation is the most $\frac{44}{12}$ widely used technique to prepare graphene because of its low cost $\frac{45}{121}$. The final product of chamical origination is graphene oxide $\frac{46}{121}$ [\[13\].](#page--1-0) The final product of chemical exfoliation is graphene oxide 46
(CO), which needs to be reduced before it can be used as a 47 (GO), which needs to be reduced before it can be used as a 47 supercapacitor electrode. Reduction methods that have been 48 supercapacitor electrode. Reduction methods that have been 48
studied include thermal reduction [14.15] microwave and photo 49 studied include thermal reduction $[14,15]$, microwave and photo 49
reduction $[16, 19]$, chemical regnery reduction $[20, 22]$, photo 50 reduction [16–[19\],](#page--1-0) chemical reagent reduction [20–[22\],](#page--1-0) photo-
catalyst reduction [22–25] electrochemical reduction [26–29], and [51] catalyst reduction $[23-25]$, electrochemical reduction $[26-29]$, and 51
solvothermal reduction $[30, 32]$. Chemical reduction using reduc solvothermal reduction [\[30](#page--1-0)–32]. Chemical reduction using reduc-
ing agents such as hydrazine (N-H λ [20,22], sodium borobydride 53 ing agents such as hydrazine (N_2H_4) [\[20,22\]](#page--1-0), sodium borohydride 5^3
(N2BH₂) [23, 25], and bydroiodic acid (HJ) [26, 27] can be 5^4 (NaBH₄) [\[33](#page--1-0)–35], and hydroiodic acid (HI) [\[36,37\]](#page--1-0) can be 54
accomplished in several hours at relatively low temperatures 55 Corresponding author. Fax: +82 42 860 7237.
5-E-mail address: thkim@krict.re.kr (T.-H. Kim). Complished in several hours at relatively low temperatures

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56 (>100 °C). However, these reducing agents are toxic and dangerous.
57 (a) fixed parallel agents are presented to the symphonic of reduced produced 57 A facile and green approach to the synthesis of reduced graphene 58 oxide (rGO) was recently developed, which involved mixing GO 59 suith particles function that the boundary derivative contributions. ⁵⁹ with particles of metals that have lower electrochemical potentials
 $\frac{60}{25}$ than CO (such as $\frac{7}{25}$ Fe Al, Cu, and Ni) [28, 50]. The reduction rate ⁶⁰ than GO (such as Zn, Fe, Al, Cu, and Ni) [\[38](#page--1-0)–50]. The reduction rate 61 of Zn in particular is significantly promoted in acidic, alkaling or 61 of Zn, in particular, is significantly promoted in acidic, alkaline, or 62 ammonia colutions or by ultrasonic treatment [20.40.44]. In spite $\frac{62}{63}$ ammonia solutions, or by ultrasonic treatment [\[39,40,44\]](#page--1-0). In spite of these advantages fou studies have evolved the application of 63 of these advantages, few studies have explored the application of 64 this reduction method in approximately exctance. Linearly ⁶⁴ this reduction method in energy-related systems. Liu et al.
⁶⁵ evaluated rCO reduced by 7n particles for supercapacitor electro-⁶⁵ evaluated rGO reduced by Zn particles for supercapacitor electro-
⁶⁶ desin aqueous electrolyte in which rCO exhibited 116 Eq⁻¹ in KOH ⁶⁶ des in aqueous electrolyte, in which rGO exhibited 116 F g⁻¹ in KOH ⁶⁷ electrolyte [\[40\]](#page--1-0). However, the surface morphology and porosity, 68 which are important factors in the porformance of supercapacitors ⁶⁸ which are important factors in the performance of supercapacitors,
 69 of rCO reduced by Zp particles were not applyzed in detail ⁶⁹ of rGO reduced by Zn particles were not analyzed in detail.

⁷⁰ In this study we prepared mesoporous rCO (m rCO) by the

⁷⁰ In this study, we prepared mesoporous rGO (m -rGO) by the Zn
⁷¹ particle reduction method which produced significant corruption 71 particle reduction method which produced significant corrugation
 72 of the rCO sheet, m rCO was tested as an electrode in a 72 of the rGO sheet. m-rGO was tested as an electrode in a
 73 superconnector in a 1 othul 2 methylimidatelium higherations 73 supercapacitor in a 1-ethyl-3-methylimidazolium bis(trifluoro- 74 methyloulorum at $(EMIMTES)$ ionis liquid electrolyte to take ⁷⁴ methylsulfonyl)imide (EMIM-TFSI) ionic liquid electrolyte to take
 75 advantage of its mesonoresity Comparative studies of m rCO and ⁷⁵ advantage of its mesoporosity. Comparative studies of *m*-rGO and $\frac{76}{10}$ and $\frac{1}{20}$ at graphene (f graphene) were explied out and the physics flat graphene (f-graphene) were carried out and the physicochemical properties of m-rGO were studied in relation to the $\frac{77}{78}$ supercapacitor performance.

Experimental

Preparation of m-rGO 80

Graphene oxide solution was purchased at Angstron Materials 81
002-ps 0.5 wt% of CO in water). The CO solution was diluted to 82 (N002-ps, 0.5 wt% of GO in water). The GO solution was diluted to 82
0.1 wt% and acidified with bydrochloric acid (HCl) to a final HCl 83 0.1 wt% and acidified with hydrochloric acid (HCl) to a final HCl 83
concentration of 10 mM. Commercial 7n novel of (Kanto) was then 84 concentration of 10 mM. Commercial Zn powder (Kanto) was then 84
added to the CO solution in unwing amounta Masks to total Al Ti added to the GO solution in varying amounts. We also tested Al, Ti, 85
and Fe motal particles for comparison test with the same method and Fe metal particles for comparison test with the same method $\frac{86}{2}$
to $\frac{7}{2}$ particles but no significant change was observed in short $\frac{87}{2}$ to Zn particles, but no significant change was observed in short $\frac{87}{100}$
time The Zn/CO solution was bomogenized in an ultrasonic bath $\frac{88}{100}$ time. The Zn/GO solution was homogenized in an ultrasonic bath 88
for 1 min at room temperature. During ultrasonic treatment, the 89 89
color of the colution changed from dark brown to black Bosidual and 90 color of the solution changed from dark brown to black. Residual 90
7n particles were removed with avesse asid in 1 M UCL solution 91 Zn particles were removed with excess acid in 1 M HCl solution $\frac{91}{2}$ with gentle stirring for 1 day. Finally, the solution was filtered and $\frac{92}{100}$ washed with DI water until the pH of the rinse was neutral. The 93 filtered m-rGO sample was dried at 60° C overnight.

Fig. 1. (a) Digital photograph of GO/Zn dispersion before and after ultrasonic treatment, (b) carbon to oxygen atomic ratio of graphene reacted with Al, Ti, Fe, and Zn metal particles. Reaction time is 1 min in ultrasonic bath and elemental analysis is conducted by XPS survey spectrum. SEM images of (c) commercial Zn particles and (d) Zn/rGO after reduction, (e) high resolution SEM image of m-rGO after Zn etching, and (f) TEM image of m-rGO. White scale bars in the each figure indicate 10 μ m (c), 10 μ m (d), 200 nm (e), and 50 nm (f).

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