

# Benefits of Cryo-XPS for Battery Analysis

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## INTRODUCTION:

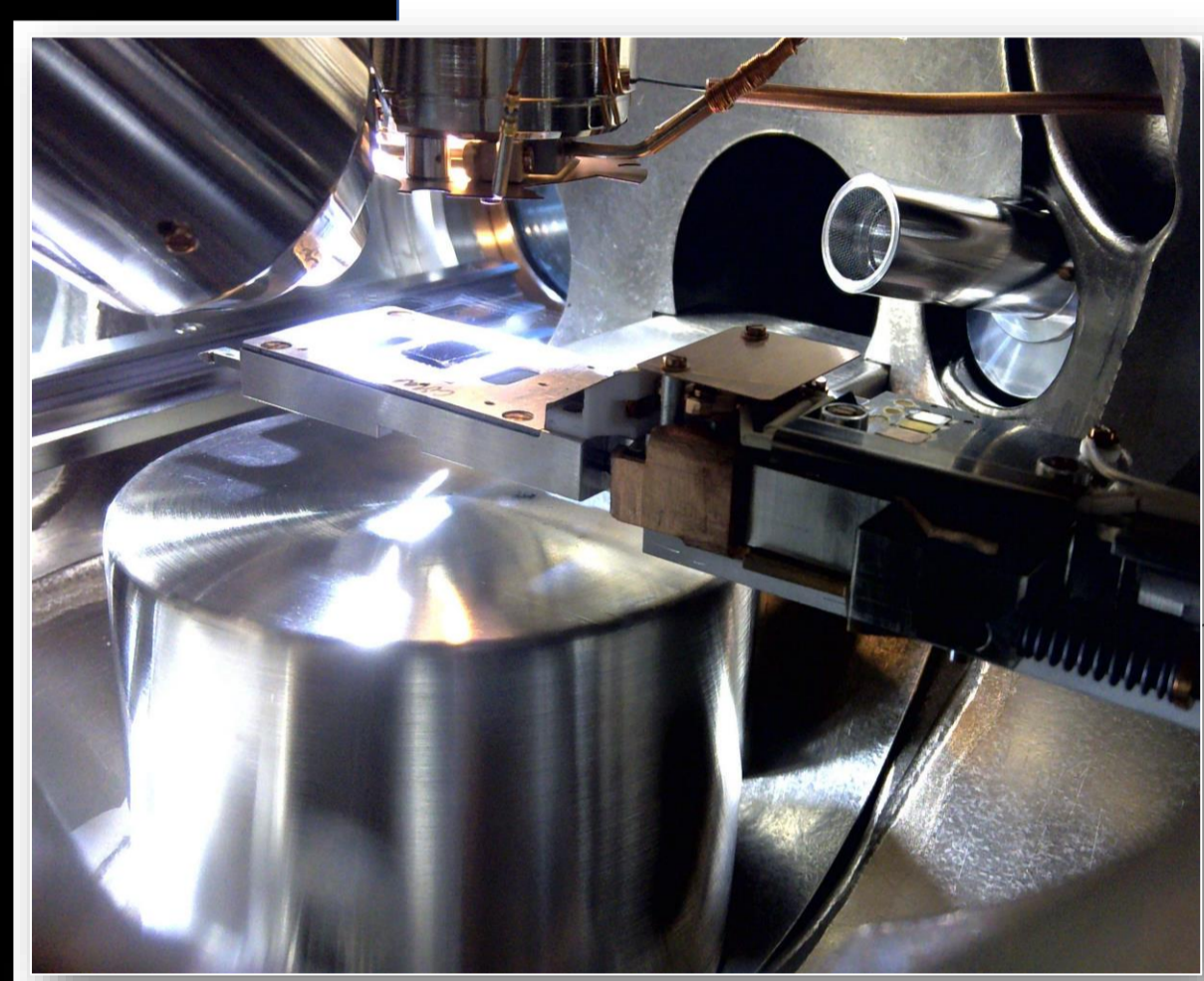
The widespread commercialization of lithium-sulfur batteries (LSBs) has encountered significant roadblocks, largely stemming from a couple of critical challenges. One of these challenges is the volumetric expansion experienced by the sulfur electrode during the battery's cyclic charge and discharge processes. The second is the notorious "shuttle effect" induced by polysulfide intermediates, which compromises the battery's performance and longevity. To surmount these obstacles, an understanding of the underlying mechanisms and the chemistry within the Lithium-Sulfur (Li-S) system is important. Here we have used XPS to scrutinize the oxidation states of both sulfur and carbon within the anode material, shedding light on the chemical intricacies at play.

## EXPLORATION: Sulfur chemistry

Sulfur exhibits oxidation states ranging from -2 to +6. For LSBs, two predominant oxidation states of sulfur may occur: +2 and 0. The former corresponds to elemental sulfur, while the latter corresponds to lithium sulfide. The emergence of higher sulfur oxidation states, notably +4 and +6, indicates the formation of polysulfide intermediates and the accompanying shuttle effect, negatively impacting the battery's performance.

## Carbon chemistry

The analysis of the carbon concentration in the material yields interesting insights into its composition and behaviour over time.



In-situ sample cooling

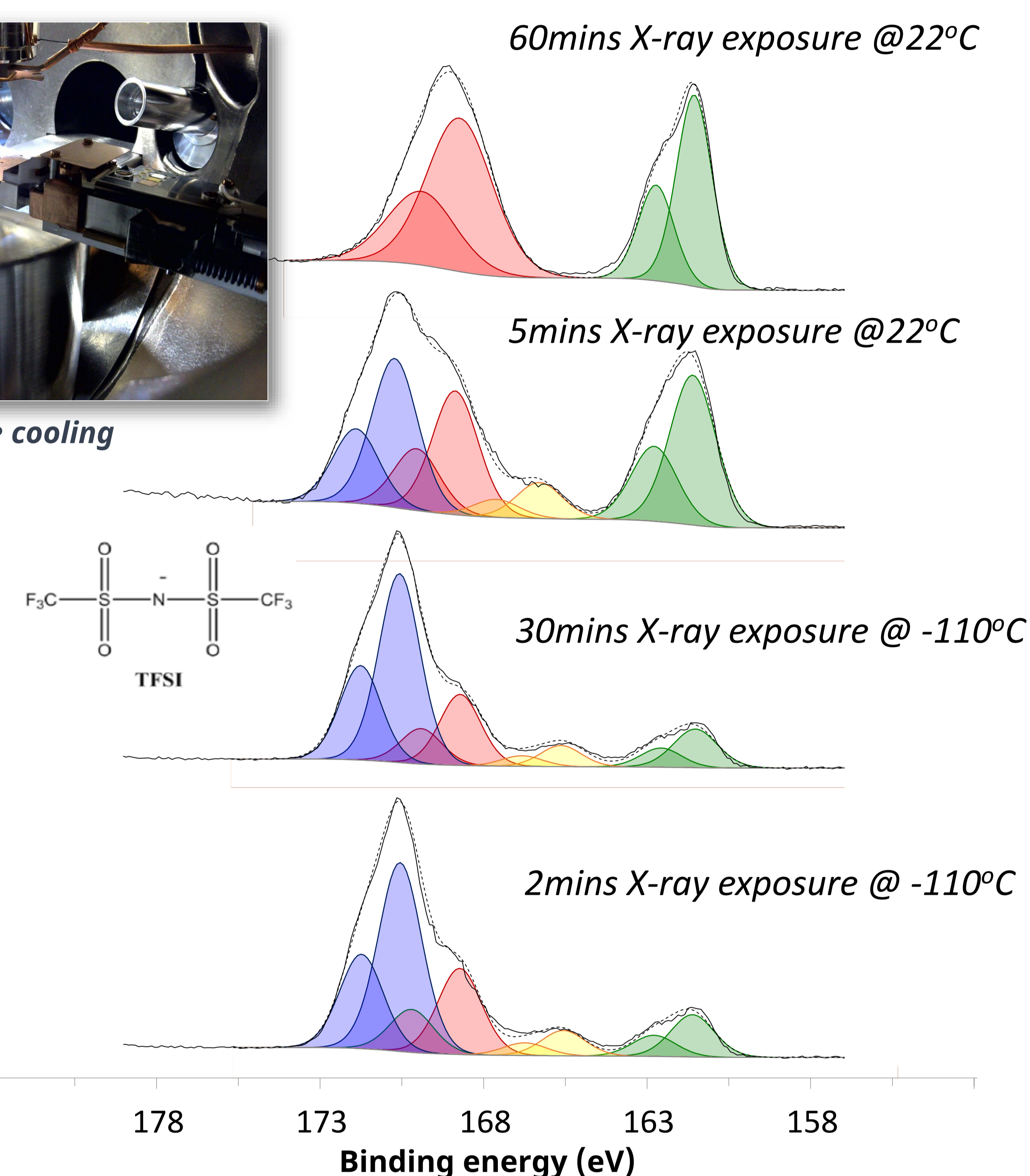


Figure 1: S 2p chemical states under different analysis conditions.

Detailed analysis of high-resolution S 2p spectra (above) for uncycled and uncharged Lithium-Sulfur Battery (LSB) materials provides valuable insights into the surface chemistry and its evolution over time. Initially, the S 2p spectrum reveals distinct chemical species on the surface.

**IL/Li<sub>2</sub>S<sub>6</sub> Electrolyte (Blue):** At the outset, the presence of the IL/Li<sub>2</sub>S<sub>6</sub> electrolyte is evident, indicated by a doublet in the S 2p spectrum at 169.9 eV (blue). This suggests that the ionic liquid (IL) components interact with the surface of the material.

**Sulfite (SO<sub>3</sub><sup>2-</sup>) or Thiosulfate (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>) Species (Red + Yellow):** In addition to the IL/Li<sub>2</sub>S<sub>6</sub>, the spectrum also displays the presence of sulfite (SO<sub>3</sub><sup>2-</sup>) or thiosulfate (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>) species (indicated in red and yellow, respectively) on the surface of the Li metal. These species are important intermediates in the sulfur redox reactions and signify the complex chemistry occurring at the interface.

**Lower Binding Energy Species (Li<sub>2</sub>S<sub>x</sub>):** Lower binding energy species are detected in the spectrum, representing Li<sub>2</sub>S<sub>x</sub> species. These are likely formed during the electrochemical processes within the LSB.

When the surface is cooled, it exhibits stability under X-rays at a power level of 150W. Over a 30-minute period, the relative composition of the different chemical states remains largely unchanged, with a minimal shift of less than 5%. As the surface warms, stability diminishes, and decomposition and radiolysis processes are initiated.

High-order sulfur species are reduced to lower-order species, particularly evident in the significant increase in lithium sulfide components (green). The IL on the surface recombines, forming surface sulfates. This recombination process is marked by a near three-fold increase in surface lithium concentration, indicating the formation of surface sulfides.

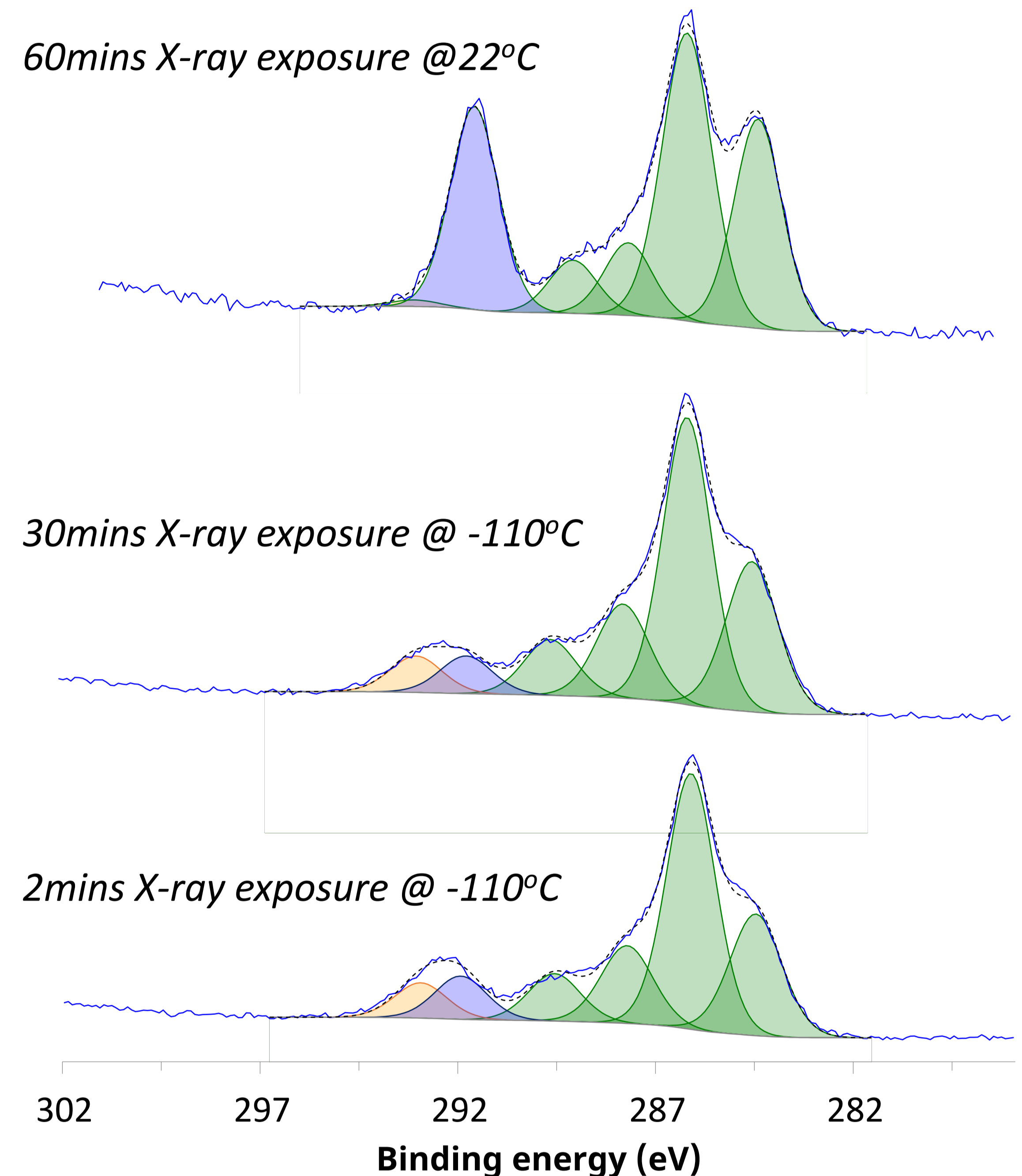


Figure 2: C 1s chemical states under different analysis conditions.

After 60 minutes of analysis at room temperature (RT), the carbon concentration exhibited a significant change, specifically halving. This substantial reduction in carbon content points to a dynamic transformation occurring within the material.

Notably, the spectral data reveals alterations in the carbon chemical environment. The CF<sub>3</sub> peak (orange peak) noticeably decreases. Concurrently, there was an observable increase in CF<sub>x</sub> species (blue peak). These changes in the carbon species and their relative proportions are indicative of a chemical transformation taking place within the material during the analysis period.

The reduction in the CF<sub>3</sub> peak suggests a decrease in the concentration of trifluoromethyl (CF<sub>3</sub>) functional groups within the material. This change may be attributed to chemical reactions, adsorption, or desorption processes happening on the material's surface or within its bulk. Conversely, the rise in CF<sub>x</sub> species indicates the emergence or enhancement of carbon species with a different chemical composition, represented by the "X" in CF<sub>x</sub>. This transformation reflects the formation of new carbon-based compounds or the alteration of existing ones, possibly in response to environmental factors during the analysis.

In summary, the observed changes in carbon concentration and the shifting balance between CF<sub>3</sub> and CF<sub>x</sub> species underscore the dynamic nature of the material's composition and chemistry. Understanding these alterations is essential for comprehending the material's properties and reactivity, and it may have implications for its applications, stability, and performance.

## CONCLUSION

XPS and more importantly cryo-XPS is very useful for analysing battery systems and other materials prone to degradation under X-rays. Further studies are necessary to understand the effects of X-ray exposure.