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The effects of multi-functional groups from PVA and ternary multisilicon copolymer on diffusion dialysis

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ABSTRACT

Ternary multisilicon copolymers are prepared from copolymerization of acrylic acid, sodium styrene sulfonate and γ-methacryloxypropyl trimethoxy silane, from which functional groups of –Si$(OCH_3)_3$, –COOH and –SO_3Na are obtained respectively. The acidic –COOH groups may induce gel during copolymerization, and thus sufficient solvent needs to be used. The –Si$(OCH_3)_3$ groups can crosslink with polyvinyl alcohol (PVA) to yield cation exchange hybrid membranes.

The membranes have the ion exchange capacity of 1.01–2.26 mmol/g, water uptake of 39.1–59.7%, swelling degrees of 108–339% in 65 °C water after 192 h, and swelling degrees of 254–344% in 65 °C alkaline solution after 60 h. Membrane with proper ratios of multi-functional groups can sorb 1.4 mol/L NaOH in 1.0 mol/L NaOH solution. The membranes are used in diffusion dialysis (DD) process for alkali recovery from NaOH/Na_2WO_4 solution. The dialysis coefficients of NaOH (U_{OH}) are in the range of 0.013–0.021 m/h at room temperature, with the separation factors of 15–23. The high U_{OH} values indicate the superiority of multi-functional groups. The –OH, –COOH and –SO_3Na groups from PVA and multisilicon copolymer chains may have coupling effects on the transport of both Na^+ and OH^- ions.

1. Introduction

Large amount of acid or alkali waste solution is produced from industrial processes, such as hydrometallurgy, electronic products processing, papermaking and production of biological products. The acid or alkali solution can be treated with diffusion dialysis (DD) membrane process due to its unique advantages, such as low energy assumption [1], simple construction of the apparatus [2], no pollution, continuous operation, and recoverable alkali or acid [3]. Besides, DD can be used to separate acid or alkali mixture with similar electrochemical properties but different sizes, such as the mixture of amino acid and HCl [4], as well as weak acids such as lactic acid and propionic acid [5].

The DD researches are mainly focused on three aspects, as shown in Scheme 1. Firstly, DD devices have been developed such as batch and continuous devices. The batch device is mainly used for laboratory research, in which the ions in the dialysate side diffuse through the membrane into the water (diffusate) side [6]. Continuous device, on the other hand, consists of several dialysate and diffusate cells through which the waste solution and water flow by pumping [7]. Hence the continuous device can be used for industrial production and separation fields. Recently, spiral wound DD devices are also developed by our research group [8]. The spiral wound DD devices have the advantages of light weight, high utilization of membrane area, and low concentration polarization. Secondly, waste solutions containing various ions are separated, especially for acidic waste solutions such as H_2SO_4 [3,7]. The alkaline waste solutions are seldom reported except in our research group such as NaOH/Na_2WO_4 [9]. The few reports are mainly attributed to the lack of suitable cation exchange membranes, for the permeability of commercial membranes is at a low level [9]. The permeability needs to be elevated through the design of novel membrane structures. Hence in the final, the membrane structures are investigated to elevate DD performances and to know more about DD mechanisms.

The effects of membrane structures on DD performances are generally summarized as following (Scheme 1). (1) The membrane charge density, though often regarded as essential for other applications such as fuel cell and electrodialysis, has less effect on DD performances [10]. This is because both anion and cation such as Na^+ OH^- need to be transported through the membrane, which is different from the other applications. (2) Organic–inorganic hybrid membranes are prepared. The inorganic phase of silica particles can elevate the permeability in some cases, for there may be some interstices between organic and inorganic phases [9,11].

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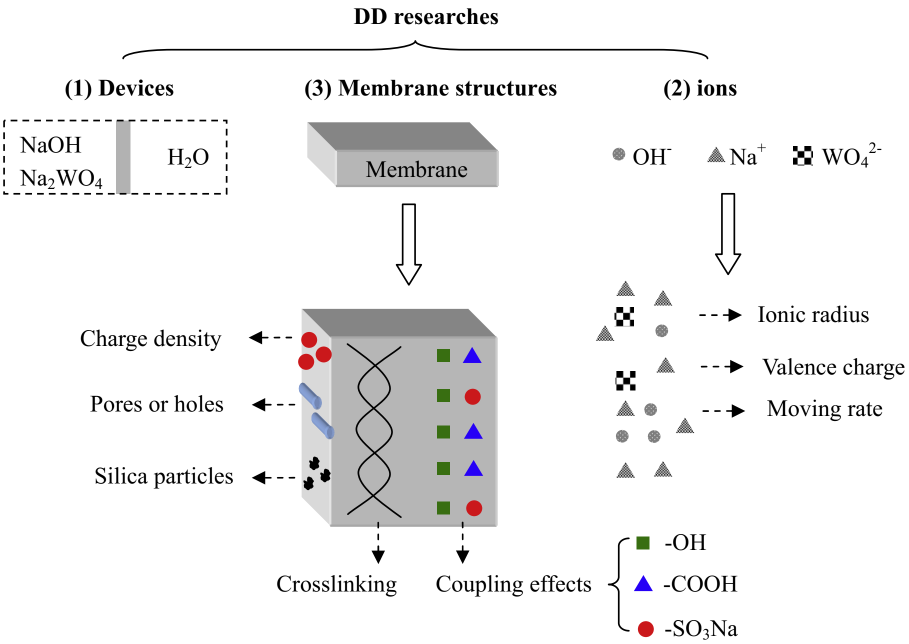

Scheme 1. DD researches in three aspects, including the development of DD devices, the separation of different waste solutions, and the design of membrane structures.

For example, the inorganic phase can elevate proton conductivity within hybrid membranes [12]. (3) The micropores within membrane matrix can accelerate the ion transport rate [13]. Interestingly, the silica particles and micropores, if with proper content, sizes and under proper temperature, can even enhance membrane selectivity [11]. (4) The crosslinking degree and phase separation have more complex effects on DD process [14]. (5) Double functional groups, including ion exchange group and –OH group, are combined to accelerate the transport of both cation (Na^+) and anion (OH^-). For example, groups of –OH/–COOH [15] or $–OH/SO_3$-Na have been combined in our previous reports [14]. The –COOH or $–SO_3Na$ groups can transfer Na^+ ions through ion exchange process, while the –OH groups may be effective to the transport of H^+ or OH^- ions through weak interactions such as hydrogen bonds.

Different functional groups can be combined through blending and sol–gel process between polyvinyl alcohol (PVA) and multisilicon copolymers. Multisilicon copolymer has a long main chain, and many branched chains with plenty of functional groups such as $–Si(OCH_3)_3$ and ion exchange groups, which are similar to the stem, branch, acetabula and fruit of a vine from bionic aspect, respectively [15,16]. The $–Si(OCH_3)_3$ groups can crosslink with the –OH groups of PVA (PVA-OH), while the ion exchange groups can be varied to adjust membrane performance. In our primary work, multisilicon copolymers containing one type of ion exchange groups had been developed to prepare PVA-based hybrid membranes. The membranes have favorable stability and acceptable DD performances. Their permeability is comparable with that of commercial DF-120 anion exchange membrane (0.009 m/h at 25 °C for $HCl/FeCl_2$ solution [11]), which is widely used in DD process for acid recovery. However, their permeability is still much lower than those of PVA-based anion exchange membranes in acid recovery (0.075 m/h at room temperature, [16]).

In our following work, a ternary multisilicon copolymer, which contains both anhydride and $–SO_3Na$ groups, was prepared to develop PVA-based hybrid membranes [10]. The membranes have favorable permeability (0.011–0.019 m/h), with the separation factors of 13.9–27.6 for $NaOH/Na_2WO_4$ solution. However, the ternary multisilicon copolymer has three main defects in membrane preparation and performance. Firstly, as the content of anhydride group is fixed at 25%, the effects among different functional groups are difficult to be compared. Secondly, the polarity of anhydride group is insufficient in the ternary multisilicon copolymer, which restricts its compatibility with PVA aqueous solution. The insufficient compatibility would reduce membrane homogeneity, and thus the obtained membrane has white "powder" on its surface after drying. Finally, though the anhydride groups can be gradually transformed into –COOH groups, the transformation can not hinder the initial inhomogeneous sol–gel reaction. The initial inhomogeneity would further impede the homogenous dispersion of copolymer chains within aqueous PVA solution, which may weaken the "coupling effects" among different functional groups during DD process.

The present work is a further development of ternary multisilicon copolymer for preparing PVA-based hybrid membranes. The present ternary multisilicon copolymers are prepared from acrylic acid (AA), sodium styrene sulfonate (SSS) and γ-methacryloxypropyl trimethoxy silane (γ-MPS), which provide the copolymers with functional groups of –COOH, $–SO_3Na$ and $–Si(OCH_3)_3$. The $–Si(OCH_3)_3$ groups can crosslink with PVA to enhance membrane stability. The –COOH groups, instead of previous anhydride groups, can overcome the previous defects. Firstly, the content of –COOH, together with other functional groups, will be adjusted to develop different copolymers. Secondly, as the –COOH groups have higher polarity and can also combine with PVA-OH groups through weak interactions, the sol–gel process between the copolymer and PVA aqueous solution is homogenous all the time. Finally, the obtained hybrid membranes may not only be homogeneous, but may also have higher DD performances due to the homogeneous dispersion among –OH, –COOH and $–SO_3Na$ groups. The contents of –OH, –COOH and $–SO_3Na$ groups are adjustable, which may have coupling effects on DD process. The DD performances, correlated with the copolymer and membrane structures, will be fully investigated.

2. Experimentals

2.1. Materials

Polyvinyl alcohol (PVA, polymerization degree of 1750 ± 50), acryl acid (AA) and N,N-dimethyl formamide (DMF) were supplied by Shanghai Sinopharm Chemical Reagent Co. Ltd. (China).