

Electrochemical Growth of β -Ni(OH)₂ and NiOOH on Ni Electrodes at Well-defined Polarization Potential, Polarization Time, and Temperature Conditions
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Electro-oxidation of Ni electrodes in aq. KOH is examined as a function of the polarization potential ($0.5 \leq E_p \leq 1.6$ V), polarization time (t_p up to 3 hrs), and temperature ($283 \leq T \leq 348$ K). Under these conditions, β -Ni(OH)₂ and NiOOH oxides can exist at two different potential regions. The oxide growth behaviour is influenced by the experimental conditions (E_p , t_p , and T), and in general, increase in E_p , t_p and/or T leads to increases the oxide layer thickness. At the potential region of β -Ni(OH)₂ oxide formation, two processes take place: (i) transformation of α -Ni(OH)₂ (which is formed at less positive potentials) to β -Ni(OH)₂ and (ii) oxidation of metallic Ni below the surface to β -Ni(OH)₂. This results in the formation of multilayer film of β -Ni(OH)₂ which cannot be easily reduced to metallic Ni [1,2] or in some cases is considered to be electrochemically non-reducible [3,4]. Reliable measurements of the rate of formation of β -Ni(OH)₂ require application of non-electrochemical techniques. Ultra high vacuum (UHV) depth profiling is used to measure the thickness of the hydroxide layer under well-defined E_p , t_p and T conditions. X-ray photoelectron spectroscopy (XPS) spectra are recorded periodically during profiling process to control progress in sputtering process by monitoring the chemical composition of the surface layer exposed to the ion beam. Application of the oxide growth theories to our data indicate that the development of the β -Ni(OH)₂ layer follows inverse logarithmic growth kinetics according to Mott-Cabrera model. The kinetics of the Ni oxidation was determined on the basis of film thickness, d -1 vs. Log t_p relation. The driving force of the process is the strong electric field that is established across the oxide layer. The strength of the electric field is in the range of $0.015 - 0.197 \times 10^9$ V m⁻¹.

The mechanism of Ni(OH)₂ oxidation to NiOOH in basic solutions was studied for nickel electrodes under well-controlled conditions (E_p , t_p , and T). The oxidation is electrochemically irreversible and the process is treated according to Randles-Sevcik equation. Oxidation of Ni(II) to Ni(III) is controlled by transport (diffusion) of protons inside the solid phase [5,6]. A linear relation was determined between the peak current density (j_p) and the square root of the potential scan rate ($v^{1/2}$) for the entire range of E_p , t_p and T . For metallic nickel, the calculated values of the diffusion coefficient are in the range of $8.1 \pm 0.2 \times 10^{-12}$ and $4.3 \pm 0.2 \times 10^{-12}$ cm² s⁻¹ for the anodic and the cathodic process, respectively. The activation energy (E_a) values for the diffusion processes are in the range of 23 ± 2 and 26 ± 2 kJ mol⁻¹ for the anodic and the cathodic process, respectively. Chronoamperometry measurements show comparable values of D and E_a .

References

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