ISE ARRAYS WITH IMPROVED DYNAMIC RESPONSE AND LIFETIME

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ABSTRACT

Poly(vinylchloride) (PVC) based ion-selective electrodes (ISEs) exhibit poor substrate adhesion and often fail due electrolytic shunts around the membrane. Silicone rubber (SR) based ISEs have improved surface adhesion, solving the shunt problem, but they have over 15x larger impedances. This increased impedance yields noisy signals and long response times. An ion-selective electrode array with on-chip CMOS buffers was implemented to negate the effects of the silicone rubber membrane's increased impedance. The array was implemented using post-CMOS thin-film fabrication techniques. Theoretical calculations for ISE response time are presented and experimentally verified. Results demonstrated that the dynamic response of on-chip buffered ISEs was 7.5x faster than conventional electrodes, even though they were 225 times smaller. The silicone rubber ISEs demonstrated a 40x increase in lifetime versus PVC membranes, functioning properly for more than 120days.

INTRODUCTION

Poly(vinylchloride) (PVC) is a commonly used membrane in ion-selective electrodes (ISEs) due to its superb electrochemical properties. PVC, however, has poor mechanical adhesion to the silicon substrates often used in micropotentiometric sensors [1]. Poor adhesion is the leading cause of failure in solid-state potentiometric sensors [2]. Membrane matrices having better mechanical properties have been previously investigated. Of these, silicone rubber (SR) has shown exceptional adhesive strength to silicon nitride substrates [3-5].

Compared to PVC, silicone rubber membranes have larger source impedances. Conventional ion-selective electrodes can utilize silicone rubber membranes because the ISEs have large surface areas, and impedance is inversely proportional to area [6]. Solid-state ISE arrays, however, use small geometries which results in ISEs having large impedances, slow responses, and poor detection limits [5]. Membrane impedance may be reduced by engineering the membrane composition. Adding lipophilic salts and various plasticizers can reduce impedance, but they also reduce adhesion [4-5].

In this work, the impedance, response, and lifetime of several silicone rubber membranes were investigated. A solid-state ISE array with on-chip CMOS buffers was developed to enable the use of silicone rubber micropotentiometric sensors. The array was fabricated using a commercial CMOS process and the electrodes and membranes were post-processed on top of the electronics. The membranes were characterized on three electrodes including: conventional liquid junction, passive solid-state, and the CMOS-inter-

Figure 1. Unity-gain buffer.

Table I. Measured unity-gain buffer characteristics.

Specification	Conditions	Value
Supply		+/- 1.5 V
Power	$R_{load} = 1M\Omega$	0.9 mW
Open-loop gain	Simulated	100 dB
Closed-loop gain	$R_{load} = 1M\Omega$	-0.98 V/V
3dB Bandwidth	$C_{load} = 13$ pF	2.1 MHz
Input Impedance	Freq = 0 Hz	> 20 G Ω
Output Impedance		< 100 Ω
Input Common Mode Range		2.6 V
Output Swing	$R_{load} = 1M\Omega$	2.6 V
Slew Rate	$C_{load} = 13$ pF	20 mV/ μ s
Settle Time (1 V step)	$C_{load} = 13$ pF	3.5 μ s
Area		0.023 mm ²

grated solid-state electrodes. A model of the ISE response was developed and experimentally verified. Lifetime of the various devices was also examined.

EXPERIMENT

Arrays of CMOS op-amps, configured as unity-gain buffers, were fabricated in an AMI Semiconductor (Pocatello, ID) 0.5 μ m, 3V, CMOS process. The folded-cascode op-amps incorporated rail-to-rail input and output stages. Figure 1 shows the schematic of the buffers. Table I lists the measured performance of the unity-gain buffer.

Each die was designed to have six ion-selective electrodes with a 400 μ m diameter membrane and a 200 μ m diameter Ag/AgCl electrode. The electrode arrays were fabricated on top of the active die using CMOS-compatible, thin-film processing techniques. Fig-

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Figure 2. Cross-section of an active ISE.

Figure 2 shows a cross-section of the completed devices. After delivery from the foundry, the CMOS devices were patterned for interconnect deposition and subjected to a short reactive-ion etch (RIE) to improve step coverage and patterning. A layer of Ti/TiN (40/80nm) was sputter-deposited to prevent interdiffusion between the aluminum and platinum layers. A layer of Ti/Pt (10/1000nm) was then evaporated onto the die and patterned using liftoff. A passivation layer of 400°C PECVD silicon nitride (800nm) was then deposited. Contact openings through the nitride were etched using RIE. Ti/Ag (20/650nm) was then sputter deposited and patterned using liftoff. Thin wells (12µm high) were patterned in SU-8. The SU-8 was cured at 150°C and became a permanent feature on the die. Next, the arrays were diced and bonded. The wirebonds were covered with a two step polymer coating of a silicone elastomer (MED-4211, NuSil Silicon Technology, Santa Barbara, CA) and silicone rubber (RTV3140, Dow Chemical, Midland, MI). Finally, the Ag electrodes were chloridized by submersion in 1M FeCl₃. Passive electrode arrays of identical size were similarly fabricated.

Three different silicon rubber (RTV3140) potassium-selective membranes (labeled K1-K3), and a PVC potassium-selective membrane (K4) were made according to Table II. The common additive potassium tetrakis[3,5-bis(p-chlorophenyl)borate (KTP-CIPB) and plasticizer dioctylsebacate (DOS) were incorporated into the membranes to study their effects on altering the membrane impedance and performance. The membranes were dissolved in tetrahydrofuran (THF) and dispensed into the SU-8 rings. The rings ensure a repeatable membrane thickness (≈12µm thick). The solvent was allowed to evaporate over several days, leaving behind the selective polymer membrane. Microphotographs of completed devices are shown in Figure 3.

RESULTS AND DISCUSSION

The impedance of the membranes on the different electrode types was recorded using electron impedance spectroscopy (EIS) in a solution of 50mM Tris-H₂SO₄, pH 7.4 plus 0.1M KCl. The results of the EIS experiments were averaged over four different devices

Table II. Membrane compositions.

Components	K1	K2	K3	K4
Matrix	RTV3140 198 mg	RTV3140 198 mg	RTV3140 198 mg	PVC 66 mg
Additive: KTPCIPB	0.6 mg			
Plasticizer: DOS		13.3 mg		133 mg
Ionophore: valinomycin	2.0 mg	2.0 mg	2.0 mg	2.0 mg

Figure 3. (a) Scanning electron micrograph of four ISEs cast into the SU-8 containment rings. (b) Microphotograph of an active ISE showing the buffer op-amp and selective membrane.

Table III. Measured membrane impedances in MΩ

Electrode Type	Area (mm ²)	K1	K2	K3	K4
Conventional	28.3	555	127	601	
Solid-State (passive)	0.13	8766	4600	7967	307

and are shown in Table III. The impedance of the active devices could not be measured because of the on-chip buffer, but their impedance should match that of the passive devices. The passive electrodes had impedances well into the gigaohm range even with the various additives. Comparatively, the average impedance of the PVC-based membrane was 307MΩ. These results demonstrate that the silicone rubber membranes were nearly 15x higher resistance.

The selectivity of the membranes was characterized using the matched potential method [7], and the results are shown in Table IV. The selectivity coefficient is a measure of the ratio of primary to interfering ion activity that results in an identical potential change of the sensor. The results indicate that the potassium-selective silicone rubber membranes are over four orders of magnitude more selective towards potassium than the most of other ions examined. The selectivity of the membranes is affected by the addition of the lipophilic salt. The results show that the selectivity is compromised the most in the lowest impedance silicone rubber membrane, K2.

The dynamic response of an ISE can be simulated using a two-time-constant model. The solution/membrane system has an intrinsic time constant, τ_1 [8]. The corresponding dynamic potential change of the membrane is given by

$$\Delta V_{mem}(t) = \frac{RT}{zF} \ln\left(\frac{a_f}{a_i}\right) \left[1 - \exp\left(-\frac{t}{\tau_1}\right) \right] \quad (1)$$

where t is time, R is the gas constant, T is temperature, z is the charge number of the ion, F is Faraday's constant, a_f is the final activity of the ion, and a_i is the initial activity of the ion. A second time-constant, τ_2 , is formed by the membrane impedance in series with the input capacitance of the measuring circuit, C_{load} , as shown in Figure 4. Assuming an instantaneous change in activity, the change in output voltage can be derived from Figure 4 such that

$$\Delta V_{out}(t) = \frac{RT}{zF} \ln\left(\frac{a_f}{a_i}\right) \left[1 + \frac{\tau_2 \exp\left(-\frac{t}{\tau_2}\right)}{\tau_1 - \tau_2} - \frac{\tau_1 \exp\left(-\frac{t}{\tau_1}\right)}{\tau_1 - \tau_2} \right] \quad (2)$$

Note that the effective impedance of the reference electrode is negligible compared to the resistance of the membrane. A commercial

Table IV. Measured selectivity coefficients.

Selectivity log ($K_{k,j}$)	Na^+	Ca^{2+}	Mg^{2+}	NH_4^+
K1 Membrane	< -5.0	< -5.0	-4.2	-2.0
K2 Membrane	-4.8	-4.6	-3.9	-1.9
K3 Membrane	< -5.0	< -5.0	-4.1	-2.0

Figure 4. Simple model for ISE dynamic response.

15-channel pH meter (Kosentech, South Korea), with a measured input capacitance of 1nF, was used for recording. The active devices' input capacitance was approximately 100fF. Table V lists the corresponding time constants. Since the active devices minimize τ_2 , τ_1 was empirically fit using the active devices' response. Figure 5 shows both the theoretical and experimentally measured dynamic responses to a decade change in concentration of K^+ . The experiments were conducted in a solution of 50mM Tris- H_2SO_4 , pH 7.4. Voltage offsets of the responses were eliminated mathematically before plotting. The figure clearly demonstrates the response time dependence on the membrane impedance and load capacitance. The active ISEs responded, on average, nearly 200x faster than passive ion-selective electrodes. The CMOS-buffered ISEs, which are 225x smaller than the conventional electrodes, were 7.5x faster than the conventional electrodes.

Figure 6 shows the measured calibration curves for the potassium-selective electrodes in a solution of 50mM Tris- H_2SO_4 , pH 7.4. At room temperature, the theoretically calculated slope for potassium-selective electrodes is 59mV/dec. The percent error of the measured slope versus this ideal slope was 5% and 19% for the active and passive devices, respectively. The standard deviation of the slope was 0.7mV/dec for the active ISEs while the standard deviation of the slope was 3.0mV/dec for the passive sensors.

Figure 7 plots the slope of the calibration curve versus soaking time. The PVC membrane failed after 3days in 50mM Tris- H_2SO_4 , pH 7.4, while the passive silicone rubber membrane survived nearly 50days before unexpectedly failing. All six of the passive ISEs failed on the same day indicating some catastrophic failure on the die. This failure is most likely unrelated to failures in

Table V. Measured time constants in ms.

Electrode Type	K1		K2		K3	
	τ_1	τ_2	τ_1	τ_2	τ_1	τ_2
Conventional	0.9	560	0.5	130	0.8	600
Solid-State (passive)	0.9	8800	0.5	4600	0.8	8000
Solid-State (active)	0.9	0.9	0.5	0.5	0.8	0.8

Figure 5. Theoretical and measured dynamic response for the K2 and K3 membranes on the three electrode types.

the ion-selective electrodes themselves. The active ISEs with silicone rubber membranes functioned properly for more than 120days.

CONCLUSION

The measured characteristics of the ion-selective electrodes are summarized in Table VI. The impedance of the silicone rubber membranes was shown to be 15x more resistive than PVC membranes. Incorporation of additives such as lipophilic salts into the membrane were unsuccessful at lowering the impedance below 1G Ω . CMOS-integrated ISE arrays were fabricated using thin-film post-processing techniques to enable the use of the high-resistance

Figure 6. Measure calibration curves for the ISEs.

Table VI. Summary of measured ISE characteristics.

Membrane	Electrode Type	Impedance (M Ω)	Slope (mV/dec)	Response Time 95% (s)	Detection Limit (μ M)	Lifetime (days)
K1	conventional	555	56.0	5	14	>120
	passive	8766	44.1	234	17	46
	active		56.5	1	9.4	>120
K2	conventional	127	56.0	12	17	>120
	passive	4600	49.8	130	12	46
	active		55.9	1	10	>120
K3	conventional	601	56.5	22	15	>120
	passive	7967	48.6	250	15	46
	active		55.0	3	9.9	>120

Figure 7. Measured lifetime of SR and PVC membranes.

silicone rubber membranes in micropotentiometric sensors. Results indicated that the buffered ISEs had a 200x faster response than passive potentiometric sensors. The active devices were even faster than conventional electrodes while occupying 225x smaller area. The active ISEs improved the slope and linearity of the response versus the passive sensors. The active, SR-based ISEs survived for more than 120days with a response within 5% of ideal and a detection limit of 10 μ M. Response times, detection limits, and lifetimes for the economically fabricated active sensors were far superior to those of conventional and passive microelectrodes.

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