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Electrochemical Deposition of Pt-(Fe, Co, Ni) Alloys: Self-terminated growth to underpotential co-deposition

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The electrodeposition of Pt alloy films is examined and compared to the characteristics of the constituent elements. Pt deposition at negative potentials revealed an unanticipated self-terminating characteristic that enables controlled deposition of Pt monolayer films from a K_2PtCl_4-NaCl electrolyte.[1] Despite the deposition overpotential being in excess of -1 V, Pt deposition is quenched at potentials just negative of proton reduction by alteration of the double layer structure induced by a saturated surface coverage of underpotential deposited hydrogen, (H_{upd}).[1] The surface may be reactivated for Pt deposition by stepping the potential to more positive values where H_{upd} is oxidized and fresh sites for adsorption of $PtCl_4^{2-}$ become available. Periodic pulsing of the potential enables sequential deposition of two dimensional (2-D) Pt layers to fabricate films of desired thickness relevant to a range of advanced technologies in a manner that is tantamount to wet atomic layer deposition (ALD). In the presence of iron group metals, the H_{upd} induced suppression is lifted by underpotential deposition of the iron group metal as revealed in voltammetric studies of singular surfaces and thin film deposition studies of binary $Pt_{100-x}Ni_x$ and $Pt_{100-x}Co_x$ alloys.[2,3] Bulk alloy formation is facilitated by ongoing Pt deposition that incorporates the iron group metal in accord with the excess enthalpy of alloy formation. The performance of these materials as electrocatalysts will also be briefly detailed.[4,5]

1. Y. Liu et al., Science, 338, 1327 (2012).
2. J.J. Mallett et al. J. Electrochem. Soc,155, D1 (2008).
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5. T.P. Moffat et al, J. Electrochem. Soc., 156, B238 (2009).