

L-Ascorbic acid as an alternative fuel for direct oxidation fuel cells

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Received 24 January 2007; received in revised form 7 February 2007; accepted 8 February 2007

Available online 24 February 2007

Abstract

L-Ascorbic acid (AA) was directly supplied to polymer electrolyte fuel cells (PEFCs) as an alternative fuel. Only dehydroascorbic acid (DHAA) was detected as a product released by the electrochemical oxidation of AA via a two-electron transfer process regardless of the anode catalyst used. The ionomer in the anode may inhibit the mass transfer of AA to the reaction sites by electrostatic repulsion. In addition, polymer resins without an ionic group such as poly(vinylidene fluoride) and poly(vinyl butyral) were also useful for reducing the contact resistance between Nafion membrane and carbon black used as an anode, although an ionomer like Nafion is needed for typical PEFCs. A reaction mechanism at the two-phase boundaries between AA and carbon black was proposed for the anode structure of DAAFCs, since lack of the proton conductivity was compensated by AA. There was too little crossover of AA through a Nafion membrane to cause a serious technical problem. The best performance (maximum power density of 16 mW cm^{-2}) was attained with a Vulcan XC72 anode that included 5 wt.% Nafion at room temperature, which was about one-third of that for a DMFC with a PtRu anode.

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Keywords: L-Ascorbic acid; Polymer electrolyte fuel cell; Electrochemical oxidation; Dehydroascorbic acid; Carbon black; Crossover

1. Introduction

Direct methanol fuel cells (DMFCs), in which methanol solution is directly supplied to the anode, have been actively developed as power sources in portable electronic devices such as mobile phones and portable PCs, as alternatives to rechargeable batteries [1–3]. The use of methanol as a fuel offers several advantages, including high energy density for fuel storage, theoretically complete oxidation to CO_2 , and low cost. However, there are still several obstacles to the practical use of DMFCs, such as the need for Pt-based catalysts due to the large overvoltage toward the electrooxidation of methanol [4], large methanol crossover through the polymer membrane [5], and the toxicity of methanol and by-product species, i.e. formaldehyde and formic acid.

We have been trying to identify alternatives to methanol for use in direct-PEFCs [6]. The main purpose of this study is to solve the technical problems in DMFCs described above and

to propose a variety of micropower sources with different output scales and characteristics for application in novel fields. For medical applications, which are expected to be one of the most important markets for micropower sources in the near future, the demand for safety is predominant. On that point, we reported for the first time the possibility of using environmentally and biologically friendly L-ascorbic acid (AA), well known as vitamin C, as a fuel for direct-PEFCs [7]. Direct AA fuel cells (DAAFCs), in which AA solution is directly supplied to the anode, offer several advantages compared to DMFCs. In particular, DAAFCs do not require a precious metal anode and do not release any toxic product.

Although many studies have been reported on the electrochemical oxidation of AA in the field of fundamental electrochemistry and its application to electrochemical sensors, there are few research reporting on the use of AA in fuel cells. The electrochemical oxidation of AA has been widely studied on Pt [8], Au [9], and Hg [10] or carbon electrode [11,12]. In our recent study, DAAFCs using carbon black with a large surface area as an anode were developed and demonstrated that anodic performance was dominated by the electrochemically active surface area of the carbon electrode [13].

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Recently, biofuel cells, in which glucose is oxidized to gluconolactone by glucose oxidase, have also been reported as power generators for implantable devices, such as artificial organs, microsurgery robots, and in situ sensors [14–16]. Glucose is an attractive fuel for both in vivo use and as a biomass energy resource. There has also been interest in the use of bioethanol transformed by the fermentation of biomass, i.e. glucose as a fuel for vehicle engines or PEFCs to reduce carbon dioxide emissions [17,18]. AA is also a biomass-derived fuel, and can be obtained from the fermentation or chemical conversion of D-glucose. Thus, the investigation of DAAFCs may contribute to its application as a regenerative fuel.

In the present study, the fundamental characteristics of DAAFCs were investigated in comparison with DMFCs. Quantitative analysis of the product species during the operation of DAAFCs was carried out to determine the stoichiometry. AA crossover through a Nafion membrane was evaluated in comparison with methanol. The structure of the carbon electrode and the formation of a reaction site in the anode of DAAFCs are also discussed based on the effect of polymer resins and their content when used as binders.

2. Experimental

2.1. Materials

Unsupported catalysts, Pt, Ru, Pd, Ir, Rh, and PtRu black (Johnson-Matthey, specific surface area is typically $20 \text{ m}^2 \text{ g}^{-1}$), were used as electrocatalysts to prepare membrane electrode assemblies (MEAs) in DAAFCs. Vulcan XC72 (Cabot), which is a typical carbon black with a BET surface area of $254 \text{ m}^2 \text{ g}^{-1}$, was used after heating at 180°C for 3 h under vacuum. Three types of polymer resins were used as binders to prepare an electrode layer: poly(vinylidene fluoride) (PVDF, average $M_w = 534,000$, Aldrich), poly(vinyl butyral) (PVB, average polymerization degree: 2300–2500, Wako), and Nafion solution (5 wt.% solution in a lower aliphatic alcohol and water, Aldrich). Nafion membranes (equivalent weight: $1100 \text{ g equiv.}^{-1}$, sulfonic acid form, DuPont) with different thicknesses [Nafion 117 ($183 \mu\text{m}$), 115 ($127 \mu\text{m}$), 112 ($51 \mu\text{m}$)] were used as polymer electrolyte membranes after pretreatment with 3% H_2O_2 and 1 M H_2SO_4 at 80°C . All other chemicals were analytical grade and used as received.

2.2. Electrochemical measurements in electrolyte solution

The electrochemical oxidation of AA on glassy carbon (GC) electrodes was examined by the rotating disk electrode technique. A GC disk electrode (3 mm diameter) was polished to a mirror finish with $0.05 \mu\text{m}$ alumina powders. The GC disk electrode was coated with a $0.1 \mu\text{m}$ Nafion layer (Aldrich 5 wt.% solution) and then dried at 150°C , and served as the working electrode. Cyclic voltammetry (CV) was conducted in a conventional three-electrode arrangement with a working electrode, a reversible hydrogen electrode (RHE) for reference, and a Pt spiral counter electrode under an Ar atmosphere at 25°C . CVs were recorded in $0.5 \text{ M AA} + 0.5 \text{ M H}_2\text{SO}_4$ under a cyclic potential

sweep from 0.05 to 1.0 V versus RHE at 1 mV s^{-1} . An electrochemical analyzer with a rotating disk electrode set-up (ALS, model 660A and RDE-2) was used and the working electrode was rotated at 2500 rpm during all measurements.

2.3. Fabrication and evaluation of DAAFCs

Pt, Ru, Pd, Ir, Rh, and PtRu black used as anode catalysts were suspended in Nafion solution and the obtained slurry was spread on a PTFE sheet. The anode layers (catalysts 3.0 mg cm^{-2} , Nafion 10 wt.%) were prepared after drying in a vacuum at 80°C for 1 h. Vulcan XC72 electrodes (Vulcan XC72, 0.3 mg cm^{-2}) with various Nafion contents were also prepared by suspending Vulcan XC72 powders with appropriate amounts of Nafion same as the anode layers with metal catalysts. Pt black powder used as a cathode catalyst was mixed with a polytetrafluoroethylene (PTFE) emulsion (Daikin Polyflon) and heated at 360°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. Membrane electrode assemblies (MEAs) were prepared by decal transfer [19] of the electrode layers onto both sides of a Nafion membrane.

MEAs were sandwiched between two carbon-cloths (E-TEK) used as gas-diffusion media. DAAFC performance was evaluated using a single cell with a geometric electrode area of 10 cm^2 at room temperature and at atmospheric pressure. A 0.5 M AA aqueous solution was delivered to the anode at 4 ml min^{-1} , while humidified oxygen was supplied to the cathode (100 ml min^{-1}). The current–voltage behaviors were measured galvanostatically and the internal resistance of the cell was determined by the current interruption method with a current pulse generator (Hokuto Denko HC-113) and a digital multimeter. The individual electrode potentials were detected versus a standard hydrogen electrode (RHE) connected to the periphery of the anode side by a 1 M H_2SO_4 electrolyte junction as shown previously [20].

2.4. Product analysis of DAAFCs

The exhausted liquid from the anode outlet in DAAFCs was analyzed by a high-performance liquid chromatograph (HPLC) system (Shimadzu LC-VP series) that consisted of solvent delivery units (LC-10ADvp), a column oven (CTO-10Avp), a UV–vis detector (SPD-10Avp) and a system controller (SCL-10Avp). The concentrations of AA and DHAA in the fuel reservoir were determined during the steady-state operation of DAAFCs at 20 mA cm^{-2} under the circulation of 50 ml of 0.5 M AA aqueous solution at 4 ml min^{-1} in the anode. One-milliliter aliquots of the fuel solution were withdrawn at regular time intervals and quantitatively analyzed by HPLC as follows. Quantitative analysis of DHAA by direct UV-detection is very difficult, since DHAA does not show a clear absorption maximum and has little absorbance, in contrast to AA which shows strong absorbance at 265 nm. Therefore, the following post-column technique with derivatization by reagents was adopted for the simultaneous determination of AA and DHAA. One-milliliter

aliquots of sample solution were injected into a Shim-pack SCR-102H (8 mm internal diameter, 300 mm length) column thermostatted at 40 °C and eluted with 2 mM HClO₄ aqueous solution at 0.8 ml min⁻¹. After column separation, the eluate was mixed with a reagent solution composed of 100 mM NaBH₄ and 100 mM NaOH at 40 °C. By this post-column process, each component was reduced to its derivatives, which have maximum absorbance at 300 nm and could be quantitatively determined by the UV detector. The cathode side was thoroughly washed with 30 ml of distilled water after the steady-state operation of DAAFCs for 4 h. AA and DHAA in the solution recovered from the cathode side were analyzed by the same method as for that in the fuel reservoir for the anode side.

2.5. Evaluation of crossover current of DAAFCs

MEAs with PtRu anodes were used to compare the crossover of AA and methanol through the Nafion membrane under the same conditions. MEAs were fixed in single cells with a RHE connected by a 1 M H₂SO₄ electrolyte junction as in the performance test of DAAFCs. A 0.5 M AA aqueous solution was fed to the anode at 4 ml min⁻¹, while humidified nitrogen instead of oxygen was supplied to the cathode (100 ml min⁻¹). AA crossover to the cathode side through a Nafion membrane was evaluated using an electrochemical analyzer (ALS, model 660A) with a power booster (ALS, Amp Booster model 680) by the same method as for examining methanol crossover [21]. Positive potentials were applied step-wise to the cathode and the oxidation current was measured after waiting for 180 s until a steady state was reached at each potential, with an anode and RHE acting as counter and reference electrodes, respectively. The electrooxidation current of AA reaches a transport-controlled limiting value at high potentials, which reflects AA permeation flux through the membrane.

3. Results and discussion

3.1. *I*-*V* performance of DAAFCs with various anode catalysts

The performance of DAAFCs with various anode catalysts was compared. Fig. 1(a) shows the cell voltage versus current plots for DAAFCs using Pt, Ru, Pd, Ir, Rh, PtRu (3.0 mg cm⁻², Nafion 10 wt.%), and Vulcan XC72 (0.3 mg cm⁻², Nafion 5 wt.%) as anode catalysts. The differences in cell performance with the different anode catalysts can be explained by the electrochemically active surface area formed by the catalysts and Nafion electrolyte rather than by the specific catalytic activities. Previous studies have suggested that the oxidation current of AA is dominated by the electrochemically active surface area of the electrode [13]. The largest surface area electrochemically active to the AA oxidation is expected to be formed with Vulcan XC72, which has a 10-fold greater BET surface area than metal black catalysts. It is consistent with the fact that Vulcan XC72 showed the best performance compared to metal catalysts in Fig. 1. The maximum power densities of DAAFCs varied from 2 to 16 mW cm⁻², as shown in Fig. 1(b). For com-

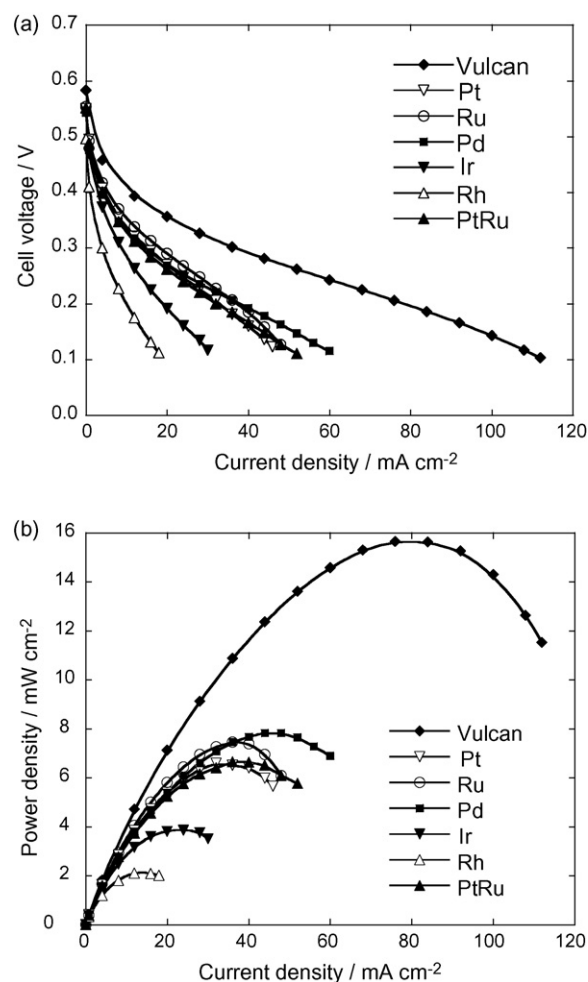


Fig. 1. Cell voltage (a) and power density (b) versus current density plots of DAAFCs using Pt, Ru, Pd, Ir, Rh, PtRu black, and Vulcan XC72 as anodes at room temperature and atmospheric pressure. Membrane: Nafion117, cathode: 3 mg cm⁻² Pt-PTFE black; AA concentration and flow rate: 0.5 M and 4 ml min⁻¹.

parison, the performance of DMFCs was also evaluated under the same experimental conditions with the same MEAs as for DAAFCs by supplying 1 M methanol aqueous solution to the anode side instead of 0.5 M AA. PtRu showed the best catalytic activity for methanol oxidation as described previously [6]. The maximum power density of the DMFC with a PtRu anode was 50 mW cm⁻², which is about three times larger than that for the DAAFC with a Vulcan XC72 anode.

3.2. Products analysis of DAAFCs

The exhausted liquid from the anode outlet was analyzed by HPLC during the operation of DAAFCs with various anodes. Only AA and DHAA were observed, and no other chemicals were detected for any of the MEAs with various anode catalysts. The time-course of the AA and DHAA concentrations in the fuel reservoir during the operation of DAAFCs at constant current density of 20 mA cm⁻² was followed by HPLC and is plotted in Fig. 2(a) and (b). A monotonous decrease and increase in the AA and DHAA concentrations in the fuel reservoir, respectively,

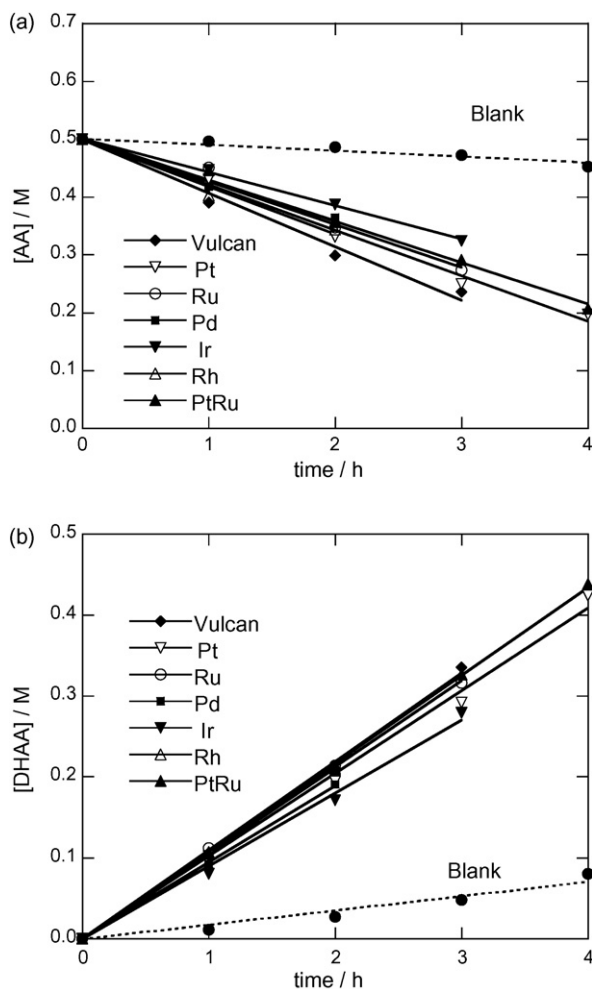
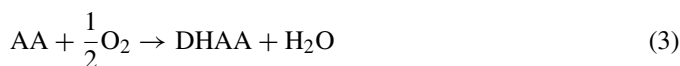
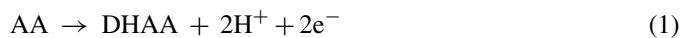


Fig. 2. Changes in AA (a) and DHAA (b) concentrations in the fuel reservoir over time during the steady-state operation of DAAFCs at 20 mA cm^{-2} under the circulation of 50 ml of 0.5 M AA at 4 ml min^{-1} on the anode side. Membrane: Nafion 117; anode: Pt, Ru, Pd, Ir, Rh, PtRu black (3 mg cm^{-2}), and Vulcan XC72 (0.3 mg cm^{-2}); cathode: 3 mg cm^{-2} Pt-PTFE black; operating conditions: room temperature and atmospheric pressure.

were observed for all of the anode catalysts with time. This indicates that AA was consumed and oxidized into DHAA during the operation of DAAFCs. However, AA is readily oxidized into DHAA not only by the electrochemical reaction but also by atmospheric oxygen. Therefore, a blank test was carried out to determine the effect of the oxidation of AA by atmospheric oxygen in the fuel reservoir and the circulation line. Plots denoted as blank in Fig. 2 represent the time-course of the AA and DHAA concentrations via a non-electrochemical process. The practical amounts of AA consumed and DHAA produced via the electrochemical reaction can be evaluated by subtracting those consumed and produced via the non-electrochemical reaction. The number of electrons related to AA oxidation was calculated using the electric charge and faraday constant to be 2.2 ± 0.4 and 1.8 ± 0.3 based on the changes in the concentrations of AA and DHAA, respectively. The anodic reaction can be estimated as a two-electron oxidation of AA to DHAA, as described by Eq. (1). The total reaction of DAAFCs was explained by Eq. (3) in combination with the cathode reaction in Eq. (2). The theo-

retical voltage of the fuel cell can be calculated to be 0.758 V from the redox potentials of 0.471 and 1.229 V for Eqs. (1) and (2), respectively, under standard conditions:



Some papers have described the existence of other reactions such as the hydrolysis of DHAA to diketogulonate, and its degradation to 5- and 4-carbon species [22]. However, those reactions were not related to redox in operating DAAFCs. The anodic reaction (Eq. (1)) is the same as the metabolic conversion of AA, and the hydrolysis of DHAA can also occur in vivo. These product analyses confirmed that DAAFCs were very safe power sources in which both the fuel and evolved products were harmless. On the other hand, the cathode side was washed with distilled water after the operation of DAAFCs at constant current density of 20 mA cm^{-2} for 4 h and then AA and DHAA in the solution were analyzed by HPLC. The experimental results suggest that the amounts of AA and DHAA in the solution recovered from the cathode side were too small to affect on the stoichiometry of AA oxidation.

3.3. Structures of carbon electrodes as anodes for DAAFCs

Carbon black is the most promising anode for DAAFCs because of its large active surface area and conductivity, as described above. The oxidation current of AA on carbon black depends on the actual active surface area of the carbon electrode and a specific functional group is not needed to increase the electrooxidation reactivity of carbon black [11]. In the present study, the preparation of carbon anodes with a large surface and the ready mass transfer of AA was investigated by optimizing the Nafion content used to support proton conductivity in the anode layer. Fig. 3 shows the cell voltages (a) and anode potentials obtained after correcting internal resistance (b) of DAAFCs using a Vulcan XC72 anode with various Nafion contents. The cell voltage strongly depended on the Nafion content in the anode layers, even with the same carbon black at the same loading as an anode (Fig. 3(a)). These differences result from the differences in the anode potentials, as shown in Fig. 3(b). The carbon black layer containing 5 wt.% of Nafion gave better cell performance due to suppression of the anode potential compared to that prepared without Nafion ionomer (Nafion 0 wt.% in Fig. 3). It suggests that Nafion ionomer in the anode layer improves the contact between Nafion membrane and the anode layer. However, higher contents of Nafion (10 and 16 wt.%) strongly increased the anode potential and consequently decreased the cell voltage. A Nafion content of 16 wt.% particularly inhibited the oxidation of AA to give a maximum current density of only a few mA cm^{-2} .

The optimum content of Nafion ionomer was investigated using supported and unsupported PtRu catalysts in an anode layer for DMFCs. A previous study reported that the optimum

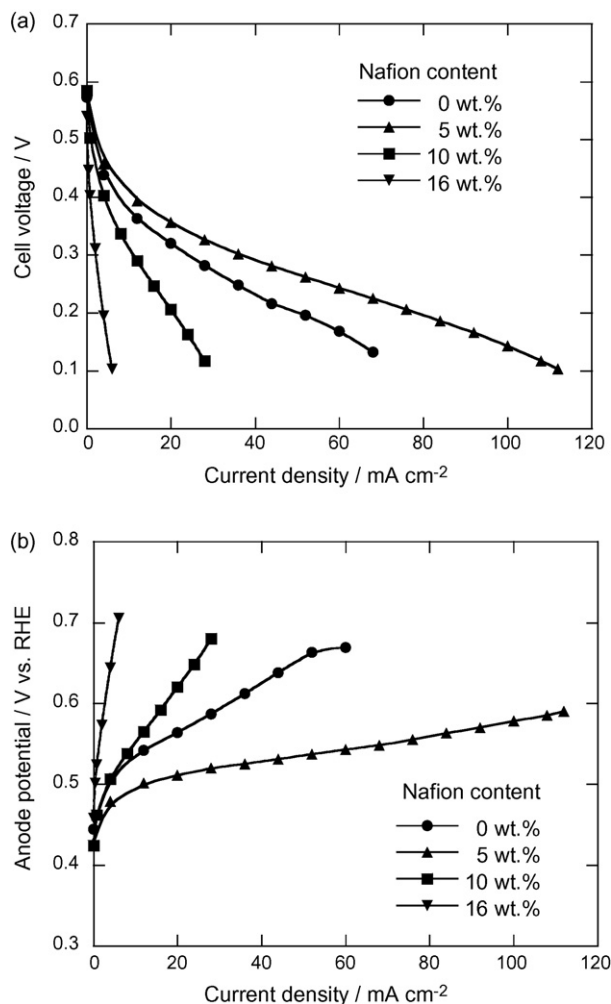


Fig. 3. Cell voltage (a) and anode potential free of internal resistance loss (b) vs. current density plots of DAAFCs using Vulcan XC72 with various Nafion contents as anodes at room temperature and atmospheric pressure. Membrane: Nafion117; cathode: 3 mg cm⁻² Pt-PTFE black; AA concentration and flow rate: 0.5 M and 4 ml min⁻¹.

content of Nafion ionomer was 60 wt.% for PtRu catalysts supported on carbon and no significant dependence was observed from 4 to 20 wt.% for PtRu black [23]. The optimum content of Nafion for Vulcan XC72 can be estimated to be more than 10 wt.%, since Vulcan XC72 (254 m² g⁻¹) has a 10-fold greater surface area than PtRu black (20 m² g⁻¹) and more Nafion is needed to cover the electrode surface. However, the experimental results showed that the appropriate content of Nafion was much smaller in DAAFCs than that estimated from the results obtained in DMFCs.

To explain this unusual behavior for the carbon anode in DAAFCs, the effect of a Nafion coating on the electrode on AA oxidation was investigated by the CV technique in electrolyte solution. Fig. 4 shows CVs of GC electrodes that have been unmodified and modified with a Nafion layer of 0.1 μm in 0.5 M AA + 0.5 M H₂SO₄. Although the oxidation current starts to increase at 0.6 V to reach a current density of 75 mA cm⁻² at 1.0 V on bare GC, the current density decreased to 11 mA cm⁻² at 1.0 V upon the modification of GC with Nafion. This is

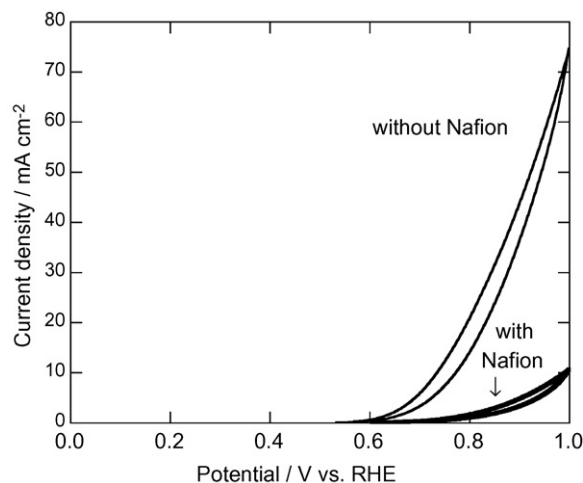


Fig. 4. Cyclic voltammograms of glassy carbon electrodes that have been unmodified and modified by a 0.1 μm Nafion layer in 0.5 M AA + 0.5 M H₂SO₄ solution obtained by the rotating disk electrode technique. Sweep rate: 1 mV s⁻¹; temperature: 25 °C; rotation rate: 2500 rpm.

due to inhibition of the mass transfer of AA by the Nafion layer formed on the electrode. In many studies, electrodes were modified with Nafion to eliminate the effect of coexisting AA which interferes with the electrochemical determination of neurotransmitters such as dopamine and serotonin [24]. It has been suggested that Nafion, which is a negatively charged perfluorinated polymer with sulfonate, excluded AA from the electrode surface by electrostatic repulsion. In DAAFCs, Nafion used as a binder in an anode layer may inhibit the effective oxidation of AA. As a result, the optimum amount of Nafion in the anode layer of DAAFCs was turned out to be 5 wt.% in Fig. 3.

Other fluoro- and butyral resins without any ionic group, PVDF and PVB, were used as binders in the anode as alternatives to Nafion. A comparison of anode performance with different binder contents indicated that 5 wt.% gave the best results for both PVDF and PVB, as with Nafion. Fig. 5 compares the cell voltages of DAAFCs using Vulcan XC72 anodes with 5 wt.%

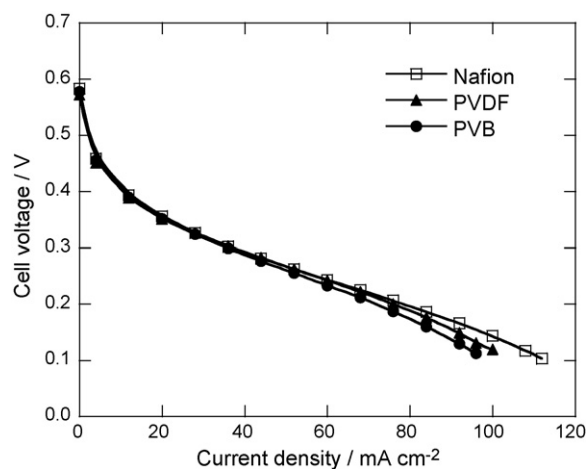


Fig. 5. Cell voltage vs. current density plots of DAAFCs using Vulcan XC72 anodes with 5 wt.% of Nafion, PVDF, and PVB as binders at room temperature and atmospheric pressure. Membrane: Nafion117; cathode: 3 mg cm⁻² Pt-PTFE black; AA concentration and flow rate: 0.5 M and 4 ml min⁻¹.

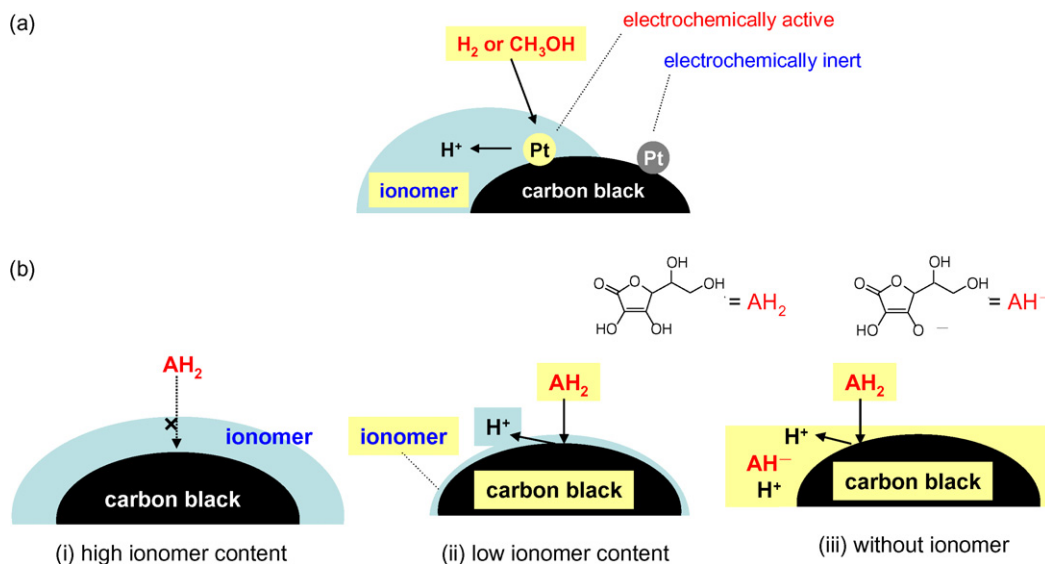


Fig. 6. Schematic drawing of the reaction boundaries in the anodes of DMFCs (a) and DAAFCs (b).

of Nafion, PVDF, and PVB. There was no obvious difference in the cell voltages between the three types of binders. In the case of typical PEFCs or DMFCs, ionomer is necessary to maintain large proton conductivity and to increase the reaction sites in the catalyst layer for both the anode and cathode. In contrast, ionomer is not necessary on the anode side of DAAFCs. The reason for the similar output of DAAFCs even without ionomer may be that slightly dissociated AA compensates lack of the proton conductor. The formation of reaction sites in the anode of DAAFCs can be explained by comparison to the findings in hydrogen-fueled PEFCs or DMFCs (Fig. 6). Fig. 6(a) shows the typical structure of an anode of PEFCs or DMFCs, in which nano-sized Pt particles are deposited on a carbon support. Only Pt particles covered with ionomer are electrochemically active and the anodic reaction takes place at only three phase boundaries among a catalyst particle, ionomer, and substrate (hydrogen or methanol). On the other hand, the anode structure of DAAFCs is quite different from that of PEFCs or DMFCs. Although the oxidation of AA potentially occurs on carbon black, a thick Nafion layer covering carbon black reduces the activity toward AA oxidation because of inhibition of the mass transfer of AA through the Nafion layer by electrostatic repulsion (Fig. 6(b)-(i)). An appropriate content of Nafion in the anode (5 wt.%) improves the contact between Nafion membrane and the anode layer with facile access of AA to the electrode surface (Fig. 6(b)-(ii)). Even if a polymer resin without proton conductivity is used to prepare the anode layer, AA is slightly dissociated to ascorbate and proton to act as a proton conductor instead of an ionomer (Fig. 6(b)-(iii)). Further studies on the increase in reaction sites in three dimensions and optimization of the anode structure in DAAFCs are now under progress.

3.4. Crossover effects of DAAFCs

The crossover of AA through a Nafion membrane was evaluated to compare this fundamental characteristic of DAAFCs

with that of DMFCs. The oxidation current densities of the permeation of AA through a Nafion membrane from an anode were detected at a cathode and plotted as crossover current densities versus applied voltages in Fig. 7. The crossover current density of AA increases in the order Nafion 117 < 115 < 112 with a decrease in the membrane thickness, based on the results shown in the inset in Fig. 7. A similar tendency was observed for methanol crossover. However, comparison of the crossover current density between AA and methanol using the same membrane suggests that the crossover of AA is about 100-fold less than that of methanol. Therefore, the crossover of AA in DAAFCs using a membrane with a certain thickness may not be as serious a problem as in DMFCs. This observation may be related to the fact that the Nafion resin in the anode limits access by AA, as described above.

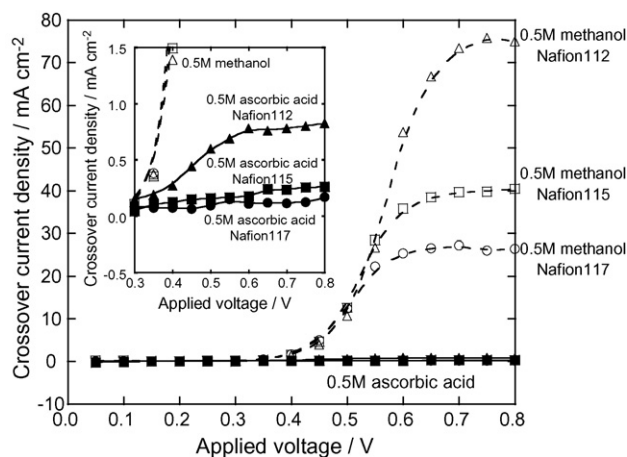


Fig. 7. Crossover current densities of direct fuel cells using 0.5 M AA and 0.5 M methanol as fuels with membranes of various thicknesses at room temperature and atmospheric pressure. Anode catalyst: PtRu black (3 mg cm^{-2}); cathode catalyst: Pt-PTFE black (3 mg cm^{-2}); cathode gas: humidified N_2 (100 ml min^{-1}); fuel: 0.5 M AA or methanol (4 ml min^{-1}). The inset shows a magnification of the 0.3–0.8 V region.

4. Conclusions

The fundamental characteristics of DAAFCs, in which AA is used as an alternative fuel for PEFCs, were investigated in terms of cell performance, product analysis, and AA crossover. The best performance was attained using a Vulcan XC72 anode and the maximum power density reached 16 mW cm^{-2} , which was about one-third of that for DMFCs with a PtRu anode under the same operating conditions. The product analysis suggested that the anode reaction was two-electron oxidation from AA to DHAA, the same as in its metabolic conversion. Thus, DAAFCs could be safely used as portable power sources, since both the fuel and product are non-toxic. The energy density of AA is lower than those of alcohol fuels, although AA is attractive fuel from the point of its safety. Therefore, the utilization of DAAFCs as a power supplier with small output power such as wearable sensors for medical use is appropriate. The crossover of AA through a Nafion membrane was about 100-fold less than that of methanol, although crossover increased with a decrease in the membrane thickness, similar to the results with methanol. The anode structure of DAAFCs was also investigated in terms of the appropriate binders and their content in the anode layer. Obvious differences between DAAFCs and DMFCs were observed for the formation of the reaction site. Nafion ionomer in the anode may inhibit the mass transfer of AA to the electrode surface. The oxidation of AA in DAAFCs may occur at the two-phase boundaries between carbon black and substrate (AA), since AA acts not only as a fuel but also as a proton conductor. Optimization of the design and construction of carbon electrodes is still necessary to increase the reaction sites and achieve the ready mass transfer of AA.

Acknowledgments

This study was supported by the Industrial Technology Research Grant Program in 2004 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan. The authors thank Mr. Kazuya Sako, Ms. Eriko Kasugai,

Ms. Yoshiko Murai, and Ms. Yumiko Hayashi for their kind support with the experiments.

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