

Ion-Selective Electrodes with Three-Dimensionally Ordered Macroporous Carbon as the Solid Contact

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Electrodes with three-dimensionally ordered macroporous (3DOM) carbon as the intermediate layer between an ionophore-doped solvent polymeric membrane and a metal contact are presented as a novel approach to solid-contact ion-selective electrodes (SC-ISEs). Due to the well-interconnected pore and wall structure of 3DOM carbon, filling of the 3DOM pores with an electrolyte solution results in a nanostructured material that exhibits high ionic and electric conductivity. The long-term drift of freshly prepared SC-ISEs with 3DOM carbon contacts is only 11.7 $\mu\text{V}/\text{h}$, and does not increase when in contact with solution for 1 month, making this the most stable SC-ISE reported so far. The electrodes show good resistance to the interference from oxygen. Moreover, in contrast to previously reported SC-ISEs with conducting polymers as the intermediate layer, 3DOM carbon is an electron conductor rather than a semiconductor, eliminating any light interference.

Ion-selective electrodes (ISEs) have become a routine tool in chemical analysis.^{1–5} They are attractive for applications in clinical diagnostics, process control, and environmental monitoring. With a view to both mass fabrication and measurements in small volumes, the miniaturization of ISEs has attracted considerable interest. Conventional ion-selective microelectrodes⁶ are based on an ion-selective membrane separating the sample solution from the inner reference electrode, which is immersed in an inner solution. However, the use of an inner solution impedes further miniaturization since attempts to minimize the volume of the internal electrolyte solution encountered considerable difficulties.⁷ In contrast, electrodes without an inner solution are less fragile, do not dry out, and are more robust to external pressure. This has led to the development of several types of solid-contact ion-selective electrodes (SC-ISEs).

The first reported SC-ISEs were commonly referred to as coated-wire electrodes (CWEs).⁸ In a CWE, a sensing polymeric

membrane is directly coated onto a metallic conductor. These electrodes exhibit limited long-term stability and have only been used as detectors in certain specific areas, such as capillary electrophoresis⁹ and flow injection analysis.¹⁰ The instability of the measured potential can be attributed to the “blocked” interface between the sensing membrane and the metallic conductor, which is characterized by an ill-defined phase boundary potential that often depends on oxygen and other redox-active components of the sample.¹¹ Many efforts have been made to solve this problem, e.g., by using an inner Ag/AgCl reference electrode and replacing the internal electrolyte solution with a hydrogel-based electrolyte.^{12,13} However, hydrogel-based ISEs have limitations related to water uptake/release and the corresponding volume changes of the hydrogel layer.⁷

A completely different method to modify the “blocked” interface is to use an intermediate layer with suitable redox and ion-exchange properties that permits charge transfer between the electronic conductor and the sensing membrane. A redox-active self-assembled monolayer (SAM) between the membrane and the inner Au electrode was reported to lead to a stable system because of a well-defined pathway for charge transfer.¹⁴ However, one limitation of monolayers is their inherently low redox capacitance. In order to minimize the polarizability of the solid contact, a sufficiently high redox capacitance of the intermediate layer is required.¹⁵ Conducting polymers that possess this higher redox capacitance have been investigated, such as poly(pyrrole) (PPy),^{16–20} poly(aniline) (PANI),^{21,22} poly(thiophene) (PT),^{23,24} and several of

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their derivatives. Some of the electrodes using these polymers as an intermediate layer have been reported to be sensitive to CO₂ and pH, such as in the case of PPy, PANI, and poly(3-octylthiophene) (POT).^{25–32} For PANI, partial conversion from its conducting to its nonconducting emeraldine salt form was found during long-term measurements (1–3 months),³³ which results in a decrease of the electrode potential. Moreover, some polymers, such as PT, are organic semiconductors with a suitable band gap for photon absorption, giving SC-ISEs that are photoresponsive.³⁴ Some of the lowest reported potential drifts that have been achieved based on SC-ISEs are 85 $\mu\text{V/h}$ for SAM-contacted electrodes,³⁵ 100 $\mu\text{V/h}$ for hydrogel-based electrodes, and 30 $\mu\text{V/h}$ for PPy-contacted electrodes.¹⁸ In view of long-term monitoring under circumstances where frequent recalibration must be avoided, a further reduction of signal drift is highly desirable. In this context, we have tested three-dimensionally ordered macroporous (3DOM) carbon as a new material for SC-ISEs.

3DOM carbon consists of a skeleton of glassy carbon surrounding a periodic array of uniform spherical pores that are interconnected in three dimensions. This structure is prepared by colloidal crystal templating, a process in which a close-packed array of monodisperse spheres—here, poly(methyl methacrylate) (PMMA) spheres—is infiltrated by a fluid precursor that is processed to form a solid skeleton. Porosity is introduced by removal of the template spheres. Typical pore sizes in these materials are on the order of a few hundred nanometers, and skeletal walls are tens of nanometers thick. Many different 3DOM materials have been produced by colloidal crystal templating, including metals, oxides, and polymers.³⁶ The open, periodic structure benefits applications such as photonics, catalysis, bio-glasses, and separation.³⁶ 3DOM carbon produced by carbonization of a templated resorcinol–formaldehyde (RF) sol–gel precursor has recently been studied as a potential anode material for lithium ion batteries.^{37–40} This glassy carbon architecture has several properties that make it promising also for sensor applications. 3DOM carbon can be prepared in monolithic form and is

strong enough to be handled and polished to a desired thickness. The final structure has a well-connected wall structure that is electronically conducting, with typical conductivity values of 0.2–0.3 S·cm⁻¹.⁴⁰ Filling of the continuous void space with an electrolyte allows for ionic conductivity through the monolith.

In the present work, 3DOM carbon has been used for the first time as the intermediate layer of SC-ISEs to stabilize the potential difference between the ionophore-doped solvent polymeric sensing membrane and a metallic conductor. An excellent potential stability of this new type of SC-ISEs is reported.

EXPERIMENTAL SECTION

Reagents. Sensing membranes: high molecular weight poly(vinyl chloride) (PVC) and 2-nitrophenyl octyl ether (2-NPOE) were purchased from Fluka (Buchs, Switzerland), valinomycin was from Sigma (St. Louis, MO), and potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (KTTPB) was from Dojindo (Kumamoto, Japan). Deionized and charcoal-treated water (18.2 M Ω ·cm specific resistance) obtained with a Milli-Q PLUS reagent-grade water system (Millipore, Bedford, MA) was used for all sample solutions. The potassium, sodium, and iron salts were obtained from Mallinckrodt Baker (Paris, KY). All chemicals were used as received.

3DOM carbon: methyl methacrylate (MMA) (99%), 2,2'-azobis(2-methylpropionamide) dihydrochloride (AMPD, 97%), and resorcinol (99+%) were purchased from Aldrich (Milwaukee, WI), sodium carbonate (anhydrous, 99.7%) was from Mallinckrodt Baker, and formaldehyde (37% in H₂O) was from Fisher Scientific (Pittsburgh, PA). Ni mesh was obtained from Dexmet (Branford, CT).

For comparison, highly oriented pyrolytic graphite (HOPG) (SPI-2), purchased from SPI Supplies (West Chester, PA), was used as an intermediate layer.

Substrate Preparation. 3DOM carbon monoliths were prepared by colloidal crystal templating with monodisperse PMMA spheres. PMMA spheres with diameters of 420 nm were synthesized by surfactant-free emulsion polymerization of MMA at 70 °C, initiated by AMPD, as previously described.⁴¹

The sphere suspension was poured into a large crystallization dish, covered, and allowed to undergo gravitational settling. The cover was then removed, and the water was allowed to evaporate, forming opalescent PMMA pieces. 3DOM carbon was prepared by a slight modification of published methods.^{37,39} The carbon precursor solution was prepared by stirring resorcinol (3.3 g), formaldehyde (4.5 mL solution), and sodium carbonate (60 mg) in a 60:120:1 molar ratio at room temperature for 20 min. Several PMMA pieces with dimensions of approximately 1 cm × 1 cm × 0.2 cm were placed in a small crystallization dish. The RF solution was deposited with a pipet around the PMMA pieces to cover the bottom of the dish but not the PMMA pieces. The dish was covered, and the solution infiltrated the PMMA pieces by capillary action. Once the RF solution reached the top of the PMMA pieces, they were placed in a sealed plastic bottle and kept at 85 °C for 3 days. The PMMA/RF composites were then transferred to a porcelain boat and heated under flowing nitrogen with a heating ramp of 5 °C·min⁻¹ to 900 °C. The temperature was kept at

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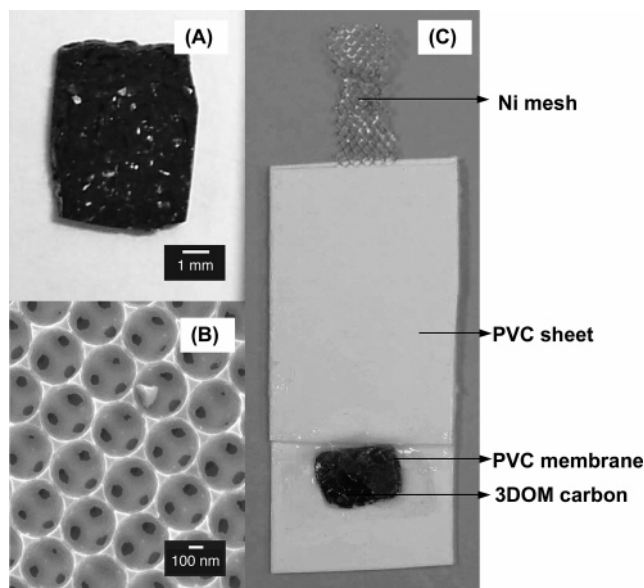


Figure 1. (A) Photograph of monolithic 3DOM carbon. (B) SEM image of 3DOM carbon. (C) Photograph of 3DOM carbon-contacted ISE.

900 °C for 2 h and then reduced back to room temperature with a cooling rate of 10 °C·min⁻¹. This process removes the PMMA template and carbonizes the precursor, leaving a porous glassy carbon skeleton with 360 nm diameter pores connected by 90 nm diameter windows. Before use, the 3DOM carbon monoliths were wet polished with 320 grit sandpaper to remove the untemplated crust and to produce the desired thickness (≈ 0.25 mm). The carbon monoliths were then attached to a piece of Ni mesh using RF as the adhesive. The molar ratios of the RF components were the same as above, but the mixture was stirred and heated at low temperature until it became viscous enough to use. A small amount of the RF was used to attach the carbon to the Ni mesh, which was then clamped between two microscope slides, placed in a sealed plastic bottle, and kept at 85 °C overnight for RF curing. The electrical conductivity of monolithic macroporous carbon was measured to be 0.34 S·cm⁻¹ at room temperature with the four-probe van der Pauw method.⁴² The probes were attached to the sample using Ag paste as an adhesive (Ted Pella, Redding, CA).

Membranes. Valinomycin-doped K⁺-ISE membranes were prepared according to a standard procedure by pouring a tetrahydrofuran (THF) solution of 200 mg of the membrane components into a glass dish (31 mm i.d.) and letting the THF evaporate slowly at room temperature over 24 h. The same type of membrane containing 32.8% (w/w) PVC, 65.6% 2-NPOE, 1.0% valinomycin, and 0.6% KTFPB was used for all experiments. The thickness of the resulting membranes was approximately 100 μ m.

Electrode Fabrication. SC-ISEs were prepared by inserting a small piece of 3DOM carbon between a Ni mesh and a PVC membrane (Figure 1). The 3DOM carbon was glued onto the Ni mesh, and a section of the Ni mesh was embedded between two PVC sheets, which served as the substrate for the whole setup. Finally, the 3DOM carbon was covered with a PVC membrane. A solution of PVC in THF was used to tightly glue the two PVC sheets together and to cover all still exposed Ni mesh and 3DOM

carbon, ensuring that there was no direct contact between the ionophore-doped PVC membrane and the Ni mesh and between the 3DOM carbon and the sample solution. All electrodes were conditioned in a 100 mM KCl solution for 24 h prior to measurements.

EMF Measurements. Potentials were monitored with an EMF 16 potentiometer (Lawson Labs, Malvern, PA) controlled with EMF Suite 1.02 software (Fluorous Innovations, Arden Hills, MN) at room temperature (25 °C) in stirred solutions. The external reference electrode consisted of a double-junction Ag/AgCl electrode with a 1 M LiOAc bridge electrolyte and 3 M KCl as reference electrolyte. All measurements of long-term stability were performed with temperature-controlled samples, using a water bath. All emf values were corrected for liquid-junction potentials according to the Henderson equation.⁴³ Activity coefficients were calculated with a two-parameter Debye–Hückel approximation.⁴⁴

RESULTS AND DISCUSSION

To characterize the novel solid-contact ISE with 3DOM carbon (Ni/3DOM carbon/PVC) as contact layer between a nickel metal lead and ionophore-doped PVC membranes, their ionic response, long-term drift characteristics, and the stability to redox and light interferences were determined. They are compared in the following to the responses of several other electrode setups. SC-ISEs with a layer of HOPG replacing the 3DOM carbon were prepared analogous to the 3DOM carbon-contacted ISEs and are referred to in the following as Ni/HOPG/PVC electrodes. SC-ISEs made of a Ni mesh covered directly with an ionophore-doped plasticized PVC membrane but without an intermediate layer (Ni/PVC) and a Ni mesh coated with 3DOM carbon but lacking the PVC membrane (Ni/3DOM carbon) were also investigated for comparison.

Ionic Response. The ionic responses of SC-ISEs with the different electrode assemblies were measured in KCl solutions. Calibration curves (Figure 2) were obtained by repeated dilution of the sample with pure water, starting from a 100 mM KCl solution. As predicted by theory for an electrode based on a solvent polymeric membrane doped with K⁺-selective valinomycin as ionophore, the Ni/3DOM carbon/PVC electrode exhibited a Nernstian response to K⁺. The observed detection limit of 10^{-6.2} M is similar to detection limits of SC-ISEs as observed in the past but could probably be lowered by preventing direct exposure of the electrode to solutions of high K⁺ activity.²⁰

While the Ni/HOPG/PVC and Ni/PVC electrodes lack the ion- and electron-conducting intermediate layer between the electron conductor (Ni) and ion conductor (PVC membrane) and would not be expected to give stable long-term responses, they did provide Nernstian responses to K⁺ with slopes of 58.1 mV/decade for the Ni/HOPG/PVC electrode in the range from 10^{-1.1} M to 10^{-5.2} M and 56.4 mV/decade for the Ni/PVC electrode in the range from 10^{-1.1} M to 10^{-5.5} M. This can be explained by the short time span required for the measurement of a calibration curve and is consistent with previous observations for comparable CWEs (see above). More surprising was the response of the Ni/3DOM carbon electrode, which exhibited a slope of 48.6 mV/

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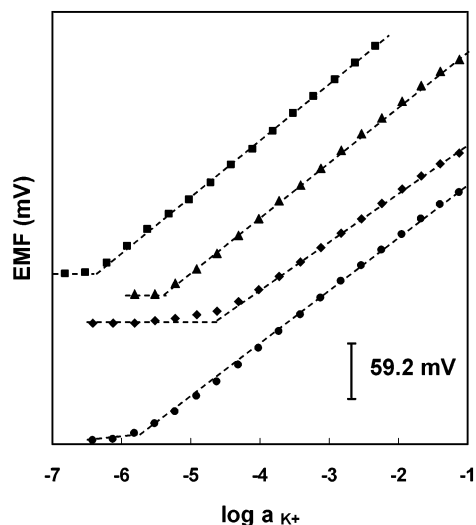


Figure 2. Potentiometric K^+ response curves of SC-ISEs with different electrode assemblies in KCl solutions: (■) Ni/3DOM carbon/PVC, (▲) Ni/HOPG/PVC, (◆) Ni/3DOM carbon, (●) Ni/PVC. For clarity, response curves have been shifted vertically relative to one another.

Table 1. Redox Response of Different Electrode Assemblies as Given by the Slopes of the EMF versus $\log([Fe(III)]/[Fe(II)])$

substrate	slope mV/decade
Ni/3DOM carbon	57.2 ± 0.2
Ni/3DOM carbon/PVC	1.43 ± 0.40
Ni/HOPG/PVC	0.70
Ni/PVC	4.16

decade in the range from $10^{-1.1}$ M to $10^{-4.3}$ M. This response may be related to K^+ intercalation into 3DOM carbon or very low concentrations of oxygen-containing functional groups on the surface of 3DOM carbon.³⁹

Redox Response. For each electrode assembly, the redox interference was investigated by measuring the cell potential in solutions of the redox couple Fe(III) and Fe(II) in various ratios with a constant ionic strength (100 mM KCl). The sum of the concentrations of Fe(II) and Fe(III) was kept constant (1 mM), and the Fe(II)/Fe(III) ratio was changed from 4:1 to 1:4. The results are shown in Table 1. A Nernstian response to the Fe(II)/Fe(III) redox couple was observed at the 3DOM carbon-coated Ni electrode because 3DOM carbon is an electron conductor and can be considered as an extension of the Ni electrode. Evidently, this redox response would be considered an interference for an SC-ISE. In contrast, all electrodes coated with PVC membranes showed no redox interference, which is consistent with the lack of electron transport through the valinomycin-doped plasticized PVC membranes.

Potential Stability. The potential stability of all SC-ISEs was studied by comparing the potential drift for different electrode assemblies in 100 mM KCl solution at a constant temperature (25 °C) controlled with a thermostat. To assess the contribution of the reference electrode to the measured potentials, the potential of one reference electrode was measured relative to a second identical reference electrode. This measurement showed a residual drift of $7.5 \mu V/h$ over 80 h. While this value is not the drift

Table 2. Potential Stability of Different Freshly Prepared Electrode Assemblies in 100 mM KCl Solution

substrate	drift $\mu V/h$
Ni/3DOM carbon	210 (over 96 h)
Ni/3DOM carbon/PVC	11.7 (over 70 h)
Ni/HOPG/PVC	77.0 (over 96 h)
Ni/PVC	280 (over 144 h)

associated with one individual reference electrode, it suggests that the residual drift associated with one reference electrode is at least on the order of $7.5 \mu V/h$. In comparison, the potentials of 3DOM carbon-contacted ISEs relative to the same reference electrode were very stable (see Table 2). Their potential drifts over 70 h were only $11.7 \pm 1.0 \mu V/h$ or 0.28 ± 0.02 mV/day (average for three electrodes). The potential stabilities were rechecked after the electrodes were kept in 100 mM KCl solution for 1 month. The potential drift of the 3DOM carbon-contacted ISE was still very small ($10.8 \mu V/h$ over 185 h), while the potential drift of the Ni/HOPG/PVC electrode worsened further (from $77.0 \mu V/h$ over 96 h to $114.6 \mu V/h$ over 144 h).

Other solid contacts that have been reported to be used in SC-ISEs exhibited significantly larger potential drift, e.g., the potential drifts were $30 \mu V/h$ (over 72 h) and $100 \mu V/h$ (over 72 h) for PPy- and hydrogel-contacted ISEs, respectively.¹⁸ In contrast, the potential drift of the electrode with HOPG as the intermediate is much larger ($77.0 \mu V/h$), indicating the presence of a “blocked” interface due to the absence of an ion/electron conductor. With $280.0 \mu V/h$, the potential drift of the Ni/PVC electrode between the polymeric membrane and the Ni electrode was even worse.

The high stability of the 3DOM carbon-contacted SC-ISEs reported here is related to the bicontinuous electron- and ion-conducting structure of the interlayer. On one hand, the well-interconnected wall structure of the 3DOM carbon provides a continuous pathway for electron conduction. On the other hand, ionic conductivity is provided by a continuous network of interconnected pores that are filled with the ionophore-doped solvent polymeric phase containing the cationic valinomycin complexes and the tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate as ionic species.^{38,39} The 3DOM carbon/polymer composite interlayer shares the mixed ion- and electron-conducting property with semiconducting polymers but lacks the photon sensitivity and surface hydrophilicity that many of the latter exhibit. Moreover, the bicontinuity of the two phases appears to be an excellent means to prevent delamination of the electron and the ion conductor.

Effect of Oxygen and Carbon Dioxide on the Potential Stability. Interferences from O_2 and CO_2 have been reported for several SC-ISEs. Both gases can easily permeate through the polymeric membrane. While CO_2 can affect the local pH at the surface of the metal contact (or more generally, the electron conductor), it has been reported that the formation of an oxygen half-cell can affect the phase boundary potential at that surface.⁴⁵ The PPy-contacted ISEs show different levels of interference from

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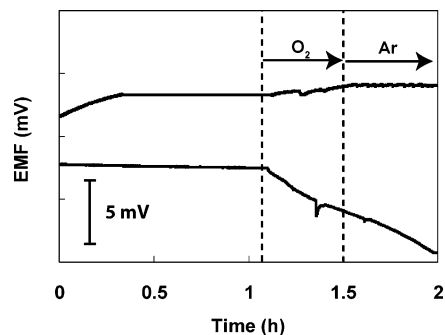


Figure 3. Effect of oxygen on the potential stability of SC-ISEs with different electrode assemblies in 100 mM KCl solution: (top) Ni/3DOM carbon/PVC, (bottom) Ni/HOPG/PVC.

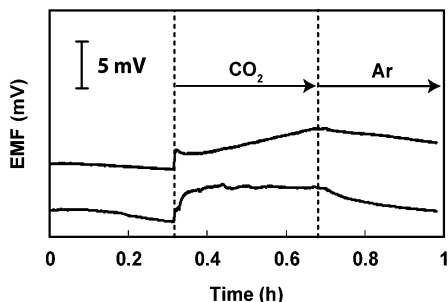


Figure 4. Effect of carbon dioxide on the potential stability of SC-ISEs with different electrode assemblies: (top) Ni/3DOM carbon/PVC, (bottom) Ni/HOPG/PVC.

O₂ depending on the type of doping ion and the PPy film thickness.^{16,46}

In this study, a possible interference of O₂ on the K⁺ response was tested by immersion of the electrodes into 100 mM KCl solution and alternating saturation of the solution with O₂ and Ar by bubbling the respective gas into the solution while recording the electrode potentials. As shown in Figure 3, a small potential increase of 0.82 ± 0.02 mV was observed upon O₂ exposure of 3DOM carbon-contacted electrodes. Figure 3 also shows a -2.6 ± 0.1 mV drift over 30 min for a HOPG-contacted electrode, which is more than 3 times larger than for the 3DOM-contacted electrode but still better than expected in the presence of an ill-defined interfacial potential. Indeed, even for a PPy-coated glassy carbon electrode coated with a valinomycin-doped solvent polymeric membrane, a drift of 25 mV/h was reported in the literature.⁴⁶

CO₂ has been shown to interfere with SC-ISEs by altering the local pH at the solid contact.^{25–31} For this study, the effect of CO₂ on the K⁺ response was determined by bubbling CO₂ emitted from dry ice into a 100 mM KCl solution (see Figure 4). Both the 3DOM carbon- and the HOPG-contacted ISE show a larger potential drift (11.8 ± 1.5 mV/h and 12.8 ± 1.6 mV/h, respectively) than in the case of O₂. The sensitivity to CO₂ of the 3DOM carbon-contacted ISE is of the same magnitude as for poly(3,4-ethylenedioxythiophene)-contacted SC-ISEs (8 to ~ 10 mV/h) and less than for PPy-contacted electrodes (25 to ~ 30 mV/h).⁴⁶

Test for an Aqueous Layer at the 3DOM Surface. The formation of an aqueous layer between the polymeric sensing membrane and the underlying contact, as for example reported for highly plasticized PVC membranes with PPy contacts, not only

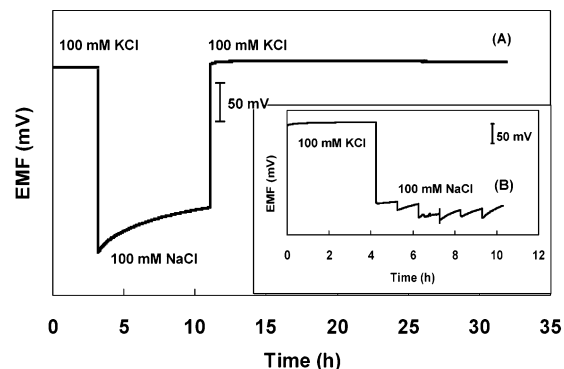


Figure 5. Response of a 3DOM carbon-contacted K⁺-selective electrode: (A) At $t = 3.2$ h, the conditioning solution (100 mM KCl) was exchanged for 100 mM NaCl; at $t = 11.0$ h, the sample was replaced by the conditioning solution. (B) At $t = 4.3$ h, the conditioning solution (100 mM KCl) was exchanged for 100 mM NaCl, which was then replaced five times by fresh 100 mM NaCl solution in intervals of 60 min.

causes mechanical failure but also leads to chemical hysteresis caused by the distribution of ions or carbon dioxide into this aqueous layer. Fibbioli et al. suggested that such a thin aqueous layer was the main source of potential instability of SC-ISEs and proposed a method to test for the presence of such an aqueous layer.⁴⁷ Potential drifts upon replacing the primary ions in the measuring solution with discriminated interfering ions, or the reverse, are indicative of the presence of an aqueous layer between the solid contact and the membrane. The presence of an aqueous layer is indicated by a positive potential drift when changing from primary ions to interfering ions and a negative potential drift when changing from interfering ions to primary ions. This can be explained by transport of the relevant ions from the sample through the ionophore-doped membrane into the aqueous layer and vice versa.

Corresponding experiments were carried out for SC-ISEs with 3DOM carbon as the solid contact (Figure 5). Upon conditioning of electrodes in 100 mM KCl solution for 24 h, the solution was changed to 100 mM NaCl. As soon as the solution was changed, an instantaneous emf shift of -220 mV was observed (curve A). This is caused by the change in the phase boundary potential at the PVC/outer sample solution interface and reflects the membrane selectivity. Over the next several hours, a positive drift was observed (curve A). However, no negative potential drift was observed when the sample solution was changed back to 100 mM KCl. On the basis of the theory of Fibbioli et al., the existence of an aqueous layer would be indicated by a positive potential drift when changing from K⁺ to Na⁺ and a negative potential drift when changing back from Na⁺ to K⁺ (see, e.g., Figure 3 in ref 47). Evidently, our results differ from what is expected as there is no drift on the return to K⁺. To understand the reason for the positive potential drifts, the potential was recorded while the electrode was kept in 100 mM KCl solution for 24 h, and the solution was then changed to 100 mM NaCl solution, followed by repeated replacement of the solution with fresh 100 mM NaCl every 60 min (Figure 5, curve B). Each time the NaCl solution was replaced, a drop of potential was observed, indicating a contamina-

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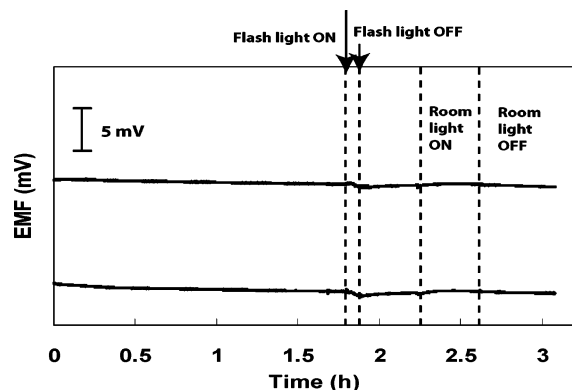


Figure 6. Effect of light on the potential stability of SC-ISEs with different electrode assemblies in 100 mM KCl solution: (top) Ni/3DOM carbon/PVC, (bottom) Ni/HOPG/PVC.

tion of the NaCl solution with K^+ continuously leaching from the PVC membrane. This is the main reason for the potential drifts upon changing to NaCl solution. The only evidence that might indicate an aqueous layer is that the potential upon return to 100 mM KCl is 4 mV higher than for the initial KCl solution and that there is some carbon dioxide interference (see above). The comparatively small size of both effects suggests that the hydrophobic surface of 3DOM carbon as prepared in this study suppresses the formation of an aqueous layer. We are currently investigating whether the 4 mV difference can be further reduced by chemical modification of the 3DOM carbon surface.

Effect of Ambient Light on the Potential Stability. SC-ISEs can be photoresponsive if the intermediate layer between the polymeric membrane and the underlying metal electrode is an organic semiconductor with a suitable band gap. To investigate the light sensitivity, electrodes prepared in this study were immersed into a 100 mM KCl solution. Continuously recorded potentials are presented in Figure 6. During the experiment, the whole electrochemical cell was kept in the dark until the electrodes were exposed either to a flashlight for 6 min or to ambient room light for 20 min, followed each time by a return to

the dark. In both experiments, no significant drift was observed, indicating that the 3DOM carbon-based layer is insensitive to light.

CONCLUSIONS

This paper presents a new approach to fabricate SC-ISEs by using 3DOM carbon. Our results show that the 3DOM carbon layer containing the ionophore-doped polymeric phase is capable of both ionic and electronic charge transfer. The 3DOM carbon-contacted electrode provided a good Nernstian response to potassium, with a detection limit of $10^{-6.2}$ M, which is similar as for typical SC-ISEs with conducting polymer contacts. Importantly, the 3DOM carbon-contacted electrode was found to exhibit a greatly improved long-term potential stability, and it had good resistance to the interferences from O_2 and light. Interestingly, there was no clear evidence for the formation of an aqueous layer, which is probably the result of the rather hydrophobic character of the surface of 3DOM carbon. In conclusion, the excellent potential stability makes 3DOM carbon-contacted electrodes promising for miniaturization and mass fabrication. We are currently studying the impedance properties of 3DOM carbon to better understand its surface chemistry and the effect of its high interfacial capacitance on the response behavior and offset voltage of these SC-ISEs.

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