

Spatial Distributions of Polymer and Mobile Species in Poly(o-toluidine) Films

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Poly(o-toluidine) (PoT) is a member of the poly(aniline) family of conducting polymers. PoT has attractive electronic properties (1), demonstrated through electrochemical impedance data (2),(3). The associated redox-driven film ion and solvent population changes have been monitored using the electrochemical quartz crystal microbalance (EQCM), both alone (4) and in conjunction with probe beam deflection (PBD) (5),(6),(7).

The general observation was that ion and solvent transfers (5) and the dynamics thereof (6),(7) vary in a complex manner with electrolyte composition, notably pH. In order to rationalise these effects, which are crucial to a range of applications, we sought to obtain a more detailed picture of film composition and structure. In particular, we wished to determine the *absolute* populations of mobile species within the film and their spatial distributions. We have used neutron reflectivity as an *in situ* technique to acquire such information for electrodes modified with osmium polyvinylpyridine complexes (8) and with conducting polymer bilayers (9). More recently we demonstrated that the method could be applied to PoT films under potential control (10) and we now use this method to explore the effect of pH on film structure and composition.

PoT films were potentiodynamically deposited onto Au thin film electrodes (supported on single crystal quartz blocks (10)) from o-toluidine monomer solutions in aqueous H₂SO₄, as described previously (4). Typically, 35-45 cycles (between 0.0 and 0.8 V vs Ag/AgCl, at $v = 100\text{mV s}^{-1}$) were used to generate films in the thickness range 25-90 nm, an optimum range for the neutron reflectivity measurements. Neutron reflectivity experiments were performed using the TAS-8 spectrometer (Riso National Laboratory, Denmark) and the CRISP and SURF instruments (ISIS Facility, UK). Data fitting was performed with the Parratt32 program, used with the permission of Hahn-Meitner Institut.

With the advantages of isotopic substitution of the aqueous solvent ("contrast variation"), we are able to interpret the data in terms of the spatial distributions (perpendicular to the interface) of polymer and solvent. We report this information as a functions of perchloric acid electrolyte concentration (pH) and thickness for fully reduced films. All films show a relatively dense (high polymer volume

fraction) interior and a relatively diffuse (high solvent volume fraction) region at the polymer / solution interface. Upon increasing the acid concentration from 0.01 M to 1 M, the films swell (by up to 20%) due to additional solvent permeation. Further increase in acid concentration (to 5 M) results in a slight additional film swelling, but decreased solvent volume fraction, which we attribute to permeation of perchloric acid. These effects are seen for films of different thickness.

These *absolute* mobile species population data, notably for solvent within the film, bring new insights to redox-driven *relative* population changes determined using the EQCM and PBD techniques. The ion populations determine the sources and sinks of species able to move in order to satisfy the electroneutrality condition, and the solvent population influences the rates of transport of these species within the film. The sensitivity of the dynamics of coupled electron/ion and solvent transfer to the ambient medium will be discussed in terms of the corresponding variations in film structure and composition.

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