

THE THERMODYNAMICS OF SOLID SOLUTIONS OF Ni(II)/Ni(IV) OXO COMPOUNDS

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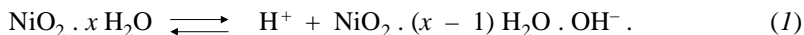
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The measured data of equilibrium and rest potentials of higher nickel oxo compounds, E' (converted for 25 °C and $a_{\text{H}_2\text{O}} = a_{\text{KOH}} = a_{\text{H}_2} = 1.0$) selected in the range of the overall oxidation number of $2.0 < z_{\text{Ni}} \leq 3.6$, were newly evaluated with the aid of a simplified model of the quasi-binary solid solutions $\text{Ni}(\text{OH})_2/\text{Ni}(\text{OH})_4$ assuming unlimited miscibility. It was found that the dependence of E' on the composition of the redox system can be described by a Nernst equation in the entire range of z_{Ni} investigated, where the activity coefficients of individual components are expressed by relations for regular solutions. The so calculated activities of considered components showed positive deviations from the ideal behaviour of the solid solutions. All results obtained were discussed in more detail assuming the non-existence of Ni(III) oxo compounds in such solid solutions.

Key words: Equilibrium potential; Activity coefficients; "Nickel oxide" electrode.

Our previous study of the thermodynamics of higher solid nickel oxo compounds¹ had shown that the evaluation of critically selected data from different authors²⁻⁷ for the equilibrium and rest potentials of higher nickel oxo hydroxo compounds in the range of the oxidation number $z_{\text{Ni}} = 2-3.6$ was in good agreement with the simple model of non-ideal solid solutions of $\text{Ni}(\text{OH})_2$ and $\text{NiO}_2 \cdot x \text{H}_2\text{O}$ ($x = 1-2$) with unlimited miscibility. In conformity with the increasing electrical conductivity of these systems with rising oxidation number z_{Ni} , it was assumed that non-conducting $\text{Ni}(\text{OH})_2$ is present in a completely undissociated form, whereas $\text{NiO}_2 \cdot x \text{H}_2\text{O}$ is completely dissociated into the first stage according to the scheme



A similar model among others had been used earlier by Barnard and coworkers⁸ for the same system in the range of $z_{\text{Ni}} = 2.0-3.0$ with NiOOH as the oxidized form.

In order to determine quantitatively the non-ideal behaviour of this system in the range of $z_{\text{Ni}} = 2.0-3.6$, the dependence of the activity coefficients of individual compo-

nents (*i.e.* Ni(OH)_2 and $\text{NiO}_2 \cdot x \text{H}_2\text{O}$) on the overall composition of the system was expressed in a first approximation by an empirical relation according to Margules. This purely empirical treatment of measured data led to the following thermodynamic data for the reversible course of the simplified electrochemical overall reaction



$E_{(2)}^0 = 1.3250 \text{ V}$ and $\Delta G_{(2)}^0 = -255.68 \text{ kJ mol}^{-1}$ at 25°C (ref.¹). These values were used to determine the following values of the hypothetical substance $\text{NiO}_2 \cdot x \text{H}_2\text{O}$ at 25°C : $\Delta G_{\text{f}}^0 = -202.02 - 237.141x \text{ kJ mol}^{-1}$, so that $\Delta G_{\text{f}}^0(\text{Ni(OH)}_4) = -637.30 \text{ kJ mol}^{-1}$, and furthermore $\Delta H_{\text{f}}^0(\text{Ni(OH)}_4) = -844 \text{ kJ mol}^{-1}$ and thus $S^0(\text{Ni(OH)}_4) = 139 \text{ J mol}^{-1} \text{ K}^{-1}$.

The interaction constant $A = 4\,866.7 \text{ J mol}^{-1}$ (ref.¹), characterising the non-ideal behaviour of the system under study, gave a critical temperature of $T_c = A/2R = 292.7 \text{ K}$. This value, denoting the limiting temperature below which solid solution separation into two phases with different composition can take place¹⁰, was slightly below the average measurement temperature (25°C). This result could be regarded as supporting our idea that in this system solid solutions with unlimited miscibility of both main components in the whole measured range of $z_{\text{Ni}} = 2.04\text{--}3.6$ were present. On the contrary, Barnard and coworkers^{2,3} explained the almost constant values of reversible or rest potentials of this system in the range of $z_{\text{Ni}} = 2.25\text{--}3.0$ by the co-existence of two separated phases containing nickel in higher and lower states of oxidation.

The insertion of alkaline cations into the lattice with higher oxidation number of nickel – mostly in the range of $z_{\text{Ni}} \geq 3.0$ (ref.⁹), was not taken into consideration in the calculations for the sake of simplicity. In our opinion, however, this phenomenon can be regarded as a partial neutralization of the acidic Ni(IV) component, *i.e.* partial exchange of alkaline cations with the dissociated protons of the solid solution, and not as an intercalation.

However, the purely empirical evaluation of measured data¹ does not sufficiently satisfy the theoretical requirements, because the value of $\lim_{X_2 \rightarrow 1} (da_2/dX_2) \neq 1$ (where a_2 represents the total activity and X_2 the mole fraction of the Ni(IV) component, *i.e.* $\text{NiO}_2 \cdot x \text{H}_2\text{O}$). It was therefore attempted here to evaluate the same data (see Table I in ref.¹) with the aid of a modified model corresponding more to the theoretical requirements.

CALCULATIONS

The new evaluation of measured data of the equilibrium and rest potentials of higher nickel oxo hydroxo compounds in the range of the oxidation number $2.0 < z_{\text{Ni}} < 3.6$ (converted for 25°C and $a_{\text{KOH}} = a_{\text{H}_2\text{O}} = a_{\text{H}_2} = 1.0$, see Table I in ref.¹) was based on the simplified assumption that the solid system – irrespective of the possible presence of

alkaline cations at $z_{\text{Ni}} > 3$ – can be represented as a solid solution of $\text{Ni}(\text{OH})_2$ and $\text{Ni}(\text{OH})_4$ with unlimited miscibility. In such a quasi-binary mixed hydroxide system, the anionic sublattice may be regarded as consisting only of OH^- ions, irrespective of the form in which the individual components can be transferred into aqueous solution, so that their anion mole fraction $X_{\text{OH}^-} = 1.0$ irrespective of the actual oxidation number z_{Ni} in the entire theoretically possible range of $2.0 < z_{\text{Ni}} < 4.0$. However, the total number of OH^- ions increases per mole unit of the redox system with rising oxidation number z_{Ni} . In accordance with the oxidation number, z_{Ni} , and irrespective of the possible dissociation scheme of $\text{Ni}(\text{OH})_4$ or $\text{Ni}(\text{OH})_2$, the cationic sublattice is formed by Ni^{2+} and Ni^{4+} whose spatial distribution can obviously be regarded as random. Under these conditions, the following relations for regular solutions derived for analogous solid solutions of mixed oxide systems^{10,11} can be used. They describe the dependence of the activity coefficients of the individual main components on the composition of the non-ideal quasi-binary system:

$$\log \gamma_1 = (A/(2.3 RT))X_2^2 \quad (3)$$

and

$$\log \gamma_2 = (A/(2.3 RT))(1 - X_2)^2, \quad (4)$$

where γ_1 and $X_1 = 1 - X_2$ represent the activity coefficient and the mole fraction of $\text{Ni}(\text{OH})_2$ while γ_2 and X_2 are analogous quantities of $\text{Ni}(\text{OH})_4$ in the solid solution.

Accordingly, the dependence of the equilibrium potential of the electrochemical overall reaction



on composition of the solid solution can be expressed by the following equation:

$$E' = E^0 - (2.3 RT/2F) \log ((1 - X_2)/X_2) + (A/(2F))(1 - 2X_2), \quad (6)$$

where E' is measured equilibrium potential of the redox system (converted for 25 °C and $a_{\text{H}_2\text{O}} = a_{\text{KOH}} = a_{\text{H}_2} = 1.0$). After introducing the expression

$$\phi = E' + (2.3 RT/2F) \log ((1 - X_2)/X_2) \quad (7)$$

a linear equation is thus obtained

$$\phi = E^0 + k(1 - 2X_2) \quad (8)$$

with $k = A/2F$. The equation (8) was used to correlate experimental data (see Table I in ref.¹) using the relation

$$X_2 = (z_{\text{Ni}} - 2)/2 \quad (9)$$

(see Fig. 1). The linear regression (after elimination of two points showing the greatest deviations) led to the following values $E^0 = 1.3233 \pm 0.0078$ V and $k = 0.012525$. This gave $A = 2416.8$ J mol⁻¹ for the interaction parameter. Thus E^0 value is almost identical with that value calculated earlier¹ ($E^0 = 1.3250$ V). The newly calculated interaction parameter led to the critical temperature $T_c = A/2F = 145.3$ K, which is distinctly lower than the average measuring temperature 25 °C. This result clearly supports our explanation concerning the formation of solid solutions of Ni(OH)₂/Ni(OH)₄ without any miscibility gap in the range of $2.0 < z_{\text{Ni}} \leq 3.6$.

The new value of the standard potential of electrochemical cell reaction (5), $E^0 = 1.3233 \pm 0.0078$ V, gives $\Delta G_{(5)}^0 = -255.35 \pm 1.50$ kJ mol⁻¹ at 25 °C. Using $\Delta G_f^0(\text{H}_2\text{O}) = -237.141$ kJ mol⁻¹ according to ref.¹² and $\Delta G_f^0(\text{Ni(OH)}_2) = -457.7$ kJ mol⁻¹ (corrected according to ref.¹), $\Delta G_f^0(\text{Ni(OH)}_4) = -676.63 \pm 1.50$ kJ mol⁻¹ ($= \Delta G_f^0(\text{NiO}_2 \cdot 2 \text{H}_2\text{O})$) and

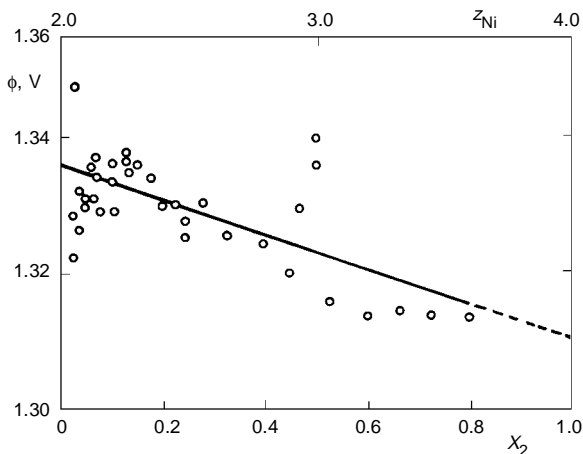


FIG. 1
Plot of ϕ vs X_2 for the system of solid solutions of Ni(OH)₂/Ni(OH)₄ at 25 °C

$\Delta G_f^0(\text{NiO}_2 \cdot x \text{H}_2\text{O}) = -202.35 \pm 1.50 - 237.141 x \text{ kJ mol}^{-1}$ was obtained for individual hypothetical forms of NiO_2 hydrates not precisely known. As it is seen, all these hypothetical forms of NiO_2 can be regarded as thermodynamically equivalent.

On the basis of the results presented above it was also possible to calculate the activities of individual main components of quasi-binary solid solutions, $a_{\text{Ni}(\text{OH})_4}$ and $a_{\text{Ni}(\text{OH})_2}$, for the given range of z_{Ni} , X_2 and the temperature of 25 °C:

$$\begin{aligned} \log a_{\text{Ni}(\text{OH})_2} &= \log (1 - X_2) + (A/2.3RT) X_2^2 = \\ &= \log (1 - X_2) + 0.42324 X_2^2 \end{aligned} \quad (10)$$

and

$$\begin{aligned} \log a_{\text{Ni}(\text{OH})_4} &= \log X_2 + (A/2.3RT) (1 - X_2)^2 = \\ &= \log X_2 + 0.42324 (1 - X_2)^2. \end{aligned} \quad (11)$$

The dependence of the activities of the two main components on the composition of solid solutions in the range of $z_{\text{Ni}} = 2.0\text{--}3.6$, *i.e.* of $X_2 = 0\text{--}0.8$, is shown in Fig. 2. As can be seen, both curves show distinct positive deviations from ideal behaviour. It can also be observed that for $X_2 \rightarrow 0$ the relation between X_1 and $a_{\text{Ni}(\text{OH})_2}$ follows Raoult's law, whereas the relation between X_2 and $a_{\text{Ni}(\text{OH})_4}$ corresponds to Henry's law. Analogous reciprocal behaviour could be obviously expected in the second limiting case for $X_2 \rightarrow 1$. However, all attempts to prepare sufficiently stable solid solutions of such

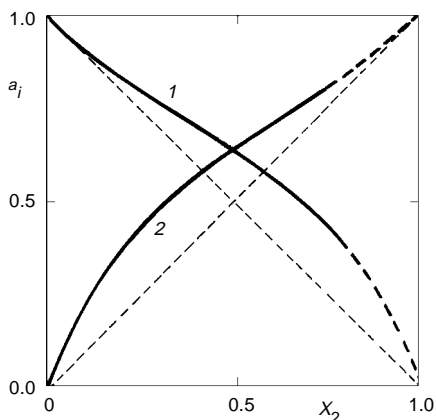


FIG. 2
Plot of the activity $a_{\text{Ni}(\text{OH})_2}$ (1) and $a_{\text{Ni}(\text{OH})_4}$ (2) vs X_2 in the system of solid solutions of $\text{Ni}(\text{OH})_2/\text{Ni}(\text{OH})_4$ at 25 °C under the given simplified assumptions

composition failed so far. Nevertheless, it may be seen from Fig. 2 that the evaluation of the experimental data according to the simplified model of the quasi-binary solid solutions of Ni(II)/Ni(IV) hydroxides satisfies the theoretical requirements for the first order systems.

DISCUSSION

It should be emphasized that the model of quasi-binary solid solutions $\text{Ni}(\text{OH})_2/\text{Ni}(\text{OH})_4$ represents a simplification only, since the experimentally observed insertion of alkaline cations in the crystal lattice could not be included into the model due to a lack of appropriate thermodynamic data. The insertion of alkaline cations into the lattice of higher-oxidized solid solutions of $\text{Ni}(\text{OH})_2/\text{Ni}(\text{OH})_4$ appears to be according to our opinion¹, partial neutralisation of dissociable H^+ cations from the acidic Ni(IV)-component (equivalent with cationic exchange between the solid solution and aqueous alkali solution of appropriate concentration) rather than an intercalation as assumed *e.g.* in ref.¹³. However, a complete and unambiguous clarification of all these problems requires further meticulous measurements using suitable methods, as it was also stated in the recent paper¹⁴. The reliable measurements are difficult because the equilibrium and rest potentials of such systems at $z_{\text{Ni}} > 2.1$ are already above the equilibrium potential of the oxygen electrode in alkaline solutions¹ so that the electrochemical processes establishing the equilibrium potential of the Ni(II)/Ni(IV) oxo system in alkaline solutions are always accompanied by oxygen evolution. The Ni(II)/Ni(IV) oxo system is known as a very effective electrocatalyst for anodic oxygen evolution from aqueous alkaline solutions. Its mechanism is explained *e.g.* in ref.¹⁵. As the nickel valency of the catalytically acting centres is continuously changed between the higher and lower value, it is difficult to establish a true equilibrium composition, especially for higher values of $z_{\text{Ni}} > 3.0$. It therefore appears doubtful whether a rigorous establishment of equilibrium and its unambiguous determination will be possible at all for such reaction conditions in the system studied. On the other hand, it is quite comprehensible that several metastable modifications were identified in previous studies of higher nickel oxo compounds (survey *e.g.* in refs^{9,16}).

CONCLUSION

On the basis of our previous¹ and present work we assume that the higher nickel oxo compounds with the overall oxidation number $2.0 < z_{\text{Ni}} \leq 3.6$ are solid non-ideal solutions of Ni(II)/Ni(IV) oxo compounds without participation of Ni(III) components. Their thermodynamic behaviour was described with the aid of a simplified model of solid regular solutions of $\text{Ni}(\text{OH})_2/\text{Ni}(\text{OH})_4$ with unlimited miscibility in the investigated range of $2.0 < z_{\text{Ni}} \leq 3.6$. These conclusions are in accordance with the previous experimental findings by different authors stating that the dependence of the equi-

brum and rest potentials of this system on the overall oxidation number z_{Ni} exhibits a broad plateau in the range of $z_{\text{Ni}} = 2.3\text{--}3.2$. This contradicts to the up to date almost commonly accepted idea of existence of Ni(III) oxo compounds as an individual chemical substance. It was also theoretically outlined in the previous paper¹.

The mathematical correlation of critically selected reversible or rest potentials measured earlier by different authors, using a simplified model of quasi-binary solid solutions of $\text{Ni}(\text{OH})_2/\text{Ni}(\text{OH})_4$, enabled to calculate standard thermodynamic data of hypothetical pure nickel dioxide and its hydrates, *i.e.* NiO_2 and $\text{NiO}_2 \cdot x \text{H}_2\text{O}$ ($x = 1, 2$) at 25 °C. The newly calculated data are almost the same as those obtained in our previous paper¹.

The calculated values of the activities of the two main components of solid solutions $\text{Ni}(\text{OH})_2/\text{Ni}(\text{OH})_4$ showed that both exhibit distinct positive deviations from ideal behaviour. In solid solutions with low content of $\text{Ni}(\text{OH})_4$, *i.e.* for $X_2 \rightarrow 0$, the relation for $a_{\text{Ni}(\text{OH})_2}$ vs X_1 obeys Raoult's law and that for $a_{\text{Ni}(\text{OH})_4}$ vs X_2 follows Henry's law. The course of these relations for the reverse case $X_2 \rightarrow 1.0$ is up to date unknown.

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