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POWER SOURCES 7

RESEARCH AND DEVELOPMENT IN NON-MECHANICAL ELECTRICAL POWER SOURCES

Proceedings of the 11th International Symposium
held at Brighton, September 1978

SPONSORED BY THE JOINT SERVICES
ELECTRICAL POWER SOURCES COMMITTEE

Edited by
J. THOMPSON



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POWER SOURCES 7

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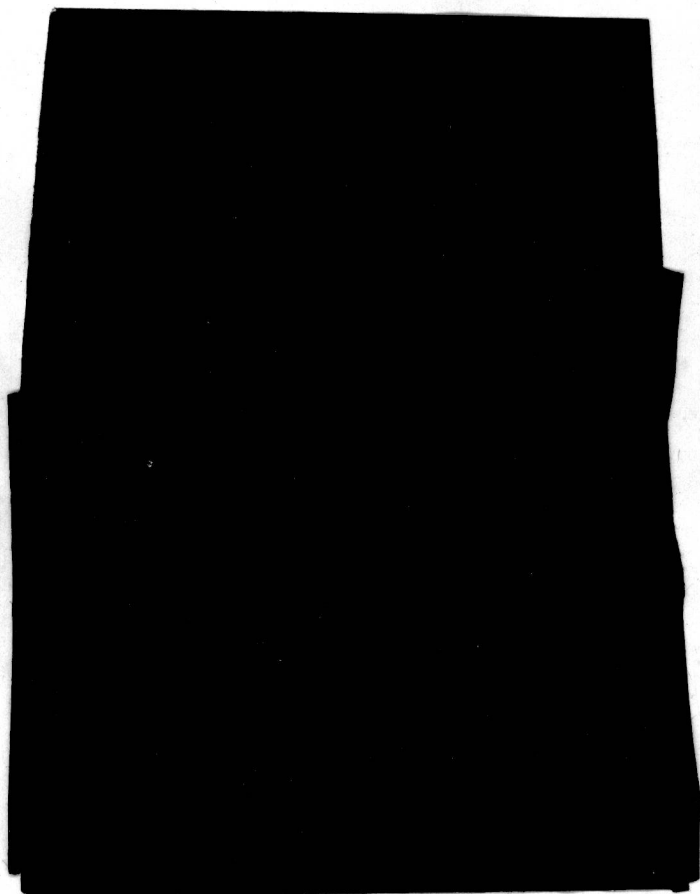
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PREFACE

THE Power Sources series of books records the proceedings of the International Power Sources Symposia which are held at two-yearly intervals. Power Sources 7 contains the 49 papers presented at the 11th Symposium held at Brighton in September 1978 and an edited record of the discussion which followed each paper.

Since their inauguration in 1958 the Symposia, organized by a committee representing British commercial and government organizations, have continued to attract delegates from many countries such that in 1978 some 450 delegates from 30 countries attended the four-day meeting.

The Symposia provide a forum for people engaged in research, development and the use of electrical power sources (other than rotating machinery) to present and discuss their work. Within the scope of the Symposia no other restriction is placed on the subject of papers offered for presentation in order that these published proceedings may represent as realistically as possible the current state of progress in the continuously expanding field of power sources. To stimulate discussion of the papers presented, delegates representing mainly industry, universities and government establishments, are furnished with pre-prints in advance of the Symposium.

The publication of Power Sources 7 results from the work of its contributors, the efforts of each of my colleagues on the Symposium Committee and the organizations they represent, and the many people to whom I am indebted for the organization and work involved in the recording and transcription of the discussion. The reader will recognize in this book the format evolved over many years by my predecessor as editor, D. H. Collins.

Farnborough
January 1979

J.T.

THE FRANK M. BOOTH AWARD

In 1970, the Frank M. Booth Award was established. Named after the founder of the Symposia, the award has the form of a silver medallion engraved on one side with the name of the recipient and the year in which it was awarded, and on the other with the symbolic representation of non-mechanical electrical power, international interest and persons in conference.

The award is made to persons who have made outstanding contributions to the advancement of Power Sources either technically or by increasing the effectiveness of the Symposia.

Previous recipients of the award have been:

Dr M. Barak	}	1960/1970
Dr P. Reasbeck		
Mr A. L. Taylor		
Mrs Jeanne Burbank		1970
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The 1978 award was made to Professor H. R. Thirsk of the University of Newcastle upon Tyne for his outstanding contributions in the field of electrochemistry and active involvement in the Symposia over many years.

Papers presented at the Symposia:

1. "The rate and nature of phase changes at electrode surfaces",
M. FLEISCHMANN and H. R. THIRSK, 1958.
2. "The reversible potential of the manganese dioxide electrode",
B. G. LEVER, A. K. COVINGTON and H. R. THIRSK, 1960.
3. "Review of paper to be presented in 1964",
M. FLEISCHMANN and H. R. THIRSK, 1962.
4. "The behaviour of electrodes of the second kind",
G. W. D. BRIGGS, M. FLEISCHMANN and H. R. THIRSK, 1964.
5. "Properties of some potassium-containing-manganese dioxides",
J. AMBROSE, A. K. COVINGTON and H. R. THIRSK, 1968.
6. "The kinetics of the silver/silver rubidium iodide electrode",
R. D. ARMSTRONG, T. DICKINSON, H. R. THIRSK and R. WHITFIELD, 1972.
7. "The solubility and diffusion of iodine in AgRbI_5 ",
R. D. ARMSTRONG, T. DICKINSON, H. R. THIRSK and R. WHITFIELD, 1972.
8. "The anodic behaviour of indium/bismuth alloys in alkaline solution",
R. D. ARMSTRONG, T. DICKINSON, B. MACFARLANE and H. R. THIRSK,
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1

MORPHOLOGICAL AND KINETIC STUDIES ON LEAD DIOXIDE ELECTRODES

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ABSTRACT

Electrochemical studies on lead dioxide electrodes have established the kinetic mechanisms involved in the charge-discharge cycle of the lead-acid battery positive plate. Scanning electron microscopy, X-ray and thermal analysis were used to examine the morphological changes that occur during cycling of the positive active material. The chemical, electrochemical, physical and structural data indicate the electrochemical processes responsible for the development of the reticulate and coralloid structures observed in some plates after specific cycle duty.

INTRODUCTION

The electrochemistry group of the Corrosion and Protection Centre has, for the past few years, been investigating the anodic corrosion and film formation on lead and lead alloys. The adhesion of the corrosion product to the grid alloy is an important consideration in terms of shedding and charge acceptance, but of equal importance are the related phenomena of cohesion of the active material to the corrosion product and the morphological changes of the lead dioxide during the cycle life of the plate. The present paper presents a review of some of our data which is relevant to the structural and electrochemical changes observed during cycling.

The cycle limitations of the lead dioxide electrode has ensured that it continues to be the subject of extensive research, however the system is still incompletely understood. Many investigations have been concerned with the initial plate formation processes from lead and lead oxides but it is only recently that the structural changes during cycle life plus the related electrochemical mechanisms have received more attention. Caulder and Simon (Caulder, 1974; Simon, 1974, 1975) have shown that in automotive battery plates an electrochemically inactive form of lead dioxide is produced and a coralloid

structure develops during cycling. These observations on the microscale can also be linked to plate data on the macroscale (Yamaura *et al.*, 1973, 1974) to describe the gradual deterioration that occurs during the life of the plate.

The fundamental electrochemical mechanisms responsible for the above observed structural changes are outlined below, the preliminary data was obtained using potentiostatic conditions with both experimental and paste type electrodes. Comparison of constant current cycling and constant potential cycling of the active material were then shown to be valid. The electrocrystallization processes occurring during the phase changes $\text{PbO}_2 \rightleftharpoons \text{PbSO}_4$ are therefore analysed in the context of the change of active material morphology.

PRELIMINARY EXPERIMENTS ON LEAD AND ELECTRODEPOSITED β -LEAD-DIOXIDE

Potentiostatic Anodization of Lead Electrodes

Pure lead electrodes of 1 cm² exposed area were prepared by gravity casting 99.99% pure lead rods which were then machined into electrode discs. The discs were annealed at 100°C for 72 h and after attaching a copper conducting wire to one side they were embedded in epoxy resin with the front face exposed. This face was microtomed to 1 μm and gently abraded on 600 grade paper in running water. It was then polished to $\frac{1}{4}$ μm on a selvylt cloth on a polishing wheel, using "Hyprez" fluid as a lubricant; the electrode was washed in acetone, methylated spirit, carbon tetrachloride and dried in a cold blast of air. The lead specimen was finally etched using a mixture of equal amounts of 15% w/v solution of ammonium molybdate and a solution made from 27 ml of concentrated nitric acid in 100 ml of distilled water. Cotton wool was soaked in the etching solution and gently swabbed over the electrode surface until a well-defined crystal surface appeared. The electrodes were then washed in distilled water and dried with clean tissue paper.

The electrode was pre-cathodized in 5 M sulphuric acid at -1200 mV with respect to a $\text{Hg}/\text{Hg}_2\text{SO}_4/5 \text{ M H}_2\text{SO}_4$ reference electrode for two hours to remove any surface oxide prior to immersion in the 5 M sulphuric acid solution for the potentiostatic transient measurements. The solutions used throughout were prepared from "Analar grade" reagents and triple-distilled water. All potentiostatic pulse measurements were carried out in 5 M sulphuric acid. The solutions were deoxygenated with nitrogen (B.O.C. "white spot") before use.

A Wenking potentiostat (type 70TS1) was used in conjunction with a Chemical Electronics waveform generator (type RB1) to supply a single square wave potential pulse for the transient measurements. Pulse lengths of greater than 40 s were obtained by switching to the "d.c." position before the end of the

original time limit. The current-time transients were recorded both on a storage oscilloscope, "Tektronix" (type 564) and a Chart recorder "Leeds and Northrup" (speedomax type XL 681).

A typical transient for the conversion of the lead to lead sulphate and then to lead dioxide is shown in Fig. 1. Analysis of the initial decay gave the i vs $t^{-1/2}$

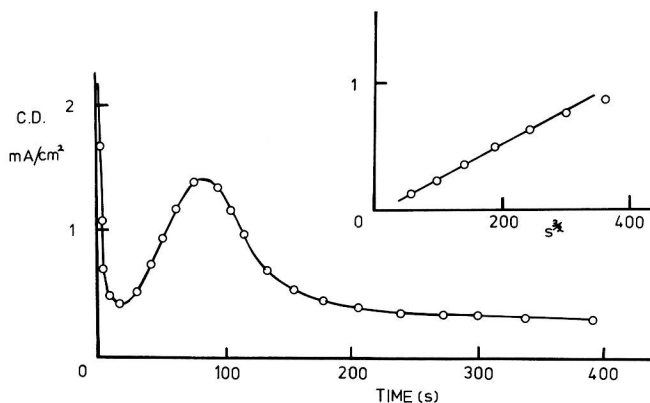


FIG. 1. Current-time transient of the oxidation of lead to β -lead-dioxide. Potential stepped from -1200 mV to $+1500$ mV vs $\text{Hg}/\text{Hg}_2\text{SO}_4$ in $5\text{ M H}_2\text{SO}_4$ at 30°C .

relationship normal for the dissolution-precipitation mechanism for the formation of a lead sulphate film (Archdale and Harrison, 1972). Of more interest to the present paper is the rising transient for the conversion of the lead sulphate to lead dioxide (Rana, 1975). Analysis of this transient inset of Fig. 1, shows the i vs $t^{3/2}$ relationship (Thirsk and Harrison, 1972) typical for an electrocrystallization process involving a progressive three-dimensional nucleation with a slow diffusion step, probably involving the solution diffusion of an electroactive species. The decay part of this transient was exponential showing impingement and overlap of the growing phase, the β -lead-dioxide centres.

The Discharge and Charge Kinetics of Electrodeposited β -Lead-dioxide

For the current-time transient measurements β -lead-dioxide electrodes were prepared by electrodeposition onto a gold-wire electrode of diameter 0.1 cm and length 2.5 cm. The gold electrode was cleaned with dilute nitric acid and was then washed with triple-distilled water. The β -lead-dioxide electrodeposited from a solution of 10 g l^{-1} of lead nitrate and 15% nitric acid (Ikari, Yoshizawa and Okada, 1959) for 48 h using a platinum foil cylinder of height 2.5 cm and diameter 5 cm as counter-electrode. The solution was gently stirred with a magnetic stirrer during electrodeposition. An average current density of 1 mA cm^{-2} consisting of 20% a.c. (peak to peak) at 50 Hz superimposed on the

d.c. was used which produced a strongly adherent layer of the lead dioxide. The electrical circuit consisted of a Wenking 70 TS1 potentiostat used as a galvanostat, in conjunction with an Advance a.c. generator (type H-1). The electrodeposited electrodes were washed well and soaked in triple-distilled water.

For the potentiostatic transient measurements an electrode was introduced into a cell containing nitrogen-saturated, 5 M sulphuric acid maintained at 30°C. A preset potential of +1500 mV, with respect to the Hg/Hg₂SO₄ electrode in the same electrolyte, was applied and maintained for one hour, by which time the preconditioning anodic current was virtually steady. The flow of nitrogen was stopped before taking measurements on discharge. The data for the initial potentiostatic discharge of the electrodeposited β -lead-dioxide is shown in Fig. 2 and the discharge pulse duration was 10 s. The current-time

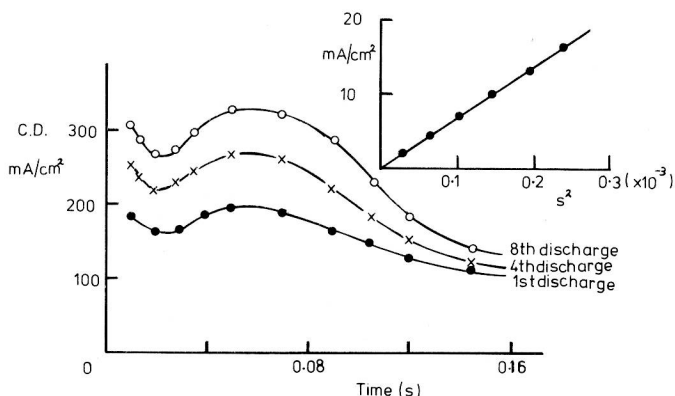


FIG. 2. Discharge transients on electrodeposited β -lead-dioxide. The potential stepped from +1500 mV to +990 mV vs Hg/Hg₂SO₄ during the cycling.

curves had two transients; the first shows an initial falling current approximately proportional to $t^{-1/2}$. This current was then subtracted from the observed curve in order to analyse the rising electrocrystallization transient. The inset in Fig. 2 shows that the growth current is proportional to t^2 (Munasiri, 1977).

The initial discharge reaction of β -lead-dioxide and the formation of lead sulphate therefore occurs via two routes; a diffusion controlled outer layer discharge by a dissolution-precipitation mechanism i vs $t^{-1/2}$, the diffusion being through pores in the growing lead sulphate layer and an electrocrystallization reaction of the underlying or inner layer of lead dioxide, i vs t^2 , by a two-dimensional, progressive nucleation and growth of lead sulphate, the slowest step being at the growing crystal. Recharge of the electrodeposited electrode also shows two transients (Fig. 3), an initial decay followed by a rising