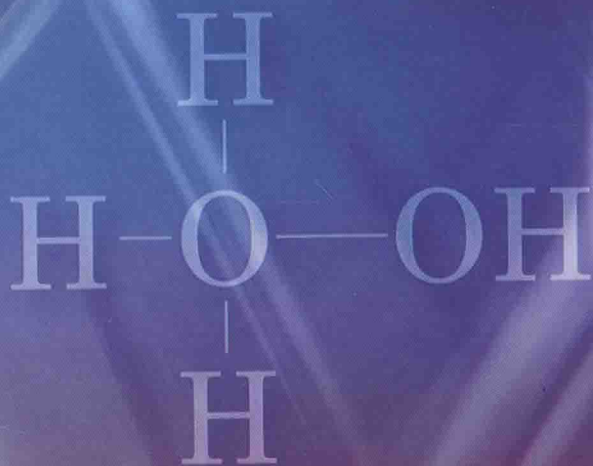


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A. S. Arico ♦ V. Baglio
V. Antonucci



Direct Methanol Fuel Cells

NOVA

ENERGY SCIENCE, ENGINEERING AND TECHNOLOGY SERIES

DIRECT METHANOL FUEL CELLS

ANTONINO S. ARICO
VINCENZO BAGLIO
VINCENZO TONUCCI

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A. S. Arico, V. Baglio and V. Antonucci

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PREFACE

This book 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 in this book with particular regard to fabrication methodologies for the manufacturing of catalysts, electrolytes membrane-electrode assemblies, stack hardware and system design.

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 book 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.

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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 book 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.

Chapter 2

2. BASIC ASPECTS OF DIRECT METHANOL FUEL CELLS

2.1. 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 CO₂ 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.

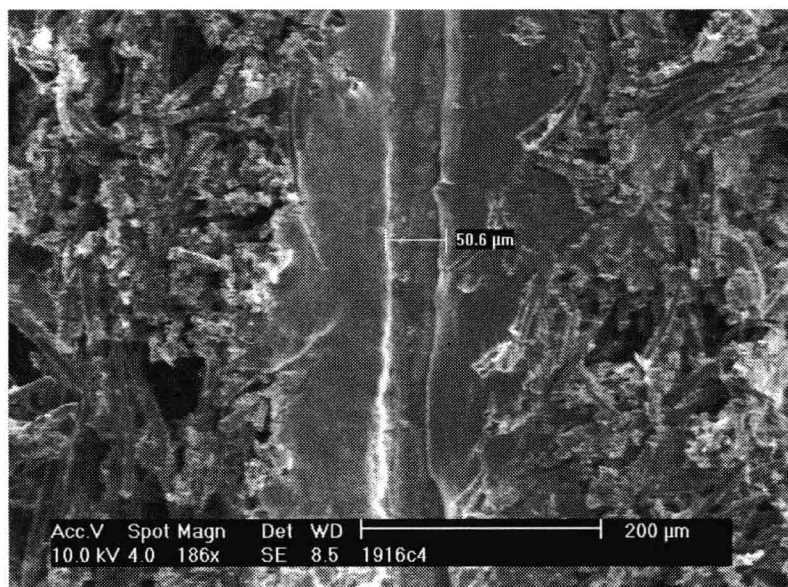


Figure 1. SEM micrograph of a DMFC membrane and electrode assembly equipped with Nafion 112 membrane.

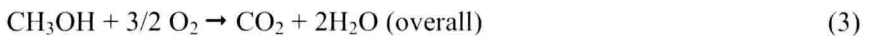
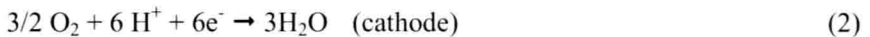
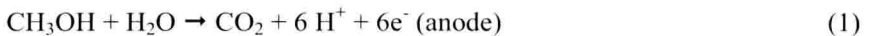
In the literature it is usually made a distinction between “active” and “passive” operation mode [5]. In the active mode, the auxiliaries such as pumps, blowers, sensors etc. are used to supply reactants and to control the stack operation in order to optimize working conditions. This allows to achieve the most appropriate electrical characteristics. In the passive mode, there are no energy consuming auxiliaries (excluding step-up DC/DC converters) and the reactants reach the catalytic sites by natural convection or by effect of the capillary forces or due to the concentration/partial pressure gradient. The system is more simple than in the active mode; no significant amount of power from the stack is thus dissipated on auxiliaries, but, the operating conditions may not be optimal to achieve the best efficiency and performance.

DMFCs usually operate at temperatures below 100°C. This leads to significantly lower power density and lower efficiency than a PEMFC operating with hydrogen because of the slow oxidation kinetics of methanol, in this temperature range, and methanol crossover from the anode to the cathode. [2-4] Typical perfluorosulfonic acid membranes used in the present DMFCs, such as Nafion (DuPont), are permeable to methanol transport, thereby reducing significantly the fuel utilization efficiency of the device. An increase of the power density can be achieved by raising the fuel cell operating temperature to increase

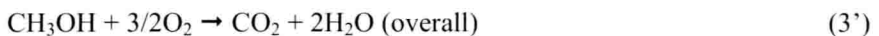
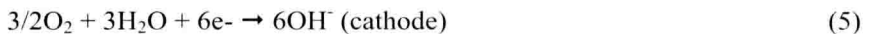
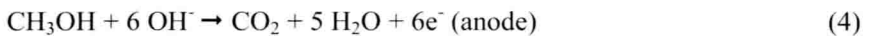
the kinetics of methanol oxidation and to reduce the coverage of its oxidation intermediates on the anode catalyst. Unfortunately, typical membranes experience significant membrane dehydration at higher temperatures, leading to high ohmic drop and poor cell performance [2]. Furthermore, for some applications such as portable systems, low operating temperatures are preferable. There are alternative membranes that can extend the operating temperature above 100 °C such as phosphoric acid doped polybenzimidazole or composite membranes [2]. Thus, it can be affirmed that polymer electrolyte membrane DMFCs can operate from ambient temperature up to 200 °C, depending on the membrane. The membrane determines the optimum performance in a specific temperature range.

However, what is required for the DMFC is an optimal operation in a wide temperature range. In the presence of a protonic membrane, the DMFCs are directly fed with methanol/water mixture at the anode. Methanol is directly oxidized to carbon dioxide although it is not excluded the possible formation of compounds such as formaldehyde, formic acid and other organic molecules. The formation of such organic molecules decreases the fuel utilization in the process.

A scheme of the overall reaction process occurring in a DMFC equipped with a proton conducting electrolyte is outlined below:



In the presence of an alkaline electrolyte, this process can be written as follows:



The thermodynamic efficiency of the process is given by the ratio between the Gibbs free energy, i.e. the maximum value of electrical work (ΔG°) that can be obtained and the total available energy for the process, i.e. the enthalpy (ΔH°). Under standard conditions:

$$\eta_{\text{rev}} = \Delta G^\circ / \Delta H^\circ ; \text{ reversible energy efficiency} \quad (6)$$

with

$$\Delta G^\circ = \Delta H^\circ - (T \cdot \Delta S^\circ); \quad (7)$$

and

$$\Delta G^\circ = -nF \cdot \Delta E_{\text{rev}} \quad (8)$$

ΔE_{rev} is the electromotive force. At 25°C, 1 atm and with pure oxygen feed the reversible potential for methanol oxidation is 1.18 V [3]. It does not vary significantly in the operating range 20°-130 °C and 1-3 bar abs. pressure.

Usually, the open circuit voltage of a polymer electrolyte direct methanol fuel cell is significantly lower than the thermodynamic or reversible potential for the overall process. This is mainly due to methanol cross-over that causes a mixed potential at the cathode and to the irreversible adsorption of intermediate species at electrode potentials close to the reversible potential. The coverage of methanolic species is larger at high cell potentials i.e. at low anode potentials. This determines a strong anode activation control that the overall polarization curve (Figure 2). This can be observed in a polarization plot (Figure 2) where the terminal voltage of the cell is deconvoluted into the anode and cathode polarizations according to the equation:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \quad (9)$$

The anodic potential, the cathodic potential and the terminal cell voltage can be measured simultaneously by using a proper reference electrode. This can be a dynamic hydrogen electrode (DHE) formed by two small circular pieces of electrodes, in close contact with the membrane; hydrogen is forced to evolve on one of these small electrodes, which is used as a reference, by applying a small current. These electrodes are electrically insulated from the anode and cathode current collectors but are humidified by draining a small amount of liquid from the main compartments through a channel (Figure 3). Alternatively, the anode polarization can be measured in the driven mode, in an independent experiment carried out in the same conditions of the overall polarization curve. The cathode curve is mathematically calculated from equation 9. In the driven mode hydrogen is fed to the cathode that acts as both counter and reference electrode. This is also the usual mode to carry out in-situ cyclic voltammetry experiments for the anode.

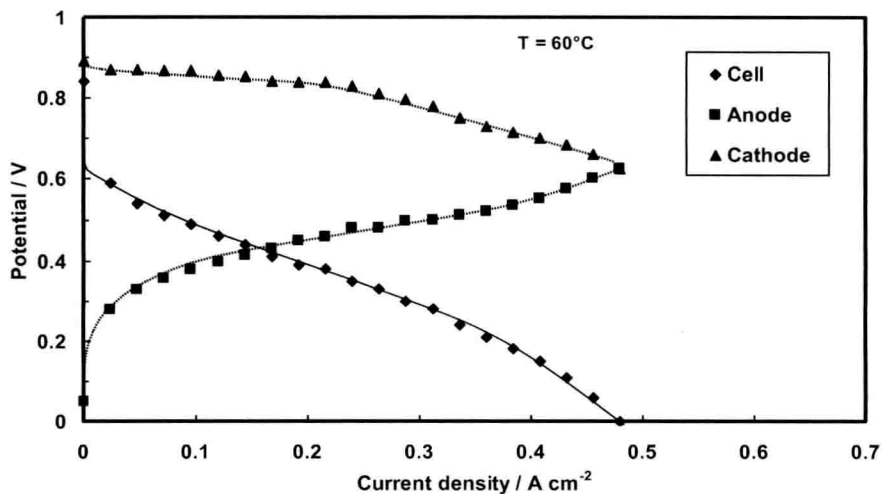


Figure 2. Single cell and in-situ half-cell electrode polarizations for a DMFC operating at 60 °C, ambient pressure, with 1 M methanol at the anode and air feed at the cathode.

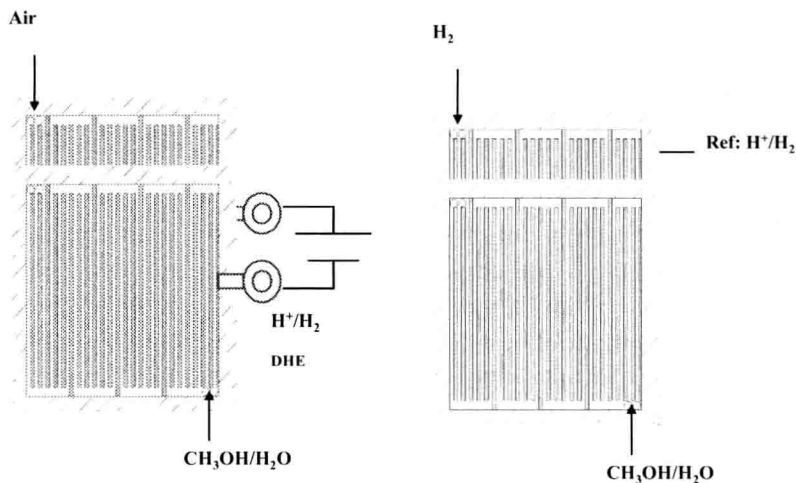


Figure 3. Reference electrode configurations for in-situ half-cell electrode polarization measurements.

Besides the strong activation control at the anode, the effect of the mixed potential on the cathode polarization curve is clearly observed in Figure 2. The onset potential for the oxygen reduction in the presence of methanol cross-over is below 0.9 V versus the reversible hydrogen electrode (RHE). This is much lower