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Al-ZnO / CuO_CFRP ORGANIC STRUCTURAL AUXILIARY ENERGY STORAGE SYSTEM FOR ELECTRIC VEHICLE

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ABSTRACT

Electric vehicles (EVs) have tremendous potential in the context of curtailing greenhouse gas emissions within the transportation sector. The main drawbacks of the EVs are: battery pack increased weight, limited range and required additional electricity generation source to charge the batteries. The contribution of the coal plant to the production of electricity is 57% and emissions 1.4 kg / kWh, while gasoline 35% and 1.2 kg / kWh respectively. Nanocomposite technology in automotive industries makes the vehicle more energy efficient, by cutting the emission with reducing weight. The main objective of this study is to develop a structural energy storage system using aluminum-doped zinc oxide / copper oxide carbon fibre reinforced polymer (Al-ZnO/CuO_CFRP) sandwiched 70gsm/20gsm paper dielectric structural organic super-capacitor (OSC) for EV body panel. A conceptual laboratory model has been developed to find the suitability of structural Al-ZnO/CuO_CFRP OSC as EV body panel, which is considered as the energy generation and storage system. The OSC has considered as the roof panel of EV and it has tested at a solar temperature of 30^0C. The test results show that the energy conversion efficiency (ηec) of 19%, voltage (V_{oc}) 2800 mV, current density (J_{sc}) 522 mA/cm^2, capacitance (C) 20.15 μF/cm^2, energy density (E_d) 120 Wh/kg, and power density (P_d) 29 kW/kg. It would be able to reduce EV battery size by 15%, weight 7.5% and battery charging power 9%. Furthermore, the OPSC-EV roof panel would contribute to the reduction of greenhouse gas (GHG) emission 25% and help transport the population with a low level of carbonization.

Keynotes: Organic energy storage system; Nanocomposite technology; solar renewable energy; Electric vehicle; Greenhouse gas reduction

INTRODUCTION

The multifunctional nano-filler conductive polymer structure of the EV provides greater potential to save energy and weight reduction if combined with features and functions. These materials enhance the engineering system features from their superior performance (Cao et al., 2017; Rahman et al., 2014, Deka et al., 2016). An organic solar plate created with a carbon-stimulating conductive polymer carrying capacitors serves as a stronger and lighter EV body panel as well as energy generation from solar heat-trapping and helps to recharge batteries. This will reduce the battery charge time, extend battery life and make vehicle energy efficient. The main objective of this study is to develop a structural capacitor using aluminum-doped zinc oxide / copper oxide carbon fibre reinforced polymer (Al-ZnO/CuO_CFRP) sandwiched 70gsm/20gsm paper dielectric structural organic super-capacitor (OSC) for EV body panel. A conceptual laboratory model has been developed to find the suitability of structural Al-ZnO/CuO_CFRP OSC as EV body panel, which is considered as the energy generation and storage system. A non-conducting material is known as dielectric, is essential between the materials, which prevents the electron transfer with the electrode surface. However, it will be only through the electric circuit. The dielectric capacitor charged by the electron transfer therefore it takes less time to charge compare to the batteries. The electrodes are made of a permeable material and a greater surface area.

The common characteristics of a super-capacitors are fast charging & discharge processes and exhibit low self-discharging [Zhang et al., 2010]. By using environmental materials several research has been conducted on super-capacitors focused on increasing power and energy densities. Carbons and metal oxides, filler conducting polymers are the electrodes of super-capacitor. Graphene-based materials using CNTs have shown immense theoretical and practical advantages: high surface area, excellent conductivity and specific capacitance of 730 mAh/g [Yoo et al., 2008]. Graphene has many similarities to CNTs in structure and properties including large surface area including large-surface area (2630 m^2 / g) [Liu et al., 2010, Novoselov et al., 2005] and excellent mechanical properties [Rahman et al., 2020] and carrier mobility (15,000 cm^2 / Vs). Theoretically, the capacitance of EDLC of a graphene electrode can reach up to 550 F / g, the highest value of intrinsic capacitance among all carbon-based electrodes [Bia et al., 2012], a specific supercapacitor with a specific capacitance of 135 [deg.] C and 99 [deg. Wh / kg at room temperature and 136 Wh / kg at 80 ° C) [Liu et al., 2010]. Recently, super-capacitors with high specific capacitance (276 F / g), power density (20 W / cm^3, 20 times higher than that of the activated carbon counterpart, energy density (1.36 mWh / cm^3), 2 times higher than that of the activated carbon counterpart) [Jaidev et al., 2012].

Super-apacitors are called electrochemical capacitors (ECs) are considered as a promising energy storage devices and have been applied in hybrid electric vehicles (HEV)/electric vehicle power-supply devices [Chen et al, 2014]. Nanotechnology is an enabling technology for energy storage. Particularly, carbon nanotubes and graphene sheets have been playing an important role in the development of supercapacitors [Zhang et al., 2009; Zhu et al., 2011]. Activated carbon materials have a high surface area limited energy density (4-5 Wh / kg) and power density (1-2 kW / kg).

The authors [Sirshova et al., 2013] developed multifunctional structural super-capacitors using carbon fiber electrodes. Transition-metal oxides and their alloys have been fascinating to develop the high efficient organic super-capacitor/ultracapacitor due to their unique physical and chemical properties. Zinc oxide (ZnO) with wide optical band gap (3.37 eV at room temperature), large band gap energy (60 meV) is a potential metal oxide for the photovoltaic super-capacitor (Caglar et al., 2006, Yakuphanoglu et al., 2007). ZnO optical performance can be improved with doping by the dopant like (Al, In, Ga, etc). Aluminum (Al) doped zinc oxide (AZO) is very useful for the fabrication of optoelectronic devices, heterojunction and superlattices, and detectors (Zhang et al., 2010). The optical band gap energies of thin films were determined based on transmission spectra and it is found that the band gap energy is increased with increasing Al doping concentration (Ahmed et al., 2014).

CuO is considered as one of the suitable materials for super-capacitor due to its chemical stability, large surface area, higher hole mobility, relatively high specific capacitance (674 mAh/ g) and eco-friendly [Dar et al., 2015, Zhan et al., 2015].

The mechanical and electrical properties of the dielectric capacitors are affected by materials of the electrodes and dielectrics and electric breakdown strength (EBD) [Carlson et al., 2011]. Electrical breakdown (EBD) occurs when the voltage applied across an electrical insulator exceeds the breakdown voltage and current flows through it, which makes the insulator electrically conductive. Polymer films having EBD as superior to impregnated papers. In addition, the capacitances of specimens are observed to decrease with the increase in thickness of dielectric separators. The CFRP electrode layers were manufactured from 0.125mm thick prepreg weaves. The prepregs were a $245g/m^2$ (Carlson et al, 2010).

METHODOLOGY

An organic super-capacitor (OSC) has been made with Al doped ZnO filler polymer reinforced with carbon fibre (Al-ZnO_CFRP) as p-type semiconductor, CuO filler polymer reinforced with carbon fibre (CuO_CFRP) as n-type semiconductor (SC) with sandwiched the 70gsm paper film dielectric or 20gsm paper film soaked with Na_2SO_4 aqueous solution. Once sandwiched has been completed the OSC been tested with a solar temperature of 30°C which is called the state-of-charging, SoC(T) of OSC and discharge OSC with electrical load is called state-of-discharge, SoD(t). The SoC(t) happens when the photon of solar heat strikes the Al-ZnO_CFRP, its energy is given to an electron in the cystal lattice of CuO_CFRP where the free electrons to move from n-type to p-type SC through the external circuit. Thus higher solar heat creates electron hole and causes the more electron flow from the CuO_CFRP to Al-ZnO_CFRP. The electron can flow through the surface of the separator (dielectric). However, it flows through the external electrical circuit. The electrical wire has been placed both in p-type and n-type during fabrication for developing electrical circuit. The performance of the OSC has been measured with capacitance, μF, open circuit voltage, V_{OC} (v), current density, J_{SC} (mA/m^2), power density, W/m^2 or $W/_{kg}$, energy density, Wh/m^2 or Wh/kg and the energy conversion, η_{ecs} (t).
The open circuit voltage reduces increases with increasing the temperature. Mathematically Voc can be defined using the equation (Bagienski e al., 2012):

$$V_{oc} = E_g - \frac{\sigma_n^2 + \sigma_p^2}{2kT} - kT \ln\left(\frac{N_n N_p}{np}\right) \tag{1}$$

The current density can be defined as,

$$J_{sc} = \left(\frac{1}{A_{sample}}\right)\frac{v_{oc}}{R}\left(1 - e^{-t/RC}\right) \tag{2}$$

The energy storage efficiency as a function of time of charge, t is defined as η_{ecs} (t) = E_{store}(t)/ E_{light} (t) where E_{store} is the energy stored in the supercapacitor at time t and E_{light} (t) light energy received by the solar cell. The light energy, E_{store} (t) =P_{light} * t where P_{light} is the solar power, the solar power in this study is considered as 1000W/m^2. The specific energy store can be defined as,

$$E_{spc} = \frac{1}{A_s} C v_s \left[1 - e^{-t(\tau)/RC}\right] \tag{3}$$

where, v_s (τ) is the charging voltage of the capacitor which is developed due to the variation of the solar temperature and the fill factors of the cell and $t_c(\tau)$ is the charging time of the supercapacitor with solar power. The total energy stored to the super-capacitor can be defined as,

$$E_{T(stored)}(t) = \frac{1}{A_s} CVoc\left(1 - e^{-t(\tau)/RC}\right) \tag{4}$$

where, A_t is the area of the cell (module), m^2, R total saturated resistance of the cells, and C is the capacitance. The efficiency of the energy conversion of the OSC can be defined as,

$$\eta_{ece}(t) = \frac{\int_0^t V_{oc}(t) * i_{sc}(t)\, dt}{P_{light} * t} * 100\% \tag{5}$$

The time of full charge can be estimated as, $t_c = CV_{oc}/I_{sc}$ where, V_{oc} is the open circuit voltage, I_{sc} is the short circuit current. The voltage generation of the solar cell can be estimated as, $V_{pv} = V_{oc} + R_s I_{sc} = Q_{sc}/C_{sc} + R_s I_{sc}$.

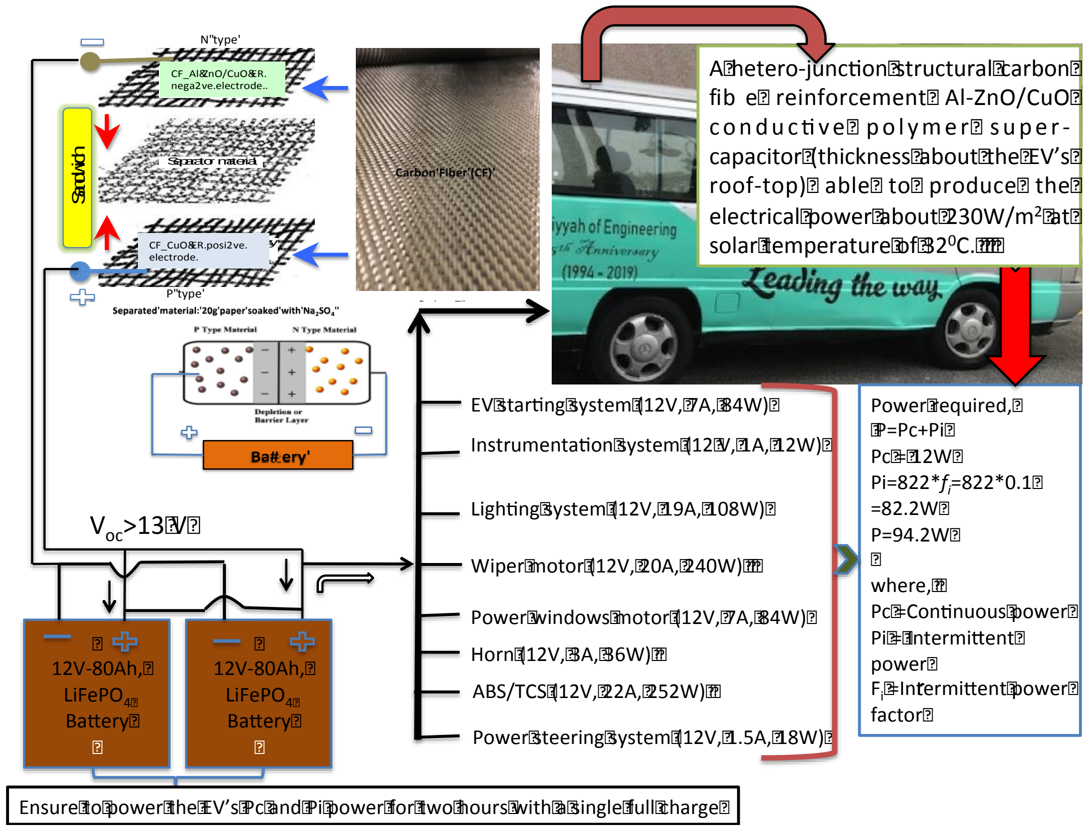


Figure 1: Model of structural capacitor

DEVELOPMENT of SUPER-CAPACITORS

Different mixture compositions were made and tested accordingly to justify the best mixture percentages as shown in Table 1. All the composition has been taken in weight percentage (wt%). For example, a 10% mixture means 10g nano-particles was mixed with 60g epoxy and 30g hardener. The ratio of epoxy to hardener is always 2:1 in all the cases as recommended by the manufacturer of epoxy resin. The different mixture has been made to identify the best composition for the OPSC.

Table 1. Composition of nano-conductive polymer super-capacitor

Electrode	Mixture (M)			
CF & P-type SC	M1 (wt.%)	M2 (wt.%)	M 3 (wt.%)	M4 (wt.%)
Epoxy+hardener	95	90	70	64
ZnO	5	10	30	30
Al	10	20	25	30
CF & N-type SC	M1 (wt.%)	M2 (wt.%)	M 3 (wt.%)	M 4 (wt.%)
Epoxy+hardener	95	90	70	64
CuO	5	10	30	30

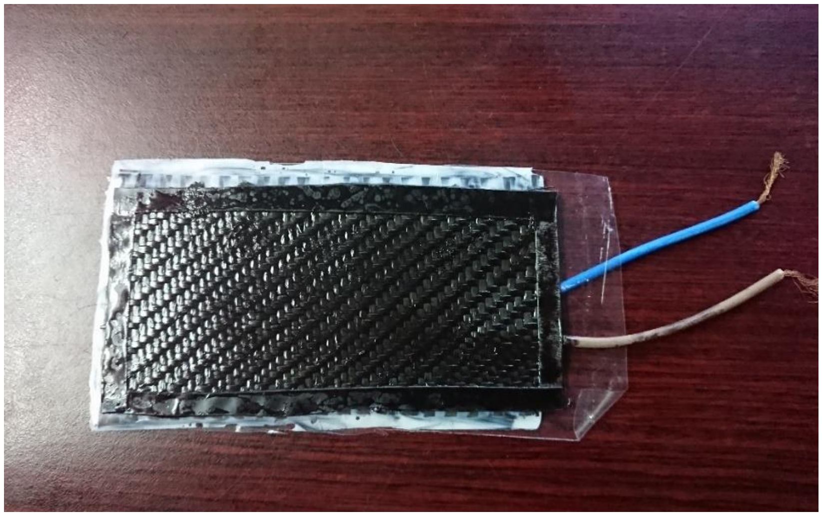


Figure 2: A smaple of developed organic photo-supercapacitor with 20gsm paper soaked in Na_2SO_4 [sample of size (10cmx4.5cm), mass 0.009kg]

The organic super-capacitor (OSC) has been designed and developed for the EV as a body panel to generate electricity from solar energy and store. It is made with aluminum zinc oxide (Al-ZnO) and copper oxide (CuO) conductive polymer reinforced by carbon fibre (CF) and dielectric as separator/salt aquous electrolyte. The basic design principle of OSC is to enhance the optical absorption and/or reduce loss during electron transport to cenvert the solar energy into electric energy and store. The nano Al-ZnO structure is employed to improve the performance of OSC by increasing the exciting generation effect in quantum dots, creating large surface area, generating unique optical effects, conduction and improving the electron transport and/or electron collection. The Al-ZnO nanostructure is made in a shape of nanowires, which has less defects in the material. Therefore, this single crystalline phase causes the much higher electron mobility and highly efficient in electron transport. CF fabrics derived from π-Carbon (240g / m2) 0.25 mm thick were used for the development of OPSC (Figure 1). The CF acts like a common OPSC electrode.

To enlarge the specific surface area of the CF electrodes, the CFs was activated by HNO_3 at 90 ° C for about 2 hours on the side that was in contact with the dielectric. Epoxy resin and hardener were selected based on their compatibility with carbon fibers. The transparent epoxy resin and hardener came in a package with a recommended mixing ratio of 2: 1 and a complete curing time of 24 hours between 25 ° C and 30 ° C.
The CF electrodes were reinforced with nano Al-ZnO epoxy for the negative electrode to facilitate high electron mobility as a type n semiconductor with a bandgap energy of 3.2 eV to 3.4 eV and epoxy-filled nano-CuO to the positive electrode to facilitate bore / positive charge movement as a p-type semiconductor with a band range from 1.2 eV to 1.8 eV (Dhara et al, 2016). By incorporating these nanoparticles into the opposite electrodes, they increased the conductivity of the CF electrodes. The zinc oxide (ZnO) nanoparticles (size 10 nm) were supplied by Chemetal SDN, BHD, Malaysia. The

copper oxide nanoparticles (CuO) (size 50 nm) were from Sigma-Aldrich. Both samples come with the risk of handling P273 and the environmental risk H411. The dielectric film was placed between the ZnO doped ER added to one side of the CF and the CuO doped ER added to the side of another thin CF layer. The sample of the OSC laboratory scale which is made with 30wt.% doped with 30wt.% ZnO/CuO reinforced with carbon fibre polymer and 70gsm dielectric paper film has shown in Figure 2 and Figure 3 shows the developed double layer OSC 30wt.% doped with 30wt.% ZnO/CuO reinforced with carbon fibre polymer and 20gsm dielectric paper film soaked with aqueous Na_2SO_4.

RESULT AND DISCUSSION

The number of samples of OSC, size of the sample thickness 2mm, area (10 cm*4.5 cm) of 0.0045 m^2, mass 9g (all samples of 70gsm dielectric) and mass 12g of 30% ZnO/CuO double 20gsm paper soaked with aqueous Na_aSO_4, has been with different composition of C-ZnO and CuO and dielectric materials (20gsm, and 70gsm, non-aqueous paper film and Na_2SO_4 soaked paper film). Initially the terminals of the final sample of OSC for different composition has been short circuited to be ensured no charge was stored in OPSC. Then it has been tested both indoor and outdoor environment. The OSC indoor testing has been made using the fluorescent lamps with temperature of 27°C and outdoor was in solar temperature of 32^0C and 34°C at 13.20 and 13.50 Malaysia time respectively. A multimeter was attached to the terminals of the sample to be tested. The results has been recorded in every 10 seconds until 5 minutes for each of the samples at solar temperature in the range of 20-34°C at samples were taken at an interval of 10 seconds for 5 minutes to investigate the performance of OPSC at a solar temperature of 20-34°C.

EV's energy efficiency has been made with considering the roof-top thichkness xxmm, width 30 cm and length 100cm. The area of the roof top 0.3 m^2 to estimate the power generation by the OSC from trapping the solar heat and store. The store power is considered to charge the battery which could be used to meet the power demand auxiliary electrical system stated. The solar power conversion efficiency is estimated based on the ratio of the power generated by the OSC to the input power of the solar 1000 W/m^2.

Performance parameters of the OPSC such as open circuit voltage (V_{oc}), short-circuit current (J_{sc}), state-of-charge (SoC) and power density (P_d), energy density has been measured for two different samples (i) paper film dielectric; (ii) Na_2SO_4 aqueous soaked paper film which is considered as EDLC. The average power conversion efficiency of 11 samples with different composition was found 14.5%. It is concluded FF fall drop, leading to the reduction of Jsc, Voc and conversion efficiency.

Figure 3 shows the charging /discharging of the Al-ZnO/CuO_CFRP OSC of sample size 0.0045 m^2. The OSC has been charged under the solar heat of 32^0C for 5 minutes. It was found the OSC has been reached the maximum charging voltage (i.e open circuit voltage, V_{OC}) level of 0.25V for 30% Al, 0.18 for 20% Al, and 0.11V for 10% Al at 60s. The Voc of the 30% Al-ZnO/CuO_CFP is more than others because of optical band gap (E_g) of the films is increased with increasing Al concentration. Which increases the electrical conductivity, mobility carriers and carrier concentration of the films.

Connecting a 1.5V lithium-ion battery has checked the discharge VOC. It is found that the OSC has fast charging in 40-50s but discharge slowly until 100s. Maximum Voc is found 2.2V for 30%Al-30%ZnO/CuO_CFRP super-capacitor. By considering the maximum discharge voltage of a sample 2.2V*60%=1.32V and connecting 10 samples in series, total 13.2 V will be available to charge the battery. Therefore, it could be concluded that by using the EV's roof-top as a structural super-capacitor, only a 12V battery can be charged.

Figure 4 shows the state-of-charging, SoC(t) and state-of-discharging, SoD(t) of the OSC of different doped percentage of Al with ZnO. Curve of SoC(t) and SoD(t) implies that the charging of the OSC is faster while the SoD(t) is slower. It could be concluded that the losses of the OSC is very low as OSC able to store the power until state of charge condition arises. This is an advantage of OSC over the conventional super-capacitor. In all of the cases of Al% doped with ZnO reaches the maximum charge level at 50 s. while, due to the 30 wt. % CuO_CFRP hold the charge for a longer time to discharge as the copper oxide (CuO) oxides has anti-ferromagnetic, electrochemical deposition, and high temperature superconducting with low band gap energy of 1.2-1.9 eV and high hole electron mobility and absorb the charge from the Al doped ZnO_CFRP. The nano-composites 30-40 wt. % CuO filler polymer shows high conductivity due to interfacial polarization.

Current density of OSC depends on the solar heat. Higher solar heat causes the more electrical pressure, which causes the higher density. Maximum current was recorded for the each of the sample of 70gsm dielectric OSC about 0.14A for the 30% Al-ZnO/CuO_CFRP (Figure 5) which is almost double than the 20% Al-ZnO/CuO_CFRP SC. The same result shows in Figure 6(a). Figure 6(b) shows that the EDLC has contributed more J_{sc} over the dielectric OSC. However, it is difficult to maintain the aqueous Na_2SO_4 concentration for the EDL-OSC. This is because of the increment of carrier density and hole mobility. However by arranging the samples 60 in parallel to get the thickness of the EV rooftop of 120 mm with 2 mm OSC module, the current will be 60*0.14 or 8.4 A. The battery will charge with 8.4 A current which would not generate any heat in the structural OSC. The instantaneous power generates 110 W.

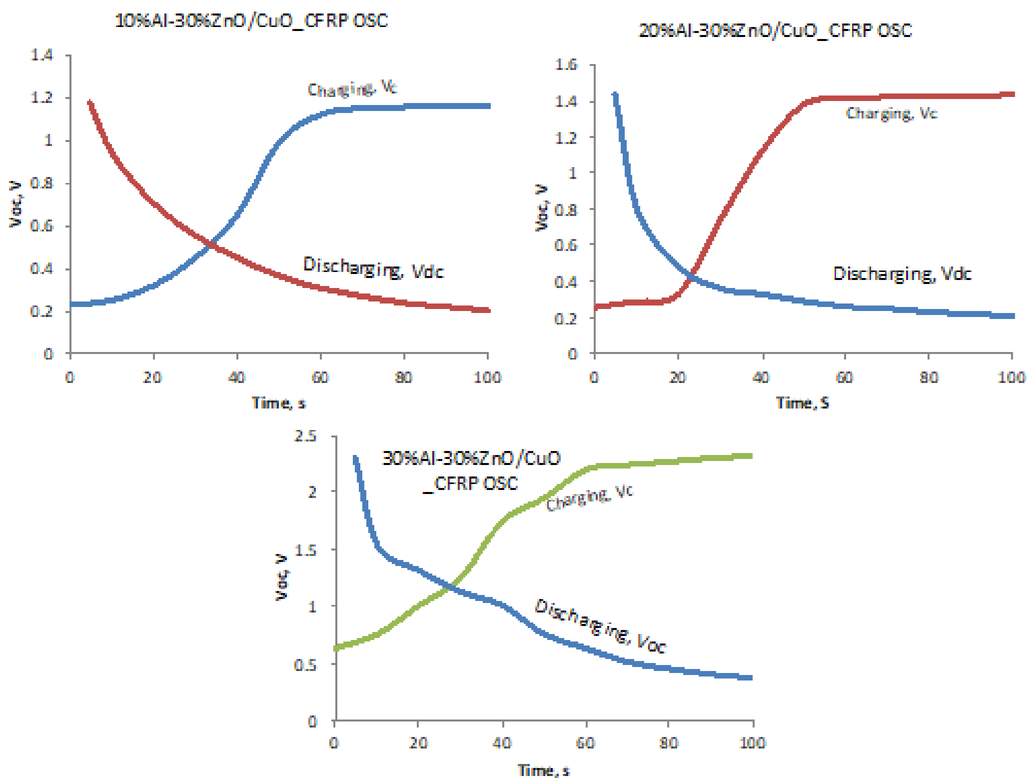
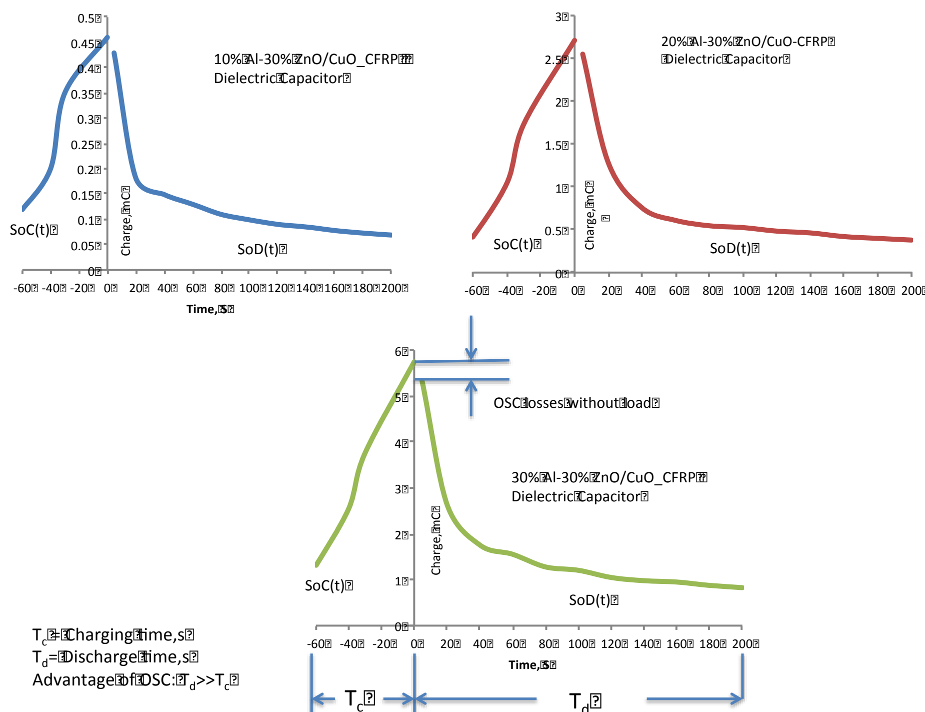
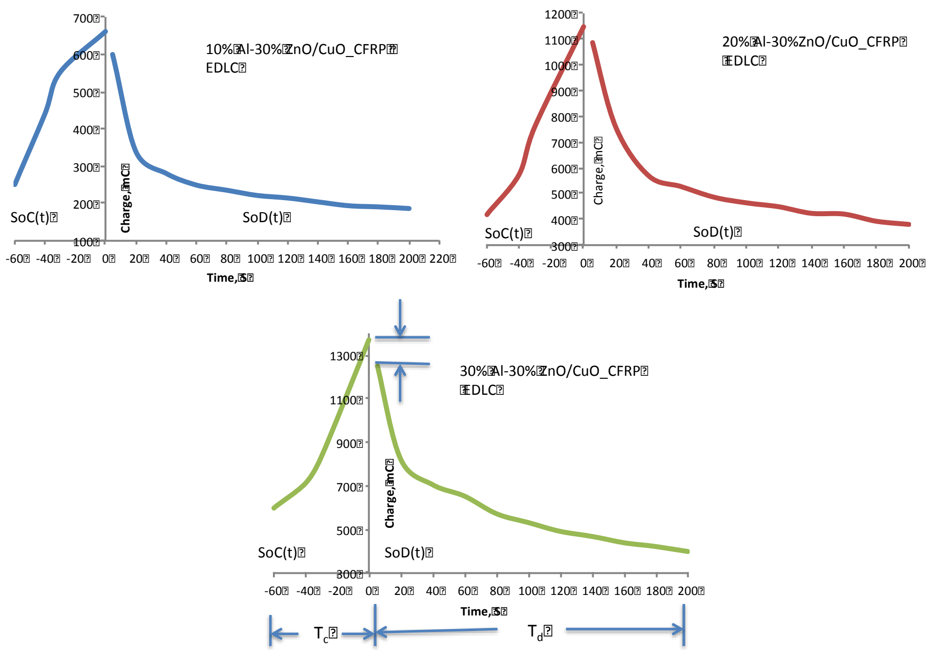


Figure 3: Open circuit voltage (V_{oc}) of OSC.



(a) Dielectric 70gsm paper film-supercapacitor



(b) EDLC-20gsm paper soaked with aqueous Na2SO4

Figure 4: Charge level of Al-ZnO/CuO-CFRP super-capacitor both in charging/discharging

Table 2: Capacitance of capacitor

Capacitance, µF	**Weight % of Al doped with 30% ZnO/CuO, OSC**		
	10% Al-ZnO/CuO	**20% Al-ZnO/CuO**	**30% Al-ZnO/CuO**
(i) 70gsm paper dielectric OSC, capacitance (µF)			
Capacitance (µF)/m^2	0.55	2.1	6.1
(ii) 20gsm paper soaked with Na_2SO_4 OSC, capacitance (µF)			
Capacitance (µF)/m^2	346	510	578

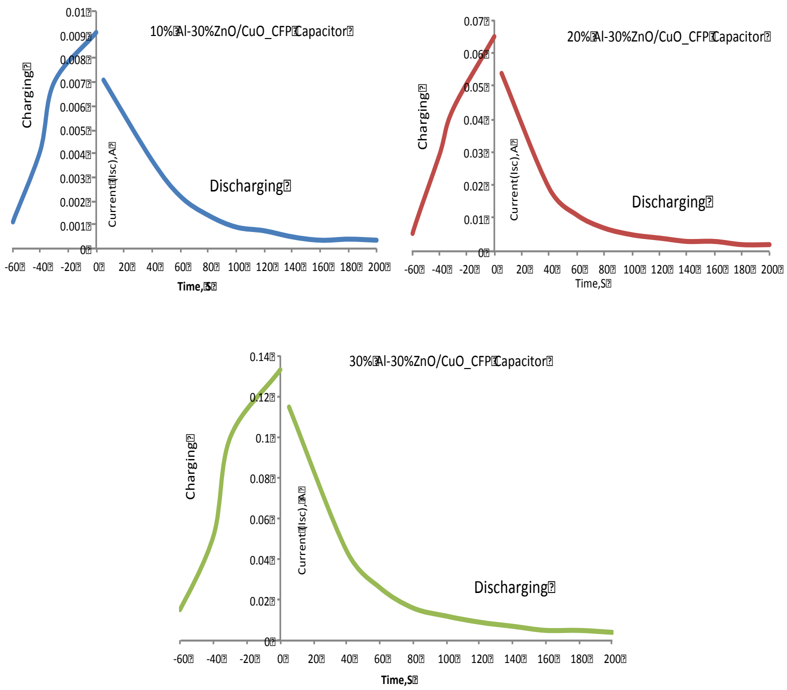


Figure 5: Short circuit current (I_{SC}) of dielectric super-capacitor

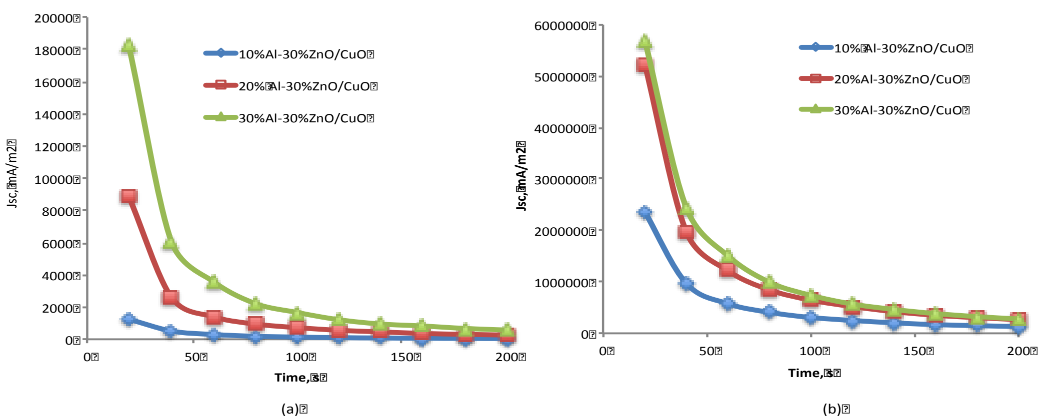


Figure 6: Short circuit current density of Al-ZnO/CuO_CFRP super-capacitor with (a) 70gsm paper dielectric (b) 70gsm paper soaked with Na_2SO_4

The power density of Al-ZnO/CuO_CFRP OSC defines as the rate at which power is discharged from the OSC. Figure 7 shows the power density of the OSC both for the dielectric and electric double layer OSC. EDL-OSC always dominant more power density due to the easier exchanging of protons through the surface and electrons through the circuit. However, it is difficult to maintain the Na_2SO_4 aqueous level of the separator.

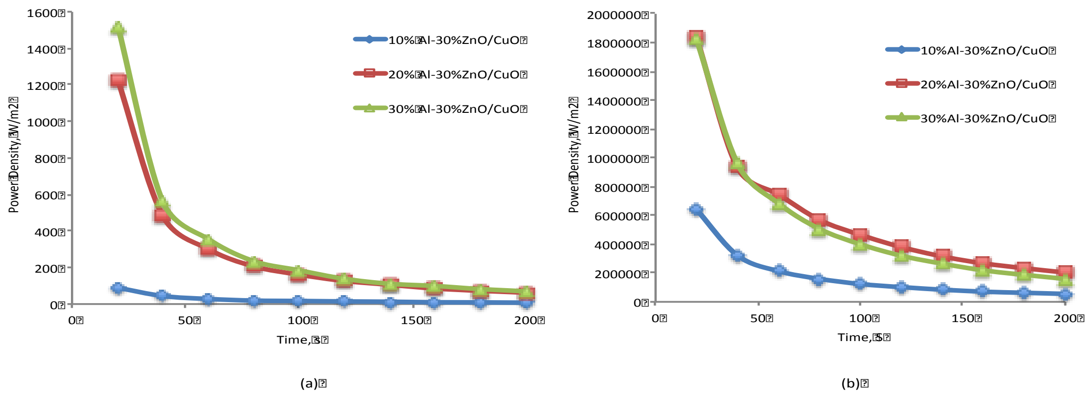


Figure 7: Power density of Al-ZnO/CuO_CFRP super-capacitor with (a) 70gsm paper dielectric (b) 70gsm paper soaked with Na_2SO_4

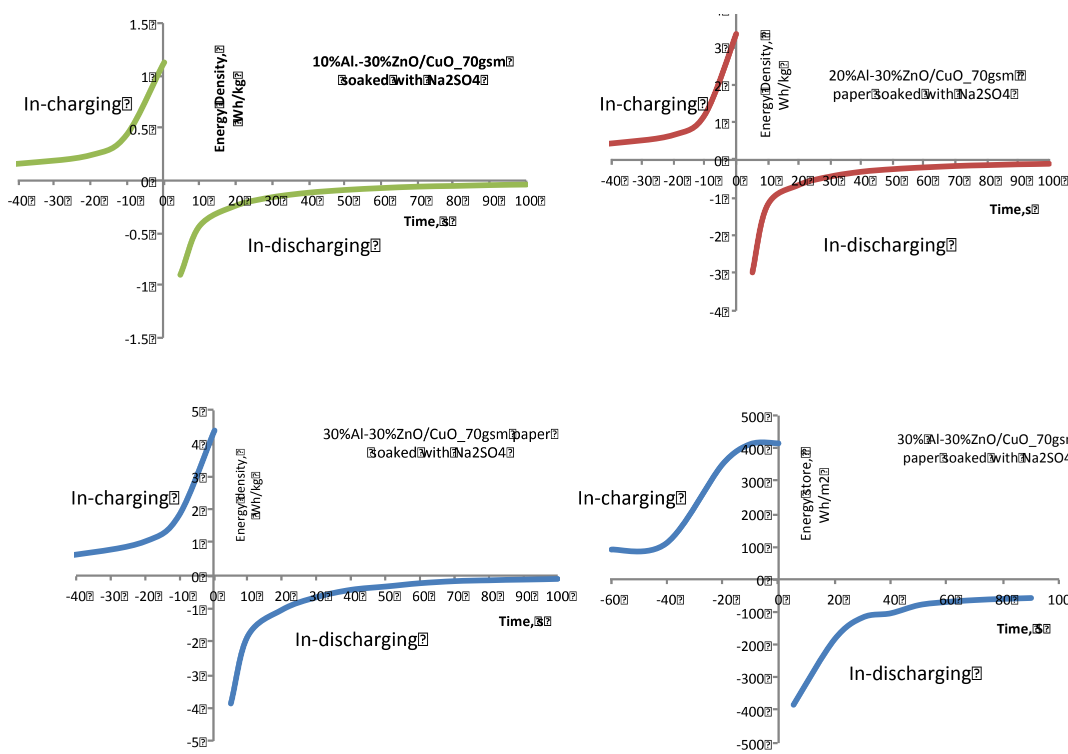


Figure 8: Energy density during charging and discharging for OPSC with Na_2SO_4 soaked paper dielectric

Impact of Al-ZnO/CuO_CFRP OSC on EV Sustainability

Vehicle sustainability means to provide the sustainable mobility to the society in a manner to the least reduction/zero greenhouse emission. Vehicle sustainable depends on the vehicle weight and energy system. The electric vehicle power system weight is about 320 kg for 33 kWh batteries including thermal management system (Rahman et al., 2017, 2018) and body (body on frame) about 150 kg (23% of cub weight) (Lotus engineering, 2010). By using the structural super-capacitor, the car body weight can be reduced to 100 kg and size of battery power system can be reduced to 30 kWh and weight 50 kg. The EV will be benefited by sum of 100 kg, which will make the EV energy efficient and reduce the emission. Figure 1 shows the contribution of the hetrojunction 30 wt. % Al doped with 30 wt. % ZnO/30wt. % of CuO_CFRP with 70gsm paper dielectric super-capacitor. The hetrojunction dielectric super-capacitor has been made based on the thickness of the EV roof-top thickess. Experimental result shows that OPSC able to develop the open-circuit voltage (V_{OC}) about 13.2 V and short circuit current density (J_{sc}) of 122 A/m^2 under the solar heat of temperature 32^{0}C.Therefore, the 30wt.%Al-30 wt.%ZnO/CuO-CFRP with dielectric OSC able to develop the power density of 2160 W/m^2 and energy density of 477 Wh/m^2 and or 4.7 Wh/kg which implies that the 30wt.%Al-30 wt.%ZnO/CuO-CFRP OSC able to generate maximum power 483.1 W at 32°C and store the energy 143 Wh. EV needs 94W power to operate the auxiliary power system. The OSC able to power the EV directly without storing the power into the battery.

CONCLUSION

The conclusion has been based on the conceptual OSC laboratory-scale testing in solar temperature 32°C. OSC has found a potential organic super-capacitor, although it has 11.5% efficiency, which is less than the efficiency of CNT and graphene-based supercapacitor. However, the performance of OSC can be enhanced by soaking a dielectric paper film with aqueous Na_2SO_4 and increasing the dopant percentage with the principal filler metal oxide (ZnO) of polymer. Increasing the dopant wt.% of Al with ZnO_CFRP, which will transfer more photodynamic energy through the dielectric surface and energize the electron-hole mobility, can increase energy density and power density. At the discharge stage, OSC performance has decreased by 3-5% without using a load in the circuit and it could be more if the dopant percentage increases, which is the result of higher conductivity of super-capacitor. The OSC for EV is a promising multifaceted structure that can reduce power consumption and emissiondue to the cut-weight of structure and reduction of traction.

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