doi:10.1017/S1431927614009325
Microsc. Microanal. 20 (Suppl 3), 2014


# X-ray and Electron Energy Loss Spectroscopy in Liquids in the Analytical S/TEM

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As in-situ studies of dynamic processes in gases and liquids in the transmission and scanning transmission electron microscope (TEM/STEM) become routine [1] the need to go beyond imaging to more fully characterize complex microstructures during in-situ experiments becomes paramount. The use of both x-ray energy dispersive (XEDS) and electron loss spectroscopy (EELS) in conventional (vacuum) TEM is now routine. During gas/solid in-situ studies EELS has been used successfully [2], however, this has not been the case for studies in liquids [3] and XEDS has only recently been successful reported [4]. This is due to two factors namely: 1) multiple inelastic scattering in the liquids making EELS impractical and 2.) physical limitations which virtually preclude x-ray measurements in conventional liquid cell S/TEM holders. Recent modifications to holders and optimization of detectors has allowed us to overcome the former limitation [4]. In this work we present results using a modified Protochips Poseiden P200 holder in an FEI Tecnai F20 and CM200F TEMs operated at 200 kV. Nanoparticle specimens were encapsulated between a pair of 50 nm thick SiN windows having a nominal 150 nm gap in a commercial $Si/SiN_x$ eCell surrounded by both gaseous and liquid media.

Figure 1 shows a comparison of EELS spectrum from a fully hydrated and an air filled (dehydrated -liquid absent) SiN windowed eCell, illustrating succinctly the effects of multiple inelastic scattering. In both cases the eCell was allowed to equilibrate over 12 hours under 1 ATM of pressure in both the air filled (liquid absent) and fully hydrated condition. Due to bowing of the window under these pressures the thickness of the gap and the corresponding space filling environmental media (air or liquid) cannot be independently determined, but based upon the experimentally measured $t/\lambda$ values of 1.4 (air filled) and 5.2 (fully hydrated) values in excess of 150 nm are expected. The large inelastic scattering peak at ~ 140 eV precludes any core loss spectroscopy by EELS (Fig. 1) when liquid is present, while O, N, and Si EELS core loss edges are detectable in the air filled state (Fig. 1), core loss profiles were not visible in the fully hydrated condition. In contrast, Figure 2 shows corresponding x-ray spectra for the same conditions air filled (Fig 2a) vs hydrated (Fig. 2b), the presence of liquid water , as well as the SiN window components are easily detected by virtue of the $O_K$ , $N_K$, and $Si_K$ x-ray emission lines. The presence of liquid water can be verified by the integrated intensity of the Oxygen signal and can be gauged by the Si/O ratio which for the two extremes are ~ 30:1 (Air) and ~ 0.5:1 ($H_2O$) respectively. Figure 2c and 2d show illustrative XEDS data when the $H_2O$ in the eCell is replaced by Ethanol ($C_2H_5OH$) and Dichloroethane ($CH_2ClCH_2Cl$). The variation in the composition of the liquid is revealed spectroscopically by the varying intensities ( or lack thereof) of $C_K$, $O_K$, and $Cl_K$. Lastly, figure 3 shows an typical spectra recorded in the fully hydrated state of Au and Ag nanoparticles deliberatedly suspended in liquid water during these studies. To date spatial resolutions ~ 10 nm have been obtained.

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[5] Research supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357 at the Electron Microscopy Center of Argonne National Laboratory.and the BP 2013 DRL Innovation Fund.

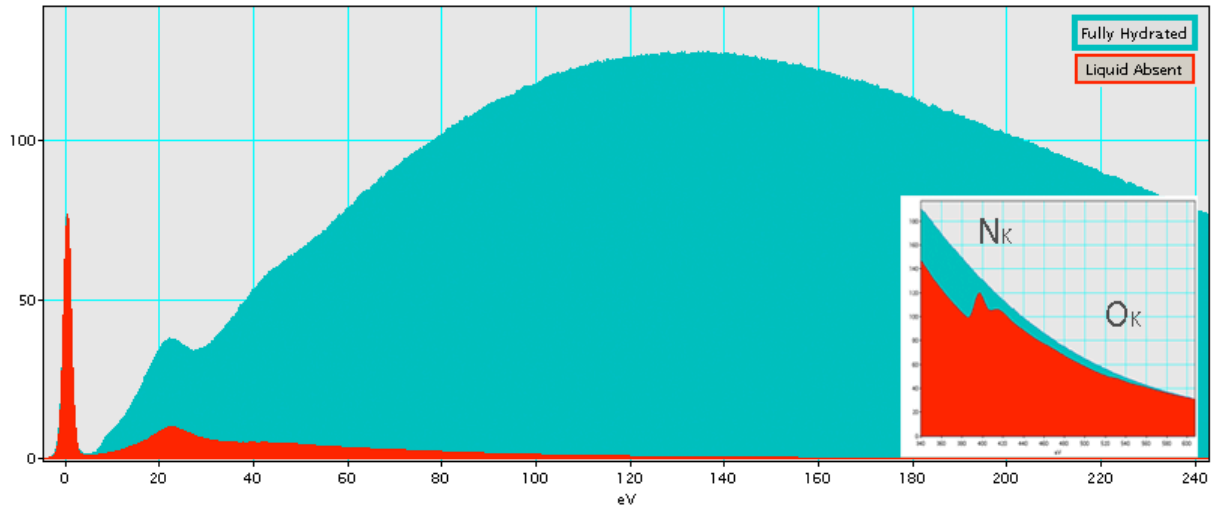


Figure 1. EEL spectra from a fully hydrated (green) and air filled (red) $SiN_x$ eCell ($t/\lambda = 5.2$ and 1.4 respectively), spectra are normalized at the zero loss peak. Fully hydrated = $H_2O$, liquid absent media = air @ 1 ATM. Inset: background normalized spectral profiles for $N_K$ and $O_K$ regions for air filled (red), and hydrated eCell (green) . NK and OK core loss edges not measurable for hydrated case (green) due to the large multiple scattering background. $O_K$ for air filled is measurable after background subtraction.

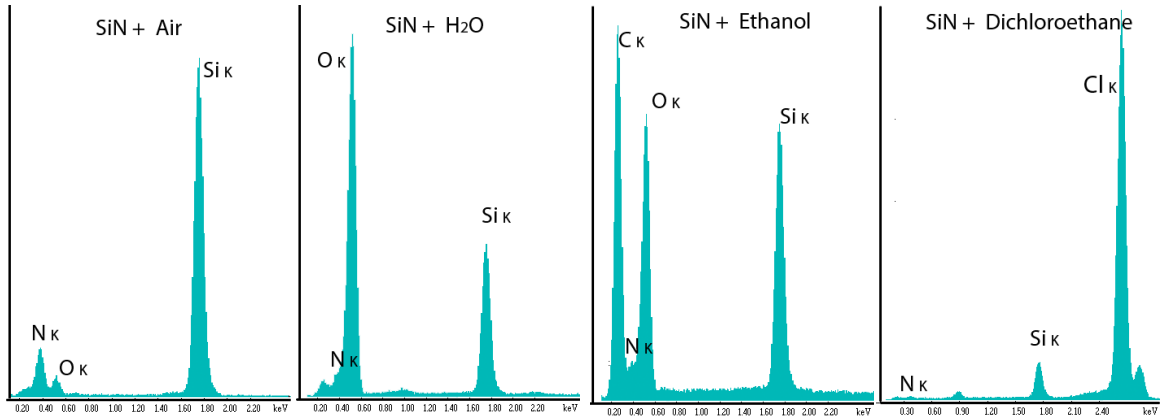


Figure 2. XED spectra from SiNx eCell with the ~ 150 nm gap filled by a). Air, b.) $H_2O$ c.) Ethanol($C_2H_5OH$) d.) Dichloroethane ($CH_2ClCH_2Cl$). All environmental media at nominally 1 ATM pressure.

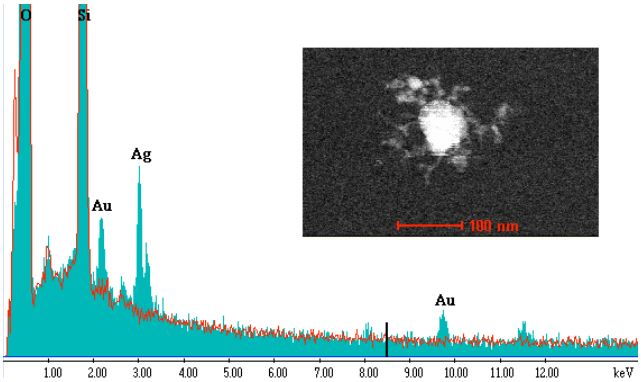


Figure 3.) XED Spectra from drifting Au and Ag nanoparticle array in $H_2O$. Shown is a XED spectra (green) recorded from the nanoparticle array captured by following the floating particles in liquid compared to a corresponding background (red) spectrum recorded under identical conditions from a neighboring region which was devoid of nanoparticles and consisted only of the $SiN_x/H_2O$ media.

https://doi.org/10.1017/S1431927614009325 Published online by Cambridge University Press