

DEVELOPMENT OF METHODS OF REDUCING ELECTRICAL ENERGY CONSUMPTION IN HYDROGEN PRODUCTION BY ELECTROLYSIS

Kozin L.F., Manilevich F.D.*, Mashkova N.V., Kutsyy A.V.

Institute of General & Inorganic Chemistry of Ukrainian NAS,

prosp. Palladina, 32/34, 03680 Kiev 142, Ukraine

Fax: 38 (044) 424 3070

E-mail: fedor@ionc.kar.net

Introduction

Among the known hydrogen production methods, electrolysis of aqueous alkaline solutions is distinguished by environmental safety and high purity of produced hydrogen. The feedstock consumed in this hydrogen production is water, which is regenerated after the use of hydrogen as a energy carrier. However, a considerable expenditure of electrical power is required to produce hydrogen by electrolysis, therefore electrochemical isolation of hydrogen from water is used at present mainly only when high-purity hydrogen is needed [1, 2].

The electrical power consumption for electrolysis at predetermined current magnitude is determined by electrolyzer voltage, which includes several main components in accordance with the following formula:

$$U = E_T + |\eta_c| + |\eta_a| + IR, \quad (1)$$

where E_T is the difference in thermodynamic equilibrium potentials between anode and cathode ($E_T = 1.229$ V at 25°C [1]), η_c and η_a are cathodic and anodic overpotentials respectively, IR is ohmic voltage loss. Under the conditions of real electrolysis of alkaline solutions with hydrogen and oxygen evolution, the electrolyzer voltage is almost a factor of 2 higher than the E_T value. According to formula (1), an obvious way of reducing the electrolyzer voltage is reduction of the overpotential of the cathodic and anodic processes, which was the aim of this work.

Results and discussion

The overpotential values of hydrogen evolution at the cathode (η_c) with other electrolysis conditions being equal depend on the nature and condition of the electrode surface. Platinum metals have the lowest η_c values. At such relatively inexpensive metals as Ni, Co, Mo and W, cathodic hydrogen evolution takes place at higher η_c values than at platinum metals but at lower values than at the other metals. In the present work, to reduce the overpotential of hydrogen evolution at nickel and cobalt, it is proposed to modify their surface with binary alloys of these metals with molybdenum and tungsten. The possibility of using titanium,

which is widely used in chemical industry as a structural material, has also been examined as a cathodic substrate.

Alloys were electrodeposited on the surface of cathodic substrates from alkaline and slightly alkaline electrolytes at elevated temperatures. Thin deposits of Co-Mo alloys with a Mo content of about 86 %, Ni-W alloys with a W content of about 33 % and Ni-Mo alloys with a Mo content of about 25 % have been obtained. To enhance alloy-to-titanium adhesion, Rowland effect was employed in addition to mechanical polishing, defatting and etching of titanium in a HNO_3 -HF mixture, to which end Trilon B was added to the electrolytic solution. In the presence of Trilon B in the solution, the surface oxides dissolve, and the titanium electrode surface is activated.

Fig. 1 shows plots of hydrogen evolution current density against overpotential, which have been obtained on an unmodified nickel rotating disk electrode (RDE) (980 rpm) and on a nickel RDE modified with Ni-W and Ni-Mo alloys. It can be seen that the overpotential of hydrogen evolution at modified electrodes is much lower than at unmodified one, Ni-Mo alloy being a more efficient depolarizer than Ni-W alloy.

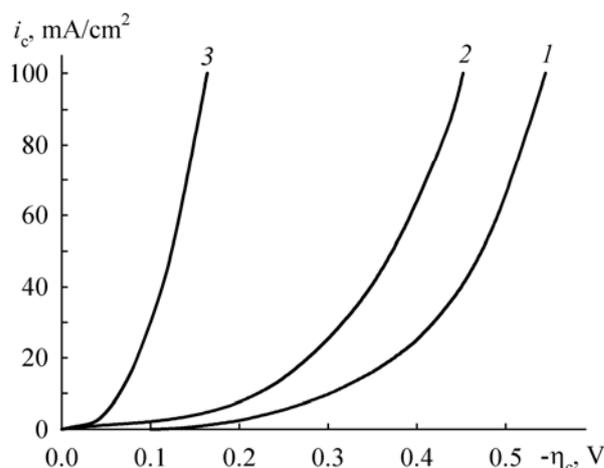


Fig. 1. Potentiodynamic (4 mV/s) polarization curves of hydrogen evolution from a 30 % KOH solution (65°C) at the following cathodes: (1) Ni, (2) Ni modified with Ni-W alloy, (3) Ni modified with Ni-Mo alloy.

In Fig. 2, plots of hydrogen evolution current density against overpotential, obtained on an unmodified plate-like titanium cathode activated in a HNO₃-HF mixture and on a titanium cathode modified with Co-Mo alloy are juxtaposed.

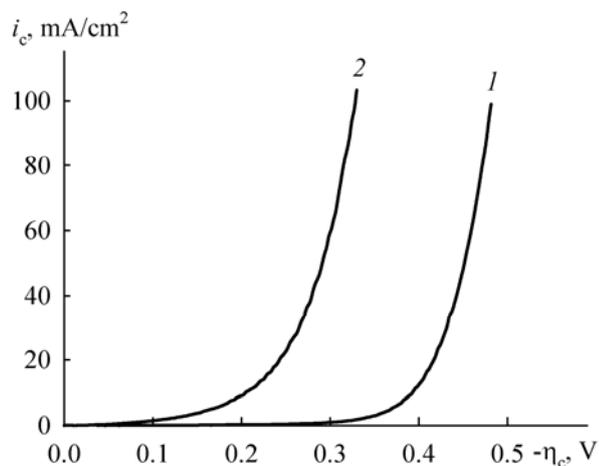


Fig. 2. Potentiodynamic (5 mV/s) polarization curves of hydrogen evolution from 30 % KOH solution (20°C) at the following cathodes: (1) Ti, (2) Ti modified with Co-Mo alloy.

The reasons of the observed depolarization of hydrogen evolution at modified electrode in comparison with unmodified one may be more extended alloy surface (see Fig. 3) and its catalytic activity in hydrogen evolution reaction.

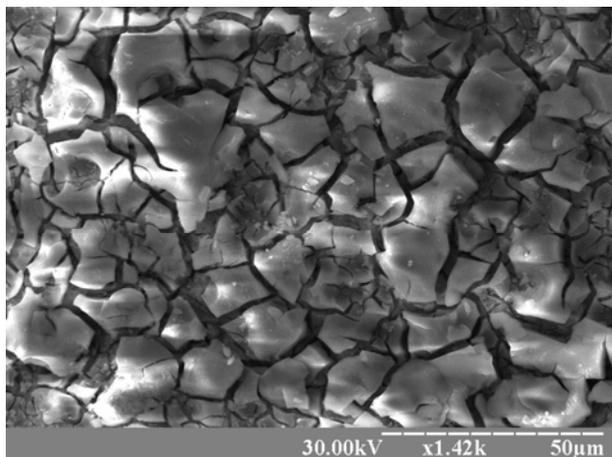


Fig. 3. Micrograph of the surface of Co-Mo alloy on a titanium cathode.

Thus, after the surface modification of titanium described above, it can also be used as cathodes in electrolyzers for hydrogen production.

To reduce the overpotential of the anodic process (η_a), gases-depolarizers, which oxidize at anodes at overpotentials lower than that of anodic oxygen evolution, were used in addition to anode

surface modification with alloys with low η_a values. It has been shown, e.g., that passing natural gas along the nickel anode surface leads to a decrease of 65 mV in η_a at a current density of 10 mA/cm² at 65°C.

To enhance the depolarizing action of hydrogen in the case of anodic oxygen evolution, it is proposed to generate hydrogen directly on the electrode surface by using ac pulse electrolysis.

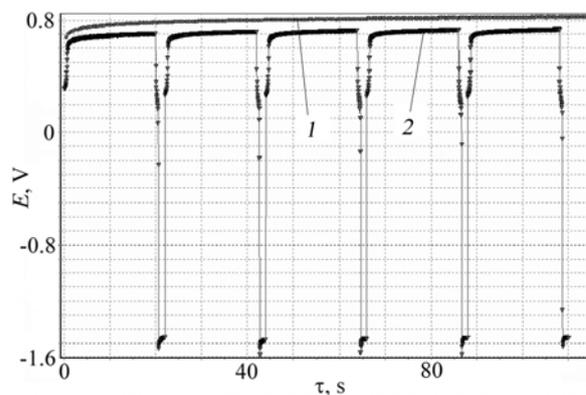


Fig. 4. Chronopotentiograms of a nickel electrode in the case of stationary ($i_a = 50 \text{ mA/cm}^2$) (1) and ac pulse ($i_a = 50 \text{ mA/cm}^2$, $\tau_a = 20 \text{ s}$; $i_c = 50 \text{ A/cm}^2$, $\tau_c = 2 \text{ s}$) (2) electrolysis in a 30 % KOH solution (20°C).

The chronopotentiograms juxtaposed in Fig. 4 indicate that the maximum overpotential of each anodic pulse is lower by 100-120 mV that overpotential in the case of stationary electrolysis, and that the average value of η_a in case of pulse electrolysis does not exceed 70 % of η_a in case of stationary electrolysis.

Conclusions

1. Efficient depolarizers of cathodic hydrogen evolution from alkaline solutions are alloys of subgroup VIb metals (Mo, W) with iron family metals electrodeposited on the electrode surface.
2. A considerable reduction in the overpotential of anodic oxygen evolution from alkaline solutions is possible if gases-depolarizers and ac pulse electrolysis are used.
3. By combining different methods for the depolarization of electrode processes, a considerable saving of electrical power can be achieved in electrochemical hydrogen production.

References

1. Kozin L.F. and Volkov S.V., Hydrogen Power Engineering and Ecology, Naukova Dumka, Kyiv (2002). – 336 p.
2. Kozin L.F. and Volkov S.V., Modern Power Engineering and Ecology. Problems and Prospects, Naukova Dumka, Kyiv (2006). – 776 p.