Experimental Report
Quantitative texture analysis of redox-stimuli responsive poly(ferrocenylsilane) nanoporous membranes
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Experimental team: Kaihuan Zhang, Julius G. Vancso, Laura Folkertsma, Orsolya Czakkel
Local Contact: Gudrun Lotze

Redox responsive nanoporous membranes can be readily formed via electrostatic complexation between poly(ferrocenylsilane) PFS-based poly(ionic liquid)s and poly(acrylic acid) in a variety of morphologies. Coating the membrane onto the surface of an electrode or other substrates results in a switching surface with redox-stimuli responsivity due to the charge and porous nature of the membrane layer. This system has a high application potential in membrane technology and bioengineering science (e.g. permeability switching and protein screening). The superficial and cross-sectional properties, both in a static and dynamic way have been characterized by atomic force microscopy (AFM) and scanning electron microscopy (SEM). However, the in-depth properties of the membranes can be revealed only via scattering techniques, owing to the partially closed porosity and the thinness of the samples. By the proposed small angle X-Ray scattering experiment we intend to reveal in details the bulk static morphology of the membranes, as well as by time resolved in-situ studies the kinetics of their stimuli responsive behaviour.
The samples have been prepared at the MESA+ Institute for REF Nanotechnology, at the University of Twente, The Netherlands. We have performed both off-line and online measurements. For the off-line measurements, to explore the bulk morphology of the membranes, 100-500 μm thick PFS-based nanoporous membranes were deposited on 0.5 mm thick glass window supports (diameter of 15 mm), and previously reduced or oxidised. We have compared several membranes, coming from different batches to examine the reproducibility of the preparation process.
In the second part of the experiment we have performed the in-situ measurements. A home-made electrochemical cell have been built before the experiment. This was installed onto the sample stage and the SAXS response of the membranes has been followed during the reduction/oxidation cycles.
The analysis of the in-situ measurements is still ongoing. The evaluation of the off-line data revealed that oxidation/reduction indeed induces an opening/closing in the network structure. Typical response curves and pore sizes deduced from Porod analysis are presented in Figure 1 and Table 1. A publication including the results from the off-line data is under preparation.

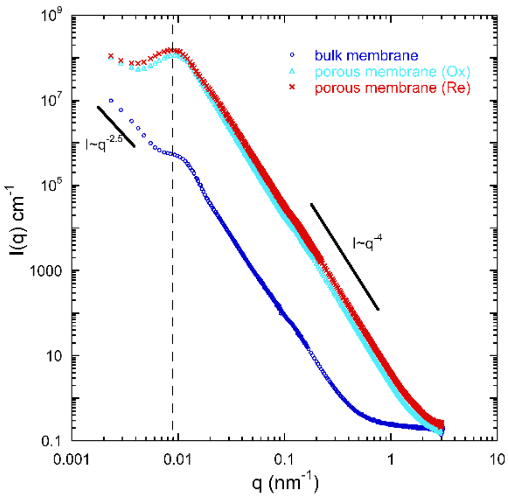

Figure 2 SAXS intensity curves of the bulk (circles), oxidized porous (triangle) and reduced porous (cross) membranes. The dashed line shows the position of the correlation peak maxima in the porous membranes ($q=0.009$ nm^{-1}).

Table 1. Pore characteristics of the membranes from SAXS measurements

	Bulk	Oxidized	Reduced
Rmax (nm)	203 ± 0.3	195 ± 2	197 ± 10
Rpore (nm)	10.6 ± 0.9	125.9 ± 15.4	97.4 ± 11.5