Polymer xxx (2015) 1–8

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Probing rough composite surfaces with atomic force microscopy: Nafion ionomer in fuel cell electrodes

Oleksandr Trotsenko [a], Roland Koestner [b], Yuri Roiter [c,1], Alexander Tokarev [a], Sergiy Minko [a,*]

[a] Nanostructured Materials Lab, University of Georgia, Athens, GA, 30602, USA
[b] GM Powertrain Engineering, Pontiac, MI, 48340, USA
[c] Department of Chemistry, Clarkson University, Potsdam, NY, 13699, USA

ARTICLE INFO

Article history:
Received 31 July 2015
Received in revised form
3 November 2015
Accepted 9 November 2015
Available online xxx

Keywords:
Nafion
Adhesion
Fuel cell electrodes
AFM
PeakForce QNM

ABSTRACT

Optimizing Nafion loading and surface distribution of Nafion in the fuel cell electrode is critical for the fuel cell performance for minimizing ohmic and mass transport overpotentials. An atomic force microscopy method is used here for a qualitative and a quantitative discrimination between the ionomer and Pt in the fuel cell electrode. This work describes a methodology for the analysis of complex composite surface of fuel cell electrodes and discrimination of different materials on the electrode surface. The reported methodology could be extended for imaging composite rough surfaces when contrast is based on mechanical properties, adhesion and electrical conductivity.

1. Introduction

Commonly used methods for mapping composite surfaces on the nanoscale include energy-dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) associated with electron microscopy methods. However, probing materials with high energy electrons could be distractive for the material structures especially made of organic substances. For example, fluorinated organic materials including fluoropolymers are sensitive to electron beam radiation [1]. Damage caused by interactions of the electron beam with the polymer includes bond breaking, free radical formation and crosslinking, and eventually formation of amorphous carbon [2]. This damage induces structural and chemical changes, as was demonstrated for polymer electrolyte fuel cell (PEFC) membranes [3]. At the same time, high doses are required for EDS or EELS to obtain a spectroscopic map of the surface with a high resolution. A number of strategies were developed [1,3,4] to minimize beam induced damages including cooling samples and selection of special substrates. However, electron microscopy techniques remain destructive yet to the fluoropolymer samples and could change their structure and chemical composition. This problem has attracted recent attention in the light of the development of fluoropolymer, specifically Nafion based, electrodes for hydrogen fuel cells. The PEFC electrodes are complex composite materials made of carbon black nanoparticles decorated with Pt nanoclusters coated with a Nafion ionomer. The tiny details of the structure of the composite electrode are critically important for understanding of the mechanisms of mass transport to the electrode surface. The latter problem is currently considered as a major source of energy losses associate with fuel cell cathodes. Thus, less damaging methods for mapping of the ionomer on the surface of fuel cell electrodes are highly demanded.

Atomic force microscopy (AFM) is a powerful and versatile tool to study interfaces and surfaces [5,6]. For the last decades, many AFM based methods have been developed for estimation of mechanical, electrical, magnetic and chemical properties of materials surfaces at nano- and microscopic levels [7–10]. Recently developed software packages enabled simultaneous acquiring combinations of physical properties of the mapped surfaces. For example, adhesion characteristics, mechanical response, and electrical properties can be measure while mapping with Bruker PeakForce QNM and TUNA [11,12] extensions.

* Corresponding author.
E-mail address: sminko@uga.edu (S. Minko).
[1] Current address: The Procter & Gamble Company, Cincinnati, Ohio, 45224, USA.

http://dx.doi.org/10.1016/j.polymer.2015.11.021
0032-3861/

Please cite this article in press as: O. Trotsenko, et al., Probing rough composite surfaces with atomic force microscopy: Nafion ionomer in fuel cell electrodes, Polymer (2015), http://dx.doi.org/10.1016/j.polymer.2015.11.021

Adhesion forces measured with AFM in the air originate from chemical and physical interactions of the probe with the sample. The latter includes van der Waals forces and capillary force generated by the humidity condensed on the probe tip and the sample. The capillary force strongly alternates the tip–surface interactions and could result in inconclusive results of AFM mapping in the humid atmosphere. However, even in the presence of condensed water a chemical contrast was reported based on pull-off forces [13]. It was demonstrated that adhesion measurements at relative humidity (RH) above 50% are not essentially dependent on humidity [13]. The chemical contrast originates from the fact that the pull-off force depends on the water contact angle on the surface of the sample. Hydrophobic surfaces demonstrate lower experimental pull-off force in the air than hydrophilic surfaces. According to Sedin and Rowlen [13], the measured force (F_{meas}) includes four contributing forces: the tip–sample interaction in vapor (F_{stv}), the tip-sample interaction in liquid (F_{stw}), and the capillary force (F_{cap}) which is a sum of the surface tension (F_t) and the force caused by pressure difference (F_p). The terms F_{stv} and F_{stw} may be calculated using Derjaguin approximation for separation of a spherical tip (1) with an apex radius R_t and a flat sample (2) in the presence of the third phase (3, vapor or liquid) [14]:

$$F_{stv/w} = 2\pi R_t(\gamma_{13} + \gamma_{23} - \gamma_{12})$$

where γ_{13} is the tip-vapor and γ_{12} is the tip-water interfacial tension, and γ_{23} is the water-vapor interfacial tension.

For both hydrophilic tip and sample, the capillary force dominates over F_{stw} [15] and:

$$F_{meas} \approx F_{stv} + \frac{F_t + F_p}{1 + e^{-[(RH - RH')/m]}}$$

where RH is the relative humidity, RH' is the transition point relative humidity when the capillary forces prevail, m – is the slope of the transition. F_t and F_p depend on contact angles of water (Fig. 1):

$$F_t = 2\pi R_t \gamma_w \sin(\psi)\sin(\psi + \theta_1)$$

$$F_p = -2\pi H \gamma_w R_t^2 \sin^2(\psi)$$

where R_t is the radius of curvature of the tip, γ_w is the surface tension of water, ψ is the filling angle, θ_1 is the contact angle for water on the AFM tip, θ_2 is the contact angle for water on the flat substrate, and H is the local mean curvature as defined for a circular approximation of the meniscus (Fig. 1)

$$H = \left(\frac{1}{r_1} - \frac{1}{r_2}\right) = \frac{1}{2R_t}\left[-\left(\frac{\cos(\theta_1 + \psi) + \cos(\theta_2)}{1 - \cos(\psi)}\right) + \frac{\sin(\theta_1 + \psi)}{\sin(\psi)}\right]$$

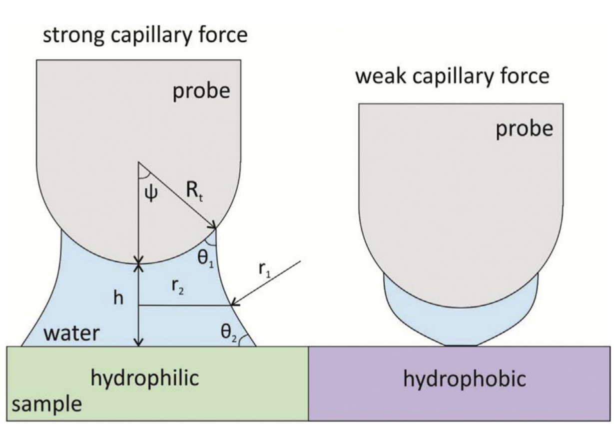

Fig. 1. Schematic of a capillary bridge formed between the AFM tip and the sample with hydrophilic and hydrophobic surface properties. R_t is the radius of curvature for the AFM tip, ψ is the fill angle, r_1 and r_2 are the principal radii of curvature of the meniscus, θ_1 is the contact angle for water on the AFM tip, and θ_2 is the contact angle for water on the sample surface.

Both types of interactions $F_{stv/w}$ and F_{cap} are surface specific. Therefore, the measured pull-off force depends on contact angle for water on the surface. The force is greater for a hydrophilic surface than for a hydrophobic surface. This simple analysis explains the origin for the chemical contrast when mapping composite surfaces made of materials with different wetting behavior.

Mechanical properties of the samples such as Young's modulus can be mapped on the nanoscale using PeakForce QNM tapping technique [7]. In the tapping mode Derjaguin–Muller–Toporov (DMT) model is explored for the unloading of the probe in the contact with the substrate for each data point. Comparing to Hertzian model, the DMT model takes into account adhesive forces [16] and describes elastic contact deformation of a ball (tip apex) and a plane surface [17]. However, if multicomponent thin films are scanned, the sample thickness and sample composition should be considered [8,18]. The DMT model is not applied in cases when the relatively soft polymer material is confined by a hard substrate underneath or aside of the structural features. This may introduce an error in the calculation of modulus. Thus, probing mechanical properties of composite surfaces enables imaging with nanomechanical contrast.

In this work we used nanomechanical contrast between a Nafion ionomer and Pt with the deformation channel. By keeping maximum loading force constant, we distinguish ionomer from Pt by higher deformation of the polymer comparing to the hard substrate.

A local surface conductivity of the mapping sample is measured when a bias voltage is applied between a conducting tip and the sample, and the electrical current is measured. Specifically, from a current–time plot during the PeakForce TUNA Tapping oscillation cycle three characteristics are collected: peak current, cycle-average current, and contact-average current. Peak current is the current when maximum force is applied to the probe. Cycle-average current are current averaged for the entire oscillation cycle when the tip touches the surface and when it is off the surface. Contact-averaged current is the current averaged for the period when the tip is in contact with the sample as judged from the force–separation curve. When the tip is brought in direct contact with a conductive substrate, usually the maximum current is observed [11]. Tip-sample contact area impacts the magnitude of the current, i.e. when the sample is deformed, or multiple contact between probe and rough sample occurs. However, if tip touches dielectric polymer no electrical current is detected. Offline analysis of the current maps is used to calculate statistics of the electrical properties of different regions, the spatial distribution of the properties. The data are used for study of the correlation of mechanical, topographic and electrical properties [11].

The described above mechanisms of the tip-substrate interactions create the background for the analysis of composite surfaces studied with AFM probes using different modes of the probe-substrate interactions on flat substrates. The interpretation of the AFM data becomes much less conclusive on rough surfaces when the tip-substrate contact area varies with dimensions of the topographical features on the surface [19,20]. Very small topographical features may not affect the probe-substrate interactions while structures with dimensions comparable with the probe size could much stronger contribute to the variations in probe-substrate interactions. Surface topographical structures are typically irregular