Temperature dependence studies on the electro-oxidation of aliphatic alcohols with modified platinum electrodes

PANADDA KATIKAWONG[a]*, TANAKORN RATANA[b] and WARET VEERASAI[a]

[a]Department of Chemistry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand
[b]Department of Industrial Chemistry, Faculty of Applied Science,
King Mongkut's University of Technology North Bangkok, Bangkok 10800, Thailand
e-mail: pana_a@hotmail.com

Abstract. Temperature dependence on the electro-oxidation of methanol, ethanol and 1-propanol in 0·5 M H_2SO_4 were investigated with Pt and PtRu electrodes. Tafel slope and apparent activation energy were evaluated from the cyclic voltammetric data in the low potential region (0·3–0·5 V vs SHE). The CV results provided Tafel slopes for alcohols in the range of 200–400 mV dec^{-1} which indicated a difference in the rate determining step. The decrease in Tafel slope was only observed in the case of methanol for the Ru-modified Pt electrode. This indicates that Ru improves the rate of determining step for methanol while hindering it for the other alcohols. The electrochemical impedance spectroscopy was also used to evaluate the electro-oxidation mechanism of alcohols on these electrodes. The simulated EIS results provided two important parameters: charge transfer resistance (R_{ct}) and inductance (L). The R_{ct}^{-1} and L^{-1} represent the rate of alcohol electro-oxidation and rate of desorption of intermediate species, respectively. These values increased with the increasing of temperature. The results from two techniques were well agreed that the electro-oxidation of methanol was improved by raising the temperature and ruthenium modification.

Keywords. Cyclic voltammetry; electrochemical impedance spectroscopy; activation energy; fuel cell; alcohol.

1. Introduction

The use of hydrogen carrier like alcohol as alternative fuels in the direct alcohol fuel cell (DAFC) appears that they are advantageous for two main reasons: (i) easy storage of liquid fuels and (ii) their high theoretical mass energy density, for example; 6·1 and 8·0 kWh kg^{-1} for methanol and ethanol, respectively. An emerging technology of DAFC uses liquid alcohols without an external fuel processing unit such as methanol, ethanol and propanol which made them more versatile in many portable products.[1–5] DAFCs generate power through the direct oxidation of alcohol in conjunction with the reduction of oxygen (in air). The major challenges faced in DAFC are (i) methanol crossover which can only be overcome by developing new membranes; (ii) slow electrochemical kinetics at electrode/electrolyte interfaces which can only be overcome by develop-

ing new electrocatalysts for both anode and cathode.[5–7] To date, Pt-based catalyst have been shown to improve the efficiency of DAFC in acidic electrolyte.[5–9] Many metals such as Ru, Pd, Sn or Rh exhibit co-catalytic activity with Pt for the oxidation of alcohol via the bifunctional mechanism.[5] The understanding of the relationship between the reaction pathway and their electrocatalytic activity at elevated temperature is necessary for developing the new catalyst in DAFC.

In this work, cyclic voltammetry (CV) was used to provide kinetic data while electrochemical impedance spectroscopy (EIS) was used to distinguish different elementary steps of the reaction process at desired bias potentials. The electro-oxidation of aliphatic alcohols including; methanol, ethanol, 1-propanol on the well-defined Pt-based electrode were performed in the temperature range of 25 to 60°C. Based on CV data, the kinetic parameters such as Tafel slope and apparent activation energy were evaluated. Through the analysis of EIS spectra,
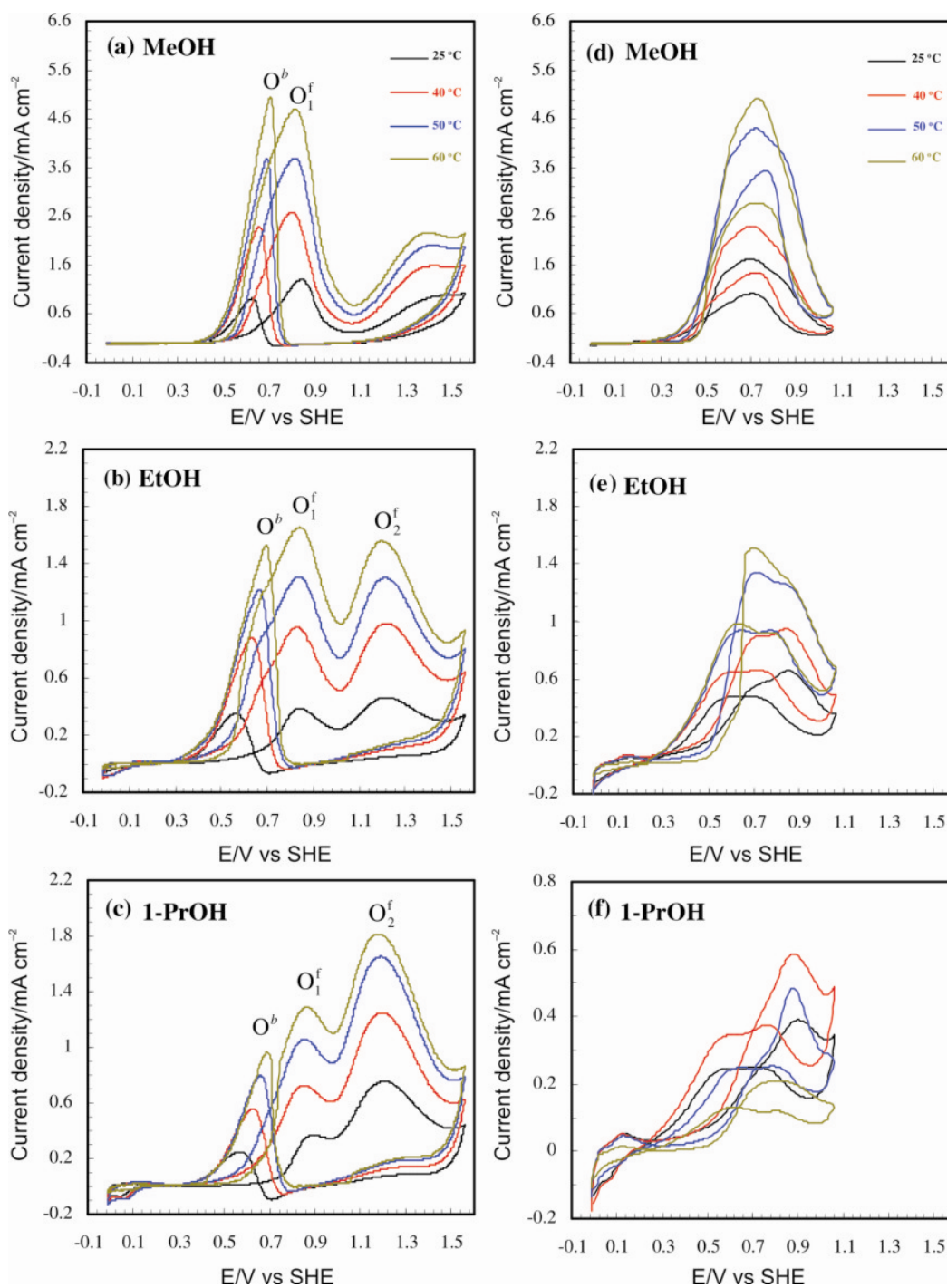
---

*For correspondence

Figure 1. Cyclic voltammograms at different temperatures with p-Pt electrode (a–c) and p-PtRu electrode (d–f) in 0·25 M methanol, 0·25 M ethanol, and 0·25 M 1-propanol. Scan rate = 0·05 V s^{-1}.

we obtained the inverse charge transfer resistance and inverse inductance values which can be correlated with the rate of electro-oxidation of alcohols and the rate of desorption of intermediate species, respectively. Additionally, the reaction pathway of aliphatic alcohols (C_1–C_3) is proposed and discussed in this study.

2. Experimental

2.1 *Chemicals*

All analytical grade chemicals were used in this work without further purification. The solution was prepared in deionized water (18·2 MΩ cm, Milli-Q-

system, Milford, Massachusetts, USA). The 0·25 M methanol, ethanol and 1-propanol (Merck, Germany) were prepared in 0·5 M of H_2SO_4 (Merck, Germany).

2.2 *Preparation of the modified electrodes*

The platinized platinum (p-Pt) electrode was prepared on a platinum wire (i.d. = 2·5 mm). The electrode surface was electrochemically activated by cycling the potential between 0 and 1·15 V vs SHE at scan rate of 50 mV s^{-1} in 0·5 M H_2SO_4. Then, the CV was applied by cycling potential between −0·1 and −0·45 V vs SHE for 10 scans in 13 mM H_2PtCl_6 (Fluka, Switzerland). After platinizing step, the electrode was polarized at −0·5 V vs SHE for 5 min in 0·5 M H_2SO_4 in order to eliminate chloride ions from the electrode surface.

The ruthenium modified Pt electrode (p-PtRu) was prepared by electrodeposition technique. After the electrochemically activated step, the p-Pt electrode was immersed in 10 mM $RuCl_3$ (Aldrich, USA) and fixed potential at −0·07 V vs SHE for 100 s.

2.3 *Electrochemical measurements*

The electrochemical measurements were investigated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) using a three electrode cell with temperature control unit. The working electrode was a p-Pt or a p-PtRu electrode and the counter electrode was a Pt rod. The Ag/AgCl electrode was used as reference electrode ($E = 0·206$ V vs SHE).[10] All potentials are given with respect to the standard hydrogen electrode (SHE). The electrochemical experiments were carried out under nitrogen atmosphere and measured with the AUTOLAB PGSTAT30 with FRA2 module (Eco Chemie B.V., The Netherlands), which was controlled by GPES and FRA software. The working electrode was activated by cycling potential between 0 and 1·15 V vs SHE at scan rate of 50 mV s^{-1} until the reproducible CV patterns were obtained. The cell temperature was controlled between 25 and 60°C within ± 0·2°C.

The electrochemical impedance spectra were recorded in the frequency range of 10 kHz to 8 mHz. The amplitude of single sinusoidal modulation voltage was setting at 0·05 V. All EIS spectra were recorded with bias potential of 0·4–1·0 V vs SHE.

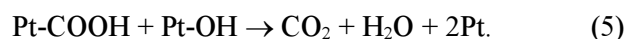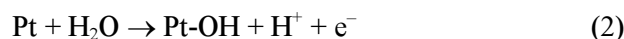## 3. Results and discussion

3.1 *Cyclic voltammetry (CV)*

Cyclic voltammograms of methanol, ethanol and 1-propanol on a p-Pt electrode at different temperatures (25, 40, 50 and 60°C) are shown in figures 1a–c. The oxidation peaks of the CV presented as O_1^f and O_2^f for the first and the second anodic peaks in the forward potential scan and O^b for the cathodic peak in the backward potential scan. At 25°C, the first anodic peak (O_1^f) appears around 0·84 V vs SHE with lower onset potential ($E_{onset} = 0·62$ V vs SHE), which was well agreed with the beginning of the methanol electro-oxidation via adsorbed intermediates on Pt/C electrode as reported by Lee *et al.*[11] The O^b peak appears around 0·69 V vs SHE which was attributed to the re-oxidation of the intermediate species. The effect of temperature in the range of 25 to 60°C showed the increasing in the anodic current density with increasing temperature. Moreover, a negative shift in the onset potential was also observed.

The electro-oxidation pathway of methanol consists of two processes necessary to complete the oxidation in different potential regions. First, hydrogen atom is discarded from the Pt surfaces at potential around 0·2 V and methanol can be adsorbed on the Pt surface as follows:

$$Pt\text{-}H + CH_3OH \rightarrow Pt\text{-}COH + 4H^+ + 4e^-. \quad (1)$$

The second process requires the dissociation of water on vacancy of Pt sites which is the oxygen donor for the oxidation of the intermediate species to form CO_2 at the potential above 0·45 V.[12] The effect of increasing temperature may be explained from the increasing rate of both processes as follows:
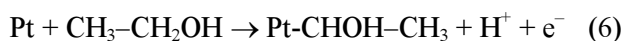
$$Pt + H_2O \rightarrow Pt\text{-}OH + H^+ + e^- \quad (2)$$

$$Pt\text{-}COH + Pt\text{-}OH \rightarrow Pt\text{-}CO + H_2O + Pt \quad (3)$$

$$Pt\text{-}CO + Pt\text{-}OH \rightarrow Pt\text{-}COOH + H^+ + e^- \quad (4)$$

$$Pt\text{-}COOH + Pt\text{-}OH \rightarrow CO_2 + H_2O + 2Pt. \quad (5)$$

For the electro-oxidation of ethanol on p-Pt electrode at 25°C in figure 1b, the O_1^f, O_2^f and O^b peaks were found at 0·83, 1·23 and 0·56 V vs SHE, respectively. The presence of O_2^f peak was assigned as the oxidation of alcohol with Pt oxide surface. More negative potential value in O^b peak than the observed in re-oxidation peak of methanol were found. It was suggested that the intermediate species of ethanol

Table 1. Electrochemical data at various temperatures of the three aliphatic alcohols oxidation on p-Pt and p-PtRu (θ_{Ru} = 0.6) electrodes.
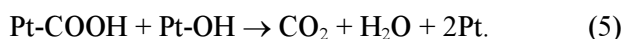
Temperature (°C)	Onset potential (V vs SHE)	Peak potential, E_p (V vs SHE)			Current density, J (mA cm^{-2})			Tafel slope (mV dec^{-1})	Activation energy (kJ mol^{-1})
		O_1^f	O_2^f	O^b	O_1^f	O_2^f	O^b		
25	0.62/0.47	0.84/0.69	–	0.63/0.70	1.16/1.58	–	0.99/0.91	178/74	70.4/54.4
40	0.57/0.46	0.80/0.70	–	0.65/0.71	2.45/2.21	–	2.42/1.31	118/65	
50	0.56/0.43	0.80/0.70	–	0.69/0.76	3.44/4.03	–	3.85/3.19	97/54	
60	0.55/0.40	0.81/0.71	–	0.70/0.70	4.34/4.63	–	5.15/2.51	83/71	
25	0.60/0.48	0.83/0.71	1.23	0.56/0.58	0.32/0.31	0.28	0.41/0.37	211/165	52.2/22.5
40	0.54/0.48	0.82/0.71	1.21	0.63/0.58	0.69/0.6	0.43	0.92/0.49	277/157	
50	0.54/0.53	0.82/0.71	1.21	0.66/0.61	0.91/1.03	0.53	1.24/0.67	227/173	
60	0.54/0.51	0.83/0.69	1.23	0.69/0.61	1.21/1.24	0.61	1.53/0.72	181/194	
25	0.74/0.49	0.86/0.69	1.19	0.56/0.55	0.14/0.16	0.34	0.34/0.16	398/241	32.8/17.1
40	0.62/0.52	0.82/0.70	1.19	0.62/0.55	0.30/0.26	0.64	0.61/0.21	277/261	
50	0.57/0.56	0.82/0.70	1.19	0.65/0.60	0.44/0.44	0.80	0.83/0.15	263/283	
60	0.54/0.53	0.82/0.71	1.18	0.69/0.58	0.59/0.47	0.81	0.97/0.09	225/311	

Note: The data in this table were presented as p-Pt/p-PtRu electrodes.

oxidation should differ from those intermediates of methanol oxidation. Ethanol should produce more reaction intermediates such as acetaldehyde and acetic acid which can be adsorbed strongly on the Pt surface than methanol.[1,11,13,14] The oxidation pathway of ethanol on p-Pt electrode can be explained by the following mechanism:[1]

$$Pt + CH_3–CH_2OH \rightarrow Pt\text{-}CHOH–CH_3 + H^+ + e^- \quad (6)$$

$$Pt\text{-}CHOH–CH_3 \rightarrow Pt\text{-}CHO–CH_3 + H^+ + e^- \quad (7)$$

$$Pt\text{-}CHO–CH_3 \rightarrow Pt\text{-}CO–CH_3 + H^+ + e^- \quad (8)$$

$$Pt\text{-}CO–CH_3 + Pt \rightarrow Pt\text{-}CO + Pt\text{-}CH_3 \quad (9)$$

and then

$$Pt\text{-}CO + Pt\text{-}OH \rightarrow Pt\text{-}COOH + H^+ + e^- \quad (4)$$

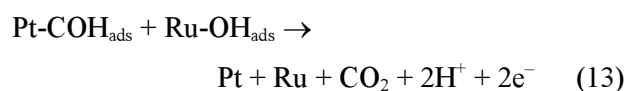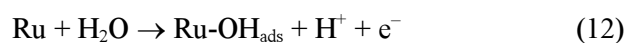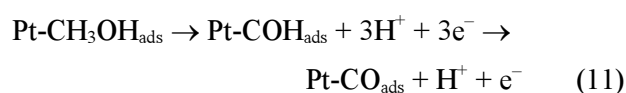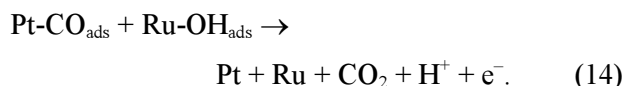$$Pt\text{-}COOH + Pt\text{-}OH \rightarrow CO_2 + H_2O + 2Pt. \quad (5)$$

Cyclic voltammograms in figure 1c of the electro-oxidation of 1-propanol showed the onset potential around 0.74 V vs SHE which was more positive than other alcohols. This may be attributed to the de-protonation of 1-propanol during adsorption, suggested by Rodrigues *et al.*[15] The 1-propanol was oxidized at potential higher than 0.5 V and was detected the oxidation product by DEMS and FTIR techniques.[15,16]

The relativities of electro-oxidation of alcohols estimated from the current density of O_1^f peak are in the order: methanol > ethanol > 1-propanol at the same temperature. The increasing in the anodic current with the number of carbon atom in aliphatic alcohol indicates that it is more difficult to cleave

C–C bond to be adsorbed CO (CO_{ads}) and then also produce many reaction intermediate species.[13] These adsorbed intermediates inhibit the electro-oxidation reaction and lead to increase the onset potential and decrease in current density as summarized in table 1. However, the electro-oxidation efficiency for all alcohols increased when the temperature was raised. This indicates that the increasing temperature can enhance the rate of electro-oxidation of alcohols.

Figures 1d–f show the CV of the electro-oxidation of methanol, ethanol and 1-propanol with Ru modified platinized platinum (p-PtRu) electrode with Ru coverage (θ_{Ru}) of 0.6 at various temperatures. For the electro-oxidation of methanol, the higher in current density of O_1^f peak and lower in current density of O^b peak were observed when compared with p-Pt electrode. The E_{onset} around 0.47 V vs SHE was also obtained at 25°C (see table 1). These results suggested that the major roles of Ru promoter were to increase the OH_{ads} species or active H_2O on the Ru surface which CO_{ads} was loosely bound with the Pt surface. This mechanism is known as the bifunctional mechanism.[11,17]

$$Pt + CH_3OH_{solution} \rightarrow Pt\text{-}CH_3OH_{ads} \quad (10)$$

$$Pt\text{-}CH_3OH_{ads} \rightarrow Pt\text{-}COH_{ads} + 3H^+ + 3e^- \rightarrow$$
$$Pt\text{-}CO_{ads} + H^+ + e^- \quad (11)$$

$$Ru + H_2O \rightarrow Ru\text{-}OH_{ads} + H^+ + e^- \quad (12)$$

$$Pt\text{-}COH_{ads} + Ru\text{-}OH_{ads} \rightarrow$$
$$Pt + Ru + CO_2 + 2H^+ + 2e^- \quad (13)$$

$$Pt\text{-}CO_{ads} + Ru\text{-}OH_{ads} \rightarrow$$

$$Pt + Ru + CO_2 + H^+ + e^-. \qquad (14)$$

With the increasing temperature, the increasing in peak current and unchanged in the position of O_1^f peak was also observed. These results were similar with both ethanol and 1-propanol.

In order to compare the activity of the electro-oxidation of alcohols on p-Pt and p-PtRu at different temperatures, the Tafel slope (b) and apparent activation energy (E_a) were estimated from CV data[3] in low potential range (0·4–0·6 V) and also summarized in table 1. For p-Pt electrode, the Tafel slope (b) is in the order: methanol < ethanol < 1-propanol at 25°C and decreases with the increasing of the temperature. It is well known that the Tafel slope corresponds to the rate determining step as well as the number of electron transfer steps that precede it. The electro-oxidation of alcohols with the higher carbon atoms (C_2–C_3 alcohols) occur via complicate reactions compared with the C_1 alcohols. These reactions produced many adsorbed intermediate species and blocked the active site of Pt surface. The intermediate species can be removed when increasing temperature, corresponded to the decreasing of Tafel slope.

Arrhenius plots of logarithm of exchange current density ($\log J_0$) versus the reciprocal of temperature (T^{-1}) provided the apparent activation energy from the slope of linear fitted as shown in figure 2. The apparent activation energy of methanol, ethanol and 1-propanol at p-Pt electrode were 70·4, 52·2 and 32·8 kJ mol^{-1}, respectively. These values were in agreement with the results reported by Lee *et al.*[11] The higher activation energy of methanol than ethanol and 1-propanol imply that the electro-oxidation process of methanol consists of the different pathways. For p-PtRu electrode, the apparent activation energy was lower than those found in p-Pt electrode. This result indicated that Ru sites improved the electro-oxidation of all alcohols, especially for methanol and ethanol.

3.2 *Electrochemical impedance spectroscopy (EIS)*

The EIS technique was performed in order to study the reaction activity of the alcohol electro-oxidation.[4,18,19] The methanol oxidation showed different Nyquist plot patterns with various potentials at 25°C as shown in figure 3. The different Nyquist patterns imply that the mechanism of the electro-oxidation reaction differ at various potentials. The Nyquist plot shows the 'capacitive loop' and 'inductive loop' in the high and low frequency range, respectively. The diameter of both loops decreased with increasing potential from 0·4 to 0·6 V vs SHE in quadrant I. It is known that the size of capacitive loop imply the rate of reaction. Moreover, the rate of poisoning intermediate species can be considered from the appearance of inductive loop.[4]
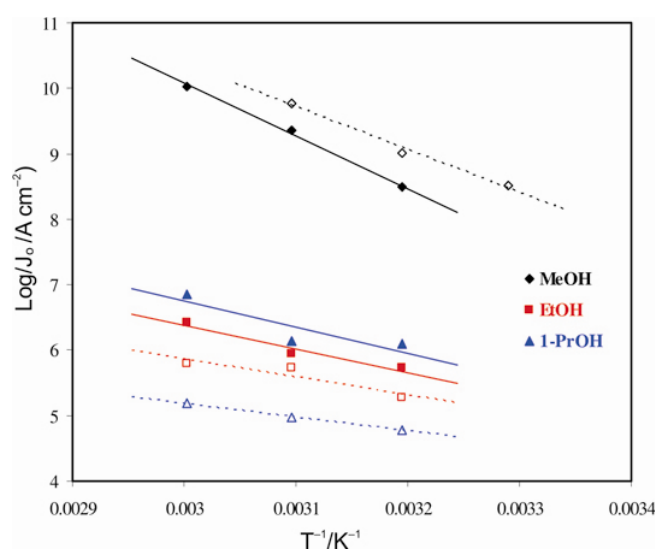

Figure 2. Arrhenius plot for methanol, ethanol and 1-propanol at p-Pt (solid line) and p-PtRu (dash line) electrodes.
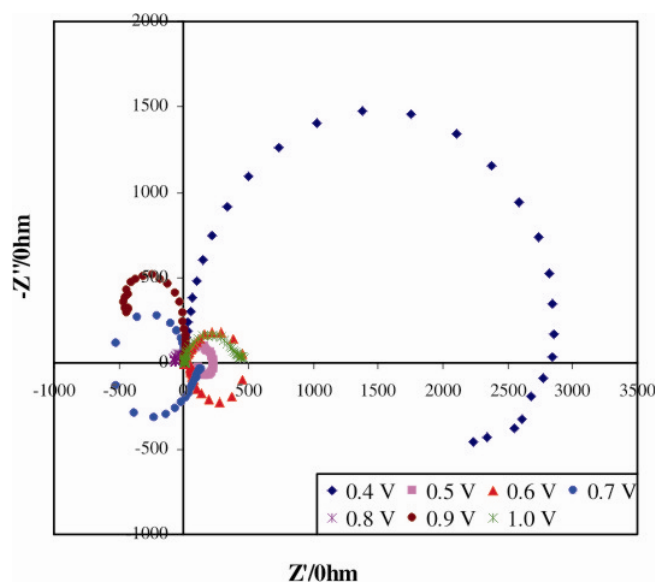

Figure 3. Nyquist plots for 0·25 M methanol in 0·5 M H_2SO_4 with p-Pt electrode at different bias potential (0·4–1·0 V vs SHE).
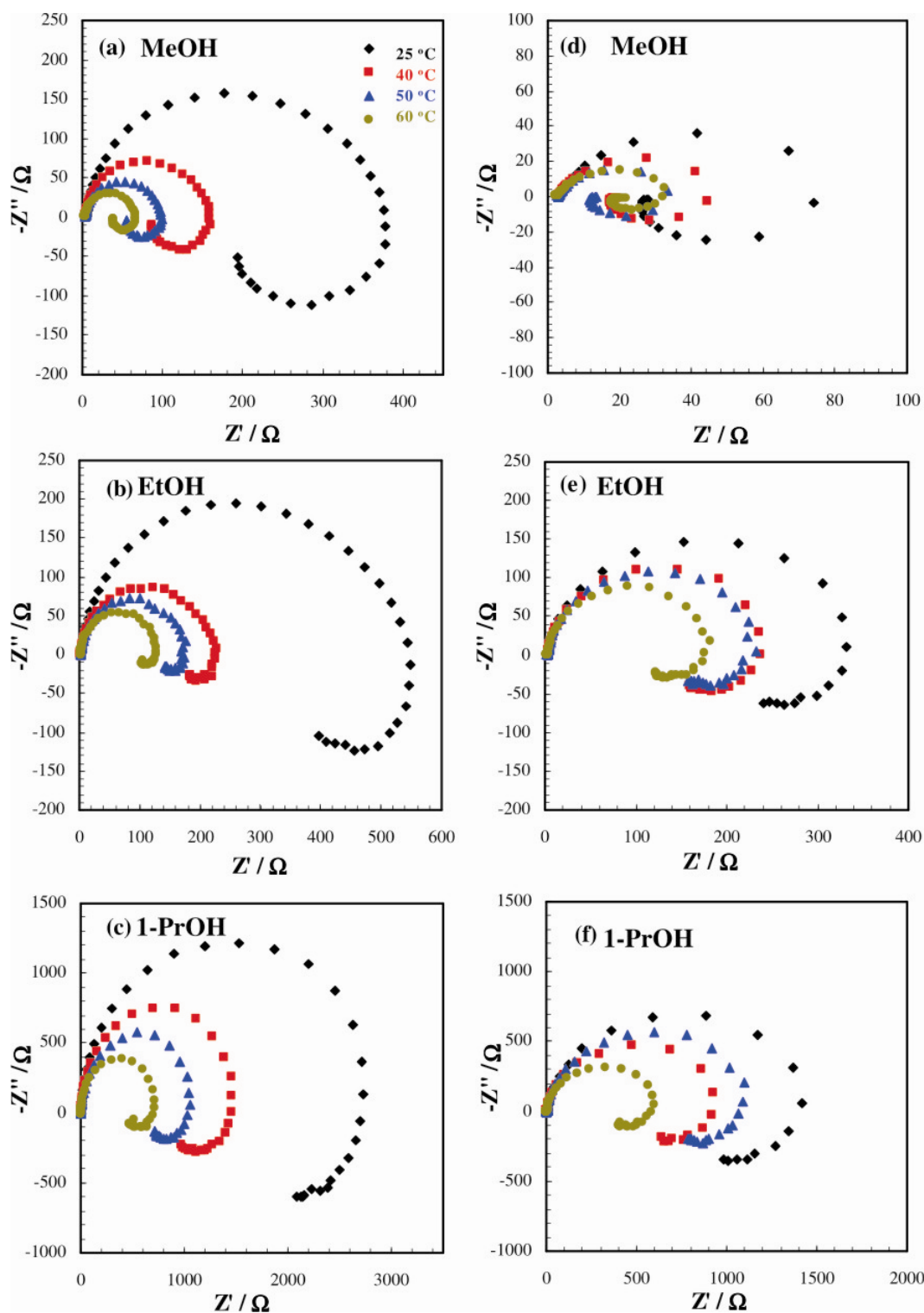
Figure 4. Nyquist plots at different temperatures with p-Pt electrode and (a–c) and p-PtRu electrode (d–f) in 0·25 M methanol, 0·25 M ethanol, and 0·25 M 1-propanol.

At the potential of 0·5 V vs SHE was considered as the occurrence of intermediate species. This provided the direct electrochemical evidence for the fact that CO_{ads} was being oxidized on the Pt surface,[20] so we selected this bias potential for EIS study in this work. At the potential of 0·5 V, the Nyquist plots for methanol, ethanol and 1-propanol in 0·5 M H_2SO_4 on a p-Pt electrode at various tempera-

tures are shown in figures 4a–c. The diameter of capacitive loop decreased with increasing the temperature.
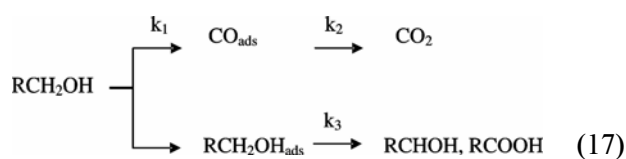
The equivalent circuit model in figure 5 is used for fitting the EIS spectra,[19] and the two important parameters were used including: charge transfer resistance (R_{ct}) and inductance (L). The relationship between impedance values (Z) and fitting parameters can be expressed as shown in equation (15)–(16):

$$Z = R_S + \left(\frac{1}{Z_F} + Y(j\omega)^n \right)^{-1} \qquad (15)$$

$$\frac{1}{Z_F} = \frac{1}{R_{ct}} + \frac{1}{R_L + j\omega L}, \qquad (16)$$

where R_s is the solution resistance, Z_F is the faradaic impedance, ω is the angular frequency, Y_0 and n are two components of constant phase element (Q_{CPE}), R_{ct} is the charge transfer resistance, R_L is the inductive resistance, L is the inductance.

The reaction steps of the electro-oxidation of alcohol pathways can be simplified in the following scheme:

$$RCH_2OH \longrightarrow \begin{array}{l} \xrightarrow{k_1} CO_{ads} \xrightarrow{k_2} CO_2 \\[2ex] \xrightarrow{} RCH_2OH_{ads} \xrightarrow{k_3} RCHOH, RCOOH \end{array} \qquad (17)$$

where R is hydrogen or any alkyl group.

The first pathway occurs via dehydrogenation to COads which is the major intermediate species of the methanol electro-oxidation. Then, CO_{ads} is oxidized with OH_{ads} or H_2O_{ads} to CO_2. The another pathway is the direct oxidation of alcohol to form acid or aldehyde which is observed by *in situ* FT-IR techniques.[21,22] Above reaction pathway can explain from the relation of the reciprocal of charge-transfer resistance (R_{ct}^{-1}) and inverse of inductance (L^{-1}). The
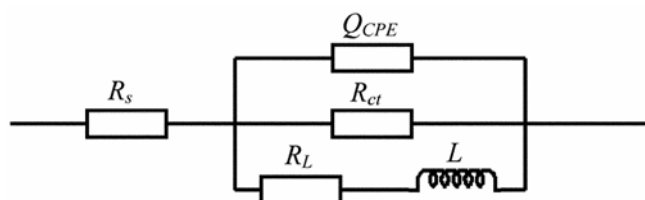

Figure 5. Equivalent circuit used for simulating the EIS spectra for the alcohol electro-oxidation on p-Pt and p-PtRu electrodes at different temperatures.

physical meaning of R_{ct}^{-1} or the reciprocal of charge transfer resistance is the overall reaction rate when the concentration of intermediate on electrode surface is kept constant. The L^{-1} can assume as the rate of oxidation for desorption of intermediate species on electrode surface, which mainly is CO_{ads}.

Figure 6 shows the temperature dependent for R_{ct}^{-1} and L^{-1} values of C_1–C_3 alcohols on the p-Pt and p-PtRu electrodes. These results show that R_{ct}^{-1} and L^{-1} values increase with the rising temperature. The R_{ct}^{-1} and L^{-1} of methanol, ethanol and 1-propanol decreased with the increasing the number of carbon atom in alcohol chains. It is corresponded with the decreasing in anodic current observed from CV results. It is possible that the breaking C–C bond process to CO_{ads} is difficult in the first pathway. Moreover, the smaller in L^{-1} values of both ethanol and 1-propanol than methanol also indicated the slower in the desorption rate of adsorbed species on the Pt surface.[23] It is possible that the numbers of CO_{ads} decreased or the other intermediate species were strongly adsorbed and inhibited electro-oxidation process. Moreover, it is possible that the adsorbed species could be further oxidized another oxidation pathway. According to the lower in apparent activation energy values of both ethanol and 1-propanol, it is indicated that the electro-oxidation of these alcohols occur via the second pathway. Because of the activation energy of the CO_{ads} oxidation should be higher than the C–C breaking bond.

The enhancement effect of Ru modified Pt surface on the electro-oxidation of methanol are also found in figure 6. The L^{-1} value increased with the excessively increasing temperature. This result suggested that the adding of Ru can improve the electro-oxidation of methanol and the strong adsorbed CO_{ads} can be easily oxidized to CO_2. This effect is also found in the ethanol oxidation, while 1-propanol oxidation is not significantly different.

4. Conclusions

The effect of temperature on the electro-oxidation of all alcohols on p-Pt and p-PtRu electrodes was explored by cyclic voltammetry and electrochemical impedance spectroscopy. The increase in anodic current and decrease in R_{ct} value indicated that the reaction rate would be enhanced at higher temperature. The major roles of Ru sites were to increase the water adsorption and OH_{ads} formation on Ru site. From the Arrhenius analysis, the activation energy
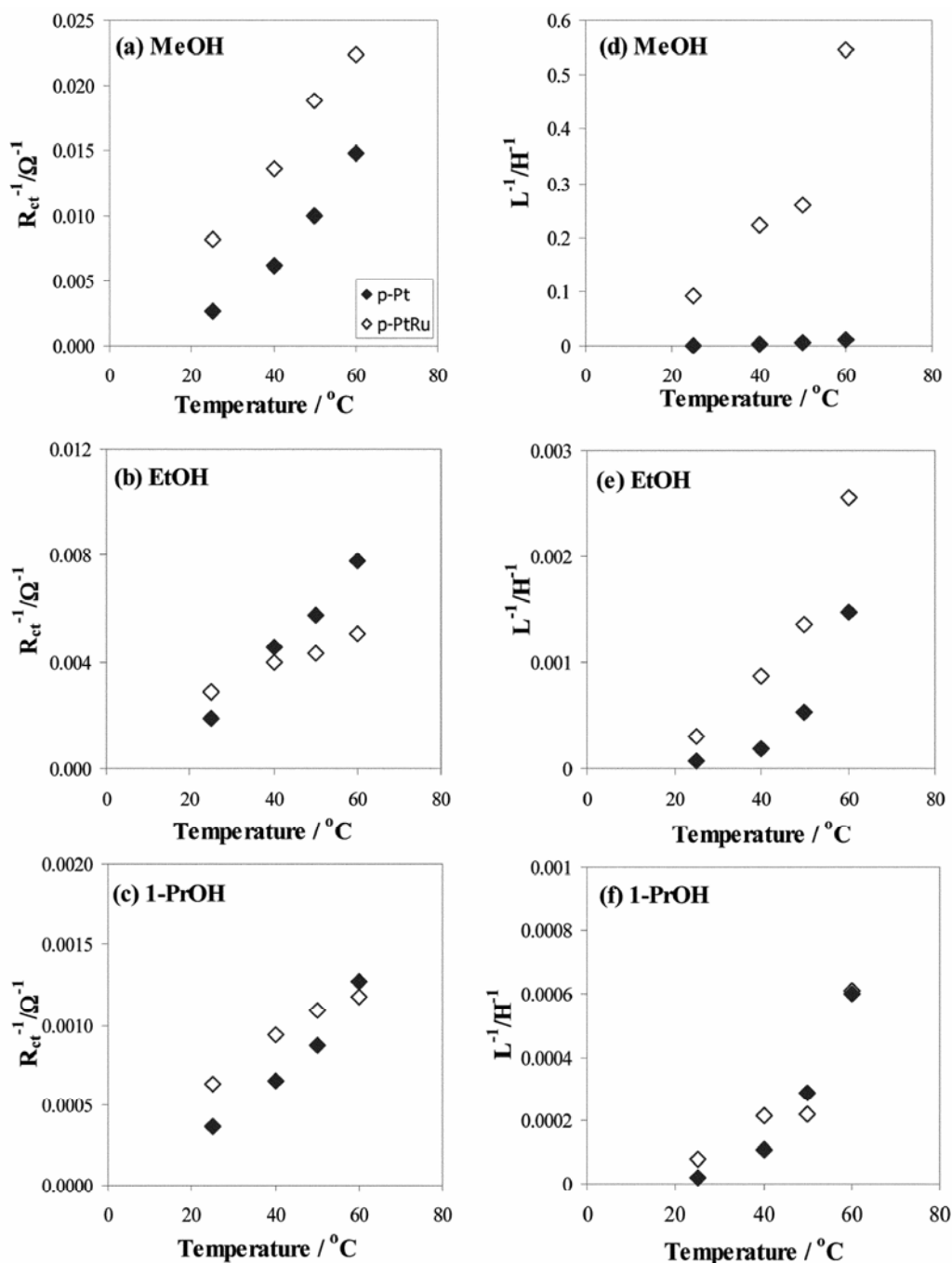
Figure 6. Plot of R_{ct}^{-1} (**a–c**) and L^{-1} (**d–f**) versus temperature for the electro-oxidation of 0·25 M methanol, 0·25 M ethanol, and 0.25 M 1-propanol on (♦) p-Pt and (◊) p-PtRu electrodes.

of methanol, ethanol and 1-propanol electro-oxidation on p-Pt electrode were 70·4, 52·2 and 32·8 kJ mol^{-1}, respectively. It is possible to explain that both ethanol and 1-propanol also occur via the C–C bond breaking pathway and lead to the lower of E_a value. The EIS results shown that the electro-oxidation of methanol prefer occurs via the electro-oxidation of CO_{ads} species, while ethanol and 1-propanol occur via the oxidation of alcohol (RCH_2OH_{ads}) to acid or aldehyde. The R_{ct}^{-1} and L^{-1} values were higher when modified surface electrode by Ru, especially for methanol and ethanol oxidation. However, the Ru modified surface cannot improve the electro-oxidation of 1-propanol.

Acknowledgements

References

1. Gupta S S and Datta J 2006 *J. Electroanal. Chem.* **594** 65
2. Zhou W J *et al* 2004 *J. Power Sources* **126** 16
3. Wu G, Li L and Xu B-Q 2004 *Electrochim. Acta* **50** 1
4. Otomo J, Li X, Kobayashi T, Wen C-J, Nagamoto H and Takahashi H 2004 *J. Electroanal. Chem.* **573** 99
5. Lamy C, Lima A, LeRhun V, Delime F, Coutanceau C and Léger J-M 2002 *J. Power Sources* **105** 283
6. Song S, Zhou W, Liang Z, Cai R, Sun G, Xin Q, Stergiopoulos V and Tsiakaras P 2005 *Appl. Catal. B: Environmental* **55** 65
7. Liu H, Song C, Zhang L, Zhang J, Wang H and Wilkinson D P 2006 *J. Power Sources* **155** 95
8. Dubau L, Hahn F, Coutanceau C, Léger J-M and Lamy C 2003 *J. Electroanal. Chem.* **554–555** 407
9. Léger J-M, Rousseau S, Coutanceau C, Hahn F and Lamy C 2005 *Electrochim. Acta* **50** 5118
10. Waszczuk P, Wieckowski A, Zelenay P, Gottesfeld S, Coutanceau C, Léger J-M and Lamy C 2001 *J. Electroanal. Chem.* **511** 55
11. Lee C-G, Umedab M and Uchida I 2006 *J. Power Sources* **160** 78
12. Burstein G T, Barnett C J, Kucenak A R and Williams K R 1997 *Catal. Today* **38** 425
13. Schmidt V M, Ianniello R, Pastor E and González S 1996 *J. Phys. Chem.* **100** 17901
14. Colmati F, Antolini E and Gonzalez E R 2006 *J. Power Sources* **157** 98
15. Rodrigues IdA, Souza J P I D, Pastor E and Nart F C 1997 *Langmuir* **13** 6829
16. Pastor E, Wasmus S, Iwasita T, Arévalo S MCGl and Arvia A J 1993 *J. Electroanal. Chem.* **350** 97
17. Gojković SLj, Vidaković T R and Đurović D R 2003 *Electrochim. Acta* **48** 3607
18. Chakraborty D, Chorkendorff I and Johannessen T 2006 *J. Power Sources* **162** 1010
19. Hsing I-M, Wang X and Leng Y-J 2002 *J. Electrochem. Soc.* **149** A615
20. Ciureanu M, Wang H and Qi Z 1999 *J. Phys. Chem.* **B103** 9645
21. Kabbabi A, Faure R, Durand R, Beden B, Hahn F, Léger J-M and Lamy C 1998 *J. Electroanal. Chem.* **444** 41
22. Vigier F, Gloaguen F, Léger J-M and Lamy C 2001 *Electrochim. Acta* **46** 4331
23. Ratana T 2005 The mechanistic study of the electro-oxidation reaction of small organic molecules on modified Pt electrodes by electrochemical impedance spectroscopy and other techniques (Ph.D. Dissertation). Mahidol University, Bangkok, Thailand