

Effect of silicon carbide particle size in the electrolyte matrix on the performance of a phosphoric acid fuel cell

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Abstract

Silicon carbide (SiC) powders with two different particle sizes were dispersed in de-ionized water containing 13–3 wt.% of polytetrafluoroethylene (PTFE) as a binder. The slurries were ball-milled for 24 h and tape-cast on the cathode or anode catalyst layer for making the electrolyte matrix layer. The matrix layers were characterized by measuring pore distribution and surface morphology. The effects of fine SiC particle and PTFE content on the electrolyte uptake of the matrix layers were examined. Addition of fine particle to coarse particle and high PTFE content decreased significantly the electrolyte uptake. The electrolyte matrix layer with the mixed powder of fine and coarse particles showed a good cell performance due probably to high bubble pressure and good contact between matrix and electrodes. By using the mixed powder with fine particle size, a thin matrix layer can also be fabricated, which decreases the cell internal resistance and so increases cell performance. The effect of the formed matrix over the cathode and over both the cathode and anode, on the cell performance was investigated. Gas starvation studies indicate that a cell with matrix coated on both the anode and cathode catalyst layers is less susceptible to reactant gas starving effects. Especially, coating the matrix on the anode catalyst layer can minimize the observed effect due to hydrogen starvation. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Fuel cells to generate direct current from a fuel and an oxidant gas are well known. Such cells comprise a fuel electrode spaced apart from an oxidant electrode with an electrolyte-retaining matrix layer disposed between them. The overall cell performance and life of such cells is often governed by the morphology of the electrolyte-retaining matrix layer [1]. In phosphoric acid fuel cells, the amount of polytetrafluoroethylene (PTFE) binder used to prevent the movement of the silicon carbide (SiC) particles in the cell, is one of the deciding factors of the electrolyte-retaining capacity of the matrix layer [2].

Apart from this, the intimate contact between the matrix and electrode surfaces, which is necessary to maximize catalyst utilization by uniform distribution of electrolyte [3], and thickness, with structural integrity throughout the surface [4], are also important for an optimum cell performance. Therefore, the purpose of this research is to summarize the results from the physical characterization of the formed matrix and single cell tests to find out the effect of SiC particle size in the formed matrix layer on electrodes on the cell performance.

2. Experimental

The characterization of the as-received SiC powders was carried out using Coulter particle size analyzer. Matrix layers containing PTFE as a binder to an amount of about 13–3 wt.% were prepared using a PTFE emulsion (60 wt.% in solid, DuPont). Two different commercial SiC powders (Lonza and Alfa Aesar) were used to prepare the matrix layers. Hereafter, SiC (Lonza) and SiC (Alfa Aesar) will be referred as SiC-L and SiC-A, respectively. The slurries were ball-milled for 24 h and cast over the cathode and anode to the desired thickness with a doctor blade instrument. Coated matrix layers were sintered in air at 295 °C for about 5 min. In order to measure the absorption of the electrolyte as a function of PTFE content in the matrix, respective matrix layers with an area of 5 cm² were made to be in contact with the electrolyte for 24 h at a temperature of 150 °C. The volume of the absorbed electrolyte was calculated by dividing the weight difference before and after the electrolyte absorption by the specific gravity of the electrolyte. The microstructure of the formed layers was observed with SEM (SL-30 Philips) and analyzed using a mercury intrusion porosimeter (Micromeritics 9400 series). Impedance analysis of the cells with the respective matrix was done at an open circuit voltage, with a Solartron analyzer setup. The performance analysis of the matrix layers was studied by

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assembling unit cells of 100 cm^2 geometric area. The catalyst loading was about 0.5 and 0.25 mg cm^{-2} for cathode and anode, respectively and the preparation procedure was described elsewhere [5]. The working temperature of the cell was $200 \text{ }^\circ\text{C}$ and the flow rates of fuel gas and air were 1000 and $3500 \text{ cm}^3 \text{ min}^{-1}$, respectively.

3. Results and discussion

The particle size distribution (PSD) of the commercial SiC-L and SiC-A samples is shown in Fig. 1. The respective distribution curves shows that the PSD of the as-received samples is bimodal in nature for both the powder samples. The particle size ratio between the coarse (mean diameter: $2.106 \text{ }\mu\text{m}$) and fine (mean diameter: $0.268 \text{ }\mu\text{m}$) of the SiC-L powder is about 10 and their particle weight ratio is 45/55. Even though it is reported in the literature [6], that their size and weight ratios are more favorable for a close packed structure, our previous experimental results [5] were different from this finding. This may be due to the presence of PTFE, irregular shape of the SiC particles and no use of dispersing agent.

To circumvent the above-mentioned packing problem, SiC-A powder having greater vol.% of smaller particle size ($0.186 \text{ }\mu\text{m}$ mean size) is added to an amount of 23 wt.% to the parent SiC-L powder. The amount of SiC-A powder added was selected on the basis of the electrolyte uptake of the matrix layer with 13 wt.% PTFE and 0.040 mm thickness, as shown in the Fig. 2. The increase of SiC-A from 23 to 24 wt.% resulted in a twice the decrease in electrolyte uptake values that resulted from a decrease from 22 to 23 wt.%. Moreover, the cells exhibited low performance when the added ratio was above or below this level, may be due to low electrolyte and gas cross over. The volume distribution curve of the SiC-A as shown in Fig. 1 (curve b), indicates a perfect non-intersecting bimodal distribution [7]

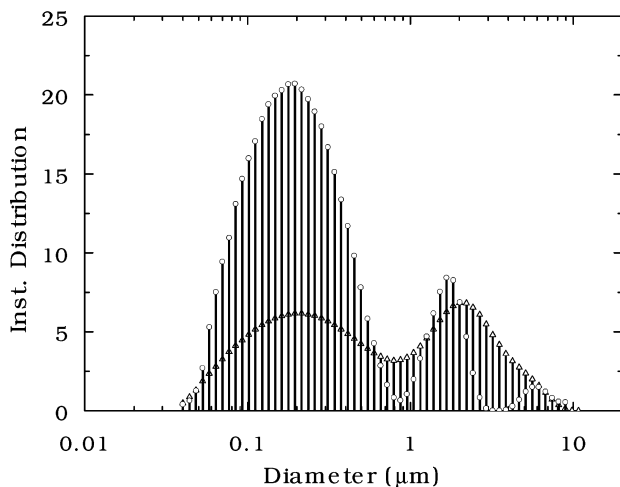


Fig. 1. Particle size distribution of as-received: (a, Δ) SiC-L; and (b, \circ) SiC-A powders.

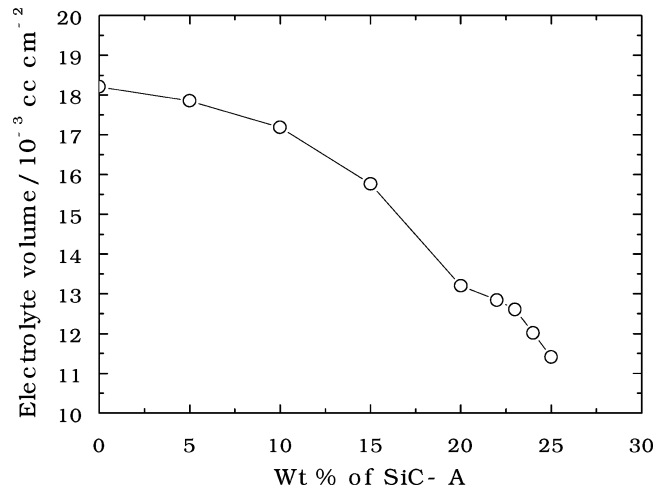


Fig. 2. Electrolyte uptake of the 0.03 mm thick SiC matrix layer with various wt.% of SiC-A to SiC-L with 13 wt.% PTFE.

with mean equivalent spherical diameter of 0.186 and $1.680 \text{ }\mu\text{m}$, along with negligibly small amount of particles in the higher diameter range. The vol.% ratio between the fine and coarse particles is $72.58/27.42$, indicating the presence of an excess of fine particles.

The performance of the cell having matrix layer prepared with SiC-L powder alone is better up to a current density of 80 mA cm^{-2} , than the cell having matrix layer prepared with mixed (SiC-L + 23 wt.% SiC-A) powder and above this current density the reverse order in performance is observed as shown in Fig. 3. The surface morphology of matrix layers with SiC-L and SiC-L + 23 wt.% SiC-A coated on the identical electrodes are shown in Fig. 4a and b, respectively. It is clear that the surface morphology of the matrix prepared with mixed powders is more closely packed, due to the presence of an excess of lower size particles, than the layer prepared with SiC-L alone. Since the matrix thickness (0.040 mm) was same in both cases, the

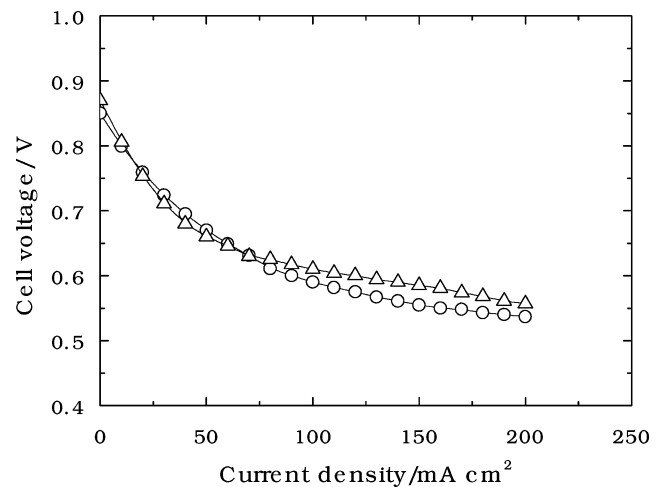


Fig. 3. Cell voltage-current density plot for H_2/air single cell with (\circ) single powder (SiC-L) and (Δ) mixed powder (SiC-L + SiC-A) matrix.

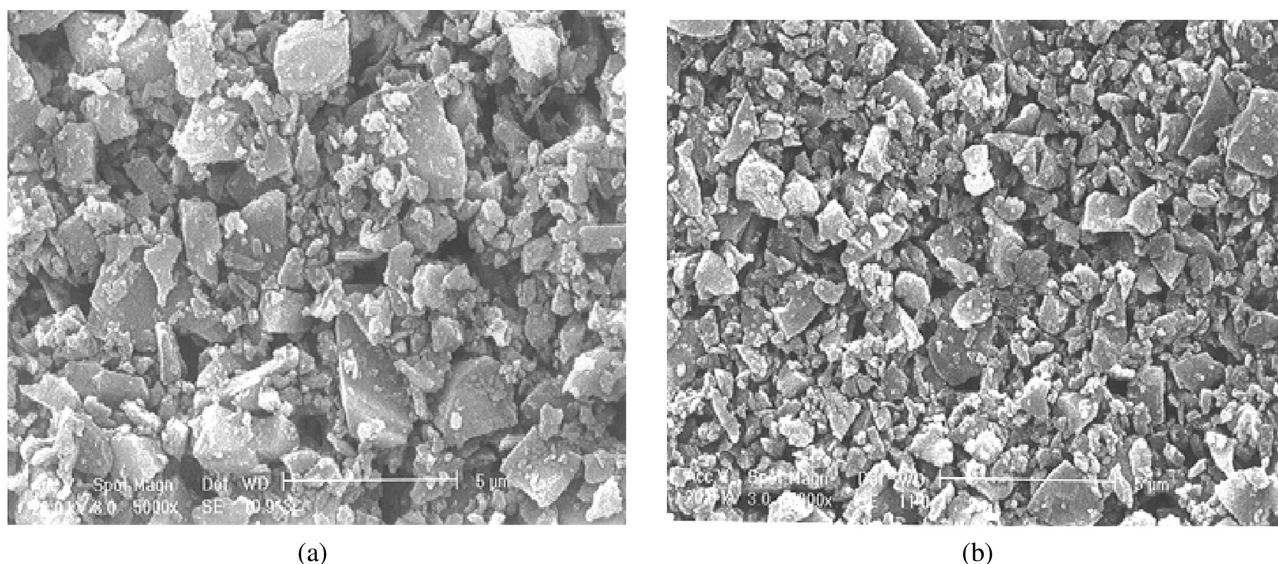


Fig. 4. Surface morphology of SiC matrix layer prepared with (a) single (SiC-L) and (b) mixed powder (SiC-L + SiC-A).

observed low performance below 80 mA cm^{-2} , may be due to an increase in internal cell resistance caused by the reduction in total pore area from 19.431 (for single SiC-L powder) to $11.884 \text{ m}^2 \text{ g}^{-1}$ (mixed powder SiC and SiC-A powder), calculated from the respective mercury intrusion data, which is shown in Fig. 5. Comparing the respective incremental intrusion versus diameter graph, as shown in Fig. 5, can substantiate the above argument. The reduction of macro pores ($>50 \mu\text{m}$) in the matrix layer prepared with mixed powder (SiC-L + SiC-A) indicates the effectiveness of the addition of the second powder (SiC-A) on the macro pores, which are responsible for low bubble pressure and electrolyte hold-ability. The enhanced performance above 80 mA cm^{-2} may be caused by the increased number of active pores of the anode and cathode exposed to the electrolyte and due to good bubble pressure barrier. Upon

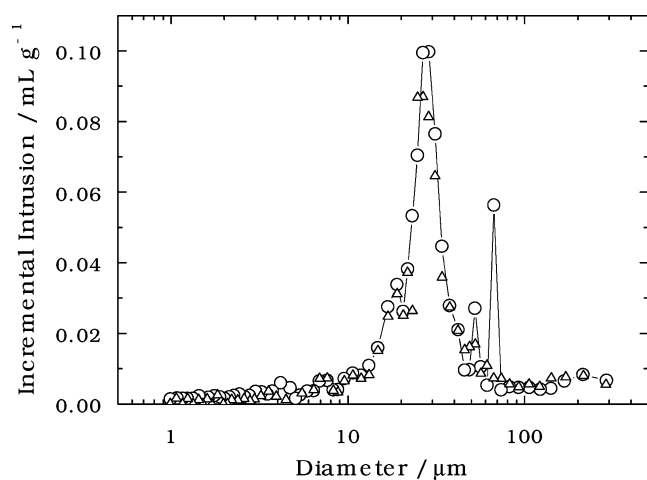


Fig. 5. Pore size distribution of the SiC matrix layer prepared with (○) single powder (SiC-L) and (△) mixed powder (SiC-L + SiC-A)

the above findings, the following changes in the matrix layer were made to improve the cell performance at all current density levels. The PTFE content (from 13 to 3 wt.%) and the matrix thickness (from 0.040 to 0.030 mm) were reduced in order to increase the uptake of electrolyte and decrease the internal cell resistance. When the PTFE content in the matrix was reduced below 3 wt.%, the adherence of the matrix to the catalyst layer was poor. Moreover, free movement of the matrix material in and around the surface was observed while impregnating with electrolyte, so the lower limit of PTFE was fixed at 3 wt.%.

Fig. 6 shows the effect of above modification in the matrix on the cell performance. A single cell with a matrix layer of 0.030 mm thick having 3 wt.% PTFE displayed good performance. The effect of the above changes in the matrix layer is well understood by comparing the respective

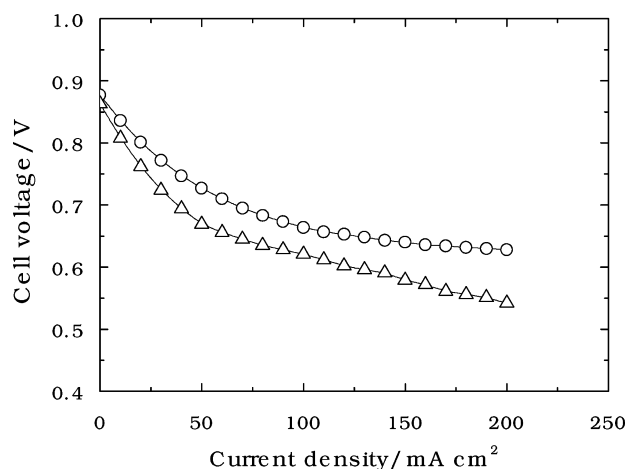


Fig. 6. Effect of PTFE content and thickness of the mixed powder matrix layer on the cell performance (△) PTFE 13 wt.%, thickness 0.04 mm and (○) PTFE 3 wt.%, thickness 0.03 mm.

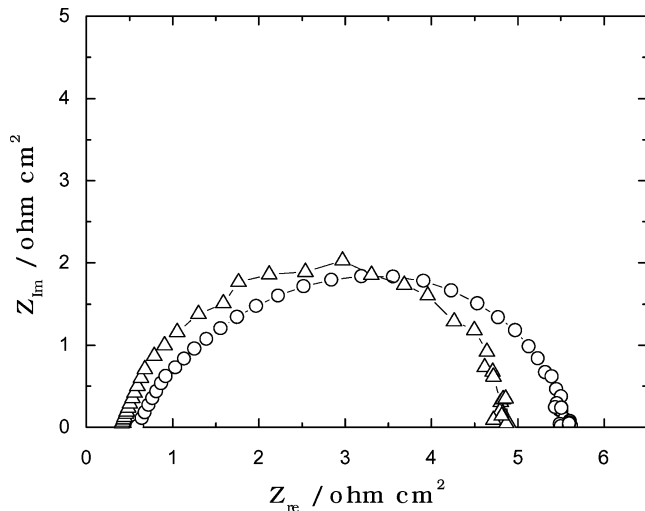


Fig. 7. Impedance spectra of the single cell having matrix layer prepared with (○) single powder (SiC-L) and (△) mixed powder (SiC-L + SiC-A).

complex plane impedance plot as shown in Fig. 7. Apart from the observed constant phase element (CPE) with a theoretical slope of 45° on the high frequency range indicating that the electrolyte infiltrates into the narrow pores [8], the entire semicircle is shifted towards lower values on reducing the thickness and PTFE content of the matrix. It can be noted that the calculated double layer capacitance value for the cell having 0.030 mm thick and low PTFE matrix is 0.03796 F, which is ~ 10 times higher than the 0.002978 F, for the cell with 0.040 mm thick matrix and high PTFE content. Thus, the significant influence of PTFE in the matrix layer on the improvement of the cell performance can be well understood by comparing the respective double layer capacitance values [9].

In all the experimental single cells, the open circuit voltage rose to 0.930–0.945 V as soon as air and hydrogen

were passed over the respective electrodes, and then reduced to 0.820–0.840 V within a few seconds and remained stable there. Even though it is not possible to make clear the reason for this immediate drop in open circuit voltage, the probable reasons are gas cross-over [10] and change in optimal percentage of electrolyte occupation at the electrodes which provide proper balance of three phase elements, gas, solid and electrolyte [11] before and after the supply of the reactant gases.

In order to substantiate the above argument, the effect of changes in the reactant gases on the cell at open circuit voltage conditions was analyzed using impedance spectroscopy as shown in Fig. 8. Curve a of the impedance spectrum was taken at a constant flow rate 3500 and $1000 \text{ cm}^3 \text{ min}^{-1}$ of air and hydrogen, respectively. Spectrum b was taken at the same flow rates of the reactant gases after 1 min interruption of both the gases simultaneously. Except with a small suppression in the height of the arc, an appreciable change in the spectrum compared to that of 'curve a' is not observed, indicating no appreciable change in the three phase elements of the electrodes. The very low difference between the respective C_{dl} values as shown in Table 1 confirms the above finding. On the other hand, re-supply of air or hydrogen without disturbing the counter gas flow, after stopping the supply of hydrogen and air individually for a minute has a pronounced effect, as shown by the spectra c and d. From the respective curves c and d for air and hydrogen, it is clear that the starving effect of hydrogen on the spectrum is more pronounced than that observed with air. Moreover, it can be seen from Fig. 8 and Table 1 that the high frequency loop is not affected by the starving effect, exhibiting almost same R_Q value for all experimental conditions. On the other hand, the low frequency side was affected by gas starvation indicative of a change in mass transfer coefficient due to a difference in the concentration boundaries at the three-phase contact [12,13] before and after gas

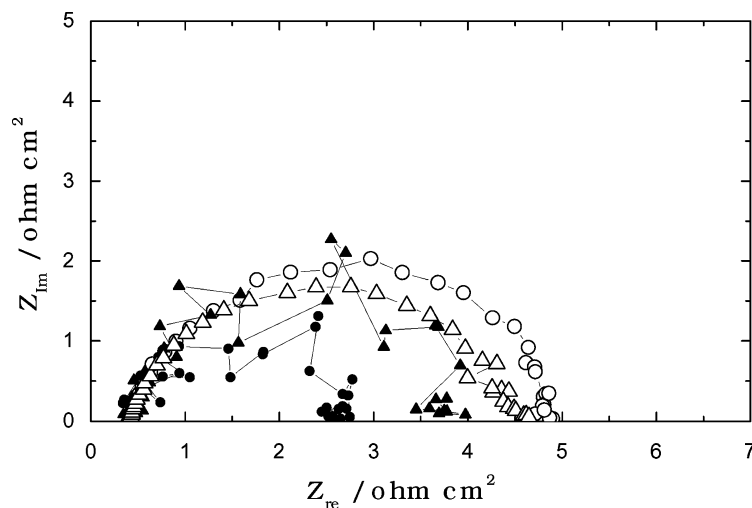


Fig. 8. Impedance spectra of the single cell with mixed powder matrix layer (a, ○) before subjecting to gas starving (b, △) after subjecting to simultaneous gas starving of H_2 and air, (c, ▲) after air and (d, ●) after H_2 starving.

Table 1

Observed effect of gas starvation on the electrical properties of the single cell, as measured from the impedance spectroscopy experiments

	No starvation	Simultaneous starvation of air and hydrogen	Air starvation only	Hydrogen starvation only
R_{Ω} (ohm)	0.4118	0.4140	0.4094	0.4108
R_p (ohm)	4.4410	4.1087	3.2321	2.2692
C_{dl} (F cm ⁻²)	0.0379	0.0395	0.1250	0.1600

starvation. The curves c and d shows experimental scattering of the measured values. This was attributed to the unstable three-phase contact while doing the measurements. When sufficient time (15 min) was given for three-phase stabilization after gas starvation, the response resulted in a considerably smooth curve. Even at a constant current density of 100 mA cm⁻², the effect of hydrogen starvation with a voltage gain of 20–25 mV is more pronounced than that for air. The observed low gas starvation effect for air (8–10 mV gain) may be due to the role played by the matrix layer, which is usually formed on the cathode catalyst surface, favoring intimate contact between the cathode and the matrix surface rather than between the anode and the matrix. Because of this intimate contact, the electrolyte at the cathode/matrix interface is less susceptible to air starvation, resulting in no appreciable change in the percentage of electrolyte occupation and three-phase contact at the cathode catalyst structure. Apart from this intimate contact between the matrix and the catalyst layers, with identical electrodes and experimental test conditions, the pore structure of the matrix is also important in controlling the distribution of the electrolyte in the respective electrodes [14].

To verify the above findings, single cells were assembled with a matrix coated over both the anode and cathode catalyst layers. The thickness of the coated matrix on the respective electrodes is 0.030 mm. On assembling into a

cell, the total thickness of the matrix came to 0.060 mm. As shown in Fig. 9, when both the anode and cathode were coated with single powder (SiC-L), the open circuit voltage rose to 0.88 V. On the other hand, if the anode was coated with mixed powder (SiC-L + 23 wt.% SiC-A) and the cathode with the single powder (SiC-L), the open circuit voltage rose to 0.92 V and exhibited a good cell performance. The better OCV was because of the good bubble pressure barrier offered by the mixed powder matrix coating on the anode. The good performance was considered to be due to the effective distribution of the electrolyte, in maintaining a stable three-phase contact between the anode and the matrix layer. Even though a further raise in open circuit voltage to 0.95 was observed when both the electrodes were coated with mixed powder (SiC-L + 23 wt.% SiC-A) matrix, overall cell performance was poor due to increase in the internal cell resistance caused by a decrease in the volume of electrolyte, compared to other types of matrix coatings. At a constant current density of 100 mA cm⁻², the starving effect due to hydrogen of the cell having anode coated with mixed powder, is very low (5 mV gain). This illustrates the achievement of better electrolyte management and stable three-phase contact, when compared to the cells having an anode coated with the single matrix powder (12–15 mV gain) and an anode without matrix coating (20–25 mV gain). The decreasing order of starving effect due to hydrogen gas was found to be, anode without matrix coating > anode

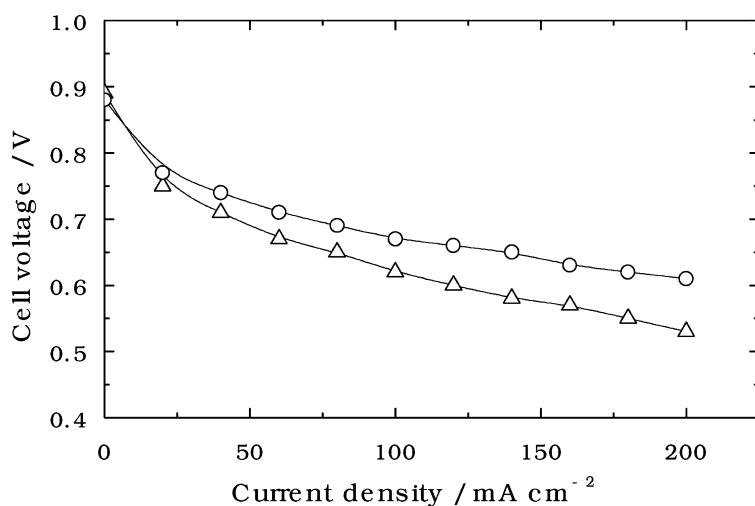


Fig. 9. Effect of matrix coating over both anode and cathode catalyst layers on the cell performance (○) anode coated with mixed powder (SiC-L + SiC-A), cathode single powder (SiC-L) matrix, and (△) anode and cathode coated with single powder (SiC-L) matrix.

coated with single powder > anode coated with mixed powder.

On summing up all the above experimental results, it can be concluded that the matrix parameters such as particle size, preparation method, porosity, pore size distribution, binder content, thickness and intimate contact between the electrodes and matrix layers are all inter-related to each other in deciding the over all cell performance with an identical electrode and experimental test conditions.

4. Conclusions

The electrolyte quantity in the matrix layer can be adjusted by changing SiC particle size distribution and the PTFE content in the matrix layer without sacrificing the wettability and structural integrity of the matrix layer. The pore structure of the matrix can be conveniently modified by increasing ratio of fine particles to coarse, with respect to reduction in matrix thickness so that the performance loss due to gas cross over can be minimized. The pore structure of the matrix layer can affect not only the internal cell resistance, but also the three-phase contact at the catalyst electrodes. The pronounced effect of hydrogen gas starvation on cell performance, an indication of improper electrolyte management in the anode catalyst layer, can

be reduced to a greater extent by providing a matrix coating over the anode catalyst layer also.

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