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Simultaneous quartz microbalance and mirage effect studies of poly(3-methoxythiophene) electrosynthesis and electrochemical characterisations

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ABSTRACT

This work characterises the electropolymerisation of 3-methoxythiophene and presents an electrochemical study of poly(3-methoxythiophene) by cyclic voltammetry using different electrolytes in solvent mixture of water-acetonitrile (3:1, v/v) at 25 °C. Simultaneous measurements of the mirage effect and the quartz microbalance were also performed. This study evaluated the influence of cations on the electrochemical properties of monomers and polymers and allowed us to observe an anomalous behaviour of the synthesised polymer in the presence of potassium ions (K^+) when compared with other cations. The reversibility of the polymers was also evaluated with respect to the various electrolytes and was observed the influence of the polymer film thickness (deposited mass) on its electrochemical properties.

1. Introduction

Organic electronics is currently one of the most promising technological fields [1,2]. The possibility of obtaining low-cost, flexible materials and conjugated polymers (CPs) is promising in several areas, such as the development of flexible solar cells [3], polymeric light-emitting diodes [4], transistors, and other applications.

The electrochemical properties of these materials must be determined for their application in the electronics. The factors affecting these properties should be determined, along with the influence of the external environment on the properties of the final material. It is also necessary to assess the properties and redox behaviours of CPs in electrochemical cells during electropolymerisation.

In this study, the electropolymerisation of the monomer 3-methoxythiophene (MOT) was evaluated using cyclic voltammetry. The same anion was used as the electrolyte (perchlorate ion, ClO_4^-), and but different alkaline metal cations (Li^+, Na^+, K^+, Rb^+, and Cs^+) were employed to evaluate the influence of the cation size. Studies of the mirage effect and the quartz microbalance were conducted simultaneously during the electropolymerisation and electrochemical characterisation of the film. The flow of the electroactive species/electrolytes during the electropolymerisation of 3-methoxythiophene was monitored, and the electrolytes were characterised while analysing the redox behaviour of PMOT to obtain important information on the influences of the electrolyte on the growth of the film and the electrochemical profile of the materials.

One can find in the literature studies about the influence of ionic exchanges on properties of inorganic films deposited on the surface of electrodes, such as Prussian blue derivatives [5–8]. However these works, that show the input and output cations of the film due to changes in the oxidation state of iron in the material structure, not study the ion exchange during the electrodeposition.

2. Experimental

2.1. Reagents and solvents

Lithium perchlorate ($LiClO_4$), sodium perchlorate ($NaClO_4$), potassium perchlorate ($KClO_4$), rubidium perchlorate ($RbClO_4$), caesium perchlorate ($CsClO_4$)) and 3-methoxythiophene were purchased from Aldrich. The acetonitrile used to prepare the electrolyte solution was obtained from Vetec. All solutions were prepared using distilled water.

2.2. Utilised apparatus

The system used for this study was adapted from the literature [9,10]. The electrochemical data were obtained using a digital Omnimetra PG-39 potentiostat. The electrochemical cell consisted of a glass cuvette with an optical pathlength of 30 mm

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obtained from Biocell and three electrodes. A quartz crystal AT-cut 5 MHz QCM (Stanford Research Systems) with a circular film of platinum/titanium (Pt/Ti) was used as the working electrode. A platinum wire was used as the auxiliary electrode, and a silver wire was used as the quasi-reference electrode. A QCM200 from Stanford Research Systems was used as the quartz microbalance.

The mirage effect apparatus consisted of a 633 nm, 2 mW HeNe laser. The laser beam diameter at the lens focal point was approximately 32 μm, and the beam was parallel to the working electrode. The positive deflections indicated that the ions diffused within the solution to the electrode surface, whereas the negative deflections indicated that the ions diffused from the electrode surface to the bulk solution.

2.3. Poly(3-methoxythiophene) electrodeposition and characterisation by quartz microbalance, cyclic voltammetry and mirage effect

The poly(3-methoxythiophene) (PMOT) electrodeposition was performed as described in a previous work [11]. A 35 mmol L^{-1}

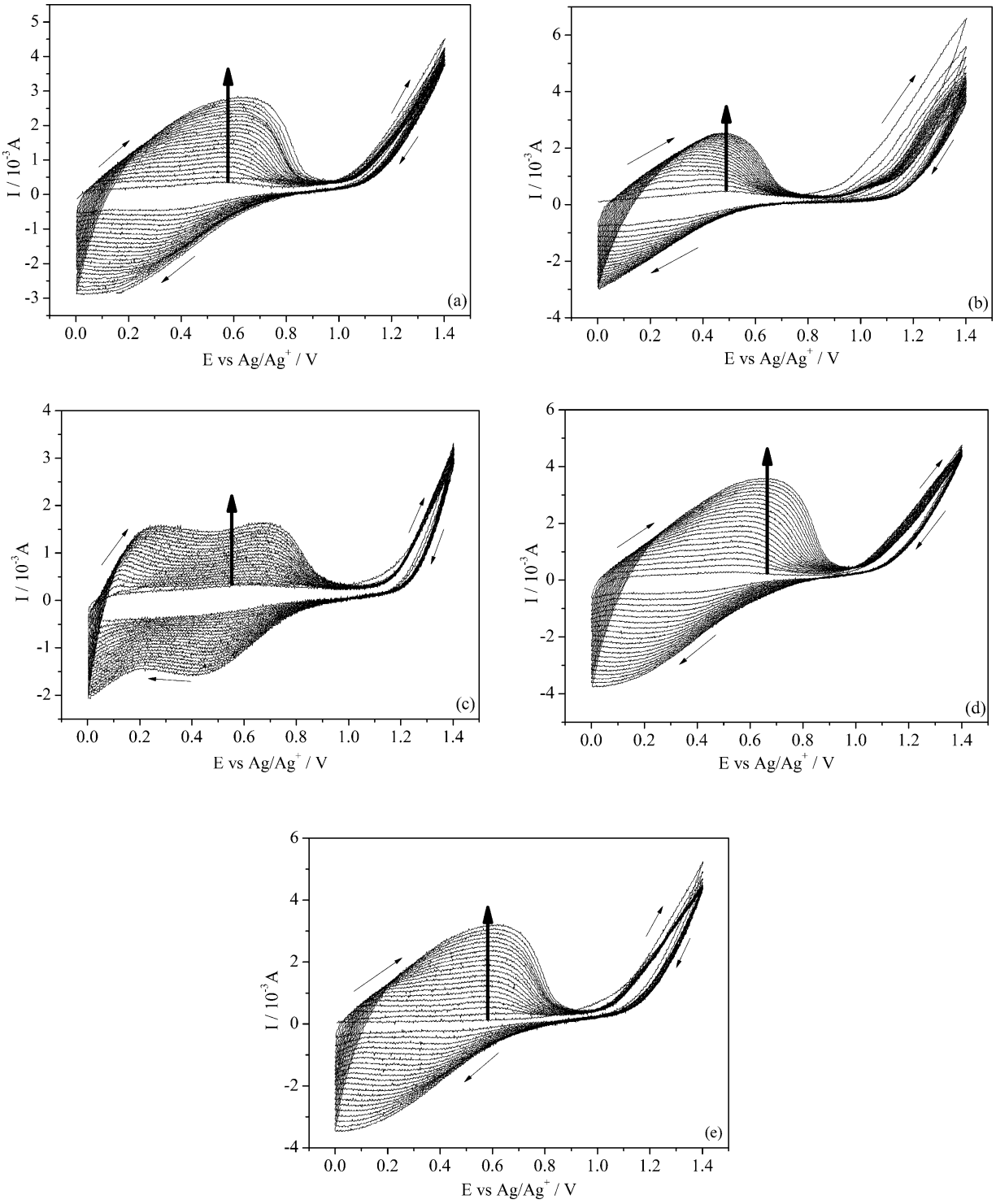

Fig. 1. PMOT electrodeposition voltammograms with different electrolytes: (a) $LiClO_4$, (b) $NaClO_4$, (c) $KClO_4$, (d) $RbClO_4$, and (e) $CsClO_4$.