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Influence of the physical properties and handling of silica gel modified carbon paste electrodes on the phase transfer of solved Cu(II) ions

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Abstract

Carbon paste electrodes (CPE) modified with natural minerals might be utilised to mimic adsorption/desorption reactions at natural interfaces. As a step towards this aim, several properties and application conditions of CPEs, modified with silica gel, were tested for their influence on phase transfer reactions of solved Cu(II)–tetrammine complex ions.

The peak current recorded during the anodic stripping of adsorbed Cu(II) species increased with increasing diameter of the circular electrode surface. A silica gel content of 29 mass percent yielded the highest peak current at otherwise constant exposition conditions. A substitution of graphite by glassy carbon did not enhance the electrode sensitivity. The peak current increased with increasing exposition time (up to 20 min) and with decreasing size of the modifier particles. Typically between 12% and 22% of the solved Cu ions were adsorbed onto the electrode surface and between 15% and 20% of this Cu fraction was subsequently removed by stripping and electrode regeneration. Despite the incomplete electrode regeneration the mass transfer ratios of the Cu(II) species were relatively constant during several application cycles.

Keywords: Silica gel modified carbon paste electrode; Adsorption; Desorption; Phase distribution; Copper(II) ions; Cu(II)–tetrammine complex; Voltammetry

1. Introduction

Chemically modified carbon paste electrodes (CMCPEs) are especially useful in the determination of traces of metal species and organic compounds. The analyte is first bound at the electrode surface via a non-electrochemical interaction with the embedded modifier, e.g. chemical reaction or adsorption process, so that a sensitive and/or a selective accumulation is achieved. Usually modifiers for the determination of metal cations are organic polymers [1–3], complexing agents [4–8], ion exchangers [9–11], crown ethers [12,13] or minerals [14–18]. Normally the modifier is directly embedded in the paste of the electrode, which consists of a homogeneous mixture of graphite and nujol [19,20].

Mostly the fixation of metal ions is achieved under open-circuit conditions after immersion of the polished electrode into the sample solution. To reach high adsorption rates and high detection sensitivity, the sample matrix is modified with respect to the sample pH, the ionic strength and the presence of complexing agents.

Phase transfer reactions at solid–liquid interfaces, e.g. interfaces between natural waters and sediments, are of great importance for environmental processes. The transfer mechanisms are similar or almost identical to those occurring at electrode integrated mineral particles under open-circuit conditions. First investigations verified that CMCPEs are suitable to mimic adsorption processes occurring at natural solid–liquid interfaces [15,21–23]. Walcarius et al. [24] have demonstrated the good reliability of electroanalysis (stripping voltammetry using modified carbon paste electrode) for studying the sorption of Hg-species on aminopropyl-grafted silica particles. Svegl and Ogorevc modified carbon paste electrodes (CPE) with different soils and found a correlation between the cation exchange capacity of the solids and the voltammetric stripping signal of Cu resulting from the Cu ions adsorbed on the electrode surface [25].

Our investigation ties to the work of Walcarius especially, who had examined the silica gel–CPE/Cu(II)–tetrammine system with respect to the reaction variables pH value, NH_3 concentration, redox potential, electrolysis time and composition of the

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regeneration solution [22,26,27]. Our study is focused on several open questions, i.e. the optimisation of the electrode design and preparation, the standardisation of the electrode handling including precondition and regeneration steps and the systematic determination of the analytical reproducibility. For the first time an attempt was made to calculate the mass balance of the phase transfer of Cu(II) ions between the electrode and the various contact solutions.

2. Experimental

2.1. Apparatus

All CMCPE experiments were carried out using the potentiostat Polarecord E 626 (Metrohm) with the 663 VA Stand (Metrohm). The three-electrode system was completed by an Ag/AgCl/3 M KCl reference electrode and a glassy carbon auxiliary electrode.

All voltammetric measurements for Cu determination were made with a VA Processor 663 (Metrohm) in connection with a 694 VA-Stand (Metrohm). The electrode compartment consisted of a Hg drop electrode, an Ag/AgCl/3 M KNO_3 reference electrode and a Pt-wire as a counterelectrode.

Complementary measurements of the Cu solute concentration were performed with a graphite furnace AAS (Spectra AA 640, Varian) using the resonance line of 324.8 nm and a slit width of 0.5 nm.

2.2. Chemicals and reagents

Spectral carbon powder (type RW-C, Ringsdorff Werke), glassy carbon (spherical powder, type 1, 20–50 μm; Johnson Matthey), silica gel from Merck with different particle sizes (15–40 μm, 40–63 μm, 63–100 μm and 63–200 μm) and paraffin oil (Merck) were used for the preparation of the CMCPE. All other chemicals were of analytical grade (Merck).

Ultrapure water obtained with a Milli-Q-system (Millipore) was used to prepare all solutions.

A standard stock solution of Cu(II) (1000 mg l^{-1}; Merck) was used to prepare working standards by serial dilution.

2.3. Preparation of the working electrode

Silica gel modified carbon pastes were prepared by using of 1.2 g of carbon powder, 0.6 g of paraffin oil and different amounts of silica gel according to the following procedures:

A. Carbon powder and silica gel particles were carefully hand mixed with a glass rod for 10 min. After addition of paraffin oil the mixture was homogenised.
B. Carbon powder and silica gel particles were suspended in 10 ml of CH_2Cl_2. The suspension was carefully stirred until the CH_2Cl_2 has evaporated. After addition of paraffin oil the mixture was homogenised and dried overnight.
C. Carbon powder, paraffin oil and silica gel particles were together suspended in 10 ml of CH_2Cl_2 and slowly mixed until the solvent has evaporated. The homogenous mixture was dried overnight.

The bodies of the electrodes consisted of a teflon rod (diameter 15 mm) with a circular bore hole at one end. The diameters ranged from 2.8 mm to 10 mm having a depth of 30 mm for insertion of the paste. Contact was made with a copper wire (diameter 1 mm) mounted in the centre of the rod.

To obtain a new electrode surface the copper wire was turned and the excess paste was stripped off. Then the electrode surface was polished on a smooth paper.

2.4. Analytical procedures

2.4.1. Voltammetric measurements with the CMCPE

2.4.1.1. Pretreatment of the electrode. Every freshly prepared CMCPE was activated by performing of 6 or more test cycles including all steps of the whole measuring procedure.

2.4.1.2. Adsorption. The pretreated CMCPE was placed into an exposition cell filled with 5 ml or 20 ml of the Cu containing ammoniacal (0.5 M NH_3) exposition solution. The copper content of the solution varied between 0.05 μg ml^{-1} and 10 μg ml^{-1}. The adsorption of the formed Cu(II)–tetrammine complex was allowed to proceed within prefixed time periods (t_{ex}, 1–20 min) under constant stirring of the solution and open-circuit conditions. Then the electrode was removed, rinsed with pure water and placed into the voltammetric cell.

2.4.1.3. Voltammetric measurements. The CPCME was immersed into the scanning solution (10 ml or 40 ml of 0.1 M HNO_3) and immediately a potential of −0.2 V was applied under stirring of the solution. A differential pulse voltammogram was recorded from −0.2 V to 0.4 V after a pre-electrolysis time of 60 s and an equilibration time of 20 s. The scan rate was 10 mV s^{-1} and the pulse height 50 mV.

2.4.1.4. Regeneration of the electrode surface. The remaining electrochemically active Cu(II) fraction was removed from the surface applying a constant potential of 0.4 V without replacing the acidic solution used before. The gradual decrease of the Cu content was controlled by scanning voltammograms. The same electrode surface was used for the next adsorption experiment.

2.4.2. Determination of the Cu mass transfer

For the balance of the Cu mass transfer between the liquid phase and the electrode surface the Cu content was measured in the liquid phase independently from the CMCPE with HMDE anodic stripping voltammetry and AAS.

3. Results and discussion

3.1. Preparation of the CMCPE

Different methods of the electrode preparation are described in the literature [3,19,28,29]. Three procedures of the homogenisation of the electrode components, i.e. graphite, silica gel and