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The evolution of hydrogen on cobalt-molybdenum coating: polarization characteristics

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It is shown that good quality deposits of cobalt–molybdenum alloys may be produced using pulse plating and it is demonstrated that such coatings on titanium have a low overpotential for hydrogen evolution under typical brine electrolysis conditions.

1. Introduction

In many industrial electrochemical processes, the hydrogen evolution reaction takes place as the main cathodic reaction (water electrolysis, chlorate and chlorine production, etc.). Besides the electrochemical activity and corrosion stability, cost is a major criterion for the selection of suitable electrocatalysts. We have therefore studied non-noble transition metal electrocatalysts with the objective of at least matching the activities achieved using noble metals [1–7]. The most widely investigated electrocatalysis are mixed transition metal oxides [3, 8, 9], the plated and co-plated transition metals [10, 11], and chemically modified single metal systems such as sulphided nickel [12–14]. The few results given in the open literature, show that the best activity is achieved with co-plated transition metals or their oxides and this technology is the subject of two European patent applications [15, 16]. In these patents, the electrodes were prepared by alternately coating a substrate with a nickel or cobalt compound and with molybdenum or tungsten compounds. These compounds were decomposed thermally to the corresponding oxides. The mixed oxide layer was then cured in a reducing atmosphere at suitable temperatures. On the other hand Jakšić *et al.* [17] have reported that the addition of cobalt and molybdenum salts in sodium chloride solutions results in depolarization of the cathodic evolution of hydrogen on graphite and titanium. Recently, it has been shown that good quality deposits of cobalt and molybdenum alloys can be obtained using pulsed electrolysis [18, 19].

2. Experimental details

The coating examined here was prepared, as described earlier [18], on either a titanium or steel substrate; the frequency of the pulsed potential was 10^4 Hz, the effective current density was 25 mA cm^{-2} and the plating time 1 h. Hydrogen evolution was examined at 80° C in three types of solution: 30% NaOH, 15% NaOH + 15% NaCl and 300 g dm^{-3} NaCl, corresponding to typical solutions employed in brine electrolysis. The potentials are referred to the standard hydrogen electrode. The ohmic drop of the electrolyte was determined by using a Stonehart BC-1200 potentiostat, a PAR 175 programmer and a Nicolet 206 oscilloscope.

3. Results

The polarization characteristics of the cobalt–molybdenum coating are presented in Fig. 1. The corresponding curves for the substrates are also shown for the sake of comparison. It is evident that a cobalt–molybdenum coating exhibits an extremely high catalytic activity for the hydrogen

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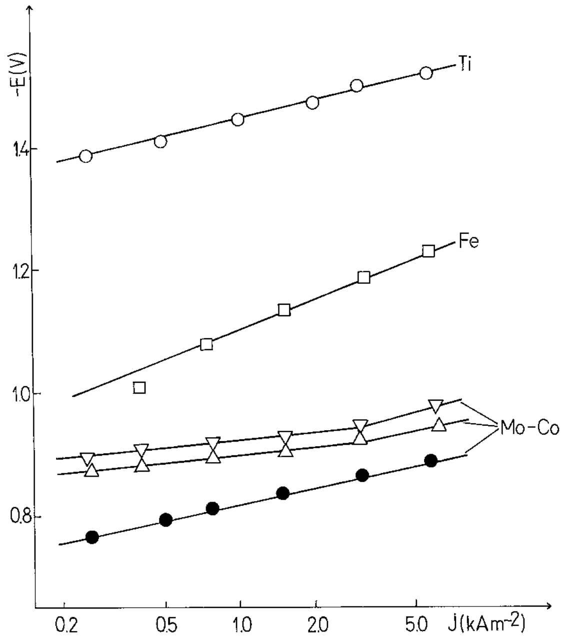

Fig. 1. The polarization curves for hydrogen evolution reaction at 80° C: ● – Co–Mo in 300 g dm^{-3} NaCl; △ – Co–Mo in 15% NaOH + 15% NaCl; ▽ – Co–Mo in 30% NaOH; □ – steel substrate in 300 g dm^{-3} NaCl; ○ – titanium substrate in 300 g dm^{-3} NaCl.

evolution reaction. The substrate has no effect on the activity of the coating. For practical use, the hydrogen overvoltage at high current densities is so small that practically no further improvements, such as an increased surface area, are needed.

No explanation for the activity of cobalt–molybdenum coating can be offered before the investigation of its structure is completed. Coatings of different composition have been prepared in order to elucidate the role of each constituent.

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