

The design of advanced thin-film catalysts for electrooxidation of formic acid

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Successful development of catalysts for electrochemical formic acid oxidation (FAO) requires finding an optimal balance between catalytic performance (activity/stability/selectivity) and the catalyst cost. While platinum is one of the most active catalyst materials for FAO, it suffers from performance loss at low overpotentials due to poisoning with CO, which is one of the intermediates formed in the so-called indirect path of FAO.

In this work, we explored the synergistic effects of the supporting material and annealing temperature on the performance of Pt thin films over Cr support for FAO in acidic media. In an attempt to reduce the proneness of Pt to poisoning species i.e. CO and improve the catalytic performance of Pt/Cr at low potentials in the formic acid oxidation reaction, the as-prepared catalyst was modified using controlled thermal treatment. The influence of thermal treatment on the surface morphology was monitored using atomic force microscopy (AFM). The catalyst was electrochemically characterized with cyclic voltammetry and oxidation of CO monolayer, while the performance of the catalyst was tested in formic acid oxidation reaction.

Based on the obtained results it was concluded that the improved activity on the annealed Pt/Cr system is a consequence of surface reconstruction of Pt film with predominant (111) orientation. Compared to other facets, the (111) facet selectively favors the oxidation of HCOOH via the direct path, avoiding the formation of CO_{ad} at low potentials. Moreover, the Pt (111) facets offer improved stability of the catalyst compared to the as-prepared polycrystalline film. Finally, the Cr substrate also experiences improved stability after annealing, presumably due to the formation of a protective oxide layer. Thus, with the successful choice of the supporting material and annealing temperature, we were able to create a thin film catalyst with improved activity, selectivity and stability, challenging conventional trade-offs in electrocatalysis.

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