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## Article (Special Column on Electrocatalysis for Fuel Cells)

# Improving the efficiency of a direct ethanol fuel cell by a periodic load change



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## ABSTRACT

We present a simple method to increase the efficiency of a direct ethanol fuel cell by a periodic modulation of the load (pulsed mode). The fuel cell was periodically short circuited with a resistor ( $1\ \Omega$ ) for a few seconds (high load period) followed by a low load period of up to 100 s when the resistor was disconnected. The open circuit voltage (OCV) values before and after the short circuit of the cell showed an increase of up to 70 mV. The higher OCV was due to the oxidation and removal of strongly adsorbed CO during the electric short circuit when the electric potential of the anode was increased to be close to the cathode potential. The depoisoned anode surface was much more active directly after the short circuit. The slow decrease of the OCV observed after the short circuit was caused by the subsequent poisoning of the anode surface, which can be neutralized by another short circuit. In general, a stable increase in cell performance was obtained by repetition of the electric short circuit. The data showed that the pulse mode gave an increase in the power generated by the direct ethanol fuel cell by up to 51% and was 6% on average. It is anticipated that this mode of operation can be used also in different types of polymer electrolyte membrane fuel cells where CO poisoning is a problem, and after optimization of the parameters, a much higher gain in efficiency can be obtained.

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## 1. Introduction

Direct ethanol fuel cells (DEFCs) are a subclass of polymer electrolyte membrane fuel cells (PEMFCs) that have many potential advantages over other types of fuel cells (FCs), but currently there are no anode, cathode, and membrane materials that give a high efficiency [1–8]. Three important obstacles are: (1) low activity of the anode and cathode catalysts [2–5,9–12], (2) low durability of the membrane, especially at elevated temperature [13–15], and (3) permeability of the membrane to fuel and oxidizer [15–17]. Even with the most active anode catalysts, which are noble metal nanoparticles, ethanol oxidation only occurs with a high overpotential and gives a low se-

lectivity to  $\text{CO}_2$  [18–23], the product of the complete oxidation of ethanol. Different approaches have been tested to increase the activity of the anode and cathode catalysts, including changing the catalyst support [8] and the preparation of ultra-pure [24] and bi- or multicomponent catalysts [10–12, 25–28]. Changes in cell design, including membraneless cells, have also been proposed to increase efficiency [29,30].

It is known that the incomplete electrooxidation of ethanol on Pt leads to CO as one of the products [31]. CO strongly adsorbs on the surface of the Pt electrode and significantly decreases its catalytic activity [31]. It has been also observed that alloying Pt with other metals can increase the catalytic activity by a bifunctional mechanism. In bimetallic systems, ethanol

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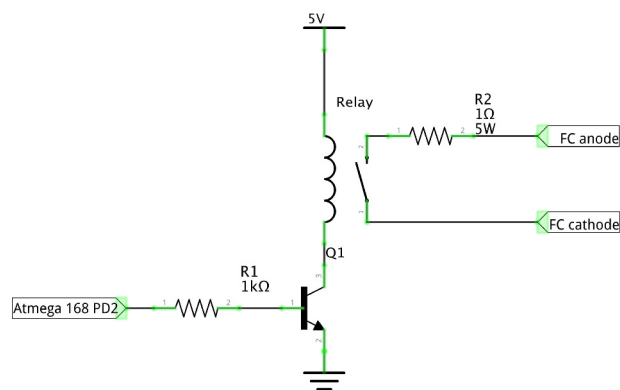
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adsorbs on Pt while the second metal provides adsorbed OH groups. When CO is produced, adsorbed OH groups facilitate its removal by the oxidation of CO to CO<sub>2</sub>. This mechanism was described for the first time by Watanabe and Motoo [32,33] for methanol electrooxidation on Pt-Ru, but it is valid also for ethanol electrooxidation. The main difference is that in the case of ethanol electrooxidation, the OH groups on the second metal promote the formation of acetic acid (another product of the incomplete oxidation of ethanol) [16,23], which is a dead end for the electrooxidation of ethanol in low temperature fuel cells [34,35]. This is why another method for the removal of CO from the catalyst surface is needed for DEFCs. Here we present a simple method to de-poison the anode catalyst surface by a momentary increase of the anode potential, which caused the oxidation and removal of adsorbed CO from the catalyst surface. As a result, an increase in the open circuit voltage (OCV) and in the amount of power generated was observed.

## 2. Experimental

Analytical grade 96% ethanol (POCH, Gliwice, Poland) and MilliQ (18 MΩ cm) water were used to prepare the ethanol solution (anode fuel). The anode catalyst (4–6 nm Pt or 1:1 Pt-Ru nanoparticles, 20% metal loading on Vulcan XC-72) and cathode catalyst (4–6 nm Pt nanoparticles, 40% metal loading on Vulcan XC-72) were manufactured by BASF. High purity (N5.2) O<sub>2</sub> from Air Products Inc. (Poland) was used as the cathode gas. Fuel cells from Fuel Cell Technologies Inc. were used, which consisted of two graphite plates with a single serpentine flow pattern and 10 cm<sup>2</sup> active area. The cell voltage and current were controlled using an EG&G Princeton Applied Research 362 Scanning Potentiostat and collected using a National Instruments NI USB-6211 data acquisition card connected to the *I* and *E* monitors of the potentiostat. Fuel was fed by a peristaltic pump at 1.56 cm<sup>3</sup>/min flow rate. The fuel cell membrane-electrode assembly (MEA) preparation has been described elsewhere [19]. The membrane-electrode assemblies were prepared by painting the catalyst suspension onto DuPont Nafion 117 pretreated by boiling in 0.5 mol/L H<sub>2</sub>SO<sub>4</sub> for 3 h prior to the catalyst deposition. For the anode, either Pt or Pt-Ru nanoparticles with 20% metal by mass on Vulcan XC-72 (BASF) or a loading of 1 mg (metal)/cm<sup>2</sup> was used. For the cathode, Pt nanoparticles with 40% Pt by mass on Vulcan

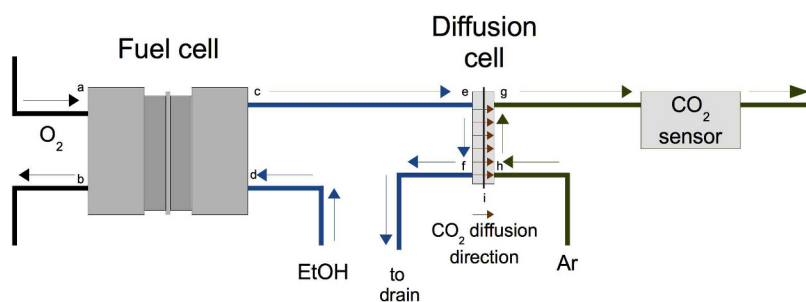


**Fig. 1.** Electronic schematic of the interface used for short circuiting the cell with a resistor (1 Ω).

XC-72 or a loading of 1 mg (metal)/cm<sup>2</sup> was used. The catalyst suspension used for the anode and cathode was prepared using water and 5% Nafion solution in ethanol (Aldrich) (1:1 by volume). The amount of liquid in the suspension was adjusted to give 30% by weight of Nafion in the dried total catalyst mass after deposition. Gas diffusion layers (10 cm<sup>2</sup> pieces of carbon paper from Toray) were added on both sides of the membrane before cell assembly.

The fuel cell was short circuited using a resistor (1 Ω 5W). The use of a small resistance was to simulate a low resistance load. The short circuit current was not measured. To give a periodic shorting of the fuel cell, a mechanical relay (Panasonic TX2SA-5V) controlled by an Atmel ATmega 168 microcontroller and a simple program for the microcontroller were used. A simple electronic interface to drive the mechanic relay from the microcontroller was made (Fig. 1), which consisted of a current limiting resistor (R1) and a general purpose NPN transistor (BC548) to drive the relay.

CO<sub>2</sub> amount was recorded using a GE Measurement & Control/GE Sensing Telaire T6615 NDIR 0–2000 ppm CO<sub>2</sub> sensor. A diffusion cell was used to separate gaseous CO<sub>2</sub> from the liquid product leaving the fuel cell anode. The diffusion cell consisted of two cavities, 10 mm wide, 100 mm long, and 1 mm deep, separated by the semipermeable Nafion 112 membrane (Fig. 2(i)) with inlet and outlet connections at both ends. One half (one cavity) of the diffusion cell was connected directly to the fuel cell anode outlet (Fig. 2, port c connected to port e), and the



**Fig. 2.** Schematic drawing of the experimental set-up. (a) FC cathode inlet; (b) FC cathode outlet; (c) FC anode outlet; (d) FC anode inlet; (e) diffusion cell liquid inlet (connected to FC anode outlet); (f) diffusion cell liquid outlet; (g) diffusion cell gas outlet; (h) diffusion cell gas inlet; (i) semipermeable Nafion 112 membrane. Liquid fuel path is marked in blue, and path of carrier gas (Ar) and CO<sub>2</sub> from the FC anode (gaseous) is marked in green. Brown arrows in the diffusion cell mark the direction of CO<sub>2</sub> diffusion from the liquid leaving the FC anode outlet to the carrier gas (Ar) stream.

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