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Recent Developments in XPS – Microspectroscopy, Spectromicroscopy, Lateral and Depth Information towards Cutting-Edge Solid Electrolytes and Biomaterials

David J. Surman[1], Chris Moffitt[1] and Jonathan D. P. Counsell[2]

[1.] Kratos Analytical Inc. 100 Red Schoolhouse Road, Building A, Chestnut Ridge, New York, 10977, USA
[2.] Kratos Analytical Ltd, Wharfside, Trafford Wharf Road, Manchester, M17 1GP, UK

Commercially available XPS instruments were introduced in the latter half of the twentieth century and have become an established analytical tool in the fields of surface science and surface analysis. Instruments typically comprise of a monochromated aluminium K-alpha X-ray source for exciting core-shell and bonding electrons the kinetic energies of which are subsequently analysed in a hemispherical electron analyser. Traditional applications of the technique include heterogeneous catalysis, nuclear engineering and semiconductor devices. The strength of XPS lies in its inherently quantitative nature. In recent times the technique has increasingly been applied in novel areas of research such as biomaterials, soft matter and organic electronics. The desire to apply XPS to these new areas has resulted in several technique developments such as charge-neutralisation, small-spot analysis on the micron scale and novel depth-profiling techniques. A major milestone was the recent introduction of Argon cluster ion sources allowing for the first time the depth profiling of organic and soft-materials. Here we will discuss several systems which highlight both the novelty and wide reaching applications of these analytical evolutions.

Research into new biomaterials has grown exponentially especially in the field of cardiovascular research therapy with rapid developments in stent technology. Originally stents were made of steel however these have been replaced with a new range made from bio-resorbable polymers. Problems such as thrombosis and hyperplasia still remain as the pathological responses to the implantation of foreign devices. To suppress this immune response and that of overgrowth and subsequent restenosis anti-inflammatory drugs are now loaded onto the surface of stent implants. The stents in this study are made of polylactic acid (PLA) dosed with an anti-inflammatory drug with the molecular formulae $C_{51}H_xNO_{13}$. Here we investigate the concentration of anti-inflammatory drug coated on the surface. Small-spot microspectroscopy combined with low-energy Argon cluster depth profiling was applied to fully characterise the stent surface for drug concentration and layer thickness (see figure 1). Analysis was also performed on stents submerged in buffer solution (PDMS) for different lengths of time (1–3 months) to see the effects on ageing and the propensity for the drug to migrate into solution with time — conventionally the solution would be analysed using HPLC however in this study we reanalyse the eluted surface of the stent [1]. The variations in drug concentration with depth and ageing will be discussed in detail. Of particular importance for the analyst was the ability to perform small-area analysis whilst still achieving a low limit of detection for the low drug loading.

Developments into energy storage materials have expanded the use of batteries including micro devices. Lithium phosphorous oxynitride (LiPON) is widely used in solid state micro-batteries due to low electronic conductivity, increased durability to cycling and ease of preparation. Despite the widespread use of LiPON much is still unknown regarding Nitrogen bonding and Li mobility. We apply XPS to analyse small surface features and sputter depth profile to understand the surface and bulk chemistry of LiPON films formed via atomic-layer deposition (ALD) [2]. The elemental composition as a function of depth is probed and comparisons are made between the results obtained from conventional monatomic

Ar^+ depth profiling and Ar_n^+ cluster depth profiling. The use of cluster ions for depth profiling is shown to provide a more accurate determination of the Li distribution through the thin film materials as well as the ability to retain the true chemical state of the nitrogen species (see figure 2).

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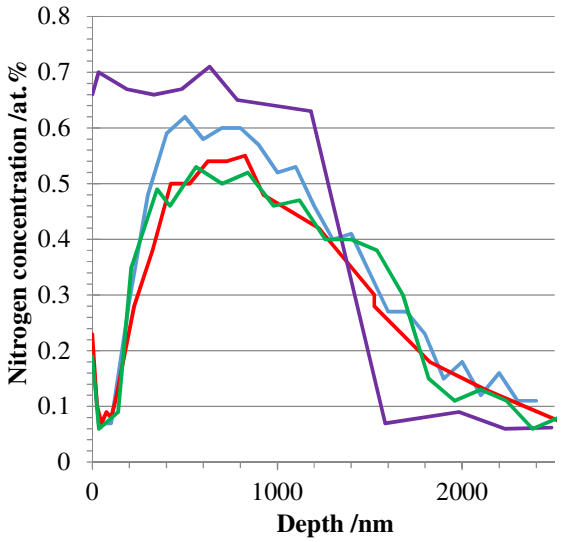

Figure 1. 10 kV Ar_{1000}^+ depth profile for unused polymer stent (purple); 1 month PBS (baby-blue); 2 month PBS (parakeet) and 3 month PBS (scarlet).

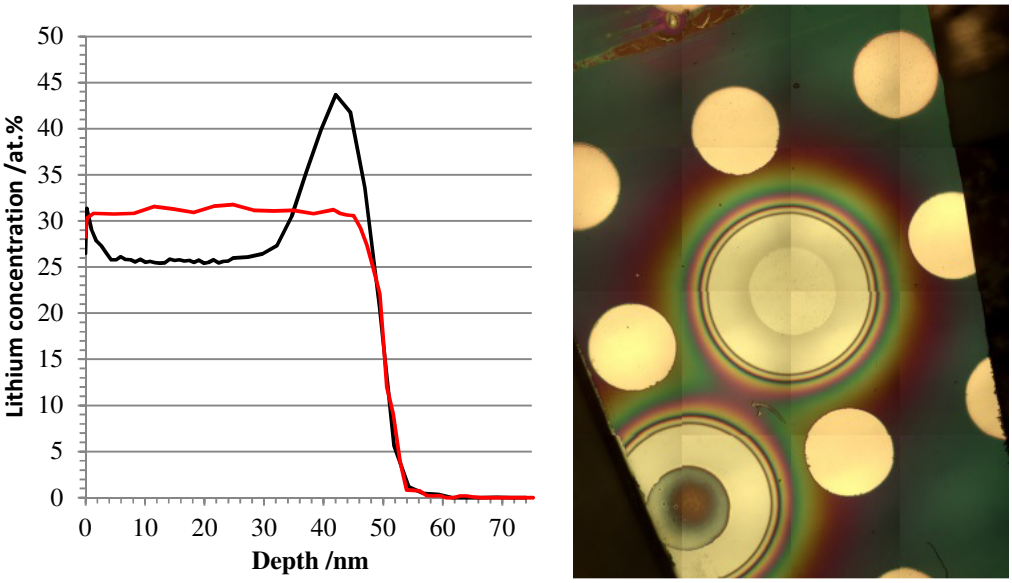

Figure 2. Left: Lithium concentration of LiPON layer depth profiled with monatomic (black) and cluster (red) ions. Right: Optical microscope image of battery micro-stacks.

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