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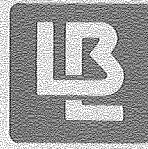
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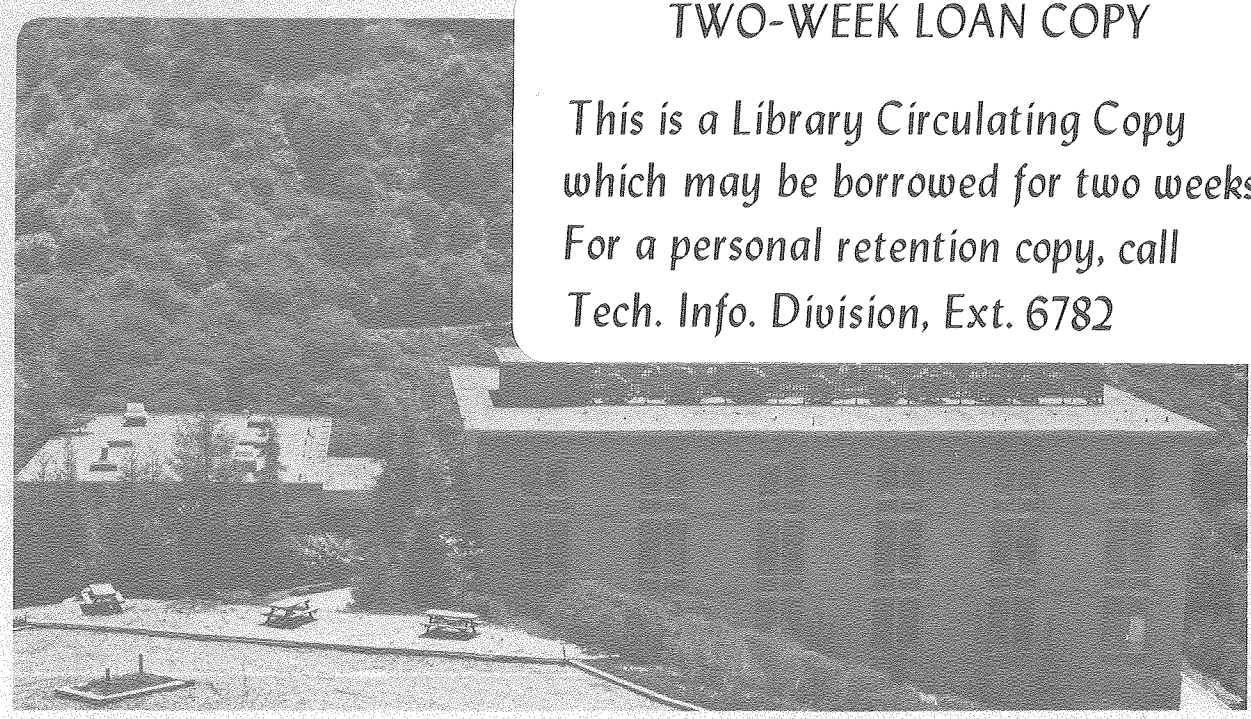
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ELLIPSOMETRY OF SULFATE FILMS ON LEAD
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The growth of PbSO_4 films has been studied using fast in situ automatic ellipsometry. Parameters describing film structure and mechanism of growth have been obtained from measurements. Films are followed from initial nucleation on clean planar electrodes until they are about $0.5 \mu\text{m}$ thick. Constant anodic current (0.1 A/m^2 to 13 A/m^2) and open circuit conditions have been used in H_2SO_4 solutions (1.3 to 5.0M). Experiments were performed under free convection and laminar flow conditions.

Ellipsometer data have been analyzed using a multiparameter fit which models the surface as plano-parallel layers of porous material. Film porosity represents the overall void space between crystals. Thickness of layers is established from porosity and a material balance; refractive index is derived from volume averaging solid anodic product and electrolyte within the pores.

Film porosity, as derived from ellipsometer measurements, is influenced by three experimental variables: applied current density, H_2SO_4 concentration, and flow conditions over the electrode. Conditions which lead to a higher supersaturation of anodic species at the interface leads to a greater number density of crystals which is reflected in reduced porosity. This observation is consistent with a solution precipitation mechanism.

Current efficiency for solid film formation ranges from 75 to 90%. The balance of current forms material which apparently remains "solubilized". Supersaturated ionic species cannot account for the required fluxes away from the surface (necessary high Pb^{+2} concentrations are precluded by potential measurements). The presence of a colloidal species during anodic oxidation of Pb in H_2SO_4 has been indicated previously [2,3]. Scattering of light from large crystals must be considered when discussing ellipsometer-derived film current efficiency. Crystals having dimensions near the wavelength of light ($1/3$ to $1/2 \mu\text{m}$) are optically less visible since part of the incident beam entering them is scattered in non-specular directions.

Formation of new anodic products at the Pb/ PbSO_4 electrode is signaled by a sudden rise in potential during constant current oxidation and a simultaneous change in the slopes of optical parameters ψ and Δ (relative amplitude and relative phase difference) as seen in figure 1, point a. At point b, the current is interrupted (open circuit) and slopes of ψ and Δ are momentarily zero, indicating transient passivation of the electrode. The potential falls to values associated with basic lead sulfates (-0.56 to -0.63V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$ corresponding to $4\text{PbO}\cdot\text{PbSO}_4$ and $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$). At point c, ψ and Δ resume changing due to film formation from corrosion of lead at open circuit. These findings are consistent with the theory that basic sulfates are produced anodically in small amounts and can

passivate the lead electrode [4]. Depassivation occurs when basic sulfates dissolve.

Open circuit corrosion rates were evaluated from ellipsometer measurements at different acid concentrations for periods of up to five minutes. A square dependence on water concentration has been found. This agrees with Lander's data which were obtained from gravimetric measurements over many hours [5].

The cathodic reduction of sulfate films can be observed as a reversal of ψ vs Δ obtained during the previous anodic cycle. Reduction apparently terminates with the onset of H_2 evolution as ψ and Δ no longer change even though they are far from the starting point corresponding to clean Pb. In other words, a large fraction of $PbSO_4$ remains on the surface, apparently unavailable for reduction. Loss of rechargeability is usually attributed to sulfation (formation of "hard" lead sulfate). Recrystallization of $PbSO_4$ deposits which occurs after many cycles over periods of weeks or months leads to sulfation. This does not explain the loss of reduction capability observed here. Present findings suggest that reduced material utilization may also be due to changes on the lead surface (instead of in the sulfate layer) which result in preferred H_2 evolution.

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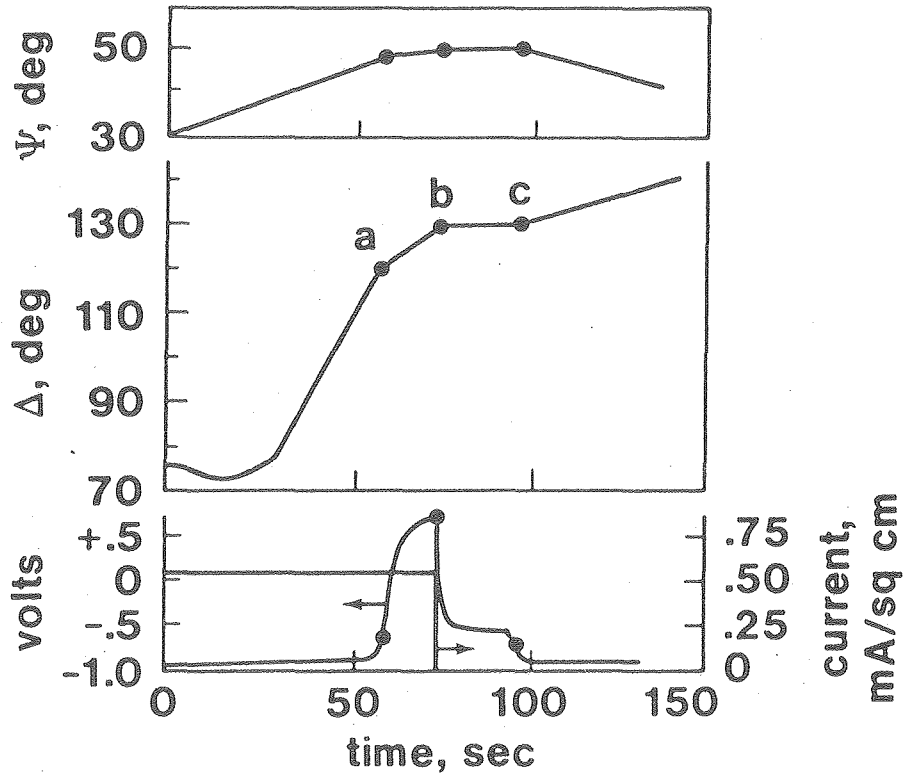


Fig. 1 Potential and optical transients observed during high potential oxidation (a to b) and passivation (b to c). Volts are measured against Hg/Hg₂SO₄ electrode in the same solution (3.1 M. H₂SO₄) as the working electrode. Depassivation occurs at c where ψ and Δ resume changing after arrest between b and c.

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