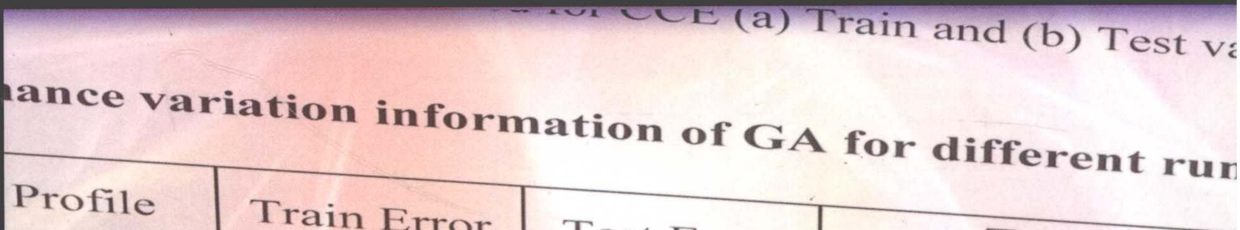
# Applied Electrochemistry



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Chemistry Research and Applications Series

Vijay G. Singh
Editor

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CHEMISTRY RESEARCH AND APPLICATIONS SERIES

# APPLIED ELECTROCHEMISTRY

VIJAY G. SINGH
EDITOR

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CHEMISTRY RESEARCH AND APPLICATIONS SERIES

# APPLIED ELECTROCHEMISTRY

# CHEMISTRY RESEARCH AND APPLICATIONS SERIES

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# PREFACE

This new and important book gathers the latest research from around the globe in the study in the dynamic field of electrochemistry and highlights such topics as: electrochemical applications of modified electrodes in wastewater treatment, corrosion and protection of magnesium and its alloys as a biomaterial, electrochemical hydrogen storage, analysis of electrochemical reactor performance and others.

Chapter 1 - The candidate fuel for fuel cells is usually considered hydrogen. However, at present, no suitable large-scale infrastructure exists for hydrogen production, storage and distribution. Significant efforts have been addressed in the last decades to the direct electrochemical oxidation of alcohol and hydrocarbon fuels. Organic liquid fuels are characterized by high energy density whereas the electromotive force associated to their electrochemical combustion to $CO_2$ is comparable to that of hydrogen combustion to water. Among the liquid organic fuels, methanol has promising characteristics in terms of reactivity at low temperatures, storage and handling. Accordingly, a methanol-feed proton exchange membrane fuel cell would help to alleviate some of the issues surrounding fuel storage and processing for fuel cells. Technological improvements in direct methanol fuel cells (DMFCs) are thus fuelled by their perspectives of applications in portable, transportation and stationary systems especially with regard to the remote and distributed generation of electrical energy. This chapter deals with an analysis of materials issues, status of technologies and potential applications of direct methanol fuel cells. The principle of operation of direct methanol fuel cells and the status of knowledge in the basic research areas are presented. The technology of direct methanol fuel cells is discussed with particular regard to fabrication methodologies for the manufacturing of catalysts, electrolytes membrane-electrode assemblies, stack hardware and system design.

Chapter 2 - Electrochemical deposition of Al, Pb, Mn, Al-Pb and Al-Mn alloys from basic and acidic molten $AlCl_3$-NaCl-KCl mixture on graphite and aluminum electrodes have been extensively studied by electrochemical methods. The deposition of aluminum was found to proceed via a nucleation/growth mechanism in basic melt, while it was found to be diffusion controlled in acidic melt. A model based on random birth and deterministic growth of monolayers is proposed, where the growth of the edges of the layer are assumed to follow a propagation law. Two-dimensional (2D) nucleation and growth of aluminum proceeding through instantaneous and a multitude of progressive steps followed the initial double layer charging. Transition from 2D to three-dimensional (3D) processes has been observed under more cathodic potentials. The kinetic parameters were obtained in the light of Bewick, Fleischmann and Thirsk (BFT) theory an also Armstrong, Fleischmann and Thirsk (AFT) model. The high frequency impedance data measures the rate of the charge transfer reaction of $AlCl_4^-$ reduction while the low frequency features signifies the growth mode of deposits. The inductive response observed in the course of polycrystalline deposition reflects the activation of electrode area while a capacitive loop appears in regular growth. Depending on the current density and $AlCl_3$ concentration (acidic or basic melt) different aluminum morphologies appear but silver bright, compact, and very stable metallic form of aluminum deposit was obtained in acidic melt with KI addition as surfactant. The deposition of aluminum was found to proceed via a nucleation/growth mechanism, while the depositions of lead and manganese were found to be diffusion controlled. The deposition processes of lead and manganese on Al substrates were controlled by 3D nucleation and growth. Under more cathodic potential, the saturation number density of the formed lead nuclei and also the efficiency of the use of the available surface nucleation sites increased. In basic solutions, in the presence of $PbCl_2$ smoother and non-porous aluminum are formed.

Chapter 3 - Increased concentrations of organic pollutants in waters can result from the growth of certain industrial activities. In order to develop a fast electrochemical method to quantitatively determine the concentrations of such pollutants, new electrode materials are required. This review will focus on the preparation, characterization, and electrochemical behaviour of advanced carbon-based composite electrodes, i.e., expanded exfoliated graphite-epoxy, carbon nanofiber-expanded graphite-epoxy, expanded graphite-epoxy, and expanded graphite-polystyrene. Scanning Electron Microscopy (SEM) has been used to determine the physical distribution of the carbon particles within the insulating matrices epoxy or polystyrene. Expanded graphite-epoxy composites were used as the host material for a Cu or Ag-modified zeolite. Selected organic molecules were chosen to represent target pollutants in aqueous solutions, i.e., thiourea for sulfur-based impurities, glucose for carbohydrates, and urea for nitrogen-based impurities. In addition, 4-chlorophenol as priority pollutant set by EU and by USEPA and oxalic acid as a result of the partial degradation of 4-chlorophenol were selected as well. The electrochemical characterization and application of these composite electrodes were carried out by using cyclic voltammetry, linear-scan voltammetry, chronoamperometry, differential pulse voltammetry, and multiple pulsed amperometry. The zeolite-modified electrodes exhibit improved sensitivity for the detection of 4-chlorophenol and improved catalytic activity for the detection of urea and glucose. The presented composite electrode materials and the selected electrochemical methods reveal that the fast determination of the concentrations has been achieved.

Chapter 4 - This chapter sheds some light on the use of modified electrodes in some vital processes related to environmental and energy conversion systems. It highlights the use of modified electrodes (planar and porous) in the remediation of industrial waste water contaminated with nitrate ions or lead ions using modified Au electrodes and porous electrochemical reactor operating in a flow regime, respectively. Additionally, this porous flow-through electrode system has also been used for the production of hydrogen gas from flowing alkaline electrolytes. Our results concerning this issue will be briefly outlined.

The second part of this chapter describes our recent researches on the development of tailor-designed nanoparticles-based electrocatalysts with controllable size and crystallographic orientation, for reactions of relevance to, among others, the polymer electrolyte membrane (PEM) fuel cell, e.g., oxygen reduction and evolution reactions as well as formic acid oxidation. This includes the fabrication and characterization of chemically/electrochemically-prepared metallic nanoparticles (e.g. Au) and metal oxide nanostructures (e.g. manganese oxide) onto various substrates and their applications as electrocatalysts.

Chapter 5 - Electrochemical methods are a promising alternative for the treatment of wastewaters containing organic pollutants. The main advantages of these processes include environmental compatibility, versatility, energy efficiency, safety, selectivity, amenability to automation and cost effectiveness. Particular attention has been place in the anodic oxidation, based on the electrogeneration of hydroxyl radicals directly at the anode surface from water discharge. It has been generally observed that the nature of the electrode material strongly influences the efficiency of the anodic oxidation process. While for classical anode materials (e.g.: Pt, C or $IrO_2$) the oxygen transfer reactions are slow and characterized by low faradic yields and current loss due to $O_2$ evolution, the use of anodes with high oxygen overpotential, like lead dioxide ($PbO_2$) or boron-doped diamond (BDD), favors the degradation and enhances the current efficiency. $PbO_2$ has been extensively used to decompose organic contaminants owing to its high electrical conductivity, high oxygen overpotential and chemical inertness and low cost comparing with other anodic materials. The use of high performance anodic materials like $PbO_2$ electrode can achieve high efficiency and lower the operating cost. This paper presents a critical review of efficient electrochemical technologies developed to treat effluents for environmental protection using $PbO_2$ anodes. Fundamentals and main applications of electrochemical direct and indirect oxidation with this anode are summarized and discussed. The influences of structure, experimental conditions and metal support on the process efficiency and comparison with other anodic materials are reported. Recent progress of emerging surface modifications by the incorporation of dopants which improve the electrocatalytic activity of $PbO_2$ electrodes, were examined.

Chapter 6 - The principles and advantages of photoelectrochemical oxidation of organic pollutants are briefly presented and the electrochemical methods for the preparation of $TiO_2$ and $WO_3$ single component or bicomponent photocatalysts over conducting substrates are reviewed. The latter include anodization of the corresponding metals (Ti, W), anodic or cathodic electrosynthesis ($TiO_2$) and cathodic electrodeposition ($WO_3$). Particular emphasis is given in the discussion of: *i.* Cathodic electrosynthesis/electrodeposition methods, *ii.* The properties of bicomponent $TiO_2$-$WO_3$ catalysts in view of their enhanced activity under both UV and visible light illumination, *iii.* The use of practical substrates such as stainless steel (SS) and *iv.* The photoelectrolysis of typical pollutants. In that direction, results obtained in the authors' laboratories are presented. These include the electrochemical preparation of $TiO_2/WO_3/SS$ photoelectrodes, their microscopic, spectroscopic and photoelectrochemical (photovoltammetric) characterization as well as their use in a small batch photoreactor for the photoelectrocatalytic removal of model organics (oxalate, chlorophenol, dyes).

Chapter 7 - Cathodic hydrogen evolution on a rotating silver disc electrode was studied from aqueous solutions of polybasic acids (EDTA, citric, pyrophosphoric and phosphoric) , as well as monobasic acetic acid at different pH values. A theoretical analysis was carried out to calculate the abundance of undissociated and dissociated species as a function of pH, using literature values of the dissociation constants. It was found that in some pH range each of the species exists in virtually 100% abundance. Hence, the kinetics of hydrogen discharge from the acids anions could be investigated separately. The aim was to establish whether hydrogen atoms bound in the undissociated acid and in the acid anions participate in the reaction as hydrogen donors. The galvanostatic pulse method was used to establish Tafel plots. Diffusion limiting currents proportional to the total concentration of the acid are found pointing to the participation of the latter in the process. In order to distinguish between (a) evolution of hydrogen via hydronium ions arising from dissociation of the acid or acid anions, and (b) direct involvement of hydrogen bound in those species, a diagnostic criterion is found in the pH dependence of the current density at a constant potential, or potential at constant current density. The analysis resulted in the conclusion that mechanism (b) is operative.

Chapter 8 - A set of modified $PbO_2$ anodes doped with the oxides of Bismuth and Cobalt were prepared by the means of electrodeposition in nitrate solutions. These electrodes were characterized in terms of their morphological (SEM) and structural (XRD) features. The electrochemical activities of these modified electrodes were investigated by means of cyclic voltammetry and bulk electrolysis and compared with undoped $PbO_2$ electrode. The Ti/Bi-$PbO_2$ anode had the highest overpotential of 1.75 V (vs SCE) for oxygen evolution. Both XRD patterns and SEM images demonstrated that the incorporation of Bi could diminish the size of the crystal particles. Oxidants such as hydroxyl radical, hydrogen peroxide were determined, and their amount was proportional to the electrocatalyitc activities of modified $PbO_2$ anodes. Electrocatalytic oxidation of o-nitrophenol was conducted by using these anodes as anode and stainless steel sheet as cathode. Ti/Bi-$PbO_2$ anode displayed not only excellent electrocatalytic performance but also low energy consumption. The Ti/Bi-$PbO_2$ anode is a promising anode for the treatment of organic pollutants. Furthermore, the electrocatalytic oxidation of o-nitrophenol (o-NP), m-nitrophenol (m-NP) and p-nitrophenol (p-NP) has also been studied at Bi-doped lead dioxide anodes on acid medium by cyclic voltammetry and bulk electrolysis. The results of voltammetric studies indicated that these nitrophenol isomers were indirectly oxidized by ·OH radical in the solutions. Within the present experimental conditions used (50 mg of nitrophenol $L^{-1}$, pH 4.3, 30 mA $cm^{-2}$, 303 K), the complete decomposition of nitrophenols (NPs) was achieved. The electrocatalytic oxidation of NPs lay in the order: o-NP>m-NP> p-NP. Molecular configuration including the electron character and hydrogen bonds of NPs significantly influenced the electrocatalytic oxidation of these isomers. Hydroquinone, catechol, resorcinol, benzoquinone, aminophenols, glutaconic acid and maleic acid and oxalic acid have been detected as soluble products during the electrolysis of NPs. The possible degradation pathways of these isomers were proposed. The first stage is the release of nitro group from the aromatic rings. As a consequence, hydroquinone, catechol, resorcinol and benzoquinone are formed. These organic compounds are oxidized initially to carboxylic acids (Glutaconic acid, maleic acid and oxalic acid) and later to carbon dioxide and water. Simultaneously, the reduction of NPs to aminophenols takes place at the cathode.

Chapter 9 - The paper considers some circumstances that can make difficult the application of conventional electrochemical methods in assessing corrosion rate in practice. In these cases the determined values of polarization resistance are often apparent values that when inserted in the equation of Stern-Geary, give erroneous estimates of corrosion rate. It is paid attention to when there is (a) an uneven distribution of the electrical signal applied during the electrochemical measurements, as with large reinforced concrete structures in civil engineering, that complicates the obtainement of true polarization resistance values. Another circumstance that can complicate the estimates is (b) the occurrence of other processes different from the corrosion process, resulting in the over-estimation of corrosion rate values, for example in the presence of redox processes and high capacitive values. Finally, (c) gravimetric mass losses and electrochemical corrosion estimates in the case of Mg and its alloys shows sometimes important discrepancies. The metal surface exposed to corrosive media does not seem to respond to a normal electrochemical behavior. Formation of $Mg^+$ ions, partial disintegration of the sample in fine metal particles and a possible chemical attack independent of the electrochemical one offer possible explanations for this behavior.

Chapter 10 – Biomaterials are used to treat, complete, enlarge or replace living tissues or organs. Two of the most important properties of biomaterials are their biocompatibility and their biofunctionality. Magnesium is a biomaterial of great clinical importance for osteosynthesis and the manufacturing of stents. Its low density, its mechanical properties – which are closer to those of bone than other metals – and in particular, the biocompatibility of the liberated ions make it potentially suitable. Furthermore, its degradability would avoid the need for a second operation to remove it once the bone has healed. Knowledge of the magnesium degradation rate is of great interest since it is linked to the material's stability time as a support. Although research has been performed on magnesium corrosion in industrial environments, little is known about its behaviour in biological fluids.

Chapter 11 - The use of hydride-forming metal alloys as hydrogen storage materials offers to provide high volumetric energy densities comparable to that of liquid hydrogen. Nickel-metal hydride (Ni/MH) batteries employ this type of metal alloy electrode for advanced electricity storage systems in electric vehicles. Advances in the compositional design of different alloy electrodes for use in Ni/MH batteries are described in this manuscript. A report is included on the physicochemical properties of these electrochemical hydrogen-storage materials and their application to hybrid cars.

Chapter 12 - Two-sample multivariate tests of distribution-free (i.e. nonparametric) statistics, and the multivariate analog of normal distribution-based test of difference between two means, are presented for a probabilistic evaluation of electrochemical process/reactor performance. A conventional electrolytic hydrogen peroxide producing process is employed for numerical illustration. The difference between two operational protocols (or modes): e.g. non-flow, and batch, or tank-flow and tubular-flow, etc. but whose exact nature is immaterial for statistical analysis is determined by considering the effect of the protocols on the cathodic current density (CD) and the current efficiency (CE) in terms of CD/CE data strings, randomly observed over test periods of the same fixed length.

The analysis involves permuted variates of Hotteling's $T^2$- statistics and related F-statistics, maximum-of-two-sided T-statistics (TMA) and the maximum-of-one-sided T-statistics (TM). Since nonparametric statistical tests are prone to yield more conservative results than distribution-based tests, inferences drawn from critical comparisons are not always straightforward, especially when the response variable sets are of unequal size.

The major and primarily technological, utility of the subject matter for the electrochemical analyst/engineer lies in the technical decision-making aspects of selecting the proper mode of operation.

Chapter 13 - Chlor-alkali (CA) production is the largest industrial scale electro synthesis. One of the major issues confronting the chlor-alkali industry is the high power consumption, i.e. about $1.5\times10^8$ MWh of electricity per year. Cell voltage and current efficiency are two most important process parameters proportional to the power consumption of a CA plant. Therefore, the process evaluation is important from industrial point of view in order to quantify the impact of process variables on these two parameters. At the same time, prediction of the cell voltage and current efficiency can facilitate achieving the optimum conditions which will further reduce the intercalary costs of trial and error experiments.

This paper presents the development of Non-parameter Regression Methods including Artificial Neural Network (ANN), Genetic Algorithm Optimization (GA) and Support Vector Machine (SVM) models for the prediction of cell voltage and caustic current efficiency (CCE) versus various operating parameters in a lab scale chlor-alkali membrane cell. Implementation of such methods would enable the operators of chlor-alkali membrane cell units to figure out their optimum process conditions and benefit from the savings in time and energy.

The predictions of new ANN, GA & SVM models exhibited to fit the experimental data with the lowest mean absolute percentage (MAPE) as well as standard deviation (SD) errors. It was also found that the developed models are not only capable to predict the voltage and current efficiency but also to reflect the impacts of the other process parameters on the same functions. The predicted cell voltages and current efficiencies using these models were found to be close to the measured values. According to the obtained results, SVM model is suitable for the prediction of current efficiency with an average deviation (for test validation data) of 1.53% while GA & ANN models are suitable for the prediction of cell voltage with an average deviation of 1.21% & 1.27%, respectively.

Chapter 14 - Some analytical applications of the catalytic effect exerted on the electrochemical oxidation/reduction of selected species in solution by inorganic solids containing immobile redox-active centers are described. Substrate/catalyst and catalyst/substrate reaction/regeneration and substrate-catalyst adduct formation mechanisms are described. Electrocatalytic activity of cerium-doped zirconias on the oxidation of methylenedioxyamphetamine (MDA) and light-driven electrocatalytic activity of spiropyran attached to zeolite Y with respect the oxidation of 1,4-dihydrobenzoquinone are presented. Chiral electrocatalysis exerted by monoclinic cerium-doped zirconias on the oxidation of mandelic acid is also discussed.

Chapter 15 - The aluminium and its alloys are suitable and candidate materials for general purpose and structural applications due to low density, high specific strength and inertness at ambient atmosphere. Aluminium, as indicated by its position in the electromotive force series, is thermodynamically an active metal. It develops a protective strongly bonded thin oxide film, if damaged, repairs immediately in most of the environments. The stability of this protective oxide layer is governed by the environment and its conditions. The break down of the oxide passive film results in localized corrosion and environmental assisted cracking (EAC).

The chapter deals with the discussion of various forms of corrosion e.g. pitting, galvanic, intergranular, environmental assisted cracking, such as stress corrosion cracking (SCC), hydrogen embrittlement (HE) and corrosion fatigue (CF) of 2xxx, 7xxx, 8xxx and other series of aluminium alloys. The effects of the corrosive media, the presence of active species, the oxygen content, the amount of depolarizers and temperature etc. have been dealt in discussing the corrosion behaviour of these alloys. Further, the relationships among the solution-potential, the alloy composition and the microstructural constituents present in the alloy of various tempers, and retrogressed and reaged (RRA) states of have been incorporated. Corrosion processes and their preventive methods have also been highlighted.

In this chapter, a special emphasis has been given in discussing SCC of precipitation hardenable aluminium alloys. High strength aluminium alloys are susceptible to SCC in the maximum strength peak aged (T6 or T8) tempers, although over-aged (T7) tempers exhibit acceptable resistance. But, over aged temper has lower strength requiring over-sized components. Hence, a novel heat treatment retrogression and reaging (RRA) which finds the solution to overcome the problem, has been dealt in detail. It has been observed that RRA tempers have resulted in retaining peak aged temper strength and at the same time exhibited maximum SCC resistance. The SCC results have been explained with the help of microstructural features of the various tempers of aluminium alloys. Hydrogen embrittlement phenomenon, at applied cathodic potentials, has also been discussed.

Chapter 16 - Data concerning electrochemistry of molybdenum in melts are considered and generalized. Data about mechanisms of metal electroreduction and electrodeposition in form of different cathode deposits are discussed and systematized. The state of art in these areas is analyzed, and prospectives are discussed.

# CONTENTS

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*Chapter 1*

# MATERIALS ISSUES, STATUS OF TECHNOLOGIES AND POTENTIAL APPLICATIONS OF DIRECT METHANOL FUEL CELLS

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## ABSTRACT

The candidate fuel for fuel cells is usually considered hydrogen. However, at present, no suitable large-scale infrastructure exists for hydrogen production, storage and distribution. Significant efforts have been addressed in the last decades to the direct electrochemical oxidation of alcohol and hydrocarbon fuels. Organic liquid fuels are characterized by high energy density whereas the electromotive force associated to their electrochemical combustion to $CO_2$ is comparable to that of hydrogen combustion to water. Among the liquid organic fuels, methanol has promising characteristics in terms of reactivity at low temperatures, storage and handling. Accordingly, a methanol-feed proton exchange membrane fuel cell would help to alleviate some of the issues surrounding fuel storage and processing for fuel cells. Technological improvements in direct methanol fuel cells (DMFCs) are thus fuelled by their perspectives of applications in portable, transportation and stationary systems especially with regard to the remote and distributed generation of electrical energy. This chapter deals with an analysis of materials issues, status of technologies and potential applications of direct methanol fuel cells. The principle of operation of direct methanol fuel cells and the status of knowledge in the basic research areas are presented. The technology of direct methanol fuel cells is discussed with particular regard to fabrication methodologies for the manufacturing of catalysts, electrolytes membrane-electrode assemblies, stack hardware and system design.

## 1. INTRODUCTION

Fuel cells have reached a mature level of technology. These systems appear now ready for electro-traction, portable power sources, distributed power generation and stationary applications [1]. The high thermodynamic efficiency and the near zero emission levels make them an attractive alternative to internal combustion engines, batteries and thermal combustion power plants. Like storage batteries, fuel cells deliver energy by consuming electroactive chemicals, but differ significantly in that these chemicals are delivered on-demand to the cell. As a result, a fuel cell can generate energy continuously and for as long as the electroactive chemicals are provided to the cell. The candidate fuel for fuel cells is usually considered hydrogen. However, at present, no suitable large-scale infrastructure exists for hydrogen production, storage and distribution. Significant efforts have been addressed in the last decades to the direct electrochemical oxidation of alcohol and hydrocarbon fuels. Organic liquid fuels are characterized by high energy density, whereas, the electromotive force associated to their electrochemical combustion to $CO_2$ is comparable to that of hydrogen combustion to water [1-3]. Among the liquid organic fuels, methanol has promising characteristics in terms of reactivity at low temperatures, storage and handling. Accordingly, a methanol-feed proton exchange membrane fuel cell would help to alleviate some of the issues surrounding fuel storage and processing for fuel cells. Technological improvements in direct methanol fuel cells (DMFCs) are thus fuelled by their perspectives of applications in portable, transportation and stationary systems especially with regard to the remote and distributed generation of electrical energy [4-5]. Methanol is cheap and it can be distributed by using the present infrastructure for liquid fuels. It can be obtained from fossil fuels, such as natural gas or coal, as well as from sustainable sources through fermentation of agricultural products and from biomasses. With respect to ethanol, methanol has the significant advantage of high selectivity to $CO_2$ formation in the electrochemical oxidation process [1-3].

Thus, the direct methanol fuel cell is a technology receiving a great deal of attention because of specific advantages it has over hydrogen-based fuel cell systems. As above mentioned, hydrogen-based systems for mobile applications require new technologies and new infrastructure for fuel storage, delivery, and handling safety. Liquid fuels can greatly simplify handling, furthermore, they are characterized by energy density larger than hydrogen stored as a compressed gas or metal hydride. Alternatively, hydrogen can be supplied by converting hydrocarbon and alcohol fuels, but a DMFC still presents a much simpler system for mobile applications by eliminating the need for a fuel processor.

However, despite these practical system benefits, DMFCs are characterized by a significantly lower power density and lower efficiency than a polymer electrolyte fuel cell (PEMFC) operating with hydrogen because of the slow oxidation kinetics of methanol and methanol cross-over from the anode to the cathode [1-3].

This chapter deals with an analysis of the history, current status of technology, potential applications and techno-economic challenges of direct methanol fuel cells. The basic aspects related to DMFC operation are presented with particular regard to thermodynamics, performance, efficiency and energy density characteristics. The historical development of DMFC devices and components is analyzed with special regard to the study of catalysts and electrolytes. The status of knowledge in the basic research areas is presented and particular emphasis is given to required breakthroughs. The section on fundamentals is focused on the electrocatalysis of the methanol oxidation reaction and oxygen electro-reduction. To this regard, particular relevance is given to the interpretation of the promoting effects for methanol oxidation and on the features that govern methanol tolerance for oxygen reduction catalysts. The technology section deals with the fabrication methodologies for the manufacturing of membrane-electrode assemblies, stack hardware and system design. The recent efforts in developing DMFC stacks for both portable and electro-traction applications are reported.

## 2. BASIC ASPECTS OF DIRECT METHANOL FUEL CELLS

### 2.2. Fuel Cell Process

The core of the present direct methanol fuel cells is a polymer electrolyte ion exchange membrane. The electrodes (anode and cathode) are in intimate contact with the membrane faces. A scanning electron micrograph of a DMFC MEA is shown in Figure 1. The electrodes usually consist of three-layers: catalytic layer, diffusion layer and backing layer, but there are also several different configurations. The catalytic layer is composed by a mixture of catalyst and ionomer and it is characterized by a mixed electronic-ionic conductivity. The catalysts are often based on carbon supported or unsupported PtRu and Pt materials at the anode and cathode, respectively. The membrane as well as the ionomer consists, in most cases, of a perfluorosulfonic acid polymer. The diffusion layer is usually a mixture of carbon and Polytetrafluoroethylene (Teflon). The hydrophobic properties of this layer are determined by the need to transport oxygen molecules to the catalytic sites at the cathode or to favor the escape of $CO_2$ from the anode. The package formed by electrodes and membrane is called "membrane and electrode assembly" (MEA). The overall thickness of this package is generally smaller than one millimeter. Each MEA forms a cell. Several cells are usually connected in series to form a fuel cell stack that is integrated in a system which contains the auxiliaries allowing stack operation and delivering of the electrical power to the external load.

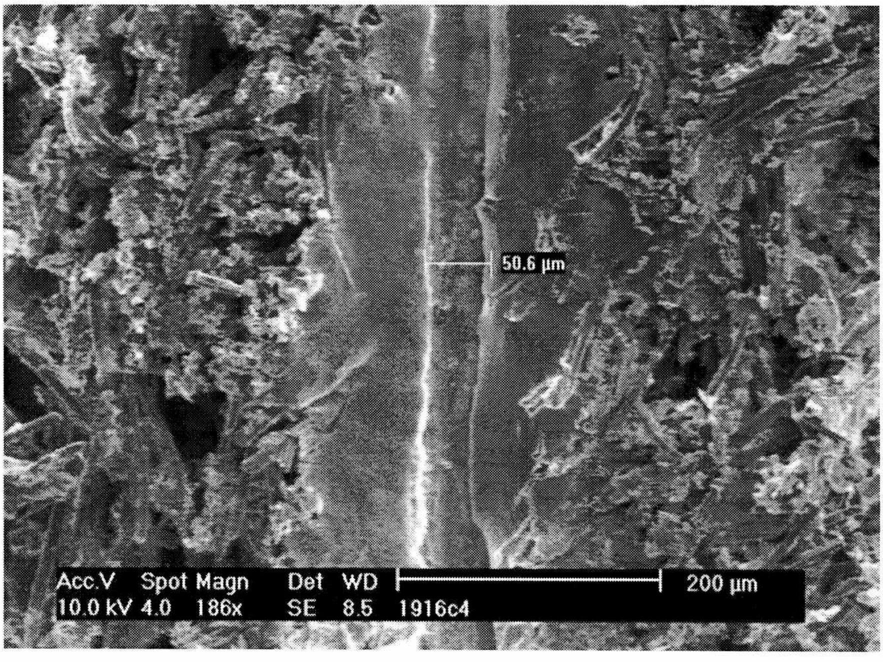

Figure 1. SEM micrograph of a DMFC membrane and electrode assembly equipped with Nafion 112 membrane.