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Nanocomposite Carbon-PDMS Membranes for Gas Separation

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Abstract

Polydimethylsiloxane (PDMS) composites containing variable weight amounts of carbon black (CB) have been synthesized as membranes to evaluate the effect of CB concentration on gas selectivity and separation. The membranes were used in conjunction with a commercial semiconducting methane (CH_4) gas sensor that had a strong cross-talk with hydrogen (H_2) gas. The selectivity of the CB-PDMS composite membranes for gas separation was tested using CH_4 and H_2 . It was found that at 6 wt% of CB in PDMS, the permeability of CH_4 was significantly and selectively attenuated through the composite membrane. This work demonstrates that CB is an effective additive for tuning H_2/CH_4 gas selectivity of the composite membranes. The selectivity is attributed to a chemical transition occurring with increasing CB doping, which was observed by vibrational spectroscopy measurements.

Keywords: polydimethylsiloxane (PDMS); carbon black (CB); nanocomposite membrane; hydrogen (H_2); methane (CH_4); selectivity; separation ; FTIR; Raman.

1. Introduction

Blocking an environmentally harmful gas or purifying a useful gas is required for many industrial, environmental, and biomedical applications [1,2]. Additionally, gas separation techniques are showing increasing demand for many sensing processes [3-5]. Many of the current gas sensor technologies suffer significantly from cross-talk and interferences of non-target gas species [6-9]. For example, semiconducting H_2 gas sensors commonly show cross-talk with other reducing gases such as CO and CH_4 [6,7]. Gas separation is also essential to selective sensing technologies, as the presence of interfering gas species can be harmful, even corrosive, to the gas sensing elements. For instance, the presence of gas species such as SO_2 and gaseous HCl, which produce strong acidic environments, can reduce the lifetime of optical CO_2 gas sensors [10].

Amongst conventional methods for gas separation, membrane technology has been widely embraced and commercially adopted, due to its efficiency and cost [2,11-13]. These gas selective membranes are also becoming increasingly incorporated in semiconducting and electrochemical sensors. Such selective membranes are used: (a) within the sensor package, reducing the effect of non-desired gases on the sensitive element of the gas sensors, or (b) as coating layers formed on the surface of the gas sensitive layers in semiconducting sensors [5] or on the surface of electrodes in electrochemical sensors [8,14].

Polymer science has increasingly provided new grounds for creating novel membrane technologies [13]. One of the polymers commonly used for developing gas selective membranes is polydimethylsiloxane (PDMS) [15-17]. PDMS is widely utilized in micro-devices and systems, due to its versatile and favorable properties, which include nontoxicity, biocompatibility, flexibility, low cost, and ease of fabrication [18]. Also advantageously amongst polymers manufactured industrially, PDMS has the highest gas

permeability [17,19,20]. However, polymers with high permeability are generally less selective to gas species [13], and similarly PDMS is also a non-selective polymer, allowing most of the gases to effectively permeate through the material.

In order to enhance polymers selectivity, researchers have been considering the use of fillers for creating unique composites [21]. Adding these fillers can offer composites the capability of tuning properties such as conductivity, strength and, for our purpose, gas selectivity. Selectivity within polymers can be achieved using many types of fillers including metal oxides [22], and metals [23] as well as a host of other inorganic and organic fillers [24].

Carbon-based fillers such as carbon nanotubes (CNTs), carbon black (CB) and graphene, have been added to PDMS and other polymers to evaluate the effect on their properties [25]. Several investigations have been conducted on the incorporation of CNTs into PDMS for gas separation applications [26,27]. For instance, Kim *et al.* [26] have demonstrated that CNTs, if used in membranes, have the ability to separate gases. Their study has shown that CNT-based membranes have altered permeability to methane (CH₄).

Most commonly, the CB particles have been used as fillers to prolong the lifespan of PDMS and to create polymers with tunable electrical and thermal conductivities [28]. In a commercial sense, CB particles are also regularly used in PDMS-based rubber tires in the automobile industry [29]. It has been shown that the infiltration of CB into the polymer matrix enhances the stability of PDMS [30]. Additionally, it has also been demonstrated that the incorporation of carbon-based fillers within PDMS increases selectivity of the resultant membranes [28].

The intent of this study is to verify the hypothesis of increased separation of methane (CH₄) and hydrogen (H₂) utilizing CB-PDMS nanocomposites. The membranes are used in conjunction with a semiconducting commercial gas sensor that shows strong responses to both H₂ and CH₄. The hypothesis is tested by producing and testing composite

membranes consisting of CB dispersed within PDMS. Our assumption is based on the well-known fact that carbon has a high affinity to hydrogen atoms [31]. As a result, introducing CB into PDMS should alter the selectivity of the membrane against H₂ and CH₄ at different concentrations of CB in the composite. In this work, the gas separation properties of the nanocomposite membranes were evaluated, and correlated to their chemical structure, using vibrational spectroscopy.

2. Experimental

2.1 Membrane preparation

Four different CB-PDMS nanocomposite membranes were prepared with CB weight percentages ranging from 2 wt% to 15 wt%. First, the PDMS (Sylgard 184, Dow Corning) was prepared using 10:1 mixture of the base polymer and the curing agent. Next, CB powder (Vulcan XC72R, Cabot Inc.) was added to the PDMS matrix at the desired percentage by weight (2%, 6%, 10%, and 15%). The mixtures were then vigorously mixed until homogeneous pastes were obtained. After that, these pastes were placed in a vacuum oven at 60 °C for ~10 minutes for degassing. Finally, 7 g of the pastes were casted and levelled on glass plates of 100 mm × 15 mm dimensions and cured at room temperature for over 2 days. This resulted in membranes with similar thicknesses of 0.08±0.02 mm.

2.2 Characterization of CB-PDMS membranes

The pure, reference PDMS and the nanocomposite CB-PDMS membranes were characterized by electron microscopy and vibrational spectroscopy techniques. The membrane cross-section was studied using FEI Nova NanoSEM scanning electron microscope. The Fourier transform infrared (FTIR) spectra of PDMS and CB-PDMS membranes were recorded using a Thermo Nicolet 6700 spectrophotometer at a resolution of 4 cm^{-1} . A Renishaw InVia Raman spectrometer was used for performing micro-Raman characterization of the samples, which were analyzed at 633 nm wavelength with a laser power of 1.7 mW and with 20 s exposures over 3 accumulations.

2.3 Gas sensing setup

To measure the permeability and selectivity of these membranes to CH_4 and H_2 , a gas chamber setup was custom designed as shown in Figure 1. The setup is made of a main gas chamber with the dimensions of $17\text{ cm} \times 12\text{ cm} \times 5\text{ cm}$. The gas chamber has an inlet and outlet that allow the target gases to enter and leave. The chamber also has a 0.5 cm radius recess, where the membrane under investigation is placed. Outside the chamber, a commercial gas sensor is fixed against this membrane (see inset of Figure 1). The sensor and membrane is sealed in a way that only the diffused gas from the chamber and through the membrane can affect the sensor. A commercial and accurately calibrated CH_4 semiconducting gas sensor (TGS 2611, Figaro, Inc., USA) was used in these experiments in order to continuously measure gas concentration that passed through the membrane to interact with this sensor. This sensor was chosen as, in addition to CH_4 , it also shows a strong response to H_2 . This cross-response is desirable because the sensor can be practically used for assessing the selectivity of the different membranes to CH_4 and H_2 . According to the data sheet for TGS 2611 CH_4

sensor, response of this device to CH₄ is approximately 1.5 times larger than its response to H₂ for the same concentration of the gases (this ratio is only accurate in the range of 0.5% to 1.0% of these gases in ambient air).

A mass flow controller (MKS Instruments, Inc., USA) is used to feed the chamber with gas. The sensor measurements were acquired using a custom-made data acquisition system and analyzed using a MATLAB software-based program.

3. Results and Discussion

The nanocomposite CB-PDMS membranes were characterized using electron microscopy and vibrational spectroscopy techniques, to determine the characteristics of the CB-PDMS bonds at different CB concentrations.

3.1 Membrane Characterization by Microscopy and Vibrational Spectroscopy

3.1.1 Cross-sectional electron microscopy

Scanning electron microscopy (SEM) was used in order to examine the morphology of the membranes as well as the distribution of the CB nanoparticles into the polymer. For CB-PDMS nanocomposites lower than 10 wt%, samples were coated with gold to prevent charging, as they had a very low electrical conductivity [31].

Figure 2 shows the SEM micrographs of the prepared CB-PDMS composites. It was observed that particle dispersion was reasonably homogenous for all samples. The size and shape of the particles appeared irregular ranging in the order of 70 to 110 nm. Visually it was seen that as the concentration of CB increased in the polymer, the

dominant PDMS structure with CB particles changed to a composite structure. No exceptional morphological behavior was observed after the addition of CB particles at different concentrations.

3.1.2 FTIR studies

Figure 3 shows the FTIR spectra of pure PDMS and for different CB-PDMS composites. In the FTIR spectrum of pristine PDMS [32], $-\text{CH}_3$ deformation vibration signatures, appear between $1400\text{--}1420\text{ cm}^{-1}$ and between $1240\text{--}1280\text{ cm}^{-1}$. The latter peak can be observed in Figure 3 at 1240 cm^{-1} and this appear to have a minor back shift as the percentage of CB increases in PDMS. A broad, multi-component peak ranging from $930\text{ to }1200\text{ cm}^{-1}$, corresponding to symmetrical Si--O--Si stretching is also present. The peak at 918 cm^{-1} decreases and shifts to significantly lower wave numbers as the concentration of CB increase in PDMS. At 6 wt% CB in PDMS, the ratio between the two transmissions at 918 cm^{-1} and 944 cm^{-1} changes (peaks with marked region in Figure 3). Similar to previous reports [32-34], Si--C bands and rocking peaks for $\text{Si}(\text{CH}_3)_2$ are observed in $825\text{--}865$ and $785\text{--}815\text{ cm}^{-1}$ regions, respectively.

3.1.3 Raman spectroscopy studies

The Raman spectrum of our PDMS membrane is presented in Figure 4(a), with peaks that agree with typical PDMS spectra presented in previous works [35]. It has a Si--O--Si symmetric stretching peak at 488 cm^{-1} . The Si--CH_3 symmetric rocking appears around 607 cm^{-1} . At 708 cm^{-1} and 787 cm^{-1} , Si--C symmetric stretching and CH_3 asymmetric rocking appear, respectively. CH_3 symmetric rocking, symmetric bending, asymmetric bending, symmetric stretching, and asymmetric stretching show around 862 , 1262 , 1412 , 2907 , and 2965 cm^{-1} , respectively [35].

After incorporating CB into PDMS, the Si–O–Si symmetric stretching band at 488 cm^{-1} of the pure PDMS appears to fadeout as the concentration of CB increases [Figure 4(b)]. It is also observed that at 6 wt% the 607 cm^{-1} the Si–CH₃ symmetric rocking is the weakest of all mixtures.

In contrast, pure CB powder has two first-order peaks around 1350 and 1580 cm^{-1} which correspond to disordered and crystalline (graphitic) carbon, respectively [36]. These bands are relatively equal in the CB-PDMS composites. It can be seen from Figure 4(b,c) that as the concentration of CB increases, the intensity of these peaks increases. The peaks around 620 cm^{-1} are attributed to Si–C stretching band.

3.2 Gas permeability and selectivity

The permeability and selectivity of the membranes were tested at different concentrations of CH₄ and H₂ in ambient air, using the mass flow controller setup that was presented in Section 2.3. The measurements were conducted while the membranes were kept at room temperature and the Figaro sensor was biased as recommended (5 V DC applied to its heater) by the manufacturer and, during the gas exposure, the resistance across it was measured every 10 s. In order to assess the gas permeability and cross talk for the membranes, the mass flow controller generated gas streams of different concentrations of CH₄, H₂, and their mixtures in ambient air were pumped into the chamber. First, 0.5% and 1.0% H₂ (in ambient air) were pumped, followed by ambient air after each cycle to allow for the sensor recovery. Subsequently, 0.5% and 1.0% CH₄ (also in ambient air) were pumped into the chamber, similarly with ambient air between the two cycles for recovery. At the end, a mixture of 0.5% H₂ and 0.5% CH₄ were pumped to observe the effect of a mixed gas environment.

The exposure time for which different gas concentrations were pumped into the chamber was 15 min for CH₄ and 10 minutes for H₂ (due to its relatively faster gas diffusion through the membranes), while the ambient air for recovery was pumped for 20 and 30 min in between and after exposures, respectively. It was observed that the exposure time of 10 min was also sufficient for the mixture of CH₄ and H₂.

As these gases were pumped into the chamber, the commercial CH₄ sensor behind the different membranes was used for measuring the concentrations of the analyte gases that passed through the membranes (Figure 1). Employing the commercial sensor in conjunction with the pure PDMS and nano-composite CB-PDMS membranes, when subject to different gas species and concentrations, the relative permeability ratios of different membranes for various gas species were determined. The dynamic response of sensing system at different concentrations of gases is shown in Figure 5, where the variation in resistance of the commercial sensor R_s as a function of gas exposure over time is presented. All measurements were taken at room temperature.

As can be seen in Figure 5, for 2, 6, and 15 wt% CB-PDMS composites, the response magnitudes and their trends were fairly similar upon exposure to both 0.5% and 1.0% H₂ and fell within the maximum and minimum 50% range of the values. Additionally, at these mixtures the baselines were quite stable. However, at 10 wt% CB composite and to a lesser degree for the pure PDMS, the baselines gradually shifted upwards and were not as stable. This effect resulted in a change in the value of R_s when the H₂ concentration increased, which disordered the H₂ response trend. The baseline shift effect was dramatically reduced after repeated measurements, when both the membranes and sensor reached a high degree of stability.

To assess the membranes' gas selectivity and their relative permeability for each gas species, we obtained the normalized permeability for each case (Figure 6). First,

responses of the sensor/membrane systems to H_2 gas was multiplied by 1.5 due to the fact that the Figaro gas sensor response to a H_2 gas concentration is 1.5 less than that of the same concentration of CH_4 . Second, the response of the system incorporating 2 wt% CB in PDMS membrane to H_2 was used as the base for the normalization, as it provided the largest response. It should be considered that before the normalization the responses of the membranes to H_2 gas was multiplied by 1.5 due to the fact that the Figaro gas sensor response to a H_2 gas concentration is 1.5 less than that of the same concentration of CH_4 . As can be seen in Figure 6, the presence of CB in PDMS has slightly enhanced the permeability to H_2 through the composite membranes. This is in agreement with our earlier hypothesis that carbon-loading enhances H_2 diffusion, as carbon has an affinity to H_2 . Conversely, embedding CB in PDMS has significantly attenuated the permeability of the membranes to CH_4 . The optimum condition for almost completely blocking CH_4 diffusion, while allowing the passage of H_2 , was obtained at 6 wt% CB loading.

As described in Section 3.1.2 and revealed from our FTIR investigations (Figure 3), at 6 wt% CB in PDMS, the ratio between the two transmissions at 918 cm^{-1} and 944 cm^{-1} changes. This appears to relate to the membrane permeability to CH_4 as we have more non-polymerized bonds between Si and O, which facilitate the interaction of CH_4 with the membrane. Moreover, Si–C bands around $825\text{--}865\text{ cm}^{-1}$ and rocking in $Si(CH_3)_2$ in $785\text{--}815\text{ cm}^{-1}$ were also observed. These changes suggest that the 6 wt % CB PDMS composite is a transition point, where the chemical bond structure starts to change. This transitory structure appears to be responsible for CH_4 blockage. As the concentration of CB increases, the CB-PDMS bonds start to become increasingly cross-linked, which again enables CH_4 permeation [37].

From the Raman spectra (Figure 4), it was seen that at 6 wt% the Si– CH_3 symmetric rocking is the weakest, in comparison to the other CB concentrations. As a result, it is

likely that at this concentration, Si establishes the optimum number of bonds with the carbon from the CB matrix.

The results obtained from the vibrational spectroscopy analyses (FTIR and Raman) both suggest and support that Si–O bond plays a major role in the membrane permeability characteristics. As the concentration of CB reaches 6 wt%, a chemical transition exists, where the number of non-polymerized Si–O bonds increase, which appears to relate to the prevention of CH₄ molecules from passing through the composite membrane. Moreover, as the concentration of CB reaches 15 wt%, the microscopy and vibrational spectra indicate that PDMS is significantly modified resulting in a new composite material.

4. Conclusion

In this work, a number of weight concentrations of CB in CB-PDMS nanocomposite membranes were fabricated. The effect of the CB concentration on membrane selectivity to CH₄ and H₂ was studied. It was found that in general the presence of CB in PDMS enhances the selectivity of the membranes toward H₂ over CH₄. A specific, optimal weight ratio of CB (6 wt%) in PDMS was found to produce nanocomposites with increased selectivity to permeation of H₂ by efficient blocking of CH₄. Such selective permeability membranes can enable *in situ* selective H₂ gas measurement, using low cost semiconducting gas sensors, as most semiconducting gas sensors are also sensitive to CH₄ and other gas species. We plan to extend this study in the future by testing these membranes in both aqueous environments.

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Figure Captions

Figure 1: Gas sensing setup depicting location of the gas selective membrane and the gas sensing module (not to scale).

Figure 2: Cross sectional SEM micrographs of CB-PDMS nanocomposite membranes of different concentrations, showing distribution and particle size, respectively for: 2 wt% CB in **(a)** and **(b)**; 6 wt% CB in **(c)** and **(d)**; and 15 wt% CB in **(e)** and **(f)**.

Figure 3: FTIR spectra for the pure PDMS and nanocomposite CB-PDMS membranes.

Figure 4: Micro-Raman spectra for: **(a)** pure PDMS; **(b)** three different CB concentrations in CB-PDMS nanocomposite membranes; and **(c)** marked wavenumber range in **(b)**.

Figure 5: Dynamic response of the sensor-membrane system on exposure to different gas concentrations and mixtures.

Figure 6: Normalized relative permeability of CB-PDMS membranes to various concentrations of CH₄ and H₂ in ambient air.

Figure 1
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