Electrochemical Behaviour of Hydrogen in Low-Viscosity Phosphonium Ionic Liquids

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The electrochemical and diffusive properties of hydrogen in low-viscosity phosphonium ionic liquids were investigated by the electrochemical methods such as cyclic voltammetry and chronoamperometry. The hydrogen redox reactions were concluded to be a quasi-reversible system in phosphonium-based ionic liquids. The diffusion coefficients of hydrogen in these ionic liquids were of the order of 10^{-10} m^2 s^{-1} at 25 °C. Additionally, the obtained activation energy of the diffusion process for hydrogen was 11.2 – 15.9 kJ mol^{-1} estimated from the temperature dependence of the diffusion coefficients.

A new type of proton conducting medium such as triethylphosphonium bis(trifluoromethylsulfonyl)amide was synthesized by the neutralization reaction, because the trialkylphosphine-based ionic liquids with good stability at higher temperature and high conductivity were appropriate candidates. This proton conducting membrane containing the ionic liquids with trialkylphosphine-based cations and the polyvinylidenefluoride-co-hexafluoropropylene has been fabricated in the present study. The proton conducting membrane exhibits relatively high ionic conductivity along with good mechanical stability.

Key words: Ionic Liquid; Phosphonium Cations; Hydrogen; Diffusion Coefficients.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are emerging as one of the most promising and environment friendly alternative devices in various transport, stationary, and portable applications [1]. The Nafion perfluorinated ionomeric membrane generally applied in these PEMFCs possess high ionic conductivity, good thermal and chemical stability, excellent mechanical strength, etc. [2]. PEMFCs are generally operated at 80 °C under fully hydrated conditions. However, the poisoning problem of the platinum catalyst by carbon monoxide still remains the performance of the fuel cell. This harmful situation would be recovered by operating the fuel cell at higher temperature. However, the Nafion membrane could not be used at higher temperature, because the conductivity of the Nafion membrane drastically decreases above 80 °C due to the loss of humidity. Therefore, some different alternative membranes which could be used at temperatures above 100 °C have been developed recently [3 – 5].

As one of the hopeful approaches for this problem, in recent, ionic liquids (ILs) due to several kinds of their unique properties such as high conductivity, low vapour pressure, wide temperature liquid range, good thermal and chemical stability, etc. are focused on the significant candidates. In addition, ILs containing various amide anions, which are stable in air and moisture, are receiving much attention due to their potential applications in many diverse fields [6]. They generally consist of a combination of organic cations such as imidazolium, pyridinium, pyrrolidinium, ammonium, sulfonium, and phosphonium, and bulky and soft anions, such as CF_3SO_3, $N(CF_3SO_2)_2$, PF_6, and BF_4 [7, 8]. As a large number of combinations of anions and cations are possible, so the physicochemical properties of ILs can be controlled by a suitable choice of the composition of the IL. In recent, the ILs composed of relatively small phosphonium cations [9, 10] were in particular focused on the novel ILs in comparison with the nitrogen based aromatic and aliphatic cations, because the phosphonium ILs have significantly low viscosity and high ionic conductivity, which are practical advantages for various applications. However, there were few reports about the electrochemical behaviour of hydrogen in phosphonium ILs and the proton conduction electrolytes using this kind of ILs. Therefore the electrochemical and diffusive properties of hydrogen were investigated in phosphonium-based ILs in this study. In addition, the proton conducting gel polymer electrolyte using trialkylphosphine-based ILs was fabricated, and we investigated the applicability for the PEMFCs.

2. Experimental

2.1. Preparation of Phosphonium-Based ILs

The trialkylphosphine-based ILs such as $[\mathrm{P_{XXXH}}][\mathrm{TFSA}]$ ($X = 2,4,8$) are schematically illustrated in Figure 1. These proton conducting materials were prepared from the following process. Triethylphosphonium bis(trifluoromethylsulfonyl)-amide $(\mathrm{C_2H_5})_3\mathrm{P}\text{-}\mathrm{N(SO_2CF_3)_2}$, $[\mathrm{P_{222H}}][\mathrm{TFSA}]$ were prepared by the neutralization reaction of triethylphosphine $(\mathrm{C_2H_5})_3\mathrm{P}$ (TEP) with 1,1,1-trifluoro-N-(trifluoromethyl)sulfonyl-methane-sulfonamide $\mathrm{HN(SO_2CF_3)_2}$ (HTFSA). TEP was supplied by Nippon Chemical Industrial Co., Ltd. (trade name Hishicolin® P-2, 20% toluene solution). HTFSA was used as purchased from Kanto Chemical Co., Inc. The neutralization reaction of TEP with HTFSA was carried out in a toluene/water biphasic medium at 80 °C to obtain the corresponding TFSA salt. The resulting crude liquid was separated and then purified by washing with pure water and *n*-hexane several times. The liquid obtained was dried under high vacuum for at least 12 h at 100 °C and was stored in an argon atmosphere glove box. The products were confirmed by ^{1}H, ^{13}C, ^{19}F, and ^{31}P nuclear magnetic resonance (NMR) spectra. The water contents in the sample, which was measured by using a Karl Fischer moisture titrator (Kyoto Electronics Manufacturing Co., Ltd., MKC-610), was less than 50 ppm.

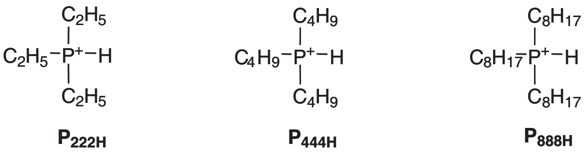

Fig. 1. Schematic illustration of the proton conducting molecular structure.

The preparation of quaternary phosphonium-based ILs such as $[\mathrm{P_{222Y}}][\mathrm{TFSA}]$ ($Y = 5,8,12$) [9, 10] was carried out according to the procedure described in the recent paper. The synthesized ILs were dried in a vacuum chamber at 393 K for 72 h. The preparation of comparative quaternary ammonium ILs such as $[\mathrm{N_{222Y}}][\mathrm{TFSA}]$ ($Y = 5,8,12$) was basically followed by the similar procedure as for phosphonium ILs.

2.2. Electrochemical Measurements

All electrochemical measurements such as cyclic voltammetry (CV) and chronoamperometry (CA) were connected with an electrochemical analyzer (ALS-660B, BAS Inc.). For the electrochemical measurements a cylindrical cell composed of a three-electrode system was used. A platinum (Pt) electrode with 1.6 mm inside diameter was employed as working electrode. This working electrode was washed with a diluted acid solution and polished with a diamond paste (1 µm) and an alumina paste (0.05 µm) before the measurements. A platinum wire with 1 mm inner diameter was used as counter electrode. As reference electrode, a silver wire immersed in 0.1 mol dm^{-3} tetrabutyl ammonium perchlorate/acetonitrile solution with a Vycor glass separator was applied for all measurements. The hydrogen (GL Sciences Inc., 99.99%) was introduced into the ILs in an air-tight cell. The bubbling of hydrogen was maintained until the hydrogen redox peak current in CV showed a constant value.

2.3. Fabrication of Ionic Liquid-Polymer Gel Electrolytes

Polymer electrolyte membranes containing polyvinylidenefluoride-co-hexafluoropropylene (PVdF-HFP, Kynar flex 2751) and several kinds of ILs with ammonium and phosphonium cations were mixed with 4-methyl-2-pentanone (Wako Chem. Co. Ltd., 99.9%) and fabricated by the solution casting method. PVdF-HFP was dissolved in 4-methyl-2-pentanone and then the IL was added in stoichiometric quantities along with continuous stirring to obtain a homogeneous viscous solution which was then poured in polypropylene dishes. The solvent was allowed to evaporate slowly resulting in the formation of polymer electrolytes in the form of free-standing films which were dried under vacuum for 24 h.

The ionic conductivity of the membranes was determined in a hermetic cell by means of complex impedance measurements over the frequency range from 1 Hz to 100 kHz at an AC amplitude of 5 mV. The measurements were conducted at controlled temperatures ranging from 25 – 150 °C. The samples were thermally equilibrated at each temperature for at least 0.5 h prior to the measurements. The bulk resistance of the polymer electrolyte was obtained from the impedance spectrum, and then the ionic conductivity was calculated. The variation of the ionic conductivity with temperature was studied by placing the cell in a temperature controlled furnace.

3. Results and Discussion

3.1. Diffusion Coefficients of Hydrogen in Phosphonium-Based ILs

The cyclic voltammogram of $2H^+/H_2$ in $[P_{2225}][TFSA]$ containing saturated hydrogen is shown in Figure 2. An anodic and a cathodic peak current at -0.47 and -0.66 V was assigned to the oxidation and the reduction of hydrogen, respectively. The anodic and cathodic peak current densities were almost proportional to the square root of the sweep rates, which indicated that the mass transport process was almost controlled by the diffusion process. However, the peak width between anodic and cathodic peaks was approximately 190 mV at $0.10\ \mathrm{V\,s^{-1}}$ and therefore relatively larger than the theoretical value for a reversible reaction with one electron transfer even though the drop in resistance current was physically compensated. Thus, the hydrogen redox reaction would be evaluated as a quasi-reversible system. The chronoamperogram of $2H^+/H_2$ in $[P_{2225}][TFSA]$ containing saturated hydrogen is shown in Figure 3. The limiting current density in CA was observed under a potential less than -0.7 V. The current density is inversely proportional to the square root of time as represented by Cottrell's equation [11],

$$i(t) = \frac{nFD^{1/2}C^*}{\pi^{1/2}t^{1/2}}, \tag{1}$$

where i is the current as a function of time t, D the diffusion coefficient, n the number of electrons, F Faraday's constant, C^* the bulk concentration of the electroactive species, respectively. The calculated diffusion coefficients of hydrogen are listed in Table 1. The diffusion coefficient of hydrogen in phosphonium ILs is relatively larger than that in corresponding am-

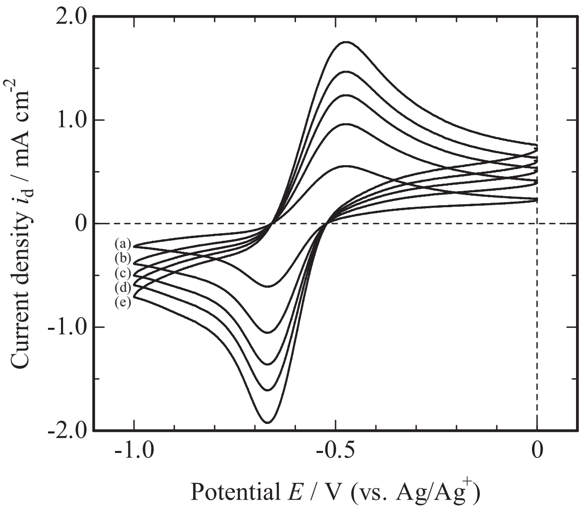

Fig. 2. Cyclic voltammograms of $2H^+/H_2$ using a Pt electrode in $[P_{2225}][TFSA]$ containing saturated hydrogen at 25 °C with various sweep rates: (a) 0.01, (b) 0.03, (c) 0.05, (d) 0.07, and (e) $0.10\ \mathrm{V\,s^{-1}}$.

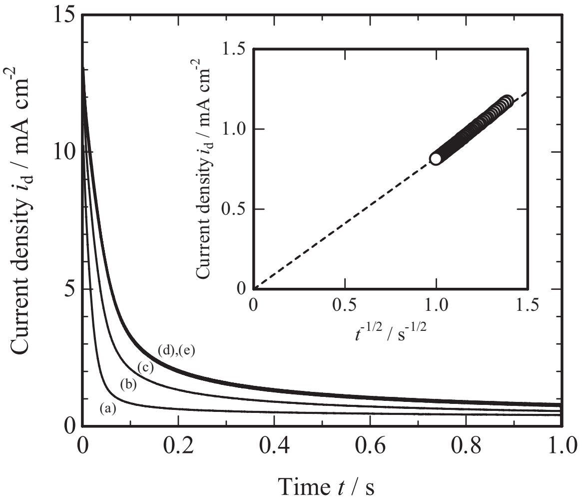

Fig. 3. Chronoamperograms of $2H^+/H_2$ using a Pt electrode in hydrogen-saturated $[P_{2225}][TFSA]$ containing saturated hydrogen at 25 °C with various potentials: (a) -0.5 V, (b) -0.6 V, (c) -0.7 V, (d) -0.8 V, and (e) -0.9 V.

Table 1. Diffusion coefficients (D), vistosity (η), and Stokes radius (r_s) for hydrogen in TFSA-based ILs.

Cation species	D at 25 °C 10^{-10} [$m^2 s^{-1}$]	η [mPa s]	r_s [nm]
P_{2225}	4.4 ± 0.2	88	0.056
P_{2228}	3.2 ± 0.2	129	0.053
P_{22212}	2.0 ± 0.3	180	0.061
P_{222H}	9.3 ± 0.2	40	0.047
P_{444H}	5.3 ± 0.3	75	0.046
P_{888H}	1.9 ± 0.3	160	0.048
N_{2225}	2.2 ± 0.2	172	0.058
N_{2228}	1.6 ± 0.3	217	0.063
N_{22212}	1.1 ± 0.3	316	0.063
N_{222H}	6.2 ± 0.2	62	0.047
EMI	5.5 ± 0.3 [19]	34 [20]	0.047
BMI	8.8 ± 0.4 [19]	52 [20]	0.114
N_{2226}	3.2 ± 0.3 [19]	167 [21]	0.134
P_{66614}	2.9 ± 0.3 [19]	450 [22]	0.326
BMP	1.8 [14]	70	0.173
N_{1116}	4.6 [14]	135	0.035

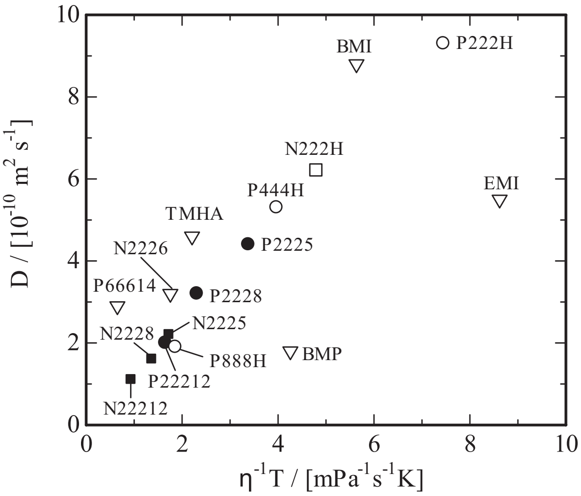

Fig. 4. Relationship between the diffusion coefficients of hydrogen and the inverse of the viscosity in TFSA-based ILs at 25 °C.

monium ILs. This result is explained by the electrostatic interaction around hydrogen in phosphonium ILs which is weaker than that of ammonium ILs. The fast diffusion of hydrogen also can be correlated with the weak interaction between hydrogen and organic species consisting of ILs, while the metallic species such as rare earths [12] in phophonium ILs have a diffusion coefficient of the order of 10^{-12} $m^2 s^{-1}$. In addition, the diffusion process of hydrogen is not influenced by the apparent viscosity of ILs as presented in Figure 4. This behaviour is consistent with the diffusion of oxygen [13, 14] in TFSA-based ILs, because there is almost no electrostatic interaction between the organic ions and the hydrogen or oxygen molecules. We conjecture that the trialkylphosphine-based cations can be assisted by the mass transport of the hydrogen molecule, because the diffusion coefficients of hydrogen in trialkylphosphine-based ILs are relatively larger than those in quaternary phosphonium-based ILs.

In the Stokes–Einstein relation [15], for a simple diffusing species, a linear relationship is expressed between the diffusion coefficients and the inverse of viscosity,

$$\frac{D\eta}{T} = \frac{k}{6\pi r_s}, \tag{2}$$

where η is the viscosity, T the absolute temperature, k the Boltzmann constant, and r_s the hydrodynamic radius of the diffusing species, respectively. This relationship is commonly followed in conventional molecular solvents and also for organic molecules in ILs. The Stokes radii seemed to be diversely scattered, and this result indicates that the Stokes–Einstein relation can not be applied for hydrogen species due to the small size of the hydrogen molecules.

The temperature dependence of the diffusion coefficient for hydrogen in trialkylphosphine-based ILs and quaternary phosphonium ILs is shown in Figure 5. The diffusion coefficients of hydrogen in both trialkylphosphine and quaternary phosphonium-based ILs are elevated linearly with increasing temperature. The diffusion coefficient is related with the temperature by the Arrhenius equation represented in the following equation:

$$D = A \exp\left(-E_a/RT\right), \tag{3}$$

where A is the pre-exponential factor and E_a the energy of activation. The logarithmic plot of the diffusion coefficients against the inverse of the temperature resulted in an almost straight line and the apparent activation energy of the diffusion process was calculated from the obtained slopes as tabulated in Table 2. The activation energies of hydrogen diffusion in quaternary phosphonium-based ILs are in good agreement with those for [N_{1116}][TFSA] [14] and [BMP][TFSA] [14]. As for the comparison of

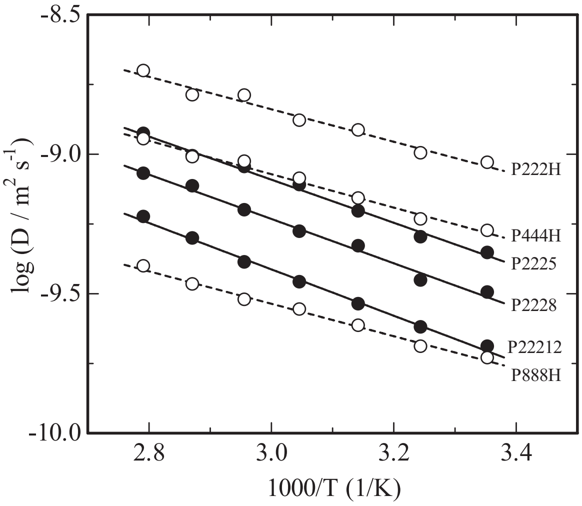

Fig. 5. Temperature dependence of the diffusion coefficients for hydrogen in trialkylphosphine and phosphonium-based ILs containing saturated hydrogen.

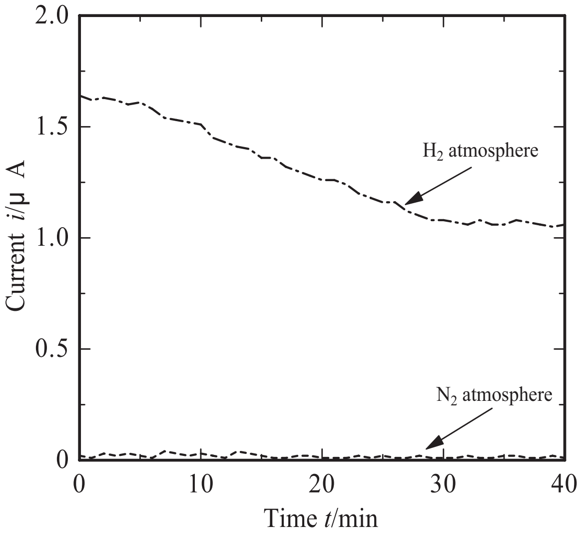

Fig. 6. Direct current observed during potentiostatic polarization of PVdF-HFP + [P_{222H}] under hydrogen or nitrogen atmosphere.

Table 2. Activation energies (E_a) of the diffusion process for hydrogen in TFSA-based ILs.

Cation species	E_a [kJ mol^{-1}]	Ref.
P_{2225}	14.8	This work
P_{2228}	15.2	This work
P_{22212}	15.9	This work
P_{222H}	11.2	This work
P_{444H}	11.5	This work
P_{888H}	11.2	This work
BMP	16.3	[14]
N_{1116}	19.3	[14]

phosphine- and phosphonium-based ILs, the activation energies for trialkylphosphine-based ILs such as [P_{XXXH}][TFSA] ($X = 2,4,8$) are lower than those for quaternary phosphonium-based ILs such as [P_{222Y}][TFSA] ($Y = 5,8,12$). Thus above result would indicating that the interaction between the hydrogen and the organic spices is weaker, and the proton in trialkylphosphine-based ILs is helpful for the diffusion transfer of the hydrogen.

3.2. Preparation of Gel Polymer Electrolyte Using Alkylphosphine-Based ILs

According to the above descriptions, the [P_{XXXH}][TFSA] ($X = 2,4,8$) are suitable candidates for ionic conducting materials. Therefore, we prepared the gel polymer electrolyte by mixing these trialkylphosphine-based ILs with PVdF-HFP. The simple fabrication process by the solution casting method allowed us to obtain the transparent and chemically stable membrane. The proton conductivity of the fabricated membranes was investigated by the direct current method at hydrogen or nitrogen atmosphere. The current was directly measured by each electrode attached with the membrane composed of PVdF-HFP and [P_{222H}][TFSA] as shown in Figure 6. The current of the membrane was merely observed in the hydrogen atmosphere and the result was expressed for the evidence of the proton conducting membrane.

The dependence of ionic conductivity on temperature for this membrane is shown in Figure 7. The ionic transport behaviour for the temperature dependence is of Arrhenius-type, and this behaviour can be described occasionally by the Vogel–Tammann–Fulcher (VTF) equation [16],

$$\sigma = AT^{-0.5}\, e^{B/T-T_0}\,, \tag{4}$$

where A is the pre-exponential factor, T_0 a reference temperature, and B a pseudo-activation energy for the charge-carriers motion. This VTF equation is a phenomenological way to interpret ion transport data in

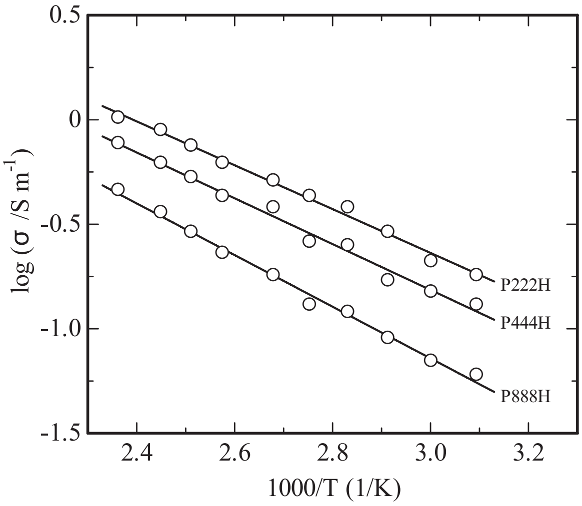

Fig. 7. Dependence of the ionic conductivity of gel polymer electrolytes for PVdF-HFP + trialkylphosphine-based ILs upon the reciprocal temperature.

polymer electrolytes. In particular, VTF behaviours of viscosity and ionic conductivity have been reported for ILs [17]. In this study, the calculated activation energy in trialkylphosphine-based electrolytes was similar to the value for the pyrrolidinium-based electrolytes [18]. Finally, the ionic conductivity of polymer electrolytes increased proportionally with temperature and reached a value of $1.02 \cdot 10^{-2}$ S m^{-1} at 150 °C. Thus, this new low-viscosity IL-based membrane blended [P_{XXXH}][TFSA] ($X = 2,4,8$) with PVdF-HFP was developed in this study. In comparison to Nafion-based polymer films, although the proton conductivity would not be high around room temperature due to the large transport losses in the electrode, this proton conducting electrolytes would be applicable for PEMFCs at higher temperature.

4. Conclusion

The oxidation and reduction reactions of hydrogen in phosphonium-based ILs proceeded a quasi-reversible system. The calculated diffusion coefficients of hydrogen in phosphonium-based ILs were relatively larger than those in ammonium-based ILs. This fact resulted in the electrostatic interaction between anion and cation in phosphonium-based ILs which was weaker than that in ammonium-based ILs, associated with low viscosity and high conductivity in phosphonium ILs compared with ammonium ILs. Moreover, the diffusion coefficients of hydrogen in TFSA-based ILs gradually increased with elevating temperature, and the temperature dependence of the diffusion process for hydrogen obeyed the Arrhenius equation.

Novel proton conducting media such as triethylphosphonium bis(trifluoro methylsulfonyl)amide were synthesized and the diffusion properties of these materials were investigated. The diffusion coefficients of hydrogen in low-viscosity ILs were drastically larger. Moreover, the activation energies were estimated from the temperature dependence of the diffusion coefficients. Furthermore, the novel gel polymer electrolytes fabricated by the proton conducting trialkylphosphine-based ILs and PVdF-HFP exhibited high ionic conductivity and possessed sufficient mechanical strength, transparency, and flexibility. These new materials based on trialkylphosphine-based ILs were a hopeful candidate for the application of polymer electrolyte membrane fuel cells.

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