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A new alkyl-imidazole polymer prepared as an inonic polymer electrolyte by in situ polymerization of dye sensitized solar cells

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Abstract

A new imidazole polymer was synthesized in order to develop an ionic polymer electrolyte for quasi-solid-state dye sensitized solar cells (DSCs). The polymers are prepared by co-polymerization of alkyl-bis(imidazole)s and diiodoalkyls. The resultant polymer can be regarded as a molten salt type polymer because the polymer chains consist of alkyl-midazolium salts. This polymer is suitable for quasi-solidification of electrolytes in DSCs by in situ polymerization because the polymerization reaction proceeds even in solutions containing iodine. A photon to electron conversion efficiency of the cell containing the ionic polymer electrolyte is 1.3% under a light intensity of 100 mW cm^{-2} (air mass 1.5).

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1. Introduction

Dye sensitized solar cells (DSCs) have been intensively investigated since the discovery of high efficient cells [1]. DSCs are regarded as promising alternative candidates for conventional silicon solar cells because of their simple structure and relatively high photon to electron conversion efficiency. However, improvement in the long term stability of DSCs is an important requirement for practical use of DSCs as a reliable energy device. The low stability of DSCs is attributed to two reasons: (1) evaporation of the liquid electrolyte solvent and (2) leakage of liquid electrolyte at high temperatures.

Recently, room temperature molten salts (RTMS) have received attention because of their remarkable properties including nonvolatility, chemical and thermal stability and high ionic conductivity. The evaporation durability of liquid electrolytes can be improved by the use of RTMS as an electrolyte solvent (ionic liquid electrolyte). Since the discovery of air stable RTMS [2], various investigations have been carried out to apply ionic liquid electrolytes to electrochemical devices such as DSC [3,4]. On the other hand, research on matrix materials solidifying liquid electrolytes has also been undertaken to improve the leakage durability of liquid electrolytes. Furthermore, ionic gels and ionic polymer electrolytes prepared by incorporating ionic liquid electrolytes into matrix materials have been investigated to improve the leakage and evaporation durability of the electrolytes. Various materials, ethylene oxide copolymer [5,6]; polyvinylpyridine cross-linked copolymer [7]; viniliden–propylene copolymer [8,9]; organic molecular [10]; inorganic particles [11] have been used as matrices for ionic gels and ionic polymer electrolytes to fabricate quasi-solid-state DSCs.

We have investigated imidazole polymers that are suitable for quasi-solidification of ionic liquid electrolytes by in situ polymerization. In general, quasi-solid-electrolytes have difficulty permeating into the pores of TiO_2 electrodes because of high viscosity. However, this problem can be solved by thermal polymerization after permeation of the monomer and electrolyte into the pores of the TiO_2 electrode [7].

Imidazole polymers are prepared by co-polymerization of alkyl-bis(immidazole)s (**1**) and alkyl-bis(halogen)s (**2**) according to the reaction shown in Scheme 1. The resultant polymer (**3**) can be regarded as a molten salt type polymer

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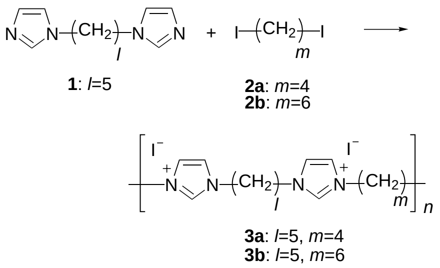
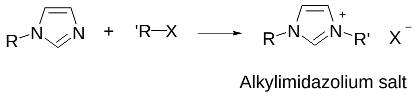


Scheme 1. Schematic of alkylimidazolium polymerization.



Scheme 2. Reaction of alkylimidazolium salt formation.

because the polymer chains consist of alkyl-midazolium salt. Several molten salt type polymers have been prepared by radical polymerization of vinyl derivatives containing an imidazolium salts [12,13]. On the other hand, the polymerization reaction of **1** with **2** proceeds by alkylimidazolium salt formation, which is a general method for preparation of imidazolium salt type RTMS (Scheme 2). Polymer **3** has several beneficial features for preparation of ionic polymer electrolytes: (i) reactivity of the monomer molecule can be controlled by modification of the alkyl chain length and reaction temperature; (ii) the polymerization reaction proceeds even in solutions containing iodine; (iii) degradation of electrolytes by the addition of polymer is minimized because (a) by-products are not produced by the polymerization reaction, (b) addition of polymerization initiator is not required and (c) changes in the chemical properties are small due to the structural resemblance of polymer **3** to imidazolium salt type RTMS. Above all (i) and (ii) are important properties of monomers to prepare ionic polymer electrolytes by in situ polymerization.

Here, we report the properties of synthesized alkylimidazolium polymers and results of ionic polymer electrolyte application to DSC.

2. Experimental

1,1′-(1,5-Pentamethylene)bis(imidazole) (**1**) was prepared by a coupling reaction of 1,5-dibromopentane with 2 mol of imidazole potassium salt in tetrahydrofuran (THF) according to procedures described previously [14]. 1,4-Diiodobutane (**2a**) and 1,6-diiodohexane (**2b**) were purchased from Avocado Research Chemicals and used without further purification.

Equimolar mixtures of monomers **1** and **2a** or **1** and **2b** were prepared. The monomer mixtures were heated at 25 and 100 °C to accelerate the polymerization reaction. The polymerization test was also carried out using equimolar monomer mixtures **1** and **2a** containing 0.32 M (M = mol dm^{-3}) iodine. As an index for the degree of polymerization, the viscosity of monomer mixtures was evaluated by measuring the peel-off strength, namely, the force necessary to separate a pair of glass plates (area: 1.0 cm^2) after polymerization of 2 μl of the monomer mixture between the glass plates.

The reaction times of the imidazolium salt formation were tested using 50 mmol of equimolar mixtures of 1-methylimidazole and alkyliodides (methyliodide, buthyliodide or hexyliodide).

Three ionic polymer electrolytes with different polymer concentrations were prepared; the first ionic polymer electrolyte (0.47 M) was composed of iodine (0.30 M), **1** (0.47 M) and **2a** (0.47 M) in 1-methyl-3-(3-methylbutyl)-imidazolium iodide (**4**); the second ionic polymer electrolyte (1.1 M) was composed of iodine (0.30 M), **1** (1.1 M) and **2a** (1.1 M) in **4**; the third ionic polymer electrolyte (1.9 M) was composed of iodine (0.30 M), **1** (1.9 M) and **2a** (1.9 M) in **4**. Liquid and ionic liquid electrolytes were also prepared to compare with the ionic polymer electrolytes. Their compositions were as follows, liquid electrolyte: iodine (0.05 M), lithium iodide (0.10 M), 4-*tert*-butylpyridine (0.50 M) and 1,2-dimethyl-3-propylimidazolium iodide (0.30 M, Shikoku Corp.) in 3-methoxyacetonitrile; ionic liquid electrolyte: iodine (0.30 M) in **4**. The **4** is a novel RTMS, used as a solvent and an iodide anion (I^-) source in the ionic liquid and ionic polymer electrolytes was synthesized in our laboratory.

Fabrication method of the TiO_2 photoelectrode is outlined below. TiO_2 colloidal paste (Ti-nanoxide T, particle size: 13 nm, Solaronix) was spread on a fluorine-doped tin oxide conducting glass electrode (FTO, Asahi Glass). A mixed suspension of ZrO_2 (0.08 g, JRC-ZEO-1: particle size 36 nm), TiO_2 (0.8 g, JRC-TIO-5: particle size 0.5–1 μm, JRC-ZEO-1 and JRC-TIO-5, reference catalysts obtained from the Catalysis Society of Japan), cellulose polymer (0.08 g, Marpolose 60MP-50, Matsumoto Yushi Seiyaku), polyethylene glycol (0.80 g) and water (4 ml) was applied on the TiO_2 layer as a light scattering layer. After sintering at 450 °C for 30 min, the TiO_2 electrodes were soaked into a 0.3 mM solution of ruthenium dye [15] (N719, Solaronix) in a solvent of acetonitrile and *tert*-butanol (volume ratio: 1:1) at room temperature for 12 h. The thickness of the TiO_2 layer was 6 μm and that of the ZrO_2 layer was 5 μm. The TiO_2 electrodes coated with ionic polymer electrolyte were placed on a counter electrode (Pt sputtered FTO) to assemble solar cell. The cell was fixed in a holder and placed at 25 °C to allow permeation of the ionic polymer electrolyte into the TiO_2 electrode. Then the cell was heated at 100 °C to accelerate the polymerization reaction.

Photocurrent–voltage curves were measured at room temperature (20–25 °C) under simulated sunlight (AM 1.5, 100 mW cm^{-2}). The active area of the TiO_2 photoelectrode was 0.50 cm^2 and unsealed type solar cells were used for all the measurements.

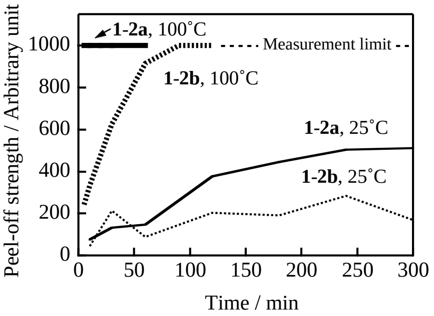


Fig. 1. Time-course for peel-off strength of monomer mixtures **1**–**2a** and **1**–**2b** heated at 25 or 100 °C.

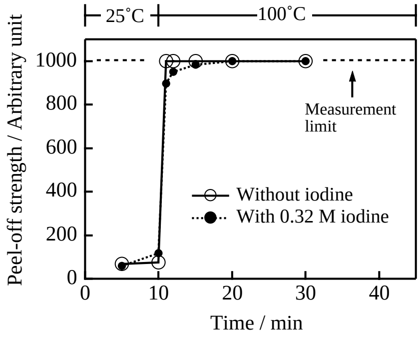


Fig. 2. Changes in peel-off strength of monomer mixtures **1**–**2a** and **1**–**2a** with 0.32 M (M = mol dm^{-3}) iodine by change in temperature from 25 to 100 °C.

3. Results and discussion

The monomer mixtures **1**–**2a** and **1**–**2b** are not clear solutions, but transparent solids were obtained when the polymerization reactions were completed. Fig. 1 shows the results of the peel-off test of monomer mixtures at temperatures of 25 and 100 °C. The peel-off strength of **1**–**2a** is larger than that of **1**–**2b** at each temperature because the polymerization reaction became faster in proportion to the reactivity of the monomer molecules. The monomer **2a**, containing short alkyl chain, showed higher reactivity than **2b**. A similar relationship between alkyl chain length and molecular reactivity was also observed in the imidazolium salt formation reaction shown in Scheme 2. Several examples of differences in the reaction time until the end of the imidazoliun salt formation at 20 °C are given below, 1,3-dimethylimidazolium iodide (DMImI: R=CH_3, R′=CH_3, X=I) 5 min; 1-butyl-3-methylimidazolium iodide (BMImI: R=CH_3, R′=C_4H_9, X=I) 22 h; 1-hexyl-3-methylimidazolium iodide (HMImI: R=CH_3, R′=C_6H_{13}, X=I) 40 h. The reaction time of BMImI and HMImI at 100 °C is 4 and 7 min. Fig. 1 also shows that in the same monomer mixture, the peel-off strength at 100 °C is larger than at 25 °C because the polymerization reaction is accelerated at the high temperature. From these results, it was found that the reactivity of the monomer molecule is controllable through adjustment of the alkyl chain length (l or m, Scheme 1) and reaction temperature. The control of reactivity of a monomer molecule is an important consideration for application of monomers to in situ polymerization.

The monomer mixture **1**–**2a** was used as a polymerization reagent in the following experiments because of its short polymerization time at a high temperature.

Fig. 2 presents the results of the peel-off test for monomer mixtures **1**–**2a** without iodine and **1**–**2a** with 0.32 M iodine. In both cases, although the peel-off strength at 25 °C was low, this strength rapidly increased with an increase in the degree of polymerization by heating the monomer mixture at 100 °C. It is apparent from this results that monomer mixture **1**–**2a** is suitable for in situ polymerization of DSC electrolytes because the polymerization reaction is accelerated at high temperatures even if the solution contains iodine. In general, vinyl monomers are difficult to polymerize in DSC electrolytes because radical intermediates are deactivated by iodine [16]. On the other hand, the polymerization reaction of **1** with **2a** was not inhibited by iodine because the reaction proceeds with the formation of imidazolium salt.

Fig. 3 shows the time-course for the peel-off strength of ionic polymer electrolytes at three polymer concentrations (0.47, 1.1, 1.9 M, M = mol dm^{-3}). Peel-off strength became larger with an increase in polymer concentration and heating time at 100 °C. However, conversion efficiency decreases according to an increase in polymer concentration and heating time (Fig. 4) because the increase in viscosity causes a decrease in the ionic conductivity of the electrolytes. Although the use of ionic polymer electrolytes **1**–**2a** cause a decrease in conversion efficiency, the cell fabrication becomes easy because viscous electrolytes act as an adhesive. Viscous polymer electrolytes have advantages and also disadvantages for DSCs. Depending on the purpose, the important thing for a polymer electrolyte is that the polymer concentration is controlled to adjust the balance between conductivity and viscosity.

In Fig. 4, the conversion efficiencies decreased immediately when the cells were heated at 100 °C. This was

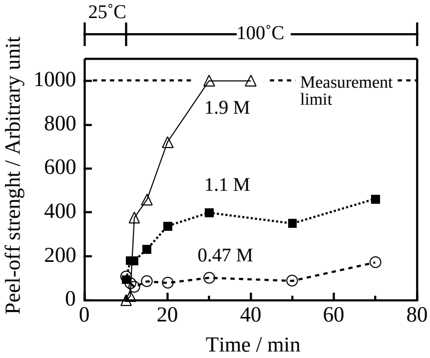


Fig. 3. Time-course for peel-off strength of ionic polymer electrolytes at different polymer concentrations (0.47, 1.1 and 1.9 M, M = mol dm^{-3}).

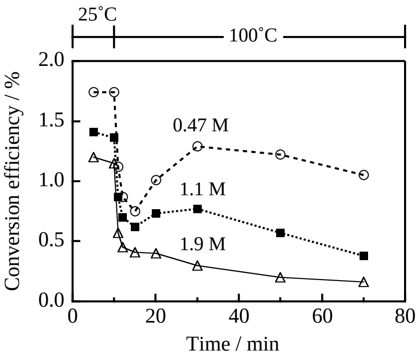


Fig. 4. Time-course for conversion efficiency of the cells with ionic polymer electrolytes at different polymer concentrations (0.47, 1.1 and 1.9 M, M = mol dm^{-3}).

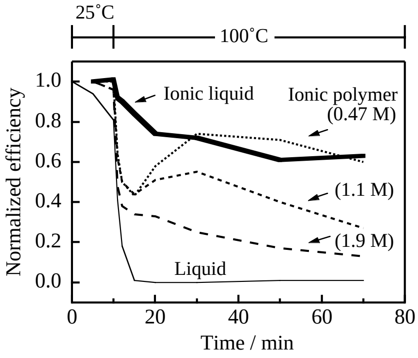


Fig. 5. Time-course for normalized conversion efficiency of cells with various electrolytes.

probably due to the evaporation of the remaining **2a** (bp 108 °C) in the ionic polymer electrolyte.[2]

Fig. 5 shows the time-course for normalized conversion efficiency of DSCs with various types of electrolytes. In the case of the liquid electrolyte, the efficiency decreased immediately as the cell was heated at 100 °C because of the evaporation of the electrolyte. In the case of the ionic liquid electrolyte, the evaporation of the solvent did not occur and heat stability of the cell was improved. However, the efficiency decreased slowly because iodine leaked out of the electrolyte at the edge of the solar cell. In the 0.47 M ionic polymer electrolyte, conversion efficiency decreased instantly at the start of heating at 100 °C. However, the efficiency was recovered at approximately 30 min and the efficiency was kept at almost the same value as the ionic liquid electrolyte. Other ionic polymer electrolytes (1.1, 1.9 M) showed lower efficiencies because viscosity of the electrolytes became higher with the higher polymer concentration.

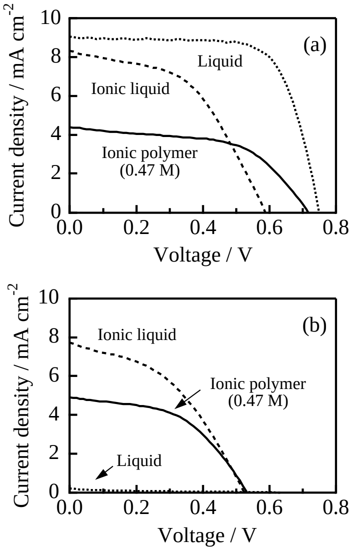


Fig. 6. Photocurrent density (*J*)–voltage (*V*) curves of cells with ionic polymers, ionic liquid or liquid electrolytes: (a) *J*–*V* curves of cells heated at 25 °C for 5 min; (b) *J*–*V* curves of cells heated at 25 °C for 10 min and then heated at 100 °C for 20 min. The measurements were taken under simulated sun light (AM 1.5, 100 mW cm^{-2}).

Fig. 6(a) shows the photocurrent density (*J*)–voltage (*V*) curves of DSCs heated at 25 °C for 5 min. Fig. 6(b) shows the *J*–*V* curves of the cells heated at 25 °C for 10 min and then 100 °C for 20 min. The cell characteristics are summarized in Table 1(a) and (b) (V_{oc}: open circuit voltage; J_{sc}: short circuit photocurrent density; FF: fill factor; η: conversion efficiency). Change in the *J*–*V* curves of the liquid electrolyte between Fig. 6(a) and (b) was drastic. However, changes in the ionic liquid electrolyte was small because evaporation of solvent did not occur. The reduce performance of the cell is attributed to evaporation of iodine. In Fig. 6(a), the ionic polymer electrolyte showed a large V_{oc}, almost the same value as that of the liquid electrolyte, because monomers act as solvent increasing ionic conductivity.

Table 1
Characteristics of the cell photocurrent density–voltage curves shown in Fig. 6

Electrolyte	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	η (%)
(a) Heating at 25 °C for 5 min				
Liquid	0.74	9.1	0.72	4.8
Ionic liquid	0.58	8.5	0.49	2.4
Ionic polymer (0.47 M)	0.71	4.4	0.56	1.7
(b) Heating at 25 °C for 10 min and 100 °C for 20 min				
Liquid	0.63	0.2	0.14	0.02
Ionic liquid	0.52	7.7	0.43	1.7
Ionic polymer (0.47 M)	0.53	4.9	0.50	1.3

V_{oc}: open circuit voltage; J_{sc}: short circuit photocurrent density; FF: fill factor; η: conversion efficiency; M = mol dm^{-3}.

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[2] The evaporation of **2a** causes a decline in the electrical contact between the electrode and electrolyte because of the generation of small holes in the electrolyte. After finishing evaporation, the holes were filled with an electrolyte and electrical contact was recovered. A recovery of the efficiency was clearly observed in 0.47 and 1.1 M ionic polymer electrolytes (Fig. 4). But the recovery of the 1.9 M ionic polymer electrolyte was small because of the high viscosity and low conductivity of the 1.9 M ionic polymer electrolyte.

However, the V_{oc} decreased to the same value as that of the ionic liquid electrolyte after heating at 100 °C for 20 min because the monomers were consumed in the polymerization reaction.

4. Conclusion

Polymers consisting of alkylimidazolium salts were developed by these experiments. The reactivity of monomers can be controlled by adjusting the alkyl chain length in the monomer molecules and the reaction temperature. These polymers are suitable for fabricating ionic polymer electrolytes by in situ polymerization in DSCs because the polymerization reaction occurs even in solutions containing iodine. Although the conversion efficiency is decreased, solidification of the electrolyte by alkyl-imidazole polymers is still promising for the development of quasi-solid-state DSC.

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