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Electrocatalytic activity of simple and modified Fe–P electrodeposits for hydrogen evolution from alkaline media

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ABSTRACT

Electrodeposition of Fe–P, Fe–P–Pt and Fe–P–Ce into copper substrates is carried out under galvanostatic conditions. The influence of the current density on the composition of the deposits and the current efficiencies for the electrodeposition processes are determined. Preliminary data indicate that addition of formic acid to the electroplating bath improves the current efficiency for electrodeposition. Electrocatalytic activities of the heat-treated plated materials are investigated by dc polarisation and ac impedance techniques for the hydrogen evolution reaction (HER) in 1 M NaOH solution at 298 K. Steady-state polarisation curves and electrochemical impedance spectroscopy data show that improved catalytic activities for the HER are due to an increase in the effective surface area, a change in surface features upon heat treatment, the partial contribution of the Pt component, and the electrocatalytic synergism with Fe imposed by the Ce co-deposit. Cathodic potentiostatic measurements for medium time operation indicate that the electroplated materials are stable even in moderately aggressive alkaline solutions.

1. Introduction

An outstanding factor of energy dissipation and high cost in electrolytic hydrogen production concerns the relatively low electrodes efficiency. An improvement in this efficiency is a fundamental aspect in electrocatalysis.

One of the most significant electrocatalytic processes is the hydrogen evolution reaction (HER). HER has received wide attention because of its importance in both fundamental and technological electrochemistry [1–17]. From a pure technological aspect the cost of electrolytic hydrogen is directly dependent on the voltage used to operate the electrolyser at significant current densities. As for the operational voltage it depends on the overpotentials for the cathodic (hydrogen evolution) and anodic (oxygen evolution) reactions, and on the internal resistance of the cell. Thus, from an electrochemical point of view, the problem to be tackled for decreasing the cost of hydrogen is related to the reduction of the overpotentials of the electrode reactions.

This decrease in the overpotentials can be accomplished by a suitable choice of materials with high electrocatalytic activity for the reactions. To be of technological interest, new materials with high electrocatalytic activity must have a cost comparable to that of traditional materials used in conventional monopolar water electrolysers (mild steel cathodes and nickel plate anodes). Therefore HER has been extensively studied in alkaline media on different types of electrodes in order to obtain electrocatalytic materials that are active, efficient and stable [18–23]. The materials must also exhibit good stability towards highly corrosive cell electrolytes (e.g. H_3PO_4, H_2SO_4 or NaOH). The activity of electrocatalytic materials has usually been improved by either increasing the ratio between the real and geometric surface area of the electrode or by a synergetic combination of electrocatalytic components.

In electrochemical systems, amorphous metallic alloys have been the object of several studies because of their enhanced corrosion resistance and their generally good catalytic activity towards complex electrochemical reactions like the HER. Of the several available preparation methods, electrodeposition is particularly attractive due to its simplicity, low cost, and the possibility of obtaining electrodes with larger areas. The most widely studied and used alloys for the HER in alkaline media are conventional and modified Ni and Co alloys [3,11,21,24–28], namely the nickel–phosphorous (Ni–P) electrodeposited amorphous alloys [29], in which phosphorous acts as the amorphism-causing additive. In many cases, these electrode materials lose catalytic activity after a few cycles of operation because of surface contamination and instability in the electrolyte solutions. Therefore, it is of interest to see whether amorphous alloys based on Fe show a good electrocatalytic activity towards the HER. Fe–P

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amorphous alloys have interesting mechanical, magnetic, and electrical properties [30–40], but the number of electrolytes known to have been used for the deposition of Fe–P amorphous alloys is relatively small [29,41,42].

The present work deals with electrochemical studies of the HER on Fe–P, Fe–P–Pt and Fe–P–Ce electroplated materials in alkaline solution. Their electrocatalytic activities towards the HER in 1 M NaOH at 298 K are examined by dc polarisation and ac impedance methods. 6 M KOH solutions would be more realistic relative to the actual water electrolysis in industrial conditions, but the selected working electrolyte provides relatively good basis for comparison. The preparation of the electrode materials by electrodeposition and their characterisation is also described.

2. Experimental

2.1. Sample preparation

All solutions were prepared by using AR grade chemicals and either distilled water or dimethylsulfoxide (DMSO). Table 1 gives the composition of the plating bath solutions and the working conditions.

As the oxidation–reduction potential of cerium (Ce) is very negative, an organic solvent (DMSO) was used for the Fe–P–Ce deposition. Thin films were electrodeposited onto copper (99.9%) foils of 0.025 mm thickness, with an exposed surface area of 0.785 cm^2 (1 cm diameter). Before deposition, the surface was washed with trichloroethylene followed by water. Thereafter, the surface was homogenised with emery paper down to grade 6/0, and rinsed with distilled water. The electrodeposition baths were found to have a pH of 1.0–2.0. Formic acid was added as an additional complexing agent to increase the current efficiency and improve the quality of the coatings [43–45]. A Nafion membrane was used to separate the cathode and anode compartments. Of course, Nafion is perfectly acceptable for the present measurements, but it is senseless for water electrolysis due to its high price. Electrodeposition was carried out at room temperature under constant current density which was controlled from 20 to 900 mA cm^{-2}. Most experiments were conducted with a total input charge of 900 coulombs cm^{-2}. Some deposits were further heat-treated following the procedure suggested by Shafia Hoor et al. [42] (623 K, 5 h, 10^{-6} mbar). Current efficiency at the copper cathodes was always less than 100% due to hydrogen evolution, so the actual weight gain (or deposit thickness) together with the current efficiency were calculated by using Faraday's law of electrolysis, and the volumetric amount of hydrogen evolved during deposition. Physical techniques (e.g. XRD, EDX, AES, SEM) were used to characterise the deposits (with and without heat treatment) in terms of sample composition, surface morphology, and microstructure.

Table 1
Bath compositions and operating conditions.

Fe–P deposition	
$FeSO_4 \cdot 7H_2O$	150 g l^{-1}
NaH_2PO_2	7 g l^{-1}
Glycine	8.5 g l^{-1}
Oxalic acid	0.5 g l^{-1}
$MnSO_4$	3 g l^{-1}
$CuSO_4$	0.2 g l^{-1}
Formic acid	50 ml l^{-1}
Fe–P–Pt deposition	
$Fe(NH_4)(SO_4)_2 \cdot 12H_2O$	40 g l^{-1}
NaH_2PO_2	10 g l^{-1}
$H_2(PtCl_6) \cdot 6H_2O$	3 g l^{-1}
$(NH_4)_2SO_4$	80 g l^{-1}
K_2SO_4	20 g l^{-1}
Sodium citrate	45 g l^{-1}
Citric acid	30 g l^{-1}
Boric acid	40 g l^{-1}
Formic acid	50 ml l^{-1}
Fe–P–Ce deposition	
$FeCl_2$	40 g l^{-1}
NaH_2PO_2	10 g l^{-1}
$Ce(CH_3SO_3)_3$	22 g l^{-1}
NH_4Cl	40 g l^{-1}
$(NH_2)_2CO$	180 g l^{-1}
CH_3COOH	12 mg l^{-1}
Sodium citrate	45 g l^{-1}
Citric acid	30 g l^{-1}
Boric acid	40 g l^{-1}
Formic acid	50 ml l^{-1}

Cathode, copper foil; temperature, 298 K; current, 150–700 mA; time, 15–75 min.

2.2. Electrochemical measurements

The electrochemical measurements were performed in a conventional two-compartment double-walled glass cell. The experiments were carried out in 1 M NaOH electrolyte solution at 298 K. A large platinum (Pt) foil (10 cm^2) served as counter electrode. The reference electrode was a saturated calomel electrode (SCE); all indicated electrode potentials were calculated *a posteriori* against the RHE reference. N_2 gas was bubbled into the cell for 1 h before each test. For the conventional dc measurements, the electrochemical cell was controlled by a Princeton Applied Research potentiostat equipped with IR compensation. Measurements were initiated after the 1-h gas bubbling. Impedance spectra were recorded at overpotential of −200 mV in the H_2 evolution region with a Solartron frequency response analyser. Data acquisition and processing was performed on a computer system with the associated software package. The impedance measurements were carried out in the frequency range 50 mHz–50 kHz with a constant ac voltage amplitude of 10 mV.

3. Results and discussion

3.1. Sample analysis

XRD patterns for most of Fe–P, Fe–P–Pt and Fe-P-Ce deposits confirm that the electrodeposits are amorphous. Metallographic analysis shows that the prepared samples appear uniform with neither local discontinuities in composition that could affect electrochemical measurements, nor contamination from bath solutions. Most surfaces of untreated samples consist of nodular lumps, which turn rough on heat treatment. SEM of Fe–P–Ce samples reveal black dendrite crystals of Fe surrounded by grey and white nonstoichiometric Ce_2Fe_{17} and CeP phases; the dendritic crystals disappear on heat treatment. Table 2 shows the composition of heat-treated films produced at different current densities with a total input charge of 900 coulombs cm^{-2}, as determined by EDX. When applying current densities lower than 200 mA cm^{-2} it was observed that a higher overpotential was accompanying the deposits formation. Therefore, our attention was directed for currents in the range 200–900 mA cm^{-2}. Clearly, these high values also decreased the time of the electrodeposition operation.

Since the instrument has no capability to detect carbon, the composition reported is on a carbon-free basis. The Fe–P deposits were found to contain oxygen by AES. EDX dot mapping of the deposited Fe–P–Pt(Ce) alloys with respect to Pt(Ce) also reveal that Pt(Ce) are evenly distributed throughout the surfaces. This rather homogeneous distribution testified by the EDX measurements agrees well with the theory of the hypo-hyper-*d*-interelectronic bonding of transition metal ions and atoms [46]. The Ce content of the deposits was found to increase with the current density. Since Ce