

Operando Electrochemical-TERS Study to Unveil Structure-Activity Relationships in Li-Ion Batteries

■ Background and Challenges

When subjecting Li-ion batteries to repetitive charge/discharge cycles, the migration of lithium ions between the two electrodes generates a series of electrochemical transformations over the active material surfaces and at the interfaces between them and the electrolyte, which influences the battery performance in terms of efficiency, stability and longevity. Tracking in real time the chemical and physical processes that follow these reactions is crucial for understanding if and how the battery components are modified, and how to optimize the overall quality of the battery itself. Among different *in situ* or *operando* techniques that could yield this kind of information, Raman spectro-electrochemistry has the advantage of coupling the chemical sensitivity of vibrational spectroscopy with the precise electrical control of the charge/discharge

process via a potentiostat throughout the measurements. Moreover, when implementing this setup in a scanning probe microscope, not only the spectro-electrochemical information can be additionally correlated to the sample morphology, but the Raman resolution can be improved beyond the diffraction limit to reach a nano-scale precision.

This note will present an example of a successive *operando* study performed with this setup^[1] as part of the European project Harvestore^[2], focused on the development of devices for energy harvesting and storage. Thanks to the coupling of nanoRaman with electrochemistry, the local reactivity of a cathode materials for Li-ion batteries could be probed in real time, thus showing its morphology-dependent efficiency during the charge/discharge process.

■ HORIBA's option for TERS in liquid and electrochemical conditions

All HORIBA's Raman microscopes can be coupled to an atomic force microscopy (AFM) setup via a dedicated optical platform. When the Raman laser is redirected towards a plasmonic AFM probe, this acts as a new nano-source of light and can be used to perform tip-enhanced Raman spectroscopy (TERS). As a result, the scattered signal is amplified up to a factor of 10^5 - 10^6 , while the resolution improves down to the nanometre scale.

Recently, HORIBA designed a cell and a set of accessories (Figure 1) for facilitating AFM-TERS measurements in liquid media, as well as under electrochemical (EC) conditions. For this purpose, the cell can indeed be set up in a fully functional three-electrode configuration and controlled externally by a potentiostat, thus enabling *in situ/operando* spectro-electrochemical material characterization with nanoscale precision.

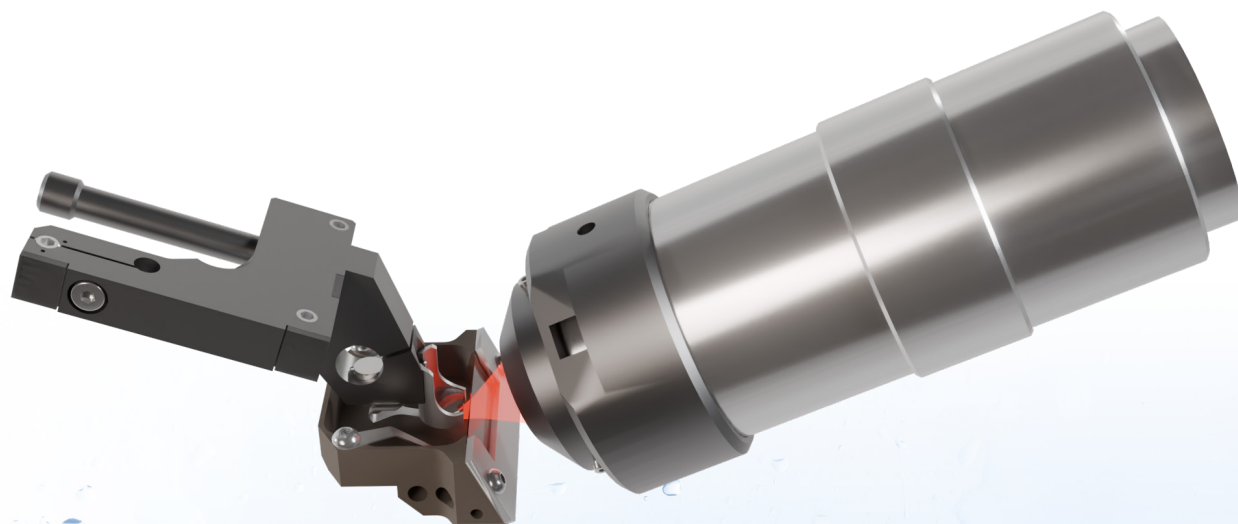


Figure 1. Setup for AFM-TERS in liquid environment.

The EC-TERS analysis presented here were performed on a model cathode material, LiMn_2O_4 , deposited in a thin film over a platinum-coated substrate. An aqueous solution of 1M Li_2SO_4 was used as supporting electrolyte, while two platinum wires were used as the reference and the counter electrodes inside the AFM cell.

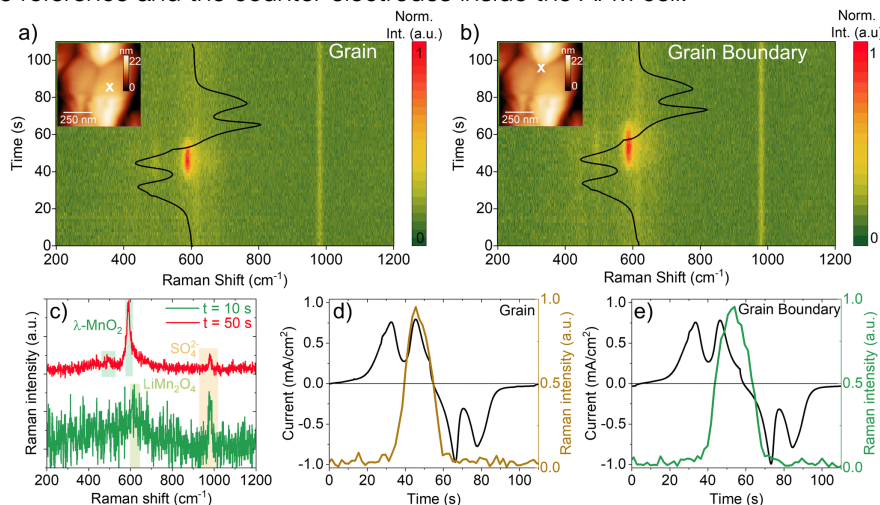


Figure 2. TERS time maps acquired while sweeping the potential over a (a) grain and (b) grain boundary of LiMn_2O_4 , shown in the insets of each map (1 s acquisition/spectrum, 638 nm laser at ~ 3 mW of power). The black profile superposed to the maps represents the current density variation as a function of time, recorded while scanning the potential from 0.5 to 1.05 V vs Pt (5 mV/s scan rate). (c) EC-TERS spectra extracted before ($t=10$ s, green) and after ($t=50$ s, red) delithiation of LiMn_2O_4 on the grain: the band centred at 590 cm^{-1} is indeed characteristic of the fully-delithiated $\lambda\text{-MnO}_2$ phase. The intensity variation of this band as a function of time is plotted, superposed to the corresponding current intensity curve, in (d) for the grain and (e) for the grain boundary.

Figures 2a-b shows two TERS maps recorded on a single spot of an LiMn_2O_4 grain and grain boundary, respectively, while changing the potential over the sample surface. The variation of the current density with the time is also illustrated, superposed to the spectra. At the beginning of the measurements, the spectral signature shows a single band at about 980 cm^{-1} (Figure 2c), attributed to the SO_4^- cation of the electrolyte solution. No spectral changes occur at the onset of the first anodic peak in the current signal. On the contrary, in correspondence of the second oxidation peak a more intense and sharper band appears at 590 cm^{-1} (Figure 2c), which vanishes again with the first reduction peak. This band reveals indeed the presence of $\lambda\text{-MnO}_2$, the fully-delithiated form in which LiMn_2O_4 transforms when the battery discharge is complete, and that switches back reversibly during the charging process (cathodic potential/current).

Interestingly, while in the grain the 590 cm^{-1} band appears exactly at the onset of the oxidation peak (Figures 2d), in the grain boundary the appearance of the band is delayed of about 6 seconds. This observation can be explained by a higher Li-ion diffusivity in this zone, which would lead in turn to a slower accumulation of delithiated product and therefore in a delay on the manifestation of its Raman signature. This hypothesis, previously proposed in the literature^[3], confirms on one side the deep structure-activity relationship of LiMn_2O_4 , whose knowledge is essential for building robust and efficient battery devices, and on the other side the capabilities of operando EC-TERS in unveiling electrochemical transformations with a great spatial sensitivity.

References

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2. Further information can be found on the Harvestore project website
3. R. Wang, X. Chen, Z. Huang, J. Yang, F. Liu, M. Chu, T. Liu, C. Wang, W. Zhu, S. Li, S. Li, J. Zheng, J. Chen, L. He, L. Jin, F. Pan, Y. Xiao, "Twin boundary defect engineering improves lithium-ion diffusion for fast-charging spinel cathode materials", *Nat Commun*, 2021, 12, 3085

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