CRYOPREPARATION FOR INTERFACIAL ATOM-PROBE ANALYSIS

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A cryopreparation technique from the biological literature has been adapted for analysis of a liquid-solid interface in the Imaging Atom-Probe (IAP). Although adsorption at the vacuum-solid interface has been studied in great detail, little is known about adsorption at the liquid-solid interface or the nature of the interface, itself. It is clear that problems of lubrication, wear and corrosion, the integrity of medical protheses and the operation of biological sensors could benefit from a three-dimensional nanoscale mapping of the liquid-solid interface. This capability is provided by a modification of the Imaging Atom-Probe mass spectrometer [1]. The Imaging Atom-Probe extends the capabilities of the original Atom-Probe Field Ion Microscope by providing a large field of view without the necessity for tip movement or the use of field ion imaging [2-3]. This paper describes an improved version of a procedure described previously to create a layer of vitreous ice at the apex of a field-emitter tip [4]. The creation of vitreous ice is essential because crystal formation and solute partitioning of the liquid is eliminated, thereby providing an accurate snapshot of the interface at the instant the liquid solidifies. A novel cryotransfer technique was developed to preserve the vitreous ice layer at 78K and keep the layer contaminant free until the conditions for Imaging Atom-Probe analysis are established.

Vitrification is performed under liquid nitrogen vapor in a dewar as shown schematically in Figure 1. A field emitter tip is etched at one end of a wire that is inserted into a capillary tube for stability and handling. The other end of the wire emerges from the tube and is etched to a sharp point, creating a dart-like structure. The tube is held by a tension spring, positioning the tip apex in the center of a 20 µl drop of the desired liquid. When spring tension is released the capillary tube is plunged into a container of liquid ethane at 102 K where the dart-like structure is supported by a layer of foam at the bottom of the container. The liquid layer at the tip apex His vitrified by the rapid gravity plunge and the instantaneous cooling of the tip apex when it enters the cryogen. A cooling rate of ≈105 K/s is required for vitrification until a temperature of ~135 K is reached [5]. Liquid ethane is used to minimize the Leidenfrost phenomena [6]. Figure 2 shows the dewar in which vitrification is performed.

The cryotransfer procedure employes a custom split “tweezer”, cooled to 78K with liquid nitrogen, as shown in Figure 3. After vitrification the capillary tube holding the tip is inserted into an anode assembly held at 78K where the tip is isolated in liquid nitrogen vapor inside a cathode shield (see insert).

An IAP has been modified for cryotransfer as shown in Figure 4. The modified IAP consists of a flat-bottomed glass “cold finger”, cooled to 78K in a LN_2 dewar. The cold finger is O-ring sealed to a chamber incorporating a drift tube, a dual microchannel plate assembly (CEMA), a turbopump station and a viewport to photograph the phosphor screen of the CEMA. A magnetic field removes the steel ball from the cathode shield after pump-down to 10^{-9} Torr, exposing the tip for IAP analysis.

Evidence for vitrification of aqueous 1N KCL solutions have been reported previously using a field desorption image [7]. Here, we present the first evidence for vitrification of an aqueous interface using Field-Ion Tomography in which a three dimensional reconstruction of an interface can be created [8].

References

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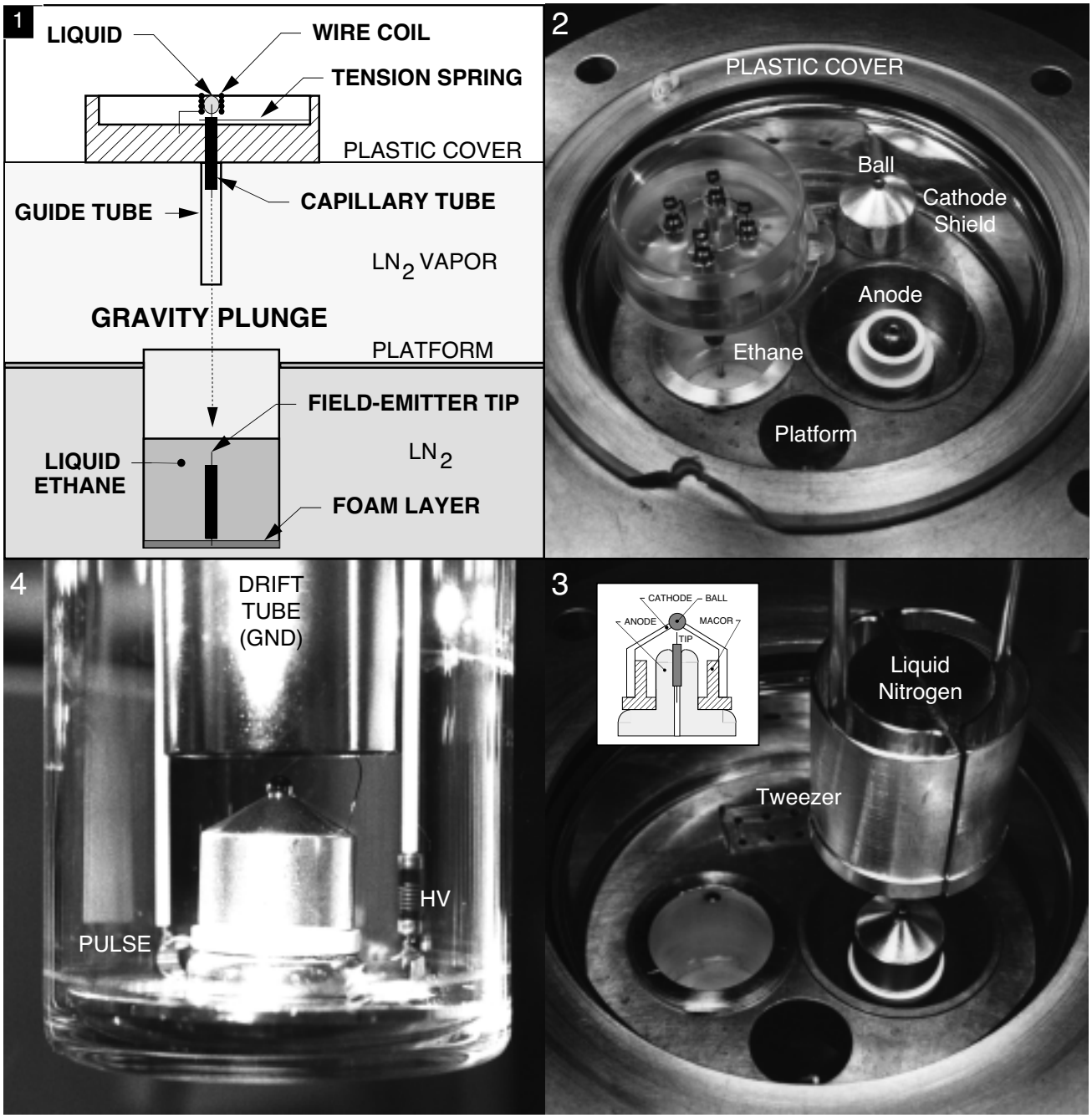

FIG. 1. Vitrification. A metal wire protrudes ≈ 2 mm from each end of a Ø2 mm capillary tube, positioned by a tension spring. A field-emitter tip, at one end of the wire, is centered in a liquid droplet. When spring tension is released, the capillary tube falls through a guide tube and is plunged into liquid ethane at 102 K, vitrifying the liquid layer on the tip apex.

FIG. 2. Apparatus. A metal platform is cooled to 78K inside a dewar containing liquid nitrogen. The platform supports a liquid ethane container and an anode assembly consisting of a metal tip holder, a macor insulator and a separate cathode shield (with a Ø1 mm aperture closed by a steel ball).

FIG. 3. Cryotransfer: A "tweezer" with a LN_2 reservoir is used to pick up and enclose the anode assembly (see insert). The tip is isolated and exposed only to LN_2 vapor during transfer to the IAP.

FIG 4. IAP cold finger (dewar removed). After pump-down the ball is removed by a magnetic field.