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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, 10,000 to 50,000, of the membrane has been achieved to separate hydrogen from carbon monoxide. The permeability constant of hydrogen through the ceramic membrane was about 46,000 Barrer at the room temperature, which is about the same as Pd-Ag membrane at 400c.

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 but energy intense operation. Metal alloys or composite metal membrane have been used for hydrogen purification. But 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 decrepitaiton 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 glass coating on coarse substrate is by the sol-gel process. Coarse substrate can be metal frit or ceramic filter materials. The pore size of the thin dense layer is controlled by the conditions of sol-gel coating process and the heat treatments. Heat treatment including microwave makes the coating dense.

Parallel approach has been taken.

> (1) *Composite metal hydride*, sol-gel coating on metal hydride to form a packing material for hydrogen separation from other gases by absorption of hydrogen only; (2) *Ceramic membrane filter*, sol-gel coating on coarse substrates to form a filter membrane that only hydrogen can pass through but no other gases.

Composite metal hydride has been produced. Tests show that the selectivity of hydrogen to carbon monoxide is in the rage of 10,000 to 50,000. It can be used for absorption based hydrogen separation process.

Current focus is on the development of ceramic membrane filter.

Filter Fabrications

A. Sol-Gel Formulations

The sol-gel technique has been well published in the literature (1-10). The technique starts 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 solution in alcohol, M-(OR)4 in ROH, and water-alcohol solution are mixed to make several reactions:

Hydrolysis reaction: (OR)3-M-OR + HOH = (OR)3-M-OH + ROH

Water Condensation: (OR)3-M-OH + (OR)3-M-OH = (OR)3-M-O-M-(OR)3 + H2O

Alcohol Condensation:(OR)3-M-OH + (OR)3-M-OR = (OR)3-M-O-M-(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 form 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.

B. Sol-gel filter Formation

The viscous sol is drip 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. In general, elevated temperature gives broader pore distribution.

C. Heat Treatment

Heat treatments make densification of the sol-gel coating. 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 from 200 to 600C. Further treatments are done by a microwave oven.

Experimental Results

A. Pore Distribution

Pore size distributions are measured on sol-gel coating materials by BET gas adsorption. This method can not be able to measure the pore size smaller than 15 A. True selectivity depends on the size of narrow channels between the pore to pore, not on the pore size itself. However, the distribution of pore size may indicate the quality of the coating. Typical pore size distributions are summarized in Table 1. Coating with a narrow pore size distribution has good selectivity over 10,000, but the coating with broader distribution show poor selectivity less than 5.

Table 1. Pore Size Distribution (in nm)

High Selectivity Coating		**Low Selectivity Coating**	
Peak location	**Half width**	**Peak location**	**Half width**
2.5	**1.2**	**1.3**	**4.5**
1.3	**1.2**	**2.3**	**30.**
1.7	**0.5**	**3.2**	**30.**
1.9	**1.0**	**8.0**	**60.**
2.2	**0.8**		

B. Performance Testing

The permeation rates of hydrogen through filter are measured to test the performance of the sample. The pressurized hydrogen gas is allowed to flow through the filter to a constant lower pressure. The flow rates are determined. The results are compared with the flow rate of typical Pd-Ag membrane in Figure 1. At the low pressure, samples tested have about same permeability constant with Pd-Ag membrane.

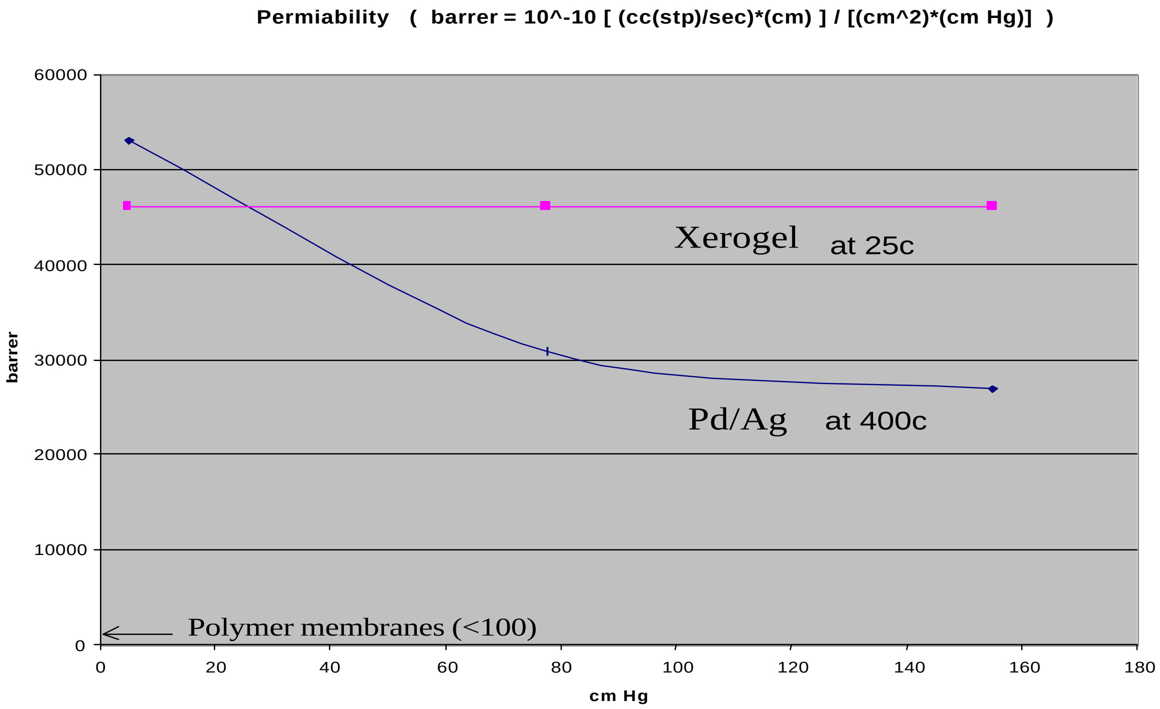

Figure 1 - Permeability

Conclusion

Ceramic membrane filter can be produced by a sol-gel process. Tests show promising results. Improvement on defect free, large filter is in progress.

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