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Journal of Power Sources 103 (2001) 147–149

JOURNAL OF
POWER
SOURCESwww.elsevier.com/locate/jpowsour

Short communication

Fe–P and Fe–P–Pt co-deposits as hydrogen electrodes in alkaline solution

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Received 5 March 2001; accepted 25 May 2001

Abstract

Fe–P and Fe–P–Pt alloys for use as electrodes for alkaline water electrolysis are prepared by an electroplating technique which employs an acidic complex bath solution. After heat treatment, the plated alloys act as effective electrocatalytic materials by lowering the hydrogen overpotential sufficiently. The improved electrocatalytic activity is due to an increase in effective surface area, a change in surface features upon heat treatment, and the presence of traces of platinum. Electrodes of the plated alloys are stable even in a highly corrosive electrolytic medium (6 M KOH). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Fe–P; Fe–P–Pt alloy; Electrocatalytic; Hydrogen evolution; Hydrogen overpotential; Heat-treatment

1. Introduction

Deteriorating urban air-quality, growing dependence on unsustainable energy sources, and global warming are forcing the replacement of petroleum-fueled, internal combustion-engined vehicles. To this end, many non-conventional energy sources are under development. The hydrogen–oxygen fuel cell is a prime example and there is extensive literature on its development [1]. As a consequence, there is much interest in the electrolytic production of hydrogen from alkaline water electrolysis by using electrode materials with low hydrogen overpotential [2]. These electrode materials must exhibit high intrinsic electrocatalytic activity or high effective surface area, in addition to good stability towards highly corrosive cell electrolytes (e.g. H_3PO_4 , H_2SO_4 or KOH) and an affordable cost. It is very difficult for a single electrode material to meet all these requirements.

Several electrode materials based on modification of nickel surfaces by co-deposition of other elements have been developed [3–6]. In many cases, these electrode materials lose catalytic activity after a few cycles of operation because of surface contamination and instability in the working electrolyte solutions. As a part of a broad program on the electrocatalytic preparation and characterization of suitable electrode materials for fuel cell technology [7–9], this study reports investigations on Fe–P and Fe–P–Pt alloys as cathode materials for alkaline water electrolysis. The

plating bath solutions are optimized to obtain alloys of good quality. Surface characterization of the plated samples is undertaken and catalytic activity and stability are evaluated by a polarization technique.

2. Experimental

All solutions were prepared by using AR grade chemicals and distilled water. Alloys were deposited on copper (99.9%) foils (2 mm × 2 mm × 0.5 mm). Before deposition, the surface was washed with trichloroethylene followed by water. Next, the surface was polished with emery paper down to grade 6/0, and washed with dilute H_2SO_4 and then with water. The surface morphology and microstructure of the deposited alloy were investigated by means of scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. Polarization measurements were carried out in a three-compartment glass cell with stainless-steel sheet (SS 316) and Hg/HgO/ OH^- as an auxiliary electrode and a reference electrode, respectively. Steady-state polarization curves were obtained galvanostatically in the range 1–100 mA cm^{-2} (potentiostat/galvanostat model EG&G PAR 273A). The experimental procedures have been described in detail elsewhere [10].

3. Results and discussion

Investigations were made with various complexing agents in the plating bath solution at a definite concentration of Fe

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Table 1
Bath composition and operating conditions

Bath composition (m l ⁻¹)	Fe–P	Fe–P–Pt	Operating conditions
(NH ₄) ₂ Fe(SO ₄) ₂ ·H ₂ O	0.20	0.20	Cathode: copper foil
H ₂ (PtCl ₆)·6H ₂ O	–	5.0 (mM)	Temperature: 323 K
NaH ₂ PO ₂ ·H ₂ O	0.25	0.25	Potential: –1900 mV
(NH ₄) ₃ C ₆ H ₅ O ₇	0.30	0.30	Time: 60 min
Boric acid (g l ⁻¹)	30	30	pH: 3.0

and Pt ions and at different pH values, current densities and temperatures. The resulting data were used to optimize the plating bath solution and the working conditions (Table 1) so that Fe–P and Fe–P–Pt alloys of good quality were obtained. Before using the alloys as electrodes (cathode), their surface morphology and structure were evaluated.

Electron micrographs of Fe–P–Pt without and with heat treatment are shown in Fig. 1(A) and (B), respectively. The untreated surface consists of nodular lumps (Fig. 1(A)). On heat treatment, recrystallization leads to increased roughness of the alloy film surface (Fig. 1(B)). EDX dot mapping

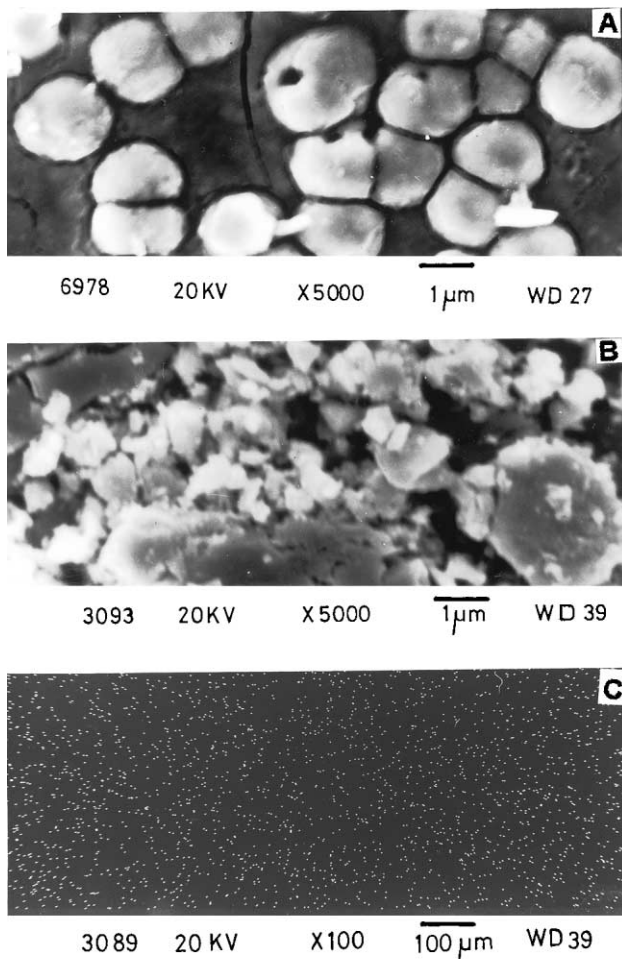


Fig. 1. Electron micrographs of: (A) Fe–P–Pt without heat treatment; (B) Fe–P–Pt with heat treatment (5 h, 723 K); (C) EDX: Pt dot mapping.

Table 2
XRD analysis of Fe–P–Pt_(94–4–2) alloy

Before heat treatment			After heat treatment ^a		
2θ	d (Å)	Phase	2θ	d (Å)	Phase
43.465	2.0803	Cu(1 1 1)	31.299	2.8174	FeP ₄ (1 3 0)
46.844	1.9121	FeP(1 1 4)	31.904	2.7653	FeP ₄ (0 0 2)
47.385	1.9169	Cu(2 2 0)	40.409	2.2005	Fe ₃ P(3 2 1)
50.535	1.8046	Fe(1 1 1)	43.152	2.0667	Cu(1 1 1)
74.245	1.2769	Cu(2 2 0)	43.963	2.0304	Fe ₃ P(4 2 0)
89.985	1.0895	Fe(3 1 1)	44.041	2.0270	Feα(1 1 0)
95.295	1.0431	Fe(2 2 0)	45.181	1.9784	Fe ₃ P(4 1 1)
			53.039	1.7021	FeP ₄ (1 1 3)
			64.049	1.4332	Feα(2 0 0)
			73.521	1.2699	Cu(2 0 0)
			90.732	1.0868	Fe ₃ P ₂ (1 1 2)

^a 623 K, 5 h, 10⁻⁶ mb.

of the deposited Fe–P–Pt alloy with respect to Pt (Fig. 1(C)) reveals that platinum is evenly distributed throughout the surface. The significant phases of as-plated and heat-treated samples were identified by XRD analysis (Table 2).

The electrocatalytic activity of Fe–P and Fe–P–Pt alloys with respect to the hydrogen evolution reaction (HER) is found to be critically dependent on the surface morphology, composition of the alloy (especially the amount of platinum), and the post-treatment. Cathodic, steady-state, current–potential curves were obtained at 323 K in 6 M KOH. The corresponding Tafel diagrams are shown in Fig. 2 and the respective Tafel parameters are given in Table 3. It is important to note that the values of overpotentials (η) at 100 mA cm⁻² (Table 3) are significantly lower, even at lower temperature, than those commonly reported for mild steel (~380 mV) [11].

In particular, appreciable electrocatalytic activity for hydrogen evolution on Fe–P–Pt (heat-treated) is revealed

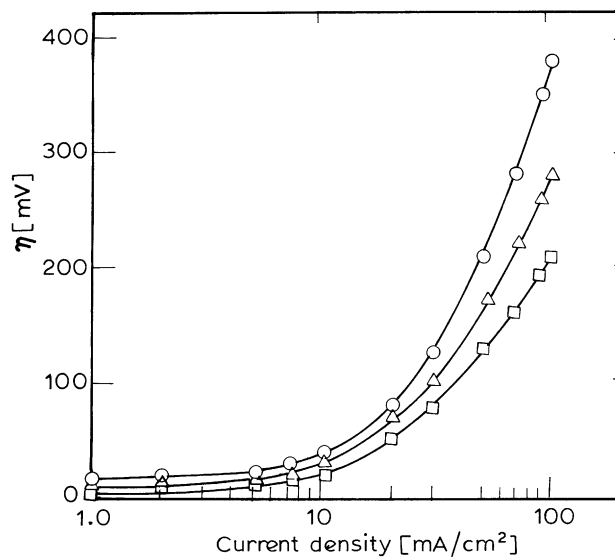


Fig. 2. Polarization diagrams for HER on deposited alloys in 30% KOH at 323 K: (○) Fe–P; (△) Fe–P–Pt; (□) Fe–P–Pt (heat-treated).

Table 3
Electrochemical parameters for hydrogen evolution on Fe–P and Fe–P–Pt alloys in 30% KOH at 323 K^a

System	b_c (mV)	i_0 (mA cm ⁻²)	i_{corr} (μ A cm ⁻²)	η_{100} (mV)
Fe–P	150.0 (170.0)	8.0 (8.5)	0.10 (0.07)	382.0 (360.0)
Fe–P–Pt	200.0 (210.0)	9.0 (10.0)	0.04 (0.30)	282.0 (210.0)

^a Values for heat-treated samples deposited at –1900 mV are given in parenthesis.

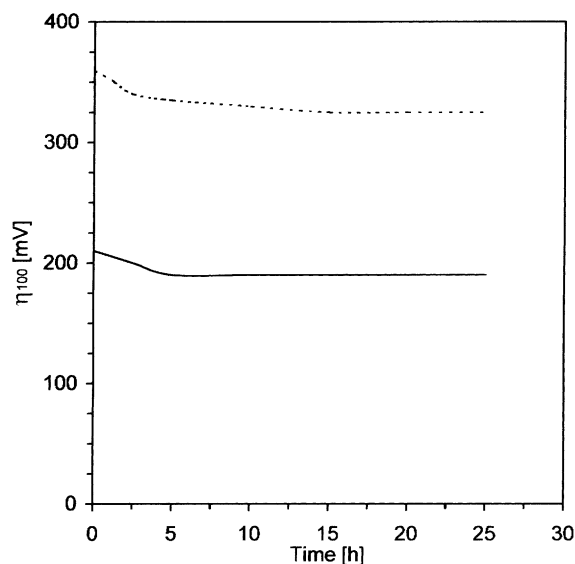


Fig. 3. Variation of overpotential with time during hydrogen evolution on coated alloys (heat-treated) in 30% KOH at 323: (—) Fe–P–Pt; (---) Fe–P.

by a reduction in overpotential of about 170 mV with respect to the value for mild steel. This indicates that the alloy shows good performance as a cathode material. Moreover, the material proves to be very stable, e.g. the electrode maintained the same electrocatalytic activity even after long term operation up to 25 h (Fig. 3) under conditions analogous to those nearly prevailing in industrial water electrolysis. One of the most important parameters in the evaluation of electrocatalysts is the real surface area. A qualitative indication of the increase in surface roughness by heat treatment supports the dependence of catalytic activity on surface area. Nevertheless, an intrinsic electrocatalytic activity effect cannot be explained only through increase in the effective surface area. XRD data with heat-treated samples support

the presence of new phases which modify the electronic and structural properties of the substance over the near-surface region and thus influence the electrocatalytic activity for hydrogen evolution.

4. Conclusions

Suitable plating baths are developed to electroplate Fe–P and Fe–P–Pt alloys which act as electrocatalysts during alkaline water electrolysis. Electrocatalytic activity depends on effective surface area, surface morphology, the composition and heat treatment of the electrode. The electrodes are stable even on prolonged electrolysis. Trace amounts of platinum in the bulk material, Fe–P, lowers considerably the hydrogen overpotential.

Acknowledgements

The authors wish to thank the University Grants Commission (UGC), New Delhi, for financial assistance to carry out this work under the COSIST program.

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