Slot-Die Coating of a Formamidinium-Cesium Mixed-Cation Perovskite for Roll-to-Roll Fabrication.

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Most solution-processed perovskite solar cells (PSCs) fabricated using scalable techniques are based on 3-dimensional perovskites, ABX_3, where typically A is a cation or mixture of cations such as methylammonium (MA), formamidinium (FA) or caesium (Cs), B is lead(II) or tin(II), and X is chloride, bromide, iodide anions or combinations thereof. PCEs of up to 14.1% have been reported for small-area PSCs (active area 0.16 cm^2) produced using R2R processes on flexible substrates [1-3]. PSCs fabricated using a perovskite layer containing only the MA cation generally show lower stability to high temperatures and constant illumination than when the perovskite layer comprises the FA cation or a mixture of cations, e.g. FA/Cs cations [4-7]. A problem with using FA as the sole organic cation in the perovskite formulation is that higher phase-transformation temperatures (>150 °C) are required during processing [4, 8-10]. Partial substitution of the FA content with Cs to give perovskite compositions $FA_{1-x}Cs_xPbI_3$ has been found to reduce the phase-transformation temperature of the perovskite layer, as well as resulting in improved PSC environmental stability [6, 7].

In the present work, nitrogen flow was used as a means to promote perovskite nucleation and crystallisation for the preparation of high quality $FA_{0.91}Cs_{0.09}PbI_3$ perovskite films using spin-coating or slot-die coating methods under ambient laboratory conditions. The addition of methyl ammonium chloride (MACl) to the perovskite formulation reduced the temperature required for the formation of the desired perovskite α-phase to less than 160 °C [11, 12]. The best-performing PSCs in this work were obtained by adding 2-(2,3,4,5,6-pentafluorophenyl)ethylammonium iodide (FEAI) to the precursor formulation, which improved the PSCs stability.[13]

The PV parameters for the PSCs (active area 0.2 cm^2) comprising the slot-die coated perovskite layers produced with or without 0.15 mol% FEAI additive in the precursor formulation are presented in **Figures 1a-d.** The PCEs for the devices comprising a slot-die coated perovskite layer containing 0.15 mol% of FEAI additive (average PCE: 17.4%, champion PCE: 18.4%) were higher than comparable devices that did not contain FEAI in the perovskite formulation (average PCE: 16.8%, champion PCE: 17.6%) (**Figure 1a**).

For both device types there was minimal hysteresis between the forward and reverse *J-V* scans (**Figure 1e**). Furthermore, a PSC composed of a slot-die coated perovskite layer using a 0.15 mol% FEAI additive level displayed a stable PCE of 17.9%, short-circuit photocurrent (J_{sc}) of 21.3 mA cm^{-2}, and an open-circuit voltage (V_{oc}) of 0.87 V under maximum power point (MPP) conditions for over 600 seconds when measured in a nitrogen filled glove box (**Figure 1f)**.

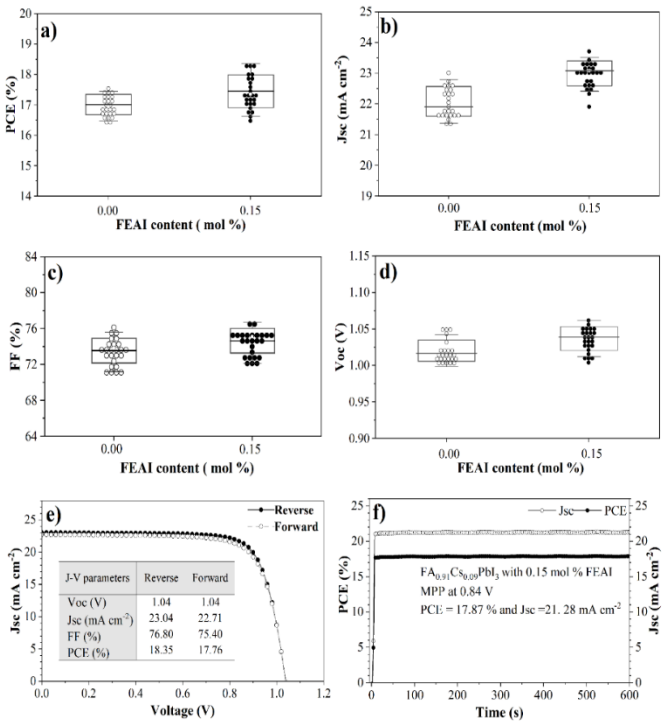

Figure 1. Photovoltaic parameters of PSCs prepared on glass substrates using slot-die coating of perovskite layers with or without 0.15 mol% FEAI. **a)** PCE, **b)** J_{sc}, **c)** FF, and **d)** V_{oc}. **e)** *J-V* curves of the champion device fabricated with 0.15 mol% FEAI. **f)** MPP of the champion device at 0.84 V for 600 seconds. The architecture of these PSCs was glass/ITO/SnO_2/perovskite/Spiro-OMeTAD/Au(20 nm)/Ag(80 nm).

Encapsulated PSC devices having a gold metal electrode (80 nm) and a slot-die coated perovskite layer produced either with or without FEAI in the precursor solution were measured at MPP under constant 1-sun illumination for 1000 h (**Figure 2**).

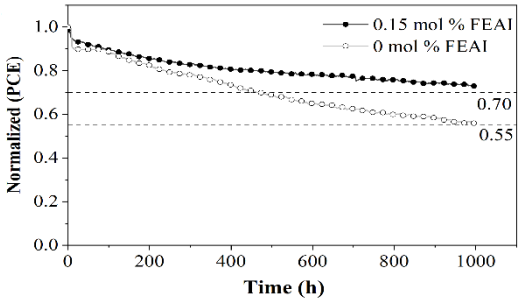

Figure 2. Stability of encapsulated PSCs under constant 1-sun illumination for 1000 h in an ambient laboratory atmosphere. Devices comprise a slot-die coated perovskite formulation with or without 0.15 mol% FEAI.

The initial PCE of the PSC produced without FEAI additive decreased by around 45% over this period, whereas use of 0.15 mol% FEAI in the perovskite formulation resulted in a device showing only a 30% decrease in PCE (**Figure 2**). The higher stability of the PSC having the slot-die coated perovskite film and containing the FEAI additive may be related to the decrease in the defect density in the perovskite film induced by the addition of the FEAI. A similar effect has been reported for PSCs where *n*-butylammonium or phenylammonium cations were used as additives. [6, 14].

For the fabrication of flexible perovskite solar cells (f-PSCs), the R2R slot-die coater comprises a slot-die coating head to which the perovskite formulation is channelled via a syringe pump, and a N_2 outlet fitted with a flowmeter (**Figure 3a**). After coating, the perovskite layer was annealed at 135 °C for around 3 minutes. A coating speed of 0.1 m min^{-1} was used to ensure sufficient

residence time of the substrate on the hot plates to achieve an annealing time of approximately three minutes. Under these conditions it was possible to obtain the fully cubic perovskite phase, which has previously been one of the primary difficulties in forming high-quality perovskite films on PET substrates (**Figure 3b)**. The R2R-processed perovskite films consisted of dense, compact grains (**Figure 3c**), similar to those derived from the spin-coated or slot-die coated perovskite films on glass-based substrates.

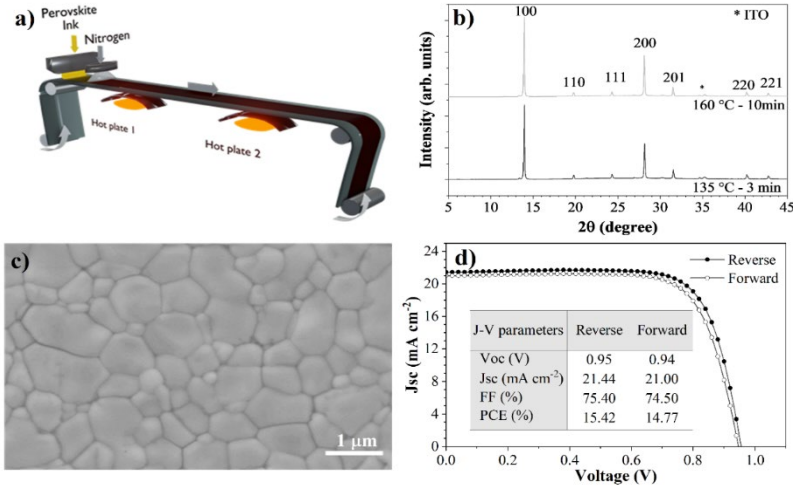

Figure 3. **a)** Schematic illustration of the slot-die coating process using a continuous R2R system. **b)** XRD patterns of the perovskite films annealed at 160 °C for 10 minutes and 135 °C for 3 min using the R2R process on a flexible PET substrate. **c)** SEM image of the perovskite film fabricated using the R2R system. **d)** *J-V* curves of a device fabricated using R2R printing, comprising the structure of OPV8/SnO_2/$FA_{0.91}Cs_{0.09}PbI_3$/Spiro-OMeTAD/Au (80 nm). The SnO_2, perovskite and Spiro-OMeTAD layers were also coated using the R2R system under ambient laboratory conditions without humidity control (up to 50% RH).

The PV parameters for the PSCs (device area 0.2 cm^2) fabricated using the R2R approach are summarized in **Figure 4**. The PCEs were in the range of approximately 12-15%, with the best-performing device having a PCE of 15.4% (V_{oc} 0.95 V, J_{sc} 21.4 mA cm^{-2}, FF 75.4%). These photovoltaic parameters are lower than that obtained for the slot-die coated devices on the glass substrates. These differences could be related to substrate wettability and surface smoothness which affected the quality of the printed SnO_2 and Spiro layers. This is amongst the highest PCEs reported to date for PSCs fabricated using a FA-Cs perovskite formulation where all layers apart from the metal anode are fabricated using R2R processing [1, 3, 15], low temperature annealing (<140 ºC), and ambient laboratory conditions without humidity control (25 °C, 40-50% RH). Notably, there was also minimal hysteresis between the forward and reverse scans. We note that the stability of the flexible devices on PET would be lower than the devices fabricated on glass substrates. The lower stability arises from PET having a higher permeability to oxygen and water than glass substrates, which can lead to degradation of the device components [10].

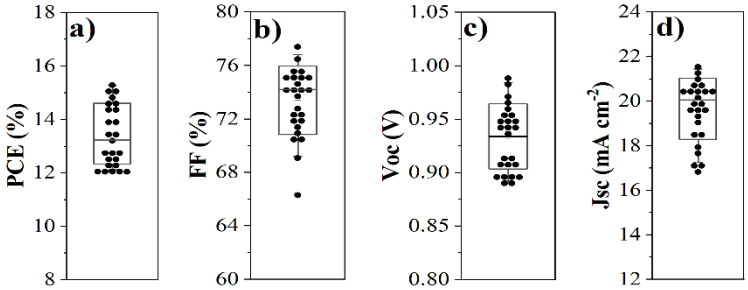

Figure 4. **a)** PCE, **b)** FF, **c)** V_{oc}, and **d)** J_{sc} distributions for 25 devices fabricated using the R2R system under ambient laboratory conditions. The device structure was PET/OPV8/SnO_2/$FA_{0.91}Cs_{0.09}PbI_3$/Spiro-OMeTAD/Au (80 nm).

In conclusion, the feasibility of applying a facile nitrogen-flow strategy for slot-die coated high-quality $FA_{0.91}Cs_{0.09}PbI_3$ perovskite films on a flexible PET film substrate under R2R conditions has been demonstrated, even when using relatively low annealing temperatures (135 °C). Inclusion of FEAI in the perovskite formulation also improved the stability of encapsulated PSCs comprising a slot-die coated perovskite layer fabricated on a rigid glass-based substrate, which retained 70% of their original PCE after 1000 h of continuous 1-sun illumination at maximum power point. Conventional n-i-p configuration PSCs comprising a perovskite layer R2R slot-die coated on a PET film substrate under ambient laboratory conditions produced devices having a maximum PCE of more than 15%, which is amongst the highest values reported for flexible PSCs fabricated using R2R. This work provides an insight into the processing conditions needed to produce high-quality $FA_{0.91}Cs_{0.09}PbI_3$ perovskite layers in a continuous R2R process, paving the way for upscaling the fabrication of high-performance and stable PSCs.

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