

Upscaling of polymer solar cells

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Summary of Key Findings

This report investigates the potential and challenges for all-polymer solar cells to be produced using scalable coating processes. Three systems are studied, two all-polymer blends (J52:N2200 and J71:PNDI-T10) and a novel polymer non-fullerene acceptor (NFA) system (PTQ10:ITIC-Br). The effect of increasing cell area from 0.045 cm² to 1.0 cm² for active layers prepared via spin-coating is first investigated. Decreases in efficiency are seen which are attributed to increased series resistance. Smaller cells are also found to benefit from “edge-effects” where carriers generated outside the nominal active area are collected. For spin-coated cells, efficiencies of ~6% for J52:N2200 cells, ~5% for J71:PNDI-T10 cells and ~9% for PTQ10:ITIC-Br cells are achieved. J52:N2200 and PTQ10:ITIC-Br cells produced by blade-coating, a scalable coating process, are described. For the J52:N2200 system a ~5% power conversion efficiency is achieved for 1.0 cm² blade coated cells while an efficiency of ~9% could be maintained for 1.0 cm² blade-coated PTQ10:ITIC-Br cells. For all-polymer solar cells, leakage current was found to decrease with active area for spin-coated cells, but increased with active area for blade-coated cells. For the polymer/NFA system studied leakage current was found to increase with active area for both spin-coated and blade-coated cells. Our findings demonstrate the potential for these systems to be coated at scale. Strategies to mitigate series resistance and improve the uniformity of blade-coated layers will help boost the efficiency of large area, scalably coated cells.

Introduction

A key attraction of polymer solar cells is the potential for high-throughput reel-to-reel printing that may enable the large scale fabrication of polymer solar cells at low cost.^{1,2} Much of the research into polymer solar cells is still at the academic (university) level, with devices produced using small-scale processes such as spin-coating that are not readily scalable. Indeed, the conditions of spin-coating are very different to that of printing, meaning that laboratory-scale results are often not easily reproduced in printed modules.³ Much of the early work on upscaling of polymer solar cells has focused on polymer/fullerene solar cells, where one component is a small molecule (fullerene derivative). Thus only one component, namely the polymer, is able to substantially affect the rheological properties of the solution which needs to be carefully tuned to ensure processability. Furthermore the crystallisation of the small molecule component during the longer coating time that accompanies printing may adversely affect film uniformity. An attraction of all-polymer solar cells is that they are based on a blend of two semiconducting polymers. Thus the rheological properties of the formulation are easier to tune, and it is more likely that optimum morphologies produced with spin-coating are replicated with large area coating. As cell area is increased, additional issues can be encountered such as increased series resistance. Furthermore, small cells when tested in a laboratory setting can benefit from “edge-effects” whereby charges can be collected from outside the nominal active area. The small active area of lab cells also has larger uncertainties, meaning that

so-called “champion cells” may not actually be performing any better, but rather may be benefitting from a larger active area than expected.

In this report, we investigate some of the issues facing the scaling up of polymer solar cell fabrication. First, we investigate the effect of increasing the nominal active area of our standard lab-scale cells from 0.045 cm² to 0.21 cm² to 36 cm² and finally to 1.0 cm². Secondly, we compare cells fabricated via blade-coating (a scalable process whose conditions are similar to those use in large scale manufacturing) to those fabricated using spin-coating. We find that the performance of blade-coated cells compare favourably to those of spin-coated cells indicating the potential for the large-scale reel-to-reel printing of these materials.

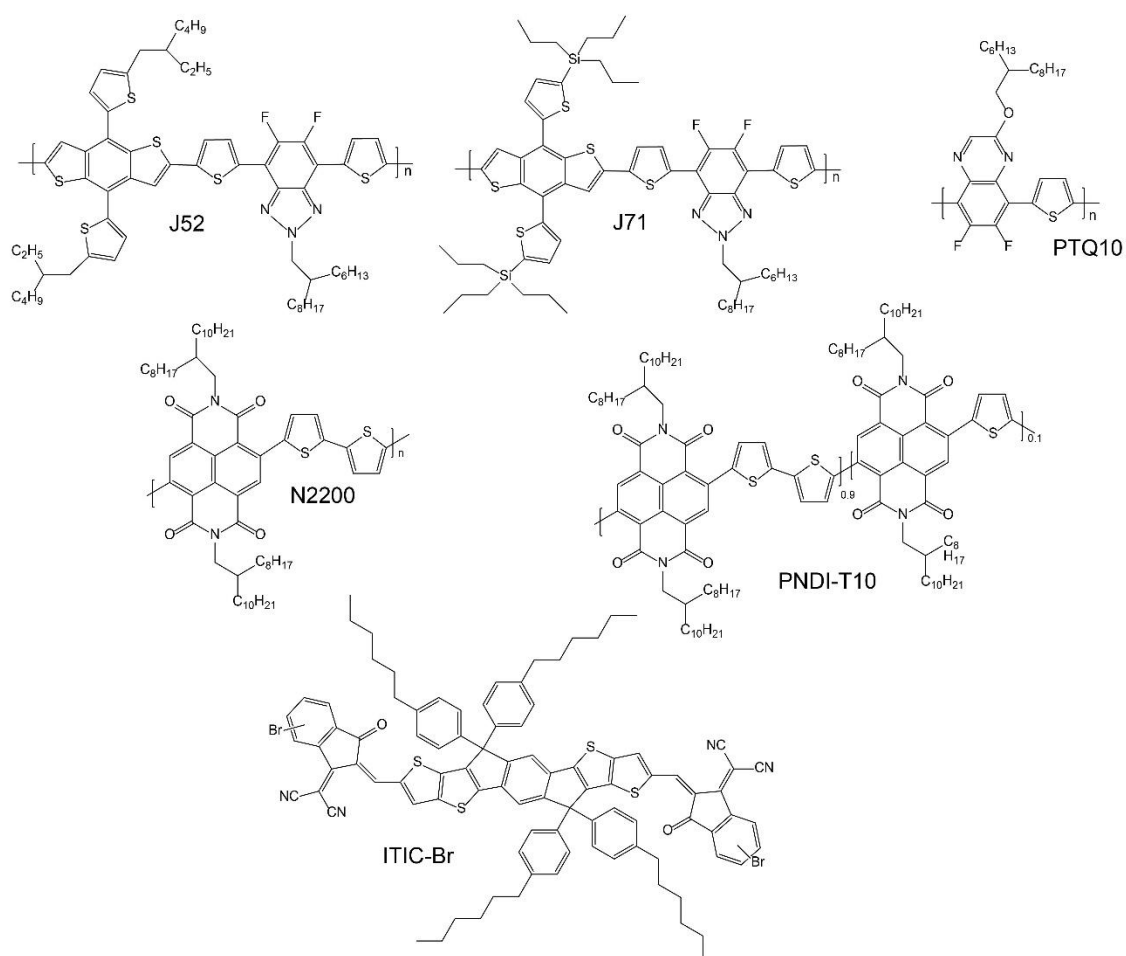


Figure 1 Chemical structures of the materials used in this study.

Methodology

Materials

Figure 1 presents the chemical structures of the materials used in this study. J52 ($M_n = 16$ kDa, $\bar{D} = 2.5$) and PTQ10 ($M_n = 41$ kDa, $\bar{D} = 2.1$) were purchased from 1-Material Inc. N2200 (also known as P(NDI2OD-T2)) was purchased from Raynergy Tek ($M_n = 32$ kDa, $\bar{D} = 2.1$). PNDI-T10 ($M_n = 17$ kDa, $\bar{D} = 2.6$) and ITIC-Br were synthesised in-house at Flinders University.

Device fabrication and characterisation

Solar cells were fabricated with an inverted architecture: ITO/ZnO/PEIE/active layer/MoO_x/Ag. ITO-coated glass substrates were cleaned firstly by sonication for 10 minutes in acetone, followed by sonication for another 10 minutes in isopropanol before oxygen plasma cleaning for 10 minutes. A 0.1 M ZnO precursor solution was prepared by dissolving 160 mg of zinc acetate dehydrate in 61 mg of ethanolamine and 10 mL of 2-methoxyethanol with vigorous stirring for 12 hours for the hydrolysis reaction at 60 °C. A 0.1 M ZnO precursor solution was then spin-coated onto cleaned ITO-coated glass at 3000 rpm for 30 s and annealed on a hot plate at 200 °C for 30 minutes to form a thin conducting layer. A PEIE layer was subsequently spin coated on top of the ZnO layer at 5000 rpm for 30 s and annealed on a hot plate at 110 °C for 15 mins to form a thin hole-blocking layer. The active layers of the solar cells were coated via spin-coating or blade-coating, with the optimum conditions specified in Table 1. Blade coating was performed in air using a home-made blade coater based on coater described by Stafford et al.⁴ Finally, a 13 nm MoO_x layer with a 100 nm Ag layer was thermally deposited. All top electrode layers were deposited via thermal evaporation in vacuo ($\sim 10^{-6}$ mbar) through a shadow mask to define electrodes with an active area of either 0.045 cm², 0.21 cm², 0.36 cm² or 1.0 cm². Devices were encapsulated with epoxy resin and glass cover slides before being moved from the glove box for testing. Current density–voltage (*JV*) characteristics for all devices were measured using a Keithley 2635 source meter. A Photo Emission Tech model SS50AAA solar simulator, simulating an AM1.5G radiation spectrum with 100 mW/cm² irradiance, was used. The intensity of the simulator was calibrated with a silicon reference cell with a KG3 glass filter. External quantum efficiency (EQE) was measured using a spot size smaller than that of the device active area. An Oriel Cornerstone 130 monochromator was used to disperse light from a tungsten filament (Newport 250 W QTH). Prior to measurement, this system was calibrated using a Thorlabs FDS-100CAL photodiode placed at the exact location of the devices during measurements.

Table 1. Summary of the optimum coating parameters for spin-coated and blade-coated cells.

System	Weight ratio	Casting solvent	Concentration (mg/mL)	Spin-speed / blade coating speed	Substrate / stage temperature
J52:N2200 spin-coating	1:1	Chlorobenzene	16	4000 rpm	Room temp.
J52:N2200 blade-coating	1:1	Chlorobenzene	32	13 mm/s	70 °C
J71:PNDI-T10 spin-coating	1:1	2-MeTHF	14	8000 rpm	Room temp.
PTQ10:ITIC-Br spin-coating	1:1	Chlorobenzene	20	1000 rpm	Room temp.
PTQ10:ITIC-Br blade-coating	1:1	Chlorobenzene	48	40 mm/s	70 °C

Results

For this study three systems were chosen: (i) J52:N2200, (ii) J71:PNDI-T10 and (iii) PTQ10:ITIC-Br. J52:N2200 and J71:PNDI-T10 are promising all-polymer systems whereas PTQ10:ITIC-Br is a novel polymer/small molecule non-fullerene acceptor (NFA) system. J52:N2200 and J71:PNDI-T10 were chosen because of their reasonable efficiencies and good stability compared to other systems studied. The PTQ10:ITIC-Br system is of interest as a PTQ10 is a low-cost donor polymer that can be synthesised via a 2-step reaction from inexpensive starting materials.⁵ The pairing of PTQ10 with ITIC-Br is novel and a separate scientific study on this new pairing will be reported separately.

Figure 2 presents a photograph of the evolution of device size and geometry. 12 mm by 12 mm substrates were initially used for small area devices with a nominal active cell area of 0.045 cm². Subsequently a larger 19 mm by 19 mm geometry was adopted with two different active cell areas

of 0.21 cm² and 0.36 cm². Finally, a different shadow mask geometry was adopted that provided cells of area 0.21 cm², 0.36 cm² and 1.0 cm² on the one substrate.

The effect of increasing cell size on devices produced by spin-coating of the active layer is considered first. The light and dark current density – voltage (*JV*) curves of J52:N2200, J71:PNDI-T10 and PTQ10:ITIC-Br solar cells for different cell active areas are shown in Figure 3. The corresponding performance parameters are summarised in Tables 2 to 4.

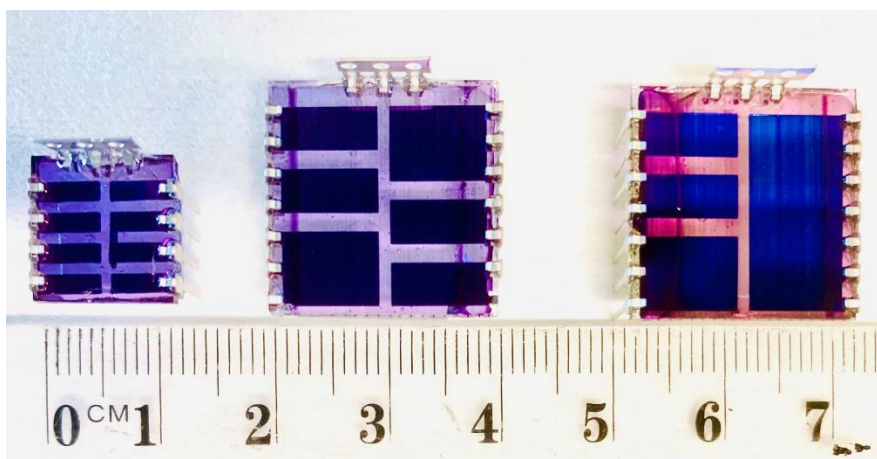
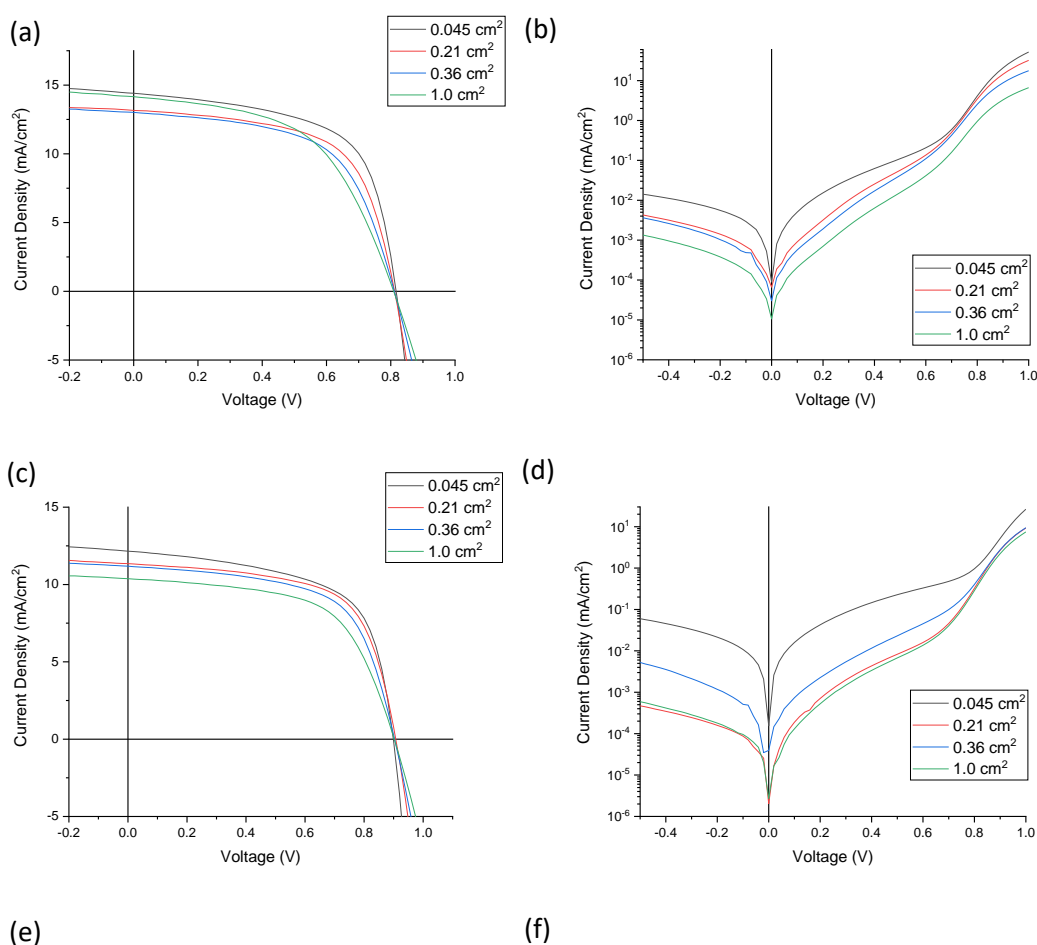


Figure 2 Devices with different size and geometry, (left) 0.045 cm², (middle) 0.21 cm², 0.36 cm² (right) 0.21 cm², 0.36 cm² and 1.0 cm²

For spin-coated J52:N2200 cells, Figure 3(a), a systematic drop in PCE is observed going from 0.045 cm² active area to 1.0 cm² active area, with PCE dropping from 7.3% to 6.0%. The open circuit voltage (V_{oc}) maintained a constant value of 0.81 V for all cell sizes. Cell fill factor (FF) was observed to systematically decrease with increasing cell area, decreasing from FF = 0.63 for an active area of 0.045 cm² to FF = 0.53 for an active area of 1.0 cm². This decrease in fill factor is most likely due to an increase in cell series resistance, with the slope of the *JV* curve at open circuit voltage systematically decreasing with increasing cell area. J_{sc} shows a more complicated behaviour, with the 1.0 cm² cell exhibiting a higher J_{sc} than the 0.21 cm² and 0.36 cm² cells, but slightly lower than that of the 0.045 cm² cell. These observations seem to indicate that increases in series resistance with increasing cell active area are the main cause of decreasing efficiency with increasing active area. Encouragingly the dark leakage current, Figure 3(b), actually decreases with increasing cell area, indicating that high-quality films which are essentially pin-hole free for cm²-sized devices can be realised.

For spin-coated J71:PNDI-T10 cells, Figure 3(c), a similar story emerges. PCE is again found to systematically decrease from 6.75% (0.045 cm² cell area) to 5.10% (1.0 cm² cell area). In this case J_{sc} also systematically decreases with increasing cell area. V_{oc} , however, is again essentially constant, but a more dramatic drop in FF is seen, going from FF = 0.69 (0.045 cm² cell area) to FF = 0.54 (1.0 cm² cell area). In our cell optimization, the solvent 2-methyltetrahydrofuran (2-MeTHF) which is a marginal solvent for PNDI-T10 was found to optimise small area cells compared to the solvent chlorobenzene which was used for J52:N2200. 2-MeTHF however has a high volatility which may not make it as suitable for large area coating. Thus while increased series resistance will also be contributing to the decreased cell efficiency with increasing active area, a suboptimal morphology for J71:PNDI-T10 films produced by spin-coating from 2-MeTHF on larger substrates may also be an issue. Similar to the J52:N2200 cells, the leakage current, Figure 3(d), was also suppressed in larger area cells.

For the spin-coated PTQ10:ITIC-Br cells, Figure 3(e), a more pronounced drop in cell efficiency with increasing active area is seen. Whereas for J52:N2200 a relative decrease in PCE of 17% was seen, and a relative decrease in PCE of 25% was seen, for PTQ10:ITIC-Br a 36% relative drop in PCE is seen, which decreases from an absolute value of 14.5% to 9.2%. Although a similar decrease in FF is seen, dropping from $FF = 0.67$ to $FF = 0.52$, a more pronounced drop in J_{SC} is seen which goes from $J_{SC} = 23.3 \text{ mA/cm}^2$ for the 0.045 cm^2 cell to 17.1 mA/cm^2 for the 0.36 cm^2 cell. In our optimisation, the PTQ10:ITIC-Br system was found to be especially sensitive to processing parameters such as spin-speed, so these variations may be related to variations in film microstructure when upscaling. Edge effects also seem to be playing a strong role, given the discrepancy between the measured J_{SC} (23.2 mA/cm^2) and the integrated J_{SC} based on EQE data (17.4 mA/cm^2) for the 0.045 cm^2 PTQ10:ITIC-Br cell. This discrepancy (33% overestimate) suggests that the carries in the PTQ10:ITIC-Br system have relatively high diffusion lengths enabling carries to be collected from further outside the active area of the cell. For comparison, the all-polymer systems have experimental J_{SC} values for the 0.045 cm^2 cells that are $\sim 17\%$ higher than the integrated EQE values. Looking at the dark current of the PTQ10:ITIC-Br cells, an increase in leakage current with increasing active area is seen, which is very different to what was seen for the two all-polymer systems. Indeed, the leakage current at -0.5 V increases by a factor of 1,000 going from 0.045 cm^2 cell area to 1.0 cm^2 cell area. This pronounced increase in leakage current with active area for the PTQ10:ITIC-Br system suggests that film quality and uniformity is inferior to that of the two all-polymer systems studied.



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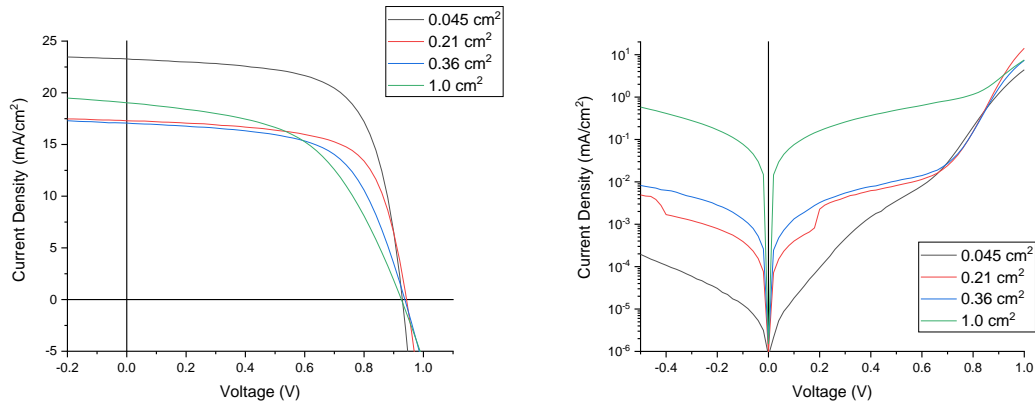


Figure 3. Light JV curves (left) and dark JV curves (right) of spin-coated J52:N2200, (a, b), J71:PNDI-T1, (c, d) and PTQ10:ITIC-Br, (e, f), solar cells produced by spin-coating for different active area size.

Table 2. Summary of the optimised performance parameters for spin-coated J52:N2200 cells as a function of cell area.

Cell area (cm ²)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
0.045	14.4	0.81	0.63	7.26
0.21	13.2	0.81	0.62	6.57
0.36	13.0	0.81	0.59	6.18
1.0	14.1	0.81	0.53	6.05

Table 3. Summary of the optimised performance parameters for spin-coated J71:PNDI-T10 cells as a function of cell area.

Cell area (cm ²)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
0.045	12.16	0.90	0.69	6.75
0.21	11.35	0.91	0.64	6.57
0.36	11.18	0.91	0.61	6.23
1.0	10.37	0.91	0.54	5.10

Table 4. Summary of the optimised performance parameters for spin-coated PTQ-10:ITIC-Br cells as a function of cell area.

Cell area (cm ²)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
0.045	23.27	0.93	0.67	14.5
0.21	17.29	0.94	0.67	10.96
0.36	17.07	0.93	0.62	9.82
1.0	19.03	0.93	0.52	9.21

The J52:N2200 and PTQ10:ITIC-Br systems were selected for blade coating trials. While J71:PNDI-T10 blends were found to give good efficiencies, the optimisation of spin-coated cells relied upon the use of the highly volatile solvent 2-MeTHF which was found not to be suitable for blade-coating. Figure 4 presents the light *JV* and dark *JV* data of J52:N2200 and PTQ10:ITIC-Br cells as a function of cell active area with performance parameters summarised in Tables 5 and 6. Discussing the J52:N2200 blade coated cells first, similar performance was achievable for cell areas up to 0.36 cm². Fill factor show a similar drop off with increasing cell area, which can again be mostly attributed to increased series resistance. The blade coated cells did exhibit lower V_{oc} , with the larger area cell showing a V_{oc} of 0.79 compared to 0.81 V for spin-coated cells. This decrease in cell VOC could be due to increased leakage current, with blade-coated cells exhibiting increasing dark current with increasing active area, opposite to what was seen for spin-coated cells. This suggests that film uniformity in blade coated layers needs to be improved to preserve the performance achieved in spin-coated layers. The lower efficiency of the 1.0 cm² blade coated cell (5.1%) compared to the 1.0 cm² spin-coated cell (6.0%) is mainly due however to the lower J_{sc} of the blade-coated cell. This lower JSC may be associated again with film uniformity and in particular being able to maintain an optimum active layer thickness over a large area. For the cells prepared here, the substrate was not much larger than the cell active area; it is hard to maintain film uniformity at the edges of the substrate so shifting to larger substrates may overcome this issue.

For the blade-coated PTQ10:ITIC-Br cells, a PCE of 9.0% was achieved for an active area of 1.0 cm^2 which compares favourably with that achieved via spin-coating (9.2%). Similar trends in FF, J_{SC} and V_{OC} were seen for blade-coated PTQ10:ITIC-Br cells with increasing active area as for spin-coated cells. Leakage current again increased with increasing active area as seen for spin-coated cells. Larger leakage current was seen for the 1.0 cm^2 PTQ10:ITIC-Br cell compared to the 1.0 cm^2 J52:N2200 cell.

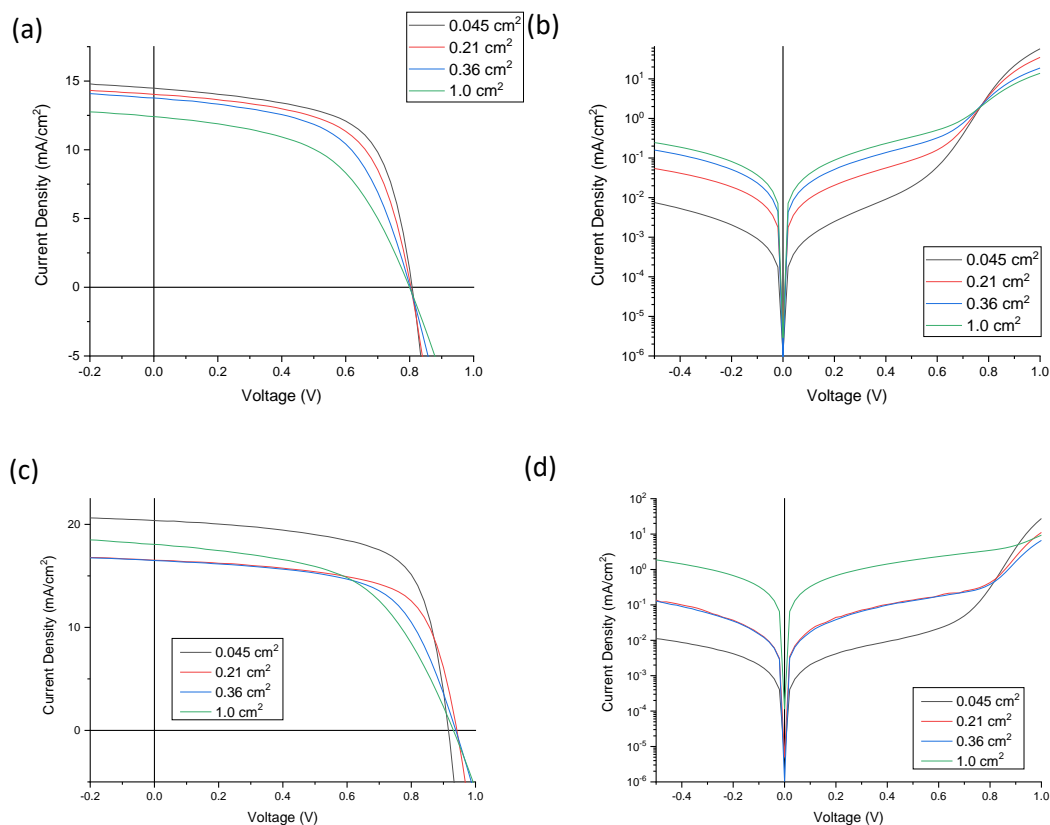


Figure 4. Light JV curves (left) and dark JV curves (right) of blade-coated J52:N2200, (a, b) and PTQ10:ITIC-Br, (c, d), solar cells produced by spin-coating for different active area size.

Table 5. Summary of the optimised performance parameters for blade-coated J52:N2200 cells as a function of cell area.

Cell area (cm ²)	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	PCE (%)
0.045	14.48	0.80	0.64	7.35
0.21	14.03	0.80	0.61	6.82
0.36	13.77	0.80	0.57	6.27
1.0	12.41	0.79	0.52	5.14

Table 6. Summary of the optimised performance parameters for spin-coated PTQ-10:ITIC-Br cells as a function of cell area.

Cell area (cm ²)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
0.045	20.37	0.92	0.67	12.51
0.21	16.52	0.94	0.66	10.23
0.36	16.50	0.94	0.61	9.49
1.0	18.06	0.93	0.54	9.04

Conclusions

The potential for three polymer solar cell systems to be fabricated on the cm² scale has been investigated. Cells produced by blade-coating were found to perform favourably compared to those produced by spin-coating. The decrease in efficiency with increasing active area was largely due to increases in series resistance and losing the benefits of “edge-effects” in small scale cells. For spin-coated cells, efficiencies of ~6% for J52:N2200 cells, ~5% for J71:PNDI-T10 cells and ~9% for PTQ10:ITIC-Br cells were achieved. For the J52:N2200 system a ~5% efficiency was achieved for 1.0 cm² blade coated cells while an efficiency of ~9% could be maintained for 1.0 cm² blade-coated PTQ10:ITIC-Br cells. Issues facing large area blade-coated cells include increased leakage current and maintaining film uniformity. Strategies to mitigate series resistance in large area cells in general will also boost the efficiency of large area devices.

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