A novel route for electrosynthesis of CuCr_2O_4 nanocomposite with p-type conductive polymer as a high performance material for electrochemical supercapacitors

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Abstract

In this work, supercapacitive performance of polypyrrole copper chromate nano particles (Ppy/CuCr₂O₄ NPs) was studied. CuCr₂O₄ NPs with the average size of 20 nm were synthesized simply by hydrothermal method and the composite electrodes were then electropolymerized on the surface of glassy carbon electrode. Common surface analysis techniques such as scanning electron microscopy (SEM), transmission electron microscopy(TEM) and Fourier transform infrared (FTIR) were used to study the morphology and structure of the composite. Furthermore, for electrochemical evaluation of composite electrodes, techniques including cyclic voltammetry (CV), galvanostatic charge discharge (CD) and impedance spectroscopy (EIS) were used. Using cyclic voltammetry, the specific capacitance values of Ppy and Ppy/CuCr₂O₄ NPs were calculated to be 109 and 508 F g⁻¹, respectively. Results show that using CuCr₂O₄ NPs in the structure of polymeric films led to increased specific capacitance of composite electrodes more than four times that of poly pyrrole. Increasing the conductivity and stability of composite electrodes through continuous cycles are the other advantages of using CuCr₂O₄ NPs as active materials in a polymeric structure.

Keywords:

Poly pyrrole, CuCr₂O₄ NPs, Supercapacitors, Electropolymerization, Nanocomposite

1 Introduction

Nowadays, exhausting fossil fuels have attracted much attention to developing renewable energy and energy storage devices such as electrochemical capacitors (ECs)[1, 2] . ECs are one of the most well-known energy storage groups, which can fill the gap between the batteries and capacitors [3] . Active materials and energy storage mechanisms are two major groups studied by scientists. Carbon materials, metal oxides and conductive polymers (CPs) are three categories of active materials, which have been used in ECs. The first stores the electrical energy at the double layer interface and the others store the energy by a charge transfer reaction [4, 5]. The most famous CPs reported as EC electrodes are polyaniline, polypyrrole (Ppy), polythiophene and its derivatives [6, 7]. Among these, Ppy has attracted much more attention owing to its features such as ease of synthesis, chemical stability and cost effective production [8, 9]. Generally, CPs suffer from poor stability during continuous cycles due to mechanical collision of counter ions by polymer filaments in dope/undope procedure [10, 11]. It has been shown that the combination of CPs with active nano materials is one of the useful solutions for this problem. Furthermore, the contribution of charge storage process can improve the capacity of the composite electrodes. Many papers have been published about using metal oxides in CP networks to form hybrid electrodes [12, 13]. Nowadays, combined metal oxides are a novel class of active materials, which show an efficient electrochemical behavior. The presence of mixed valence metal cations can provide higher electronic conductivity and electrochemical activity in comparison with single component materials [14-18]. Among the various mixed metal oxides, CuCr_2O_4 is an interesting chromate spinel because of its low cost and non-toxic nature. Recently, this spinel has been used as a photocatalyst in the oxidation of organic compounds such as toluene [19], benzene [20], glycerol [21] etc. Using as active materials in lithium batteries is one the

electrochemical applications of CuCr_2O_4 . However, there is no report on the possibility of employing CuCr_2O_4 active material for ECs. Therefore, the feasibility of Cr based compounds as active materials for ECs remains interesting. In our previous studies, CPs have been used as a conductive base for metal oxide nano materials [22-25]. In this work, the application of CuCr_2O_4 NPs, as active materials for application in ECs is reported for the first time. For this purpose, the polypyrrole/ CuCr_2O_4 nano particles (Ppy/ CuCr_2O_4 NPs) composite electrodes were electrochemically synthesized and their supercapacitive performance in 0.1 M H_2SO_4 solution were thoroughly investigated.

2 Experimental

All the chemicals used in this work, purchased from Merck Chemical Co., were of analytical grade and were used without any further purification. Double distilled water was used throughout the experiments.

2.1 Material characterization and electrochemical evaluation

Electrochemical experiments were carried out using an Autolab General Purpose System PGSTAT 30 (Eco-chime, Netherlands). A conventional three electrode cell with a glassy carbon electrode with an area of 0.03 cm^2 served as the working electrode. A platinum wire and an Ag/AgCl reference electrode (Argental, 3 M KCl) were used as the counter and reference electrodes, respectively. The EIS experiments were conducted in the frequency range between 100 kHz and 15 mHz with a perturbation amplitude of 5 mV.

Morphological investigations of the polymeric films were carried out using SEM (Philips XL 30). The Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 6700 spectrophotometer with the sweeping range of $500\text{--}4500 \text{ cm}^{-1}$ at a 4 cm^{-1} resolution with KBr as compressed slices. X-ray diffraction patterns were obtained from an X-ray diffractometer (PANalytical X'Pert-Pro) with a Cu-K α mono-chromatized radiation source and a Ni filter. The transmission electron microscopy (TEM) was performed using a CEM 902A ZEISS transmission electron microscope with an accelerating voltage of 80 kV.

2.2 Synthesis of CuCr_2O_4 nano particles

Firstly, 15.4 g of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 5.54 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were dissolved in 50 ml of distilled water to make a 1M solution of the corresponding nitrates. The prepared nitrate solution

was then introduced into another beaker containing 50 ml of distilled water at 60°C together with NaOH (1M). During precipitation, the pH was kept constant at 7. After the reaction was complete, the precipitation was aged in mother liquor for 5 h. After drying at 90 °C, the product was calcined at 500 °C for 5 h.

2.3 Synthesis of the electrodes

Ppy/CuCr₂O₄ NP composite was synthesized by CV technique in 1 M KCl solution containing pyrrol monomer (0.1 M), CuCr₂O₄ NPs (0.2 wt.%) and sodium dodecyl sulfate (0.005 M) dispersed in solution by sonication. The ppy electrode was synthesized in the same solution without CuCr₂O₄ NPs and sodium dodecyl sulfate. Electropolymerizations were conducted by 10 cycles at the sweep rate of 50 mV/s in the potential range of 0 to 1 V. The mass of Ppy films was approximated assuming a current efficiency of the electropolymerization process of 100%, using Faraday's law [25].

3 Results and discussion

Fig. 1 presents the TEM and SEM images of CuCr_2O_4 NPs and composite electrodes, respectively. As observed, the average size of CuCr_2O_4 NPs was obtained about 20 nm (Fig.1 (A)) and these nano particles dispersed in the Ppy network to form composite electrodes (Fig. 1(B)). As illustrated, nano particles are uniformly distributed in the Ppy structure, showing that the electrochemical synthesis of Ppy/ CuCr_2O_4 NPs has been successful. Distribution of nano particles in the structure of Ppy film can enhance the active surface of nano particles and therefore increase the active sites for charge transfer reaction.

Figure 1. TEM images of CuCr_2O_4 NPs (A) inset: histogram of size distributed, SEM images of Ppy/ CuCr_2O_4 NPs electrode (B).

Fig. 2(a) presents the XRD patterns of the CuCr_2O_4 NPs, Ppy and composite electrodes. The typical peaks of CuCr_2O_4 NPs corresponding to (112), (211), (202), (224) and (303) related to the hexagonal structure appear in the pattern at 31° , 35° , 38° , 65° and 56° , respectively (JCPDS 05-0657). By insertion of CuCr_2O_4 NPs in the structure of Ppy, these diffraction peaks remain in XRD pattern of composite electrodes and get sharper indicating the structural strength of composite materials **Error! Reference source not found.** presents the FT-IR spectra of CuCr_2O_4 NPs, Ppy and composite electrodes. As it can be observed, the characteristic peak located at 3435 cm^{-1} is due to N-H stretching vibration, which is consistent with the literature data. The characteristic peaks located at 1634 and 1460 cm^{-1} are assigned to the asymmetric and symmetric stretching modes of the PPY ring, respectively [26]. Furthermore, the peak located at 1044 cm^{-1} is attributed to C-H deformation vibrations of Ppy. According to our previous papers [27, 28], the spectra of composite electrodes are similar to those of polymeric ones in the main peaks although the different intensity suggests the interaction between the Ppy and CuCr_2O_4 nanoparticles.

Figure 2. X-ray diffraction spectra of the hydrothermally synthesized CuCr₂O₄ NPs, Ppy and composite electrodes (a). FT-IR spectra of CuCr₂O₄ NPs, Ppy and Ppy/CuCr₂O₄ NPs(b).

CV is one of the electrochemical techniques used for describing the electrochemical nature of various electrodes [29, 30]. Fi. 3(a) shows the CVs of polymeric and composite electrodes in 0.1 M H₂SO₄. Very highly efficient supercapacitive behavior of Ppy/CuCr₂O₄ NPs can be observed in CV curves. As the figures show, CuCr₂O₄ NPs have enhanced the electrochemical performance of composite electrodes compared with the polymeric one. Increasing the capacitance of electrodes, stability of current and their symmetrical shape are some advantages of using CuCr₂O₄ NPs in Ppy network. The specific capacitance (SC) values of the electrodes were calculated from the CV curves according to the following equation:

$$C = \frac{I}{mv} \quad (1)$$

where I is the current, m is the mass of reactive material and v is the potential scan rate. The SC of Ppy and Ppy/CuCr₂O₄ NPs calculated by equation (1) are 168 and 725 F/g, respectively. Enhancing the SC of composite electrode nearly five times is an evidence of the synergistic effect between CuCr₂O₄ NPs and Ppy network.

Figure 3. CVs of Ppy and composite electrodes at the scan rate of 25 mV/s (a), CVs of Ppy/CuCr₂O₄ NPs electrodes at various scan rates (b), SC of Ppy and Ppy/CuCr₂O₄NPs as a function of scan rate (c), CD curves of Ppy and Ppy/CuCr₂O₄ NPs electrodes at the current density of 2.2 A/g (d), CD curves of composite electrodes at various current densities (e) and variation of SC of composites against current density(f).

To study the kinetic reversibility and electrochemical performance of the composite electrode in various sweep rates, CVs of Ppy/CuCr₂O₄ NPs electrode were recorded at different scan rates from 5 to 300 mV s⁻¹ (Fig. 3b). As illustrated, at low scan rates, the CVs of composite electrode exhibit a typical quasi-rectangular shape indicating good charge propagation at the electrode/electrolyte interface. With increasing the scan rate, current response increased accordingly and the CV curves maintained their quasi-rectangular shape with small distortions, which shows good performance of composite electrode in various dope- undope rates.

Fig. 3(c) shows the SC variation of both electrodes as a function of scan rate over the range of 5 –300 mV in 0.1 M H₂SO₄ solution. As observed, with increasing the scan rate, SC of both electrodes decreased, which is related to the slow diffusion of ions in the matrix electrode. This phenomenon leads to inaccessibility of deeper porosities for joining in dope – undope process and results in non-ideal rectangular shapes of CVs at high scan rates [31-33].

Galvanostatic charge/discharge (CD) method was used to highlight the capacitance characteristic of Ppy/CuCr₂O₄NPs composite electrodes. CD diagrams of Ppy and Ppy/CuCr₂O₄NPs electrodes are shown in Fig. 3(d). Symmetrical triangle curves of two electrodes indicate the good reversibility of the both electrodes in charge and discharge processes [34].

Here, SC has been measured according to the charge/discharge curves using Eq. (2).

$$SC = \frac{I}{\left(-\frac{\Delta E}{\Delta t}\right)m} \quad (2)$$

where I is the applied current, $-\Delta E/\Delta t$ is the slope of the discharge curve after the voltage drop at the beginning of each discharge (ESR) and m is the mass of electrodes. As observed, the perfect electrochemical behavior of two electrodes can result from the symmetrical shape of CD diagrams. The SCs of Ppy and Ppy/CuCr₂O₄ NPs calculated by Eq. (2) are 168 and 750 F/g, respectively. These results confirm the data obtained from CV technique. One of the critical

points, which must be considered, is the role of CuCr_2O_4 NPs in Ppy network. Whereas the magnitude of CuCr_2O_4 NPs is very low, increasing in SC of composite electrodes is very high suggesting a synergistic effect between CuCr_2O_4 NPs and Ppy matrix. The electrochemical performance of composite electrode can be explained by the charge transfer of Cr from III to VI in acidic media, which results in increasing the SC of composite electrodes. Another reason considered in describing the electrochemical performance of composite electrodes is the uniform distribution of CuCr_2O_4 NPs in polymer matrix, which increases the surface area of nano particles and enhances their reactivity [35]. Fig. 3 (e) presents the CD diagrams of Ppy/ CuCr_2O_4 NPs composite electrodes at different current densities. As observed, by increasing the current density, the time needed to reach the cut off potential decreased, which is related to intercalation of ions at the surface of active materials. On the other hand, at low specific currents, all the porosities in electrode/electrolyte interface have can be reacted with ions [29]. The variations of SC against current density are shown in Fig. 3(f). As observed, the maximum SC for composite electrodes is obtained for the current density of 2.2 A/g.

Another feature of electrochemical supercapacitor electrodes is their stability during continuous cycles. Fig. 4(a) presents the stability of two electrodes using continuous CVs in 0.1 M H_2SO_4 at the scan rate of 50 mV/s. As observed, Ppy electrode loses its capacitance to nearly 50% of the initial value in the time range of 0-35000 seconds. However, this phenomenon does not occur in the composite electrode. The pattern shows that by using CuCr_2O_4 /NPs in the structure of polypyrrole, the stability of electrode enhanced owing to increased mechanical resistance of composite material through continuous cycles or charge/discharge process.

EIS is one of most useful techniques used to study the electrochemical performance of ECs [36-45]. Fig. 4(b) presents the Nyquist diagrams of two electrodes in 0.1 M H_2SO_4 solution under

open circuit potential (OCP) conditions. As observed, both diagrams have a semicircular arc in high frequency range followed by a vertical line along the imaginary axis corresponding to the ideal capacitor. The intercept of both diagrams in real part is related to solution/electrode resistance (R_s), which shows that the composite electrode has a lower resistance compared to the polymeric one. Charge transfer resistance (R_{ct}) for the two electrodes can be studied by semicircular arc of Nyquist diagrams [28]. As illustrated in Fig. 4(b), composite electrodes have a very lower R_{ct} against compared with Ppy resulting from the easier charge transfer reaction due to the insertion of $CuCr_2O_4$ NPs in the structure of Ppy. Both electrodes exhibit a nearly linear branch in the low frequency region indicating a decrease in diffusion resistance of the electrolyte ions in the electrode matrix, as expected for a capacitor. The low frequency capacitance (C_{lf}) of each film was determined from the imaginary component of impedance (Z'') at low frequency versus the inverse of frequency (f), using Eq. (3).

$$C_{lf} = \frac{1}{(2\pi f Z'')} \quad (3)$$

From this equation, the SC of Ppy and Ppy/ $CuCr_2O_4$ electrodes were calculated as 160 and 580F/g, respectively. These results showed that the SC of composite electrodes is more than three times higher than that of the polymeric one.

Figure 4. Variation of the stability of two electrodes as a function of time at a scan rate of 50 mV/s (f) in 0.1M H_2SO_4 solution (a) and Nyquist diagrams of Ppy and Ppy/CuCr₂O₄ electrodes in 0.1 M H_2SO_4 under OCP conditions (b).

Conclusion

In this work, the electrochemical performance of polypyrrole CuCr₂O₄ nanoparticle composite electrode was studied. The results show that using CuCr₂O₄ NPs caused increasing of the capacitance and stability of polymeric electrodes during 1200 consecutive cycles. Increasing the conductivity of composite electrode is another feature of using this nano material in the structure of polypyrrole. Considering the very low magnitude of CuCr₂O₄ NPs in composite structure and very high specific capacitance, the synergistic effect between CuCr₂O₄ NPs and polypyrrole is suggested.

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Copper Chromate

Electrosynthesis

Pseudocapacitor