Copolymer electrode self-modified with fullerene C₆₀

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Abstract

A copolymer of polystyrene-acrylonitrile was modified with fullerene C₆₀ using gamma irradiation technique to produce a new copolymer with high quality in physical and chemical properties and using to fabrication a working electrode alternative for the modification of commercial working electrode in cyclic voltammetric technique (such as glassy carbon electrode, Pt, Au electrode). The new copolymer electrode self-modified with C₆₀ (CESMC₆₀) was characterized electrochemically by cyclic voltammetric method using a standard solution of 0.3 mM K₄[Fe(CN)₆] in 1 M KCl to evaluate the redox current peaks of Fe(II)/Fe(III). The electrochemical and physical properties of the new fabrication electrode has good hardness, insoluble in aqueous and non-aqueous solvent, electrochemical stability, resistance to high temperatures and different pH. It was found that 0.3 mM of K₄[Fe(CN)₆] in 1 M KCl of the new electrode at different concentration using reagent, scan rate, pH, temperature, electrolytes, stability and reliability. The new electrode was given encouraging properties for using in high-precision analysis and resuscitates commercial electrodes such as glassy carbon electrode, platinum electrode, gold electrode, and so on.

Keywords: cyclic voltammetry, copolymer electrode modified C₆₀, K₄[Fe(CN)₆], redox process

Kulcsszavak: ciklikus voltametria, C₆₀ módosított kopolimer elektróda, K₄[Fe(CN)₆], redox eljárás

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1. Introduction

Some scientists were manufactured high quality electrodes from conductive polymer which were used in the device of cyclic voltammetry and pH meter [1-3] and reference electrode [4].

IUPAC was upheld the modification of electrodes with conductive and semiconductive polymers to enhancement of the redox current peaks in cyclic voltammetric technique [5,6]. The modification of electrode in cyclic voltammetry was performed as chemical sensors and biosensors [7].

Fullerene C₆₀ film as single wall on gold electrode was studied in cyclic voltammetric technique which characterization in this method [8,9]. Some polymer synthesis with nanoparticles like poly(methyl methacrylate) complex with Fullerene C₆₀ using as organic solar cell [10-12].

The use of C₆₀ with the polymer composition has been gotten a polymer with different recipes for the polymer and that irradiation under vacuum pressure and at 300 °C to produce different spectral of conductive polymer [13]. C₆₀ and carbon nanotubes (CNT) were deposited with the polymer to production of new recipes on the polymer where the polymer gave the new specification in photovoltaic cells manufacturing [14].

Some of researches were studied an application of important biosensors using fullerene C₆₀, the new biosensor electrode with nanomaterials which has a functionalization in electrochemical applications [15,16].

Polymer-fullerene was synthesized and characterized by cyclic voltammetric technique to observation of energetic offsets which has up to value of 150 meV, this energy contribute for improving performance of the polymer solar cells [17].

New electrochemical sensors were used in detection of ions in voltammetric analysis by modification of electrode with metalloporphyrin dimer – fullerene C₆₀ [18].

Cyclic voltammetry was studied the modification glassy carbon electrode with single wall carbon nanotube and chitosan as a sensor to determination of acetaminophen, uric acid and ascorbic acid in human serum and urine medium with satisfactory results [19].

Cyclic voltammetry and differential pulse voltammetry were studied the modification gold electrode with fullerene-pyrrolidine to analysis the electrochemical characterized of the synthesized fullerene derivatives [20].

A thin film of C₆₀ with nano-TiO₂ on the electrode was determined the photocurrent efficiency photoactive of the polycrystalline TiO₂ and decreases the recombination effect [21].

In this work, a new fabrication of copolymer electrode self-modified with C₆₀ as alternative working electrode using in cyclic voltammetric technique was characterized.

2. Experimental

2.1. Synthesis of copolymer modified with fullerene C₆₀

The copolymer was manufactured process of polystyrene – acrylonitrile modified with Fullerene C₆₀ using gamma-irradiation by ferrous ammonium sulfite (FAS) as a catalyst. The minimization of the copolymer production was the following:

- 0.25% (w/w) of the catalyst FAS
- 80% (w/w) of monomer (acrylonitrile)
- 1.5 MRD dose of gamma-irradiation
- 2 g of polymer (polystyrene)
- 1 mg of Fullerene C₆₀

Fig. 1 shows the mechanism reaction as a suggestion [22].

Fig. 1 Suggested reaction mechanism of copolymer modified with fullerene C_{60}
1. ábra Kopolimer módosítása C_{60} fullerénnel – javasolt reakció mechanizmus

2.2. Fabrication of copolymer electrode self-modified with fullerene C_{60} (CESMC $_{60}$)

The new fabrication working electrode (CESMC $_{60}$) has been fabricated by a diameter of 5 mm of the material of copolymer manufacturer, and entered into a hole works in the center of the piece of the copolymer restaurant and prove to the wire of platinum 1 cm length where it executes a very small part of the other party, and the other part links with copper wire and all parts covered with glass tube and prove with epoxy adhesive, as shown in Fig. 2.

Fig. 2 Copolymer electrode self-modified with fullerene C_{60}
2. ábra C_{60} fullerénnel módosított kopolimer elektróda

2.3 Instrument and electrochemical analysis methods

EZstat series (potentiostat/galvanostat) NuVant Systems Inc. pioneering electrochemical technologies USA were used in this study. An Ag/AgCl (3 M NaCl) and platinum wire (1 mm diameter) were used as a reference and counter electrodes, respectively. The new fabrication working electrode CESMC $_{60}$ was used in this study.

Cyclic voltammetric cell was used in this technique by adding 10 ml of electrolyte in the quartz cell and immerse three electrodes in the supporting electrolyte, then all the electrodes was connected with potentiostat to finding the results of analysis by the cyclic voltammogram using personal computer as a soft ware of the analysis results.

2.4 Reagents

The following reagents were used: KCl powder purity from SCRC (China), potassium hexacyanoferrate II $K_4[Fe(CN)_6] \cdot 3H_2O$ from Fluka AG Chem. (Fabrik CH-9470 Buchs Germany) and other chemicals in high purity from the manufactures. All reagents were prepared by deionized

distilled water. All experimental analysis in cyclic voltammetry cell was dissolved oxygen remove with pure nitrogen gas bubbling for 10 to 15 min to avoid the peroxide producing from the oxidation of oxygen in the water of the solution in the cyclic voltammetric cell.

2.5. Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) was used to examine the morphology of the copolymer of polystyrene-acrylonitrile and the copolymer modification with fullerene C_{60} as shown in Fig. 3a and 3b, respectively.

Fig. 3. Scanning Electron Microscopy (SEM) of (a) the copolymer of polystyrene-acrylonitrile only (b) the copolymer of polystyrene-acrylonitrile modification with C_{60}
3. ábra Pásztázó elektronmikroszkópos (SEM) felvételek (a) poliszti-rén-akrilnitril kopolimer (b) C_{60} fullerénnel módosított poliszti-rén-akrilnitril kopolimer

3. Results and discussion

3.1. Electrochemical properties of the copolymer electrode self-modified with fullerene C₆₀

3.1.1. Effective of potential area

It can be compared to the potential area that are in commercial working electrode such as glassy carbon electrode (GCE), Platinum electrode (Pt-electrode), gold electrode (Au-electrode) with a new fabrication copolymer working electrode in 0.1 KCl electrolyte. It was noted that the new average potential area of the CESMC₆₀ is larger than GCE where the average potential area of CESMC₆₀ covers -1.8 to +2.0 V while the average potential area of GCE covers -1.5 to +1.8 V. It can also note that the presence of redox current peaks at commercial electrodes compared with flat area at CESMC₆₀.

3.1.2. Effect of CESMC₆₀ on the current and potential for redox current peaks in K₄[Fe(CN)₆]

Commonly it was used a compound of 1mM K₄[Fe(CN)₆] in the calibration of the cyclic voltammetric technique, when using in aqueous solutions. Good redox current peaks Fe(III)/Fe(II) were found to the CESMC₆₀. Where it was noted that the separation potential between redox peaks value ΔE_{pc-a} = 200 mV in aqueous solution 0.1M KCl and this is that the electrode used in the reaction is almost reversible type of interaction of Fe(II)/Fe(III) which is an acceptable value. As for the ratio of the cathode to the anode (I_{pa}/I_{pc}) it was approximately equal to 1, which represents the value of the reversible electrode as shown in Fig. 3.

Fig. 4 cyclic voltammogram of 0.3mM K₄[Fe(CN)₆] in 1M KCl as a supporting electrolyte using CESMC₆₀ as working electrode versus Ag/AgCl as reference electrode at scan rate 100 mVs⁻¹

4. ábra Ciklikus voltammogram: CESMC₆₀ munkaelektroda 0.3mM K₄[Fe(CN)₆] 1M KCl oldatban, Ag/AgCl referencia elektróddal; mintavételi sebesség 100 mVs⁻¹

3.2. Effect of scan rate on the CESMC₆₀

The different scan rates (0.01 – 0.1 Vs⁻¹) was studied for the CESMC₆₀ in a solution of 1M KCl as a supported electrolyte and 0.3 mM K₄[Fe(CN)₆]. It has been observed that the redox current peaks of Fe(II)/Fe(III) increased with increasing the scan rate which get heterogeneous kinetics phenomenon as shown in Table 1 [23].

A rational linear relationship between Log(I_{pa}) and Log(SR) of the CESMC₆₀ 0.3 mM K₄[Fe(CN)₆] which described by the equation: $y=0.4835X - 2.1379$, $R^2 = 0.9976$.

The slope of graph in Fig. 5 is 0.48 which is destination compatible with theoretical slope of 0.5 for diffusion controlled process [24].

Fig. 6 shows the relationship between oxidative potential and scan rate of Fe(II)/Fe(III) at the new fabrication working electrode, the oxidation current peak of 63mV at low scan rate (10mV/sec) was increased linearly to 279mV at high scan rate (100mV/sec) as described in the equation: $Y=2338.3X+63.013$ ($R^2=0.9476$).

From Fig. 6 the intercepts at zero current or scan rate produces zero current potential (E₀, 1) of 63mV for the process of Fe(II)/Fe(III) at CESMC₆₀ [25].

Scan rate (Vsec ⁻¹)	E _{pc} (V)	E _{pa} (V)	I _{pc} (A)	I _{pa} (A)	ΔE= E _{pa} -E _{pc} (V)	Ratio I _{pa} /I _{pc}	Df (Cm- 2sec-1)
0.01	-0.274	0.052	-0.0194	0.144	0.222	0.74	1.59x10 ⁻¹⁰
0.02	-0.338	0.111	-0.0269	0.212	0.227	0.79	1.72x10 ⁻¹⁰
0.03	-0.384	0.141	-0.0320	0.259	0.243	0.81	1.71x10 ⁻¹⁰
0.04	-0.419	0.170	-0.0361	0.298	0.249	0.83	1.70x10 ⁻¹⁰
0.05	-0.447	0.198	-0.0394	0.327	0.249	0.83	1.64x10 ⁻¹⁰
0.06	-0.471	0.217	-0.0424	0.356	0.254	0.84	1.62x10 ⁻¹⁰
0.07	-0.498	0.238	-0.0447	0.381	0.260	0.85	1.59x10 ⁻¹⁰
0.08	-0.509	0.247	-0.0472	0.406	0.262	0.86	1.58x10 ⁻¹⁰
0.09	-0.534	0.263	-0.0493	0.427	0.271	0.87	1.55x10 ⁻¹⁰
0.10	-0.542	0.279	-0.0515	0.446	0.263	0.87	1.52x10 ⁻¹⁰

Table 1. Scan rate, potential, current, peak potential separation, peak current ratio and diffusion coefficient (D_f) for Fe(II)/Fe(III) in KCl solution using CESMC₆₀
1. táblázat Mintavételi sebesség, potenciál, áramerősség, elválasztó csúspotenciál, csúcs áramerősség arány és diffúziós tényező (D_f); Fe(II)/Fe(III) KCl oldatban CESMC₆₀ elektróddal

Fig. 5 Plot of Log (anodic current peak) of 0.3 mM K₄[Fe(CN)₆] in 1M KCl at fabrication working electrode CESMC₆₀ versus Ag/AgCl and different SR (0.01- 1 Vs⁻¹)

5. ábra Anódos csúcs áramerősség logaritmus ábrázolása: CESMC₆₀ munkaelektroda 0.3mM K₄[Fe(CN)₆] 1M KCl oldatban, Ag/AgCl referencia elektróddal; mintavételi sebesség 0.01- 1 Vs⁻¹

Fig. 6 Plot of anodic potential peak of 0.3 mM K₄[Fe(CN)₆] in 1M KCl at fabrication working electrode CESMC₆₀ versus Ag/AgCl and different SR (0.01- 1 Vs⁻¹)

6. ábra Anódos csúcs potenciál logaritmus ábrázolása: CESMC₆₀ munkaelektroda 0.3mM K₄[Fe(CN)₆] 1M KCl oldatban, Ag/AgCl referencia elektróddal; mintavételi sebesség 0.01- 1 Vs⁻¹

3.3. Calculation of diffusion coefficient (D_f)

The diffusion coefficient of the oxidation reaction for ferric ions to ferrous ions through cyclic voltammetry at the CESMC₆₀ can be calculated by Eq. (1) and from the data in Table 1 and Eq. (1) [26,27]:

$$I_{pa} = 2.69 \times 10^5 (n)^{3/2} A C_0 (D_f)^{1/2} (v)^{1/2} \quad (1)$$

Where:

I_{pa} is oxidative current peak, A is the area of the electrode, F is Faraday, C_0 is the concentration, v is the scan rate and D_f is the diffusion coefficient of the reacting species.

It was found that the D_f values of Fe(II)/Fe(III) in the 0.1M KCl as supporting electrolyte has average value of the $D_f = 1.622 \times 10^{-10} \text{ cm}^2 \text{sec}^{-1}$ of the oxidative current peak of $K_4[Fe(CN)_6]$ when used the new fabrication working electrode CESMC₆₀ that means the heterogeneous transfer of electron through the electrolyte by nanomaterials fullerene C_{60} in the modified working electrode which acts as electro-catalyst for the enhancement of the processing the Fe(II)/Fe(III) in the electrolyte by increasing of scan rate against to the diffusion coefficient values as shown in Table 1 [28,29].

3.4. The influence of different temperatures on the CESMC₆₀

The influence of different temperatures on the new fabrication electrode was used the redox current peaks value of output potential using $K_4[Fe(CN)_6]$ and increasing the temperature from 10 °C to 80 °C. The logarithm of current versus inverse temperature depends on the Arrhenius equations [24]:

$$\sigma = \sigma^0 \exp(-E^* / RT) \quad (2)$$

$$D = D^0 \exp(-E^* / RT) \quad (3)$$

Where:

σ / D - is the quotient of connectivity

σ^0 / D^0 - is the quotient of the standard connectivity

E^* - is the activation energy

R - is the ideal gas constant

T - is the temperature in Kelvin

The activation energy which needed to oxidizing the Fe(II) to Fe(III) was found as $E^* = 1.05 \text{ kJmol}^{-1} \text{K}^{-1}$ with less value than using other electrodes such as grafted polymer electrode in the same operation as $E^* = 1.75 \text{ kJmol}^{-1} \text{K}^{-1}$ [30]. Also, the stability of GPE at high temperature has high resistance than other working electrodes [31-38].

3.5. Sensitivity of CESMC₆₀ in low detection limit at different concentrations

The new fabrication working electrode CESMC₆₀ of the polarization of high sensitivity in the detection of low concentrations of solutions of $K_4[Fe(CN)_6]$ in 0.1M KCl solution as a supporting electrolyte, where it can be seen as a good sensor for low concentrations of chemical compounds with high sensitivity ($R^2 = 0.9822$ for anodic current peak and $R^2 = 0.9834$ for cathodic current peak) of the CESMC₆₀ for both oxidation-reduction current peaks as shown in Figs. 7 and 8 respectively.

Fig. 7 Plot of anodic current peak of different concentrations (0.3-1mM) $K_4[Fe(CN)_6]$ in 1M KCl at fabrication working electrode CESMC₆₀ versus Ag/AgCl and SR 100 mVs⁻¹

7. ábra Anódos csúcs potenciál különböző koncentrációk esetén: CESMC₆₀ munkaelektroda 0.3mM $K_4[Fe(CN)_6]$ 1M KCl oldatban, Ag/AgCl referencia elektróddával; mintavételi sebesség 100 mVs⁻¹

Fig. 8 Plot of cathodic current peak of different concentrations (0.3-1mM) $K_4[Fe(CN)_6]$ in 1M KCl at fabrication working electrode CESMC₆₀ versus Ag/AgCl and SR 100 mVs⁻¹

8. ábra Katódos csúcs áramerősség különböző koncentrációk esetén: CESMC₆₀ munkaelektroda 0.3mM $K_4[Fe(CN)_6]$ 1M KCl oldatban, Ag/AgCl referencia elektróddával; mintavételi sebesség 100 mVs⁻¹

3.6. Stability and reliability of CESMC₆₀

The potential cycling of the redox current peaks of the modified working electrode CESMC₆₀ in 0.3 mM $K_4[Fe(CN)_6]$ with 1M KCl was carried out during cyclic voltammetry. Continuous potential cycling did not seem to affect the redox current peak of the new working electrode, since the faradic activity appears reliable even after ten times, and the relative standard deviation (RSD) of the cathodic current peak of the new fabrication electrode is $\pm 4.16\%$ as shown in Table 2. Table 3 shows the reliability of CESMC₆₀ as working electrode at SR is 100 mV s⁻¹ for anodic current peak of 0.3 mM $K_4[Fe(CN)_6]$ in 0.3 M KCl and the RSD is $\pm 3.34\%$.

Fig. 9 Cyclic voltammogram of ten times for redox current peaks of CESMC₆₀ in 0.3 mM $K_4[Fe(CN)_6]$ with 1 M KCl at SR 100mVs⁻¹

9. ábra Tíz ciklusos ciklikus voltammogram: CESMC₆₀ munkaelektroda 0.3mM $K_4[Fe(CN)_6]$ 1M KCl oldatban, mintavételi sebesség 100 mVs⁻¹

Fig. 9 shows the cyclic voltammogram of redox current peaks of 0.3 mM $K_4[Fe(CN)_6]$ in 1M KCl for ten times of Fe(II)/Fe(III) which illustrate the good stability of the cyclic voltammogram of the new fabrication working electrode by overlapping the lines.

Numbers	I_{pc} (uA)	Mean	RSD
1	-49.0		
2	-48.9		
3	-47.9		
4	-47.5		
5	-46.9		
6	-45.5		
7	-45.8		
8	-44.8		
9	-44.4		
10	-43.4	-46.41	±4.16%

Table 2. Reliability of CESMC₆₀ as working electrode at SR is 100 mVs-1 for cathodic current peak of 0.3 mM $K_4[Fe(CN)_6]$ in 1 M KCl
2. táblázat CESMC₆₀ munkaelektroda megbízhatósága katódos csúcs áramerősségre; 0.3mM $K_4[Fe(CN)_6]$ 1M KCl oldatban, mintavételi sebesség 100 mVs-1

Numbers	I_{pa} (uA)	Mean	RSD
1	40.9		
2	41.0		
3	42.2		
4	42.5		
5	42.7		
6	43.4		
7	43.7		
8	44.5		
9	44.7		
10	44.8	43.02	±3.34%

Table 3. Reliability of CESMC₆₀ as working electrode at SR is 100 mVs-1 for anodic current peak 0.3mM $K_4[Fe(CN)_6]$ in 1 M KCl
3. táblázat CESMC₆₀ munkaelektroda megbízhatósága anódos csúcs áramerősségre; 0.3mM $K_4[Fe(CN)_6]$ 1M KCl oldatban, mintavételi sebesség 100 mVs-1

3.6. Study the CESMC₆₀ at different pH

The new fabrication CESMC₆₀ was studied at different pH in aqueous solution for both acidic and alkaline medium as shown in Table 4. It was observed that the fabrication electrode properties of the redox current peaks for Fe(II)/Fe(III) in 0.3 mM $K_4[Fe(CN)_6]$ with 1M KCl as a supporting electrolyte have the same affective against to the acidic and alkaline medium by increasing the current peak against to increasing of acidity and the same phenomena increasing the current peak versus ton increasing the alkaline medium as shown in Table 4 and Figs. 10 and 11.

pH	E_{pc} V	E_{pa} V	I_{pc} mA	I_{pa} mA
3	-544	263	-47.2	41.3
4	-531	228	-50.4	41.9
5	-553	238	-49	41.3
6	-574	279	-51.2	41.9
7	-534	247	-49.4	40
8	-506	347	-55.4	48.1
11	-580	317	-48.6	42.3

Table 4. Relationship between pH and redox current and potential peaks of 0.3 mM $K_4[Fe(CN)_6]$ with 1 M KCl at CESMC₆₀
4. táblázat Kapcsolat a pH érték, a redox csúcs áramerősség és csúcs potenciál között; CESMC₆₀ munkaelektroda 0.3mM $K_4[Fe(CN)_6]$ 1M KCl oldatban

Fig. 10 Plot of anodic current peak of 0.3 mM $K_4[Fe(CN)_6]$ in 1M KCl at fabrication working electrode CESMC₆₀ against to pH using Ag/AgCl as reference electrode and SR 0.1 Vs-1

10. ábra Anódos csúcs áramerősség ábrázolása: CESMC₆₀ munkaelektroda 0.3mM $K_4[Fe(CN)_6]$ 1M KCl oldatban, Ag/AgCl referencia elektróddával; mintavételi sebesség 0.01 Vs-1

Fig. 11 Plot of cathodic current peak of 0.3 mM $K_4[Fe(CN)_6]$ in 1M KCl at fabrication working electrode CESMC₆₀ against to pH using Ag/AgCl as reference electrode and SR 0.1 Vs-1

11. ábra Katódos csúcs áramerősség ábrázolása: CESMC₆₀ munkaelektroda 0.3mM $K_4[Fe(CN)_6]$ 1M KCl oldatban, Ag/AgCl referencia elektróddával; mintavételi sebesség 0.01 Vs-1

4. Conclusions

A new fabrication working electrode CESMC₆₀ was manufactured and characterized electrochemically in the laboratory of cyclic voltammetry. All chemical and physical properties was studied using 0.3 mM $K_4[Fe(CN)_6]$ in 1M KCl for redox current peaks of reversible reaction of Fe(II)/Fe(III). It was found an enhancement current peak of the CESMC₆₀ for redox process of Fe(II)/Fe(III) was observed compared to the GCE about ten times, also extended potential area working region between 2.0 to -2.0 V for the new electrode. The sensitivity of the fabrication electrode has high detection analysis using cyclic voltammetry significantly depend on the different concentration, pH, temperature, scan rates, and Stability and reliability. It was determined the diffusion coefficient (D_f) of the CESMC₆₀ in the 0.3 mM $K_4[Fe(CN)_6]$ in 1M KCl which has average value $1.6 \times 10^{-10} \text{ cm}^2 \text{ sec}^{-1}$.

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