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ACTIVATION ENERGY OF ELECTRON TRANSFER STEP OF HYDROGEN EVOLUTION REACTION ON NICKEL IN AQUEOUS LITHIUM AND CESIUM HYDROXIDE

By

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Abstract

The real activation energies of the discharge of Li^+ and Cs^+ ions on nickel which is a constituent step of the hydrogen evolution in alkaline solutions have been found to fall in the range 2.5~3.5 kcal/mole, including Na^+ ion, insensitive to the difference in the real hydration free energies of these ions. These close values of the activation energy have been explained based on a compensation effect of the hydration free energies of these ions on the initial and final free energy states of the step.

Introduction

As reported previously, the electron transfer step of the hydrogen evolution reaction on nickel in aqueous sodium hydroxide solution consists of the discharge of sodium ion¹⁾ and its activation energy is 2.5 kcal/mole.

On the other hand, the real hydration energies of alkali metal ions are known to be quite different depending on their ion radii, as reported by Randles.²⁾ It is interesting to know whether the difference of the real hydration energies of these ions is reflected on the activation energies of the discharge of these ions or not. In the present work the activation energies of the Li^+ and Cs^+ ions on the nickel hydrogen electrode will be determined experimentally in lithium and cesium hydroxide solutions and they will be discussed in connection with the molal standard real free energies of hydration of these ions.

Experimentals

The electrolytic cell was made of quartz glass and a nickel foil, apparent surface area 1.0 cm², was used as the test electrode after heat treatments

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invacuum. The time constant τ_1 of the discharge of Li^+ and Cs^+ ions and the double layer capacity C_D were determined at the reversible hydrogen electrode potential by the galvanostatic transient method^{1,3-5)} in 0.23 N LiOH and 0.11 N CsOH aqueous solutions in the range of temperature 0~30°C. The polarization resistance r_1 and the exchange current i_{10} of the discharge step were evaluated from the equations $\tau_1 = C_D \cdot r_1$ and $i_{10} = RT/F \cdot r_1$. The activation energy of the step was determined from the temperature dependence of i_{10} .

Results

The C_D value changes with temperature in LiOH and CsOH solutions as in the case of NaOH, as shown in Fig. 1. The temperature dependence of C_D may reasonably be attributed to the intrinsic structural change of the double layer, as discussed previously.¹⁾ There was no η -dependence of C_D in these solutions as in the case of NaOH solution, where η denoted the overvoltage of the overall reaction. The roughness factor of the electrode determined from the comparison of C_D value at 25°C with that for mercury electrode,⁶⁾ 18 $\mu\text{F}/\text{cm}^2$, was found to be 1.03 or 1.08 in LiOH or CsOH solution. All kinetic parameters are referred to the true unit area of the electrode surface determined from the roughness factor.

The experimental values τ_1 , r_1 and i_{10} at 25°C at $\eta=0$ are shown in Table 1. In this Table the values of parameters are normalized to those in the solutions of mean activity 0.1. For comparison, the values for Na^+ ¹⁾ are also shown in this table. The parameters for platinum hydrogen electrode^{3,7,8)} are shown in Table 2. As seen from these tables, there is little difference of i_{10} among these ions both in the cases of nickel and platinum electrodes.

The temperature dependence of i_{10} for Li^+ and Cs^+ ions is shown in Fig. 2. The values of the real activation energies A_{10} calculated from Fig. 2 are respectively 3.5 and 3.2 kcal/mole for Li^+ and Cs^+ ions, and A_{10} for Na^+ is 2.5 kcal/mole¹⁾, as reported previously. It should be noted that the difference in the real hydration energies of these ions does not reflect on

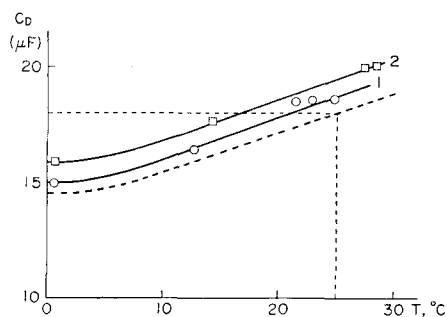


Fig. 1. Temperature dependences of C_D per apparent unit area on Ni at $\eta=0$ in 0.23 N LiOH_{aq} . (curve 1) and 0.11 N CsOH_{aq} . (curve 2) and C_D per true unit area calculated from the roughness factor (broken line) for both solutions.

Activation Energy of Electron Transfer Step of H.E.R. on Ni in LiOH_{aq} and CsOH_{aq}

the real activation energies of the discharge of these ions.

The i_1 value for Li⁺ ion is kept constant in the range on η from 0 to -300 mV at temperatures between 0 to 20°C as in the case of Na⁺ ion, as shown in Fig. 3. The reason of this constancy of i_1 has already been explained in a previous work based on a compensation effect of the adsorbed alkali metal atom⁹.

TABLE 1. Time constant τ_1 , polarization resistance r_1 and i_{10} of the electron transfer step on Ni at $\eta=0$ and $T=25^\circ\text{C}$ in LiOH_{aq}, NaOH_{aq} and CsOH_{aq} of mean activity 0.1.

Cation	$\tau_1, \mu \text{ sec}$	$r_1, \Omega \cdot \text{cm}^2$	$i_{10}, \text{mA/cm}^2$
Li ⁺	150	8.3	3.1
Na ⁺	210	11.7	2.2
Cs ⁺	200	11.2	2.3

TABLE 2. Time constant τ_1 , polarization resistance r_1 and i_{10} of the electron transfer step on Pt at $\eta=0$ and $T=25^\circ\text{C}$ in LiOH_{aq}, NaOH_{aq} and CsOH_{aq} of mean activity 0.1.

Cation	$\tau_1, \mu \text{ sec}$	$r_1, \Omega \cdot \text{cm}^2$	$i_{10}, \text{mA/cm}^2$
Li ⁺	70	3.9	6.6
Na ⁺	90	5.0	5.0
Cs ⁺	110	6.1	4.2

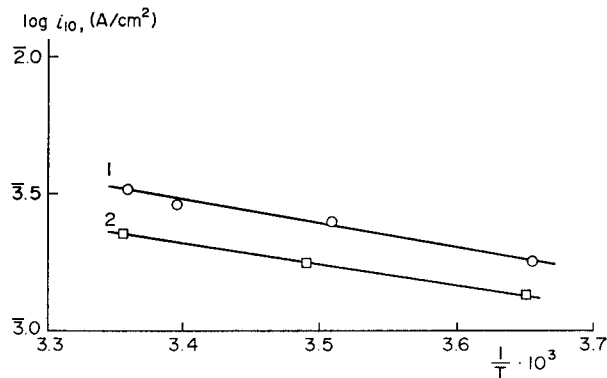


Fig. 2. Temperature dependences of the exchange current i_{10} of the electron transfer step on Ni in 0.23 N LiOH_{aq}. (curve 1) and 0.11 N CsOH_{aq}. (curve 2).

R. NOTOYA and A. MATSUDA

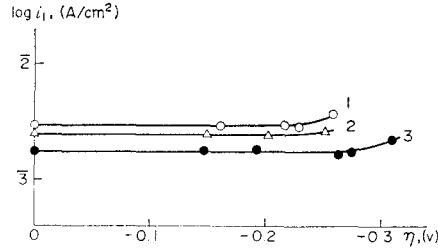


Fig. 3. η -dependence of the current of the discharge step $\log i_1$ in 0.23 N LiOH_{aq} . at temperatures = 0.8°C (●), 14°C (△) and 19°C (○).

Discussion

The rates of the formation of adsorbed alkali metal atoms through the discharge of ions are quite close to each other and the real activation energies fall in the range 2.5–3.5 kcal/mole for Li^+ , Na^+ and Cs^+ ions, whereas the standard free energies of hydration of these ions are 122.1 kcal/mole for Li^+ , 98.2 kcal/mole for Na^+ and 67.8 kcal/mole for Cs^+ ion²⁰. Therefore the hydration state of the ions does not reflect on the rate and activation energy of the discharge of these ions. This result may be explained by a compensation effect between the standard free energies of the initial and final states of the step.

Let us consider the standard free energy of the initial state \mathcal{F}_i° and the molal free energy of the final state \mathcal{F}_f of the discharge of an alkali metal ion M^+ at the reversible hydrogen electrode potential which are referred to the standard states of gaseous alkali metal ion and electron. \mathcal{F}_i° and \mathcal{F}_f may be given by the following equations,

$$\mathcal{F}_i^{\circ} = \bar{\mu}_{M^+, \text{aq}}^{\circ} + \bar{\mu}_e^{\text{H}} - \bar{\mu}_{M^+, \text{g}}^{\circ} - \bar{\mu}_e^{\circ}, \quad (1)$$

$$\mathcal{F}_f = \mu_{M(\text{a})} - \bar{\mu}_{M^+, \text{g}}^{\circ} - \bar{\mu}_e^{\circ}, \quad (2)$$

where $\bar{\mu}_i$ is the electrochemical potential of i , subscript aq and g mean aqueous and gaseous states respectively, superscript \circ means the standard state, superscript H means the reversible hydrogen electrode and $M(\text{a})$ is the adsorbed alkali metal atom. The difference $\bar{\mu}_{M^+, \text{aq}}^{\circ} - \bar{\mu}_{M^+, \text{g}}^{\circ}$ means by the definition the molal real free energy of hydration of M^+ ion $\alpha_{M^+, \text{aq}}$, *i. e.*,

$$\bar{\mu}_{M^+, \text{aq}}^{\circ} - \bar{\mu}_{M^+, \text{g}}^{\circ} = \alpha_{M^+, \text{aq}}. \quad (3)$$

$\mu_{M(\text{a})}$ is given by the following equilibrium relation at the reversible hydrogen electrode potential,

$$\mu_{M(\text{a})} = \bar{\mu}_{M^+, \text{aq}}^{\circ} + RT \ln a_{M^+} + \bar{\mu}_e^{\text{H}} \quad (4)$$

Activation Energy of Electron Transfer Step of H.E.R. on Ni in LiOH_{aq} and CsOH_{aq}

where α_{M^+} is the activity of M^+ ion. Substituting (3) and (4) into (1) and (2), we have

$$\mathcal{F}_i^{\circ} = \alpha_{M^+,aq} + \bar{\mu}_c^{\text{II}} - \bar{\mu}_{e,g}^{\circ}, \quad (5)$$

$$\mathcal{F}_f = \alpha_{M^+,aq} + \bar{\mu}_e^{\text{II}} - \bar{\mu}_{e,g}^{\circ} + RT \ln \alpha_{M^+}. \quad (6)$$

From the comparison of \mathcal{F}_f and \mathcal{F}_i° for different kinds of alkali metal atoms $M_i(a)$ and $M_j(a)$ in the alkali hydroxide solutions of same activity, it is found that

$$\mathcal{F}_{f,M_j(a)} - \mathcal{F}_{f,M_i(a)} = \alpha_{M_j^+,aq} - \alpha_{M_i^+,aq} = \mathcal{F}_{i,M_j^+}^{\circ} - \mathcal{F}_{i,M_i^+}^{\circ}. \quad (7)$$

It can be concluded from Eq. (7) that the difference of the free energies of final states for two different kinds of alkali metal atoms equals the difference of the real free energies of hydration of these ions in the initial state, *i. e.* there exists a compensation effect between the initial and final states.

In this way, we can expect that the real free energy of hydration of an alkali metal ion does not reflect on the activation free energy of the discharge of the ion, insofar as the Brönsted relation holds between the two quantities, or we can expect almost the same rate for the discharge of different kinds of alkali metal ions at a constant electrode potential, as experimentally verified in the preceding section. Strictly speaking, the Brönsted relation should be applied to the difference between the standard free energy of the initial state and the free energy of the final state which does not include the entropy term due to the distribution of $M(a)$ on the electrode surface. However, this term may be given by the surface coverage θ of $M(a)$ as $RT \ln(\theta/1-\theta)^{10}$ which can be neglected in the expression of $\mu_{M(a)}$ when θ is not close to zero or unity.

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