

LETTERS

Temperature Effects in the Enantiomeric Electro-Oxidation of D- and L-Glucose on Pt{643}^S

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The temperature dependence of the enantioselective adsorption of D- and L-glucose on a chiral Pt{643}^S electrode is reported. The contribution to the electro-oxidation current of the initial adsorption of the glucose molecule on {111} terrace sites is used to determine a difference in the activation energy of adsorption between D- and L-glucose on Pt{643}^S. A value of approximately 1.4 kJ mol⁻¹ is obtained. When this value is converted into a diastereomeric product ratio, the mole percentage of the major product is evaluated as being 64%. Although small, it is speculated that optimization of the average terrace width of the chiral electrode surface will lead to an increase in the stereoselectivity of the reaction. These measurements constitute the first quantitative determination of enantiomeric selectivity at a metal electrode in the absence of a chiral promoter.

Introduction

In a recent paper,¹ we asserted that all kinked single-crystal surfaces are chiral.¹ Although kinked surfaces had already been postulated as being chiral by McFadden et al.,² the criterion used by these authors to identify the nature of the chirality in terms of asymmetric kink sites (the junction of steps of unequal magnitude) did not take into account the individual symmetry of {111}, {100}, and {110} sites comprising the kink. Hence, only certain kinked surfaces were considered chiral by these authors.² The stereogenic center actually results from consideration of the "handedness" of kink sites. Using an analogy with the Cahn–Ingold–Prelog sequence rules found in introductory

textbooks on organic chemistry,³ the kink site is viewed from above (i.e., from the vacuum or electrolyte phase) and the Miller indices of the individual sites comprising the kink are given the priority {111} > {100} > {110}. If the sequence of sites comprising the kink taken in the order {111} → {100} → {110} runs clockwise, the surface is denoted *R* (from the Latin "rectus"). If, however, the sequence {111} → {100} → {110} runs anticlockwise, the surface should be denoted *S* (from the Latin "sinister"). In the present study, we investigated the temperature dependence of the D-glucose and L-glucose electro-oxidation rate on the chiral Pt{643}^S surface. Previous work in our laboratory has demonstrated that the rate of adsorption of glucose

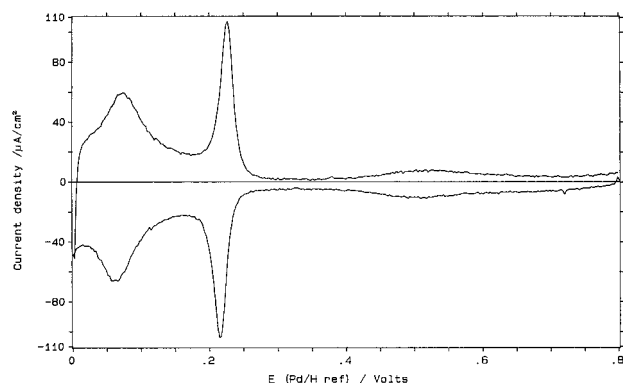
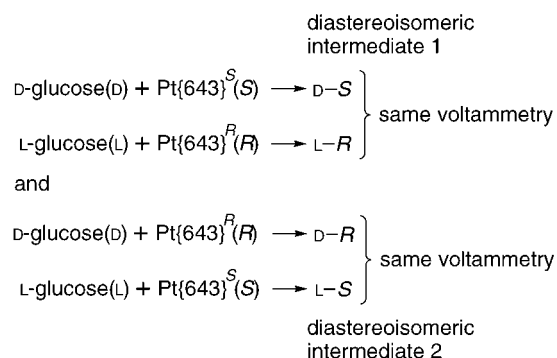


Figure 1. Cyclic voltammogram of Pt{643}^S in 0.1 M sulfuric acid. Sweep rate = 50 mV/s. Potentials referenced to a saturated palladium–hydrogen electrode.

on Pt{643} depends both on the stereochemistry of the glucose molecule and also on the stereochemistry of the electrode surface. In fact, a classical diastereomeric result was obtained in that two distinct voltammetric responses were observed associated with the adsorption processes:



Clearly if one determines the activation energy for the formation of diastereomeric intermediates 1 and 2 separately, the difference in the activation energy between these two values $\Delta(\Delta E)$ may be used to calculate a diastereomeric product ratio Q .⁴

$$\Delta(\Delta E) = -RT \log_e Q \quad (1)$$

For a McKenzie–Prelog or Cram asymmetric synthesis, Q is given by the mole ratio of the diastereomeric products $[P]/[N]$, where P refers to the like combination of configuration at the two chiral centers (R,R) or (S,S) and N to the corresponding antipodal combination (R,S) or (S,R).⁴ Hence, one may evaluate the relative stereoselectivity (the mole percentage of the major adsorption diastereomeric product) from $\Delta(\Delta E)$.

In the present letter we report, for the first time, an estimate for the difference in activation energy between D- and L-glucose adsorption on a chiral platinum surface. Such experiments allow enantiodifferentiation at solid surfaces to be investigated in a new and fundamental manner.

Previous electrochemical investigations of glucose electro-oxidation are extensive and include studies on polycrystalline⁵ and crystalline electrodes.⁶ The structure-sensitive nature of glucose oxidation, particularly in relation to the dependence of the oxidation rate on terrace width, was emphasized in ref 7. Furthermore, glucose oxidation was demonstrated to occur via a dual-path mechanism whereby, in parallel with the formation of a “reactive” intermediate, adsorbed carbon monoxide is generated which blocks active sites and if not removed at more positive overpotentials, eventually quenches all electrocatalytic activity.⁷

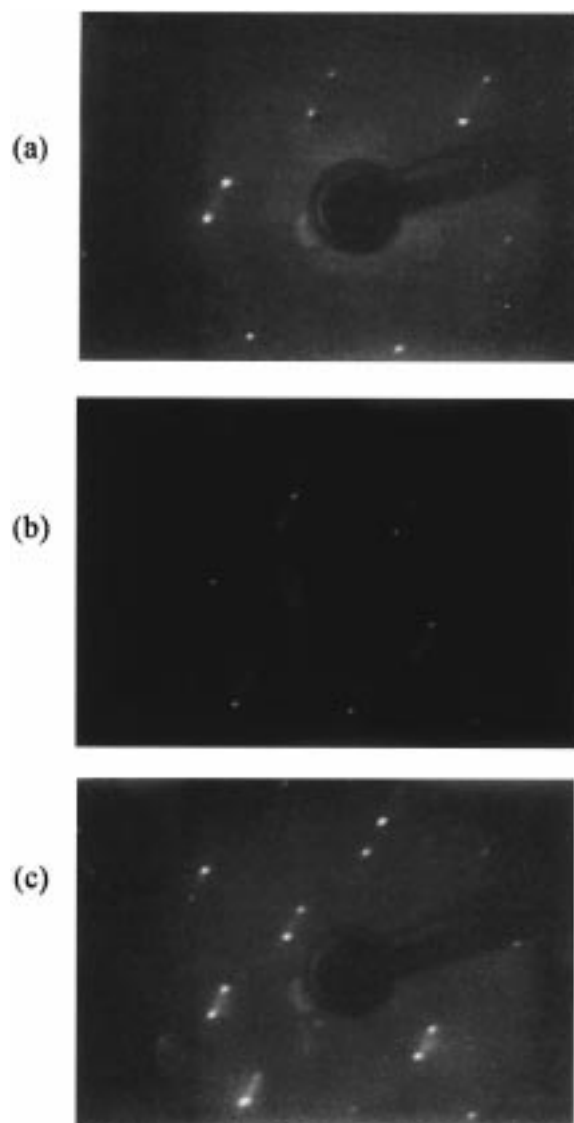


Figure 2. LEED patterns obtained from a clean Pt{643}^S surface at (a) $E_p = 78$ eV, (b) $E_p = 119$ eV, and (c) $E_p = 134$ eV.

Experimental Section

The Pt{643}^S bead electrode used in these experiments was prepared using the method developed by Clavilier et al.⁸ The crystal diameter was approximately 3 mm, and the clean, well-ordered surface was obtained by flame-annealing and subsequent cooling in a H₂/H₂O atmosphere. Clean transfer of the platinum crystal from the cooling vessel to the electrochemical cell was achieved using a droplet of ultrapure water attached to the electrode to protect the active surface from the ambient environment and in order to form a meniscus contact with the electrolyte solution. The achiral Pt{211} and Pt{111} bead electrodes also utilized in this study were prepared in exactly the same manner. Two identical electrochemical cells for cyclic voltammetry measurements were used in tandem, containing aqueous acidic solutions of D- and L-glucose, the cell design having been described previously.⁷ The cells were contained within a water tank thermostated at either 273 or 293 K. Sulfuric acid solutions were prepared from ARISTAR-grade concentrated acid (BDH) using ultrapure water from a Millipore Milli-Q system. The D- and L-glucose were purchased from Aldrich and Fluka (99.9% purity), respectively. To allow for mutarotation,³ glucose solutions were prepared at least 12 h prior to any

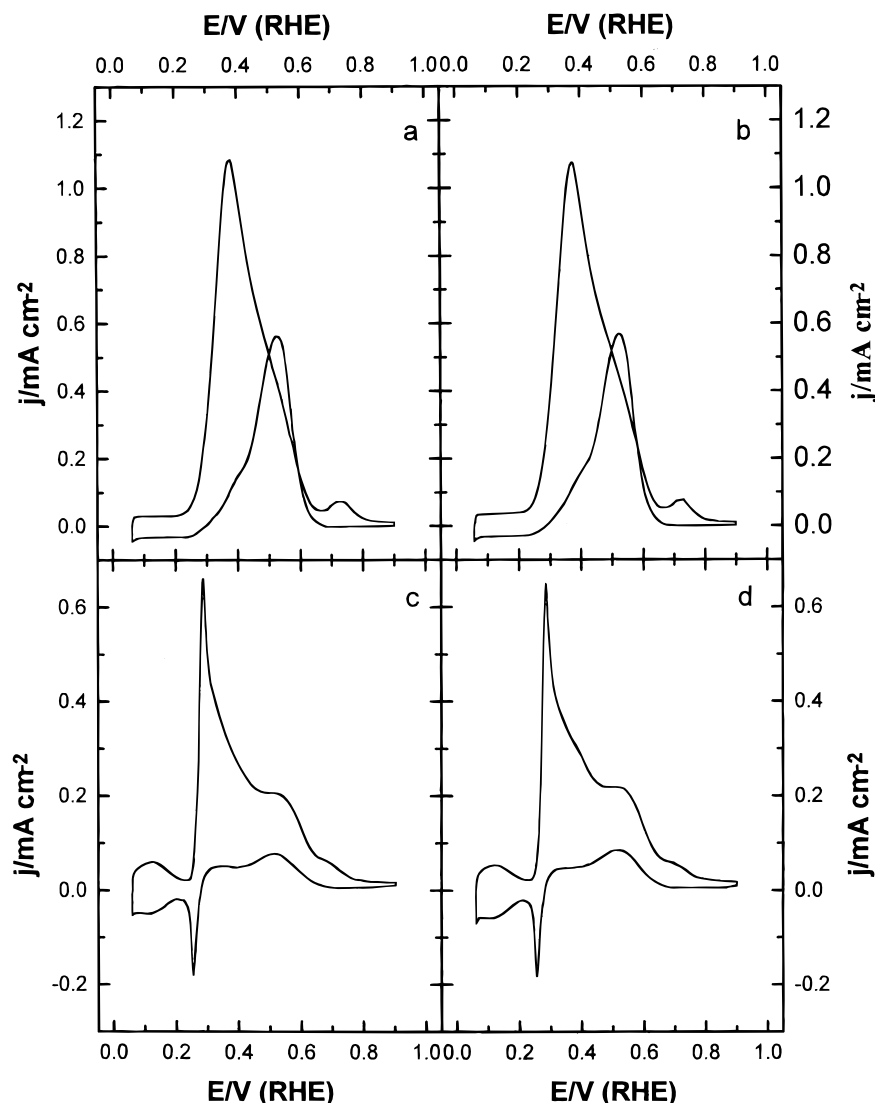


Figure 3. Pt{111} voltammogram in (a) 0.05 M sulfuric acid + 5×10^{-3} M D-glucose, (b) 0.05 M sulfuric acid + 5×10^{-3} M L-glucose. Pt{211} voltammogram in (c) 0.05 M sulfuric acid + 5×10^{-3} M D-glucose, (d) 0.05 M sulfuric acid + 5×10^{-3} M L-glucose. Sweep rate = 50 mV/s.

electrochemical measurements to enable time for equilibration between α - and β -glucose moieties present in aqueous solution. All electrolyte solutions were degassed for 30 min before each experiment to remove dissolved oxygen. The UHV-electrochemical transfer system used for LEED and Auger electron spectroscopy (AES) characterization of the Pt{643}^S bead electrode has already been described in ref 11. Electrochemical potentials are quoted with reference to a hydrogen electrode contained within the electrolytes except for Figure 1, in which the potential scale is quoted with reference to a saturated palladium–hydrogen electrode.

Results and Discussion

Structural Characterization of Pt{643}^S. Figure 1 illustrates the voltammetric response of a hydrogen-cooled Pt{643}^S electrode in contact with 0.1 M sulfuric acid. It is evident that three adsorption peaks can be identified. The broad peak situated between 0.35 and 0.7 V may be assigned to ionic adsorption from solution onto {111} terraces.¹⁰ The narrower, more intense peak at 0.22 V has been shown to be associated with $n\{111\} \times \{100\}$ step sites.¹⁰ Hence, the presence of {100} adsorption sites on Pt{643} is confirmed. Similarly, the peak at 0.06 V has been

demonstrated to be characteristic of $\{111\} \times \{111\}$ sites or more straightforwardly “110” sites.¹¹ Therefore, all of the adsorption sites predicted to be present on an unreconstructed Pt{643} surface are observed experimentally. If one takes into consideration the fact that the area under each peak reflects the surface concentration of a particular site, the cyclic voltammogram in Figure 1 is entirely consistent with an unreconstructed Pt{643}. However, to confirm these deductions using a more direct structural probe, the Pt{643}^S bead electrode was transferred to an ultrahigh-vacuum (UHV) chamber for analysis using LEED and AES. After a short anneal at 1000 K in 10^{-6} mb of oxygen for 10 min followed by heating the crystal to 1300 K in vacuo, no surface impurities could be detected by AES, confirming that the crystal was clean. The LEED pattern obtained from the clean surface at 298 K is shown in Figure 2. The diffraction spots were sharp with negligible diffuse scattering, attesting to the good crystalline order of the surface. In microfacet notation, the Pt{643} surface becomes Pt $3\{111\} \times \{310\}$, i.e., a three-atom wide {111} terrace separated by {310} steps. The splitting of the integral order diffraction spots is a manifestation of the step periodicity. In particular, the direction and magnitude of splitting is identical to the LEED photographs presented in ref 2 for the Ag{643} chiral surfaces.

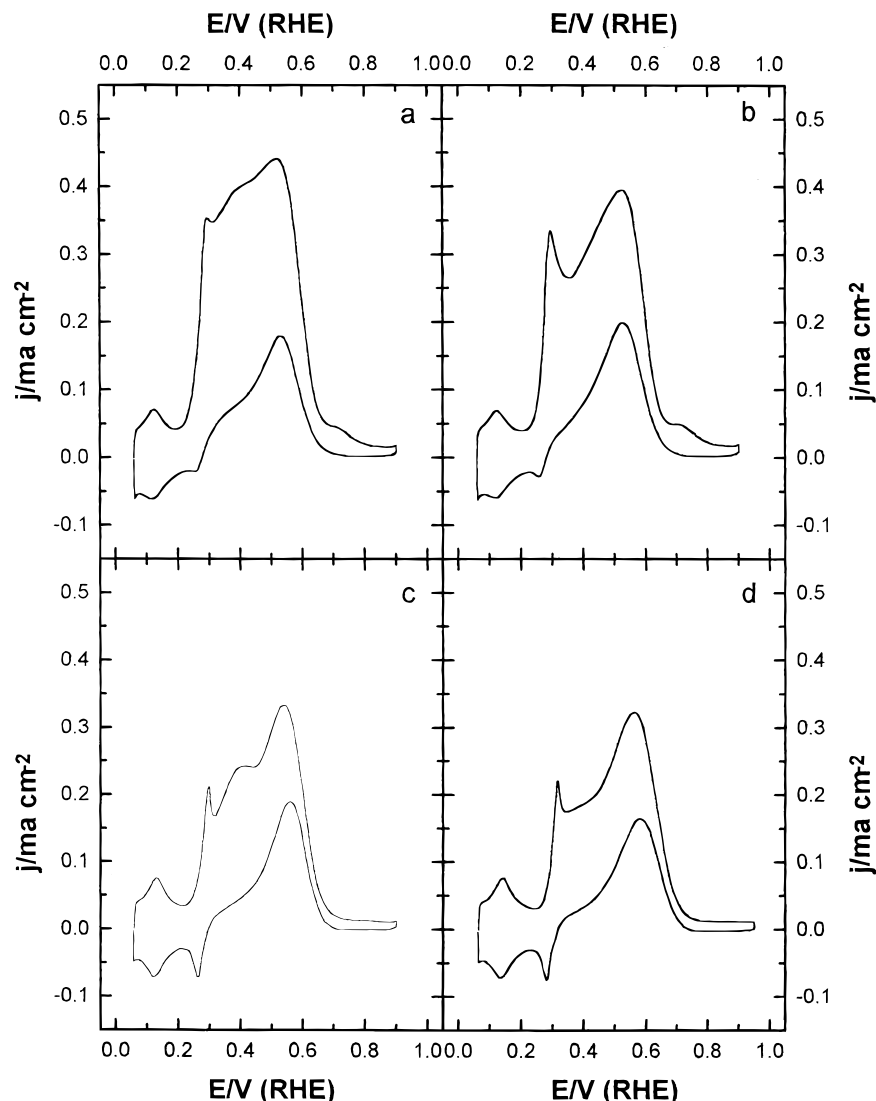


Figure 4. Pt{643}^S voltammogram in (a) 0.05 M sulfuric acid + 5×10^{-3} M D-glucose (293 K), (b) 0.05 M sulfuric acid + 5×10^{-3} M L-glucose (293 K), (c) 0.05 M sulfuric acid + 5×10^{-3} M D-glucose (273 K), (d) 0.05 M sulfuric acid + 5×10^{-3} M L-glucose (273 K). Sweep rate = 50 mV/s. In contrast to Figure 3, a clear enantiomeric difference in oxidation rate at 0.3 V is observed using the kinked electrode surface.

Therefore, taking into account both voltammetry and LEED, the crystalline structure of the electrode is confirmed as being {643}.

Temperature Effects and Chiral Discrimination in Glucose Oxidation on Pt{643}^S. To demonstrate that kink sites are essential for the observation of an enantiomeric effect in the adsorption of glucose, it is first necessary to show the absence of such effects in achiral surfaces. Figure 3 shows the first electro-oxidation sweep of D- and L-glucose using the kink-free platinum surfaces Pt{111} and Pt{211}. Pt{211} may alternatively be written as Pt 3{111} \times {100}, and it possesses the same three-atom wide average terrace width as Pt{643}^S. The peaks at 0.27 and 0.35 V may be assigned to adsorption of glucose at {100} \times {111} steps and {111} terraces, respectively.⁷ The greater magnitude of the electro-oxidation currents at 0.35 V for Pt{111} relative to Pt{211} has been attributed to the increased rate of adsorption of glucose as {111} terrace width increases.⁷ More importantly, however, in the context of the present study, is the fact that for both Pt{111} and Pt{211}, the electro-oxidation of D- and L-glucose are indistinguishable. In contrast, Figure 4 shows the electro-oxidation of D- and L-glucose using Pt{643}^S at 293 and 273 K. Irrespective of the relative intensities of the various voltammetric peaks (and hence

the detailed mechanism), it is evident that the voltammetry of D-glucose on Pt{643}^S is *different* from that of L-glucose. The largest difference may be ascribed to the peak at 0.35 V. Since the concentration of D- and L-glucose is the same in both cases, the difference in voltammetry is asserted to be a chiral discrimination associated with the symmetry (*R* or *S*) of the surface. In addition, it is clear that decreasing the temperature decreases the absolute magnitude of the rate of electro-oxidation (smaller anodic currents at 273 K compared to 293 K) while increasing the resolution of the individual electro-oxidation peaks (compare the potential region between 0.3 and 0.45 V at 273 and 293 K, particularly for D-glucose). To calculate an activation energy for the adsorption of D-glucose on Pt{643}^S, a deconvolution program is used to break down the different contributions to the total electro-oxidation. One could, of course, take the absolute value of the current density at 0.39 V as a measure of the reaction rate. However, to avoid the possibility of errors associated with overlap between the various peaks, a deconvolution procedure was employed. Three Gaussian peaks were sufficient to account for the electro-oxidation profile. The magnitude of the electro-oxidation peak at 0.39 V is the key difference between D- and L-glucose adsorption on Pt{643}^S and, as mentioned earlier, is also a measure of the rate of

adsorption of glucose. Hence, if the rate of D-glucose adsorption is measured at 293 and 273 K, an activation energy barrier of 9.4 kJ mol^{-1} is evaluated. Repeating the above deconvolution procedure for L-glucose, electro-oxidation using the same three Gaussian peak contributions at 293 and 273 K gives rise to an activation energy barrier for L-glucose adsorption on $\text{Pt}\{643\}^S$ of 8.0 kJ mol^{-1} . Because the uncertainty on the slope of a line between two points is unknown, one may deduce that the free-energy difference between the corresponding precursor transition states $\Delta(\Delta E)$ is approximately $9.4 - 8.0 = 1.4 \text{ kJ mol}^{-1}$. Using this value in eq 1, the diastereomeric product ratio Q for the glucose electro-oxidation at 298 K is determined to be 1.8. This in turn may be translated into a mole percentage of the major diastereomeric product of 64%. Although this value is small (50% would be zero enantiomeric effect), it is clear that glucose electro-oxidation is critically dependent on the average terrace width of the single-crystal electrode, and hence, it is speculated that this value may be increased by suitable geometrical manipulation of terrace width and kink geometry. In this way, enantioselectivity at solid surfaces may be examined at a fundamental level. Future work will be directed toward examining the role of chiral adsorption sites in asymmetric heterogeneous catalysis and how chiral promoters interact with the kink sites of catalyst materials.

Conclusion

The interaction of chiral $\text{Pt}\{643\}^S$ with D- and L-glucose results in a differential in the activation energy for adsorption of approximately 1.4 kJ mol^{-1} . This corresponds to a diastereomeric product ratio of 1.8 and a mole percentage of major diastereomeric product of 64%. These measurements constitute the first quantitative determination of chiral selectivity at a metal surface in the absence of a chiral promoter.

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