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Dependence of the electric field on the specific surface conductivity of PbO_2 , $3PbO \cdot PbSO_4$ and $4PbO \cdot PbSO_4$

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Abstract

Our investigation is based on the relationship between the electric field and the surface conductivity of PbO₂, 3PbO · PbSO₄ and 4PbO · PbSO₄, and is evaluated at different temperatures and duration times. We used a suspension of each sample in a weak solution of H_2SO_4 (2.5×10⁻⁶ M) which has been titrated with a stronger acid solution of H_2SO_4 (1.58×10⁻³ M). The conductivity was measured during agitation, \vec{K} , and during sedimentation, K. When $\vec{K}/K = 1$, the iso-conductivity point under these specific conditions was analysed. The electrical field influenced the displacement of the particles in the solution.

Keywords: Lead sulfate; Lead dioxide; Surface conductivity

1. Introduction

This paper is based on the relationship between the electrical field and the specific surface conductivity of PbO_2 samples which have been submitted to different thermal treatments.

Wien (cited in Ref. [1]) discovered that for an electrical field of high intensity, the electrical conductivity increased until reaching a certain limit. Dukhin and co-workers [2,3] based their work on the polygorskite clay particles in suspension (non-acid solution), in order to determine the iso-conductivity, the specific surface conductivity and also to study the movement of particles. This study was carried out on very light particles, which are easy to keep in suspension.

In order to obtain a good specific surface conductivity, we sought an ideal agitation the PbO_2 particles being too heavy to get a good suspension.

2. Theory

2.1. Electrical conductivity of colloids

The colloidal conductivity is [2,3]

$$\tilde{K} = F^{-1}K \tag{1}$$

in the case of a very high concentration of the electrolyte or in the case of non-charged colloidal particles. K is the con-

0378-7753/97/\$17.00 © 1997 Elsevier Science S.A. All rights reserved *PII* \$0378-7753(96)02503-7 ductivity of the dispersed medium, \bar{K} is the conductivity in a stirred medium; F is the coefficient of the electrical resistance obtained from the the surface geometry of the pores.

2.2. The effect of a change in conductivity

The electrical current lines passing round the surface of non-conductive particles become longer which means that there is a decrease in specific conductivity of the system, because F is greater than unity [4]. The electrical field polarizes the particles and has an impact on their movements, leading to an increase in conductivity of the thin electrical double layer.

$$xa \gg 1 \text{ and } P \ll 1$$
 (2)

$$K_{\rm iso} = \frac{X'}{a(2+4.5P)} \tag{3}$$

where P represents the fraction of big particles in the solution. K_{iso} is considered as the point where the factors decreasing/increasing the conductivity are in balance

$$X' = K_{iso}a(2 + 4.5P)$$
(4)

where X' is the specific surface conductivity and a the mean half diameter of the particles.

In this case the thickness of the electrical double layer of the colloidal particles is defined as

$$x = 3.06C^{-0.5} \times 10^{-10} \text{ (m)}$$
⁽⁵⁾

where C is the concentration of the solution and x the thickness of the electrical double layer [4-6].

3. Experimental

3.1. Procedure and experimental condition

Thermal treatments used for the different samples were made in order to follow the changes in specific surface conductivity versus temperature.

We used the suspension of each PbO₂ sample in a solution of weak acidity based on H_2SO_4 (2.5×10⁻⁶ M). This solution was titrated with a more concentrated solution of H_2SO_4 $(1.58 \times 10^{-3} \text{ M})$. The conductivity was measured during stirring (\bar{K}) and then during sedimentation (K). The iso-conductivity was calculated under the condition $\bar{K}/K = 1$, in order to find the specific surface conductivity which depends on the electrical field, $X' = F(E^2)$.

The results obtained are illustrated below.

4. Discussion

It has been observed that, for PbO₂, the specific surface conductivity (X') decreased with increasing both the thermal treatment time and the temperature (Fig. 1), while for Fig. 2 the increase in X' depended on the increase of both the tem-

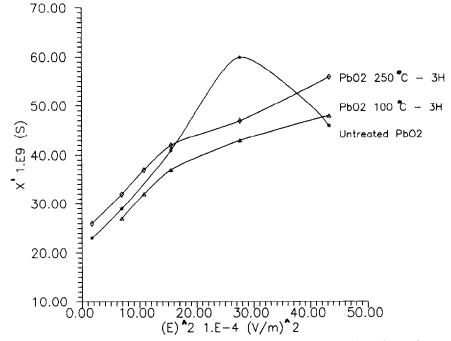


Fig. 1. The specific surface conductivity as a function of the square of the electrical field of the PbO₂ sample.

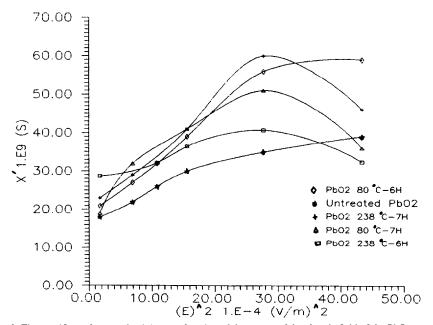


Fig. 2. The specific surface conductivity as a function of the square of the electric field of the PbO2 sample.

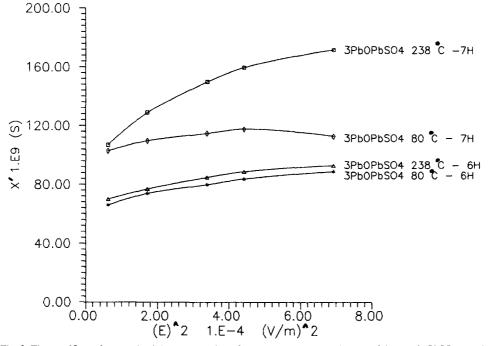


Fig. 3. The specific surface conductivity as a function of the square of the electric field of the 3PbO · PbSO₄ sample.

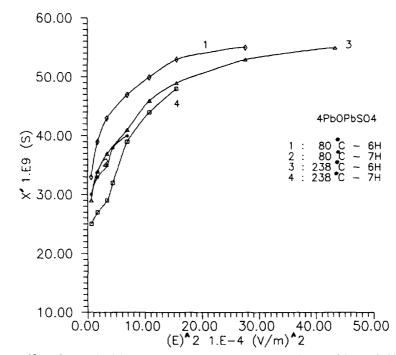


Fig. 4. The specific surface conductivity as a function of the square of the electric field of the 4PbO · PbSO₄ sample.

perature and the electrical field. It can be noticed that the highest value reached by the specific surface conductivity (X') was that of untreated PbO₂ (60×10^{-9} S). The specific surface conductivity as well as the applied electrical field increased also. Fig. 3 dealing with the sample 3PbO · PbSO₄, showed that the specific surface conductivity increased with the electrical field, the thermal treatment time and the temperature. In Fig. 4, dealing with the sample of 4PbO · PbSO₄, one may observe that for a thermal treatment time of 6 h, the specific surface conductivity (X') decreased when the temperature.

perature increased. However, the other values of X' increased with increasing the thermal treatment.

We have to know that each value of the applied electrical field corresponds to a different value of solution concentration. On the other hand, for each volume of H_2SO_4 a substantial increase in the conductivity (K) can be observed while increasing the electrical field. We thought that the lead dioxide was ionized by H⁺ (dissociated from H_2SO_4). Thus, for the stabilization of the sol, the lead dioxide granule attracts the anions, i.e. SO_4^{2-} , to its surface to form a fixed layer. If

the whole charge of the particles is not zero, the specific surface conductivity increases with increasing solution concentration. Once the equilibrium is reached, the ratio $\bar{K}/K < 1$, i.e., when the number of the ions in the dispersive medium increases and the thickness of the diffusive layer decreases. The influence of the mutual attraction of the ions is charaterized by the current intensity.

This attraction may be more important than the influence of the increase in the total concentration of the electrolyte. In this case the specific surface conductivity decreases with an increase in the concentration of the solution.

5. Conclusions

The increase or decrease in specific surface conductivity is related to the electrical field and also to the number of H^+ ions (dissociated from H_2SO_4) located at the surface of the sample of the lead dioxide. The greater is the surface contact of the sample the greater is the number of ionized particles, implying a high mobility, thus an ideal specific surface conductivity. However, the non-charged particles and an excess of hydronium concentration causes a diminution of the specific surface conductivity because the mobility of the ions decreases.

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