

# Study of electrolyte management in phosphoric acid fuel cells

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## Abstract

Acid volume changes in phosphoric acid fuel cells were investigated. Compared with cells which were kept in a constant humidity and temperature environment without operation, those operated under variable operating conditions showed a relatively rapid rate of acid volume change. Cell resistance increased drastically when the acid volume in the operating cell dropped below  $30 \mu\text{l}/\text{cm}^2$ . It would seem that the dependance of internal resistance on operating temperature can be used to estimate the amount of acid in the cell during operation.

## Introduction

In phosphoric acid fuel cells, considerable variation may occur in the volume of phosphoric acid. Thus, it is important to undertake volume management in order to achieve a satisfactory performance level from the fuel cell under different operating conditions. For example, should the volume of phosphoric acid electrolyte increase appreciably through water absorption, then electrolyte will tend to leak into the gas-diffusion layers and out of the fuel-cell stack. This results in lowered cell characteristics. By contrast, should the volume of electrolyte decrease significantly through evaporation, then a considerable increase in the cell resistance and/or the cross-over of the process gases may occur. This again gives rise to deterioration in the cell characteristics.

Cell performance and life are affected by catalyst activity, the ability of the cell to retain acid, and the operating conditions, as well as by other factors. The effect on electrode performance of acid absorption in the catalyst layer has been investigated [1, 2]. The influence of this absorption on acid movement and balance in the cell, as well as on cell performance and endurance, has also been examined [3].

This study investigates the change in acid volume during storage and the resultant effects on cell operation and performance.

## Experimental

### *Cell construction*

Figure 1 is a schematic of the cell unit. This consists of an air electrode, a fuel electrode and an electrolyte matrix. Both electrodes comprised a carbon-supported

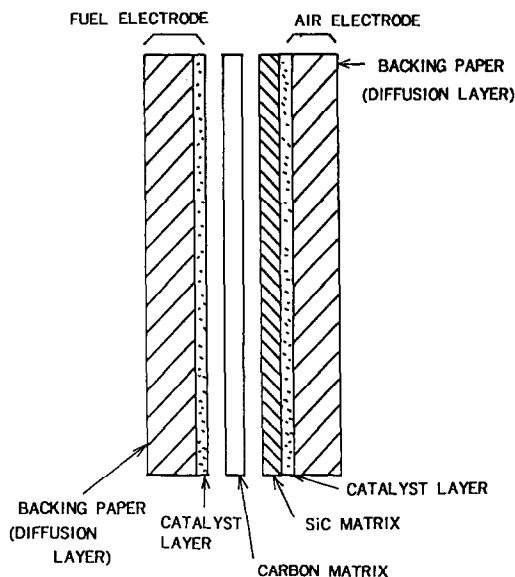


Fig. 1. Cell construction.

platinum catalyst with a platinum loading of 10 wt.% (Vulcan XC-72R, Cabot Ltd.), PTFE (30J, Du Pont-Mitui Fuluoro Chemicals Ltd.), and a porous carbon substrate (E-715, Kureha Kagaku Kogyo Ltd.). The thickness and porosity of the substrate were 0.4 mm and 70–75%, respectively. The substrate was impregnated by FEP dispersion (120, Du Pont-Mitui Fuluoro Chemicals Ltd.) and waterproofed by heating in air at 350 °C for 30 min. The FEP content in the resulting substrate was 30 wt.%. The catalyst layer was prepared by kneading the catalyst and PTFE together. The PTFE content in the catalyst layer was 40 wt.%. The catalyst layer was pressed onto the carbon substrate, then heated in air at 360 °C for 30 min. The electrode thickness and platinum loading were, respectively, 0.45 mm and 0.2 mg cm<sup>-2</sup> for the fuel electrode, and 0.55 mm and 0.5 mg cm<sup>-2</sup> for the air electrode.

The electrolyte matrix was composed of an SiC matrix and a carbon matrix in order to increase the amount of acid in the cell. The SiC layer was formed on the cathode by preparing a slurry made from a SiC (no. 1200, Showa Denko Ltd.) and PTFE dispersion (6CJ, Du Pont-Mitui Fuluoro Chemicals Ltd.). The mixture was spread on the cathode (using a doctor blade method) and then heated in air at 360 °C for 30 min. The thickness of the SiC layer was 0.2 mm.

The carbon matrix was prepared using a mixture made by kneading the carbon (Vulcan XC-72, Cabot Ltd.) and PTFE. The PTFE content was 3 wt.% and the thickness of the carbon matrix layer was 0.3 mm.

#### Storage test

A cell was assembled from the above active components. The electrolyte was 100 wt.% phosphoric acid (Rasa Kogyo Ltd.). A single cell was loaded with 2.1 g (84 mg cm<sup>-2</sup>) electrolyte. The specific gravity of the acid was 1.87 [4].

The cell construction is shown in Fig. 2. The active area of the electrodes was 25 cm<sup>2</sup>. The cell was placed between inner-manifold carbon separators.

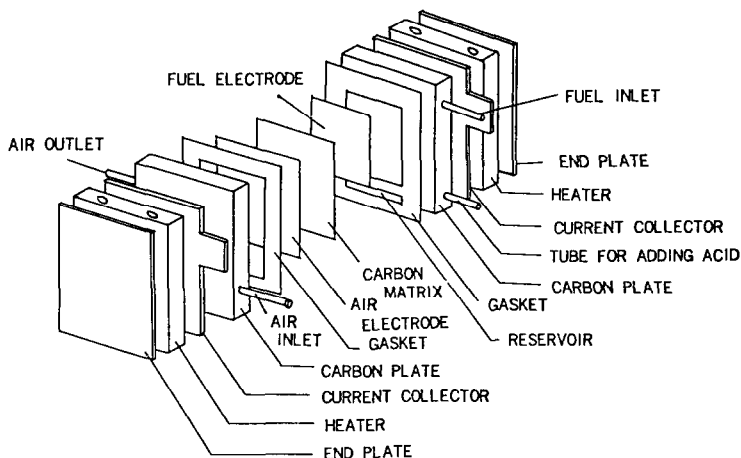


Fig. 2. Single cell construction with 25 cm<sup>2</sup> electrodes.

The cells were located in a dry room (at a constant humidity of 10% r.h.) without operation. A storage temperature of 50, 80, or 120 °C was achieved by means of heater plates.

The specific volume of the acid was calculated from the weight gain of the cell unit. This assumes that the weight changes were a result of water absorption from the air.

#### *Cell test*

The cell test was carried out at 180 °C, 1 atm. and 100 mA cm<sup>-2</sup>. An air flow (7.5 stoich; humidity=12.8 mm Hg) was introduced into the cathode, and hydrogen gas (1.5 stoich) into the anode.

To study the effects of changes in acid volume on cell performance, a cell was operated within the temperature ranges 180 to 210 °C and 180 to 90 °C. The quantity of acid in the cell was 54 mg cm<sup>-2</sup>.

The cell voltage was monitored continuously and the internal resistance was measured using a milliohmmeter (model 4328A, Yokogawa-Hewlett-Packard Ltd.).

#### *Acid analysis*

The cells were disassembled after testing, and the acid content of each component was examined by neutralizing the phosphoric acid (following test procedure: JIS K9005).

## **Results and discussion**

#### *Change in acid volume on storage*

The storage test was carried out to investigate the rate of the change in acid volume when cells were kept at constant humidity and temperature without operation.

The data were obtained at 50, 80 and 120 °C at a constant 10% r.h. The results, given in Fig. 3, show that the acid specific volume increased for the first 50 h and then became constant. The specific volumes at 50, 80, and 120 °C after 1000 h were 0.579, 0.562, and 0.537 ml g<sup>-1</sup>, respectively. These values were nearly equal to those for phosphoric acid under the same conditions [5].

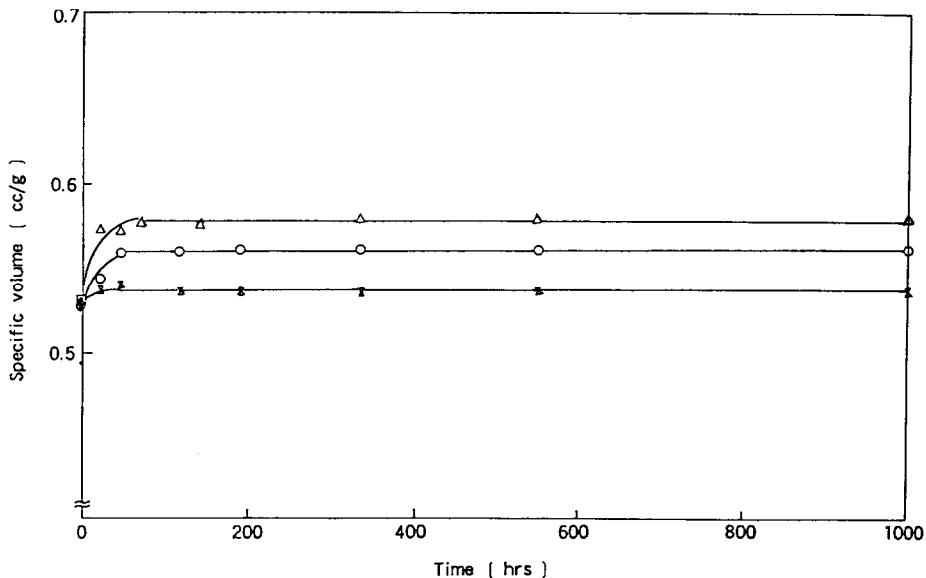


Fig. 3. Changes in specific volume of phosphoric acid at various temperatures ( $^{\circ}\text{C}$ ): ( $\Delta$ ) 50; ( $\circ$ ) 80; ( $\otimes$ ) 120.

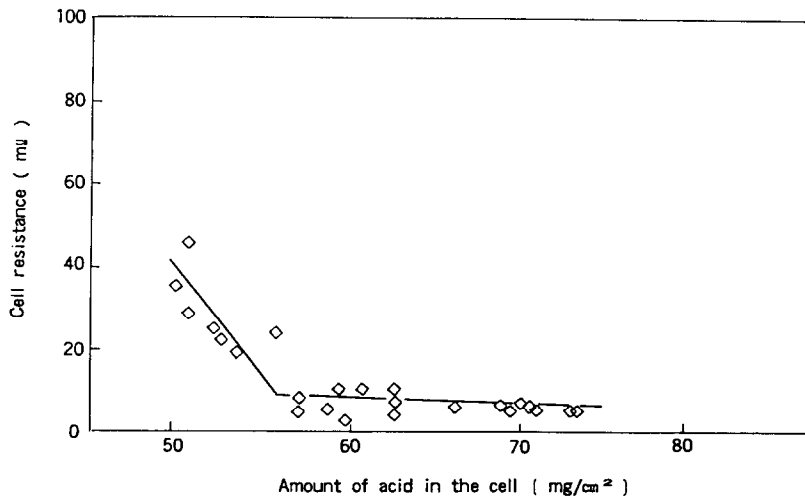


Fig. 4. Relationship between cell resistance and amount of acid in cell.

#### *Amount of acid and cell internal resistance*

Figure 4 shows the relationship between the amount of acid and the internal resistance for cells that were operated and then disassembled. The internal resistance was  $<10\text{ m}\Omega$  when the amount of acid in the cell was between  $55\text{ and }75\text{ mg cm}^{-2}$ . A dramatic increase in the resistance was observed, however, when the amount of acid dropped below  $55\text{ mg cm}^{-2}$ .

### Change in cell internal resistance with temperature

A study was made of the effect of the amount of acid in the cell on the internal resistance at different operating temperatures. The results are shown in Fig. 5.

When the amount of acid in the cell is  $58.9 \text{ mg cm}^{-2}$  (i.e.,  $> 55 \text{ mg/cm}^{-2}$ ), see curve (a), the internal resistance decreases as the operating temperature is increased. This is due to the increased electrical conductivity of the phosphoric acid. On the other hand, in cases (b)–(e), where the amount of acid in the cell is  $< 55 \text{ mg cm}^{-2}$ , the internal resistance increases as the cell operating temperature is raised.

As shown in Fig. 4, the cell resistance increases sharply when the amount of acid in the cell drops below  $55 \text{ mg cm}^{-2}$ . It appears that the acid volume decreases considerably at higher temperatures, and thereby causes an increase in cell resistance.

### Changes in cell performance over time

In order to examine the influence of changes in acid volume on cell performance, the cell was operated within temperature ranges 180 to 210 °C and 180 to 90 °C. The amount of acid in the cell was  $54 \text{ mg cm}^{-2}$ . The findings are presented in Figs. 6 and 7, respectively. It can be seen that the cell voltage and internal resistance change with temperature, and then stabilize within 1 h. The acid volume changed more rapidly during cell operation than during storage due to water production.

### Acid volume during cell operation

The specific volume of acid at different operating temperatures was calculated using the acid vapour pressure data available in the literature [5], extrapolated values of the acid vapour pressure, and simplified assumptions [6]. The results of these calculations are presented in Table 1. The acid volume in the cell at a given operating temperature can be calculated from the acid specific volume at that temperature and the amount of the acid in the cell.

Figure 8 shows the relationship between internal resistance and the calculated acid volume at different operating temperatures. It can be seen that the cell resistance

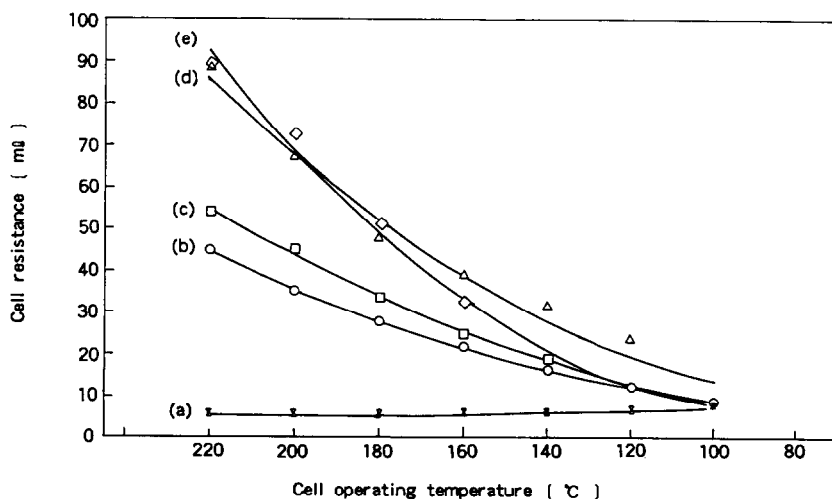


Fig. 5. Relationship between cell operating temperature and cell resistance. Amount of acid ( $\text{mg cm}^{-2}$ ) in the cell: (a) 58.9; (b) 54.0; (c) 51.0; (d) 50.6; (e) 49.1.

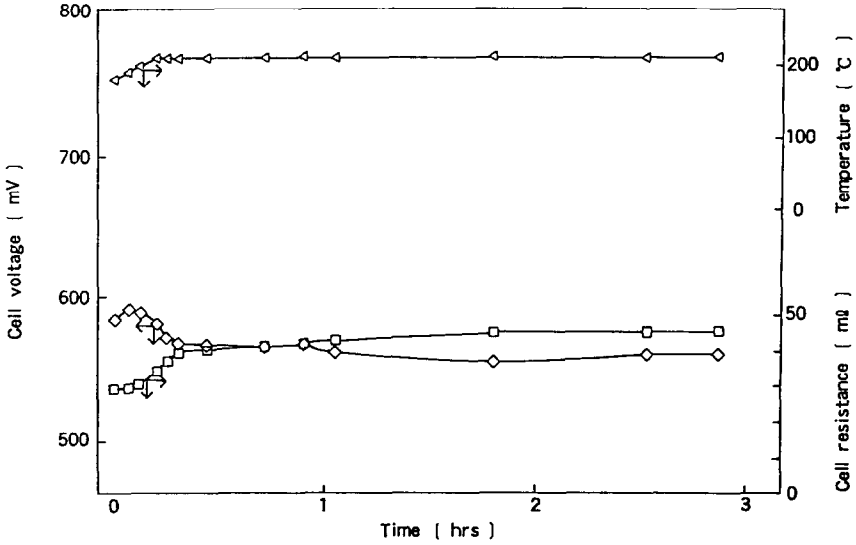


Fig. 6. Changes in cell voltage and cell resistance for shift in cell operating temperature from 180 to 210 °C. (□) resistance; (◇) voltage; (◁) temperature.

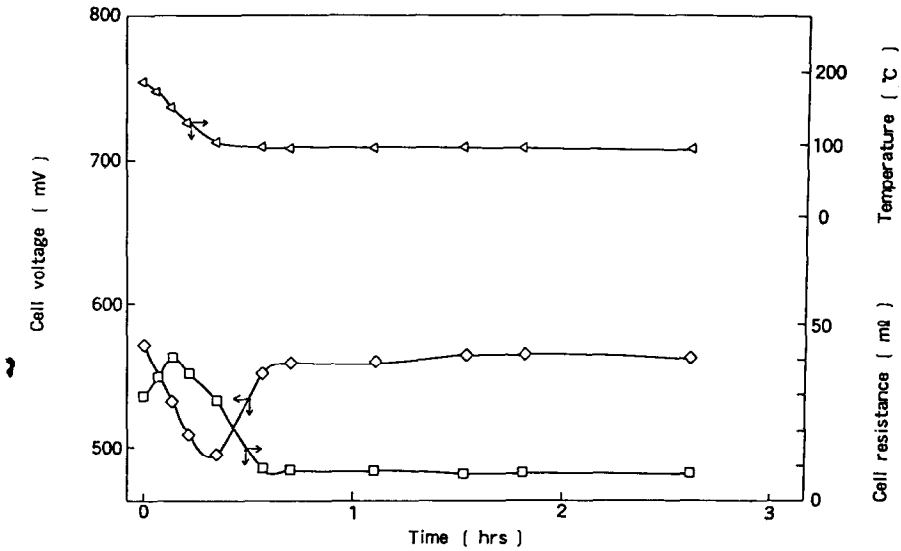


Fig. 7. Changes in cell voltage and cell resistance for shift in cell operating temperature from 180 to 90 °C. (□) resistance; (◇) voltage; (◁) temperature.

increases sharply when the acid volume in the cell drops below  $30 \mu\text{l cm}^{-2}$ . This situation is nearly the same as that for a cell with an acid content of  $55 \text{ mg cm}^{-2}$ , as shown in Fig. 4. It would appear that the dependence of internal resistance on operating temperature can be used to estimate the amount of acid in the cell during operation.

TABLE 1

Calculated specific volume of phosphoric acid

Temperature (°C)	Specific volume (ml g <sup>-1</sup> )
100	0.616
120	0.590
140	0.575
160	0.564
180	0.557
200	0.551
220	0.546

Air 7.5 stoich (12.8 mm Hg).

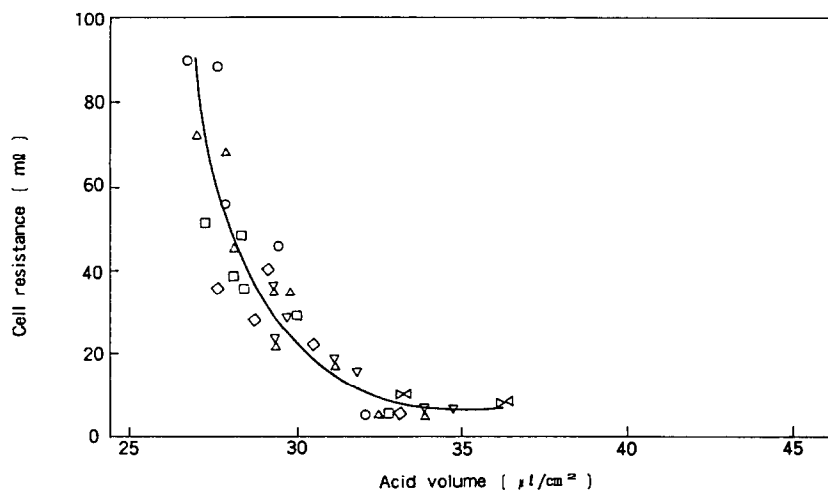


Fig. 8. Cell resistance as a function of calculated acid volume. Cell operating temperature; (⋈) 100; (∇) 120; (⊗) 140; (◇) 160; (□) 180; (△) 200; (○) 220.

### Conclusions

Compared with cells that were stored in an environment of constant humidity and temperature, those operated under variable conditions exhibit a relatively rapid change in acid volume.

There was a marked increase in cell resistance when the acid volume in the operating cell fell below 30  $\mu\text{l cm}^{-2}$ . It is concluded that the dependence of internal resistance on operating temperature can be used to estimate the amount of acid in the cell during operation.

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