

二甲醚电氧化增强电化学表面积的研究

邵玉艳 尹鹤平* 高云智

(哈尔滨工业大学应用化学系, 哈尔滨 150001)

关键词: 电化学表面积; 二甲醚; 电氧化

中图分类号: O646.54

文献标识码: A

文章编号: 1001-4861(2005)07-1060-05

Electrochemical Surface Area Enhanced by Dimethyl-ether (DME) Electrooxidation

SHAO Yu-Yan YIN Ge-Ping* GAO Yun-Zhi

(Department of Applied Chemistry, Harbin Institute of Technology, Harbin 150001)

Abstract: The electrochemical surface area (ESA) of the half-membrane electrode assembly (HMEA) and dimethyl-ether (DME) electrooxidation on the HMEA were examined by cyclic voltammetry (CV). The ESAs of the electrode before and after DME electrooxidation were calculated from the integrated charge during the adsorption (and/or desorption) of atomic hydrogen minus the charge for the double layer charging in $0.5 \text{ mol} \cdot \text{L}^{-1} \text{ H}_2\text{SO}_4$. The increase in ESA was observed, and this was attributed to the change of catalyst layer structure, leading to a more effective contact between catalysts and the electrolyte Nafion.

Key words: electrochemical surface area (ESA); dimethyl-ether (DME); electrooxidation

0 Introduction

Fuel cells employing polymer (e.g., Nafion membranes) as the electrolyte are receiving increasing attention. The membrane-electrode assembly (MEA), comprising of a proton conducting membrane sandwiched between two gas diffusion electrodes (GDE), is the heart of the fuel cell^[1]. The GDE consists of carbon black supported Pt electrocatalyst and the backing layer, such as carbon paper or carbon cloth. It has been established that optimal electrochemical kinetics are achieved only when a three-phase interface for protons, electrons, and gases exists^[2]. Only catalysts located in this region is electrochemically active, and by inference not all catalyst in the catalyst layer is uti-

lized. Catalyst utilization and the electrode performance are thus determined by the electrochemically active surface, also called electrochemical surface area (ESA). Cyclic voltammetry (CV) has been frequently used to estimate the ESA by adsorption of atomic hydrogen in acidic media^[3~5]. The ESA is calculated from the amount of charge (Q_H) passed during the adsorption (and/or desorption) of atomic hydrogen. The calculation is based on two commonly accepted assumptions^[6]. First, each proton is able to occupy one site on the available Pt surface; second, all sites that are active and accessible will be occupied by hydrogen atoms during the transition from proton adsorption to hydrogen evolution (or hydrogen adsorption to proton desorption), that is, the ratio of adsorbed hydrogen

收稿日期: 2004-11-08。收修稿日期: 2005-03-14。

国家自然科学基金资助项目(No.20476020), 黑龙江省自然科学基金资助项目(No.B0201), 哈尔滨工业大学科学基金资助项目(No.HIT200139)。

*通讯联系人。E-mail: yingphit@hit.edu.cn

第一作者: 邵玉艳, 男, 26 岁, 博士生, 研究方向: 燃料电池和电催化。

atoms to the active Pt sites is 1:1. Using the proportionality constant $210 \mu\text{C} \cdot \text{cm}^{-2}$, the charge (Q_{H}) can be converted to the surface area.

In this work, a large increase of the ESA was found due to dimethyl-ether (DME) electrooxidation on the electrode, and *vice versa*. DME has many advantages for applications in fuel cells^[7-10]: high energy density, easy to handle (to store and convey), nontoxic, etc. Performance enhancement of direct dimethyl-ether fuel cell (DDFC) attributed to methanol or CO preconditioning was observed by Mench et al^[7]. Performance enhancement by methanol preconditioning was also observed in formic acid fuel cells^[11,12]. The authors attributed the enhancement phenomenon to changes in the structure of the anode layer, pore alignment and porosity increase in the cast Nafion film due to CO_2 bubbles. They implied that the increase of ESA had little effect on the performance enhancement of fuel cells. In this work the half-membrane electrode assembly and the gas diffusion electrode (without Nafion membrane) were studied using a half-fuel cell system.

1 Experimental

1.1 Materials

All the chemicals were of analytical grade. H_2PtCl_6 and HCHO were used as received. Carbon black (Vulcan XC-72) was pre-oxidized using O_3 for the preparation of the catalyst Pt/C (40wt%)^[13,14]. The Nafion-117 membranes (Electrochem Inc., USA) were pretreated in 3% hydrogen peroxide aqueous solution and $0.5 \text{ mol} \cdot \text{L}^{-1}$ sulphuric acid in sequence^[15]. Carbon papers (Toray, Japan) were hydrophobized using 20wt% PTFE emulsion. The 5wt% Nafion solution (Electrochem Inc., USA) was used as received. The purity of DME was 99.99%. All the solutions were prepared using superpure water ($18.2 \text{ M}\Omega \cdot \text{cm}$ resistivity, Millipore Milli-Q system).

1.2 Half-membrane electrode assembly

The half-membrane electrode assemblies (HMEA) were prepared by hot-pressing a gas diffusion electrode (GDE) with Pt loading of $0.7 \text{ mg} \cdot \text{cm}^{-2}$ on one side of the pretreated Nafion-117 membrane with a pressure of 5 MPa at 130°C ^[1]. The gas diffusion electrode was composed of three layers, namely, the backing layer (70wt% carbon paper and 30wt% PTFE), the diffusion layer (80wt% carbon black and 20wt%

PTFE), and the catalyst layer (80wt% Pt/C and 20wt% Nafion). The HMEAs were stored in deionized water for further use.

1.3 Electrochemical measurements

The electrochemical measurements were conducted in a half-fuel cell setup^[1,16], as shown in Fig.1. The working electrode (HMEA or GDE, $2.3 \times 2.3 \text{ cm}^2$) was held vertically in a chamber filled with $0.5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$ with the Nafion membrane exposed to the electrolyte solution. The counter electrode (a Pt foil of 3.5 cm^2) was placed in a compartment separated from the WE compartment by a Nafion 117 membrane^[17], so that it prevented the hydrogen generated at the counter electrode from interfering with the WE process^[16]. The reversible hydrogen electrode (RHE) was used as the reference electrode and was placed in the WE compartment with a distance of *ca.* 1.0 cm away from the WE. Usually the WE backside compartment was filled with water in order to prevent oxygen from interfering with the WE process^[18].

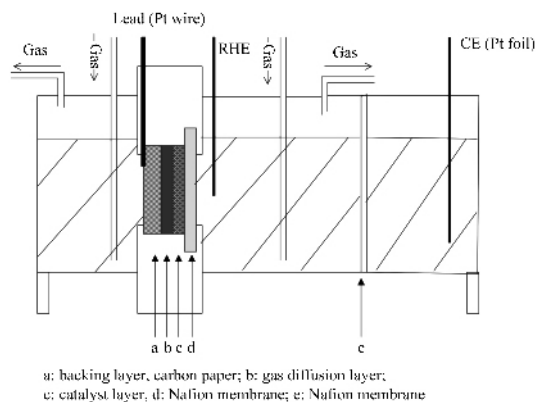


Fig.1 Schematics of the half-cell setup with a half-membrane electrode assembly (HMEA) or gas diffusion electrode (GDE) as a working electrode ($2.3 \times 2.3 \text{ cm}^2$), a RHE as a reference electrode, and a Pt foil as a counter electrode

The counter electrode compartment is separated from the working electrode compartment by a Nafion-117 membrane.

The procedures used in the electrochemical experiments were: (i) the supporting electrolyte solution of $0.5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$ and the WE backside water were saturated with Ar for at least 30 min, then cyclic voltammetry experiments between $0.05 \sim 1.0 \text{ V}$ were carried out until a steady CV curve was recorded; (ii) the WE backside water was saturated with DME ($1.5 \text{ mol} \cdot \text{L}^{-1}$)^[10], and the cyclic voltammetry experiments

were carried out until a steady CV curve was performed, with all CV curves recorded; (iii) the WE backside DME solution was replaced with water, and then the water was saturated with Ar for at least 30 min, and then CV experiments were carried out between 0.05~1.0 V. All the electrochemical measurements were carried out at 18 ± 1 °C.

2 Results and discussion

Fig.2 shows the cyclic voltammograms obtained in $0.5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$ for a HMEA before and after DME electrooxidation. The value of Q_{H} was calculated by the following equation:

$$Q_{\text{H}} = 0.5(Q_{\text{total}} - Q_{\text{dl}}),$$

where Q_{total} and Q_{dl} are the charge by the hydrogen adsorption/desorption curve and the capacitive charge due to double layer charging, respectively^[19]. It is reasonable to assume that a higher ESA implies a higher catalytic activity, because more catalyst sites are available for the reaction^[6,20]. The roughness factor (RF) was calculated by dividing the ESA by the geometric area ($2.3 \times 2.3 \text{ cm}^2$) of the electrode. The RFs for the HMEA before and after DME electrooxidation were 76.8 and 113.1, respectively. The RF, implying the electrochemical surface area, was increased by ca. 48% after DME electrooxidation. In Fig.3, the current of DME electrooxidation kept increasing with potential cycling until the 10th cycle, which also implied that the electrocatalytic activity was improved with potential cycling. The peak current shown in the 10th CV was higher by ca. 40% than that shown in the 1st CV. After the 10th and the 11th CVs were recorded, step iii experiments were carried out (Experimental section). The recorded CV (inset) showed that the ESA was not changed, implying that the peak current given in DME electrooxidation CV had a positive correlation with the ESA. And the enhanced performance of DME electrooxidation at the HMEA could be attributed to the increase of the ESA. Mench et al^[7] attributed the enhanced performance to the adsorbed CO that was not consumed by the reaction and somehow accelerated the DME electrooxidation process. In methanol-preconditioned formic acid fuel cells^[11,12], the authors attributed the enhancement phenomenon to changes in the structure of the anode layer, pore alignment and porosity increase in the cast Nafion film due to CO_2

bubbles. On the contrary, they implied that the increase of ESA had little effect on the performance enhancement of fuel cells because they observed a very small change (increased by 2.2%) in ESA^[11]. At the peak potential (around 0.85 V vs RHE), CO is oxidized. Pore alignment may contribute to the current increase. We do observe CO_2 bubbles formed on the backside of the HMEA. CO_2 bubbles may cause the anode catalyst layer to reconstruct, leading to an effective contact between catalyst and cast Nafion, so the ESA was increased. A 48% increase of ESA only

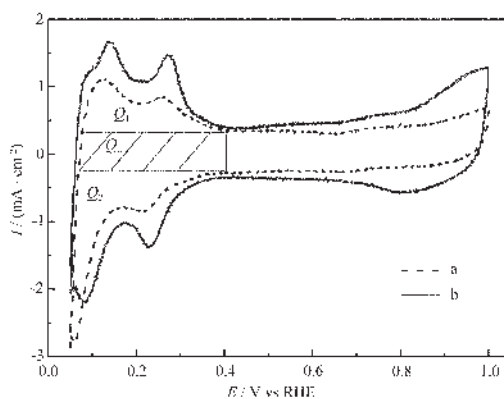


Fig.2 Cyclic voltammograms at half-membrane electrode assembly (HMEA) in $0.5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$ solution a: before DME electrooxidation (step i); b: after DME electrooxidation (step iii). Sweep rate: $10 \text{ mV} \cdot \text{s}^{-1}$, at 18 ± 1 °C. Q_1 , Q_2 , and Q_{dl} are the integrated charge used to calculate the electrochemical surface area.

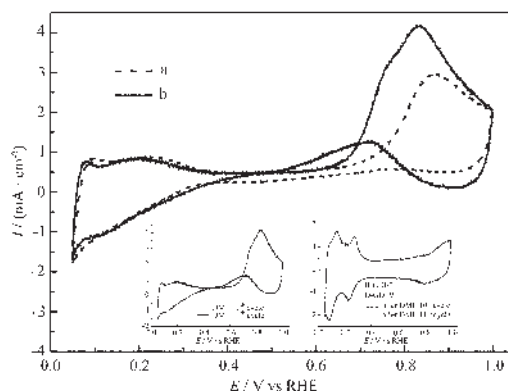


Fig.3 Potential cycle effect on DME electrooxidation at HMEA and the electrochemical surface area a: 1st cycle of DME electrooxidation, b: 10th cycle of DME electrooxidation. Sweep rate: $10 \text{ mV} \cdot \text{s}^{-1}$, at 18 ± 1 °C. The insets show a steady CV of DME electrooxidation and no change in the ESA.

led to a 40% increase in the peak current. This implied that not all the catalyst sites accessible to protons were effective in DME electrooxidation. The onset potential of DME electrooxidation was observed to be finally shifted to a more negative potential.

Similar results were observed for the gas diffusion electrode. The RFs calculated from the ESA divided by the geometric area were 82.2 and 105.8 for the GDE before and after DME electrooxidation, respectively, with an increase by 28.7% (Fig.4). The peak current shown in DME electrooxidation CV (Fig. 5) was increased by 34%. This implied that some factors in addition to ESA change during DME electrooxidation enhanced the electrode catalytic activity. A change could be seen in the feature of hydrogen adsorption/desorption region (Fig.4). In the initial CV, the hydrogen adsorption-desorption peaks appeared to be broad and featureless; it was presumed that the Pt (111) was the predominant facet in the catalyst surface^[21]. But the peaks changed into one like that on a usual polycrystalline Pt electrode in acid, which implied that the percentage of Pt(110) and Pt(100) increased during DME electrooxidation^[21]. It is known that various Pt single crystal planes show different catalytic activity toward some organic molecules' electrooxidation. We have shown that Pt(111) electrode had a poor performance toward DME electrooxidation^[22], and DME electrooxidation on other planes of

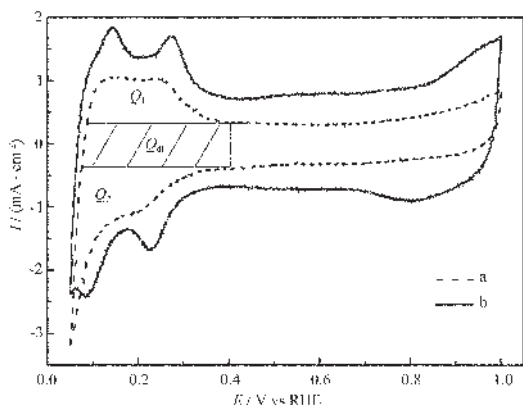


Fig.4 Cyclic voltammograms at gas diffusion electrode in $0.5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$ solution

a: before DME electrooxidation (step i);

b: after DME electrooxidation (step iii).

Sweep rate: $10 \text{ mV} \cdot \text{s}^{-1}$, at $18 \pm 1^\circ \text{C}$. Q_1 , Q_2 , and Q_3 are the integrated charge used to calculate the electrochemical surface area.

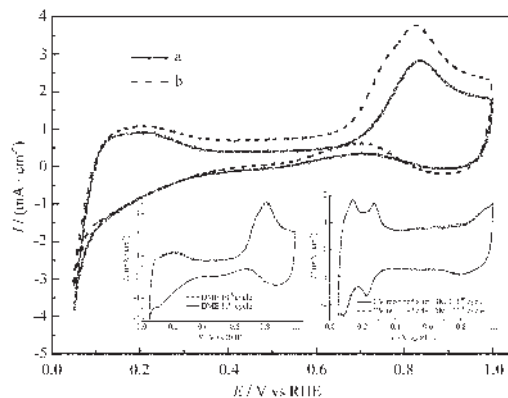


Fig.5 Potential cycle effect on DME electrooxidation at GDE and the electrochemical surface area

a: 1st cycle of DME electrooxidation,

b: 10th cycle of DME electrooxidation.

Sweep rate: $10 \text{ mV} \cdot \text{s}^{-1}$, at $18 \pm 1^\circ \text{C}$. The insets show a steady CV of DME electrooxidation and no change in the ESA.

Pt are under study. The increase of the peak current might be partly attributed to the change in catalyst predominant facets.

Jiang et al^[19] showed a decrease in the ESA and the capacitive current when Nafion was the bulk electrolyte in comparison with the bulk electrolyte of $0.5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$. In our work, the hot-pressed Nafion membrane seemed to have little effect on ESA, even with a decrease of ESA when GDE directly contacts with $0.5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$ (RF=105.8 for GDE compared with RF=113.1 for HMEA). This could be attributed to the flood of HMEA because both sides of HMEA were exposed to aqueous solutions (one was $0.5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$, and the other was Ar saturated water or DME aqueous solution).

3 Conclusions

Half fuel cell systems can simulate fuel cells under flooded conditions and provide valuable information on available ESAs. The electrochemical surface area of HMEAs increases after DME electrooxidation, and vice versa. This increase of ESA was attributed to the changes in the catalyst layer of HMEA, which made the contact between catalyst and Nafion more effectively. Not all the ESA sites associated with hydrogen adsorption/desorption are shown to be effective for DME electrooxidation. This implies that protons accessible sites are not equal to those of DME

molecules. The ESA increase was also observed for GDEs after DME electrooxidation. This could be attributed to the change in the catalyst layer and the facet change on catalyst surface.

References:

- [1] Navessin T, Holdcroft S, Wang Q, et al. *Journal of Electroanalytical Chemistry*, **2004**,**567**:111~122
- [2] Litster S, McLean G. *Journal of Power Sources*, **2004**,**130**:61~76
- [3] Li W, Zhou W, Li H, et al. *Electrochimica Acta*, **2004**,**49**:1045~1055
- [4] Murthi V S, Urian R C, Mukerjee S. *J. Phys. Chem. B*, **2004**, **108**:11011~11023
- [5] Xiong L, Manthiram A. *Electrochimica Acta*, **2004**,**49**:4163~4170
- [6] Stevens D A, Dahn J R. *J. Electrochem. Soc.*, **2003**,**150**(6): A770~A775
- [7] Mench M M, Chance H M, Wang C Y. *J. Electrochem. Soc.*, **2004**,**151**(1):A144~A150
- [8] Muller J T, Urban P M, Hulderich W F, et al. *J. Electrochem. Soc.*, **2000**,**147**(11):4058~4060
- [9] Tsutsumi Y, Nakano Y, Kajitani S, et al. *Electrochemistry*, **2002**,**70**(12):984~987
- [10] SHAO Yu-Yan(邵玉艳), YIN Ge-Ping(尹鸽平), GAO Yun-Zhi(高云智), et al. *Wuji Huaxue Xuebao(Chinese Journal of Inorganic Chemistry)*, **2004**,**20**(12):1453~1458
- [11] Ha S, Rice C A, Masel R I, et al. *Journal of Power Sources*, **2002**,**112**:655~659
- [12] Rice C., Ha S., Masel R.I., et al. *Journal of Power Sources*, **2003**,**115**:229~235
- [13] Kim H, Park J, Lee W. *Catalysis Today*, **2003**,**87**:237~245
- [14] Zhou Z, Zhou W, Wang S, et al. *Catalysis Today*, **2004**,**93**~**95**:523~528
- [15] Costamagna P, Yang C, Bocarsly A B, et al. *Electrochimica Acta*, **2002**,**47**:1023~1033
- [16] Reeve R W, Burstein G T, Williams K R. *Journal of Power Sources*, **2004**,**128**:1~12
- [17] Tamizhmani G, Dodelet J P, Guay D, et al. *Journal of Electroanalytical Chemistry*, **1998**,**444**:121~125
- [18] Pozio A, Francesco M D, Cenni A, et al. *Journal of Power Sources*, **2002**,**105**:13~19
- [19] Jiang J, Kucernak A. *Journal of Electroanalytical Chemistry*, **2004**,**567**:123~137
- [20] Sasikumar G, Ihm J W, Ryu H. *Journal of Power Sources*, **2004**,**132**:11~17
- [21] Prabhuram J, Zhao T S, Wong C W, et al. *Journal of Power Sources*, **2004**,**134**:1~6
- [22] SHAO Yu-Yan(邵玉艳), GAO Yun-Zhi(高云智), YIN Ge-Ping(尹鸽平). In *12th Conference of the Electrochemical Society of China*(第 12 届全国电化学会议). Shanghai, Nov. **2003**.A065