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Note

PERIODIC VARIATION OF EXCHANGE CURRENT DENSITY OF HYDROGEN ELECTRODE REACTION WITH ATOMIC NUMBER

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The works on hydrogen electrode reaction have been increasingly accumulated during the last decade. These works are much more reliable than earlier ones, inasmuch as the special precaution has been taken against contaminations of solution and electrode surface. Survey of the results shows that the activity of metals for the reaction in terms of the exchange current density, i_0 (Acm^{-2}), varies in a wide range, namely from $\log i_0 = -1.2$ on Pd to -12.9 on Pb and even on the same metal, from -3.15 to -7.04 on Au (*cf.* Table 1).

Such variations in the activity may be caused by several factors such as bulk property of electrode material, surface state of the electrode and solution.

The present note is concerned with the relation of the exchange current density of various metals to their position in the Periodic Table and with the decision of the determining factor of the activity.

Review of the Experimental Results

Table 1 shows results of observations as well as their experimental conditions reported mainly during these ten years.[1~61] The exchange current density, i_0, was determined by extrapolating the current density, i, at $\eta=0$ according to the TAFEL equation

$$\eta = a + b \log i ,$$

where η is the overvoltage**) and a or b the constant. Logarithm of the exchange current density is plotted in Fig. 1 against the atomic number of electrode material, where ⊸, ⨯ or ⊙ represents the values obtained respectively in acidic, alkaline or neutral solution. In case where two linear parts appear in $\eta \sim \log i$ plot, i_0 was determined by extrapolating i from the part of the lower η.**)

Table 1 and Fig. 1 are commented upon as follows.

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**) Overvoltage is defined in this paper as the negative of potential of the test electrode referred to that of the reversible hydrogen electrode in the same environment.

TABLE 1. List of reported values of

Electrode			Solution		Temp. (°C)
Metal	Form	Treatment	Concn.	Pre-electrolysis	
Ag			1.0 N HCl	1 A·cm^{-2}, 3.1 ×10^4 Coulomb	Room temp.
	Wire	Chem. polished, heated in H_2 at 600°C for 2~3 hr.	5 N HCl	1 A·cm^{-2}, 10^5 Coulomb	
	Wire	Chem. polished	1 N H_2SO_4	conducted, no details	
	Wire	Sealed into glass bulb	1 N NaOH	10 mA·cm^{-2}, 20 hr.	30
	Wire	Heated in H_2 at 700°C for 1 hr., sealed into glass bulb	0.4 N HCl	10 mA·cm^{-2}, 60 hr.	23±2
	Wire	Sealed into glass bulb	0.1 N NaOH	10 mA·cm^{-2}, > 2 days, 0.1 A·cm^{-2}, 36 hr.	25
	Single or poly-crystal	Electropolished, held in hot H_2 for a few days, gently anodized	2 N H_2SO_4	conducted, no details	Room temp.
	Wire	Sealed into glass bulb	0.1 N HCl 0.1 N DCl	0.1 A·cm^{-2}, 24~36 hr.	26±1
	Foil	Heated in H_2 at 450°C for 24 hr., sealed with paraffin	2 N H_2SO_4	0.1 A, 60 hr.	Room temp.
	Wire	Sealed by Teflon, anodic, cathodic polarizations	1.11 or 0.26 N NaOH	30 mA, 60 hr.	21±2
Au	Wire	Anodic polarization	8 N H_2SO_4		
	Bead	Anodic, cathodic polarizations (40 mA, 200 sec.)	2 N H_2SO_4	50 mA, a week	29±1
	Wire	Sealed into glass bulb	0.1 N HCl 0.1 N NaOH	27 mA·cm^{-2}, 42 hr. 180 mA·cm^{-2}, 43 hr.	
	Foil	Cleaned chemically	0.1 N HCl	conducted, no details	
	Wire	Sealed into glass bulb	0.1 N DCl 0.1 N HCl	0.1 A·cm^{-2}, 24~36 hr.	26±1

log i_0 and b on various metals.

Rest potential[a)]	Range of observation in log i (A·cm^{-2})	b (mV)	log i_0 (A·cm^{-2})	log i[b)] (A·cm^{-2})	Reference
	−6∼−1	60±5 130±5	−5.4±0.4 (−3.7±0.4)		BOCKRIS & CONWAY 1 (1952)
	−3∼+2	120	−5.3		BOCKRIS & AZZAM 2 (1952)
	−4∼−2	110	−5.7*		GERISCHER & MEHL 3 (1955)
	−7.5∼−3	120	−6.50		AMMAR & AWAD 4 (1956)
	−7∼−3	57±2 101±9	−6.6 −5.35		BOCKRIS, AMMAR & HUQ 5 (1957)
	−7∼−2	122	−6.5		DEVANATHAN, BOCKRIS & MEHL 6 (1959)
+0.35∼+0.45 V, occasionally 0∼+18 mV	−7.5∼−2.7	59 116	−6*		ANTONIOU & WETMORE 7 (1959)
	−5.5∼−2	72±7 12(5)±5 72±7 122±5	−6.10±0.2 −4.80±0.15 −7.05±0.2 −5.40±0.15		CONWAY 8 (1960)
	−2.3∼−1.3	120	−5.4		GOSSNER, LÖFFLER & SCHWAB 9 (1961)
4.5±0.9 mV	−5∼+1	43±2 309±5	−5.35±0.4		YAMAZAKI & KITA 10 (1965)
	−3∼−1	130	−3.15		BREITER, KAMMERMAIER & KNORR 11 (1956)
	−3∼−0.5	27	−3.4*		SCHULDINER & HOARE 12 (1957)
Value of r. h. e.	−5.63∼−2.41# −5.92∼−3.68#	71 97 119	(−6.83) −5.64 −7.04		PENTLAND, BOCKRIS & SHELDON 13 (1957)
Value of r. h. e.	−6∼−3	123	−5.5*		IVES 14 (1959)
	−5∼−1.5	120±5 110±5	−6.23±0.22 −5.60±0.18		CONWAY 8 (1960)

Electrode			Solution		Temp. (°C)
Metal	Form	Treatment	Concn.	Pre-electrolysis	
	Wire	Sealed with paraffin or araldite, scraped with sharp glass bar	2 N H_2SO_4		20
Bi	Plate	Previously polarized	0.9 N HCl 0.9 N H_2SO_4 0.9 N $HClO_4$	conducted, 20~25 hr.	
Cd	Wire	Heated in H_2 at 200°C	0.5 N H_2SO_4	1 mA·cm^{-2}, 15~20 hr.	Room temp.
Cu	Wire	Sealed into glass bulb	0.1 N HCl 0.01 N NaOH	75 mA·cm^{-2}, 37 hr. 0.36 mA·cm^{-2}, 14 hr.	
	Wire	Heated to red hot in H_2, sealed into glass bulb	0.1 N HCl	0.25 A·cm^{-2}, 24 hr.	38 ± 1
		Sealed into glass bulb	0.1 N HCl 0.1 N DCl	0.1 A·cm^{-2}, 24~36 hr.	
Fe	Wire	Sealed into glass bulb	0.01 N HCl 0.1 N NaOH	18 mA·cm^{-2}, 36 hr. 25 mA·cm^{-2}, 35 hr.	
	Wire	Sealed into glass bulb	0.5 N HCl 0.5 N DCl	15 mA·cm^{-2}, 20 hr.	
	Cylindrical	Mounted on Teflon holder, etched in 0.5 M H_2SO_4	0.5 M H_2SO_4	conducted, no details	25.00 ± 0.03
Ga	Solid Liquid		0.1 N HCl	conducted, no details	20.5 35
	Solid Liquid		1 N H_2SO_4		28 32
Hg	Pool	Redistillation	1.005 N HCl		25 ± 0.02
	Pool	Triply distilled, then distilled in vacuum	0.1 N HCl	conducted, no details	21 ± 0.1
	Pool	Purified in vacuum apparatus	0.1 N HCl	conducted, no details	0
	Pool		0.1 M HCl solution of H_2O, CH_3OH, C_2H_5OH, n-C_3H_7OH		20 ± 0.5

Periodic Variation of Exchange Current Density of Hydrogen Electrode Reaction

Rest potential[a)]	Range of observation in log i (A·cm^{-2})	b (mV)	log i_0 (A·cm^{-2})	log i[b)] (A·cm^{-2})	Reference
	−3∼−1	116±4	−5.36		GOSSNER & LÖFFLER 15 (1963)
	−7∼−1	118±5 101±5 100±5	− 9.32 −10.45 −10.4	−5.07* −5.2* −5.35* at η=0.5 V	PALM & PAST 16 (1964)
	−5∼−2	135±12	−10.77±0.75		BOCKRIS & SRINIVASAN 17 (1964)
	−4.51∼−3.47#	114±8	−6.84		PENTLAND, BOCKRIS & SHELDON 13 (1957)
	−5.19∼−3.75#	107±6	−6.09		
	−5∼−1		−6.21*		CONWAY, BEATTY & DEMAINE 18 (1962)
	−5.5∼−2 −5.5∼−2	120±5 120±5	−6.7±0.15 −7.6±0.15		CONWAY 8 (1960)
	−4.06∼−3.19#	118±15	−6.29		PENTLAND, BOCKRIS & SHELDON 13 (1957)
	−4.09∼−2.16#	120±2	−6.06		
		133±4 134±4	−5.18±0.1 −5.77±0.14		BOCKRIS & KOCH 19 (1961)
	−3.9∼−1.6	118	−5.65*		KELLY 20 (1965)
	−6∼−3	113 93	−10.0 −10.1		CHRISTOV & RAJĆEVA 21 (1962)
	−5∼−3	95 95	− 9.9* −10.0*		SABO & BAGOTSKAJA 22 (1963)
	−4.6∼−1	118±2	−11.53±0.05		BÉTHUNE 23 (1949)
	−6∼−1	116	−12.11*		POST & HISKEY 24 (1950)
	−11∼−8	α=0.54 α=1.54			MITUYA 25 (1956)
		117 107 104 102	−11.8 −11.5 −10.8 −10.8		MINC & SOBKOWSKI 26 (1959)

Electrode			Solution		Temp. (°C)
Metal	Form	Treatment	Concn.	Pre-electrolysis	
Hg (cont'd)	Drop	Triply distilled	0.1 N $HClO_4$	1 mA·cm^{-2}, overnight	25
	Pool	Redistilled, anodic polarization in HNO_3–$Hg_2(NO_3)_2$, distillation in vacuum	1 N HCl solution of CH_3OH 1 N DCl solution of CH_3OD	conducted, no details conducted, no details	27
In			0.1 M $HClO_4$	1 mA·cm^{-2}, overnight	25
	Cylindrical	Electropolished in 2 : 1 mixture of CH_3OH and HNO_3 at 0.3 mA·cm^{-2}, cathodic polarization at $\eta = 1$ V overnight	0.1 M $HClO_4$ 0.01 M $HClO_4$	10 mA, 16 hr.	30.0 ± 0.2
Mo	Wire	Flushed in vacuum, sealed into glass bulb	0.1 N HCl 0.1 N NaOH	75 mA·cm^{-2}, 37 hr. 0.24 A·cm^{-2}, 71 hr.	
Nb			1 N HCl		
	Plate	Polished with emery paper, cathodic polarization (5 mA·cm^{-2}, 1 hr.)	1 N H_2SO_4 1 N NaOH	10 mA·cm^{-2}, 6 hr.	
		Polished with emery paper, cathodic polarization (5 mA·cm^{-2}, 96 hr.)	1 N H_2SO_4 1 N NaOH	10 mA·cm^{-2}, 6 hr.	
	Sheet (passive state)	Purified by a zonerefining method, mounted in Teflon holder, cleaned in HCl	0.145 N HCl	4~5 mA, 50 hr.	25 ± 0.1
Ni	Wire	Sealed into glass bulb	1.0 N HCl 0.1 N NaOH	0.1 A·cm^{-2}, 18 hr.	20 ± 0.5
	Disk	Electrodeposition 15 mA·cm^{-2}, 10 min.	0.5 M $NiSO_4$		45 ± 0.05
	Single crystal (100) (110) (111)	Anodic treatment in 70% H_2SO_4	0.1 N $HClO_4$ 0.15 N $HClO_4$ 0.15 N $HClO_4$		25
	Cross section of rod	Polyethylene sleeved	2 N NaOH	25 mA, 3~4 hr.	26~28
	Wire	Sealed into glass bulb	0.1 N HCl 0.1 N DCl	0.1 A·cm^{-2}, 24~36 hr.	25

Periodic Variation of Exchange Current Density of Hydrogen Electrode Reaction

Rest potential[a)]	Range of observation in $\log i$ (A·cm^{-2})	b (mV)	$\log i_0$ (A·cm^{-2})	$\log i^{b)}$ (A·cm^{-2})	Reference
	−4 ~ −1.7	118	−11.82		BUTLER & MAKRIDES 27 (1964)
	−4 ~ −2	119*	−10.8*		CONWAY & SALOMON 28 (1964)
	−4 ~ −3	119*	−11.3*		
	−3.5 ~ −1.15	118	−11.85	−2.75 at $\eta = 1$ V	BUTLER & MAKRIDES 29 (1964)
	−6.3 ~ −2.8	$\alpha = 0.530 \pm 0.04$ $\alpha = 0.48 \pm 0.02$	-11.19 ± 0.07 -10.8 ± 0.3		BUTLER & DIENST 29 a (1965)
	−5.52 ~ −3.48 −3.34 ~ −1.80 −4.74 ~ −3.72 −3.58 ~ −2.10	80 ± 4 104 ± 4 80 ± 3 116 ± 8	−7.30 −6.40 −7.35 −6.35		PENTLAND, BOCKRIS & SHELDON 13 (1957)
	−3 ~ −1	110	−9*		BOCKRIS 62 (1947)
	−5 ~ −2.3	low 130 low 140	— −6.75 — −7.50		ROTINYAN & KOZHEVNIKOVA 29 b (1963)
	−5 ~ −2.3	low 120 low 140	— −6.33 — −6.15		
	−6 ~ −2	57 343	−8.06		JONCICH, STEWART & POSEY 29 c (1965)
	−6 ~ −2.3 −7.7 ~ −3.3	109 ± 9 101 ± 4	-5.4 ± 0.1 -6.4 ± 0.2	−3.56* at $\eta = 0.2$ V −4.7* at $\eta = 0.2$ V	BOCKRIS & POTTER 30 (1952)
	−3 ~ −1.3	120	−6.1		YEAGER, Cels, YEAGER & HOVORKA 31 (1959)
	−6 ~ −3	100 155 150	−4.85 −5.2 −5.2	−3.0* −3.9* −3.9* at $\eta = 0.2$ V	PIONTELLI, BICELLI & VECCHIA 32 (1959)
	−6 ~ −1	100*	−4.9*	−2.9* at $\eta = 0.2$ V	DEVANATHAN & SELVARATNAM 33 (1960)
	−5 ~ −1.35	118 ± 3 124 ± 3	-5.87 ± 0.15 -6.35 ± 0.15	−4.3* −4.7* at $\eta = 0.2$ V	CONWAY 8 (1960)

Electrode			Solution		Temp. (°C)
Metal	Form	Treatment	Concn.	Pre-electrolysis	
Ni (cont'd)		Heated to red hot in H_2, sealed into glass bulb	0.1 N HCl	0.25 A·cm^{-2}, 24 hr.	38±0.1
	Cylinder	Anodic (10~100 mA·cm^{-2}) and cathodic (2 mA·cm^{-2}, 5 min.) polarization	0.1 N NaOH	10~15 mA·cm^{-2}, 18~124 hr.	30
	Small sphere	Sealed into glass bulb	0.95 N NaOH	3.5 mA, 48~72 hr.	22±1
	Cross section of rod	Mounted in Pyrex holder by Kel-F wax, polishings, treated by chromic acid/sulfuric acid	1 M $HClO_4$ pH=0.04 1 M $NaClO_4$+0.01 M NaOH pH=10.8	30 mA, 6 hr.	25±0.1
	Single crystal (100) (110) (111)	Chem. polished	4 N KOH		
	Wire	Heated in H_2 at 700°C	0.5 N H_2SO_4 0.5 N NaOH	1 mA·cm^{-2}, 15~20 hr.	Room temp.
	Evaporated film		NaOH pH=13.68	20~30 mA·cm^{-2}, 30~50 hr.	Room temp.
Pb		Cathodic polarization (0.1~1 mA·cm^{-2})	0.1~0.01 N H_2SO_4		20
			1 N H_2SO_4 1 N HCl		
	Wire	Chem. polished	0.5 N H_2SO_4 0.5 N NaOH	1 mA·cm^{-2}, 40 hr. 1 mA·cm^{-2}, 16 hr.	Room temp.
Pd	Wire	Anodic polarization	2 N H_2SO_4		Room temp.
	Bead β-phase	Anodic (5 mA, 15 min.), cathodic (50 mA, 30 min.) polarizations	1.05 N H_2SO_4 pH=0.40	conducted, no details	39±1
		Anodic (10 mA, 30 min.), cathodic (50 mA, 30 min.) polari- zations	0.514 N H_2SO_4 +0.5 N Na_2SO_4 pH=0.84	conducted, no details	39±1
	Membrane, α-phase	Anodic polarization (10 mA, 45 min.)	2 N H_2SO_4 pH=0 0.3 N H_2SO_4+0.7 N Na_2SO_4 pH=0.9	conducted, no details	31±2
	Wire	Sealed into glass bulb	0.1 N HCl 0.1 N NaOH	0.24 A·cm^{-2}, 13 hr. 0.12 A·cm^{-2}, 38 hr.	

Periodic Variation of Exchange Current Density of Hydrogen Electrode Reaction

Rest potential[a)]	Range of observation in log i (A·cm^{-2})	b (mV)	log i_0 (A·cm^{-2})	log i[b)] (A·cm^{-2})	Reference
	−5∼−1	95*	−5.24	−3.1* at $\eta=0.2$ V	CONWAY, BEATTY & DEMAINE 18 (1962)
0±2 mV	−6∼−2.5	89	−5.03	−2.73* at $\eta=0.2$ V	MAKRIDES 34 (1962)
	−3∼+2	104±9	−5.32	−3.7* at $\eta=0.2$ V	KITA & YAMAZAKI 35 (1963)
	−6∼−1.2 −5∼−1.5	125 105	−5.7 −5.0	−4.1* −3.05* at $\eta=0.2$ V	HUQ & ROSENBERG 36 (1964)
	−5.5∼−2	89∼93	−5.0	−3.0* at $\eta=0.2$ V	WEININGER & BREITER 37 (1964)
		124±10 96±10	−5.22±0.53 −6.10±0.10		BOCKRIS & SRINIVASAN 17 (1964)
	−4.8∼−0.8	90*	−5.1*	−2.9* at $\eta=0.2$ V	MATSUDA & OHMORI 38 (1962)
	−6.6∼−2.8	118	−12.9*		JOFA 39 (1945)
	−4.2∼−0.5	120 117	−12.7 −12.9		PALM & PAST 40 (1962)
	−5∼−1.3	125±14 129±4	−11.33±1.40 −6.47±0.26	−2.9 at $\eta=0.2$ V	BOCKRIS & SRINIVASAN 17 (1964)
	−4.4∼0	29 0	−2.7		CLAMROTH & KNORR 41 (1953)
	−2.0∼−0.5 −2.0∼−0.6	40 0 42 126	−1.25*	−0.9* at $\eta=0.05$ V	HOARE & SCHULDINER 42 (1955)
+49.5 mV	−4.5∼+0.5 −4.5∼+1.4	(42) 124 (30) 125	−1.2* −1.85*	−0.75* at $\eta=0.05$ V −1.4* at $\eta=0.05$ V	HOARE & SCHULDINER 43 (1957)
Value of r. h. e.	−2.89∼−1.41* −4.13∼−3.08*	99 125	−3.25 −5.01		PENTLAND, BOCKRIS & SHELDON 13 (1957)

Electrode			Solution		Temp. (°C)
Metal	Form	Treatment	Concn.	Pre-electrolysis	
Pd (cont'd)	Wire α-phase	Sealed into glass bulb	0.1 N HCl 0.1 N DCl	0.1 A·cm^{-2}, 24~36 hr.	26±1
	Membrane		2 N H_2SO_4		20
	Wire	Palladized	1.0 N HCl		25±0.2
	Bead		0.05 M NaOH+ 0.22 M Na_2SO_4	5~10 mA, a week	25±1
Pt	Wire		1 N H_2SO_4		20
	Wire	Heated in H_2 at 600°C for 10 min., anodic polarization (0.1 A·cm^{-2}, 10 sec.)	1 N HCl	0.1 A·cm^{-2}, 10 hr.	23±2
	Wire	Anodic (0.01 Coulomb·cm^{-2}), cathodic polarizations	0.1 N NaOH	10 mA·cm^{-2}, 25~30 hr.	25
	Bead	Anodic polarization	1 N H_2SO_4	5~10 mA, overnight	25±1
			1 N H_2SO_4	conducted, 15 hr.	25.0
	Small sphere	Soaked in chromic+sulfuric acid mixture for 24 hr., anodic and cathodic polarization (0.1 A·cm^{-2}, 5 sec.)	0.5 M HCl	10 mA·cm^{-2}, 18 hr.	25±0.5
	Wire	Platinized	0.1 N HCl 0.1 N DCl	0.1 A·cm^{-2}, 24~36 hr.	26±1
	Wire	Heated in H_2, sealed into glass bulb, anodic polarization (10 mA·cm^{-2}, 10 sec.)	0.5 N HCl 0.5 N DCl	15 mA·cm^{-2}, 20 hr.	
	Foil	Anodic polarization (1~2 mA·cm^{-2}), cathodic polarization (i<1 mA·cm^{-2}) till potential reached the value of r. h. e.	0.1 N Na_2CO_3 pH=11	conducted, 15 hr.	25±0.5
	Wire	Anodic polarization	0.5 N H_2SO_4 0.5 N NaOH	1 mA·cm^{-2}, 15~20 hr.	Room temp.
Re	Wire	Mounted in Teflon holder, cleaned in HCl	0.037 N HCl 0.145 N HCl	4~5 mA, 50 hr.	25±0.1
Rh	Wire	Sealed into glass bulb	0.01 N HCl 0.01 N NaOH	conducted, no details 6 mA·cm^{-2}, 20 hr.	

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Rest potential[a)]	Range of observation in log i (A·cm^{-2})	b (mV)	log i_0 (A·cm^{-2})	log i[b)] (A·cm^{-2})	Reference
	−5∼−1.5 −5∼−2.2	(25±3) 110±10 (25±3) 120±10	−2.8* −3.7*	−2.4* at η=0.05 V −3.3* at η=0.05 V	CONWAY 8 (1960)
	−4∼−2	120	−3.2*	−2.7* at η=0.05 V	SHIRATORI 44 (1961)
	−3.4∼0	29.5	−2.5*	−0.8* at η=0.05 V	BARTON & LEWIS 45 (1962)
±0.5 mV	−4.8∼−2.2	126	−3.25*		SCHULDINER 46 (1954)
<+2 mV	−7∼−2	129	−3.65*		VETTER & OTTO 47 (1956)
	−3∼−1	29±1	−3.0		BOCKRIS, AMMAR & HUQ 5 (1957)
	−5∼−3	114±11	−4.17		AMMAR & DARWISH 48 (1959)
±0.5 mV	−4∼−0.6	25	−3.1*		SCHULDINER 49 (1959)
	−4∼−0.4	26*	−3.6*		YEAGER 50 (1959)
Value of r. h. e.	−3.4∼−1	27.8±1.4	−2.59±0.09		PARSONS 51 (1960)
		30±2 31±2	−3.16±0.1 −3.33±0.1		CONWAY 8 (1960)
		29±3 26±6	−3.33±0.14 −3.62±0.45		BOCKRIS & KOCH 20 (1961)
	−5.5∼−1	58±2 260±60	−3.83 −2.58		HISANO 52 (1963)
		30±1 117±8	−3.53±0.05 −4.06±0.09		BOCKRIS & SRINIVASAN 17 (1964)
	−6∼−2	43 29.2	−4.95 −5.14		JONCICH, STEWART & POSEY 29 c (1965)
Value of r. h. e.	−3.38∼−3.08# −4.18∼−3.51#	55±3 119±3	−3.80 −4.85		PENTLAND, BOCKRIS & SHELDON 13 (1957)

Electrode			Solution		Temp. (°C)
Metal	Form	Treatment	Concn.	Pre-electrolysis	
Rh	Bead	Anodic, cathodic polarizations	1 M H_2SO_4	conducted, no details	27 ± 1
	Bead	Anodic, cathodic polarization (0.3 A·cm^{-2}, 90 min.)	2 N H_2SO_4		25 ± 1
	Wire	Anodic polarization (10 mA·cm^{-2})	0.5 N H_2SO_4	1 mA·cm^{-2}, 15~20 hr.	Room temp.
Si	Single crystal (111) n and p types	Treated with solutions; HF : HNO_3 = 1 : 2 and 42% HF	2 N H_2SO_4		20
			2.5 N HF		
Te	Rod		1 N HCl	30~40 mA·cm^{-2}, 20 hr.	30
Ti			0.5 M NaCl		30
	Wire	10 min. in hot 1 N NaOH, 1~2 min. in hot 2 N H_2SO_4, polished with glass powder	1 N H_2SO_4 1 N HCl		
	Plate	10 min. in hot 1 N NaOH, 1~2 min. in hot 2 N H_2SO_4, cathodic polarization in 2 N H_2SO_4 (5 mA·cm^{-2}, 1 hr.)	2 N H_2SO_4		
W	Wire	Heated in H_2 at 600°C for 2~3 hr.	5 N HCl	1 A·cm^{-2}, 10^5 Coulomb	25
	Wire	Heated in vacuum at 3000°C for 1 min., in H_2 at 1000°C for 2~3 min.	0.1 N HCl	10 mA·cm^{-2}, 60 hr.	23 ± 2
		Cleaning with molten $NaNO_3$	0.5 N HCl 0.5 N DCl	15 mA·cm^{-2}, 20 hr.	
	Wire	Cleaning with molten $NaNO_3$, heating in H_2 at 200°C	0.5 N H_2SO_4 0.5 N NaOH	1 mA·cm^{-2}, 15~20 hr.	Room temp.
Zn			1 N H_2SO_4		20

*; Values estimated from figures.
( ); Uncertain values.
#; The region where a straight TAFEL line is observed.
a); Values of rest potential are referred to the reversible hydrogen electrode (r. h. e.) in the same solution and hydrogen atmosphere.
b); Values of this column are those at a given overvoltage.

Periodic Variation of Exchange Current Density of Hydrogen Electrode Reaction

Rest potential[a)]	Range of observation in log i (A·cm^{-2})	b (mV)	log i_0 (A·cm^{-2})	log i[b)] (A·cm^{-2})	Reference
	−5∼−0.5	27.5	−3.0*	−1.3* at $\eta=0.05$ V	SCHULDINER 53 (1960)
	−3.5∼0	120	−1.85*	−1.75* at $\eta=0.05$ V	HOARE 54 (1960)
		28±2	−3.22±0.06		BOCKRIS & SRINIVASAN 17 (1964)
	−6∼−1	180	−6.0	−3.9* at $\eta=0.5$ V	EFIMOF & ERUSALIMCHIK 55 (1959)
	−6∼−1	170	−7.7*	−4.7* at $\eta=0.5$ V	EFIMOF, ERUSALIMCHIK & SOKOLOVA 56 (1962)
	−6∼−2	53 115	−10.1* − 6.4*	−2.1* at $\eta=0.5$ V	AMMAR & AWAD 57 (1956)
	−5.7∼−2.7	154	−8.45*	−5.1* at $\eta=0.5$ V	HACKERMAN & HALL 58 (1954)
	−5∼−2.5	135 130	−6.07 −6.30	−2.5* −2.4* at $\eta=0.5$ V	KOLOTYRKIN & PETROV 59 (1957)
	−5∼−1.5	119	−8.15*	−4.0* at $\eta=0.5$ V	PETRENKO 60 (1962)
	−3∼+2	110	−5.0		BOCKRIS & AZZAM 2 (1952)
		60±3 105±13	−6.11 −5.55		BOCKRIS, AMMAR & HUQ 5 (1957)
		70±5 112±9 69±6 101±4	−7.87±0.31 −6.30±0.23 −8.34±0.27 −7.10±0.42		BOCKRIS & KOCH 20 (1961)
		84±6 116±3 80±1 100±4	−6.63±0.22 −5.90±0.09 −7.53±0.10 −6.60±0.26		BOCKRIS & SRINIVASAN 17 (1964)
	−4.6∼−1.8	120	−10.8*		ROTINYAN, FEDOTIEFF & SOK 61 (1957)

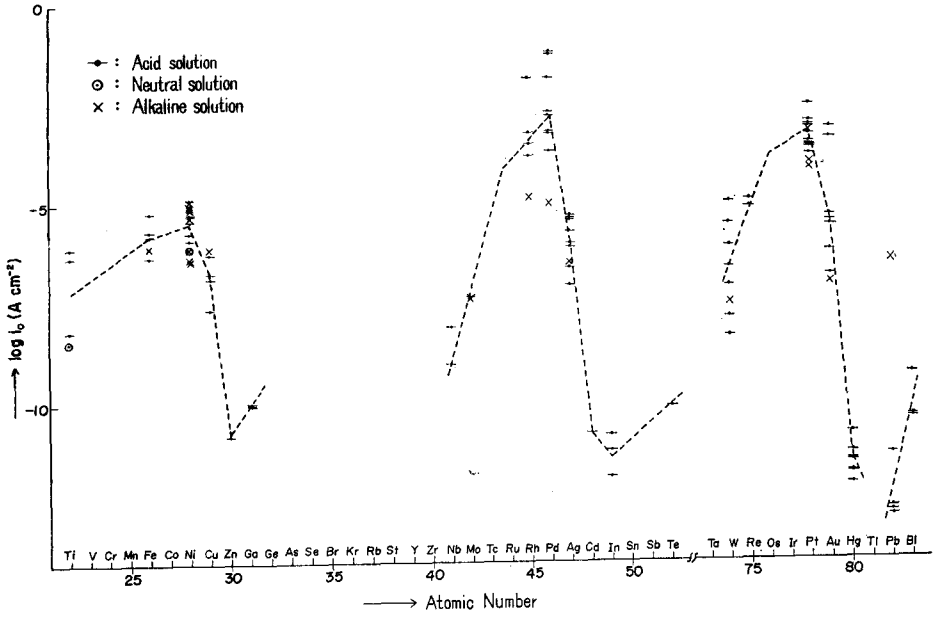

Fig. 1. Log i_0 as a function of atomic number.
-•-; Values in acidic solution, ×; Values in alkaline solution,
⊙; Values in neutral solution.

(1) *Periodicity of the activity*:

The results on the same metal flucuate considerably, especially in case of Rh, Pd, W, Au and Pb but still the log i_0-values of the respective metals studied are basically a periodic function of the atomic number as shown by the dotted lines in Fig. 1 for the three long periods of the Periodic Table; in other words, the activity increases first with increase of atomic number, reaches the maximum at metals of Group VIII, decreases quite sharply with the minimum at metal of IIB or IIIB, and then increases again with further increase of the atomic number. The activity varies quite similarly in the second and the third long periods, revealing a precise periodicity. It may be noted that the third metal of the triad of Group VIII shows a tendency to have the highest activity.

The similar periodicity has been suggested by BOCKRIS[62] and recently by KHOMUTOV[63] with regard to the hydrogen overvoltage of metals at a certain definite current density. However, in the former work, the periodicity in the first long period is incomplete because of lack of observations and in the latter, those only in hydrochloric or sulfuric acid are included. Moreover, only one or two values for each metal are used in their works, which appears insufficient in view of the following points, (2) and (3).

(2) *Effect of the composition of solution on the activity*:

The $\log i_0$-value of the same electrode metal fluctuates by *ca.* 2 in most of the cases apparently without correlation with pH, whereas the $\log i_0$-values of Rh, Pd and Pb in alkaline solution deviate from those in acidic solution by *ca.* 6 at most. The latter group of metals might need be re-examined, their observations in alkaline solution being extremely scanty. The activity is apparently independent of anion of acids within the fluctuation as seen for example, in the case of Ni in Table 1, where the values of $\log i_0$ are -5.4 (1 N HCl)[30], -5.78[8] and -5.24[18] (0.1 N HCl), -5.22 (0.5 N H_2SO_4)[17], -4.85 (0.1 N $HClO_4$)[32], -5.2 (0.15 N $HClO_4$)[32] and -5.7 (1 M $HClO_4$)[36].

The activity appears to have similarly no correlation with the solvent of electrolyte solution as exemplified by $\log i_0$-value of mercury electrode, *i.e.* -11.8, -11.5, -10.8 or -10.8 respectively in 0.1 M HCl solution of water, methyl alcohol, ethyl alcohol or n-propyl alcohol.[26] The values of $\log i_0$ in heavy water are, however, smaller in all cases than those in ordinary water and the difference on the same metal varies from the greatest value, 0.95 of Ag to the least one, 0.17 of Pt, being 0.55 on an average.[8,20]

(3) *Effect of treatment of electrode*:

Electrode of nickel, which is one of the metals studied most in detail, has a wide variety of treatment as seen from the third column of Table 1, *i.e.* reduction of wire in hydrogen atmosphere, electrodeposition of Ni from $NiSO_4$ solution, anodic or chemical polishing of single crystal, quenching of the melt in helium atmosphere, evaporation of Ni on glass wall, *etc.* It is noticed from Fig. 1 that the values of $\log i_0$ of nickel electrodes of the above treatments are not largely different from each other. Hence, the activity appears to depend not so much on the treatment as on the atomic number. The same is the case with most of other metals.

PIONTELLI *et al.*[32] and WEININGER *et al.*[37] observed TAFEL lines individually on (100)-, (110)- and (111)-lattice planes of f. c. c. crystal of Ni; the observation of the former with anodically treated electrodes leades to $\log i_0$-values of the respective lattice planes which differ by 0.34 at most, while that of the latter with chemically polished electrodes to the practically coincident values.

(4) *Homogeneity and heterogeneity of surface*:

It is of interest that the activity of mercury conforms to the periodicity as seen in Fig. 1, since the surface of liquid metal is taken to be homogeneous, whereas that of solid metals possibly heterogeneous, owing to grain boundaries, steps, kinks, inperfections, *etc.* In the case of gallium, the activity is of little difference at temperatures slightly above or below the melting point of 29.78°C as shown in Table 1 and in conformity with the periodicity as well.

These facts indicate that the heterogeneity of surface, if any, could not be a predominant factor of hydrogen electrode as the active center theory suggests.

Discussion

The above mentioned points lead us to conclude that bulk property of the electrode is the determining factor of the activity of hydrogen electrodes. In other words, the activity of a metal depends not so much on solvent, electrolyte and its composition as on the atomic number of the electrode material. The activity also does not depent within the fluctuation of results on the surface treatment as well as on liquid or solid state of the electrode. Hence, the geometry of the surface is also of the secondary importance.

HORIUTI and the present author[64] have studied theoretically the difference of activity among the principal lattice planes, *i.e.* (110)-, (100)- and (111)-lattice planes of Ni and concluded that the current density is exceedingly large on the (111)-lattice plane over the region of overvoltage where the TAFEL line is experimentally observed, suggesting an importance of the geometrical factor. This conclusion may be reconciled with that of the present paper referring to the experimental results of GOMER *et al.*[65] and GERMER *et al.*[66] that the three principal lattice planes are nearly equally exposed in area, since then the observed current density is approximately the average of the current densities on the individual principal lattice planes but not one of the latter current densities which are theoretically[64] considerably different from each other. This proposition requires that even in the case of experiments as reported to have been conducted with a single lattice plane, the exposed surface is not the single lattice plane in atomic scale, which ought to be further investigated.

Now the question arises from the above conclusion as to what property of metal effects essentially the activity. Many physical properties such as latent heat of sublimation, melting-point, density, metallic radius and work function are known to show periodic gradations on passing through the long period. The correlation between the activity and the properties of metal is now under investigation in this laboratory.

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