JOURNAL OF APPLIED ELECTROCHEMISTRY **15** (1985) 727–735

Preparation and reproducibility of a thermal silver–silver chloride electrode

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Received 20 July 1984; revised 9 October 1984

A new 'dry way' method for the preparation of thermal-type Ag–AgCl electrodes for prolonged accuracy studies is presented. Freshly prepared electrodes were compared with equilibrated Ag–AgCl electrodes selected as reference standards. Bias potential tests allowed a restricted interval for the different factors intervening in the process of preparation to be established with a view to obtaining reference electrodes stable in time. This study has been completed with the superficial observation of the electrodes by microphotographic techniques, and a correlation between the electrochemical behaviour and superficial characteristics is verified.

1. Introduction

Although the hydrogen electrode has been chosen to define the scale of standard potentials its use presents many practical difficulties. Other more readily prepared and more easily controlled electrodes are therefore generally employed. These electrodes, called 'reference electrodes', substitute the SHE satisfactorily and have found a wide range of applications both in theoretical and practical studies due to their characteristics of electrochemical reversibility, high exchange current (i_0) and minimum polarization on small currents.

One of the best known and generally accepted is the second-kind Ag–AgCl electrode, reversible to the Cl^- ion in agreement with

$$Ag_{(s)} + Cl^-_{(aq)} \rightleftharpoons AgCl_{(s)} + e \qquad (1)$$

The simplicity of the equilibrium, the solid nature of the metal and the physical properties (adherence, porosity, etc.) of the solid phase AgCl on the silver give this electrode obvious advantages over the calomel electrode in many applications.

The monographs by Janz and Taniguchi [1] and Janz [2], devoted to this electrode, compile very complete information on its preparation, characteristics and behaviour. Different methods for its manufacture have been described in which electrolytic processes, chemical processes alone or a combination of both are used, Pt being commonly employed as a support or base of the components of the electrode. The single anodizing of Ag wires has also been advocated [3].

Different types of electrode are thus obtained, the degree of coincidence of which has occasionally been verified. Smith and Taylor [4] confirm that the reproducibility among them is of the same order, with an average deviation of 0.02 mV. However, the paper by Bates and Macaskill [5] establishes that the present inaccuracy of the standard potential $E^0_{Ag-AgCl}$ (vs SHE) is 0.2 mV, recommending the use of the $Pt(H_2)$–HCl 0.01 M, AgCl–Ag cell emf as a practical rule for the standardization of these electrodes.

The existence of specific effects on the different methods of preparation and even within them is evident. In an attempt to explain these differences, possible contaminations brought about by the use of solutions (Pt silver-plating step in media with CN^-, anodizing step with KCl or HCl solutions, washing operations, etc.) have been mentioned.

The complexity of the recommended methods of preparation and the current commercialization of instrumental techniques are responsible for the fact that many research workers depend

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on electrodes supplied by the manufacturers of the instruments they use. This leads to the consideration of two important facts: the confident acceptance of such electrodes and the dependence from habit on this source of supply and restocking which may prove expensive.

In our interest in establishing a technique which would permit the preparation in simple operations of Ag–AgCl electrodes of correct and stable response of the potential, i.e. the objective of this work, attention was centred on the 'thermal' method proposed by Rule and La Mer [6] and developed in detail by other authors [7–9]. This review allowed modifications to be introduced which greatly facilitated preparation, while a study was carried out by electrochemical methods (bias potential tests) and superficial observation (SEM (scanning electron microscopy) and XES (X-ray energy spectrometry)) allowing the optimum conditions of their behaviour to be determined.

2. Experimental details

2.1. *Products*

2.1.1. Ag_2O. The method of preparation described by Taniguchi and Janz [10] and Janz [2], with analytical grade $AgNO_3$ and NaOH as starting materials, was adopted. The Ag_2O was precipitated by adding a solution of NaOH to a vigorously stirred solution of $AgNO_3$; stirring was continued until homogeneity and complete precipitation was achieved. Thorough washing of the resulting precipitate was then required to ensure the removal of water soluble impurities. The final aqueous paste was transferred to a weighing bottle and submitted to vacuum drying at 100–120° C for several days with periodic interruptions to disperse the product with a stainless steel spatula. The dry product was ground in an agate mortar and finally stored.

2.1.2. $AgClO_3$. The product was obtained by an exchange reaction with concentrated solutions (approximately 10 M) of analytical grade $AgNO_3$ and $NaClO_3$ and was recrystallized three times in aqueous medium. Precipitation was achieved by slowly pouring the $AgNO_3$ solution with mild shaking onto the hot $NaClO_3$ solution (85° C) in an Erlenmeyer. The mixture was allowed to cool and was kept overnight at 3–5° C to complete the crystallization of the $AgClO_3$. After decanting, the crystals were dissolved by heating with a minimum amount of water and recrystallization again, this operation being repeated twice further. Finally the crystals were washed quickly with conductivity water in a sintered glass funnel by suction and were oven-dried at 100° C, being dispersed at intervals with a spatula to obtain a loose product. The salt thus obtained was stored in an amber glass bottle.

2.1.3. KCl. The analytical grade salt was purified in accordance with the instructions of Janz [2] in order to reduce its bromide content to a minimum.

2.1.4. Hg_2Cl_2. Calomel was prepared by chemical precipitation as recommended by Hills and Ives [11] with a view to the formation of the pearly calomel–mercury skin in the dry state.

2.1.5. Electrode base. Ag and Pt wires, purity not below 99.95%, 0.25–1.0 mm in diameter and 2.5–3.0 cm in length were used. After washing in hot acetone and distilled water they were annealed by heating at 800° C for 2 h and slowly cooled in the furnace.

2.2. *Method of preparation of the electrodes*

Weighed amounts of Ag_2O and $AgClO_3$ were ground and well mixed in an agate mortar and transferred to moulds in the form of small Pyrex glass tubes (inner diameter 2.5 mm, length 3 cm, closed at one end and with a flat inner-bottom) (Fig. 1a). The mixture was lightly pressed with a flat-ended glass rod to a height of 2 cm and the Pt or Ag wire was finally inserted at the centre to a depth of 1.0–1.5 cm. The glass moulds were placed in cylindrical holes 2 cm deep in a stainless steel block (diameter 5 cm, height 2.5 cm) in order to ensure homogeneous heating. The block was set in the centre of an electric tube furnace with a horizontal heating chamber and the temperature was raised slowly over 30–40 min to the desired value. When decomposition was completed in accordance with the programme the mixture was left to cool in the furnace for several hours.

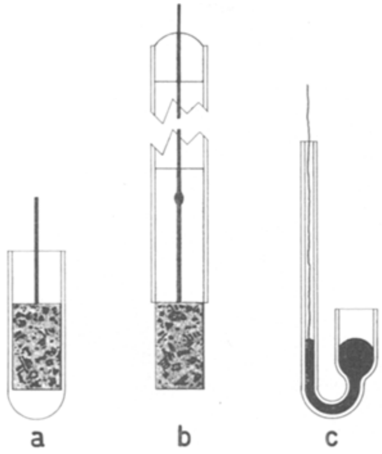


Fig. 1. (a) Solid mixture inside the mould with metal base at the centre; (b) the finished electrode; and (c) calomel electrode.

The operations which followed were: (a) extending the free end of the Pt or Ag wire by soldering to an 8–10 cm auxiliary Cu wire of the same diameter; (b) separating the moulding tube either directly (there is generally no adherence) or by breaking it by pressing lightly in a screw clamp or with a gentle blow of a hammer; and (c) providing the electrode with a system of insulation to facilitate handling.

In our study this last stage was readily solved by means of a Pyrex glass tube of small diameter to protect both the solder and free Pt or Ag wire, both ends being carefully sealed with bicomponent epoxy resin (Fig. 1b).

2.3. *Control techniques*

2.3.1. Thermal decomposition. The decomposition was found in every case to correspond stoichiometrically to the loss expected (within 1%) by weighing the mould, the amount of mixture and the electrode.

2.3.2. Electrochemical techniques. A glass vessel (750 ml volume), with seven openings in the lid in which the series of electrodes were arranged by means of stoppers, was employed for the intercomparative electrochemical study. The electrolytic solution was KCl (0.1 M) saturated with AgCl. The measurements of bias potential among the electrodes were displayed by means of a Keithley 191 DMM Digital Multimeter with an input impedance of over 1000 MΩ. In the range of measurement of d.c. voltage the accuracy was 0.007%. The studies were carried out among electrodes of the same series (an average of four) in order to establish their reproducibility, and among electrodes from different series to determine stability and/or deviation from the potential and to compare them with an electrode previously selected as reference. In order to verify the goodness of the potential of the electrodes the emf of the cell without the liquid junction ($Hg–Hg_2Cl_{2(s)}$, KCl (0.1 M), $AgCl_{(s)}–Ag$) was checked using calomel electrodes (Fig. 1c), prepared following the method recommended by Hills and Ives [11]. Contact with the tridistilled Hg was with a Pt wire. At 25° C the emf of the cell, independent of the concentration of Cl^-, was 45.7 ± 0.1 mV [12–13].

2.3.3. Superficial techniques. The study of the superficial topography of the electrodes was carried out with a Hitachi S-450 scanning electron microscope. The analysis of the X-ray region of the electromagnetic spectrum was performed with an X-ray S-4004 unit together with a Kevex Micro-X 7000 X-ray spectrometer.

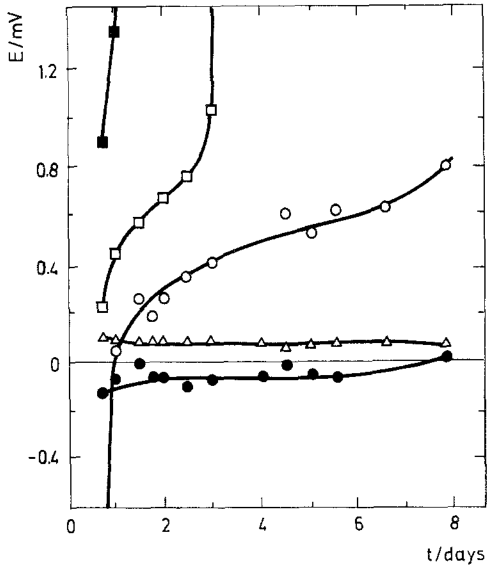


Fig. 2. Effect of increasing $Ag_2O:AgClO_3$ weight relationships on equilibrium of fresh thermal electrodes: ○, 3:1; □, 5:1; △, 7:1; ●, 9:1; ■, 12:1. (vs a selected aged reference electrode.)

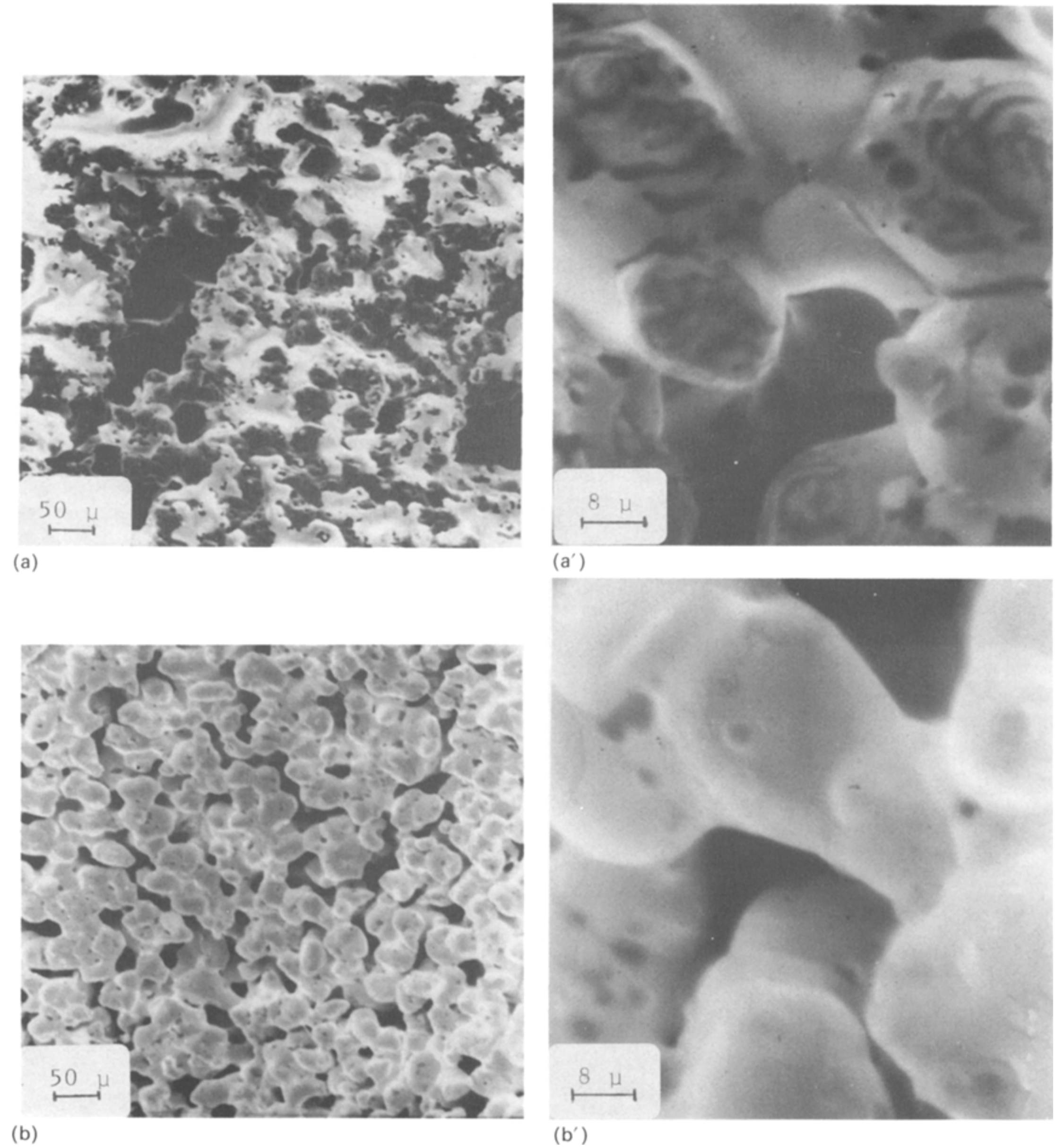


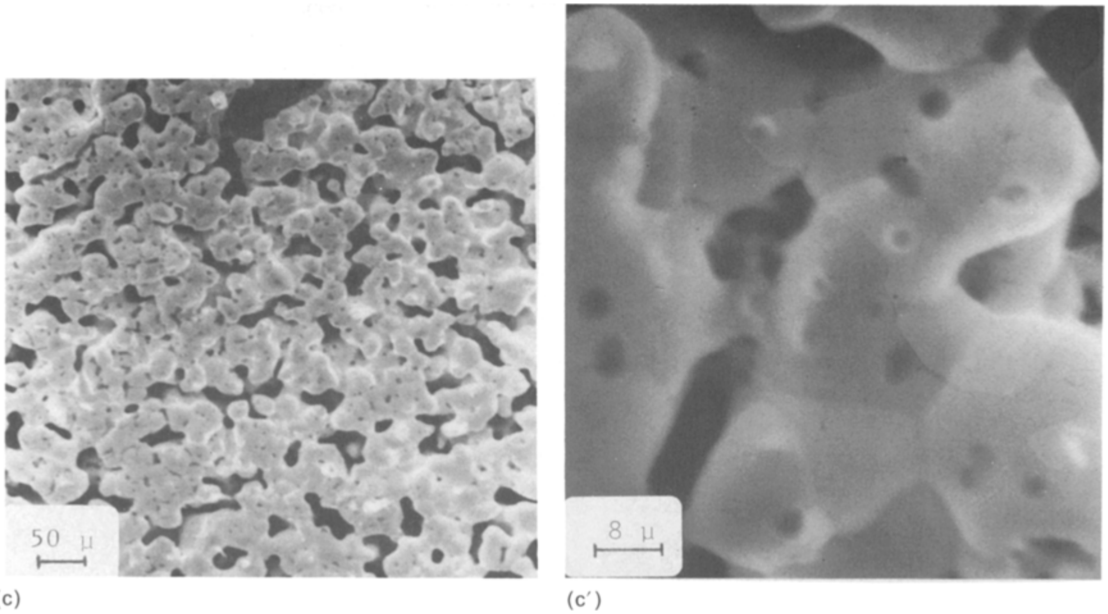
Fig. 3. Effect of increasing Ag_2O:$AgClO_3$ weight relationships on superficial morphology of fresh thermal electrodes: (a), (a′) 3:1; (b), (b′) 7:1; (c), (c′) 12:1.

3. Results

The influence of the main factors involved in the method of preparation of the electrodes on their subsequent electrochemical behaviour (accuracy, stability and reproducibility) and the correlation with superficial structural characteristics (morphology, porosity, etc.) were analysed experimentally.

3.1. *Composition of the mixture*

The electrochemical control defined a zone of optimum composition of the Ag_2O:$AgClO_3$ mixtures based on the performance of the electrodes and corresponding to the ratios 7:1 and 9:1 in weight. Beyond these limits the stability of the potential decreases and deviations are observed (Fig. 2). The SEM microphotographs



(c) (c′)

Fig. 3 continued.

(Fig. 3) of freshly prepared electrodes show how the structure varies as the proportion of Ag in the electrode increases. In the optimum range the morphology is more open and porous in comparison with the compact and cemented forms of the other compositions.

3.2. *Decomposition temperature*

The study of bias potentials showed a difference (Fig. 4) between (a) 'warm' electrodes (decomposition temp ⩽ 500° C) and 'hot' electrodes (decomposition temp ⩾ 720° C), which showed good stability although there was divergence between them; and (b) those obtained at intermediate temperatures (approximately 650° C), the behaviour of which was clearly unstable. The reproducibility and stability in the value of the emf of the cell without the liquid junction demonstrated the superior behaviour of the 'warm' electrodes in comparison to the 'hot' ones. The SEM analysis (Fig. 5) showed the open structure of the 'warm' electrodes and also the loss of porosity as the temperature of decomposition increased. Around 720° C porosity again increased although the structure becomes denser.

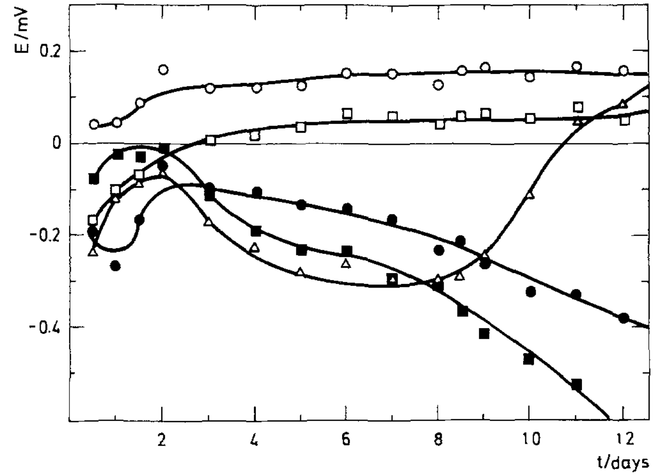


Fig. 4. Effect of increasing decomposition temperature (° C) on equilibrium of fresh 7:1 thermal electrodes: ○, 445; □, 500; △, 650; ●, 720; ■, 780.

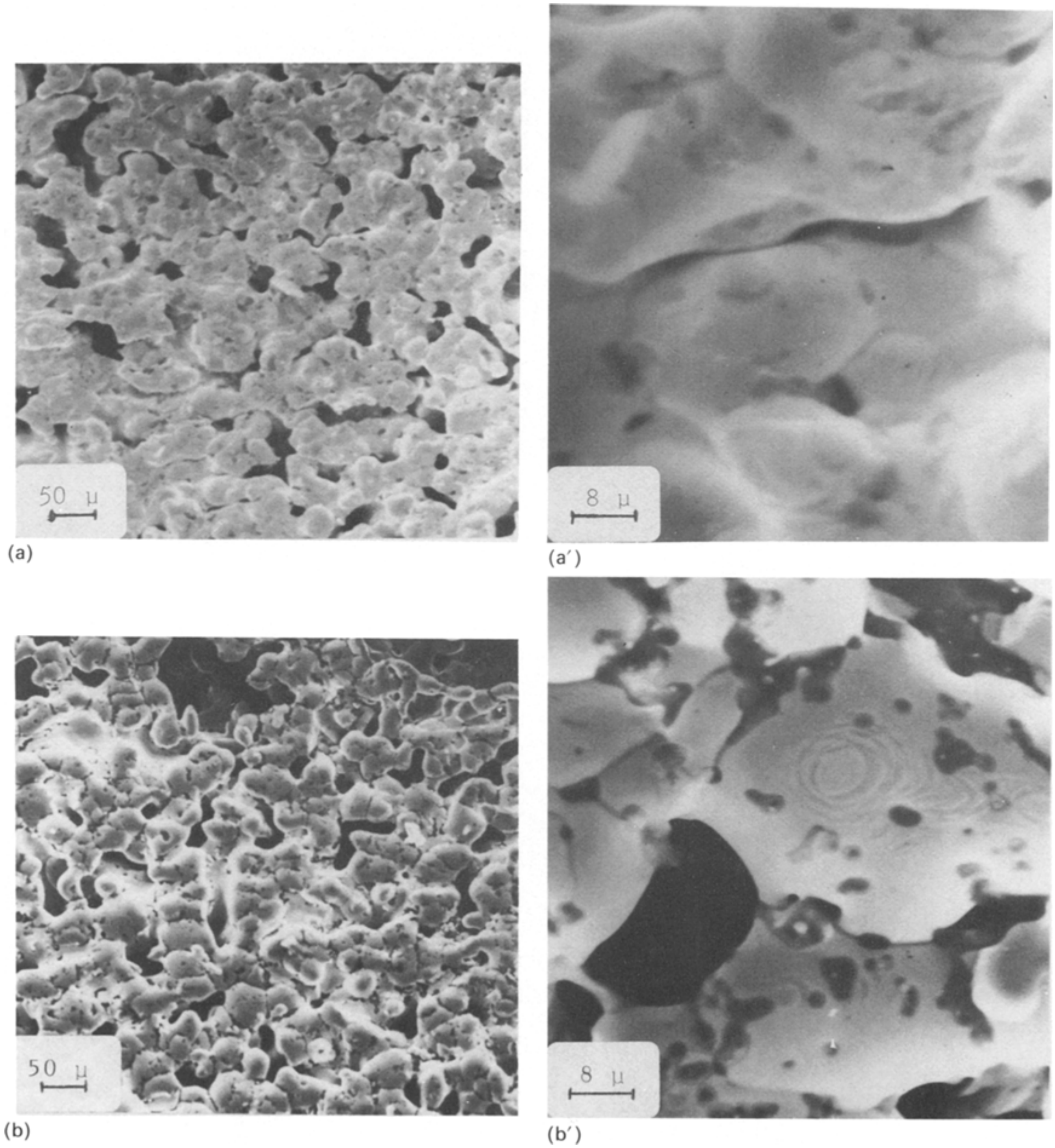
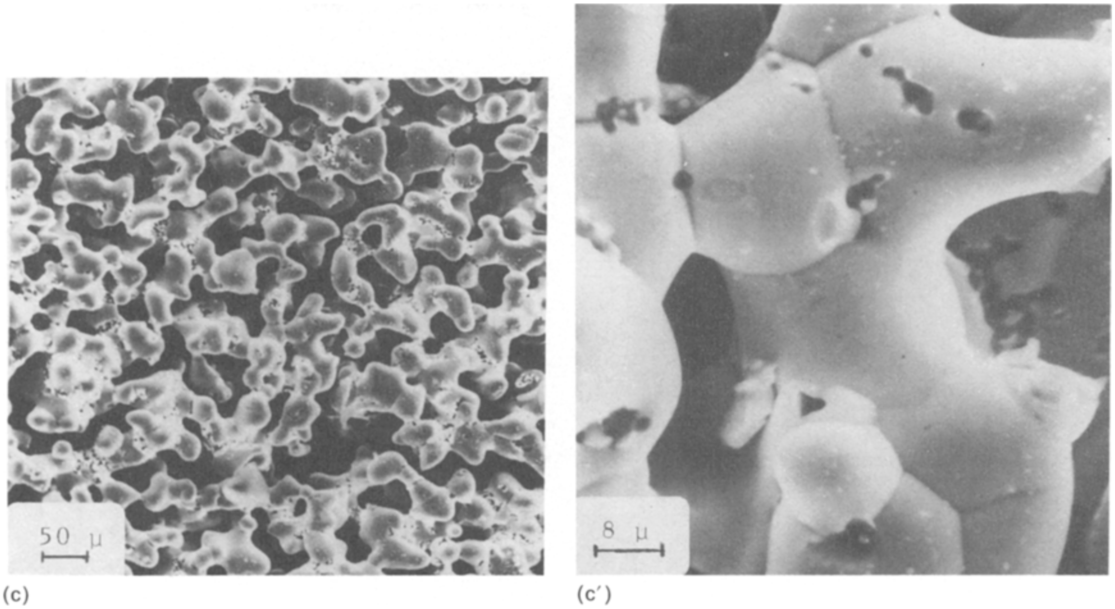


Fig. 5. Effect of increasing decomposition temperature (° C) on superficial morphology of fresh 7:1 thermal electrodes: (a), (a′) 500; (b), (b′) 650; (c), (c′) 780.

3.3. *Decomposition time*

Experiments in which the decomposition temperature was maintained within the range of 7–120 min showed no significant changes in the behaviour of the electrodes. The potential showed a good degree of coherence and deviation was below $\pm 0.1\,\mathrm{mV}$. The SEM observation confirmed that the covering of AgCl did not affect the morphology of the primary superficial structures although some cementing of the pores was detected when the decomposition time was prolonged to 120 min.



(c) (c′)

Fig. 5 continued.

3.4. *Ageing of the electrodes*

The stability of the bias potentials was verified satisfactorily over a period of three months at $E < 50\ \mu V$ with electrodes prepared under the composition and temperature conditions considered 'optimum' (Fig. 6). The information provided by the SEM micrographs proved very interesting (Fig. 7), confirming the dynamic nature of the electrochemical equilibrium of the electrodes in the electrolytic solution as the regular and 'levelling' evolution of the superficial elements became apparent without the loss of the original open and porous basic structure. However, over much longer periods of use compact zones were observed resulting from the deterioration of the aforementioned initial structures.

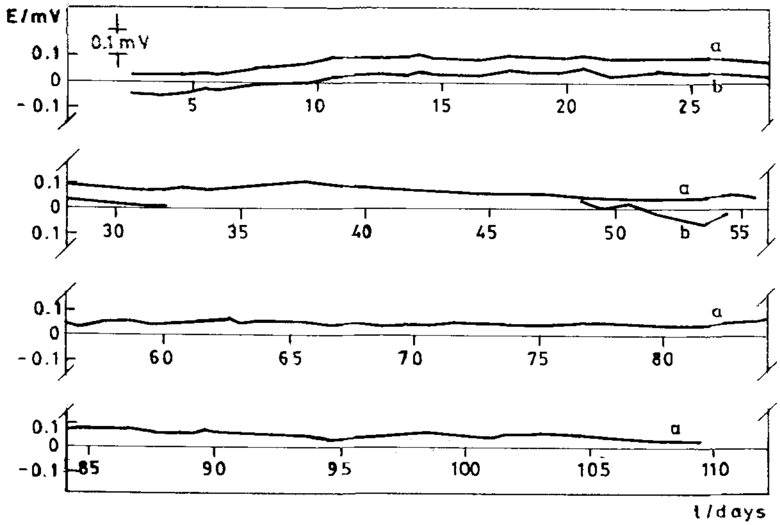


Fig. 6. Equilibrium of fresh thermal electrodes (7:1 and 500° C).

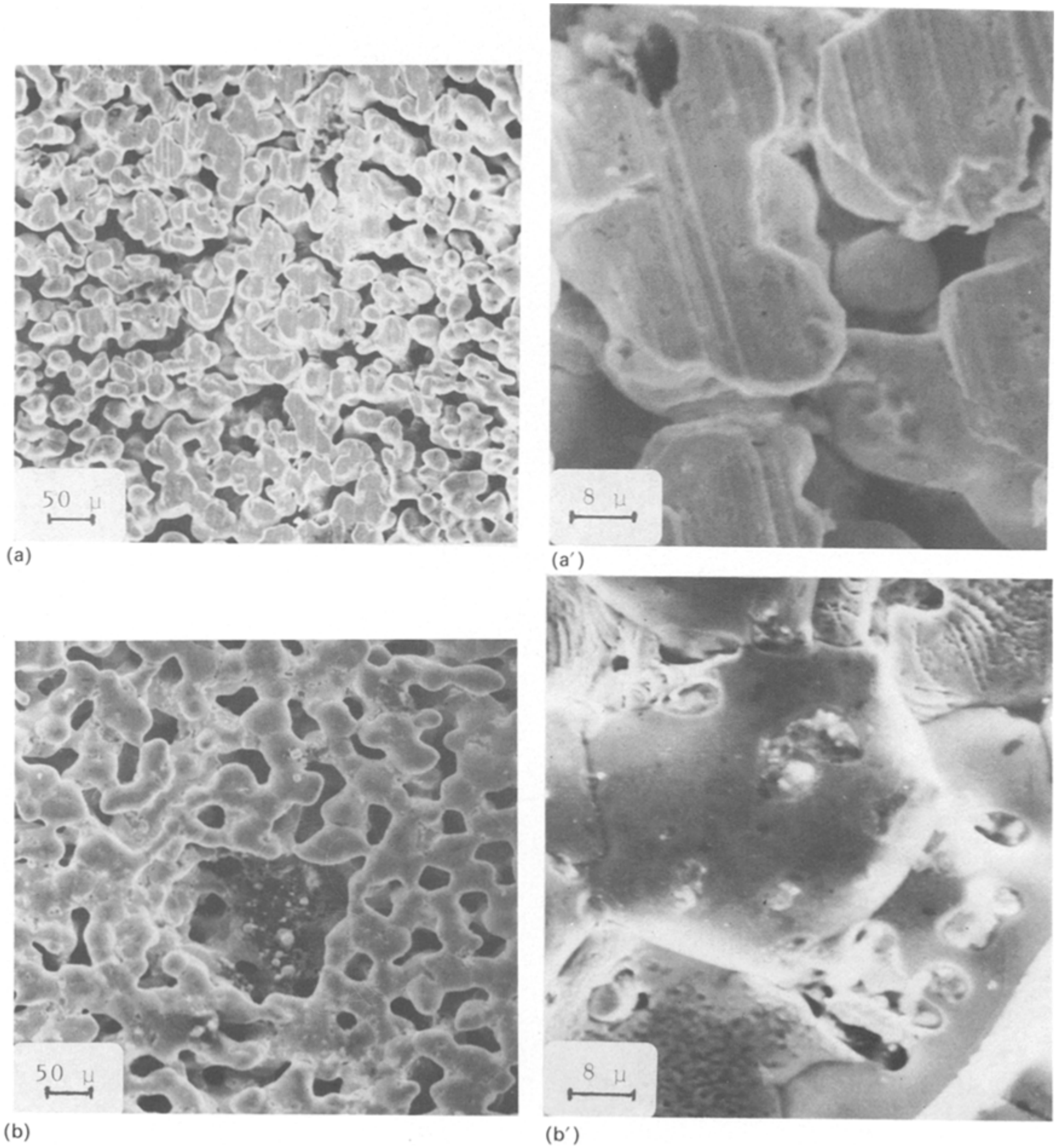


Fig. 7. Effect of ageing on superficial morphology of thermal electrodes (7:1; 500° C and 7 min): (a) 1 month in 1 M KCl solution; (b) 2 months in saturated KCl solution.

3.5. *Metal base*

The nature of the metal wire (Pt or Ag), whether previously annealed or not, and the thickness of the wire do not bring about significant modifications in the behaviour of the electrodes. Anomalies in the functioning of defective electrodes in which the wire was visible at the surface could be observed occasionally. Studies of electrodes with tungsten wires led to unstable and unsatisfactory results.

4. Discussion

The essential modification that this method of preparation provides to 'thermal' Ag–AgCl elec-

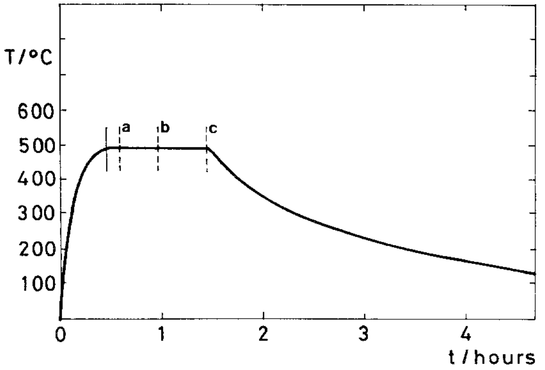


Fig. 8. Typical temperature–time plot of the thermal process. Decomposition time (min): (a) 7; (b) 30; (c) 60.

trodes consists of the application of the so-called 'dry way' rather than the traditionally used wet paste of both components. Using this method the pre-drying operation is avoided as well as the associated uncontrolled effects of cracking which affect the macroscopic form of the electrode and the superficial structure. The homogeneity of the mixture achieved by joint grinding of the components in the mortar is satisfactory as shown in the XES distribution maps of the Ag and Cl atoms, independent of the proportion of both components and/or the decomposition temperature.

The lesser influence of the decomposition time pointed out in Section 3.3 can be attributed to the procedure followed whereby heating of the furnace was interrupted and the electrodes allowed to cool spontaneously inside, a process which took place over a long period of time (Fig. 8). It should be noted that at a temperature above 400° C the mixture decomposed quickly and the melting point of AgCl is 450° C.

The SEM method of superficial microscopic observation, jointly applied with the electrochemical measurements in the study of the electrodes, provides valuable information. These observations allow interpretation of the 'good' behaviour of the electrodes in terms of a series of properties such as:

(a) Formation of porous and open morphological structures dependent on the composition of the Ag_2O–$AgClO_3$ mixture.

(b) Existence of primary forms of Ag with homogeneous covering of the AgCl phase governed by the temperature of decomposition.

(c) Regular evolution of the rounded forms during ageing without loss of the fundamental structure.

Acknowledgements

The Edaphology Department (University of La Laguna) is gratefully acknowledged for running microphotographic techniques.

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