Probing chemical pathways in polymer membranes despite electron beam damage

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Reverse Osmosis (RO) membranes are used for seawater desalination in the oil and gas industry. These membranes are made of a polyamide (PA) 'active' layer, around 100-500 nm thick, a polysulfone (PSf) support and a polyester backing layer. The PA layer is thought to control ion flow through the membrane yet very little is understood about how that is achieved at the nanoscale. A number of techniques have been used to try to characterise the PA layer but none of them have the spatial and energy distribution necessary for nanoscale chemical mapping. Here we test whether scanning transmission electron microscopy EELS (STEM-EELS) techniques can be used to map chemical functionality across flat RO membranes with nm-scale resolution. We argue that, despite the high electron flux required during acquisition, careful comparison to dose-managed control experiments on standards together with multivariate analysis post-processing techniques can be used to extract useful information about the distribution of functional chemistry from spectra acquired from damaged PA.

Practically, commercial RO membranes are very rough making them difficult to characterise. For this reason, in-house prepared 10 nm thick PA membranes prepared via an interfacial polymerisation technique, were used for this study. STEM EELS studies were carried out on a Nion UltraSTEM 100MC 'HERMES' monochromated transmission electron microscope at SuperSTEM (Daresbury, UK). The microscope was operated at 100 kV with a probe size of 0.9 Å and convergence and collection semi angles of 31 and 44 mrad respectively.

First, chemical maps of C, N and O K-edges, the main components of the membranes, were obtained. From the nitrogen signal the exact width of the membrane could be established as N is only present in the membrane itself. Control beam damage studies were carried out on large areas (800 nm x 800 nm) of plan-view samples so that the degree of damage on the C K-edge could be assessed. The parameters required to avoid detection of beam damage effects were impractical for obtaining chemical information with a pixel size of 2 nm. However, with higher electron fluences (e.g. 3-10 x 107 e/Å2 per probe size or 6-10 x 103 e/Å2 per pixel size), whilst damage occurred to the carbon bonds, the dominant features in the fine structure of the C K-edge were in fact still present and variations could be mapped across the PA membrane with a spatial sensitivity of 2 nm. Application of multivariate analysis to the raw high electron fluence data made it possible to assign peaks related to specific co-ordination environments by comparison with the control data fine structure.

This work shows that despite severe electron beam damage evident by the loss of fine structure of the C K-edge, information about functional chemistry within the PA can still be achieved. This suggests that spectra obtained where the electron flux has been high, may still be interpreted provided care is taken to assess the extent of possible beam damage and carry out control experiments. With continued advancement of technologies such as stable cold stages, high frame rate cameras and direct electron detection capabilities it should become easier to map functional chemistry across radiation sensitive soft materials with nm-scale high spatial and energy resolution.

Keywords:

Polymers, EELS, beam-damage, chemical pathways