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Degradation of silicone rubbers with different hardness in various aqueous solutions

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ABSTRACT

Durability is one of the remaining challenges for practical application of proton exchange membrane fuel cells. Seals or gaskets around perimeters of each cell in a fuel cell stack are important to prevent leakage of reactant gases, avoiding the decay in utilization of gases and in overall cell performance. In this study, degradation of silicone rubbers, often used as sealing material in fuel cells, with different hardness in various aqueous solutions is investigated. Although the weight loss increases with the increase in hardness, the durability seems enhanced with the increase in hardness, as revealed by the variation of surface morphology and mechanical properties of silicone rubbers before and after exposure to acidic aqueous solutions. It also turns out that the degradation of silicone rubbers can be catalyzed by protons, leading to severe corrosion of materials in strong acidic environment. The results described in this study may provide guidance to evaluation or selection of silicone rubbers as seals for PEMFC applications.

1. Introduction

As concerns mount on limited energy sources and ecological challenges, it is essential to develop alternative, renewable, and environmentally friendly sources of energy to meet the changing and growing global energy demands. Fuel cell, particularly proton exchange membrane fuel cell (PEMFC) that is an electrochemical device directly converting the chemical energy of a fuel into electricity, emerges as a promising alternative to the depleting fossil energy sources due to its green nature, high energy density, and wide range of applicability including automotive and stationary application [1,2]. Nonetheless, the durability of PEMFC remains a major challenge towards its commercial viability and has attracted great attention from researchers worldwide [3,4].

PEMFC stack is assembled by connecting each single cell in series, which consists of membrane electrode assembly, gas diffusion layer, gaskets, and bipolar plates with flow channels for reactant gases. In general, one PEMFC stack contains several tens to even several hundreds of single cells, depending on the designed power of the stack. For each cell, gaskets or seals have to be used around the perimeters to prevent the leakage of reactant gases from the active area. If any seal or sealing material degrades during fuel cell operation, a leakage leading to mixture of reactant gases can occur. This will not only affect the performance of fuel cells and the utilization of fuel gases, but may also bring the danger of burning from the mixture of hydrogen and oxygen (air). Thus, the stability and durability of sealing materials are of great importance for fuel cell applications.

Considering the operation conditions and key materials of a typical PEMFC, the seals are often exposed to acidic aqueous solution, humid air, mechanical stress, and elevated temperatures (65–80 °C) as well. In addition, if small ions leach out of the sealing materials, they can migrate to the surface of polymer electrolyte membrane or catalyst and affect the proton conductivity or catalytic activity respectively. Therefore, sealing materials for PEMFC applications should be stable and durable during the operation of fuel cells throughout the entire life of designed fuel cells [5–7].

Although the suitable sealing materials in PEMFC strongly depend on the conditions for stack assembly and operation conditions of the stack, It is generally realized that the hardness (Shore A) of sealing materials in the range of 20–60 is suitable for PEMFC application [8]. Silicone rubbers have attracted much attention as

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sealing materials in PEMFCs because of their low cost, good mechanical properties, wide temperature ranges for application as well as easy manufacturing process [9–14]. Extensive studies have been conducted on the variation of chemical and mechanical properties of silicone rubbers while exposed to different environments [15–25]. As sealing material for PEMFC applications, Chao and co-workers have systematically studied the degradation behavior of silicone rubbers exposed to solutions simulating fuel cell environment and accelerated durability test solutions [26–32]. They found that silicone rubbers corrode severely with the increase in acidity of exposed solutions and the degradation of silicone rubbers was attributed to both chemical decomposition of silicon based backbone and leaching of fillers. Schulze et al. observed that small particles were released from silicone rubbers after operation of an assembled fuel cell [33]. The released small particles could further migrate to the surface of membrane at anode side and migrate to interface of gas diffusion layer and catalyst layer, leading to the decay of the overall fuel cell performance. Generally, most of the works reported in literature are focused on the degradation mechanism of silicone rubbers under different conditions or the comparison of silicone rubbers with other elastic materials. However, the degradation of silicone rubbers with different hardness has not been reported.

In this study, degradation of silicone rubbers with different hardness exposed to various aqueous solutions was investigated. Considering the elastic properties required for practical fuel cell applications [8], three silicone rubbers with Shore hardness of 30, 40, and 50 were selected. It turned out that the degradation of silicone rubbers could result in weight loss and voids or cracks on the surface of tested materials because of the chemical decomposition of silicon based backbone and leaching of fillers. With the increase in hardness, silicone rubbers became more durable in tested aqueous solutions. The results described here may provide guidance for evaluation or selection of silicone rubbers as seals for PEMFC applications.

2. Experimental

Methylvinyl silicone rubbers with hardness of 30, 40, 50 (Shore A) used in this study have thickness of 0.5 mm and were purchased from For long Silicone Rubber Products Co. Ltd (China). Reagent grade acetic acid, sulfuric acid (98%), and hydrofluoric acid (48%) were received from Sinopharm Chemical Reagent Co. Ltd (China). Water was de-ionized through a Milli-Q system (Barnsted Nanopore, resistivity = 18.0 MΩ cm^{-1}). Prior to degradation tests, silicone rubbers were flushed with de-ionized water to clean the surface.

Aqueous solution to simulate the operation environment of proton exchange membrane fuel cells (denoted as simulated solution) consists of 98% H_2SO_4 and 48% HF diluted in de-ionized water. The final composition was 12 ppm H_2SO_4, 1.8 ppm HF, and de-ionized water. The pH value of this simulated solution was 3.35, that is close to the fuel cell environment [34]. The strong acid solution used in this study also consists of 98% H_2SO_4 and 48% HF diluted in de-ionized water. The final composition is 1.0 M H_2SO_4, 1.8 ppm HF, and de-ionized water. An acetic acid solution with pH of 5.0 was employed as weak acid.

All the tested specimens have square-shape with dimensions of 7.0 cm in both length and width. The samples were submerged into solutions in different containers placed in an oven for degradation test. Since the typical PEMFC is operated at temperature range of 65–80 °C, degradation tests of silicone rubbers were carried out at 80 °C. The degraded samples were taken out after a specific time period and thoroughly rinsed with de-ionized water and dried in air for further analysis. The overall exposure time was 15 days for samples exposed to strong acid solution and 30 days for other aqueous solutions.

The weight of samples was measured using electronic balance (Mark MW3, Boyue Instrument Co.) with resolution of 1.0 mg. The contents of silicon and calcium in aged solution were determined on Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, Optima 5300DV, Pekin–Elmer). The wavelength is in the range of 165–782 nm with a resolution of 0.006 nm. Mechanical property of silicone rubbers were tested at room temperature using an Electromechanical Universal Testing Machine (WDW-1C, Shanghai Hualong Co., China). Samples were measured at a strain rate of 50 mm per minute. Fourier transform infrared spectra (FTIR, Bio-Rad FTS 300) were recorded with a resolution of 4 cm^{-1} to investigate the chemical degradation of silicone rubbers. Surface morphology of silicone rubbers before and after degradation in desired solutions was examined using scanning electron microscopy (SEM, JEOL JSM-5610LV).

3. Results and discussion

After exposure to desired solutions, the percentage of weight loss of the tested sample, defined as the ratio of weight change before and after degradation test to the initial weight of the tested samples, was first investigated. Fig. 1a displays the percentage of weight loss of silicone rubbers with different hardness as a function of exposure time in simulated solution. It can be clearly seen that all the tested samples gradually lost weight with the increase in exposure time in simulated solution. Furthermore, with the increase in the hardness of silicone rubbers, the weight loss becomes more significant. As can be seen from Fig 1a, after exposure to simulated solution for 30 days, the weight loss for materials with hardness of 30 is about 0.98% whereas it is about 1.8% for materials with hardness of 50. Since the environment during PEMFC operation is acidic, the weight loss of silicone rubber with hardness of 40 was also investigated in different acidic conditions, as shown in Fig 1b. It is apparent that the weight loss of the tested material increased with the increase in acidity of the exposed solution, reaching 2.1% in strong acid solution even within 15 days. However, even when exposed in de-ionized water, the tested material also lost weight after a certain period of time. Typically, fillers including silicon dioxide and calcium carbonate are often impregnated into silicone rubbers to improve their mechanical properties. While exposed to aqueous solution, the polysiloxane backbone of silicon rubbers swells up and causes the fillers to leach out, leading to the weight loss of the tested materials. In addition, the existence of F^- in both simulated and strong acid solutions could also result in the chemical decomposition of silicone rubbers under acidic environment. Thus, the weight loss in strong acid aqueous solution is more pronounced.

As the leaching of fillers from silicone rubber is closely related to the swelling of the silicone rubber, the volume expansion properties of silicone rubbers in different aqueous solutions were further investigated. Fig 2a displays the volume expansion ratio, defined as the ratio of volume change before and after exposure in solution to the initial dry volume of tested samples, as a function of exposure time in simulated solutions. Clearly, after 30 days of exposure to simulated solution, all the tested silicone rubbers swelled, reaching the volume expansion percentages of 18.3%, 17.7%, and 16.0% for silicone rubbers with hardness of 30, 40, and 50, respectively. The swelling of silicone rubbers indicates that the fillers in silicone rubbers can leach out from the bulk materials, resulting in the weight loss of tested materials. Although the swelling degree of silicone rubber with hardness of 50 is the lowest one due to the high density of cross-linking, the highest weight loss value for the sample with hardness of 50, as described in the above paragraph,