



Effect of black catalyst ionomer content on the performance of passive DMFC

Mohammad Ali Abdelkareem^a, Takuya Tsujiguchi^b, Nobuyoshi Nakagawa^{b,*}

^a Advanced Technology Centre (ATEC), Gunma University, 1-5-1 Tenjin, Kiryu, Gunma 375-8515, Japan

^b Department of Chemical and Environmental Engineering, Gunma University, 1-5-1 Tenjin, Kiryu, Gunma 375-8515, Japan

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ABSTRACT

The effect of the ionomer content in the catalyst layers of both the anode and the cathode with the black catalyst on the performance of a passive DMFC was investigated in order to increase the power output of the passive DMFC. *In situ* cyclic voltammetry has been carried out to evaluate the electrochemically active surface area, ECSA and the catalyst utilization. Under the passive conditions, ionomer content had a significant effect on both the mass transport and the ECSA. The optimum ionomer content was affected by the operating current density whether at anode or at cathode. Under low current density region, i.e., activation over voltage region, 20 wt.% showed the highest performance at the anode and the cathode, and the cell performance in this region was varied in accordance with the results of the ECSA. Under high current density region, i.e., mass transport over voltage region, lower ionomer content, 10 and 15 wt.%, had the highest cell performance at the anode and the cathode, respectively. The decrease in the optimum ionomer content at high current density was related to the low mass transport of methanol at the anode, and the flooding at the cathode at the high ionomer contents. The optimum ionomer content whether at anode or at cathode was 20 wt.%, from the power density point of view. The catalyst utilization was 10% and 25% at optimum conditions at the cathode and the anode respectively.

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1. Introduction

There is a great interest in the development of direct methanol fuel cells (DMFCs), because of their high theoretical energy density that is suitable for mobile electric devices and automobiles. However, the commercialization of the DMFC was hindered by many obstacles such as the methanol crossover, MCO and the high over voltage at the electrodes [1–5]. The microstructure of the catalyst layer plays a key factor in fuel cell performance. The reaction and the mass transport as well as ohmic over-voltages of the DMFC are affected by the ionomer content in the catalyst layer where the ionomer prepares the active reaction sites, the so-called three-phase boundary, by contacting it with the catalyst particles. In this three-phase boundary layer, the ionomer layer acts as channels for ion transport between the membrane and the reaction sites, while the open pores act as channels for the mass transport of the reactants and/or products to or from the reaction sites, respectively. With increasing the ionomer content, the channels for proton transport increase but the open pores available for mass transport decrease.

The addition of the ionomer affects the number of reaction sites, where hydrogen protons are generated or consumed, and the channels for the ionic path based on the mixing and the distribution

structures of the catalyst with the ionomer. These structures determine the effective ionic conductivity of the catalyst layer and the number of effective reaction sites.

At the same time, the addition of the ionomer affects the mass transport whether to or from the reaction active sites or to the electrolyte membrane. With the increasing ionomer content, the catalyst utilization will increase. A further increase in the ionomer content results in the formation of a thick ionomer layer on the catalyst, thereby the access of the reactants or the products to or from the active sites decreases, therefore, the catalyst utilization decreases. Hence, there is an optimum ionomer content which is a compromise among the high number of effective reaction sites, the high effective ionic conductivity and the low mass transport resistance [6–10]. Moreover, the ionomer content influences the hydrophobic and hydrophilic pore distribution in the catalyst layer so its content affects the transport of the liquid and gas phases [11].

In a PEMFC, many studies have been carried out to investigate the optimum ionomer content [6–15]. The best results have been reported at different ionomer loadings by different researchers, and it generally ranged from 30 to 40 wt.% of the catalyst loading.

The optimum ionomer content in the catalyst layer of DMFC is considered to be different from that in the PEMFC because of the high mass transport resistance. At the anode of DMFC, methanol has a low diffusion coefficient, compared to that of hydrogen gas in the PEMFC, as well as the difficulties of the releasing of the CO₂. At the cathode, MCO, in DMFC, not only causes a mixed potential and flooding, but also consumes the oxygen required for the oxy-

* Corresponding author. Tel.: +81 277 30 1458; fax: +81 277 30 1457.
E-mail address: nakagawa@cee.gunma-u.ac.jp (N. Nakagawa).

Table 1

List of the previous studies that investigated the optimum ionomer content in the catalyst layer for the DMFC.

Electrode	Catalyst	Preparation method	Catalyst loading (mg cm ⁻²)	Conc. (M)	Temp. (K)	Operation mode	Optimum NAF (wt.%)	Ref.	
Anode	PtRu black (1:1)	C paper treated	–	2 M	383	Active	36	Chu et al. [16]	
		Decal	2+/-0.3	1 M	353	Active	6.5	Thomas et al. [17]	
		Decal	3.9	1 M	353	Active	7	Dohle et al. [18]	
		–	3	2 M	353	Active	4	Kim et al. [19]	
		Decal/CCM	3	1 M	348	Active	15	Zhao et al. [26]	
	PtRu (53%)/C	–	–	3	2 M	353	Active	60	Kim et al. [19]
		PtRu (40%)/C	CCM	1	1	353	Active	25	Krishnamurthy et al. [20]
		Pt40 Ru20/CNT	C cloth, vacuum filtration	4	1 M	–	Active	63	Jeng et al. [25]
		PtRu (60%)/C	Decal	2	1 M	343	Active	20–40	Wannek et al. [27]
		Pt20 Ru10/C	Spraying, C paper treated	2	1 M	313	Active	>60	Birry et al. [28]
Cathode	Pt black	Decal	2.5+/-0.5	1 M	353	Active	10.5	Thomas et al. [17]	
		CCM, C paper and MPL	–	–	–	Active	33	Krishnamurthy et al. [21]	
	Pt/C	CCM, C cloth and MPL	1.2	H2	333	Active	22	Liu et al. [22]	
	Pt (20 & 40%)/C	CCM, C paper and MPL	2	1 M	353	Active	33	Krishnamurthy et al. [20,21]	

CCM, catalyst coated membrane; MPL, micro porous layer.

gen reduction reaction. Both results in additional oxygen transport limitations at the cathode surface.

Many studies have been done to determine the optimum ionomer content for the DMFCs [16–27] as shown in Table 1. As obvious from the table, the optimum ionomer content varied from one study to another depending on the preparation method, catalyst type, diffusion media and also the operating conditions. The catalyst layers with the same composition produced on different substrates, i.e., (decal sheets, gas diffusion layers or directly on membranes), resulted in different mass transport limitations. Therefore, different optimum ionomer content was expected. The black catalyst prepared by the decal methods realized a low optimum ionomer content of less than 15 wt.% [17,18,26]. This is because, in the decal method, catalyst ink with the ionomer was first applied on a non-porous sheet without any permeation loss of the ionomer. Higher ionomer contents were required in the other preparation methods [16,21] and/or for the supported catalyst [19–21,25,26,28], in which a catalyst ink was applied on a porous diffusion media, i.e., a microporous layer (MPL), carbon paper or carbon cloth. A large portion of the ionomer permeates through these layers, therefore, a relatively large amount of the ionomer was used in the catalyst layer. If a vacuum was used during the preparation, the ionomer loss by permeation would be increased and higher ionomer content was required [25]. The supported catalyst is nanoparticles finely distributed on a carbon support that requires a higher ionomer content to provide enough contact between the catalyst and the ionomer [21]. Moreover, the operating conditions, such as cell temperature [11,22] reactant flow rate [22] and methanol concentration affect the mass transport, therefore, the optimum ionomer content.

Recently, a passive DMFC that absorbs methanol from a built in methanol reservoir by an osmotic action and breathes O₂ from the surrounding air by natural diffusion and convection, has been demonstrated and investigated by some researchers [29–42]. Under the low cell temperatures around 298 K used for passive conditions, the resistance to mass transport becomes high in comparison to that at high temperature around 353 K, used for the active conditions. At the cathode, the accumulation of water blocks the openings of the cathode and blocks the O₂ supply, and at a high current density, flooding is quite severe and significantly depresses the cell performance. At the anode, the low diffusion of methanol and the CO₂ release, at low cell temperature, limit the methanol supply. Under these high mass transport resistances, the optimum ionomer content for the passive DMFC is expected to be lower than that for the active conditions. Up to now, there has been no report about the optimum ionomer content in the passive DMFC.

Under the passive conditions, carbon cloth was widely used as the diffusion layer to enhance the mass transport and black catalyst was used to increase the catalyst activity. *In situ* cyclic voltammetry measurements were usually done at the actual operating temperature. This study has been carried out to clarify the optimum ionomer content in a passive DMFC using the black catalyst, PtRu at the anode, Pt at the cathode and carbon cloth as the diffusion layer. Polarization and *in situ* cyclic voltammetry measurements have been carried out to investigate the effect of the ionomer content on the cell performance and evaluate the electrochemically active surface area ECSA, respectively.

2. Experimental

2.1. MEA preparation

The MEA, which uses carbon cloth (35% Teflonized, ElectroChem, Inc.) as the anode and cathode backing layers, was prepared in the following manner: 3–4 mg cm⁻² of carbon black, Ketjen black, containing 10% PTFE, a microporous layer MPL, was prepared on the surface of the carbon cloth.

Pt black of 2 nm particle size (HiSPEC 1000, Johnson Matthey Fuel Cells, Co., Ltd.) and PtRu black of 2.72 nm particle size (HiSPEC 6000, Johnson Matthey Fuel Cells, Co., Ltd.) were used as the catalyst for the cathode and the anode, respectively. Catalyst ink was prepared by dispersing an appropriate amount of the catalyst in a solution of de-ionized water, isopropyl alcohol and a 5 wt.% Nafion solution (Wako, Inc.). The ink was then precipitated on the surface of the carbon cloth with the MPL using a micropipette to form the catalyst layer. The catalyst loading was around 4 mg cm⁻² in each electrode. For the anode catalyst layer, five different electrodes containing 10, 15, 20, 30 and 40 wt.% of the ionomer were prepared as the anodes while the ionomer content in the cathode catalyst layer was fixed at 30 wt.%. For the cathode catalyst layer, four different electrodes containing 10, 15, 20 and 30 wt.% of the ionomer were prepared as the cathodes in which the ionomer content in the anode catalyst layer was fixed at 20 wt.%.

Nafion 112 was used as the electrolyte membrane. The MEA was then fabricated by sandwiching the membrane between the anode and the cathode and hot pressing them at 408 K and 5 MPa for 3 min.

2.2. Electrochemical measurements

2.2.1. Measurement of cell performance

The MEA was placed in a plastic holder as shown in Fig. 1. In the anode compartment, a methanol reservoir, 22 mm wide, 22 mm

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