

**EFFECT OF GELLING ON THE ELECTROCHEMICAL
BEHAVIOUR OF Pb/PbSO₄ ELECTRODE IN
MAINTENANCE -FREE LEAD-ACID BATTERIES**

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Dedicated to

My Parents

and

Teachers

CERTIFICATE

This is to certify that the work discussed in the thesis entitled " EFFECT OF GELLING ON THE ELECTROCHEMICAL BEHAVIOUR OF Pb/PbSO₄ ELECTRODE IN MAINTENANCE -FREE LEAD-ACID BATTERIES" by Mr. M. P. Vinod for the degree of Doctor of Philosophy was carried out under my supervision in the Physical Chemistry Division of National Chemical Laboratory, Pune. To the best of my knowledge, the present work or any part thereof, has not been submitted for the award of any other degree.



Dr. K. Vijayamohan

(Research Guide)

COMPUTERISED

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(M.P. Vinod)

List of symbols

C_{dl}	Double-layer capacitance
E^r	Equilibrium potential of the Working electrode versus Hg/Hg_2SO_4 , 4. 8 M H_2SO_4 .
f	F/RT where F is the Faraday constant, R , the universal gas constant and T the absolute temperature
I_0	Exchange current density
$I_{0, Pb}$	Exchange current density for Lead electrode reaction
$I_{0, H}$	Exchange current density for Hydrogen Evolution Reaction
$I_{0, O}$	Exchange current density for Oxygen Evolution Reaction
I_{cor}	Corrosion Current
α	Cathodic energy transfer coefficient
α_H	Cathodic energy transfer coefficient for Hydrogen Evolution Reaction
α_{Pb}	Cathodic energy transfer coefficient for Lead electrode reaction
α_O	Cathodic energy transfer coefficient for Oxygen Evolution Reaction
β	Anodic energy transfer coefficient
β_H	Anodic energy transfer coefficient for Hydrogen Evolution Reaction
β_{Pb}	Anodic energy transfer coefficient for Lead electrode reaction
β_O	Anodic energy transfer coefficient for Oxygen Evolution Reaction
E^{cor}	Corrosion Potential
n	Number of electrons involved in the rate determining step of an electrochemical reaction
R_{ct}	Charge transfer resistance for a particular reaction
R_0	Ohmic resistance
C	Capacity
C/n	Capacity derived by 'n' hr rate
η	Overpotential, defined as $E - E^r$
$I_{p, a}$	Anodic peak current
$I_{p, c}$	Cathodic peak current
$E_{p, a}$	Anodic peak potential
$E_{p, c}$	Cathodic peak potential

Abbreviations

MF	Maintenance-Free
EV	Electric Vehicle
SPV	Solar Photo-Voltaic
OCV	Open-Circuit Voltage
DOD	Depth of Discharge
HER	Hydrogen Evolution Reaction
UPS	Uninterruptable Power Supplies
RAPS	Remote Area Power Supplies
SOC	State-of-Charge
EMF	Electro Motive Force

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Chapter 1

INTRODUCTION

This introductory Chapter discusses both the elementary aspects and the current trends in Maintenance-Free Lead-acid Batteries with special emphasis on gelled systems. This chapter also gives the major objectives and the overall organisation of the present investigation.

1. 1. Electrochemical Energy Storage

Electrochemistry plays a crucial role in both generation and storage of energy.¹⁻³ Electrochemical methods of energy storage possess several advantages over other modes of energy storage such as fly wheels, pumped water hydroelectric generators and compressed gas generators. The inherent advantages of electrochemical energy generation methods are that they are not subject to Carnot limitations. More significantly, electrochemical methods are also environmentally acceptable,⁴ since they avoid some of the major disadvantages of thermal (pollution problems), nuclear (safety hazards) and hydroelectric (deforestation) energy conversion technologies. In addition, the controlled transformation, storage and use of stored energy permits the conservation and distribution of resources, in a more effective way. Finally, such improvements in energy storage will release the technical and economical pressures on the total energy system by simplifying the storage and distribution of electricity, as well as by enabling the introduction of electric vehicles (EV) on a massive scale in the near future.⁵⁻⁸

Electrochemical power sources, allow the direct conversion of the free energy of a chemical reaction to electrical energy. Such a conversion of chemical energy stored in the active materials into electrical energy takes place by electrochemical oxidation-reduction reactions, involving flow of electrons through an external circuit. The electrochemical cell essentially consists of an anode, which sustains an oxidation reaction and a cathode, which sustains a reduction reaction contained in an electrolyte which provides ionic path for electrical conduction. Commercial systems also contain a separator between the anode and the cathode to prevent accidental electronic shorts between these electrodes. A schematic description of such an electrochemical power source indicating all these different components is shown in Figure 1.1

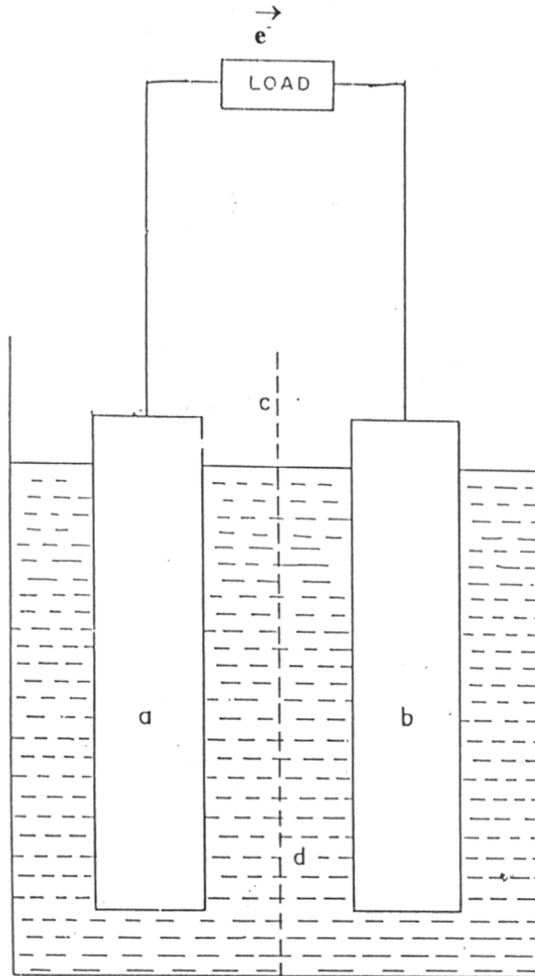


Figure 1. 1. Schematic description of an electrochemical power source, during discharge (a) Anode, (b) Cathode, (c) Separator and (d) Electrolyte.

The electrochemical power Sources, can be broadly classified in to three types; fuel cells, primary batteries and secondary batteries.

Fuel cells are electrochemical devices which convert the free energy change of a chemical reaction directly to electrical energy in an essentially invariant electrode-electrolyte system.⁹⁻¹¹ They operate continuously in the discharge mode and the reactants have to be supplied from outside. The Hydrogen-Oxygen fuel cell utilising potassium hydroxide or phosphoric acid electrolytes is one of the most common examples. Depending on the type of electrolyte employed, fuel cells can be conveniently classified into Alkaline fuel cells, Acid fuel cells, Molten carbonate fuel cells, Solid oxide fuel cells and Proton exchange membrane fuel cells. Some of these systems such as phosphoric acid fuel cells have reached commercial maturity in recent times while continued attempts are being made to improve other types. The major advantages of these systems are their high efficiency, environment-friendly operation, low solution resistance, easy transportation and low day-to-day maintenance. However, their difficulties like electrode degradation, uncertainty in lifetime, activation and concentration polarisation, and ohmic losses, hamper their wider commercial applications, although several electrocatalysts have been recently developed to alleviate some of the problems.⁹⁻¹¹

Primary batteries are devices which work only in the discharge mode and therefore are to be discarded after use.¹² However they act as a convenient and inexpensive source of power for several common devices and the important advantages include long shelf-life, high energy density, and user-friendly design. Common examples are Leclanche cell ($\text{Zn}/\text{NH}_4\text{Cl}/\text{MnO}_2$), Zn/MnO_2 alkaline cell and different type of Lithium cells¹³ such as Li/MnO_2 , Li/SO_2 and Li/SOCl_2 .

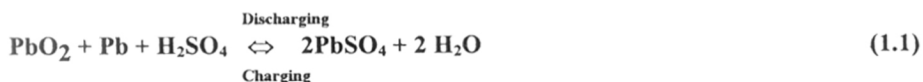
Secondary batteries are electrochemical devices which work on both charged and discharged modes.¹⁴ During discharge they deliver electrical energy to an external load

through the simultaneous occurrence of electron-transfer reactions at the electrodes. They can be recharged and discharged several times in a cyclic manner and the recharging is carried out using an external power supply by reversing the direction of current. Some of the common examples include Lead-acid¹⁵⁻¹⁸, Nickel/Cadmium¹⁹, Lithium/Iron Sulphide²⁰⁻²¹ and Sodium-Sulphur.²²

1. 2. Lead-acid Batteries

Lead-acid battery is one of the most widely used electrochemical power Sources. This has several favourable characteristics as a low cost rechargeable battery and hence is successful in a variety of applications such as automobile starting, Uninterruptable Power Supplies (UPS) and industrial traction.²³

The lead-acid battery consists of a positive electrode of lead dioxide and a negative electrode of finely divided lead, both being supported on a grid of lead-antimony alloy. The electrodes are separated by an insulating porous barrier and both the electrodes and separator are in contact with 2-4 M sulphuric acid as the electrolyte. The electrochemical reactions during charge/discharge are represented as,



This reaction is thermodynamically reversible and the theoretical energy density amounts to 165 Wh/Kg corresponding to an emf of 2.0 V. However only 30-40 Wh/Kg (at 5 hr. rate, i.e., C/5) is realised in practice mainly due to the incomplete faradaic conversion of the active materials and also because of the weight of grids, connectors and containers. The cycle life normally varies from 300 to 1800 depending on the depth of discharge (DOD) and the average charge efficiency during cycling is about 75 %. There are several kinds of lead-acid batteries depending on the internal design variables and there is a wide

variation among them with respect to their electrical performance, service life, reliability level, maintenance-requirement and cost.

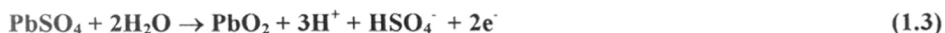
1.2.1. Electrochemical reactions During Charge- discharge Process

Various processes such as dissolution, precipitation, deposition and corrosion always occur in a lead-acid battery regardless of whether it is in charged/discharged or open-circuit conditions^{15,16}. It is necessary to differentiate the various electrochemical reactions under these conditions in order to understand at which stage a given process becomes dominant and also how it affects the overall performance of the battery. In addition, a knowledge of the details of these reactions will possibly help to suppress some of the parasitic reactions associated with self-discharge processes.

During charging, the negative electrode sustains a reduction reaction,



while, the positive electrode undergoes an oxidation of PbSO₄ to lead(IV) oxide as,



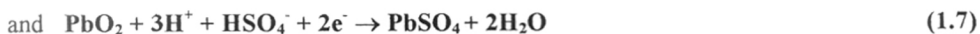
Once the charging is complete, overcharging can occur and the electrode reactions on the negative and positive electrodes respectively are,



As a consequence, both hydrogen and oxygen are evolved on lead and lead oxide electrodes respectively and in a flooded cell, the concentration of sulphuric acid continues to increase along with concomitant changes in specific gravity.

During the discharge of the cell, the reverse reactions of (1.2) and (1.3) occur on negative and positive electrodes respectively, i.e.;





Nevertheless, overdischarge can cause both (1.3) and (1.5) to occur on the negative electrode while (1.2) and (1.4) on the positive electrode. Similarly, charge-stand can cause (1.5) and (1.7) to occur simultaneously on the positive electrode, while, the negative electrode may allow a combination of (1.4) and (1.6). These reactions constitute the well known self-discharge processes occurring on the positive and negative electrodes respectively. On the contrary, discharge-stand can cause reactions (1.4) and (1.6) to occur simultaneously on the positive as well as negative electrodes and after extended discharge-stand negative electrode reversibility may be permanently lost.¹⁶

1. 2. 2. Limitations of Conventional Lead-acid Batteries

Because of the use of antimony containing grids which cause high rate of self-discharge, the shelf-life of a conventional lead-acid battery is relatively poor. For example, the self-discharge rate is about 20-30 % of its nominal capacity per month and this self discharge rate may be decreased to about one fourth of it by using non-antimony grids and suitable additives. The self-discharge process involves both hydrogen and oxygen evolution, resulting to considerable loss of water from the electrolyte. This is the major reason why conventional lead-acid batteries need periodic maintenance like topping up of the electrolyte level by water addition and periodic charging to compensate self-discharge. Another important disadvantage of conventional lead-acid batteries is its poor tolerance to discharge-stand, demanding a mandatory charging after deep-discharge. This along with the need for avoidance of overcharge requires extensive maintenance and care during usage.

The charge acceptance of a conventional lead-acid battery is also low due to the parasitic hydrogen evolution reaction (1.4) arising from the low hydrogen overpotential of

antimony present in the grid.²⁴ Corrosion induced dissolution of antimony from the positive plate can further decrease the charging efficiency. Thus a reduction in the antimony content not only increases the charge acceptance but also reduces the self-discharge rate. For example, a reduction in the antimony content from 4.5 wt % to zero in automotive batteries has resulted in a 10 % reduction in the gassing rate.²⁵ However, replacement of Sb-Pb alloys by other composition such as Pb-Ca-Sn has been found to affect the cycle life adversely although other desirable features of Sb, such as increased hardness, improved castability and enhanced adhesion of the active material to the grid are retained.

1.3. Maintenance-Free Lead-acid Batteries

Maintenance-Free Lead-acid batteries, as the name indicates are capable of long-term silent operation in a permanent location without any special attention.²⁶⁻⁴⁹ Thus there is no need for the periodic control and adjustment of water level. Furthermore, periodic recharging after extended storage is not necessary due to the low self-discharge rate and this along with avoidance of overcharge make this system superior.

The gas evolution rate is significantly reduced by the special use of low antimony or antimony free grids. Consequently these systems experience little loss of water during their expected life. Choosing a suitable alloy⁵⁰⁻⁶³ for grids without affecting the performance under deep discharge conditions is one of the crucial steps in the design of MF lead-acid batteries. Several innovations over the last three decades in the form of improved separators and the technology of the manufacturing processes have contributed significantly in the development.⁶⁴ These MF lead-acid batteries have become more and more important in recent years due to their application possibilities in remote area power supplies and also for portable electronic appliances.

1.3.1. Various types of maintenance free lead-acid batteries

Depending on the cell construction, separator structure, and amount of electrolyte employed, there are three types of maintenance-free lead-acid batteries. The first one namely the flooded electrolyte type⁶⁵⁻⁶⁶ usually has tubular positive plates and excess of electrolyte to compensate the loss of water during cycling. Special features such as spill-proof vents with spray arrestors, recombination catalyst plugs are also present in some of these batteries. The major limitations of these systems include capacity fading due to electrolyte stratification, poor tolerance to discharge and relatively low gravimetric and volumetric energy density and mechanical inconvenience due to the presence of large amount of acid electrolyte.

The second type of maintenance-free absorbed electrolyte⁶⁷⁻⁷⁹ battery operates on an internal oxygen cycle. Since these batteries are positive limited, there is no hydrogen evolution at the negative electrode at any state-of-charge while oxygen evolution is possible during charge or discharge. The oxygen is continuously and efficiently consumed by the negative electrode as represented by the reaction (1.8).



The amount of acid electrolyte is carefully chosen so that all the amount is adsorbed in the pores of the electrodes and separator and there is no free electrolyte. Hence the proper selection of the separator is extremely important for this types of cells and recent developments related to glass fibre mat technology offer several advantages. Due to the presence of electrolyte starved conditions, loss of water during overcharging is negligible and no topping up is required. The use of low antimony or antimony-free grids reduces the

life limiting processes at the electrodes and also recombination catalysts plugs can be included in the design.

One of the major limitations of adsorbed type of MF batteries arises due to the incomplete filling of the pores of the separator by the electrolyte. Consequently, the non-equilibrium concentration gradients in the capillary of the separator may cause problems of non-uniform mass transfer and current density variations between the upper and lower parts of the cell. In addition, there is also variation in top-of-charge voltages and currents due to the change in the negative electrode overpotential attributed to different levels of oxygen recombination.⁷²

1 . 4. Maintenance-free Gelled Electrolyte Batteries.

Although immobilisation of the electrolyte was originally attempted for safety reasons, i.e., to avoid acid spillage, later several other advantages were realised in terms of battery performance.⁸⁰⁻⁹⁴ Consequently gelled maintenance-free lead-acid batteries became very important and several common features of other MF lead-acid batteries were incorporated into this.

The selection of gelling agent is one of the crucial steps in designing a MF gelled type lead-acid battery. Several requirements are to be satisfied by the gelled electrolyte and some of them include, (i) high gel stiffness, (ii) good gel distribution, (iii) ability to keep the correct amount of acid between the electrodes and (iv) low viscosity for a reasonable time in the beginning. The gelling agents generally used for this purpose are inorganic and organic compounds which render the sulphuric acid electrolyte immobile. More significantly, the evolution of gases (mostly oxygen) during the initial cycles generate fissures in the interpenetrating gel structure, providing a pathway for the convective diffusion of oxygen prior to recombination. Commonly employed inorganic gelling agents

Table 1.1. Comparison of the performance of gelled and flooded Lead-acid batteries.

Parameter	Gelled Type	Flooded Type	Reference
Capacity (C/ 5 rate)	46 Wh/Kg	36 Wh/Kg	84
Cycle life (80 % DOD)	450 cycles	120 cycles	87
Specific Gravity Difference between top and bottom*	0.0	0.1	84
Gassing rate (After 1hr Charging)	15 cm ³ /Ah	150 cm ³ /Ah	84
Shelf life	Two years	Three months	87

* After five cycles with a cell of 350 Ah capacity.

are silica based compounds which generates a three dimensional net work in the electrolyte. Typical examples include finely divided silica, sodium silicate, amorphous silica, colloidal silica etc. In addition, several organic acid resistant gelling agents like phenolic resins and polyacrylamides have also been attempted.²⁵

1.4.1. Advantages of Gelled Batteries

One of the inherent benefits of a gelled lead-acid battery is the minimisation of acid stratification. Electrolyte stratification is a common phenomena when flooded cells are cycled with low charging voltages so that no gas evolution takes place and density gradients are established between the top and bottom portion of the electrolyte. This can lead to the premature failure of the batteries due to the reduction in capacity through electrolyte limitations as well as due to short life through corrosion and passivation problems in the lower part of the electrode. Gelled electrolyte systems are virtually unaffected by stratification since the electrolyte remains immobile in the pores of the gel. For example, flooded electrolyte cells of 350 Ah capacity shows a specific gravity difference of 0.1 between top and bottom portion of the container after five cycles, while gelled batteries indicate no such change in specific gravity.⁸² Interestingly, similar cells using adsorptive gas mat technology show only 50 % specific gravity change. This specific gravity change indicate a clear superiority of gelled batteries over adsorbed electrolyte type.

Gelling of the electrolyte does not harm the electrical performance of the battery and it has been observed that these type of MF batteries give a superior capacity at low temperature. This is mainly due to the depolarisation of the negative plate by oxygen reduction during charging and a higher charging voltage is attained for the positive electrode. This enhancement in oxygen reduction presumably arising from the formation of cracks in the gel, favourably affects the mass-transfer characteristics of the oxygen from the

positive to the negative electrode. Since reduction of oxygen is preferred over hydrogen evolution, rate of self-discharge is considerably suppressed. For example, gassing rate of gelled batteries is less than 10% of that of the flooded type and consequently electrolyte loss is negligible.⁸²⁻⁸⁷

Other advantages of gelled batteries include flexibility, portability, improved cycle life, enhanced capacity and good charging efficiency. In addition, gelling of the electrolyte is also found to improve the mechanical strength of the electrodes by preventing shedding of the active materials. Some of these advantages are summarised in Table 1.1.

1.4.2. Special Applications of Gelled Batteries

Due to the above advantages, MF batteries are suitable for several special applications that are not possible with their conventional counter parts. For example, these batteries can be used in vibrating environments due to their spill-proof design, and suitability for deep-discharge applications indicate promise for special applications such as electric vehicle propulsion,⁵⁻⁸ load levelling and solar energy storage.⁹⁵ Since there is no periodic maintenance, gelled batteries are found to be suitable for emergency power systems like Uninterruptable Power Supplies (UPS),²³ stand alone power systems⁹⁶ and other applications including emergency lighting and telecommunication.

1. 4. 3. Limitations of Gelled Batteries

One of the major limitations of gelled batteries is the lack of control over generation, size and stability of the micro cracks and fissures in the gel. There will always be regions with and without cracks and the distribution of various sizes of fissures are not easily controllable. This kind of an irregularity will lead to uneven oxygen transport and this may be manifested as non-uniform current distribution leading to active material migration and

related difficulties. These problems become more serious for applications requiring high depth of discharge. Another major limitation of gelled battery is the enhanced internal resistance due to the presence of silicate network in the electrolyte. The reduced levels of ion transport rates in the gelled phase leads to high internal impedance which obstructs high- rate discharge and fast recharging.

1.4.4. Effect of Gelling on the Behaviour of PbO_2 Electrode

Although there are plenty of studies related to the effect of gelling on the performance of lead-acid batteries, the influence on the performance of individual electrodes are not many.⁹⁷⁻¹⁰⁹ Gelling of the electrolyte is known to decrease the capacity of the positive electrode by 15% and a comparison of the discharge curve indicates that the anodic overpotential for PbO_2 formation reaction is increased due to the presence of silicate ions in the electrolyte. The details regarding the effect of gelling on the kinetic parameters of these reactions are not available in spite of their importance in maintenance-free batteries. Similarly, the effect of oxygen evolution on PbO_2 electrode also requires further investigations especially due to the significance of oxygen recombination in these systems.

1.4. 5. Effect of Gelling on the Behaviour of Pb/PbSO_4 Electrode

The addition of gelling agents such as sodium silicate affect the performance of negative electrode in different ways.¹¹⁰⁻¹¹⁹ First, the capacity of the electrode is enhanced significantly (20 %), and this has been explained using depassivation effect of silicate ions on the lead electrode surface during anodic polarisation.⁸⁸

With the introduction of gelled type, valve regulated lead-acid batteries in mass production, the question of influence of these gel on the kinetics of the electrode processes has attained crucial importance. Although reports on the effect of gelling agent on the kinetics of Pb/PbSO_4 electrode reaction are scanty, the effect on the kinetics of hydrogen

evolution reaction has been extensively investigated.⁸¹ Gelling is found to generally suppress the rate of hydrogen evolution reaction and this effect has been explained using complexation of silicate ions.⁸¹

The effect of gelling on the morphology of negative electrode has also not been completely analysed. Since the capacity and the cycle life of Pb/PbSO₄ electrode are favourably affected by gelling, the depassivation of silicate ions will be naturally reflected in the morphology of electrodes kept at discharged conditions. The gel structure has a retarding effect on the crystallisation of the sulphate film on the passivating layer. This suggests a loosening of the passivation of PbSO₄ layer by silica particles present in the zone of PbSO₄ crystallisation.

1. 5. The present study

From the above critical review, it is clear that several aspects pertaining to the effect of gelling on the electrochemical behaviour of Pb/PbSO₄ electrode are not completely elucidated, despite the extensive use of silicate ions during the last three decades. Although the benefits due to gelling in improving capacity and cycle-life are known for several years; the exact mechanism is not clearly understood and a theoretical correlation of electrode kinetic parameters is lacking. Any inhibition of self-discharge kinetics as obtained from such a study will be useful in improving the shelf-life of these M-F batteries and also designing cells for special applications like pulsed discharge.^{120,121}

The present study is an attempt to provide some of these information and the major objectives are;(a) to investigate the effect of gelling agents in the self-discharge kinetics of Pb/PbSO₄ electrode,(b) to compare the kinetic parameters of both lead electrode and hydrogen evolution reaction in gelled and flooded electrolyte using galvanostatic potential-time transients,(c) to establish a method for predicting the SOC of gelled batteries in a non-

destructive manner, (d) to understand how gelling affects the morphology of the Pb/PbSO₄ electrode reaction, (e) to estimate the variation of exchange current density with state-of charge with and without gelling agent, (f) to make an experimental and theoretical investigation of the open-circuit potential-time transients of Pb/PbSO₄ electrode with and without gelling., (g) to analyse the potential dependence of double layer capacitance of Pb/PbSO₄ electrode with and without gelling and (h) to determine the uncompensated ohmic drop of Pb/PbSO₄ electrode with and without gelling agent.

This thesis comprises of five chapters. After a brief introduction to the general features of sealed batteries, Chapter 1 deals with the current trends in MF lead-acid batteries. The primary emphasis is on the change in the kinetics of the Pb/PbSO₄ electrode by sodium silicate additives ; this electrode is more significant because of its crucial contribution towards self-discharge.

In Chapter II, the technique of open-circuit potential relaxation from a prior pre-polarised state has been employed to study the kinetics of Pb/PbSO₄ electrode in flooded and gelled electrolytes. The significant features governing the relaxation have been quantitatively analysed to obtain a correlation between the state-of-charge of the electrode and its potential recovery time constants. The study provides a method for estimating the variation of exchange current density of the lead electrode and hydrogen evolution reactions at various SOC values with and without gelling agents.

Chapter III is concerned with the electrode kinetics of Pb/PbSO₄ and hydrogen evolution reactions on porous lead electrodes in sulphuric acid using a quantitative analysis of galvanostatic transients in the linear polarisation domain. Significant changes have been observed in the electrode kinetics with the addition of sodium silicate as a thixotropic agent. The effect on charge-transfer and ohmic components of the Pb/PbSO₄ reaction and charge

transfer components of the hydrogen electrode reaction are analysed with the help of a pore-plugging model. This study allows a non-destructive determination of electrode-kinetic parameters and the contribution of internal resistance to pore-plugging ; more significantly, the conclusions are relevant to other porous battery electrodes also.

Chapter IV deals with the variation of double layer capacitance and exchange current densities of the Pb/PbSO₄ electrode reaction at various SOC values calculated using the phenomenology outlined in chapter III. In addition, the potential-dependence of double layer capacitance has been evaluated as a function of SOC, Interesting changes have been observed in these kinetic parameters as a result of immobilisation of the electrolyte. This analysis also gives a direct determination of the uncompensated resistance of the porous Pb/PbSO₄ electrode originating from the variation of SOC, obtained by comparing the theoretical potential-time transients with experimental data. This method is non-evasive and can be used to predict the SOC of general maintenance-free batteries.

In chapter V, the effect of immobilising sulphuric acid with sodium silicate as the gelling agent on the electrochemical behaviour of lead in sulphuric acid is studied using a combination of electrochemical methods such as Cyclic Voltammetry(CV), charging curve technique, Tafel polarisation technique and surface spectroscopic methods including X-ray photoelectron spectroscopy(XPS) and scanning electron microscopy(SEM). The CV studies indicate a 700 mV shift in the hydrogen evolution potential due to gelling while the well-known reversible Pb/Pb²⁺ couple is found to be thermodynamically disfavoured. A significant change in the double layer capacitance by 600 μFcm^{-2} , probably due to the contribution of silicate adsorption in the interfacial region has been observed. In addition, the exchange current density for hydrogen evolution reaction (HER) as calculated from the Tafel plots are 1.35×10^{-6} and $1.31 \times 10^{-8} \text{ A cm}^{-2}$ for free and gelled electrolyte respectively, revealing the

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kinetic suppression of HER. However, XPS studies give no evidence for chemisorption of silicate on the lead surface, although the SEM analysis shows an appreciable change in the surface morphology.

These results clearly suggest the benefits of improving capacity and charge efficiency offered by immobilising the electrolyte. By using this additives better tolerance to discharge stand and longer service life are also obtained. More significant is the suppression of self-discharge kinetics as revealed by the order of magnitude change of exchange current density of HER. There is clearly an active participation of the gelling agent in controlling the morphology and the kinetics of Pb/PbSO₄ electrode. Although these studies are based on macroscopic models, which do not give molecular level information about interfacial activity, the results are believed to be useful for designing MF lead-acid batteries with gelled electrolyte.

1. 6. REFERENCES

1. C. Starr, M. F. Searl and S. Alpert., Science, **256** (1992) 981.
2. M. Barek (ed.), Electrochemical power Sources, Peter Peregrines, Stevenage (1980)
3. T. E. Rummery, D. F. Torgerson and A. G. Wilyord (eds.), ACS symposium series, **783** (1970) p. 303.
4. P. M. Bersier, L. Carlson and J. Bersier, Topp. Curr, Chem., **170** (1994) 113.
5. T. Ochiai, J. Power Sources, **33** (1991) 291.
6. B. L. McKinney., B. K. Mahata and K. R. Bullock, in K. R. Bullock and D. Pavlov(eds.) Advances in Lead-acid batteries, Proc. Vol. 84-14, The Electrochemical Society, Pennington, NJ, USA, 1984, p. 426.
7. S. V. Jemsen and O.G. Nissen, Int. Electric Vehicle Symp. Oct. 1986, Washington, D.C., USA.
8. D. Pavlov, in 'Power Sources, for Electric Vehicle,' edited by B. D. Mc Nicol. and D. A. J. Rand., Elsevier, Amsterdam, Oxford, (1984) p. 113.
9. K. V. Kordesch. and G. R. Simader, Chem. Rev. , **95** (1995)191.
10. D. Linden., "Handbook of Batteries and Fuel Cells", McGraw-Hill Book Co., New York, (1984).
11. K. V. Kordesch, J. Electrochem., Soc., **125** (1978) 77.
12. G. W. Heise and N. Caboon, " The primary Battery", John Wily and Sons, New York, 1971.
13. H. V. Venkatasetty., "Lithium Battery Technology" Wiley-Interscience, New York (1984).
14. S. V. Falk and A. J. Salkind, " Alkaline Storage Batteries", John Wily and Sons, New York, (1969).
15. G. W. Vinal, Storage Batteries, 4th ed. John Wily and Sons, New York, (1955).
16. H. Bode, " Lead-Acid Batteries", Wily-Interscience, New York, (1984)
17. E. Voss, J. Power Sources, **30** (1990) 7.
18. K. R. Bullock, J. Electrochem., Soc., **142** (1995) 1726.
19. G. Lander, "Sealed Nickel/Cadmium Batteries" VARTA Batteries, A. G. Led, (1982).

20. W. Li, J. R. Dahn, D. S. Wainwright, *Science*, **264** (1994) 1115.
21. G. Dstoia (Ed) *Lithium Batteries*, Elsevier, Amsterdam (1994)
22. J. L. Sudworth, *J. Power Sources*, **11** (1984) 143.
23. G. D. Brownlie, *J. Power Sources*, **23** (1988) 211.
24. A. A. Jenkins, W. C. Maskell and F. L. Tye, *J. Power Sources*, **19** (1987) 75
25. G. Posch, *J. Power Sources*, **33** (1991) 127.
26. M. Maja and N. Penazzi, *J. Power Sources*, **31** (1990) 115.
27. H. Dietz, S. Voss, H. Doring, J. Garche and K. Wiesener, *J. Power Sources*, **31** (1990) 107.
28. E. Voss, U. Hullmeine and A. Winsel, *J. Power Sources*, **30** (1990) 33.
29. S. Venugopalan, *J. Power Sources*, **46** (1993) 1.
30. S. Venugopalan, *J. Power Sources*, **48** (1994) 371.
31. A. Cerny and V. Koudelka, *J. Power Sources*, **31** (1990) 183.
32. E. Voss, *J. Power Sources*, **24** (1988) 171.
33. J. Mrha, J. Jindra, M. Musilov, B. L. Tesnter, I. A. Aguf and R. V. Mustaffin, *J. Power Sources*, **32** (1990) 303.
34. C. Bohle and R. Kiessling, *J. Power Sources*, **31** (1990) 145.
35. L. Lundstrom et al., *Surface Science*, **64** (1977) 497.
36. R. H. Newnham, *J. Power Sources*, **52** (1994) 149.
37. M. Shiomi, K. Takahashi and M. Tsubota, *J. Power Sources*, **42** (1993) 173.
38. J. F. Cole, *J. Power Sources*, **40** (1992) 1.
39. J. S. Symanski, B. K. Mahato and K. R. Bullock, *J. Electrochem., Soc.*, **135** (1988) 548.
40. E. Nann, *J. Power Sources*, **33** (1991) 93.
41. J. Mrha, K. Micka, J. Jindra and M. Musilova, *J. Power Sources*, **27** (1989) 91.

42. M. Iwata, Progress in Batteries and solar cells, **8** (1989) 231.
43. S. A. Awad and Z. A. Elhady, J. Electroanal. Chem. , **20** (1969) 79.
44. A. H. Taylor, F. Goebel and J. Ginger, Power Sources, **4** (1972) 541,
45. J. P. Carr and N. A. Hamspon, Chem. Rev. , **72** (1972) 679.
46. P. Ruetschi, J. Electrochem Soc., **120** (1973) 331.
47. M. K. Dimitrov and D. Pavlov, J. Power Sources, **46** (1993) 203.
48. D. Pavlov, J. Power Sources, **42** (1993) 345.
49. W. Greife, J. Power Sources, **19** (1987) 201.
50. D. Pavlov, J. Power Sources, **48** (1994) 179.
51. G. Richter, J. Power Sources, **33** (1991) 285.
52. S. Clerici and N. Penazzi, J. Power Sources, **31** (1990) 157.
53. S. Zhao, Y. Lu, Z. Zhang and Z. Jlang, J. Power Sources, **31** (1990) 163.
54. W. F. Gillian , J. Power Sources, **19** (1987) 133.
55. B. E. Kallup and D. Berndt, in K. Bullock and D. Pavlov(eds.), Advances in Lead-Acid Batteries, Electrochemical Society, Pennington, NJ, **84** (1984) 214.
56. B. Jiang, Y. Lu, S. Zhao and W. Gu and Z. Zhang, J. Power Sources, **31**(1990)169.
57. D. Pavlov, A. Dakhouche and T. Rogachev, J. Power Sources, **30** (1990) 117.
58. N. E. Bagshaw, J. Power Sources, **53** (1995) 25.
59. K. H. Cristian and R. Ackermann, J. Power Sources, **31**(1990) 151.
60. J. Manders, J. Power Sources, **38** (1992) 197.
61. B. Culpin, A. F. Hollenkamp and D. A.J. Rand, J. Power Sources, **38** (1992) 63.
62. T. Rogachev, J. Power Sources, **23** (1988) 331.
63. L. Mrha, J. Jindra and M. Musilova, J. Power Sources, **31** (1990) 139.
64. J. W. Reitz, J. Power Sources, **19** (1987) 181.

65. J. M. Stevenson and J. L. Dyson, *J. Power Sources*, **40** (1992) 39.
66. J. Alzieu, N. Koechlin and J. Robert, *J. Electrochem. Soc.*, **137** (1987) 1881.
67. K. Peters, *J. Power Sources*, **43** (1993) 155.
68. R. Egeling, *Progress in Batteries and Solar Cells*, **4**(1982)77.
69. M. Maja and N. Penazzi, *J. Power Sources*, **25** (1989) 229.
70. M. Maja and N. Penazzi, *J. Power Sources*, **25** (1989) 99.
71. J. Magyar, H. A. Kepros and R. F. Nelson, *J. Power Sources*, **31** (1990) 93.
72. R. F. Nelson, *J. Power Sources*, **31** (1990) 3.
73. N. E. Bagshaw, *J. Power Sources*, **31** (1990) 23.
74. I. Nikalov, G. Papazov, D. Pavlov, T. Vitanov and V. Naidenov, *J. Power Sources*, **31** (1990) 60.
75. S. Sarkar and I. N. Basumallick, *J. Power Sources*, **31** (1990) 89.
76. S. A. Crouch Jr. and J. W. Reitz, *J. Power Sources*, **31** (1990)125.
77. W. B. Brecht and N. F. O'Leary, in *INTELEC ,1988 Conf. Proc. IEEE*, 1988, pp 35-42.
78. S. Atlung, B. Z. Christiansen, *J. power Sources*, **52** (1994) 201.
79. J. Mrha, J. Jindra and M. Musilova, *J. Power Sources*, **32** (1990) 303.
80. M. A. Dasoyan and I. A. Aguf, *Modern Theory of Lead-Acid Batteries*, Energiya, Leningrad (1975).
81. K. Vijayamohanam, S. Sathyanarayana and S. N. Joshi, *J. Power Sources*, **30**(1990) 169.
82. H. Tuphorn, *Proc. Electrochem. Soc.*, **84** (1984) 441.
83. H. Tuphorn, *J. Power Sources*, **31** (1990) 57
84. H. Tuphorn, *Rev. Gen. Electr.*, **3** (1990) 45.
85. K. Eberts, in D. H. Collins (Ed.), *Power Sources*, 2, Pergamon, Oxford, 1970, 69.
86. H. Tuphorn, *J. Power Sources*, **23** (1988) 143.

87. B. Culpin, M. W. Pilling and F. A. Fleming, J. Power Sources, **24** (1988) 127.
88. H. Tuphorn Proc. 3rd Int. Lead-acid Battery Seminar, Orlando, (1989).
89. N. K. Grigalyuk, T. P. Chizhik and I. A. Aguf, Russ. J. Appl. Chem., **57** (1984) 432.
90. A. M. Hardman, R. T. Hopwood, J. E. Manders, D. A. J. Rand, J. W. Reitz and H. Tuphorn, J. Power Sources, **23** (1988) 258.
91. J. Strebe, B. Reichman, B. Mahato and K. R. Bullock, J. Power Sources, **31**(1990) 43.
92. K. Higashimoto, A. Miura, T. Hayakawa and A. Komaki, Prog. Batteries Solar Cells, **8** (1989) 268.
93. H. Dietz, M. Radwam, J. Garche, H. Doring and K. Weisener, J. Appl. Electrochem. , **21** (1991) 221.
94. B. Culpin and D. A. J. Rand, J. Power Sources, **36** (1991) 415.
95. O. Ikkala and A. Nieminen, J. Power Sources, **31** (1990) 321.
96. A. T. Hollenkamp, W. G. A. Balsing, J. A. Hamilton and D. A. J. Rand, J. Power Sources, **31** (1990) 329.
97. H. Doring, J. Garche, H. Dietz and K. Wiesner, J. Power Sources, **30** (1990) 121.
98. N. K. Dimitrov, J. Power Sources, **31** (1990) 121.
99. D. Pavlov and E. Bashtavelova, J. Power Sources, **31** (1990) 243.
100. E. Voss, U. Hullmeine and A. Winsel, J. Power Sources, **30** (1990) 33.
101. H. Doring, J. Garche, H. Dietz and K. Weisener, J. Power Sources, **30** (1990) 41.
102. D. Bastavelova, J. Power Sources, **31** (1990) 243.
103. E. Meissner and E. Voss, J. Power Sources, **33** (1991) 231.
104. T. Rogachev, J. Power Sources, **23**(1988) 331.
105. J. Garche, E. Voss, R. F. Nelson and D. A. J. Rand, J. Power Sources, **36**(1991) 40
106. K. Takahashi, M. Tsubota, K. Yonezu and K. Ando, J. Electrochem Soc., **130** (1983) 2144.

107. A. M. Hardman, J. Power Sources, **23** (1988) 127.
108. J. Burbank. J. Electrochem Soc., **118** (1971) 525.
109. S. Sternberg, V. Branzoi and L. Apateanu, J. Power Sources, **30** (1990) 177.
110. V. Iliev and D. Pavlov, J. Appl. Electrochem., **15** (1985) 39.
111. M. Johnson, S. R. Ellis, N. A. Hampson, F. Wilkinson and M. C. Ball, J. Power Sources, **22** (1988) 11.
112. L. A. Avaca, E. R. Gonzalez, G. T. Filho and C. V. D'Alkaine, J. Power Sources, **30**(1990)161.
113. S. Sternberg, V. Branzoi and L. Apateanu, J. Power Sources, **30**(1990)177
114. S. Gust, E. Hameenoja, J. Ahl, T. Laitinen, A. Savonen, G. Sundholm, J. Power Sources, **30**(1990),185.
115. G. Hoffman and W. Vielstich, Prog. Batteries Solar cells, **5** (1984) 170.
116. B. K. Mahato, J. Electrochem., Soc., **127** (1980) 1679.
117. A. LeMehaute, J. Appl. Electrochem., **6**(1979)543.
118. G. J. Szava, J. Power Sources, **23** (1988) 119.
119. B. Hall and G. A. Wright and I. G. Mawston, J. Power Sources, **30** (1990)193.
120. R. M. LaFollette, and D. N. Bennion, J. Electrochem. Soc., **137**(1990)3693.
121. R. M. LaFollette and D. N. Bennion, J. Electrochem. Soc., **137**(1990)3701.

Chapter 2

EFFECT OF GELLING ON THE OPEN-CIRCUIT POTENTIAL - TIME TRANSIENTS OF Pb/PbSO₄ ELECTRODES AT VARIOUS STATES-OF-CHARGE*

The technique of open-circuit potential relaxation from a prior pre-polarised state has been employed to study the kinetics of the Pb/PbSO₄ electrode in 4.8 M. sulphuric acid. The significant features governing the relaxation have been quantitatively analysed to obtain a correlation between state-of-charge of the electrode and its potential-recovery time constant. The effect of immobilising the electrolyte has also been included due to its relevance in making sealed maintenance-free batteries. The study provides a method for estimating the variation of exchange current density of the Pb/PbSO₄ and hydrogen evolution reactions at various states-of-charge with and without added gelling agents.

*A paper based on this study has appeared in the J. Appl. Electrochem., **24** (1994) 44.

2.1. INTRODUCTION

Measurement and analysis of the relaxation of open-circuit potential provides useful information regarding the interfacial characteristics of electrochemical reactions¹⁻⁶. Specifically, this includes capacitance behaviour of the electrode-solution interface,³⁻⁷ kinetic and mechanistic behaviour of the electrode reactions⁸⁻¹⁰ and potential-dependent adsorption pseudo-capacitance associated with the coverage variation of chemisorbed species etc. This technique is especially important when steady state measurements are difficult due to the time dependence of overpotential or the variation of coverage by adsorbed species with potential and time. This difficulty is often realised in several experimental systems such as corroding battery electrodes, other film-covered interfaces and electrodes with attached gas bubbles.

The open-circuit potential (OCP) relaxation technique has been employed successfully for the past two decades for various battery electrodes such as PbO_2 ⁸, NiOOH ^{6,7,9}, Mg^{10} , Fe^{11} and Zn^{12} . A similar understanding of the mechanism governing the transients of the Pb/PbSO_4 electrode in sulphuric acid electrolyte is both of theoretical and practical interests. Although the technique of the OCP-time transient has been employed for the Pb/PbSO_4 electrode in sulphuric acid by Pavlov¹³, the objective was to analyse the mechanism of passivation along with the alkalisiation of solution in the pores subsequent to the formation of PbO and basic PbSO_4 . The transients were found to be governed by processes associated with the disappearance of alkalisiation in the pores.

As the modern trend to develop sealed maintenance-free lead-acid batteries with gelled or absorbed electrolytes continues, it is of practical importance to analyse the effect of gelling on the electrode kinetics of the Pb/PbSO_4 electrode. Furthermore, this analysis of OCP decay with or without gel can provide a correlation between the parameters of self-

discharge kinetics and the observed potential-recovery time constants. The latter aspect will be useful for improving the shelf life of maintenance-free batteries and also in designing cells for special purposes like pulsed discharge.^{14,15}

In this chapter an analysis of the open-circuit potential-time transients of Pb/PbSO₄ electrodes is attempted at various states-of-charge (SOC); the effect of immobilising the electrolyte using sodium silicate gel on the kinetics of Pb/PbSO₄ electrode is also investigated. In addition, the study provides a means to estimate self-discharge rate from the slope of such OCP- time transients.

2.2. EXPERIMENTAL DETAILS

Positive and negative lead-acid plates were obtained in cured and formed condition from the production line at UB-MEC Batteries Ltd, India. All the electrodes were made using the same grid materials namely, Pb-Ca(0.08%)-Sn(0.5%), in order to exclude possible effects of interaction by corrosion products. Negative limited test cells with excess sulphuric acid (4.8 M) electrolyte were assembled with two positive counter electrodes arranged on either side of the working electrode. AnalaR grade reagents and Millipore water were used throughout the experiments.

The potential of the working electrode was measured against a Hg/HgSO₄, H₂SO₄ (4.8 M) reference electrode. The reference electrode was connected to the test cell with a capillary bridge filled with sulphuric acid (4.8 M) and provided with a closed ungreased stopcock. The bridge terminated in a luggin type capillary tip aligned close to the centre of the working electrode. All potentials are reported relative to this reference electrode. The electrode potentials were measured, corrected to ± 0.1 mV, by connecting a buffer amplifier with unit gain and substantially high input impedance ($10^{13} \Omega$) between the working and reference electrodes.¹⁶

The electrodes were given an initial soaking of 10 hrs. in 4.8 M sulphuric acid and then the cell was subsequently subjected to galvanostatic charging and discharging (C/10 rate) for five cycles to stabilise the capacity. The discharge and charge cut-off points for these cycles were -0.85 and -1.2 V respectively. The SOC was calculated on the basis of the stabilised capacity at the end of the fifth cycle. At the end of the sixth charge, the cells were given the same amount of over-charge(20%), kept at OCP for 30 min. and then discharged at the C/10 rate. At the end of discharge potential-time data were collected at room temperature ($25 \pm 1^\circ\text{C}$). The experiments were repeated at each SOC values with immobilised electrolyte, prepared by using sodium silicate (5 gm dm^{-3}) as the gelling agent.¹⁷

2. 3. RESULTS AND DISCUSSION

Figures 2.1 and 2. 2 show data for the OCP recovery of the Pb/PbSO₄ electrode following the interruption of a prior anodic polarisation in flooded and gelled electrolyte, respectively, at various state-of-charge (SOC) values. The instantaneous variation in the electrode potential caused by the ohmic drop makes the transient very steep at the onset. This recovery appears to be faster in the case of flooded electrolyte at all SOC values. Subsequent to this initial steep drop, the potential varies slowly with time, approaching the equilibrium value asymptotically. The physicochemical processes governing this relaxation are independent of SOC as the attainment of equilibrium is fairly fast and is complete within 15 seconds. This is in contrast to the PbO₂ electrode in which the relaxation time is constant, as well as the equilibrium potential varies with SOC.⁸ Moreover, the variation over longer times is much faster for the case with immobilised electrolyte, indicating the increased hindrance to mass transfer. This is more pronounced at lower SOC values. For example, in the case of flooded electrolyte, 95% of the relaxation is complete within 20

seconds, even at an SOC of 0.05, but it requires several minutes for the gelled electrolyte case.

Figures 2.3 and 2.4 show the OCP-time transients for the flooded and gelled electrolytes subsequent to the interruption of the cathodic current. The main features are similar to those for the anodic case, suggesting that a similar reaction, the reduction of PbSO_4 to Pb , controls the relaxation kinetics. However, in the case of all SOC values,

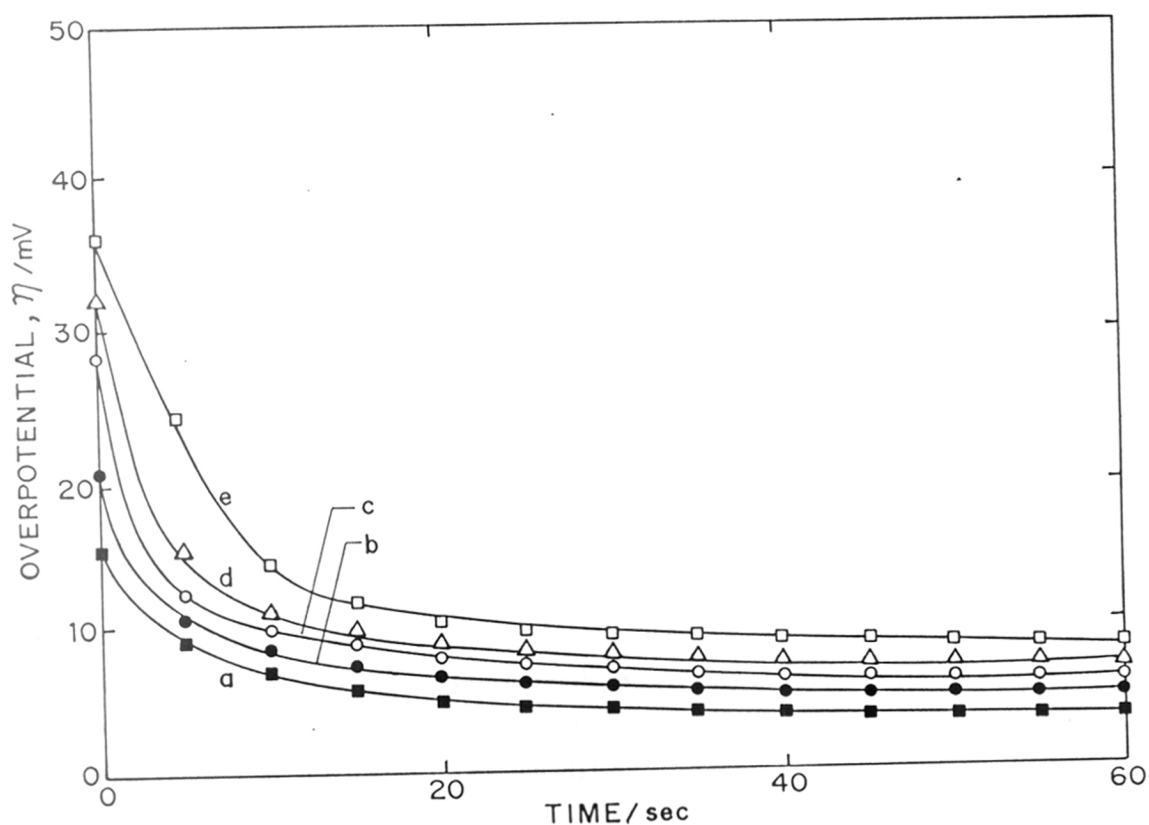


Figure 2.1. Open-circuit potential-time transients following the interruption of a prior anodic polarisation of Pb/PbSO_4 electrode in 4.8 M sulphuric acid at various SOC values; (a) 0.995, (b) 0.8, (c) 0.5, (d) 0.2 and (e) 0.05.

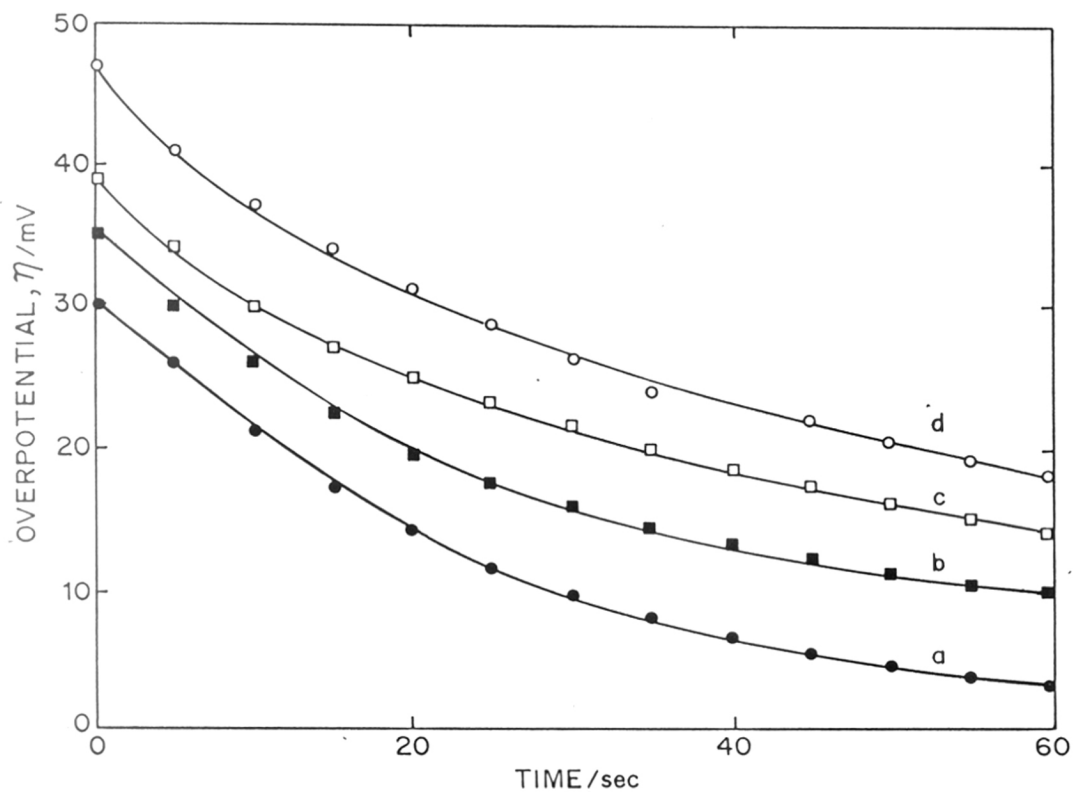


Figure 2.2. Open-circuit potential-time transients following the interruption of a prior anodic polarisation of Pb/PbSO₄ electrode in 4.8 M gelled sulphuric acid at various SOC values : (a) 0.8, (b) 0.5, (c) 0.2 and (d) 0.05

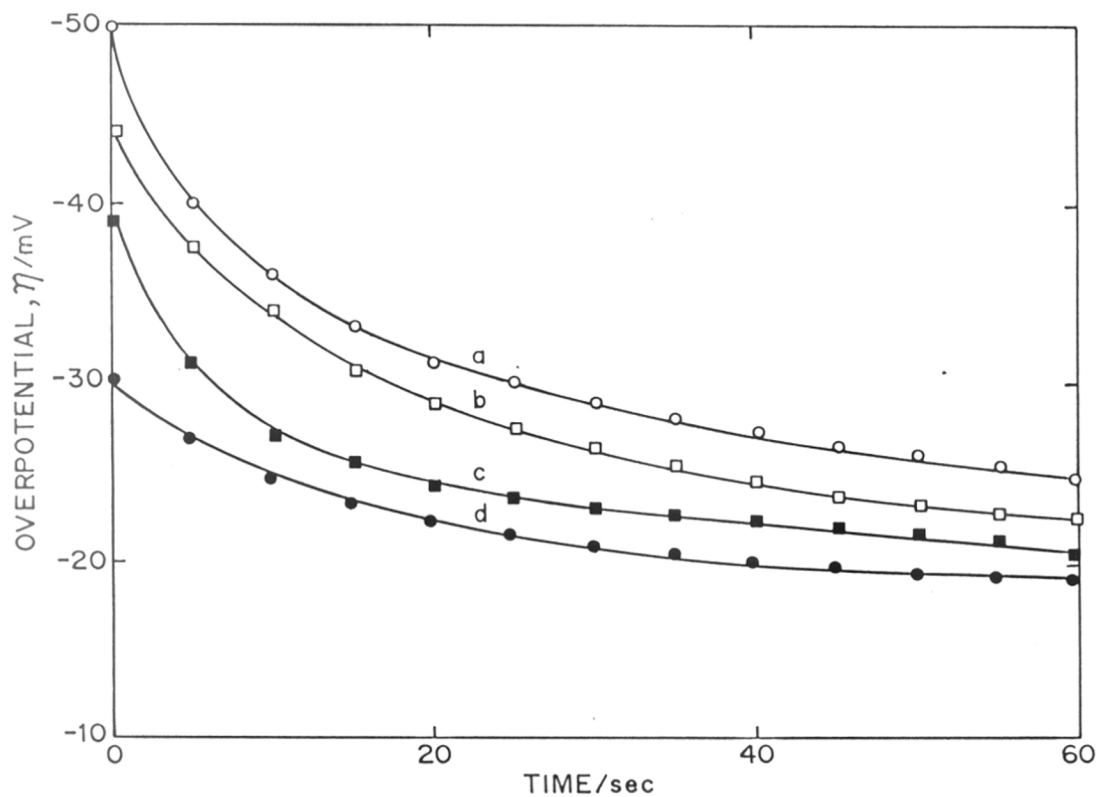


Figure. 2. 3. Open-circuit potential-time transients following the interruption of a prior cathodic polarisation of Pb/PbSO₄ electrode in 4.8 M sulphuric acid at various SOC values:(a) 1, (b) 0.8, (c) 0.5 and (d) 0.2.

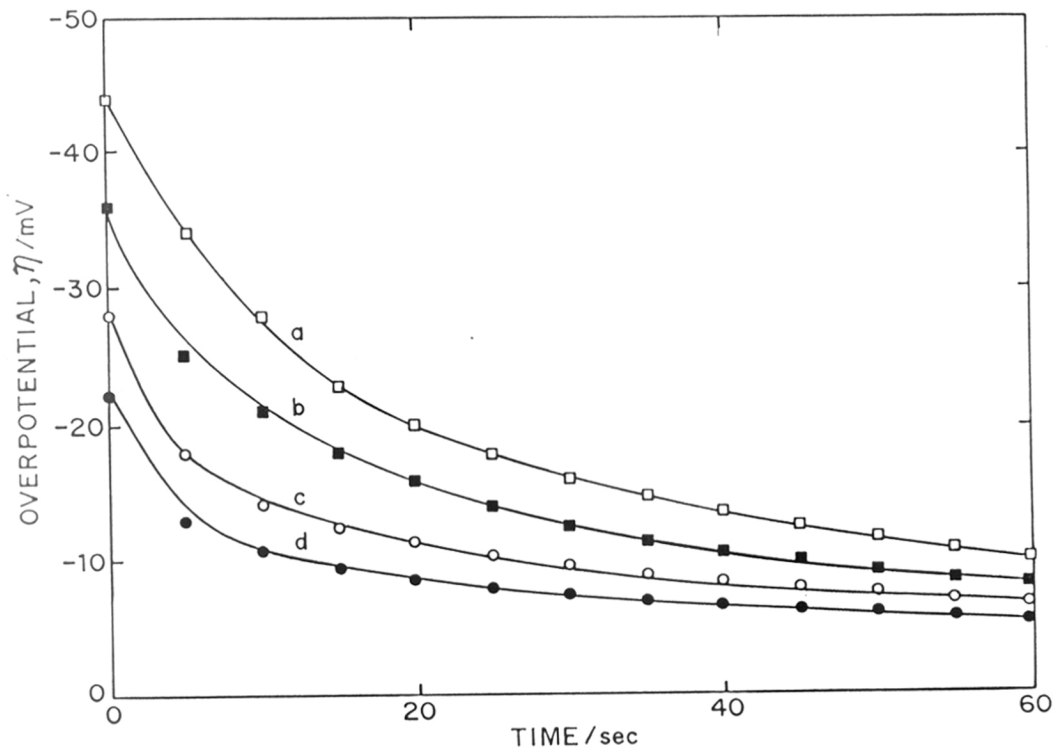


Figure. 2. 4. Open-circuit potential-time transients following the interruption of a prior cathodic polarisation of Pb/PbSO₄ electrode in 4.8 M gelled sulphuric acid at various SOC values : (a) 1, (b) 0.8, (c) 0.5 and (d) 0.2.

except perhaps the case of the lowest one (0.2), the possibility of simultaneous hydrogen evolution and PbSO_4 reduction contributing to the relaxation is more likely. Although these transient patterns progressively change with SOC, the immobilisation has very little effect at high SOC values on the cathodic recovery curves, unlike the cases represented in Figures 2.1 and 2.2.

2.3.1 Theoretical analysis of OCP transients

Several electrochemical reactions can possibly occur on a Pb/PbSO_4 electrode under open-circuit conditions.¹⁸ Among these, the important potential-determining reactions are as follows,



The Pb/PbSO_4 , H_2SO_4 electrode under open-circuit is in a steady state when current flows between the Pb/PbSO_4 and $1/2\text{H}_2/\text{H}^+$ electrodes. That is, the observed potential is a corrosion potential (mixed potential) having a contribution from anodic lead dissolution and cathodic hydrogen evolution. This is especially significant at higher SOC values, where, the concentration of PbSO_4 is small compared to that of lead. The potential relaxation from a steady state value during polarisation to such a mixed potential following the interruption of the current in a galvanostatic mode can be expressed by the mutual compensation of faradaic and non-faradaic currents. That is,

$$-C_{dl} (d\eta/dt) + \Sigma I_{\text{faradaic}} = 0 \quad (2.4)$$

where C_{dl} is the double layer capacity, I_{faradaic} is the potential-dependent current for various faradaic processes such as reactions (2.1), (2.2) and (2.3) and η is the overpotential undergoing relaxation. The value of η also determines the magnitude of the open-circuit self discharge current. The resistance polarisation can be considered to be absent as the net

current is zero. Under these circumstances the relaxation of the OCP following current interruption can be analysed with the help of electrochemical reactions (2.1), (2.2) and (2.3) by using Equation (2.4).

$$-C_{dl}(d\eta/dt) + I_{o,Pb}[\exp(-\alpha_{Pb}f\eta_{Pb}) - \exp(\beta_{Pb}f\eta_{Pb})] + I_{o,H}[\exp(-\alpha_Hf\eta_H) - \exp(\beta_Hf\eta_H)] + I_{o,O}[\exp(-\alpha_Of\eta_O) - \exp(\beta_Of\eta_O)] = 0 \quad (2.5)$$

where, $I_{o,Pb}$, $I_{o,H}$ and $I_{o,O}$ are the exchange currents for reactions 2.1, 2.2 and 2.3 respectively. Similarly α and β are the apparent cathodic and anodic energy transfer coefficients; η_{Pb} , η_H and η_O are the overpotentials defined as $E - E_{Pb}^r$, $E - E_H^r$ and $E - E_O^r$ respectively and f is defined as nF/RT , where n is the number of electrons involved in the respective reactions and F , R and T have their usual significance.

Equation (2.5) is valid only if mass transfer polarisation is negligible for all the faradaic reactions. A high concentration of sulphuric acid (4.8 M) employed in the experiment and invariance of the observed OCP decay patterns with stirring suggest the absence of mass transfer control.

As a first approximation, one may avoid the third term in Equation (2.5) because of kinetic reasons.* Oxygen mass transfer is a relatively slow process; in addition, the electrolyte is likely to be saturated with hydrogen initially at least at high SOC values, due to corrosion of the lead electrodes. Hence, the oxygen reduction may be neglected and Equation (2.5) becomes

$$-C_{dl}(d\eta/dt) + I_{o,Pb}[\exp(-\alpha_{Pb}f\eta_{Pb}) - \exp(\beta_{Pb}f\eta_{Pb})] + I_{o,H}[\exp(-\alpha_Hf\eta_H) - \exp(\beta_Hf\eta_H)] = 0 \quad (2.6)$$

*Although the possibility of oxygen reduction can not be strictly ruled out in a maintenance-free battery with glass fibre separator or in a stirred cell with oxygen evolution from PbO_2 electrodes, its relative contribution is negligible¹⁹ as $I_{o,Pb}/I_{o,O} \gg 10^4$.

An examination of the observed OCP-time transients indicates that the hydrogen evolution reaction is in the Tafel domain in the potential ranges under consideration [$\eta_H \gg RT/nF$], hence the above Equation can be modified to

$$-C_{dl} (d\eta/dt) + I_{o,Pb} [\exp(-\alpha_{Pb} f \eta_{Pb}) - \exp(\beta_{Pb} f \eta_{Pb})] + I_{o,H} [\exp(-\alpha_H f \eta_H)] = 0 \quad (2.7)$$

This expression is the governing Equation for OCP transients of the Pb/PbSO₄ electrode in sulphuric acid at various SOC values. It includes the charge transfer polarisation of the reversible Pb/PbSO₄ system and the irreversible cathodic hydrogen evolution reaction (HER), compensated by the non-faradaic component expressed by the first term. This expression can be used for the analysis of OCP-time transients subsequent to cathodic as well as anodic interruption as follows.

During the relaxation from a prior anodic polarisation, the lead electrode (unless its SOC is near zero) attains a mixed or corrosion potential, E^{cor} , with lead dissolution occurring with hydrogen evolution. The measured potential approaches E^{cor} as $(d\eta/dt)$ approaches zero. At high SOC values as little PbSO₄ is present in the electrode surface, the PbSO₄ reduction can be neglected in comparison with dissolution of Pb during the relaxation from anodic polarisation. Hence Equation (2.7) becomes,

$$-C_{dl} (d\eta/dt) - I_{o,Pb} [\exp(\beta_{Pb} f \eta_{Pb})] + I_{o,H} [\exp(-\alpha_H f \eta_H)] = 0 \quad (2.8)$$

And consequently the corrosion current is

$$I_{cor} = I_{o,Pb} [\exp(\beta_{Pb} f (E^{cor} - E_{Pb}^r))] = I_{o,H} [\exp(-\alpha_H f (E^{cor} - E_H^r))] \quad (2.9)$$

where the overpotential for the lead dissolution and hydrogen evolution are substituted by the respective shift from their reversible values.

Substituting $I_{o,Pb}$ and $I_{o,H}$ into eqn.(2.8) and simplifying

$$- C_{dl} (d\eta / dt) - I_{cor} \{ \exp[\beta_{Pb} f(E-E^{cor})] \} + I_{cor} \{ \exp[-\alpha_H f(E-E^{cor})] \} = 0 \quad (2.10)$$

In the potential domain where $E - E^{cor} \ll 1/f$ eqn.(10) can be linearised to get

$$(d\eta / dt) = - [I_{cor}(\alpha_H + \beta_{Pb})f/C_{dl}]E + [I_{cor}(\alpha_H + \beta_{Pb})f/C_{dl}] E^{cor} = 0 \quad (2.11)$$

Thus a plot of $(d\eta / dt)$ vs. E will be a straight line with a slope of $I_{cor}(\alpha_H + \beta_{Pb})/C_{dl}$. Furthermore, this slope and intercept can be used to calculate the double layer capacitance and corrosion current with a prior knowledge of α_H and β_{Pb} values.

For the case of lower SOC values, although HER is thermodynamically possible, the presence of a large amount of $PbSO_4$ demands Pb^{2+} reduction as the major potential determining reaction. This is further supported by the fact that exchange currents are much larger for Pb^{2+} reduction in comparison with that for HER [i.e., $I_{0,Pb}/I_{0,H} > 10^3$].¹⁹ Also, experimentally HER is not observed during the decay except at SOC equal to unity. Under these circumstances Equation (2.7) can be written as

$$- C_{dl} (d\eta / dt) + I_{o,Pb} [\exp(-\alpha_{Pb} f \eta_{Pb})] - I_{o,Pb} [\exp(\beta_{Pb} f \eta_{Pb})] = 0 \quad (2.12)$$

Assuming $\alpha_{Pb} = \beta_{Pb} = \alpha$ the above expression can be written as,

$$- C_{dl} (d\eta / dt) + 2I_{o,Pb} \sinh(\alpha f \eta_{Pb}) = 0 \quad (2.13)$$

The solution of this differential Equation is,

$$\ln[\tanh(\alpha_{Pb} f \eta_{Pb}/2)] = -(2I_{o,Pb} f/C_{dl})t + \text{constant} \quad (2.14)$$

Hence by plotting $\ln[\tanh(\alpha f \eta_{Pb}/2)]$ against t , the exchange current density for the $Pb/PbSO_4$ system can be calculated from the slope. Furthermore, any change in the slope due to immobilisation can be attributed to the variation of $I_{o,Pb}$, assuming that C_{dl} does not vary appreciably with immobilisation. Alternatively, if η is very small compared to $1/\alpha f$ eqn.(2.12) can be linearised to obtain

$$- C_{dl} (d\eta / dt) - I_{o,Pb} f \eta_{Pb} = 0 \quad (2.15)$$

with the additional assumption $(\alpha_{Pb} + \beta_{Pb})$ equal to unity. This gives,

$$\ln(\eta) = - (I_{o,Pb}f)/C_{dl} t + \text{constant} \quad (2.16)$$

Hence a plot of $\ln(\eta)$ against t will be straight line with a slope of $-I_{o,Pb} f/C_{dl}$, during relaxation over longer times.

In the case of OCP-time transients subsequent to a prior cathodic polarisation the analysis is more complicated due to the variation of coverage of absorbed hydrogen with potential. However, for the special case of SOC of unity (relaxation from prolonged over-charging) the coverage variations can be neglected and the rate of the $Pb/PbSO_4$ reaction is practically zero compared to the rate of hydrogen evolution. Moreover, mass transfer polarisation can be neglected for hydrogen evolution in acid media as limiting currents are very high. In this situation eqn.(2.7) can be approximated as

$$-C(d\eta/dt) + I_{o,H} \exp(-\alpha_H f \eta_H) = 0 \quad (2.17)$$

Solution of this Equation gives,

$$\exp(\alpha_H f \eta_H) = -(\alpha_H f I_{o,H}/C)t + \text{constant} \quad (2.18)$$

Hence a plot of $\exp(\alpha_H f \eta_H)$ against time should be a straight line with a slope of $-(\alpha_H f I_{o,H})/C$, for the special case of SOC equal to unity.

For other SOC values, the cathodic case is similar to that of the anodic and a similar treatment will give a linear relation between $\ln(\eta)$ and time, whose slope and intercept can be used to calculate the kinetic parameters.

2.3.2 Comparison of theory with experimental data

Figures 2.5 and 2.6 show plots of $d\eta/dt$ against E at high SOC values using the data from Fig 2.1 and Fig 2.2. respectively. The linearity shown in the case of SOC 0.995 and 0.8 are in good agreement with the analysis expressed in eqn.(2.11). In addition, I_{cor} calculated on the basis of these slopes and apparent geometrical area (with the values of C , α_H and β_{Pb} taken from literature¹⁹) are $1.5 \times 10^{-7} \text{ A cm}^{-2}$ and $0.4 \times 10^{-7} \text{ A cm}^{-2}$ for flooded

and gelled electrolytes respectively. This decrease in corrosion rate is an added advantage in designing maintenance-free batteries using immobilised electrolyte. The deviation from linearity over the larger potential range is more prominent at low SOC values, as the reverse reaction, namely reduction of PbSO_4 to Pb , may also contribute; this was neglected during the derivation of eqn.(2.11).

However, at low SOC values eqn.(2.14) must be used and plots of $\ln [\tanh (\alpha f \eta_{\text{pb}}/2)]$ against t are shown in Fig.2.7 and 2.8 for flooded and gelled electrolytes respectively. The range of linearity is larger for the case of lower SOC values which

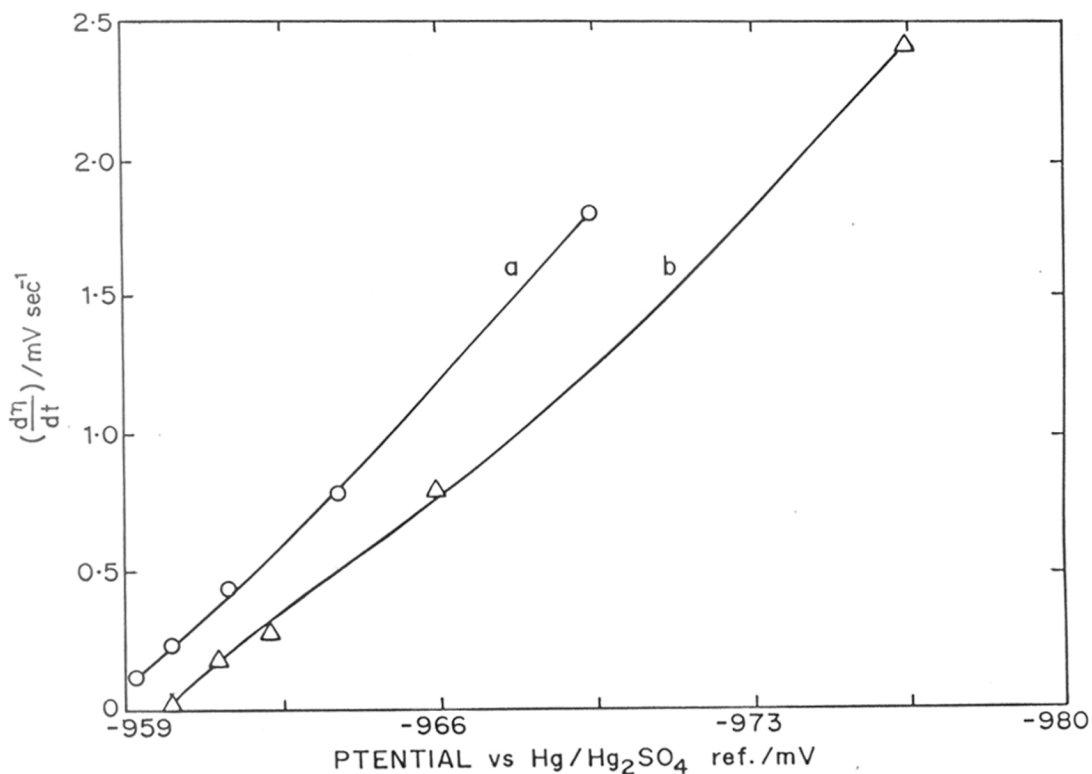


Figure 2.5. $(d\eta/dt)$ vs. E plots using the data from Fig.2.1 at various SOC values: (a) 0.995 and (b) 0.8.

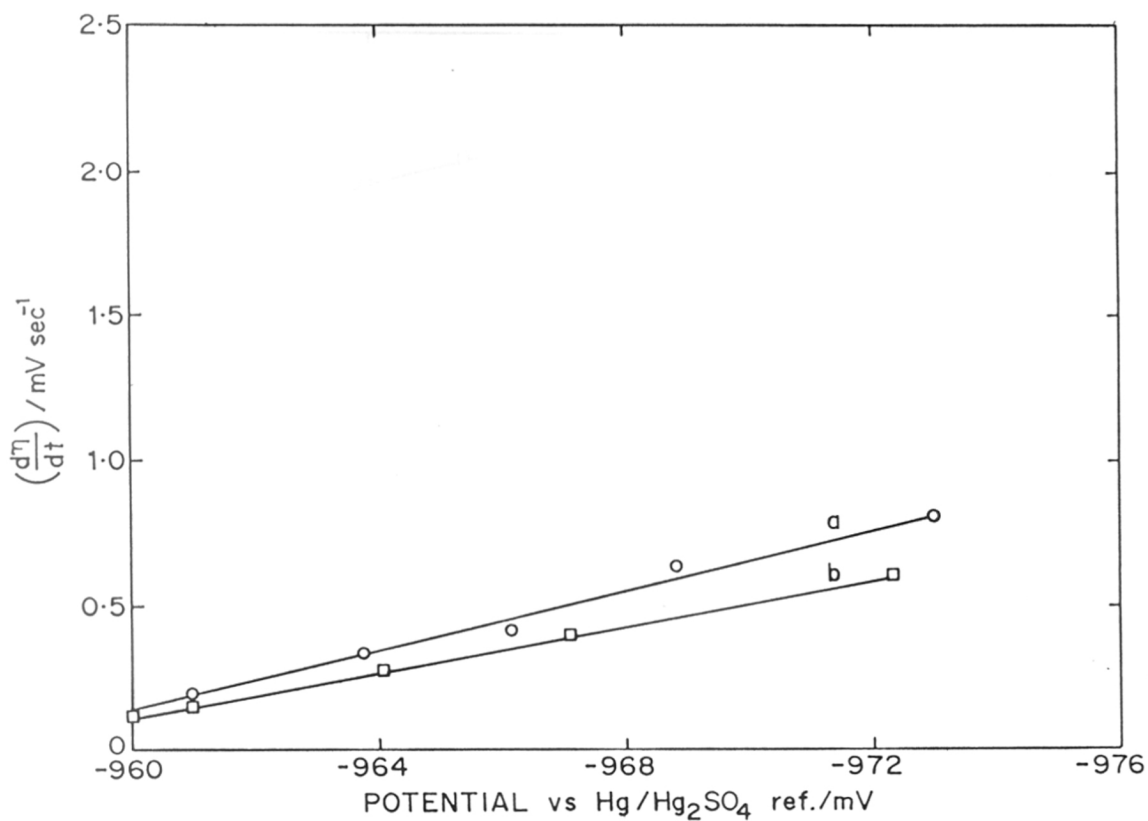


Figure 2. 6. $(d\eta/dt)$ vs. E plots in gelled electrolyte using the data from Figure 2.2 at various SOC values: (a) 0.8 and (b) 0.5

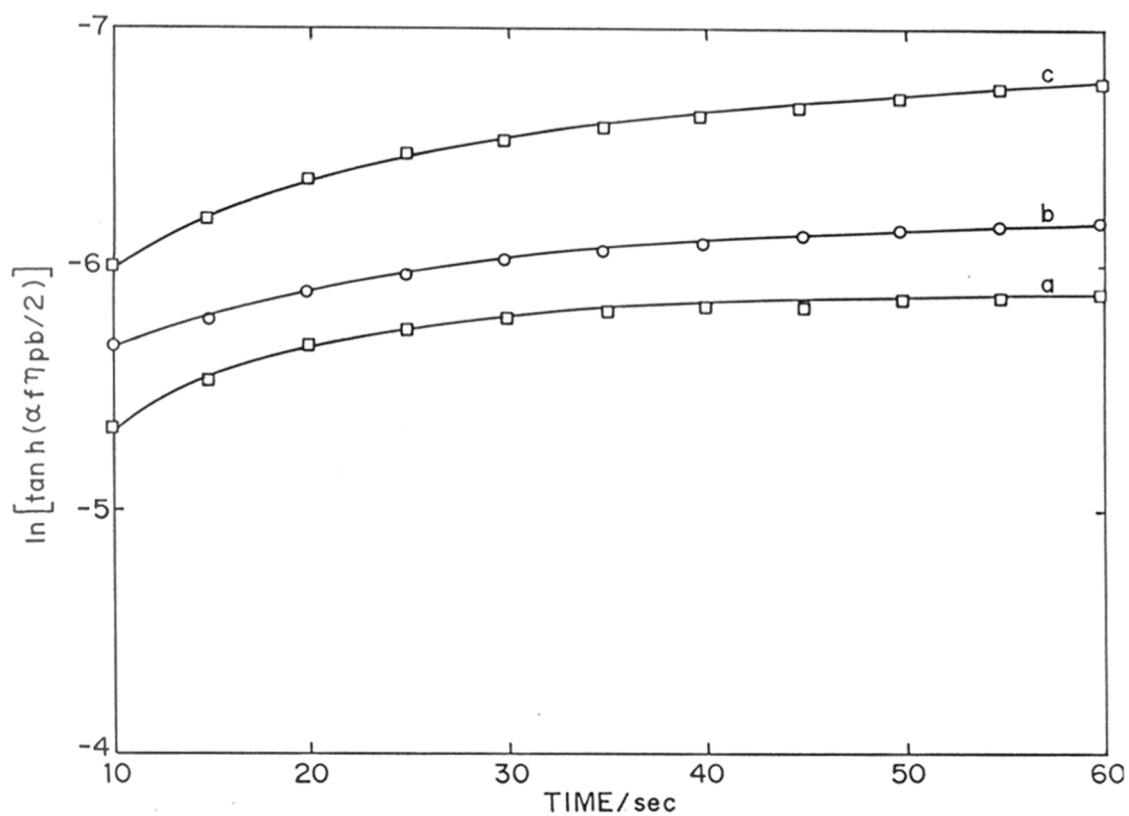


Figure 2. 7. $\ln [\tanh(\alpha_{pb}f\eta_{pb}/2)]$ vs. t plots using the data from Figure 2.1 at various SOC values: (a) 0.05, (b) 0.2 and (c) 0.5

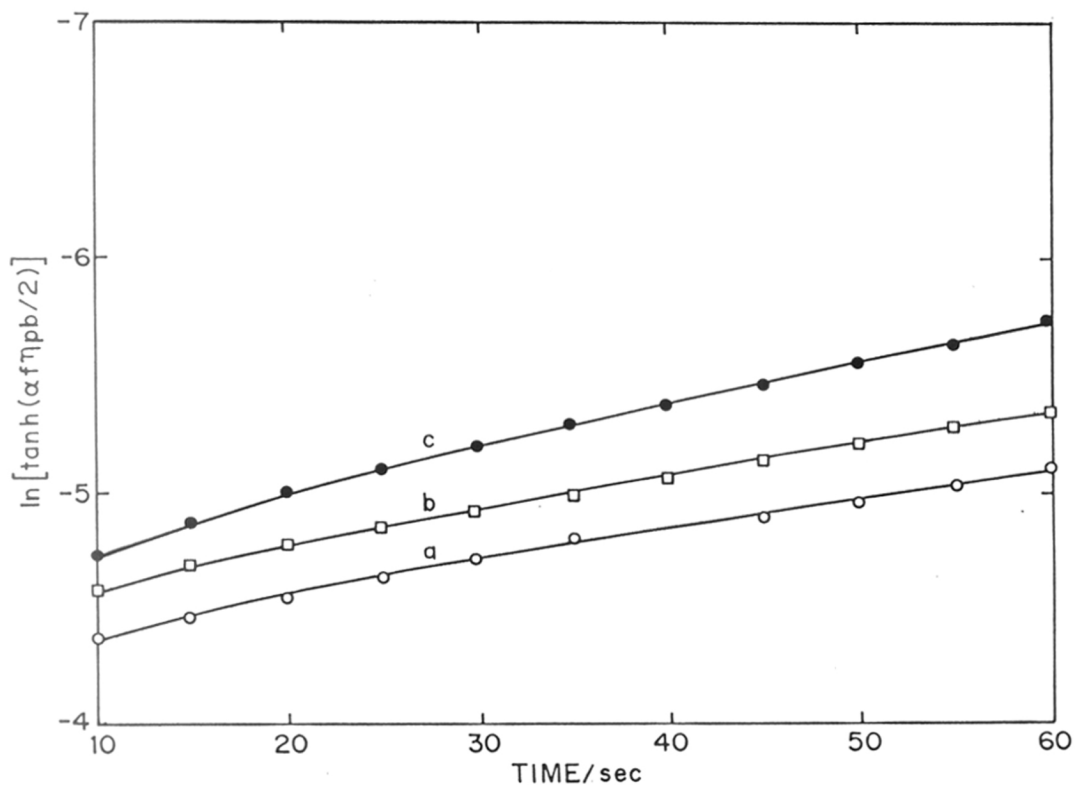


Figure 2. 8. $\ln [\tanh(\alpha_{pb} f \eta_{pb}/2)]$ vs. t plots of OCP relaxation from a prior anodic polarisation of Pb/PbSO₄ electrode in 4.8 M gelled sulphuric acid using the data from Figure 2.2 at various SOC values: (a) 0.05, (b) 0.2 and (c) 0.5.

substantiates the validity of eqn.(2.14). Furthermore, as the slope of these lines are independent of the area of the porous electrode, the variation of slope with SOC can be attributed to the variation of electrochemical reaction rate at different SOC values. Typical values of $I_{o,Pb}$ calculated on the basis of these plots and the apparent geometrical area (by taking the values of C , α_H and β_{Pb} from the literature¹⁹) are $5.1 \times 10^{-8} \text{ A cm}^{-2}$ and $1.2 \times 10^{-8} \text{ A cm}^{-2}$ for flooded and gelled electrolytes respectively. Although the magnitude of these values are small in comparison with reported values,^{14,19} it is reasonable to expect this on the basis of enhanced actual area due to porosity. This decrease in the exchange current density and extent of linearity change at a particular SOC value can be attributed to the effect of gelling agents like silicate ions on interfacial charge transfer. This, of course, assumes that the double layer capacitance is not changed by the addition of gelling agents, which is not necessarily true. The same conclusions can be obtained by plotting $\ln(\eta)$ vs. t as implied by eqn.(2.16).

Figure 2.9 shows plots of $\exp(\alpha_H f \eta_H)$ vs. t for OCP- relaxation from a prior cathodic polarisation at unit SOC using the data from figures 2.3 and 2. 4. The excellent linearity over a large time domain supports the assumptions involved in the treatment. The $I_{o,H}$ values calculated from the slopes are $2.2 \times 10^{-9} \text{ A cm}^{-2}$ and $1.5 \times 10^{-9} \text{ A cm}^{-2}$ for flooded and gelled electrolyte respectively. The slope change due to gelling is insignificant, indicating the absence of any electro-catalytic effects on HER by sodium silicate.

Plots of $\ln(\eta)$ against t for OCP-relaxation from a prior cathodic polarisation at various SOC values for Pb/PbSO₄ electrode in flooded and gelled electrolyte are shown in Figures 2.10 and 2. 11 respectively. The large initial deviation from linearity, as predicted by eqn.(2.16), may be attributed to the preference of lead dissolution over hydrogen

evolution. The possibility of interference from mass transfer cannot be ruled out completely as Pb^{2+} deposition may occur under diffusion limited conditions, which are not involved in

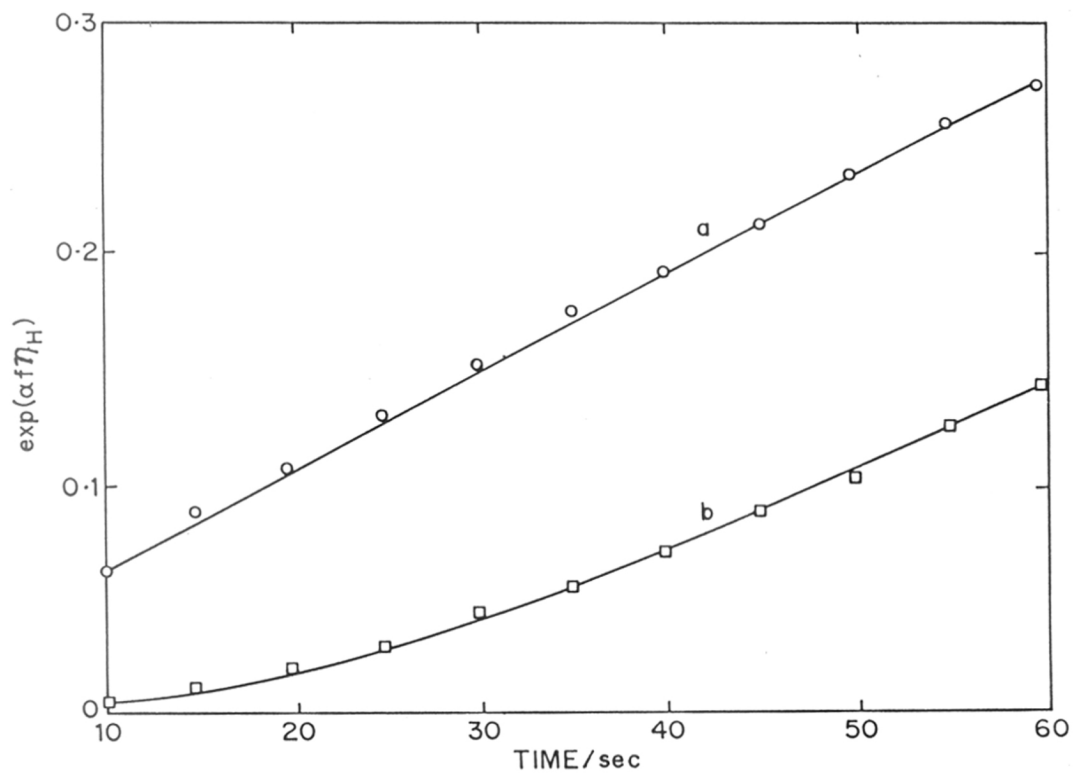


Figure 2. 9. $\exp(\alpha_{\text{Pb}} f \eta_{\text{Pb}}/2)$ Vs t plots at unit SOC using the data from Figure 2. 3 and Figure 2.4 ; (a) and (b) represent flooded and gelled electrolyte respectively.

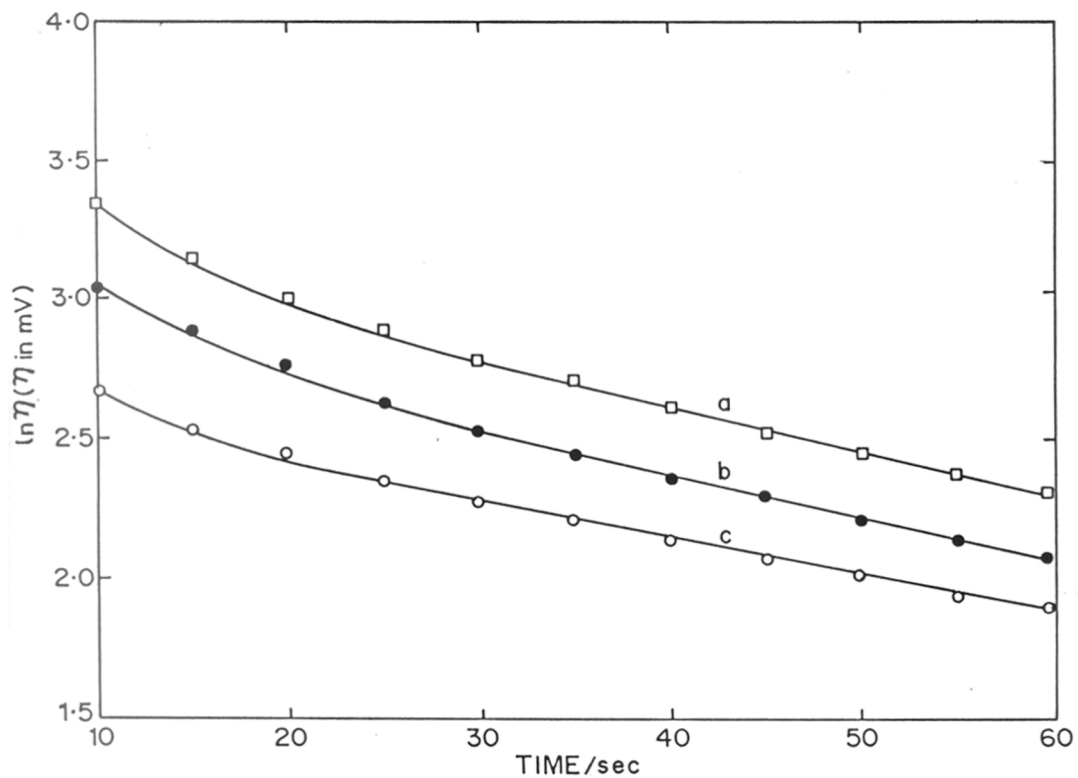


Figure. 2. 10. $\ln(\eta)$ Vs t plots for OCP relaxation from a prior cathodic polarisation using the data from Figure 2.3. at various SOC values: (a) 0.8, (b) 0.5 and (c) 0.2.

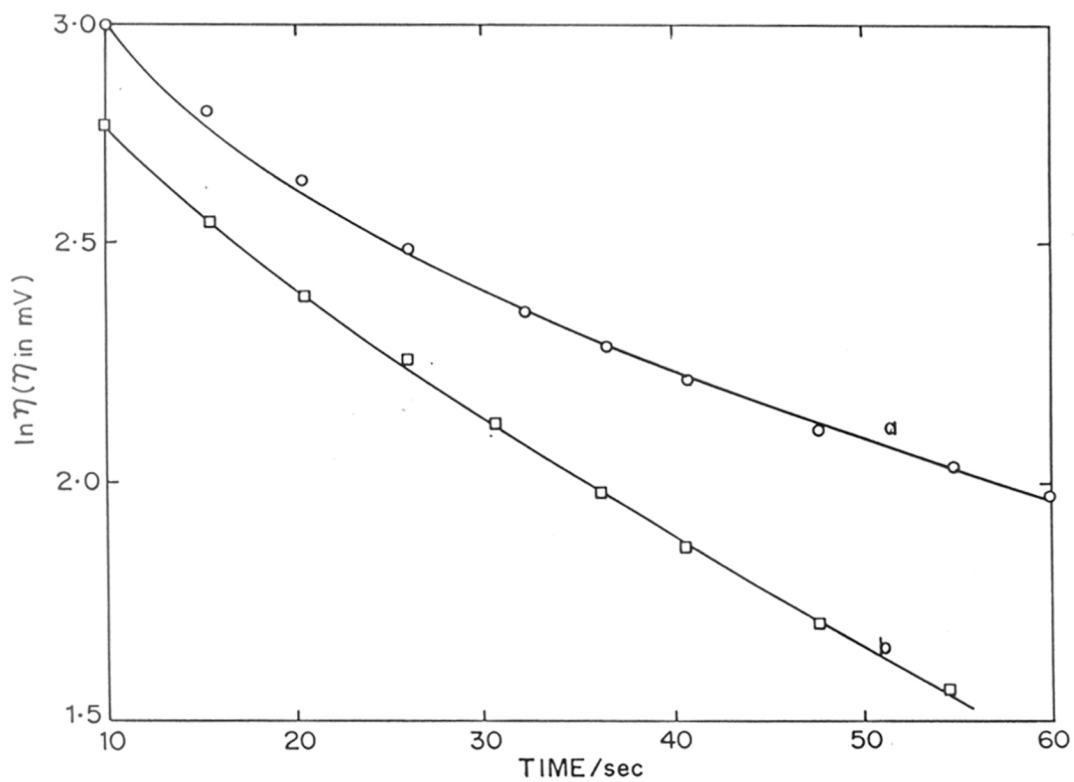


Figure 2. 11. $\ln(\eta)$ Vs t plots for OCP relaxation using the data from Figure 2.4 at various SOC values: (a) 0.5 and (c) 0.2.

the theoretical analysis. The viscosity effects due to immobilisation of the electrolyte may also be important. The extent of deviation is less for the gelled electrolyte as there is increased hindrance for mass transfer especially at lower SOC values. The slope and intercept of these plots can also be used to calculate the kinetic parameters, with a prior knowledge of double-layer capacitance and apparent transfer coefficients.

2. 4. CONCLUSION

A quantitative analysis of OCP-time transients of the Pb/PbSO_4 electrode in gelled and flooded sulphuric acid shows that there is a substantial change in the self-discharge kinetics of the Pb/PbSO_4 electrode as a result of immobilisation. This change in the rate of both Pb/PbSO_4 and hydrogen electrode reactions will be especially useful in designing maintenance-free lead-acid batteries with gelled electrolytes.

2.5. REFERENCES

1. G. H. Kelsall, in 'Techniques in Electrochemistry, Corrosion and Metal Finishing -a hand book (edited by A. T. Kuhn) John Wiley New York (1987) P.43.
2. D. A. Harrington and B.E Conway, J. Electroanal. Chem., **221** (1987) 1.
3. J. A. Butler and J. F. Armstrong, Trans. Faraday. Soc., **29** (1938) 126.
4. A. N. Frumkin, Acta Physicochem. URSS., **18** (1943) 23.
5. H. B. Morley and F. E. W. Wetmore, Can. J. Chem., **34**(1956) 359.
6. B. E. Conway and P. L. Bourgault, Can. J. Chem, **37** (1959) 292.
7. B. E. Conway and P. L. Bourgault, Trans. Faraday. Soc., **58** (1962) 593.
8. P. Ruetschi, J. Electrochem. Soc., **120**(1973) 331.
9. P. L. Bourgault and B. E. Conway, Can. J. Chem., **38** (1960) 1557.
10. B. V. Ratnakumar and S. Sathyanarayana, J. Power Sources, **12** (1984) 39.
11. K. Vijayamohan, A. K. Shukla and S. Sathyanarayana, J. Power Sources, **21**(1987) 53
12. T. P. Driske, J. Appl. Electrochem., **1** (1971) 27.
13. D. Pavlov, Electrochim. Acta., **13** (1968) 2051.
14. R. M. LaFollette and D. N. Bennion, J. Electrochem. Soc., **137** (1990) 3693.
15. J. Sterbe, B.Reichman, B.Mohato., K. R. Bullock., J. power. Sources., **31** (1990) 43.
16. K. Vijayamohan, A. K. shukla and S. Sathyanarayana, Eletrochim. Acta,**36** (1991)369.
17. M. Barek, 'Electrochemical Power Sources', Peter Peregrine, Stevenage, (1980) p. 290
18. D. Pavlov in 'Power sources for Electric vehicles', (edited by B. D. Mc Nicol and D.A.J Rand) Elsevier, Amsterdam, Oxford (1984) p.113.
19. T.F.Sharpe, in 'Encyclopaedia of Electrochemistry of the Elements', vol.1,(edited by A. J. Bard), Marvel Decker Inc., New York (1973) P. 308.

EFFECT OF GELLING ON THE ELECTRODE KINETICS OF Pb/PbSO₄ AND HYDROGEN ELECTRODE REACTIONS IN MAINTENANCE-FREE LEAD-ACID BATTERIES*

The electrode kinetics of Pb/PbSO₄ and hydrogen evolution reactions on porous lead electrodes in sulphuric acid has been studied using a quantitative analysis of galvanostatic transients in the linear polarisation domain. Significant changes have been observed in the kinetics with the addition of thixotropic agents, like sodium silicate which are often employed in the manufacture of maintenance-free lead acid batteries. The effect of these thixotropic agents on the charge-transfer and ohmic components of Pb/PbSO₄ reaction and charge transfer components of hydrogen electrode reaction are analysed with the help of a "pore-plugging" model. This study allows a nondestructive determination of electrode kinetic parameters and internal resistance contribution from pore-plugging useful for designing maintenance-free lead-acid batteries.

* A paper based on this study has appeared in J. Power Sources, 50 (1994) 67.

3. 1. INTRODUCTION

The advent of sealed maintenance-free batteries in recent years has increasingly lead to the use of immobilised and absorbed electrolytes,¹⁻³ with or without catalytic recombination plugs. In the former, the loss of oxygen and hydrogen (produced during charge or overcharge of the respective positive and negative electrodes) is sought to be minimised either by oxygen-hydrogen recombination on a suitable catalyst in the vent plug or by oxygen reduction on porous lead of the negative electrode. In the latter immobilisation of the electrolyte is necessary and is achieved by using an artificial thixotropic agent such as sodium silicate to the electrolyte so that the amount of electrolyte can be controlled to achieve electrolyte-starved conditions, where gas evolution is minimum. However, addition of this thixotropic agent will have other implications such as increased ohmic resistance, change on the interfacial kinetics due to adsorption of silicate ions, formation of cracks in the electrolyte and gas entrapment. In addition, a progressive loss of hydrogen from the cell can cause drying out of the gel, resulting in electrolyte imbalance followed by eventual cell or battery failure. Although pressure-regulated valve cells with gelled electrolyte are commonly used for several float applications, none of the above problems have been systematically analysed, except for the effect of thixotropic agents on hydrogen evolution kinetics⁴. More importantly, recent studies^{5,6} indicate the suitability of the lead-acid system for pulsed discharge and this demands a careful analysis of the effect of gelling on the ohmic drop, especially if maintenance-free (MF) gelled systems is to be used for these and other high-rate applications. Addition of silicate ions is also known to cause favourable changes in shelf-life and cycle life of lead-acid batteries.

In the second chapter, the gelling of the electrolyte is found to suppress the self discharge kinetics of Pb/PbSO_4 electrode kinetics. In order to substantiate these results a

study on the kinetics of the lead electrode and hydrogen electrode reactions in gelled and flooded electrolyte systems is presented in this chapter. Within the range of open-circuit potentials observed for Pb/PbSO₄ system, the hydrogen evolution reaction (HER) could be considered to be in the Tafel domain and the lead electrode reaction occurring in a quasi-reversible manner. Considering this, the galvanostatic transients of Pb/PbSO₄ electrode in gelled and flooded electrolyte have been quantitatively analysed in the linear polarisation domain. From such an analysis of the build-up and decay region of the transients, several useful parameters like double layer capacitance and exchange current density of both lead and hydrogen electrode reactions have been obtained. More specifically, the plugging of the pores of the Pb/PbSO₄ electrode due to the accumulation of the discharged products, PbSO₄, resulting in a high IR drop has also been incorporated as a parameter in the analysis; the progressive variation of this parameter with battery state-of-charge (SOC) has been used to account for the pore plugging, a phenomenon which is known to even limit the capacity of several battery electrodes.^{6,7} The significant changes in pore-plugging with gelling at a low state-of-charge (SOC) have also been evaluated after neglecting any local alkalisiation in the pores.^{8,9}

3.2. EXPERIMENTAL DETAILS

Negative and positive pasted plates (5.5 X 3 X 0.1 cm³) used in this study were obtained in cured and formed condition, and the experimental details are described in chapter 2.

Initially all these electrodes were soaked in 4.8 M H₂SO₄ for 10 hrs. and then subject to galvanostatic charging and discharging at C/10 and C/8 rates respectively. This was continued for five cycles to stabilise the measured capacity values and this constant value is used for all SOC calculations. All the cells were then given the same

amount of overcharge (20%) kept at open-circuit for 30 min. and polarised with appropriate current densities such that a steady-state could be obtained in few minutes within the linear polarisation range. On attaining the steady-state, the current was interrupted and the open-circuit potential (OCP) versus time transients were measured till the original equilibrium value was restored. The experiments were repeated using various current densities selected on the basis of causing negligible SOC change (i.e., $\int Idt \ll \text{SOC}$).

Galvanostatic potential-time transients were obtained at various SOC values such as 1, 0.5 and 0.05 by keeping the current densities at constant values. Similar experiments were conducted with separate electrodes at various SOC values and current densities in an immobilised electrolyte. The later was prepared by using sodium silicate (5gm/l) as a thixotropic agent.^{10,11}

3. 3. RESULTS AND DISCUSSION

The data for potential-time transients taken at various current densities in the linear polarisation domain for gelled and flooded electrolytes at unit SOC are presented in Figures 3.1 and 3. 2 respectively. During both the cathodic and the anodic polarisation, the build-up and decay transients were followed, till a steady-state was reached within an overpotential of less than 10 mV to ensure a linear polarisation domain. Similar plots for low SOC value (0.05) are shown in Figures 3. 3. and 3. 4. respectively. In all these cases, the potential tends to reach the steady-state value asymptotically with time and this time is longer for higher current densities. Significant difference can be observed between the cathodic and anodic transients at a given SOC value. Moreover, the transient patterns are less steeper for the low SOC value case irrespective of the nature of the polarisation. In the case of cathodic polarisation at unit SOC value, the pattern is different from that of the other curves. This deviation can be attributed to the contribution of the HER on the

electrode kinetics which is insignificant at low SOC values. In addition, significant changes are observed in the anodic patterns at a SOC of 0.05, indicating the importance of ohmic drop arising due to the accumulation of insulating PbSO_4 in the pores of the electrode.

The transient patterns in the gelled electrolyte is basically the same as that obtained in the flooded electrolyte. However, the build-up and decay transients are much steeper for the gelled electrolyte for a particular SOC value. This can be attributed to the increased hindrance of mass transfer that is brought about by the presence of interpenetrating net work of polysilicic acid gel. Variation of the transient patterns with SOC values is also observed in the gelled electrolyte. The explanation of this behaviour is the same as that discussed above for flooded electrolyte.

3.3.1. Phenomenological model for galvanostatic transients

Various electrochemical reactions are known to occur on a Pb/PbSO_4 electrode under open-circuit conditions as described in details in chapter 2. Among these the major potential-determining reactions are,



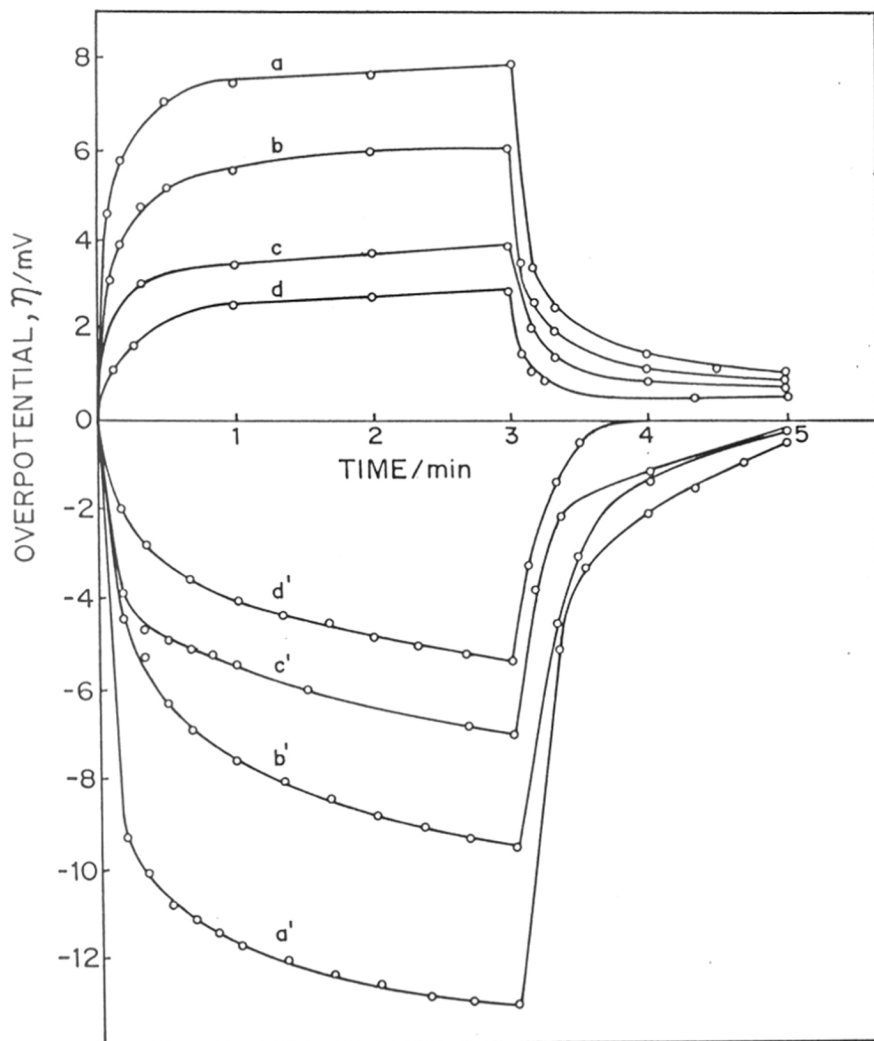


Figure 3.1. Galvanostatic potential-time transients at various current densities for flooded electrolyte at SOC = 1; a,b,c,d corresponds to anodic transients and a',b',c' and d' corresponds to cathodic transients at 60, 45, 30 and 15 $\mu\text{A cm}^{-2}$ respectively.

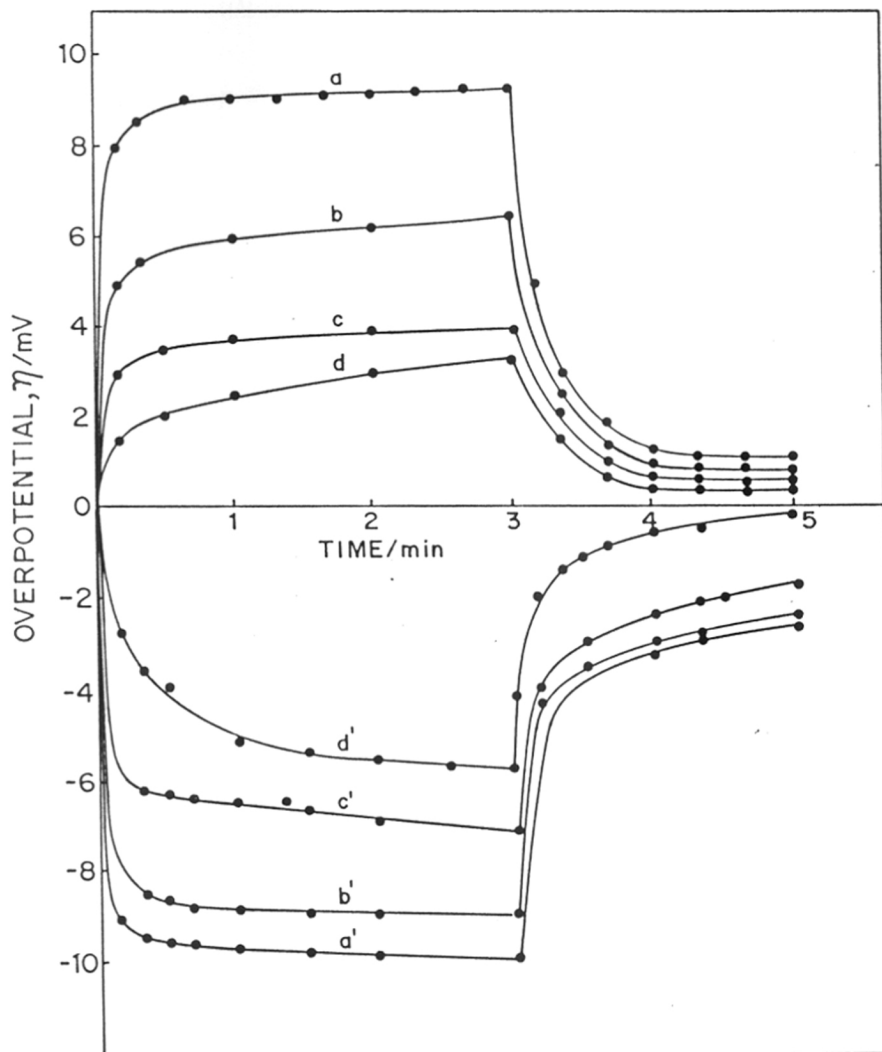


Figure 3. 2. Galvanostatic potential-time transients at various current densities for gelled electrolyte at SOC = 1; a,b,c,d corresponds to anodic transients and a',b',c' and d' corresponds to cathodic transients at 60, 45, 30 and 15 $\mu\text{A cm}^{-2}$ respectively.

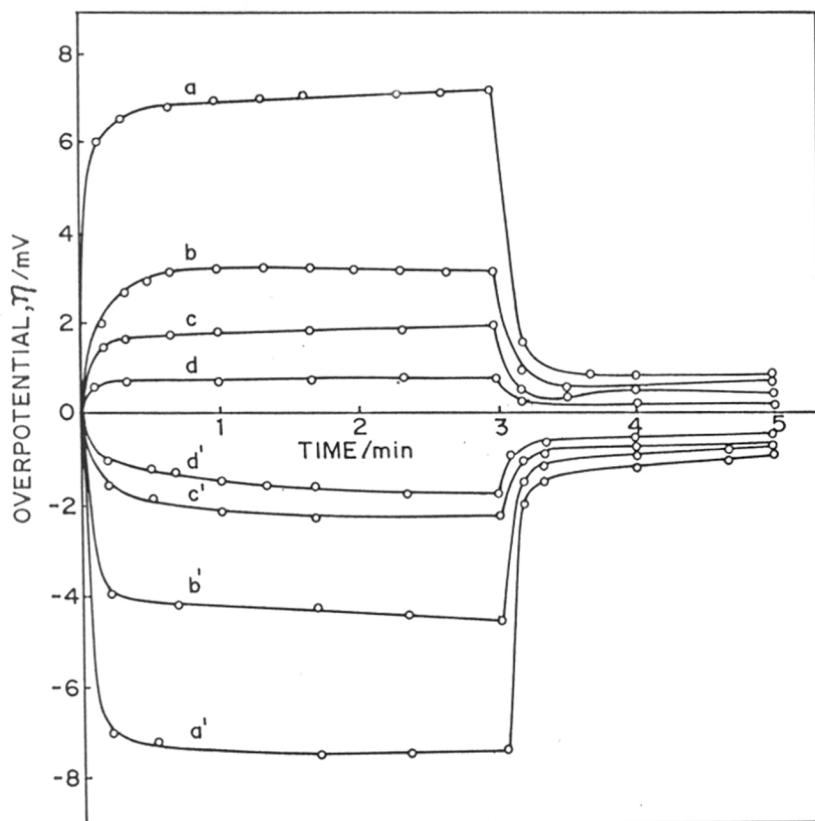


Figure 3.3. Galvanostatic potential-time transients at various current densities for flooded electrolyte at $\text{SOC} = 0.05$; a,b,c,d corresponds to anodic transients and a',b',c' and d' corresponds to cathodic transients at 60, 45, 30 and $15 \mu\text{A cm}^{-2}$ respectively.

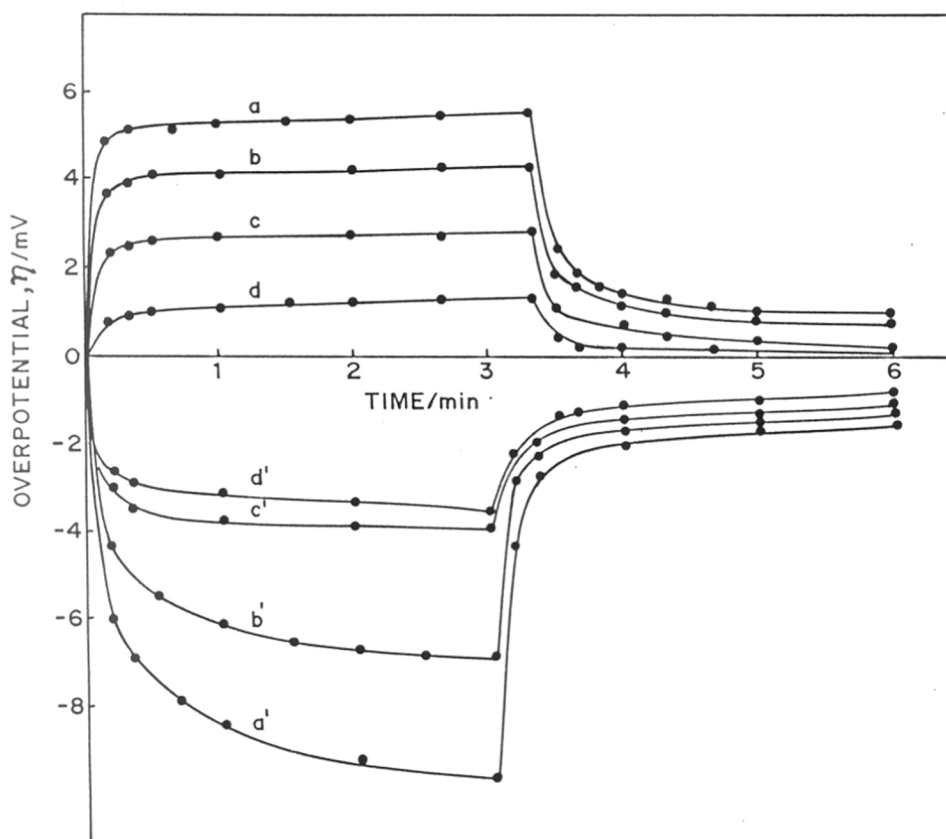


Figure 3. 4. Galvanostatic potential-time transients at various current densities for gelled electrolyte at SOC = 0.05; a,b,c,d corresponds to anodic transients and a',b',c' and d' corresponds to cathodic transients at 60, 45, 30 and 15 $\mu\text{A cm}^{-2}$ respectively.

The respective reversible potentials of these reactions in 4.8 M sulphuric acid are - 0.9716, - 0.6186 and + 0.6116 V vs. Hg/Hg₂SO₄, H₂SO₄ reference electrode. Among these reactions, the oxygen reduction reaction can be neglected due to the following kinetic reasons. The dissolution of oxygen from the atmosphere and its supply to the electrode surface by diffusion is a relatively slow process in a quiescent solution. More importantly, a constant evolution of hydrogen as observed experimentally at open-circuit will make the electrolyte likely to be saturated with hydrogen in the beginning especially at high SOC values. The general current-potential relation for the remaining two reactions can be written as

$$I = -C_{dl} (d\eta / dt) + I_{o,Pb} [\exp(-\alpha_{Pb} f \eta_{Pb}) - \exp(\beta_{Pb} f \eta_{Pb})] + I_{o,H} [\exp(-\alpha_H f \eta_H)] \quad (3.4)$$

Where, the first term corresponds to the non-faradaic current with C_{dl} as the double layer capacitance and the second and third terms correspond to faradaic currents associated with reaction (3.1) and (3.2) respectively; α_{Pb} and α_H are the overpotentials for reactions (3.1) and (3.2) defined as $E - E_{Pb}^r$ and $E - E_H^r$ respectively; $I_{o,Pb}$ and $I_{o,H}$ are the respective exchange current densities; α_{Pb} , β_{Pb} , α_H and β_H are the apparent charge-transfer coefficients for the corresponding reactions and f is given by nF/RT with n as the number of electrons involved in the respective rate-determining steps.

Equation (3.4) is valid only if mass transfer polarisation can be considered to be negligible for the faradaic reactions. A high concentration of sulphuric acid (4.8 M) and invariance of transients with stirring justifies this assumption. In addition, the time dependent diffusional contributions are rendered insignificant by a judicious choice of

experimental conditions. The current density is selected to be extremely small (approximately $C/500$ where C is the nominal capacity of the electrode) for a duration of only few minutes. These two criteria imply that the diffusional polarisation is negligibly small compared with the charge transfer and ohmic components even at the end of each experiment. This can be further supported by the following approximate calculation.

In the linear polarisation domain, the magnitude of the diffusional polarisation is given approximately by $(RT/nF) \ln(1-I/I_L)$, where I_L is the instantaneous limiting current. This limiting current could be as high as 20 C rate, or perhaps the short-circuit current for charged lead-acid batteries.¹² The diffusional polarisation is therefore less than few microvolts (i.e., $< 0.05\%$) in our experimental results. A close examination of the observed potential-time transients reveals that the HER could occur irreversibly in the linear polarisation domain of Pb/PbSO₄ electrode. Hence for overpotentials less than 10 mV, the above equation can be written as :

$$I = -C_{dl} (dE/dt) - I_{o,Pb} [(\alpha_{Pb} + \beta_{Pb}) f(E - E_{Pb}^r)] + I_{o,H} [\exp(-\alpha_H f(E - E_H^r))] \quad (3.5)$$

This equation includes the quasi-reversible nature of Pb/PbSO₄ reaction, along with the charge-transfer components of the HER in a Tafel domain. Simplification of equation (3.5) gives :

$$I = -C_{dl} (dE/dt) - I_{o,Pb} \gamma f(E - E_{Pb}^r) + I_{o,H} [\exp(-\alpha_H f(E - E_H^r + E_{Pb}^r - E_{Pb}^r))] \quad (3.6)$$

where, $\gamma = (\alpha_{Pb} + \beta_{Pb})$. Equation (3.6) can be written as :

$$I = -C_{dl} (dE/dt) - I_{o,Pb} \gamma f(E - E_{Pb}^r) + [\exp(-\alpha_H f(E_{Pb}^r - E_H^r))] Q \quad (3.7)$$

with Q as a constant defined as $I_{o,H} \exp[-\alpha_H f(E - E_{Pb}^r)]$

Thus :

$$I = -C_{dl} (dE/dt) - I_{o,Pb} \gamma f(E - E_{Pb}^r) + Q [1 - \alpha_H f(E - E_{Pb}^r)] \quad (3.8)$$

On simplification the expression yields :

$$I = -C_{dl} (dE/dt) - f(E - E_{Pb}^r) (\gamma I_{o,Pb} + \alpha_H Q) + Q \quad (3.9)$$

Generally, for porous battery electrodes, as SOC decreases during discharge, the ohmic resistance of accumulated products in the pores progressively increases. The later is known to limit the capacity.^{6,7} In such a situation, the ohmic component (due to this SOC dependence) is a significant parameter to be accounted while designing porous electrodes for high rated applications. This is of special significance for MF battery electrodes especially with immobilised electrolytes as one of the key parameters to be optimised is ohmic drop due to the nonconducting materials (PbSO₄ along with the gel) inside the pores. Considering this, the observed electrode potential E, with correction for this porous electrode resistance R_o would be (E+IR_o), where R_o will depend only on the SOC of the electrode along with any changes that are induced by electrolyte immobilisation.

Hence above equation can be written as,

$$I = -C_{dl} d(E+IR_o)/dt - f(E-E_{Pb}^r + IR_o) [(\gamma I_{o,Pb} + \alpha_H Q) + Q] \quad (3.10)$$

This expression can be considered as the governing equation for both build-up and decay transients of Pb/PbSO₄ system in the linear polarisation domain, which includes charge transfer and ohmic components of lead electrode reaction along with the charge transfer polarisation of the hydrogen evolution reaction. Since R_o is assumed to vary only with SOC, the eqn.(3.10) can be used to analyse the above two components of the electrode kinetics. This is especially true for MF battery electrodes.

Now By taking $K = f(\gamma I_{o,Pb} + \alpha_H Q)$, at any SOC, since R_o is a constant equation 3.10 can be written as :

$$I = -C_{dl} d(E+IR_o)/dt - (E - E_{Pb}^r + IR_o) K + Q \quad (3.11)$$

on rearranging :

$$I = -C_{dl}/(1+KR_o) (dE/dt) - K(E - E_{Pb}^r)/(1+KR_o) + Q/(1+KR_o) \quad (3.12)$$

This expression contains two unknowns (namely R_o and K) and can be solved using the following strategy. If at a particular SOC value, two different values of current are taken (i.e., I' and I''), one of which is zero and corresponding to open circuit conditions, two equations can be formulated as follows.

$$I' = -C_{dl}/(1+KR_o) (dE'/dt) - K(E' - E_{Pb}^r)/(1+KR_o) + Q/(1+KR_o) \quad (3.13)$$

$$I'' = -C_{dl}/(1+KR_o) (dE''/dt) - K(E'' - E_{Pb}^r)/(1+KR_o) + Q/(1+KR_o) \quad (3.14)$$

By comparing the slopes of the decay and build-up transients at the same potential, (i.e., $E' = E''$) the magnitudes of the $C_{dl}/(1+KR_o)$ could be calculated from equations 3.13 and 3.14.

$$C_{dl}/(1+KR_o) = (I' - I'') / (dE'/dt - dE''/dt) \quad (3.15)$$

Using these $C_{dl}/(1+KR_o)$ values, the double layer capacitance can be calculated from equation (3.11), which on rearranging gives,

$$C_{dl} (dE/dt) = -I(1 + KR_o) - K(E - E_{Pb}^r) + Q \quad (3.16)$$

Therefore if (dE/dt) is plotted against $E - E_{Pb}^r$, a straight line should be obtained with a slope of $-K/C_{dl}$ and an intercept of $[Q - I(1 + KR_o)]/C_{dl}$. Furthermore, C_{dl} and K can be calculated by using the exchange current density and Tafel slopes that have been reported from the HER^{4,13}. This is especially useful to compute R_o and exchange current density of Pb/PbSO₄ reaction at various SOC values. The variation in R_o and C_{dl} at fixed SOC values can now be correlated to the effect of gelling. The resulting data could be useful for the design of MF lead-acid batteries.

3. 3. 2. Comparison of theory with experimental data

Figures 3. 5 to 3. 8 show dE/dt vs. η plots for gelled and flooded electrolytes at three representative SOC values namely 1, 0.5 and 0.05. The linearity shown in all the cases is in excellent agreement with the model suggested by eqn (3.16). Furthermore, the slopes and intercepts of these curves provide estimates of R_o with known $C/(1 + KR_o)$ values. Given the large number of data points used and the range as well as direction of the current, the mean deviation of about $\pm 2\%$ in each case suggests that the $C/(1+KR_o)$ values are fairly reliable.

The double layer capacitance, exchange-current density and R_o thus calculated are given in Table 3. 1. The double layer capacitance values remain unchanged with respect to gelling for a given SOC value. This probably indicates the absence of any specific adsorption of silicate ions; the change of capacitance with SOC is more prominent, but the area change and the potential-dependent adsorption-pseudocapacitance may play a complex role to cause this. For gelled electrolytes, the $I_{o,Pb}$ values exhibit a gradual decrease at a particular SOC. This may be attributed to the increased contribution of diffusional resistance in the presence of gelling.

Although the magnitude of C_{dl} in Table 3. 1 appears to be larger than the usual values for metal/solution interface, it is quite possible that the surface roughness factor associated with porous electrodes cause this deviation. Considering a medium value for the surface area of few m^2g^{-1} and a 10^3 to 10^4 fold increase in the apparent area due to porosity⁷, the double layer capacitance can be estimated to be 6 to 60 $\mu F/cm^2$. This values are close to those reported for lead in sulphuric acid.¹³

In contrast to both $I_{o,Pb}$ and C_{dl} the ohmic resistance (R_o) in Table 3. 1. shows a significant variation due to gelling as well as to SOC change. Addition of thixotropic

agents obviously increases the ohmic drop and this effect is more pronounced at a low SOC, such as 0.05. Furthermore, the variation of R_o with SOC can be attributed to the increased hindrance of charge transfer as a result of accumulation of insulating $PbSO_4$ in the pores of the electrode. The gelled electrolyte with $SOC = 0.05$ gives the highest value.

Table 3. 1. Double layer Capacitance (C_{dl}), exchange-current densities ($I_{o,Pb}$) and ohmic resistance for gelled and flooded Pb/PbSO₄ system at various state-of-charge (SOC)

Electrode type	SOC	C_{dl} (F cm ⁻²)*	$I_{o,Pb}$ (A cm ⁻²)*	R_o (Ω)*
Flooded, anodic	1	0.06	1.38×10^{-5}	18.43
	0.5	0.02	9.45×10^{-6}	39.45
Flooded, Cathodic	0.5	0.09	1.08×10^{-5}	28.84
	0.05	0.05	5.71×10^{-6}	115.47
Gelled, anodic	1	0.05	1.44×10^{-6}	39.65
	0.5	0.02	2.78×10^{-6}	42.44
Flooded Cathodic	0.5	0.08	4.21×10^{-6}	140.27
	0.05	0.04	1.93×10^{-6}	415.85

* Calculated on the basis of apparent geometrical area (33 cm²)

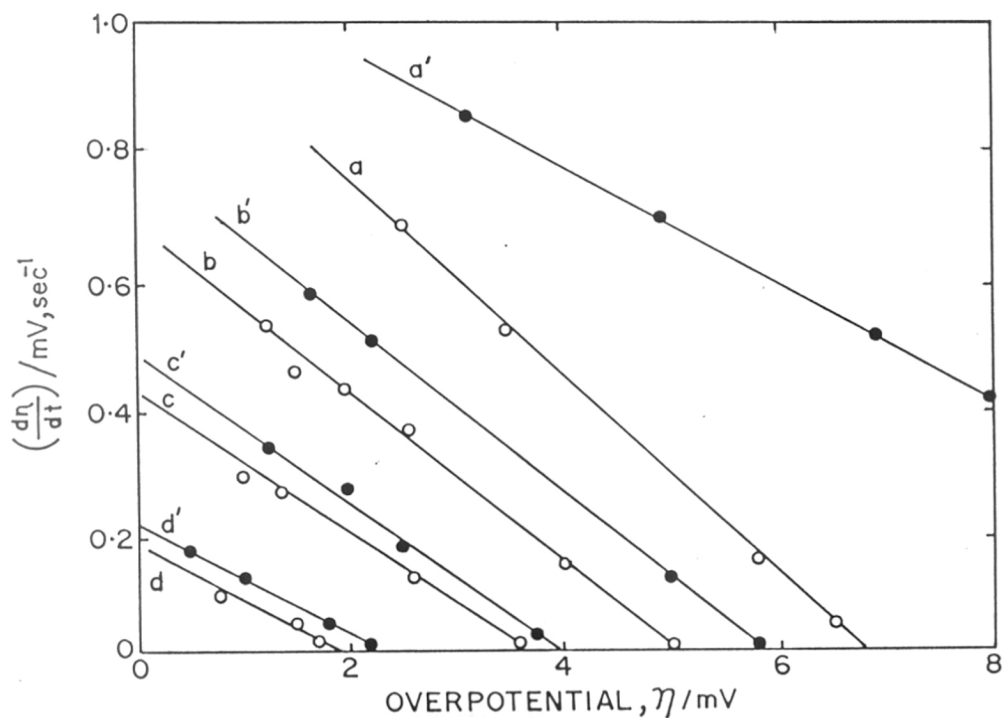


Figure 3. 5. Plot of dE/dt vs η for flooded and gelled electrolyte as derived from the anodic transients at unit SOC using the data from Figure 3. 1 and Figure 3. 2; blank and filled circles indicate flooded and gelled electrolytes respectively.

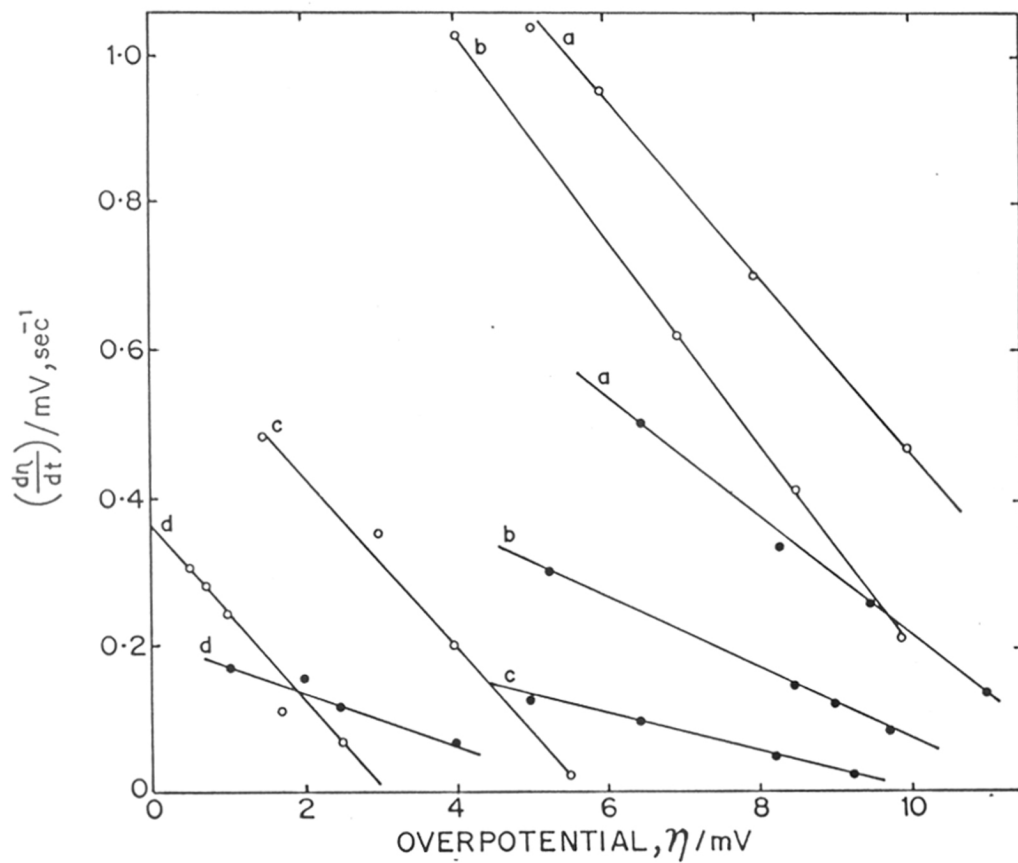


Figure 3. 6. Plot of dE/dt vs η for flooded (blank circle) and gelled (filled circle) electrolytes as derived from the anodic transients at SOC = 0.5; corresponding to various current densities: (a) 60, (b) 45, (c) 30 and (d) 15 $\mu \text{A cm}^{-2}$.

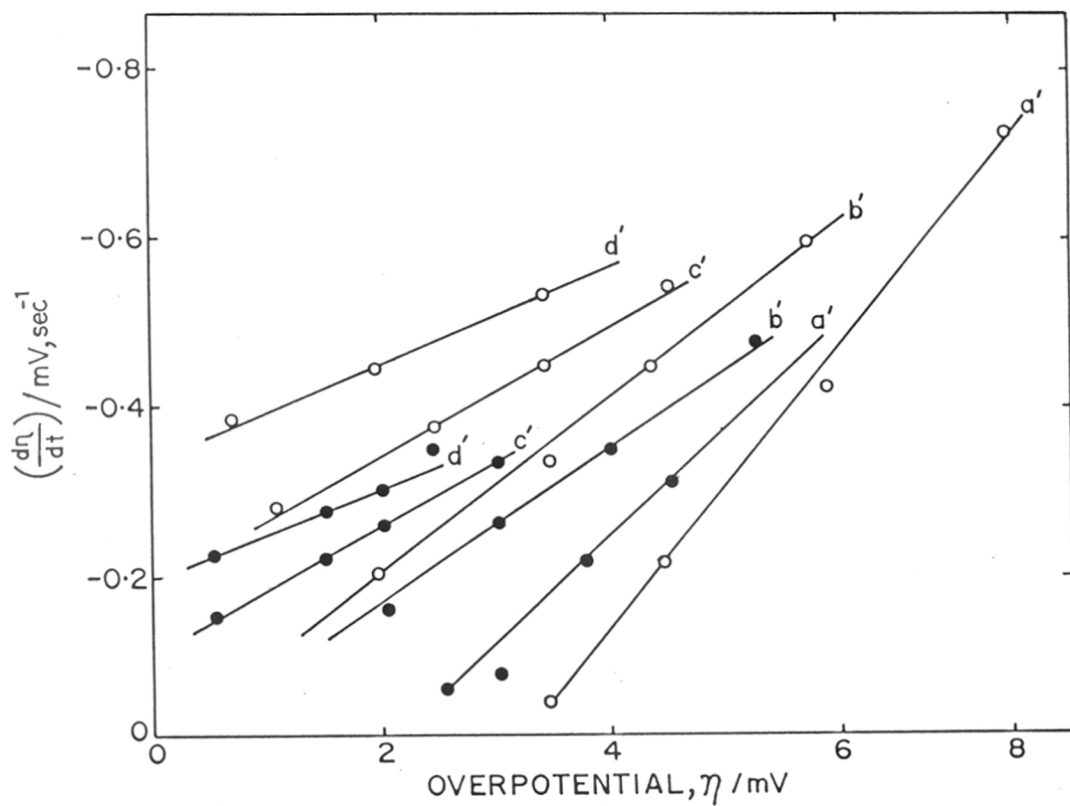


Figure 3. 7. Plot of dE/dt vs η for flooded (blank circle) and gelled (filled circle) electrolytes as derived from the cathodic transients at SOC = 0.5 corresponding to various current densities: (a') 60, (b') 45, (c') 30 and (d') 15 $\mu\text{A cm}^{-2}$.

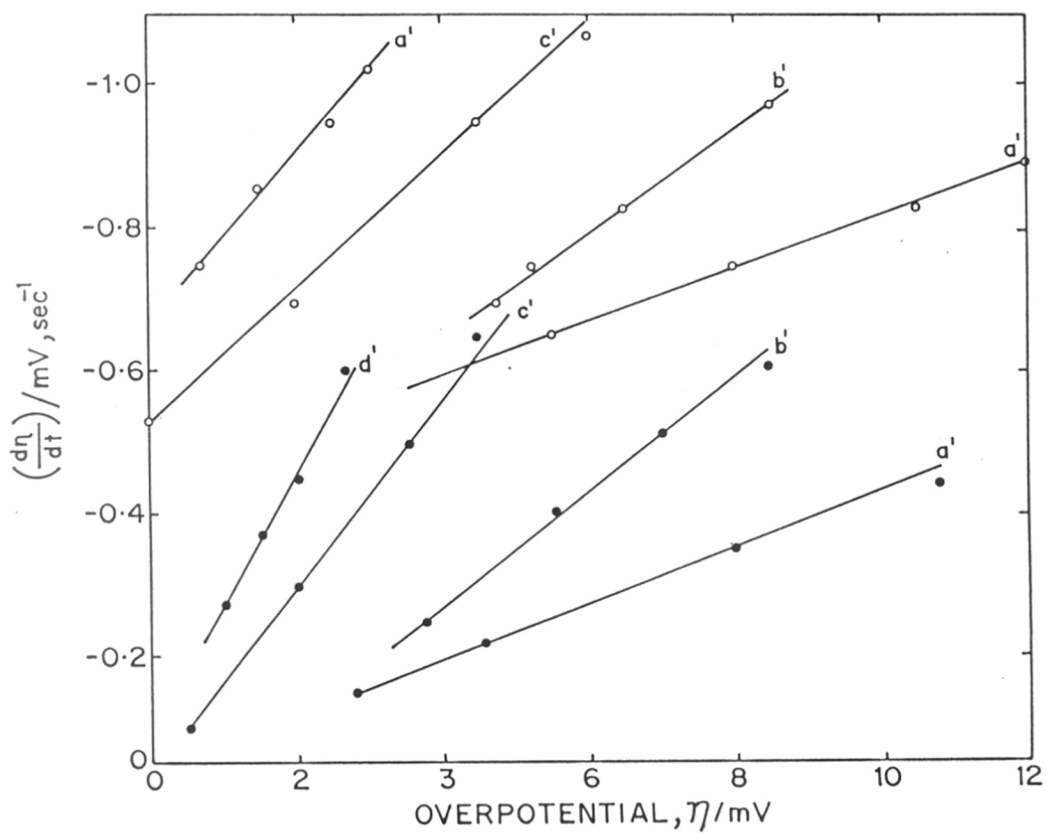


Figure 3. 8. Plot of dE/dt vs η for flooded (blank circle) and gelled (filled circle) electrolytes as derived from the cathodic transients at SOC = 0.05 using data from Figures 3.3 and 3.4.

of ohmic resistance due to pore-plugging (namely, 415Ω) and hence, is unsuitable for deep-discharge applications.

The above results confirm the importance of ohmic drop due to pore plugging. This aspect is general for all types of porous electrodes. Since most of the battery electrodes are porous in nature, the above analysis is helpful in estimating the extent of pore plugging without any *a priori* assumptions regarding the detailed geometry of the porous electrode. Moreover, R_o has special significance in designing maintenance-free batteries using immobilised electrolyte as it manifests the sum total of the ohmic losses that occur in the pores by pore-plugging and immobilisation-induced changes.

3. 4. Limitations of the model

The quasi-reversibility of Pb/PbSO₄ system assumed in deriving eqn.(3.11) may not be universally valid, especially for cathodic polarisation at an SOC equal to unity. For example, the charging efficiency at this SOC will be very poor and current passed will be completely utilised for the reaction (3.2). Similarly, at an SOC close to zero there is very little amount of lead for anodic reaction and, hence, during charging all the faradaic currents will be consumed only for reaction (3.1) and departure from quasireversibility can be reflected in the initial deviation from linearity in experimental plots. Variation of R_o with SOC will not be uniform at these limiting SOC values. Thus, the model is most appropriate close to SOC = 0.5, where cathodic as well as anodic schemes indicate mutual validity.

Another important limitation is imposed by neglecting the role of adsorbed hydrogen. The coverage-induced variation of exchange-current densities, capacitance and R_o values are also not included. This is because equation (3.4) is valid only if the reaction of interest does not involve an adsorbed intermediate or, more importantly, the adsorbed

intermediate is not participating in the rate-determining step. This cannot be strictly true as the silicate ion is known to adsorb on the electrode and thereby changing the electrode kinetics. Lastly the effect of adsorption pseudocapacitance is also ignored in the present analysis.

In spite of the above limitations, the assumptions involved in the model are quite general for most battery electrodes and the estimation of the internal ohmic-drop due to pore-plugging may provide a useful physical insight in to the design of MF batteries. Furthermore, all of the kinetic parameters are obtained by polarising the electrode less than 10 mV, with negligible SOC change. Hence, the analysis can be considered as a non-destructive method for obtaining kinetic data.

3. 5. CONCLUSION

A quantitative analysis of potential-time transients of porous Pb/PbSO_4 electrode in gelled and flooded sulphuric acid demonstrates numerous key features that are useful for designing maintenance-free batteries. This analysis, despite its non-destructive nature, provides several important kinetic parameters for both the lead and the hydrogen electrode reactions. Furthermore, the effect of accumulation of non-conducting discharged products as well as the addition of thixotropic agents in the electrolyte, has been incorporated as resistance parameters by developing a model based on pore-plugging. The study shows that this resistance component can affect significantly the design of maintenance-free lead-acid batteries.

3. 6. REFERENCES

1. M. Maja and N. Penazzi, J. Power Sources, **25** (1989) 99.
2. A.M. Hardman, J. Power Sources, **23** (1988) 127.
3. J. Sterbe, B. Reichman, B. Mohato and K.R. Bullock, J. Power Sources, **31** (1990) 43.
4. K. Vijayamohanan, S.N. Joshi and S. Sathyanarayana, J. Power Sources, **30** (1990) 169.
5. R.M. Lafollette and D.N. Bennim, J. Electrochem. Soc., **137** (1990) 3692.
6. K. Micka and I. Rousar, Electrochim. Acta, **29** (1984) 1411.
7. J. Newman and W. Tiedemann, AIChE. J., **21** (1975) 25.
8. D. Pavlov, Electrochim. Acta, **13** (1968) 2151.
9. D. Pavlov in , P.113,"Power Sources for Electric vehicles" B.D. McNicol and D.A.J. Rand (eds.) Elsevier, Amsterdam,1984.
10. M. Barak(ed.),Electrochemical power Sources, Peter Pergines Ltd. Stevenage, 980, P.290.
11. R. Iler, "The Chemistry of Silica", John Wiley, New York, 1979, P.287.
12. S. Okazaki, S. Higuchi, N. Kubota and S. Takahashi, J. Appl. Electrochem., **16** (1986) 513.
13. T. F. Sharp, in A.J. Bard(ed.), *Encyclopaedia of electrochemistry of elements*, vol.1 , 1973, p.308.

Effect of gelling on battery
**EFFECT OF GELLING ON THE DOUBLE-LAYER CAPACITANCE,
EXCHANGE CURRENT DENSITY AND UNCOMPENSATED
RESISTANCE OF THE Pb/PbSO₄ ELECTRODE REACTION***

Galvanostatic transients in the linear polarisation domain have been used to analyse the variation of double-layer capacitance and exchange current densities of the Pb/PbSO₄ electrode reaction at various states-of-charge (SOC) values. From these data, the potential-dependence of double-layer capacitance has been evaluated as a function of SOC. Interesting changes have been observed in the double-layer capacitance and exchange current densities as a result of immobilisation of the electrolyte. A direct determination of the uncompensated resistance of porous Pb/PbSO₄ electrode as promoted by variation in the SOC has also been obtained by comparing the theoretical, potential-time transients with experimental data. This method is non-evasive and can be useful in predicting SOC of maintenance-free batteries.

* Papers based on this study have appeared in J. Power Sources, **52** (1994) 135 and J. Appl. Electrochem., **25** (1995) 80.

4.1 INTRODUCTION

The effect of adsorption on the electrode kinetics of specific reactions has received considerable attention in recent years because it can provide significant information in determining the fundamental behaviour of modified electrodes.¹⁻⁴ Determination of the adsorption-induced effects on both faradaic as well as non-faradaic processes occurring on the electrode-electrolyte interface can be useful for designing electrocatalytic electrodes for several cases such as electro-synthesis,⁵ electroanalytical sensors,⁶ batteries and fuel cells,⁷ photoelectrolysis, corrosion inhibition⁸ etc. For example, adsorption-induced irreversibility at low coverage,⁹ underpotential deposition¹⁰⁻¹² and adsorption-dependent pseudocapacitance¹³ are well known in several systems and recent studies¹⁴ indicate the remarkable advances in understanding the electronic and structural changes on well-defined single crystal surfaces as a result of adsorption-induced reconstruction.¹³⁻¹⁵ Some of the adsorbed species influence the electrode kinetics only through a change in the double layer structure, while others show specific chemical interactions with substrate, solvents and other adsorbates. Both inhibition and enhancement of electron transfer have been observed in a variety of reactions.¹⁶

Since the adsorbed species can have a strong influence on the charge transfer kinetics of several reactions this can some times be used to improve the performance of existing electrochemical devices. For example, one class of rechargeable lead-acid batteries for maintenance-free applications employ thixotropic agents such as sodium silicate for immobilising the electrolyte. Although these additives have been extensively in use for about three decades, their influence on the electrode kinetics of the Pb/PbSO_4 reaction has not been investigated so far except perhaps the effect on hydrogen evolution kinetics.¹⁷ In addition, the utilisation of both negative (Pb/PbSO_4) and positive ($\text{PbO}_2/\text{PbSO}_4$)

electrodes has been found to be significantly affected by adsorbed silicate ions as shown by the change in capacity values during their discharge.¹⁸ As a consequence, the gelled electrolyte obtained shows several superior design features, compared to the conventional flooded-type, such as minimum gas evolution due to electrolyte starving, increased corrosion resistance, increased safety against acid spills etc.

Although Lead-acid batteries with immobilised electrolyte with or without gas recombination catalysts have been used increasingly in maintenance-free applications, their large scale utilisation has been hindered to a certain extent by the uncertainties in the states-of-charge (SOC) determination. As SOC of a battery indicates the ratio of residual capacity at a given instant to the maximum available capacity, a knowledge of it is specially significant for maintenance-free system in rural applications (such as storage of solar energy) where SOC change due to progressive self discharge limits their practical behaviour. Hence, an accurate and non-evasive method of determining the SOC of such systems is highly desirable for large scale applications. A knowledge of the SOC can be extremely useful in predicting the residual capacity and more significantly, it can help in increasing the cycle life by proper control of the degree of charge and depth of discharge in each case.

The present methods of SOC determination¹⁹ suffer from the following limitations. Density measurements are so crude and does not reflect the SOC accurately; as it can predict the SOC only within about 10% over the useful portion of the discharge curve. In addition, the density of acid inside the pores often show drastic differences to that in the bulk of the solution and the use of gelled electrolytes and hermetically sealed units preclude the use of density measurements for estimating the SOC.²⁰ Impedance methods require sophisticated instruments and is too complicated to apply on a routine basis.

Moreover, the interpretation is ambiguous as the behaviour of porous electrodes often can not be represented by any unique equivalent circuit of passive elements. Conventional IR measurements using large current are proven to give inaccurate results as the pores of the electrodes with several resistive and reactive components, some of which may be time dependent thereby causing non-stationary behaviour. More importantly, change of composition during these tests are often responsible for large errors.

Lastly, the prediction of SOC on the basis of equilibrium values of open-circuit voltage is more relevant for negative limited cells and difficulties arise due to significant battery-to-battery variations. The preferred SOC measuring test should be fast, simple to use and should not cause any change in the fundamental parameters of the electrochemical system i.e., it should permit well-defined and variable criteria for the noninvasive aspects to be set out at the beginning and during the test.

The effects of these immobilising agents on the double-layer capacitance and exchange current density of the Pb/PbSO₄ electrode are analysed in chapter 3, by using potential-time transients. In this chapter, using the same formalism, adsorption-induced changes in exchange current density are evaluated at various SOC so that the insights obtained from such an analysis can be used to control the depth of discharge to attain higher cycle life for practical systems. This study also provides a novel non-destructive method to predict the SOC of maintenance-free lead-acid batteries as derived from the galvanostatic transients in the linear polarisation domain. This technique is of marked importance for evaluating SOC variation due to progressive self-discharge during their applications.

4.2. EXPERIMENTAL DETAILS

Both the positive and negative electrodes used in this study were obtained in factory cured and formed conditions, and the experimental details are described in chapter 3. Initially, all the electrodes were soaked in 4.8 M sulphuric acid for 10 h and then subjected to galvanostatic charging and discharging at C/10 and C/8 rates respectively. This was continued for five cycles to obtain stable capacity values and this constant value was used for all SOC calculations. All the cells were then given the same amount of overcharge (20%), kept at open circuit for 30 min. and polarised with appropriate current densities such that the steady state could be obtained in few minutes within the linear polarisation domain ($\eta < 10$ mV). On attaining the steady state, the current was interrupted and the potential transients were measured until the original equilibrium value was restored. The experiments were repeated using various current densities selected on the basis of causing negligible change in the SOC of the electrode ($< 0.01\%$). Similar transients were also obtained at other SOC values such as 0.8, 0.5, 0.2 and 0.05 by keeping the current density, as constant. These experiments were then repeated with separate electrodes at the same SOC values and current densities in an immobilised electrolyte. The latter was prepared by adding sodium silicate as a thixotropic agent, due to its well known property of existing at low pH as polysilicic acid²¹

4.3. RESULTS AND DISCUSSION

4.3.1. Analysis of Potential-time Transients

The expression for build-up and decay transients for Pb/PbSO₄ electrode in sulphuric acid obtained from the theoretical analysis in chapter 3 (equation 3.10) is

$$I = -C_{dl}(d(E+IR_o)/dt) - f(E-E_{pb}^r + IR_o)(\gamma I_{o,Pb} + \alpha_H Q) + Q \quad (4.1)$$

On recasting with a constant $K = f(\gamma I_{o,Pb} + \alpha_H Q)$ we have,

$$I = -1/(1 + KRo) [C_{dl}(dE/dt) + K(E - E_{pb}^r) - Q] \quad (4.2)$$

This expression of potential-time transients is valid only if diffusional contribution to overpotential is negligible. A high concentration of sulphuric acid (4.8 M) and invariance of potential time patterns with stirring supports this assumption. More importantly, the current densities and time domain are selected to be extremely small so that time dependent diffusional contributions are rendered insignificant; Although the diffusional polarisation is negligible due to these factors, when SOC is too high or too low, mass transfer becomes important and hence equation (4.2) is invalid. In the intermediate range of SOC ($0 < SOC < 1$) the above equation can be used to calculate both unknowns, Ro and K (which contains $I_{o,Pb}$). Since both are expected to vary with SOC (as SOC indicates the ratio of oxidant to reductant) at a particular SOC, the build-up and decay(open-circuit) transients can be expressed as,

$$I = -1/(1 + KRo) [C_{dl}(dE/dt) + K(E - E_{pb}^r) - Q] \quad (4.3)$$

$$0 = -1/(1 + KRo) [C_{dl}(dE'/dt) + K(E' - E_{pb}^r) - Q] \quad (4.4)$$

Subtracting eqn.4.3 from eqn. 4.4 we have,

$$I = -1/(1 + KRo)[C_{dl}(dE/dt) - (dE'/dt)] - K(E - E') \quad (4.5)$$

This equation may be solved to get $C_{dl}/(1 + KRo)$ values and Ro can be calculated by using the slopes and intercepts of dE/dt plot against $E - E_{pb}^r$ at various C_{dl} values and the reported values of $I_{o,H}$ and $I_{o,Pb}$ on porous lead electrode.¹³ The validity of these equations have been confirmed earlier by the expected linear plots at both high and low SOC values obtained in chapter 3 (Figures 3.5 and 3.6). If the potential is selected in such a way that the slopes of the decay and build up transients can be compared at the same potential, $C_{dl}/(1 + KRo)$, can be obtained as

$$C_{dl}/(1 + KRo) = I / [(dE'/dt) - (dE/dt)] \quad (4.6)$$

From these $C_{dl}/(1+KR_o)$ values, the double-layer capacitance can be easily obtained by plotting dE/dt against η according to eqn.(4.6) which on suitable rearrangement, gives,

$$C_{dl} (dE/dt) = -I (1 + KR_o) - K (E - E_{Pb}^r) + Q \quad (4.7)$$

Thus by measuring the slopes of build-up (dE'/dt) and decay (dE''/dt) transients at a particular potential, $C_{dl}/(1+KR_o)$ values at various SOC values can be calculated. Furthermore, with these known $C_{dl}/(1+KR_o)$ values and the slopes and intercepts of a plot of (dE/dt) versus $E - E_{Pb}^r$, C_{dl} values can be calculated as a function of SOC. More specifically, the exchange current densities of Pb/PbSO₄ reaction at various SOC can be calculated by using the reported value of $I_{o,H}$ for HER on porous lead electrodes.²³

This evaluation of the fundamental kinetic parameters of Pb/PbSO₄ reaction could be useful for designing maintenance-free lead-acid batteries. The study of the variation of these parameters with immobilisation of electrolyte would also help to improve their cycle life at high depths of discharge.

Although this analysis helps in calculating the kinetics parameters namely C_{dl} and $I_{o,Pb}$, the real utility is in calculating the potential dependence of the double layer capacitance at a given SOC, as this gives valuable information regarding effects of adsorption. In addition, if adsorption of silicate causes any irreversibility, it will be reflected in the value of $I_{o,Pb}$, especially at lower SOC values.

4.3.2 Comparison of model with experimental data

Typical potential-time transients at various current densities (in the domain of η less than 10 mV) for gelled and flooded electrolytes at SOC = 0.5 are shown in figures 4.1 and 4.2 respectively. The potential tends to reach the steady state value asymptotically with time and this time increases with an increase in the deviation from equilibrium.

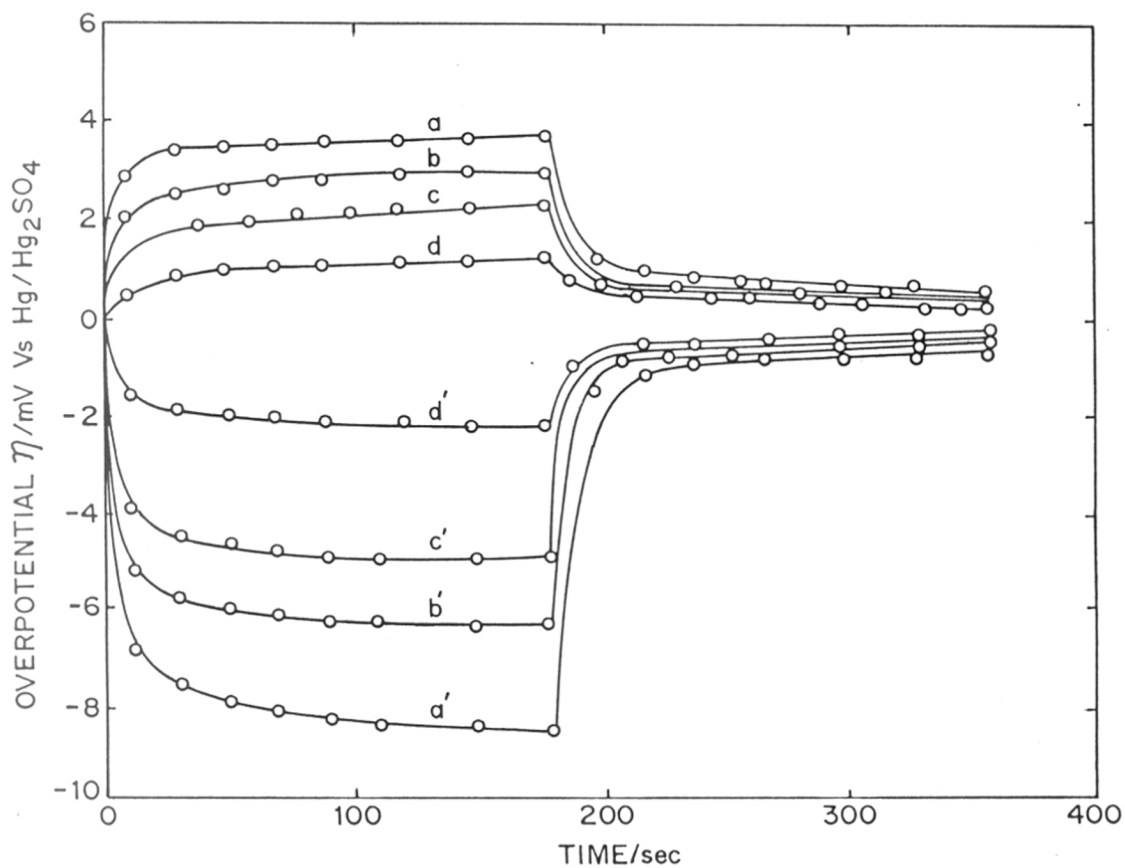


Figure 4. 1. Galvanostatic Overpotential-time Transients at various current densities for flooded electrolyte at SOC = 0.5 ; a,b,c,d corresponds to anodic transients and a', b', c' and d' corresponds to cathodic transients at current densities of 60, 45, 30 and 15 μAcm^{-2} respectively.

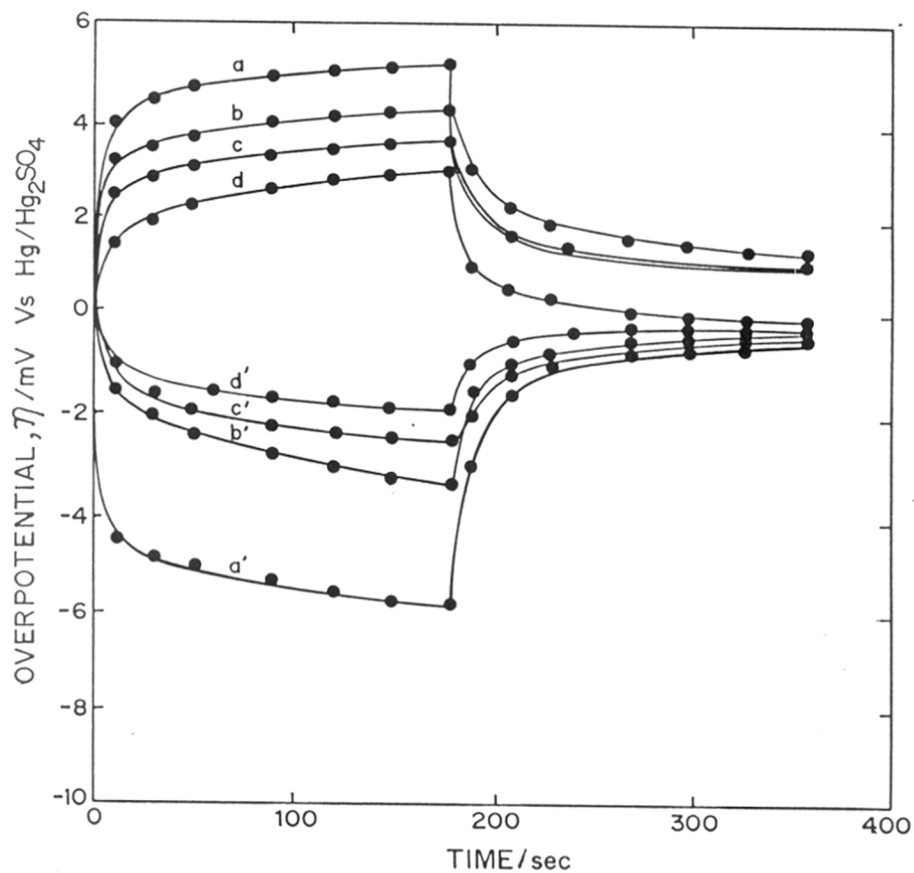


Figure 4. 2. Galvanostatic Overpotential-time Transients at various current densities for immobilised electrolyte at SOC = 0.5 ; a,b,c,d corresponds to anodic transients and a', b', c' and d' corresponds to cathodic transients at current densities of 60, 45, 30 and 15 μAcm^{-2} respectively.

In addition, the build-up and decay patterns are much steeper for the gelled electrolyte. This may be attributed to the increased hindrance of mass transfer due to the presence of interpenetrating net work of polysilicic acid gel.

Comparison of the transients in figures 4.1 and 4.2 illustrates that under cathodic polarisation the overvoltage is higher when the electrodes are immersed in H_2SO_4 solution than in the case of H_2SO_4 gel. Under cathodic polarisation, hydrogen evolution reaction contributes more to the observed current (eqn.4.2) and the electrocatalytic effects of silicate adsorption for hydrogen evolution reaction¹⁷ is mainly responsible. In contrast, under anodic polarisation, the electrode in H_2SO_4 gel has higher overvoltage than that in H_2SO_4 solution as the predominant contribution under anodic polarisation is due to the formation of PbSO_4 . This is consistent with the observation of lower exchange current densities for reaction 3.1 in gelled electrolyte compared to that in H_2SO_4 solution.

Figures 4.3 and 4.4 show the variation of $I_{o, \text{Pb}}$ for the Pb/PbSO_4 system on changing the SOC of the electrode. These $I_{o, \text{Pb}}$ values were calculated on the basis of C_{dl} and K values obtained from the slopes of the figures 4.1 and 4.2. These changes are consistent, indicating a change in the charge transfer kinetics of the electrode reaction with the ratio of the electroactive species. Probably the variation of $I_{o, \text{Pb}}$ with activities of Pb(II) and Pb(0) with a correction for the change of activity of sulphuric acid may explain this variation. Irrespective of the source of the data (i.e, from cathodic or anodic transients) a large change is observed at SOC close to 1 corresponding to the onset of ideal polarisability under these conditions. Similar behaviour may be expected as SOC tends to zero, but the measurements were not conducted due to irreversible degradation of the

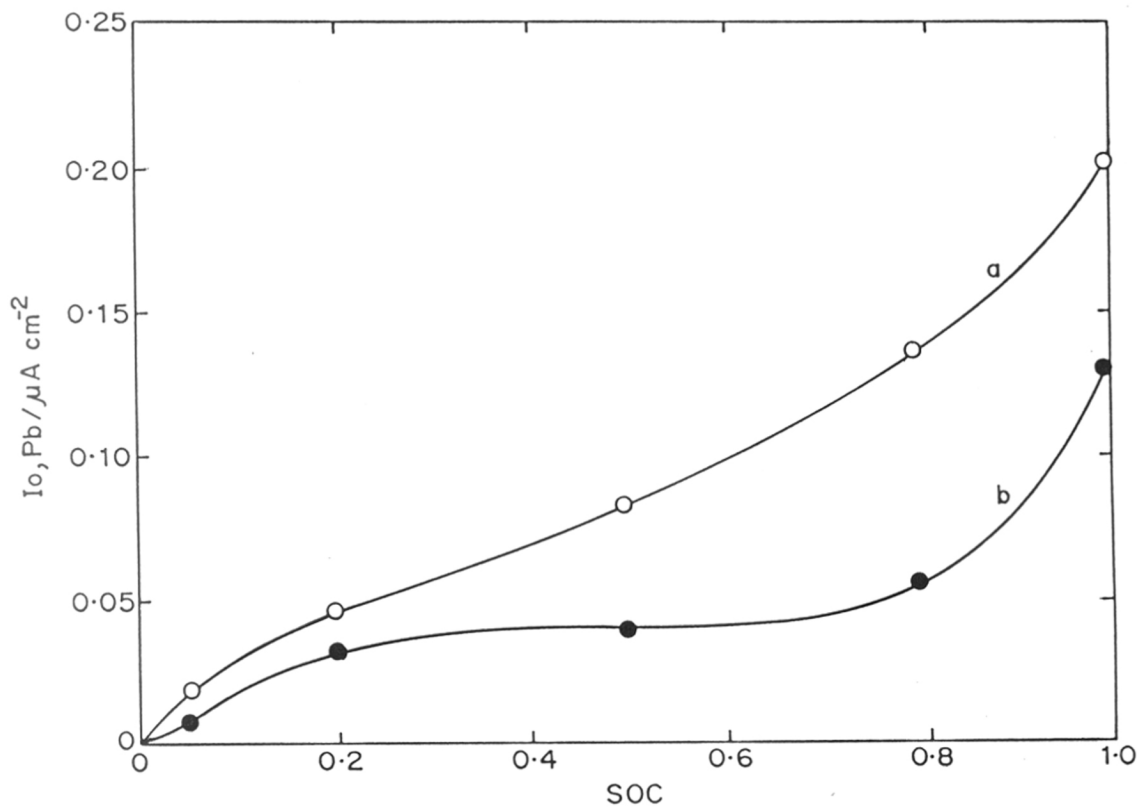


Figure 4. 3. Variation of $I_{o, Pb}$ with SOC obtained from the data from a prior cathodic polarisation case. 'a' corresponds to flooded electrolyte and 'b' corresponds to immobilised electrolyte.

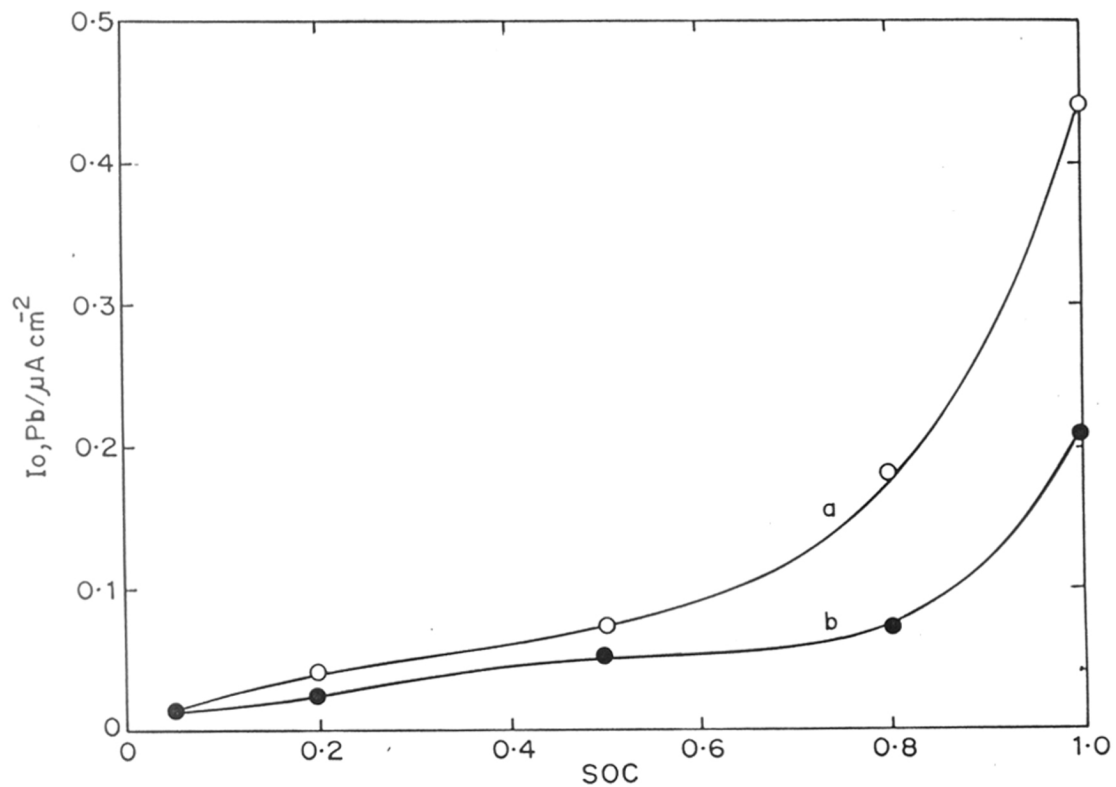


Figure 4. 4. Variation of $I_{o,Pb}$ with SOC obtained from the data from a prior anodic polarisation case. 'a' corresponds to flooded electrolyte and 'b' corresponds to immobilised electrolyte.

electrode. The difference in the magnitude for the cathodic and anodic cases can be ascribed to the contribution from expected hydrogen evolution reaction.

The variation of double-layer capacitance (calculated on the basis of apparent geometrical area) with SOC values for a prior anodic polarisation case for the gelled and non gelled electrolyte is shown in figure 4. 5. The variation from 0.2 to 0.8 is the representation of actual change as higher SOC will have pseudocapacitance contribution from adsorbed hydrogen. Since Pb/PbSO₄ electrode operates as an electrode of second kind, through the dissolved Pb(II) species, the reversible potential is practically independent of SOC and the double layer will be practically compact (Helmoltz type) due to the high ionic strength of the electrolyte.²⁴ Hence, the double-layer capacitance should not vary appreciably in the range of 0.2 to 0.8 SOC values as electrolyte depletion (including local alkalisiation in the pores) and adsorbed hydrogen can cause deviations at lower and higher SOC values.

The average value of C_{dl} is less for gelled due to the adsorption of bulky silicate ions since the C_{dl} value is an indication of the area of the active material. Although, this area is smaller for gelled electrolyte this trend is further enhanced in the case of SOC = 0.2, and the reduction in C_{dl} is mainly due to the effects of adsorbed silicate ions especially at low SOC values where the silicate is masked by a large amount of PbSO₄ insulating layer. This decrease may be explained by the specific chemical interaction between Pb²⁺ ions and silicate ions causing large leakage in capacitance.

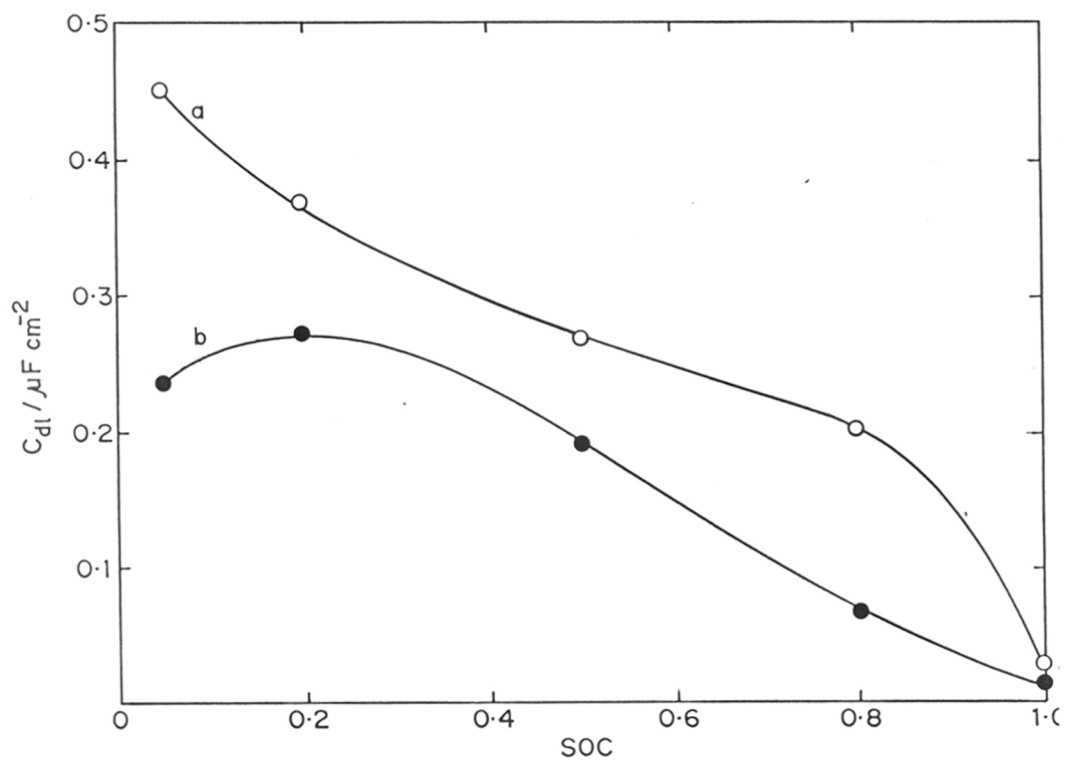


Figure 4. 5. Variation of C_{dl} with SOC values for a prior anodic polarisation case 'a' corresponds to flooded electrolyte and 'b' corresponds to immobilised electrolyte.

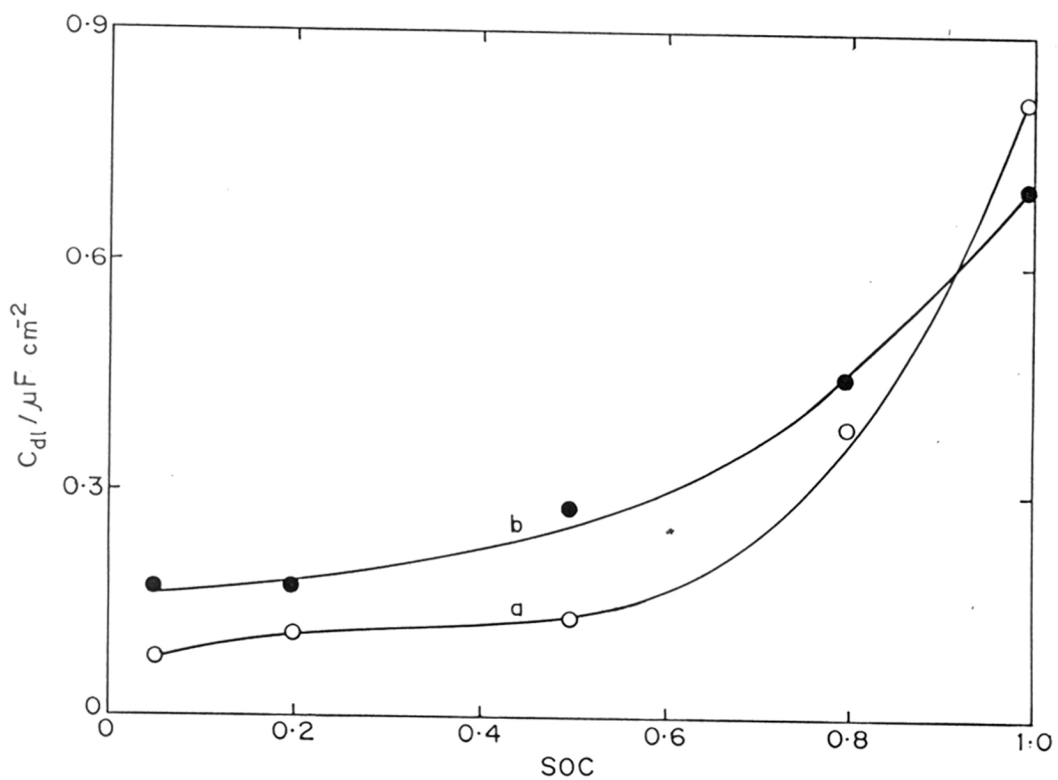


Figure 4. 6. Variation of C_{dl} with SOC values for a prior cathodic polarisation case 'a' corresponds to flooded electrolyte and 'b' corresponds to immobilised electrolyte.

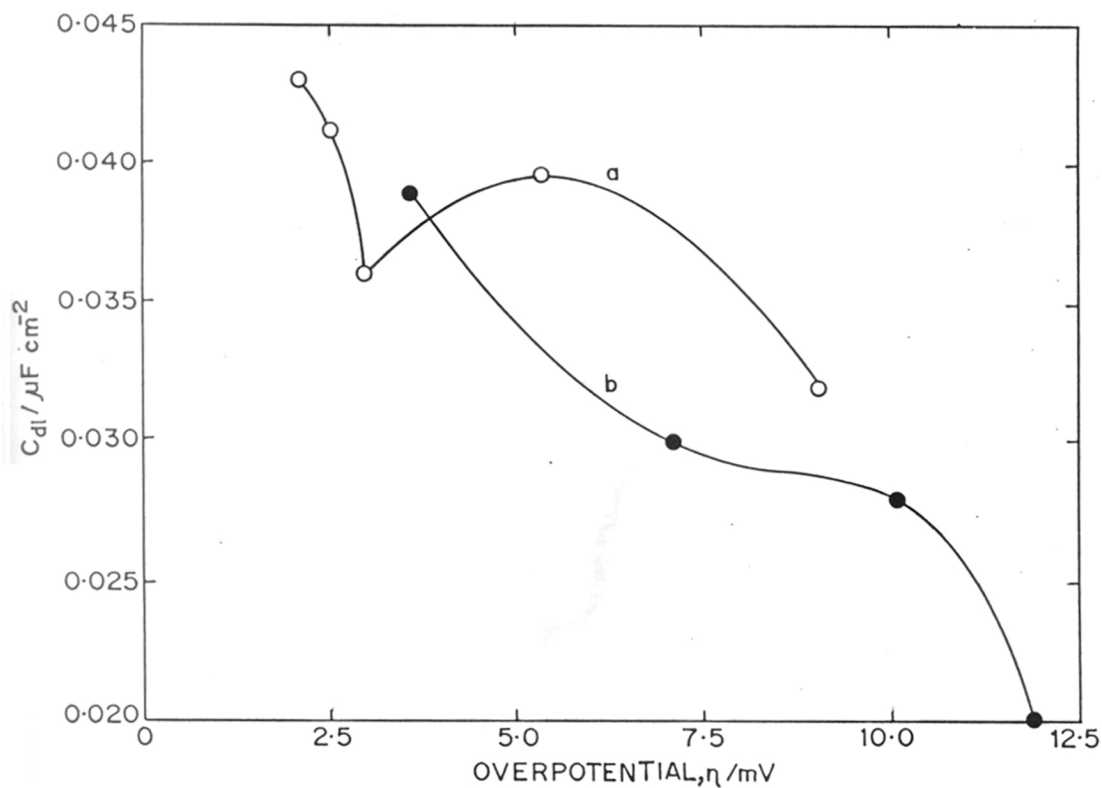


Figure 4.7. Variation of R_o with SOC values for a prior anodic polarisation case 'a' corresponds to flooded electrolyte and 'b' corresponds to immobilised electrolyte.

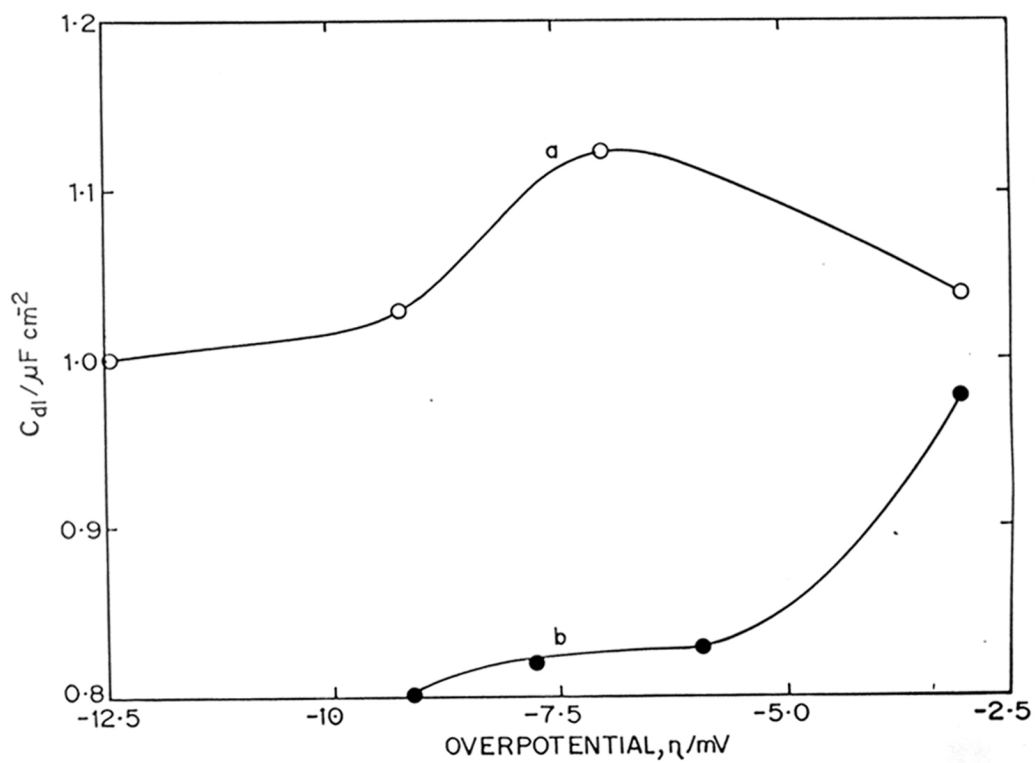


Figure 4.8. Variation of R_o with SOC values for a prior cathodic polarisation case 'a' corresponds to flooded electrolyte and 'b' corresponds to immobilised electrolyte.

Figure 4.6 shows the variation of double layer capacitance with SOC values for a prior cathodic polarisation case. The large increase at unit SOC can be attributed to the contribution from adsorbed hydrogen which is negligible at very low SOC values. Similar trends with lower capacitance values are observed for the data from a prior anodic polarisation case as shown in figure 4.7. This is expected since adsorption pseudocapacitance of hydrogen is not contributing in the anodic case. This change is in agreement with the observed cathodic shift in open circuit due to gelling (from -959 mV to -975 mV).

Although the specific adsorption of silicate ions is expected to increase the capacitance, the capacitance seems to decrease as the potential becomes more cathodic. This trend can be attributed to the accumulation of insulating PbSO_4 on the pores of the electrode thus preventing the specific adsorption of silicate ions. This is increasingly clear for more anodic potentials.

The capacitance versus potential curve derived from potential-time transients during cathodic polarisation at unit SOC is shown in Figure 4.8. In this case the contribution of hydrogen adsorption can also be significant, especially at high SOC values. Decrease in capacitance is also observed as a result of gelling. This effect can be attributed to the co-operative adsorption of silicate ions and hydrogen, where the adsorbed silicate ions can electrocatalytically enhance the adsorption of hydrogen.

A comparison of figures 4.7 and 4.8 shows that the capacitance values are larger when obtained from the data for a prior cathodic polarisation. During anodic polarisation, the variation of coverage with potential (due to the accumulation of insulating PbSO_4 in the pores) is mainly responsible for the capacitance changes.

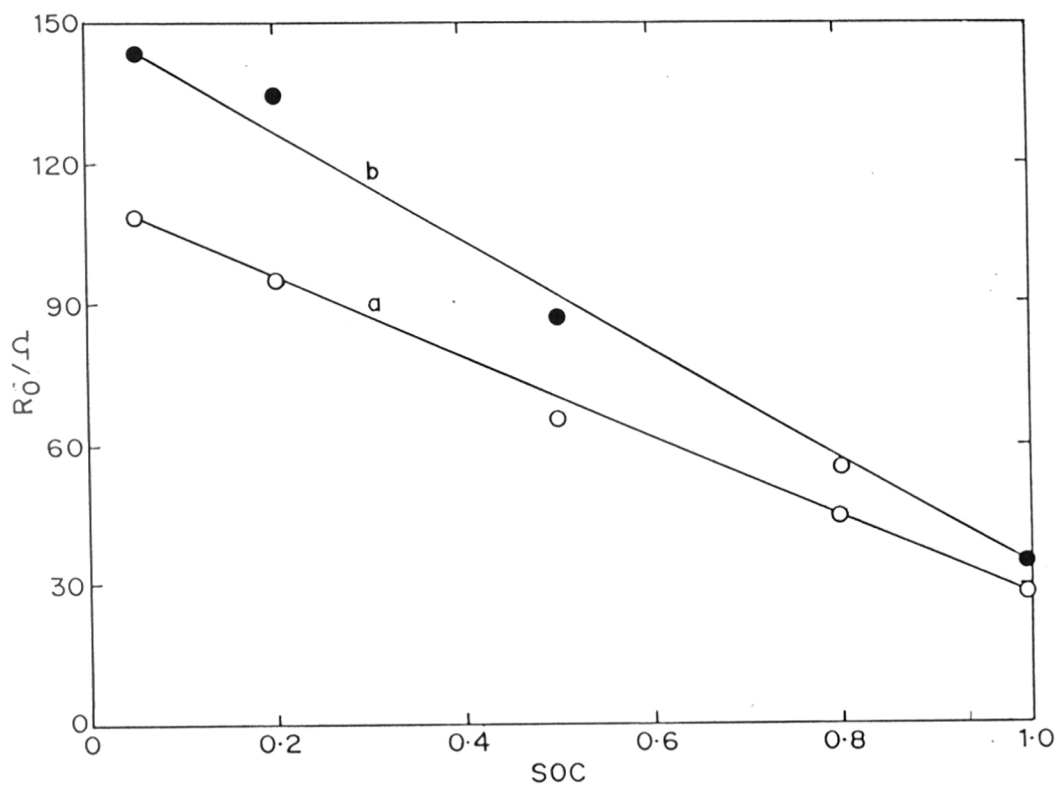


Figure 4. 9. Variation of R_o with SOC derived from the data of a prior anodic polarisation: (a)flooded electrolyte, and (b) immobilised electrolyte.

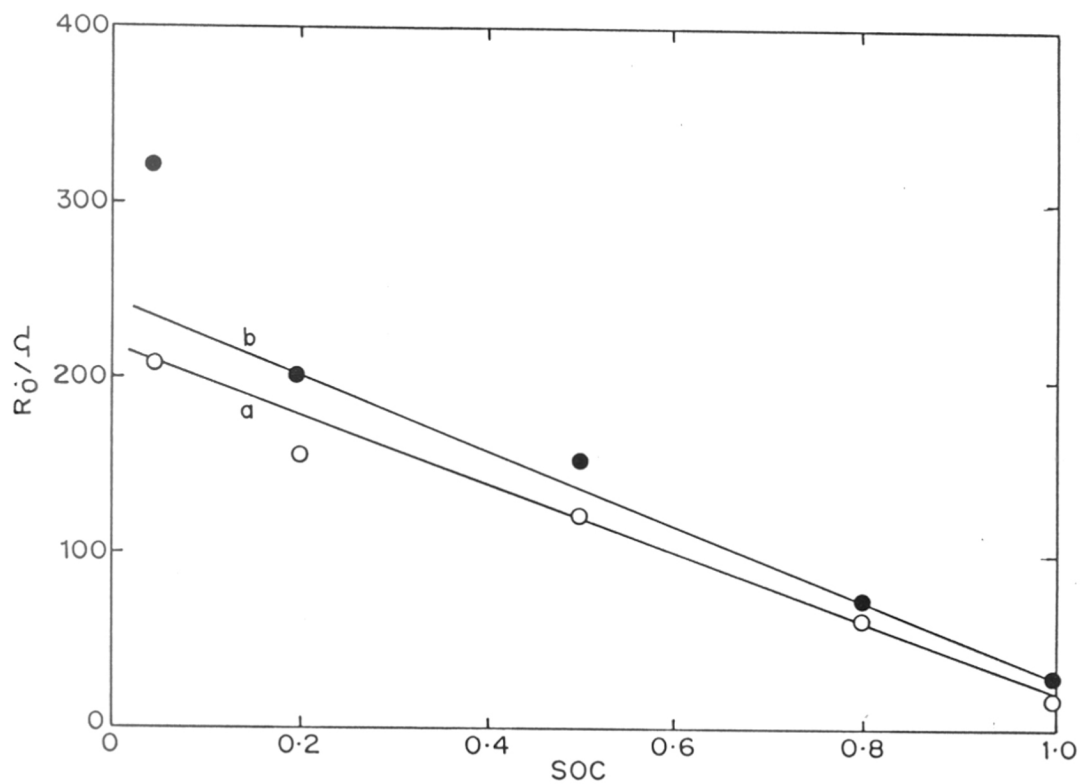


Figure 4. 10. Variation of R_o with SOC derived from the data of a prior cathodic polarisation: (a) flooded electrolyte, and (b) immobilised electrolyte.

Figures 4. 9 and 4. 10 show the uncompensated resistance versus SOC curve derived from the data for prior anodic and cathodic potential-time transients respectively. For the purpose of comparison, values for the immobilised electrolyte are also included in the same figures. The variation of R_o generally reflects, the change in the concentration of the electrolyte with SOC and or the accompanying change in the ohmic resistance of the active materials. In sharp contrast to the cathodic case, the anodic case shows large variation at extremely low SOC values as the amount of insoluble $PbSO_4$ that is accumulated in the pores of the electrode is large. As the SOC increases the density of acid in the pores increases and consequently, the resistance decreases. This explanation may be further supported by the enhanced effect in immobilised electrolyte. In addition, similar behaviour is generally observed for the variation of acid density with SOC.¹⁴ Linearity over a range of SOC from 0.2 to 0.8 confirms that above resistance is actually the ohmic part of the internal resistance and has no contribution from the charge-transfer component R_{ct} as shown by the separation of the two terms in equation (4.2). Furthermore, the variation of charge transfer resistance with SOC can be appreciated from it's relation with the exchange current, viz.,

$$R_{ct} = RT / nFI_{o,Pb}$$

As $I_{o,Pb}$ is proportional to $C_O^{1-\alpha}$ and C_R^α , where C_O and C_R refer to the concentrations of active materials. Although, this agreement is strictly true only for a homogeneous solid solution, useful information can be obtained as the SOC is an indication of the relative amounts of charged materials., the SOC can be considered to be non-linear with respect to charge-transfer resistance. More specifically, an approximate functional dependence of the form, $R_{ct} \propto 1/ SOC (1-SOC)^{1/2}$ can be obtained from the additional assumption of $\alpha = 0.5$.

One of the significant features of the above data is that the variation of the uncompensated resistance is almost linear with SOC especially if the latter is not very small. Thus, the R_o method can be used to measure the SOC of lead-acid batteries by simply measuring the uncompensated resistance. This prediction of SOC is generally considered as one of the basic requirements for large-scale applications of maintenance-free lead-acid batteries. As a design implication, it can be seen that the rapid fall of R_o at low SOC in the anodic case is more important for normal operation, namely discharge. Improvement of this design aspects is very useful, especially for pulsed and high-rate applications.

4. 4. Limitations of the model

One of the major assumptions involved in deriving Eqn. 4.14, i.e., the quasireversibility of the $PbSO_4$ system, may not be universally valid, especially because near the vicinity of open-circuit potential both lead dissolution and cathodic hydrogen evolution reaction will occur at equal rates, due to self-discharge (corrosion) process. For cathodic polarisation at high SOC values this quasireversibility may not be valid as hydrogen evolution is the only possible reaction and current passed is completely utilised for Reaction 3. 2. Similarly, at very low SOC values all the faradaic currents are completely used for Reaction 3. 1., and departure from the quasireversibility may be expected. As a consequence the model is not expected to be valid at both high (close to unity) and low (close to zero) SOC values.

Another major disadvantage of the above model arises from neglected adsorption induced pseudocapacitance. This is more important for cathodic polarisation as adsorbed hydrogen can contribute largely to all parameters estimated using the above model. More specifically, the coverage induced variations of exchange current density and C_{dl}

values contain large errors. Lastly, at high SOC values $I_{o, Pb}$ estimated using this model will reflect the corrosion currents for Pb/PbSO₄ system rather than the true $I_{o, Pb}$. In contrast, at lower SOC values the estimated exchange current will have more significant contribution from Pb/PbSO₄ system, particularly for cathodic polarisation as hydrogen evolution cannot occur since there is very little, if any, free lead present.

4. 5. CONCLUSION

The behaviour of Pb/PbSO₄ electrode in maintenance-free lead-acid batteries has been successfully investigated. A quantitative analysis of the potential-time transients explains the observed effect of adsorbed silicate ions on the exchange current densities and double-layer capacitance of the system. These results are useful in understanding the potential dependence of the double layer capacitance at particular SOC values. A systematic analysis of these variation provides a useful non-destructive method for the determination of SOC of maintenance-free lead-acid batteries. The technique is especially significant for immobilised or hermetically sealed systems.

4. 6. REFERENCES

1. D. A. J. Rand and R. Woods, *J. Electroanal. Chem.*, **29** (1971) 31.
2. R. W. Murray, in 'Electroanalytical chemistry' Vol 13, Bard, A.J. Ed. Marcel Decker, New York, (1984), p.191.
3. T. F. Evans, T. Kuwana, M.T. Heme and P. Royer, *J. Electroanal Chem.*, **80** (1977) 409.
4. M.P. Soriaga(Ed)'Electrochemical Surface Science; Molecular Phenomena at Electrode., American Chemical Society, Washington DC. (1988) P.8.
5. A . M. Couper, Derek Pletcher and Frank C. Walsh, *Chem Rev.*, **90** (1990) 837-865.
6. J. Janata, *Anal. Chem.*, **64**(1992) 196R-219R.
7. K. Vijayamohan, A.K. Shukla and S. Sathyanarayana, *J. Electroanal. Chem.*, **289** (1990) 55.
8. J. S. Buchanan, N.P. Freestone and L.M. Peter., *ibid*, **182** (1985) 383.
9. M. P. Soriaga, *Chem. Rev.*, **90** (1990) 771-793.
10. D. M. Kolb, in *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 2,(H. Gerisher, C. W. Tobias, Eds.) John Wiley and Sons, New York, (1984) p.125.
11. O. M. Magnussen, J. Motlos, O. M. Kolb and J. Behn, *Phys. Rev. Lett.*, **64** (1990) 2929.
12. T. Machiga, M. Honbo, K. Itaya, *J. Electroanal. Chem.*, **315** (1991) 275.
13. S. L. Yau, C. M. Vitus, B. C. Schardt, *J. Am. Chem. Soc.*, **112** (1990) 3677.
14. R. L. Mc Carley, A. J. Bard, *J. Phys. Chem.*, **95**(1991) 9618.
15. N. J. Tau, S. M. Lindcas, *J. Phys. Chem.*, **96** (1992) 5213.
16. R. Parson and J. Vander Noot, *J. Electroanal Chem.*, **257** (1988) 9.
17. K. Vijayamohan, S.N. Joshi and S. S. Sathayanarayana, *J. Power Sources*, **30**(1990) 169.
18. H. Tuphron, *J. Power Sources*, **23** (1988), 143-155.

19. S. Sathyanarayana, S. Venugopal and M. L. Gopikanth, J. Appl. Electrochem., **9** (1979) 125.
20. R. delevie. Adv. Electrochem. Engg., **6** (1967) 239.
21. R. Iler, 'The Chemistry of Silica' p. 287, John Wiley & Sons New York, (1979) p.287.
22. K. Vijayamohan, A. K. Shukla and S. Sathyanarayana, J. Electroanal. Chem., **295** (1990) 59-70.
23. T. F. Sharp in Encyclopaedia of electrochemistry of elements vol 1. edited by (A.J. Bard), Marcel Decker, New York, (1973) p.308.
24. P. Delahay 'Double Layer and Electrode Kinetics', Wiley-Interscience New York (1965), Ch. 2.
25. H. Bode, "Lead-Acid Batteries", Wiley, New York (1977), pp 26.

Chapter 5

EFFECT OF GELLING ON THE SURFACE STRUCTURE OF POROUS LEAD ELECTRODE IN SULPHURIC ACID

Effect of immobilising the electrolyte using thixotropic agents such as sodium silicate on the electrochemical behaviour of lead in sulphuric acid is studied using electrochemical methods such as Cyclic Voltammetry (CV), charging curve technique, Tafel polarisation and surface spectroscopic methods including X-ray Photo Electron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM). CV studies indicate a 700 mV cathodic shift in the Hydrogen evolution potential as a result of gelling while the well known reversible Pb/Pb^{2+} couple is found to be thermodynamically disfavoured (100 mV and 50 mV shift for the Pb dissolution and Pb^{2+} reduction reactions respectively). In addition, a significant change in double layer capacitance by $600 \mu\text{Fcm}^{-2}$ is observed at the same potential probably due to the contribution of silicate adsorption in the interfacial region. Exchange current density for Hydrogen evolution reaction calculated from Tafel plots are $1.35 \times 10^{-6} \text{ Acm}^{-2}$ and $1.31 \times 10^{-8} \text{ Acm}^{-2}$ for flooded and gelled electrolytes respectively, which reveal the kinetic suppression of HER. However, XPS studies give no evidence for chemisorption of silicate on the Lead surface, although SEM analysis shows appreciable change in the surface morphology.

* A paper based on this study has been accepted in the J. Appl. Electrochem. (In press)

5. 1. INTRODUCTION

Gels provide a unique environment which cannot be envisaged by their parent solid or liquid parts from which they are generally derived.¹ Use of gels as media for chemical reactions provides a unique way of controlling nucleation, growth, and any type of phase transitions during the reactions by controlling their viscosity. Both organic and aqueous types of gels are currently used for several chemical, physical and biological applications. For example, electrically readable polymeric gels are used for controlled-drug delivery systems² and also for understanding certain intermolecular interactions.³ Gelled systems are also successfully used for diffusion-limited aggregation in a wide range of phenomena such as electrodeposition⁴, random dendritic growth⁵, fluid-fluid displacement in porous media⁶, dielectric breakdown⁷ and for biological process such as the growth of nerve cells and blood vessels.⁸ Yet another application involves in catalysis, where mixed metal oxide such as vanadium silicate xerogels are prepared and tested for catalytic activity for reaction like alkene oxidation.⁹

These gelled systems are also found to offer several advantages in electrochemical applications^{10,11} They can be used either to immobilise an electroactive substance at an electrode surface or as a polymer electrolyte itself. Gels are particularly suitable for electrochemical systems where, dimensional changes occur on electrode as a result of electrochemical reactions like dissolution since they are deformable and can accommodate such changes. In addition gels of silica and transition metal hydroxides are appropriate media for performing electrochemistry due to the high content of free solvent. Therefore, it was a natural development of such studies to prepare modified electrodes from such gels. In a recent study, glucose oxidase was incorporated along with a water sol using

ferrocene as a mediator in silica gels and its electrocatalytic activity was studied by following the electrochemistry of ferrocene.¹²

One specific application of gels in electrochemical system is in sealed maintenance-free (MF) lead-acid batteries,^{13,14} where, the electrolyte is being immobilised with organic or inorganic thixotropic agents.¹⁵ The original reason for immobilising the electrolyte was to avoid acid spillover from batteries especially under stringent conditions like that in an aircraft. Subsequently, it was observed that due to the partial drying out, such gels exhibit improved gas recombination characteristics. These gelled systems do not require periodic topping up of the electrolytes for two main reasons. First, the amount of hydrogen produced is less compared to the flooded electrolyte and more importantly the oxygen released at the positive electrode migrates to the negative through cracks in the gelled electrolytes leading to recombination with the highly active lead surface. Thus the electrolyte loss is very negligible in gelled electrolyte systems. These type of gelled batteries are found to be especially suitable for severe duty such as Remote Area Power Supplies (RAPS) where a well defined charging regime is not available.

An analysis of OCP-time transients at various state-of-charge shows substantial changes in the self-discharge kinetics of the negative electrode as a result of gelling as discussed in Chapter 2. In addition, double layer capacitance (C_{dl}) and uncompensated resistance (R_u) measurements as discussed in chapters 3 and 4 also reveal an enhancement of both these parameters in gelled electrolytes. As a result, it is also important to see how the kinetic effects are related to the morphology of the active material in order to understand the benefits of gelling in improving cycle life. The present study is aimed at understanding the effect of immobilisation of the electrolyte on the surface structure of the negative electrode. In addition, the results of earlier chapters regarding the kinetics of

Pb/PbSO₄ electrode has been analysed using a judicious choice of conventional electrochemical methods such as Cyclic Voltammetry, Tafel polarisation and charging curve methods with modern surface spectroscopic techniques such as X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM).

5. 2. EXPERIMENTAL DETAILS

Negative and positive pasted plates (5.5 X 3 X 0.1 cm³) used in this study were obtained in cured and formed condition and the experimental details are described chapter 2. In brief, negative limited test cells with excess sulphuric acid (4.8 M) electrolyte were assembled with two positive counter electrodes (PbO₂) arranged on both side of the working electrode along with a Hg/Hg₂SO₄, H₂SO₄ (4.8 M) reference electrode. All the electrodes used in the present study were made with the same grid material namely Pb-Ca(0.08%)-Sn(0.5%) in order to preclude the possible effects of interaction by corrosion products of the grid. The reference electrode was connected to the test cell with a Luggin capillary tip aligned close to the working electrode to minimise the uncompensated resistance due to the solution.

5. 2. 1. Cyclic Voltammetric studies

The Cyclic voltammetric studies were carried out in 0.1 M sulphuric acid solution using a lead electrode of geometric area 0.02 cm² in a three electrode single compartment set up with Hg/Hg₂SO₄, H₂SO₄ reference electrode and a platinum foil counter electrode. All the experiments were carried out in an argon atmosphere at a temperature of 25±1°C controlled by a thermostat using a PAR 173 potentiostat coupled with a PAR 175 function generator and the data were recorded on a RE0091 X-Y recorder. The experiments were then repeated with an immobilised electrolyte having the same sulphuric acid concentration. The latter was prepared by adding sodium silicate as gelling agent (5g/L).¹⁶

5. 2. 2. Tafel Polarisation studies

Tafel polarisation was carried out using PAR 173 galvanostat. Prior to the measurements, the working electrode compartment was deaerated in the cell with pure argon, and the working electrode was then introduced immediately and kept at a current density of (1 Acm^{-2}) from the moment of insertion in the electrolyte to prevent spontaneous corrosion, i.e., from creating a build-up of Pb^{2+} ions in solution for 10 to 15 min. After this polarisation treatment at high current densities, the electrode was found to attain a stable open-circuit potential. The steady-state potential for the highest current density was recorded first and subsequently steady-state potentials for other current densities were recorded in descending order by decreasing the current densities in steps. The experiments were repeated with gelled electrolyte.

5. 2. 3. Charging curve methods

Charging curve measurements¹⁷ were carried out using similar electrodes used for CV and Tafel polarisation measurements. The electrode was first cathodically polarised using appropriate current densities to the potentials corresponding to the Ideal Polarised Region (IPE) of lead in sulphuric acid as obtained from the CV results. Potential build-up with time was recorded for smallest current density and (dE/dt) was calculated from the slope of E-t curves with extrapolation to zero time. The experiments were then repeated with gelled electrolytes.

5. 2. 4. Scanning Electron Microscopy (SEM)

SEM of the Pb/PbSO_4 electrode from completely discharged and overcharged conditions were taken in a Leica Cambridge Stereoscan 440 model from M/S Leica, Cambridge, UK. The Samples were mounted on a standard specimen mounting stub and then coated by a conducting thin layer of gold by vacuum deposition to prevent charging of

the specimen. For comparative study, the electron beam parameters were kept constant while analysing all the lead samples. The micrographs of the samples with 10 kV EHT and 200 nA beam current were recorded by a 35 mm camera attached on the high resolution recording unit.

5. 2. 5. X-ray Photoelectron Spectroscopy

X-ray Photoelectron spectroscopy (XPS) of the porous lead electrode from fully discharged and fully charged state with flooded and gelled electrolytes were carried out in a V.G. Scientific ESCA-3-MK-2 electron spectrometer with Mg-K α X-ray source (non-monochromatic). For the present measurements, the anode was operated at a constant pass energy of 50 eV. All the spectra were recorded with similar spectroscopic parameters. Binding energy (B. E) scale was calibrated by determining the B.E of Au 4f_{7/2} (84 eV), Ag 3d_{3/2} (368.4) and Cu 2p_{3/2} (932.4) levels using spectroscopically pure metals from Johnson-Matthey, London. The B. E values (measured to an accuracy of 0.2 eV) were in good agreement with literature values. The resolution in terms of the full width at half maximum (FWHM) of the Au 4f_{7/2} level was 1.6 eV.

5. 3. RESULTS AND DISCUSSION

5. 3. 1. Cyclic Voltammetric studies

Figure 5.1 represents typical Cyclic voltammograms of lead electrode in sulphuric acid (0.1 M) with and without immobilisation of the electrolyte at a representative scan rate of 10 mV/sec. Although commercial lead-acid batteries use 2-5 M sulphuric acid as electrolyte, 0.1 M is selected to keep mild conditions in CV. A comparison of the two voltammograms indicates a drastic change in the electrochemical behaviour of lead as a result of immobilisation of the electrolyte.

More specifically, the peaks for both lead dissolution (-950 mV) and deposition (-1000 mV) are flattened while the peak currents are increased in the gelled electrolyte and these effects are more pronounced for the deposition peak. The onset of HER is shifted by 700 mV cathodically as a result of gelling (-1.5 to -2.2 V). In addition, a small anodic peak is observed for voltammograms with gelled electrolyte, possibly arising from the adsorbed hydrogen as the peak height is found to increase by holding the potential at the HER region for few seconds and also since this is not observed at high scan rates. In order to avoid the formation of insoluble PbSO_4 and also to eliminate the complication from adsorbed hydrogen, the anodic and cathodic limits of the CV's were fixed at -0.8 V to -1.2 V respectively for further experiments. The typical cyclic voltammograms thus obtained for gelled and flooded electrolyte at a scan rate of 10 mV/sec are shown in figure 5.2a-b where the distortion due to gelling is particularly prominent. Interestingly, lead dissolution peak is shifted from -956 mV to -856 mV as a result of gelling, while reduction peak is shifted from -1000 mV to -1044 mV. Major contribution of this shift is perhaps from IR drop as evidenced by a 40 Ω increase in the internal resistance of the cell with the addition of gelling agent as discussed in chapter 3 and 4. This increased internal resistance can approximately shift the reduction potential cathodically by 40 mV (for 1 mA current). This is in further agreement with the flattening of the wave observed in the gelled electrolyte as the peak widths for both lead deposition and dissolution are increased. For example, ΔE_p of the cathodic peak is increased from 8 mV to 48 mV by immobilisation (at the scan rate of 10 mV/sec) while the anodic peak is expanded from 20 mV to 48 mV in the gelled electrolyte. The influence of gel is more pronounced in the case of reduction peak, as the species from the solution is diffusing to the electrode surface and getting deposited

there. This process is more influenced by the gel due to nucleation than the anodic process in which the dissolution is from the electrode surface.

Figure 5.3 shows the comparison of the anodic and cathodic peak current variations with square root of scan rate in flooded and gelled electrolytes respectively. There is a drastic enhancement in both cathodic and anodic peak currents as a result of gelling, in spite of the slower diffusion, and this increase is significantly more for the anodic peak than the cathodic one in the gelled electrolyte. For example, at a scan rate of 10 mV/sec $I_{p,a}$ is increased from 136 mA to 900 mA while $I_{p,c}$ is increased from 30 mA to 48 mA in gelled electrolyte possibly due to the electrocatalytic effect of silicate ions. This is more significant since the ohmic drop due to gelling is expected to cause a reduction in all peak currents.

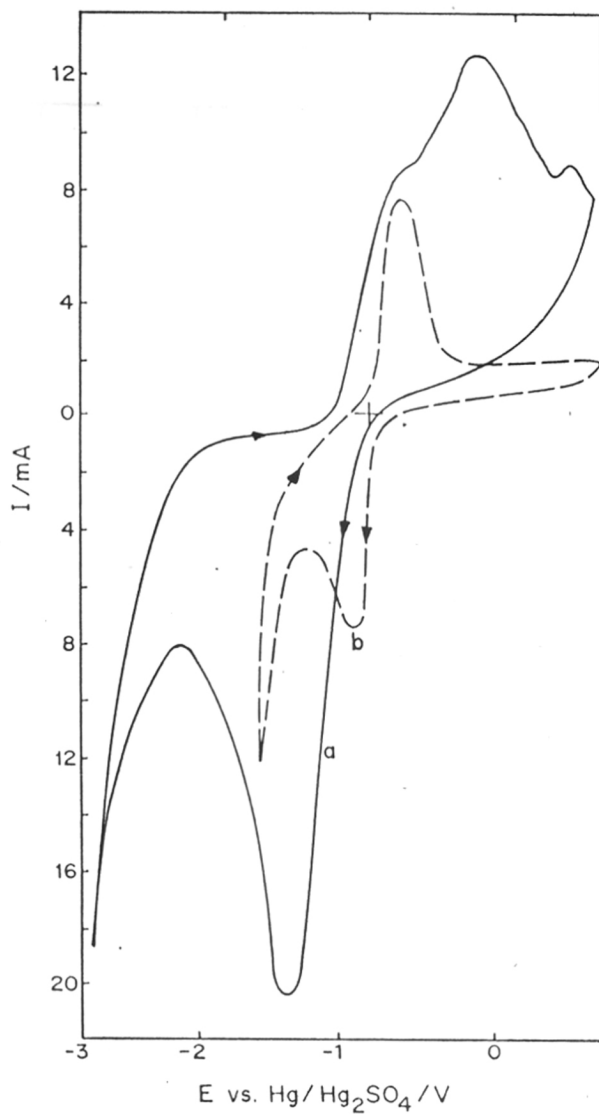


Figure 5.1. Cyclic voltammograms of lead electrode (0.02 cm^2) in sulphuric acid (.1 M) at a scan rate of 10 mV sec^{-1} with (a) and without (b) immobilisation of the electrolyte in a potential region of -3 to +0.5 V.

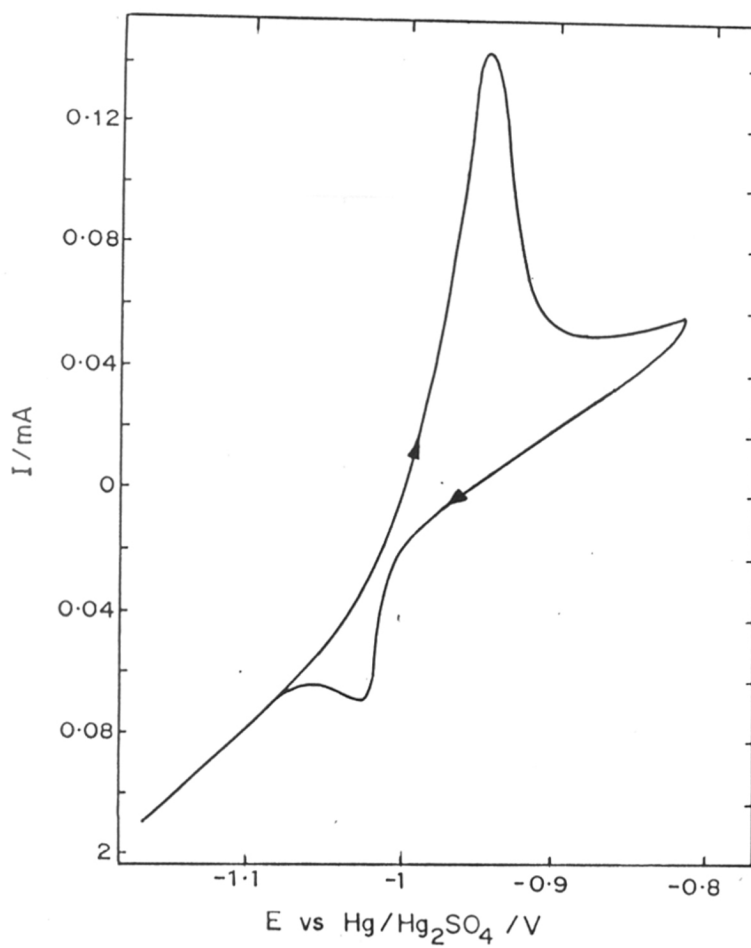


Figure 5.2a. Cyclic voltammograms obtained for flooded electrolyte at a scan rate of 10 mV sec^{-1} in the potential region of -1.2 to -0.6 V.

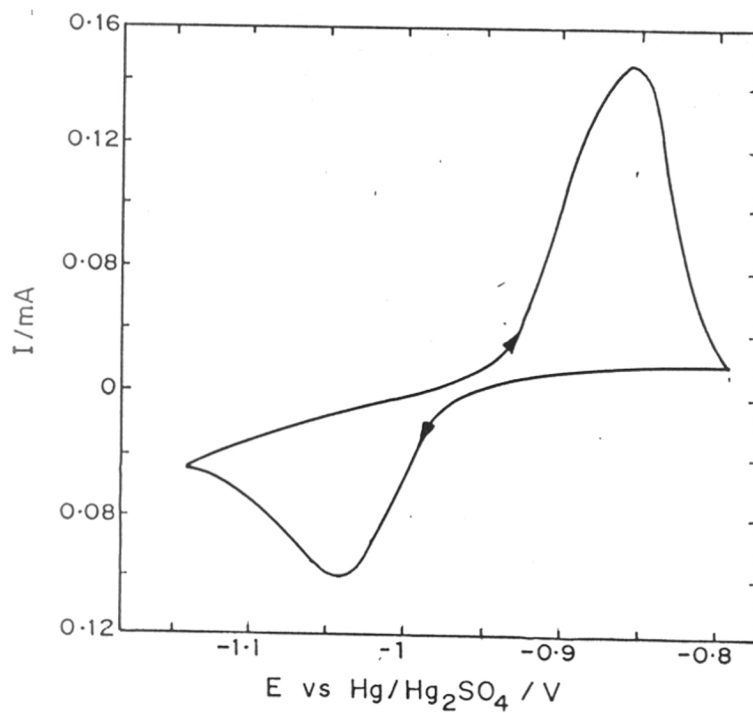


Figure 5.2 b. Cyclic voltammograms obtained for gelled electrolyte at a scan rate of 10 mV sec^{-1} in the region of -1.2 to -0.6 V.

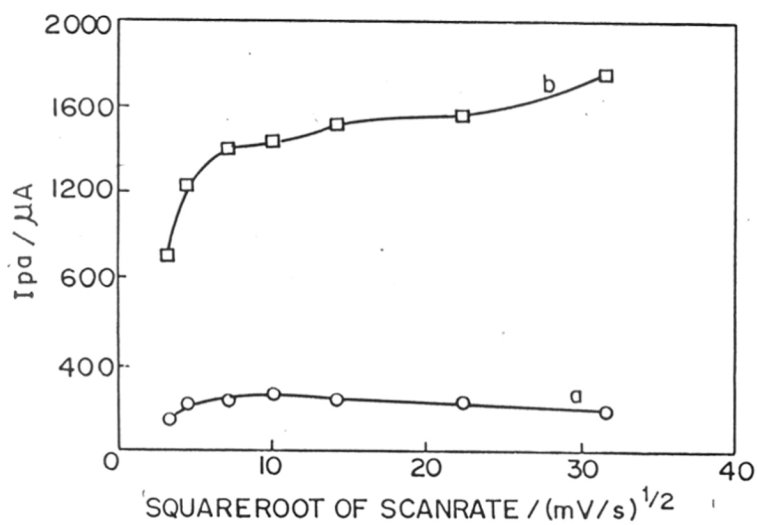


Figure 5. 3. Variation of anodic peak current with square root of scan rate in flooded (a) and gelled (b) electrolytes respectively.

5. 3. 2. Charging curve studies

Charging curve method is a standard procedure for estimating double-layer capacitance of any electrode/electrolyte interface¹⁷⁻¹⁹ in the ideal polarised region. The high hydrogen overpotential of lead facilitates the use of charging curve for the study of lead electrode/sulphuric acid interface in a limited cathodic region. The observed charging curve for the free and immobilised electrolyte in this region is shown in Figure 5. 4, indicating that there is an over all increase in double layer capacitance as a result of immobilisation. The corresponding C_{dl} values calculated using the geometrical area of the electrode for the free and immobilised electrolyte are $1400 \mu\text{Fcm}^{-2}$ and $2000 \mu\text{Fcm}^{-2}$ respectively. These values are very high compared to the capacitance values for normal electrode/electrolyte interface and the anomalous values are due to the surface roughness factor.^{20 -21} Since the lead electrode used for both cases have same size there is no reason for such a drastic change in surface roughness and therefore the result indicates that the double-layer capacitance values are enhanced significantly in gelled electrolyte. This enhancement can be explained by the fact that the double layer will be compact in the gelled electrolyte compare to the flooded electrolyte, due to increased hindrance of charge separation from the adsorbed silicate network, leading to a pronounced. Helmholtz type behaviour rather than diffused behaviour.

5. 3. 3. Tafel Polarisation methods

Steady-state, potentiostatic, cathodic Tafel polarisation plots for the Pb electrode in gelled and normal electrolyte (Figure 5.5) are recorded in the descending order of current densities. The Tafel slopes are found to be 120 and 170 mV respectively for gelled and flooded electrolyte respectively. The exchange current density $i_{0,H}$ for HER calculated from the intercepts on the basis of apparent geometrical area are $1.35 \times 10^{-3} \text{ mA cm}^{-2}$ and

$1.31 \times 10^{-3} \text{ mA cm}^{-2}$ for flooded and gelled electrolytes respectively showing that the gel suppresses HER. This is in complete agreement with the cyclic voltammetric studies where a 700 mV cathodic shift is observed in HER as a result of immobilisation. This suppression can be due to two major reasons; the gelling may affect the mass transfer of H^+ ions to the electrode surface by complexing of silicate ions, and more importantly, the silicate network may be changing the surface properties of lead electrode and thereby suppressing the chemisorption of protons at the Pb electrode surface. Another main reason for the difference in Tafel behaviour in gelled and free electrolyte is due to the enhanced diffusion of oxygen through cracks present in the gel, leading to the chemical oxidation of lead surface. It is well known in gelled batteries that, Oxygen can diffuse through the cracks to cause recombination at the lead electrode surface.²² This can suppress HER and leads to a large shift in HER potential observed in gelled electrolyte.

5. 3. 4. Scanning Electron Microscopy

It is well-known that the activemass of negative electrode in a lead-acid battery contains a primary skeleton and a secondary structure.^{23, 24} The primary structure is emerging during the formation stage, where, the lead oxide and the basic sulphates are reduced to metallic lead. The use of the expander enhance the formation of secondary structure. Since gelling of the electrolyte is known to improve the capacity of the negative electrode²⁵, it is expected that gelling will influence the secondary structure more effectively than the primary structure.

Scanning electron micrograph of samples from overcharged and deeply discharged electrodes with and without immobilisation of the electrolyte respectively are shown in

Figure 5.6a- 5.6d.. This clearly demonstrates the drastic effect of gelling on the morphology of Pb electrode²³ both in charged and discharged states. The SEM of the electrode from the fully charged state (Figures 5.6 a to 5.6 b) shows that the particles obtained in the case of gelled electrolyte is 10 times larger than that obtained from a free electrolyte. This can be attributed to the effect of gelling on nucleation and growth involving Pb^{2+} ions in the solution, as the growth rate will depend on the rate of mass transfer of Pb^{2+} ions. Gelling is known to control the nucleation and growth of crystals in other systems due to its unique control of viscosity. Gelling will naturally hinder the rate of mass transfer to the electrode surface and in the free electrolyte the rate of nucleation is much faster than growth. This will lead to the formation of less number of big crystals rather than large number of small crystals. Interestingly, a reverse trend is observed on the morphology of completely discharged electrode due to gelling, since the PbSO_4 particles are smaller and more uniformly deposited in comparison with the electrode from a flooded electrolyte. Since a finer particle size and more uniform distribution increase the utilisation of the reactive material, this could be used to explain the enhanced capacity of negative electrode due to gelling.

5. 3. 5. X-ray Photoelectron Spectroscopy

Significant changes in the surface morphology observed in gelled electrolyte together with the substantial changes in the fundamental electrochemistry of lead as a result of gelling demands the characterisation of the surface composition by XPS. Chemisorbed species are in general²⁵ stable at ultrahigh vacuum conditions used in the XPS measurements thus permitting their identification and quantification. The binding energy for Pb $4f_{7/2}$ and $4f_{5/2}$ signals corresponding to samples in the fully charged state are near 138.6 eV, the signals are found to enhance with gelling (Figure 5. 7). Significant changes are not observed

in the surface chemistry of lead in the gelled electrolyte. This is probably because the Pb-O--Si bond formed in solution may not be strong enough to withstand the ultrahigh vacuum conditions of the XPS spectroscopy. Similar results are also obtained for samples taken from a deeply discharged cell.

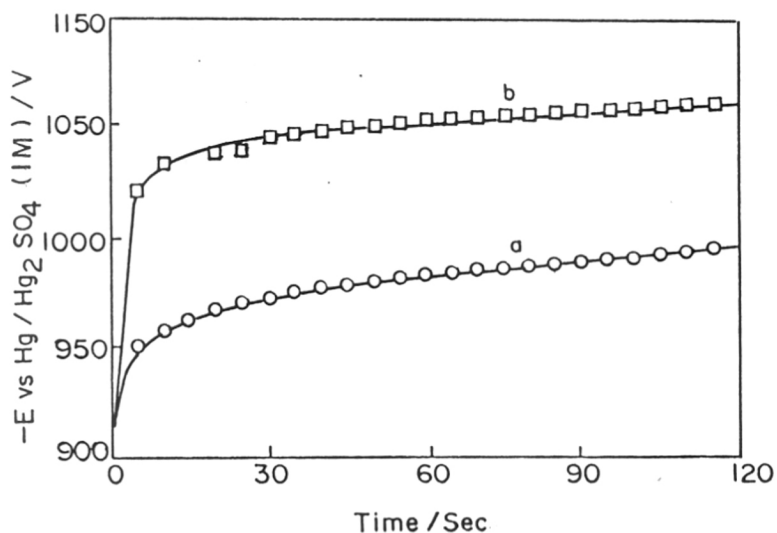


Figure 5. 4. Charging curve for the lead electrode in a) flooded and b) immobilised 1 M sulphuric acid electrolyte.

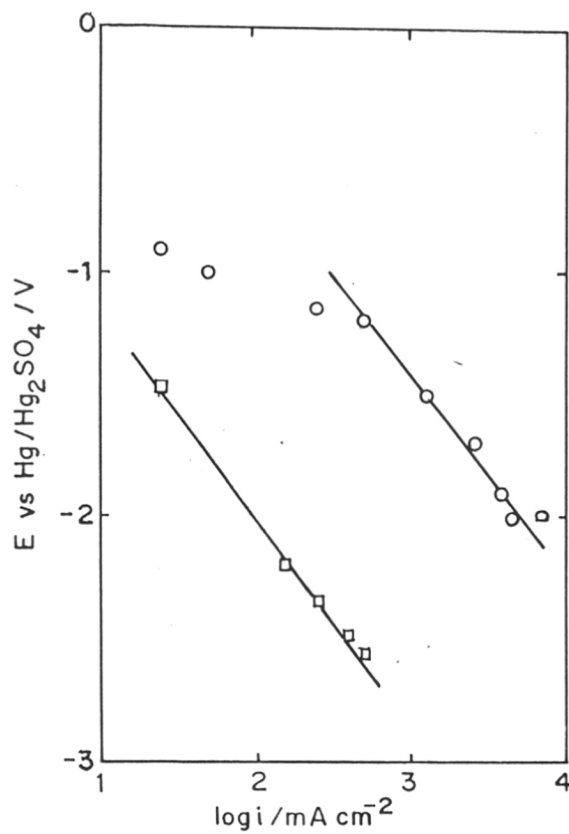


Figure 5.5. Steady-state potentiostatic Tafel polarisation curve in the cathodic region for the flooded (a) and immobilised (b) electrolytes.

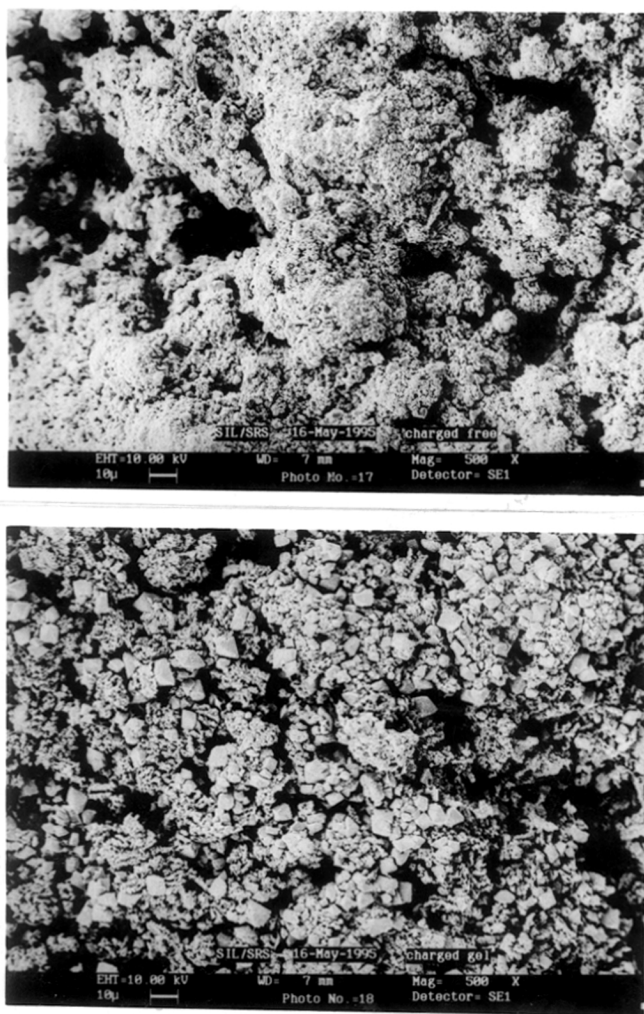


Figure 5. 6.(a,b) Scanning Electron Micrographs for Pb/PbSO₄ electrodes from a fully charged cell in flooded and gelled electrolytes respectively.

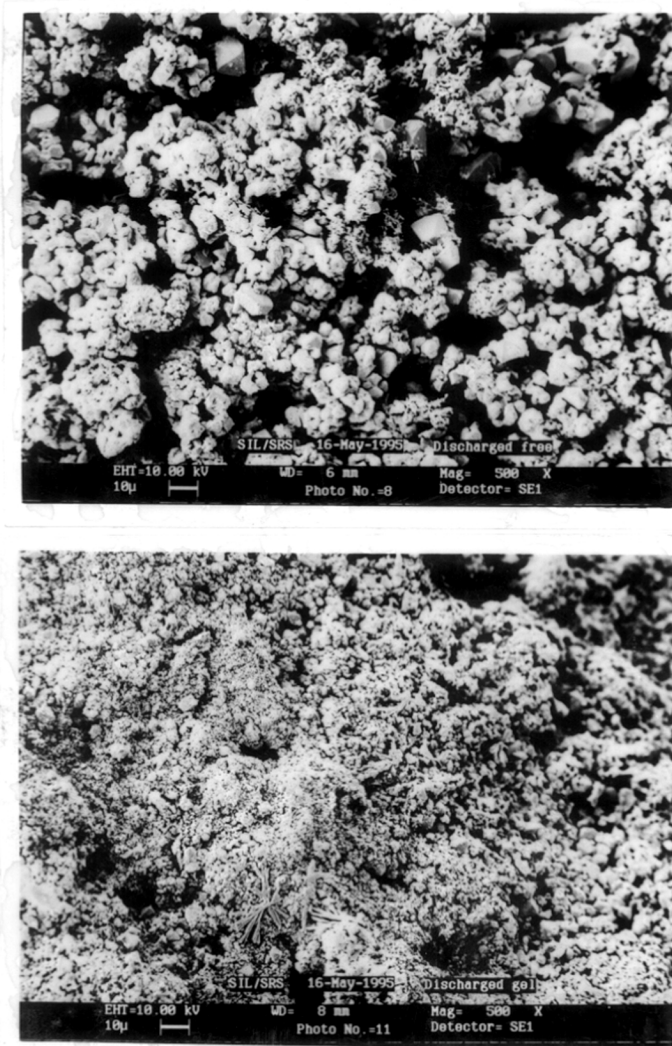


Figure 5. 6.(c,d) Scanning Electron Micrographs for Pb/PbSO₄ electrodes from a fully discharged cell in flooded and gelled electrolytes respectively.

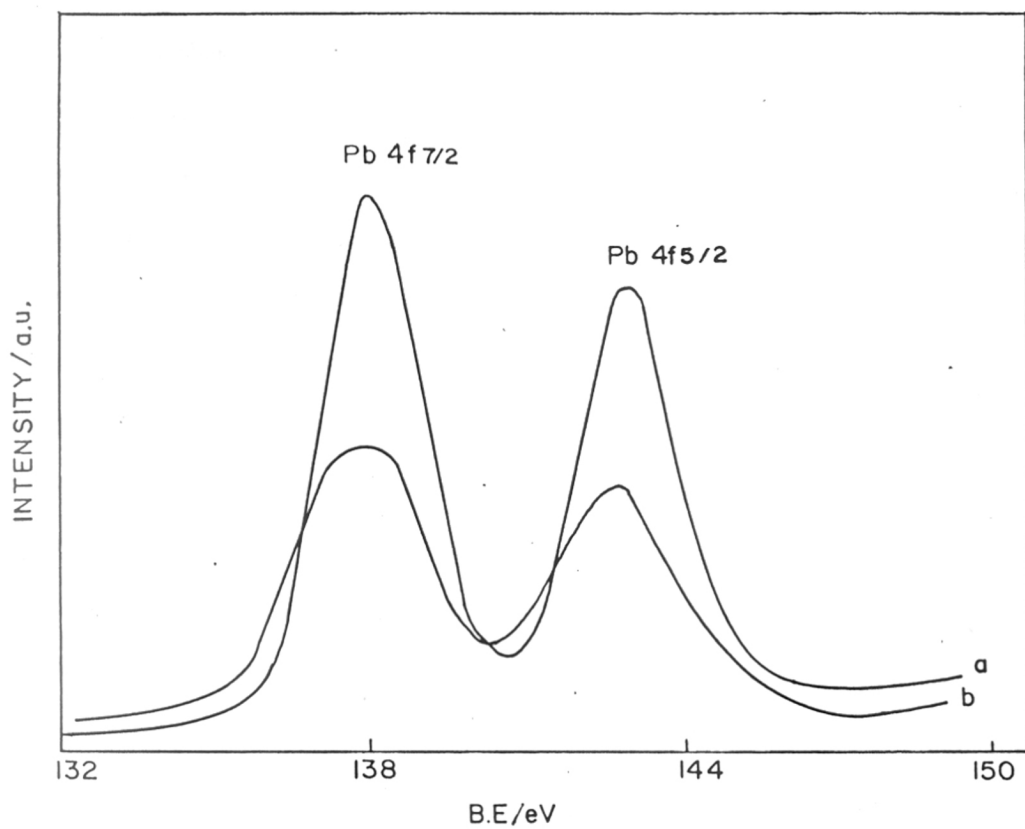


Figure 5. 7. Pb 4f_{7/2} and Pb 4f_{5/2} X-ray photoelectron spectra of Pb electrode obtained from a fully discharged cell with a) gelled electrolyte b) flooded electrolyte.

5. 4. CONCLUSION

A combined application of Cyclic Voltammetry, charging curve methods and Tafel polarisation along with XPS and SEM studies indicates a drastic change in the surface electrochemistry of lead as a result of the immobilisation of the electrolyte. Although both lead deposition and dissolution become thermodynamically less favourable, both peak currents are interestingly increased with immobilisation. Double-layer capacitance measurements using the charging curve method show that a major contribution of this increase is from the change in the interfacial structure. Tafel polarisation studies prove that the HER reaction is suppressed by the addition of silicate and this is further confirmed by the Cyclic Voltammograms, where a 700 mV cathodic shift in HER is observed as a result of immobilisation. SEM studies indicate a drastic change in morphology of the porous Pb/PbSO₄ electrode surface as a result of gelling, although XPS studies give no clear proof for chemisorption of silicate ions on the lead electrode surface. These results are important in understanding the operations of sealed MF lead-acid batteries.

5. 5. REFERENCES

1. I. A. E. Alexander and P. Johnson, Colloid science, Clarendon press, Oxford (1949).
2. I. C. Kwon, Y. H. Bae and S.W. Kim, Nature, **354** (1991)291.
3. E.Tschida, and K. Abe, Adv. Polym. Sci., **45** (1982)1.
4. K. Ignatova and J. Nikolova, Bull. Electrochem. Soc., **8** (1992)266.
5. G. Daccord and R. Lenormand, Nature, **325**(1987)41.
6. J. Nittmann, G. Decord, H. E. Stankey., Nature, **314**(1985)141.
7. L. Nilemeyer, L. Pietronero and H. J. Weismann, Phys. Rev. Lett., **52**, (1984) 1033.
8. N. P. Pavletich and C. O. Paboo, Science, **252**(1991)809.
9. R.Newmann and L. E. Michael, Appl. Cat A , **122**(1995)85.
10. "Electrochemical science and technology of polymers", R. G. Linford, ed., vol **1-2**, Elsveir applied Sciences New York. (1987).
11. M. E. Armand, J. J. Chabagno and M. J. Duclot., Fast ion transport in solids. eds. P. Vashishta, J.N. Mundy and G. K. Shenoy, North-Holland, Amsterdam, (1979).
12. M. T. Reetz, A. Zonta and J. Simpelkamp., Angew. Chem.Int. Ed. Engl., **34**(1995)301.
13. K. Vijayamohanan, S.N. Joshi and S. S. Sathayanarayana, J. Power Sources, **30**(1990)169.
14. H. Tuphron, J. Power Sources, **23**,(988)143.
15. G. Posch, J. Power Sources, **33**(1991)127.
16. R. Iler, 'The Chemistry of Silica' p. 287, John Wiley, New York, (1979).
17. P. Delahay 'Double layer and electrode kinetics', Chapter 2, Wiley-Interscience New York (1965).
18. C. H. Preshreg Jr., and S. Schuldimer, J. Electrochem. Soc., **180** (1961) 985.
19. P. E. Bowden, Proc. Roy. Soc., **125A**(1929) 446.

20. R. delevie. Adv. Electrochem. Electrochem. Engg., **6** (1967)239.
21. J. Newman and W. Tiedemann, AlchE. J., **21** (1975)35.
22. R. H. Newnham, J. Power. Sources., **52** (1994)149.
23. D. Pavlov and Z. Dinev, J. Electrochem Soc., **127** (1980) 855.
24. V. Ilev and D. Pavlov, J. Appl. Electrochem., **15** (1985) 39.
25. A. T. Hubbard, Langmuir, **6** (1990) 97.

List of Publications

1. Effect of gelling on the Open-circuit potential against time transients of Pb/PbSO₄ electrode at various states of charge.

M. P. Vinod and K. Vijayamohanan, **J. Appl. Electrochem.**, 24 (1994) 44.

2. Effect of gelling on the electrode kinetics of the Pb/PbSO₄ and hydrogen electrode reactions in maintenance-free lead-acid batteries

M. P. Vinod and K. Vijayamohanan, **J. Power Sources**, 50 (1994) 67.

3. A Novel non-destructive method for the prediction of state - of-charge of maintenance-free lead-acid batteries.

M. P. Vinod and K. Vijayamohanan, **J. Power Sources**, 52 (1994) 135.

4. Effect of silicate adsorption on the double layer capacitance and exchange current density of Pb/PbSO₄ electrode reaction.

M. P. Vinod and K. Vijayamohanan, **J. Appl. Electrochem.**, 25 (1995) 80.

5. An unusual electron transfer behavior of ferrocene in micelles.

B. K. Jha, B. D. Kulkarni, **M. P. Vinod** and K. Vijayamohanan,

Chem. Phys. Letters 240 (1995) 442.

6. Catalytic selective oxidation of aniline with hydroperoxides over molecular sieves :Investigations into the reaction of alkyl amines and aryl amines.

S. Suresh, Reni Joseph, B. Jayachandran, A. V. Pol, **M. P. Vinod**, A. Sudalai, H.

R. Sonawane and T. Ravindranathan., **Tetrahedron** 51 (1995) 11305.

7. Environment dependent redox behavior of Vanadium containing molecular sieves

N. Venkatathiri, **M. P. Vinod**, K. Vijayamohanan, and S. Sivasankar, **J. Chem. Soc.**

Faraday. Trans, 92 (1996) 473

8. Silicon Based Light emitting gels,

M. P. Vinod and K. Vijayamohanan **Appl. Phys. Lett.**, 68 (1996) 81.

9. A Novel efficient synthesis and charecterisation of Cr-silicalite 1

T. Selvam and **M. P. Vinod**, **Appl. Cat A**, 1996 (134) L197.

10. Mechanism of Humidity Sensing Properties of Ti Doped MgCr_2O_4 Ceramics

S. S. Pingale, S. F. Patil, **M. P. Vinod**, G. Pathak and K. Vijayamohanan ,

Mater. Chem. Phys., 46(1996)72.

11. Catalytic and Electrocatalytic Oxidation of Aniline to Nitrobenzene Over Vanadium Silicate Molecular Sieves: VS-1 Using t-Butyl Hydroperoxide as the oxidant.

T. Selvam, **M. P. Vinod** and K. Vijayamohanan, **React. Kint. Cat. Lett.**, 1996 (In Press)

12. Effect of Gelling on the Surface Structure of Porous Electrode in Sulfuric Acid

M. P. Vinod, A. B. Mandle, S. R. Sainker and K. Vijayamohanan,

J. Appl. Electrochem (In Press)