Experimental Report

Proposal:	**9-11-1595** **Council:** 4/2012
Title:	Dynamics of polyaniline depositionand solvation as a function of electrochemical control function

This proposal is a new proposal

Researh Area: Chemistry

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Samples: SiO2/Au/[C6NH5]n.ClO4,D2O/D2O,HClO4

Instrument	Req. Days	All. Days	From	To
FIGARO User-supplied	4	3	30/11/2012	03/12/2012

Abstract:

We propose specular NR measurements on polyaniline films during their deposition by different electrochemical control functions (potentiostatic, potentiodynamic and galvanostatic) known to generate films of different characteristics and, in devices, different performance. These will combine steady-state measurements of the films at intermediate states of deposition and dynamic experiments performed at the limits of time resolution of the FIGARO reflectometer. Issues addressed are variations in solvent population and spatial distributions of polymer and solvent within the growing films as functions of electrochemical control function and parameters. These outcomes relate directly to film uniformity, mechanical and electronic integrity, and internal transport processes that govern device switching times.

It has been observed that the choice of electrodeposition method as well as other elements of the deposition protocol such as supporting electrolyte or monomer concentration can affect the electrochemical and structural properties of the polymer film produced.

The deposition of the polymer itself went well from an electrochemical perspective: polyaniline (PAni) films were successfully grown on the gold surfaces, using each of the three techniques, within the confines of the neutron cell; however the reflectometry data was surprisingly disappointing. Initially it was thought that the growth was not occurring yet a film was definitely produced with a thickness that should have been within, and eventually beyond, the resolution of the neutron data. Despite this, the reflectivities suggested that the final state of the polymer films were hardly different from the bare gold electrodes.
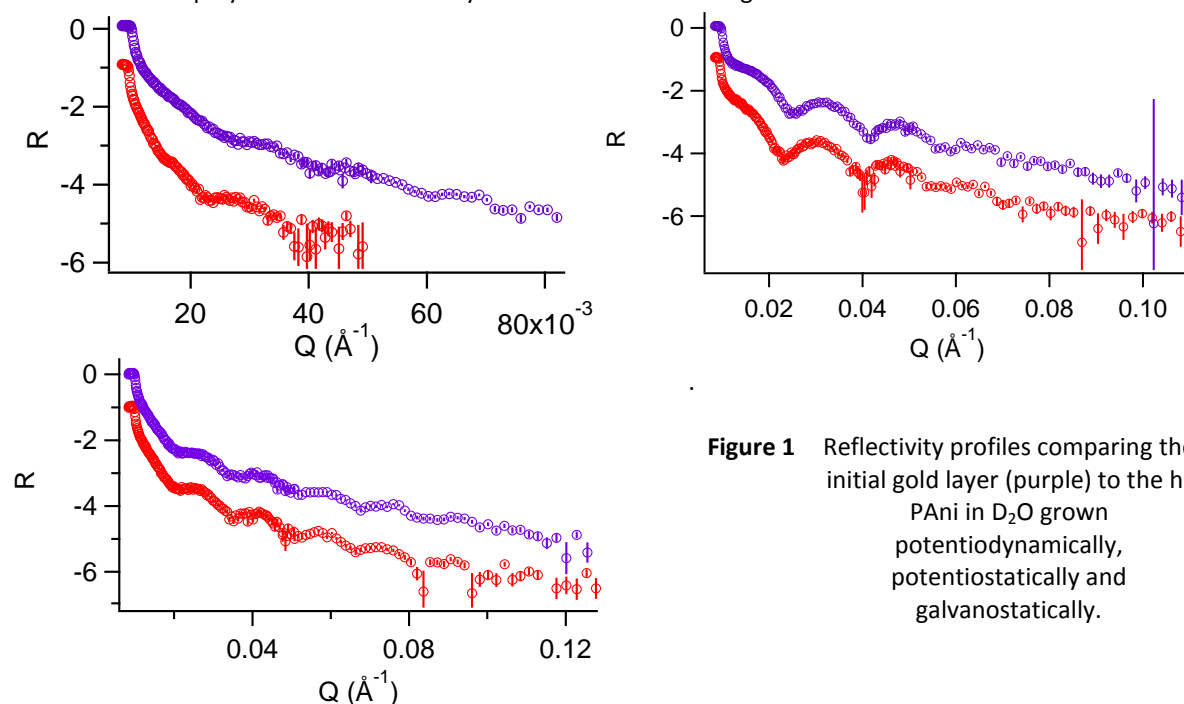

Figure 1 Reflectivity profiles comparing the initial gold layer (purple) to the h-PAni in D_2O grown potentiodynamically, potentiostatically and galvanostatically.

Subsequent modelling of the PAni film parameters obtained through atomic force microscopy revealed that the contrast situation was not optimal for hydrogenous PAni in D_2O.
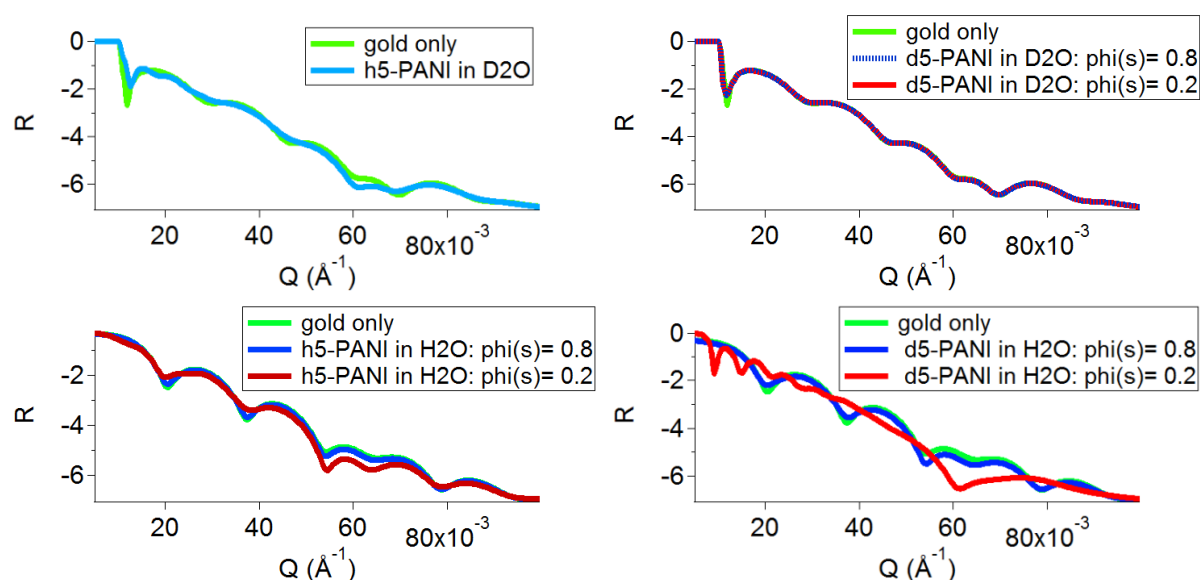

Figure 2 Reflectivity profile simulations comparing a 600 Å PAni film with the bare gold electrode. The PAni film has been modelled with maximum and minimum possible solvation levels expected during growth of 0.80 and 0.20, respectively.

Fortunately another monomer, deuterated pyrrole, was available with a very different scattering length density. Two samples were produced, each deposited using a different electrochemical method. In this case the reflectometry data closely resembled the modelled data, clearly showing fringes shifting to lower values of q with increasing film thickness. Furthermore, although the two films were grown to a similar thickness, they displayed different structural features which may be caused by differences in solvation or roughness. It has long been believed that these different deposition methods are responsible for different electrochemical features in films, this data will hopefully give us insight into what structural differences cause these features.
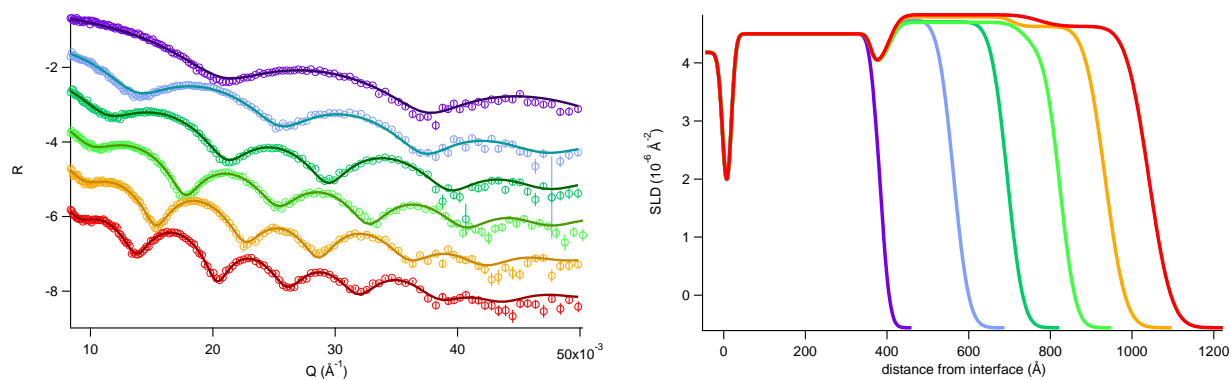

Figure 3   Reflectivity and SLD profiles showing the potentiodynamic growth of d_3-polypyrrole on a gold surface where the purple traces are the bare gold surface and the red traces are the fully formed films.

Charlotte Beebee a PhD student at the ILL was awarded extra time on FIGARO during her time at the ILL to complete the other 2 growth mechanisms for d_3-polypyrrole. The results from her extra time are detailed below.
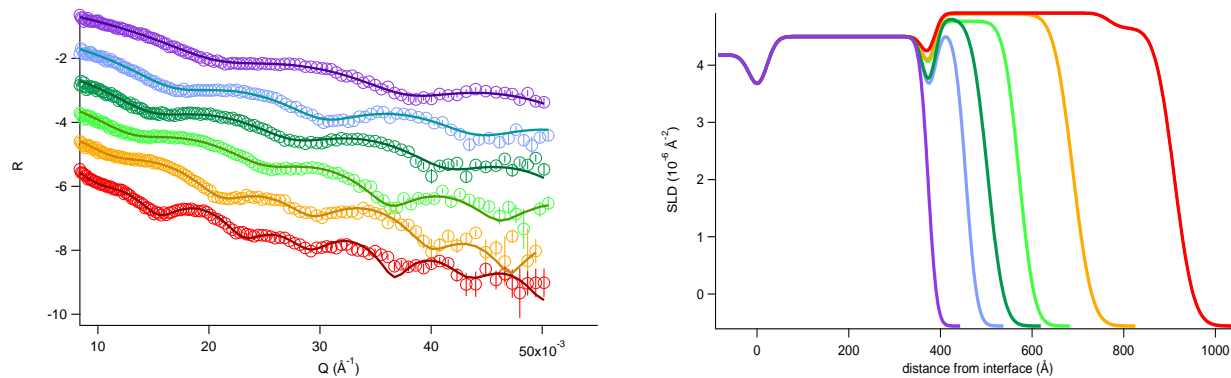

Figure 4   Reflectivity and SLD profiles showing the potentiostatic growth of d_3-polypyrrole on a gold surface where the purple traces are the bare gold surface and the red traces are the fully formed films.

Figure 5   Reflectivity and SLD profiles showing the galvanostatic growth of d_3-polypyrrole on a gold surface where the purple traces are the bare gold surface and the red traces are the fully formed films.
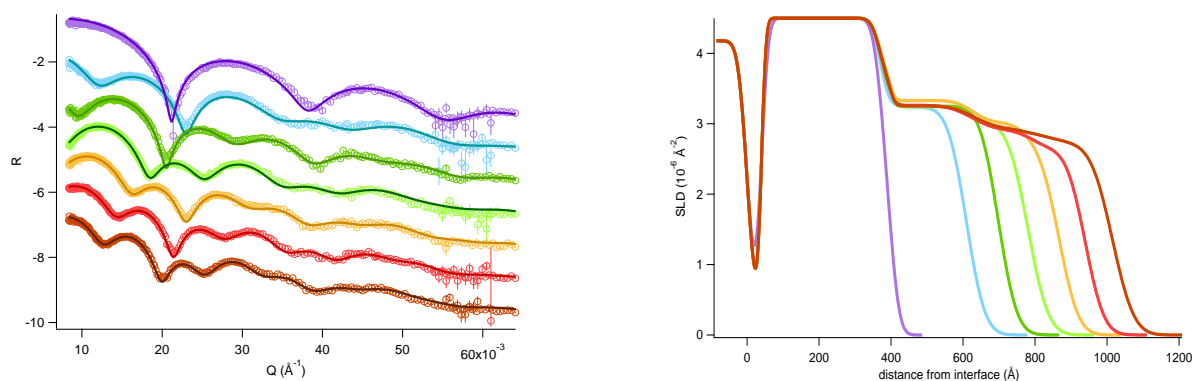
The potentiodynamic growth resulted in a film that was evenly solvated at every stage as shown in **figure 3**. The SLD profile of the film following the first growth step indicates that the film has an SLD of 4.75×10^{-6} $Å^{-2}$ which suggests a solvent volume fraction of 0.29 for a SLD_{dPPy} of 6.93×10^{-6} $Å^{-2}$. Each of the subsequent growth steps produces a further layer of polymer with the same SLD and therefore the same level of solvation.

On the other hand, the potentiostatic growth suggests a more solvated film in the first stages of growth but quickly reaches a homogeneous level of solvation as the deposition progresses as illustrated in **figure 4**. In this case the film reaches a 'bulk' solvation state after the fifteenth deposition step and a total charge density of 3.6 mC cm^{-2}. The solvent volume fraction was 0.28 in the bulk, increasing slightly to 0.31 at the polymer/solution interface in the final growth stage.

The galvanostatic growth, from the same monomer concentration, displayed a similar growth to the potentiostatic method, with the SLD profiles showing a more solvated film in the early stages of growth. **Error! Reference source not found.** shows the progression to a more homogeneous film was more gradual in this case, only reaching a 'bulk' solvent content at the fourth growth step after a charge density of 5.08 mC cm^{-2}. The overall SLD of the film was higher than both the potentiodynamic and potentiostatically grown films, suggesting that the galvanostatic growth results in a more compact film since it displays a slightly lower solvent volume fraction of between 0.23 and 0.26.