THE ELECTRODEPOSITION MECHANISM OF RHENIUM

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In [1] we showed that the curves plotting rhenium current efficiency versus current density have maxima.

An increase in current density usually speeds up the reduction of the more electronegative ion. However, the equilibrium potential of rhenium is more positive than that of hydrogen. It may be supposed that this law is due to activation of the electrode's surface. If we assume that the surface is nonuniform and that different reactions take place mainly in different regions of it (reduction of rhenium ions occurring on active areas free from impurities), the active surface of freshly deposited rhenium must increase with current density; this means that the current efficiency of the metal (A%) will increase. We may thus infer that A is related to the degree of activity of the electrode surface: the current efficiency of the metal increases with increasing activity of the electrode surface. The overall area of an electrode's active surface may be considered as the resultant of two factors: adsorption of foreign particles (reversible or irreversible), hindering reduction of metal ions, and activation of the electrode surface.

The electrode surface is greatly affected by the electrolyte composition, current density and other factors. In the electrodeposition of rhenium, sulfuric acid and ammonium sulfate are evidently activators of the electrode surface; they either prevent oxidation of the freshly-deposited rhenium surface or promote solution of oxides, thereby speeding up the reduction of perrhenate ions.

The state of the electrode surface also affects the rate of reduction of hydrogen ions, but to a lesser extent than that of rhenium ions [2].

The effect of the state of the surface on the metal's current efficiency increases up to a certain limit, after which the rate of reduction of the metal ions is limited by diffusion.

The effect of the state of the electrode surface on the metal's current density along the rising branch of the (i, A) curve is confirmed by experimental data on electrodeposition of rhenium by an intermittent current. It is clear that adsorption of foreign particles on the electrode surface will be greater with electrolysis by an intermittent current than by a steady current, thereby decreasing the metal's current efficiency. In fact, experiments showed that electrolysis by intermittent current does reduce the metal's current efficiency, the reduction becoming greater with the frequency of interruption. * It may be supposed that during brief breaks in current the electrode will not be passivated and that during this process the current efficiency will reach the same value as during deposition with a steady current.

Simple calculations show that at current density 1 amp/cm^2, corresponding to electrodeposition of rhenium, the mean time required for renewal of the electrode surface by a monoatomic layer of rhenium is $\sim 10^{-3}$ sec. It may be supposed that the electrode's active surface would not be greatly passivated during a break of this length, and that the current efficiency would not be less than for electrolysis without a break in current.

The aim of the present paper was to verify the proposed activation mechanism of electrodeposition of rhenium and determine the rate of passivation of the electrode surface; We used electrolytes with the following compositions (g/liter):

* The reduction in current efficiency cannot be attributed to solution of rhenium when the current is switched off; our observations [2] indicate that this does not occur in this electrolyte.

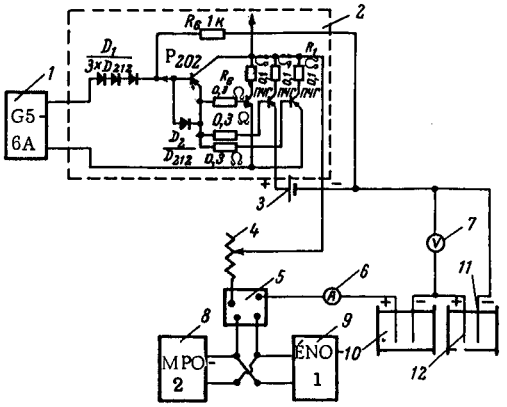

Fig. 1. Electronic inertialess apparatus: 1) G5-6A square-pulse generator; 2) composite triode switch; 3) NKN-22M storage batteries; 4) rheostat; 5) shunt; 6) ammeter; 7) voltmeter; 8) MPO-2 oscillograph; 9) ÉNO-1 oscillograph; 10) coulometer; 11) cathode; 12) anode.

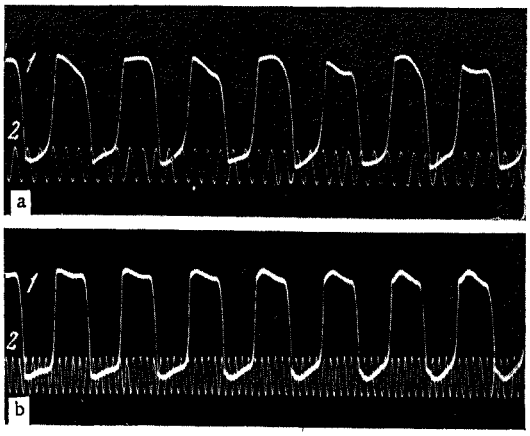

Fig. 2. Pulse shape at different ratios of current duration to current break (sec); a) 1/50: 1/50; b) 1/300: 1/300; 1) pulse shape; 2) 500-cps time marker.

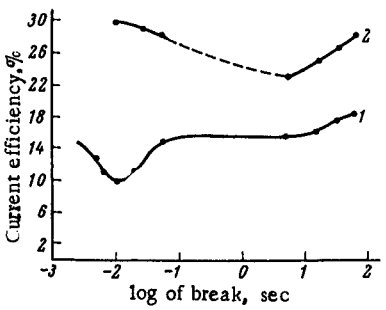

Fig. 3. Current efficiency of rhenium versus duration of break, for electrolytes of composition 1 and 2.

1. Ammonium perrhenate, 50
   Sulfuric acid, 25

2. Ammonium perrhenate, 50
   Sulfuric acid, 25
   Ammonium sulfate, 40

Electrolysis was performed at current density 1 amp/cm^2 temperature 70°, and electrolysis/dead period ratio 1:1; the total electrolysis time was 15 min.

To obtain an intermittent current with different pulse frequencies we set up two apparatuses, each of which enabled us to perform experiments in a certain frequency range. The steady-current source consisted of alkaline storage batteries connected in series; the quantity of electricity passed (in amp-h) was measured with a coulometer.

To obtain pulses in the range 120-5 sec, we used a KÉP-12U electropneumatic control device as time relay; this enabled current up to 15 amp to be passed.

Shorter pulses (50 msec – 50 μsec) were obtained with an electronic inertialess apparatus (cf. Fig. 1). The steady current was switched on and off by a system consisting of a composite triode switch with power triodes connected in parallel [3]. The time relay was a G5-6A square pulse generator. The pulse shape (Fig. 2) was monitored by an ÉNO-1 cathode-ray oscillograph and recorded by an MPO-2 loop oscillograph.

The results are plotted in Fig. 3. It will be seen that during electrodeposition of rhenium from electrolyte 1 by an intermittent current, the minimum on the curve plotting metal current efficiency versus duration of the current break is at 10^{-2} sec. The current efficiency rises with a decrease in the break; this obviously indicates that the renewed surface of the cathode is not completely passivated within this period. It will also be seen that a break of $\sim 10^{-3}$ sec is required for the electrode to reach its initial state. These results are therefore evidence in favor of the "activation mechanism" of the electrodeposition of rhenium, and they show that the metal's current efficiency depends on the state of the electrode surface.

The state of the electrode surface clearly depends on the additives present in the electrolyte. If the ammonium sulfate added to the electrolyte in electrodeposition of rhenium activates the electrode surface, its addition must increase the mean electrode passivation time; i.e., the minimum on curve 2 (Fig. 3) must be displaced towards greater durations. In fact, in the presence of ammonium sulfate the minimum current efficiency is in the range 1/20-5 sec * while in absence of this additive the minimum is at 1/100 sec.

* There are no points on curve 2 in the range 1/20 - 5 sec, owing to lack of a current interrupter in this time range.

Ammonium sulfate therefore activates the electrode surface. By this experiment we have shown that in some cases electrolysis by intermittent current enables us to determine the rate of passivation of the electrode surface.

LITERATURE CITED

1. A. A. Nikitina, Z. A. Solov'eva, Z. M. Sominskaya and A. T. Vagramyan, Elektrokhimiya, 1, 750, (1965).
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3. T. A. Glazenko, Transistorized pulse amplifiers in Electric Drives, Energiya, Moscow-Leningrad, p. 35 (1965).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of the first issue of this year.
