Experimental report

11/03/2022

Proposal: **9-11-1986** **Council:** 4/2020

Title: Ionic liquid post-treatment effecton water uptake of PEDOT:PSS films

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: PEDOT:PSS

Instrument	Requested days	Allocated days	From	To
D17	4	4	25/06/2021	29/06/2021

Abstract:

By combining so-called ionic liquids with conducting polymers a novel approach for TE materials is realized. The polymer blend poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) consists of two ionically bound polymers. Recently, it was discovered that ionic liquids could be used to complement the binary nature of PEDOT:PSS, in order to simultaneously enhance both Seebeck coefficients and electrical conductivities. However, PEDOT:PSS films are very hygroscopic and thus swell via incorporation of water molecules in a humid atmosphere. In turn, the film thickness changes and the conductivity is affected. In the proposed experiment we want to investigate the kinetics of water uptake by PEDOT:PSS films post-treated with ionic liquids: a) EMIM DCA, b) EMIM TCB and c) EMIM BF4 in 3 different concentrations in THF (0.01, 0.l1 and 0.3 M). TOF neutron reflectivity will be used to probe the water distribution inside the films and the water uptake kinetics.

Ionic liquid post-treatment effect on water uptake of PEDOT:PSS films

(Proposal 9-11-1986)

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Thermoelectric (TE) generators provide a seminal technique to reduce energy dissipation and combat the steadily increasing energy demand worldwide, due to their ability to directly convert heat waste into electrical power. Especially organic TE materials, like the polymer blend poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS), have gained huge interest, as they allow the large-scale production of lightweight, non-toxic, mechanical flexible and potentially cheap TE devices with an intrinsically low thermal conductivity. In recent years, research was focusing on the further improvement of the TE properties of PEDOT:PSS through different treatment approaches, for example the very promising post-treatment of PEDOT:PSS thin films with ionic liquids (ILs).[1-3] ILs are organic ionic compounds with melting points below 100 °C and in this case allow for twofold modification of the properties of PEDOT:PSS thin films. The improvement in Seebeck coefficient originates from interactions between the conducting polythiophene PEDOT and the organic anions of the ILs. On the other hand, the electrical conductivity increases due to short-range morphological rearrangement within the films, which allows for improved charge transport. The combination of increased Seebeck coefficients and electrical conductivities yields higher achievable output power values, which makes treatment of PEDOT:PSS films with ILs a promising route for enhanced organic thermoelectric properties. Previous studies in our group have shown that the TE performance of these IL post-treated PEDOT:PSS thin films is greatly influenced by the ambient humidity. Therefore, with *in-situ* neutron reflectometry (NR) at the D17 instrument we investigated the effect of IL post-treatment on the water uptake of PEDOT:PSS thin films.

For the experiment, PEDOT:PSS was spin-coated onto cleaned Si substrates and thermally annealed. Afterwards the prepared PEDOT:PSS film was soaked in the IL post-treatment solution using three different IL: a) 1-ethyl-3-methylimidazolium dicyanamide (EMIM DCA), b) 1-ethyl-3-methylimidazolium tetracyanoborate (EMIM TCB) and c) 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM BF_4) in 3 different concentrations in water for 1 min. The IL post-treated PEDOT:PSS film was mounted into our custom made humidity chamber to realize the controlled water uptake. To have contrast, D_2O was used to establish the humid atmosphere.

In-situ NR measurements were performed in time-of-flight (TOF) mode with a wavelength band of 2 to 30 Å at the D17 instrument at the ILL. The sample-detector distance (SDD) was set to 3.1 m. To cover a large q_z range, the reflectivity curves for the films in equilibrium were acquired at two different incident angles (san 0.5° and 2.5°) with a total counting time of 45 min. To follow the kinetics of the thin film during the exchange of atmospheres, reflectivity data was repeatedly recorded at a fixed incident angle (san 1.0°) with a time resolution of 5 s. This high time resolution allowed the observation of the thin films response during the D_2O hydration cycle. In order to avoid the oversaturation of the detector during the absorption of volatile compounds with high SLD, the count rate was recorded for each kinetic run. If it exceeded the preset value of 15000 c/s, a change in the TOF angle was triggered (san 1.0° to 1.5°). The reverse of the TOF angle setting was triggered, if the count rate felt beneath a set value.

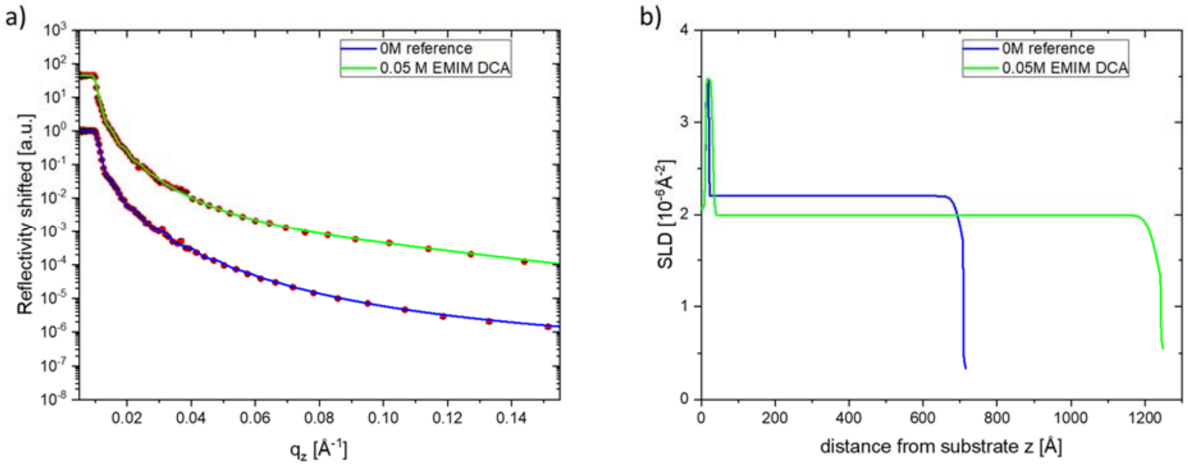

Figure 1. *a) Example of NR curves of the PEDOT:PSS thin films in the dry equilibrium state (symbols) shown with model fits for untreated 0M reference (blue line) and post-treated with 0.05M EMIM DCA (green line). b) Corresponding SLD profiles, untreated 0M reference (blue line) and post-treated with 0.05M EMIM DCA (green line), with Si substrate located at z = 0 Å.*

The NR data of the dry untreated and 0.05M EMIM DCA post-treated PEDOT:PSS film in equilibrium (Figure 1a, red dots) exhibit weak Kiessig fringes, indicating that the polymer films are homogenous but rough. An initial three-layer model is used to describe the dry films on the Si substrate. The theoretical reflectivity curve generated by the model is represented by the blue and green lines in Figure 1a, whereas the respective resulting scattering length density (SLD) profiles along the dry film vertical are shown in Figure 1b. The Si near layer consists of the SiO_2 with a thickness of 15 Å and a SLD value of 3.47×10^{-6} $Å^{-2}$. The next layer is the PEDOT:PSS film. It has a thickness of 700 Å and a SLD value of 2.20×10^{-6} $Å^{-2}$ for the 0M reference film and a thickness of 1230 Å and a SLD value of 1.99×10^{-6} $Å^{-2}$ for the 0.05M EMIM DCA post-treated film. The top layer at the air interface is only around 1 Å thick, has a lower SLD value than the polymer layers and is used to mimic the density gradient along the surface normal in the box model approach, due to loose chain ends and loops at the surface.

Figure 2a shows the applied D_2O humidity cycle, which increased the humidity in three steps (40, 70 and 100% RH). It was realized by respectively enriching the dry N_2 carrier gas flow with a D_2O saturated vapor. The thermostat used to equilibrate the vapor generation and humidity chamber was set to 25 °C. Selected NR curves from the beginning (bottom) to the end (top) of a hydration cycle in D_2O are shown in Figure 2b. The observable shift in the position of the critical edge towards higher q_z values indicates an absorption of D_2O into the polymer layer. This D_2O absorption appears to be stronger for the 0.05M EMIM DCA post-treated film (right NR curves), where at 100 %RH D_2O the film even seems to somehow collapse or form a new intermediate layer. This trend is matching well with the previously observed change of the TE performance for IL post-treated PEDOT:PSS thin films at high humidity values. However, to better understand this behavior and to enable the publication of the results, further data analysis is ongoing.

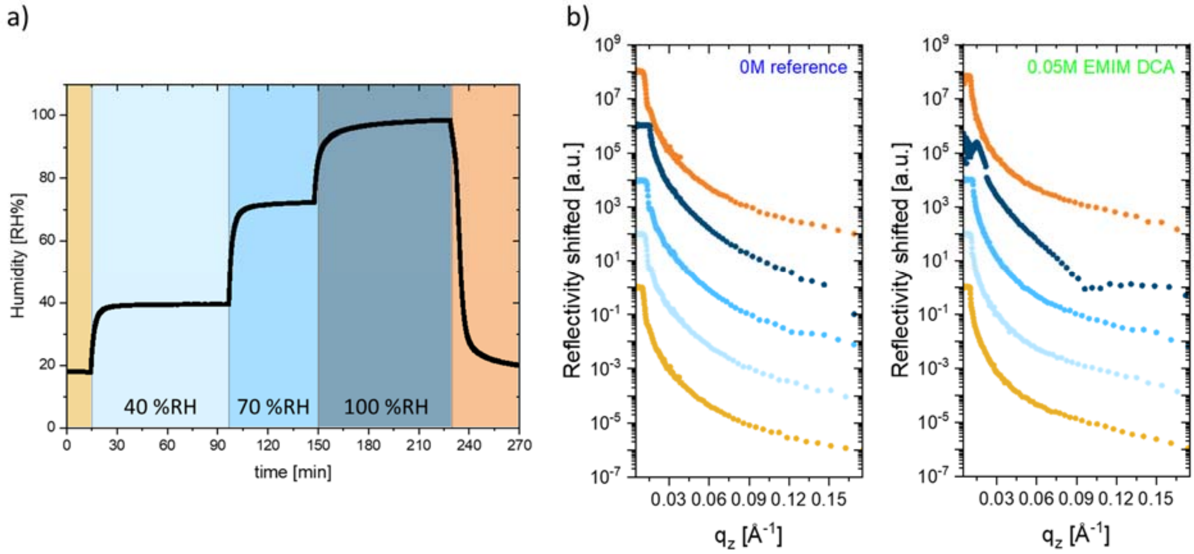

Figure 2. *a) Applied D_2O vapor humidity cycle at 25 °C for investigating the water uptake of the PEDOT:PSS thin films. b) NR curves of the untreated 0M reference (left) and the 0.05M EMIM DCA post-treated (right) PEDOT:PSS thin films in equilibrium state at different D_2O humidity. Selected NR curves are respectively shown from the beginning (bottom) to the end of the humidity cycle (top).*

References

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