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SupercapBattery performances of rGO/NiO/PPy nanocomposite in ionic liquid electrolyte

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Abstract **–** In this study, 3 different materials were combined to form hybrid nanocomposite for SupercapBattery applications. reduced graphene oxide (rGO), Nickel oxide (NiO), 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}= 1724.61 $F \times g^{-1}$ at 2 $mV \times s^{-1}$ (electrode weight was obtained as 42,7 mg).

Keywords – Long-Term Stability, 2032 Coin Cell, Energy Density, GCD Measurements

I. INTRODUCTION

Supercapacitors are called as electrochemical energy storage devices. They have attracted considerable attention during the past decades due to their advantages over conventional dielectric capacitors [1]. Unlike batteries, supercapacitors store their energy in an electrostatic field rather than in chemical form [2, 3]. In supercapacitors applications, conducting polymers are generally used. Batteries have long cycle life and high energy density [4, 5].

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 mass loading of electrode of 42.7 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 [6].

B. rGO synthesis

A microwave oven was performed to reduce GO at 180 Watt and 20 min. So, rGO was obtained by centrifuged 3 times using DI water and ethanol [7].

C. NiO synthesis

$NiNO_3 \times 6H_2O$ nanoparticles were synthesized by sol-gel method and NiO was obtained 17,4 g $NiNO_3 \times 6H_2O$ (0,3 M) dissolved in 200 ml DI water with a magnetic stirrer. Then drop by drop into the $NiNO_3 \times 6H_2O$ solution in a magnetic stirrer at 75 ^oC at 300 rpm until a homogeneous green color. 1.3 M, 200 ml NaOH solution prepared in a seperate beaker was added dropwise to the mixture at 70 oC. Then

product obtained in two phases was filtered to obtain a green colored gel [8]. The resulting gel was dried at 110 oC for 24 h. Samples prepared to obtain NiO in powder from with a single dispersion were crushed in a mortar and black NiO nanoparticles, which were obtained with a heating rate of 4 ^{o}C /min at 400 oC in a muffle furnace and purified with DI water, methyl and ethyl alcohol.

Fig. 1 Synthesis pictures for Nickel oxide.

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 ^{o}C for 1.5 h [9].

Fig. 2 Synthesis pictures for polypyrrole.

E. *Electrochemical performances of SupercapBattery device*

rGO/NiO/PPy nanocomposite were measured by CV, GCD and EIS measurements.

F. *CV measurements*

CV plots of rGO/NiO/PPy nanocomposite at different scan rates from 1000 mV×s^{-1} to 2 mV×s^{-1} were given in Figure 3.

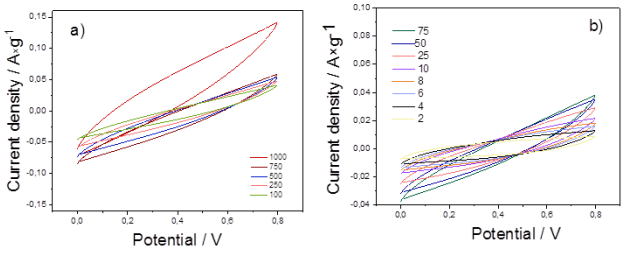

Fig. 3 CV plots of rGO/NiO/PPy nanocomposite at different scan rates, a) 1000-100 mV×s^{-1}, b) 75-2 mV×s^{-1}.

The lowest specific capacitance was obtained as C_{sp}= 21.27 F×g^{-1} at 1000 mV×s^{-1}. However, the highest specific capacitance was found as C_{sp}= 1724.61 F×g^{-1} at 2 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 3).

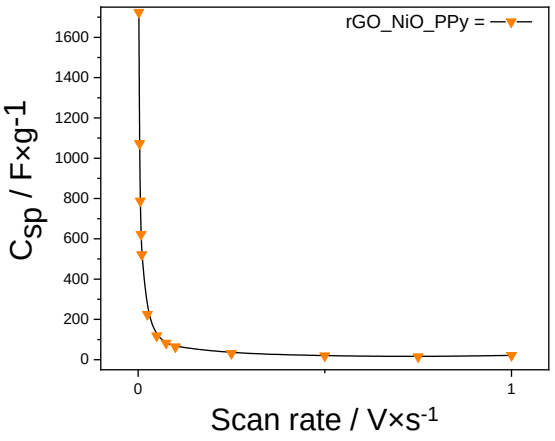

Fig. 4 C_{sp} vs. Scan rate plot of rGO/NiO/PPy nanocomposite at different scan rates from 1000 to 2 mV×s^{-1}.

G. *GCD measurements*

GCD plots of rGO/NiO/PPy nanocomposite was given at constant current density from 0.1 A×g^{-1} to 10 A×g^{-1} as shown in Figure 5. The highest specific capacitance was obtained as C_{sp}= 1.66 F×g^{-1} at 0.1 mA by GCD measurements.

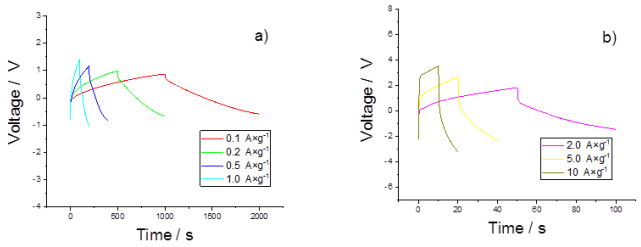

Fig. 5 GCD plots of rGO/NiO/PPy nanocomposite at constant current density from 0.1 A×g^{-1} to 10 A×g^{-1}.

H. *EIS measurements*

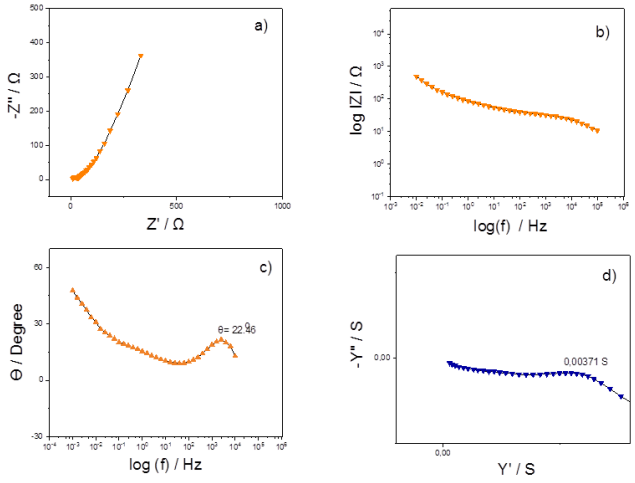

Fig. 6 EIS plots of rGO/NiO/PPy nanocomposite a) Nyquist plot, b) Bode-magnitude plot, c) Bode-phase plot, d) Admittance plot.

EIS plots of rGO/NiO/PPy nanocomposite were given in Figure 6. Specific capacitance was obtained as C_{sp}= 1.03 F×g^{-1} from Nyquist plot. Double layer capacitance and phase angle were obtained as C_{dl}= 0.27 F×g^{-1} and θ= 22.46^{o} at 3179.99 Hz from Bode-magnitude and Bode-phase plots, respectively. Admittance plots defined conductivity of nanocomposite material (Y″= 0.00371 S).

İ. Stability tests

The stability plots of the rGO/NiO/PPy nanocomposite for 2032 coin cell were given charge/discharge device performances for 1000 cycles (Fig. 7). The first capacitance value after 1000 charge/discharge performances were obtained as 102.63% in ionic liquid in 2032 coin cell. The initial capacitance value was exceeded to 100% due to the wettability and electrode activation process depending on the cycle increase [10, 11].

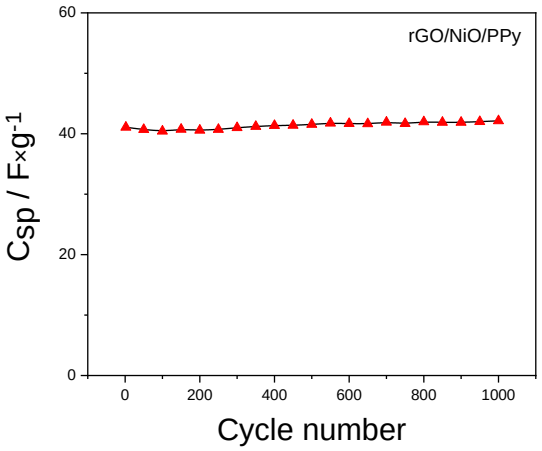

Fig. 7 Stability tests of rGO/NiO/PPy nanocomposite at a scan rate of 100 mV×s^{-1}, 1000 charge-discharge measurements.

II. RESULTS & DISCUSSION

SupercapBattery device performances were obtained by 2032 coin cell. The highest energy and power densities were obtained as E= 1.31 Wh×kg^{-1} at 10 mA and P= 484.77 W×kg^{-1} at 10 mA. EIS data were also presented as θ= 22.46^{o} at 3179.9 Hz and 102.63% for initial capacitance preservation for 1000 charge-discharge measurements.

III. CONCLUSION

Our results have demonstrated that rGO/NiO/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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