

Supporting Information

for

Solid-Contact Ion-Selective and Reference Electrodes

Covalently Attached to Functionalized Poly(ethylene terephthalate)

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Materials

AgCl, KCl, LiCl, NaCl, LiOH, LiAlH₄, KOH, 1.0 M NaOH, 1.0 M HCl, KH₂PO₄, K₂HPO₄, FeCl₃, lithium acetate, methyl methacrylate, ethylene glycol dimethacrylate, butyl acrylate, 1,6-hexanediol diacrylate, 2,2-dimethoxy-2-phenylacetophenone, 2-(dimethylamino)ethyl methacrylate, ethanol, hexanes, diethyl ether, methacryloyl chloride, potassium *tert*-butoxide, basic alumina, valinomycin, and potassium tetrakis(4-chlorophenyl) borate were purchased from Sigma-Aldrich, Ag wires (0.05 mm diameter, $\geq 99.9\%$) and Ag foil (0.05 mm thick) from Alfa Aesar, 1-octyl-3-methylimidazolium bis-(trifluoromethyl sulfonyl)imide, and 1-dodecyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide from Ionic Liquid Technologies, a pH glass electrode from Hanna Instruments, a 3UV lamp from Analytik Jena, poly(ethylene terephthalate) (PET) sheets (0.127 mm thick) and poly(ethylene terephthalate glycol) (PETG) sheets (1.59 mm thick) from McMaster-Carr Supply Company, 8331 silver conductive epoxy adhesive from MG Chemicals, and quartz glass plates (15 × 15 cm², 3,2 mm thick) from Fisher Scientific. Methyl methacrylate, ethylene glycol dimethacrylate, butyl acrylate, 1,6-hexanediol diacrylate, and 2-(dimethylamino)ethyl methacrylate were filtered through basic alumina before use. All other chemicals were used as received.

Preparation of AgCl-coated Ag Foil

Ag ribbons (cleaned in 0.1 M HCl for 15 min) were transferred into a 1.0 M FeCl₃ and 0.10 M HCl solution. After stirring for 10 minutes, the resulting AgCl-coated Ag foil ribbons were rinsed with H₂O and dried.

Contact Angle Measurements

Contact angles were measured with a contact-angle goniometer (Erma, Tokyo, Japan) with three drops (4, 6, 8 μL) of purified H_2O or 10.0 mM phosphate buffer ($\text{pH} = 12.3$). Averages were computed from six advancing contact-angle measurements at three separate locations on the PET or PETG surfaces.

Potentiometric Measurements

All potentials were measured at room temperature in stirred solutions with an EMF 16 potentiometer (Lawson Labs, Malvern, PA, USA) controlled with EMF Suite 1.02 software. All potentials were measured relative to a free-flowing double-junction reference electrode¹ with a 3.00 M KCl bridge electrolyte and AgCl-saturated 3.00 M KCl reference electrolyte (DX200, Mettler Toledo, Switzerland). The bridge electrolyte was changed to 1.00 M lithium acetate for measurements with K^+ -selective electrodes.

Free-Standing Ionic-Liquid Reference Membranes

Reference membrane disks (1.0 cm diameter) were mounted onto Philips-type electrode bodies (Glasbläserei Möller, Zürich, Switzerland). The inner filling solution was 1.0 mM KCl, saturated with 1-octyl-3-methylimidazolium bis-(trifluoromethyl sulfonyl)imide, into which a AgCl-coated Ag wire was inserted as inner reference electrode.

H^+ -Selective Electrodes

Solid-contact H^+ -selective electrodes were fully submerged for conditioning in 10.0 mM phosphate buffer ($\text{pH} = 7.1$) for 12 h before potentiometric measurements. H^+ -selective electrodes were not conditioned for measurements presented in Figure 5. To measure calibration curves, the electrodes were placed in a 10.0 mM potassium phosphate buffer solution ($\text{pH} = 7.1$), and after approximately 10 min the pH was adjusted by addition of aliquots of 1.0 M NaOH until the lower

limit of detection was reached. This was followed by addition of aliquots of 1.0 M HCl until the upper detection limit was reached. The pH was monitored with a pH glass electrode.

Selectivities were measured using the fixed interference method.² Electrodes were placed in solutions containing 1.0 mM potassium phosphate buffer (pH = 7.1) and 0.10 M LiCl, NaCl, or KCl. The pH was adjusted by additions of 1.0 M LiOH, NaOH, or KOH, respectively, until the lower limit of detection was reached.

K⁺-Selective Electrodes

Solid-contact K⁺-selective electrodes were fully submerged for conditioning in 1.00 mM KCl for 24 h before potentiometric measurements. To measure calibration curves, the electrodes were placed in deionized purified water, and the concentration of KCl was adjusted by additions from 10.0 mM and 1.00 M KCl stock solutions. Selectivity was measured using the fixed interference method.² Electrodes were placed in solutions containing 0.10 M LiCl or NaCl. KCl concentrations were adjusted by additions from 10.0 mM and 1.00 M KCl stock solutions.

Resistance Measurements

Electrical resistances of solid-contact reference electrodes were measured with a three-electrode setup using a Solartron 1255B frequency response analyzer with an SI 1287 electrochemical interface (Farnborough, Hampshire, U.K.) controlled by ZPlot software (Scribner Associates, Southern Pines, NC).³ Measurements were performed at the open circuit potential with an AC amplitude of 10 mV in 100 mM KCl. Data was collected using a Pt foil (3×3 cm²) counter electrode and a AgCl/Ag wire reference electrode. All data fits were performed using Mathematica 10.1 software (Champaign, IL).

Electrical resistances of solid-contact H⁺-selective and K⁺-selective electrodes were measured with the known shunt method.⁴ The potentials (E_1) of the electrodes were first measured in a 10.0 mM

potassium phosphate buffer solution (pH = 7.1) for H⁺-selective electrodes or 1.00 mM KCl for K⁺-selective electrodes versus a free-flowing double-junction reference electrode. The potentials (E_2) were measured a second time after the electrodes were individually shorted to the free-flowing double junction reference electrode through a 10 M Ω resistor. Resistances were calculated as $10 \text{ M}\Omega \times (E_1 - E_2) / E_2$.

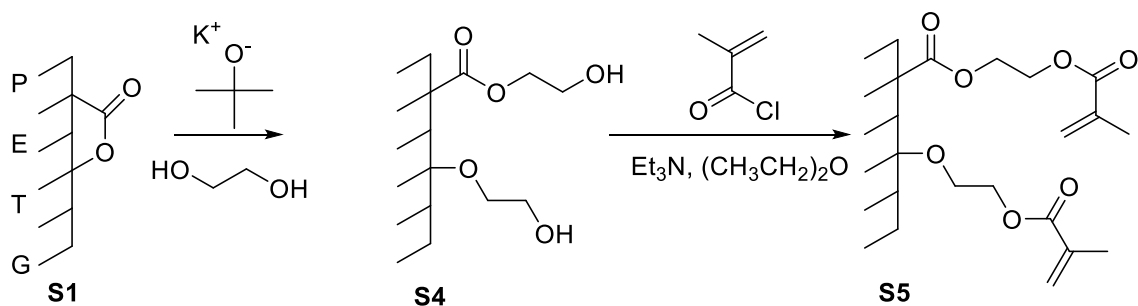


Figure S1. Surface functionalization of PETG using potassium *tert*-butoxide/ethylene glycol solutions. Synthetic details are described in the Experimental Section of the manuscript.

Table S1: Contact angles of H_2O and 10 mM phosphate buffer (pH = 12.3) on non-functionalized and differently functionalized PETG. Results are reported with 95% confidence intervals ($n = 6$).

PETG Surface ^a	H_2O	10 mM Phosphate Buffer (pH = 12.3)
S1	71.1 ± 2.0	72.0 ± 1.8
S4	61.3 ± 1.5	63.2 ± 1.2
S5	72.7 ± 1.5	75.8 ± 1.8

^a Surface types as shown in Figure S1.

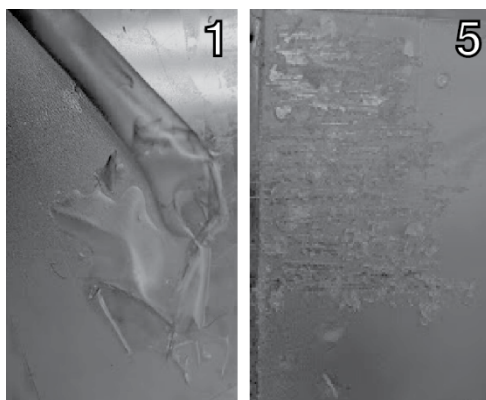


Figure S2. Attachment of crosslinked butyl acrylate membranes to non-functionalized PET, **1**, (left) and functionalized PET, **5** (right): Polymer membranes could be removed from **1** in one piece with little effort but could not be removed from **5**. The right panel shows scratch marks on **5** that resulted from forceful attempts of removal with tweezers (image contrast enhanced for improved visibility).

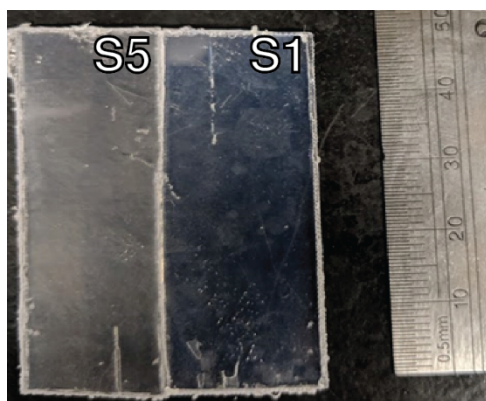


Figure S3. Crosslinked butyl acrylate membranes on non-functionalized PETG, **S1**, (right) and functionalized PETG, **S5**, (left) prior to removal attempts.

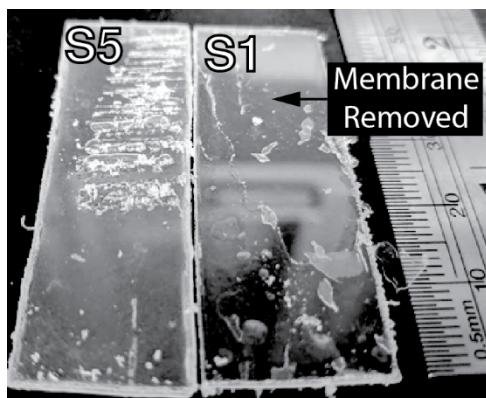


Figure S4. Adhesion of crosslinked butyl acrylate membranes to non-functionalized PETG, **S1**, (right) and functionalized PETG, **S5** (left). Polymer membranes could be easily removed from **S1** but all efforts to remove them from **S5** failed. The left PETG shows scratches on **S5** that resulted from failed attempts of removal with tweezers.

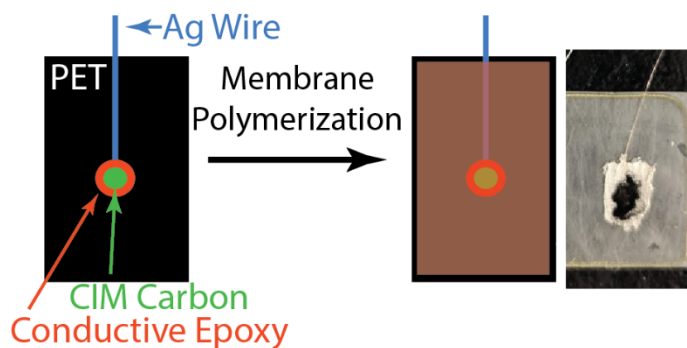


Figure S5. Schematic and image of the fabrication of a solid-contact H^+ -selective electrode.

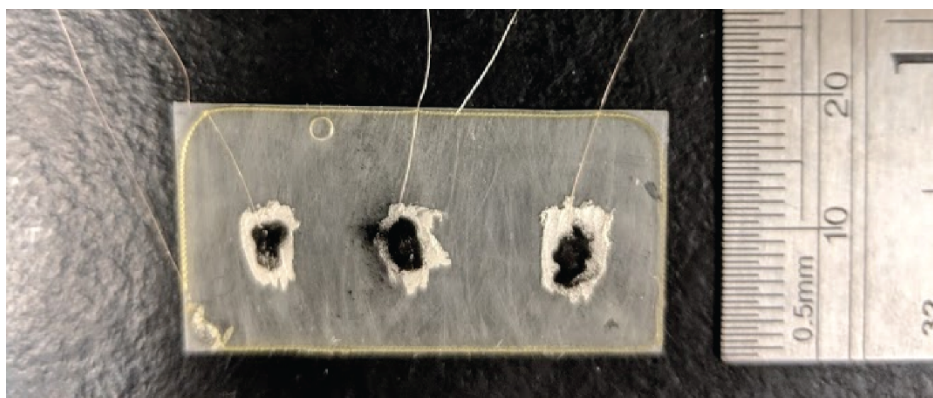


Figure S6. Image of a PET construct with three solid-contact H⁺-selective electrodes (prior to cutting into three separate pH electrodes).

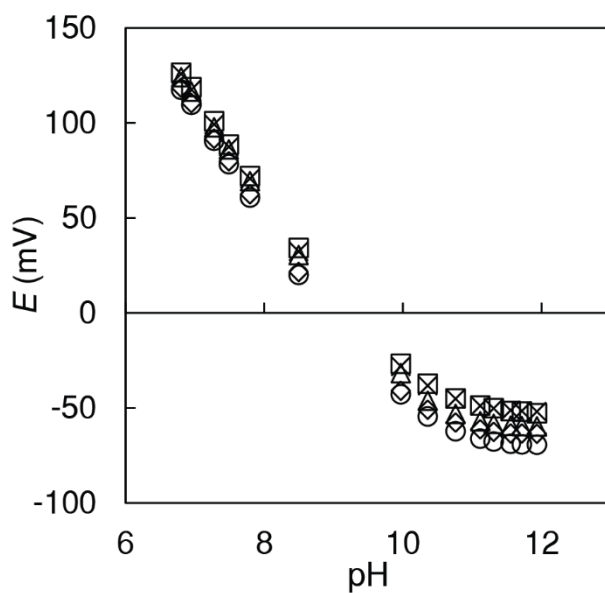


Figure S7. Measured potentials, E , of solid-contact H⁺-selective electrodes as a function of solution pH. The initial solution was 1.0 mM phosphate buffer with 100 mM KCl (pH = 7.1). The pH was then raised stepwise with aliquots of 1.0 M KOH. The pH shown on the x-axis was measured using a pH glass electrode. Black symbols represent E values of individual electrodes. E was measured relative to a free-flowing double-junction reference electrode. All E values are corrected for liquid junction potentials at the free-flowing double junction.

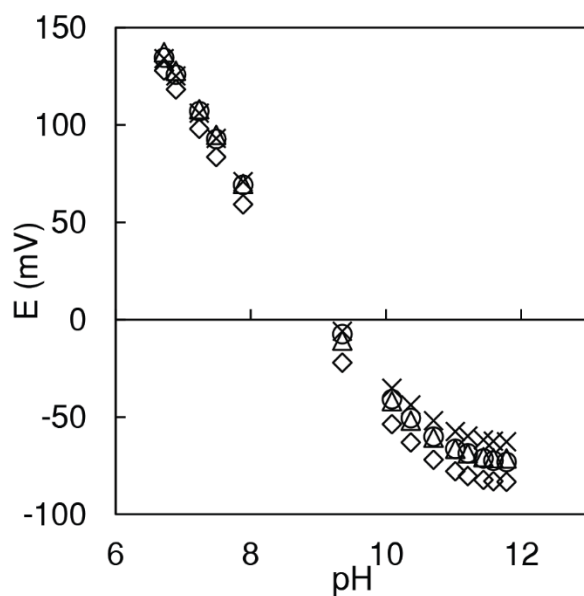


Figure S8. Measured potentials, E , of solid-contact H^+ -selective electrodes as a function of solution pH. The initial solution was 1.0 mM phosphate buffer with 100 mM LiCl (pH = 7.1). The pH was raised stepwise with aliquots of 1.0 M LiOH. The pH shown on the x-axis was measured using a pH glass electrode. Black symbols represent E values of individual electrodes. E was measured relative to a free-flowing double-junction reference electrode. All E values are corrected for liquid junction potentials at the free-flowing double junction.

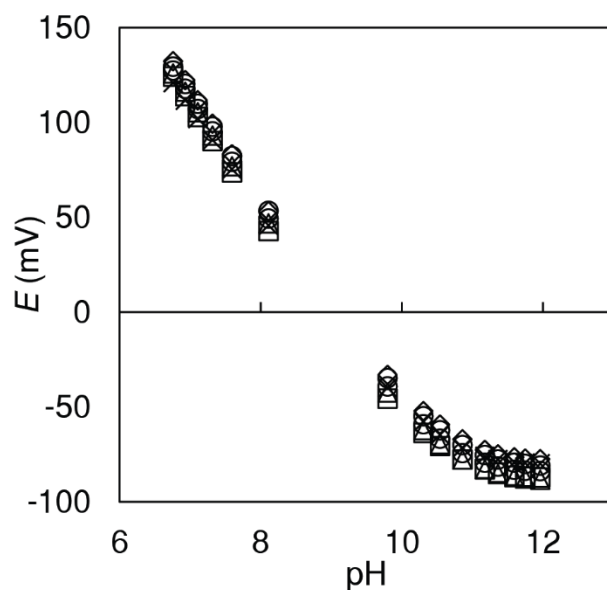


Figure S9. Measured potentials, E , of solid-contact H^+ -selective electrodes as a function of solution pH. The initial solution was 1.0 mM phosphate buffer with 100 mM NaCl (pH = 7.1). The pH was then raised stepwise with aliquots of 1 M NaOH solution. The pH shown on the x-axis was measured using a pH glass electrode. Black symbols represent E of individual electrodes. E was measured relative to a free-flowing double-junction reference electrode. All E values are corrected for liquid junction potentials at the free-flowing double junction.

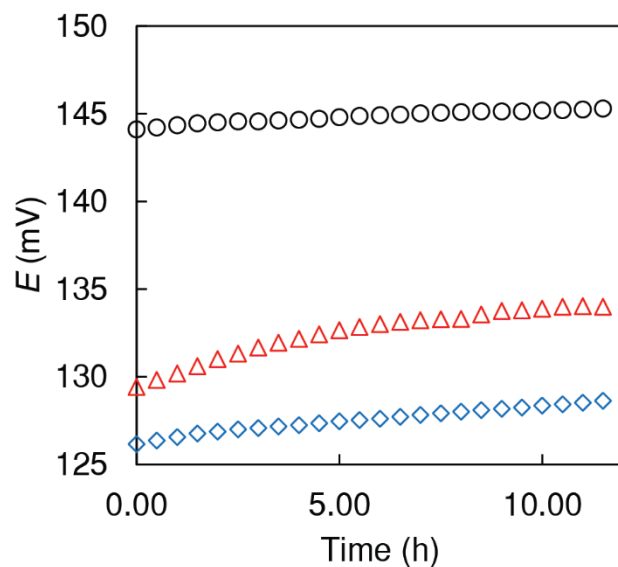


Figure S10. Potentials, E , of solid-contact H^+ -selective electrodes over time in a 10.0 mM phosphate buffer solution (pH = 7.1). Empty black circles, blue diamonds, and red triangles are H^+ -selective electrodes with functionalized PET, **5**.

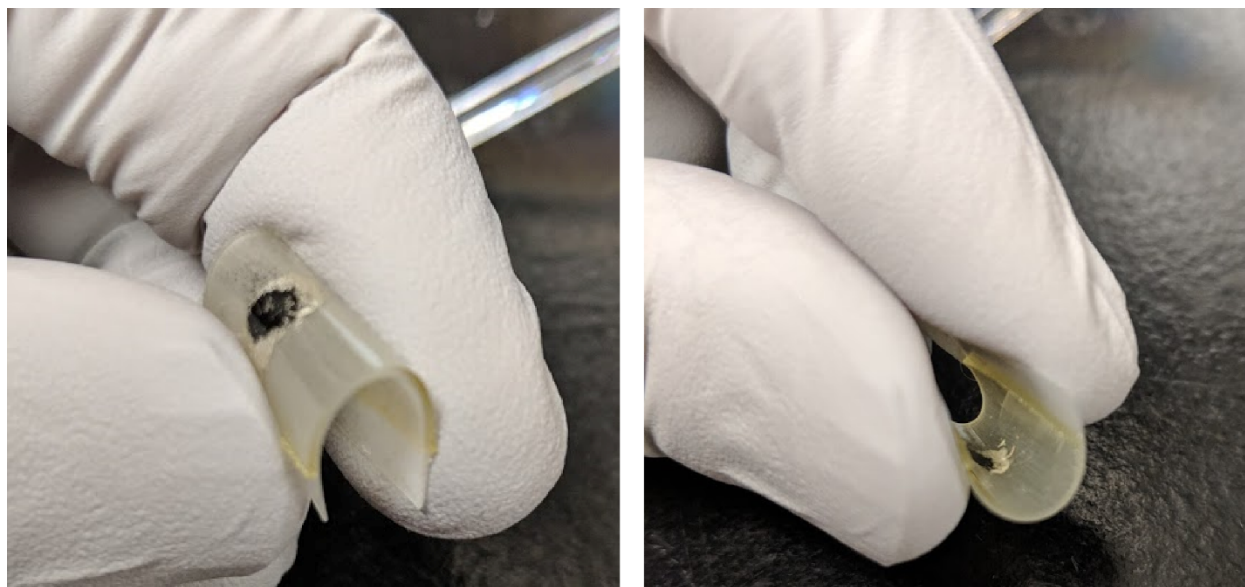


Figure S11. Images showing bending of solid-contact H^+ -selective electrodes. Bending was repeated approximately 100 times over 5 minutes with each electrode.

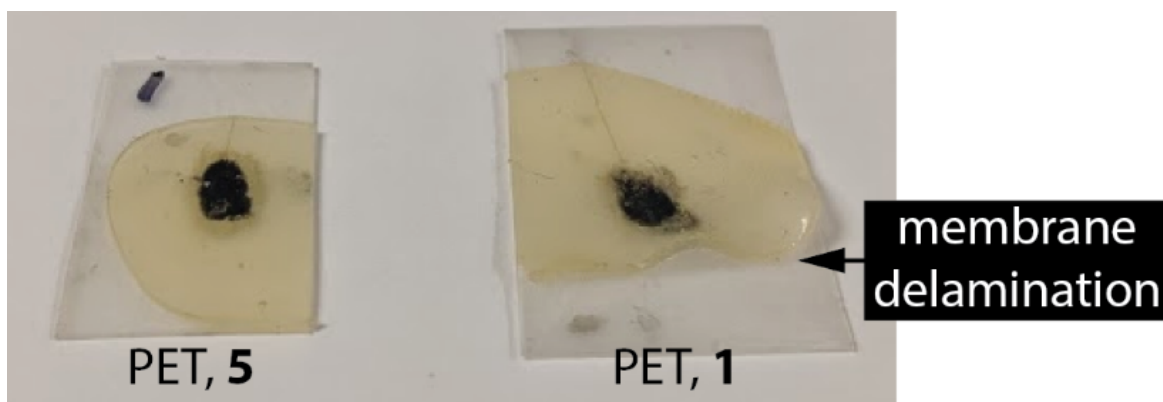


Figure S12. Images taken after repetitive bending of H^+ -selective electrodes after submersion in H_2O for three days. Numbers in the Figure correspond to PET functionalization of Figure 3. Black arrow points to delamination of the H^+ -selective membranes from non-functionalized PET, 1.

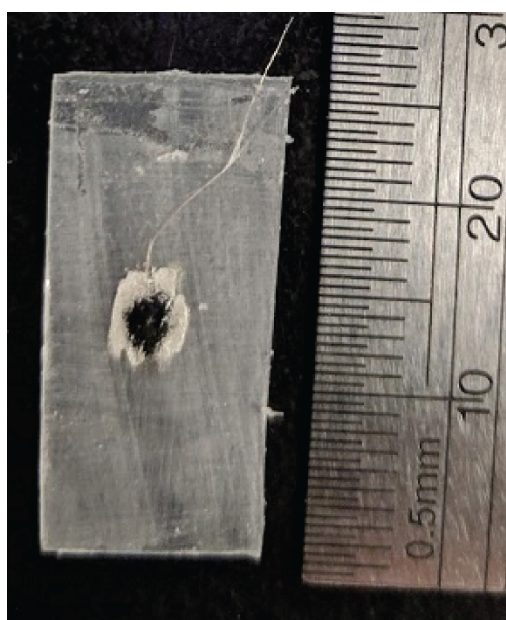


Figure S13. Image of a PET construct with a solid-contact K^+ -selective electrode.

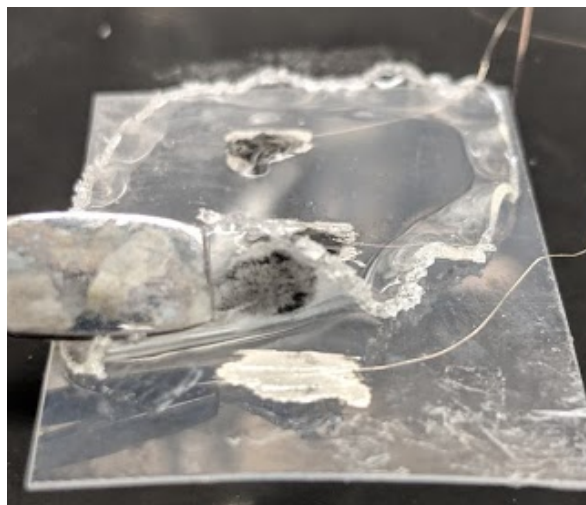


Figure S14. Image of a K^+ -selective electrode on non-functionalized PET, **1**. The membrane delaminated from the PET during removal of the device from quartz glass plates after polymerization.

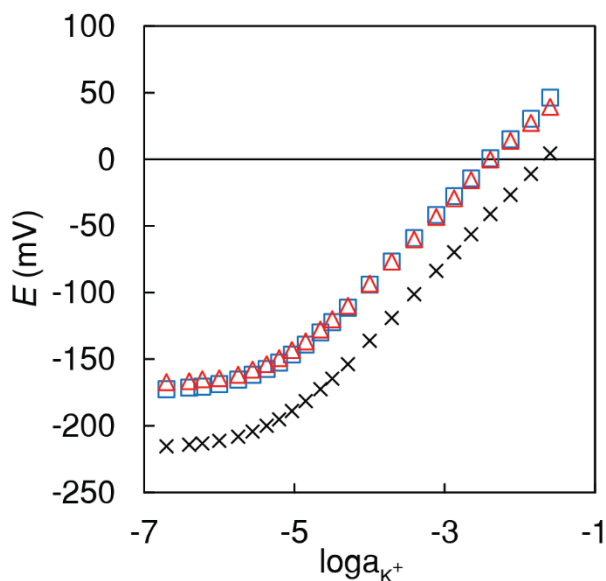


Figure S15. Potentials, E , of solid-contact K^+ -selective electrodes as a function of K^+ activity. The three symbols represent value of three individual but identically prepared solid contact electrodes. E was measured relative to a free-flowing double-junction reference electrode with 1.00 M lithium acetate bridge electrolyte. All E values are corrected for liquid junction potentials at the free-flowing double junction.

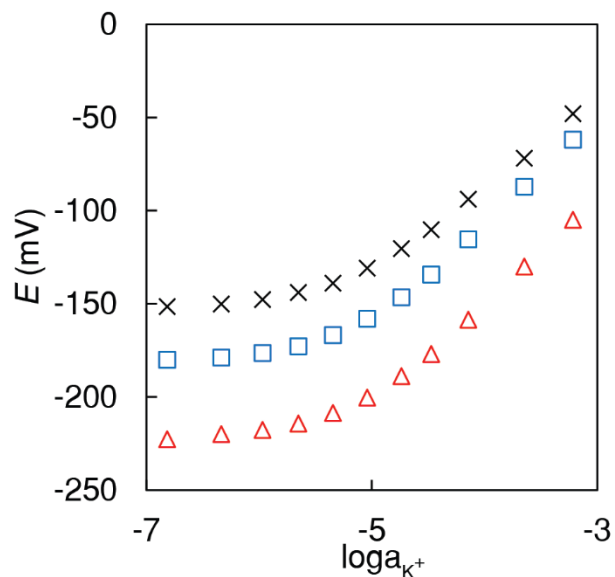


Figure S16. Measured potentials, E , of solid-contact K^+ -selective electrodes as a function of the K^+ activity in a 100 mM LiCl background. The three symbols represent values of three individual but identically prepared solid-contact electrodes. E was measured relative to a free-flowing double-junction reference electrode with 1.00 M lithium acetate bridge electrolyte. All E values are corrected for liquid junction potentials at the free-flowing double junction.

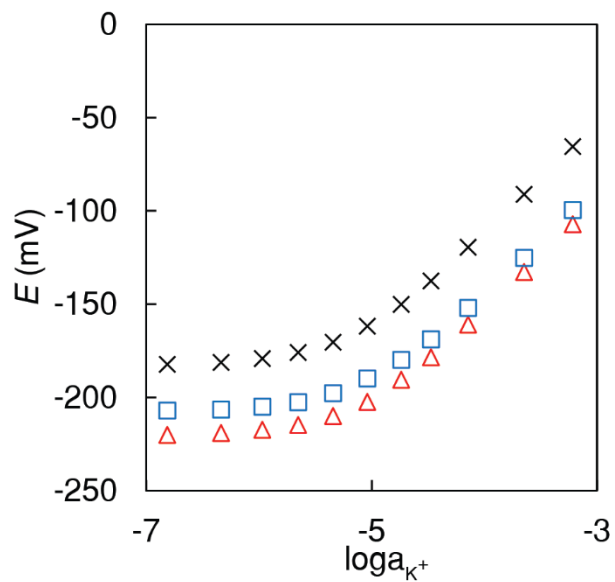


Figure S17. Measured potentials, E , of solid-contact K^+ -selective electrodes as a function of the K^+ activity in a 100 mM NaCl background. The three symbols represent values of three individual but identically prepared solid-contact electrodes. E was measured relative to a free-flowing double-junction reference electrode with 1.00 M lithium acetate bridge electrolyte. All E values are corrected for liquid junction potentials at the free-flowing double junction.

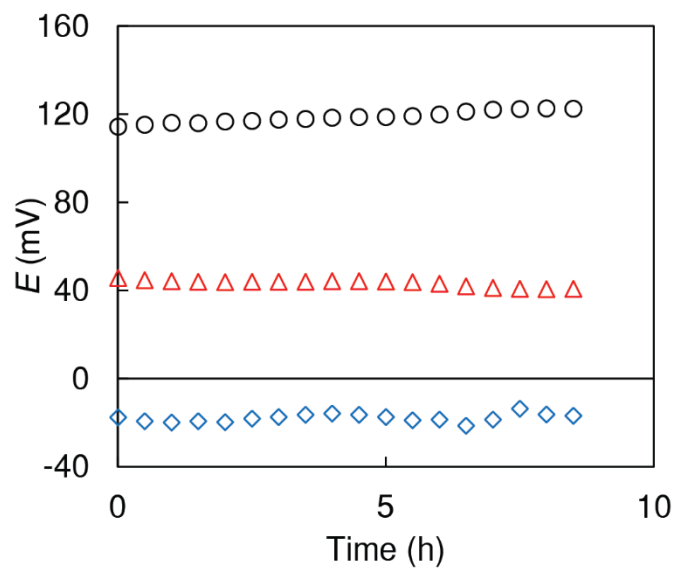


Figure S18. Potentials, E , of solid-contact K^+ -selective electrodes over time in a 10.0 mM KCl solution. Empty black circles, blue diamonds, and red triangles are H^+ -selective electrodes with functionalized PET, **5**.

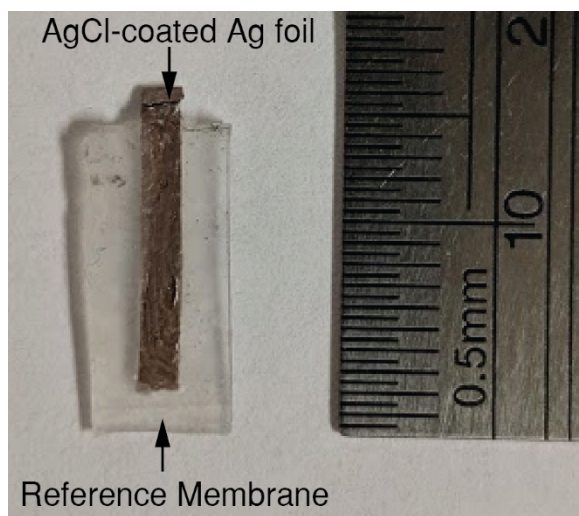


Figure S19. Image of a solid-contact reference electrode.



Figure S20. Image of a bent solid-contact reference electrode.

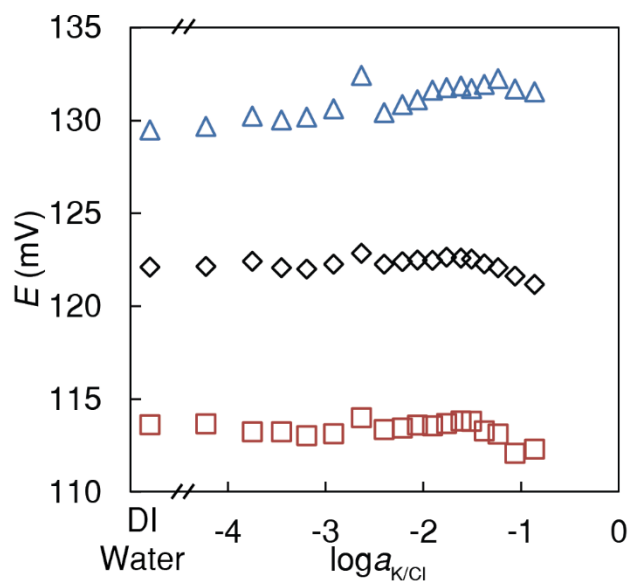


Figure S21. Potentials of solid-contact reference electrodes as a function of the K^+/Cl^- activity in KCl solutions. E was measured relative to a free-flowing double-junction reference electrode. All E values are corrected for liquid junction potentials at the free-flowing double junction. Blue triangles, red squares, and black diamonds represent data for three individual electrodes.

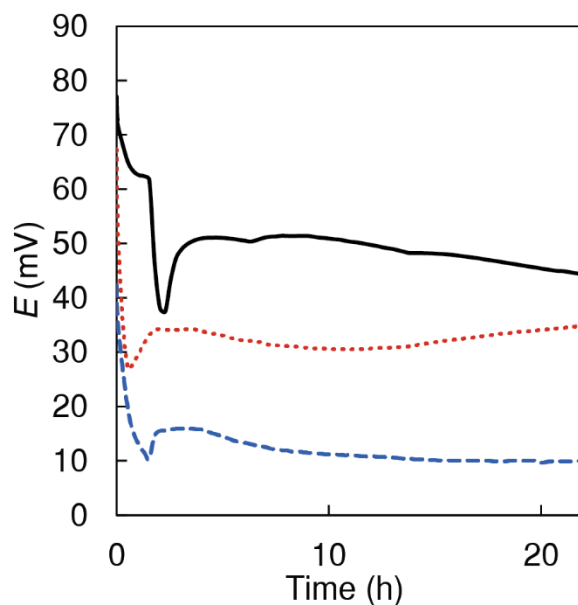


Figure S22. Measured potentials, E , of solid-contact reference electrodes with ionic-liquid-doped reference membranes over time in an aqueous solution saturated with 1-octyl-3-methylimidazolium bis-(trifluoromethyl sulfonyl)imide. Solid black, dotted red, and dashed blue lines represent data for three individual electrodes.

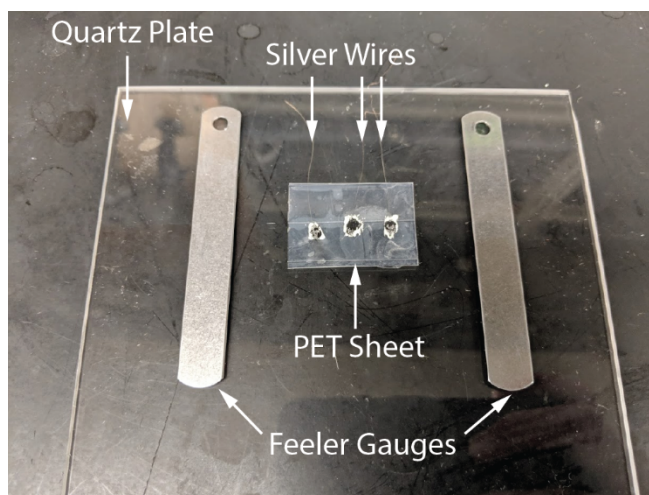


Figure S23. Device fabrication: PET sheet (center) with three Ag wires, CIM carbon (black), and sensing membrane, attached to a quartz glass plate with double-sided adhesive (not visible). See Figure S24 for more details.

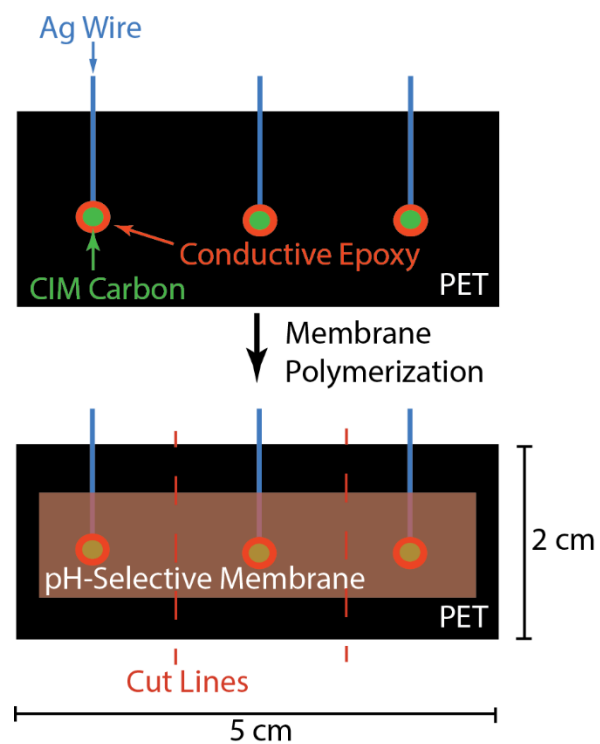


Figure S24. Schematic of PET construct with three solid-contact H^+ -selective electrodes (prior to cutting into three separate reference electrodes).

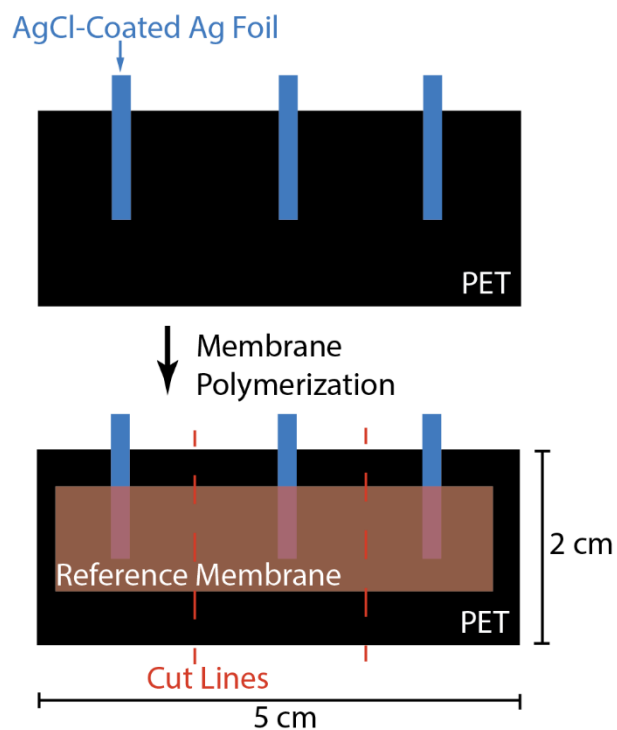


Figure S25. Schematic of PET construct with three solid-contact reference electrodes (prior to cutting into three separate reference electrodes).

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