

Short communication

# The enhancement effect of $\text{Eu}^{3+}$ on electro-oxidation of ethanol at Pt electrode

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Received 16 July 2007; received in revised form 28 August 2007; accepted 30 August 2007

Available online 4 September 2007

## Abstract

It is reported for the first time that the slow electrochemical kinetics process for the electro-oxidation of ethanol can be promoted by changing the electrochemical environment. The electro-oxidation of ethanol at a Pt electrode in the presence of  $\text{Eu}^{3+}$  cations was studied and an enhancement effect was exhibited. Cyclic voltammetry experiment results showed that the peak current density for the electro-oxidation of ethanol was increased in the presence of  $\text{Eu}^{3+}$  in the ethanol solution. A preliminary discussion of the mechanism of the enhancement effect is given. This is based on a CO stripping experiment, which shows that either the onset potential or the peak potential of CO oxidation is shifted negatively after adding  $\text{Eu}^{3+}$  to the solution.

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**Keywords:** Ethanol; Electro-oxidation;  $\text{Eu}^{3+}$ ; CO

## 1. Introduction

Direct ethanol fuel cells (DEFCs) have been widely investigated in recent years for their potential application as portable power sources due to the intrinsic advantages of ethanol compared to methanol, such as its non-toxicity and the ease with which it can be obtained from raw material at low cost [1–7]. Currently, the main obstacle facing DEFC development is the slow anode kinetics of the electro-oxidation of ethanol [8]. The complete ethanol anodic oxidation process is a 12-electron transfer process, leading to many adsorbed intermediates and byproducts. Adsorbed CO has been readily detected at potentials below its oxidation potential during the complex process. The majority of studies have examined the correlation between CO adsorption and the inhibition of catalytic activity of Pt based catalysts used for ethanol oxidation. It has been shown that oxidation of ethanol in the bulk solution commenced only after removal of the adsorbed CO intermediate [9–14]. The CO-like intermediate fragments produce an auto-inhibition or poisoning phenomenon, which dramatically affects the oxidation process. It is necessary

to propose more active and selective anode catalysts for ethanol oxidation [7].

One approach to overcome this shortcoming is to deliberately introduce species to the electrochemical reaction environment which enhance the activity of the catalysts as well as weaken CO poisoning. Pt-M (Ru, Sn, W, Pd, Rh, Re, Mo, Ti, Ce) catalysts have been investigated and discussed in the review by Antolini [1]. According to Pauling metallic bonding theory, the catalytic activity of the catalyst is closely related to the condition of the d-orbit, as characterized by the d-% (the percentage of the d-orbit). The d-% can be regarded as a measure of the utilization of the free d-orbit in the chemical adsorption, which is the so-called “electronic factor” in the electrical catalyst. Most of the secondary metals used in the Pt/M(oxide) catalysts for organic molecules are the group of elements with abundant d-orbits such as Pt/Ru, Pt/Ru/W, Pt/Ru/Os. Ln transition metal elements belonging to Group IIIB in the Periodic Table of Elements have electronic configurations of the type  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^m 5s^2 5p^6 5d^m 6s^2$ . It is obvious that the rare earth elements and their ions have abundant d-orbit electrons and can catalyze the oxidation of ethanol when combined with Pt. In this work we report for the first time the discovery that the rare earth element europium, added as a trace element to the electrochemical system, exhibits

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an obvious promotional effect on ethanol electro-oxidation. The CO adsorbed onto the Pt electrode can easily be oxidized at a more negative potential in the presence of  $\text{Eu}^{3+}$  in the electrochemical surroundings and consequently the rate of electro-oxidation of ethanol is clearly enhanced.

## 2. Experimental details

### 2.1. CO stripping experiment

The CO stripping experiment was conducted in  $\text{Eu}^{3+} + 0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  solution with the potential scanned at a rate of  $10 \text{ mV s}^{-1}$ . CO was introduced into the cell for at least 0.5 h to allow complete adsorption of CO on to the electrode whilst maintaining a constant voltage of 0.11 V (vs. Ag/AgCl). Excess CO was then purged with  $\text{N}_2$  for at least 0.5 h.

### 2.2. Cyclic voltammetry experiments

The cyclic voltammetry (CV) experiments were carried out using a potentiostat/galvanostat (EG&G Model 273A) coupled to a personal computer and using the software provided by EG&G.

CV measurements were carried out in a traditional triple electrode system using a platinum cylinder with area  $7.065 \text{ mm}^2$  as the working electrode, a platinum wire as the counter electrode and Ag/AgCl as the reference electrode. CV was performed in a solution of  $0.5 \text{ mol L}^{-1} \text{ CH}_3\text{CH}_2\text{OH}$  and  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  after adding different concentrations of  $\text{Eu}^{3+}$  cations. The electrolyte was saturated with  $\text{N}_2$  before the measurement. The surface of the working electrode was cleaned electrochemically by cycling the potential in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ . During the experiment the potential ranged from  $-0.2$  to  $1.2 \text{ V}$ .

## 3. Experiment results and discussion

### 3.1. CO stripping voltammograms results and discussion

The CO stripping voltammograms for the oxidation of adsorbed CO (corresponding to a saturation coverage) in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  and  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4/0.005 \text{ mol L}^{-1} \text{ Eu}^{3+}$  are shown in Figs. 1 and 2, respectively. In  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ , the onset potential of CO oxidation was close to 0.6 V and the oxidation peak occurred at 0.7 V. In  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4/0.005 \text{ mol L}^{-1} \text{ Eu}^{3+}$ , the onset potential of CO oxidation was reduced by 300 mV, i.e. close to 0.3 V, while the peak occurred at 0.6 V.

Both the onset potential of CO oxidation and the CO oxidation peak in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4/0.005 \text{ mol L}^{-1} \text{ Eu}^{3+}$  shifted negatively. The negative shift is clearly attributed to the presence of  $\text{Eu}^{3+}$  at a lower potential compared with platinum. The negative shift means that the oxidation process from CO to  $\text{CO}_2$  is easier in the presence of  $\text{Eu}^{3+}$ . In addition, the oxidation of adsorbed CO occurred over a relatively large potential range (0.3–0.7) on Pt/ $\text{Eu}^{3+}$  compared with pure platinum (0.6–0.7), indicating further oxidation of the adsorbed CO with the addition of  $\text{Eu}^{3+}$ .

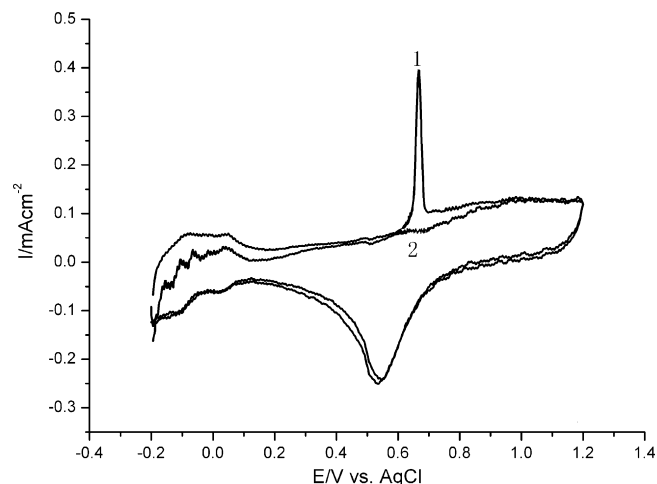
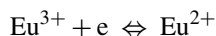


Fig. 1. CO stripping voltammograms of platinum in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ . 1, The first scan; 2, the second scan. Scan rate:  $10 \text{ mV s}^{-1}$ .

Electrons can be transferred between the two different valences of europium,  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$



Metal ions with variable valence can provide an easy way to speed up a reaction by decreasing the activation energy barrier through the coordinating of the metal ion with the other reactant; this facilitates electron transfer [15,16]. The coordination not only attracts an electron from the substrate and the inter-coordinate, but also releases an electron to form a free radical and ion. It is favorable to enhance the catalytic reaction of free radical and ion. It is well known that rare earth ions show a strong tendency to coordinate with oxygen atoms, so can form stable coordination compounds with CO via the oxygen atom [17].

According to the Lewis acid and alkali theory,  $\text{Eu}^{3+}$  is a Lewis acid which can attract the electron from CO to form a  $\sigma$  bond  $\text{Eu}-\text{CO}$ . As CO binds to  $\text{Eu}^{3+}$ , the full d orbitals of the carbon in CO overlap with the  $\sigma$  orbitals of Eu [18] and an electron will flow

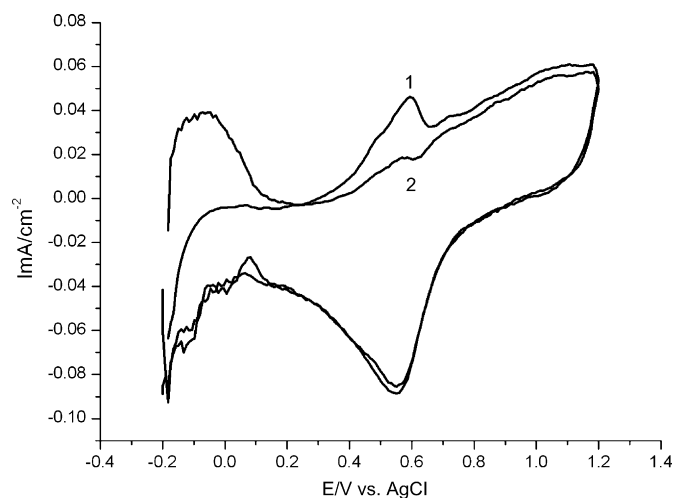


Fig. 2. CO stripping voltammograms of platinum in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 0.005 \text{ mol L}^{-1} \text{ Eu}^{3+}$ . 1, The first scan; 2, the second scan. Scan rate:  $10 \text{ mV s}^{-1}$ .

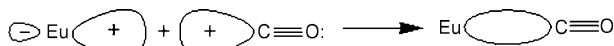


Fig. 3. The  $\text{Eu} \leftarrow \text{C} \sigma$  bond formed with a single electron from the carbon atom.

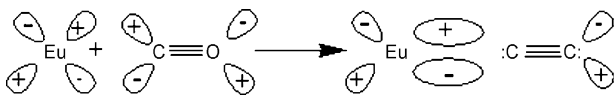


Fig. 4. The  $\text{Eu} \rightarrow \text{C} \pi$  bond.

to the carbon from the Eu atom, as illustrated in Fig. 3. There is enough pushing electron force in Eu to push the electrons back to the coordinate to reduce its electronic charge according to Pauling's Electric Neutral Theory. When the full  $d\pi$  orbitals overlap with the empty  $p\pi^*$  orbitals of CO, the electron will feed back from Eu to the coordinate, as illustrated in Fig. 4, so weakening the C–O band. This accords with the experiment results showing that both the onset potential and the peak potential of CO electro-oxidation are shifted negatively.

### 3.2. CV experiment result and discussion

Fig. 5 shows the CV curves for ethanol and ethanol with  $0.005 \text{ mol L}^{-1} \text{ Eu}^{3+}$  cation in aqueous solution, respectively. It can be seen from Fig. 5 that the oxidation peak current density for the case with  $\text{Eu}^{3+}$  cations in solution increases compared to that without  $\text{Eu}^{3+}$ . This can be attributed to the effect of  $\text{Eu}^{3+}$  in enhancing the catalyst for the electro-oxidation of ethanol. Different concentrations (0.1, 0.01, 0.001, 0.005,  $0.0001 \text{ mol L}^{-1}$ ) of  $\text{Eu}^{3+}$  were added in the electrolyte; from Fig. 6 we can see that  $0.005 \text{ mol L}^{-1}$  of  $\text{Eu}^{3+}$  shows the best result.

The increase of current shown in Fig. 5 can be explained in two ways. Firstly, after the adsorption of the  $\text{Eu}^{3+}$ , there is a kind of surface coverage of Pt- $\text{Eu}^{3+}$  on the platinum, which inhibits the formation of the oxide membrane of platinum (Pt-OHads and Pt-Oads). There is then more opportunity for the ethanol molecule to react with platinum on the surface of the

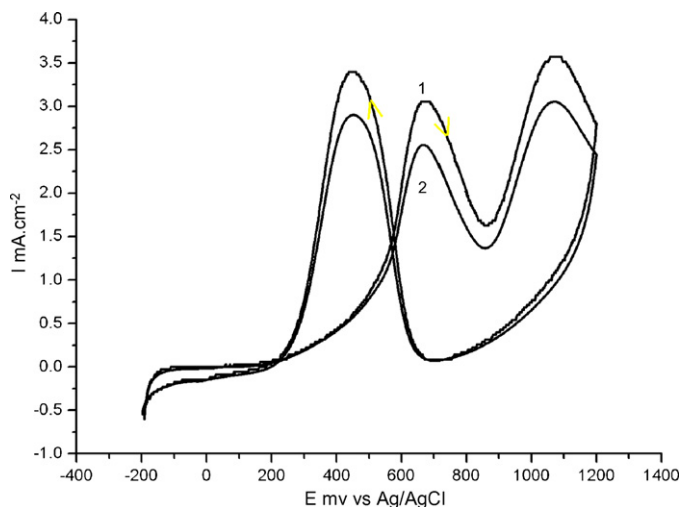


Fig. 5. Cyclic voltammograms for Pt electrode in electrolyte of: 1,  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 0.5 \text{ mol L}^{-1} \text{ CH}_3\text{CH}_2\text{OH} + 0.005 \text{ mol L}^{-1} \text{ Eu}^{3+}$ ; 2,  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 0.5 \text{ mol L}^{-1} \text{ CH}_3\text{CH}_2\text{OH}$ ; scan rate:  $20 \text{ mV s}^{-1}$ .

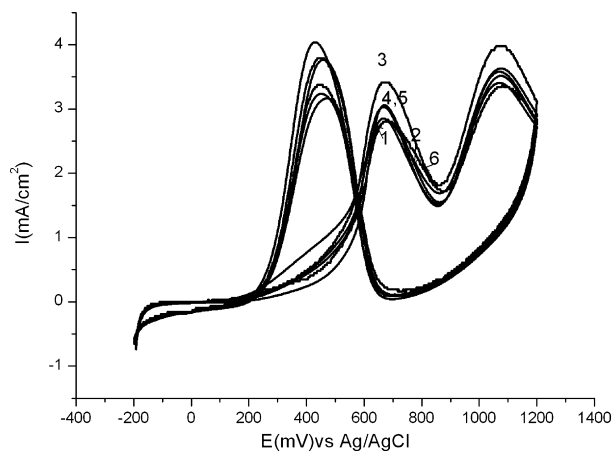


Fig. 6. Cyclic voltammograms for Pt electrode in electrolyte of  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 0.5 \text{ mol L}^{-1} \text{ CH}_3\text{CH}_2\text{OH}$  with different concentrations of  $\text{Eu}^{3+}$  cation; the concentrations are 2,  $0.0001 \text{ mol L}^{-1}$ ; 3,  $0.0005 \text{ mol L}^{-1}$ ; 4,  $0.001 \text{ mol L}^{-1}$ ; 5,  $0.005 \text{ mol L}^{-1}$ ; 6,  $0.01 \text{ mol L}^{-1}$ . Scan rate:  $20 \text{ mV s}^{-1}$ .

electrode; in this way the electro-oxidation reaction of ethanol is enhanced. Secondly, the enhancement effect is also related to the promotion of CO oxidation by the addition of  $\text{Eu}^{3+}$  to the ethanol solution, by cleaning of the platinum surface and preventing it from being poisoned. The cleaned platinum will promote the electro-catalytic activity of ethanol.

### 4. Conclusion

It has been discovered that the slow electro-oxidation of ethanol can be promoted by changing the electrochemical environment. The rare earth ion  $\text{Eu}^{3+}$  exhibited an enhancement effect on CO and ethanol electro-oxidation with the CO electro-oxidation potential shifted negatively by 300 mV. In a suitable concentration,  $\text{Eu}^{3+}$  played a key role in the enhancement effect. A possible mechanism is assumed to be that  $\text{Eu}^{3+}$  weakens the C–O bond of the intermediate CO produced from the electro-oxidation of ethanol and then favors the oxidation of the poison. Thus, it enhances the total electro-oxidation process of ethanol.

### Acknowledgements

This work was supported by High Technology Research Program (863 program 2003AA517060, 2006AA03Z224, 2007AA05Z143) of Science and Technology Ministry of China, the National Natural Science Foundation of China (20373068, and Key Project 20433060).

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