

16<sup>th</sup>–21<sup>st</sup>  
JUNE 2019

# WEEM-2019

International  
**WORKSHOP**  
on Electrochemistry  
of Electroactive Materials

BOROVETS,  
BULGARIA



June 18, Tuesday

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**Morning session**

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**Subsession I: Electroactive polymers IV**

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**T. Schoetz**

*Understanding the charge storage mechanism of conductive polymers as hybrid battery-capacitor materials in ionic liquids*

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**A. Pailleret**

*Deepening of the characterisation of the electrochemo-mechanical behavior of conducting polymers using electrochemical atomic force microscopy*

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**J.P. Correia**

*Evaluation of the pseudocationic doping character of PEDOT:PSS towards Na<sup>+</sup> exchange. Discrimination of the mass transfer processes by coupling EQCM and PBD data*

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**Subsession II: Electroactive polymers V**

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**A.R. Hillman**

*Effect of deposition electrochemical control function on solvent content and spatial profile within conducting polymer films*

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**O.L. Gribkova**

*The role of polyelectrolytes during electrosynthesis of conductive polymers*

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**P. Chulkin**

*Electrochemical impedance spectroscopy monitoring of charge transport in conductive polymer film*

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## Effect of deposition electrochemical control function on solvent content and spatial profile within conducting polymer films

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The electrochemical deposition and properties of conducting polymer films and their application in electronic, optical, sensing and energy storage devices have attracted huge interest. However, the literature describing this research contains many apparent inconsistencies: nominally the same material prepared by different researchers is commonly found to have different properties. This is problematic in the development of these materials for practical applications. Qualitatively, this is often attributed to variations in film structure, but without defining the nature of these variations, their origins or their resilience (or otherwise) to redox cycling that would be typical of a functioning device.

One hypothesis that has been invoked is that different electrochemical control functions result in different nucleation and growth mechanisms and/or dynamics, generating films with different internal spatial structures and solvent profiles. However, since electrochemical techniques, spectroscopic methods and surface imaging methods are unable to probe these aspects, there has been little evidence produced to test this hypothesis.

Here we describe the use of *in situ* neutron reflectivity (NR) measurements to determine both overall film solvent content and its spatial profile through polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT) films. The NR technique is sensitive to isotopic substitution ("contrast variation"), which we exploit via H/D substitution in polymer or solvent (*e.g.*, *d*<sub>4</sub>-pyrrole polymerised from H<sub>2</sub>O solution) to provide contrast between the polymer and solvent components of the film. Measurements were made under conditions that generated films of similar *total* polymer population to eliminate effects due solely to film thickness.

In both PPy and PEDOT cases, we determined quantitative film solvation (both spatially resolved and integrated) for films deposited under potentiostatic (PS), potentiodynamic (PD) and galvanostatic (GS) conditions. These observations provide insights into film homogeneity and evolution during deposition, and the sharpness of the film/solution interface. *During deposition*, the effect of electrochemical control function is greater for PPy than for PEDOT. The longevity of these distinctions was explored *via* analogous observations *subsequent to deposition* (after transfer to background electrolyte), during which the films were redox cycled and allowed to relax. Interestingly, the outcomes for PPy and PEDOT were quite different. We discuss these findings in the context of applications in which film solvent distribution controls the dynamics of mobile species transport (*e.g.* dopant in an electro/optical device or analyte in a sensor) and of polymer spinal motion (*e.g.* in an actuator).

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