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# How Can Direct Methanol Fuel Cell Benefit from Carbonate Media

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**Abstract:** The kinetics of methanol oxidation and oxygen reduction in 0.5 mol/L  $K_2CO_3$  were compared with those in 0.5 mol/L  $H_2SO_4$ . Experiments revealed that carbonate media could be more beneficial to direct methanol fuel cell (DMFC). Firstly, both electrode reactions show better performance in the carbonate than in the acid; secondly, materials other than noble metals become possible to be used as the anodic and cathodic catalysts; thirdly, the potential decrease caused by methanol crossover could be depressed by using metal oxide catalysts not stable in acid, such as  $MnO_2$ .

**Key words:** Direct methanol fuel cell, Carbonate media, Electrocatalysis

**CLC number:** TM 911.4 O 646

**Document code:** A

## 1 Introduction

Direct methanol fuel cell (DMFC) is expected to be an ideal power source for the electric vehicle and portable electronic devices in the new century. Although much progress has been made in recent years<sup>[1~4]</sup>, The performance and cost of DMFC still cannot satisfy the requirement of commercial applications at present. What have been impeding the development of DMFC most are the electrocatalytic inefficiency and the methanol crossover<sup>[3,4]</sup>.

Until now, anodic catalysts reported to be active for the methanol oxidation are almost based on noble metals, especially Pt. Pure platinum tends to be easily poisoned by the reaction intermediates; alloys of platinum with different metals, typically such as Ru, Sn, Os, etc.<sup>[5~8]</sup>, are reported to be more active. Among these alloys, Pt-Ru is the only one incontrovertibly showing an obvious synergistic effect<sup>[5,6]</sup>. However, Pt-Ru catalysts are still not sufficiently active and have been proved unstable for long-term use<sup>[9]</sup>. Studies of the anodic catalyst have now been intensively focused on the Pt-Ru alloys<sup>[10,11]</sup>, but no remarkable progress has been made so far.

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The ideology of current researches on the anodic catalyst is predominantly based on the theory of bifunctional mechanism<sup>[12]</sup>. According to this theory, Pt is the basic catalyst and the second metal is incorporated to act as a promoter by forming oxygen-containing species on the electrode surface so that the reaction intermediates can be further oxidized at lower potentials. In this sense, ruthenium appears to be the best promoter found so far. It is notable that the process of dissociative adsorption of methanol molecules on the platinum surface may also become the rate-limiting step when the subsequent reactions have been accelerated<sup>[13]</sup>. However, the dissociative adsorption step seems difficult to be modified as long as Pt is used as the basic catalyst.

In DMFCs using Nafion membrane or other acidic solid polymer electrolytes, platinum is also used as the cathodic catalyst for oxygen reduction. Methanol molecules are rather easy to cross the membrane and they can react on the platinum-catalyzed cathode, resulting in a decrease of the electromotive force of the fuel cell<sup>[14]</sup>. Since it seems unlikely for an ideally methanol-tight solid polymer electrolyte membrane to emerge in the near future, methanol-insensitive cathodic catalysts are highly desired.

Efforts have been made to search for catalysts more active and/or cheaper than Pt or known Pt-based catalysts for use in DMFC<sup>[15~18]</sup>, unfortunately no significant breakthrough have been achieved. Actually, in the strong acidic media currently used in DMFC, including protonated Nafion, the platinum based catalysts are the only acceptable catalysts because of stability consideration. It is clear that the main advantage of acidic media is to expel the CO<sub>2</sub> produced by the anodic reaction; however the disadvantages are the reduce in electroactivity in comparison with alkaline media and a very limited choice of electrode materials.

The use of alkaline electrolytes seems very attractive as long as electrocatalytic activity is in concern<sup>[19]</sup>, but it is not practical. The most serious drawback with alkaline electrolytes is their progressive consumption by the CO<sub>2</sub> generated during operation. A promising cure for this situation, as Parsons suggested<sup>[19]</sup>, is to develop DMFC in carbonate or bicarbonate solutions which uptake less or no carbon dioxide.

The aim of this preliminary study is to ascertain and demonstrate how DMFC could benefit from carbonate media. Bicarbonate may be produced in the carbonate solution but it will be readily decomposed at temperatures above 65 °C which is within the working temperature range of DMFC. In this study, both the anodic oxidation of methanol and the cathodic reduction of oxygen were found to show better performances in the carbonate medium (0.5 mol/L K<sub>2</sub>CO<sub>3</sub>) than in acidic medium (0.5 mol/L H<sub>2</sub>SO<sub>4</sub>). Furthermore, materials other than noble metals become possible to be used as the catalysts. For example, manganese dioxide can be used as cathodic catalyst to effectively depress the negative potential shift of the cathode due to coexistence of methanol.

## 2 Experimental

Cyclic voltammetric and steady-state polarization measurements were carried out in 0.5 mol/

L  $\text{H}_2\text{SO}_4$  and 0.5 mol/L  $\text{K}_2\text{CO}_3$  at 60 °C to evaluate the electrocatalytic activity. The electrolyte was deoxygenated by bubbling pure argon through the cell. All chemicals used were of analytical-pure grade, and solutions were prepared with twice distilled water.

In the anode studies, three electrodes were tested for methanol oxidation, i. e., a Pt foil (geometric area ca. 0.4 cm<sup>2</sup>), an Au micro-disk ( $\varnothing$  30  $\mu\text{m}$ ) and a Pt/C thin powder layer electrode. The thin powder layer electrode was made from platinized carbon powder (Pt 20 w %) adhered on a Teflon bonded acetylene black sheet covering a metal disk electrode ( $\varnothing$  0.3 cm). Two gas diffusion electrodes (1 cm<sup>2</sup> apparent area) were tested for oxygen reduction in air. The same Teflon bonded acetylene black sheet was used as the gas-diffusion layer. The catalytic layers were adhered thin Pt/C powder layer and Teflon bonded  $\text{MnO}_2$  catalysed carbon, respectively. A reversible hydrogen electrode (RHE)<sup>[20]</sup> filled with the same solution as in the electrolytic cell was used as the reference electrode. Since the thermodynamic equilibrium potentials for the anodic and cathodic reactions in DMFC have the same pH dependence, this reference electrode is convenient for comparing the kinetics of a reaction in solutions of different pH values.

### 3 Results and Discussion

#### 3.1 Anodic oxidation of methanol in $\text{K}_2\text{CO}_3$ solution

As illustrated in Fig. 1, the cyclic voltammogram obtained for a smooth Pt electrode in  $\text{K}_2\text{CO}_3$  is similar to that in  $\text{H}_2\text{SO}_4$  to some extent, but several differences were also observed. The most important difference is a negative shift of the current peak in carbonate compared to the acid, indicating that carbonate medium is beneficial to the methanol oxidation. The other differences include the disappearance of the hysteresis in low potential region (0.3 ~ 0.6 V) and the anodic peak at higher potentials (1.3 ~ 1.6 V) in the carbonate. Very similar results (not shown) were obtained with the thin layer Pt/C powder electrode. These observations may be indicative of differences in reaction mechanisms in the different electrolytes.

#### 3.2 Possibility of non-Pt based anodic catalyst

As mentioned in Introduction, Pt-based catalysts are the only acceptable catalysts for strong acidic media for stability consideration. However, many kinds of compounds are stable in carbonate media, thus the electrode material can be no more limited to the noble metals. In our studies, some composite metal oxides, such as spinel  $\text{NiCo}_2\text{O}_4$ , were found able to catalyze the methanol oxidation, but they are not sufficiently active at present. Further studies are carrying out in our lab.

An interesting result was the dramatic change in the catalytic activity of gold when the electrolyte was switched from the acid to carbonate. As shown in Fig. 2, Au exhibits a notable activity for the methanol oxidation in  $\text{K}_2\text{CO}_3$  whereas it is completely inactive in the same potential range (with respect to the RHE in the same solution as in the cell) in  $\text{H}_2\text{SO}_4$ . Although the performance of Au is not so good as that of Pt, this result encourages searching for the anodic catalyst

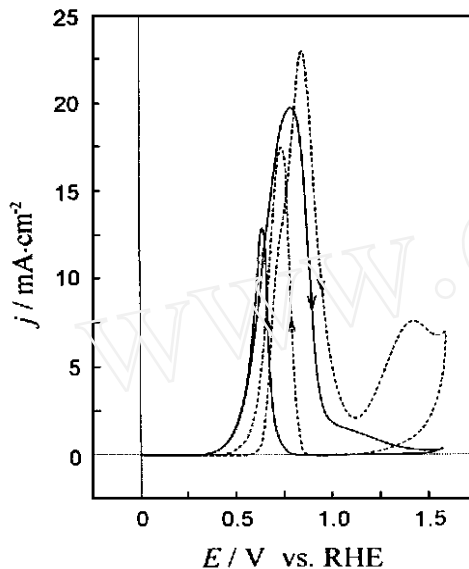


Fig. 1 Cyclic voltammograms of methanol oxidation on smooth Pt electrode at 60 and 50 mV/s in 1 mol/L CH<sub>3</sub>OH. The supporting electrolytes are 0.5 mol/L K<sub>2</sub>CO<sub>3</sub> (solid line) and 0.5 mol/L H<sub>2</sub>SO<sub>4</sub> (broken line), respectively

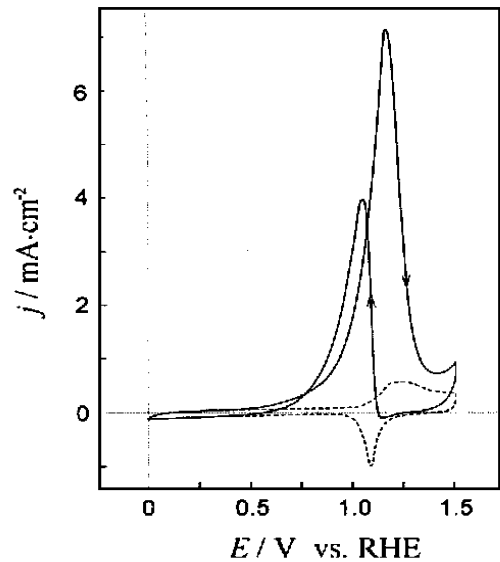


Fig. 2 Cyclic voltammograms of Au micro-disk electrode at 60 and 50 mV/s in 0.5 mol/L K<sub>2</sub>CO<sub>3</sub> in the presence (solid line) and absence (broken line) of CH<sub>3</sub>OH (1 mol/L)

among materials other than Pt-based ones.

### 3.3 Cathodic reduction of oxygen at Pt/ C in K<sub>2</sub>CO<sub>3</sub> solution

Fig. 3 shows that oxygen reduction at the gas-diffusion electrode catalyzed with a thin layer of Pt/ C powder is slightly more favored in K<sub>2</sub>CO<sub>3</sub> than in H<sub>2</sub>SO<sub>4</sub>. This result together with the result in 3.1 indicates that K<sub>2</sub>CO<sub>3</sub> is an electrolyte as good as (or even slightly better than) H<sub>2</sub>SO<sub>4</sub> in terms of reaction kinetics for the Pt catalyzed anodes and cathodes for DMFC.

### 3.4 Methanol-insensitive catalyst for the cathodic oxygen reduction

Transition metal macrocycle catalysts have been proposed as methanol-insensitive cathodic catalysts<sup>[17,18]</sup>, but their efficiency and stability are still not satisfactory. In carbonate media, some oxides not stable in acidic media become hopeful candidates for methanol-insensitive cathodic catalysts. For demonstration, Fig. 4 compares the polarization curves of the gas-diffusion electrode catalyzed with MnO<sub>2</sub> in the presence and absence of methanol, showing that the methanol effect was almost completely depressed.

### 3.5 The drawbacks of carbonate media and possible solutions

Carbonate media seem quite beneficial to DMFC according to above discussions. Two main drawbacks are low conductivity and the tendency for carbonate to precipitate in pores of gas-diffusion electrodes. The solution to the former might be an addition of highly conductive salts. The

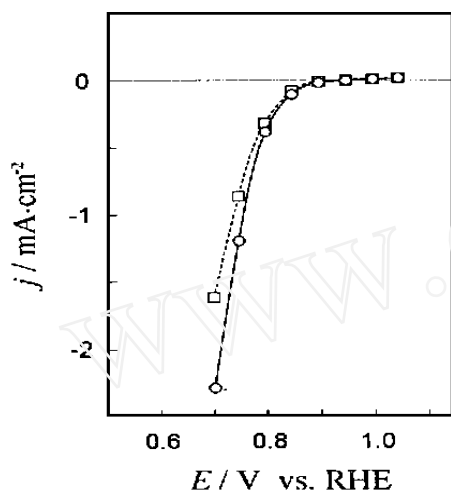


Fig. 3 Steady-state polarization curves of oxygen reduction at thin layer Pt/C catalyzed air electrode at 60 °C in 0.5 mol/L  $K_2CO_3$  (circle) and 0.5 mol/L  $H_2SO_4$  (square), respectively

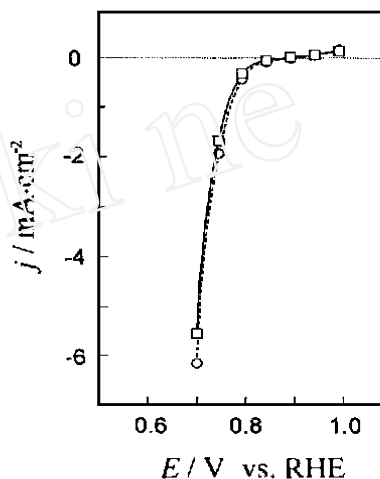


Fig. 4 Steady-state polarization curves of oxygen reduction at  $MnO_2$  catalyzed air electrode at 60 °C in the absence (circle) and presence (square) of methanol (1 mol/L) in 0.5 mol/L  $K_2CO_3$

problem of salt precipitation might be overcome if water management is treated as carefully as with the membrane-type DMFC.

#### 4 Summary

The comparative studies have proved carbonate system to be a hopeful approach to DMFC. In summary, as long as kinetics is in concern, carbonate appears as good as or slightly better than sulfuric acid. Since more materials are stable in carbonate than in strong acids, there is a much greater variety of materials to be chosen for the catalysts for carbonate systems, including the urgently demanded methanol-insensitive cathodic catalysts. The disadvantages associated with carbonate may be circumvented with relevant measures. Therefore, the carbonate approach is well worth further studies.

#### Acknowledgement

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# 直接甲醇燃料电池如何获益于碳酸盐介质

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**摘要:** 本文通过比较 0.5 mol/L  $K_2CO_3$  与 0.5 mol/L  $H_2SO_4$  中甲醇阳极氧化与氧阴极还原的动力学, 探讨直接甲醇燃料电池 (DMFC) 使用碳酸盐介质的可能性. 实验表明, 碳酸盐介质比传统的酸性介质具有更多的优点: 1) 在碳酸盐介质中, 电池的阴阳极反应性能比在酸中的高; 2) 非贵重金属材料有可能被用作阴阳极催化剂; 3) 由于可能使用对甲醇不敏感的金属氧化物 (如  $MnO_2$ ) 作阴极催化剂, 甲醇穿透隔膜于阴极放电的难题有望克服.

**关键词:** 直接甲醇燃料电池; 碳酸盐介质; 电催化