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# Use of a sub-gasket and soft gas diffusion layer to mitigate mechanical degradation of a hydrocarbon membrane for polymer electrolyte fuel cells in wet-dry cycling



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#### HIGHLIGHTS

- Mechanical durability of the HC membranes was measured by the DOE wet-dry protocol.
- The membrane in the edge region of the MEA was ruptured due to stress concentration.
- Mechanical rupture strain of membrane was significantly reduced after 30,000 cycles.
- New MEA edge configuration reinforced by a sub-gasket and a soft GDL was developed.
- Mechanical durability was improved more than 100 times due to the reinforcements.

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#### G R A P H I C A L A B S T R A C T



#### ABSTRACT

The mechanical durability of hydrocarbon (HC) membranes, used for polymer electrolyte fuel cells (PEFCs), was evaluated by the United States Department of Energy (USDOE) stress protocol involving wetdry cycling, and the degradation mechanism is discussed. The HC membrane ruptured in the edge region of the membrane electrode assembly (MEA) after 300 cycles due to a concentration of the mechanical stress. Post-test analysis of stress-strain measurements revealed that the membrane mechanical strain decreased more than 80% in the edge region of the MEA and about 50% in the electrode region, compared with the pristine condition. Size exclusion chromatography (SEC) indicated that the average molecular weight of the HC polymer increased slightly, indicating some cross-linking, while the IEC decreased slightly, indicating ionomer degradation. As a result of two types of modifications, a sub-gasket (SG) and a soft gas diffusion layer (GDL) in the MEA edge region, the mechanical stress decreased, and the durability increased, the membrane lasting more than 30,000 cycles without mechanical failure.

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#### 1. Introduction

Polymer electrolyte fuel cells (PEFCs) have attracted much attention due to their expected application in residential cogeneration systems and automotive power sources, with the possibility of reducing CO<sub>2</sub> emissions. For the commercial use of these applications, it is essential to reduce the material and manufacturing costs of PEFCs and to guarantee long-term durability.

Hydrocarbon (HC) membranes are expected to be nextgeneration PEFC membrane alternatives to conventional perfluorinated membranes (e.g., Nafion), due to their low process cost, environmentally-friendly materials, flexible polymer modification, and low through-membrane gas permeability [1,2]. However, it is necessary to improve their proton conductivity, chemical durability and mechanical durability to the same levels as those for the perfluorinated membranes under practical fuel cell operating conditions.

To overcome these drawbacks, HC membranes have been developed intensively for many years. The polymer composition and morphology have been modified in order to maintain high proton conductivity, even under low humidity conditions. Recent progress has revealed that multiblock copolymers composed of sulfonated hydrophilic segments and hydrophobic segments show much enhanced proton conductivity [3]. The highly concentrated sulfonation in the hydrophilic segments of the multiblock poly (arylene ether)s resulted in proton conductivity comparable to that of the perfluorinated membranes, even under low humidity conditions [4–6].

The oxidative stability of the HC membrane is also a key issue for the chemical durability [7,8]. The introduction of electronwithdrawing sulfone or ketone groups as well as sulfonic acid groups into the hydrophilic parts improved the oxidative stability of the bulk membranes [9]. Recently, we have proposed a new HC membrane that is composed of a sulfonated polybenzophenone poly (arylene ether ketone) (SPK) copolymer (Fig. 1) [10]. This membrane showed higher radical tolerance and chemical durability than those of conventional HC membranes due to the introduction of chemically stable hydrophilic components into the polymer chain [11]. Even after a chemical durability evaluation for 980 h, the loss in molecular weight (Mw) of the SPK polymer was only ca. 6%, and the MEA maintained high performance due to a suppression of the specific adsorption of the membrane degradation products on the cathode catalyst.

It is also required for the membranes to have enhanced mechanical durability. Under practical fuel cell operating conditions, the membrane swells and shrinks repeatedly in the cell due to temperature and humidity cycles. These cycles cause mechanical stress of the membrane, which results in the irreversible deformation or rupture of the membrane [12]. In the literature, there have been few reports on the durability of HC membranes during humidity cycling [13,14]. To enhance the mechanical durability, HC membranes were modified to have higher mechanical strength, or they were reinforced with materials that had high mechanical strength characteristics [15–19]. Gross et al. prepared membranes consisting of sulfonated poly(arylene ether ketone) triblock copolymers with different morphologies and compared the RH cycle durability [20]. A block copolymer showed higher durability than that of a random copolymer, and a membrane with a low degree of lamellar orientation showed higher durability than that with highly oriented lamellae. MacKinnon et al. measured the RH cycle durability for both PFSA and HC membranes [21]. The PFSA membrane was more robust compared to the HC membranes, due to its lower modulus and higher elasticity. Mivatake et al. measured the mechanical durability of sulfonated polyimide (SPI) membranes by means of an evaluation method involving wet-dry cycles, similar to the United States Department of Energy (USDOE) protocol [22,23]. It was revealed that the membrane mechanical properties and gas impermeability deteriorated only slightly after 10,000 cycles, even though the membrane was hydrolyzed to a certain extent. In our work however, when the same cycle evaluation was conducted with an SPK membrane, the membrane ruptured mechanically less than 100 cycles. The membrane ruptured in the edge region of the membrane-electrode assembly (MEA), and thus it was concluded that there was specific membrane degradation in that region.

In the present work, the mechanical degradation mechanism of HC membranes and various strategies to enhance the mechanical durability, including reinforcing modifications, are discussed, focusing particularly on the edge configuration of the MEA. Three types of edge configurations of the MEA were prepared, and the effect on the durability during mechanical stress was evaluated for each. During the durability cycling, the mechanical degradation of the HC membranes was analyzed by monitoring the percentage of H<sub>2</sub> gas crossover through the membranes. In the post-test analysis, the membrane mechanical properties were analyzed by size exclusion chromatography (SEC). Based on these results, the mechanical degradation degradation degradation degradation mechanical degradation mechanical degradation mechanical degradation mechanical degradation mechanical degradation degradation mechanical degradation mechanical degradation de

#### 2. Experimental

#### 2.1. Membrane electrode assembly (MEA) configuration

The SPK membrane (ca. 30 µm thick) was prepared according to the method described previously [10]. The ion exchange capacity (IEC) of the SPK membrane was 1.59–1.84 meq g<sup>-1</sup>, as determined by titration. Carbon-supported Pt–Ru anode material and Pt–Co cathode catalyst, TEC61E54 and TEC36E52, respectively, were purchased from Tanaka Kikinzoku Kogyo. The catalyst slurry was prepared by mixing the catalyst, a perfluorosulfonated ionomer (equivalent weight = 909 g eq<sup>-1</sup>, Asahi Glass Co., Ltd.) (dry basis) solution, and solvents, which consisted of water and ethanol. Catalyst layers (CL) were made by spraying the slurry directly on the membrane. The Pt loadings of the anode and cathode were 0.3 mg cm<sup>-2</sup> and 0.6 mg cm<sup>-2</sup>, respectively. The geometric CL electrode area was 36 cm<sup>2</sup> (6 cm × 6 cm). The resulting catalystcoated membrane (CCM) was annealed at 160 °C for 5 min.

The MEAs were constructed by sandwiching the CCM between two gas diffusion layers (GDL) with microporous layers. Two types of GDL were used for the durability cycling. The first type was a conventional paper GDL (240  $\mu$ m, SGL-25BCH, SGL Carbon Group Co., Ltd.). The second was a soft-type GDL, which was prepared by the procedure described below.

According to work of Yamauchi and Tsuji [24,25], the soft GDL was prepared as follows. The GDL slurry was prepared by mixing



Fig. 1. Chemical structure of sulfonated polybenzophenone poly (arylene ether ketone) (SPK) block copolymer.

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