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# SEPARATION MEMBRANE DEVELOPMENT

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## Abstract

A ceramic membrane has been developed to separate hydrogen from other gases. The method used is a sol-gel process. A thin layer of dense ceramic material is coated on a coarse ceramic filter substrate. The pore size distribution in the thin layer is controlled by a densification of the coating materials by heat treatment. The membrane has been tested by permeation measurement of the hydrogen and other gases. Selectivity of the membrane has been achieved to separate hydrogen from carbon monoxide. The permeation rate of hydrogen through the ceramic membrane was about 20 times larger than Pd-Ag membrane.

## Background

Billions of standard cubic feet of hydrogen are consumed every day by the refinery industry alone. Demand for hydrogen is continue growing in recent years. In the hydrogen recovery and production, separation of hydrogen from other gases is important part of process. PSA is main separation method. Metal alloys or composite metal membrane have been used for hydrogen purification. Metal is sensitive to poisonous gases. Ceramic membrane, inert to poisonous gas, is desirable.

The sol-gel encapsulated metal hydrides, developed at Savannah River Technology Center have solved the problem of decrepitation of metal hydride particle. The pore size of the sol-gel coating can be tailored to discriminate between $H_2$ (2.89A) and CO (3.76A) on the basis

of molecular size in much the same manner that silica membranes have been shown to have the ability to separate hydrogen and nitrogen.

## Overall Approach

Overall objective is to develop and demonstrate a thin dense glass coating on a coarse ceramic substrate which allow hydrogen to easily permeate through but no other gases. The process of the glass coating is formed by the sol-gel process. The pore size of the thin dense layer are controlled by a heat treatment which densify the coating.

## Filter Fabrications

### Sol-Gel Formulations

The sol-gel technique has been well published in the literature (ref . 1-9). The technique stars with the hydrolysis of an organo-metallic compound. The hydrolyzed compound is polymerized via water and alcohol condensations and dried by removing water and the solvent. An acid or base is used to catalyze the polymerization reaction. The heat treatment following the drying step is used to further modify the final product. The reactions involved are generally as follows:

Organo-metallic Compound:

$$M\text{-}(OR)4$$

Hydrolysis:

$$(OR)4\text{-}M\text{-}OR + H2O = (OR)3\text{-}M\text{-}OH + ROH$$

Water Condensation:

$$(OR)3\text{-}M\text{-}OH + (OR)3\text{-}M\text{-}OH = (OR)3\text{-}M\text{-}O\text{-}M\text{-}(OR)3 + H2O$$

Alcohol Condensation:

$$(OR)3\text{-}M\text{-}OH + (OR)3\text{-}M\text{-}OR = (OR)3\text{-}M\text{-}O\text{-}M\text{-}(OR)3 + ROH$$

where M is metal such as Si, Al, or Ti and R for an alkyl group (-CxH2x+1) in most case -C2H5 or -CH3.

The first solution is formed by mixing one part ethanol into 2 part tetraethyl orthosilicate (TEOS). The second solution is formed by mixing 2~5 part of ethanol to one part of water. Acidity of second solution is adjusted by adding HCl until the PH is in the range of 1 to 2.5. The second solution is added to the first solution while stirring continuously to for sol. The sol is then covered and allowed to age for 2~24 hours which allows the sol, initially a water-like consistency to become viscous. This viscous sol is used to make thin coating.

### Sol-gel filter Formation

The viscous sol is coated on a course substrate (silica or alumina). Next step is the drying to evaporate water and alcohol formed by a polymerization. The filter then allowed to gel completely for few days. The drying can be done either by evaporation at room temperature or in a ventilated oven at elevated temperature.

### Heat Treatment

The dried sample can be heat treated under vacuum to vary the pore size. While the sample in under the vacuum, its temperature is raised to a target value and maintained for 2 hours. The target temperature used are 200, 300. 400, and 600C. Further treatments are done by a microwave oven. Heat treatment densify the coating.

## Experimental Results

### Performance Testing

The performance of the sample has been tested by measuring the permeation rate of hydrogen through filter. The pressurized hydrogen gas is allowed to flow through the filter to a constant lower pressure. The flow rate are determined. The results are compared with the flow rate of typical Pd-Ag membrane in Figure 1. At low pressure range, sample tested was about 20 time larger permeation rate than typical Pd-Ag membrane.

## Conclusion

Hydrogen filter are produced by a sol-gel process. Preliminary test shows promising results. Improvement on defect free, large filter is in progress.

## References


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**Figure 1 Permeability for Hydrogen**

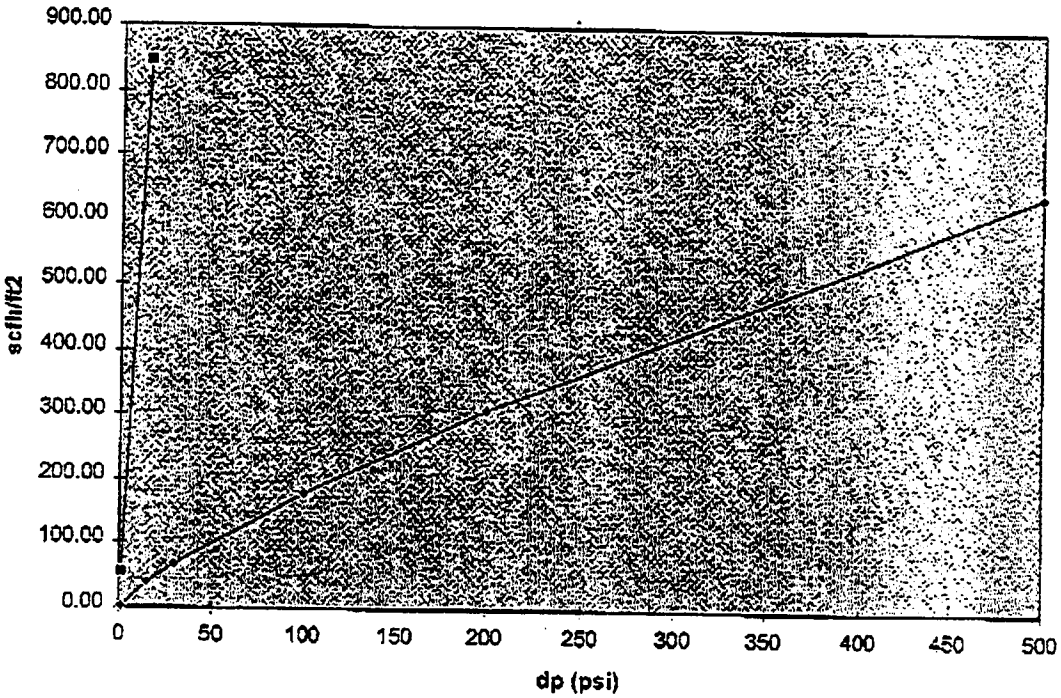

**Figure 1 Permeability for Hydrogen**