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— Note —

DETERMINATION OF INTERMEDIATES OF HYDROGEN EVOLUTION REACTION ON NICKEL IN AQUEOUS BARIUM AND CALCIUM HYDROXIDES BY ATOMIC ABSORPTION SPECTROSCOPY

By

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Abstract

It was observed by the spectroscopic method that barium or calcium atoms were deposited on the nickel hydrogen electrode respectively from aqueous $Ba(OH)_2$ or $Ca(OH)_2$ solutions as the intermediate species of the hydrogen evolution reaction.

It has been suggested on the basis of the galvanostatic transient studies of the hydrogen evolution reaction on platinum and nickel in alkaline or neutral solutions containing alkali metal or alkali earth metal ions that the metal electrons transfer directly to these ions and that the main part of the hydrogen overvoltage is the change of surface potential of the electrode due to the accumlation of the intermediate metal atoms produced by the electron transfer step.[1~7]

The present work is concerned with a direct identification of the intermediate metal atoms on the electrode surface under polarization by means of the atomic absorption spectroscopy with reference to the nickel hydrogen electrode in aqueous barium or calcium hydroxide solutions.

Experimental procedure: Nickel plates of 99.9% purity and of geometrical area, 150 and 40 cm^2, were used as the test electrode in aqueous 0.01 N barium or calcium hydroxide. The nickel plate was purified in concentrated hot HCl solution after washing with ethyl alcohol and twice distilled water, and washed with twice distilled water several times, and then evacuated at 500°C and reduced with hydrogen at the same temperature. The nickel plate thus prepared was immersed in aqueous $Ba(OH)_2$ or $Ca(OH)_2$ solution under hydrogen stream and was used as the test electrode. The test electrode first showed the potential about 300 mV more positive than the reversible hydrogen electrode potential,

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but it attained the reverseble hydrogen potential after several times of repeated cathodic polarization each for a few seconds.

The test electrode was cathodically polarized at a fixed potential for 15 min.-3 hours in the test solution. It was then taken out under polarization from the solution and transferred to a cell containing 0.01N NaOH saturated with atmospheric hydrogen. Upon contact with the solution it was cathonically polarized for a few seconds under the same condition as in the test solution in order to remove the residual test solution from the surface. The electrode was transferred into a small glass vessel filled with 2 N HCl solution and the electrode surface was dissolved into the solution. This solution was concentrated by evaporation to a definite constant volume suitable for the absorbance measurement by an atomic absorption spectrophotometer (Westinghouse Electric Co. Type AA-70). The wave length of the spectrum line used for the absorbance measurement was 5336 Å for barium and 4227 Å for calcium. The absorbance of these lines was unaffected by the presence of Na^+ and Cl^- ions in the solution. The spectrophotometer was sensitive to 2 ppm for barium and 0.05 ppm for calcium, and its reliability was ±10%. The calibration curves of the absorbance obtained from the standard solution of $BaCl_2$ and $CaCl_2$ are shown in Fig. 1.

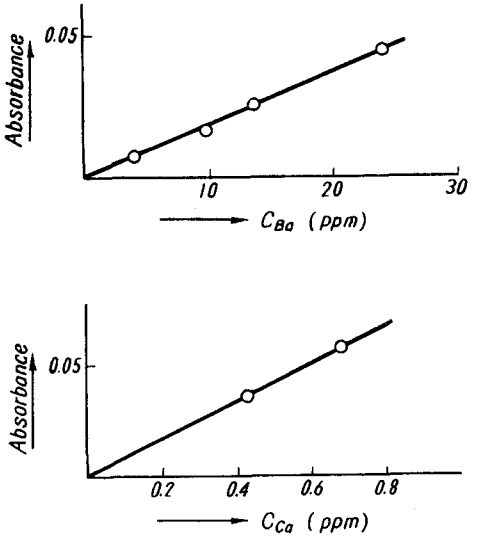

Fig. 1. Calibration curves of a spectrophotometer Ba and Ca.

Typical examples of the absorbance of the solutions which dissolved surface layers of the test electrodes after the polarization at different overvoltages in aqueous 0.01 N $Ba(OH)_2$ and 0.01 N $Ca(OH)_2$ are shown respectively in Fig. (2 a) and (2 b). The background absorbance of the pure hydrochloric acid used for the dissolution of the test electrode is also shown in these Figures. It can be

seen from Fig. 2 that barium and calcium are deposited on the electrode surface during the polarization. This supports the previous conclusion from the galvanostatic transient studies that the surface concentration of the metal deposit increases with negative displacement of the hydrogen overvoltage.

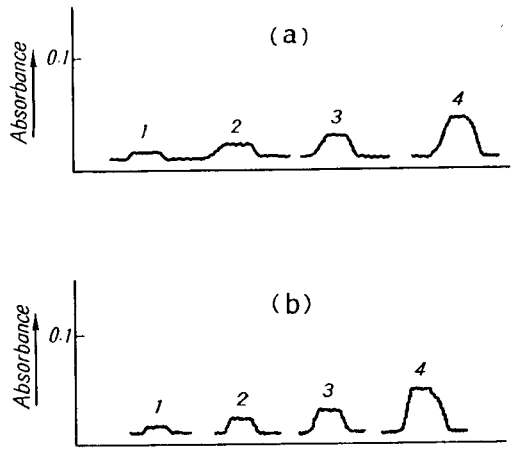

Fig. 2. Absorbance of the solutions which dissolved surface layer of the nickel electrode after polarization at different overvoltages,
(a) for Ba ions: (1) background, (2) $\eta=0$ mV, (3) $\eta=-50$ mV, (4) $\eta=-100$ mV.
(b) for Ca ions: (1) background, (2) $\eta=0$ mV, (3) $\eta=-50$ mV, (4) $\eta=-120$ mV.

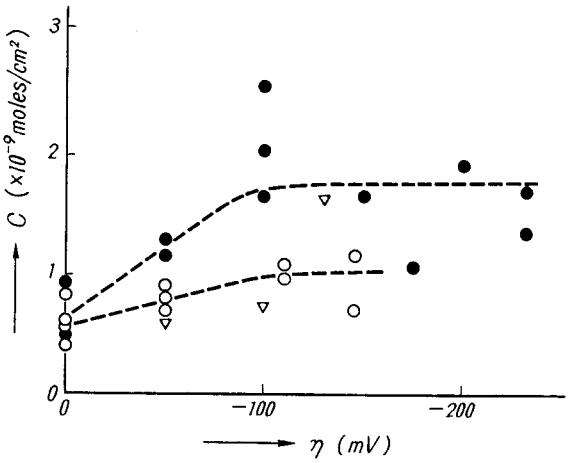

Fig. 3. Surface concentration of Ba and Ca atoms per true unit area as a function of overvoltage. (●) Ba atoms obtained after polarization for 15 min., (○), (▽) Ca atoms obtained after polarization for 15 min. and 3 hours respectively.

The surface concentration of barium or calcium atoms referred to true unit area are shown in Fig. 3 as a function of the hydrogen overvoltage. Points in this Figure are taken with different nickel plates. The data are rather scattered, but it is seen that the surface concentration of both Ba and Ca increases with negative shift of the hydrogen overvoltage up to about -100 mV and then reaches a plateau. The surface concentration of barium exceeds a monolayer coverage, but that of calcium is less than that of barium.

From the comparison of the results of the kinetic studies of the hydrogen evolution reaction in aqueous $Ba(OH)_2$[7] with those of the spectroscopic studies, it may be concluded that the intermediate barium atom produced by the electron transfer step composes a major part of the hydrogen overvoltage at the current density lower than the exchange current density of the electron transfer step i_{10}. Further investigation is needed to explain the presence of a minimum in the double layer capacitance *vs.* overvoltage curve Fig. 3 in the previous work[7].

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