

Electronic Supplementary Information

The effect of Bi adsorption on CO oxidation inside 1.8 nm Pt pores

Thomas F. Esterle, Andrea E. Russell and Philip N. Bartlett

Experimental Section

The surfactant, octaethylene glycol monododecyl ether ($C_{12}EO_8$) (98% purity) was purchased from Fluka. Hexachloroplatinic acid hydrate (HCPA, 99.9% purity) and bismuth oxide (Bi_2O_3 , 99.9% purity) were purchased from Aldrich. The compounds were used as received. All solutions were prepared with deionised water from a Whatman Still and RO 50 water purification system (18 M Ω cm). 1 M sulphuric acid solutions were diluted from concentrated sp. gr. 1.84 acid (95% purity) purchased from Aristar. 0.6 M perchloric acid solutions were diluted from concentrated sp. gr. 1.54 Acid (60% purity) purchased from Fluka. The argon, nitrogen and carbon monoxide gases used were of high purity grade (Boc gases, 99.9% purity). Electrochemical deposition and cyclic voltammetry in sulphuric acid to clean the electrode surfaces were carried out on an EG&G model 263A potentiostat/galvanostat using a three electrode cell. Experiments for the electrooxidation of carbon monoxide were performed with an Uniscan Instruments model PG580 potentiostat/galvanostat. The three electrode system consisted of the working electrode, a large area platinum gauze and either a homemade saturated calomel reference electrode (SCE) or a homemade saturated mercurous sulphate reference electrode (SMSE). The saturated calomel reference electrode was used for the electrochemical deposition of platinum whereas the saturated mercurous sulphate was used for the cyclic voltammetry experiments.

The plating mixture was a ternary system of surfactant ($C_{12}EO_8$), water and H_2PtCl_6 . The constituents were heated in a sealed vial to 40 °C for 30 min then stirred in order to produce a homogeneous mixture. The vial was again sealed (to avoid the evaporation of water) and placed in the oven at 40 °C for a further 30 min. The template mixture contains 42 wt% $C_{12}EO_8$, 29 wt% H_2PtCl_6 and 29 wt % deionised water.

The formation of the H_1 hexagonal lyotropic liquid crystalline phase was confirmed by using an Olympus BH-2 polarized light microscope equipped with a Linkam TMS90 heating/cooling stage and control unit. The experiment consisted of preparing a thin film of mixture between a cover slip and a glass slide.

Pt disc electrodes (500 μ m in diameter) sealed into glass were used in all the experiments. The electrodes were polished using silica carbide papers and alumina slurries of 1 μ m and 0.3 μ m particle size on a Buehler microcloth to obtain a mirror finish. The Pt disc were characterised in 1 M sulphuric acid. Around 30 cycles were necessary to remove the impurities at the surface of the electrode and obtain a stable cyclic voltammogram in sulphuric acid between -0.65 V and 0.85 V vs. SMSE.

The electrodeposition of the mesoporous Pt film was carried out at room temperature (23 - 27 °C) under potentiostatic conditions as previously reported¹. The potential was stepped from +0.6 to -0.1 V vs. SCE and held that potential until the desired deposition charge (6.27 mC) was passed (typically 6 - 12 min). The resulting films were first cleaned in isopropanol and then soaked in water for several hours to remove the surfactant.

For the CO stripping studies, CO gas was bubbled through 1 M sulphuric acid for 30 min with the electrode held at -0.65 or -0.6 V vs. SMSE to ensure that carbon monoxide molecules adsorbed on the Pt surface reach equilibrium. Nitrogen gas was sparged through the solution for 15 min in order to remove all traces of CO from the bulk while maintaining the electrode potential unchanged. Two stripping voltammograms were then recorded scanning between -0.65 and 0.85 V vs. SMSE. The first scan shows the CO stripping peak and the second scan is considered as a blank to demonstrate that all of the adsorbed CO has been oxidised.

The adsorption of bismuth on the Pt surface was carried out by immersing the electrode for a period of time (2 - 3 min) at open circuit in 0.6 M perchloric acid containing the dissolved bismuth salt (10 mM); the procedure was adapted from Clavilier *et al.*². The electrode was rinsed with deionised water and then immersed in the solution containing only sulphuric acid to record the CO stripping voltammogram.

Electrochemical Characterisation

Cyclic voltammetry in 1 M sulphuric acid was performed for polished and H₁ mesoporous Pt electrodes until stable cyclic voltammograms were obtained. Fig. S1 shows such a stable cyclic voltammogram for a polished Pt electrode and a H₁ mesoporous Pt electrode of the same diameter recorded in 1 M sulphuric acid between -0.65 and 0.85 V vs. SMSE. The currents for the polished Pt electrode have been multiplied by 42 so as to match the currents in the double layer region at -0.3 V for the H₁ mesoporous Pt to aid comparison. The electroactive surface areas calculated from the hydrogen desorption peaks were 0.0048 cm² for the polished Pt and 0.220 cm² for the H₁ mesoporous Pt³. Cyclic voltammetry in sulphuric acid for a platinum electrode reveals the crystal facets present at the surface. The features displayed on the voltammogram for the oxide formation/stripping and for the hydrogen desorption/adsorption regions are identical for each electrode and are characteristics of a polycrystalline electrode made up of low index facets as indicated in the literature⁴⁻⁶.

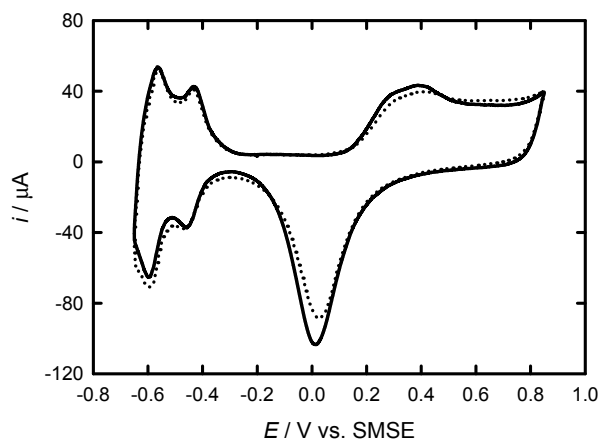


Fig S1. Cyclic voltammograms of a C₁₂EO₈ mesoporous platinum film electrode deposited onto a platinum disc electrode (solid line) and a polished polycrystalline platinum disc electrode (dotted line) (both 500 μm in diameter) in 1 M sulphuric acid recorded at 200 mV s⁻¹. The solution was deaerated by purging with argon for at least 20 min prior to the measurements. The currents for the polished polycrystalline platinum electrode have been multiplied by 42 to match the currents in the double layer region.

CO stripping voltammetry on platinum can also provide information regarding the crystalline structure of the Pt surface as reported in the literature⁷⁻¹⁴. Fig. S2 shows a CO stripping voltammogram of a polished Pt electrode in 1 M sulphuric acid. In this case CO was adsorbed at -0.6 V vs. SMSE and the solution was purged with nitrogen gas to remove CO from the solution before recording the CO stripping voltammogram. The subsequent cycle was used to verify that all the carbon monoxide was stripped off the surface.

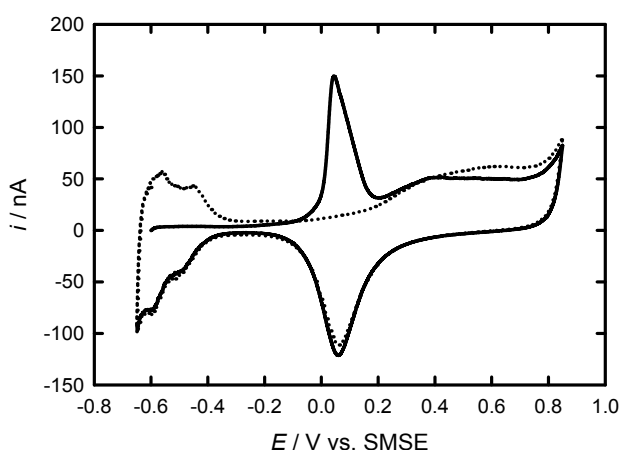


Fig. S2 CO stripping voltammogram (solid line) for a polished polycrystalline Pt electrode (500 μm in diameter) recorded in 1 M sulphuric acid, scan rate 10 mV s⁻¹. CO was adsorbed at -0.6 V with CO bubbling for 30 min and then the solution was sparged with N₂ for 15 min before recording the stripping. Second cycle (dotted line).

The CO stripping voltammogram for the polished Pt electrode is consistent with results for polished Pt electrodes found in the literature¹⁵. The absence of features in the hydrogen desorption region and the presence of a single CO stripping peak is observed on the first cycle. The restoration of the hydrogen desorption peaks and the absence of CO stripping peaks confirm the entire removal of the adsorbed CO monolayer on the second cycle.

Fig. S3 shows a CO stripping voltammogram of a H₁ mesoporous Pt film in 1 M sulphuric acid where CO was adsorbed at –0.65 V vs. SMSE and the solution was purged with nitrogen gas. The subsequent cycle was used to verify that all the carbon monoxide was stripped off the surface. The first scan shows a pre-wave and a main CO stripping peak divided into a main peak (denoted as peak I) and a shoulder (denoted as peak II). Peak I occurs at 0.01 V vs. SMSE, which is about 50 mV lower than the peak for the polished Pt electrode. The onset for CO oxidation starts at -0.3 V vs. SMSE, lower than for the polished Pt electrode (0.0 V vs. SMSE). The analysis of these peaks has been described in our previous paper concerning CO oxidation on mesoporous Pt. The pre-wave was attributed to the reaction of CO near the trough sites with oxygenated species, such as OH, adsorbed on the trough sites¹. The trough sites are the Pt sites situated at the inner corner of the pore where the pore walls intersect.

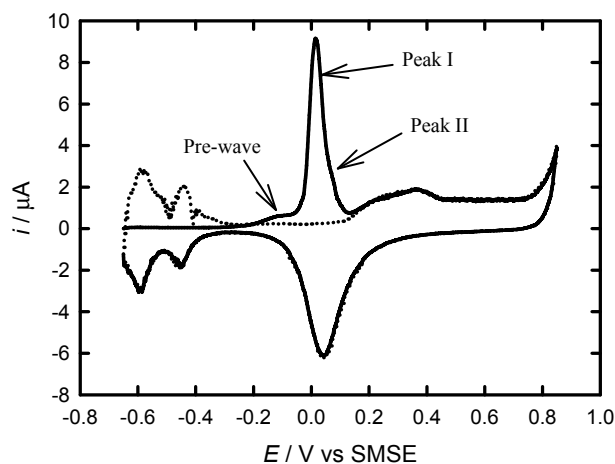


Fig S3. CO stripping voltammogram (solid line) of a mesoporous platinum film electrode (charge = 6.27 mC, 500 μm in diameter) on a polished platinum electrode in 1 M sulphuric acid. CO was adsorbed at -0.65 V with CO bubbling for 30 min and then the solution was sparged with N₂ for 15 min before recording the stripping. Second cycle (dotted line). The scan rate was 10 mV s⁻¹.

References

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