

Supplementary Information for

**Transport and accumulation of ferrocene tagged poly(vinyl chloride) at
the buried interfaces of plasticized membrane electrodes**

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Materials

Glassy carbon (GC) coupons (10 mm x 10 mm) were purchased from SPI Supplies/Structure probe, Inc. (Terrigal, NSW) and mounted as electrodes in high vacuum compatible epoxy resin, Varian Torr Seal (Albuquerque, New Mexico). Electrical connection was made using Kapton insulated silver plated copper wire, 0.025 cm in diameter, purchased from Accu-Glass Products, Inc. (Valencia, CA). High vacuum compatible epoxy and Kapton insulated wire were essential, to avoid excessive outgassing of electrodes in the ultrahigh vacuum chamber of the electron spectrometer.

All reagents including native PVC were purchased from Sigma Aldrich Australia Ltd. Aqueous solutions were prepared by dissolving the appropriate salts in Milli-Q water (18.2 MΩ.cm). The FcPVC polymer utilized in this work (with 6 mol% of Fc dopant) was prepared through modification of the PVC side chains with azide groups and subsequent introduction of ferrocene moieties using a “click chemistry” approach, as described elsewhere by Bakker and co-workers¹. Membrane cocktails were prepared with FcPVC via dissolution of FcPVC, DOS and ETH 500 in 1 mL of THF (viz., about 50 mg in the proportions of 35 wt.% FcPVC, 55 wt.% DOS and 10 wt.% ETH500) in sandwich membranes, or FcPVC, DOS and NaTFPB in 1 mL of THF (viz., about 50 mg in the proportions 35 wt.% FcPVC, 62 wt.% DOS and 3 wt.% NaTFPB) in the membranes utilized in aqueous electrolyte studies, noting that 250 μL of membrane cocktail was deposited onto a 12 mm diameter epoxy mounted glassy carbon electrode, so as to provide a nominal membrane film thickness of 200 μm².

Electrochemical measurements

Electrochemical measurements were undertaken on an Autolab PGSTAT 101 potentiostat (Eco-Chemie) workstation. A standard three-electrode electrochemical cell utilizing a GC coupon working electrode, a Ag/AgSCN wire reference electrode and platinum wire auxiliary electrode was used in all electrochemical studies in liquid electrolytes. Note that due to the instant deposition of AgSCN material on the Ag/AgCl wire on exposure to 0.1 M KSCN solution, the practical reference electrode used in this study was Ag/AgSCN. In solid-state electrochemical measurements, a two-electrode system employing a membrane drop cast onto a GC coupon electrode was sandwiched between this electrode and another GC coupon electrode by the application of a gentle pressure between Teflon bars.

SR-XPS/NEXAFS measurements

After chronoamperometry at 500 mV versus the Ag/AgSCN wire reference electrode for 180 seconds, the sample was rinsed in a jet of Milli-Q water, and transferred into the introduction chamber of the SR-XPS/NEXAFS instrument where it was pumped down for 7 hours prior to transfer into the sample preparation and ultimately the electron analyzer chamber of the instrument. SR-XPS and NEXAFS measurements were carried out on the soft X-ray spectroscopy beamline (141D) at the Australian Synchrotron, Victoria, Australia. XPS measurements were carried out using a photon energy of 900 eV and an electron spectrometer pass energy of 20 eV. The instrument was calibrated with

gold calibrant using the Au 4f_{7/2} peak at a binding energy of 85.15 eV. Charging of the FcPVC membranes during photoionization was corrected against the graphitic-like C 1s peak of the membrane at 284.6 eV. The L-edge Fe NEXAFS spectra were measured in both the surface-sensitive total electron yield (TEY) and bulk-sensitive fluorescence yield (FY) modes. The NEXAFS spectra were normalised against variations in the incident photon flux that are simultaneously recorded on the beamline³. Argon ion sputtering was used in depth profiling of the FcPVC films, noting that a sputtering rate of 0.5 μM/min was obtained by sputtering a FcPVC film of known thickness. SR-XPS and NEXAFS analyses were performed at each sputtering time until the glassy carbon substrate electrode had been reached, noting that the entire depth profiling experiment took approximately 2 days to complete.

Reference

- 1 M. Pawlak, E. Grygolicz-Pawlak and E. Bakker, *Anal. Chem.*, 2010, **82**, 6887.
- 2 V. Bhakthavatsalam and E. Bakker, *Electroanalysis*, 2008, **20**, 225.
- 3 B.Y. Zhan, E. Holmstrom, R. Lizarraga, O. Eriksson, X. Liu, F. Li, E. Carlegrim, S. Stafstrom and M. Fahlman, *Adv. Mater.*, 2010, **22**, 1626.