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Investigations of Intermediate-Temperature Alkaline Methanol Fuel Cell Electrocatalysis Using a Pressurized Electrochemical Cell

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1. Introduction

Direct methanol fuel cells (DMFCs) possess obvious advantages over traditional hydrogen fuel cells in terms of hydrogen storage, transportation, and the utilization of existing infrastructure. However, the commercialization of this fuel cell technology based on the use of proton-conductive polymer membranes has been largely hindered by its low power density owing to the sluggish kinetics of both anode and cathode reactions in acidic media and high cost owing to the use of noble metal catalysts. These could be potentially addressed by the development of alkaline methanol fuel cells (AMFCs). In alkaline media, the polarization characteristics of the methanol electrooxidation and oxygen electroreduction are far superior to those in acidic media (Yu et al., 2003; Prabhuram & Manoharan, 1998). Another obvious advantage of using alkaline media is less-limitations of electrode materials. The replacement of Pt catalysts with non-Pt catalysts will significantly decrease the cost of catalysts. Recently, the AMFCs have received increased attention (Dillon et al., 2004). However, these fuel cells are normally operated at temperature lower than 80 °C. In this low temperature range, both methanol electrooxidation and oxygen electroreduction reactions are not sufficiently facile for the development of high performance AMFCs. Considerable undergoing efforts are now focused on the development of highly active catalysts for accelerated electrode reactions.

Alternatively, increasing temperature has been proven as an effective way to accelerate electrode reactions. The changes of the reaction rates with increasing temperature are strongly determined by the values of activation energy, as described by the Arrhenius equation. More obvious changes are expected for the methanol electrooxidation in alkaline media than in acidic media since reported values of the activation energy are higher in alkaline media (Cohen et al, 2007). Additionally, increasing temperature may decrease concentration polarization, Ohmic polarization, and CO poisoning of the catalysts. All these advantages can contribute to the performance improvement of the AMFCs.

Further finding of increasing temperature for the methanol oxidation is that methanol can be efficiently converted with water in the aqueous phase over appropriate heterogeneous catalysts at temperatures near 200 °C to produce primarily H₂ and CO₂ (Huber et al., 2003;

Cortright et al., 2002). The aqueous-phase reforming (APR) process eliminates the need to vaporize both water and the oxygenated hydrocarbon, which reduces the energy requirements for producing hydrogen. Moreover, the formation of CO could be minimized since the APR occurs at temperatures and pressures where the water-gas shift reaction is favorable. The APR of methanol on supported Pt over 200~265 °C results in the production of H₂ at a usually high selectivity of around 99% as follows (Davda et al., 2005):



During the methanol APR, trace amount of methane is the side product and the use of more basic/neutral catalyst favors H₂ production. The methanol APR indicates that sluggish methanol oxidation reaction which has plagued low temperature AMFCs, could become highly facile in alkaline/neutral media at temperatures close to 200 °C where the APR of methanol is triggered. Substantially accelerated electrooxidation of methanol would make it possible to achieve low anode overpotentials. Therefore, the investigations of the electrooxidation of methanol in an intermediate-temperature range over the methanol-boiling temperature (around 80 °C) and the triggering temperature of the methanol APR (about 200 °C) would be of academic and practical importance for the development of high performance AMFC technology. This intermediate temperature range has been rarely used because of the limitation of boiling points of both methanol and water.

Our research efforts have been focused on the investigations of fuel cell electrocatalysis in alkaline media in the intermediate-temperature range of 80 to 200 °C for accelerated anode and cathode reaction kinetics, and the development of high performance AMFCs. In this work, we have successfully developed a pressurized electrochemical cell by modifying a Parr autoclave which can be operated at pressure up to 2000 psi and at temperature up to 200 °C. An Ag/AgCl electrode has been identified as a suitable internal reference electrode with good stability in this intermediate temperature range. It has been found that the methanol oxidation and oxygen reduction reactions can be significantly accelerated in aqueous alkaline media with increasing temperature. The former is characterized by an onset overpotential of less than 0.1 V at 150 °C for substantial methanol electrooxidation at Pt. Furthermore, highly facile methanol oxidation and oxygen reduction reactions have been also achieved at non-Pt electrodes. This accelerated kinetics of both the methanol oxidation and oxygen reduction reactions provides fundamental support for the development of novel methanol fuel cells. Accordingly, high performance intermediate-temperature alkaline methanol fuel cells using Pt and non-Pt electrocatalysts have been successfully demonstrated.

2. Experimental

2.1 Pressurized electrochemical cell

The pressurized electrochemical cell was constructed by modifying a 300 ml Parr autoclave equipped with a 200 ml glass liner, as shown in Fig. 1 (A) and (B). The working electrode was prepared by mechanically depositing high-surface-area catalysts onto a gold disk electrode of 0.5 mm in diameter, following a powder-rubbing procedure (Kucernak & Jiang, 2003), Fig. 1 (C). The mass of the catalyst layer was measured by dissolving the rubbed layer in boiling aqua regia, followed by removing the excess acid and measuring inductively

coupled plasma-atomic emission spectroscopy (ICP-AES) spectra. A 15 cm length Pt wire of 0.5 mm in diameter was used as the counter electrode. Three kinds of Ag-based reference electrodes were evaluated as the internal reference electrode under our conditions by monitoring the changes of both hydrogen- and oxygen-electrochemistry on measured voltammograms for a Pt electrode in 0.5 mol dm^{-3} potassium hydroxide (KOH) at varying temperature. It was found that the Ag/AgCl reference provides the most reproducible results while both Ag wire quasi-reference electrode and Ag/Ag₂O electrode were inapplicable. The Ag/AgCl reference electrode was introduced into a glass tube containing 0.1 mol dm^{-3} HCl which was separated from KOH solution in the working electrode chamber by a microporous ceramic pellet fixed at the top end of the glass tube. The potentials of the Ag/AgCl were measured versus a reversible hydrogen electrode (RHE) at varying temperature in a hydrogen atmosphere. In the following sections, all potentials reported were referred to the RHE unless otherwise stated.

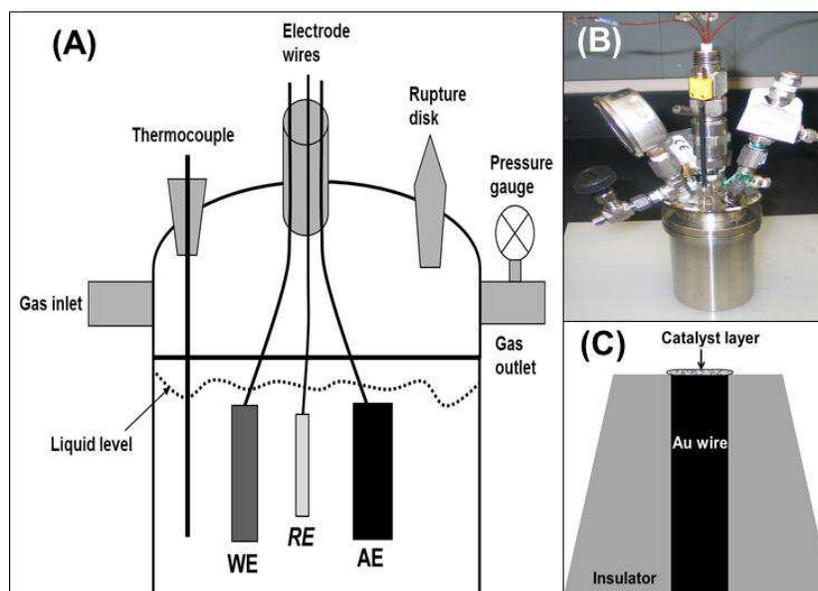


Fig. 1. A pressurized electrochemical cell based on a modified Parr autoclave. Schematic diagram of the cell (A); Image of the cell (B); and Schematic structure of a working electrode (C).

2.2 Instruments and materials

Both voltammetric and chronoamperometric measurements were performed using Autolab general purpose electrochemical system (Ecochemie, Netherland). A lab-constructed single-cell system with temperature control, gas flow rate and pressure control, and liquid flow rate and pressure control constructed was used for the measurements of fuel cell performance.

All chemicals and materials were used as received without further purification. All solutions were prepared from methanol (>99.9%, Aldrich) or KOH (>85%, Aldrich) with deionized water (18.2 M Ω cm). Unsupported electrocatalysts were used in voltammetric and chronoamperometric measurements, including Pt black (Alfa, S.A. typically $27 \text{ m}^2 \text{ g}^{-1}$), Pd black (Alfa, S.A. typically $20 \text{ m}^2 \text{ g}^{-1}$) and Ag nanopowder (Alfa, 20-40 nm). Carbon supported Pt (Fuel Cell Store, 60 wt% Pt/C) and carbon supported Pd (Sigma-Aldrich, 30

wt% Pd/C) were used for the preparation of gas diffusion electrodes with carbon-cloth as the diffusion layer. All gases used were of research grade.

2.3 Electrochemical measurements

During the measurements of base voltammograms and methanol electrooxidation, high-purity nitrogen was introduced into the electrochemical cell to inhibit vaporization of the liquid phase at elevated temperature, and gas-phase pressure was set at 300 psi unless otherwise stated. Background voltammograms were measured in 0.5 mol dm^{-3} KOH at 50 mV s^{-1} . All methanol oxidation experiments were carried out in 0.5 mol dm^{-3} KOH + 0.5 mol dm^{-3} methanol. Steady-state voltammograms for the methanol oxidation were recorded at a scan rate of 10 mV s^{-1} . The measurements of the chronoamperograms were performed by stepping potential from -1.1 V where no methanol oxidation occurs to a given value where methanol is oxidized. For the purpose of comparison, the oxidation of hydrogen was investigated under similar conditions by introducing high-purity hydrogen into the electrochemical cell to equilibrate with the solution of 0.5 mol dm^{-3} KOH solution at 200 psi. All oxygen reduction experiments were carried out in 0.5 mol dm^{-3} KOH solution equilibrated with 300 psi high purity O_2 . To investigate the electrochemical oxidation of CO, high purity CO was introduced into the electrochemical cell with the pressure set at 300 psi.

3. Results and Discussion

3.1 Ag/AgCl reference electrode

Base cyclic voltammograms for a high-surface-area Pt-coated Au disk in 0.5 mol dm^{-3} KOH solution as a function of temperature are shown in Fig 2. Analogous to literature results, three characteristic zones corresponding to hydrogen electrochemistry, double layer and oxygen electrochemistry are observed. The peaks associated with hydrogen adsorption/desorption in the hydrogen electrochemistry zone over -1.15 to around -0.60 V are negatively shifted as the temperature is increased, accompanied by obvious decrease in the peak currents at higher temperature. The decrease in these peak currents and the double layer currents observed in a narrow potential range over -0.60 V to -0.50 V suggest that the electrochemical surface area of the electrodes is decreased at higher temperature. This could be caused by the accelerated adsorption of electrolyte components and/or impurities onto the electrode surface, resulting in the blocking of some electrode surfaces. In the oxygen electrochemistry zone over -0.5 to approximately 0.2 V , the potential of the cathode peak corresponding to the reduction of surface oxides is slightly shifted as the temperature is increased from 20° to 150°C . All these facts are indicative of the possibility of using the Ag/AgCl electrode as the internal reference electrode in aqueous KOH solution at elevated temperature.

The standard potential of the Ag/AgCl electrode in aqueous solution containing chloride has been measured in a wide temperature range over 0 to approximately 300°C , and its temperature dependence has been analyzed by several groups (Öijerholm et al., 2009; Greeley et al., 1960). Based on the standard potential of the Ag/AgCl electrode of around 0.23 V vs. standard hydrogen electrode (SHE) and the reversible hydrogen potential in 0.5 mol dm^{-3} KOH solution (-0.81 V vs. SHE) at 20°C , the value of the onset potential for hydrogen evolution would be around -1.04 V vs. Ag/AgCl if the hydrogen evolution

overpotential on Pt is neglected. This value is very close to our measured value (-1.1 V). This agreement between the calculated value and measured value suggests that the Ag/AgCl electrode satisfactorily functions as the internal reference electrode in hydroxide solution. This is also supported by the characters of the hydrogen and oxygen electrochemistry for Pt electrode at elevated temperature.

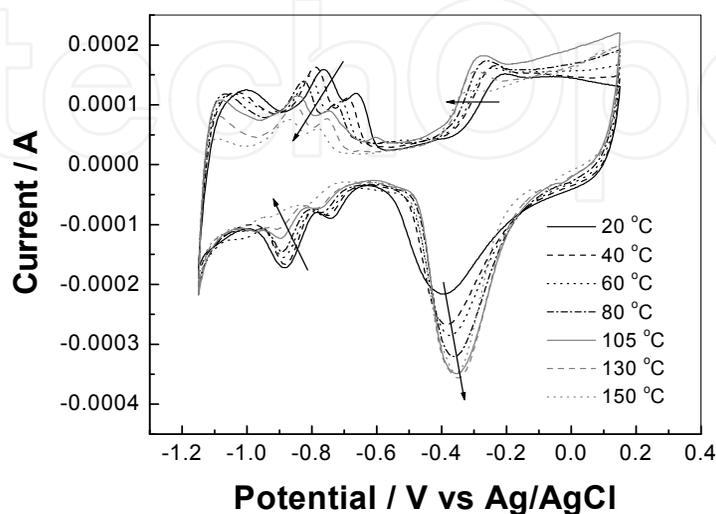


Fig. 2. Cyclic voltammograms for a high-surface Pt-coated Au disk electrode of 0.5 mm diameter in 0.5 mol dm^{-3} KOH at a scan rate of 50 mV s^{-1} as a function of reaction temperature.

To further evaluate the suitability of using the Ag/AgCl electrode as the internal reference in the wide temperature range of our interest, the cyclic voltammograms for a high-surface-area Pt-coated Au disk in 0.5 mol dm^{-3} KOH solution equilibrated with 200 psi H_2 are measured and shown in Fig. 3. The positive-going scans are characteristic of fast-rising currents at lower overpotentials, followed by slow-rising currents and limiting currents at higher overpotentials. These characteristics are similar to literature results for H_2 oxidation at Pt electrodes in aqueous base solution (Bao & Macdonald, 2007; Schmidt et al., 2002). Increasing reaction temperature clearly increases the limiting currents. These changes are mainly caused by the concentration changes of dissolved H_2 as a function of the temperature. The potential value at zero current ($E_{\text{H}_2, I=0}$) measured in Fig. 3 is negatively shifted by around 40 mV as the temperature is increased from 20 to 150 °C.

The reversible potential of hydrogen reaction depends upon the reaction temperature and the pH value of the reaction medium as follows:

$$E_{\text{H}_2}^0 = \frac{-2.303RT}{F} \text{pH} \quad (2)$$

where T is in K. Substituting $\text{pH}=13.69$ (corresponding to $0.5 \text{ mol dm}^{-3} \text{ OH}^-$) and the values of R and F into Equation 2 results in its simplification as follows:

$$E_{\text{H}_2}^0 = -2.7 \times 10^{-3} T \quad (3)$$

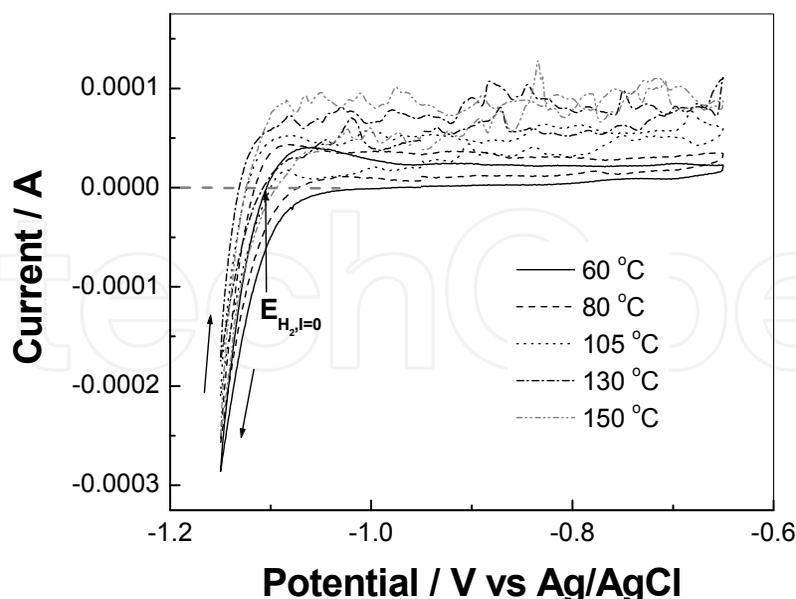


Fig. 3. Temperature dependence of cyclic voltammograms for a high-surface Pt-coated Au disk electrode of 0.5 mm diameter in 0.5 mol dm⁻³ KOH equilibrated with 200 psi H₂ at a scan rate of 10 mV s⁻¹.

According to Equation 3, the reversible hydrogen potential (*RHE*) should be negatively shifted with increasing temperature. At 20°C, the value is -0.81 V, and it is expected to be -1.14 V at 150°C. This means that a negative reversible potential shift should be around 0.33 V as the reaction temperature is increased from 20° to 150°C if the potential of the Ag/AgCl reference electrode is a constant independent upon the temperature. Because the value of $E_{H_2, I=0}$ is a signature of the reversible hydrogen potential, its shift with increasing temperature should be theoretically similar to that of the *RHE* if the Ag/AgCl reference electrode potential remains constant. However, Fig. 3 demonstrates that increasing temperature from 20° to 150°C produces a negative shift of only around 40 mV, much lower than 0.33 V. Therefore, the small $E_{H_2, I=0}$ shift strongly indicates that the potential of the Ag/AgCl reference electrode would have a temperature dependence similar to that of the *RHE*. This consistence provides a big convenience to investigate the kinetics of fuel cell reactions in a wide temperature range using an internal Ag/AgCl reference electrode since the Ag/AgCl reference electrode could be used as an equivalent of the reversible hydrogen electrode.

The potential difference between the Ag/AgCl electrode and the *RHE* is experimentally measured in a H₂ atmosphere. Fig. 4 shows the temperature dependence of the potential difference. It is clearly seen that the difference is less dependent upon the reaction temperature in comparison to the individual *RHE*. A potential difference of around 80 mV as the temperature is increased from 20 to 150 °C. The temperature dependence of their potential difference could be linearly approximated as follows:

$$\Delta E = E_{Ag/AgCl} - E_{RHE} = -4.4 \times 10^{-4} T - 0.980 \quad (4)$$

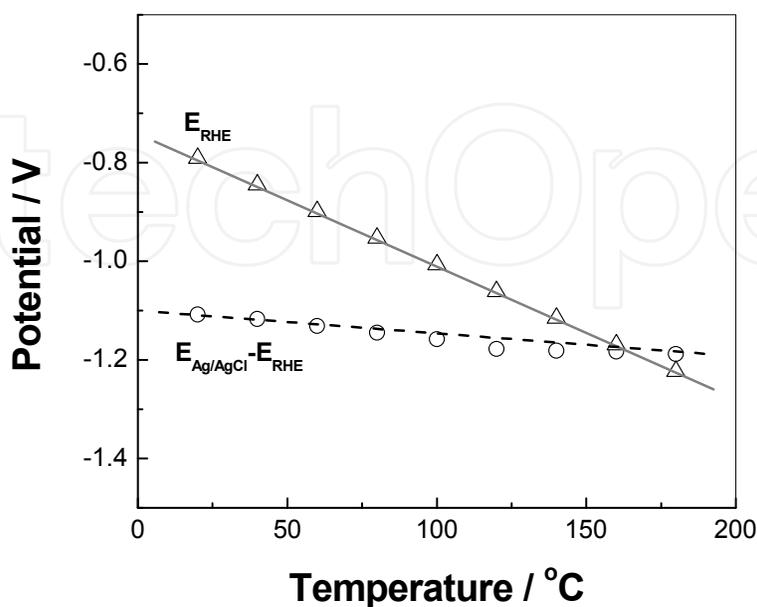


Fig. 4. Temperature dependence of calculated *RHE* potential and measured potential difference between *Ag/AgCl* electrode and *RHE*.

In Equation 4, the first term is much smaller than the second term being a constant. This supports that the temperature dependence of the *Ag/AgCl* electrode is similar to that of the *RHE*. Therefore, the *Ag/AgCl* electrode can be approximated as an equivalent of the *RHE* in preliminary investigations. The variations of measured electrode potentials with temperature are signature of the changes in the reaction kinetics. For the kinetic analysis, all potentials can be corrected to the *RHE* scale according to Equation 4.

3.2 Methanol electrooxidation

Cyclic voltammograms for a high-surface-area Pt-coated Au disk electrode in 0.5 mol dm^{-3} KOH solution containing 0.5 mol dm^{-3} methanol as a function of temperature (Fig. 5) clearly show that the onset potentials of substantial methanol electrooxidation are negatively shifted by increasing temperature. Because this prominent negative potential shift with increasing temperature is not caused by the potential shift of the reference electrode, it is reasonably believed that the electrooxidation of methanol is substantially accelerated. To assess the kinetics of methanol electrooxidation, we have compared the onset potentials for methanol oxidation and H_2 oxidation (Fig. 3) under similar conditions. The value of their onset potential difference is significantly decreased with increasing temperature. At $150 \text{ }^\circ\text{C}$, a typical value is approximately 60 mV. It is well accepted that the hydrogen oxidation is highly facile on Pt, this value indicates that highly facile electrooxidation of methanol can be achieved on single-element Pt electrocatalyst in aqueous alkaline solution in the intermediate-temperature range.

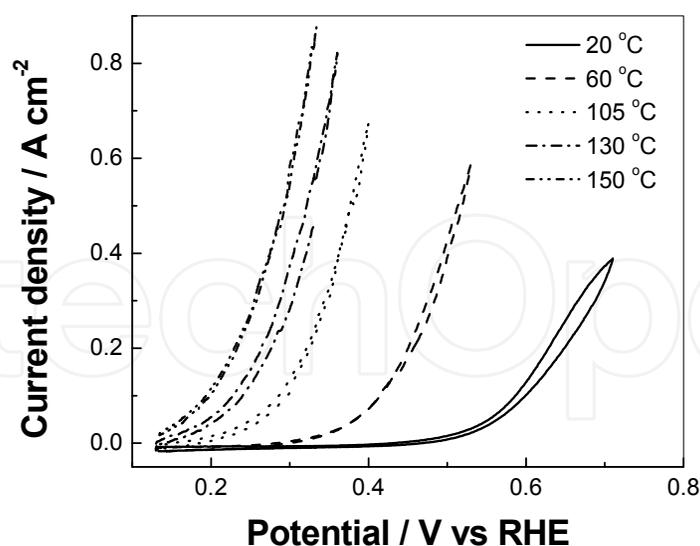


Fig. 5. Temperature dependence of cyclic voltammograms for a high-surface Pt-coated Au disk electrode of 0.5 mm diameter in 0.5 mol dm⁻³ KOH + 0.5 mol dm⁻³ CH₃OH at a scan rate of 10 mV s⁻¹.

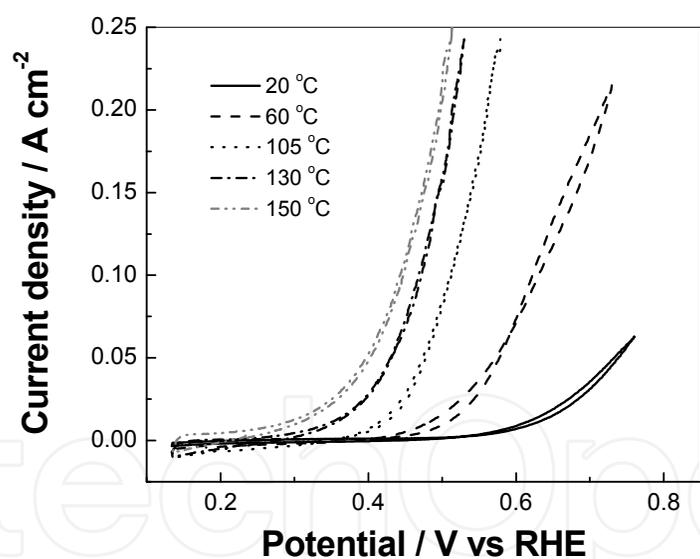


Fig. 6. Temperature dependence of cyclic voltammograms for a high-surface Pd-coated Au disk electrode of 0.5 mm diameter in 0.5 mol dm⁻³ KOH + 0.5 mol dm⁻³ CH₃OH at a scan rate of 10 mV s⁻¹.

Cyclic voltammograms for a high-surface-area Pd-coated Au disk electrode in 0.5 mol dm⁻³ KOH solution containing 0.5 mol dm⁻³ methanol as a function of temperature are shown in Fig. 6. Similar temperature dependence is observed. Increasing temperature significantly shifts the onset overpotential for methanol electrooxidation to more negative potentials. The value of the onset overpotential is decreased from 0.52 V to approximately

0.20 V when the temperature is increased from 20 °C to 150 °C. Although these values are higher compared to those measured at Pt electrode under the similar conditions, the value of 0.20 V would suggest that Pd is highly active toward the methanol oxidation. It is therefore prospective to replace Pt with Pd in alkaline methanol fuel cells for decreased cost since Pd is normally three times cheaper than Pt. Moreover, the activity of Pd-based catalysts could be further improved by introducing metal oxides to Pd or alloying Pd with other metal elements.

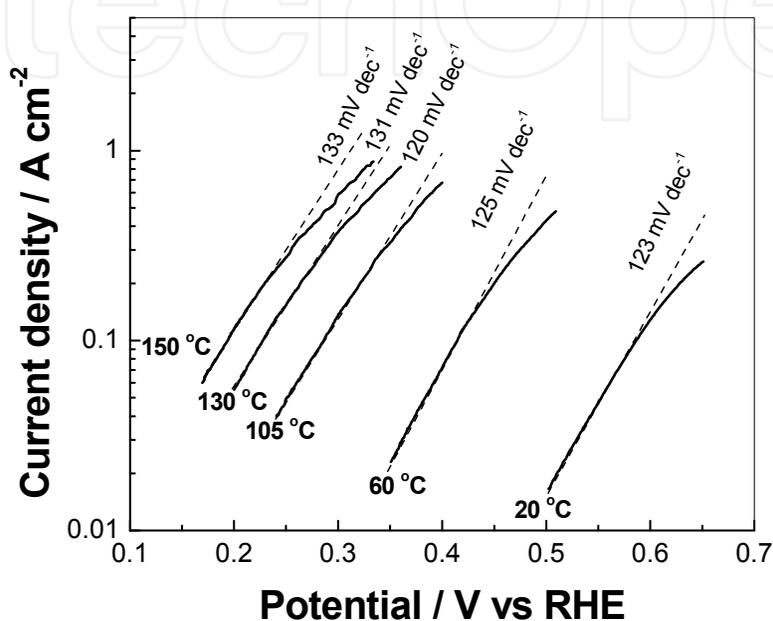


Fig. 7. Tafel plots for methanol electrooxidation at a high-surface Pt-coated Au disk electrode of 0.5 mm diameter in 0.5 mol dm⁻³ KOH + 0.5 mol dm⁻³ CH₃OH as a function of reaction temperature with data extracted from the positive-scans in Fig. 5.

Tafel plots for the methanol electrooxidation at the high-surface-area Pt electrode in a solution of 0.5 mol dm⁻³ KOH and 0.5 mol dm⁻³ CH₃OH as a function of temperature are shown in Fig. 7. The values of measured Tafel slopes range from 120 mV dec⁻¹ to 133 mV dec⁻¹ in the intermediate-temperature range over 20 to approximately 150 °C. These values are in agreement with literature results obtained under similar conditions at a platinized Pt electrode and single crystal Pt(110) and Pt(111) electrodes (Tripković et al., 1998 & 2002). It has been proposed that the chemical reaction between the surface intermediate HCO_{ad} and OH_{ad} is the rate-determining step and the overall rate equation for the methanol electrooxidation could be written as follows (13):

$$j = A c_{\text{CH}_3\text{OH}}^{0.5} c_{\text{OH}}^{0.5} \exp\left(\frac{\alpha F}{RT} \eta\right) \quad (5)$$

where A is a constant and other terms have their normal meanings. From this expression, a Tafel slope ranging from 120 to 164 mV dec⁻¹ as the temperature is increased from 20 to 150 °C could be obtained, which fits with the experimental data shown in Fig. 7.

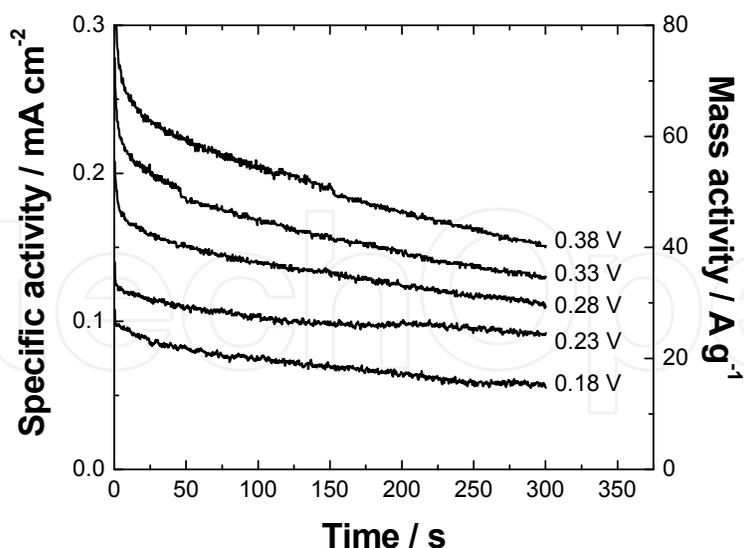


Fig. 8. Dependence of chronoamperometric curves at a controlled potential at 150 °C for a high-surface Pt-coated Au disk electrode of 0.5 mm diameter in 0.5 mol dm⁻³ KOH + 0.5 mol dm⁻³ CH₃OH upon polarization time.

The activity of high-surface-area Pt toward the methanol electrooxidation in aqueous KOH solution at 150 °C is evaluated using chronoamperometry. The current-time transients at controlled potentials are shown in Fig. 8. The mass activity was estimated from measured pseudo steady-state chronoamperometric current upon a polarization of 300 s. This figure shows that pseudo current densities can be attained even at 0.18 V vs RHE. This indicates that methanol can be dominantly oxidized to non-poisoning products in alkaline media even at low overpotentials. The activity of Pt is rather high, characterized by a mass activity of 14.9 A g⁻¹ and a specific area activity of 0.05 mA cm⁻² at an overpotential of 0.18 V. This fact is important for the improvement of the anodic reaction kinetics. In this figure, the activity decays are slow at low overpotentials and they become fast at high overpotentials. The slow decays may be caused by the surface blocking of Pt electrode owing to the adsorption of surface poisons (Matsuoka et al., 2005). Analogous to methanol oxidation in acidic media, CO has been also proposed as the predominant surface poison formed in the methanol oxidation in alkaline media. Additionally, progressive carbonation of the solution caused by CO₂ produced by oxidation reaction may decrease the pH value of the solution close to the electrode surface, leading to a decrease in reactivity. It is reasonable to attribute the progressive carbonation for the fast activity decays.

3.3 CO electrooxidation

Adsorption and oxidation of CO on Pt surfaces in aqueous electrolytes has been extensively studied, primarily because of the importance of CO as a catalyst poison and also as a reaction intermediate (Garcia & Koper, 2011; Spendelow et al., 2006). The onset of CO oxidation on Pt occurs at lower overpotentials alkaline media than in acidic media. However, all these studies have been performed at low temperature. Here we have investigated the oxidation of dissolved CO in alkaline media in the intermediate

temperature range. Fig. 9 shows the temperature dependence of cyclic voltammograms for a high-surface Pt-coated Au disk electrode of 0.5 mm diameter in 0.5 mol dm⁻³ KOH equilibrated with 300 psi CO. The voltammetric characters for the oxidation of dissolved CO in the alkaline media are significantly different from those reported for adsorbed CO. The CO oxidation commences at around 0.23 V vs RHE at 60 °C. The oxidation current initially increases with increasing potential until a maximum current is reached at approximately 0.65 V. Further increase in the potential results in sudden oxidation current decrease. These facts interestingly indicate that the oxidation of CO proceeds on oxide-free Pt surface and the formation of the surface oxide inhibits the CO oxidation since the formation of the surface oxide on Pt commences at around 0.65 V (Fig. 2). These are quite different from literature results for the oxidation of adsorbed CO on Pt in acidic and alkaline media since the latter is normally triggered by the formation of surface oxide.

Increasing temperature substantially increases the CO oxidation at the oxide-free Pt surface and diminishes the onset overpotential. At temperature higher than 130 °C, the onset overpotential is approximately 0.15 V. This value is lower than those potentials used for the chronoamperometric measurements for the methanol oxidation on Pt (Fig. 8). Therefore, the current decays are less likely to be caused by the formation of surface CO as a catalyst poison.

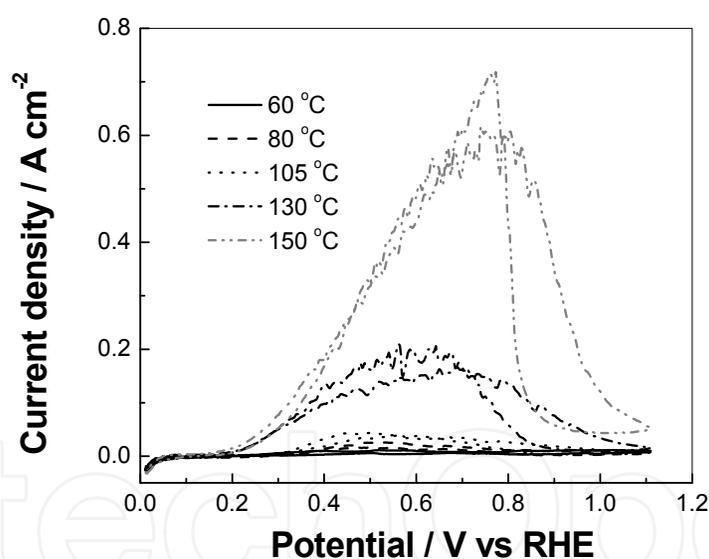


Fig. 9. Variation of cyclic voltammograms for a high-surface Pt-coated Au disk electrode of 0.5 mm diameter in 0.5 mol dm⁻³ KOH equilibrated with 300 psi CO as a function of reaction temperature.

We have also investigated the oxidation of dissolved CO at the Pd electrode. Fig. 10 shows the temperature dependence of cyclic voltammograms for a high-surface Pd-coated Au disk electrode of 0.5 mm diameter in CO-saturated 0.5 mol dm⁻³ KOH. The temperature dependence of the CO oxidation is more complicated at the Pd electrode than at the Pt electrode. At temperature lower than 105 °C, the oxidation of dissolved CO is very slow. A broad oxidation wave can be seen in the double layer region. However, the CO oxidation is

inhibited at more positive potentials. This behaviour becomes more pronounced at 130 °C. The onset of the oxidation occurs at 0.20 V. Further increasing temperature causes substantial changes in the voltammograms. At 150 °C, the onset potential for the CO oxidation is shifted negative to approximately 0 V vs RHE. This value is much lower than the onset potential (0.2 V) for the methanol oxidation under similar conditions (Fig. 6). Moreover, the oxidation current is increased with increasing potentials even in the oxide formation region. These strongly suggest that the CO oxidation is more facile than the methanol oxidation at the Pd electrode at 150 °C. Therefore, it is highly likely that methanol can be oxidized to non-poisoning products rather than surface poison CO under our conditions.

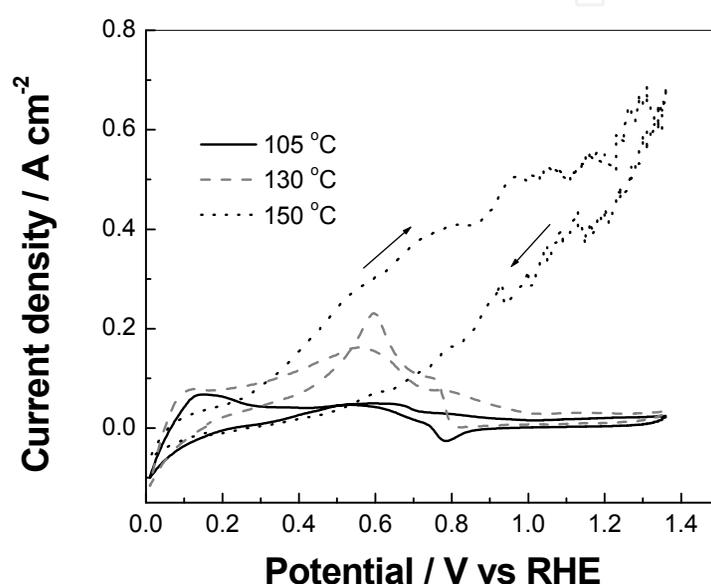


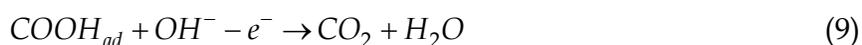
Fig. 10. Variation of cyclic voltammograms for a high-surface Pd-coated Au disk electrode of 0.5 mm diameter in 0.5 mol dm⁻³ KOH equilibrated with 300 psi CO as a function of reaction temperature.

It is well accepted that the oxidation of the adsorbed CO at Pt and Pd follows a Langmuir-Hinshelwood mechanism with the reaction between adsorbed CO and surface OH as the rate-determining step as follows (Spendelow et al., 2004):



This mechanism suggests that the substantial oxidation of adsorbed CO occurs in the oxide-formation potential region. However, cyclic voltammograms in Figs. 9 and 10 show that the CO oxidation occurs at the oxide-free electrodes and is inhibited by the oxide formation. The CO oxidation is also likely to proceed via the following mechanism:





A theoretical *Tafel* slope of around 167 mV dec⁻¹ will be expected at 150 °C if the electrochemical formation of COOH_{ad} is the rate-determining step. This value is close to our experimental value of 138 mV dec⁻¹ measured from the polarization region over 0.2 to 0.35 V shown in Fig. 9 at the same temperature.

3.4 Oxygen electroreduction

Pt is the most used and active catalyst for the oxygen reduction reaction (*orr*) and all of the Pt-group metals reduce oxygen in alkaline media according to the 4-electron process (Lima & Ticianelli, 2004). Silver has been studied as a potential replacement of Pt due to its high activity for the *orr* and its low cost. The *orr* occurs with the participation of 2 and 4-electron processes, depending on its oxidation state and electrode potential (Kotz & Yeager, 1980). Moreover, the size of the Ag particles affects the different catalytic activity for these two processes (Demarconnay et al., 2004).

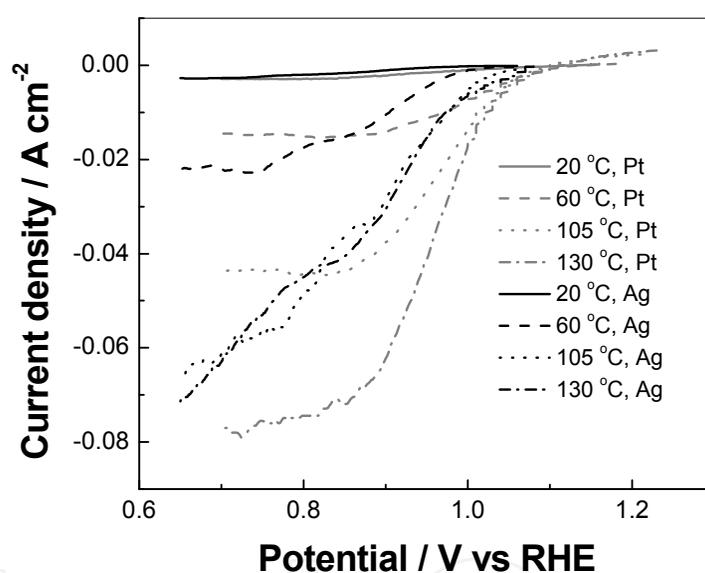


Fig. 11. Temperature dependence of polarization curves at a scan rate of 10 mV s⁻¹ for a high-surface Pt (in gray) and Ag (in black) coated Au disk electrode of 0.5 mm diameter in 0.5 mol dm⁻³ KOH equilibrated with 300 psi O₂.

We have compared the activities of Pt and Ag for the *orr* in alkaline media in the intermediate temperature range. Fig. 11 shows the temperature dependence of voltammograms for high surface area Ag and Pt coated gold disk electrode of 0.5 mm in diameter in 0.5 M KOH solution equilibrated by 300 psi O₂. At both Pt and Ag electrodes, the values of the current density at lower overpotentials are substantially increased with increasing temperature with obvious positive shift of the onset potential. At higher overpotentials, a limiting current plateau is observed and it is increased with increasing temperature. The increase of the limiting current is probably caused by higher O₂ diffusion efficient and concentration in the aqueous solution at higher temperature.

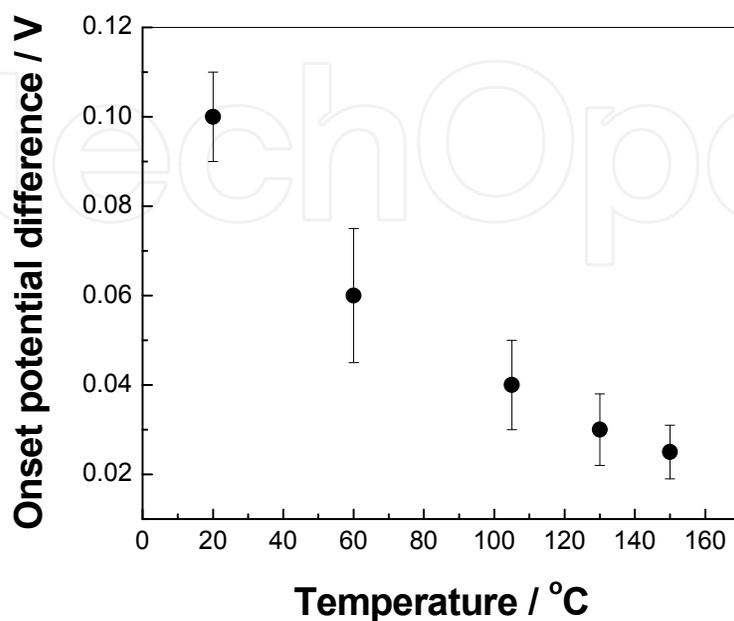


Fig. 12. Temperature dependence of onset polarization potential difference for the *orr* on Pt and Ag with data taken from Fig. 11.

The onset potential difference for the *orr* at Ag and Pt as a function of reaction temperature is shown in Fig. 12. Their potential difference is obviously decreased with increasing temperature. At room temperature, the difference is approximately 0.10 V. It falls in a range of 0.02 to 0.03 V when the temperature is higher than 130 °C. This indicates that Ag is a very promising electrocatalyst for the *orr* in the intermediate temperature range. Although the stability of Ag in alkaline media is questioned, a few strategies have been proven efficient to this issue.

3.5 Single cell performance

Based on the above fundamental studies, an intermediate-temperature alkaline methanol fuel has been developed and its performance is measured using a single-cell system with temperature control, gas flow rate and pressure control, and liquid flow rate and pressure control.

The performance of the novel fuel cell utilizing commercial Pt/C as both anode and cathode catalysts under optimized operating conditions is demonstrated in Fig. 13. The peak power density seen at around 280 mA cm⁻² reaches 90 mW cm⁻². This value is much higher than a typical value of around 50 mW cm⁻² of the state-of-the-art DMFCs using Nafion[®]-based proton-conducting membranes and PtRu anode catalysts (Dillon et al, 2004).

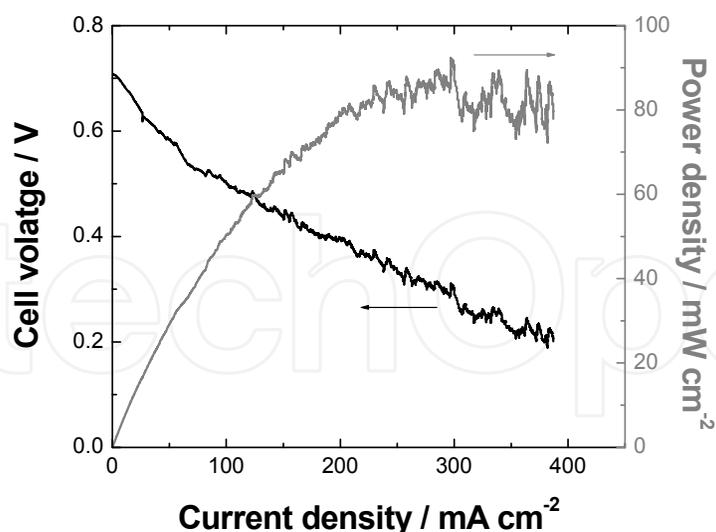


Fig. 13. Dependence of cell voltage and power density on current density for an intermediate-temperature alkaline methanol fuel using Pt/C for both anode and cathode and operated at 120 °C. Anode feed: 2 mol dm⁻³ CH₃OH + 2 mol dm⁻³ KOH; cathode feed: 120 SCCM O₂.

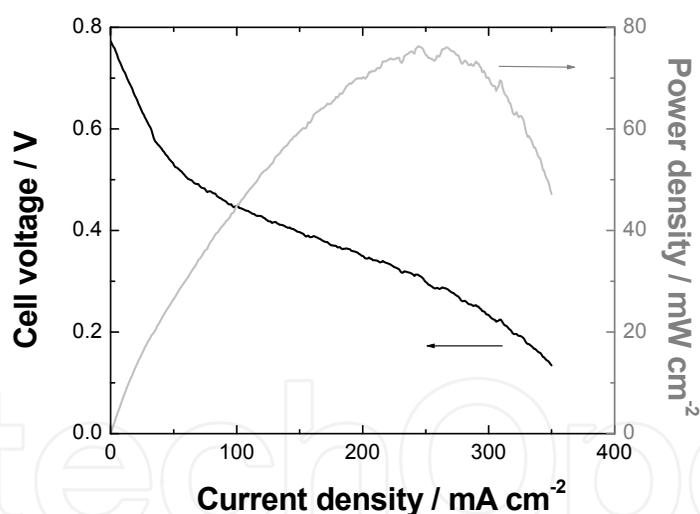


Fig. 14. Dependence of cell voltage and power density on current density for an intermediate-temperature alkaline methanol fuel using Pd/C for anode and Ag/C for cathode operated at 140 °C. Anode feed: 2 mol dm⁻³ CH₃OH + 2 mol dm⁻³ KOH; Cathode feed: 120 SCCM O₂.

To evaluate the potential of using non-Pt catalysts in the novel fuel cell, the performance of the fuel cell utilizing Pd/C anode and Ag/C cathode has been measured and is shown in Fig. 14. It is characterized by a peak power density of around 75 mW cm⁻² seen at around 260 mA cm⁻². This performance is comparable to that of the fuel cell utilizing Pt catalysts. Therefore, significant cost reduction would be expected for the novel fuel cell without the

cost of the performance because Pd and Ag are much cheaper than Pt. Further cost reduction will be dependent up the advance of the non-noble catalysts for the methanol oxidation and the *orr*.

4. Conclusion

Increasing temperature has been proven as an effective way to accelerate fuel cell reactions. To investigate the fuel cell reactions in the intermediate temperature of 80 to 200 °C, we have developed a pressurized electrochemical cell based on a modified commercial Parr autoclave which can be pressurized up to 2000 psi. In this electrochemical cell, aqueous electrolyte solutions and liquid fuels can exist in their liquid forms in the intermediate-temperature range at varying balance pressure. This makes the investigations of intermediate-temperature fuel cell electrocatalysis possible. To further address experimental challenges, we have evaluated three kinds of Ag-based electrodes as an internal reference electrode in basic media and have found that the Ag/AgCl electrode could act as the internal reference electrode with satisfactory stability. To facilitate the investigations of the fuel cell reactions on high-surface-area electrocatalysts, a powder-rubbing procedure has been used to mechanically deposit the electrocatalysts onto a gold substrate of 0.5 mm in diameter. Based upon these efforts, well-developed cyclic voltammograms and chronoamperograms for the electrochemical methanol oxidation and oxygen reduction in the intermediate temperature range have been obtained.

It is encouragingly found that the methanol electrooxidation in alkaline media on high-surface-area Pt and Pd electrodes can be substantially accelerated by increasing temperature, characterized by obvious decrease in the onset overpotential with increasing temperature. Moreover, CO could be oxidized at lower onset potentials than methanol in the intermediate temperature range under similar conditions. This strongly indicates that CO is no longer a poison limiting the methanol oxidation. Replacement of Pt with Pd produces no substantial decrease in the activity towards the methanol oxidation. For the electrochemical oxygen reduction, silver demonstrates a high activity in the intermediate temperature range which is comparable to that of high surface area Pt. This indicates the possibility of using non-Pt catalysts in intermediate-temperature alkaline methanol fuel cells. Our preliminary fuel cell studies demonstrate the high performance of intermediate-temperature alkaline methanol fuel cell with Pt and non-Pt catalysts.

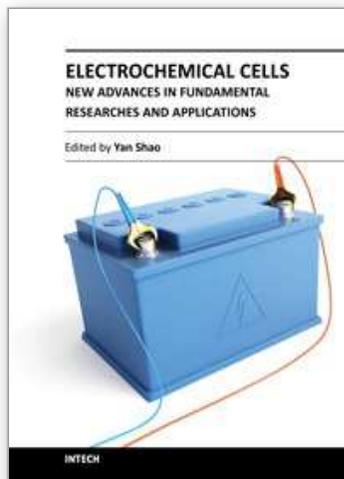
5. References

- Yu, H., Scott, K. & Reeve, W. (2003). A Study of the Anodic Oxidation of Methanol on Pt in Alkaline Solutions. *Journal of Electroanalytical Chemistry*, Vol.547, No.1, (April 2003), pp. 17-24, ISSN: 00220728
- Prabhuram, J. & Manoharan, R. (1998). Investigation of Methanol Oxidation on Unsupported Platinum Electrodes in Strong Alkali and Strong Acid. *Journal of Power Sources*, Vol.74, No.1, (July 1998), pp. 54-61, ISSN: 03787753
- Dillon, R., Srinivasan, S., Aricò, S. & Antonucci, V. (2004). International Activities in DMFC R&D: Status of Technologies and Potential Applications. *Journal of Power Sources*, Vol.127, No. 1-2, (March 2004), pp. 112-126, ISSN: 03787753

- Cohen, J., Volpe, D. & Abruña, H. (2007). Electrochemical Determination of Activation Energies for Methanol Oxidation on Polycrystalline Platinum in Acidic and Alkaline Electrolytes. *Physical Chemistry Chemical Physics*, Vol.9, No.1, (January 2007), pp. 49-77, ISSN: 1463-9076.
- Huber, W., Shabaker, W. & Dumesic, A. (2003). Raney Ni-Sn Catalyst for H₂ Production from Biomass-derived Hydrocarbons. *Science*, Vol.300, No.5628, (June 2003), pp. 2075-2077, ISSN: 00368075
- Cortright, D., Davda, R. & Dumesic, A. (2002). Hydrogen from Catalytic Reforming of Biomass-derived Hydrocarbons in Liquid Water. *Nature*, Vol.418, No.6901, (August 2002), pp. 964-967, ISSN: 00280836
- Davda, R., Shabaker, W., Huber, W., Cortright, D. & Dumesic, A. (2005). A Review of Catalytic Issues and Process Conditions for Renewable Hydrogen and Alkanes by Aqueous-phase Reforming of Oxygenated Hydrocarbons over Supported Metal Catalysts. *Applied Catalysis B: Environmental*, Vol. 56, No. 1-2, (March 2005), pp. 171-186, ISSN: 09263373
- Kucernak, A. & Jiang, J. (2003). Mesoporous Platinum as a Catalyst for Oxygen Electroreduction and Methanol Electrooxidation. *Chemical Engineering Journal*, Vol.93, No.1, (May 2003), pp. 81-90, ISSN: 13858947
- Öijerholm, J., Forsberg, S., Hermansson, P. & Ullberg, M. (2009). Relation between the SHE and the Internal AgAgCl Reference Electrode at High Temperatures. *Journal of the Electrochemical Society*, Vol.156, No.3, pp. P56-P61, ISSN: 00134651
- Greeley, S., Smith Jr., T., Stoughton, W. & Lietzke, H. (1960). Electromotive Force Studies in Aqueous Solutions at Elevated Temperatures. I. The Standard Potential of the Silver-silver Chloride Electrode. *Journal of Physical Chemistry*, Vol.64, No.5, pp. 652-657, ISSN: 00223654
- Bao, J. & Macdonald, D. (2007). Oxidation of Hydrogen on Oxidized Platinum. Part I: The Tunneling Current. *Journal of Electroanalytical Chemistry*, Vol.600, No.1, (February 2007), pp. 205-216, ISSN: 00220728
- Schmidt, J., Ross Jr., N. & Markovic, M. (2002). Temperature Dependent Surface Electrochemistry on Pt Single Crystals in Alkaline Electrolytes: Part 2. The Hydrogen Evolution/Oxidation Reaction. *Journal of Electroanalytical Chemistry*, Vol.524-525, No.3, (May 2002), pp. 252-260, ISSN: 00220728
- Tripković, V., Popović, D., Momčilović & D., Dražić, M. (1998). Kinetic and Mechanistic Study of Methanol Oxidation on a Pt(110) Surface in Alkaline Media. *Electrochimica Acta*, Vol.44, No.6-7, (November 1998), pp. 1135-1145, ISSN: 00134686
- Tripković, V., Popović, D., Momčilović, D. & Dražić, M. (1998). Kinetic and Mechanistic Study of Methanol Oxidation on a Pt(100) Surface in Alkaline Media. *Journal of Electroanalytical Chemistry*, Vol.448, No.2, (May 1998), pp. 173-181, ISSN: 00220728
- Matsuoka, K., Iriyama, Y., Abe, T., Matsuoka, M. & Ogumi, Z. (2005). Electro-oxidation of Methanol and Ethylene Glycol on Platinum in Alkaline Solution: Poisoning Effects and Product Analysis. *Electrochimica Acta*, Vol.51, No.6, (November 2005), pp. 1085-1090, ISSN: 00134686
- García, G. & Koper, M. (2011). Carbon Monoxide Oxidation on Pt Single Crystal Electrodes: Understanding the Catalysis for Low Temperature Fuel Cells. *ChemPhysChem*, Vol.12, No.11, (August 2011), pp. 2064-2072, ISSN: 14394235

- Spendelow, S., Goodpaster, D., Kenis, A. & Wieckowski, A. (2006). Mechanism of CO Oxidation on Pt(111) in Alkaline Media. *Journal of Physical Chemistry B*, Vol.110, No.19, (May 2006), pp. 9545-9555, ISSN: 15206106
- Spendelow, S., Lu, Q., Kenis, A. & Wieckowski, A. (2004). Electrooxidation of Adsorbed CO on Pt(1 1 1) and Pt(1 1 1)/Ru in Alkaline Media and Comparison with Results from Acidic Media. *Journal of Electroanalytical Chemistry*, Vol.568, No.1-2, (July 2004), pp. 215-224, ISSN: 00220728
- Lima, B. & Ticianelli, A. (2004). Oxygen Electrocatalysis on Ultra-thin Porous Coating Rotating Ring/Disk Platinum and Platinum-Cobalt Electrodes in Alkaline Media. *Electrochimica Acta*, Vol.49, No.24, (September 2004), pp. 4091-4099, ISSN: 00134686
- Kötz, R & Yeager, E. (1980). Raman Studies of the Silver/Silver Oxide Electrode. *Journal of Electroanalytical Chemistry*, Vol.111, No.1, (July 1980), pp. 105-110, ISSN: 00220728
- Demarconnay, L., Coutanceau, C. & Léger, M. (2004). Electroreduction of Dioxygen (ORR) in Alkaline Medium on Ag/C and Pt/C Nanostructured Catalysts - Effect of the Presence of Methanol. *Electrochimica Acta*, Vol.49, No.25, (October 2004), pp. 4513-4521, ISSN: 00134686

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