



HAL
open science

Sensing as the key to battery lifetime and sustainability

Jiaqiang Huang, Steven Boles, Jean-Marie Tarascon

► **To cite this version:**

Jiaqiang Huang, Steven Boles, Jean-Marie Tarascon. Sensing as the key to battery lifetime and sustainability. *Nature Sustainability*, 2022, 5 (3), pp.194-204. 10.1038/s41893-022-00859-y. hal-03843308

HAL Id: hal-03843308

<https://hal.science/hal-03843308v1>

Submitted on 8 Nov 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Sensing as the key to battery lifetime and sustainability

Jiaqiang HUANG^{1,2}, Steven T. BOLES^{3,4} and Jean-Marie TARASCON^{1,2,*}

¹Collège de France, Chimie du Solide et de l'Energie—UMR 8260 CNRS, Paris, France.

²Réseau sur le Stockage Electrochimique de l'Energie (RS2E)—FR, CNRS 3459, Amiens, France.

³Department of Electrical Engineering, The Hong Kong Polytechnic University, Kowloon, Hong Kong SAR, China.

⁴Department of Energy and Process Engineering, Faculty of Engineering, NTNU – Norwegian University of Science and Technology, Trondheim, Norway

* Corresponding author: J.-M. Tarascon: jean-marie.tarascon@college-de-france.fr

Preface

Recent economic and productivity gains of rechargeable batteries have cemented their dominance in energy-intensive societies. With demand soaring, enhancing battery performance through continuous monitoring is essential to limiting their environmental footprint. While some benefits of sensing have been known for a century, the convergence of fiber optic techniques with new battery platforms is poised to change the industry as a wealth of chemical, thermal, and mechanical data will transform the utilization strategies for new and used lithium-ion devices alike. This Review highlights recent advances and associated benefits with a focus on optical sensors that could improve the sustainability of batteries.

Introduction

Perhaps no technology better represents the sustainability challenges of the 21st century than that of rechargeable batteries¹⁻³. Lead-acid and nickel metal-hydride batteries are mature technologies with nearly closed-loop supply chains and excellent materials recovery/reusability, but lithium-based batteries have ousted their predecessors due to the insatiable and sophisticated demands across many industries, combined with the ongoing internet of things (IoT) communications revolution. At their current pace, lithium-ion battery (LIB) pack prices are projected (<https://about.bnef.com/blog/battery-pack-prices-cited-below-100-kwh-for-the-first-time-in-2020-while-market-average-sits-at-137-kwh/>) to drop below €85 per kWh by 2023, a threshold that is believed to render batteries competitive with internal combustion engines in the automotive sector. Such utilization of rechargeable batteries may lead to significant decreases in CO₂ emissions for the power and transport sectors, which accounts for 23% and 16% of global emissions in 2017, respectively³. Thus, while the promise of improved carbon neutrality and “macro-level” impact due to further adoption of Li-ion batteries is excellent, short-sighted considerations for their reusability or repurposing means that maximizing the quality, reliability, lifetime, and safety (QRLS) of cells and systems is essential establishing device-level sustainability. Major research initiatives and funding sources⁴ are

responding accordingly and are now focused on “greening” Li-ion batteries⁵ through eco-designed materials and electrodes, re-thinking battery recycling approaches¹, and expanding the quest for passive, non-disruptive diagnostic techniques that can demonstrably improve device performance². However, the latter case of battery monitoring is a complex problem that must decode an intrinsic competition between main and parasitic faradaic chemical reactions and phase transitions, together with electronic and ionic transport limitations. Parasitic reactions will lead to phenomena⁶ such as uncontrolled growth of solid electrolyte interphase (SEI), electrode cracking, metal dissolution, shuttling of redox contaminants, and lithium plating. Not only are all these phenomena detrimental to cell performance, but poor diagnostic abilities lead to an over-reliance on imperfect data to establish safety margins and a systematic under-utilization of cells and batteries, depicted in Fig. 1a.

In the laboratory, numerous characterization techniques have been developed to untangle the underlying science of batteries which enlist sophisticated instrumentation⁷⁻¹⁰ and can ideally operate *in operando*, or as a cell is cycled. However, these analytical techniques rely on special equipment and cell designs that cannot be deployed directly in commercial cells¹¹. In the field, monitoring of current (I), voltage (V), and impedance (R) parameters constitute the basic data elements of today’s battery management systems (BMS). Surprisingly, regarding electric vehicle (EV) applications, temperature and its gradient (which essentially govern the battery chemistry and lifetime¹²) are not presently measured at cell level directly, but at the module level. Analog temperature sensors¹³⁻¹⁶ are being explored for individual-cell sensing, but their size and necessary wiring have hampered their integration. However, even with precise knowledge of cell temperature, BMS units are still relegated to inferring reliability and performance using statistical approaches. While such estimation is adequate for ‘disposable’ electronics, an EV battery may comprise $\sim 1/3$ of the vehicle cost, so the pursuit of high-value information leading to increased battery service life is clearly justified. Ideally, new cell level sensors will allow us to monitor chemical-physical-thermal metrics (*in operando* with notable time and spatial resolution), which lead to more accurate state of charge (SoC) and state of health (SoH) estimates along with early-failure indicators.

The benefits of battery diagnostics are clear, so it is no surprise that the field is blooming with multi-sensing approaches that this review will modestly attempt to cover. We will begin by giving a brief history of battery sensing, followed by its recent evolution: We will discuss acoustic approaches prior to mainly focusing on optical sensing as it paves the way to previously inaccessible chemical and mechanical metrics. This discussion will be accompanied by a number of examples both from the literature and from our own work, which convey the need for combining electrochemistry, photonics, and data science. We will conclude by providing our perspective on the future of the field and what we view as enabling a “lab-

on-fiber” analytical platform for field battery monitoring and a new generation of sustainable energy storage.

Box 1 | Glossary of key technical terms

| | | | | | |
|-------|----------------------------------------|------|--------------------------------------------|------|----------------------------|
| AE | Acoustic emission | LIB | Lithium-ion battery | SMF | Single mode optical fiber |
| BMS | Battery management system | LPG | Long period grating | SoC | State of charge |
| CEI | Cathode electrolyte interphase | MOF | Microstructured optical fiber | SoH | State of health |
| DMC | Dimethyl carbonate | NPS | Nano-plasmonic sensor | SoP | State of power |
| EIS | Electrochemical impedance spectroscopy | PCF | Photonic crystal fiber | SoS | State of safety |
| EV | Electric vehicle | QRLS | Quality, reliability, lifetime, and safety | SPR | Surface plasmon resonance |
| FBG | Fiber Bragg grating | RI | Refractive index | TFBG | Tilted fiber Bragg grating |
| FOEWS | Fiber optic evanescent wave sensor | SEI | Solid electrolyte interphase | ToF | Time-of-flight |
| IoT | Internet of things | SEM | Scanning electron microscope | | |

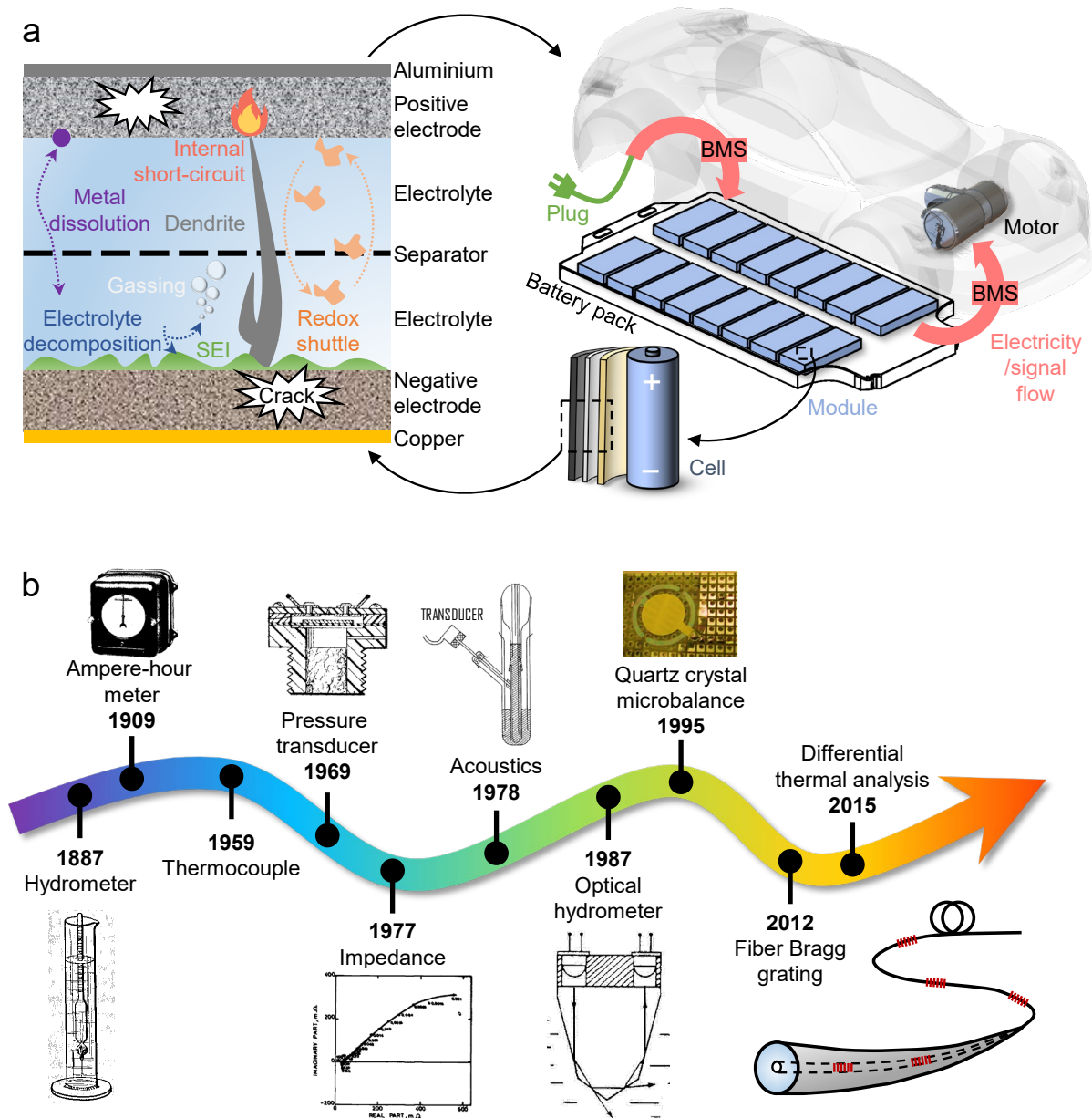


Fig. 1 | Sensing overview. **a**, Major physio-chemical sources of battery dysfunction at the component and the cell level with an emphasis on the gap that exists in going from lab to system applications. **b**, Timeline of some key milestones for the battery sensing techniques of interest.

Overview

Historically, as early as batteries were put into the market, scientists have been challenged to design monitoring techniques¹⁷⁻²³ to determine their SoC, SoH, and state of power (SoP) (chronologically summarized in Fig. 1b). Pb-acid batteries were an ideal starting point and playground for developing methods for diagnosing these parameters since the specific gravity, viscosity, and refraction index of the electrolyte each vary in proportion with the extent of electrochemical reaction, and the electrolyte can be readily sampled non-destructively. Going back to 1887, hydrometers were used to determine the specific gravity of the electrolyte^{17,24}, with higher SoC corresponding to denser electrolyte, because the H₂SO₄ in electrolyte is consumed during battery discharge and vice versa. Optical hydrometer sensors²², whose working principle relies on correlating the attenuation amplitude of an optical signal to the refractive index of its surrounding electrolyte, were similarly developed for estimating SoC of Pb-acid batteries. Other approaches include the design of quartz crystal microbalance sensors^{23,25} for real-time monitoring of changes in the square root of the density-viscosity product ($\sqrt{\rho\eta}$) of electrolyte²⁵ during battery cycling to estimate SoC.

Due to the various limitations of these sensors, the technology has been effectively supplanted by diagnostic methods utilizing electrochemical techniques. Beyond the voltmeter and the ampere-hour meter¹⁸ implemented long ago, the use of electrochemical impedance spectroscopy (EIS) or pulse methods allows for the contact and charge-transfer resistances and their contribution to the cell overpotential to be tracked. These can reveal detrimental effects of ageing, such as increased contact resistance due to electrode fracturing or interface growth. It is worth mentioning that alternating current impedance²⁰ characterization, as a non-destructive technique, has been widely used in telecom central offices over the years to follow the SoC and SoH of Pb-acid batteries. This non-invasive EIS technique has also been successfully extended to other battery chemistries including Li-ion. As a contemporary technology, Li-ion cells have benefited from third reference electrode²⁶, high precision chargers²⁷ to cycle batteries while adjusting charge-discharge currents, sweeping voltage windows, and temperature profiles. Through the exploitation of this rich electrochemical data, freewares²⁸ have been developed to help track QRLS issues.

Analytical instrumentation^{29,30} has also spectacularly evolved over the past decades to enable precise quantification of the evolving inorganic and organic species within Li-based electrolyte, as it is closely linked to battery longevity. These approaches allow for the determination of salts and solvent concentration variations, but typically require cell disassembly and significant laboratory infrastructure. These limitations were recently overcome using a non-destructive differential thermal analysis technique³¹

(<https://www.novonixgroup.com/>) that briefly consists of tracking variations of the liquidus and solidus features of the electrolyte, together with their associated enthalpies. Since changes to these parameters stem from the composition and amount of the electrolyte, implications can be made for the SoH of the battery. However, the heating and cooling (with liquid nitrogen) requirements may prevent it from *operando* monitoring in the field.

Gas formation, electrode swelling and SEI overgrowth, are severe problems linked to cell ageing, and each gives rise to cell volume expansion. Archimedes' *in situ* gas analysers³², whereby a cell is immersed in a fluid and a force sensor allows its buoyancy to be quantified as volume, have mainly been used to measure gas build-up stemming from the first charge-discharge (*i.e.*, formation) cycles. *In situ* microscopy¹⁰, electrochemical dilatometry³³, X-ray computed tomography³⁴, and mechanical stress measurements³⁵, can also probe the reversible expansion of insertion and alloy electrodes, as well as irreversible expansion concomitant with prolonged cycling. In essentially all cases, these techniques require specially designed cells to monitor expansion. Moving towards complete cells, one of the most accessible techniques employed to track volumetric expansion during cycling relies on *operando* pressure measurements with strain gauges mounted on cells. Dahn's group reported a variation of this measurement to decouple gassing from swelling for accurate monitoring of the SEI growth by adding a protruding gas bag to a pouch cell³⁶. Implementing such pressure measurements on various Li-ion NMC(NCA) with either graphite or C/Si composite electrodes, they succeeded in spotting the irreversible volume expansion caused by SEI growth and in ranking the performance of different Li-ion chemistries via capacity retention and irreversible pressure growth. Unfortunately, although elegant, it remains to be seen if this approach can be implemented commercially.

Acoustic sensing

Passive acoustic sensing: Beyond the degradation mechanisms stemming from electrolytes, the mechanical evolution of electrodes often leads to fracture events and a corresponding release of energy. These events consequently emit acoustic waves that depend on intrinsic material characteristics (crystallographic structure, grain size, and phase transformations³³, etc.), in addition to stresses arising during cycling^{37,38}, as depicted in Fig. 2a. Thus, acoustic emission (AE) characterization, as a non-destructive and passive technique, appears well-suited for tracking an electrode material that undergoes phase transitions and repeatedly expands and contracts during cycling, resulting in a range of crack types and locations. AE is broadly used³⁹ in civil structures for early detection of damage (cracks, fatigue) in concrete construction, and in aerospace to support predictive maintenance via strain mapping of aerospace parts. However, AE has had difficulties establishing itself in the field of batteries in spite of work dating back to the 1970s when it was used to study the breakdown of beta-alumina electrolyte²¹ in high-temperature sodium-sulphur batteries. Nevertheless, it regained interest in the 1990s, following the

work by Ohzuku *et al.* where Li/MnO₂ coin cells were mounted with an acoustic transducer attached to the cell casing via a silicon grease³⁷. Analyzing the collected acoustic emission signals produced by the cell during cycling, the authors spotted events that they ascribed to electrode electrochemical grinding, phase transitions, or gas evolution, and further hinted at the feasibility of such analytical tool to predict or forewarn of cell failure. This laid the foundation for the more recent use of AE sensing within the field of batteries to probe SEI formation, Li-driven volume changes in graphite³³ and Si⁴⁰ electrodes, as well as chemo-mechanical effects in layered oxide electrodes. As highlighted by Choe *et al.*⁴¹, with LiCoO₂/C cells, two types of AE events could be unveiled over two different frequency regions, based on waveform analysis, which when combined with scanning electron microscope (SEM) measurements, were assigned to LiCoO₂ fracture and SEI growth, respectively. Of course, the AE spectra will depend on cell chemistry, as highlighted by a recent study on LiNiO₂/Li cells⁴² where three distinct types of acoustic events are discerned during cycling. In addition to particle fracture, the growth of a cathode electrolyte interphase (CEI) at the positive electrode was also evidenced. However, cell voltage guidance together with complementary EIS and SEM measurements, were necessary to distinguish these phenomena. So despite the highly sensitive technique being relatively easy to apply, its difficulty resides in the complexity of linking observed events with their physical origin, unless complemented by additional analytical techniques.

Active acoustic sensing: New studies are employing acoustic ultrasound characterization, which is an active, but non-destructive technique that relies on the use of two piezoelectric transducers⁴³⁻⁴⁶: one sensor injects acoustic waves of a defined frequency into the battery when cycling, while the other one records the wave after it has travelled through the battery medium, see Fig. 2b. Its propagation velocity and amplitude attenuation not only depend on the properties (moduli, density, thicknesses, and porosity) of the anodes, cathodes, separators, and current collector layers that the wave is crossing (bearing in mind that at each interface the waves will be in part reflected and transmitted) but also on the electrolyte loading or residual gas bubbles. Although complex, these variables can be simulated via the elastic wave propagation theory, while the time-of-flight (ToF) vs. amplitude spectra of received pulses are temporally recorded upon cycling⁴⁷. From this information, a link between the ultrasonic spectra and SoC can be inferred. An explicit illustration⁴⁷ is conveyed via an operando study of commercial LiCoO₂/C pouch cells that were interrogated in their various SoC by employing pulses of 200 kHz. Both the amplitude and ToF of one peak of the rectified, received pulses showed a linear dependence on the SoC⁴⁷ and can enable the construction of models for predicting the SoH⁴⁸.

A more simple and practical way of using ultrasound within the field of batteries was recently illustrated by J. Dahn *et al.*, who developed an ultrasonic imaging apparatus^{49,50} that consists of a pair of movable ultrasonic transducers positioned on each side of the pouch cell with the whole cell immersed in silicone

oil for ultrasonic coupling, shown in Fig. 2c. With the attenuation of the transmitted signal being drastically different between dried, wetted or gas-containing electrodes, the authors succeeded in visualizing the electrolyte distribution within the cell as a function of impregnation time and electrolyte content by monitoring the amplitude of the transmitted wave. Moreover, cycling the Li-ion NMC/C cells with either different temperatures, cut-off voltages, or electrolytes, they could detect the early stages of gassing and confirm the number of cycles before the cell dries up. Thus, it offers the possibility of using ultrasonic imaging for assisting with electrolyte filling of Li-ion pouch cells, as well as tracking cell performance over time. This could be of great help for online inspection in LIB manufacturing facilities, provided that means are offered to manage the silicone oil inclusion.

Altogether, the sensors described so far (temperature, strain gauge, electrochemical, and acoustic) have different merits and enable access to key metrics for monitoring the ageing of commercial batteries under simulated working conditions. However, most of these sensing techniques, with the exception of acoustic ones, can barely access more than a single metric with precision. Acoustics are indeed prolific for visualizing consequences of mechanical effects but suffer from an inability to distinguish the exact sources. Furthermore, they do not provide direct access to invaluable temperature or thermodynamics observables. On the other hand, the development of optical sensing permits access to conjoined physical-thermal-chemical parameters that are essential not only for tracking the dynamic chemistry of parasitic reactions, but also for predicting cell end of life or anticipating thermal runaway.

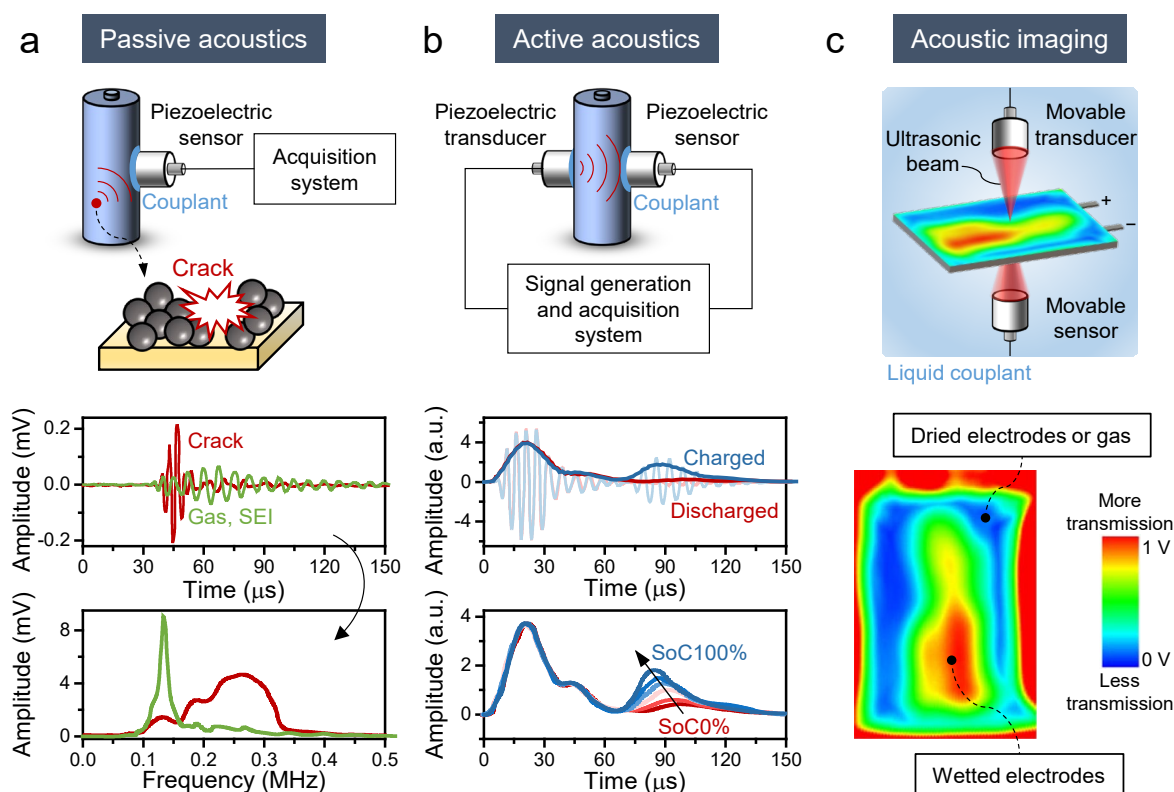


Fig. 2 | Acoustic sensing. a-c, The schematic illustrations showing the experimental set-ups and typical signals of non-destructive passive and active acoustic sensing in (a) and (b), respectively, with the acoustic imaging in (c). The Fourier analysis of the representative waveform signals (top) in (a) unravels two frequency events (bottom) that are related to the gas bubbles accompanied by SEI growth and the electrochemical crack of the positive electrode, respectively³⁸. (b) shows the smoothed data (dark lines) of the pristine acoustic response (shallow lines) in a Li-ion cell (top) with a strong correlation between the SoC and both the amplitude and the ToF of one peak (bottom)⁴⁷. Lastly, the acoustic imaging of a pouch cell⁵⁰ is shown in (c). Taking advantage of the different attenuation properties between wetted and dried cells or in gases, contour maps were obtained for distinguishing these regions, hence enabling tracking of electrolyte wetting and battery ageing.

Optical sensing

Optical fiber Bragg grating sensor: The rise of telecommunications technology based on optical fibers and optoelectronic devices has led to the successive development of optical sensors for a range of applications in the engineering and medical sectors⁵¹. The diversity of optical sensing methods lies in various physical phenomena by which light interacts with matter by either scattering (Brillouin⁵², Rayleigh⁵³, or Raman⁵⁴ scattering), diffraction, or absorption. For fibers, these interactions can either occur along the complete fiber length or be intentionally localized, leading to distributed or quasi-distributed sensors⁵¹. Fiber Bragg grating (FBG) optical sensors, for example, have a periodic modification of the refractive index inscribed over a finite distance in a single mode optical fiber (SMF).

SMF-FBG sensors, with the Bragg grating region acting as a reflector for a specific wavelength λ_B (Fig. 3a), are a mature technology used in many applications, including construction/assembling/infrastructure sectors for structural health monitoring⁵¹. They operate by correlating the wavelength dependence of the signal (λ_B) with the local temperature (T), pressure (P), and strain (ϵ) of the surrounding environment⁵⁵. Amongst their advantages, they are immune to electromagnetic interference, environmentally compatible, electrically insulating, lightweight with a small form factor, and additionally offer the possibility of multiplexed, multi-parameter sensing⁵¹. Owing to such benefits, SMF-FBG sensors have been inserted in fuel-cell stacks for thermal and water management via the combined monitoring of local temperature and humidity (with a polymer coating) under transient operating conditions⁵⁶.

SMF-FBG sensors have also been used in the field of batteries^{57,58}, owing to the pioneering works of PARC (a Xerox company)⁵⁹, Pinto's group^{60,61}, and others. FBGs were shown to be perfectly suitable for achieving reliable cell temperature images of Li-ion pouch and cylindrical cells under real working conditions⁶²⁻⁶⁴ (Fig. 3c), hence enabling access to the electrochemical-driven temperature gradient within the cell core and probing the effects⁶¹ of overcharge or external short-circuit on temperature. Besides monitoring the temperature with high sensitivity and space resolution, FBGs are also sensitive to strain

(ε)⁶⁵⁻⁶⁷, and two sensors (such as two FBGs^{65,66} or one FBG + one Fabry-Perot sensor⁶⁷) can be used to decouple ε and T . By cleverly configuring pairs of FBGs, PARC demonstrated in their seminal work^{65,66} that embedded FBGs sensors in large-format lithium-ion pouch cells for EV's applications are the ideal option to monitor strain and temperature over various operational and safety-critical scenarios. Based on the accuracy of the strain measured by FBGs, they were able to reach estimates of SoC of the pouch cells with an error of less than 2.5% under different temperature conditions and dynamic cycling, while also being able to predict the capacity up to 10 cycles ahead with approximately an error of 2% or lower⁶⁶. Thus, it implies that the cell capacity can be inferred by strain measurement. PARC also demonstrated the viability to further embed a FBG sensor within the graphite electrode in a liquid pouch cell and convert strain into stress for tracking its changes⁶⁸ (Fig. 3d). A successful extension of this approach to solid-state batteries is presently underway with the feasibility of monitoring stress evolutions both at interfaces and within the solid composite electrodes, hence providing guidance for electrode designs and cell assembling configurations in highly anticipated solid-state batteries.

In spite of the insights from SMF-FBGs discussed above, which correlate observables with battery SoC or SoH, the correlation between the observables and the underlying chemistry was not established. Recently, our group⁵⁵ partially closed this gap by pairing a SMF-FBG with another FBG written in a microstructured optical fiber (MOF-FBG), which by virtue of its air-hole pattern design offers a high sensitivity to hydraulic pressure. This renders possible the precise decoupling of temperature and pressure within the cell during cycling⁵⁵ (Fig. 3b). Using 18650 commercial Na-ion cells relying on the NVPF/C cell chemistry, we demonstrate the feasibility of tracking chemical events, such as the formation of SEI together with the evolution of parasitic chemical reactions. Moreover, via the use of multiple FBG sensors, a novel operando optical calorimetry method was developed based on a thermal model that enabled us to indirectly determine/quantify heat flows generated by the cells under different uses⁵⁵ (Fig. 3e). Unlike the isothermal calorimetry⁶⁹, it enables the access to heat capacity contributions and thus the full parameterization of battery thermal models. Taken together, these findings allow interfacial reactions to be monitored and offer a scalable solution for screening the role of electrolyte additives during the SEI/CEI formation, as was recently proven by the identification of a high-performance electrolyte for Na-ion cells⁷⁰. Moreover, knowledge of the cell's thermodynamic parameters extracted by this technique is of paramount importance to design battery thermal management systems⁷¹.

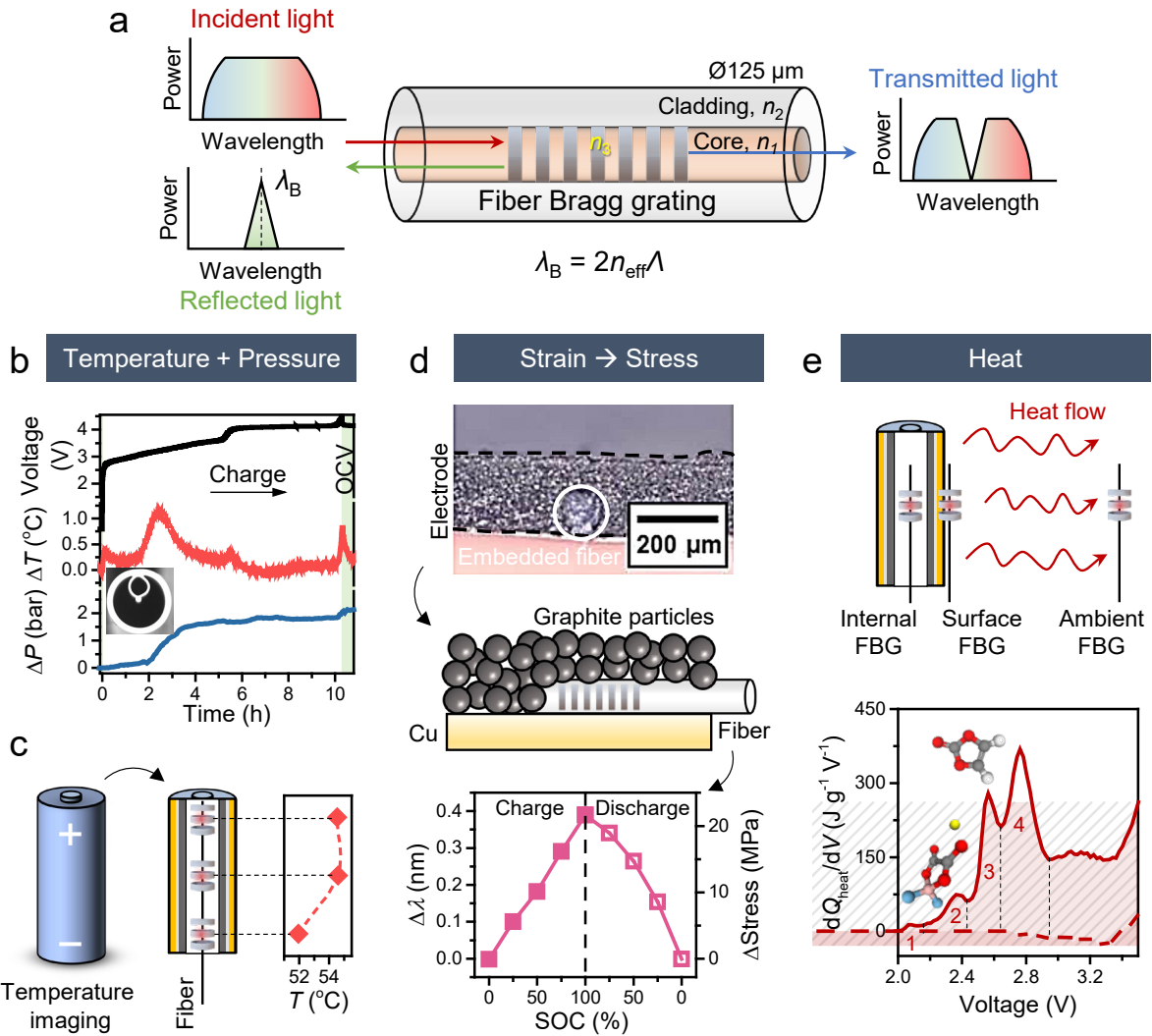


Fig. 3 | Optical sensing relying on FBGs. **a-e**, The working principle of FBG sensors is described in **(a)** together with examples showing their benefits to operando monitor temperature **(b, c)**, pressure **(b)**, strain/stress **(d)**, and heat **(e)**. As shown in **(a)**, the incident light is injected into the fibre core, and the fibre Bragg grating selectively reflects a characteristic peak at $\lambda_B = 2n_{\text{eff}}\Lambda$ with n_{eff} and Λ being the effective refractive index of the grating and the Bragg grating period, respectively. Due to the dependence of n_{eff} and Λ on T , P , and ϵ , the FBG sensor can monitor T , P , and ϵ by tracking λ_B shift. The variations of T and P , as deduced by combining FBGs written in SMF and MOF fibers⁵⁵, are shown in **(b)** with in **(c)** a cell temperature imaging obtained using an array of FBGs on the same fiber⁶³. **(d)** shows the use of FBG embedded inside the graphite electrodes to determine stress evolution inside the electrode during cycling⁶⁸. **(e)** shows the FBG's positioning for performing optical calorimetry and accessing the heat associated with the various steps (indexed by "1" to "4" in the figure) of the cascade reactions leading to the formation of the SEI⁵⁵.

Fiber optic evanescent wave sensor: To access rich chemical information pertaining to electrode materials, Li inventory, or electrolyte properties such as the refractive index (RI), we must escape from the situation in which the light is confined within the fiber core, as previously described. Measuring RI changes necessitates an optical sensing principle that relies on the evanescent field interaction at the

boundary between the fiber and the surrounding medium, as with fiber optic evanescent wave sensor (FOEWS). This calls for design modification of the optical fiber so that the light propagating in the direction of the fiber axis can partly escape from the core and reach the fiber/surrounding interface (Fig. 4a). One solution to achieve evanescent waves penetrating the external medium for distances on the order of hundred nanometers is to partially or totally remove the fiber cladding through etching⁷², polishing, or even by directly writing FBGs on the cladding⁷³. Another approach has relied on either increasing the grating period (~500 nm to tens/hundreds of μm) or tilting the grating plane of FBGs, leading to two other types of devices called long period grating (LPG)⁷⁴ and tilted fiber Bragg grating (TFBG)⁷⁵ sensors (Fig. 4b), respectively. Bearing in mind that the light in the cladding modes of these devices is penetrating the fiber environment, LPG and TFBG are sensitive to the surrounding RI , hence enabling real applications in gas/liquid detection⁷⁶, (bio-)chemical sensing⁷⁷, and in the field of electrochemistry such as supercapacitors⁷⁸.

Progress in this direction of chemical environment sensing within the field of batteries is illustrated by a study⁷³ dealing with RI measurements in 5 Ah Li-ion (NMC/C) pouch cells by using an FBG inscribed into the etched cladding of an optical fiber. A marked correlation between fading cell capacity and changes in the optical signals could be obtained. However, with this approach, several intertwined parameters (T , RI , and ϵ) are measured at once, thus rendering the quantification of RI infeasible⁷³. To overcome this complexity, a recent study⁷⁹ has injected a TFBG into the central void of pre-drilled commercial 18650 Na-ion cells to remove the sensitivity to ϵ . Unlike the sole peak pertaining to FBG and LPG detection, the rich features in TFBGs spectra facilitate the decoupling of multiple parameters, such as T and RI under real working conditions. By tracking changes of the RI during the formation cycle that are related to the variation of electrolyte characteristics in various electrolytes, it was feasible to trace decomposition pathways (e.g., the formation of sodium methoxide and dimethyl oxalate in the presence of dimethyl carbonate (DMC)) and comment on electrolyte stability during cycling. Copious electrolyte degradation can occasionally provoke particle precipitation that leads to modification of the electrolyte turbidity. This can be spotted as well by TFBGs due to the particulate-induced optical scattering and absorption. Thus, it is possible with TFBGs to monitor a cell's SoH with the advantage of avoiding the delicate process of cladding etching. Additionally, since each resonance peak responds differently to RI , T , and ϵ , the multiple modes of TFBG offer a viable platform to acquire at the same time multiple observables that can be decoupled from each other (e.g., quantifying internal pressure as an additional observable by inscribing TFBGs on a MOF fiber).

Plasmonic sensors, which in this context, can be viewed as optical fibers covered by a thin metallic layer which excites a surface plasmon resonance (SPR)⁸⁰, are naturally sensitive to the RI of the fiber's surrounding environment. Since a change in RI can be linked to a change in physical or chemical

composition, SPR sensors can be used for *operando* monitoring of physio-chemical changes in a penetration radius of a couple hundreds of nm to 1 micron around the sensor⁸¹. One possible embodiment of a SPR sensor consists of a fiber containing a TFBG, coated with a metal layer (typically, Au, Ag, etc.) in Fig. 4c, offering a better *RI* sensitivity than bare TFBGs. Thus, in 2018, Guo and Albert *et al.* demonstrated the use of a TFBG-SPR sensor to monitor the SoC of a supercapacitor⁷⁸, since the electrolyte concentration varies with SoC in a supercapacitor (anions adsorb at one electrode, while cations adsorb at the other). Alternatively, in a nano-plasmonic sensor (NPS), the continuous metal coating is replaced by a structured nanocoating or array of nanoparticles⁸². This allows the NPS to probe local surface plasmon resonances⁸³, enabling the sensing of molecular binding and conformation⁸⁴. Dealing with the field of energy, the use of the plasmonic approach for monitoring hydrogen insertion into the intermetallic compounds is worth mentioning⁸⁵. The present center of activities around nano-plasmonic sensing is intimately linked to progress in materials and nanoscience for adjusting the optical response of metallic nanostructures by engineering the dimension, size, shape, or dielectric environment⁸². Turning to the field of batteries, researchers from the company Insplorion (<https://www.insplorion.com/en/battery-sensor/>) are presently implementing a NPS approach in commercial batteries so as to record in real-time physio-chemical changes such as the variations in Li-ion concentration of the electrolyte. Moreover, an array of NPS sensors should be a good tool for transport properties determination⁸⁶, essential to electrochemical modeling.

Despite the potential benefit of accessing *RI*, there is a constant uncertainty about which specific characteristics of the electrolytes that are being measured, about changes due to specific electrolyte degradation, or variation of the salt or solvent concentration within the electrolyte. Unfortunately, the cell remains a black box regarding its dynamic chemistry. Are optical sensors capable of revealing such chemistry? This may indeed be one of the most promising aspects of such sensors when we remember that many spectroscopic techniques, such as Raman⁸⁷, phosphorescence⁸⁸, and infrared absorption spectroscopies, rely on the use of evanescent waves as well. A step towards this direction was taken once it was realized that the lithiation of graphite electrode is associated with a transmittance in the near infrared band (750 - 900 nm) within the SiO₂ fiber transmittance region (0-3 μm). Thus, by extending the FOEWS from *RI* to spectroscopic measurements, the changes in graphite⁷² optical properties can be detected. With these FOEWS, it is possible to assess the SoC of graphite, and further estimation of the SoH by monitoring the loss of Li inventory upon cycling becomes feasible. It was then logical to use FOEWS sensors to probe the electrolyte and to identify the nature and formulae of the chemical species forming during cell formation, which is critical to understanding the SEI growth and for providing a means to improve it. A difficulty, however, resides in the absorbing wavelength domain of such molecules that is beyond the transmittance domains of SiO₂ fibers⁸⁹. One solution to this is to use chalcogenide (sulfides,

selenides, and tellurides) glass fibers that can transmit light within the 2 – 12 μm wavelength range⁸⁹ (Fig. 4d). In one example, $\text{Te}_2\text{As}_3\text{Se}_5$ glass fibers were passed through the central voids of 18650 Na-ion cells and connected to an infrared optical signal generator and detector, while the cells (each with different electrolyte formulations) were electrochemically cycled⁹⁰. From the analysis of the collected spectra during the formation cycle and long cycling, the growth of additional infrared bands in cells containing DMC-based electrolytes leads to the ability to quantify Na-alkyl carbonates and Na-methoxy species. This ability to record the appearance of chemical species and even quantify them during battery formation and cycling by infrared absorption spectroscopy opens the way to an enhancement of battery lifetime and improved prospects for sustainability.

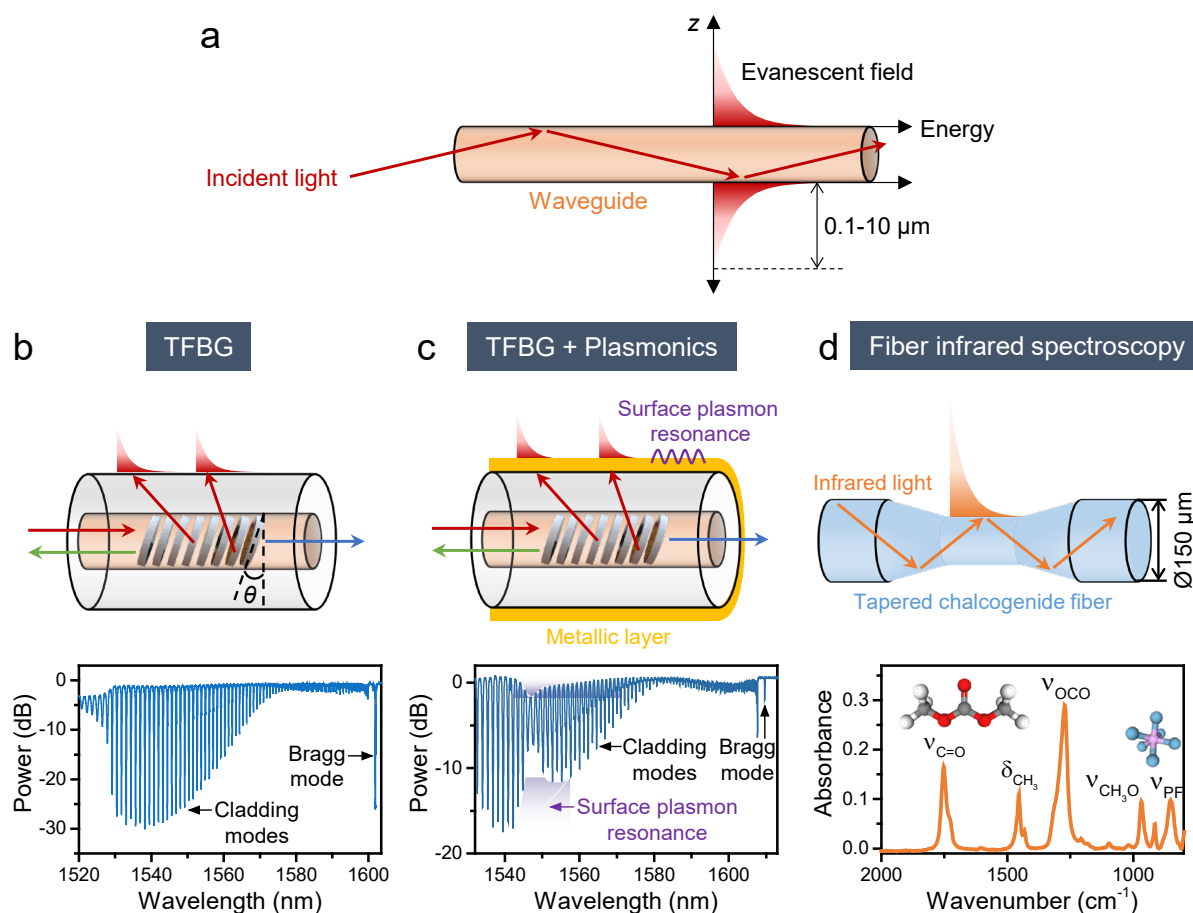


Fig. 4 | Optical sensing based on evanescent waves. a-d, The fundamental principle of FOEWS in (a) with the various sensors (b-d) working on this principle. As depicted in (a), the light propagates in the waveguide and the electromagnetic field away from the surface decays evanescently in the z-direction with a penetration depth^{81,83,91} on the order of 0.1 to 10 μm , enabling the interactions of light with the surrounding media. A schematic illustration of a TFBG sensor is shown in (b) together with a typical resonance spectrum, out of which a few metrics (T , ϵ , and R/I) can be deduced from the respective wavelength shift of each resonant peak. (c) is a derived version of (b) on which a thin plasmonic metallic film was deposited to stimulate the surface plasmon resonance, providing better sensitivity to R/I than the neat TFBG. Lastly, a tapered chalcogenide fiber for conducting an operando measurement in a commercial cell during cycling under real working conditions is shown in (d) together with an accompanied collected infrared absorption spectrum.

Outlook

New optical sensors are rapidly improving the feasibility for tracking key physical-chemical-thermal metrics and relating them to the SoC, SoH, SoP, and state of safety (SoS) of batteries. Aside from state estimation, the sensors can instantaneously identify catastrophic failures and extreme abuses. The various sensing approaches considered are neutral to cell chemistry since they can be used either in non-aqueous environment (Li(Na)ion, Li-S, solid-state batteries) or in aqueous environment (Zn-MnO₂, etc.).

Nevertheless, we must recognize that there are still a number of issues to be addressed prior to putting some of these advances into practice, but such challenges may also lead to new opportunities, as discussed below. Firstly, the usefulness of new fiber-based devices will only be meaningful if the lifetime of the sensor is greater than that of battery. This then calls for a thorough investigation of the long-term chemical stability of silica or chalcogenide-based fibers and of the metal plasmonic coatings in the harsh chemical nature of fluorine-based battery environments. This stability issue can be expected to be even more problematic for bare fibers. Naturally, this is a factor that we must anticipate by developing innovative chemical coatings having extremely high chemical and thermal stability, without compromising their optical properties.

Secondly, it is important for practical reasons to make optical sensors an integral part of the battery and not simply an add-on, but the relative manufacturing cost vs. benefit will determine which sensing approaches are deployed in packaged products, and which are relegated to internal R&D units. However, we can note that in the field of composites structures (pressure vessel and others), embedding single or multi-axis fiber grating strain sensor arrays is common practice. Furthermore, we note how the battery industry is presently trending towards individual cells with larger capacity and larger cost (*e.g.*, 18650 → 46800 or reducing number of pouch/prismatic cells in pack), increasingly justifying the incorporation of new functionality and the use of optical multiplexing to interrogate sensor arrays, while bypassing wiring constraints. Within this context, it is worth highlighting the cost analysis by *Alamgir et al.* from PARC⁶⁵ in 2016 which anticipated that a fiber-optic-sensing-based BMS would be comparable and competitive with an electrical sensing BMS. The study also noted that the cost of optical sensing, owing to multiplexing of the optical signals, does not scale up linearly with the number of cells, as is the case of electrical sensing.

The combination of innovations in sensor fabrication, along with advancements in data processing, may help in realizing a “lab-on-fiber” analytical platform for battery monitoring in the field. Pushing further this “lab-on-fiber” concept for chemical insights, one can envision the inscribing of FBGs or TFBGs on chalcogenides or even coupling acoustic transducers to FBG receivers in order to enhance strain imaging resolution, as done in aerospace⁹², or vice versa for photoacoustic approaches alike in medicine. With widespread adoption, addressing such a “lab-on-fiber” in a WiFi-type mode would be ideal. Relevant

experience may be gained from wireless, portable fiber optic interrogation systems in the medical⁹³ and aerospace⁹⁴ fields. Though encouraging, miniaturization and cost reduction of the interrogation system are still in need for battery applications, requiring close partnering with experts in optical hardware and signal processing.

Optical multisensory will also greatly benefit from the fiber materials engineering advancements, such as preparing a wide variety of fibers differentiated by their size (reaching less than a few microns facilitates their incorporation into coiled or flat electrodes), their nature (SiO_2 , chalcogenides, or even polymers), and their morphology. For example, two “butterfly” MOFs with different angular orientations were embedded within composite materials for assessing the three-dimensional strain field⁹⁵. Together with the emergence of MOF having various air-hole shapes, photonic crystal fibers (PCFs, a subgroup of MOF) bearing a central core, either hole or solid, surrounded by a cladding consisting of a periodic arrangement of microscopic capillaries⁹⁶ (Fig. 5a), provide unique sensing opportunities. They offer the possibility of infusing sub- μL liquids⁹⁷ within their open channels, hence drastically increasing the evanescent field penetration and therefore rendering PCF ideal for chemical detection via UV-vis, infrared, and Raman spectroscopies (Fig. 5b). PCFs are being widely exploited for the development of biosensors for molecular recognition⁹⁸ (Fig. 5c) and have been recently used for the first time in the field of batteries to follow the evolution of electrolyte by Raman spectroscopy during cycling⁹⁷ (Fig. 5b). Bearing in mind that PCF can also be made with chalcogenides fibers, infrared experiments are equally feasible but await to be realized.

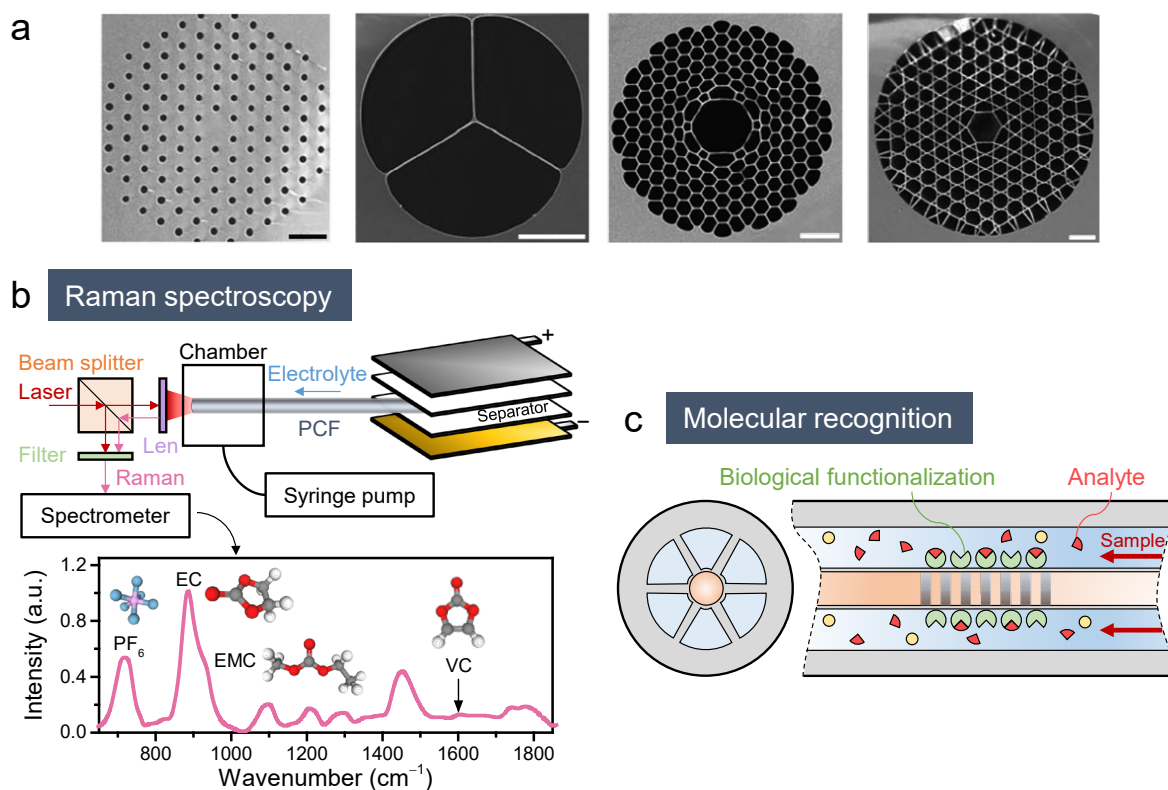


Fig. 5 | Fiber engineering. a-c, Advances in the realization of diversified PCFs⁹⁶ are shown in (a, scale bars from left to right correspond to 5, 20, 10, 20 μm , respectively) together with the first reported experiment in the field of batteries using such a type of fiber in (b) and the applications in biosensors in (c). A schematic of the set-up for conducting operando Raman spectroscopy with PCF sensors to monitor the electrolyte evolution upon cycling is shown in (b) with a collected Raman spectrum⁹⁷. Lastly, the benefit of using fiber capillary through the microfluidics set-ups for designing biosensors is shown in (c) for molecular recognition as well as the possible inspiration to extend such experiments to the field of batteries to sense specific, important molecules. Note that the surfaces of the capillaries can be functionalized for various purposes.

Thirdly, transmission and reception of the colossal amount of data obtained by sensing into BMS is another indispensable aspect to consider. The communication interfaces of the sensor must be viewed as an integrated aspect and have to be taken into account upstream, such that the sensor and cell are effectively co-designed. The development of intelligent responsive BMS and of state function estimators relies on the full exploitation of information available from the cell. To bring this fascinating field to fruition, subsequent advances dealing with both hardware and software are needed. The proper transfer functions and modeling tools (including the first-principle and other multiscale multiphysics models⁹⁹) must wisely use the sensing information read-out either at the cell, module, or pack level. For this to happen, the setting of a multisensory integration platform that fuses established models and state indicator algorithms developed via artificial intelligence (AI)⁹⁹ is essential. One plausible solution, as depicted in Fig. 6, is that data will be transferred from the battery in real time via IoT to feed a digital twin¹⁰⁰ in the cloud (*i.e.*, computationally-intensive multi-parameter model), which accurately calculates the state functions and relays information back to the BMS unit for improved operation. Although optimistic, such models would dramatically benefit from the increase in available information compared to today's off-line approach. In short, optical multisensory techniques open a new era for battery research that is solely limited by our imagination.

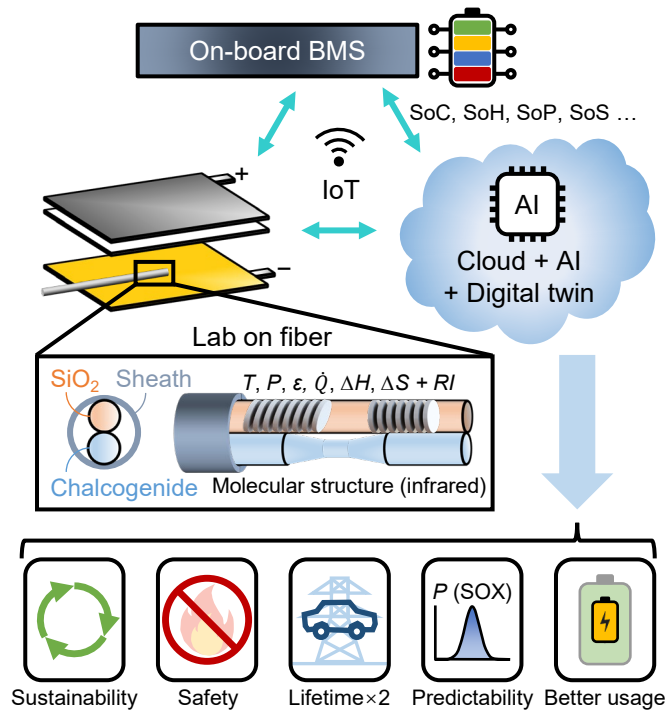


Fig. 6 | Projecting in the future. The “lab-on-fiber” concept combining FBG, TFBG, and chalcogenide infrared sensors is synergized with the cloud, AI, and digital twins to fully exploit the sensing information and offer critical read-outs of SoC, SoH, SoP, and SoS, etc. at the cell, module, or pack level for the intelligent and responsive BMS. The convergence of these cross-disciplinary approaches will result in long-life, highly reliable, and nearly fully sustainable batteries.

The development of these diagnostic tools coupled with advanced BMS methods will present the new possibility of approaching a battery’s theoretical performance during real-time operation. By offering accurate information and importantly, *information history*, batteries will become not only friendlier to the users, but also more valuable and less interchangeable. This approach can boost their wide acceptance in transport and other applications, some of which (*e.g.*, aerospace and defense) may be earlier adopters due to their more aggressive operational requirements and higher cost tolerance than EVs. As we have discussed, the monitoring of the battery metrics at the material level (T, P, ϵ), at the electrolyte level (RI and parasitic chemical species), and at the interface level (SEI) would allow us to enhance battery reliability and sustainability. This can, in theory, lead to a securitized table of the metrics and states, or perhaps even a blockchain-backed record, which is essential for it to become an energy-asset and optimize its service life. For example, current vehicle-to-grid scenarios expect that energy will be transferred back to the power grid from the battery of an electric car. Sensing mastery can verify the battery functional status through an electronic passport⁵, which then confirms the eligibility to ‘plug-in’. Similarly, knowledge of thermodynamic metrics provided by optical microcalorimetry will help to achieve the fastest or least-damaging charge rates in a safer way. Equally, it would allow for an online evaluation and optimization of internal cell balancing, in turn allowing for a finer tuning of, for example, maximum

charging power. Altogether, we have argued how the injection of embedded sensing technologies capable of performing spatial and time-resolved monitoring will give new life and shine light into old batteries. We anticipate that future optical sensing will lead to smarter and greener batteries. This is timely, since based on European new directives⁵, governments may even move to bind industry to control specific metrics in batteries in the coming years, hence facilitating industrial cooperation. We thus hope that this review will arouse interests and curiosity from a wide range of disciplines together with diversified industries beyond the battery sector because significant multidisciplinary challenges remain to realize a miniaturized optical fiber sensing platform. In the end, the practical success of *operando* monitoring of batteries will depend on the ambition and efficiency of the cross-fertilization between different scientific and industrial actors.

Correspondence and requests for materials should be addressed to J.-M.T.

Acknowledgments

We are truly thankful to Laura Albero Blanquer, Charlotte Gervillié, Julien Bonafacino, Jacob Joseph Lamb, Alexis Grimaud, and Charles Delacourt for their critical reading of the manuscript as well as to Lionel Quézel for sharing all of his expertise on FBG sensors. Equally, our thanks extend to Hwa-Yaw Tam and Tuan Guo for in-depth discussion of various aspects of optical sensing. We are also indebted to Fu Liu for providing the TFBG spectra and the fruitful discussions. We acknowledge BATTERY 2030+ funded by the European Union's Horizon 2020 research and innovation program under Grant agreement No. 957213, and the funding from the International Balzan Prize Foundation via the 2020 Balzan Prize to Jean-Marie Tarascon. Lastly, we would like to thank the Collège de France for making all 2020 Tarascon's lectures relating to this review available free of charge via the following link: <https://www.college-de-france.fr/site/jean-marie-tarascon/course-2020-2021.htm>

Competing interests

The authors declare no competing interests.

References

- 1 Larcher, D. & Tarascon, J. M. Towards greener and more sustainable batteries for electrical energy storage. *Nat. Chem.* **7**, 19-29 (2015).
- 2 Grey, C. & Tarascon, J. Sustainability and in situ monitoring in battery development. *Nat. Mater.* **16**, 45 (2017).
- 3 Bruder Müller, M., Sobotka, B. & Waughray, D. A Vision for a Sustainable Battery Value Chain in 2030. (World Economic Forum, Switzerland, 2019).
- 4 Fichtner, M. *et al.* Rechargeable Batteries of the Future—The State of the Art from a BATTERY 2030+ Perspective. *Adv. Energy Mater.*, 2102904 (2021).

- 5 European Union. Proposal for a regulation of the European parliament and of the
council concerning batteries and waste batteries, repealing Directive 2006/66/EC and
amending Regulation (EU) No 2019/1020. (Brussels: European Commission, 2020).
- 6 Birkl, C. R., Roberts, M. R., McTurk, E., Bruce, P. G. & Howey, D. A. Degradation
diagnostics for lithium ion cells. *J. Power Sources* **341**, 373-386 (2017).
- 7 Blanc, F., Leskes, M. & Grey, C. P. In situ solid-state NMR spectroscopy of
electrochemical cells: batteries, supercapacitors, and fuel cells. *Acc. Chem. Res.* **46**,
1952-1963 (2013).
- 8 Ilott, A. J., Mohammadi, M., Schauerma, C. M., Ganter, M. J. & Jerschow, A.
Rechargeable lithium-ion cell state of charge and defect detection by in-situ inside-out
magnetic resonance imaging. *Nat. Commun.* **9**, 1776 (2018).
- 9 Sathiya, M. *et al.* Electron paramagnetic resonance imaging for real-time monitoring of
Li-ion batteries. *Nat. Commun.* **6**, 1-7 (2015).
- 10 Huang, J. Y. *et al.* In situ observation of the electrochemical lithiation of a single SnO₂
nanowire electrode. *Science* **330**, 1515-1520 (2010).
- 11 Li, W. *et al.* Peering into Batteries: Electrochemical Insight Through In Situ and
Operando Methods over Multiple Length Scales. *Joule* **5**, 77-88 (2021).
- 12 Spitthoff, L., Shearing, P. R. & Burheim, O. S. Temperature, Ageing and Thermal
Management of Lithium-Ion Batteries. *Energies* **14**, 1248 (2021).
- 13 Knobloch, A. *et al.* Fabrication of multimeasurand sensor for monitoring of a li-ion
battery. *J. Electron. Packag.* **140**, 031002 (2018).
- 14 Amietszajew, T. *et al.* Hybrid thermo-electrochemical In Situ instrumentation for lithium-
ion energy storage. *Batteries & Supercaps* **2**, 934-940 (2019).
- 15 Martiny, N. *et al.* Development of an all kapton-based thin-film thermocouple matrix for
in situ temperature measurement in a lithium ion pouch cell. *IEEE Sens. J.* **14**, 3377-
3384 (2014).
- 16 Li, S. *et al.* Optimal cell tab design and cooling strategy for cylindrical lithium-ion
batteries. *J. Power Sources* **492**, 229594 (2021).
- 17 Bright, C. T. *et al.* Remarks on "On reversible lead batteries and their use for electric
lighting". *J. Soc. Telegraph-Eng. Electr.* **16**, 184-218 (1887).
- 18 Lanphier, R. C. THE AMPERE-HOUR METER FOR ELECTRIC VEHICLES.
Transactions (Society of Automobile Engineers) **6**, 371-393 (1911).
- 19 Mas, J. A. Battery charging system and transducer therefor. US patent 3,460,019
(1969).
- 20 Keddam, M., Stoyanov, Z. & Takenouti, H. Impedance measurement on Pb/H₂SO₄
batteries. *J. Appl. Electrochem.* **7**, 539-544 (1977).
- 21 Worrell, C. & Redfern, B. Acoustic emission studies of the breakdown of beta-alumina
under conditions of sodium ion transport. *J. Mater. Sci.* **13**, 1515-1520 (1978).
- 22 Nagai, Y., Tomokuni, Y. & Matsui, T. in *INTELEC'87-The Ninth International
Telecommunications Energy Conference.* 640-647. DOI:
610.1109/INTLEC.1987.4794631.
- 23 Garrard, W. N. C. & Charlesworth, J. M. Application of the quartz crystal microbalance
to measurement of the concentration of electrolyte in lead/acid batteries. *J. Power
Sources* **56**, 19-23 (1995).
- 24 Black, N. H. & Davis, H. N. *Practical physics; fundamental principles and applications
to daily live.* 79 (Macmillan, 1922).
- 25 Cao-Paz, A. M., Rodríguez-Pardo, L., Fariña, J. & Marcos-Acevedo, J. Resolution in
QCM sensors for the viscosity and density of liquids: application to lead acid batteries.
Sensors **12**, 10604-10620 (2012).
- 26 Dollé, M., Orsini, F., Gozdz, A. S. & Tarascon, J.-M. Development of reliable three-
electrode impedance measurements in plastic Li-ion batteries. *J. Electrochem. Soc.*
148, A851 (2001).
- 27 Smith, A. J., Burns, J. C., Trussler, S. & Dahn, J. R. Precision Measurements of the
Coulombic Efficiency of Lithium-Ion Batteries and of Electrode Materials for Lithium-Ion
Batteries. *J. Electrochem. Soc.* **157**, A196 (2010).

- 28 Dahn, H. M., Smith, A., Burns, J., Stevens, D. & Dahn, J. User-friendly differential voltage analysis freeware for the analysis of degradation mechanisms in Li-ion batteries. *J. Electrochem. Soc.* **159**, A1405 (2012).
- 29 Gireaud, L., Grugeon, S., Laruelle, S., Pilard, S. & Tarascon, J. M. Identification of Li Battery Electrolyte Degradation Products Through Direct Synthesis and Characterization of Alkyl Carbonate Salts. *J. Electrochem. Soc.* **152**, A850 (2005).
- 30 Horsthemke, F., Winkler, V., Diehl, M., Winter, M. & Nowak, S. Concept for the Analysis of the Electrolyte Composition within the Cell Manufacturing Process: From Sealing to Sample Preparation. *Energy Technol.* **8**, 1801081 (2020).
- 31 Day, R. *et al.* Differential thermal analysis of Li-ion cells as an effective probe of liquid electrolyte evolution during aging. *J. Electrochem. Soc.* **162**, A2577 (2015).
- 32 Aiken, C. *et al.* An apparatus for the study of in situ gas evolution in Li-ion pouch cells. *J. Electrochem. Soc.* **161**, A1548 (2014).
- 33 Ohzuku, T., Matoba, N. & Sawai, K. Direct evidence on anomalous expansion of graphite-negative electrodes on first charge by dilatometry. *J. Power Sources* **97**, 73-77 (2001).
- 34 Michael, H. *et al.* A Dilatometric Study of Graphite Electrodes during Cycling with X-ray Computed Tomography. *J. Electrochem. Soc.* **168**, 010507 (2021).
- 35 Al-Obeidi, A., Kramer, D., Boles, S. T., Mönig, R. & Thompson, C. V. Mechanical measurements on lithium phosphorous oxynitride coated silicon thin film electrodes for lithium-ion batteries during lithiation and delithiation. *Appl. Phys. Lett.* **109**, 071902 (2016).
- 36 Louli, A., Ellis, L. & Dahn, J. Operando pressure measurements reveal solid electrolyte interphase growth to rank Li-ion cell performance. *Joule* **3**, 745-761 (2019).
- 37 Ohzuku, T., Tomura, H. & Sawai, K. Monitoring of particle fracture by acoustic emission during charge and discharge of Li/MnO₂ cells. *J. Electrochem. Soc.* **144**, 3496 (1997).
- 38 Didier-Laurent, S., Idrissi, H. & Roué, L. In-situ study of the cracking of metal hydride electrodes by acoustic emission technique. *J. Power Sources* **179**, 412-416 (2008).
- 39 Mizutani, Y. *et al.* *Practical Acoustic Emission Testing*. (Springer, 2006).
- 40 Rhodes, K., Dudney, N., Lara-Curzio, E. & Daniel, C. Understanding the degradation of silicon electrodes for lithium-ion batteries using acoustic emission. *J. Electrochem. Soc.* **157**, A1354 (2010).
- 41 Choe, C.-Y., Jung, W.-S. & Byeon, J.-W. Damage evaluation in lithium cobalt oxide/carbon electrodes of secondary battery by acoustic emission monitoring. *Mater. Trans.* **56**, 269-273 (2015).
- 42 Schweidler, S., Bianchini, M., Hartmann, P., Brezesinski, T. & Janek, J. The sound of batteries: an operando acoustic emission study of the LiNiO₂ cathode in Li-ion cells. *Batteries & Supercaps* **3**, 1021-1027 (2020).
- 43 Sood, B., Osterman, M. & Pecht, M. in *2013 IEEE Symposium on Product Compliance Engineering (ISPCE)*. 1-6. DOI: 10.1109/ISPCE.2013.6664165.
- 44 Hsieh, A. *et al.* Electrochemical-acoustic time of flight: in operando correlation of physical dynamics with battery charge and health. *Energy Environ. Sci.* **8**, 1569-1577 (2015).
- 45 Robinson, J. B. *et al.* Spatially resolved ultrasound diagnostics of Li-ion battery electrodes. *Phys. Chem. Chem. Phys.* **21**, 6354-6361 (2019).
- 46 Robinson, J. B. *et al.* Identifying Defects in Li-Ion Cells Using Ultrasound Acoustic Measurements. *J. Electrochem. Soc.* **167**, 120530 (2020).
- 47 Gold, L. *et al.* Probing lithium-ion batteries' state-of-charge using ultrasonic transmission—Concept and laboratory testing. *J. Power Sources* **343**, 536-544 (2017).
- 48 Davies, G. *et al.* State of charge and state of health estimation using electrochemical acoustic time of flight analysis. *J. Electrochem. Soc.* **164**, A2746 (2017).
- 49 Deng, Z. *et al.* Ultrasonic Scanning to Observe Wetting and “Unwetting” in Li-Ion Pouch Cells. *Joule* **4**, 2017-2029 (2020).
- 50 Louli, A. *et al.* Diagnosing and correcting anode-free cell failure via electrolyte and morphological analysis. *Nat. Energy* **5**, 693-702 (2020).

- 51 Udd, E. & Spillman Jr, W. B. *Fiber optic sensors: an introduction for engineers and scientists*. (John Wiley & Sons, 2011).
- 52 Kurashima, T., Horiguchi, T. & Tateda, M. Distributed-temperature sensing using stimulated Brillouin scattering in optical silica fibers. *Opt. Lett.* **15**, 1038-1040 (1990).
- 53 Hartog, A. & Payne, D. in *8th European Conference on Optical Communication (ECOC-8)* (1982).
- 54 Dakin, J., Pratt, D., Bibby, G. & Ross, J. Distributed optical fibre Raman temperature sensor using a semiconductor light source and detector. *Electron. Lett.* **21**, 569-570 (1985).
- 55 Huang, J. *et al.* Operando decoding of chemical and thermal events in commercial Na (Li)-ion cells via optical sensors. *Nat. Energy* **5**, 674-683 (2020).
- 56 David, N., Wild, P., Jensen, J., Navessin, T. & Djilali, N. Simultaneous in situ measurement of temperature and relative humidity in a PEMFC using optical fiber sensors. *J. Electrochem. Soc.* **157**, B1173 (2010).
- 57 Han, G. *et al.* A review on various optical fibre sensing methods for batteries. *Renew. Sust. Energ. Rev.* **150**, 111514 (2021).
- 58 Su, Y.-D., Preger, Y., Burroughs, H., Sun, C. & Ohodnicki, P. R. Fiber Optic Sensing Technologies for Battery Management Systems and Energy Storage Applications. *Sensors* **21**, 1397 (2021).
- 59 Raghavan, A., Kiesel, P. & Saha, B. Monitoring and management for energy storage devices. US patent 9,203,122 (2015).
- 60 Leitão, C., Novo, C., Yang, G., Tang, C. & Pinto, J. in *Latin America Optics and Photonics Conference 2012*. LS2C.1. DOI: 10.1364/LAOP.2012.LS1362C.1361 (OSA).
- 61 Yang, G., Leitão, C., Li, Y., Pinto, J. & Jiang, X. Real-time temperature measurement with fiber Bragg sensors in lithium batteries for safety usage. *Measurement* **46**, 3166-3172 (2013).
- 62 Nascimento, M., Paixão, T., Ferreira, M. S. & Pinto, J. L. Thermal mapping of a lithium polymer batteries pack with FBGs network. *Batteries* **4**, 67 (2018).
- 63 Huang, J., Alberio Blanquer, L., Gervillie, C. & Tarascon, J.-M. Distributed Fiber Optic Sensing to Assess In-Live Temperature Imaging Inside Batteries: Rayleigh and FBGs. *J. Electrochem. Soc.* **168**, 060520 (2021).
- 64 Fleming, J. *et al.* Development and evaluation of in-situ instrumentation for cylindrical Li-ion cells using fibre optic sensors. *HardwareX* **3**, 100-109 (2018).
- 65 Raghavan, A. *et al.* Embedded fiber-optic sensing for accurate internal monitoring of cell state in advanced battery management systems part 1: Cell embedding method and performance. *J. Power Sources* **341**, 466-473 (2017).
- 66 Ganguli, A. *et al.* Embedded fiber-optic sensing for accurate internal monitoring of cell state in advanced battery management systems part 2: Internal cell signals and utility for state estimation. *J. Power Sources* **341**, 474-482 (2017).
- 67 Nascimento, M. *et al.* Internal strain and temperature discrimination with optical fiber hybrid sensors in Li-ion batteries. *J. Power Sources* **410**, 1-9 (2019).
- 68 Bae, C. J., Manandhar, A., Kiesel, P. & Raghavan, A. Monitoring the strain evolution of lithium-ion battery electrodes using an optical fiber Bragg grating sensor. *Energy Technol.* **4**, 851-855 (2016).
- 69 Downie, L. & Dahn, J. Determination of the voltage dependence of parasitic heat flow in lithium ion cells using isothermal microcalorimetry. *J. Electrochem. Soc.* **161**, A1782-A1787 (2014).
- 70 Desai, P. *et al.* Deciphering Interfacial Reactions via Optical Sensing to Tune the Interphase Chemistry for Optimized Na-Ion Electrolyte Formulation. *Adv. Energy Mater.* **11**, 2101490 (2021).
- 71 Wahl, M. S. *et al.* The Importance of Optical Fibres for Internal Temperature Sensing in Lithium-ion Batteries during Operation. *Energies* **14**, 3617 (2021).

- 72 Ghannoum, A. *et al.* Optical characterization of commercial lithiated graphite battery electrodes and in situ fiber optic evanescent wave spectroscopy. *ACS Appl. Mater. Interfaces* **8**, 18763-18769 (2016).
- 73 Nedjalkov, A. *et al.* Refractive Index Measurement of Lithium Ion Battery Electrolyte with Etched Surface Cladding Waveguide Bragg Gratings and Cell Electrode State Monitoring by Optical Strain Sensors. *Batteries* **5**, 30 (2019).
- 74 James, S. W. & Tatam, R. P. Optical fibre long-period grating sensors: characteristics and application. *Meas. Sci. Technol.* **14**, R49 (2003).
- 75 Albert, J., Shao, L. Y. & Caucheteur, C. Tilted fiber Bragg grating sensors. *Laser Photonics Rev.* **7**, 83-108 (2013).
- 76 Marrec, L. *et al.* in *Europe Oceans 2005*. Vol. 2, 1276-1278. DOI: 1210.1109/OCEANSE.2005.1513243
- 77 Guo, T., Liu, F., Guan, B.-O. & Albert, J. Tilted fiber grating mechanical and biochemical sensors. *Opt. Laser Technol.* **78**, 19-33 (2016).
- 78 Lao, J. *et al.* In situ plasmonic optical fiber detection of the state of charge of supercapacitors for renewable energy storage. *Light Sci. Appl.* **7**, 34 (2018).
- 79 Huang, J. *et al.* Monitoring battery electrolyte chemistry via in-operando tilted fiber Bragg grating sensors *Energy Environ. Sci.* **14**, 6464-6475 (2021).
- 80 Sharma, A. K., Jha, R. & Gupta, B. D. Fiber-Optic Sensors Based on Surface Plasmon Resonance: A Comprehensive Review. *IEEE Sens. J.* **7**, 1118-1129 (2007).
- 81 Raether, H. Surface plasmons. *Springer Tracts Mod. Phys.* **111**, 1 (1988).
- 82 Anker, J. N. *et al.* Biosensing with plasmonic nanosensors. *Nat. Mater.* **7**, 442-453 (2008).
- 83 Willets, K. A. & Duyne, R. P. V. Localized Surface Plasmon Resonance Spectroscopy and Sensing. *Annu. Rev. Phys. Chem.* **58**, 267-297 (2007).
- 84 Larsson, E. M., Langhammer, C., Zorić, I. & Kasemo, B. Nanoplasmonic probes of catalytic reactions. *Science* **326**, 1091-1094 (2009).
- 85 Nugroho, F. A. A. *et al.* Metal-polymer hybrid nanomaterials for plasmonic ultrafast hydrogen detection. *Nat. Mater.* **18**, 489-495 (2019).
- 86 Newman, J. & Chapman, T. W. Restricted diffusion in binary solutions. *AIChE J.* **19**, 343-348 (1973).
- 87 Yamanaka, T. *et al.* Ultrafine Fiber Raman Probe with High Spatial Resolution and Fluorescence Noise Reduction. *J. Phys. Chem. C* **120**, 2585-2591 (2016).
- 88 Fujimoto, S., Uemura, S., Imanishi, N. & Hirai, S. Oxygen concentration measurement in the porous cathode of a lithium-air battery using a fine optical fiber sensor. *Mech. Eng. Lett.* **5**, 19-00095 (2019).
- 89 Yang, G. *Structure and physical properties of chalcogenide glasses* Doctoral thesis, Université de Rennes 1, (2012).
- 90 Tarascon, J.-M., Gervillie, C., Boussard, C., Zhang, X.-H. & Adam, J.-L. Method for operando characterization of chemical species within a battery using infrared spectroscopy. EP21306068.4 (2021).
- 91 Larkin, P. *Infrared and Raman spectroscopy: principles and spectral interpretation*. (Elsevier, 2017).
- 92 Udd, E. High speed fiber grating sensors for structural monitoring. *SPIE Sens. Technol. + Appl. XI* **9098** (2014).
- 93 Ogawa, K. *et al.* Wireless, Portable Fiber Bragg Grating Interrogation System Employing Optical Edge Filter. *Sensors* **19**, 3222 (2019).
- 94 Mendoza, E., Kempen, C., Sun, S. & Esterkin, Y. Light weight, high-speed, and self-powered wireless fiber optic sensor (WiFOS) structural health monitor system for avionics and aerospace environments. *SPIE Opt. Eng. + Appl.* **9202** (2014).
- 95 Sonnenfeld, C. *et al.* Microstructured optical fiber Bragg grating as an internal three-dimensional strain sensor for composite laminates. *Smart Mater. Struct.* **24**, 055003 (2015).
- 96 Cubillas, A. M. *et al.* Photonic crystal fibres for chemical sensing and photochemistry. *Chem. Soc. Rev.* **42**, 8629-8648 (2013).

- 97 Miele, E. *et al.* Operando Raman analysis of electrolyte changes in Li-ion batteries with hollow-core optical fibre sensors. DOI: 10.21203/rs.21203.rs-531818/v531811 (2021).
- 98 Bertucci, A. *et al.* Detection of unamplified genomic DNA by a PNA-based microstructured optical fiber (MOF) Bragg-grating optofluidic system. *Biosens. Bioelectron.* **63**, 248-254 (2015).
- 99 Vegge, T., Tarascon, J. M. & Edström, K. Toward Better and Smarter Batteries by Combining AI with Multisensory and Self-Healing Approaches. *Adv. Energy Mater.* **11**, 2100362 (2021).
- 100 Wu, B., Widanage, W. D., Yang, S. & Liu, X. Battery digital twins: Perspectives on the fusion of models, data and artificial intelligence for smart battery management systems. *Energy AI* **1**, 100016 (2020).