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# ENHANCEMENT OF CATHODIC HYDROGEN EVOLUTION REACTION THROUGH THE USE OF PROTON CARRIERS (A BRIEF-REVIEW)

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*The paper is a mini-review on the enhancement of the hydrogen evolution reaction (HER) through the use of proton carriers. Results obtained based on the research of the catalytic effect of amines on cathodic HER have been presented. The best results have been obtained on Pt in 0.5 M $H_2SO_4$, where aniline as proton carrier was used. In this case, an emphasis was laid on the increase of exchange current density $i_o$ from 2.9 A $m^{-2}$, in blank $H_2SO_4$, to 67.6 A $m^{-2}$ in the presence of $10^{-2}$ M aniline. At the same time, the Gibbs absorption energy goes to show that proton carriers are adsorbed on the metal surface by weak physical bond. Also, correlations between catalytic effect and molecular parameters of proton carrier molecules have been accomplished.*

***Keywords**: hydrogen evolution, proton carriers, aniline, catalytic effect, electro-catalysis.*

## INTRODUCTION

Approaches to the topic are explained as being due to the fact that hydrogen is still considered to be an excellent energy carrier and fuel of the future. The point is that in the combustion process of hydrogen inside engines there is just water without carbon dioxide. Unfortunately, most widely used methods for hydrogen production are based on coal gasification, or cracking and reforming of hydrocarbons, processes that produce not only hydrogen, but huge quantity of carbon dioxide as well. For example, if hydrogen is obtained by steam reforming of methane per each 1 ton of $H_2$, a quantity of 5.5 tons of $CO_2$ is discharged into atmosphere [1]. Moreover, in coal gasification technology, 11 tons of $CO_2$ are emitted into environment per each 1 ton of $H_2$ produced [2].

It should be noted that water splitting by electrolysis is a *green* procedure; however, it is limited by essential electric energy consumption. That's why the research into the cathodic hydrogen evolution is still important. There is a great number of studies into the enhancement of water electrolysis process with due regard for electro-catalytic effect of electrode materials on both anodic and cathodic processes, including various aspects of oxygen and hydrogen evolution. From this point of view, a question of the enhancement of hydrogen evolution with the help of catalysts in the electrolyte solution remains to be little-studied.

The aim of the paper is to present a mechanism of catalytic effect of proton carriers on cathodic hydrogen evolution reaction HER in acid solutions, as well as the latest achievements on this track.

## PRINCIPLES OF ELECTROCATALYSIS BY PROTON CARRIERS

The catalytic effect of proton carriers on HER has been noted many years ago, particularly in polarographic studies into dropping mercury electrode where an essential shift of polarographic wave of HER towards more positive potentials was revealed to result from high hydrogen over-potential [3]. Albumin was one of the first organic bases analyzed as proton carriers. Its effect on HER was initially interpreted as proton transfer bridge between electrolyte solution and mercury surface [4]. Later on, studies touched upon other organic compounds, including peptides and proteins [5-7]. Similar phenomenon was reported by Tamamushi et al. conformably to methylviologen [8].

Frumkin was the first to have suggested a consistent mechanism of this catalytic effect [9]. In his view, organic bases are directly involved in the cathodic process, and the charge transfer step is a reversible reaction as is seen from the equation below (1):

$$\text{BASE-H}^+ + e^- \rightarrow [\text{BASE-H}], \qquad (1)$$

where BASE is the organic compound (proton carrier).

Neutral chemical species [BASE-H], which are adsorbed on the metal surface, release molecular hydrogen in an irreversible reaction (2).

$$2[\text{BASE-H}] \rightarrow H_2 + 2\text{BASE} \qquad (2)$$

Further, neutral molecules BASE pass over to the solution, where they are protonated again.

Stackelberg et al. proposed a more elaborate mechanism, unfolded in four steps [10-12]:

$$H_3O^+(aq) \rightarrow H_3O^+(ads) \qquad (3)$$

$$\text{BASE}(ads) + H_3O^+(ads) \rightarrow [\text{BASE-H}]^+(ads) + H_2O \qquad (4)$$

$$[\text{BASE-H}]^+(ads) + e^- \rightarrow \text{BASE-H}(ads) \qquad (5)$$

$$2\text{BASE-H}(ads) \rightarrow H_2 + 2\text{BASE}(ads) \qquad (6)$$

The above mentioned authors assumed that at low current densities the rate determining step is the charge transfer (5), whereas at high current densities the organic base protonation (4) becomes the slow step.

Stackelberg mechanism differs essentially from Frumkin one. In Stackelberg mechanism, organic base molecules are permanently blocked on the metal surface by adsorption, while Frumkin mechanism assumes that proton carrier molecules are desorbed after the charge transfer and protonated in the electrolyte solution. Therefore, only Stackelberg mechanism may be considered as heterogeneous catalysis, whereas Frumkin mechanism has a homogeneous step.

For several decades, the influence of proton carriers on HER has been studied specifically on dropping mercury electrode given that the surface of this kind of electrode is perfectly reproducible, and the over-potential for HER is significant. However, from practical standpoint, metals displaying higher over-potential for HER are improper as cathodes in water electrolysis. In this circumstance, for some time past studies on catalytic effect of organic bases like amines have been extended on metals with lower over-potential for HER. Systematic studies started with the effect of benzylamine (BA) on HER on copper [13]. Further, studies embraced various aromatic amines: aniline (A), N-methylaniline (MA), N-ethylaniline (EA), N,N-dimethylaniline (DMA), N,N-diethylaniline (DEA), 2-toluidine (oT), 3-toluidine (mT) and 4-toluidine (pT) at low current densities [14], and also at high current densities similar with those applied in commercial water electrolysers [15].

The *volcano curve* for HER shows that the strength of Au-H bond is close to that of Fe-, Ni- and Co-H bonds, and consequently Au should present a similar effect on the recombination of hydrogen atoms like iron group metals [16]. It offers the possibility to use Au in order to develop a bifunctional catalyst for HER in acid media. That’s why, the effect of methylamine (MAm), aniline (A) and 4-chloroaniline (PCA) as proton carriers has been studied conformably to gold [17]. The most interesting results, taking into account practical insights, have been obtained on platinum, using BA and A [18].

## KINETICS OF *HER* CATALYZED BY PROTON CARRIERS

As a rule, the rate determining step in the cathodic HER is the charge transfer, even at higher current densities. In this circumstance, parameters that characterize the kinetics of the cathodic process are the exchange current density $i_o$ and cathodic transfer coefficient 1- α, usually determined by Tafel slope method. Useful information about the kinetics of cathodic HER may be obtained by electrochemical impedance spectroscopy (EIS). Experimental data provided by EIS provide directly charge transfer resistance $R_{ct}$, which is a function of over-potential, cathodic transfer coefficient and exchange current density.

Results obtained on Cu, Au and Pt, in 0.5 M $H_2SO_4$ in the absence/presence of amines ($10^{-4}$ M) are shown in Table 1 [13,14,17-20].

According to Table 1 results, it transpires that in the presence of proton carriers the values of 1-α decrease. This may be explained as being due to the fact that 1-α is a measure of coordinates that characterize the activated complex at metal – solution interface. The decrease of the 1-α is unfavorable for the kinetics of electrode process, according to Butler-Volmer equation, however, this effect is offset by significant rise in the exchange current density $i_o$.

Data presented in Table 1 show that the catalytic effect of examined amines depends essentially on their molecular structure, following which molecular parameters of protonated amines have been identified (Table 2) [13,15, 18,20]. Quantum calculations were carried out in order to evaluate molecular volume and dipole moment, as well as coverage surface and frontier orbital energy (highest occupied molecular orbital – HOMO and lowest unoccupied molecular orbital – LUMO). For this purpose, GAUSIAN 09 package was used [21, 22].

The coverage area of methyl ammonium is the smallest, and consequently much greater is the number of these ions to be adsorbed on the electrode. This fact gives weight to higher concentrations of protons at the interface metal-electrolyte solution, and as a result, higher exchange current density. Even if coverage area of $AH^+$ and $PCAH^+$ is very close, $i_o$ in the presence of $PCAH^+$ is higher than in the presence of $AN^+$, because Cl atom has an electron-withdrawing inductive effect which produces a supplementary charge separation. As a result, the dipole moment for $PCAH^+$ is larger together with higher ordered orientation of $PCAH^+$ [18].

**Table 1.** Kinetic parameters of HER.

| Proton carrier | Cathode | 1-α | $i_o$[A m$^{-2}$] | $R_{ct}$·10$^4$ [Ω m$^2$] | Overpotential [V] | Reference |
|---|---|---|---|---|---|---|
| Blank | Cu | 0.64 | $2.0110^{-5}$ | 47.2 | -0.75 | 14, 19 |
| BA | Cu | 0.43 ($10^{-2}$ M) | $1.7810^{-2}$ | 5.7 | -0.50 | 13, 19 |
| A | Cu | 0.48 | $2.8510^{-3}$ | 23,6 | -0.50 | 14, 19 |
| MA | Cu | 0.56 | $6.5310^{-4}$ | 33.7 | -0.50 | 14, 19 |
| EA | Cu | 0.58 | $6.8010^{-4}$ | 32.5 | -0.50 | 14, 19 |
| DMA | Cu | 0.58 | $7.6310^{-4}$ | 31.1 | -0.50 | 14, 19 |
| DEA | Cu | 0.46 | $1.9110^{-3}$ | 28.2 | -0.50 | 14, 19 |
| oT | Cu | 0.50 | $2.7010^{-3}$ | 27.4 | -0.50 | 14, 19 |
| mT | Cu | 0.50 | $2.8110^{-3}$ | 24.8 | -0.50 | 14, 19 |
| pT | Cu | 0.51 | $1.5110^{-3}$ | 30.2 | -0.50 | 14, 19 |
| Blank | Au | 0.52 | 0.29 | 52.3 | -0.20 | 17, 20 |
| A | Au | 0.44 | 8.00 | 7.5 | -0.20 | 17, 20 |
| MAm | Au | 0.37 | 33.3 | 0.6 | -0.20 | 17, 20 |
| PCA | Au | 0.41 | 20.5 | 3.4 | -0.20 | 17, 20 |
| Blank | Pt | 0.68 | 2.98 | 0.43 | -0.25 | 18, 20 |
| A | Pt | 0.54 ($10^{-2}$ M) | 67.6 | 2.58 | -0.25 | 18, 20 |
| BA | Pt | 0.57($10^{-2}$ M) | 22.9 | 2.35 | -0.25 | 18, 20 |

**Table 2.** Molecular parameters of protonated amines.

| Protonated amine | Molecular volume [Å$^3$] | Dipole moment [D] | Molecular coverage [Å$^2$] | HOMO –LUMO [eV] | Reference |
|---|---|---|---|---|---|
| $AH^+$ | 95.3 | 7.12 | 30.9 | -6.3 | 18, 20 |
| $BAH^+$ | 106.8 | 9.85 | 51.5 | -5.8 | 13 |
| $MAmH^+$ | 36.1 | 2.22 | 21.5 | -11.3 | 18, 20 |
| $PCAH^+$ | 108.6 | 12.3 | 30.9 | -5.7 | 18, 20 |
| $MAH^+$ | 109.6 | 6.32 | 45.0 | -6.5 | 15 |
| $DMAH^+$ | 129.8 | 5.3 | 58.5 | -6.6 | 15 |

Another fact that has to be taken into account when revealing the electrode reaction mechanism is the Gibbs free energy of adsorption $G_{ads}$. For example, in case of DMA, $G_{ads}$ calculated from Langmuir adsorption isotherm is about -10 kJ mol$^{-1}$. This value is consistent with weak physical adsorption [15].

Results presented above suggest an improved mechanism derived from Stackelberg one [18]:

In the first step, ammonium is formed by amine protonation in the bulk of solution:

$$H_2N–X\ (aq) + H_3O^+(aq) \rightarrow H_3N^+–X(aq) + H_2O \qquad (7)$$

In the electrolyte solution, ammonium ions migrate towards cathode, where they are adsorbed on the metal surface together with nitrogen atoms oriented toward the metal surface, according to the dipole moment. That means the best position for the charge transfer process:

$$H_3N^+–X(aq) \rightarrow H_3N^+–X(ads) \qquad (8)$$

Due to the adsorption process, a higher concentration of ammonium ions is achieved. In these conditions, at low current densities, the hydrogen over potential is low and the charge transfer occurs according to the reaction:

$$H_3N^+–X(ads) + e^- \rightarrow H(ads) + H_2N–X(ads) \qquad (9)$$

The recombination step of HER could occur chemically [Tafel step (10)] or electrochemically [Heyrovsky step (11)]:

$$2H(ads) \rightarrow H_2(ads) \qquad (10)$$

$$H_3N^+–X(ads) + H(ads) + e^- \rightarrow H_2(ads) + H_2N–X(ads) \qquad (11)$$

At higher current densities (high over potential), hydronium ions discharge becomes possible:

$$H_3O^+(ads) + e^- \rightarrow H(ads) + H_2O \qquad (12)$$

followed by Tafel (10) or Heyrovsky desorption (13):

$$H(ads) + H_3O^+(ads) + e^- \rightarrow H_2(ads) + H_2O \qquad (13)$$

As a consequence, the hydronium ions discharge is characterized by local pH rise in the solution adjacent to the cathode up to values that allows hydrolysis of ammonium ions:

$$H_3N^+–X(ads) + H_2O \rightarrow H_2N–X(ads) + H_3O^+(ads) \qquad (14)$$

This reaction helps to keep up high values of hydronium ions concentration. Note that neutral amines diffuse into the bulk solution where the re-protonation reaction (11) occurs.

## CONCLUSIONS

The catalytic effect of some protonated amines on HER has been compared through the use of kinetic parameters of the electrode process 1-α and $i_o$. The presence of protonated amines in the electrolyte solution predetermines a decrease of 1-α; however, this unfavorable effect is offset by essential growth of $i_o$. Thereby, an overall result of proton carriers' effect is the diminution of hydrogen over-potential. The catalytic function of amines might be associated with molecular parameters of protonated amines, following which the dipole moment and coverage surface are instrumental in the process. Proceeding from the results above, an improved mechanism has been suggested.

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# *ИНТЕНСИФИКАЦИЯ РЕАКЦИИ КАТОДНОГО ВЫДЕЛЕНИЯ ВОДОРОДА С ИСПОЛЬЗОВАНИЕМ ПЕРЕНОСЧИКОВ ПРОТОНА (КРАТКИЙ ОБЗОР)*

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*Статья является кратким обзором работ по интенсификации реакции выделения водорода с использованием переносчиков протона. Представлены результаты, полученные при изучении каталитического эффекта аминов на упомянутую реакцию. Наилучшие результаты были получены на Pt в 0.5 М $H_2SO_4$ с использованием анилина как переносчика протона. В этом случае наблюдалось увеличение плотности тока обмена $i_o$, с 2.9 $Am^{-2}$ до 67.6 $Am^{-2}$в $H_2SO_4$ в присутствии $10^{-2}$М анилина. В то же время значения адсорбционной энергии Гиббса показывают, что переносчики протона адсорбируются на поверхности металла с помощью слабых физических связей. Как правило, наблюдаются корреляции между каталитическим эффектом и молекулярными параметрами переносчиков протона.*

**Ключевые слова:** *выделение водорода, переносчики протона, анилин, каталитический эффект, электрокатализ*

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