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Catalytic water dissociation using hyperbranched aliphatic polyester (Boltorn® series) as the interface of a bipolar membrane

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Abstract

The effect of hyperbranched aliphatic polyester (Boltorn® series) on the water dissociation in bipolar membranes was firstly investigated in this paper. The bipolar membranes were prepared by immersing the anion exchange layer in a hyperbranched aliphatic polyester solution and then coating on the layer a polyphenylene oxide (SPPO) solution. The SEM observations proved the existence of hyperbranched aliphatic polyester at the membrane intermediate layer. The adsorption amount was evaluated by the oxygen content via XPS. The junction thickness of the prepared bipolar membrane was determined by electrochemical impedance spectroscopy (EIS), and the membrane performances were evaluated by current–voltage curves. The results showed that the amount and generation of Boltorn® series, and temperature all affected I–V behaviors of the fabricated bipolar membranes, and the former two played the critical role. These effects were explained on the basis of the water dissociation theory and the characteristics of hyperbranched aliphatic polyester.

Keywords: Bipolar membrane; Catalytic water dissociation; Intermediate layer; Hyperbranched aliphatic polyester

1. Introduction

Electrodialysis with bipolar membranes (EDBM) is a type of technology which is based on "design for the environment (DFE)" and "Green Chemistry" [1]. It can conduct some new synthetic processes and achieve the maximal utilization of resources and pollution prevention by flexibly coupling with other traditional technologies. It can realize closing loops by recovering or regenerating the waste effluents from chemical industries, food industries, etc. [1–5]. For an EDBM system, the most significant component is bipolar membrane (BM). However, earlier preparation of a bipolar membrane was conducted by directly combining anion-exchange and cation-exchange layers [6]. The membrane prepared as such does not have satisfactory performances for applications, and thus this bipolar membrane technology has not developed at a desirable pace ever since its preparation a half century ago [7].

Most applications of bipolar membranes are based on their ability to dissociate water into protons and hydroxyl ions. The process was also called water dissociation or splitting, a phenomenon which was firstly observed in conventional electrodialysis above the limiting current density [8]. Thus, the improvement on the performance finally focuses on the mechanism studies of catalytic water splitting. It is well known that the water splitting does not take place in the solution but mainly in the membrane phase. Based on the general observations, Simons stressed that the water splitting was caused by a reversible protonation of weakly basic groups of the anion exchange layer, i.e., tertiary amines [9]. He further showed that (1) water splitting could be suppressed by methylation of tertiary amines into quaternary amines, (2) degradation of quaternary ammonium groups in a strongly basic environment led to the formation of tertiary amines, and (3) water splitting in cation-exchange membranes can be analogously obtained when weakly acidic groups exist in the membrane phase [9–11]. Following the reasoning of Simons, the water dissociation in a bipolar membrane was symbolized by the following reactions (chemical reaction model):

$$B + H_2O \Leftrightarrow BH^+ \cdots OH^- \Leftrightarrow BH^+ + OH^-, \quad (1)$$

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$$BH^+ + H_2O \Leftrightarrow B\cdots H_3O^+ \Leftrightarrow B + H_3O^+, \quad (2)$$

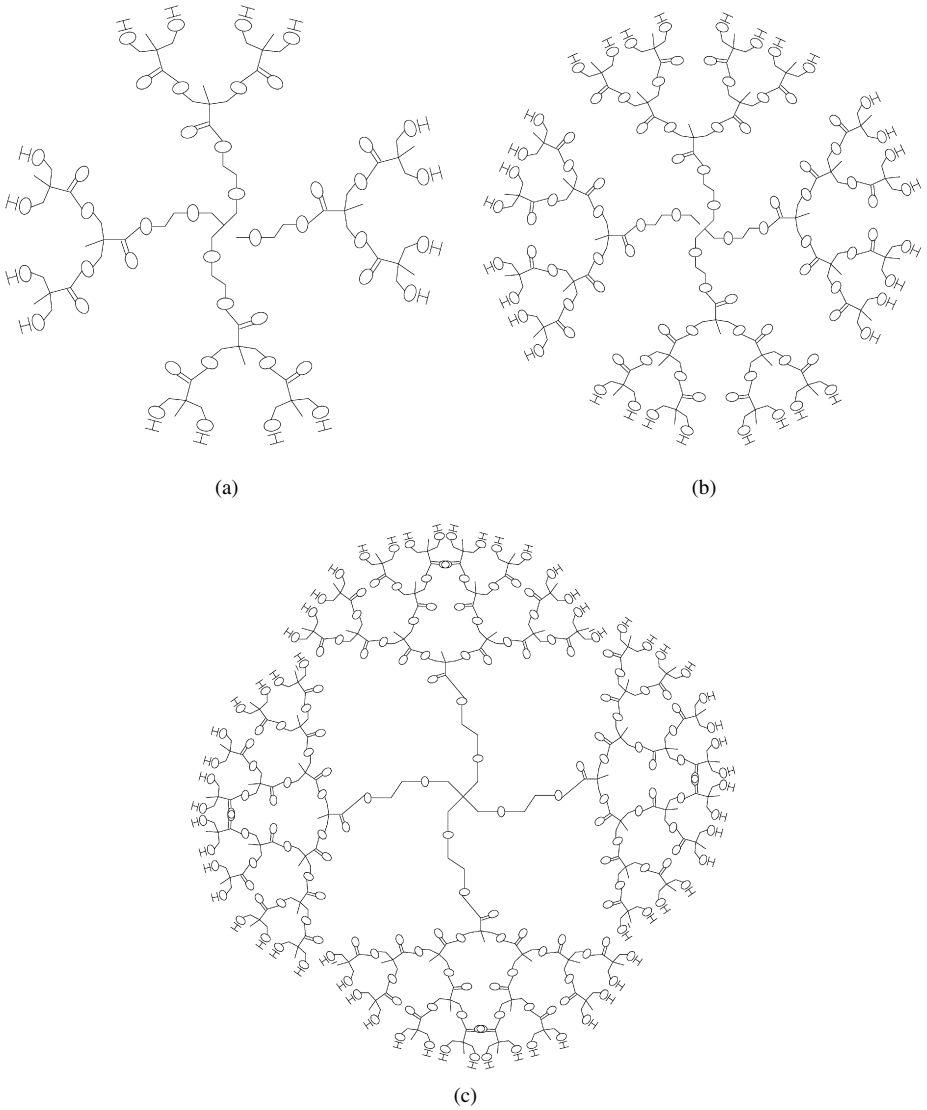
or

$$A^- + H_2O \Leftrightarrow AH\cdots OH^- \Leftrightarrow AH + OH^-, \quad (3)$$

$$AH + H_2O \Leftrightarrow A^-\cdots H_3O^+ \Leftrightarrow A^- + H_3O^+, \quad (4)$$

where BH^+ and A^- stand for the positive and negative catalytic centers, respectively. These equations demonstrate that water splitting can be considered a type of proton-transfer reaction between water molecules and functional groups or chemicals [8,11]. According to this chemical reaction model, the performance of bipolar membranes were improved by introducing a third contact region or catalytic layer between the original two ion-exchange layers, which contains weak acids or the corresponding bases, such as amino groups, pyridines, carboxylic acids, and phenolic and phosphoric acid groups [9–12]. For example, Tanioka et al. suggested that amino groups, if inserted in the interface region, could catalyze water splitting through the proton transfer reaction [13]. In addition, due to the amphoteric characteristics, some inorganic substances or metallic compounds (such as ruthenium trichloride, chromic nitrate, indium sulfate, iron hydroxide/oxide, and hydrated zirconium oxide [14–19]) have been reported to have the same catalytic function if they are introduced into the junction of a bipolar membrane.

In our previous work, the starburst dendrimer polyamidoamine (PAMAM) were synthesized and used as bipolar membrane intermediate layer to catalyze water splitting. It was found that, whether it is used alone or as a complex with transitional metals, the starburst dendrimer polyamidoamine can apparently improve water splitting because of its plentiful amino groups. The limitation on this kind of material is the high cost and the difficulty of its synthesis [20]. To further investigate the relation between water splitting and the chemical composition of intermediate layer, in this paper, we try to explore the possibility of some new materials—hyperbranched aliphatic polyesters (Boltorn® series, Fig. 1)—to modify the interface in bipolar membrane. The Boltorn® series possess abundant hydroxyl groups. For examples, Boltorn®



(a) (b)

(c)

Fig. 1. Idealized formula of (a) Boltorn® H20, (b) Boltorn® H30, and (c) Boltorn® H40.