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Double cross-linking PVA-SiO_2 hybrid membranes for alkali recovery

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ABSTRACT

Non-charged PVA-SiO_2 hybrid membranes are prepared through sol-gel process among polyvinyl alcohol (PVA) and double cross-linking agents, which are selected from four types of alkoxysilanes including tetraethoxysilane (TEOS), tetramethoxysilane (TMOS), γ-aminopropyl triethoxysilane (APTEOS) and methacryloxypropyl trimethoxy silane (MPS). The double cross-linking agent can combine their advantages including different hydrolysis rates of $-OC_2H_5$ and $-OCH_3$ groups, high compatibility of $-NH_2$, and polymerizable C=C bonds.

The $-NH_2$ group from APTEOS can enhance membrane homogeneity, thermal stability and flexibility due to its compatibility with PVA–OH groups. The membranes have high selectivity (62–101) but low permeability in diffusion dialysis process for separating NaOH/Na_2WO_4 solution. Single type of $-Si(OCH_3)$ groups produces large silica particles (1.5–5μm), which reduce membrane stability but enhance permeability. The membrane has low strength and flexibility, and high swelling degrees in 65 °C water (373–408%) and weight loss percentage in 65 °C NaOH solution (25.8–28.7%). The permeability can reach up to 0.0076–0.0092 m/h but the selectivity is only 23.7–25.0 at 20–40 °C. The combination of $-Si(OCH_3)$ and $-Si(OC_2H_5)$ groups (TEOS and MPS) can obtain high strength and flexibility (20.3 MPa, 571%), acceptable swelling degrees (232–279%) and balanced permeability and selectivity (0.0043–0.0071 m/h, 45–110). Hence, double cross-linking agents can be combined to prepare optimized neutral membranes for diffusion dialysis.

1. Introduction

Alkali waste is produced in many industrial processes such as paper, leather, printing & dying, tungsten ore smelting and man-made fiber industries [1–5]. The alkali waste, though can be treated by conventional methods such as neutralization, concentration and burning, would consume large amount of energy and cause further pollution. As compared, diffusion dialysis (DD) provides convenient way to separate alkali (NaOH) from the alkaline solution. The NaOH component transports through a membrane under concentration gradient, while other components are rejected due to their low activity [6]. Hence, the DD process is low energy consumption and environmental friendly [7].

The membrane, as a key factor to determine the DD efficiency, needs high alkaline resistance, NaOH permeability and selectivity. Conventional cation exchange membranes are composed of three phases including a hydrophobic region of membrane matrix, an active region of ion exchange groups and an interstitial region [8]. The ion exchange groups can transport counter ions (Na^+) through ion exchange process, while the hydrophobic region is less likely to transport any ions. Hence, the co-ions (OH^-) can only be leaked through the interstitial region with high resistances including friction and electrostatic repulsion from the active region ($-SO_3^-$) [9]. Therefore, the permeability of NaOH is low for conventional cation exchange membranes such as sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) membranes (0.002 m/h [10]).

Polyvinyl alcohol (PVA) based membranes have favorable NaOH permeability due to its linear alkyl chains and high density of $-OH$ groups (22.7 mmol/g). The alkyl chains are less hydrophobic than the aromatic chains of commercial membranes, which weaken the interface between active and interstitial regions. The $-OH$ groups are hydrophilic and can form weak interactions such as hydrogen bonds with OH^- ions, and thus are regarded as assistant functional groups to transport OH^- ions. Hence, the PVA is cross-linked with various multisilicon copolymers to prepare cation exchange membranes [9]. The DD performances seem to be less affected by the membrane charge densities, and thus

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Nomenclature

List of symbols

Codes	full name or meaning
PVA	polyvinyl alcohol
TEOS	tetraethoxysilane
TMOS	tetramethoxysilane
APTEOS	γ-aminopropyl triethoxysilane
MPS	methacryloxypropyl trimethoxy silane
Membrane E-T	membrane cross-linked with TEOS and TMOS
Membrane E-A	membrane cross-linked with TEOS and APTEOS
Membrane E-M	membrane cross-linked with TEOS and MPS
Membrane T-M	membrane cross-linked with TMOS and MPS
Membrane T-A	membrane cross-linked with TMOS and APTEOS
Membrane A-M	membrane cross-linked with APTEOS and MPS
DD	diffusion dialysis
U_{OH}	dialysis coefficients of NaOH
S	separation factor
SPPO	sulfonated poly(2,6-dimethyl-1,4-phenylene oxide)
IEC	ion exchange capacity
SEM	scanning electron microscope
m_1	weight of the fresh and dry membrane sample
m_2	weight of the wet sample after immersed in 65 °C NaOH solution for 60 h
m_3	weight of the dry sample after immersed in 65 °C NaOH solution for 60 h
TS	tensile strength
E_b	elongation at break
W_R	water uptake
LER	linear expansion ratio
IDT	initial decomposition temperature
T_d	thermal degradation temperature

non-charged hybrid membranes are prepared for application in DD process [11].

The non-charged hybrid membranes are prepared from the sol-gel process of PVA and methacryloxypropyl trimethoxy silane (MPS), which show the dialysis coefficient of NaOH of 0.0069–0.0127 m/h, and the separation factor of 19–92 for NaOH/Na_2WO_4 solution [11]. However, membrane cross-linked with MPS is inhomogeneous with the silica particles of 2–4 μm, and is unstable in alkaline solution with the weight loss as high as 35.6%. Besides, permeability and selectivity can not be balanced for a certain membrane. For example, membrane with high selectivity (92.7) has low permeability (0.0069 m/h), while high permeability (0.0127 m/h) corresponds to low selectivity (19.1).

Alkoxysilane, due to its typical chain and functional group, has own advantages and inherent defects. For example, tetraethoxy silane (TEOS) contains four Si—OC_2H_5 groups, while the tetramethoxysilane (TMOS) contains four Si—OCH_3 groups, as shown in Scheme 1. All the groups can take part in sol-gel reaction with PVA to form silica network. Hence, TEOS and TMOS may have favorable cross-linking ability. However, the four Si—OR groups are not well compatible with PVA aqueous solution especially for Si—OC_2H_5 group due to its lower polarity, which induces phase separation between organic and inorganic phases [12]. Though the compatibility can be improved by the acid catalyst [13], the obtained membrane would change color during heat treatment due to the loss of PVA–OH groups and the emergence of unsaturated bonds [14]. γ-aminopropyl-triethoxysilane (APTEOS) contains three —Si(OR) groups with a —NH_2 group, which may have higher compatibility with PVA. Hence, different alkoxysilanes need to be combined to prepare optimized membranes.

Therefore, in this work, four types of alkoxysilanes are selected including TEOS, TMOS, APTEOS and MPS (Scheme 1), from which double alkoxysilanes are cross-linked with PVA to prepare non-charged hybrid membranes. The double alkoxysilanes may combine their advantages of different functional groups, including the different sol-gel rates of $Si(OCH_3)$ and $Si(OC_2H_5)$ groups (without acid catalyst), the compatibility of —NH_2, and the polymerizable C=C bonds. The combination may obtain optimized membranes in morphology, mechanical and thermal stability, swelling and alkaline resistances. The non-charged hybrid membranes will be potentially applied in DD process for alkali recovery.

2. Experimental

2.1. Materials

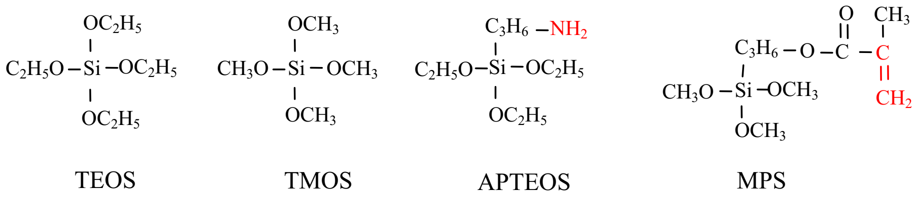
Polyvinyl alcohol (PVA) was supplied by Shanghai Sinopharm Chemical Reagent Co., Ltd. (China). The average degree of polymerization was 1750 ± 50. Tetraethoxy silane (TEOS), NaOH and Na_2WO_4 were supplied by Shanghai Sinopharm Chemical Reagent Co. Ltd. (China). Tetramethoxysilane (TMOS) was purchased from Nanjing Jingtianwei Chemical Co. Ltd. γ-aminopropyl-triethoxysilane (APTEOS) was bought from Hangzhou Jessica chemical reagents Co., Ltd. Methacryloxypropyl trimethoxy silane (MPS) was bought from Tianchang Anhui green chemical assistant co., Ltd. The other regents were from domestic chemical reagents company and of analytical grade. Distilled water was used throughout.

The alkoxysilanes need to be sealed to avoid moisture in the air, for little water would induce sol-gel reaction within Si—OR groups. Besides, the residual APTEOS in the sampler needs to be washed with ethanol timely.

PVA solution (5 wt%) was prepared by dissolving 42.4 g PVA in 760 mL water at room temperature for one day, then heated to 102 °C at the rate of 8 °C/h and kept at 102 °C for around 2.5 h. The dissolved solution was cooled to 65 °C before use.

2.2. Membrane preparation

Two kinds of alkoxysilanes were separately dropped into 65 °C PVA solution (200 mL) within 5 min. The mixture solution was continuously stirred at 65 °C for 12 h. The solution was cast onto



Scheme 1. Chemical structures of the four types of alkoxysilanes.