Polypyrrole-Organoclay Nanocomposites for Gas Sensors

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ABSTRACT

Polypyrrole (PPy) was synthesized in the presence of octadecylammonium-montmorillonite (OC-MMT) 1-9 wt% using ferric chloride as an initiator. The product obtained was the intercalated nanocomposites. The synthesized PPy and its nanocomposites were tested as gas sensors for volatile organic gases important for agricultural applications; i.e. CO_2, CH_4 and C_2H_4. The resistance of the nanocomposite in each gas was presented as sensitivity and cross sensitivity for the mixed gas. The response time for all materials was found to be within 1.5-2.5 minutes. Sensitivity of pure PPy is the highest for C_2H_4 followed closely by methane and the least is CO_2. Sensitivity to CO_2 was decreased as OC-MMT content increased but for methane, the sensitivity is about steady at 3 wt% OC-MMT. Ethylene sensitivity reduces with OC-MMT content that brings high barrier property. There was a critical OC-MMT content at 3 wt% that showed the highest sensitivity for methane and ethylene. At the critical content, doping the PPy nanocomposite with DBSA resulted in increasing conductivity for ethylene and carbon dioxide. For the mixed gas system, CH_4: CO_2 and C_2H_4:CO_2, the positive cross sensitivity increases with increasing methane or ethylene gas pressure as well as increasing OC-MMT content.

Key words: polypyrrole, nanocomposites, gas sensor, organoclay, doping

1. INTRODUCTION

Polypyrrole (PPy) was synthesized in the presence of octadecylammonium-montmorillonite (OC-MMT) 1-9 wt% using ferric chloride as an initiator to result the intercalated nanocomposites. The prepared nanocomposites were tested for conductivity in the presence of carbon dioxide (CO_2), methane (CH_4) and ethylene (C_2H_4) gases. These gases are not only important as volatile organic gases but also as the gases involving in agricultural production e.g. biogas, growth and photosynthesis of plants and fruits. The gas sensors for these gases are currently needed e.g. to monitor biogas emission and control methane recovery process; and to monitor ripening of mot commercialvegetables and fruits like tomatoes, green apples, and bananas. The ability to be gas sensing materials for the prepared nanocomposites were presented in term of sensitivity which is the percentage of the change in resistance and the resistance prior to the exposure to such gases.

2. EXPERIMENTAL

2.1 Materials

Pyrrole was purchased from Merck and was purified by vacuum distillation and stored in a refrigerator at about 4°C before use. Iron (III) chloride $FeCl_3.6H_2O$ (an oxidizing agent), dodecyl benzenesulfonic acid sodium salt (a doping agent) and octadecylamine (OC) were purchased from Fluka. Sodium montmorillonite (Na-MMT) with cation exchange capacity of 119 meq/ 100g was supplied by Kunimine Industrial Co., Ltd., Japan. Carbon dioxide 99.8% purity, methane 99.0-99.99% purity (2000 psig) and ethylene 99.9% purity (fill pressure 80 psig) were purchased from Thai Industrial Gas Public Company and used as received.

2.2 Synthesis of Polypyrrole (PPy)

Polypyrrole and its nanocomposites were chemically synthesized as mentioned earlier in the previous paper [1]. The samples were prepared in the pellet form (1.3 cm diameter) using Hydraulic Press, GRASEBY SPECAC (8 bars pressure for 2 min).

2.3 Electrical Resistance Measurement

Electrical resistance of the obtained pure PPy and PPy/OC-MMT nanocomposites were determined by a Keithley Electrometer Model 6517. Under ambient air atmosphere, an AC voltage of 10 volt was applied for at least 60 seconds and the resulting resistance was then measured. For measuring resistance of samples under CO_2, CH_4, C_2H_4 atmosphere, the pressure of gas was set at 0.1-0.3 bars (output pressure from gas tank). The mixed gas between CO_2+CH_4 and CO_2+C_2H_4 was also tested at different ratios of supplied pressure.

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3 RESULTS AND DISCUSSION

The resistances of the circular disks (0.5 mm thick) of pressed powder PPy and PPy/OCT-MMT nancomposites were measured by electrometer. The result in Figure 1 shows the equilibrium resistance (about 864.1 ohms or conductivity 4.72×10^{-3} S/cm) of

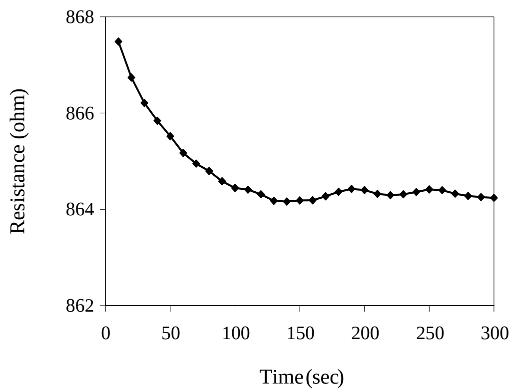
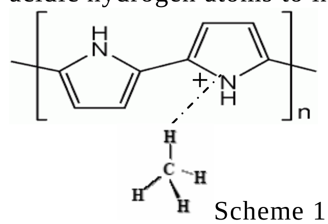


Figure 1 Resistance to 0.1 bar CO_2 at various times for pure PPy of 0.5mm thick

pure PPy in carbon dioxide atmosphere is achieved at about 100 s. This measured time, so called “response time”, is considered to be suitable for sensor application. The equilibrium resistances of pure PPy and its nanocomposites in each specified gas are presented in Figure 2. This shows that the sensitivity sign is sometime positive (resistance in the test gas is greater than resistance in ambient air) for carbon dioxide monitoring and mostly is negative (resistance in the test gas is lower than that measured in ambient air) for both ethylene and methane. The sensitivity values varies between -1% to 1%. The sensing efficiency measured by the equilibrium resistance depends on the chemical attraction between the gas and sensing materials (PPy and its nanocomposites) that influence the conductivity of the sensing materials.

3.1 Sensitivity to Different Gases

The interested gases to be monitored are nonpolar; i.e. carbon dioxide (CO_2) and two hydrocarbon gases, methane (CH_4) and ethylene (C_2H_4). While in CO_2, pure PPy shows positive sensitivity but negative sensitivity in methane and ethylene suggesting that PPy becomes more conductive in strongly reduced gases (hydrogen-rich gases). Proton in these reduced gases is rather acidic and can be located near to the lone pair electron of nitrogen atom in PPy to enhance conductivity (Scheme 1). However, it can be expected that ethylene can be adsorbed to PPy as well as methane because of the double bond can pull electrons and make more acidic hydrogen atoms to interact with nitrogen atoms.



Scheme 1 CH_4 adsorption on PPy

Only when carbon dioxide combines with moisture, proton and bicarbonate are created and the protonation of PPy can be formed to bring up conductivity. But in our case, this process is rather less dominant so that the resistance increases.

When 1-9 wt% OC-MMT was intercalated to PPy, intercalated nanocomposites with less moisture absorption (80% reduction in moisture content) were obtained. The gas diffusion through sensing materials becomes harder due to increasing tutorial path in the presence of clay platelets. Increasing conductivity or decreasing sensitivity in the presence of CO_2 is found with increasing OC-MMT content because the primary amine can capture CO_2 and produce proton [2]. For methane gas, the sensitivity is less dependent on OC-MMT content. This is attributed to its better diffusion and adsorption that gets to the limit due to increase in barrier property with increasing clay content. Ethylene sensitivity or conductivity decreases with clay content because the diffusion of ethylene is slower than that of methane [3] and thus retarding the absorption of ethylene. Therefore, at critical OC-MMT content of 3 wt% and beyond, the arrangement of clay platelets is well formed to retard the gas diffusion effectively.

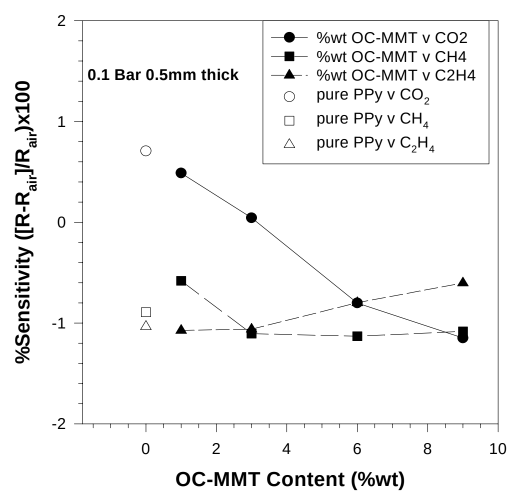


Figure 2 Effect of OC-MMT content on the sensitivity toward each gas (CO_2, CH_4 and C_2H_4 at 0.1 bar) of PPy and its nanocomposites at 0.5 mm thick

3.2 Effect of Dopant

As DBSA was doped on the PPy/ 3 wt% OCT-MMT nanocomposites, the conductivity to each measured gas is shown in Figure 3. It is clear that the conductivity of the doped nanocomposites is altered by gas absorption in the order of ethylene > methane > carbon dioxide dependent on the interactive strength of the hydrogen atoms. Moreover, the resistance of the doped nanocomposites to CO_2 gas is higher than that of undoped nanocomposites (864 ohms). The insufficient doping ability of DBSA in the presence of the nanoclay, OCT-MMT is possibly due to the intercalation of DBSA in the clay galleries and thus shielding its molecules from protonating PPy. Moreover, the proton in the acid group may exchange with sodium ions of the clay and thus reducing number of active doping molecules. This makes slight increased resistance. The response time is delayed to 150 s to get the equilibrium response.

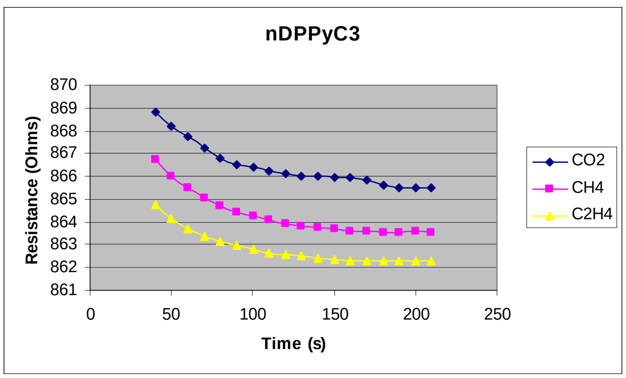


Figure 3 Resistance to 0.1 bar CO_2, CH_4 and CH_4 v.s. response time (room temperature) for doped PPy/OC-MMT 3 wt% (nDPPyC3) of 0.5mm thick (n = 1:1 molar ratio H^+/N)

Figure 4 showed the effect of dopant molar ratio H^+/N on the sensitivity of the PPy/OC-MMT 3 wt% nanocomposite (PPyC3). Without doping its sensitivity in carbon dioxide gas is almost zero. After doping, the conductivity increases and its sensitivity becomes higher in negative values. This possibly due to more water absorption by DBSA and thus producing proton from the reaction between moisture and CO_2. Increasing doping ratio to 1 makes more DBSA intercalation and lose its doping function. For ethylene, its sensitivity after doping is similar to that of undoped one, about "-1". For methane, the sensitivity (closer to zero) is also reduced by doping. This is due to moisture absorption. Further increasing dope ratio, the sensitivity is slightly better for methane and slight changed for ethylene because of DBSA intercalation.

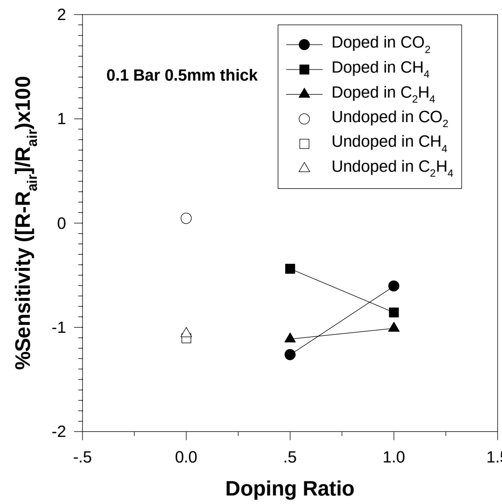


Figure 4 Effect of doping ratio on the sensitivity of PPyC3

Cross sensitivity to CO_2 is showed in Figures 5-6. As increasing OC-MMT content, the cross sensitivity of the mixed gases, CH_4/CO_2 or C_2H_4/CO_2, also increases. Besides the cross sensitivity becomes higher with increasing gas pressure (0.1-0.3 bars). The cross sensitivity is greater than 100% when pressure of methane increases or OC-MMT content increases. This shows good selectivity to methane. Increased pressure enhances the diffusion of gases through the nanocomposite.

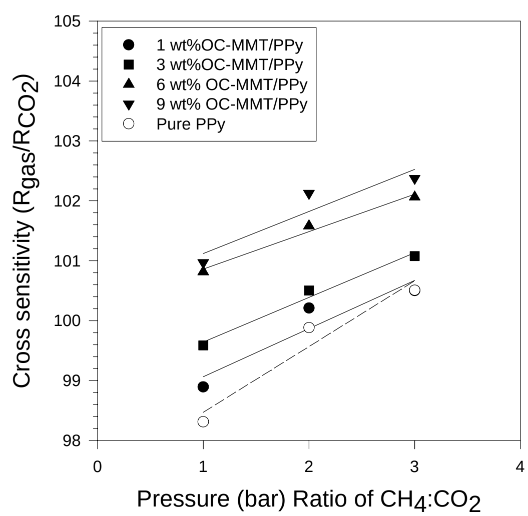


Figure 5 cross sensitivity (bottom) of the mixed gases CH_4:CO_2 at pressure ratios 1:1, 2:1 and 3:1 dependent on OC-MMT content

Resistance of CO_2 reduce relatively faster than that of methane making higher sensitivity. Increasing clay content also induces higher cross sensitivity because of higher barrier to methane but more amine to capture CO_2 making more conductivity. The cross sensitivity is linearly changed with the gas pressure suggesting that the materials are good for sensor application for the mixed gas.

Similar results were observed for ethylene as shown in Figure 6. The cross sensitivity is linearly changed with gas pressure and increased with increasing OC-MMT content. The values of cross sensitivity becomes greater than 100% at 3 wt% OC-MMT. The slopes are rather shallower than those of methane: CO_2 gases suggesting that their resistance are not much different at each gas pressure. This reveals that ethylene adsorption is more dependent on its diffusion than methane; if the pressure is high, diffusion is enhanced and thus increase in cross sensitivity is found. When barrier effect is increased, the resistance becomes higher and cross sensitivity is increased.

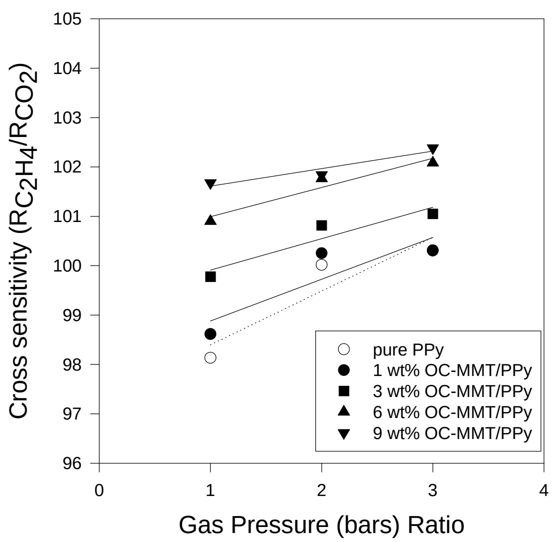


Figure 6 cross sensitivity (bottom) of the mixed gases C_2H_4:CO_2 at pressure ratios 1:1, 2:1 and 3:1 dependent on OC-MMT content

4 CONCLUSION

The PPy-organoclay nanocomposites gave the equilibrium conductivity within 100-150 s. Carbon dioxide gas has high positive sensitivity that reduces with clay content. Methane sensitivity was almost steady over 1-9 wt% OC-MMT/PPy nanocomposites while ethylene becomes less sensitivity with increasing OC-MMT content. The different responses from three gases to PPy and PPy nanocomposites are due to different adsorption mechanism and diffusion rate. Cross sensitivities for both gas mixtures positively increase with gas pressure and OC-MMT content revealing the resistances of PPy/OC-MMT nanocomposites either in methane or ethylene atmosphere.are greater than that in carbon dioxide environment. In other words, the conductivity in carbon dioxide environment is higher with increasing organoclay or amine content and gas pressure. In this work, DBSA doping has two effects on conductivity of PPy and its nanocomposites; i.e. increased moisture absorption (thus bring more increase in conductivity in CO_2 environment but poor conductivity to methane and ethylene) and partial intercalation into clay galleries (so losing its efficiency to dope PPy and thus lowering conductivity in methane and ethylene).

5 ACKNOWGEMENT

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