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Sensing of Acetone Vapours using Pvdzr Composite

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An actual problem of medical diagnostics is that the determination of acetone concentration in air exhaled by persons. For industrial health and safety, environmental monitoring and process control Gas detection instruments are needed. Conducting polymer composites have various industrial applications. The most dangerous pollutants released each year by anthropogenic sources are benzene, toluene, nitrogen oxides, hydrogen sulfide or ammonia They have harmful effects both on human beings and animals. People may develop a headache, fatigue and even narcosis when the concentration of acetone in air is higher than 10,000 ppm. Hence, detecting and measuring acetone concentrations in the workplace or human body are necessary for our safety and health. Gas sensors play vital role in detecting, monitoring and controlling the presence of hazardous and poisonous gases in the atmosphere at very low concentrations. In the present work, a pasty solution of PVDF/ZrO_2 was coated on glass plates using an Apex Spin Coating unit (SCU 2005) and the samples were tested for gas sensing. For this study, acetone, ethanol and ammonia gases were used and the electrical resistance of polymer composites over the vapours were determined using MECO 603 digital multimeter. The vapours of acetone were detected by the sensor. The sensing cycle is reversible upto to two cycles. In order to validate the selectivity of the gas sensor, polymer composite plates were exposed to ammonia and ethanol vapours which do not show any response. The PVDF / ZrO_2 (PVDZr) composites were characterized by using PXRD, FTIR and SEM. The results show that the thick film of PVDZr composite can function as a very good gas sensor for acetone vapours.

1. Introduction

Composite materials are complex materials whose components differ strongly from each other in properties. PVDF has been widely used in many fields, such as ultrafiltration and microfiltration membranes, electrode binder in lithium ion batteries, microwave transducers and its unique applications as piezoelectric and pyro electric materials. It's strong piezoelectric response, chemical and mechanical durability make it a valuable material for sensors and actuators. A Polymer host (PVDF) is doped with metal oxides enhance the conductivity (Li, 2009). The conductivity is related to the glass transition temperature, T_g and is further related to the inter-linking of the polymer chain. Zirconia (ZrO_2) is an oxide which has a high tensile strength, high hardness and corrosion resistance. Zirconia based ceramics are routinely used in structural applications in engineering, such as manufacture of cutting tools, gas sensors, refractories and structural opacifiers (Rajendran t al., 2006; Spadavecchia et al., 2000; Wang et al., 2010; Zeng and Liu, 2010; Ryabtsev et al., 1999; zhang et al., 2006; Dupare et al., 2011). Various types of acetone sensors based on different sensing principles such as, semiconductor sensors (Anno et al., 1995), chemiluminescence-based sensors (Hashmi et al., 2002), optical –fibre sensors (Utsunomiya et al., 1993) and piezoelectric sensors (Bene et al., 1998) have been fabricated. In practical use, sensors have to be studied with respect to the 's' criteria of gas sensors namely sensitivity, selectivity, stability and speed. However, regarding these criteria many gas sensors do not sufficiently fulfill the requirements. Also, these sensors still have some short-comings such as low selectivity, short life time, unsuitability and low sensitivity. Successful attempts have been made by a number of groups to overcome these problems by investigating semi conducting metal oxides operated at higher temperatures. This includes materials like $BaTiO_3$, $SrTiO_3$, Ga_2O_3, WO_3, Nb_2O_3, MoO_3 and CeO_2 with operating temperatures being typically between 400 and 900 °C (Barko and Hlavay, 1998). The present work reports the results of the gas sensing behavior of a sensor developed using thick film of PVDZr composites which shows a maximum response to the test gas at room temperature.

2. Materials and methods

2.1 Materials used

Polyvinylidene difluoride (PVDF) (Alfa Aesar), Zirconium dioxide (ZrO_2) (Fischer Scientific, India) and N,N Dimethyl formamide (DMF) (Fischer Scientific, India). All chemicals used were of Analar grade and were used as received from the supplier without further purification.

2.2 Preparation of PVDZr Composites

PVDZr composites were prepared by sol gel method (Fleischer and Meixner, 1997).

2.3 Preparation of PVDZr composite thick films for gas sensing

A pasty solution of PVDF/ZrO_2 was coated on glass plates using an Apex Spin Coating unit (SCU 2005) and the samples were sintered in a hot air oven for about 30 minutes at 80 °C. Then these plates were used for gas sensing. Two parallel copper wires were fitted onto the corners of the glass strips. These wires act as electrodes to detect the presence of gas. The samples were placed in a closed chamber. The experiment was performed at room temperature (30 ^{o}C). For this study, acetone, ethanol and ammonia gases were used and the electrical resistance of polymer composites over the vapours were determined using MECO 603 digital multimeter.

2.4 Response of composites to vapours

The responsiveness, S, of the composites to acetone, ethanol and ammonia vapours can be determined from the equation,

$$S = R_t / R_o \quad (1)$$

Where R_o is the initial resistance value of the sensor, and R_t is the maximum steady state response value of the sensor when it was exposed to the analyte vapour (Devikala et al., 2013).

2.5 Characterisation techniques

The X-ray diffraction pattern (XRD) and Scanning Electron Microscopy (SEM) are the basic techniques required to find out the phase and purity of the composite materials. The XRD patterns of polymers and polymer composites were recorded using Philips X'Pert pro diffractometer. The FTIR spectrums of polymers and polymer composites were recorded using Shimadzu FTIR spectrophotometer. The SEM images of polymers and polymer composites were recorded using Hitachi Scanning Electron Microscope SU1510.

3. Results and discussion

3.1 XRD

The sharp crystalline diffraction peaks noticed in pure PVDF, have become less prominent in case of composites. The intensity of the peak at 38.0^{o}, is gradually decreased. As the ZrO_2 content increases, the characteristic composite peaks at 30.26, 50.37, 50.70, 60.2 corresponding to the tetragonal phase ZrO_2, are obviously pronounced, and the peaks corresponding to PVDF diminish. The broad peak at region of 2θ = 15-20°, showing the main crystalline property of PVDF disappears when ZrO_2 content increases. This shows that a small amount of PVDF may exist in the composite samples with higher ZrO_2 content (Figure 1 (i) – (iii)). The average crystallite size is found to be 0.1367 µm.

3.2 FTIR

In the composite PVDZr , the peaks due to ZrO_2 at 2204, 2192, 2169, 1973, 1683, 1651, 1434, 750, 686, 665, 650 and 520 cm (Wei et al., 2009)$^{-}$ are shifted to 2225, 2187, 2160, 1964, 1685, 1652, 1415, 737, 677, 667, 650, 642 and 518 cm^{-1} respectively. This suggests the presence of ZrO_2 in the composite. PVDF characteristic peaks are also observed in the composite at 1189, 533 and 491 cm^{-1} respectively. In addition, some new peaks are also formed. The shifts in the pure PVDF and pure ZrO_2 indicate that some interactions have occurred. This may be due to the interaction between the CF_2 groups of PVDF and oxygen atoms of ZrO_2. On adding ZrO_2, significant changes in the spectral features in terms of the appearance of new peaks and the disappearance of existing peaks are observed (Figure 2 (i) - (iii)).

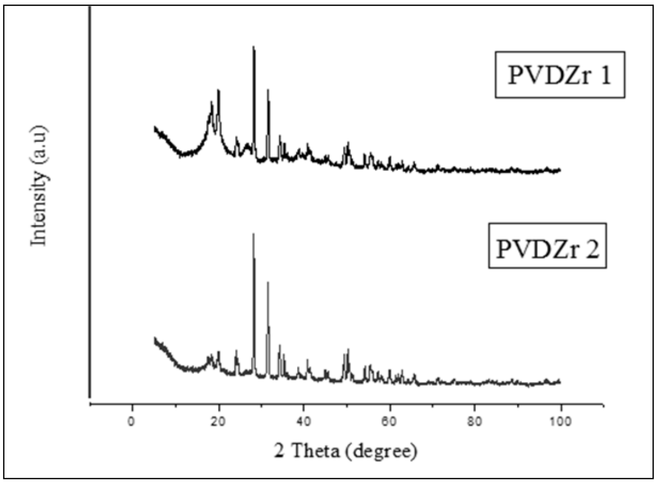

Figure 1: (i) XRD patterns of PVDZr 1 and 2

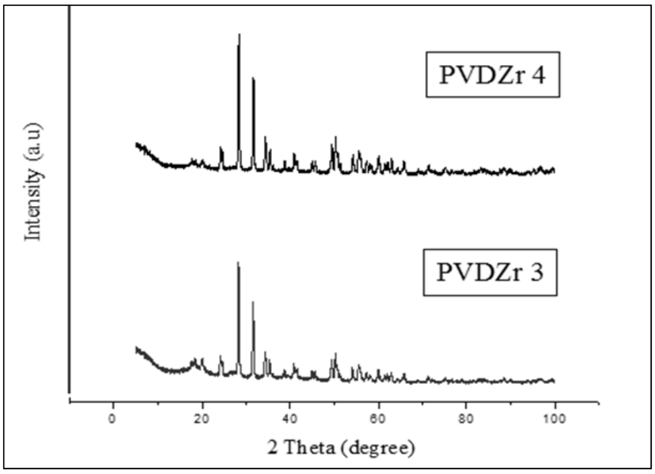

Figure 1: (ii) XRD patterns of PVDZr 3 and 4

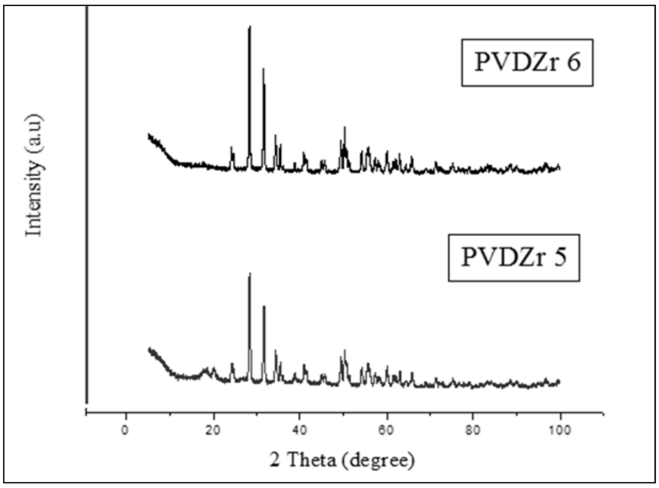

Figure 1: (iii) XRD patterns of PVDZr 5 and 6

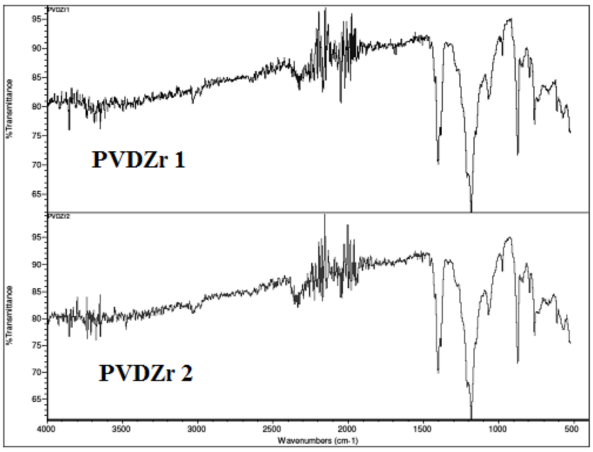

Figure 2: (i) FTIR spectra of PVDZr 1 and 2

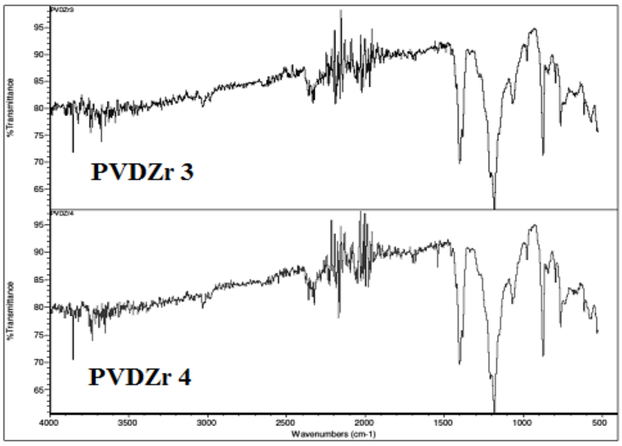

Figure 2: (ii) FTIR spectra of PVDZr 3 and 4

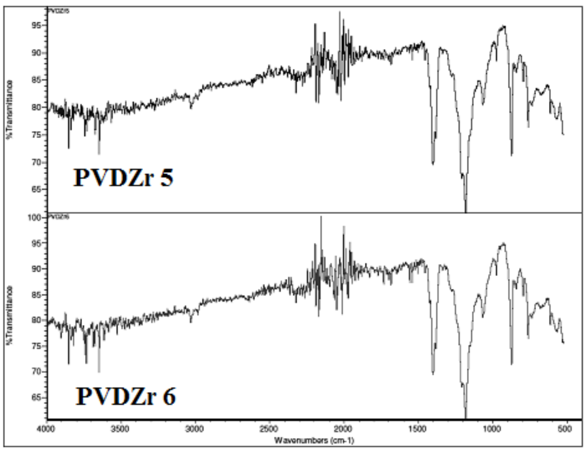

Figure 2: (iii) FTIR spectra of PVDZr 5 and 6

3.3 Gas sensing

The sensor has been tested for a continous two subsequent cycles to test it stability. It was found that the resistance could return to the base line after each cycle (Dee et al., 2009). The resistance, responsiveness and sensitivity of the composite-based sensor obtained from the response and recovery curves are summarized in Table 1. The response time of the polymer composite sensor is 12 seconds. The fast response time may be due to the fast reaction rate between the test gas and adsorbed oxygen. The films exhibited fast response time and recovery time when compared to the reported (Zhao et al., 2006; Luo et al., 2002). As soon as the film is transferred from the flask full of the saturation acetone vapour to dry air, the resistance immediately decreased to the original value, indicating that the film reversibility responds to acetone vapour.

Table 1: Sensor response of PVDZr composites to acetone vapour

PVDF/ZrO_2 composites	Ro MΩ (Initial resistance)	Rt MΩ (Maximum steady state resistance)	R_t/R_o (Sensitivity)
PVDZr 1	52	4200	89
PVDZr 2	48	4000	92
PVDZr 3	46	3900	94
PVDZr 4	42	3600	96
PVDZr 5	40	3400	98
PVDZr 6	33	3200	99

4. Conclusion

A gas sensor based on PVDZr has been developed and the experimental results are evaluated. The resistance of the polymer composite got extremely increased in acetone vapours and reached equilibrium over time. The addition of ZrO_2 to PVDF has increased the conductivity of the PVDZr composites. The results have shown that composites have potential application for detecting acetone selectively at room temperature.

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