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Manganese(III) Porphyrin as Electrocatalyst for Hydrogen Evolution Reaction

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Abstract: *5,10,15,20-tetraphenyl-21H,23H-porphine manganese(III) chloride (Mn(TPP)Cl) has been evaluated as electrocatalyst for Hydrogen Evolution Reaction (HER) in the presence of triethylamine hydrochloride (Et_3NHCl) as source of proton. The direct reduction of Et_3NHCl on vitreous carbon electrode occurs at E_p -1.6 V vs Ag/AgCl in $[Bu_4N][BF_4]$-CH_3CN. Interestingly, in the presence of Mn(TPP)Cl as electrocatalyst the reduction potential shifts to -1.20 V. Based on gas chromatography analysis, the formation of H_2 gas, with a current efficiency of ca. 58% after 2 h, is observed with a yield of 8 µmoles and a turnover of 2.5. However, the chemical yield at carbon electrode was about 35%. These results reflect the exquisite electrocatalytic efficiency of Mn(TPP)Cl in Hydrogen Evolution Reaction (HER).*

Keywords: Porphyrin; electrocatalysis; hydrogen , manganese(III)I complex, porphyrin

1. INTRODUCTION

The using of hydrogen as sustainable energy has attracted significant attention, primordially because of its innocent impact on the environment with energy conversion free of CO_2 emission. However, the main problem resulting from its production remains in the release of CO_2, a gas which is considered as the main responsible of the climate change [1-6].In order to encounter this major problem, researchers are interested in developing many other methods for hydrogen production including water splitting and proton reduction. Moreover, the hydrogen is often seen as an environmentally-friendly energy carrier for the future [7-8].

Generally, the Hydrogen Evolution Reaction (HER) requires the use of catalyst in order to decrease the overpotential which refers to the potential difference between the electrodes [9-14]. Platinum (Pt) is the predominant catalyst, which has the great exchange current density of 4.5 x 10^{-4} A/cm^2, and the Tafel slope smaller than 30 mV/decade[15,16]. However, the expensive price of platinum urges researchers to find an alternative cheap and abundant metal for HER.

The use of transition metal complexes as electrocatalysts for the reduction of proton into hydrogen presents a stirring challenge for chemists. Knowing that the hydrogen evolution reaction (HER; $2H^+ + 2e^- \leftrightarrow H_2$) is ↔ a central process in the global biological energy cycle which is catalysed by [Fe-Fe]- and [Ni-Fe]-hydrogenase enzymes, an interesting strategy was to mimic the functionality of hydrogenase [17-23]. Many research groups have followed this strategy in order to discover new and inexpensive electrocatalytic materials. Most of these H_2ase mimics display proton reduction activity in organic solvents, but they often display low efficiency and stability and require a relatively high overpotential [24,25]. Moreover, in the course of finding the suitable catalyst, there were several attempts to use molecular hybrid complexes such as cobalt-, iron-,osmium- or ruthenium- porphyrins[26]. Bhugun *et al.* reported on the catalysis of electrochemical reduction of proton by using an iron *meso*-tetraphenylporphyrin (TPP) in the presence of Et_3NHCl as source of proton[27]. Herein we have discovered that importantly Mn(TPP)Cl can be used as catalyst for the proton reduction into hydrogen at -1.2 V vs Ag/AgCl in $[NBu_4][BF_4]$-CH_3CN (0.2 mM) using triethylamine hydrochloride (Et_3NHCl) as source of proton.

2. EXPERIMENTAL

Mn(TPP)Cl and Et_3NHCl were purchased from Aldrich and used as received. Acetonitrile (CH_3CN) 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 a vitreous carbon working electrode (CPE) (0.07 cm^2), a platinum wire as the auxiliary electrode (2 cm^2) and Ag^+/AgCl as a reference electrode.

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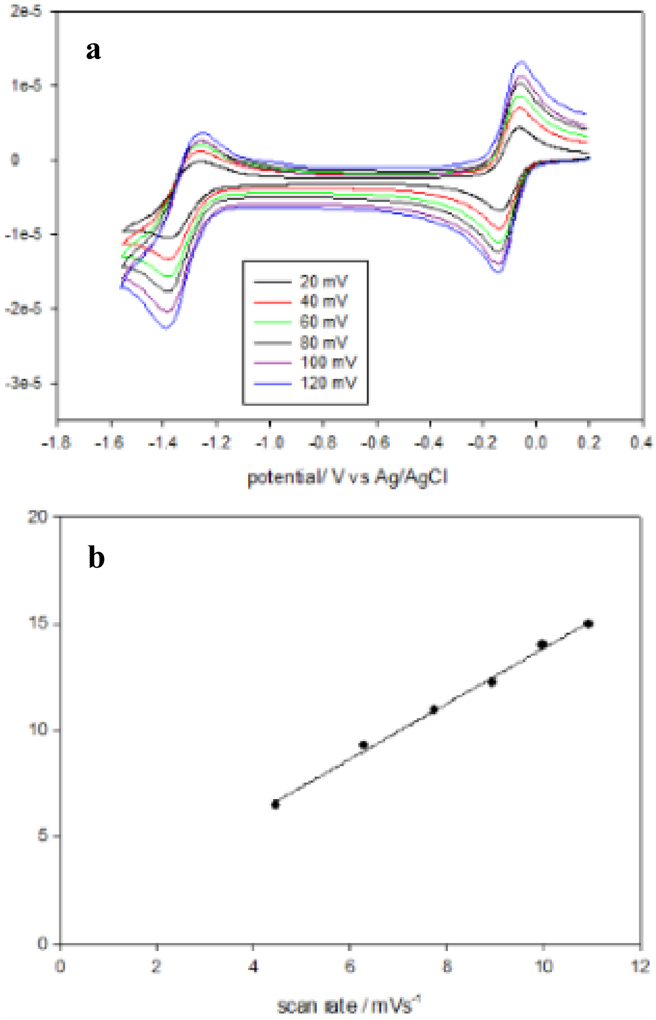

Figure 1. a) Cyclic voltammograms of 0.25 mM Mn(TPP)Cl in 0.1M $[Bu_4N][BF_4]$-MeCN, run at different scan rate. b) The plot of i_p^{red} *versus* $v^{1/2}$.

The electrolysis cell containing 14 ml of a solution of electrolyte $[NBu_4][BF_4]$, 0.2 M in CH_3CN, was degassed with argon gas.5 ml of this solution were placed in the working electrode compartment. About 9-10 ml of gas phase takes place at the working electrode part. 0.25mM of catalyst Mn(TPP)Cl was added and stirred under Ar in the electrochemical cell.

The electrolysis was carried out at -1.2 V *vs* Ag^+/AgCl and the current was recorded during the course of electrolysis *vs* time. The charge passed was recorded and the electrolysis was stopped when the current decayed after 2 h.

Gas chromatography 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. 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.

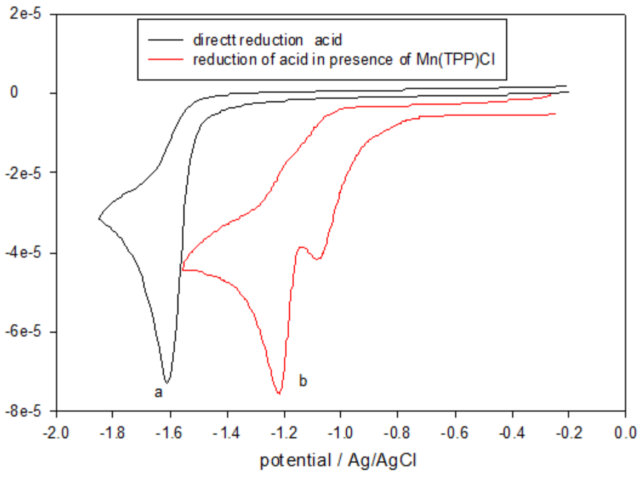

Figure 2. a) Cyclic voltammogram of catalyst-free direct reduction of acid in 0.028 mM of Et_3NHCl (black line) and b) in the presence of 0.25 mM Mn(TPP)Cl in $[Bu_4N][BF_4]$-CH_3CN (red line), scan rate 100 mVs^{-1} at a vitreous carbon electrode under Ar.

3. RESULTS AND DISCUSSION

3.1. Electrochemical behiever of Mn(TPP)Cl in acetonitrile

The cyclic voltammogram (CV) of Mn(TPP)Cl in 0.1 M $[Bu_4N][BF_4]$-MeCN exhibits two well-defined Mn-reduction bielectronic waves (Figure 1a). These consecutive electron processes, at -0.15 V and -1.3 V vs Ag/AgCl, are formally attributed to Mn/Mn^- andMn^-/Mn^{2-}, respectively. The primary reduction process is electrochemically reversible and diffusion controlled one-electron transfer (Figure 1b). The plots of the peak current of first wave ${}^{1}i_p^{red}$ *versus* $v^{1/2}$ is linear with intercept close to zero. It proves that there is no complicated mass transfer control of one electron-transfer rate. Furthermore, the separation of the peak potential $1E_{p\text{-}red}$-$1E_{pox}$ is about 65 mV which is close to the theoretical value of 59 mV expected for a reversible one-electron transfer process. The diffusion coefficient for Mn(TPP)Cl was estimated from cyclic voltammetry data (D = 7.2× 10-5 cm^2s^{-1}) using flowing equation[28-30].

$$I_p = -\,(2.69\times10^5)\; n^{3/2}\, C_0^{\infty}\; D^{1/2} v^{1/} C_0^{\infty}{}^{2}$$ Randles-Sevcik Equation

3.2. The Dependence of the catalytic current for proton reduction

The cyclic voltammetry of free-catalyst Et_3NHCl in 0.1 M $[NBu_4][BF_4]$-CH_3CN (control experiment) at vitreous carbon electrode were carried out (Figure 2a). It shows that the direct reduction of the acid occurs at E_p -1.6 V *vs* Ag/AgCl. Interestingly, in presence of catalyst Mn(TPP)Cl, this redox potential E_p shifts about 400 mv towards the positive potentials. It occurs at-1.20 V *vs* Ag/AgCl (Figure 2b).

In the figure 3a, we observe that the catalytic current of second process reduction at -1.2 V vs Ag/AgCl becomes irreversible with the increment of the concentration of acid, which is consistent with the electrocatalytic proton reduction. These observations are fully

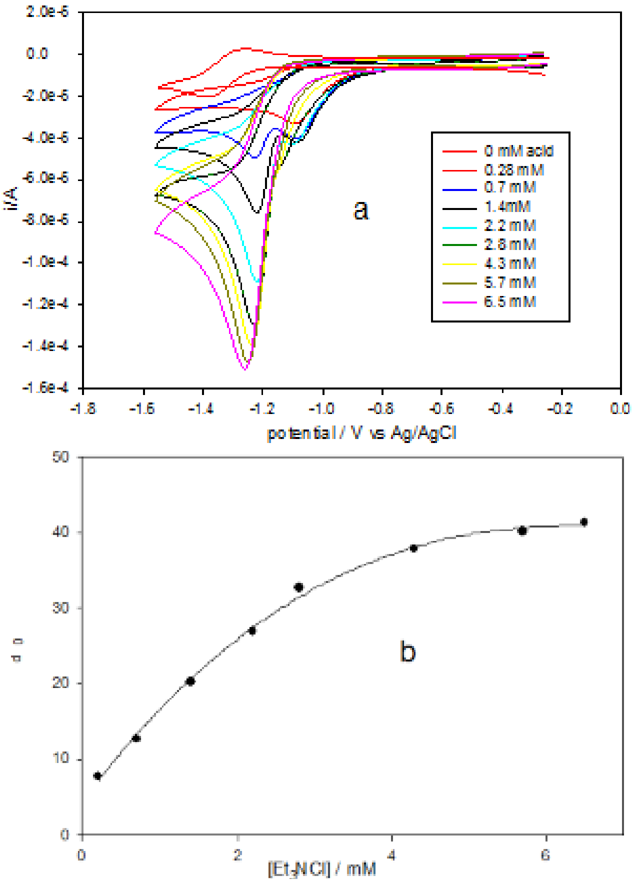

Figure 3. a) Cyclic voltammetry of 0.25 mM [Mn(TPP)Cl] in [Bu4N][BF4]-CH_3CN, scan rate 100 mVs^{-1} at a vitreous carbon electrode under Ar in the presence of various concentrations of Et_3NHCl, b) The effect of the acid concentration on i_{cat}/i_0 ratio for the second reduction wave.

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 V *vs* Ag/AgCl [27]. However, removal of the electrode after cycling in the presence of acid and Mn(TPP)Cl, washing and transferring to fresh electrolyte containing acid gives a current response indicative of the formation of catalytic film on the electrode surface. In addition, the figure 3b shows the relationship between i_{cat}/i_o and the increasing of the concentration of acid at -1.2V. The peak catalytic current(i_{cat}) is measured at 100 mVs^{-1} in the presence of acid while the peak current (i_o) is measured for the first reduction one-electron step at the same scan-rate in the absence of proton source. It is clear that at vitreous carbon the values of i_{cat}/i_o become independent of the acid concentration at *ca* 4mM. Apparently, the lower acid concentration reduction is observed close to the second reduction potential catalyst at -1.3 V.As the acid concentration is increased, the peak current shift more positive to reaches -1.2V.

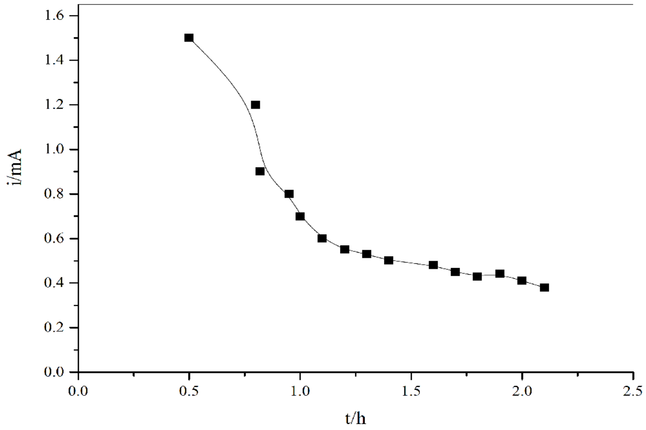

Figure 4. The relationship between the current and charge passed.

Following the approach of Dubois and co-worker, the rate constant can be estimated using i_{cat}/i_o data and the relationship shown in the following equation[31].

$$K_{obs}= 0.1992(Fv/RTn^2)(i_{cat} / i_o)^2$$

Where *F, R* and *T* are the Faraday constant, the gas constant and the temperature respectively, and *n* is the number of electrons.

The rate constant (k^c_{cat}, 25 °C) for catalysis at vitreous carbon electrode is estimated to be1124 s^{-1} from the magnitude of i_{cat} / i_o in the acid independent regime.

3.3. Preparative electrocatalysis

Preparative bulk electrolyses reduction of protons in the presence of Mn(TPP)Cl was carried out in closed-system at -1.25 V *vs* Ag/AgCl (0.2 mM-[NBu_4][BF_4]-CH_3CN; 296K) using 6.5 mM of Et_3NHCl as source of protons. The charge passed was monitored during the course of experiment and the working electrode compartment was stirred at a constant rate during electrocatalysis. Figure 4 shows the relationship between the current and charge passed. During the course of proton reduction, the initial current rapidly decayed to a plateau about 40% of the initial current before falling off towards the end of electrolysis. The gas chromatography (GC-TCD) test confirms the formation of H_2 with a current efficiency of ca 45% after 2 h and the yield of H_2 was5.8 µmoles. No H_2 was formed at -1.2 V vs Ag/AgCl in the presence of 6mMEt_3NHCl without Mn(TPP)Cl (control experiment) (Table 1).

Table 1. Results of electrocatalysis of proton reduction during the course of 2 h in presence of Mn(TPP)Cl and control experiment

	CPE Potential (Ag/AgCl)	Number of moles of catalyst µmole	Time of experiment/h	Charge coulomb /C	Current efficiency* H_2	Tunover Number H_2
In the presence of Mn(TPP)Cl	-1.25	1.25	2	5.4	45	4.8
Control experiment	-1.25	0	2	0.12	0	0

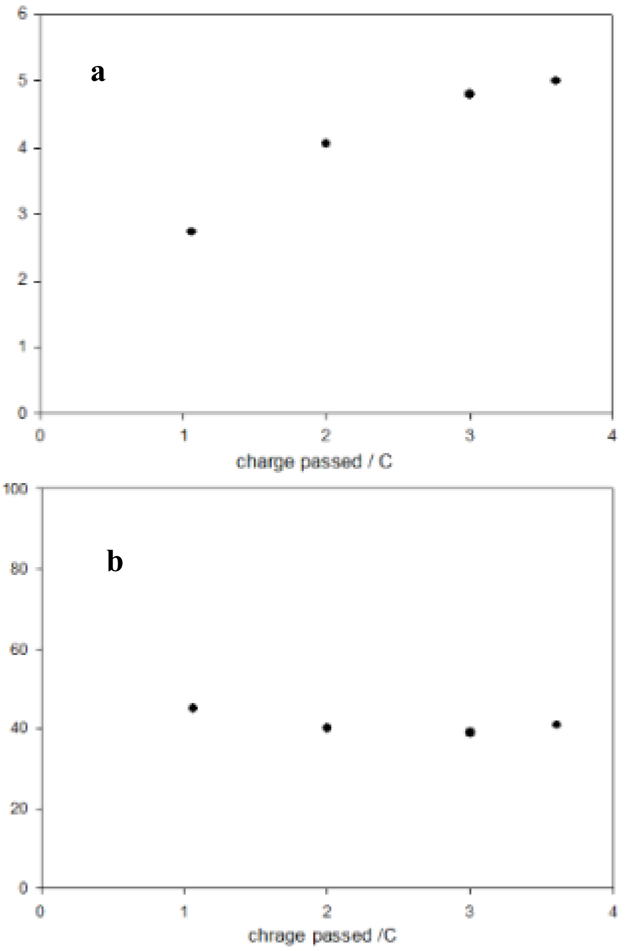

Figure 5. a. The yield of dihydrogen as a function of charge passed, b. The current efficiency *versus* charge passed. In electrolysis, 28.5μmoles acid was used.

In a separate experiment under the same conditions, the yield of H_2 was monitored by gas chromatography as a function of electrolysis time and the current efficiency versus of charge passed. Figure 5a shows the yield of dihydrogen as a function of charge passed and figure 5b shows The current efficiency versus charge passed. It is clear that the yield of H_2 increased steadily in the first phase of the electrolysis and dropped off in the latter stages as the acid was consumed. The chemical yield of dihydrogen at the end of electrolysis based upon the total acid available was 35%, electrochemical results are shown in Table 2. At the end of the electrolysis, a charge of 3.6 coulombs was passed and 5 μmoles of dihydrogen was detected in the headspace of the catholyte by thermal conductivity gas chromatography.

4. CONCLUSIONS

In summary, we have proved that Mn(TPP)Cl can be used as electrocatalyst for the conversion of proton into H_2 at carbon electrode (CPE). The cyclic voltammogram of Mn(TPP)Cl at carbon electrode displays two successive reversible reduction processes; first reduction at -0.15 V and the second reduction at -1.3 V vs Ag/AgCl. This study has allowed us to conclude that the potential of the second reduction wave is suitable for the reduction of protons into dihydrogens. The electrolysis of proton reduction was performed in $[Bu_4N][BF_4]$-CH_3CN on carbon electrode at room temperature for 2 h in the presence of Et_3NHCl. The current efficiency to convert proton to dihydrogen was about 42-45%, the chemical yield at carbon electrode was 35% and the turnover (T. N.) number is 2.5 over ca 2 h. Further studies will focus on the use of transition metal complexes of derivatized TPP.

5. ACKNOWLEDGMENT

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Table 2. Current efficiency and turnover numbers for electrocatalytic reduction of protons by Mn(TPP)Cl

Time/h	0.08	0.9	1.3	1.6
Number of μmoles of H_2	2.70	4.05	4.80	5.00
Current efficiency %	45	40	39.5	42
Chemical yield %	19	28.4	33.6	35
T.N	0.2	1.03	1.73	2.5
Charge passed C	1	2	3	3.6
μmole of electrons	10.36	20.72	31.1	37.3

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