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Low catalyst loaded ethanol gas fuel cell sensor

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ABSTRACT

Fuel cell sensors with polymer electrolyte membrane for ethanol gas concentration measurement in human exhaled breath were studied for the purpose of reduction of platinum (Pt) catalyst loading in both sensor electrodes and decreasing the sensor production cost. The sensors with Nafion electrolyte and different catalyst loading electrodes including 10, 20, 30, and 40% Pt/C with 0.1, 0.2, 0.25, and 0.3 mg/cm^2 Pt loadings, respectively, were fabricated and tested in this study. The results confirm that the sensor catalyst loading can be reduced by approximately 130 times compared to the catalyst loading in commercial sensors without notably changes on the sensor performance. In addition, fabrication of sensors with very low Pt loading on the cathode side is possible and can be economically favorable for manufacturing ethanol gas sensors. It also has been shown that the peak current density measurement method, which expedites the sensor recovering time, can be used for low catalyst loading sensors due to the observation of very good linearity behavior of the sensor with changing the ethanol gas concentration.

1. Introduction

Accurate, rapid and low-cost alcohol detection and quantification is required for applications such as ethanol gas concentration measurement in human breath, clinical analysis, foods and beverages industries, and agricultural and environmental analyses [1,2]. The ethanol gas concentration measurement in exhaled breath of vehicle drivers is essential for determination of the blood alcohol concentration in drunk drivers. For this purpose, the electrochemical-based/fuel cell sensors was introduced in 1970s [3,4]. Although gas chromatography [5,6], infrared [7–9], and semiconductor [10–12] techniques are commercially available, the breath ethanol measurements are usually performed by fuel cell sensors [13] due to their acceptable accuracy, linearity, sensitivity and selectivity, portable field-based size, moderate-cost, and rapid response time to expedite the assessment of vehicle drivers [14]. Although the available fuel cell sensor technology is acceptable to measure the ethanol gas concentration, this technology has not been updated for many years. Despite significant progress that has been made in the fields of nano-technology, catalysts, and fuel cells in the past decade, commercial fuel cell sensors are still based on 1970s technology. At present, the platinum (Pt) catalyst content in fuel cell sensors is very high (manufacturing cost issue) and liquid phosphoric or sulfuric acid [15,16] is used as their electrolyte (safety issue). The recent advances in proton exchange membrane fuel cells (PEMFCs) [17–20] can lead researchers to the next generation of fuel cell sensors that are highly accurate, safe and cost-effective [21,22].

Fuel cells are electrochemical devices, which can directly convert the chemical energy of some fuels (in this study the fuel is ethanol gas) to electricity [23,24]. It has been reported that PEMFCs with solid polymer electrolytes can be successfully used with direct ethanol fuel [25–30]. The PEMFC can be used as the ethanol gas sensor such that the magnitude of generated current determines the feed ethanol gas concentration. PEMFCs are comprised of two electrode catalysts, which usually contain a precious metallic catalyst such as platinum [31], or platinum- ruthenium [32]. The electrodes are separated by an electrolyte membrane such as Nafion [33], or Titania-Nafion composite [34]. In this study PEMFC was used as a sensor to measure ethanol gas concentration in simulated breath of drunken drivers. The obtained current response of the sensor was measured as a function of blood alcohol concentration (BAC). The BAC is the ethanol content in grams divided by blood volume in deciliters. The permissible legal detection limit of BAC for non-business and business drivers are 0.08% and 0.04%, respectively in most states of the United States, which correspond to 208 and 104 ppm ethanol in human breath [35]. It is noted that the ratio of alcohol concentration in blood to alveolar air is 2100:1 [36,37]. and SEM micrographs of a typical GDE used is illustrated in Fig. 1

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Table 1
Characteristics of different gas diffusion electrodes used in this study.

Catalyst	Pt catalyst loading (mg/cm^2)	ECSA[a] (m^2/g)	Thickness (μm)				Pt in 1.8 cm^2 electrode (mg)
			CL[c]	MPL[d]	GDL[e]	GDE[f]	
10% Pt/C	0.10	105	10	70	310	390	0.18
20% Pt/C	0.20	90	10	70	310	390	0.36
30% Pt/C	0.25	80	9	70	310	389	0.45
40% Pt/C	0.30	60	8	70	310	388	0.54
20% Pt/C	0.03	90	2	70	310	382	0.05
Commercial sensor	32	30[b]	10	Electrolyte thickness: 1 mm			57.27[g]

[a] ECSA: electrochemical active specific surface area.
[b] The value is the reported surface area for Platinum black by vendor.
[c] CL: catalyst layer.
[d] MPL: micro porous layer.
[e] GDL: gas diffusion layer.
[f] GDE: gas diffusion electrode (GDE = CL + MPL + GDL).
[g] Commercial sensor electrode area was 1.21 cm^2. The amount of Pt loading for electrode area of 1.8 cm^2 was extrapolated.

Although some researchers have shown the possibility of using PEMFC sensors with solid polymer electrolyte to measure ethanol gas concentration [21,22,38], no study has been done so far to show the effect of catalyst loading on the performance of these sensors and how much the catalyst loading in commercial sensors can be decreased if their fabrication technology is updated. The objective of this study is to answer these questions. For this purpose, the solid polymer electrolyte membrane (Nafion) and electrodes containing carbon-supported Pt catalyst were employed to fabricate the PEMFC sensors. These sensors were used to measure ethanol gas concentration in the simulated exhaled human breath. Electrodes with different Pt catalyst loading were examined to investigate the effect of Pt loading on performance of fresh sensors. The fresh sensor in this study denotes a sensor tested in the same day that the membrane electrode assembly (MEA) has been fabricated. It is noted that in addition to the catalyst loading [39] that is the purpose of this study, the type of catalyst [40] and the electrode microstructure [41–45] can play important roles in performance determination of any electrochemical systems, including fuel cell sensors. The type of catalyst, the electrode microstructure, durability and environmental tests, and improvement of polymer electrolytes for fuel cell sensors are ongoing studies in Advanced Energy & Sensor Lab.

2. Sensor fabrication, experimental setup and testing

2.1. PEMFC sensor fabrication

The MEA of PEMFC ethanol gas sensor consists of solid polymer electrolyte sandwiched by two electrodes. Electrodes are basically gas diffusion electrodes (GDE, Fuel Cells Etc.) comprised of Vulcan carbon-supported Pt catalyst (HiSpec 3000 and 4000, Alfa Aesar/Johnson Matthey) and Nafion ionomer spread on woven carbon cloth (GDL-CT, CeTech) as the gas diffusion layer (GDL). GDEs with 10, 20, 30, and 40% Pt/C with Pt loading of 0.1, 0.2, 0.25, and 0.3 mg/cm^2, respectively, were used as the sensor electrodes (It should be noted that 10% Pt/C, 0.1 mg/cm^2 Pt and 30% Pt/C, 0.25 mg/cm^2 Pt GDEs were customized by authors with the exact same catalyst and GDL type with the other GDEs). The ratio of Nafion ionomer to Pt was held constant at 3:2 for all GDEs. The characteristics of all GDEs used in this study including their electrochemical active specific surface area (ECSA) are listed in Table 1. (The ECSA values were calculated and reported by the catalyst layer provider.)

Nafion 115 with the thickness of 127 μm (Fuel Cells Etc.) was used as the solid electrolyte membrane for fabrication of MEAs. Prior to fabrication, Nafion membrane requires impurity removal (cleaning) by the following steps. Nafion was immersed in boiling 3 wt% H_2O_2 aqueous solution for 1 h. Then, it was rinsed in DI water several times, followed by boiling in DI water for 1 h. The Nafion membrane cleaning was continued by immersing in boiling 1 M H_2SO_4 aqueous solution for another hour. Finally, the Nafion membrane was rinsed several times with DI water and stored in DI water at room temperature prior to its usage in sensor fabrication.

The electrodes and activated Nafion membranes were cut precisely by laser cutter machine (VLS2.30 Versa Laser) in a circular shape with the diameter of 15 mm (Area ≈ 1.8 cm^2). It should be noted that Nafion membranes should be cut slightly larger than electrodes to prevent short-circuiting. Nafion 115 was then placed between two electrodes and was compressed using a hot press (MTI Corporation), which applied 10 MPa (or 2.5 kN) of pressure at 100 °C for 1.5 min to complete the MEA fabrication. The fabricated MEA should be sandwiched between two current collectors (0.01 in. thick stainless steel metal grid, McMaster) to improve the current collection from the sensor's electrodes. In order to ensure good contact between current collectors and electrodes and to min-

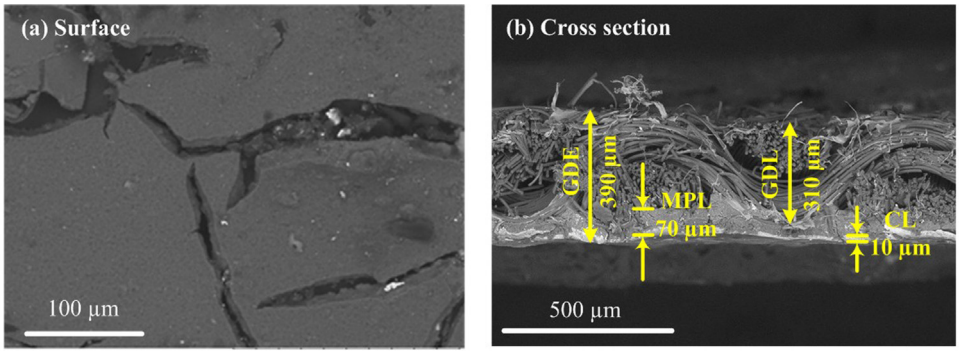

Fig. 1. SEM micro porous structure of a typical sensor electrode (a) surface, (b) cross section view.