

# *Lanthanum–molybdenum coating for hydrogen evolution on titanium*

N. V. KRSTAJIĆ, M. D. SPASOJEVIĆ, R. T. ATANASOSKI

*Institute of Electrochemistry, ICTM, 11000 Belgrade, Yugoslavia*

Received 6 November 1981, Revised 12 May 1983

---

There is practical interest in the use of titanium as a cathode material in brine electrolysis processes. The overvoltage of hydrogen evolution on titanium is, however, very high and, at the same time, hydrogen penetrates the bulk of the metal. Here, a new type of catalytically active coating has been applied on the surface of titanium in order to overcome these problems. The coating consists of a mixture of the thermal decomposition products of lanthanum chloride and sodium molybdate. The coating has been tested for 18 months of continuous operation. No change in the overvoltage gain (of 0.4 V at  $3 \text{ kA m}^{-2}$ , as compared with pure titanium) nor change in the properties of the bulk metal have been noticed during this period.

---

## 1. Introduction

The use of titanium as a cathode in brine electrolysis processes is prevented by two shortcomings.

1. Titanium surfaces are poor catalysts for the hydrogen evolution reaction (h.e.r.) and 2. titanium suffers from hydrogen embrittlement. If these drawbacks were overcome it would allow improved electrode arrangements and cell designs. For instance, a bipolar electrode made solely of titanium could be constructed and the need for cathodic protection, while the cell is not in operation, could be avoided. The results achieved so far in this area (e.g. alloying of titanium with palladium) give room for further improvements of the properties of titanium for hydrogen evolution.

For several years now, successful attempts have been made in our Institute to catalyse hydrogen evolution at titanium by addition of cobalt and molybdenum ions to the electrolyte [1, 2]. In this work a rather different approach has been adopted. A molybdenum–lanthanum-based coating has been applied to the surface of the titanium by a thermal decomposition method [3]. The aim of this communication is to present the method of preparation of the lanthanum–molybdenum coating and to give a short account on the results obtained for hydrogen evolution.

## 2. Experimental details

Titanium electrodes were etched in boiling 20% hydrochloric acid for 20 min to provide a key for the coating. Aqueous solutions of lanthanum chloride ( $20 \text{ g dm}^{-3}$ ) and sodium molybdate ( $20 \text{ g dm}^{-3}$ ) have been subsequently painted and fired on the etched titanium surface. In order to get total surface concentration of  $10 \text{ g m}^{-2}$  of the elements, five layers of each have been applied. After applying each layer, the electrode was fired at  $500^\circ \text{C}$  for 10 min. Finally, the electrode was annealed at the same temperature for 2 h. As a result of such treatment, a compact, adherent, dark coating has been obtained. The percentage ratio of lanthanum against molybdenum varied from 0–100%, and was typically 30 : 70 wt %.

The polarization characteristics have been recorded in  $300 \text{ g dm}^{-3}$  sodium chloride solution at various temperatures. The performance of etched titanium without coating has been recorded for the purpose of comparison. The life test has been performed in chlorate production conditions: pH = 6–7 maintained by phosphate buffer,  $300 \text{ g dm}^{-3}$  NaCl, current density of  $3 \text{ kA m}^{-2}$ , and  $60^\circ \text{C}$ .

## 3. Results

The polarization characteristics of the electrodes

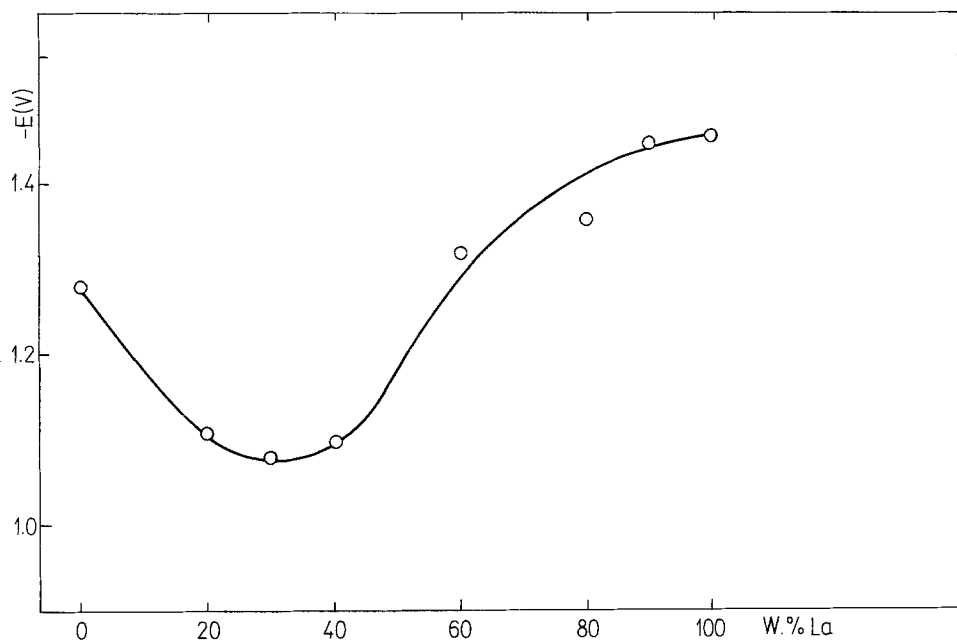


Fig. 1. The dependence of the potential on weight per cent La-Mo coatings at  $3 \text{ kA m}^{-2}$  ( $300 \text{ g dm}^{-3}$  NaCl,  $80^\circ \text{C}$ ).

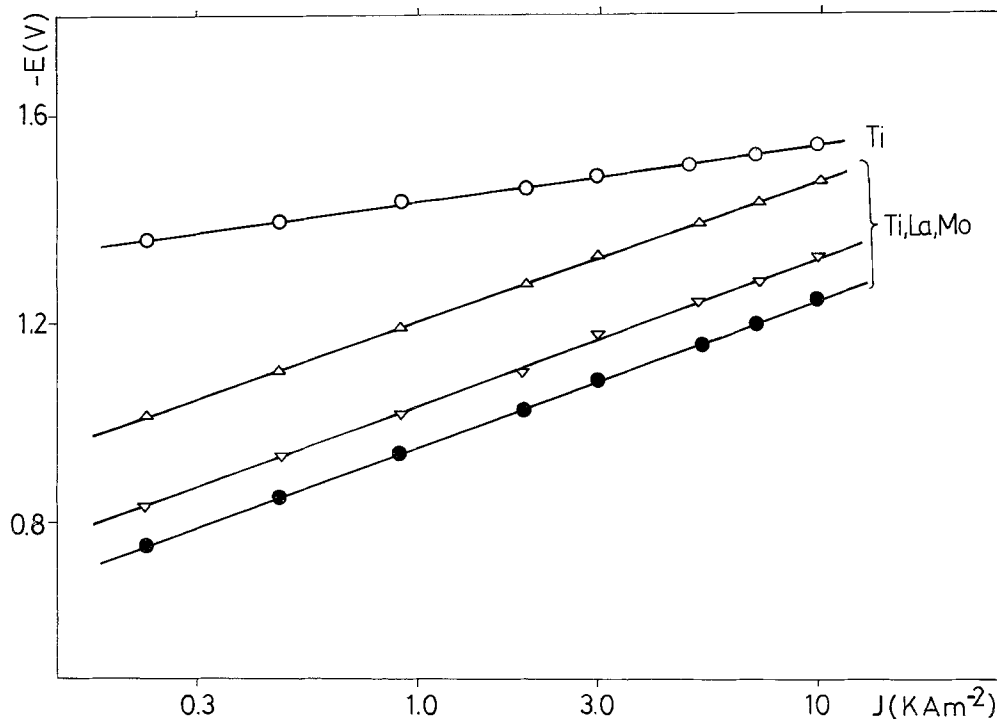


Fig. 2. The polarization characteristics of pure titanium and titanium coated with lanthanum and molybdenum (30 wt% La) run at various temperatures;  $\circ$  -  $80^\circ \text{C}$  of titanium;  $\triangle$  -  $25^\circ \text{C}$ ,  $\nabla$  -  $60^\circ \text{C}$ ,  $\bullet$  -  $80^\circ \text{C}$  of coated titanium ( $300 \text{ g dm}^{-3}$  NaCl).

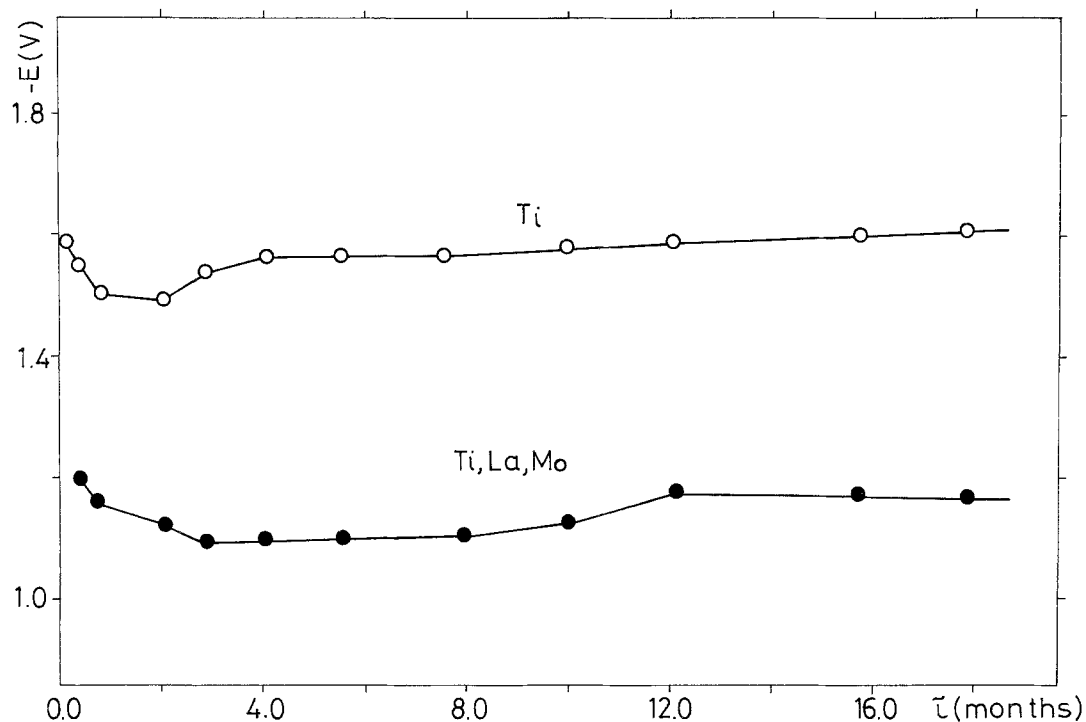


Fig. 3. The polarization change in long term experiments at  $3 \text{ kA m}^{-2}$  ( $300 \text{ g dm}^{-3} \text{ NaCl}$ ,  $60^\circ \text{ C}$ ); ○ - titanium, ● - coated titanium.

were found to be strongly dependent on the chemical composition of the coatings (Fig. 1). The most active surface for hydrogen evolution is that with a ratio of lanthanum to molybdenum of

30 : 70 wt % in the coating. The polarization characteristics of this cathode and of uncoated titanium in pure chloride solution, at various temperatures are shown in Fig. 2. The activity of

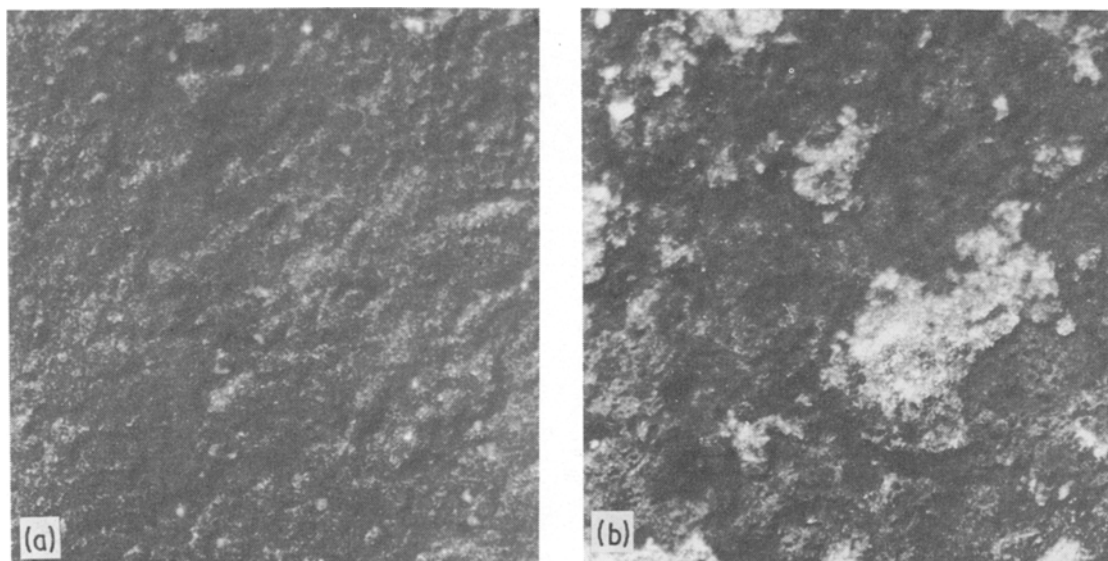


Fig. 4. The appearance of coated (a) and uncoated (b) titanium after 7 months of operation, magnification 40.

La–Mo-coated titanium is better than the activity of the uncoated surface by 0.6 V, at  $0.25 \text{ kA m}^{-2}$  at  $80^\circ \text{C}$ . At current densities of practical interest, e.g. at  $3 \text{ kA m}^{-2}$ , the La–Mo coating exhibits depolarization of some 0.4 V.

The polarization characteristics of the samples remain unchanged during continuous operation and the electrode potential varied between  $-1.1$  to  $-1.2 \text{ V}$  vs SHE at  $3 \text{ kA m}^{-2}$ , while that for the uncoated samples was between  $-1.6$  to  $-1.7 \text{ V}$  (Fig. 3). The physical appearance of the samples after seven months of operation is unchanged (Fig. 4). Contrary to this, the surface of uncoated titanium is extremely rough and dark, as compared to the appearance before the experiment.

X-ray analyses reveal the presence of different types of oxides of lanthanum, molybdenum and titanium as well as molybdate and titanate of lanthanum.

#### 4. Conclusion

It seems that titanium can be satisfactorily acti-

vated by lanthanum–molybdenum coating for brine electrolysis processes.

Potentials of  $-1.1$  to  $-1.2 \text{ V}$  at  $3 \text{ kA m}^{-2}$  are obtained, which compares favourably to potentials obtained with mild steel. The activity is high for long periods of time. Judging by the physical appearance of the coating, hydrogen embrittlement is not evident. A further account of the behaviour and properties of the coating will be reported later. No evidence of the use of this type of material in electrochemical processes has so far been found in the literature.

#### References

- [1] J. Jakšić, V. Komnenić, R. Atanasoski, R. Adžić, *Elektrokhimiya* **13** (1977) 1355.
- [2] M. Jakšić, Č. Lačnjevac, R. Atanasoski, R. Adžić, Proceedings of the Oronzio De Nora Symposium, Venice (1979) p. 57.
- [3] Yugoslav Patent Application 2079/79.