Smarter Batteries Based on New Embedded Sensors for In-Live Monitoring of Their Chemical and Physical Evolution

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2020 Balzan Prize for Environmental Challenges: Materials Science for Renewable Energy

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Monitoring the dynamic chemical and thermal state of a cell during operation is crucial in order to make meaningful advancements in battery technology as safety and reliability cannot be compromised. There are two objectives to this project. The first proposes to diversify sensor configuration either by using titled optical fiber grating (TFBG) or Au-coated FBGs to probe the fiber surrounding chemical media. Additionally, we will envision the chemical functionalization of the fiber cladding or the injection of fluorescence or IR probes with optical readout for the identification of chemical species. The second aim deals with the implementation of FBGs within a solid-state battery to monitor strain, pressure, and decomposition reactions developing at interfaces, and to enable the development of this technology, which is a hot topic in today's battery research. Altogether, these studies, which will involve collaboration between the Collège de France and the Hong Kong Polytechnic University, should enable in-live monitoring of the state of health of the battery while increasing its overall performance. They will also offer a second life to the battery. Both are essential to increase battery sustainability and lower their CO_2 footprint.

Research Advances 2020-2023

Executive summary

As society moves towards a sustainable and electrified future, it is crucial to increase battery lifetime, safety and reliability under working conditions, as these figures of merits cannot be compromised. This requires a paradigm shift in battery monitoring. Thanks to the support of the Balzan Foundation support we were able to take up this challenge and open up a new avenue of research direction, aimed at developing smart batteries by injecting sensing and self-repair functionalities to improve their quality, reliability, and lifespan, thereby reducing their environmental footprint. Key advances have been made over the past three years. Firstly, we demonstrated the operational decoding of chemical and thermal events in commercial Na(Li)-ion cells via fiber Bragg grating (FBG) sensors and developed a new optical calorimetry technique to access battery thermodynamic metrics. In addition, using a tilted fiber grating (TFBG), we were able to access the kinetics of the chemical reactions involved during battery functioning. However, our latest coup is the use of operando infrared fiber evanescent wave spectroscopy to monitor the chemical evolution of the electrolyte in 18650- and pouch-format Na-ion and Li-ion batteries, enabling chemical species to be identified under real working conditions. This first in the field of batteries has had an impact on a global scale (10 articles in high impact journals; 5 patents; widespread media coverage). This transformational change in battery diagnostics is attracting interest from materials producers, battery makers, and users as evidenced by the large number of partnership requests we received.

Research and societal context of the study

As one of the most versatile energy storage technologies, batteries play a central role in the ongoing transition from fossil fuels to renewable energies. They have become key enablers for the deployment of electric transportation and the use of decentralized renewable energy sources. Our increasing dependence on batteries calls for an accurate monitoring of the battery functional status to increase their quality, reliability, and lifetime. Battery performances are mainly governed by nature and dynamic interfaces that are rooted in temperature-driven reactions with unpredictable kinetics. Surprisingly, although monitoring temperature is essential for enhancing the battery cycle life, it is not directly measured today at the cell level in EV (Electrical Vehicles) applications. So fundamental science is sorely needed to provide a better knowledge/monitoring of the battery’s physical/chemical parameters (temperature, pressure, strain, parasitic reactions) during cycling in order to understand science beyond the nucleation/growth of interfaces for enhancing their performances.

Keeping in mind that batteries are becoming the heart of our daily lives together with the increasing social demands for highly reliable and long-life batteries, back in 2020, as laureate of the Balzan’s prize, I proposed a disruptive approach to target those social expectations. It consists in injecting smart embedded sensing technologies into the battery in order to perform spatial and time-resolved monitoring, with the possibility of transmitting information in and out of the cells alike, as is done in medicine during surgery via the use of optical fibers. So far, sensing activities within the field of batteries have mainly relied on the use of sensors placed outside rather than inside the cells, hence limiting the knowledge of internal chemical/physical parameters, which are of paramount importance for monitoring battery lifetime. Thus, we developed implantable sensors that can measure, via non-disruptive approaches, multiple parameters such as temperature (T), pressure (P), strain (□□, electrolyte composition (x), electrode breathing (□V), and heat flow (q) with high sensitivity at various locations within the cells.

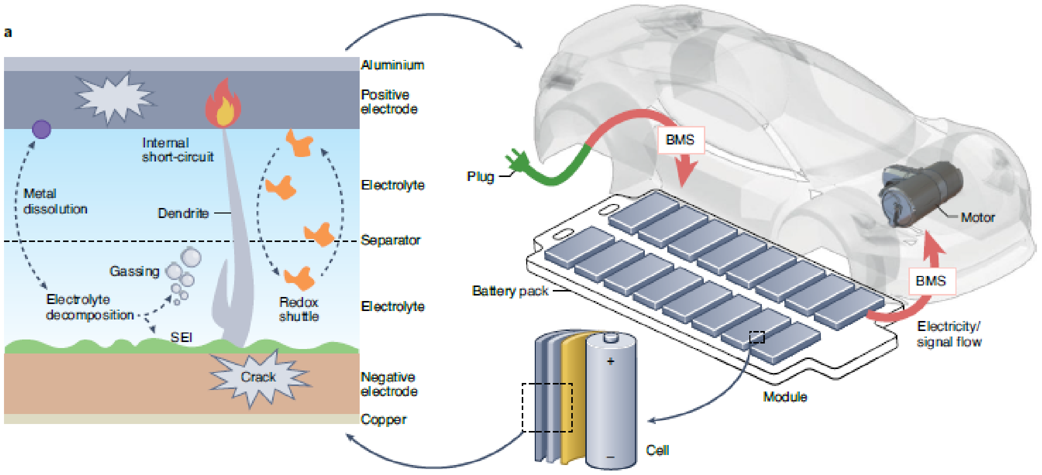


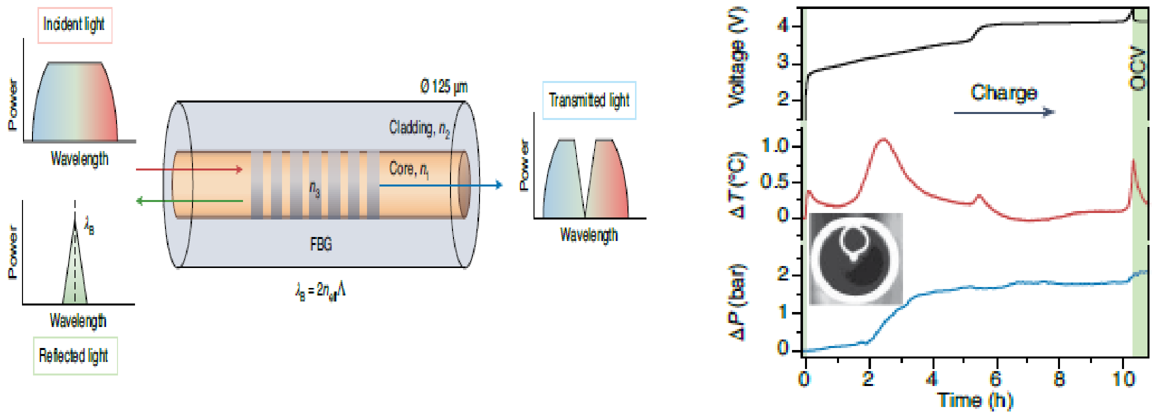
Figure. 1: Sensing overview. Major physical-chemical sources of battery dysfunction at the component and cell level, with an emphasis on the gap that exists in going from the laboratory to system applications.

Achievements

Inspired by the field of medicine within which fibers are used to transmit and receive signals during the operation, our group has injected optical sensors inside the battery to monitor, with high sensitivity and accurate space resolution, changes in multiple metrics, such as chemical composition, strain, temperature and pressure. A chronological account of our progress follows.

2019 -2021: Fiber Bragg Grating sensors *(FBGs).*

Spectacularly, using conjointly optical Fiber Bragg Grating sensors inscribed in a single mode fiber (SMF-FBG) or in Microstructure Optical Fiber (MOF-SBG), we demonstrated 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 uses. Unlike isothermal calorimetry, 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 to screen 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 cells. We expanded the versatility of this analytical approach by implementing it to different battery chemistry (Li-ion , Na-ion) as well as different cell configurations (18650 vs; pouch cells). Moreover, knowledge of the cell's thermodynamic parameters extracted by this technique is of paramount importance to design battery thermal management systems. We further demonstrated the effectiveness of using optical sensing calorimetry to equally measure the temperature and heat of NMC/C commercial pouch batteries under different test conditions, hence revealing information regarding the kinetics, safety limits during fast charging, overcharging, and under real driving applications as the Worldwide Harmonized Light Vehicles Test Procedure (WLTP).



<u>Figure 2:</u> Optical sensing relying on FBGs. The working principle of FBG sensors is shown in the left. The incident light is injected into the fiber core and the FBG selectively reflects a characteristic peak at $\lambda B = 2n\text{eff}\Lambda$, where $n$eff and Λ are the effective refractive index of the grating and the Bragg grating period, respectively. Owing to the dependence of $n$eff and Λ on T, P and ε, the FBG sensor can monitor T, P and ε via tracking the λB shift. The variations of T and P as deduced by combining FBGs written in SMF and MOF fibers are shown on the left (with the inset showing the cross-section of a MOF).

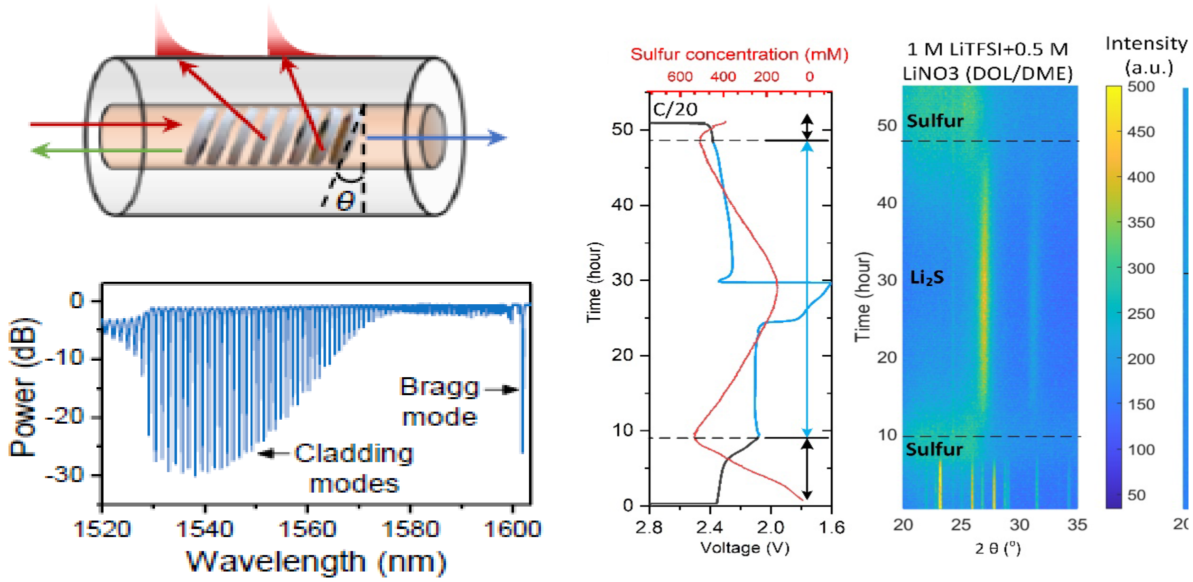
Moreover, the intrinsic chemical, mechanical, and thermal robustness of FBG sensors suggests that the operando techniques we developed and protected by three patents can be extended to other energy storage devices (such as fuel cells and supercapacitors) as well as other important applications (such as catalysis and water-splitting), to achieve fundamental advancements in the academia and industry fields alike.

2021 -2023: Tilted Fiber Bragg Grating Sensors (TFBGs)

At this stage we were still lacking chemical information pertaining to electrode materials, Li inventory, or electrolyte properties surrounding the fibers such as its refractive index (*RI*) which is affected by parasitic chemical reactions occurring during cell cycling. To overcome our limitation, we needed to 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 observation 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 tilt the grating plane of FBGs, leading to another type of device called tilted fiber Bragg grating (TFBG) sensors. Keeping in mind that the light in the cladding modes of TFBG penetrates the fiber environment, TFBG is sensitive to the surrounding *RI*, hence our idea to apply this approach to the field of battery monitoring.

We injected a TFBG into the central void of pre-drilled commercial 18650 Na-ion cell. Unlike the sole peak pertaining to FBG, the rich features in TFBGs spectra facilitates 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.

Just recently, we described and showed the use of TFBG sensors to track, via the monitoring of both temperature and refractive index metrics, electrolyte-electrode coupled changes that fundamentally control lithium sulfur batteries. Through quantitative sensing of the sulfur concentration in the electrolyte, we demonstrated that the nucleation pathway and crystallization of Li2S and sulfur governs the cycling performance, hence establishing a correlated relationship between the capacity fading and dynamic of dissolution/precipitation of polysulfides over cycling and at different cycling rates. In parallel, we could decode, via GITT experiments, the chemical kinetic and thermodynamic response of soluble polysulfide in electrolyte and access the dynamic disproportionation process linked to the transport flux of soluble species.



<u>Figure. 3:</u> **Optical sensing based on evanescent waves.** As depicted in the schematic illustration of a TFBG sensor (top); the light propagates in the waveguide and the electromagnetic field away from the surface decays evanescently in the *z* direction with a penetration depth of the order of 0.1–10 µm, enabling the interactions of light. Underneath is the associated typical resonance spectrum from which a few metrics (*T*, *ε* and RI) can be deduced from the respective wavelength shift of each resonant peak. *θ* indicates the tilting angle of grating planes relative to the cross-section of the fiber. On the right is operando measurement of a lithium sulfur battery by TFBG and XRD at C/20. Note that the changes in the electrolyte refractive index (RI) correlate nicely with the dissolution of S into polysulfide's (RI) increase) and its precipitation in Li_2S (RI decreases).

With this technique, a critical milestone is achieved, not only towards developing chemistry-wise cells (in terms of smart battery sensing leading to improved safety and health diagnostics), but further towards demonstrating that the coupling of sensing and cycling can revitalize known cell chemistries and break open new directions for their development. Additionally, since each resonance peak responds differently to *RI*, *T*, and *ε*,the multiple modes of TFBGs 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). This constitutes a key advance towards our dream of realizing our "lab-on-fiber" analytical platform for battery monitoring.

2022 – 2023$^+$: Tilted Fiber Bragg Grating Sensors (TFBGs)

We previously showed that physical metrics (such as temperature and pressure) were accessible through the incorporation of optical sensors (FBGs) into practical batteries. Similarly, by monitoring the evolution of the electrolyte refractive index (RI) we could capture the chemical dynamics of batteries involving intertwined reaction pathways between electrolytes and electrodes but failed to determine the chemical species involved in the processes, because the measurement is blind to the fiber's chemical environment. To overcome this, it was necessary to find a way for some of the light carried by the fiber to escape the fiber and spy on its surroundings. Having this in mind, we developed an approach that takes advantage of the evanescent field created at the surface of the optical fiber and uses a chalcogenide rather than silica fiber to transport light in the infrared (IR) region to detect the molecular signatures of chemical species in the electrolyte and electrode materials.

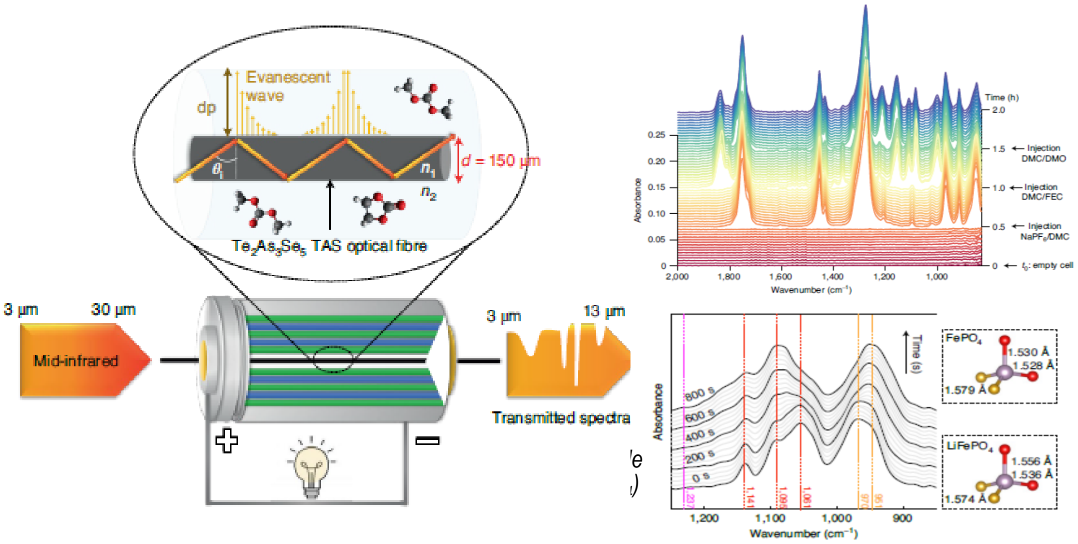


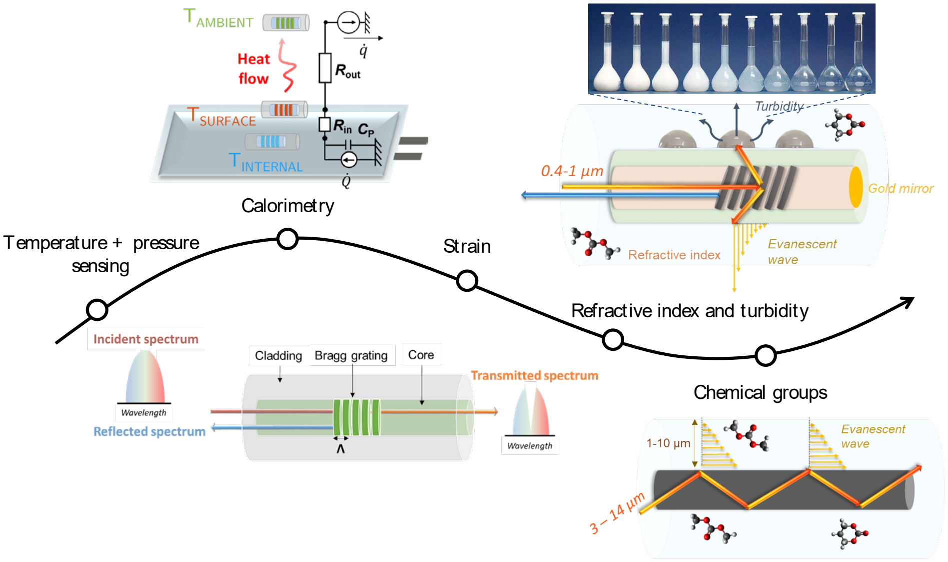
Figure. 4: **Operando IR fire evanescent wave spectroscopy.** Schematic of IR light propagation via total internal reflections (where θi is the incident angle of the light) through the $Te_2As_3Se_5$ (TAS) fiber core (where d is the fiber diameter). At the fiber surface, an evanescent wave is created, the depth of penetration (Dp) of which depends on θi and on the refractive indexes of the fiber ($n1$) and its surrounding medium ($n2$). The TAS fiber is passed through the central void of an 18650 jelly-roll, allowing for IR-FEWS operando measurements of the electrolyte while cycling the battery. On the top right, the IR-FEWS absorbance spectra as a function of time, obtained via the use of a commercial Na-ion cell hosting the TAS fiber while in the bottom the stacked IR-FEWS absorbance spectra at different values of the lithium content x in Li_xFePO_4 are shown.

Practically, a chalcogenide $Te_2As_3Se_5$ fiber is first passed through the core of a 18650 Li-ion (Na-ion) cell and the IR spectra are recorded operando while the cell is charged or discharged, enabling the identification of chemical species in the surrounding medium of the fiber. Using this knowledge, we succeeded in revealing mechanisms underpinning electrolyte degradation during cycling and the role of additives, thereby providing insight into the nature of the SEI, the dynamics of solvation, and their complex interrelations. Aside from revealing chemical species involved in parasitic electrolyte degradation, our analytical approach provides insight into insertion processes and the Li(Na) inventory within the cell upon cycling. This is a first in the field of batteries, so it is not surprising that this work is attracting worldwide attention and media coverage (see end of the document). Moreover, this approach can also be applied to other energy-storage devices (such as fuel cells and supercapacitors). Put simply, if a new electrolyte additive is proposed, how can one understand what it does? In the past, this answer would be crudely extracted from capacity and cycling data. With our approach, one can monitor the solvation, dissociation, coordination and formation of chemical species from the moment the electrolyte is prepared and/or put into the cell.

However, like for many discoveries, our IR-FEWS approach can be improved by drawing inspiration from other fields. For example, it is necessary to address the engineering limitations due to the brittleness of the $Te_2As_3Se_5$ fibers and the engineering of apertures in the cell to avoid perturbing the venting valve while preserving airtightness. Compared with FBG sensing, an additional difficulty is the limitation to a single measurement per spectrometer. However, this problem might be surmountable, as ongoing studies on optical switches have already enabled a single IR channel to periodically monitor multiple fibers. Finally, different decomposition and formation reactions can induce counteractive effects on the IR signal, making deconvolution of the spectra challenging. Methods based on machine learning could be one route to quantifying the degradation of different solvents during operando measurements. These challenges are presently addressed by exploring different fiber compositions and morphologies, including hollow core fibers through national and international partners (University of Rennes and of Hong-Kong, respectively) and by establishing collaborations with experts in data treatment (SAFRAN).

Conclusions and perspectives

Altogether, our work provides a comprehensive understanding of the fundamental mechanisms and performance characteristics of batteries through optical sensing. We have highlighted the opportunities offered by optical sensing through access to a wide range of physical-chemical observables (P, T, e, RI, Li^+ content) (Fig. 5) to optimize battery formation steps and electrolyte formulations on an industrial scale, resulting in time and cost savings. Furthermore, we showed the feasibility of ranking various battery chemistry with respect to worldwide-recognized EV driving tests (WLTP). Lastly, as never before, we have been able to monitor the dynamic chemistry of commercial batteries in real time using infrared fiber spectroscopy, enabling us to better understand the parasitic reactions occurring at the electrodes and in the electrolyte.



<u>Figure 5:</u> ***Operando*** **battery diagnostics of commercial cells.** Operando access to chemical and physical metrics in commercial cells *via* optical sensing. Fibers Bragg Grating sensors (FBGs) inscribe on single mode optical Fiber (SMF) are used for physical metrics (T, P, □), thermodynamic observables □H, Cp, while Titled Fiber Bragg gratings (TFBGs) measure changes in Refractive index and turbidity. Last IR Optical spectroscopy to determine the nature of molecular parasitic species is done *via* chalcogenide fibers.

Access to these different observables could be a preliminary step towards integrating batteries in electric vehicles, where new design packs are emerging. Overall, spatial and time-resolved optical fiber monitoring will give new life and shine light into old batteries. As optical sensors become increasingly ubiquitous in our environment, they can be utilized to monitor other aspects of the vehicle, such as tires, and ultimately, in a more connected world, we can obtain accurate information about our batteries at any time. This is timely, as based on new European Union directives, governments may even move to force industry to control specific metrics in batteries in the coming years. In the light of these advances, optical monitoring has aroused the interest and curiosity of a wide range of disciplines and industries beyond the battery field. New opportunities are emerging: a miniaturized fiber optic sensing platform has yet to be realized. Intense cross-fertilization between different scientific and industrial players will be essential to ensure the practical success of operando monitoring of batteries.

What happens next? A full mastering of battery diagnostic via optical sensing so as to realize our “lab-on- fiber” dream will require a deeper understanding of the science beyond the observed measurements, as well as clever ways to make such a new diagnosis approach practical and widely used in next generation of EVs or in new grid designs. To meet these challenges, our roadmap for the upcoming 2 to 3 years is as follows:

- Firstly, we plan to explore coating SiO2 fibers with functionalized polymers to design sensors with specific spatial chemical sensitivity or a thin Au layer to trigger plasmonic surface effects and lower the detection threshold of ions and molecules. A more futuristic approach will be to deposit a transparent, metallic ITO coating on a chalcogenide fiber with the hope of simultaneously performing electrochemical charges and discharges while visualizing SEI growth by IR optical spectroscopy.
- Secondly, we need to simplify data acquisition and analysis to transform optical calorimetry into a user-friendly diagnostic technique for battery manufacturers interested in optimizing electrolyte formulations, simplifying formation protocol testing, classifying cathode electrochemical stability, etc. Here to handle the large amount of data generated by this remote sensing we are setting up collaborations with experts (S. Mallat) in data processing, machine learning and artificial intelligence.
- Thirdly, last but not least, to ensure successful implementation of this optical tool in practical batteries, we need to miniaturize our interrogator device while still being able to address it remotely via Wi-Fi or Bluetooth. We initiate research towards this direction through a collaboration with Professor Tam, University of Hong Kong, who is a world expert in the development of miniaturized optical interrogators and wireless sensing for medical applications.

All these efforts are being carried out in parallel to develop intelligent and responsive battery management systems in conjunction with industrial electric vehicle manufacturers in order to realize prototyping. The results will be presented in the next report.

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