IN SITU IR-ATR-SPECTROSCOPY OF ELECTRODE SURFACES

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Résumé - Dans ce papier on présente une méthode rapide pour l'étude *in situ* des surfaces d'électrodes en contact avec un électrolyte, utilisant la spectroscopie infra-rouge à transformée de Fourier. On étudie les réactions électrochimiques de substances organiques polymérisées conductrices, par spectroscopie en réflexion totale atténuée utilisant des éléments réflecteurs semiconducteurs recouverts de couches minces métalliques évaporées. On discute quelques résultats sur le processus d'oxydation de films de polymères hétéroatomiques sur des couches minces de platine.

Abstract - In this paper a fast method for *in situ* investigations of electrode surfaces in contact with an electrolyte using Fourier transform infrared spectroscopy is demonstrated. With attenuated total reflection spectroscopy (ATR) using semiconducting reflection elements with evaporated thin metal layers the electrochemical reactions of conducting polymerized organic substances are investigated. Some results on the oxidation process of heteroaromatic polymer films on thin platinum layers are discussed.

In the last years extensive research work has been done in the field of *in situ* investigations of electrodes in contact with an electrolyte /1/. A characteristic point of all proposed and applied techniques is the possibility to characterize an electrode in contact with an electrolyte at definite potentials or during controlled electrochemical experiments, e.g. cyclic voltammetry.

Most of these methods use electromagnetic waves as stimulation and detection signals, e.g. light in the uv or visible spectral range (ellipsometry, reflection spectroscopy) or infrared radiation. Spectroscopic investigations in the infrared spectral range can yield information about the molecular structure of the electrode surface and the strength of the chemical bonds of adsorbed species.

Some methods have been developed, such as EMIRS (electrochemically modulated infrared reflectance spectroscopy) /2/ and IRRAS (infrared reflectance absorption spectroscopy) /3/. Another approach to obtain the infrared spectra of an electrode surface is the attenuated total reflection spectroscopy (ATR) /4/. In this case semiconducting reflection elements, e.g. germanium, silicon or cadmium telluride, are used. The working electrode in electrochemical cells consists of one of these reflection elements covered with a thin metallic layer /5/. This metallic layer can be used as a substrate material for other reactions, e.g. polymerization of organic substances. For our investigations of the oxidation reactions of polymerized heteroaromatic substances (3-methylthiophene and thiophene) we use thin platinum layers. By means of Fourier transform infrared spectroscopy rapid changes of the surface during dynamic electrochemical experiments can be detected.

In figure 1 the typical radiation path in the spectroelectrochemical cell is demonstrated. The cell is made from teflon and is constructed as a flow cell, as de-

Fig. 1: Path of radiation in the spectroelectrochemical equipment.

scribed earlier /6/. The counter electrode is a platinum foil, the reference electrode a saturated calomel electrode (SCE) or a silver/silvernitrate electrode in acetonitrile. After improving the sealing of the cell it was possible to work with an evacuated spectrometer (FTIR spectrometer Bruker IFS 113V, Karlsruhe, FRG) to eliminate instabilities caused by flushing the instrument with inert gas. The electrochemical equipment consisted of a potentiostat (60TB, Jaisle, FRG), a sweep generator (PPRI, HiTekInstruments, UK) and a X-Y-plotter (29000A3, Bryans, UK).

The polymerization reactions were performed in a 0.4 molar solution of 3-methylthiophene or thiophene in acetonitrile with tetrabutylammoniumperchlorate (0.1 molar) as supporting electrolyte. The polymerization starts at anodic potentials (+1.5 V against SCE, respectively +1.3 V against Ag/AgNO₃ in the case of thiophene) and the polymers are produced in the conducting oxidized form on the platinum layer. The oxidized forms were reduced to the non-conducting neutral forms by applying a potential of 0.0 V against SCE (-0.5 V against Ag/AgNO₃) on the working electrode. The obtained polymer film can be oxidized and reduced repeatedly during cyclic voltammetric experiments. The potential sweep applied to the cell was 2 mV/sec, the potential limits were 0.0 V and +1.0 V against SCE for 3-methylthiophene, in the case of thiophene -0.5 V and +1.0 V against Ag/AgNO₃. Interferograms were measured during the oxidation and reduction half cycle. In a potential range of about 30 to 40 mV a number of interferograms were added and stored on a disk. This adding of interferograms before performing the Fourier transformation is necessary to improve the signal/noise ratio of the spectra.

In figure 2a the cyclic voltammogram of a polythiophene layer on the platinum electrode is displayed. Figure 2b shows the infrared spectra obtained during the oxidation. The reference spectrum for this plot, which is subtracted from each curve, is the spectrum of the electrolyte and was recorded before starting the polymerization. The absorption of the polymer on the platinum electrode increases very strongly during the oxidation process and is related to the change in the electrical behaviour. Furthermore some typical vibration bands occur additionally to the bands of the neutral form. The strong intensity of the bands growing during the oxidation may be explained by a vibronic intensity enhancement effect similar to the effect obtained during the doping process of polyacetylene /7/.

In figure 3 the infrared spectra measured during the oxidation process of a poly-3-methylthiophene layer on a platinum electrode is displayed. The insert shows the cyclic voltammogram of this layer. In this case the reference spectrum is the spectrum of the neutral form of the polymer in contact with the electrolyte. Corresponding to the increase of the electrical conductivity the infrared absorption of the film increases and some characteristic vibration bands occur during the oxidation process. These bands have no counterparts in the neutral form and increase with the electrochemical oxidation process. Additionally the intensities of some bands grow with different rates during the oxidation process. A band at 1100 cm⁻¹ occurs in the high oxidation state. This band is associated with the ClO₄⁻ anion /8/, and results from the intercalation of perchlorate anions into the polymer film during the oxidation process /9/. An exact interpretation of all

Fig. 2a: Current density/potential curves:

----- electrochemical polymerization of thiophene (sweep rate 2 mV/sec)

—— oxidation and reduction of the polythiophene layer (sweep rate 2 mV/sec)

Fig. 2b: ATR-IR-spectra recorded during the oxidation of polythiophene. Each spectrum originates from 20 added interferograms. Reference spectrum: electrolyte solution. The inserted potential values refer to the cyclic voltammogram in Fig. 2a.

Fig. 3: ATR-IR-spectra recorded during the oxidation of poly-3-methylthiophene. Each spectrum originates from 128 added interferograms, reference spectrum is the spectrum of the neutral form of poly-3-methylthiophene.

The insert shows the cyclic voltammogram of the oxidation and reduction of the poly-3-methylthiophene layer.

vibration bands of the polymer and of their behaviour during the oxidation process (shift of the maxima e.g.) cannot be described at this moment, but work is carried out to get more information about the structure and the normal vibration modes of these organic conducting polymers.

The ATR spectroscopy in combination with a fast Fourier transform equipment allows to get information of an electrode surface in the infrared spectral range during dynamic electrochemical experiments and is suitable for the characterization of reaction products and the elucidation of reaction mechanisms.

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