

Short Communication

## Electrocatalytic Hydrogen Evolution Reaction Using meso-tetrakis-(pentafluorophenyl)porphyrin iron(III) chloride

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Received: 24 April 2016 / Accepted: 12 October 2016 / Published: 12 December 2016

This study focuses on the electrochemical catalysis of proton reduction into hydrogen using meso-tetrakis-(pentafluorophenyl)porphyrin iron(III) chloride in the presence of Et<sub>3</sub>NHCl. Indeed, the direct reduction of Et<sub>3</sub>NHCl on vitreous carbon electrode occurs at E<sub>p</sub> -1.6 V vs Ag/AgCl in [Bu<sub>4</sub>N][BF<sub>4</sub>]-CH<sub>3</sub>CN, whereas the reduction potential shifts to -1.3 V vs Ag/AgCl in the presence of Fe(PFTPP)Cl. Based on the gas chromatography analysis, the formation of H<sub>2</sub>, with a current efficiency of *ca.* 58% after 3.8 h, is achieved with a yield of 8 μmoles and a turnover number of 8 while the chemical yield was about 80%. These results reflect the effect of the presence of electron withdrawing pentafluorophenyl groups around the metal in Fe(PFTPP)Cl.

**Keywords:** electrocatalysis; hydrogen; iron complex, porphyrin

### 1. INTRODUCTION

Since hydrogen is considered as a clean energy carrier for the future, the conversion of proton into hydrogen is widely studied by researchers [1-6]. The electrochemical reduction of proton from acidic solution using metal electrodes is an attractive area. However the electrochemical overpotential (potential difference between electrodes) needs to be reduced using catalysts in order to enhance the hydrogen production [7-12]. The catalysis of the Hydrogen Evolution Reaction (HER) at low potential using transition metal complexes presents a challenge for chemists. As known, the HER ( $2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2$ ) is a common and important process in biochemical system, which occur by coupled electron and proton-transfer reactions. The conversion of H<sup>+</sup> to H<sub>2</sub> is performed in nature by hydrogenase and nitrogenase enzymes. Mimics of [Fe-Fe]- and [Ni-Fe]-hydrogenase enzymes, have been widely developed in the aim to test their effectiveness toward HER. Several research groups have achieved pioneering work for the discovery of novel and cheap electrocatalytic materials. Henderson has

examined the protonation reactions of reduced clusters and the generation of dihydrogen by using several heterometals (eg. Fe, Mo, W, Ni) [13-18]. Bhugun *et al.* [19] reported on the catalysis of electrochemical reduction of proton by using an iron *meso*-tetraphenylporphyrin (TPP) in the presence triethylamine as source of proton. In this context, much effort has been focused on the development of novel model of porphyrin mimics such as cobalt-, iron-, osmium- or ruthenium- porphyrins [20,21].

This study focuses on the use of meso-tetrakis-(pentafluorophenyl)porphyrin iron(III) chloride [Fe(PFTPP)Cl] as a catalyst in HER, because it posses four strong electron withdrawing pentafluorophenyl groups which decrease the electron density at the metal center. The aim is to study the electrocatalysis of proton reduction into hydrogen using Fe(PFTPP)Cl at vitreous carbon electrode in the presence of triethylamine hydrochloride (Et<sub>3</sub>NHCl) as source of proton.

## 2. EXPERIMENTAL

Fe(PFTPP)Cl and Et<sub>3</sub>NHCl were purchased from Aldrich and used as received. Methyl cyanide (CH<sub>3</sub>CN) was purified by distillation over calcium hydride.

Cyclic voltammetry experiments were carried out using an Autolab PGSTAT 30 potentiostat. A conventional three-electrode arrangement was employed, consisting of vitreous carbon working electrode (0.07 cm<sup>2</sup>) and Ag<sup>+</sup>/AgCl reference electrode separated by a glass frits from a platinum wire auxiliary electrode (2 cm<sup>2</sup>).

The electrolysis cell containing 14 ml of the electrolyte [NBu<sub>4</sub>][BF<sub>4</sub>] solution (0.2 M in CH<sub>3</sub>CN) was degassed with argon gas. 5 ml of this solution was placed in the working electrode compartment. About 9-10 ml of gas phase take place at the working electrode part. 0.20 mM of catalyst Fe(PFTPP)Cl was added and stirred under Ar in the electrochemical cell. The working electrode has a surface of 1 cm<sup>2</sup>.

The electrolysis was carried out at -1.3 Ag<sup>+</sup>/AgCl and the current was recorded during the course of electrolysis verses the time. The charge passed was recorded and the electrolysis was stopped when the current decayed after 3.8 h.

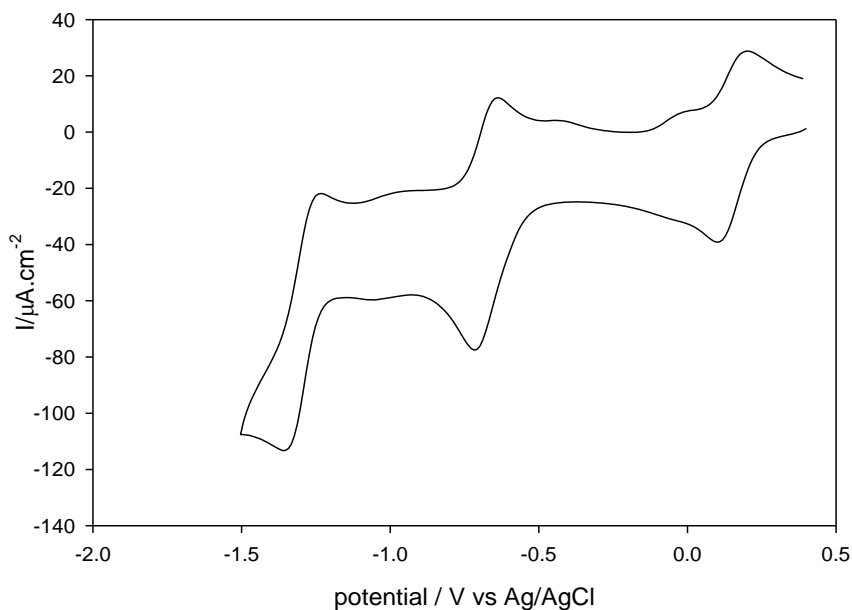
Gas chromatography (GC) was carried out using a Perkin–Elmer Clarius 500 instrument fitted with a 5Å molecular sieve column (800/100 mesh, 6'x1/8") and thermal conductivity detector (TCD). The operating conditions were: 80 °C oven temperature, 0.5 ml injected volume, and 10 min retention time. The external standard calibration was performed same day.

## 3. RESULTS AND DISCUSSION

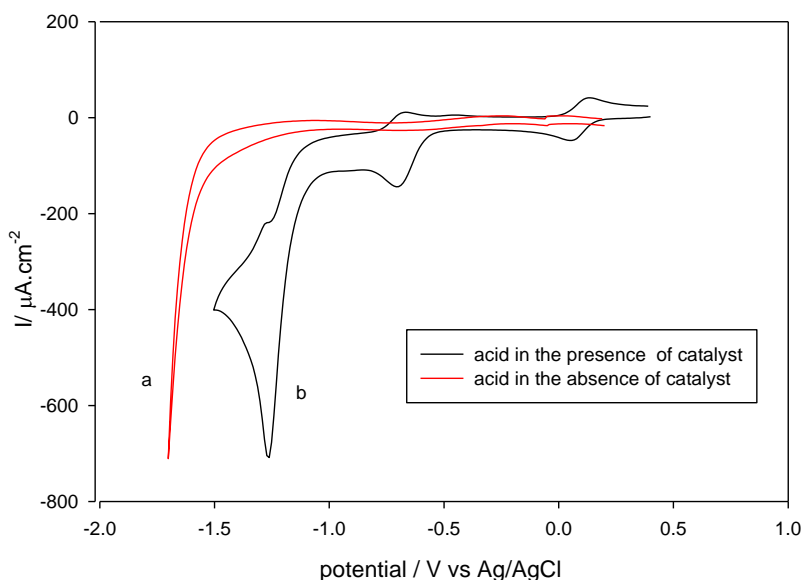
### 3.1. Cyclic voltammetry of iron(III) porphyrin complex

Cyclic voltammogram of Fe(PFTPP)Cl at vitreous carbon in [NBu<sub>4</sub>][BF<sub>4</sub>] electrolyte solution (0.1 M in CH<sub>3</sub>CN) exhibits three successive reversible one-electron reduction processes [22]. Those steps, observed at potentials E<sub>1/2</sub>= 0.1, -0.68, and -1.3V *versus* Ag/AgCl, are formally corresponding to

Fe(III)/Fe(II), Fe(II)/Fe(I) and Fe(I)/Fe(0) processes respectively (Figure 1). Importantly, the direct reduction of Et<sub>3</sub>NHCl on vitreous carbon electrode occurs at  $E_p = -1.65$  V vs Ag/AgCl while under the same conditions but in the presence of **Fe(PFTPP)Cl** catalyst we observe a shift of +350 mV at *ca.* -1.3 V vs Ag/AgCl, as shown in figure 2.



**Figure 1.** Cyclic voltammograms of 0.20 mM **Fe(PFTPP)Cl** at vitreous carbon electrodes (0.07 cm<sup>2</sup>) in MeCN containing 0.1M [NBu<sub>4</sub>][BF<sub>4</sub>].



**Figure 2.** a) Cyclic voltammogram of catalyst-free direct reduction of acid in 20 eq of Et<sub>3</sub>NHCl and b) in the presence of 0.20 mM **Fe(PFTPP)Cl** in [Bu<sub>4</sub>N][BF<sub>4</sub>]-CH<sub>3</sub>CN scan rate 100 mVs<sup>-1</sup> at a vitreous carbon electrode (0.07 cm<sup>2</sup>) under Ar.

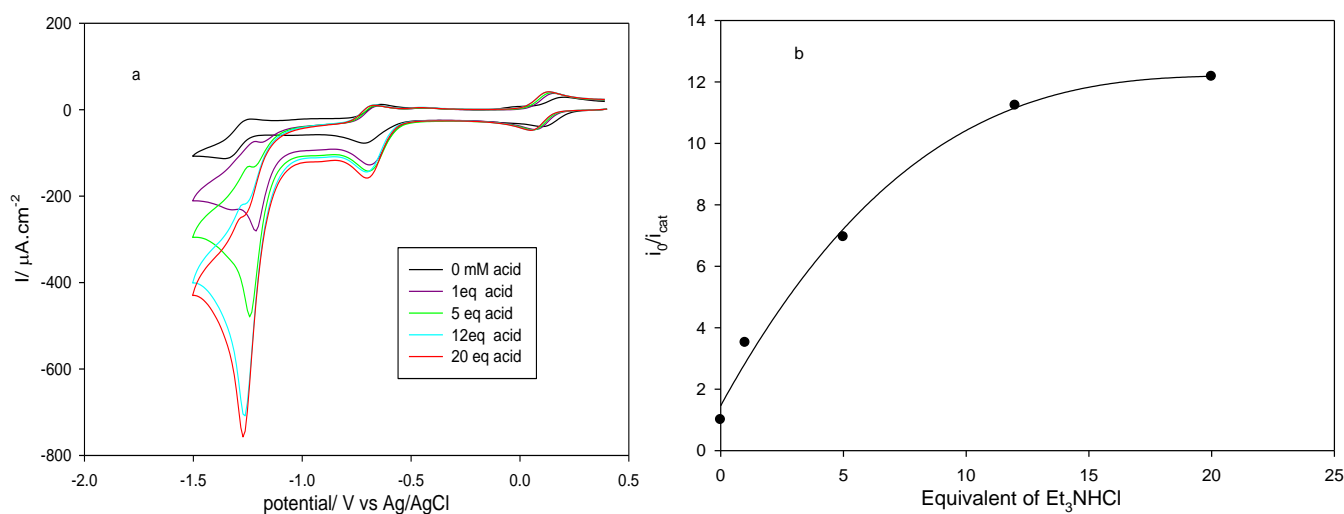
Upon addition of the acid, the wave of Fe(III)/Fe(II), remain unchanged and there is small increase in the peak current at the wave Fe(II)/Fe(I) may be related to the trace amount of water in acid. However, hydrogen was not formed when the preparative bulk electrolyses were carried out at  $-0.9\text{ V vs Ag/AgCl}$ . The wave of Fe(I)/Fe(0) becomes irreversible in the presence of  $(\text{Et}_3\text{NHCl})^+$ , and the peak current increase dramatically with the increasing of acid concentration (Figure 3). These observations are fully in accordance with those reported earlier by Bhugun and coworkers who studied the catalysis of electrochemical hydrogen evolution by **Fe(TPP)Cl** at about  $-1.6\text{ V vs Ag/AgCl}$  [19]. Other iron-based complexes have been found to electrocatalytically generate hydrogen at about  $1.17\text{ V}$  and  $1.18\text{ V vs SCE}$  and  $\text{Fc}^+/\text{Fc}$  ( $\text{Fc}$  = Ferrocene), respectively, but using trifluoroacetic acid (TFA) as source of protons which is a much stronger acid than  $\text{Et}_3\text{NHCl}$  [23, 24].

However, removal of the electrode after cycling in the presence of acid and the catalyst, washing and transferring to fresh electrolyte containing acid gave a current response indicative of the formation of a catalytic film on the electrode surface.

In the presence of  $\text{Et}_3\text{NHCl}$ , very large catalytic current is observed in Fe(I)/Fe(0) at  $-1.3\text{ V vs Ag/AgCl}$  which is about 13 times larger than cyclic voltammetry of **Fe(PFTT)Cl** alone. However, the catalytic current tends towards a plateau at  $[\text{Et}_3\text{NHCl}]^+ \geq 1.2\text{ eq}$  which is indicative of an acid independent kinetic regime figure 3a.

Kinetics of electrocatalytic proton reduction was investigated; figure 3b shows the ratio of  $i_{\text{cat}}/i_0$  at the virtues carbon electrode *versus*  $[\text{Et}_3\text{NHCl}]$ . The peak current,  $i_{\text{cat}}$ , is that measured at  $100\text{ mVs}^{-1}$  and  $i_0$  is that for the peak current for Fe(I)/Fe(0) before addition of acid at same scan- rate. It is clear that the values of  $i_{\text{cat}}/i_0$  become independent of the acid concentration at *ca* 12eq ( $12\mu\text{mole}$ ). The rate constant ( $k_{\text{cat}}^c$ , room temperature) for the catalysis at carbon electrode is calculated to be  $114\text{ S}^{-1}$  for the magnitude of  $i_{\text{cat}}/i_0$  equation 1.

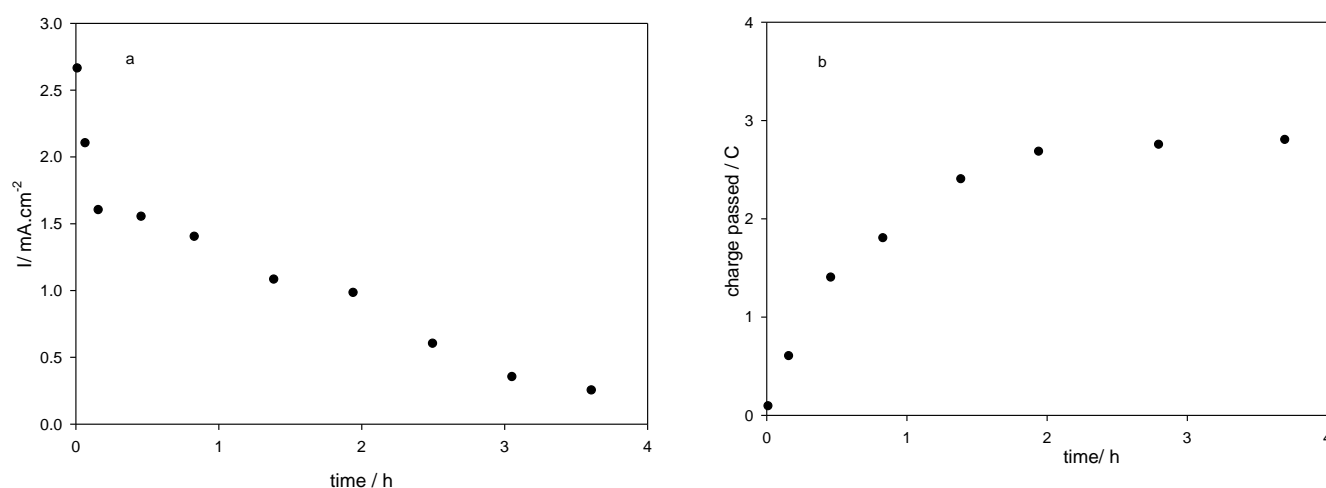
$$K_{\text{obs}} = 0.1992 \left( \frac{F v n^2}{RT} \right) \left( \frac{i_{\text{cat}}}{i_0} \right)^2 \quad [25]$$



**Figure 3.** a) Cyclic voltammetry of  $0.20\text{ mM [Fe(PFTTP)Cl]}$  in  $[\text{Bu}_4\text{N}][\text{BF}_4]\text{-CH}_3\text{CN}$ , scan rate  $100\text{ mVs}^{-1}$  at a vitreous carbon electrode ( $0.07\text{ cm}^2$ ) under Ar in the presence of various concentrations of  $\text{Et}_3\text{NHCl}$ , b) The effect of the acid concentration on  $i_{\text{cat}}/i_0$  ratio for the second reduction wave.

### 3.2. Preparative –scale electrolysis at carbon electrode

Electrocatalytic reduction of proton into dihydrogen was carried out in 0.1M [Bu<sub>4</sub>N][BF<sub>4</sub>]-MeCN at room temperature in the presence of Et<sub>3</sub>NHCl on carbon electrode (1 cm<sup>2</sup>) in an H-type cell figure 4a. The concentration of catalyst was 0.2 mM (1 μmoles) and the solution contains 20 eq. Et<sub>3</sub>NHCl. Based on the cyclic voltammograms of Fe(PFTPP)Cl, applied potentials for electrolyses were set at -1.3V *versus* Ag/AgCl. The gas of dihydrogen was collected of the gas phase of the cell, and analysed using GC-TCD. When the current had decayed to *ca* 5% of the initial current. Electrolyses were typically terminated after 3.8 h which allowed *ca* 8 turnovers and gave 8 μmoles of dihydrogen yield, Plot of current versus charge-passed is shown by Figure 4b which is indicative of loss of the catalyst at longer times.



**Figure 4.** a) Current density versus electrolysis time. b) Charge passed *versus* electrolysis time. The electrode has a surface of 1 cm<sup>2</sup>.

**Table 1.** Current efficiency, chemical yield and turnover number of electrocatalytic reduction of proton catalysed by Fe(PFTPP)Cl at carbon electrode.

	Number of moles of catalyst /μmole	Time experiment	Charge passed /C	Number of moles of H <sub>2</sub> / μmole	Chemical yield %	Current efficiency %	T.N
In the presence of Fe(PFTPP)Cl	1	3.8	2.7	8	80	58	8
Control experiment	0	4	0.4	0.1	1	5	0

CPE potential *vs* Ag/AgCl = -1.3V; Number of moles of acid /μmole = 20

The chemical yield of dihydrogen at the end of electrolysis based upon the total acid available was 80%, and the current efficiency for H<sub>2</sub> production after 3.8h was fairly constant at 58%. No H<sub>2</sub> was detected when bulk electrolysis was performed in the absence of the catalyst at 1.3V *versus*

Ag/AgCl. Table 1 summarises the results for the four Fe(PFTPP)Cl in terms of charge passed, H<sub>2</sub> yields, current efficiency, chemical yield and number of turnovers, T.N. The presence of electron withdrawing pentafluorophenyl groups around the metal in Fe(PFTPP)Cl has great beneficial effects on the performance of the catalyst. Therefore, while using Fe(TPP)Cl as a catalyst for HER and Et<sub>3</sub>NHCl as source of proton, the applied potential was -1.6 V *versus* SCE. However, Bhugun *et al.* have electrocatalytically produced H<sub>2</sub> with current efficiency more than 95 %. This high efficiency has been recorded because of the applied potential higher than -1.30 V [19].

#### 4. CONCLUSION

We have successfully highlighted that Fe(PFTPP)Cl, having four strong electron withdrawing pentafluorophenyl groups, is a great electrocatalyst for the conversion of proton into hydrogen at carbon electrode in [Bu<sub>4</sub>N][BF<sub>4</sub>]-CH<sub>3</sub>CN electrolyte solution at 23 °C. The cyclic voltammogram of Fe(PFTPP)Cl at carbon electrode exhibits three successive reversible reduction waves; at 0.1 V, -0.68 V and -1.3 V *vs* Ag/AgCl. The direct reduction of Et<sub>3</sub>NHCl on vitreous carbon electrode occurs at E<sub>p</sub> = -1.65 V *vs* Ag/AgCl. Based on this study we could conclude that the potential of the third reduction wave of Fe(PFTPP)Cl at -1.3 V is suitable for the reduction of protons into dihydrogens. This has resulted in a shift of 350 mV to more positive potential. In addition, comparing to Fe(TPP)Cl catalyst, we observed here a shift of + 300 mV. The electrolysis of proton reduction was carried out in [Bu<sub>4</sub>N][BF<sub>4</sub>]-CH<sub>3</sub>CN on carbon electrode at room temperature for 3.8 h in the presence of Et<sub>3</sub>NHCl. The current efficiency to reduce proton into dihydrogen was about 58%, the chemical yield was 80% and the turnover number is 8 over ca 3.8 hour.

#### ACKNOWLEDGMENTS

The author would like to thank Research Deanship, University of Hail, Kingdom of Saudi Arabia, for providing research fund (1410-BA).

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