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Sol-gel based surface modification of electrodes for electro analysis

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Abstract

In chemical analysis and electrochemical catalysis modified electrodes have been used in a wide range. In addition to the several methods of electrode modification reported in literature, the sol-gel route offers a possibility of preparing ceramic like films under rather mild conditions. This enhances the possibility of incorporation of temperature sensitive particles such as enzymes, microorganisms, proteins and several other biomolecules into such composite layers, resulting in very inert and stable matrices useful for analytical applications.

The present paper, in addition to providing an overview of the various analytical applications of sol-gel processes, presents the fabrication and evaluation, of a novel sol-gel based potentiometric sensor for pH measurement. The performance characteristics of the sol-gel based pH sensor is evaluated using buffers in the pH range 2–10 prepared using standard buffer compositions reported in literature. The results show a linear correlation between negative logarithm of hydrogen ion concentration and measured millivolt response.

Keywords: Sol-gel; pH sensor

Contents

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1. Introduction

The sol-gel process, which has been a method for the production of ceramic materials for more than one and a half century is gaining importance [1–5] because it provides rather convenient and simple means to incorporate heat sensitive materials including organic molecules and active proteins, in porous ceramic materials. It has been rapidly developed over the years because of its ability to form inorganic–organic hybrids. "Sol-Gel" refers to a process by which largely inorganic polymers are synthesized. A "Sol" is a dispersion of colloidal particles and a "Gel" is an interconnected polymeric network formed by the assembly of the sol. [6]

The main aim of this paper is to provide an overview of the various analytical applications of sol-gel processes reported in the literature and throw some insight into sol-gel chemistry. A practical approach to fabrication of pH sensing electrode based on classical quinhydrone redox system, wherein sol-gel chemistry provides a firm footing in arriving at the composition and stable design of the sensing electrode is demonstrated.

2. Sol-gel technology

2.1. Process

The term sol-gel describes a broad class of processes by which gels are produced from colloidal suspensions, or sols. As the name implies it involves, the manufacture of inorganic matrices through the formation of colloidal suspension and gelation of the sol to form a set gel which after drying form the "dry gel" state (xerogel). [5] After the formation of xerogel various additives in the name of dopants are added into the matrix for obtaining desired properties.

The sol-gel process occurs through four stages viz.

1. hydrolysis and poly-condensation
2. gelation
3. drying
4. high temperature treatment

They are best explained as below.

2.2. Hydrolysis and poly-condensation

The reaction proceeds by hydrolysis of alkoxide precursors under acidic or basic condition followed by poly-condensation of hydroxylated monomer to form a porous gel. [7] Traditionally organic reagents are immobilized in silica gel matrices by impregnation or by using the high reactivity of surface silanol groups to anchor the reagents by covalent bonding. In recent years, a novel doping method has been introduced, where the dopants are incorporated in the sol-gel glass at the early stages (or even before initiation) of the polymerisation step. The surface property of the xerogel can be modified by using a precursor compound containing the silicon carbon bond, as it remain unchanged during hydrolysis and poly-condensation. [5] Further the functional group (R) remains exposed at the surface of porous structure that is denoted by the general formula.

$$(1-\mathrm{y})\mathrm{Si}(\mathrm{O}R')_4 + (\mathrm{y})R\mathrm{Si}(\mathrm{O}R')_3 + (4-x-y)\mathrm{H_2O} \rightarrow R_y\mathrm{SiO}_x(\mathrm{OH})_{4-y-2x} + (4-y)R'\mathrm{OH}$$

where $0<y<1$ and $0<x<2$.

2.3. Gelation

The gel point is defined as the point at which the entire solid mass becomes inter connected, at the initial stages of polymerisation, the silanol functional groups at the surface of the growing particles are partly deprotonated, and their negative charge provides a repulsion barrier that stabilizes the sol. Later, solvent evaporation and water consumption by alkoxysilanes hydrolyses the concentrated solution and destabilizes the suspension. Thus the rigidity of the product is increased. [6]

2.4. Drying, aging, and fracture prevention

During the last stages of gelation, water and the organic solvent evaporate from the glass cavities and the volume of the solid matrix shrinks gradually. During the drying phase, some of the larger pores are emptied while smaller pores remain wetted by the solvent. The final product obtained is a porous glasslike solid termed as "Xerogel". [6] Thus, when the dry xerogel is formed, dopants remain physically encapsulated within in the porous glass matrix but maintain their ability to interact with species that diffuse into the matrix. [8]

2.5. High temperature treatments and densification

A xerogel is the desirable end product for most sensing applications, although a final high temperature step may be required for densification, improving the electrical conductivity, or obtaining a desirable crystallographic structure. [5] Also the high temperature treatment facilitates more amount of liquid to be displaced from the pores, making the solid network denser and pore less. [6]

2.6. Sol-gel doping

In this procedure the organic, inorganic or biological moieties are mixed with sol-gel precursors. [8] After gel formation the dopants remain entrapped in the porous gel. Since sol-gel polymerisation can be conducted under near ambient, and neutral conditions, using a process that does not involve free radical formation, sol-gel doping provides a convenient way to incorporate delicate organic compounds and even active proteins or sensitive biological entities into or onto inorganic matrices.

2.7. ORMOSIL or ORMOCER formation

Ormosil (organically modified silicates) or more generally, the so-called ormocers (organically modified ceramics) are produced from hydrolysable monomers containing desirable organofunctional groups (e.g., covalently attached via Si–C bonds). They are organic–inorganic copolymers exhibiting wide range of chemical, electrical and mechanical properties. [9,10] With the addition of ionic salts they provide favourable conditions for ionic conductivity, based on their amorphous character and thermal stability. They are used as polymer electrolytes in high energy density secondary batteries.

2.8. Impregnation

It was found that the diffusion coefficients of organic compounds in silicate films are low due to tiny fractures and defects. So polymeric dopants or surfactants are introduced for compensating the diffusion value. Another possible way is to introduce heterogeneity by incorporating polymeric or inorganic phase.

Further this sol-gel process can be differentiated into organic and inorganic process.

3. Sol-gel inorganic process

In sol-gel inorganic process, ceramic polymer precursors are formed in solution at ambient temperature, shaped by casting, film formation or fibre drawing at optimum temperature and then consolidated to furnish dense glasses of polycrystalline ceramic. The most common sol-gel processes employ alkoxides of elements such as silicon, boron, titanium and aluminium. In alcohol–water solution the alkoxide groups are removed stepwise by hydrolysis under acidic or basic catalysis and replaced by hydroxyl groups, which then form–M–O–M–linkages. Gelation occurs as the growing polymers link together to form a network that spans the entire solution volume. At this gel point, both the viscosity and the elastic modules increase rapidly. The gel can then be dried by evaporation to form a xerogel or by super critical fluid extraction to give an aero-gel.

4. Sol-gel organic process

Heat sensitive organic molecules and active proteins can be incorporated in porous ceramic molecules. Most sol-gel techniques use water and low molecular weight alkoxysilanes such as tetramethoxy silane (TMOS), tetraethoxy silane or an equivalent organometallic alkoxide (such as tetraisopropoxy titanium or trisopropoxy aluminium) as sol-gel precursor. The poly-condensation of alkoxy silane, involves three reactions Viz., hydrolysis, of the ester, silanol–silanol condensation and silanol–ester condensation.

5. Carbon ceramic electrodes

While discussing the aspects of sol-gel technique it is customary to mention about another important class in sol-gel is the carbon ceramic electrodes (CCE). They are prepared by mixing graphite powders with sol-gel precursors, which results in a porous brittle composite matrix after gelation and drying. They find a wide variety of electrochemical applications. Incorporation of hydrophobic dopants facilitates a degree of hydrophobicity and a controlled section of the electrode to be wetted by the electrolyte and the hydrophilic dopants increase the wetted section of electrodes.

6. Applications

In addition to outlining various synthesis methods for the preparation of CCEs with unique characteristics, we present a gist of various applications of CCEs in electrochemistry, electro-analysis, biosensing, electro-catalysis, gas electrodes and energy storage devices. [8] However their application is focussed in the fields of chemical sensors and biosensors. [11] The analytical applications of silica modified electrodes are comprehensively reviewed. [12]

6.1. Electro analysis

Until now most electrochemical applications of CCEs were devoted to amperometric electroanalysis. For this purpose redox mediator, concentrating ligands, catalysts and biocatalysts can appropriately modify the properties of CCE's. The promising applications of CCEs in

1. electrochemical flow detection
2. stripping analysis of metals
3. pH electrodes
4. potentiometry

have been demonstrated by several authors and the topic has been reviewed by Rabinovich and Lev. [8]

6.2. Electrocatalysis

With the addition of trace metals or organometallic catalysts the electrocatalytic activity of graphite is improved and thereby its selectivity and sensitivity is also increased. The electrodes thus obtained are

1. inert metal and inorganic doped electrodes
2. organic and organometallic catalysts and mediator doped electrodes
3. polyoxometallates doped electrodes
4. inorganic binder electrodes by catalysis.

6.3. Gas electrodes

They can also function as gas electrodes. [9] They have a porous structure, permeable for gaseous compounds so that the gas feed can be introduced through the back side of the electrode, diffuse through it and react at the solid–liquid interface. They found use in fuel cells, batteries, electromachining and gas sensing. The different types of electrodes are oxygen, ammonia and nitrite/nitrogen dioxide sensors. [8]

6.4. Biosensing

The encapsulation of sensitive biochemical moieties in sol-gel materials is an area of interest due to the biocompatibility of silicates. With appropriate selection of sol-gel precursors and co-dopants the enzymes can be stabilized and prevented from denaturation. Various biochemicals like lactate oxidase, aminoacide oxidase, hydrogen peroxidase, glucose oxidase, tyrosinase, and xanthine oxidase are encapsulated. In a comprehensive review on analytical application of silica modified electrodes, with 30 references [12], the implication of the presence of silica or chemically modified silica is highlighted with special emphasis on enzyme immobilisation for biosensing application, accumulation of electro-active analytes prior to voltammetric determination and also some information on the screen printed electrodes involving sol-gel chemistry for the production of disposable amperometric biosensors. The application of CCEs are numerous and so we just elucidate a few important applications of them in the field of biosensing. Some of the important biosensing applications are:

6.4.1. Glucose and cholesterol

With the advent of sol-gel technology and the subsequent finding that biomolecules withstand the harsh preparation conditions such as use of acid catalyst and alcoholic solvents, tremendous activity has been generated in the area of sol-gel based biosensors [14–16].The attractive feature of these sol-gel derived carbon composite enzyme electrodes has been its rigidity combined with its easy surface renewal. Moreover tunable porosity of sol-gel carbon composite electrodes can be used for imparting diffusional constraints and hence for extending the linear dynamic range of these amperometric biosensors [17]. The half-life of glucose oxidase at 63 °C increased upon immobilization 200 fold. [14,15] Obviously the graphite particle incorporated glucose shows an amperometric signal due to good conductivity and a better porosity of the sol-gel network. [16] With the immobilization of cholesterol oxidase (ChO_x) in a layer of silica sol-gel matrix on the top of a Prussian blue modified glassy carbon electrode the biosensor for glucose was prepared with high stability and low cost. [13]

6.4.2. Horse Radish Peroxidase (HRP)

The immobilization of Horse Radish Peroxidase (HRP) and ferrocene in a thin sol-gel inert matrix has led to the development of mediated hydrogen peroxide sensitive amperometric biosensor with low operating potential, enhanced selectivity, fast response and low cost. [18] However leaching of the soluble ferricinium-ion leads to low stability, which is overcome by using hydrophobic ferrocene derivatives as mediator. Later a novel GEC-Os HRP sol-gel biosensor was developed for determining a range of phenolic compounds with the detection limits even within the micro-molar region and the response times were within 11–29 s for all compounds. [19] The SiO_2/Nb_6O_5 mixed oxide proved to be an efficient support for HRP immobilization for biosensor construction to detect several phenol compounds in a flow system. [20]

6.4.3. Nitrite sensor

A new type of silicomolybdate-methlysilicate-graphite composite material was prepared and used for the fabrication of an amperometric nitrite sensor. The sensor thus obtained has a high sensitivity, long-term stability and surface reproducibility. [21]

6.4.4. Insulin

Insulin sensing is of great importance in clinical diagnosis because it serves as a predictor of diabetes of insulinoma and trauma. Various difficulties such as low sensitivity, less stability, high detection limit, difficult and expensive methods of preparation combined with high leachability of the immobilized reagents, non-renewable and polishable nature, are encountered in conventional electrodes. But the versatility of sol-gel based organically modified electrodes is a natural choice in the fabrication of amperometric electrodes. [22]

6.4.5. Energy storage applications

The CCEs obtained through sol-gel process also find applications in energy storage devices since they can perform well under high current density and high capacity in controlled environment. Because of the ability to incorporate sulfonic groups in the silicate network sol-gel silicates and ormosils are among the most efficient solid-state electric conductors. In secondary lithium ion batteries graphite powder-MTMOS based CCEs serve as lithium intercalation anode and super capacitors. The fabrication of Yttria stabilized zirconia (YSZ) film and yttria doped ceria (YDC) substrate composite electrolyte by a sol-gel coating method and its compatibility in solid oxide fuel cell that can be operated under 800 °C was evaluated. [23]

7. Metal Ceramic Composite Electrodes (Metal-CCEs)

A new metal ceramic electrode comprising gold powder homogeneously dispersed in a modified silica matrix, which couples the favourable electron transfer kinetics of gold surfaces with the regeneration, bulk modification and versatile features of sol-gel derived gold biosensors has been described for the first time. [24]

8. Photoconducting materials

The incorporation of the optically active organic molecules within the matrix results in a novel sol-gel material with photoconductive properties. [25] In another study [27] silica gel films prepared by the sol-gel route was used to modify platinum and transparent indium oxide electrodes. Ruthenium complex incorporated into a gel layer and the ruthenium cation retains electrochemical and photochemical activity. Thus it is a very promising route for the preparation of photoconductive materials.

9. Advantages

The advantages of this technique are innumerous and we have mentioned a gist of them in a brief manner. Its ability to form organic–inorganic hybrids and other composites materials combined with the versatility of tailoring thin film configurations under near ambient conditions make it especially attractive for diverse fields of electrochemistry. [9] This versatility is well revealed with the help of CCEs. The modified electrodes posses the following desirable properties.

1. large potential window
2. low and almost constant background current over a large potential window
3. fast kinetics for a large number of electrochemical mediators
4. stable and reproducible response even after prolonged immersion in the electrolyte
5. high signal background current

It also provides a convenient way to incorporate heat sensitive materials including organic molecules and active proteins, in porous ceramic materials. [5] The silica based matrices while rendering support to the matrix also enhances the physical rigidity and high abrasion resistance; negligible swelling; chemical inertness; high biodegradational, photochemical and thermal stability and excellent optical transparency and low intrinsic fluorescence. It also provides flexibility in shaping sensor configurations and immobilizing organic reagents in porous supports and manipulating the physiochemical characteristics of their ceramic products. They can be doped with complexing reagents or enzymes as platforms for chemical and biochemical sensors. [6] Biomolecules, which could denature outside the limited pH, are encapsulated thereby protecting them from hostile environment and their stability and reactivity is preserved. Modified electrodes can be produced by sol-gel route in four different ways as reported below:

i) Incorporation of modifying particles into electrode body.
ii) Direct attachment of modifying particles.
iii) Applications of films from modifying particles.
iv) Incorporation of modifying particles into the supporting matrix. [26,27] Their versatility makes them attractive for the preparation of electrochemical devices in particular a graphite electrode, which is renewable/polishable or disposable sensor. [12] As reported earlier it is the simplest process to prepare glassy materials at room temperature. [7]

Sol-gel technology has also unique advantages for the fabrication of ceramic films or fibres. It does not require costly equipment, allows a lower processing temperature and can control microstructure and chemical composition easily.

This method is an excellent process for producing highly proton-conductive solid materials because the gel materials prepared by this method contains a large number of micro pores filled with liquid, which can be utilized for fast portion transfer. [24] Also with suitable modification they can be employed in photochemistry, analytical chemistry and in biotechnology. [28] Even miniature electrodes can be easily prepared using this route. [8]

9.1. Limitations

The notable drawbacks are fragility and hydrolysis at high pH, which are due to the intrinsic properties of the silica matrices; high gelation temperatures which preclude their use in laboratory and analytical applications. [5] the non-transparency of CCE prevents their use in dual optical electrochemical sensing modes and in electrochemical luminescence (ECL). Another constraint is that, it cannot be covered with a selective film and mechanically polished for potentiometric applications.

9.2. Controlling factors

A large number of process variables can be used to control average pore size and the distribution of pore sizes, specific surface area, mass fractal dimension, concentration of silanol groups, and other structural characteristics of xerogels. [5] The pH and the H_2O: Si molar ratio is the most significant process parameters. Higher pH accelerates the hydrolysis and condensation while very low pH (<2) makes the dissolution of the silica particles negligible.

As carbon powder is used as for dispersion in the electrodes, which are held by the binder, different carbon powders have different volume conductivity. [8]

In the case of enzyme trapped sol-gel biosensor, the non-conducting nature of the sol-gel matrix and long diffusion path length of the substrate, the response times are relatively longer. [17] In the case of hydrogen peroxide biosensor, horseradish peroxidase (HRP) is sandwiched between two thin tetramethoxy silane sol-gel films. The sol-gel based solid electrolytes posses' good conductivity only at moderately high temperature. [29]

10. Measurements of pH with surface modified electrodes

As an example to illustrate the usefulness of sol-gel modification in electroanalysis, the design and working of a sol-gel based potentiometric pH sensor is reported in this communication. From literature it is inferred that among various reference electrodes used, the redox quinhydrone electrode is reported to be more a technique rather than an electrode. When hydroquinone and p-benzoquinone (1:1 molar mixture) are added to a sample

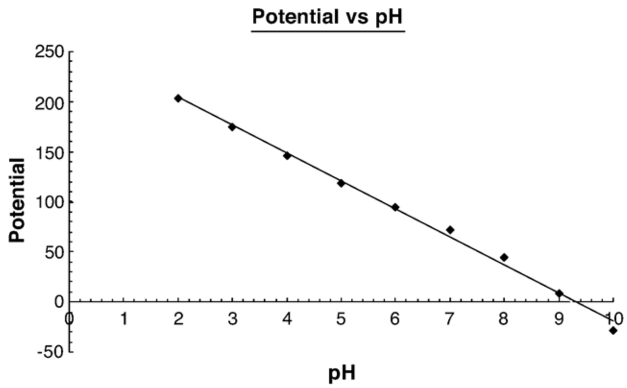

Fig. 1. The slope is found top be 28.6 mV for a decade change in concentration.

solution a pH dependent oxidation–reduction couple is formed between quinone and quinol and this redox potential is measured with a platinum electrode. Quinhydrone forms a reversible oxidation–reduction couple when dissolved in water. Hydrogen ions participate in the reaction between quinone and hydroquinone creating pH dependant equilibrium. The redox potential of the resulting equilibrium is proportional to the pH of the solution. A new class of sol-gel derived carbon–silica composite electrodes useful in potentiometric, amperometric, and biosensing applications is proposed. [30] The importance of this method is well explained [31].

The present investigation attempts to incorporate the advantages of sol-gel method in the design of sturdy, carbon based quinhydrone electrode as an alternative to the conventional glass electrode now employed for the measurement of hydrogen ion concentration in solution.

10.1. Method of preparation of pH sensor

Graphite was powdered to a size of 250 μm. 2 g of this powder and 0.67 g of quinhydrone in the ratio 3:1 was grounded in a mortar. The resulting powdered mixture should be fairly well mixed and fine. Then 1.0 ml of sol-gel precursor tetraethoxysiliane was added and mixed well with 1.5 ml of methanol as solvent. Also 0.05 ml of 0.1 M sulphuric acid was added to enhance conductivity of the matrix. The paste is mixed thoroughly till a desired viscosity is obtained and filled in an empty glass electrode by capillary action without any air voids.

The prepared electrode is dried overnight and its response with various pH buffers was observed. It was found that they have a Nerstian behaviour with a slope of $59/n$ where n is the number of electrons and in our case it is 2 for quinhydrone. The results are shown in the graphical presentation (Fig. 1).

10.2. Discussion

This paper discusses the steps involved in the processes of producing gels followed by the various doping process carried out for their stability and for attaining the desired property of a sensor. The sol-gel process as stated can be classified into organic and inorganic process. Then an important class in sol-gel chemistry i.e. Carbon Ceramic electrode is also briefly discussed followed by a discussion of various applications of sol-gel processes. Their applications are mainly focused on the sensors. However their applications in other fields are also worthy of mentioning. The most important application of sol-gel is their use as super capacitors and as separators in solid-state batteries. Also a new class of modified sol-gel carbon composite electrodes based on the encapsulation of complexing ligands is also described. Such modified electrodes couple the versatility and tunability of sol-gel processes with the advantages of the preconcentration/ voltammetric strategy. Material synthesis experiments using sol-gel chemistry, suitable for chemical sensing is developed for the undergraduate curriculum. [6] Sol-gel technology is proving to be an efficient tool for obtaining organic–inorganic hybrid materials useful in diverse analytical applications. The structural rigidity of the sol-gel polymer modified electrodes compared to pure polymer network films enhances the application prospects and also the molecular level combination of organic and inorganic components into the polymer matrix. [8] A new type of organically modified sol-gel/chitosan composite material has been synthesized and used as a matrix for enzyme immobilization. [32] This material is reported to be biocompatible and stabilize the microenvironment around the enzyme.

Evolution of sol-gel technology, a melt less metal for the formation of silicon metal oxides, and the subsequent invention of sol-gel doping technique provided analytical chemists with the possibility to tailor supporting inorganic matrices with the versatility that was traditionally attributed to organic polymer. [30] Sol-gel derived ceramics have wide analytical application in biosensing, chromatography, photometric sensing and other application.

11. Conclusion

The gels and xerogels of silica prepared by the sol-gel processes are interesting materials for electrode modification because of their electro-inactiveness in aqueous medium. They are also used for the entrapment and encapsulation of various biological specimens and enzymes. The sensors exhibit good chemical and mechanical stability and excellent reproducibility. They posses a distinct advantage of polishing in the event of surface fouling. The experimental work, concentrating on the fabrication of pH sensors, which has some unique advantages over conventional sensors like glass electrodes are industrially important. With more involvement and research in this field could develop much more sophisticated and advanced sensors.

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