

Optofluidic hollow-core fibres as Raman sensors for Li-ion battery chemistry

E. Miele,^{a,b} W. M. Dose,^{b,c} I. Manyakin,^a M. H. Frosz,^d C. P. Grey,^b J. J. Baumberg,^a and T. G. Euser^{a,*}

a. NanoPhotonics Centre, Cavendish Laboratory, Department of Physics, University of Cambridge, UK

b. Department of Chemistry, University of Cambridge, United Kingdom

c. Department of Engineering, University of Cambridge, Cambridge, United Kingdom

d. Max Planck Institute for the Science of Light, Erlangen, Germany

* e-mail: te287@cam.ac.uk

ABSTRACT

We demonstrate a fibre-optic sensing method capable of monitoring chemical changes within Li:ion cells under real working conditions. Our technique is based on optofluidic single-ring hollow-core fibres, which uniquely allow light to be guided at the centre of a microfluidic channel. We integrate the fibres into working Li:ion cells, use them to take sub-microlitre samples of the electrolyte liquid, and analyse these by background-free Raman spectroscopy to identify early signs of battery degradation. Our approach complements existing battery monitoring systems and will enable us to identify degradation mechanisms that currently limit the lifetime and capacity of state-of-the-art energy storage systems.

Keywords: fibre-optic sensors, Raman-spectroscopy, photonic crystal fibre

To develop the next-generation of safe, high-capacity, Li:ion batteries [1–2], it is essential to understand the complex interplay of chemical and physical processes and degradation mechanisms that occur under operating conditions [3]. Batteries are commonly investigated using electrochemical impedance spectroscopy and cyclic voltammetry that offer no direct information on the chemical processes within the device. Optical spectroscopy can shed light on battery chemistry, but is currently limited to the use of half battery-cells demanding access windows or post-mortem analysis, and thus offers limited insight in degradation processes under operating conditions.

Here we present a fibre-optical sensing method capable of in-situ and in-operando monitoring of battery devices under real working conditions. Using Raman spectroscopy, we identify degradation products by their vibrational bonds [4]. Our approach is based on optofluidic single-ring hollow-core fibres (HC-fibres) that uniquely allow light to be guided at the centre of a liquid-filled microchannel [5]. The use of HC-fibre strongly reduces the background Raman signal generated by the silica glass core in conventional fibre probes [6,7]. One fibre end is embedded in a working battery cell and used to sample and analyse sub-microlitre volumes of the electrolyte by background-free Raman spectroscopy. Similar to a laboratory blood test, the concentrations of chemicals within the electrolyte provide unique information on the *state-of-health* of a battery. For example, the data in Figure 1(d) shows clear Raman peaks related to ethylene carbonate (EC) and the important battery additive vinylene carbonate (VC), offering a direct insight in the formation of the Solid Electrolyte Interface, a key buffer layer that largely forms during its first electrochemical cycle, and whose stability is key to longevity (or capacity retention) of the device. We are currently extending this work to study a range of different degradation mechanisms.

ACKNOWLEDGEMENTS

This work was supported by the Faraday Institution [grant number EP/S003053/1].

REFERENCES

- [1] K. Kang, Y. S. Meng, J. Bréger, C. P. Grey, G. Ceder, *Science* **311**, 977 (2006).
- [2] S. Goriparti, E. Miele, C. Capiglia, *Journal of Power Sources* **257**, 421 (2014).
- [3] C.P. Grey and M. Tarascon, *Nature Materials* **16**, pp. 45-56 (2017).
- [4] D. Chen, D M. A. El-Sayed, M. Liu, *Chemistry of Materials* **27**, 6608 (2015).
- [5] A. M. Cubillas, S. Unterkofler, T. G. Euser *et al.*, *Chem. Soc. Rev.* **42**, 8629 (2013).
- [6] F. Benabid, J. C. Knight, G. Antonopoulos, P. St. J. Russell, *Science* **298**, pp. 399-402 (2002).
- [7] D. Yan, J. Popp, M. W. Pletz and T. Frosch, *ACS Photonics* **4**, 138 (2017).

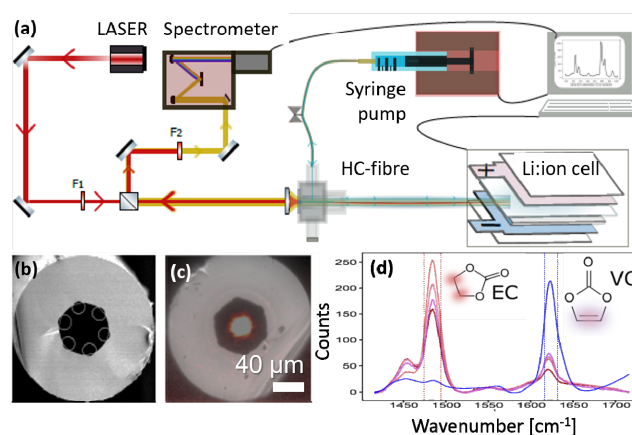


Fig. 1: (a) Raman setup for battery sensing. (b) SEM of HC-fibre, (c) measured mode at 785 nm in an electrolyte-filled core, (d) Raman bands of VC and EC.