The application of power-generating fuel cell electrode materials and monitoring methods to breath alcohol sensors

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ABSTRACT

A state-of-the-art fuel cell-based breath alcohol sensor (BrAS) testing station was developed and used to test electrocatalysts typically employed in power generating fuel cells for ethanol sensing. Sensor membrane-electrode assemblies (MEAs) were prepared with 20% Pt/C electrocatalysts and their sensitivity were compared to that of a commercial BrAS MEA that employs high loadings of Pt black. Using these Pt/C sensor MEAs, we were able to achieve raw sensitivity factors that approach that of the commercial sensor despite using 97% less Pt. The design of our test cell and station enabled *in situ* monitoring of MEA health through cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements in an operating sensor. MEAs prepared from Pt/C display a faster rate of sensor decay compared to the commercial sensor. CV and EIS measurements confirm that this loss is due to a combination of adsorbed intermediates on the anode surface as well dehydration of the catalyst layer. Sensitivity was completely restored by simple rehydration and potential cycling.

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1. Introduction

In recent years, there has been increased interest in the determination of breath compounds in medicine and clinical toxicology [1], since the analysis of volatile compounds in human breath makes it possible to observe several chemical processes in the body through a minimally invasive process. Measurements of breath alcohol concentration (BrAC) are prevalent for enforcing drinking and driving laws. While the analysis of blood alcohol concentration (BAC) is required for conviction in a court of law, routine analysis requires the use of portable and easy-to-operate devices that can be used by police agencies. The measurement of BrAC is a valid method because the alcohol concentration in alveolar air is proportional to the alcohol concentration in blood, with this relationship being 2100:1 (BAC/BrAC) [2]. This blood/breath factor has been used to calibrate breathalyzer devices, and it has become generally accepted for legal purposes to produce readings directly in BAC units [3]. It is illegal to operate a motor vehicle in Canada with a blood alcohol concentration (BAC) greater than 0.08 g/dL, which is equivalent to 80 mg of ethanol per 100 mL of blood. Similar laws are in place in most jurisdictions around the globe. Law enforcement agencies perform mandatory roadside breath alcohol tests on suspected offenders using approved devices. In recent years, devices such as these have been built into vehicles in the form of an alcohol ignition interlock, which will only allow a vehicle to be operated if the driver tests negative for alcohol in their system. A growing number of jurisdictions require alcohol interlock devices to be installed in a convicted offender's vehicle, especially repeat offenders.

Breath alcohol measurements have been accomplished using different approaches, such as solid-state sensing [4], infrared spectrometry [4,5], electrochemical oxidation [2,4], biosensors [4,6], gas chromatography [4,7], multi-sensor array (semiconductors and infrared devices) [8] and colorimetry [9]. Of all those types of devices, electrochemical fuel-cell style sensors have received the most attention and wide spread deployment due to their portable nature allowing easy deployment for real-time measurements in the field. These devices allow *in situ* data analysis and avoid time-consuming sampling, transportation, and storage steps.

Electrochemical fuel-cell type breath-alcohol sensors (BrAS) get their name due to the similarity to direct alcohol fuel cells commonly studied for power generation. A schematic diagram of an electrochemical BrAS is shown in Fig. 1. The electrochemical sensor consists of two platinum electrodes sandwiched across a polymer electrolyte membrane (PEM) to form what is called the membrane-electrode assembly (MEA). A fixed volume of ethanol vapour is aspirated into the anode compartment where it is oxidized to

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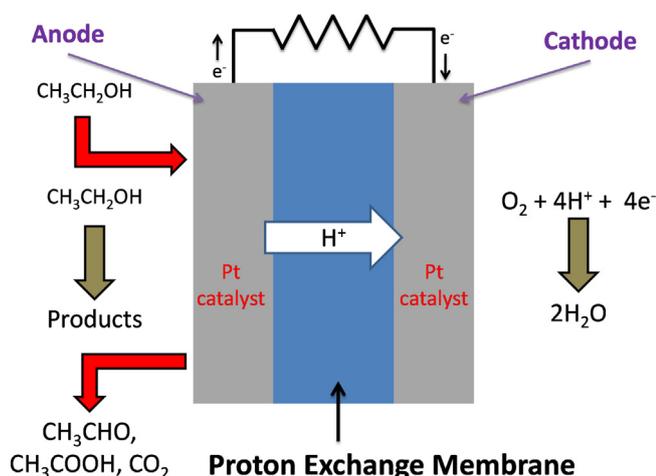 *E-mail address:* Brad.Easton@uoit.ca (E.B. Easton).

Fig. 1. Schematic diagram of an electrochemical breath alcohol sensor (BrAS).

several possible products; mainly acetaldehyde, acetic acid and possibly CO_2 [10]. Protons migrate through the PEM and electrons are transported through the external circuit and into the cathode compartment where they combine with oxygen (from air) to form water. The current (or charge) transferred is measured for each injection and is proportional to the concentration/amount of ethanol introduced into anode compartment. Thus, after calibration, the sensor can determine ethanol concentrations in unknown samples, including BrAC levels in humans.

Despite the commercial success of these sensors over the last three decades, there is ample need and opportunity for improvement in the performance, durability and cost of the MEAs. While there are many examples of ethanol sensor devices in the recent literature [2,11], very few correspond to cell configurations that are similar to those used in the commercial device. In many cases, these reports involve sensing ethanol using an alkaline electrolyte or directly sampling ethanol containing liquids (as opposed to vapor). Typical commercial sensor MEAs employ a porous polyvinyl chloride (PVC) membrane that is filled with H_2SO_4 (aq) [12,13]. Each electrode contains extremely large amounts of Pt black catalyst (7–14 mg/cm^2) and employ a Teflon binder, as shown in Fig. 2A. Our analysis of these MEAs demonstrated that there is a high degree of Pt agglomeration, meaning there is an extremely low electrochemically active surface area (ECSA) and very poor utilization of Pt [14]. Significant advances in MEA materials for power generation fuel cells have occurred over the last 25 years that have not been investigated or validated for applicability to these sensor formulations. For example, advances in Pt nanoparticle catalyst preparations and electrode structure optimization has resulted in increased fuel cell performance with drastically lower Pt loadings, typically 0.5 mg cm^{-2} or less [15]. Moreover, several reports have shown that Pt or Pd-based alloy catalysts can improve ethanol oxidation in alkaline media [16–18]. Furthermore, there have been significant advances related to *in situ* electrochemical diagnostic measurements that can assess MEA health in operating fuel cells. To the best of our knowledge, such materials and diagnostic methods have not been investigated nor validated for applicability to these sensor formulations.

In this paper, we have compared the sensing behavior obtained using typical power-generating MEA materials with that obtained using current commercial devices. Electrodes were prepared using two different commercially available carbon support Pt fuel cell catalyst. In order to facilitate these measurements, a sensor cell and testing station was constructed that could accommodate cell testing of different MEA materials as well as diagnostic cyclic voltammetry and electrochemical impedance spectroscopy mea-
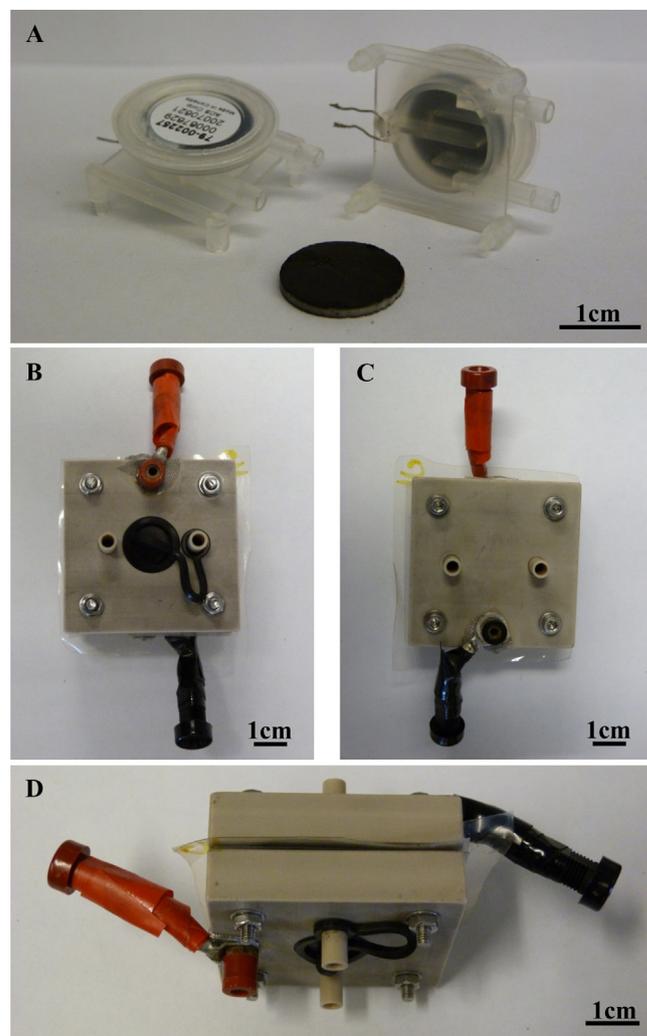

Fig. 2. Photograph of (A) the commercial sensor cell and Dräger MEA. Photographs of the (B) cathode (C) anode side and (D) assembled UOIT cell.

surements. Through these measurements, the influence of catalyst selection on sensitivity and stability was assessed.

2. Methods and materials

2.1. Materials

E-TEK 20% Pt on Vulcan XC72 carbon black was purchased from BASF and is hereafter referred to as E_{20}. Johnson Matthey HiSpec 3000 20% Pt on carbon black was purchased from Alfa Aesar and is hereafter referred to as JM_{20}. Both of these catalysts are composed of Pt nanoparticles dispersed onto a carbon support. Ethanol (95%) was obtained from Commercial Alcohols Inc. Isopropyl alcohol and sulfuric acid (98%) were obtained from Sigma–Aldrich. Commercial alcohol sensor cells, pumps and MEAs were donated by Alcohol Countermeasure Systems Corp.

2.2. Commercial MEA and commercial sensor cell

2.2.1. Characterization of the commercial MEA

The commercially sourced sensor unit employed MEAs manufactured by Dräger. The MEA employs porous polyvinyl chloride (PVC) membrane filled with sulfuric acid [12]. Each side of the PVC membrane is coated with a Pt-based catalyst layers. Optical microscope images were obtained using a National Digital Microscope