

Nanomechanoelectrical characterization applications in fuel cells and organic photovoltaics

This article describes two nanoindentation based techniques, and demonstrates their utilities in fuel cells and organic photovoltaics (OPVs) that have a high dependence of performance on the internal nanoscale structure. We demonstrate that Modulus Mapping™ and nanoECRTM techniques can be utilized to study the nature and extent of phase separation in an advanced - proton exchange membranes (PEM) and polymer based OPV device active layers, respectively. While both techniques are extensions and supportive of nanoindentation based mechanical testing, each serves unique purposes. The former technique that uses aspects of nanoDMATM and in-situ SPM imaging, was utilized to observe and quantify the phase separation behavior on an advanced PEM in the lateral direction, while the latter was used to illustrate the photovoltaic behavior at a certain depth in an OPV active layer, by nanoindentation and simultaneous measurement of electrical characteristics in dark as well as under illumination. We believe that phase-separation knowledge discovery resulting from such nano-mechano-electrical characterization can be very critical towards the development of high quality and high efficiency alternative energy devices such as hydrogen fuel cells and OPV devices.

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Nanoscale phase separation in PEM and OPV devices

Low proton conductivity and poor mechanical properties of the proton exchange membrane (PEM) are the two main obstacles

preventing greater commercialization of the polymer electrolyte fuel cells¹. Conductive probe-AFM and phase current correlation microscopy have been utilized to evaluate the electrochemical active area and aqueous domains present at the surface of an

operating membrane². Currently the performance of the state-of-the-art membranes, including perfluorosulfonic acid polymers (PFSA) such as Nafion® is limited to temperatures below 80 °C. Hence, work is in progress towards attaining operating capabilities at higher temperatures that could allow better efficiencies and less sensitivity to catalyst poisoning. For this, ongoing hydrogen fuel cell research is inclined towards developing 'advanced-PEM' that would maintain high level of efficiency even at processing conditions such as high temperature annealing³. However, there is a demand for characterization technology to better understand the nature and extent of the resulting nano and microscale phase separations in PEM, which in turn could inform the optimal processing conditions to produce next-generation PEMs.

In the case of OPV devices, conjugated polymer based OPV devices have been studied extensively due to the promise of low-cost and roll-to-roll manufacturability. The solution-processed active layer in such OPVs usually consists interpenetrating donor and acceptor organic species in so called bulk-heterojunction architecture. The morphology and phase-separation in these active layers critically affects the performance of the resultant solar cell⁴. Techniques such as AFM, TEM and XPS have been utilized to elucidate the lateral and vertical nanoscale phase separation in these films. In general, it is difficult to predict the morphology and phase information of a solution-processed film due to its sensitive dependence on the choice of materials, processing parameters, and inherent interfacial instabilities^{5,6}. Factors like type and extent of annealing, solvents, and blending ratios have been studied and linked to attaining acceptable nanoscale morphology of the device active layer^{7,8,9,10}. However, there remains a need to fine tune these understandings via more precise correlations between the nanoscale structural nature and resultant photovoltaic performance of a macroscale OPV device.

Subsequent paragraphs of this article present further detail on an established nano-mechano-electrical testing approach that can be utilized towards precisely studying nano and microscale phase separation observed in advanced-PEM samples and polymer based OPV device active layers.

Functional and non-functional polymer phase separation in advanced-PEMs using Modulus Mapping technique

Increasing interest towards developing advanced membrane-electrodes assembly (MEA) and its success are limited by poor understanding of the proton transport mechanisms of the PEM fuel cells. Superior proton transport capability depends on the optimization of the PEM material properties, which in turn will impact its mechanical endurance from the macro scale down to the submolecular level. Hence, a variety of processing conditions with common methodologies such as heating, boiling, annealing, and drying are continuing to be incorporated to obtain better hydration properties in the PEMs. This knowledge is

especially critical considering the task of the electrochemical catalysis that PEMs support while undergoing micro to nanoscale phase separation within itself during its processing and operational stages. PEM process optimization in turn amounts to optimization in proton conductivity and mechanical endurance to a desired level. To attain this, there is clearly a requirement for a proven technology to help determine the nature and extent of the resulting phase separation between the membrane constituents, which in turn also depends on the molecular and submolecular material properties. This section of this article focuses on performing Quasi-static nanoindentation to elucidate the phase separation details by studying the membrane material's mechanical properties on a non-commercial advanced-PEM with a functional and non-functional polymer blend in its formulation chemistry. The advanced-PEM sample was annealed at 200 °C for 30 minutes prior to soaking in water for at least 2 hrs before performing nanomechanical testing.

A Hysitron TI 950 TriboIndenter™ equipped with the nanoDMA II and Modulus Mapping options was used for the nanomechanical characterization study of the 'advanced-PEM' and for the electrical characterization of the OPV device active layer TI 900 equipped with a nanoECR option was used. The instrument included an environmental enclosure that helps shield the system from ambient airflow, thermal, acoustic effects and electric signal effects (in case of nanoECR option). X and Y – axis stages with 500 nm encoder resolution and a Z-axis stage with a 13 nm step size were used to position a standard diamond Berkovich probe (~ 100 nm radius of curvature) in the areas of interest on the sample. The nanoindentations were performed in the load control mode and a load of 10 µN was applied in all experiments.

As mentioned, the Modulus Mapping technique¹¹ was used to quantify the complex, loss, and storage moduli on the PEM surface. The probe, with this technique, maps the surface using the phase and amplitude information it derives by oscillating at a selected frequency between 10 and 300 Hz in contact with the surface. Fig. 1 shows images obtained for each particular modulus including a line profile to demonstrate the ability to quantify the storage modulus values across that particular region on the 'advanced-PEM' sample.

The in-situ SPM image shown in Fig. 2, along with the hardness and reduced modulus values obtained by quasi-static nanoindentation on the same area of the 'advanced PEM' surface further confirms phase separation represented by two different ranges of hardness and reduced modulus values. Using the instrument's 'click script' feature, indentations were performed at desired locations on the advanced-PEM surface as seen in Fig. 2. The indent seen in the center of the image is representative of the size of indents performed at each of the other marked positions on the sample.

Several force versus displacement plots denoting loading, holding at the maximum load, and unloading were obtained at both phases and are as shown in Fig. 3. The separation in force displacement plots indicated the different hardness (H) and modulus (E_r) values

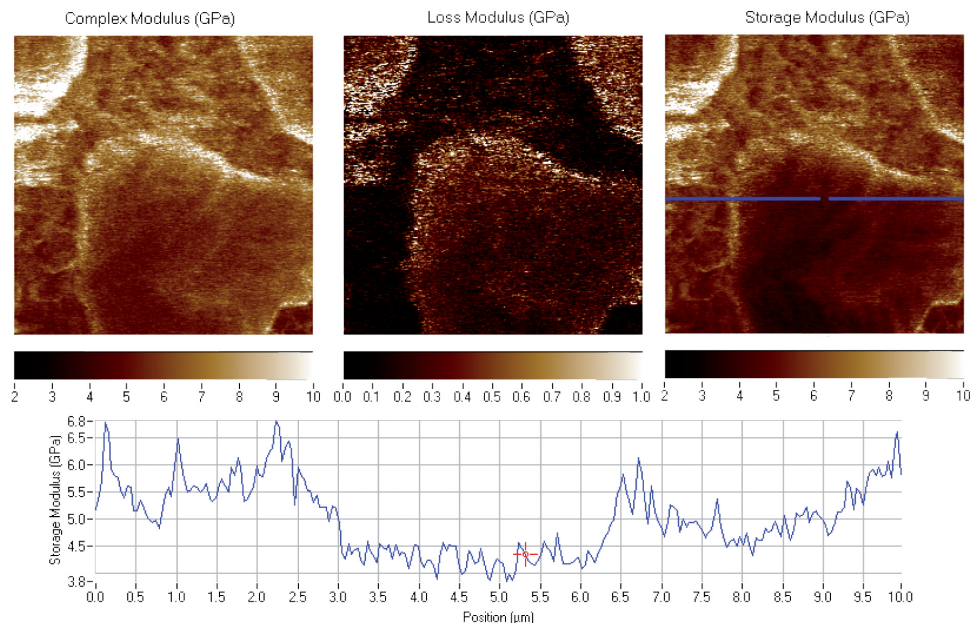


Fig. 1 Modulus Mapping images showing complex, storage, and loss moduli maps of a 10 μm region of the advanced-PEM sample. A line profile across the storage Modulus Map is also shown.

that were the characteristics of the functional and non-functional polymer components of the advanced-PEM. The measured average H values were 90 MPa and 40 MPa for the functional and non-functional polymeric regions, respectively. Similarly, 1600 MPa and 645 MPa were the average E_r values measured for the functional and non-functional polymeric regions, respectively. These quasi-static modulus values are

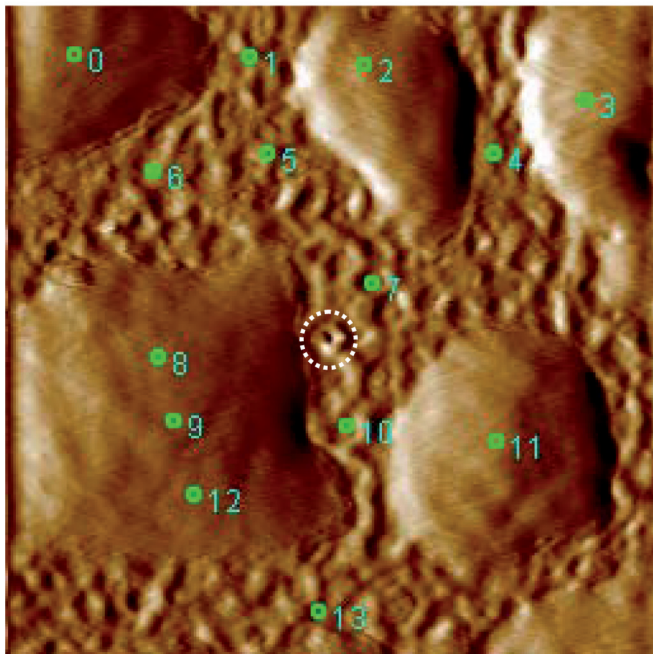


Fig. 2. 10 μm gradient SPM image showing where the indents were placed on the advanced-PEM sample using the instrument's click-script Piezo Automation feature.

less than the values determined using Modulus Mapping technique because of the sinusoidal modulation of the center plate of the force-displacement transducer at 200 Hz. Hence, the significant difference in the material property values observed within the same sample area, coupled with the morphological in-situ SPM image has together served as a measure of the nature and extent of phase separation within the 'advanced-PEM'. The size of the irregular and intermittently present non-functional polymeric regions were approximately 6 to 8 μm . Variations in the volume percent of the non-functional polymer will lead to variations in the phase separation size. Hence, the PEM processing optimization and the optimal polymer blend can both be achieved in the development of an 'advanced-PEM' with the incorporation of a systematic nanomechanical testing approach.

Horizontal and vertical phase separation study using nanoECR on an OPV device

OPV cells/devices are promising candidates for the next generation of solar-electric conversion. Today, OPV devices are sitting at the brink of commercialization with power conversion efficiencies approaching 8%¹². Further progress will come from not only newer organic materials that can harvest more solar spectrum in an efficient way, but also from more detailed understanding of the underlying physical phenomena and properties of these materials.

As mentioned, behavior of macroscale solar cell devices is intricately linked to their nanoscale structure. When the OPV active layer is coated from solution as in the case of polymer based OPVs, phase separation occurs between the electron donating and electron accepting species in state-of-the-art bulk heterojunction devices.

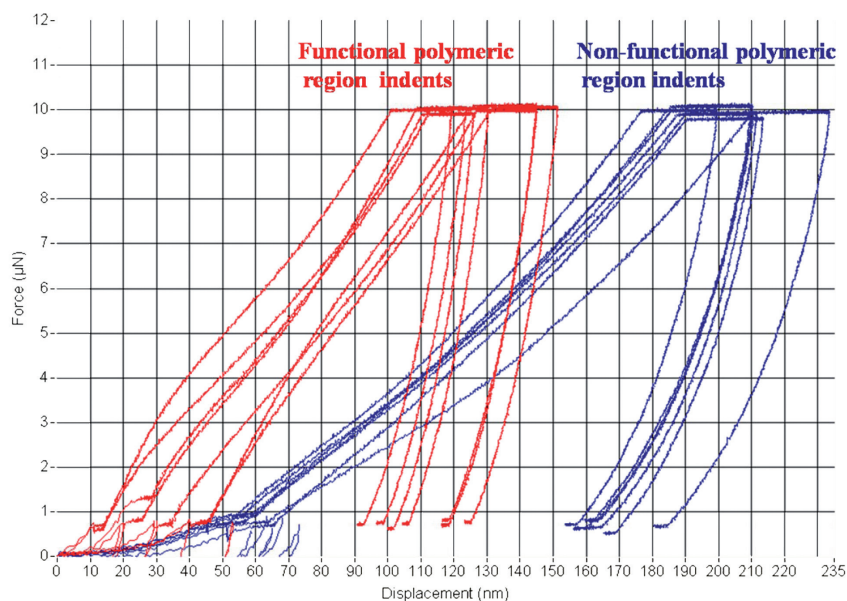


Fig. 3. Force-displacement curves obtained from the click-script Piezo Automation indents show the softer non-functional polymer regions (in blue) and harder functional polymer regions (in red) on the membrane sample.

Such separations happen both in horizontal and vertical directions, and are critical for all the important characteristics of the device, like open-circuit voltage, short-circuit current, and fill factor¹³. Nanoscale characterization techniques that are typically used for these devices are AFM and TEM¹⁴. AFM yields information about the lateral (horizontal) phases in these thin films, and TEM has been utilized to visualize them vertically. In another embodiment, conductive AFM has also been utilized to map the charge transport phenomenon in the lateral direction¹⁵.

The nanoECR technique¹⁶ employs a nanoscale electrical contact resistance tool as another option with Hysitron's TriboIndenter system and has been utilized in this section of the article. With this

system, a conductive Boron-doped diamond probe with a nominal resistivity of 3.3 Ω-cm for standard mechanical and electrical testing was used. An electric flow through this probe is driven by the biasing sample stage and a voltage/current source meter. The nanoECR technique demonstrates the ability to render the conventional nanoscale characterization of OPVs to an even more sophisticated level by providing simultaneous and quantitative topographic data, material property based phase separation information, and electrical characterization in both lateral and vertical directions. The schematic of a nanoECR set up is as shown in Fig. 4.

In a typical experiment, a conductive probe vertically indented the thin photovoltaic film (setup is shown in Fig. 4) with a pre-specified

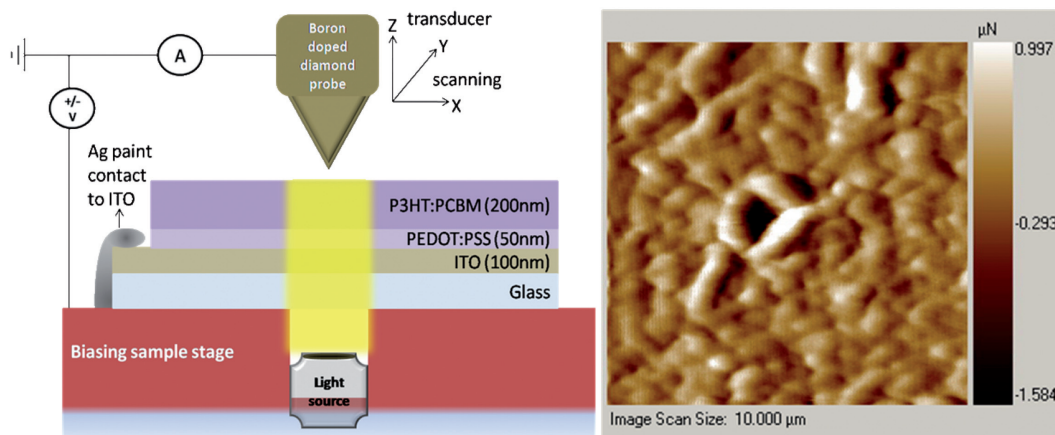


Fig. 4 Schematic of nano-mechano-electrical characterization using nanoECR on an OPV device sample (left) and in situ SPM imaging of the indented active layer area (right)

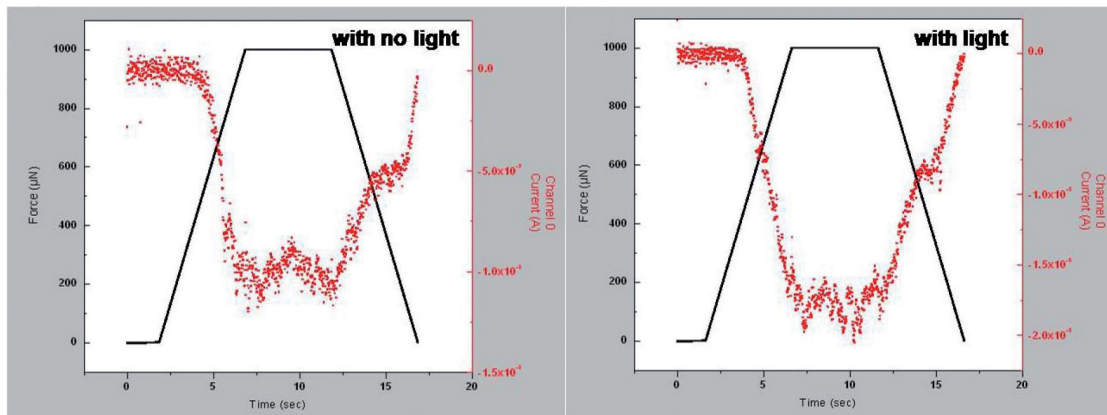



Fig. 5 Current-voltage profile obtained on the polymer based OPV active layer (a) with no light and (b) in light.

force, or to a desired depth. Current-voltage (I-V) characteristics were then measured as the probe traverses to that depth (loading), and is retracted (unloading). This can be performed both in dark and illuminated conditions to shed light on photovoltaic phenomenon at the nanoscale, both in vertical and lateral directions for the OPV active layer. In principle, as the probe progresses into and out of a thin film, the vertical phase transformations in the organic film can also be tracked, which in turn can be linked with the corresponding electrical characteristics. The hardness and the reduced modulus of the active layer were found to be approximately 0.35 ± 0.03 GPa and 60 ± 20 GPa, respectively. Deviations in modulus values across different locations on the film represent variabilities in separation for the given blend of polythiophenes and fullerene derivatives in the active layer. Fig. 5 shows the aforementioned characterization curve, wherein, the probe indents with a force of $1000 \mu\text{N}$, current is measured through the OPV active layer structure at a bias of -0.2V . Total magnitude of current obtained under illumination exceeds the magnitude of current in the dark by at least 60%. Although the increase in current under illumination is expected, detailed analysis regarding the origin of the peaks in the current between 5 and 15 seconds, the shoulder around 15 seconds, and their correlation with nanoscale structure will be reported elsewhere. However, combination of such vertical and lateral phase separation information collected using NanoECR can not only offer fundamental insights about these materials, but will also help in optimizing the material processing steps during fabrication, which can

potentially lead to obtaining the best performance from a given set of materials.

Conclusions

The quasi-static nanoindentation, Modulus Mapping, and nanoECR techniques have clearly demonstrated the ease with which nanoscale lateral and vertical phase separation information can be acquired. The study can be further extended to determine and understand the hydrated and dehydrated phase separations in PEM. Similarly, precise blend phase separation in the OPV active layer can be studied and its optimization can be attained with the help of the nanoindentation based Modulus Mapping technique. These techniques are not only on par with similar techniques that have followed the paradigm shift towards being highly beneficial but are also experiencing higher demand due to the increase in the desire for products that produce, conserve, and sustain clean energy. More so because these alternative energy producing products have evolved towards considering the sophistication that nanotechnology offers to its basic functioning. Certainly, the future of such cost saving alternative energy technologies depends on the embracing of such newer and proven techniques. 

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