CARBON 77 (2014) 933–938

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journal homepage: www.elsevier.com/locate/carbon

Graphene oxide membrane for liquid phase organic molecular separation

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ARTICLE INFO

Article history:
Received 28 February 2014
Accepted 3 June 2014
Available online 13 June 2014

ABSTRACT

The selective permeation of organic solvents and water through graphene oxide (GO) membranes has been demonstrated. Water was found to permeate through GO membranes faster than various alcohols. The permeation rates of ethanol, 1-propanol and 2-propanol (IPA) are about 80 times lower than that of water. Taking advantage of the differences in the permeation rates, we separated water from the alcohols and obtained alcohols with high purity. For ethanol and 1-propanol, binary solutions of the alcohol and water were filtered efficiently to produce alcohols with concentration of about 97%. However, the selectivity of the filtration of methanol is significantly lower than those of the other alcohols. To understand the mechanism we followed the structural changes in the GO membranes by X-ray diffraction analysis. From the X-ray diffraction results we speculate that the selectivity of the permeation of water and alcohols is closely related to the molecular sizes of the solvents and their polarity. In order to demonstrate the potential applications of this process for the selective removal of water from aqueous organic mixtures, we performed the separation of water from a bio-oil containing 73% of water. The majority of the water was filtered out resulting in a higher purity bio-oil.

1. Introduction

The carbon atoms in graphene are so tightly bonded that no gas molecules can permeate through the one atom thick membrane of graphene [1–4]. If atomic defects are generated in the membrane through oxidation or chemical reaction methods, some gas or liquid molecules can pass through it depending on the sizes of the defects and the molecules, which suggests that graphene membranes can be used as molecular filters [5–8]. However, single layer graphene membranes with defects are mechanically too weak to be used in large volume molecular separation. In contrast, graphene oxide (GO) paper with a stack structure [9] has good chemical stability, excellent mechanical stiffness and strength [10–12], and can easily be produced with large sizes for macroscale applications [13,14]. Functional groups in the GO structure open gaps between the stacked platelets that are approximately 1 nm wide [15]. These gaps in GO paper can act as nanopores for molecular transport [16], and, depending on the gap size or functional groups in the GO membrane, can permit the selective passage of gas or liquid molecules through the pores [17–19]. Thus GO membranes

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http://dx.doi.org/10.1016/j.carbon.2014.06.007
0008-6223/

can be used as molecular sieves. One of the interesting studies which has been done recently reported that GO membrane does not permit the permeation of helium gas molecules whereas water molecules can pass through it easily due to the hydrophilic characteristics of the material [17]. Although that experiment demonstrated the possibility of the selective filtration of gas molecules using GO membranes, their sieving characteristics with respect to liquid phase molecules have not been investigated systematically. Chemical feed stock, solvents, and the products of reactions in the liquid phase are often complex mixtures of organic solvents and water [20]. The separation of these mixtures remains a difficult task for industry, and is mostly performed by energy-consuming distillation techniques [21,22] sometimes combined with the use of entrainers [23,24]. Very recently, Tang et al. [25] and Talyzin et al. [26] demonstrated the selective permeation of water and ethanol through GO membranes. In this context GO membranes can offer many advantages in liquid phase separations because of their inherent porous structures that creates pathways for the selective passage of different molecules resulting in the separation on the basis of their permeation rates. The immediate advantages are higher selectivity, lower energy consumption, moderate cost to performance ratio, and modular design.

In this study, we assessed the effectiveness of graphene oxide membranes in the liquid phase separation of mixtures of alcohol and water. First, we measured the permeation rates of water and various alcohols with varying carbon numbers, then performed filtering experiments on water and alcohol mixtures in order to observe the selective permeation of the liquid molecules and to investigate the mechanism behind the selectivity. The permeation rate of water was found to be higher than those of the alcohols and we speculate that this is due to the differences in their molecular sizes and polarity. We also tested the filtration of a mixture of many kinds of organic molecules [27] and water and showed that it is feasible to use GO as a versatile liquid phase filter membrane.

2. Experimental procedure

GO were prepared with modified Hummer's method and characterized by using various methods (Figs. S1–S5) [28–30]. Graphene oxide membranes were prepared by filtering diluted graphene oxide dispersions through a PTFE filter with 0.5 μm pore size [31,32]. The thickness of the membranes was approximately 5 μm for all experiments (Fig. S6). These membranes were all prepared from GO solutions of the same concentration and quantity, and thus their thicknesses were almost identical. A series of liquid phase permeation experiments were conducted with a modified vacuum filtering device and the GO membranes, as shown in the schematic diagram in Fig. S7. Although freestanding GO membranes possess sufficient mechanical strength for the applications tested in our experiments, we used GO membranes on top of PTFE substrates to extend their life time and check their reusability. The permeation rates of methanol/ethanol/propanol and water through the PTFE filter were observed to be five orders of magnitudes higher than those through the GO membranes, so the rate of permeation through the GO/PTFE stack filter structure is determined by the GO membranes. The permeation rates were calculated by following the changes in the density as well as weight loss of the water/alcohol mixtures over a time of one day.

3. Results and discussion

We varied the alcohol concentration in water from 0 to 100 wt.% in order to investigate the filtration selectivity. Here, alcohol concentrations of 0 wt.% and 100 wt.% correspond to pure water and pure alcohol. The permeation rates of the pure alcohols were found to be much lower than that of water, as shown in Fig. 1. The permeation rates of pure water and the pure alcohols are as follows; water: methanol: ethanol: IPA: 1-propanol = 1:0.19:0.017:0.015:0.012 (see Fig. S8 for clear comparison between alcohols). The methanol permeation rate is the highest of those of the alcohols.

As the concentration of alcohol in the solutions of water and ethanol/isopropanol/1-propanol decreases, the permeation rate of the alcohol increases (Fig. 1(b)–(d)). We speculate that water assists the permeation of the alcohols because these alcohols dissolve in water. Pure ethanol/isopropanol/1-propanol molecules pass through the nanochannels in GO paper quite slowly compared to water, as mentioned above. However, when they are mixed with water, water molecules adhered to these alcohol molecules through van der Waals bonds or hydrogen bonds can drag the alcohol molecules through the nanogaps between the GO flakes, which usually have a size of approximately 1 nm, because of the high affinity between water and the functional groups in GO. If the solubility of the alcohol in water is lower, this mechanism is likely to be less effective. Hence we also tested mixtures of water and alcohols with large molecular sizes, i.e., butanol and pentanol.

These alcohols can be mixed with water to concentrations of approximately 7.6 wt.% (1-butanol) and 2.2 wt.% (1-pentanol) in water at 20 °C [33]. We added the alcohols to the solutions up to the highest possible concentrations in water and the filtration results of the two alcohols are shown in Fig. S9 along with other alcohols. In the filtering test, since the permeation rate of water is much higher than these alcohols, some of the alcohol is separated from the solution as water permeates and we observed the formation and level change of boundary of water and the undissolved alcohol. The permeation of the alcohols with higher molecular weight is almost completely blocked by the GO film and the permeation rate 1 or 2 orders lower than other alcohols, so the unfiltered solutions are almost pure alcohol (i.e., the mass and density of the unfiltered liquid are the same as those of the alcohol previously added into the binary mixture). These results show that the solubility of the alcohol in water is important for GO paper permeation.

The trend in the permeation rates for the components of the solutions of methanol and water is opposite to those for the other three alcohol mixtures with water (Fig. 1(a)). As the concentration of methanol in the mixtures increases, the methanol permeation rate increases. These results indicate that water prevents the permeation of methanol through the GO membrane.