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Fundamental studies on the intermediate layer of a bipolar membrane. Part VI. Effect of the coordinated complex between starburst dendrimer PAMAM and chromium (III) on water dissociation at the interface of a bipolar membrane

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Abstract

Starburst dendrimer polyamidoamine (PAMAM) is an ellipsoidal tree-like macromolecule with a well defined structure and many more amino groups than conventional macromolecules, which can be used to catalyze water dissociation in a bipolar membrane according previous work. The purpose of this research is to discover the effect of the coordinated complex between PAMAM G4 and Cr(III) on water dissociation in a bipolar membrane. The coordinated reaction between G4 and Cr(III) was investigated by UV–VIS absorption spectroscopy, and finally the molar ratio Cr(III)/G4 was chosen as 20. The I-V curves showed that the coordinated complex could be applied to accelerate water dissociation in a bipolar membrane, and the accelerative or catalytic effect was more prominent than separated G4 or Cr(III). Furthermore, the V-t curves showed that the coordinated complex in the intermediate layer was comparatively chemically stable, namely G4 had the function of fixing Cr(III) ions in the intermediate layer. Thus, it is expected that a bipolar membrane with high efficiency and comparative stability can be prepared by applying the coordinated complex between G4 and Cr(III) as the intermediate layer.

Keywords: Bipolar membrane; Water dissociation; Intermediate layer; Polyamidoamine; Chromium

1. Introduction

A bipolar membrane, which consists of an anion selective layer, a cation selective layer and a contact region between the two layers, has been applied in industries for resource recovery, pollutant control and chemical processing with a simple process, high efficiency, and low waste disposal [1,2]. The contact region, also referred to as the intermediate layer, is the region where the desired water dissociation reaction actually

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occurs [3], and thus the charged groups and structures in this region should be modified elaborately to improve the performance of a bipolar membrane; especially, a catalyst should be imported. To date, it is well accepted that the proper catalysts include the weak acids/bases such as amino groups, pyridine, carboxylic acid, phenolic and the phosphoric acid group [4,5] as well as heavy metal salts such as ruthenium trichloride, chromic nitrate, indium sulfate, hydrated zirconium oxide, etc. [6–8].

Recently, some functional macromolecules have been used for the interfacial laver of bipolar membranes. It was found that hydrophilic polyethylene glycol [9], low concentration polyvinyl alcohol [10] and low concentration gelatin doped with AgCl [11] are effective in catalyzing water dissociation; however, both amphoteric bovine serum albumin [12] and high concentration polyvinyl alcohol [10] are retardants for water dissociation. Especially, when the starburst dendrimer polyamidoamine (PAMAM), an ellipsoidal tree-like macromolecule with a well defined structure and many more amino groups than conventional macromolecules, is used as the intermediate layer of a bipolar membrane, both the generation and concentration of PAMAM strongly affect the characteristics of the bipolar membranes, and there is a transitional concentration for various generations to catalyze water dissociation effectively [13].

The advantage of using macromolecules as an intermediate layer is that the catalytic function can last much longer than heavy metal ions that may leach out of the intermediate layer and cause an increase in water dissociation voltage after comparatively short periods [6,7]. To reduce the leaching, two methods have been proposed: the anion- and/or cation-exchange membrane is firstly immersed in a slurry of metal salt in hot caustic soda instead of a solution of metal salt, or the prepared bipolar membrane is post-treated by circulating hot caustic soda near the membrane [6,7]. These methods may cause destruction of

the anion-exchange layer with the quaternary amine group. It is well known that most heavy metal ions can form a coordinated complex with some macromolecules such as the abovementioned PAMAM [14,15]. Thus, some questions emerge: what is the effect of the coordinated complex formed between PAMAM and metal ions on water dissociation in a bipolar membrane? Does there exist a synergistic effect between PAMAM and metal ions on water dissociation? In order to find the answers, bipolar membranes with a coordinated complex between PAMAM G4 and chromium (III) as the intermediate layer were prepared and the effect on water dissociation was fully investigated. Here, the reason of choosing the chromium (III) ion is that it is a more effective catalyst for water dissociation in a bipolar membrane than other metal ions [6,7].

2. Experimental

The quaternary ammonium type heterogeneous anion-exchange membrane (Model 3362BW) (Shanghai Chemical) was used with a thickness 0.42 mm, water content 35%, ion exchange capacity 1.8 meg/g-dry, area resistance 12Ω -cm² and permselectivity of 89%. Sulfonated poly(phenylene oxide) (SPPO) was obtained from the Shangdong Ocean Chemical Industry Scientific Research Institute with an ion-exchange capacity of 2.1 meq/g-dry. Dark green chromic chloride ($[Cr(H_2O)_4Cl_2]Cl\cdot H_2O$) with analytical purity was provided by Shanghai Chemical Reagent. It has an acidic aqueous solution which is due to hydrolyzation (some multi-nuclear Cr(III) complexes bridged by the hydroxyl ion are produced) [16]. PAMAM G4 dendrimers, based on an ethylenediamine core, were obtained from Dendritech (Midland, MI, USA). The characteristic data of PAMAM G4 include molecular weight 6900, number of primary amine groups 32 and number of total tertiary amine groups 30 (including 16 outmost tertiary amine groups and Download English Version:

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