# Development of Site Specific Cryogenic Specimen Preparation and Transfer of Frozen Liquids for Complementary High-Resolution Analysis by Scanning Transmission Electron Microscopy and Atom Probe Tomography

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# Development of Site Specific Cryogenic Specimen Preparation and Transfer of Frozen Liquids for Complementary High-Resolution Analysis by Scanning Transmission Electron Microscopy and Atom Probe Tomography

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There has been considerable interest in the high-resolution analysis of solid-liquid interfaces, for instance, electrolyte/electrode within battery materials. Such analyses would be greatly facilitated through the use of freezing the system prior to sample preparation and thus preserving the native environment [1]. Carrying out analysis of complex 3D nanoscale microstructures on systems involving light elements such as lithium can be independently challenging for both scanning transmission electron microscopy (STEM) and atom probe tomography (APT), where their combination is necessary to gain the necessary insights into structure and composition. APT requires high aspect ratio, needle shaped specimens with an apex diameter generally less than 100 nm, with the region of interest sufficiently close to the apex that it will be contained within a typical analysed volume of 50 nm x 50 nm x 80 nm. As such, APT specimens are electron transparent at STEM achievable voltages and hence suitable for STEM imaging and spectroscopy-based analysis, although there can be challenges with non-uniform thicknesses from curved tip geometries.

The complementarity of STEM followed by APT analyses has been showcased on a number of material systems and is now relatively common across many institutions [2]. APT samples that are intended for complementary STEM analysis can be formed from electropolished bulk needles in the case of appropriate metals/alloys or more commonly placed by focused-ion beam (FIB) liftout onto metal needles and the exposed topmost sections of TEM half grids. The transfer between STEM suitable holders and APT suitable holders is still, for the most part, a manual process and yield loss through mechanical handling even under ambient conditions can be a significant issue.

Significant advances in cryogenic STEM and associated cryogenic FIB liftout specimen preparation and cryogenic transfer have been made [3] but there are challenges associated with adapting these protocols to allow subsequent APT analysis. APT specimens require a more robust connection to the support structure than STEM samples due to the high thermal and electrical conductivity requirements, along with increased mechanical stability for the high stress conditions encountered during APT analysis. Cryogenic FIB specimen preparation for APT of frozen liquids and liquid solid interfaces has been shown to be viable using liquid deposition onto pre-made needles , “satellite dish” of liquids infused into nanoporous substrate and combined redeposition/cryogenic gas-injection system (GIS) approaches [4] but there is scope for optimisation for complementary STEM analysis. Analyses of frozen liquids by APT has generally required including a significant section of conductive substrate within the final sample and minimising the amount of frozen liquid at the apex, limiting the application of the technique to very relatively low volumes within a material system, or facing the issue of poor analytical performance [4].

Maintaining cryogenic conditions and reducing contamination during the multiple stages of sample preparation, transfer and analysis between respective instruments is a significant engineering and logistical challenge. The development of reliable and reproducible process flows for this is achievable but requires increased communication and significant investment of time and resources from user groups and instrument manufacturers, as can be seen from advances in cryogenic sample preparation and analysis in the life sciences.

Recently, we demonstrated a cryogenic liftout process using in situ sputtered metal from a cryogenic micromanipulator to be a viable method for site specific FIB liftout for APT. APT data obtained using this novel technique was found to be have comparable quality to calibration samples, showing mechanical stability in addition to the required thermal and electrical conductivity. The process flow can be readily adopted by those familiar with standard FIB liftout for APT and tests across a wide number of material systems requiring various levels of cryogenic sample preparation and transfer are underway. As the method can be used with a similar level of flexibility as room temperature FIB liftout, it is also suitable for mounting samples onto pre-made needles or TEM half grids.

This approach has now been applied to the full cryogenic FIB liftout and successful APT analysis of water ice with 0.1 M NaCl solution without any conductive substrate included within the sample. This development demonstrates the viability of site specific cryogenic sample preparation for complementary STEM and APT analysis of a wide range of frozen materials, justifying further investigation into robust transfer protocols to take full advantage of these combined techniques [5].

## References

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