Preparation of Synthetic Membranes
Outline

Introduction
- Types of inorganic membranes
- Advantages/disadvantages over polymeric membranes

General scheme for the preparation of inorganic membranes
- Sol–gel process
- Membrane modification
- Zeolite membranes
- Glass membranes
- Metal membranes
- Carbon membranes
Types of inorganic membranes

- Ceramic membranes
- Zeolite membranes
- Carbon membranes
- Glass membranes
- Metallic membranes
Inorganic membranes- materials

Ceramic membranes:
- Mainly various oxides of alumina, titania or zirconia
- By sol-gel process

Metal membranes:
- Palladium, silver and their alloys

Carbon membranes

Glass membranes
- Silicon oxide or silica, SiO$_2$, by leaching on demixed glasses

Zeolite membranes
- Ordered porous, narrow pore size

Composite membranes
Inorganic membranes: morphology

Symmetric & Asymmetric
- Dense membranes
- Porous membranes
- Ordered porous membranes
  - Zeolites
  - mesoporous silica
  - MOF structures
Inorganic composite membrane

**Critical Separation (selective) Layer(s)**
- Pore Size: 0.4-5nm
- Thickness: single or multiple thin layers
- Materials: Oxides
- Uses: RO, nanofiltration & molecular sieving

**Primary Layer**
- Pore Size: 0.005-0.5 µm
- Thickness: 1-20 µm
- Materials: oxides, carbides, nitrides, metals, metal alloys, and carbon
- Uses: Ultrafiltration & microfiltration

**Porous Support/Substrate**
- Pore Size: 0.5-50 µm
- Thickness: >400 µm
- Materials: Metals, metal alloys, oxides, carbides, nitrides, intermetallics
- Uses: Depth filter & surface-cake filter
Advantages of inorganic membranes

High thermal stability
  ◦ Compatible with high-temperature operations, membrane reactors.

High chemical stability
  ◦ good corrosion resistance, allowing very aggressive cleaning,

Biocompatibility
  ◦ Pharmaceutical and food industry.

Not compact under high pressures

High mechanical strength

Long lifetime
Disadvantages of inorganic membranes

- High capital costs
- Britleness
- Low membrane surface per module volume
- Complex preparation methods
- Difficult membrane-to-module sealing at high temperatures
- Difficult to scale up
- Poor reproducibility
Synthesis of inorganic membranes,

Ref: 1.11 Basic Aspects in Inorganic Membrane Preparation in Comprehensive membrane science and engineering, Enrico Drioli and Lidietta Giorno, Volume 1, 2010, Elsevier
General Scheme for Inorganic Membrane Synthesis
The sol-gel process

**Sol–gel** is a general process which converts a colloidal or polymeric solution (*sol*) to a gelatinous substance (*gel*).

**Sol** is a colloidal suspension (microscopically dispersed evenly) of very small solid particles in a continuous liquid medium. Examples include blood, pigmented ink, and paint.

**Gel** can be defined as a 3-D network structure, and the compactness of the structure depends on the pH, concentration and natural of ions to stabilize the colloid suspension.

Sol-gel involves the hydrolysis and condensation of alkoxide or salt precursors in an organic solvent with an appropriate amount of water.

Preparation of ceramic membranes of different shapes with a mesoporous structure (~100nm)
- Thick films/ Thin films/ Fibers
Sol-gel process & shaping

Sol-Gel Technologies and Their Products

Ferdowsi University of Mashhad
Two sol-gel routes

- Colloid suspension route
- Polymeric gel route

Process:
- Hydrolysis + condensation (polymerization) of a precursor
- Required membrane structure can be controlled by process conditions
- Drying is critical in the formation of membranes
Two main sol–gel routes

- **Colloidal route**
  - Metal salt or metal-organic precursors
  - Water
  - Sol (colloidal particles)
  - Membrane coating
  - Hydrolysis
  - Condensation

- **Polymeric route**
  - Organic
  - Sol (polymeric)
  - Drying
  - Sintering
  - (Pure inorganic membrane)
Colloid suspension route:

Sol solution: precise control of the hydrolysis & condensation conditions (precursor concentration, and acid or basic catalysis, etc.)
- Membrane pore size depends on the conditions of the hydrolyzing / condensation process and of the calcination temperature.
- Rapid hydrolyzing & condensation with excess of water
- The rapid condensation causes the formation of medium-sized nanoparticles of the order of 20–100nm
- Addition of organic binder materials to relax the stress during drying (e.g. PVA)
- Sol coated to obtain certain shape of membranes

Coated on support with top layer pores in the order of the sol particles.

Gelling of the sol, formed membrane dried and calcined at an appropriate temperatures
Polymeric sol–gel route: 
Producing fine pores of microporous membrane layers

Same precursors, but only partially hydrolyzed using less than the stoichiometric amount of water

Hydrolysis is kept slower

Polymeric sol is transparent containing small nanometersized inorganic polymeric structures < 5nm

Coating the support and interlayer with binder
  - binders create very large voids in the coated layer after thermal treatment.
  - A polymeric network forms (gel)
Membrane modification

Top layer densification for GS and RO

Catalytic functionalization

Hydrophobization
  - bonding specific organic compounds with varying hydrophobic tails

Fig. III-59 Surface modification of ceramic membranes

(a) Internal deposition of pores by mono-multi-layer;
(b) pore-plugging of nanoparticles;
(c) coating layer on top of the membrane
(d) constrictions at sites in the toplayer
Template-mediated process

For sharp pore size & pore size distribution

- Insert passive organic template agents (uniform size)
- Eliminate (e.g. burning out) the templates for a directly related porous structure

Figure: Schematic representation of the formation of a membrane layer using passive organic templates in a polymeric gel (left) and in a colloidal gel (right).
Ordered porosity

By structure-directing agents

- Self-assembly of surfactants

Figure: Formation of a membrane layer using a hexagonal liquid-crystal phase as template.
(a) The situation in the wet gel. (b) The pore formation in the heat-treated gel.
Surfactant Self-assembly

Figure 1: Surfactant shapes and various self-assemblies in colloidal solution.

a, Cone-shaped surfactant resulting in
b, normal micelles.

c, Champagne cork shaped surfactant resulting in
d, reverse micelles

e, Interconnected cylinders.
f, Planar lamellar phase.
g, Onion-like lamellar phase.
Zeolite Membranes

Zeolites: microporous crystalline alumina-silicate with a uniform pore size

Built up by a 3-D network of SiO$_4$ and AlO$_4$ with very defined pore structure (several Å)

Main problems as membrane materials

- low gas fluxes:
  - thick zeolite layers for pinhole-free and crack-free zeolite layer.
  - Overcome: use thin layer supported on others.

- negative thermal expansion:
  - zeolite shrinks at high temperature where the support continuously expands!!!
  - Problems in the attachment of the zeolite layer to the support and the connection of the individual micro-crystals within the zeolite layer.
Some properties of zeolites

Zeolite A
- 3D pores
- High amount of Al - very hydrophilic
- Pore size depends on types of cations

Silicate-1
- 2D pores
- Non Al – very hydrophobic
- Non charge, pure silica zeolite,

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<th>pore size (Å)</th>
<th>Si/Al</th>
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<td>5.1 - 5.6</td>
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<td>Faujasite</td>
<td>7.4</td>
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Glass membranes

- Containing SiO$_2$, B$_2$O$_3$ and Na$_2$O
- Miscibility gaps observed from 1300-1500°C cooled down to 500-800°C

- Phase separation in Vycor regions
- Demixing:
  - SiO$_2$ rich phase remains,
  - B$_2$O$_3$ rich phase leached out (pores)
- Pore sized controlled by temperature
- Advantages
  - Narrow pore size distribution
  - Easy modified surface

Fig. III-61 Ternary phase diagram of the system SiO$_2$, B$_2$O$_3$ and Na$_2$O
Glass membranes with surface modification

- Reduced pore size: 0.2 - 2.4 nm
- Knudsen diffusion → surface diffusion or solubility diffusion mechanism
- Increased selectivity of n-C_4H_{10}/N_2 and n-C_4H_{10}/CH_4
- High permeability and selectivity for chlorine
Dense metal Membranes

Casting and rolling
- a sequence of alternate rolling and annealing steps to reach the required thickness

Vapor deposition
- physical (PVD) or sputtering & chemical vapor deposition (CVD)
- spray coating

Electroplating
- a metal or its alloy in a plating bath with the support as cathode

Electroless plating
- autocatalyzed decomposition or reduction of a few metallic salt
Pd membranes

Palladium membranes: hydrogen separation
- High solubility and permeability for hydrogen
- Infinite $H_2$ selectivity
- But expensive and brittle
  - Pd/Ag alloy used to reduce cost and increase toughness
- Low permeability
  - Composite membrane with very thin Pd layer

Composite palladium membrane:
- A thin layer of palladium on a tantalum or vanadium support film and a porous substrate, such as a ceramic or stainless steel
- Reduced material costs (tantalum and vanadium are less expensive).
- Improved mechanical strength
- Possibly higher flux (tantalum and vanadium are quite permeable to hydrogen)

A major problem: surface poisoning effects
Carbon membranes

Pyrolysis of polymer precursor in the absence of $O_2$:
- polyimide, cellulose, etc.

Figure: Process diagram (left) and picture of the carbonization rig
Carbon membranes

The pores vary in size, shape and connectivity
- depending on the morphology of precursors and the chemistry of its pyrolysis

Figure: The precursor hollow fiber membranes (a), pyrolyzed carbon membranes (b) and an idealized structure of a pore in a carbon material (c)
Inorganic-organic Hybrid membranes