Design of a new UV/Vis-spectroelectrochemical measuring system

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Aims

Electrochemical measuring techniques are used in different areas of chemical research and industry. These methods do not deliver structural information of generated products. Therefore electrochemistry is combined with spectroscopical techniques to obtain structural information.
The aim of this project is to develop a novel electrochemical measuring system for spectroscopical analysis of products formed on rotating disc electrodes.

Experimental Arrangement

The measuring system consists of a rotating (ring) disc elektrode, a fibre-optic light guide and a motorised positioning unit for the optical part. A schematic drawing of the system is shown in fig. 1. Fig. 2 presents the preliminary measuring system.

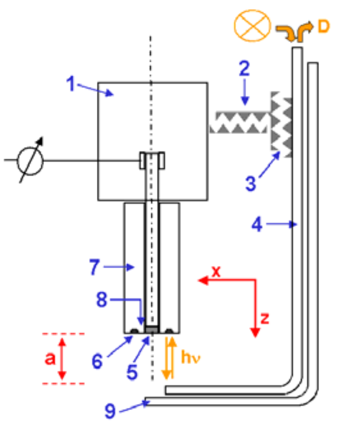

Fig. 1: Schematic drawing of the experimental arrangement

1: rotating-electrode-drive
2: x-positioning
3: z-positioning
4: fibre-optic light-guide
5: disc-electrode
6: ring-electrode / mirror
7: sheath
8: insulating ring
9: Haber-Luggin-probe
a: variable distance between light guide and electrode

The light guide is placed beneath the rotating electrode. The electrode material (preferably platinum or gold) either in the disc or in the ring is used as a mirror to reflect the light. Accurate positioning of the light guide is obtained using the positioning system.

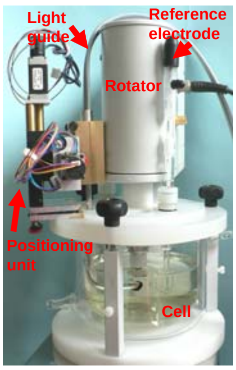

Fig. 2: Preliminary model of the measuring system including rotator, positioning unit, spectroscopic part and electrochemical cell.

The two types of electrodes and the position of the light beam are shown schematically in fig. 3.

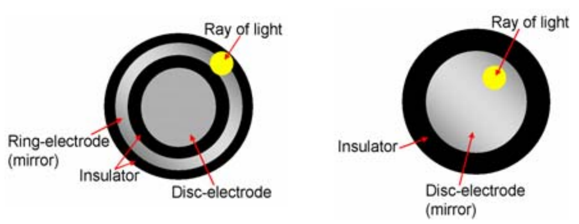

Fig. 3: Schemes of a rotating ring disc elektrode (left) and a rotating disc elektrode (right).

With this system reaction products from the disc can be detected spectroscopically on the ring. They are transported radially to the outside of the electrode.
Corrosion products and precipitation of reaction products can be observed spectroscopically on the disc electrode.

Results

The functionality of the system was verified electrochemically and spectroscopically. Potassium ferrocyanide ($K_4[Fe(CN)_6]$) was used as test solution. The pale yellow potassium ferrocyanide ($K_4[Fe(CN)_6]$) is oxidized to form orange ferricyanide in front of the electrode. The resulting changes in absorption in the visible range can be detected spectroscopically.

The presence of the light guide in front of the electrode does not cause significant changes in the electrochemical behaviour compared to measurements without light guide.

The ideal distance between electrode and light guide was determined. The z-position of the light guide was therefore varied while spectroscopic measurements were carried out. The extinction increases with increasing distance but linearity is obtained only up to 2 mm distance.

Subsequently the solution was observed spectroscopically while cyclovoltammetric measurements were carried out. Changes in colour can be observed in correspondance with the applied potential (fig. 4).

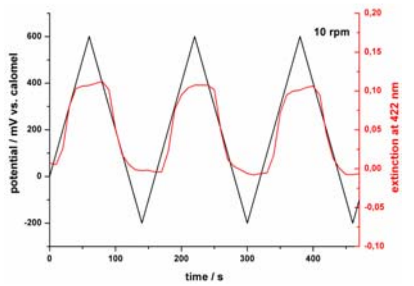

Fig. 4: Spectroelectrochemical measurements in ferrocyanide-solution. The rotation of the electrode was 10 rpm. The absorbance varies corresponding to the applied potential.

Additionally the influence of the rotation rate on the stability of the spectroscopic signal was examined. The intensity of the spectroscopic signal depends on the rotation rate of the electrode. The signals become weaker with increasing rotation rates. Stable results can be obtained up to 200 revolutions per minute. The UV/VIS-spectra of the oxidation-product (ferricyanide) measured at different rotation rates are shown in fig. 5. Best spectroscopic results were obtained by light reflection directly at the disc electrode.

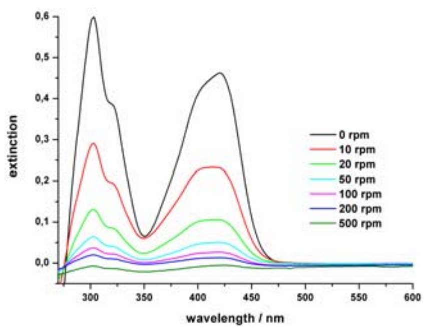

Fig. 5: UV/VIS-spectra of electrochemically produced ferricyanide measured at different rotation rates.

Summary

- The functionality of the new spectroelectrochemical system was demonstrated.
- Electrochemically produced substances can be characterized spectroscopically.
- The light guide has to be placed close to the electrode to obtain the best spectroscopic results.
- Stable spectroscopic signals can be achieved up to 200 revolutions per minute.
- Further experiments will be carried out to demonstrate the suitability for studies of electrode kinetics.