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# Fabrication and Empirical Analysis of Graphene Dispersion/ Activated Carbon on Conductive Networks in Porous Graphite Felt Supercapacitor for Fast Charging Regenerative Braking in EV

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# Abstract

Supercapacitors are a promising candidate for regenerative braking system due to their inherent fast charging and high-current/temperature tolerance capabilities. However, most supercapacitors suffer from high weight to capacitance ratio, which averts the use of supercapacitors in regenerative braking in electric vehicles. This research proposes a new lightweight supercapacitor electrode fabrication, which consists of networking conductive layers of graphene dispersion and activated carbon in porous graphite felt using conductive ink. The composite electrode showed a specific capacitance up to 170 F g-1 or 13 F g-1 from completed device in type iii deep eutectic solvent electrolyte, which gave the starting voltage of 2.3 V. The submersion fabrication alleviated the fabrication compare to brush method and production time was reduced to under 3 minutes of physical preparation.

# Introduction

An increase in the use of electric propulsion in road vehicles in recent years has expanded interests in various methods to improve the efficiency for longer mileage and lower cost of the vehicle. This has opened for an opportunity for the regenerative braking system, which recovers partial kinetic energy to storable energy1. In the case of most electric cars, lithium-ion batteries are used, because of the presence for vehicle propulsion2. However, regenerative braking system's high-power transient charging that occurs during braking is problematic for lithium-ion batteries, lithium-ion batteries are intolerant in high-temperature, which can be caused by high current flow during the charging period3,4. This can cause significant degradation, influencing the performance and lifetime of the electric vehicle4.

Supercapacitors, in its nature, has lower energy density and highpower density compare to a typical battery5, which is why it is not found common as other power storing devices that need extensive charging. However, in regenerative braking system, complementary features batteries and supercapacitors can be effectively used due to supercapacitor benefits of fast charging and high tolerance in current and temperature6. Current commercial supercapacitors usually suffer from high weight to capacitance ratio, since most applications does not require any weight constraints, such as grid power buffer and voltage stabilizer in electronics7,8,9. However, in electric vehicles, reducing the weight of the vehicle is crucial for longer mileage of the car, which has averted the use of supercapacitors in the regenerative braking system9. Attributed by advancements in material science, such as the implementation of carbon nanotube and graphene in the electrode, have increased supercapacitor's capacity and voltage consistently over the years8,14. However, majority of researching supercapacitor cannot be produced for commercial use, because cost and safety of the supercapacitor and the methodology are usually not considered 15. Usage of these unfamiliar materials has an extremely high cost for commercial use and assembling methods of these supercapacitors is difficult, which adds to the cost variable due to the fabrication time15,16.

Recent development of large-scale fabrication of graphene dispersion has made possible to purchase graphene slurries at lower cost, which can be utilized in electrode system. Even though there are multiple reports on the fabrication of graphene dispersion, the knowledge of the application is still very limited. This research demonstrates the use of graphene dispersion with activated carbon to construct conductive networks in 3D porous electrode composite, which has on average 3 times better overall device specific capacitance of up to 13 Fg-1, compare to current commercial supercapacitors. The use of choline chloride based deep eutectic solvent has served an alternative to ionic liquid giving starting voltage of 2.3V and increasing the safety factors during fabrication and simplifying the electrolyte fabrication process.

#### Results

### Scalable Fabrication of Supercapacitor

The schematic of the entire process to form the supercapacitor, which was done with the perspective of scalable manufacturing process was given in Fig. 1b Fig 1a shows the implementation of different materials in the electrode during the fabrication. During the initial process, graphite felt is submerged in conductive ink made from graphene dispersion and activated carbon, which is prepared in advanced for faster process. The electrode composite was dried for 25 minutes before electrolyte coating on the top electrode surface. Activated carbon and graphene dispersion is used to construct the conductive ink, which allows for high surface area and high conductivity. Fig. 2a and Fig 2b shows SEM image of the activated carbon and Fig. 2c and Fig. 2d shows SEM image of the graphene dispersion.

### **Electrode Characteristics**

Pre-fabrication electrode testing were conducted to find the best ratio for conductive ink fabrication, which is used to build the test supercapacitor on following stage. It has been shown in previous researches that conductive network of graphene nanoplatelets in the dispersion helped space the activated carbon, which is proven for faster ion transportation and better access to pores20. Also, researches shows graphene nanoplatelet contained composite showed 23.5 times higher thermal conductivity than that of just powder AC21. Activated carbon and graphene dispersion were empirically tested in different ratios of each other to test variables that impacts the capacity of the supercapacitor. Electrode electricity conductivity was measured using different integer weight ratios of AC and GD in Fig. 3a. Because activated carbon used in this research was semi-conductive, increasing GD weight increased the conductivity of the electrode. GD and AC weight ratios of 1:8, 1:7, 1:6, and 1:5 showed high conductivity in the range of 3 to 6 ohm/ cm2. Surface area of 1 gram showed to be 1800 m2/g based on the materials technical data sheet and electrode surface area was calculated based on the weight ratio of AC and GD in Fig. 3b. Electrode conductivity and surface area positively impacts the capacity of the supercapacitor, however the two variables did not correspond due to low conductivity of the activated carbon. Increase usage of activated carbon increased the surface area of the electrode but decreased the conductivity and vice-versa for increasing graphene dispersion ratio in the conductive ink. Empirical analysis was performed, in which, total of 16 supercapacitors with different ratios of graphene dispersion and activated carbon were constructed to test the capacity of each electrode ratios. 36 electrode sizing 1 cm2 were prepared and the submersion fabrication showed in Fig. 3c was used to construct the supercapacitor. 1 ml of sodium sulfate aqueous electrolyte were coated on each of the electrode and low current of 20 mA was used to charge the supercapacitor for 30 seconds before testing the capacity. The usage of sodium sulfate electrolyte and low current charging helped with stability and accuracy of the data, since it resulted in lower capacitance than normal testing condition. Fig. 2c shows that using the range of 3:2.5 to 4:3 ratios of graphene dispersion and activated carbon respectively showed the highest capacity of 1.2 to 1.4 farads. The range of these ratios were used to fabricate supercapacitors for capacitance measurement.

#### **Supercapacitor Capacitance**

Supercapacitor's most important requirement is high capacitance and low weight ratio with capacitance. All the tests were performed with galvanostatic charge and discharge technique, since data accuracy usually greater than cyclic voltammetry measurements. Current during charging was first measured to approximate the maximum charging rate and charging time estimation during the research. All current decreased as supercapacitor voltage value gets closer to the charging voltage. As seen in Fig. 4a, initial charging is very fast as current value loose half of its value at about 30 seconds of charging. After the 30 second mark, the current drop is much slower. Charging the supercapacitor over 10 V started bubbling of electrolyte and the current value did not decrease and no charge was shown during discharging. Fig. 4b shows the relationship between voltage and time when different current is applied. The specific capacitance was calculated using the following.

# $C_{c} = I * \Delta t / \Delta V * m (Fg^{-1})$

Where, Cs is the overall specific capacitance, I is the discharging current,  $\Delta t$  is the time in seconds it takes to discharge to certain voltage,  $\Delta V$  is the voltage difference, and m is mass of the supercapacitor. Overall specific capacitance is including weight of the entire supercapacitor including the Kapton tape insulation. This was measured instead of electrode weight specific capacitance, since overall specific capacitance gave more realistic idea of capacitance. The voltage curve constantly decreased, which confirm the EDLC characteristics of the samples. The supercapacitor mass was 2.5 grams, which showed the overall specific capacitance of 8.67 Fg-1, 7.46 Fg-1, and 5.68 Fg-1 when 20 mA, 40 mA, and 60 mA were used to discharge respectively. The specific capacity decreased as discharge current increased, primarily due to the contribution of Ohmic drop. The current discharge test was also performed to 20 F commercial supercapacitor (8.5g), which showed overall specific capacitance of 2.27 Fg-1 when discharging at 20 Ma, which meant the research supercapacitor showed about 4 times better specific capacitance in respect to the weight. With the perspective of supercapacitor usage in regenerative braking, repetitive chargedischarge testing were performed as can see in Fig. 4c and Fig. 4d. The two supercapacitors in two graphs were charged and discharged at same voltage and current. Fig. 4c was performed right after fabrication and Fig. 4d was performed 3 hours after fabrication. Previous researches show that poor performance of supercapacitor is mainly caused by sluggish desolvation of ions at the pore opening and low ion migration within the pores25. After 3 hours, it was seen that supercapacitor sample's voltage increased slightly by 0.1 - 0.2volts, which led to increase in capacity. Fig. 4e shows low current discharge and coulombic efficiency rate, which was calculated with equation 1. Supercapacitor was seen to discharge at faster voltage

values during the initial discharge phase (2.7 V to 1.2 V), which lasted for 200 seconds, but after 200 seconds, the voltage drop was significantly lower, with 0.65 V difference in the time range of 4000 seconds, which showed capacitance of 92.3 Farads or overall specific capacitance of 12.8 F g-1, which was about 1.5 times better than capacitance when discharging at 20 mA. Columbic efficiency was calculated using the ratio of discharge specific capacitance and charge specific capacitance. The efficiency was shown to be 96.30%, which shows high reversibility of electrode material for long term performance in supercapacitor. Also, the columbic efficiency showed that the supercapacitor did not provoked additional chemical reactions, such as decomposition of the electrolyte, which degrades supercapacitor life. Fig. 4f shows the charge-discharge ratio during high voltage input. Voltage range in the range of 5 V to 9 V were tested, however supercapacitor did not break down and still showed energy potential. Charging current value showed that above 9 volts, the charging characteristic of current became abnormal, however Fig. 4a does not show the effect of high charging rate for the capacity of the supercapacitor. Generally, as charging voltage increased, capacity decreased, which can be seem from decrease in discharge time. Charging to 5 V, 6 V, 7 V, 8 V, and 9 V showed capacitance of 6.24 F, 6.13 F, 5.31 F, 5.2 F, and 5.16 F respectively. The difference in capacity was not significant but charging over 6 V showed 0.82 F in lower capacity, which was relatively lower than charging below 6 V. Electrolyte breakdown was tested with temperature sensor and bubbling voltage rates, which were performed simultaneously. Fully assembled supercapacitors were charged at different voltages, starting from 2 V and incrementing 2 V until 12 V, which was the maximum allowed voltage during the experiment condition. The electrode size was 6 cm2 and the height was 0.5 cm2 and the volume was 3 cm2. Shown in Fig. 5, charging at 2 V, 4 V, and 6 V, did not show significant temperature change and the average temperature in respect to charging voltages were 31.5 °C, 32.28 °C, and 32.47 °C. Starting at 8 V, electrode temperature increased to 33.81 °C, 10 V resulted in 36.22 °C, and 12 V resulted in 38.28 °C. This experiment showed that charging the sample supercapacitors above 6 volts was possible but led to faster degradation of the supercapacitor.

### Conclusion

Optimizing high-surface area activated carbon and graphene nanoplatelet mixture to create supercapacitor resulted in 4 times higher capacitance compare to commercial supercapacitors in similar mass. It can be seen that the specific capacitance is not superior compare to other researches,21,22,23 however the supercapacitor was constructed with the perspective of lower-cost materials and fast manufacturing abilities. By using this novel composite electrode and type iii deep eutectic solvent, the developed supercapacitor not only exhibit high capacity and physically lightweight, but also possess repeatability with excellent columbic efficiency that are comparable to commercial supercapacitors.

# Method

#### Preparation of Current Collector/Electrode

To develop the fastest method of fabrication possible, conductive ink

is prepared. 35g of 5 wt% graphene dispersion (XFNano) is sonicated in 20 kHz for 15 minutes. 30g of activated carbon (XFNano) is than added to the dispersion and the mixture is moved to magnetic stirrer for 2 minutes at 300 rpm. Commercial graphite felt (Zibo Ouzheng Carbon Co.) is than submerge in the aqueous mixture until all the felt pores are wet. A 3 cm3 graphite felt takes 7 ml of conductive ink. To minimize leaking of the ink in the graphite felt, the felt is held in air for 5 minutes, giving the outer layer of the conductive ink dry. The electrode is rested for heatbed 60°C for 20 minutes. The remaining conductive ink can be used several times for this method. The conductive ink mixture with 35g of 5 wt.% graphene dispersion and 30g of activated carbon was used 6 times to construct the complete electrode system for the 10 cm2 supercapacitor. The dry electrode shows outer layer resistance of 0.85  $\Omega$ /cm2. Deep eutectic solvent electrolyte is constructed with choline chloride and ethylene glycol with the mole ratio of 1:2 respectively. The solution was heated on 80°C until they dissolved and formed uniform solution. Fabrication of the electrode composite is completed after 10 ml of electrolyte is coated on both electrode and rested for 3 hours for better distribution of electrolytes in the electrode. When the conductive ink is prepared in advanced, the entire electrode construction takes 3 minutes of physical fabrication by hands and 55 minutes of drying time.



(a) Schematic illustration of composite electrode and electrolyte synthesis. Activated carbon and graphene dispersion ink is represented with yellow spheres and electrolyte is represented with red and blue spheres. (b) Manufacturing perspective of the supercapacitor fabrication. 1) Conductive ink and graphite felt is prepared. 2) Graphite felt is submerged in the ink for 5 seconds.
3) Electrode composite is dried for 20 minutes in 60°C. 4) 10 ml of Electrolyte is Coated per 6 cm2.



(a-b) Sem image of the structural characterization of activated carbon with different magnification. (c-d) Sem image of graphene dispersion slurry at different magnification.

(a) Outer shell electrode with different weight ratios of activated carbon

and graphene dispersion's resistance is measured. (b) Surface area of the electrode based on the amount of electrode material is calculated using data numbers. (c) 1 cm2 supercapacitors are built using different weight ratios of activated carbon and graphene to find the capacitance.





Supercapacitor charging temperature measurement in different temperature after 30 seconds, (a) 2 V (b) 4 V (c) 6 V (d) 8V (e) 10 V (f) 12 V.

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