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Conducting polymer effects on hybrid S-rGO/CuO/polymer nanocomposites for SupercapBattery devices

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Abstract – In this study, 3 different materials were combined to form hybrid nanocomposite for SupercapBattery applications. Sulfur (S) doped reduced graphene oxide (S-rGO), copper (II) oxide (CuO), and different conducting polymers such as polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT) and polypyrrole (PPy) were used as a one of the components of nanocomposites. Electrochemical performances were performed by cyclic voltammetry (CV), galvanostatic charge / discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements. EIS measurements were analyzed by Nyquist, Bode-magnitude, Bode-phase, and Admittance plots. Long-term stability tests were obtained by CV method using 1000 charge/discharge performances at a scan rate of 100 $mV \times s^{-1}$. The highest specific capacitance was calculated as C_{sp}= 171.63 $F \times g^{-1}$ at 2 $mV \times s^{-1}$ (electrode weight was obtained as 12,8 mg) for S-rGO/CuO/PEDOT nanocomposite.

Keywords – Supercapbattery, Hybrid Nanocomposite, S-rGO/CuO/PANI, Admittance Plot, Specific Capacitance

I. Introduction

The energy storage devices like supercapacitors and batteries are the most used favorable technologies in a portable electronics and hybrid vehicles [1, 2]. A nanocomposites with specific architectures have been intensively given as advanced electrodes in supercapacitors (SCs), like carbon materials, metal oxides / nitrides, and conductive polymers [3-5].

In this study, S-doped reduced graphene oxide (S-rGO), copper (II) oxide (CuO), and 3 different conducting polymers (polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT) and polypyrrole (PPy) were used as a hybrid electrode material for supercapbattery devices.

II. Materials and Method

Electrochemical measurements were performed with 2032 coin-type cells. The slurry was obtained by mixing the as-synthesized materials, acetylene black and *N*-methyl-2-pyrrolidone (NMP) as a solvent for materials. Polyvinyl pyrrolidone (PVP) was performed by binder. Then the slurry was pasted onto Al and Cu foils and dried at 60 °C in a vacuum oven for 12 h. The electrolyte was ionic liquid (IL). And the mass loading of electrodes of 13.1, 12.8 and 21.8 mg for S-rGO/CuO/PANI, S-rGO/CuO/PEDOT and S-rGO/CuO/PPy nanocomposites, respectively. Galvanostatic charge/discharge, rate performance and cyclic performances were tested between 0.0 and 0.8 V by using ivium-vertex potentiostat-galvanostat instrument.

A. GO and rGO synthesis

Graphene oxide (GO) was synthesized from graphite powder according to modified Hummers method [4].

B. S-rGO synthesis

In literature, the conductivity of GO increases by doped of S and N elements [7, 8]. As a result, S doped GO have a superior performance compared

to other additives (N, B or P) in terms of capacitor performance [9]. 5 ml Na_2S was mixed in various sources (0.5 M). It was synthesized in a microwave oven at 180 Watt and 20 min. So, S-GO was obtained by centrifuged 3 times [10].

C. *CuO synthesis*

Copper (II) oxide (CuO) nanoparticles were synthesized by ultrasonication and precipitation by heat treatment method. For the synthesis form, 4.8 g of Copper (II) sulfur penta hydrate ($CuSO_4 \times 5H_2O$) was dissolved in 200 ml of DI water. 200 ml is added dropwise to the mixture containing 0.2 M NaOH and ultrasonication treatment at 60 ^oC for 2 hours. The dark brown precipitate was decanted by centrifugation and washed several times with DI water and kept in an oven at 80 ^oC for 1 night and CuO nanoparticles were obtained.

D. *Polyaniline (PANI) synthesis*

Aniline (0.2 ml) and sodium dodecyl benzene sulphate (SDBS, 3.3 g) as a surfactant will be mixed with 0.06 ml of H_3PO_4 in 10 ml of DI water in an ice-bath. The resulting ANI/H_3PO_4 salt will be added to the 0.46 g / 5 ml DI water soluble ammonium persulfate (APS) mixture. Polymerization will continue in the ice-bath for 12 h. A green colour solid PANI will be formed. The resulting solid PANI will be dried by DI water and ethyl alcohol [11].

E. *Poly(3,4-ethylenedioxythiophene) (PEDOT) synthesis*

Polyvinylpyrrolidone (PVP, 30 mg) was placed in 20 ml of DI water in 250 ml flask and dispersed by ultrasonication device for 30 min. EDOT monomer (80 mg) and naphthalene-1, 5-disulfonic acid tetra hydrate (60 mg) were added into the flask and mixed for 30 min. Ammonium persulfate (APS, 500 mg) was added to the flask and mixed. The polymerization was carried out at room temperature for 15 h. As a result, PEDOT in solid form was obtained and dried in vacuum oven for 15 h at 60 ^oC by filtration through cellulose membrane.

F. *Polypyrrole (PPy) synthesis*

Polypyrrole was synthesized by chemical oxidation polymerization method. Pyrrole monomer, potassium dichromate ($K_2Cr_2O_7$) was used as oxidizer and H_2SO_4 as additive. Chemical polymerization was carried out by adding 1 M H_2SO_4 and 1 M pyrrole monomer solution dropwise addition to the above solution. Polymerization was carried out with constant stirring for 24 h with ice-bath condition. After the obtained product was filtered and washed with DI water. The black colored PPy powders were dried in an oven at 100 ^oC for 1.5 h [12].

III. Results & Discussion

G. *Electrochemical performances of SupercapBattery device*

Electrochemical performances of S-rGO/CuO/PANI, S-rGO/CuO/PEDOT and S-rGO/CuO/PPy nanocomposites were performed by CV, GCD and EIS measurements.

H. *CV measurements*

CV plots of S-rGO/CuO/PANI, S-rGO/CuO/PEDOT and S-rGO/CuO/PPy nanocomposites at different scan rates from 1000 $mV \times s^{-1}$ to 100 $mV \times s^{-1}$ were given in Figure 1.

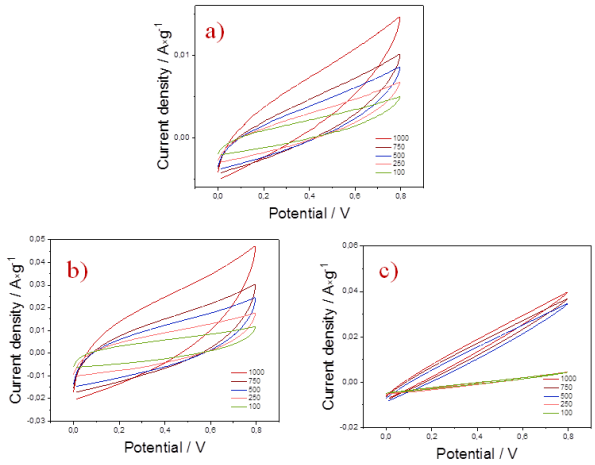

Fig. 1 CV plots of a) S-rGO/CuO/PANI, b) S-rGO/CuO/PEDOT and c) S-rGO/CuO/PPy nanocomposites at different scan rates from 1000 to 100 $mV \times s^{-1}$.

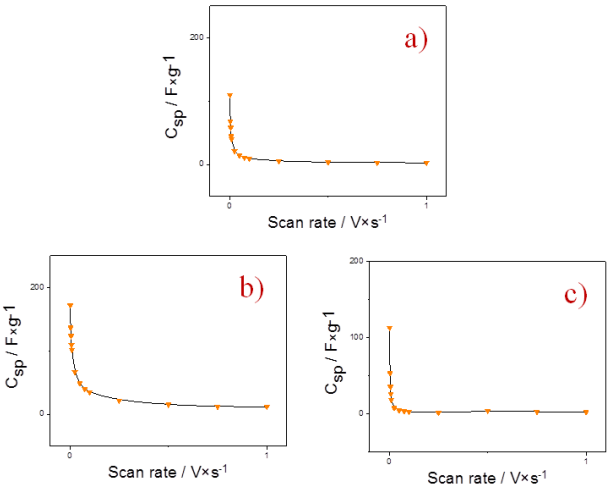

Fig. 2 C_{sp} vs. Scan rate plot of a) S-rGO/CuO/PANI, b) S-rGO/CuO/PEDOT and c) S-rGO/CuO/PPy nanocomposites at different scan rates from 1000 to 2 mV×s^{-1}.

The highest specific capacitances were presented as C_{sp}= 109.73 F×g^{-1}, C_{sp}= 171.63 F×g^{-1} and 113.10 F×g^{-1} at a scan rate of 2 mV×s^{-1} for S-rGO/CuO/PANI, S-rGO/CuO/PEDOT and S-rGO/CuO/PPy nanocomposites, respectively. The lowest specific capacitances were obtained for highest scan rates (1000 mV×s^{-1}). The specific capacitances were taken as C_{sp}= 2.61 F×g^{-1}, C_{sp}= 11.74 F×g^{-1} and 2.11 F×g^{-1} at a scan rate of 1000 mV×s^{-1} for S-rGO/CuO/PANI, S-rGO/CuO/PEDOT and S-rGO/CuO/PPy nanocomposites, respectively. When the scan rate increases, the specific capacitances were decreased due to the lower charge accumulation on electrode surface and in Helmoltz plane region.

I- GCD measurements

GCD plots of S-rGO/CuO/PANI, S-rGO/CuO/PEDOT and S-rGO/CuO/PPy nanocomposites were given at constant current density from 0.1 A×g^{-1} to 1.0 A×g^{-1} as shown in Figure 3. The highest specific capacitance was obtained as C_{sp}= 4.91 F×g^{-1} at 5 mA for S-rGO/CuO/PANI nanocomposite by GCD measurements. In addition, it was obtained as C_{sp}= 2.00 F×g^{-1} at 10 mA for S-rGO/CuO/PEDOT nanocomposite by GCD method. Moreover, the highest specific capacitance was obtained as C_{sp}=27.92 F×g^{-1} at 10 mA for S-rGO/CuO/PPy nanocomposite by GCD method.

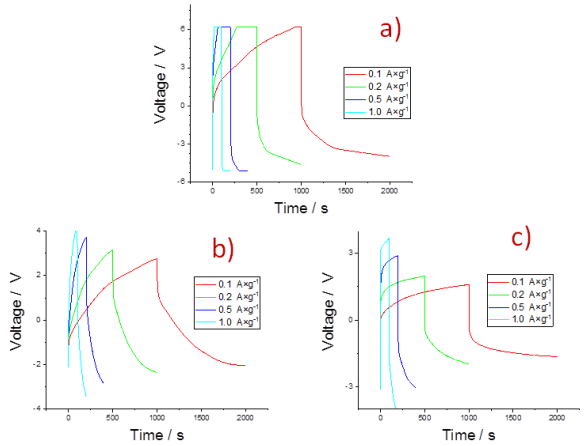

Fig. 3 GCD plots of a) S-rGO/CuO/PANI, b) S-rGO/CuO/PEDOT and c) S-rGO/CuO/PPy nanocomposites at constant current density from 0.1 A×g^{-1} to 10 A×g^{-1}.

İ-EIS measurements

EIS plots of S-rGO/CuO/PANI, S-rGO/CuO/PEDOT and S-rGO/CuO/PPy nanocomposites were given in Figure 4. Specific capacitance was obtained as C_{sp}= 7.26×10^{-2} F×g^{-1} for S-rGO/CuO/PANI nanocomposite, C_{sp}= 0.174 F×g^{-1} for S-rGO/CuO/PEDOT nanocomposite and C_{sp}= 1.35×10^{-3} F×g^{-1} for S-rGO/CuO/PPy nanocomposite obtained from Nyquist plot (Fig.4).

Double layer capacitance (C_{dl}) and phase angle (θ) were obtained as C_{dl}= 0.018 F×g^{-1} and θ= 44.92º for S-rGO/CuO/PANI nanocomposite obtained from Bode-magnitude and Bode-phase plots, respectively. The other C_{dl} and θ values were obtained as C_{dl}= 0.088 F×g^{-1} and θ= 48.13º for S-rGO/CuO/PEDOT nanocomposite and C_{dl}= 0.0081 F×g^{-1} and θ= 64.17º for S-rGO/CuO/PPy nanocomposites, respectively (Fig.5 & 6). Admittance plots defined conductivity of nanocomposite materials as Y″= 0.00536 S for S-rGO/CuO/PANI, Y″= 0.00634 S for S-rGO/CuO/PEDOT and Y″= 0.00869 S for S-rGO/CuO/PPy nanocomposites as shown in Figure 7.

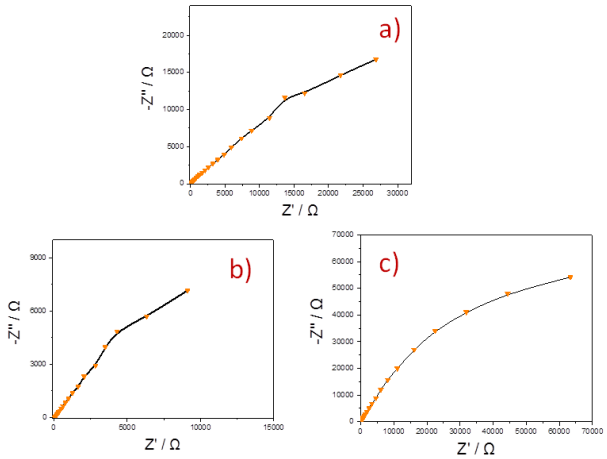

Fig. 4 EIS plots of Nyquist plots a) S-rGO/CuO/PANI, b) S-rGO/CuO/PEDOT and c) S-rGO/CuO/PPy nanocomposites.

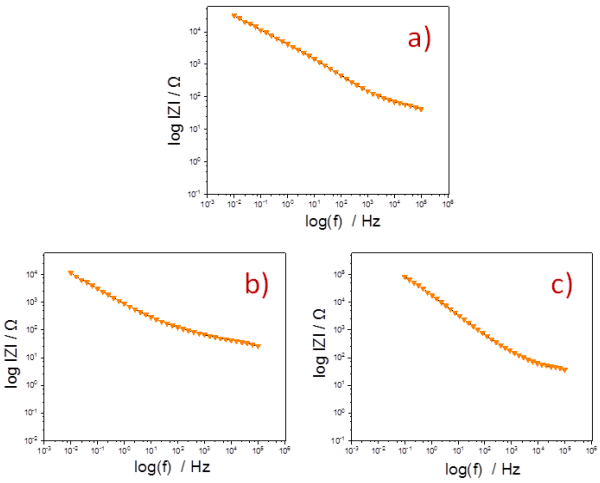

Fig. 5 EIS plots of Bode-magnitude plots a) S-rGO/CuO/PANI, b) S-rGO/CuO/PEDOT and c) S-rGO/CuO/PPy nanocomposites.

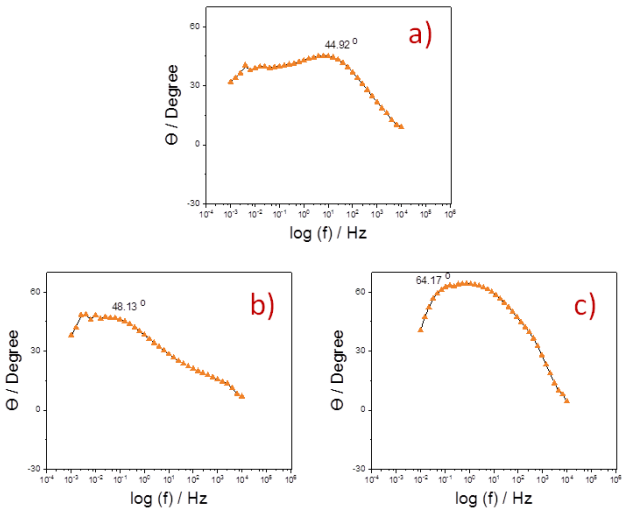

Fig. 6 EIS plots of Bode-phase plots a) S-rGO/CuO/PANI, b) S-rGO/CuO/PEDOT and c) S-rGO/CuO/PPy nanocomposites.

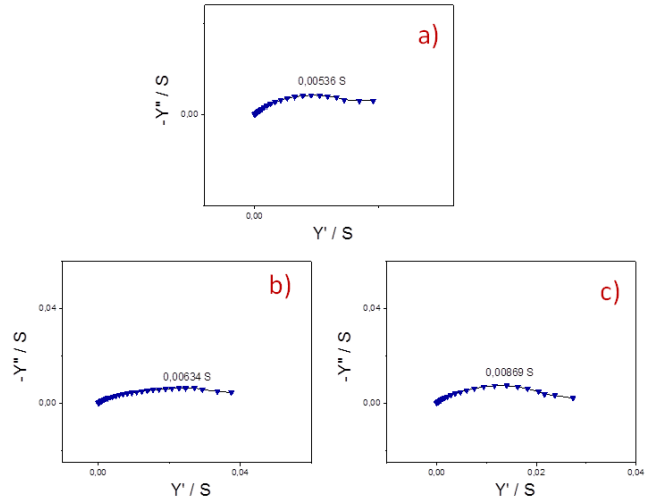

Fig. 7 EIS plots of Admittance plots a) S-rGO/CuO/PANI, b) S-rGO/CuO/PEDOT and c) S-rGO/CuO/PPy nanocomposites.

J- Stability tests

The stability graphs of the S-rGO/CuO/PANI, S-rGO/CuO/PEDOT and S-rGO/CuO/PPy nanocomposites for 2032 coin cell electrodes were given charge/discharge device performances for 1000 cycles (Fig.8). The first capacitance value after 1000 charge/discharge performances were obtained as 79.55% for S-rGO/CuO/PANI nanocomposite, 25.76% for S-rGO/CuO/PEDOT nanocomposite and 71.23% for S-rGO/CuO/PPy nanocomposites in ionic liquid in 2032 coin cell.

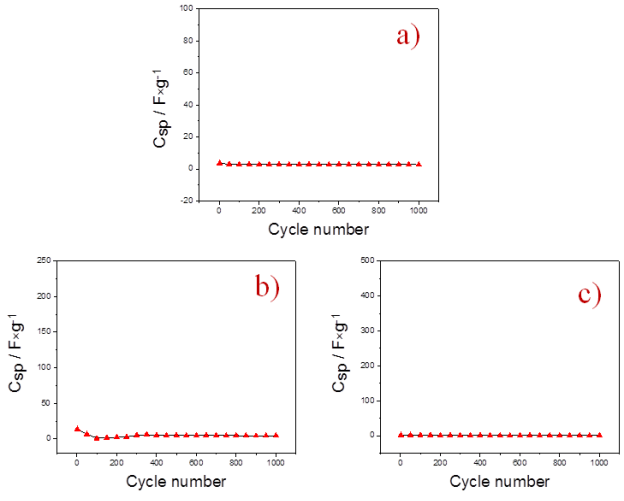

Fig. 8 Stability tests of a) S-rGO/CuO/PANI, b) S-rGO/CuO/PEDOT and c) S-rGO/CuO/PPy nanocomposites. The measurements were taken at a scan rate of 100 $mV \times s^{-1}$, 1000 charge-discharge measurements.

CONCLUSION

SupercapBattery device performances were obtained by 2032 coin cell. The highest energy and power densities were obtained as E= 5.63 $Wh \times kg^{-1}$ at 0.1 mA, 6.67 $Wh \times kg^{-1}$ at 2 mA and 1.97 $Wh \times kg^{-1}$ at 1 mA and P= 293.89 $W \times kg^{-1}$ at 5 mA, P= 1493.75 $W \times kg^{-1}$ at 10 mA and P= 134.95 $W \times kg^{-1}$ at 2 mA for S-rGO/CuO/PANI, S-rGO/CuO/PEDOT and S-rGO/CuO/PPy nanocomposites, respectively.

Phase angles were also presented as θ= 44.92º, θ= 48.13º and θ= 64.17º from EIS data. The highest initial capacitance preservation was obtained as 79.55% for S-rGO/CuO/PANI nanocomposite for 1000 charge-discharge measurements.

Our results have demonstrated that S-rGO/CuO/PANI, S-rGO/CuO/PEDOT and S-rGO/CuO/PPy nanocomposites for 2032 coin cell electrodes will be considered as a promising symmetrical electrode materials for the next generation of supercapacitor applications.

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