

Proceeding Paper

Solution-Processed Organic Light-Emitting Electrochemical Cells (OLECs) with Blue Colour Emission via Silver-Nanowires (AgNWs) as Cathode [†]

Katie Court ^{1,*}, Sasikumar Arumugam ^{1,2} , Yi Li ¹, Martin D. B. Charlton ³, John Tudor ¹, David Harrowven ² and Steve Beeby ¹ 

¹ Smart Electronic Materials and Systems Research Group, School of Electronics and Computer Science (ECS), University of Southampton, Southampton SO17 1BJ, UK; S.Arumugam@soton.ac.uk (S.A.); Yi.Li@soton.ac.uk (Y.L.); mjt@ecs.soton.ac.uk (J.T.); spb@ecs.soton.ac.uk (S.B.)

² Synthesis, Catalysis and Flow Group, School of Chemistry, University of Southampton, Southampton SO17 1BJ, UK; dch2@soton.ac.uk

³ Sustainable Electronic Technology Group, ECS, University of Southampton, Southampton SO17 1BJ, UK; mdbc@ecs.soton.ac.uk

* Correspondence: K.L.Court@soton.ac.uk

[†] Presented at the 3rd International Conference on the Challenges, Opportunities, Innovations and Applications in Electronic Textiles (E-Textiles 2021), Manchester, UK, 3–4 November 2021.

Abstract: Organic light-emitting polymers can be formulated into solutions that can be printed in ambient atmospheres and cured at low temperatures of <120 °C. The deposition techniques that can be employed include spin coating, spray coating and ink-jet printing. This provides the possibility of fabricating OLECs onto a range of flexible substrates including textiles, hence enabling wearable electronics. In addition, the utilization of different polymers could produce light-emitting textiles in a range of colors. This work details the optimisation steps and challenges involved in the fabrication of OLECs on Indium Tin Oxide (ITO) glass prior to the transfer of the process onto a textile. A blue-emitting polymer Merck (NCMP) is used for the active layer and the device fabrication process is carried out at low temperatures in an ambient atmosphere. Working devices have been created on ITO glass to achieve the top blue emission with the next phase being the transfer onto textile. Blue OLECs emission peak is captured at 520 nm with brightness of ~25 cd·m⁻².

Keywords: light-emitting electrochemical cells; spray coating; light-emitting textiles; solution processed



Citation: Court, K.; Arumugam, S.; Li, Y.; Charlton, M.D.B.; Tudor, J.; Harrowven, D.; Beeby, S.

Solution-Processed Organic Light-Emitting Electrochemical Cells (OLECs) with Blue Colour Emission via Silver-Nanowires (AgNWs) as Cathode. *Eng. Proc.* **2022**, *15*, 21. <https://doi.org/10.3390/engproc2022015021>

Academic Editors: Kai Yang and Russel Torah

Published: 24 June 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The development of electronic textiles (E-textiles) has been a particular area of interest since 2010 among both academia and industrial researchers. The various e-textiles applications include: healthcare, the military, and wellbeing, and textile light emission within the visible wavelength is of significant interest due to the fact that it is typically used for communication and signal information [1].

A conventional approach to achieve light emission on textiles has been to incorporate light-emitting devices [2], for example, light-emitting diodes (LEDs), by attaching them onto standard textiles as a carrier. However, this approach has limited technological novelty and changes the original texture of the textile permanently. As a recent alternative approach, light-emitting yarn has been used as it can be woven into the textile during fabrication to achieve a built-in light-emitting textile [3]. This approach also has its limitations on physical deformation from the yarn geometry and limitation on the light emission from the wrap and weft orientation. Another recent approach is to integrate the individual or a number of LEDs into a single yarn, then to sew or weave it into textile [4]; however, this approach limits the light-emitting textile to a single point or a set of single-point light

source. So far, the state-of-the-art fabrication method to achieve the light-emitting textile is to deposit, for example, via a solution process, each functional layer of the light-emitting device directly onto the textile. This approach is typically used in LEDs and light-emitting electrochemical cells (LECs) [5]. However, this process presents significant challenges and requires multi-disciplinary contributions from synthetic chemistry, material science, printing techniques and ink formulation.

In this research work, we report the early-stage experimental results of a blue colour-emitting material, based on an ITO-coated glass substrate with top emission. This achieved light emission and its fabrication process has been optimised for the migration from an ITO-coated glass substrate to a textile substrate. The key novelties arising from this work are to optimise the fabrication process to make it suitable for transfer to the standard textile, whilst having limitations in the maximum processing temperature of 120 °C. At the same time, top emission is required for the textile substrate, as bottom emission is not suitable for non-transparent nor translucent textile substrates. The first blue LECs based on conjugated polymers were reported by Pei et al. in 1996 [6]. LECs fabricated with the highly efficient poly[9,9-bis(3,6-dioxaheptyl)-fluorene-2,7-diyl] (BDOH-PF), exhibited bright sky-blue emissions, with a max brightness of 190 cd·m⁻², under 3.1 V. Edman and co-workers introduced a tri-layer device structure of LECs showing excellent performances, with blue emissions peaking at the 450 and 484 nm regions with high efficiency of 5.3 cd·A⁻¹ at a low drive voltage of 5 V [7]. The authors reported blue emission on and via the ITO glass substrate previously [8], which led to this further research work, demonstrating the spray coating of AgNWs as a translucent top electrode for blue emission via the top electrode. To date, no such blue emission devices have been reported to be able to meet the above criteria for the fabrication process migration to textile substrates for future textile blue light emission.

2. Materials and Device Fabrication

Prior to the device fabrication, the blue colour-emitting active layer formulation was prepared by making three separate 10mg/ml in cyclohexanone (~99%, Gillingham, UK) master solutions of the blue light-emitting polymer (NCMP, Livilux, Merck KGaA, Darmstadt Germany); an ion-dissolving polymer, Trimethylolpropane ethoxylate (TMPE-OH, average Mn ~450 g/mol, Sigma Aldrich, Gillingham, UK); and a salt, potassium trifluoromethanesulfonate (KTF, ~98%, Sigma Aldrich, Gillingham, UK). The solutions were prepared and heated with magnetic stirring until dissolved. They were then blended in a ratio of NCMP:TMPE:KTF of 1.0:1.0:0.2. The blend was left to stir overnight at room temperature to ensure it was homogenous before use.

The device optimisation and fabrication work were carried out in an ambient atmosphere on pre-coated patterned indium tin oxide (ITO) glass substrates (sourced from Gulo Glass, LuoYang, China). The substrates were cleaned by subsequent immersion in acetone, iso-propyl alcohol and deionised water. After drying with compressed air, they were exposed to a 15 min ultraviolet (UV) Ozone treatment using a Novascan benchtop ozone cleaner (PSD-UV4 with OES-1000D, Boone, NC, USA) in order to achieve the correct surface energy for the following PEDOT:PSS (Clevios P VP AI 4083, Heraeus, Leverkusen, Germany) layer. The PEDOT:PSS solution was spin coated onto the cleaned ITO and annealed on a hotplate at 120 °C for 20 min. The active layer formulation, the preparation of which has already been described, was deposited on top of the PEDOT:PSS layer by spin coating; this was also annealed on a hotplate at 120 °C for 30 min. The top electrode was either sputter coated silver in a vacuum chamber at 2×10^{-2} mbar, or spray coated AgNWs (Dycotec, Calne, UK). In both cases, the electrodes were deposited through a shadow mask. Conductive paint was applied to the electrode contacts to achieve a reliable contact during measurement. The devices were then encapsulated with a UV-curable epoxy (Norland, NOA 61) and a cover slip in order to protect the cells from oxygen and moisture during the measurement process. Figure 1a shows a schematic of the OLEC architecture and Figure 1b shows an image of one of the devices fabricated with the silver nano-wires top electrode.

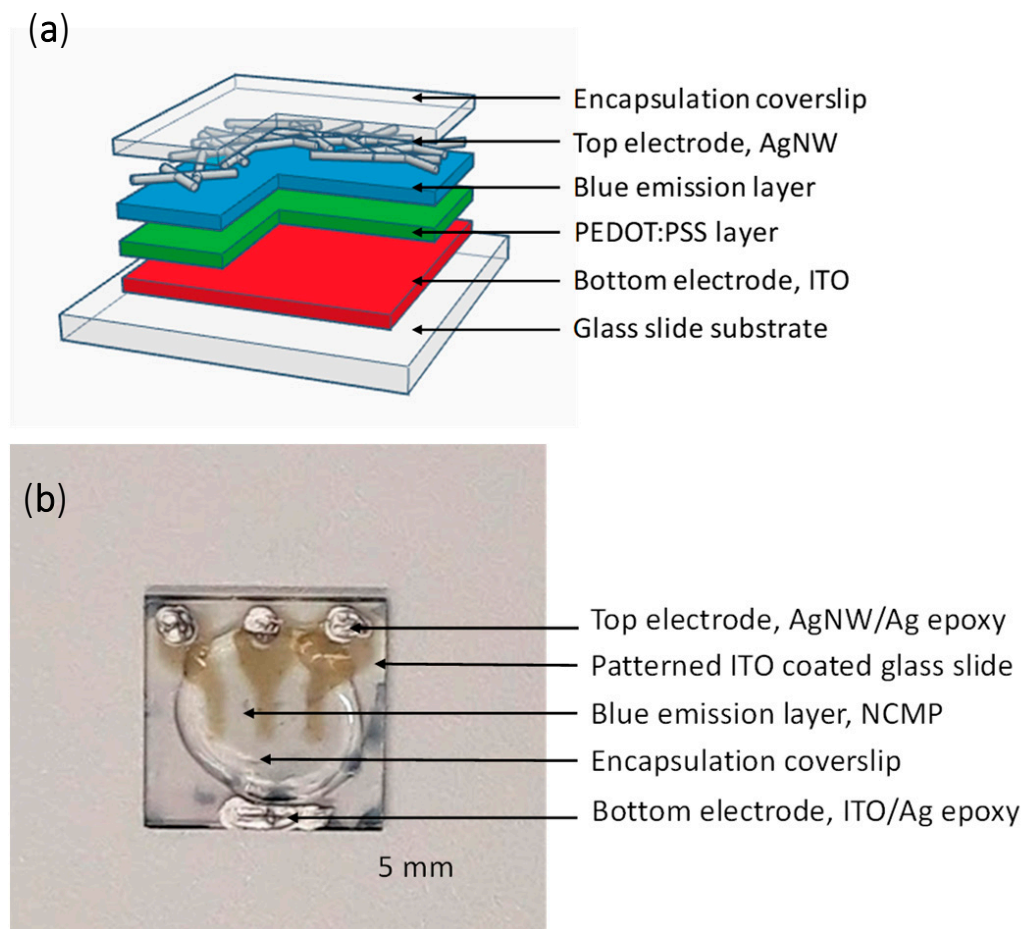


Figure 1. (a) Shows a pictorial schematic of the solution processed device architecture. (b) Image of the fabricated blue-emitting device.

3. Results and Discussion

Each step of the LEC fabrication process was studied in order to improve device performance and reproducibility. This has so far included optimising the coating and annealing conditions for both the PEDOT:PSS and active layers to yield layer thicknesses of 100 nm and 150 nm, respectively. The formulation preparation and ratio of components has also been studied as well as different post-fabrication annealing and encapsulation methods to improve the device lifetime during measurement. The reference device optimisation work used a sputter-coated silver electrode; then, the next stage of the process was studied with the solution processable top electrode formulations (AgNWs) in order to provide an entirely solution-processable process for when it is transferred onto a textile substrate. The optical properties of the blue emitter were also assessed, using an ultraviolet/visible (UV/Vis) spectrophotometer, and photoluminescence (PL) by laser excitation, as shown in Figure 2a, whereas Figure 2b shows the EL spectrum of the biased OLECs with the AgNWs top electrode, indicating the peak of 520 nm within the blue region. The peak of the emission corresponds with a wavelength of 520 nm, which corresponds to a brightness measurement of $\sim 25 \text{ cd}\cdot\text{m}^{-2}$. Figure 2c shows one of the fabricated devices (reference device) lit up with a bright blue light during measurement. The image of the AgNW lit-up devices is not available in this submission.

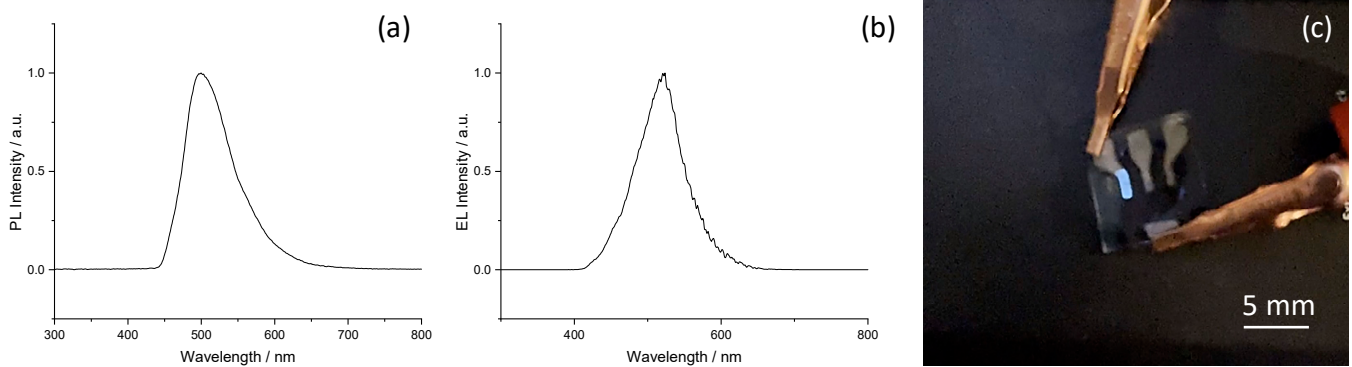


Figure 2. (a) Photoluminescent (PL) intensity spectrum obtained by laser excitation on the Merck NCMP in cyclohexanone solution, (b) electroluminescent (EL) intensity spectrum obtained by electrical bias at 6 V on the NCMP OLEC (spectrometer integration time of 500 μ s), (c) the NCMP Merck blue-emitting device (reference device) lit up during measurement with a brilliant blue.

4. Conclusions

Blue-emitting OLEC devices have been fabricated using a process in which all steps were solution processed and in an ambient atmosphere. ITO pre-coated glass substrates were used for this initial optimisation work and the next steps will be to transfer the process onto a textile substrate. A commercially available blue-emitting polymer was utilized as the active layer, and by achieving the correct layer thicknesses for both the PEDOT:PSS and blue-emitter layers, bright light emission with good junction resistance (<1 k Ω) was achieved. A silver nano-wire spray coating formulation was used as a top electrode was used to achieve a solution-processed top electrode instead of the traditional sputter-coated silver. It can be seen from the image of the device that more work is needed to make more translucent cells for the top electrode for potential migration to textile substrates.

Author Contributions: K.C. and S.A. mainly did the lab work on fabrication; Y.L. did the measurement and characterization of the blue colour light emitting electrochemical cells. K.C., Y.L. and S.A. did the experimental plan, interpreted the collected data and prepared the manuscript. M.D.B.C. contributed his optical lab facilities for all the measurement. J.T. joined the technical discussion and proofread the proceeding. D.H. is the budget holder for the project. S.B. is the team leader and supervised the project. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the EPSRC Funding, Functional Electronic Textiles for Light Emitting and Colour Changing Applications (EP/S005307/1), Zepler institute Stimulus Fund 2017, Functional Electronic Textiles for Light Emitting Applications via Light Emitting Electrochemical Cells (517719107) and ERDF Interreg Program (EU), Smart Textiles for Regional Industry and Smart Specialisation Sectors (SmartT).

Data Availability Statement: Data available upon request, please contact the author.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Komolafe, A.; Zaghari, B.; Torah, R.; Weddell, A.S.; Khanbareh, H.; Tsikriteas, Z.M.; Vousden, M.; Wagih, M.; Jurado, U.T.; Shi, J.; et al. E-Textile Technology Review—From Materials to Application. *IEEE Access* **2021**, *9*, 97152–97179. [[CrossRef](#)]
2. Ciquino, M.; Prontera, C.T.; Pugliese, M.; Giannuzzi, R.; Taurino, D.; Gigli, G.; Maiorano, V. Light-Emitting Textiles: Device Architectures, Working Principles, and Applications. *Micromachines* **2021**, *12*, 652. [[CrossRef](#)] [[PubMed](#)]
3. Komolafe, A.; Torah, R.; Wei, Y.; Nunes-Matos, H.; Li, M.; Hardy, D.; Dias, T.; Tudor, M.; Beeby, S. Integrating Flexible Filament Circuits for E-Textile Applications. *Adv. Mater. Technol.* **2019**, *4*, 1900176. [[CrossRef](#)]
4. Hardy, D.A.; Moneta, A.; Sakalyte, V.; Connolly, L.; Shahidi, A.; Hughes-Riley, T. Engineering a Costume for Performance Using Illuminated LED-Yarns. *Fibers* **2018**, *6*, 35. [[CrossRef](#)]
5. Arumugam, S.; Li, Y.; Pearce, J.; Charlton, M.D.B.; Tudor, J.; Harrowven, D.; Beeby, S. Spray-Coated Organic Light-Emitting Electrochemical Cells Realized on a Standard Woven Polyester Cotton Textile. *IEEE Trans. Electron. Devices* **2021**, *68*, 1717–1722. [[CrossRef](#)]

6. Pei, Q.; Yang, Y.; Yu, G.; Zhang, C.; Heeger, A.J. Polymer Light-Emitting Electrochemical Cells: In Situ Formation of a Light-Emitting p–n Junction. *J. Am. Chem. Soc.* **1996**, *118*, 3922–3929. [[CrossRef](#)] [[PubMed](#)]
7. Tang, S.; Sandström, A.; Fang, J.; Edman, L. A Solution-Processed Trilayer Electrochemical Device: Localizing the Light Emission for Optimized Performance. *J. Am. Chem. Soc.* **2012**, *134*, 14050–14055. [[CrossRef](#)] [[PubMed](#)]
8. Arumugam, S.; Li, Y.; Court, K.; Piana, G.; Charlton, M.; Tudor, J.; Harrowven, D.; Beeby, S. Solution processed blue light emitting electrochemical cells fabricated and encapsulated fully in ambient environment. In Proceedings of the 2021 IEEE International Conference on Flexible and Printable Sensors and Systems (FLEPS), Virtual, 20–23 June 2021; pp. 1–4.