

Characterization of Reference Electrode Ag/AgCl Dry Type by Cyclic Voltammetry

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ABSTRACT

In the present work the characterisazion of reference electrode Ag/AgCl type dry by 0.01 M [Fe(CN)₆]^{3-/4-} in 0.1 M KCl using the technique of cyclic voltammetry at potential range of -0.2 to 0.8 V and scan rate variation.. The anodic (E_{pa}) and the cathodic (E_{pc}) peak potentials. as well as the corresponding anodic (i_{pa}) and cathodic (i_{pc}) peak currents. were obtained at different scan rates (10. 20. 25. 50. 100. and 200) mV/s . The half-wave potentials (E_{1/2}) of the [Fe(CN)₆]^{4-/} [Fe(CN)₆]³⁻ couple in the investigated solvent media have been evaluated. I_p versus v^{1/2} have been calculated using the Randles-Sevcik equation.

Keywords: cyclic voltammetry. half-wave potential. reference electrode Ag/AgCl.

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I. INTRODUCTION

One of technique in modern analytical chemistry that can be used to indicate electroactive species and to give information about the analyte is obtained from measurement of the Faradaic current as a function of the applied potential is cyclic voltammetry. At this limiting potential the direction of the potential scan is reversed and the same potential range is scanned in the opposite direction (hence the term "cyclic"). Consequently, the species formed by oxidation on the forward scan can be reduced on the reverse scan. This technique is accomplished with a three-electrode arrangement: the potential is applied to the working electrode with respect to a reference electrode while an auxiliary (or counter) electrode is used to complete the electrical circuit^{1,2}. Cyclic voltammetry is a method in which information about the analyte is obtained from measurement of the Faradaic current as a function of theapplied potential. The current response over a range of potentials is measured, starting at an initial value and varying the potential in a linear manner up to a limiting value. At this limiting potential the direction of the potential scan is reversed and the same potential range is scanned in the opposite

direction (hence the term "cyclic"). Consequently, the species formed by oxidation on the forward scan can be reduced on the reverse scan. This technique is accomplished with a three-electrode arrangement: the potential is applied to the working electrode with respect to a reference electrode while an auxiliary (or counter) electrode is used to complete the electrical circuit.

The present article reports the results from an electrochemical investigation of the [Fe(CN)₆]^{4-/} [Fe(CN)₆]³⁻ couple in KCl 0.1 M using the technique of cyclic voltammetry. All experiments were undertaken at different scan rates (10. 20. 25. 50. 100. and 200) mV/s and cyclic variation. The purpose of the present work is characterisazion of reference electrode Ag/AgCl dry type by cyclic voltammetry to enlarge the available knowledge on the electrochemical behavior.

II. EXPERIMENTAL SECTION

II.1. Chemicals

All the chemicals and solvents used in the present study were of Sigma-Adrich. was purchased from Sigma-Aldrich. The solvents used on this study were KCl. The chemical used on this study was dilute 0.01 to 0.005 M

$K_3Fe(CN)_6/K_4Fe(CN)_6$ in KCl 0.1 M solvent as a working solution.

II.2. Experimental

All electrochemical experiments were undertaken with a potentiostat from eDAQ with disc Platinum (Pt) working electrode (1 mm). Pt wire (0.5 mm) as counter electrode. and dry type Ag/AgCl as reference electrode. Therefore, all values of potential are automatically reported with respect to the redox potential of Ag/AgCl. For the electrochemical experiments, the electrolyte temperature was the room temperature of about 25°C.

III. RESULT and DISCUSSIONS

Characterization of the reference electrode Ag/AgCl self-made by cyclic voltammetry

Initial characterization performed using cyclic voltammetry versus Ag/AgCl reference electrode using 0.1 KCl in aqueous as the electrolyte on the potential range of -0.8 to 0.5 V and at scan rate of 100 mV / as shown in Figure 1.

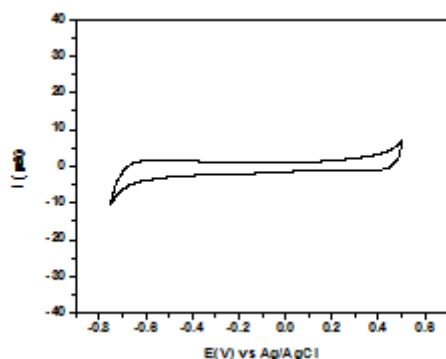


Figure 1. Voltamogram of disc Pt using 0.1M KCl as the electrolyte on potential range -0.8V to 0.5V

It is seen that there is no oxidation and reduction peak in the applied potential range. It indicates that disc Pt is electrochemically stable and there is no contamination of other analytes that can undergo redox reactions in the applied potential range on the cyclic voltammetry system.

Characterization of reference electrode Ag/AgCl also analyzed using a solution of 0.005 M $[Fe(CN)_6]^{3-/4-}$ in 0.1 M KCl. The characterization in using the same solution by varying the scan rate (figure 2a and 2b) is also shown that the current is proportionate to the increased of scan rate which indicates the good performance of the working electrode for delivering the current. The cyclic

voltammetric parameters for $K_3Fe(CN)_6/K_4Fe(CN)_6$ 0.005 M in KCl 0.1 M in water at 298 K are summarized in Table 1 and 2. all potential values are reported versus the Ag/AgCl reference electrode was made by myself and commercial eDAQ dry type.

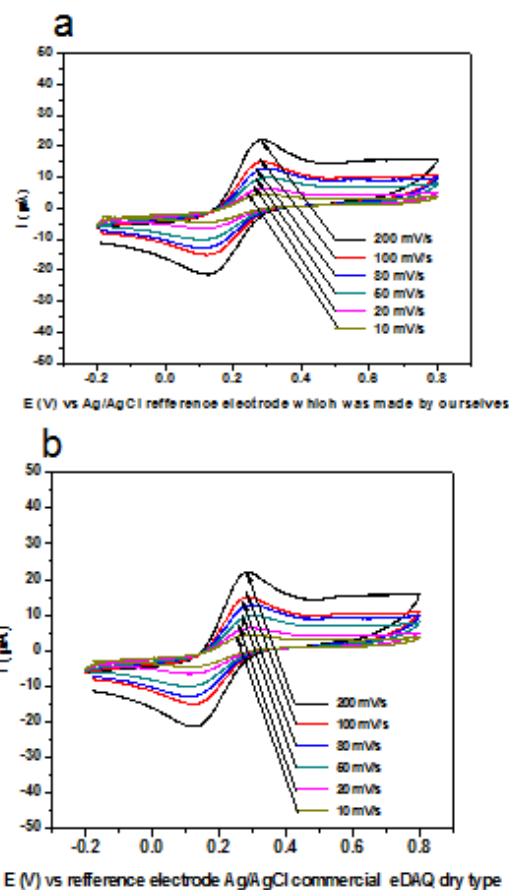


Fig. 2 Cyclic voltammograms vs Ag/AgCl reference electrode at a platinum electrode showing the effect of the scan rate on the electrochemistry of $K_3Fe(CN)_6 / K_4Fe(CN)_6$ system 0.005 M in KCl 0.1 M at 298 K; (2a) vs Ag/AgCl was made by myself. and (2b). vs Ag/AgCl was commercial eDAQ dry type

The reference electrode must have a fixed electrode potential during the measurement. To comply with these requirements the self-made Ag/AgCl electrode has done characterization using $K_3Fe(CN)_6/K_4Fe(CN)_6$ cyclic voltammetry.

Table 1. Scan rate (v). anodic (E_{pa}) and cathodic (E_{pc}) peak potentials a anodic and cathodic current ratio (i_{pa}/i_{pc}). anodic and cathodic peak separation (ΔE_p) and half-wave

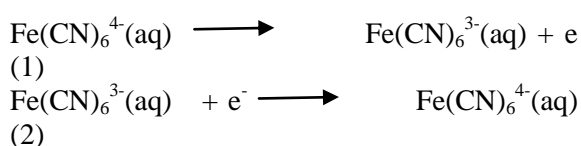
potential a ($E_{1/2}$) for $K_3Fe(CN)_6/K_4Fe(CN)_6$ KCl at 298 K versus Ag/AgCl which was made system at concentration of 0.005 M in 0.1 M by myself

v (mV/s)	Ag/AgCl of the self - made						
	Δi_{pa} (μA)	Δi_{pc} (μA)	ipa/ipc	E_{pa} (mV)	E_{pc} (mV)	$(E_{pa} - E_{pc})$ (mV)	$(E_{pa} + E_{pc})/2$ (mV)
10	4.4	-3.6	-1.2	284	112	172	198
20	5.8	-4.8	-1.2	286	113	173	200
50	7.7	-7.5	-1.0	292	116	176	204
80	9.7	-9.9	-0.9	294	116	178	205
100	11.9	-11.7	-1.0	302	120	182	211
200	17.4	-16.4	-1.1	302	128	174	215

Table 2. Scan rate (v). anodic (E_{pa}) and cathodic (E_{pc}) peak potentials a anodic and cathodic current ratio (ipa/ipc). anodic and cathodic peak separation (E_p) and half-wave potential a ($E_{1/2}$) for $K_3Fe(CN)_6/K_4Fe(CN)_6$ system at concentration of 0.005 M in 0.1 M KCl at 298 K versus Ag/AgCl commercial eDAQ dry type.

v (mV/s)	Ag/AgCl dry type						
	Δi_{pa} (μA)	Δi_{pc} (μA)	ipa/ipc	E_{pa} (mV)	E_{pc} (mV)	$(E_{pa} - E_{pc})$ (mV)	$(E_{pa} + E_{pc})/2$ (mV)
10	3.7	-3.2	-1.1	266	110	156	188
20	5.2	-4.3	-1.2	268	114	140	191
50	7.4	-6.8	-1.1	274	116	152	195
80	9.4	-8.8	-1.1	272	122	156	197
100	11.0	-10.4	-1.1	276	128	162	202
200	16.7	-13.9	-1.2	276	130	166	203

Representative cyclic voltammograms of $K_3Fe(CN)_6/K_4Fe(CN)_6$ system in KCl 0.1 M in water are shown in Figs. 2. The voltammograms illustrate that as the voltage becomes more positive, an anodic peak current (ipa) is observed at the anodic peak potential (E_{pa}), indicating that $Fe(CN)_6^{4-}$ is converted to its oxidized form $Fe(CN)_6^{3-}$ according to reaction 1. During the return scan, the voltage becomes less positive and the process is reversed; consequently, reduction of $Fe(CN)_6^{3-}$ is now occurring and a cathodic peak current (ipc) is observed at the cathodic peak potential (E_{pc}).



The $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ couple exhibits reversible oxidation of the investigated in KCl 0.1 M in water media. The anodic and cathodic peak separation (E_p) in the cyclic voltammograms was found to be in the range between -0.20 V (the ideal value that is indicative of one-electron oxidation) and 0.80 V (Table 1). The peak current ratio of the reverse and the forward scans is equal to unity ($ipa/ipc = 1.0$). It was also found that the peak currents were essentially constant for several cycles (Fig.3).

The redox potential for a couple is better expressed as the half-wave potential ($E_{1/2}$) rather than by the anodic peak (E_{pa}) or cathodic peak (E_{pc}) potentials, because both E_{pa} and E_{pc} change with the scan rate whereas $E_{1/2}$ is independent of the scan rate. The halfwave potential ($E_{1/2}$) of the $[Fe(CN)_6]^{4-}/$

$[\text{Fe}(\text{CN})_6]^{3-}$ couple was determined according to the following equation:

$$E_{1/2} = E_{pa} - (\Delta E_p)/2$$

where E_{pa} is the anodic peak potential and E_p is the potential difference between the anodic and cathodic peaks ($E_p = E_{pa} - E_{pc}$). Cyclic voltammograms of $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ couple in KCl 0.1 M in water solution are shown in Figs. 2 (a) and (b) with variation scan rate. The data obtained from these curves are summarized in Table 1 and 2. The values of the half-wave potential ($E_{1/2}$) were found to be independent of the scan rate, as was expected for a reversible system.

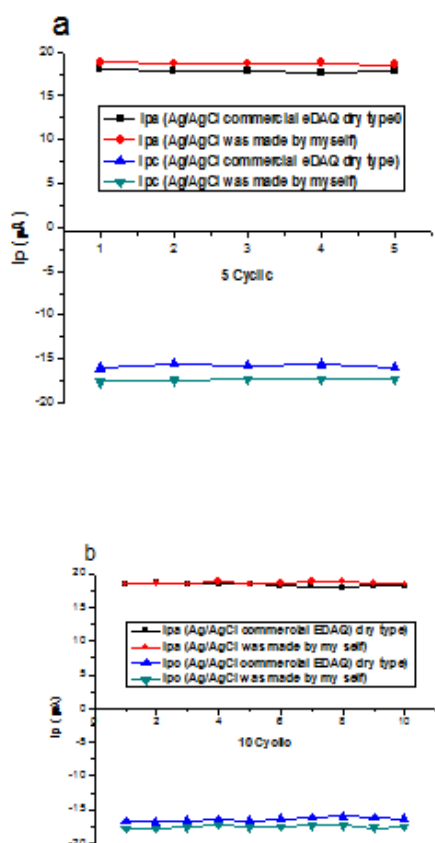


Fig. 3 Curves I_{pa} and I_{pc} versus repeating cyclic of cyclic voltammogram $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ system 0.005 M in KCl 0.1 M vs Ag/AgCl was made by myself and commercial eDAQ dry type at 100 mV/s; (3a) 5 cyclic (3b). 10 cyclic
 Figure 3 (a) and (b) shows that the results are reproducible to the application of repeating cyclic which indicate the stability of the working electrode, and electrolyte solution and analytes during measurement. From this

characterization, we identified the oxidation and reduction peak as the analyte is in the range - 0.20 to 0.80 V.

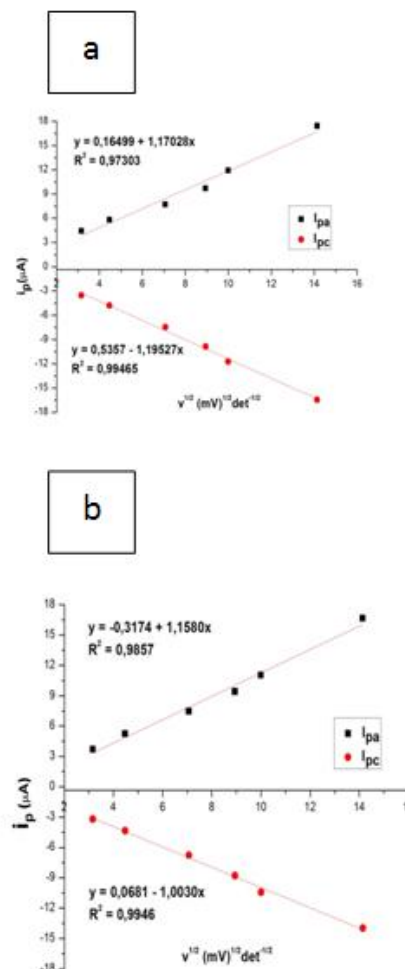


FIG. 4 CURVES I_{pa} AND I_{pc} VERSUS $v^{1/2}$ OF CYCLIC VOLTAMMOGRAM $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ SYSTEM 0.005 M IN KCL 0.1 M; (3A) VS AG/AGCL WAS MADE BY MYSELF (3B). COMMERCIAL EDAQ DRY TYPE

Characterization using the same solution by varying the scan rate (figure 4a and 4b) is also shown that the current is proportionate to the increased of scan rate which indicates the good performance of the working electrode for delivering the current⁶. The peak current for a reversible process is described by the Randles-Sevcik equation^{7, 8}, which assumes that mass transport occurs only by a diffusion process

$$I_p = 268,600 n^{3/2} A D^{1/2} C v^{1/2}$$

where i_p is the peak current (in A), n the number of electron equivalents exchanged during the oxidation/redox reversible process (electron stoichiometry), A the active surface area of the working electrode (cm^2), D the

diffusion coefficient ($\text{cm}^2 \cdot \text{s}^{-1}$), c the bulk concentration of the diffusing species ($\text{mol} \cdot \text{cm}^{-3}$), v the voltage scan rate ($\text{V} \cdot \text{s}^{-1}$), F Faraday's constant, and R the universal gas constant.

In the present work, a plot of the anodic (i_{pa}) and the cathodic peak current (i_{pc}) against the square root of the scan rate ($v^{1/2}$) results in a straight line that passes through the origin with a slope proportional to the square root of the diffusion coefficient ($D^{1/2}$).

Based on result of electrochemical parameter i_{pa}/i_{pc} is closer to 1 (involving 1 electron in the $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ system), so that both comparing electrodes can be used. However, according to visual observation, reference electrode Ag/AgCl was made by myself is decreasing by time. This happens due to its partition porosity, giving a possibility for the electrode's KCl solution to contaminate the analyte. Meanwhile, reference electrode Ag/AgCl commercial dry type has Cl^- source on its surface that comes from the $K_{sp}^{1/2}$ AgCl's solubility in the solution used.

IV. CONCLUSION

Based on the characteristic result electrochemical parameter i_{pa}/i_{pc} is closer to 1 (involving 1 electron in that system) of the both reference electrode Ag/AgCl (was made by myself and commercial eDAQ dry type) to 0.01 and 0.005 M $(\text{Fe}(\text{CN})_6)^{3-/4-}$ system in KCl 0.1 M in water using work and auxiliary electrode Pt, so that both reference electrode Ag/AgCl can be used. But there are some weakness of electrode Ag/AgCl was made by myself, such as leaky cell membrane (effect of porosity to Cl^- concentrations in analyte solution) and to require replenishment of 0.1 M KCl solution. Whereas reference electrode Ag/AgCl commercial eDAQ dry type has a source of Cl^- ions on the electrode surface from the solubility ($K_{sp}^{1/2}$) AgCl in various the solution used. For the subsequent work, reference electrode Ag/AgCl commercial dry type was used in different types of solvents.

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