

Steady State Experimental Evaluation
of a Novel Raney-Ni/PTFE Gas Diffusion
Electrode in an Alkaline Fuel Cell

by

Khan Abbas A. Khan

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMICAL ENGINEERING

June, 1993

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

U·M·I

University Microfilms International
A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600



Order Number 1354019

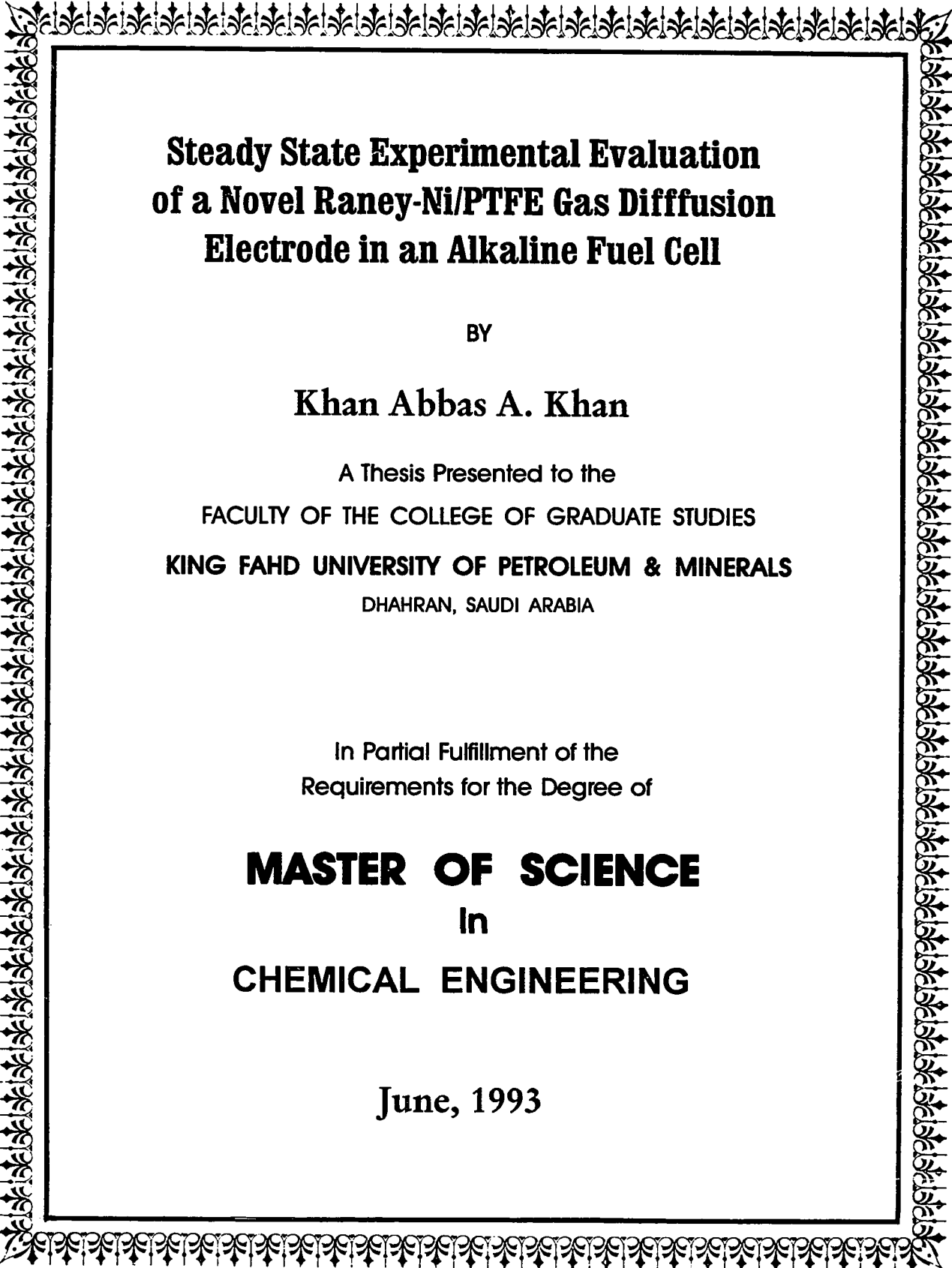
**Steady state experimental evaluation of a novel Raney-Ni/PTFE
gas diffusion electrode in an alkaline fuel cell**

Khan, Khan Abbas A., M.S.

King Fahd University of Petroleum and Minerals (Saudi Arabia), 1993

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106





**Steady State Experimental Evaluation
of a Novel Raney-Ni/PTFE Gas Diffusion
Electrode in an Alkaline Fuel Cell**

BY

Khan Abbas A. Khan

A Thesis Presented to the
FACULTY OF THE COLLEGE OF GRADUATE STUDIES
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE
In
CHEMICAL ENGINEERING

June, 1993

KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS
DHAHRAN 31261, SAUDI ARABIA

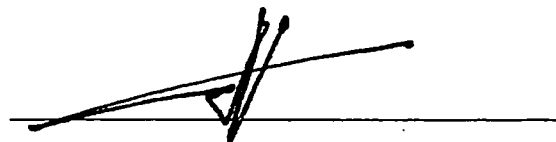
COLLEGE OF GRADUATE STUDIES

This thesis, written by *ABBAS ALI A. KHAN* under the direction of his thesis advisor and approved by his thesis committee, has been presented to and accepted by the Dean of the College of Graduate Studies, in partial fulfillment of the requirements for the degree of *MASTER OF SCIENCE IN CHEMICAL ENGINEERING*

Thesis Committee



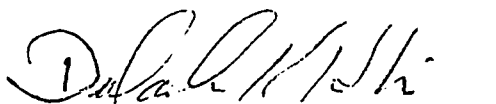
Chairman (Dr. Selahattin Gultekin)



Co-Chairman (Dr. Muhammad A. Al-Saleh)



Member (Dr. Abdullah S. Al-Zakri)



Dr. Dulaihan K. Al-Harbi
Department Chairman



Dr. Ala H. Al-Rabeh
Dean, College of Graduate Studies



Date: 10-7-93

THIS IS DEDICATED TO MY
BROTHERS

ACKNOWLEDGMENT

I would like to sincerely thank my thesis advisor, Dr. Selahattin Gultekin for his invaluable guidance and co-operation during the course of my studies. I am grateful to my co-advisor, Dr. Muhammad Al-Saleh for his excellent guidance and constant encouragement throughout this thesis. I am also indebted to Dr. Abdullah Al-Zakri for his critical comments, fruitful suggestions and generous assistance in this project. I would like to thank Dr. Dulaihan Al-Harbi, Chemical Engineering Department Chairman for his marvelous assistance during my research work. Special thanks are also due to my friends Aleem Paracha and Saleem ur-Rahman for their help in the project. I am grateful to all the faculty members and graduate students of Chemical Engineering Department who made my stay in the university pleasant and memorable one.

ABBAS ALI A. KHAN

Dhahran/Saudi Arabia

June 1993

TABLE OF CONTENTS

| | Page |
|-----------------------|------|
| List of Figures..... | iv |
| List of Tables..... | vi |
| Nomenclature..... | vii |
| ABSTRACT-Arabic..... | viii |
| ABSTRACT-English..... | ix |

Chapter 1-INTRODUCTION

| | |
|--|----|
| 1.1 Basic Concept of a Fuel Cell..... | 1 |
| 1.2 Advantages and Disadvantages of Fuel Cells..... | 3 |
| 1.3 Applications of Fuel Cells..... | 4 |
| 1.4 Classification of Fuel Cells..... | 4 |
| 1.5 H ₂ /O ₂ Alkaline Electrolyte Fuel Cell (AFC)..... | 7 |
| 1.6 Fuel Cell Electrodes..... | 8 |
| 1.7 Overpotential Concept..... | 8 |
| 1.8 Objectives | 11 |

Chapter 2- LITERATURE REVIEW ON H₂ ELECTRODE 13

Chapter 3-ELECTRODE KINETICS AND ELECTROCATALYSIS

| | |
|---|----|
| 3.1 Introduction..... | 20 |
| 3.2 Current-Potential Relation at a Single Electrode..... | 20 |

| | | |
|-----|--------------------------------------|----|
| 3.3 | Electrocatalysts..... | 22 |
| 3.4 | Design of Electrodes..... | 24 |
| 3.5 | Electrode study Techniques..... | 25 |
| 3.6 | Importance of Half Cell Studies..... | 28 |

| | |
|---|-----------|
| Chapter 4-REVIEW OF MATHEMATICAL MODELS FOR POROUS FUEL CELL ELECTRODES..... | 30 |
|---|-----------|

**Chapter 5-ELECTRODE MANUFACTURE AND
CHARACTERISTICS**

| | | |
|-----|---|----|
| 5.1 | Manufacture of H ₂ Anodes..... | 36 |
| 5.2 | Surface Area..... | 39 |
| 5.3 | Mercury Intrusion Porosimetry..... | 42 |
| 5.4 | Scanning Electron Microscopy(SEM)..... | 45 |
| 5.5 | Inductively Coupled Plasma-AES..... | 51 |
| 5.6 | Estimation of Electrochemically Active Surface Area | 51 |
| 5.7 | Estimation of Electrode Macroporosity..... | 53 |

Chapter 6-EXPERIMENTAL SETUP AND PROCEDURE

| | | |
|-----|--|----|
| 6.1 | Experimental Half Cell Setup..... | 56 |
| 6.2 | Activation of the Raney-Ni Electrode..... | 58 |
| 6.3 | Polarization and IR Drop Measurement | 59 |

Chapter 7-EXPERIMENTAL RESULTS AND ANALYSIS

| | | |
|------|--|----|
| 7.1 | Polarization Measurements Results..... | 65 |
| 7.2 | Application of Spherical Raney-Catalyst Grain model..... | 76 |
| 7.3 | Estimation of Kinetic Parameters..... | 77 |
| 7.4 | Apparent Activation Energy..... | 80 |
| 7.5 | Discussion of Polarization Results..... | 84 |
| 7.6 | Experimental Results for Long Term Performance Test..... | 86 |
| 7.7 | Application of Deactivation Model..... | 88 |
| 7.8 | Estimation of Deactivation Constants..... | 93 |
| 7.9 | Characterization of Deactivated Electrode..... | 95 |
| 7.10 | Discussion of Deactivation Results..... | 96 |

| | |
|------------------------------------|-----|
| Chapter 8-CONCLUSIONS | 102 |
|------------------------------------|-----|

| | |
|--|-----|
| Chapter 9-RECOMMENDATIONS | 104 |
|--|-----|

| | |
|-------------------------|-----|
| REFERENCES | 105 |
|-------------------------|-----|

| | |
|-------------------------|-----|
| APPENDICES | 109 |
|-------------------------|-----|

LIST OF FIGURES

| Figure | Page |
|---|------|
| 1.1 Schematic Diagram of a Fuel Cell..... | 2 |
| 1.2 Typical Plot of Cell Potential and Current..... | 10 |
| 3.1 Schematic Representation of a Hydrogen Half Cell..... | 29 |
| 5.1 Schematic Representation of Felt Rolling into Metal Net..... | 38 |
| 5.2 EDS Spectra for the Metal Mesh..... | 46 |
| 5.3 EDS Spectra for the Electrolyte Facing Side of Electrode..... | 47 |
| 5.4 EDS Spectra for the Gas Facing Side of Electrode..... | 48 |
| 5.5 SEM Micrograph of the Active Layer of Electrode..... | 49 |
| 5.6 SEM Micrograph of the Cross-section of Electrode..... | 50 |
| 6.1 A Schematic diagram of the Half Cell Assembly..... | 57 |
| 6.2 Circuit Diagram for the Galvanostatic Polarization Expt..... | 60 |
| 6.3 Current Interruption Method for IR Drop Measurement..... | 61 |
| 6.4 Circuit Diagram for the Potentiostatic Experiments..... | 64 |
| 7.1 Reproducibility runs with the Old Electrode at 35°C & 65°C | 66 |
| 7.2 Reproducibility Run at 45°C..... | 67 |
| 7.3 Electrolyte Resistance as a Function of Temperature..... | 68 |
| 7.4 Steady State Polarization Curve For H ₂ Oxidation Reaction at 25°C..... | 70 |
| 7.5 Steady State Polarization Curve For H ₂ Oxidation Reaction at 35°C..... | 71 |
| 7.6 Steady State Polarization Curve For H ₂ Oxidation Reaction at 45°C..... | 72 |
| 7.7 Steady State Polarization Curve For H ₂ Oxidation Reaction at 55°C..... | 73 |
| 7.8 Steady State Polarization Curve For H ₂ Oxidation Reaction at 65° | 74 |

| | | |
|------|---|----|
| 7.9 | Steady State Polarization Curve For H ₂ Oxidation | |
| | Reaction at 75°C..... | 75 |
| 7.10 | Logarithm of current density Vs 1/T for Constant η | 82 |
| 7.11 | Exchange current density as a function of temperature..... | 87 |
| 7.12 | Potentiostatic Long Term Performance Test at 25°C..... | 89 |
| 7.13 | Potentiostatic Long Term Performance Test at 45°C..... | 90 |
| 7.14 | Potentiostatic Long Term Performance Test at 75°C..... | 91 |
| 7.15 | Galvanostatic Long Term Performance Test at 75°C | 92 |
| 7.16 | Logarithm of current density as a function of time on stream | 94 |
| 7.17 | SEM Micrograph of Deactivated Electrode from mesh side | 98 |
| 7.18 | EDS spectra for the Deactivated Electrode..... | 99 |

LIST OF TABLES

| Table | Page |
|---|------|
| 1.1 Possible Applications Of Fuel Cells..... | 5 |
| 1.2 Fuel Cells Classification Based on Electrolyte..... | 6 |
| 3.1 Techniques for Fuel Cell Electrode Research..... | 26 |
| 5.1 B.E.T. Surface Area for the Fresh Electrode..... | 41 |
| 5.2 Pore Volume by Hg Intrusion Porosimetry..... | 43 |
| 5.3 Pore Size Distribution for the Fresh Electrode..... | 44 |
| 5.4 ICP-AES Analysis for the Fresh Electrode..... | 52 |
| 5.5 Comparison of Characteristics of New electrode with Old | 55 |
| 7.1 Average Electrolyte as a Function of Temperature..... | 68 |
| 7.2 Temperature-independent Input Parameters for Spherical Raney-Catalyst Grain Model..... | 78 |
| 7.3 Temperature-dependent Input Parameter for Spherical Raney-Catalyst Grain Model..... | 79 |
| 7.4 Kinetic Parameters for Hydrogen Oxidation Reaction at various Temperatures..... | 81 |
| 7.5 Apparent Activation Energy at Different Overvoltages..... | 83 |
| 7.6 Apparent Deactivation Constants at different Temperatures. | 96 |

Nomenclature

| | | |
|----------------|---|--|
| A | = | External surface area of electrode, cm ² |
| \bar{a} | = | Electrode activity |
| C ₀ | = | Solubility of hydrogen in KOH, mol/cm ³ |
| D _L | = | Effective diffusion coefficient of H ₂ in electrolyte flooded pores |
| E _a | = | Apparent activation energy for H ₂ oxidation reaction |
| F | = | Faraday constant |
| f ^o | = | Active surface area of electrode per unit volume, cm ⁻¹ |
| I | = | Total current, Ampere |
| i | = | Current density, mA/cm ² |
| i ₀ | = | Exchange current density, mA/cm ² |
| K _d | = | Deactivation rate constant |
| L | = | Electrode thickness, cm |
| n | = | Number of electrons transferred |
| R | = | Average radius of catalyst grain, cm |
| t | = | Time on stream, hr |
| T | = | Absolute temperature |
| z | = | Stoichiometric number |

Greek Letters

| | | |
|-------------------------|---|---|
| α | = | Charge transfer coefficient |
| ϵ_{mac} | = | Macroporosity of the electrode |
| ϵ_{mic} | = | Microporosity of the electrode |
| η | = | Measureable overpotential on the electrolyte side, mV |
| θ | = | Contact angle |
| κ_e | = | Effective ionic conductivity, $\Omega^{-1}\text{cm}^{-1}$ |
| ξ | = | Dimensionless electrode thickness |
| ϕ | = | Dimensionless overvoltage |

ملخص الأطروحة

الاسم : عباس علي خان

عنوان الأطروحة : تقييم تجريبي لاقطاب نيكل اسفنجي غازية جديدة عند حالة الاستقرار في خلايا الوقود القلوية.

التخصص : هندسة كيميائية

التاريخ : يونيو ١٩٩٣

أجريت قياسات استقطابية عند حالة الاستقرار لقطب نيكل اسفنجي غازي جديد، ومطلي بأول أكسيد النحاس، و قد تم رصد أداء القطب على المدى الطويل في نصيف خلية تحتوي ٤٥٪ من محلول هيدروكسيد البوتاسيوم . ضخ غاز هيدروجين نقى لنصف الخلية تحت ضغط ١.٤ بار، وغيره الحرارة من ٢٥°م إلى ٧٥°م، يعزى الأداء الأفضل (الاستقطاب أقل) عند كثافات تيار كهربائي عالية لاضافة النحاس للقطب.

تم تطبيق نموذج داني الكروي لامتزاز وذلك لتقرير:

الوسائط الكايناتيكية، كثافات التيار المتبادلة، و معامل انتقال الشحنة للقطب. ووجد أن قيم كثافات التيار المتبادلة تحت درجات حرارة مختلفة تتراوح ما بين ١.٦ X ١٠ إلى ١.١ X ١٠-٤ أمبير/سم^٢ وه علامة أسية مع درجة الحرارة. وجد أيضاً أن طاقة التنشيط الظاهرية للقطب تساوي ٢٨ كيلوجول/مول، وهي أقل من القيم المنشورة. أما طاقة التنشيط الأقل لتفاعل أكسدة الهيدروجين فإنها تعني نشاطاً أعلى لمثل هذا النوع من الاقطاب.

على المدى الطويل بينت الاختبارات أن جهداً قطبياً أعلى من ٥٠ ملي فولت يُسبب تقليلاً سريعاً لنشاط القطب حُسبت ثوابت التقليل الظاهري للنشاط فكانت تتغير ما بين ٠.٠٤، إلى ٠.٣٦، لكل ساعة، وكان معدل تقليل النشاط أكثر عند درجات حرارة أعلى .

درجة الماجستير في العلوم

جامعة الملك فهد للبترول والمعادن

الظهران ، المملكة العربية السعودية

ABSTRACT

Steady state polarization measurements on specially prepared Raney-Ni/PTFE gas diffusion electrode impregnated with copper oxide were carried out. The long term performance of the electrode was also investigated in a half cell setup with 25% KOH solution. Pure hydrogen gas was fed to the half cell at a pressure of 1.4 bar. The electrolyte temperature was varied from 25°C to 75°C. The better performance (less polarization) at higher current densities is attributed to the addition of copper to the electrode.

Spherical Raney-catalyst grain model was applied to determine the kinetic parameters, exchange current density(i_0) and charge transfer coefficient(α) for the electrode. The values found for the exchange current densities at various temperatures were 6.6×10^{-6} to 3.1×10^{-4} Acm^{-2} . Exchange current density followed an exponential relation with temperature. Apparent activation energy for the electrode was found to be 28 kJ/mol lower than that reported in the literature. The lower activation energy for hydrogen oxidation reaction implied higher electroactivity of the electrodes of this type.

Long term performance tests showed that electrode overpotential greater than 50 mV cause rapid deactivation of the electrode. The apparent deactivation constants estimated for the electrode varied from 0.004 hr^{-1} to 0.032 hr^{-1} . The rate of deactivation is more at higher temperatures.

Chapter 1

INTRODUCTION

1.1 Basic Concept of a Fuel Cell

Fuel cell is an electrochemical device which converts the energy of chemical bonding to electrical energy. Unlike conventional batteries, fuel cells are fed continuously with their appropriate reactants a fuel and an oxidant. The reactants are stored outside the cell. Fuel cell comprises of two electrodes which are immersed in an electrolyte. The fuel which is a reducing agent such as hydrogen is fed to the anode. The oxidizing agent (air or oxygen) is fed to the cathode. (see fig. 1.1)

The oxidation of fuel at the anode and simultaneous reduction of oxidant at the cathode causes a potential difference. This potential difference promotes electron flow in an external circuit, where a load is connected. Thus useful work is obtained from a cell by physical separation of the electrode processes. To keep the electrode electrolyte invariant the reaction products are discarded.(1)

Theoretically any spontaneous chemical reaction could be used in a fuel cell. Because of unlimited supply of oxygen in the air combustion reactions are usually preferred for fuel cells. Most systems under development rely on hydrogen as the fuel.(1)

In practice, voltages of 0.7-0.8 V can be obtained in fuel cells with current densities of 100-300 mAcm⁻² of electrode surface(2). Fuel cells are

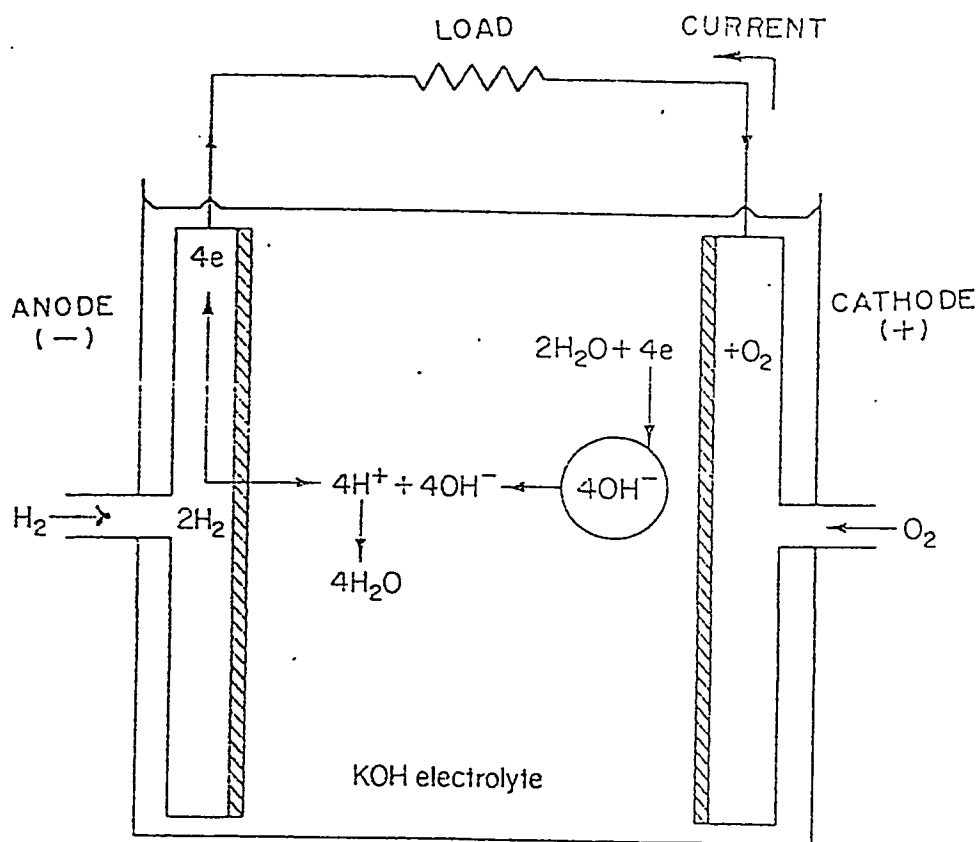


Fig. 1.1 Schematic Representation of a Fuel Cell

usually connected in series or in parallel to obtain higher voltages or currents. Such an arrangement is called a fuel cell stack.

1.2 Advantages and Disadvantages of fuel cells

Fuel cell operation is not dependent on flow of heat between sources and sinks hence it is not subject to Carnot limitations. In fuel cells 100% efficiency can be approached through appropriate design. Because of high thermodynamic efficiency, energy produced per unit weight is relatively high.(3)

Besides high energy production of electrical energy, the fuel cell has several other advantages. There are no moving parts involved so no friction losses. Atmospheric pollutants produced are minimal(4). The operation of a fuel cell is quite simple and reliable.

Within broad limits, efficiency of a fuel cell is independent of size. Therefore smaller modular units could be installed in areas of high electrical demand. This results in decreased in power line investment and transmission losses. Waste heat from fuel cell can be used for space heating ,raising steam . The combined efficiency for electricity and heat production can be as high as 98%.(5)

The disadvantages of fuel cell include actual efficiency, reliability and overall cost. Sources of irreversible behavior such as ohmic losses and sluggish kinetics limit fuel cell efficiency below 50% . The specific power obtained from a fuel cell is very low. Other disadvantages of fuel cell include larger weight and volume of gas fuel storage system, liquification expenses for the fuel, cleaning requirements for the reactants ,deactivation of electrode catalyst etc.(6)

1.3 Applications of Fuel Cells

The major applications of fuel cells can be divided into Remote power, Portable power and Electric utility applications(7). Table 1.1 gives potential fuel cell applications. Remote power applications include space missions, submarine applications, navigational aids, automated weather stations remote beacons, pipeline cathodic protection systems and communication system. Portable power applications are mostly for military purposes. Electric utility applications could further be classified as (a)on-site power plants (40-400kW) close to the point of energy demands,(b)electric utility power plants (5-50MW) located at utility substations with the option of the waste thermal energy being used for commercial heating,(c)electric utility power plants (100-500 MW)located at large central stations. Other possible applications of fuel cells could be to power electric vehicles and emergency power supply.(7,8)

At present very few of this applications are commercialised. With the advancement of technology in future these applications will become economically viable.(9)

1.4 Classification of Fuel Cells

Fuel cells can be configured in many ways with a variety of electrolytes,electrodes, fuels, operating temperatures and catalyst involved. Fuel cells are generally classified according to electrolyte type, since the electrolyte limits the operating temperature range and together these tend to define the fuel option. Table 1.2 gives classification of fuel cells based on electrolyte (10).

Table 1.2 Fuel Cell Classification Based On Electrolyte

| Electrolyte | Operating temperature (°C) | Fuel | Oxidant |
|-----------------------|----------------------------|--------------------------------------|--|
| Aqueous acid | 150-220 | Hydrogen | Air, O ₂ (pure) |
| Phosphoric acid | <100 | Indirect methanol, hydrocarbon, coal | Indirect H ₂ O ₂ |
| Solid polymer | <260 ^a | Hydrogen, hydrazine | O ₂ (pure) |
| Aqueous alkaline | 600-700 | Indirect ammonia | Indirect H ₂ O ₂ |
| Molten carbonate salt | 1000-1100 | Direct methane or methanol | Air ^b |
| Solid oxide | | Indirect methanol, hydrocarbon, coal | Air |
| | | Hydrogen | |
| | | Direct methane or methanol | |
| | | Indirect methanol, hydrocarbon, coal | |

^a For long life with inexpensive materials, temperatures are limited to less than 100°C.

^b Also requires CO₂ to complete cathode reaction.

Table 1.1 Possible Applications of Fuel Cells

| Application | Efficiency | | Emissions/noise | | Cost |
|----------------|---------------|-----------|-----------------|---------------|------|
| | Weight/volume | Fuel cost | Environmental | Detectability | |
| Remote | | | | | |
| Space | 2 | 3 | 3 | 3 | 3 |
| Submarine | 1-2 | 2 | 3 | 2 | 2-3 |
| Portable | | | | | |
| Military | 1-2 | 3 | 3 | 2 | 2-3 |
| Recreational | 3 | 2 | 3 | 3 | 1 |
| Utility | | | | | |
| Small (<1 MW) | 3 | 2 | 2 | 3 | 1-2 |
| Large | 3 | 2 | 2 | 3 | 2 |
| Other | | | | | |
| Emergency | 3 | 3 | 2 | 3 | 1 |
| Transportation | 1 | 2 | 2 | 3 | 1 |

^a 1, Very important, difficult to achieve targets.

2, Very important, targets achievable.

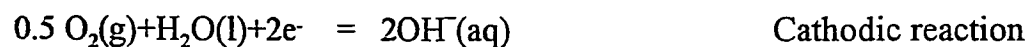
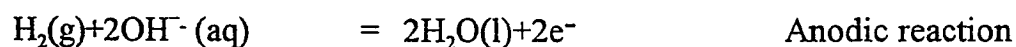
3, Relatively unimportant (compared with other requirements).

1.5 H₂/O₂ Alkaline Electrolyte Fuel Cell(AFC)

Alkaline electrolyte fuel cells can be operated at much lower temperatures(<120° C) using less concentrated alkali (usually 25-30 % KOH). The lower temperature helps in retaining the electrolyte on matrices and also increases the life of other components.(11)

The advantages of AFC are higher performance and reduced cost. The major disadvantage is the degradation of electrolyte caused by CO₂,CO present in air or in fuel gas. The removal of CO₂,CO gas results in decrease in efficiency of an alkaline fuel cell.(12)

In this thesis work the electrolyte used is KOH in the temperature range 25°C to 75° C. In a H₂/O₂ alkaline fuel cell the reactions taking place on the anode and cathode are as follows (9),



1.6 Fuel Cell Electrodes

A good electrode structure must be able to bring gas and electrolyte together so that the reaction can be easy and fast and must be able to keep them apart to prevent undesirable mass transfer e.g. bubbling, floating, weeping. Bringing gas and electrolyte with maximum effectiveness requires an enlarged surface and a porous structure(13). Typical gas diffusion electrodes involve 3 phases namely gas, electrolyte and catalyst. A gas diffusion electrode for a liquid electrolyte contains several layers frequently a backing layer or gas diffusion layer, an electrocatalyst layer and a conducting grid or perforated metal foil for support and current conduction. The gas diffusion layer serves as a barrier between the electrolyte and the gas phase. In the gas-diffusion electrode, reactant gas is supplied to the active sites of the electrode by a diffusion process thereby producing higher current densities(14).

Platinum group metals(usually Pt, Ag, Ni) are important electrocatalysts used for alkaline fuel cell electrodes. In alkaline fuel cells Raney-Ni is commonly used as the catalyst in the anode section while Raney-Ag is used in the cathode section(9).

1.7 Over Potential Concept

The flow of electric current through a fuel cell changes the potential of the electrode from its equilibrium value. This is called polarization. The difference between polarization potential E_p and equilibrium potential E_e both with respect to the same reference electrode is known as the overvoltage of the electrode. The overvoltage is represented by the symbol η at a given current density.

Thus

$$\eta = E_p - E_r \quad (1.1)$$

If the cathode is polarized then it is called cathodic polarization and it is given a negative sign. In the opposite case of anodic polarization, anodic overvoltage is positive.

The overvoltage represents efficiency loss in an electrochemical device.

The polarization losses(fig. 1.2) include the following(11),

1. Activation Polarization This represents energy losses associated with the electrode reactions. For electrochemical reactions the activation energy lost in overcoming the energy barrier takes the form

$$\eta_{act} = a + b \ln i \quad (1.2)$$

Where η_{act} is the activation polarization, a, b are constants and i is the current density.

2. Ohmic polarization It represents the summation of all the ohmic losses within the cell, including electronic impedances through electrodes, contacts, and current collectors and ionic impedances through the electrolyte. These losses follow ohms law ($V = IR$).

3. Concentration polarization It represents the energy losses associated with mass transfer effects. For example the performance of an electrode reaction may

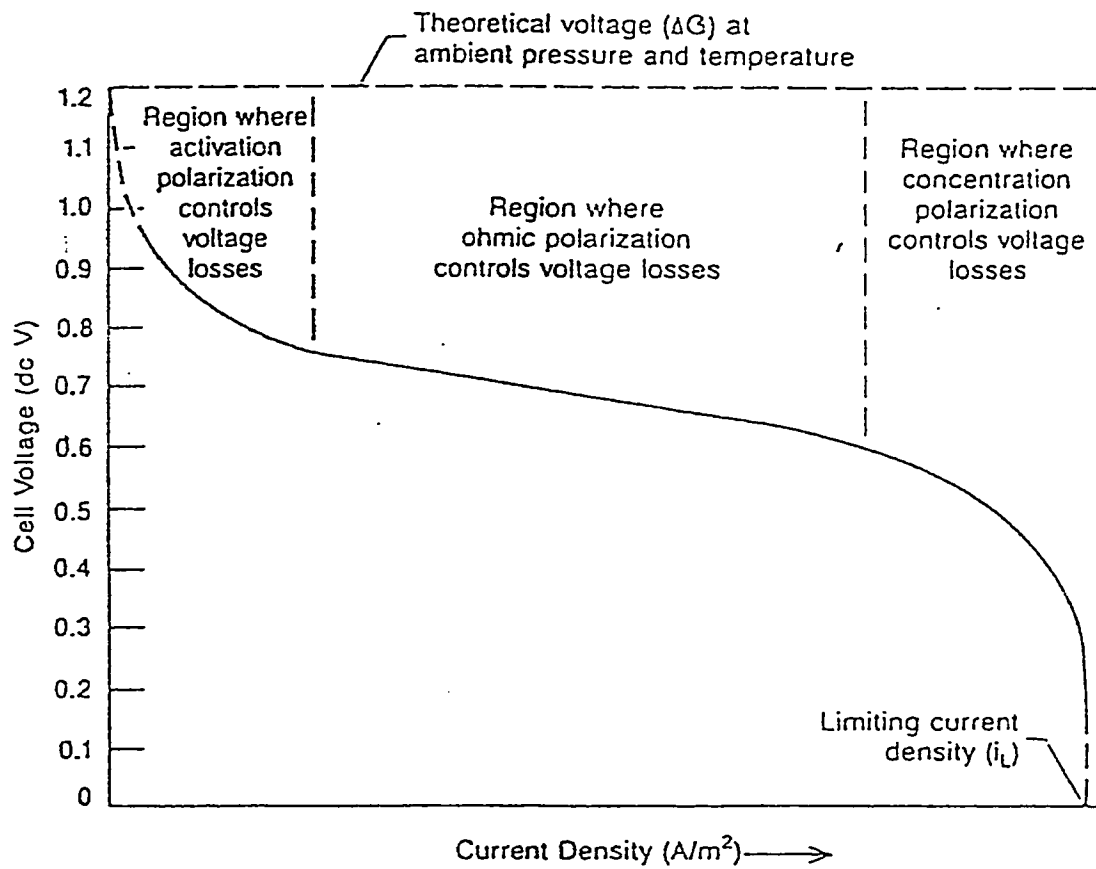


Fig. 1.1 Typical Plot of Cell Potential and Current

be inhibited by the inability of the reactants to diffuse toward, or of products to diffuse away from, the reaction site. In fact at some current, the limiting current density i_L where the current is completely limited by the diffusion process(see fig 1.2).

The performance of a fuel cell is given by the following equation

$$E = E_r - \eta_{c,act} - \eta_{a,act} - \eta_{c,con} - \eta_{a,con} - IR_i \quad (1.4)$$

Where E_r is the reversible potential, η_{act} and η_{conc} terms represent the activation and concentration overpotential at the corresponding electrodes and IR is the ohmic overpotential.

At temperatures below 200°C activation overpotential is the main cause of efficiency losses in fuel cells. The hydrogen overpotential is low compared to oxygen overpotential in acid as well as in alkaline electrolyte fuel cells. Therefore oxygen overpotential is responsible for the departure of the cell potential from the reversible value at desired current densities.

1.8 Objectives

The research objectives of this dissertation are as follows

- 1) Testing the operability of the equipment and electronic instruments involved.
- 2) Reproducing the steady state polarization behavior of Ni/PTFE gas diffusion electrode used by Celikar(15) at 35°C and 55°C.

- 3) Investigating the steady state polarization behavior of a new Ni/PTFE gas diffusion electrode in the temperature range of 25°C -75°C with pure hydrogen gas in a half cell setup.
- 4) Investigating the long term performance of this new Raney Ni/PTFE electrode.
- 5) Characterization of the fresh and used electrodes by SEM, ICP-AES, BET surface area measurement.
- 6) Determination of exchange current density, charge transfer coefficient by the application of mathematical model developed earlier by Celikar et al.(15).
- 7) Determination of the apparent activation energies for the electrochemical reaction taking place on the electrode.
- 8) Determination of the apparent and intrinsic deactivation constants at various temperatures.

Chapter 2

LITERATURE REVIEW ON H₂ ELECTRODE

The maximum power density obtained from alkaline fuel cells has undergone many advances in recent years due to improved catalyst and electrode materials, and also due to operating conditions and fuel cell design. Theoretical understanding of the electrochemical reactions taking place at the catalyst surface and the influence of electrode structure has improved in recent years(16). Despite all these advances the production of fuel cell electrode is more of an art than a scientifically well founded process.

Kordesh(17) has given a comprehensive review of fuel cell developments during the period 1951-1976. Bacon(18) first produced a biporous electrode with a stable meniscus to be used as an anode in a H₂/O₂ fuel cell. In Bacon's biporous electrode the coarse pore layer is for the gas side and the fine pore layer is for the electrolyte side.

Double skeleton(DSK) electrodes are developed by pressing and sintering carbonyl nickel powder with Raney nickel powder. DSK electrodes were first produced in former West Germany. DSK electrodes have high catalytic activity of Raney powder and the mechanical rigidity and electrical conductivity of bulk metals. DSK Bacon electrodes were made entirely of the electrocatalyst.

Most of the porous electrodes employed in fuel cell research are produced by deposition of the catalyst on a substrate. A typical porous fuel cell

electrode consists of a metal screen, electrocatalyst, catalyst support and the binder(19). In alkaline fuel cells for anode mostly Ni, Cu screens are used while PTFE is used as a binder.

In H_2/O_2 alkaline fuel cell Raney-Ni alloy is used for hydrogen electrode and Raney-Ag alloy for oxygen electrode. Aluminum present in the alloy is leached out by using caustic solutions. So far in the open literature only one paper describes the method of fuel cell electrode preparation.(20).

Mund et al.(21) used 5 % titanium containing Raney-nickel catalyst which showed superior performance from Electrochemical activity and stability point of view. The catalyst layer in the electrode was supported by asbestos covering layer on the electrolyte side and by a metal screen on the gas side. They have measured the polarization resistance as a function of catalyst loading and studied the influence of electrolyte temperature on polarization behavior. Impedance measurements have also been used to characterize the electrodes.

Ewe et. al.(22) studied the preservation of Raney-nickel and of various blended Raney-nickel catalyst by slow oxidation of samples in atmospheric oxygen followed by controlled heat treatment and reduction. They have found that undoped 1% Ti alloyed Raney nickel gave the best current voltage performance. Catalyst doped with Fe or Mo have been observed to deteriorate under preservation. The method of preservation is useful when it causes a strong increase of exchange current density with insignificant decrease of surface diffusion.

Tomido and Nakabayash(23) prepared hydrogen electrodes of fuel cell by an innovative method. They sprayed molten aluminum by an acetylene-oxygen

flame gun on both sides of a spongy plate of nickel as substrate. The spongy nickel electrodes were activated by alloying at 50°C to 75°C and leaching the aluminum from the alloy in alkaline solution. With the experimental results they concluded that spongy Raney nickel electrode have very low polarization resistance.

The influence of contact pressure on the performance of supported gas diffusion electrodes in alkaline H_2/O_2 fuel cells has been studied by Ewe et.al(24). A half cell assembly with variable contact pressure facility is constructed and used to measure the polarization of Raney-Ni and Raney-Ag electrodes as a function of contact pressure in KOH electrolyte. They have found that the current densities at constant polarization are increased significantly by the optimization of the contact pressure.

Ewe et. all (25) found that the catalytic properties of Ti doped by Raney Ni (for hydrogen anodes of alkaline fuel cells) could be improved by $Ni(OH)_2$ surface coating which is obtained by carefully optimized oxidation. It is observed that $Ni(OH)_2$ content of 5-6 % increased the attainable current density by a factor of 3 to 4. Also it is observed that the exchange current densities increased significantly up to a $Ni(OH)_2$ content of 5 % but remained constant with further increasing the $Ni(OH)_2$ percentage. As a continuation of this study it has also been shown that oxide surface coating may be stabilized by an annealing of the slowly air oxidized and $Ni(OH)_2$ coated catalyst in hydrogen at 35°C, followed by an air oxidation again(26). It is observed that the formed mixture of NiO and $Ni(OH)_2$ coated improved the catalytic properties and structure. The optimum annealing parameters were determined. The experiments were carried out using a Ti-containing Raney-Ni as catalyst with 6M KOH electrolyte operating at 80°C.

In a following study, Ewe et.al.(27) studied the aging rate of annealed catalyst which was found to be very small at polarization below a critical value of 50mV. Aging rates increased exponentially when polarization was above 50mV. The best catalyst with the lowest aging rate under $\mu\text{V/hr}$ was prepared by using a Raney-Ni(containing 2 % Ti)catalyst with 4-6% initial Ni(OH)_2 content, which was heat treated in hydrogen atmosphere at 35 $^\circ\text{C}$ for 5 minutes. Brennecke et.al (28) studied the kinetics of the electrodes used by Ewe (24,25)by means of impedance measurements. A sine wave generator and a potentiometer regulator was used in the measurements.

Kenjo(29)used a PTFE bonded Raney Ni hydrogen electrode prepared by milling a PTFE dispersion with caustic -leached Raney metal with subsequent calendar rolling of the electrode paste into sheets. The electrode polarization were measured in 6M KOH electrolyte at 62 $^\circ\text{C}$. The influence of the pressure of the press machine and of the PTFE content on the polarization have been investigated. The polarization resistance as a function of catalyst loading is also determined. It was observed that the polarization resistance decreases with the catalyst loading in the manner to be expected from the reaction mechanism of the gas diffusion through electrolyte film.

Kenjo and Nakajima(30)measured the polarization characteristics of PTFE bonded Raney-Ni hydrogen electrode as a function of the catalyst layer. The polarization curve of the electrode was analyzed based on the electrolyte film. With the thickening of the catalyst layer the performance of the electrodes approached asymptotically to an upper limit. The catalytic activities of Raney-Ni catalysts are enhanced with progression of the polarization while the resistivity of

the electrolyte film remains essentially constant. A slight surface oxidation for the Raney-Ni is understood to be responsible for the enhanced catalytic activities.

Canday and Foilloux (31) used a passivated Raney powder which is mixed with a slurry of PTFE(85.5 % and 12.5% respectively)and sprayed into nickel-grid support. The wafer obtained is heated to sinter the fluorinated plastic which acts as a binder. They also prepared another electrode where the water repelling effect was obtained by charcoal particles with fluorinated oil. The binding material in this case was polyvinylidene fluoride. The electrode was characterized in 5M KOH by using an impedance technique.

Markina et. all (32) prepared a NiCO_2O_4 electrode(nickel -cobalt spinels) by thermal decomposition of a mixture of nickel hydroxide and cobalt hydroxide. Moren (33) developed a cell for determining structure parameters such as interstice tortuosity, film tortuosity, effective specific film resistance, effective pore length ,mean film thickness, and film area on operating porous gas diffusion electrodes. Ni electrodes and 5M KOH solution were used in the experiments.

Padyukova(34) studied the state of hydrogen in a Raney-Ni catalyst prepared from Ni-Al alloys(40 -60 mass % Ni) having different degrees of dispersion by using thermal desorption and potentiodynamic measurements. It was found that the composition of the Ni-Al alloys and their particle size have important influence on the adsorption behavior of the Raney-Ni.

Kenjo(35) found that the tenth percent of chromium markedly enhances and stabilizes the activity of Raney-Ni. Hydrogen electrodes catalyzed with chromium dope are prepared and their polarization characteristics are measured. It

was found that the chromium doped Raney Ni was more active than the Titanium-doped catalyst and it provided a high activity over a wide range of the dopant content.

Mund et. al(36)prepared Raney-Ni electrodes which contained 2% Ti. The Raney catalyst powder obtained from Raney alloy had a BET area of 80 m^2/g . A mean pore radius of 2×10^{-7} cm is found in the catalyst particles. They have found that the steady state current voltage characteristics of supported Raney-Ni hydrogen anodes are linear up to a polarization of 0.1V in 6M KOH as electrolyte. The influence of the electrolyte temperature on the current -voltage relation is also studied with a catalyst loading of 0.1 g/cm^2 . The influence of the electrolyte concentration on polarization is drastic and observed to lead in diluted alkali to limiting current behaviour. Impedance characteristics were also studied.

Pattabiraman et.all(37)studied the preparation and polarization characteristics of hydrogen and oxygen gas diffusion electrodes for use in low temperature alkaline fuel cells. The electrodes they fabricated had a geometric surface area of 30 cm^2 and employed skeletal Ni obtained from Ni-Al alloy containing Ti promoter as electrocatalyst for hydrogen electrode. The hydrogen electrode was found to show a high polarization beyond 30 mA/cm^2 .

Grune(38)studied the dynamic behavior of porous gas diffusion electrodes in fuel cells. In this study all measurements were carried out in a half cell with electrodes having 1 cm^2 external surface area ,using 6M KOH as electrolyte at 80°C.

Abramzon et. al(39) developed a technique to determine the specific activity of disperse Ni catalysts. The specific activity of the type of Nickel catalyst examined is practically independent of the way of preparation.

Jenset et. al(20) have given the production steps of Raney-Ni based PTFE bonded hydrogen anodes for lightweight alkaline fuel cells. The Raney-Ni catalyst has been made by leaching the Ni-Al alloy and additional stabilisation. The electrode is fabricated by mixing the catalyst with copper oxide for enhancing the electronic conductivity and aqueous PTFE emulsion as hydrophobic binder. Based on the experimental findings they concluded that a load of approximately 8-9% PTFE and 15 weight % copper gives optimal performance. They showed that at an overpotential of 100mV the optimized hydrogen anode exhibits at negligible excess hydrogen pressure(1.02 bar) a current density of nearly 400 mA/cm² at 80°C in 30 weight % KOH. They also showed the long term performance of the electrode.

Chapter 3

ELECTRODE KINETICS AND ELECTROCATALYSIS

3.1 Introduction

The real efficiency of an electrochemical energy producing device such as an AFC depends upon the power per unit weight. The power per unit weight also depends on the rate of electrochemical reaction taking place at the electrode. Thus electrode kinetics determines the real efficiency of an AFC.

Electrocatalysis is the enhancement of a particular electrode reaction by the appropriate choice of electrode material. The Electrocatalytic reaction depends upon the nature of the electrode, presence of an electric field across the electrode-electrolyte interface and nature of the electrolyte. Electrocatalyst is a material which makes electrode reaction cost effective.

3.2 Current-Potential relation at a single Electrode

The reaction rate in electrode kinetics is measured by the current density at the electrode. Thus the current across 1 cm² of electrode surface gives the reaction rate. By Faraday's law the reaction rate is(40)

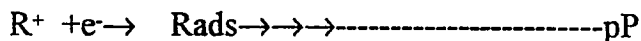
$$r = \text{reaction rate in mole sec}^{-1} = -\frac{dz}{dt} = \frac{I}{nF}$$

and per 1 cm² of the electrode of area A, the reaction rate is

$$r = \frac{I}{AnF} = \frac{i}{nF} \quad (3.1)$$

Thus the current density is a direct measure of the reaction rate.

Consider the following electrochemical reaction



Let the first reaction which is charge transfer step be rate determining. In this case the relation of the electrode potential to the current is given by(41)

$$i = i_0 \left[\exp\left\{\frac{\alpha F \eta}{RT}\right\} - \exp\left\{-\frac{(1-\alpha) F \eta}{RT}\right\} \right] \quad (3.2)$$

Equation 3.2 is called the Butler-Volmer relation. It is a standard model that describes the current - overpotential relationship for an electrode at a given temperature, pressure and concentration of reacting species.

If the overpotential is large and positive, then the first exponential term in equation 3.2 is much larger than the second term. In this case of large anodic polarization the equation 3.2 simplifies to

$$i = i_0 \exp\left(\frac{\alpha \eta}{RT}\right) \quad (3.3)$$

where i_0 is the exchange current density, α is transfer coefficient and η is overpotential.

It is remarkable to note that for a change in overpotential by 0.5 V, the reaction rate changes by 4 to 8 orders of magnitude. Electrocatalysis is the science of minimizing the overpotential terms given by equation 3.3.

Equation 3.3 can also be written as

$$\eta = a + b \ln i \quad (3.4)$$

expression 3.4 is called the Tafel equation. The Tafel parameters are characteristics of the electrode and are obtained experimentally from a plot of η Vs $\log i$.

In the case of small overpotential ($|\eta| < RT/F$) the Butler-Volmer equation can be linearised as

$$i = \frac{2i_0 \alpha F \eta}{RT} \quad (3.5)$$

3.3 Electrocatalysts

Electrocatalysts are selected or designed for each electrode reaction from a knowledge of the chemical and structural properties of potential catalyst materials. If the mechanism of the same overall reaction is different on various substrates. Then depending on the value of overpotential, one or other is a better substrate from the practical point of view. Owing to a different mechanism of the reaction resulting in transfer coefficient α being different. (42)

Factors which determine Electrocatalytic activity are as follows (43)

1) Chemical composition of the Catalyst

Electrocatalysts are always based on transition metal atoms or ions. Therefore the design of an electrocatalyst requires the placing of the transition metal in a matrix which optimizes unpaired electron density and the spacing of transition metal centers. For transition metal species unpaired d-electrons and unfilled d-orbitals are available for forming bonds with adsorbates. The catalyst is most effective when the bond is of intermediate strength. Geometric arrangement of the catalyst centers is also important. The geometric and electronic factors are dependent on each other. Together they decide the relationship between the catalytic activity and chemical composition.

2) Real surface area

The current density for an electrode can be increased by deliberately creating a rough surface. By making electrode surface rough the area available for electrochemical reaction is greatly increased as compared to planar surface.

3) The catalyst support

Commonly electrocatalysts are expensive and are therefore prepared either in the form of small particles dispersed on a cheaper substrate or as a thin layer.

4) Catalyst structure on an atomic scale

Size and shape of small centers the presence of grain boundaries, lattice defects and special sites e.g. kinks, edges or screw dislocation also determine Electrochemical activity.

A good electrocatalyst should have

- a) High exchange current density and /or
- b) A low Tafel slope.
- c) A tendency to inhibit side reactions.
- d) Stability

3.4 Design of Electrodes

Any practical electrode should have high activity for the desired reaction which is stable over a long period of time. This generally means the ability to deliver a current-density of 0.1-1 A cm² at an acceptable overpotential of less than 100mV and this performance must be maintained for the service interval of the cell. The requirements for light weight AFC are as follows,

1. Operating Temperature should be less than 100°C
2. Operating pressure should be less than 4 atm.
3. Insensitivity to impurities in feed gas.
4. O.C.V. should be at least 90 % of reversible E.M.F.
5. High Exchange current density, limiting current density
6. Low overvoltage
7. High gas consumption efficiency i.e. maximum conversion of feed gas
8. High performance at operating load
9. Inexpensive
10. Sufficient life time

Factors which lead to the loss of electrode activity are

- 1) Mechanical erosion or damage during servicing or handling.
- 2) Corrosion in the electrolysis medium either when the cell is on load or standing on open circuit.
- 3) Poisoning by side reactions or adsorption of an impurity from the electrolyte medium.
- 4) Re crystallization leads to loss in surface area.

The electrode material must show the desired selectivity. In practice the selectivity is based on kinetics rather than thermodynamics.

The electrodes used in AFC are porous in structure. The porous electrode is made by compressing onto a conducting grid a mixture of the catalyst, a conducting powder and a hydrophobic material e.g. PTFE. The gas is then passed over the back of the electrode so that a three phase interface between gas, electrolyte and catalyst is formed within the pores.

Gas consuming porous AFC electrodes have a triple layered structure. The active electrode surface constitutes the primary(chemical) structure of the active electrode surface. The secondary structure consisting of the inner surface of the catalyst or its support is determined by the fine porosity($d_p = 1-10 \text{ nm}$). The third structure is the intermeshed dual system of coarser pores ($d_p > 5\mu\text{m}$) between the catalyst particles one part of which is hydrophobic and conducts the gases into fuel cell electrode supplying the electrode wetted catalyst -particles with gas, whereas the second, hydrophilic pore system containing the electrolyte enables the passage of ionic currents towards the counter electrode.(16)

3.5 Electrode study Techniques

Steady state and unsteady state techniques are used for the study of fuel cell electrodes(44). Table 3.1 gives the various techniques that are commonly employed in fuel cell electrode research. Any change in one of the variables e.g. pressure, temperature, concentration etc. in an electrochemical reaction will cause a time dependent change on other variable. All these variables reach a steady state after a certain period of time. Steady state electrochemical techniques are used to

TECHNIQUES FOR FUEL CELL ELECTRODE RESEARCH

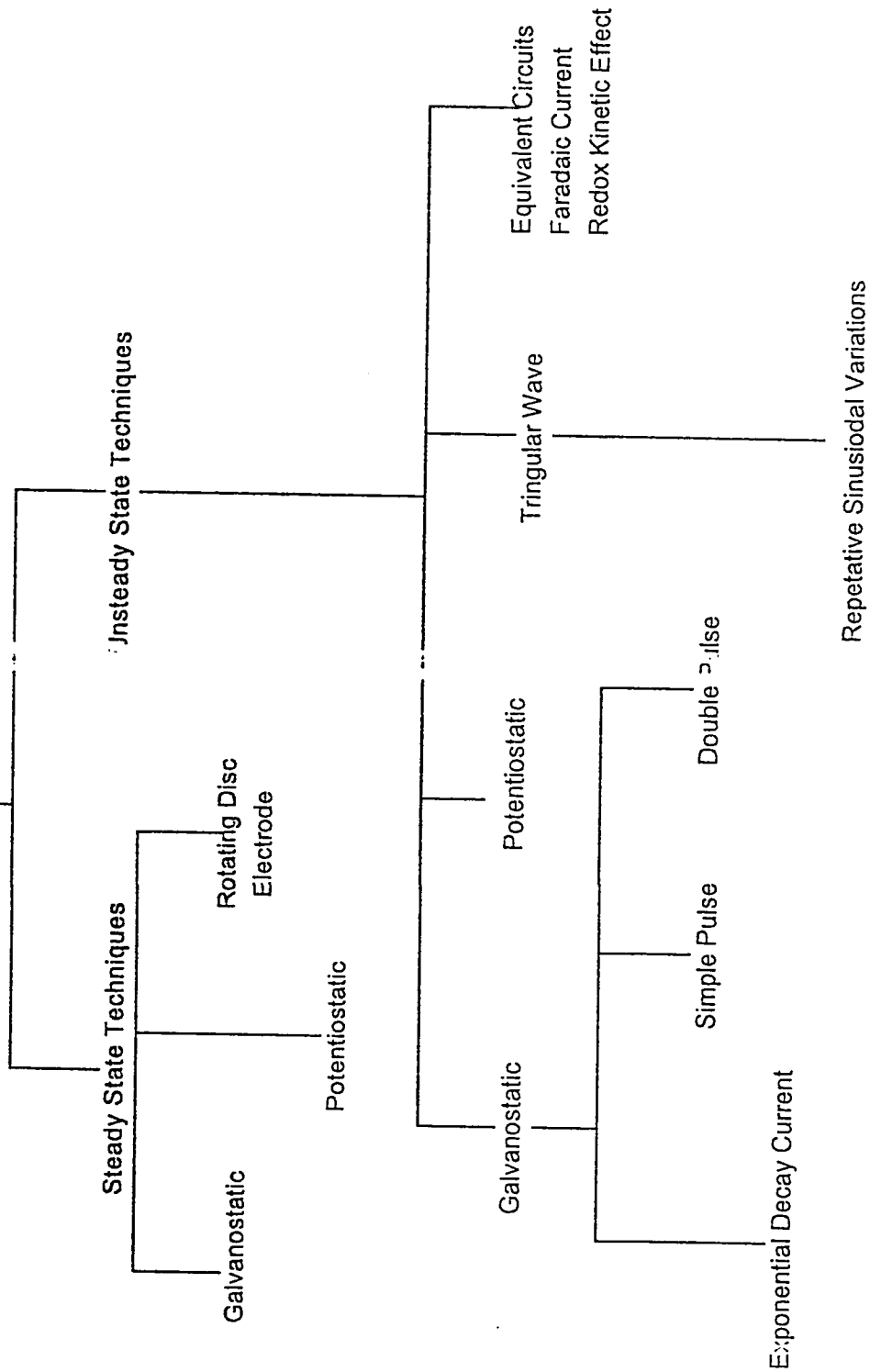


TABLE 3.1 : TECHNIQUES FOR FUEL CELL ELECTRODE RESEARCH
 Single Complete Cathodic - Anodic Sweeps

study the functional relationship between variables. Polarization curves (current density Vs potential curves) provide useful information on suitable working potentials, possible current densities and current efficiencies. Steady state polarization curves are utilized to get kinetic information on the overall reaction, reaction orders and to determine charge transfer coefficients, exchange current densities and limiting current densities.

In steady state technique there are again two methods namely galvanostatic and potentiostatic. In galvanostatic method the electrochemical reaction is forced to proceed at a chosen rate by keeping the current flow constant. In this method the current required is changed in steps through a galvanostat and the corresponding potential at the working electrode is measured against a reference electrode under steady state conditions.

In potentiostatic method a potentiostat is used to keep the potential between the working and reference electrode constant at a chosen value by allowing a passage of current through the working and counter electrode. The required voltage values are then changed in steps and each time corresponding current is allowed to come to steady state.

In a non deactivating system, under steady state conditions the galvanostatic and potentiostatic polarization techniques give same results. In this work galvanostatic method is used to investigate the performance of specially prepared Raney-Ni hydrogen electrode for AFC.

Unsteady state techniques are used to get double layer capacity, adsorption coverage, diffusion coefficients etc.

3.6 Importance of Half Cell Studies

Half cell measurements give information about the magnitude of activation, concentration and ohmic polarization occurring in each electrode. The ohmic polarization is measured separately by IR drop measurement techniques. The activation and ohmic polarization are isolated by analyzing the polarization curves. Using a half cell, the reaction at each electrode is studied separately. In this case current is supplied from an external source to the working electrode. The overall reaction taking place in a half cell is different from that occurring in complete cell. A schematic diagram of the half cell used in this study is given in Fig. 3.1.

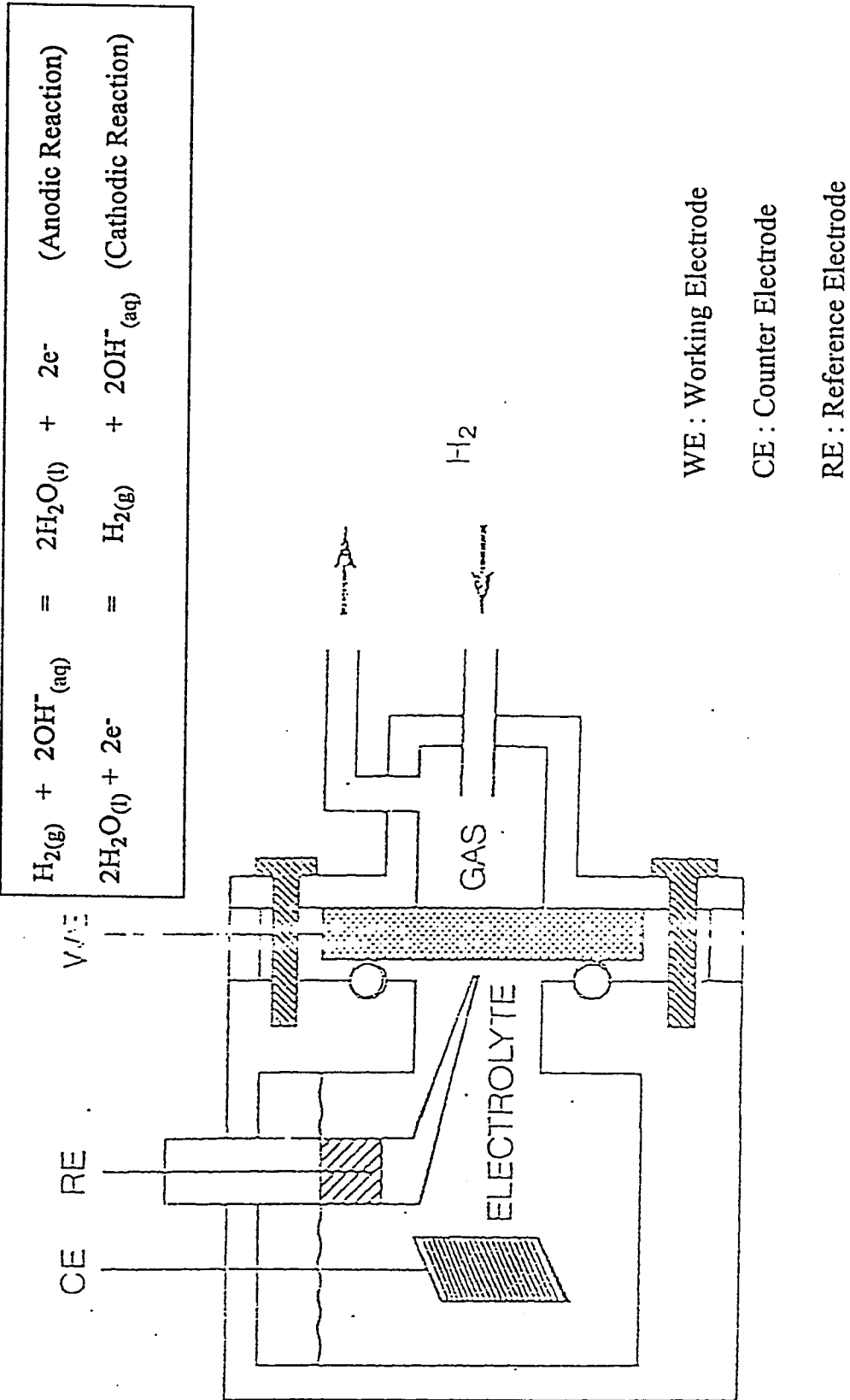


Fig. 3.1 Schematic Representation of a Hydrogen Half Cell

Chapter 4
***REVIEW OF MATHEMATICAL MODELS FOR POROUS FUEL
CELL ELECTRODES***

In order to increase the power density in alkaline fuel cell the activation, concentration and ohmic polarization should be made as small as possible. In order to determine the polarization behavior of electrodes numerous and expensive tests need to be performed. Moreover, the interaction among the three types of polarization causes difficulties in isolating the characteristics of a particular type of polarization. Mathematical models of AFC electrodes can help in determining how changes in parameters and operating conditions affect the various types of polarization, which subsequently influence the performance of a fuel cell.

The AFC electrode models can help in identifying the parameters and concepts that limit the performance of the fuel cell based on today's state-of-the-art technology. The mathematical model can also be used to investigate the effect of hypothetical advances in technology on the predicted performance.

The exact theoretical analysis of porous electrode is difficult to carry out because of the following reasons,

- (1) Precise knowledge of the structural details of electrode is unavailable.
- (2) Non-linear multidimensional and coupled equations describing the mass transport and partial distributions.
- (3) Difficulties encountered in defining the three phase boundaries.

Because of these problems idealizations of various types have been used in the modeling. Thus in the literature there are many models due to diversified design of porous gas diffusion electrodes, controlling factors and operating regimes(42). The models which are mostly used for the description of current-potential relation are the following:

1. Simple Pore Model
2. Thin Film and Meniscus Models
3. Hydrophobic Electrode Models
4. Hydrophilic Electrode Models
5. Cylindrical Gas Pore Model
6. Flooded Agglomerate Model

In the simple pore model developed by Austin et.all (45) it is assumed that the reactant gas diffuses into the pores, dissolves in the electrolyte and further diffuses in solution to reach the catalytic sites where the three-phase boundary of solid -liquid-gas comes into contact.

Experiments with partially submerged electrodes show that the electrode reaction occurs mainly in a region where the electrolyte forms a thin meniscus and a film at the electrode-gas interface. This film helps in molecular diffusion of the gaseous reactant through the thin film of the electrolyte. This is the basis of Thin film and Meniscus model.(46)

Hydrophobic electrode models can be classified into three basic types(47). In the first type hydrophobic gas pores are formed by agglomerates of PTFE in a hydrophilic medium consisting of catalyst particles separated by the

electrolyte. In the second type hydrophobic pores are formed by agglomerates of catalyst located in a hydrophobic medium consisting of PTFE particles with the space occupied by the gas. In the third type the contact angle at the boundary of the liquid is determined by PTFE concentration at the surface of gas pores. The activity of hydrophobic electrode is determined not only by the pressure difference but by the hydrophobizer concentration. The polarization distribution in the electrode is determined by solving differential equations which involve a probability factor of the position of PTFE grains in crystal lattices.

Hydrophilic electrode models include dual porosity models and the models of intersecting capillaries. The dual porosity model treats a porous electrode as containing both wide and narrow pores. The wide pores are filled with gas but their walls are covered with a solution film, and the narrow ones are flooded. Models of intersecting capillaries assumes that the current generation is localized in the neighborhood of intersection of pores.(48)

The pressure differential between the gas and electrolyte solution determines the distribution of gas and liquid and the electrochemical activity of hydrophobic electrodes. The performance characteristics of hydrophobized electrodes depend upon the degree of hydrophobization. The Cylindrical gas pore model was proposed to explain the fact that as Teflon concentration is increased the electrochemical activity goes through a maximum.

In the cylindrical gas pore model suggested by Burshtein et.all (49) and Chirkov(50) gas filled pores are assumed to be circular cylinders of constant radius. These cylinders are assumed to be arranged in a regular manner with walls composed of a mixture of PTFE and catalyst moistened with the electrolyte.

Lampinen, M. J. and Viitanen, M. (51) have proposed a mathematical model in which the agglomerates of catalytic particles are described as cylinders whose axes are perpendicular to the surface of the electrode. The model takes into account the diffusion of gas, the electrochemical reaction taking place, ionic ohmic drop in the cylinder and also electronic ohmic drop due to the finite conductivity of solid materials. The structure of fuel cell electrode can be optimized by this model.

In the agglomerate model the catalyst particles and liquid filled pores coexist in a homogeneous continuum surrounded by the gaseous species. Giner's(52) model accounts for the diffusion of a dissolved gaseous species with electrochemical reaction in a cylindrical agglomerate and considers the variation in the solution phase potential. The model doesn't take into consideration the gas phase and solid phase resistances. The Giner's model predicts the performance of the electrode as a function of agglomerate radius and catalyst utilization for low current density. Cutlip's analytical model (53) considers mass-transport process occurring in gas diffusion electrodes. In this model catalyst effectiveness factors are used to modify the electrocatalyst based on different shape factors. Cutlip's model predicts that the coupling of the gas-phase diffusional resistance and electrode thickness strongly influence the limiting current density.

Iczkowski and Cutlip (54) proposed a fairly complete model of a three-phase electrode. This model accounts for the gaseous diffusion resistance, solution phase diffusional resistances, and solid and liquid potential variations. Based on this model they suggested that the gas diffusion resistance is about 38% and ohmic loss in the electrolyte contributes 48% of the total voltage drop in fuel cell cathode.

Celikar et. all (55) have proposed flooded Raney catalyst grain model to describe the working mechanism of PTFE - bonded Raney catalyst gas diffusion electrodes. In this model Raney metal catalyst grains in the electrode are considered to be spherical in shape and flooded with electrolyte during operation and are surrounded by hydrophobic gas pores. Analytical equations are derived to evaluate the performance of a single catalyst grain in the presence of diffusion limitations. The current generation expression for each grain is then combined with the potential distribution differential equation to predict the complete electrode performance. The radial degree of utilization of the spherical grains for current generation and also the degree of utilization of the whole electrode in the axial direction can be investigated by the model equations. This model predicts the polarization behavior in terms of experimentally measurable properties e.g. porosity's, current density, potential catalyst loading, electrode thickness.

Kimble and White(56) have for the first time proposed a complete mathematical model of an alkaline fuel cell that contains both the electrodes and the separator. This model assumes a macro homogeneous, three phase electrode structure to describe the processes occurring in the solid, liquid, and gaseous phases of the anode, separator and cathode regions. This model accounts for the one-dimensional transport of reactant gases, water vapor, solution phase concentrations, solid and solution potential variations, and the volume - average velocity. Limitations to attain high power densities are given and methods to increase the maximum attainable power density are suggested based on the model.

In a following paper Kimble and White (57) have carried out parameter sensitivity and optimal design analysis for a hydrogen/oxygen alkaline fuel cell. The optimal electrode thicknesses for the anode and cathode reaction layers and

the gas and liquid phase porosity in the cathode reaction layer are determined by maximizing the power density. Based on the model prediction the authors suggest a significant improvement in the fuel cell performance can be achieved by increasing the gas - liquid interfacial area followed by increasing the Electrochemical activity and decreasing the separator thickness.

Yang and Bjornbom (58) have developed a mathematical model for alkaline fuel cell cathode by using concentrated solution transport theory. The model assumes an electrode with two layers: gas supply layer and reaction - active catalyst layer. Application of this model is useful in understanding humidity content management during electrode operation.

Chapter 5

ELECTRODE MANUFACTURE AND CHARACTERISTICS

5.1 Manufacture of Hydrogen Anodes

At present production of fuel cell electrode requires experience and a very good knowledge of material properties. As the volume of research in this area is increasing electrode manufacture will become a scientifically well founded process.

For the production of hydrogen anodes from Raney-nickel for lightweight alkaline fuel cell pulverized aluminum-nickel alloys are taken. These alloys are then leached with KOH solution to remove aluminum. This leaching process results in a highly porous structure. Large amounts of adsorbed hydrogen is found in freshly leached Raney nickel. This adsorbed hydrogen is then removed by slow and controlled oxidation before further processing the material.

Polytetrafluorethylene(PTFE) in powder or aqueous emulsion form is used as a binder in AFC electrode manufacture. This PTFE binder provides cohesion between the catalyst particles and firm mechanical contact of the catalyst with the supporting metal screen. The hydrophobic material for the gas conducting pore system is also provided by PTFE.

The depyrophorised and thermally stabilized catalyst and PTFE powder is then intensively blade-milled. This through mixing produces a fluffy mass by which the catalyst and PTFE particles become indistinguishable from each other. This mixture of catalyst and PTFE is then mixed with Cu_2O . The fluffy mass is

then cold rolled into a felt. This cold rolling process results in cross linking of the catalyst particles by PTFE-fibers which is brought about by stress and friction from the initially globular PTFE- particles. This cold rolling of the mixture is the most important step in the production of AFC electrodes. This is where the art factor in the manufacture of fuel cell electrode comes into picture. A very good knowledge of material properties and experience is required for cold rolling step.(59)

When PTFE in powder form is used then the process of electrode manufacture is called dry method. While the manufacturing process with PTFE emulsion is called wet method.(9)

High rolling pressure and strain are required for dry method than wet method. High rolling pressures and stress are supposed to induce a layered structure of the electrode and in particular alignment of the PTFE fibers parallel to the electrode surface. The felt is then rolled onto a metallic screen (fig. 5.1). The metallic screen can be of nickel or copper. The metallic screen acts as a support and current collector. Since at the potential of the hydrogen anode Ni or Cu is immune to corrosion. The thickness of the PTFE bonded Raney-nickel felt for the hydrogen anode should not exceed 0.5 mm for optimum performance. The mesh width of the net and diameters of the metallic wire are of the same or comparable size. The freshly prepared electrodes require cathodic conditioning before using them in AFC. The cathodic conditioning reduces the added Cu_2O with the formation of a highly metallic, highly conductive, copper deposits within the fuel cell electrode. In this way a homogeneous deposition of copper in the electrode matrix is achieved. This cathodic treatment also leads additionally to partial reduction of nickel oxide.(60)

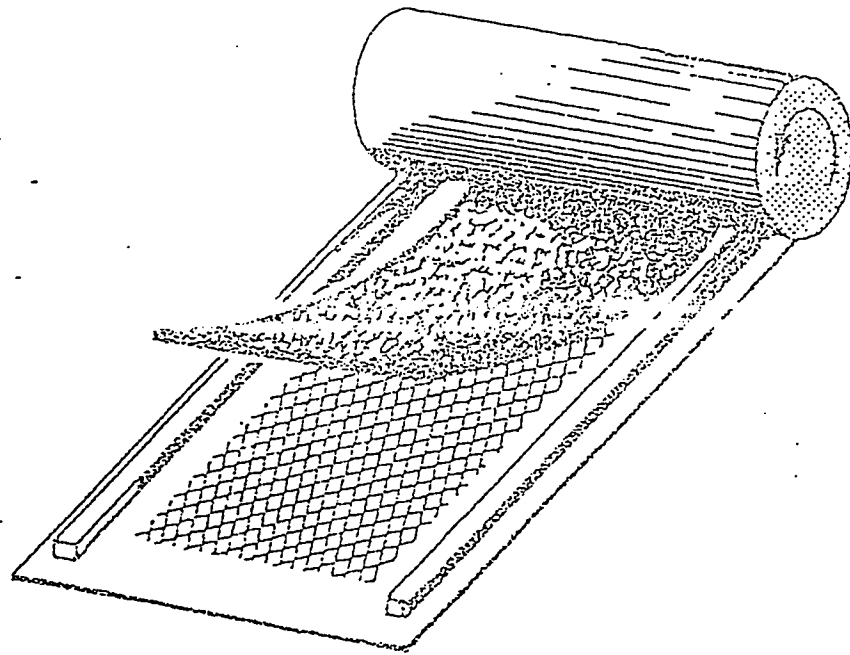


Fig. 5.1 Schematic Representation of Felt Rolling into Metal Net

The novel Raney-Ni/PTFE gas diffusion electrodes used in this study were characterized by a number of techniques which were:

1. BET surface area by nitrogen adsorption
2. Mercury Intrusion Porosimetry
3. Scanning Electron Microscopy
4. Inductively Coupled Plasma(ICP)- Atomic Energy Spectrometry

These characterization results were later used to estimate the physical parameters required for flooded spherical Raney-Ni catalyst grain model developed earlier by Celikar et. all (15). The characterization of the electrode was carried out in the Research Institute of the King Fahd University of Petroleum and Minerals.

5.2 Surface Area

The basic theory behind measuring total surface area of porous structure is by adsorption of a particular molecular species from a gas or liquid onto the surface. If conditions are so adjusted that a complete adsorbed layer, averaging one molecule thick, can be established and the area covered per molecule is known. Then the quantity of adsorbed material gives directly the total surface area of the sample.

In BET surface area by nitrogen adsorption method, the amount of nitrogen adsorbed at equilibrium at the normal boiling point(-195.8°C) is measured over a range of nitrogen pressures below 1atm.

Extension of Langmuir adsorption isotherm to multilayer adsorption gives the following expression for the volume of nitrogen adsorbed at pressure P.

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_m C P_0}$$

Here P_0 is saturation pressure of adsorbate gas at the experimental temperature and C is a constant which is related exponentially to the heat of adsorption and liquefaction of the gas. More accurate determination of the surface area requires higher C values.

A plot of $P/V(P_0 - P)$ against P/P_0 gives a straight line. The reciprocal of the sum of slope S and intercept I of this line gives volume, V_m of gas adsorbed in monolayer. By knowing the average area occupied by an adsorbed molecule the surface area to the catalyst is then calculated. For nitrogen at -195.8°C the surface area per gram is $4.35 \times 10^4 V_m$.

The equipment used for the determination of BET surface area of the new electrode was SORPTOMATIC. In this instrument the volume of the gas adsorbed was obtained by measuring the decrease in pressure resulting from the adsorption of a portion of a known gas volume. Predetermined constant volumes of nitrogen were introduced in an evacuated empty burette and kept at liquid nitrogen temperature. After introducing the sample in test chamber a part of nitrogen introduced was adsorbed and the pressure of the gas in equilibrium with the portion adsorbed were recorded. Comparison of the values of pressures with empty

Table 5.1 B.E.T. Surface Area for the Fresh Electrode

| SORPTOMATIC | B.E.T. |
|---------------------------|---------------|
| DATE | 3/2/93 |
| OPERATOR | |
| SAMPLE | A-CHE (FRESH) |
| MONOLAYER THICKN. (A) | 4.3 |
| SATUR./LIM. PRESS. (TORR) | 760 |
| ADS.MOL.MASS (G/MOL) | 28 |
| ADS.LIQ.DENS. (G/CM3) | .808 |
| BUR.TEMPERATURE (C) | -195.82 |
| OPERAT.PRESS. (TORR) | 800 |
| TOTAL INTRODUCTION | 8 |
| RED. INTRODUCTION | 8 |
| REDUCTION FACTOR | .5 |
| BUR.CONST.(CM3/TORR) | .1 |
| SAMPLE MASS (G) | .1047 |
| SAMP.DENS. (G/CM3) | 2 |

CORRECTED BUR. COSTANT (CM3/TORR) = .0993392

ADSORPTION VALUES

| P ADS (TORR) | P/PO ADS | VI (CM3) | V ADS (CM3/G) | T (A) | P/(PO-P) |
|--------------|----------|----------|---------------|-------|----------|
| 67.5 | 0.089 | 7.88 | 4.130 | 5.5 | .023601 |
| 143.4 | 0.189 | 15.76 | 5.329 | 6.2 | .043641 |
| 218.2 | 0.287 | 23.64 | 6.912 | 6.8 | .058267 |
| 293.6 | 0.385 | 31.52 | 8.285 | 7.5 | .075979 |
| 368.4 | 0.485 | 39.41 | 9.662 | 8.2 | |
| 444.9 | 0.585 | 47.29 | 10.858 | 9.1 | |
| 517.3 | 0.681 | 55.17 | 13.278 | 10.1 | |
| 594.2 | 0.782 | 63.05 | 14.128 | 11.7 | |
| 59.0 | | | | | |

VOLUME (MONOLAYER)..... 5.47891 (CM3/G)

SPEC.SURF.AREA..... 23.9409 (M2/G)

BET C VALUE..... 19.9255

TOT. VOL. INTRODUCED.... 63.05 (CM3)

burette gives the gas volume adsorbed at the various equilibrium pressure and hence the isotherm could be calculated.

The results of BET surface area determination of the new electrode by nitrogen adsorption are given in table 5.1.

5.3 Mercury Intrusion Porosimetry

Mercury does not wet most surfaces and therefore doesn't penetrate most pores at atmospheric pressures. Mercury intrusion porosimetry is based on this nonwetting behavior of Hg in capillary. If the contact angle between liquid and solid, θ is greater than 90° , the interfacial tension opposes the entrance of liquid into pores. This opposition is overcome by external pressure. For a cylindrical pore the force opposing entrance to the pore acts along the circumference and equals $-2\pi r\sigma\cos\theta$, where σ is the surface tension. The external pressure, which opposes this force, acts over the entire pore cross-sectional area and equals πr^2P . At equilibrium the two forces are equal and pore radius is given by

$$r = \frac{-2\sigma\cos\theta}{P}$$

Mercury intrusion porosimetry was applied to the new electrode to measure the macroporosity which consisted of pores bigger than 50 Å in size. In this method the porous electrode was placed in a cell and evacuated. Hg was then injected into the pores at various pressures and the volume of Hg taken up was obtained as a function of pressure. The results of Hg intrusion porosimetry are given in table 5.2 and 5.3. The total macroporosity for the new hydrogen anode was estimated as $0.0057\text{cm}^3/\text{g}$.

C
A
C

Table 5.2 Pore Volume by Hg Intrusion Porosimetry

PORE SIZE, SURFACE, PARTICLE SIZE DISTRIBUTION

| DATE | 10-2-68 | | | | | | |
|------------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| OPERATOR | SAA | | | | | | |
| SAMPLE | FRESH CHE | | | | | | |
| CONTACT ANGLE | 141.2 | | | | | | |
| SURF. TENS. (DYNES/CM) | 480 | | | | | | |
| PRESSURE MAX. (BAR) | 2000 | | | | | | |
| RELAT. VOLUME (CM ³ /G) | 15 | | | | | | |
| CAP. RADII (MM) | 1.5 | | | | | | |
| COMPRESS. (BAR) | 1.1730E-05 | | | | | | |
| MERCURY HEIGHT (MM) | 100 | | | | | | |
| SAMPLE MASS (G) | .28 | | | | | | |
| SURF. TENS. (G/CM ²) | 2 | | | | | | |
| REL. VOL. (%) | REL. VOL. (%) | REL. VOL. (%) | REL. VOL. (%) | REL. VOL. (%) | REL. VOL. (%) | REL. VOL. (%) | REL. VOL. (%) |
| PORE SIZE (MM) | PORE SIZE (MM) | PORE SIZE (MM) | PORE SIZE (MM) | PORE SIZE (MM) | PORE SIZE (MM) | PORE SIZE (MM) | PORE SIZE (MM) |
| SURF. AREA (CM ² /G) | SURF. AREA (CM ² /G) | SURF. AREA (CM ² /G) | SURF. AREA (CM ² /G) | SURF. AREA (CM ² /G) | SURF. AREA (CM ² /G) | SURF. AREA (CM ² /G) | SURF. AREA (CM ² /G) |
| 0.71 | 4.54 | 15221.3 | 1.55 | 3.04 | 3.0 | 10 | 19.3 |
| 1.41 | 5.44 | 14526.6 | 3.47 | 6.38 | 3.0 | 45 | 23.0 |
| 2.12 | 5.44 | 11955.3 | 5.28 | 9.72 | 3.3 | 75 | 20.5 |
| 2.83 | 7.24 | 10545.1 | 7.11 | 13.07 | 3.4 | 110 | 24.5 |
| 3.53 | 8.54 | 8339.2 | 8.91 | 16.38 | 3.3 | 151 | 40.3 |
| 4.21 | 9.74 | 7327.4 | 10.71 | 19.70 | 3.3 | 197 | 48.1 |
| 4.95 | 10.63 | 7174.3 | 12.53 | 23.04 | 3.3 | 247 | 50.7 |
| 5.65 | 12.03 | 6339.8 | 14.33 | 26.34 | 3.2 | 304 | 55.7 |
| 6.35 | 12.95 | 5999.7 | 16.15 | 29.68 | 3.3 | 366 | 61.7 |
| 7.07 | 13.93 | 5475.4 | 17.96 | 33.02 | 3.3 | 432 | 66.2 |
| 7.78 | 14.93 | 5106.9 | 19.78 | 36.25 | 3.3 | 503 | 71.0 |
| 8.49 | 16.53 | 4614.5 | 21.56 | 39.64 | 3.3 | 580 | 77.4 |
| 9.19 | 17.53 | 4351.4 | 23.38 | 42.97 | 3.3 | 664 | 83.4 |
| 9.90 | 18.93 | 4029.7 | 25.17 | 46.28 | 3.3 | 753 | 89.1 |
| 10.60 | 19.82 | 3846.9 | 26.99 | 49.62 | 3.3 | 847 | 94.6 |
| 11.31 | 21.82 | 3479.6 | 28.75 | 52.88 | 3.3 | 946 | 100.0 |
| 12.02 | 23.27 | 3269.9 | 30.55 | 56.16 | 3.2 | 1050 | 100.0 |
| 12.72 | 25.52 | 2928.1 | 32.31 | 59.40 | 3.2 | 1176 | 117.7 |
| 13.43 | 27.03 | 2771.1 | 34.06 | 62.65 | 3.2 | 1301 | 127.5 |
| 14.14 | 31.03 | 2453.6 | 35.79 | 65.77 | 3.1 | 1442 | 138.2 |
| 14.84 | 34.83 | 2190.4 | 37.46 | 68.87 | 3.1 | 1596 | 153.9 |
| 15.55 | 40.53 | 1882.4 | 39.06 | 71.81 | 2.9 | 1766 | 168.8 |
| 16.26 | 45.63 | 1672.0 | 40.60 | 74.80 | 3.0 | 1850 | 164.5 |
| 16.96 | 54.13 | 1409.5 | 42.16 | 77.50 | 2.7 | 2169 | 208.5 |
| 17.57 | 63.43 | 1202.8 | 43.59 | 80.13 | 2.6 | 2407 | 238.2 |
| 18.38 | 74.63 | 1022.3 | 44.93 | 82.61 | 2.5 | 2671 | 263.3 |
| 19.08 | 91.03 | 838.1 | 46.04 | 84.64 | 2.0 | 2935 | 284.1 |
| 19.79 | 102.53 | 703.0 | 47.10 | 86.59 | 1.9 | 3235 | 300.5 |
| 20.50 | 127.12 | 606.1 | 48.10 | 88.43 | 1.9 | 3570 | 335.2 |
| 21.21 | 149.63 | 529.9 | 48.93 | 89.95 | 1.5 | 3895 | 354.2 |
| 21.94 | 202.13 | 291.3 | 51.00 | 93.08 | 0.9 | 5438 | 354.5 |
| 22.45 | 302.13 | 229.8 | 52.17 | 95.61 | 0.4 | 8064 | 407.2 |
| 22.95 | 360.13 | 211.8 | 53.28 | 98.12 | 0.3 | 9372 | 404.3 |
| 23.86 | 394.13 | 193.6 | 52.58 | 96.07 | 0.5 | 6280 | 308.4 |
| 27.57 | 426.13 | 179.0 | 52.97 | 97.38 | 0.7 | 6716 | 436.0 |
| 28.27 | 461.13 | 155.5 | 53.22 | 97.85 | 0.5 | 7022 | 365.3 |
| 28.98 | 496.13 | 153.8 | 53.48 | 98.31 | 0.5 | 7350 | 329.4 |
| 30.69 | 573.13 | 133.6 | 53.55 | 98.32 | 0.4 | 7745 | 395.8 |
| 31.10 | 608.13 | 125.5 | 53.91 | 99.11 | 0.2 | 8012 | 256.1 |
| 31.81 | 645.13 | 118.3 | 54.07 | 99.41 | 0.3 | 8294 | 271.7 |
| 32.51 | 686.13 | 111.2 | 54.07 | 99.41 | 0.0 | 8284 | 0.0 |
| 33.22 | 719.13 | 106.1 | 54.39 | 100.00 | 0.6 | 8220 | 605.8 |
| 33.93 | 756.13 | 99.6 | 54.39 | 100.00 | 0.0 | 8200 | 0.0 |
| 34.64 | 810.13 | 94.2 | 54.39 | 100.00 | 0.0 | 8200 | 0.0 |
| 35.34 | 854.13 | 89.2 | 54.39 | 100.00 | 0.0 | 8200 | 0.0 |
| 36.05 | 902.13 | 84.0 | 54.39 | 100.00 | 0.0 | 8200 | 0.0 |
| 36.76 | 953.13 | 80.0 | 54.39 | 100.00 | 0.0 | 8200 | 0.0 |
| 37.46 | 998.13 | 75.4 | 54.39 | 100.00 | 0.0 | 8200 | 0.0 |
| 38.17 | 1048.13 | 71.3 | 54.39 | 100.00 | 0.0 | 8200 | 0.0 |
| 38.88 | 1114.13 | 63.5 | 54.39 | 100.00 | 0.0 | 8200 | 0.0 |
| 39.58 | 1174.13 | 65.0 | 54.39 | 100.00 | 0.0 | 8200 | 0.0 |
| 40.29 | 1228.13 | 62.1 | 54.39 | 100.00 | 0.0 | 8200 | 0.0 |
| 41.00 | 1292.13 | 59.5 | 54.39 | 100.00 | 0.0 | 8200 | 0.0 |
| 41.70 | 1363.13 | 55.2 | 54.39 | 100.00 | 0.0 | 8200 | 0.0 |
| 42.41 | 1436.13 | 55.0 | 54.39 | 100.00 | 0.0 | 8200 | 0.0 |
| 43.12 | 1432.13 | 53.1 | 54.39 | 100.00 | 0.0 | 8200 | 0.0 |
| 43.82 | 1509.13 | 50.5 | 54.39 | 100.00 | 0.0 | 8200 | 0.0 |
| 44.53 | 1524.13 | 49.1 | 54.39 | 100.00 | 0.0 | 8200 | 0.0 |
| 45.24 | 1515.13 | 47.2 | 54.39 | 100.00 | 0.0 | 8200 | 0.0 |
| 45.94 | 1602.13 | 45.7 | 54.39 | 100.00 | 0.0 | 8200 | 0.0 |
| 46.65 | 1731.13 | 44.1 | 54.39 | 100.00 | 0.0 | 8200 | 0.0 |
| 47.36 | 1773.13 | 42.9 | 54.39 | 100.00 | 0.0 | 8200 | 0.0 |

54.0

SPECIFIC SURFACE AREA (M²/G) = .283 (CYLINDRICAL MODEL)

Table 5.3 Pore Size Distribution for the Fresh Electrode

| Pore Size | % Pores |
|------------------|---------|
| 37 - 100 °A | 0 % |
| 100 - 1000 °A | 17 % |
| $10^3 - 10^4$ °A | 70 % |
| $> 10^4$ °A | 13 % |

5.4 Scanning Electron Microscopy (SEM)

In SEM an electron spot of about 5 nm minimum is focused on the sample. This spot is then moved over a small area by means of a set of deflecting coils. This area is displayed highly magnified on a cathode ray tube (CRT) screen by causing currents passing through the scanning coils to pass through the corresponding deflecting coils of the CRT while the electrons emitted from the sample are collected, amplified and used to modulate the brightness of the CRT. By verifying the orientation of the specimen with respect to the signal detector, a light/dark effect is produced forming a three-dimensional effect.

The SEM analysis of the electrode was carried out to observe the morphology of the electrode sample and perform EDS analysis for the active layer and metal mesh. The samples were cut and mounted on holders of JSM-840 type SEM, with the help of a double sided adhesive tape. Carbon conducting paint was applied to make the sample conductive. The samples were observed on the CRT screen and energy dispersive spectral (EDS) analysis was performed. After this the samples were coated with a thin layer of gold and micrographs were taken. Two micrographs of the sample were taken to show the cross-sectional area, mesh side or electrolyte facing side. EDS spectra and semiquantitative analysis data was obtained for the mesh and for the electrolyte facing side and back side or gas facing side (figs. 5.2, 5.3, 5.4).

From figs. 5.5 and 5.6 the average grain size and thickness of active χ layer of the electrode sample was estimated to be

Average catalyst grain diameter = 10 μ m (fig. 5.5)

Average Thickness of Active layer = 380 μ m (fig. 5.6)

TN-55000 UPM Date: 01/11/2001 Time: 10:17
Subject: EDS VFS = 8192 10.240

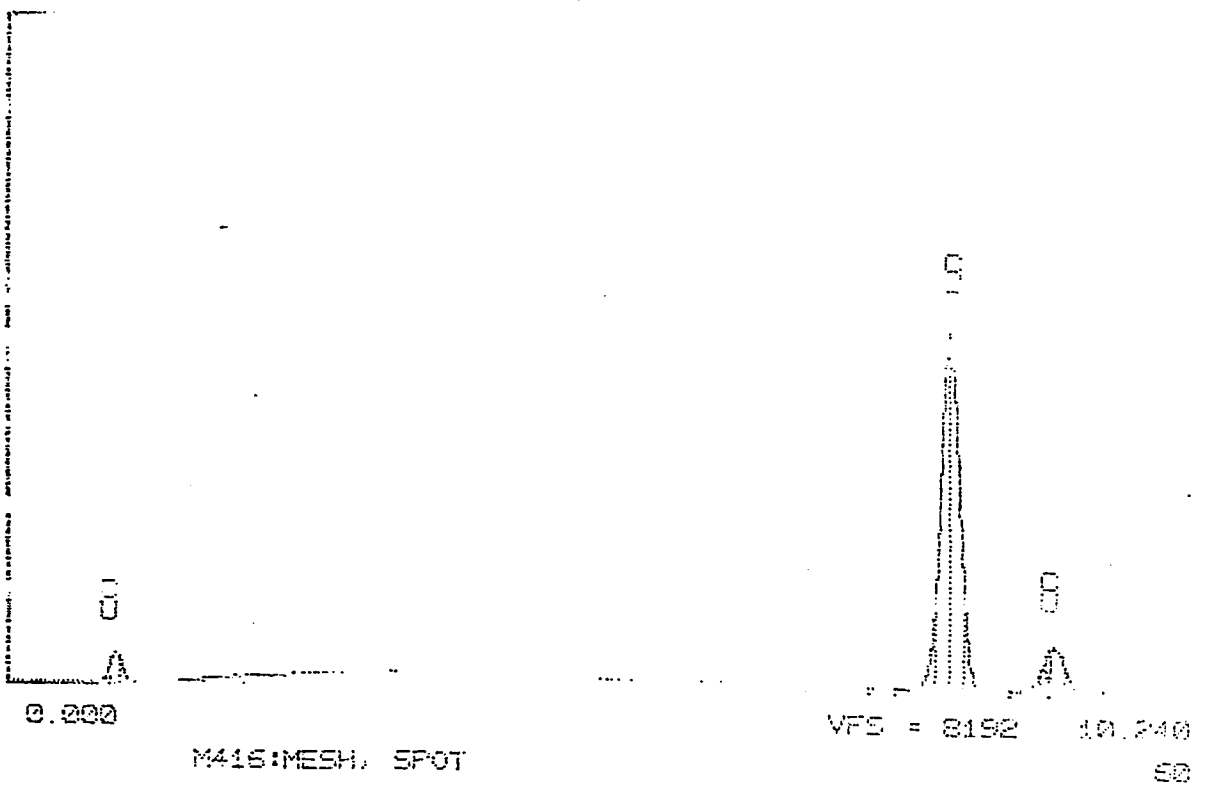


Fig. 5.2 EDS Spectra for the Metal Mesh

S00: S00

SEMI-QUANTITATIVE ANALYSIS: M415: SQUARE, ADNA
EL NDRY. K-RATIO

CU-K 3.18185 +- 0.98215

AL-K 3.20962 +- 3.28821

NI-K 0.50051 + 0.98480

ZAF CORRECTION 20.30 KV 40.80 Degs

No. of Iterations 2

| --- | K | III | IV | VF | ZAF | ATOM% | WT% |
|------|-------|-------|-------|-------|-------|-------|--------|
| CU-K | 0.191 | 1.048 | 0.998 | 1.000 | 1.041 | 15.75 | 13.52 |
| AL-K | 0.039 | 0.244 | 0.291 | 0.290 | 0.047 | 6.15 | 2.87 * |
| NI-K | 0.628 | 0.998 | 1.000 | 1.110 | 0.974 | 77.10 | 78.61 |

* - High Absorbance

S01.

TN-5500 LPM - Saudi Arabia JSM-840

SUN 21-FEB-93 11:37

Gunsch: 0.000KV = 0

ROI

(3) 0.390: 0.040

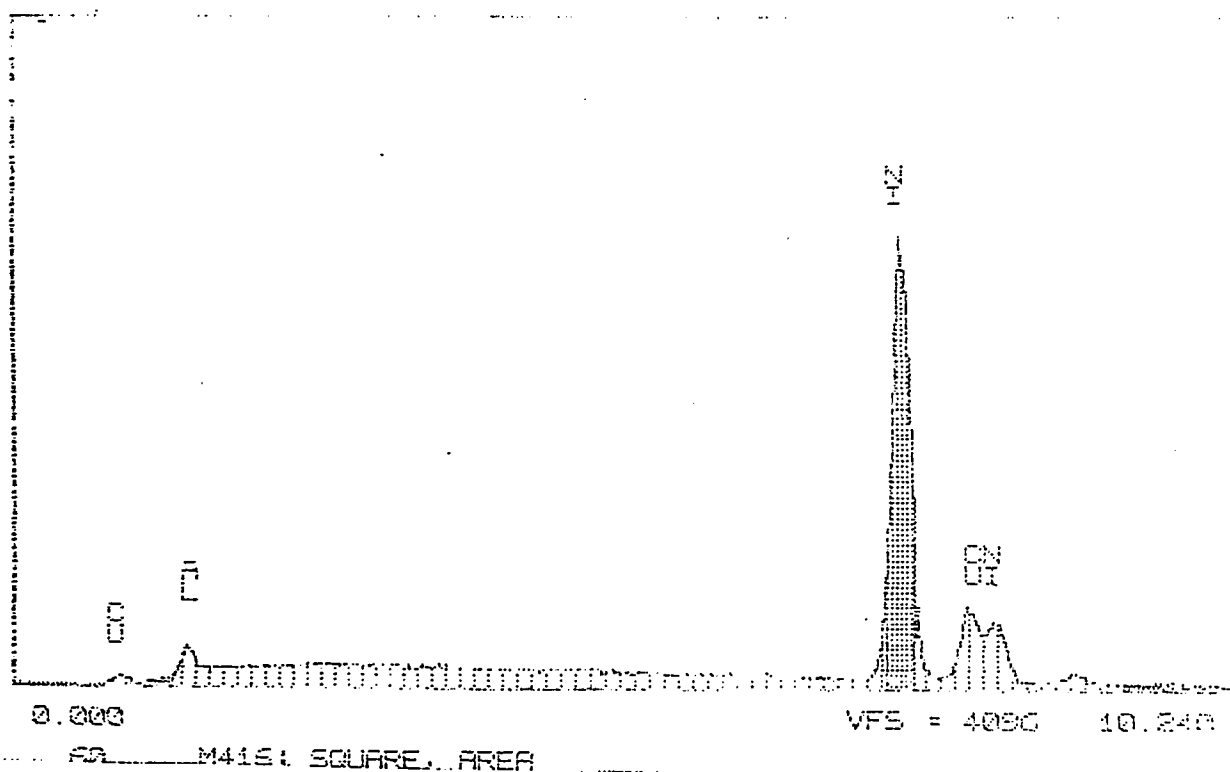


Fig. 5.3 EDS Spectra for the Electrolyte Facing Side of Electrode

889

SEM-QUANTITATIVE ANALYSIS: M416: BACKSIDE, AREA
EL NORM. K-RATIO

CU-K 0.23425 +- 0.00243

AL-K 0.00928 +- 0.00021

NI-K 0.75143 +- 0.00389

ZAF CORRECTION 20.00 KV 40.00 Degs

No. of Iterations 1

| --- | K | (Z) | (A) | (F) | (ZAF) | ATOM.% | WT.% |
|------|-------|-------|-------|-------|-------|--------|-------|
| CU-K | 0.234 | 1.848 | 0.998 | 1.000 | 1.000 | 21.64 | 28.81 |
| AL-K | 0.009 | 0.941 | 3.249 | 0.999 | 0.009 | 5.99 | 2.78 |
| NI-K | 0.751 | 0.991 | 1.000 | 1.000 | 0.991 | 72.17 | 78.41 |

* - High Absorbance

889:

T-3000 UPM - Saudi Arabia JSM-840

SUN 21-FEB-03 11:4

Cursor: 0.000keV = 0

ROI

(1) 9.100e: 9.640

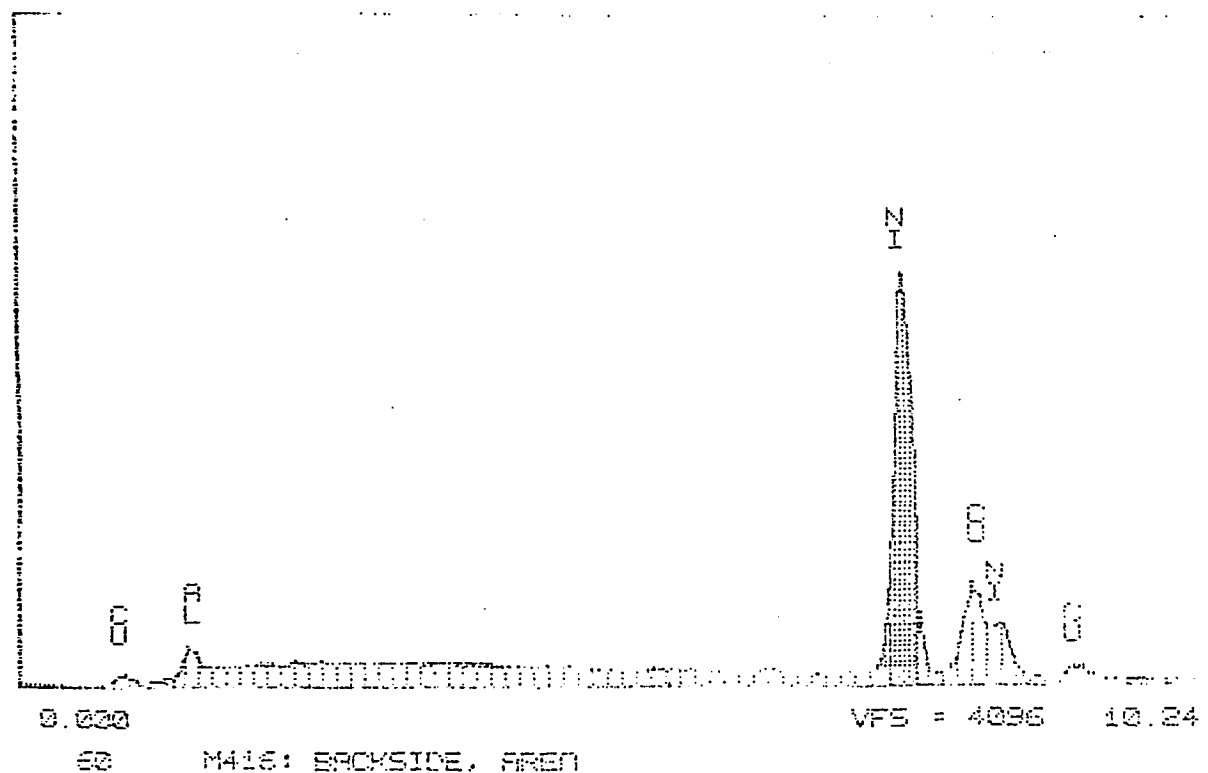


Fig. 5.4 EDS Spectra for the Gas Facing Side of Electrode

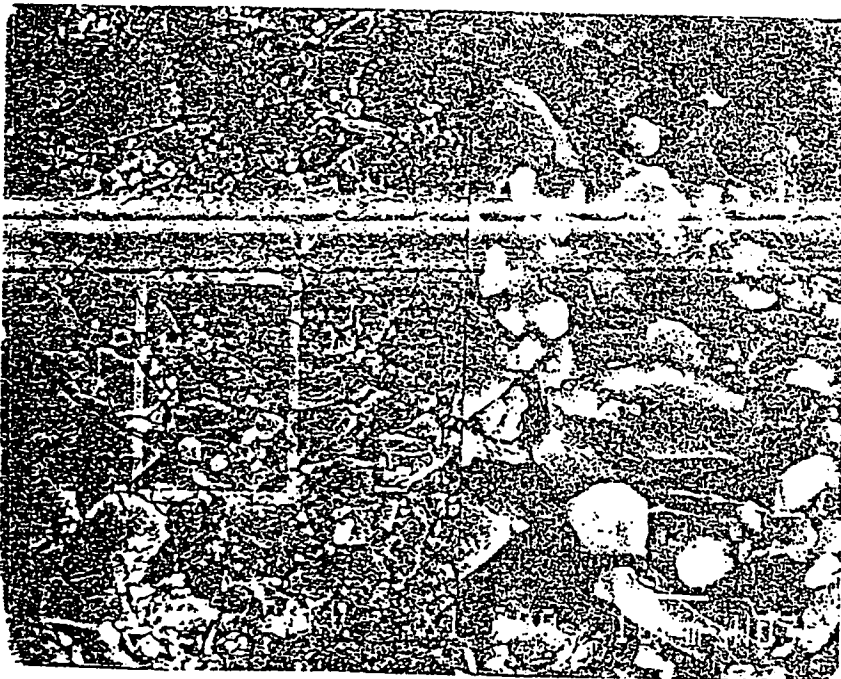


Fig. 5.5 SEM Micrograph of the Active Layer of Electrode



Fig. 5.6 SEM Micrograph of the Cross-section of Electrode

5.5 Inductively Coupled Plasma -AES

ICP-AES analysis gives very accurate determination of the composition of the sample. For this analysis the electrode sample was separated from its metal mesh. The sample was weighed in a digital balance then digested with 25 % HCl under low heat until only white film particles were left. Sample was finally diluted in 5% HCl and screened by ICP to check what elements were there. Final analysis was carried out by ICP which was calibrated with four levels of mixed standards containing the elements that were found from screen test. The results are given in table 5.4.

These results showed that about 27 % PTFE was present in the electrode. This result helped in determining the catalyst loading which was calculated to be 0.08278 g/cm^2 .

5.6 Estimation of Electrochemically Active Surface Area

For estimating electrochemically active surface area a piece of the electrode having external surface area of 4 cm^2 was cut. This piece of electrode was then weighed on a digital balance. After this the copper mesh was separated very carefully from the electrode piece and weighed. From the difference between the total weight and the metal mesh the weight of the active layer in the electrode piece was calculated as follows,

| | |
|--|------------|
| Total weight of 4 cm^2 electrode piece | = 0.6341 g |
| Weight of copper mesh | = 0.1807 g |
| \therefore weight of active layer in the electrode | = 0.4534 g |

Table 5.4 ICP-AES Analysis for the Fresh Electrode

| Elements | % By Weight |
|----------|-------------|
| Al | 3.30 % |
| Cu | 7.80 % |
| Ni | 62.0 % |
| Cr | < 0.05 % |
| Ti | < 0.01 % |
| Fe | < 0.05 % |
| Mn | < 0.05 % |

From the BET surface area measurement an area of 24 m²/g based on total weight was measured. The corrected BET surface area based on the active layer for the electrode was

$$S_{\text{BET}}(\text{corrected}) = \frac{24 (0.6341)}{(0.4534)} \text{ m}^2/\text{g}$$

$$= 33.56 \text{ m}^2/\text{g}$$

Surface area based on unit volume of the electrode was calculated as

$$f^{\circ} = S_{\text{BET}}(\text{corrected}) \rho (1 - \theta)$$

$$= 33.56 \times 4.1175 \times (1 - 0.4)$$

$$= 8.3 \times 10^5 \text{ cm}^2/\text{cm}^3$$

5.7 Estimation of Electrode Macroporosity

For estimation of macroporosity a 4 cm² square piece of electrode was carefully cut and weighed on a digital balance. The weight of this sample was found to be 0.6341 g. Hence the area of 1 g of electrode becomes 6.3081 cm². The product of electrode thickness with the area gave volume of 1 g of electrode to be 0.2429 cm³/g. Thirty copper wires of 200 μm diameter and 1 cm length (L) were counted in 1 cm² piece of electrode. From this the volume of wire in 1 g of the electrode was calculated as

$$\begin{aligned} \text{Volume of wire in 1 cm}^2 \text{ of electrode} &= 30\pi D^2 L/4 \\ 1 \text{ cm}^2 \text{ of the electrode} &= 0.009425 \text{ cm}^3 \\ 1 \text{ g of electrode} &= 0.05945 \text{ cm}^3 \end{aligned}$$

$$\begin{aligned}\text{Hence corrected volume of active layer} &= 0.2429 - 0.05945 \\ &= 0.1834 \text{ cm}^3\end{aligned}$$

From Hg intrusion porosimetry the total pore volume was found to be $0.0544 \text{ cm}^3/\text{g}$. The electrode macroporosity was given by the ratio of void volume which was obtained from Hg intrusion porosimetry divided by the corrected volume. Thus

$$\begin{aligned}\text{Macroporosity}(\epsilon_{\text{mac}}) &= \frac{.00544}{0.1834} \\ &= 0.2966\end{aligned}$$

Table 5.5 gives comparison between the characteristics of previous electrode and the new electrode.

Table 5.5 Comparison of Characteristics of the New Electrode with Previous Electrode

| Characteristics | Previous Electrode | New Electrode |
|-----------------------------------|------------------------------------|------------------------------------|
| Avg. Grain Radius(R) | 20 μ m | 5 μ m |
| Electrode Thickness(L) | 320 μ m | 380 μ m |
| Macroporosity(ϵ_{mac}) | 0.2 | 0.3 |
| Active Surface Area(f^a) | 5.4 $\times 10^5$ cm ⁻¹ | 8.3 $\times 10^5$ cm ⁻¹ |
| BET Surface Area(S) | 30 m ² /g | 33.56 m ² /g |
| Catalyst loading | 7 kg/m ² | 8 kg/m ² |
| Cu Content (%) | 0 % | 7.8 % |

Chapter 6

EXPERIMENTAL SETUP AND PROCEDURE

6.1 Experimental Half Cell Setup

A schematic diagram of the half cell assembly used for investigating the performance of the specially prepared Raney-Ni hydrogen electrode is shown in fig.6.1. The half cell is fabricated from plexiglass. It has a gas chamber and an electrode chamber. The gas chamber has an inlet and outlet for the gas while the electrode chamber houses the electrode, a ring shaped PTFE sealing and two nickel wire current collectors. The electrode chamber is screwed to the gas chamber with stainless steel screws. The half cell is mounted into a PTFE container which is filled with 25% KOH solution. A 2.5cm × 2.5cm nickel plate which is welded onto a nickel rod is used as a counter electrode. The counter electrode is fixed onto the plexiglass lid of the PTFE container. As the electrolyte medium is basic therefore a Hg/HgO reference electrode is used. The reference electrode is placed near the electrode in the cell in such a way that shielding effects are minimized. The gas inlet and outlet of the gas chamber are sealed by PTFE tape. The incoming gas is introduced at the side of the chamber while the outgoing gas leaves from the top. The level of water in the back pressure regulator is adjusted to 10 - 15 cm height. A Brooks gas flow controller is used to control the flow rate of hydrogen through the cell. The outlet gas pressure from the hydrogen gas cylinder is kept at 1.4kg/cm². The hydrogen gas used in this work has a purity of 99.99%.

The outlet gas stream from the half cell is bubbled through an adjustable height of water column acting as back pressure regulator. The entire half cell

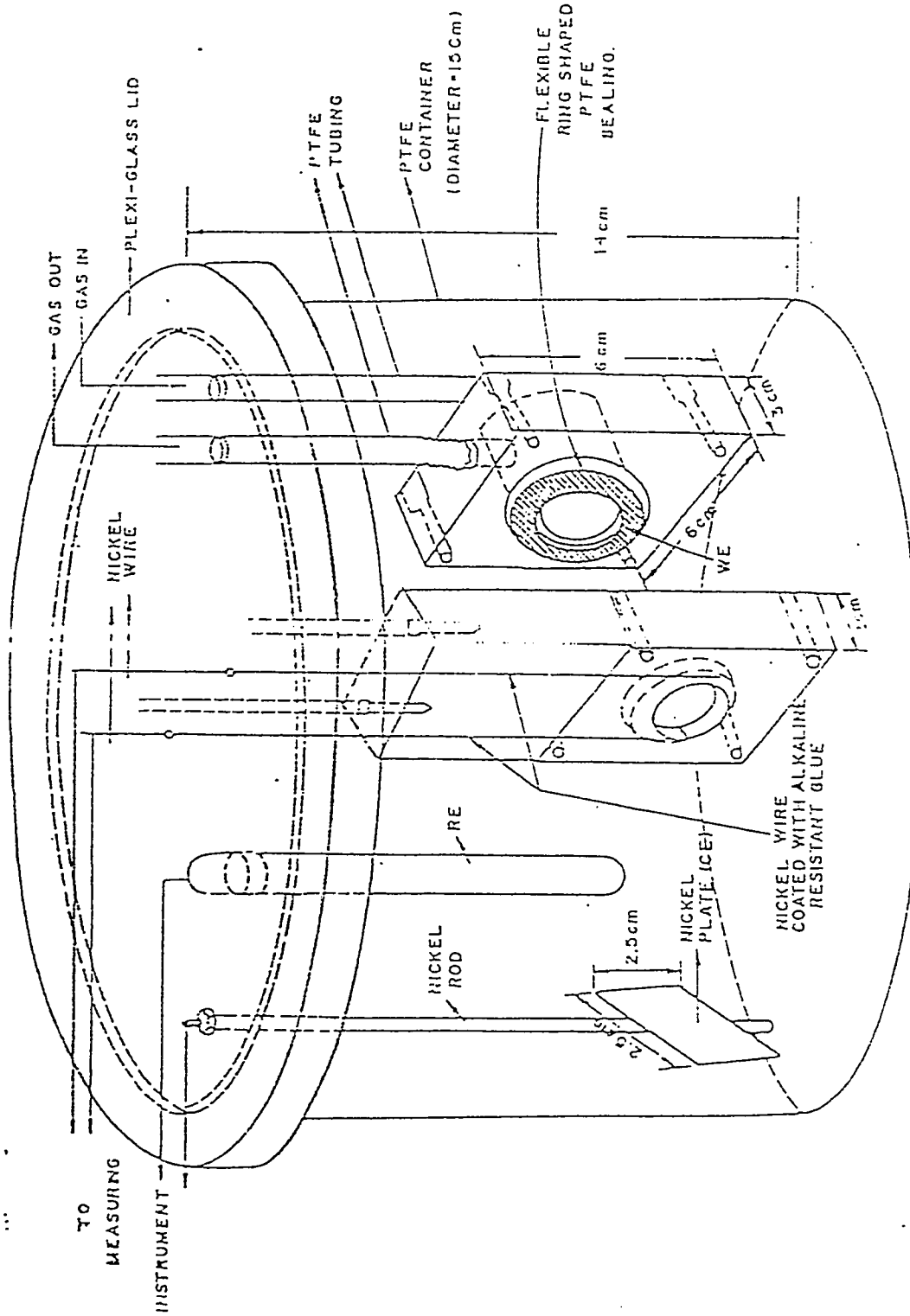


Fig. 6.1 A Schematic diagram of the Half Cell Assembly

assembly is placed in a thermostat water bath for doing experiments at different electrolyte temperatures.

The geometric surface area of the circular shaped electrode used is 6 cm^2 and it is placed in the half cell in such a way that the mesh side faces the electrolyte. Nickel wire current collectors are used to connect the working electrode to external circuit. A Wenking type POS73 potentiostat is used to apply a desired load of current to the working electrode by choosing suitable external resistances. The external resistor is fixed to an interface board. The interface board is also equipped with a solid state relay. Digital multimeter of type METER M-4650 are used as high impedance DC voltmeter and ammeter in the circuit. A dual channel digital storage oscilloscope (Philips ,PM 3302) with a maximum sampling rate of 20 MHz is used for IR drop measurement by current interruption technique using the solid state relay (Teledyne SSP p/N type with 4-10V DC control).

6.2 Activation of the Raney-Ni Electrode

Activation of the Raney-Ni electrode was carried out to precondition the electrode. The activation process results in reduction of the nickel oxide. The activation was done by passing a cathodic current of 25 mA, the electrode being fully immersed in 25% KOH electrolyte.

For the purpose of activation, a circular shaped electrode of diameter 3.6 cm is cut from the electrode sheet and placed in the electrode chamber in such a way that the metallic mesh touches the current collector wires. A ring shaped PTFE sheet was placed on top of the electrode. The ring acts as a sealing. Then the two pieces of the half cell were brought together and screwed with stainless steel

screws. The gas connections were done and the half cell mounted on the plexiglass lid was slowly lowered into a 25% KOH solution in a PTFE container. The PTFE container was then placed in a thermostat water bath. The level of water in the back pressure regulator was adjusted between 10-15 cm so that neither the gas bubbles in the electrolyte nor the electrolyte leaks into the gas compartment.

The external circuit was connected galvanostatically and a current of 25mA was passed through the cell for 48 hours at 25°C. During activation the electrode potential stayed around -945mV with respect to Hg/HgO reference electrode. Upon stopping the cathodic current the electrode potential falls down to about -922mV.

6.3 Polarization and IR drop Measurements

The working electrode was polarized by changing the settings of the potentiostat and passing anodic current through the cell (fig. 6.2, 6.3). A DC interruption technique which was developed at KFUPM was used to measure the IR drop losses. This IR drop technique utilizes the fact that ohmic overvoltage decays 100 times faster than activation, concentration overvoltage.

The potentiostat was used as a galvanostat by using an external resistor R_1 whose value determines the current range to be controlled. This resistor was placed between the working electrode and its potentiostatic lead was connected to the point where the external resistor was linked to the working electrode. A solid state relay in series with a milliammeter was connected to the working electrode of the half cell. Potential difference between the working and reference electrode was measured by a high impedance voltmeter.

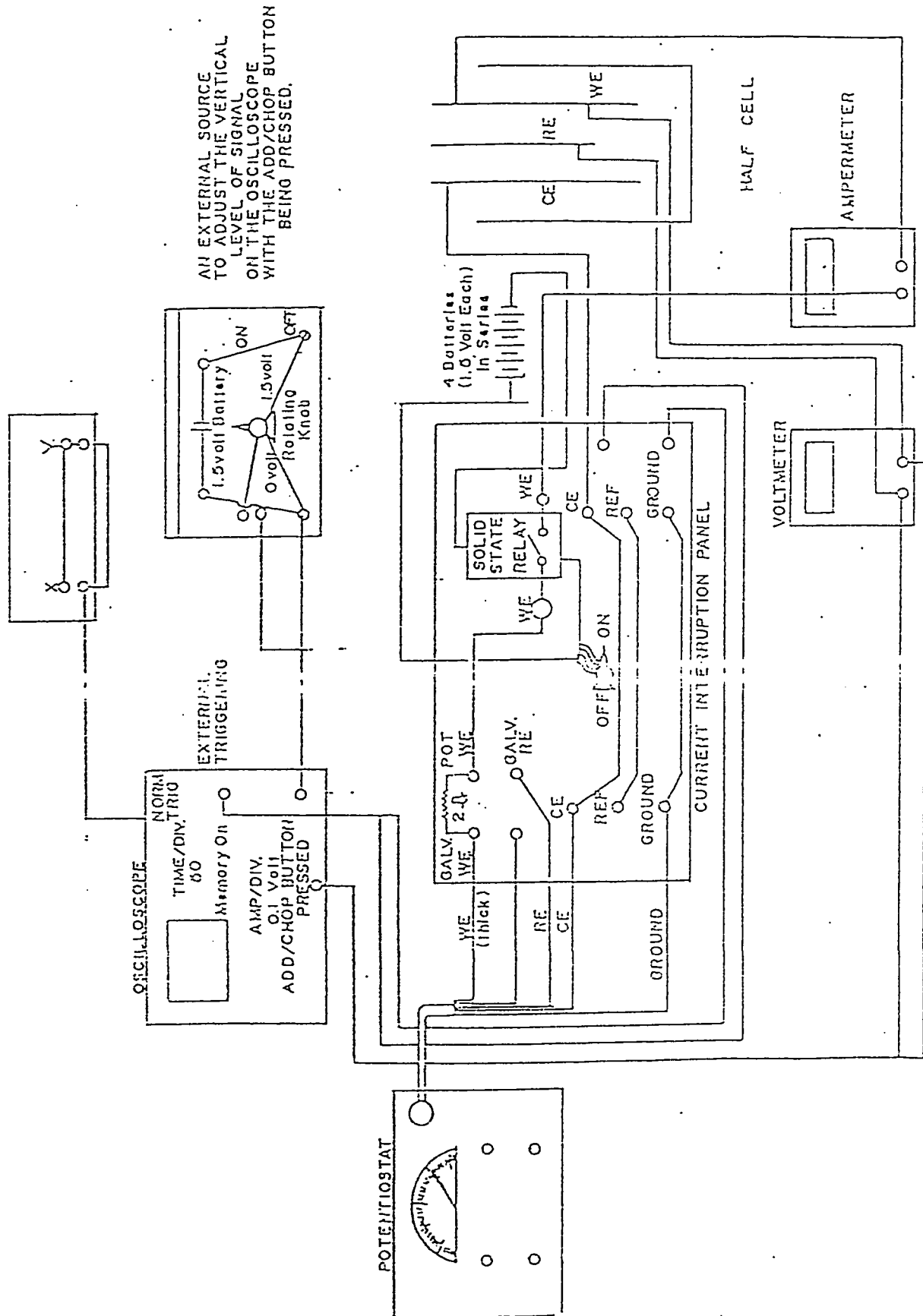


Fig. 6.2 Circuit Diagram for the Galvanostatic Polarization Experiments

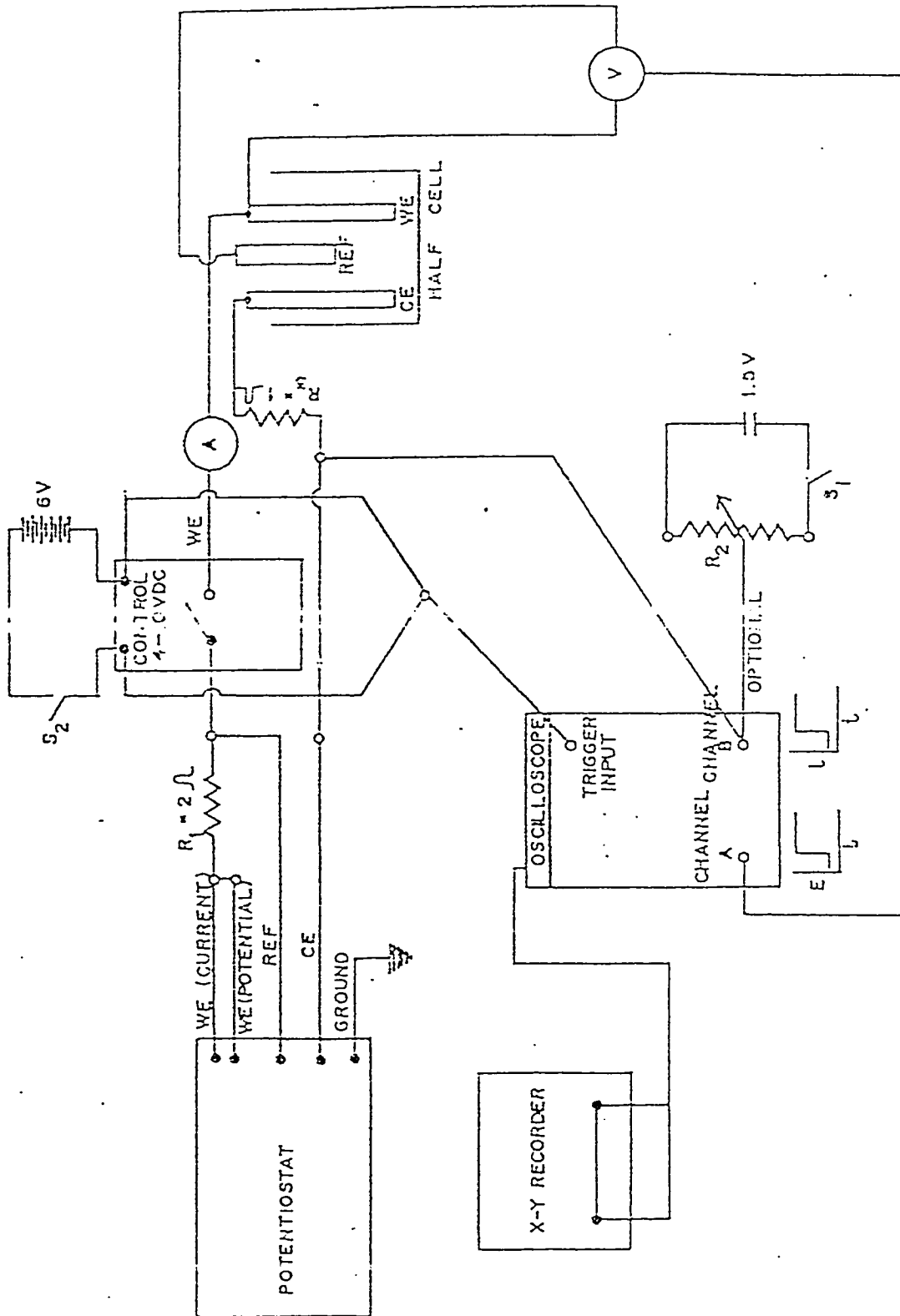


Fig. 6.3 Current Interruption Method for IR Drop Measurement

A dual channel digital storage oscilloscope was used to monitor the working electrode potential and cell current through channels A and B ,respectively. The position of the signal in the Y direction was adjusted by depressing the normal triggering switch and by adjusting the amplifier A and B switches accordingly. The level signal on the oscilloscope was turned slowly till the signal is caught at its present time base values. The cell current transient was recorded as a voltage drop across an accurately known resistor , R_3 . Mechanical switch S_2 when opened ,activates the batteries in series which then deenergizes the relay breaking the circuit current. Without using any pulse generator, switch S_2 was simultaneously used for pre-triggering the oscilloscope with shielded concentric cables. In addition the oscilloscope itself has built in four levels of pre triggering before the event which are namely zero, two, three, four quarter on the screen. Either one quarter or one half pre triggering was used in all the experiments. All the connecting wires to the instruments were kept as short as possible to minimize the pickup of stray capacitances and inductances.

The initial instantaneous jump of the voltage recovery upon going from an operating load to open circuit was recorded as the IR drop in the half cell. At oscilloscope sweep rates of 50ms/div. ,sharp steps corresponding IR drop was easily recorded and measured. It was observed that this event is completed in about 30-35msec. The reproducible delay in the opening of the solid state relay and the adjustment of level of the signal provided a ready synchronization with oscilloscope sweep rate at a present trigger level. The signal was digitally recorded in the memory of the oscilloscope and then plotted on an X-Y plotter. A variable resistor R_2 , a mechanical switch S_1 , and a 1.5 V battery was connected in series to adjust the vertical level of signal in channel B. This was optional and only

necessary when high sensitivities of deflection per division were required in the vertical direction of the screen.

Thus the experimental procedure involved loading the working electrode with a current density and measuring the resulting potential of the electrode with respect to Hg/HgO reference electrode. The IR drop measured from the oscilloscope and the XY plot of voltage against time. The same process was repeated at different current densities and at different electrolyte temperatures.

For the long term electrode performance test the half cell was connected to the potentiostat in potentiostatic mode. In potentiostatic mode a predetermined overvoltage was applied to the working electrode so as to pass a constant current through the counter and working electrode. Fig. 6.4 gives the circuit diagram for the potentiostatic experimental setup. The decay of this current was then followed as function of time.

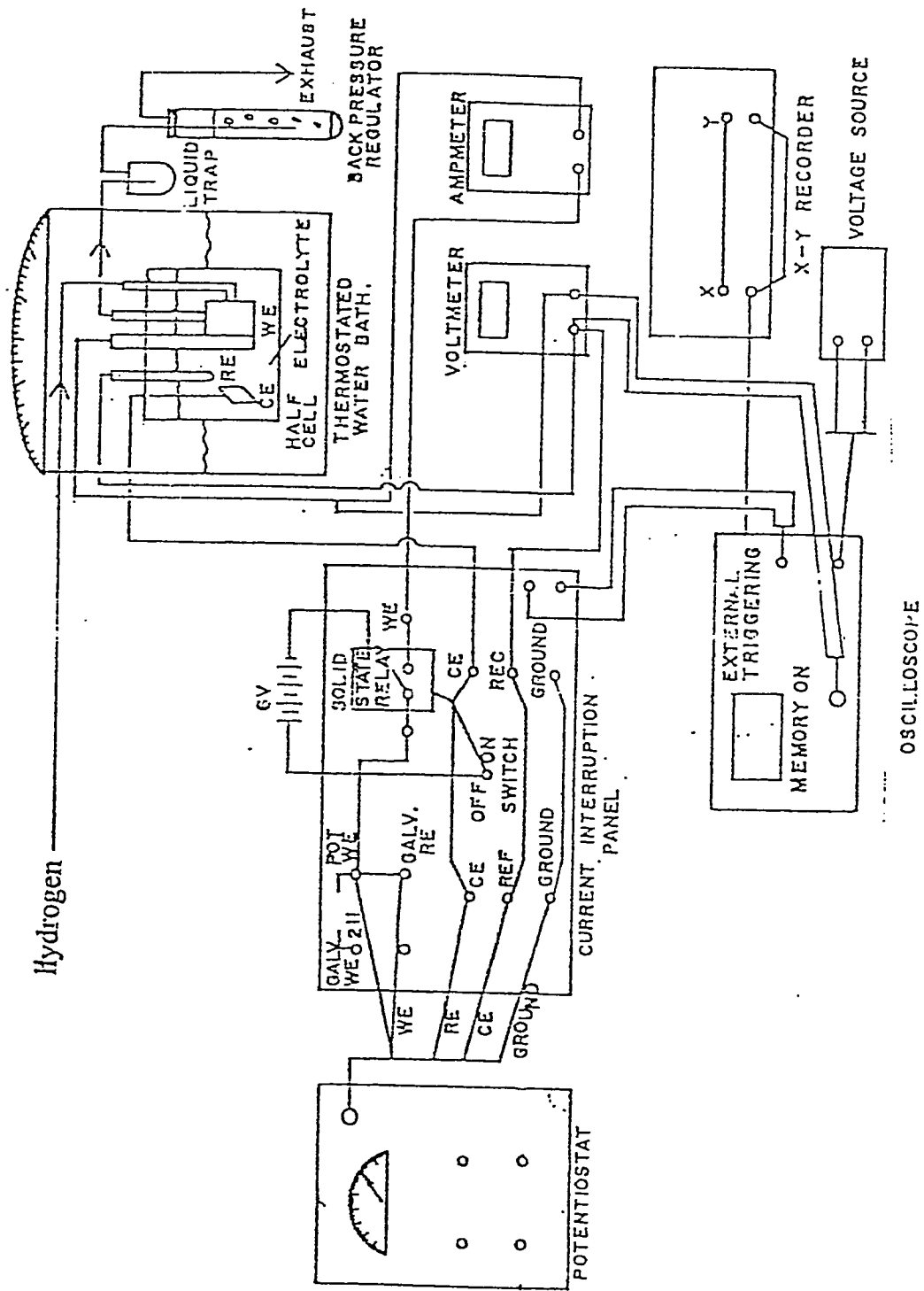


Fig. 6.4 Circuit Diagram for Potentiostatic Experiments

Chapter 7

EXPERIMENTAL RESULTS AND ANALYSIS

7.1 Polarization Measurements Results

In order to ascertain the validity of experimental setup galvanostatic polarization runs were carried out with the old electrode. Fig. 7.1 shows the reproducibility run carried out with the old electrode at 35°C and 65°C as compared to the previous data(15). The measured cell current was divided by the electrode external surface area to get the current densities. Fig. 7.2 shows the reproducibility run carried out with another piece of the new electrode. This run was carried out to ascertain the homogeneity of the electrode.

The voltage drop in the electrolyte(IR) was measured by current interruption method. The electrolyte resistance was calculated by dividing IR drop by the measured cell current. Fig. 7.3 shows the electrolyte resistance at various temperatures. Table 7.1 gives the average electrolyte resistance at various temperatures (25°C-75°C). Steady state galvanostatic polarization curves obtained for the new electrode at various temperatures in the half cell setup are shown in figs. 7.4 to 7.9. The open circuit voltage read on the voltmeter and IR drop voltage measured by current interruption method was subtracted from the polarized electrode potential to get IR free overpotential.

$$\text{IR free overpotential} = E_p - \text{O.C.V.} - IR$$

For the polarization curves this overvoltage versus the current densities at various temperatures were plotted.

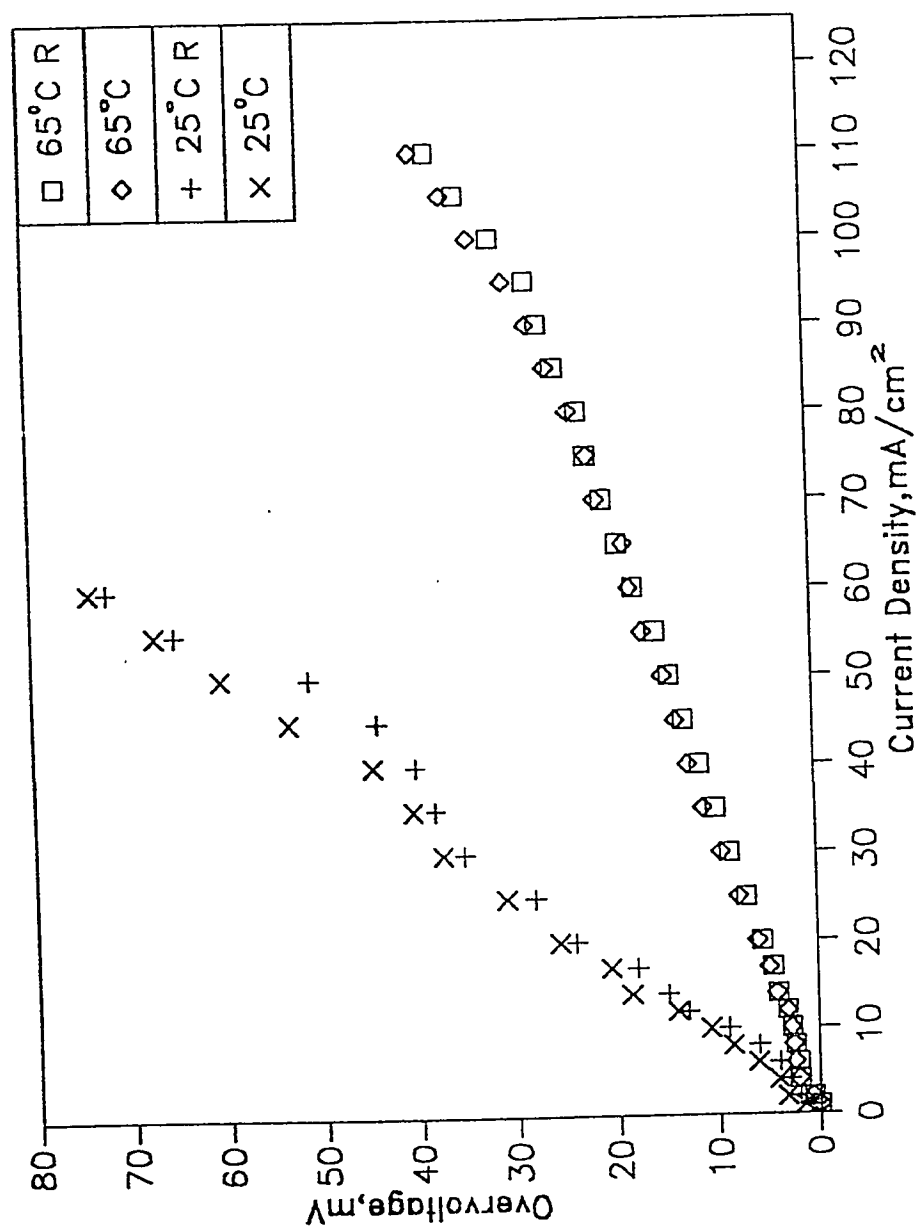


Fig. 7.1 Reproducibility Runs with the Old Electrode at 35°C and 65°C

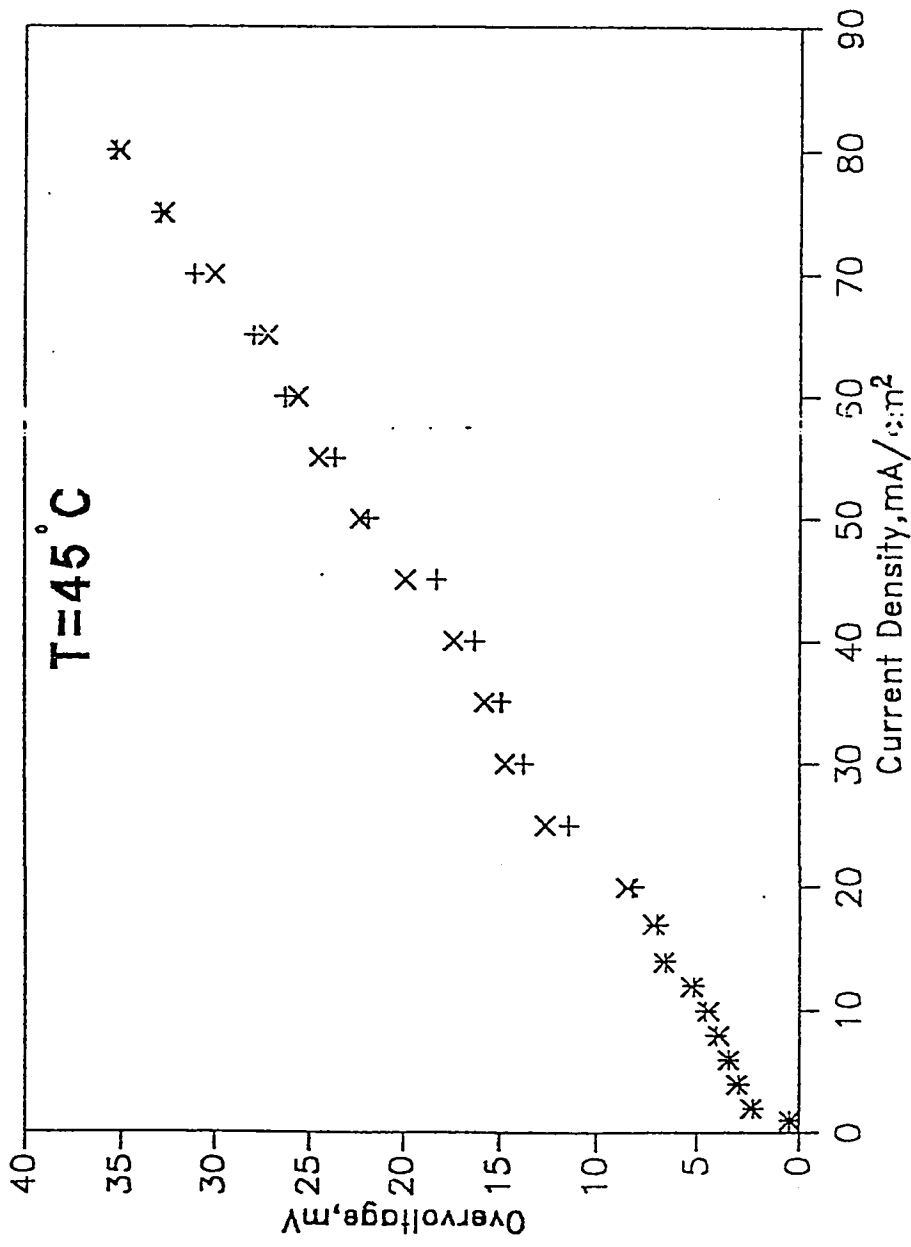


Fig. 7.2 Reproducibility Run with the New Electrode at 45°C.

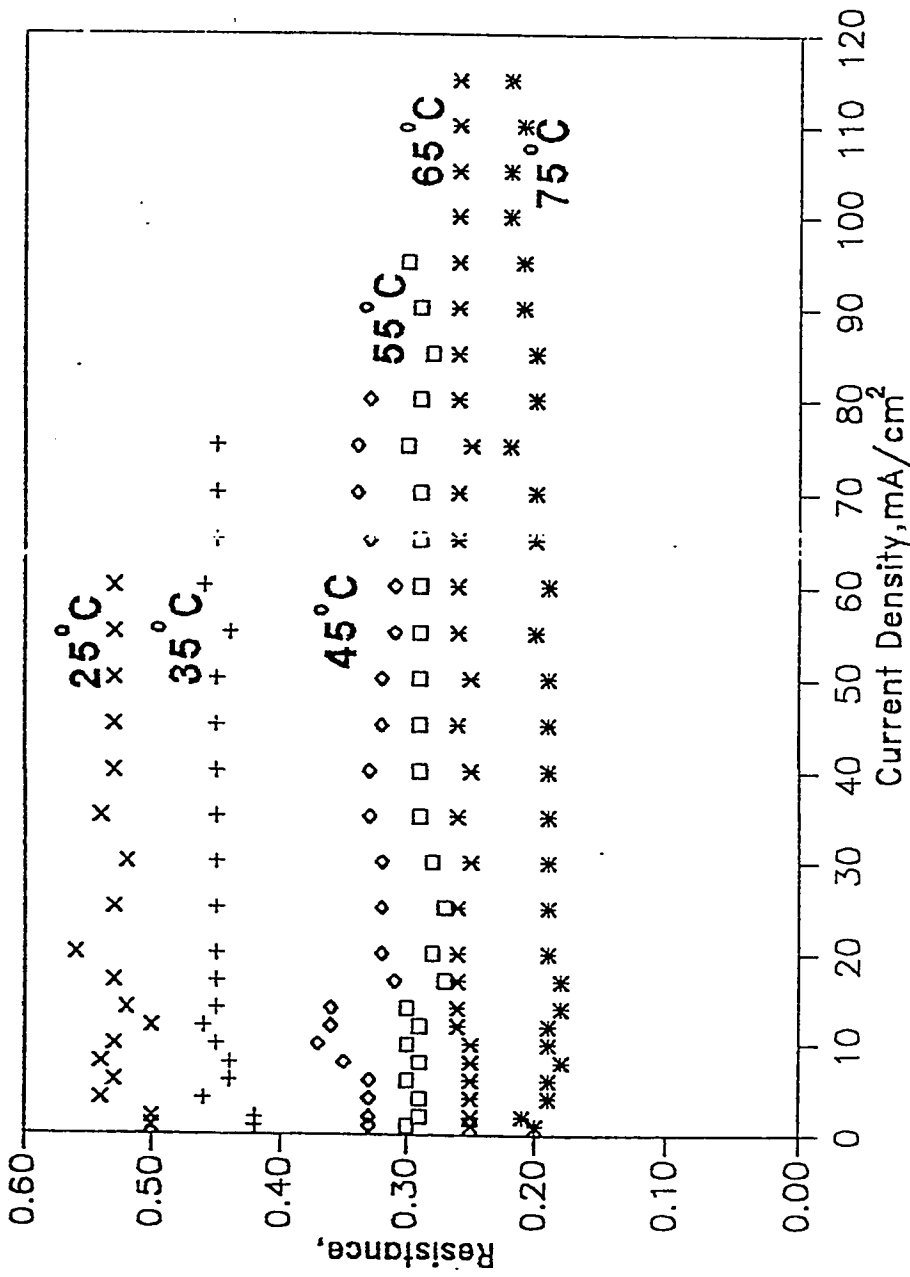


Fig. 7.3 Electrolyte Resistance as a Function of Temperature.

Table 7.1 Electrolyte Resistance as a Function of Temperature

| Temperature (°C) | Electrolyte Resistance (Ω) |
|---------------------|--|
| 25 | 0.527 |
| 35 | 0.447 |
| 45 | 0.331 |
| 55 | 0.2904 |
| 65 | 0.2565 |
| 75 | 0.1969 |

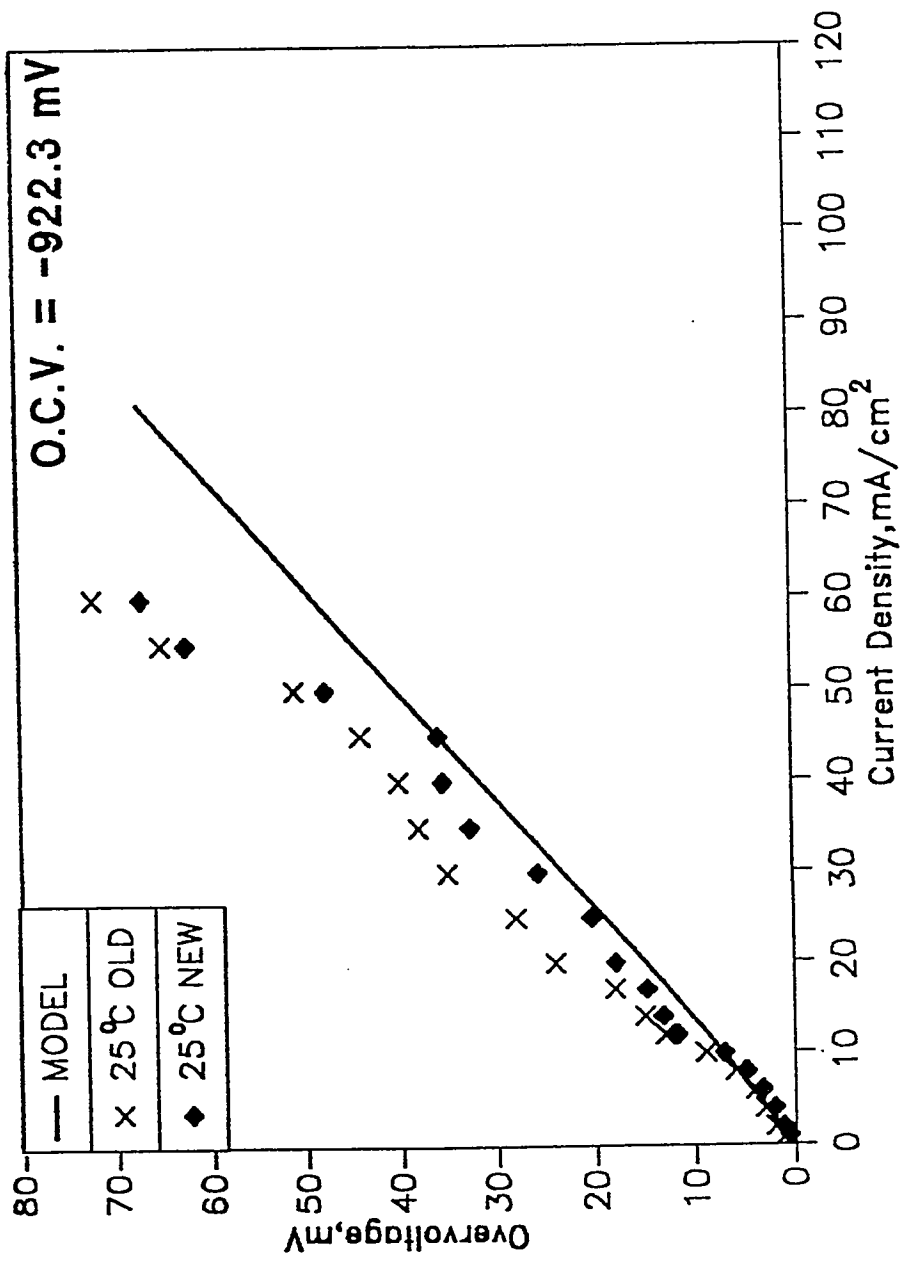


Fig. 7.4 Steady State Polarization Curve for Hydrogen Oxidation Reaction at 25°C.

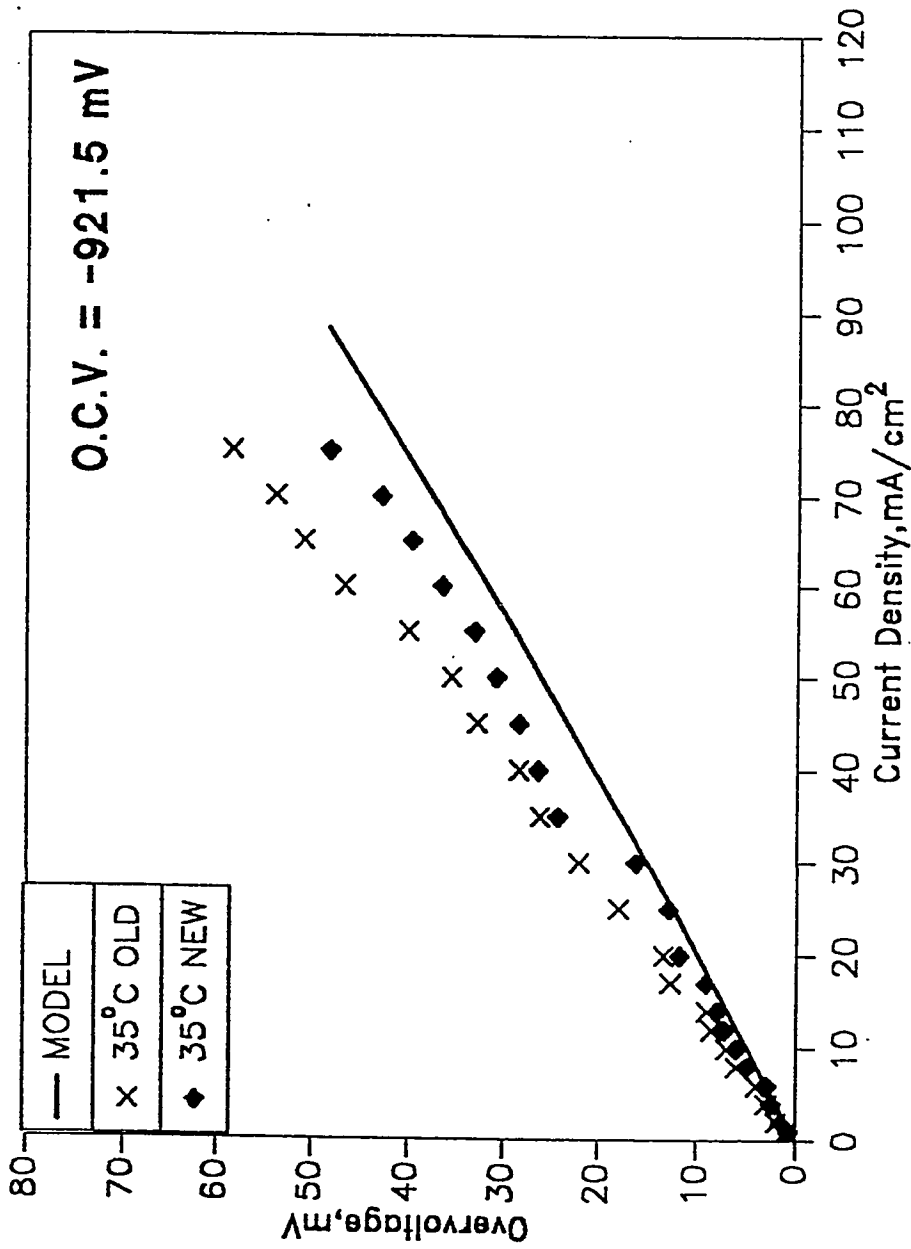


Fig. 7.5 Steady State Polarization Curve for Hydrogen Oxidation Reaction at 35°C.

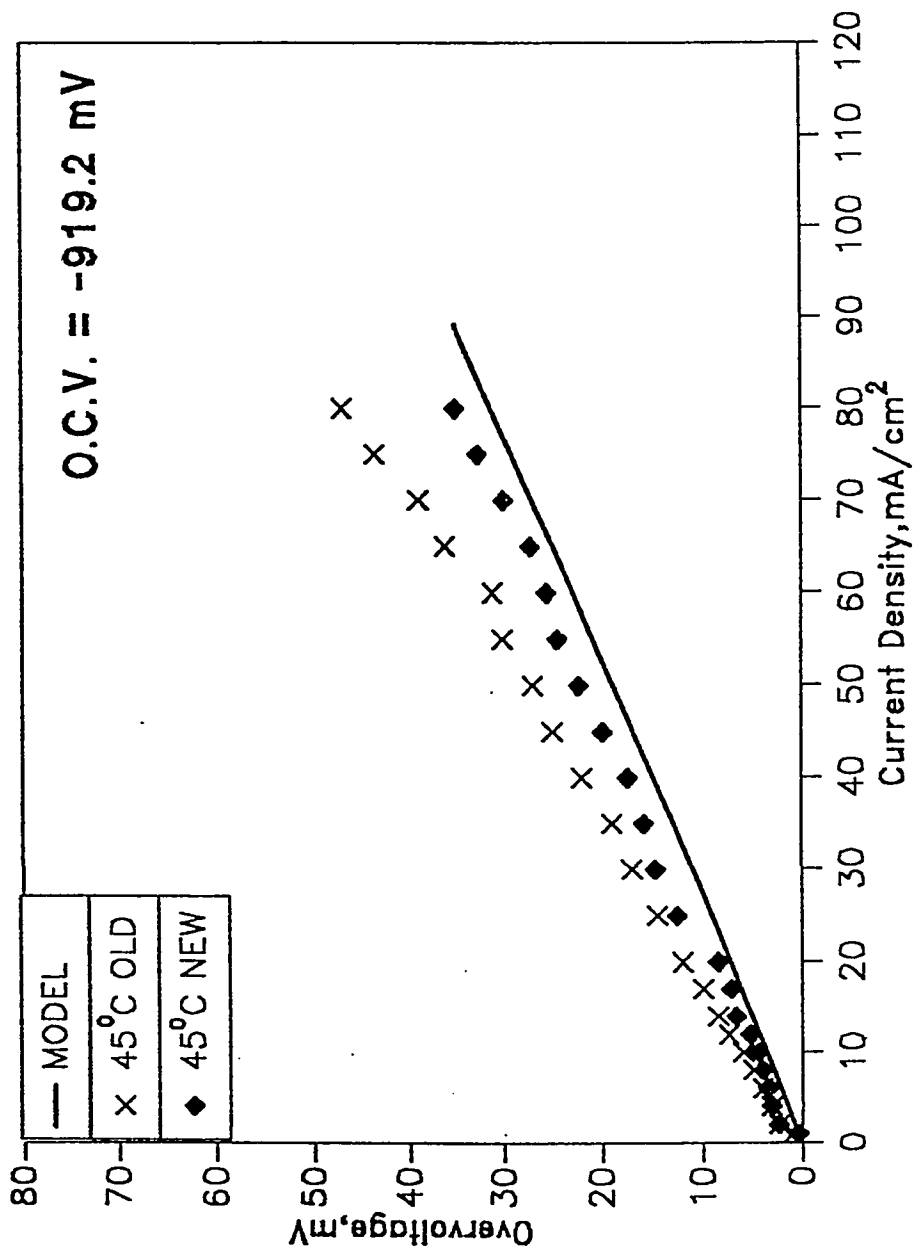


Fig. 7.6 Steady State Polarization Curve for Hydrogen Oxidation Reaction at 45°C.

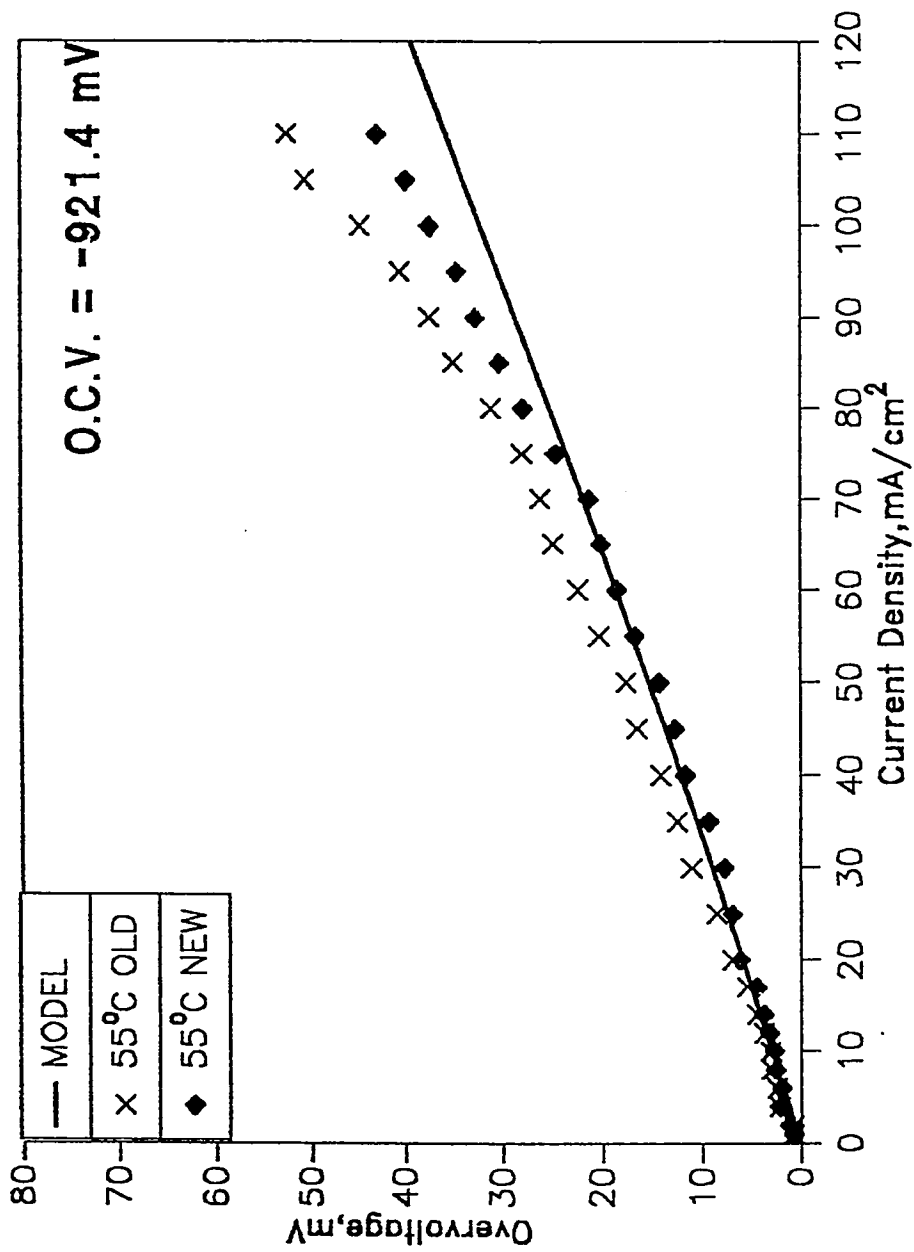


Fig. 7.7 Steady State Polarization Curve for Hydrogen Oxidation Reaction at 55°C.

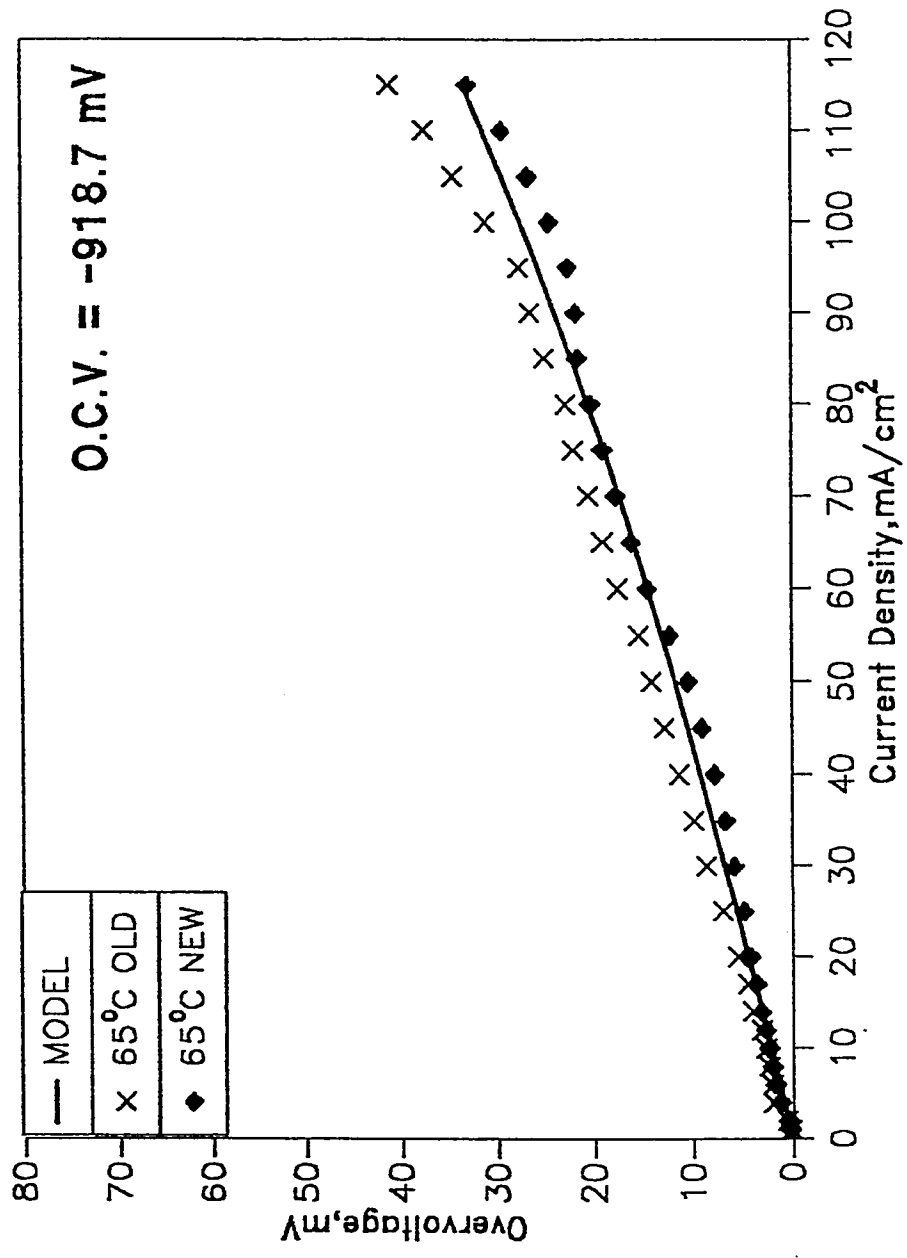


Fig. 7.8 Steady State Polarization Curve for Hydrogen Oxidation Reaction at 65°C.

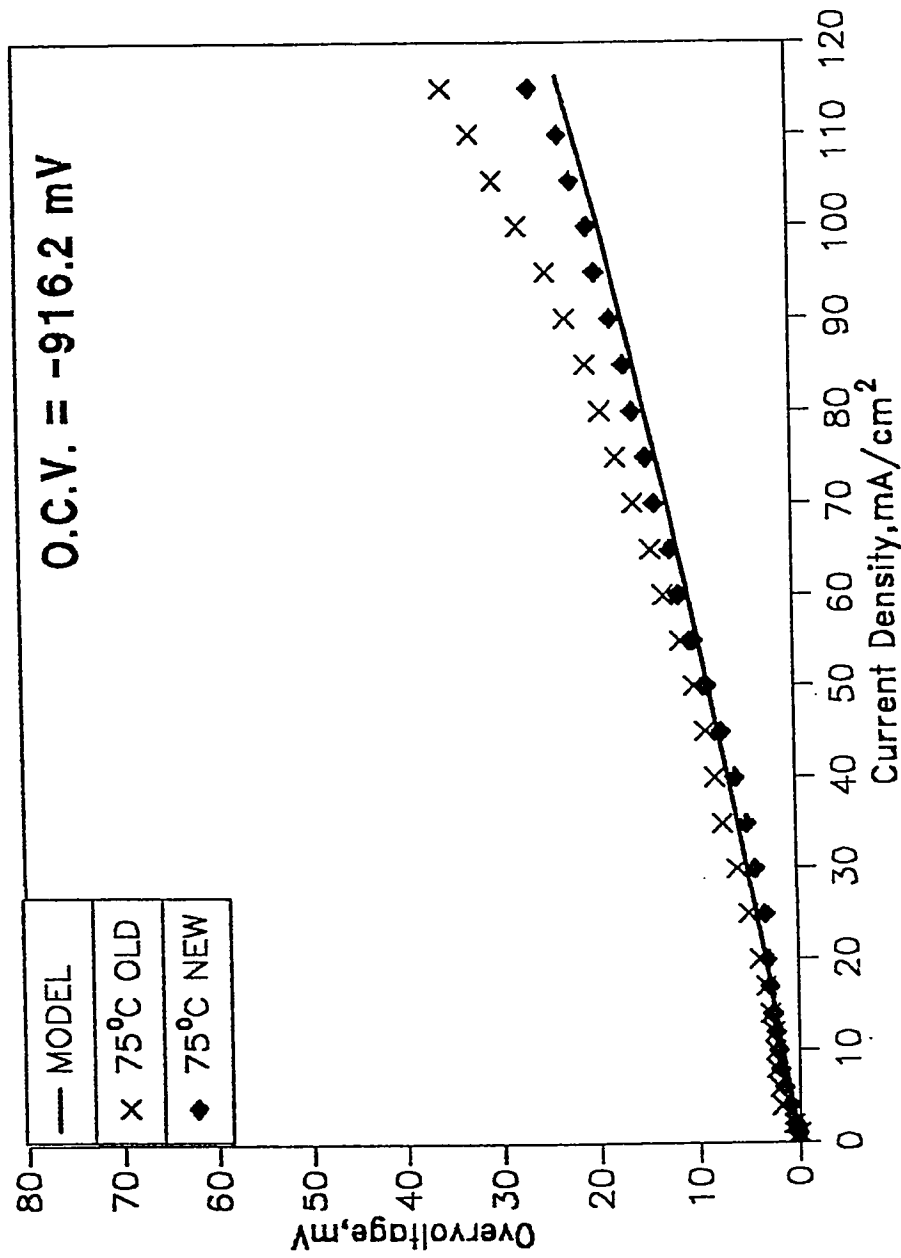


Fig. 7.9 Steady State Polarization Curve for Hydrogen Oxidation Reaction at 75°C.

7.2 Application of Spherical Raney Catalyst Grain Model

The spherical Raney catalyst grain model developed earlier (15) was applied to estimate the charge transfer coefficients and exchange current densities for the new electrode at different temperatures. The following model equation in dimensionless form ,

$$\frac{d^2\phi}{d\xi^2} = \frac{2nFD_0L^2}{\eta\kappa R} C_0 \left(1 - e^{-\frac{zF}{RT}\eta_0\phi}\right) \left[\sqrt{\frac{ia}{nFD_0C_0}} \exp\left(\frac{\alpha zF\eta_0}{2RT}\phi\right) \coth\left\{R\sqrt{\frac{ia}{nFD_0C_0}} \exp\left(\frac{\alpha zF\eta_0}{2RT}\phi\right)\right\} - \frac{1}{R} \right] \quad (7.1)$$

with dimensionless boundary conditions is used for the parameter estimation.

$$\text{B.C. 1} \quad \xi = 0 \quad \phi = 1$$

$$\text{B.C. 2} \quad \xi = 1 \quad \frac{d\phi}{d\xi} = 0$$

Here,

$$\phi = \text{Dimensionless overvoltage} = \frac{\eta}{\eta_0}$$

$$\text{and} \quad \xi = \text{Dimensionless electrode thickness} = \frac{x}{L}$$

η_0 is the measurable overvoltage at the electrolyte side of the electrode and L is thickness of the electrode.

difference method. The electrode current density at the electrolyte side of the electrode is given by

$$j(x) = -\kappa_e (1-\epsilon_{\text{mac}}) \left. \frac{d\eta}{dx} \right|_{x=0} \quad (7.2)$$

Tables 7.2 and 7.3 gives respectively the temperature independent and temperature dependent input parameters used in the solution of equation 7.1.

Based on these parameters and experimental overvoltage values the model equation was solved to get theoretical current densities. The solid lines in figs. 7.4 to 7.9 also represents the current densities as predicted by the model.

7.3 Estimation of Kinetic Parameters

The spherical Raney-catalyst grain model was used to determine the kinetic parameters by comparing the predicted current density values with the observed experimental values and minimizing the sums of the squares of the difference between these two quantities. N data points from the experimental polarization curve were chosen and the objective function, S which was defined as the sum of the squares of the error

$$S = \sum_1^N (i_{\text{cal}} - i_{\text{exp}})^2$$

Table 7.2: Temperature -independent input parameters for Spherical Raney-Catalyst Grain Model

| | |
|-----------------------|---|
| Stoichiometric Number | $z=1$ |
| Electrons Transferred | $n=2$ |
| Electrode Thickness | $L=380\mu\text{m}$ |
| Avg. Grain Radius | $R=5\mu\text{m}$ |
| Macroporosity | $\epsilon_{\text{mac}}=0.3$ |
| Microporosity | $\epsilon_{\text{mic}}=0.4$ |
| Tortuosity | $\tau_{\text{mic}}=2$ |
| Active Surface Area | $f^{\circ}=8.3 \times 10^5 \text{ cm}^{-1}$ |
| BET surface Area | $S=33.56 \text{ m}^2/\text{g}$ |
| Catalyst Density | $\rho=4.117\text{g}/\text{cm}^3$ |

Table 7.3: Temperature -dependent input parameters for Spherical Raney-Catalyst Grain Model

| Temperature (°C) | 25 | 35 | 45 | 55 | 65 | 75 |
|--|----------------------|----------------------|----------------------|-----------------------|-----------------------|-----------------------|
| Effective Diffusivity D_L (cm ² /s)* | 1.6×10^{-5} | 1.8×10^{-5} | 2.0×10^{-5} | 2.11×10^{-5} | 2.32×10^{-5} | 2.52×10^{-5} |
| Solubility Co (mol/cm ³) | 2.0×10^{-7} | 1.7×10^{-7} | 1.4×10^{-7} | 1.2×10^{-7} | 0.92×10^{-7} | 0.7×10^{-7} |
| Effective Electrical Conductivity κ_e ($\Omega^{-1} \text{cm}^{-1}$)* | 0.254 | 0.300 | 0.344 | 0.390 | 0.434 | 0.480 |

* Estimated from correlations in literature

was evaluated by assuming a particular set of exchange current density (i_0) and charge transfer coefficient (α) values. The assumed values of i_0 and α had upper and lower constraints based on physical considerations. At each temperature experimental data points were chosen on each polarization curve and the minimization procedure was carried out. Table 7.4 gives the best fitting values for i_0 and α .

7.4 Apparent Activation Energy

The apparent activation energy, E_a for an electrochemical reaction is given at constant electrode potential by

$$E_a = \frac{R(\ln i_2 - \ln i_1)}{\frac{1}{T_2} - \frac{1}{T_1}} \quad (7.3)$$

The potential of the reference electrode is dependent upon the temperature hence only apparent activation energies can be estimated.

The apparent activation energies for the new electrode for hydrogen oxidation reaction at overpotential, $\eta = 10$ mV, 25 mV and 50 mV were obtained from a plot (fig. 7.10) of logarithm of current density against the reciprocal of temperature. Table 7.5 gives the apparent activation energy for the electrode at different over voltages.

Table 7.4 Kinetic Parameters for Hydrogen Oxidation Reaction

| Temperature °C | Charge Transfer Coefficient (α) | Exchange Current Density (i_0) mA/cm² |
|---------------------------|--|--|
| 25 | 0.57 | 6.6 E-6 |
| 35 | 0.59 | 15.1 E-6 |
| 45 | 0.60 | 31.0 E-6 |
| 55 | 0.61 | 52.7 E-6 |
| 65 | 0.63 | 118.5 E-6 |
| 75 | 0.65 | 310.0 E-6 |

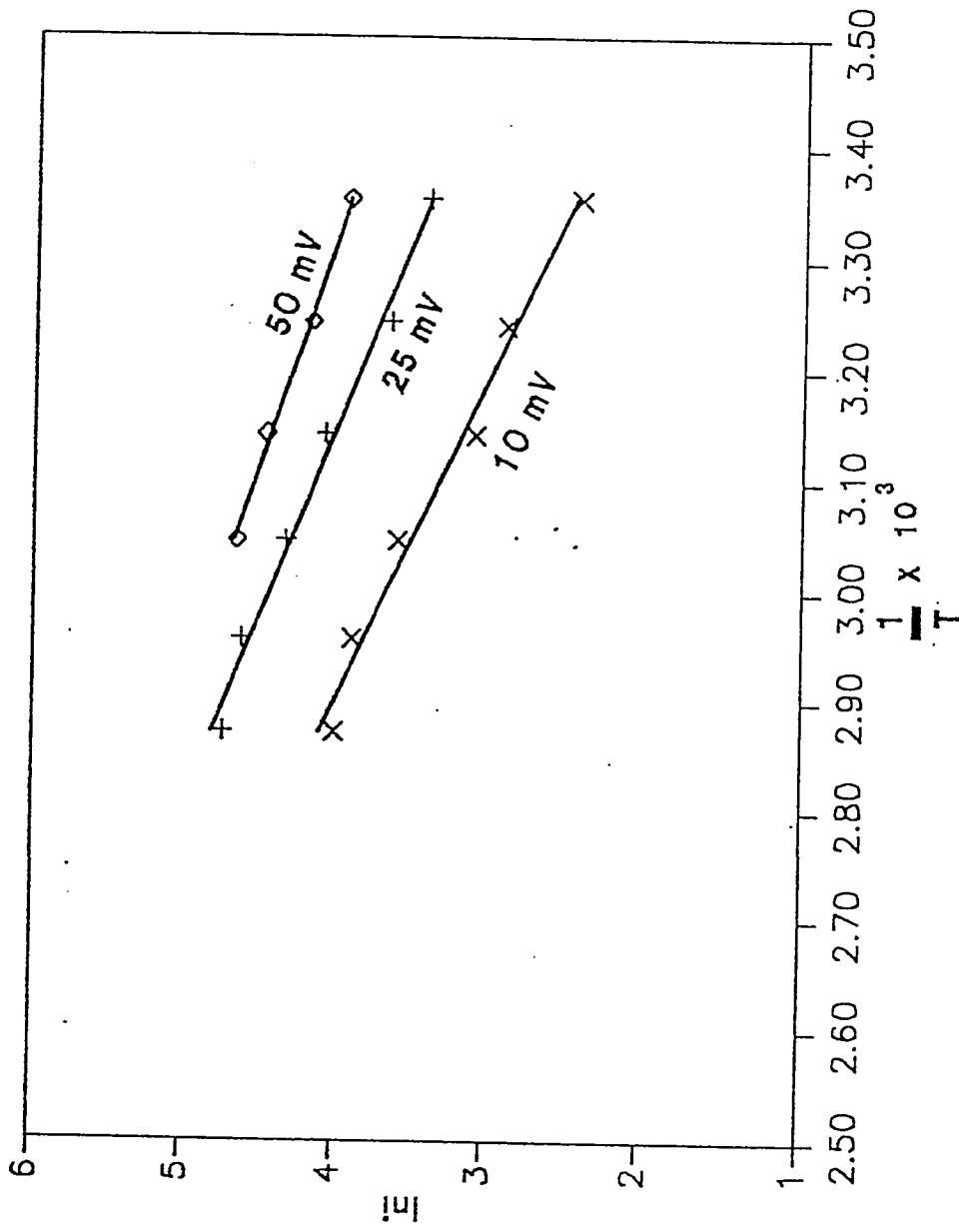


Fig. 7.10 Logarithm of Current Density(i) Vs $1/T$ for constant Overvoltage(η)

Table 7.5 Apparent Activation Energy at different Overvoltages

| Overvoltage (mV) | Apparent Activation Energy (kJ/mol) |
|-----------------------------|--|
| 0 | 27.9 |
| 10 | 24.45 |
| 25 | 20.10 |
| 50 | 16.52 |

7.5 . Discussion of Polarization Results

It can be seen from figs. 7.4 to 7.9 that with increasing current density the IR free overvoltage i.e. losses also increase. For the range of current densities investigated it appears that the current density varies almost linearly with overpotential. This behavior is due to the fact that at lower polarization activation overpotential is very high while concentration and ohmic overpotentials are small.

From the figures it can be clearly discerned that the overvoltage at a given current density decreases with increase of electrolyte temperature. The reason behind this decrease in overvoltage at higher temperatures is still not clear. It is proposed that several different but partially co-operative and partially opposing processes are responsible for the experimentally observed phenomena of decrease in overvoltage with increase of temperature. Some of these processes are,

1. Change in electrolyte / gas hold up of the electrolyte.
2. Increase of electrolyte conductivity with increase of temperature.
3. Increase of exchange current density and charge transfer coefficient with temperature.

At 75°C the new electrode is able to support a current density of 115 mA/cm² at an overpotential of 24 mV(fig 7.9).While the old electrode could support the same current density at an overpotential of 35 mV. Under the experimental conditions kept for this study the overpotentials were always less than 70 mV. The polarization curve for the new electrode is always lower than that for the old electrode especially at higher current densities. This means the polarization resistance of the new electrode is smaller than the old electrode at

decrease in contact resistance(less Ohmic Polarization) brought about by copper present in the active layer and conducting grid. The new electrode also has a higher Electrocatalytic activity.

Fig. 7.3 shows the ohmic resistance of the electrolyte at various temperatures as a function of current density. From the figure it can be seen that the electrolyte resistance decreases with increase of temperature. This is because of the fact that at higher temperature the conductivity of KOH is more. In fact the conductivity of KOH increases more than twice from 25°C to 75°C as can be seen from the figure.

At 25°C (fig. 7.4) the electrode is not able to support current densities which are higher than 60 mA/cm². This implies that this is a limiting current density for the new electrode at 25°C. Thus the present value of limiting current density at 25°C makes the operation of the new electrode at room temperature very uneconomical. A through study of factors which affect the limiting current density is required to explain this decrease in limiting current density with decrease of temperature. The new electrode starts showing better performance at 55°C (fig. 7.6).

The apparent activation energy found for the new electrode at an overpotential of 10 mV is 28.63 kJ/mol. The activation energy for the new electrode at zero polarization is estimated to be 27.9 kJ/mol. For the previous electrode the activation energy was 31.35 kJ/mol. The lower value of activation energy indicates that lower activation energy results in lower polarization resistance. Which means better performance.

The kinetic parameters namely exchange current densities (i_0) and charge transfer coefficients (α) were estimated at different temperatures by using the spherical flooded Raney catalyst grain model and the experimental polarization curves. Table 7.4 gives the values of i_0 and α for the new electrode. The exchange current density follows an exponential relation with temperature (fig.7.11). The exchange current densities and charge transfer coefficients estimated for the new electrode are greater than those for the previous electrode. For example at 75°C the i_0 for the new electrode is found to be 3.10×10^{-4} A/cm² while for the old electrode it was 2.80×10^{-4} A/cm². The addition of Cu₂O to the catalyst is responsible for bringing about this increase in the exchange current density.

7.6 Experimental Results for Long Term performance Test

Steady state potentiostatic long term performance tests were carried out for the new electrode at various temperatures. The voltage between the test electrode and reference electrode was kept constant and current (i.e. Reaction rate) was monitored as a function of time.

For plotting the potentiostatic transient current decay experimental results the concept of Residual Electrode Activity (R.E.A.) was used. Residual electrode activity (R.E.A.) is defined as the ratio of electrode current density at any time = t to the initial electrode current density at time = 0. Thus,

$$\text{R.E.A.} = \frac{i_{t=t}}{i_{t=0}}$$

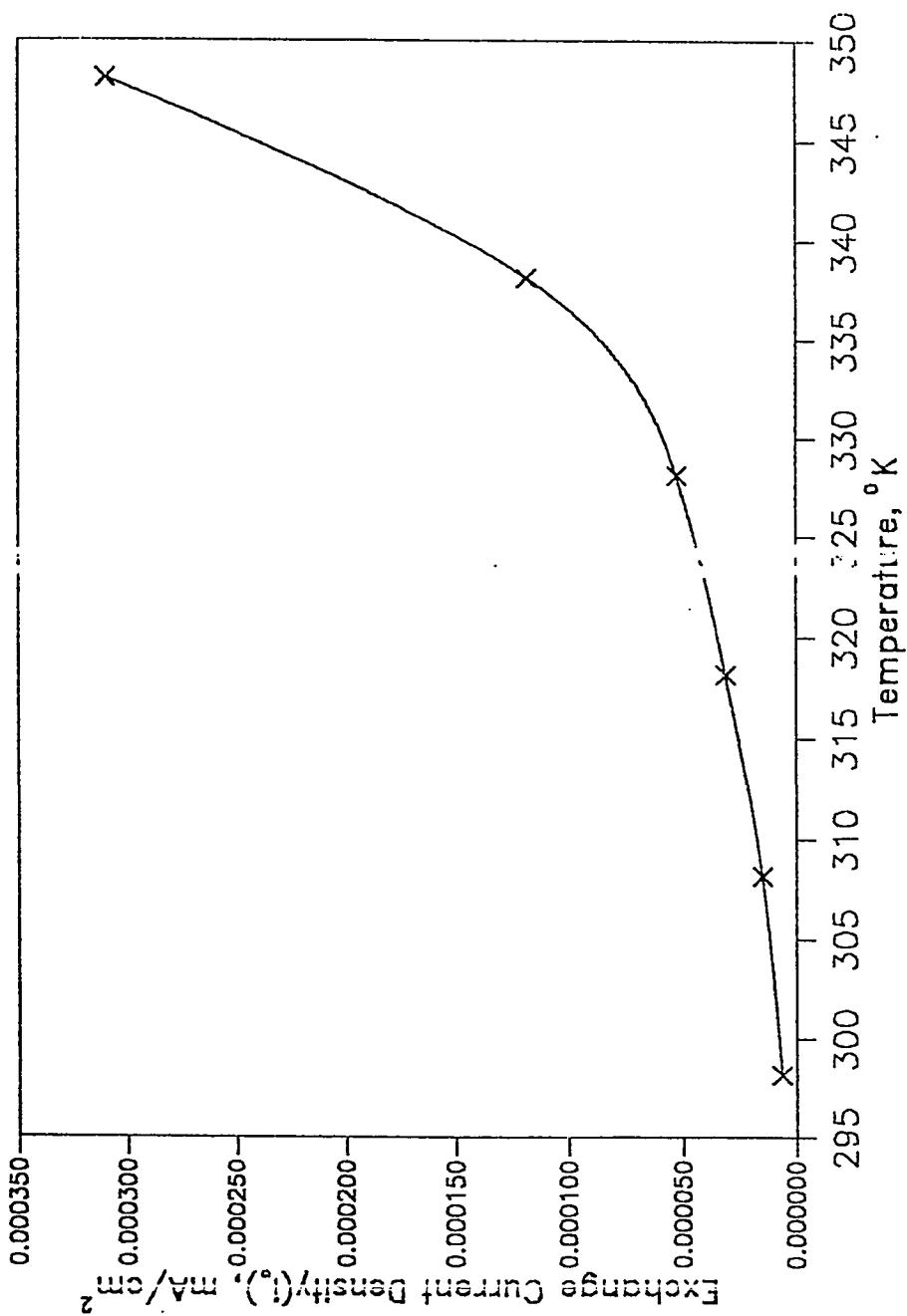


Fig. 7.11 Exchange Current Density as a Function of Temperature

Figs. 7.12 to 7.14 show the results of potentiostatic long term performance test on the new electrode at various temperatures.

Galvanostatic steady state long term performance test of the new electrode was also carried out for the new and previous electrode. For this particular test the current flowing through the half cell was kept constant and the potential of the test electrode was observed as a function of time. Fig. 7.15 shows the result of galvanostatic long term study.

7.7 Application of Deactivation Model

The spherical flooded Raney catalyst grain model has been modified to study the effect of deactivation phenomena in gas diffusion electrodes. The deactivation model assumes a first order reactant-gas-concentration-independent deactivation. The activity of the catalyst is then at any time t is given by

$$\bar{a} = \bar{a}_0 \exp(-Kat) \quad (7.4)$$

Where a_0 the activity of the catalyst at zero time as unity. The equation 7.4 can be written as

$$\text{R.E.A.} = \exp(-k_d t) \quad (7.5)$$

The time dependent electrode current densities for an isothermal gas diffusion electrode with no gas diffusion limitation in the macropores is given by the following expression,

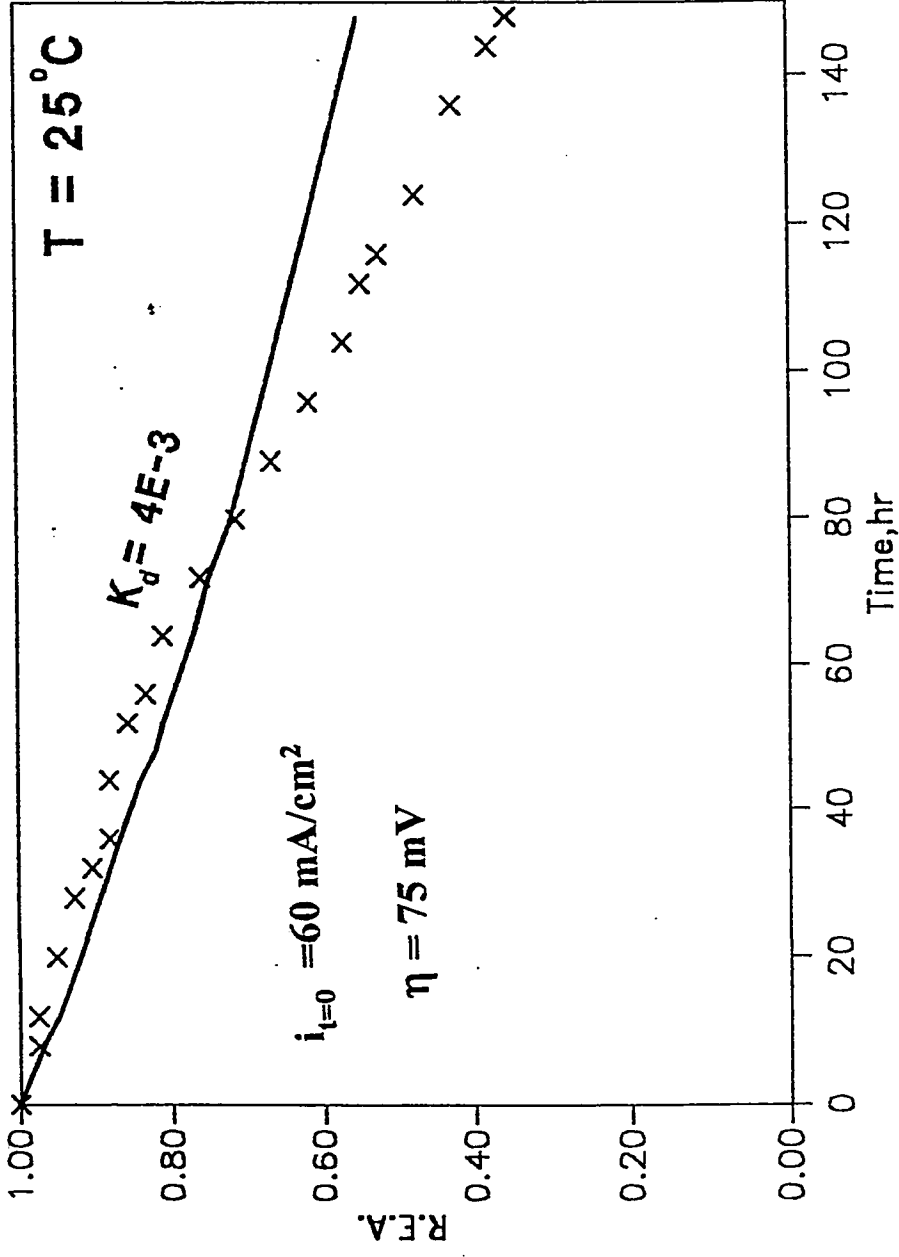


Fig. 7.12 Potentiostatic Long Term Performance Test at 25°C

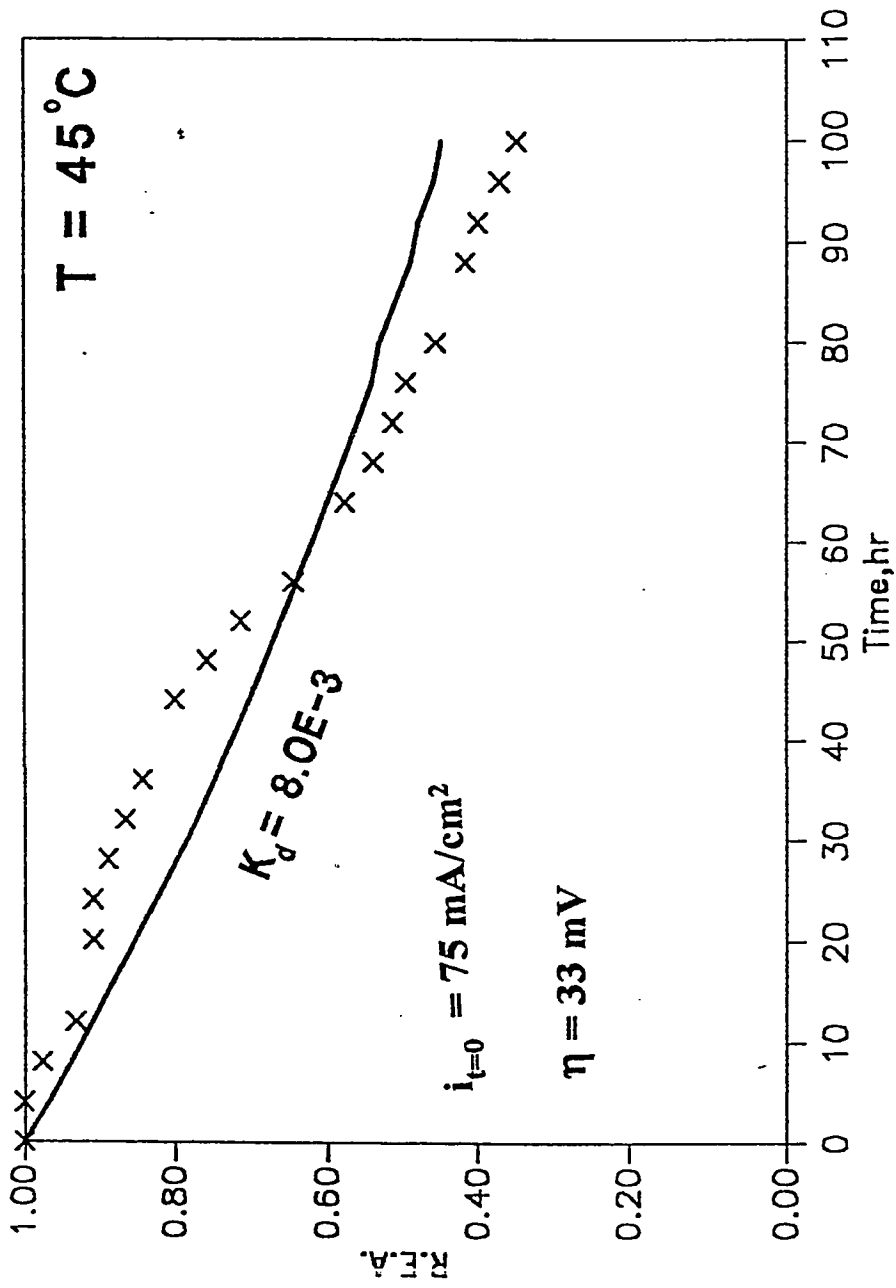


Fig. 7.13 Potentiostatic Long Term Performance Test at 45°C

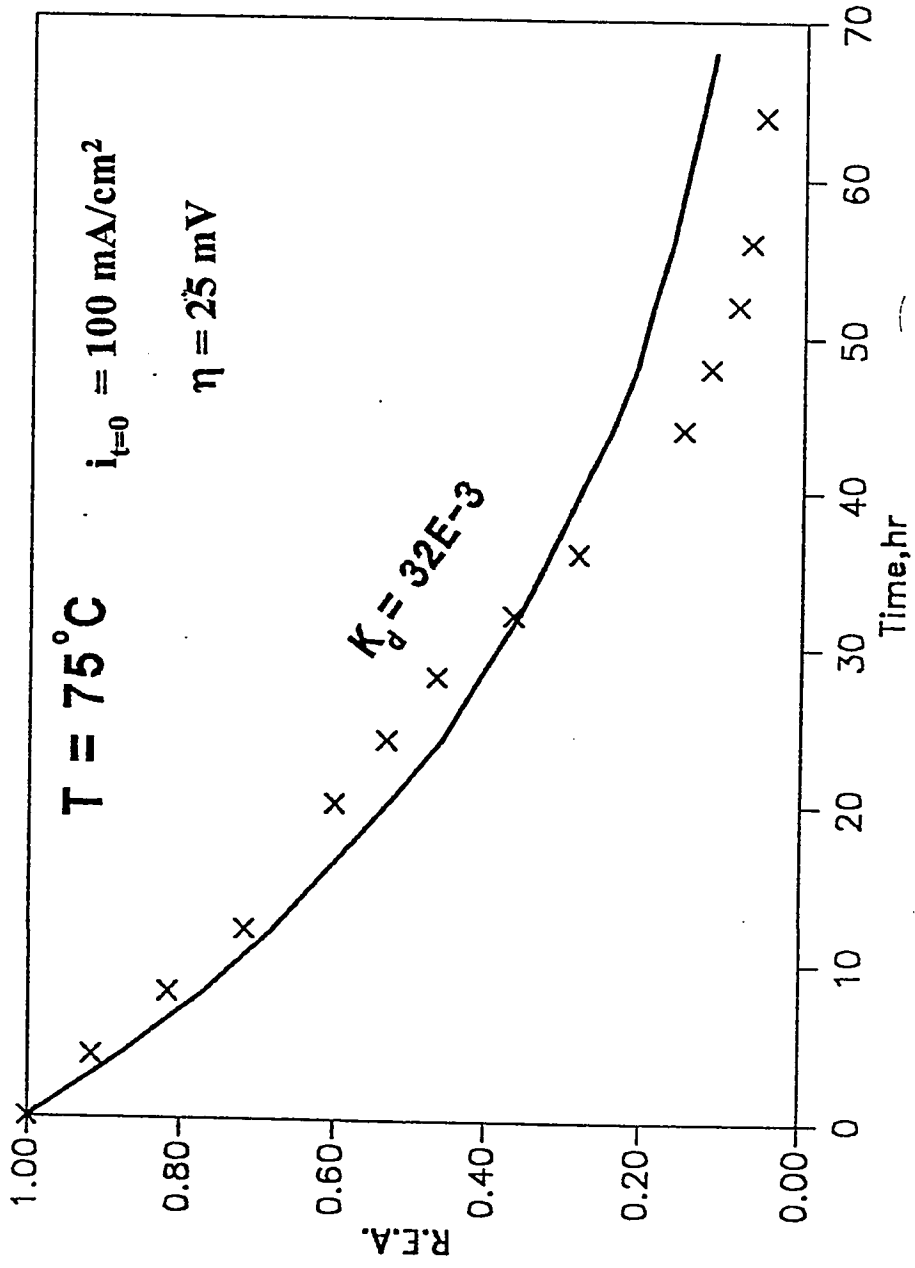


Fig. 7.14 Potentiostatic Long Term Performance Test at 75°C

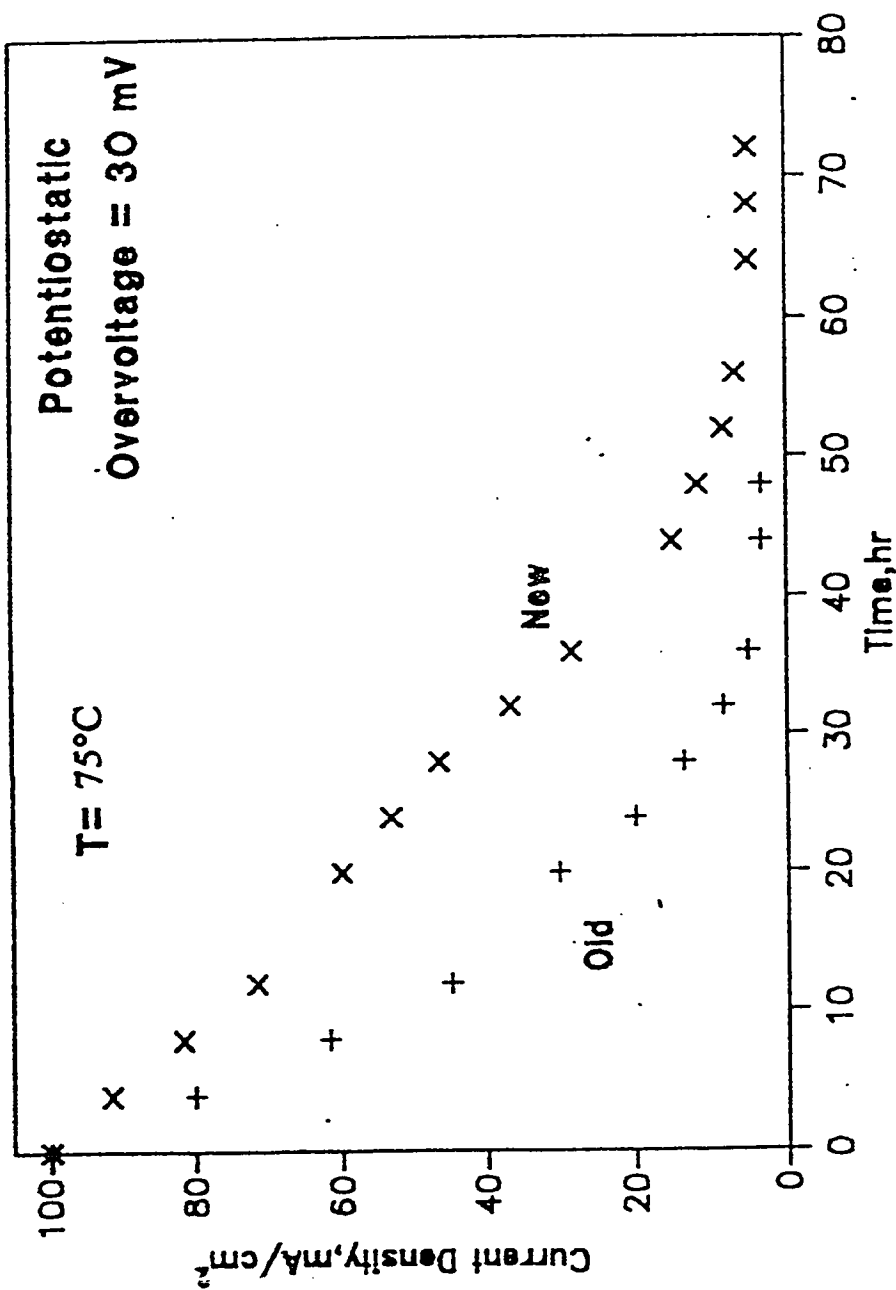


Fig. 7.15 Potentiostatic long term performance of the new and old electrode at 75°C

$$\frac{d^2\eta}{dx^2} = \frac{2nFD_L}{\kappa R} C_o \left(1 - \frac{A_3}{A_2}\right) \left[\sqrt{\frac{i_o f^o}{nFD_L}} \exp\left(\frac{-K_d t}{2}\right) \sqrt{\frac{A_2}{C_o}} \right. \\ \left. \coth\left\{ \sqrt{\frac{i_o f^o}{nFD_L}} \exp\left(\frac{-K_d t}{2}\right) \sqrt{\frac{A_2}{C_o}} R \right\} - \frac{1}{R} \right] \quad (7.6)$$

with the boundary conditions as

$$\text{B.C.1} \quad x=0 \quad \eta = \eta_o$$

$$\text{B.C.2} \quad x=1 \quad \frac{d\eta}{dx} = 0$$

here,

$$A_2 = \exp\left(\frac{\alpha z F}{RT} \eta\right)$$

$$A_3 = \exp\left[\frac{-(1-\alpha)zF}{RT} \eta\right]$$

Equation 7.6 when solved with the above boundary conditions and a set of parameters including deactivation rate constant gives the time decay of electrode current densities.

7.8 Estimation of Deactivation Constant

The rate of reaction for an electrochemical reaction is given by current density. The decay of the electrode current density is assumed to be exponential with time. Therefore for estimating the apparent deactivation constant logarithm of the current density was plotted against time on stream. Fig. 7.16 gives the best fit

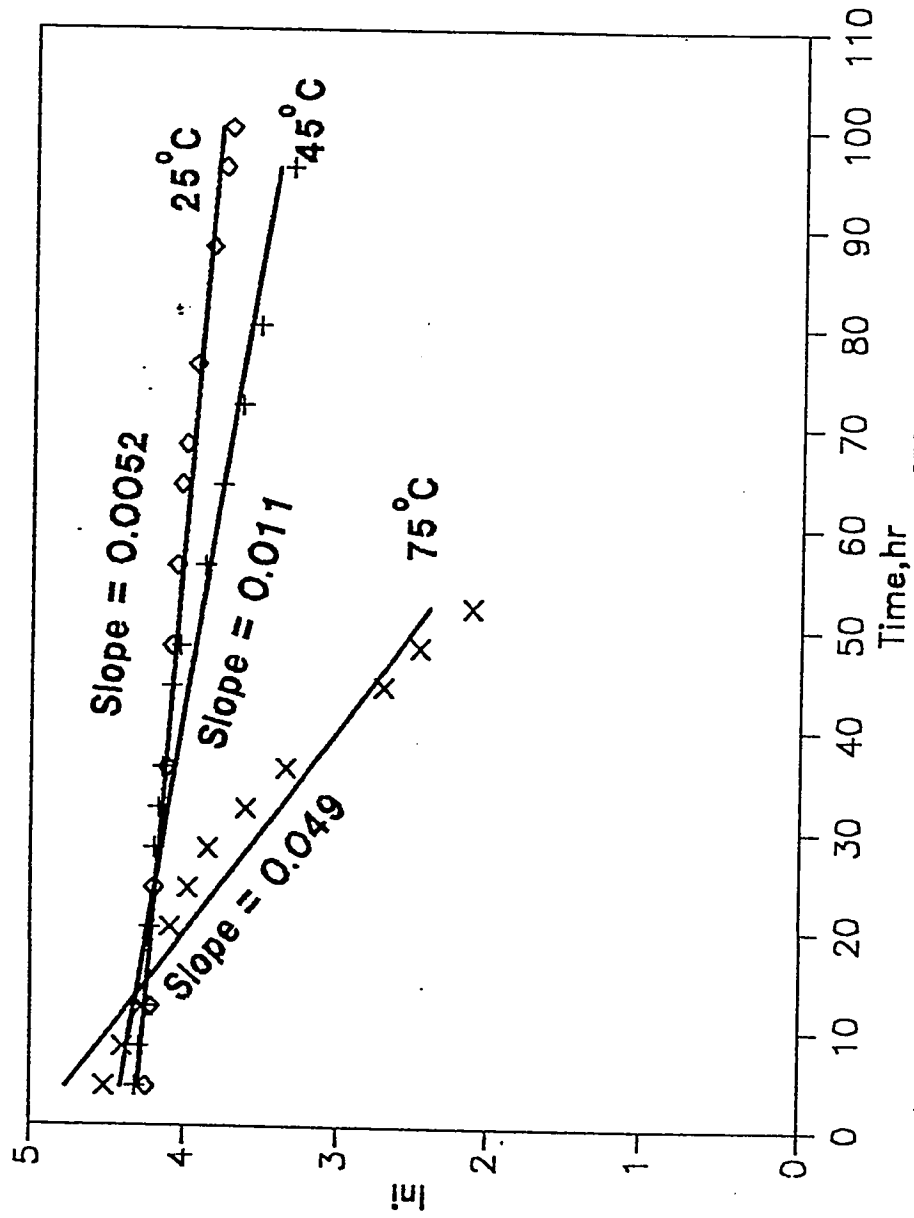


Fig. 7.16 Logarithm of Current Density as a Function of time on stream.

line to the $\ln i$ versus t data. From the slopes of these lines the apparent deactivation constants are estimated at each temperature.

For estimating the deactivation constant by the modified spherical Raney catalyst grain model. The model was fit to the experimental R.E.A. versus time data by curve fitting with the deactivation rate constant (Figs. 7.12 to 7.14). The deactivation rate constant was determined by a similar approach as that was used for estimating i_0 and α . However in this case the calculated and experimental current densities were functions of time only. The experimental R.E.A. versus time plots were used as a basis for the model equation to fit. N data points were chosen from the experimental curve and the function, $S = \sum (i_{\text{cal}} - i_{\text{exp}})^2$ was evaluated by assuming a particular value of K_d . In this case there was only one parameter for curve fitting therefore it was not possible to predict the new steady state reached by the electrode upon deactivation. Table 7.6 gives the apparent deactivation constants at three different temperatures.

7.9 Characterization of Deactivated Electrodes

The deactivated Raney-Ni/ PTFE electrode has been characterized by

1. BET Surface Area Measurement
2. X Ray Diffraction
3. Scanning Electron Microscopy

The main purpose behind carrying out this characterization was to find morphological and chemical changes due to deactivation. BET surface area measurement gave the surface area of the deactivated electrode sample to be $16.32 \text{ m}^2/\text{g}$. The BET surface area for the fresh electrode was $24 \text{ m}^2/\text{g}$. The decrease in surface area of the electrode can be correlated with the deposition of

Table 7.6 Apparent Deactivation Constants at Different Temperatures

| Temperature °C | App. Deactivation Constant (Model) hr⁻¹ | App. Deactivation Constant(Plot) hr⁻¹ |
|---------------------------|---|---|
| 25 | 4.0 E-3 | 5.2 E-3 |
| 45 | 8.0 E-3 | 11.0 E-3 |
| 75 | 32.0E-3 | 49.0 E-3 |

KOH on the micropores. There was no K in the fresh electrode. The XRF analysis confirmed the presence of potassium in the deactivated sample. Fig. 7.17 gives a micro graph of the deactivated sample from the mesh side. Fig. 7.18 gives EDS spectra for the deactivated sample.

7.10 Discussion of Deactivation Results

The performance of a gas diffusion electrode depends on two main factors namely,

1. A suitable micro geometrical structure to have maximum gas-liquid interfacial area.
2. Improvement of the local intrinsic activity of the surface by using appropriate electrocatalyst.

The structure of the active layer or the reaction layer where electrochemical reaction occurs constitutes the most important part of a gas diffusion electrode. The steps which could control the current produced are

- a) The supply of reactant gas to gas side of active layer.
- b) Diffusion of reactant gas through the active layer to gas-liquid interface.
- c) Diffusion of dissolved gas from gas-liquid interface to catalyst clusters.
- d) Reaction at catalyst clusters.

The slowest step is the diffusion of dissolved gas to the catalyst clusters located throughout the reaction layer. More gas-liquid interfacial area throughout the reaction layer reduces the gas diffusion distance and thus improves the performance of gas diffusion electrode.



Fig. 7.17 SEM Micrograph of the Deactivated Electrode from mesh side.

SEEE\ETUP SSG

SSQ: SSG

SEMI-QUANTITATIVE ANALYSIS: M416: SAMP B, SQUARE
EL NORM. K-RATIO

CU-K 0.43581 +/- 0.00347
AL-K 0.00198 +/- 0.00014
NI-K 0.51388 +/- 0.00330
K -K 0.04636 +/- 0.00054

ZAF CORRECTION 20.00 KV 49.00 Degr

No. of Iterations 1

| | K | [Z] | [A] | [F] | [ZAF] | ATOM.% | WT.% |
|------|-------|-------|-------|-------|-------|--------|--------|
| CU-K | 0.435 | 1.032 | 1.000 | 1.000 | 1.032 | 48.47 | 44.13 |
| AL-K | 0.002 | 0.934 | 3.754 | 2.999 | 3.048 | 2.58 | 1.19 * |
| NI-K | 0.513 | 0.988 | 1.000 | 1.000 | 0.988 | 49.43 | 49.69 |
| K -K | 0.047 | 0.986 | 1.101 | 0.775 | 1.000 | 1.10 | 0.80 |

* - High Absorbance

SSQ:

: TN-5500 LPM - Saudi Arabia JSM-040

SUN 21-FEB 8X 11:40

: Cursch: 0.0000KV = 0

: ROJ

: (1) 0.000: 9.640

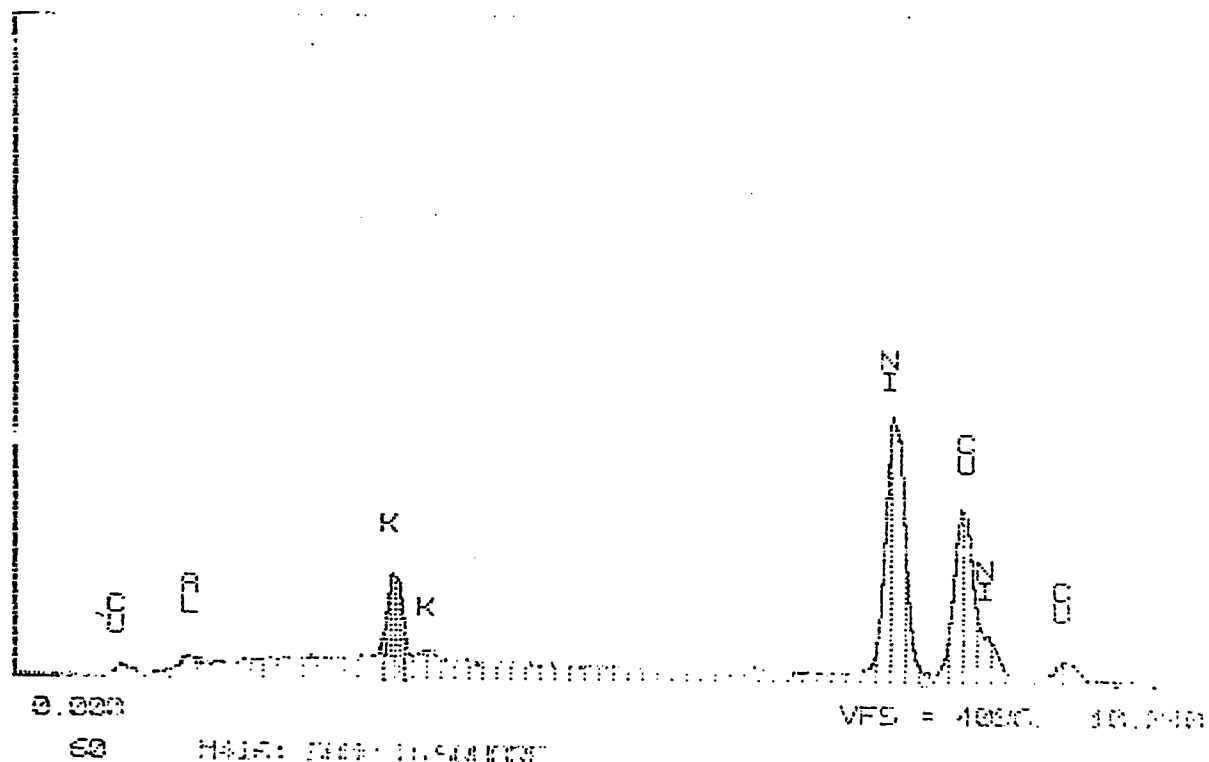


Fig. 7.18 EDS Spectra for the Deactivated Electrode.

The decay of electrode current density (figs. 7.12 - 7.14) with time on stream is a cumulative effect of combination of several independent processes.

Ewe, Justi and Selbach(26) have reported that the method of heat treatment employed during catalyst preparation affects stability of fuel cell electrodes. During catalyst preparation after leaching out Al- fraction of the basing Raney-Ni sponge obtained is dried in vacuum. This drying is accomplished by slow air oxidation of the sponge. This air oxidation of the catalyst produces α - $3\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ which is very active but unstable. Therefore further complicated heat treatment is done to convert α - hydroxide to more stable NiO. Not all α -hydroxide gets converted into NiO. During this heat treatment process a recrystallization of the strongly disordered Raney-Ni sponge occurs.

Maximovitch and Durand (61) have confirmed that α - $3\text{Ni}(\text{OH})_2$ has a passivating effect on the hydrogen oxidation reaction. Moreover due to recrystallization of Raney-Ni sponge coarser catalyst grains are formed(26). Electrodes fabricated from coarser catalyst grains show lower performance due to slow hydrogen diffusion into the catalyst particles(20).

Uneven current and potential distribution in the active layer leads to electrode corrosion. Because of heterogeneity of the electrode structure the current and potential distribution in the active layer are uneven. Therefore in some regions the local overvoltage may be quite high. This high overvoltage results in the anodic dissolution of copper thereby causing deactivation.(20)

Inability of hydrogen to reach the minor fractions of electrode. In the active layer macropores are filled with gas while micropores are flooded with

electrolyte. Not all hydrogen can reach the smaller pores of the active layer because of slow diffusion. The initial heat of adsorption for hydrogen on Raney-Ni is approximately 90 kJ/mol(62). This initial high heat of adsorption results in the evaporation of the electrolyte. This evaporated electrolyte then subsequently cools down and deposits on the gas diffusion pores. This deposition of electrolyte on the gas pores offers diffusion resistance to the diffusion of hydrogen. The gas diffusion process being slowest controls the generation of current in gas diffusion electrode.

Rotenberg and Srinivasan(63) have shown that KOH solution affects the hydrophobicity of PTFE. They carried out contact angle measurement experiments with KOH solution and teflon. They concluded that with increase in temperature and KOH concentration, PTFE undergoes chemical changes e.g. change of roughness. Thus the chemical change in hydrophobicity of PTFE brought about by KOH solution results in depletion of gas diffusion macropores. This affects the rate of current production.

Atmospheric carbon dioxide dissolves in KOH solution and reacts with it. The reaction of CO_2 with the hydroxyl ions to form carbonate species which can precipitate and may block the micropores of Raney-Ni electrode. It can also stay as liquid and reduce the ionic conductivity of the electrolyte. Lower wettability and pH rise in the carbonate - containing electrodes results in lower performance when compared with pure KOH solution.(64)

The extent to which each of the above factors affect the decay of electrode current density requires further in-depth study of deactivation phenomena.

BET surface area measurement for the spoiled electrode indicate less surface area as compared to the fresh electrode. A significant part of the change in surface area is also brought about by the evaporation of water and deposition of KOH on the pores after removing the electrode from half cell. The presence of K in the active layer of the electrode has been confirmed by SEM and XRF analysis.

From figs. 7.12 to 7.14 it can be observed that initially the deactivation is slow. As the time on stream increases the deactivation becomes more rapid. This suggests the possibility of two deactivation mechanisms. This behavior can be explained by considering the diffusion resistance of the feed gas in the active layer of the electrode. Initially high heat of adsorption evaporates electrolyte. With increase of time on stream the KOH deposited in the pores increases diffusion resistance. Hence the rate of deactivation also increases.

From figs. 7.12 to 7.14 it can be easily seen that the decay of current density is more at higher temperature than at lower temperature. This behavior can be explained by the fact that at higher temperature more KOH gets evaporated. Also at higher temperatures nickel hydroxide is more unstable. It gets converted into NiO which passivates the electrode.

Table 7.6 gives the values of apparent deactivation constants at different temperatures estimated from $\ln i$ versus t plot and the deactivation model. From the table it can be deduced that the apparent deactivation constant estimated from the plot is lower than that of deactivation constant obtained by the deactivation model. This discrepancy is due to the negligence of mass transfer terms in the modified

spherical Raney catalyst grain model. From this it can be concluded that the diffusion limitation plays an important role in the deactivation behavior.

From potentiostatic long term performance test (ref. fig. 7.15) performed on the new and previous electrode it can be observed that the previous electrode decays faster than the new electrode. Copper impregnation adds to the stability of the new electrode. The activity of the new electrode for hydrogen oxidation at 75°C becomes very small in about 60 hrs while the previous electrode gets destroyed in 40 hrs at the same temperature. Thus it can be conferred that the long term performance of the new electrode is better than that of the previous electrode.

Chapter 8

CONCLUSIONS

1. The polarization of the new electrode is found to be less as compared to the electrode used in earlier studies in our laboratory. The performance of the new electrode is higher at higher current densities. Copper impregnation and improved micro geometry of the new electrode contribute to its better performance. The use of Cu mesh instead of Ni mesh reduces the contact resistance of the new electrode.
2. The values found for the exchange current densities for the new electrode were 6.6 E-6 A/cm^2 (@ 25°C) and 3.1 E-4 A/cm^2 (@ 75°C). While the charge transfer coefficient varied from 0.57 to 0.65 in the temperature range studied. The kinetic parameters namely exchange current density and charge transfer coefficient estimated for the hydrogen oxidation reaction on this new electrode are higher than that of the previous electrode. The higher value of the kinetic parameters for the new electrode gives less activation energy(28 kJ/mol). This shows better electrocatalytic activity.
3. The deactivation constant varied from 4 E-3 hr^{-1} at 25°C to 32 E-3 hr^{-1} at 75°C The deactivation constant estimated for the new electrode increases with temperature. Higher temperature and higher current densities are detrimental to the life of electrode. Copper improves the stability of the new electrode.

Chapter 9

RECOMMENDATIONS

1. The polarization behavior of the electrode should be investigated for higher current densities so as to obtain limiting current densities.
2. Impedance spectroscopy with an appropriate impedance model should be applied to the electrode so as to analyze the contribution of Ohmic, Faradaic and mass transport resistances to the effective impedance of the electrode.
3. The performance of electrode prepared by Dry Method and Wet Method should be investigated to arrive at the optimum fabrication technique. Attention should be paid to improve the gas-liquid interfacial area.
4. Raney - Ni should be alloyed with some other metals like Cr, Ti and impregnated with Copper to improve the electrocatalytic activity.
5. The effect of electrolyte concentration on the exchange current density and deactivation constant should be studied.
6. A deactivation model which takes into account the diffusion of reactant gas should be developed.

REFERENCES

1. Srinivasan, S. "Fuel Cells for Extraterrestrial and Terrestrial Applications." *J. of Electrochem. Soc.*, 136/2, 1989:41C-48C.
2. Kleywegt, G., J. and Willem L., Driessen. "Fuel Cells Revisited." *Chemistry In Britain*, May 1988:447-450.
3. Lindstorm, O. "Fuel Cell Technology and Applications." *Chemtech* Aug. 1988 :490 - 495
4. Walsh, M., P. "The importance of fuel cells to address the global warming Problems" *J. of Power Sources*, 29, 1990:13-28.
5. Benjamin, T., J. Camara and Marianowski. "Handbook of Fuel Cell Performance " USDOE contract no. EC-77-C-03-1545:1980.
6. Prentice, G. "Fuel Cells: Principles and Prospects." *Chemtech*, Nov. 1984:684-694.
7. Broek, Vanden H. "Alkaline Fuel Cells at ALENCO." *J. Power Sources*, 29, 1990:201-206.
8. "Recent Developments in Fuel Cells", *J. Electrochem. Soc.* 139/10 October 1992:3008-3010.
9. Applby, A. J. and Foulkes, F. R. 'FUEL CELLS HANDBOOK.' Van Nostrand Reinhold, N. Y., 1989.
10. Bacon, Francis T. "The Fuel Cell: Some Thoughts and Recollections." *J. Elechem. Soc.* Jan., 1979:7C-17C..
11. Fickette, A., P. "Fuel Cells." *Encyclopedia of Physical Science and Technology*, Vol. 5, Academic Press Inc. 1987:629-639.
12. Strasser, K. "The Design of AFC." *J. Power Sources*, 29, 1990:149-168.
13. Linden, D. "Handbook of Batteries and Fuel Cells." Mc-Graw Hill, 1983.

14. Kordesh, K. and Jehangir, S. *Electrochimica Acta* 29, 1989:1984-1988.
15. Celikar, H. "Effect of carbon monoxide, carbon dioxide and nitrogen on the electrokinetics of Gas Diffusion Electrodes in Hydrogen/Oxygen Alkaline Fuel Cells." PhD Dissertation, KFUPM, OCT:1990.
16. Hammett, A. and Troughton, "Electrocatalysis and the Direct Methanol Fuel Cell." *Chemistry and Industry*, July 1992:482-483.
17. Kordesh, K. V., *J. Electrochem. Soc.*, 125(3), 1978:77C.
18. Bacon, F. T., Adams, A. M. and Watson, R. G. H., *FUEL CELLS*, Chap. 4, Ed. W. Mitchell, Academic Press, 1963.
19. Niedrich, L. and Alford, H. R., *J. Electrochem. Soc.*, 112, 1977:117.
20. Jenseit, W., Khalil, A., Wendt, H., *J. of Applied Electrochemistry*, 20:1990:893.
21. Mund, K., Richter, G., Von Sturm, F., *Journal Electrochem. Soc.*, 124(1), 1977
22. Ewe, H., Justi, E., Schmidt, A., *Energy Conversion*, 14, 1975:35.
23. Tomido and Nakabayashi, *J. Electrochem. Soc.* 136(11), 1989:3296
24. Ewe, H., Justi, E., Schmidt, A., *Energy Conversion*, 20, 1980:75.
25. Ewe, H., Justi, E., Selbach, H., *Energy Conversion and Management*, 23:1983:245.
26. Ewe, H., Justi, E., Selbach, H., *Energy Conversion and Management*, 4:1984:89.
27. Ewe, H., Justi, Selbach, H., *Energy Conversion and Management*, 24:1984:94.
28. Brennecke, P., W., Ewe, H., Justi, and Selbach, *Energy Conversion and Management*, 24:1984:98.
29. Kenjo, T., *Bulletin Chemical Soc. Japan*, 54:1981:2553.
30. Kenjo, T., *Bulletin Chemical Soc. Japan*, 56, 1983:1.
31. Candy, J. P., and Foilloux P., *J. Chemical Soc. Faraday Trans.* 79, 1983:823.

32. Markina, E., L., Tarasevich, M., R., Efremov, B., *Electrochimica Acta*, 24, 1988:93.
33. Moren, C., J., *Journal Electrochem. Soc.* 132(2)1985:383.
34. Padyukova, G., L. et al. *Electrochimica Acta*, 22, 1986:247.
35. Kenjo, T., *J. Electrochem. Soc.*, 132(2), 1985:383.
36. Mund, K., Richter, G., Van Strum, "Electrocatalysts for the Reactions in AFC." *Proceedings workshop on 'Electrocatalysis of Fuel Cell Reactions. Vol. 79- 2, Eds. Graday, Srinivasan, Dudley, 1978:67.*
37. Pattabiraman, R. et al. *Transaction of the SAEST*, 22(1), 1987:25.
38. Grune, H., Siemens, F., *Entwickl-Ber*, 12(5), 1983:285.
39. Abramson O. , S., Chernyshov, Pshenickov, *Electrochimica Acta*, 12(11), 1976.
40. Al-Saleh , Gultekin, Zakri and Celikar., "Kinetics of Electrochemical Reactions: An Overview." *Proceedings of Third National Meeting of Chemist KFUPM, March, 1989:537-548.*
41. Heitz, E. and Kreysa, G., "Principles of Electrochemical Engineering." *Extended version of a DECHEMA Experimental Course, FRG, 1986.*
42. Tilak, B. V., Yeo and Srinivasan. "Comprehensive Treatise of Electrochemistry." *Plenum Press, 1981:39.*
43. Bockris, J.O.M and Reddy, A.K.N., "Modern Electrochemistry." Vol. 2 *Plenum Press , 1970.*
44. Bockris, J.O.M. and Srinivasan, S. "Fuel Cells: Their Electrochemistry." *Chapter 9, McGraw Hill , 1969:469-510.*
45. Austin, L.G., Ariet, M., Walker, Woods, Comyan, *IEC Fundamentals* 4:1965:321.
46. Chan, K. Y., Efthymiou, G. S., Cochetto, J.F. *Electrochimica Acta* 32, 1987:1227.
47. Chirkov, Yu.G., *Soviet Electrochemistry*, 8, 1972:358.
48. Pshenichnikov, A.G., Kruyukov, Yu.K., Burshtein, R.Kh., Astakhov, I.I.,

- Surikov, V.V. *Soviet Electrochemistry*, 12, 1976:1183.
49. Burshtein, R.Kh., Dribinskii, A.V., Tarasevich, M.R., Chimadzhev, Yu.A., Chirkov, Yu.G., *Soviet Electrochemistry*, 7, 1971:1762.
50. Chirkov, Yu. G., *Soviet Electrochemistry*, 11, 1975:36.
51. Lampinen, M.J. and Viitanen M. "A Mathematical Model and Optimization of the Structure for Porous Air Electrodes." *J. Power Sources*, 32, 1990:207.
52. Giner, J., "From Electrocatalysis to Fuel Cells." Ed. G. Sandstede, University of Washington Press, Seattle, 1972.
53. Cutlip, M.B. "An Approximate Model for Mass Transfer with Reaction in Porous Gas Diffusion Electrodes." *Electrochimica*, 20, 1975:767-772.
54. Iczkowski, R.P. and Cutlip, M.B. "Voltage Losses in Fuel Cell Cathodes." *J. Electrochemical Soc.* 127, 1980:1433-1440.
55. Celikar, H., Al-Saleh, M.A., Gultekin, S. and Al-Zakri, A.S. "Mathematical Model for the Performance of Raney Metal Gas Diffusion Electrodes." *J. Electrochemical Society*, 138/6, 1991:1671-1681.
56. Kimble, M.C. and White, R.E. "A Mathematical Model of a Hydrogen/oxygen Alkaline Fuel Cell." *J. Electrochemical society*, 138/11, 1991:3370-3382.
57. Kimble, M.C. and White, R.E. "Parameter Sensitivity and Optimization Prediction of a Hydrogen/Oxygen Alkaline Fuel Cell Model." *J. Electrochem Society*, 139/2, 1992:478-484.
58. Yang, Shian-Cherng and Bjornbom, P. "Modeling and Simulation of the Operation of AFC cathode by using concentrated electrolyte transport theory." *Electrochimica Acta*, 37/10, 1992:1831-1843.
59. Bolvin, K., Longhi, P. and Shnurnberger in *Fuel Cell Seminar Abstract*, Long Beach California, 1988:164.

60. Jung, M. and Dohren, H. V. DBP 1258 , 398 1968.
61. Maximovitch, S. and Durand, R. J. Electroanal. Chem. 149,1983:237-277.
62. Satterfield, C. N. " Heterogeneous Catalysis" MIT press, Cambridge, 1991.
63. Rotenberg, Y. and Srinivasan, S. J. Electroanal. Chem. 213, 1986:43-51.
64. Striebel, K. A., McLarnon, F. R. and Cairns, E. J., Journal Electrochem. Society, vol. 137, No. 11, Nov.1990:3360-3367.

Appendix A

STEADY STATE EXPERIMENTAL DATA

Temperature = 25°C

O.C.V= -922.3 mV

| Current Density (mA/cm ²) | Electrode Potential Hg/HgO (mV) | IR Drop (mV) | IR Free Overpotential (mV) | Ohmic Resistance (Ω) |
|---------------------------------------|---------------------------------|--------------|----------------------------|----------------------|
| 1 | -918.7 | 3 | 0.6 | 0.50 |
| 2 | -915.1 | 6 | 1.2 | 0.50 |
| 4 | -907.2 | 13 | 2.1 | 0.54 |
| 6 | -900.0 | 19 | 3.3 | 0.53 |
| 8 | -891.5 | 26 | 4.8 | 0.54 |
| 10 | -883.2 | 32 | 7.1 | 0.53 |
| 12 | -874.5 | 36 | 11.8 | 0.50 |
| 14 | -865.1 | 44 | 13.2 | 0.52 |
| 17 | -853.5 | 54 | 14.8 | 0.53 |
| 20 | -836.4 | 68 | 17.9 | 0.56 |
| 25 | -823.0 | 79 | 20.3 | 0.53 |
| 30 | -802.6 | 94 | 25.7 | 0.52 |
| 35 | -774.7 | 115 | 32.6 | 0.54 |
| 40 | -759.9 | 127 | 35.4 | 0.53 |
| 45 | -741.4 | 145 | 35.9 | 0.53 |
| 50 | -716.6 | 158 | 47.7 | 0.53 |
| 55 | -682.9 | 177 | 62.4 | 0.53 |
| 60 | -662.3 | 193 | 67.0 | 0.53 |

Temperature = 45°C

O.C.V= -919.2 mV

| Current Density (mA/cm ²) | Electrode Potential Hg/HgO (mV) | IR Drop (mV) | IR Free Overpotential (mV) | Ohmic Resistance (Ω) |
|---------------------------------------|---------------------------------|--------------|----------------------------|----------------------|
| 1 | -916.7 | 2 | 0.5 | 0.33 |
| 2 | -912.8 | 4 | 2.4 | 0.33 |
| 4 | -908.1 | 8 | 3.1 | 0.33 |
| 6 | -903.7 | 12 | 3.5 | 0.33 |
| 8 | -898.2 | 17 | 4.0 | 0.35 |
| 10 | -892.7 | 22 | 4.5 | 0.37 |
| 12 | -887.9 | 26 | 5.3 | 0.36 |
| 14 | -882.5 | 30 | 6.7 | 0.36 |
| 17 | -880.0 | 32 | 7.2 | 0.31 |
| 20 | -872.7 | 38 | 8.5 | 0.32 |
| 25 | -858.6 | 48 | 12.6 | 0.32 |
| 30 | -846.5 | 58 | 14.7 | 0.32 |
| 35 | -833.4 | 70 | 15.8 | 0.33 |
| 40 | -821.8 | 80 | 17.4 | 0.33 |
| 45 | -812.3 | 87 | 19.9 | 0.32 |
| 50 | -800.9 | 96 | 22.3 | 0.32 |
| 55 | -792.7 | 102 | 24.5 | 0.31 |
| 60 | -781.6 | 112 | 25.6 | 0.31 |
| 65 | -762.0 | 130 | 27.2 | 0.33 |
| 70 | -745.2 | 144 | 30.0 | 0.34 |
| 75 | -734.5 | 152 | 32.7 | 0.34 |
| 80 | -724.1 | 160 | 35.1 | 0.33 |

Temperature = 35°C

O.C.V= -921.5 mV

| Current Density (mA/cm ²) | Electrode Potential Hg/HgO (mV) | IR Drop (mV) | IR Free Overpotential (mV) | Ohmic Resistance (Ω) |
|---------------------------------------|---------------------------------|--------------|----------------------------|----------------------|
| 1 | -918.2 | 2.5 | 0.8 | 0.42 |
| 2 | -915.0 | 5 | 1.5 | 0.42 |
| 4 | -908.0 | 11 | 2.5 | 0.46 |
| 6 | -902.5 | 16 | 3.0 | 0.44 |
| 8 | -895.5 | 21 | 5.0 | 0.44 |
| 10 | -888.5 | 27 | 6.0 | 0.45 |
| 12 | -881.5 | 33 | 7.2 | 0.46 |
| 14 | -875.5 | 38 | 8.0 | 0.45 |
| 17 | -866.4 | 46 | 9.1 | 0.45 |
| 20 | -855.7 | 54 | 11.8 | 0.45 |
| 25 | -840.6 | 68 | 12.9 | 0.45 |
| 30 | -824.2 | 81 | 16.3 | 0.45 |
| 35 | -803.3 | 94 | 24.2 | 0.45 |
| 40 | -787.2 | 108 | 26.3 | 0.45 |
| 45 | -771.1 | 122 | 28.4 | 0.45 |
| 50 | -755.7 | 135 | 30.8 | 0.45 |
| 55 | -743.4 | 146 | 33.1 | 0.44 |
| 60 | -723.0 | 165 | 36.5 | 0.46 |
| 65 | -710.8 | 174 | 39.7 | 0.45 |
| 70 | -694.6 | 188 | 42.9 | 0.45 |
| 75 | -675.2 | 204 | 48.3 | 0.45 |

Temperature = 55°C

O.C.V= -921.4 mV

| Current Density (mA/cm ²) | Electrode Potential Hg/HgO (mV) | IR Drop (mV) | IR Free Overpotential (mV) | Ohmic Resistance (Ω) |
|---------------------------------------|---------------------------------|--------------|----------------------------|----------------------|
| 1 | -918.8 | 1.8 | 0.8 | 0.30 |
| 2 | -916.7 | 3.5 | 1.2 | 0.29 |
| 4 | -912.2 | 7 | 2.2 | 0.29 |
| 6 | -908.4 | 11 | 2.0 | 0.30 |
| 8 | -904.8 | 14 | 2.6 | 0.29 |
| 10 | -900.7 | 18 | 2.7 | 0.30 |
| 12 | -897.2 | 21 | 3.2 | 0.29 |
| 14 | -892.6 | 25 | 3.8 | 0.30 |
| 17 | -888.9 | 28 | 4.5 | 0.27 |
| 20 | -882.2 | 33 | 6.2 | 0.28 |
| 25 | -875.4 | 39 | 7.0 | 0.27 |
| 30 | -863.6 | 50 | 7.8 | 0.28 |
| 35 | -850.0 | 62 | 9.4 | 0.29 |
| 40 | -839.7 | 70 | 11.7 | 0.29 |
| 45 | -828.6 | 80 | 12.8 | 0.29 |
| 50 | -819.1 | 88 | 14.3 | 0.29 |
| 55 | -808.7 | 96 | 16.7 | 0.29 |
| 60 | -796.9 | 106 | 18.5 | 0.29 |
| 65 | -787.3 | 114 | 20.1 | 0.29 |
| 70 | -776.1 | 124 | 21.3 | 0.29 |
| 75 | -761.8 | 135 | 24.6 | 0.30 |
| 80 | -754.5 | 139 | 27.9 | 0.29 |
| 85 | -743.1 | 148 | 30.3 | 0.29 |
| 90 | -726.7 | 162 | 32.7 | 0.30 |
| 95 | -721.8 | 165 | 34.6 | 0.29 |
| 100 | -712.0 | 172 | 37.4 | 0.29 |
| 105 | -697.6 | 184 | 39.8 | 0.29 |
| 110 | -686.6 | 192 | 42.8 | 0.30 |

Temperature = 65°C

O.C.V= -918.7 mV

| Current Density (mA/cm ²) | Electrode Potential Hg/HgO (mV) | IR Drop (mV) | IR Free Overpotential (mV) | Ohmic Resistance (Ω) |
|---------------------------------------|---------------------------------|--------------|----------------------------|----------------------|
| 1 | -916.9 | 1.5 | 0.3 | 0.25 |
| 2 | -915.2 | 3 | 0.5 | 0.25 |
| 4 | -911.4 | 6 | 1.3 | 0.25 |
| 6 | -907.6 | 9 | 1.8 | 0.25 |
| 8 | -904.3 | 12 | 2.1 | 0.25 |
| 10 | -900.0 | 16 | 2.4 | 0.25 |
| 12 | -896.7 | 19 | 2.7 | 0.26 |
| 14 | -893.2 | 22 | 3.2 | 0.26 |
| 17 | -887.7 | 27 | 3.7 | 0.26 |
| 20 | -883.1 | 31 | 4.3 | 0.26 |
| 25 | -874.5 | 39 | 4.9 | 0.26 |
| 30 | -867.6 | 45 | 5.8 | 0.25 |
| 35 | -857.7 | 54 | 6.7 | 0.26 |
| 40 | -850.6 | 60 | 7.8 | 0.25 |
| 45 | -839.3 | 70 | 9.1 | 0.26 |
| 50 | -824.7 | 76 | 10.5 | 0.25 |
| 55 | -822.0 | 84 | 12.4 | 0.26 |
| 60 | -809.8 | 94 | 14.6 | 0.26 |
| 65 | -800.2 | 102 | 16.2 | 0.26 |
| 70 | -790.6 | 110 | 17.8 | 0.26 |
| 75 | -785.3 | 114 | 19.1 | 0.25 |
| 80 | -774.1 | 124 | 20.3 | 0.26 |
| 85 | -763.8 | 133 | 21.6 | 0.26 |
| 90 | -756.6 | 140 | 21.8 | 0.26 |
| 95 | -747.8 | 148 | 22.6 | 0.26 |
| 100 | -739.9 | 154 | 24.5 | 0.26 |
| 105 | -727.7 | 164 | 26.7 | 0.26 |
| 110 | -719.0 | 170 | 29.4 | 0.26 |
| 115 | -706.4 | 179 | 33.0 | 0.26 |

Temperature = 75°C

O.C.V= -916.2 mV

| Current Density (mA/cm ²) | Electrode Potential Hg/HgO (mV) | IR Drop (mV) | IR Free Overpotential (mV) | Ohmic Resistance (Ω) |
|---------------------------------------|---------------------------------|--------------|----------------------------|----------------------|
| 1 | -914.8 | 1.2 | 0.2 | 0.20 |
| 2 | -913.2 | 2.5 | 0.5 | 0.21 |
| 4 | -910.7 | 4.5 | 1.0 | 0.19 |
| 6 | -907.7 | 7 | 1.5 | 0.19 |
| 8 | -905.3 | 9 | 1.9 | 0.18 |
| 10 | -903.1 | 11 | 2.1 | 0.19 |
| 12 | -899.9 | 14 | 2.3 | 0.19 |
| 14 | -897.6 | 16 | 2.6 | 0.18 |
| 17 | -895.3 | 18 | 2.9 | 0.18 |
| 20 | -891.1 | 22 | 3.1 | 0.19 |
| 25 | -883.9 | 29 | 3.3 | 0.19 |
| 30 | -878.0 | 34 | 4.2 | 0.19 |
| 35 | -870.2 | 41 | 5.0 | 0.19 |
| 40 | -864.1 | 46 | 6.1 | 0.19 |
| 45 | -856.8 | 52 | 7.4 | 0.19 |
| 50 | -849.4 | 58 | 8.8 | 0.19 |
| 55 | -840.1 | 66 | 10.1 | 0.20 |
| 60 | -834.7 | 70 | 11.5 | 0.19 |
| 65 | -825.9 | 78 | 12.3 | 0.19 |
| 70 | -817.4 | 85 | 13.8 | 0.20 |
| 75 | -808.6 | 93 | 14.6 | 0.20 |
| 80 | -801.3 | 99 | 15.9 | 0.22 |
| 85 | -793.5 | 106 | 16.7 | 0.20 |
| 90 | -784.2 | 114 | 18.0 | 0.20 |
| 95 | -778.7 | 118 | 19.5 | 0.21 |
| 100 | -766.0 | 130 | 20.2 | 0.21 |
| 105 | -760.4 | 134 | 21.8 | 0.22 |
| 110 | -753.2 | 140 | 23.0 | 0.21 |
| 115 | -740.2 | 150 | 26.0 | 0.22 |

Appendix B

Long Term Performance Experimental Data

Mode of Polarization: Potentiostatic

O.C.V. = -920.1 mV

Overvoltage = 25 mV

Temperature = 70°C

| Time (hour) | Current Density (mA/cm ²) |
|----------------|--|
| 0 | 100 |
| 4 | 91.7 |
| 8 | 81.7 |
| 12 | 71.7 |
| 20 | 60.0 |
| 24 | 53.3 |
| 28 | 46.7 |
| 32 | 36.7 |
| 36 | 28.3 |
| 44 | 15.0 |
| 48 | 11.7 |
| 52 | 8.3 |
| 56 | 6.7 |
| 64 | 5.0 |
| 68 | 5.0 |
| 72 | 5.0 |

Mode of Polarization: Potentiostatic

O.C.V = -919.5 mV

Overvoltage = 33 mV

Temperature = 45°C

| Time (hour) | Current Density (mA/cm ²) |
|----------------|--|
| 0 | 75.0 |
| 4 | 75.0 |
| 8 | 73.3 |
| 12 | 70.0 |
| 20 | 68.3 |
| 24 | 68.3 |
| 28 | 66.7 |
| 32 | 65.0 |
| 36 | 63.3 |
| 44 | 60.0 |
| 48 | 56.7 |
| 52 | 53.3 |
| 56 | 48.3 |
| 64 | 43.3 |
| 68 | 40.0 |
| 72 | 38.3 |
| 76 | 37.3 |
| 80 | 34.3 |
| 88 | 31.0 |
| 92 | 30.0 |
| 96 | 28 |
| 100 | 26.3 |
| 104 | 26.3 |

Mode of Polarization: Potentiostatic

O.C.V. = -922.3 mV

Overvoltage = 75 mV

Temperature = 25°C

| Time (hour) | Current Density (mA/cm ²) |
|----------------|--|
| 0 | 70.0 |
| 4 | 70.0 |
| 8 | 68.3 |
| 12 | 68.3 |
| 20 | 66.7 |
| 24 | 66.7 |
| 28 | 65.0 |
| 32 | 63.3 |
| 36 | 61.7 |
| 44 | 61.7 |
| 48 | 60.0 |
| 52 | 60.0 |
| 56 | 58.3 |
| 64 | 56.7 |
| 68 | 55.0 |
| 72 | 53.3 |
| 76 | 51.7 |
| 80 | 50.0 |
| 88 | 46.7 |
| 92 | 45.0 |
| 96 | 43.3 |
| 100 | 41.7 |
| 104 | 40.0 |
| 112 | 38.3 |
| 116 | 36.7 |
| 120 | 35.0 |
| 124 | 33.3 |
| 128 | 30.0 |
| 136 | 30.0 |
| 140 | 28.3 |
| 144 | 26.7 |
| 148 | 25.0 |

Mode of Polarization: Galvanostatic

O.C.V.=917.2 mV

Current Density(i)=100 (mA/cm²)

Temperature = 70°C

| Time (hour) | Overvoltage (mV) |
|----------------|---------------------|
| 0 | 22.7 |
| 4 | 22.8 |
| 8 | 22.7 |
| 12 | 23.2 |
| 20 | 26.5 |
| 24 | 28.9 |
| 28 | 30.6 |
| 32 | 35.7 |
| 36 | 43.6 |
| 44 | 55.3 |
| 48 | 63.6 |
| 52 | 77.8 |
| 56 | 92.6 |
| 64 | 107.5 |
| 68 | 500 |
| 72 | 1200 |

SAMPLE CALCULATIONS

Galvanostatic Polarization Run at 45°C

Open Circuit Voltage (O.C.V.) = -919.2 mV

Galvanostatic Current (I) = 300 mA

Geometric Area of Electrode(A) = 6 cm²

Current Density (i) = 50 mA/cm²

Circuit Voltage (C.V.) = -800.9 mV

IR Drop in the Electrolyte = 96 mV

Electrolyte Resistance = IR Drop/ I

= 96/300

= 0.32 Ω

IR free Overvoltage (η) = C.V. + IR -O.C.V.

= -800.9 - 9.6 + 919.2

= 22.3 mV

| | | |
|---|--|----------|
| C | | H2500010 |
| C | PARAMETERS @ 25 C | H2500020 |
| C | | H2500030 |
| C | \$JOB | H2500040 |
| C |SPECIFICATIONS FOR PARAMETERS | H2500050 |
| C | IMPLICIT REAL*8(A-H,O-Z) | H2500060 |
| | INTEGER LDYFIN,LDYINI,MXGRID,NEQNS,NINIT | H2500070 |
| | PARAMETER (MXGRID=100, NEQNS=2, NINIT=40, LDYFIN=NEQNS, | H2500080 |
| | * LDYINI=NEQNS) | H2500090 |
| C | | H2500100 |
| C | | H2500110 |
| | INTEGER I, J, NCUPBC, NFINAL, NLEFT, NOUT | H2500120 |
| | REAL CONST, ERREST(NEQNS), FCNBC, FCNEQN, FCNJAC, FLOAT, | H2500130 |
| | * PISTEP, TOL, XFINAL(MXGRID), XINIT(NINIT), XLEFT, | H2500140 |
| | * XRIGHT, YFINAL(LDYFIN,MXGRID), YINIT(LDYINI,NINIT), | H2500150 |
| | * CURR(NINIT),RACURR(NINIT),XPRIM(NINIT) | H2500160 |
| C | ... | H2500170 |
| | LOGICAL LINEAR, PRINT | H2500180 |
| | INTRINSIC FLOAT | H2500190 |
| | EXTERNAL BVPFD, CONST, FCNBC, FCNEQN, FCNJAC, UHACH | H2500200 |
| C | ... | H2500210 |
| C | SET PARAMETERS | H2500220 |
| C | ... | H2500230 |
| | ETA0=0.075 | H2500240 |
| | EPS=0.30 | H2500250 |
| | EXCH1=6.60E-06 | H2500260 |
| | ALPHA=0.57 | H2500270 |
| | BARK=0.254 | H2500280 |
| | R=0.5E-03 | H2500290 |
| | T=298.15 | H2500300 |
| | DEA=0.004 | H2500310 |
| | TIM=20.0 | H2500320 |
| | CONCO=2.0E-07 | H2500330 |
| C | ALPHA=1.40 | H2500340 |
| | DBAR=1.60E-05 | H2500350 |
| | NLEFT = 1 | H2500360 |
| | NCUPBC = 0 | H2500370 |
| | TOL =0.01 | H2500380 |
| | XLEFT = 0.0 | H2500390 |
| C | XRIGHT = 0.020 | H2500400 |
| | XRIGHT = 0.385E-01 | H2500410 |
| | PISTEP =0.0 | H2500420 |
| | PRINT = .FALSE. | H2500430 |
| | LINEAR = .FALSE. | H2500440 |
| | EN=2.0 | H2500450 |
| | Z=1.0 | H2500460 |
| | CM2CM3=8.3E+05 | H2500470 |
| C | | H2500480 |
| C | ... DEFINE XINIT AND YINIT | H2500490 |
| C | | H2500500 |
| | DO 10 I=1,NINIT | H2500510 |
| | XINIT(I)=XLEFT + FLOAT(I-1)*(XRIGHT-XLEFT)/FLOAT(NINIT-1) | H2500520 |
| C | YINIT(1,I)=0.4*(XINIT(I)-XLEFT)*(XRIGHT-XINIT(I)) | H2500530 |
| C | CHANGE THE VALUE OF ETA0 FOR DIFFERENT VALUES IN THE STAT. BELOW | H2500540 |
| | YINIT(1,I)=0.0584-0.005*FLOAT(I) | H2500550 |

```

BARK=0.254
R=0.5E-03
F=96484.56
CONCO=2.0E-07
DBAR=1.6E-05
Z=1.0
GASC=8.314
T=298.15
EXCH1=6.60E-06
ALPHA=0.57
CM2CM3=8.30E+05
C    ALPHA=1.40
DEA=0.004
TIM=20.0
C
C.....CALCULATION OF C1,C2,C3,C4
C
C1=(2.0*DBAR*EN*F*CONCO)/(BARK*R)
C2=(Z*F)/(GASC*T)
C3=SQRT((EXCH1*CM2CM3*EXP(-DEA*TIM))/(EN*F*DBAR*CONCO))
C4=(ALPHA*C2)/2.0
CC1=TANH(C3*R*EXP(C4*Y(1)))
CC2=EXP(-C2*Y(1))
CC3=EXP(C4*Y(1))
C
C.....DEFINE PDE
C
DYDX(1) = Y(2)
DYDX(2) = C1*(1.0-EXP(-C2*Y(1)))*(C3*EXP(C4*Y(1))*1.0/
*       TANH(C3*R*EXP(C4*Y(1)))-1.0/R)
C    WRITE(7,*)'Y(2)= ',Y(2),'Y(1) = ',Y(1)
C    WRITE(7,*)'DYDX ',DYDX(2),Y(2),Y(1)
RETURN
END
C
C
SUBROUTINE FCNJAC (NEQNS,X,Y,P,DYDPY)
C    IMPLICIT REAL*8(A-H,O-Z)
INTEGER NEQNS
REAL X,Y(NEQNS),P,DYDPY(NEQNS,NEQNS),C1,C2,C3,C4,C5,EN,F,BARK,
*    R,DBAR,Z,GASC,T,EXCH1,CM2CM3,ALPHA
REAL TANH,SINH,EXP,SQRT
INTRINSIC TANH,SINH,EXP,SQRT
C
C.....DEFINE PHYSICAL PARAMETERS
C
C    WRITE(7,*)'FCNJAC'
EN=2.0
BARK=0.254
R=0.5E-03
F=96484.56
CONCO=2.0E-07
DBAR=1.6E-05
Z=1.0
GASC=8.314

```

H2501110
H2501120
H2501130
H2501140
H2501150
H2501160
H2501170
H2501180
H2501190
H2501200
H2501210
H2501220
H2501230
H2501240
H2501250
H2501260
H2501270
H2501280
H2501290
H2501300
H2501310
H2501320
H2501330
H2501340
H2501350
H2501360
H2501370
H2501380
H2501390
H2501400
H2501410
H2501420
H2501430
H2501440
H2501450
H2501460
H2501470
H2501480
H2501490
H2501500
H2501510
H2501520
H2501530
H2501540
H2501550
H2501560
H2501570
H2501580
H2501590
H2501600
H2501610
H2501620
H2501630
H2501640
H2501650

```

T=298.15
EXCH1=6.60E-06
ALPHA=0.57
CM2CM3=8.30E+05
C ALPHA=1.40
DEA=0.004
TIM=20.0
C
C.....CALCULATION OF C1,C2,C3,C4,C5
C
C1=(2.0*DBAR*EN*F*CONCO)/(BARK*R)
C2=(Z*F)/(GASC*T)
C3=SQRT((EXCH1*CM2CM3*EXP(-DEA*TIM))/(EN*F*DBAR*CONCO))
C4=(ALPHA*C2)/2.0
C5=C4-C2
C
C... DEFINE D(DYDX)/DY
C
DYPDY(1,1)=0.0
DYPDY(1,2)=1.0
C DYPDY(2,1)=C1*C3*C4*EXP(C4*Y(1))*(1.0/TANH(C3*EXP(C4*Y(1))))+
C * (-C3)*EXP(C4*Y(1))*1.0/SINH(C3*EXP(C4*Y(1)))**2.0
C * +C1*C3*C5*EXP(C5*Y(1))*(1.0/TANH(C3*EXP(C4*Y(1))))+
C * (-C3)*EXP(C5*Y(1))*1.0/SINH(C3*EXP(C4*Y(1)))**2.0
C * -C1*(-C2)*EXP(-C2*Y(1))
DYPDY(2,1)=C1*C3*C4*EXP(C4*Y(1))*(1.0/TANH(C3*R*EXP(C4*Y(1))))+
* (-C3)*R*EXP(C4*Y(1))*1.0/SINH(C3*R*EXP(C4*Y(1)))**2.0
* +C1*C3*EXP(C5*Y(1))*(1.0/TANH(C3*R*EXP(C4*Y(1))))+
* (-C3)*R*C4*EXP(C4*Y(1))*1.0/SINH(C3*R*EXP(C4*Y(1)))**2.0
* +(C1*C2*EXP(-C2*Y(1)))/R
DYPDY(2,2)=0.0
C WRITE(7,*)'DYPDY ',DYPDY(2,1),Y(2),Y(1)
RETURN
END
C
C
C SUBROUTINE FCNBC (NEQNS,YLEFT,YRIGHT,P,F)
C IMPLICIT REAL*8(A-H,O-Z)
C INTEGER NEQNS
C REAL YLEFT(NEQNS), YRIGHT(NEQNS), P,F(NEQNS)
C.....DEFINE BOUNDARY CONDITIONS
C
C WRITE(7,*)'FCNBC'
C CHANGE THE VALUE OF ETA0 FOR DIFFERENT VALUES IN THE STAT. BELOW
F(1)=YLEFT(1)-ETA0
F(2)=YRIGHT(2)
RETURN
END

```

H2501660
H2501670
H2501680
H2501690
H2501700
H2501710
H2501720
H2501730
H2501740
H2501750
H2501760
H2501770
H2501780
H2501790
H2501800
H2501810
H2501820
H2501830
H2501840
H2501850
H2501860
H2501870
H2501880
H2501890
H2501900
H2501910
H2501920
H2501930
H2501940
H2501950
H2501960
H2501970
H2501980
H2501990
H2502000
H2502010
H2502020
H2502030
H2502040
H2502050
H2502060
H2502070
H2502080
H2502090
H2502100
H2502110
H2502120
H2502130
H2502140