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S-rGO/Fe_2O_3/PPy nanocomposite formation for 2032 SupercapBattery Applications

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Abstract **–** In this study, 3 different materials were combined to form hybrid nanocomposite for SupercapBattery applications. Sulfur doped reduced graphene oxide (rGO), iron (III) oxide (Fe_2O_3), and polypyrrole (PPy) were used as a component 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}= 125.33 $F \times g^{-1}$ at 10 $mV \times s^{-1}$ (electrode weight was obtained as 20,9 mg).

Keywords – Supercapbattery, Polypyrrole, 2032 Coin Cell, Power Density, Cyclic Voltammetry

I. INTRODUCTION

Both supercapacitors and batteries are used in energy systems [1]. Supercapacitors or ultracapacitors have attracted attentions because of their high power density, high charge/discharge capability and rates, and long stability performances [2]. However, batteries have long energy density and long cycle life performances. So, we combine both of these devices as a supercapbattery systems. In this study, S-rGO/Fe_2O_3/PPy nanocomposite was used as an electrode materials in Al ve Cu electrodes. A facile and environmentally friendly approach was obtained for the synthesis of S-doped reduced graphene oxide/Fe_2O_3/polypyrrole nanocomposite hybrids. Energy storage mechanism is based on Faradic redox reactions of heteroatom-doped carbons [3], transition metal oxides [4], sulfides [5] or nitrides [6] and conductive polymers [7].

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 ^oC in a vacuum oven for 12 h. The electrolyte was ionic liquid (IL). And the total mass loading of electrode of 20.9 mg. 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 [8].

B. *S-rGO synthesis*

In literature, the conductivity of GO increases by doped of S and N elements [9, 10]. As a result, S doped GO have a superior performance compared to other additives (N, B or P) in terms of capacitor performance [11]. 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 with DI water and methanol [12].

C. *Fe_2O_3 nano-material synthesis*

$FeCl_3 \times 6H_2O$ (1.5 g) was dissolved in 2 ml of HCl solution (30 ml). This mixture was obtained as pH= 11 adding dropwise to 25% NH_4OH solution (75 ml) with stirring of solution. Afterwards, 2 ml of HCl was added dropwise until pH=2 and the mixture was stirred for 2h. Then by centrifugation and the collected solid was washed with DI water to remove access NH_4OH. The obtained product was dried at 80 ^oC for 8 h. Thus, Fe_2O_3 nanomaterials was synthesized [13, 14].

D. *Polypyrrole 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 [15].

E. *Electrochemical performances of SupercapBattery device*

S-rGO/Fe_2O_3/PPy nanocomposite were measured by CV, GCD and EIS measurements.

F. *CV measurements*

CV plots of S-rGO/Fe_2O_3/PPy nanocomposite at different scan rates from 1000 mV×s^{-1} to 2 mV×s^{-1} were given in Figure 1.

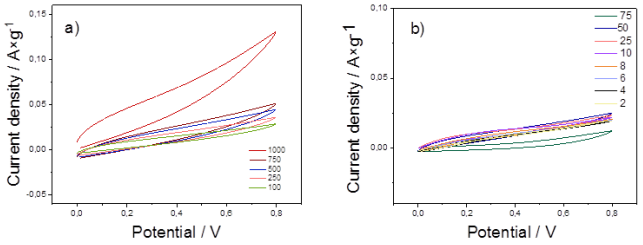

Fig. 1 CV plots of S-rGO/Fe_2O_3/PPy nanocomposite at different scan rates, a) 1000-100 mV×s^{-1}, b) 75-2 mV×s^{-1}.

The lowest specific capacitance was obtained as C_{sp}= 10.59 F×g^{-1} at 500 mV×s^{-1}. However, the highest specific capacitance was found as C_{sp}= 125.33 F×g^{-1} at 10 mV×s^{-1}. There is a logarithmic decrease by increasing of scan rate due to fast ion movement from one compartment to another compartment (Figure 2).

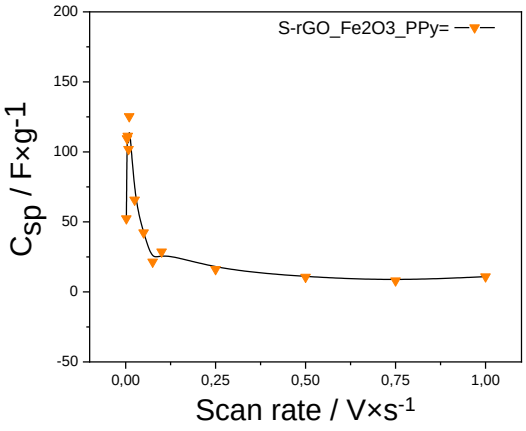

Fig. 2 C_{sp} vs. Scan rate plot of S-rGO/Fe_2O_3/PPy nanocomposite at different scan rates from 1000 to 2 mV×s^{-1}.

G. *GCD measurements*

GCD plots of S-rGO/Fe_2O_3/PPy nanocomposite was given at constant current density from 0.1 A×g^{-1} to 10 A×g^{-1} as shown in Figure 3. The highest specific capacitance was obtained as C_{sp}= 4.51 F×g^{-1} at 0.1 mA by GCD measurements.

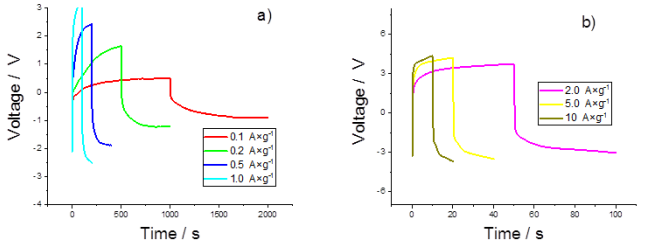

Fig. 3 GCD plots of S-rGO/Fe_2O_3/PPy nanocomposite at constant current density from 0.1 A×g^{-1} to 10 A×g^{-1}.

H. EIS measurements

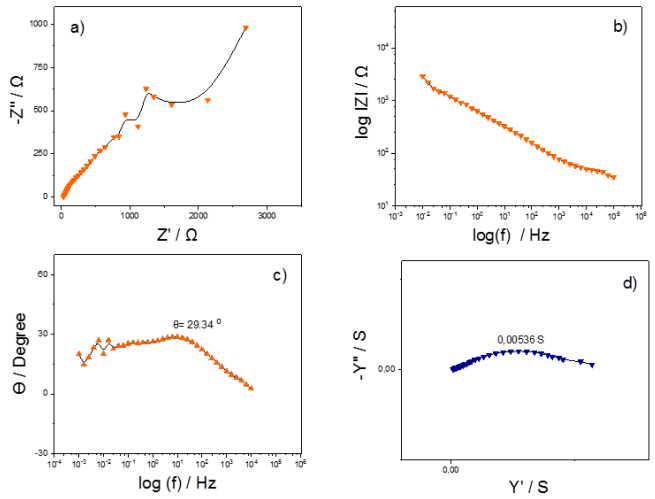

Fig. 4 EIS plots of S-rGO/Fe_2O_3/PPy nanocomposite a) Nyquist plot, b) Bode-magnitude plot, c) Bode-phase plot, d) Admittance plot.

EIS plots of S-rGO/Fe_2O_3/PPy nanocomposite were given in Figure 4. Specific capacitance was obtained as C_{sp}= 0.776 F×g^{-1} from Nyquist plot. Double layer capacitance and phase angle were obtained as C_{dl}= 0.076 F×g^{-1} and θ= 29.34º at 12.26 Hz from Bode-magnitude and Bode-phase plots, respectively. Admittance plots defined conductivity of nanocomposite material (Y″= 0.00536 S).

İ. Stability tests

The stability plots of the S-rGO/Fe_2O_3/PPy nanocomposite for 2032 coin cell were given charge/discharge device performances for 1000 cycles (Fig.5). The first capacitance value after 1000 charge/discharge performances were obtained as 73.82% for the SS electrode in ionic liquid in 2032 coin cell.

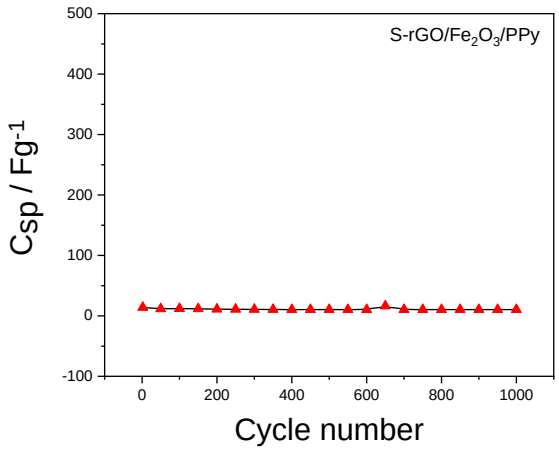

Fig. 5 Stability tests of S-rGO/Fe_2O_3/PPy nanocomposite at a scan rate of 100 mV×s^{-1}, 1000 charge-discharge measurements.

III. Results & Discussion

SupercapBattery device performances were obtained by 2032 coin cell. The highest energy and power densities were obtained as E= 1.82 Wh×kg^{-1} at 1 mA and P= 517.94 W×kg^{-1} at 10 mA. EIS data were also presented as θ= 29.34º at 12.26 Hz and 73.82% for initial capacitance preservation for 1000 charge-discharge measurements.

IV. Conclusion

Our results have demonstrated that S-rGO/Fe_2O_3/PPy nanocomposites will be considered as a promising symmetrical electrode materials for the next generation of supercapacitor applications. Our target is to focus on the overall supercapbattery device performance in energy storage applications in portable and wearable electronic, transport, electrical and hybrid vehicles.

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