

Dedicated to Professor Dr. ALEXANDRU T. BALABAN, member of the Roumanian Academy on the occasion of his 75th anniversary

ELECTROCHEMICAL BEHAVIOUR OF DIMETHYL ETHER IN ALKALINE SOLUTIONS AT 298 K

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Dimethyl ether (DME) is a potential fuel for direct oxidation fuel cells, that has interesting advantages comparative with hydrogen, alcohols (especially methanol) and other possible candidates used in fuel cells at room temperature. The paper describes the electrochemical behaviour of DME in 0.5 M KOH solution saturate with oxygen using a Pd electrode. At this anode the electrochemical oxidation of DME is a complex process, implying a preceding chemical reaction. The anodic reactions during the potential sweep were studied and some electrochemical parameters were determined.

INTRODUCTION

Due to safety and technological barriers associated with the use of hydrogen and methanol as fuel, significant effort has been directed to searching for an alternative to these combustibles.

Owing to its molecular simplicity, disposability (as it is a secondary product for hydrocarbon reforming) and ease of oxidation, dimethyl ether (DME) is ideal for replacing hydrogen and methanol as fuel in fuel cells.¹⁻⁹ Benefits of the use of DME for fuel cells include:

a) high electron transfer number of 12 for complete oxidation (we remind that for CH₃OH this is 6 and for H₂ 2), resulting in reduced theoretical fuel requirement; its theoretical energy density is 8.2 kWh/kg;

b) lack of the C-C bond makes a complete direct electro-oxidation possible with minimal kinetic losses, compared to other more complex compounds;¹⁰

c) the toxicity and handling properties are similar to those of propane or butane; therefore, the existing infrastructure and handling technologies can be used to store and transport DME. Comparatively, methanol is very toxic upon skin contact and ingestion;¹¹

d) DME decomposes in the atmosphere in several tens of hours; therefore, DME is neither a greenhouse gas, nor does it degrade the ozone layer.¹²

The present study is part of a systematic investigation program focused on the electrochemistry of dimethyl ether in alkaline solution in the presence of molecular oxygen at room temperature. The purpose of this part is to examine the electrochemical behaviour of dimethyl ether in 0.5 M KOH solution saturate with oxygen at a Pd electrode and to elucidate the kinetics of the anode process of DME electro-oxidation.

MATERIALS AND METHODS

The methods and techniques used for the DME electrochemical studies were as usual. The employed technique for establishing the mechanism and kinetics of the electrochemical process in the electro-oxidation of DME was cyclic voltammetry.^{13,14}

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The electrochemical investigation was carried out using a PRT 20-10X Tacussel potentiostat controlled by means either of an interface and an IBM compatible computer or by a signal generator E 0507. The storage of data from the voltammetry cell electrodes as well as their processing were achieved by means of a software developed in our laboratory. Also, the Linseis (X, Y, t) LY 1600 recorder was used to registered the cyclic voltammograms.

The cell containing the three electrodes was made of glass. The anode was made of spectral Pd with a surface area of $16 \cdot 10^{-2} \text{ cm}^2$ introduced in a Teflon sheath to accurately delimit the surface area. The reference electrode was standard calomel electrode (SCE), whereas the auxiliary electrode was a Pt foil with a large surface area.

The supporting electrolyte consisted in a 0.5 M KOH solution saturated with O_2 in which DME is introduced; all chemicals were of advanced purity so that no previously purification was needed. The voltammetric runs were performed at $298 \pm 0.1 \text{ K}$ temperature.

RESULTS AND DISCUSSION

Fig.1 and Fig. 2 show typical cyclic voltammograms for the electrochemical oxidation of DME ($44 \cdot 10^{-5} \text{ mol/cm}^3$) in 0.5 M KOH at a Pd electrode.

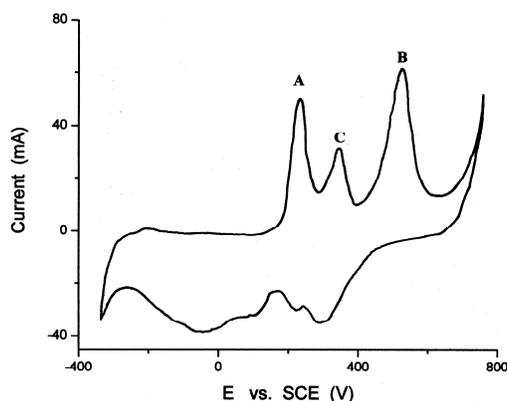


Fig. 1 – Cyclic voltammogram recorded at the electrooxidation of DME on a Pd electrode in 0.5 M KOH supporting electrolyte. Concentration of DME is $44 \cdot 10^{-5} \text{ mol/cm}^3$; $T = 298 \text{ K}$; sweep rate $v = 20 \text{ mV/s}$.

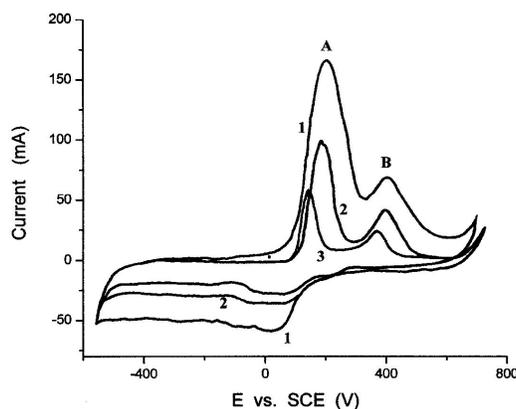
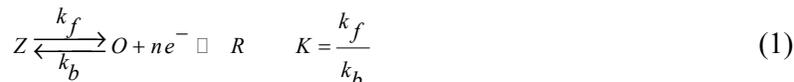


Fig. 2 – Cyclic voltammograms recorded at a Pd electrode in 0.5 M KOH solution for various sweep rates: 1) $v = 100 \text{ mV/s}$; 2) $v = 200 \text{ mV/s}$; 3) $v = 400 \text{ mV/s}$. Concentration of DME is $44 \cdot 10^{-5} \text{ mol/cm}^3$; $T = 298 \text{ K}$.

One can notice three distinct peaks on the anodic branches of the voltammograms, corresponding to three individual electrochemical processes. Examining the cyclic voltammetry data given by Table 1, we

suppose that the electrochemical processes have a preceding chemical reaction, as presented in the reaction sequence (CE mechanism):



where: K is an equilibrium constant;

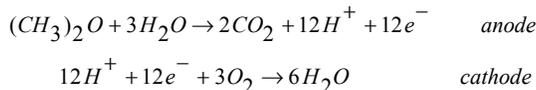
k_f and k_b are the reaction rate constant (forward and respectively backward).

Table 1

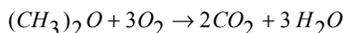
Some electrochemical data at DME electrooxidation in alkaline solution obtained from Fig. 1. Surface area of the Pd anode: 0.16 cm^2 ; $T = 298 \text{ K}$

Anodic parameters	Peak a	Peak b	Peak c
E_{p_a} mV	220	378	640
i_{p_a} mA	48	31	62
$E_{p_a} - E_{p_{a/2}}$ mV	Exp	25	25.6
	Th	28.2	28.2

The most probable chemical reaction in this case is a reaction between DME and water with formation of an unknown structure intermediary product (methoxy-methyl radicals – $[\text{CH}_3\text{OCH}_2]^*$; methoxy-methyl peroxide – $[\text{CH}_3\text{OCH}_2\text{O}_2]^*$ were identified).⁷ Thus, the overall DME electrochemical oxidation process could be described by the following reactions:



or, by summation:



According to the thermodynamic data (standard Gibbs free energy) for the total combustion of DME ($\Delta G_{\text{reac}} = -1362 \text{ kJ mol}^{-1}$) 12 electrons are involved, and the equilibrium potential determined thereby is 1.18 V.¹¹

Our voltammetric results confirm this supposition based on literature data that the fact DME electro-oxidation is a 12 electron transfer process. In this case, water is an indispensable reaction component because in the absence of the water the DME electro-oxidation does not take place.^{15,16}

It is known that for a preceding chemical reaction for the electrochemical process, the peak potential, E_p , shifts cathodically and increases with the sweep rate v , whereas the current function parameter i_p / \sqrt{v} decreases as v increases.¹⁷⁻²³ From our experimental data we determined that i_p / \sqrt{v} ($\text{mA cm}^{-2} \text{ V}^{-1/2} \text{ s}^{-1/2}$) decreases from the value of 149.2 for $v = 50 \text{ mV/s}$ to 146.2 for $v = 100 \text{ mV/s}$ and to 143.5 mV for $v = 200 \text{ mV/s}$.

This kind of electrochemical process was also confirmed by the experimental data presented in Fig. 3 and Table 2, where before each voltammograms a short-circuit of 1 hour was performed.

Theoretically, when the preceding chemical reaction is a fast process, a diffusion-controlled wave results because the chemical reaction has no influence on the flow of the electroactive species on the electrode. In this case, the peak potential is cathodically shifted depending on the value of the equilibrium constant K ; the dependence is expressed as:

$$E_p = E_{1/2} + \frac{RT}{nF} \ln \frac{K}{1+K} \quad (2)$$

where: $E_{1/2}$ is the half-wave potential; the other symbols have their common significances.

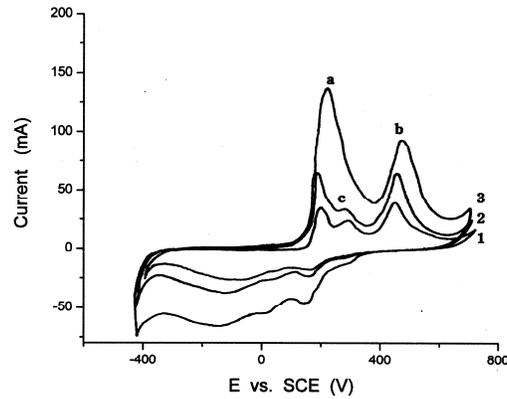


Fig. 3 – Cyclic voltammograms recorded at a Pd electrode in 0.5 M KOH supporting electrolyte after 1 hour short-circuit between anode–cathode. Initial concentration of DME is $44 \cdot 10^{-5}$ mol/cm³; T = 298 K; sweep rates: 1) $v = 100$ mV/s; 2) $v = 200$ mV/s; 3) $v = 400$ mV/s.

Table 2

Some voltammetric data at DME electrooxidation in alkaline solutions, obtained from Fig.3. Surface area of the Pd anode: 0.16 cm²; T = 298 K

Anodic Peak		Voltamogram		
		1	2	3
a	E_p , mV	220	236	254
	i_p , mA	32	68	146
b	E_p , mV	440	458	480
	i_p , mA	45	56	96
c	E_p , mV	378	396	-----
	i_p , mA	28	30	-----

The shift is depending with $\frac{RT}{nF} \ln \frac{K}{1+K}$ and if the equilibrium constant is too large, there will be no thermodynamic potential shift. This means that O is the predominant species in solution, meaning that the most probable electrochemical species present in solution are the obtained products between DME and water.

The confirmation that the anode process is reversible with a soluble species is in good agreement with the experimental and theoretical values of parameter ΔE_{pa} , given by the expression:²²

$$\Delta E_{pa} = E_{pa} - E_{pa/2} = -1.10 \frac{RT}{nF} \quad (3)$$

where: E_{pa} is the anodic peak potential; $E_{pa/2}$ is the anode half peak potential, and n is the number of exchanged electrons.

This agreement is illustrated in Table 2.

Furthermore, the voltammogram in Fig. 4 recorded at a high sweep rate, of 800 mV/s, presents only two distinct peaks, corresponding to two reversible electrode processes, where both reactants and products are soluble.

The analysis of the dependence between the electrochemical parameters determined from this figure, evidences that the number of electrons transferred in this reaction is variable: in the case of peak A three electrons are transferred whereas in the case of peak B, two electrons are transferred.

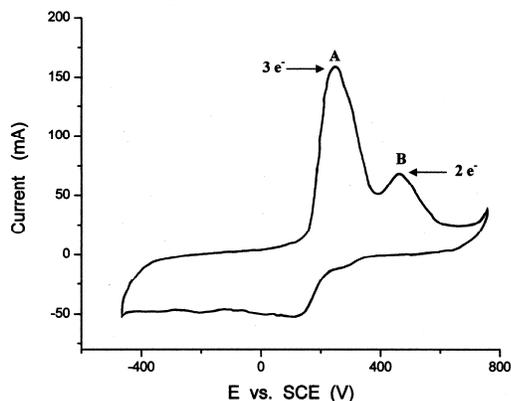


Fig. 4 – Typical cyclic voltammogram recorded at a Pd electrode in 0.5 M KOH solution. Concentration of DME is $44 \cdot 10^{-5} \text{ mol/cm}^3$; $T = 298 \text{ K}$; sweep rate $v = 0.800 \text{ V/s}$.

In the absence of an appropriate chemical analysis, the chemical nature of these compounds is obscure and we cannot advance any hypothesis about their chemical structure.

CONCLUSIONS

The DME electro-oxidation process in alkaline solution at room temperature is a complex and less known mechanism. The present study has demonstrated that DME electro-oxidation is a reversible process with a preceding chemical reaction. However, the value of the equilibrium constant of this reaction is important, because it controls both the electrode potential value where the overall process takes place and the concentration of the electro-chemically predominant species in solution.

For more information on the DME electro-oxidation in alkaline media an intensive study of the electrolyte chemistry is necessary as well as the determination of the nature of the intermediary products.

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