

Juan Carlos Gonzalez-Rosillo

Beatrice Laurenti, Francesco Chiabrera, Alex Morata, Albert Tarancón

Catalonia Institute for Energy Research (IREC), Jardins de les Dones de Negre 1, Planta 2, 08930, Sant Adrià del Besòs, Barcelona, Spain.

jcgonzalez@irec.cat

Nanoscale imaging of grain boundaries in ceramic energy devices and operando battery chemistry via Tip-Enhanced Raman Spectroscopy

Electroceramic materials for energy conversion and storage derive their functional performance from chemical and structural processes occurring at the nanoscale, particularly at surfaces, interfaces, and grain boundaries. Experimentally accessing these regions under realistic conditions remains challenging due to the spatial resolution limits of conventional non-destructive techniques. Tip-Enhanced Raman Spectroscopy (TERS) overcomes these limitations by combining the chemical sensitivity of Raman spectroscopy with the nanometric precision of scanning-probe microscopy, enabling chemical imaging below 20 nm. In this contribution, we demonstrate how TERS addresses these challenges through three key methodologies applied to energy devices. First, we resolve nanoscale surface degradation, tracking Sr segregation and carbonate formation on functional oxides. Second, we overcome substrate and geometry limitations by using freestanding thin-film membranes to probe the vertical interfaces of multi-phase, vertically aligned nanocomposites (VAN), revealing oxygen vacancy accumulation at these internal boundaries. Finally, we present operando liquid-cell TERS during cyclic voltammetry of LiMn_2O_4 thin-film cathodes, combined with 2D finite element method (FEM) simulations. This synergistic approach directly visualizes and models accelerated electrochemical phase evolution at single grain boundaries, demonstrating the unique power of nanoscale operando Raman to resolve local structure-property relationships in operando energy systems.

References

- [1] J.M. Sojo-Gordillo et al., *Small*, 19, (2023), 2206339.
- [2] J.C. Gonzalez-Rosillo et al., *Chem. Mater*, 36, (2024), 6144-6153.
- [3] J. Sirvent et al., *ACS Appl. Energy Mater.*, 8, (2025), 7022-7037.
- [4] B. Laurenti et al., *EES Batteries*, 1, (2025), 1147-1157.

Figures

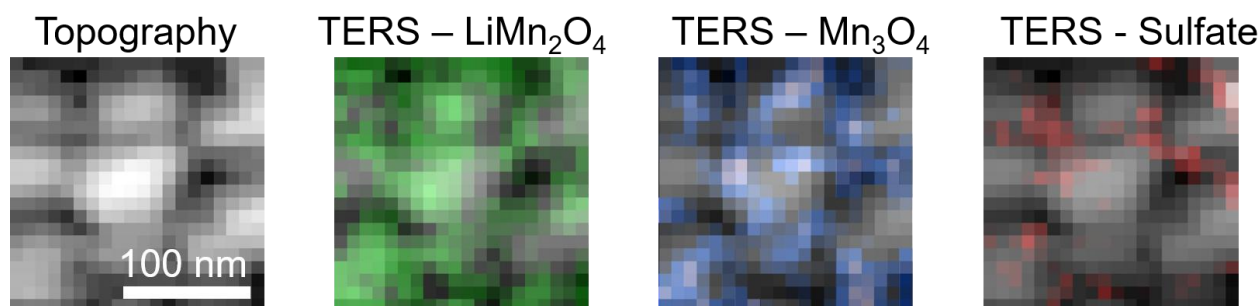


Figure 1: Ex-situ TERS of an LiMn_2O_4 thin-film battery cathode after cycling in 1M Li_2SO_4 aqueous electrolyte.