

Surface Characterisation and  
Electrochemical Behaviour of Well-  
Defined Pt-Pd(111) Single Crystal  
Surfaces: A Comparative Study Using  
Pt(111) and Palladium-modified Pt  
(111) Electrodes.

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Abstract

The need to understand the key structural parameters governing the electrocatalytic behaviour of metal surfaces continues to provide a strong impetus towards fundamental studies of electroadsorption [1]. To this end, systematic variation of surface crystallography [2] and surface modification of well-defined electrodes by adatoms [3] has often been employed to delineate these electrocatalytic trends [4]. However, very few electrocatalytic studies of bi-metallic alloy single crystal electrodes have been reported [5,6]. Since electronic perturbations associated with alloy phases are almost certainly connected with several high performance catalysts [7], this relative lack of fundamental experimental data constitutes a significant weakness on the part of the surface science approach to electrochemistry. In order to improve this situation, we have embarked upon a research program which utilises a simple modification of the Clavilier method of single crystal manufacture to prepare a series of well-defined bi-metallic bead electrodes. For example, by adding palladium carefully to the molten bead formed from a melted platinum wire, it is possible to control very precisely the bulk composition of the Pd-Pt single crystal that is formed upon cooling. In the present study, two Pd-Pt(111) alloy surfaces have been prepared (containing 6.25% and 25% palladium) and characterised both in UHV using LEED, AES and ISS and electrochemically using cyclic voltammetry (CV). Comparison has been made with the voltammetric response of Pt(111) and Pt(111) modified with a monolayer of palladium adatoms [Pd/Pt(111)]. Both alloy crystals when clean and thermally annealed in UHV give rise to sharp (1x1) LEED patterns. AES and ISS revealed that a surface enrichment in palladium takes place in agreement with an earlier study using polycrystalline Pd/Pt alloy samples [8]. Gentle ion etching of the thermally equilibrated surface (to remove the selvedge region) followed by AES and ISS analysis established that the bulk composition was in precise agreement with the nominal composition determined during crystal manufacture and hence confirming the soundness of the method. Electrochemical CV investigation of the alloy beads in aqueous

solutions of perchloric acid, perchloric acid containing chloride ions (see figure 1), CO saturated perchloric acid and copper chloride revealed a systematic and smooth graduation of response when compared with Pt(111) and Pd/Pt(111). In figure 1 for example, CV features associated with specific adsorption of chloride ions on "Pt-like" and "Pd-like" regions may readily be identified and a scaling in their intensity as a function of surface palladium composition is highlighted. Nonetheless, some deviations from the systematic trends are found for the monolayer Pd/Pt(111) surface which is known from previous electrochemical measurements [3] to be quite distinct electrochemically from bulk Pd(111).

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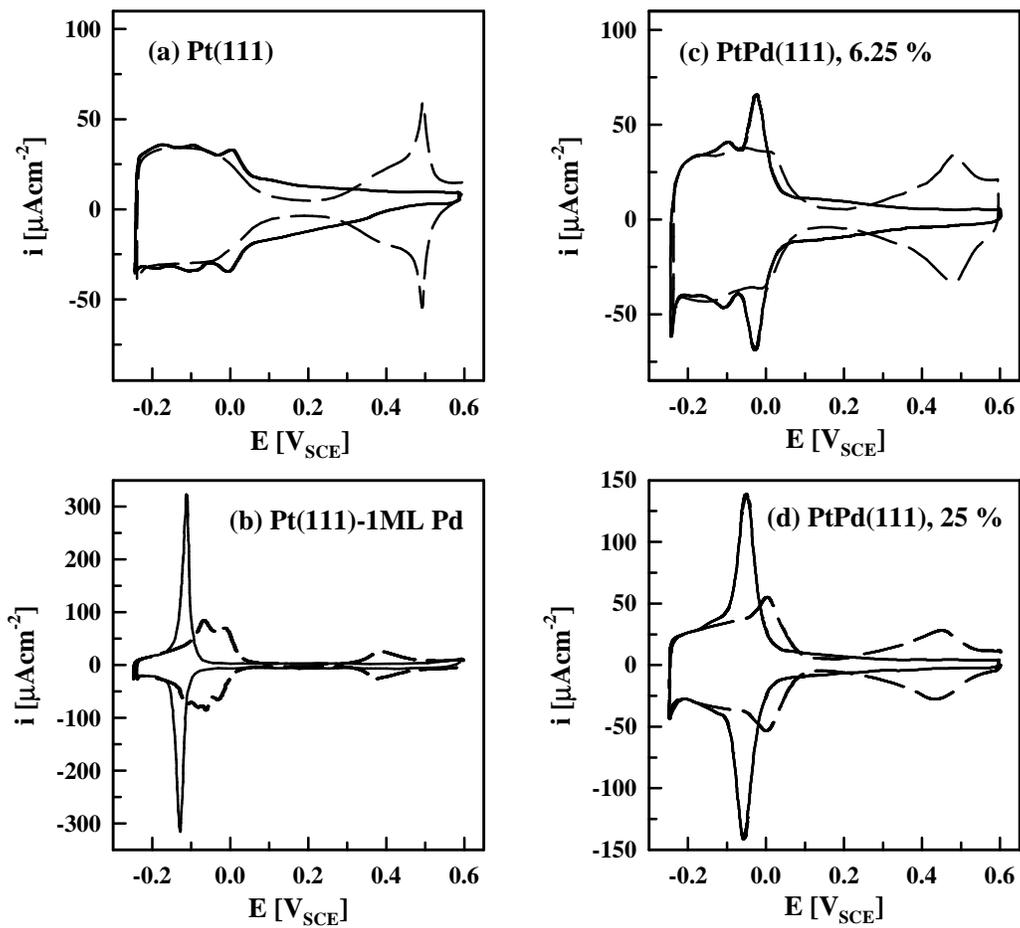


Figure 1. Cyclic voltammetry of (a) Pt(111), (b) Pt(111)-1ML Pd, (c) PtPd(111), 6.25%, (d) PtPd(111), 25%, sweep rate = 50 mV/s. (----) = 0.1M Perchloric Acid, (—) = 0.1M Perchloric Acid with added chloride anions.