

Short Communication

Effect of storage conditions on the performance of phosphoric acid fuel cells

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Abstract

In this study, start/stop tests have been conducted on small, single cells at various storage temperatures. Cell service-life has been observed, along with changes in the distribution of phosphoric acid in the cell components that accompany fluctuations in the phosphoric acid volume. The results show that, with each repetition of the operation-storage cycle, the volume of phosphoric acid changes (i.e., increases/decreases). This behaviour influences both the cell service-life and the phosphoric acid distribution in the cell components. Therefore, in order to attain stable cell performance for a long period, it is necessary to optimize the conditions under which cells are stored.

Introduction

In phosphoric acid fuel cells, considerable variation may occur in the volume of the phosphoric acid electrolyte. Proper electrolyte volume management is essential if the performance level of a phosphoric acid fuel cell is to be maintained under different operating conditions.

In situations where the volume of phosphoric acid electrolyte increases considerably through the absorption of water, the electrolyte tends to leak into the gas-diffusion layers and out of the fuel-cell stack. This results in lowered cell characteristics. By contrast, the volume of phosphoric acid electrolyte decreases significantly through evaporation, then a considerable increase in cell resistance and/or cross-over of the process gases may occur. Again, this causes deterioration in the cell characteristics.

Cell performance and life are affected by catalyst activity, the ability of the cell to retain acid, the operating conditions, and other factors. Attempts have been made [1–3] to understand the effect of acid absorption in the catalyst layer on electrode performance, as well as the causes of reduced cell performance during start/stop tests [3, 4]. The influence of the acid absorbency of the electrode on acid movement and balance in the cell, cell performance, and endurance has also been examined [5].

This work involves an investigation of the effects of acid volume changes, brought about by repeated start/stop cycling, on the acid distribution in the cell components and, ultimately, on cell performance itself.

Experimental

Cell construction

Figure 1 shows the construction of the cell unit. This consists of an air electrode, a fuel electrode and an electrolyte matrix. Both electrodes comprised a carbon-supported platinum catalyst with a platinum loading of 10 wt.% (Vulcan XC-72R, Cabot, Ltd.), polyfluoroethylene (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 (tetrafluoroethylene-hexafluoropropylene copolymer) 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 was 40 wt.%. The catalyst layer was pressed onto the carbon substrate and then heated in air at 360 °C for 30 min. The electrode thickness and platinum loading were 0.45 mm and 0.2 mg cm⁻², respectively, for the fuel electrode, and 0.55 mm and 0.5 mg cm⁻² for the air electrode.

The electrolyte matrix was composed of an SiC matrix and 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 by SiC (#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, 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 from a mixture that was 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.

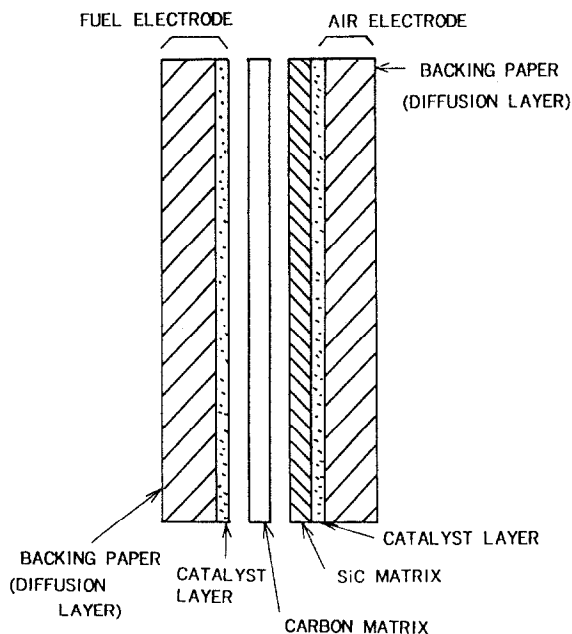


Fig. 1. Cell construction.

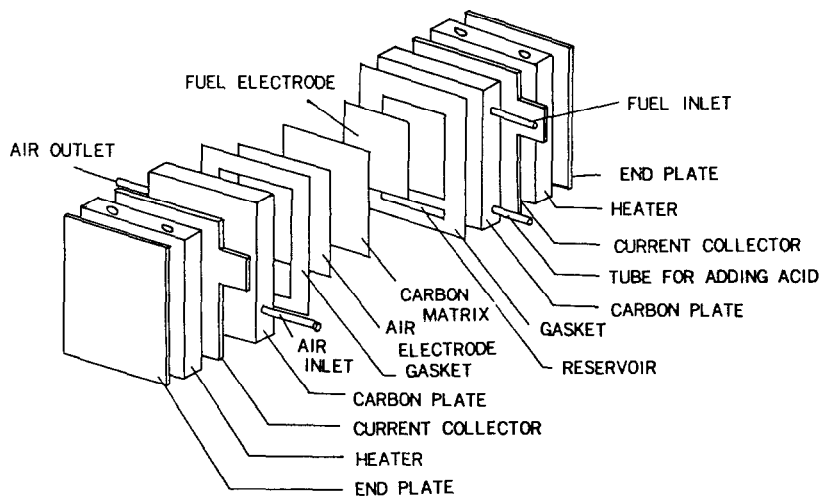


Fig. 2. Construction of a single cell with 25 cm² electrodes.

Purge test

A cell was assembled using the active components described above and an electrolyte of 100 wt.% phosphoric acid (Rasa Kogyo, Ltd.). A single cell was loaded with 2.1 g (84 mg cm⁻²) of electrolyte. The specific gravity of the acid was 1.87 [6]. The cell construction is shown in Fig. 2. The active area of the electrodes was 25 cm². The cell was placed between inner-manifold carbon separators.

Non-operating cells were located in a vessel which was filled with nitrogen. The storage temperature was maintained at 50, 80, and 120 °C by means of heater plates. The specific volume of the acid was calculated from the weight gain of the cell unit. It was assumed that weight changes were a result of water absorption from the vessel atmosphere.

Accelerated life test

To simulate the actual operating sequence that would occur in a typical fuel cell, a start/stop cycle that included start-up/shut-down procedure was adapted for accelerated cell-life testing.

Cell start-up was achieved by first heating to 200 °C in nitrogen flow, feeding process gases to the cell after shutting off the nitrogen, and then loading a direct current resistance to maintain a constant current density of 100 mA cm⁻². An air flow (7.5 stoich.; 12.8 mm Hg humidity) was introduced into the cathode, and hydrogen gas (1.5 stoich.) into the anode. The cell voltage was monitored continuously. The internal resistance was measured by a milliohmmeter (Model 4328 A, Yokogawa-Hewlett Packard, Ltd.). The cell was operated for approximately 8 h, and then shut down. The latter was carried out by first leaving the external electrical load, turning off the heater plate, changing the feed gases from process to nitrogen, and then allowing the cell to cool to the storage temperature. Cell storage involved removing the gas-feeding tube of the cell, covering the cell with a vessel, and then purging the vessel with nitrogen. The storage temperature was maintained at 50, 80 and 120 °C by means of heater plates.

Two start/stop cycling frequencies were selected. One cycle was performed 5 times per week (short-term storage) while the other was of varying frequency (long-term storage).

Acid analysis

The cells were disassembled after testing, and the acid content in each component was examined by neutralizing the phosphoric acid (JIS K9005).

Results and discussion

Change in acid volume during purge test

Purge testing was conducted in order to investigate the rate of change in the specific acid volume under storage conditions at 50, 80, and 120 °C. The results in Fig. 3 show that the acid specific volume increased for the first 100 h, and then became stable. The specific volumes after 330 h were 0.590, 0.562 and 0.538 cm³ g⁻¹, at 50, 80 and 120 °C, respectively.

Changes in acid distribution after purge test

The acid content in each component after the purge test was examined in order to determine the effect of acid volume changes on the acid distribution. Figure 4 gives the acid distribution in each cell component after 330 h at 120, 80 and 50 °C. The electrode was composed of a catalyst layer and a gas-diffusion layer. The acid occupation of the electrodes varied slightly. There was a tendency for part of the electrode acid to leak into the gas-diffusion layer at 50 °C.

The electrolyte consisted of an SiC matrix and a carbon matrix. The acid occupation of these matrices did not differ significantly. With the increase in the volume of

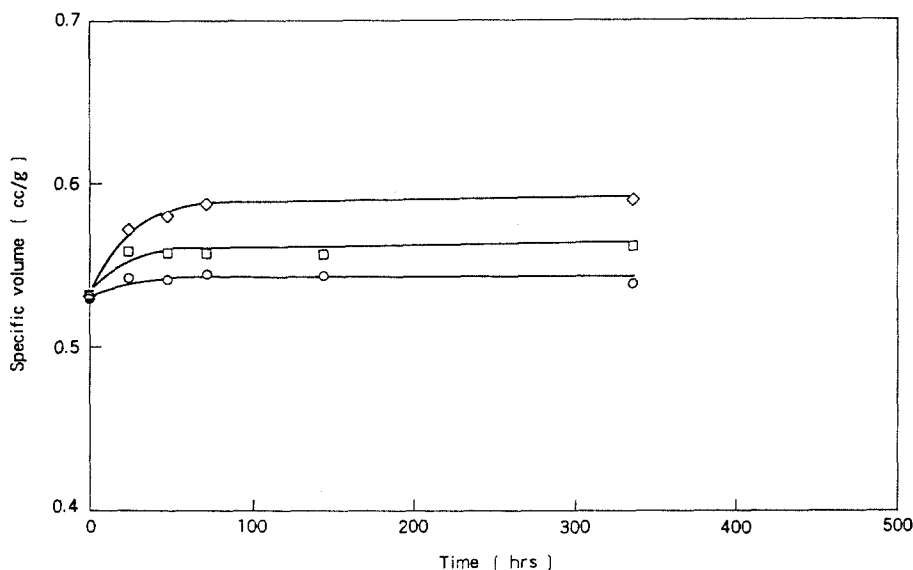


Fig. 3. Changes in specific volume of phosphoric acid at various storage temperatures: (◇) 50 °C; (□) 80 °C; (○) 120 °C.

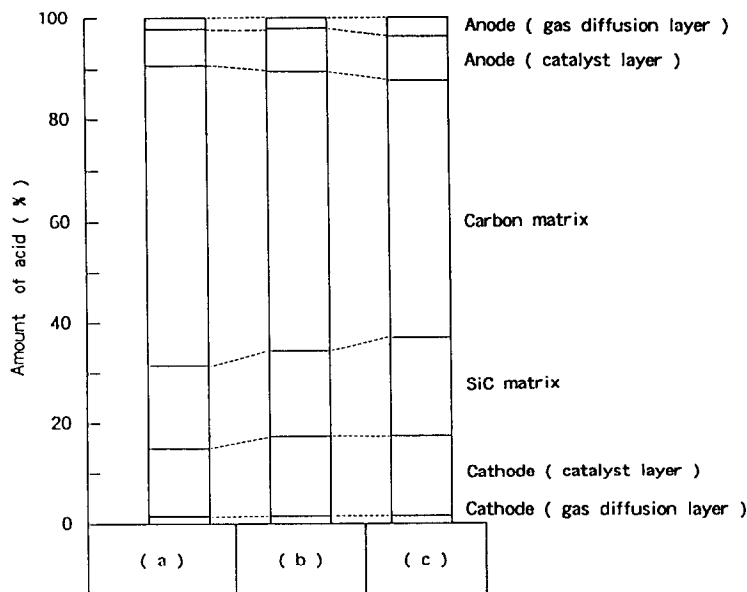


Fig. 4. Acid distribution in each cell component at various storage temperatures: (a) 120 °C; (b) 80 °C; (c) 50 °C.

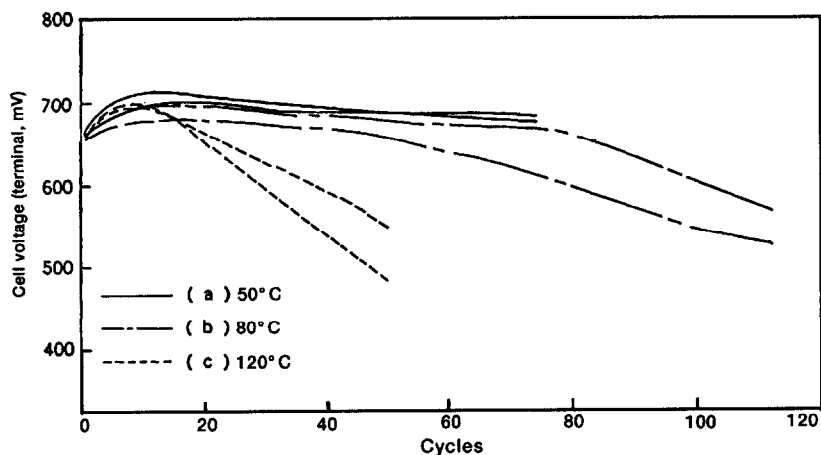


Fig. 5. Accelerated life-test at short-term storage and the temperatures listed.

phosphoric acid at low temperatures, there was a corresponding decrease in the ratio of the fluids in the two parts of the electrolyte layer.

Effects of storage conditions on cell performance

Cell performance under short-term storage is reported in Fig. 5. There was a marked difference between storage at 120 °C and at other temperatures (i.e., 50 or 80 °C). Storage at high temperature caused a sharp fall in cell performance, with a maximum cell service-life of only 50 cycles. On the other hand, at a storage temperature

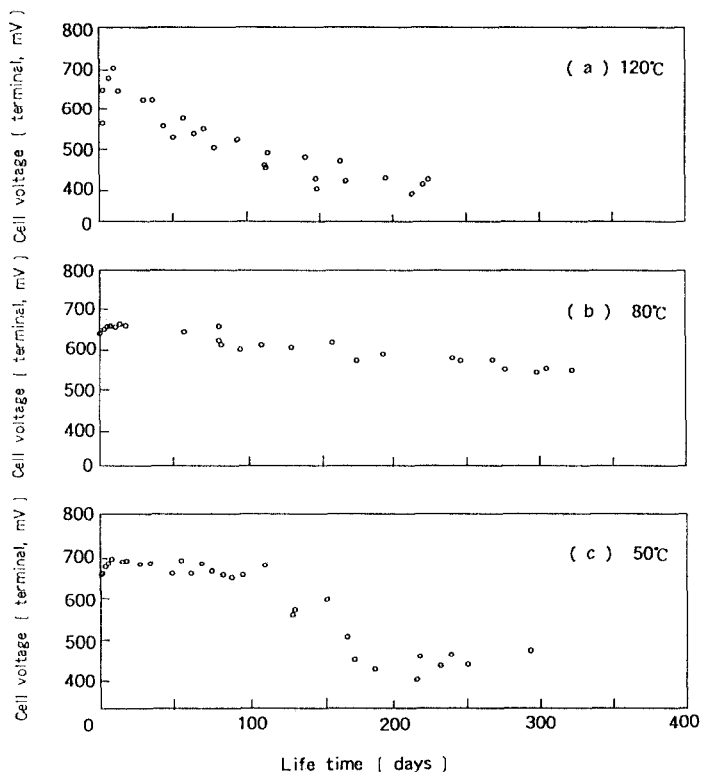


Fig. 6. Accelerated life test at long-term storage and the temperatures listed.

of 50 °C, the cell service-life remained stable up to about 80 cycles with good cell performance. After that, however, a sudden decline occurred which prevented further cell operation. Under 80 °C storage, the cell performance was inferior to that at 50 °C, although the service-life was stable up to ~110 cycles.

The corresponding performance data, under long-term storage are given in Fig. 6. The experimental points represent cell performance during operation, and the gaps between those points show the storage periods. In qualitative terms, the effect of storage temperature on cell performance was the same as that for short-term storage. That is to say, there was an initial marked drop in cell characteristics when the storage temperature was 120 °C. At 50 °C, the cell service-life was stable up ~100 days, with good cell performance, but then declined suddenly. For 80 °C storage, the cell service-life was stable over a long period. In each case, however, the decline in cell performance that accompanies the repetition of the operation-storage cycle was more rapid than that observed under short-term storage.

Changes in acid distribution after cell operation

The acid content in each component was examined to determine changes in acid distribution after cell operation under either short-term or long-term storage conditions. The results are presented in Figs. 7 and 8, respectively.

As in the case of the purge test without cell operation, there was only a small variation in the acid occupation of the electrodes. Again, part of the electrode acid

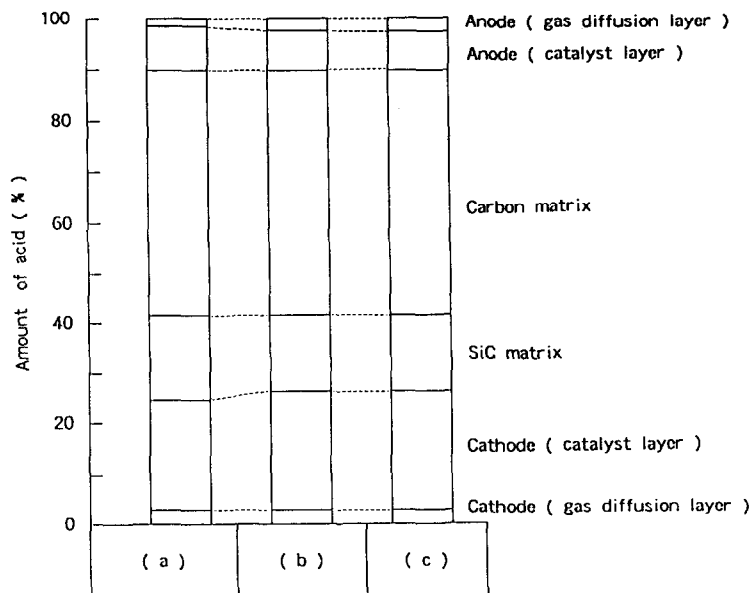


Fig. 7. Acid distribution in each cell component of terminated cell at short-term storage: (a) 120 °C; (b) 80 °C; (c) 50 °C.

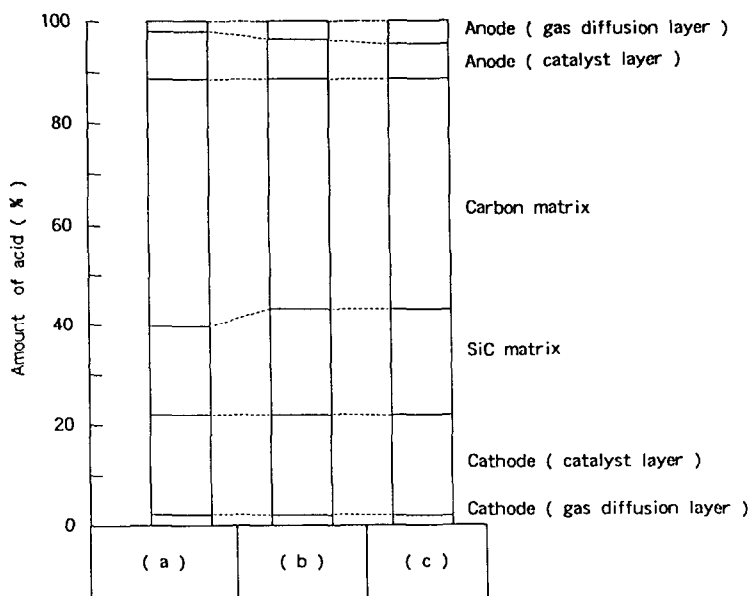


Fig. 8. Acid distribution in each cell component of terminated cell at long-term storage: (a) 120 °C; (b) 80 °C; (c) 50 °C.

tended to leak into the gas-diffusion layer at a low temperature, i.e., 50 °C; the effect was virtually identical under both short- and long-term storage conditions.

Change in acid volume during start/stop cycle

With each start/stop cycle, there is believed to be a change (increase/decrease) in the volume of phosphoric acid. This affects not only the cell service-life but also the amount and distribution of phosphoric acid in the cell components. Accordingly, the cell service-lives are presented in Figs. 5 and 6 from the standpoint of phosphoric acid volume changes.

The specific volume of acid during operation was calculated using acid vapour-pressure data available in the literature [7], extrapolated values of the acid vapour pressure, and simplified assumptions [8]. The calculated acid specific volume under cell-operating conditions was $0.551 \text{ cm}^3 \text{ g}^{-1}$. Figure 9 gives a comparison of phosphoric acid specific volume during cell operation and purge test under storage conditions. Compared with the specific volume during cell operation ($0.551 \text{ cm}^3 \text{ g}^{-1}$), that under 120 °C storage conditions is low ($0.538 \text{ cm}^3 \text{ g}^{-1}$). This indicates a decrease in the phosphoric acid volume. Conversely, the data for 80 and 50 °C storage (i.e., 0.562 and $0.590 \text{ cm}^3 \text{ g}^{-1}$, respectively) are indicative of an increase in the volume of phosphoric acid. With each repetition of the cycle, there is believed to be a change (increase/decrease) in the volume of phosphoric acid.

If the operating conditions are taken as a standard, the volume changes under 50, 80, and 120 °C storage were +7.1, +2.0, and -2.4%, respectively. A plus (+) denotes a volume increase, and a minus (-) indicates a decrease.

When the specific volume of phosphoric acid was lower under storage than during operation, as in the case of 120 °C storage (volume change: -2.4%), there was a marked drop in cell performance, as shown in Figs. 5 and 6. If, on the other hand, the specific volume of phosphoric acid was greater under storage than during operation, as in the case of 50 or 80 °C storage (respective volume changes: +7.1 and +2.0%), the cell characteristics were stable for a period and then declined suddenly. The degradation in service-life characteristics was proportional to the volume difference between operation and storage conditions. The latter, in turn, was dependent upon the storage temperature.

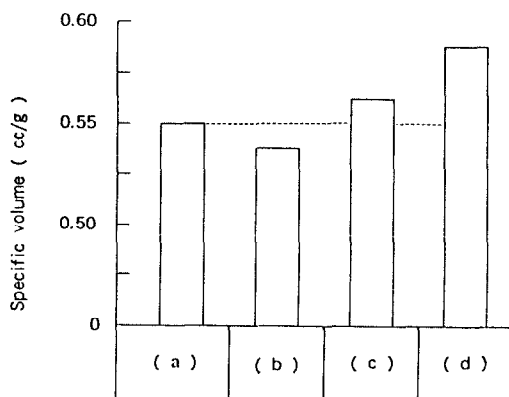


Fig. 9. Comparison of specific volume of phosphoric acid during cell operation and storage: (a) cell operation; (b) storage at 120 °C; (c) storage at 80 °C; (d) storage at 50 °C.

In terms of cell configuration, Figs. 7 and 8 reveal that the rate of phosphoric acid fluid distribution in the gas-diffusion layers increased. This occurred in proportion to the lowering of the storage temperature and the increase in the specific volume of phosphoric acid. Thus it is concluded that the sharp decline in cell performance is due to defective reactive-gas diffusion that accompanies the increase in the rate of phosphoric acid fluid apportionment in the gas-diffusion layers of the electrodes.

The storage characteristics of cells in a continuous discharge mode are more stable than those in an intermittent discharge mode. Since there is almost no change in the volume of phosphoric acid in the continuous discharge mode, it is considered that stable cell characteristics can be obtained by maintaining a near-constant specific volume of phosphoric acid during both operation and storage. Further, it is suggested that the specific volume of phosphoric acid should be greater during storage than during operation. Further studies are necessary, however, to determine a method and a control strategy for achieving such a condition.

Conclusions

In this study, start/stop tests were conducted on small, single cells at various storage temperatures. The service-life was observed, along with changes in the distribution of phosphoric acid in the cell components that accompanied phosphoric acid volume fluctuations. The results showed that with each repetition of the operation-storage cycle, the volume of phosphoric acid changed (increased/decreased). This influenced not only the cell service-life but also the phosphoric acid distribution in the cell components.

When the specific volume of phosphoric acid under storage was less than that during operation, there was a sharp fall in cell performance. By contrast, when the phosphoric acid specific volume was greater during storage than operation, the cell performance remained stable for a period, but then dropped suddenly. The deterioration in service-life characteristics was proportional to the volume difference between operation and storage conditions. It is concluded that decline in cell performance is due to defective reactive-gas diffusion that accompanies the increase in the rate of phosphoric acid fluid distribution in the gas-diffusion layers of the electrodes.

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