Electrochemical characterization of polymeric sensor of poly-acrylonitrile self-modified with carbon nanotubes (CNT)

Szén nanocsövekkel (CNT) módosított poliakrilnitril elektrokémiai jellemzése

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Abstract

A new conductive material was fabricated from polymer (poly-acrylonitrile) modified with carbon nanotubes. The polymeric material was used to produce of self – modified electrode in cyclic voltammetry. It is well known that when using solid electrodes in electrochemistry, especially in cyclic voltammetry, the electrode works independently in electrolytic conductivity. Therefore, we modify the electrode using carbon nanotubes or other nanomaterials to increase electrical conductivity and obtain high oxidation – reduction current peaks with clear chemical reaction comparing with the electrode in its natural state, (such as glass electrode, platinum electrode, gold electrode and other commercial electrodes). The modification of commercial electrode with carbon nanotubes was acted either mechanical method (manually) by modifying the working electrode with multi attachment of the electrode surface with carbon nanotube (about 30 times). The fabrication electrode is characterized by its special properties, as it is inert, with high potential area, excellent reliability, high hardness, resist to high temperature, water and organic solvents, its low cost (relative to the commercial electrode), non-toxicity, high stability and high accuracy in the analysis of oxidation-reduction process. And has high sensitivity to the chemicals, pollutants and has excellent selectivity. Keywords: cyclic voltammetry, poly-acrylonitrile, CNT, polymer self-modified with CNT

Kulcsszavak: ciklikus voltammetria, poliakrilnitril, szén nanocsövek (CNT), CNT-vel módosított polimer

1. Introduction

Some advanced techniques in conductive polymers were presented using nanoparticles within to produce different applications in the electrochemical field [1-5], such as working electrode of cyclic voltammetry with high electro-conductivity [6].

It was observed that in mixed nanomaterials, high damping can be achieved by using friction between the nanotubes and the polymeric material. The aim of this research is to study the damping properties in the structures of the mixed material supported by nanotubes of various rubber ratios. The damping properties of samples for pipe ratios between 0-0.6% were studied and tested in practice. By comparing the raw material of the base and the base with the additive, it was observed that the damping was improved by adding nanotubes to the mixture. Practical results showed that the maximum damping ratio (damping factor) was 0.4% of carbon nanotubes [7].

The effect of carbon nanotubes on the electrical properties of polyvinyl chloride has been studied. Examples of polyvinyl chloride composites and carbon nanotubes prepared using thermal pressing technology. Weight ratios of carbon nanotubes are (0, 5, 10 and 20) wt.%. The results show that continuous electrical conductivity increases with increasing weight ratios of carbon nanotubes. Continuous electrical

conductivity also changes with increasing temperature for different concentrations of carbon nanotubes. The activation power of the continuous electrical conductivity decreases with increasing the concentration of carbon nanotubes [8].

Carbon nanotubes were used to strengthen the epoxy mixture with polysulfide and assessed the tensile and wear characteristics. In order to achieve a better evaluation of properties, several ratios of nanomaterials were used and mixed with epoxy resin. Poly sulfide was then added to the mixture. Nanocarbon coefficient has increased from 245-273 MPa and the tensile strength of 30.5-38.9 MPa and fracture stress from 12.4% to 14.2%. Electronic elements [9].

Carbon nanotubes were employed using covalent recruitment and in two phases. The employed carbon nanotubes were coated with copper metal using (Electroless coating process). Three groups of superposed copper nanoparticles were prepared using powder technology with different weight ratios of carbon nanotubes. The first group contained carbon nanotubes as they were, the second group contained the employed carbon nanotubes, while the third group contained coated carbon nanotubes. The comparison of these samples showed that the coating process significantly improved the hardness and wear resistance of the superposed nanomaterial. The improvement

in properties can be attributed to increased adhesion to the ground and dispersion of carbon nanotubes. SEM, XRD, and FTIR were used to characterize the coating process as well as to characterize metal-based nanomaterials [10].

2. Experimental

2.1 Apparatus

Cyclic voltammetry (CV) was performed with an EZstat apparatus (NuVant Systems, USA) consisting of an electrochemical cell connected to a computer [11]. Reference silver chloride electrodes were placed in 3mol potassium chloride. A 1mm platinum wire used as counter control electrodes [12]. A glassy carbon electrode (GCE) was polished with alumina solution and ultrasonic waterpath 10 min to maintain performance and remove impurities [13-15].

2.2 Materials

Poly-acrylonitrile was received from SCRC, (China), carbon nanotubes (purity 99%) were supplied by Fluka company (Germany), Potassium ferrous cyanide $K_4Fe(CN)_6$ (Merck Sante SAS, Germany), KCl, $KClO_4$, K_2SO_4 , K_2HPO_4 , and KNO_3 (Technicon chemicals, Tournai, Belgique). deionized water and added 0.1 mM of $K_4Fe(CN)_6$ solution in a cyclic voltammetric cell with the GCE, reference and counter electrodes immersed in the fluid as shown in Fig. 1.

Fig. 1 Cyclic voltammetry experimental setup
1. ábra Ciklikus voltametria kísérleti összeállítása

2.2.1 Manufacture of poly-acrylonitrile modified with carbon nanotubes (CNT)

Poly-acrylonitrile was modified with carbon nanotubes were manufactured using the thermal method [16].

2 g of poly-acrylonitrile was mixed with 1 mg of carbon nanotubes using 50 mL of chloroform as a solvent and heated at 50 °C with continuous mixing using a magnetic bar (magnetic bar) for 72 hours for use in diagnostic analyzes and electrode fabrication.

2.2.2 Fabrication of self-modified polymer with carbon nanotubes

The working electrode is made of self-modified polymer with carbon nanotubes by taking a piece of it in a circular diameter of 5 mm and a thickness of 2 mm. The other is connected with a copper wire and all the parts are covered with a glass tube and fixed with epoxy adhesive as shown in Fig. 2.

Fig. 2 Poly-acrylonitrile self-modified with CNT as working electrode
2. ábra CNT-vel módosított poliakrilnitril munkaelektroda

2.3 Characterization studies of the new modified polymer

2.3.1 FTIR infrared spectra

The infrared spectra of the poly-acrylonitrile alone is shown in Fig. 3 and its comparison with the polymer modified carbon nanotubes in Fig. 4.

Fig. 3 Infrared spectrum of poly-acrylonitrile
3. ábra A poliakrilnitril infravörös spektrum elemzésének eredménye

Fig. 4 Infrared spectrum of polyacrylonitrile after modification with carbon nanotubes
4. ábra A CNT-vel módosított poliakrilnitril infravörös spektrum elemzésének eredménye

3.2.2 X-ray study of the new modified polymer

The study of X-ray spectra of the polymer material (poly-acrylonitrile) emerged of two peaks as shown in Fig. 5 comparing with the modified polymer material with carbon nanotubes which showed the emergence of a new third summit in the polymer composition of the nanomaterial as shown in Fig. 6.

3.2.3 Study of polymer modification with nanomaterials

One of the three methods indicated by Manas, 2006 and Zinco, 2010 was used to modify the polymers either by the free radicals of the gamma rays, the ionic method or the thermal method. The thermal method was adopted in the preparation of the modified polymeric material with nanomaterials. The composition of the nanomaterial entry through the poly-acrylonitrile was proposed as per the scheme proposed in Fig. 7 [17].

Fig. 5 X-ray spectrum of poly-acrylonitrile
5. ábra A poliakrilnitril röntgenspektruma

Fig. 6 X-ray spectrum of poly-acrylonitrile after modification with carbon nanotubes
6. ábra A CNT-vel módosított poliakrilnitril röntgenspektruma

Fig. 7 Proposed formula for carbon nanotube-modified poly-acrylonitrile
7. ábra A CNT-vel módosított poliakrilnitril javasolt formulája

3. Results and discussion

3.1 Effect of potential area

The potential area of the polymeric electrode (polymer modified with carbon nanoparticle) was compared with commercial working electrode such as glassy carbon electrode (GCE) in KCl 1 molar solution. It was noted that the area of potential of the polymer electrode is greater than the potential area of the glassy carbon electrode. The polymer electrode covers an area of -1.8 to +2.0 volts, while the commercial electrode (GCE) covers an area of less than -1.5 to +1.8 volts.

3.2 Effect of different electrodes

The standard 0.1 molar compound of $K_4[Fe(CN)_6]$ was used to calibrate the cyclic voltammeter in aqueous solutions. Oxidation - reduction peaks of the iron were observed in Fe

(III) / Fe (II) as shown in Fig. 8 of the both working electrodes, modified polymer electrode and glassy carbon electrode (GCE). It was observed that the potential difference between the oxidation and reduction peaks is $E_{pc-a} \approx 100$ mV and the ratio of the current value of the cathode-to-anode peaks (I_{pc} / I_{pa}) is equal to 1, which represents the standard value of the reversible electrodes.

Fig. 8 Cyclic voltammogram of 0.1M Fe ions in 0.1M KCl using (green line) polymer electrode modified with CNT and (red line) glassy carbon electrode
8. ábra 0.1M KCl-ben lévő 0.1M Fe ion ciklikus voltammogramja CNT-vel módosított polimer elektródát használva (zöld) valamint karbon elektródát használva (piros)

3.3 Effect of scan rates on self - modified polymer electrode

At the different scan rates (0.01 - 0.1 Vs-1) of 0.1 mM $K_4[Fe(CN)_6]$ in 0.1 M KCl solution the CV were studied using polymer electrode modified with CNT manufactured in the laboratory. It has been observed that the electric current of the oxidation and reduction peaks of Fe(III)/Fe(II) increases with increasing scanning rate, which indicated that the phenomenon of heterogeneous kinetics is shown in Fig. 9. When plotting oxidation and reduction (I_{pa} and I_{pc}) versus scan rate, a straight line was shown as in Fig. 9 and 10 respectively, and the sensitivity values were high because the graphical line matched the device results [18].

Fig. 9 Cyclic voltammogram of 0.1M $K_4[Fe(CN)_6]$ in 0.1M KCl at different scan rates (red line) SR=0.1 mV/sec (green line) SR=0.01 mV/sec using polymer electrode modified with CNT.
9. ábra 0.1M KCl-ben lévő 0.1M $K_4[Fe(CN)_6]$ ciklikus voltammogramja CNT-vel módosított polimer elektródát használva különböző mintavételi sebességeken (Zöld: SR=0.1 mV/sec; Piros: SR=0.01 mV/sec)

3.4 Measurement of Fe(II)/Fe(III) in different concentration

The new electrode is a highly sensitive electrode in detecting low concentrations of aqueous solutions and, as evidenced by the use of the standard solution $K_4[Fe(CN)_6]$ in a 0.1M KCl solution.

Fig. 10 Plot the oxidation current peak of $K_4[Fe(CN)_6]$ at different scan rates on working electrode of polyacrylonitrile self-modified with CNT
10. ábra $K_4[Fe(CN)_6]$ oxidációs áramcsúcsa különböző mintavételi sebesség mellett CNT-vel módosított polimer elektródot használva

Fig. 11 Plot the reduction current peak of $K_4[Fe(CN)_6]$ at different scan rates on working electrode of polyacrylonitrile self-modified with CNT
11. ábra $K_4[Fe(CN)_6]$ redukciós áramcsúcsa különböző mintavételi sebesség mellett CNT-vel módosított polimer elektródot használva

Fig. 12 Cyclic voltammogram of $0.1M K_4[Fe(CN)_6]$ at different concentrations in $0.1M KCl$ using polymer electrode self-modified with CNT at $SR=0.1 mV/sec$ versus $Ag/AgCl$
12. ábra $0.1M K_4[Fe(CN)_6]$ ciklikus voltammogramja CNT-vel módosított polimer elektródot használva különböző koncentrációk mellett ($SR=0.1 mV/sec$; vs. $Ag/AgCl$)

3.5 Study the polymer self-modified with CNT in different pH

The CV technique demonstrated the high sensitivity of the synthesized electrode in different pH levels (for both acidic and alkaline medium) on the oxidation and reduction peaks

of $1 mM K_4[Fe(CN)_6]$ in $0.1 M KCl$ as an electrolytic solution on the self-modified polymer with carbon nanotubes where shows in Fig. 13, a significant sensitivity in various acidic and basic solutions. Fig. 14 shows the relationship between the pH medium against to oxidation current peak of the iron ions.

Fig. 13 Cyclic voltammogram of $0.1M K_4[Fe(CN)_6]$ in $0.1M KCl$ using polymer electrode modified with CNT in alkaline pH and acidic medium at $SR=0.1 mV/sec$ versus $Ag/AgCl$
13. ábra $0.1M KCl$ -ben lévő $0.1M K_4[Fe(CN)_6]$ ciklikus voltammogramja CNT-vel módosított polimer elektródot használva savas és lúgos közegben ($SR=0.1 mV/sec$; vs. $Ag/AgCl$)

Fig. 14 Plot of oxidation current peak of $K_4[Fe(CN)_6]$ at different pH (acidic and alkaline) using polymer electrode self-modified with CNT against to $Ag/AgCl$ as reference electrode and scan rate at $0.1Vsec^{-1}$
14. ábra $K_4[Fe(CN)_6]$ oxidációs áramcsúcsa különböző pH (sav és lúgos) mellett CNT-vel módosított polimer elektródot használva vs. $Ag/AgCl$ mint referencia elektróda ($SR = 0.1Vsec^{-1}$)

3.6 Effect of different electrolytes

The different electrolytic solutions have a clear effect on the oxidation and reduction peaks of $1 mM K_4[Fe(CN)_6]$ in terms of the current as well as voltage when using the polymer electrode. It was found that the highest degrees of the electric current was increased the oxidation and reduction peaks according to the following sequence:

Anodic current: $KCl > KClO_4 > K_2SO_4 > K_2HPO_4 > KNO_3$

Cathodic current: $KCl > KClO_4 > KNO_3 > K_2SO_4 > K_2HPO_4$

On this basis, the best electrolyte solution supported in the study of the modified polymer with carbon nanotubes is KCl .

3.7 Scanning Electron Microscopy (SEM) for polymer modified with CNT

The scanning electron microscopy of the polymer modified with carbon nanotubes have been studied as shown in Fig. 15.

It was noted that the figure shows the surface of the electrode was overlapped, impermeable, compact and punctuated by strings represented by carbon nanotubes.

Fig. 15 SEM of polymer modified with CNT

15. ábra A CNT-vel módosított polimer pásztázó elektronmikroszkóp alatt

3.8 Study Atomic Force Microscopy (AFM) of polymer modified with CNT

Fig. 16 shows the atomic force microscopy of the surface of the synthetic electrode in the regular image of the polymer, which overlaps with carbon nanotubes and highly homogeneity and regulation was the high proportion of the measurement of carbon nanotubes of 20-100 nanometers as shown in Fig. 17.

Fig. 16 AFM of the polymer modified with CNT

16. ábra A CNT-vel módosított polimer atomerő-mikroszkóp alatt

3.9 Study of reproducibility and stability of self-modified polymer with carbon nanotubes

The potential and current stability of the new electrode was studied by the standard solution of $K_4[Fe(CN)_6]$ in KCl

solution. The CV is obtained by proving the redox peaks in the relation between current and voltage. Fig. 19 shows the overlapping of cyclic voltammogram of ten times of redox peaks of $Fe(II)/Fe(III)$, which indicated the stability of the new fabricated electrode.

Fig. 17 The diagram of the percentage average dimension of nanoparticles in the polymer modified with CNT from AFM analysis

17. ábra A CNT-vel módosított polimer nanorészecskék méretének százalékos eloszlása az AFM elemzés alapján

Fig. 18 Cyclic voltammogram of $0.1M K_4[Fe(CN)_6]$ in $0.1M KCl$ at ten times using polymer working electrode modified with CNT

18. ábra $0.1M KCl$ -ben lévő $0.1M K_4[Fe(CN)_6]$ ciklikus voltammogramja 10-szer ismételve CNT-vel módosított polimer elektródát használva

4. Conclusions

The new polymeric working electrode was manufactured because of its importance in the analysis of electrochemistry, especially in the cyclic voltmeter can be used in several aspects:

1. Used as an alternative to commercial solid electrodes used in the cyclic voltmeter because it is better than electrochemical analysis (in terms of electrical conductivity).
2. It can be used as an alternative to electrodes used in acidity measurement (pH meter).
3. The electrode can be used as a self-modified carbon nanotube in the rotary electrode technique which can be used with high efficiency by electrolysis since the oxidation and reduction current at high value.

References

- [1] Muhammed, M.R., Wee, T.T, Mohamad, Z.B. and Anuar, B.K., 2010. Electrochemical Characterization of the Redox Couple of $[\text{Fe}(\text{CN})_6]^{3-}$ $\text{Fe}(\text{CN})_6]^{4-}$ Mediated by a Grafted Polymer Modified Glassy Carbon Electrode, *Journal of Chemical Engineering of Japan*, 43(11), pp.927-931. <https://www.jstage.jst.go.jp/browse/jcej>.
- [2] Wee, T.T, Muhammed, M.R., Mohamad, Z.B. and Anuar, B.K., 2011. Electrochemical Reduction of Manganese Mediated by Carbon Nanotubes/Li⁺ Modified Glassy Carbon Electrodes, *Asian journal of chemistry*, 23(6), pp. 2401 – 2406. www.asianjournalofchemistry.co.in/.
- [3] Muhammed, M.R., Wee, T.T, Mohamad, Z.B. and Anuar, B.K., 2012. Synthesis and characterization of grafted acrylonitrile on polystyrene modified with activated carbon using gamma-irradiation, *Scientific Research and Essays*, 7(7), pp. 790-795. www.academicjournals.org/sre/.
- [4] Muhammed Mizher Radhi, Emad A. Al-Mulla, Copolymer electrode self-modified with fullerene C_{60} , *Journal of Silicate Based and Composite Materials*, 2018/5 § Vol. 70, No. 5, 134-139. <https://doi.org/10.14382/epitoanyag-jsbcm.2018.25>
- [5] Muhammed, M.R., Hanaa, N.A., Majid, S.J. and Emad, A.J., 2017. Electrochemical Effect of Ascorbic Acid on Redox Current Peaks of CoCl_2 in Blood Medium, *Nano Biomed. Eng.*, 9(2), pp 103-106. <https://doi.org/10.5101/nbe.v9i2.p103-106>.
- [6] M. M. Radhi, W. T. Tan and A. J. Haider, 2012. Electrochemical Characterization of the Redox Couple of Fe(II)/Fe(III) Mediated by a Grafted Polymer Electrode in Non-aqueous Electrolyte, *Int. J. Electrochem. Sci.*, 7. www.electrochemsci.org/.
- [7] Adnan, N.A., Mahmood A.E., 2016. Effect of Carbon Nanotube on Damping Characteristic of Epoxy Polysulfide Blend Composite. 2016, *Engineering and Technology Journal*, 34(1), pp. 73-84.
- [8] Ramadhan, Z.A., Ahmed H., Majeed, A., and Alaa, J., 2012. Synthesis and study the electrical properties of carbon nanotubes- polyvinylchloride composites, *Iraqi Journal of Physics*, 10(18), pp. 147-150.
- [9] Adnan, N., Ibtihal, A.A., Ekhlas, E.K., 2014. Diyala journal of engineering sciences, characteristics and properties of epoxy/polysulfide composite materials reinforced by carbon nanotubes, 7(3), pp. 106-119.
- [10] Ahmed, A.M., Abdul, Q.F., 2014. Righdan Mohsen Namus, *Surface Modification of Multiwall Carbon Nanotubes for Metal Matrix Nanocomposite Applications*, *Engineering and Technology Journal*, 32(7) Part (A) *Engineering Pages*: 1859-1869.
- [11] Instruction manual, CV 50W, version 2, Bioanalytical system Inc. USA (1996).
- [12] Bard, A.J., Faulkner, L.R., 2001. *Electrochemical Methods: Fundamentals and Applications*, 2nd Ed. Wiley, New York.
- [13] Compton, R.G., Spaman, R.A., Riley, D.J., Wellington, R.G., Eklund, J.C., and Fisher, A.C., 1993. *Electroanal. Chem.* 344, pp. 235.
- [14] Abdullah, A.A., 2013. Electrochemical studies of copper fatty amides complex in organic medium. *Res. Chem. Intermed.*, 39(6), pp. 2817-2823. <https://doi.org/10.1007/s40090-015-0053-9>
- [15] Abdul-Amir, Y.K., Radhi, M.M., and Al-Mulla E.A., 2017. Use of nano-sensors of the interferences between Pb(II) with each of Mg(II) , Zn(II) , Mn(II) , Ca(II) , Co(II) and PO_4^{3-} in blood medium: An electrochemical study. *Nano Biomed. Eng.*, 9(3): 199-207. <https://doi.org/10.5101/nbe.v9i3.p199-207>.
- [16] Manas C., 2006. *Introduction to polymer science and chemistry: a problem solving approach*, USA: CRC press.
- [17] Beaujuge, P.M., Reynolds, J.R., 2010. Color control in pi-conjugated organic polymers for use in electrochromic devices. *Chemical Reviews*. 110(1), pp. 268-320. <https://doi.org/10.1021/cr900129a>
- [18] Muhammed, M.R., Hanaa, N.A., Sura, A.A., Emad, A.J., 2015. Electrochemical oxidation effect of ascorbic acid on mercury ions in blood sample using cyclic voltammetry, *Journal International Journal of Industrial Chemistry*, Volume 6(4) 311-316. www.springer.com/chemistry/industrial

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