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Electro-Oxidation of Glycerol on Platinum Modified by Adatoms: Activity and Selectivity Effects

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Abstract Antimony irreversibly adsorbed on a carbon supported platinum electrode oxidizes glycerol selectively to dihydroxyacetone with a lower onset potential (ca. 150 mV) and a higher peak current density (ca. 170 %) compared to clean Pt/C. Pb, In, and Sn also promote the catalytic activity of glycerol oxidation, however the reaction pathway towards the primary alcohol oxidation remains unchanged. Higher surface coverage by adatoms on Pt/C generally increases the activity of glycerol oxidation.

Keywords Glycerol · Dihydroxyacetone · Antimony · Platinum · Electrocatalysis

1 Introduction

Glycerol, a surplus byproduct of biodiesel, is an attractive and versatile feedstock as it is nontoxic, edible, and biodegradable [1, 2]. Valorisation of glycerol in generating valuable C_3 chemicals such as dihydroxyacetone (DHA), glyceraldehyde, and glyceric acid is viewed with particular interest to avoid rather expensive processes such as refining and distillation [2–6]. DHA, the product of secondary alcohol oxidation, is economically the most interesting one among the various target compounds due to its wide applications, especially in the cosmetic industry as a self-tanning agent [3, 7]. To date, DHA is produced by a fermentation process due to high yield, selectivity and quality requirements [3]. However microbial oxidation suffers from a low glycerol concentration and a long operating time [3, 7]. Recent advances in the catalytic oxidation of glycerol with Pd based homogenous catalyst report promising conversion (97 %) and selectivity (99 %) in the presence of benzoquinone as an oxidant within 15 min at room temperature [5]. Alternatively, in heterogeneous catalysis, Pt–Bi bimetallic catalyst has been shown to be a good candidate offering high conversion and selectivity towards DHA at low pH and mild operating conditions, among several monometallic (Pt, Pd, Au) [8, 9] and bimetallic catalysts (Pt–Bi, Au–Pt) [4, 9–12]. Electrocatalysis may offer additional advantages owing to the highly precise control of the oxidizing conditions through the electrode potential [6, 13–21]. Our previous study, following the electrocatalytic approach, revealed for the first time that a Pt/C electrode in a Bi-saturated solution at a carefully chosen potential is capable of oxidizing glycerol to DHA with 100 % selectivity [19]. As an attempt to gain more insight into active and selective conversion of glycerol to DHA by the Pt-M bimetallic catalyst system, it is important to study the trends and inherent relationships as to how the different metallic adatoms such as Sb, Pb, Sn, and In promote the electrocatalytic glycerol oxidation, as well as their effects on the product distribution.

In this paper, we demonstrate the enhanced activity and selectivity of glycerol conversion by incorporating adatoms (Sb, Pb, Sn, and In) onto the surface of a carbon-supported platinum (Pt/C) electrode in acidic solution by correlating the voltammetry with online HPLC product analysis. Two methods of reversible and irreversible modification have been used. Our results show that irreversibly deposited Sb on Pt/C is the most promising modifier for DHA formation

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with a low onset potential (ca. 150 mV than on pure Pt) and enhanced peak current density (ca. 170 %) compared to unmodified Pt/C. Although Pb, Sn, and In on Pt/C also promote the catalytic activity of glycerol oxidation, the reaction pathway towards the primary alcohol oxidation to generate glyceraldehyde as a dominant reaction product remains unchanged.

2 Experimental Section

Electrochemical measurements were carried out in a standard three-electrode cell controlled by a potentiostat/galvanostat (μ-Autolab Type III). A thin-film electrode with 3 nm Pt/C nanoparticles (50 wt%, Tanaka) was fabricated by loading defined amounts of nanoparticle suspension (10 μL) in water (1 mg mL^{-1}) onto a polished glassy carbon substrate, subsequently dried by purging Ar at room temperature. In order to confirm the electrochemically active surface area of the loaded catalyst, a blank voltammogram was recorded before each experiment. A large Pt plate was employed as a counter electrode and a reversible hydrogen electrode (RHE) as a reference. Oxidation of glycerol was performed in a mixture of glycerol (0.1 M, analytical grade) and 0.5 M H_2SO_4 under deaerated conditions by purging Ar.

For the Pt/C surface modification, analytical grades of Sb (Sb_2O_3, Sigma-Aldrich), Pb ($Pb(ClO_4)_2$, Acros), Sn ($SnCl_2 \bullet 2H_2O$, Merck), and In ($In_2(SO_4)_3$, Sigma-Aldrich) were used. Irreversible adsorption of adatoms was performed by placing the freshly prepared Pt/C electrode in contact with a 1 mM solution of Pb, Sn, and In, and Sb-saturated 0.5 M H_2SO_4 solutions for a set amount of time. After rinsing the electrode with water, each coverage is determined by recording the suppression of the hydrogen region [22], and then transferred to the electrochemical cell. For reversible adatom adsorption/desorption, 1 mM adatoms (Pb, Sn, and In) and a sufficiently large amount of Sb_2O_3, which corresponds to a concentration of ca. 10^{-4}–10^{-3} M, were introduced directly into the electrochemical cell. A freshly prepared Pt/C electrode was kept at a constant potential of 0.1 V for different times, after which the surface coverage is measured by the suppression of the hydrogen region in a blank solution, before applying it for glycerol oxidation.

The reaction products during voltammetry were collected and analyzed with an online HPLC system as described in our previous work [19–21, 23]. Sample volumes of 30 μL were injected into the columns in series of Aminex HPX 87-H (Bio-Rad) and Sugar SH1011 (Shodex) with diluted sulfuric acid (0.5 mM) as eluent. The selected temperature of column oven was 85 °C. Details of system configuration are described elsewhere [20, 21].

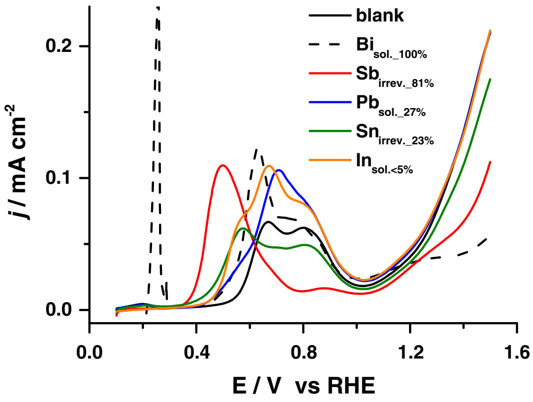

Fig. 1 Glycerol oxidation (0.1 M) on Pt/C electrodes modified by $Sb_{irrev.}$ ($\theta_{sb} = 81$ %), $Pb_{sol.}$ ($\theta_{Pb} = 27$ %), $Sn_{irrev.}$ ($\theta_{Sn} = 23$ %), and $In_{sol.}$ ($\theta_{In} < 5$ %) in comparison with blank and $Bi_{sol.}$ ($\theta_{Bi} = 100$ %) in 0.5 M H_2SO_4, with a scan rate of 1 mV s^{-1}

3 Results and Discussion

The glycerol oxidation on Pt electrode in acidic condition is relatively sluggish and generates glyceraldehyde as one of the dominant products without apparent C–C bond splitting in the potential window between 0.4 and 1.0 V (vs. RHE) [19–21]. Above 1 V, however, PtO_x activates the cleavage of the carbon–carbon bond to form mainly formic acid and glycolic acid followed by carbon dioxide formation from formic acid oxidation [19, 20]. Bismuth in the solution ($Bi_{sol.}$) blocks active sites for primary alcohol oxidation, lowers the onset potential (ca. 50 mV), and enhances the turnover frequency (ca. 180 %) compared to Pt/C blank by forming a Bi-related active site on the surface poised for secondary oxidation [19]. However, a constant and full coverage of Bi on the Pt/C surface is essential to obtain optimal activity and selectivity towards DHA for a PtBi catalyst prepared by the irreversible modification method [19].

Shown in Fig. 1 are the linear sweep voltammetry curves of 0.1 M glycerol on the Pt/C catalyst with several adatoms on the Pt surface or in the solution of 0.5 M H_2SO_4. As can be seen from the comparison of the six voltammograms, irreversibly deposited antimony ($Sb_{irrev.}$) on Pt/C shows significantly lowered onset potential (ca. 150 mV) and enhanced peak activity (ca. 170 %) compared to unmodified Pt/C. Interestingly, $Sb_{irrev.}$ on Pt/C shows a comparable turn over frequency but a lower onset potential (ca. 100 mV) than that of bismuth, which is considered the best surface modifier on Pt catalyst [4, 10–12]. Irreversible modified Sn ($Sn_{irrev.}$) on Pt/C also lowers the onset potential, starting at 0.35 V, the same potential of $Sb_{irrev.}$, but the current density is lower than that of unmodified Pt/C. Lead ($Pb_{sol.}$) and indium ($In_{sol.}$) dissolved

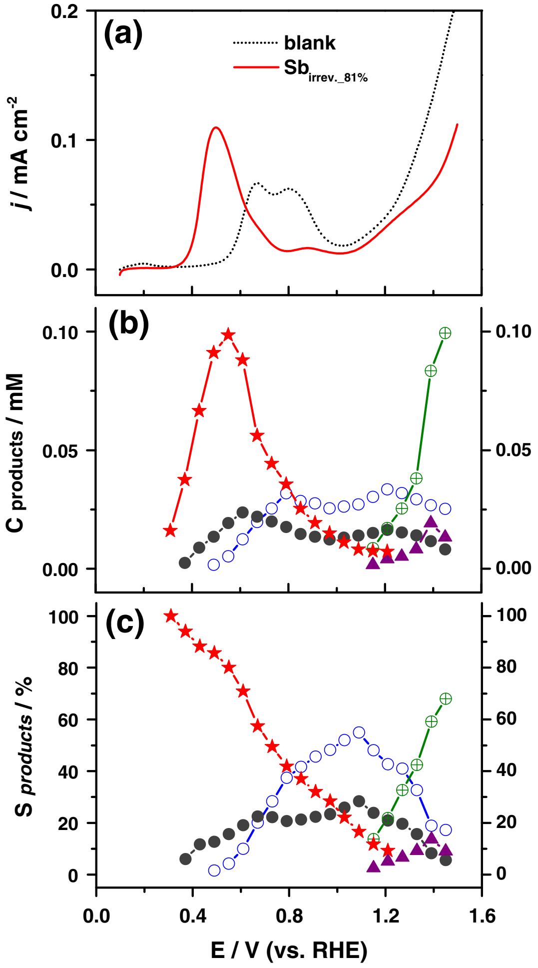

Fig. 2 Glycerol oxidation (0.1 M) on Pt/C electrode modified by Sb$_{\mathrm{irrev.}}$ ($\theta_{\mathrm{sb}} = 81$ %) in 0.5 M H_2SO_4: **a** current density profile at a scan rate of 1 mV s^{-1}, **b** concentration changes of reaction products, and **c** selectivity (%) of products as a function of potential. *white circle* glyceraldehyde, *asterisk* DHA, *blackcircle* glyceric acid, *black up-pointing triangle* glycolic acid, *circled plus* formic acid

in solution show comparable activities in terms of onset potential and peak current density to those of Bi$_{\mathrm{sol.}}$.

The effect of antimony on the product distribution of glycerol oxidation is shown in Fig. 2, which compares the positive-going potential sweeps and the associated product spectrum as detected by online HPLC at 1 mV s^{-1}. A Sb$_{\mathrm{irrev.}}$ on Pt/C electrode ($\theta_{\mathrm{sb}} = 81$ %) is obtained by dipping a freshly prepared Pt/C electrode in Sb-saturated solution for 3 min, after which the electrode is rinsed by water and the surface coverage of Sb is measured by recording the suppression of the hydrogen region before the electrochemical oxidation of glycerol. The presence of antimony (Sb$_{\mathrm{irrev.}}$) on Pt/C surface enhances the glycerol oxidation as shown by a peak at 0.5 V and the magnitude of this peak is strongly related to the surface coverage of Sb on Pt/C (see Supporting Information, Fig. S1). The results from HPLC analysis confirm that Sb$_{\mathrm{irrev.}}$ on Pt/C electrode is selective in oxidizing the secondary alcohol, and the main product observed is DHA with a selectivity of more than 80 % in between 0.35 and 0.55 V. At higher potentials, a similar product distribution as on Pt/C blank is obtained, ascribed mainly to the oxidative desorption of the adsorbed Sb [24, 25]. However Sb in the solution (Sb$_{\mathrm{sol.}}$) results in a complete inhibition of glycerol oxidation (see Fig. S1), whereas Bi$_{\mathrm{sol.}}$ maximizes the activity [19]. Interestingly, glyceric acid is observed as the second oxidation product from ca. 0.35 V, which is at a lower potential than the detection of glyceraldehyde formation. Since glyceraldehyde is expected to be the first reaction intermediate or product in the primary alcohol oxidation pathway and DHA is not oxidized to glyceric acid on PtSb (and PtBi) as proved by a separate experiment (see Fig. S2), it is obvious that antimony on Pt surface interferes and accelerates glycerol oxidation to glyceric acid via glyceraldehyde in the low potential range mainly on unmodified Pt sites. Arsenic (As), which features above Sb in the periodic table, also adsorbs on Pt sites. However irreversibly modified As on Pt/C mainly suppresses glycerol oxidation at low potentials before the surface oxide formation, and glyceraldehyde and glyceric acid were observed as dominant products on oxidized Pt surface (>1.0 V). (See Fig. S3).

Shown in Fig. 3 are the products formed during glycerol oxidation as detected by online HPLC in the presence of other adatoms (Pb$_{\mathrm{sol.}}$, Sn$_{\mathrm{irrev.}}$, and In$_{\mathrm{sol.}}$) on Pt/C surface or in the solution. Panels (b) in Fig. 3 show that there is no strong effect of adatoms on the product distribution of glycerol oxidation compared to Pt/C blank. The only significant difference is that the presence of Pb ($\theta_{\mathrm{Pb}} = 27$ %) in the solution generates DHA near the onset potential. Additionally, we were able to observe a small amount of 2-hydroxypropanedial (glucic acid) as one of oxidation products from Pb, Sn, and In modified Pt/C electrodes, whereas 2-hydroxypropandial is not observed either in the absence of modifiers [19–21, 23] or in the presence of Bi [19]. This could suggest that an adatom on the Pt surface anchors glyceraldehyde and oxidizes another primary alcohol rather than the secondary. The maximum surface coverage of Pb ($\theta_{\mathrm{Pb}} = 27$ %) is achieved by underpotential deposition for 3 min at 0.1 V in 1 mM Pb solution and the increase of the glycerol oxidation activity is proportional to the surface coverage. However irreversibly modified Pb on Pt/C partially blocks glycerol oxidation (see Fig. S4). In contrast to Pb, irreversibly adsorbed Sn (Sn$_{\mathrm{irrev.}}$, $\theta_{\mathrm{Sn.}} = 27$ %) on Pt/C enhances the glycerol oxidation activity, whilst a reversible system of Sn in solution (Sn$_{\mathrm{sol.}}$) completely suppresses the glycerol oxidation, similar to Sb (see Fig. S5). In$_{\mathrm{irrev.}}$ on Pt/C inhibits the activity of glycerol oxidation similar to Pb. However an enhanced activity from In$_{\mathrm{sol.}}$ is observed although almost no surface coverage

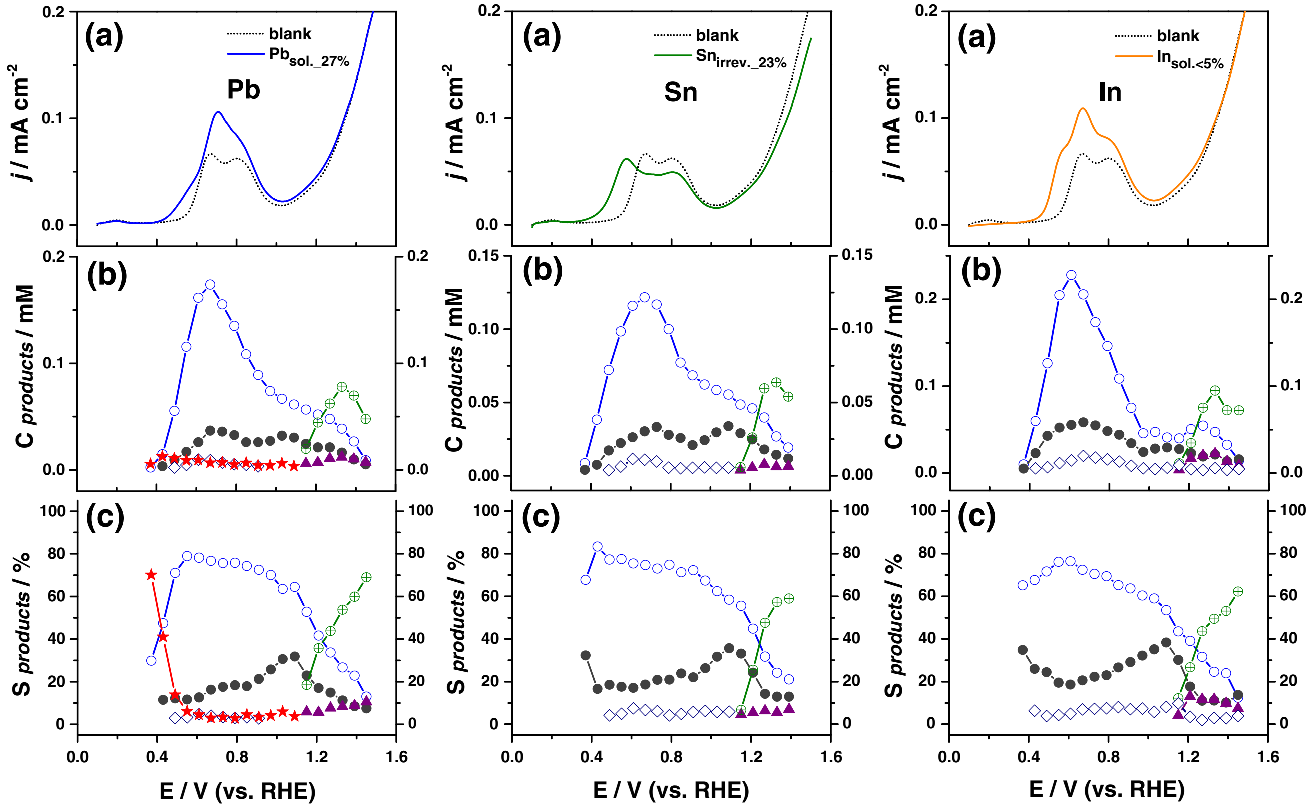

Fig. 3 Glycerol oxidation (0.1 M) in 0.5 M H_2SO_4 for and a Pt/C electrode in 1 mM Pb solution (in sol., $\theta_{Pb} = 27$ %), a Sn-modified Pt/C (irrev., $\theta_{Sn} = 23$ %), and a Pt/C electrode in 1 mM In solution (in sol., $\theta_{In} < 5$ %): **a** current density profile at scan rate of 1 mV s^{-1},**b** concentration changes of reaction products, and **c** selectivity (%) of products as a function of potential. *white circle* glyceraldehyde, *asterisk* DHA, *white diomond* 2-hydroxypropanedial, *blackcircle* glyceric acid, *black up-pointing triangle* glycolic acid, *circled plus* formic acid

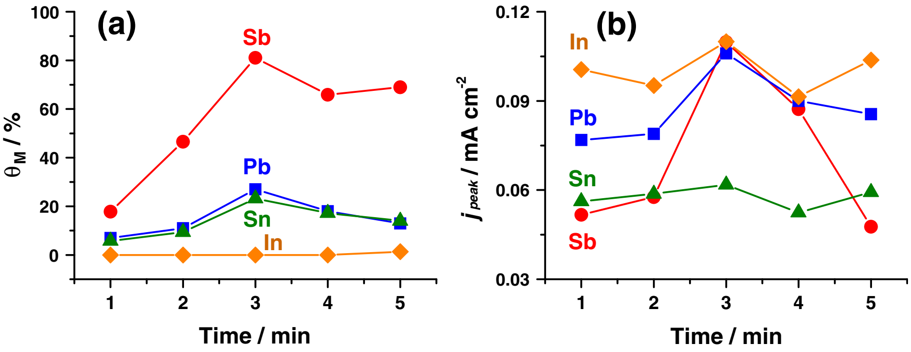

Fig. 4 **a** Surface coverage (θ_M, %) of Pt/C electrode by adatoms and **b** peak current density (j_{peak}, mA cm^{-2}) of glycerol oxidation in 0.5 M H_2SO_4 as a function of modification time. Sb and Sb: irreversible modification, Pb and In: reversible modification

is obtained from $In_{sol.}$ regardless of surface modification time. (see Fig. S6).

As shown above, the irreversible/reversible adsorption of the adatoms Sb, Pb, Sn, and In is not able to achieve a 100 % surface coverage on Pt/C electrode as Bi does. However we found that Pt/C electrode modified for 3 min by both methods gives the highest activity of glycerol oxidation, except for indium, as shown in Fig. 4. This general relationship suggests that a higher surface coverage leads to a higher activity, although the change of the surface coverage by adatoms as a function of time remains to be understood.

4 Conclusions

Pt-M bimetallic systems were developed to significantly enhance the activity and the selectivity of electro-oxidation of glycerol through the reversible/irreversible addition of adatoms (Sb, Pb, Sn, and In). A Pt/C electrode onto which antimony is irreversibly adsorbed is the most promising as it is capable of oxidizing glycerol selectively to DHA with a lower onset potential (ca. 150 mV) and with an enhanced peak current density (ca. 170 %) compared to a unmodified Pt/C. $\mathrm{Pb}_{\mathrm{sol.}}$, $\mathrm{In}_{\mathrm{sol.}}$, and $\mathrm{Sn}_{\mathrm{irrev.}}$ on Pt/C promote the electrocatalytic oxidation of glycerol, however the reaction pathway remains unchanged towards the primary alcohol oxidation to generate glyceraldehyde as a dominant reaction product. Although $\mathrm{Sb}_{\mathrm{irrev.}}$ shows a highly potent and remarkable activity, even higher surface coverage should be reached by other methods including overpotential deposition, since the activity of glycerol oxidation is strongly dependent on surface coverage by adatoms.

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