

Evaluation of the Nafion effect on the activity of Pt–Ru electrocatalysts for the electro-oxidation of methanol

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Abstract

The influence of the Nafion ionomer as a proton conductor on the platinum–ruthenium (Pt–Ru) alloy electrocatalyst for the electro-oxidation of methanol was investigated using combinatorial electrochemical methods. The most active composition of the Pt–Ru alloy electrocatalysts for the electro-oxidation of methanol was Pt(54.5)Ru(45.5), and the most active composition of the Pt–Ru–Nafion electrocatalysts for the electro-oxidation of methanol was metal (Pt:Ru = 1:1, molar ratio):Nafion = 63.6:36.4, wt.%. The electrochemical properties of the electrodes were compared using cyclic voltammetry, impedance spectroscopy and a performance test of a direct methanol fuel cell (DMFC). When the Nafion was added to the Pt–Ru alloy electrocatalyst, the initial activation potential decreased about 80 mV versus RHE, and the methanol electro-oxidation activity simultaneously increased. In a CO poisoning experiment, the CO was desorbed at a lower potential (lower than 130 mV versus RHE) when the Nafion was present. These results suggest a synergistic effect of Nafion-active metal catalysts for the electro-oxidation of methanol.

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1. Introduction

A direct methanol fuel cell (DMFC) is one of the most attractive power sources for a variety of wide applications from vehicles to portable electrical equipment, due to the simplicity of the system and the adaptability of the liquid fuel (methanol). Therefore, extensive studies on DMFCs have been carried out [1–3], mainly aiming at improving its poor performance compared with that of polymer electrolyte membrane fuel cells (PEMFCs) supplied with hydrogen. However, the main drawbacks limiting the practical realization of DMFC are the high overpotential at the anode catalyst, combined with the necessity of operating at low temperatures, the poisoning arising from carbonyl group-containing intermediate compounds adsorbed on the anode, and the high cost of preparing the precious metal electrode [4–6]. In order to solve these problems, considerable efforts have been made in search for a DMFC anode catalyst, especially for methanol electro-oxidation [7–9]. To date, Pt–Ru alloy catalysts are still considered the most active

catalysts to improve the effective polarization characteristics of methanol electro-oxidation for DMFCs [10–14].

Combinatorial chemistry, while most popularly used in the discovery of biochemicals and pharmaceuticals, has also for many years been used to identify and optimize inorganic materials of complex compositions [15,16]. The combinatorial method entails the synthesis of large libraries of compounds, in which composition or processing conditions are systematically varied, followed by screening for a particular property of interest. Recently, this approach has been used with some success in the discovery of a new electrocatalyst [17], and sophisticated methods for rapid screening of catalyst libraries have now been developed [18].

As DMFCs require platinum (Pt) or platinum alloy catalysts as an active material in their electrodes, it is important to increase the reaction sites in the catalytic layer and, thus, to improve electrode performance. Since the polymer membrane used for the electrolyte is a solid phase, it does not penetrate deeply into the electrode as does a liquid, therefore the reaction area is limited to the contact surface between the electrode and membrane. To increase this contact surface area, ionomers like Nafion are impregnated into the catalytic layer [19,20].

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In the present study, an examination is performed to evaluate the influence of the Nafion ionomer in the platinum–ruthenium (Pt–Ru) alloy electrocatalyst on the methanol electro-oxidation using a combinatorial electrochemistry method. To elucidate the electrochemical properties of the electrodes, which contain different compositions of Nafion ionomer, cyclic voltammetry, impedance spectroscopy and a direct methanol fuel cell performance test were used.

2. Experimental

2.1. Factorial method

Fig. 1 shows the experimental scheme of combinatorial scanning method for finding the active catalysts for methanol electro-oxidation activation. Electrode arrays were prepared by dispersing 0.5 M aqueous solutions of two metal salts (H_2PtCl_6 , RuCl_3 , Aldrich) and Nafion ionomer (5 wt.% Nafion solution, Aldrich) onto a Teflon-coated Toray carbon sheet, using manually prepared solution mixtures. The completed array was reduced by 0.5 M sodium borohydride, and the reduced array was thoroughly washed with nanopure water. Fig. 2 shows the combinatorial electrode array map of Pt–Ru alloy catalysts and Pt–Ru–Nafion ternary catalysts for methanol electro-oxidation. To measure the methanol electro-oxidation potential of CO adsorption on the array with this combinatorial method, we adsorbed CO gas onto the selected composition (the most active composition) by immersion of the array that contained the selected composition into the CO purged electrolyte solution for 5 h.

The electrolyte solution was composed of 100 μM quinine as a proton indicator, 6 M of reactant methanol, and the diluted H_2SO_4 which was added to adjust the pH to 7. The potential-step experiments were carried out using a potentiostat/galvanostat controlled by an IBM PC. Each composition

Table 1

The composition of Pt–Ru–Nafion anode (wt.%)

	Metal (Pt + Ru(Pt:Ru = 1:1, molar ratio)) (%)	Nafion (%)
Anode-1	100	0
Anode-2	91	9
Anode-3	66	34
Anode-4	40	60

was used as a working electrode. Cyclic voltammetry experiments were conducted between -0.2 and 0.8 V RHE at a sweep rate of 1 mV/s. The most active working electrode was selected by the brightest spot of the array obtained by fluorescence emission excited by UV of 254 nm [17].

2.2. Electrochemical experiments

To evaluate the Nafion ionomer loading on the Pt–Ru alloy catalyst, we prepared anodes, having different loadings of Nafion as shown in Table 1. As shown in Fig. 2, Anode-1, Anode-2, Anode-3, and Anode-4 are designated the position on the array as A1, A2, A3, and A4, respectively corresponding to the composition of the combinatorial array. The Nafion ionomer content was varied from 0 to 60%. A single direct methanol fuel cell was operated at a temperature of 110°C , with an active area of 1 cm^2 . The feed flow rate of the anode was 1.8 ml/min of 2 M methanol solution, and cathode gas (oxygen) was maintained at 300 ml/min with an external pressurization of 2 atm. To analyze the DMFC anode impedances, the anode was supplied with a 2 M aqueous solution of methanol at the 1.8 ml/min flow rate. The cathode was operated on hydrogen: this served as a reference and counter electrode. For impedance measurements, the current was modulated by a small sinusoidal signal so that the potential amplitude did not exceed 15 mV.

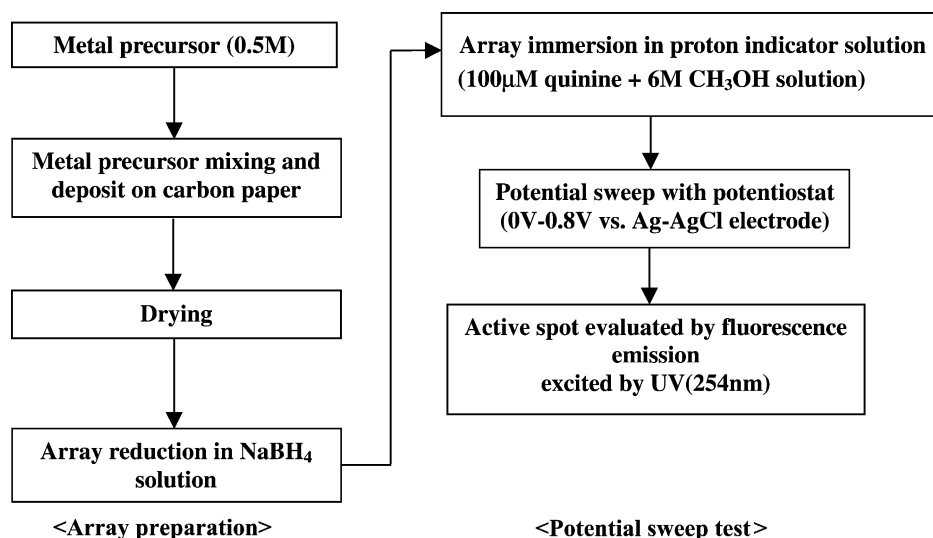


Fig. 1. Experimental scheme of the combinatorial scanning for the methanol electro-oxidation catalyst.

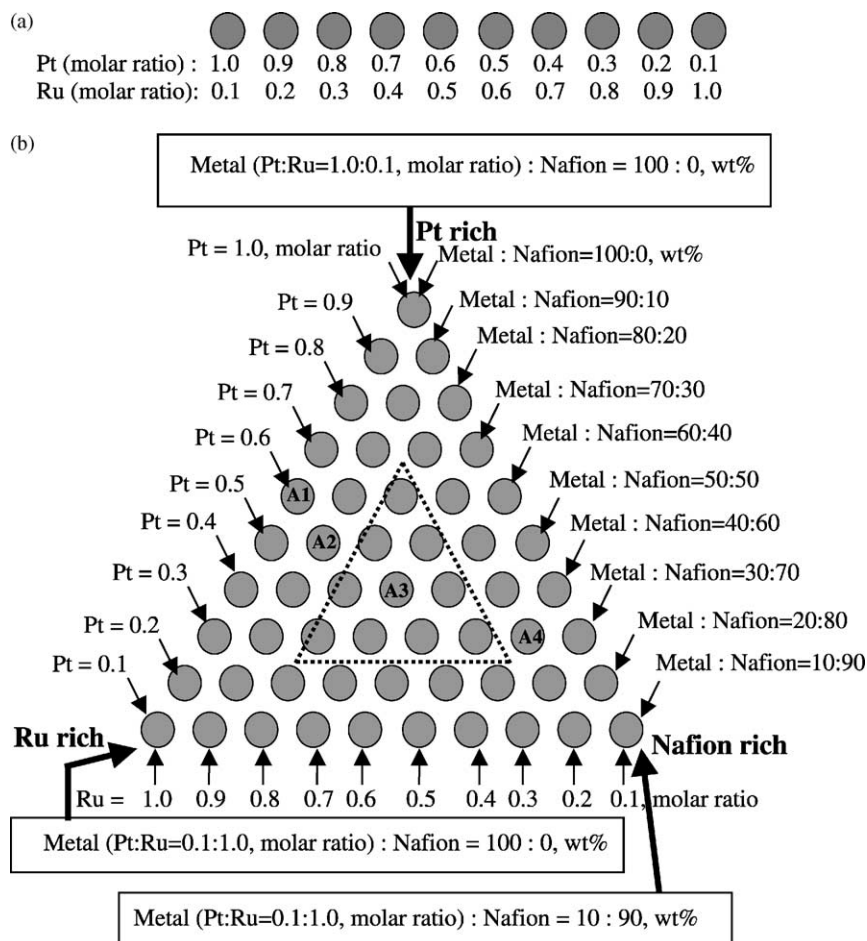


Fig. 2. Combinatorial array for methanol electro-oxidation; (a) Pt–Ru alloy catalyst, (b) Pt–Ru–Nafion ternary catalyst. Note: inside of dotted area denotes the active compositions for methanol electro-oxidation.

Impedance spectra were usually obtained at frequencies between 40 kHz and 3 mHz [21]. The cyclic voltammetry experiments were carried out at 25 °C in a conventional three-electrode cell, with a 0.5 M H₂SO₄ + 0.5 M CH₃OH oxygen free (purged and blanked with nitrogen) electrolyte solution. The prepared anodes were mounted into a Teflon holder containing a platinum ring as current collector and a platinum mesh was used as counter electrode. An Ag/AgCl reference electrode was placed next to the cell and connected to the main compartment through a Luggin capillary whose tip was placed close to the working electrode surface. The electrochemical cell was connected to an AUTOLAB FRA2 impedance analyzer for electrochemical impedance spectroscopy and an AUTOLAB potentiostat/galvanostat for cyclic voltammetry.

3. Results and discussion

The fluorescence images of Pt–Ru alloy and Pt–Ru–Nafion ternary electrodes for methanol electro-oxidation at different activation voltages are shown in Fig. 3. The activity of methanol electro-oxidation was measured by the

intensity of fluorescence and the active compositions of catalysts are shown in Fig. 2 as a dotted area. Among them, the most active composition was Pt(54.5)Ru(45.5), and the initial activation potential was started from 0.2 V without Nafion. When the Nafion ionomer was added into the Pt–Ru alloy electrocatalyst, the initial activation potential was lower by about 80 mV than that of the electrocatalyst without Nafion ionomer but the atomic ratio of Pt and Ru in the most active composition was not changed. As a result, the most active composition for the methanol electro-oxidation was (Pt:Ru(1:1), molar ratio:Nafion = 63.6:36.4, wt.%), and this result is in accord with the result by E. Passalacqua et al. [22]. Fig. 4 shows the evaluation of the Nafion effect on the methanol electro-oxidation activity in the Pt–Ru electrocatalyst by combinatorial electrochemistry. Below the temperature of 120 °C, the initial methanol electro-oxidation potential was not changed, but it was increased drastically over the temperature 120 °C. The high potential for CO oxidation may be mainly caused by the modification of the acid characteristic of the Nafion. It is well known that Nafion has a high proton conducting capability due to the acid sites in Nafion ionomer and that it decreases abruptly above 120 °C. From these result, we can suggest a synergistic

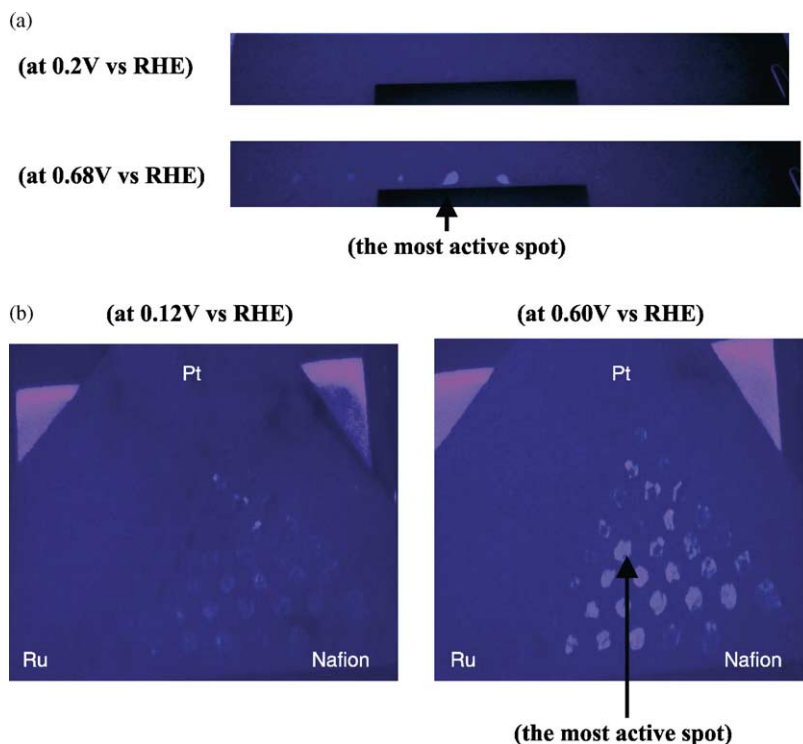


Fig. 3. Combinatorial array and screening results by fluorescence imaging. Active compositions for methanol electro-oxidation are shown as bright spots; (a) Pt–Ru, (b) Pt–Ru–Nafion.

effect of the electro-oxidation of methanol on the Pt–Ru–Nafion electrocatalyst. This is similar to the bifunctional mechanism in petrochemical catalysts.

To compare the electrochemical properties with varying Nafion composition, we prepared four representative DMFC anodes, which loaded different amounts of Nafion ionomer onto the Pt–Ru catalysts. Anode-1 contains no Nafion ionomer, Anode-2 contains 9% Nafion ionomer (Pt + Ru(Pt:Ru

= 1:1, molar ratio):Nafion = 91:9, wt.%), Anode-3 contains the 34% of Nafion ionomer (Pt + Ru(Pt:Ru = 1:1, molar ratio):Nafion = 66:34, wt.%), and Anode-4 contains high amount of Nafion ionomer (Pt + Ru(Pt:Ru = 1:1, molar ratio):Nafion = 40:60, wt.%).

Fig. 5 shows the cyclic voltammograms on the prepared anodes in the 0.5 M methanol + 0.5 M H₂SO₄ electrolyte solution at 25 °C. The forward sweep of the cyclic

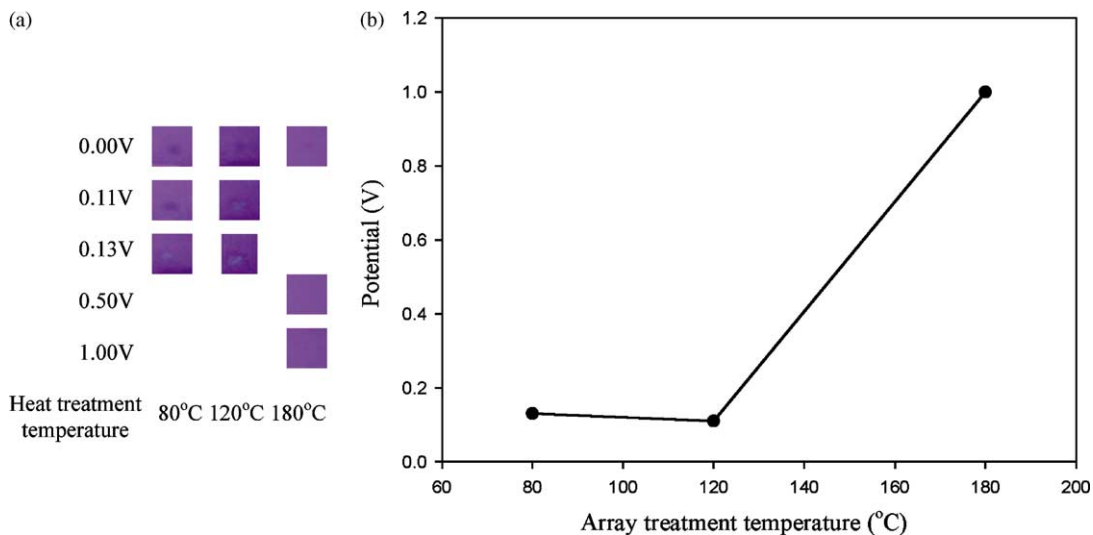


Fig. 4. Effect of heat treatment on the initial methanol oxidation potential of CO poisoned Pt–Ru–Nafion catalyst at 25 °C. (Note: Pt:Ru(1:1, molar ratio):Nafion = 66:34); (a) initial activation spots appeared by combinatorial scanning test, (b) initial activation potential for methanol electro-oxidation.

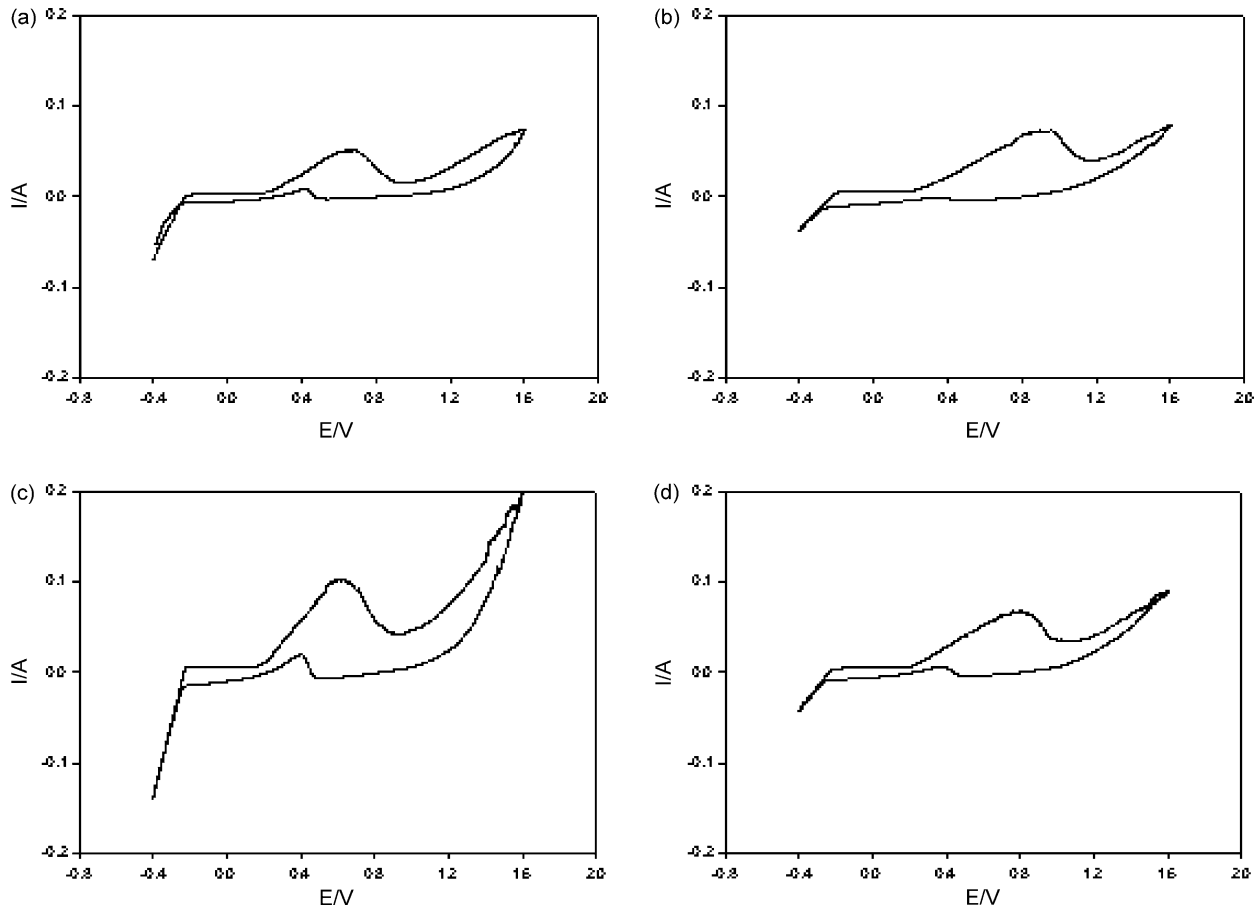
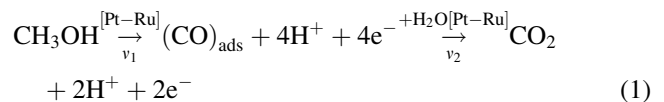


Fig. 5. Cyclic voltammograms of the Pt–Ru–Nafion electrodes in electrolyte solution (0.5 M methanol + 0.5 M H₂SO₄); (a) Pt + Ru:Nafion = 100:0, (b) Pt + Ru:Nafion = 91:9, (c) Pt + Ru:Nafion = 66:34, (d) Pt + Ru:Nafion = 40:60 (Note: Pt:Ru = 1:1, molar ratio).

voltammograms of the prepared anodes in 0.5 M methanol + 0.5 M H₂SO₄ solution are shown in Fig. 6. The electro-oxidation of methanol started ca. 179 and 136 mV at Anode-1 and Anode-3, respectively. The initial electro-oxidation potential of methanol on Anode-3 shifted negatively more than 43 mV compared with Anode-1. In addition, the methanol electro-oxidation current of Anode-3 at 1.6 V is much larger than that of Anode-1. The current increase in the forward sweep was due to the electro-oxidation of methanol. After the current peak, we observed a decrease in the electro-oxidation current due to the formation of oxide on the Pt–Ru surface, which decreases the number of active sites on the electrode surface [23]. These results suggest that the Nafion ionomer greatly affected the kinetics of methanol electro-oxidation. It promoted the electro-oxidation of methanol as observed in bifunctional catalysts. Namely, protonic sites on Nafion enhanced the methanol electro-oxidation when it was incorporated with in the metallic sites.

Fig. 7 shows impedance spectra of DMFC anodes. In our experiments, mass-transport limitations have been eliminated by using very high fuel flow rates (over 20 times the stoichiometric rate). It is known that the magnitude of the semicircle in the DMFC anode impedance is related to the

resistance due to the methanol electro-oxidation kinetics [21,24]. The magnitudes of the semicircles were 11.17 and 8.61 Ω cm² for Anode-1 and Anode-3, respectively. This shows a reduction in the resistance due to methanol electro-oxidation due to the addition of the Nafion(34%) in Anode-3. The methanol electro-oxidation can be assumed to follow Eq. (1):



Methanol is adsorbed, mainly on the Pt–Ru sites, with a rate v_1 to give (CO)_{ads} as the dominating intermediate species. Oxidative removal of the adsorbate v_2 is rate-limiting under conditions relevant to fuel cell operation [11,24]. The addition of Nafion may provide protonic sites due to the metallic site and this combination could promote the CO oxidation by supply in a protons to the metallic sites. It is important to increase the removal rate of CO, which inhibits the kinetics of electro-oxidation of methanol on the Pt–Ru electrocatalyst. To confirm the effect of Nafion ionomer on the CO removal in the Pt–Ru electrocatalyst, Pt–Ru electrocatalysts containing different compositions of Nafion

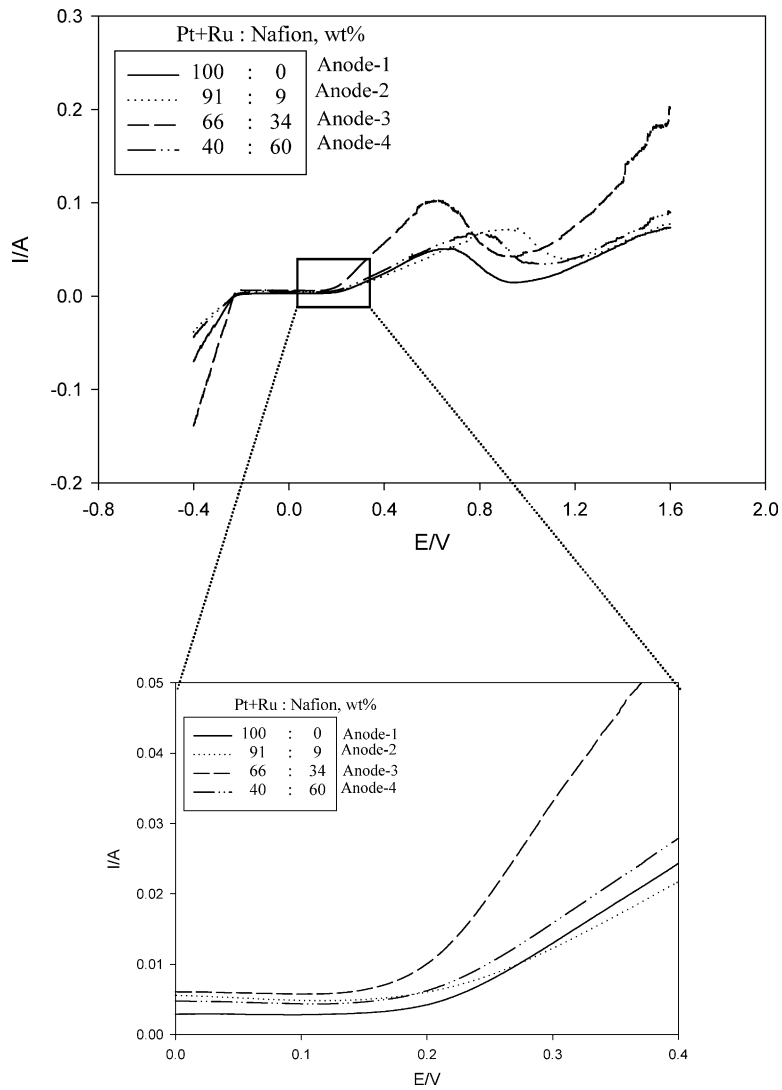


Fig. 6. The forward sweep of the cyclic voltammograms of the Pt–Ru–Nafion electrodes in electrolyte solution (0.5 M methanol + 0.5 M H₂SO₄) (Note: Pt:Ru = 1:1, molar ratio).

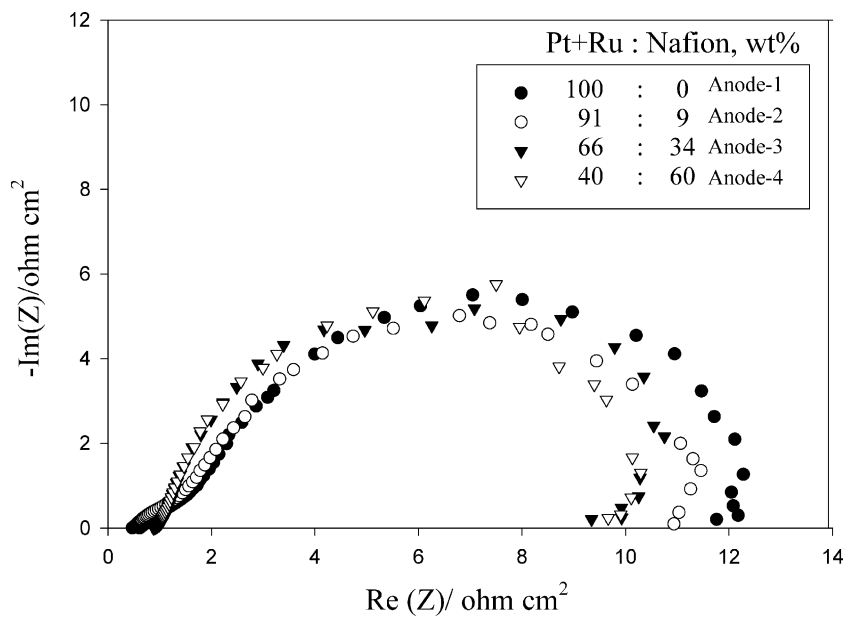


Fig. 7. Impedance spectra of Pt–Ru–Nafion electrodes (Note: Pt:Ru = 1:1, molar ratio).

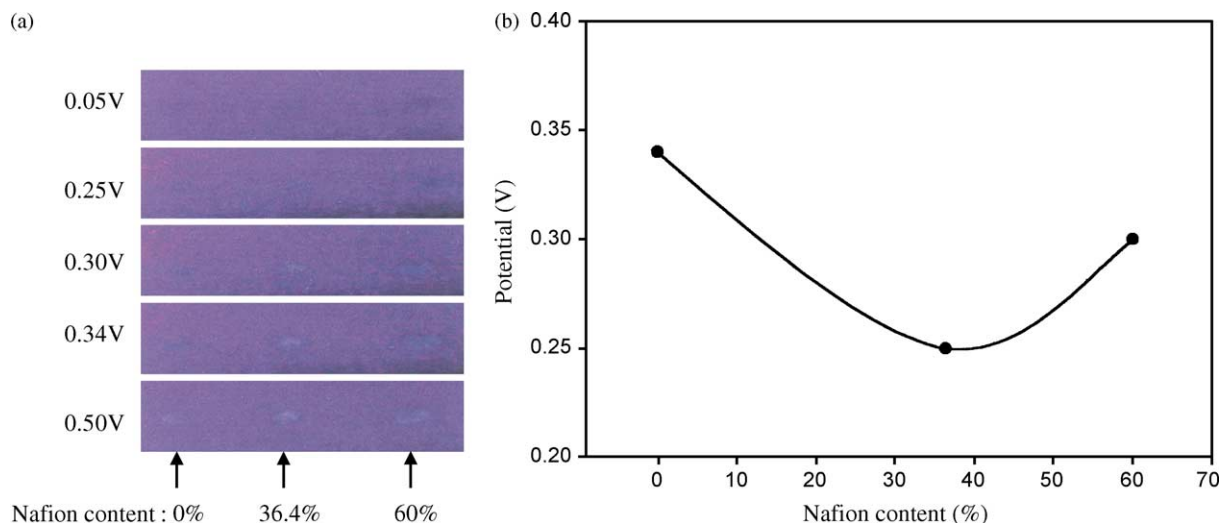


Fig. 8. Initial methanol oxidation potential of CO poisoned Pt–Ru–Nafion catalysts at 25 °C by changing the Nafion contents. (Note: Pt:Ru = 1:1, molar ratio); (a) combinatorial scanning test results, (b) initial activation potential for methanol electro-oxidation.

ionomer (0, 36.4, 60%) were poisoned with CO gas. Then we observed the initial methanol electro-oxidation potential of the CO poisoned Pt–Ru–Nafion electrodes. Fig. 8 shows the initial methanol electro-oxidation potential changes with the Nafion ionomer content from 0 to 60%. When the Nafion ionomer content was 36.4%, the initial methanol electro-oxidation potential of Pt–Ru electrocatalyst with CO poisoning was about 130 mV higher than that of Pt–Ru electrocatalyst without CO poisoning. By loading the 34.6% of Nafion ionomer onto the platinum–ruthenium alloy electrocatalyst, the initial methanol electro-oxidation potential was decreased about 90 mV. These results proved that CO desorption rate was increased by loading the Nafion ionomer

onto the platinum–ruthenium alloy catalyst, and there is an optimum composition of Nafion ionomer (30–40%) to enhance the CO desorption rate.

Fig. 9 shows the single direct methanol fuel cell performance with the four different amounts of Nafion ionomer loaded anode at the temperature of 110 °C. The performances of MEA samples at 0.4 V were shown in Table 2. When the Nafion ionomer was loaded onto the electrode, the performance was increased from 158 mA/cm² (Anode-1) to 218 mA/cm² (Anode-3), but it was slightly decreased at the excessive of Nafion content (60%). 30–40 wt.% of Nafion on Pt–Ru catalysts seemed to be the optimum to increase the single cell performance.

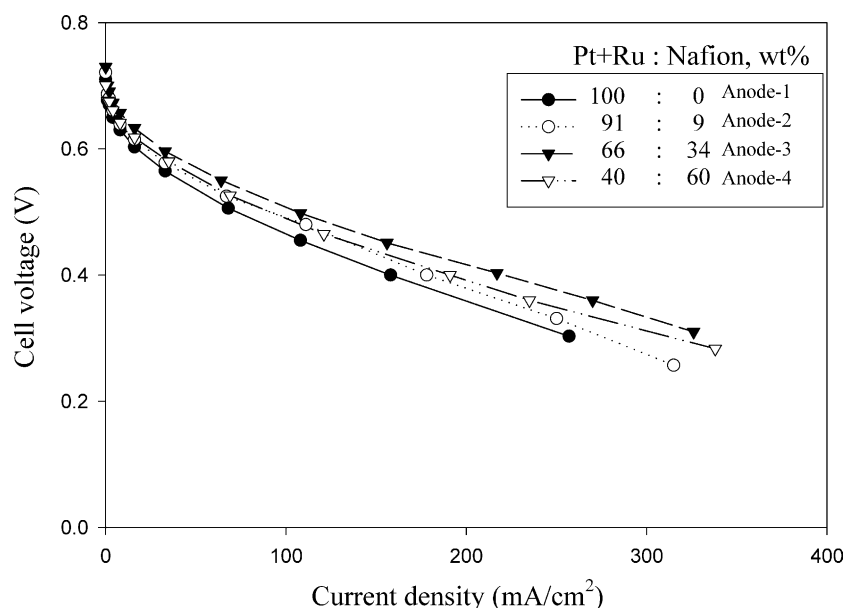


Fig. 9. The single cell performance of the Pt–Ru–Nafion electrodes at 110 °C, (fuel: 2 M methanol solution, 1.8 ml/min, O₂: 300 ml/min, 2 atm).

Table 2
Characteristics of electrochemical parameters of Pt–Ru–Nafion anodes on methanol oxidation

Electrochemical parameters	Anode-1	Anode-2	Anode-3	Anode-4
Initial methanol oxidation potential (mV)	179	164	136	154
Methanol oxidation current at 1.6 V (mA)	73	78	201	90
Current density at 0.4 V (mA/cm ²)	158	178	218	191

4. Conclusions

The effect of Nafion ionomer on the Pt–Ru alloy electrocatalyst was evaluated by using a factorial scanning method. The most active composition of Pt–Ru–Nafion electrocatalyst on the methanol electro-oxidation was [Pt/Ru(1/1):Nafion = 63.6:36.4, wt.%]. By adding Nafion, the initial methanol electro-oxidation potential of the Pt–Ru alloy was decreased, and simultaneously, a high methanol electro-oxidation current was obtained at 1.6 V. These observations suggest a synergistic effect of methanol electro-oxidation on Nafion-active metal (Pt–Ru) catalysts. In addition the Nafion proved to be effective to desorb the CO desorption on Pt–Ru catalysts in the methanol electro-oxidation process. The optimum composition of Nafion ionomer was about 30–40 wt.% to improve the fuel cell performance.

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