Experimental Report

19/09/2014

Proposal: **9-11-1641** **Council:** 10/2012

Title: Study of the growth and solvation of PEDOT films as a function of electrochemical deposition methodology

This proposal is a new proposal

Researh Area: Materials

Main proposer: **BEEBEE Charlotte**

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Samples:
PEDOT $C_6H_4O_2S$
d-PEDOT $C_6D_4O_2S$

Instrument	Req. Days	All. Days	From	To
FIGARO User-supplied	4	4	28/02/2013	04/03/2013

Abstract:

We propose specular NR measurements of the deposition of the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) using three different electrochemical methods. This will allow us to determine the kinetics of film growth and characterize the structural differences of the films as a function of electrochemical deposition technique. The structural results will allow for the correlatation of the variations in polymer density, ion distribution and solvent population within the polymer matrix to observed differences in film behaviour and electrochemical properties.

It has been observed that the choice of electrodeposition method (ref) as well as other elements of the deposition protocol such as supporting electrolyte (ref) or monomer concentration (ref) can affect the electrochemical (ref) and structural properties (ref) of the polymer film produced. The NR measurements of the potentiodynamic growth of PEDOT reveal, at a first glance, a film deposition with regular growth intervals:

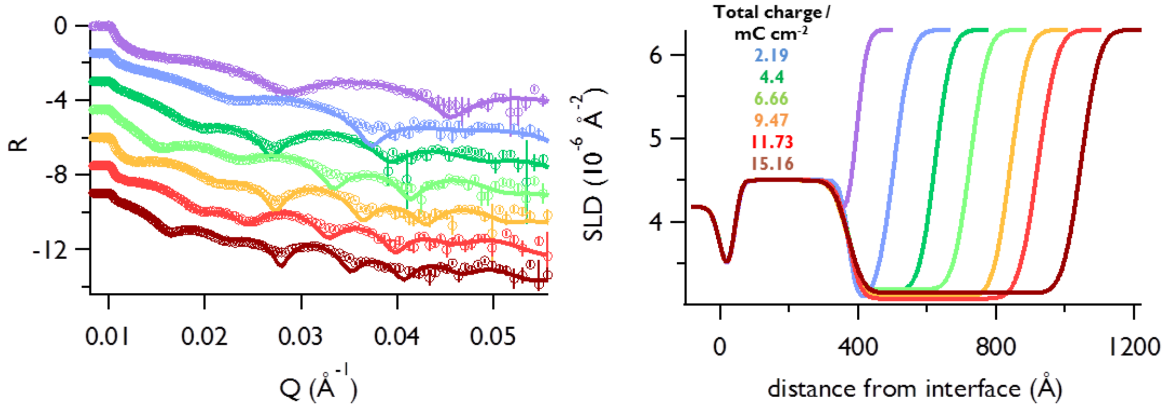

Figure 1 Potentiodynamic growth of (single layer models); the purple trace is the gold measurement prior to deposition.

Evaluation of the SLD of the polymer layer in these fits indicate a consistently solvated state with a solvent volume fraction of between Φ_s ~ 0.2 – 0.23. The final three growth stages can, however, be fitted with a model that divides the polymer layer into two layers that can fit independently. The other stages of growth do not fit with such a model and converge to a single layer therefore it can be concluded that these early stages produce a homogeneously solvated film. On the other hand, the later stages of growth reveal a divide between the polymer layer at the gold/polymer interface and the outer layer at the polymer/solution interface. The latter become progressively more solvated as the growth progresses while the former retains a slightly lower volume fraction of solvent. These models can be seen in **Figure** . The orange trace, after a growth charge density of 9.47 mC cm^{-2}, shows the film presenting a very low volume fraction of solvent of Φ_s ~ 0.13 throughout the bulk of the film with the polymer/solvent interface modelled using an additional layer and significant roughness parameter.

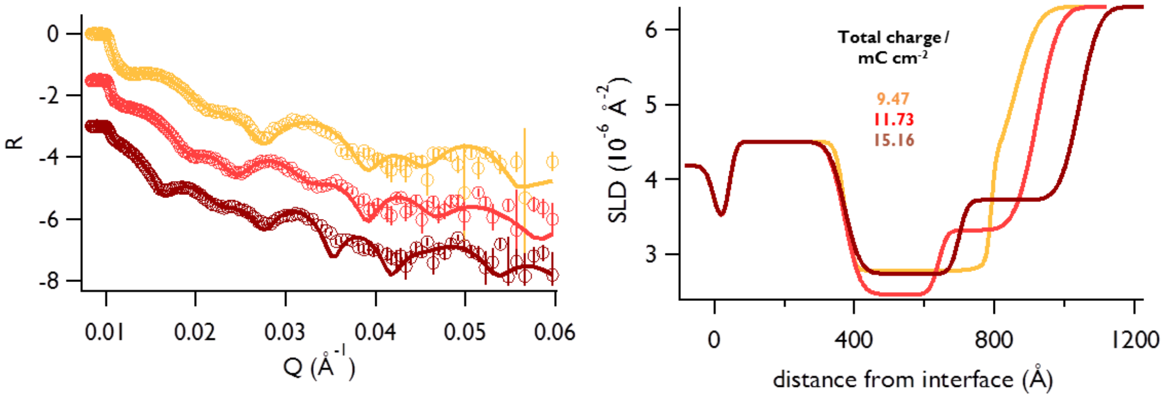

Figure 2 Final stages of the potentiodynamic growth of PEDOT (multilayer model).

The red trace shows the film, after further growth cycles, now presenting very distinct inner and outer layers with significantly different levels of solvation. The layer at the gold/polymer interface has an SLD indicating a solvent volume fraction of just Φ_s ~ 0.05, whereas the outer layer has a volume fraction of Φ_s ~ 0.26. Finally, the last growth stage has an inner and outer layer solvation of Φ_s ~ 0.12 and Φ_s ~ 0.36 respectively.

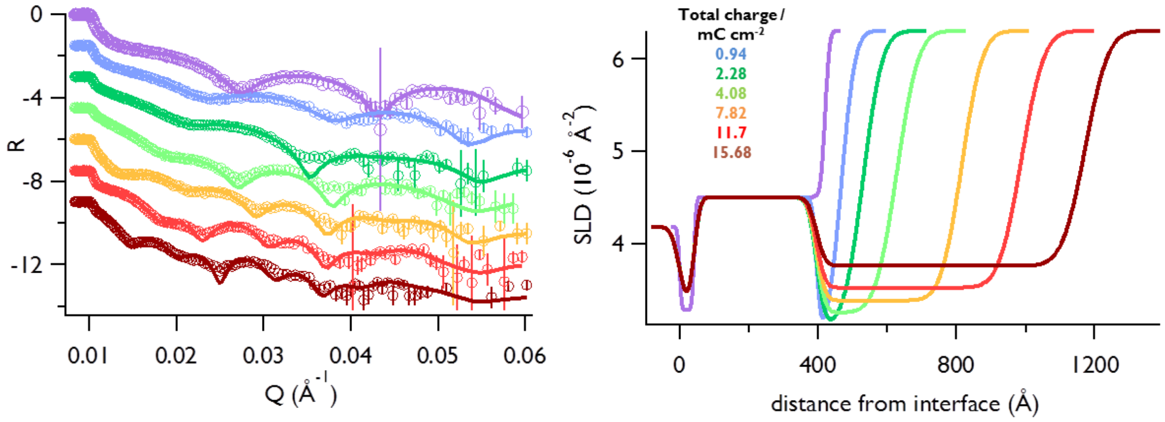

Figure 3 Potentiostatic growth of PEDOT; the purple trace is the gold measurement prior to deposition.

The potentiostatic growth of PEDOT presented a slightly different growth pattern with regards to solvation throughout the growth stages. As shown in **Figure** , the early deposition intervals present a polymer layer with a low SLD which gradually increases with each deposition step. In terms of solvation, this translates to an initial solvated state of approximately Φ_s ~ 0.2 which progresses to Φ_s ~ 0.3 and eventually Φ_s ~ 0.37 in the final growth stage.

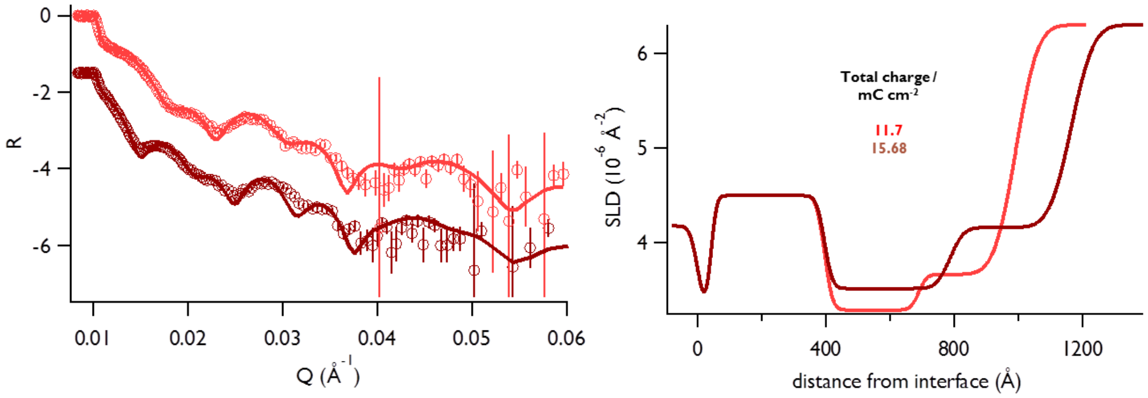

Figure 4 Final stages of potentiostatic growth of PEDOT (multilayer model).

The NR measurements of the galvanostatic growth of PEDOT reveal a very slight increase in the degree of solvation as the growth progresses. This can be observed in the SLD profiles presented in **Figure**, where the SLD remains unchanging in the early stages of growth before increasing slightly in the last two growth intervals. The volume fraction of solvent in the first three growth steps is consistently Φ_s ~ 0.33, before increasing to Φ_s ~ 0.35 and Φ_s ~ 0.38 in the penultimate and final stages respectively.

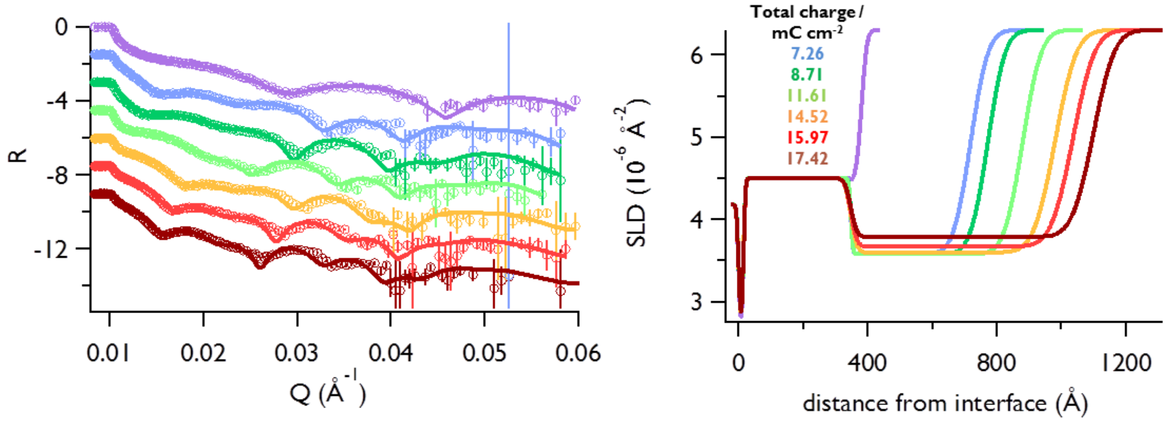

Figure 5 Galvanostatic growth of PEDOT; the purple trace is the gold measurement prior to deposition.

Although the last three growth stages can be fitted to a multi-layered polymer model, the fit converges to an SLD profile in which the film is homogenously solvated, with a volume fraction of Φ_s ~ 0.35 – 0.37, but presents a large roughness at the polymer/solution interface as shown in **Figure** . Thus the solvation level of the film does not change significantly from the single layer models. This would suggest that the galvanostatic film presents a more consistent structure throughout the growth.

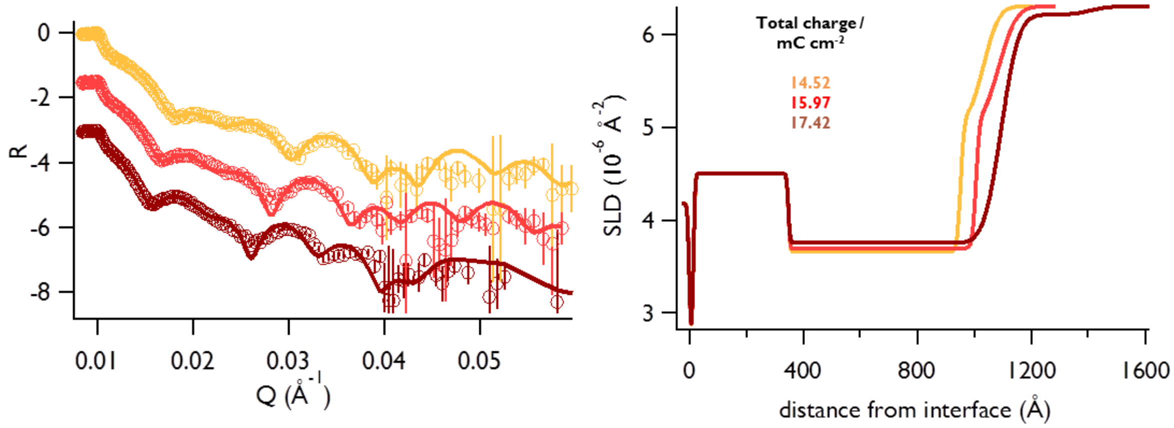

Figure 6 Final stages of galvanostatic growth of PEDOT (multilayer model).

Each film was cycled in fresh electrolyte following deposition then held in an oxidised and reduced state to examine the effect of charging and discharging on the internal structure of the film. Once again, the NR data could be fitted using a single layer to model the polymer film and the results are presented in **Figure** alongside the SLD profiles of the final growth stage for each electrochemical control function.

Overall, the films presented no significant structural changes and, in fact, showed almost identical SLD profiles to those of the final growth stages. Only the potentiodynamically grown film exhibited a slight increase in the level of solvation of the film from a solvent volume fraction of Φ_s ~ 0.22 after growth to between Φ_s ~ 0.24 – 0.26 in the redox states. This film also presented a slightly rougher interface at the boundary between the polymer and the solution.

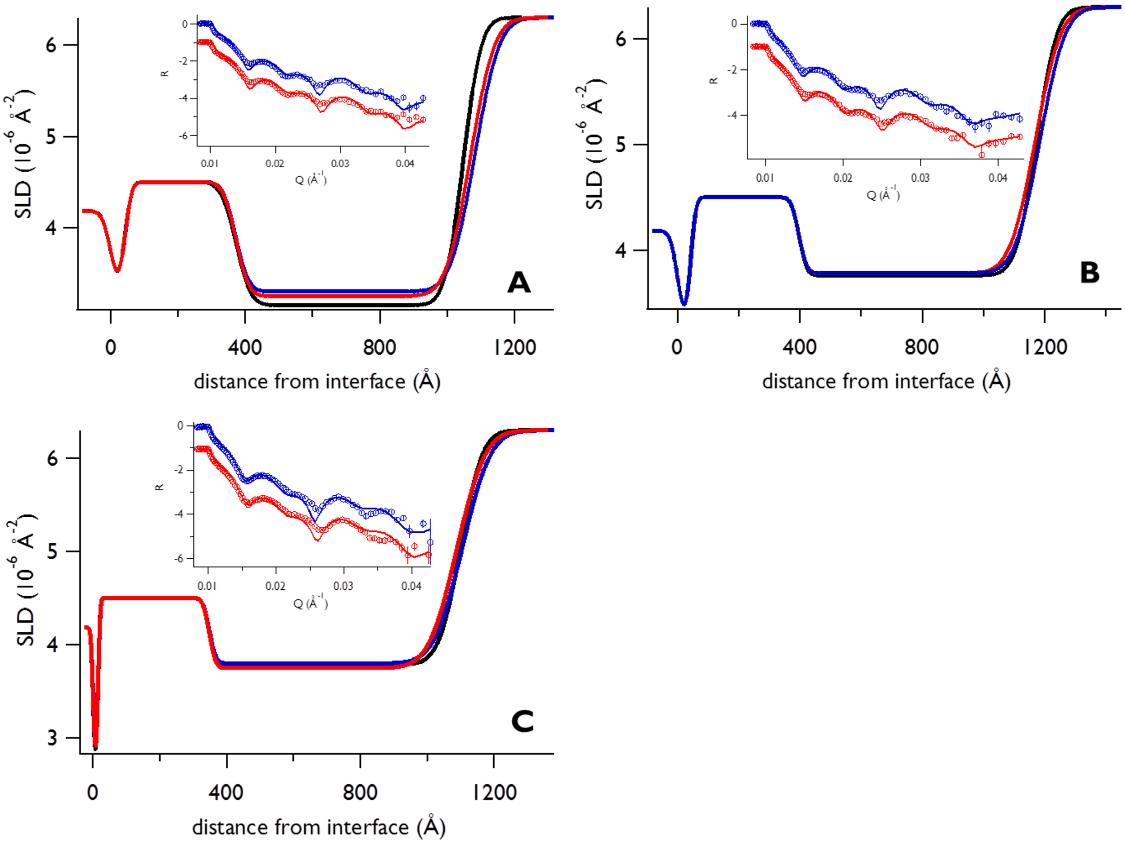

Figure 7 SLD profiles of the films produced under potentiodynamic (A), potentiostatic (B) and galvanostatic (C) conditions, measured at the open circuit potential following the final growth stage (black), held oxidized at E = 0.4 V (blue) and reduced at E = -0.5 V (red); insets show the corresponding reflectivity data and fits from which these are derived. The model consisted of a single polymer layer with a rough outer interface.