SUPPLEMENTARY INFORMATION

Reagents

Tetrahydrofuran (anhydrous, ≥ 99.9%, inhibitor-free) was purchased from Sigma-Aldrich Australia. Silver ionophore IV O,O''-bis[2-(methylthio)ethyl]-*tert*-butylcalix[4]arene, calcium ionophore IV N-dicyclohexyl-N',N'-dioctadecyl-3-oxapentaneamide, sodium tetrakis [3,5-bis(trifluoromethyl)phenyl]borate (NaTPFB), bis(2-ethylhexyl) adipate (DOS), and poly (vinyl chloride) (PVC) Selectophore reagents were obtained from Fluka. Silver nitrate (AR grade) solutions from Univar were prepared using milli-Q and/or deuterated water.

Silicon Wafer Substrates

Cylindrical n-type silicon wafers (100 mm diameter, 10 mm thick, orientation 111, scratch /dig of 40/20) with a deep optical polish on one face and a flatness of < 20 lambda were purchased from Crystran LTD, United Kingdom.

Ion-selective electrode (ISE) Membrane Preparation and Deposition

ISE membranes for NR studies were prepared in a clean room. Silicon wafers were rinsed with high purity ethanol to remove surface dust and lint prior to sonification in ethanol for 5 minutes. Samples were dried in a stream of high purity nitrogen gas.

A PVC film was prepared by spin-coating at 2000 rpm for 2 minutes with a solution of 0.278 wt.% PVC-ISE cocktail in THF comprising the silver ionophore (1.83 wt.%) or calcium ionophore (1.00 wt.%), NaTFPB (0.51 or 0.60 wt.%), DOS (65.11 or 65.90 wt.%) and PVC (32.55 or 32.5 wt.%). The PVC ISE-coated wafer was annealed in a vacuum oven at 60 ^{o}C and 1.0 kPa for 45 minutes.

Silver nitrate solutions (1 mM) were made up in D_2O, milli-Q water, and a D_2O / milli-Q water mixture with a ratio of 0.582: 0.418 respectively.

Electrochemical Impedance Spectroscopy (EIS)

ORION double-junction sleeve reference (Model 900200), platinum counter and ISE working electrodes were connected to a Princeton Applied Research PARSTAT 2263 portable potentiostat. EIS experimental control and data acquisition were performed using a personal computer running the PowerSINE software, and EIS data were collected at the open circuit potential using an A.C. amplitude of ±10 mV rms and a frequency range of 100 kHz–10 mHz..

Secondary Ion Mass Spectromertry (SIMS)

All SIMS spectra and images were collected on a CAMECA IMS 5f instrument housed at the Australian Nuclear Science and Technology Organization (ANSTO), Lucas Heights, Sydney. A Cs^+ primary ion source (10 keV) was used to generate secondary ions. A primary beam diameter of ~30 μm was rastered over an area of 250 x 250 μm and an analytical area of 60 μm was used in all measurements.

X-Ray Reflectometry (XR) and Neutron Reflectometry (NR)

XR was performed on a PVC ISE-coated wafer in air at a wavelength 1.541 Å to ascertain the starting film thickness and roughness.

Although the Si wafers used in this study almost certainly comprised a 5-10 Å thick layer of native oxide, this oxide film does not contribute strongly to the NR reflectivity, as compared to the 200 Å thick polymer ISE film, so it was deemed unnecessary to include it in the fitting of the NR reflectivity data.

Figure S1 presents theoretically modelled NR reflectivity curves for a silicon wafer coated with 200 Å of PVC ISE in a D_2O electrolyte (see Fig. S2a) as well as a 120 Å underlayer of D_2O between the silicon wafer and the 200 Å film of PVC ISE (see Fig. S2b). It is important to note that the modelling assumed atomically flat and perfectly homogeneous or pure films, and the results clearly showed a superposition of NR interference fringes for the PVC film and the intermediate D_2O layer.

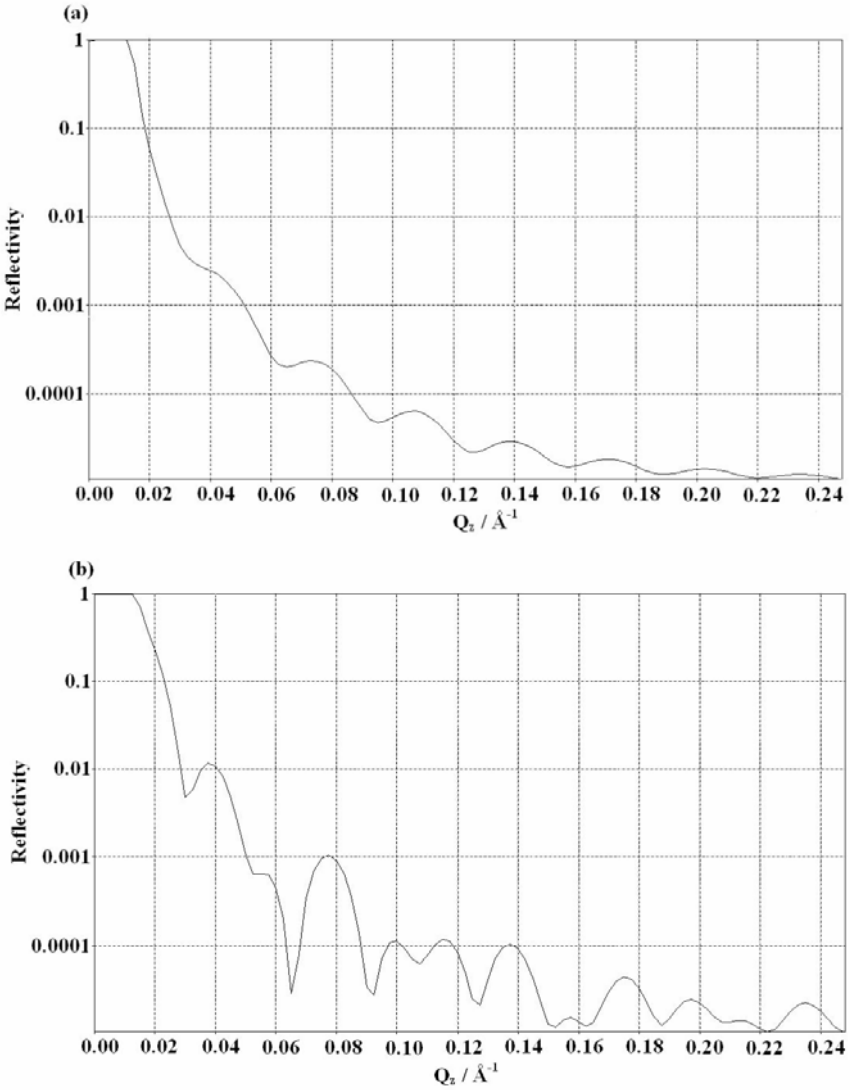

Figure S1: Modelled NR curves in a D_2O electrolyte for (a) 200 Å of PVC ISE film and (b) 200 Å of PVC ISE film also comprising an underlayer of 120 Å of D_2O.

NR experiments were conducted at a wavelength 2.43 Å. A custom-built cell (see Figure S2) enabled in-situ experiments on the PVC-ISE film as it bathed in solution. NR measurements were performed on wafers in varying media including air, D_2O, a H_2O/D_2O mixture, and H_2O. All solutions contained 1 mM of silver nitrate.

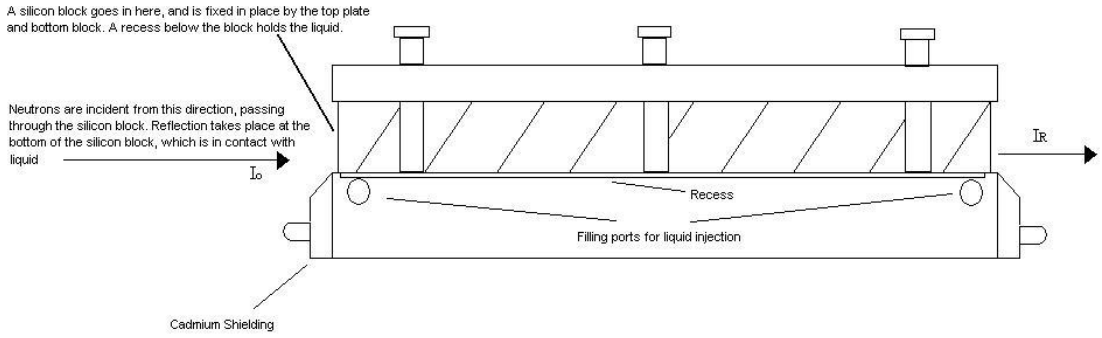

Figure S2: Schematic diagram of the specialized cell used in the neutron reflectometry experiments.

Table S1 presents the modelling results for the NR data of the PVC ISE using a two-layer construction comprising an underlayer of water and an overlayer of PVC ISE. It can be seen that the PVC film possesses a neutron scattering length density (NSLD) consistent with a combination of the PVC ISE and water which is slightly roughened due to neutron scattering from polydisperse water and the surrounding PVC ISE matrix, and an underlying water layer commensurate with an intermediate NSLD value for water and the plasticizer that is roughened due to the exudation of polydisperse plasticizer nanodroplets into the water layer.

Table S1: NR best-fit parameters for the PVC ISE aged in 1 mM silver nitrate in D_2O, D_2O/H_2O and H_2O.

Membrane	Material	Thickness (Å)	NSLD ($Å^{-2}$)	Roughness (σ / Å)
PVC D_2O	Si	N/A	2.07E-06	34.4
	D_2O Layer	99.3	1.60E-06	15.1
	PVC	172.6	4.84E-07	3.7
	D_2O	N/A	6.36E-06	N/A
PVC D_2O/H_2O	Si	N/A	2.07E-06	37.0
	D_2O/H_2O Layer	109.9	1.13E-06	14.6
	PVC	167.1	1.10E-07	0.1
	D_2O/H_2O	N/A	3.36E-06	N/A
PVC H_2O	Si	N/A	2.07E-06	15.0
	H_2O Layer	110.3	1.48E-06	8.0
	PVC	164.1	-1.88E-07	1.1
	H_2O	N/A	-5.59E-07	N/A