PÔSTER - RESUMO - DISPOSITIVOS ELETRÔNICOS, ELETROQUÍMICOS, SUPERCAPACITORES E BATERIAS

REAL-TIME ELECTROCHEMICAL SPECTROSCOPY MEASUREMENTS IN ITO/POLYANILINE ELECTRODES USING GPE ANALYSIS

Arthur Da Silva Zimermann (Ic); Ufsc (arthurzimermann0902@gmail.com)

Carleane Patrícia Da Silva Reis (carleanepsreis@gmail.com)

Maria Luisa Sartorelli (mluisa.sartorelli@gmail.com)

Françoise Toledo Reis (ftoledoreis@gmail.com)

In the context of the National Institute for Organic and Sustainable Electronics network, the focus of our team is the production and characterization of polymeric semiconductor electrodes for application in ionotronic devices such as batteries, supercapacitors, electrochemical light-emitting cells, and organic electrochemical transistors. Ionotronics is an emerging technology that explores the coupling between the ionic and electronic nature of materials, including modifications in their structure, composition, and their properties. A key aspect of these systems is the role of the electrode/electrolyte interface and the ability of ions to move along or across them. Therefore, determination of the capacitance of the electrodes is essential for device optimization. However, given the complexity of such interfaces, particularly when polymeric electrodes are involved, traditional dynamic analysis methods, such as cyclic voltammetry and charge/discharge tests, are insufficient for a complete description. Electrochemical impedance spectroscopy (EIS) is a perturbation technique which is able to distinguish between faradaic and non-faradaic phenomena

occurring at distinct frequencies. In this work, we employed a new impedance analysis method, developed at LabSiN/UFSC, named Generalized Phase Element (GPE), which extracts capacitance and resistance values of dispersive materials, without requiring interpretation through preconceived models [1, 2]. The GPE method performs differential analysis of impedance spectroscopy data, enabling nearly instantaneous and frequency dispersion-free determination of capacitance and conductivity. Through GPE, real-time characterization of non-stationary interfaces becomes possible, opening opportunities for studying systems that evolve over time under external parameters such as electric field, temperature, or illumination. This allows quantification of charge accumulation and transfer processes across different frequency ranges, providing information about active charge carriers. In this work electrochemical polymerization of aniline (PANI) was carried out on indium tin oxide (ITO) substrates, using trifluoroacetic (TFA) or nitric (HNO3) acid as dopants, while simultaneously acquiring 60 consecutive electrochemical impedance spectra (Autolab/Metrohm potentiostat with FRA module). A fixed electric potential of +0.8 V/SCE was applied throughout the process, to promote oxidation of the aniline monomer. The objective was to monitor, in real time, the evolution of the electrochemical response during formation of the PANI film. Morphological characterization by scanning electron microscopy (SEM) revealed formation of a fibrillar PANI network (200–500 nm diameter), homogeneously covering the electrode surface. This fibrillar morphology is directly associated with high specific surface area, which favors charge storage and transfer processes. Sequential impedance measurements showed a transition from the dominance of ITO to PANI behavior. A capacitance plateau at low frequencies (1–2 Hz), between 1–5 mF/cm², was observed, along with a high-frequency plateau (300 Hz–10 kHz), between 4–5 μF/cm². The low-frequency plateau may arise from two simultaneous processes: (i) formation of the electrical double layer around PANI fibers and (ii) protonation of PANI, leading to polaron/bipolaron formation. Temporal analysis showed an increase in this capacitance, which is consistent with the increased volume of deposited PANI. Meanwhile, the real impedance decreased, shifting the system’s characteristic frequency to values below 1 Hz. The high-frequency capacitance plateau does not change significantly with time, but shifts toward higher frequencies, most likely due to reduced real impedance as the polymer film thickens.

Acknowledgements: INCT/INEO, FAPESP (2025/27044-5), CNPq (408449/2024-1) and CAPES.

[1] M. L. Sartorelli et al. “Model-free impedance analysis of electrodes with a 2D+1D

dispersion of time constants”, Eletrochimica Acta 390 (2021) 138796.

[2] A. M. C. Gomes et al. “The electrochemical hydroxylation of H-terminated n-Si as revealed by a generalized phase analysis of EIS: Real time detection”, Journal of the

Electroanalytical Chemistry 984 (2025) 119025.

Palavras-chave: electrochemical impedance spectroscopy; polyaniline; generalized phase element analysis; real-time electrochemical characterization; capacitive processes.