

Study of Pt Dissolution During Formic Acid Oxidation on Thin Films Deposited via Surface Limited Redox Replacements

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Current understanding of Pt catalysts dissolution has been based on the variety of studies on carbon supported nanoparticles in the background solutions and under conditions relevant for the oxygen reduction reaction.^{1,2} Although much has been explored over decades, our fundamental understanding of the Pt-oxide induced dissolution is still incomplete. A need for more active fundamental research of Pt stability and dissolution³ has been recognized by recent in-situ studies on single crystal surfaces⁴ and monitoring by inductively coupled plasma mass spectrometry (ICP-MS).^{4,5}

Most of the studies on Pt-based catalysts for formic acid oxidation (FAO) have been focused on their activity and effect of CO poisoning with little attention on Pt dissolution and related long-term performance. The effect and role of organic fuels on Pt durability has been reported but has not been explored in details so far.^{6,7} In this work we present first quantitative analysis of the Pt dissolution during FAO using 2D epitaxial thin films grown via Surface Limited Redox Replacement (SLRR) of Pb UPD. The SLRR method of Pt deposition allowed precise control of thickness of epitaxial layers that enabled controlled Pt loss measurements and the surface-science based electrocatalytic analysis of catalyst performance.

Long-term catalytic performance of Pt films of different thicknesses (5-30 ML) was examined by potential cycling in 2M HCOOH + 0.1M HClO₄ solution at sweep rate of 0.05 V/s over an extended potential range limited positively by the onset of Pt oxidation. The monitoring of Pt activity marked by several distinctive stages during surface dissolution, as illustrated in Figure 1, showed clear proportionality between overall life and thickness of the catalyst. The steady loss of Pt during cycling was confirmed by XPS compositional analysis while ex-situ characterizations by SEM and AFM at characteristic stages of the activity decay revealed dramatic morphological changes (Figure 1).

The analysis of FAO activity decays of Pt films of different thickness were used to estimate an average Pt dissolution rate of $272 \pm 30 \text{ ng.cm}^{-2}.\text{h}^{-1}$. For comparison, identical experiments performed in the absence of formic acid showed about 4-5 times lower Pt dissolution rate, in the range of $61 \pm 8 \text{ ng.cm}^{-2}.\text{h}^{-1}$. These results show significant impact of the FAO on the dissolution rate and suggest possible role of reaction intermediates on the dissolution of Pt.

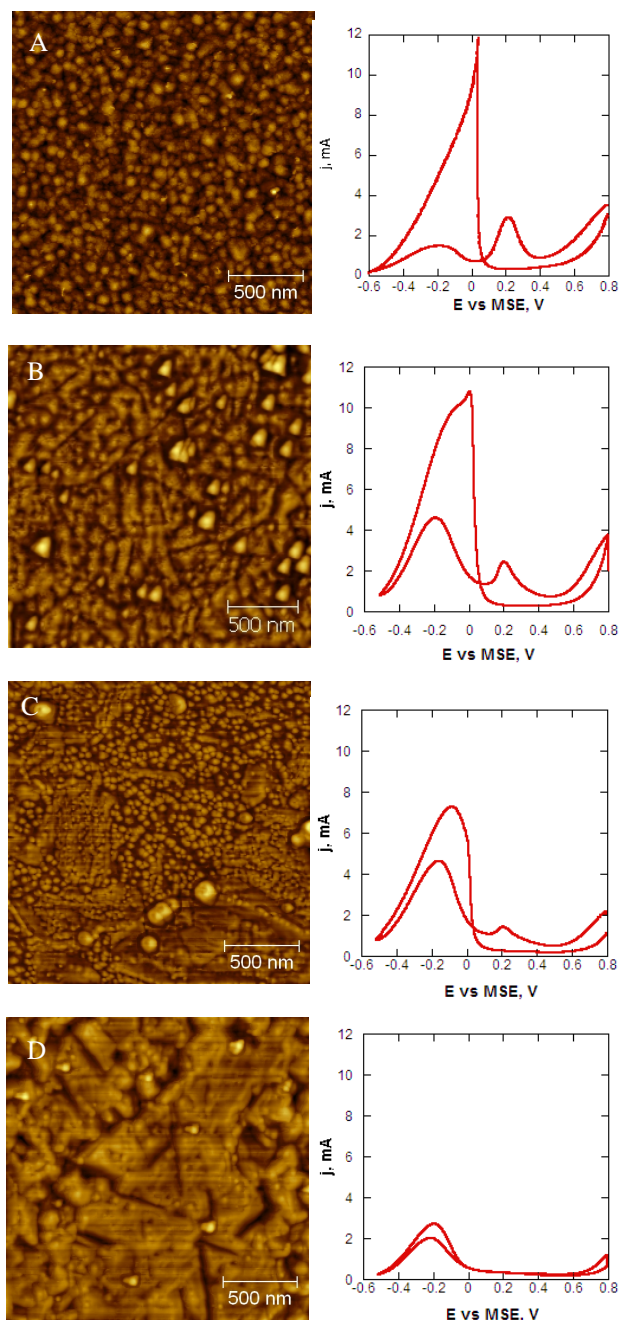


Figure 1. AFM images ($2 \times 2 \mu\text{m}$) and cyclic voltammetry curves of 10 ML Pt film grown on Au films using SLRR at different stages (i.e. after time t) of potential cycling in 0.1 M HClO₄ + 2 M HCOOH with the scan rate of 0.05 V/s. (A) $t = 0$ h; (B) $t = 8$ h; (C) $t = 17$ h; (D) $t = 28$ h.

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