Short communication

Passive direct methanol fuel cells fed with methanol vapor

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Abstract

A vapor fed passive direct methanol fuel cell (DMFC) is proposed to achieve a high energy density by using pure methanol for mobile applications. Vapor is provided from a methanol reservoir to the membrane electrode assembly (MEA) through a vaporizer, barrier and buffer layer. With a composite membrane of lower methanol cross-over and diffusion layers of hydrophilic nanomaterials, the humidity of the MEA was enhanced by water back diffusion from the cathode to the anode through the membrane in these passive DMFCs. The humidity in the MEA due to water back diffusion results in the supply of water for an anodic electrochemical reaction with a low membrane resistance. The vapor fed passive DMFC with humidified MEA maintained 20–25 mW cm^{-2} power density for 360 h and performed with a 70% higher fuel efficiency and 1.5 times higher energy density when compared with a liquid fed passive DMFC.
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Keywords: DMFC; Vapor feed; Humidified MEA; Passive DMFC; Composite membrane

1. Introduction

The direct methanol fuel cell (DMFC) is an attractive candidate for mobile power sources, such as Notebook PCs, handheld PCs, cellular phones, PDAs, etc., because of its advantageous properties including easy fuel storage, low operating temperature and simple design. Despite these advantages, the performance of DFMCs still does not meet strict requirements for commercialization in size, noise level, and weight. In particular, the typically large volume of DMFCs is largely due to their inefficient performance because of low catalytic activities and methanol cross-over. In this study, we adopted a vapor fed passive system to improve the energy density by using pure methanol fuel and removing the active components.

Controlling the transport processes of water, methanol, and air is the key to enhancing the efficiency of the fuel cell, which in turn makes possible the reduction of the size of DFMCs. There has been a lot of research to reduce the volume of DMFCs by controlling the fuel supply methods, such as control of the diffusivity in methanol and water, water recycling to fuel tank, or development of diffusion layers [1–3]. Another attempt was to use natural convection or capillary forces to supply air or liquid methanol fuel instead of using active components such as pumps or compressors, which led to reduction in noise. In the work of Fukunaga et al., vapor fed DMFCs have been suggested because of higher activities and the usage of highly concentrated fuel [4–6]. However, in their work, the water and methanol were vaporized and supplied with a carrier gas at high temperature, and then the active components for vapor supply cannot exclude the size problem of DMFCs. To increase the energy density and eliminate the active components for the fuel supply, transporting methanol fuel was proposed for passive DMFCs [7–9]. In those passive DMFCs, highly concentrated methanol fuel was stored as a liquid phase in a fuel reservoir and then transported as a vapor or liquid phase by diffusion or wicking from a fuel reservoir to the membrane electrode assembly (MEA) under ambient conditions. For an effective fuel cell, the anode catalysts should react with water as well as methanol [10]. The water required for methanol oxidation, in passive DMFCs, was carefully supplied by controlling the diffusion selectivity or the water back diffusion from the cathode through the membranes [7,11,12], and water back diffusion effects were proven by developing hydrophobic microporous layer with carbon particles and/or Teflon for cathode diffusion electrodes in the previous work.

In the present work, we used vapor fed passive DMFCs to get high energy density, high fuel efficiency and no noise. Humid-

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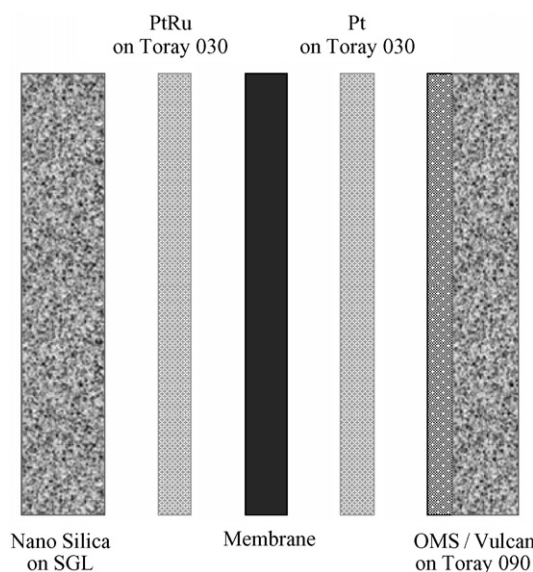Fig. 1. Schematic diagram of the MEA for a vapor fed passive DMFC.

Fig. 2. Schematic diagrams for a vapor fed passive DMFC.

ified MEAs were prepared with a composite membrane and diffusion layer for water back diffusion and methanol vapor [13]. We observed that the humidified MEA worked successfully under these conditions. Maximum power was found to be 36 mW cm^{-2} and was maintained around 25–30 mW cm^{-2} over 360 h. This humidified MEA showed a durability over 15 days in the vapor fed passive DMFC, which indicates that the MEA was humidified with the water from cathode reduction.

2. Experimental

Catalyst layers were prepared by a squeezing method. PtRu black (HIGHSPEC 6000) and Pt black (HIGHSPEC1000) were used as the catalyst for the anode and cathode, respectively. A composite membrane was fabricated by the solution casting method to have a thickness of 50 μm [14]. Loadings of PtRu and Pt on the anode and cathode catalyst layers were 8 mg cm^{-2}. The anode diffusion layer was prepared on a carbon backing layer with nano silica particles of 4–5 nm and a polyvilyldiene fluoride (PVDF) mixture whose weight ratio was 7:3. At the cathode side, a mixture of carbon particles (Vulcan XG 72) and polytetrafluoro ethylene (PTFE) was first sprayed onto the carbon backing layer with a loading of 2 mg cm^{-2} carbon base. Then, the mixture of ordered mesoporous silica of 300 nm with 10 nm pores and PVDF was loaded by spraying. SGL plain paper was used as the anode backing layer and Toray 090 (40 wt.% PTFE) for the cathode backing layer. Gold-coated nickel mesh made of thin wires was used as a current collector. A schematic diagram of humidified MEA configuration are shown in Fig. 1. All layers are hot pressed at 1 tonnes for 1 min and then at 2.2 tonnes for 3 min at 125 °C.

3. Results and discussions

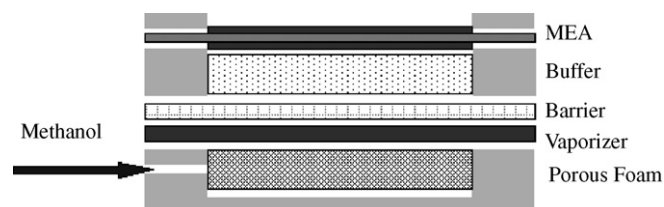The vapor fed system for the passive DMFCs is shown in Fig. 2. Here, liquid methanol is supplied to the system by a

syringe pump at the rate of 0.3 cm^3 h^{-1} for a continuous supply of methanol from the fuel reservoir or cartridge to the system. Firstly, methanol is provided to the porous foam, which is a porous pulp with 0.2 cm of thickness from 3 M$^{®}$, next the pulp absorbs liquid methanol, then methanol vapor is formed, finally vapor is diffused through the vaporizer and the barrier to the buffer layer. The buffer layer is a fired alumina which has pores of 30–40 μm, a thickness of 0.2 cm, and a porosity of 35–40% and was proposed as a MEA supporter as well as a controller of the methanol vapor diffusivity. A hydrophobic barrier, which was suggested to resist water transport from the MEA to a pulp foam or vaporizer, is a porous Teflon membrane from Whatman$^{®}$, which has pores of 10 μm and thickness of 200 μm, and the vaporizer is Nafion 112 membrane from DuPont$^{®}$ for methanol vapor diffusion. Vaporizer, barrier, and buffer layer verify delivery of methanol as a vapor phase and control the diffusion rate. Every component was designed to have 3.3 cm × 3.3 cm dimensions. Total volume of the vapor fed passive DMFC was 4.3 cm^3 except the housing, MEA, and the syringe pump. Poly (Methyl methacrylate) was used as a housing material.

The vapor transport varies with the characteristics of the vaporizer, barrier, and buffer layer because of the functions of the permeability and thickness of vaporizer, barrier, and buffer layer. The feeding rate of liquid methanol is also one of the important factors for controlling the vapor transport. The barrier and vaporizer can be replaced with other kinds of materials, which have selectivity for methanol and water, and also the buffer layer can be exchanged with other porous rigid materials with the consideration for vapor transport. In the present vapor fed passive DMFCs, the methanol vapor transport through the vaporizer, barrier, and buffer layer were optimized to get a power density of 20–30 mW cm^{-2}.

The humidified MEAs were assembled with the vapor and liquid fed passive DMFCs and their open circuit voltages (OCVs) were recorded as shown in Fig. 3. The OCV of the vapor fed passive DMFC (VFP-D) was stabilized at 0.52 V, and increased to 0.6 V with enough fuel, then finally decreased to 0.56 V due to an increase of methanol cross-over after 1 h. In the case of the liquid fed passive DMFC (LFP-D), the OCV started at 0.68 V and stabilized at 0.53 V after a certain decreasing period. The temperatures in the LFP-D and VFP-D were 43–45 °C and 38–40 °C, respectively, and the LFP-D showed a higher temperature than the VFP-D, which resulted from a higher methanol cross-over of the liquid fuel supply [15,16]. The differences in OCVs and temperatures indicate that methanol cross-over is more serious in the LFP-D than in the VFP-D. To exclude the effects of accumulated methanol and water on the OCV, the polarizations of
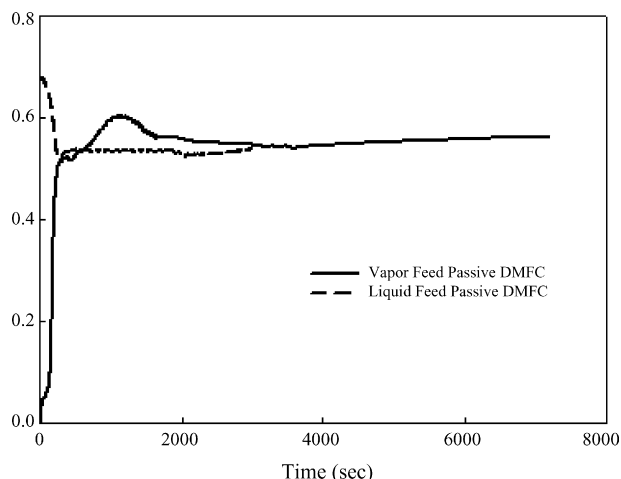
Fig. 3. Open circuit voltage of the humidified MEA in a vapor fed passive DMFC.

MEAs were measured after 1000 mA of current for 1 h. The VFP-D produced a maximum power density of 36 mW cm^{-2} and the LFP-D showed 48 mW cm^{-2} as shown in Fig. 4. It is known that higher methanol cross-over leads to a lower OCV and cell performance at low current densities with the liquid-fed methanol fuels [15,16]. However, the performance of VFP-D, which showed a higher OCV value than LFP-D, was lower than that of LFP-D, even at low current densities. Even though the OCV in VFP-D showed a higher value due to lower methanol cross-over [4–6], the LFP-D showed a higher fuel cell performance than the VFP-D because of the higher catalytic activities with lower concentration methanol solution and the induced higher temperature. Furthermore, the MEA resistance in the LFP-D was also lower than that in the VFP-D because the membrane and MEA were filled with liquid fuel, especially water. The VFP-D, in this work, had a limitation of water supply for lowering fuel concentration and membrane resistance. In spite of a higher MEA resistance and lower catalytic activities, the VFP-D showed 36 mW cm^{-2} without any supplied water, which came up to 80% of the power density of the LFP-D. However,
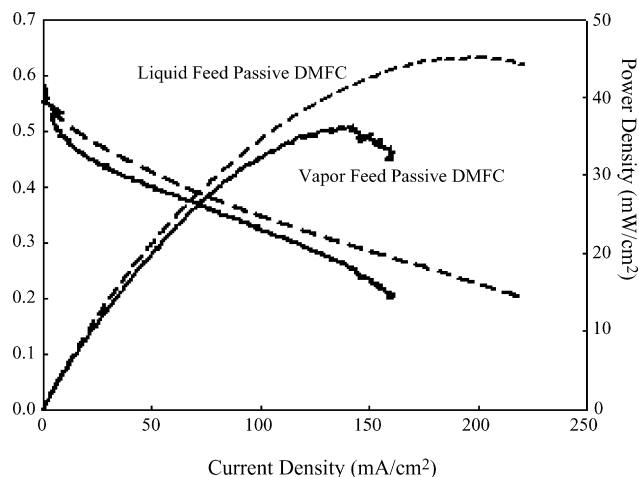

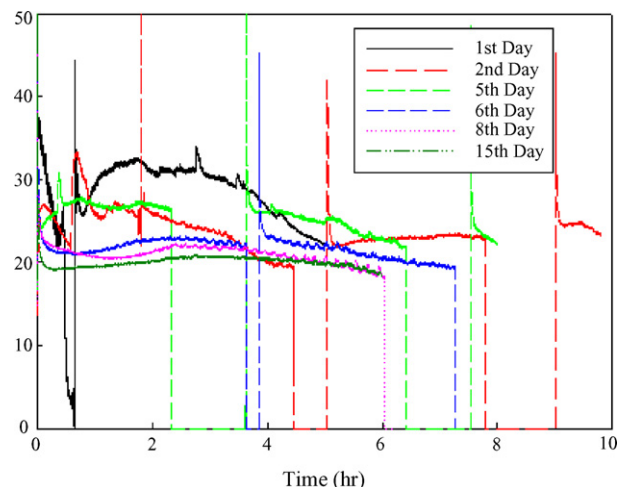Fig. 4. Polarization properties of the MEA in a vapor fed passive DMFC and liquid fed passive DMFC.

Fig. 5. Performances of the MEA at 0.3 V in a vapor fed passive DMFC.

the performance in VFP-D showed a fluctuation below 0.25 V due to mass transport limits. Because there are no mass transfer limits for air for getting ~50 mW cm^{-2} as shown in Fig. 4, the mass transfer limits in the VFP-D were inferred to be the methanol vapor supply limit. This indicates that if one wants to get a much higher power density from a VFP-D, the MEA should be designed to have better transfer of methanol fuel.

The VFP-D was also measured for long term stability, which was operated at 0.3 V as shown in Fig. 5. With a rate of 0.3 cm^3 h^{-1} of liquid methanol by a syringe pump, the cell performance was tested and operated discontinuously. The fuel was supplied only when the VFP-D was operated. The discontinuous operation was to confirm the humidification of MEA and to check whether the MEA could sustain the humidity without water being supplied from the cathode electrochemical reaction. The sustainability of the humidity in the MEA is an important factor for long term stability of the VFP-D because water is essential for the methanol oxidation reaction and lower MEA resistance [10]. The performance on the first day showed over 30 mW cm^{-2} and an impedance of 68 mΩ, then it decreased to 25 mW cm^{-2} on the fifth day. Finally, the performance remained stable at 20 mW cm^{-2} with 80 mΩ of impedance until the 15th day. The decline of performance results from the dryness of the MEA. Fuel at the anode became highly concentrated due to the lack of humidity in the MEA, and acceleration of methanol cross-over took place in turn, followed by a temperature increase from unwanted reactions, which causes a deteriorating circle [15,16]. The resulting increase of methanol cross-over reduced the fuel cell performance significantly. And also the lack of humidity increased the resistance of the MEA and reduced the fuel cell performance, which was inferred from the lower ionic conductivity of the membrane.

From the experiments, the VFP-D showed a fuel efficiency of 57%, which was obtained from 4 h of operation at 0.2 W with 0.3 cm^3 h^{-1} of methanol. The fuel efficiency is obtained from the equation, $E_{MeOH} = E_{MeOH,rxn}/E_{MeOH,supplied}$, where $E_{MeOH,rxn}$ is the product of power and time, and $E_{MeOH,supplied}$ is the energy from supplied methanol. And the energy density is obtained with the equation as $E_{MeOH,rxn}/(V_{system} + V_{fuel})$, $E_{MeOH,rxn}$ is the
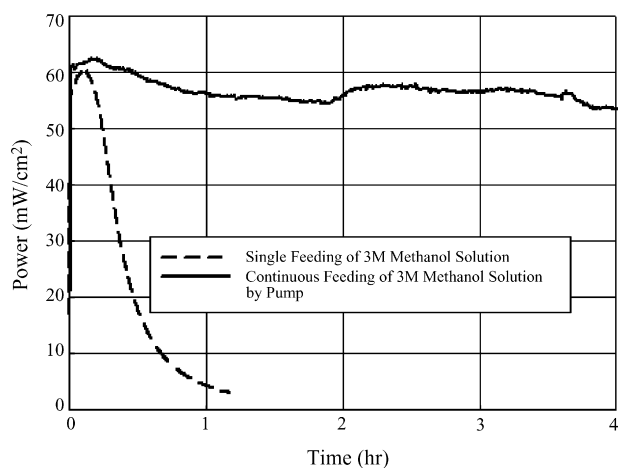
Fig. 6. Performances of the MEA in a liquid fed passive DMFC.

energy produced, V_{system} the volume of fuel delivery, and V_{fuel} is the volume of fuels. The energy density of $0.145 \, Wh \, cm^{-3}$ was obtained with the volume of vapor fed system, $4.3 \, cm^3$, and supplied fuel, $1.2 \, cm^3$. The LFP-D produced the energy density of $0.05 \, Wh \, cm^{-3}$, which was calculated from $0.27 \, mW$ with $5 \, cm^3$ single feed of $3 \, M$ methanol solution as shown in Fig. 6. The performance of the LFP-D with continuous feed of $3 \, M$ methanol by pump was also measured, which indicates that the energy density was $0.095 \, Wh \, cm^{-3}$ for $4 \, h$ operation and the fuel efficiency was 38%. If the volume of the active component is considered, the energy density rapidly decreased below $0.095 \, Wh \, cm^{-3}$. From these results, the vapor fed passive DMFC with humidified MEA shows a higher fuel efficiency and energy density at ambient conditions than the LFP-D.

4. Conclusions

A vapor fed passive direct methanol fuel cell system with a humidified membrane electrode assembly is proposed to achieve high energy density and high fuel cell efficiency simultaneously.

A porous fired alumina, porous foam, barrier, and vaporizer were used for feeding and controlling methanol in the vapor phase. The humidified MEA, with a composite membrane of lower methanol cross-over and diffusion layers of hydrophilic nano-materials, can force the water back diffusion from the cathode to the anode through the membrane. The VFP-D with a humidified MEA showed $20–30 \, mW \, cm^{-2}$ for 15 days with a maximum power of $36 \, mW \, cm^{-2}$. The VFP-D showed 70% higher fuel efficiency and 1.5 times higher energy density for a 4 h operation than the liquid feed passive DMFC. However, for applications in small electronics, the vapor fed passive DMFC should be considered to perform much higher energy density and longer stability with more innovative and strategic approaches.

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