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Applications Note

Benefits of Cryo-XPS for battery analysis

MO528(A)

Keywords XPS, battery materials, cryo-XPS

Overview

Comparisons between standard and cryo-XPS have been made to scrutinize the oxidation states of both sulphur and carbon within the anode material of lithium-sulphur batteries (LSBs), providing valuable insights into the surface chemistry and its evolution over time. 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. However, as the surface warms, stability diminishes and decomposition and radiolysis processes are initiated. This highlights the importance of cryo-XPS for materials prone to degradation under X-rays.

Introduction

The widespread commercialization of lithium-sulphur 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 sulphur 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-Sulphur (Li-S) system is important. Here we have used XPS to scrutinize the oxidation states of both sulphur and carbon within the anode material, shedding light on the chemical intricacies at play.

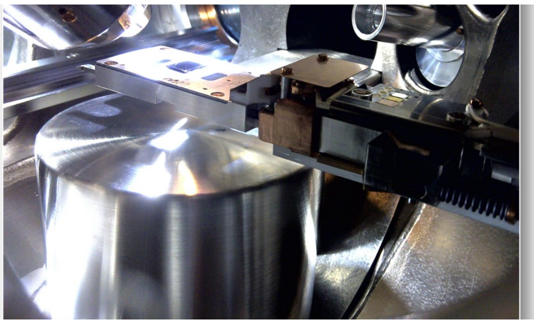
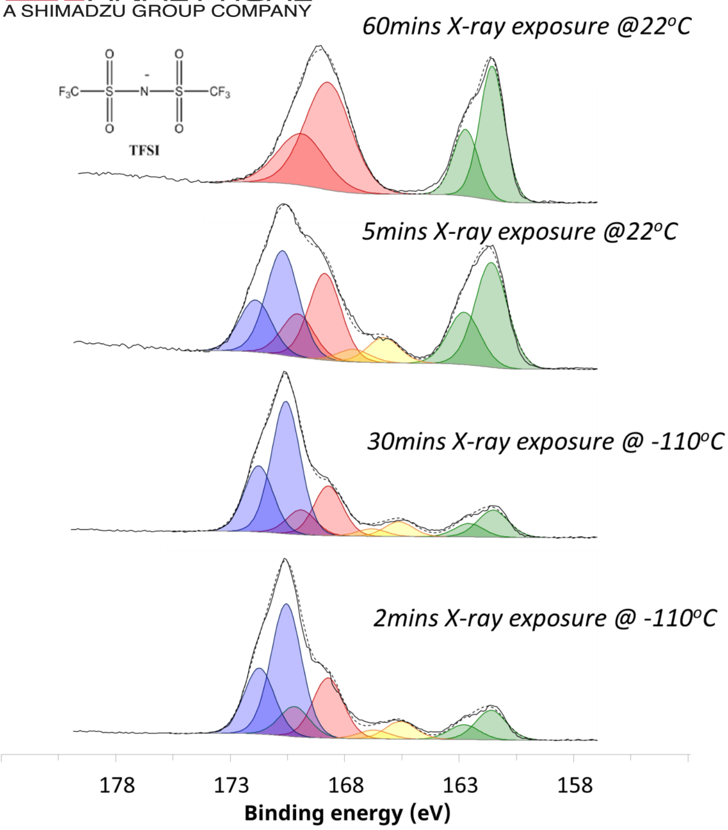


Figure 1: In-situ sample cooling.

Experimental

Sulphur Chemistry

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



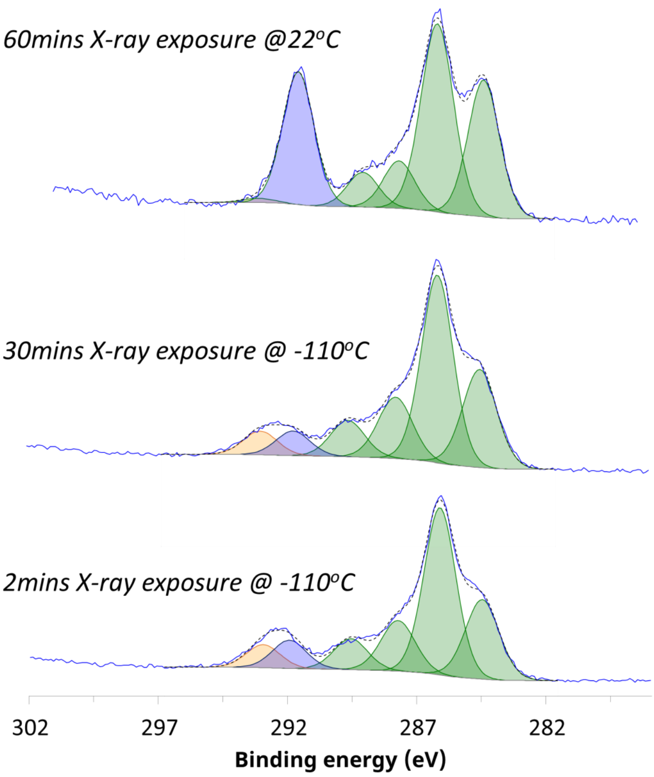


Figure 2: S 2p chemical states under different analysis conditions

Figure 3: C 1s chemical states under different analysis conditions

Detailed analysis of high-resolution S 2p spectra (Fig. 2) for uncycled and uncharged 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/Li2S6 Electrolyte (Blue): At the outset, the presence of the IL/ Li_2S_6 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.

Sulphite (SO_3^{2-}) or Thiosulfate ($S_2O_3^{2-}$) Species (Red + Yellow): In addition to the IL/Li_2S_6, the spectrum also displays the presence of sulphite (SO_3^{2-}) or thiosulphate ($S_2O_3^{2-}$) species (indicated in red and yellow, respectively) on the surface of the Li metal. These species are important intermediates in the sulphur redox reactions and signify the complex chemistry occurring at the interface.

Lower Binding Energy Species (Li_2S_x): Lower binding energy species are detected in the spectrum, representing Li_2S_x 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 sulphur species are reduced to lower-order species, particularly evident in the significant increase in lithium sulphide components (green).

The IL on the surface recombines, forming surface sulphates.

This recombination process is marked by a near three-fold increase in surface lithium concentration, indicating the formation of surface sulphides.

Carbon Chemistry

The analysis of the carbon concentration (Fig. 3) in the material yields interesting insights into its composition and behaviour over time.

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_3 peak (orange peak) noticeably decreases. Concurrently, there was an observable increase in CF_X 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_3 peak suggests a decrease in the concentration of trifluoromethyl (CF_3) 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_X species indicates the emergence or enhancement of carbon species with a different chemical composition, represented by the "X" in CF_X. 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_3 and CF_X 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 caused by X-rays. Further studies are necessary to understand the effects of X-ray exposure.

Related documents online:

MO495 High throughput XPS analysis of Na-Fe-Mn-O cathodes for Ni-ion batteries

MO496 XPS analysis of solid-electrolyte interphase layer formed on a lithium-ion battery negative electrode

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