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Electrical conductivity responses and interactions of poly(3-thiopheneacetic acid)/zeolites L, mordenite, beta and H_2

Kaneungnit Thuwachaowsoan [a], Datchanee Chotpattananont [a], Anuvat Sirivat [a,*], Ratana Rujiravanit [a], Johannes W. Schwank [b]

[a] *Conductive and Electroactive Polymer Research Unit, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330, Thailand*
[b] *Conductive and Electroactive Polymer Research Unit, Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109-2136, USA*

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Abstract

Poly(3-thiopheneacetic acid), P3TAA, was chemically synthesized via an oxidation polymerization and doped with perchloric acid. Composites were fabricated from P3TAA and zeolites, zeolites L (L), mordenite (MOR), and beta (BEA) through random dry mixing. The electrical conductivity response toward H_2 was investigated for the effects of zeolite contents, zeolite type, cation type, and cation concentration. Negative electrical conductivity response and sensitivity generally occur when exposed to H_2 relative to N_2. A weaker interaction is suggested to occur between H_2 and the polaron or the bipolaron species relative to the interaction between N_2 and active sites of the doped P3TAA. For the effect of zeolite content, the composite with 20% (v/v) MOR has the highest electrical conductivity sensitivity value. The reduction of sensitivity values occurs with increasing MOR zeolite concentration from 20 to 50% (v/v); this arises from the diminishing active sites available for the interaction between H_2 and the polaron or the bipolaron species. For the composites with 20% (v/v) L, MOR and BEA, the electrical conductivity sensitivity increases with decreasing Al content because of a lesser interaction between H_2 and the zeolite, and consequently a greater interaction between H_2 and the active sites on the polymer chain. The higher electronegativity and smaller ionic radius of Li^+ loaded into the MOR zeolite framework causes the lowering of electrical conductivity sensitivity than the composites loaded with Na^+ and K^+. For composites with zeolite L loaded with Na^+ at 0, 15, 20, 30 and 50 mole%, the electrical conductivity sensitivity increases with increasing Na^+ content up to 30 mole% and decreases beyond that.

Keywords: Polythiophene; Gas sensor; Conductive polymer; Zeolite L; Zeolite modenite; Zeolite beta

1. Introduction

Hydrogen is a promising alternative fuel since it can be used completely pollution-free and can readily be produced from renewable energy resources. It is efficient energy since it contains more chemical energy per weight than hydrocarbon fuels. Uses of hydrogen can be found in many applications such as in fuel cell, in gas run diesel engines, and in microturbines. Moreover, hydrogen is an important raw material for the aerospace, chemical, semiconductor, and many other sectors [1]. However, hydrogen is lighter than air and it can easily lead to explosive build ups. To detect minute gas leaks and to evaluate the efficiency of various combustion processes, H2 sensor is a necessary safety device. In addition, there have been demands for accurate and dedicated sensors to provide precise process control and automation in manufacturing processes, and to monitor environmental pollution; a new generation of sensing materials and sensor technology is acute [2].

Recently, there have been interests in using conductive polymers in gas sensing materials, as alternatives to metal or metal oxide sensing films. Conductive polymers can offer a variety of advantages for sensor applications over the metallic or ceramics counterparts: conductive polymers are relatively low cost materials and lighter; their fabrication techniques are relatively simple and straightforward since there are no needs for clean room and high temperature processes; they can be deposited on various types of substrates and can be operated at lower applied voltage in many conditions; these materials exhibit moderately fast reversible electrical conductivity changes when exposed to gases or vapors at room temperature; they have flexibility

* Corresponding author. Tel.: +66 2 218 413; fax: +66 2 611 7221.
E-mail address: anuvat.s@chula.ac.th (A. Sirivat).

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in molecular architectures such as side chain attachments, and modifications by charged or neutral particles either in the bulk or on the surface [3].

Several conductive polymers have been used as gas sensing materials. Polypyrrole (PPy) is the one of the most interesting amongst many conductive polymers known due to its relatively high environmental stability and the eases in synthesizing and doping with various dopants [4]. Polyaniline (PANI) has several interesting features such as inexpensiveness ease to process, high yield, and excellent chemical stability [5]. Another conductive polymer, polythiophene, is also a candidate gas sensor material. It has good mechanical properties, high electrical conductivity, and environmental stability in both doped and pristine forms [6]. There have been other works related to the uses of conductive polymers for gas and vapor sensing applications [7–14].

Zeolites have emerged as alternative candidates for gas and chemicals sensing materials. Zeolite, a class of microporous aluminosilicate crystals, contains molecular-sized void spaces within their crystal structures. Because of their unique structures, zeolites and related microporous materials possess molecular-sieving property, which have widely been utilized as catalysts, ion-exchanges and adsorbents. As a sensing layer, zeolites are very advantageous due to its high thermal stability and chemical resistance. Characteristic molecular sieving properties have been explored and utilized in gas sensing applications to detect toxic gases and other large organic molecules [8–22].

Combining the advantages of the two materials, we propose to combine a conductive polymer, poly(3-thiopheneacetic acid), with a variety of zeolites to be used as selective gas sensors. The effects of zeolite type, zeolite concentration, cation type, and cation concentration on electrical conductivity response of composites were investigated along the line of previous work [23,24]. We specifically selected zeolites L, mordenite, and beta as the mesoporous dispersed phases since they have nearly the same pore sizes but different Si/Al ratios and hence distinct structures.

2. Experimental

2.1. Materials

3-Thiopheneacetic acid, 3TAA (AR grade, Fluka) was used as the monomer and anhydrous ferric chloride, $FeCl_3$ (AR grade, Riedel-delHean) was used as the oxidant as received. Chloroform, $CHCl_3$ (AR grade, Lab-Scan), methanol, CH_3OH (AR grade, Lab-Scan) and dimethyl sulfoxide (DMSO) were dried over CaH_2 for 24 h under the nitrogen atmosphere and then distilled and used as solvents. Hydrochloric acid, HCl (AR grade, Lab-Scan) was used to neutralize and to precipitate the polymer synthesized. Sulfuric acid, H_2SO_4, was used to protect the oxidative decomposition of monomer. Diethyl ether and deionized water were used to extract and to wash materials. Sodium hydroxide, NaOH, was used as the hydrolyzing agent. Perchloric acid, $HClO_4$ (AR grade, Panreac Quimica), was used as received as the dopant.

Zeolites L, modenite and beta, having K, Na and H as the cations, respectively, were purchased from Tosoh Corp. (Japan).

Nitrogen (TIG) was used as the carrier gas hydrogen (TIG, 99.999%) was used as the target gas.

2.2. Synthesis of poly(3-thiopheneacetic acid) (P3TAA)

Poly(3-thiopheneacetic acid) was synthesized by the oxidative coupling polymerization according to the method of Kim et al. [25]. 10.0 g of 3-thipheneacetic acid (3TAA) was refluxed for 24 h in 50 ml of dry methanol with 1 drop of concentrated H_2SO_4, to protect the oxidative reaction of the monomer at the carboxylic acid group during polymerization. Then methanol was evaporated and the residue was extracted with diethyl ether. The extract was washed with deionized water, dried with anhydrous $MgSO_4$, and filtered. The 3-thiophene methyl acetate (3TMA) was recovered after evaporation of diethyl ether by a rotating evaporator.

The prepared monomer, 3TMA, of 10 mmol was dissolved in 20 ml chloroform and then added dropwise to a solution of 40 mmol ferric chloride in 30 ml chloroform under nitrogen atmosphere. The reaction was carefully maintained at 0 °C (±0.5 °C) for 24 h. The mixture was precipitated by pouring in an excess amount of methanol. Then the precipitate was washed with methanol and deionized water to remove the residual oxidant and the oligomers after filtering. Finally, P3TMA was obtained.

P3TMA was hydrolyzed by heating 0.5 g precipitate in 50 ml of 2.0 M NaOH solution for 24 h at 100 °C. Poly(3-thiopheneacetic acid) (P3TAA) was obtained by neutralization and precipitation in a dilute HCl solution. P3TAA was repeatedly washed with deionized water before vacuum drying at room temperature for 2 days.

2.3. Characterization method

Undoped and doped poly(3-thiopheneacetic acid) powders were identified for their functional groups by a FT-IR spectrometer (Thermo Nicolet, Nexus 670) operated in the absorption mode with 32 scans and a resolution of ±4 cm^{-1}, covering a wavenumber range of 4000–400 cm^{-1}. UV–vis absorption spectrophotometer (Shimadzu, UV-2550) was used to identify the successfully doped poly(3-thiopheneacetic acid). Measurements were taken in the absorbance mode in the wavelength range of 200–800 nm.

A thermal gravimetric analyzer (DuPont, model TGA 2950) was used to investigate the thermal property of undoped and doped poly(3-thiopheneacetic acid) (P3TAA) from 30 to 800 °C with a heating rate of 10 °C/min under air condition.

Scanning electron micrographs were taken with a scanning electron microscope (JEOL, JSM-5200) to determine the morphology of poly(3-thiopheneacetic acid), zeolites, and polythiophene/zeolite composites.

The average particle size and the standard size distribution of poly(3-thiopheneacetic acid) and the zeolites were determined by using a particle size analyzer (Malvern, Masterizer X).

Crystallinity and structures of poly(3-thiopheneacetic acid) and zeoloite powders were identified by an X-ray diffractometer (Phillips, Rigaku).