

## Understanding Heteroaromatic Molecular Adsorption by Lead Underpotential Deposition and Electrochemical Quartz Crystal Microbalance

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Underpotential Deposition (UPD) is usually the first stage of metal deposition on a metal substrate. In UPD process, a submonolayer to several monolayers of a foreign metal adatom deposits onto another metallic substrate at potentials positive to the reversible Nernst potential. One of the important findings at both single and polycrystalline surfaces is that UPD is very sensitive to surface structure of the substrate crystal. Using cyclic voltammetry (CV) to follow UPD deposition and stripping of lead from single crystal gold, Hamelin et al.<sup>1,2,3,4,5</sup> and Adzic et. al.<sup>6</sup> showed that the number of UPD peaks, peak potentials, peak heights, and peak widths were characteristic of the surface's crystallographic orientation. In certain case, cyclic voltammograms (CVs) obtained at a single crystal electrode show more complex and detailed features than those obtained at a polycrystalline electrode. We believe that this difference is primarily caused by the higher sensitivity of cyclic voltammetry on single crystal substrates. The presence of grain boundaries and surface defects that are prevalent on polycrystalline electrodes allows the cyclic voltammetry only to detect the predominant processes occurred on polycrystalline substrate. Thus, we assume that the CV response at a polycrystalline metal surface is the weighted sum of the CV responses attributable to the **predominant** individual single crystal crystallites composing the surface. Therefore, the surface "signature" of UPD processes could be used to study chemisorptions of organic molecules through their effect on a concurrent UPD process at both single crystal and polycrystalline electrodes. Consequently, by using different UPD probes for a selected metal, we can identify the primary metal surface sites participating in concurrent adsorption process from changes in the UPD isotherm. This isotherm information will provide the basis for elucidating the interaction of organic molecules with a metal surface; in particular the molecular orientation and surface coverage of the organic adsorbate will be correlated with the modified surface's electrochemical reactivity. A major attraction of the UPD probe technique arises because of the availability of different, unique UPD metals that can be selected to study a specific system. In selecting a UPD probe, electrolyte composition must be considered, as well as possible chemical interactions with the adsorbate. In this paper, Pb underpotential deposition process in conjunction with *in situ* Electrochemical Quartz Crystal Microbalance (EQCM) was used to investigate the adsorption properties of 1,10-phenanthroline, 4,7-phenanthroline and phenanthridine heteroaromatic molecules on Au polycrystalline electrode substrate. All these three heteroaromatic compounds adsorbed over the potential range (-0.34 V to +0.44V vs Ag/AgCl) on Au. The effects that the adsorption of these molecules had on the Lead UPD process indicate that 4,7 phenanthroline and phenanthridine are site selectively adsorbed on Au (110) sites. 1,10 phenanthroline doesn't show as strong site selective adsorption as 4,7 Phenanthroline and

phenanthridine. Adsorption of 4,7 phenanthridine stabilized the Pb UPD processes on Au (111) sites. It is not detected that Pb can react with adsorbed 1,10 Phenanthroline to form a surface complex on Au. The molecular orientation and site selectivity of those organic molecules for adsorption and the properties of the resulting electrode surface are also characterized. Our study indicates UPD process not only can be used as a probe for in-situ investigation of phenomena at solid-liquid interfaces but also we believe that by selecting appropriate pairs of UPD metal and organic adsorbates, new electrode surfaces, with desirable properties can be developed.

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### References

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