

인산형 연료전지의 전해질 매트릭스 성능 개선 연구

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1. Introduction

Fuel cells to generate direct current from a fuel and an oxidant gas are well known. In phosphoric acid fuel cells the amount of poly-tetra-fluoro-ethylene (PTFE) binder used to prevent the movement of the silicon carbide (SiC) particles in the cell, is one of the deciding factor of the electrolyte retaining capacity of the matrix layer[1]. Apart from this, the intimate contact between the matrix and electrodes surface, which is necessary to maximize catalyst utilization by uniform distribution of electrolyte, and thickness with structural integrity throughout the surface [2], 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 effects of ball milling process and SiC particle size on the electrolyte matrix property.

2. Experimental

The characterization of the as received SiC powders was carried out using coulter particle size analyzer. Zeta potential of the matrix slurry manufactured by ball milling and conventional processes were measured in order to confirm particle distribution. Matrix layers containing PTFE as a binder to an amount of about 13 to 3 wt%(solid) were prepared using 60 wt% (solid) PTFE emulsion(DuPont). Two different commercial SiC powders SiC-L(Lonza) and SiC-A(Alfa Aesar) were used to prepare matrix layers. The slurries were ball milled and cast over the cathode and anode to the desired thickness with doctor blade instrument. Coated matrix layers were sintered in air. In order to measure the absorption of the electrolyte with respect to 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.

3. Results and Discussions

The pH of the SiC powder dispersed in de-ionized water is about 6.5. Addition of 13 wt. % PTFE increased the pH of the slurry to about 7.4. The experimentally observed iso-electric point (IEP) value of SiC approaching pH 2 is in good agreement with values reported in literature. IEP of the particles, also known as zero point charge (ZPC), is the pH at which the particle has net

zero charge. Due to absence of the electrostatic repulsive forces between the particles at IEP, the slurry will flocculate exhibiting high viscosity. Thus the repulsive forces between the particles are important in determining particle interactions and dispersion.

The variation of pH (< 5), little away from the IEP resulted in no appreciable difference in zeta potential between the slurries prepared by two different mixing methods. As pH increases above 5, difference in zeta potential is observed, with little more negative values for the slurry prepared by ball milling procedure. The synergetic effect due to ball milling and pH is clear, because their use moves the zeta potential to high values by facilitating good dispersion and ultimately by increasing the facility of the charges to cover the surface. Upon this experimental finding, the ball milling method was subjected to further investigations.

The dependence of zeta potential on milling time at a pH 7.4 was studied. As the milling time increases, absolute value of zeta potential increases and attains a maximum value of 20 mV, after 24 h milling. No further noticeable change in zeta potential value, with more increase in milling time was observed, indicative of optimum dispersion and surface charge coverage of the particles in the slurry. This informs that the minimum milling time required for an optimum dispersion is 24 h.

The particle size distribution(PSD) of the commercial SiC-L and SiC-A samples is as shown in Fig 1. The particle size ratio between the coarse (mean diameter 2.106 μm) and fine (mean diameter 0.268 μm) of the SiC-L powder is about 10 and their particle weight ratio is 45/55. Even though it is reported in literature[3], our previous experimental results[4] 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.

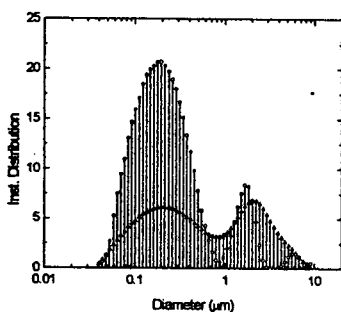


Fig 1 Particle size distribution of as received, (Δ) SiC-L and, (\circ) SiC-A powders

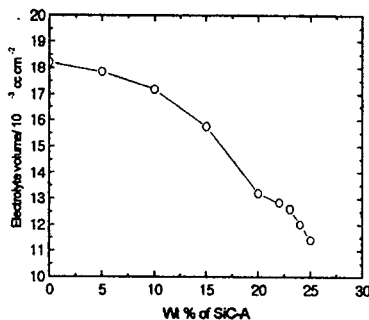


Fig 2 Electrolyte uptake of the 0.03 mm thick SiC matrix layer with addition of various wt % of SiC-A to SiC-L with 13wt % PTFE

To circumvent the above said packing problem, SiC-A powder having greater volume % of smaller particle size (0.186 mean size) is added to an amount of 23wt % to the parent SiC-L powder. This wt % was selected on the basis of electrolyte uptake of the matrix layer with 13wt % PTFE and 0.040 mm thick, as shown in the Fig 2. The increase in addition of SiC-A from 23 to 24wt % resulted in twofold decrease in electrolyte uptake values than from 22 to 23wt %.

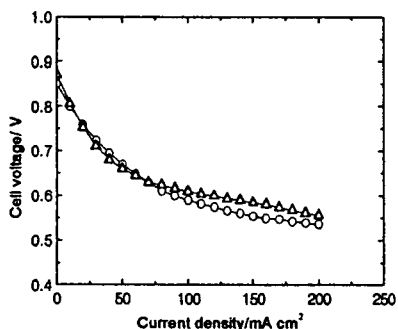


Fig 3 Cell voltage- Current density plot for H₂/air single cell with (O) single powder (SiC-L) and (Δ) mixed powder (SiC-L+SiC-A) matrix

Moreover cells exhibited low performance when the added ratio was above or below this level, may be due to low electrolyte and gas cross over respectively. 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+ 23wt %SiC-A) powder and above this current density reverse order in performance is observed as shown in Fig 3. The SEM of SiC-L and SiC-L+ 23wt % SiC- matrix layers coated over the identical electrodes are shown in Fig.4a and 4b respectively. From the Figs it is clear that the surface morphology of the matrix prepared with mixed powders is closely packed due to the presence of excess amount of lower size particles,

than the layer prepared with SiC-L alone. Since both the matrix thickness(0.040 mm) was same, the observed low performance below 80 mAcm⁻², may be due to increase in internal cell resistance by reduction in total pore area from 19.431 (for single powder matrix) to 11.884 m²/g due to the effect of fine particle size of SiC-A, on the pore structure as calculated from the respective mercury intrusion data, which is shown in Fig 5. The enhanced performance above 80mA cm⁻² may be caused by an effect relating to the number of active pores of the anode and cathode exposed to electrolyte and because of low dilution/poisoning effect of the reactant due to good bubble pressure barrier.

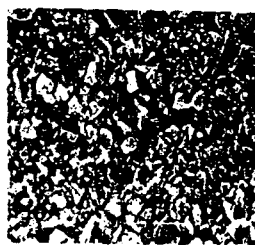


Fig 4a and 4b SEM of SiC matrix layer prepared with (a) single (SiC-L) and (b) mixed powder (SiC-L+SiC-A)

of fine particle size of SiC-A, on the pore structure as calculated from the respective mercury intrusion data, which is shown in Fig 5. The enhanced performance above 80mA cm⁻² may be caused by an effect relating to the number of active pores of the anode and cathode exposed to electrolyte and because of low dilution/poisoning effect of the reactant due to good bubble pressure barrier.

Upon the above findings, the following changes in the matrix layer were made to improve the cell performance at all current density levels. PTFE content from 13 to 3wt % and 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

respectively. When the PTFE content in the matrix was reduced below 3wt %, the adherence of the matrix to that of the catalyst layer was poor. More over 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 3wt %. Fig 6 Show the effect of above modification in the matrix on the cell performance. The effect of the above changes in the matrix layer is well understood by comparing the respective 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[5], the entire semicircle is shifted towards lower values on reducing the thickness and PTFE content of the matrix.

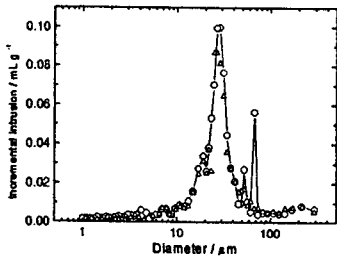


Fig 5 Pore size distribution of the SiC matrix layer prepared with (○) single powder (SiC-L) and (△) mixed powder (SiC-L+SiC-A)

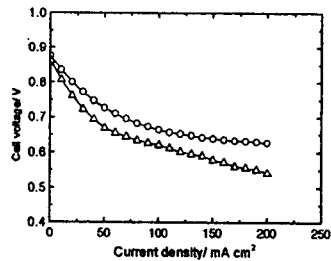


Fig 6 Effect of PTFE content and thickness of the mixed powder matrix layer on the cell performance (△) PTFE13wt %, thickness 0.04 mm and (○) PTFE 3wt %, thickness 0.03mm

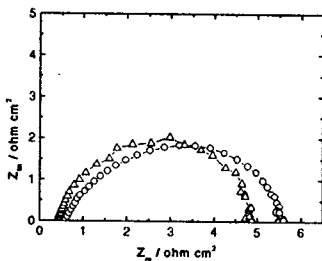


Fig 7 Impedance spectra of the single cell having matrix layer prepared with (○) single powder (SiC-L) and (△) mixed powder (SiC-L+SiC-A)

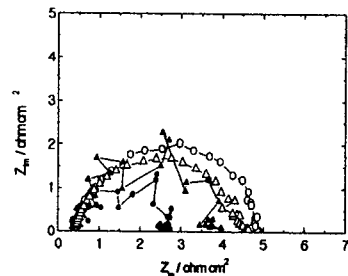


Fig 8 Impedance spectr of the single cell with mixed powder matrix layer (○) before subjecting to gas starving (△) after subjecting to simultaneous gas starving of H₂ and air, (▲) after air and (●) after H₂ starving.

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 farad, which is ~10 times higher than 0.002978 farad, for the cell with 0.040 mm thick matrix and PTFE content higher than by 4 orders in magnitude. Thus the significant influence of PTFE on the electrolyte distribution in the matrix layer on the improvement of the cell performance can be well understood by comparing the respective double layer capacitance values. In all our experimental single cells, open circuit voltage rose to 0.930 to 0.945 V as soon as air and hydrogen were passed over the respective electrodes and reduced to 0.820 to 0.840 V within few seconds and remained stable there on. Even though it is not possible to single out the reason for this immediate drop in open circuit voltage, the probable important reasons are gas cross over [6] and change in optimal percentage of electrolyte occupation at the electrodes which provide proper balance of three phase elements, gas, solid and electrolyte 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. Since the spectrum was recorded at open circuit voltage mass transfer impedance is uniform. On the other hand, low frequency side was affected by gas starvation indicative of change in mass transfer coefficient due to difference in concentration boundaries at three-phase contact before and after gas starvation. Even at constant current density of 100mA cm^{-2} , the effect of hydrogen starvation on the cell voltage is more pronounced than that for air with a voltage gain of 20 to 25 mV. The observed low gas starvation effect for air (8 to 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 than between anode and 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. To verify the above findings, single cells were assembled with 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, total thickness of the matrix came to 0.060 mm. As shown in Fig 9 when both the anode and cathode is given matrix coating with single powder (SiC-L), open circuit voltage rose to 0.88 V. On the other hand if the anode is coated with mixed powder (SiC-L+23wt % SiC-A) and cathode with single powder (SiC-L), open circuit voltage rose to 0.92 V and exhibited over all good cell performance. Even though further raise in open circuit voltage to 0.95 was observed when both the electrodes were coated with mixed powder (SiC-L+23wt % SiC-A) matrix, over all cell performance was poor may be due to increase in internal cell resistance due to decrease in volume of electrolyte, compared to other types of matrix coatings, which is not shown in the fig. At a constant current density of 100mA cm^{-2} is very low (5 mV gain) informing about the achievement of better electrolyte management and

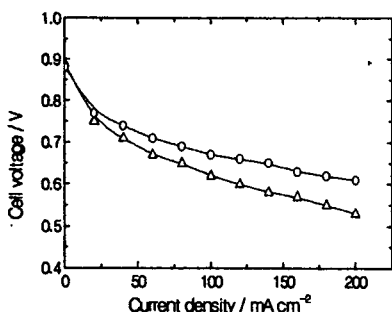


Fig 9 Effect of matrix coating over both anode and cathode catalyst layers on the cell performance (○) anode coated with mixed powder (SiC-L+ SiC-A), cathode single powder (SiC-L) matrix, and (△) anode and cathode coated with single powder (SiC-L) matrix

balling time and pH, which is confirmed by zeta potential. The single cell with ball milled electrolyte matrix showed also high cell performance. It is concluded from these results, that the ball milling method is preferable to the mechanical stirring procedure for preparing SiC slurry. The electrolyte quantity can be adjusted by changing the PTFE content without sacrificing the wet-ability and structural integrity of the matrix layer. The pore structure of the matrix can be conveniently modified by increasing the wt% of fine particles to that of 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 matrix coating over the anode catalyst layer.

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stable three-phase contact, when compared to the cells having anode coated with single matrix powder (12 to 15 mV gain) and anode without matrix coating (20 to 25 mV gain).

4. Conclusions

Effect of ball milling in making silicon carbide slurry for electrolyte matrix of phosphoric acid fuel cell were studied by measuring zeta potential and particle size distribution, and by analyzing cell performance. The ball milled slurry indicated a better particle distribution as compared to conventional mechanical stirring method, and the particle distribution of the slurry depends on