Journal of Chemical Reactivity and Synthesis 2024: 14(3) 201-209

Research Article

The Investigating and comparing the spectroscopic impedance of the electrode modified by polypyrrole in the presence of chromium, copper and iron

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ARTICLE INFO:

Received:
25 January 2025

Accepted:
28 February 2025

Available online:
18 May 2025

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ABSTRACT

In this research, the synthesis of pyrrole polymer on graphite electrode has been investigated by cyclic voltammetry method in the potential range of -0.8 to 1.2 V in phosphoric acid, including calcium chloride as an electrolyte support, and the impedance technique has been used to determine the conductivity properties and resistance of 3 elements chromium, copper and iron are used. The Nyquist curves of each element at specific voltages and in a set of voltages have been discussed individually and comparatively, and these results have been obtained that at a certain voltage, the charge transfer resistance of the copper element has decreased compared to chromium and increased compared to iron. And the iron element has the lowest load transfer resistance value, and in checking the voltage set, we came to the conclusion that the lowest load transfer resistance of the iron element and the voltage is 0.2.

Keywords: spectroscopic impedance, polypyrrole, chromium, copper; iron.

1. Introduction

In the impedance technique, the electrochemical cell is stimulated by an alternating signal with a small amplitude (about 5 mV). Another advantage of this technique is that it is possible to obtain resistance and capacitance information, which is a part of the nature of any electrochemical system and is performed on the surface of the electrode[1-3]., such as studying corrosion of metals and determining the mechanism of reactions responsible for corrosion, it is also possible to study the nature of the charge and the mass at the electrode/solution interface. examined the contract[4-6]. The basis of this method is applying the potential of the electrochemical cell and receiving the response in the form of a current; But it should be noted that each electrochemical cell is actually a set of resistors (solution resistance, coating resistance on the electrode, etc.) and capacitors (electrical double layer capacitor, etc.); Therefore, the applied potential and current are distributed in the circuit, and the impedance technique has the ability to determine the equivalent circuit and evaluate each of its elements[1, 7].

As a result of applying an alternating potential of an electrochemical cell and the intensity of the resulting current, a phase difference appears, as a result of which different parts of the equivalent circuit can be recognized. Electrochemical cell is actually an electric circuit that consists of resistors and capacitors such as solution resistance, electrode surface coating resistance, double layer capacitor.

2. Experimental

Materials, Equipment, and Method

Pyrrole with the formula (C_4H_4NH) was distilled under low pressure in a nitrogen atmosphere and the resulting colorless liquid with a purity of 99.9%, a molecular weight of 67.09 gr/mol and a density of 0.97 gr/ml was stored at 5 degrees Celsius. Calcium chloride and phosphoric acid are also used without purification. all the above items had the label of the German company Merck. Potentiostat and galvanostat device Ivium Compact State model made in the Netherlands is used for electrosynthesis. 1.8 mm pencil tip made by Gaj Educational Institute was used as the working electrode and platinum blade as auxiliary electrode and Ag/AgCl electrode as reference electrode in electrochemical synthesis.

Electrosynthesis of pyrrole on the tip of a graphite pencil in the potential range of -0.8 V to 1.2 V with a sweep speed of 100 mV/s from a solution with a volume of 10 ml containing 50 mM monomer, 1 M phosphoric acid and 1 M calcium chloride was performed.

Spectroscopic impedance spectra were prepared in a separate solution containing 10 ml of iron, chromium or copper solution and 1 M potassium chloride as an electrolyte support, and the modified graphite electrode was placed in the solution together with the reference electrode and the platinum electrode, and the impedance It is obtained by the device in the potential range of -0.2 V to 1 V and the frequency range of 0.01 to 10,000 Hz.

3. Results and Discussion

Investigating spectroscopic impedance in the oxidation potential of any modified electrode

Since they do not show an obvious current at a certain potential, therefore, the spectroscopic impedance was investigated at any oxidation potential [8-10]. According to Figures 1 to 3, the oxidation potential for chromium solution is 0.42 V, copper solution is 0.3 V, and iron solution is 0.7 V.

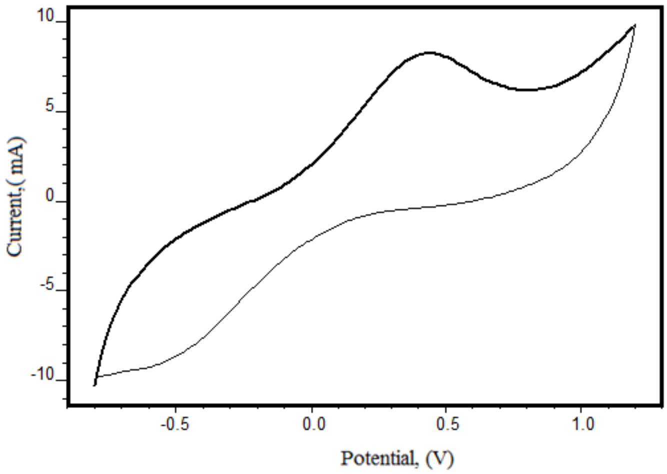

Fig. 1. Cyclic voltammogram of the electrode modified by polypyrrole in 0.1 molar chromium solutions in the presence of potassium chloride

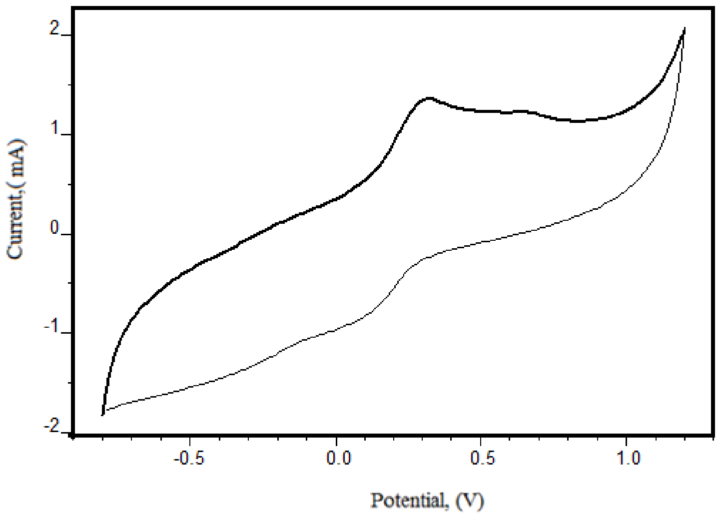

Fig. 2. Cyclic voltammogram of the electrode modified by polypyrrole in 0.1 molar solutions in the presence of potassium chloride

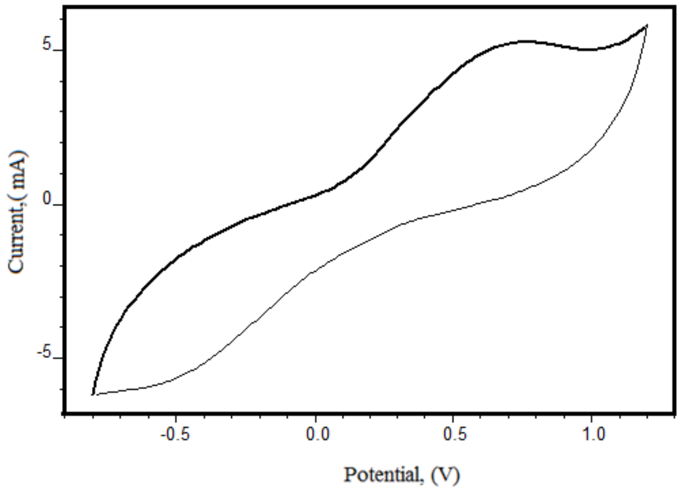

Fig. 3. Cyclic voltammogram of the electrode modified by polypyrrole in 0.1 M iron solutions in the presence of potassium chloride

Impedance spectroscopy of electrosynthesized polypyrrole in the presence of chromium, copper and iron

Figure 4 shows the Nyquist impedance spectroscopy curve of electrosynthesized polypyrrole in the presence of 0.1 M solutions of chromium, copper and iron along with potassium chloride as an electrolyte support in aqueous medium.

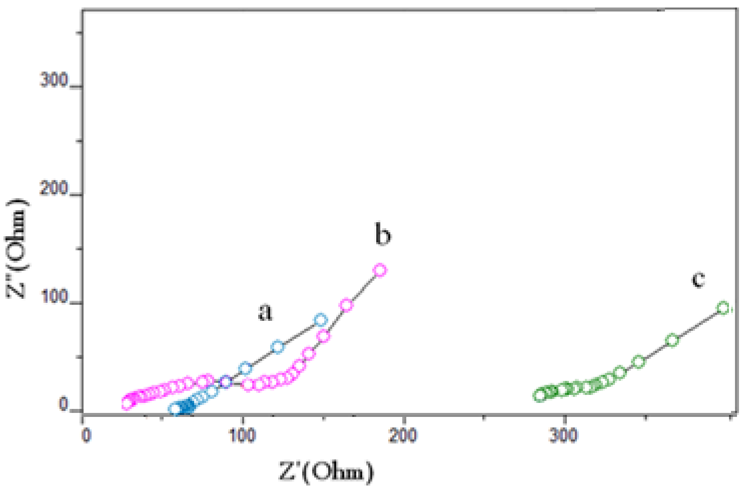

Fig. 4. .Nyquist impedance spectroscopic curve of electrode modified by polypyrrole in 0.1 M solutions a) iron b) chromium c) copper in the presence of potassium chloride as a support in aqueous medium at a voltage of 0.6

According to the placement of these elements in the periodic table from left to right, the load transfer resistance decreases; Therefore, the load transfer resistance of copper is lower than chromium; Iron also has a lower charge transfer resistance than chromium, but the charge transfer resistance of iron is lower than copper, which is because iron is considered a paramagnetic element [11-13].

According to Table 1, the charge transfer resistance for 0.1 M solutions, chromium is 90 ohms, for copper is 31 ohms, and for iron is 9 ohms in the presence of potassium chloride as an electrolyte support. The conductivity of group IB elements (such as copper) is higher than other metals, which is due to the fact that d 3 level orbitals are full, so the effect of covering the nucleus increases in it and causes the force of the nucleus to decrease relative to the valence layer and the electron to move freely According to Table 1, the charge transfer resistance for 0.1 M solutions, chromium is 90 ohms, for copper is 31 ohms, and for iron is 9 ohms in the presence of potassium chloride as an electrolyte support. The conductivity of group IB elements (such as copper) is higher than other metals, which is due to the fact that 3d level orbitals are full, so the effect of covering the nucleus increases in it and causes the force of the nucleus to decrease relative to the valence layer and the electron to move freely.

In this circuit, Rs is the solution resistance, Rp is the charge transfer resistance or polarization resistance, Q is the capacitance of the electric double layer, and W is the Warberg impedance and represents the diffusion element in the circuit[14, 15].

Table 1. The results of spectroscopic impedance spectrum of the electrode modified by polypyrrole in the presence of 0.1 M, chromium, copper and iron solutions at 0.6 voltage

	R_s (Ohm)	R_p (Ohm)	Q(F)	N	W
Cr	1/15	90	$2/00\times10^{-6}$	$7/00\times10^{-1}$	$4/72\times10^{+1}$
Cu	2/4	31	$4/00\times10^{-6}$	$7/03\times10^{-1}$	$9/04\times10^{+1}$
Fe	1/7	9	$6/02\times10^{-6}$	$7/02\times10^{-1}$	$4/27\times10^{+1}$

Studying and checking the impedance curves of chromium, copper and iron solutions

Figure 5 shows the changes of real impedance in terms of potential for 0.1 M chromium solution, as can be seen, the lowest amount of load transfer resistance for chromium solution is at 0.1 volts.

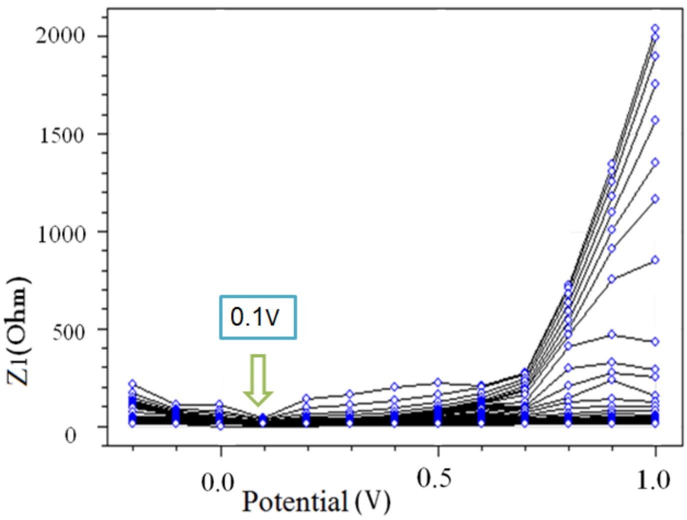

Fig. 5. True spectroscopic impedance curve of electrode modified by polypyrrole in 0.1 M chromium solution

In copper solution, the lowest charge transfer resistance is in the potential range of 0.4-0.1 volts, which is shown in figure 6.

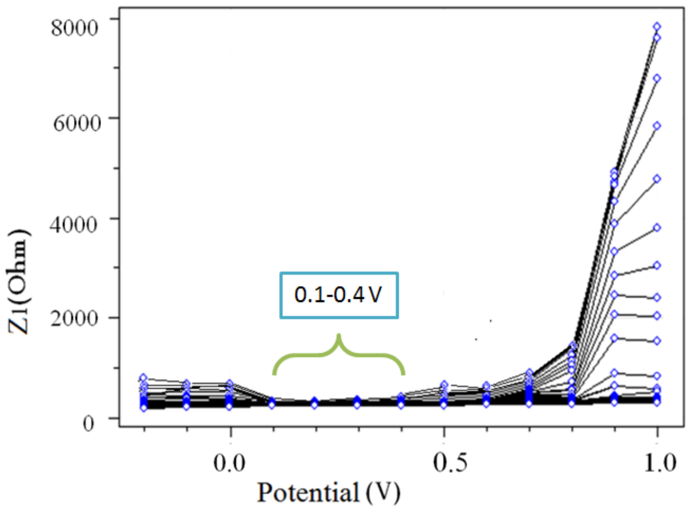

Fig. 6. True spectroscopic impedance curve of the electrode modified by polypyrrole in 0.1 M copper solution

Investigation of impedance curves of 0.1 M iron solutions Figure 7 show that the lowest charge transfer resistance in 0.1 M iron solution is at 0.7 volts.

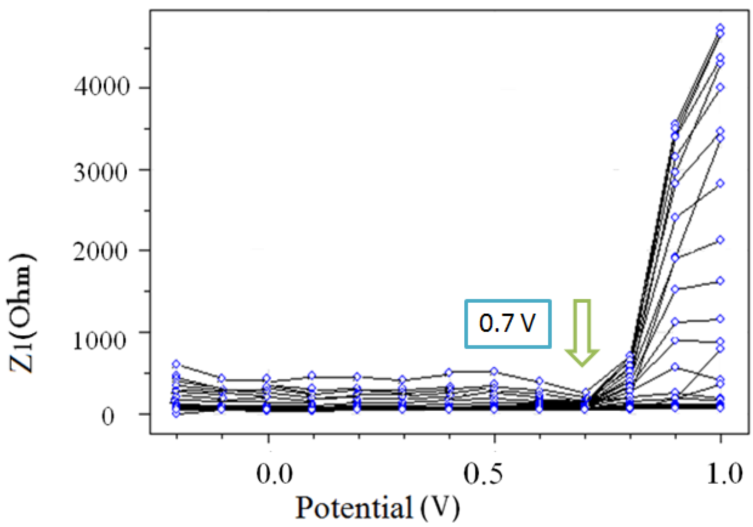

Fig. 7. True spectroscopic impedance curve of the electrode modified by polypyrrole in 0.1 M iron solution

According to the results obtained from the impedance curves, it can be concluded that the charge transfer resistance of the polypyrrole film of the copper element has decreased compared to chromium due to the filling of the 3d layer and has increased compared to iron, and the iron element has the lowest charge transfer resistance due to It has paramagnetic properties, and in the analysis of the voltage set, we came to the conclusion that the lowest charge transfer resistance is the polypyrrole film for the iron element.

4. Conclusion

In this research, the spectroscopic impedance of graphite electrode modified by pyrrole homopolymer in the presence of chromium, copper and iron has been investigated.

According to the results obtained from the spectroscopic impedance curves of the graphite electrode modified by pyrrole homopolymer, the conductivity of group IB elements (such as copper) is higher than other metals, which is due to the filling of d-aligned orbitals and the presence of one-electron orbitals in the valence layer.

Chromium, compared to copper, due to the half-filled d orbitals, the single electron in the valence layer cannot easily escape from the nucleus; For this reason, it has lower conductivity than copper, and therefore, the load transfer resistance of copper is lower than that of chromium. Due to its paramagnetic property, iron has a lower R_P value than the other two elements.

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