**A Surface Study of Self-Assembled Monolayer (SAM)-Based Solid Contact (SC) Polymeric Ion Sensors**

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**Abstract**

Self-assembled monolayers (SAMs) of ferrocene (Fc) have been utilized as solid contacts (SCs) in polymeric ion sensors.  The SAM Fc films on glassy carbon (GC) substrates were prepared using a click chemistry approach, with the thicknesses and molecular orientations of SAM films determined using photon energy dependent synchrotron radiation-X-ray photoelectron spectroscopy (SR-XPS) [1] and angle-resolved-near edge X-ray absorption fine structure (AR-NEXAFS) spectroscopy [2]. With oxidation of SAM redox centres in the native films, changes in the Fc SAM have been probed using SR-XPS and NEXAFS edge spectra [3]. However, we have also derived rich information such as the injection of Fe 3d states from Fe redox centres using valence band spectroscopy (VBS) [4], and changes in near linear plots of densities of states (DOS) near to the Fermi edge that are symbolic of the Seebeck coefficients for thermoelectronic conduction and oxidative doping of SAMs using VBS [4]. It is shown that an anchoring of the Fc molecule to the GC substrate prevents mobility of the Fc molecule and overcomes the electrochemical irreversibility of dissolved Fc in membranes. We also demonstrate that SAM molecular orientation effects, which may be controlled by electrode polarization, are critical to SAM electrochemistry and their concomitant efficacy in SC systems. Last, we show that a minimization of thermally excited capillary waves can reduce a mixing of membrane and Fc SAM components in SCs, thereby enabling a washing and replacement of spent sensing films on Fc SAM SCs – a critical factor in the longevity of sensors of this type.

**References**

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