Mechanisms and kinetics of electrode processes at bismuth and antimony film and bare glassy carbon surfaces under square-wave anodic stripping voltammetry conditions

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ABSTRACT

Mechanism and kinetics of anodic stripping electrode processes of Zn(II), Cd(II) and Pb(II) at bismuth (BiFE) and antimony (SbFE) film as well as bare glassy carbon (GCE) electrodes have been studied with respect to our recent published theoretical considerations developed for square-wave voltammetry (SWV). Mechanistic aspects of electrode reactions have been elucidated by a qualitative comparison of simulated and experimental data for three different electrode reaction mechanisms, i.e. simple anodic stripping mechanism, anodic stripping mechanism coupled with adsorption of metal analyte ions, and mechanism affected by interactions within the particles of the metal deposit on the electrode surface. The electrode kinetics has been estimated by the method of quasireversible maximum and by analyzing the peak potential separation between forward and backward SW components, under variation of the SW amplitude. Electrode mechanisms and kinetics are different at bismuth compared to antimony film electrodes. The electrode reactions of Pb(II) and Cd(II) at BiFE involve adsorption phenomena, while electrode processes of all three analytes are free of adsorption at SbFE. At BiFE, the electron transfer standard rate constants of all three analytes are quite comparable, ranging within the interval from 1 to 3 cm s^{-1}. At SbFE the electrode kinetics of Cd(II) and Pb(II) are almost the same, while the electrode reaction of Zn(II) is significantly slower. Our results showed that the kinetics of all examined electrode reactions are slower at SbFE as compared to those observed at BiFE.

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1. Introduction

Electrochemical techniques have been proven to be versatile tools for trace metal determination. Among them, stripping voltammetry is particularly powerful method due to effective preconcentration of the analyte prior to the detection (stripping) step, thus being attributed with a remarkable sensitivity and associated low detection limits [1]. Performance of a stripping voltammetric procedure depends primarily on the appropriate choice of the working electrode. Hence, the electrode material, its surface morphology, as well as the knowledge of the electrode mechanisms, are among the critical factors determining the analytical performance.

Different substrates, most frequently a variety of carbon materials and metals, have been employed for the fabrication of working electrodes. In particular, glassy carbon electrode (GCE) has gained wide acceptance due to its convenient electrical/electroanalytical and mechanical properties and the ease of operation. During the last four decades glassy carbon electrodes have been extensively utilized, either as a bare electrode, or being a subject of a surface modification [2–4]. Mercury film electrode (MFE), typically prepared by using GCE as a substrate, has been traditionally used in voltammetric and potentiometric stripping analysis of metal ions, because of its extremely favourable signal-to-background ratio and overall electroanalytical performance [5,6]. However, mercury related electrodes are associated with well-known drawbacks concerning toxicity, handling and disposal of mercury. Fortunately, a bit more than a decade ago, a novel bismuth film electrode (BiFE) was developed as a convenient alternative to the MFE [7]. This pioneering work provoked a plethora of studies focused on non-mercury film electrodes for trace metal analysis. In order to find the most suitable and desired analytical performance, different

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configurations of bismuth electrodes have been employed for measuring metal ions [8–12] as well as miscellaneous organic compounds relevant to the environment, medicine, etc. [13,14]. Subsequently, another novel metal film electrode, the antimony film electrode (SbFE) was also introduced a few years ago [15]. Similar to their bismuth analogue, the antinomy based electrodes are attributed with acceptable characteristics for electroanalytical (stripping) analysis such as an auspicious performance in more acidic media, a favourably negative potential for hydrogen evolution process, and unexpectedly low stripping signal of the antimony itself [16–22].

While the overall analytical performance of BiFEs and SbFEs has been already thoroughly examined, systematic mechanistic and kinetic studies at these electrodes are still missing. Recently, an attempt was made to develop a phenomenological theoretical background to rationalize some of possible electrode mechanisms [23] under conditions of square-wave voltammetry (SWV) [24,25]. In the present communication we apply the recent theory [23] to characterize the anodic stripping electrode mechanisms of Pb(II), Cd(II) and Zn(II) from mechanistic and kinetic point at both BiFEs and SbFEs, while the mechanism of Pb(II) was studied at bare GCE as well.

2. Experimental

2.1. Apparatus

Anodic stripping voltammetric (ASV) measurements were performed with the modular electrochemical workstation (Autolab, Eco Chemie, Utrecht, The Netherlands) equipped with PGSTAT12 driven by GPES software (Eco Chemie). A three-electrode configuration was used, consisting of a bismuth or antimony film modified or a bare glassy carbon disc electrode ($d = 2$ mm), Ag/AgCl (KCl 3 M), and a platinum wire as the working, reference, and counter electrode, respectively. All electrochemical experiments were carried out in a 20 mL one-compartment voltammetric cell at conditioned room temperature ($23 \pm 1 °C$).

2.2. Reagents

Standard stock solutions of bismuth(III), antimony(III), cadmium(II), lead(II), and zinc(II) (1 g L^{-1}, atomic absorption standard solution) were obtained from Aldrich and diluted as required. A 0.1 M sodium acetate buffer solution (pH 4.5) served as the supporting electrolyte for experiments with BiFEs, while 0.01 M HNO$_3$ solution was the supporting electrolyte for experiments with SbFEs. Water used to prepare all solutions was first deionized and then further purified via an Elix 10/Milli-Q Gradient unit (Millipore, Bedford, MA).

2.3. Procedures

ASV measurements were performed by the in situ accumulation of bismuth or antimony film together with target metal ions in the presence of dissolved oxygen. Prior to its use, the glassy carbon disc electrode was polished with a 0.05 μm alumina slurry on a polishing pad and rinsed with water. The polished working electrode was immersed into a 20 mL electrochemical cell containing either 0.1 M acetate buffer solution and 20 μM of Bi(III) ions (for studies at in situ BiFEs), or 0.01 M HNO$_3$ solution containing 20 μM of Sb(III) ions (for studies at in situ SbFEs).

At BiFEs the accumulation potential of -1.4 V was applied without stirring, in order to obtain the metal deposit morphology as uniform as possible, being in accordance with the theoretical assumptions upon which the theoretical model is based [23]. The anodic stripping voltammogram was recorded by applying a positive-going square-wave potential scan with a potential step of usually 2 mV and with a frequency and an amplitude as denoted in each experiment. Aliquots of the target metal ion standard solution were introduced after recording the background stripping voltammogram. Prior to the next cycle, a 30 s conditioning step at +0.3 V under stirring conditions was used to remove completely the accumulated metals and bismuth film.

For experiments with Pb(II) at bare GCE, the same procedure has been followed as for BiFEs, only the supporting electrolyte was free of Bi(III) ions.

A similar procedure was applied at SbFEs, composed of an electrochemical accumulation step at -1.3 V for a period of 120 s without stirring, which was followed by a square-wave voltammetric scan from -1.3 V to +0.3 V. Prior to each ASV measurement, the cleaning step was applied by holding the working electrode at the potential of +0.3 V for 20 s, while stirring the solution.

3. Results and discussion

3.1. Theoretical considerations

The recent theoretical treatment of anodic stripping voltammetric processes at BiFEs [23] under conditions of SWV encompassed three different mechanisms: (i) *simple anodic stripping mechanism* in which the metal analyte ions are the subject of diffusion mass transport following the stripping step, (ii) *adsorption mechanism*, in which the diffusion mass transport is coupled with a partial adsorption of the analyte ions on the Bi-film surface, and (iii) *adsorption-interaction mechanism* in which, besides adsorption and diffusion, the role of interactions (attractive or repulsive) between accumulated metal particles have been taken into account. The latter mechanism is the most general one, providing a basis for detail qualitative description of the majority of the experimental data. The previous two simpler mechanisms could be considered as limiting cases of adsorption-interaction mechanism. More specifically, if the degree of interactions is insignificant the adsorption-interaction mechanism simplifies to the adsorption mechanism and further, if the adsorption is insignificant, the system eventually converges to the simple anodic stripping mechanism.

The stripping voltammetric features of the adsorption-interaction mechanisms are predominantly controlled by the interaction parameter $\zeta = a\sqrt{D/f}(c_M^*/\Gamma_{max})$, where a is Frumkin interaction parameter, D is diffusion coefficient of the metal analyte ion, f is frequency of the SW potential modulation, c_M^* is bulk concentration of the metal analyte, and Γ_{max} is maximal surface concentration of the metal deposit on the electrode substrate. Indeed, the degree of interactions depends mainly on the Frumkin interaction parameter, as a typical dimensionless constant for a given experimental system with $a < 0$ and $a > 0$ for repulsive and attractive interactions, respectively, and the fractional coverage of the electrode surface with accumulated metal particles. In addition, all parameters controlling the surface coverage, i.e. the analyte concentration, time and potential of the accumulation, diffusion coefficient, and the SW frequency, further affect the degree of interactions. The presence and type of interactions can be determined by a simple analysis of the net anodic SW voltammetric peak potential (E_p) variation with the accumulation time and/or concentration of the analyte. When attractive or repulsive forces are operative the peak potential shifts towards less or more negative potentials, respectively, which can be easily examined by increasing either or both metal analyte concentration or deposition time. Another diagnostic criterion can be based on the evolution of the quasireversible maximum (QRM) as a function of the concentration or accumulation time. In Fig. 1 it is clearly shown that the position of the QRM is affected by the analyte concentration in the presence of interactions, which is not the case for the system free of interactions. The