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Compact and flexible hydrocarbon polymer sensor for sensing humidity in confined spaces

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ARTICLE INFO

Article history:
Received 9 June 2014
Received in revised form
8 October 2014
Accepted 19 October 2014
Available online 7 November 2014

Keywords:
Sulfonation
Ion conduction
FTIR
DMA
Humidity sensor
Fuel cells

ABSTRACT

Hydrophilic polymers generally respond reversibly to changes in humidity and hence can behave as humidity sensors. A hydrocarbon based polymer, Sulfonated Poly (ether ether ketone) (SPEEK) has been investigated as humidity sensor. Sensors of size 2 mm × 4 mm with inter-digitated gold electrodes were fabricated using photolithography technique. The resistance change was noted at varying relative humidity in a humidity chamber. The polymeric membrane was characterized using Fourier Transform Infrared Spectroscopy for the functional groups and with a Dynamic Mechanical Analysis for flexibility. The sensor showed a fast response time of approximately 20 s. Low hysteresis, good cyclability and repeatability were observed for the sensor. As an application to test in confined spaces the sensor was placed inside narrow proton exchange membrane fuel cell gas flow fields for humidity mapping of the cathode plates while operating the cell. For a fuel cell operating at 50 °C with dry and humidified fuel gas (dry oxidant) the sensor placed at the centre of the cathode shows an RH of 30–40% and 60–90% respectively at different current densities.

Introduction

Humidity sensors are important for environmental monitoring of humidity and are used in fuel cells, food quality and storage, meteorological studies, air conditioning systems, for feedback control in household electrical appliances such as drying machines and microwave ovens. These sensors are of varied types made from various polymers, ceramics, metal oxides, etc. [1–3]. Parameters that are generally monitored to measure the humidity of the environment include changes in resistance/capacitance/optical sensing of the material of the sensor. Humidity sensors based on solid polymer electrolytes offer many advantages such as long-term stability, reliability, ease of processing and low fabrication cost [4]. Polymers like polyimide, polystyrene, perflourosulfonate ionomer like Nafion, poly vinyl alcohol, poly ethylene oxide, and polyaniline have been used as sensing material in humidity sensors [5,6].

Sulfonation is a powerful and versatile process, which can be used to simultaneously render polymers proton conductive and hydrophilic in nature [7]. Few sulfonated polymers used for sensing moisture are polyimide, polystyrene and poly ether ether ketone [8]. Nafion series of polymers show good water uptake properties and can fit well as sensors [9]. However, they have not been practically used as humidity sensor, probably because of their poor adhesion on a sensor substrate, resulting in the poor durability [10] and also few random

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http://dx.doi.org/10.1016/j.ijhydene.2014.10.085

experiments reveal excess swelling of Nafion under humid conditions. Sulfonated polyimide has also been found to show changes in resistance with humidity. Ueda et al. [10] found that sulphonated polyimide based sensors showed excellent durability against water, humidity, heat, etc. These sensors also had a fast response time of 1 min for humidification from 30% to 90% and a relatively slow response time for the dehumidification cycle.

Polyether ether ketone (PEEK) is semi-crystalline and possesses high thermal stability. It can withstand temperatures up to 200 °C. It possesses good toughness, chemical resistance, mechanical properties and film forming capabilities [11,12]. PEEK is hydrolysis resistant, so sulfonation provides the moisture sensing ability to the polymer. The good dimensional stability and sulfonation of the polymer makes it a strong candidate as humidity sensor. In the present study, PEEK was sulfonated and a sensor based on this material was developed for humidity sensing in confined spaces especially for fuel cell applications.

Humidity measurements in fuel cells are important as (i). Membrane conductivity and hence performance is dependent on the state of hydration of the membrane, (ii). Humidity measurements help in analyzing the state of humidity of the cells after a long shut down or start up (iii). Particular dry spots in the membrane, which are one of the reasons for membrane degradation, can be identified by humidity mapping of the cell according to which the gas flow field design could be optimized.

Most of the study on humidity measurement in fuel cells is based on the average value obtained by monitoring the humidity at the inlet and outlet of the cells. Very few attempts have been made to study the humidity at any particular point in the fuel cell. Placing sensors inside a fuel cell flow field is a challenging task. Hinds et al. [13] have attempted to place a metal-oxide based humidity sensor in various points in a fuel cell by drilling extra grooves in the flow field. Using this technique they observed that the anode gas humidity increased considerably due to back diffusion of water from the cathode. Lee et al. [14] fabricated humidity sensor for *in-situ* fuel cell application by using a polyimide based sensor hot pressed onto the membrane itself. They found that the optimal performance of the fuel cell was obtained at 50 °C, 75% humidity and 50 ml/min flow rate for the reactant gases. In the present work, attempts have been made to measure the humidity at the centre of the flow field plate to understand the spot humidity due to electro-osmotic drag and back diffusion when the fuel cell is operated with dry gases and when one of the inlet gases have been humidified. The objective has been achieved by placing a low cost sensor based on sulphonated poly (ether ether ketone) at the centre of the oxidant gas flow fields along the grooves of a fuel cell to measure the relative humidity inside.

Experimental

Sulfonation process of PEEK

PEEK (Gatone) was purchased from Gharda Chemicals Ltd., (Mumbai), India. Concentrated sulfuric acid (*E. Merck*) was used as sulfonating agent. The polymer was stirred in the sulfonating agent for 20 h in a round bottomed flask at ambient conditions of air atmosphere and 30 °C. The sulfonated polymer was recovered by precipitating the solution in ice cold de-ionized water. The precipitate was repeatedly washed in de-ionized water to remove the excess acids. SPEEK obtained was dried at 50 °C, dissolved in Dimethyl Formamide (DMF) and cast as membrane (of thickness 0.1 mm). The membrane was dried at around 50 °C–70 °C for few hours in vacuum. The dried membrane was soaked in 0.5 M H_2SO_4 for 1hr to remove DMF and washed with water and dried again [15,16]. Fig. 1 shows the chemical structure of SPEEK.

Characterization of SPEEK

Ion exchange capacity and degree of sulfonation

The titration technique was used to determine the IEC of the membranes. Firstly, the membranes in the acid form (H^+) were converted to the sodium form by immersing the membranes in a 1 M NaCl solution for 24 h to exchange the H^+ ions with Na^+ ions. Then, the exchanged H^+ ion in the solution was titrated with a 0.01 N NaOH solution. The Degree of Sulfonation (DS %) was calculated from the IEC obtained and the molecular weights of PEEK and SPEEK monomers [17,18].

$$DS = (IEC/1000)/((1 - M_{SPEEK} \times IEC/1000)/M_{PEEK} + IEC/1000) \quad (1)$$

where M_{PEEK} and M_{SPEEK} denote the molecular weights of PEEK and SPEEK respectively.

Water swelling

To measure the weight differences between the fully-hydrated polymer and the dry polymer, the polymer was immersed in distilled water for 24 h at 30 °C till it attained equilibrium, and after quickly dry-wiping the surface of the polymer to remove excess water, it was weighed as M_{wet}. The polymer was then dried at 100 °C for a few hours and the weight M_{dry} was determined (by weighing the polymer to constant mass). The water swelling (*WS* %) of the polymer was calculated using the formula:

$$WS\% = (M_{wet} - M_{dry})/M_{dry} * 100 \quad (2)$$

Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of film samples were obtained from Perkin Elmer Spectrum One FTIR Spectrometer in order to identify and

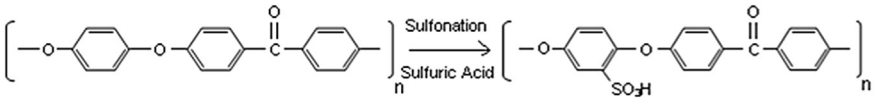

Fig. 1 – PEEK sulfonation reaction.