

Research on bioorganic fuels as power sources

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ABSTRACT

This paper deals with the kind of the bioorganic fuel cells that are equipped with or without ion exchange membranes. The bioorganic materials of interest are alcohols (methanol, ethanol) and glucose, which are obtained from renewable energy sources such as biomass. The operation temperatures of the direct fuel cells cover from room temperature up to 150 °C. The direct bioorganic fuel cells belong to the subject area of 'Advanced fuel cells' of the Working group 4 in the EU COST Action 543 among the collaborating Universities and Institutes. Bioorganic fuel cells are suitable for application in small portable power sources, such as backups, battery chargers and in electronic devices. A number of current and earlier works are summarised and advances are highlighted in this area with special emphasis on glucose as a fuel.

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1. Introduction

Bioorganic fuel cells are nowadays of great importance because they allow the use of renewable energy sources obtained from biomass products as a fuel for a direct and sustainable use in small units of power sources. The direct use of different biofuels in fuel cells avoids the need for storage, handling, need of safety measures and transportation as compared to fuel hydrogen. There exist three types of direct fuel cells obtained from bioorganic materials that can operate within the temperatures intervals from room temperatures up to 150 °C and they are mainly classified as follows: 1) direct fuel cells with an electrolyte contained in either anion exchange (AEM) or proton exchange membranes (PEM) [1-4], 2) direct fuel cells with either proton exchange membranes or membrane-less with microbial tissues or enzymes [5-7], and 3) direct fuel cells with the fuel mixed in the liquid electrolyte together [8]. The direct alcohol fuel cells as a fuel produce higher current densities up to several tens of mA cm⁻², much higher than the current densities achievable with the glucose fuel cells. Moreover, glucose and alcohol fuel cells differ in the possibilities of employing selective ion exchange membranes. In this paper, we will compare the three different types of fuel cells, with emphasis on the direct alcohol fuel cell using AEM or PEM, and will summarize the R&D effort for glucose fuel cells in an alkaline medium.

2. Types of direct bioorganic fuel cells

2.1. The anion and proton exchange membrane fuel cells with alcohols as the fuel

The liquid-fed direct alcohol (methanol and ethanol) fuel cells especially obtained from renewable energy sources are

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promising candidates for portable power supply given the relatively simple system design, handling, volume and cell operation [9,10]. The primary advantage of the direct electrooxidation of alcohols is that that liquid fuel has a high specific energy, i.e., 6 and 8 kW h kg⁻¹ for pure methanol and ethanol, respectively, making storage and refuelling easy. In both the AEM and PEM fuel cells, both methanol and ethanol are consumed at the anode with Pt and Pt alloy as catalysts dispersed on high surface area carbons or other carbonaceous materials. The low-current densities associated with the oxidation reactions of the alcohols are mainly ascribed to the slow kinetics and mechanisms involving a number of steps and intermediate products, adsorption of the intermediate CO on Pt sites, non-facile dissociation of the bonded carbon atoms, release of CO₂ as a reaction product leading to a formation of carbonate with the alkaline electrolyte as well as fuel crossover through the membranes to the cathode side resulting not only the loss of fuel efficiency but also creation of mixed potential at the cathode side [11-19].

In order to suppress the deleterious effect of CO on Pt in the form of catalyst poisoning, another metal of the oxophilic type is added to promote the oxidation of CO to CO2. Different supports and alloys of PtRu, Pt/WC, Pt/WO_x, ternary (Pt-Ru-Os, Pt-Ru-Ir) and quaternary (Pt-Ru-Os-Ir, Pt-Ru-Ir-Sn) have been applied to enhance the reaction rate of methanol oxidation [11,13,14,20,21]. Furthermore, inorganic fillers of hygroscopic materials, such as silica, titania, zirconia or alumina have been included in a synthesis of the proton conducting membranes so that to reach high temperatures and to achieve i) faster electrode kinetics ii) higher level of hydration and easier water-thermal management iii) lower impact of CO are maintained [22-25]. Currently anion exchange membranes have been employed in direct methanol or ethanol as a viable method to avoid the drawbacks associated with PEM or liquid alkaline electrolyte as mentioned above. The AEM is less prone to carbonisation due to the oxidation reaction of methanol and incoming carbon dioxide with air.

Alcohols have a relatively high specific energy capacities 5019 Ah kg⁻¹ (pure methanol) and 6981 Ah kg⁻¹ (pure ethanol). The anodic oxidations of methanol and ethanol as well as the respective cathodic reactions in PEM and AEM are described in equations (1) and (2). The equilibrium cell voltages ΔE_o for standard conditions at 25 °C are 1.21 V (methanol) and 1.15 V (ethanol), respectively.

obtained with methanol in PEMFC as a fuel compared to DEFC with ca 50 mW cm⁻² [3,4,26,27]. Low power densities from 2 to 16 mW cm⁻² have been reported for the AEM with methanol and ethanol supplied at the anode in various concentrations [1,2,28–30].

2.2. Direct fuel cells with glucose

There are three different kinds of fuel cells, where glucose is oxidized at the anode and these are called i) enzymebased fuel cells ii) microbial fuel cells also called collectively as biofuel cells and iii) abiotic fuel cells. All fuel cells convert the chemical energy to electrical energy with the help of the catalytic reactions either by enzymes, microbes or inorganic metals or mixtures of organic molecules supported on carbon. The biofuel cells use whole living organisms or purified enzymes to act as specific and active catalysts [5-7]. Since most enzymes and microbes are electrochemically inactive to electron transfer to the electrode, redox mediators or chemical modification are needed to facilitate this interaction [31-33]. Furthermore, a cation selective membrane serves as a separator in biofuel cells or non-compartmentalization between the anode and cathode is also used in enzyme-based systems [5,34]. Microbial fuel cells can be used for power generation from sources such as sewage sludge, sediments or waste water [35], while enzyme fuel cells find applications in miniaturized devices for implantable appliances, sensors, drug delivery, microchips and small portable power supplies [36,37]. The power densities in biofuel cells are very low with current densities of few microamperes making them inadequate to be used for harnessing more energy from glucose. Moreover, the complexity of the systems, durability, sludge formation, enzyme or microbe stability, mass transfer problems (proton and electron transfer and diffusion of fuel), etc. render the biofuel cells to be addressed in order to find applications in a number of functions and niches.

Glucose as a fuel has a relatively high specific energy capacity 3572 Ah kg⁻¹ when compared with direct hydrazine fuel cell (3345 Ah kg⁻¹) or direct formic acid fuel cell (1165 A h kg⁻¹). However, this theoretical value is based on full transfer in an alkaline medium of the 24 electrons appearing in Eq. (3).

PEM	AEM		
$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$	anode	$CH_3OH + 6OH^- \rightarrow CO_2 + 5H_2O + 6e^-$	(1)
$1.5O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$	cathode	$1.5O_2 + 3H_2O + 6e^- \rightarrow 6OH^-$	(1)
$CH_3OH + 1.5O_2 \rightarrow CO_2 + 2H_2O$	overall cell	$CH_3OH + 1.5O_2 \rightarrow CO_2 + 2H_2O$	
PEM		AEM	
$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$	anode	$C_2H_5OH + 12OH^- \rightarrow 2CO_2 + 9H_2O + 12e^-$	(2)
$3O_2 + 12H^+ + 12e^- \rightarrow 6H_2O$	cathode	$3O_2 + 6H_2O + 12e^- \rightarrow 12OH^-$	(2)
$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$	overall cell	$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$	

Power densities from 4.5–360 mW cm⁻² depending on temperature ranges (from room T to 150 °C), concentration of methanol (1 or 2 M) or type of oxidant (air or oxygen) were

$C_6H_{12}O_6 + 24OH^- \rightarrow 6CO_2 + 18H_2O + 24e^-$	anode	
$6O_2 + 12H_2O + 24e^- \rightarrow 24OH^-$	cathode	(3)
$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$	overall cell	

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