Durability of Sulfonated Phenylene Poly(arylene Ether Ketone) Semiblock Copolymer Membrane in Wet-Dry Cycling for PEFCs

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The mechanical durability of sulfonated poly (phenylene) (SPP) membrane, used for polymer electrolyte fuel cells (PEFCs), is an issue of importance. The membranes need to have adequate mechanical properties to withstand the wet-dry cycles of the fuel cell. The SPP membrane is composed of a sulfonated benzophenone poly(arylene ether ketone) (SPK) semiblock copolymer. The mechanical properties of the SPP membrane were analyzed in wet-dry cycling experiments. The SPP membrane exhibited higher durability than that of the SPK membrane. The oxidative stability of the SPP membrane is also a key issue for the commercial use of the polymer electrolyte fuel cells.
The sample was dried at 105 °C under vacuum for 6 hours, and the thickness of the sample was measured quickly, and the thickness of the sample was measured at three sites. The dimensional change ratios of the membrane are defined as follows:

\[ D_y = \frac{L_{t,y} - L_{t,d,y}}{L_{t,d,y}} \times 100 \]  
\[ D_x = \frac{L_{t,x} - L_{t,d,x}}{L_{t,d,x}} \times 100 \]

where \( D_y \) and \( D_x \) are the dimensional change ratios of the in-plane direction and through-plane (thickness) direction, respectively, \( L_{t,y} \) and \( L_{t,x} \) are the sums of the lengths of the four sides of the sample under wet and dry conditions, respectively, and \( L_{t,w,y} \) and \( L_{t,d,y} \) are the mean values of thickness of the sample under wet and dry conditions, respectively.

**Experimental**

**Analysis of membrane mechanical properties.**—The tensile strength of the membrane was measured by use of an Imada Seisakusho SVZ-50NB-5R2 universal test machine. The measurement was conducted according to the procedure described previously. The dimensional change of the membrane was measured by a wet-dry test. The membrane was cut into a rectangular shape (20 mm × 30 mm). The sample was dried at 105 °C under vacuum for 6 hours, and the lengths of the four sides and the thickness (three sites) of the sample were measured. After immersing in ultrapure water at 25 °C for 15 hours, the sample was sandwiched between two glass plates and the lengths of all four sides were measured. Water on the sample was wiped off quickly, and the thickness of the sample was measured at three sites. The dimensional change ratios of the membrane are defined as follows:  

\[ D_y = \frac{L_{i,y} - L_{i,d,y}}{L_{i,d,y}} \times 100 \]  
\[ D_x = \frac{L_{i,x} - L_{i,d,x}}{L_{i,d,x}} \times 100 \]

where \( D_y \) and \( D_x \) are the dimensional change ratios of the in-plane direction and through-plane (thickness) direction, respectively, \( L_{i,y} \) and \( L_{i,x} \) are the sums of the lengths of the four sides of the sample under wet and dry conditions, respectively, and \( L_{i,w,y} \) and \( L_{i,d,y} \) are the mean values of thickness of the sample under wet and dry conditions, respectively.

**MEA preparation for cell performance and durability test.**—The SPP membrane (ca. 30 μm thick) was prepared according to the method described previously. The ion exchange capacity (IEC) of the SPP membrane was 2.31 mmol/g, as determined by \(^1\)H NMR spectra. \(^1\)H NMR spectra were obtained on a JEOL RESONANCE JNM-ECA400 instrument using deuterated dimethyl sulfoxide (DMSO-d6) as a solvent and tetramethylsilane (TMS) as an internal reference. Next, catalyst-coated membrane (CCM) was prepared by mixing the catalyst, ionomer and solvent and spraying the catalyst slurry on the membrane, according to the procedures described in our previous reports. The Pt loadings of the anode and cathode were controlled at 0.3 mg/cm² and 0.6 mg/cm², respectively. The geometric electrode area of the catalyst layer (CL) was 36 cm² (6 cm × 6 cm). The MEAs were constructed by sandwiching the CCM between two gas diffusion layers (GDL) with microporous layers (MPL). A conventional paper GDL (240 μm, SGL-25BCH, SGL Carbon Group Co., Ltd.) was used for both electrodes. A sub-gasket (SG) film, which was a 38-μm thick polyphenylene sulfide (PPS) sheet, was introduced in the edge region of the MEA. This MEA edge configuration was applied in order to accelerate the mechanical degradation of the membrane, even though the durability using the paper GDL was lower than that using a soft GDL, as described in our previous report. The MEA was mounted in a single-cell holder composed of two carbon separator plates with ribbed single-serpentine flow channels. Photographic and schematic images of the MEA and the fabrication process are shown in Fig. 2. The specific information of the separator flowfields is listed in Table I. The cell was fastened to generate a force of 10 kgf cm⁻². The compressive force was passively controlled by optimizing the amount of the spring strain in the cell when it was fastened. The compressive force was measured by inserting pressure-sensitive paper in the cell.
The dimensional changes of the membrane.—The dimensional change ratios for the SPP, SPK, and Nafion membranes are listed in Table I. The dimensional change ratios were determined by multiplying the H₂ percentage and the cathode inlet flow rate.

Post-test analyses.—After the durability cycling, the cells were disassembled, and both the SG and GDL were removed from the MEA. The ruptured regions of the membrane were identified by means of a helium gas leak test. The thickness changes of the membrane after durability cycling were analyzed by cross-sectional SEM. A field emission scanning electron microscope (FE-SEM) (SU-8020, Hitachi High-Technologies) was used to take SEM images with an accelerating voltage of 2 kV. The molecular weight of the SPP polymer was measured by use of an SEC system equipped with two TOSOH TSKgel α-M and α-3000 columns and a Shodex RI-71 refractive index detector. N,N-dimethylformamide (DMF) containing 0.05 M LiCl and 0.01% HCl was used as the eluent at a flow rate of 0.8 mL min⁻¹. The average molecular weight was calibrated with standard polystyrene samples. DMA measurements of the SPP membrane (5 × 30 mm) were conducted with an ITK DV A-225 dynamic viscoelastic analyzer. The measurements were conducted at the gauge length of 20 mm, strain amplitude of ~0.01 mm, which is 0.05% of the gauge length, and a frequency of 10 Hz. The humidity dependence of the storage modulus (E' (Pa)), loss modulus (E'' (Pa)), and tan δ at 80°C was tested at a humidification rate of 1% RH /min.

Table I. Separator flowfields of a single cell.

| Separator | Anode | Cathode |
|-----------|-------|---------|
| Channel   | Flowpath type | Width | Depth | Number of flowpaths | Number of turns | Land | Width |
|           | Serpentine | 1 mm  | 1 mm  | 2                  | 20              | 1 mm | 1 mm  |
|           | Serpentine | 1 mm  | 1 mm  | 6                  | 6               | 1 mm | 1 mm  |
in Table II. The in-plane dimensional change of the SPP membrane was approximately half that for the SPK membrane, and the through-plane dimensional change of the SPP membrane was relatively close to that of the SPK membrane. Unlike SPK, SPP does not include keto groups in the hydrophilic segments and thus forms a more rigid, linear structure than that of SPK. Consequently, the molecular motion of SPP is restricted, and the free volume between SPP polymer strands is likely to be smaller than that for SPK, resulting in lower water uptake. Thus, it was assumed that the membrane swelling and shrinking were restricted, and the SPP membrane exhibited lower in-plane dimensional change than the SPK membrane. As reported in previous works, the mechanical stress and irreversible deformation occurring during wet-dry cycles can be accelerated by the in-plane dimensional changes, especially under the compressed conditions in the cell. Hence, the SPP membrane can experience reduced degradation during wet-dry cycling due to the low in-plane dimensional change ratio.

**Cell performances of SPK membrane and SPP membrane.**—Fig. 3 shows the i-V curves and ohmic resistances of the cells utilizing SPK and SPP membranes under 80% C and 50% RH condition. Although the performances of the cells utilizing the HC membranes were lower than that for NRE211, the SPP membrane cell exhibited slightly higher performance than that for the SPK membrane in all current density regions. The ohmic resistance of the SPP membrane was slightly lower than that of the SPK membrane, due to the slightly higher proton conductivity of the SPP membrane under low humidity conditions.

**Durability evaluation by USDOE stress protocol.**—Fig. 4 shows the results of the USDOE durability cycling for each membrane. The results for SPK and Nafion-NRE211 have already been reported in the previous work. The initial \( H_2 \) crossover percentages for SPP, SPK and NRE211 were 0.01%, 0.02% and 0.24% respectively, indicating very low gas permeabilities for the HC membranes. In the SPP membrane, the \( H_2 \) crossover percentage remained less than 0.2% until 20,000 cycles and then gradually increased. The durability cycling was stopped at 27,000 cycles when the \( H_2 \) crossover percentages reached 2%, indicating clear membrane degradation. The SPP membrane exhibited more than 5-fold longer durability than the SPK membrane, and the durability met the USDOE target of 20,000 cycles for fuel cell vehicle usage, indicating that SPP is one of the more promising candidates for PEFC membranes.

**Post-test analysis of membrane mechanical properties.**—After the durability evaluation, the SPP membrane cell was disassembled, and the membrane degradation and mechanical properties were analyzed. Figs. 5a and 5b show photographic and schematic images of an MEA using an SPP membrane after durability cycling. A large crack in the membrane was observed in the top edge region of the electrode, and there were many small cracks observed around most of the edge region. The crack region of the membrane was the edge of the SG film, where the paper GDL overlapped the SG film, as shown in Fig. 5b. The region of the membrane degradation was the same as that for the SPK membrane observed in our previous work.

To investigate the crack regions in detail, the helium leakage was checked in 36 regions in the plane of the MEA (Fig. 5c). The arrow in Fig. 5c represents the same position of the arrow in Fig. 5a, and the outer periphery bars represent the amount of leakage in the near-SG edge region. Typically, the leakage rates were less than \( 1.0 \times 10^{-3} \) Pa m\(^3\)/s in the pristine membrane, while the rate increased to more than \( 1.0 \times 10^{-2} \) Pa m\(^3\)/s in the ruptured region of the deteriorated membrane. The leakage rates for the SPP membrane after durability cycling were increased in all regions. In particular, the membrane in the peripheral region of the electrode severely deteriorated and exhibited a much higher leakage rate, more than \( 1.0 \times 10^{-1} \) Pa m\(^3\)/s, indicating clear cracks. This result can be attributed to the fact that the cell fastening stress was concentrated in the peripheral region due to the uneven thickness of the MEA (Fig. 5b). The concentration of cell fastening stress in the SG edge region was also observed with pressure-sensitive paper (Fig. 5d); the red-colored regions indicated higher compression. The thickness in this region was relatively higher than that of other regions, because the GDL, using a hard paper, was located on the SG film. Furthermore, the degradation could be accelerated by membrane swelling and shrinking under wet-dry cycling.

Fig. 6 shows cross-sectional SEM images of the SPP membrane before and after durability cycling. Membrane cracks were observed at the SG edge in the peripheral region (Fig. 6d). The average thicknesses of the pristine membrane, post-test membrane in the electrode region, and post-test membrane in the peripheral region near the cracks were 27 \( \mu \)m, 25 \( \mu \)m, and 27 \( \mu \)m, respectively (Table III). As a previous study has reported, no severe thinning or creep of the membrane was observed.

The mechanical properties of the SPP membrane were analyzed by use of the tensile tester. The stress-strain curves of the SPP and SPK membrane were compared before and after durability cycling.
(Fig. 7). The tensile tests were conducted three times on the pristine membrane but only once on the membrane after the durability cycling due to the limitation of the sample size. The pristine SPP membrane exhibited higher stress and lower strain percentages than those for the SPK membrane at the rupture point. This is most likely due to the rigid chemical structure of SPP. After the durability evaluation of 27,000 cycles for the SPP membrane, the strain percentages at the rupture point were significantly decreased, and the degrees of decrease were different in each region. The rupture strain percentage in the electrode region, which was in contact with the paper GDL, retained about 50% of the value for the pristine membrane. On the other hand, the values in the peripheral region, which was in contact with the SG, decreased significantly, to less than 10% of the pristine value. The membrane rupture strain represents the degree of irreversible deformation. These trends were also observed in the SPK membrane, and the degradation mechanism of the SPP membrane was considered to be the same as that for the SPK membrane. It was assumed that the membrane in the peripheral region ruptured due to the stress concentration of the cell compressive force and the irreversible deformation of the membrane by swelling and shrinking during the wet-dry cycles. The humidity gradient between the electrode region and the peripheral region could accelerate the mechanical degradation at the SG edge. However, the durability of the SPP membrane was enhanced significantly, most

| SPP membrane       | Thickness (μm) |
|---------------------|----------------|
| pristine            | 27             |
| electrode region    | 25             |
| peripheral region   | 27             |

Table III. Average thickness of the pristine SPP membrane and the membrane in the electrode region and the peripheral region after durability cycling.

![Cross-sectional SEM images of (a) pristine SPP membrane; (b) membrane in the electrode region; (c) membrane in the peripheral region; (d) crack region of the membrane in the SG edge of the peripheral region after durability cycling.](image)

![Tensile strengths of the SPK membrane and SPP membrane in pristine form and in the electrode region and peripheral region after durability cycling.](image)
likely due to the higher mechanical strength and lower dimensional change in comparison with those of the SPK membrane, even though the fracture strain of the SPP membrane was lower than that of the SPK membrane. The tensile strength and elongation to break of the pristine NRE211 membrane were 23–28 MPa and 250–310% respectively. It was assumed that NRE211 exhibited higher durability than SPK due to the longer strain (Fig. 7) and lower dimensional change ratio (Table II) than SPK. Furthermore, the SPP membrane exhibited higher durability than NRE211 due to the higher stiffness of SPP.

**Post-test analysis of SPP polymer properties.**—The chemical state of the SPP polymer before and after the durability cycling was examined by use of SEC analysis. The SEC measurements were conducted twice on the membrane after durability cycling, and there were no significant differences (Table IV). The SEC curves, weight-averaged molecular weight ($M_w$) and number-averaged molecular weight ($M_n$) values for the SPP polymers are shown and listed in Fig. 8 and Table IV. In the electrode region after the durability cycling, the $M_w$ for the SPP polymer was higher than that of the pristine polymer. The increase in $M_w$ might be due to ionic cross-linkages between the SPP polymer chains, as also observed for the SPK polymer. On the other hand, $M_w$ in the peripheral region decreased significantly, by more than 70% from the pristine value, which could have been caused by structural changes of the SPP membrane, such as a morphological change of the hydrophobic/hydrophilic phase-separated structure, structural changes due to the ionic cross-linkage, and polymer chain breakage. It was assumed that the decrease of $M_w$ in the peripheral region could result in the decrease of the membrane stiffness, and the increase of the apparent $M_w$ in the electrode region due to ionic cross-linkage could not result in an increase in membrane stiffness because of the relatively weak bonding via sulfonic acid groups (Fig. 7). The IEC values of the SPP polymer, which were evaluated by $^1$H NMR (Table IV), decreased in the peripheral region, whereas there was negligible change in the electrode region. It was considered that not only the chain breakage of SPP polymer but also the hydrophilic segments were lost in the peripheral region due to their lower mechanical strength and higher dimensional change as a result of water uptake, as compared to the hydrophobic segments. In the TEM/EDX measurement, Si, which probably dissolved from the gasket, was detected at low levels in the peripheral region (data not shown), and, as shown by Zoppi et al., this could also make the membrane brittle and accelerate the mechanical degradation.

The DMA of the SPP membrane was carried out before and after the wet-dry cycling, and the humidity dependence of each membrane was compared (Fig. 9). In the pristine condition, both $E'$ (storage modulus) and $E''$ (loss modulus) values for the SPP membrane were higher than those for the SPK membrane. Furthermore, unlike the SPK membrane, the SPP membrane did not exhibit any peaks in $E''$ and $\delta (E''/E')$ that could be ascribed to a glass transition resulting from the humidity cycling. Even after the durability cycling, both $E'$ and $E''$ curves exhibited nearly the same behavior in each region. It is concluded that the SPP membrane was more durable during the wet-dry cycling than the SPK membrane, i.e., the wet-dry cycling durability was superior. After the DOE durability cycling, even though the strain of the SPP membrane decreased significantly, the modulus of the membrane did not change in either the electrode region or the peripheral region. It was assumed that the change of the membrane modulus could be difficult to show, because the membrane became very brittle and could rupture during the wet-dry cycling soon after the

### Table IV. $M_n$, $M_w$, and IEC of the SPP membrane in pristine form and in electrode region and peripheral region after durability cycling.

| SPP membrane | $M_n$ (kDa) | $M_w$ (n = 2) (kDa) | IEC (mmol/g) |
|--------------|------------|--------------------|--------------|
| pristine     | 7          | 161                | 2.31         |
| electrode    | 43         | 203 (203)          | 2.26         |
| peripheral   | 19         | 46.1 (46.3)        | 2.04         |

![Figure 8. SEC curves for the SPP polymer of the pristine membrane and the membrane in the electrode region and peripheral region after the durability cycling.](https://example.com/f8.png)

![Figure 9. DMA analyses of the SPK and SPP membranes before and after the durability cycling: (a) $E'$ (storage modulus), (b) $E''$ (loss modulus), and (c) $\delta$ at 80°C as a function of RH.](https://example.com/f9.png)
strain of the membrane reduced dramatically and the plastic region of the membrane was nearly completely lost, as in the peripheral region, as shown in Fig. 7.

The results of the degradation analyses indicated that the SPP membrane ruptured mechanically due to the concentration of cell fastening stress in the peripheral region and the membrane irreversible deformation occurring during wet-dry cycling. The strain of the SPP membrane in the peripheral region decreased significantly, and the membrane became brittle. Furthermore, both Mw and IEC values of the membrane were changed significantly after the cycling. It was assumed that the mechanical degradation of the SPP membrane could have been accelerated by morphological changes of the hydrophobic/hydrophilic phase-separated structure, ionic cross-linkages of the polymers, polymer chain-breakage, and the presence of contaminants. For further durability enhancement of the membrane, it is necessary to reduce the dimensional change ratio and to enhance the mechanical stiffness. The polymer structure should be modified to restrict the polymer swelling by cross-linking the polymers or introducing a core substrate as a reinforcement. In another approach, the mechanical stress of the membrane caused by cell compressive forces should be reduced by decreasing these forces or by using a soft GDL instead of the hard paper GDL in order to reduce the stress concentration of the membrane in the peripheral region.

Conclusions

The mechanical durability of the SPP membrane was evaluated by use of the USDOE wet-dry cycling protocol. The SPP membrane exhibited remarkable stability during the wet-dry cycling, lasting more than 20,000 cycles without mechanical failure, which was more than 5-fold longer durability than that for the SPK membrane. Due to the rigid structure of the SPK polymer and smaller free volume between SPK polymer strands, the SPP membrane exhibited 2-fold higher mechanical stiffness and 50% lower dimensional change ratio than those for the SPK and Nafion-NRE211 membranes. Furthermore, unlike the SPK membrane, the SPP membrane exhibited minor dependency of the storage Mw and moduli and tan δ. These mechanical properties were able to enhance the wet-dry cycling durability of the SPP membrane by reducing both irreversible deformation and mechanical stress that would have resulted from shrinking and swelling. However, in the post-test analyses, the SPP membrane ruptured in the peripheral region of the MEA, which was the same region as that for the SPK membrane. The SPP membrane maintained only 10% of elongation at break in the peripheral region but 50% in the electrode region, compared with the pristine condition, indicating the presence of mechanical degradation in the peripheral region. Furthermore, the Mw value of the SPP membrane decreased by ca. 70%, and IEC decreased by ca. 12% in the peripheral region, indicating structural change of the SPP polymer and elimination of sulfonic groups, respectively. The membrane was concluded to have undergone deterioration in the peripheral region most probably due to the stress concentration resulting from cell compression and membrane deformation during the wet-dry cycling.

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