

Spontaneous Bi-modification of polycrystalline Pt electrode: fabrication, characterization, and performance in formic acid electrooxidation

Vilija Pautienienė · Loreta Tamašauskaitė-Tamašiūnaitė · Aloyzas Sudavičius · Giedrius Stalnionis · Zenonas Jusys

Received: 20 August 2009 / Revised: 23 November 2009 / Accepted: 25 December 2009 / Published online: 11 February 2010
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Abstract Spontaneous modification of polycrystalline Pt by irreversibly adsorbed bismuth was performed in BiCl_3 solution in concentrated hydrochloric acid under open-circuit conditions. After spontaneous modification, followed by extensive rinsing with water and drying, the surface was characterized using X-ray photoelectron spectroscopy and electrochemistry. Bi-oxy(chloride), oxide species, and metallic Bi were found at a submonolayer coverage on the Pt surface after spontaneous modification. The electrochemical response of Bi-modified polycrystalline Pt electrode in sulfuric acid solution exhibits a complex multi-peak feature, which is resulting in about constant redox charge (Bi species coverage) in the potential region from 0 to 0.9 V (vs. a standard hydrogen electrode). The spontaneously Bi-modified Pt catalyst in model studies exhibits a superior activity towards formic acid oxidation at fuel cell anode relevant potentials. The catalytic effect of bismuth oxy-species is explained in terms of both inhibition of CO_{ad} formation and oxidation of CO_{ad} in reaction with Bi-oxy-species.

Keywords Pt · Surface modification · Bi · Formic acid · Electrooxidation

V. Pautienienė · L. Tamašauskaitė-Tamašiūnaitė · A. Sudavičius · G. Stalnionis
Institute of Chemistry,
A. Goštauto 9,
LT-01108 Vilnius, Lithuania

Present address:

Z. Jusys (✉)
Institute of Surface Chemistry and Catalysis, Ulm University,
Albert-Einstein-Allee 47,
D-89069 Ulm, Germany
e-mail: zenonas.jusys@uni-ulm.de

Introduction

Formic acid oxidation had been intensively studied as a model electrocatalytic reaction related to fuel cell (direct formic acid or methanol fuel cells) applications (for detailed reviews see [1–4]). Oxidation of formic acid was proposed to occur via a ‘parallel-path mechanism’, namely, a direct oxidation to CO_2 via a reactive intermediate (‘direct pathway’) and via dissociative adsorption to form CO_{ad} and its subsequent oxidation (‘indirect pathway’) [1, 3, 5]. The overall oxidation rate and contribution of individual pathways were found to be dependent on the electrode surface structure and composition [1–3], the latter being possible to modify by irreversibly adsorbed submonolayers of foreign metals, such as Bi, Pb, Sn, Tl, etc. [1, 5–12]. The controlled noble metal surface modification is usually achieved by underpotential deposition (UPD) or (electro) reduction of pre-adsorbed metal ion precursor [13], while for some metal ions, such as Bi^{3+} or Sn^{2+} , their irreversible adsorption on Pt surface occurs spontaneously, i.e., without applying an external current [14–18].

In previous publications, we have reported a spontaneous modification of polycrystalline Pt surface via irreversible adsorption of tin and tin oxy-species, and the performance of resulting modified electrode in oxidation of C-1 organic molecules [19, 20]. In the present communication, we will further explore our approach for spontaneous Pt surface modification by bismuth. After a brief description of experimental procedures, we present and discuss physical and electrochemical characterization of the catalyst, and compare the electrocatalytic activity of spontaneously Bi-modified Pt vs. unmodified-polycrystalline Pt electrode in electrooxidation of formic acid.

Experimental

The solution of BiCl_3 (ca. 3.5 M) was freshly prepared by dissolving BiCl_3 in concentrated HCl (both from Lachema, Czech Republic) to avoid hydrolysis of bismuth chloride. A spontaneous modification of the clean polycrystalline Pt foil surface was carried out by (1) immersing a clean polycrystalline Pt electrode into BiCl_3/HCl solution under open-circuit conditions at room temperature for 2 min, and (2) subsequent extensive rinsing of the surface by pure water. All procedures were performed at ambient temperatures under a naturally aerated environment. After Pt surface modification and rinsing, the samples were dried in Ar stream (99.999%, ElmeMesser Gaas, Germany) and the X-ray photoelectron spectroscopy (XPS) analyses of the modified surface at a representative region were performed using a spectrometer ESCALAB-MKII VG Scientific (UK) with Mg K_α X-ray radiation source (300 W) and Ar^+ ion gun ($20 \mu\text{A cm}^{-2}$).

Electrochemical measurements were performed in a standard three electrode electrochemical cell filled with deaerated by Ar (99.999%, ElmeMesser Gaas, Germany) 0.5 M H_2SO_4 (Lachema, Czech Republic) supporting electrolyte or that containing 1 M of formic acid. Analytical grade chemicals and triply distilled water were used to prepare the solutions. All the experiments were performed at room temperature. The electrochemical data were acquired using a computerized system containing potentiostat PI-50-1 and a function generator PR-8 (Russia). The working electrode was Pt foil of 2 cm^2 ($1 \times 1 \text{ cm}$) geometric area, counter electrode: Pt sheet of ca. 2 cm^2 area ($1 \times 1 \text{ cm}$), reference electrode: $\text{Ag}/\text{AgCl}/\text{KCl}_{\text{sat}}$ (all potentials are quoted vs. a standard hydrogen electrode, SHE).

Results and discussion

XPS characterization

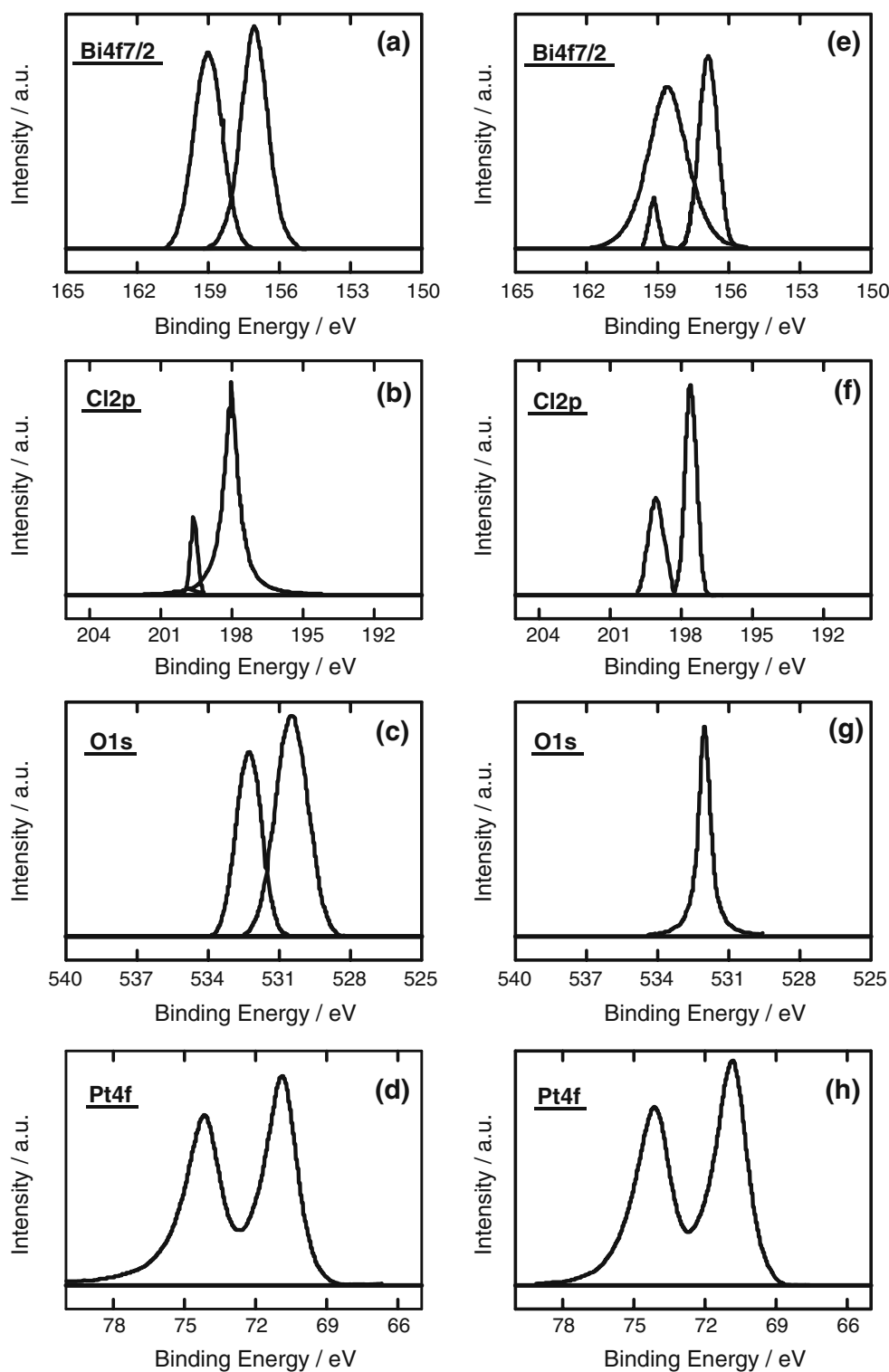
The XP spectra of spontaneously modified polycrystalline Pt confirm the presence of irreversibly adsorbed bismuth species on the Pt surface. The spontaneously modified Pt/Bi surface contains ca. 25 at.% of oxygen, ca. 51 at.% of Pt, ca. 15 at.% of Bi (both metallic and oxidic) and about 9 at.% of Cl (anion from the modifying solution), which overall indicates a submonolayer coverage of modifying species developed after the spontaneous modification (Table 1). Upon the Ar^+ sputtering down to 4 nm the modifying layer is gradually removed, resulting in a corresponding decrease of oxygen, Bi (to ca. 1 at.%) and Cl (below 1 at.%) content, and a corresponding increase in Pt content (up to 97 at.%).

The surface layer was found to be dominated initially by Bi-oxychloride/oxide and metallic bismuth (not shown), while with Ar^+ sputtering two peaks in Bi 4f spectra can be clearly resolved, corresponding to metallic Bi at lower binding energies (BE) and bismuth oxychloride(hydroxide)/oxide at higher BE (Fig. 1a), in agreement with the XPS spectra of PtBi intermetallic compounds [21, 22]. With further Ar^+ sputtering, bismuth oxide (major component) and bismuth oxychloride (minor component) contribute to the higher BE peak, with metallic Bi becoming dominant (Fig. 1e). Correspondingly, Cl 2p peak after 30 s Ar^+ sputtering constitutes of two components (Fig. 1b), which could be related to chloride anions and Bi-oxychloride. With further Ar^+ sputtering and the higher BE component becomes clearly resolved (Fig. 1f). The oxygen 1s doublet for (hydr)oxide/hydrochloride in the XP spectra after 30 s Ar^+ sputtering (Fig. 1c) turns to a single peak at ca. 532 eV (Fig. 1g),

Table 1 XPS analysis of the elemental composition of the modifying layer after spontaneous modification of polycrystalline Pt surface by bismuth species and corresponding composition after Ar^+ sputtering (rate 4 nm min^{-1})

Ar^+ sputter time/s	Element	Composition/at.%	E_b (Bi4f _{7/2})/eV
0	Pt	51	159.3 and 157.0
	O	25.2	
	Bi	14.7	
	Cl	9.1	
30	Pt	65.8	158.9 and 157.0
	O	30.25	
	Bi	3.0	
	Cl	0.95	
60	Pt	96.8	159.1, 158.5, and 156.8
	O	1.5	
	Bi	1.1	
	Cl	0.6	

Fig. 1 Representative X-ray photoelectron spectra of spontaneously Bi-modified polycrystalline Pt after 30 s (**a–d**) and 60 s (**e–h**) Ar^+ sputtering (2 and 4 nm sputter depth, correspondingly) for binding energies of bismuth 4f (**a, e**), chlorine 2p (**b, f**), oxygen 1s (**c, g**) and platinum 4f (**d, h**)



which, in combination with corresponding Bi4f and Cl 2p spectra, could be related to removal of bismuth oxychloride/hydroxide upon sputtering. The Pt 4f XP spectra (Figs. 1d,h) indicate a submonolayer coverage of modifying species.

The XPS data confirm the presence of both metallic bismuth and its oxy-species on the Pt surface after

spontaneous modification under open-circuit conditions. This finding is in agreement with previously reported data for irreversible Bi-adsorption on Pt electrode [14–17], where reduction of bismuth ions to metal was assigned (depending on the Pt electrode pretreatment) to interaction of either pre-adsorbed hydrogen [14] or hydroxy species [15].

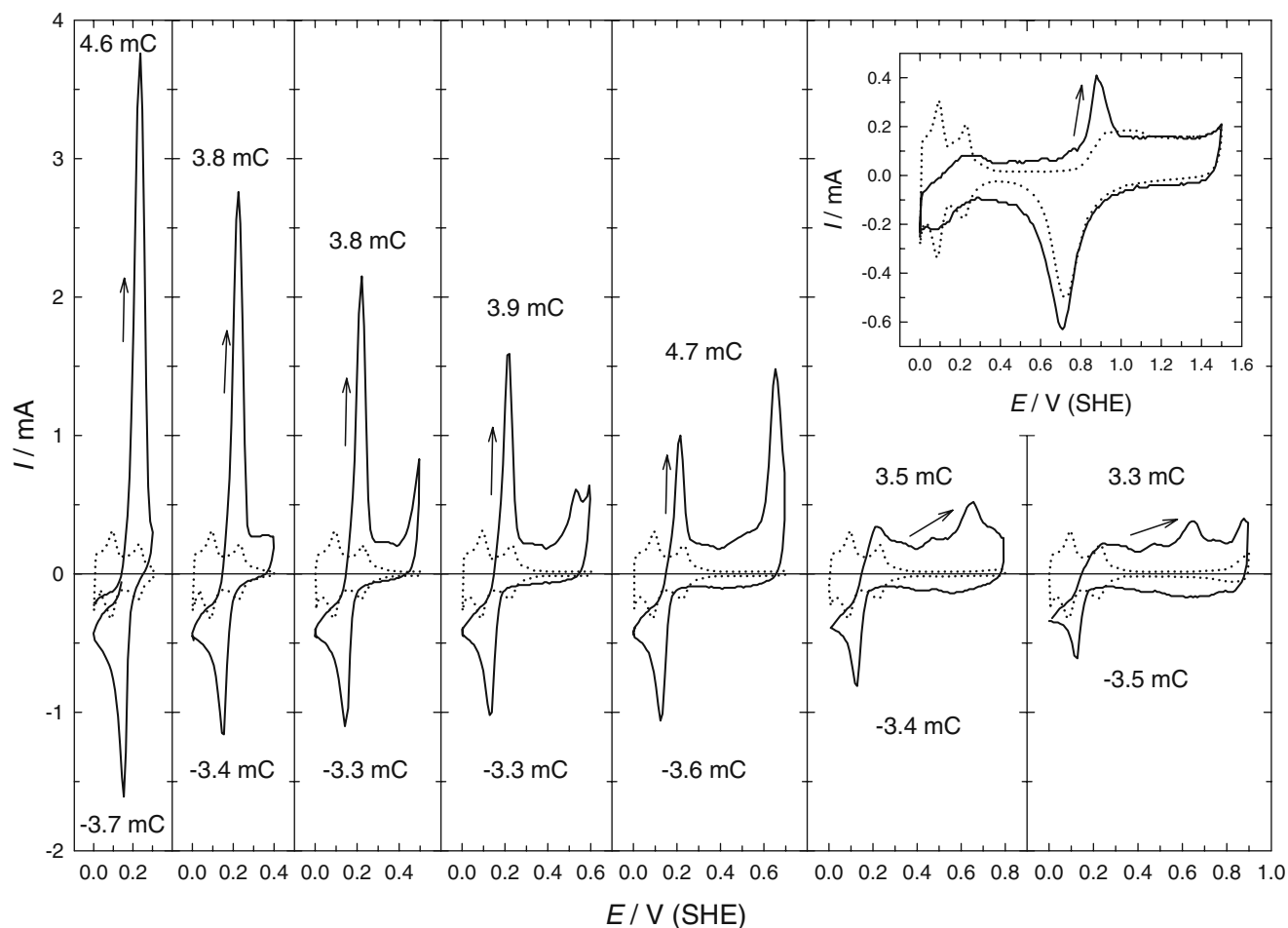


Fig. 2 Cyclic voltammograms for the clean polycrystalline Pt electrode (*dotted lines*) and Bi-modified polycrystalline Pt electrode (*full lines*) in 0.5 M H₂SO₄ solution with a progressive increase (increment of 0.1 V) in the upper potential limit from 0.3 to 0.9 V. Room temperature, potential scan rate 50 mV s⁻¹. The charges for

integration of corresponding currents within the applied potential window are listed in the figure. *Inset* base CV of pc-Pt and a stable CV Bi-modified pc-Pt electrode in 0.5 M H₂SO₄ solution for the upper potential limit of 1.5 V

Electrochemical characterization

Bi-modified pc-Pt electrode was immersed at 0 V vs. SHE and held at this potential for ca. 5 min, then the electrode potential was scanned to progressively more positive values, gradually increasing the upper limit. Hydrogen adsorption/desorption features, typical for a clean polycrystalline Pt electrode in sulfuric acid solution (Fig. 2, dotted lines) are largely suppressed on Bi-modified Pt electrode in the potential region 0–0.2 V, confirming the presence of blocking species on the Pt surface (Fig. 2, full lines). Scanning further the Faradaic current steeply increases and passes a pronounced anodic peak centered at ca. 0.25 V. After the potential reversal at 0.3 V, an equally expressed although about twice lower quasi-reversible narrow cathodic peak appears at ca. 0.15 V. An integration of the positive and negative current features results in the charges of ca. 4.6 and –3.7 mC, respectively (see corresponding numbers listed in Fig. 2), which could be indicative of some loss of bismuth-

modifying species from the surface, although the rotating ring-disk electrode measurements [13] suggest that metallic Bi is mainly converted to (hydr)oxide upon oxidation rather than dissolving. Some higher oxidation current (charge) in the first positive-going scan can be due to lower oxidation state Bi-oxy-species developed when holding the electrode at 0 V for 5 min prior to the potential scan. The reversibility of the above peaks clearly indicates the formation of a redox couple of Bi-oxy-species on the Pt surface. Similar redox peaks were reported for irreversibly adsorbed Bi on Pt(111) electrode in presence of chloride [11] or bulk PtBi alloy [22], whereas Bi-modified polycrystalline Pt electrode does not exhibit these features as reported previously [18]. The above redox couple could be attributed of the adsorbed Bi-oxychloride in agreement with the XPS findings (see Fig. 1a,b,e,f).

The second positive-going scan results in a significantly lower anodic current peak, compared to the first scan, although the charge under the potential scan to 0.4 V is

about equal to that measured for the preceding cathodic peak (see second panel in Fig. 2). The increase in the upper potential limit (see corresponding panels in Fig. 2) causes a further decrease of the above redox peaks, whereas new anodic peaks are developing at more positive potentials (at ca. 0.5, 0.65 and 0.9 V), which could be interpreted as a gradual conversion of Bi-oxychloride to Bi-hydroxy/oxy surface species. Overall, the resulting multi-peak feature developed in the positive-going potential scan could be attributed to the transformations of the adlayer [13]. The corresponding negative-going scans are nearly featureless due to the overlap of the peaks resulting in a broad double-layer type response, which is typical for oxophilic metals. Importantly, the integration of positive- and negative-going scans results in similar overall charges in the positive limit range from 0.3 to 0.9 V, which is indicative for development of a relatively stable irreversibly adsorbed residual Bi-oxy-species adlayer on polycrystalline Pt electrode surface, as evident from the largely suppressed H-UPD features of polycrystalline Pt electrode even after opening the electrode potential window up to 1.5 V (see inset in Fig. 2), in agreement with [6–8, 13]. However, the coverage of the residual Bi-adlayer cannot be quantified from the H-upd charge due to the overlap of the redox peaks related to Bi-oxy-species and the H-upd features [23].

Formic acid oxidation

Figure 3 shows formic acid oxidation on unmodified pc-Pt electrode (dotted line), the first (dashed line) and the fifth cycle (solid line) for Bi-modified pc-Pt electrode (corresponding Tafel plots in the positive-going scan for a clean pc-Pt and Bi-modified pc-Pt electrode are shown in the inset). Formic acid oxidation is inhibited over pc-Pt electrode at lower potentials since the electrode surface is partly poisoned by CO_{ad} species formed due to dissociative adsorption of formic acid as confirmed by in-situ IR spectroscopy studies [1, 24, 25]. Recent spectro-electrochemical studies suggest that electrooxidation of formic acid proceeds via a direct pathway at low potentials, while at higher potentials both oxidation of CO_{ad} species and a direct pathway are operative resulting in CO_2 formation [24–26].

The first positive-going scan for Bi-modified pc-Pt electrode results the anodic current maximum at ca. 0.25 V (Fig. 3, dashed line), which could be attributed to oxidation of both formic acid and bismuth oxy-species, similar to the analogous response for the positive-going potential scan in the supporting electrolyte (Fig. 2, full line). After that, the Faradaic current drops to the values similar to those for unmodified pc-Pt electrode at ca. 0.4 V, whereas with further potential increase a tremendous increase in formic acid oxidation current occurs, resulting

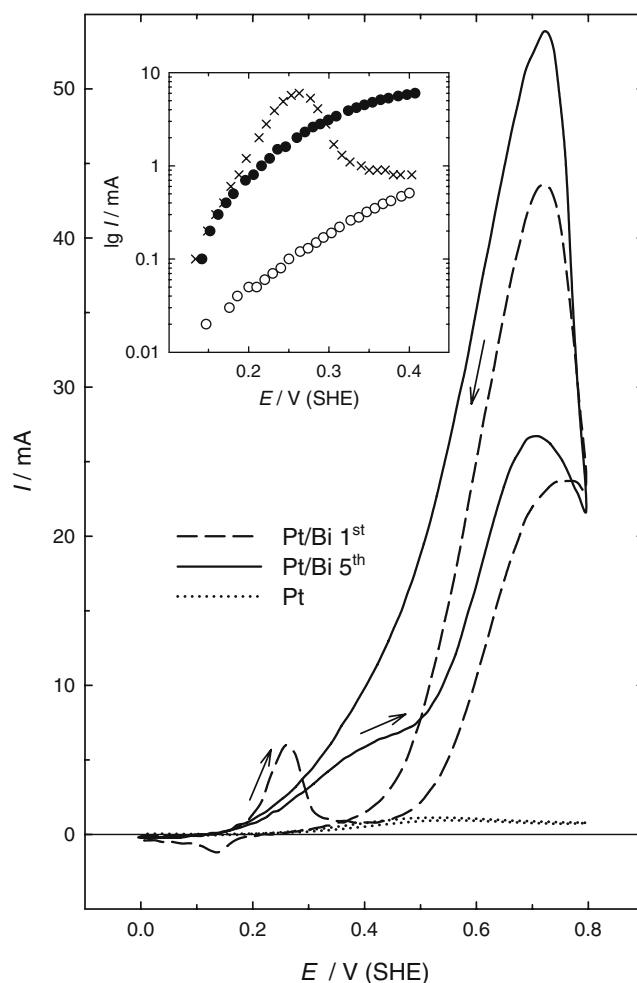


Fig. 3 Formic acid oxidation on the clean polycrystalline Pt electrode (dotted lines) and Bi-modified Pt electrode: first (dashed line) and fifth (solid line) cycle. Solution: 0.5 M H_2SO_4 +1 M HCOOH. Room temperature, potential scan rate 50 mV s^{-1} . Inset Tafel plot for formic acid oxidation in the positive-going scan over unmodified pc-Pt (open circles) or over Bi-modified pc-Pt electrode (crosses first scan, filled circles fifth scan)

in a current peak at ca. 0.75 V. A further current increase in the negative-going scan is because of a lower steady state CO_{ad} coverage due to its oxidative removal and/or lower CO_{ad} formation rate. Then, the Faradaic current decays faster due to re-poisoning of the electrode surface by CO_{ad} , reaching at ca. 0.3 V the activity similar to that for unmodified pc-Pt electrode. With further potential scans in the same potential window, the anodic current peak at 0.25 V is decreasing (not shown), while the oxidation current at higher potentials is increasing. The Faradaic current response for Bi-modified pc-Pt electrode in the fifth cycle (Fig. 3, solid line) exhibits the onset of formic acid oxidation at ca. 0.1 V, followed by an ill-resolved plateau at around 0.4 V of about tenfold higher current, compared to unmodified pc-Pt, and ca. 50-fold higher currents at more positive potentials.

A comparison of the electrocatalytic activity of an unmodified (open circles) and Bi-modified pc-Pt electrode for the first (crosses) and the fifth (filled circles) positive-going scan for formic acid oxidation is shown in the inset of Fig. 3. The increase in the current of Bi-modified Pt electrode in the first positive-going scan could be largely related to oxidation of modifying Bi-species as discussed above, while at higher potentials the performance of the modified electrode becomes similar to that of unmodified pc-Pt electrode. In contrast, the fifth positive-going scan for formic acid oxidation over Bi-modified electrode exhibits ca. tenfold higher current over the entire potential window compared to unmodified Pt electrode, demonstrating a superior catalytic activity of Bi-modified polycrystalline Pt electrode at the potentials relevant to fuel cell anode operation. The change in the activity of Bi-modified electrode can be explained by the variation of the adlayer coverage and/or their oxidation state [8, 13, 27]. An improved activity of Bi-modified pc-Pt electrode for formic acid oxidation could be attributed to site-blocking for formic acid dehydration to form CO_{ad} [28], the presence of Bi-oxy-species required for CO_{ad} oxidation [8], or weaker CO_{ad} bonding to Pt in presence of Bi [29–31].

Summary

The spontaneous modification of polycrystalline Pt surface by Bi-species in hydrochloric BiCl_3 solution and a subsequent rinsing of the surface with water results in formation of irreversibly adsorbed submonolayer of Bi-oxychloride/oxide and metallic Bi. The electrochemical signature of the modified electrode in sulfuric acid solution shows distinct redox features, which are decreasing when scanning the electrode potential to more positive values with development of new oxidation peaks at higher potentials, whereas the overall oxidation/reduction charge remains unchanged over a wide potential range indicating a relative stability of the adlayer. Bi-modified polycrystalline Pt electrode fabricated by irreversible adsorption of Bi-species in hydrochloric acid solution exhibits a superior activity for formic acid oxidation at low potentials relevant to fuel cell anode operation. The proposed method could be easily adopted for modification of realistic carbon-supported Pt nanoparticle catalysts.

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