Chapter Two

2.1 The sol-gel technology

Treated as a scientific curiosity in 1845 when Ebellmen reported the synthesis of hydrous silica from silicon ester for the first time the field of sol-gel is receiving much attention nowadays. Over the last thirty-five years, this area of science has been extensively studied and its practice is now relatively well known. The principle advantages of sol-gel processing include the ability to achieve oxygen and ionic stoichiometry during the formation reaction, to synthesize complex composition single-phase materials to form higher purity products using high purity reagents and to provide coatings over complex geometries including the insides of tubes. However, these advantages are to put in balance with the raw materials high cost, the long processing time involved the non uniformity of the films and the formation of cracks up on drying.

As its name indicates, the principle of the sol-gel techniques consists of converting the sol, which is a suspension of colloidal or polymeric particles in a solvent, into a semi solid phase known as gel. Commonly, the most preferred starting reagents are metal alkoxides, with general formula:
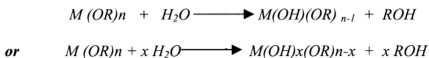
M (OR) $_n$
Where M= metal
R= alkyl group such as methyl (CH30, ethyl C2H5), propyl (C3H7)
or butyl (C4H9)
n= the valence of the metal atom.

The transition form of sol to gel involves two key steps, hydrolysis and condensation. Hydrolysis occurs by introducing water in the sol. In this process, the alkoxides groups (OR) are replaced stepwise with hydroxyl groups (OH), as summarized in the following equations.

$$M\,(OR)n \;+\; H_2O \longrightarrow M(OH)(OR)_{n-1} \;+\; ROH$$

$$or \qquad M\,(OR)n + x\,H_2O \longrightarrow M(OH)x(OR)n\text{-}x \;+\; x\,ROH$$

2.2 Sol-gel process

The sol-gel process is based on the hydrolysis and condensation of molecular precursors. These molecular precursors are usually metal alkoxides. However, hydrolyzed metal ions in aqueous solutions exhibit also sol-gel transition. This technique is very convenient for the synthesis of oxides or multicomponent oxides such as ceramics or glasses. The crystalline structure and the atomic homogeneity can be tailored by controlling the process parameters. Usually, complete crystallized structures are obtained at lower temperatures than those of conventional ceramic processes. The preparation of thin films from sol-gel solutions is today one of the main applications of the sol-gel technique for the deposition of oxides with a wide variety of properties. The most technologically important aspects of sol-gel processing that prior to gelation, the sample solution is ideal for preparing thin films by common processes such as, dipping, spinning and spraying process. In the sol-gel process, the precursors, (starting compounds) for preparation of colloid consist of a metal alkoxides or metal halides such as tetraprophyl orthosilane, tetra ethyl orthosilicate and silicon tetra chloride.

Those are appendages not including another metal or metalloid atom. For example common precursors for aluminum oxide and silicon dioxide are compounds such as $Al(NO_3)_3$ and $C_4H_{16}O_4Si_4$ (tetraethoxy silane). The latter alkoxide is an example of an alkoxide, the class of precursors most widely used in sol gel research.
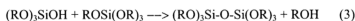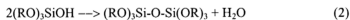
In sol-gel processing metal alkoxides are popular precursors because they react readily with water. The reaction is hydrolysis, because hydroxyl ions becomes attached to the metal atom, as in the following reaction:

$$HO\text{-}Si\,(OR)_3 + H2O \longrightarrow Si(OH)_4 + ROH$$

In above equation the 'R' represents a proton or other ligands (if 'R' is an alkyl, then OR is an alkoxy group and ROH is alcohol)

2.3 Sol-gel research

An area of research in Dr Misni's colloid laboratory is the use of sol-gel technology to fabricate materials for optical applications. In the sol-gel process, a sol is first formed by mechanically well mixed a liquid alkoxide precursor, such as tetramethoxy silane (TMOS) or tetraethoxysilane (TEOS), water, a co-solvent, and an acid catalyst at room temperature. During this step, alkoxide groups are removed by acid catalyzed hydrolysis reactions (eq. 1). Networks of O-Si-O linkages are formed in subsequent condensation reactions involving hydroxyl groups (eqs. 2 and 3).

$(RO)_3SiOR + H_2O \longrightarrow (RO)_3SiOH + ROH$ \hspace{1cm} (1)

$2(RO)_3SiOH \longrightarrow (RO)_3Si\text{-}O\text{-}Si(OR)_3 + H_2O$ \hspace{1cm} (2)

$(RO)_3SiOH + ROSi(OR)_3 \longrightarrow (RO)_3Si\text{-}O\text{-}Si(OR)_3 + ROH$ \hspace{1cm} (3)

Depending upon the water-alkoxide molar ratio R, temperature, and solvent, further condensation leads to different polymeric structures such as linear, entangled chains, clusters, and colloidal particles. The resulting sol is cast into a mold, whereupon gelation causes a solid in the shape of the mold to be formed. The gel is aged (syneresis) in the pore liquid for a period of time to allow the gel network to strengthen. The gel is then dried under atmospheric conditions to remove the liquid. Sol-gels prepared in this way are called xerogel glasses. These glasses have large surface-to-volume ratios, high pore connectivity, and narrow pore size distributions. The glasses can be doped with a variety of organic/inorganic materials during the mixing stage of the sol-gel process. The glasses can be in the form of monoliths or thin films. These doped glasses can be studied by a variety of optical techniques, including UV-vis absorption, fluorescence, and Raman spectroscopy. Sol-gel processes refer to the hydrolyses of, e.g., $Si(OR)_4$ to form SiO_2, and have been recently explored to make mixed metal oxides and to dope functional groups or molecules in oxide solid matrices. The oxide materials produced by such hydrolysis processes are called sol-gel materials.

2.4 Hydrolysis reaction mechanism

The hydrolysis reaction of TEOS, the common abbreviation for the chemical $Si(OC_2H_5)_4$, variously known as tetraethoxysilane and tetraethyl orthosilicate- may be summarized as:
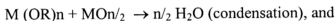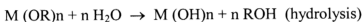
$$Si(OC_2H_5)_4 + 4 H_2O \rightarrow Si(OH)_4 + 4 C_2H_5OH$$
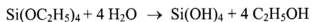
The $Si(OH)_4$ then condenses into SiO_2 by the following reaction:

$$Si(OH)_4 \xrightarrow{heat} SiO_2 + 2H_2O$$

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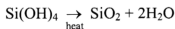
Therefore, the overall reaction for sol-gel silica glass formation using TEOS is:

$$Si(OC_2H_5)_4 + 4\,H_2O \rightarrow Si(OH)_4 + 4\,C_2H_5OH.$$

More generally the reactions for sol-gel glass formation using an alkoxide of a metal M

with valence "n" are:

$$M\,(OR)n + n\,H_2O \rightarrow M\,(OH)n + n\,ROH \text{ (hydrolysis)}$$

$$M\,(OR)n + MOn/_2 \rightarrow n/_2\,H_2O \text{ (condensation), and}$$

$$M\,(OR)n + n/_2\,H_2O \rightarrow MOn/_2 + n\,ROH \text{ (overall)}$$

The result is an interconnected, porous network of $MOn/_2$ that must be dried and sintered

to form a glass.

The hydrolysis rate was found to depend upon many factors. Indeed, the reaction

can favorably be promoted by an increase in the charge density on the metal; the number

metal ions bridged by a hydroxo- or oxo-ligand, and the size of the alkyl groups.

Conversely, inhibition occurs as the number of hydroxo-ligand coordinating M increases

or when the temperature or water and solvent concentration tend to favor the reveres

reaction (esterification).

The hydrolysation of the metal alkoxide particles is usually catalyzed by addition

of an acid or base. In acidic solution, the hydrolysis reaction proceeds by electrophilic

attack as illustrated in the following reaction mechanism 1. For tetraorethoxysilane

precursors, this mechanism features the attraction of a protonated water molecule (H_3O^+)

to the negatively charged oxygen in the more basic alkoxide groups resulting in the

substitution of an alkoxide group (OR) by an hydroxide group (OH). Conversely, in basic

solution the hydrolysis mechanism occurs by nucleophilic substitution. In this case, the

positively charged metal (M^+) is preferentially attacked by a negatively charged

hydroxide (OH⁻) leading to the deprotonation of an hydroxo ligand as shown in the following reaction mechanism 2.
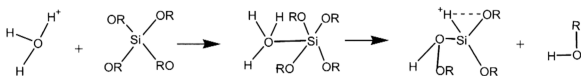
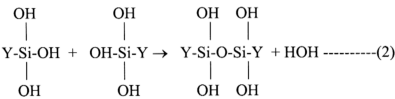**Mechanism 1: Acid catalyzed hydrolysis by electrophilic reaction mechanism**
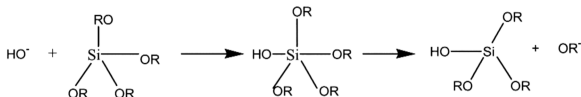
Mechanism 2: Base-catalyzed hydrolysis by nucleophilic reaction mechanism

2.5 Silane chemistry

In order for a sol-gel coating to be effective, it must be adhere to its substrates. A silane coupling agent may be used to promote this type of adhesion. The general formula for a silane coupling agent is X_3SiY, where X is a hydrolysable group and Y is an organic functional group that bonds with either the substrate or another silane molecule following its condensation reaction. The initial hydrolysis reactions occur when water attacks the X hydrolysable groups as follows:

$$X_3SiY + 3H_2O \rightarrow (OH)_3SiY + 3XOH \text{ -------------------- (1)}$$
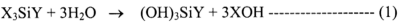
The subsequent condensation reaction produces chains of silanol molecules and bonding with substrate. The following reaction shows an example of a single condensation reaction linking two siloxanol molecules.

$$
\begin{array}{cccccc}
\text{OH} & & \text{OH} & & \text{OH} & \text{OH} \\
| & & | & & | & | \\
\text{Y-Si-OH} & + & \text{OH-Si-Y} & \rightarrow & \text{Y-Si-O-Si-Y} & + \text{HOH} \text{ ----------(2)} \\
| & & | & & | & | \\
\text{OH} & & \text{OH} & & \text{OH} & \text{OH}
\end{array}
$$

2.6 Sol-gel applications

Since the early 1980's a better understanding and mastery of the sol-gel process has opened broad avenues for technological applications. There exist a multitude of areas, as diverse as biological support or large mirrors for laser weapons in space, where the sol-gel technique is employed. The many area of interest are best summarized as below.

The applications for sol-gel derived products are numerous. Powders and thin films can be used for electronic, optical, and electro-optic components and devices, such as substrates, capacitors, memory devices, IR detectors, and wave-guides. Both optical and refractory fibers are used for fiber optic sensors and thermal insulation, respectively. Antireflection coatings are also used for automotive and architectural applications. Glass monoliths and inorganic/organic hybrids are under development for lenses, mirror substrates, graded index optics, optical filters, sensors, passive and nonlinear active wave-guides, and lasers. Membranes for separation and filtration processes also are being investigated.

In this section, emphasis will be placed on three promising commercial niches where the sol-gel process has been proved a competitive technique. These three areas deal with the production of ceramic powders, glass and coating.

In the ceramic industry, advances in wet chemical techniques have created considerable enthusiasm mainly because of their potential to the produce ceramic powders. The driving force behind the use of sol-gel stems, from the ability to prepare

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powders with a high purity, very fine spherical shape, and narrow distribution of particle size. A high degree of purity is achievable since extremely pure starting materials are commercially available. However, their high energy cost production may be limiting factor if saving energy (one of the chief advantage of the sol gel process) is considered. The fine spherical shapes (e.g. 1 μm), which yield a higher chemical activity and the correct particle size hardly attainable by milling are of prime important for the densification of ceramics and are routinely obtainable through the use of colloidal or acid catalyzed sols. It is well known to the ceramist that these important characteristics are key features for sintering to higher density and at temperature much lower than those required in conventional to radius of the particles and that for a given rate, the sintering temperature decreases with the particle size.

Another area where the sol-gel technique has sparked widespread interest is the glass industry as evidenced by the large number of publications on TEOS or its related products. The glass industry can benefit from sol-gel technology for two main reasons. First, it is possible to manufacture high-priced existing products, such as titanium silicate glasses or graded index optical fibers, more cheaply and with larger quality. It is noted that only expensive glass products are targeted since the high cost of raw materials (silicon or metal alkoxides are employed rather than silicon or metal oxides) makes large quantity production commercially non viable. Therefore, the sol-gel process is by no means a substitute for heavy industrial procedures such as the production of flat glass and fiberglasses. However, when high priced articles are concerned, sol-gel can be and alternative over conventional methods owing to some of its unique properties, that include high purity raw materials and low sintering

temperatures. In this case considerable energy, saving can be achieved because the porous structure of the gel dose not requires the attainment of liquid temperatures to form the glass. The reason that makes the sol-gel science appealing to the glass industries lie in its potential innovativeness. Indeed, a wide range of new products with desirable properties cannot be obtained through the traditional melt route. For example, in contrast with classic processes, controlled hydrolysis polymerization reactions can allow significant structural variation in the glass network without compositional alteration. Wide perspectives for the synthesis of glass with novel composition are opened since melt-related problems such as liquid immiscibility, phase separation, or crystallization upon cooling, are now suppressed.

Finally the third area of application, which is also the oldest commercial exploitation of the sol-gel technique, deal with the preparation of coatings. Industrial applications include the development of thin films with specific mechanical, optical or electrical properties, as well as chemical or physical protective properties. There exist at least three coating methods, which are: spin coating, dip coating, and spray coating. In the following paragraph, only the first technique is presented for it the most relevant of current study. The advantages of using the sol-gel and spin coating techniques for deposition of thin film are well known and include the ability to coat complex shapes and large surfaces compared to vacuum coating technique.

The disadvantages of the method lie in the high cost of the starting reagents, the long processing time involved, and the shrinkage and non-uniformity of the coatings. The preparation of the sol usually requires a partial hydrolysis and the use

of acid catalysts to synthesize a low viscosity medium with linear polymeric chains. To form good uniform coatings, the spreading of solution on substrates should be kept smooth and stabilization. However, the surface tension must also be considered. For multi-component systems, it was reported that the rate of hydrolysis varied from a component to another. Therefore, to obtain films with uniform chemical composition, great care is required to allow bonds between the different alkoxides to form. Unfortunately, the hydrolysis of multi-component system is complex and very little is known for this subject.