# Ce-dope Effect of Crosslinked Membranes using Highly Sulfonated Polyphenylsulfone (PPSU) Ionomers

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Aiming to achieve carbon neutrality by 2050, research into $CO_2$ utilization for energy generation is gaining momentum. Furthermore, research into alternative materials is required due to PFAS (Per-and poly-fluoroalkyl substances) regulations. We are conducting research into the application of SPPSU (Sulfonated Polyphenylsulfone) ionomer electrolyte membranes as a non-fluorinated electrolyte with the aim of contributing to a carbon-neutral society [1]. SPPSU ionomers are used as electrolyte membranes for fuel cells, water electrolysis, RFBs, and electrolysis of organic and inorganic materials [1]. In this study, we prepared a crosslinked electrolyte membrane (CSPPSU: Crosslinked Sulfonated Polyphenylsulfone) using an ionomer with two sulfonic acid groups per PPSU unit (SPPSU(2S)), and report on the physical and chemical properties and fuel cell performance of the Ce-dope and Fenton test membranes. The synthesis of SPPSU(2S) ionomer and the membrane preparation process for the crosslinked membrane have been reported previously [1]. Ce-dope and Fenton test methods were also performed using references [2]. The stability of the CSPPSU membrane and the Ce-doped CSPPSU membrane was examined at 80°C for 2 h using a Fenton solution (3% $H_2O_2$ + 2 ppm Fe). Table 1 shows the results of the water uptake (WU, %), ion exchange capacity (IEC, meq/g), flexural modulus (Mpa) from stress-strain measurements, electrical conductivity, and fuel cell properties for the CSPPSU membrane, the Ce-doped CSPPSU membrane, and the Ce-doped CSPPSU membrane after the Fenton test. The membrane maintained its flexibility even after the Fenton test, confirming that Ce-doping improved the chemical stability of the CSPPSU membrane against the Fenton solution. Ce-doping increased the IEC and WU of the CSPPSU membrane, but its mechanical properties became slightly more rigid. Furthermore, conductivity measurements at 80°C and with varying relative humidity (RH) showed that Ce-doping of the CSPPSU membrane reduced its conductivity by approximately 13% compared to before Ce-doping. After the Fenton test, a further 39% decrease in conductivity was observed. Single fuel cell evaluation was performed using these membranes. Comparing the voltage and resistivity of the CSPPSU membrane, the Ce-doped CSPPSU membrane, and the Ce-doped CSPPSU membrane after the Fenton test at a cell temperature of 80°C, RH 100%, and a current density of 0.5 A/cm$^2$, the differences before and after Ce-doping were nearly identical. However, cell characteristics using membranes after the Fenton test showed a decrease in voltage and an increase in resistivity. These experimental results showed that Ce-doping of the CSPPSU membrane improved its resistance to Fenton.

Table 1. Properties of CSPPSU, Ce-doped CSPPSU, and Ce-doped CSPPSU membranes after Fenton test.

| CSPPSU membrane | | CSPPSU membrane | Ce-doped CSPPSU | Fenton tested Ce-doped CSPPSU |
|---|---|---|---|---|
| IEC (meq/g) | | 3.3 | 4.8 | 3.4 |
| $WU_{swell}$ (%) | | 74 | 229 | 345 |
| Flexural modulus (Mpa) | | 803 | 949 | 956 |
| Conductivity, (80°C, 80% RH, mS/cm) | | 31 | 27 | 19 |
| IV (80°C/80°C/80°C, 100% RH) at 0.5 A/cm$^2$ | Voltage (V) | 0.569 | 0.579 | 0.530 |
| | Resistivity (mohm cm$^2$) | 348 | 349 | 353 |

*Lab NR212 membrane measurement data; conductivity, 80°C, 80% RH: 31 mS/cm; single cell test, 80°C, 100% RH: 0.64 V, 245 mohm cm$^2$ at 0.5 A/cm$^2$.

Reference

[1] J. Kim, 25th Topical Meeting of the International Society of Electrochemisty, Toledo, Spain, 12 – 15/May, **2019**, Program book p. 13; J. Kim, 25th Topical Meeting of the International Society of Electrochemisty, Toledo, Spain, 12 – 15/May, **2019**, Program book p. 49; J. Kim etal., membranes, DOI: 10.3390/membranes10020031, **2020**, 10, 31-44; J. Kim, etal,; Japan patent no. 6548176, EU patent no. EP3340350, US patentno. US1086215; J.Kim, A. Ohira, membranes, DOI: 10.3390/membranes11050330, **2021**, 11, 330-342; J.Kim, etal, membranes, DOI: 10.3390/membranes11110861, **2021**, 11, 861-873; J. Kim, membranes, DOI: 10.3390/membranes14080173, **2024**, 14, 173-184; J. Kim, Key Engineering Materials, DOI: 10.4028/p-61Ktlv, **2025**, 1039, 47-52.

[2] H. Lee, et al; J. Power Source, **2015**, 295, 221 – 227.