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Hollow fiber contained hydrogel-CA membrane contactor for carbon dioxide removal from the enclosed spaces

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ABSTRACT

Control of CO_2 level within a certain range is one of the most important tasks in life support systems, such as spaceship and submarine. In order to control the membrane liquid evaporation into the gas phase for the hollow fiber contained carbonic anhydrase (CA) and its buffer membrane contactor (buffer-CA HFCLM), a poly(acrylic acid-co-acrylamide) (poly(AA-co-AM)) hydrogel showing biocompatibility is synthesized for the immobilization of CA. The hollow fiber contained hydrogel-CA membrane contactor (hydrogel-CA HFCLM) is then prepared for the comparison of operating stability and CO_2 removal efficiency with that of buffer-CA HFCLM. The results show that the loss of the membrane liquid is alleviated while the water-rich ambience is still retained by holding the water molecule within the network of the hydrogel. The hydrogel-CA HFCLM in combining both advantages of CO_2 facilitated transport using CA and the poly(AA-co-AM) hydrogel as facilitators shows higher CO_2 removal capability, reducing CO_2 from 0.52 vol.% in the inlet feed gas to under 0.09% while the buffer-CA HFCLM only reducing CO_2 to 0.32% under the same operating conditions. Consequently, as a safer and more reliable CO_2 removal system, the hydrogel-CA HFCLM deserves to be further studied.

1. Introduction

Control of carbon dioxide (CO_2) is crucial for all crew inhabited space-flight missions. Air revitalization requires safe and reliable CO_2 extraction systems characterized by small volume, low mass, low rate of energy use, minimal use of consumables, and little or no crew time for operation and maintenance [1]. For applications at low CO_2 concentration (<1 vol.%) and near ambient temperature, carbonic anhydrase (CA) is the most efficient catalyst for CO_2 hydration and dehydration, with a turnover number of 10^6 mol CO_2 mol^{-1} (CA) s^{-1} [2]. Using CA as a facilitator, the design of an immobilized liquid membrane (ILM), a supported liquid membrane (SLM) or a contained liquid membrane (CLM) has shown the potential to remove CO_2 from the closed spaces [3]. Compared to the ILM/SLM, the membrane stability of CLM design has been enhanced greatly by holding the aqueous solution within the interstitial space of hydrophobic surfaces [4]. In the hollow fiber contained liquid membrane (HFCLM), not only the failure due to evaporation in an ILM or SLM design is minimized because the direct access to the fluid allows replenishment of a high vapor pressure solvent, but also merits in the ease of scalability and the wide pressure difference are demonstrated due to its structural geometry [2,4]. Nevertheless, the HFCLM design does have its risk in humidity control and pore wetting with respect to pressure fluctuations for the sweep gas mode [4]. The evaporation of the liquids into the gas phase is still apparent considering that the feed gas is normally not completely humidified in the space-walk applications [5].

A strategy when aqueous solution is used as the CLM fluid is to humidify both the feed and sweep gas streams simultaneously, or to stabilize the membrane by continuously supplying the liquid to membrane system. For instance, polysulfone humidifier was first used to control the feed and sweep gas humidity, and later a reservoir was adopted to continuously supply the core liquid to a CLM design [6]. Another alternative is to use low volatility and hygroscopic liquids, such as glycerol as the major component in the CLM fluid. Hydrophilic hollow fiber-based glycine-Na-glycerol CLM was experimentally studied by Chen et al. for the separation of CO_2 from a humid mixture of CO_2–N_2 [7,8]. Despite that all those membranes show remarkably high CO_2 permeance and selectivity of CO_2 versus O_2 and N_2, their separation properties are degraded if the relative humidity of inlet feed and sweep gases or the core liquid level are not controlled [6–8]. The water extent in the CLM will decrease significantly with a decrease in feed relative humidity. The decreased water content in the CLM will drastically increase the liquid-phase viscosity which can be responsible for the observed decrease in CO_2 and N_2 permeances [9]. Therefore, much work is still needed to

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ensure sufficient safety tolerance for those CO_2 extraction systems potentially applied in the spaces.

In contrast, the highly water-swollen membrane (hydrogel membrane), with its characteristic of the network configuration, might not only obtain a high permeation rate because the mobility of the gas through the membrane is high, but also effectively prevent the loss of membrane liquid by holding the water molecules within the network of hydrogel, thus dramatically enhancing the gas permeability, the mechanical stability and operation stability of the membrane [10]. Water-swollen hydrogel membranes prepared with poly(vinyl alcohol) (PVA)–poly(acrylic acid) (PAA) were used for the separation of CO_2 from CO_2–N_2 mixture of 20/80 vol.%, and the separation factors toward CO_2 were about 100 and the permeabilities of CO_2 ranged from 3.35×10^{-9}–3.35×10^{-10} mol m^{-2} s^{-1} Pa^{-1}. These membranes were stable at least up to 12 h [11]. Another two water-swollen hydrogel membranes for gas separation were also prepared with PVA-glutaraldehyde (GA) and Na-alginate-PVA-GA, respectively, followed by the crosslinking of the active layer by a solution-based method [12,13]. According to the concept of CO_2 facilitated transport separation, a CA immobilized PVA hydrogel membrane had been prepared and studied by Xu et al. in our group [14]. Nevertheless, still two problems remain for the CA hydrogel membrane to be used as the CO_2 separation system presently. One is the relatively lower activity of the immobilized enzyme. For example, Xu et al. found that half of the activity was left once CA was immobilized with the PVA using the GA as a crosslinking agent, and only one third was retained after a week. The other is the relatively poorer permeability and selectivity of the prepared coating layer of the hydrogel membrane [14]. Although, PVA is a well known material having good mechanical property and hydrophilicity, its swelling ratio is found generally no more than 100% [12,13]. Note that the behavior of gas permeation properties of hydrogel membrane was reported to be parallel to the swelling behavior of the coating layer in water [12,13], it is expected that the CO_2 permeation rates through membranes might increase exponentially if the water content in the membranes can be increased significantly, thereby alleviating the sensitivity of the CLM to the relative humidity of inlet feed and sweep gases. Therefore, an effective CO_2 extracting system calls for a proper hydrogel. It should not only absorb a large amount of water, thus increasing the gas permeance, but also overcome the evaporation of the fluid by holding the water molecule within the network of hydrogel, thereby improving its operating stability. In particular, for the CLM using CA as a facilitator, the ambient microenvironment formed by the network configuration of the hydrogel should also be biocompatible in order to maintain the high activity of CA itself.

Unlike PVA, the polymer superabsorbents, such as PAA-based resin, can absorb a large amount of water. Poly(acrylic acid-co-acrylamide) (poly(AA-co-AM)) irradiated in a ^{60}Co γ-source showed maximum swelling as large as 3000 times its own weight [15]. The driving force for the water absorption of the superabsorbent is not only by the capillary adsorption, but also by the secondary forces between various polymer chains, including hydrogen bonding, coulombic force, Van der Waals force, electron donating and accepting interaction, or hydrophobic interaction in aqueous medium [15]. As a result, the absorbed water is hardly removable even under certain degree of pressure, and thereby the loss of membrane liquid might be mitigated considerably for the hydrogel to be used as CLM. Also the state of water in the hydrogel was observed to be mainly composed of free water besides the freezable-bound and non-freezing water using differential scanning calorimetry (DSC) and nuclear magnetic resonance (NMR) analysis [16]. It indicates that a majority of water entrapped within the network of the hydrogel remains unchanged, except for its difficulty in evaporation into the gas phase. Consequently, it is likely that the CA enzyme entrapped in the hydrogel is similar with that dissolved in its buffer system, with the result that higher enzyme activity is retained even if it is swollen or immobilized by the hydrogel particle. Actually, the effective crosslinking network of the PAA-based hydrogel had been reported to be the most favorable circumstances for the cell immobilization in comparison with the usual carriers, such as Na-alginate [17]. The microenvironment created by the matrix and pores of carriers will offer protection to the entrapped cell or enzyme.

In this paper, a series of poly(AA-co-AM) superabsorbents were first synthesized and characterized for the investigation of their biocompatibility by the immobilization culture of a microalga, *Spirulina platensis*. The hydrogel which could be compatible with the *S. vulgaris* was then selected to swell the aqueous CA solution. Based on the effects evaluation of buffer-CA HFCLM under varying operating conditions, a hydrogel-CA HFCLM contactor was finally prepared for the low concentration CO_2 removal test in order to compare its operating stability and CO_2 removal efficiency with that of the buffer-CA HFCLM. To the best of our knowledge, no work has been reported on low concentration CO_2 removal by the HFCLM using poly(AA-co-AM) hydrogel-swollen CA as the facilitator.

2. Experimental

2.1. Synthesis and characterization of poly(AA-co-AM)

2.1.1. Synthesis of poly(AA-co-AM) superabsorbent

Poly(AA-co-AM) superabsorbent was produced using acrylic acid (AA) and acrylamide (AM) with ammonium persulfate (APS) as the initiator by free radical polymerization. AA, AM, *N*,*N*′-methylene-bis-acrylamide (Bis), APS, urea and Span-60 were from Shanghai Chemical Reagent Supply Station. Cyclohexane and isopropyl alcohol were of reagent grade.

The synthesis of superabsorbent by inverse suspension technique was conducted in a flask equipped with a mechanical stirrer, condenser, thermometer, dropping funnel and nitrogen line. The cyclohexane dispersed by Span-60 was added into reactor and stirred for 15 min firstly. After AA was neutralized by NaOH to the designated degree, such as 85%, 90%, 95% or 100% in the bath of ice-water, a solution of AA, AM, APS and urea was added dropwise within 20 min. The mixture was then heated to 45 °C and maintained for 1 h. The isopropyl alcohol of 2 ml was added for the control of molecular weight at the end of the first heated stage. After another 1 h reaction at 55 °C, the system was dewatered by azeotropic distillation. Finally, the product was precipitated in methanol and vacuum dried at 80 °C to a constant weight [18]. The chemical structure and reaction routes for poly(AA-co-AM) superabsorbent are illustrated in Scheme 1.

2.1.2. Characterization of poly(AA-co-AM) superabsorbent

2.1.2.1. FTIR. The active function groups of the prepared superabsorbent were measured with IR (E.S.T.560, USA Nicolet), and the spectras of —COOH, —COONa and —CONH$_2$ were analyzed.

2.1.2.2. Measurement of absorbency. An accurately weighed 0.5000 g sample of the superabsorbent was allowed to soak in water or 0.9% NaCl aqueous solution at room temperature until the swelling equilibrium was reached. The swollen superabsorbent was then separated from unabsorbed water by screening through a 100-mesh sieve. The hydrogel on the sieve was then allowed to leach for 10 min and the absorbency Q was expressed in grams of water retained in the gel by a gram of dried gel.

$$Q = \frac{m_2 - m_1}{m_1} \tag{1}$$