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Research Paper

Temperature and humidity effect on aging of silicone rubbers as sealing materials for proton exchange membrane fuel cell applications

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HIGHLIGHTS

- Aging of silicone rubbers with different hardness was investigated.
- Existed water molecules from humidified gases can accelerate the aging process.
- Silicone rubber with hardness of 40 is more suitable as sealing materials.
- Silicone rubbers can be used as sealing materials below 80 °C but not above 100 °C.

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ABSTRACT

Durability and reliability of seals around perimeter of each unit are critical to the lifetime of proton exchange membrane fuel cells. In this study, we investigate the aging of silicone rubbers with different hardness, often used as sealing materials for fuel cells, subjected to dry and humidified air at different temperatures. The aging properties are characterized by variation of permanent compression set value under compression, mechanical properties, and surface morphology as well. The results show that aging of silicone rubbers becomes more severe with the increase in subjected temperature. At temperature above 100 °C, silicone rubbers are not suitable for fuel cell applications. The existed water molecules from humidified gases can accelerate the aging of silicone rubbers. Among the tested samples, silicone rubber with hardness of 40 is more durable than that with hardness of 30 and 50 for fuel cells. The change of chemical structure after aging suggests that the aging of silicone rubbers mainly results from the chemical decomposition of cross-linker units for connection of polysiloxane backbones and of methyl groups attached to silicon atoms.

1. Introduction

Fuel cell, particularly proton exchange membrane fuel cell (PEMFC) that is an electrochemical device directly converting the chemical energy of a fuel into electricity has been considered as a promising alternative power sources to the depleting fossil energy sources because of its high energy density, zero-emission, quick start-up, and wide range of applicability including automotive and stationary applications [1]. However, the reliability of PEMFC is of great concerns toward its practical applications [2], as well as durability [3]. And both of them have attracted much attention from researches around the world [4].

Typically, a single fuel cell consists of membrane electrode assembly, gas diffusion layer, gaskets, and bipolar plates with flow channels for reactant gases. One PEMFC stack may contain several tens to even several hundreds of single cells, depending on the designed power of the stack. For each cell, gaskets made of elastomeric materials have to be applied around the perimeters to prevent the leaching of reactant gases from the active area [5]. In addition, the sealing materials may have great impacts on the oxygen permeation fluxes of oxygen permeating membranes. Experimental study of three different types of dense oxygen permeating membranes with typical electronic conductivity was conducted by Chen et al. [6]. If the sealing material degrades during fuel cell operation, the leakage of reactant gases can not only affect

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the overall performance of fuel cells and the utilization of fuel gases, but also may cause the danger of burning from the mixture of hydrogen and oxygen (air). Thus, the stability and reliability of sealing materials are critical to fuel cell applications.

With the state-of-the-art of PEMFC technology, humidified gases are generally required to ensure the effective proton conduction through the electrolyte membranes [7]. Although the operating temperature is typically in the range of 60–80 °C, PEMFC may also be stored in very low temperature to −40 °C, depending on the region of fuel cells used. Graiver et al. [8] studied the fate and effects of silicones used as sealing materials for PEMFC in different environment conditions. In addition, sealing materials for PEMFCs should be reliable and durable under compressed conditions during both storage and operation of fuel cells throughout the entire life of designed fuel cells [9].

Silicone rubbers have extensively used as sealing materials in PEMFCs because of their clear advantages over other materials [10]. These advantages include low cost, good mechanical properties, wide temperature ranges for application as well as easy manufacturing process. Cleghorn et al. [11] conducted a 3-year continuous operation test to study the overall performance of PEMFC, and they found that the silicone was typically reduced by approximately 25 μm. A comparison analysis of the characteristics of surface wettability, hydrophobicity and recovery ability between EPDM rubber and silicone rubber as sealing materials in PEMFC was conducted with experimental study. These experiments ranged from contact angle, surface hydrophobicity to equilibrium state [12]. A kind of modified silicone rubber was presented and used as high voltage outdoor insulators, and the modified silicone rubber showed excellent performance compared with traditional silicone rubber [13]. The gas sealability of silicone rubber as the adhesive between the anode bipolar plate and the membrane assembly was investigated by Ehsani et al. [14]. From these experimental measurements, the presented development of the silicone adhesive bonded anode bipolar plate/membrane assembly unit showed very good sealing performance of the designed air breathing PEMFC stack.

Variation of chemical and mechanical properties of silicone rubbers subjected to different environments has been studied and reported by different research groups in the world [15]. Wu et al. [16] introduced platinum catalyst and nitrogen-containing silane to improve the thermal stability of silicone rubber. The synergistic effect and mechanism were also analyzed. Cui et al. [17] used a prony series to predict the compression stress performance at different strain levels. The temperature superposition accumulated with time was studied, and a master curves was generated to predict the service life of this sealing material used in PEMFCs. The estimated lives in water and in air were also compared. Mechanical properties were well investigated with both experimental test and simulation study in the work presented by Lin et al. [18]. The influence of thermal effect on the mechanical properties of silicone rubbers was experimentally studied by Chagnon et al. [19]. The mechanical behaviors of filled and unfilled silicone rubbers were both investigated in their study. The mechanical ageing of filled silicone rubbers was also study by Zakaria et al. [20]. Acid–aging characteristics and chemical degradation were studied by Kim et al. [21]. Chemical degradation and aging mechanisms were conclude from a simulated and three accelerated PEMFC environments [22]. Similar work was also conducted by another research group [23]. The results showed that the main mechanism of degradation was acid hydrolysis. Through systematic studies on degradation of silicone rubbers exposed in different solutions, Chao and coworkers revealed that silicone rubbers degraded in acidic solutions by chemical decomposition of silicon based backbone and leaching of fillers [24]. The effect of water on life prediction of liquid silicone rubber seals was also investigated by their group [25], as well as pressure and periodic variation of temperature [26]. Schulze et al. [27] observed the release of small particles from silicone rubbers after operation of an assembled fuel cell, which in turn affects the proton conduction through membrane and the overall cell performance. However, most of literature works focused on the degradation or aging of silicone rubbers subjected to aqueous solutions at temperatures simulated fuel cell operation.

We have recently shown the degradation of silicone rubbers with different hardness subjected to the simulated solution of fuel cells [28] and subjected into the cathode outlet solutions [29]. As one of the series of paper related to the degradation of silicone rubbers as sealing materials for fuel cells, in this study, degradation of silicone rubbers with different hardness subjected to different humidified air at different temperatures was investigated. Considering the elastic properties required for practical fuel cells, three silicone rubbers with Shore hardness of 30, 40, and 50 were selected. It turns out that aging of silicone rubbers is more severe with the increase in temperature and silicone rubbers are not suitable as seals for PEMFC operated above 80 °C. The existed water molecules from humidified gases can significantly accelerate the degradation of silicones rubbers. The results revealed that silicone rubber with hardness of 40 is more suitable for PEMFC applications than silicone rubbers with hardness of 30 or 50. The results described here may provide guidance for evaluation or selection of silicone rubbers as seals for PEMFC applications.

2. Experimental

Methylvinyl silicon rubbers with hardness of 30, 40, 50 (Shore A) used in this study have thickness of 0.5 mm and were purchased from Forlong Silicone Rubber Products Co. Ltd. (China). Water used for humidifying air was deionized through a Milli-Q system (Barnsted Nanopore, resistivity = 18.0 MΩ cm^{-1}). Prior to aging tests, silicone rubbers were flushed with de-ionized water to clean the surface. In general, the aging tests were carried out in a testing chamber (GDJS-150, Wuxi Zhuocheng Instrument Co. China) with controllable temperature and relative humidity.

The permanent compression set value (*PCSV*) was calculated based on variation of thickness before and after compression. The compression experiments were carried out using a homemade setup. Silicone rubbers were cut to 10 mm × 10 mm pieces. The test sample was placed in the compression setup and the compression ratio was kept at 25%. The whole setup was then placed in the testing chambering at preset temperature and relative humidity. After desired period of time, the setup was taken out from the chamber and the sample was released from the setup. The tested silicone rubber was then kept in air for 30 min to ensure spring back thoroughly before determining the final thickness. Each measurement was repeated three times and the mean value of final thickness was used for calculation of *PCSV*.

Mechanical property of silicone rubbers were tested at room temperature using an Electromechanical Universal Testing Machine (WDW-1C, Shanghai Hualong Co., China). Samples with 10 mm in width and 40 mm in length were measured at a strain rate of 50 mm per minute at room temperature before and after aging tests. Surface morphology of silicone rubbers before and after aging in desired conditions was examined using scanning electron microscopy (SEM, JEOL JSM-5610LV, Japan). Fourier transform infrared spectra (FTIR, Bio-Rad FTS 300, US) were recorded with a resolution of 4 cm^{-1} to investigate the chemical degradation of silicone rubbers.

3. Results and discussion

One principal parameter to evaluate the sealing properties of elastomeric material is the permanent compression set value