

Surface Energy and Water Sorption Characterization of Fuel Cell Components at Different Relative Humidity Conditions

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Introduction

Proton exchange membrane fuel cells (PEMFC) are an expanding area of research for use as low pollution power generators. The relative humidity (RH) of the feed stream is a critical parameter affecting PEMFC performance. If the hydration level is too low, the polymers exhibit greatly reduced ionic conductivity [1] and proton transport will be insufficient. Alternatively, if the hydration level is too high, excess water can flood the pores in the Gas Diffusion Layers (GDLs) and catalyst layers, eventually leading to blockage of reaction sites or reactant transport impediments within the electrode structure [2,3]. Therefore, characterizing thermodynamic properties of wetting, such as internal surface energy, over a range of RHs is vital to the successful development of PEMFC components.

Surface energy determines the wetting affinity of liquid water for both the membrane, as related to electro-osmotic drag and back diffusion of water, and GDL, as related to water removal and retention from a fuel cell. These wetting phenomena occur on a nanometer scale for the membrane and are controlled by the type and extent of anionic chemistry (i.e. sulfonate or phosphonate groups) of the polymer side chains. As for GDL wetting, it occurs mainly on a micrometer (substrate) to sub-micrometer (bilayer coating) scale and may vary widely depending on whether water is wetting externally (from catalyst layer to GDL or visa versa) or internally (along a network of pores formed by the carbon fibers). In addition, GDLs are treated with a hydrophobic fluoropolymer (PTFE or FEP) to create a dual wetting characteristic of hydrophobic and hydrophilic regions for the internal pore surface. The proper balance of hydrophobic and hydrophilic regions, for both the GDL and membrane, must be maintained throughout the life of the PEMFC.

Materials and Methods

This study investigates the surface energies of proton exchange membranes and GDLs using Inverse Gas Chromatography (IGC) and water sorption properties using Dynamic Vapor Sorption (DVS). IGC is a well-known tool for the characterization of particulates, fibers, and films. A detailed explanation of the theory is given in Reference [Error! Bookmark not defined.]. The surface energies of two different proton exchange membranes, Nafion 1135 and BPSH-30, and three different GDLs (same fiber substrate with different hydrophobic treatments) were measured at

DVS is a well-established method for the determination of vapor sorption isotherms. The DVS instrument used for these studies measures the uptake and loss of vapor gravimetrically using the SMS Ultrabalance with a mass resolution of at least $\pm 0.1 \mu\text{g}$. The water vapor sorption properties were measured on the two PEM and three GDL samples between 0 and 95% RH at 25 °C.

Results and Discussion

As the humidity was increased, the dispersive surface energy of the two proton exchange membranes decreased (29.5 mJ/m² at 10% RH to 23.0 mJ/m² at 90% RH for the BPSH-30 sample; 29.1 mJ/m² at 10% RH to 27.7 mJ/m² at 90% RH for the Nafion 1135 sample), suggesting that preferential wetting of the hydrophilic side chains occurred. In contrast, the specific surface energies of the membranes increased with increasing humidity (5.3 mJ/m² at 10% RH to 15.3 mJ/m² at 90% RH for the BPSH-30 sample; 14.3 mJ/m² at 10% RH to 22.4 mJ/m² at 90% RH for the Nafion sample). DVS studies show the membranes sorb significantly more water as the humidity increases (over 13% change in mass). The relatively high mass increases indicate water uptake is dominated by bulk water absorption. Coupled with the changes in surface energy with humidity, the high water uptakes indicate the membranes' properties are greatly affected by the amount of water vapor present.

Similar surface energy experiments were performed for three GDLs at the same conditions. The GDLs contained the same fiber type (Toray TGP-H 060 substrate) with different hydrophobic treatments: "plain" (no PTFE, no bilayer), "BA" (5 wt% PTFE substrate, no bilayer), and "bilayer" (5/23 wt% PTFE substrate/bilayer). For all three GDL samples the dispersive surface energy decreases with increasing humidity. For the specific surface energies, the trends are more complex. While the BA GDL shows an increase in specific surface energy with increasing humidity, the Plain and Bilayer samples generally decrease with increasing humidity. The decrease in specific surface energies may be due to competitive adsorption between water on the surface and the IGC probe molecules. Water molecules may be preferentially adsorbing to higher energy sites, leaving lower energy areas exposed to the probe molecules. The water sorption isotherms indicate the surfaces are much more hydrophobic than the membranes. The two membranes (BPSH-30 and Nafion 1135) uptake over 14% of their weight in water, while the GDL samples sorb less than 0.12% of their dry weights in water.

Significance

Surface energies and water uptakes were measured for several membranes and GDLs over a range of RHs. For the proton exchange membranes, the dispersive surface energy decreased, while the specific free energies increased, with increasing humidification. For the GDL samples, the dispersive surface energy decreased as the humidity increased. The humidity effects on the GDL specific surface energies were more complex: the Plain and Bilayer samples specific surface energies decreased, while the BA specific surface energy increased from 10 to 90% RH. Similar experiments could be applied to other fuel cell components (PEM, GDL, catalysts, etc.) over a wide range of temperature and humidity conditions.

References

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