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Pt/Ti electrode preparation methods: application to the electrooxidation of isopropanol

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Abstract

Platinum coatings on Ti were prepared by a two-step process: partial thermal decomposition of chloroplatinic acid followed by electroreduction of the coating. Effects of preparation temperature and of cathodic polarization on the roughness factor were studied. Roughness factors greater than 570 were achieved, leading to an enhancement of the activity towards isopropanol electrooxidation in 1 M H_2SO_4.

1. Introduction

Several methods have been reported for the preparation of platinum based electrodes, namely, electrodeposition, thermal decomposition and chemical reduction of platinum compounds [1]. The influence of the crystalline structure, surface texture and grain size of the Pt electrodes on the distribution of reactive and poisoning intermediates of the electrooxidation of organics has been extensively studied [2]. To enhance the electrochemical activity for methanol and ethanol electrooxidation, highly dispersed Pt catalysts have been prepared; for example, Pt based glassy or porous carbons [3–5], bimetallic catalyst deposited on Ti [6], Pt based polymer matrix [7, 8], Pt-proton exchange membrane [9] etc.

In this paper the preparation of platinated titanium (Pt/Ti) electrodes is described by a two step process: partial thermal decomposition of chloroplatinic acid followed by an electroreduction of the coating. We report the effects of preparation temperature and of the cathodic polarization on the electrochemically active surface area. The electrocatalytic behaviour of this type of electrodes in the isopropanol electrooxidation is studied.

2. Experimental details

2.1. *Electrode preparation*

The Ti base metal was sand blasted then etched in boiling HCl (30%) for 30 min. Pt/Ti electrodes were prepared by depositing $10\,\mu l$ H_2PtCl_6 (0.2 g in 5 ml isopropanol, Fluka 38% Pt) on 1 cm^2 (geometric) pretreated Ti surface, followed by drying in an air oven at 90 °C for 10 min and heating in a preheated furnace at various temperatures ranging from 90 °C to 500 °C for 5 min. By repeating this procedure, 10 subsequent layers were deposited. Four electrodes were prepared (**1**, **2**, **3** and **4**) at 500 °C, 350 °C, 230 °C and 90 °C, respectively. All these electrodes were further electrochemically conditioned by cathodic polarization under galvanostatic conditions (-100 mA cm^{-2}) for 10 min in 1 M H_2SO_4 under stirring. The final platinum loading was about 2 mg cm^{-2}.

2.2. *Electrode characterization*

The electrodes were characterized in 1 M H_2SO_4 by cyclic voltammetry in a conventional three-electrode cell. The measuring equipment comprised a PAR270 potentiostat monitored by M270 software. The reference electrode was $Hg/Hg_2SO_4/K_2SO_4$ sat (640 mV vs NHE), all potentials are reported with respect to NHE. A Pt wire was used as counter electrode. All voltammograms reported correspond to the 5th cycle. The electrochemically active electrode areas (‘active area’) were estimated by intregration of the charge due to hydrogen adsorption in the anodic sweep between 0.0 and 0.35 V after substracting the double layer charge. A theoretical charge of $Q_H = 210\,\mu C$ for hydrogen adsorption over 1 cm^2 (geometric) of platinum was used. A roughness factor, f_r, is defined as the ratio of the electrochemically active and the geometric surface area ($f_r = A_{active}/A_{geom}$) [9].

The surface morphology was studied by scanning electron miscroscopy SEM (Jeol 6300F). XRD patterns were performed with a Siemens D500 diffractometer using CuKα.

3. Results and discussion

3.1. *Effect of the temperature on the electrochemically active surface area*

Typical cyclic voltammograms of the Pt/Ti electrodes in 1 M H_2SO_4 are shown in Figure 1. In the anodic scan, the electrochemical ionisation of adsorbed H takes place between 0 and 0.35 V, followed by the surface oxidation of the Pt metal from 0.70 to 1.5 V. In the reverse sweep, the peak associated with platinum oxide reduction appears at around 0.7 V then the peak of H deposition below 0.25 V. After 10 min of cathodic polarization at -100 mA cm^{-2}, an enhancement of current density is obtained. Even for electrode **4**, prepared at 90 °C, which presents no electrochemical activity in the first five cycles, great electroactivity can be induced by cathodic polarization (Table 1 and Figure 2(a)).

Figure 2(a) shows the effect of the preparation temperature and the cathodic polarization upon the roughness factor f_r. In the case of electrode **1**, prepared at 500 °C, the cathodic polarization has no significant effect on the roughness factor ($f_r \simeq 30$, Table 1). Electrodes **2** and **3** prepared at lower temperature ($T = 350$ °C and 230 °C) give systematically higher active area and polarization causes a large increase in the roughness factor.

Weight loss was observed after polarization for electrodes **3** and **4** ($T \leq 230$ °C) (Figure 2(b)). With the exception of electrode **4** (prepared at 90 °C), the final platinum loading obtained (1.9 mg cm^{-2}) corresponds roughly to the theoretical value calculated with 100% yield for the thermal decomposition of H_2PtCl_6 (1.5 mg cm^{-2}) [10]. The lower residual platinum loading of electrode **4** (1 mg cm^{-2}) can be related to a lack of adherence of the deposit, as observed on the SEM images (Figure 3). Indeed, at 500 °C (electrode **1**), the photograph reveals a high density of globular particles of different sizes. This film seems to be stable under polarization and looks like that observed with Pt/Ti prepared by direct electrolysis [6]. When the temperature decreases, the films become more compact and cracks appear after polarization, which are increasingly deep as the temperature decreases. However, the XRD patterns show the complete decomposition of H_2PtCl_6 to metallic Pt at $T \geq 350$ °C.

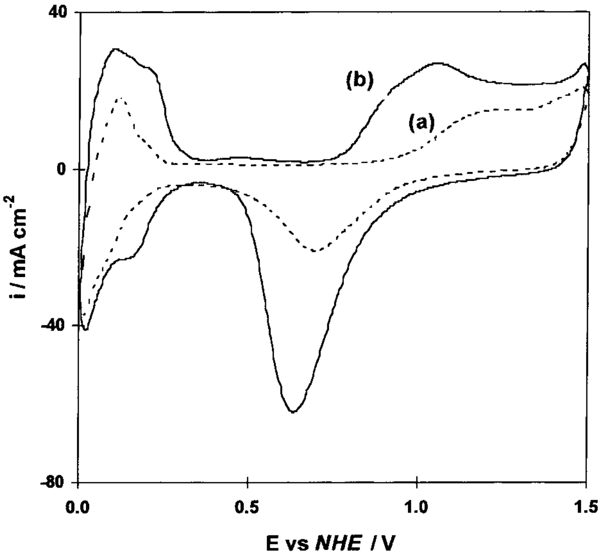

Fig. 1. Cyclic voltammograms of Pt/Ti (electrode **3**, 230 °C) in 1 M H_2SO_4, scan rate 50 mV s^{-1}: (a) before and (b) after cathodic polarization at -100 mA cm^{-2} during 10 min under stirring. Current density is referred to the geometric area.

Table 1. Pt/Ti electrode characteristics

Electrode	Preparation TD (T/°C) +CP	f_r	Reference
1	500	36	[*]
	+CP	36	[*]
2	350	68	[*]
	+CP	280	[*]
3	230	200	[*]
	+CP	570	[*]
4	90	0	[*]
	+CP	390	[*]
Pt/Ti	electrodeposition	24	[6]
Pt/Pt	electrodeposition	4–50	[2]
Pt/C	220/air	48	[4]
	220/H_2	68	[4]
Pt/PEM	chemical reduction	690	[9]

TD Thermal decomposition of H_2PtCl_6/isopropanol (200 mg/5 ml), 10 × 10 μl, 90 °C/5 min, T/5 min,

CP Cathodic polarization: 100 mA cm^{-2}/10 min under stirring

[*] This work

These results confirm that decomposition of H_2PtCl_6 is complete in air at 350 °C, but at the same time sintering is taking place at higher temperatures [4], leading to a decrease in the roughness factor (Figure 2(a)). Indeed, in the case of electrode **1**, the value ($f_r = 36$) is close to that reported for a Pt/Ti electrode prepared by electrodeposition [6] (Table 1).

Preparation at lower temperatures causes a partial decomposition of the precursor. Polarization under hydrogen evolution completes this decomposition to metallic Pt giving rise to a higher electrochemically active surface area (Figure 2(a)). An interesting point is that the temperature of 230 °C (electrode **3**), where the highest increase in cathodic activation was obtained, corresponds to that reported by Biswas for Pt/C prepared by heat treatment under hydrogen (Table 1) [4]. However, in our case, a much greater active surface area ($f_r = 570$) can be achieved, of the same order of magnitude as that reported by Lamy for Pt/PEM electrodes [9] (Table 1).

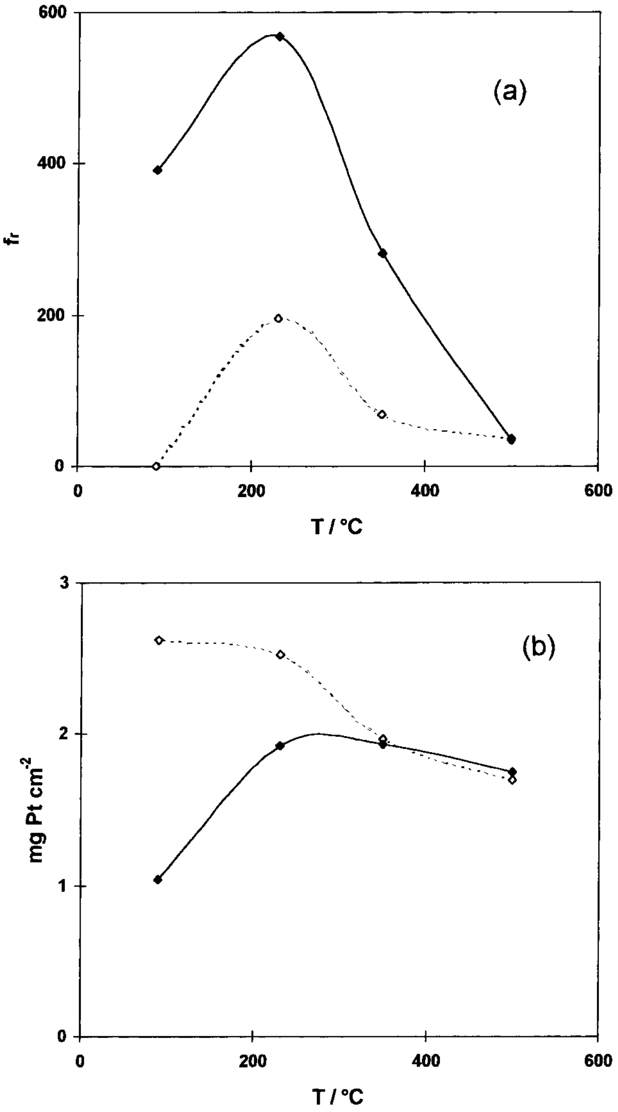

Fig. 2. (a) Effect of the preparation temperature upon the roughness factor (f_r) of Pt/Ti electrodes: (◇) before and (◆) after polarization (-100 mA cm^{-2}). (b) Effect of the preparation temperature upon the Pt loading on Pt/Ti electrodes: (◇) before and (◆) after cathodic polarization (-100 mA cm^{-2}).

3.2. *Isopropanol electrooxidation*

When Pt/Ti electrodes were used in solution containing isopropanol, the voltammograms exhibit three new oxidation peaks. In the positive scan, the peaks i_1 and i_2 appear at about 0.52 and 1.30 V (Figure 4). In the back scan, an anodic peak i_3 appears at a lower potential than that of peak i_1. The peak intensities are calculated as a difference between measured current densities in the presence and absence of alcohol (Figure 4). Both the potential and the intensity of the peaks vary with several parameters such as preparation temperature, cathodic polarization, concentration of isopropanol and electrolyte temperature (Table 2, Figures 5 and 6). For the evaluation of the activity in electrooxidation of isopropanol, the current density i_2 was chosen and reported in Figures 5, 6(b) and 7.

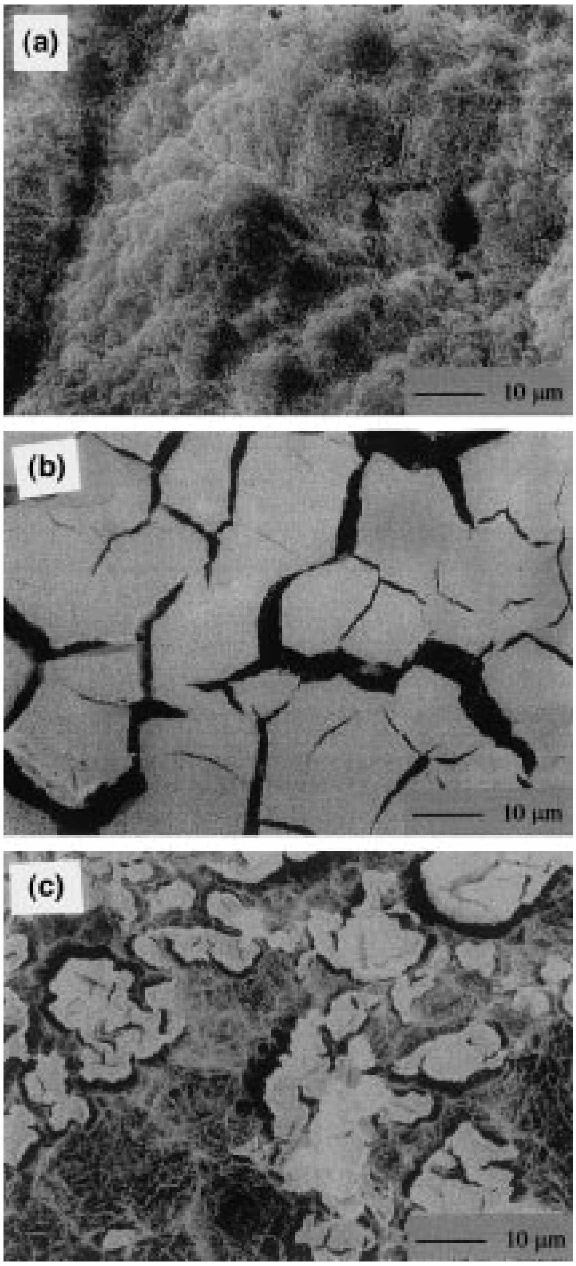

Fig. 3. SEM images of Pt coating after polarization (-100 mA cm^{-2}) on Pt/Ti electrodes **1**, **3** and **4**.

Table 2 shows the effect of preparation temperature on the current densities (referred to the geometric area) of electrooxidation of isopropanol. Before the cathodic polarization, the electrooxidation current densities remain very low. In particular, electrode **4** (90 °C) exhibits no electroactivity and the other electrodes present electrooxidation current densities around 20 mA cm^{-2} in 1 M isopropanol. After the cathodic polarization, a shift in the oxidation peaks towards less anodic potentials is generally observed and a noticeable enhancement of current density ($\Delta i_2 = 50$–90 mA cm^{-2} in 1 M isopropanol) is observed for electrodes **2** and **3** prepared at 230 and 350 °C, respectively. However, with electrode **4** (90 °C), even after the cathodic polarization, current densities remain very low. The same effects are illus-

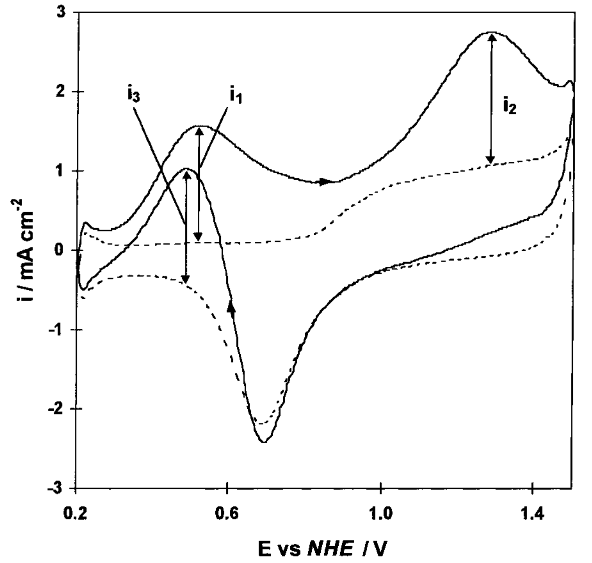

Fig. 4. Typical cyclic voltammograms of oxidation of isopropanol on Pt/Ti electrodes ($v = 50$ mV s^{-1}). Illustration for the determination of i_1, i_2 and i_3; solid line: 1 M H_2SO_4 + 0.1 M isopropanol; dashed line: 1 M H_2SO_4.

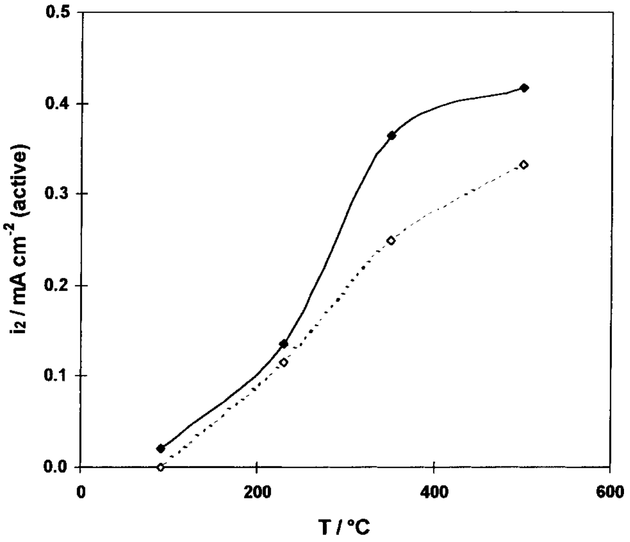

Fig. 5. Variation of the current peak density i_2 (referred to the active area) in the presence of 1 M isopropanol as a function of preparation temperature; (◇) before and (◆) after cathodic polarization (1 M H_2SO_4, $v = 50$ mV s^{-1}).

trated in Figure 5 where the current densities i_2 referred to the electrochemically active area are plotted. For all studied electrodes after cathodic polarization, the electrocatalytic current densities vary linearly with isopropanol concentration.

The electroactivity of electrodes **1** to **3** seems to correlate with their roughness factor (Figure 5). This confirms the conclusion of Nart et al. that the roughness and morphology of the surface determine the mechanism of electrooxidation of isopropanol on electrodeposited platinum electrodes [11].

It is known that oxidation of isopropanol on Pt is a surface sensitive reaction involving dehydrogenation of isopropanol to acetone [12–14]. Electrocatalytic performance of Pt electrodes would certainly depend on the electrolyte temperature (T_{el}). As previously observed by Raicheva [15], temperature increase leads to changes in the shape of the cyclic voltammogram (Figure 6). All anodic currents increase with temperature increase. Peak 3 shifts regularly to more anodic potentials with increasing temperature and a new peak appears at 0.9 V at temperatures higher than 50 °C. Linear correlation is obtained on plotting $\log i_2$ vs $1/T_{el}$ (Figure 6(b)), the apparent activation energy being 24 kJ mol^{-1} in good agreement with that found at a smooth Pt electrode [15]. This suggests that the catalytic activities for Pt/Ti and smooth Pt electrodes towards isopropanol electrooxidation exhibit similar behaviour concerning the rate determining steps, which are probably adsorption processes.

Deactivation of electrodes **1** and **2**, possessing different roughness factors (f_r), has been followed by chronoamperometry under stirring at various electrolyte temperatures (T_{el}) (Figure 7). The potential was fixed at E_2, because it does not change with T_{el} while this is not the case for E_1 and E_3 (Figure 6). The decrease in i_2 with time shows that deactivation depends on T_{el} and f_r. At the same temperature (i.e., $T_{el} = 60$ °C), it clearly appears that an increase in f_r leads to a lower deactivation rate. In the same way, an increase in T_{el} slows down the deactivation effect.

Table 2. 1 M isopropanol electrooxidation characteristics on Pt/Ti electrodes in 1 M H_2SO_4, 50 mV s^{-1}, 25 °C

Electrode	Preparation TD (T/°C) +CP	Peak 1		Peak 2		Peak 3	
		i_1 /mA cm^{-2}	E_1 /mV	i_2 /mA cm^{-2}	E_2 /mV	i_3 /mA cm^{-2}	E_3 /mV
1	500	18	520	12	1300	25	490
	+CP	22	520	15	1290	28	480
2	350	11	490	17	1340	12	500
	+CP	136	510	102	1230	149	450
3	230	11	510	23	1370	18	500
	+CP	92	590	77	1320	152	580
4	90	–	0	0	–	0	–
	+CP	9	550	8	1300	12	510

The current density is referred to the geometric area

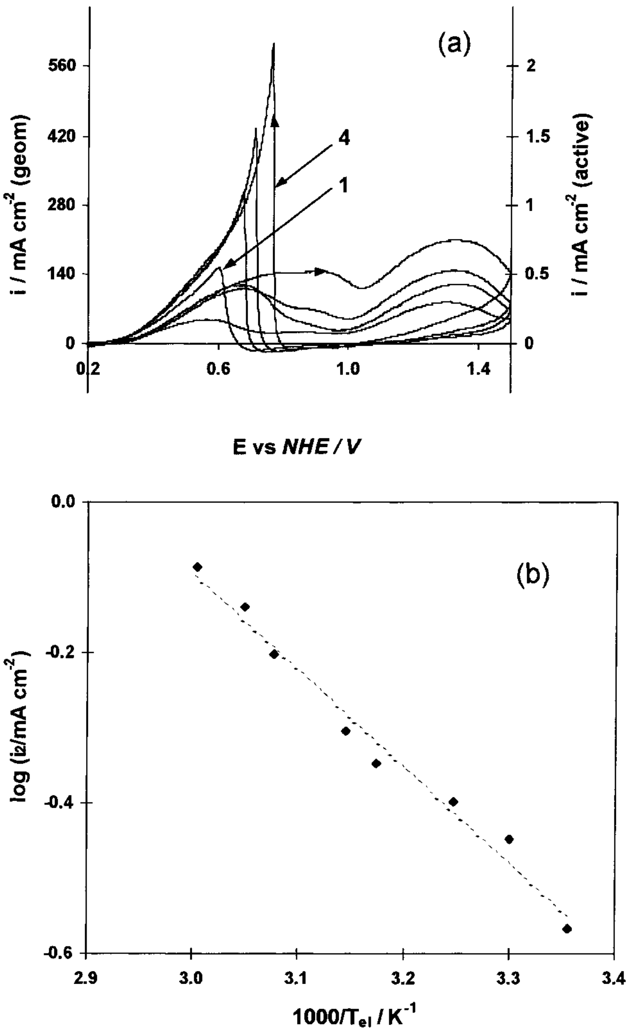

Fig. 6. (a) Cyclic voltammograms of electrode **2** (350 °C) in 1 M isopropanol as a function of electrolyte temperature (T_{el}): (**1**) 25 °C, (**2**) 35 °C, (**3**) 45 °C, (**4**) 55 °C (1 M H_2SO_4, $v = 50$ mV s^{-1}). (b) Plot of log i_2 vs $1/T_{el}$ (referred to the active area) in 1 M isopropanol (1 M H_2SO_4, $v = 50$ mV s^{-1}).

4. Conclusion

Platinum coatings on Ti were prepared by a two-step process: partial thermal decomposition of chloroplatinic acid followed by electroreduction of the coating. The cathodic treatment leads to a significant increase in the electrochemically active area. Depending on the preparation temperature, roughness factors up to 570 were obtained. Such electrodes exhibit enhanced electrochemical activity in oxidation of isopropanol mainly due to the high active surface. The electrocatalytic process appears to be similar to that proposed for a smooth Pt electrode; however, the deactivation process is slowed down with increasing surface roughness.

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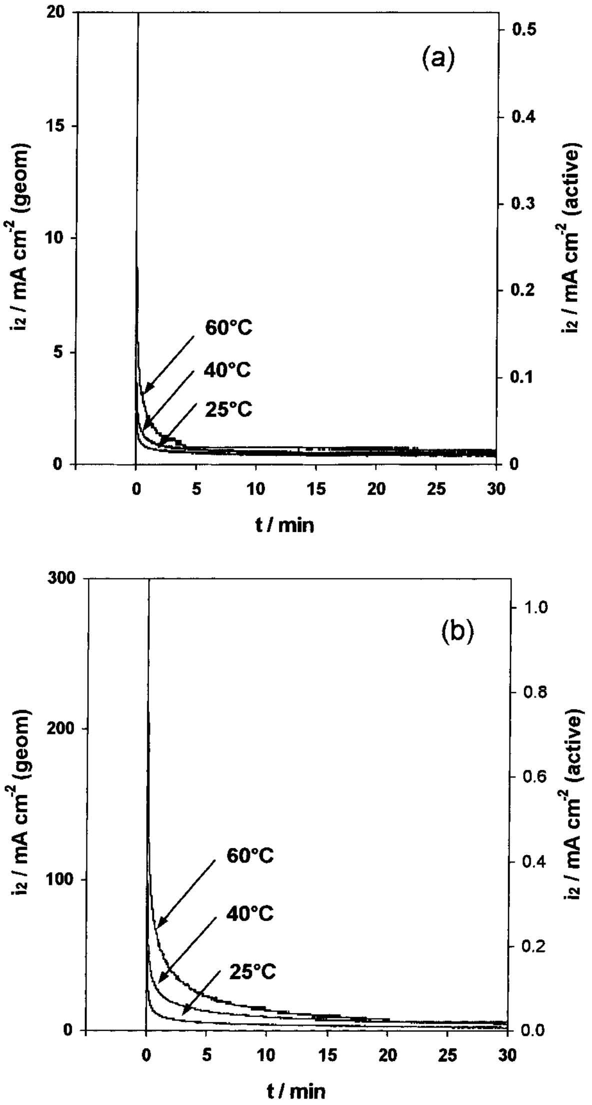

Fig. 7. Chronoamperometry at E_2 in 1 M isopropanol: (a) electrode **1** (500 °C) and (b) electrode **2** (350 °C). Influence of electrolyte temperature T_{el} (60, 40 and 25 °C).

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