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Electrocatalytic Hydrogen Production using Cu(II), Fe(III) and Co(III) complexes with Pyridoxal-thiosemicarbazone (PLTSC) derived ligand: A comparative study

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In the present work, we made comparative studies of the electrocatalytic performance toward proton reduction of Cu(II), Fe(III) and Co(III) complexes with pyridoxal-thiosemicarbazone (PLTSC) ligand. Knowing that the direct reduction of CH_3COOH on the surface of vitreous carbon electrode occurs at Ep = -1.8 V vs Ag/AgCl in $[Bu_4N][BF_4]$-DMF solution, the presence of Fe(III), Cu(II) or Co(III) complex significantly shifts the peak potential to the more positive values, Ep = -1.42, -1.48, and -1.63 V, respectively *vs* Ag/AgCl. In the presence of acid, the peak current values for Fe(III), Cu(II), and Co(III) complexes was increased of about 2.6 , 7.2 and 2.2 times, respectively compared to the acid-free solution. This indicates the superiority of the Cu(II) complex for hydrogen production compared to Fe(III) and Co(III) complexes.

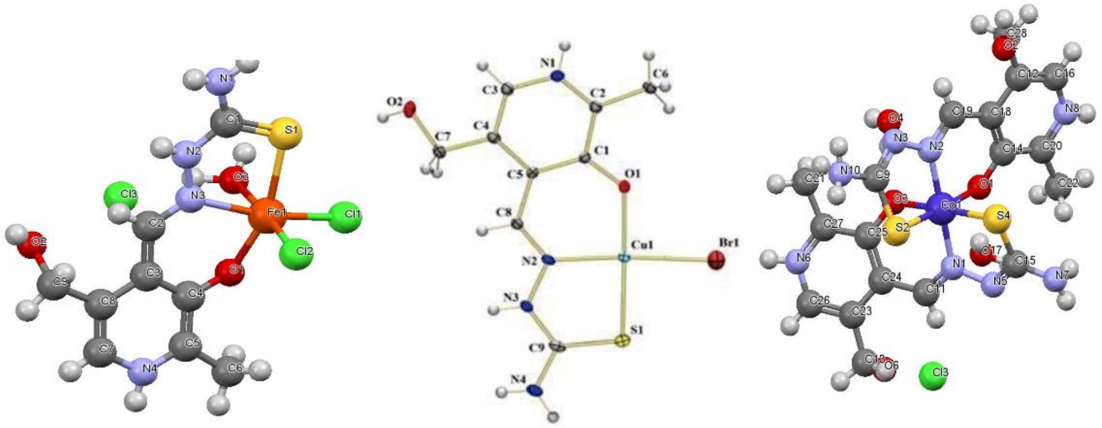
Keywords: Electrocatalysis; hydrogen production; Pyridoxal-thiosemicarbazone, Transition metal complexes

1. INTRODUCTION

Currently, the researchers focus their effort on hydrogen production as hydrogen is considered as suitable energy alternative for the future. A part of those research uses one of the most common strategies to produce hydrogen which is the electrochemical proton reduction technique [1-6]. This technique is very appealing as it is fast and inexpensive. As known, the direct reduction of proton (CH_3COOH) to convert to hydrogen usually take place at a high potential around Ep = -1.85 V vs Ag/AgCl. Therefore, the researchers are looking for a suitable electrocatalyst to shift the reduction potential of proton to more positive values. To reach this aim, the organometallic complexes have been synthesized and used in much past research, for example, hydrogen production was studied by Henderson using clusters complexes that contain different transition metals such as Fe, Mo, W, Ni, etc.

[7-12]. In the same way, Bhugun et al. [13] reported hydrogen production at low potential by using an iron meso-tetraphenylporphyrin (TPP) and triethylamine as source of proton. Alenezi and co-group [14-15] focused on the study of hydrogen production by using different metal complexes such as porphyrins, thio-smicarbazone and other clusters. In the same area, Violeta Jevtovic et all., reported that the hydrogen evolution reaction performance of Co(II) and Co(III) complexes is enhanced because of the presence of pyridoxal (thio)semicarbazones [16-17].

In the present study, we used the complexes $Fe(PLTSC)Cl_2(H_2O)]Cl$ [18], $[Cu(PLTSC)Br]\cdot H_2O$ [19] and $[Co(PLTSC\text{-}H)_2]Cl\cdot H_2O$ [20]. The Iron complex [18] has an octahedral structure, a mono-ligand complex. The Copper complex [19] has square-planar geometry, a mono-ligand complex while the cobalt complex [20] has octahedral coordination, but this one is bis-ligand complex. (Picture 1.)



a) b) c)

Picture 1. Molecular structures for complexes: a) $Fe(PLTSC)Cl_2(H_2O)]Cl$ [18], b) $[Cu(PLTSC)Br]\cdot H_2O$ [19], and c) $[Co(PLTSC\text{-}H)_2]Cl\cdot H_2O$ [20] with PLTSC ligand

Herein, we report the electrochemical study of the hydrogen evolution reaction (HER) using three complexes of Cu(II), Fe(III) or Co(III) containing PLTSC ligand. The acetic acid (CH_3COOH) was used as a source of proton. The electrocatalytic efficiency and activity of the three complexes were compared.

2. EXPERIMENTAL

The Cu(II), Fe(III) and Co(III) complexes were synthesized and characterized according to previously reported procedures [18-20]. Acetic acid (CH_3COOH) and Dimethylformamide (DMF) were purchased from Sigma Aldrich. DMF was purified by distillation over calcium hydride. Cyclic voltammetry experiments were carried out using an Potentiostat /galvanostat (Autolab PGSTAT 128N) and NOVA 1.10 software was used for recording and fitting the electrochemical experiment results. A conventional three-electrode arrangement was employed, consisting of vitreous carbon working electrode (0.07 cm^2) and Ag/AgCl reference electrode separated by a glass frit from a platinum wire auxiliary electrode (2 cm^2).

3. RESULTS AND DISCUSSION

3.1 Cyclic voltammetry of Cu(II),Fe(III) and Co(III) complexes

The electrochemical study of Cu(II), Fe(III) and Co(III) complexes was carried out at vitreous carbon in $[NBu_4][BF_4]$ electrolyte solution (0.1 M in DMF). The Table 1 shows the peak potentials of the studied complexes versus Ag|AgCl. The $[Cu(PLTSC)Br]^{\cdot}H_2O$ displays two one-electron reduction peaks, at E_p= -0.3 V and -1.42 V versus Ag/AgCl which are assigned to redox couples Cu(II)/Cu(I) and Cu(1)/Cu(0) respectively (Figure 1A). On the other hand, $Co(PLTSC\text{-}H)_2]Cl\ {}^{\cdot}\ H_2O$ shows three reduction waves at E_p= -0.62 V, -0.98 V and -1.63V versus Ag/AgCl corresponding to Co(III)/Co(II) , Co(II)/Co(I) and Co(I)/Co(0) respectively. It is worth noting that the first wave is a one electron reduction but the second reduction is more than one electron which may be related to both second reduction of cobalt and Pyridoxal-thiosemicarbazone ligand (PLTSC) (Figure 1B). The complex $Fe(PLTSC)Cl_2(H_2O)]Cl$ exhibits three reduction waves, the first one is a one-electron process at E_p= -0.15 V, the second reduction wave appears at -1.25 V and the third one at E_p= -1.48 V versus Ag/AgCl corresponding to Fe(III)/Fe(II), Fe(II)/Fe(I) and Fe(I)/Fe(0) (Figure 1C).

Table 1. Potentials of reduction waves of $Fe(PLTSC)Cl_2(H_2O)]Cl$, $[Cu(PLTSC)Br]^{\cdot}H_2O$ and $[Co(PLTSC\text{-}H)_2]Cl^{\cdot}H_2O$ versus Ag|AgCl[NBu4][BF4]–DMF.

Complexes	$Fe(PLTSC)Cl_2(H_2O)]Cl$			$[Cu(PLTSC)Br]^{\cdot}H_2O$		$[Co(PLTSC\text{-}H)_2]Cl^{\cdot}H_2O$		
Redox couple	Fe(III)/Fe(II)	Fe(II)/Fe(I)	Fe(I)/Fe(0)	Cu(II)/Cu(I)	Cu(I)/Cu(0)	Co(III)/Co(II)	Co(II)/Co(I)	Co(I)/Co(0)
E /V Ag^+/AgCl	0.15	-1.25	-1.48	- 0.30	-1.42	-0.62	-0.98	-1.63

Figure 1 shows the plot of the peak current (I_p) for the reduction waves of the studied complexes versus the square root of the scan-rate, $\nu^{1/2}$. The relationship between Ip and $\nu^{1/2}$ confirms that all process in the complexes is diffusion controlled. Plots of Ip versus $\nu^{1/2}$ for the Fe(I)/Fe(0), Cu(I)/Cu(0) and Co(I)/Co(0) displayed a similar linear dependence. The diffusion coefficient for Fe(I)/Fe(0), Cu(I)/Cu(0) and Co(I)/Co(0) are estimated from the cyclic voltametric data as 7.48×10^{-5} , 3.4×10^{-5} and 5.71×10^{-5} $cm^2\ s^{-1}$ receptively using equation 1.1 [21].

$$I_p= -(2.69\times10^5)\ n^{3/2}\ \ 1^{/2}\ D^{\ 1/2}\ v^{\ 1/2} \qquad 1.1$$

Where, I_p the peak current density $A.cm^{-2}$, D in $cm^2.s^{-1}$, v is in $V.s^{-1}$, c_0 Bulk is in $mol.cm^{-3}$ and n is the number of electrons transferred in the rate controlling step.

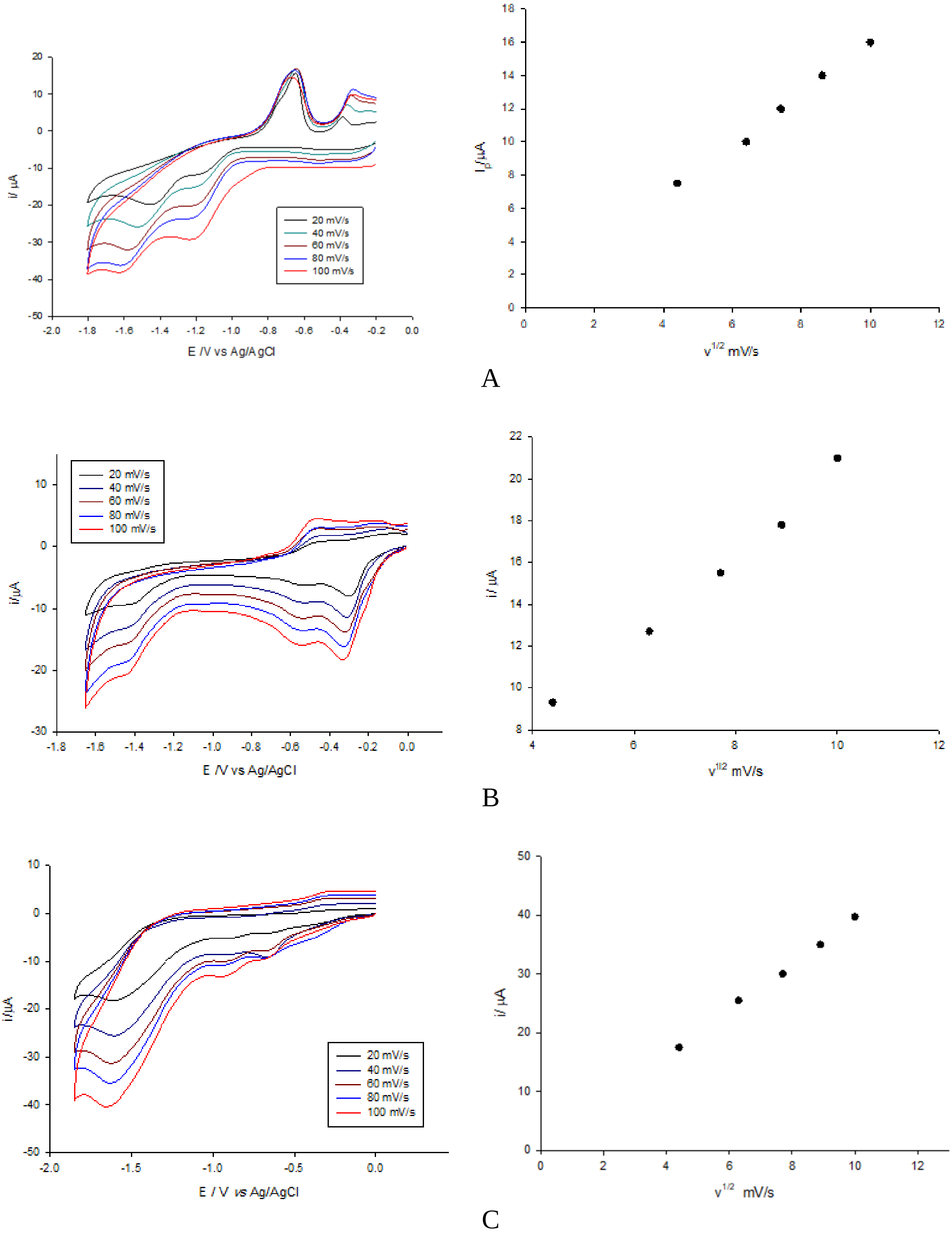


Figure 1. Cyclic voltammograms of 0.22 Mm a) Fe(PLTSC)$Cl_2(H_2O)$]Cl b) [Cu(PLTSC)Br]·H_2O (c) [Co(PLTSC-H)$_2$]Cl·H_2O at carbon electrode, at different scan-rates in DMF containing 0.1M [NBu_4][BF_4]. Plot of ip red for the Fe(I)/Fe(0) Cu(I)/Cu(0) and Co(I)/Co(0), couple versus the square-root of the scan-rate

3.2. Effect of acetic acid (CH_3COOH) on CV of Fe(III), Cu(II) and Co(III) complexes

The cyclic voltammetry plots of Fe(III), Cu(II) and Co(III) PLTSC complexes in DMF containing 0.1M $[NBu_4][BF_4]$ in the presence of different concentration of CH_3COOH under argon are shown in figure 3. It is worth noting that the peak current of the last reduction wave in the presence of acid become a large catalytic process.

Cyclic voltammetry of $Fe(PLTSC)Cl_2(H_2O)]Cl$ in the presence of CH_3COOH, shows an increases in the peak current for Fe(I)/Fe(0) wave at -1.48 V *vs* Ag/AgCl which is about 2.5 times higher compared to the peak current for $Fe(PLTSC)Cl_2(H_2O)]Cl$ in the absence of acid. The catalytic current tends towards a plateau at 4.3 mM of CH_3COOH. While, the dependence of the catalytic current of $[Cu(PLTSC)Br]{\cdot}H_2O$ for proton reduction is at -1.42 V versus Ag/AgCl, when the acid concentration increases the peak current increases until a maximum of 7.2 times higher compared to the peak current in the presence of $[Cu(PLTSC)Br]{\cdot}H_2O$ without acid and it stops increasing at an acid concentration of about 4.8 mM. In the other hand, the third peak of $[Co(PLTSC\text{-}H)_2]Cl{\cdot}H_2O$ Co(I)/Co(0) also increased in presence of different concentration of CH_3COOH, at -1.63 V versus Ag/AgCl and the peak current increase to 2 times more than the peak of $[Co(PLTSC\text{-}H)_2]Cl{\cdot}H_2O$ alone in presence of 4.2 mM CH_3COOH. To compare between the three studied complexes in activity as catalyst for proton production, Cu complex is more active than both $Fe(PLTSC)Cl_2(H_2O)]Cl$ and $[Co(PLTSC\text{-}H)_2]Cl{\cdot}H_2O$.

As known, the direct reduction of acetic acid on the carbon electrode surface in DMF at Ep = -1.85 V vs Ag/AgCl Figure 2. However, In the presence of the studied complexes, the potential shifted to more positive values; $Fe(PLTSC)Cl_2(H_2O)]Cl$ by (370 mV), $[Cu(PLTSC)Br]{\cdot}H_2O$ (430 mV) and $Co(PLTSC)Cl_2(H_2O)]Cl$ by (220 mV).

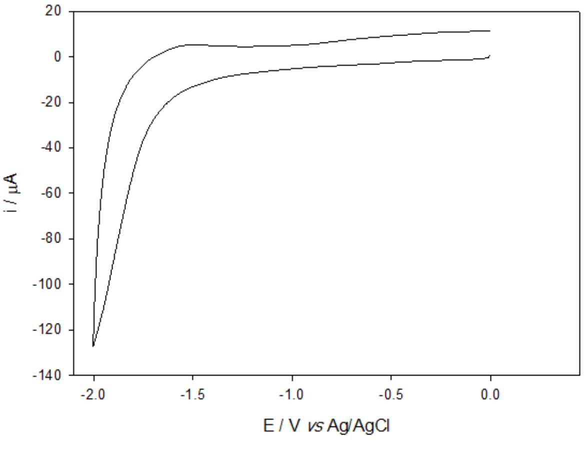


Figure 2. Cyclic voltammetry of 2 mM CH_3COOH in $[Bu_4N][BF_4]$-DMF, scan rate 100 mVs^{-1} at a vitreous carbon electrode.

It was found that the addition of the acid led to irreversible reduction waves in all the complexes, corresponding to Fe(I)/Fe(0) , Co(I)/Co(0) and Cu(I)/Cu0) In addition to this, peak current also increase dramatically (Figure 3). These observations are fully in accordance with those reported by Bhugun and coworkers who studied the catalysis of electrochemical hydrogen evolution by Fe(TPP)Cl at about -1.65 V *vs* Ag/AgCl using trifluoroacetic acid (TFA) as source of protons[21] .

Table 2. Potentials of reduction wave of CH_3COOH versus Ag|AgCl[NBu4][BF4] –DMF.

Reduction of CH_3COOH	**Potential /V *vs* Ag|AgCl[**	**Shift**
Direct reduction	-1.85	0
In presence of Fe(PLTSC)$Cl_2(H_2O)$]Cl	-1.48	370 mM
In presence of [Cu(PLTSC)Br]$\cdot H_2O$	-1.42	480 mM
In presence of [Co(PLTSC-H)$_2$]Cl$\cdot H_2O$	-1.63	220 mM

Electrocatalytic kinetics of proton reduction was also examined by the relations between the concentration of acetic acid *versus* i_{cat}/i_0 at the virtues carbon electrode. The peak current for Fe(I)/Fe(0), Cu(I)/Cu(0) and Co(I)/Co(0) is that measured at 100 mVs^{-1} before and after addition of acid at the same scan- rate. It is noted that the values of i_{cat}/i_0 become independent of the acid concentration at around *3* mM for all complexes.

Table 3. The rate constants (kcat, 25 °C) of the catalysis of the different electrocatalyst complexes, at glassy carbon electrode (3.6 mM CH_3COOH)

Complex	i_p/i_0	Rate constant (k_{obs}) / s^{-1}
Fe(PLTSC)$Cl_2(H_2O)$]Cl	2.6	5.3
[Cu(PLTSC)Br]$\cdot H_2O$	7.2	40.2
Fe(PLTSC)$Cl_2(H_2O)$]Cl	2.2	3.8

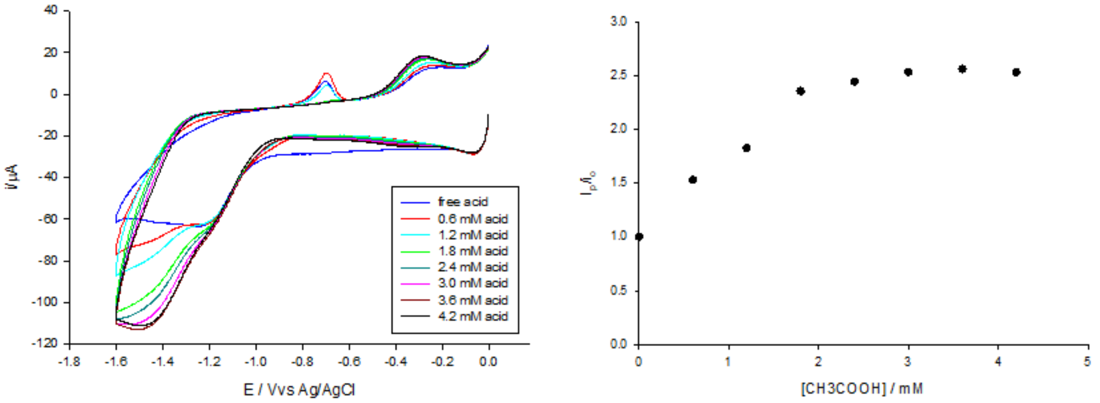
The rate constant (k^c_{cat} , room temperature) for the catalysis at carbon electrode the presence of Fe(PLTSC)$Cl_2(H_2O)$]Cl , [Cu(PLTSC)Br]$\cdot H_2O$ and [Co(PLTSC-H)$_2$]Cl$\cdot H_2O$ found to be 5.3 s^{-1}, 40.2 s^{-1} and 3.8 S^{-1}. Using the approach developed by Dubois [22] the rate constants were predicted and the i_p/i_o data, based on the equation below (F is the Faraday constant, R is the gas constant, T is the temperature, i_p is the peak catalytic current, io is the peak current in the nonexistence of acetic acid and n is the number of electrons).

$$K_{obs} = 0.1992\ (Fvn^2/RT) \times (i_{cat}/i_0)^2 \ \ldots\ldots.\ (1)$$

Table 3 shows the rate constants (kcat, 25 °C) of the catalysis of the different electrocatalyst complexes, at glassy carbon electrode (3.6 mM CH_3COOH).

Figure 3 shows that the Cyclic voltammetry of complexes which used for this study in $[Bu_4N][BF_4]$-DMF, scan rate 100 mVs^{-1} at a vitreous carbon electrode (0.07 cm^2) under N_2 in the presence of various concentrations of CH_3COOH. It is noted in all complexes the peak catalytic current became in depend on concentration of acid around 3.6 mM. Also, we found In DMF a precipitate is formed about 5-6 mM of the acid for all complexes.

The Table 3 shows the comparison of the catalytic performance toward HER of the various studied complexes and some reported electrocatalysts. It is worth noting that the type of catalyst plays important role on the shifting of potential for the selected proton source. For example, the highest shifting toward positive value was reported for Co (TFPP) that was used as catalyst (542 mV) and Fe (TPP)Cl exhibited lower shift (180 mV) under the same conditions.



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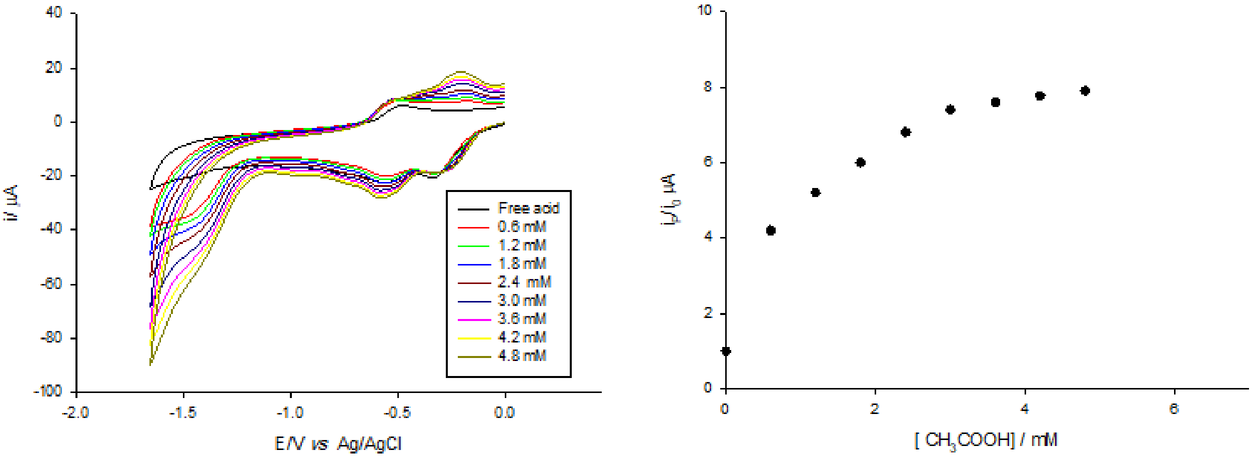

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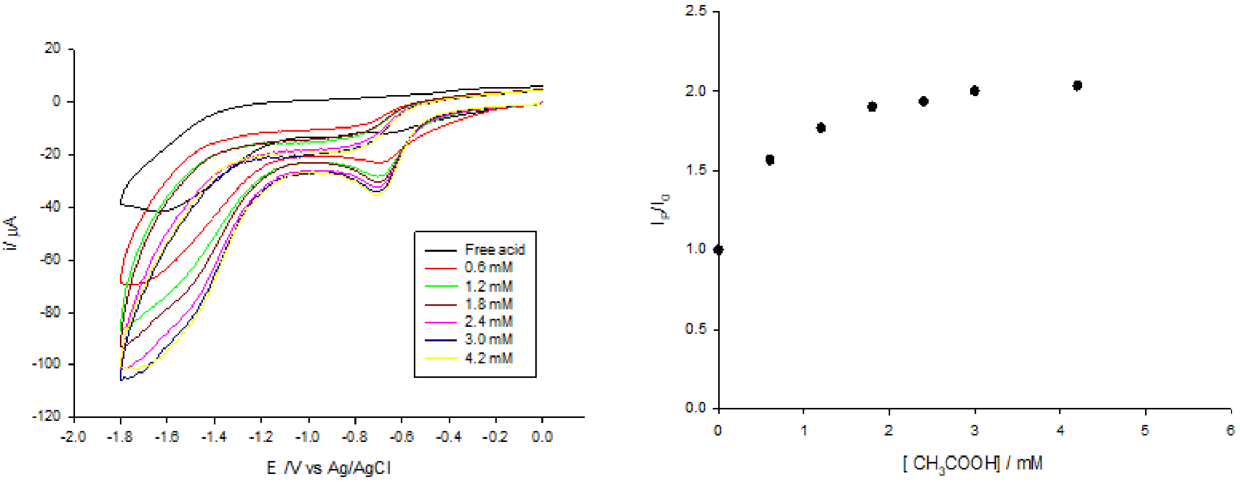

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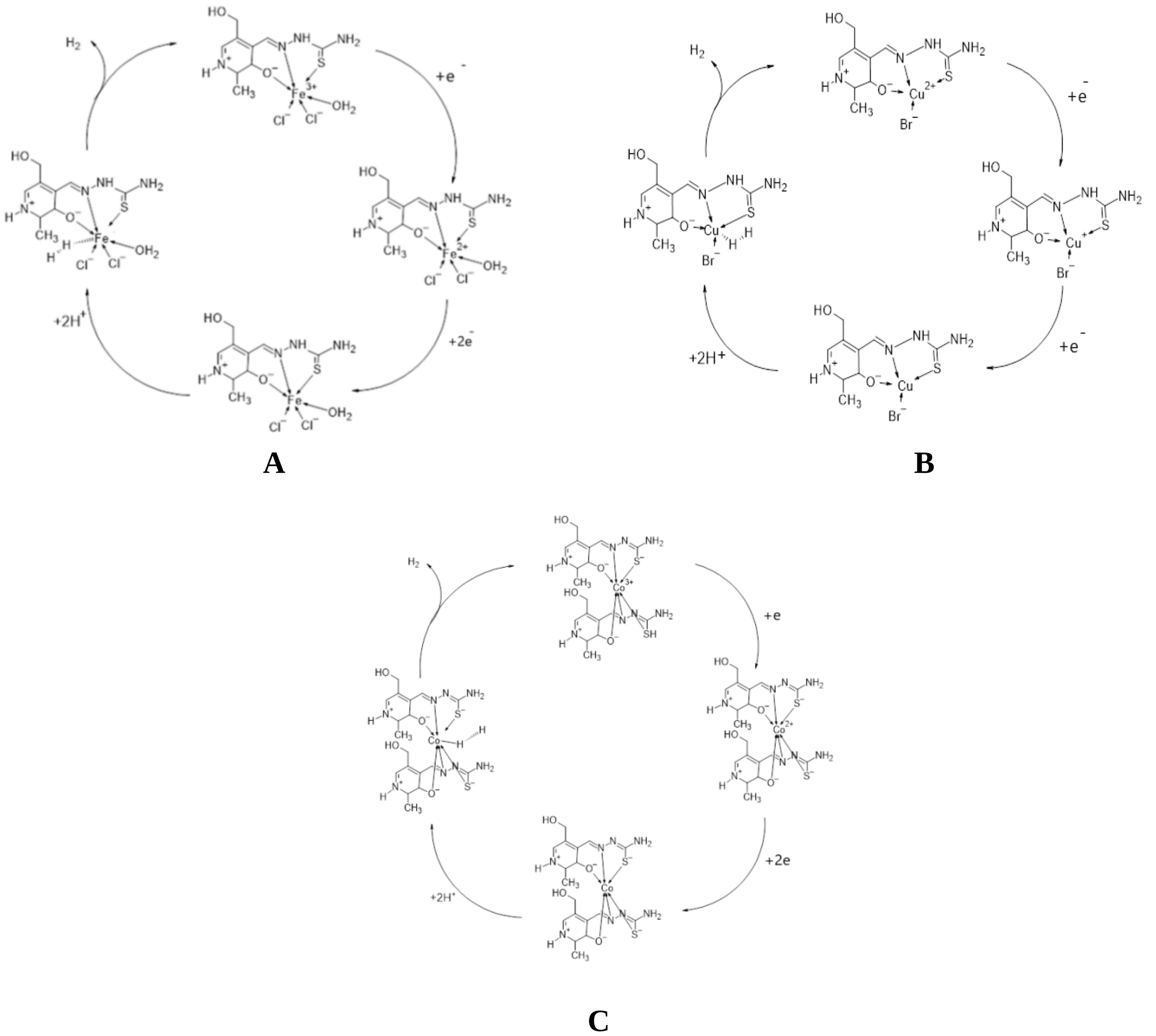
Figure 3. a) Cyclic voltammetry of a) Fe(PLTSC)Cl_2(H_2O)]Cl b) Cu(PLTSC)Cl_2(H_2O)]Cl (c) Co(PLTSC)Cl_2(H_2O)]Cl in [Bu4N][BF4]-DMF, scan rate 100 mVs^{-1} at a vitreous carbon electrode (0.07 cm2) under N_2 in the presence of various concentrations of CH_3COOH

Table 4. Comparing the effect of various complexes on HER.

Complex	**Proton source**	**Potential of catalyst-free direct reduction**	**Condition**	**Potential of reduction of acid in the presence of catalyst**	**Potential shifting**	**Ref.**
Fe(PLTSC)Cl_2(H_2O)]Cl	AcOH	-1.85 Ag/AgCl	[NBu_4][BF_4]–DMF	-1.48 Ag/AgCl	370 mV	This work
[Cu(PLTSC)Br]·H_2O	AcOH	-1.85 Ag/AgCl	[NBu_4][BF_4]–DMF	-1.42 Ag/AgCl	480 mV	This work
Co(PLTSC)Cl_2(H_2O)]Cl	AcOH	-1.85 Ag/AgCl	[NBu_4][BF_4]–DMF	-1.63 Ag/AgCl	220 mV	This work
Mn (TPP)Cl	AcOH	-1.85 Ag/AgCl	[NBu_4][BF_4]–DMF	-1.3 Ag/AgCl	450 mV	[14]
Fe (TPP)Cl	AcOH	-1.85 Ag/AgCl	[NBu_4][BF_4]–DMF	-1.60 Ag/AgCl	180 mV	[14]
Co (TFPP)	AcOH	-1.81 Ag/$AgNO_3$	[NBu_4]ClO_4–DMF	-1.45 V Ag/$AgNO_3$	542 mV	[21]
Fe(PFTPP)Cl	TEA	-1.6	[NBu_4][BF_4]–ACN	-1.3 V Ag/AgCl	300 mV	[15]
ACN = Acetonitrile, AcOH = Acetic acid, DMF = Dimethylformamide, LTD = 2,6-lutidine, TEA = Triethylamine						

3.3.Mechanism of HER

Depends on last HER studies, we have tried to make a possible mechanism of Fe(III), Cu(II) and Co(III) complexes-mediated HER (Scheme 1). The reduction of proton in presence of metal complexes was reported by many studies [16-21]. It is suggested that H_2 production take place when the metal undergoes multi electron reduction. In this study, all the metal ions convert to metal(0) before bond to the proton to produce hydrogen (Scheme 1). For Fe(III) and Co(III), the first step consists of a one-electron reduction followed by a two-electrons reduction. Afterward, the Fe(0) and the Co(0) bind to two protons before the formation of H_2 that get eliminated to regenerate the Fe(III) or Co(III) catalyst. For the Cu(II) complex, the mechanism is similar except for the reduction from Cu(II) to Cu(0) as it is a divalent metal.



Scheme 1. Possible mechanism of HER by (a) Fe (III), b) Cu(II) and (c) Co(III) complexes.

4. CONCLUSION

The electrocatalytic performance of $Fe(PLTSC)Cl_2(H_2O)]Cl$, $[Cu(PLTSC)Br]{\cdot}H_2O$ and $[Co(PLTSC\text{-}H)_2]Cl{\cdot}H_2O$ for proton reduction into hydrogen was evaluated in $[Bu_4N][BF_4]$-DMF using acetic acid as source of proton. As known, the direct reduction of $[CH_3COOH]$ on vitreous carbon electrode occurs at Ep = -1.8 V *vs* Ag/AgCl but in the presence of Fe $(PLTSC)Cl_2(H_2O)]Cl$,

$[Cu(PLTSC)Br]\cdot H_2O$ or $[Co(PLTSC\text{-}H)_2]Cl\cdot H_2O$ the reduction of proton was shift to the more positive values at room temperature at -1.48, -1.42 and -1.63 V Ag/AgCl. In addition, the rates constant (k^c_{cat}, room temperature) for the catalysis at carbon electrode in presence of $Fe(PLTSC)Cl_2(H_2O)]Cl$, $[Cu(PLTSC)Br]\cdot H_2O$ and $[Co(PLTSC\text{-}H)_2]Cl\cdot H_2O$ are found to be 5.3 S^{-1}, 40.2 S^{-1} and 3.8 S^{-1} respectively.

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