*Supporting Information*

# Hydrogels Doped With Redox Buffers as Transducers for Ion-Selective Electrodes

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## Supplementary Experimental Details

Poly(vinyl alcohol), $M_w$ ~195,000 g/mol, was purchased from Fluka (Buchs, Switzerland). *N,N*-Dimethylformamide and dimethylsulfoxide were purchased from Sigma-Aldrich (St. Louis, MO). Potassium ferricyanide, potassium ferrocyanide, and KCl were purchased from Fisher (Waltham, MA). Gold disk electrodes were purchased from CH Instruments (Austin, TX). Deionized water (18 MΩ cm) was obtained using a MilliQ Plus purification system (Millipore Sigma, Burlington, MA).

Gold disk electrodes were polished over slurries of alumina powder, first with 0.3 and then 0.05 µm particles, on polishing pads. Electrodes were then cleaned with hot piranha solution (3:1 sulfuric acid to 30% hydrogen peroxide) for one minute, sonicated in water and ethanol, and then dried with nitrogen. *Caution: piranha solution is a strong oxidizing reagent, is highly corrosive, and should be handled with care.*

Electrodes were conditioned in potassium chloride solution overnight before calibration. Drift experiments were measured in 100 mM KCl solution. Potentiometric measurements were conducted on a 16 channel Lawson potentiometer with EMF Suite 1.03 software. Potentials were measured against a free-flowing double-junction reference electrode (DX200, Mettler Toledo, Switzerland) with a 3.0 M KCl saturated AgCl inner solution and 1.0 M LiOAc outer solution. Activity coefficients for the primary ion were calculated using a 2-parameter Debye–Hückel equation[1] and liquid junction potentials were calculated using the Henderson equation.[2]

**Change in $E^0$ with ratio of ferrocyanide to ferricyanide for electrodes with PVA hydrogels and hydrophilic ion-exchange membranes**

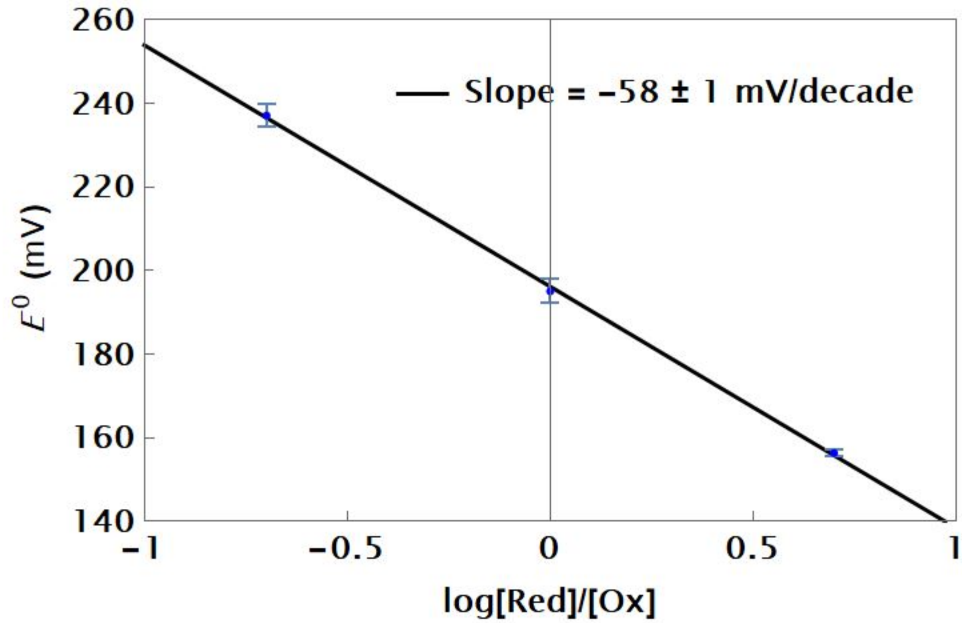


**Figure S1**: Dependence of $E^0$ on ratio of ferrocyanide to ferricyanide for electrodes with hydrophilic cation exchange membranes and inner filling solutions comprising PVA and varying concentrations of ferrocyanide/ferricyanide redox buffer (total concentration 20 mM). The $E^0$ values in this figure are corrected for the change in potassium concentration in the gel that accompanies the change in the ratio of ferrocyanide to ferricyanide.

**Change in $E^0$ with ratio of ferrocyanide to ferricyanide for electrodes with PVA hydrogels and plasticized PVC membranes**

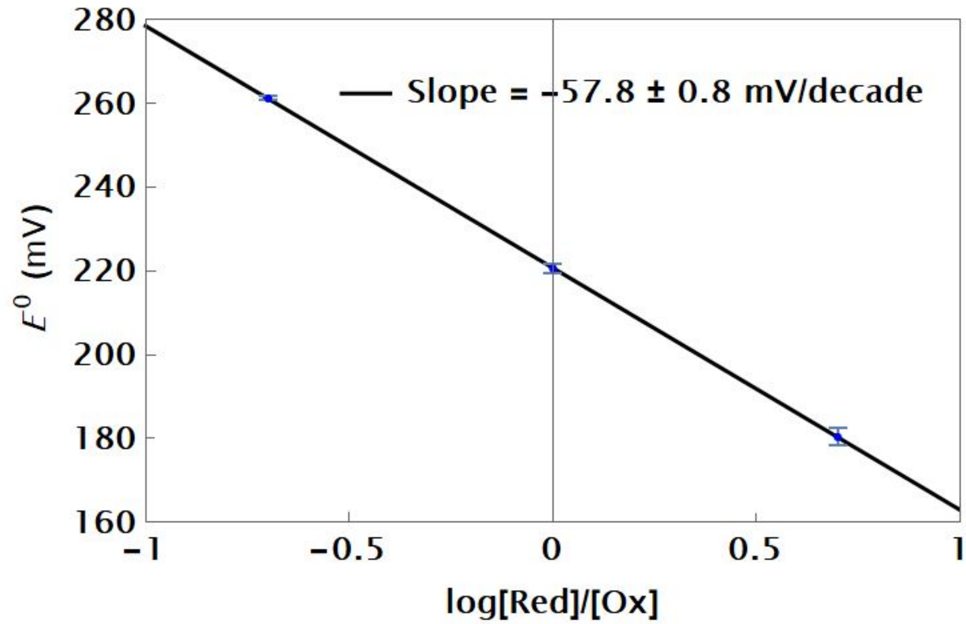


**Figure S2**: Dependence of $E^0$ on ratio of ferrocyanide to ferricyanide for electrodes with plasticized PVC membranes and inner filling solutions comprising PVA and varying concentrations of ferrocyanide/ferricyanide redox buffer (total concentration 20 mM). The $E^0$ values in this figure are corrected for the change in potassium concentration in the gel that accompanies the change in the ratio of ferrocyanide to ferricyanide.

**Long-term drift of electrodes with redox buffer loaded PVA hydrogels**

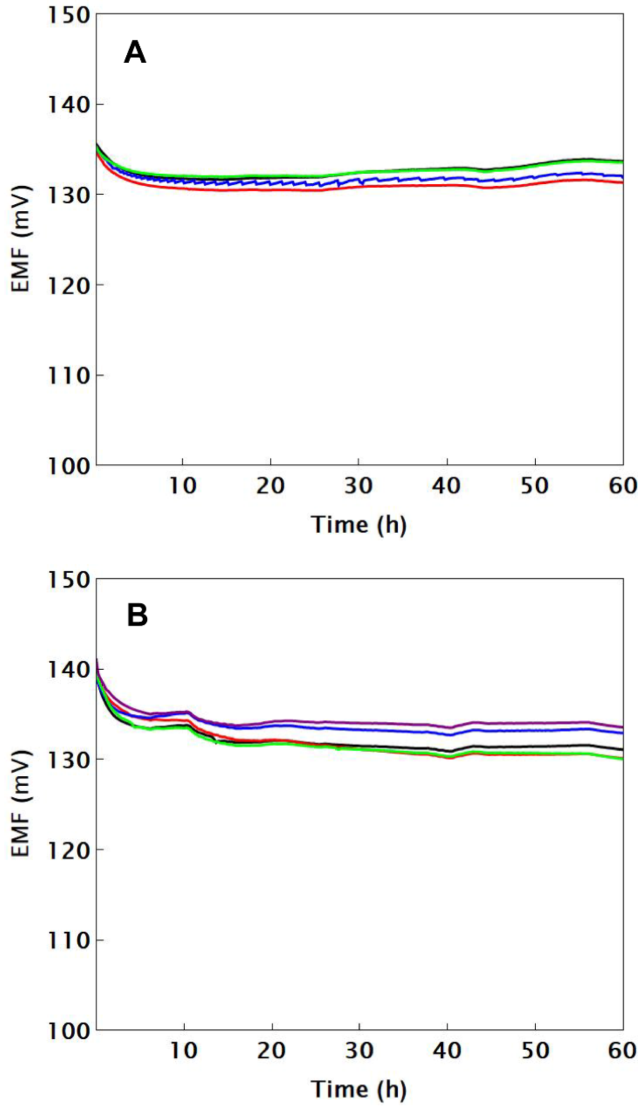


**Figure S3:** Potential versus time data over the first 60 h after exposure to 100 mM KCl solution for (A) plasticized PVC membranes and (B) hydrophilic ion-exchange membranes, backed by a PVA hydrogel containing redox buffer (10 mM potassium ferricyanide, 10 mM ferrocyanide). All electrodes in part (A) were measured simultaneously and all electrodes in part (B) were measured simultaneously. In each case, the drift is rather small, with a drift between 15 and 60 h after exposure to 100 mM KCl of 40 ± 13 μV/h for plasticized PVC membranes and –20 ± 16 μV/h for hydrophilic membranes.

**Table S1:** Average potential value and standard deviation at 10, 30, and 60 h after exposure to 100 mM potassium chloride solution for both PVC and hydrophilic membrane electrodes with inner filling solutions comprising a PVA hydrogel and redox buffer (10 mM potassium ferricyanide, 10 mM potassium ferrocyanide). The data in this table corresponds to that in Figure S3.

| Time After Exposure to Solution | Average Potential (mV ± Standard Deviation) |
|---|---|
| PVC Membranes (N=4) | |
| 10 h | 131.5 ± 0.6 |
| 30 h | 131.9 ± 0.8 |
| 60 h | 132.8 ± 1.2 |
| Hydrophilic Membranes (N=5) | |
| 10 h | 134.4 ± 0.8 |
| 30 h | 132.2 ± 1.3 |
| 60 h | 131.5 ± 1.6 |

Table S1 shows the average value of the potential at 10, 30, and 60 h after exposure to solution for both the PVC and hydrophilic membrane electrodes. Although the average value of the potential stays essentially constant for both sets, the electrodes with PVC membranes have a smaller standard deviation than those with hydrophilic membranes at each time after exposure to solution. However, this difference in standard deviation between the two sets of electrodes is very small, indicating that the differences between the two systems is less obvious when performing experiments where the sample concentration does not change rapidly. For both types of membranes, the standard deviation increases as time goes on.

**Drift of electrodes with redox buffer loaded PVA hydrogels in high and low osmotic pressure solutions**

**Table S2:** Average drifts over various time periods after exposure to KCl solutions for electrodes (N=3) with either plasticized PVC or hydrophilic membranes, and PVA gels containing 10 mM $K_4[Fe(CN)_6]$ and 10 mM $K_3[Fe(CN)_6]$. From 0 to 22.2 h (20 h for the hydrophilic membranes), the sample was 160 mM KCl, after which it was switched to 0.1 mM KCl. Shown in the right-most column are drifts as predicted based on assumptions described in the main text.

| Concentration of KCl in Sample (mM) | Time Period (h) | Average Drift (µV/h ± Standard Deviation) | Expected Drift (µV/h) |
|---|---|---|---|
| | *PVC Membranes* | | |
| 160 | 0-10 | -500 ± 200 | |
| 160 | 10-22 | 20 ± 20 | -0.7 |
| 0.1 | 25-30 | -1000 ± 400 | |
| 0.1 | 30-46 | 234 ± 8 | 0.3 |
| | *Hydrophilic Membranes* | | |
| 160 | 0-10 | 280 ± 80 | |
| 160 | 10-20 | 7 ± 100 | -100 |
| 0.1 | 21-25 | -1200 ± 400 | |
| 0.1 | 25-46 | 400 ± 200 | 50 |

**References**


1. Meier, P. C., 2-parameter Debye-Hückel approximation for the evaluation of mean activity-coefficients of 109 electrolytes. *Anal. Chim. Acta* **1982,** *136*, 363-368.
2. Morf, W. E., *The principles of ion-selective electrodes and of membrane transport*. Elsevier, New York, 1981.