

Distribution, segregation and chemical state identification of Lithium salts on Cu electrodes

Keywords

Electrode, depth profile, selected area spectroscopy, imaging

Application Note MO448(A)

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Introduction

Rechargeable metal-based batteries (Li, Na and Al) are among the most versatile platforms for high-energy storage. Unfortunately however there are several pitfalls for these energy storage systems, one of which is deposition and dendrite formation during repeated cycles of charge and discharge. Many studies have been performed in search of a dendrite-free, deposition-free system for lithium batteries using novel materials such as 3D structures and carbon nanofibers.^[1,2]

Here we will explore the distribution of Lithium in different chemical environments on electrode surfaces. We employ conventional surface analysis techniques (XPS) to yield large area, quantitative, information regarding the distribution of surface species. To explore the lateral and depth distribution of Li we also utilise XP imaging and Argon cluster depth profiling.

Experimental

XPS was performed using the state-of-the-art AXIS spectrometer. Survey spectra were acquired over a large energy range of 0 to 1200 eV. The co-axial charge neutraliser was used to mitigate against charge build-up. Depth profiling was performed using Argon cluster ions (20kV Ar₅₀₀⁺).^[3] High spatial resolution XPS images were acquired over a large surface area using stitched imaging mode. This imaging mode combines fast parallel imaging with stage movements. In this example a 3x3 stitched image using a 400µm field of view provided an image of 1.2 x 1.2 mm. Small-spot spectroscopy was performed using a 110 micron diameter aperture and the total acquisition time for each survey spectrum was 4 minutes. After synthesis of the electrodes, CV experimentation was performed via the three electrode system.^[4]

Results

XPS survey spectra were acquired for different areas of the electrode surface (figure 1). Peak identification showed the presence of expected elements - Mg, Li, Cu, O and C on the surface post experiment, also present were low levels of other elements, most probably contamination – F, Na, Cl, S (see table 1).

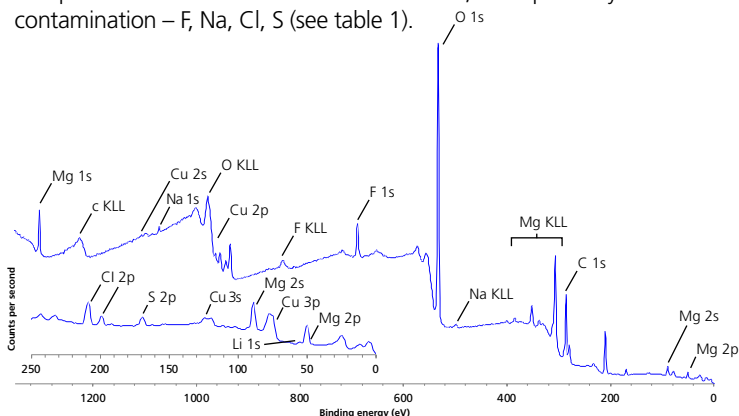


Figure 1: Large area survey spectrum of electrode surface.

Table 1: Surface quantification of as-received electrode surface.

| Element | Quantification |
|---------|------------------|
| | Atomic conc. [%] |
| Mg | 3.91 |
| Cu | 3.79 |
| O | 55.00 |
| F | 5.15 |
| C | 20.81 |
| S | 0.99 |
| Cl | 0.53 |
| Na | 0.24 |
| Li | 9.57 |

The distribution of Li into the bulk of the electrode surface was further explored using Argon cluster depth profiling. A high-energy cluster (20kV Ar₅₀₀⁺) ion was used to allow for quick, deep, depth profiling whilst limiting the migration of light Li ions – a common issue with monatomic Argon depth profiling. Figure 2 shows the distribution of surface species as a function of etch time.

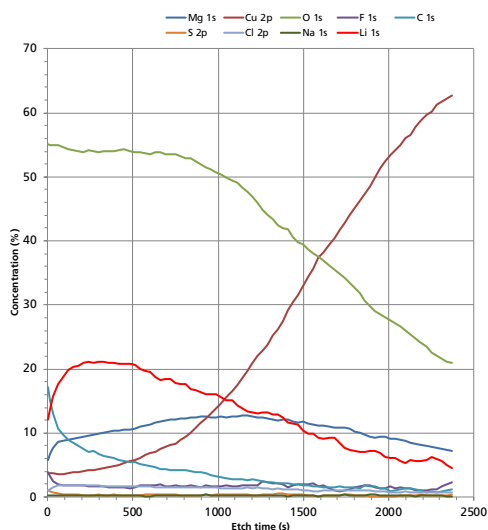


Figure 2: 20 kV Ar₅₀₀⁺ depth profile of electrode surface.

After the first few etch cycles the concentration of Li increases to >20 at.%. Further sputter removal of surface material shows a decrease in Li concentration. This indicates that Li is segregated into the uppermost region of the electrode surface and the Li concentration decreases once the depth profile had reached the interface with the Cu bulk electrode surface. There is little evidence to suggest that Li has migrated deeper into the electrode.

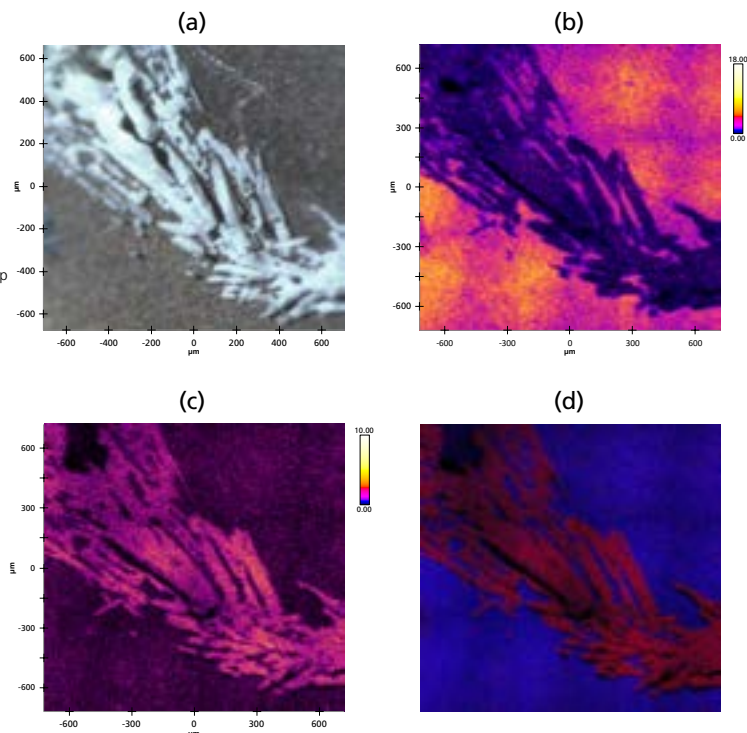


Figure 3: (a) Optical microscope image of surface crystallites; (b) XPS stitched image of Mg; (c) XPS stitched image of Cl; (d) overlay of Mg (blue) and Cl (red).

Using the in-situ optical microscope on the analysis chamber it was possible to identify white crystallite structures on the electrode surface (figure 3a). By acquiring peak-minus-background stitched images at fixed energies for different elements it is possible to observe the relative distributions and accumulations of particular species on the surface. XPS images were acquired for several of the elements identified in the survey spectrum to investigate the composition of these crystallites (figure 3b-c). Here we can see that there is a higher concentration of Cl on the crystallite regions when compared to the rest of the electrode surface. Conversely there is a decrease in the atomic concentration of Mg. A combined overlay image of the two elemental XPS images highlights the distinctive distribution differences of the elements (figure 3d).

Using the XPS images for navigation it was possible to acquire small-spot, selected area spectroscopy both on and off the crystalline regions (figure 4). Elemental quantification from the electrode and crystalline survey spectra are shown in Table 2.

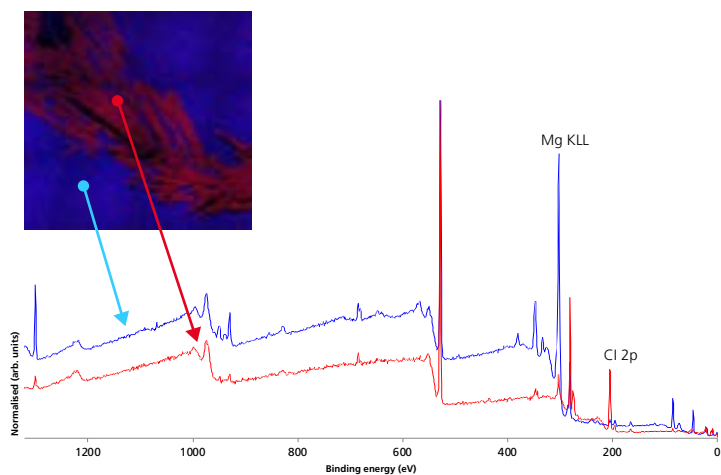


Figure 4: 110 micron small-spot survey spectra on electrode (blue) and crystallite (red) areas.

Table 2: Surface quantification of electrode and crystallite areas.

| Element | Quantification | |
|---------|------------------|-------------------|
| | BLUE (electrode) | RED (crystalline) |
| Mg 1s | 5.24 | 0.97 |
| Cu 2p | 2.46 | 0.36 |
| O 1s | 50.49 | 42.30 |
| F 1s | 3.79 | 1.52 |
| C 1s | 31.59 | 34.56 |
| S 2p | 1.18 | 0.46 |
| Cl 2p | 2.66 | 10.75 |
| Li 1s | 2.00 | 8.97 |
| Na 1s | 0.59 | 0.11 |

As indicated from the images we see a high accumulation of Cl on the crystalline areas along with a significantly higher concentration of Li. The atomic concentration of F, S, Na were depleted in the crystalline regions. To further elucidate the nature of these crystalline areas high energy resolution, chemical state, spectra were acquired (figure 5)

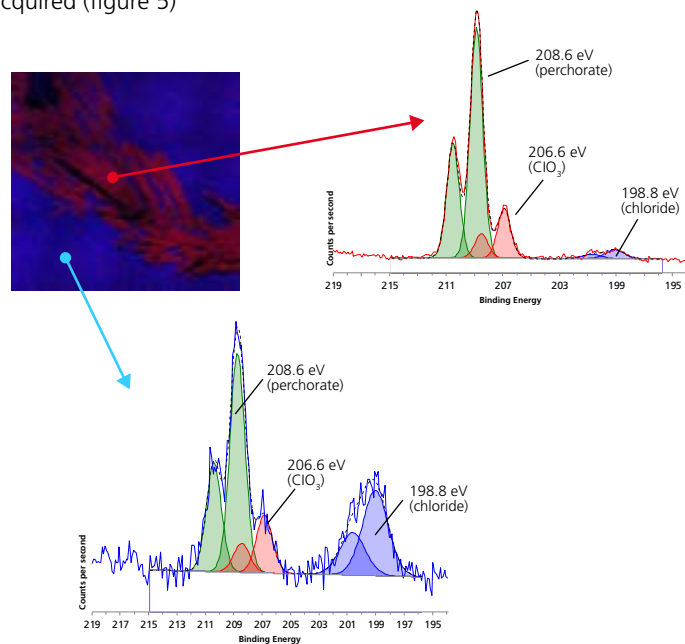


Figure 5: 110 micron small-spot spectroscopy of Chlorine 2p region for electrode (blue) and crystallite (red) areas.

As expected there is a significantly higher Cl signal for the crystalline areas. Peak-fitting analysis of both spectra indicates three different chemical environments for Cl: perchlorate ion (208.6 eV), chlorate (206.6 eV) and chloride (198.8 eV). For the crystalline areas the most dominant chemical state of chlorine is in the perchlorate ion. This along with the increased concentration of Li in this region (and decreased concentrations of other non-electrode surface species) indicates that the white crystalline species is Lithium perchlorate.

Conclusion

XPS was used to investigate the distribution of Li and other surface species on Cu electrode surfaces. Applying argon cluster depth profiling it was possible to observe that the Li is contained within the surface of the electrode and has not penetrated into the bulk. Crystalline species were identified on the surface of the electrode as Lithium perchlorate.

Acknowledgements

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