Hydrogen Overvoltage of Zirconium*

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In the preceding papers^(1,2), the hydrogen overvoltage of titanium was measured in 1N H₂SO₄, 1N NaOH and in 1N KOH and it was found that the Tafel's equation holds for the metal, where, according to the surface treatment and temperature (25°, 40° and 60°C), $a=0.5\sim0.7$, $b=0.12\sim0.23$ in 1N H₂SO₄, $a=1.4\sim1.6$, $b=0.20\sim0.27$ in 1N NaOH and $a=1.4\sim1.8$, $b=0.18\sim0.26$ in 1N KOH. These results were confirmed by M.E. Straumanis et al⁽⁵⁾, and by K. Aotani⁽⁶⁾. The metal also proved to be effective as a new cathode material for electrolytic reduction³⁾.

In the present paper, the hydrogen overvoltage of zirconium was measured and the similarity to titanium has been noticed. The pieces employed here were cut from the commercial zirconium sheet of the Firth Sterling Co. of U.S.A., the composition of which is announced as shown in Table 1. and which received the following three treatments.

- A. as degreased by CCl₄
- B. polished with emery 06 and degreased in CCl₄
- C. pickled in 0.05% HF for 30 sec. and rinsed.

The measurement was done by direct method with Pt anode (2×1 cm²), zirconium cathode (2×1 cm²) and with calomel electrode for 1N H₂SO₄ and with mercuric oxide electrode for 1N NaOH respectively as reference.

Zr | 1N H₂SO₄, 1N H₂SO₄ tip, satd. KCl, satd. KCl, Hg₂Cl₂ | Hg

Zr | 1N NaOH, 1N NaOH tip, 1N NaOH, 1N NaOH, HgO | Hg

The cell was of metacryl resin, the cathode and anode compartments being 6×5.5×5.5 cm³ and 6×2×5.5 cm³ respectively, separated by Saran diaphragm.

A freshly prepared sample is first electrolyzed for 24 h with 1 A/dm² at room temperature in order to eliminate trace impurities in the electrolyte and to stabilize the surface conditions and then held at 25°C for 1 h. The current is then lowered to 0.05 A/dm² and after 20 min. duration, the cathode polarization is measured. Measurements at 0.1, 0.25, 0.50, 0.75, 1.00, 1.25 and 1.50 A/dm² are carried out

Table 1 Chemical Composition of Zirconium Sample

Al	0.030 %	Pb	0.005 %
Fe	0.020	Ti	0.008
Cr	0.020	V	0.002
Mg	0.050	C	0.060
Mn	0.040	Hf	2~2.51
N	0.010	Zr	balance
Ni	0.010

Fig. 1 Hydrogen overvoltage and current density in 1N H₂SO₄, 25°C.

Fig. 2 Hydrogen overvoltage and current density in 1N H₂SO₄, 45°C.

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Fig. 3 Hydrogen overvoltage and current density in 1 N NaOH, 25°C.

Fig. 4 Hydrogen overvoltage and current density in 1 N NaOH, 45°C.

continuously in the same way. Then the temperature is raised to 45°C.

The results are shown in Fig. 1~4.

The Tafel's constants a and b as determined from the data at 1.00 and 0.10 A/dm² are shown in Table 2 and 3.

Table 2 Hydrogen Overvoltage η and Current Density I in 1 N H₂SO₄

Surface condition	25°C	45°C
A	$0.75 + 0.21 \log I$	$0.65 + 0.20 \log I$
B	$0.79 + 0.23 \log I$	$0.69 + 0.21 \log I$
C	$0.67 + 0.18 \log I$	$0.54 + 0.15 \log I$

Table 3 Hydrogen Overvoltage and Current Density I in 1 N NaOH₄

Surface condition	25°C	45°C
A	$1.66 + 0.22 \log I$	$1.57 + 0.20 \log I$
B	$1.74 + 0.26 \log I$	$1.62 + 0.20 \log I$
C	$1.63 + 0.21 \log I$	$1.52 + 0.20 \log I$

The value of the overvoltage at each point as calculated from the equation is in good agreement with the experimental value within the error of ± 3 mV. Thus, the Tafel's equation holds in the range of 45~25°C and of 0.05~1.00 A/dm².

The values are lower for the rough surfaces as is usually the case. The abnormally high values of a in alkaline solutions have already been observed in the case of titanium and the similarity to titanium is also noticed in the case of zirconium.

The electrolyte in which electrolysis was carried out at 1 A/dm² and at 25°C for 60h was concentrated by evaporation and spectroscopically analyzed but zirconium and hafnium were not detected at all. Zirconium cathode is stable in these solutions while titanium cathode was slightly attacked as described in the previous paper¹⁾. Moreover, the Microvickers Hardness was measured for zirconium cathode as shown in Fig. 5 and Table 4 of the Japanese original paper. The values are larger at edges and corners where the current distribution is greater. The average hardness was 299 MHV which is very much larger than that of the untreated original piece, 228 MHV.

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