Characterization and performance analysis of SIC matrix layer of phosphoric acid

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Characterization and Performance Analysis of SiC Matrix Layer of Phosphoric Acid Fuel Cell

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1. Introduction

A very common electrolyte retaining matrix material for phosphoric acid fuel cell is the Silicon Carbide (SiC) powder [1,2]. The SiC powder was formed into a layer of required thickness with Polytetra fluro ethylene (PTFE) as a binder. Thus the formed layer should exhibit some important properties [3-7] like wet-ability, hold-ability and a good bubble pressure barrier for the reactant gases. Even at this advanced stage, works are going on in developing a suitable electrolyte retaining matrix layer for PAFC, indicating that the method of preparing the matrix is still an art rather than a science. More over most of the fundamental problems in making the matrix layer were not addressed properly or proprietary, we feel that it will be appropriate to study and discuss these problems, so that this art can be made as science.

Accordingly in this research work, preparation [8], physical and electrochemical characterization of the electrolyte retaining matrix layer prepared with SiC powder are reported.

2. Experimental

Commercial SiC powder (Lonza) was used in this research. The powder characteristics are summarized in Table I. Particle size distribution (PSD) of the as received commercial SiC and in the slurry state was measured with Light Scattering spectrophotometer meter. The resin used-as a binder was 13 wt % PTFE (60 solid wt % emulsion from DuPont) for studying the zeta potential variation with pH and for making electrolyte retaining matrix layers as an initial measure to optimize the matrix structure at the possible maximum level of the PTFE content for a good structural integrity. Above this wt% of PTFE, wet-ability to electrolyte of the heat-treated matrix was very poor even after 24 h of contact with electrolyte at room temperature. Wet-ability of the matrix with the electrolyte were measured by keeping one edge of the respective samples of same dimension in contact with the electrolyte at room temperature.

The slurry was prepared by dispersing required amount of SiC powder in de-ionized water. To this dispersion PTFE emulsion was added and mixed with hand for few minutes to initiate proper mixing, followed by two different mixing methods. Ball milling and mechanical stirring method were used for this purpose. For ball milling, plastic container with ceramic balls and for mechanical stirring, glass beaker with a teflon covered magnetic stirring rod were used. Mixing time varied from 6 h to 24 h. The solid content of the slurry was limited to 65wt % (including PTFE solid) in tape casting experiment to obtain optimum viscosity. Zeta potential values of the particles in the slurry were measured with light scattering spectrophotometer (Model ELS-8000). For studying the pH effect on zeta potential, the slurry pH was adjusted to a desired value by the addition of required amount of HCl or NH_4OH. Zeta potentials of the slurries were measured by the addition of very small amount of the slurry to the solution, the ionic strength of which was adjusted to 10mM NaCl. Doctor blade method was used to coat the slurries upon the catalyst layer, with a matrix coating thickness of about 0.040 mm. Coated layers were sintered in air at 295 ^{0}C for about 5 minutes. Scan Electron Microscopy (SEM; model SL-30, Philips) was used to study the surface morphology of the coated matrix layer.

The performance characteristics of the coated layer were evaluated by assembling into a single cell of 100 cm^2 geometric area. Before assembling into a cell, the matrix layers were impregnated and kept in contact with phosphoric acid at a temperature of 150 ^{0}C for 24 h. The method of preparing the catalyst electrodes, with an optimum catalyst loading of 0.25 and 0.5 mg cm^{-2}, for anode and cathode respectively, was as described elsewhere [9]. Working temperature of the assembled cells was 200 ^0C, with air as an oxidant and hydrogen as a fuel gas.

3. Results and Discussion

Fig 4a shows the resulting bimodal particle size distribution for the as received commercial SiC powder used in the present study. From the figure, it is clear that the sample contains wide range of particle size as shown in Table.1 with a mean equivalent spherical diameter of 1.266 μm. When comparing the sizes of the peaks, the peak at 0.268 μm is broader than the peak at 2.106 μm, indicating the presence of excess of particle size sub population at 0.268 μm. Such sub population distributions may have influence on the slurry stability if not dispersed properly resulting in agglomeration of primary particles [10].

The pH of the SiC powder dispersed in de-ionized water is about 6.5. Addition of 13 wt % of PTFE, increased the pH of the slurry to about 7.4. The results of the zeta potential measurements at various pH of the slurries prepared by ball milling and mechanical stirring are shown in Fig 1. The experimentally observed iso-electric point (IEP) value of SiC approaching pH 2 is in good agreement with values reported in literature [11]. Iso-electric point 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 these two methods of mixing: As pH increase 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 [12] and ultimately 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 pH 7.4 was studied and reported in Fig 2. 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 increase in milling time was observed, indicative of optimum dispersion and surface charge coverage of the particles in the slurry. The linear dependence of zeta potential on milling time and a limiting type after 24 h milling, informs that the minimum milling time required for an optimum dispersion is 24 h.

The electrolyte retaining matrix layers were prepared according to the procedure as described in experimental part and schematically shown in Fig 3. The sintering temperature of the matrix layer was optimized from electrolyte wettability results with heat-treatment temperature. The obtained results indicates that even though a good bonding between the matrix and the catalyst surface was exhibited with 13wt% of PTFE than with 1 wt%, the matrix layers were not at all wettable in nature, when sintered between 330 to 350 ^{0}C for about 10 to 15 minutes, irrespective of the PTFE content due to the high hydrophobic nature of the heat-treated matrix. When PTFE content was reduced to 0.5 wt%, matrix layer was wetted completely after 24h at 30 ^{0}C, with total loss in structural integrity. In order to maintain structural integrity and bonding strength, the PTFE content in the matrix layer was kept at 13wt % and to increase the wettability the heat treatment temperature was lowered and optimized at 295 ^{0}C. Thus the matrix surface containing 13-wt % PTFE, which were sintered at 295 ^{0}C completely wetted with in 24 h of contact with the electrolyte at 30 ^{0}C. At this sintering temperature the wettability of the matrix to electrolyte and bonding between the matrix and the catalyst layer were found to be optimum.

The following conclusions can be drawn by comparing the particle size distribution curves of the respective slurries prepared by ball milling and mechanical stirring method as shown in Fig 4. The particle size distribution in the slurry prepared by mechanical stirring method (Fig 4c), exhibited tri-modal like distribution with a well-separated particle size profile. On the other hand the intensity profile of the particles in the lower size region is closer for the slurry prepared by ball milling (Fig 4b), indicating particle size distribution approaching bimodal type. The observed tri-modal distribution in mechanically mixed slurry may be due to formation of separate agglomerates between the particles in the range 0.4 to 2 μm with a mean particle size of about 1.13 μm. This value is in good agreement with the value as exhibited in Fig 4. These agglomerates were de-agglomerated to some extent by use of ball milling procedure resulting in maintaining individual particle size to a greater extent not only in this region but also at the higher region of 10 μm. In both the cases it is clear that the dispersion of agglomerated particles below 0.3 μm size, is less susceptible to variation in mixing procedure, informing the limitation of the use of physical mean in dispersing lower size particles.

From the SEM observations of the cross section view of the coated matrix layer as shown in Fig 5 it can be concluded that the slurry prepared by ball milling procedure coated uniformly. The non-uniform surface layer of the matrix coated with mechanically mixed slurry may be due the improper dispersion of the particles as exhibited by the lower zeta potential value. The probability of agglomerate formation is also high as shown in Fig 4c resulting in non-smooth run to make matrix layer having an uneven surface without batch consistency.

In order to have a better understanding of the correlation between the physical property of the slurry and the performance characteristics of the matrix layer, cells were assembled having matrix layers prepared with slurries milled for different time periods of 6, 12, 18, and 24 h. Fig 6 Show the effect of the matrix layer prepared from the respective slurries, on the cell performance, at an open circuit condition and at a constant current density of 100 mA cm^{-2}. It is evident that under both conditions, the cell performance is improved with an increase in milling time and reached a maximum for the layer prepared with the slurry milled for 24 h, where the particles in the slurry possessed a maximum zeta potential of –20 mV (Fig 2). In absence of dispersing agents, except that found in PTFE emulsion, the particle dispersion in the slurry is dependant on milling time, which is evident from the increase in absolute zeta potential values with milling time. As discussed earlier, this optimum dispersion of the particles may be achieved in stages with respect to ball milling time. More over this variation in particle dispersion is reflected in the matrix structure when formed into cast layer. The difference in matrix structure may be attributed to non-uniform distribution of the particles and agglomerates when ball milled for lower time periods, favoring wide variation in pore structure. Over all performance data of the cells with matrix layer prepared by different mixing procedures is shown in Fig 7. The observed over all increase in performance of the cell having matrix layer prepared by ball milling procedure confirms the above findings. Moreover, the main factor responsible for the gain in open circuit voltage from 0.810 to 0.850 V was resistance for gas mixing by better particle packing promoted by bi-modal than tri-modal [13] particle size distribution in the slurry prepared by ball milling procedure.

In order to find out the effect of preparation variables on the cell life, short-term (200 h) performance at a constant current density of 100mA cm^{-2} was investigated and reported in Fig 8. Apart from low cell performance, the voltage of the cell with matrix prepared by mechanical mixing of the slurry is only stable up to about 40 h and decayed with a total voltage loss of about 90 mV after 100 h of study. On the other hand, the performance of the cell having matrix layer prepared by ball milling the slurry is stable within this short-term study. Even though the life of the cell is dependent on many factors such as corrosion of active material, electrolyte conductivity change with time, flooding, loss of electrolyte due to edge seal leak and vaporization. In our present study flooding, is considered to be the probable reason in this short-term life test. Under identical electrode condition flooding depends on the ability of the matrix structure to hold the electrolyte uniformly throughout its surface [14]. On the other hand if the electrolyte hold-ability is time dependant due to wide variation in pore structure as shown in Fig 9 and varied along the matrix structure, electrode reaction will be affected accordingly due to variation in three-phase contact at the electrode due to excess movement of electrolyte into the gas diffusion layers [15] and loss of electrolyte at some places in the matrix layer. On the basis of the above argument, it can be concluded that, the ability of the matrix prepared by ball milling procedure to hold the electrolyte uniformly in its structure throughout its surface may be more due to less number of big pores as shown in Fig 9, resulting in better cell life. This uniformity was achieved due to optimum dispersion of the matrix particles in the slurry by ball milling method. All the above results suggest a close relationship between the particles state in the slurry and the properties of the formed layer, stressing the necessity of a proper tailoring of the SiC slurry.

Even though the observed cell performance is lower than that reported in literature, a good correlation between the physical properties of the particles in the slurry and preparation parameter variables to that of the cell performance and life were obtained.

4. Conclusions

The variation of zeta potential value of the SiC particles with respect to change in pH value of the slurry prepared by two different mixing methods were measured and compared.

The particles in the slurry prepared by ball milling procedure exhibited high absolute zeta potential value indicative of good dispersion.

From the experimental results of the effect of milling time on the zeta potential value, it can be concluded that optimum dispersion of the particles is achieved after 24 h milling.

Over all cell performance and life is found to depend on the structure of the matrix in turn depend on the particle state in the slurry. The cell with a matrix layer prepared by ball milling the slurry showed better performance and life, than the cell having matrix layer prepared by mechanically stirring the slurry.

A good correlation between the physical properties and preparation parameter variables to that of the cell performance and life were obtained.

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Table 1. Particle size distribution data of as received SiC powder

Mean	1.266 μm				
Median	0.512 μm				
% <	10	25	50	75	90
μ m	0.0998	0.185	0.512	1.949	3.369

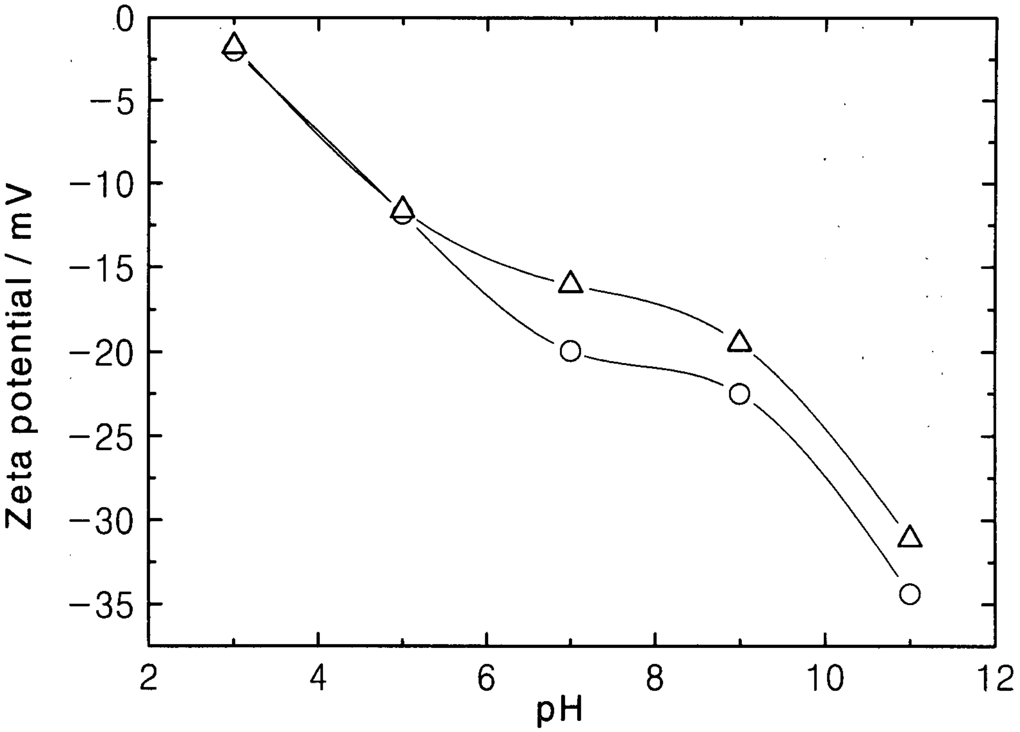

Fig 1. Effect pH of the SiC slurry on the zeta potential, (0) ball milling and (Δ) mechanical stirring method

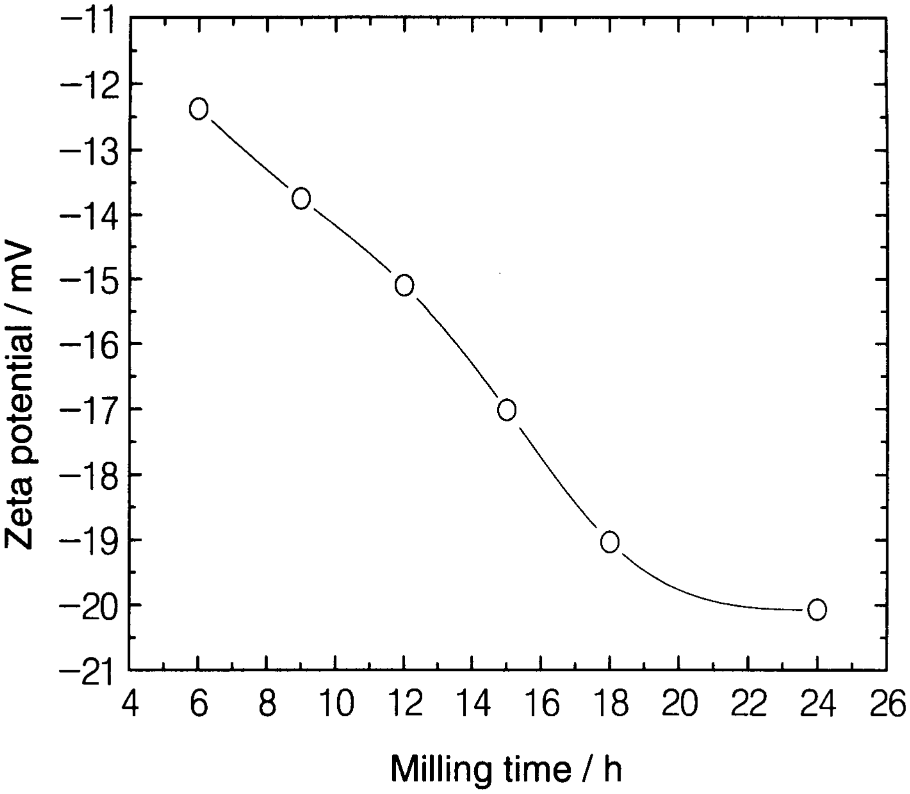

Fig 2. Effect of ball milling time on zeta potential of SiC particles in the slurry

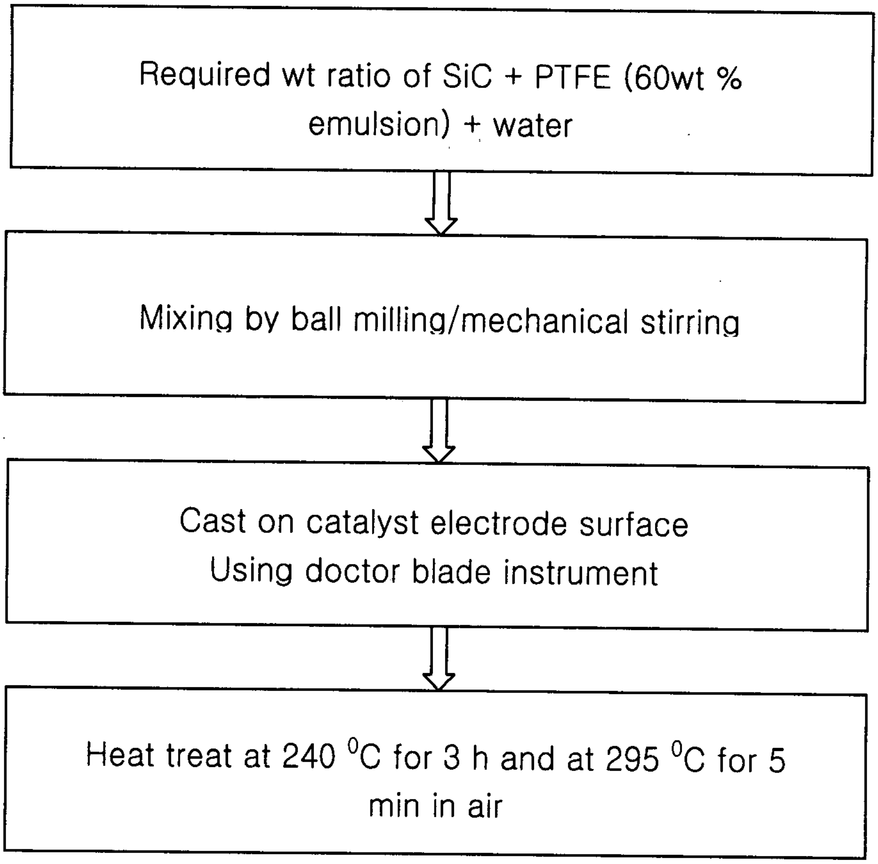

Fig 3. SiC matrix preparation procedure by doctor blade coating method

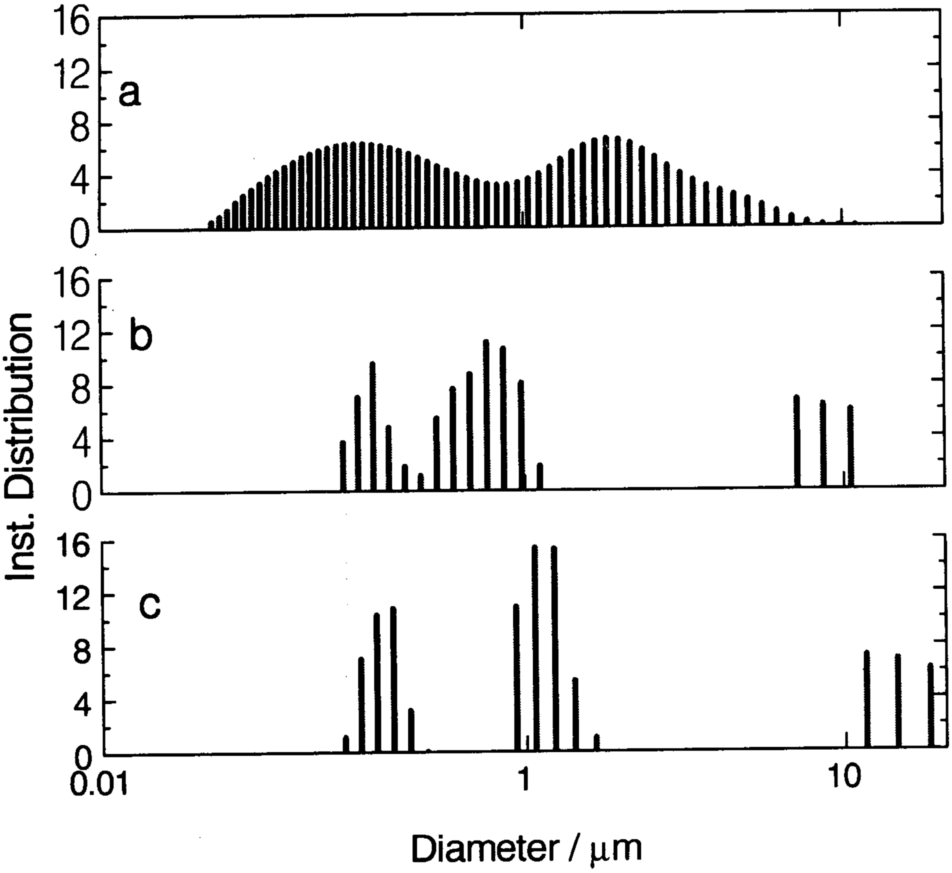

Fig 4. SiC particle size distribution, a) as received and without PTFE, b) after ball milling and c) mechanical mixing with PTFE

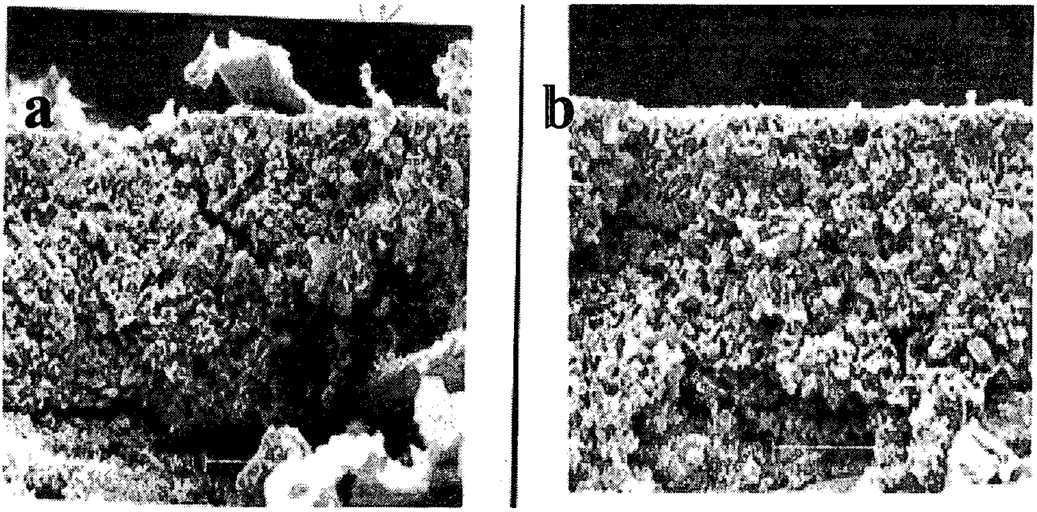

Fig 5. Scan Electron Micrographs of cross section view of SiC matrix layer a) Slurry prepared by mechanical stirring and b) ball milling method

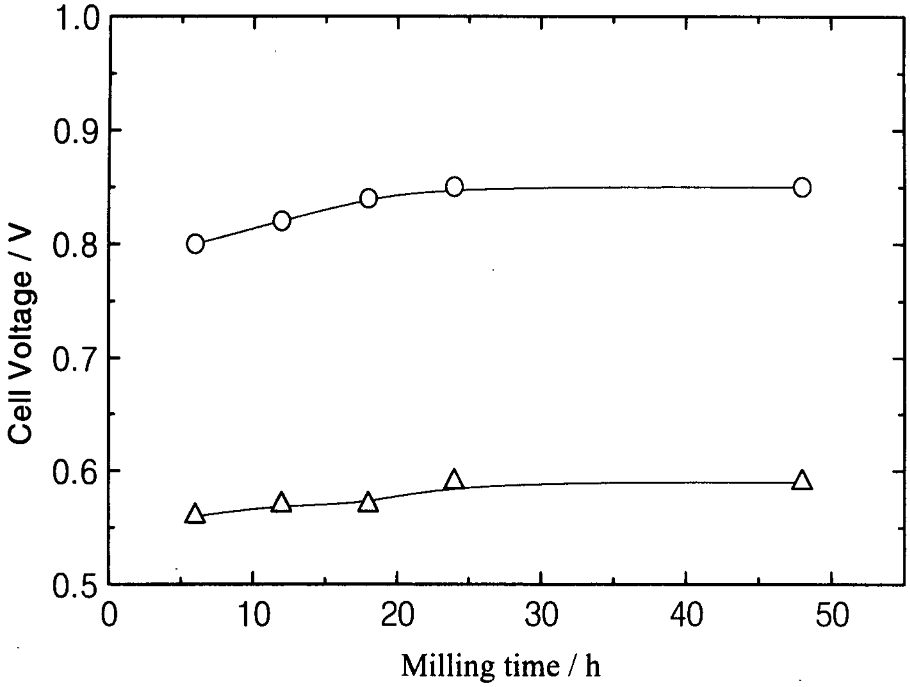

Fig 6. Effect of milling time on open circuit voltage (0) and on cell voltage (Δ) at a constant current density of 100 mA cm^{-2}

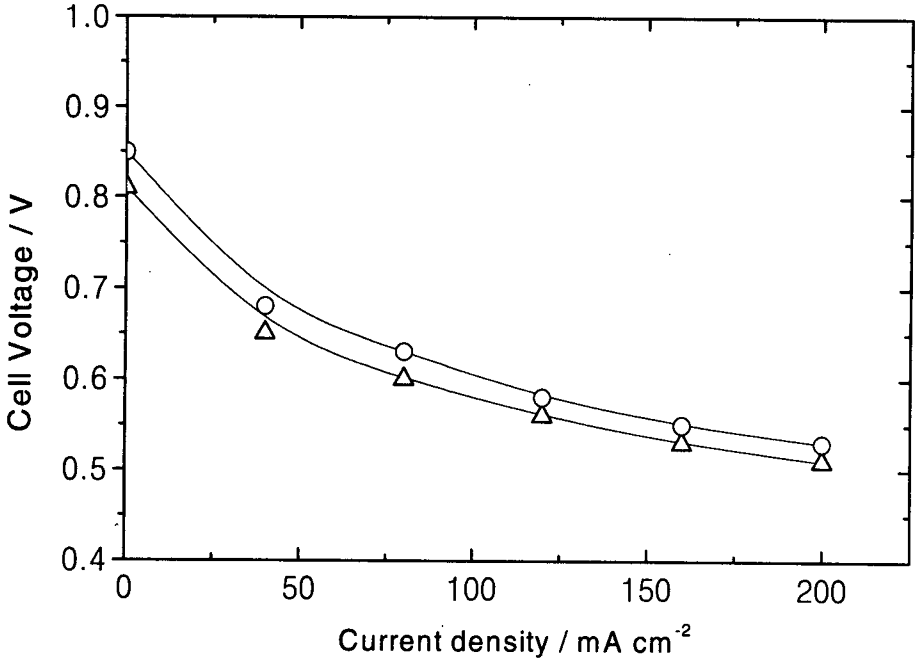

Fig 7. Effect of preparation method of SiC matrix on cell performance (0), ball milling and (Δ), mechanical stirring method

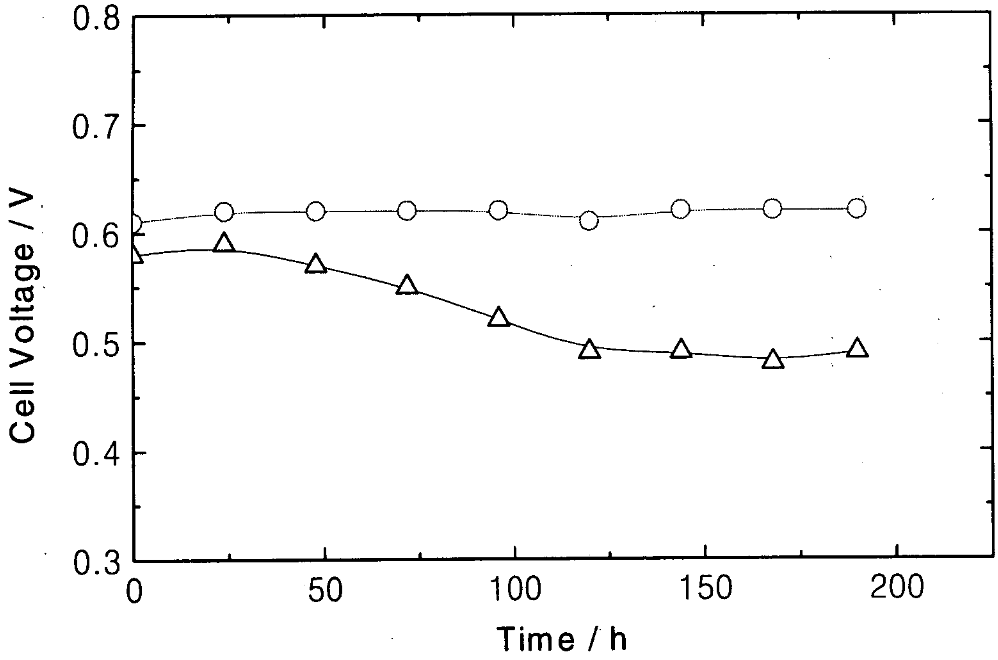

Fig 8. Effect of preparation method of SiC matrix on cell life (0), ball milling and (Δ), mechanical stirring method