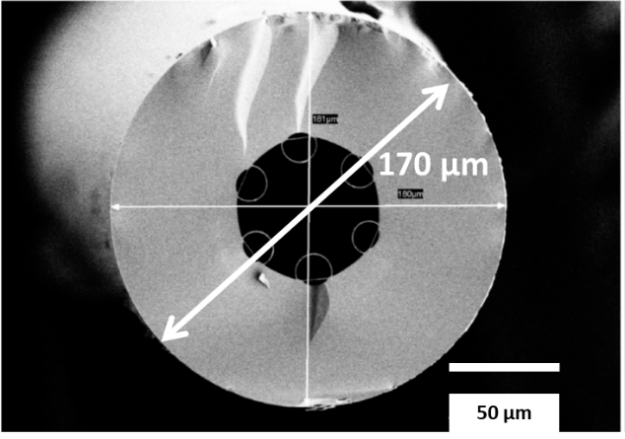
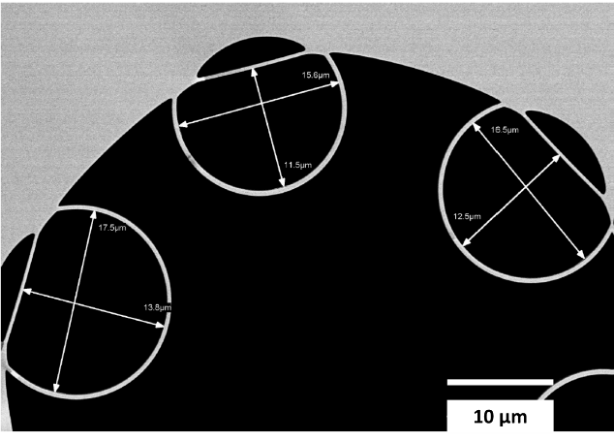
# Supplementary Information for:

**Operando Raman analysis of electrolyte composition in Li-ion batteries with hollow-core optical fibre sensors**



**a**

**b**

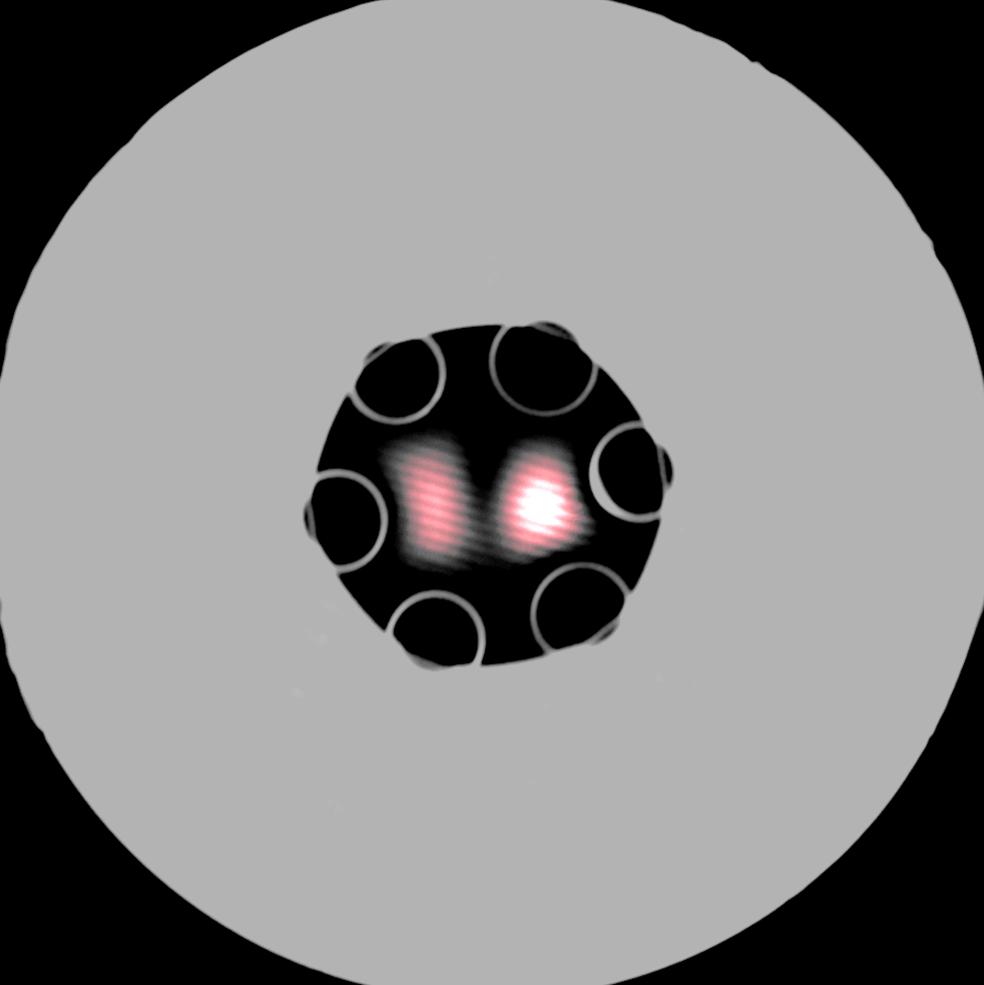
***Supplementary Figure 1 | SEM Images of hollow-core fibre.*** *(****a****) Fibre comprises a single ring negative curvature fibre with outer diameter of 174 μm and internal hollow-core diameter measuring 36 μm, with (****b****) 6 internal capillaries of 16 μm in diameter.*

***Supplementary Figure 2 | Fibre transmission properties at 785 nm.*** *Transmitted optical modes at   
785 nm for three filling materials with different refractive indices: (****a****) air, (****b****) IPA, and (****c****) EC:EMC (3:7). The CCD images are overlaid with optical microscope images taken in the same setup, using a white-light source to illuminate the glass cladding structure. The transmitted power was measured using a Si photodiode power meter with typical values between 10% and 20% for refractive indices between 1.37 and 1.42.*

T= 10%

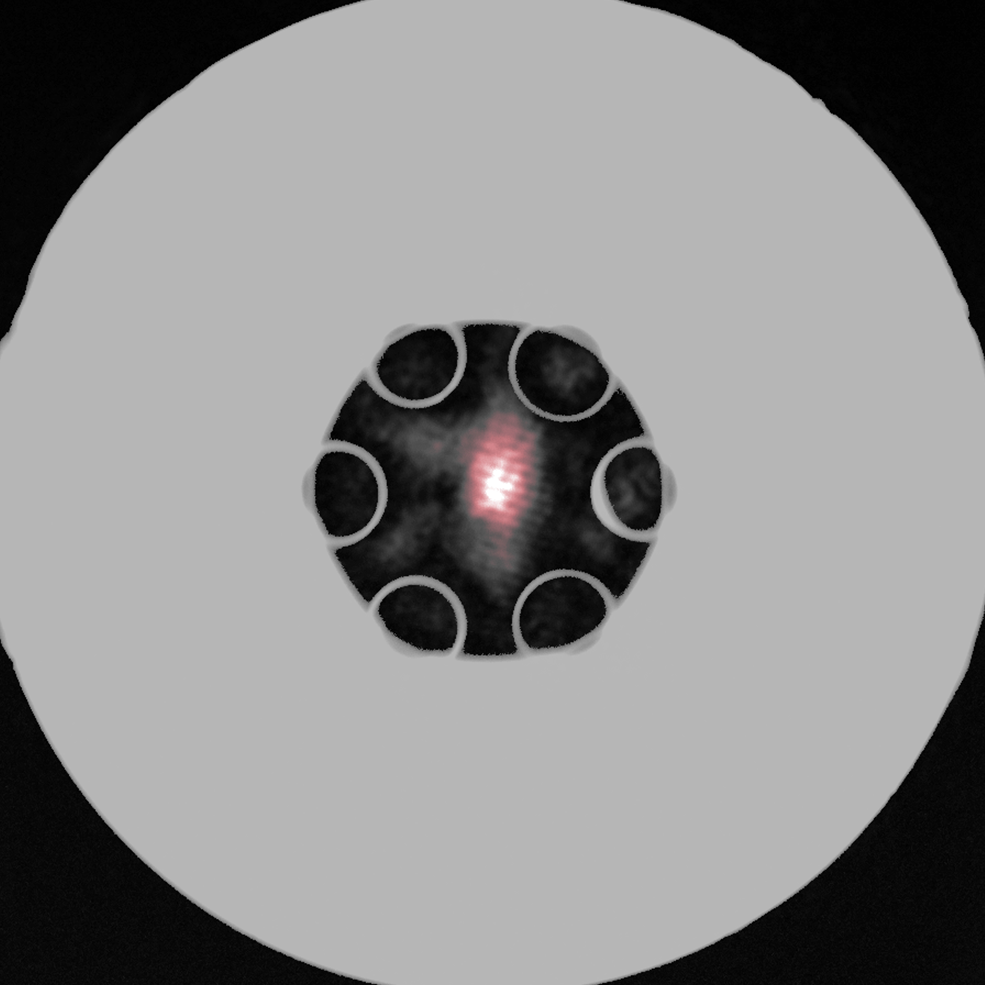
T= 20%

T= 7%



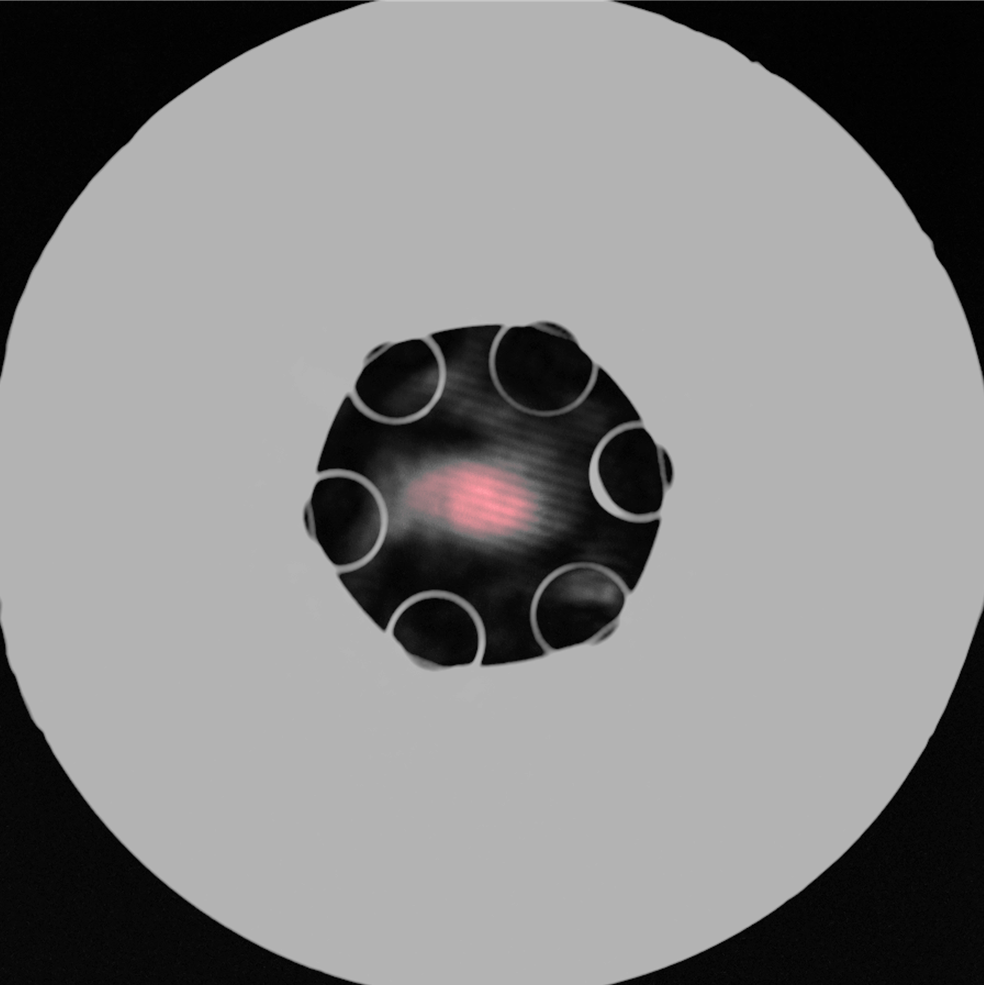
**a**

n = 1.00



**b**

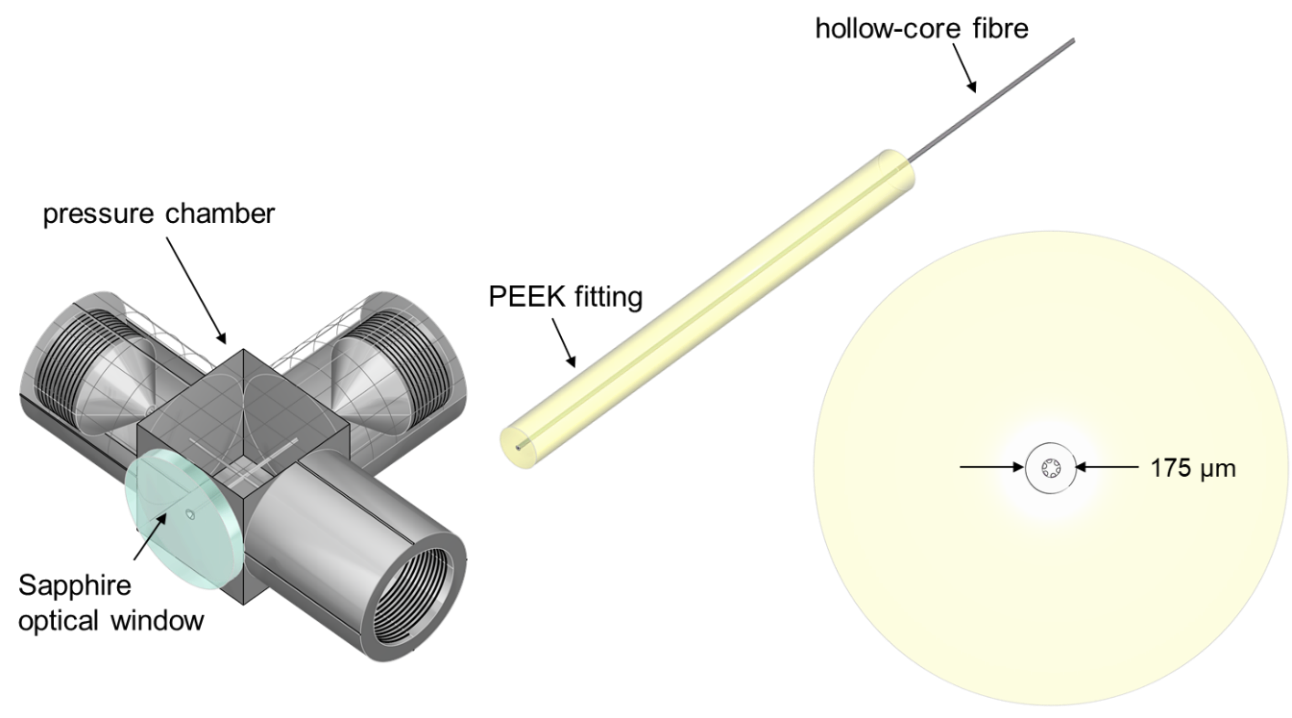
n = 1.377



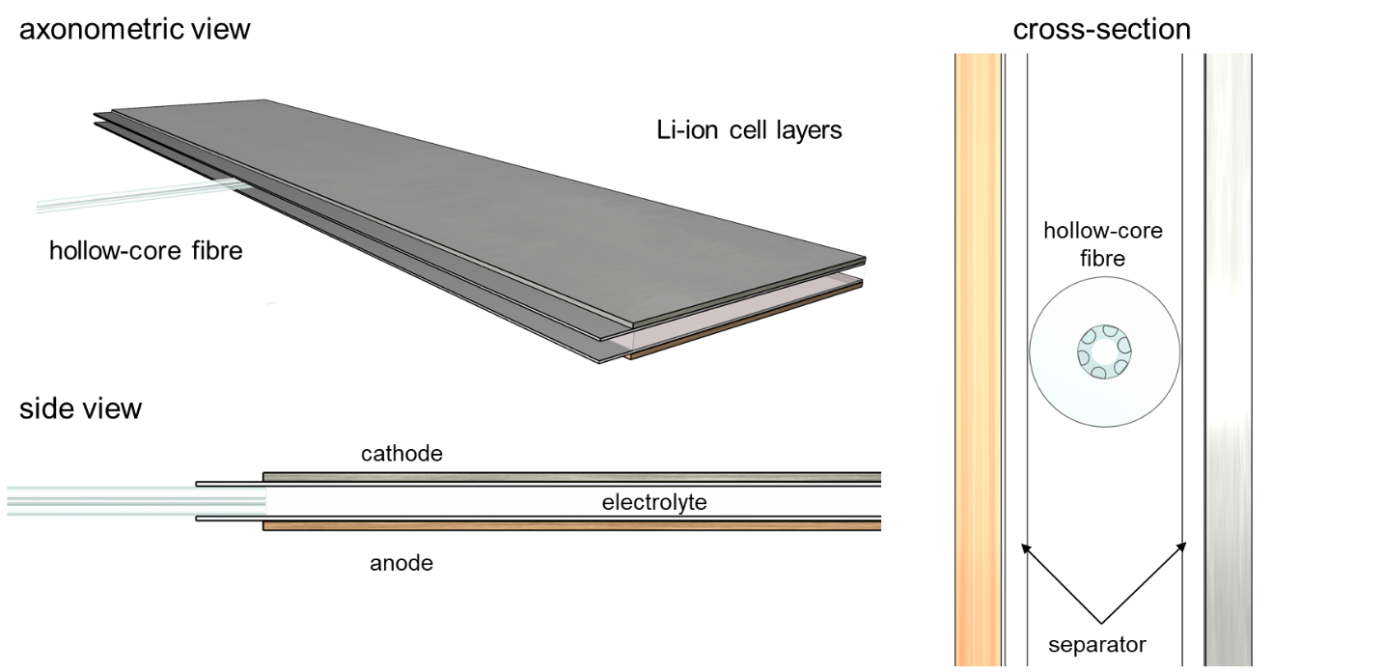
30μm

**c**

n = 1.39



***Supplementary Figure 3 | Ultralow dead-volume pressure chamber for light coupling and microfluidic actuation****. A HPLC tee-connector (Idex UH-422) is customized to connect the fibre to the syringe pump, while allowing for optical access. A 1 mm thick sapphire optical access window (Edmund optics #43-366) is mounted to the cell using optical adhesive. The fibre is connected to an access port by embedding it in a 1/16” outer diameter, 229 µm inner diameter PEEK sleeve (Upchurch F-227), and fixed with a finger-tight fitting (Upchurch F-120, not shown).*

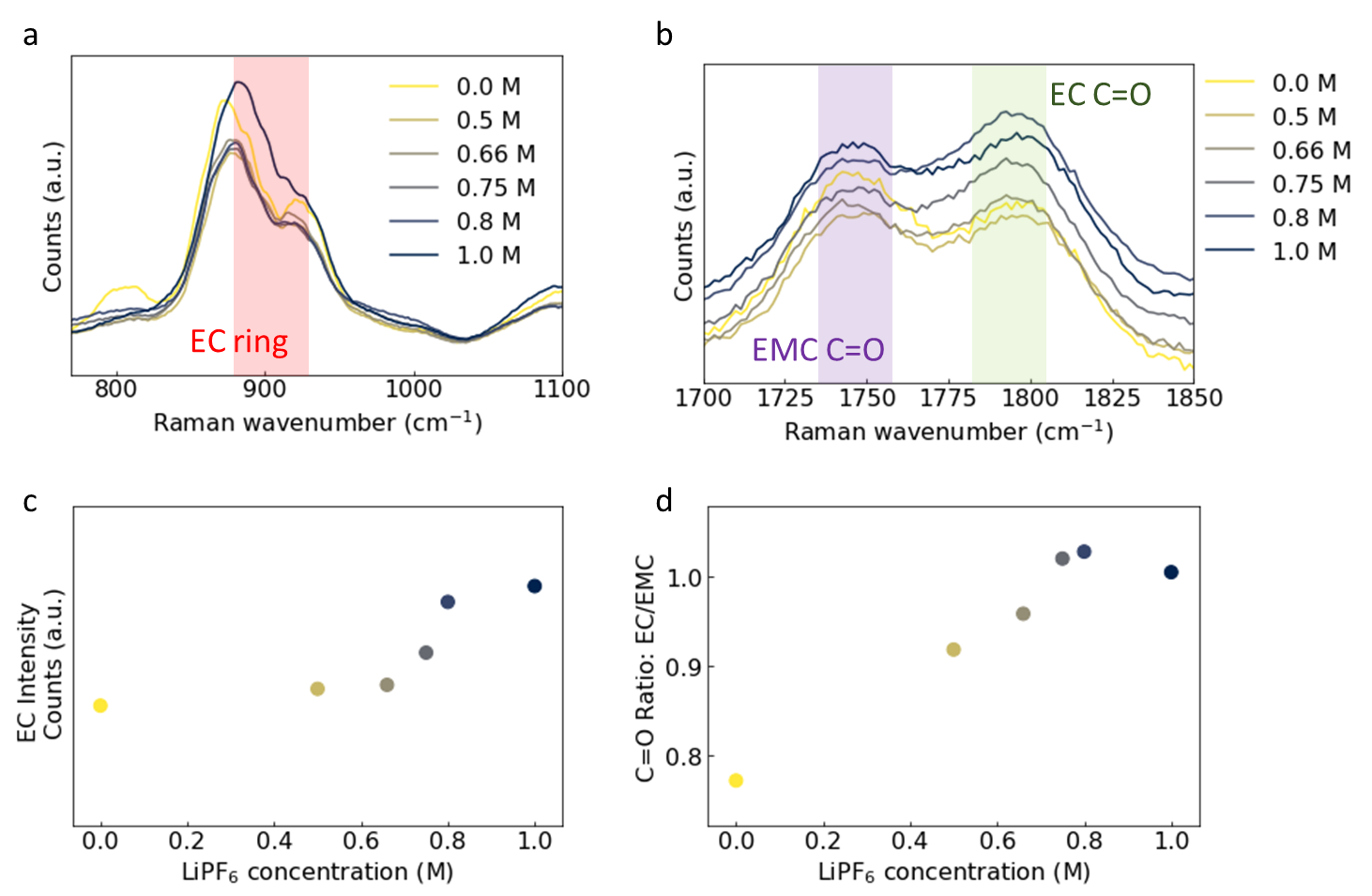


**a**

**c**

**b**

***Supplementary Figure 4* |*Li-ion cell stack geometry and assembly.*** *(****a-b****) The hollow-core fibre is embedded in the electrolyte compartment, protected by two 25 µm-thick layers of monolayer PE polymer separator (MTI). (****c****) Cross-section of the hollow-core fibre position within the cell. The outer diameter of the fibre is 174 µm.*

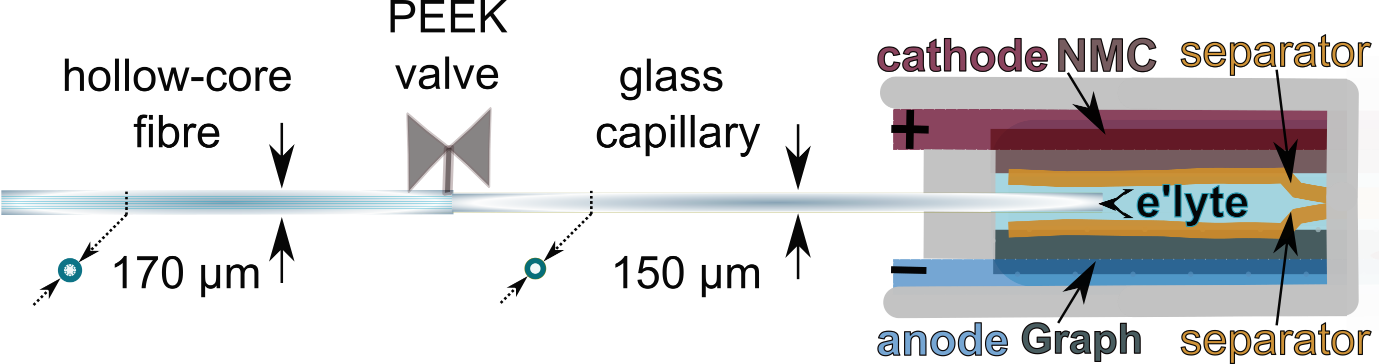


***Supplementary Figure 5 | Ex-situ calibration of Raman response.*** *The effect of Li concentration on the EC/EMC Raman spectra is studied by infiltrating prepared solutions of LiPF6 salt in EC:EMC (3:7 (v)) in the HC-fibre sensor. (****a-b****) The EC breathing mode (shaded area in (****a****)) and the EMC- and EC C=O stretch modes (shaded areas in (****b****)) are measured for a range of [LiPF6] concentrations between 0 and 1.0 M. The EC breathing mode (****c****) as well as the ratio between the EC and EMC (C=O) stretching modes (****d****) are observed to increase with [LiPF6].*

A picture containing clock

Description automatically generated

***Supplementary Figure 6 | Representative measurements on different Li-ion pouch cells.****Both experiments in (****a-b****) display a step increase in EC breathing mode intensity during charging   
(as in* ***Fig. 3*** *in main text), as well as a reduction in signal due to bubble formation at higher voltages (shaded areas). Sections* I-III *correspond to the same parts of the cycle as in* ***Fig. 4*** *in the main text.*



***Supplementary Figure 7 | Alternative microfluidic configuration for a Li-ion cell.*** *The drawing depicts the stack layers arrangement and the position of the coated glass capillary used for experiments discussed in* ***Fig. 6*** *in the main text. This configuration allows for separation between the hollow-core used for Raman detection and the capillary used for sampling the LP57 (VC-free) electrolyte.*

***Supplementary Movie 1 | Gas bubble trapped in hollow-core fibre.***

<https://youtu.be/G7Jn4_sGrN8>