In-situ thermal analysis of Pyrolyzed Polyacrylonitrile Film using operando ToF-SIMS

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Emerging technologies increasingly depend on complex multifunctional materials whose performance and reliability are strongly governed by their chemical composition, interfacial chemistry, diffusion behavior, degradation pathways, and thermally induced transformations. Understanding these mechanisms is essential for both fundamental research and industrial implementation; however, the structural and chemical complexity of advanced materials remains difficult to probe using conventional characterization techniques.

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) has become a powerful surface analytical technique capable of providing highly sensitive elemental and molecular information from surfaces, interfaces, thin films, and three-dimensional architectures. Recent advances in ToF-SIMS instrumentation now enable operando investigations under realistic reaction environments, offering new opportunities to directly monitor dynamic thermal and chemical processes in functional materials.

In this work, we present an operando thermal analysis methodology based on ToF-SIMS for investigating thermally driven reactions through controlled in-situ heating during analysis. As an initial demonstration, a reference polystyrene film is annealed to illustrate how operando thermal SIMS can probe both physical and chemical transformations. We then investigate pyrolyzed polyacrylonitrile (pPAN) films, a conductive binder widely used in lithium-ion batteries. Owing to its high elasticity, pPAN has shown significant potential for silicon-based anodes. Here, we examine the evolution of aromatic and aliphatic secondary ion fragments as a function of temperature and demonstrate how their relative intensity ratio can be used to monitor the pyrolysis behavior of the material under various annealing conditions. The ToF-SIMS results are correlated with thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) and Fourier-transform infrared spectroscopy (FTIR) to validate the operando thermal analysis approach.