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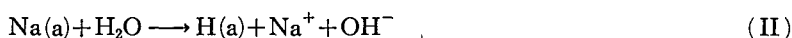
INTERMEDIATES OF HYDROGEN EVOLUTION REACTION ON NICKEL IN AQUEOUS SODIUM HYDROXIDE

By

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According to Pshenichnikov, Burshtein and Kovalevskaya¹⁾ the surface of the nickel hydrogen electrode in anodic polarization region in aqueous NaOH is covered with adsorbed hydrogen atoms whose activity corresponds to the hydrogen overvoltage and the surface coverage nearly equals unity at the neighborhood of the reversible potential. On the other hand, we reported previously^{2,3)} that the hydrogen evolution reaction on nickel in aqueous NaOH occurs as the sequence of the following elementary steps, including the intermediate species Na(a) and H(a),



and that the hydrogen overvoltage is caused by both the charging up of the double layer and the surface potential produced by the adsorbed intermediate species.

The purpose of the present work is to clarify, on the basis of the differential capacity measurements, which of the intermediates, Na(a) or H(a), plays an important role in the establishment of the hydrogen overvoltage in cathodic polarization region.

The differential capacity C was estimated from the decay curve of overvoltage after switching off a constant polarizing current by the following equation,⁴⁾

$$C = \left(\frac{i}{\dot{\eta}} \right)_{\eta} \quad (1)$$

where $\dot{\eta}$ is the time derivative of overvoltage and i is the rate of the removal of the intermediate species from the electrode surface which may be identified with the current density at the steady state polarization. The value of the starting overvoltage of the decay curve was fixed at -500 mV or -800 mV. A typical

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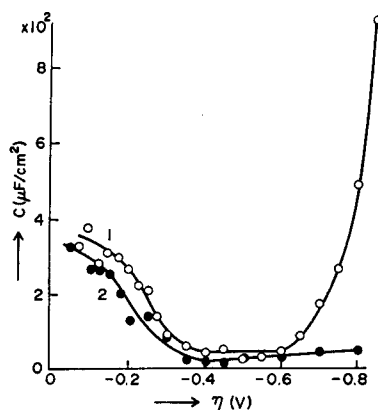


Fig. 1. Differential capacity C vs. η . 1—1N NaOH, 2—0.5N NaOH + 0.5N NaNO_3 .

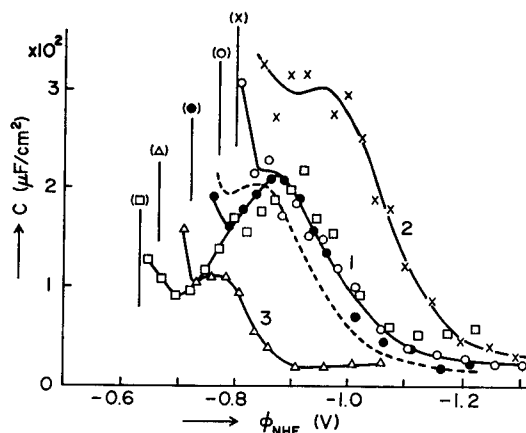


Fig. 2. Differential capacity C vs. ϕ . 1—0.1N Na^+ solutions: (○) 0.1N NaOH, (●) 0.09N NaClO_4 + 0.01N NaOH, (□) 0.1N NaClO_4 + 0.0005N NaOH, 2—1N NaOH, 3—0.01N NaOH, dashed line—0.1 N LiOH.

C — η curve obtained from the decay curves in 1N NaOH is shown

by curve 1 in Fig. 1. As seen from this Figure, a pseudocapacity hump appears both in low and high overvoltage regions at $-\eta < 400$ mV and $-\eta > 600$ mV, and the double layer region is observed between the two humps.

The pseudocapacities taken in NaOH or NaOH+ NaClO_4 solutions of different pH and pNa are plotted in Fig. 2 against the electrode potential ϕ referred to the N.H.E. The vertical line in this Figure shows the reversible potential in each solution. Curve 1 in Fig. 2 shows the C — ϕ relations in the solutions of 0.1N Na^+ ion concentration, but with different values of pH. As seen from this curve, the values of C strongly depend on ϕ , but independent of pH of the solution. From the comparison of the curves 1, 2 and 3 in Fig. 2, it can also be seen that the hump in the low overvoltage region becomes higher as the concentration of Na^+ ion increases, although the electrode potential at the maximum of the C — ϕ curve shows a slight shift toward negative side. These experimental results may be explained based on the assumption that the pseudocapacity observed in the low overvoltage region is caused by the adsorbed Na atom produced by the electron transfer step (I). The small increment of pseudocapacity appeared in the vicinity of the reversible potential is unreliable because of the insufficient accuracy of measurements in this region.

The marked increase of the pseudocapacity was also observed when the polarization time was prolonged before the start of the decay curve, which suggested the penetration of Na(a) into the bulk of the electrode. This phenomenon was remarkable in the case of evaporated nickel film electrode at which the

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maximum value of pseudocapacity attained $1700 \mu\text{F}/\text{cm}^2$ in 1N NaOH.⁴⁾

The atomic absorption spectroscopic method⁵⁾ is available for the detection of the intermediate alkali metal atom on the electrode surface, but this method is not applicable in the case of Na atom because of difficulties of eliminating Na impurities from the spectroscopic measurement system. However, as the $C-\varphi$ curve in aqueous LiOH resembled that in aqueous NaOH in shape as illustrated in Fig 2, the detection of Li atom accumulated on the nickel electrode surface during the electrolysis was carried out by the spectroscopic method, LiOH being used as electrolyte in place of NaOH. The results are shown in Fig. 3. It can be seen from this Figure that the adsorbed Li atom increases with the increase of overvoltage. Therefore, it may be concluded in the cathodic region that the major intermediate species of the hydrogen evolution reaction in alkaline solutions is the adsorbed alkali metal atom, and not the adsorbed hydrogen atom which is different from the cases in anodic region reported by Pshenichnikov *et al.*

The pseudocapacity in high overvoltage region $-\eta > 600 \text{ mV}$ in 1N NaOH disappeared when NO_3^- ion was added in the solution, as seen from curve 2 in Fig. 1. Since NO_3^- ion is known to be a scavenger for hydrated electrons,⁶⁾ the appearance of the pseudocapacity hump in aqueous NaOH in this region may be explained by assuming the back diffusion to the electrode of the hydrated electron which is produced by a direct transition of electron from the electrode into solution in the high overvoltage region.

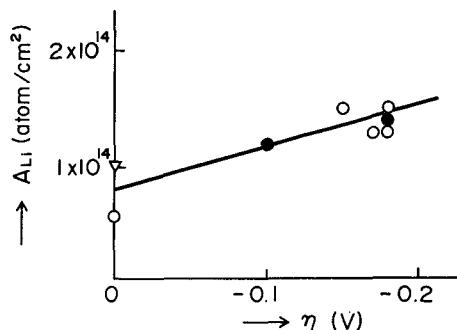


Fig. 3. Surface concentration of Li atoms A_{Li} vs. η in 0.01N LiOH. Polarization time: (∇) 3 sec., (\bullet) 3 hr., (\circ) 24 hr.

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