CYCLIC VOLTAMMETRIC STUDIES ON THE LEAD ELECTRODE IN SOME AQUEOUS SOLUTIONS

A Thesis Presented By

Abd El-Kader Saty Mohamed Osman

B. Sc. , M. Sc.

For The Award Of The Degree

Of

PHILOSOPHER DOCTOR OF SCIENCE

" Chemistry "

Department Of Chemistry

Faculty of Science - Ain Shams University

1991

Approval Sheet

Of The Thesis Entitled

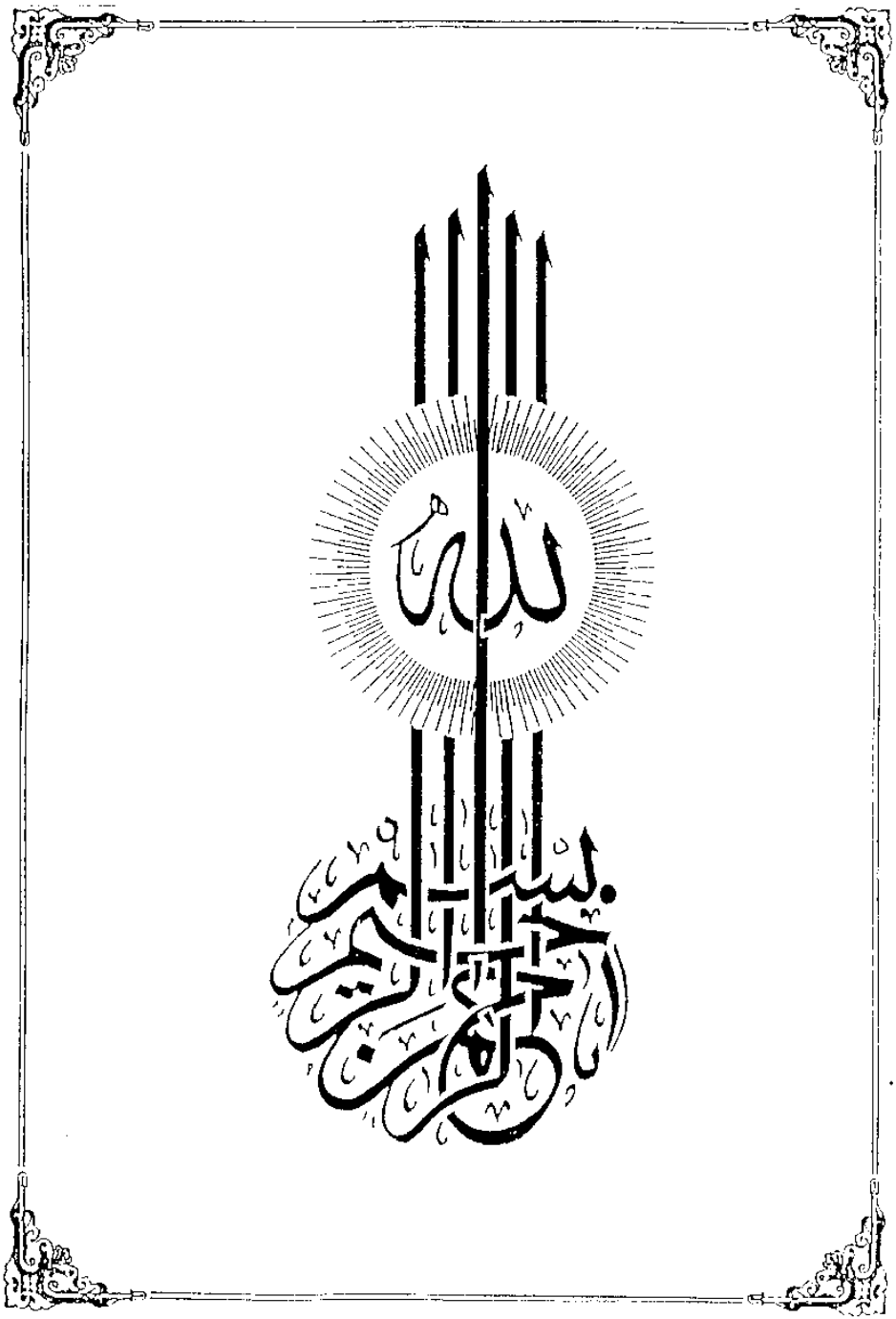
" CYCLIC VOLTAMMETRIC STUDIES ON THE LEAD ELECTRODE IN SOME AQUEOUS SOLUTIONS " .

Supervisors :	Signature
Prof. Dr. S . S . Abd El Rehim	.....
Prof. Dr. S . M . Abd El Wahaab	.....
Prof. Dr. A . M . Abd El - Halim	.....
Ass. Prof. Dr. M . H . Fawzy	.....

Credit

Prof. Dr. N . M . Guindy

Head of Chemistry Department



ACKNOWLEDGEMENT

The author would like to express his thanks and gratitude to Prof. Dr. S. S. Abd El Rehim and Prof. Dr. S. M. Abd El Wahaab , for their kind help and encouragement .

The author is greatly indebted to Prof. Dr. A. M. Abd El - Halim for suggesting the present work and for his valuable guidance , continuous interest and discussion without which the present work could not have been conducted .

The author wishes to express his thanks and gratitude to Ass. Prof. Dr. M. H. Fawzy for his kind help and interest .

Many thanks to Prof. Dr. N. M. Guindy , Head of the Department of Chemistry and to the staff Members of the Chemistry Department for the concern they paid to this thesis .

CONTENTS

AIM AND SCOPE OF THE PRESENT WORK

AIM AND SCOPE
OF THE PRESENT WORK

The Ag / AgCl electrode is used as an effective cathode in sea - water activated batteries which employ a Mg - alloy anode . In spite of the high cost of silver and its irrecoverable loss during use , non - silver electrodes were recently developed . Particularly , the Pb / $PbCl_2$ electrode is recommended as an economical substitute for the Ag / AgCl electrode . In practice , the Pb / $PbCl_2$ electrode is prepared by various means such as hot - pressing , cold - pressing and fusion casting techniques . In fact , the performance characteristics of the substitute electrode , prepared by any of these methods , are still inferior to those of the Ag / AgCl electrode . This may be due partially to the specific properties of $PbCl_2$ and partially to the method of its preparation .

On the other hand , the basic electrochemistry of the lead electrode in aqueous HCl and NaCl solutions has been extensively studied by galvanostatic and potentiostatic techniques but investigated to a minor extent by cyclic voltammetry . In conclusion , the results of these investigations showed that the overall anodic reaction leads to the formation of a passivating thin layer of $PbCl_2$ on the surface of the lead anode . In addition , a feature worthy of attention is that sea - water activated batteries are generally subjected to repeated cycles of charge and discharge analogous to those occur in a cyclic voltammetry experiment .

For these reasons , the first and second parts of the present thesis are devoted to investigate , in more details , the cyclic voltammetric behaviour of the lead electrode in aqueous HCl and NaCl solutions , respectively . Actually , some developed types of measurements have been performed in this investigation . Moreover , examination of the as - formed $PbCl_2$ surface - layers by scanning electron microscopy and X - ray diffraction analysis has been carried out . Accordingly , the present study could be effective in thickening of the passivating $PbCl_2$ surface - layer and hence may lead to exploring a new route for electrochemical preparation of an improved Pb / $PbCl_2$ electrode .

Unfortunately , the anodic behaviour of the lead electrode in aqueous bromide and iodide solutions has not received adequate attention . However , very few literature have been published in this respect . Therefore , the third and fourth parts of the present thesis are directed to throw more light onto the cyclic voltammetric behaviour of the lead electrode in aqueous NaBr and NaI solutions , respectively . In addition , the produced $PbBr_2$ and PbI_2 surface - layers were investigated by electron microscopy and identified by X - ray diffraction analysis . These two parts of the thesis were undertaken to achieve the following two purposes . Firstly , to integrate our intensive study on the cyclic voltammetric behaviour of the lead electrode in the conventional aqueous halide (chloride , bromide and iodide) solutions . Secondly , to provide some original data concerning preparation of the Pb / $PbBr_2$ and Pb / PbI_2 electrodes by electrochemical means . The latter data may be helpful in development of the less common Pb / $PbBr_2$ - Br_2 and Pb / PbI_2 - Mg

accumulators .

The fifth part of the thesis deals with application of the Pb / $PbCl_2$ electrode , prepared by cyclic voltammetry under selected conditions , in a pilot sea- water activated cell (or battery) . The discharge curves of the cell have been examined as a function of some operating variables . Accordingly , the performance characteristics of the cell have been discussed and evaluated .

CHAPTER - 1

INTRODUCTION

1.INTRODUCTION

1.1 The passivation phenomenon

Passivation is an unusual phenomenon observed during the corrosion of certain metals and alloys . It can be defined as a loss of chemical reactivity under certain environmental conditions . More specifically , the term is applied to the sometimes observed transformation of a corroding unstable surface to a passive stable surface by the superimposition of a double - layer field which would accelerate the metal dissolution reaction rather than hinder it , i . e. by a shift of the electrode potential in the positive direction . This phenomenon of enforced passivation [1] seems unnatural or at least unexpected . Passivation results as a process of formation of an insoluble oxide , hydroxide or solid salt in contact with the metal . Protection of the metal will be complete where the film of deposit is absolutely adherent and non - porous .

The behaviour of metal anodes at which an insoluble layer is formed has been discussed in detail by Müller [2] . He suggested that crystals formed by supersaturation of the solution near the anode grew sideways of the surface during the low overpotential passivation period . When this covering was completed there was an abrupt rise in the potential of the electrode due to the increased current density in the pores of the salt layer leading to the production of higher valency - metal compounds and / or oxygen evolution .

The variations in the passivation time (at a certain potential) could then be ascribed to differing thickness of the layer at the moment of completion , and also to variation in the amount of lead salts lost by convection during the formation of the thicker layers .

The relation between the applied current density (j) and the time of passivation (t_p) was also studied by Müller and Machu [3] and Kabanov [4] and the following relation was found to apply :

$$j^a \cdot t_p = \text{constant}$$

If the above relation is written as :

$$\log t_p = \text{constant} - a \log j$$

it is evident that the plot of $\log t_p$ against $\log j$ should be linear with a slope equals - a .

The electrochemical behaviour of an active - passive metal renders a reasonable explanation for the formation of a passive surface layer [5] . The electrode potential - current density (E - j) curves for an active - passive metal show an interesting pattern as can be seen in Fig. 1. When the potential is shifted starting from the corrosion potential E_{corr} (the zero current potential) , the dissolution current increases . The metal ions pass into the solution according to the reaction :