IJIREEICE
ISSN (Online) 2321 – 2004
ISSN (Print) 2321 – 5526
INTERNATIONAL JOURNAL OF INNOVATIVE RESEARCH IN ELECTRICAL, ELECTRONICS, INSTRUMENTATION AND CONTROL ENGINEERING
Vol. 3, Issue 12, December 2015

Sensor Applications Using Sol-Gel Technique

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Abstract: We prepared sol-gel samples by hydrolysis of tetraethyl orthosilicate (TEOS). FTIR studies are done on the samples heated at different temperatures to confirm the glassy network. Porosity studies confirmed the pore size of around 22nm. Acid /Alkali indicators like methyl orange, phenolphthalein and universal indicator doped sol-gel glasses are prepared. These glasses can be used as acid/alkali reversible solid indicators. V-I characteristics are drawn for these glasses using a diode laser photo detector set up. These glasses find application as a solid-pH sensor. Samples are also prepared by doping them with suitable chemicals which find application as a sensor for industrial chemical leakage.

Key words: sol-gel process, industrial chemical sensor, pH sensor, porosity studies.

INTRODUCTION

Sol-gel processing is a low temperature method which is used for the fabrication of inorganic or composite organic materials such as glasses, thin films, ceramics or powdersof high homogeneity and purity [1]. It is based on the mixing of liquid reactants on molecular scale and solidification of solution into a porous amorphous oxide gel. Sol-gel process for the synthesis of glass and ceramics has attracted increasing scientific and technological interest.

Structural studies of sol-gel silica glass

In this paper we describe about the structural modification during the gel to glass transition. Structural properties of sol-gel glass such as characteristics of porous width and FTIR spectra of sol-gel glasses have important role in determining the glassy network. We have prepared sol-gel glass samples at room temperature, 100°C, 200°C, 500°C and 800°C. The FTIR spectrums of these glass samples were taken. The hydrolysis and polymerization of the prepared glass sample have investigated. The hydrolysis of tetraethyl orthosilicate (TEOS) with Si-OH groups which react with other Si-OH groups through polycondensation, gives us a three-dimensional silica network.

Silica sol-gel glasses are porous materials whose pore size can be tailored effectively. On comparison to size of the piece material considered the pores must be extremely small.[2]. The porous glass can be produced in high quality and with pore sizes ranging from 1 nm up to millimetre order. Incorporation of nanomaterials in the body of sol-gel glasses opens a wide field of applications. Most of the porous materials do not have uniform pores. The pore size distribution is also an important property. Moreover the narrow pore size distribution, i.e., uniform pore size is required for filters and bioreactor beds.

Study of pH indicator in sol-gel silica glass

Recently,it has been proposed that the determination of pH has a wide range importance in the medical, environmental and biotechnological fields **[**3**]**.pH is defined as the negative logarithm to base 10 of the activity of the hydrogen ion [4]. pH indicator is a halochromic material added to a solution that changes the pH of the solution. Because of subjective determination of colour, pH indicators are susceptible to imprecise readings. We have prepared indicator such as phenolphthalein, methyl orange and universal indicator doped sol-gel glass samples at room temperature. Also we have identified that the indicator doped glass shows reversible characteristics. By using a laser diode-photo detector set up we have measuredthe variation of current with respect to voltage, which is due to the high variation of colour in acidic and alkali medium. The change in colour is due to the change in pH values of the indicator.

Industrial Chemical Leakage sensor

The sol-gel derived chemical sensors have blossomed since the mid-1980's. Sol-gel derived matrices as host provide better stability, flexibility, optical transparency and permeability[5-8].However, sensor technology is a multidisciplinary field and more and more scientists are now crossing discipline boundaries thus new research groups are being set up [9].Chemical sensors are developed for a large variety of applications such as industrial hygiene, process control, clinical diagnostics and more recently home land security. This paper summarizes the effort that we have made on implementing the sol-gel technology in sensor applications. We proposed that sol-gel glass doped with certain chemicals, act as a sensor to detect the industrial chemical leakage. Because of the ease of fabrication and design flexibility, studies in optical chemical sensor are an attracting research field [10].

EXPERIMENTAL

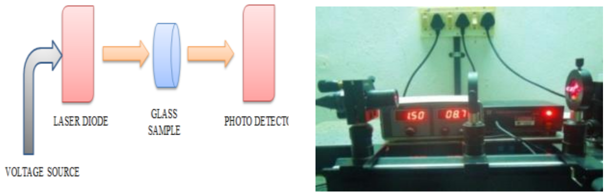
Preparation of sol-gel silica glass samples

Sol-gel silica glasses were prepared [11] by the hydrolysis of tetraethyl orthosilicate (TEOS). Mix 6 ml of tetraethyl orthosilicate (TEOS) with 2 ml of water (H_2O) &2 ml of ethanol (C_2H_5OH) and the mixture was stirred magnetically. After preparation, samples were dried at room temperature for 5 days. Samples heated at different temperatures using hot air oven. The FTIR spectra were taken using the Shi madzu FTIR spectrometer.

Preparation of indicator doped glass samples

Mix 6 ml of tetraethyl orthosilicate (TEOS) with 0.5 ml of methyl orange, 2 ml of water (H2O) & 2 ml of ethanol (C_2H_5OH). After stirring the complex gel using a magnetic stirrer, they kept at room temperature, dried for 5 days. Thus methyl orange doped glass samples were prepared.

Continue the process by replacing phenolphthalein and universal indicator. Set up a circuit as shown in figure 1.

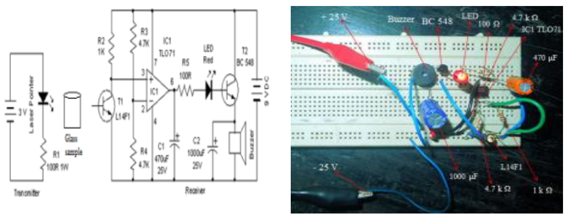


(a) (b)

Figure 1: (a) schematic diagra9m of pH sensor set up (b) original set up of pH sensor

Preparation of chemical doped glass samples for the industrial chemical leakage sensor

In order to prepare transparent silver nitrate doped glass sample, first mix 6 ml of tetraethyl orthosilicate (TEOS) with 1 ml of silver nitrate solution, 2 ml of water (H_2O) & 2 ml of ethanol (C_2H_5OH) and stir the complex gel using a magnetic stirrer. They were kept under room temperature, dried for 5 days. Thus the silver nitrate doped glass samples prepared. Same process is repeated for the preparation of barium chloride and copper sulphate. The leakage can be identified by the help of an alarm circuit (shown in figure 2) that can sense the light beams falls on it. The basic idea is that when certain chemical falls on the prepared sample, the glass loses its transparency and turns into opaque. The so prepared sample was kept between a laser source and the alarm circuit as shown in the figure 2(a). When few drops of chemical (example-hydrochloric acid) fall on the sample the transparent glass sample turns opaque. This sudden change will switch on the alarm circuit.



(a) (b)

Figure 2: (a) schematic diagram of chemical sensor set up (b) original set up of chemical sensor using photo detector

RESULT AND DISCUSSION

FTIR spectrum analysis

In summary, the gel at room temperature shows a wide bands in the IR spectrum characteristic of adsorbed water and Si-OH stretching vibration(bands at 3000- 3800 cm^{-1} and 1645 cm^{-1}). It is observed that the intensity of these bands show substantial decrease above 200 °C and have negligible intensity in the high temperature annealed samples. These results confirm that a substantial portion of the water and residual organic molecules in dried silica gels have been removed above this temperature.

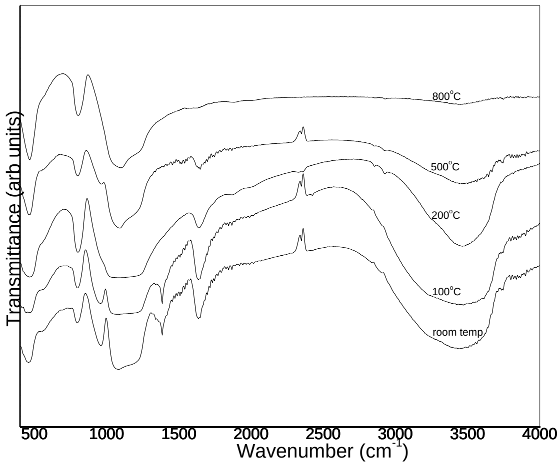


Figure 3: FTIR spectrum of sol-gel glass at different temperature

IR peaks(cm^{-1})	Assignments
3800-3000	V_{OH} of absorbed water
1635	V_{OH} of water absorbed on to Si-OH with hydrogen bonding
1385	δCH_3 Symmetric bend
1180	Si-O-Si Symmetric stretch
1085	Si-O-Si Anti-symmetric stretch
960	Si-OH Anti symmetric stretch
798	O-Si-O Bend
460	Si-O-Si Bend

Table 1: FTIR band assignments of sol-gel glass at different temperature

Porosity studies:

The interpretation of adsorption-desorption isotherms provides information on the texture of the adsorbent. The main parameters which can be measured are surface area, pore volume and pore size. We have investigated using single point estimation, t-Plot model, Langmuir model, BET model and BJH method [12].

The following tables (table 2-4) show their characteristics at room temperature.

Surface area

Method	Surface area(m^2/g)
Single point surface area at p/p^o= 0.313019540	658.9452
BET surface area	667.2386
Langmuir surface area	104.04309
t-Plot	Micropore: 146.3620 External: 520.8765
BJH adsorption (cumulative surface area of pores between 17 nm and 3000 nm width)	336.1924
BJH desorption (cumulative surface area of pores between 17 nm and 3000 nm width)	358.5095

Table 2: Estimation of surface area

DOI 10.17148/IJIREEICE.2015.31207

IJIREEICE

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ISSN (Print) 2321 – 5526

INTERNATIONAL JOURNAL OF INNOVATIVE RESEARCH IN ELECTRICAL, ELECTRONICS, INSTRUMENTATION AND CONTROL ENGINEERING
Vol. 3, Issue 12, December 2015

Pore volume

Method	Pore volume (cm^3/g)
Single point adsorption (total pore volume of pore less than1231.755 nm width at p/p^o=0.984173850)	0.362509
t-Plot	(micro pore) 0.085923
BJH adsorption (cumulative surface area of pores between 17 nm and 3000 nm width)	0.185024
BJH desorption (cumulative surface area of pores between 17 nm and 3000 nm width)	0.191079

Table 3: Estimation of pore volume

Pore size

Method	Pore size obtained (nm)
Adsorption average pore width (4 V/A)	21.7319
BJH adsorption average pore width(4 V/A)	22.014
BJH desorption average pore width(4 V/A)	21.319

Table 4: Estimation of pore size

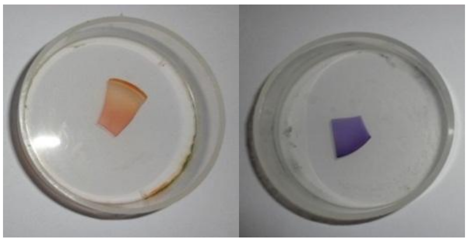
Where, p-equilibrium pressure, p^o- saturated vapour pressure
The main parameters (surface area, pore volume and pore size) have been found out using six calculation methods: Langmuir model, BET model, single point method, t-Plot method, BJD adsorption and BJD desorption methods. Average pore size was found to be around 22 nm while pore volume and surface area was around $0.20cm^3/g$& $330m^2/g$. these results indicates that sol-gel glasses are in nano-regime.

Reversible characteristics of indicator doped sol-gel glasses

We have identified that at room temperature indicator doped glass shows reversible characteristics. However the performance is not long lasting. It degenerate after a couple of reactions. Phenolphthalein doped glass degenerate fastly hence it can be reused up to five times while methyl orange and universal indicator doped glass lasts its reversible property up to twelve or thirteen times. The following figures (figure 4-6) shows images of indicator doped glass in acid medium and in alkali medium.

(a) (b)
Figure 4: Methyl orange doped glass in (a) acid medium & (b) alkali medium

(a) (b)
Figure 5: Phenolphthalein doped glass in (a) acid medium & (b) alkali medium



(a) (b)
Figure 6: Universal indicator doped glass in (a) acid medium & (b) alkali medium

V-I Characteristics of indicator doped glasses
Here we have tabulated (tables 5-7) and plotted (figure 7-9) the current –voltage relation of certain indicator doped sol-gel glasses.

1. Methyl orange doped glass in acid and alkali medium

Voltage (V)	Current (mA)	
	Acid Medium	Alkali Medium
1.5	12.5	10.2
2.0	14.6	12.2
2.5	16.6	14.1
3.0	18.4	15.7
3.5	20.1	17.2
4.0	21.6	18.5
4.5	23	19.7
5.0	24.3	20.7
5.5	25.5	21.7
6.0	26.6	22.5
6.5	27.8	23.2

Table 5: Methyl orange doped glass in acid and alkali medium

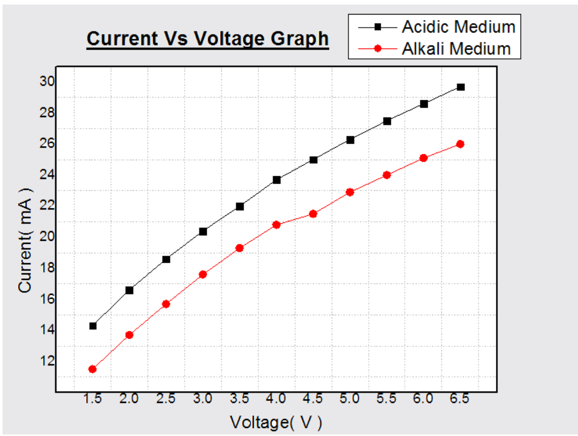


Figure 7: Current Vs Voltage graph of methyl orange doped glass sample

DOI 10.17148/IJIREEICE.2015.31207

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2. Phenolphthalein doped glass in acid and alkali medium

Voltage (V)	Current (mA)	
	Acid Medium	Alkali Medium
1.5	14.3	11.5
2.0	16.6	13.7
2.5	18.6	15.7
3.0	20.4	17.6
3.5	22	19.3
4.0	23.7	20.8
4.5	25	21.5
5.0	26.3	22.9
5.5	27.5	24
6.0	28.6	25.1
6.5	29.7	26

Table 6: Phenolphthalein doped glass in acid and alkali medium

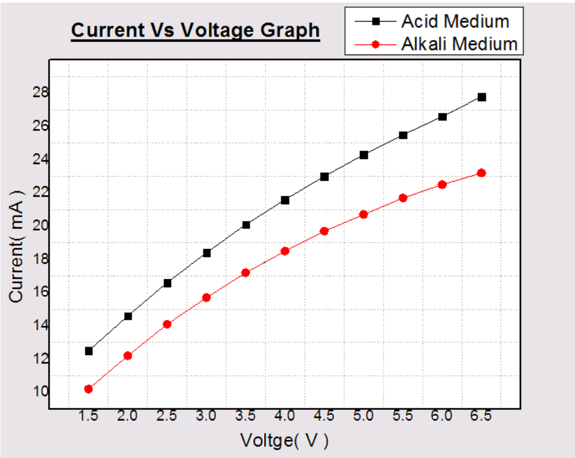


Figure 8: Current Vs Voltage graph of phenolphthalein doped glass sample

3. Universal indicator doped glass for pH5, pH7 and pH10

Voltage (V)	Current (mA)		
	pH5	pH7	pH10
1.5	11.8	13.7	14.4
2.0	13.9	16.1	16.8
2.5	15.8	18.3	19.0
3.0	17.6	20.2	21.0
3.5	19.1	22	22.9
4.0	20.6	23.6	24.3
4.5	22	25	26.1
5.0	23.3	26.3	27.5
5.5	24.6	27.6	28.9
6.0	25.6	28.5	30.9
6.5	26.7	29.5	31.1

Table 7: Universal indicator doped glass for pH 5, pH 7 and pH 10

The above diagrams shows that the current variation with voltage can be used to study the transition of indicator doped glass from acid to alkali medium. The approximate range of pH value can be determined because of the strong colour change of indicator doped glasses in acid and alkali medium.

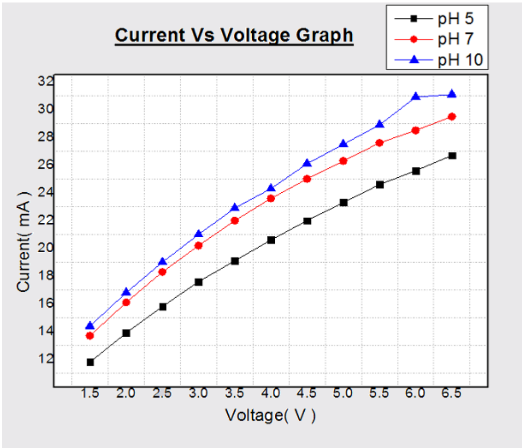


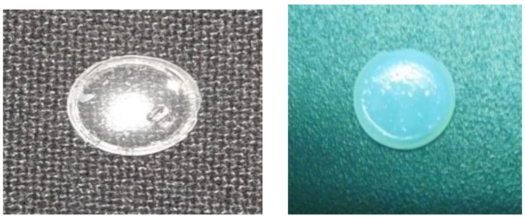
Figure 9: Current Vs Voltage graph of universal indicator doped glass sample

Chemical sensor

In this study we have identified the leakage of two chemicals one hydrochloric acid (HCl) and the other sodium chromate (Na_2CrO_4).We have prepared transparent sol-gel samples doped with silver nitrate ($AgNO_3$) solution using sol-gel technique. When few drops of hydrochloric acid (HCl) solution falls on the sample, the sample turns opaque due to the following reaction,

$$HCl + AgNO_3 \rightarrow AgCl + HNO_3$$

This is an ideal sensor to detect thehydrochloric acid(HCl) leakage (figure 10).



(a) (b)

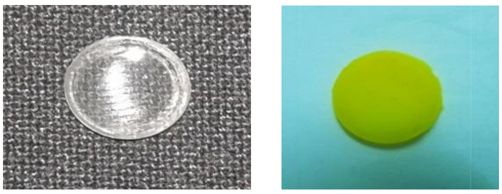
Figure 10: Images of $AgNO_3$ doped glass sample (a) before and (b) after dropping HCl solution

Similarly, sodium chromate (Na_2CrO_4) leakage can also be detected by using barium chloride ($BaCl_2$) doped transparent samples figure 11). The reaction is given by,

$$Na_2CrO_4 + BaCl_2 \rightarrow BaCrO_4 + 2NaCl$$

Na_2CrO_4 solution dropped on the transparent samples turns it opaque due to the presence of the barium chromate ($BaCrO_4$). The copper sulphate doped transparent sample is also found to exhibit this opaque property (figure 12) by the following reaction,

$$Na_2CrO_4 + CuSO_4 \rightarrow Na_2SO_4 + CuCrO_4$$



(a) (b)

Figure 11: Images of $BaCl_2$ doped glass sample (a) before and (b) after dropping Na_2CrO_4 solution

DOI 10.17148/IJIREEICE.2015.31207

IJIREEICE

ISSN (Online) 2321 – 2004
ISSN (Print) 2321 – 5526

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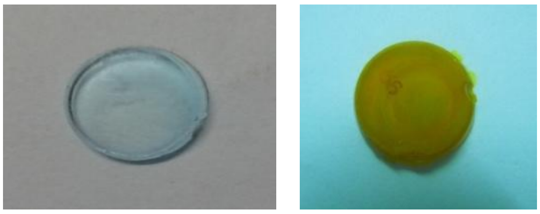

(a) (b)

Figure 12: Images of $CuSO_4$ doped glass sample (a) before and (b) after dropping Na_2CrO_4 solution

Response time measurement:

Type of glass sample	Response time (sec)
$AgNO_3$ doped	1.0 – 3.0
$BaCl_2$ doped	2.0 – 3.0
$CuSO_4$ doped	3.0 – 4.0

Table 8: Estimation of response time for the glasses

Since the response time of these glass samples (table 8) are very short the sensor is highly sensitive to the leakage of HCl and Na_2CrO_4 solutions.
We found that the leakage of hydrochloric acid and sodium chromate solutions can be determined using sol-gel technique. The set up can be extended for sensing other chemicals in industries by doping the glass with suitable dopants. The thin films prepared using this technique find immense potential in sensing other chemicals using smart device.

CONCLUSION

The structural studies like FTIR spectrum analysis and porosity studies of glass samples were done to confirm the rigid glassy network and nanopore size of the sample. The indicators like methyl orange, phenolphthalein and universal indicator were incorporated in glass samples and its reversible characteristics were studied. Hence a solid-pH sensor was proposed. Leakage of certain industrial chemicals were identified and reported. And a practical working model was constructed.

ACKNOWLEDGEMENT

Authors would like to thank principal, Sacred Heart College Thevara for providing infrastructure facilities and **Dr. Jose K. B,** Associate Professor, Department of Chemistry for chemical preparations.

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