Effect of tin concentration on the electrical properties of ceramic membranes used as separators in electrochemical reactors

M. García-Gabaldón [a], V. Pérez-Herranz [a,*], E. Sánchez [b], S. Mestre [b]

[a] Departamento de Ingeniería Química y Nuclear, Universidad Politécnica de Valencia, Camino de Vera s/n, 46022 Valencia, Spain
[b] Instituto de Tecnología Cerámica, Universidad Jaume I, Campus Universitario Riu Sec, 12006 Castellón, Spain

ARTICLE INFO

ABSTRACT

This paper deals with the study of different microporous ceramic membranes used as separators in electrochemical reactors to treat the activating solutions coming from the electroless plating of polymers. The main component of these solutions is Sn(IV) in HCl as diluting agent, then, the effect of the complex species formed between Sn^{4+} and Cl^- ions on the electrical properties of the membranes has been studied.

The porosity of the membranes was modified by changing the manufacturing pressure, P, and by the addition of starch to the alumina–kaolin matrix. In the absence of starch the pore-size distribution becomes more uniform with the increase of the manufacturing pressure, and lower porosities and average pore sizes were obtained. On the other hand, the porosity and the average pore size increase with the addition of starch to the alumina–kaolin matrix, but pore-size distribution was less uniform and becomes bimodal with two different characteristic pore diameters.

Independently of the manufacturing pressure and the starch percentage, for the rinse water solutions is convenient to keep low concentrations of Sn(IV), since higher values of the effective electrical conductivity of the membrane were obtained, whilst for treating the activating-wasted baths is better to maintain concentrations of Sn(IV) lower than 0.1 M in order to reach high values of the effective electrical conductivity of the membrane.

1. Introduction

The presence of separators in electrochemical reactors is essential when reagents or products of one electrode process are susceptible to reaction at the counter electrode [1]. In the particular case of the electrochemical recovery of the tin present in the activating solutions coming from the electroless plating of polymers, the use of a separator is justified in order to prevent the oxidation of Sn(II) at the anode which would lead to the loss of current efficiency in the overall process. However, the separator introduces an ohmic drop which contributes to the increase of the overall cell voltage.

There are varieties of materials used as separators in electrochemical reactors, such as ion-exchange membranes and microporous ceramic membranes. Ion-exchange membranes separate ions from solution depending on their polarity and number of charge. The application of these membranes in electrochemical processes has been limited by the poor chemical stability of the materials, membrane fouling and concentration polarization which may lead to the increase of the electrical resistance and

to the precipitation of metallic hydroxides on the membrane surface [2–4]. These constrains limit the service time and ensure these type of membranes can only be used in dilute solutions [5]. Consequently, in certain processes is more convenient to work with ceramic membranes instead of ion-exchange membranes, since, although ceramic separators present less selectivity than ion-exchange membranes, they are more stable in severe alkaline or acidic media and to the action of oxidizing agents [2,5,6], and they present long life in service due to the ability to be cleaned.

Microporous ceramic membranes act as barriers to convection and diffusion due to their small pore size but permit the transport of solvent, solutes and ions through hydraulic permeability, which ensure electrical continuity through the system. In the absence of fouling and concentration polarization, the permeability of the ceramic membranes and the efficiency of the separation process are mainly determined by the membrane pore structure, i.e. the porosity and pore-size distribution. The application of ceramic membranes in pollution prevention, resource recovery and waste treatment activities is increasing due to their excellent mechanical strength and tolerance to solvents, as well as pH, oxidation and temperature extremes [7,8]. In addition, the amphoteric properties of ceramic surfaces result in uniquely versatile membranes for water and wastewater treatment [9,10].

* Corresponding author. Tel.: +34 96 3877632; fax: +34 96 3877639.
E-mail address: vperez@iqn.upv.es (V. Pérez-Herranz).

In a previous work [11] the effect of the structural parameters (porosity and pore-size distribution) on the effective electrical conductivity of the ceramic membranes was studied for different ceramic membranes in HCl media. In all cases, the effect of the surface conductivity could be neglected and the electrical properties of the membranes, i.e. effective electrical conductivity (κ_{eff}) and conductivity factor (f_c), were mainly affected by the porosity (ε), if the pore-size distribution was uniform. A correlation between the conductivity factor and the porosity was also obtained.

In the case of the activating solutions of the electroless plating of polymers, they are mainly composed of $SnCl_2$ and $PdCl_2$ in HCl as diluting agent, where tin is the major specie. As a consequence of palladium reduction, and because of direct oxidation by air, Sn(II) is oxidized to Sn(IV), which may form complex species in the presence of chloride ions. On the other hand, Sn(IV) presents a high tendency to form hydroxyl complexes at moderate pH values [12,13]. Those different complex species formed possess different size and mobility, and consequently, may affect the values of the effective electrical conductivity of the ceramic membranes, since their concentration inside the pores may be quite different from that in solution. On the other hand, the quantity of palladium present in both the wasted and diluted activating baths is about 100 times lower than the amount of tin present in the same baths, therefore, the effect of palladium on the electrical parameters of the membranes can be considered negligible. In this way, the present paper deals with the study of the effect of Sn(IV) concentration on the electrical parameters of the same ceramic membranes as those studied previously [11] for a concentration range of Sn(IV) similar to that occurring in the activated-wasted baths and in the rinse water solutions of the activating solutions of the electroless plating of polymers.

2. Experimental

2.1. Preparation of the ceramic membranes

The manufacturing process and the pore structure characterization of the separators is described in more detail in a previous work [11]. The ceramic membranes used were synthesized from a mixture of alumina (provided by Alcoa Alumina Española, S.A.) and kaolin (from Caobar, S.A.), proportioned so as to produce a raw material composition that was readily procesable by uniaxial dry pressing, which was the forming method chosen. The manufacturing pressure (P) was varied from 250 to 900 kg cm^{-2} and organic matter (starch from potatoes, Fluka, A.G.) was added to the alumina–kaolin matrix within a range of 0–20%. After sintering, the density, ρ, thickness, e, porosity, ε, average pore diameter, $d_{p_{av}}$ and pore-size distribution were determined. Table 1 presents the main characteristics of the ceramic membranes used in the present work.

Table 1
Characteristics of the ceramic membranes

| Separator	% starch	P (kg cm^{-2})	ρ (g cm^{-3})	e (cm)	$d_{p_{av}}$ (μm)	ε
S-0-250	0	250	1.60	0.67	0.37	0.500
S-0-500	0	500	1.79	0.66	0.28	0.483
S-0-700	0	700	1.86	0.64	0.27	0.456
S-0-900	0	900	1.90	0.62	0.26	0.428
S-5-250	5	250	1.59	0.71	0.43	0.546
S-5-500	5	500	1.68	0.68	0.33	0.520
S-10-250	10	250	1.51	0.71	0.46	0.584
S-10-500	10	500	1.55	0.71	0.38	0.567
S-15-250	15	250	1.33	0.78	0.52	0.624
S-15-500	15	500	1.44	0.72	0.40	0.576
S-20-250	20	250	1.23	0.79	0.68	0.632
S-20-500	20	500	1.33	0.73	0.51	0.632
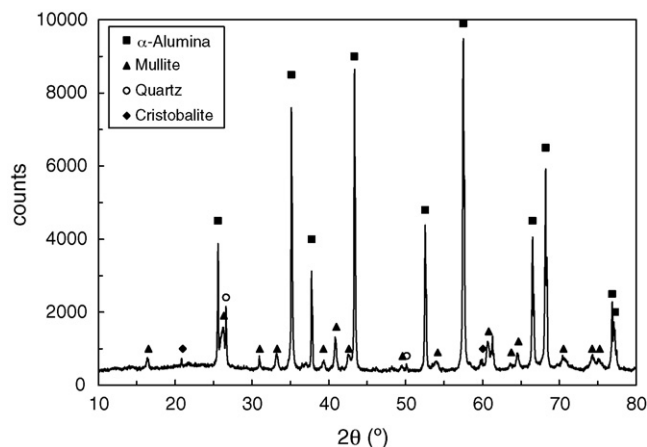
Fig. 1. XRD analysis of the membranes synthesized after 4 h treatment at 1200 °C.

Pore-size distribution was determined by Mercury Intrusion Porosimetry on a Micromeritics, Model Autopore III porosimeter and the surface morphology of the membranes was observed by scanning electron microscopy (Phillips XL50). The crystalline phases present in the ceramic materials were determined by X-ray diffraction (XRD) on a Phillips, Model PW 1840 diffractometer. The XRD analysis of the membranes synthesized after 4 h of treatment at 1200 °C (Fig. 1) revealed that the presence of cristobalite was negligible, and α-alumina and mullite were the predominant crystalline phases. A large quantity of cristobalite can give rise to cracks in the membrane during the cooling stretch of the thermal treatment, and hence affects the mechanical strength and the pore-size distribution [14].

2.2. Electrical measurement

A schematic diagram of the experimental arrangement can be seen in Fig. 2. The electrochemical cell consisted of two Pyrex glass chambers with the ceramic membrane placed between them. Prior to use, the membranes were submerged in 1 M HCl for 24 h to remove impurities and then were washed with distilled water. The solution under consideration was forced through the membrane by current imposition for 4 h.

Two 12.57 cm^2 Ag/AgCl discs being parallel to the membranes were fixed at the end of each compartment. These two Ag/AgCl discs
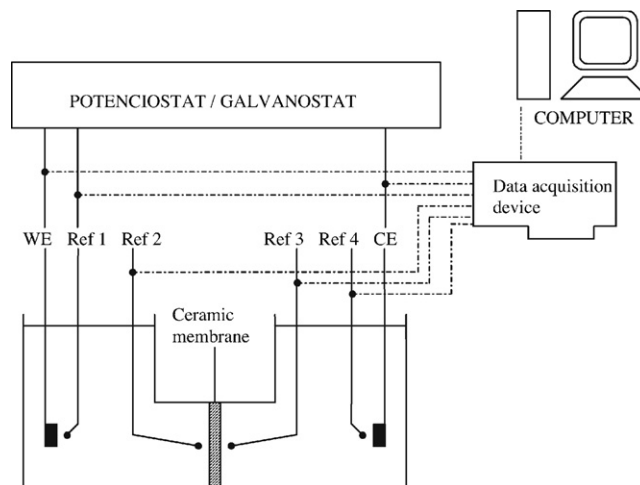

Fig. 2. Schematic of the experimental arrangement.