

## LITHIUM-DOPED SILK FIBROIN FILMS FOR APPLICATION IN ELECTROCHROMIC DEVICES

Rui F. P. Pereira<sup>1,2,\*</sup>, F. Sentanin<sup>3</sup>, A. Pawlicka<sup>3</sup>, M. Manuela Silva<sup>1</sup> and Verónica de Zea Bermudez<sup>2,4</sup>

<sup>1</sup>Chemistry Centre, University of Minho, 4710-057 Braga, Portugal

<sup>2</sup>Department of Chemistry, University of Trás-os-Montes e Alto Douro, 5001-801 Vila Real, Portugal

<sup>3</sup>Instituto de Química de São Carlos, Universidade de São Paulo, 13566-590 São Carlos, SP, Brazil.

<sup>4</sup>CQ-VR, University of Trás-os-Montes e Alto Douro, 5001-801 Vila Real, Portugal

\*corresponding author: rpereira@quimica.uminho.pt

**Keywords:** silk fibroin, electrochromic devices, lithium doped films, solid electrolytes.

### Abstract

Silk fibroin (SF) is a commonly available natural biopolymer produced in specialized glands of arthropods, with a long history of use in textile production and also in health cares. The exceptional intrinsic properties of these fibers, such as self-assembly, machinability, biocompatibility, biodegradation or non-toxicity, offer a wide range of exciting opportunities [1].

It has long been recognized that silk can be a rich source of inspiration for designing new materials with tailored properties, enhanced performance and high added value for targeted applications, opening exciting new prospects in the domain of materials science and related technological fields, including bio-friendly integration, miniaturization and multifunctionalization. In recent years it has been demonstrated that fibroin is an excellent material for active components in optics and photonics devices. Progress in new technological fields such as optics, photonics and electronics are emerging [2,3].

The incorporation of polymer electrolytes as components of various devices (advanced batteries, smart windows, displays and supercapacitors) offers significant advantages with respect to traditional electrolytes, including enhanced reliability and improved safety. SF films are particularly attractive in this context. They have near-perfect transparency across the VIS range, surface flatness (together with outstanding mechanical robustness), ability to replicate patterned substrates and their thickness may be easily tailored from a few nanometers to hundreds of micrometers through spin-casting of a silk solution into substrate. Moreover, fibroin can be added to other biocomponents or salts in order to modify the biomaterial properties leading to optimized and total different functions.

Preliminary tests performed with a prototype electrochromic device (ECD) incorporating SF films doped with lithium triflate and lithium tetrafluoroborate (LiTFSI and LiBF<sub>4</sub>, respectively) as electrolyte and WO<sub>3</sub> as cathodic electrochromic layer, are extremely encouraging. Aiming to evaluate the performance of the ion conducting SF membranes doped with LiTFSI and LiBF<sub>4</sub> (SF-Li), small ECDs with glass/ITO/WO<sub>3</sub>/SF-Li/CeO<sub>2</sub>-TiO<sub>2</sub>/ITO/glass configuration were assembled and characterized. The device exhibited, after 4500 cycles, the insertion of charge at -3.0 V reached -1.1 mC.cm<sup>-2</sup> in 15 s. After 4500 cycles the window glass-staining, glass/ITO/WO<sub>3</sub>/Fibrin-Li salts electrolyte/CeO<sub>2</sub>-TiO<sub>2</sub>/ITO/glass configuration was reversible and featured a  $\Delta T \cong 8\%$  at  $\lambda = 686$  nm.

### Acknowledgements

This work was supported by Fundação para a Ciência e a Tecnologia (FCT) and Feder (contracts PTDC/CTM-BPC/112774/2009, PEst-OE/QUI/UI0616/2014 and PEst-C/QUI/UI0686/2013) and COST Action MP1202 "Rational design of hybrid organic-inorganic interfaces". R.F.P.P. acknowledges FCT for a grant (SFRH/BPD/87759/2012). M. M. Silva acknowledges CNPq, for the mobility grant provided by this institution.

### References

- [1] L. B. Shi, H. X. Cai, L. K. Chen, Y. Wu, S. A. Zhu, X. N. Gong, Y. X. Xia, H. W. Ouyang and X. H. Zou *Biomaterials*, 2014, 35, 1519-1530
- [2] R. F. P. Pereira, M. M. Silva, V. de Zea Bermudez, *Macromol. Mater. Eng.* 2014, 299, DOI: 10.1002/mame.201400276
- [3] H. Tao, D. L. Kaplan and F. G. Omenetto, *Adv. Mater.*, 2012, 24, 2824-2837