



## Fuel cell-based breath alcohol sensors utilizing Pt-alloy electrocatalysts

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### ABSTRACT

Fuel cell-based breath alcohol sensors (BrAS) are routinely used to measure breath alcohol concentration (BrAC) in human subjects. The electrodes used in BrAS employ an extremely high loadings of Pt black to catalyze the half-cells reaction. Over the last two decades, significant advances in Pt-based alloy electrocatalysts for the ethanol oxidation reaction (EOR) have been made. However, these new electrocatalysts have never been examined or validated for ethanol sensing. In this study, we have fabricated fuel cell-based BrAS using Pt-Mn/C and Pt-Cu/C alloy catalysts synthesis in-house. We evaluated their sensitivity and durability in comparison to electrodes fabricated from commercial Pt/C and Pt<sub>3</sub>Sn/C catalysts. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to evaluate the quality of catalyst layers and membrane electrode assemblies (MEA) in the BrAS and to understand factors that influenced sensitivity. Among the commercial samples, Pt<sub>3</sub>Sn/C showed the highest sensitivity with slightly lower precision. The sensitivity achieved with Pt-Cu/C was significantly better than Pt-Mn/C and very similar to Pt<sub>3</sub>Sn/C. However, since the Pt-Cu alloy contains much less Pt than either commercial catalyst, it had a significantly higher Pt-mass specific sensitivity compared to all other catalysts. Therefore, these alloy catalysts could be great candidates to replace Pt black in future commercial sensors.

### 1. Introduction

There are many volatile compounds in human breath that can be used to detect compounds present in the blood which are related to the health of the subject [1–3]. Breath sampling is a very appealing method because it is non-invasive and it can be completed rapidly with high accuracy.

One of the most well-known applications of breath sampling is the breath alcohol sensing devices used for the determination of sobriety/inebriation, commonly referred to as a breathalyzer [3–9]. In these devices, the breath alcohol concentration (BrAC) in a subject's exhaled breath is determined and can be related to the ethanol concentration in blood, through the known volume ratio of 1:2100 [10]. The fuel cell-based breath alcohol sensor (BrAS) is the most commonly employed portable device. However, there are many other types of sensors systems, including solid-state sensing [3,6], infrared spectrometry [6,11], biosensors [6,12], gas chromatography [6,13], multi-sensor array (semiconductors and infrared devices) [14–18] and colorimetry [19] can be also used to measure BrAC. However, many of these devices are less portable and/or more expensive than the cell-based BrAS.

In many jurisdictions, it is illegal to operate a motor vehicle when a subject has a blood alcohol concentration (BAC) above a critical value. For example, the Criminal Code of Canada (Section 235) states that it is

a criminal offence to operate a vehicle with a BAC greater than 0.08 g/dL, which is equivalent to 80 mg of ethanol per 100 mL of blood [4]. Most jurisdictions within Canada also forbid driving at lower BAC (e.g. 0.05 g/dL), and many new drivers are not permitted any alcohol in their system at all.

To enforce these laws, law enforcement agencies typically employ a fuel cell-based BrAS for road side screening. Fuel cell-based BrAS detects ethanol electrochemically. The cell is essentially a modified version of a direct ethanol fuel cell, where a fixed volume of breath is injected into the anode compartment of the cell. If ethanol is present, it will be oxidized with a corresponding reduction of oxygen (from air) occurring at the cathode. The current or charge produced is directly proportional to the BrAC enabling the determination of BAC. The cell design employs a membrane electrode assembly (MEA) fabricated from a porous polyvinyl chloride membrane that is filled with H<sub>2</sub>SO<sub>4</sub> (aq) [20,21] and two electrodes. Each electrode contains a large amount of Pt black catalyst (7–14 mg/cm<sup>2</sup>) held together with a Teflon binder. Studies in our group have indicated that the Pt utilization is very low in the commercial sensors [4,7].

The sensor MEAs share many of the same basic characteristics of MEA used for power generation. Innovation in the power-generating fuel cell industry over the last couple of decades has resulted in a substantial decrease in required Pt loadings without sacrificing

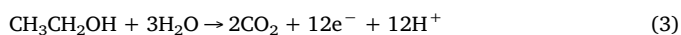
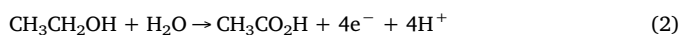
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performance. For example, numerous studies have shown that Pt loading can be extremely reduced to  $\sim 0.5 \text{ mg/cm}^2$  or less with using carbon supported Pt nanoparticles [22–33]. Furthermore, Pt-alloy catalysts such those made with Ru, Sn, Mo, Mn, Cu or Ni [25,31–42] have been shown to have enhanced activity towards both anodic and cathodic fuel cell reaction.

Despite these advances in power-generating fuel cell technology, very few of these advances have even been evaluated for BrAS applications. Recently, we have shown that carbon supported Pt electrocatalysts (Pt/C) can be used to replace high loadings of Pt black in commercial BrAS [4]. The BrAS assembled using Pt/C has illustrated raw sensitivity factors similar to the commercial sensor despite using 97% less Pt [4]. Recent work from Modjtahedi et al has found that a linear sensing response can be achieved with as little as  $0.03 \text{ mg/cm}^2$  of Pt, though a significant reduction in sensitivity factor does occur [30]. Additional studies from our group have shown how refining the MEA composition can influence sensor reliability under dry condition [43,44].

Those studies have demonstrated the viability of adapting power generating fuel cell advances towards ethanol sensing. The next evolution in this would be to employ alloy electrocatalysts to improve the ethanol oxidation reaction (EOR) kinetics at the anode. Ethanol oxidation can occur via multiple pathways:



In the case of the ethanol sensor, the first two reactions are believed to be the dominant reactions. These reactions correspond to incomplete oxidation of ethanol. Since the sensor measures current (or charge), increasing the current produced by a fixed amount of ethanol would lead to greater sensitivity. Thus, one would expect that any catalyst that favour the last reaction, one that produces 12 electrons per ethanol molecule, would be more sensitive. However, Pickup's group has demonstrated that for power generating fuel cells, the maximum  $\text{CO}_2$  production does not correspond with maximum performance below  $100^\circ\text{C}$ , since that reaction (Eq. (3)) is slower than the 2 or 4 electrode steps (Eqs. (1) and (2)) [45,46].

Pt-Sn has been perhaps the most well studied alloy catalyst for EOR, with the most active phase believed to be  $\text{Pt}_3\text{Sn}$  [29,47–50]. Our group has had better success with Pt-Mn and Pt-Cu catalysts for EOR oxidation, demonstrating about 3-times the Pt mass-specific EOR activity of Pt/C [33,39,42,51]. One key advantage of these alloy catalyst is significantly lower Pt-contents in the alloy. This, along with reduced metal loadings has the potential benefit of cost savings in the devices. Furthermore, the co-catalyst may improve the electrode's tolerance to atmospheric contaminants (e.g. CO).

In this paper, we have examined the behavior of BrAS devices constructed using in-house synthesized Pt-Mn/C and Pt-Cu/C alloy catalysts at the anode. We have compared their sensing properties to similar sensors fabricated from commercially available Pt/C and  $\text{Pt}_3\text{Sn}/\text{C}$  electrocatalysts. These catalysts were selected based on previous demonstration of high EOR activity in liquid phase. Our hypothesis is that EOR activity in the liquid phase will translate to greater sensing of ethanol in the vapour phase. Furthermore, to the best of our knowledge, this is the first report of Pt-alloy catalysts being utilized in a BrAS configuration. The influence of catalyst composition on sensor response and stability was evaluated.

## 2. Methods and materials

### 2.1. Electrocatalysts

The synthetic methods used to prepare the carbon supported

$\text{Pt}_{0.25}\text{Mn}_{0.75}$  and  $\text{Pt}_{0.25}\text{Cu}_{0.75}$  alloys are described in detail elsewhere, and are briefly described here [33,39,42]. Vulcan XC72R carbon black (Cabot Corp.) was used as the carbon support in all cases. Metal precursors were  $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$  (Aldrich),  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (Aldrich), and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (Aldrich).

Pt-Mn/C was prepared via an aqueous impregnation method. The required amounts of metal salts and carbon were dispersed in a beaker at room temperature while maintaining a pH of 3. Trisodium citrate (SC) (Aldrich) was added to the solution to control particle size and improve dispersion on the carbon support.  $\text{NaBH}_4$  was subsequently added and the mixture was left to stir overnight. The resulting powder was filtered and washed with isopropanol alcohol (IPA), acetone, and deionized water, and finally dried in an oven at  $80^\circ\text{C}$  overnight.

Pt-Cu/C was prepared via a microwave assisted polyol method. Each metal precursors and Vulcan carbon were mixed with ethylene glycol (Aldrich) using a mechanical stirrer. The solution pH was adjusted to pH 9, after which it was sonicated for 45 min to achieve a uniform suspension. The suspension was placed into a microwave oven (SANYO - 2450 MHz) and heated for 8 min and then left to cool down under continues mechanical stirring. The final product was collected via suction filtration, and washed with copious amounts of IPA, acetone, and deionized water, and finally dried in an oven at  $80^\circ\text{C}$  overnight.

Both Pt-Mn/C and Pt-Cu/C were heated treated to create catalysts more active towards the EOR. This is primarily due to the formation of more uniform alloys phases at higher temperatures. Each sample was heat treated in quartz tube under a nitrogen atmosphere at  $700^\circ\text{C}$  using a Barnstead Thermolyne tube furnace. The period of heat treatment was kept constant (1 h) for all the samples. This heat treatment procedure was determined to be optimal in our previous studies [33,39,42]. After heat treatment, the samples were cooled down under a constant flow of nitrogen gas and were preserved inside the furnace until room temperature was reached. These samples are hereafter referred to as "Pt-Mn/C-SC-HT and Pt-Cu/C-POL-HT".

Two carbon support commercial samples with 20 wt% metal loading, Pt/C (Premetek Co.) and  $\text{Pt}_3\text{Sn}/\text{C}$  (Premetek Co.), were studied and compared to the samples made in-house.

### 2.2. Sensor electrodes and MEA fabrication

Fuel cell electrodes were prepared from catalyst inks, which were produced by mixing the appropriate amounts of catalyst powder, 5 wt% Nafion solution (Dupont), water and IPA. The volumetric ratio of water/IPA was 50% and the ratio of solution to catalyst powder for producing ink was kept constant for all samples. The mixture was thoroughly mixed and then sonicated for 45 min. The ink was mechanically stirred overnight to produce a uniform mixture and the ink was further sonicated for 45 min before spray deposited using an air-brush onto carbon paper (Toray TPGH-090, 10% wet-proofing) as a gas diffusion layer. The electrodes were dried for 30 min at room temperature and then at  $80^\circ\text{C}$  overnight. Electrode had a Nafion loading of 30 wt% in all cases. The total metal loading of the catalyst layer was kept similar at ca.  $0.4 \text{ mg/cm}^2$ .

MEAs were prepared by hot-pressing ( $150 \text{ kg/cm}^2$  at  $130^\circ\text{C}$  for 120 s) two  $4\text{-cm}^2$  electrodes across a Nafion 115 membrane (Ion Power). All MEAs employed a cathode electrode fabricated from 20 wt % Pt/C powder, which had a Pt loading of  $0.43 \pm 0.05 \text{ mg/cm}^2$ . MEAs were prepared with anode electrodes fabricated from the various electrocatalysts described above. The total metal loading of anode electrodes was as follows: (a) Pt-Mn/C-SC-HT with  $0.41 \text{ mg/cm}^2$  (b) Pt-Cu/C-POL-HT with  $0.31 \text{ mg/cm}^2$  and (c)  $\text{Pt}_3\text{Sn}/\text{C}$  with  $0.33 \text{ mg/cm}^2$  metal loading.

### 2.3. Three-electrode cell measurements

All electrochemical measurements were made using a Solartron

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