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Tungsten carbide-based electrochemical sensors for hydrogen determination in gas mixtures

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Abstract

An amperometric study of gas-diffusion electrodes (GDE) catalysed by two types of tungsten carbide, $WC_{(1)}$ and $WC_{(2)}$, which differ considerably in their specific surface area (0.5 and 6 $m^2 g^{-1}$), was carried out. The H_2–air gas mixture (H_2 1–4%) measurements show that for this range of hydrogen concentration the hydrogen limiting diffusion current ($i_{d(H_2)}$) may be attained so that a curve of limiting current density against hydrogen concentration can be obtained. The response and stability of the electrode performance were compared to those of platinum catalysed GDEs. The most promising for use in amperometric hydrogen sensing is the $WC_{(1)}$ catalyst of small specific surface area. Electrodes catalysed with this catalyst show inferior response time in comparison to electrodes catalysed with the other two catalysts ($WC_{(2)}$ and Pt) but their overall stability is much better.

1. Introduction

Hydrogen is an important industrial gas which is used in fuel cells, chemical synthesis and in the food industry, but it has the disadvantage that when its concentration in air exceeds the 4% limit, the mixture becomes explosive. This hazard necessitates the use of hydrogen sensors for measurement and control of hydrogen concentration. Most direct-sensing hydrogen sensors operate on the principle of the effect of hydrogen concentration on the physical properties of the sensing material, namely, the electrical resistance of semiconductors [1–3], the effect of reaction heat generated by hydrogen catalytic oxidation on the resistance of platinum [4] and the threshold voltage of Pd-gate MOS sensors [5–7].

Electrochemical sensors constitute another large group of hydrogen sensors. Their main advantages are the simpler design and operation based on many different electrochemical techniques such as voltametry, potentiometry and amperometry. These sensors are most frequently catalysed by platinum, a catalyst with a good activity in many reactions. This property may sometimes, however, transform to a disadvantage such as pronounced influence of catalytic poisons and a likelihood of explosion under the impact of Pt on the gas mixtures with a higher percentage of hydrogen.

An alternative to the platinum catalyst for the hydrogen reaction in acid media is tungsten carbide [8, 9] which does not possess such a high activity and is thus less influenced by catalytic poisons [8].

The aim of the present work is to study the prospects of using this catalyst in electrochemical hydrogen sensors.

2. Experimental conditions

An amperometric study of GDEs catalysed with two types of WC was conducted. The first, $WC_{(1)}$, which is frequently used as an abrasive, was synthesized from W and C (graphite) by a solid-state reaction. The second, $WC_{(2)}$, well-known as a good electrocatalyst for hydrogen oxidation [8, 9], was synthesized from WO_3 and CO [10]. The synthesis conditions and the particular physicochemical parameters of these carbides are presented in Table 1.

The two carbides were selected following earlier studies [11, 12] which showed that the electrocatalytic activity of WC with respect to H_2 oxidation increased while its corrosion stability decreased with specific surface area increase and decrease in the carbon bonded to its crystal lattice. On these grounds it was expected that the two carbides would differ in their electrochemical activity (if $WC_{(1)}$ was active at all), corrosion resistivity and current-potential characteristic stability with respect to catalytic poisons. For comparison purposes another catalyst consisting of carbon (Vulcan 72XC) supported Pt (1.4%) deposited from a $H_3Pt(SO_3)OH$ solution was studied. With all these catalysts double-layered gas-diffusion electrodes ($S_{geom.} = 2\ cm^2$) were developed whose gas-diffusion layer ($d = 10^{-1}$ cm) contained

Table 1. Preparation conditions, surface area (S_{BET}) and carbon content in the crystal lattice (C_{cl}) of the investigated WC

WC	Starting materials	Temperature of carbonization /°C	S_{BET} /m^2 g^{-1}	C_{cl} /%
1	W; C	1400	0.5	6
2	WO_3; CO	800	6.4	4.77

carbon black hydrophobized with PTFE (XC) and the active layer consisted of a catalyst and XC. The electrodes were pressed at 320 °C at a pressure of $p = 300$ kg cm^{-2}. The electrochemical measurements were carried out in a three-electrode cell with a volume of 150 cm^3. The sensor electrode was positioned with its active layer onto a gelled electrolyte 5 M H_2SO_4, the counter electrode was lead and the reference electrode was Hg/Hg_2SO_4. All potentials were referred to the hydrogen electrode in the solution. The cell was fed with gas mixtures, H_2–air or H_2–Ar, prepared by means of Brooks 5850E valves. The hydrogen concentration range was from 1% to 4 vol % due to the fact that higher hydrogen concentrations in air are explosive. The total flow rate was maintained constant at 2.77×10^{-5} m^3 s^{-1} for all experiments. The experimental conditions were controlled by a custom made potentiostat with a specialised current-to-voltage converter circuitry.

Since it is well-known that besides Pt, WC is also a catalyst for the electrochemical reduction of O_2 [14], the current–potential dependencies of gas-diffusion electrodes catalysed with $WC_{(1)}$, $WC_{(2)}$ and Pt were measured in hydrogen and air to clarify whether: (i) $WC_{(1)}$ was electrochemically active; (ii) the selected GDE design was appropriate to attain the hydrogen limiting diffusion current at potentials where the partial O_2 reduction current was zero. Due to the possible oxidation of WC, resulting in a deterioration of the current–potential curves, when selecting the sensor operational mode the condition had to be fulfilled that the potential in the limiting diffusion current range did not exceed +800 mV. This is practically the steady state potential of the particular electrode in air. Under these conditions, when supplying a gas mixture containing hydrogen, a current signal emerged which was measured with an *x–t* Servogor 310 recorder.

The long term stability test of the electrodes performance was carried out by measuring the limiting current after 1000 h for $WC_{(1)}$ and $WC_{(2)}$ and 300 h for Pt samples, respectively, at potentiostatically controlled operational potentials.

3. Experimental results

Figure 1 shows the hydrogen and air current–voltage plots of the electrodes catalysed by the three catalysts under investigation. It can be seen that $WC_{(1)}$ possesses electrochemical activity with respect to hydrogen oxi-

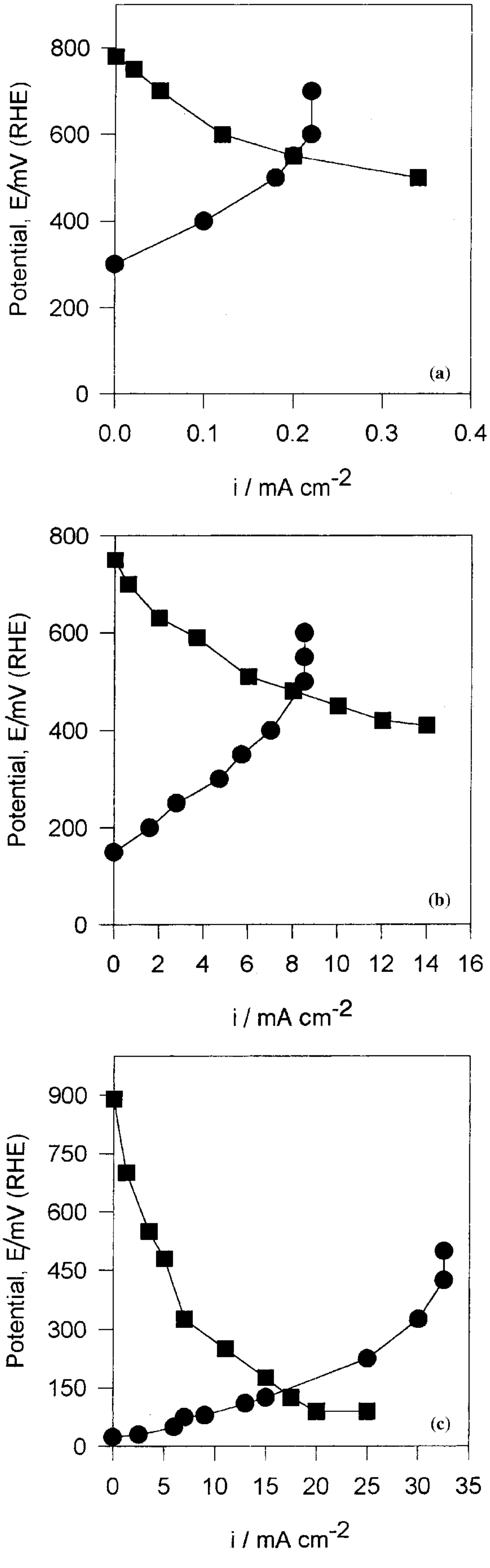

Fig. 1. Current–voltage plots of GDEs catalysed with (a) WC_1, (b) WC_2 and (c) Pt. Key: (●) hydrogen and (■) air. 5 M H_2SO_4, 20 °C.

dation and oxygen reduction. This activity is quite low but sufficient for the investigation of the possibility of using it when developing hydrogen sensors. It can also be observed that for the different catalysts the ($i_{d(H_2)}$) is reached at different potentials. As expected the lowest potential (400 mV HE) corresponds to the most active catalyst, Pt, while the highest potential (600 mV HE) corresponds to the carbide with the smallest specific surface area and stoichiometric composition, WC. From the plot it is clear that at the steady potential in air the ($i_{d(H_2)}$) current will flow for all the electrodes, i.e. the condition for $i_{d(H_2)}$ determination at $i_{(O_2)} = 0$ will be satisfied. It should be noted that the ($i_{d(H_2)}$) current for the electrode catalysed with the technical carbide is rather small. Therefore we assumed that for this electrode type there are diffusion limitations which are most probably due to the active layer structure, since the gas diffusion layers of all the electrodes are identical. Information about the diffusion limitations for the gas-diffusion electrodes may be obtained from the $\Delta E/i$ relationships. These reflect the difference of the electrode potentials at the same current density when the depolarize is either pure hydrogen or a mixture of H_2 and Ar [15]. To confirm the results the current–voltage curves were measured with pure hydrogen and a mixture of H_2 + Ar (1:1). It turned out, however, that within the current range where transport limitations occurred for the $WC_{(1)}$ catalysed electrode, the current–voltage curves of the $WC_{(2)}$ catalysed electrode were still in the activation region. This can also be observed in Figure 2. This was the reason why it was not possible to compare the diffusion limitations of the two electrode types. Experiments were conducted to optimise the structure of the $WC_{(1)}$ catalysed electrode active layer by replacing the carbon black with PTFE powder, but due to the larger specific gravity of the catalyst no positive results were achieved.

Figure 2 illustrates the amperometric signals of the investigated electrodes for a gas mixture of H_2–air with 3 vol % H_2. A time lag of 10–20 s in the signal, following the penetration of the gas mixture into the cell, is seen. As expected from the current–voltage relationships the signal from the $WC_{(2)}$ catalysed electrode was of the same magnitude as the signal from the Pt activated electrode, while that from the $WC_{(1)}$ containing electrode was two orders of magnitude lower.

Based on identical signals obtained for various hydrogen contents in the gas mixture the curves of limiting sensor current density against hydrogen concentration and of response time (mA s^{-1}) against hydrogen concentration were plotted. These relationships combined with the long term tests show whether the WC catalysed electrodes fulfil the requirements for sensor design and development. These are: (i) the possibility of giving a linear plot for a particular range of concentrations; (ii) fast response of the information signal; (iii) time related stability of the plot; and (iv) stability with respect to catalytic poisons.

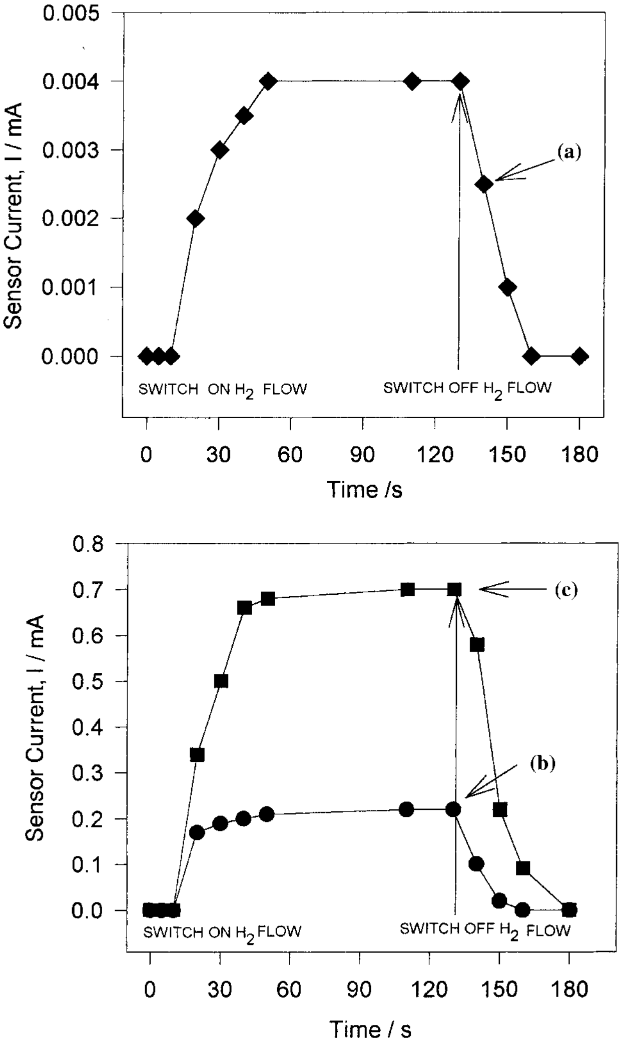

Fig. 2. Amperometric signals of GDEs catalysed with (a) WC_1, (b) WC_2 and (c) Pt. 3 vol % H_2; 5 M H_2SO_4, 20 °C; flow rate 2.77×10^{-5} m^3 s^{-1}.

Figure 3 represents the first of the above relationships for the three electrode types. The investigations were carried out in series of ten $WC_{(1)}$ and $WC_{(2)}$ and three Pt catalysed electrodes. The figure represents the average values and the corresponding dispersion.

From Figure 3 it can be seen that for both WC and Pt catalysed electrodes, the plots are linear and start at the origin. This indicates that, within the concentration range under investigation, the signals correspond to the ($i_{d(H_2)}$). It is clear that up to 4% H_2 the electrodes fulfil the first requirement for sensor development.

Figure 4 illustrates the relationship $(\mathrm{d}i/\mathrm{d}t)_{t=0}$ against H_2 concentration reflecting the sensor response time. It is clear that the $WC_{(1)}$ electrodes are inferior to the Pt electrodes with respect to reaction rate. This is not a vital disadvantage since the signal reaction with the $WC_{(1)}$ electrodes gave the hydrogen content 10–20 s following its emergence.

Figure 5 represents the initial relationships between limiting sensor current and hydrogen concentration and

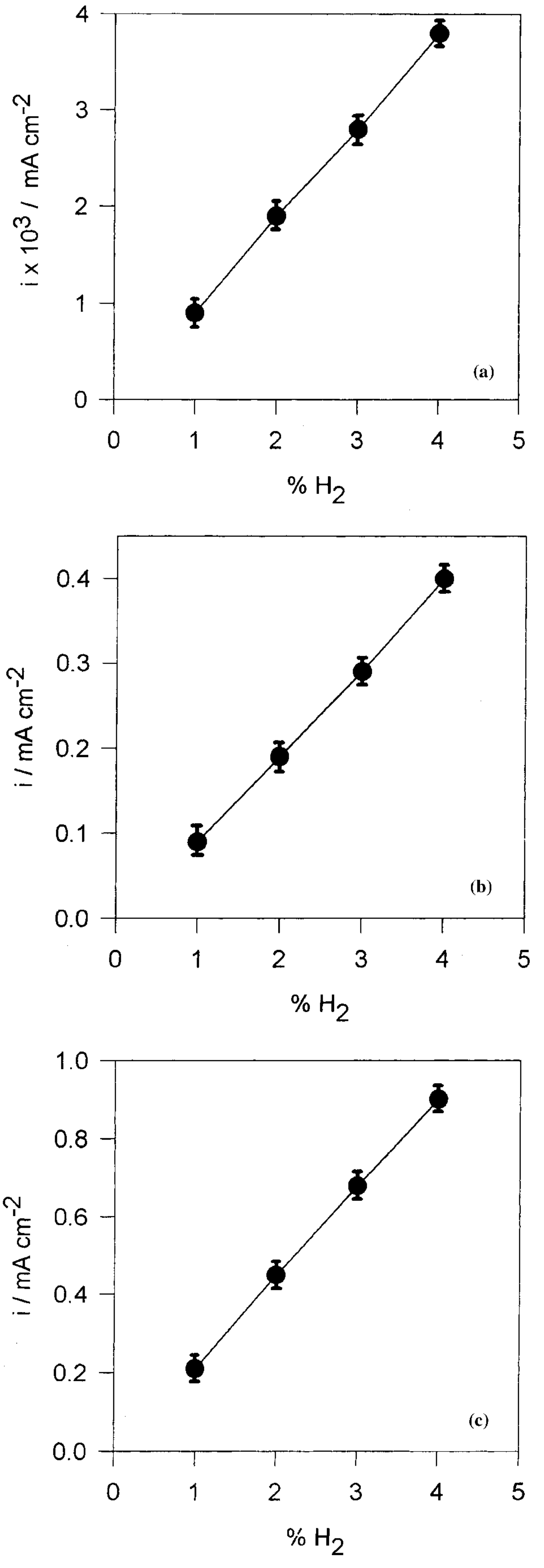

Fig. 3. Limiting current density against hydrogen concentration plots for (a) WC_1, (b) WC_2 and (c) Pt. 5 M H_2SO_4, 20 °C; flow rate 2.77×10^{-5} m^3 s^{-1}.

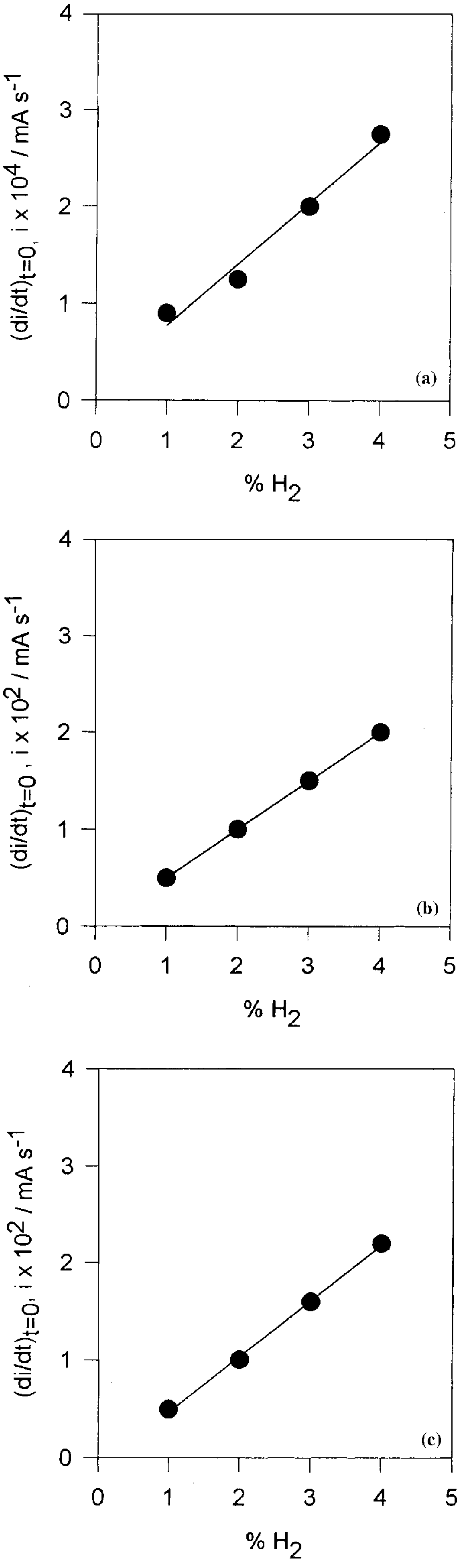

Fig. 4. Response time of limiting current density against hydrogen concentration for (a) WC_1, (b) WC_2 and (c) Pt.

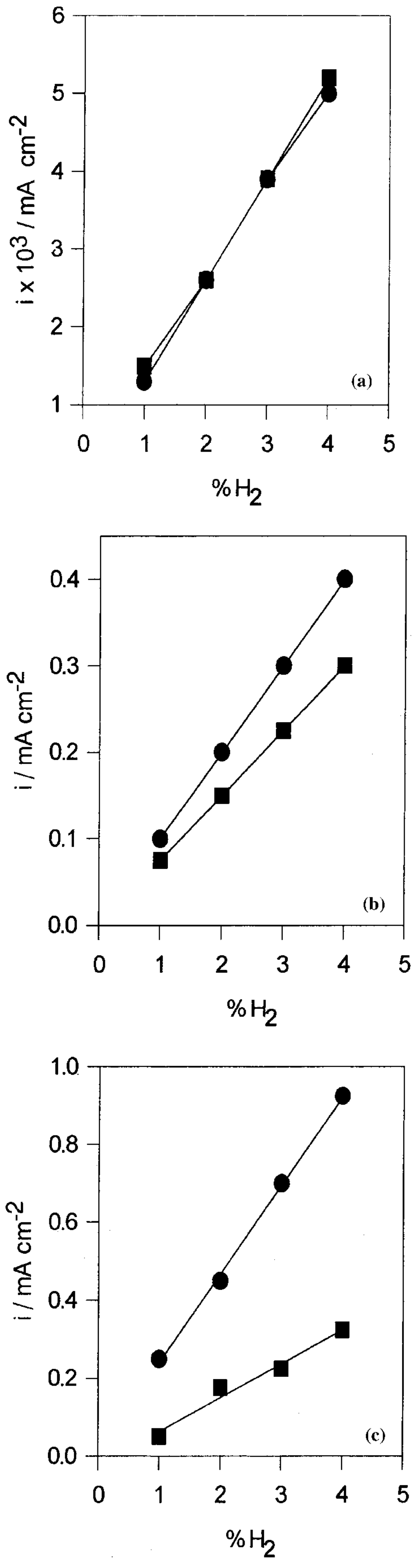

Fig. 5. Limiting current density against hydrogen concentration for (a) WC_1, (b) WC_2 and (c) Pt. Key: (●) initial, (■) after 1000 h of operation and (■) after 300 h of operation.

those after different running times: 1000 h for $WC_{(1)}$ and $WC_{(2)}$ and 300 h for Pt catalysed electrodes, respectively. It should be noted that the $WC_{(1)}$ catalysed electrode demonstrated satisfactory stability after 1000 h.

Following the first 300 operating hours the electrode catalysed with the second carbide, $WC_{(2)}$, had constant characteristics but after 1000 h the signals were weaker (Figure 5(b)). The X-ray diffractograms and the chemical analysis indicated that following this test 30% of the catalyst had been oxidised, which caused a change in electrode performance. This may be avoided if, after every measurement, the catalysed electrode is withdrawn from the electrochemical cell, which, however, would render it unusable for sensor design and development. The third, Pt-catalysed, electrode gave deteriorating performance after 300 h as indicated by the change. This was probably due to the adsorption of catalytic poisons onto the Pt. This assumption was supported by the fact that a two hour cycling of the electrode within the potential range −50 to +1350 mV resulted in resumption of the initial Pt electrode performance.

The influence of the catalytic poisons CO and NO_x on the activity of $WC_1$and WC_2 catalysed electrodes was also studied. A fourfold reduction in signal was observed 20 s after introducing 0.2 vol % CO to a mixture of H_2–air with 2 vol % H_2. The poisoning effect disappeared after purging with a mixture of air +2 vol % H_2. No influence of 0.2 vol % NO_x on the current signal was detected.

4. Conclusion

It is evident that WC of specific surface area over 1 to 2 $m^2\ g^{-1}$ is not suitable for use as a catalyst on electrodes for amperometric hydrogen sensor design. This is due to its tendency to slight corrosion at the sensor operating conditions. Much more promising is the WC obtained by solid-state synthesis employed in industrial applications with specific surface area lower than 1 $m^2\ g^{-1}$. Although the amperometric signals emitted by this type of electrode are weaker, they are more stable with time, due to their stability fowards corrosion and catalytic poisoning.

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