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Atomic Force Microscopy on Cross Sections of Fuel Cell Membranes, Electrodes, and Membrane Electrode Assemblies



Renate Hiesgen^{a,1,*}, Tobias Morawietz^a, Michael Handl^a, Martina Corasaniti^b,
K.Andreas Friedrich^{c,1}

^a University of Applied Sciences Esslingen, Kanalstrasse 33, Esslingen 73728, Germany

^b Solvay Specialty Polymers Italy S.p.A., Viale Lombardia, 20, 20021 Bollate (Mi), Italy

^c German Aerospace Center, Institute of Technical Thermodynamics, Pfaffenwaldring 38-40, Stuttgart 70569, Germany

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ABSTRACT

Using material-sensitive and conductive atomic force microscopy (AFM) on cross sections of perfluorinated and sulfonated membranes at low humidity, crystalline polymer lamellae were imaged and their thickness determined to approximately 6 nm. In the capacitive current, water-rich and water-poor areas with different phase structures were investigated. The formation of a local electrochemical double layer within the water-rich ionically conductive areas at the contact of the AFM tip with the electrolyte enabled their visibility. The large water-filled ionically conductive areas include numerous ionic domains. Under equilibrium conditions, these areas are spherical (appearing circular in the images) and with distinct size distribution. Forcing a current through the membranes (current-induced activation) led to merging of the water-filled ionically conductive areas in the voltage direction and resulted in an anisotropic ionically conducting network with flat channels. The distribution of the current in the membrane and catalytic layers of a pristine membrane electrode assembly (MEA) was analyzed. From the adhesion force mappings, an inhomogeneous distribution of ionomer in the catalytic layer was detected. Cross currents between Pt/C particles through large ionomer particles within the catalytic layer were detected and the ionomer content across an electrode was evaluated.

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1. Introduction

For polymer membrane fuel cell application mostly Nafion[®] from DuPont is used as electrolyte, but recently the importance of related materials such as AQUIVION[®] is increasing. The two ionomer materials were used as membranes and as ionically conductive components within the electrode. Nafion[®] and AQUIVION[®] are both perfluorinated polymers with sulfonated end groups at their side chains (PFSA). These materials differ in the length of their side chains, which leads to somewhat different properties based on the different nanostructures [1],[2]. Together with water, these molecules undergo a phase separation upon solidification; the sulfonated end groups cluster together to form a hydrophilic ionic phase, which is the basis of a continuous ionically conductive network. The polymer main chains also cluster

together to form bundles with a size of a few nanometers [3] and provide mechanical strength. Approximately 20% of the fluorocarbon chains are crystalline [4], thus contributing to the mechanical strength. The size of ionic phase structures has been intensively studied using scattering techniques such as small angle X-ray scattering (SAXS). A strong effect on the water content and pretreatment is generally observed, monitored by the shift of the generally broad peaks, mainly the so-called ionic peak. SAXS results indicate a value of 3 to 7 nm, which is attributed to the distance of the ionic areas [5]. Nanostructure models that fit the measured spectra for a wide range of humidity and temperature values exist; however, no consensus has been reached on the precise nanostructure.

Due to the high sensitivity of PFSA toward humidity changes, the structure determination is highly complex and controversial results have been published. It has to be noted that changes occur with time constants that comprise several orders of magnitude [6]. In addition, the structure under equilibrium and the structure under non-equilibrium conditions, such as the current flow, may differ greatly. The protons that carry the ionic current are solvated,

* Corresponding author.

E-mail address: renate.hiesgen@hs-esslingen.de (R. Hiesgen).

¹ ISE member

and depending on the conditions, one proton drags an average of 1–3 water molecules during fuel cell operation (electro-osmotic drag and permeation, see [7] and values therein). In addition, the current water exerts a mechanical pressure on the polymer.

Despite the self-assembly of the two different phases, the hydrophilic and the hydrophobic phase are a prerequisite for the formation of a continuous ionically conducting network; it may not exist in pristine PFSA, at least at lower humidity. In a previous study it was demonstrated that for the induction of a faradaic current a forced current flow was necessary, called the current-induced activation of the membrane [8]. Investigation of the PFSA structure is therefore assumed to yield different resulting nanostructures depending whether equilibrated samples or samples under or after current flow, as necessary for fuel cell operation, are analyzed.

In previous studies, mostly samples at different equilibrium states have been studied and compared to various nanostructure models. A detailed discussion of existing models can be found in [1]. Nafion[®] was first described by Gierke et al. [9], with a model of ionic clusters dispersed in a hydrophobic polymeric matrix. This model was based on the reduction of the total free energy of the polymer system, described by Eisenberg [10]. Based on the experimentally observed linear volume change with humidity, a lamellar stacking of fluorocarbon chains with ionic side groups that sandwich water layers with various thicknesses was proposed by Falk et al. [11] and Litt [12], and was further refined by Haubold [13]. Recently, Kreuer et al. predicted a lamellar structure of perfluorinated membranes, based on the experimental findings in combination with electrostatic considerations [5]. In our previous study at low humidity, we imaged for the first time a lamellar stacking of Nafion[®] and AQUIVION[®] PFSA in AFM experiments [14].

An alternative model in the literature consists of flat polymeric fibrils and bundles of aggregated polymer backbones with a bundle size of approximately 3–4 nm, aggregated to aligned crystalline structures of approximately 50 nm based on the scattering data proposed by Gebel et al. [15],[16],[17]. In this model, water surrounds the fibrillar objects and is not confined to pores. Predictions from modeling also provide input on the discussion, and recent models combine aspects from various existing models to suggest a more complicated structure, including independent bicontinuous networks of ionic clusters and fluorocarbon chains [18].

For the application of PFSA membranes in fuel cells, the ionomer/electrode interfaces play an important role because this is the location of the electrochemical reaction, and it may limit the performance of the cell. At the surface of PFSA membranes in air, the existence of a surface skin layer has been proposed by several authors and is currently accepted [19],[20]. At equilibrium conditions, this layer forms due to the different surface energies of the membrane and environment. At the membrane/air interface, a hydrophobic surface is formed. From GISAX measurements, a high crystallinity of an approximately 5-nm layer with an orientation parallel to the surface was observed [21]. From other scattering experiments, including synchrotron grazing incidence X-ray diffraction (GIXRD) and small angle X-ray scattering (GISAXS) analyses, a similar value was obtained [21],[22]. Recently, AFM measurements confirmed this thickness for the skin layer for membranes in air [23]. This highly adhesive surface phase is fluorocarbon-rich with the ionic side groups folded inwards [24]. Consequently, the surface properties of the outer surface and cross section are expected to differ significantly.

For the investigation of the PFSA nanostructure, scanning probe techniques are well suited [25],[26],[27],[28]. With advanced tapping mode techniques, the differentiation between different materials, including different phases, allows a direct imaging of

nanostructure under various temperature and humidity conditions. Using conductive AFM, analysis of the structures under non-equilibrium conditions as current flow has been conducted [8],[23],[29],[30],[31],[32]. The disadvantage of this approach is the restriction of the measurement to surface or subsurface properties and the dependence of the obtained resolution on the tip size and shape.

The electrodes of a fuel cell fulfill several functions, including high catalytic activity but also the provision of electronic and ionic conductivity and the appropriate transport of water and reactant gases. This complex functionality is normally achieved by mixing ionomer with the catalytically active nanometer platinum particles supported on carbon. The size and distribution of the components, especially of the ionomer in the catalyst layer, determines the performance and stability of the electrodes, i.e., based on the volume of the electrochemically active catalyst area, which affects the proton conductivity, mass transport, electronic conductivity, and porosity [33].

For a quantitative analysis of the electrode components, a method with a high lateral resolution is needed to image the nanosized particles and obtain a quantitative result of the composition. In the past, the ionomer content within the electrodes was mostly analyzed using transmission electron microscopy (TEM)[34,35] [36] in combination with energy dispersive elementary analysis (EDX) or energy filtering to obtain a mapping of the fluorine content. TEM-based techniques require very thin slicing and staining of the sample below 100 nm. For these techniques, staining with heavy metal atoms is often applied to enhance the scattering contrast. Artefacts such as swelling, or pore penetration with epoxy fillers may occur. Ionomer damage may occur due to electron beam radiation. The ionomer volume may shrink and change its structure due to water loss in the vacuum, a problem only avoided using cryo-TEM [37]. Modern scanning electron microscopy with increasing resolution is also able to image electrodes, including the ionomer; however, the issues of polymer radiation damage and water loss are similar to those encountered for TEM analysis, and quantitative analysis may be difficult to circumvent.

Recently, the analysis of components in fuel cell has been performed using synchrotron based soft X-ray scanning transmission microscopy (STXM) [33],[38],[39]. The chemical contrast between the elements is facilitated using the near edge X-ray absorption with a spatial resolution of 30 nm. For the samples, 100–300-nm thick ultra-microtome cut slices of membrane electrode assembly (MEA) samples were used. STXM has been used for characterizing ionomer distributions in differently applied catalyst layer structures, yielding quantitative maps of the ionomer and carbon support components [40]. Although some radiation damage is still detectable for radiation sensitive polymers such as PTFE, the advantage over energy-filtered TEM is significant using the same radiation dose.

In this study, we have two different sections. First, we employ material-sensitive and conducting AFM to analyze the structure, phase separation, and development of the continuously connected ionically conducting phase in Nafion[®] and AQUIVION[®] PFSA membranes. Here, we use AFM for detection of properties that influence the function of a fuel cell: the conductive structure of the membrane with the detection of water-rich phase using membrane cross sections and the formation of the ionically conducting network under forced current flow; the interface of the membrane which impacts the interface to the electrode and inside the electrode to the Pt/C particles with an investigation of the ionomer/ionomer interface formation and its interface properties. In the second part we report on the application of AFM for MEAs and we can clearly distinguish ionomer phase in electrodes for the first time with this method with a resolution in the nanometer range. The structure and conductivity of pristine MEA cross-sections and catalyst layers were

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