JCRS

Journal of Chemical Reactivity and Synthesis 2022: 12(4) 239-253

Research Article

Investigation of electrochemical behavior of Fe and Mn ions at the surface of electrode/electrolyte interface using electrochemical impedance spectroscopy

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ARTICLE INFO:

Received:
17 October 2022

Accepted:
29 November 2022

Available online:
15 December 2022

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ABSTRACT

Many studies have been conducted using electrochemical impedance spectroscopy (EIS) in recent decades. This is an accurate detection technique for electrochemical systems based on transmission function analysis between voltage and current. In this research, impedance, admittance, and capacitance of composite graphite electrode are investigated and compared in Mn and Fe ions solutions in sulfuric acid medium. The results indicated lower Fe impedance than Mn and admittance greater than that of Mn, indicating a greater Fe conductivity than Mn. Additionally, higher capacitance of Fe than of Mn was because of higher electric characteristics of Fe as compared to Mn. These techniques have been an alternative for cyclic voltammogram (CV) and mainly help in the quantitative determination of kinetic and transmission parameters. Valuable data are obtained using Electrochemical impedance spectroscopy (EIS). Therefore, it can be concluded that EIS is a detecting technique for describing and evaluating the behavior of intermediary elements at the surface of electrode/electrolyte.

Keywords: Admittance; Capacitance; Cyclic voltammogram; Manganese(II) sulfate; Iron(II) sulfate.

1. Introduction

Carbon electrode has many applications and advantages because of easy access, good polarization, high contact surface, low price, as well as chemical and thermal capacities. Many studies have been conducted using electrochemical characteristics of carbon surface and spectroscopy impedance [1].

Electrochemical impedance spectroscopy (EIS) is a proper technique of examining many physical and chemical parameters in liquids that are obtained using Wheatstone bridge and dielectric permeability of aqueous solutions, organic fluids, and oxides through which the dependence of frequency on impedance can be determined (for example, determination of conductivity, dielectric constant, and interfacial properties of sample) Valuable electrochemical information can be obtained using the relationship between EIS data and equivalent circuits[2]. The rapid estimation of the corrosion rate in complex systems is one of the advantages of spectroscopic impedance, since, by drawing the impedance spectrum and matching it with an electrical circuit, polarization resistance can be obtained. This feature is very important in complex systems, such as effluent factories that have several known or unknown chemicals

[2-4]. EIS is an electrochemical method in which potential range is low and current response is measured; and other electrochemical factors and corrosion rate can be discussed using the relationship between voltage and current. EIS is a powerful method of studying the phenomena in electrode or electrolyte gap. The Randles' model can be used to obtain this goal including R_s, R_{ct}, and Z_w elements that signify solution resistance, charge transfer resistance, and Warburg impedance, respectively. R indicates resistance and depending on charge or mass transfer is denoted as Rs and Rct [3, 5, 6].

A remarkable factor in EIS studies is the use of small sinus potential on carbon electrochemical properties using spectroscopy of impedance over the past 10 years.This is an effective and reliable technique of extracting information on electrochemical characteristics of electrochemical systems such as double-layer capacity (Q), diffusion impedance, charge transfer determination, and resistance against solution[7, 8].

Another important parameter is the double layer capacity (Q). This capacity (Q) check point in the EIS is the interface between the electrode/electrolyte, which forms the characteristics of the two-layer structure. Various capacities of two layers generally depend on frequency. This dependence is often referred to as a capacitive dispersion (the distribution of indirect current at the electrode/electrolyte interface leads to capacitive dispersion) [9].

Double- layer capacity study is one of the important aspects of electrode and electrolyte materials processes. Since different ions have different double-layer capacities, they exhibit different strengths for the double-layer capacity (Q) [10, 11].

EIS and capacitance are dependent on the applied potential of the electrode and are obtained as frequencies of the alternative current (AC) signal and is one of the general techniques in corrosion studies that provide useful information on the interface between the electrode / electrolyte films and their electrical properties [12, 13].

Admittance is the reverse of impedance. In principle, the required data can be analyzed at the frequency domain or time under consideration. Impedance measures AC in circuits while admittance shows flowed current in circuits. Admittance is a criterion for conductivity showing easiness of current movements in circuits [14, 15].

In this research, spectroscopic impedance of graphite electrode was studied in the presence of Fe and Mn ions. Therefore, in order to remove the medium effect on spectrophotometric impedance of graphite electrode, sulfuric acid was used for both ions. For this purpose, ions were dissolved in a similar solvent to remove the effect of the solvent in creating different resistance; and only the effect of the present of ions in the solution on electrode impedance was studied. Moreover, the effect of ion transfer elements on conductivity and electric activity of graphite electrode was studied.

2. Experimental

2.1. Materials

Iron(II) sulfate, manganese sulfate ($MnSO_4$) and 96 % w/w Sulfuric acid (H_2SO_4) were from Merck. All solutions were prepared with water from a MilliQ-MilliRho purification system and had a typical pH of 6.5. Separate solutions of 0.001 M iron(II) sulfate and 0.001 M $MnSO_4$ in molar sulfuric acid are prepared right before the experiments before the electrochemical measurements.

2.2. Equipment

Electrochemical measurements were performed in a one-compartment cell with a three electrode configuration. The three-electrode cell consists of 2B pencil graphite (1.8 mm diameter) (Staedtler Lumograph, Germany) as working electrode and Pt electrode was used as the counter electrode against a pseudo Ag/AgCl reference electrode.

2.3. Procedure

Cyclic voltammetry (CV) was carried out with use of a Potentiostat/Galvanostat (Ivium Technologies, Netherlands) by a computer equipped with the Ivium Soft Software package. Electrochemical impedance spectroscopy (EIS) measurements were taken using the (Compact State; Ivium Technologies, Netherlands) controlled by a computer equipped with the Ivium Soft software package. EIS was performed using the following parameters: amplitude of 0.01 V; frequency range of 100 Hz to100000 HZ.

3. Results and discussion

3.1. Cyclic voltammetry of iron(II) solution

Fig. 1a indicates the cyclic voltammogram of 1 M sulfuric acid containing 0.001 M Iron(II) sulfate on the composite graphite electrode with a scan rate of 100 mV s^{-1} at potential range of -0.8 to 1.2 V. As obvious from Fig. 1a, only a couple of oxidation peaks and reduction are observed, implying reaction reversibility; this is because electrode transition reaction happens in the electrode surface without any prior or subsequent reaction. Fig 1b shows the CV of 1 M sulfuric acid on composite graphite electrode. As observed, when a graphite electrode is put in 1 M sulfuric acid, no peak is seen. The anodic peak in the forward scan and the cathodic peak in the reverse scan in Fig. 1a correspond to the conversion of Fe^{2+} to Fe^{3+} and vice versa.

In reversible reactions, currents ratios are equal and they stay the same by changing the sweep speed (equation 1). Since this is the law of the system and current ratio is 1, this reaction is reversible. Therefore, the mentioned half-reaction is reversible on Composite graphite working electrode in sulfuric acid.

$$\frac{I_p^a}{I_p^c} = \frac{3.4\times10^{-4}}{3.4\times10^{-4}} = 1 \qquad \text{Eq. 1}$$

Moreover, reaction reversibility is obtained using the Tomes Criterion (equation 2). Tomes Criterion is differences between $E_{1/4}$ and $E_{3/4}$ (ΔE_{TC})

$$E_{1/4} = E_{1/2} + \frac{0.0592}{n}\log\frac{I_d - I_d/4}{I_d/4} \Rightarrow E_{1/4} = E_{1/2} + \frac{0.0592}{n}\log 3$$

$$E_{3/4} = E_{1/2} + \frac{0.0592}{n}\log\frac{I_d - 3I_d/4}{3I_d/4} \Rightarrow E_{3/4} = E_{1/2} + \frac{0.0592}{n}\log\frac{1}{3} \qquad \text{Eq. 2}$$

$$\Delta E = E_{1/4} - E_{3/4} = \frac{0.0565}{n}$$

In the voltammogram, $E_{1/4} = 0.39$ V , $E_{3/4} = 0.33$ V and ΔE_{TC} (Peak potential differences between $E_{1/4}$ and $E_{3/4}$) using the Tomes criterion technique is 0.06, which implies the reversibility of the reaction, since the ΔE_{TC} value for the reversible reaction is 60/n mV. Therefore, the results indicate the reversibility of the reaction.

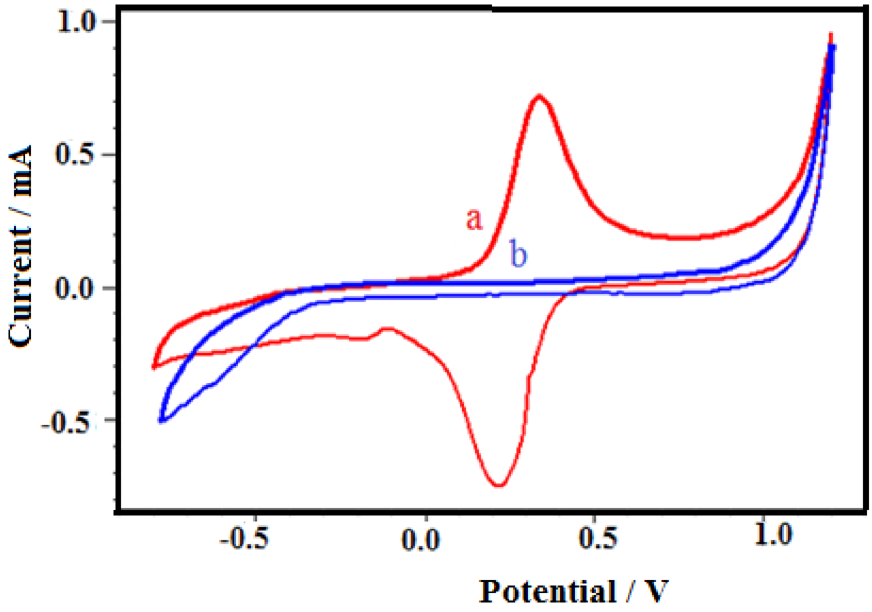

Fig. 1. The CVs of composite graphite electrode (a) in 1 M sulfuric acid containing 0.001 M Iron(II) sulfate (b) in 1 M sulfuric acid. The potential is cycled between −0.8 and +1.2 V (vs. Ag/AgCl) at a scan rate of 100 mV/s.

Fig. 2 shows the CVs of Composite graphite working electrode in 0.001 M Iron(II) sulfate solution in 1 M sulfuric acid with different scan rates in the potential area of -0.8 to 1.2 V. As shown in Fig. 2, not only the potential difference between the anodic and cathodic peaks (ΔE_p) does not change with increasing the scan rates, but the anodic peak current (Ipa) directly proportional to the square root of the scan rates, which implies that the electrode process is mainly controlled by the diffusion.

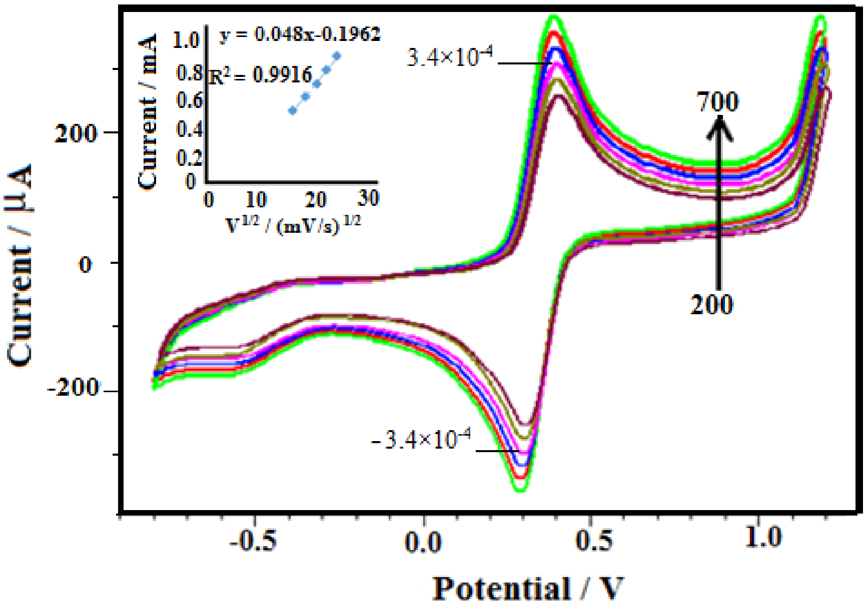

Fig. 2. The CVs of composite graphite electrode in 1 M sulfuric acid containing 0.001 M Iron(II) sulfate at scan rates of 200,300,400,500,600,700 mV/s. Inset shows the plot of I_{pa} vs. $\upsilon^{1/2}$

3.2. Cyclic voltammetry of Mn solution

Fig. 3a shows the CVs obtained from 0.001M manganese (II) sulfate in 1 M sulfuric acid medium on composite graphite electrode at a scan rate of 100 mV s^{-1} at potential area of -0.8 to1.2 V. usually, two reduction processes are performed in the forward scan, which is due to the conversion of Mn^{+2} to Mn^{+3} and Mn^{+4}; while with an increase in the concentration of sulfuric acid, the conversion process is only from Mn^{+2} to Mn^{+3}. As observed, just one pair of oxidation-reduction is seen that is related to the half-reaction peak of Mn^{+2} to Mn^{+3}.

Fig. 3b shows the CVs obtained from in 1 M sulfuric acid medium without in the presence manganese (II) sulfate on composite graphite electrode. As seen, when graphite electrode is put in 1 M H_2SO_4, no peak is observed. The studied reaction is quasi-reversible because the behavior of a quasi-reversible system is similar to that of a reversible system in low sweep rates. However, the behavior of a quasi-reversible system is similar to that of an irreversible system in high sweep rates. In a quasi-reversible system, the Redox reaction is performed with excessive voltage, and also the electron transfer reaction at the electrode surface occurs without any additional reaction. In a quasi-reversible reaction, if α = 0.5, the ratio of anodic and cathodic currents (I_p^a/I_p^c) is equal to one (equation 3).

$$\frac{I_p^a}{I_p^c}=\frac{8\times10^{-4}}{8\times10^{-4}}=1 \qquad \text{Eq. 3}$$

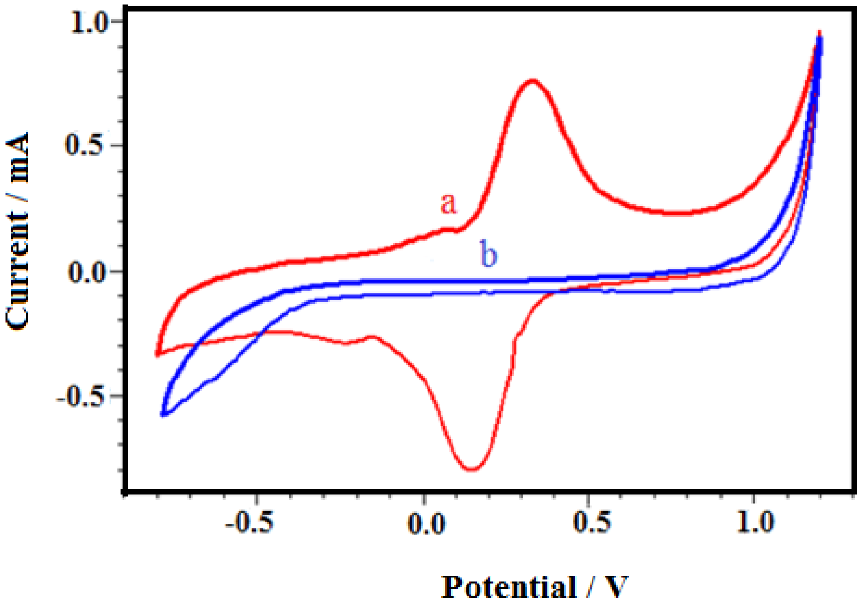

Fig. 3. The CVs of composite graphite electrode (a) in 1 M sulfuric acid containing 0.001 M manganese sulfate (b) in 1 M sulfuric acid. The potential is cycled between −0.8 and +1.2 V (vs. Ag/AgCl) at a scan rate of 100 mV/s.

Fig. 4 shows different scan rates on composite graphite electrode in sulfuric acid solution containing manganese sulfate in a potential range of -0.8 to 1.2 V. As shown in Fig. 4, the ΔEp is greater than 0.18 V (Ea=0.15 V, Ec=0.33 V), which increases with increasing scan rate, which implies a quasi-reversible reaction.

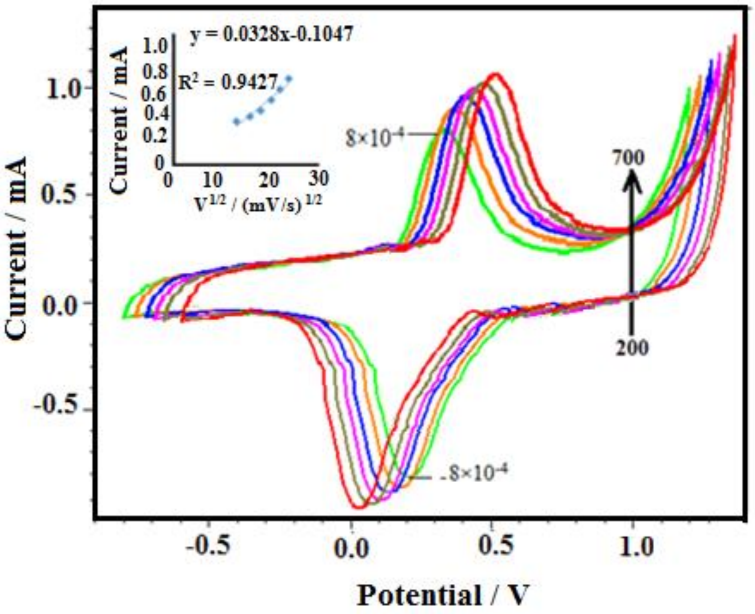

Fig. 4. The CVs of composite graphite electrode in 1 M sulfuric acid containing 0.001 M Manganese sulfate at scan rates of 200, 300, 400, 500, 600, 700 mV/s. Inset shows the plot of I_{pa} vs. $\upsilon^{1/2}$

3.3. Impedance, Capacitance and Admittance of Manganese(II) sulfate and Iron(II) sulfate

In this research, graphite electrode was used in a similar solution of 1 M sulfuric acid containing different ions in order to evaluate the effect of different ions in making resistance. The spectroscopic impedance of Composite graphite electrode in the presence of two solutions (one containing Mn and the other containing Fe) with similar conditions showed the following:

The value of charge transfer resistance at constant potential 0.3 V is 70 Ω for manganese and 25 Ω for iron. Since the electrical conductivity of the solutions is due to the displacement of the ions, ion concentration, ion charge, and ion mobility. Therefore, the difference in the conduction value of the ions depends on the size of the ions and their hydrated degree.

Ionic conductivity value is the criterion of its mobility under the influence of an electric field; through this, the ability of ions for electricity transfer in solutions can be predicted Consequently, lower resistance against charge transfer leads to more charge transfer and increased electric conductivity, and facilitates redox transfers. Based on calculations, the ionic conductivity of Iron(II) sulfate is more than that of manganese sulfate; this is due to the charge transfer resistance of Iron(II) being less than that of manganese(II). When a working electrode is put in solution, ions with higher mobility permeate inside the working electrode and are less hydrated. Therefore, impedance exits from ideal capacitive mode and shows non-ideal capacitive behavior; this is because less Warburg impedance to transfer protons in a double layer leads to better permittivity in the electrode surface and also, better load transfer. Warburg impedance shows the ion permittivity process.

Therefore, since higher Warburg impedance is obtained in a test for Mn 700 (1/Ω sqrt (Hz)) than for Fe 400 (1/Ω sqrt (Hz)), it confirms better permittivity of Fe ion on the electrode surface as compared to Mn ion. When an oxide film is formed on a piece through permittivity, the corrosion rate is controlled by permittivity; and reaction speeds controlled by high concentrations of cation or low concentration of anion result in permittivity or concentration polarization, respectively. Solution resistance is obtained as 55 Ω and 11 Ω for Mn and Fe, respectively. The higher solution resistance in Mn is due to less diffusion; this is because higher solution resistance reduces mass transfer for electrode permittivity processes adjacent to the electrode and hence, there is less diffusion.

Since the double-layer has electron exchange characteristics and is created at the solid-liquid interface, the transfer of ions in the double layer to the ions on the solid surface is due to the diffusion phenomenon Since the electron exchange property is higher in Fe than in Mn, the double-layer capacity (Q) is 1.9×10^{-7} F and 1×10^{-5} F for Mn and Fe, respectively. The double-layer formed in electrode/electrolyte interface level is very important in EIS. By studying the double-layer of water and ion electrolyte, it has been concluded that double-layer capacity (Q) depends on frequency. N (Degree of electrode surface roughness or cell geometry) is the capacity of the acceptor layer (acceptor concentration). The lower the acceptor concentration, the more is the charge transfer resistance. Based on studies, the lower acceptor concentration in Mn (8.9×10^{-1}) as compared to Fe (7.8×10^{-1}) increases solution resistance and charge transfer resistance in Mn. The Nyquist diagram can explain Randles' cell, Warburg impedance, and capacitive responses at low frequencies. Charge is transferred and electron is exchanged at the level of pores and areas where oxidation occurs at the electrode surface and impedance detects electrode or electrolyte interface properties as a collection of real (Z) and imaginative (Z ') resistances. Fig. 5 shows Composite graphite electrode impedance in Mn and Fe solutions. Table I is the values of the Randles'equivalent circuit elements obtained by fitting the experimental results from the Nyquist plots in 1 M sulfuric acid containing 0.001 M Iron(II) sulfate and 0.001 M manganese sulfate at 0.25 V.

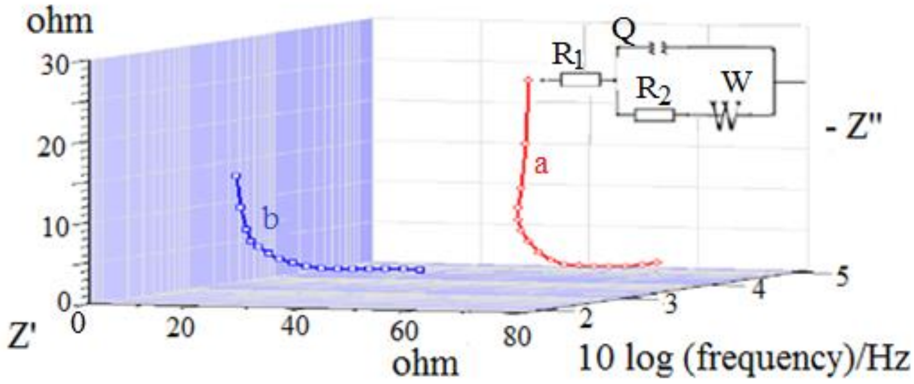

Fig. 5. Nyquist plots of composite graphite electrode in (a) Manganese(II) sulfate (b) Iron(II) sulfate. The ac potential amplitude was 10 mV and frequency range used was from 100 kHz to 100 Hz.

Table I. The best fitted values of the Randles' equivalent circuit elements simulated from impedance data for graphite electrode (a) in 1 M sulfuric acid containing 0.001 M Iron(II) sulfate (b) in 1 M sulfuric acid containing 0.001 M manganese sulfate.

	Element	R_s (Ω)	R_{ct} (Ω)	W (1/Ω sqrt (Hz)	Q (F)	N
a	Fe	1.1×10^{1}	2.5×10^{1}	4×10^{2}	1×10^{-5}	7.8×10^{-1}
b	Mn	5.5×10^{1}	7×10^{1}	7×10^{2}	1.9×10^{-7}	8.9×10^{-1}

When EIS occurs only in one frequency, some physical characteristics that are effective in creating electrical properties are damaged and, in some cases, an incorrect estimation of the performance of concentration factors are obtained such as bandwidth potential and so on. Capacity can be calculated from Equation 4 by knowing the frequency at the highest point of the circle.

Equation 4: $C = \frac{1}{WR_p}$

Since for Fe, $R_p = 2.5\times10^{1}$ Ω and $w = 4\times10^{2}$ (1/Ω sqrt (Hz)), its capacitance was obtained as $C = 1\times10^{-4}$ F; and since for Mn, $R_p = 7\times10^{1}$ Ω and $w = 7\times10^{2}$ (1/Ω sqrt (Hz)), its capacitance was obtained as $C = 204\times10^{-7}$ F. The higher capacitance of Fe as compared to Mn shows that iron is more electrically charged than Mn.

Impedance is a criterion for persistence showing opposition to the current of electrons in a circuit while admittance shows easiness of electron movements. In standard admittance techniques, capacity is only measured for low voltage that depends on electrochemical parameters and can give information on electrode kinetic, corrosion current, and electrosorption. The admittance is obtained by equation 5.

$$Y = \frac{wc}{\sqrt{1 + w^2 c^2 Rs^2}} \qquad \text{Eq. 5}$$

Since $w = 4\times10^{2}$ (1/Ω sqrt (Hz)), $C = 1\times10^{-4}$ F, and $R_s = 11$ Ω for Fe, obtained admittance for Fe is $Y = 0.0366\ \Omega^{-1}$; and since $w = 7\times10^{2}$ (1/Ω sqrt (Hz)), $C = 204\times10^{-7}$ F, and $R_s = 55$ Ω for Mn, obtained admittance for Mn is $Y = 0.0112\ \Omega^{-1,}$ which shows higher conductivity of Fe as compared to Mn. In Fig. 6, Diagram (a) shows Mn admittance and Diagram (b) shows Fe admittance in 1M sulfuric acid.

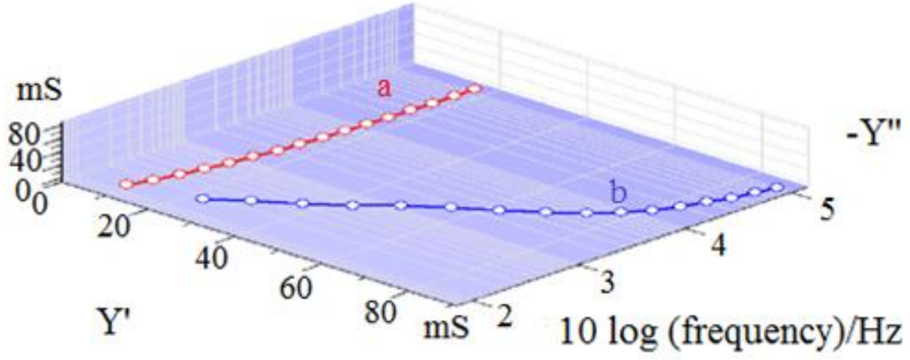

Fig. 6. Admittance of composite graphite electrode in (a) Manganese(II) sulfate (b) Iron(II) sulfate. The ac potential amplitude was 10 mV and frequency range used was from 100 kHz to 100 Hz.

4. Conclusions

EIS is one of the most effective and reliable techniques of extracting information on electrochemical characteristics of electrochemical systems such as solution resistance, charge transfer resistance, double-layer capacity (Q) and Warburg impedance. This technique is powerful for electrochemical systems based on analysis of transfer function between voltage and current, which has higher stimulation than frequency during current (or voltage) and is compared by voltage (or current) response [16, 17]. In this research, Composite graphite electrode was used in Iron(II) sulfate solution and manganese(II) sulfate was used in 1M sulfuric acid to examine different resulted resistances by intermediary elements and then, to obtain impedance, admittance, and capacitance. Admittance is the opposite of impedance, which is measured at small AC voltages. Obtained admittance is 0.0366 Ω^{-1} for Fe and 0.0112 Ω^{-1} for Mn. Higher admittance for Fe as compared to Mn shows higher conductivity of Fe than of Mn; this is because Fe impedance is lower than Mn impedance based on obtained results since impedance for Fe and Mn is 25 Ω and 70 Ω, respectively. Examining capacitance is 1×10^{-4} F for Fe and 204×10^{-7} F for Mn, which shows that capacitance of Fe, is higher than that of Mn due to its higher electric characteristics. Therefore, it can be concluded that EIS is a detecting technique for describing and evaluating the behavior of intermediary elements.

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