

# Studies on methanol fuel cell

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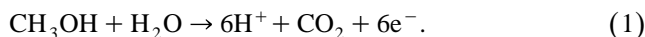
## Abstract

A fuel cell using methanol dissolved in 6 N KOH solution with (Fe(III) and Al(III)) and without treated graphite cathode at ambient temperature (25°C) was studied for the following parameters: (a) current–voltage behaviour at ambient temperature; (b) voltage drop with time; (c) methanol concentration as a function of time; (d) carbon dioxide generation as a function of time; (e) effect of catalyst on the performance of the cell. The OCV of the cell was 0.273, 0.850 and 1.4 V, while current density was 0.5, 4.52 and 17.2 Am<sup>-2</sup> with untreated and treated (Fe(III) and Al(III)) graphite electrode, respectively. The highest current density was 180 Am<sup>-2</sup> at 0.3 V and 540 Am<sup>-2</sup> at 1.04 V for Fe(III) and Al(III), respectively. Polarisation was found to be higher in Al(III) than Fe(III)-treated graphite electrode due to the low heat of adsorption of Al(III) [406 kJ mol<sup>-1</sup> vs. 518 kJ mol<sup>-1</sup> for Fe(III)]. The catalytic oxidation of methanol in terms of electrical energy output shows efficiency of about 78% for Al(III) and 80% for Fe(III)-treated graphite electrode. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Methanol; Polarisation; Efficiency; Catalysis; Adsorption

## 1. Introduction

Methanol is an attractive liquid fuel because it is relatively cheap, easily stored and handled, readily available, soluble in aqueous electrolytes and has a high caloric value. The electrochemical oxidation of methanol produces carbon dioxide,



The rate of oxidation of methanol in alkaline medium is higher than acidic medium but the carbon dioxide that is formed reacts with alkali to form carbonate and bicarbonate to lower the concentration of the electrolytes and this affects the performance of the cell.

The search for a more effective methanol oxidation catalyst was actively pursued by several investigators [1] during the early 1970s, notably at Shell Research in England [2–5] and Hitachi in Japan [6]. Hitachi in 1985 was on the point of commercializing a small direct methanol fuel cell unit utilizing SPE membrane to reduce the problem of

methanol conversion [7]. Theoretical reversible cell potential  $E^\circ$  of different fuels is given in Table 1.

Methanol fuel cells were studied by various workers in aqueous KOH solution as shown in Table 2.

Methanol fuel cells in acidic medium were studied [11–13]. In alkaline electrolytes, the depletion of electrolyte strength takes place due to the adsorption of CO<sub>2</sub> gas, which is not possible in acidic medium. Oxidation of methanol, however, is difficult in acidic electrolyte [14].

Gregory [15] recommended the use of strongly acidic or strongly basic electrolytes in order to avoid concentration polarisation.

In alkaline electrolyte, the oxidation of methanol takes place in various steps [16] as shown in Table 3.

Oxygen from air is the most convenient and economical oxidant for the oxidation process [17].

The object of this study was to develop a low-cost active catalyst for a methanol fuel cell in alkaline medium, which will have a low activation energy for reaction and low temperature coefficient, hence allowing the possibility of higher power output during oxidation at ambient tem-

Table 1  
Theoretical electrode cell potential, relative cost and wattage

Fuel	Useful energy (MJ/Kg)	Gram/Faraday	Relative cost (MJ)	Wattage (h/g)
Methanol	21.8	05.633	03.3	5.90
Hydrazine hydrate	12.0	12.50	16.8	3.47
Ammonia	20.9	05.67	03.6	5.73

perature. Hydrophobic carbon electrodes were chosen for the following reasons:

- (i) Porous carbon electrodes have light weight.
- (ii) Surface area is large.
- (iii) Adsorption of catalyst takes place easily.

## 2. Experimental

### 2.1. Apparatus

The schematic diagram of the experimental set-up is given in Fig. 1. It consisted of two graphite electrodes, in which the cathode is treated with Ag(I) while the anode is treated with Fe(III) and Al(III) ions. The electrodes were 1 cm long (exposed portion) and had a cross-sectional area of 1 cm<sup>2</sup>. Both the electrodes were placed 2 cm apart from each other and were kept in a 500-ml beaker containing 300 ml of 6 N KOH solution and 15 ml methanol. The electrodes were connected to a variable resistance box and digital microammeter in series and digital d.c. micro volt-meter in parallel.

### 2.2. Preparation of electrodes

The carbon electrodes were prepared out of graphite powder (M/S Lilly), acid-washed, and then washed in boiling water until they were free from ions and pressure-dried and moulded using an epoxy resin binder. The electrodes were then equilibrated for 12 h with saturated solution of Ag(I), Fe(III), and Al(III) ions in an acid medium, then washed and dried, and finally baked at 150°C.

Table 2  
Comparative performance of methanol fuel cell

Sl. no.	References	Anode	Cathode	OCV (V)	Current density (Am <sup>-2</sup> )
1	Armours Research Foundation	Ni sheet coated with Ni–Al alloy	Raney Ni	0.70	1000.00
2	Wynn [8]	Platinised porous carbon	Hallow carbon impregnated with Ag Co and Al	0.25	80.00
3	Hunger [9]	Undisclosed	Undisclosed	0.50	10.00
4	Murray and Grimes [10]	Ni-sheet impregnated with Pt/Pd	Ni-sheet impregnated with Ag	0.40	15.00

Table 3  
Oxidation of methanol in alkaline solution and its standard electrode potential

Electrode reactions	E° (V) at 25°C
Overall reaction CH <sub>3</sub> OH + 8OH <sup>-</sup> = CO <sub>3</sub> <sup>2-</sup> + 6H <sub>2</sub> O + 6e <sup>-</sup> .	
CH <sub>3</sub> OH + 2OH <sup>-</sup> = HCHO + 2H <sub>2</sub> O + 2e <sup>-</sup>	0.595
HCHO + 3OH <sup>-</sup> = HCOO <sup>-</sup> + 2H <sub>2</sub> O + 2e <sup>-</sup>	1.070
HCOO <sup>-</sup> + 3OH <sup>-</sup> = CO <sub>3</sub> <sup>2-</sup> + 2H <sub>2</sub> O + 2e <sup>-</sup>	1.010

### 2.3. Method

Electrochemical oxidation of methanol at ambient temperature was carried out and following measurements were made.

(i) The current–voltage behaviour of the experimental set-up with Ag(I)-impregnated graphite cathode and (a) untreated graphite, (b) Fe(III)-impregnated graphite, and (c) Al(III)-impregnated graphite anode was measured as a function of concentration of KOH solution and time during continuous run of the cell.

(ii) Qualitative tests were performed in the alkaline methanol solution after prolonged continuous run of the cell showed only the presence of CO<sub>2</sub> (as alkali carbonate) with Al(III)-catalysed graphite anode but the presence of CO<sub>2</sub> (as alkali carbonate) and formic acid was detected in the case of Fe(III)-catalysed anode.

(iii) During oxidation of methanol, the evolved CO<sub>2</sub> was absorbed in the electrolyte, and then determined by titration against a standard acid solution. The amount of methanol consumption was determined [18].

## 3. Results

Fig. 1 gives the schematic diagram of the experimental set-up. The current–voltage relationship for the oxidation of methanol in 6 N KOH solution using Ag(I)-catalysed graphite cathode and anode containing of (i) carbon alone, (ii) treated with Fe(III), and (iii) Al(III) is shown in Fig. 2. Fig. 3 gives the change in voltage of the cell as a function of concentration of the electrolyte with and without treated

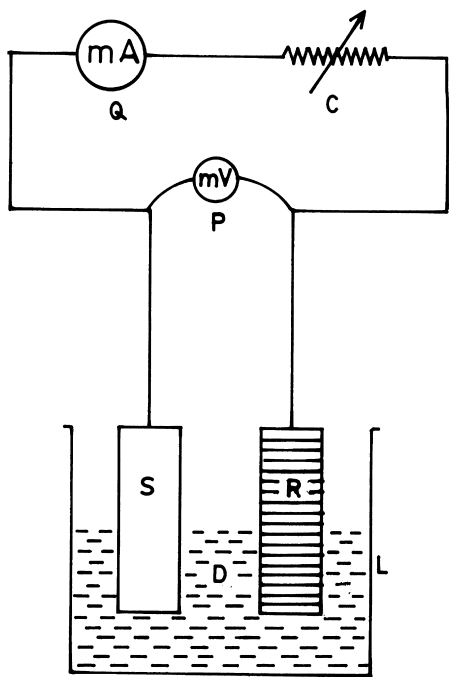


Fig. 1. Schematic diagram of the experimental set-up. Q: Digital microammeter. C: Variable resistance box. P: Digital micro voltmeter. S: Ag(I)-treated graphite cathode. R: Treated graphite anode. D: 6 N KOH solution. L: Pyrex beaker.

anode. Fig. 4 shows the current–voltage relation as a function of time for the continuous running of the cell for 24 h. Fig. 5 gives the time dependence of OCV, CO<sub>2</sub> evolution and methanol consumption in the presence of Fe(III)- and Al(III)-catalysed anode. Fig. 6 indicates the evolution of CO<sub>2</sub> gas against methanol consumption dur-

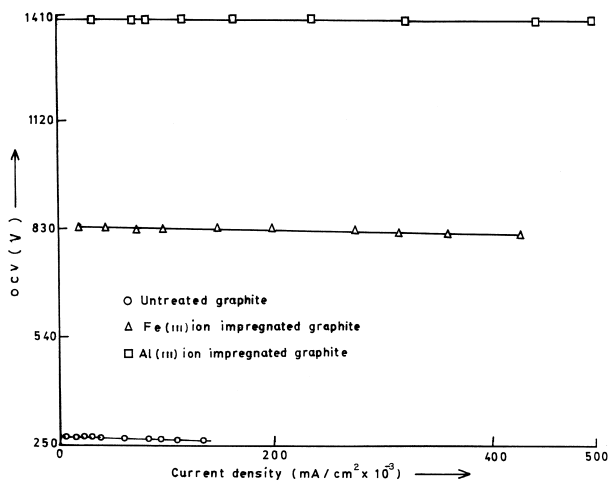


Fig. 2. Current–voltage relationship for methanol fuel with Ag(I)-catalysed graphite cathode, and (i) untreated graphite (ii) that was treated with Fe(III) and (iii) Al(III) ions.

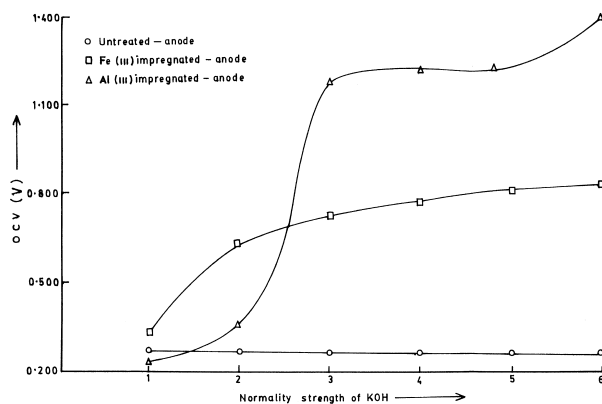


Fig. 3. Change in OCV with concentration of KOH solution.

ing the oxidation process in the presence of the treated graphite anode.

4. Discussion

The catalytic activity of Fe(III)- and Al(III)-impregnated electrode is reflected in Fig. 2. Experimental results show that the oxidation of methanol followed Eq. (1) with Al(III) and favors equations shown in Table 3 with Fe(III)-catalysed electrodes. Complete oxidation of methanol is possible in case of Al(III) but the formation of carbon dioxide with HCOO<sup>-</sup> ion in the case of Fe(III) is observed. This is probably due to higher HCOO<sup>-</sup> activation energy of Al(III) [20.4 kJ mol<sup>-1</sup>] compared to Fe(III)

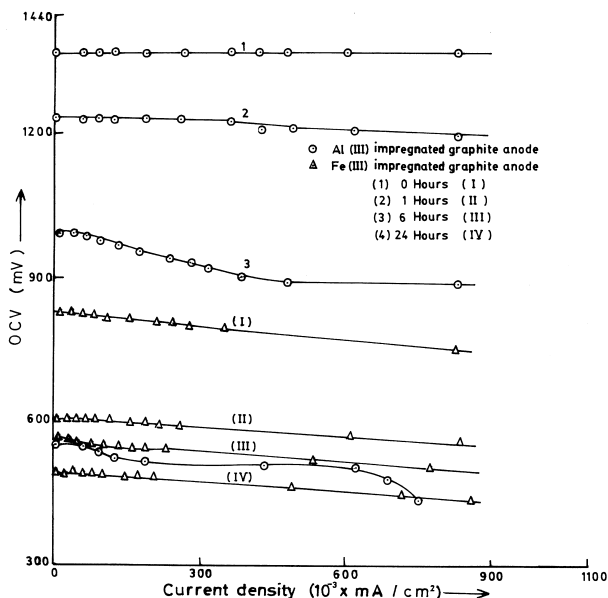


Fig. 4. Current–voltage relationship for methanol fuel cell with Al(III)- and Fe(III)-impregnated graphite anode and Ag(I)-impregnated graphite cathode in 6 N KOH solution.

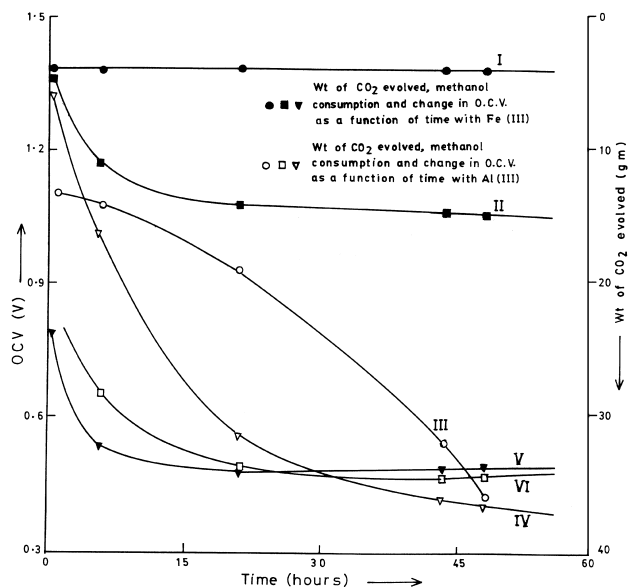


Fig. 5. Time dependence of OCV, CO<sub>2</sub>, evolution, and methanol consumption.

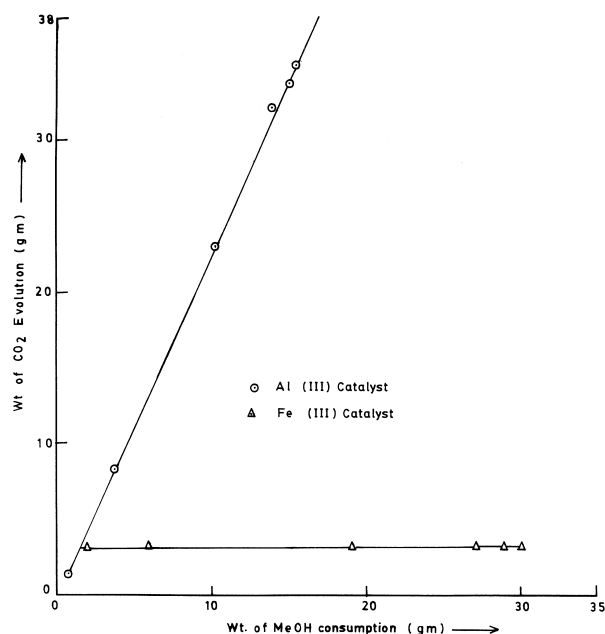


Fig. 6. Weight of methanol consumption vs. CO<sub>2</sub> evolution.

[18.8 kJ mol<sup>-1</sup>] [19]. The electrocatalytic activities of these ions are probably due to adsorption on the carbon electrode or formation of an interlamellar compound. This is followed by an electron exchange process with the electrode material.

From Fig. 3, it can be seen that OCV is a function of the electrolyte concentration up to certain limits for both the catalysed electrodes, and then after the OCV remains constant. This is due to the high-temperature coefficient of the electrolyte with increase in concentration. Fig. 4 gives the mode of polarisation, which occurs more in Al(III) than Fe(III), probably due to more ready reaction with the electrolyte. The weight of carbon dioxide evolution, methanol consumption and change in OCV as a function of time during continuous run of the cell is shown in Fig. 5. The drop in OCV is sharper for Al(III) than Fe(III) [Fig. 5IV and V] due to the amphoteric nature of aluminum, high activation energy and low heat of adsorption (405 kJ mol<sup>-1</sup>). Fig. 5(III) also reflects that the amount of carbon dioxide evolution is a function of time for Al(III) but not for Fe(III)-catalysed electrode [Fig. 5(I)], which is why the

consumption of methanol is faster with Al(III) than Fe(III) [Fig. 5 (VI) and (II)].

## 5. Conclusion

The comparative performance of the experimental set-up is given in Table 4.

(i) Catalysed graphite electrode performs as effectively, indeed even better, than metal electrodes for the activation of fuels and oxidant molecule.

(ii) Conversion efficiency [20] from chemical to electrical energy is about 78% and 80% with Al(III) and Fe(III), respectively.

(iii) The impregnated ions may remain adsorbed or from interlamellar compounds with graphite and probably provide appropriate geometrical configuration for the activation of reactant.

(iv) Table 4 indicates that Al(III) gives better initial performance, although Fe(III) is more suitable for prolonged use.

Table 4  
Comparative performance of the experimental set-up

Sl. no.	Anode	Cathode	OCV (V)	Drop in voltage (V)	Max. current density (Am <sup>-2</sup> )	Efficiency (%)	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta E$ (kJ mol <sup>-1</sup> )
1	Untreated graphite	graphite treated with Ag(I)	0.27	–	–	–	–	–
2	Fe(III)-treated	graphite treated with Ag(I)	0.85	0.36	180	80	518	18.8
2	Al(III)-treated	graphite treated with Ag(I)	1.4	0.36	540	78	406	20.4

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