

Rapid evaluation of the electrooxidation of fuel compounds with a multiple-electrode setup for direct polymer electrolyte fuel cells

Naoko Fujiwara*, Zyun Siroma, Tsutomu Ioroi, Kazuaki Yasuda

*Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST),
1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan*

Received 31 August 2006; received in revised form 23 October 2006; accepted 26 October 2006
Available online 4 December 2006

Abstract

Electrochemical oxidation of fuel compounds in acidic media was examined on eight electrodes (Pt, Ru, PtRu, Rh, Ir, Pd, Au, and glassy carbon) simultaneously by multiple cyclic voltammetry (CV) with an electrochemical cell equipped with an eight-electrode configuration. Direct-type polymer electrolyte fuel cells (PEFCs), in which aqueous solutions of the fuel compounds are directly supplied to the anode, were also evaluated. The performances of direct PEFCs with various anode catalysts could be roughly estimated from the results obtained with multiple CV. This multiple evaluation may be useful for identifying novel fuels or electrocatalysts. Methanol, ethanol, ethylene glycol, 2-propanol, and D-glucose were oxidized selectively on Pt or PtRu, as reported previously. However, several compounds that are often used as reducing agents show electrochemical oxidation with unique characteristics. Large current was obtained for the oxidation of formic acid, hypophosphorous acid, and phosphorous acid on a Pd electrode. L-Ascorbic acid and sulfurous acid were oxidized on all of the electrodes used in the present study. © 2006 Elsevier B.V. All rights reserved.

Keywords: Electrochemical oxidation; Cyclic voltammetry; Alcohol; Electrocatalyst; Polymer electrolyte fuel cell

1. Introduction

Direct methanol fuel cells (DMFCs), which are methanol-fueled polymer electrolyte fuel cells (PEFCs), have attracted much attention as alternative power sources for portable electric devices such as cellular phones and laptop PCs [1,2]. The advantages of DMFCs compared to hydrogen-fueled polymer electrolyte fuel cells (PEFCs) are a high energy density for fuel storage and the simplicity of their subsystem requirements. Convenient sources of micropower that can be worn or implanted with electric devices are also desired to support our increasingly information-oriented society. The medical industry will be one of the most important markets for sources of micropower in the near future. Micropower generators for artificial organs, microsurgery robots, and in situ sensors are some examples of such medical applications. Greater safety will be needed for the practical use of direct-type PEFCs as micropower sources in medical devices. One approach to improving safety is to develop

direct PEFCs with biologically friendly fuels instead of toxic methanol.

Many previous papers have reported the application of various fuels other than methanol to direct PEFCs. Ethanol [3], 2-propanol [4], and ethylene glycol [5] have all received attention as typical alternatives because of their high energy densities. However, the complete oxidation of these alcohols to CO₂ by breaking the C–C bond was so difficult that the main product species of direct PEFCs supplied with ethanol, 2-propanol, and ethylene glycol were acetaldehyde, acetone, and glycolaldehyde, respectively [6,7]. Direct PEFCs with polyhydric alcohols [8], borohydride [9], and hydrazine [10] were investigated under alkaline conditions, in the expectation of enhanced electrode kinetics of fuel oxidation and oxygen reduction or a reduction of fuel crossover. Direct PEFCs that use 2-propanol [4,11], borohydride [9,12], hydrazine [13], and formic acid [14,15] have all exhibited higher power densities than DMFCs.

We have already reported direct L-ascorbic acid fuel cells (DAAFCs), in which L-ascorbic acid solution is supplied directly to the anode [16]. DAAFCs offer several advantages compared to DMFCs. L-Ascorbic acid, also known as Vitamin C, is an environmentally and biologically friendly compound. Carbon

* Corresponding author. Tel.: +81 727 51 9653; fax: +81 727 51 9629.
E-mail address: n-fujiwara@aist.go.jp (N. Fujiwara).

black can be used as the anode and no toxic product is released in DAAFCs [17].

The purpose of the present study was to identify novel fuels for use in direct PEFCs and good catalysts with high activity toward electrochemical oxidation. Chemical compounds that are used as reducing agents in chemical processes such as electrodeless plating and chemical syntheses were considered candidates for fuels in direct PEFCs. The oxidation of these chemical compounds was systematically examined on electrodes that were resistant to corrosion in acidic medium to find appropriate pairs of anode catalysts and fuel compounds. This paper introduces a multiple-electrochemical method for the rapid evaluation of the electrochemical oxidation of fuel compounds. The performances of direct-type PEFCs using these fuel compounds were also evaluated to confirm the correlation between the electrooxidation behaviour of the compounds in electrolyte solution and in PEFCs. As a result, several combinations of fuel compounds and anode catalysts showed interesting behaviours that were different from those of typical alcohol fuels.

2. Experimental

2.1. Materials

Methanol, ethanol, ethylene glycol, 2-propanol, D-glucose, formaldehyde, formic acid, oxalic acid, citric acid, L-ascorbic acid, tartaric acid, sulfurous acid, hypophosphorous acid, and phosphorous acid were used as fuel compounds for direct-type PEFCs. All of the chemicals were analytical grade and used as received. Unsupported catalysts, Pt, Ru, PtRu, Rh, Ir, and Pd black (Johnson–Matthey, specific surface area is typically $20\text{ m}^2\text{ g}^{-1}$) were used as electrocatalysts both for the multiple evaluation of electrooxidation in electrolyte solution and to prepare membrane electrode assemblies (MEAs) in PEFCs.

2.2. Multiple-electrochemical measurements in acidic media with an eight-electrode setup

Catalyst-modified glassy carbon (GC) electrodes used for electrochemical measurements in $0.5\text{ M H}_2\text{SO}_4$ solution were prepared by the following method as described by Schmidt et al. [18]. GC disk electrodes (3 mm diameter) were polished to a mirror finish with $0.05\text{ }\mu\text{m}$ alumina powder. Aqueous suspensions containing 4 mg ml^{-1} of precious metal black were dispersed ultrasonically. Three microliters of the metal black suspensions were dropped onto the GC substrate. After the water evaporated, the GC electrode was coated with a $0.1\text{-}\mu\text{m}$ layer of Nafion (Aldrich 5 wt.% solution), and then dried at $150\text{ }^\circ\text{C}$ for 1 h.

Multiple cyclic voltammetry (CV) was conducted in an electrochemical cell equipped with an eight-working-electrode configuration, as shown in Fig. 1. A reversible hydrogen electrode (RHE) for reference and a Pt spiral counter electrode were centered in the cell and eight working electrodes were arranged around them. GC electrodes modified with Pt, Ru, PtRu, Rh, Ir, and Pd black as described above, Au (3 mm diameter), and unmodified GC electrodes served as working electrodes. A multichannel potentiostat (VMP-80, Princeton Applied Research)

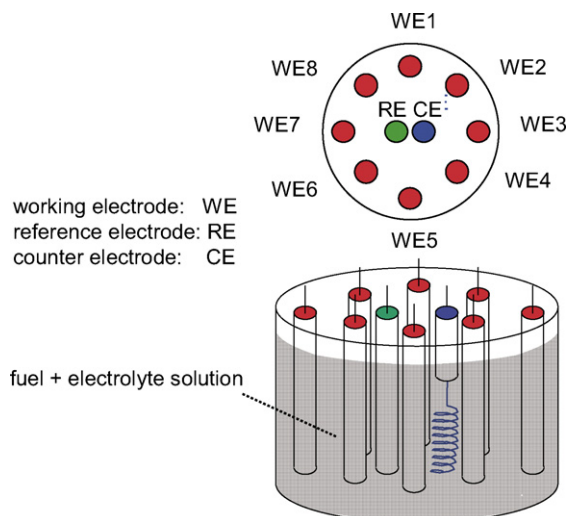


Fig. 1. Electrochemical cell equipped with an eight-working-electrode configuration.

with eight independent potentiostats was connected to the electrochemical cell. In the potentiostat the counter electrode is set to the ground and the working and reference electrodes are floating. Therefore, CVs on eight different electrodes can be obtained simultaneously in a single cell using common counter and reference electrodes without interference in the electric circuit. All measurements were carried out under an Ar atmosphere at $25\text{ }^\circ\text{C}$.

2.3. Fabrication and evaluation of direct-type PEFCs

Unsupported metal catalysts (Pt, Ru, PtRu, Rh, Ir, and Pd black) were suspended in Nafion solution and spread on PTFE blanks to prepare anode layers (metal 3 mg cm^{-2} , Nafion 10 wt.%). Pt black powder used as a cathode catalyst was mixed with a polytetrafluoroethylene (PTFE) emulsion (Daikin Polyflon) and heated at $360\text{ }^\circ\text{C}$ for 1 h. The obtained Pt–PTFE black (PTFE 7 wt.%) was used to prepare cathode layers (Pt 3 mg cm^{-2} , Nafion 10 wt.%) by the same method as for the anode. MEAs were prepared by decal transfer [19] of the electrode layers onto both sides of a Nafion-117 (DuPont) membrane.

MEAs were sandwiched between two carbon-cloths (E-TEK) used as gas-diffusion media. An aqueous solution of fuel compounds was delivered to the anode at 4 ml min^{-1} , and air was spontaneously diffused to the cathode as the oxidant. Fuel cell performance was evaluated using a single cell with a geometric electrode area of 10 cm^2 at room temperature and at atmospheric pressure using a current pulse generator (Hokuto Denko HC-113) and a digital multimeter.

3. Results and discussion

3.1. Rapid evaluation of the electrooxidation of fuel compounds with a multiple-electrochemical technique

CVs of eight electrodes (Pt, Ru, PtRu, Rh, Ir, Pd, Au, and GC) in electrolyte solution could be obtained simultaneously with

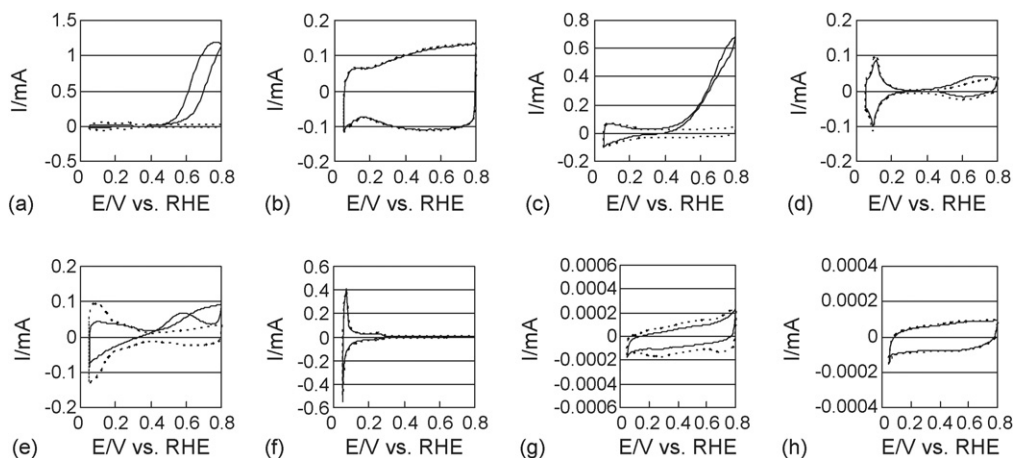


Fig. 2. Cyclic voltammograms in 0.5 M H_2SO_4 (····) and 0.5 M methanol + 0.5 M H_2SO_4 (—) solution on Pt (a), Ru (b), PtRu (c), Rh (d), Ir (e), Pd (f), Au (g), and GC (h) electrodes. Sweep rate: 20 mV s^{-1} , temperature: 25°C .

this multiple-electrochemical technique using the electrochemical cell shown in Fig. 1. Before data were obtained by multiple CVs, electrochemical measurements with conventional three-electrode configuration were carried out. The detected currents were so small (a few mA) that only small amounts of reaction products were formed on the working electrode. Therefore, the products formed on one working electrode did not interfere with the reaction on the next neighbor working electrode under these experimental conditions. In fact, it was confirmed for some fuels that the obtained CVs with the multiple-electrochemical technique were same as those obtained in the conventional three-electrode configuration without interference in the electric circuit and by reaction products. Multiple CVs obtained in 0.5 M H_2SO_4 solution containing 0.5 M of methanol, L-ascorbic acid, or phosphorous acid are shown as examples in Figs. 2–4, respectively. Fig. 2 shows CVs in 0.5 M methanol + 0.5 M H_2SO_4 at a sweep rate of 20 mV s^{-1} and 25°C . Subtracting of the currents in 0.5 M H_2SO_4 from those in 0.5 M methanol + 0.5 M H_2SO_4 gives the results of methanol oxidation. Large oxidation currents were obtained on Pt and PtRu electrodes and methanol was slightly oxidized on Ir and Rh electrodes (Fig. 2). Ru, Pd, Au and GC had no reactivity toward the electrochemical ox-

idation of methanol. These behaviors are consistent with many previous studies which have shown that Pt-based metal exhibited high activities for methanol oxidation [20]. The catalytic activities of Pt and PtRu for the electrochemical oxidation of ethanol, ethylene glycol, 2-propanol, and D-glucose were remarkably the same as those for methanol, despite the differences in each current value. In contrast to the electrochemical oxidation of the alcohols, different behaviors were observed in Fig. 3, which shows multiple CVs in 0.5 M L-ascorbic acid + 0.5 M H_2SO_4 . Anodic currents start to increase at around 0.5 V versus RHE and reach a few mA during the positive sweep up to 0.8 V on all electrodes. This behavior suggests that all of the eight electrodes including Au and unmodified GC show large activity toward the electrooxidation of L-ascorbic acid. The multiple CVs in 0.5 M phosphorous acid + 0.5 M H_2SO_4 are shown in Fig. 4. The catalytic activities for the electrooxidation of phosphorous acid were in the order $\text{Pd} > \text{PtRu} > \text{Pt}, \text{Rh} > \text{Ir} > \text{Ru}$, based on the oxidation current obtained in Fig. 4. The oxidation of phosphorous acid did not proceed on a Au or GC electrode.

Multiple evaluations were also carried out for the oxidation of formaldehyde, formic acid, oxalic acid, citric acid, tartaric acid, sulfurous acid, and hypophosphorous acid. Completely

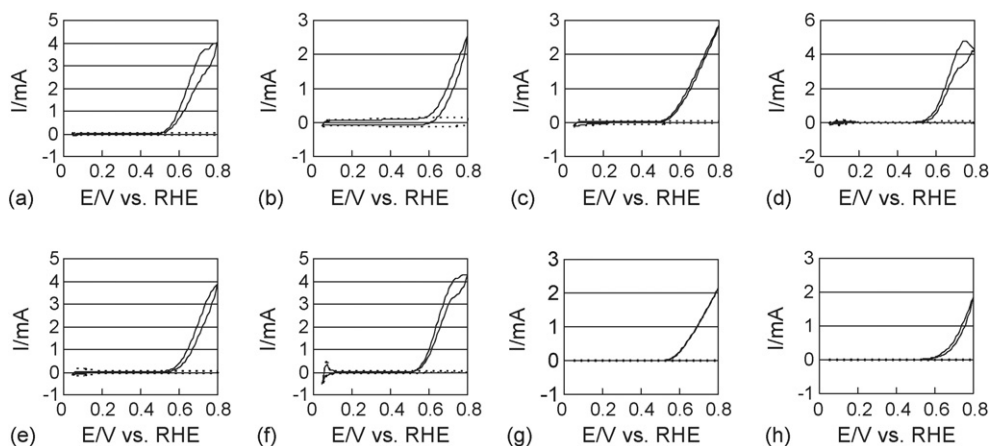


Fig. 3. Cyclic voltammograms in 0.5 M H_2SO_4 (····) and 0.5 M L-ascorbic acid + 0.5 M H_2SO_4 (—) solution on Pt (a), Ru (b), PtRu (c), Rh (d), Ir (e), Pd (f), Au (g), and GC (h) electrodes. Sweep rate: 20 mV s^{-1} , temperature: 25°C .

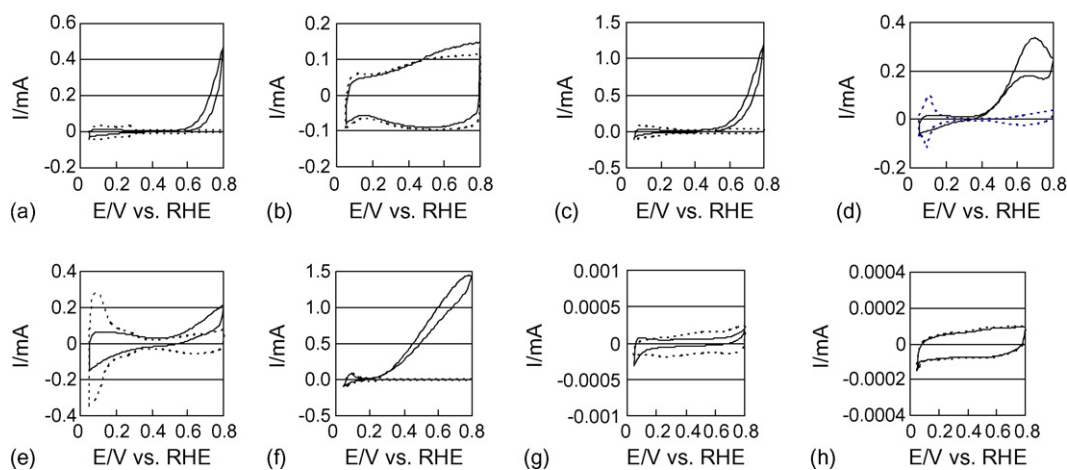


Fig. 4. Cyclic voltammograms in 0.5 M H_2SO_4 (---) and 0.5 M phosphorous acid + 0.5 M H_2SO_4 (—) solution on Pt (a), Ru (b), PtRu (c), Rh (d), Ir (e), Pd (f), Au (g), and GC (h) electrodes. Sweep rate: 20 mV s^{-1} , temperature: 25°C .

different current-potential behaviors indicating current peaks at different potentials were observed, depending on the fuel compounds and electrodes. It is unreliable to compare the current at some fixed potential for evaluating the electrooxidation. In the present study, the peak currents obtained in each CV were chosen for the systematical comparison of their electrochemical oxidation. Oxidation currents were calculated by subtracting currents in 0.5 M H_2SO_4 from those in 0.5 M H_2SO_4 containing the fuel compounds, and their maximum values during the positive sweep from 0.05 to 0.8 V versus RHE are summarized in Fig. 5. Effective oxidation currents for the oxidation of methanol, ethanol, ethylene glycol, 2-propanol, and D-glucose were only

observed on Pt or PtRu electrodes, as mentioned above. Several fuel compounds, so-called reducing agents, gave results different from those with alcohol fuels, as shown in Fig. 5. The peak currents for the oxidation of formaldehyde on Pt and PtRu, formic acid on Pt, PtRu and Pd, L-ascorbic acid on Pt, Ru, PtRu, Rh, Ir, Pd, Au, and GC, sulfurous acid on Pt, PtRu, Rh, and Pd, hypophosphorous acid and phosphorous acid on Pd were remarkably greater than those for methanol on Pt or PtRu. In addition, L-ascorbic acid and sulfurous acid were oxidized on all eight of the electrodes used in this study. On the other hand, no oxidation currents were observed for the CVs in oxalic acid, citric acid, or tartaric acid, which showed that all eight electrodes were inactive toward oxidation. These experimental results show that several combinations of fuel compounds and anode catalysts may be suitable for use in direct PEFCs.

3.2. Evaluation of direct PEFC performance with various fuel compounds

Seven different membrane electrode assemblies (MEAs) with Pt, Ru, PtRu, Rh, Ir, and Pd for anode catalysts or without any anode catalyst were prepared and then used for the performance evaluation. Aqueous solutions of methanol, ethanol, ethylene glycol, D-glucose, formaldehyde, formic acid, oxalic acid, citric acid, L-ascorbic acid, tartaric acid, sulfurous acid, hypophosphorous acid, and phosphorous acid were supplied to the anode side of the direct PEFCs using each MEA. DMFCs, which are typical direct PEFCs, worked with Pt, PtRu, and Ir anode, but did not work with the other anodes. The best performance was shown with a PtRu anode, which has been used as an anode catalyst for DMFCs in many previous studies [21]. The superior performance of PtRu and Pt anodes and the order PtRu > Pt was commonly observed for direct PEFCs fueled with alcohol, such as methanol, ethanol, ethylene glycol, and 2-propanol. The maximum power density of 23 mW cm^{-2} was obtained at room temperature for the direct PEFC that used 2-propanol as a fuel with a PtRu anode, which is much better performance than for a DMFC with a PtRu anode (16 mW cm^{-2}). The maximum power density of the direct D-glucose fuel cell with a PtRu anode was

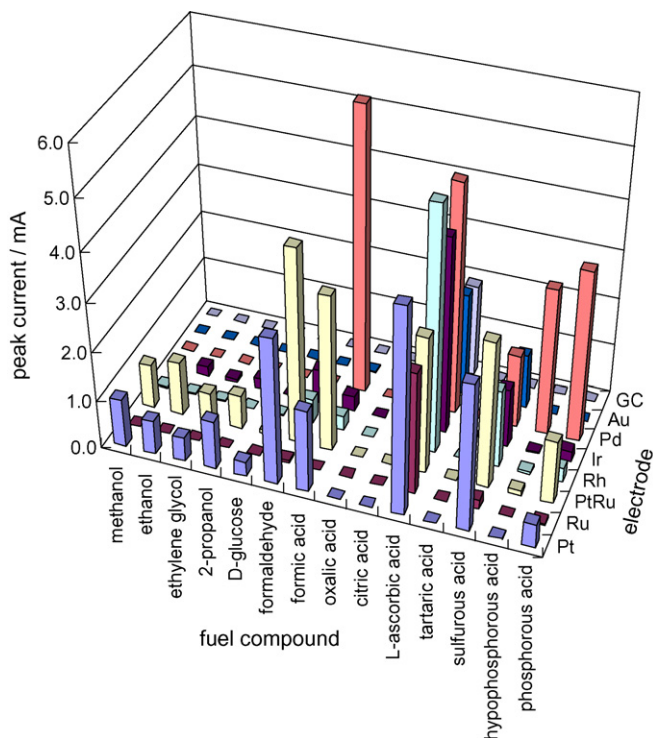


Fig. 5. Oxidation current of fuel compounds on various electrodes obtained in multiple-cyclic voltammograms at 25°C .

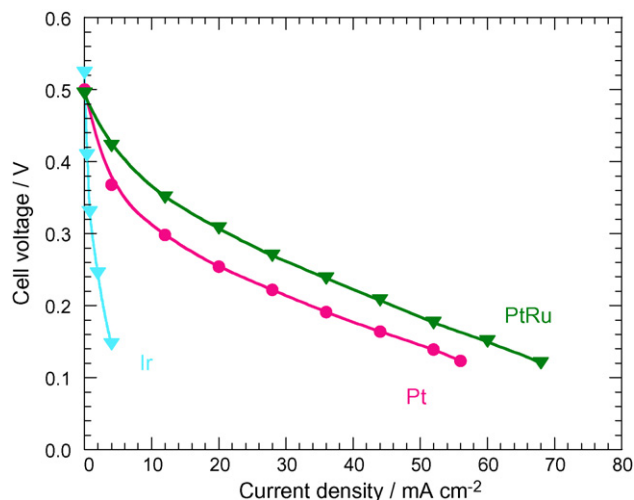


Fig. 6. Cell voltage vs. current density plots of direct formaldehyde fuel cells with various anode catalysts (3 mg cm^{-2}) at room temperature and atmospheric pressure. Cathode catalyst: Pt-PTFE black (3 mg cm^{-2}), membrane: Nafion-117, fuel: 1.0 M aqueous solution of formaldehyde (4 ml min^{-1}).

smaller by one order of magnitude than those of the direct alcohol fuel cells, although they all showed their best performance with PtRu and Pt.

Fig. 6 shows the cell voltage versus current density plots of direct PEFCs using 1.0 M aqueous solution of formaldehyde with Pt, PtRu, and Ir anodes at room temperature. Catalytic activities of the anode for the direct formaldehyde fuel cells were greater in the order $\text{PtRu} > \text{Pt} \gg \text{Ir}$, which is consistent with the results obtained by the multiple-electrochemical measurements. This trend for the selectivity of the anode catalysts was similar to that described above for direct alcohol fuel cells.

The performance of direct PEFCs using a 1.0 M aqueous solution of formic acid at room temperature is shown in Fig. 7 as cell voltage versus current density plots. The direct formic acid fuel cells worked with five different anode catalysts, although they showed very different catalytic behaviors based on the open

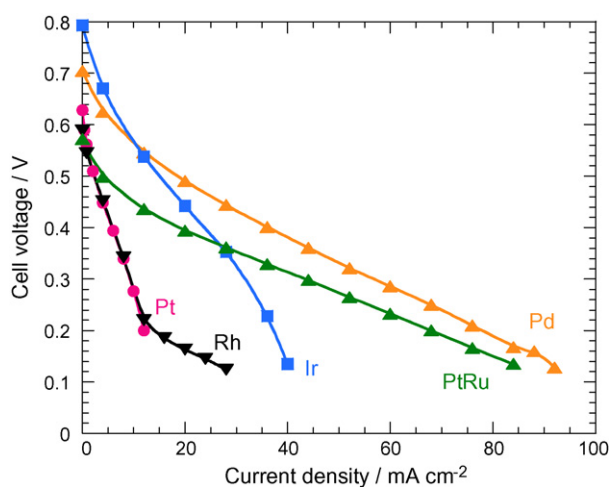


Fig. 7. Cell voltage vs. current density plots of direct formic acid fuel cells with various anode catalysts (3 mg cm^{-2}) at room temperature and atmospheric pressure. Cathode catalyst: Pt-PTFE black (3 mg cm^{-2}), membrane: Nafion-117, fuel: 1.0 M aqueous solution of formic acid (4 ml min^{-1}).

circuit voltage and observed current density. A maximum power density of 17 mW cm^{-2} was obtained with a Pd anode, and this was almost equal to that for a DMFC with a PtRu anode. Previous papers have reported the high activity of Pd electrode for the oxidation of formic acid [15], and the present study supports these previous results.

Direct PEFCs fueled with oxalic acid, citric acid, and tartaric acid did not work with either anode catalysts or without catalyst, as expected from the finding with multiple CVs that all of the eight electrodes used in this study were inactive toward oxidation. On the other hand, direct PEFCs fueled with L-ascorbic acid worked with all six of the electrodes used in this study and even without catalyst. The maximum power densities of the direct L-ascorbic acid fuel cells were in the range of $3\text{--}6 \text{ mW cm}^{-2}$, and varied with the anode catalyst. Direct PEFCs that used an aqueous solution of sulfurous acid also generated power both with any catalyst and without an anode catalyst, although the maximum power densities were small, in the range of $0.1\text{--}0.8 \text{ mW cm}^{-2}$.

The relatively high activity of a Pd anode was confirmed for direct PEFCs with some fuel compounds, such as formic acid, L-ascorbic acid, sulfurous acid, hypophosphorous acid, and phosphorous acid. Fig. 8 shows the cell voltage–current density plots of direct PEFCs with a Pd anode. The open circuit voltages varied from 0.44 to 0.74 V depending on the supplied fuel compounds. The maximum power densities were 17 mW cm^{-2} (formic acid), 6 mW cm^{-2} (L-ascorbic acid), 0.8 mW cm^{-2} (sulfurous acid), 1 mW cm^{-2} (hypophosphorous acid), and 3 mW cm^{-2} (phosphorous acid).

Fig. 9 summarizes the performance of direct PEFCs using different combinations of fuels and anode catalysts at their maximum power densities. The selectivity of anode catalysts in direct PEFCs reflects the catalytic activities for the electrochemical oxidation of fuel compounds obtained by multiple-CVs.

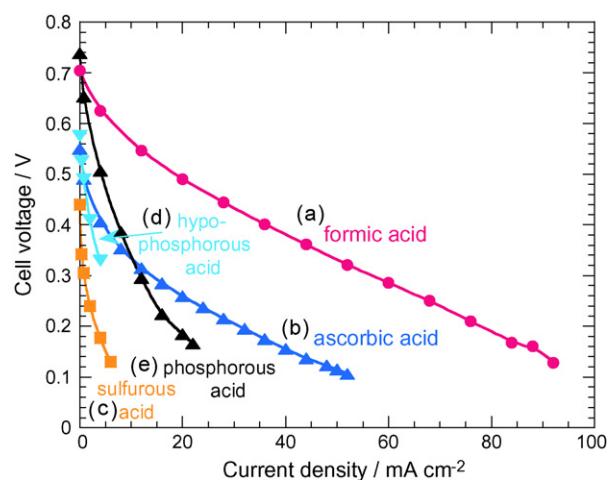


Fig. 8. Cell voltage vs. current density plots of direct type-PEFCs using aqueous solution (4 ml min^{-1}) of 1.0 M formic acid (a), 1.0 M L-ascorbic acid (b), 0.05 M sulfurous acid (c), 0.5 M hypophosphorous acid (d), and 1.0 M phosphorous acid (e) as fuels at room temperature and atmospheric pressure. Anode catalyst: Pd black (3 mg cm^{-2}), cathode catalyst: Pt-PTFE black (3 mg cm^{-2}), membrane: Nafion-117.

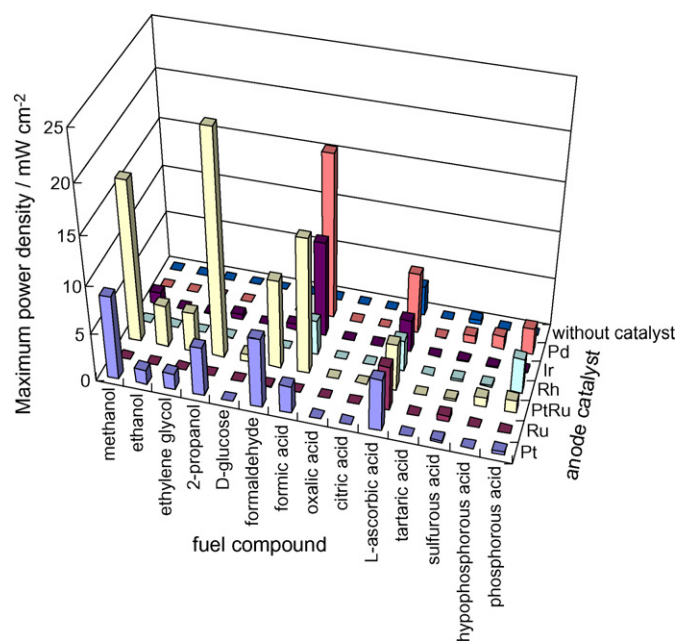


Fig. 9. Maximum power densities of direct type-PEFCs with various fuel compounds and anode catalysts at room temperature and atmospheric pressure.

The histograms in Figs. 5 and 9 show some common features, as well as a few differences. Direct PEFCs with methanol and PtRu, 2-propanol and PtRu, and formic acid and Ir showed excellent performance compared to their peak currents obtained by the electrochemical experiments in H_2SO_4 solution. In contrast, the maximum power densities of the direct PEFCs that used L-ascorbic acid, sulfurous acid, hypophosphorous acid, and phosphorous acid as fuels were much smaller than the expected values from the peak currents summarized in Fig. 5. One possible explanation for this difference is the differences in the effective potential region between the two experiments. The multiple-CV experiments were carried out in a potential sweep from 0.05 to 0.8 V versus RHE and the maximum oxidation currents in this potential range are summarized in Fig. 5. However, the direct PEFCs work below an anodic potential of 0.5 V and therefore the large peak current in the potential range of 0.5–0.8 V versus RHE obtained in multiple-CVs does not contribute to the fuel cell performance. Peak currents of a few mA listed in Fig. 5 for the oxidation of L-ascorbic acid and sulfurous acid were obtained beyond 0.7 V versus RHE, which does not correspond to the anodic potential range for direct PEFCs. In addition, the formation of reaction sites in the electrocatalysts and the diffusion of fuel compounds or product species should also be considered to explain the performance of direct PEFCs. The crossover of fuels may also be an important point that explains the discrepancy between Figs. 5 and 9. Large crossover of fuels through the polymer electrolyte membrane significantly decreases the cell voltage and output power. Some electrocatalysts may not show strong activity for the electrooxidation of fuel compounds in direct PEFCs because of these factors. The multiple-electrochemical technique proposed in the present study may be useful for the primary screening of electrocatalysts used in fuel cells, despite the slight discrep-

ancy in the results obtained in electrolyte solution and real cells.

4. Conclusions

A method for the rapid evaluation of electrocatalysts by the simultaneous examination of eight electrodes (Pt, Ru, PtRu, Rh, Ir, Pd, Au, and GC) was established. Electrochemical oxidation of fuel compounds in acidic media on eight different electrodes was evaluated simultaneously with multiple-electrochemical measurements to identify novel fuels for use in direct PEFCs. Methanol, ethanol, ethylene glycol, 2-propanol, and D-glucose were oxidized selectively on Pt and PtRu. On the other hand, formic acid, hypophosphorous acid, and phosphorous acid were oxidized effectively on Pd, and L-ascorbic acid and sulfurous acid were oxidized on all eight electrodes. Direct PEFCs using various fuel compounds were fabricated and their performance was evaluated. The performance of direct PEFCs could be roughly estimated from the results of multiple-electrochemical measurements in electrolyte solution, although additional considerations were necessary in terms of enlarging the reaction sites and the facile diffusion of fuels and products to elucidate catalytic activities in direct PEFCs.

Acknowledgments

This study was supported in part by the Industrial Technology Research Grant Program in 2004 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan. The authors thank Ms. Yoshiko Murai, Mr. Kazuya Sako and Ms. Eriko Kasugai for their kind support with the experiments.

References

- [1] S. Motokawa, M. Mohamedi, T. Momma, S. Shoji, T. Osaka, *Electrochem. Commun.* 6 (2004) 562.
- [2] H. Qiao, T. Kasajima, M. Kunitatsu, N. Fujiwara, T. Okada, *J. Electrochem. Soc.* 153 (2006) A42.
- [3] C. Lamy, S. Rousseau, E.M. Belgsir, C. Coutanceau, J.-M. Léger, *Electrochim. Acta* 49 (2004) 3901.
- [4] D. Cao, S.H. Bergens, *J. Power Sources* 124 (2003) 12.
- [5] E. Peled, V. Livshits, T. Duvdevani, *J. Power Sources* 106 (2002) 245.
- [6] J. Wang, S. Wasmus, R.F. Savinell, *J. Electrochem. Soc.* 142 (1995) 4218.
- [7] G. Horányi, V.E. Kazarinov, Y.B. Vassiliev, V.N. Andreev, *J. Electroanal. Chem.* 147 (1983) 263.
- [8] K. Matsuoka, Y. Iriyama, T. Abe, M. Matsuoka, Z. Ogumi, *J. Power Sources* 150 (2005) 27.
- [9] Z.P. Li, B.H. Liu, K. Arai, S. Suda, *J. Electrochem. Soc.* 150 (2003) A868.
- [10] K. Yamada, K. Yasuda, N. Fujiwara, Z. Siroma, H. Tanaka, Y. Miyazaki, T. Kobayashi, *Electrochem. Commun.* 5 (2003) 892.
- [11] Z. Qi, M. Hollett, A. Attia, A. Kaufman, *Electrochem. Solid-State Lett.* 5 (2002) A129.
- [12] Z.P. Li, B.H. Liu, K. Arai, K. Asaba, S. Suda, *J. Power Sources* 126 (2004) 28.
- [13] K. Yamada, K. Asazawa, K. Yasuda, T. Ioroi, H. Tanaka, Y. Miyazaki, T. Kobayashi, *J. Power Sources* 115 (2003) 236.
- [14] Y. Zhu, S.Y. Ha, R.I. Masel, *J. Power Sources* 130 (2004) 8.
- [15] Y. Zhu, Z. Khan, R.I. Masel, *J. Power Sources* 139 (2005) 15.
- [16] N. Fujiwara, K. Yasuda, T. Ioroi, Z. Siroma, Y. Miyazaki, T. Kobayashi, *Electrochem. Solid-State Lett.* 6 (2003) A257.

- [17] N. Fujiwara, S. Yamazaki, Z. Siroma, T. Ioroi, K. Yasuda, *Electrochem. Commun.* 8 (2006) 720.
- [18] T.J. Schmidt, H.A. Gasteiger, G.D. Stäb, P.M. Urban, D.M. Kolb, R.J. Behm, *J. Electrochem. Soc.* 145 (1998) 2354.
- [19] M.S. Wilson, S. Gottesfeld, *J. Appl. Electrochem.* 22 (1992) 1.
- [20] A. Hamnett, *Catal. Today* 38 (1997) 445.
- [21] V. Rao, P.A. Simonov, E.R. Savinova, G.V. Plaksin, S.V. Cherepanova, G.N. Kryukova, U. Stimming, *J. Power Sources* 145 (2005) 178.