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Microscopic in situ diffuse reflectance spectroelectrochemistry of solid state electrochemical reactions of particles immobilized on electrodes

Abstract An instrumental setup is described which allows electrochemical measurements to be performed with solid particles immobilized on the surface of a graphite electrode with in situ recording of diffuse reflectance spectra under an incident light microscope. The instrument used includes a special electrochemical cell and a microscope which is interfaced by a light guide to a transputer-integrated photodiode-array spectrometer allowing measurements ranging from 320 to 950 nm with a resolution of 3.2 nm/pixel and a PC-interfaced potentiostat. The $0R_0$ geometry of the optical arrangement and the use of crossed polarization filters for blocking specular reflectance makes it possible to use the Kubelka-Munk function for quantifying the optical measurements. The above instrument has been used for the study of the electrochromic system of solid silver octacyanomolybdate(IV/V) adjacent to a silver nitrate solution. The in situ diffuse reflectance spectroelectrochemical measurements prove that the electrochemical reaction starts at the graphite/sample interface and then advances into the bulk of the sample towards the sample/electrolyte interface. The ratios Red:Ox determined by spectrometry and chronocoulometry as a function of electrode potentials are identical.

Key words Spectroelectrochemistry · Diffuse reflectance spectrometry · Solid state electrochemistry · Voltammetry · Microscopy

Introduction

To acquire a complete understanding of chemical processes, the application of in situ combinations of different techniques has proved to be very powerful. This holds true also of electrochemical reactions where

a number of special restrictions exist. Thus, electrochemical reactions are often performed at ambient temperature and pressure, and they require a metal/electrolyte solution interface. There are several restrictions which prevent the real-time in situ application of all vacuum spectrometric techniques employing electrons, ions or atoms for excitation or detection. Optical spectroscopy in the UV-VIS range lends itself very well for in situ studies of electrochemical reactions, provided the reacting species are soluble and absorb light [1]. If the redox pair is confined to a solid phase, optical spectrometry can be applied using optically transparent electrodes, e.g. indium-tin oxide layers on glass [2]. However, the coating of optically transparent electrodes with a solid electrochromic substance is an art in its own right, and there are no generally applicable ways of doing this. Further, the optically transparent electrodes can easily impair the electrochemical response because of high ohmic resistance. It would be highly desirable to have a technique on hand which allows the electrochromism of solids to be studied without facing the above-mentioned restrictions and difficulties, even on a microscale, if possible, with single particles having a size between 10 and 100 μm . In the present paper, a combination is described which meets all these requirements and is based on the following approach:

1. The solid particles of the studied compound are immobilized by mechanically embedding them in the soft surface of a polished graphite electrode (abrasive stripping voltammetry technique [3, 4])
2. The electrode is mounted in an appropriate electrochemical cell which allows the surface to be observed under an incident light microscope equipped with polarizing filters.
3. The incident light microscope is interfaced by a light guide to a diode array spectrometer.

The electrode surface is illuminated by the 100 W halogen incandescent lamp of the microscope, and the spectrometer measures the diffuse reflected light from the electrode surface, provided that the detection of the

specular reflectance is minimized by polarizing filters. The performance of this method combination has been studied using silver octacyanomolybdate and octacyanotungstate as electrochromic compounds. This real-time in situ VIS-reflectance spectroelectrochemistry allows new insights into the mechanism of the observed solid-state electrochemical reactions to be obtained.

Experimental

Chemicals

Silver octacyanomolybdate(IV) was prepared by precipitating stoichiometric amounts of silver nitrate with a potassium octacyanomolybdate(IV) [5] solution. Silver octacyanomolybdate(V) was precipitated from a potassium octacyanomolybdate(V) solution which was prepared by oxidizing potassium octacyanomolybdate(IV) with permanganate. The results of chemical analysis were as follows: $C_{\text{exp.}}/C_{\text{calc.}}$ 12.64/13.06, $N_{\text{exp.}}/N_{\text{calc.}}$ 14.50/15.33 for $\text{Ag}_4[\text{Mo}^{\text{IV}}(\text{CN})_8]$, which agrees with literature [6], and $C_{\text{exp.}}/C_{\text{calc.}}$ 15.05/15.31, $N_{\text{exp.}}/N_{\text{calc.}}$ 17.26/17.93 for $\text{Ag}_3[\text{Mo}^{\text{V}}(\text{CN})_8]$. There are no data accessible on the solubility of silver octacyanomolybdate, but the latter is generally regarded as extremely insoluble.

All electrolyte solutions were prepared with twice-distilled and ion-exchanged water. The electrolyte salts were of analytical grade: Silver nitrate (VEB Feinchemie Apolda, former GDR), Prussian blue (Heyl Chem.-pharm. Fabrik, Berlin, Germany). For the preparation of mixtures of Prussian blue with magnesium oxide, different ratios of both substances were mixed in a ball mill for twenty minutes.

Experimental setup for in situ diffuse reflectance spectroelectrochemical measurements

Figure 1 schematically shows the experimental setup for spectroelectrochemical measurements. The instrumentation consists of four main parts: (A) potentiostat, (B) incident light microscope, (C) spectrometer, (D) cell unit.

A Potentiostat

The electrochemical measurements were performed with an Autolab PGSTAT 20 (ECO-Chemie, Utrecht, Netherlands) interfaced to a 386 PC.

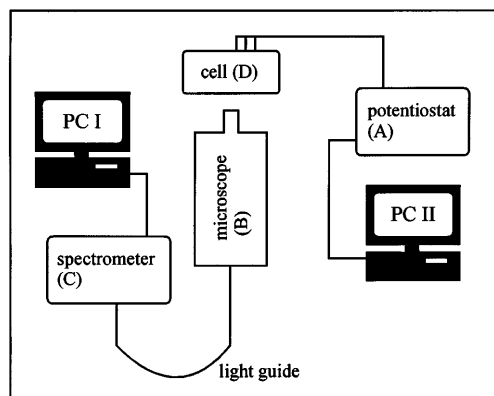


Fig. 1 Schematic view of the instrumentation for in situ diffuse reflectance spectroelectrochemical measurements

B Microscope

A Leitz Laborlux 12 POL S incident light microscope (Leica Mikroskopie und Systeme Germany) with a 100 W halogen incandescent lamp serving as an interface between electrochemistry and spectrometry (Fig. 2). Two crossed linear polarizing filters minimized the detection of specular reflectance. The above setup allowed the reflected light to be guided either to the oculars (to choose a sample spot and to control the focus) or to the spectrometer. The spectrometer is coupled via fiber optics. The microscope allowed a 500-fold magnification, but in conjunction with the electrochemical cell the maximum magnification was 200. This restriction is a result of the distance between the electrode surface and the objective lens caused by the glass window and the electrolyte layer between them.

C Spectrometer

The spectrometer was a transputer-integrated diode array system (TIDAS) (J&M Analytische Mess- und Regeltechnik, Ahlen, Germany) with a spectral range of 320–950 nm. The number of photo-diodes was 256 and the resolution 3.2 nm/pixel. The spectrometer was interfaced to a Pentium personal computer.

D Cell unit

Figure 3 shows a cross section through the electrochemical cell. The cell body is made of acrylic. The electrochemical setup is realized by a conventional three-electrode arrangement. The reference electrode (RE) is a silver/silver chloride electrode (3 mol/l KCl, $E = 208$ mV versus the standard hydrogen electrode, SHE); the auxiliary electrode (AE) is a platinum wire. A paraffin-impregnated graphite electrode, PIGE, served as a working electrode (WE).

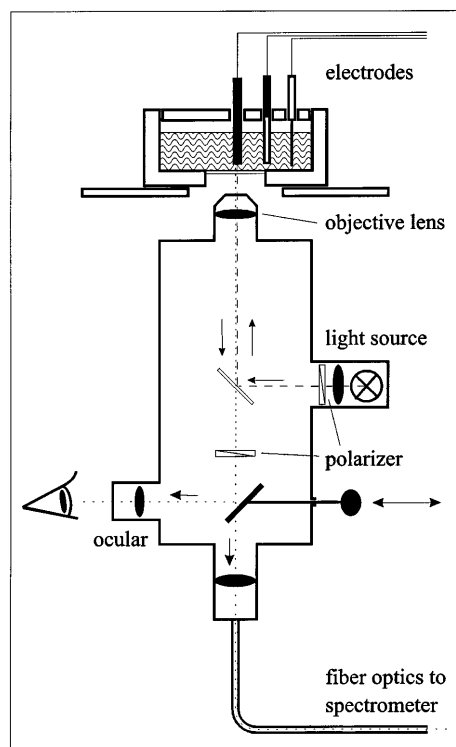


Fig. 2 Cross section of the incident light microscope and the electrochemical cell

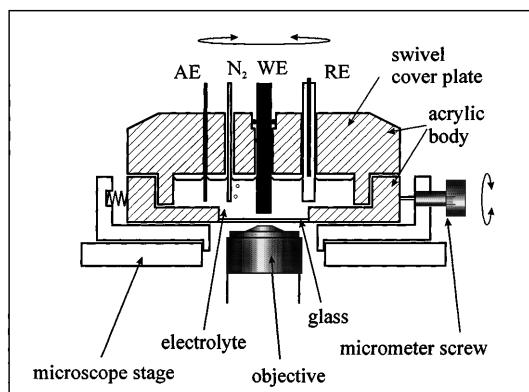


Fig. 3 Cross section of the electrochemical cell for in situ reflectance spectroelectrochemistry

The immobilization of solid particles on the surface of the working electrode was achieved in the usual manner [3, 4], i.e. small amounts of the sample powder were placed onto a clean surface (e.g. glass plate or filter paper) and the surface of the electrode was gently rubbed or pressed on the sample. For varying the thickness of the layer of immobilized particles, several electrodes were prepared, and the appropriate layers were singled out by microscopic measurements.

The electrode is then introduced into the cell through the cover plate in such a way that the lower electrode surface is parallel to the glass window at the bottom of the cell. This glass plate (3 mm thick) enables the observation of the electrode surface via the microscope. The use of a 20-fold magnifying objective results in a 200-fold magnification (using 10-fold magnifying oculars). If the latter objective is used, a surface area of about 0.7 mm² will be accessible for spectrometry. This area can be reduced to 0.05 mm² by closing an aperture. With the help of a micrometer screw, the entire cell can be moved in one direction (*x*) to adjust the sample spot to the optics. The electrode sits in the center of a swivel cover plate which, when turned by 90°, allows an adjustment in the perpendicular direction (*y*) just with the same micrometer screw. On the opposite site of the micrometer screw, a spiral spring presses against the electrochemical cell body.

The instrumental setup comprising the incident microscope and the spectrometer leads to a $0^\circ R_0$ geometry of the optical path. This means that the incident and reflected light beams are exactly in the azimuth. For measuring the diffuse reflected light, the large amount of regular reflected light had to be minimized. Therefore, two polarizing filters (foils) were arranged in crossed position (90°). The optical properties of this very unusual configuration had to be studied before an application with regard to an electrochemical problem became possible.

Experimental setup for ex situ spectrometry

For the recording of remission spectra of dry substances, approximately 20 mg of the diluted sample were sandwiched between two glass plates of 3 mm thickness. This "sandwich" then replaced the electrochemical cell on the microscope stage and the sample spot was adjusted to be in the focus of the microscope lens. Magnesium oxide served as a reference substance.

Chronocoulometric measurements

Chronocoulometry was used to determine the ratio of Mo(IV) to Mo(V). Therefore, the amount of consumed charge was measured after certain potential steps. This experimental approach has been published elsewhere [7].

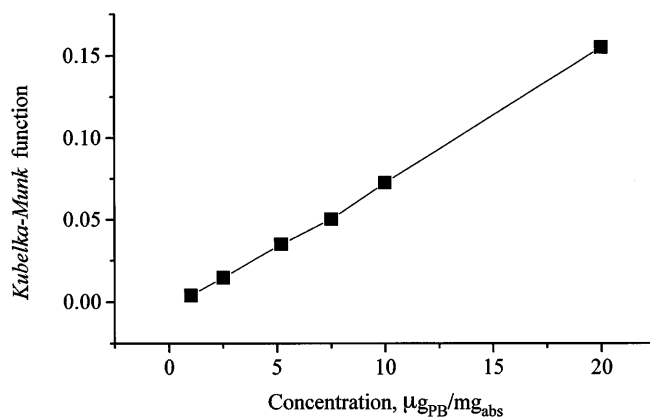


Fig. 4 Dependence of the Kubelka-Munk function on the concentration of Prussian blue in magnesium oxide at a wave length of 690 nm

Results and discussion

Optical and spectrometric characterization of the instrumentation

Test of the validity of the Kubelka-Munk function for ex situ measurements

As the present setup strongly deviates from that of conventional diffuse reflectance spectrometry [8], the question arises whether the Kubelka-Munk function (Eq. 1) is followed, at least for small concentrations of the absorbing compound in a thick layer of solid material. The Kubelka-Munk function $F(R_\infty)$ takes into account the two major processes (a) light absorption and (b) light scattering:

$$\frac{K}{S} = \frac{(1 - R_\infty)^2}{2R_\infty} \equiv F(R_\infty) \quad (1)$$

(K = absorption coefficient, S = scattering coefficient, R_∞ = reflectance of a sample of infinite thickness).

This was tested by measuring a number of powder samples containing different concentrations of Prussian blue in magnesium oxide. The Kubelka-Munk function was then calculated for a wavelength of 690 nm. The result shown in Fig. 4. $F(R_\infty)$ is linear up to a concentration of 20 $\mu\text{g}/\text{g}$ MgO. The slope in the double logarithmic plot is 1.1, which agrees reasonably well with the expected direct proportionality between the concentration of the colored compound and the Kubelka-Munk function. These experiments show that the optical arrangement with a directed and spot-like illumination and measurement of the reflected light at 0° relative to the incident beam yields results which obey the Kubelka-Munk theory to a remarkable extent. Thus, the optical requirements are met for using the Kubelka-Munk function for a quantification of solid-confined redox pairs.

Applicability of the Kubelka-Munk function to in situ measurements

The Kubelka-Munk function has been derived for determining diluted solid compounds in a thick layer [9]. In the case of in situ spectroelectrochemical measurements of mechanically immobilized microparticles, it is neither possible to dilute the compound nor will the thickness of the layer always be sufficient to cover the electrode optically. Taking silver octacyanomolybdate(IV) and -(V) as examples, the results of in situ spectrometry are compared to the spectra of dry and MgO-diluted samples. Figure 5a shows the Kubelka-Munk functions of silver octacyanomolybdate(IV) and -(V) recorded ex situ with the MgO-diluted and dry compounds. For the sake of comparison, Fig. 5b depicts the Kubelka-Munk functions of these two compounds when they are immobilized as microparticles on the surface of a paraffin-impregnated graphite electrode. In this case the electrode was also covered by a layer of an aqueous 0.1 M AgNO₃ solution as electrolyte. A comparison of Fig. 5a with 5b reveals that the dry and MgO-diluted samples give a much better resolved spectrum than the undiluted compounds covered with an electrolyte film. The effect of the electrolyte solution on the resolution is negligible as this solution

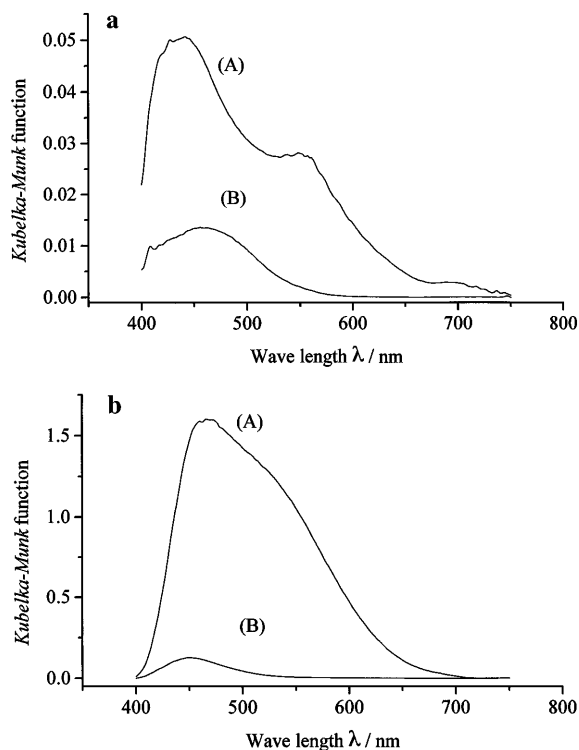


Fig. 5a, b Kubelka-Munk functions of (A) silver OCM(V) and (B) silver OCM(IV) (a) Spectra of the dry compounds diluted in MgO (1:50) and measured ex situ. (b) Spectra of Ag OCM(IV,V) immobilized on a graphite electrode, covered by a layer of 0.1M AgNO₃ and measured in situ. The oxidized species Ag OCM(V) was electrochemically formed from Ag OCM(IV)

layer mainly alters light scattering, which depends much less on wavelength than does the absorption. From what is known about the solution spectra, the absorption bands of Ag₄[Mo^{IV}(CN)₈] are d ↔ d transitions [10]. The spectrum of Ag₃[Mo^V(CN)₈] is most probably due to a Mo^V ↔ Ag^I charge transfer as the intense color is only observed in the solid compound and not in OCM(V) solutions.

The most important conclusion from the above comparison of the spectra in Fig. 5 is that the in situ recording of the spectra of the pure compounds on the electrode surface allows an unambiguous identification of the redox pairs, although the resolution is slightly impaired. It will later be shown that the Kubelka-Munk values which are measured during the continuous oxidation of solid octacyanomolybdate(IV) to -(V) are almost linearly correlated with the concentration of the absorbing species in the solid matrix.

The Kubelka-Munk $[F(R)_\lambda]$ values have been used for the calculation of the Red:Ox ratio as follows:

$$\frac{c_{\text{ox}}}{c_{\text{red}}} = \frac{\frac{(F(R) - F'_{\text{red}})}{(F'_{\text{ox}} - F'_{\text{red}})}}{\left(1 - \frac{(F(R) - F'_{\text{red}})}{(F'_{\text{ox}} - F'_{\text{red}})}\right)} \quad (2)$$

($F'_{\text{ox/red}}$ are the values of the Kubelka-Munk function at 530 nm for $c_{\text{ox}} = 1$ and $c_{\text{red}} = 1$, $F(R)$ is the actual value of the Kubelka-Munk function for a certain Red:Ox ratio.)

Spectroelectrochemistry of silver octacyanomolybdate (IV/V)

Figure 6 depicts cyclic voltammograms of silver OCM(IV) in a silver nitrate electrolyte solution. With silver nitrate as the electrolyte, the following chemical reversible redox system can be observed:

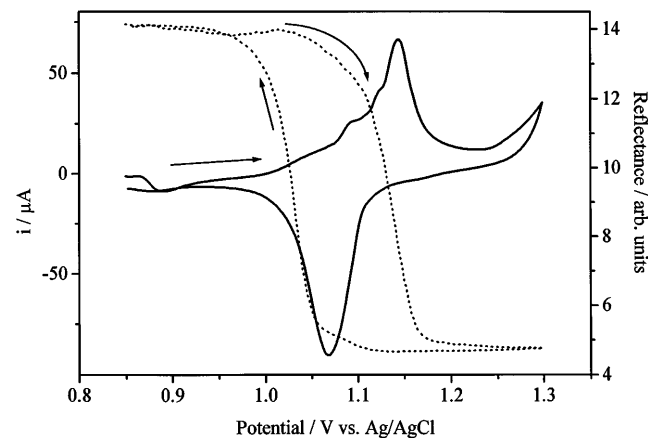


Fig. 6 Cyclic voltammogram (full line) of Ag OCM(IV/V) in 0.1 M AgNO₃ (scan rate 1 mV/s) and the trace of the reflectance measured in situ (dotted line, $\lambda = 550$ nm) versus potential. The thickness of the Ag OCM(IV/V) layer was about 10 μm

$\{\text{Ag}_4[\text{Mo}^{\text{IV}}(\text{CN})_8]\} \rightleftharpoons \{\text{Ag}_3[\text{Mo}^{\text{V}}(\text{CN})_8]\} + \text{Ag}^+ + \text{e}^-$
(The species enclosed by braces are solid.)

In the case of potassium ions containing electrolytes, it is more difficult to control the electrode reaction, as at positive potentials an irreversible destruction of the solid compound occurs [11] which does not appear with an electrolyte containing silver ions. This will be described in detail in a forthcoming paper. The cycling of silver OCM between the +4 and +5 oxidation states of molybdenum is accompanied by a pronounced electrochromism, with the +5 compound possessing a larger absorption (see Fig. 5). Therefore, Fig. 6 also includes traces of the absolute intensity of reflected light at 550 nm as a function of the potential. This figure shows cyclic voltammograms for two different layer thicknesses with reflectance recorded in situ. For a better analysis of the main features of the reflectance measurement, the dR/dE derivative is more straightforward. Figure 7 shows that for a thin layer (about 1 μm thickness) the dR/dE ratio closely follows the current of the cyclic voltammogram with almost equal

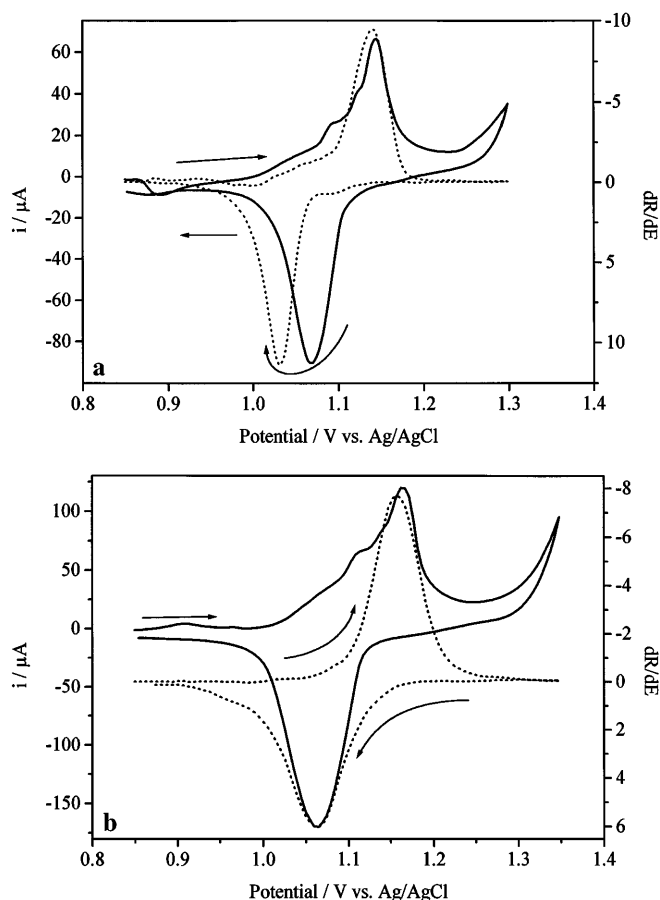


Fig. 7a, b Cyclic voltammogram (full line) of Ag OCM(IV/V) in 0.1 M AgNO_3 (scan rate 1 mV/s). First derivative of the reflectance over the dR/dE potential (dotted line) versus potential. (a) The reflectance was measured for a sample layer of about 10 μm thickness (b) The reflectance was measured for a sample layer of about 1 μm thickness

positions of the peaks. However, for a thick layer (10 μm), the dR/dE value is strongly retarded during the reduction but closely follows the current during the oxidation. Even the fine structure of the oxidation currents is visible in the dR/dE curve in the case of the thick layer. From Fig. 7, it follows that the determination of the formal potential of an electrochromic redox pair by diffuse reflectance measurements is feasible. The necessary prerequisite for this is that the layer thickness is small, as only in this case is there a coincidence of peak potentials between optical and electrochemical measurements. The retardation of the dR/dE dependence on the potential scale for the case of a thick sample layer can easily be derived from the schematic drawing in Fig. 8. In principle, one could suppose that the oxidation of solid Ag OCM(IV) may start either at the graphite-sample interface or at the sample-electrolyte interface. The same holds true of the reduction of Ag OCM(V). However, only in the case where the reaction advances from the graphite-sample interface into the sample can one explain the optical behavior as follows: Upon oxidation, a layer of higher optical density grows from the graphite OCM interface, and the incident light beam can fully penetrate the upper layer of optically less dense Ag OCM(IV). Thus, the incident light will be less reflected the thicker the Ag OCM(V) layer becomes. If the opposite case were true, i.e. if the optically less transparent layer grew from the solution OCM interface downwards, the reflectance would decrease to its minimum before the electrochemical reaction reaches the graphite interface. Obviously, this does not happen. But, upon reduction of the optically dense Ag OCM(V), especially in the case of a thick sample layer, the effect of electrochemical reduction is mirrored by the reflection only with strong retardation. This is the result of a growth of the optically less dense layer from the graphite interface in the direction of the solution interface. These in situ measurements give a clear answer to the question of how the solid state electrochemical reactions proceed geometrically. The reason for this growth mechanism is most probably that the compounds have a low electronic

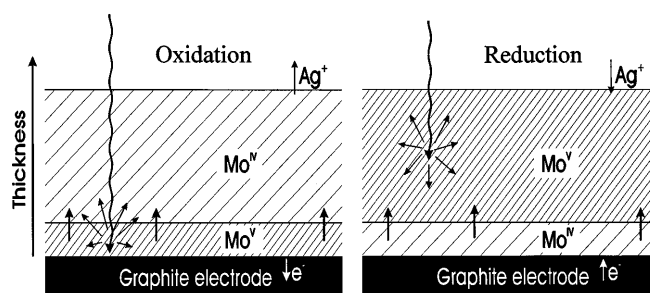


Fig. 8 Schematic drawing of a model for layer growth and light penetration for the processes of oxidation and reduction of silver octacyanomolybdate immobilized on an electrode surface. This scheme is based on the fact that the absorption coefficient of Ag OCM(IV) is much smaller than that of Ag OCM(V)

conductivity, which prevents the sample phase from assuming the potential of the graphite. The size of the Ag OCM(IV) crystals is so small that no single crystals are visible under the microscope. This means that the measurements were performed with patches of crystals, which raises the question whether the growth mechanism is valid only on a macroscopic scale. A difference between the microscopic and macroscopic growth mechanisms would only be understandable if there were a very slow intercrystal reaction rate, which is rather unlikely.

Figure 9a,b shows plots of the logarithm of the Red:Ox ratio as derived from multistep chronocoulometric measurements and also from in situ diffuse reflectance spectro-electrochemical measurements. Both methods practically yield the same results. Starting with the reduced form of $\text{Ag}_4[\text{Mo}^{\text{IV}}(\text{CN})_8]$ and stepping the potential in the positive direction (Fig. 9a), the slope of this plot is almost Nernstian (68 mV) over a limited potential range, i.e. between 1.02 and 1.1 V. At more positive potentials the plot deviates strongly from the Nernstian slope. When the experiment starts with the oxidized form and potential steps are made in the negative direction (Fig. 9b), then the chronocoulometry gives a slope of 65 mV in the same potential range as in the case of oxidation. The non-Nernstian slope of $\log(\text{Mo}^{\text{V}}/\text{Mo}^{\text{IV}})$ vs. E at potentials between 1.1 and 1.18, i.e. around the anodic peak potential (cf. Figs. 6 and 7) will be described in a forthcoming paper.

Conclusions

This study shows that microscopic diffuse reflectance spectroelectrochemistry can be performed with solid compounds on an electrode surface. Such measurements can substantially help to elucidate the mechanism of electrode reactions. They facilitate the study of electrochromic systems, as there is no need to deposit the electrochromic compound on the surface of transparent electrodes.

In the case of silver octacyanomolybdate, microscopic reflectance spectroelectrochemistry showed that the electrode reaction always starts at the graphite/compound interface and advances toward the compound/solution interface. Optical measurements are in very good agreement with chronocoulometric measurements.

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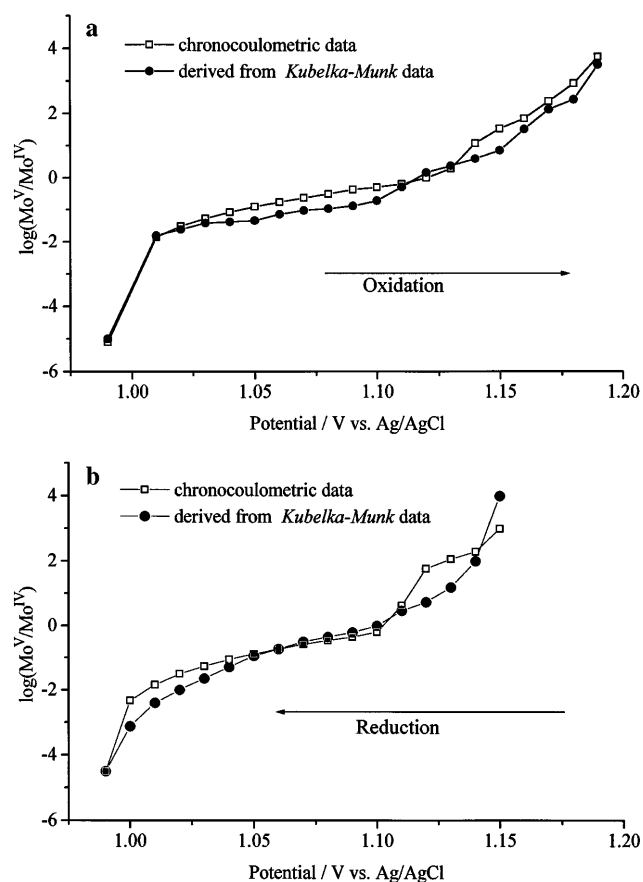


Fig. 9a, b Comparison of the plots $\log(c_{\text{ox}}/c_{\text{red}})$ versus the electrode potential as determined by chronocoulometry (squares) and from the Kubelka-Munk function (at 530 nm) of the in situ diffuse reflectance spectrometry (circles)

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