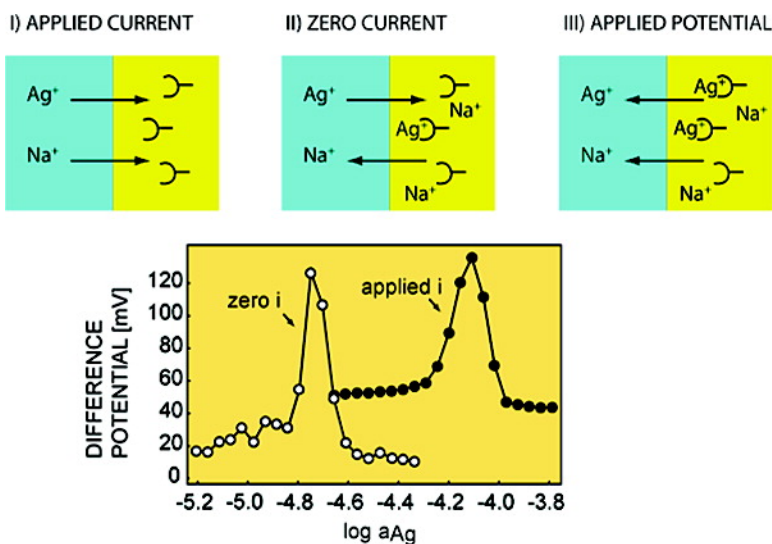


Pulstrodes: Triple Pulse Control of Potentiometric Sensors

Sergey Makarychev-Mikhailov, Alexey Shvarev, and Eric Bakker

J. Am. Chem. Soc., **2004**, 126 (34), 10548-10549 • DOI: 10.1021/ja047728q • Publication Date (Web): 05 August 2004

Downloaded from <http://pubs.acs.org> on April 1, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 8 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Pulstrodes: Triple Pulse Control of Potentiometric Sensors

Sergey Makarychev-Mikhailov, Alexey Shvarev, and Eric Bakker*

Department of Chemistry, Auburn University, Auburn, Alabama 36849

Received April 20, 2004; E-mail: eric.bakker@auburn.edu

The concept of so-called pulstrodes is introduced where a multipulse electrochemical excitation signal is imposed onto an ionophore-based ion-selective liquid membrane operating on the basis of assisted ion transfer voltammetry principles.¹ This yields a tunable potential difference signal that is independent of the reference electrode potential and gives a significantly larger sensitivity than predicted classically on the basis of the Nernst equation.

Ion-selective electrodes normally obey the Nernst equation, which predicts that a 10-fold sample activity change of a monovalent ion yields a ca. 59 mV change in the observed electromotive force. For ions of higher valency, this sensitivity is proportionally smaller. A second important limitation of ion-selective electrodes is the direct dependence of the electromotive force on the reference electrode. The required bridge electrolyte and well-defined liquid junction of such reference electrodes require high maintenance and do not lend themselves easily to miniaturization. Since very few reports on well-defined and -understood liquid junction-free reference electrode concepts have been published in the past decades,² this remains an important fundamental problem. Today, potentiometric sensors with extremely high selectivity³ and detection limits down to the low parts per trillion range are available,^{4–6} but the two challenges mentioned above remain important bottlenecks of modern ion-selective electrode research.

Earlier work has already described or utilized zero current ion fluxes with ion-selective electrode membranes by passive counterdiffusion processes. When a less preferred hydrophilic ion in the membrane spontaneously exchanges with the analyte ion in the sample, a large so-called super-Nernstian response slope is observed in a critical concentration range.^{7,8} While interesting analytical applications have been proposed on the basis of this unusual response principle,^{7–9} such spontaneous processes are difficult to control in classical zero current potentiometry because of the continuously changing diffusion layer thickness in the membrane phase.¹⁰

We introduce here a novel response principle to impose a defined concentration polarization on the sample side of the membrane while the system can still be interrogated at zero current. The measurement principle is illustrated in Figure 1 with a silver-selective membrane containing a bis-thioether functionalized *tert*-butyl calix[4]arene ionophore as a model system.¹¹ This ionophore is known to possess an excellent selectivity over alkali metals.¹² A controlled cathodic current pulse I of defined magnitude and duration is first imposed, which leads to a flux of sample cations in direction of the ion-selective membrane.¹³ At high silver concentrations, the imposed flux can be fully maintained by silver ions, but as the concentration is lowered, other sample ions (sodium) must also be extracted. The inner solution of the membrane contained a high concentration of a hydrophilic salt (10 mM NaCl) to minimize the depletion of the co-extracting anion into the inner membrane side during the cathodic pulse. As recently established,¹³ the potential during this current pulse can be monitored for direct

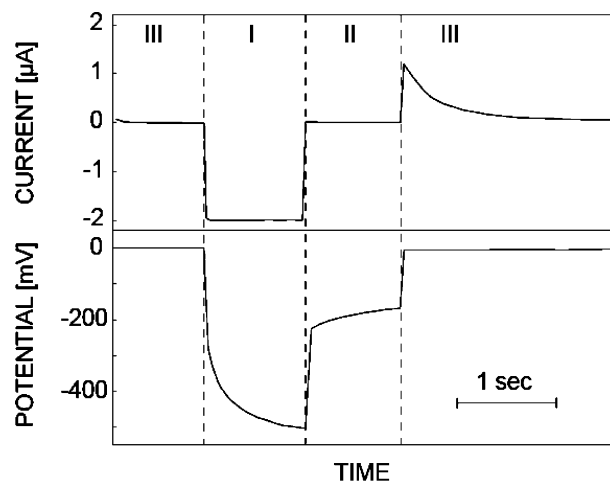


Figure 1. Time profile of the triple pulse experiment to control the ion-selective electrode. Pulse I applies a cathodic current to generate a defined ion flux in the direction of the membrane (the potential may be measured at the end of this pulse as mode I). Pulse II is a zero-current measurement pulse (mode II). Pulse III is a potential controlled baseline pulse for regeneration of the membrane. Subsequent current pulses may have different amplitudes for differential detection as shown in Figure 2.

detection purposes, and a reversible sensor for the polyion protamine was proposed on the basis of this principle.¹⁴ Here, however, the cathodic pulse I is followed by a zero current measurement pulse II. During this pulse, the previously extracted background ions are allowed to exchange with silver ions from the sample according to zero current counterdiffusion transport principles. This leads to a super-Nernstian response slope at lower concentrations than during the cathodic pulse I, without any iR drop. Note that the second mechanism is analogous to that observed in zero current potentiometry^{5,15} but that the amount of exchangeable ions is instrumentally controlled during pulse I.¹³ All extracted ions are again expelled from the membrane during a baseline potential pulse III (of 10-fold duration compared to the uptake pulse to ensure effective membrane renewal, see ref 16) before this triple pulse sequence is repeated. The magnitude of this potential pulse III, which should be close to the open circuit potential, was chosen as 0 V vs Ag/AgCl. By applying subsequent cathodic current pulses I of different magnitude, the amount of extracted ions can be varied, which leads to a reproducible shift in the super-Nernstian response region. The difference potential from two subsequent pulses may also be used as the analytical signal.

As shown in Figure 2A, the two response modes of the membrane (potentials at the end of pulse I and pulse II) can be simultaneously monitored during the same pulse sequence. In this example, current pulses I of alternating magnitude (-9 and $-10 \mu\text{A}$; current density -72 and $-80 \mu\text{A}/\text{mm}^2$) were imposed. The potential readings at the end of each current pulse I are shown in Figure 2A (mode I) as a function of the logarithmic silver activity in the sample. So-called super-Nernstian response regions are observed for the two pulses,

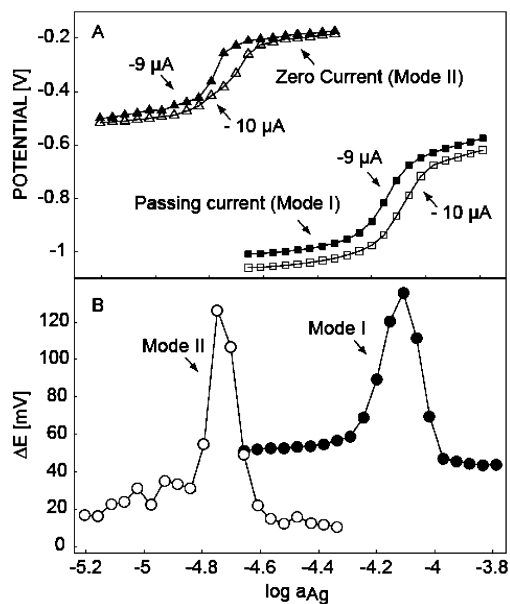


Figure 2. (A) Observed potentials for two subsequent current pulses of indicated amplitudes, measured at the end of the pulse (mode I) and during the following zero current measurement pulse (mode II). The super-Nernstian response region of interest is shifted for mode II (see text). (B) Difference potential of the data shown in (A).

separated by about 0.1 logarithmic activity units because of the amplitude difference of the applied current. Clearly, a critical range exists where the imposed flux starts to be maintained predominantly by silver ions, not only by background ions, which dominate the flux at low concentrations. In this activity range, the super-Nernstian response slope for silver ions is observed. The difference potential from the data in Figure 2A is shown in Figure 2B (mode I), and the data illustrate that a peak-shaped response with a very high sensitivity of about 60 mV per 10% activity change is observed, which corresponds to 10 times the Nernstian slope. As shown in the Supporting Information, the potential responses were reproducible.

The second measurement principle is introduced by the zero current pulse II applied just after each current pulse I. As shown in Figure 1, the initial potential change is indicative of the iR drop across the membrane, which now must be zero. At zero current, no net ion flux across the interface can occur. The potential change shown in Figure 1 is observed because of the continuous diffusion of ions away from the interface in direction of the membrane bulk. At sample concentrations below the super-Nernstian response region shown in Figure 2A (mode I), the concentration of extracted silver ions during the galvanostatic pulse is significantly smaller than that of background ions (the imposed ion flux is much larger than what can be maintained by silver flux alone). These ions readily exchange with silver ions during the zero current pulse, inducing a concentration polarization of silver at the sample side of the interface that is based on zero current counterdiffusion principles. The resulting potentials sampled at the end of the zero current pulse are also shown in Figure 2A (mode II). The super-Nernstian regions, obtained after the two current pulses of -9 and -10 μA , are now shifted to lower concentrations compared to those at mode I, and the potentials are of smaller magnitude because no iR drop is observed. Figure 2B (mode II) shows the potential difference of the data in Figure 2A. The sensitivity of the experiment is now

even larger than that observed with mode I, reaching about 100 mV for less than 0.1 logarithmic activity change. This corresponds to a nearly 20-fold sensitivity increase relative to classical zero current potentiometry, obtained here at zero current as well.

One single experimental protocol, shown in Figure 1, can be used to shift the high-sensitivity region of the electrode by orders of magnitude. By varying the duration of each of the two pulses I and II and the magnitude of the galvanostatic pulse I (-1 to -15 μA and 0.1-s to 1.0-s pulse durations), the measuring range was shifted by about 4 orders of magnitude, from less than 10^{-7} M to more than 10^{-4} M (see Supporting Information). The direct potential reading during the galvanostatic pulse (mode I) is most useful for monitoring changes at concentrations in the near millimolar range. The potential reading during the zero current pulse (mode II) is attractive for trace-level analysis or for systems where the membrane resistance is relatively large or unstable (see Supporting Information).

Note that the difference potentials shown in Figure 2B are independent of the reference electrode potential and are highly attractive for the realization of miniaturized sensor systems. Approximate potential control is still required during the baseline potential pulse III, without which the membrane could not be accurately renewed between the measurement pulses. The potential of the reference electrode or of a third measuring pulse (at a different applied current) is also needed to quantify the sign of the activity change in the differential mode.

Acknowledgment. We acknowledge NIH (EB002189 and GM071623) and ACS-PRF for financial support. S.M.-M. thanks the Danish Academy of Technical Sciences (ATV) and PBI-Dansensor A/S for a PhD fellowship (Grant EF 908) to travel to Auburn for this research.

Supporting Information Available: Tunability of calibration curves, reproducibility and selectivity data, experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Homolka, D.; Hung, L. Q.; Hofmanova, A.; Khalil, M. W.; Koryta, J.; Marecek, V.; Samec, Z.; Sen, S. K.; Vanysek, P.; Weber, J.; Brezina, M.; Janda, M.; Stibor, I. *Anal. Chem.* **1980**, *52*, 1606–1610.
- (2) Diamond, D.; McEnroe, E.; McCarrick, M.; Lewenstam, A. *Electroanalysis* **1994**, *6*, 962–971.
- (3) Bühlmann, P.; Pretsch, E.; Bakker, E. *Chem. Rev.* **1998**, *98*, 1593–1687.
- (4) Sokalski, T.; Ceresa, A.; Zwickl, T.; Pretsch, E. *J. Am. Chem. Soc.* **1997**, *119*, 11347–11348.
- (5) Ceresa, A.; Radu, A.; Peper, S.; Bakker, E.; Pretsch, E. *Anal. Chem.* **2002**, *74*, 4027–4036.
- (6) Bakker, E.; Pretsch, E. *Anal. Chem.* **2002**, *74*, 420A–426A.
- (7) Fu, B.; Bakker, E.; Yun, J. H.; Yang, V. C.; Meyerhoff, M. E. *Anal. Chem.* **1994**, *66*, 2250–2259.
- (8) Ceresa, A.; Pretsch, E.; Bakker, E. *Anal. Chem.* **2000**, *72*, 2050–2054.
- (9) Vigassy, T.; Ceresa, A.; Badertscher, M.; Morf, W. E.; de Rooij, N. F.; Pretsch, E. *Sens. Actuators B* **2001**, *76*, 477–481.
- (10) Mathison, S.; Bakker, E. *J. Pharm. Biomed. Anal.* **1999**, *19*, 163–173.
- (11) Ion-selective membranes (8 mm² exposed area) were microporous Celgard membranes (25 μm thick, 0.2 μm pore size, Celgard, Charlotte, NC) doped with 0.8 wt % silver ionophore *O,O'*-bis[2-(methylthio)ethyl]-*tert*-butylcalix[4]arene and 10 wt % lipophilic inert electrolyte tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH 500) in bis(2-ethylhexyl) sebacate (DOS).
- (12) Bakker, E. *Anal. Chem.* **1997**, *69*, 1061–1069.
- (13) Shvarev, A.; Bakker, E. *Anal. Chem.* **2003**, *75*, 4541–4550.
- (14) Shvarev, A.; Bakker, E. *J. Am. Chem. Soc.* **2003**, *125*, 11192–11193.
- (15) Morf, W. E.; Badertscher, M.; Zwickl, T.; de Rooij, N. F.; Pretsch, E. *J. Phys. Chem. B* **1999**, *103*, 11346–11356.
- (16) Jadhav, S.; Meir, A. J.; Bakker, E. *Electroanalysis* **2000**, *12*, 1251–1257; Bakker, E.; Meir, A. J. *SIAM Rev.* **2003**, *45*, 327–344.

JA047728Q