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LONG-TERM RELIABILITY EVALUATION OF FLUORORESIN GASKET FOR ELECTRODE OF AUTOMOTIVE LITHIUM-ION BATTERY USING SIMULATION

JIHONG LIU*, TAKAHISA AOYAMA†, HAYATO TSUDA† AND MASAMICHI SUKEGAWA†

* Technology and Innovation Center
Daikin Industries, Ltd.
1-1 Nishi-Hitotsuya, Settsu, Osaka 566-8585, Japan
E-mail: jihong.liu@daikin.co.jp, www.daikin.com

† Chemicals Division
Daikin Industries, Ltd.
1-1 Nishi-Hitotsuya, Settsu, Osaka 566-8585, Japan
E-mail: takahisa.aoyama@daikin.co.jp, www.daikin.com

Key words: Fluororesin, Gasket, Sealing Pressure, Maximum Principal Strain, Elasto-Plastic and Creep Properties, Finite Element Method.

Abstract: *In this paper, we proposed a simulation method based on the finite element method using an elasto-plastic model and a creep model to evaluate the changes in fluororesin properties with time. The validity of the proposed simulation method was verified by comparing the simulation results with the experiment results for the compression set of fluororesin PFA (Perfluoroalkoxy Copolymer). Furthermore, with the proposed simulation method, we evaluated the long-term reliability of PFA gaskets for the electrodes of automotive lithium-ion batteries.*

1 INTRODUCTION

In recent years, in order to prolong life of automotive lithium-ion (Li-ion) batteries for electric vehicles, fluororesin such as PFA (Perfluoroalkoxy Copolymer), which has excellent electrolyte resistance, electrical insulation properties, climate resistance and low moisture permeability, is being used as a material for gaskets around electrodes [1]. Since the reliability such as sealing performance and strength properties of automotive Li-ion battery gaskets must be guaranteed for 10 years or more, the long-term reliability evaluation of fluororesin gaskets has become an important issue.

In this paper, we proposed a simulation method based on the finite element method (FEM) using a combined material model, which is composed of an elasto-plastic model and a creep model, to evaluate the changes in fluororesin properties with time. We verified the validity of the simulation method by comparing the simulation results with the experiment results for the compression sets of fluororesin PFA. Moreover, we clarified that it is possible to quickly evaluate the long-term reliability of gaskets for electrodes of automotive Li-ion batteries when shapes of the gaskets, electrodes and lids change without relying on prototype tests, and realize an optimum gasket structure design in a short time.

2 PERFORMANCE REQUIREMENTS FOR AUTOMOTIVE Li-ION BATTERY GASKETS

Figure 1 shows a schematic diagram of a prismatic-type automotive Li-ion battery. Gaskets used in Li-ion batteries act as seals to prevent electrolyte from leaking out and moisture in the air from infiltrating the battery. The gaskets also provide electrical insulation to prevent the positive and negative electrodes from making contact and causing short circuits. To ensure the safety and life-span of the batteries, sealing and insulation functions of automotive Li-ion battery gaskets must be guaranteed for 10 years or more. Battery gaskets must also possess restoring force to maintain the shape of the seal under adverse conditions, such as high temperatures and long-term stresses, which can cause creep deformation. When a gasket is tightened, the restoring force generated by tightening creates seals between the gasket and the electrode and between the gasket and the lid. In designing automotive Li-ion battery gaskets, it is an important task to evaluate the long-term reliability of gaskets to ensure the required sealing pressure while suppressing the maximum strain in gaskets.

Battery gaskets have traditionally been made of rubbers. For many years, it was not considered possible to produce the gaskets from other polymers. Fluororesin like PFA, however, possesses excellent electrolyte resistance, electrical insulation and climate resistance in addition to low moisture permeability. The material wedges into the concavities on metal surfaces, and can form seals, even on rough surfaces without the use of treatment agents or adhesives. Even at a low temperature of −40°C or when exposed to a long-term high temperature of 65°C, the PFA retains its restoring force and maintains its sealing performance. In addition, the amount of swelling of PFA in response to electrolyte is less than one-tenth that of rubbers. Therefore, deterioration of material properties of PFA due to swelling is small, and long-term reliability improvement of its gaskets can be expected.

3 MATERIAL PROPERTIES OF FLUORORESIN PFA

In this paper, we assumed that the time dependence of the mechanical properties of PFA can be represented by a combined material model, which is composed of an elasto-plastic

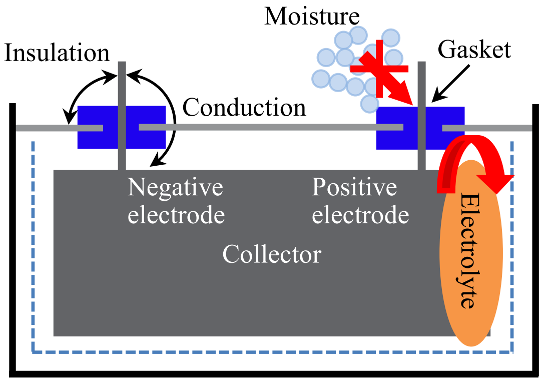


Figure 1: Schematic diagram of a prismatic-type automotive Li-ion battery showing gaskets

model and a creep model. The elasto-plastic model is assumed to meet the von Mises yield criteria and isotropic hardening rule, and is approximated by multiple lines, and the creep model is characterized by the modified time hardening creep model [2]. In particular, the elasto-plastic model of PFA is prepared based on the tensile stress-strain diagrams at a normal temperature of 23°C and a high temperature of 65°C, and the creep model of PFA is created based on the results of compression creep tests with different stress levels at the corresponding temperatures. The modified time hardening creep model is shown in the following equation (1).

$$\varepsilon_{crep} = C_1 \sigma^{C_2} t^{C_3+1} e^{-C_4/T} / (C_3 + 1) \tag{1}$$

where, ε_{crep} is cerrp strain, σ is stress, T is temperature and C_1, C_2, C_3, C_4 are parameters identified from the compression creep experiment results. In particular, the values of the parameters C_1, C_2, C_3 are identified by fitting the cmpression creep experiment results at the normal temperature and the high temperature to the equation (1), with the parameter C_4 representing the temperature dependency of the creep characteristic set to 0.

3.1 Compression set test for PFA

In this paper, we verify the validity of the combined material model by comparing simulation results of the compression sets of PFA over time with the experiment results.

The compression set [3] of a material is the permanent deformation remaining after removal of a force that was applied to it. The term is normally applied to soft materials such as elastomers, and is considered as an important property for gasket materials. Compression set is normally measured in two ways: compression set under constant force in air (A) and compression set under constant deflection in air (B).

In compression set B, the specimen is compressed to 75% of its original height for a set time and at a set temperature. Compression set B is defined as the percentage of original specimen thickness after it has been left in normal conditions for 30 minutes. C_B, the compression set B is given by

$$C_B = [(t_o - t_i)/(t_o - t_n)] \times 100 \tag{2}$$

where, t_o is the original specimen thickness, t_i is the specimen thickness after testing and t_n is the spacer thickness or the specimen thickness during the test.

In this paper, we expand and apply the method of compression set test B to fluororesin PFA to evaluate its permanent deformation characteristics. Figure 2 shows the detailed procedure of the compression set test for fluororesin PFA.

1) Compress the cylindrical specimen by 25% using a jig at a normal temperature of 23°C and hold it for 30 minutes.
2) Place the specimen in a furnace at a high temperature of 65°C and hold it for a set time.
3) Remove the specimen from the furnace after the set time and cool it naturally at the normal temperature for 3 hours.
4) Release the specimen from the jig and leave it at the normal temperature for another 30 minutes, then measure the thickness of the specimen.
5) Calculate the compression set from the change in the thickness of the specimen using the equation (2).

3.2 Verification of the combined material model

Figure 3 shows the compression set results of simulations and experiments for the specimens of fluororesin PFA. The simulation results are obtained by FEM based on the combined material model and the experiment conditions described above. A good correlation was found between the compression set results of simulations and experiments over 50,000 hours (about 5.7 years). Since the simulation results and the experiment results are in good agreement, we can conclude that the proposed simulation method and the combined material model are valid and effective for evaluating time-dependent deformation behaviors fluororesin PFA.

By using the proposed simulation method and the combined material model, it is possible to evaluate the long-term reliability of fluororesin PFA gaskets having different shapes and structures quickly without relying on experiments.

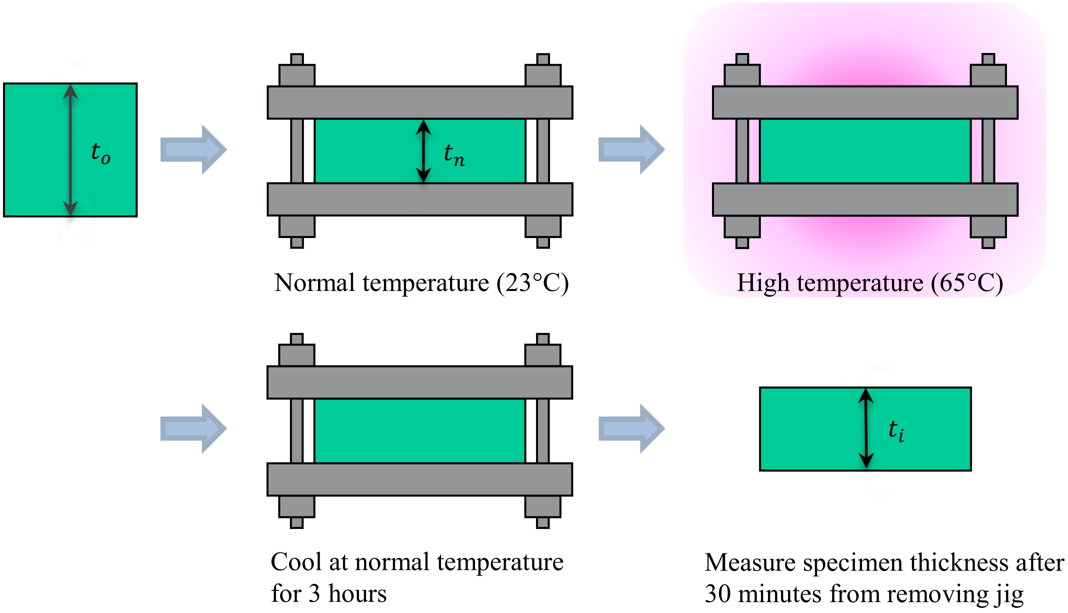


Figure 2: Procedure of the compression set test for fluororesin PFA

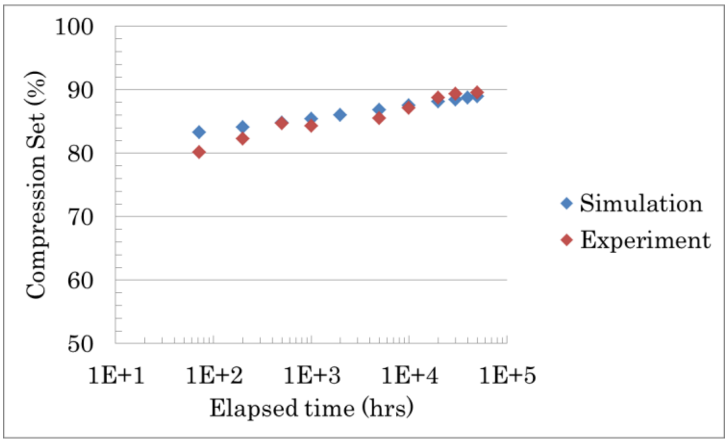


Figure 3: Compression set results of simulations and experiments for fluororesin PFA

4 SIMULATING GASKET RELIABILITY

In general, a gasket with a uniform cross-sectional thickness is used. In order to reduce variations in tightening of gasket and to increase the sealing pressure, it is common to make protrusions on the tightening members. Because it takes a lot of time to create and test physical prototypes, little research had been done on the effects of changing protrusion shapes and distances between the protrusions, and the limits of physical testing mean that we had to rely on trial-and-error methods to improve gasket designs.

In this section, we use the above-described simulation method and the proposed combined material model of fluororesin PFA to obtain a better understanding of the effects of age-related change and to learn how changing the protrusion shapes and distances between protrusions could improve efficiency and life expectancy of PFA gaskets.

4.1 Effects of protrusion shapes

Figure 4 shows a schematic half cross-sectional shape of a gasket structure for an electrode of a Li-ion battery. Here, the dimensions of the gasket are referred to the reference [4]. In this paper, we assumed that the gasket, the lid and the electrode have geometrical axial symmetry, and there is a protrusion on the lid, and the protrusion tip has an arc shape. Based on these assumptions, the simulations of the gasket tightening process and sealing performance change over time after the gasket tightening can be performed by a two-dimensional axisymmetric finite element model.

In the simulation, the lid and the electrode are assumed to be rigid because they have remarkably higher rigidity than the gasket. In the tightening process of the gasket, it is assumed that the electrode is completely fixed, and the reinforced displacement in the axial direction is applied to the lid. The maximum axial reinforced displacement of the lid is the same as the height of the protrusion. Moreover, the friction coefficients of the contact surfaces between the gasket and the lid, between the gasket and the electrode are set to 0.2. FEM code ANSYS is used in the simulations.

In this section, we show the aging changes of sealing performance of fluororesin PFA gaskets obtained by using the simulation method. The gaskets are tightened at the normal temperature (23°C) and moved to a furnace (65°C) an hour later.

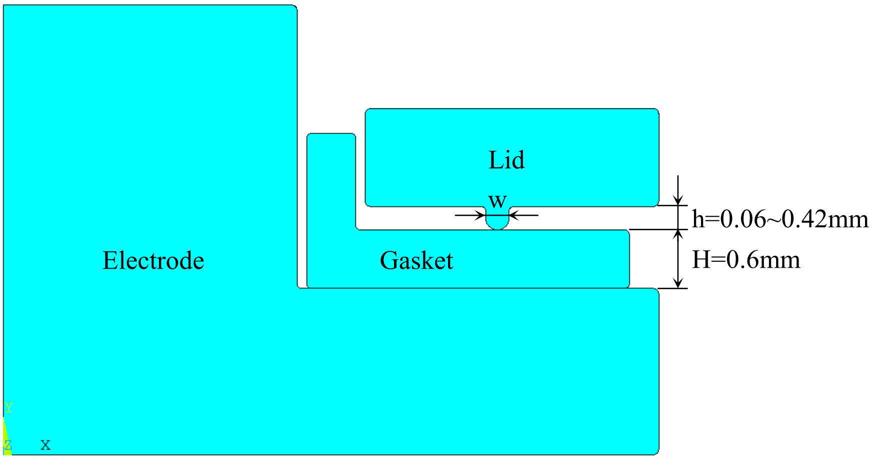


Figure 4: Cross-sectional shape of a gasket structure with a protrusion on the lid

The changes with time in the maximum gasket sealing pressure on the electrode side and the lid side are shown in Fig. 5 in the case where the protrusion height is 0.18mm and the width is 0.36mm (h0.18; w0.36). According to these results, it is obvious that a larger sealing pressure is generated on the lid side with a protrusion than on the electrode side without protrusion. It is also found that the sealing pressure on both the lid side and the electrode side greatly decrease after the gasket was moved to the furnace, but the differences in the sealing pressures between the lid side and the electrode side become smaller. In addition, the maximum sealing pressures after 90,000 hours (about 10.3 years) on the electrode side and the lid side are 3.2MPa and 8.6MPa, respectively, which are sufficient for sealing the electrodes of the automotive Li-ion batteries where required sealing pressure is 1MPa.

The distributions of the sealing pressures with time on the lid side and the electrode side are shown in Fig. 6. Judging by these results, it is seen that the distribution shapes of the sealing pressures do not change with time, but the maximum sealing pressures decrease with time. It is also found that the maximum sealing pressures on the lid side are generated slightly inside the protrusion, not directly below the protrusion, and the maximum sealing pressures on the electrode side occur inside the protrusion as well. In addition, it should be noted that the sealing pressure distributions shown at the end of Fig.6 are the results when the internal pressure of 1MPa is applied to the Li-ion battery after 90,000 hours. In this case, the maximum sealing pressures on the electrode side and the lid side are 3.2MPa and 8.8MPa, respectively, which are sufficient for sealing pressures for the automotive Li-ion batteries.

Figure 7 shows the changes with time in the maximum first principal mechanical strain, creep strain and total strain of the gasket when the protrusion height is 0.18mm and the width is 0.36mm. Here, the true strain is used and the maximum first principal total strains are calculated by the following equation (3). Based on these results, it is clear that the mechanical strains and the creep strains increase with time. It is also found that the strains do not change significantly after the gasket is moved to the furnace. This is caused by the fact that the gasket is tightened and cannot deform freely. The maximum first principal strain of the gasket is about 0.83 after 90,000 hours, it is much less than 1.61 of PFA breaking strain.

$$\varepsilon_{total} = ln\left[exp(\varepsilon_{mech}) + \exp(\varepsilon_{crep}) - 1\right] \tag{3}$$

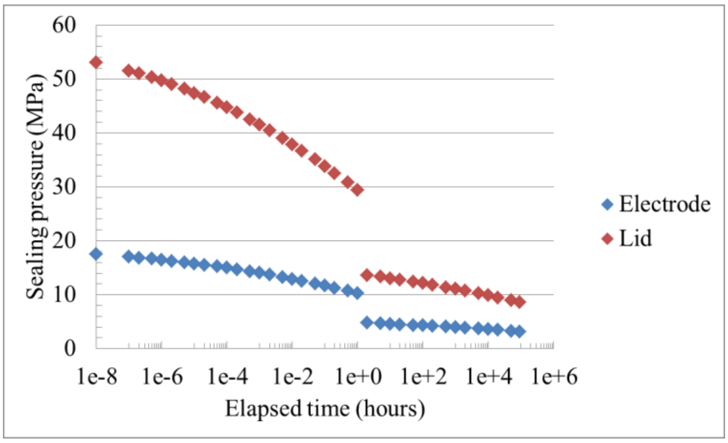
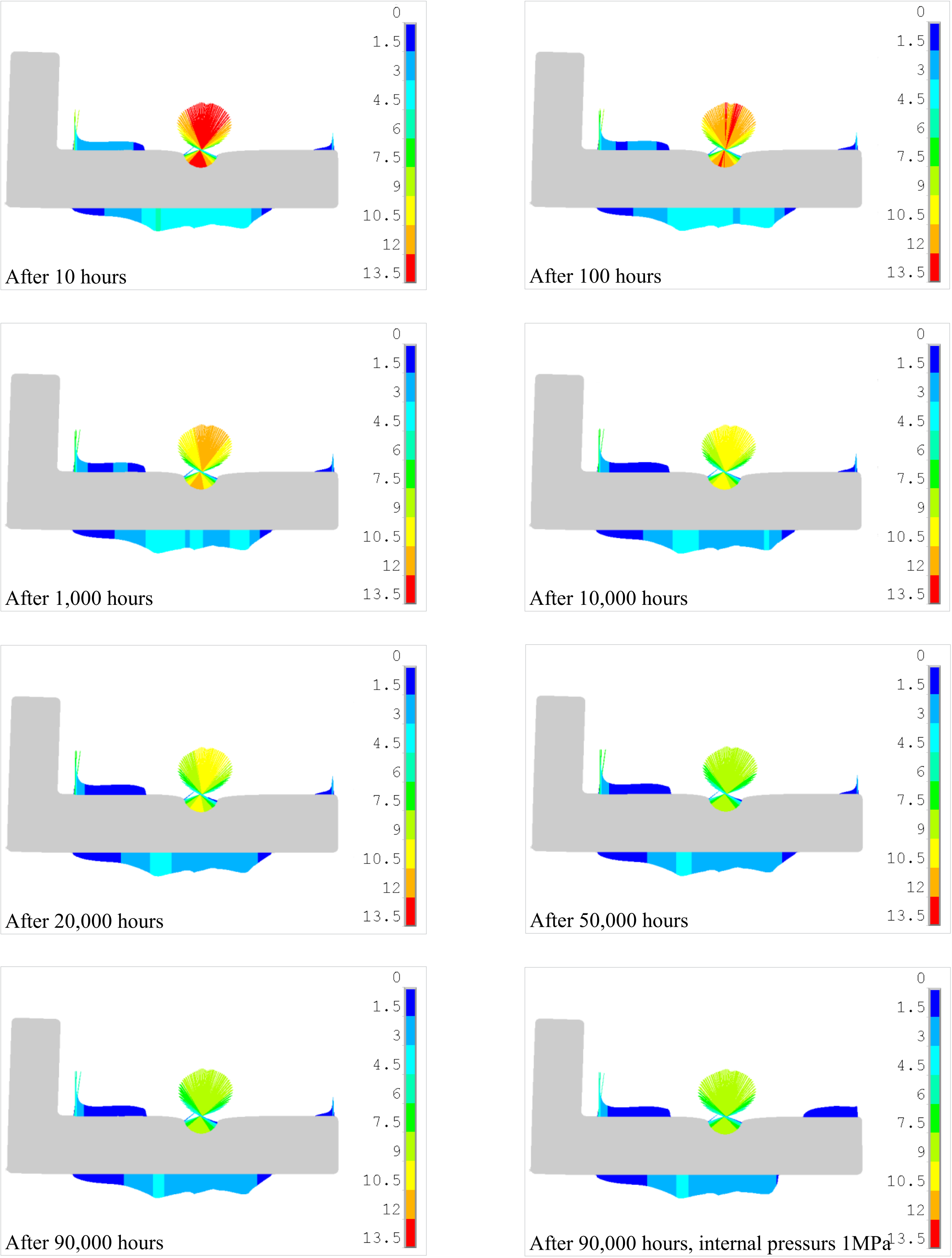


Figure 5: Changes with time in the gasket sealing pressures on the electrode side and the lid side (h0.18; w0.36)



After 10 hours

After 100 hours

After 1,000 hours

After 10,000 hours

After 20,000 hours

After 50,000 hours

After 90,000 hours

After 90,000 hours, internal pressurs 1MPa

Figure 6: Distributions of sealing pressures with time on the lid side and the electrode side (h0.18; w0.36)

Figure 8 shows the changes in the sealing pressures of the gasket after 90,000 hours due to the differences in the protrusion shapes (h/w) and the tightening ratios (h/H), and Fig. 9 shows the corresponding maximum first principal strains. Here, the vertical axis in Fig. 8 represents

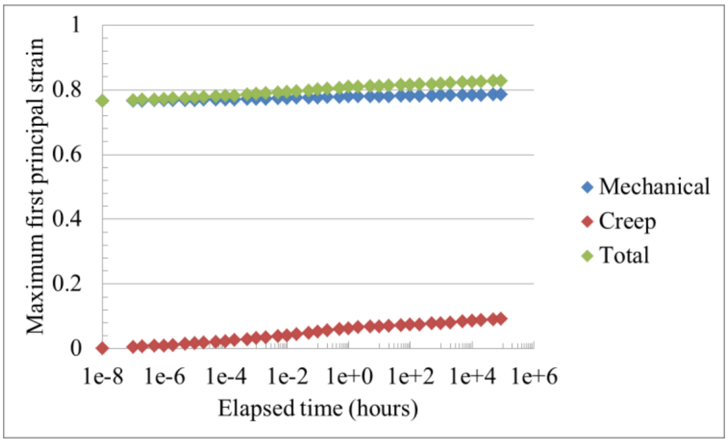


Figure 7: Changes with time in the maximum first principal strain of the gasket (h0.18; w0.36)

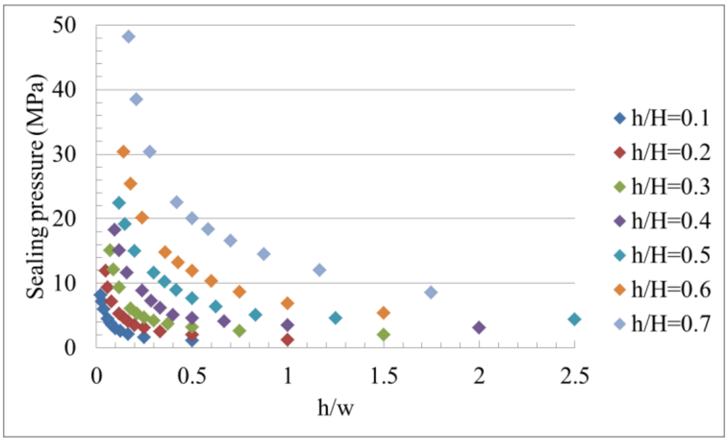


Figure 8: Sealing pressures of gaskets after 90,000 hours with a protrusion on the lid

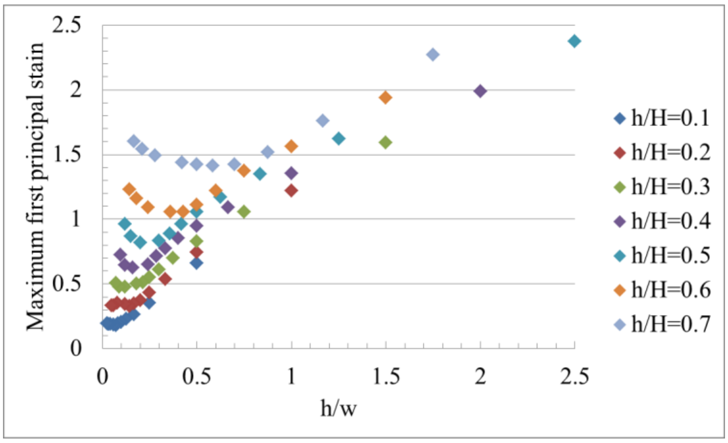


Figure 9: Maximum first principal strains of gaskets after 90,000 hours with a protrusion on the lid

the smaller of the maximum sealing pressures on the lid and the electrode side, the vertical axis in Fig. 9 means the total strains which are calculated by the equation (3). Based on these results, it is found that the gasket can secure the required sealing pressures while suppressing the maximum strains even after 90000 hours if the h/w and h/H are in the range of 0.1 to 0.7, and in the range of 0.1 to 1.0.

4.2 Effects of distances between protrusions

Figure 10 shows a schematic half cross-sectional shape of a gasket structure which has one protrusion on the lid and one on the electrode. In this section, the cross-sectional shape of the protrusion is assumed to be semicircular, and the simulation conditions are the same as above. Now, we show the effects of the distances between the protrusions on the aging changes of the sealing performance of fluororesin PFA gaskets obtained by using the simulation method.

Figure 11 shows the changes in the sealing pressures of the gasket after 90,000 hours (about 10.3 years) due to the differences in the distances between protrusions (d/H) and the tightening ratios (2h/H), and Fig. 12 shows the corresponding maximum first principal strains. As mentioned in the above section, the vertical axis in Fig. 11 represents smaller values of the maximum sealing pressures on the lid and the electrode side, and the vertical axis in Fig. 12 means the total strains calculated by the equation (3). According to these results, it is observed that the sealing pressures after 90,000 hours decrease as the tightening ratios (2h/H) increase in the range of 0.1 to 0.5. It is considered that this is because the stress relaxation of the PFA increases rapidly as the tightening ratio increases. However, the sealing pressures increase again when the tightening ratios is greater than 0.5. On the other hand, it is found that the maximum strains after 90,000 hours increase as the tightening ratios increase in the range of 0.1 to 0.8. It is revealed that the sealing pressures and maximum strains after 90,000 hours fluctuate greatly if d/H is in the range of 1 or less and 2h/H in the range of 0.5 or more

It is also confirmed that the sealing pressures and the strains approach nearly constant values when d/h is greater than 1.5, especially for the tightening ratios in the range of 0.1 to 0.7. Therefore, it is concluded that if d/H is in the range of 1.5 or more and 2h/H is in the range of 0.1 to 0.7, the sealing pressures and the maximum strains after 90,000 hours can be maintained at appropriate values, which are suitable for sealing automotive Li-ion batteries.

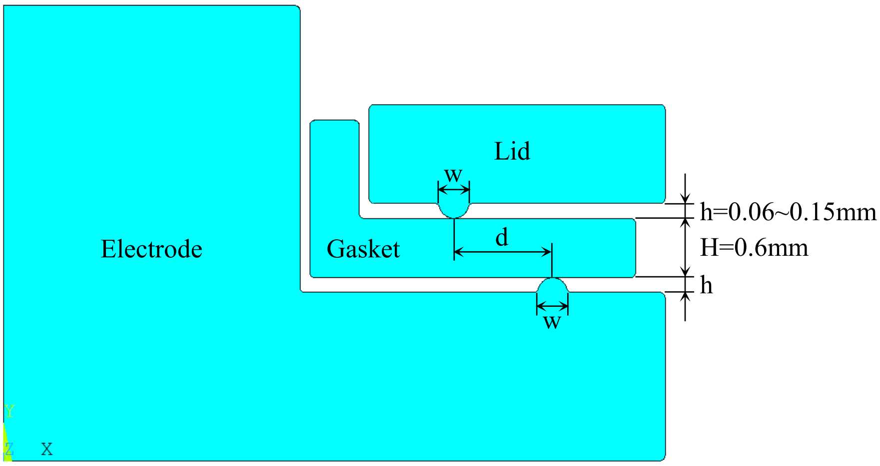


Figure 10: Cross-sectional shape of a gasket structure with protrusions on the lid and the electrode

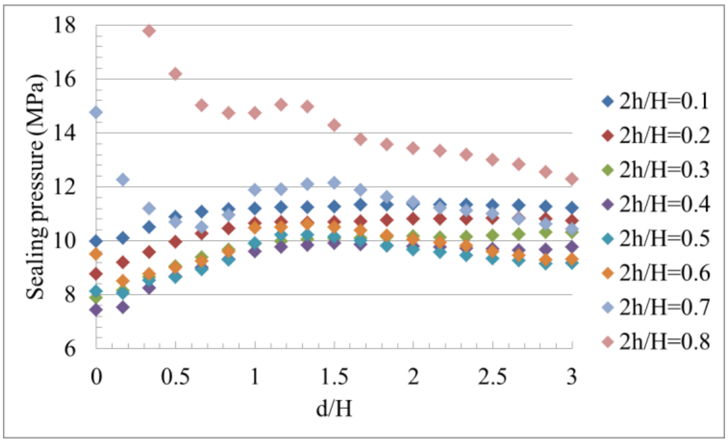


Figure 11: Sealing pressures of gaskets after 90,000 hours with protrusions on the lid and the electrode

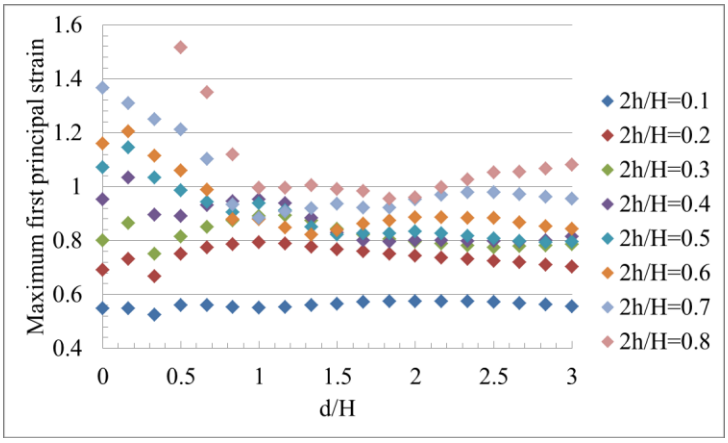


Figure 12: Maximum first principal strains of gaskets after 90,000 hours with protrusions on the lid and the electrode

5 CONCLUSIONS

- A Simulation method based on the finite element method using a combined material model which is composed of an elasto-plastic model and a creep model is established to evaluate the changes in fluororesin PFA properties with time. The elasto-plastic properties are modeled with a multilinear isotropic-hardening elastic-plastic model meeting the von Mises yield criteria, and creep properties are modeled with the modified time-hardening creep model.
- The validity of the simulation method and the combined material model for PFA is verified by comparing the simulation results of compression sets over 5 years with the experiment results.
- Based on the established simulation method, the influence of protrusion shapes and distances between protrusions on the long-term reliability of the PFA gasket is clarified, and PFA gasket structures that can maintain the required sealing pressures while reducing the maximum principal strains are revealed.
- Using the established simulation method, it is possible to quickly evaluate the long-

term reliability of PFA gaskets for automotive Li-ion batteries when shapes of gaskets, electrodes and lids change without relying on experiments, and realize an optimum gasket design in a short time.

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