Sensors and Actuators B 183 (2013) 617–626

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Methanol selective gas sensor based on nano-structured conducting polypyrrole prepared by electrochemically on interdigital electrodes for biodiesel analysis

Mohsen Babaei, Naader Alizadeh*

Department of Chemistry, Faculty of Science, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran

ARTICLE INFO

Article history:
Received 8 December 2012
Received in revised form 9 April 2013
Accepted 11 April 2013
Available online 19 April 2013

Keywords:
Nano-structured
Polypyrrole
Conducting polymer
Methanol gas sensor
Biodiesel

ABSTRACT

Nano-structured conductive polypyrrole (NCP) has been prepared by constant current electrodeposition on interdigital electrodes (IDEs) in the presence of an anionic dopant (PPy-X) and has been investigated as a gas sensor. The effects of the electrochemical conditions and dopant type (perchlorate and para toluene sulfonate) on sensing behavior of the PPy-X gas sensor toward the aliphatic alcohols vapor have been studied. The PPy-ClO_4 has been demonstrated to have fast response time (<1 s), high calibration sensitivity, high selectivity, and good reproducibility to the methanol in ambient temperature. The calibration sensitivity order of the PPy-ClO_4 for aliphatic alcohol vapors has been revealed as: methanol $\gg$ ethanol > 1-propanol > 2-propanol. Therefore, the PPy-ClO_4 can be successfully utilized as a selective sensor for detection of methanol (DL = 0.03%, mass/mass). It has been found in all of cases that the normalized electrical resistance directly correlates with the concentration of aliphatic alcohols in gas phase. Based on the obtained calibration curve linear range of about 0.15–2.01% (mass/mass) and 0.61–17.62% (mass/mass) was obtained for methanol at 30 °C and 120 °C sensing temperatures, respectively. The PPy-ClO_4 gas sensor has been applied for determination of residual methanol content in the biodiesel samples. The results are in good agreement with values obtained by GC/MS method.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Increasing environmental concerns are leading energy policies to promote research in the field of new alternative fuels, among them is biodiesel. Biodiesel is an alternative fuel similar to conventional or 'fossil' diesel. It can be produced from straight vegetable oil, animal oil/fats, tallow and waste cooking oil. The process used to convert these oils to biodiesel is called transesterification. From a chemical point of view, making biodiesel is defined as a reaction between an alcohol and a long-chain fatty acid; methanol is the most processable one [1]. The content of methanol is one of the parameters usually has been presented in quality control of the biodiesel. The amount of methanol in biodiesel is regulated by the European biodiesel standards EN-14214 (test method EN-14110), the limit being 0.2% (mass/mass), and by the ASTM D6751-07a (test method D93 or EN-14110), the limit being 0.2% volume [2]. Excess of methanol facilitates the formation of large carbon deposits in the engine, decreases heating value, increases fuel consumption, delays ignition (thus decreasing engine power and energetic content), and decreases initial temperature of the distillation curve as well as the flash point due to its volatility, causes problems during start-up in cold weather, inhibits complete separation of glycerol, induces metal corrosion (particularly of aluminum), increases the deterioration of the rubber components of the vehicle's fuel system, and increases production cost [3]. Based on the above mentioned disadvantages of excess methanol in biodiesel, finding an accurate, reproducible, and direct method to determine the amount of methanol presents in biodiesel is of great importance.

Several analytical methods have been developed for determination of the residual alcohol in biodiesel. Mittelbach et al. [4] have reported the determination of methanol in biodiesel by derivatizing agent and injecting into a gas chromatograph capillary column, flame ionization, and mass spectrometric instruments. Felizardo et al. [5] have reported the development of calibration models for water and methanol in biodiesel. Some other groups including Paraschivescu et al. [6] have used headspace solid phase microextraction (SPME) to determine the amount of methanol. Araujo et al. [7] have used a methodology based on flow analysis and hydrophilic membrane-based extraction for determination of methanol in biodiesel samples. Some other researchers have utilized NIR spectroscopy, which needs the use of chemometric tools. More recently, Boog et al. [8] have determined the residual alcohol in biodiesel through its flash point. However, many of these methods are often complicated and time consuming or require expensive equipments. Thus, there is an important demand for simple, low-cost, sensitive, and rapid alternative methods for determining the methanol in biodiesel samples.

---

* Corresponding author. Fax: +98 21 82883455.
E-mail address: alizaden@modares.ac.ir (N. Alizadeh).

0925-4005/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.snb.2013.04.045

Chemical sensors such as chemiresistor gas sensors [9] and surface acoustic wave (SAW) sensors [10,11] have important applications in the area of environmental monitoring, public security, automotive application, and medical diagnosis. A wide range of organic and inorganic materials are used as sensing elements. Inorganic materials such as metal oxides have been used extensively [12]. One of the practical problems with metal oxide-based sensors is the need to adopt high operating temperatures. In recent years, conducting polymers and their derivatives, have received much attention as candidates for gas sensors due to increasing concerns for gas detection in the fields of industrial, agricultural production, environment monitoring, etc. [13–16]. These polymers possess the advantages of low cost, easy preparation, ready modulation of their sensing properties by varying their chemical structure, and being able to operate at room temperature [17]. Polyacetylene, polypyrrole (PPy), polythiophene (PTh), polyaniline (PANI) and their derivatives are the most commons of such kind of polymers. Compared with bulk conducting polymers, nano-structures conducting polymers are expected to display improved performance in technological applications because of the unique properties arising from their nanometer-scaled size: high conductivity, large surface area, and light weight [18]. To improve the performance, conducting polymers usually has to be nano-structured [19–21]. Conducting polymers nano-materials can be synthesized through chemical or electrochemical routes. Chemical reactions usually produce powdery nano-materials and can be easily scaled up. On the other hand, electropolymerization restricts the reactions on the surfaces of the electrodes, and the nano-structures of conducting polymers are usually deposited on the electrode surface as a film. Furthermore, in many cases, nano-structures grow along the direction of the electric field to form oriented structures. The electrochemical polymerization reaction rate can be controlled easily by the applied potential or current density. The amount of products can also be controlled by the integrated charges used for electrosynthesis. The morphology and properties of the nano-materials can also be modulated by controlling the electropolymerization conditions. Therefore, electrochemical polymerization is a one-step and effective technique for producing conducting polymers nano-materials with controlled morphologies and properties [22].

Until now, a number of sensors and sensor arrays based on conducting polymers have been developed for the detection of a wide variety of gases ranging from organic vapors including $CHCl_3$ [23], alcohols [24], amines [25,26], pyridines [13], dimethyl sulfoxide [14], to inorganic vapors such as NO_2 [27,28], NH_3 [29–32], HCl [33,34], H_2S [35,36] and H_2O [37]. Among the numerous conducting polymers prepared to date, nano-structured PPy is the one, which has been extensively studied. Conducting PPy nano-materials have received considerable attention in sensors because of remarkable physical and chemical characteristics originating from their small dimensions and high surface area [38–45]. Hernandez et al. [46] fabricated a gas sensor based on single PPy nanowire. Reports also showed the sensitivity, to a certain extent, was dependent on the diameter of the one-dimension nano-materials [45,47]. However, the diameter of the PPy nanowire used as gas sensor is often over hundreds of nanometers. Small diameter and high density PPy nanowire arrays will present a significantly high surface-to-volume ratio which will result in high sensitivity [48,49]. Jang and co-workers [45] reported sensing behaviors of PPy nanotubes prepared in reverse microemulsions and the effects of transducer size and transduction mechanism, the electrical response of PPy nanotubes to analyte (NH_3 vapor) was strongly dependent on their diameters. The PPy nanotube sensors showed conspicuously enhanced responses compared with conventional PPy. Currently, the focus is on the development of sensors for various organic pollutant vapors/gaseous molecules [43].

The reasons for this intense focus on PPy certainly lie in the fact that the monomer (pyrrole) is easily oxidized, water soluble, commercially available and capable of yielding excellent sensitivity via enhanced interaction with the analytes and permits rapid adsoption/desorption kinetics for analytes, leading to fast response/recovery time even at room temperature. PPy has been extensively studied owing to its excellent conductivity, high yield in redox process, gas sensing ability, optimum performance at room temperature, response to a wide range of volatile organic compounds (VOCs) and environmental stability [50]. Herein, we have synthesized the nano-structured PPy via electropolymerization on the surface of an interdigital electrode (IDE) and investigated the application of the prepared film as a selective methanol gas sensor. It provides a direct method to rapidly and quantitatively determines the amount of free methanol in biodiesel samples that is different from the current US standard for methanol determination, ASTM D6751 which uses the flash point (closed cup) measurement (test method D93) and from the European standard which uses the headspace GC method (test method EN-14110).

2. Experimental

2.1. Chemicals and reagents

Pyrrole (Fluka, Switzerland) was distilled and stored in a refrigerator in dark prior to use. Acetonitrile, methanol, ethanol, 1-propanol, 2-propanol and other organic compounds used in this research were purchased from Merck (Darmstadt, Germany). Tetrabutylammonium perchlorate (TBAP), para-toluene sulfonic acid (p-TSA), and anhydrous sodium sulfate were purchased from Fluka. All chemicals (except for pyrrole) were of analytical reagent grade and used without purification.

2.2. Apparatus

Electrochemical polymerization of pyrrole was carried out using Behpajuh (BHP 2061-C model) potentiostat (Isfahan, Iran). An one-compartment electrochemical cell including IDEs as the working electrode (substrate consisted of a flat 10 mm × 10 mm fiber glass printed circuit board prepared by electroless deposition with a five pairs interdigitated Au parallel lines with 200 μm width and spacing, electrode surface = 0.17 cm^2) from Yeganeh PCB (Mashad, Iran), a platinum sheet (20 mm × 10 mm) as the counter electrode and Ag/AgCl, as the reference electrode were used for preparation of the polymer. IDEs were cleaned with methanol and acetone by using ultrasonic bath for 10 min and was subsequently washed with distilled water to remove the impurity and dried at the oven at 90 °C before the experiments. Prior to each electrochemical polymerization, all solutions were deoxygenated by purging them with nitrogen for 10 min.

Constant current method is used for electrochemical deposition of PPy-X conducted in 5 mL solution containing 0.1 mol L^{-1} pyrrole and 0.1 mol L^{-1} of anion dopant ($X = ClO_4^-$ and p-TS^-) in acetonitrile solution .The current used for electrochemical deposition was 5, 10, and 15 mA for 200 s, 100 s and 67 s respectively. It has been found that the charge passed during the polymerization was 1 C, in all of the electropolymerization experiments. The applied current fully controls the thickness and response behavior of the deposited sensing film. Several PPy-X gas sensors were prepared in order to examine the influence of electropolymerization conditions such as current density, time of deposition, and dopant type on the response behavior of gas sensor. After the polymerization, the substrate was taken from the reaction solution and thoroughly washed with acetonitrile and then distilled water and finally dried for 4 h at 90 °C in the oven.

Download English Version:

https://daneshyari.com/en/article/743094

Download Persian Version:

https://daneshyari.com/article/743094

Daneshyari.com