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NHI-Acid Concentration Membranes

Membrane Recommendations for the S-I Cycle

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NHI-Acid Concentration Membranes
Membrane Recommendations for the S-I Cycle
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Scope: The purpose of this report is to make recommendations concerning the applicability of specific membrane materials for acid concentration processes to the Sulfur-Iodine (S-I) thermochemical cycle integrated laboratory scale (ILS) demonstration.

Introduction

Acid concentration membrane processes have been studied for possible inclusion in the Sulfur-Iodine integrated laboratory scale (S-I ILS) demonstration. The need for this technology is driven by the chemical processes required for economical water splitting using the S-I cycle. Of the chemical processes inherent to the S-I cycle that have been identified as targets for deployment of membrane technology, three have been studied during the past three fiscal years as a part of the DOE Nuclear Hydrogen Initiative. First, the ability to concentrate hydriodic acid (HI) and iodine mixtures was sought as a method for aiding in the isolation of HI away from water and iodine. Isolated HI would then be delivered to the HI decomposition process for liberation of product hydrogen. Second, an extension of this technology to sulfuric acid was proposed to benefit sulfuric acid decomposition recycle. Third, decomposition of HI to form hydrogen is equilibrium limited. Removal of hydrogen, utilizing Le Chatelier's principle, will increase to overall conversion and thus increasing the efficiency of the S-I cycle.

Recommendations

HI Concentration. Experiments have been conducted into determining the applicability of membrane processes for the removal of water from HI and iodine. Membrane technology can be utilized in two ways. First, separations can be based on molecular size using controlled pore size membranes. Adroit selection of membrane materials will allow the removal of "smaller" molecular species from "larger" ones. Much of this technology can be found in water desalination where either polymer or ceramic membranes formed with tightly controlled pore sizes are used in reverse osmosis. Reverse osmosis employs a pressure gradient across a membrane to counter natural osmotic forces that would normally encourage equalization of concentrations upstream and downstream of the membrane. The pressure gradient forces water out of the feed creating a more concentrated feed zone and a less concentrated permeate zone.

Second, membrane separations can be performed using solubility differences between permeant and rejectate. In this type of separation, the desired permeant selectively sorbs into the membrane substrate while the non-selected component is rejected. In this type of separation, a driving force for permeation is provided through the introduction of a concentration gradient. An example of this type of membrane process is pervaporation. In pervaporation, a feed flow is provided across the surface of the membrane. This flow can be nearly ambient pressure or some pressurization can be applied. To provide a concentration across the membrane, permeants are removed from the back side of the membrane. Most typically, removal of permeants is provided through vacuum, although this work has shown that a dry sweep gas also may be used. The goal is to maintain a less that saturated environment on the membrane back side. Active removal of permeants from the membrane provides the driving force for continued sorption of permeants into the membrane from the feed solution. Selectivity is provided through mutual permeant-polymer solubility, although large differences in component vapor pressures also can play a role.

Selection of membrane materials for this project required an appreciation of the physical and chemical conditions. HI is highly corrosive and the addition of iodine to aqueous HI solutions increases its corrosive behavior. The desired temperature range is from 120 ºC to 350 ºC. From a thermal perspective, ceramic membranes would be preferred. However, ceramic membranes operate using size exclusion and the molecular size differences between the various feed components are not significant. Moreover, ceramic materials at the relevant temperatures generally are not stable. Thus, polymeric materials appeared to be the most rational way forward.

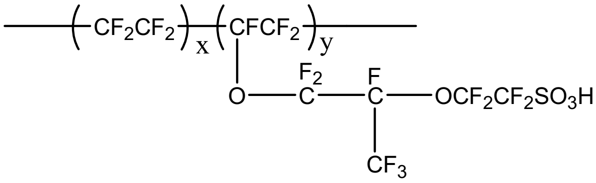

Fig.1 Chemical structure of Nafion®.

During the course of this work, two sulfonated organic polymers were investigated for water permeability and selectivity: Nafion® and sulfonated poly[ether ether ketone] (SPEEK). Nafion® is a commercial product with a porous structure consisting of hydrophilic sulfonate groups supported by a hydrophobic perfluorinated organic structure, Fig 1. Nafion® membrane sheets are available in thicknesses of 50 µm and 180 µm. This is significant because thinner membranes generally exhibit higher fluxes as compared to thicker ones, and a comparison between the two thicknesses can provide insight into the process. Nafion® materials swell approximately 25% in water, testifying to their water affinity. Significant work has been conducted on understanding the structure of Nafion® polymers with the main application of the materials being proton exchange membranes (PEMs) for fuel cells. In this role, Nafion® sorbs water and then conducts protons through hydrated channels. Nafion® polymer's ability to conduct protons is entirely dependent on the water content. One of the issues that have pushed for better PEMs is their excessive water permeability, and this capability was exploited in this work.

Another material that was investigated was SPEEK, Fig. 2. The advantage of SPEEK membranes is that they are considerably cheaper than Nafion® and their performance can be adjusted to suit a particular application. Like the Nafion® membranes, the permeability of water is dependent on the sulfonate content. Higher sulfonate group loadings result in more permeable materials.

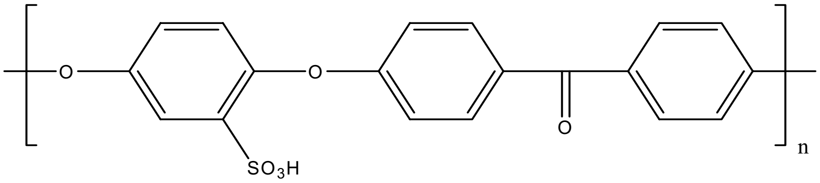

Fig. 2 Chemical structure of SPEEK.

Conversely, lower sulfonate loadings yield more hydrophobic and less permeable membranes. In this work, the SPEEK materials were formed using literature procedures for sulfonation of poly[ether ether ketone] with concentrated sulfuric acid. Sulfonation is described in terms of the ion exchange capacity (IEC). For this work, membranes were formed that had IECs ranging from 1.6 to 2.4 milliequivalents per gram of polymer (meq/g). Above 2.3 meq/g, the polymers were found to be water soluble, and thus not applicable to this separation. It also was found that the most dimensionally stable materials were in the 1.6-1.8 meq/g range, thus these were the materials that were studied. A limited collection of data was obtained on the SPEEK polymers and has been reported in the FY2006 final report for this project. A direct comparison of the two membrane formulations clearly indicates the higher performance offered by the Nafion® polymers, Table 1.

Table 1. Calculated performance data for Nafion® and SPEEK membranes at a concentration of 30 % water.

Membrane	Feed	Flux (g/m2h)	Separation Factor	Temperature (ºC)	Membrane Thickness (µm)
Nafion-112®	HI	533	1007	134	50
Nafion-117®	HI	66	1870	134	180
SPEEK 1.7	HI	72	384	131	70
Nafion-112®	HI/iodine	3615	2857	134	50
Nafion-117®	HI/iodine	1082	3571	134	180

SPEEK 1.7, which is SPEEK with an IEC of 1.7 meq/g compares to Nafion-117® favorably in terms of flux, however the separation factor, which is a measure of how well the membrane performs the separation, is nearly six fold lower in magnitude. Nafion-112® membranes are clearly superior in these tests with both fluxes and separation factor significantly higher than SPEEK 1.7. An analysis of the HI/iodine mixture data for Nafion® suggests that the addition of iodine increases membrane performance. It would be reasonable to apply this trend to the SPEEK polymers; however the performance would still be inferior to that of Nafion®

Using the currently available data, Nafion® membranes are clearly superior and do not suffer from any degradation due to the temperatures employed or the chemical aggressiveness of the feed. However, it should be noted that the amount of research performed on the SPEEK materials is limited when compared to the Nafion® membranes. There are also process questions that exist such as the optimum back side pressure and ultimate temperature at which this process can be conducted. So, it is the recommendation that Nafion® membranes will perform the desired separation under the specified process conditions. During FY 2007, investigations are on-going to address the process issues described here.

The key to better performance using Nafion® involves using thinner membranes. Comparing the Nafion-117® membrane to Nafion-112® shows that the thinner membrane gives substantially higher fluxes without any significant loss of separation factor. Thus, further improvements should be possible by using even thinner membranes. However, thinner materials are not commercially available and must be formed from Nafion® solutions.

Sulfuric Acid Concentration. Using the positive results generated from the HI concentration work, pervaporation using Nafion® membranes was applied to sulfuric acid. The need for sulfuric acid concentration was determined by the performance of the sulfuric acid decomposer, which left a significant portion of the acid intact with generated water. Recycle of the acid required concentration. Concentration is typically performed by distillation of the excess water; however distillation requires boiling of the acid. Diluted sulfuric acid is significantly more corrosive than concentrated acid especially at the vapor-liquid interface. Thus, it would be advantageous to have a process for sulfuric acid concentration without boiling.

Limited numbers of experiments have been performed to this point; however Nafion® membranes do appear to be effective membranes for removal of water from sulfuric acid. Experiments have been conducted at 100 ºC and 120 ºC with water fluxes comparable to those observed for the HI concentration. Furthermore, no significant degradation of the membrane has been observed.

Hydrogen Separation from HI and Iodine at High Temperature. Membranes for the separation of hydrogen from HI and iodine at 300 ºC are desired due to the equilibrium limited nature of the HI decomposition. A catalytic membrane reactor concept could result in increased HI decomposition efficiency by removing hydrogen as it is formed, thus shifting the equilibrium towards products and encouraging increased conversion of HI to hydrogen.

During FY2006, a series of polymers were characterized for hydrogen permeability at 300 ºC. The materials primarily consisted of commercially available polyimides and were found to hold up well to the 300 ºC temperature regime. However, the selectivity of these membranes has not been characterized. Thus, it is not possible to make a recommendation concerning the effectiveness and applicability of membranes for hydrogen separations. It is recommended that the overall concept of a catalytic membrane reactor be pursued with experimental work in future years due to the need to increase the overall conversion of HI to hydrogen and iodine. This must be done by first characterizing the ability of the membranes to perform the separation of hydrogen. Given a successful outcome of this work, combining the most effective membrane and catalyst formulations can be performed.

Summary

Recommendations have been made in this work for membrane materials that are applicable to the S-I ILS. However, selection of suitable materials does not necessarily imply that the process is reasonable for inclusion. Performance data must be included in the process models that will ultimately indicate whether S-I cycle efficiency gains may be made by inclusion of membrane separation processes. Much of this will be addressed during the FY2007 effort.