

Platinum–tin complexes as catalysts for the anodic oxidation of borohydride

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Abstract Platinum–tin complexes were prepared by the reduction of Pt(IV) with Sn(II) in HCl media and studied by light absorption spectrometry, X-ray photoelectron spectroscopy (XPS), and electron microscopy. The formation of three complexes, $\text{H}_3[\text{Pt}(\text{SnCl}_3)_5]$, $\text{H}_2[\text{Pt}(\text{SnCl}_3)_2\text{Cl}_2]$, and $\text{H}_2[\text{Pt}_3(\text{SnCl}_3)_8]$, depending on HCl and SnCl_2 concentrations, has been shown. The glassy carbon (GC) electrode modified in the complexes solutions was found to be an electrocatalyst for borohydride oxidation in a 1.0-M NaOH solution. Comparison of BH_4^- electrooxidation on Pt and on GC modified with platinum–tin complexes has shown that catalytic hydrolysis of BH_4^- did not proceed in the latter case in contrast to its oxidation on the Pt electrode, and only direct BH_4^- oxidation has been observed in the positive potentials scan. The activity of Pt–Sn complexes for BH_4^- oxidation changes with time and eventually decreases due to Sn(II), bound in the complex with Pt(II), oxidation by atmospheric oxygen. The complexes may be renewed by addition of missing amounts of SnCl_2 and HCl.

Keywords Platinum–tin complexes · Electrooxidation · Borohydride · Electrocatalyst

Introduction

Various catalytic materials such as Au, Pt, Pd, Ru, Ni, Co, and their alloys have been investigated for using low-

temperature fuel cells [1–3]. However, the purpose to increase catalytic activity of the surface using cost-effective substances remains an important problem. Colloidal metals supported on carbon by using various methods often show a higher “quality factor” than pure metals electrodes [4]. The immobilized Pt colloids via the reduction of PtCl_6^{2-} by H_2 or ethanol were found to be active catalysts for hydrogenation [5]. Colloidal Au and Au alloys supported on a glassy carbon substrate led to the maximum eight-electron oxidation of BH_4^- ; however, Au–Pt was a more active catalyst [6]. Carbon-supported platinum samples serve as catalysts for hydrolysis of NaBH_4 solution and the hydrogen generation reactions [7].

It is of interest that Pt–Sn catalysts prepared by various methods may be active in different processes. A highly active PtSn/C catalyst for a direct ethanol fuel cell was prepared by mixing precursors of Pt and Sn [8]. The results have shown that Sn exists in a multivalent state in the as-prepared sample, while only zero-valence Sn was detected after reducing in H_2/Ar atmosphere at 600 °C in the treated sample. The cyclic voltammetry (CV) technique tests indicated that the as-prepared catalyst possessed a superior catalytic activity for ethanol oxidation as compared to that of the treated sample. Pt–Sn catalyst prepared by successive impregnation of pregraphitized carbon with solutions of H_2PtCl_6 and SnCl_2 had a significant effect on the hydrogenation of the C=O bond in crotonaldehyde [9]. The catalyst prepared after reduction with H_2 contained Pt in a metallic state. A high proportion of tin remains in an oxidized state, but a relatively marked amount was reduced to Sn(0). The results obtained were explained by the promoting effect of oxidized tin species for hydrogenation of the C=O bond, whereas the formation of Pt–Sn alloy or diminishing of active Pt surface hindered the hydrogenation of a C=C bond.

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The catalytic activity of the modified Pt surface by spontaneous Sn deposition through a simple “dip-coating” method under open-circuit conditions was compared with that of a polycrystalline Pt electrode [10]. Tin oxide/hydroxide species and metallic Sn were identified on the Pt surface. Tin oxide/hydroxide were assumed to be the result of Sn(II) hydrolysis, while tin metal particles were most likely spontaneously deposited on the Pt surface due to disproportionation of Sn(II) to Sn(IV) and Sn(0). A Sn-modified Pt catalyst showed a superior activity for adsorbed CO oxidation. The methanol oxidation rate was not enhanced compared to that on the Pt electrode.

Previous studies have shown that some of platinum complexes with a SnCl_3 ligand play an important role in catalytic processes [11, 12]. The $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$ anion obtained by the reaction of $[\text{PtCl}_4]^{2-}$ with an excess of SnCl_2 was an active hydrogenation catalyst, while K_2PtCl_4 alone was not active. The presence of SnCl_3^- strongly promotes five-coordination in the chemistry of Pt(II). However, the lability of the Pt–Sn bonds very often leads to mixtures of different species in equilibrium [13]. Several different platinum–tin complexes may be formed depending on the HCl and SnCl_2 concentrations [14, 15]. It has been determined that in the solutions with the ratio $\text{Cl}(\text{II})/\text{Pt}(\text{II}) > 1,000$, the compounds of Pt(II) are formed and tin present in the complexes is not oxidized to Sn(IV) [15, 16].

Our preliminary experiments have shown that Pt–Sn complex derivatives initiate electroless copper plating on plastics while an H_2PtCl_6 solution without SnCl_2 cannot activate plastics for this process. More explicit investigations of different tin–platinum complexes activities were performed in this work using anodic oxidation of borohydride that has been investigated on a broad scale for usage in fuel cells [3, 17–21]. The anodic oxidation of borohydride, as a multi-step process, may take different reaction paths, depending on the nature of electrocatalyst, as well as on the concentrations of OH^- and BH_4^- . The character of BH_4^- oxidation on a Pt wire and on GC modified with platinum–tin complexes was also compared in this work.

Experimental

Platinum–tin derivatives were prepared using two main stock solutions: 5 mM H_2PtCl_6 and 50 mM SnCl_2 . All chemicals were analytical purity grade. The Pt(IV) solution was prepared by dissolving $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in distilled water. The Sn(II) solution was prepared by dissolving SnCl_2 in concentrated HCl under heating and then diluting with water. Freshly prepared SnCl_2 solutions were always used to minimize the effect of tin oxidation by atmospheric oxygen before Pt–Sn complexes preparation. The Pt(IV) and Sn(II) solutions, diluted to the concentrations needed,

were mixed by adding the tin salt to a platinum(IV) solution after adding of the required quantity of HCl. The platinum concentration in solutions was 0.3–0.5 mM. In order to detect changes in the composition and activity of Pt–Sn complexes occurring due to Sn(II) oxidation, the study was performed under conditions of accelerated oxidation, i.e., for every series of experiments 10 ml of complex solution was always prepared in the vessel with a surface area of 3 cm^2 . The Sn(II) concentration was estimated iodometrically.

The complexes obtained were characterized by light absorption spectra using a Perkin-Elmer Lambda 35 UV/Vis spectrometer (USA). The solutions were diluted fivefold with HCl (1:10) prior to each spectrometric measurement. It was established that such dilution did not change the shape of spectrum. Water was used as reference.

The derivatives formed in solutions were studied by electron microscopy using an electron microscope TEM MORGAGNI 268. The platinum–tin solutions for investigations of the nanoparticles formed were dropped on a copper net preliminary covered by a carbon film.

Elemental analysis of platinum–tin complexes adsorbed on GC was studied by X-ray photoelectron spectroscopy (XPS). Plates of GC were immersed into the solutions of platinum–tin complexes for 5 min, rinsed with water, and dried. The Pt–Sn/GC plates after BH_4^- oxidation and after reverse scan were rinsed and dried in the same way. XPS measurements were performed on a spectrometer ESCA-LAB MK II (VG Scientific, UK). The non-monochromatic Al $K\alpha$ X-ray radiation ($h\nu = 1486.6 \text{ eV}$) was used for excitation and the Al twin anode was operated at 14 kV and 20 mA emission current. The analyzer was operated at the constant pass energy (20 eV). The base pressure in the analysis chamber was kept below $5 \times 10^{-6} \text{ Pa}$. The photoelectron take-off angle was defined as the angle between the electron analyzer and the specimen's surfaces and was set in order to obtain the maximum intensity of collected spectra of Pt4f, Sn3d, O1s, Cl2p, and C1s. The spectrometer energy scale was calibrated by reference to Ag3d5/2 line at $368.0 \pm 0.1 \text{ eV}$ and Au4f7/2 — at $83.8 \pm 0.1 \text{ eV}$.

Cyclic voltammetric curves were recorded using a computerized potentiostat PI-50-1.1, a sweep generator PR-8 and two digital voltmeters B7-46/1 (Russia) in a standard three-electrode electrochemical cell. A glassy carbon (GC) (SU-1200) working electrode (apparent surface area 0.636 cm^2), a Pt-wire counter electrode and an Ag/AgCl/ KCl_{sat} reference electrode were used. The Pt wire was also used as a working electrode in some experiments to elucidate Sn(II) and Sn(IV) influence on the anodic oxidation of borohydride.

A modification of the Pt wire with Sn(II) ions was carried out by its immersing for 5 min into a fresh solution containing 20 mM SnCl_2 and subsequent rinsing with distilled water. For the Pt modification with Sn(IV), the

same solution was used after complete oxidation of Sn(II) to Sn(IV) by atmospheric oxygen. The GC surface prior to all measurements was refreshed by its polishing with diamond paste (1 μm particle size). The final cleaning of the electrode was performed in an acetone solution. After the treatment, the GC electrode was modified by immersing for 5 min in the Pt–Sn complex solution, then rinsed with distilled water and placed in the cell.

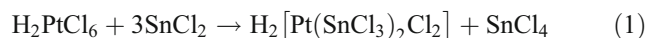
The electrochemical experiments of anodic oxidation of 50 mM sodium borohydride (NaBH_4 powder, 98.5%, ACS Reagent grade, Sigma-Aldrich) were carried out in a 1.0-M NaOH (p.a. Chempur) solution at a potential scan rate of 10 mV s^{-1} .

Results and discussion

Formation of platinum–tin complexes

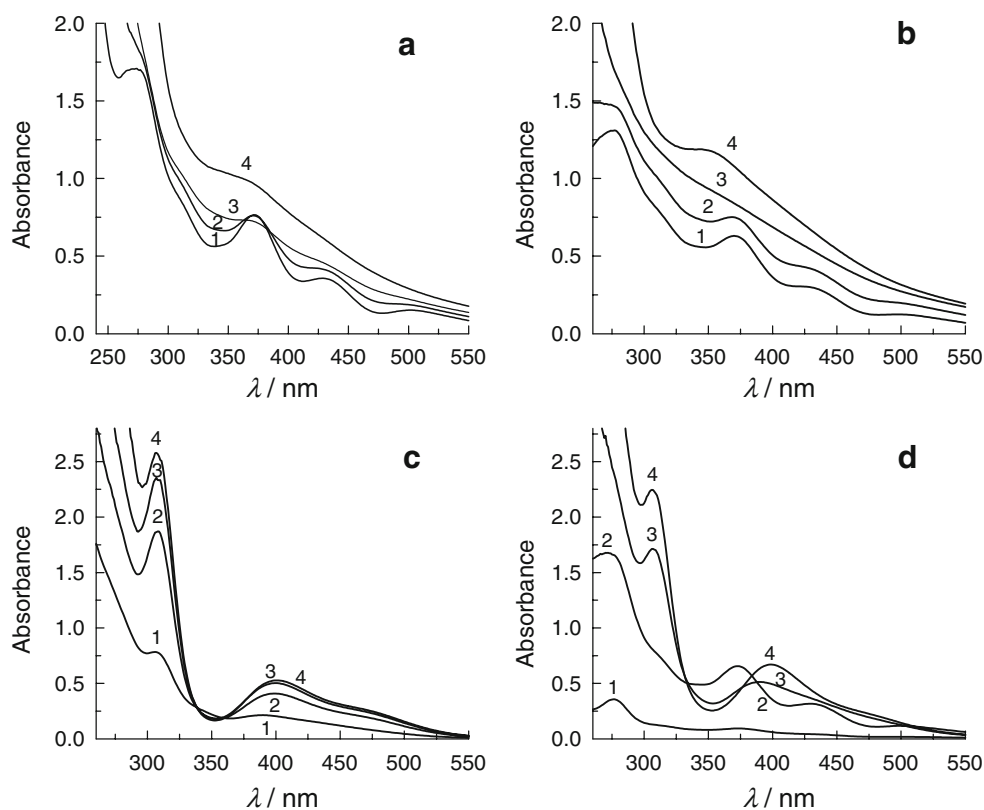
The stability of platinum derivatives obtained by the reduction of 0.3–0.5 mM H_2PtCl_6 solutions with Sn(II) in the hydrochloric acid medium depends on the initial SnCl_2 and HCl concentrations. When the Sn(II)/Pt(IV) ratio is lower than 5, a brown turbid and unstable solution is formed. The complex obtained at HCl concentrations lower

than 10 mM is unstable as well. Therefore, stable Pt–Sn derivatives may be formed only at certain initial concentrations of the reactants. Three forms of freshly prepared platinum–tin derivatives may be identified in the light absorption spectra of solutions containing initial concentrations of HCl from 0.5 to 1.1 M and SnCl_2 from 5 to 50 mM (Fig. 1). When 0.5 M HCl and 5–10 mM SnCl_2 are used, the product corresponds to the $[\text{Pt}(\text{SnCl}_3)_2\text{Cl}_2]^{2-}$ complex, which is characterized by absorption increase at 275, 375, 430, and 510 nm (Fig. 1a). Its formation may be described by the reaction:

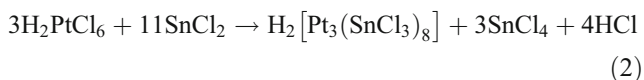


With increase in SnCl_2 concentration in the initial mixture, the light absorption of the complex obtained changes. The spectrum of a dark brown solution formed at a SnCl_2 concentration of 50 mM has no maximum and is similar to the spectrum of spherical 10-nm particles of the metallic Pt [22]. However, according to the binding energy of platinum in this complex with Sn(II) and in the other complexes obtained in this study (72–73 eV) [15, 16], it corresponds to Pt(II), so, this complex hardly can be expressed by the formula $[\text{Pt}_3\text{Sn}_8\text{Cl}_{20}]^{-4}$ with Pt(0), as it was proposed earlier [23]. For the formation of this

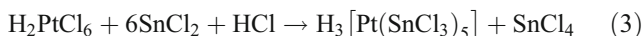
Fig. 1 Dependence of Pt–Sn complexes light absorption on Sn(II) concentration (mM): 1–5, 2–10, 3–20, 4–50; Pt(IV)—0.3 mM, HCl (M): **a** and **b**—0.5, **c** and **d**—1.1 M; **a** and **c**—as-prepared, **b** and **d**—after 2 days. Solutions diluted 1:4 with HCl 1:10



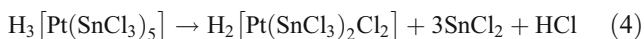
complex, a higher concentration of SnCl_2 is necessary; therefore, the reaction of its formation might be as follows:



This complex prepared at a low HCl/SnCl_2 ratio is not sufficiently stable; it tends to precipitate after some time. This is seen from an increased light absorption after 2 days in Fig. 1b. When the initial HCl concentration is higher than 1 M, the light absorption spectrum always shows the formation of $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$ complex, the amount of which, clearly seen from the height of the maximums at 310 and 400 nm (Fig. 1c), increases with increase in the initial SnCl_2 concentration. The complex formed at a low SnCl_2 concentration (5 mM) is unstable; it fades after 2 days because of lack of SnCl_2 (Fig. 1d). The solution prepared with 20–50 mM SnCl_2 remains stable much longer (6–7 days). The formation of this complex may be described as follows:



This platinum–tin complex changes with time. An increase in temperature accelerates this transition:



The transition of $\text{H}_3[\text{Pt}(\text{SnCl}_3)_5]$ complex to $\text{H}_2[\text{Pt}(\text{SnCl}_3)_2\text{Cl}_2]$, and $\text{H}_2[\text{Pt}(\text{SnCl}_3)_2\text{Cl}_2]$ to $\text{H}_2[\text{Pt}_3(\text{SnCl}_3)_8]$, observed with time proceeds due to $\text{Sn}(\text{II})$ oxidation with atmospheric oxygen. The highest rate of $\text{Sn}(\text{II})$ oxidation is observed in solutions with the highest HCl concentration in solutions with and without platinum (Fig. 2). In our

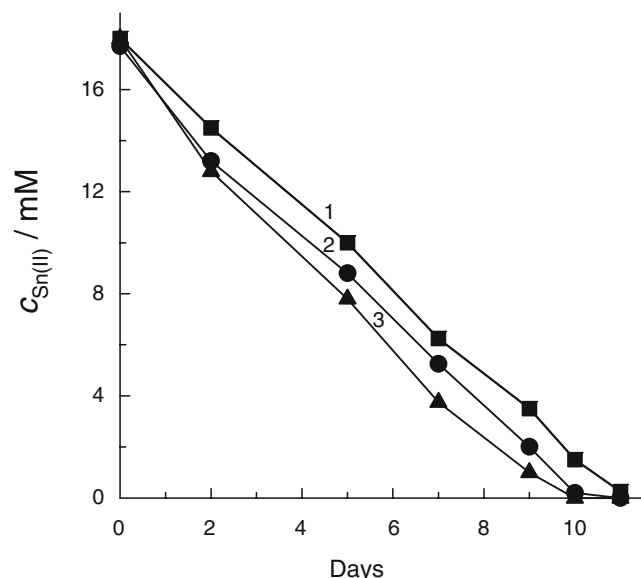
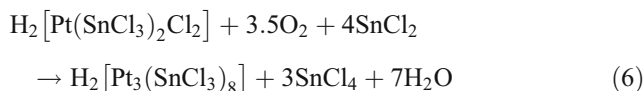
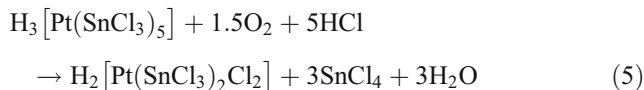
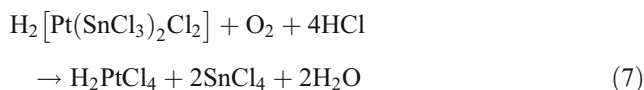


Fig. 2 Decrease in $\text{Sn}(\text{II})$ concentration with time. Other initial concentrations in solution: $\text{Pt}(\text{IV})$ 0.5 mM, HCl (M): 1–0.5, 2–0.7, 3–1.0

experiments, performed under the conditions of accelerated oxygen access, $\text{Sn}(\text{II})$ oxidation proceeds very rapidly. The correspondent changes in the spectra of the complexes are seen in Fig. 3. The $\text{H}_3[\text{Pt}(\text{SnCl}_3)_5]$ complex, formed with the highest HCl concentration, changes to $\text{H}_2[\text{Pt}(\text{SnCl}_3)_2\text{Cl}_2]$ and eventually disintegrates when the ratio of the residual $\text{Sn}(\text{II})$ to platinum in the solution remains lower than 5. The changes in complexes composition, seen in Fig. 3, may be expressed by these equations:



When the excess of $\text{Sn}(\text{II})$ being in the solution is oxidized, the $\text{H}_2[\text{Pt}(\text{SnCl}_3)_2\text{Cl}_2]$ complex discolours with transition to PtCl_4^- :

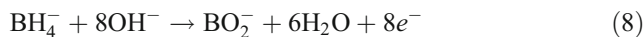


This fact confirms that $\text{Pt}(\text{II})$ in these complexes is bound to $\text{Sn}(\text{II})$. After the addition of the missing amounts of $\text{Sn}(\text{II})$ and HCl (compared with the initial ones) to the solutions, the spectra of which are shown in Fig. 3c, all the complexes recover their initial colors and the spectra of the complexes obtained become close to the initial ones (compare Fig. 3a,d).

Electron microscope images of platinum–tin compounds (Fig. 4) show that the size of nanoparticles becomes smaller with increase in HCl concentration in the reaction mixture. This is conditioned by the complex state in the solution. Especially fine nanoparticles are observed when HCl concentration is higher than 1 M and the $\text{H}_3[\text{Pt}(\text{SnCl}_3)_5]$ complex is formed. With transition of this complex to the $\text{H}_2[\text{Pt}(\text{SnCl}_3)_2\text{Cl}_2]$, nanoparticles become coarser. The size of nanoparticles diminishes with increase in SnCl_2 and HCl concentrations in the initial mixture. This is natural, because in this case reaction (4) shifts to the formation of $\text{H}_3[\text{Pt}(\text{SnCl}_3)_5]$.

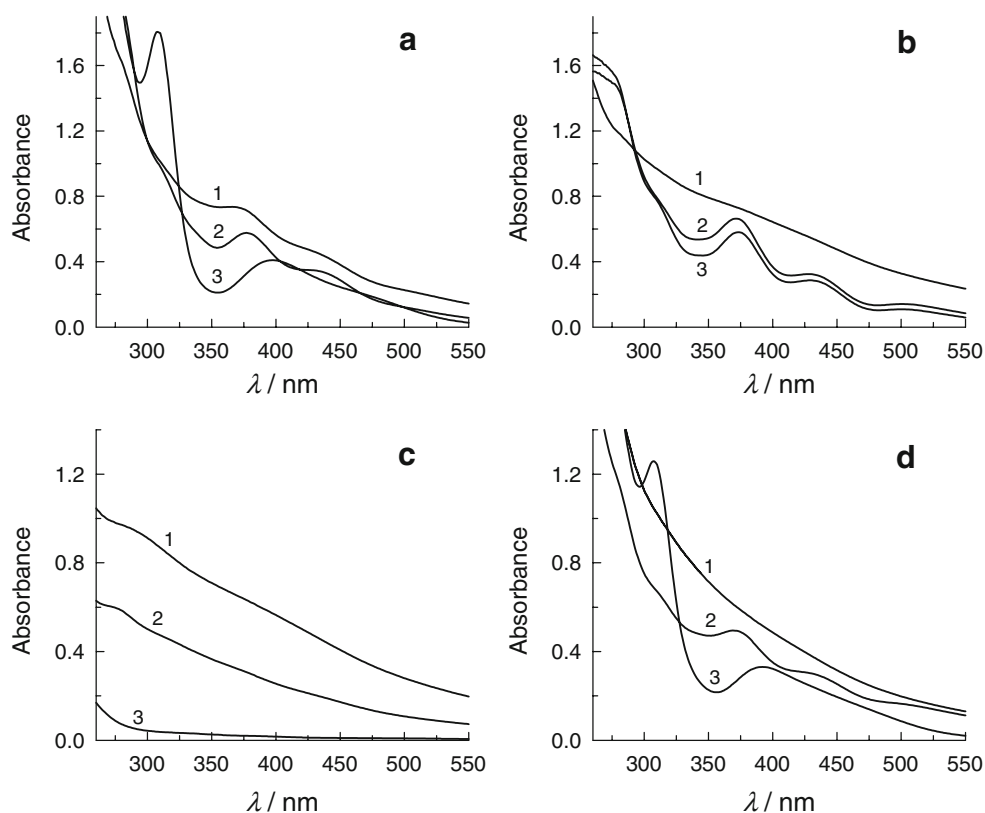
Cyclic voltammetry of borohydride on Pt

Based on previous studies of BH_4^- electrooxidation on Pt [20, 21, 24, 25], an ideal eight-electron oxidation:

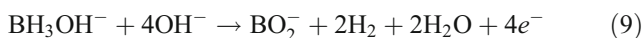


is not effective because the catalytic hydrolysis of borohydride occurs, and BH_4^- oxidation involves several steps. Although

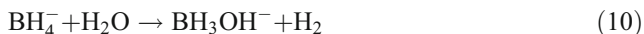
Fig. 3 Light absorption of the Pt–Sn complexes containing the initial concentrations: Pt(IV)—0.5 mM, Sn(II)—20 mM, HCl (M): 1–0.45, 2–0.7, 3–1.1, (a) as-prepared, (b) after 5, (c) after 11 days, (d) after adjusting Sn (II) and HCl concentrations. Solutions diluted 1:4 with HCl 1:10



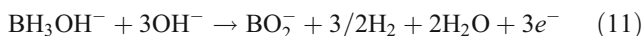
only eight hydroxide ions are theoretically needed for each borohydride ion, the overall reaction for the BH_4^- oxidation on Pt shows a four-electron process [25]:



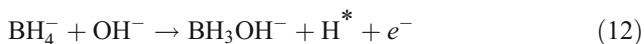
The open-circuit potential of Pt electrode in a 50-mM NaBH_4 solution in a 1.0-M NaOH medium is -1.0 V versus $\text{Ag}/\text{AgCl}/\text{KCl}_{\text{sat}}$, and the first peak (a) (Fig. 5a, solid line) observed at about -0.7 V is due to the electrooxidation of hydrogen generated by catalytic hydrolysis of BH_4^- :



The second peak (b), hardly discernible at -0.2 V, can be attributed to the electrooxidation of a rather stable intermediate BH_3OH^- :



A distinct peak (c) appears at more positive potentials, i.e., between 0 and 0.1 V. This peak and a low wave in the backward scan are associated with BH_4^- direct oxidation [20, 25]. A sharp peak (d), seen in the reverse scan, belongs to the oxidation of BH_3OH^- intermediate that could be also produced in BH_4^- electrooxidation:



The wave of BH_3OH^- oxidation coalesces with the H_2 oxidation wave, discernible at -0.7 V.

The CV of BH_4^- oxidation on the Pt electrode modified in a SnCl_2 solution distinguished by good adsorption (Fig. 5a, dotted lines) differs from the CV discussed previously. The wave of H_2 ionization (a^1) in this case is noticeably shifted to more positive potentials and the value of anodic current is reduced nearly threefold, in comparison with that obtained using pure Pt as a catalyst. This shows that Sn(II) or, maybe, Sn(0), which might be formed spontaneously on Pt due to the disproportionation of Sn (II) [10], inhibits the catalytic hydrolysis of borohydride and oxidation of hydrogen on Pt. The second two peaks of BH_4^- oxidation on the Pt modified with Sn(II) (b^1 and c^1) are only slightly lower compared with those on pure Pt. In the reverse scan the CVs recorded with and without tin species are practically identical, due to oxidation of the major part of Sn(II) in the positive scan and removal of oxidation products from the electrode. Consequently, the influence of the adsorbed tin species on the borohydride oxidation on the Pt electrode is almost insignificant in the following positive potentials scans.

The character of cyclic voltammetry curves of BH_4^- oxidation on the Pt wire modified in a Sn(IV) solution (Fig. 5b) is identical to that observed on pure Pt (Fig. 5a), indicating that the inhibiting action is not characteristic of Sn(IV).

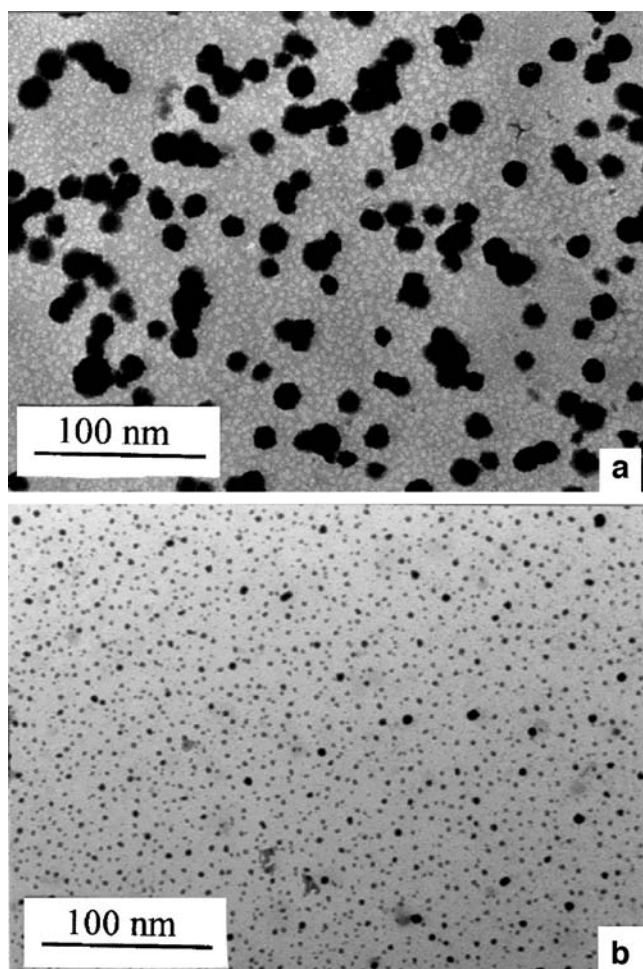


Fig. 4 TEM images of the particles of Pt–Sn complexes prepared in solutions containing the initial concentrations: Pt(IV)—0.3 mM, Sn(II)—50 mM, HCl (M): **a**—0.5, **b**—1.0

Cyclic voltammetry of BH_4^- on glassy carbon modified with Pt–Sn complexes

Any oxidation of BH_4^- in a 1.0-M NaOH solution was not observed in a wide potential range up to 0.8 V on a bare GC electrode and on GC modified in SnCl_2 or H_2PtCl_6 solutions separately at the same concentrations and pH as they were in the Pt–Sn complex solutions, whereas GC modified in Pt–Sn complex solutions is a catalyst for borohydride electrooxidation.

The colloid solution of $\text{H}_2[\text{Pt}_3(\text{SnCl}_3)_8]$ prepared with the lowest HCl concentration (less than 0.5 M) is active as prepared. However, after 3–4 days the coagulation of the complex begins, and its activity drops. The electrooxidation of BH_4^- on the GC modified in this solution versus the time passed after its preparation is shown in Fig. 6 a. The open-circuit potential of the GC modified in a $\text{H}_2[\text{Pt}_3(\text{SnCl}_3)_8]$ solution is about -0.6 V, therefore, the anodic oxidation of BH_4^- starts at potentials more positive than those in the

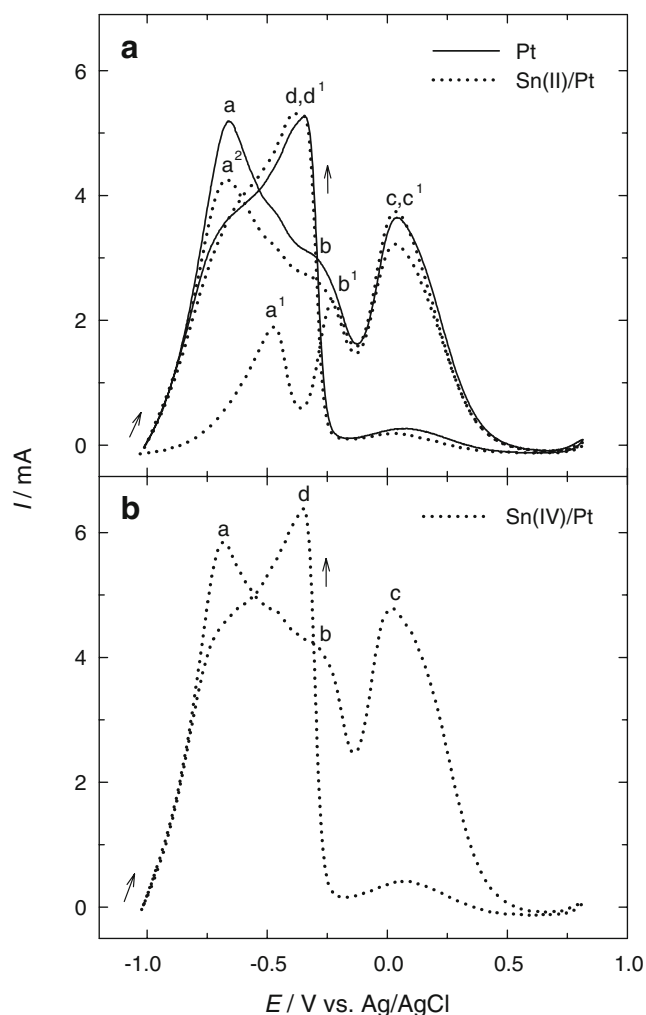


Fig. 5 Cyclic voltammograms of 50 mM NaBH_4 in 1.0 M NaOH (**a**) on the Pt wire electrode and on Pt wire, modified in 20 mM Sn(II); (**b**) on Pt wire modified in 20-mM Sn(IV) solutions. 25 °C, scan rate 10 mV s^{-1}

case of its oxidation on pure Pt, and only one oxidation wave (peak 1) is observed over the potential range between -0.6 and 0.8 V (in the positive direction). This shows that catalytic hydrolysis, characteristic of BH_4^- oxidation on pure Pt, is indistinctive for BH_4^- oxidation catalyzed by the studied platinum–tin complexes. Obviously, only a direct oxidation of BH_4^- is distinctly observed on GC modified with the Pt–Sn complex. A following decrease in activity of the modified surface at more positive potentials may be attributed to the adsorbed intermediates of the oxidation and to hampered BH_4^- ions adsorption. An anodic wave in the reverse scan, only sometimes observable at potentials more negative (about 0 V) than those in the positive scan, is likely associated with the direct oxidation of BH_4^- . This process is impeded by removal of oxidation products. A well-defined peak (1^1) appears at -0.2 to -0.3 V, similar to the BH_3OH^- oxidation peak in the case of BH_4^- oxidation

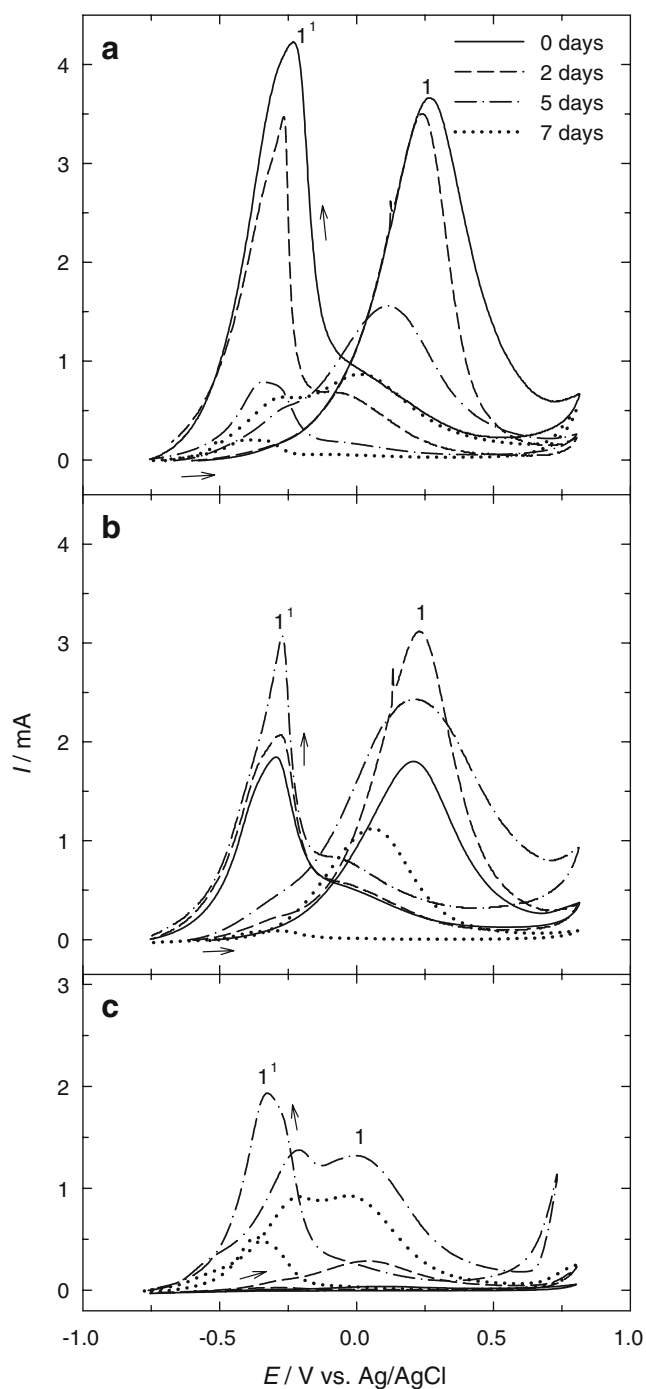
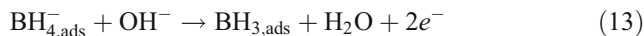


Fig. 6 First scans of cyclic voltammograms of 50 mM NaBH₄ in 1.0 M NaOH on GC modified in the solutions dependently on solutions aging. The initial concentrations: Pt(IV) 0.5 mM, Sn(II) 20 mM and HCl (M): (a) 0.45 (complex [Pt₃(SnCl₃)₈]²⁻); (b) 0.7 ([Pt(SnCl₃)₂Cl₂]²⁻); (c) 1.1 ([Pt(SnCl₃)₅]³⁻). Scan rate 10 mV s⁻¹, 25 °C

on pure Pt. It seems that this peak is related to catalytic activity of the electrode surface modified with the oxidation products of BH₄⁻, obtained in the positive oxidative scan. The reaction mechanism may involve the adsorption step similar to that proposed for borohydride oxidation on Au

[18], also non-catalytic for BH₄⁻ hydrolysis, according to which the intermediate borane (BH₃) formed during the oxidation of BH₄⁻ (Eq. 13) adsorbs on the electrode before combining with OH⁻ to BH₃OH⁻:



Therefore, the straight peak seen in the reverse scan may be attributed to the oxidation of BH₃ adsorbed on the electrode.

The open-circuit potential of the system and the peak of BH₄⁻ oxidation, catalyzed by the H₂[Pt₃(SnCl₃)₈] complex, slightly shift to more negative potentials with the colloid aging (Table 1, Fig. 6a). This potential shift testifies some increase in surface activity, probably, related to a gradual decrease in Sn(II) excess, unbound in the complex with platinum, on the GC surface. This assumption may be confirmed by studying successive scans of BH₄⁻ oxidation on the same modified GC surface. As shown in Fig. 7a, the peaks of BH₄⁻ oxidation in the second and third scans in the positive direction are shifted to more negative potentials compared with that in the first scan, and occur at -0.1 to 0 V. A similar value for the direct BH₄⁻ oxidation on Pt was obtained by Gyenge [20] and Martins et al. [25]. The rise in the anodic current of BH₄⁻ oxidation in the second positive and reverse scans also indicates an increase in the modified GC surface activity, probably due to the oxidation of Sn(II) excess in the first positive scan.

Similar results of BH₄⁻ anodic oxidation were obtained when the GC was modified in a H₂[Pt(SnCl₃)₂Cl₂] complex solution, containing initial Pt(II) and Sn(II) concentrations identical to those in the above-described H₂[Pt₃(SnCl₃)₈] complex, but at a somewhat higher HCl concentration (Table 1, Figs. 6b, and 7b). Only in the first positive scan the anodic current of BH₄⁻ oxidation, catalyzed by a freshly prepared H₂[Pt(SnCl₃)₂Cl₂] complex, was lower. With the complex aging (10–20 h), its activity increases due to the oxidation of Sn(II) excess. The anodic current of BH₄⁻ oxidation in the second scan was always higher, evidently due to the oxidation of unbound Sn(II) in the first positive scan. Since the H₂[Pt(SnCl₃)₂Cl₂] complex may be prepared by varying the Sn(II) and HCl ratio, it is interesting to examine the influence of the initial SnCl₂ concentration in the solution for GC modification on BH₄⁻ anodic oxidation. Table 2 shows that with increase in Sn(II) concentration in the Pt–Sn complex solution used for GC modification, the open-circuit potential shifts in the direction of positive potentials and the anodic current in the first scan decreases, showing the inhibiting action of Sn(II). In the second scan, when unbound Sn(II) ions are already oxidized to Sn(IV), the above-mentioned characteristics of BH₄⁻ oxidation show increase in surface activity, practically the same for all studied initial Sn(II) concentrations in the solution.

Table 1 Change in the characteristics of BH_4^- electrooxidation on Pt–Sn/GC dependently on the ageing of Pt–Sn complexes

Days	$[\text{Pt}_3(\text{SnCl}_3)_8]^{2-}/\text{GC}$			$[\text{Pt}(\text{SnCl}_3)_2\text{Cl}_2]^{2-}/\text{GC}$			$[\text{Pt}(\text{SnCl}_3)_5]^{3-}/\text{GC}$		
	E_0, V	E_1, V	$E_{\text{rev.}}, \text{V}$	E_0, V	E_1, V	$E_{\text{rev.}}, \text{V}$	E_0, V	E_1, V	$E_{\text{rev.}}, \text{V}$
0	-0.58	0.26	-0.25	-0.52	0.21	-0.29	-0.48	0.08	-
2	-0.60	0.24	-0.27	-0.60	0.22	-0.28	-0.60	0.03	-0.30
5	-0.66	0.11	-0.35	-0.62	0.21	-0.27	-0.75	0	-0.33
7	-0.70	0	-0.38	-0.68	0.07	-0.35	-0.78	-0.02	-0.38

The data are taken from CVs of Fig. 4.

E_0 open circuit potential, E_1 potential at which maximum current is achieved in the first positive scan, $E_{\text{rev.}}$ in the reverse scan.

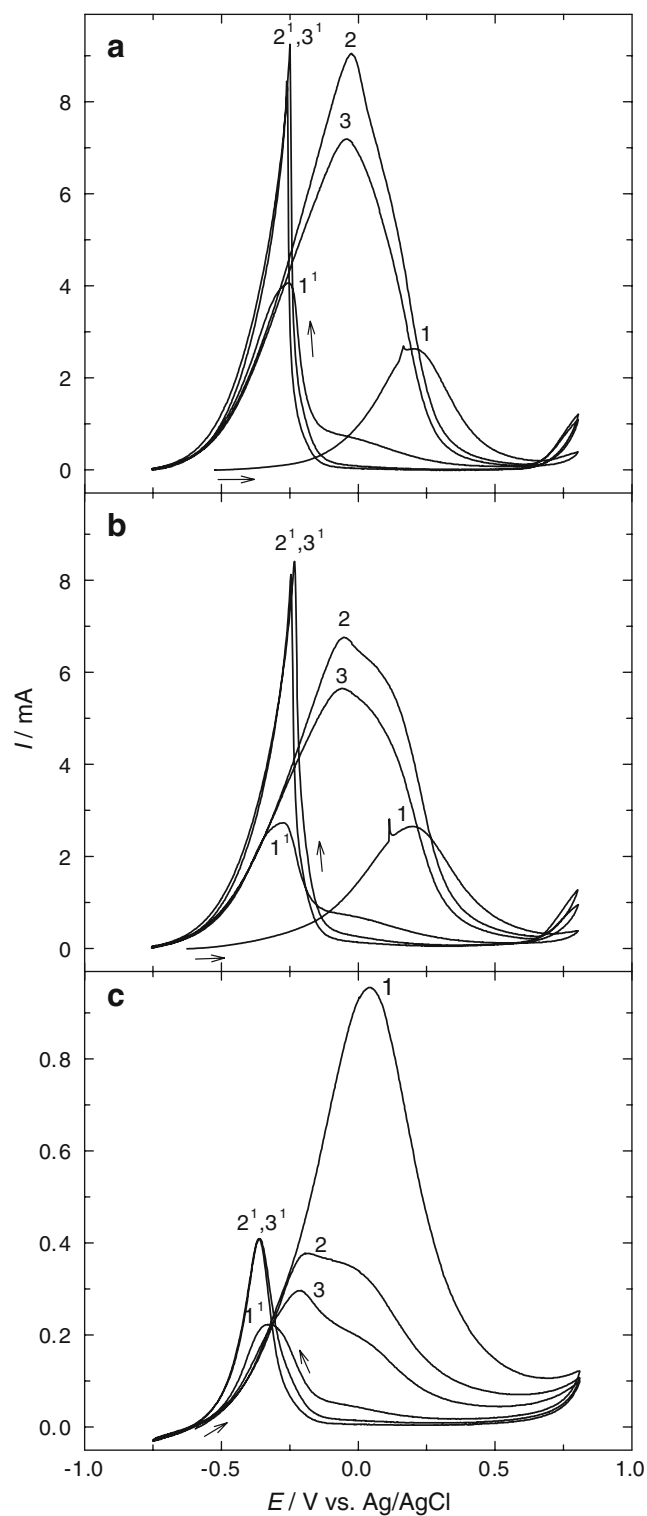


Fig. 7 Three first scans of cyclic voltammograms of 50 mM NaBH_4 in 1.0 M NaOH on GC modified in the solutions, containing the initial concentrations: Pt(IV) 0.5 mM, Sn(II) 20 mM and HCl (M): (a) 0.45 (complex $[\text{Pt}_3(\text{SnCl}_3)_8]^{2-}$); (b) 0.7 ($[\text{Pt}(\text{SnCl}_3)_2\text{Cl}_2]^{2-}$); (c) 1.1 ($[\text{Pt}(\text{SnCl}_3)_5]^{3-}$). Scan rate 10 mV s^{-1} , 25°C

Table 2 Influence of the initial SnCl₂ concentration in the solution of [Pt(SnCl₃)₂Cl₂]²⁻ complex adsorbed on GC on the characteristics of BH₄⁻ electrooxidation

SnCl ₂ , mM	E ₀ , V	E ₁ , V	E ₂ , V	E _{rev} , V	I ₁ , mA	I ₂ , mA
5	-0.60	0.22	-0.09	-0.28	3.1	6.1
10	-0.55	0.23	-0.04	-0.27	2.5	7.1
20	-0.62	0.24	-0.10	-0.29	1.8	6.8

Other initial concentrations: 0.5 mM Pt(IV); 0.7 M HCl.

E₀ open circuit potential, I₁ and I₂ maximum currents in the first and second positive scan, E₁ and E₂ potentials at which the max currents are achieved, E_{rev} potential at which maximum current are reached in the reverse scan.

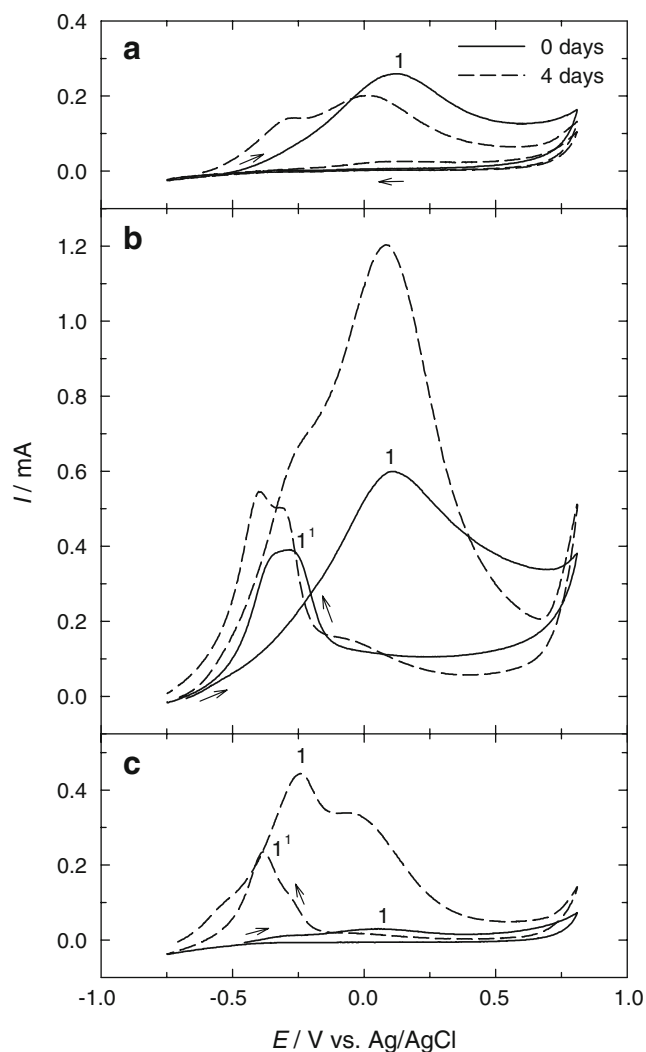


Fig. 8 First scans of cyclic voltammograms of 50 mM NaBH₄ in 1.0 M NaOH on GC modified in the complex solutions soon after adjusting Sn(II) and HCl to the initial concentrations and after 4 days. The initial concentrations: Pt(IV) 0.5 mM; Sn(II) 20 mM; HCl (M): (a) 0.45 (complex [Pt₃(SnCl₃)₈]²⁻), (b) 0.7 ([Pt(SnCl₃)₂Cl₂]²⁻), (c) 1.1 ([Pt(SnCl₃)₅]³⁻). Scan rate 10 mV s⁻¹, 25 °C

The platinum in the H₃[Pt(SnCl₃)₅] complex prepared with HCl concentrations higher than 1 M is five-coordinated, in contrast to the both Pt–Sn four-coordinated complexes whose activities in BH₄⁻ oxidation was characterized above. The reason determining the low catalytic activity of GC modified in this solution (Figs. 6c and 7c, Table 1) may be related to the difficulties of borohydride penetration to Pt(II) adsorbed on GC. Another cause for the low activity of H₃[Pt(SnCl₃)₅] may be insufficient adsorption of thin particles formed at high HCl concentrations (Fig. 4b) on GC surface. The activity of the complex increases with time when the particles in solution grow coarser due to gradual transition to the [Pt(SnCl₃)₂Cl₂]²⁻ complex with four-coordinated Pt.

The access of oxygen to the solution, which promotes degradation of Pt–Sn complexes, determines a drop in activity. The GC becomes active again for borohydride oxidation after modification in adjusted Pt–Sn complexes solutions by addition of missing amounts of SnCl_2 and HCl. The character of CVs obtained is close to those discussed above (Fig. 8). The lowest activity was observed for the adjusted $\text{H}_3[\text{Pt}(\text{SnCl}_3)_5]$ complex; its activity increases with complex transition to $\text{H}_2[\text{Pt}(\text{SnCl}_3)_2\text{Cl}_2]$ with time. Supposedly, the activities of the complexes would be higher if the oxygen present in the solutions was eliminated before the adjustment, or its excess in the solutions were minimized.

X-ray photoelectron spectroscopy investigations of the platinum–tin complexes adsorbed on GC did not show noticeable changes in the catalyst state during borohydride anodic oxidation from its open-circuit potential up to +0.4 V and in the reverse scan up to –0.6 V (Fig. 9). The data indicate that the platinum remains in a bivalent state after the positive potential scan and it is not reduced to zerovalent in the reverse scan. According to XPS, it is unlikely that the state of the tin on the electrode would be changed. Some changes in the spectra of the chlorine, observed in the positive scan, may be related to its partial

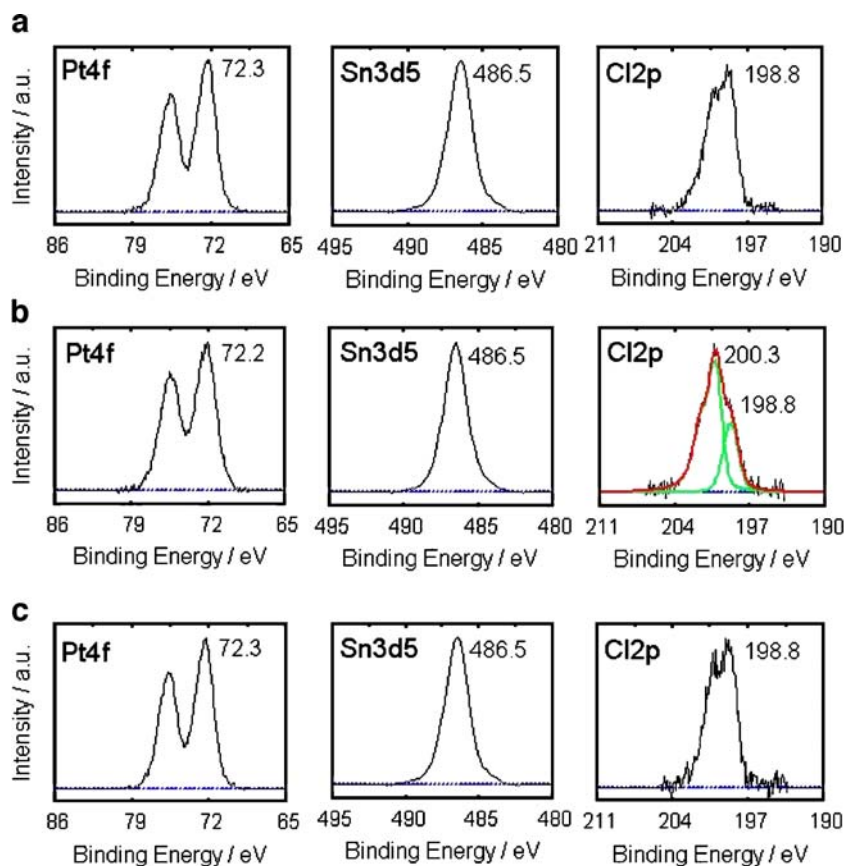
oxidation to a higher degree of valency; however, the spectrum of Cl2p observed after the reverse scan is identical to the initial one.

X-ray photoelectron spectroscopy investigations show some changes in the Sn/Pt ratio on the GC electrode during BH_4^- anodic oxidation. The initial Sn/Pt ratio in the solution was 40 (0.5 mM Pt(IV) and 20 mM Sn(II) were used for preparing $[\text{Pt}(\text{SnCl}_3)_2\text{Cl}_2]^{2-}$ complex). After GC modification, rinsing and drying, the average Sn/Pt ratio on the electrode established from several experiments decreased to 9–12 due to removal of the major part of the Sn(II) excess from GC during electrode preparation. This Sn/Pt ratio decreased by 10–20% after BH_4^- anodic oxidation but remained practically unchanged after the reverse scan. Meanwhile, the Sn/Cl ratio was unchanged during anodic BH_4^- oxidation on the modified GC electrode and after the reverse scan. Evidently, in the positive scan, unbound SnCl_2 is oxidized, maybe giving SnO_3^{2-} and ClO_3^{2-} , which are removed together.

Conclusions

Three forms of platinum–tin complexes may be obtained by the reduction of H_2PtCl_6 , with SnCl_2 depending on Sn(II)

Fig. 9 XPS spectra of Pt4f, Sn3d5, and Cl2p of Pt–Sn complex on GC modified in solution containing initial concentrations: Pt(IV) 0.5 mM, Sn(II) 20 mM and 0.7 M HCl; **(a)** initial, **(b)** after BH_4^- oxidation of 50 mM in 1.0 M NaOH up to 0.4 V; **(c)** after BH_4^- oxidation and following reverse scan up to –0.6 V



and HCl concentrations. The surface of GC modified in the Pt–Sn complex solutions containing 0.5 mM of platinum becomes an active catalyst for the electrooxidation of borohydride. The complexes with four-coordinated Pt are more active in comparison to those with five-coordinated platinum. The activity of Pt–Sn/GC in BH_4^- electrooxidation in a 1.0-M NaOH solution increases in the second positive scan due to oxidation in the first scan of the adsorbed Sn(II) excess, unbound in complex. The composition of complexes and their activity changes with time because of Sn(II) oxidation by atmospheric oxygen. The complexes may be renewed by supplementing missing amounts of SnCl_2 and HCl.

The mechanism of BH_4^- electrooxidation on Pt and on GC modified with Pt–Sn complexes is different. The Pt–Sn complexes are not catalysts for BH_4^- hydrolysis; thus, only direct BH_4^- oxidation is observed in the positive potentials scan, in contrast to its oxidation on the Pt electrode.

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