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Recent progress in direct ethanol proton exchange membrane fuel cells (DE-PEMFCs)

Shuqin Song, Panagiotis Tsiakaras *

Department of Mechanical and Industrial Engineering, School of Engineering, University of Thessaly, Pedion Areos 383 34, Greece

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Abstract

Direct ethanol fuel cells (DEFCs) belong to the family of proton exchange membrane fuel cells (PEMFCs), in which ethanol is directly used as the fuel. In the present work, the main aspects related to DEFCs such as electrocatalysts, membrane electrode assembly (MEA) preparation and their corresponding effects on the total cell performance are summarized and discussed. Furthermore, the issues about the disadvantages such as ethanol crossover and the electrolyte membrane's thermal and mechanical stability, as well as the challenges for DEFC's rapid development and commercialization are addressed.

Keywords: Direct ethanol PEMFC (DE-PEMFC); Electrocatalysts for ethanol electrooxidation; Membrane electrode assembly (MEA); Ethanol crossover

1. Introduction

It is widely recognized that *proton exchange membrane fuel cell* (PEMFC), known also as *solid polymer electrolyte fuel cell* (SPFC), possesses the advantages of quick start-up due to its low working temperature, compactness, no corrosion problems and flexibility at any orientation [1]. In this operation system, hydrogen is considered as the preferred fuel in virtue of its high activity in the anode electrochemical reaction and its environmental benignity since water is the only product of its oxidation. Considering that H_2 is not a naturally existing gaseous fuel, to date, most of hydrogen used for PEMFCs operation is from the external reforming process, leading to a bulkier and heavier system and increasing simultaneously its complexity and cost. Moreover, although the lower operation temperature is one of the advantages of PEFMC, the fuel requirement is very rigorous. Once the CO content in the hydrogen-rich gas is more than 10 ppm, an obvious decay in the cell performance will be observed. All of these problems and issues stimulate scientists and researchers to use directly the liquid fuels to feed fuel cells, avoiding in this way the difficulties and hazards associated with handle, storage, transportation and distribution of gaseous reactants such as hydrogen. This can also provide considerable weight and volume advantages over the external reforming PEMFC. Among all the investigated possible fuels up to a few years ago [2–12], methanol was the most favorite due to its relatively higher electrochemical activity compared to the other liquid fuels and much progress has been made in the different pertinent issues, including electrocatalysts, electrolyte, membrane electrode assembly and fuel cell stack of the PEMFC directly fed by methanol (DMFCs).

However, methanol is toxic for human beings and specially for optical nerve. Moreover, the sluggish anode kinetics and methanol crossover are still the main challenges to DMFC's commercialization despite that extensive efforts have been devoted. During the attempts to identify fuels for fuel cells, ethanol is considered to be an attractive and promising one at least for the following reasons: (i) its non-toxicity, (ii) natural availability, (iii) renewability, (iv) a higher power density, and (v) zero green-house contribution to the atmosphere. The last decade, a number of scientific works have been dedicated to thermodynamic [13–16] and experimental [17–42] investigation of direct ethanol fuel cells. The main part have been focused on *direct ethanol proton exchange membrane fuel cells* (DE-PEMFCs) [17–39] and only few of them on *direct ethanol solid oxide fuel cells* (DE-SOFCs) [40–42]. Especially since it was reported that PtSn shows an obviously better single DEFC

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* Corresponding author. Tel.: +30 24210 74065; fax: +30 24210 74050.
E-mail address: tsiak@mie.uth.gr (P. Tsiakaras).

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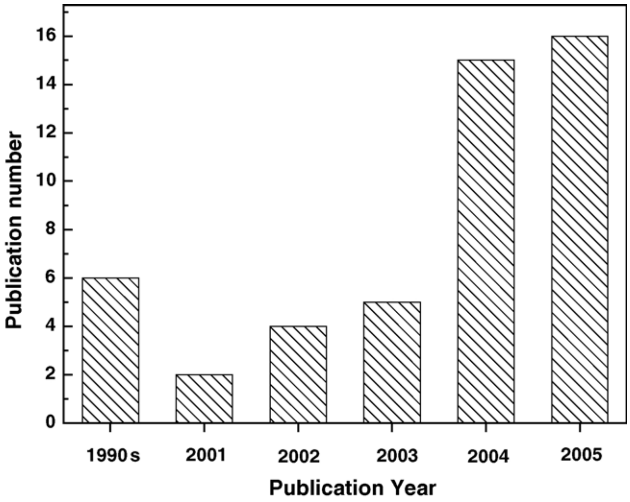


Fig. 1. Escalation of publications about low temperature direct ethanol fuel cells in the past 15 years.

performance than PtRu [17], a remarkable growth rate of the related DEFC research and development has been obtained. This can be clearly seen in Fig. 1, where the statistical results of the DEFC referred publications during the past 20 years are reported.

The objective of the present work is to provide a brief review of the state-of-the-art of the research and development of DE-PEMFCs, including the following pertinent issues: recent development of electrocatalysts for ethanol oxidation, *membrane electrode assembly* (MEA) preparation procedure, single DEFC performance and ethanol crossover phenomena. Furthermore, the performances between single DE-PEMFC, DE-SOFC, direct methanol PEMFC (DMFC) and H_2–O_2 PEMFC are compared and discussed.

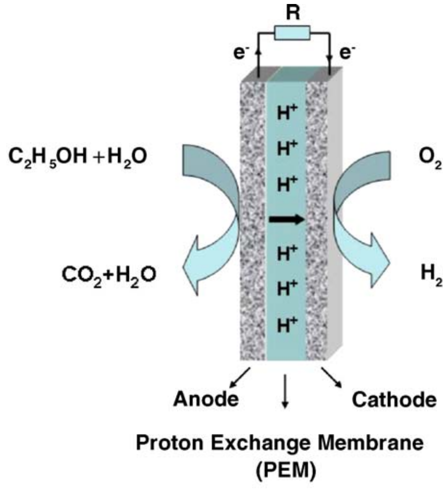
2. Anatomy and physiology of a DEFC

2.1. The working principle of a DEFC

The parts of which a direct ethanol fuel cell (DEFC) constitutes and its working principle are clearly shown in Fig. 2. The ethanol aqueous solutions are fed to the anode compartment, where with the aid of the electrocatalysts, ethanol is oxidized to produce carbon dioxide releasing simultaneously protons and electrons. Protons are then transported to the cathode through the electrolyte and electrons flow through an external circuit, and then arrive at the cathode. There, the oxidant (always air or pure oxygen) reacts with the protons and electrons transported from the anode to produce water as shown in Fig. 2. As it can be discussed below, not like H_2–O_2 PEMFC, the main overpotential loss of DEFCs is attributed to the slow reaction kinetics of ethanol electrooxidation in the anode compartment.

2.2. Electrocatalysts for ethanol electrooxidation

It is well known that the choice of the electrode material presents one of the central issues for the C_2 compounds from the practical point of view. It is also known that both catalytic activity and electronic conductivity are required for a ‘‘good’’ electrode. Moreover, the electrocatalyst effectiveness is judged more or less from its capacity for the electrooxidation of ethanol to CO_2 and water. Therefore, in view of the direct electrooxidation of ethanol in the fuel cells, the materials that could facilitate ethanol complete oxidation and shift the onset oxidation potential to lower values are of the most interest. In order to increase the catalyst surface area and decrease the catalyst loading and consequently its cost, usually, the active material is dispersed over the supports. In order to satisfy the second requirement of the electrocatalyst, a good electric conductivity, the commonly used support is carbon, especially carbon XC-72 (Cabot®) with a suitable surface area around 240 m^2/g.



Anode: $C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$

Cathode: $3O_2 + 12H^+ + 12e^- \rightarrow 6H_2O$

Total Reaction: $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

Fig. 2. The working principle of a direct ethanol fuel cell.

Platinum is recognized to be the most active material for ethanol oxidation, however, it should be noted that the self-inhibition happens in the case of Pt alone, especially in the steady state operation mode. Furthermore, in order to increase the fuel utilization and fuel cell efficiency, it is crucial to break C–C bond and provoke its complete oxidation into carbon dioxide. Therefore, a second or a third additive is adopted to modify the surface of platinum [17–23]. Fig. 3 presents the effect of different additives to Pt's activity to ethanol electrooxidation in a single DEFC. As one can distinguish that all the additives can promote more or less the platinum's electrocatalytic activity towards ethanol oxidation. The more pronounced enhancement has been observed in the case of Pt–Sn electrocatalysts. At a current density of 50 mA/cm^2, the cell voltage and the power density are increased by about three and five times respectively, comparing Pt_1Sn_1/C and Pt/C. From Table 1, it can be clearly seen that the onset potential of ethanol electrooxidation over PtSn/C is shifted to more negative values, which means easier oxidation, with respect to those over PtRu/