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Electrooxidation of acetals for direct hydrocarbon fuel cell applications[†]

O. SAVADOGO* and X. YANG
Laboratoire d'Électrochimie et de Matériaux Énergétiques, École Polytechnique de Montréal, Succ. Centre-ville, Montréal, Qc, H3C 3A7, Canada
*(*author for correspondence, fax: +1 514 340 4468; e-mail: osavadogo@mailsrv.polymtl.ca)*

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Abstract

Some acetals (e.g., methylal, ethylal and 1,3-dioxolane) were oxidized in different supporting electrolytes and on various electrodes, including oxide-based electrodes dispersed onto carbon powder. The electrooxidation of ethylal and 1,3-dioxolane was demonstrated for the first time. The fuel that exhibited the lower overvoltage from the electrooxidation curve was deduced. Then, from an analysis of the reaction products from long-term anodic experiments, the electrode reactions were deduced. It was shown that the anodic polarization of the electrooxidation of acetals in an acid medium is lower than that of methanol. Thus, acetals seem to be better fuels for fuel cell applications than methanol. It was also shown that ethylal and 1,3-dioxolane are oxidised more easily than methylal for fuel cell applications. Volcano behaviour was obtained for the plot of direct oxidation current density vs metal radius for various single noble metal electrodes. The highest current density was obtained with the Pt-based electrode. Similar behaviour was obtained with electrodes based on noble binary platinum alloys, where the electrooxidation current density increases with the difference in metal radius in each alloy (ΔR). Thus, the alloys that give the highest $|\Delta R|$, e.g. Pt–Ru and Pt–Sn, exhibit the best electrooxidation current density.

1. Introduction

The development of low-temperature (room-temperature) fuel cells fed with high-energy organic substances, such as hydrocarbons, methanol and its derivatives, is of particular importance for the integration of fuel cell technology in stationary, mobile and transportation applications. Methanol has been shown to perform relatively well [1–9], and methanol fuel cell systems have already proved to be of commercial interest, in portable applications among others. However, there are problems related to direct methanol fuel cells, the main ones being as follows: (a) low electrocatalytic activity and stability of the anodes; (b) self-poisoning effects due to strong CO-adsorption on Pt-based anodes and; (c) a high degree of methanol cross-over through the Nafion® membranes. In a study, the direct electrooxidation of dimethoxymethane (DMM, dimethylorthoformate), trimethoxymethane (TMM, trimethyl orthoformate) and trioxane (1,3,5-trioxane) was investigated at Pt, Pt–Sn and Pt–Ru electrodes [10], and the performance of these fuels in direct oxidation fuel cells was descibed using half-cells and liquid-feed polymer electrolyte fuel cells. It was shown that the fuel cells based on TMM and those based on methanol exhibited the same characteristics. The Pt–Ru alloy was shown to be a better anode material for these fuels than Pt–Sn. It was also shown that the oxidation of DMM leads to the formation of methanol and, ultimately, carbon dioxide. The electrooxidation of trioxane is preceded by an acid-catalysed hydrolysis step on Nafion® in sulphuric acid solutions. These fuels are best used without further processing in a direct liquid-feed polymer electrolyte for fuel cells [10–12]. It has been shown that trimethoxymethane can be used as an alternative fuel for a direct oxidation or, for a PBI phosphonic acid-doped polymer electrolyte fuel cell [13], and also that PBI constitutes a better proton membrane than Nafion® 117 for the direct electrooxidation of trimethoxymethane. Issues relating to fuel cross-over in methanol fuel cells are common to these fuels, but the cross-over rate of these fuels might be lower than that of methanol because they are bigger molecules than methanol. This would lead to better cathode performance. Acetals are new fuels which are fabricated from natural gas, the world's reserves of which are in terms of a promising long-lasting supply [9, 10]. There are advantages to using them as direct fuels in fuel cells: (a) they are completely electrooxidized to carbon dioxide and water; (b) their high energy content per molecule is attractive relative to that of methanol;

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(c) their boiling point, flash point and toxicity are more adequate for this application than those of methanol; (d) their cross-over rate in membranes may be lower than of methanol because of their greater size; and (e) their electrooxidation reaction involves a larger number of electrons per molecule than does the methanol electrooxidation reaction. The technology of acetal formation on a large scale is well known [14].

The aim of this work is to study the electrooxidation of some acetals (methylal, ethylal and 1,3-dioxolane) on various electrode materials, including oxide-based electrodes in an acid medium. These results are compared with the polarization curves of the electrooxidation of methanol on the same electrodes. The best types of acetals for fuel cell applications are deduced. The purpose of these exploratory studies is not however to investigate the electrode kinetics of anodic acetal oxidation.

2. Experimental details

The following electrocatalysts were used: (i) carbon-supported 10% noble metal electrocatalysts (Pt, Ru, Rh, Ir, Pd) purchased from E-TEK Corporation; (ii) carbon-supported 5% Pt (E-TEK Corporation) mixed mechanically with various oxides (RuO_2, SnO_2, MnO_2,) purchased in reagent grade from Fischer Scientific; and (iii) carbon-supported 10% binary Pt-noble metal alloy electrocatalysts (Pt–Ru, Pt–Rh, Pt–Ir, Pt–Pd) purchased in reagent grade from E-TEK Corporation. The working electrodes used for the acetal oxidation electrodes were prepared according to the following steps [15–18]: (i) each of the various electrocatalysts was mixed with an emulsion of Teflon 30 with particles 1 μm in diameter (Dupont) and Vulcan XC-72 carbon powder (E-TEK) to form a paste; (ii) the mixture was then agitated, evaporated, and dried on an aluminium foil using conventional techniques, the residue was pressed at 280 °C under 2 atm for 5 min. Typical electrode composition was 30% Teflon, and 70% carbon including the catalyst. For electrodes based on 10% Pt–Ru, the Pt–Ru catalyst loading was 3 mg cm^{-2}. For electrodes based on 5% Pt–10% RuO_2, the Pt loading was 1.4 mg cm^{-2} and RuO_2 loading was 3 mg cm^{-2}. TEM photographs of the Pt-binary alloy electrocatalysts done in previous works and prepared in the same conditions [8, 9, 18] showed that the Pt-noble crystallites are homogeneously dispersed and adhere to the carbon particles. For electrocatalysts based on Pt-oxides, the TEM photographs have shown homogeneous dispersity of the catalyst crystallites [8, 9, 18] for the various electrodes. The geometric surface area of each working electrode was about 1.3 cm^2. A platinum screen was pressed onto the electrode to act as the current collector. This surface was used in the evaluation of the current density because BET measurements carried out on the various electrodes showed that there was no significant difference in the BET surface area (with 5%) which was 1.5×10^3 m^2 g^{-1}. The counter-electrode was a platinum plate separated from the working electrode by a lugging capillary. The electrolytes were based on acetals (0.01–2 M) purchased from Lambiotte et Cie. SA were introduced into various supporting reactant grade solutions of H_2SO_4, $HClO_4$ and H_3PO_4 purchased from Fisher. The acetals were based on methylal ($((CH_3O)_2$-$CH_2)$, ethylal $((CH_3O)_2(CH_2)_3)$; and 1,3-dioxalone $(C_3H_6O_2)$. The steady-state galvanostatic polarization curves were created using a PAR potentiostat/galvanostat, Model 273, monitored by a PCs. The waiting time before recording each point of the polarization curves is 5 min.

The products of electrooxidation on the anode were analysed using an HP-5890 gas chromatograph employing a carbowax column. The sample solution from the anode side of the operating fuel cell was appropriately diluted and injected into the chromatograph.

3. Results and discussion

Figure 1 shows the direct electrooxidation polarization curves (E/i) for 1 M methanol and 1 M methylal in a supporting solution of 1 M H_2O_4. The curve for methylal oxidation is better than that for methanol. This is an indication that acetals are more easily electrooxidized than alcohols. The study of the electrooxidation of other acetals may help to sustain this result.

Figure 2 shows the quasi-steady-state polarization curves for the electrooxidation of 0.5 M ethylal of in a H_2SO_4 1 M at 25 °C on various metal electrodes. The best characteristics are obtained with the electrode based on 10% Pt. The effect of fuel concentration on polarization was also studied, and it was found that the optimum concentration of ethylal, that is, that which yields current voltage curves with the lowest overpotential is 0.5 M. For various Pt binary alloy-based catalysts and Pt/metal oxide catalysts, the overpotential of the electrooxidation of ethylal at current densities lower than 10 mA cm^{-2} increases in the order: Pt–RuO_2 < Pt–Ru < Pt–PtO_x < Pt–SnO_2, whereas at current densities higher than 10 mA cm^{-2}, Pt–Ru/C is better than (but very close to) to Pt–RuO_2/C and PtOx. For a given

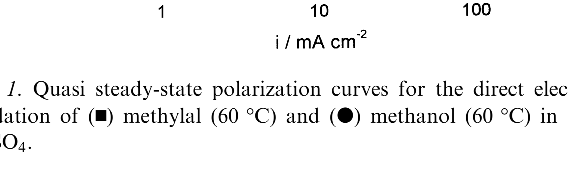

Fig. 1. Quasi steady-state polarization curves for the direct electro-oxidation of (■) methylal (60 °C) and (●) methanol (60 °C) in 1 M H_2SO_4.

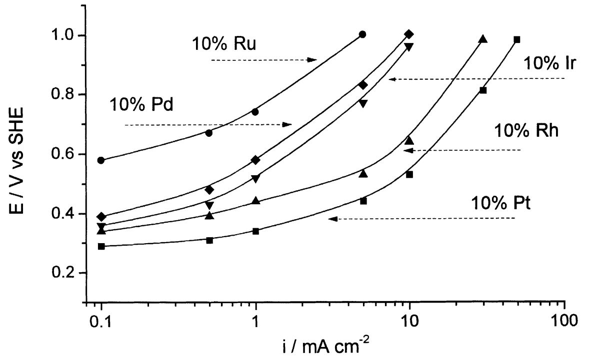

Fig. 2. Quasi steady-state polarization curves for the direct electrooxidation of 0.5 M ethylal on various single noble metals in 1 M H_2SO_4 at 25 °C.

concentration of Pt in the mixed Pt–RuO_2 catalyst, the overpotential first decreases to a minimum when [RuO_2] increases to 10% RuO_2 and then increases strongly with [RuO_2] (Figure 3). The lowest overpotential is obtained with 5% Pt–10% RuO_2. These results may be explained by the synergetic effect between Pt and the ruthenium oxides. Similar results were obtained for direct anodic methanol oxidation [8, 9]. This is now well documented.

The polarization curves for the methylal and 1,3-dioxolane in 1 M H_2SO_4 on various electrodes, including electrodes mixed with oxides, show similar trends. As examples, curves for the electrooxidation of 1,3-dioxolane on various Pt/metal oxide electrodes are shown in Figure 4. The better performances were also obtained on Pt–RuO_2 and Pt-(O_x) with the same supporting electrolyte. The bar chart representation of the electrooxidation current densities on various electrode materials obtained at 0.60 V for methylal, ethylal and 1,3-dioxolane is shown in Figure 5. For the same electrode material, the electrooxidation of ethylal performs better than that of either methylal or 1,3-dioxolane, even when the concentration of ethylal (0.5 M) is lower than that of methylal (1 M). For example, the overpotential of the electrooxidation of acetals on Pt–Ru increases in the order: ethylal < 1,3-dioxolane < methylal. But, on Pt–RuO_2; the overpotential increases in the order: ethylal < methylal < 1,3-dioxolane (Table 1).

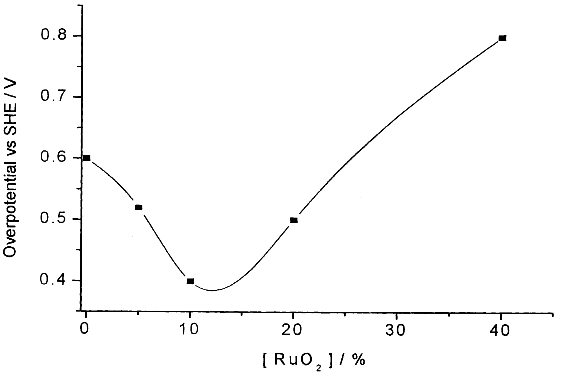

Fig. 3. Variation in electrooxidation overpotential at 5 mA cm^{-2} with [RuO_2%] loading in 5% Pt-based electrodes for the electrooxidation of 0.5 M ethylal in 1 M H_2SO_4 at 25 °C.

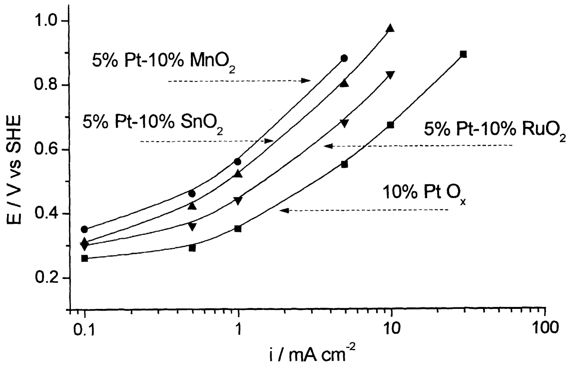

Fig. 4. Quasi steady-state polarization curves for the direct electrooxidation of 0.5 M 1,3-dioxolane on various Pt/metal oxide electrodes in 1 M H_2SO_4 at 25 °C.

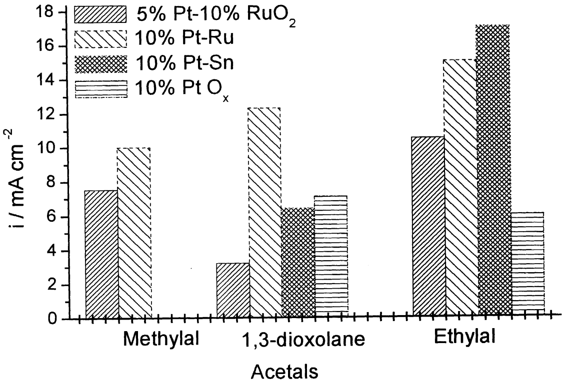

Fig. 5. Bar chart representation of direct electrooxidation current density for methylal, 1,3-dioxolane and ethylal in 1 M H_2SO_4 at 25 °C and 0.6 V vs SHE on various electrode materials.

Table 1. Values of the overpotential during the electrooxidation of methylal, ethylal and 1,3-dioxolane in 1 M H_2SO_4 at 25 °C on Pt/Ru and on $PtRuO_2$ for 20 mA cm^{-2}

Overpotential	Methylal	Ethylal	1,3-dioxolane
Pt–Ru	0.65	0.40	0.50
Pt–RuO_2	0.75	0.65	0.85

For the electrooxidation of all three acetals, 10% Pt/Ru (1:1) is a better catalyst than 5% Pt–5% RuO_2. For ethylal electrooxidation, 10% Pt/Sn (1:1) is the best catalyst and 10% PtO_x is the worst catalyst. By contrast, for 1,3-dioxolone, 10% Pt/Sn (1:1) and 10% PtO_x are comparable in terms of activity. This indicates that we may have a change of the reaction rate of the electrooxidation of the acetals according to the catalyst anode material composition. New analysis of the hydrolysis products of methylal and ethylal revealed the presence of methanol and formaldehyde [14]. However, the hydrolysis products were not detected in the electrolyte after long-term electrooxidation experiments very likely because they were anodically oxidized to carbon dioxide.

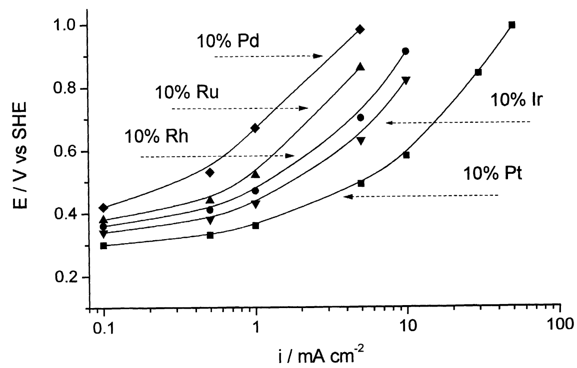

Fig. 6. Quasi steady polarization curves for the direct electro-oxidation of 0.5 M 1,3-dioxolane on various single noble metal electrodes in 1 M H_2SO_4 at 25 °C.

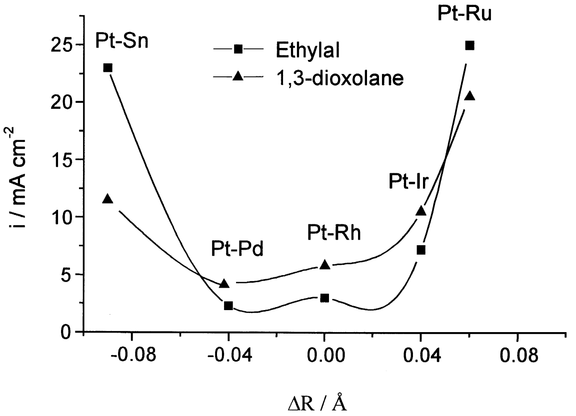

Fig. 8. Current density against ($R_{\mathrm{metal}} - R_{\mathrm{Pt}}$) for binary metals used as catalysts in the direct electrooxidation of 0.5 M acetals in 1 M H_2SO_4 at 25 °C at 0.70 V: (■) ethylal; (▲) 1,3-dioxolane.

The data in Figures 3 and 6 obtained with the noble metal catalysts are evaluated in Figure 7 by plotting the current densities a 0.70 V vs SHE against the atomic radius of their respective metal. Volcano behaviour is obtained. The highest current density was obtained with platinum and rhodium and the lowest was obtained with palladium and ruthenium. Binary alloy-based catalysts show an interesting correlation between the current density at 0.70 V vs SHE with ($\Delta R = R_{\mathrm{metal}} - R_{\mathrm{Pt}}$) as shown in Figure 8. The lowest current density is obtained when ΔR is close to zero and catalytic activity of the binary catalyst increases with $|\Delta R|$. Accordingly, the highest values of current density are obtained for Pt–Sn and Pt–Ru. The same results were obtained with methanol electrooxidation [19]. This may explain why the Pt–Ru alloy has been the best choice up to now for the methanol fuel cell anode [20, 21 and references therein] and why Pt–Sn might be intrinsically the second best active binary alloy for methanol oxidation [19, 22]. This also explain why Pt–Ru and Pt–Sn have shown to be the efficient catalysts for the electrooxidation of dimethoxymethane, trimethoxymethane and 1,3,5-trioxane [10]. Development of acetal PEM fuel cells based on these anodes is under active investigation, in particular, the relationship between the results obtained in Figure 8 and the performances of fuel cells based on these electrodes. This might help in the selection of alloys for the electrooxidation of acetals from a combination of catalytic binary alloys having particular value of ΔR. Consequently, new binary alloys could be designed for direct acetal fuel cells.

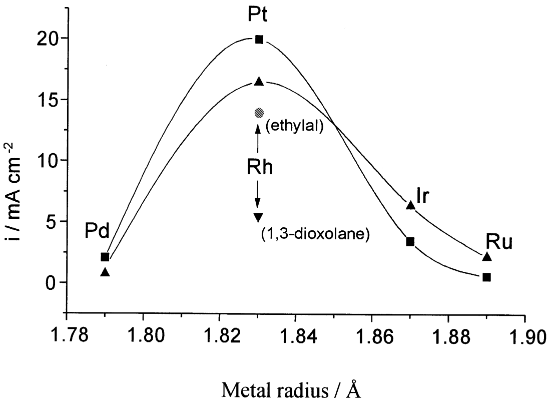

Fig. 7. Current density against radius for single noble metals used as catalysts in the direct electrooxidation of 0.5 M acetals in 1 M H_2SO_4 at 25 °C at 0.70 V: (■) ethylal; (▲) 1,3-dioxolane.

Current against overpotential curves of the electrooxidation of ethylal on Pt–Ru were drawn after various hydrolysis times (Figure 9). As may be seen, in the high current density regions, the curves improved to a measurable degree with an increase in time. At a current density of 20 mA cm^{-2}, the overpotential decreases by 200 mV after 72 h (Table 1), and the open circuit potential changes by less than 50 mV after the same amount of time (Figure 10). This improvement is very likely due to acetal hydrolysis.

This variation might be related to the change in fuel composition due to hydrolysis. Chemical hydrolysis products are certainly involved in the improvement of the acetal electrooxidation reaction. It may be seen that the electrooxidation polarization curves improved with the increase in hydrolysis time. This improvement due to the hydrolysis of ethylal was also observed for methylal and 1,3-dioxolane. Analysis of the anode effluent streams for by-products showed that carbon dioxide was the only detectable product in the case of

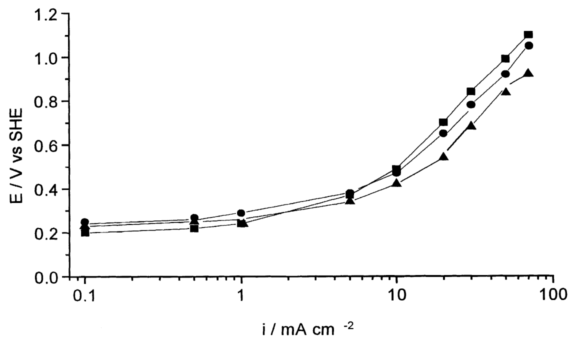

Fig. 9. Quasi steady-state polarization curves for the direct electrooxidation of 0.5 M ethylal in 1 M H_2SO_4 at 25 °C on various times of ethylal hydrolysis before electrooxidation. Key: (■) 0, (●) 24 and (▲) 72 h.

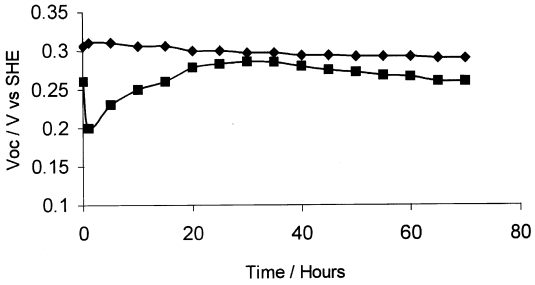

Fig. 10. Long-term stability of the open-circuit potential of the ethylal/Pt–Ru and ethylal/Pr–RuO_2 electrodes for 0.5 M ethylal in 1 M H_2SO_4 at 25 °C. Key: (◆) 5% Pt–5% RuO_2 and (■) 10% Pt–Ru.

methylal, ethylal and 1,3-dioxolane. For the acid (pH 0.5) hydrolysis of methylal, ethylal and 1,3-dioxolane over 72 h, the hydrolysis reaction products were also analysed by gas chromatographs. Methanol, methyl formate, formic acid and formaldehyde were obtained as hydrolysis by products.

The variation of the hydrolysis level with the pH was determined for methylal, ethylal and 1,3-dioxolane. The obtained results are similar as those documented by Lambiotte [14], a company which fabricates and sells acetals. These results can be summarized as follows: Acetals hydrolyse in an acid medium and in the presence of water (Table 2), but are relatively stable in a neutral or in a basic medium. At a pH level of 3.63, no detectable hydrolysis of methylal was observed in a 30–70% mixture with water at 20 °C after three months. The hydrolysis level of methylal increases when the pH level decreases. The hydrolysis level of methylal increases from 0.55% at pH 2.95 to 35.26% at pH 0.96. Similar results were obtained with ethylal, for which a hydrolysis level of 33% was shown at pH 0 and 4% at pH 1. For 1,3-dioxolane, the hydrolysis level decreases from 9% at pH 0 to 0% at pH 1 [14]. At pH 0, the hydrolysis level of methylal is higher than that of ethylal, which is higher than that of 1,3-dioxolane. Methyl formate, formic acid, methanol and formaldehyde are the main hydrolysis products of acetals [14]. The same results were obtained in this work (see the results and discussion section).

However, these hydrolysis products were not detected in the anode effluent streams. It is quite likely that the hydrolysis products could have been very easily oxidised at the anode, leaving no soluble products to accumulate in the solution. This is in agreement with results obtained on the electrooxidation of dimethyl orthoformate ($(CH_4O)_2CH_2$), trimethyl orthoformate ($(CH_3O)_3$-CH_2) and trioxane ($(CH_3O)_3$) [10].

Table 2. Percentage hydrolysis level variation with pH of acetals in H_2SO_4 during a 5 h period at 20 °C [14]

Acetals/pH	0	1	3
Methylal	52%	4%	0%
Ethylal	33%	22%	0%
1,3-dioxolane	9%	0%	0%

Based on the reaction product analysis, the following half-cell electrooxidation reactions can be proposed. This may involve the production of some hydrolysis byproducts followed by complete electroextraction to carbon dioxide.

(i) *For methylal:*
Hydrolysis:

$$(CH_3O)_2CH_2 + H_2O \xleftrightarrow{H^+} CH_2O + 2\,CH_3OH \qquad (1)$$

followed by the electrooxidation:

$$CH_2O + 2\,CH_3OH + 3\,H_2O \longleftrightarrow 3\,CO_2 + 16\,H^+ + 16\,e^- \qquad (2)$$

(ii) *For ethylal:*
Hydrolysis:

$$(CH_3O)_2(CH_2)_3 + 3\,H_2O \xleftrightarrow{H^+} 4\,CH_3OH + CH_2O \qquad (3)$$

followed by the electrooxidation:

$$CH_2O + 4\,CH_3OH + 5\,H_2O \longleftrightarrow 5\,CO_2 + 28\,H^+ + 28\,e^- \qquad (4)$$

(iii) *For 1,3-dioxolane:*
Hydrolysis:

$$C_3H_6O_2 + 2\,H_2O \xleftrightarrow{H^+} CH_2O + 2\,CH_3OH \qquad (5)$$

followed by the electrooxidation:

$$CH_2O + 2\,CH_3OH + 2\,H_2O \longleftrightarrow 3\,CO_2 + 14\,H^+ + 14\,e^- \qquad (6)$$

The above equations indicate that the complete electrooxidation of acetals produces more electrons than the complete electrooxidation of methanol:

$$CH_3OH + H_2O \longleftrightarrow CO_2 + 6\,H^+ + 6\,e^- \qquad (7)$$

The number of electrons produced by acetal electrooxidation may explain why the polarization curves of acetals are better than that of methanol. This is supported by the direct electrooxidation overpotential curves for methanol and methylal in 1 M H_2SO_4 at 25 °C and by the bar chart representation of the direct electrooxidation current density for methylal, 1,3-dioxolane and ethylal in 1 M H_2SO_4 at 20 °C (Figure 5). From Figure 1, it is shown that the curve of methylal oxidation which might involve 16 e^- is better than that of methanol which might involve 6 e^-. Whereas, for most electrocatalysts in Figure 5, the current density of the electrooxidation of ethylal which might involve 28 e^- is better than that of 1,3-dioxolane which may involve 14 e^-.

4. Conclusion

Some acetals were electrooxidized in an acid medium and the results compared to those of methanol electrooxidation. Platinum–ruthenium, platinum oxide, platinum–ruthenium oxide, platinum–tin and some platinum–metal oxide-based electrodes exhibited interesting performances for acetal electrooxidation. It has been shown that Pt–Ru, Pt–Sn, PtO_x, Pt–RuO_2, and Pt–MnO_2 can sustain the electrooxidation of ethylal and 1,3-dioxolane during the steady-state experiments without noticeable hysterisis in the polarization curves. This is an indication that these electrodes are resistant to the effects of poisoning. The electrooxidation of ethylal and 1,3-dioxolane during the steady-state experiments without noticeable hysterisis in the polarization curves. This is an indication that these electrodes are rsistant to the effects of poisoning. The electrooxidation of ethylal and 1,3-dioxolane were demonstrated for the first time. The overvoltage in the ethylal and 1,3-dioxolane electrooxidation reactions is lower than that in the methylal reactions. It was found that acetals are better fuels than methanol for direct hydrocarbon fuel cells. The determination of cross-over rates of these acetals through various solid polymer electrolyte membranes is under active investigation. Studies of the electrooxidation of other acetals are also actively under way.

This work opens the way to a new approach to the development of direct acetals PEM fuel cells, which will necessitate the development of the following related aspects:

(i) Determination of the cross-over of acetals through Nafion® 117 and other membranes.
(ii) Determination of the hydrolysis products of acetals for different hydrolysis times.
(iii) Determination of the electrooxidation products of acetals for various electrocatalyst materials.
(iv) Determination of the kinetic parameters of acetal electrooxidation.
(v) Determination of the direct acetal PEM fuel cell parameters and correlate them to physico-chemical parameters of the Pt-binary noble alloys.
(vi) Extension of this study aldehyde electrooxidation and application in PEM fuel cells.
(vii) Development of direct acetal fuel cells for portable applications etc.

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