

Preparation of Polyaniline Nanocomposite with Natural Clinoptilolite and Investigation of Its Special Properties

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Abstract:

A nanocomposite of polyaniline (PANI) with natural clinoptilolite (Clino) was prepared by chemical oxidative polymerization of anilinium cations in the presence of clinoptilolite dispersion. The PANI/Clino nanocomposite was characterized using FTIR, XRD and SEM techniques as well as electrical conductivity measurement using four point probe technique. Cyclic voltammetry analysis was used to investigate the electroactivity of PANI/Clino nanocomposite. Also solubility of the nanocomposite was determined compared to the pure PANI. Formation of the nanocomposite and incorporation of polyaniline into the clinoptilolite channels were confirmed by FTIR spectra and XRD patterns. According to the results, increasing the zeolite content of PANI/Clino nanocomposite up to 0.5% w/w, increases the electrical conductivity of the nanocomposite, but further increasing of the zeolite content causes decreasing the conductivity. Cyclic voltammetry studies showed that the nanocomposite is electroactive as well as pure PANI. Also according to the results of solubility tests, the solubility of PANI/Clino nanocomposite in N-methyl pyrrolidone solvent was improved.

Keywords: Polyaniline, Clinoptilolite, Nanocomposite

1. INTRODUCTION

Conducting polymers have become one of the most attractive subjects of investigation in last decades. Their unique properties such as electrical conductivity, reversible electrochemical behavior and possibility of both chemical and electrochemical synthesis, make them useful in the wide area of applications. These materials have been used in various technical applications, including rechargeable batteries [1, 2], chemical and electrochemical sensors [3, 4], electro-chromic devices [5], corrosion protection [6-8], removal of

toxic materials [9-11] and switchable membranes [12]. The most popular one among the conducting polymers is polyaniline (PANI) due to its acceptable chemical stability combined with relatively high level of electrical conductivity, monomer availability and ease of polymer synthesis.

Due to the fact that polyaniline exhibits extremely interesting properties and potential applications, improvement of its processability and conductivity is important. Nowadays a promising way to improve the properties of polyaniline is through the organization of the polymer chains in the

nanometer scale [13]. Many kinds of materials can be used as encapsulating host, such as zeolites, mesoporous materials and macrocycles with tubular structure [14]. Polymers may be encapsulated for a variety of reasons, but mostly is to protect materials from atmospheric and other types of chemical attack and also for separation of polymer chains to reduce inter-chain effects and improving the mechanical, thermal and chemical stabilities [15]. Zeolites are crystalline aluminosilicates with a three-dimensional ordered structure, open anion framework consisting of oxygen-sharing TO_4 tetrahedral, where T is Si or Al. Their framework structure contains interconnected voids, filled with cations which can be exchanged [16]. Encapsulation of polyaniline in the zeolite channels is a promising strategy to prepare polymer chains into the nanometer-sized of the zeolite channels, to obtain nanocomposite materials with novel special properties. The nanocomposite of polyaniline with zeolite prepared by the encapsulation method, can exhibit electronic, mechanical, chemical, and optical properties better than the pure conducting polyaniline [17-19].

In this work encapsulation of polyaniline chains in the natural clinoptilolite (Clino) channels has been reported. The produced PANI/Clino nanocomposite, with special structure, has interesting electrical conductivity and solubility properties together with reversible electrochemical behavior.

2. EXPERIMENTAL

2.1. Reagents and materials

The natural clinoptilolite used in this study was obtained from Meianah mine in East Azerbaijan, Iran. The aniline (Merck) was purified under vacuum distillation prior to use. Hydrochloric acid, methanol, ammonium hydroxide, sulfuric acid, N-methyl pyrrolidone (NMP) and ammonium persulfate were all purchased from Merck (Germany) and were used as received without any further purification.

2.2. Instrumentation

A home made four-point probe was used to measure the electrical conductivity of nanocomposite and pure polyaniline. A galvanostat/potentiostat SAMA 500 (Iran) and A three-electrode electrochemical cell system consisted of a gold coated electrode as working electrode, a platinum gauze as counter electrode and an Ag/AgCl as reference electrode were used for electrochemical experiments. A micrometer SM 1201 Teclock Corporation (Japan) was used to measure the thicknesses of polyaniline and nanocomposite films. A Scanning Electron Microscope (SEM LEO440i-England) was used to investigate the surface morphology of polyaniline and nanocomposite. A Fourier Transform Infra-Red spectroscopy (FTIR, Bruker Tensor 27-Germany) was used to investigate the physicochemical interactions between organic and inorganic phases. An X-ray diffractometer D500 Siemense (Germany) was used to study the crystallinity of the nanocomposite.

2.3. Preparation of acidic clinoptilolite

The natural zeolite rocks were first hammered to break down into smaller particles. These smaller particles were grinded and magnetically stirred for 48 hours in HCl aqueous solution (0.1 M). The slurry was filtered and washed with excess deionized water followed by drying at 150°C for a period of 2 hours. The more acidic condition of the zeolite can cause to the more strong adhesion of polymer to the zeolite [15, 18].

2.4. Synthesis of polyaniline

Chemical polymerization of aniline was carried out in an aqueous acidic solution. 8.09 g of ammonium persulfate was dissolved in 200 ml of deionized water. This solution was added dropwise to a solution of 4 ml aniline dissolved in 200 ml of HCl aqueous solution (1 M), while the reaction mixture was vigorously stirred at -2 to -5°C for a period of 6 hours. The green emeraldine hydrochloride precipitate was collected and washed repeatedly with 80/20 water/methanol solution until the under washing solution became colorless. Washing with

methanol solution causes to the removal of short low molecular weight chains and therefore improves the mechanical and electrical properties of polymer.

2.5. Preparation of PANI/Clino nanocomposite

The aniline monomer was embedded into the clinoptilolite channels and was polymerized using ammonium persulfate as initiator/oxidant. It is proposed that the weakly polar aniline finds it more difficult to penetrate into the clinoptilolite channels than a polar anilinium cation. Therefore, cation exchange reaction between H^+ in clinoptilolite structure and anilinium cation in solution was carried out. For this, clinoptilolite at weight ratios of 0.25, 0.5, 1, 2, 3, 4 and 5% w/w per aniline monomer was dispersed in 200 ml of HCl aqueous solution (1 M) containing 4 ml distilled aniline monomer. The mixture was then magnetically stirred for 48 hours at room temperature.

8.09 g of ammonium persulfate was dissolved in 200 ml of deionized water and added dropwise for a period of 6 hours to the mixture of anilinium cations and clinoptilolite dispersion. While the reaction mixture vigorously stirred at -2 to $-5^\circ C$. The obtained nanocomposite was collected and washed repeatedly with 80/20 water/methanol solution until the under washing solution became colorless.

2.6. Preparation of Films

The four point probe technique was used to measure the electrical conductivity of pure polyaniline and PANI/Clino nanocomposite free standing films. The green emeraldine hydrochloride as pure or nanocomposite was converted to the blue emeraldine base form by deprotonation (dedoping) in an aqueous ammonia solution (1M) under vigorous stirring for 4 hours. The blue precipitate was filtrated and washed with 80/20 water/methanol solution until the under washing solution became neutral. Emeraldine base powder was finally obtained after the filtrate was dried in an oven at $50^\circ C$ for 48 h.

One gram of the emeraldine base form of polyaniline or its nanocomposite was added slowly (over 5 hours) to the 40 ml of NMP solvent under magnetically

stirred condition at room temperature. It has been found that if the polyaniline powder is added too rapidly to the NMP solvent, it will be aggregate [20]. The resulting viscous solution was filtered to remove any undissolved particles. The free standing films of polyaniline or PANI/Clino nanocomposite were produced by casting the viscous solution of polyaniline or nanocomposite in NMP on the surface of glass plates (2×8 cm) followed by drying in an oven at $50^\circ C$ for 48 hours. The dried films with 20 μm thickness were removed from the glass surface by immersion in distilled water. Before conductivity measurement the prepared films were doped by immersion in aqueous solution of hydrochloric acid (1 M) for 24 hours followed by washing with excess deionized water and drying at $25^\circ C$ for 5 hours.

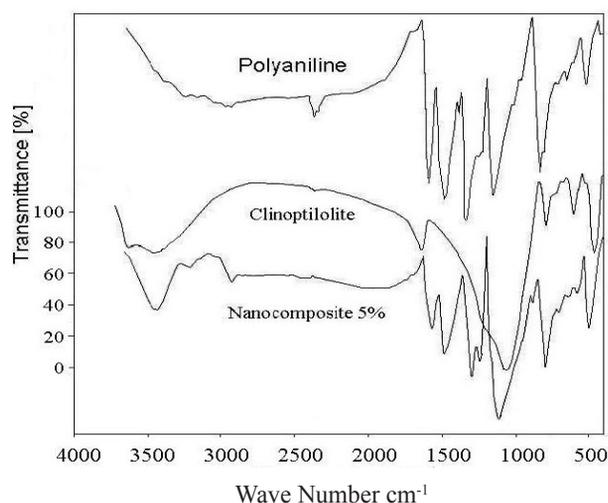


Figure 1: FTIR spectra of clinoptilolite, pure polyaniline base and PANI/Clino nanocomposite base with 5% w/w clinoptilolite content.

3. RESULTS AND DISCUSSION

3.1. FTIR spectroscopy of PANI/Clino nanocomposite

The PANI/Clino nanocomposite was characterized using FTIR technique. The characteristic peaks observed in the FTIR spectrum of PANI/Clino nanocomposite give valuable information

regarding to the conformation of polyaniline in the clinoptilolite channels and possible interactions between clinoptilolite and polyaniline. Figure 1 shows the FTIR spectra of clinoptilolite, PANI/Clino nanocomposite base with 5% w/w clinoptilolite content and pure polyaniline base. It should be mentioned that in order to obtain the clinoptilolite related peaks more sharply (for better interpretation and discussion) the nanocomposite with high clinoptilolite content (5%w/w) was used for recording FTIR spectra. FTIR spectra of PANI/Clino nanocomposite exhibit characteristic bands of polyaniline as well as of clinoptilolite which confirms the presence of both components in the PANI/Clino nanocomposite.

In the PANI/Clino nanocomposite, the observed peaks characteristic of polyaniline, were shifted to lower wave numbers, indicates complete interaction between polyaniline and clinoptilolite and also reveals the presence of physicochemical interactions, such as hydrogen bonding, between clinoptilolite and polyaniline. According to the results (Figure 1), there are noticeable changes in the absorption peaks characteristic of structural OH vibration bands for clinoptilolite and nanocomposite in the region of 3500 to 3700 cm^{-1} . These absorption bands are related to the bridging OH groups in $\equiv\text{Al}-\text{OH}-\text{Si}\equiv$ as well as other hydrogen atoms bonded to different oxygen atoms in the framework of clinoptilolite [21]. The changes in the mentioned peaks indicate that there is a complete coverage of OH groups existing in the intrachannels and extrachannels surfaces of clinoptilolite by polyaniline. The complete disappearance of the peak near to 3700 cm^{-1} is due to the complete interaction of polyaniline with OH groups (both inside and outside of the channels). When the absorption peak related to the OH group completely disappears, it means that this group is undertaken a strong interaction such as hydrogen bonding. On the other hand, the high potential of polyaniline to made hydrogen bonding or strong polar interactions, the coverage of all OH groups of clinoptilolite with polyaniline can be concluded. In other word it means that polyaniline chain have grown in and outside of the clinoptilolite channels.

3.2. X-ray diffraction pattern of PANI/Clino nanocomposite

X-ray diffraction is a versatile and non-destructive technique which is used for identification of the crystalline phases present in solid materials and for analyzing structural properties of the phases such as stress, grain size, phase composition, crystal orientation and defects. Therefore, X-ray diffraction patterns were recorded for clinoptilolite, polyaniline base and PANI/Clino nanocomposite base with 5% w/w clinoptilolite content (Figure 2). In order to obtain the clinoptilolite related peaks more sharply (for better interpretation and discussion) the nanocomposite with high clinoptilolite content (5%w/w) was used for the recording of XRD patterns. For clinoptilolite the characteristic peaks were observed at $2\theta=9.85^\circ$, 22.4° and 30.0° . Presence of these peaks in the XRD pattern of PANI/Clino nanocomposite confirms the presence of clinoptilolite in the nanocomposite composition.

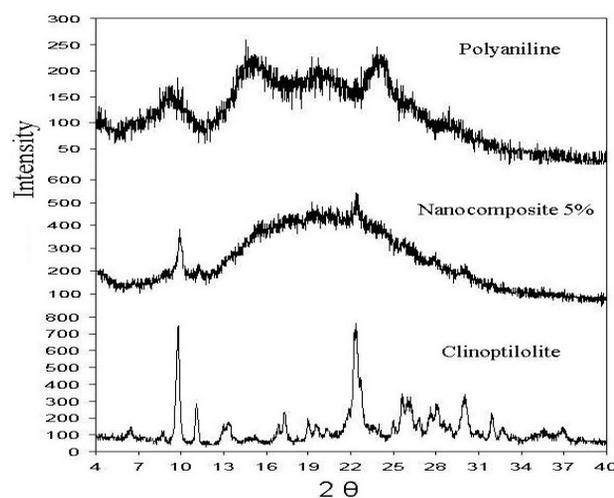


Figure 2: X-ray diffraction patterns of clinoptilolite, polyaniline base and PANI/Clino nanocomposite base with 5% w/w clinoptilolite content.

The intensity of the XRD pattern peaks can be influenced by the crystallinity or by polyaniline chains order in nanocomposite structure. According

to the XRD patterns of polyaniline (Figure 2), it can be seen that polyaniline has a relatively amorphous structure, but by encapsulation of polyaniline in the clinoptilolite channels the alignment and arrangements of polyaniline chains were significantly improved and as a result, the intensity of the peaks related to the nanocomposite were increased (Figure 2). Increasing the peaks sharpness is directly due to the increasing of the structural order in materials [22-24].

3.3. Investigation of surface morphology

The surface morphology of polyaniline, clinoptilolite and polyaniline/c clinoptilolite nanocomposite was studied using scanning electron microscopy (SEM) technique. Figure 3 shows the SEM micrographs of polyaniline, clinoptilolite and PANI/Clino (5% w/w) nanocomposite surface. In order to obtain the clinoptilolite related graphs more clearly (for better interpretation and discussion) the nanocomposite with high clinoptilolite content (5%w/w) was used for recording of SEM micrograph. SEM micrographs show that in the PANI/Clino nanocomposite with 5% w/w clinoptilolite content (Figure 3c) the alignment of polyaniline chains have been increased compared to amorphous polyaniline structure (Figure 3a). The SEM micrograph of clinoptilolite (Figure 3b) shows the layered structure of clinoptilolite with layer thicknesses in nanometer range (less than 100 nanometer). Also the SEM micrograph of nanocomposite (Figure 3c) reveals that the diameter size of polyaniline chains, grown in clinoptilolite channels, is in nanometer range.

3.4. Electrical conductivity measurement

Four point probe technique was used to measure the electrical conductivity of PANI/Clino nanocomposite films with various weight ratios (0.25, 0.5, 1, 2, 3, 4, and 5% w/w) of clinoptilolite content and the results were compared with the electrical conductivity of pure polyaniline film. The results of the electrical conductivity measurements are presented in Table 1. The isolation of the polyaniline chains into the clinoptilolite channels

and the improvement of their alignment are expected to increase its electrical conductivity. Increasing the zeolite content of nanocomposite up to 0.5% w/w, increases the conductivity of nanocomposite. However further increasing of zeolite content in nanocomposite decreases its conductivity. This is related to the intrinsic insulator characteristic of zeolite.

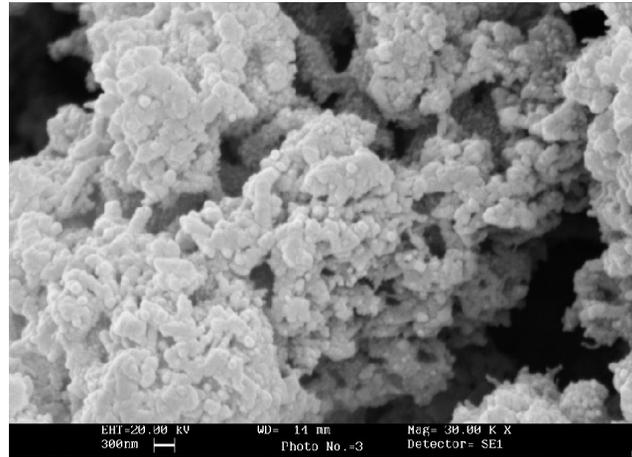
3.5. Cyclic voltammetry studies

Cyclic voltammetry studies were carried out to evaluate the electrochemical behavior of PANI/Clino nanocomposite and also to study the relation between electrochemical behavior and electrical conductivity in nanocomposite. A gold electrode (0.5×0.5 cm) coated with a thin layer (20 μm thicknesses) of nanocomposite and pure polyaniline was used as working electrode. Various solutions including HCl (1 M), H₂SO₄ (1 M) and NaCl (3.5% w/w), were used as electrolyte. Figures 4 to 6 show the cyclic voltammograms of pure polyaniline and PANI/Clino nanocomposite films with 0.5 and 5% w/w clinoptilolite content in HCl (1 M), H₂SO₄ (1 M) and NaCl (3.5% w/w) electrolytes respectively at 100 mV/s scan rate. Regarding the results, it was found that PANI/Clino nanocomposite are electroactive similar to pure polyaniline and presents two pairs of oxidation/reduction peaks in cyclic voltammogram. Also according to the results, by increasing the electrical conductivity of nanocomposite the current of peaks was also increased. Also, results showed that the electrochemical behavior of the PANI/Clino nanocomposite is completely reversible in all mentioned electrolytes.

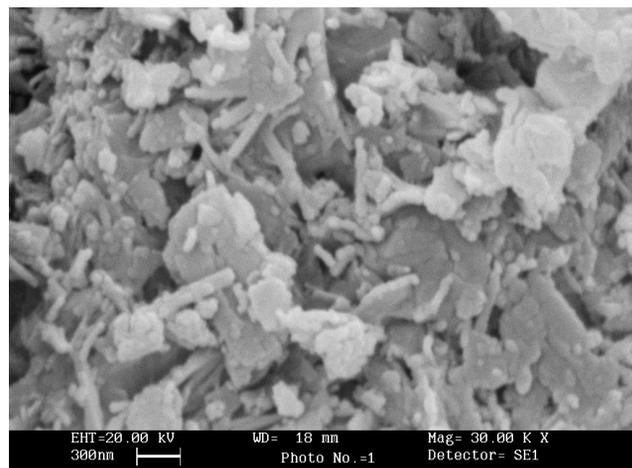
3.6. Investigation of solubility

There are relatively strong interactions between amine and imine groups of neighbor chains in emeraldine base via hydrogen bonds. This phenomenon is responsible for difficult solubility of polyaniline in various solvents [25]. Partial dissolution of polyaniline is possible only when solvent-polyaniline hydrogen bond interactions replaces to the interchain interactions. Presence of polyaniline in the clinoptilolite channels causes

(a)



(b)



(c)

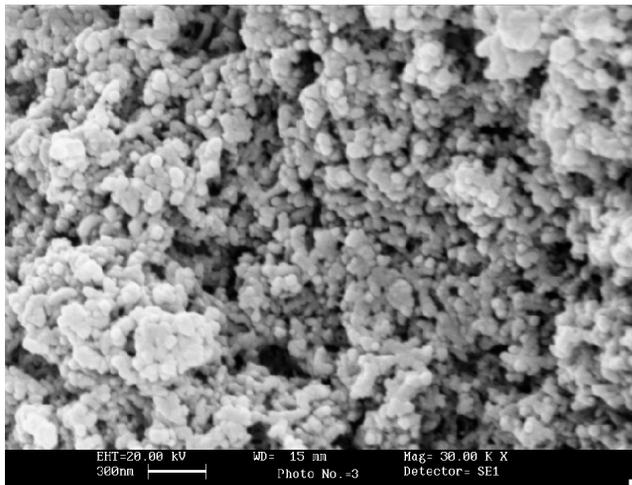


Figure 3: SEM micrographs of polyaniline base (a), clinoptilolite (b), and PANI/Clino nanocomposite base whit 5% w/w clinoptilolite content (c).

Table 1: Electrical conductivity of free standing films of pure polyaniline and PANI/Clino nanocomposite with various clinoptilolite contents (0.25-5 w/w).

| Clinoptilolite content (%w/w) | 0 (Pure PANI) | 0.25 | 0.5 | 1 | 2 | 3 | 4 | 5 |
|--------------------------------|---------------|------|-----|----|----|----|---|---|
| Electrical conductivity (S/cm) | 12 | 18 | 25 | 20 | 16 | 12 | 8 | 5 |

Table 2: Dissolution efficiency of pure polyaniline and PANI/Clino nanocomposite with various clinoptilolite contents (0.25-5 w/w) in NMP solvent (calculated using Eq. 1)

| Clinoptilolite content (%w/w) | 0 (Pure PANI) | 0.25 | 0.5 | 1 | 2 | 3 | 4 | 5 |
|-------------------------------|---------------|------|-----|-----|-----|-----|-----|-----|
| Dissolution efficiency (%) | 0.75 | 2 | 1.9 | 1.7 | 1.4 | 1.2 | 0.9 | 0.7 |

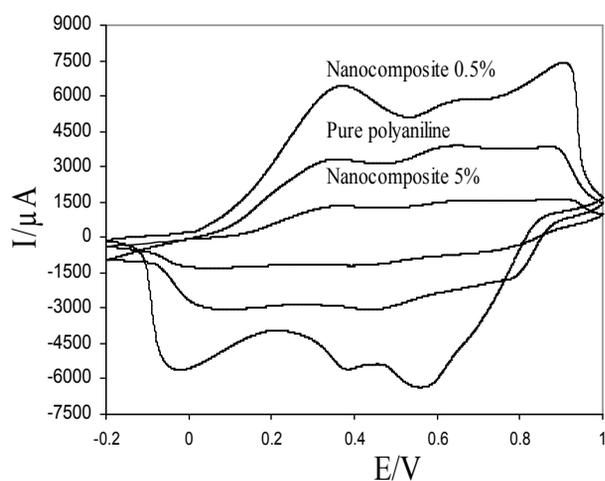


Figure 4: Cyclic voltammogram of Polyaniline and PANI/Clino nanocomposite with 0.25 and 5% w/w clinoptilolite content coated on a gold electrode (0.5×0.5 cm and $20 \mu\text{m}$ thicknesses) in H_2SO_4 solution (1 M) at 100 mV/s scan rate.

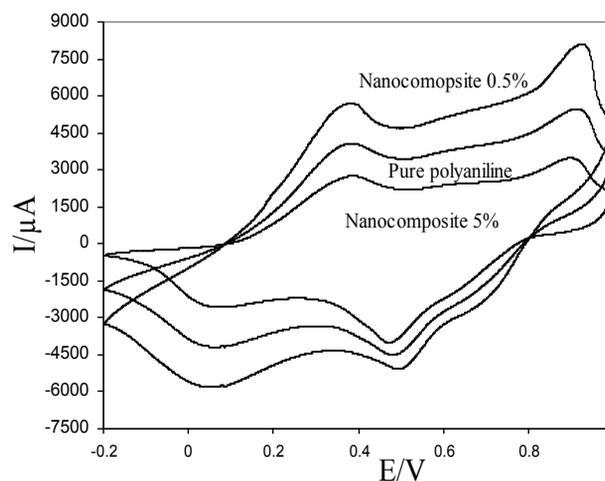


Figure 5: Cyclic voltammogram of Polyaniline and PANI/Clino nanocomposite with 0.25 and 5% w/w clinoptilolite content coated on a gold electrode (0.5×0.5 cm and $20 \mu\text{m}$ thicknesses) in HCl solution (1 M) at 100 mV/s scan rate.

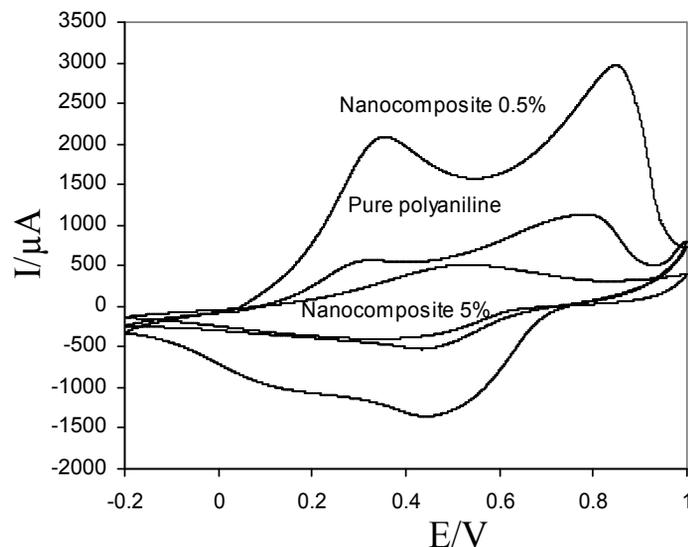


Figure 6: Cyclic voltammogram of Polyaniline and PANI/Clino nanocomposite with 0.25 and 5% w/w clinoptilolite content coated on a gold electrode (0.5×0.5 cm and $20 \mu\text{m}$ thicknesses) in NaCl solution (3.5% w/w) at 100 mV/s scan rate.

to the separation of polyaniline chains and hence diminishes the interchain interactions and increases the solubility of nanocomposite. The solubility of pure PANI and PANI/Clino nanocomposite with various clinoptilolite contents (0.25-0.5 %w/w) in NMP solvent was measured. The dissolution efficiency of polyaniline was calculated according to the equation 1:

$$D=100(W_0-W)/W_{\text{NMP}} \quad (1)$$

Where W_0 is the initial weight of polyaniline and W is the weight of polyaniline which is not dissolved and W_{NMP} is the weight of solvent. The dissolution efficiency of nanocomposite was calculated according to the equation 1. Results of the dissolution efficiency measurements were presented in Table 2. In the PANI/Clino nanocomposite the dissolution efficiency was significantly increased by the addition 0.25% w/w zeolite content. Further increasing of the zeolite content in PANI/Clino decreases its solubility, which may be due to the insoluble properties of zeolite in NMP solvent.

4. CONCLUSIONS

Results of FTIR and XRD studies confirmed the formation of nanocomposite and incorporation of polyaniline chains into the clinoptilolite channels by insitu polymerization of aniline in clinoptilolite channels. Production of polyaniline in clinoptilolite channels made isolated chains of polyaniline with higher alignment and lower interchain interactions which causes to the increasing of polyaniline solubility in NMP solvent. However increasing the clinoptilolite content of PANI/Clino nanocomposite caused to the reduction of its solubility due to the intrinsic insolubility of clinoptilolite in NMP solvent. SEM micrograph analysis confirmed the isolation and increasing the alignment of polyaniline chains in the clinoptilolite channels. Increasing the zeolite content of nanocomposite up to 0.5% w/w increases the conductivity of nanocomposite and further increasing of zeolite content, decreases its conductivity. This is related to the intrinsic insulator character of zeolite. The results of the cyclic voltammetry studies showed that the PANI/Clino nanocomposite has a reversible electrochemical

behavior in various electrolytes which is in good agreement with electrical conductivity behavior of nanocomposite.

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