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Investigation of the electrochemical behavior of ZIF-67 @ carbon nanotube and graphene oxide as potential electrode active materials for supercapacitors

A. Ghasemi Yeklangi[a], F. Rahimi[a], S. Akbari[a]*

[a]NanoSciTec GmbH, Hermann Weinhauser str. 67, Munich, 81867, Germany

Abstract

Nanocomposites composed of zeolitic imidazole framework (ZIF) and carbon nanotube (CNT) and graphene oxide (GO) have been synthesized by a simple ultrasonic method in atmospheric condition. Electrochemical techniques like cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy have been used for measuring electrochemical properties of samples using 6 M NaOH as electrolyte. Nanocomposite samples of ZIF-67 with CNT and GO showed high specific capacity of 248 F/g and 230 F/g, respectively. These values are much higher than that of absolute ZIF-67 sample. In addition to pseudocapacitance behavior, the internal resistances of nanocomposite samples are less than ZIF-67 sample that shows the beneficial effect of added carbon materials.

Keywords: *Pseudocapacitance, Zeolitic Imidazole Framework, Carbon Nanotube, Graphene Oxide, Metal-Organic Framework.*

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* Corresponding author: S. Akbari. Tel.: +49-151-664-32106   E-mail address: somayeh.akbari@nanoscitec.com

1. Introduction

Electrochemical capacitors or supercapacitors are a group of energy storage devices that are recently investigated because of their high power density and long cycle life [1]. There are two energy storage mechanisms in supercapacitors including the electric double layer capacitance, and pseudocapacitance. Electric double layer capacitance is the main electric energy storage mechanism in supercapacitors and it works based on carbon material in commercial supercapacitors [2]. Carbon materials have low capacitance despite of the long cycle life and, in the contrary, metal oxides have high capacitance due to their pseudocapacitance behavior and low cycle life [3]. Therefore, it is important to find new materials that poses these two features at the same time and improve the properties of prepared supercapacitors.

Metal-organic frameworks (MOFs) are a new group of compounds consisting of supermolecular building blocks with noteworthy specifications [4, 5]. They have one-, two- or three-dimensional structures made by coordination of metal ions and organic ligands as linkers. One of the most important properties of MOFs is porosity that causes their specific applications in the field of gas storage, gas separation, catalyst, and water softeners [6]. Recently, MOFs have attracted great attention in the field of electrochemical energy storage devices without any special chemical treatment, or after some chemical treatments and in combination with some compounds such as carbon based materials and metal oxides [7]. Their unique structures cause some more qualities like high thermal stability, uniform cavities, controllable and designable structures as well as their high surface area lead to show long cycle life and high specific capacitance when they use in preparation of supercapacitors [8].

One of the new class of MOFs are Zeolitic imidazole frameworks (ZIFs) has received considerable attention over the last few years. Like other MOFs, these materials have high thermal and chemical stability that make them suitable candidates for using in different areas such as gas absorption and gas separation [9-14]. The large surface area of ZIFs improve ion transport and the diffusion in these structures that in turn lead to boost the redox properties [15, 16]. Usually ZIFs show tetrahedral frameworks similar to zeolite topologies with transition metals (Co, Cu, Zn, etc.) in center, linked by imidazolate ligands [17]. One of the most studied ZIF materials is ZIF-67 [$Co(HMe-Im)_2$, HMe-Im=2-methylimidazolate], with a zeolite SOD (sodalite) topology.

Initially, when MOFs started to be used as a supercapacitor electrode material, Co8-MOF-5 was applied as an electrode for EDLCs [18]. Afterward, a doctor bladed Co-based MOF film was used for supercapacitor and exhibited capacitance up to 206 F/g, with 1/5% capacitance loss after 1000 cycles [19]. Thereafter, Wei et al. [20] explored a Ni-based MOF for supercapacitor electrode, and it showed large specific capacitance of 1127 F/g at rate of 0.5 A/g and long cycle life. Due to low electrical conductivity of metal-organic frameworks, many nanocomposites are made with them to increase their conductance. For instance, ZIF-67 nanocomposite with conductive polyaniline (PANI) showed good capacitance behavior and flexibility [21]. Recently a nanocomposite of ZIF-67 and graphene oxide was used for supercapacitor electrode material and exhibited 240 F/g specific capacitance [22].

Here, we synthesized nanocomposites of ZIF-67/CNT successfully and ZIF-67/GO by a simple ultrasonic method in ambient condition. The electrochemical properties of the prepared samples were electrochemically investigated by some techniques including cyclic voltammetry, galvanostatic charge/discharge, and electrochemical impedance spectroscopy.

2. Materials and Methods

2.1 Synthesis of graphene oxide

Graphene oxide (GO) was prepared by the well-known modified hummers method [23]. The produced solution was centrifuged and the resulting precipitates were dispersed in deionized water. The pH of the resulting brown solution was adjusted to 5-6 with ammonia solution to help the exfoliation of GO. The remaining graphite aggregates were removed by centrifugation at 9000 rpm. The resulting solution was dried in oven at 100°C and the remaining precipitates were gathered in the form of powder.

2.2 Synthesis of ZIF-67

For synthesis of ZIF-67 a facile room temperature method was selected according to Gross et al procedure [24], briefly 0.707 g of $Co(NO_3)_2.6H_2O$ (2.46 mmol) was dissolved in 50 ml of deionized water. Another solution was prepared by solving 3.244

g HMe-Im (39.5 mmol) and 2 g Triethylamin (TEA, 39.52 mmol) in 50 mL deionized water and was stirred until complete dissolution. Therefore, the cobalt solution was added to the HMe-Im/TEA solution and an unclear purple suspension was created; the resulting suspension was stirred for 30 minutes to let the reactions completely happen. The ZIF particles were separated via centrifugation, and the remaining clear liquid was removed, and the solid was resuspended in deionized water. The ZIF particles were stayed in deionized water for 12 hours, were separated via centrifugation, and resuspended in deionized water again. After another 12 hours, the ZIF particles were separated via centrifugation and were collected and dried in a 130°C oven. For the final preparation of ZIF-67 particles, the sample was dried and activated in a vacuum oven at 150°C for 6 hours.

2.3 Synthesis of ZIF-67/CNT and ZIF-67/GO

Nanocomposites of ZIF-67/CNT and ZIF-67/GO were synthesized with the same procedure. First, 25 mg of Multiwall carbon nanotube was added to 25 ml of DI water and sonicated for about 30 minutes. Then, 75 mg ZIF-67 was added to the suspension and sonicated for 30 min. Finally; the composite suspension was sonicated for about 30 min again. The suspension was centrifuged for 5 min with 9000 rpm and the sediments were separated. The solid remaining was dried in oven at 100°C for 12 hours.

2.4 Electrochemical measurements

Electrode materials were prepared by combining the active material, carbon black and poly (vinylidene fluoride) as binder with a weight ratio of 70:20:10. Afterward, the mixture was dispersed in N-Methyl-2-pyrrolidone (NMP) and sonicated for about 30 minutes. Sonication made the mixture hot and the solution was placed in room temperature to chill, then it was sonicated for a 30 minutes period again to get a stable and homogenous solution. The prepared solution was used for spray coating the active material on carbon paper. After each time of spraying, the sample was left to get dry and again another layer was sprayed. Finally, the electrodes were dried in vacuum oven in 100°C for 3 hours. The surface area of prepared electrodes was 1 cm^2.

Some techniques including cyclic voltammetry (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) were done using a SP-150 potentiometer (Bio-logic, France). A conventional three-electrode cell was made with a saturated calomel electrode (SCE) as reference electrode and Pt plate as the counter electrode. All experiments were performed at room temperature and in 6 M NaOH electrolyte.

2.5 Structural characterization

Powder X-ray diffraction (XRD) patterns were recorded at room temperature on a MiniFlex600 diffractometer using CuKα radiation (λ=1.54059 Å) at 40 kV and 40 mA. Scanning electron microscopy (Phenom world, Netherlands) was used for investigating topological and morphological properties of the prepared nano powders.

3. Results and discussion

3.1 Material characterization

Crystal structures of ZIF-67, ZIF-67/CNT and ZIF-67/GO samples were characterized by XRD method. Figure 1 illustrates XRD patterns of of ZIF-67, ZIF-67/CNT and ZIF-67/GO samples, respectively. The common peaks of ZIF-67 are seen in this diagram as shoen in Figure 1 (a). The XRD patterns of nanocomposite samples show the added peaks of graphitic structures in 2Θ=42°. For ZIF-67/CNT and ZIF-67/GO XRD patterns, the diffraction peaks are mostly similar to ZIF-67, because the peaks of GO and CNT are too weak in comparison with ZIF-67 peaks. SEM analysis was used to study the morphology of all samples. As we can see in Figure 2 the dodecahedral shape of ZIF-67 particles is obvious. The average size of ZIF-67 crystals is about 500 nm. Figure 3 illustrates SEM image of ZIF-67/CNT nanocomposite; the homogeneous distribution of CNTs between ZIF-67 particles is clear. The carbon nanotubes are a good platform for making ZIF-67 particles in access for electrolyte ion and prevent ZIF particles from accumulation. Figure 4 shows SEM image from nanocomposite of ZIF-67/GO sample. The sheet like structure of GO particles is clearly seen and also we can observe the uniform distribution of GO sheets between ZIF particles.
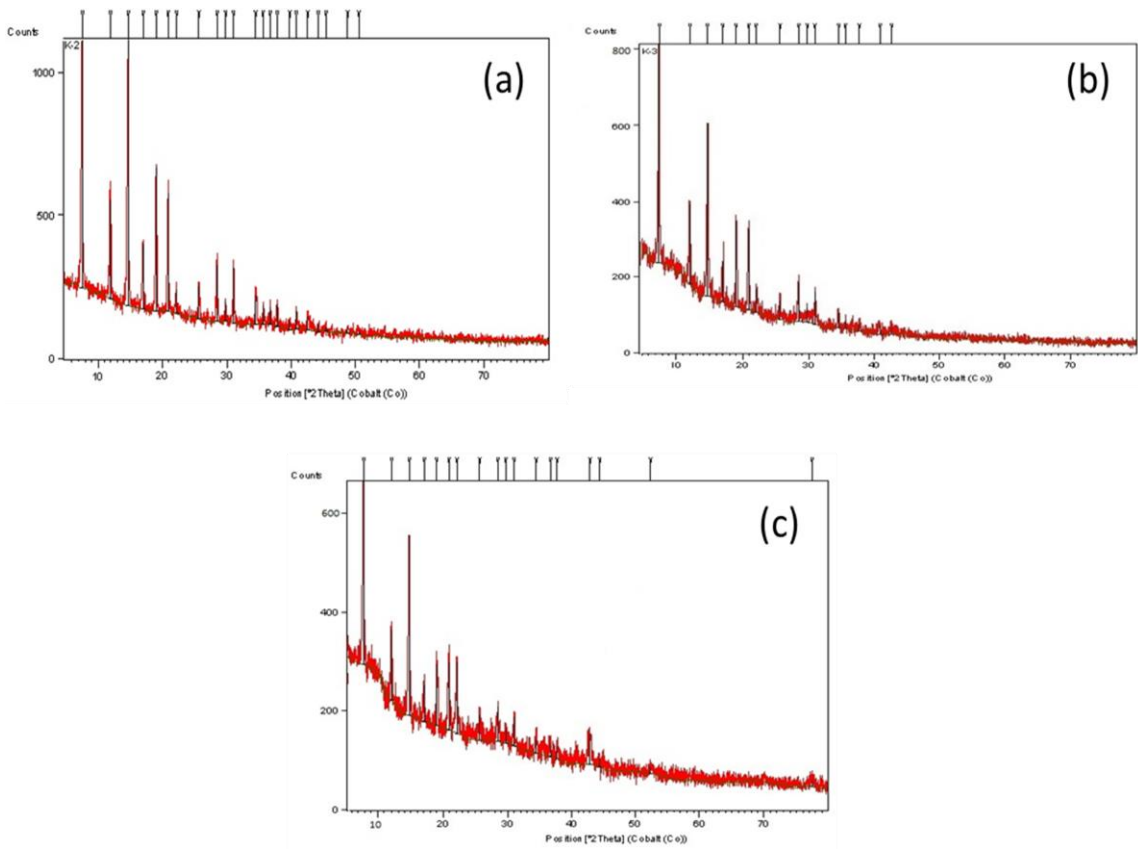
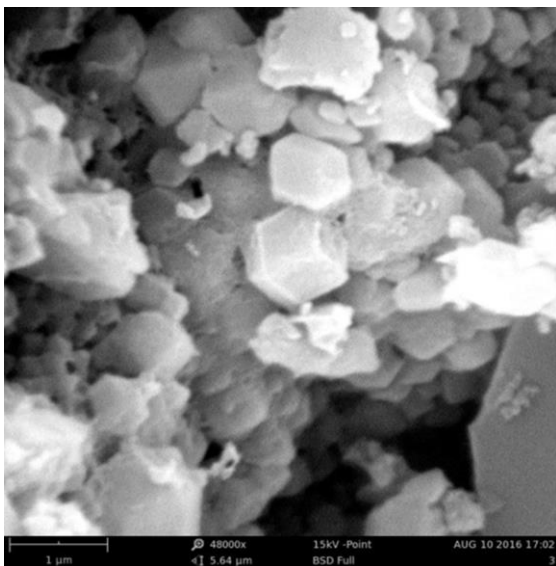Figure 1. XRD patterns of ZIF-67 (a), ZIF-67/CNT (b) and ZIF-67/GO (c) samples.

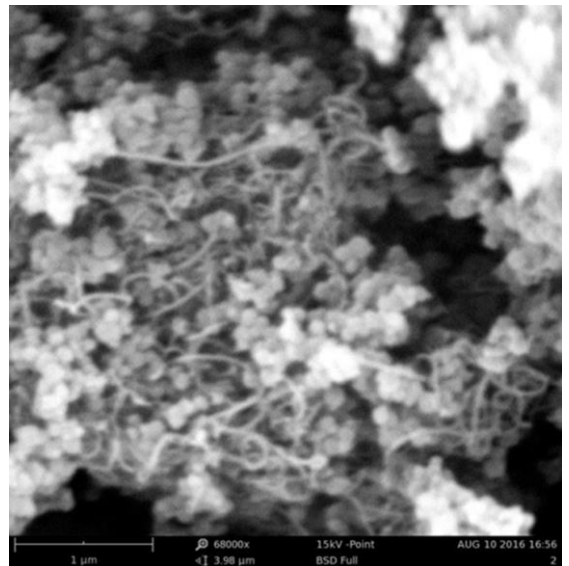Figure 2. SEM image of ZIF-67 sample
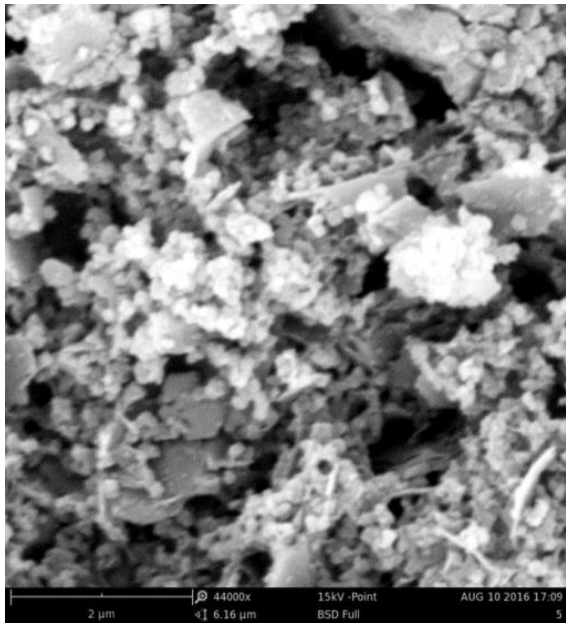

Figure 3. SEM image of ZIF-67/CNT

Figure 4. SEM image of ZIF-67/GO

3.2 Electrochemical characterization

To investigate the electrochemical characteristics of ZIF-67, ZIF-67/CNT and ZIF-67/GO, Cyclic voltammetry (CV) studies were used and results are illustrated in Figure 5. The characteristic peaks in CV curves of the ZIF-67 and nanocomposite samples propose that the capacitance reactions are based on surface charge transfer and show pseudocapacitive behavior. With increasing scan rates, the cathodic and anodic peaks of CV curves move toward higher potentials. This can be assigned to more electric polarization in higher scan rates and irreversible reactions.

According to previous studies, the peaks of ZIF-67 CV curve are related to Faradic redox reaction of Co(II) ions (Co^{2+}/Co^{3+}) in the framework, maybe intervened by the OH^- ions in the alkaline electrolyte [25].

For evaluating the power performance of the electrodes at different current densities, the following equation was used:

$$C = \frac{\int IdV}{2vm\Delta V}$$

Where C is the specific capacitance (F/g), v is the scan rate (V/s), m is the mass of active material (g), ΔV is the potential window (V) and IdV represents the area under the CV curve (W). Figure 6 shows specific capacitance of different samples with various scan rates. It is clear that specific capacitance decreases with increasing scan rate. The highest value of specific capacitance is indicated by the ZIF/CNT nanocomposite sample as it shows 248 F/g specific capacitance at scan rate of 5 mV/s and 120 F/g at 100 mV/s. Furthermore, we can see that at scan rate of 5 mV/s the pure ZIF-67 electrode shows specific capacitance of 116 F/g, about half of the amount gained for ZIG-67/CNT electrode. The ZIF-67/GO electrode also exhibited good specific capacitance of 218 F/g. At low scan rates, the specific capacitances are higher and that is because of longer time available for ions to diffuse into the pores of structures and with increasing scan rate, this time gets shorter and ions cannot go through the pores.

The galvanostatic charge/discharge curves of all electrodes are shown in Figure 7. The charge/discharge curves are not linear and there is not symmetry between the charge and discharge parts which is due to the pseudocapacitance behavior of ZIF-67.

The specific capacitance of samples can be calculated from the charge/discharge curves by the following equation:

$$C = \frac{I \times \Delta t}{\Delta V \times \Delta m}$$

Where C is the specific capacitance, I is the discharge current, Δt is the discharge time, ΔV is the potential window and Δ is the sample electroactive material mass.

The specific capacitance of ZIF-67/CNT nanocomposite at a current density of 1 A/g was measured to be 238 F/g and this value for ZIF-67/GO sample was 210 F/g while for pure ZIF-67 it was 103 F/g. The specific capacitance of nanocomposite samples is more than twice times in comparison to the pure sample with longer discharge times. The improved capacitor behavior of nanocomposite electrodes can be attributed to the increased surface area by carbon based material. In other words, the carbon nanotubes or graphene oxide particles provide an area for ZIF particles to be more in access for ions

in electrolyte. Furthermore, carbon materials form a kind of hierarchical structure that ZIF particles could lie on them, so ZIFs could exhibit all of their potential capacitance. In contrary, in the pure ZIF electrode, the ZIF particles agglomerate and most of them are not in access for electrolyte ions so the specific capacitance of pure ZIF is lower than the nanocomposite samples. Moreover, one of the most reported weaknesses of MOFs is their high electric resistance and carbon

materials help to increase their conductivity and improve their electron transport properties [26, 27].

One of the widely used tests for exhibiting electrochemical characteristics of electrode materials is electrochemical impedance spectroscopy (EIS). Figure 8 shows Nyquist plots of ZIF-67, ZIF-67/CNT and ZIF-67/GO electrode materials in the frequency range of 0.1 Hz and 100 kHz.
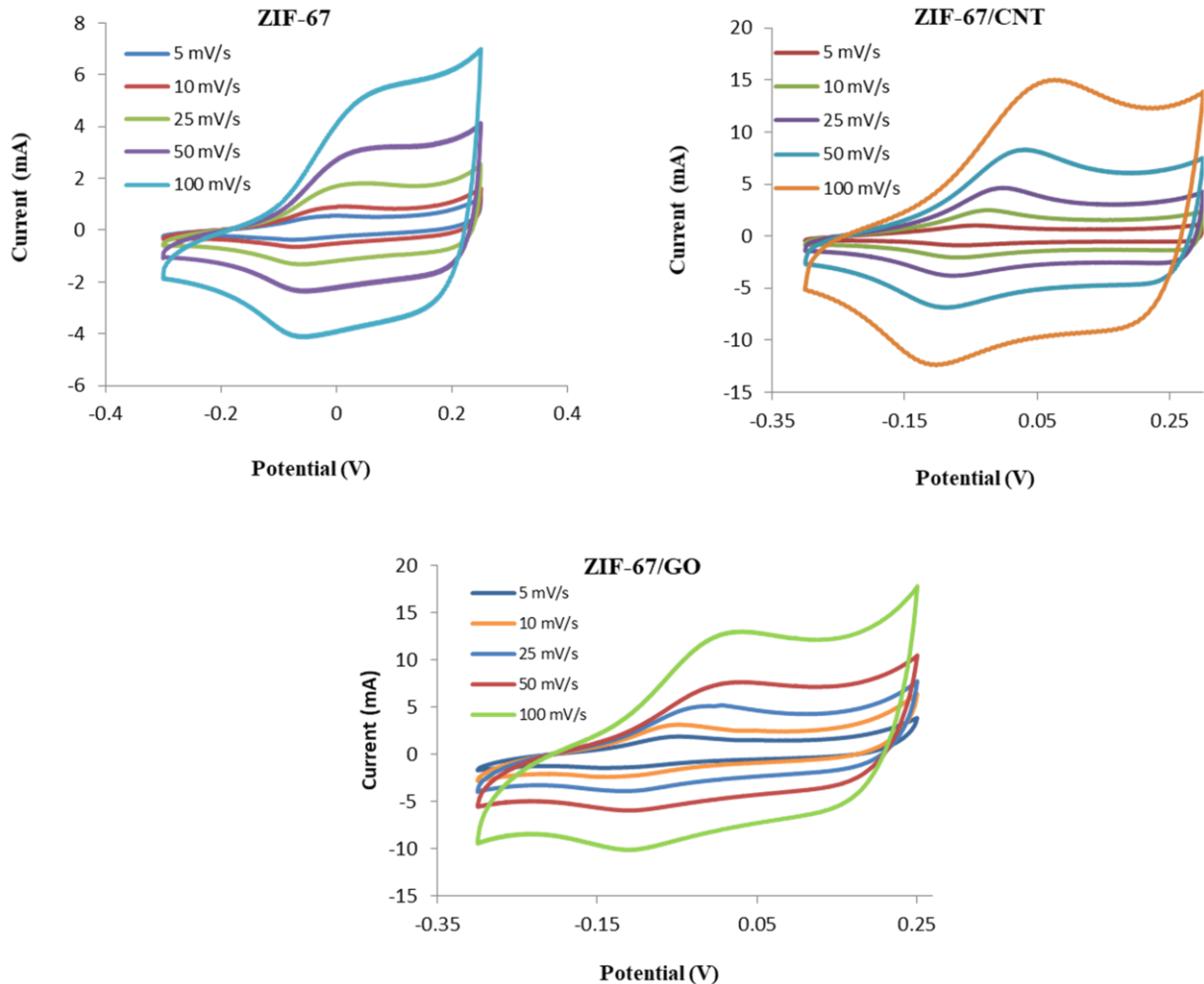

Figure 5. Cyclic voltammetry curves of ZIF-67, ZIF-67/CNT and ZIF-67/GO electrod
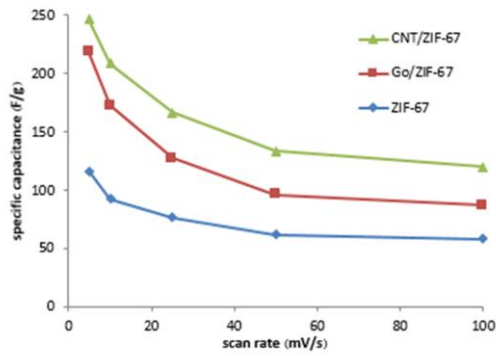
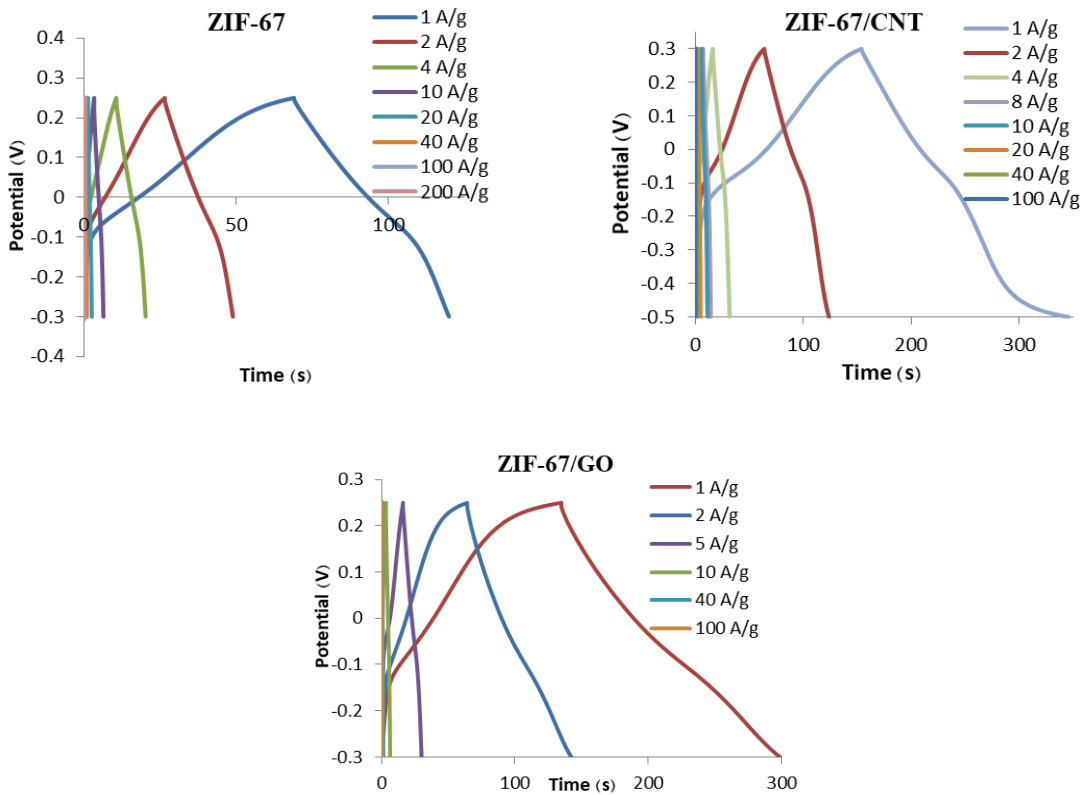Figure 6. Specific capacitance of samples with different scan rate values.

Figure 7. Charge/discharge curves of ZIF-67, ZIF-67/CNT and ZIF-67/GO samples.

There are two parts in impedance spectra of the electrodes, a quasi-semicircle at higher frequency and a linear part at lower frequency. X-axis of the diagrams show the real part of impedance and the bulk resistance (Rs) can be obtained from that axis in the high frequency range. Although, the charge transfer
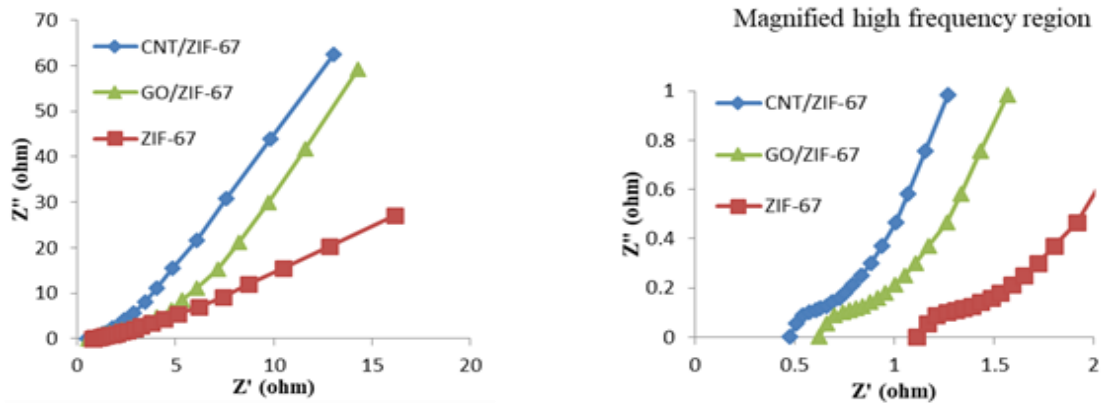
Figure 8. Nyquist plots of ZIF-67, ZIF-67/CNT and ZIF-67/GO.

resistance (Rct) on the surface of electrode with the electrolyte is obtained from the semicircle part and the diameter of the circle exhibit the magnitude of Rct. Moreover, the steeper slope at lower frequency demonstrates an ideal capacitive behavior and higher diffusion rate for ions of electrolyte. Figure 8 (magnified high frequency part) illustrates a Rs value of 0.47 Ω for ZIF-67/CNT nanocomposite and the value of 0.62 Ω for ZIF-67/GO sample while this value

for pure ZIF-67 sample is 1.1 Ω. In comparison with bare ZIF-67, the diameter of semicircles of nanocomposite samples is smaller and that's because of smaller interfacial charge transfer impedance. Moreover, the ZIF-67/CNT and ZIF-67/GO nanocomposite electrodes exhibited a steeper slope in the low frequency region in comparison with bare ZIF-67 electrode, which manifests the better diffusive impedance of OH—ions within the electrode. Finally,
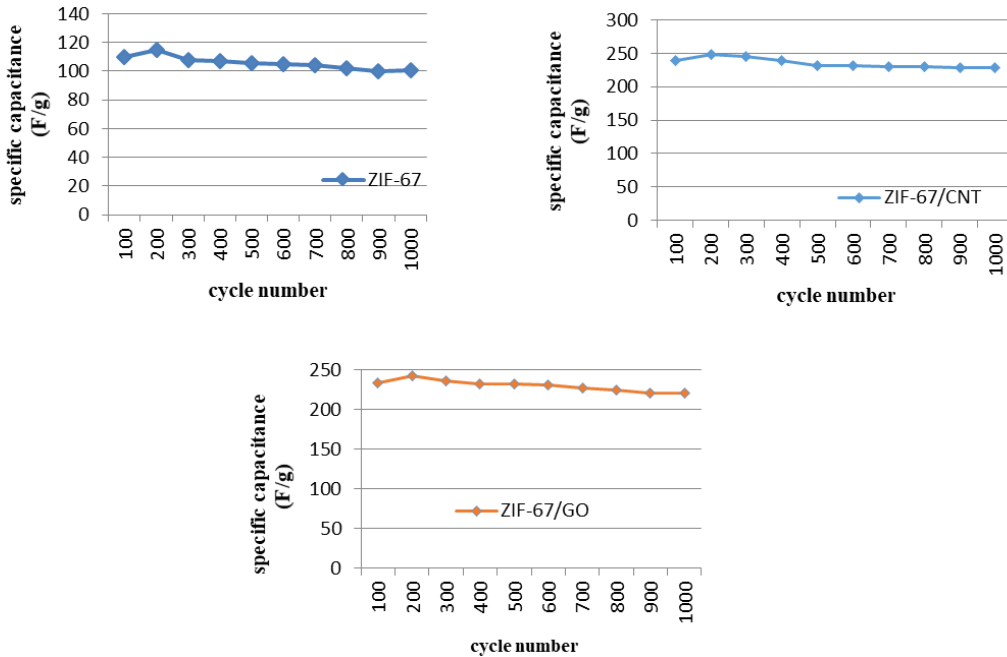

Figure 9. Cycling performance of ZIF-67, ZIF-67/CNT and ZIF-67/GO.

it can be concluded that good electrical conductivity and ion diffusion behavior of nanocomposite samples resulted in better pseudocapacity.

Another important electrochemical parameter of a pseudocapacitor electrode material is cyclic life. The cycling tests of ZIF-67/CNT, ZIF-67/GO and bare ZIF-67 electrodes are illustrated in Figure 9. As it is shown in Figure 9 the bare ZIF-67 sample exhibited about 9 percent retention in capacitance after 1000 cycles of charge/discharge with a discharge rate of 1 A/g. this amount was 4% and 5% for the ZIF-67/CNT and ZIF-67/GO nanocomposite, respectively. These values show improvement rather than previous works especially they show better cycling life for prepared nanocomposites [22, 26].

4. Conclusion

Two nanocomposites of ZIF-67/CNT and ZIF-67/GO were prepared through a simple method by aid of ultrasonic at room temperature. The resulting ZIF-67/CNT and ZIF-67/GO samples exhibited a high specific capacitance of 238 F/g and 210 F/g, respectively, at a scan rate of 5 mV/s. The capacitance was significantly enhanced, which approves that the ZIF nanocrystals on the surface of carbon nanomaterials were instrumental in improving the electrochemical characteristics of the electrode material. Also, nanocomposite electrodes showed good cycle life and capacitance retention of about 5%, after 1000 cycles. This approach can be extended to other kinds of MOFs, and also can be suitable to use in other energy storage devices and batteries.

Conflict of interest

The authors declare that they have no conflict of interest.

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