



Short Communication

Insights into the promotion effect of macrocycle molecule on HCOOH electro-oxidation

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ABSTRACT

Macrocycle molecules were found to be highly promotive to HCOOH electro-oxidation on Pt surface since 2007. But it is still not known how the macrocycle molecules induce the promotion effect. The difficulty is that it's very hard to obtain the coverage of macrocycle molecules during the reaction. In this paper, the under-potential deposited hydrogen (UPD-H) is used as the probe to measure the coverage of macrocycle molecules on Pt surface. Subsequently, the kinetics of adsorption and the promotion effect of the macrocycle molecule (copper phthalocyanine-3,4',4'',4'''-tetrasulfonic acid (CuPcTsA)) is systematically studied. We find that the coverage of CuPcTsA increases very fast at the beginning 500 s during the adsorption, and saturates after 1000 s. Usually, the activity of CuPcTsA modified Pt electrode increases with the increasing coverage of CuPcTsA under a certain CuPcTsA concentration during the range 3–25 μM. But this behavior follows different curves for different CuPcTsA concentrations. The selectivity (direct pathway to CO intermediate pathway) also increases with the increasing coverage. Surprisingly, the selectivity from different CuPcTsA concentrations follows a same curve. The order of the reaction selectivity is ~1 and ~3 for the CuPcTsA coverage lower and higher than 0.34. The desorption is not a simple reverse process of the adsorption, and has some memory of its initial state, where the desorption starts.

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1. Introduction

HCOOH is considered as a potential alternative fuel of fuel cell because it is non-toxic, highly reactive and has low crossover [1]. Currently, the catalysts in direct formic acid fuel cell (DFAFC) are mainly Pt- and Pd-based catalysts. The electro-oxidation of formic acid (EOFA) on Pt-based catalysts is usually through dual reaction pathway, which includes direct pathway and CO intermediate pathway [2,3]. For the pure Pt catalyst, the activity is very low since the EOFA is mainly through the indirect pathway where a strongly adsorbed CO intermediate is formed. In order to improve the activity, a second metal like Ru [4], Sn [5], Sb [6], Au [7], Pb [8], or Bi [9] was added as a promoter onto Pt surface.

Besides the inorganic promoters, some macrocycle molecules, such as iron-tetrasulphthalocyanine (FeTSPc) [10–12], 5,10,15,20-tetraphenyl-21H,23H-porphyrin (TAPP) [13], etc [13–17], were found to be promotive to the EOFA too. The EOFA on macrocycle molecule modified Pt electrode can totally go through

the direct pathway. In addition, the conducting polymers (CPs), such as polyfluorenes [18], and poly(5-aminoindole) [19–21], were also found to be promoters.

These organic promoters are recognized as a kind of sustainable, environmental friendly and low cost materials. Some highly active catalysts for DFAFC have been invented based on the modified Pt by these organic promoters [10–21] since 2007. But it is still not known that how the macrocycle molecules induce the promotion effect. The difficulty is that it is very hard to obtain the coverage of macrocycle molecules during the promoted reaction.

In this paper, we adopt the under-potential deposited hydrogen (UPD-H) as the probe to measure the coverage of macrocycle molecules on Pt surface. Subsequently, the kinetics of adsorption and the promotion effect of the macrocycle molecule (copper phthalocyanine-3,4',4'',4'''-tetrasulfonic acid (CuPcTsA)) is systematically studied. Many insights into the promotion effect of CuPcTsA on the EOFA are found out.

2. Experimental

All experiments were done at room temperature under ambient conditions [13]. All cyclic voltammetry (CV) tests were done in CS350 Potentiostat/galvanostat (Wuhan CORRTEST Instruments

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CO., LTD) with a three-electrode cell. The reference electrode is the Ag/AgCl/sat KCl reference electrode. All the potentials were quoted with respect to RHE reference electrode for the convenience of comparison. The counter electrode was a large area Pt plane. The working electrode is a bare Pt electrode (Diameter is 2 mm. CH Instruments, Inc), which was polished with the slurry of 0.05 μm alumina powders (CH Instruments, Inc) and was sonicated in triple-distilled water. The cyclic voltammetry (CV) was done at the scan rate of 100 mV s^{-1} under the potential region $-0.2 \sim 0.9 \text{ V}$. There were 150 cycles ($\sim 3300 \text{ s}$) of CVs were performed during the adsorption, the desorption and the EOFAs.

The adsorption was done in 0.5 M HClO_4 (Sinopharm Chemical Reagent Co., Ltd) with a certain concentration of CuPcTsA (Aldrich Co.) during a CV test. The concentration of CuPcTsA is one of 0.1, 1.0, 3.0, 5.0, 10, 15 and $25 \mu\text{M}$. Before the adsorption test, the bare Pt electrode was polished and washed carefully.

The activity test during the adsorption was done with a freshly cleaned bare Pt electrode in 0.5 M HClO_4 , 1.0 M HCOOH (Sinopharm Chemical Reagent Co., Ltd) and a certain concentration of CuPcTsA. The peak current density at around 0.35 V and 0.7 V belong to the EOFAs through direct pathway and CO intermediate pathway, respectively.

The EOFAs during the desorption was done in 0.5 M HClO_4 and 1.0 M HCOOH during a CV test. Before the desorption test, the CuPcTsA molecules adsorbed onto Pt surface through the adsorption in a certain concentration of CuPcTsA. Then the Pt electrode was washed quickly by spraying distilled water onto the electrode. In the end, the Pt electrode was immersed in 0.5 M HClO_4 and 1.0 M HCOOH to do a CV test.

A control experiment was done to prove the weak effect of EOFAs on the adsorption process of CuPcTsA. First, a freshly cleaned bare Pt electrode was immersed into the solution with 1.0 M HCOOH and $25 \mu\text{M}$ CuPcTsA to do CV test. Second, the CV test stopped at certain cycle, for example, 10th, 25th, 50th, 100th in Fig. 1B. Third, the electrode was washed and transferred into the solution with $25 \mu\text{M}$ CuPcTsA to do CV test. Fourth, the coverage for the first three cycles was calculated.

The electrochemical surface area (ECSA) was calculated by formula [22,23],

$$A = \frac{Q_H}{Q_S} \quad (1)$$

where Q_H is the UPD-H desorption charge during the adsorption or desorption of CuPcTsA, which is calculated the dash curve in Fig. 1A. Q_S is the UPD-H desorption charge of clean Pt surface, and is usually $210 \mu\text{C/cm}^2$ [22–24]. Since the adsorbed CuPcTsA can occupy the Pt sites, and block the adsorption of UPD-H, the coverage of CuPcTsA will be,

$$\theta_{\text{CuPcTsA}} = \frac{A_{\text{HUPDO}} - A_{\text{HUPD1}}}{A_{\text{HUPDO}}} \quad (2)$$

where θ_{CuPcTsA} is the coverage of CuPcTsA, A_{HUPDO} is the ECSA on clean Pt electrode, A_{HUPD1} is the ECSA during the adsorption or desorption of CuPcTsA. The integrations of the UPD-H desorption charge on Pt surface were calculated by home-written computer program. All the current density is calculated respected to the clean Pt ECSA.

3. Results and discussion

3.1. Kinetics of the adsorption of CuPcTsA and the promotion effect

Fig. 1A shows the CV curves for the bare Pt electrode (solid curve) and for the Pt electrode adsorbed CuPcTsA (dash curve) after 150 cycles of CV, and the calculation of the UPD-H desorption charge on bare Pt surface (shaded area). For the bare Pt electrode, we can see clearly sharp peak current in the potential region of UPD-H desorption. The UPD-H desorption charge on Pt surface was calculated from the shaded area, which is $10.3 \mu\text{C}$. When the bare Pt electrode adsorbed the CuPcTsA, the two sharp peaks almost disappeared. The UPD-H desorption charge dropped to $0.67 \mu\text{C}$.

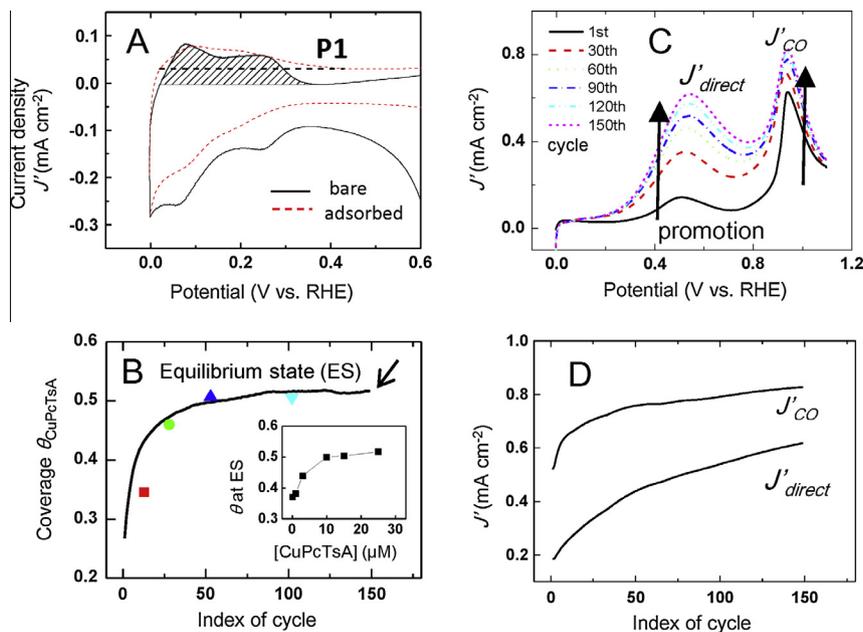


Fig. 1. Kinetics of adsorption and reaction during the adsorption of CuPcTsA. (A) CVs for the bare Pt electrode (solid curve) and for the Pt electrode adsorbed CuPcTsA (dash curve), and calculation of the UPD-H desorption charge on Pt surface (shaded area). (B) coverage θ_{CuPcTsA} variation versus time at $25 \mu\text{M}$ CuPcTsA, solid curve is θ_{CuPcTsA} in only CuPcTsA, scattered symbols are the coverage of CuPcTsA at certain index of cycle (■10th, ●25th, ▲50th, ▼100th) during the EOFAs, the inset shows the effect of the concentration of CuPcTsA on the θ_{CuPcTsA} at equilibrium state, (C) the promotion effect during the adsorption of CuPcTsA at $25 \mu\text{M}$ CuPcTsA and 1.0 M HCOOH , (D) plot of J'_{direct} and J'_{CO} versus the adsorption time. Freshly cleaned bare Pt electrode was always used in these tests. Each cycle took $\sim 22 \text{ s}$, and the total time for 150 cycles is $\sim 3300 \text{ s}$.

Fig. 1B shows an example of the coverage variation versus time during the adsorption of CuPcTsA on Pt surface at 25 μM CuPcTsA. During the beginning 23 cycles (500 s) [24], the coverage of CuPcTsA increases sharply, which means a quick adsorption process happens. At the end of the test, the coverage of CuPcTsA saturates, which implies the adsorption/desorption reaches an equilibrium state. The inset of Fig. 1B shows that the coverage at the equilibrium state increases with the increase of CuPcTsA concentration, and saturates at high concentration. The maximum coverage of CuPcTsA on Pt surface is ~ 0.5 , which means the CuPcTsA molecules will not occupy the whole surface of Pt. There are always some Pt sites are vacant for the catalysis.

Fig. 1C shows a promotion effect of CuPcTsA on the EOFA during the adsorption of CuPcTsA. The current density in both direct pathway J'_{direct} and CO intermediate pathway J'_{CO} increases with the adsorption of CuPcTsA. But the current density in CO intermediate pathway J'_{CO} increases only ~ 0.6 times after the adsorption of CuPcTsA, while the current density in direct pathway J'_{direct} increases ~ 2 times. So the promotion effect on J'_{direct} is much stronger than that on J'_{CO} shown in Fig. 1C–D.

Here, the EOFA was done in the mixture of HCOOH and CuPcTsA. So the EOFA and the adsorption of CuPcTsA occurred at the same time. The current density of each cycle in direct pathway and CO intermediate pathway can be obtained as shown in Fig. 1D at 25 μM CuPcTsA. In order to study the relationship between the coverage of CuPcTsA and the promotion effect, the coverage of CuPcTsA for each cycle is necessary to know. But it is very difficult to do in-situ measurement of coverage during the EOFA. In this paper, the coverage of CuPcTsA for each cycle is directly adopted from Fig. 1B.

The EOFA only has a weak effect on the adsorption process of CuPcTsA, since the high potential of CV is up to 0.9 V, which can clean the Pt surface in every cycle. In order to prove the weak effect, a control experiment, which is introduced in the experimental section, was done. The results are shown with some shaped symbols in Fig. 1B. We can see that the shaped symbols almost overlap with the black curve, especially for the points at the high index of cycle. So the adsorption behavior of CuPcTsA in the presence of HCOOH is similar as that in the absence of HCOOH. It is reasonable to adopt the coverage of CuPcTsA from Fig. 1B as coverage during the EOFA.

3.2. Effect of CuPcTsA coverage θ_{CuPcTsA} on the EOFA during the adsorption of CuPcTsA

The adsorption of macrocycle molecule can greatly promote the EOFA on the Pt surface shown in Fig. 1C and D. But till now, the principle problems, such as how and how much the promotion effect depends on the coverage of macrocycle molecule, are still unknown. Now, in the section above, we find a way to study the relationship between the coverage of CuPcTsA and the current density shown in Fig. 2A and B.

It can be seen that the coverage of CuPcTsA has strong promotion effect on the specific current density undergoing direct pathway J_{direct} ($J_{\text{direct}} = J'_{\text{direct}}/(1-\theta_{\text{CuPcTsA}})$) and CO intermediate pathway J_{CO} ($J_{\text{CO}} = J'_{\text{CO}}/(1-\theta_{\text{CuPcTsA}})$). The specific current density here is to describe the activity of unoccupied Pt surface. Fig. 2A shows that J_{direct} has three different trends at different concentrations of CuPcTsA. For the low concentration of CuPcTsA, i.e. 0.1 μM , J_{direct} almost does not change with the increase of coverage during the adsorption of CuPcTsA. For the mid concentration of CuPcTsA, i.e. 1.0 μM , J_{direct} decreases at first, and then increases. For the high concentration range of CuPcTsA, i.e. 3.0–25 μM , J_{direct} only monotonically increases with the coverage.

Moreover, the coverage is not the only factor for the promotion effect, because J_{direct} of different concentrations of CuPcTsA has

different values even at the same coverage. For example, at the same coverage $\theta_{\text{CuPcTsA}} = 0.3$, J_{direct} of the lower concentrations of CuPcTsA, e.g. 0.1 μM , is higher than the value 0.35 mA/cm^2 of bare Pt electrode (horizontal dot line), while J_{direct} of the higher concentrations of CuPcTsA, e.g. 25 μM , is lower. The difference may be attributed to the different adsorption types, which were generated by different adsorption rates of CuPcTsA. Fig. 2A shows that the coverage of 0.3 appears at the ~ 2 nd cycle for the highest concentration of CuPcTsA, i.e. 25 μM , while it appears at the ~ 15 th cycle for the lowest concentration of CuPcTsA, i.e. 0.1 μM . So the adsorption rate for the high concentration of CuPcTsA is much faster than that for the low concentration of CuPcTsA. Different adsorption rates usually generate different adsorption types. For example, physical adsorption is much faster than the chemical adsorption. Obviously, the physical adsorption and chemical adsorption of CuPcTsA will cause different effect on the EOFA. Therefore, different adsorption rate will contribute different activity. Interestingly, J_{CO} in Fig. 2B shows a very similar behavior as J_{direct} in Fig. 2A. The value 1.46 mA/cm^2 of bare Pt electrode (horizontal dot line) separates the J_{CO} into two populations, which belong to the low concentration range (0.1–10 μM) and the high concentration range (15–25 μM).

Unexpectedly, not as the diverse trends of the activity, the selectivity $J_{\text{direct}}/J_{\text{CO}}$ for all concentrations of CuPcTsAs only monotonically increases with the coverage, and follows a same curve in Fig. 2C. That is to say the coverage θ_{CuPcTsA} is the critical parameter for the selectivity, which does not depend on the activity, the concentration of CuPcTsA or the adsorption types. Therefore, if the coverage θ_{CuPcTsA} is fixed, the CuPcTsA of different adsorption types will promote the J_{direct} and J_{CO} simultaneously and at the same proportion. This promotion mechanism tells that it is needed to increase the coverage of promoter if one wants to suppress the formation of CO_{ad} .

But the selectivity $J_{\text{direct}}/J_{\text{CO}}$ is not linearly dependent on the coverage θ_{CuPcTsA} . The selectivity shows an accelerated increase with the increase of θ_{CuPcTsA} . Here, we build an empirical model to understand the relationship between the selectivity and the coverage θ_{CuPcTsA} . If the selectivity is proportional to $\theta_{\text{CuPcTsA}}^n$, then

$$r = r_0 + k\theta_{\text{CuPcTsA}}^n \Rightarrow \log(r - r_0) = \log(k) + n \log(\theta_{\text{CuPcTsA}}) \quad (3)$$

where r is the selectivity $J_{\text{direct}}/J_{\text{CO}}$, r_0 ($=0.24$, read from Fig. 2C) is the selectivity of bare Pt electrode, k is a constant value. The result is shown in Fig. 2D, where the points are calculated by binning the points in Fig. 2C, and the line is the model fitting. Fig. 2D shows that there is a critical point at $\theta_{\text{CuPcTsA}} = 0.34$, where the data are separated into two parts. One part below the critical coverage has a lower slope $n = 0.94 \pm 0.05$, another part has a higher slope $n = 3.30 \pm 0.29$.

3.3. The unique behavior of the selectivity during the desorption of CuPcTsA

In another situation, the EOFA was done in only HCOOH without CuPcTsA during the desorption of CuPcTsA. But the Pt electrode has already covered by CuPcTsA before the test. So the coverage of CuPcTsA become less and less with the desorption of CuPcTsA during the EOFA.

Fig. 3A shows the coverage dependent selectivity $J_{\text{direct}}/J_{\text{CO}}$ during the desorption. Interestingly, the selectivity for all concentrations of CuPcTsA decreases linearly with the decrease of the coverage. So n in Eq. (3) equals ~ 1 for this situation. But this behavior does not follow the same curve in Fig. 2C. Here, higher CuPcTsA concentration has higher selectivity shown in Fig. 3A, and has higher decay rate, i.e. higher slope k_1 , shown in Fig. 3B. So the desorption is not a simple reverse process of the adsorption,

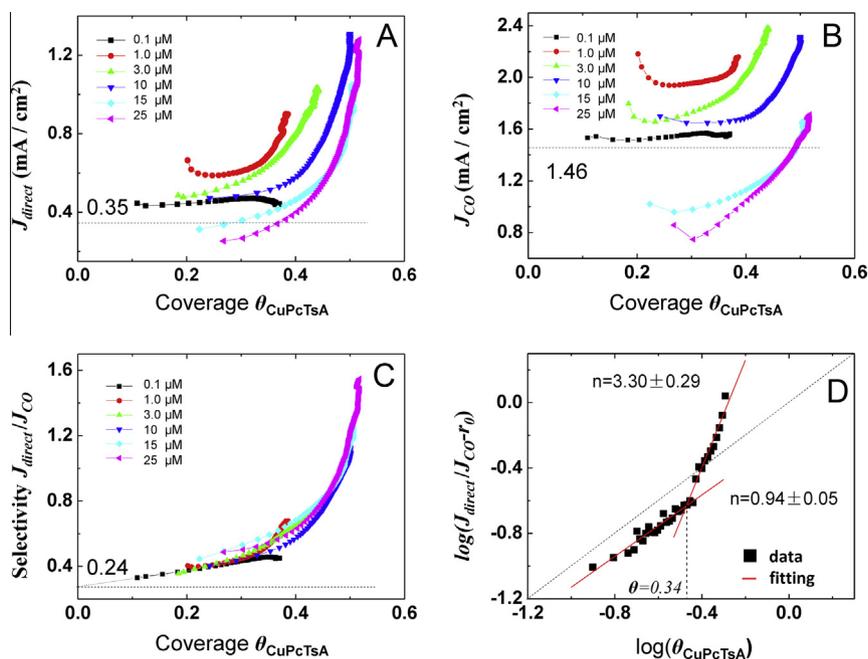


Fig. 2. Effect of $\theta_{CuPcTsA}$ on the activity and selectivity of the EOFA during the adsorption of CuPcTsA. (A) Effect of $\theta_{CuPcTsA}$ on J_{direct} , (B) effect of $\theta_{CuPcTsA}$ on J_{CO} , (C) effect of $\theta_{CuPcTsA}$ on the selectivity J_{direct}/J_{CO} , (D) model analysis. The test was done with a freshly cleaned bare Pt electrode in 1.0 M HCOOH and a certain concentration of CuPcTsA.

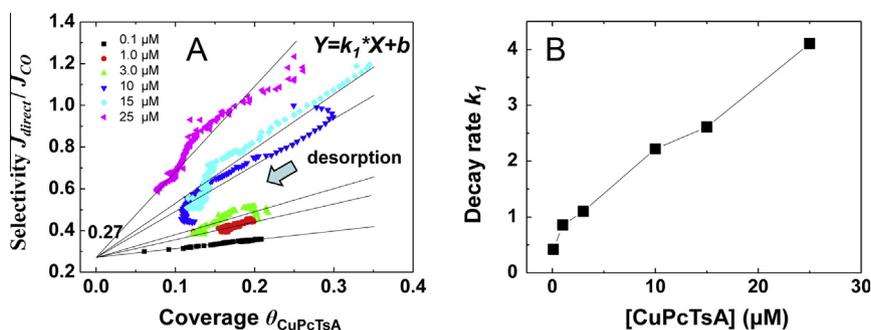


Fig. 3. CuPcTsA coverage dependent selectivity during the desorption of CuPcTsA in only support electrolyte 0.5 M HClO₄. (A) Effect of $\theta_{CuPcTsA}$ on the selectivity J_{direct}/J_{CO} , (B) decay rate of selectivity at different concentrations of CuPcTsA.

and has some memory of its initial state, where the desorption starts. From the linear fitting, we find that almost every line converges to a same point, whose J_{direct}/J_{CO} is ~ 0.27 at the coverage $\theta_{CuPcTsA} = 0$. This point is very close to the selectivity (~ 0.24) of the bare Pt electrode. Therefore, although the routes of desorption are not same, the end state of the desorption will be as same as that of the bare Pt electrode.

4. Conclusions

In this work, the kinetics of adsorption and the promotion effect of CuPcTsA on polycrystalline Pt surface is systematically studied. It is found that the coverage of CuPcTsA increases during the adsorption, and saturates at the equilibrium state. Usually, the promotion effect increases with the coverage. But the coverage is not the only factor for the promotion effect. The adsorption type plays an important role in the activity for both J_{direct} and J_{CO} too. Unexpectedly, the coverage of CuPcTsA is the critical factor for the selectivity J_{direct}/J_{CO} , which does not depend on the activity, the concentration of CuPcTsA or the adsorption types. The order of the reaction selectivity is ~ 1 and ~ 3 for the CuPcTsA coverage lower and higher than 0.34. In another situation, the selectivity degrades linearly with the desorption of CuPcTsA, and converges

to the point of bare Pt electrode. This research finds many insights into the promotion effect of macrocycle molecule, and will help us develop more highly active catalysts for DFAFC.

Conflict of interest

There is no conflict of interest.

Acknowledgments

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