



Affinity of ion-exchange membranes for HI–I₂–H₂O mixture



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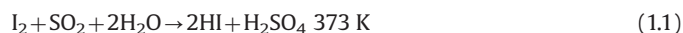
ABSTRACT

Electro-electrodialysis (EED) has been applied to thermochemical water-splitting hydrogen production iodine–sulfur process in order to enhance HI in a HI–I₂–H₂O mixture (HIx solution). In this paper, in order to understand the behavior of the components (I₂, H⁺, I[−], and H₂O) of the HIx solution in the membranes on absorption equilibrium, each component absorbed in a styrene-grafted poly-(ethylene-co-tetrafluoroethylene) (ETFE-St) membrane and Nafion 212 were evaluated. The behavior of each component in the membrane was as follows. The I₂ content in the ETFE-St membrane increased with an increase in the I₂ concentration of the immersed HIx solution, whereas I₂ absorption by Nafion 212 was minimal. The strong affinity of the ETFE-St membrane for I₂ was attributed to the formation of a charge-transfer complex with electron-donating aromatic groups. The ETFE-St membrane absorbed I[−] (also H⁺ under the neutral condition) in a HI-molality-dependent manner, whereas I[−] (H⁺) absorption by Nafion 212 was negligible. This difference was attributed to the I₃[−]-complex formation in the ETFE-St membrane, which was precluded in Nafion 212. The absorption of H₂O was greater for the ETFE-St membrane than for Nafion 212. Incorporation into Nafion 212 would not greatly stabilize H₂O while stabilizing H⁺ by a strong electrical attraction. These results accordingly clarified the affinity of the membranes for the HIx solution based on the excess Gibbs free energy calculated from the measured composition data and the estimated activity coefficients. The excess Gibbs free energy for I₂ was larger in the membranes than in the immersed solution, indicating a destabilization of I₂ in the membranes. Importantly, this difference agreed with the energy change estimated under the assumption that I₂ could form I₃[−] or the charge-transfer complex. The affinity for I₂ as well as between the sulfonic acid groups and H⁺ or H₂O is a factor determining the absorbability of the HIx solution.

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1. Introduction

The thermochemical water-splitting hydrogen production method, referred to as an iodine–sulfur (IS) process, is a promising means of energy production because it involves the use of high-temperature solar or nuclear heat with no CO₂ emission [1,2]. The basic chemical reactions involved in this process and the corresponding required temperatures are as follows:



Reaction (1.1) produces sulfuric acid and a HI–I₂–H₂O mixture (hereafter referred to as a HIx solution) from iodine (I₂), sulfur dioxide, and water (H₂O). Sulfuric acid is endothermically decomposed at elevated temperatures to produce oxygen as shown in Reaction (1.2). Gaseous HI from the HIx solution is decomposed to yield hydrogen through Reaction (1.3). In practice, the HIx solution has to be preconcentrated to allow the efficient decomposition of HI above the azeotropic equilibrium [3]. An electro-membrane separation technique, termed electro-electrodialysis (EED), has been proposed for this purpose [4–11]. EED involves electrolysis of the HIx solution in a two-compartment cell divided by a cation-exchange membrane. The iodide ion (I[−]) is generated from I₂ on the cathode by the redox reaction of I₂/I[−], whereas selective permeation of protons (H⁺) through the membrane occurs from anolyte to catholyte, thereby enhancing the HI concentration of the catholyte solution. Thus far, we have prepared new cation-exchange membranes for the EED process using radiation-induced graft polymerization and cross-linking methods, which facilitate facile control of their chemical, electrochemical, and mechanical

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properties [12–14]. These membranes allowed lower electric-power consumption compared to the commercially-available Nafion membrane [5].

The EED performance was evaluated on the basis of membrane-performance indexes [5] presented below, which were theoretically formulated by introducing the fundamental EED model [4].

$$t_+ = \left[1 + \frac{D_{I^-}^m n_{I^-}^m}{D_{H^+}^m n_{H^+}^m} \right]^{-1} \quad (1.4)$$

$$E = \frac{t_+ i l V_0 R T}{F^2 D_{H^+}^m n_{H^+}^m} \quad (1.5)$$

$$\beta = \frac{\varphi_0 S_e k T \sqrt{2 \varepsilon_0 \varepsilon_r R V_0 T} n_{H_2O}^m}{8 \pi e \eta S F D_{H^+}^m n_{H^+}^m \sqrt{n_{H^+}^m}} \quad (1.6)$$

Each of the indexes can be defined as follows: t_+ represents the permeation selectivity for H^+ with respect to I^- ; E is the cell voltage, but it is practically equated to the IR drop across the membrane, normally originating from the permeation for ions because of the other negligibly-small resistances [4,6]; and β is the quantity of water permeated with H^+ . Based on prior publications [4,6–9], these membrane-performance indexes depend on the temperature and concentration of the Hlx solution to be concentrated. Although the effect of temperature was clarified for our EED model [4], the effect of concentration on the indexes has not been elucidated. Previous research [6] suggested a deterioration of EED in terms of these indexes during prolonged operation using a Hlx solution with high HI concentration. Thus, the membrane performance is expected to be highly sensitive to the composition of the Hlx solution fed to the cell. Accordingly, the concentration dependence of the three indexes is of great interest.

It follows reason that the composition of the feed Hlx solution should influence the extent of its absorption on the ion-exchange membrane [15]. The feed is hereafter referred to as “bulk solution” in order to distinguish from the Hlx solution inside the membrane. In line with the discussion presented in the previous paragraph, varying the composition of the bulk solution leads to the absorption of different total amounts of the Hlx solution and various compositions, which directly determines the membrane-performance indexes. In fact, Eqs. (1.4–1.6) include the content of ions (i.e., H^+ and I^-) and H_2O inside the membrane. We also recognized the possibility that the diffusion in the membrane could mechanistically be related to the behavior of the components of the equilibrated solution such as the amount, the bonding state and so on [4]. Therefore, understanding the behavior of the ions and molecules in the membranes is important in order to seek optimization of the EED operation and more strict clarification of the diffusion mechanism over the future. The behavior of the components can be discussed by investigating the uptake compositions of the Hlx solution absorbed in the membrane.

In this paper, the absorption properties, i.e., the total uptake and compositions, of ion-exchange membranes are evaluated following immersion in bulk Hlx solutions of different compositions. The evaluated HI concentration range is comparable to or less than that of typical EED operation conditions (ca. 9–13 mol/kg [3]). The results of these absorption experiments are used to calculate excess Gibbs free energy for each of the ionic and molecular components, thereby allowing quantitative prediction of their absorbability in the membrane. On this basis, further insight into the affinity of the evaluated membranes for the Hlx solution is furnished.

2. Theory

The content of species i absorbed in the membrane, n_i^m ($i=H^+$, I^- , I_2 , and H_2O) under equilibrium conditions is theoretically treated for the charged ions, H^+ and I^- , and for the non-ionic molecules, I_2 and H_2O , in Sections 2.1 and 2.2, respectively.

2.1. Contents of H^+ and I^- in membrane

The chemical potentials of ion i in a solution and in a cation-exchange membrane are respectively described by [11,16]

$$\mu_i = \mu_{i,C}^\circ + RT \ln a_{i,C} + z_i F \phi \quad (2.1)$$

$$\mu_i^m = \mu_{i,C}^\circ + RT \ln a_{i,C}^m + z_i F \phi^m \quad (2.2)$$

where the standard chemical potential and activity are based on molarity. The standard states of the solution and membrane are referred to infinite dilution. These two chemical potentials equilibrate at the membrane/solution interface.

$$\mu_i = \mu_i^m \quad (2.3)$$

Thus, the following relation between the activities of H^+ and I^- can be obtained.

$$a_{H^+,C} a_{I^-,C} = a_{H^+,C}^m a_{I^-,C}^m \quad (2.4)$$

The mean activity of HI in a solution, a_{HI} , is defined as

$$a_{HI,C}^2 \equiv a_{H^+,C} a_{I^-,C} \quad (2.5)$$

The molarity-based activities of species i (including HI) in the solution and membrane are respectively defined as

$$a_{i,C} \equiv \gamma_{i,C} C_i \quad (2.6)$$

$$a_{i,C}^m \equiv \gamma_{i,C}^m C_i^m \quad (2.7)$$

Substitution of Eqs. (2.5–2.7) into Eq. (2.4) gives the following formula:

$$C_{H^+}^m C_{I^-}^m = \frac{(\gamma_{HI,C} C_{HI})^2}{\gamma_{H^+,C}^m \gamma_{I^-,C}^m} \quad (2.8)$$

The neutral condition in the membrane is given by

$$C_{H^+}^m = C_{I^-}^m + C_{-SO_3}^m \quad (2.9)$$

The concentration of species i in the membrane is thus expressed by

$$C_i^m = \frac{n_i^m}{V_0} \quad (2.10)$$

Based on Eqs. (2.8–2.10), the contents of H^+ and I^- in a cation-exchange membrane are given by

$$n_{H^+}^m = \frac{n_{-SO_3}^m}{2} + \sqrt{\frac{n_{-SO_3}^m - 2}{4} + \frac{(\gamma_{HI,C} C_{HI} V_0)^2}{\gamma_{H^+,C}^m \gamma_{I^-,C}^m}} \quad (2.11)$$

$$n_{I^-}^m = -\frac{n_{-SO_3}^m}{2} + \sqrt{\frac{n_{-SO_3}^m - 2}{4} + \frac{(\gamma_{HI,C} C_{HI} V_0)^2}{\gamma_{H^+,C}^m \gamma_{I^-,C}^m}} \quad (2.12)$$

As described in detail in Appendix A, the molarity-based activity coefficient of the ions in a solution can be converted to its mole-fraction-based counterpart.

$$n_{H^+}^m = \frac{n_{-SO_3}^m}{2} + \sqrt{\frac{n_{-SO_3}^m - 2}{4} + \frac{(d_{H_2O} V_0 \gamma_{HI,x} X_{HI})^2}{M_{H_2O}^2 \gamma_{H^+}^m \gamma_{I^-}^m}} \quad (2.13)$$

$$n_{I^-}^m = \frac{n_{-SO_3}^m}{2} + \sqrt{\frac{n_{-SO_3}^m - 2}{4} + \frac{(d_{H_2O} V_0 \gamma_{HI,x} X_{HI})^2}{M_{H_2O}^2 \gamma_{H^+}^m \gamma_{I^-}^m}} \quad (2.14)$$

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