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Electrocatalytic properties of Ni hydroxides with Zn or Co in the Ni matrix

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Akademisk avhandling för filosofie doktorsexamen i Naturvetenskap med inriktning Kemi, som med tillstånd från Naturvetenskapliga fakulteten kommer att offentligt försvaras fredagen den 7 februari 2014 kl. 10.15 i KB, Institutionen för kemi och molekylärbiologi, Kemigården 4, Göteborg.

ISBN: 978-91-628-8897-8

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Abstract

The majority of the work in this thesis has been made with the improvement of the systems for electrochemical co-generation of chemicals and electricity in mind. This is an appealing but challenging way of producing chemicals with energy as a bi-product, and is commonly referred to as “green chemistry”. In this study electrocatalytic reactions have been investigated on electrodes for which Ni is the main active species with minor addition of Zn and Co in the Ni matrix. Three important reactions have been investigated; the oxygen reduction reaction (ORR) and propenol oxidation in alkaline solution, and the proton reduction reaction (PRR) at pH 2.8. The main focus has been on the improvement of Ni based catalysts for O_2 reduction to H_2O_2 in alkaline solution. Ni has the advantage to forms a very stable oxide/hydroxide under alkaline conditions and Zn and Co are under certain conditions known to promote a $2e^-$ reduction of O_2.

A novel type of Ni-rich NiZn alloys were produced by pulse plating under anomalous deposition of Ni and Zn in a sulphate electrolyte at pH 2.8. The alloys were seen to grow in isolated 3D clusters with substantial height before the surface became completely covered. EDX measurements showed a Ni-rich alloy of Ni_xZn_{1-x} where x is between 0.14 and 0.21 depending on plating conditions. The long range order of these alloys was not possible to determine and the short range order was therefore investigated by XAFS. The result showed that the alloy was organised as a multiphase system consisting of *hcp*- and *ccp*-like structural moieties with non-homogeneous distribution of Zn, rather than the expected solid solution. The correlation of the catalytic activity between structure and proton reduction for the NiZn alloy was not unambiguous, but the reaction rate was however clearly enhanced compared to solid Ni.

The catalytic activity towards oxygen reduction in alkaline environment was studied on pulse plated Ni and NiZn. Alloying Ni with Zn clearly favoured the reaction path towards H_2O_2 and also lowered the overpotential for the reaction, even though the limiting currents indicated recessed electrode behaviour.

Direct electrochemical oxidation of propen and propenol on the pulse plated Ni and NiZn electrode was investigated in alkaline solution by CV and DEMS. The direct oxidation of propen has been reported in the literature but could not be repeated. The oxidation of propenol overlapped with oxidation of the substrate and oxygen evolution in a complex manner, with propenal as the main product. It was shown that water oxidation starts when half of the $Ni(OH)_2$ sites were oxidised to NiOOH which indicates a bi-nuclear water oxidation mechanism. A $Ni(OH)_2$/NiOOH mediated reaction mechanism was proposed in analogy with previous studies for other alcohols and amines.

To investigate the importance of the underlying Ni metal NiO was synthesised and made to an electrode by mixing it with carbon paste (CP). $Ni_{0.75}Co_{0.25}O$ and CoO were also synthesised for comparison with NiO in the reactivity towards the ORR. 67 wt% NiO in CP increased the rate constant by 25 times compared to pure CP and showed the highest overall efficiency for ORR, for which the reduction to H_2O_2 prevails.

Keywords: Redox mediated electron transfer, electrodeposition, pulse plating, Ni-rich alloy, NiZn, NiO, CoO, carbon paste electrodes, cyclic voltammetry, RRDE, DEMS, XAFS