# Effect of polymer binders in anode catalyst layer on performance of alkaline direct ethanol fuel cells

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### ABSTRACT

In preparing low-temperature fuel cell electrodes, a polymer binder is essential to bind discrete catalyst particles to form a porous catalyst layer that simultaneously facilitates the transfer of ions, electrons, and reactants/products. For two types of polymer binder, namely, an A3-an anion conducting ionomer and a PTFE-a neutral polymer, an investigation is made of the effect of the content of each binder in the anode catalyst layer on the performance of an alkaline direct ethanol fuel cell (DEFC) with an anion-exchange membrane and non-platinum (non-Pt) catalysts. Experiments are performed by feeding either ethanol ($C_2H_5OH$) solution or ethanol–potassium hydroxide ($C_2H_5OH–KOH$) solution. The experimental results for the case of feeding $C_2H_5OH$ solution without added KOH indicate that the cell performance varies with the A3 ionomer content in the anode catalyst layer, and a content of 10 wt.% exhibits the best performance. When feeding $C_2H_5OH–KOH$ solution, the results show that: (i) in the region of low current density, the best performance is achieved for a membrane electrode assembly without any binder in the anode catalyst layer; (ii) in the region of high current density, the performance is improved with incorporation of PTFE binder in the anode catalyst layer; (iii) the PTFE binder yields better performance than does the A3 binder.

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## 1. Introduction

An alkaline direct ethanol fuel cell (DEFC) directly converts the chemical energy of liquid ethanol to electricity. The most striking feature of this power source is that it uses an alkaline electrolyte membrane, rather than an acid membrane for direct methanol fuel cells (DMFC). This feature makes it possible to use non-Pt catalysts to achieve faster kinetics of both the ethanol oxidation and oxygen reduction reactions. The use of non-Pt catalysts can substantially reduce the cost of the fuel cell system. Another feature that makes the alkaline DEFC more appealing is that ethanol is a much more environmentally friendly and readily produced fuel than methanol used in DMFCs. In addition, the DEFC also possesses the advantages offered by a DMFC that include a simple and compact cell system with high specific energy, and fast refuelling. All the above-mentioned attributes make this type of fuel cell a good choice for powering portable and mobile electronic devices [1–12].

In preparing the electrodes for low-temperature fuel cells that use membrane electrolytes, a polymer binder is essential to bind discrete catalyst particles to form a porous catalyst layer that simultaneously facilitates the transfer of ions, electrons and reactants/products. In developing acid proton electrolyte membrane

fuel cells (PEMFCs) and DMFCs, Nafion®, which is a perfluorosulfonic acid polymer with high proton conductivity developed by DuPont, has proved to be the best binder in forming both the anode and cathode catalyst layers. The Nafion binder promises breakthrough not only in cell performance but also in cell durability [13–15]. Recently, Liang et al. [15] reported a simple glue method for fabricating membrane electrode assemblies (MEAs) for DMFCs with a Nafion® solution introduced between an electrode and a membrane. The experiment results indicated that the MEAs yielded better cell performance and longer durability. For the alkaline DEFC, polytetrafluoroethylene (PTFE) or Nafion® was added to the catalyst layer to serve as a binder in past investigations [3,16,17]. Yu and Scott [3] investigated an alkaline DMFC using an anion exchange polymer electrolyte membrane with PTFE as the binder in the electrodes. More recently, Scott et al. [17] used Nafion® as the binder for preparing MEAs for alkaline DMFCs.

Although both PTFE and Nafion® can bind catalyst particles so as to form a catalyst layer, they cannot conduct hydroxide ions. Hence, these two polymer materials are not a good choice as the binder for preparing MEAs for alkaline membrane fuel cells. Recently, an anion-conducting ionomer, named as A3, has been developed by Tokuyama as a binder for alkaline membrane fuel cells. Subsequently, Bunazawa and Yamazaki [18] evaluated the A3 binder and investigated the influence of its content in the anode and cathode catalyst layers for alkaline DMFCs; they found that optimum A3 content was 45.4 wt.% at both anode and cathode electrodes.
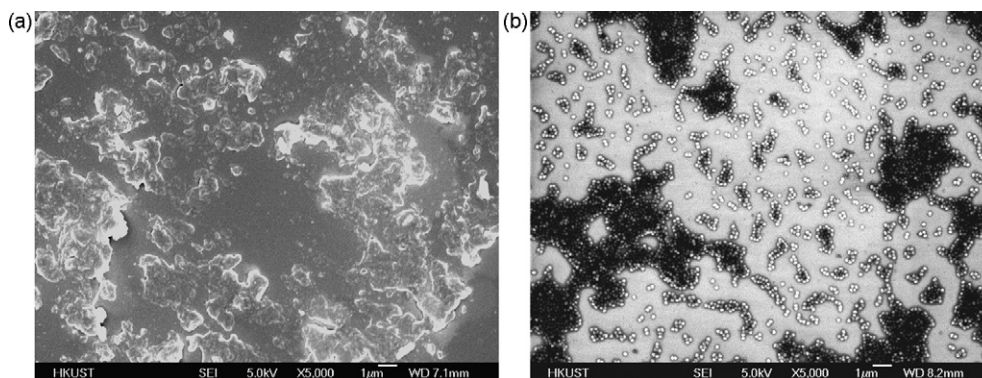
**Fig. 1.** SEM images of dried polymer binders: (a) A3 and (b) PTFE.

The objective of work reported here is to evaluate the A3 and PTFE binders for preparing the anode catalyst layer of an alkaline DEFC with an anion-exchange membrane. The experiments are performed for feeding either ethanol solution or ethanol–potassium hydroxide solution.

## 2. Experimental

### 2.1. Membrane electrode assembly

The in-house fabricated alkaline DEFC consisted of a MEA with an active area of $1.0\,cm \times 1.0\,cm$, sandwiched between a pair of current collectors. The MEA was comprised of an anion-exchange membrane (A201, Tokuyama) and two electrodes. The cathode electrode was a single-side electrode consisting of a non-platinum HYPERMEC$^{TM}$ catalyst (Acta) with a loading of $1.0\,mg\,cm^{-2}$, which was attached to a backing layer made of carbon cloth (E-TEK). On the anode, the catalyst layer was fabricated in-house by the catalyst coated substrate (CCS) method [19]. Inks were prepared by mixing non-platinum HYPERMEC$^{TM}$ catalyst (Acta) with a loading of $1.0\,mg\,cm^{-2}$ and 1-propanol as the solvent. To study the effect of binders in the anode catalyst layer, different binders (A3-solution and PTFE-emulsion) were added to the catalyst inks at various amounts from 0 to 30 wt.% (wt.% denotes a ratio of the dry weight of a binder to the weight of the catalyst layer). The catalyst inks were stirred continuously in an ultrasonic bath for 10 min such that they were well dispersed [20]. Each catalyst ink was brushed on to nickel foam (Hohsen Corp., Japan) that served as the backing layer to form an anode electrode.

### 2.2. Current collectors

For convenience of temperature control, both the anode and the cathode current-collectors were made of 316L stainless steel. A single serpentine flow-field with a 1.0 mm channel width, a 0.5 mm channel depth and a 1.0 mm rib width was machined on one side of each current-collector plate.

### 2.3. Measurement instrumentation and test conditions

The experiments were carried out in the cell test station detailed elsewhere [21,22]. At the anode, an aqueous fuel solution of 1.0 M ethanol and 1.0 M KOH was supplied by a peristaltic pump at a flow rate of $1.0\,ml\,min^{-1}$. At the cathode, 99.7% pure oxygen at ambient pressure with a flow rate of 100 standard cubic centimeters per minute (sccm) was fed without humidification. A mass flow meter (Omega FMA-7105E), along with a multiple-channel indicator (Omega FMA-5876A), was used to control and measure the oxygen flow rate. Before entering the fuel cell, the solution and oxy-

gen were preheated by means of an electrical heating rod that was installed in the anode and cathode current-collectors. The operating temperature during the experiments was set at 40 °C, which was measured by a thermocouple installed in the anode current-collector. Tests of the alkaline DEFC voltage–current (polarization) curves were controlled and measured by an electric load system (Arbin BT2000, Arbin Instrument Inc.). The cell resistance was measured by the dc-pulse method. The morphology of the anode catalyst layer was examined with a scanning electron microscope (JEOL-6700F).

Cyclic voltammetry (CV) experiments were conducted to study the effect of the binders on the anode catalyst by using a three-electrode cell assembly with a Pt foil and a Hg–HgO electrode (MMO, 1.0 M KOH) as the counter and reference electrodes, respectively. The working electrode was a glassy carbon disc (4 mm in diameter with an area of $0.126\,cm^2$) covered with a thin layer of catalyst. Typically, the catalyst ink was prepared as follows. A 5 mg sample of the catalyst with different binders was dispersed in 1 ml ethanol by sonication for 20 min. A 10 μl quantity of well-dispersed catalyst ink was pipetted on top of the glassy carbon substrate. The CV tests were then conducted at $20\,mV\,s^{-1}$ over a potential range of $-0.926$ to $0.274$ V vs. MMO in 1.0 M KOH solution. Solutions were prepared from analytical grade reagents and deionized water.

## 3. Results and discussion

### 3.1. Microstructure of binders

Fig. 1 shows SEM images of the dried polymer binders: A3 and PTFE. It can be seen that the A3 ionomer forms a film-like structure after it has been dried. Hence, it can be inferred that when A3 is mixed with catalyst particles, its inherent film structure can cause the particles to form large agglomerates, and to be covered by A3 ionomer films. By comparison, Fig. 1b shows that the dried PTFE forms a porous structure with small particles joined together. This characteristic of the PTFE microstructure suggests that when a proper amount of PTFE emulsion is added to the catalyst ink, PTFE is inclined to adhere to but not cover the catalyst particles. As a result, smaller agglomerates can be formed, and the agglomerate will not be coated by PTFE polymer. In other words, more catalytic sites can be exposed to the fuel solution for the electrode with PTFE as the binder than that with A3.

### 3.2. Effect of the A3 content in the anode catalyst layer on cell performance

The effect of A3 content in the anode catalyst layer (CL) on cell performance when feeding 1 M ethanol solution combining 1 M KOH is presented in Fig. 2. It can be seen that the cell performance
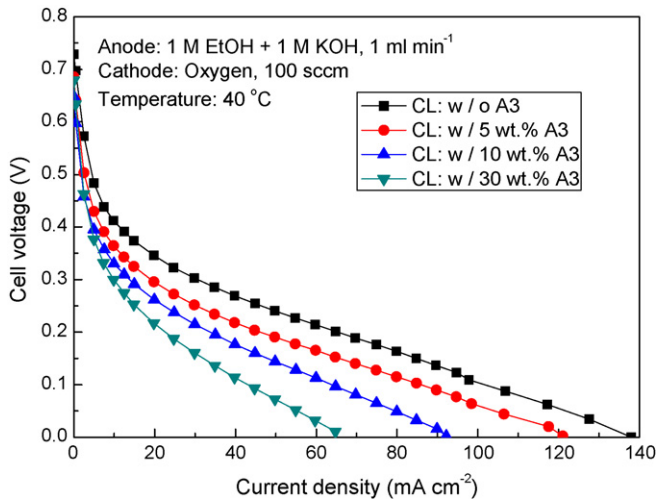
**Fig. 2.** Effect of A3 content in anode catalyst layer on cell performance.



**Fig. 3.** CV curves of anode electrode with different A3 content in 1.0 M KOH at sweep rate of 20 mV s$^{-1}$.

decreases with increase in A3 content from 0 to 30 wt.% over the whole current density region, including the activation, ohmic and concentration-controlled regions. The maximum current density is 65 mA cm$^{-2}$ with 30 wt.% A3 ionomer impregnated in the anode CL, whereas it is 138 mA cm$^{-2}$ without any A3 ionomer in the anode CL. The reason why the addition of A3 ionomer causes the cell performance to decrease is explained as follows. As discussed in the preceding section, film-like structures are likely to form when A3 ionomer is incorporated into the catalyst layer. As a result, the active sites may be covered by A3 films, leading to a decrease in the active surface area in the anode CL. The A3 films on agglomerates also increase the transport resistance of hydroxide ions, electrons and fuel in the anode CL. The above explanation can be confirmed by CV characterization of the change in catalyst activity before and after incorporation of A3. The CV curves of anode catalyst with different A3 contents are presented in Fig. 3. It can be seen that the electro-
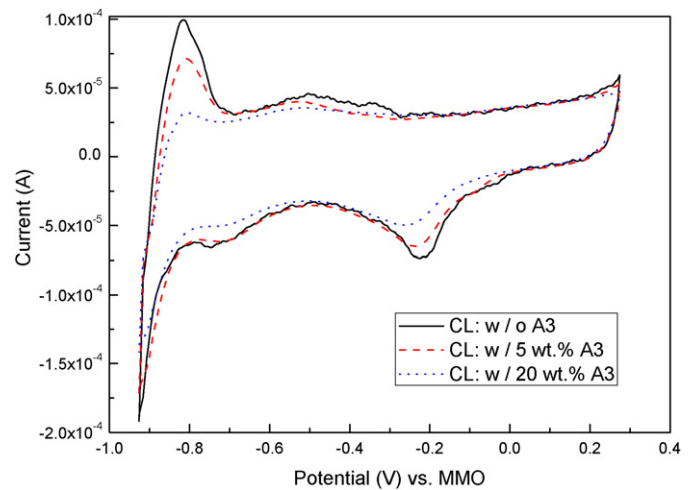
chemical active surface area (ECSA) decreases with increase in A3 content, suggesting that the A3 ionomer indeed hinders OH$^-$ ion transfer in the catalyst layer.

Fig. 4 shows SEM images of the surface morphology of the anode CL with different A3 contents. It can be seen that the porosity of the anode CL increases with increasing A3 content, which tends to enhance mass transport in the anode CL. However, the number and size of agglomerates also increase with A3 content, leading to a decrease both in the active surface area and in the mass-transport resistance of ethanol and KOH so as to decrease the maximum current density. Furthermore, the A3 coated agglomerates may impede the charge transfer of hydroxide ions and electrons into and out of the agglomerates, respectively. This can be confirmed from the measured cell resistances shown in Fig. 5, which indicate that the cell resistance increases with A3 content. As a result, the cell voltage drops quickly with increasing A3 content in the anode CL. The
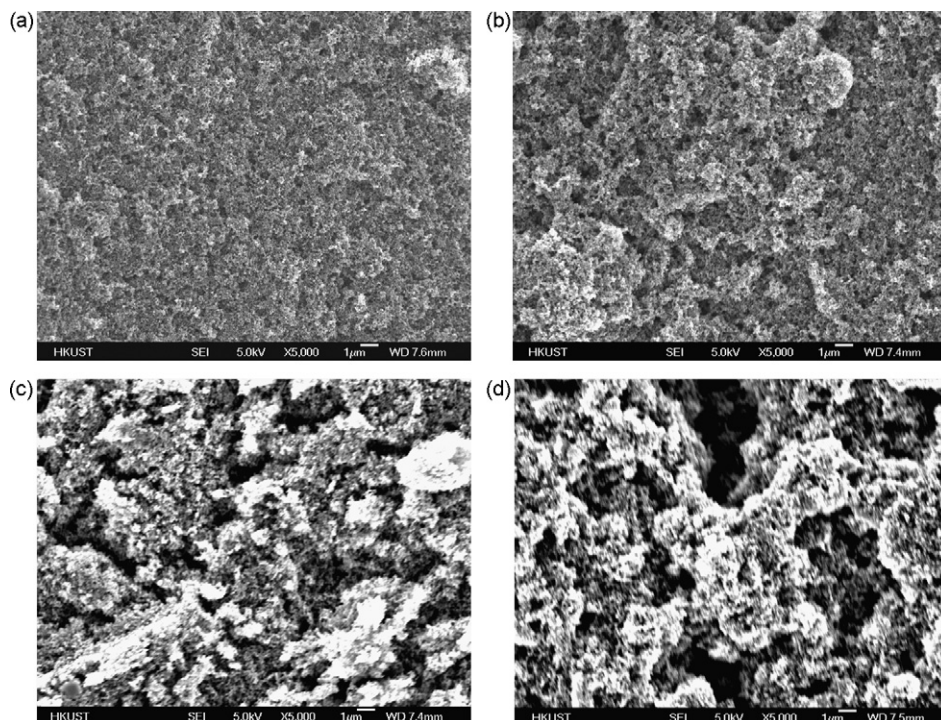


**Fig. 4.** SEM images of surface morphology of anode catalyst layer with different A3 contents: (a) 0 wt.%, (b) 5 wt.%, (c) 10 wt.%, and (d) 30 wt.%.
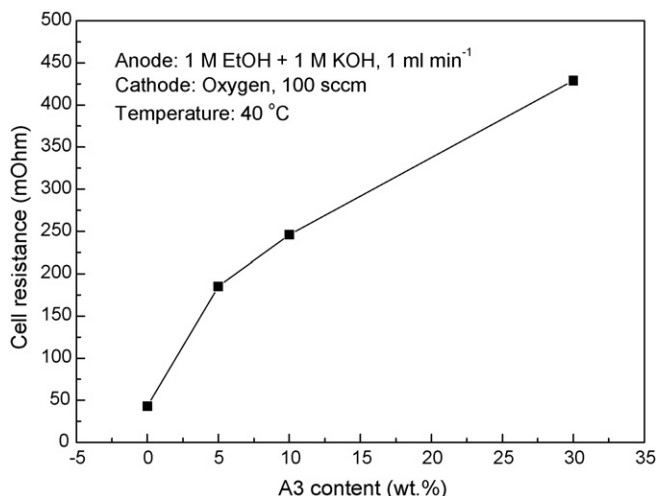
**Fig. 5.** Effect of A3 content in anode catalyst layer on cell resistance.



**Fig. 7.** Effect of A3 content in anode catalyst layer on cell performance.

results presented so far are limited to 1.0 M KOH solution, a relatively high concentration. The cell performance was also measured for different A3 contents in the anode CL with a low KOH concentration, namely, 0.10 M. The results are presented in Fig. 6 and show the same trend as in Fig. 4, i.e., the cell performance decreases with increase in A3 content. The data in Figs. 4 and 6 indicate that the ion conductivity of A3 is not sufficient in the alkaline media.

The effect of A3 content in the anode CL on cell performance when the anode is fed with 3 M ethanol solution without added KOH is shown in Fig. 7. The cell performance varies with A3 ionomer content in the anode CL, and the best performance is achieved with 10 wt.%-A3 ionomer content. The possible reason why an optimum A3 content exists is explained as follows. Use of the A3 ionomer can extend the active surface area of the anode CL as it can conduct hydroxide ions, which is beneficial to anode performance. On the other hand, excessive A3 ionomer in the anode CL hinders the transfer of ethanol and electrons to catalytic sites and thus lowers the anode performance. Therefore, there exists an optimum A3 content resulting from the transport of species, ions and electrons.

It is worth mentioning that although the incorporation of A3 ionomer in the anode CL can improve the cell performance for the case of feeding $C_2H_5OH$ solution without added KOH as shown in Fig. 7, the performance is much lower than for feeding $C_2H_5OH$ solution with added KOH as displayed in Figs. 4 and 6. This is mainly
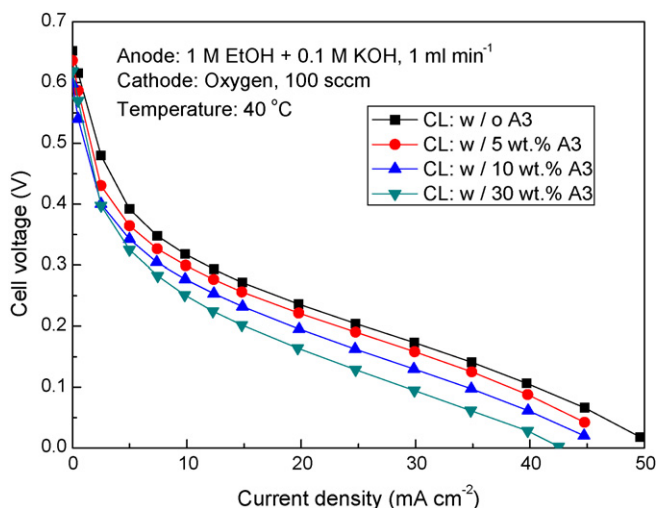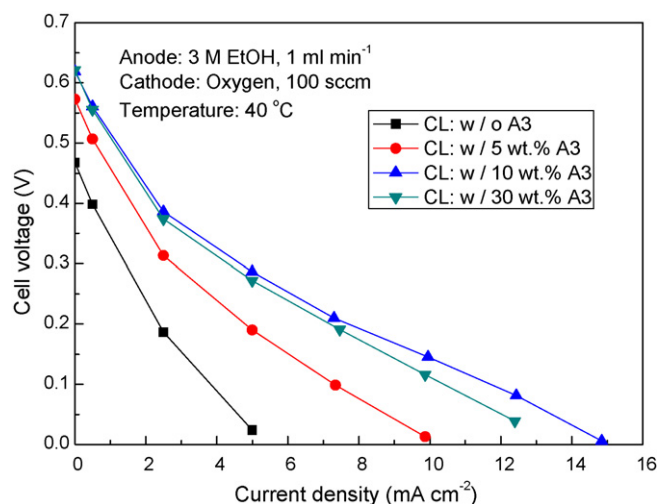
because the ion conductivity of the A3 ionomer is much lower than that of KOH solution. Hence, significant enhancement in the ion conductivity of the present anion-exchange ionomer A3 is needed. In the meantime, the microscopic structure of this ionomer should also be improved to avoid the formation of film-like surfaces when dried.

### 3.3. Effect of PTFE content in anode catalyst layer on cell performance

Fig. 8 shows the effect of PTFE content in the anode CL on cell performance. In the region of low current density, the cell performance decreases with increase in the PTFE content from 0 to 30 wt.%. The reason for this behaviour is as follows. The active surface area decreases with increase in PTFE content. As mentioned earlier, the PTFE also adheres to the catalyst particles one by one to form agglomerates, resulting in a decrease in the active surface area. This explanation can be further confirmed by CV tests of the anode catalyst with different PTFE contents, as presented in Fig. 9. The curves show that the surface area decreases with the increase in PTFE content. In addition, the incorporation of PTFE into the catalyst layer can block the transfer of hydroxide ions and electrons to the catalytic sites and hence increase the ohmic polarization loss. Fig. 10 shows the change in cell resistance with different PTFE contents,
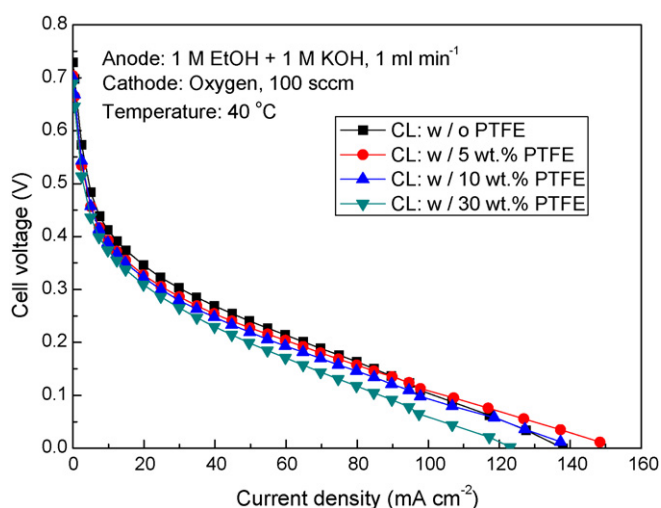


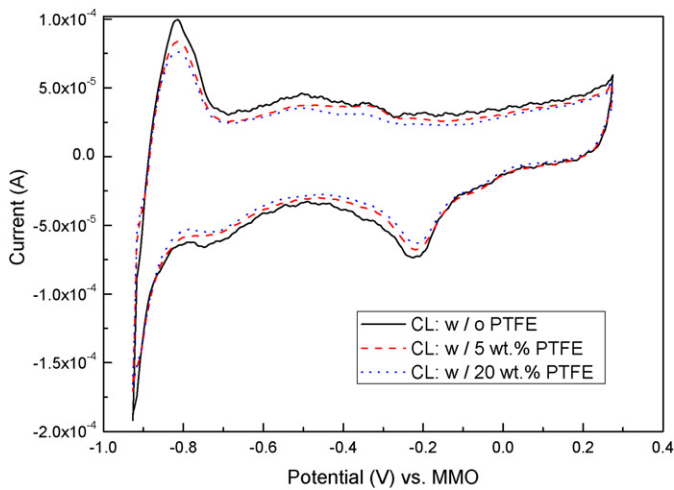**Fig. 6.** Effect of A3 content in anode catalyst layer on cell performance.



**Fig. 8.** Effect of PTFE content in anode catalyst layer on cell performance.

**Fig. 9.** CV curves of anode electrode with different PTFE contents in 1.0 M KOH at sweep rate of $20 \, mV \, s^{-1}$.



**Fig. 10.** Effect of PTFE content in anode catalyst layer on cell resistance.

which indicates that the cell resistance increases with increasing PTFE content.

With respect to the performance shown in Fig. 8 in the region of high current density. It is seen that, with increasing the PTFE content, the cell performance first increases and then decreases. The maximum current density increases and decreases, respectively, by $10 \, mA \, cm^{-2}$ and $15 \, mA \, cm^{-2}$ with 5 wt.% and 30 wt.% PTFE content in the anode CL. The change in the maximum current density can be attributed to a change in the mass-transport resistance of ethanol and KOH. The microstructure of the anode CL with different PTFE contents is given in Fig. 11. It can be seen that the number of pores in the anode CL with PTFE as a binder is more than that without PTFE, which tends to reduce the mass-transport resistance of the reactant, thereby resulting in improved cell voltages in the region of high current density. On the other hand, an excessive content of PTFE, e.g. 30 wt.% as shown in Fig. 11d, may block the pores and
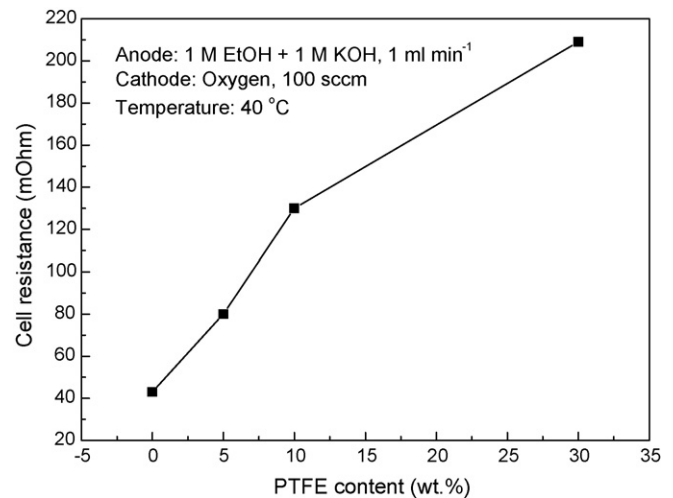
increase the mass-transport resistance. The experiments were also performed when the KOH concentration was increased to 3.0 M. The measured polarization curves are presented in Fig. 12. A trend similar to that obtained with the lower KOH concentration (1.0 M) is observed.

In summary, in the region of low current density, the cell performance decreases with increase in PTFE content, whereas in the region of high current density, the best cell performance is achieved with 5 wt.% PTFE added to the anode CL, as the mass transport of the reactant is enhanced as a result of its unique pore structure.

### 3.4. Comparison of cell performance with and without binders in anode catalyst layer

The effect of different binders with or without A3 and PTFE in the anode CL on cell performance is illustrated in Fig. 13. In the
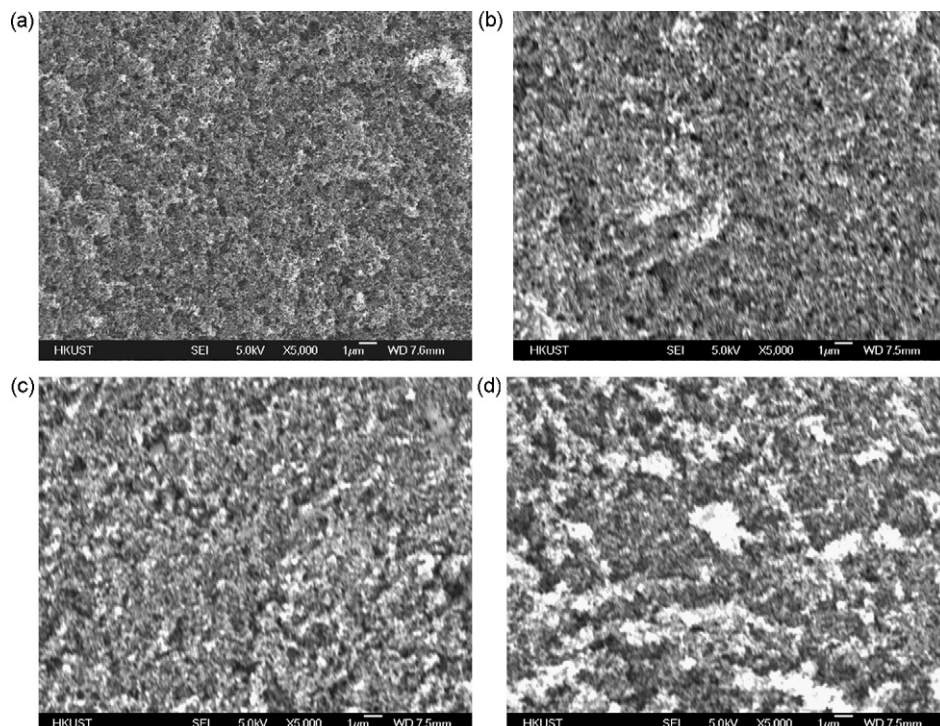


**Fig. 11.** SEM images of surface morphology of anode catalyst layer with different PTFE contents: (a) 0 wt.%, (b) 5 wt.%, (c) 10 wt.%, and (d) 30 wt.%.
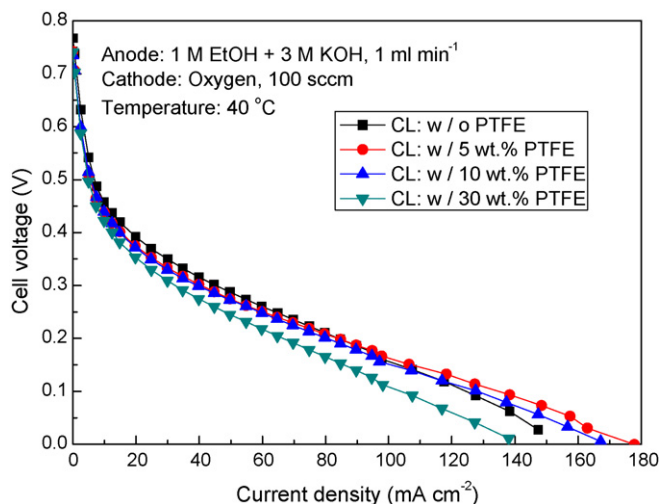
**Fig. 12.** Effect of PTFE content in anode catalyst layer on cell performance.

region of low current density, the best performance is seen without binder. The reasons, as mentioned above, are due to the loss of active sites and increase in mass- and charge-transport resistances. In the region of high current density, however, the best cell performance is achieved for a MEA with 5 wt.% PTFE in the anode CL; this is due to the enhanced mass transport of ethanol and KOH. By contrast, the cell voltage of the MEA with the same content of A3 is lower over the whole current density region as the result of the agglomerates coated by A3 with the lower ion conductivity.

### 3.5. Effect of binders in anode catalyst layer on the durability of alkaline DEFC

In the electrode, it is well understood that a binder is required to bind the catalyst particles and thereby present them from getting lost during the long-term run. Otherwise, without a binder, the cell performance will quickly degrade. An evaluation was made of cell durability with and without a binder in the anode CL. To simulate the case of the long-term run, the tests were performed by flushing the anode CL at a high flow rate. Fig. 14 shows the effects of polymer binders in the anode CL on the durability of the alkaline DEFC with and without a flushing process for 10 h at a high flow rate of 28.0 ml min$^{-1}$. At a current density of 50 mA cm$^{-2}$, the



**Fig. 13.** Performance comparison of fuel cell with anode catalyst layer containing different binders.
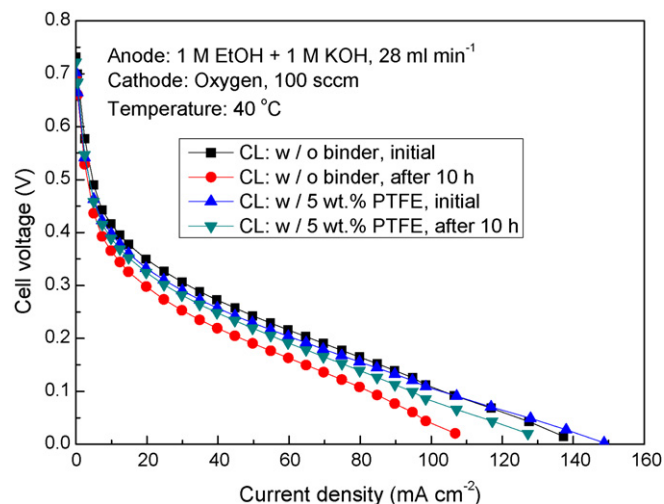


**Fig. 14.** Performance comparison of fuel cell with and without PTFE binder in anode catalyst layer before and after flushing for 10 h at flow rate of 28 ml min$^{-1}$.

MEA without the binder in the anode CL shows the high voltage of 243 mV, while the voltage drops to 191 mV after being flushed. However, when the same accelerating degradation experiments are imposed to a MEA with a 5 wt.% PTFE-impregnated anode CL, the results show that the voltage decreases by only 11 mV, from 230 to 219 mV. The reason for the voltage loss is mainly attributed to the loss of anode catalyst particles during the flushing process, leading to a decrease in the active surface area. For instance, at the current density of 5 mA cm$^{-2}$, the voltage loss of the MEA without a binder in the anode CL is more than 50 mV. By comparison, the voltage drop of the MEA with a 5 wt.% PTFE-impregnated anode CL is only 4 mV. The degradation in the performance of the MEA without binders in the anode CL is more serious than that with 5 wt.% PTFE in the anode CL, suggesting that the binder plays an important role in the anode CL in terms of MEA durability.

## 4. Conclusions

This work is concerned with the binder for preparing the MEA for an alkaline DEFC with an anion-exchange membrane and non-Pt catalysts. Two types of polymer binder have been evaluated, namely, an A3-an anion conducting ionomer and a PTFE-a neutral polymer. The effect of the content of each binder in the anode CL on the fuel cell performance has been investigated. Experiments are performed by feeding either $C_2H_5OH$ solution or $C_2H_5OH$–KOH solution. The experimental results for the case of feeding $C_2H_5OH$ solution without added KOH indicate that the cell performance varies with A3 ionomer content in the anode CL, and the best performance is obtained from a MEA with 10 wt.% A3 impregnated into the anode CL. This is because the A3 ionomer conducts hydroxide ions and extends the active surface area that results in high anode performance. However, the results for the case of feeding $C_2H_5OH$–KOH solution are more complex. First, in the region of low current density, the cell performance decreases when A3 or PTFE is incorporated as a binder in the anode CL. The decreased performance can be mainly attributed to the fact that incorporation of the polymer binder leads to a decrease in active surface area, thereby increasing the activation polarization loss. Second, in the region of high current density, the addition of PTFE with porous structures in the anode CL can enhance the mass transport of the reactant, thereby increasing the cell performance. Third, the performance of the PTFE-bonded MEA is superior to that obtained with A3 as the binder in the anode CL, since the A3 ionomer will form a dense film on the catalyst agglomerate, which results in a decrease in the active
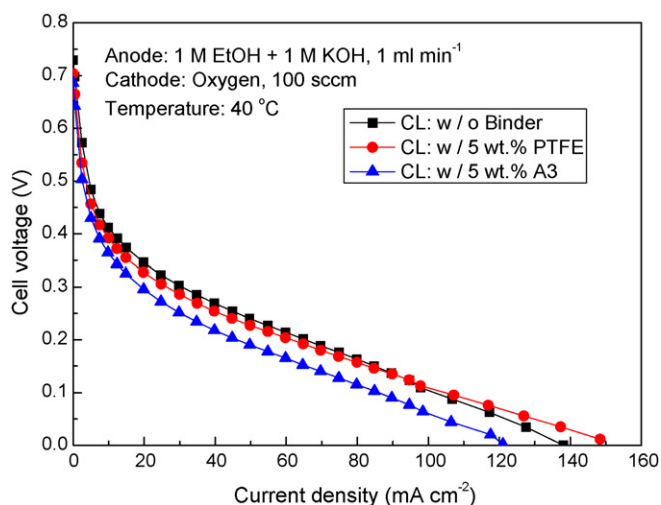
surface area. Finally, the incorporation of PTFE can further improve the durability of the MEA as the polymer can prevent the catalyst particles from being lost during long-term run of the fuel cell.

## Acknowledgements

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