Evaluation of a New Solid-State Reference Electrode Junction Material for Ion-Selective Electrodes

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ABSTRACT

The performance and properties of a new low-resistance material, Refex, suitable for use in reference electrode junctions is described. The material is a solid polyvinyl acetate that contains a very large loading of KCl (1:1 w/w KCl/PVA). Despite relatively large active surface areas in the designs studied (stand-alone reference and combination pH), leakage rates of KCl are remarkably low. pH measurements in ultrapure water and comparative measurements in common buffer solutions against standard reference electrodes confirm the stability of the potential developed across the junction to be very stable. Impedance studies verify the importance of the KCl doping for realization of the low resistance and attractive electrochemical properties of the material.

KEY WORDS: Reference electrode, Refex, Impedance, Junction potentials, Potentiometry.

INTRODUCTION

An often-neglected consideration when choosing an ion-selective electrode (ISE) system is that of a suitable reference electrode. Indeed, recent extensive reviews cite only 12 articles devoted to reference electrode considerations in potentiometric analyses [1,2] for the period 1988–1992. Conventional calomel and Ag/AgCl electrodes with free flow (capillary) or ceramic junctions are suitable for general applications, but for certain important applications such as measurement of pH in low ionic strength water or electrochemical measurements at high temperatures or pressures, the characteristics of these electrodes may not be suitable.

The fundamental consideration for a reference electrode is that it provides a stable junction potential. The maintenance of this potential is probably the factor that causes most difficulty in potentiometric measurements. In potentiometry, one monitors the cell potential (E_{cell}), which includes a contribution from the reference electrode junction potential (E_{jn}), the reference electrode half-cell potential (E_{ref}), and the ISE potential (E_{ISE}).

On transferring between solutions, the change in cell potential (ΔE_{cell}) is given by

potential in solution 1: $E_{cell(1)}$

$$= E_{ISE(1)} - E_{ref(1)} + E_{jn(1)} \quad (1)$$

potential in solution 2: $E_{cell(2)}$

$$= E_{ISE(2)} - E_{ref(2)} + E_{jn(2)} \quad (2)$$

change in cell potential: $\Delta E_{cell} = E_{cell(2)} - E_{cell(2)} \quad (3)$

Hence, the conditions

$$E_{jn(1)} = E_{jn(2)} \text{ and } E_{ref(1)} = E_{ref(2)}$$

must hold if the overall change in cell potential is to be determined solely by the ISE and, thus, enable deductions regarding the concentration or activity of the primary ion in unknown solutions to be made via the Nernst equation. The reference half-cell potential is usually unaffected by transferring from solution to solution, as it is not in direct contact with the sample solutions. However, maintenance of stable junction potentials can be a real problem in many applications and is unfortunately often overlooked as a major source of error in potentiometric measurements.

The role of the junction is to provide an electronically conducting pathway between the ISE and the reference half-cell via ion transfer from the salt bridge solution into the sample, but which does not allow bulk mixing of the bridge electrolyte and the sample solution. Commercial electrodes incorporate a porous ceramic frit, fiber wick, microcapillary, or ground sleeve to enable the salt bridge ions to diffuse slowly into the sample. In all of these junction designs, prevention of bulk mixing of salt bridge and sample ions is achieved through the use of very small areas of contact between the two so-

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lutions. For high-precision pH work, a renewable liquid junction, as in a free-diffusion junction (microcapillary), is recommended [3]. However, this type of junction is obviously unsuitable for measurements at high pressure (such as in chemical or bioreactors) as the sample would be forced into the reference electrode body and hence cause shifts in the reference half-cell potential. In addition, frits may experience residual memory effects from buffer solutions, which could give rise to errors [4]. For pure water applications, it has been recommended that the porosity of the junction be increased by reducing the length of the ceramic frit to decrease junction potentials [5]. In many situations, the reference electrode junction potential can become unstable, e.g., due to clogging or poisoning (in hostile industrial environments), dilution of the salt bridge (in pure waters), or precipitation of protein (in clinical samples) [6]. Obviously, when a very restricted diffusion path is used, as in almost all commercially available reference electrode junction designs, the susceptibility to clogging is very high, with consequent adverse affects on the stability of the liquid junction potential and the accuracy/precision of the electrochemical measurements. The solution to these problems lies in the development of junction materials with the following characteristics:

> low electrical resistance;
>
> low leakage rate of ions into sample;
>
> no permeability of ions from sample to internal electrode reference element (e.g., Ag/AgCl wire);
>
> capability of using large-area junctions;
>
> resistance to pressure and/or temperature effects; and
>
> resistance to contamination from troublesome samples (e.g., in clinical, environmental, or food analysis).

From these considerations, what clearly is needed is a solid-state material capable of forming a stable junction potential in a wide variety of media with minimal contamination of either the junction or the sample during measurements.

In routine applications, KCl is normally used as the bridge electrolyte as the almost-equitransferrent ions minimize the magnitude of the junction potential. However, a number of other electrolytes such as lithium acetate or lithium sulfate can be substituted for KCl in situations where leakage of these ions into the sample is undesirable [7]. For this reason, KCl was used as the dopant salt in the Refex polymer and in the internal reference half-cell in all the studies subsequently described.

EXPERIMENTAL

Design and Fabrication of Reference Electrodes with Refex Junctions

Samples of the KCl/vinyl ester mixture were provided by Amagruss Electrodes Ltd., Castlebar, Co. Mayo, Ireland, and used as received. The samples obtained were
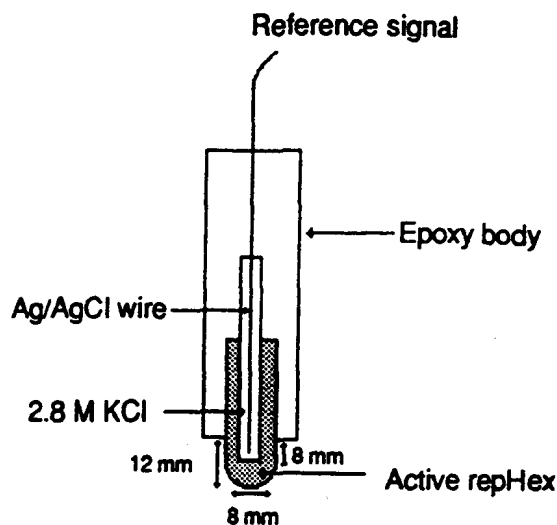

FIGURE 1. Schematic diagram of RepHex type A stand-alone reference electrode.

50% m/m KCl/vinylester resin in composition. Prior to polymerization, the material is not particularly viscous and can be preformed in molds or spun into tubes. During the curing process (24 hours typically after addition of an initiator, MEKP [2-butanone peroxide]), it becomes hard and can be machined or turned successfully even though it is quite brittle. Samples of the material and/ or complete electrodes can be obtained directly from Amagruss Electrodes Ltd., Unit 10, Castlebar Industrial Estate, Co. Mayo, Ireland.

In this research, two types of junction design were investigated.

> Type A (stand-alone reference electrode). In this design, the KCl/vinyl ester mixture was poured into a glass form with an external diameter of 10 mm. An Ag/AgCl half-cell, with a filling solution of 2.8 M KCl, was then placed in this mixture and positioned as close to the edge of the form as possible. The Refex material was allowed to cure overnight, removed from the glass form, and fixed into an epoxy body so that 12 mm of the Refex protruded (Figure 1).

> Type B (combination pH electrode). An internal pH combination electrode with four frit-restricted liquid junctions (Figure 2A) was positioned inside an epoxy body with four windows by means of an "O" ring so that the four ceramic frits were opposite the windows in the body. These windows and the pH membrane were then protected with parafilm. The body of the electrode was then inverted and filled with the Refex material. This was allowed to cure overnight to give a double-junction (DJ) design, with a Refex junction in direct contact with each of the ceramic frits (Figure 2B). A second O ring was used to seal the Refex and to help keep the glass electrode in position.
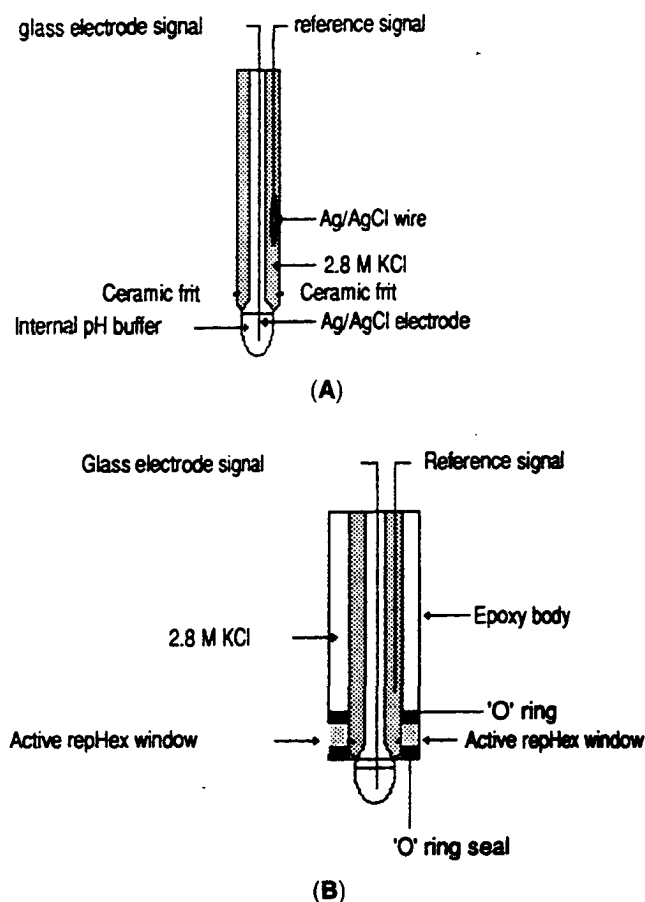
(A)

(B)

FIGURE 2. Schematic of RepHex type B combination pH electrode showing **(A)** the internal pH combination electrode and **(B)** the outer RepHex body with active RepHex windows in contact with the ceramic plugs from the combination electrode salt bridge.

Precision and Stability Studies

Measurements were made on a deionized water that had a base conductivity of 1.5 to 2.0 μS. pH and mV measurements were made using a Jenway 3040 ion-analyzer and a commercially available pH glass electrode (Amagruss Ltd.). Commercially available Orion DJ Ag/AgCl, saturated calomel electrodes (SCE) and Ag/AgCl disk electrodes were used versus the Refex electrode for general stability studies. All materials were of reagent grade and used as received.

pH measurements in deionized water were taken in both static and slowly stirred solutions. Buffers conforming to DIN 19267 standard at pH 7.00 and 4.01 (Merck, Darmstadt, Germany) were used to calibrate the electrodes. pH measurements in pure water were taken at 30 second intervals up to 10 minutes. This procedure was repeated 10 times, and the average and standard deviation were calculated in each case. All measurements were made at 25 ± 0.1°C.

Linearity of response over the pH range 2.0 to 11.9 was examined using a stand-alone (type A) Refex elec-

trode and a conventional pH glass combination electrode (innovative Sensors Inc.). Phosphate buffer solutions were made up as described by Christian [8] in 0.1 M NaCl. All potentiometric measurements were made at 25 ± 0.1°C.

Electrolyte Leakage Studies

Leakage of electrolyte from the reference electrode junctions was assessed by

1. Measuring the increase in conductivity of water in which the electrodes were immersed using a Jenway 3070 conductivity meter. This was monitored according to the following procedure:
   The Refex electrodes were soaked in deionized water for 2 to 3 days to remove any KCl that may have built up on the outer surface; 100 mL of the pure water was placed in a polycarbonate bottle, and the conductivity of the water was measured prior to insertion of the electrodes. The bottle was then sealed with parafilm to prevent any particulate contamination. During measurements, the electrode was removed, the water was stirred for 1 minute, the conductivity probe was placed in the water, and the conductivity was measured after 1 minute. The electrode was then replaced in the water and resealed until the next measurement. The leakage from the electrodes was monitored over a period of 5 days.

2. Measuring the increase of concentration of potassium ions in the water in which the electrodes were immersed, using a Dionex Ion-Chromatography system (Ion-Pac CS3 column, mobile phase 25 mM HCl/0.25 mM DAP-HCl (DL-diaminopropionic monohydrochloride)), flow rate 1.5 mL/min, and 100 mM TBAOH (Tetrabutylammonium hydroxide) as the regenerant.

The same procedure as described earlier was used except that samples (200 μL) of the deionized water were removed for analysis by the ion-chromatograph at regular intervals over a period of 4 days.

Electrochemical Impedance Measurements

In this study, the impedance spectrum of an electrode with an undoped (inactive) Refex type A junction (i.e., does not contain any KCl) was compared to that of an identical electrode with the normal doped (active) Refex junction. The measurements were performed in 0.1 M aqueous NaBF$_4$ at room temperature using a HP-9816 computer-controlled S-5720B frequency response analyzer and a NF-2000 potentiostat/galvanostat with a GPIB interface (NF Circuit Design Block Co. Ltd., Japan). The typical amplitude of the sinusoidal voltage signal used was 100 and 200 mV.

RESULTS AND DISCUSSION

pH Measurements in Deionized Water

The results obtained with the Refex A and conventional ceramic frit DJ reference electrodes are shown in Figure 3 for measurements of pH in deionized water (the same
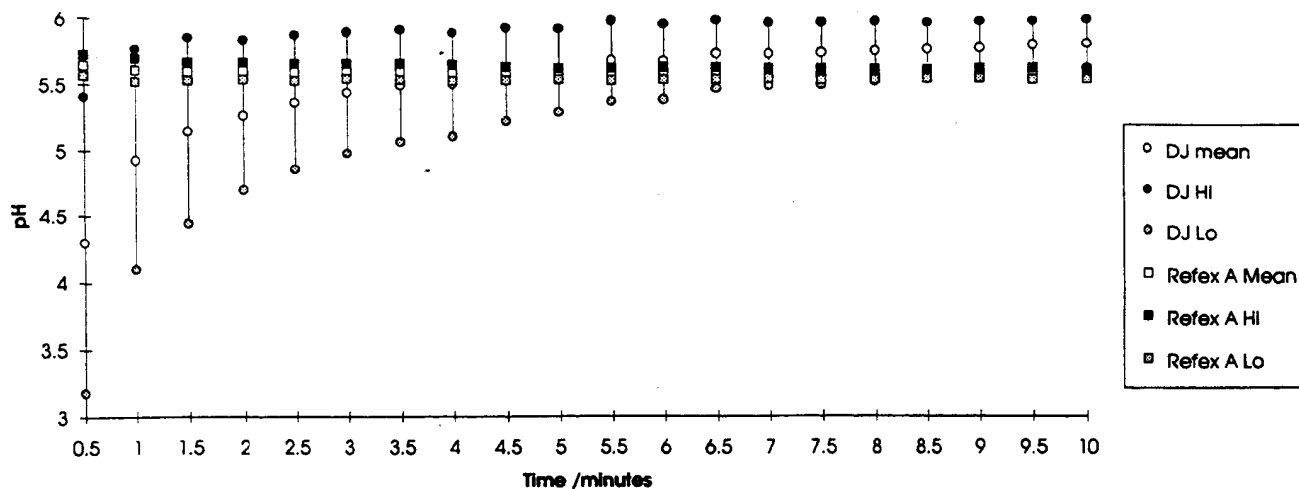
FIGURE 3. Comparison of RepHex type B and conventional combination pH electrode for pH determinations in stirred deionized water showing the mean and standard deviation for measurements taken at 30 s intervals up to 10 min (n = 10).

glass electrode was used for both sets of measurements), which was stirred slowly during the experiment. From these results, it is clear that the Refex junction gave much more precise results over the entire 10 minute measurement period compared to the ceramic frit electrode. Even after 10 minutes, the standard deviation of results obtained with the ceramic frit junction was approximately 0.18 pH. Furthermore, the mean value did not stabilize for around 6 minutes. In contrast, the cell incorporating a Refex junction gave almost instantaneously stable results with much better precision (standard deviation 0.07 pH after 0.5 minutes, decreasing to 0.035 pH after 10 minutes). Note that the range of pH values obtained in both studies (pH 5.5 to 6.0) is typical for deionized water in equilibrium with atmospheric CO_2 [9].

Stability in Buffer Solutions

The results obtained from seven studies are summarized in Table 1 and in Figure 4. Table 1 illustrates the performance of the Refex type A electrode in three commonly used buffer systems as the background concentration of NaCl is gradually raised. In these experiments, either a calomel (SCE) or Ag/AgCl reference electrode was used to check the stability of the Refex signal. In every case, the overall cell potential showed no change to within the limits of accuracy of the meter (0.1 mV), except for the boric acid buffer (pH 9.2) where the signal versus the SCE changed by around −0.3 mV during the addition of the NaCl. Furthermore, on raising the pH from 5 to 9.2, a change in overall cell potential of around +2.0 mV is obtained vs. SCE, and around −2.0 mV vs. Ag/AgCl reference electrode. These results clearly demonstrate that the Refex electrode can provide a very stable reference potential for pH measurements in these buffers, which is independent of variations in NaCl con-

centration up to 0.016 M. This is relatively small in comparison to the change of around 240 mV, which would be obtained theoretically with a pH glass electrode over the same range, and the error at <1.0% is entirely acceptable for these types of potentiometric measurements. This assumes the worst-case situation, i.e., that all the variation in the cell potential arises at the Refex junction. However, it is unclear at this stage whether the error is arising at the Refex junction or at the liquid junctions of the conventional electrodes (or both). It should also be noted that replicate measurements performed with an undoped Refex type A electrode gave very unstable signals in every case, which demonstrates the fundamental role played by the KCl in providing the very attractive properties of the doped Refex. Impedance measurements (see subsequent discussion) confirm that the high salt loading of the Refex material imparts the desirable properties, and in the absence of the salt, a classic electrical "blocked" interface of very high resistance is obtained.

Figure 4 shows the response obtained in an identical experiment performed with a Ag/AgCl disk indicator electrode and the same Refex type A reference electrode as aliquots of 1.0 M NaCl (50, 100, 200, 400, and 800 µL) were added to 50 mL 0.1 M pH 5.0 acetate buffer. Measurements were made at 1 and 2 minutes after the additions. The two curves are virtually superimposable, and the log [Cl] versus potential curves were very linear (S = 53.68 mV/decade Cl, r^2 = 0.9999 (after 1 minute), and S = 54.147 mV/decade Cl, r^2 = 1.0000 (after 2 minutes)). Clearly, these results demonstrate that the Refex electrode is capable of providing a very stable junction for pH and ion-selective measurements and is unaffected by variations in background electrolytes such as NaCl.

TABLE 1 Stability Tests for Refex Type A Stand-Alone Reference Electrode in Various pH Buffers during Addition of Aliquots of 1.0 M NaCl to 50 mL of Buffer. All Readings are in mV, Taken 1 Min and 2 Min after Immersion of the Electrodes in the Sample or Addition of the NaCl.

Volume NaCl Added (μL)	Final ([NaCl]/M)	pH 5[a]		pH 5[b]		pH 7.1[a]		pH 9.2[a]		pH 9.2[b]	
		1 (min)	2 (min)	1 (min)	2 (min)	1 (min)	2 (min)	1 (min)	2 (min)	1 (min)	2 (min)
0	0.000	2.3	2.3	−45.9	−45.9	2.3	2.4	−43.9	−43.8	0.3	N/A
50	0.001	2.3	2.3	−45.8	−45.9	2.4	2.4	−43.8	−43.9	0.3	N/A
100	0.002	2.4	2.4	−45.8	−45.8	2.3	2.4	−43.8	−43.7	0.3	N/A
200	0.004	2.4	2.4	−45.8	−45.8	2.4	2.5	−43.8	−43.7	0.2	N/A
400	0.008	2.4	2.4	−45.8	−45.8	2.4	2.4	−43.7	−43.6	0.2	N/A
800	0.016	2.4	2.4	−45.8	−45.8	2.4	2.4	−43.7	−43.6	0.2	N/A

[a] mV versus Orion DJ Ag/AgCl reference electrode.
[b] mV versus saturated calomel electrode.
N/A: results not available; pH 5.0: 0.1 M acetic acid/sodium acetate buffer; pH 7.1: 0.1 M Phosphate buffer; pH 9.2: 0.1 M Boric Acid buffer.
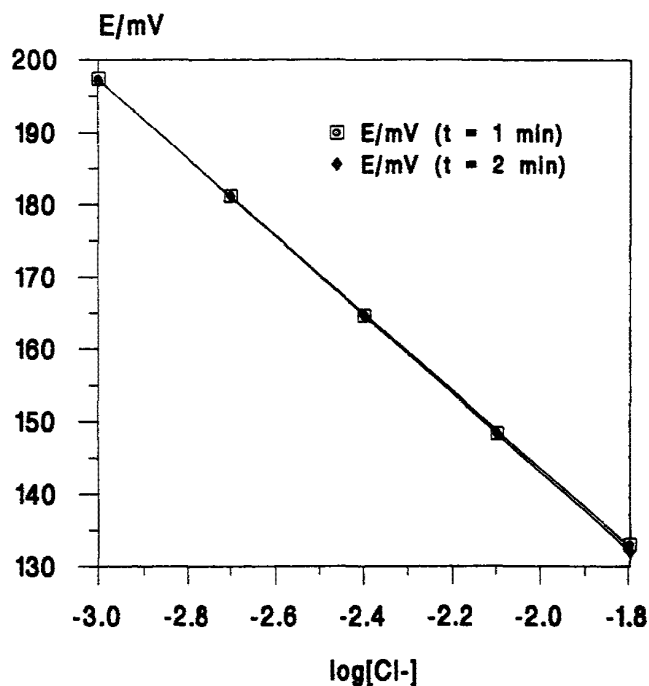

FIGURE 4. Response of Ag/AgCl disk electrode versus Refex reference electrode in 50 mL 0.1 M pH 5 acetate buffer to additions of 50, 100, 200, 400, and 800 μL of 1.0 M NaCl. Measurements taken 1 and 2 min after each addition; S = 53.68 mV/decade Cl^-, r^2 = 0.9999 (after 1 min), and S = 54.147 mV/decade Cl^-, r^2 = 1.0000 (after 2 min).

pH Linearity Studies

In order to further test the Refex electrode, its performance was examined over the pH range 2.0 to 11.9 in a constant background of 0.1 M NaCl. Three replicate sets of potential versus pH readings were taken for a

conventional pH glass combination electrode with an integral Ag/AgCl reference half-cell (fiber wick junction) over the pH range investigated, and the mean and standard deviation of the results were calculated. The reference half-cell was then disconnected from the meter and the experiment repeated using a stand-alone Refex (type A) electrode as reference for the same glass electrode. The results (Table 2 and Figure 5) show almost identical behavior over the entire range. Clearly, there is a curvature at pH values <4.0, which is independent of the reference electrode used, and is reproduced over the six experimental runs. The standard deviations obtained are smaller in almost every case (except pH 11.9) with the Refex reference electrode, while with both reference half-cells, the precision appears to deteriorate toward high pH values. The mean slope obtained (pH 6 to pH 11.9) is 58.89 mV/pH with the Refex electrode compared to 58.54 mV/pH with the combination cell. Once again, these data confirm that Refex-based reference electrodes can be used with confidence for pH measurements in place of conventional reference electrodes.

Measurements without Liquid Junction

The previous experiment was repeated using a Ag/AgCl wire (without liquid junction) versus Refex electrode type A. Hence, the only junction is that of the Refex electrode, and as the chloride ion activity is kept constant, in theory, the Ag/AgCl wire should maintain a constant potential against which variations in the Refex electrode junction potential can be detected. The results for three replicate experiments are presented in Table 3. These results show that the Refex junction again behaves very similarly to the calomel/ceramic junction electrode. In both cases, the junction potential changes by around −5.0 mV, assuming the variation to arise solely at the junction, with similar standard deviations (most of which are substantially less than 1.0 mV). Once again, this strongly suggests that the Refex junction will behave similarly to con-

TABLE 2 Comparison of a Glass Combination Electrode Performance with that of the Same Glass-Electrode Half-Cell Versus a Refex-Type A Reference Electrode[a]

pH	Glass Electrode vs. Ag/AgCl					Glass Electrode vs. Refex				
	1	2	3	Mean	SD	1	2	3	Mean	SD
2.00	250.35	248.59	246.97	248.64	1.69	255.34	257.25	257.88	256.82	1.32
4.18	162.2	158.61	169.83	163.55	5.73	165.52	168.53	164.2	166.08	2.22
6.00	62.946	63.885	75.8	67.54	7.17	72.227	69.385	70.765	70.79	1.42
8.00	-40.505	-43.166	-45.552	-43.07	2.52	-44.129	-37.134	-38.951	-40.07	3.63
10.00	-164.97	-177.72	-141.75	-161.48	18.24	-185.64	-180.55	-184.37	-183.52	2.65
11.90	-285.28	-279.36	-268.82	-277.82	8.34	-270.57	-281.61	-277.74	-276.64	5.60

[a]All figures are in millivolts; measurements taken at 25 ± 0.1°C.
SD: standard deviation.

FIGURE 5. Response curves obtained with a combination pH electrode (◊) and a Refex type A reference electrode (□) in buffer solutions (pH 2.0 to 11.9, background 0.1 M NaCl). After obtaining the combination electrode results, the in-built Ag/AgCl reference electrode was disconnected from the pH meter and replaced with the Refex electrode.

E/mV

□ mean refex
◊ mean combination

pH
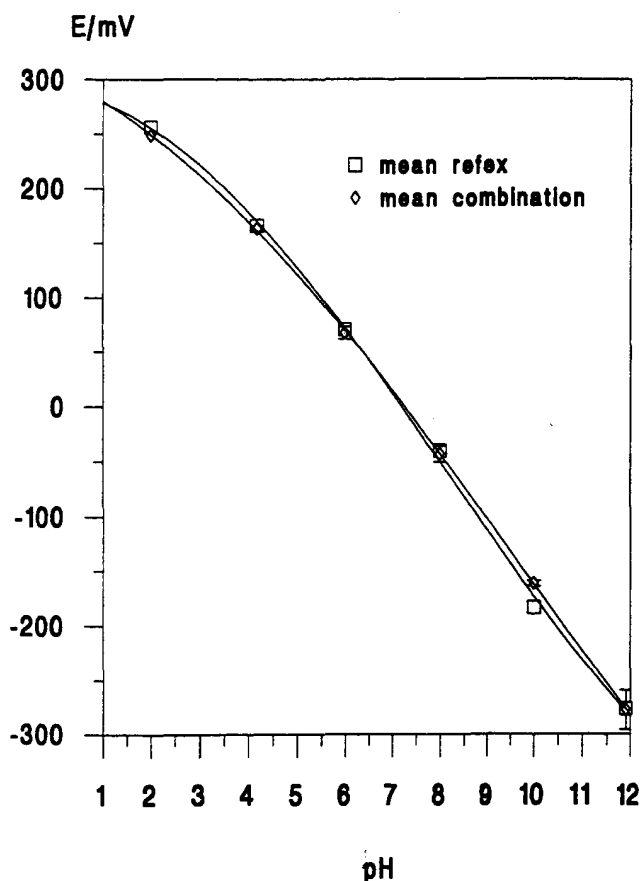
TABLE 3 Mean and Standard Deviations (n = 3) of Potentials of a Refex Type A Reference Electrode and a Calomel Reference Electrode (Ceramic Frit Junction) Measured over the pH Range 2.0 to 11.9 in a Constant Background of 0.1 M NaCl vs. Ag/AgCl Wire Electrode (without Liquid Junction)

pH	Refex		Calomel	
	Mean mV	SD	Mean mV	SD
2.00	-89.359	0.4036	-21.394	0.9745
4.18	-90.689	0.1105	-23.328	0.2239
6.00	-90.673	0.3569	-23.030	1.3408
8.00	-92.326	0.5140	-25.403	0.4446
10.00	-93.034	0.9420	-26.431	0.3720
11.90	-95.692	0.7853	-26.106	0.7785

SD: Standard deviation.

ventional reference electrode junctions in routine pH measurements.

Leakage Studies

The results of the conductivity studies are presented in Figure 6 for five reference electrodes, two with type A active Refex junctions (Refex A1 and Refex A2), two double junction Ag/AgCl reference electrodes with ceramic frit junctions (DJ1 and DJ2), and one combined glass electrode with the Refex B type junction (Refex B). The increase in conductivity brought about by leakage of KCl from the reference electrode junction into deionized water samples was greatest with the ceramic frit electrodes. This is surprising, considering the much greater junction area (see Table 4) and heavy KCl loading of the Refex electrodes. The lower leakage rate obtained with the Refex B to Refex A electrode is predictable from the smaller junction area.

These trends were confirmed by monitoring the increase in K^+ in the storage water using ion chromatography. Figure 7 shows results obtained with Refex A, Refex B, and ceramic frit junctions (DJ). Once again, the leakage of K^+ is greatest with the ceramic frit, and the general trends in the curves obtained are very similar to those obtained with the conductivity measurements,
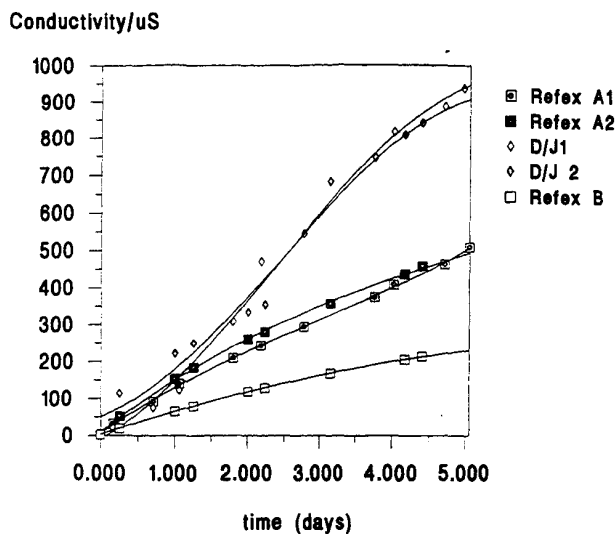
Conductivity/uS

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1000
 900                                          ⊡ Refex A1
 800                                          ■ Refex A2
 700                                          ◊ D/J1
 600                                          ◊ D/J 2
 500                                          □ Refex B
 400
 300
 200
 100
   0
     0.000  1.000  2.000  3.000  4.000  5.000
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time (days)

FIGURE 6. Changes in conductivity in deionized water solutions in contact with RepHex type A electrodes (RepHex A1 and RepHex A2), RepHex type B (RepHex B) and two ceramic frit double junction electrodes (DJ1 and DJ2) as a function of time.

confirming that it is leakage of KCl from the Refex junction that is causing the observed increase in conductivity. When the leakage rates are normalized for junction area, the rate of K^+ leakage with Refex A and Refex B junctions are almost the same at around 6.0×10^{-8} mol/h/mm^2. In contrast, leakage through the frit junction is almost three orders of magnitude higher at 2.67×10^{-5} mol/h/mm^2 (see Table 4), which is typical for junctions of this type [10,11]. Clearly, the release of KCl into sample solutions is extremely slow compared to the ceramic frit junction when normalized in terms of junction area. This is a very surprising result, in view of the heavy loading of KCl in the Refex resin and the relatively large active area over which leakage may occur. This situation offers many potential advantages:

As KCl is released from the outer boundary of the Refex junction, there remains a huge reservoir of KCl within the resin matrix. Hence, release will occur in a consistent, controlled manner over ex-

tended periods of time leading to stable, reproducible junction potentials;

stability is further enhanced by the ability to use large junction areas compared to other designs based on diffusion of KCl from an internal bridge solution that is restricted by means of a narrow capillary, a ceramic frit, or a fiber wick. Hence, clogging, coating, or blockage can be expected to be much less problematic with Refex junctions;

reduction of Refex junction areas and salt loading can be expected to produce much lower leakage rates than those observed in this study, although this may reduce the junction potential stability; and

the liquid nature of the salt-loaded resin before curing offers very flexible handling during fabrication and raises the prospect of possible applications in more specialized designs, such as a reference element in solid-state sensor manufacturing (e.g., in ISFETs or hybrid devices).

Impedance Studies

The impedance spectra for the undoped (inactive) and doped (active) electrodes with Refex type A junctions are shown in Figures 8 and 9, respectively, together with equivalent circuits for each. The results (Figure 8A) show a blocked interface effect on the inactive Refex junction as demonstrated by the extremely high impedance at low frequencies, and an unblocked Faradaic impedance with the active Refex junction (Figure 9A). The almost vertical line to the right of the semicircle in Figure 8A is typical of a blocked interface, with no fixed dc resistance and no dc current.

The equivalent circuit for the inactive Refex junction is given in Figure 8B. This shows a double-layer capacitance (C_d) in series with the bulk resistance and capacitance $(R_m$ and $C_m)$, which gives rise to the very high impedance at low frequencies.

In contrast, the impedance spectrum for the active Refex junction (Figure 9A) shows two adjacent semicircles characteristic of an unblocked interface [12], reflecting two relaxation processes with time constants (τ' and τ'') given by

$$\tau' = R_m C_m = \frac{1}{\omega'} = 0.03 \text{ ms} \qquad (4)$$

and

TABLE 4 Physical Characteristics of Junctions Investigated

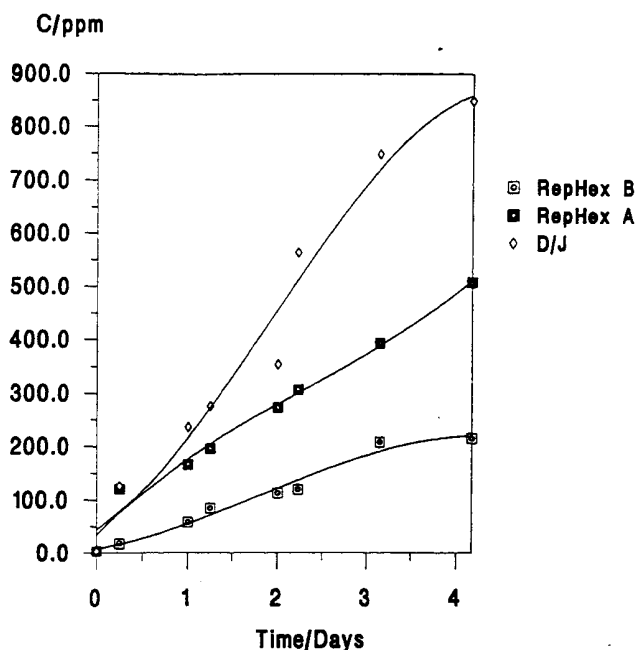| Junction Type	Dimensions (mm)	Area (mm^2)	Absolute Leakage Rate (mol K^+ hour^{-1})	Leakage Rate Normalized for Area of Contact (mol K^+ hour mm^{-2})
Refex A	Hemisphere; radius = 4.0 cylinder; height = 8.0; circumference = 25.1	301.6	1.92×10^{-5}	6.38×10^{-8}
Refex B	4 × circular windows; radius = 4.0 mm	201.1	1.18×10^{-5}	5.84×10^{-8}
Frit	Radius = 0.75 mm	1.8	4.8×10^{-5}	2.67×10^{-5}

C/ppm

FIGURE 7. Increase in potassium concentration of deionized water solutions in contact with RepHex type A, RepHex type B, and ceramic frit double junction electrodes measured by ion chromatography.

$$\tau'' = R_{ct}C_{dl} = \frac{1}{\omega''} = 0.4 \text{ ms} \qquad (5)$$

This indicates that the ion transfer at the solution/Refex interface is dictating the kinetics of the electrode response.

Note that as the frequency decreases toward dc, the impedance tends toward a fixed ohmic electrode resistance of about 9.0 kΩ, which is given by the sum of the charge transfer resistance (R_{ct}) and the bulk resistance (R_m). From the spectrum, it is evident that these resistances, as given by the radii of the two semicircles, are approximately equal and are thus approximately 4.5 kΩ each. The equivalent circuit (Figure 9B) shows an unblocked interface with a low-resistance pathway through R_{ct} and R_m at low frequencies. From these results, we can conclude that

- the excellent electronic properties of the Refex junctions are brought about by the incorporation of the KCl into the Refex polymeric matrix;

- the charge transfer mechanism occurring at the Refex junction is therefore ionic in nature;

- the doped Refex material has a very low electrical resistance at the low frequencies (essentially 0 Hz or dc) at which potentiometric measurements are made; and

- the doped Refex can be expected to have a low impedance pathway (through C_m) at high fre-

(A) Impedance Spectrum
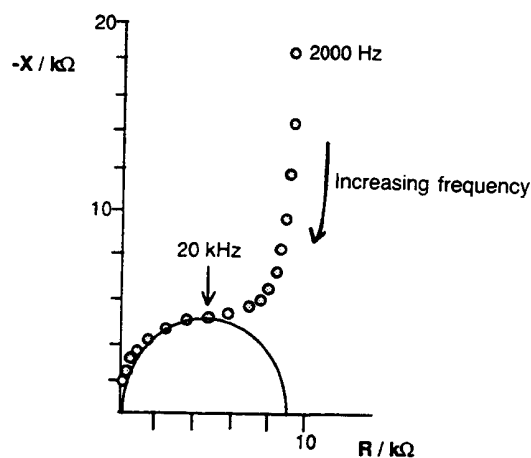
(B) Equivalent Circuit
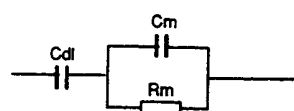
Rm = 9.2 kΩ
Cm = 1 x 10⁻⁹ F
Cdl = 4 x 10⁻⁹ F

These experiments were performed with two electrodes, one of which had a KCl doped RepHex tip (active) and the other an undoped (inactive) RepHex tip. Both had a body formed from inactive RepHex. The internal half-cell consisted of a Ag/AgCl wire in contact with 2.8 M KCl that was saturated with AgCl.

FIGURE 8. Impedance spectrum (A) and equivalent circuit (B) for inactive (undoped) RepHex type A electrode.
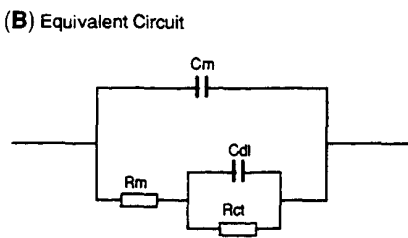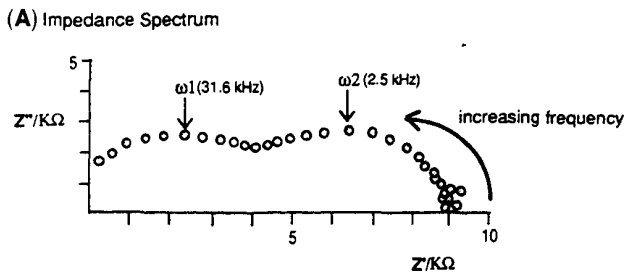
quencies. This suggests that the electrode may also be used for ac measurements.

Mechanism of Charge Transport in Refex Junctions

Figure 10 shows the charge transport processes involved at the doped Refex electrode junctions. Basically, there are five regions to consider.

Regions AQ' and AQ" are the bulk aqueous solutions on the inside (') and outside (") of the electrode. Charge transport in these regions is dominated by the diffusion of the ions present. With the internal solution, the ions are typically K^+ and Cl^-, whereas with the external solution, the charge transport will depend on the ionic composition of the samples and standards into which the electrode is placed.

Regions I' and I" are the interfaces of the Refex junction with the internal and external electrolytes, re-

(A) Impedance Spectrum

(B) Equivalent Circuit

Rm = 4.5 kΩ

$$\omega_i = \frac{1}{R_m C_m}$$

$$\omega_2 = \frac{1}{R_{cl} C_{dl}}$$

Cm = 1 x 10⁻⁹ F
Rct = 4.5 kΩ
Cdl = 1 x 10⁻⁸ F

FIGURE 9. Impedance spectrum **(A)** and equivalent circuit **(B)** for active (KCl doped) RepHex type A electrode.

FIGURE 10. Possible mechanism for charge transport processes involved at the doped Refex junctions (see text for detailed discussion).


spectively. The low impedance observed with doped (i.e., KCl containing) Refex compared to undoped Refex and the leakage studies confirm that there is efficient charge transfer occurring at both interfaces and that this involves the KCl. At present, we have no evidence to say whether the K^+ or Cl^- dominates this ion exchange process or whether each is equally involved, although the leakage studies confirm that KCl is transferred into the sample solution, albeit at a relatively slow rate.

The fifth region, bulk, is the bulk Refex material that consists mainly of the vinyl ester polymer, with a large loading of KCl (1:1 w/w KCl:Resin) and some LiCl (10:1 w/w KCl:LiCl). At present, the exact mechanism of charge transport through the bulk is not known exactly, although it is suspected to be ionic in nature for the reasons previously outlined. The very low impedance (<10 kΩ) suggests that the mechanism is relatively efficient, even though Refex is a solid, somewhat brittle material. It is clear from this research that some or all of the ions present in the Refex junction have relatively unrestricted freedom of movement, at least in the boundary regions. Given the large negative lattice enthalpies of KCl and LiCl, such freedom of movement is unlikely in a totally solid form of the salts, although lattice defects may account for some ability to hop from position to position, in a manner similar to that ascribed to the positive holes or electrons in a classical semiconductor.

Alternatively, small amounts of water may be trapped along with the salts either during the fabrication process or subsequently on standing. Hence, there is the possibility that water molecules may become bound to some ions in the resin and render them somewhat more mobile by releasing them from the lattice. These solvated ions might be able to migrate from one ionic region to another within the resin, in the direction of the potential gradient driving the process.

This low impedance is in contrast to that obtained with salt-doped Teflon. This material was investigated for solid reference junctions by Beckman Instruments some 20 years ago. Unfortunately, the salt loading could not be increased above 30% m/m as the physical characteristics of the Teflon deteriorated sharply and the electrical resistance could range up to 1.0 MΩ [13]. Another "solid" junction material is that used in Xerolyte reference electrodes (Ingold) that are commonly used in the food industry for making pH measurements. In contrast to the large contact area used in the Refex junctions studied in this research, this system makes use of a cone-shaped glass sensor tip with a small (<1.0 mm) aperture connection to the reference half-cell through a solid salt-doped gel. Presumably, this is to reduce contamination of the gel or sample due to interaction between them during measurements. Due to the hard, almost glassy nature of the Refex finish, it is possible that these electrodes would also be very suitable for pH measurements
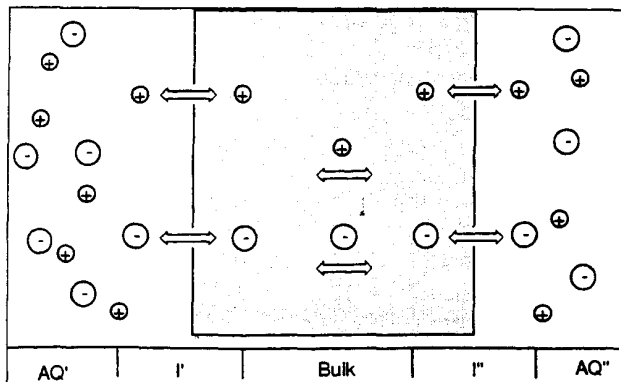
in butter, cheese, or meat that could be easily cleaned from the Refex surface, in contrast to conventional junctions that would tend to clog and become contaminated.

CONCLUSIONS

The results presented show that despite the heavy salt loading and large areas of contact of the Refex junctions investigated, leakage of KCl into sample solutions can be expected to be less than that occurring with conventional ceramic frit junctions. Careful optimization of the resin salt loading and geometry may be expected to produce junctions with lower leakage rates. pH measurements in deionized water suggest that the Refex junctions provide a junction potential that is quick to stabilize and relatively constant with time, even in very low ionic strength media. Stability also has been demonstrated over the pH range 5.0 to 9.1 in the presence of changing levels of NaCl, and overall, the performance is as good as (sometimes better than) reference electrodes based on conventional junction designs. Other users have reported excellent performance from pH-monitoring loops incorporating Refex reference electrodes in waste brine and hydrofluoric acid effluent, in contrast to previous systems that generated massive control problems [14].

Impedance measurements demonstrate that the junction resistance at low frequencies is less than 10 kΩ and that the KCl doping of the Refex resin is crucial for excellent junction properties of the material. Given the rigid (solid) nature of the material, it is quite possible that it will be less susceptible to external pressure variations than conventional junction designs based on the relatively free movement of ions across a limited area of contact. Preliminary results suggest that this is the case, and other studies with a solid contact design indicate that this material can be used successfully without the need for an internal filling solution. If these results are confirmed, then these solid-state Refex reference electrodes could have important applications in the fabrication of ISFETs and other solid-state electrochemical sensors. Work on these aspects of the material's behavior, the effect of variations of temperature and pressure, and its performance in difficult matrices is continuing and will be reported in the future.

From these experiments, it can be concluded that the Refex junctions give very stable potentials in a variety of common buffer solutions and can be used in place of conventional junction designs. The general robustness of the material coupled with the ability to use large junction areas if needed and a smooth glassy surface make it an attractive alternative to conventional junction materials, particularly for industrial applications involving troublesome media that contaminate and are difficult to remove from conventional junctions. The solid-state form should make it more resistant to external pressure fluctuations than junctions that are based on the relatively free movement of ions over small contact areas. Further research into the permeability of Refex to ions and moisture, pressure and temperature effects, and performance in a number of industrial applications is in progress.

ACKNOWLEDGMENTS

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