Direct Ion-Exchange Method for Preparing a Solution Allowing Spontaneous Perovskite Passivation via Hole Transport Material Deposition

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ABSTRACT

We propose a direct ion-exchange (DI) method for preparing a hole transport material (HTM) solution undergoing spontaneous perovskite passivation via HTM deposition and verify its applicability for the photovoltaic performance enhancement of perovskite solar cells (PSCs). The simple synthesis of a Spiro-OMeTAD HTM solution based on ion exchange via dissolving and mixing multiple solid materials in a chlorobenzene solution produces an HTM solution similar to that obtained with an n-octylammonium bis(trifluoromethanesulfonyl)imide ionic liquid functioning as a spontaneous perovskite passivator. Using the resulting HTM solution, the power conversion efficiency of PSCs was enhanced up to 23.0% without conventional post-passivation processes.

Since demonstrating a power-conversion efficiency (PCE) of approximately 10% in 2012, perovskite solar cells (PSCs) have attracted considerable attention.[1, 2] The standard configuration of a PSC (i.e., n-i-p structure) comprises a transparent conductor, electron transport material, a perovskite photoabsorber, a hole transport material (HTM), and a metal conductor; a typical PSC is fluorine-doped tin oxide (FTO)/titanium oxide (TiO_2)/perovskite/2,2',7,7'-tetrakis-(*N,N*-di-4-methoxyphenylamino)-9,9'-spirobifluorene (Spiro-OMeTAD)/Au). In the last decade, PSCs have been developed using various techniques, including methods for decreasing carrier traps in perovskite photoabsorbers. Recent progress in PSCs involves the development of a means for perovskite passivation.[3-13] The deposition process of perovskite photoabsorbers requires heating treatment, which causes defect formation, especially over the perovskite surface that is exposed to the atmosphere. Perovskite passivation, which is typically conducted by casting a passivator material over the perovskite layers, can effectively suppress the defects on perovskite surfaces and thereby enhance the photovoltaic (PV) performance of PSCs. [3-13] However, conventional perovskite passivation requires an additional process, which should be ideally skipped to increase the process efficiency of PSC fabrication.

It was recently reported that the alkyl-primary-ammonium bis(trifluoromethanesulfonyl)imide (RA-TFSI) additive for the HTM solution allows the prominent function that could not be achieved by conventional RTIL HTM additives[14-18]: spontaneous perovskite passivation in the HTM deposition process in PSCs with the standard structure (i.e., n-i-p structure). Therefore, using RA-TFSI enhances process efficiency in the PSC fabrication by skipping the conventional passivation process.[19-22] The archetype material in this series is *n*-octylammonium TFSI (OA-TFSI) room-

temperature ionic liquid (RTIL)[19-21], which exhibits spontaneous perovskite passivation: during the deposition of the OA-TFSI additive-containing HTM solution, the OA cations spontaneously passivates the perovskite taking advantage of large adsorption energy of OA cation over perovskite surface (e.g., 1.88 eV[9]), while the TFSI anions effectively induce the formation of HTM cationic radicals, thereby improving hole collection. Therefore, spontaneous perovskite passivation using OA-TFSI has recently emerged as a promising approach.

However, the synthesis of novel materials such as RTILs can be challenging for numerous PSC researchers. Moreover, dealing with high-viscosity RTILs (e.g., OA-TFSI: 572 mPa s at 298 K[21]) may cause difficulties in the preparation of HTM solutions. Therefore, the development of a means for the direct preparation of an HTM solution functioning as a spontaneous perovskite passivator is instrumental in the development of the technique of spontaneous perovskite passivation and the broadening the use of this technique in the PSC research field.

Herein, we propose and demonstrate a direct ion-exchange (DI) method for preparing an HTM solution with spontaneous perovskite passivation. The DI method was conducted as follows: first, solid materials of *n*-octylammonium chloride (OACl), Li-TFSI, and Spiro-OMeTAD HTM were dissolved and/or dispersed in chlorobenzene (CB), the formed lithium chloride (LiCl) was subsequently removed by filtration, and finally, 4-*tert*-butylpridine (TBP) was added. (Figure 1) Using the HTM solution via this DI method, the PV performance of the present PSCs was effectively improved and a PCE of up to 23.0% was achieved. Therefore, this work plays an important role in realizing spontaneous perovskite passivation and will contribute to the further development of PSCs.
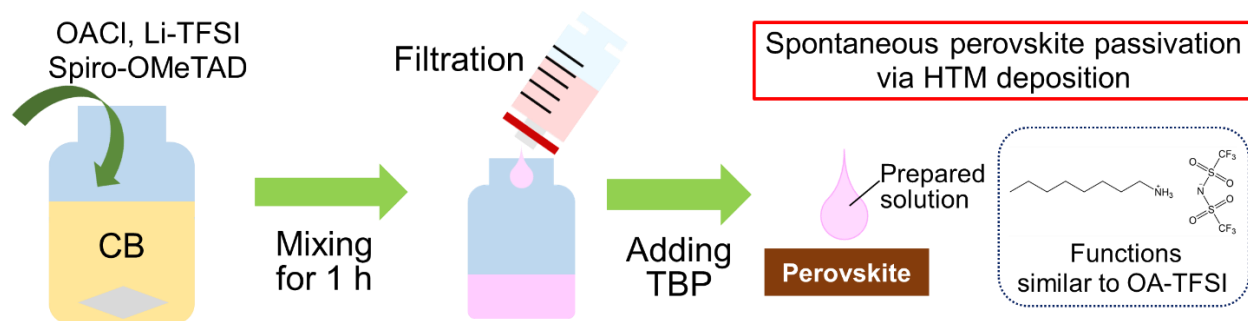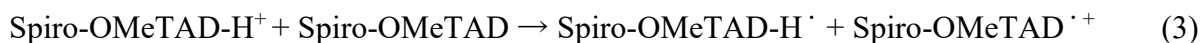
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Figure 1. Scheme of the DI method used to prepare an HTM solution that undergoes spontaneous perovskite passivation via HTM deposition

The details of the DI method are as follows. Multiple ion exchanges occurred in the first mixture of solutions comprising OACl, Li-TFSI, and Spiro-OMeTAD. The prime ion exchange between OACl and Li-TFSI proceeded (Equation 1) to form OA-TFSI and solid-state LiCl in the CB.

$$OACl + Li\text{-}TFSI \rightarrow OA\text{-}TFSI + LiCl \qquad (1)$$

OA-TFSI is extracted using a nonpolar solvent of chloroform (relative dielectric constant: 4.8) in the previous synthesis process of OA-TFSI.[19] Therefore, it is consistent that the remaining OA-TFSI in the present solvent of CB, which is nonpolar (relative dielectric constant: 5.6), and solid-state LiCl formed.

In addition to the ion-exchange reaction between OACl and Li-TFSI described in Equation 1, reactions with Spiro-OMeTAD are most likely involved in the synthesis of the HTM solution. It was recently reported that protons derived from OA cation protonates Spiro-OMeTAD[21] (Equation 2), and the reaction between protonated Spiro-OMeTAD and pristine Spiro-OMeTAD leads to the formation of Spiro-OMeTAD cation radicals (:Spiro-OMeTAD$^{.+}$, Equation 3)[16, 17, 21].

$$\text{Spiro-OMeTAD} + \text{H}^+ \rightarrow \text{Spiro-OMeTAD-H}^+ \qquad (2)$$

$$\text{Spiro-OMeTAD-H}^+ + \text{Spiro-OMeTAD} \rightarrow \text{Spiro-OMeTAD-H}^. + \text{Spiro-OMeTAD}^{.+} \qquad (3)$$

The role of the TFSI anion was to stabilize the Spiro-OMeTAD cation radicals via coordination between them (Equation 4),[11-15] and indeed, detectable Spiro-OMeTAD cation radicals were observed in the absorption spectra of the solution before filtration (Figure S3).

$$\text{Spiro-OMeTAD}^{.+} + \text{TFSI}^- \rightarrow \text{Spiro-OMeTAD}^{.+}\text{-TFSI}^- \qquad (4)$$

Accordingly, TFSI anions derived from Li-TFSI are most likely consumed via a reaction with Spiro-OMeTAD, which presumably facilitates solid-state LiCl formation. This is because this reaction (i.e., Equation 4) decreases the concentration of free TFSI anions, which can be counter anions of the Li$^+$ cations, so the reaction of Equation 1 is facilitated.

After the ion-exchange reaction described above, the formed LiCl was removed by filtration. The remaining Li content of the filtered solution was estimated to be 3.5 ppm by inductively coupled plasma, which is low considering the amount of initially added Li content (168 ppm), indicating that most of the Li species in the HTM solution were removed via filtration. It was recently reported that the addition of TBP to an HTM solution containing OA-TFSI and Spiro-OMeTAD plays a crucial role in controlling the protonation between OA cations and spiro-

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OMeTAD, in addition to improving the affinity between OA-TFSI and the HTM solution. [21] Therefore, finally, TBP was added to the HTM solution after the filtration.

The perovskite samples, including the PSCs, using an HTM solution prepared by the DI method were characterized. PSCs were fabricated by conventional methods[12, 19, 23, 24] with minor modifications (see SI for procedural details). After the deposition of a TiO_2 electron transport material onto a FTO transparent conductive glass, a formamidinium lead halide ($FAPbI_3$) perovskite layer was deposited by spin-coating. Subsequently, the Spiro-OMeTAD layer was deposited with the HTM solution via the DI method or a conventional set of additives (i.e., Li-TFSI, FK209, and TBP), and finally, the Au layer was deposited by thermal evaporation. PSCs with a standard configuration (i.e., an n-i-p structure) were obtained (Figure S1).

Figure 2 describes the characterization of samples with HTM solutions via the DI method (target) or conventional additives (reference). As the presence of OA on the perovskite surface renders the perovskite surface hydrophobic,[3, 12, 19] and contact angle (CA) measurements with water droplets for the pristine perovskite layers or that after the removal of HTMs (Figure 2a) were performed. Using the DI method, the CA over the perovskite layer ($79 \pm 1°$) became significantly large compared with that over the pristine perovskite ($55 \pm 2°$), indicating that OA cations were successfully deposited on the perovskite surface during the spontaneous perovskite passivation process. To investigate the perovskite passivation effect in suppressing defects, photoluminescence (PL) lifetime measurements for the perovskite layers after the removal of HTMs were performed (Figure 2b). The sample prepared via the DI method substantially extended the PL lifetime (953 ± 10 ns), compared with the reference (74 ± 1 ns), indicating that the

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spontaneous passivation by OA cations effectively suppressed the defects over the perovskite layer.[19, 24]

In addition, it has been reported that the Spiro-OMeTAD HTM solution with OA-TFSI, which exhibits spontaneous passivation, is also effective for the efficient formation of HTM cationic radicals, utilizing the absence of cations in the HTM core.[19, 21] As the SOMO correlating the Spiro-OMeTAD cationic radical is deeper than the HOMO of the pristine Spiro-OMeTAD, the deeper ionization energy (IE) is most likely indicative of a higher concentration of the Spiro-OMeTAD cationic radical in the HTM layer.[25] To investigate the effects of spontaneous passivation, IE measurements of the HTMs were conducted (Table 1). The HTM using the DI method resulted in a much deeper IE (5.45 eV) than that obtained with conventional additives (5.29 eV), supporting the occurrence of spontaneous perovskite passivation with the HTM solution via the DI method. Accordingly, the samples prepared using the DI method exhibited a similar trend as the reported samples containing OA-TFSI additives[19, 21], strongly suggesting a function similar to that of the OA-TFSI additive.
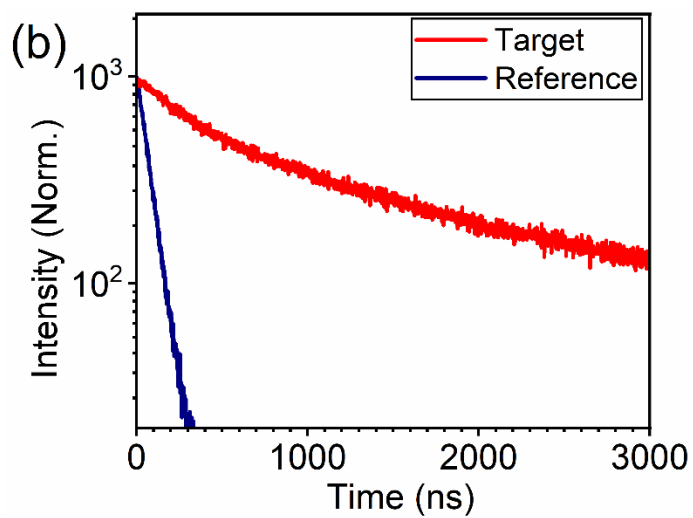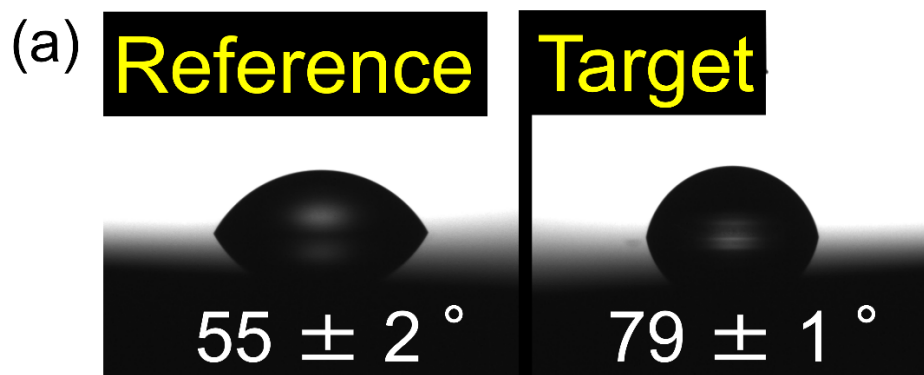
Figure 2. (a) CA of water droplets over perovskite layers after removal of HTMs, (b) PL lifetimes

of perovskite layers after removal of HTMs

Table 1. IEs of HTM layers

Sample	Ionization energy (eV)
Target	5.45
Reference	5.29

Figure 3. describes the PV performance of the PSCs. The PSCs produced using the DI method (target) exhibited considerably superior PV performance compared with the samples with conventional HTM additives (reference). The PV parameter distribution (Figure 3a) and the averaged values (Table S1) show that the target PSCs resulted in substantially higher PCEs (21.8 ± 0.8% in backward scan) than the reference PSCs (19.5 ± 0.8 in backward scan). Similarly, in the best-performing cells, the target PSC resulted in a considerably higher PCE up to 23.0% than the reference PSC up to 20.8 % (Table 2). Notably, the 23.0% PCE without the post-passivation process was relatively high in n-i-p structured PSCs and comparable to that of the previously reported PSC using the OA-TFSI additive.[19] This increase in PCE is attributed to the increase in V_{oc} (e.g., from 1.03 to 1.13 V of best-performing cells in the backward scan), representing the effectiveness of spontaneous perovskite passivation. We here note that J_{sc} in the J-V curve (Table 2) matches well with the integrated J_{sc} (Int. J_{sc}) as estimated from the EQE curve (Figure 3c). The lower difference of the target PSC (within 1% difference: J_{sc} = 25.5 mA cm^{-2} and Int. J_{sc} = 25.7 mA cm^{-2}) than the reference (approximately 2% difference: J_{sc} = 25.4 mA cm^{-2} and Int. J_{sc}: 24.8 mA cm^{-2}) might support the suppression of defects in the target sample. Besides, for long-term stability under humidity conditions (Figure S6, 30 °C, relative humidity 50%), the target PSC retained significantly higher PCE than the reference PSCs over 1000 h, owing to the resulting

hydrophobicity of perovskite surfaces via the spontaneous perovskite passivation (Figure 2a). Consequently, the utilization of the HTM solution prepared via the DI method effectively enhanced the PV performance of PSCs without conventional post-passivation treatment.
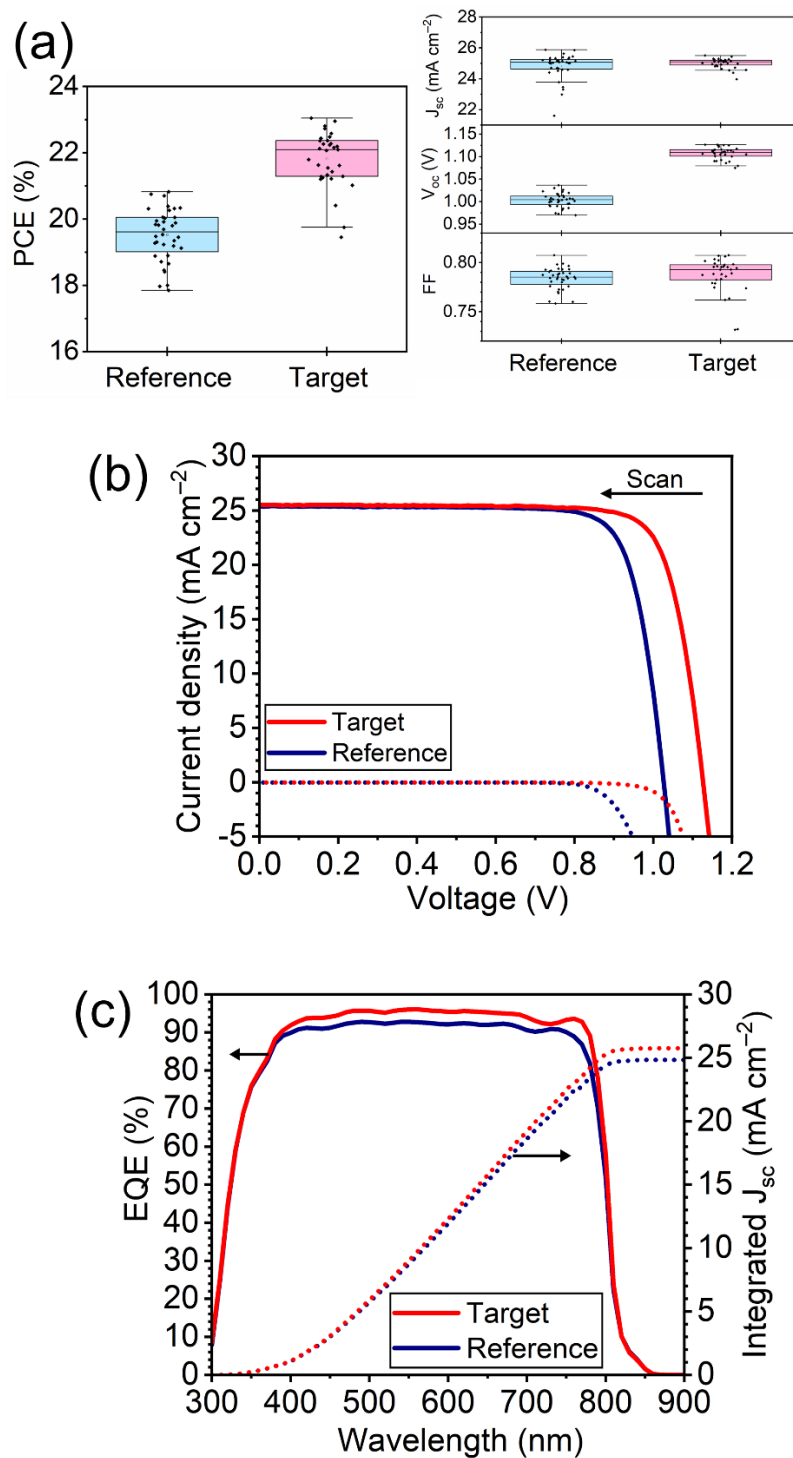
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Figure 3. (a) Distribution of PV parameters (in forward scan: Figure S4), (b) J-V curves of the best PSCs in backward scan (in forward scan: Figure S5), (c) EQE spectra

Table 2. PV parameters of PSCs

Sample	Scan	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
Target	Backward	25.5	1.13	0.80	23.0
	Forward	25.4	1.08	0.70	19.3
Reference	Backward	25.4	1.03	0.80	20.8
	Forward	25.4	0.95	0.71	17.2

In conclusion, a DI method for the simple preparation of an HTM solution exhibiting spontaneous perovskite passivation was proposed and demonstrated. Characterization of the samples fabricated using the DI method showed a trend similar to that of the OA-TFSI additive, representing the occurrence of spontaneous perovskite passivation. Moreover, the present PSCs fabricated using the DI method achieved a PCE of up to 23.0%, which is relatively high compared with the n-i-p structured PSCs without post-passivation treatments. This study provides novel insights into promising spontaneous passivation techniques, contributing to the broader adoption of this passivation method. Thus, this study will promote further advancements in PSCs.

ASSOCIATED CONTENT

Author Contributions

Naoyuki Nishimura: Conceptualization, Project administration, Investigation, Resources, Formal analysis, Writing – original draft, Writing – review & editing, **Hiroyuki Kanda:** Writing – review & editing, **Takurou N. Murakami:** Supervision, Funding acquisition, Writing – review & editing

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Supporting Information Available

Brief statement in nonsentence format listing the contents of the material supplied as Supporting Information

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Notes

There are no conflicts to declare.

ABBREVIATIONS

DI, direct ion exchange; HTM, hole transport material; PSC, perovskite solar cells; PCE, power-conversion efficiency; PV, photovoltaic; OA-TFSI, n-octylammonium TFSI; RTIL, room-temperature ionic liquid; CB, chlorobenzene; TBP, 4-tert-butylpridine; CA, contact angle; PL, photoluminescence, IE, ionization energy

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