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POTENTIAL-SWEEP STUDY FOR HYDROGEN ELECTRODE REACTION ON MERCURY

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The potential-sweep method was applied to mercury cathode in HCl, HBr, and HI aqueous solutions. Resulting current-potential curves for the hydrogen evolution reaction revealed a plateau, i.e., an almost constant current in the potential region from -0.65 to -1.0 V vs. N.H.E. which is the characteristic behaviour expected from the theoretical non-steady state analysis for the electrochemical mechanism. Effects of the sweep rate and anion are briefly discussed.

Most of the kinetic treatments are referred to the steady state of a reaction[1]. However, non-steady state treatment brings useful information when the rate-determining step of a reaction is preceded and/or followed by rapid step(s). Such a treatment was formulated and experimentally tested by Horiuti and Okamoto[2] for the hydrogen electrode reaction (H.E.R.) on Ni, and later by Gerischer and Mehl[3] on Hg, Cu, and Ni. However, their formulations have only a qualitative feature of the non-steady state.

The H.E.R. on Hg has been extensively studied by many workers from various aspects and different reaction mechanisms have been proposed. The slow discharge mechanism[4] can easily explain the Tafel slope but there seems to exist many experimental results which cannot be explained by this mechanism. For example, the prolonged evolution of hydrogen gas after electrolysis at Hg cathode[5, 6] shows that the intermediates produced by a fast step remain unreacted for a certain time and then become hydrogen gas by a slow step. Nagashima and Kita[7] observed no saturation current on Hg and excluded the catalytic mechanism. These facts lead us to deal with the electrochemical mechanism for H.E.R. on Hg, i.e.,

$$2H^{+} + e^{-} \rightarrow H_2^{+}(a) \qquad \text{(I)}$$

$$H_2^{+}(a) + e^{-} \xrightarrow{A} H_2 \qquad \text{(II)}$$

where (a) represents the adsorbed state and $\xrightarrow{A}$ the rate-determining step, respectively.

The H.E.R. on Hg has an extremely small exchange current of $10^{-12} \sim 10^{-13}$ amp/cm^2[8]. Hence, though Step (I) is faster than Step (II), the transient accumulation of $H_2^+(a)$ may take considerably long time before the steady state is reached. Consequently, it will happen that for short time observations the reaction will appear to be in a steady state, especially at low overvoltages[9]. We have thus performed the theoretical non-steady state analysis for the electrochemical mechanism[10]. Calculated results are now subjected to the experimental test by the potential-sweep method.

EXPERIMENTAL. H-type cell was used; one compartment contained a dropping mercury as a working electrode (D.M.E.) and mercury pool as a counter electrode, whereas the other contained platinized Pt foil as a reference electrode. Both compartments were separated by fritted glass and contained the same working solution in hydrogen gas atmosphere. Analytical grade reagents and doubly distilled water were used. Measurements in iodide solutions were carried out in dark to avoid the effect of light if any. Negative potential-sweep pulse was imposed to a drop of D.M.E. through potentiostat at a growth time of 3.6 sec where the drop life was controlled at 4.0 sec by mechanical knocking of the mercury column of D.M.E. Rate of mercury flow was 1.23 mg/sec. The electrical devices for the measurements are given elsewhere[11]. Change in the surface area during the pulse (less than 0.1 sec) was negligible within 2%. The current was observed by an oscilloscope through i-V transducer of operational amplifier[12].

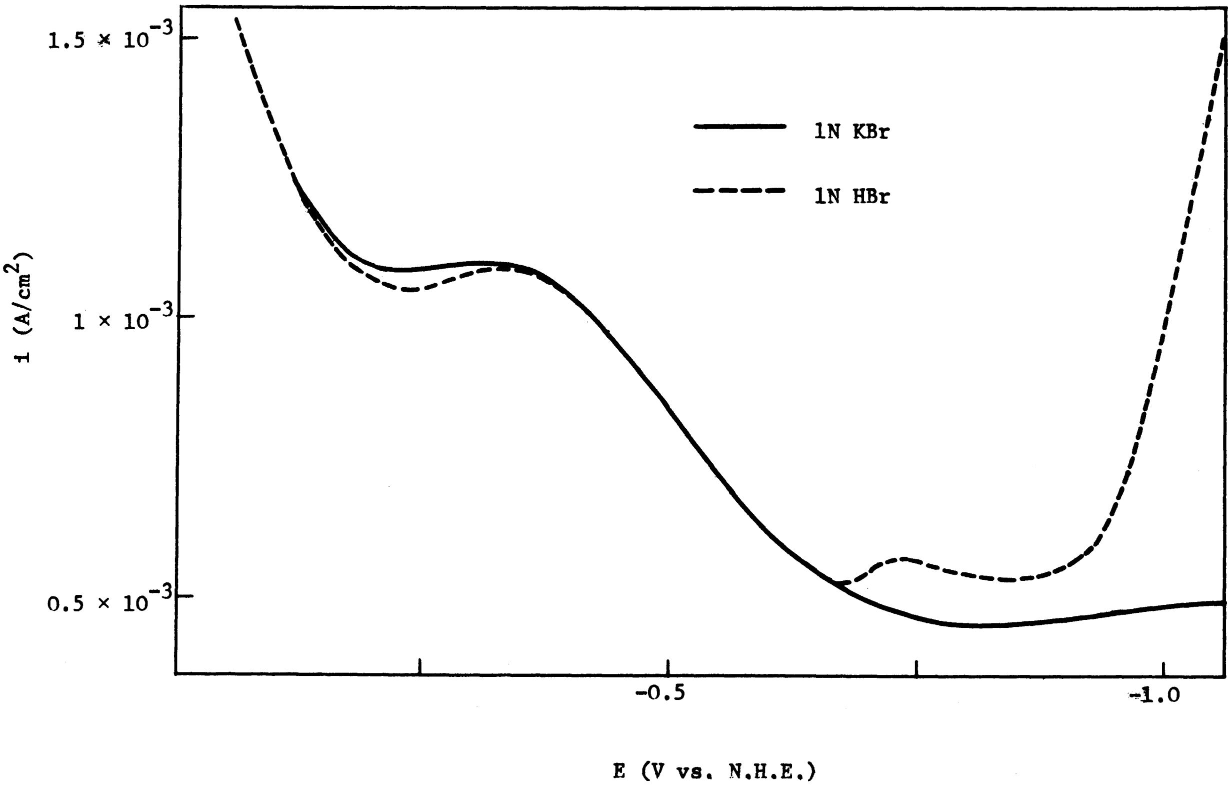

Fig. 1 Curves of current i vs. potential E with potential-sweep rate of 23.2 V/sec in 1N HBr and 1N KBr aqueous solutions at 30°C.

RESULTS. Figure 1 shows typical current-potential curves, observed with a sweep rate of 23.2 V/sec in 1N HBr and 1N KBr. Similar curves were also observed in 1N HCl and 1N KCl. Since the applied potential is in the region of the so-called ideal polarization in 1N KBr[13], the observed current in 1N KBr is ascribed only to the charging current of the double layer capacity of the electrode. The capacity calculated from the current and the sweep rate agrees very well with the result obtained by the AC-bridge method[9b]. In Fig. 1, the current in 1N HBr is identical to that in 1N KBr in the potential region between 0 and -0.65 V vs. N.H.E., and hence here only the charging of the double layer takes place in both solutions. However, at more negative potentials, the current in HBr exceeds the current in KBr. This excess current is taken as the current due to H.E.R., which is the only possible electrode reaction in this system. The double layer capacity is assumed to be the same in both solutions, as confirmed experimentally in HCl and LiCl solutions[14].

The current of H.E.R. first increases with negative polarization, becomes almost constant (called a current plateau) and then increases exponentially. The current plateau appearing from -0.65 V vs. N.H.E. in Fig. 1 can not be expected from the steady state analysis of the electrochemical mechanism[15], but has been predicted from the non-steady state analysis[10]; namely, a plateau

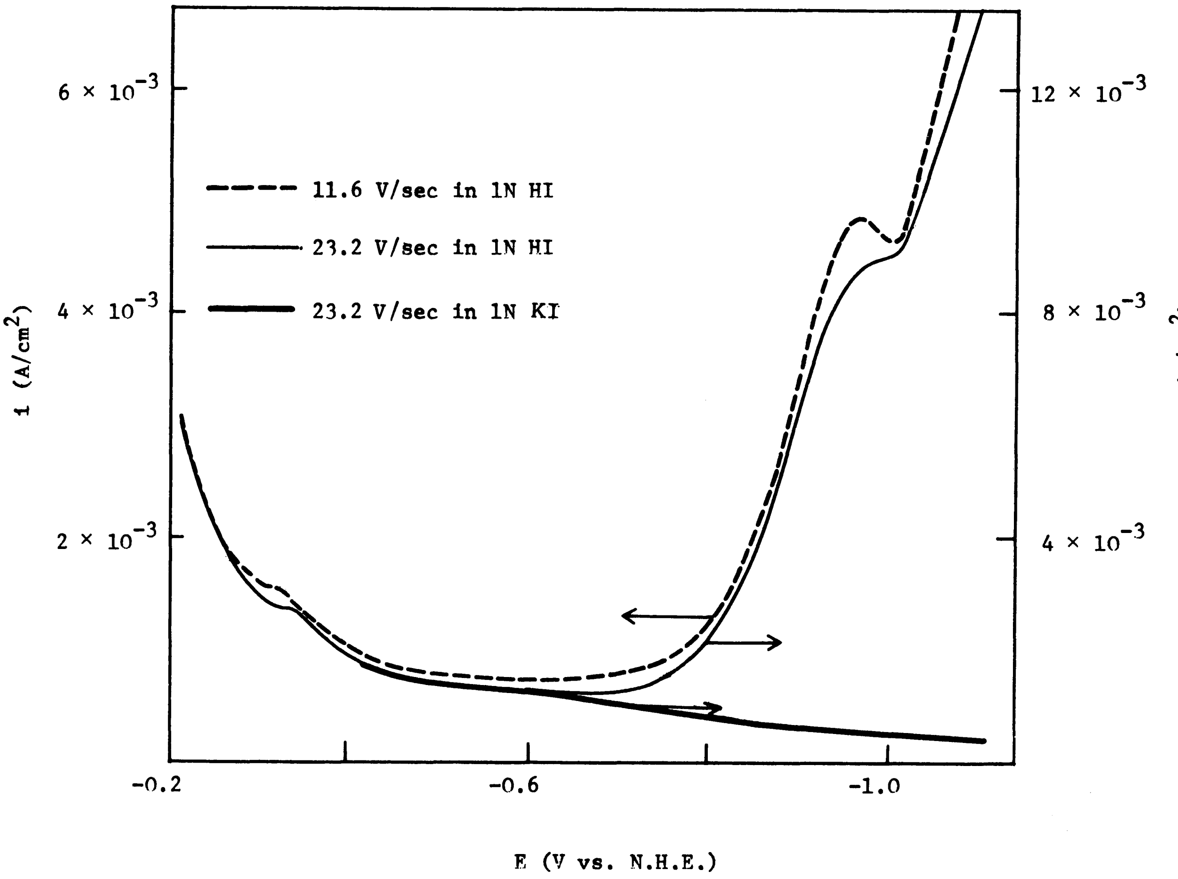

Fig. 2 Curves of current i vs. potential E with potential sweep-rates of 11.6 V/sec and 23.2 V/sec in 1N HI and 1N KI aqueous solutions at 30°C. Respective ordinates are indicated by arrows.

arises from the adsorption process of the intermediate $H_2^+(a)$ (Step (I)). Value of the plateau may be small as in Fig. 1 since the coulombic repulsive interaction between $H_2^+(a)$'s is so large that the coverage of $H_2^+(a)$ is suppressed to a great extent and approaches a limiting value at a relatively small polarization(11).

Figure 2 exhibits the current-potential curves at sweep rates of 11.6 and 23.2 V/sec in 1N HI. The curve in 1N KI at a sweep rate of 23.2 V/sec is also illustrated for comparison. In HI, a current plateau also appears between -0.65 and -1.0 V vs. N.H.E. and its value is proportional to the sweep rate. The proportional dependence satisfies the prediction of the theoretical non-steady state analysis. As seen from Figs. 1 and 2, the current plateau in HI is higher than that in HBr. According to the non-steady state analysis, the current plateau is closely related to the adsorbed state of an intermediate; the smaller the repulsive interaction between adsorbed intermediates is, the higher the current plateau is(11). Since the iodide ion is known to adsorb on Hg electrode surface stronger than bromide ion, adsorbed iodide ion is expected to reduce the repulsive interaction among $H_2^+(a)$'s, because of the counter charge of iodide ion. Hence, the current plateau will become larger in HI. This pronounced effect of adsorbed anion on the adsorbed state of an intermediate of the reaction will support that the intermediate is a positively charged species as $H_2^+(a)$.

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