# ELECTROCHEMICAL BEHAVIOR OF ZIRCONIUM IN SULFURIC ACID

1958

SovietRxiv

## Abstract

## Full Text

## Physical Chemistry

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# ELECTROCHEMICAL BEHAVIOR OF ZIRCONIUM IN SULFURIC ACID

*(Presented by Academician A. N. Frumkin, March 11, 1958)*

The few literature data currently available indicate a strong dependence of the electrochemical behavior of zirconium on the composition of the solution. According to the literature, the chemical resistance of zirconium is very high in hydrochloric acid, sodium chloride, and also in alkali solutions (1). A study of the anodic dissolution of zirconium in nitric acid showed that zirconium is passivated in this solution; moreover, the properties of the oxide films formed, consisting of monoclinic $ZrO_2$, depend on the concentration of the solution (2). In neutral sodium chloride solutions (3), zirconium is not passivated under anodic polarization; on the contrary, its complete destruction is observed. The hydrogen overvoltage curve has two bends, the upper of which (at a current density of $3 \cdot 10^{-4}$ A/cm$^2$) is explained by oxygen ionization. In a neutral sodium sulfate solution, zirconium is readily passivated under anodic polarization (current density $10^{-4}$—$10^{-5}$ A/cm$^2$).

In the present work, the cathodic and anodic behavior of zirconium was studied, as well as the change with time of its open-circuit potential in $1N$ $H_2SO_4$ at 25°.

The experiments were carried out with a zirconium rod (purity 99.99%) in a sealed glass apparatus. Before each experiment the electrode was polished with moist quartz powder and, after rapid rinsing with twice-distilled water, was immersed in the solution, which was continuously stirred with nitrogen purified from oxygen by passage over a copper catalyst. After a constant value of the potential had been established, the hydrogen overvoltage on zirconium was measured, starting from high current densities in order to reduce the oxides present on the surface. The current density was changed every 1-2 minutes in the interval from $1$—$3 \cdot 10^{-3}$ to $5$—$6 \cdot 10^{-7}$ A/cm$^2$, calculated with respect to the apparent surface. After a potential value close to the stationary one had been reached, anodic polarization was immediately switched on, and anodic curves were recorded in the same manner, first with increasing current density and then with decreasing current density. After this, on the anodically oxidized electrode, the hydrogen overvoltage curve was again recorded, starting from low current densities and proceeding to high ones.

The results obtained show that the oxide film formed on the zirconium surface

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

during prolonged exposure to air shifts the stationary potential in the positive direction. Thus, for zirconium that had been kept in air for a long time and had not been polished before the experiment, the potential has a value of $-0.17 \div -0.19$ V (against the normal hydrogen electrode), while for zirconium polished in air it is $-0.2 \div -0.3$ V. The potential of zirconium in sulfuric acid is established slowly with time, as shown in Fig. 1.

As is evident from this figure, the potential shift is especially large for an electrode that had been kept in air for a long time (Fig. 1, 1): the final magni-

the potential shift for such an electrode is equal to 0.12 V, i.e., 0.3 V more positive than the initial value. For stripped electrodes (Fig. 1, 3) the shift in the positive direction is 0.10–0.16 V. An electrode oxidized in air,

**Fig. 1.** Change in the potential of zirconium with time.
1 —after exposure to air, 2 —after exposure in a sulfuric acid solution, 3 —stripped electrode

**Fig. 2.** Curves of cathodic (*I*) and anodic (*II*) polarization of zirconium in 1 $N$ $H_2SO_4$

which was subsequently kept in sulfuric acid and then again removed into the air, acquires in 1 $N$ $H_2SO_4$ the most positive potential, rapidly established with time (Fig. 1, 2). The shift of the initial potential of stripped and unstripped zirconium electrodes in a 1 $N$ $H_2SO_4$ solution with time in the positive direction indicates the process of oxidation (passivation) of zirconium in this solution.

During cathodic and anodic polarization of zirconium in 1 $N$ $H_2SO_4$, regularities are found which indicate the great influence of oxide films. The curves of anodic and cathodic polarization on stripped zirconium are shown in Fig. 2. The discrepancy between the curves in parallel experiments in the cathodic region reaches $-0.1$ V, and in the region of anodic passivation —several tenths of a volt. On the cathodic curves an inflection is observed in the potential region from $-0.6$ V to $-0.2$ V. On both sides of the inflection the hydrogen overvoltage curve obeys the Tafel equation.

Inflections, as is known, have been observed on hydrogen-overvoltage curves for a number of metals ($^4$) when the curves are recorded slowly. These inflections are explained by the fact that, when the potential passes through a point lying somewhat more negative than the point of zero charge of the metal, its adsorption properties change; in the presence of adsorption of anions, the hydrogen overvoltage is lower than in its absence. There are no data in the literature on the point of zero charge of zirconium. From the electron work function one may expect that the zero point of zirconium should lie near $-1$ V; therefore the inflection observed by us should probably be explained by approach to the zero

Fig. 3. Hydrogen overvoltage on polished (I) and anodically oxidized zirconium (II)

Figure 2: Fig. 3. Hydrogen overvoltage on polished (I) and anodically oxidized zirconium (II)

point, strongly shifted in the positive direction under the influence of oxygen adsorption.

During anodic polarization zirconium in sulfuric acid is strongly passivated, beginning at very low current densities (1-2 $\cdot 10^{-5}$ A/cm$^2$). At current densities above $10^{-4}$ A/cm$^2$ a film is formed which has an effective ohmic resistance of the order of tens of ohms (the determination was made using direct current). This film has a golden color. On the reverse course of the anodic polarization curve, a large hysteresis is observed. Activation evidently occurs owing to dissolution of phase oxides of zirconium in sulfuric acid and to a decrease in the rate of their formation on the electrode at

decrease in anodic polarization, similarly to the case of the iron electrode ($^5$). By extrapolating the cathodic and anodic curves at current densities less than $10^{-5}$ A/cm$^2$, one can obtain the value of the self-dissolution current of zirconium in $1N$ $H_2SO_4$, equal to $2 \cdot 10^{-6}$ A/cm$^2$.

The oxide film obtained on zirconium during anodic oxidation decreases the rate of hydrogen evolution on zirconium. An increased hydrogen overvoltage in the presence of an oxide film on the metal surface was previously observed for iron ($^6$) and magnesium ($^7$) only in alkaline solutions. Figure 3 gives curves of hydrogen overvoltage on polished (curve 1) and anodically oxidized zirconium (curve 2). As can be seen from Fig. 3, the rate of hydrogen evolution on anodically oxidized zirconium is approximately 10 times less than on polished zirconium. The bend in curve 2 of the hydrogen overvoltage is also shifted toward lower current densities. At high current densities the difference between the curves decreases, evidently due to further dissolution of oxides and a slowing of their formation.

**Fig. 3.** Hydrogen overvoltage on polished (*I*) and anodically oxidized zirconium (*II*)

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Received
7 III 1958

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*Note: Figure translations are in progress. See original paper for figures.*