

Computer-aided design and manufacturing of bipolar plates for DMFC

* Huan-Chung Chiu¹, Ing-Bang Huang², Yu-Cheng Chen¹, Chun-Hsien Chiang¹
¹Department of Product Design, Transworld Institute of Technology, Taiwan
²Graduate Institute of Materials Science and Green Energy Engineering,
National Formosa University, Taiwan

ABSTRACT

This study was an application of computer-aided design and manufacturing (CAD / CAM) technology to develop and produce stainless steel bipolar plates for DMFC (direct methanol fuel cell). Surface modification on the stainless steel to reduce voltage losses due to the formation of passive layers by electroless Au plating has been demonstrated. The electroless Au plating and uncoated stainless steel bipolar plates were assembled to a direct methanol fuel cell and conduct performance testing. The methanol crossover rate of proton exchange membrane (PEM), the efficiency of direct methanol fuel cell (DMFC) and the amount of methanol electro-oxidation of the bipolar electrode at cathode side are obtained by the transient current analysis.

Keywords: DMFC, Bipolar plates, Crossover rate, Methanol

1. INTRODUCTION

Metals have good mechanical properties and chemical stability, electrical conductivity and thermal conductivity and can be recycled. Furthermore, they can be easily stamped to a desired shape to accommodate the flow channels in the fuel cell. However, in a PEMFC environment, metals are prone to corrosion and the resulting metal ions can readily migrate to, and poison, the membrane [1]. The dissolved metal ions can lower the ionic conductivity of the membrane and, thus, the performance of the PEMFC. Furthermore, any corrosion layer will lower the electrical conductivity of the bipolar plate, and increase the potential loss because of a higher electrical resistance [1].

Hence, in order to be suitable materials of bipolar plates, metals should have both a very high corrosion resistance and high electrical conductivity. Various metals such as titanium, aluminum, and stainless steel were tested as possible candidates for bipolar plates [2-8].

In this study, computer-aided design and manufacturing (CAD/CAM) technology was applied to develop and produce bipolar plates of stainless steel for DMFC (direct methanol fuel cell) application. Surface modification on the stainless steel was made by electroless Au-plating. The methanol crossover rate of PEM, the efficiency of DMFC and the amount of methanol electro-oxidation of the bipolar electrode at cathode side were estimated by measuring the transient voltage and current at the DMFC when methanol was introduced into the anode.

* Corresponding author. Tel: +886-922-562512 ;
Fax: +886-5-5370989.

2. MATHEMATICAL

Before the mathematical analysis, the following terms must be defined.

M_T : total amount of methanol charged, mole

M_{ao} : amount of methanol electro-oxidized at anode side, mole

M_{mo} : amount of bipolar plates corrosion oxidation at anode side, mole

M_{co} : amount of crossover methanol electro-oxidized at cathode side, mole

E_f : efficiency of DMFC, %

R_C : crossover rate, mol/cm²/s

t : time required for electro-oxidation current to fall from I to zero, sec

A : active area of electro-oxidation, cm²

I : current, A

n : number of electrons exchanged

F : Faraday's constant, 96480A.sec/mol

The mathematical expression of the characteristics of a direct methanol fuel cell may be simplified by the equation,

$$M_T - M_{ao} - M_T \times (1 - E_f) - R_C \times t \times A = 0 \quad (1)$$

where,

$$E_f = \frac{M_{ao}}{M_T - M_{co}} \times 100\% \quad (2)$$

and

$$\int Idt = 6F(M_{ao} - M_{co}) + 2FM_{mo} \quad (3)$$

In four experiments under identical operating conditions but different charging volumes of

methanol solution, Eq. (1) becomes the following simultaneous equations:

$$\begin{cases} M_{T1} - M_{ao1} - M_{T1} \times (1 - E_f) - R_C \times t_1 \times A_1 = 0 \\ M_{T2} - M_{ao2} - M_{T2} \times (1 - E_f) - R_C \times t_2 \times A_2 = 0 \\ M_{T3} - M_{ao3} - M_{T3} \times (1 - E_f) - R_C \times t_3 \times A_3 = 0 \\ M_{T4} - M_{ao4} - M_{T4} \times (1 - E_f) - R_C \times t_4 \times A_4 = 0 \end{cases} \quad (4)$$

Rearranging, we get:

$$\begin{cases} M_{T1} \times E_f - R_C \times t_1 \times A_1 + 3.33 \times 10^{-1} M_{mo} - M_{co} = \frac{\int_0^{t_1} I_1 dt}{6F} \\ M_{T2} \times E_f - R_C \times t_2 \times A_2 + 3.33 \times 10^{-1} M_{mo} - M_{co} = \frac{\int_0^{t_2} I_2 dt}{6F} \\ M_{T3} \times E_f - R_C \times t_3 \times A_3 + 3.33 \times 10^{-1} M_{mo} - M_{co} = \frac{\int_0^{t_3} I_3 dt}{6F} \\ M_{T4} \times E_f - R_C \times t_4 \times A_4 + 3.33 \times 10^{-1} M_{mo} - M_{co} = \frac{\int_0^{t_4} I_4 dt}{6F} \end{cases} \quad (5)$$

In spite of there are four unknown parameters M_{mo} , M_{co} , E_f and R_C in Eq.(5). However, the value of parameter M_{mo} can be set to zero due to corrosion current of stainless steel plate is much lowest when the stainless steel plate used at the anode side for DMFC. In this study, Eq. (5) can be reduced as following:

$$\begin{cases} M_{T1} \times E_f - R_C \times t_1 \times A_1 - M_{co} = \frac{\int_0^{t_1} I_1 dt}{6F} \\ M_{T2} \times E_f - R_C \times t_2 \times A_2 - M_{co} = \frac{\int_0^{t_2} I_2 dt}{6F} \\ M_{T3} \times E_f - R_C \times t_3 \times A_3 - M_{co} = \frac{\int_0^{t_3} I_3 dt}{6F} \end{cases} \quad (6)$$

The above simultaneous equations can be transformed into matrix form

$$A \times b \quad (7)$$

where

$$A = \begin{bmatrix} M_{T1} & -t_1 \times A_1 & -1 \\ M_{T2} & -t_2 \times A_2 & -1 \\ M_{T3} & -t_3 \times A_3 & -1 \end{bmatrix}, \quad X = \begin{bmatrix} E_f \\ R_c \\ M_{co} \end{bmatrix}$$

and

$$b = \begin{bmatrix} \frac{\int_0^{t_1} I_1 dt}{6F} \\ \frac{\int_0^{t_2} I_2 dt}{6F} \\ \frac{\int_0^{t_3} I_3 dt}{6F} \end{bmatrix}$$

The simultaneous equations can be easily solved by the inverse matrix:

$$X = A^{-1}b \quad (8)$$

The methanol crossover rate of PEM (R_c), the efficiency of DMFC (E_f), and the amount of methanol electro-oxidation of the bipolar electrode at cathode side can be easily computed from Eq. (8) using Microsoft Excel®.

3. EXPERIMENTAL

3.1 Computer-aided design and manufacturing of the DMFC device

The Direct Methanol Fuel Cell device consists of two supporting plates (PMMA), stainless steel bipolar plates and a membrane electrode assembly (MEA). CAD/CAM software I-DEAS was employed to do 3D solid modeling design shown in Fig. 3.1.1. Bipolar plates designed with the mirror symmetry that enables the positive and negative stacking. Every hole on the plate should be aligned each other after stacking as shown in Fig. 3.1.2. Stainless steel bipolar plates were manufactured by Japanese

Mitsubishi laser cutting machine (3500W ML3015LVPlus) as shown in Photo 3.1.1, 3.1.2 and 3.1.3.

There are two supporting plates (PMMA) of the DMFC device. One plate with 50 mm × 50 mm opening square slot is for air inlet. The part can be entirely made by laser cutting. The other plate with 7mm × 50mm × 50mm square slot is for methanol fuel tank. There is a groove closes to the square slot for placing the rubber ring to prevent leakage of methanol fuel. There are two holes at the top of square slot for injecting methanol fuel and air outlet. The CAD/CAM software SmartCAM was employed to process the tool path planning and manufacturing simulation as shown in Figure 3.1.3. Two parts were completed as shown in Photo 3.1.4.

3.2 Electroless gold – plating

Type 304 stainless steel (304SS) plates were chosen as the bipolar plates of DMFC in the research. Before electroless plating, the stainless steel plates were polished on 200, 600, 800, 1000 and 1200 grit silicon carbide papers and a final polish with 1.0µm alumina powder. The polished plates were thoroughly washed with distilled water and dried with air before passing through the procedure of electroless method. The operating conditions and steps of this method are illustrated in Fig. 3.2.1. Photo 3.2.1 is shown by the electroless gold-plating and untreated AISI 304 stainless steel bipolar plates.

3.3 Cell performance testing

The methanol crossover rate, the efficiency of direct methanol fuel cell and the amount of methanol electro-oxidation of the bipolar electrode at cathode side were measured using the experimental system shown in Fig.3.3.1. The method uses a DMFC that includes an anode chamber for the electrochemical oxidation of the methanol, a cathode chamber for the

electrochemical reduction of oxygen; a membrane electrode assembly (MEA) arranged between the anode and the cathode, and a load unit connected to the DMFC. An aqueous solution of the methanol is fed to the anode chamber while the load unit is operated at 10Ω in a loading state, enabling the methanol to crossover to the cathode, where it is oxidized. The transient voltage and current are measured using a digital-meter and the methanol crossover rate, the efficiency of direct methanol fuel cell (DMFC) and the amount of methanol electro-oxidation of the bipolar electrode at cathode side are determined from the transient current analysis. The fuel chamber (0.5 cm thick with an area of 10 cm²) was filled with 1cc, 3cc and 4cc 10 vol% aqueous methanol solution, for the first, second and third measurements, respectively. All tests were performed at an ambient temperature of 25°C and at atmospheric pressure. The voltage and current of the DMFC were monitored for approximately 36 hours to ensure a stable approach to zero current.

4. Results and Discussion

Figs. 4.1-4.4 plot the transient voltage and current of the DMFC, with each measurement performed at a different charging volume (1.1 cm³, 3.3 cm³ and 4.4 cm³) with a particular fuel solution. The fuel solution is 10%Vol methanol in water. The cell voltage response after a step change of the methanol feed concentration was performed in the dynamic experiments, reducing the methanol concentration from 10% vol to zero. The observed increase in cell voltage after a sudden decrease in the methanol feed concentration is notable. Figs. 4.1 and 4.3 demonstrate that the cell voltage (after a certain delay) first rises before falling. The voltage increases as the concentration overpotential at the anode decreases because of amounts of proton increasing. However, the quantity of methanol crossing over to

the cathode over time, results in a mixed potential, thereby lowering the overall cell voltage, although fairly small. Figs. 4.2 and 4.4 demonstrate that the transient current returns to the same shape, controlled by the reduction of oxygen in the air-breath cathode. The data in Table 4.1 were used to calculate the crossover rate (R_c), the efficiency (E_f) and the amount of methanol electro-oxidation of the bipolar electrode at cathode side (M_{co}) at various fuel charging volumes in the three tests. Crossover rates (R_c), efficiency (E_f) and amounts of methanol electro-oxidation of the bipolar electrode at cathode side (M_{co}) are $5.9\mu\text{mol}/\text{cm}^2/\text{hr}$ and $10.4\mu\text{mol}/\text{cm}^2/\text{hr}$, 22.1% and 17.8%, 27 and 32.5 mmol for coated and uncoated bipolar plates, respectively. These results may reveal the effect of Surface modification on the methanol crossover, the efficiency and the amount of methanol electro-oxidation of the bipolar electrode at cathode side of DMFC.

5. Conclusions

A relatively simple transient method to estimate of the methanol crossover rate of PEM, the efficiency and the amount of methanol electro-oxidation of the bipolar electrode at cathode side of DMFC was presented. Surface modification of the bipolar electrode plays an important role on the performance for DMFC.

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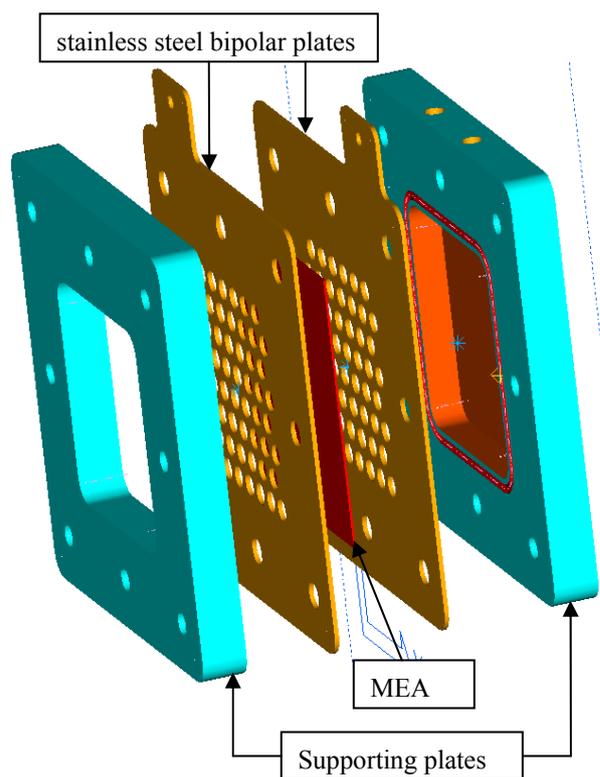


Fig.3.1.1 3D solid modeling design of DMFC device: supporting plates, stainless steel bipolar plates and MEA.

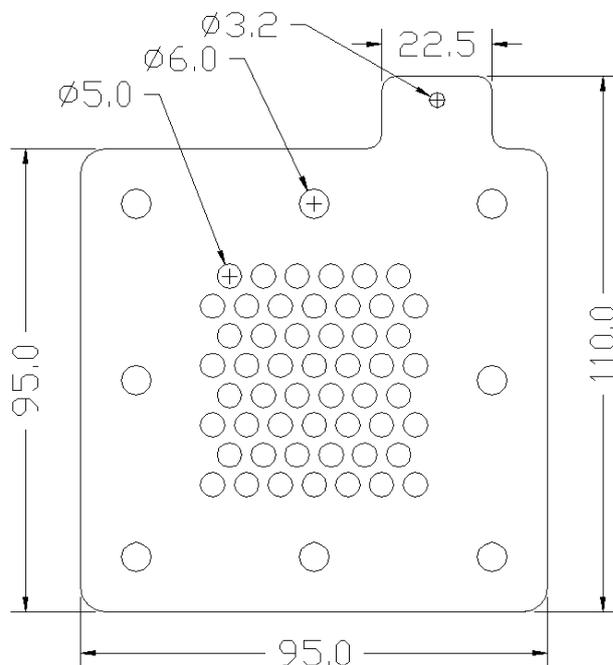


Fig. 3.1.2 Dimensions of bipolar plate



Photo 3.1.1 Mitsubishi laser cutting machine (3500W ML3015LVPlus)

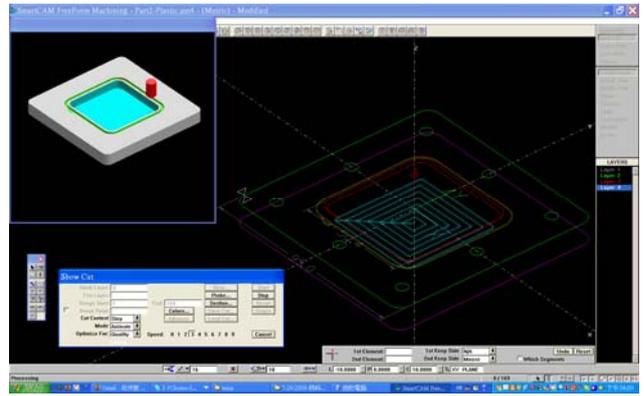


Fig. 3.1.3 Tool path planning and manufacturing simulation for supporting plate

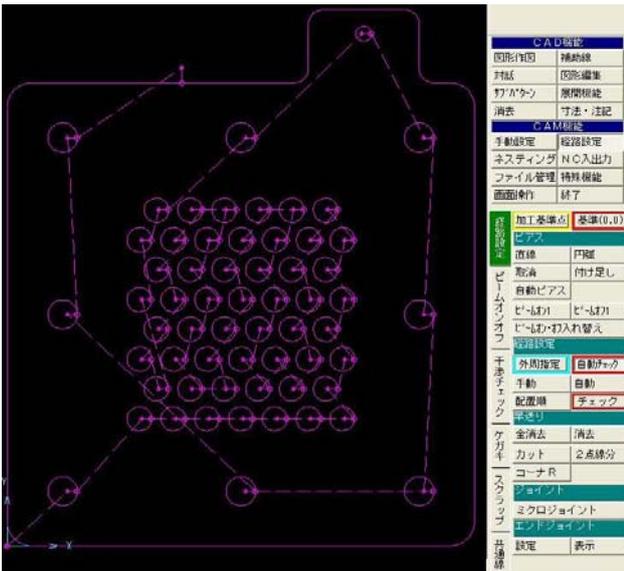


Photo 3.1.2 Laser cutting tool path simulation for bipolar plate



Photo 3.1.4 Completed two supporting plates

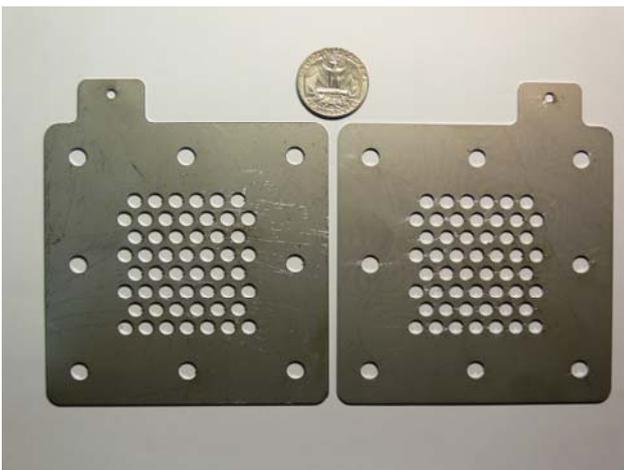


Photo 3.1.3 Completed stainless steel bipolar plates after laser cutting

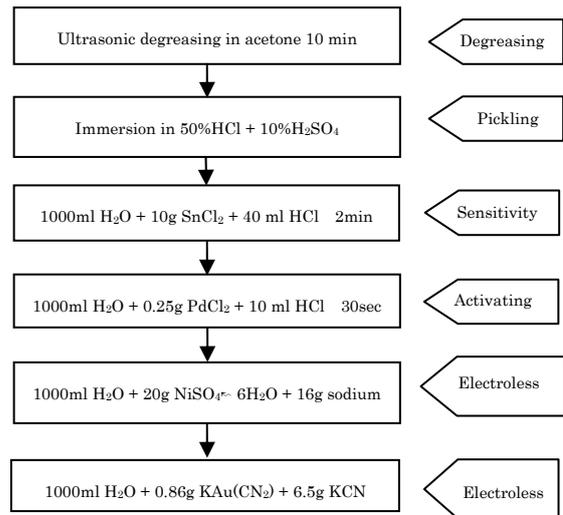


Fig.3.2.1 Flow chart of preparing the gold - plating by an electroless method

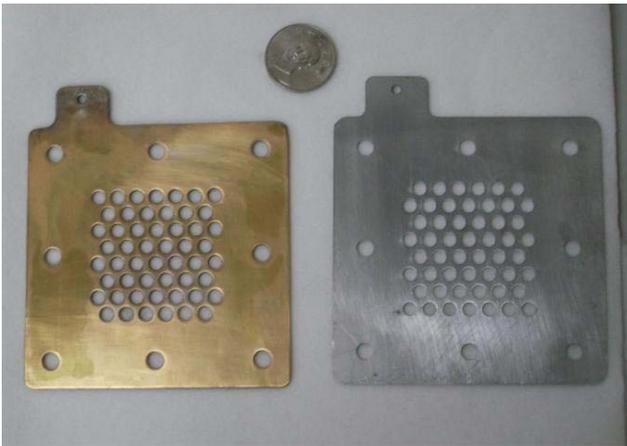


Photo 3.2.1 By the electroless gold-plating and untreated AISI 304 stainless steel bipolar plates.

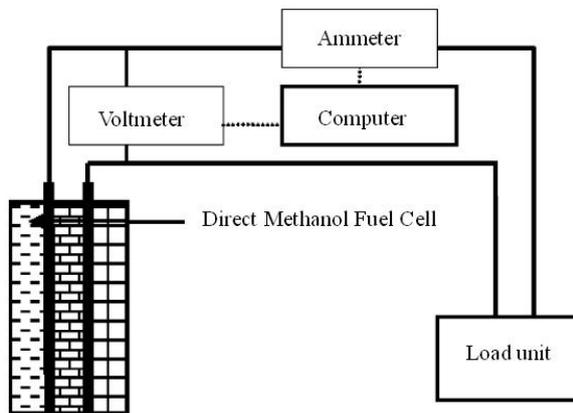


Fig.3.3.1 Block diagram of the experimental set-up

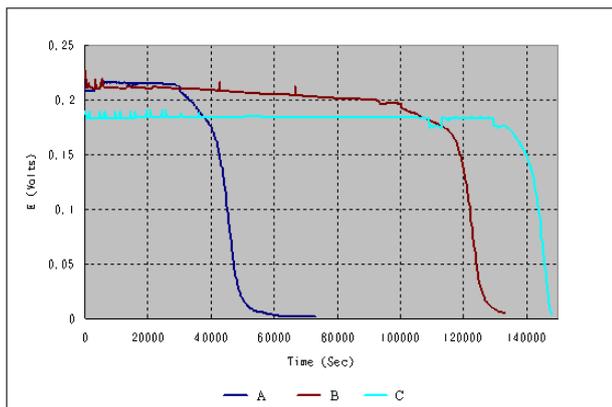


Fig. 4.1 Voltage transients monitored during electro-oxidation using 10 vol. % methanol solution for DMFC with Au coated bipolar plate at anode side: (A) 1.1 cm³, (B) 3.3 cm³ and (C) 4.4 cm³

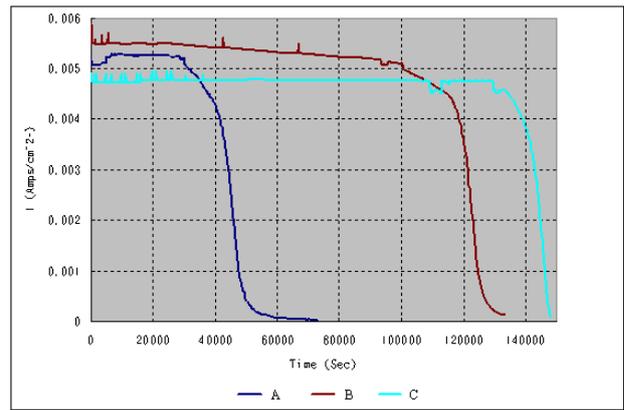


Fig. 4.2 Current transients monitored during electro-oxidation using 10 vol. % methanol solution for DMFC with Au coated bipolar plate at anode side: (A) 1.1 cm³, (B) 3.3 cm³, and (C) 4.4 cm³

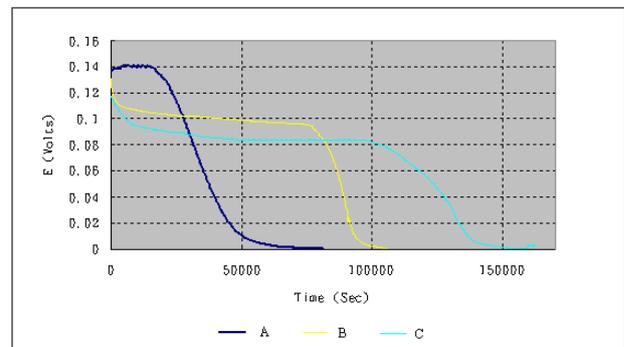


Fig. 4.3 Voltage transients monitored during electro-oxidation using 10 vol. % methanol solution with uncoated bipolar plate at anode side: (A) 1.1 cm³, (B) 3.3 cm³ and (C) 4.4 cm³

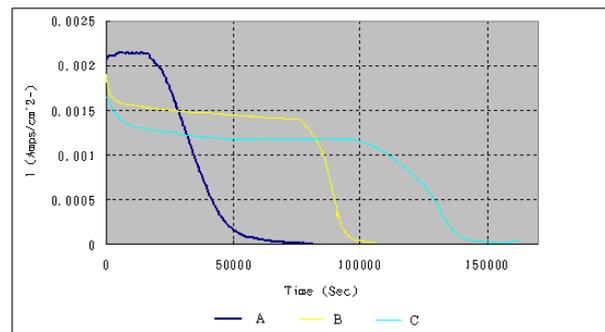


Fig. 4.4 Current transients monitored during electro-oxidation using 10 vol. % methanol solution with uncoated bipolar plate at anode side: (A) 1.1 cm³, (B) 3.3 cm³ and (C) 4.4 cm³

Table 4.1 Parameters and calculated results

Known Parameters	Test	Test	Test
	1	2	3
Methanol Concentration, vol %	10	10	10
Active area (A), cm^2	1.37	4.32	5.1
Methanol Charged, cm^3	1.1	3.3	4.4
Methanol Charged (M_T), mmol	2.7	8.2	10.9
Measured Parameters			
Time of crossover (t), as the bipolar plate with Au coating condition, hour	8.3	26.2	36
Time of crossover (t), as the bipolar plate without Au coating condition, hour	5.9	21	26.8
Analysis Results			
Amount of methanol electro-oxidation of the bipolar plate with Au coating (M_{co}) mmol	0.27		
Amount of methanol electro-oxidation of the bipolar plate without coating (M_{co}) mmol	0.325		
Crossover rate R_c , as the bipolar plate with Au coating condition mol/ cm^2 /hr	5.9E-6		
Crossover rate R_c , as the bipolar plate without Au coating condition mol/ cm^2 /hr	10.4E-6		
Efficiency E_f , %, as the polar plate with Au coating condition	22.1%		
Efficiency E_f , %, as the polar plate without Au coating condition	17.8%		