



ELECTROOXIDATION OF L-ASCORBIC ACID AND D-ISOASCORBIC ACID ON CHIRAL AND BASAL SINGLE CRYSTAL PLATINUM SURFACES

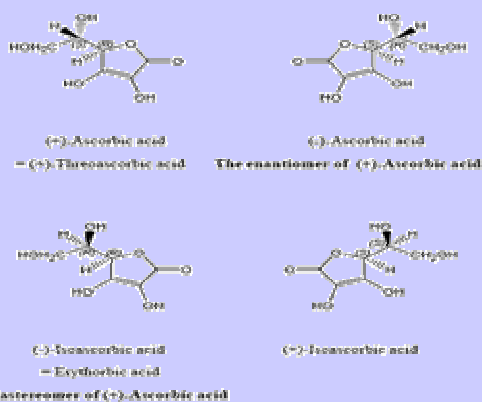
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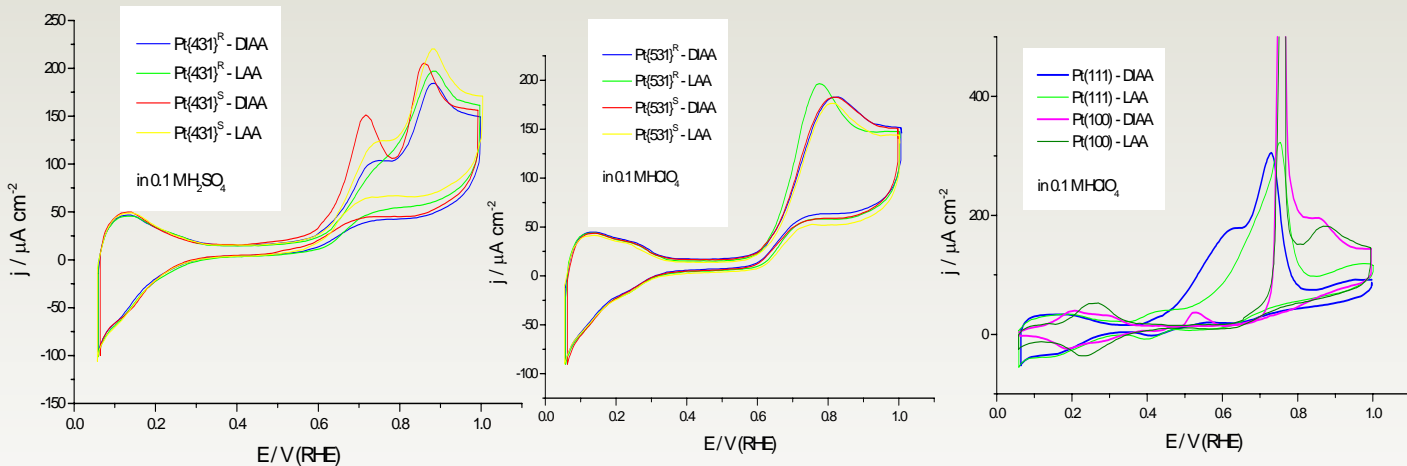
Motivation for the work: L(+)-ascorbic acid (LAA) or vitamin C is known for its important role as a component of enzymes involved in the synthesis of collagen and carnitine, and its anti-scorbutic activity. Both LAA and D(-)-isoascorbic acid (DIAA) are commercially important as antioxidant preservatives, though the biological activity of DIAA is only 5% of LAA. The electrochemistry of LAA is very well studied and there are several methods for electrochemical analysis of LAA.¹ However, there are hardly any electrochemical methods or sensors for the discrimination & selective analysis of LAA and / or DIAA.

Stereoisomers of ascorbic acid



The electrocatalytic oxidation / reduction of organic molecules on metal electrodes is often sensitive to surface atomic arrangements. For instance, the electrooxidation of sugars was found to be enantioselective on kinked single crystal, Pt² and Au³ surfaces. The purpose of this study was to check if the 'chiral' or 'basal' Pt surfaces could be useful for stereoselective recognition / oxidation of ascorbic acid stereoisomers. Pt{431}^{R&S}, Pt{531}^{R&S}, Pt{721}^{R&S} and {643}^{R&S} were the 'chiral' pairs chosen with different kink densities and terrace orientations. Pt(111), Pt(110) and Pt(100) were the basal planes used in the study.

- Both DIAA and LAA do not show any difference in CVs at any of the kinked surfaces at concentrations of 3 mM or 1 mM.
- The fine structures and differences are revealed in the voltammograms at a concentration of 0.5 mM in 0.1 M HClO₄ as well as 0.1 M H₂SO₄.
- This suggests, that adsorption at the electrode surface plays an important role and alternative oxidation pathways are possible.
- Of the kinked surfaces mentioned above, only the enantiomeric Pt{431}^{R&S} exhibit marked differences in the CVs as shown below. For the pairs of Pt{643}^{R&S}, Pt{531}^{R&S}, Pt{721}^{R&S} the CVs are similar.



- In general, the reactivity of the basal planes increases in the following order (110) < (111) < (100) with DIAA showing higher electroactivity than LAA in most cases.
- A hump followed by a peak is seen for DIAA on Pt(111), but a single peak for LAA. A return peak for DIAA is seen on Pt(100) but not for LAA. These differences could be useful in discriminating the two stereoisomers.
- The Pt {431}^{R&S} chiral pair electrodes are the only surfaces with (110) oriented terraces and the study on the basal planes revealed that this surface atomic arrangement is less favourable for the oxidation of the ascorbic acid isomers. This implies that a stereoselective effect is only visible when the extent of the electro-oxidation is less favoured.

Further experimentation needs to be done with variety of crystallographic orientations, to achieve more clear discrimination between the stereoisomers for the design of electrochemical sensors.

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