

Effect of metal cations on the reduction of oxygen on mild steel

S Muralidharan, N Palaniswamy, K Chidambaram, M Valliappan and K Balakrishnan

Central Electrochemical Research Institute, Karaikudi - 623 006, INDIA

The effect of addition of metal cations on reduction of oxygen on mild steel has been studied using a rotating electrode. The addition of zinc, manganese and cadmium ions suppresses oxygen reduction considerably.

Key words: Oxygen reduction, metal cations under potential deposition

INTRODUCTION

The understanding of the mechanism of oxygen reduction on iron is of great practical importance because of its main role in the corrosion of iron in neutral media.

Metal cations can take part in the cathodic reaction and can have the ability to accelerate or inhibit corrosion reactions. These metal cations can participate in redox reactions and thereby consume the electrons generated by the anodic reaction [1]. These metal cations can form bimetallic couples [2], bring about change in morphology of corrosion product [3], change protective oxide on surface [4] or the adsorbed cations form underpotential deposition [5].

In this present investigation, the effect of additions of metal cations like zinc, manganese and cadmium on the cathodic process of oxygen reduction on mild steel in 0.5M sodium chloride solution has been analysed using a rotating disc electrode.

EXPERIMENTAL

Mild steel electrode of area 0.282 cm² embedded in teflon was used as the test electrode. The test solutions were prepared by using Analar grade sodium chloride, zinc sulphate, manganese sulphate and cadmium sulphate with triple distilled water and the electrochemical studies have been described elsewhere [6]. Impedance measurements were carried out using EG&G PARC 5208 Two phase lockin analyzer and potentiostat model 273. The electrode was held potentiostatically at -600 mV and -850 mV vs SCE. AC signal of 10 mV amplitude was impressed at frequencies ranging from 10 kHz to 5 Hz.

RESULTS

Figure 1 shows the steady state polarisation of mild steel in 0.5M sodium chloride with and without the addition of 1×10^{-3} M ZnSO₄, 1×10^{-3} M MnSO₄ and 1×10^{-3} M

CdSO₄. The addition of ZnSO₄ shows a maximum cathodic shift in open circuit potential of the order of 70 mV. In general, addition of different metal cations suppress oxygen reduction, the maximum suppression being effected by the addition of ZnSO₄. The addition of CdSO₄ causes deposition of the cadmium on the mild steel surface. The cathodic reaction in presence of cadmium is influenced by oxygen reduction as well as cadmium deposition.

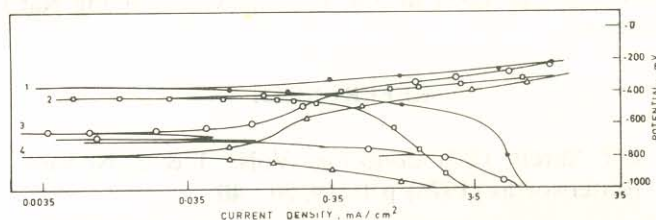


Fig. 1: Steady state polarisation of mild steel in 0.5M sodium chloride with and without the addition of 1×10^{-3} M ZnSO₄, 1×10^{-3} M MnSO₄ and 1×10^{-3} M CdSO₄

Figure 2 shows the steady state polarisation curve of mild steel in 0.5M NaCl under different speeds of electrode rotation namely 50, 100, 150 and 200 rpm. The limiting current increases with rotation indicating diffusion controlled process.

Figure 3 shows the steady state polarisation of mild steel in 0.5M NaCl with 1×10^{-3} M ZnSO₄ addition at different rotations. The addition of ZnSO₄ clearly suppresses oxygen reduction on mild steel. There is no regular increase in the limiting current with increase in rotational speed.

The steady state polarisation of mild steel in 0.5M NaCl with 1×10^{-3} M MnSO₄ under different rotating conditions is shown in Fig. 4. There is an anodic shift in current at the starting potential itself and the limiting current also does not vary linearly with rotation.

Figure 5 shows the steady state polarisation curves of mild

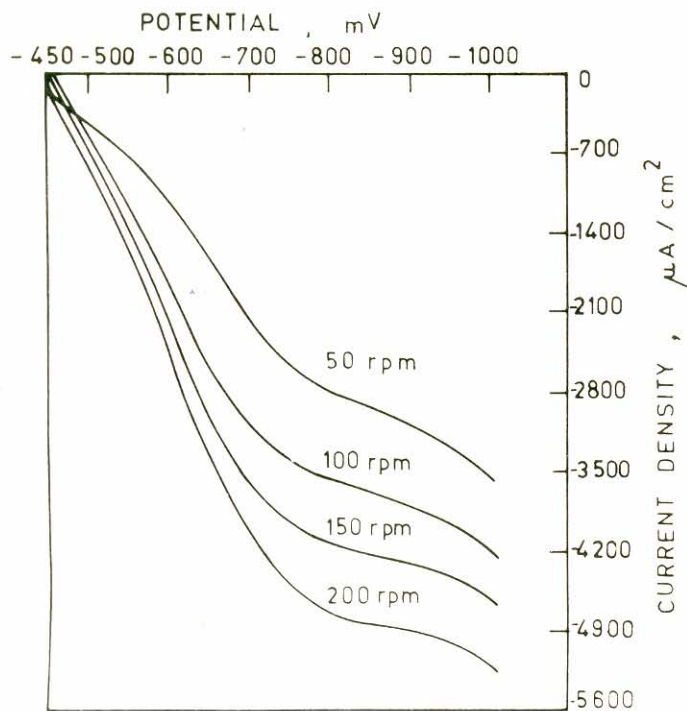


Fig. 2: Steady state polarisation of mild steel in 0.5M NaCl at different r.p.m

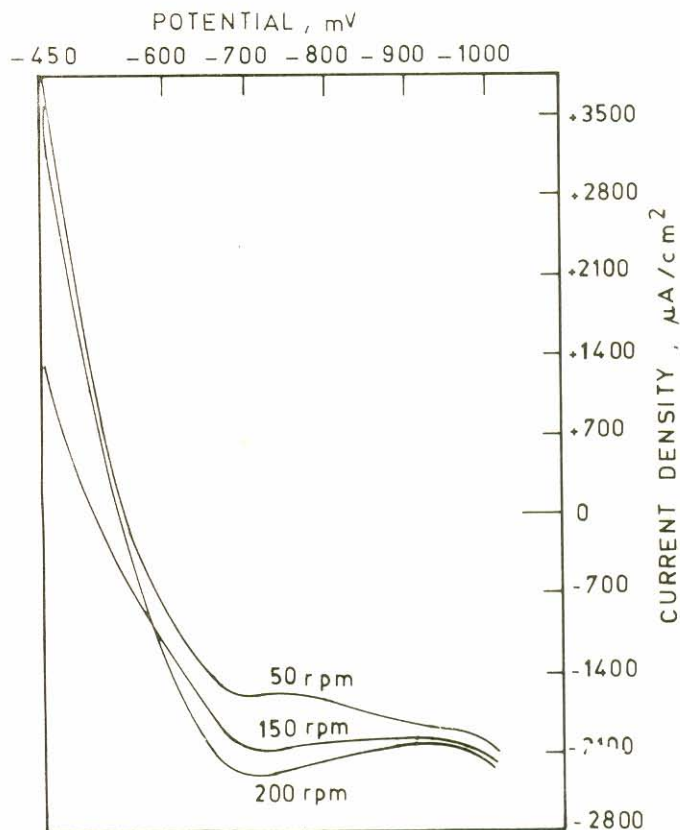


Fig. 4: Steady state polarisation of mild steel in 0.5M NaCl + 1×10^{-3} M MnSO₄ at different r.p.m.

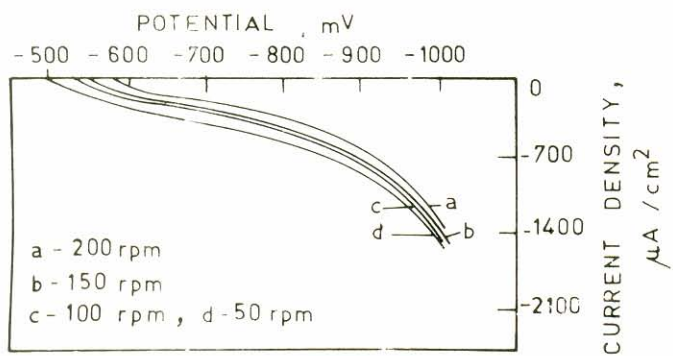


Fig. 3: Steady state polarisation of mild steel in 0.5M NaCl + 1×10^{-3} M ZnSO₄ at different r.p.m

steel in 0.5M NaCl with 1×10^{-3} M CdSO₄. Oxygen reduction is clearly suppressed by CdSO₄ with peaks corresponding to cadmium deposition. The cadmium deposition shows an anodic shift in potential with rotation.

Table I compares the solution resistance, charge transfer resistance and double layer capacitance values obtained from impedance data at two different potentials, namely, -850 mV and -600 mV vs SCE. Comparatively, addition of Zn ions enhances the solution resistance by 2 to 3 times when compared with NaCl solution alone. The addition of Mn and Cd alters the charge transfer resistance to a considerable extent. The charge transfer resistance at

-850 mV shows an increase of 60 ohms with the addition of Zn whereas Mn and Cd addition diminishes the charge transfer resistance by 90 ohms. At -600 mV the values of charge transfer resistance is maximum i.e. 776 ohms with the addition of Cd.

TABLE-I: Impedance data

System	Potential mV	R _s Ω	R _t Ω	C _{dl} F	R _{diff} Ω
MS/0.5M NaCl	-850	10	167.8	5.95×10	14
	-600	15.8	300.4	3.32×10	14
MS/0.5M NaCl + 1×10^{-3} M ZnSO ₄	-850	31.6	219.6	4.55×10	75
	-600	31.6	366.5	2.73×10	50
MS/0.5M NaCl + 1×10^{-3} M MnSO ₄	-850	12.6	76.5	1.30×10	14
	-600	12.6	303.6	3.30×10	20
MS/0.5M NaCl + 1×10^{-3} M CdSO ₄	-850	17.8	71.3	1.40×10	20
	-600	17.8	776.5	1.29×10	12

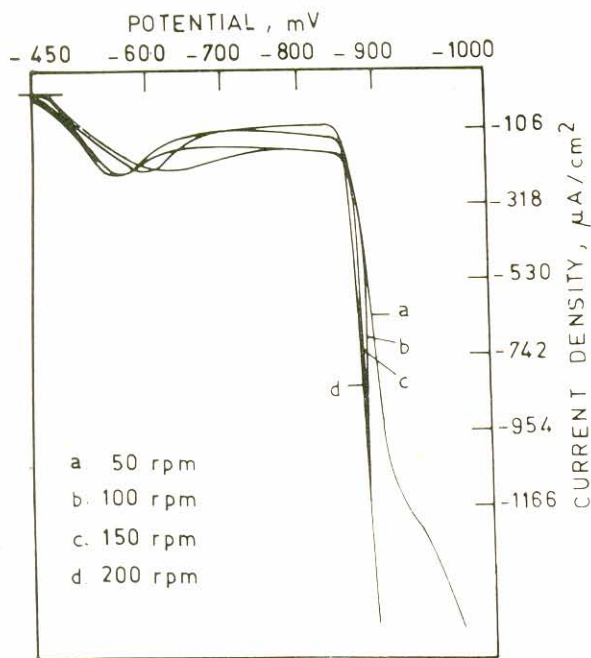


Fig. 5: Steady state polarisation of mild steel in 0.5M NaCl + 1×10^{-3} M CdSO₄ at different r.p.m.

DISCUSSION

The generalised mechanism of oxygen reduction involving a series of reaction pathways on an oxide surface as well as an oxide free surface are dealt with elsewhere [7]. In the absence of metal cations, the oxygen reduction process on mild steel in 0.5M NaCl shows the typical "S" curve indicating the diffusion controlled reaction. The addition of Zn ions markedly suppresses the processes of oxygen reduction. There is a marked increase in cathodic polarisation which can be attributed to the precipitation of Zn(OH)₂ on the cathodic areas as a result of locally elevated pH [8–10].

The addition of Mn also brings down oxygen reduction process due to complex reactions [11].

There is a possibility of Cd deposition in the scanned potential range. The observed Cd deposition potential is more positive than that of the Nernst reversible potential

indicating adatom formation at underpotentials [12].

The plots of i vs \sqrt{w} show that the oxygen reduction, which is purely under diffusion control is not only suppressed in presence of the cations but also controlled by surface reactions like hydroxide or adatom formation.

CONCLUSIONS

(1) The addition of metal cations to 0.5M NaCl solution suppresses the oxygen reduction on mild steel. (2) Zn addition shows maximum suppression of oxygen reduction; the reason may be attributed to the precipitation of Zn(OH)₂ on cathodic areas. (3) Mn addition brings down oxygen reduction by complex reactions. (4) Cd forms underpotentially deposited layers on mild steel.

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