# Improving the Sensitivity of Solid-Contact Ion-Selective Electrodes by Using Coulometric Signal Transduction

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ABSTRACT: A fundamental limitation of potentiometric ion sensors is their relatively low sensitivity due to the logarithmic dependence between potential and activity. Here we address this issue by exploring a recently developed coulometric transduction method for solid-contact ion-selective electrodes (SCISEs). Spin-coated thin-layer ion-selective membranes are used to lower the membrane resistance and shorten the response time of the SCISEs. When using coulometric transduction, an optimized design of the K^+-SCISE is able to detect a concentration change of 5 μM at a concentration level of 5 mM, corresponding to a 0.1% change in K^+ activity. This indicates that SCISEs can provide extremely high sensitivity when employing coulometric transduction. Impedance measurements show that the coulometric transduction process for the K^+-SCISE is limited by diffusion even for very thin ion-selective membranes. On the other hand, the H^+-SCISE shows a low impedance and a fast coulometric response that is related to the high mobility of H^+ in the H^+-selective polymeric membrane as well as in the solid contact layer. The coulometric transduction method was used to detect small changes of pH in seawater and found to improve the sensitivity compared to classical potentiometry. The coulometric method was briefly tested also for determining activity changes of K^+ in a serum sample.

KEYWORDS: solid-contact ISE, coulometric transduction, high sensitivity, impedance, pH, seawater
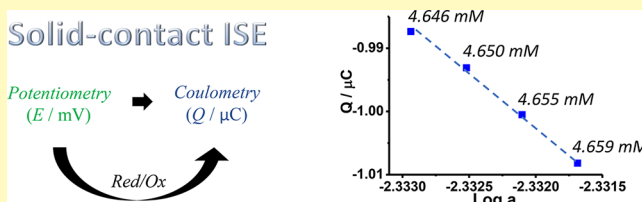
Ion-selective electrodes (ISEs) are cost-effective analytical devices that are used in various applications, including clinical diagnostics, environmental monitoring, industrial process analysis, agriculture, and food industry.[1−3] ISEs are traditionally used as potentiometric sensors, i.e., ion activity (and pH) is related to the equilibrium potential of the ISE versus the reference electrode. Under optimized conditions, ISEs show extremely low detection limits (down to 10^{-11} mol/L)[4] and a wide linear dynamic range. The durability of ISEs can be improved by using a solid internal contact,[5] such as a conducting polymer.[6] Emerging trends, including personal health monitoring,[7] will increase the demand for durable solid-contact ISEs (SCISEs) with high potential stability and high sensitivity.

A fundamental limitation of potentiometric ISEs is their low sensitivity due to the logarithmic dependence between potential and activity (Nernst equation). For example, a potential difference of 1 mV means a 4% change in ion activity for a monovalent ion (8% for a divalent ion). High sensitivity and precision are particularly relevant, e.g., in clinical analysis where the concentration intervals are extremely narrow. For example, the reference interval for Na^+ ion concentrations in human serum is from 136 mM to 145 mM.[8] In potentiometric measurements this corresponds to a potential interval of only 1.65 mV (at 25 °C). Another example is the precise measurement of pH in seawater.[9]

A coulometric signal transduction method allowing amplification of the analytical signal of SCISEs was recently introduced.[10,11] The coulometric transduction mechanism was

characterized experimentally for K^+-SCISEs[10−12] and theoretically for Cl^--SCISEs.[13] In this coulometric method, the potential between the SCISE and the reference electrode is held constant and the current between the SCISE and the counter electrode is measured.[10,11] Any change in the activity of the primary ion in solution gives a transient current signal between the SCISE and the counter electrode. The current causes oxidation/reduction of the solid-contact material and continues until the potential change of the solid contact exactly compensates the initial potential change at the ion-selective membrane/solution interface. Integration of the current−time transient gives the charge that is proportional to the potential change at the ion-selective membrane/solution interface that originated from the change in activity of primary ion in solution. The coulometric signal transduction method works specifically for solid-contact ISEs and the amplification of the analytical signal is proportional to the capacitance of the solid contact.[10−12] Since the charge is linearly proportional to the potential change, it means that the charge is proportional to the logarithm of ion activity, in analogy with potentiometry. However, the advantage of coulometry is that the charge is increased (amplified) by increasing the capacitance of the solid contact.[10−12] The practical usefulness of the coulometric method initially suffered from a long response time, due to the

relatively high resistance of the ion-selective membrane.[10,11] The membrane resistance was effectively lowered by increasing the electrode area[12] and by using a thin-layer ion-selective membrane.[13,14]

In the present work, the analytical performance of SCISEs selective to K^+ and pH are evaluated and compared by utilizing the coulometric transduction method in combination with thin-layer ion-selective membranes prepared by spin coating on top of poly(3,4-ethylenedioxythiophene) serving as an ion-to-electron transducer. The results presented in this work show that this type of SCISEs can be extremely sensitive to changes in ion activity (concentration). This approach opens up the possibility to detect minute changes in ion activity using SCISEs. Furthermore, coulometric H^+-SCISEs were evaluated for detecting small pH changes in seawater and also tested for determining activity changes of K^+ in a control serum sample.

■ EXPERIMENTAL SECTION

Materials. Valinomycin, tridecylamine (hydrogen ionophore I), 4-nonadecylpyridine (hydrogen ionophore II), potassium tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate (KTFPB), potassium tetrakis(4-chlorophenyl)borate (KTpClPB), 2-nitrophenyl octyl ether (o-NPOE), tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH-500), bis(2-ethylhexyl)sebacate (DOS), poly(vinyl chloride) (PVC), and tetrahydrofuran (THF) were purchased from Fluka and were of Selectophore purity grade. Poly(sodium 4-styrenesulfonate) (NaPSS, Mw ∼ 70 000), 3,4-ethylenedioxythiophene (EDOT, 97%), hydrogen chloride (∼37%), potassium chloride (KCl) (≥99.5%), and sodium chloride (NaCl) (≥99%) were purchased from Sigma-Aldrich. Deionized water (ELGA Purelab Ultra) was used for all the experiments. Seawater samples were collected at the seaside spot of Ruissalo, Turku, Finland (by the coast of the Baltic Sea). Whatman filter paper (589³ blue ribbon ashless, D = 110 mm, No. 300210) was purchased from Sigma-Aldrich. Control serum (Nortrol, REF 981043) and ISE calibrators 2 and 3 (REF 984035) were obtained from Thermo Fisher Scientific Oy.

Electrode Preparation. Glassy carbon (GC) disk electrodes mounted in PVC cylinders[12] were used in this work. The diameter of the GC disk electrode was 3 mm unless otherwise stated in the text. All the GC electrodes were first polished with sandpaper followed by diamond pastes with particle diameters of 15, 9, 3, and 1 μm, respectively, and finally with 0.3 μm Al_2O_3 powder. Polished electrodes were ultrasonicated for 5 min in ethanol and water baths, respectively. The aqueous polymerization solution (0.01 M EDOT + 0.1 M NaPSS) was stirred overnight to ensure complete dissolution of the monomer, and purged with N_2 gas for 15 min to remove oxygen before deposition of the PEDOT(PSS) films. Electropolymerization of the PEDOT(PSS) solid contact on the GC electrode surface was done with an Autolab general purpose electrochemical system (PGSTAT20, FRA2, AUTOLAB, Eco Chemie, B.V., The Netherlands) in a conventional three electrode cell. The GC electrode was connected as working electrode, a GC rod was used as counter electrode and a Metrohm double junction Ag/AgCl/3 M KCl/0.1 M NaPSS was the reference electrode. PEDOT(PSS) solid contacts were electrodeposited galvanostatically on GC electrode surfaces by applying 0.2 mA/cm² current for a given time.[15] The polymerization times were varied to obtain polymerization charges of 1, 10, and 100 mC.

After electropolymerization, all the GC/PEDOT(PSS) electrodes were dried overnight in air before covering them with an ion-selective membrane (ISM). SCISEs with thin-layer ISM were prepared by spin-coating the corresponding K^+ or H^+ selective membrane cocktails onto electrodes that were placed vertically with the sensing surface pointing upward in a holder on a rotator. The rotation speed was 1500 rpm and a total of 1−3 drops of membrane cocktail was added dropwise onto the rotating GC electrode surface (diameter = 3 mm). First, one drop was added, and due to rotation, most of the cocktail was swept away, so only a fraction of the drop remained on the

electrode surface. It was allowed to dry before adding the next drop. After drying, the second drop was added, and so on. For larger GC electrodes (diameter = 10 mm), the PEDOT(PSS) film was first covered with 200 μL of the membrane cocktail, and then immediately the spin-coater was switched on and set to reach the rotating speed 1500 rpm, so that excess cocktail was centrifuged away. The SCISEs with conventional thick-layer membrane were prepared by drop-casting 50 μL of the membrane cocktail onto PEDOT(PSS), without any rotation of the electrode. The composition of the K^+-selective membrane (dry weight = 15%) was 1 wt % valinomycin, 0.5 wt % KTFPB, 1 wt % ETH-500, 65.3 wt % DOS, and 32.2 wt % PVC dissolved in THF. The composition of H^+-selective cocktail (dry weight = 15%) was 1 wt % hydrogen selective ionophore II, 1 wt % KTpClPB, 68 wt % o-NPOE, and 30 wt % PVC dissolved in THF. The composition of the pH selective membrane for seawater sample measurements was 1.1 wt % hydrogen ionophore I, 0.3 wt % KTpClPB, 65.8 wt % o-NPOE, and 32.9 wt % PVC.[16]

The membranes were left to dry in air overnight followed by an overnight conditioning of the SCISEs in 0.01 M KCl (K^+-SCISEs) or 0.01 M HCl (H^+-SCISEs) or 1 mM HCl with 1 mM NaHCO₃(H^+-SCISEs)[16] before the measurements. Electrodes were stored in their conditioning solutions between the experiments.

Potentiometric and Chronoamperometric (Coulometric) Measurement. Potentiometric calibrations were performed to verify the proper functioning of the K^+-SCISEs and the H^+-SCISEs before chronoamperotric measurement. The potentiometric calibration slopes were ca. 57 ± 2 mV/log $a_{(K+)}$ (−57 ± 2 mV/pH) within the response ranges studied in this work. The linear response range was more narrow for very thin ISMs, as discussed below.

Both potentiometric and chronoamperometric (coulometric) calibrations were done using sequential dilutions of primary ion solutions with constant background electrolyte to stabilize the ionic strength. The starting solutions were 100 mL 0.01 M KCl or 0.01 M HCl with 0.1 M NaCl as background. In a typical calibration, 34.2 mL of the solution was removed and replaced with background electrolyte resulting in Δlog $a_{(K+)}$ or ΔpH of 0.18 per dilution step, following the protocol from our earlier work.[12] A Metrohm double junction Ag/AgCl/3 M KCl/1.0 M LiAc was used as the reference electrode in all potentiometric and chronoamperometric measurements.

To confirm the reversibility of the electrode response, standard addition was also used. The starting solution for K^+-SCISEs in the standard addition mode was 100 mL 0.005 M KCl with 0.1 M NaCl as the constant ionic background. Additions of 0.1 M KCl (with 0.1 M NaCl background) were made to the starting solution with a micropipette. The added volumes were 5, 10, 20, 30, and 40 μL under constant stirring of the solution. To reach equilibrium (current approaching zero) between each addition, the required time intervals between additions were 20−60 s.

Seawater samples were first filtered with Whatman filter paper to remove suspended particles as the samples were stored in the laboratory before and between pH measurements. Coulometric and potentiometric pH measurements were done in filtered seawater samples (volume = 50 mL) under constant stirring by standard addition of 0.1 mM HCl. The added volumes were 20, 30, and 40 μL. The time intervals between each addition were 100 and 120 s.

The coulometric method was evaluated further and compared with potentiometry by measuring small changes of K^+ activity in a control serum sample by using a K^+-SCISE. The K^+-SCISE was immersed in 5 mL of a control serum sample (C_{K+} = 4.4 mM) under constant stirring. Then, 360 μL of ISE calibrator 2 (C_{K+} = 6 mM) was added to obtain C_{K+} = 4.5 mM. Subsequently, 400 μL of ISE calibrator 3 (C_{K+} = 3 mM) was added to to return back to C_{K+} = 4.4 mM. Both coulometric and potentiometric measurements were performed. The time intervals between each addition were 2 min (potentiometry) and 4 min (coulometry).

Electrochemical Impedance Spectroscopy. Electrochemical impedance spectroscopy (EIS) measurements for K^+-SCISEs and H^+-SCISEs were done in 0.1 M KCl and 0.1 M HCl, respectively, at the open circuit potential (OCP) using the same Autolab (with FRA) described above, and a conventional three electrode cell. A Metrohm

single junction Ag/AgCl/3 M KCl was used as reference electrode and a glassy carbon rod as the counter electrode. The frequency range was 100 kHz−10 mHz and the excitation amplitude was 10 mV (RMS).

RESULTS AND DISCUSSION

Thin-layer K$^+$-selective membranes were spin-coated on top of the GC/PEDOT(PSS) solid contact in order to minimize the membrane resistance, thereby facilitating the ion transfer through the thin membrane and thus shortening the response time for K$^+$-SC-ISEs when applying the coulometric signal read-out method.[12,13] Typical chronoamperometric and coulometric signal responses of K$^+$-SCISEs with spin-coated thin-layer membranes are presented in Figure. 1.
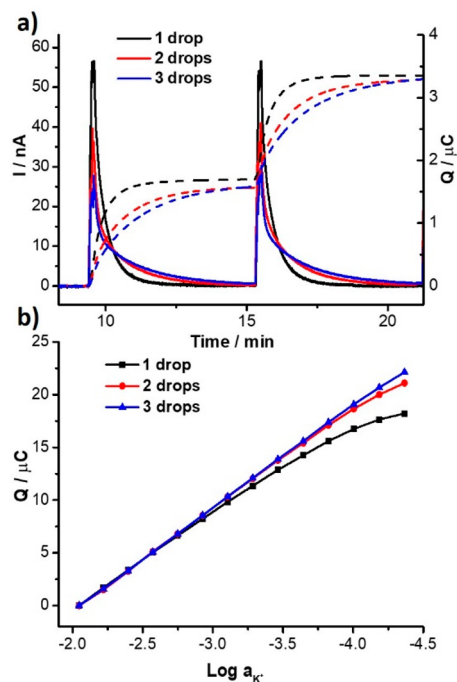
Figure 1. (a) Chronoamperograms (solid line) and the corresponding cumulated charge Q (dashed line) vs time for the K$^+$-SCISEs with 4 mC PEDOT(PSS) solid contact spin-coated by 1 drop, 2 drops, and 3 drops of the K$^+$-selective membrane cocktail. The starting solution was 10^{-2} M KCl (0.1 M NaCl as constant ionic background) and each of the 13 dilution steps correspond to Δlog a_{K+} = 0.18 (first and second dilution steps are shown). (b) Corresponding cumulated charge Q vs log a_{K+} ranging from −2 to −4.37.

Figure 1a shows an enlargement of the first and second dilution steps (Δlog a_{K+} = 0.18 per dilution step) of the chrononamperograms and the cumulated charge vs time for K$^+$-SCISEs with 4 mC PEDOT(PSS) solid contact and different thickness of the spin-coated thin-layer ISMs (1, 2, and 3 drops). The cumulated charge Q vs log a_{K+} obtained from the same experiment by integrating the current is shown in Figure 1b. The results presented in Figure 1 show that the current response of the K$^+$-SCISEs is faster for thinner ISMs, i.e., it depends on the thickness even for such thin ISMs. Figure 1 also shows that the cumulated charge Q measured during the first 5 dilution steps is the same for all the K$^+$-SCISEs in the measurement, independent of the thickness of the ISM (1, 2, or 3 drops). This shows that coulometry gives a highly reproducible response, as long as the thickness (and thus the

capacitance) of the PEDOT(PSS) solid contact is constant (in this case the polymerization charge = 4 mC). These results are consistent with the theoretical expectations for a circuit containing a resistor and capacitor in series[15] and the theoretical model presented recently.[13]

At lower concentrations (log a_{K+} < −3), a deviation from the linear charge response is observed for the K$^+$-SCISEs with the thinnest ISM prepared by spin-coating of 1 drop of membrane cocktail. The same deviation from linearity was observed also in potentiometric measurements in the case of very thin spin-coated ISMs. The detection limit was clearly worse for very thin spin-coated membrans than for "normal" thick membranes. This may indicate incomplete membrane coverage or it may also be related to a gradual exchange of K$^+$ to Na$^+$ in the bulk of the ISM when approaching the selectivity limit of the membrane (log $K_{K,Na}$). Increasing the spin-coated membrane thickness from 1 to 3 drops extended the Nernstian response to lower K$^+$ concentrations both in potentiometry and in coulometry (Figure 1b). This seems to be a fundamental limitation of very thin ISMs, which needs further studies. Nevertheless, already 3 drops of spin-coated membrane extends the linear range of the K$^+$-SCISE to log a_{K+} < −4 under the experimental conditions used here. The K$^+$-SCISE with 3 drops of spin-coated thin-layer ISM still shows a fast response and short equilibrium time compared with the conventional drop-cast thick ISM (Figure 2a).

Interestingly, the H$^+$-SCISE shows a much faster amperometric and coulometric response (Figure 2b) than the corresponding K$^+$-SCISE (Figure 2a). The cumulated charge obtained by integration of the current responses are shown as dashed lines in Figure 2. When an equilibration time of 5 min between each dilution (decrease in primary ion activity) was applied, relatively equal amounts of charge were obtained for H$^+$-SCISEs with both drop-cast (thick) and spin-coated (thin) ISMs. On the contrary, the K$^+$-SCISEs with a spin-coated (thin) ISM showed a comparatively larger amount of charge than K$^+$-SC-ISEs with a drop-cast (thick) membrane. These results indicate that the transport of H$^+$ through the bulk of the H$^+$-selective ISM and the PEDOT(PSS) solid contact is faster compared to the corresponding transport of K$^+$ in the K$^+$-SCISE. The fast response (high mobility of H$^+$) in the H$^+$-SCISE is interesting when considering that the selective ion transport in ISMs is assumed to take place in the form of ion−ionophore complexes and thus should not be dramatically faster for H$^+$ compared to K$^+$.[17] Could these results indicate that free H$^+$ contributes to ion transport in the H$^+$-selective membrane? A definite answer cannot be given at present, because in addition to ion transport in the ISM, ion transport in PEDOT(PSS) also takes place. Furthermore, an additional ion-transfer resistance at the PEDOT(PSS)/ISM interface may contribute to the overall electrode resistance.[18] So, the coulometric response can be influenced by the rate and reversibility of the oxidation/reduction of PEDOT as well as the rate and reversibility of ion transfer in the bulk and at the interfaces of the SCISE.

Increasing the thickness of the PEDOT(PSS) allows amplification of the coulometric signal, as discussed earlier.[11] The coulometric response of K$^+$-SCISEs and H$^+$-SCISEs with spin-coated thin-layer ISMs (2 drops) but with two different thicknesses of the solid contact (1 mC and 10 mC PEDOT(PSS)) are compared in Figure 3. A thicker solid contact layer corresponds to a larger amount of oxidizable/reducible material on the electrode surface, so a larger amount
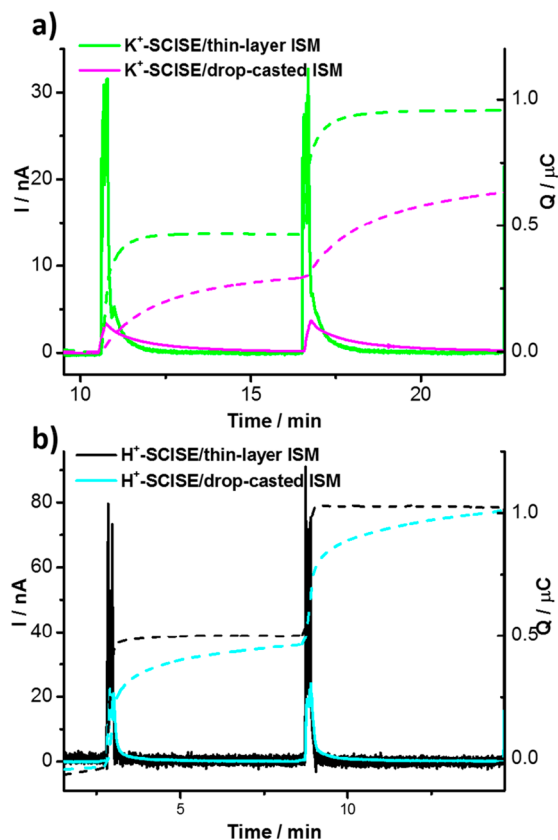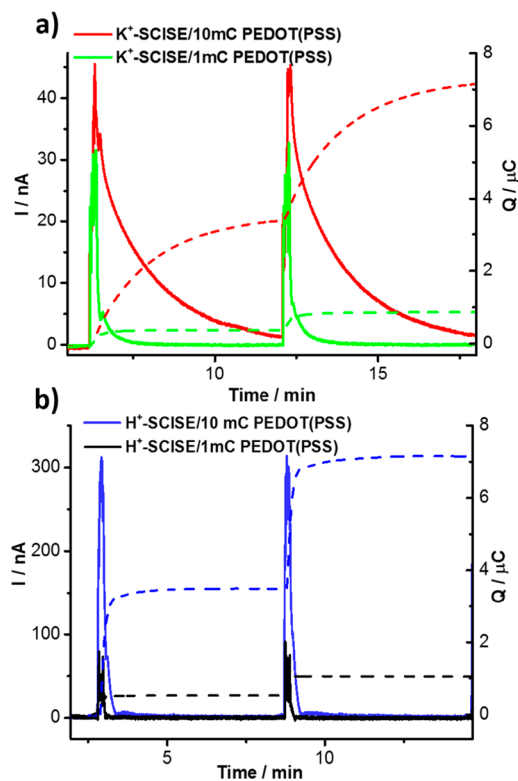
Figure 2. Chronoamperograms (solid line) and the corresponding cumulated charge Q (dashed line) vs time for (a) K+-SCISEs and (b) H+-SCISEs with constant 1 mC PEDOT(PSS) solid contact and either spin-coated thin-layer ISMs (3 drops) or drop-cast thick ISMs. The starting solution is 100 mL 10^{-2} M KCl or 10^{-2} M HCl, respectively, containing 0.1 M NaCl as constant ionic background. The first and second dilution steps ($\Delta\log a_{K+}$ = 0.18 per dilution step) are shown.

Figure 3. Chronoamperograms (solid line) and the corresponding cumulated charge (dash line) vs time for (a) K+-SCISEs and (b) H+-SCISEs with 1 mC and 10 mC PEDOT(PSS) as solid contact and spin-coated (2 drops) ISMs. The starting solutions are 100 mL 10^{-2} M KCl and 10^{-2} M HCl, respectively, containing 0.1 M NaCl as constant ionic background. The first and second dilution steps ($\Delta\log a_{K+}$ = 0.18 per dilution step) are shown.

of ions needs to be transferred to/from the PEDOT(PSS) layer for a given activity (potential) change. Increase in the thickness of the solid contact, i.e., increase in the redox capacitance of the PEDOT(PSS) layer, increases the signal amplification but also requires longer time to reach equilibrium, which is in good agreement with our previous work.[11] The results presented in Figure 3a show that the K+-SCISE with 10 mC solid contact and thin membrane does not reach equilibrium within the time frame of the experiment. Thus, a longer equilibrium time, even with the thin-layer ISM, would be required for the K+-SCISE.

The response time is illustrated further in Figure 4 showing the response to 10 successive dilution steps for the K+-SCISEs and H+-SCISEs with 10 mC PEDOT(PSS) covered with spin-coated (3 drops) thin-layer ISMs. Each dilution gives $\Delta\log a_{K+}$ or $-\Delta$pH = 0.18. It can be seen that the current peak (following the dilution) is much higher and sharper for the H+-SCISE than the K+-SCISE (Figure 4a), while the cumulated charge is very similar for both electrodes when adequate time for equilibration is also allowed for the K+-SCISE (Figure 4b). The response of the H+-SCISEs is fast and the cumulated charge curve resembles an ideal staircase, indicating full equilibration and harvesting of the complete total charge of the solid contact after each dilution step. When allowing for sufficient equilibration after each change in the primary ion
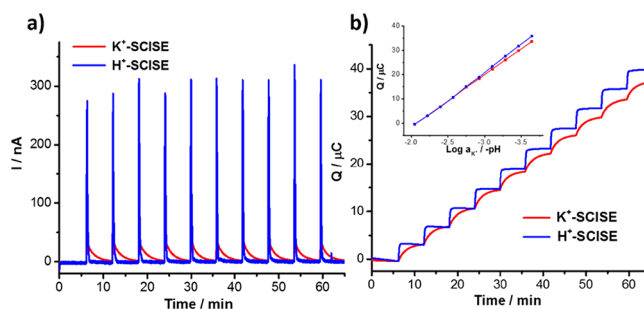

Figure 4. (a) Chronoamperograms and (b) the cumulated charge vs time for K+-SCISEs and H+-SCISEs with 10 mC PEDOT(PSS) solid contact and spin-coated (3 drops) ISM during sequential dilution steps ($\Delta\log a_{K+}$ or $-\Delta$pH = 0.18 per dilution step). The starting solution is 100 mL 10^{-2} M KCl or 10^{-2} M HCl, respectively, containing 0.1 M NaCl as constant ionic background. The cumulated charge Q vs log a_{K+} or $-$pH is shown in the inset of Figure 4b.

activity, both the K+-SCISEs and the H+-SCISEs give very similar cumulated charge, suggesting that the coulometric signal transduction principle can be used as a general approach to measure and amplify concentration changes with solid-contact ion-selective electrodes. However, as discussed above, careful attention must be given to ensure efficient ion transport processes within the entire SCISE.

Electrochemical impedance spectroscopy (EIS) measurements were performed for K+-SCISEs and H+-SCISEs with 10 mC PEDOT(PSS) as solid contact covered with spin-coated

thin-layer membranes (3 drops). The impedance spectra are shown in Figure 5. The impedance of the K$^+$-SCISE shows a
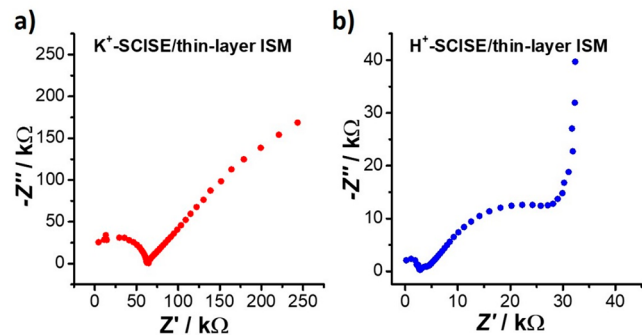

Figure 5. Impedance spectra for (a) a K$^+$-SCISE in 0.1 M KCl and (b) a H$^+$-SCISE in 0.1 M HCl. Both SCISEs had a 10 mC PEDOT(PSS) solid contact covered with a spin-coated thin-layer ISM (3 drops). The impedance measurements were done at OCP with 10 mV (RMS) perturbation amplitude and 100 kHz to 10 mHz frequency range.

high-frequency semicircle (Figure 5a). The diameter of the semicircle is ca. 65 kΩ and can be related to the bulk resistance of the spin-coated thin-layer K$^+$-selective membrane. The membrane resistance (65 kΩ) is ca. 25 times lower compared to the resistance (1.7 MΩ) of a drop-cast membrane with the same composition.[12] This indicates that the thickness of the spin-coated membranes used in this work is ca. 1−4 μm. The impedance spectrum of the K$^+$-SCISE also shows a low-frequency line with an angle of ca. 45°, corresponding to a diffusion process. This indicates that the transduction process of the K$^+$-SCISE is limited by diffusion. Such mass-transport limitations can certainly be related to the longer response time for K$^+$-SCISE in comparison to H$^+$-SCISE when utilizing the coulometric signal readout method, which is in agreement with results discussed above. On the contrary, the impedance spectrum of the H$^+$-SCISE does not show any diffusion line but an almost vertical capacitive line at low frequencies (Figure 5b). Such a capacitive response at low frequencies can be related to the redox capacitance of the PEDOT(PSS) solid contact. In this case, the imaginary impedance at the lowest frequency (10 mHz) can be used to estimate the low frequency capacitance of PEDOT(PSS) when coated with the thin-layer ion-selective membrane. The calculated low frequency capacitance of H$^+$-SCISEs with 10 mC solid contact PEDOT-(PSS) covered with thin-layer membrane is ca. 250 μF, which is comparable to the capacitance of the same thickness of a bare PEDOT(PSS) without membrane.[14] This implies that the redox capacitance of the PEDOT(PSS) solid contact can be efficiently utilized in the case of the H$^+$-SCISE during coulometric transduction. Furthermore, the overall resistance of the H$^+$-SCISE (Figure 5b) is significantly lower than for the K$^+$-SCISE (Figure 5a), which is in agreement with the faster coulometric response of the H$^+$-SCISE.

To further explore the limitations and possibilities related to the sensitivity of the coulometric method, a 100 mC PEDOT(PSS) solid contact was electropolymerized on a large-area GC electrode (diameter = 10 mm) and covered with a thin layer K$^+$-selective ISM. A large-area GC electrode and a high polymerization charge were used in order to maximize the redox capacitance of PEDOT(PSS) and thus the amplification of the coulometric signal, while a thin-layer ISM still kept the

electrode resistance sufficiently low for the K$^+$-SCISE.[12] The KCl concentration was changed within a narrow concentration range by repeated additions of small volumes (5−40 μL) of 0.1 M KCl (+0.1 M NaCl) into a 100 mL solution of 5 mM KCl (+0.1 M NaCl). The smallest additions (5 μL) gave a concentration increase of 5 μM at a concentration level of 5 mM, corresponding to a 0.1% change in K$^+$ activity. The results of the coulometric sensitivity measurement using the large area K$^+$-SCISE during such standard additions are summarized in Figure 6a-c.
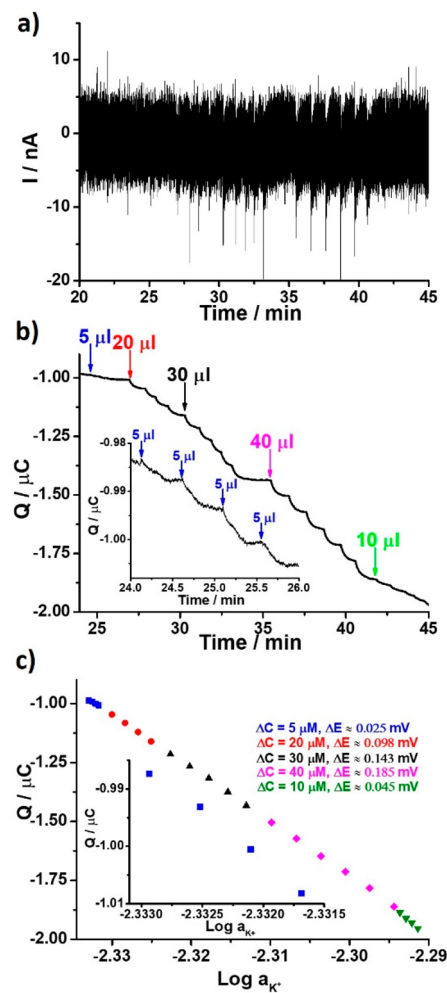

Figure 6. Response of a large-area K$^+$-SCISE (diameter = 10 mm) with 100 mC PEDOT(PSS) as solid contact and a spin-coated thin-layer ISM. Additions of 0.1 M KCl (+0.1 M NaCl) were done (volumes shown in the figure) to a 100 mL solution of 5 mM KCl + 0.1 M NaCl under constant stirring: (a) current vs time, (b) charge vs time, and (c) charge vs log a_{K^+}.

The current signal in Figure 6a contains a lot of noise, which is mainly due to the continuous magnetic stirring of the solution, the spin-coated thin-layer ISM, and the large electrode area. Interestingly, the high noise level in the current vs time response (Figure 6a) was effectively eliminated when the current was integrated over time to obtain the charge vs time response (Figure 6b). The resulting charge vs log a_{K^+} curve is close to linear in the narrow concentration range studied (Figure 6c). As shown in the inset of Figure 6b, even a 0.1% change in K$^+$ activity is detectable in the charge vs time

curve, indicating that the coulometric transduction method can be very sensitive. In potentiometric measurements a 0.1% change in K^+ activity would correspond to a potential change of only 25 μV. For comparison, it may be noted that, in conventional potentiometric measurements using a Ca^{2+}-ISE as indicator electrode and a Na^+-ISE as reference electrode, the standard deviation of the background noise was only 5 μV, while for a Ag^+-ISE as indicator electrode, the standard deviation of the background noise was 60 μV.[19]

The results shown in Figure 6 are very encouraging, suggesting that the coulometric signal transduction method can remarkably improve the sensitivity of ion detection with solid-contact ISEs. It is also highly interesting that the essential analytical information on a very noisy current signal (Figure 6a) can be obtained and visualized by simply integrating the current to obtain the charge (Figure 6b).

The sensitivity of the coulometric transduction was evaluated further and compared with potentiometry by measuring small pH changes in seawater that was collected by the coast of the Baltic Sea (Ruissalo, Turku, Finland). Results obtained by potentiometry and coulometry are compared in Figure 7. The potentiometric signal contains
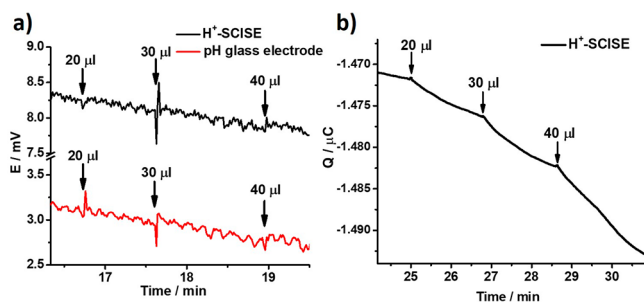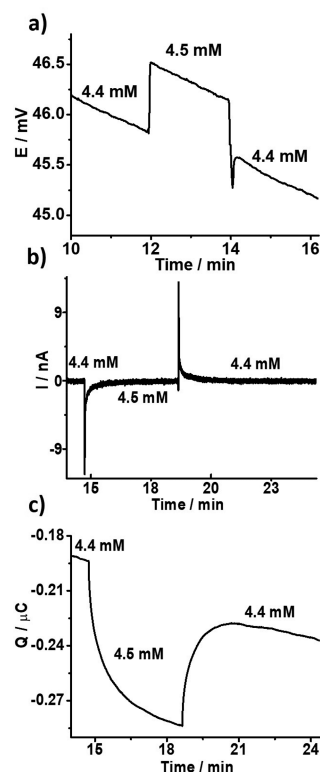

Figure 7. (a) Potentiometric response of a pH-selective glass electrode (Metrohm) and a H^+-SCISE and (b) coulometric response of a H^+-SCISE. The H^+-SCISE was based on 10 mC PEDOT(PSS) and drop cast ISM. Standard additions (20, 30, 40 μL) of 0.1 mM HCl were done to a seawater sample (50 mL) under constant stirring.

some noise and the small pH changes following standard additions are hardly visible in the potential−time curves of both the glass pH electrode and the H^+-SCISE (Figure 7a). The same standard additions give clear signals when the coulometric transduction method is used together with the same H^+-SCISE (Figure 7b). The potentiometric as well as the coulometric signals show some drift, which may be related, e.g., to slow changes in pH of the seawater sample. During potentiometry, both electrodes were measured simultaneously versus a common reference electrode. Any potential drift in the electrodes and measurement system that is not related to activity changes in the solution will inevitably decrease the accuracy of the coulometric measurement. As in potentiometric measurements, it is therefore important to ensure high stability of the SCISE and reference electrode also in coulometric measurements. Furthermore, any chemical redox reactions (e.g., due to O_2) influencing the redox state of the solid contact (PEDOT) will give a bias in the coulometric response. However, the comparison shown in Figure 7 indicates that the coulometric transduction method can improve the quality of the signal from the pH sensor in seawater close to neutral pH, especially if the drift can be eliminated. It should be emphasized further that these results

illustrate only the response to small changes in pH. Determination of the actual pH value in seawater should be performed in situ and was not attempted in this work.[16]

The coulometric method was briefly studied also for determination of K^+ changes from 4.4 mM to 4.5 mM and back to 4.4 mM in control serum samples using a K^+-SCISE. Potentiometric and coulometric measurement were done with the same single K^+-SCISE based on 4 mC PEDOT(PSS) covered with a spin-coated thin-layer K^+-selective membrane (2 drops). The potentiometric, chronoamperometric, and coulometric responses are shown in Figure 8. The potentio-

Figure 8. (a) Potentiometric, (b) chronoamperometric, and (c) coulometric response of K^+-SCISE measured in a control serum sample matrix with K^+ concentrations from 4.4 mM to 4.5 mM and back to 4.4 mM, as indicated in the figure. The K^+-SCISE was with 4 mC PEDOT(PSS) as solid contact and a spin-coated thin-layer ISM (2 drops).

metric response is fast and reversible but a potential drift is visible (Figure 8a). In addition, the chronomaperometric response is reversible (Figure 8b) but a small negative current is present, which may originate from a small potential drift also here. The coulometric signal (Figure 8c) is reversible but distorted due to the bias current in the chronoamperometric signal. These results show that the coulometric method works also in a complicated sample matrix like serum and the results illustrate the effect of potential drift. In order to fully utilize the advantages of signal amplification offered by the coulometric method it will be important to eliminate any potential drift of the SCISE (and reference electrode).

■ CONCLUSION

A recently developed coulometric transduction method for solid-contact ISEs was evaluated by comparing K^+-selective solid-contact ISEs (K^+-SCISEs) and pH-selective solid-contact

ISEs (H$^+$-SCISEs). Spin-coated ion-selective polymeric membranes were used to lower the electrode resistance and thus shorten the response time during coulometric transduction. Impedance measurements showed that the transduction process for the K$^+$-SCISE was limited by diffusion even for thin spin-coated K$^+$-selective membranes, while the H$^+$-SCISE showed a low impedance and a fast coulometric response even for thicker membranes. This was related to rapid transport of H$^+$ in the H$^+$-selective polymeric membrane and solid contact. The shape of the impedance spectrum for solid-contact ISEs correlated well with the coulometric response of the electrodes. Hence, recording an impedance spectrum of the SCISE is an extremely useful diagnostic tool to predict the performance and suitability of the SCISE for coulometric transduction. When employing coulometric transduction, the K$^+$-SCISE was able to detect a 0.1% change in K$^+$ activity, which is quite remarkable. The results obtained in this work show further that the coulometric transduction method can be applied to detect small changes of pH in seawater and small changes of K$^+$ activity in serum. However, in order to fully utilize the signal amplification offered by the coulometric method it will be important to further minimize the potential drift of the SCISE and reference electrode.

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Notes

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