

Hydrogen evolving cathodes for chlor alkali membrane electrolysers

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Efforts have been made to content the hydrogen overvoltage phenomena to near thermodynamical values. Composite metal coated electrodes were prepared and their electrochemical behaviour in 30 wt% of NaOH solutions were studied and feasibility of their use in commercial scale electrolysers were explored.

Key words: Chlor alkali, membrane electrolyser, alloy coatings, thermal coatings, service life

INTRODUCTION

From the early industrial age, electrodes with hydrogen overvoltage of about 400-500 millivolt (3 kA.M^{-2}) have been used. The rise in energy costs drew attention to the electrocatalysis and development of new energy efficient cathodes for HER [1-3]. The present paper presents a part of the work carried out in the development of low overvoltage hydrogen evolving cathodes in CECRI, Karaikudi.

EXPERIMENTAL

The catalytic coatings for HER were prepared by three different techniques (1) electroplating, (2) immersion plating and (3) thermal techniques. Alloy coatings of Ni-Mo, Ni-Co-S, Ni-Co-W, Co-Mo and Co-W-P were electrodeposited from their respective baths on nickel plated mild steel. Immersion plating process comprises contacting the electroconductive matrix (stainless steel) with an acidic solution of mixture of compounds; metal of matrix exchanges with at least some of the Pt/Ru thereby causing a deposition of Pt and/or Ru on to the matrix and finally coatings were annealed in an inert atmosphere. The thermal or pyrolitic Ni-Mo and Ni-Co alloy coatings were produced by thermally decomposing their respective chloride or nitrate dissolved in alcohol on pretreated stainless steel sheet. Electrochemical behaviour was studied in 30 wt % NaOH at 353K with PAR 273 potentiostat/galvanostat. The service life studies were made in 30 wt % NaOH at 353K at 4 kA.M^{-2} . The potentials were measured with respect to Hg/HgO under identical conditions.

RESULTS AND DISCUSSION

The electrochemical behaviour of catalytic coatings for HER in NaOH solutions, obtained by electroplating, immersion plating and thermal method are illustrated in

Fig. 1. The overvoltage performance of various coatings for HER in 30 wt % NaOH, $T = 353\text{K}$ is given in Table I.

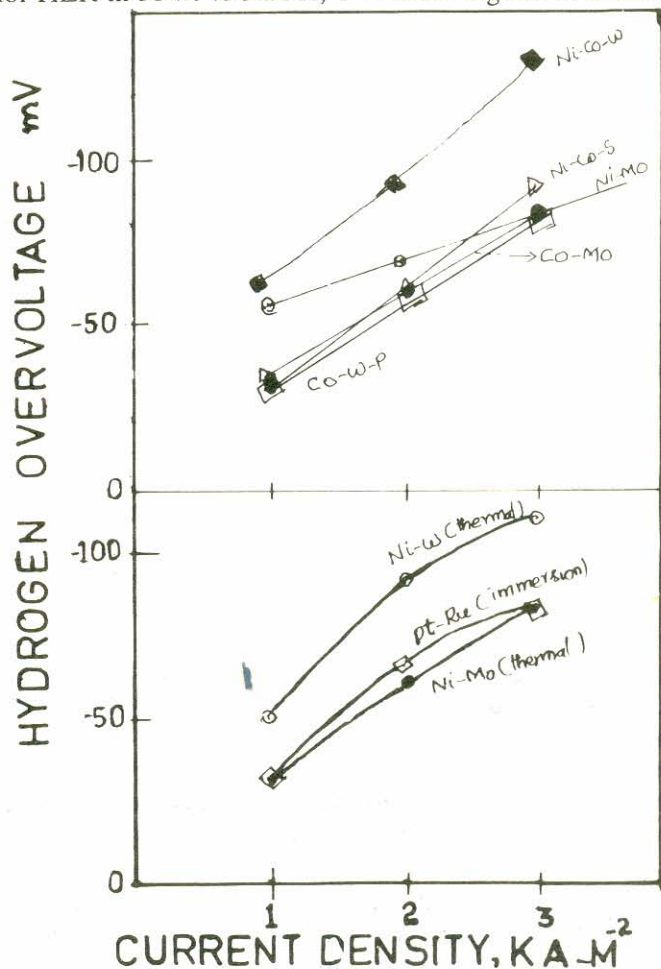


Fig. 1: Electrochemical behaviour of catalytic coatings for hydrogen evolution reaction in 30 wt % NaOH, $T = 353\text{K}$

It is found that the most promising active alloy coatings prepared by electroplating show a H_2 overvoltage of 80-100 mV (3 kA.M^{-2}). But the service life of these coatings were

TABLE-I

Cathodic coatings	Overvoltage in millivolts			Service life in hours
	1 kA.M ⁻²	2 kA.M ⁻²	3 kA.M ⁻²	
<i>Electroplated coatings</i>				4 kA.M ⁻²
Ni-Mo	55	65	80	200
Ni-Co-S	35	60	90	50
Ni-Co-W	60	90	130	50
Co-Mo	30	55	80	150
Co-W-P	30	60	80	300
<i>Immersion plated coatings</i>				
Pt-Ru	30	65	80	150
<i>Coatings by thermal method</i>				
Ni-Mo	30	60	80	3000
Ni-Co	50	90	110	250

poor and it is less than 200 hours (4 kA M⁻²) for most of electroplated coatings. And it is found that they were not stable in open circuit in NaOH solutions; Co dissolves to form cobalt hydroxide (blue colour) in Ni-Co-S and Mo with evolution of hydrogen in Ni-Mo and Co-Mo. But Co-W-P coating showed a service life of more than 300 hours and it is relatively stable in open circuit.

The Pt-Ru coatings on stainless steel obtained by immersion plating showed a hydrogen voltage of 80 millivolts (3 kA.M⁻²) but had a shorter life of 150 hours due to poorer adhesion of catalyst on the substrate.

The thermal coatings Ni-Mo and Ni-Co on stainless steel substrate, showed an overvoltage of 90-110 millivolts (3 kA.M⁻²). But Ni-Co coating has a very short life of 150 hours just as the electroplated ones and with dissolution of Co in open circuit. The service life of Ni-Mo was more than 3000 hours and there was no Mo dissolution or gas evolution observed in open circuit.

Among the low hydrogen overvoltage coatings studied, the thermally prepared Ni-Mo demonstrated a high service life and stability in open circuit. The reason for high stability and service life compared to electroplated Ni-Mo may be explained as follows. In electroplated Ni-Mo, the active sites may be in reduced form which will absorb more H₂ gas and the overvoltage shoots up [4] whereas in thermal coatings active sites are in oxidised form and hence absorption of H₂ may be comparably small.

A commercial scale 6 kA.M⁻² membrane cell with TSIA (metal anode) and Ni-Mo (thermal) coated cathode separated by cationic exchange membrane Nafion 961 was assembled and was operated at 353K for chlor alkali production. The above cell registered a cell voltage of 3.2 volts at 3 kA.M⁻² compared to cell voltage of 3.5 volts with stainless steel cathode under identical conditions. Thus a saving of 300 millivolts was effected due to the catalytic activity of Ni-Mo coating. Further work is in progress.

CONCLUSIONS

Among the low hydrogen overvoltage cathode coatings studied, Ni-Mo (thermal) was showing a service life of more than 3000 hours (4 kA M⁻²) and resulting in a saving of about 300 millivolts in actual chlor-alkali membrane cell operating conditions.

REFERENCES

1. M M Jacksic, *Int J Hydrogen Energy*, 11 (1986) 519
2. A C C Tseung, J A Antonian, D B Hibbert, *Chemistry and Industry*, 16 (1984) 54
3. N Yoshida, M Yoshiiai, E Endoh and T Morimoto, *Int J Hydrogen Energy*, 14 (1989) 137
4. M Seko, S Ogawa, H Ono and O Suzukhi, *Proc Symp Advances in Chlor-Alkali and Chlorate Industry*, The Electrochemical Society, Cincinnati, Ohio, 7-9 May, 1984, Edited by M M Silver and E M Spore, p 49