



Direct sorbitol proton exchange membrane fuel cell using moderate catalyst loadings



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ABSTRACT

Recent progress in biomass hydrolysis has made it interesting to study the use of sorbitol for electricity generation. In this study, sorbitol and glucose are used as fuels in proton exchange membrane fuel cells having 0.9 mg cm^{-2} PtRu/C at the anode and 0.3 mg cm^{-2} Pt/C at the cathode. The sorbitol oxidation was found to have slower kinetics than glucose oxidation. However, at low temperatures the direct sorbitol fuel cell shows higher performance than the direct glucose fuel cell, attributed to a lower degree of catalyst poisoning. The performance of both fuel cells is considerably improved at higher temperatures. High temperatures lower the poisoning, allowing the direct glucose fuel cell to reach a higher performance than the direct sorbitol fuel cell. The mass specific peak power densities of the direct sorbitol and direct glucose fuel cells at 65°C was $3.2 \text{ mW mg}^{-1}_{\text{catalyst}}$ and $3.5 \text{ mW mg}^{-1}_{\text{catalyst}}$, respectively. Both of these values are one order of magnitude larger than mass specific peak power densities of earlier reported direct glucose fuel cells using proton exchange membranes. Furthermore, both the fuel cells showed a considerably decrease in performance with time, which is partially attributed to sorbitol and glucose crossover poisoning the Pt/C cathode.

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1. Introduction

The abundance of biomass in the world has always generated a great deal of interest in using this natural resource as a renewable and sustainable source of power. The three main routes to obtain fuels from biomass are: *i*) gasification, *ii*) pyrolysis and liquefaction and *iii*) hydrolysis. Syn-gas ($\text{CO} + \text{H}_2$) may be obtained from gasification and may be used in the production of alkanes [1], methanol [2] or hydrogen [3,4]. Bio-oils may be obtained from pyrolysis and liquefaction and may be transformed into chemicals and other gasoline compounds with further de-oxygenation [5]. Hydrolysis may also be used to transform biomass to aqueous sugars, which later can be: *i*) fermented to ethanol [6], *ii*) aqueous-phase reformed to hydrogen [7] or *iii*) catalytically converted into other fuels [8]. On the other hand, devices that could transform the chemical energy within the biomass into electricity with fewer number of process steps could potentially bring greater benefits in terms of energy consumption, degree of complexity and time.

Polysaccharides, such as starch and cellulose obtained from food resources and woody biomass, respectively, are mainly made up by

monosaccharides, such as glucose. It has already been shown that glucose has the potential to be directly electro-oxidized in a fuel cell, generating electricity [9–15]. Furthermore, due to the abundance of glucose in the blood of humans (4–6 mM), there is a great interest in such devices to be used as implantable power generators [16].

In the context of mobile and stationary applications, glucose may readily be obtained from starch by hydrolysis, offering an abundant source of energy. On the other hand, the use of food resources as feedstock for biofuel or electricity production may be questionable due to the food-fuel supply issue. Obtaining glucose from woody biomass, such as cellulose or lignocellulose may be considered as a much more attractive alternative. However, this has been shown to be a difficult task and it is an old area of research [17]. The crystalline nature of cellulose and the network of hydrogen bonds holding it together usually require harsh conditions during hydrolysis, conditions that unfortunately often degrade the wanted product, glucose. Selective trapping of byproducts formed during cellulose hydrolysis may instead offer an opportunity to utilize and exploit the instability of glucose [17]. Acid-catalyzed hydrolysis coupled with dehydrative or reductive transformation has produced sorbitol and other polyols from cellulose in very high yields [18–20]. Such methods of producing potentially cheap sorbitol from woody biomass, e.g. from waste products formed during

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Table 1
Materials, conditions and peak performance of high-power output direct sugar abiotic fuel cells.

Peak power	Catalyst		Catalyst load		Conditions	Reference
	<i>anode</i>	<i>cathode</i>	<i>anode</i>	<i>cathode</i>		
2.8 mW cm ⁻²	PtRu	Pt	5 mg cm ⁻²	6 mg cm ⁻²	60 °C, 1 M glucose, PEM	C. A. Appleby et al. [12]
1.5 mW cm ⁻²	PtRu	Pt	3 mg cm ⁻²	3 mg cm ⁻²	20 °C, 0.5 M glucose, PEM	N. Fujiwara et al. [13]
20 mW cm ⁻²	PtRu	Pt	3 mg cm ⁻²	3 mg cm ⁻²	20 °C, 0.5 M glucose + 0.5 M KOH, AEM	N. Fujiwara et al. [13]
38 mW cm ⁻²	NiPd	HYPERMEC	3 mg cm ⁻²	1 mg cm ⁻²	60 °C, 0.5 M glucose + 7.0 M KOH, AEM	L. An et al. [10]
1.5 mW cm ⁻²	Ag/Ni	Ag/Ni			60 °C, 0.5 M glucose + 7.0 M KOH, AEM	J. Chen et al. [11]
1.4 mW cm ⁻²	PtRu	Activ. charcoal	2 mg cm ⁻²		50 °C, 0.2 M glucose + 1 M KOH solution	D. Basu et al. [9]
0.7 mW cm ⁻²	PtAu	Activ. charcoal	3 mg cm ⁻²		30 °C, 0.2 M glucose + 1 M KOH solution	D. Basu et al. [9]
4.2 mW cm ⁻²	PtPd	MnCO ₂ O ₄ /CoTPP	2.46/2.46 mg cm ⁻²	3.15/17.5 mg cm ⁻²	51 °C, 1 M glucose in KOH solution	J. P. Spets et al. [37]
2.3 mW cm ⁻²	PtPd	MnCO ₂ O ₄ /CoTPP	2.46/2.46 mg cm ⁻²	3.15/17.5 mg cm ⁻²	51 °C, 1 M sorbitol in KOH solution	J. P. Spets et al. [37]

pulp-and-paper manufacturing, make it highly relevant to study the performance of a direct sorbitol fuel cell using commercially available fuel cell components.

The electro-oxidation of glucose [21] and sorbitol [22] on Pt electrodes in neutral and acid media has been well described in the literature. It has also been studied on a number of other catalysts [23–27], as well as in alkaline media [28,29]. It is out of the scope of this paper to further study the reaction mechanisms of the electro-oxidation of glucose and sorbitol. However, it is well established that the electro-oxidation of glucose, on Pt and in acid media, proceeds via the formation of glucono- δ -lactone, which may undergo further oxidation [21,30] to form a number of different products, e.g. gluconic-, glucaric-, glucuronic-, tartaric-, glyoxylic-, formic-, oxalic- and glycolic-acids, as well as carbon dioxide and carbon monoxide [21]. Furthermore, lactone and adsorbed carbon monoxide species have been reported to block active sites on Pt, i.e. poisoning the catalyst [21,31].

Studies on the electro-oxidation of sorbitol on Pt in acidic media have shown that sorbitol is only weakly oxidized on Pt electrodes and that the direct oxidation product is actually glucose [22,32–34], which may further oxidize to gluconic-, glyoxylic- and formic-acid, and detecting traces of lactone and adsorbed CO species [34].

Although a significant amount of work has been carried out investigating the details of the electro-oxidation of glucose and sorbitol on a number of different catalysts and environments, studies concerning direct sugar fuel cells and especially direct sorbitol fuel cells are less abundant. There are primarily two design alternatives for such devices: *i*) microbial and enzymatic fuel cells and *ii*) abiotic fuel cells. Furthermore, abiotic fuel cells may: *i*) use a proton exchange membrane (PEM), *ii*) an anion exchange membrane (AEM) or *iii*) be membrane-less. Table 1 summarizes the performance and conditions of some of the best performing abiotic direct glucose and sorbitol fuel cells according to published data. As it is observed in Table 1, bi-metallic catalysts are the most commonly used anodes, as they possess a superior ability to sustain poisoning and tolerate CO compared with pure Pt [35]. Supported NiPd (NiPd/C) electrodes have shown to be very promising for glucose oxidation and have achieved the highest power densities [10]. On the other hand, all devices listed in Table 1 use rather high catalyst loadings, at both anode and cathode, which could compromise these devices cost effectiveness. It can also be noticed that the use of AEM together with a KOH solution improves the performance of the direct glucose fuel cell compared to the use of PEM. N. Fujiwara et al. [13] were able to obtain a ten-fold increase in peak power density for their device by replacing the PEM with an AEM.

Studies on direct sorbitol fuel cell are still few. J. P. Spets et al. [36] have published several studies using different bioorganic materials as fuel in a direct mode fuel cell. The device is a membrane-less fuel cell using bi-metallic PtPd catalyst at the anode. It was found that the glucose fuel cell gave higher performance than the sorbitol fuel cell (see Table 1) and that an increase in temperature considerably improved the performance of both fuel cells.

The aim of this study is to electrochemically characterize a direct sorbitol fuel cell made of commercially available PEMFC membranes and catalysts, using moderate loadings of PtRu/C catalyst at the anode. The performance of the direct sorbitol fuel cell is compared to the performance of a direct glucose fuel cell under the same conditions. This approach not only allows benchmarking the direct sorbitol fuel cell, but may also highlight some fundamental differences in the electro-oxidation of these two fuels.

2. Experimental

2.1. Preparation of MEA

Nafion™ 115 membranes (Sigma Aldrich) were pre-treated by boiling them in 3% H₂O₂, as well as in 0.5 M H₂SO₄, followed by rinsing in boiling Milli-Q water. The anode ink was prepared by mixing Tanaka TEC61E54 (29.7% Pt, 23% Ru), 5% Nafion solution, isopropanol and water. The cathode ink was prepared by mixing Tanaka, TEC10E40E (38% Pt), 5% Nafion solution, isopropanol and water. The solutions were sonicated for 1 hour and stirred overnight. The resulting ionomer to carbon ratio (I/C) in the inks were 0.9 and 0.8 for the anode and cathode, respectively. All electrodes were airbrushed over a hot plate (90 °C) while using an acetate stencil mask to control the geometrical area of the electrodes (2.4 cm²). The resulting catalyst loading of the electrodes were calculated by mass difference from the acetate stencil mask, resulting in catalyst loadings of 0.3 mg_{Pt} cm⁻² and 0.9 mg_{PtRu} cm⁻² at the cathode and anode, respectively.

2.2. Fuel cell hardware

The fuel cell had graphite current collectors with a serpentine flow field (Fuel Cells Technologies Inc.). The test bench included temperature control of the cell, humidifiers, pipes linking the humidifiers to the cell and of the pipes linking the diaphragm pumps to the cell (see Fig. 1). Gas diffusion layers (GDLs) H231516 and H2315T10AC1 (Freudenberg) were used on the anode and cathode side, respectively and the compression pressure of the cell was 2.4 bar. Cyclic voltammetry and polarization curves were carried out using a potentiostat/galvanostat Model 263A (EG&G Princeton Applied Research) controlled by CorrWare. The cell resistance was measured by electrochemical impedance spectroscopy (EIS) using an electrochemical workstation IM6 (Zahner elektrik).

2.3. Electrochemical characterization

2.3.1. In-situ cyclic voltammetry

In-situ cyclic voltammetry, using a half-cell configuration, was carried out in an effort to isolate the performance of the PtRu/C electrodes towards glucose and sorbitol oxidation. Fully humidified H₂ over the Pt/C electrode was used as combined reference/counter electrode (RE/CE), assuming negligible polarization. The cyclic

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