In Situ Variable-Temperature Liquid SIMS for Subzero Analysis

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In situ liquid time-of-flight secondary ion mass spectrometry (SIMS) technique has been invented by interfacing vacuum-based SIMS with a homemade microfluidic device of high vacuum compatibility for more than a decade, and significantly advanced with universal applicability through the utilization of the poly (ether ether ketone) (PEEK) block exhibiting exceptional chemical stability. Due to the widely demonstrated soft ionization feature, *in situ* liquid SIMS allows precise molecular discrimination of various microstructures such as ion solvation structures within both aqueous and non-aqueous liquids. Moreover, in comparison with traditional mass spectrometric tools, e.g. electrospray ionization (ESI)-MS, *in situ* liquid SIMS can directly analyze a wide range of liquid samples, even those with highly concentrated salts and/or air-sensitive liquids, without need of any sample pretreatment, which enables the detection of molecular structures of liquids in their original status. However, currently *in situ* liquid SIMS can only deal with liquid samples at room temperature.

Recently, we developed an advanced *in situ* variable-temperature liquid SIMS technique by interfacing in situ liquid SIMS with a thermal-conductive copper (Cu)-based microfluidic device that is attached on a temperature-controllable sample stage. Utilizing *in situ* variable-temperature liquid SIMS, we for the first time accessed the direct molecular evidences to discriminate the corresponding evolution of complex ion solvation structures and water structures in the subzero water-in-salt electrolyte, which may not be feasible for ESI-MS. This work opens a new avenue for bridging the gap in the knowledge of the correlations between the microscopic structures and macroscopic properties of subzero electrolytes.

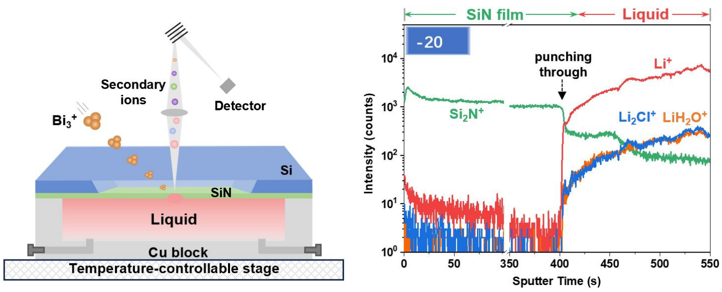

Figure 1. In Situ Variable-Temperature Liquid SIMS.

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