Enhanced performance of carbon/carbon supercapacitors upon graphene addition

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Abstract Graphene has great potential for application in capacitive energy storage devices. In this study, we have investigated the effects of employing reduced graphene oxide (rGO) either as an additional supplement or as a total replacement of carbon black, the current conductive additive used in commercial carbon/carbon supercapacitors. We also examined the impact of incorporating rGO before and during the slurry preparation. Some electrochemical and morphological studies were conducted to compare the rGO and carbon black in performance enhancement for conventional activated carbon-based electrodes. Our results have demonstrated the benefits of incorporating graphene into the current carbon/carbon supercapacitors.

Keywords Activated carbon · Enhanced performance · Reduced graphene oxide · Supercapacitor

Introduction

Supercapacitors (SC) are rechargeable capacitive electrical energy storage (EES) devices bridging the gap between dielectric capacitors and batteries. Owing to their ability to store and expend considerable amounts of electricity in relatively short period of time, SCs can be found in a wide array of applications, such as in cranes, wind turbines, airplanes, buses and trams. In addition to their outstanding

power performance, they also demonstrate very long cycle life (>1,000,000 cycles), fit-and-forget benefits and less heat generation compared to other EES devices. These outstanding properties are mainly originated from the basic operating principle of SCs by utilizing high surface area carbons (normally activated carbon in particulate form) to electrostatically accumulate and release electrolyte ions during the charging and discharging processes. Although certain metal compounds and conducting polymers have been explored to faradaically store electricity at electrode surface, activated carbon (AC)-based SCs still dominate the market due to their comparably lower cost, higher power density and longer cycle life. Such merits are mainly stemming from its electrostatic charge storage mechanism, which occurs much faster and more reversible than the faradaic processes for either metal compounds or conducting polymer-based SCs.

To further improve the performance of AC-based SCs, certain amounts of conductive additives have to be added to the AC electrodes so as to enhance their electrical conductivity to fully realize their power performance and maximize their charge storage capacity [4, 20]. The most commonly used conductive additive is carbon black (CB) for its excellent electrical conductivity. However, carbon black is known for such deficiencies as relatively low packing density, poor electrochemical performance ($<5 \text{ F g}^{-1}$) [16] and its potential carcinogenic effects.

Possible substitutes for carbon black include carbon onion, metallic carbon nanotube, and graphene. The electrochemical performance of carbon onion has been extensively studied by Gogotsi et al. [16], Pech [11, 13] who reported a specific capacitance ca. 40 F g^{-1} and some electrochemical performance improvement when carbon onion was added to AC electrode. Carbon nanotube has been widely examined as active material for supercapacitor

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electrodes, and its specific capacitance varies from 20 to 130 F g⁻¹ [1, 6, 7]. Carbon nanotubes have shown an outstanding electrical conductivity that enables the electrodes to achieve higher power density. However, caution was advised about carbon nanotube by Simon et al. [14, 15, 20] after some systematic studies of its influence on the electrochemical performance of carbon/carbon SCs. They concluded that addition of carbon nanotube leads to both a lower specific capacitance and smaller energy density. Therefore, both carbon onion and carbon nanotube have been proved to be not practical to replace carbon black.

Graphene, with a specific capacitance varying from 80 to 170 F g⁻¹ [18, 23, 29], has been regarded as a prime carbon form to possibly replace AC in SCs. However, pure graphene-based electrodes so far exhibit low packing density which severely restrains the resulting volumetric energy density, and its cost is expected to be much higher than AC. Consequently, researchers have started to hybrid graphene with AC to produce densely packed supercapacitor electrodes to improve electrochemical performance. There have been two general approaches proposed so far to incorporate graphene in AC electrodes. The first one includes mixing graphene oxide with various biomasses as the carbon source and then producing the AC/graphene composites via hydrothermal or normal activation process [3, 26, 27]. The second method involves synthesizing AC/graphene organogels through thermal reduction of graphene oxide at moderate temperature in an autoclave [22, 27]. Although there have been some encouraging reports on the improved electrochemical performance of these AC/graphene composites, they are not ready for adoption by the supercapacitor industry because of the high cost due to the inefficient processes. To align better with the current supercapacitor electrode fabrication process, a cost-effective and easy approach has to be developed to incorporate graphene into the carbon/carbon SCs.

Herein, we proposed two simple methods for the first time to incorporate graphene into the current AC electrode fabrication process: (1) adding reduced graphene oxide (rGO) directly into the AC slurry for electrode preparation or (2) producing the rGO/AC blend from graphene oxide/AC solution and then prepare the slurry. A systematic study is then conducted to find the optimal graphene content of rGO for both approaches, in comparison with the conventional electrodes with and without adding carbon blacks. From the testing results, we can demonstrate the feasibility of our approaches and show that the addition of graphene in carbon/carbon SCs is significantly beneficial.

The resultant graphene-added supercapacitor will enable a wider adoption of supercapacitors in various environmental applications. For example, when the supercapacitor is incorporated into the regenerative braking systems, it

will help to harvest the power during braking of automobiles, hybrid buses, trams, trains, etc. and later release the stored power to assist the acceleration process, thus reducing the energy consumption and greenhouse gas emission. If used in the blade pitch system of wind turbines, the reliability and stability of the produced electricity to the grid will be greatly improved. It is also suited to the intermittent power firming to alleviate the power fluctuation of the generated electricity from solar or wind farms, which will in turn promote the adoption of solar and wind energies to benefit the environment (Ciccarelli et al. [2, 9]).

Experimental

Materials and methods

In this study, we first prepared graphene oxide (GO) from natural graphite flake (99.8%, Alfa Aesar, UK) via Hummer's method [8]. Hydrazine hydrate (50–60%, Sigma-Aldrich, USA) was then used to reduce the exfoliated GO sheets into reduced graphene oxide (rGO) based on a procedure developed by Ruoff et al. [17]. Commercial activated carbon (AC) (AB-520, MTI Corporation, USA), carbon black (CB) (Super P Conductive, Alfa Aesar, UK), PTFE as adhesive both in water (60%, Sigma-Aldrich, USA) and in ethylene alcohol (99.8%, Sigma-Aldrich, USA) were obtained from their respective suppliers and used as received. The AB-520 AC has a BET surface area of ca. 2000 m² g⁻¹, a micropore size of 2.0–2.2 nm, and a pore volume ca. 0.9 cm³ g⁻¹. A highly porous nickel foam with porosity ca. 95% (MTI Corporation, USA) was used as the current collector, 6 M KOH (85%, Sigma-Aldrich, USA) as the electrolyte and cellulose filter paper (Whatman, Grade 1) as the separator for the SCs.

Based on the use of carbon black (CB), two groups of SCs, with and without CB in the electrode, were constructed. Then within each group, three further different SCs were prepared according to the use of graphene oxide (rGO), so that a total of six kind samples were prepared: (1) the original control samples coded as AC + CB + PTFE, and (2) without CB (AC + PTFE); (3) samples with rGO reduced alone and with CB (AC + rGO + CB + PTFE), and (4) without CB (AC + rGO + PTFE); (5) rGO produced in the present of AC with CB (AC/rGO + CB + PTFE), and (6) without CB (AC/rGO + PTFE). In all samples, the slurry was prepared in ethanol alcohol with 8 and 7 wt% for conductive additive and PTFE binder, respectively. The weight percent of rGO in the electrodes was varied from 0 to 20% to examine its influence on electrochemical performance. Two-electrode symmetric SCs in 6 M KOH were constructed with

industrial-level mass loadings of $10\text{--}15\text{ mg cm}^{-2}$. The finished SCs are in the form of CR 2032 button cells.

Performance characterization

The electrochemical properties of the as-constructed button cells were examined using the following tests: cyclic voltammetric (CV) (Princeton Applied Research, Model 263A), electrochemical impedance spectroscopic (EIS) (EG&G 263A), and constant current charge–discharge (CCCD) (MTI Corporation, Eight Channel Battery Analyzer) [25]. The specific capacitance, power and energy densities were calculated for a single electrode using the collective mass including that of the conductive additive and polymer adhesive PTFE based on the evaluation scheme proposed by Zhang and Pan in Ref. [24]. More specifically, the specific capacitance was calculated from total capacitance C_T normalized by the mass of both electrodes. The total capacitances C_T was derived from the CV, CCCD and EIS data based on Eqs. (1), (2) and (3), respectively, where V_0 is the rated operating potential, $V_{\text{IR-drop}}$ is the potential difference at IR drop, v is the scan rate, i is the instantaneous current, t is the time, $\text{Re}(C)$ and $\text{Im}(Z)$ are the real capacitance and imaginary impedance, respectively. In addition, the computation methods for energy and power densities are also provided in Eqs. (4) and (5), respectively, where E_D is the energy density, P_D is the power density, R_{ES} is the equivalent series resistance and Π is the total mass of both electrodes.

$$C_T = \frac{\Delta Q}{\Delta V} = \frac{\int_0^{2V_0/v} |i| dt}{2V_0} \quad (1)$$

$$C_T = \frac{I_{\text{dis}} \times \Delta t_{V_0} - 2V_0}{V_0 - V_{\text{IR-drop}}} \quad (2)$$

$$\text{Re}(C) = \frac{\text{Im}(Z)}{\omega |Z|^2} \quad (3)$$

$$E_D = \frac{1/2 C_T V_0^2}{3600 \times \Pi} \quad (4)$$

$$P_D = \frac{V_0^2}{4R_{\text{ES}} \Pi} \quad (5)$$

Moreover, scanning electron microscope (SEM, SEI XL30) was used to examine the microstructure of the as-prepared electrodes.

Results and discussion

The electrochemical performance of conventional carbon electrodes (AC + CB + PTFE) was first examined via a constant current charge–discharge (CCCD) test, resulting

in a specific capacitance of 205 F g^{-1} at a current density of 10 mA or ca. 6 mA cm^{-2} . To determine the effect and optimum graphene loading, the reduced graphene oxide (rGO) with a specific capacitance ca. 135 F g^{-1} [18] was physically added into the system at graphene contents from 0 to 20% to produce AC + rGO + CB + PTFE electrodes. The resulting specific capacitance as a function of the graphene content is shown in Fig. 1. According to the rule of mixtures, the resulting specific capacitance should have been between 205 and 135 F g^{-1} when the graphene loading increases from 0 to 100%. However, when the graphene loading is approaching 10%, the measured specific capacitance peaks at 213 F g^{-1} , indicating that a synergistic effect is occurring between rGO and AC. Three potential mechanisms may be at work. Firstly, adding proper amount of graphene into the conventional carbon electrode may have reinforced the electrical conductivity of the whole structure such that the capacitive energy storage ability of activated carbon is better performed. Secondly, the addition of rGO in the form of crumpled graphene sheet into the AC structures may facilitate the migration of electrolyte ions through the electrode, as the rGO sheets produced from a solution process have better electrolyte affiliation than the AC particles that are usually obtained through a high-temperature activation process where the oxygen containing functional groups is largely eliminated [28]. Thirdly, rGO worked more than just as a conductivity enhancer, and it also stored charges itself as an active material, as demonstrated by its much higher specific capacitance 135 F g^{-1} [18] than CB ($<5\text{ F g}^{-1}$ [16]). Consequently, rGO appears to be a promising conductive additive for activated carbon electrodes.

For a closer examination, a graphene content of 8% was chosen and a CCCD plot of the resulting

Fig. 1 Specific capacitance of conventional activated carbon electrodes at various graphene loadings from 0 to 20%

AC + rGO + CB + PTFE-based SC is presented in Fig. 2, showing the evolution of both the potential and current with time. The inset plot enlarged the potential change around its peak value of 1 V and the clearly marked IR drop. The IR drop is an indicator of resistive behavior of the cell and can be used to calculate the equivalent series resistance (R_{ES}), which is critical for the power performance of the supercapacitor. A R_{ES} of 0.97Ω or $0.57 \Omega \text{ cm}^{-2}$ was obtained for the AC + rGO + CB + PTFE cell, smaller than the R_{ES} (1.20Ω or $0.71 \Omega \text{ cm}^{-2}$) from AC/rGO + CB + PTFE cell, and R_{ES} (1.97Ω or $1.16 \Omega \text{ cm}^{-2}$) from the control sample.

The CV curves of all three supercapacitors in Fig. 3 were rather rectangular, demonstrating negligible difference among them at a scan rate of 10 mV s^{-1} . The AC/rGO + CB + PTFE cells had slightly larger specific capacitance of 200 F g^{-1} than that of both AC + rGO + CB + PTFE (197 F g^{-1}) and the control samples AC + CB + PTFE (196 F g^{-1}). Compared to the specific capacitance in Fig. 1 measured by CCCC test at 10 mA , the CV test at 10 mV s^{-1} in Fig. 3 here generally gives slightly smaller values, but the general trend is the same in both methods. Moreover, the plots show that the slope of the initial part of the CV curves increased upon the addition of graphene in both AC/rGO + CB + PTFE and AC + rGO + CB + PTFE samples, confirming a faster charging process and a smaller R_{ES} compared to those in the control sample AC + CB + PTFE.

Figure 4 presents the Nyquist plots, and the enlarged high-frequency regions (as inset) obtained from EIS test for the three supercapacitors. The equivalent circuit was inserted in the figure where R_s represents the ionic resistance of electrolytes, R_{ct} is the charge-transfer resistance, Z_w is the Warburg impedance and C_{dl} is the double-layer capacitance. Collectively, the R_{ES} was derived based on the

Fig. 2 A typical constant current charge-discharge (CCCD) plot from supercapacitors with 8% graphene loading

Fig. 3 Cyclic voltammetric (CV) plots at scan rate of 10 mV s^{-1} of the as-constructed supercapacitors with 8% graphene loading if present

Fig. 4 Nyquist plots of the as-constructed supercapacitors with 8% graphene loading if present from 0.01 Hz to 100 kHz with a magnification of the high-frequency region as inserted. Z_{img} : imaginary part of the impedance; Z_{re} : real part of the capacitance

real part of the impedance at 1 kHz and used to describe the resistance of the supercapacitors. The almost vertical curve at low frequencies suggested near-ideal capacitive energy storage behavior of the cells. A knee frequency [5] at around 385 Hz was found for all cells, indicating their similar resistive behaviors at different frequencies. This value is very close to the reported knee frequency of activated graphene-based supercapacitors at ca. 382 Hz [29]. The semicircle at high-frequency region of the Nyquist plot demonstrated a typical Warburg-like behavior resulting from the ion penetration through the porous carbon structure and the electric contact between active

materials and current collector [17]. Based on the real part of the impedance at 1 kHz, the R_{ES} of the cells can also be estimated. The AC + rGO + CB + PTFE cell displayed the lowest value of 0.43Ω or $0.25 \Omega \text{ cm}^{-2}$, while the control sample had the largest R_{ES} of 0.55Ω or $0.32 \Omega \text{ cm}^{-2}$. Compared to the R_{ES} values obtained from the IR drop of CCCD curves, the Nyquist plots gave much smaller values for the same cells. According to Zhang and Pan [24], although there are more than one ways to derive R_{ES} , the R_{ES} from the CCCD test was more accurate in describing the resistivity of the cell in actual use and is therefore used in calculating the power density of the carbon electrodes.

According to Simon et al. [19], the cell capacitance of SCs can be computed from the real part of impedance based on EIS data. Therefore, the specific capacitance of the electrodes can be likewise derived this way by simply normalizing the derived cell capacitance. A typical curve describing the change of real and imaginary parts of the specific capacitance versus frequency is shown in Fig. 5 for the AC + rGO + CB + PTFE cell. From the figure, a specific capacitance of 199 F g^{-1} was obtained, based on the real part of the complex capacitance at the lowest frequency of 0.01 Hz . This value agreed quite well with that calculated from the CV curve at 10 mV s^{-1} , yet

Fig. 5 Evolution of real and imaginary specific capacitance at various frequencies for the cell with 8% graphene loading

smaller than that from the CCCD test. Additionally, a relaxation time constant around 10 s, similar to the value of a cell constructed by Simon et al. [19], was calculated as the reciprocal of the frequency where the imaginary part of the complex capacitance reaches its maximum.

To facilitate further comparison, the above electrochemical properties of the three supercapacitors are summarized in Table 1. Although AC + rGO + CB + PTFE cell had the lowest R_{ES} in both CCCD and EIS tests, it is the AC/rGO + CB + PTFE cell that demonstrated the lowest time constant τ of 2.20 s and highest power and energy densities of 6.1 kW kg^{-1} and 7.5 Wh kg^{-1} , respectively, indicating an all-around improvement in performance. It suggests that how the graphene was added into the system will also impact on the final results; rGO reduced in the presence of AC has generated significantly better energy storage performance than rGO reduced alone.

Relative to the control cell AC + CB + PTFE ($P_{\max} = 4.0 \text{ kW kg}^{-1}$, and $E_{\max} = 7.1 \text{ Wh kg}^{-1}$), the AC/rGO + CB + PTFE cell achieved a ca. 50% in power increase with also a slightly higher energy density. Therefore, we can conclude that the incorporation of rGO material into the conventional activated carbon-based supercapacitors is able to significantly enhance the power performance by 50%, without sacrificing the energy performance of the cells. This finding may be very useful in developing next-generation high-performance supercapacitors.

Giving the superior electrical conductivity of graphene material itself, we also constructed another group of button cells to examine the possibility of replacing the carbon black entirely with rGO. The same processes were carried out to produce the supercapacitor electrodes but without adding carbon black at all, and the graphene loading was 8%, the same level as that of carbon black in conventional cells. This no-CB group of cells was tested again, and all the data are provided in Table 2.

If focused on the detailed behaviors of all three cells in Table 2, with the CV curves shown in Fig. 6a, once again the AC/rGO + PTFE cell is superior. From the Nyquist plots in Fig. 6b, similar impedance behaviors are showing for the three cells with tiny difference in R_{ES} . In addition, the cycling stability of the no-CB supercapacitors was

Table 1 Electrochemical performance of conventional activated carbon-based supercapacitors upon graphene addition

	Specific capacitance (F g^{-1})			R_{ES} (Ω)		τ (s)	$E_{\max}$ (Wh kg^{-1})	$P_{\max}$ (kW kg^{-1})
	CCCD at 10 mA	CV at 10 mV s^{-1}	EIS at 0.01 Hz	CCCD at IR drop	EIS at 1 kHz			
AC + CB + PTFE	205	196	196	1.97	0.55	3.17	7.1	4.0
AC + rGO + CB + PTFE	213	197	199	0.97	0.43	2.86	7.4	4.7
AC/rGO + CB + PTFE	215	200	201	1.20	0.50	2.20	7.5	6.1

Table 2 Electrochemical performance of supercapacitors without carbon black

	Specific capacitance (F g^{-1})		R_{ES} (Ω)		τ (s)	E_{max} (Wh kg^{-1})	P_{max} (kW kg^{-1})
	CCCD at 10 mA	CV at 10 mV s^{-1}	CCCD at IR drop	EIS at 1 kHz			
AC + PTFE	165	155	2.20	0.77	5.97	5.7	1.7
AC + rGO + PTFE	214	197	1.07	0.45	3.94	7.4	3.4
AC/rGO + PTFE	225	202	1.24	0.69	3.89	7.8	3.6

Fig. 6 CV curves at 10 mV s^{-1} (a) and Nyquist plot with the high-frequency region as inset (b) of the supercapacitors without carbon black

examined via CV test after 5000 consecutive charging and discharging cycles. All of three cells demonstrated superior cycling stability with virtually no decay. Cycling stability and CV curve comparison are illustrated in Fig. 7 using AC + rGO + PTFE cell as an example. In fact, a tiny capacity increase was observed from the CV curves,

Fig. 7 Cycling stability and CV curve comparison at 10 mV s^{-1} after 5000 cycles by using AC + rGO + PTFE cell as an example

indicating improved storage ability after 5000 recharging cycles.

Now if we keep in mind the results for AC + CB + PTFE in Table 1, the AC + PTFE cell in Table 2 shows the poorest performance out of all others. This demonstrated the importance of adding conductive additives, either CB or rGO, into the activated carbon-based supercapacitor electrodes, since an electrically conductive network is critical for the charge storage of any active material [21].

Similarly, the AC/rGO + PTFE cell demonstrated the largest specific capacitance, 225 F g^{-1} according to CCCD test, a smallest time constant τ , leading to the highest energy and power densities among the three in Table 2. This all-around performance improvement can only be attributed to the addition of rGO, which acted as both a conductivity enhancer and additional energy storage medium. It is interesting to check the effect of replacing CB with rGO as the conducting additive by comparing the AC/rGO + PTFE cell and its counterpart AC + CB + PTFE cell in Table 1: replacing CB with rGO improved the energy density from 7.1 to 7.8 Wh kg^{-1} , due to the higher specific capacitance of rGO, but lowered the power density

Fig. 8 SEM pictures of the as-prepared AC/rGO + CB + PTFE electrode

from 4.0 to 3.6 kW kg⁻¹, indicating that CB is a more conducting medium. Moreover, by comparing AC/rGO + PTFE with AC/rGO + CB + PTFE cells to check the synergy between AC/rGO and CB, the AC/rGO + PTFE cell has slightly higher energy density relative to the AC/rGO + CB + PTFE one, 7.8 versus 7.5 Wh kg⁻¹ owing again to the better specific capacitance of rGO. Nonetheless, the AC/rGO + CB + PTFE cell has higher power density 6.1 vs 3.6 kW kg⁻¹, confirming the existence of synergy in electrical conductivity between CB and rGO.

There were two major reasons for the improved electrochemical performance upon graphene addition with or without CB: (1) like CB, rGO also worked as a conductive bridging material to fill the pores in between the AC particles; (2) rGO had much higher capacitive energy storage ability than CB. This second claim has already been validated by comparing the reported specific capacitances of 135 F g⁻¹ for rGO from Ruoff et al. [18] and <5 F g⁻¹ for CB from Gogotsi et al. [16]. Herein, we examined the “bridging behavior” of rGO sheets in AC electrodes by scanning electron microscope (SEM) for AC/rGO + CB + PTFE electrode in Fig. 8, where different structural components were identified and marked. rGO once mixed into the activated carbon electrodes served as a conductive filler to seal the gaps in between the activated carbon particles as shown in Fig. 8, thus improving the electrical conductivity of the electrode structure. Also, rGO sheets could work as a flexible separator to decrease the aggregation of AC particles and then enhance the pore availability for electrolyte ions [10, 12]. With the improved electric conductive and electrolyte accessible electrode structure, the resulted SC demonstrated superior power and energy performances.

Conclusion

Given the excellent electronic properties of graphene material, two potential ways are explored in this study to incorporate graphene material into the conventional carbon/carbon supercapacitor for performance enhancement.

The first method is to use the reduced graphene oxide as a supplement, and a 50% increase in power density was achieved with only 8% graphene addition. Also by reducing graphene oxide in the presence of activated carbon, slightly higher specific capacitance 215 F g⁻¹ and energy density 7.5 Wh kg⁻¹ were obtained. Moreover, reduced graphene oxide was also examined as a possible substitute to replace carbon black. Our results demonstrated a 10% increase in energy density with a slightly suppressed power performance.

Our analysis confirmed that as a performance enhancer, graphene has much better capacitive energy storage ability yet a little lower electrical conductivity improvement ability relative to carbon black. Overall, incorporating graphene material into the conventional carbon electrodes could be an effective and practical tactic for next-generation high-power supercapacitors, which will prompt wider adoption of supercapacitors in hybrid vehicles and renewables to benefit the environment.

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