



---

Soviet-era science, translated into English

# **D. V. KOKOULINA and B. N. KABANOV**

1957

SovietRxiv

---

View the original and related papers at <https://sovietrxiv.org/items/ru-195701.98157>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

**Abstract**

**Full Text**

**PHYSICAL CHEMISTRY**

**D. V. KOKOULINA and B. N. KABANOV**

## **ON THE NEGATIVE DIFFERENCE EFFECT ON MAGNESIUM**

*(Presented by Academician A. N. Frumkin, 11 VII 1956)*

For the anodic dissolution of magnesium in aqueous salt solutions, an intensification of hydrogen evolution with increasing anodic current density is characteristic; in corrosion theory this is called the negative difference effect. The negative difference effect is observed only for active, readily oxidized metals: Mg, Al, etc. (1-4). For Mg the negative effect has been described for salt solutions, while a positive one has been described for HCl solutions (5).

There are two hypotheses explaining the negative difference effect. The first completely connects the intensification of hydrogen evolution with an increase in corrosion of the anode as a result of the destruction, during anodic polarization, of the oxide film that protects the metal (1, 3, 4, 6-8). The second hypothesis connects hydrogen evolution only with the fact that, in the anodic process, the metal partly passes into solution in a lower valence state—for example, magnesium as monovalent—while water oxidizes it to the usual valence, and hydrogen is evolved in the solution. In this case it is considered that self-dissolution of the anode during polarization practically does not occur (9, 10). The experimental data available for the magnesium anode—hydrogen evolution after switching off the current (9), direct proportionality between the rate of hydrogen evolution and the anodic current density (7, 8), the same rate of hydrogen evolution when passing continuous and commutated current of low frequency (60 cps) (9), and reduction of oxidizers at the magnesium anode—can be explained from both points of view. The existence of reduction of an oxidizer solution as anolyte flows into it, when there is no direct contact between the anode and the oxidizer solution, which would more unambiguously prove a certain stability of the ion  $Mg^+$  in solution, could be doubted, since the magnitude of the effect lies at the limit of sensitivity of the method. Thus, the factual material available up to the present time could not serve as convincing proof of the correctness of either hypothesis. In connection with this, the present work was undertaken by us.

During anodic polarization, at current densities greater than the self-dissolution current but smaller than the passivation current of magnesium in the given solution, the steady potential of a magnesium anode does not depend on the current density. However, the potential undergoes changes with time that are analogous to changes in the potential of an aluminum electrode (1). Figure 1

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

shows changes of potential with time upon changing the current density. The steady values of the potential at both current densities are almost identical; however, at the first moment after the change in current density the electrode potential proves to be different from its steady value. These changes undoubtedly indicate a change in the state of the electrode surface: immediately after a decrease or switching off of the current, the magnesium surface is, for several seconds, more active than in the stationary state under these conditions. The question remains whether this change in the state of the surface substantially affects the total rate of hydrogen evolution.

We measured the potential of the magnesium electrode and the rate of hydrogen evolution in an  $\text{MgSO}_4$  solution while passing an anodic current in pulses of rectangular form, with the intervals of current passage and interruption being identical. As can be seen from Fig. 2, the electrode potential undergoes considerable oscillations, whose amplitude depends on the pulse repetition frequency; moreover, the mean values about which the potential oscillations occur lie approximately 0.15 V more negative than the steady potential during polarization by a continuous current of the same strength.

**Fig. 1.** Change in the potential of the magnesium anode with time when the current density is changed: **1** –upon increase from 7 to 67 mA/cm<sup>2</sup>, **2** –upon decrease from 67 to 7 mA/cm<sup>2</sup>. Sections **a** and **a'** correspond to the potential at a current density of 7 mA/cm<sup>2</sup>; sections **b** and **b'** correspond to 67 mA/cm<sup>2</sup>.  $\text{MgSO}_4$  solution (1 N).

With pulsed current the anode is activated during the passage of the pulse, while during the current interruption it is passivated. At a high frequency of the pulsed current, the surface will not have time to become completely passivated during the current interruption and completely activated during current passage; in this case self-dissolution, generally speaking, should not be equal to self-dissolution under continuous passage of current.\* Therefore, if the cause of the negative difference effect is self-dissolution of the anode, then the rate of hydrogen evolution under pulsed current should differ from the rate of evolution under a direct current of the same strength. If the cause of hydrogen evolution is the chemical oxidation reaction of the ion  $\text{Mg}^+$  by water, then the rate of hydrogen evolution will be determined only by the amount of  $\text{Mg}^+$  formed per unit time, proportional to the density of the current passed, independently of the presence of current interruptions and of changes in the state of the surface.

**Fig. 2.** Change in potential during polarization of Mg by pulsed current: **1**

Fig. 3

Figure 3: Fig. 3

—1000 pulses/sec; **2**—100 pulses/sec; **3**—20 pulses/sec.  $MgSO_4$  solution (1 N). Current density in the pulse 51.3 mA/cm<sup>2</sup>.

As can be seen from Fig. 3, the rates of hydrogen evolution in an  $MgSO_4$  solution prove to be equal under continuous and pulsed passage of current, do not depend on the pulse repetition frequency or the concentration of the solution, and depend only on the density of the current passed. Although under continuous current the entire curve corresponds to an almost constant potential of  $\sim -1.75$  V vs. N.C.E., while under pulsed current of different frequency it corresponds to an oscillating potential with different mean values from  $-1.9$  to  $-2.0$  V vs. N.C.E., the rates in both cases prove equal, i.e., the rate of hydrogen evolution at the anode does not depend on the potential.

We also found hydrogen evolution on magnesium when the measured potential of the anode was 0.4-0.6 V more positive—

\* To compare rates one must compare the amount of hydrogen evolved during continuous passage of current over a certain interval of time with the amount of hydrogen evolved during intermittent passage of current over twice the interval of time. The rates of self-dissolution can be equal under continuous and pulsed passage of current only if, in the first moments of current passage in a pulse, hydrogen evolution proves to be slowed down to the same extent as it is accelerated in the first moments of current interruption, so that these processes mutually balance each other; however, such equilibration, which is preserved over a broad range of anodic-current densities and pulsed-current frequencies, is unlikely.

nonequilibrium hydrogen electrode (a 2 N  $MgSO_4$  solution with addition of 0.5 M  $K_2CrO_4$ ) at anodic-current densities of 20–30 mA/cm<sup>2</sup>. The electrode resistance, measured with alternating current, is under these conditions  $\sim 1 \Omega/cm^2$  and should not introduce appreciable distortions into the measured electrode potential. This result is consistent with the supposition that monovalent magnesium passes into solution; however, taking into account the considerable nonuniformity of the surface, the fact of hydrogen evolution at potentials more positive than the equilibrium one cannot be considered fully proved.

Fig. 3. Rate of hydrogen evolution in  $MgSO_4$  solutions as a function of anodic current density. Polarization by continuous passage of current: *a*—1 N solution; *b*—0.1 N solution. Polarization by pulsed passage of current: *v*—1 N solution, *g*—0.1 N solution (10000 pulses/sec), *d*—1 N solution (6 pulses/sec).

These two experimental facts—the independence of the rate of hydrogen evolution from the presence of current interruptions and from the electrode potential

Fig. 4

Figure 4: Fig. 4

—cannot be explained by the electrochemical process of self-dissolution at the anode, but serve as confirmation of the assumption that the elementary electrochemical act in the anodic dissolution of magnesium is a one-electron transition with formation of  $Mg^+$  ions.

We measured the rate of hydrogen evolution during anodic polarization of magnesium in a series of solutions. The results of these measurements are presented in Fig. 4. In  $NH_4Cl$  and  $HCl$  solutions, as the current density is increased, at first a decrease in the rate of hydrogen evolution is observed (a positive difference effect); with further increase in current density a minimum of the rate is observed, and then the sign of the difference effect is reversed: from positive it becomes negative, the values of the rate of hydrogen evolution being close to the values observed in neutral solutions.

Fig. 4. Rate of hydrogen evolution at an Mg anode as a function of current density: *a*— $1\text{ N } MgSO_4$ ; *b*— $4.6\text{ N } MgCl_2$ ; *v*— $5\text{ N } CaCl_2$ ; *g*— $1\text{ N } NH_4Cl$ ; *d*— $0.5\text{ N } NH_4Cl$ ; *e*— $0.039\text{ N } HCl$ ; *zh*— $0.117\text{ N } HCl$ .

On the basis of our experimental data we believe that hydrogen evolution at a magnesium anode is caused by both reasons: 1) by the reaction of chemical oxidation of the  $Mg^+$  ion by water, the rate of which  $V_1$  is proportional to the rate of dissolution of magnesium and depends on the electrode potential, the concentration and composition of the solution, and 2) by the reaction of self-dissolution of the anode, the rate of which  $V_2$  depends on the electrode potential, the state of the surface, and the composition of the solution. The total rate of hydrogen evolution, if the change in the state of the surface is neglected, is expressed by the equation:

$$V = V_1 + V_2 = \frac{6.95i(2 - n_i)}{n_i} + V_0 \exp\left(\frac{-\alpha_1 \Delta\varphi F}{RT}\right), \quad (1)$$

where  $V_0$  is the rate of hydrogen evolution without current,  $\alpha_1$  is a coefficient characterizing the cathodic process of hydrogen evolution on Mg at the given state of the surface,  $\Delta\varphi$  is the shift of the potential from the stationary value under anodic polarization,  $i$  is the density of the anodic current passed, in  $A/cm^2$ ,  $n_i$  is the effective valence of the dissolving magnesium, and 6.95 is the conversion factor for expressing the rate of hydrogen evolution in  $cm^3/cm^2 \cdot min$ .

Equation (1) approximately describes the quantitative relations observed in the evolution of hydrogen on a magnesium anode. The first term increases, whereas the second decreases with increasing anodic current density\*. Therefore a minimum should be observed on the curve  $(V, i)$ ; the presence of such a minimum indicates a change in sign of the difference effect from positive to negative. In

neutral solutions, where self-dissolution is small and the minimum should occur at tenths of mA/cm<sup>2</sup>, only an increase in the rate of hydrogen evolution is observed at all the current densities investigated, whereas in acidic solutions both effects are observed.

Hydrogen evolution at current densities considerably greater than the self-dissolution current density in each solution is practically due to a single cause: the reaction of oxidation by water of the Mg<sup>+</sup> ion (or the MgOH radical) formed during anodic polarization of magnesium. Under certain conditions, however, the increase in hydrogen evolution is partly caused by anodic activation of the metal, if such activation is possible in the given solution. Reversal of the difference effect occurs owing to the superposition of the self-dissolution reaction of Mg and the oxidation reaction of the Mg<sup>+</sup> ion.

We express our gratitude to Academician A. N. Frumkin for valuable advice.

Institute of Physical Chemistry  
Academy of Sciences of the USSR

Received  
11 VII 1956

*Proof correction note.* While our work was in press, an article by Greenblatt<sup>(11)</sup> was published on the mechanism of anodic dissolution of Mg in NaCl solution. Its results agree with our conclusions.

## CITED LITERATURE

1. N. D. Tomashov, V. N. Modestova, *Transactions of the Institute of Physical Chemistry, Academy of Sciences of the USSR*, vol. V. *Studies on the Corrosion of Metals*, 4, 75 (1955).
2. M. A. Streicher, *Trans. Electrochem. Soc.*, **93**, 285 (1948).
3. M. F. Straumanis, Y. N. Wang, *J. Electrochem. Soc.*, **102**, 304 (1955).
4. V. O. Krenig, V. N. Uspenskaya, *Proceedings of the 1st Conference on Corrosion of Metals*, Moscow-Leningrad, 1935, p. 482.
5. B. Roald, W. Beck, *J. Electrochem. Soc.*, **98**, 277 (1951).
6. E. V. Barelko, Dissertation, Moscow, 1950.
7. G. I. Ilchenko, Dissertation, Moscow, 1955.
8. N. D. Tomashov, S. K. Komissarova, M. A. Timonova, *Transactions of the Institute of Physical Chemistry, Academy of Sciences of the USSR*, vol. V. *Studies on the Corrosion of Metals*, 4, 172 (1955).

9. R. L. Petty, A. W. Davidson, J. Kleinberg, *J. Am. Chem. Soc.*, **76**, 363 (1954); M. D. Rausch, W. E. McEwen, J. Kleinberg, *J. Am. Chem. Soc.*, **76**, 3622 (1954).
10. B. D. Laughlin, J. Kleinberg, A. W. Davidson, *J. Am. Chem. Soc.*, **78**, 559 (1956); E. Rajola, A. W. Davidson, *J. Am. Chem. Soc.*, **78**, 556 (1956).
11. J. H. Greenblatt, *J. Electrochem. Soc.*, **103**, 539 (1956).

---

\* Decreases under the condition that  $\Delta\varphi$  increases. If the state of the surface is unchanged,  $\Delta\varphi$  should increase according to the equation

$$i = \frac{V_0}{6.95} \exp\left(\frac{\beta\Delta\varphi F}{RT}\right).$$

In reality, because of surface activation, beginning at a certain current density  $\Delta\varphi$  does not increase; consequently, the second term remains unchanged or even increases, since activation leads to a decrease in the hydrogen overvoltage.

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

*Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.*