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Characterization and performance analysis of silicon carbide electrolyte matrix of phosphoric acid fuel cell prepared by ball-milling method

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Abstract

The effect of ball milling in making a silicon carbide slurry for the electrolyte matrix of a phosphoric acid fuel cell (PAFC) was studied by measuring the zeta potential and the particle-size distribution, and by analyzing cell performance. The ball-milled slurry gives a better particle distribution than the conventional mechanical-stirring method, and the particle distribution of the slurry depends on balling time and pH, which is confirmed by zeta potential. A single cell with a ball-milled electrolyte matrix also displays high performance. It is concluded that the ball-milling method is preferable to the mechanical-stirring procedure for preparing silicon carbide slurries.

Keywords: Ball milling; Electrolyte matrix; Silicon carbide; Phosphoric acid fuel cell

1. Introduction

One of the most important components of the phosphoric acid fuel cell (PAFC) in terms of cell performance and lifetime is the electrolyte-retaining matrix layer [1]. The morphology of the matrix layer is dependent on the slurry properties. The best matrix material for use in PAFCs is silicon carbide (SiC) [2] with a binder, polytetra-fluroethylene (PTFE) content of about 3–15 wt.%. For good performance in a fuel cell, the electrolyte matrix must be wettable to an extent to provide good ionic conduction, must be free from pinholes and cracks in order to prevent gas cross-over, and must have good structural integrity. Some of the important physical parameters which control these properties of the matrix layer are particle-size distribution [3], solid loading [4], and the electrostatic interaction between the particles in the slurry [5–7]. Despite the diversified methods reported in literature for making ceramic slurry by the ball-milling method [8], there is no detailed research on the physical properties of SiC slurry containing a required amount of PTFE and preparation parameters. Therefore, an attempt is made here to find a satisfactory method for preparing a SiC matrix for PAFC by characterizing the slurry properties prepared by ball-milling and conventional mechanical-stirring methods, and by correlating the cell test results with the preparation parameter variables.

2. Experimental

The preparation procedure for the SiC slurry and electrolyte matrix layer is shown in Fig. 1. Commercial SiC powder (Lonza) was used in this work. The resin used as a binder was 13 wt.% PTFE (DuPont). The slurry was prepared by dispersing the required amount of SiC powder in de-ionized water. To this dispersion, PTFE emulsion was added, followed by two different mixing methods of ball milling and mechanical stirring. For ball milling, a plastic jar with ceramic balls was used, and for mechanical stirring a glass beaker with a Teflon-covered magnetic stirring bar was used. The mixing time varied between 6 and 24 h. The solid content of the slurry was limited to 65 wt.% (including PTFE solid) to obtain optimum viscosity for tape-casting experiments. The zeta potential values of the particles in the slurry were measured with a light scattering spectrophotometer (model ELS-8000). For studying the effect of pH on zeta potential, the pH of the slurry was adjusted to the desired value by the addition of the required amount of HCl or NH_4OH. The zeta potentials of the slurries were measured by the addition of a very small amount of the slurry to the solution, the ionic strength of which was adjusted to 10 mM NaCl.

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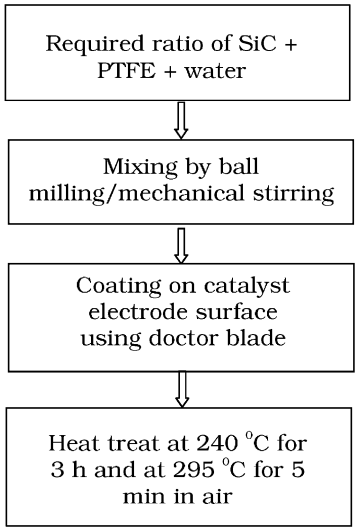

Fig. 1. Preparation procedure of SiC slurry and electrolyte matrix layer by doctor-blade process.

The doctor-blade method was used to coat the slurries on electrode catalyst layer, with a matrix-coating thickness of about 0.040 mm. The coated layers were sintered in air at 295 °C for about 5 min. Scanning electron microscopy (SEM; model SL-30, Philips) was used to study the surface morphology of the coated matrix layer. The wettability of the matrix with electrolyte was measured by keeping one edge of respective samples of the same dimension in contact with the electrolyte at room temperature. The performance characteristics of the coated layer were evaluated in a single cell of 100 cm^2 geometric area. Before assembling in a cell, the matrix layers were impregnated with phosphoric acid at a temperature of 150 °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 the anode and the cathode, respectively has been described elsewhere [9]. The working temperature of the assembled cells was 200 °C, with air as an oxidant and with hydrogen as a fuel gas.

3. Results and discussion

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 results of the zeta potential measurements at various pH values of the slurries prepared by ball milling and mechanical stirring are shown in Fig. 2. The experimentally observed iso-electric point (IEP) of SiC approaches pH 2 and is in good agreement with values reported in the literature [10]. The IEP of the particles, also known as zero point charge (ZPC), is the pH at which the particle has net zero charge. Due to the absence of electrostatic repulsive forces between the particles at the IEP, the slurry will flocculate and exhibit high viscosity. Thus, the repulsive forces between the particles are important in determining particle interactions and dispersion.

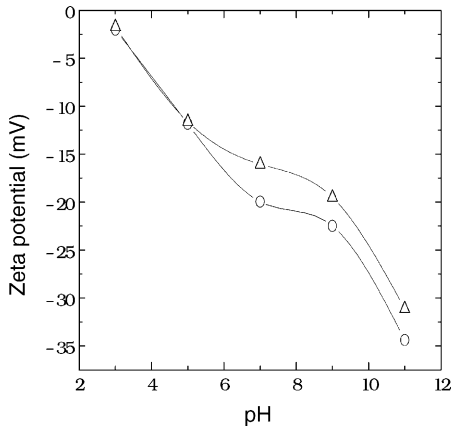

Fig. 2. Effect of pH on zeta potential of SiC particles in slurry prepared by (○) ball-milling, and (△) mechanical-stirring methods.

Variation of pH (<5) close to the IEP resulted in no appreciable difference in zeta potential between the slurries prepared by the two different mixing methods. As the pH increases above 5, a difference in zeta potential is observed. The slurry prepared by the ball-milling procedure shows slightly more negative values. The synergetic effect due to ball milling and pH is clear, namely, the shift of the zeta potential to high values by facilitating good dispersion [11] and, ultimately, by increasing the facility of the charges to cover the surface. Given this experimental finding, the ball-milling method was subjected to further investigation.

The dependence of zeta potential on milling time at a pH 7.4 was studied and is reported in Fig. 3. As the milling time increases, the absolute value of the zeta potential increases and attains a maximum value of −20 mV after 24 h of milling. There is no further noticeable change in zeta potential with increasing milling time. This is indicative of optimum dispersion and surface charge coverage of the particles in the slurry. Thus, it is concluded that the minimum milling time required for optimum dispersion is 24 h.

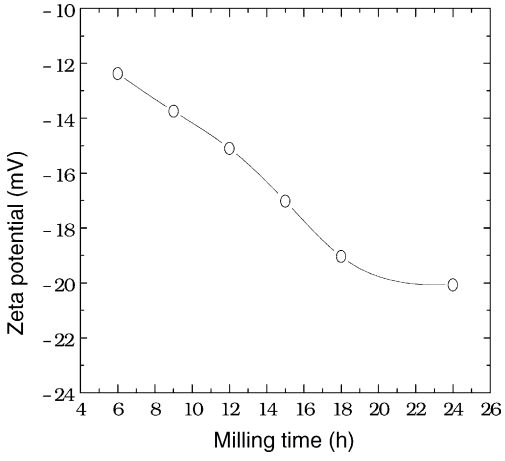

Fig. 3. Effect of ball-milling time on zeta potential of SiC particles in slurry.

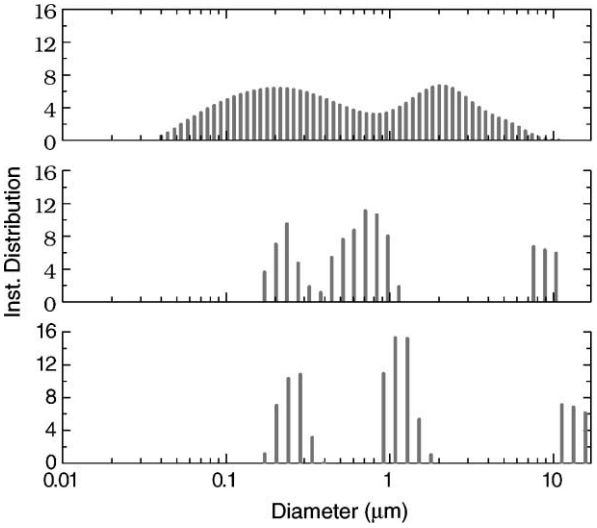

Fig. 4. Particle-size distribution of as-received SiC powder (top), and ball-milled (middle), and mechanical-stirred (bottom) SiC slurries.

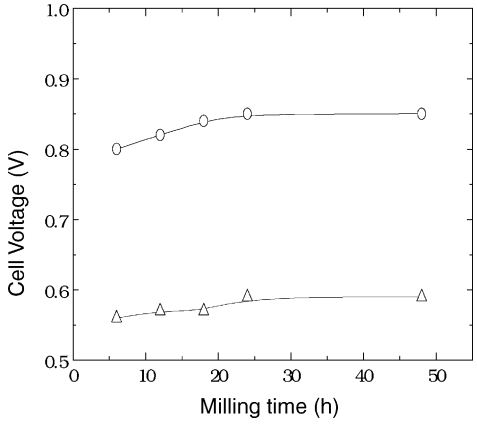

Fig. 5. Effect of ball-milling time of SiC slurry on open-circuit voltage (○), and on cell voltage (△) at constant current density of 100 mA cm^{-2}.

The particle-size distribution curves of as-received powder and the slurries prepared by the ball-milling and mechanical-stirring methods are presented in Fig. 4. The as-received SiC powder displays a bi-modal particle-size distribution and has a wide range of particle size 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, which indicates the excess presence of small particle sizes at 0.268 μm. Such excess distribution in the low particle-size region may have an influence on slurry stability, if not dispersed properly, and result in the agglomeration of primary particles [12].

The particle size in the mechanical-stirred slurry exhibited tri-modal distribution with a well-separated particle-size profile. On the other hand, the intensity profile of the particles in the slurry prepared by ball milling indicates that the particle-size distribution approaches a bi-modal type. The observed tri-modal distribution in mechanically-stirred slurry is considered to be due to the formation of separate agglomerates between the particles. These agglomerates were de-agglomerated to some extent in the high particle-size region by use of the ball-milling procedure. With both methods, it is clear that the dispersion of agglomerated particles in the low particle-size region below 0.3 μm is less susceptible to variation in the mixing procedure. This demonstrates the limitation of the use of physical means in dispersing particles of low size.

The electrolyte-retaining matrix layers were prepared according to the procedure described in Section 2 for making a single cell. The sintering temperature of the matrix layer was optimized for electrolyte wettability and bonding properties after heat treatment. The results indicate that even though a better bonding between the matrix and the catalyst surface was obtained at 13 wt.% than at 1 wt.% PTFE, the matrix layers were not at all wettable when sintered between 330 and 350 °C, irrespective of the PTFE content, due to the high hydrophobicity of the heat-treated matrix. When the PTFE content was reduced to 0.5 wt.%, the matrix layer was wetted completely after impregnated with electrolyte for 24 h at 30 °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 13 wt.%. To increase the wettability, the heat-treatment temperature was lowered and optimized at 295 °C. Thus, the matrix surface with 13 wt.% PTFE, which was sintered at 295 °C, was completely wetted with the electrolyte. At this sintering temperature, the wettability of the matrix to electrolyte and the bonding between the matrix and the catalyst layer were found to be optimum.

In order to have a better understanding of the correlation between the physical properties of the slurry and the performance characteristics of the matrix layer, cells were assembled with matrix layers prepared with slurries milled for different time periods. The effect of the matrix layer prepared from the respective slurries on the cell performance are shown in Fig. 5 for open-circuit conditions and at a constant current density of 100 mA cm^{-2}. It is evident that the cell performance is improved with increase in milling time and reaches a maximum for the layer prepared with the slurry milled for 24 h, in which the particles posses a maximum zeta potential of −20 mV (Fig. 3). All performance data of the cells with matrix layers prepared by different mixing procedures are presented in Fig. 6. The high performance of the cell with a matrix layer prepared by the ball-milling procedure confirms these findings. Moreover, the gain in open-circuit voltage from 0.810 to 0.850 V means an increased resistance to gas mixing, which is attributed to better particle packing in the ball-milling procedure promoted by a bi-modal than by a tri-modal particle-size distribution [2].

In order to determine the effect of preparation variables on cell life, the short-term performance at a constant current density of 100 mA cm^{-2} was examined and is shown in Fig. 7. The voltage of the cell with a matrix prepared with a mechanically-stirred slurry is only stable up to about 40 h

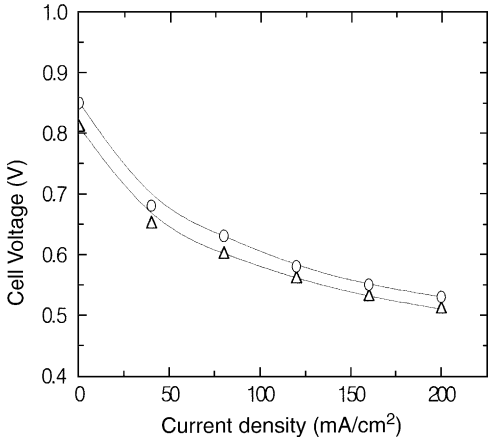

Fig. 6. Effect of preparation method of SiC matrix on cell performance: ball-milling (○), and mechanical-stirring (△) methods.

and decays rapidly with a total voltage loss of about 90 mV after 100 h of operation. On the other hand, the performance of the cell a with matrix layer prepared by the ball-milling process is stable within this short term. Even though the lifetime of the cell is dependent on many factors, such as corrosion of active material, change of electrolyte conductivity with time, electrolyte flooding, and electrolyte loss due to edge seal leaks and vaporization, electrolyte flooding is considered to be the probable reason in this short-term life test because the other factors require a longer test time to exert an effect on cell decay.

Under identical electrode conditions, electrolyte flooding depends on the ability of the matrix structure to hold the electrolyte uniformly throughout its surface [13]. During the cell operation, the electrolyte is moved into the gas-diffusion electrode layer through pores in the matrix layer, which decreases the three-phase boundary area at the electrode due to excess movement of electrolyte into the gas-diffusion layers [14], which results in a decay in cell performance. This electrolyte movement is accelerated by large pores. In Fig. 8, the matrix layer prepared by the ball-milling procedure

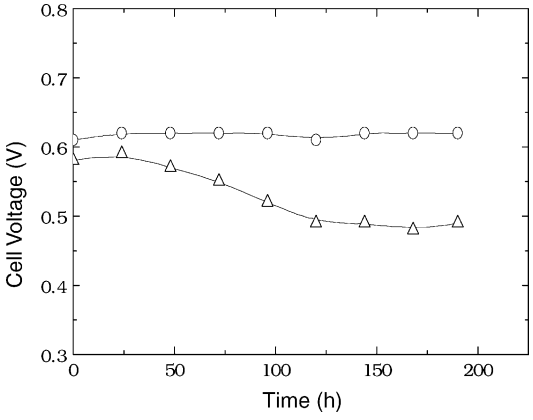

Fig. 7. Effect of preparation method of SiC matrix on cell lifetime at constant current density of 100 mA cm^{-2}: ball-milling (○), and mechanical-stirring (△) methods.

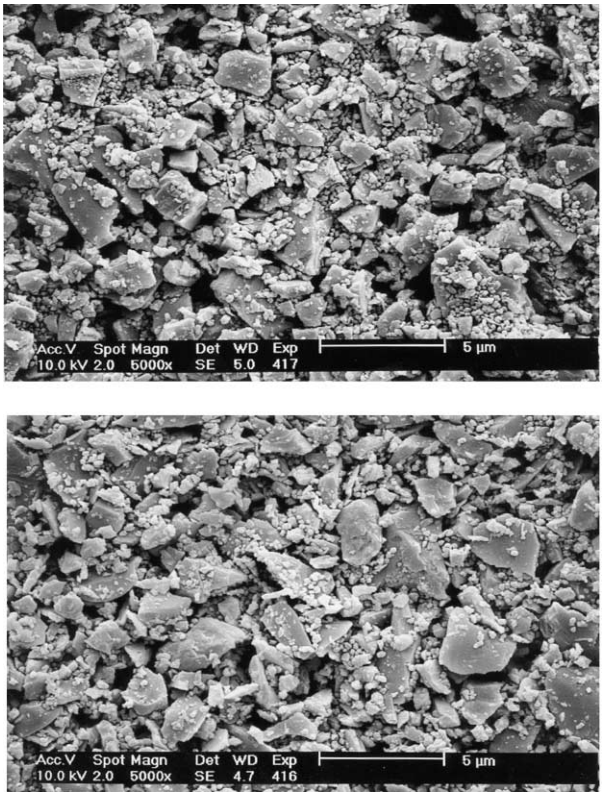

Fig. 8. Surface structure of SiC layer prepared by mechanical-stirring (top), and ball-milling (bottom) methods.

exhibits a more uniform structure but the mechanical-stirring process produces more large pores in the matrix layer. This uniformity in the ball-milling process is due to optimum dispersion of the matrix particles and agglomerates. Thus, there is less movement of electrolyte in the matrix layer prepared by the ball-milling process and this results in better cell lifetime. All these results suggest a close relationship between particle state in the slurry and the properties of the formed layer, and stresses the necessity of a proper tailoring of the SiC slurry.

4. Conclusions

The particles in slurry prepared by the ball-milling procedure exhibit high absolute zeta potential values which are indicative of good dispersion. From the experimental results of the effect of milling time and pH on the zeta potential, it can be concluded that optimum dispersion of the particles is achieved after 24 h milling in the high pH region. The cell performance and lifetime are found to depend on the particle state in the slurry, that is the structure of the matrix layer. The cell with a matrix layer prepared by the ball-milling method displays better performance and lifetime than that with a matrix obtained by the mechanical-stirring method. A good correlation between physical properties and preparation parameters of the electrolyte matrix is obtained.

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