Probing chemical pathways in polyamide reverse osmosis membranes

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Reverse Osmosis (RO) membranes are widely used for sea water desalination applications. As the cost of installing desalination plants at sea is high it has become important to have a fundamental understanding of how the membranes work so that costs can be reduced. Much effort has gone into understanding the bulk properties of the membranes, but little effort on understanding then nanoscale interactions that control ion selectivity. The membranes are made from a polyester backing layer, a polysulfone (PSf) support and a polyamide (PA) membrane which is typically 100-500nm thick in a commercial membrane. Due to the membrane's complex hierarchical structure, the controllability of ion selectivity remains unclear.

Recent work has suggested that although complex, the structure is actually made out of a single sheet of membrane about 10nm thick that has been 'crumpled'. There is also evidence that the top and bottom surfaces of the membrane are terminated with different functional groups suggesting that ion permeation pathways across the membrane may be due to chemical variations. Because of the amorphous nature of the polymer it is impossible to visualize any physical or chemical pathways using conventional transmission electron microscopy (TEM) or scanning TEM (STEM). The only method that can be used to investigate variations in chemistry on the sub nanometre scale is spatially resolved electron energy-loss spectroscopy (EELS). This, however, presents its own set of problems in the form of electron beam damage, which needs to be carefully controlled (if not mitigated) to yield meaningful conclusions.

Here we use monochromated EELS spectrum imaging to map differences in the spatial distribution of C, N and O across flat in-house fabricated 10nm membranes and rough commercially available membranes. Additionally we show clear changes in the fine structure of the C K edge in the different polymer layers (PSf, PA and resin) as well as changes across the membrane itself once electron beam damage has been taken into account. The chemical pathways that can be deduced from these findings provide us with a much clearer understanding of the transport mechanisms through the membrane.