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Preparation of activated graphene and effect of activation parameters on electrochemical capacitance

Shanthi Murali, Jeffrey R. Potts, Scott Stoller, Joono Park, Meryl D. Stoller, Li Li Zhang, Yanwu Zhu, Rodney S. Ruoff *

Department of Mechanical Engineering and the Materials Science and Engineering Program, The University of Texas at Austin, One University Station C2200, Austin, TX 78712, United States

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ABSTRACT

Activation parameters such as temperature and the amount of potassium hydroxide (KOH) were varied during the synthesis of activated microwave-exfoliated graphite oxide (a-MEGO) and the effects of these parameters on the specific surface area of a-MEGO and electrochemical capacitance of a-MEGO electrodes were investigated. At 800 °C and a KOH/MEGO mass ratio of 6.5, a maximum specific surface area of 3100 m^2/g was obtained and a high specific capacitance of 172 F/g (at 1 A/g constant current and 3.5 V maximal voltage) was measured in a two-electrode cell with a-MEGO electrodes in an organic electrolyte.

Chemical activation using alkali compounds such as KOH and NaOH is a widely used method for obtaining activated carbon materials with high specific surface areas and well developed porosity [1]. Compared to physical activation methods such as using CO_2 or steam, chemical activation aids in achieving higher yields and larger surface areas, and requires lower operating temperatures and less activation time [2]. Precursors used to obtain activated carbon materials have included coals, lignocellulosic materials, polymers, carbon nanotubes and nanofibers [3]. The resulting activated carbon materials are extensively used as adsorbents, as substrates for catalysts, electrodes in energy storage devices, etc.

Supercapacitors or electrochemical double layer capacitors (EDLCs) are energy storage devices with high power density. They operate through the separation of charges at the electrochemical interface formed between an electrode and a supporting electrolyte [4]. Various types of carbon have been explored as candidates for electrode materials, including activated and carbon-derived carbons, nanotubes, carbon fabrics, carbon onions, and reduced graphene oxide [5,6]. Recently, our group synthesized a new carbon material that was prepared by the activation of microwave-exfoliated graphite oxide (MEGO) and reported on its application as an electrode material in a supercapacitor [7]. Activated MEGO (a-MEGO) was characterized and found to possess a high electrical conductivity, a low O and H content, and is composed mostly of sp^2 bonded carbon. It exhibited a high specific surface area (SSA), as measured by the Brunauer–Emmett–Teller (BET) method [8], along with a continuous, three dimensional pore structure consisting of atom-thick walls and both micro- and mesopores. The activation was carried out by treatment of MEGO with KOH. Activation temperature and KOH/MEGO ratio are the important parameters in the synthesis process of a-MEGO. The effects of these parameters on the BET SSA of the a-MEGO was obtained and the specific capacitance of a-MEGO electrodes in 1-butyl-3-methyl-imidazolium tetrafluoroborate in acetonitrile (BMIM BF_4/AN) electrolyte. Characterizing each a-MEGO carbon in terms of SSA and gravimetric capacitance is very time consuming, and as a result a partial parametric study was done as a function of temperature at one specific KOH/MEGO mass loading (6.5), and then a more extensive study of mass loading at one specific temperature, namely 800 °C. This optimization data is also useful for tuning the specific surface area of a-MEGO for different fields of application.

* *Corresponding author:* Fax: +1 512 560 8766.
E-mail address: r.ruoff@mail.utexas.edu (R.S. Ruoff).
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The synthesis procedure of a-MEGO was as previously described [7]. Briefly, MEGO was prepared from graphite oxide (GO) by microwave exfoliation [9], then dispersed and soaked in aqueous KOH solution for 20 h. The solid cake obtained after vacuum filtration of the excess KOH was then dried. (Mixing of MEGO and KOH was done in aqueous phase rather than by physical mixing in order to get a uniform distribution of potassium ions into the carbon.) A control MEGO sample, made with the same soaking–drying process but with no KOH was also prepared, which retained 85% of its initial mass after drying. A KOH to MEGO ratio was thus calculated by assuming the MEGO in the dry KOH–MEGO mixture gave the same mass yield, i.e., 85%.

In order to study the temperature effect on activation, the activation temperature was varied from 600 to 1000 °C in increments of 100 °C for the samples with a KOH/MEGO ratio of 6.5, prepared from 7 M aqueous KOH. The effect of KOH loading was studied by increasing the molarity of KOH aqueous solutions in which the MEGO was soaked, thus increasing the KOH/MEGO ratio of the mixture. The activation temperature was maintained at 800 °C as in our previous work [7]. A horizontal tube furnace (50-mm diameter), with an argon flow of 150 sccm and working pressure of ~350 Torr was used to activate the samples in an alumina combustion boat (Coorstek Inc.). Parameters other than activation temperature and KOH loading, such as the GO precursor, the activation time of 1 h and washing procedure after the activation step were maintained as constant as possible.

SSAs were calculated in the linear relative pressure range from 0.1 to 0.3 using the BET equation from acquired N_2 adsorption isotherms. Fig. 1 shows the dependence of BET SSA of a-MEGO on activation temperature for the samples with a fixed KOH/MEGO ratio of 6.5. It has been demonstrated that, independent of the precursor, activation of 'carbon' using KOH occurs at temperatures of about 700 °C or higher [1]. Therefore, for this study, we reasoned that varying the activation temperature from 600 to 1000 °C would allow for understanding the effect of temperature on the BET SSA. At 600 °C, the BET SSA of the activated product was only

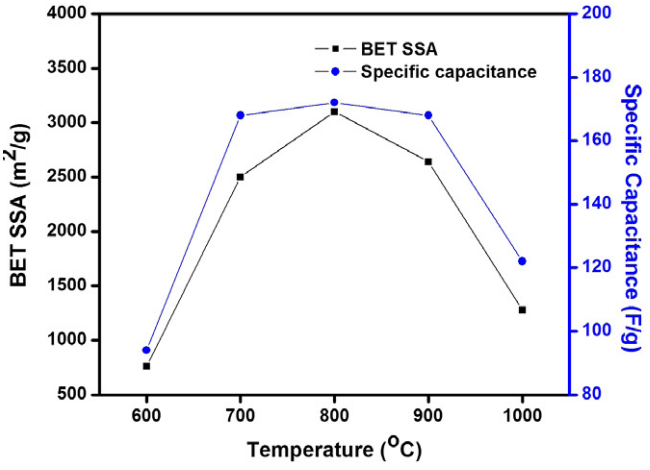

Fig. 1 – Effect of activation temperature on BET SSA and specific capacitance of a-MEGO, at a constant KOH/MEGO ratio of 6.5.

760 m^2/g. Increasing the temperature to 700 °C increased the BET SSA to 2400 m^2/g, thus more than three times the SSA at 600 °C, consistent with previous work suggesting that activation occurs at 700 °C or higher. When the temperature was increased to 800 °C, the BET SSA reached a maximum of 3100 m^2/g, which makes a-MEGO one of the highest surface area carbons studied to date. a-MEGO activated at ambient pressure at a temperature of 800 °C and KOH/MEGO ratio of 6.5 also showed a similar SSA (see Supporting information). Further increase in temperature to 900 °C yielded a SSA of 2640 m^2/g, and at 1000 °C the SSA was 1280 m^2/g. This may be due to the collapse of the porous structure during the high temperature activation process. For example, the nitrogen-sorption isotherm shown in Fig. S1 clearly demonstrated a sharp decrease of the nitrogen uptake by both micropores and mesopores for the sample activated at 1000 °C in comparison to the sample activated at 800 °C.

Electrochemical capacitance was measured by fabricating and testing a-MEGO electrodes in a two-electrode test assembly, using best practice methods [10]. Fig. 1 also shows mass normalized specific capacitances using a-MEGO electrodes in BMIM BF_4/AN electrolyte, estimated from the galvanostatic charge/discharge curve at a current density of 1 A/g. The specific capacitances follow the same trend as the BET SSA with respect to increasing activation temperature. The specific capacitance of a-MEGO electrodes obtained from activation at 700 °C was 168 F/g, 78% more than that obtained from activation at 600 °C (94 F/g). A maximum capacitance of 172 F/g was achieved for the 800 °C sample, and this is the highest capacitance achieved with a-MEGO in BMIM BF_4/AN. For activation temperatures above 800 °C, the capacitance decreased with further increases in activation temperature. Specific capacitance estimated from higher current densities (2.5 and 5 A/g) and from cyclic voltammetry (CV) at 100 and 40 mV/s follows the same trend with activation temperature. This data reinforces the correlation between high BET surface area and gravimetric capacitance for a-MEGO. Other factors such as carbon porosity, electrical conductivity, viscosity and ionic conductivity of the electrolyte are also important in determining the performance of an EDLC [4].

Chemical activation using KOH takes place by the reaction with the carbon as

$$6KOH + 2C \rightarrow 2K + 3H_2 + 2K_2CO_3 \quad (1)$$

The K_2CO_3 decomposes at 800 °C in the presence of carbon resulting in the evolution of CO_2 and CO [11]. As shown in Fig. 2, addition of KOH at a KOH/MEGO ratio of 3 doubles the BET SSA compared to the pristine MEGO control sample. The BET SSA increases with further increase in KOH loading and reached a maximum of 3100 m^2/g at a KOH/MEGO ratio of 6.5; increasing the KOH/MEGO ratio to 9 decreased the BET SSA slightly by 5%, to 2950 m^2/g. Further increases in the amount of KOH yielded a non-conductive gray/white powder (Fig. S2). A combustion elemental analysis (measured by Atlantic Microlab Inc., Norcross, GA) on this powder gave a low C/O atomic ratio of 0.3, while the C/O atomic ratios of all the other samples were in the range of 35–45. This indicated a near-complete etching of MEGO at high KOH loadings. X-ray diffraction studies (XRD, Philips X'Pert PRO, $\lambda = 1.54$ Å) indicated that this powder consisted largely of aluminum

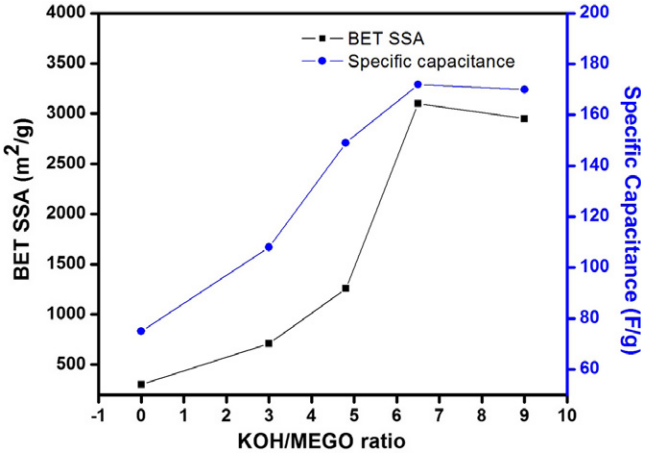

Fig. 2 – Effect of activation KOH/MEGO ratio on BET SSA and specific capacitance of a-MEGO, at a temperature of 800 °C.

hydroxide (Fig. S3). This is likely due to the KOH etching of the alumina combustion boat used as the container for the activation.

The mass-normalized capacitances of the a-MEGO with increasing KOH/MEGO ratios are shown in Fig. 2. At 1 A/g, the specific capacitance for the non-activated control sample was 75 F/g. Activation with KOH/MEGO ratios of 3 and 4.8 increased the specific capacitance to 108 and 149 F/g, respectively. At a ratio of 6.5, a maximum specific capacitance of 172 F/g was achieved. This is the same sample that was obtained in the temperature study at 800 °C. The specific capacitance seemed to plateau at a KOH/MEGO ratio of 9, decreasing only by 1% to 170 F/g. Beyond this loading, the samples were no longer conductive, as mentioned above.

Thus, for activation of MEGO with KOH, the optimized parameters for maximum SSA and maximum specific capacitance, from this partial parametric study, are an activation temperature of about 800 °C and a KOH loading of about 6.5. Fig. 3 shows representative electrochemical curves of a-MEGO at these conditions. The specific capacitances measured from the rectangular CV curves (Fig. 3a) are 150 and 154 F/g at scan rates of 40 and 100 mV/s, and the difference in capacitance of only 2% indicated good charge propagation at the high scan rate of 100 mV/s. The galvanostatic discharge at a current density of 1 A/g resulted in a specific capacitance of 172 F/g. The Nyquist plot (Fig. 3c) from frequency response analysis (FRA) of the frequency range from 1 to 10 MHz showed a fairly vertical curve indicating nearly ideal capacitor response. The magnified data in the high frequency range (Fig. 3c inset) exhibited a transition between the RC semicircle and the migration of electrolyte was observed at a frequency of about 477 Hz, corresponding to a resistance of 3.64 Ω. The electrochemical performances of all the samples are tabulated in Supporting information.

In summary, a parametric study on the activation of MEGO with KOH has been reported. The temperature and amount of KOH during activation were varied, and trends in BET SSA and electrochemical capacitance for the resulting a-MEGO were found. For a given KOH/MEGO loading level, on increasing the activation temperature from 600 °C, both the BET SSA

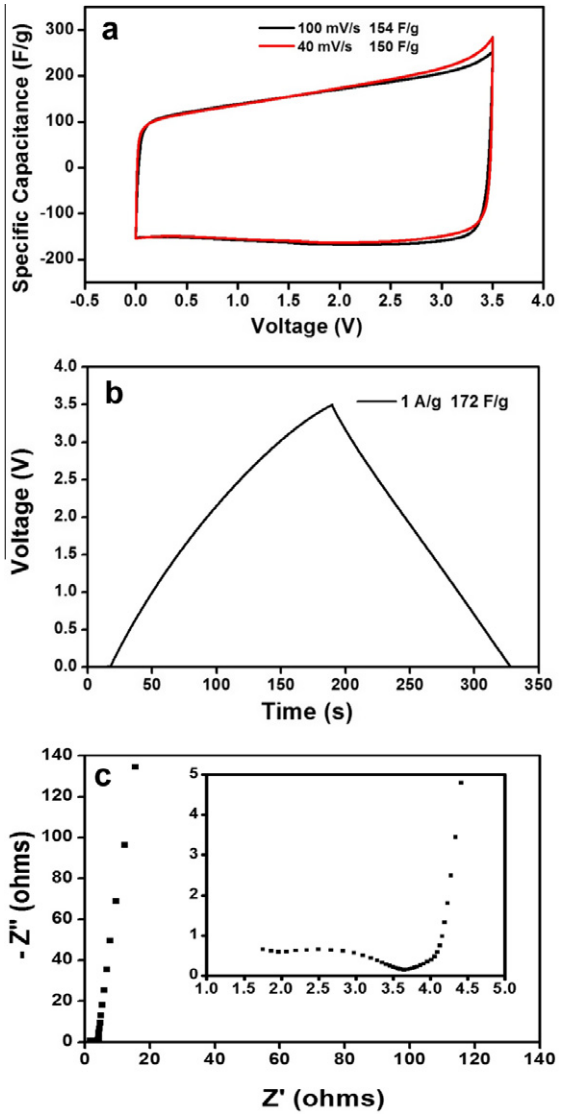

Fig. 3 – Supercapacitor performance of the a-MEGO in BMIM BF_4/AN electrolyte. (a) CV curves. (b) Galvanostatic charge/discharge curves at different constant currents. Specific capacitance values are calculated from the discharge curve for each current. (c) Frequency response analysis with magnified high frequency range in the inset.

and the gravimetric capacitance increased, reached a maximum at 800 °C and then at higher activation temperatures both decreased. The lower BET SSA and the gravimetric capacitance values at activation temperatures of 900 and 1000 °C were attributed to excess carbonization and collapse of the porous network of the a-MEGO at these temperatures. The BET SSA and specific capacitance peaked at a KOH/MEGO loading ratio of 6.5 and loading beyond a ratio of 9 rendered the product nonconductive with very small carbon content.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2012.03.014.

REFERENCES

[1] Molina-Sabio M, Rodríguez-Reinoso F. Role of chemical activation in the development of carbon porosity. Colloids Surf A 2004;241(1–3):15–25.

[2] Lillo-Ródenas MA, Cazorla-Amorós D, Linares-Solano A. Understanding chemical reactions between carbons and NaOH and KOH: an insight into the chemical activation mechanism. Carbon 2003;41(2):267–75.

[3] Marsh H, Rodríguez-Reinoso F. Activated carbon. Oxford: Elsevier; 2006.

[4] Miller JR, Simon P. Materials science – electrochemical capacitors for energy management. Science 2008;321(5889):651–2.

[5] Simon P, Gogotsi Y. Materials for electrochemical capacitors. Nat Mater 2008;7(11):845–54.

[6] Stoller MD, Park SJ, Zhu YW, An JH, Ruoff RS. Graphene-based ultracapacitors. Nano Lett 2008;8(10):3498–502.

[7] Zhu Y, Murali S, Stoller MD, Ganesh KJ, Cai W, Ferreira PJ, et al. Carbon-based supercapacitors produced by activation of graphene. Science 2011;332(6037):1537–41.

[8] Brunauer S, Emmett PH, Teller E. Adsorption of gases in multimolecular layers. J Am Chem Soc 1938;60(2):309–19.

[9] Zhu Y, Murali S, Stoller MD, Velamakanni A, Piner RD, Ruoff RS. Microwave assisted exfoliation and reduction of graphite oxide for ultracapacitors. Carbon 2010;48(7):2118–22.

[10] Stoller MD, Ruoff RS. Best practice methods for determining an electrode material's performance for ultracapacitors. Energy Environ Sci 2010;3(9):1294–301.

[11] Raymundo-Pinero E, Azais P, Cacciaguerra T, Cazorla-Amoros D, Linares-Solano A, Beguin F. KOH and NaOH activation mechanisms of multiwalled carbon nanotubes with different structural organisation. Carbon 2005;43(4):786–95.