Tungsten trioxide (WO_3) as an actuator electrode material for ISFET-based coulometric sensor-actuator systems

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Abstract

Acid or base concentrations can be determined by performing an acid–base titration with OH^- or H^+ ions, coulometrically generated by the electrolysis of water at a noble metal actuator electrode. This can be done very rapidly if the actuator electrode is in close proximity to an ISFET which is used as the indicator electrode to detect the equivalence point in the titration curve.

In order to restrict the effect of interfering redox reactions at the actuator electrode during coulometric generation, electroactive actuator materials have been studied which can exchange H^+ ions at a lower electrode potential than the potential of anodic water electrolysis.

In this paper, electrochemically grown tungsten trioxide (WO_3) is proposed as an actuator electrode material. At a WO_3 electrode, H^+ ions can be generated by a redox reaction at approximately 0.1 V versus SCE in a mildly alkaline solution (0.5–7 mM KOH) (anodic water electrolysis at a Pt electrode occurs at 1.5 V versus SCE). The observed thermodynamic and kinetic behaviour of the redox reaction is in good agreement with the theoretical predictions.

Disadvantages of WO_3 are its slow dissolution in aqueous solutions and the restriction that a titration at a WO_3 electrode can only be performed in alkaline solutions.

Introduction

Coulometric generation of H^+ or OH^- ions by the electrolysis of water at a noble metal actuator electrode permits the control of the pH at the surface of that electrode. Depending on the direction of the current through the actuator electrode, one of the following reactions occurs:

The ions thus generated are used as a titrant to perform an acid–base titration in a small volume formed by the area of the actuator electrode, typically 1 mm^2 , and the thickness of the occurring diffusion layer. Hence the measurement is carried out in a volume of a few microlitres, while the remainder of the sample solution is unaffected.

By placing a pH-sensitive ion-sensitive field-effect transistor (ISFET) in close proximity

to the actuator electrode, one can measure the resulting concentration change of H^+ or OH^- ions. The rate of this change is related to the bulk concentrations of the buffering components in the solution [1].

The sensor–actuator device is shown schematically in Fig. 1. Figure 2 shows a typical registration of a coulometric titration carried out in an alkaline solution with an

Fig. 1. Basic components of the acid–base concentration sensor.

Fig. 2. Typical coulometric titration ($t_{eq}=1.01$ s) with an ISFET–platinum sensor–actuator device in 2 mM KOH (+0.1 M KNO_3). V_{ISFET} is the ISFET amplifier output signal and V_{Pt} the Pt electrode potential.

ISFET–platinum sensor–actuator device. The actuator electrode current density was $20 \mu\text{A}/\text{mm}^2$. The equivalence time t_{eq} , i.e., the time needed to reach the equivalence point in the titration curve, depends on the acid or base concentration of the bulk. A model has been presented [2] describing the relation between t_{eq} and this bulk concentration.

The potential of the actuator electrode reaches a value of 1.5 V versus SCE during the titration. All potentials in this paper are mentioned relative to a saturated calomel electrode (SCE). A redox couple with a standard potential <1.5 V, present in the solution, might interfere with the anodic water electrolysis at the actuator electrode. Such reactions affect the actual measurement of the equivalence time; a longer time will be needed to reach the equivalence point in the titration curve, because the electron to proton efficiency of eqn. (1) decreases if this redox reaction occurs first.

This situation is shown in Fig. 3. Cl^- ions were added to the solution in which the experiment of Fig. 2 was carried out and the experiment was repeated. The reaction $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^-$ ($E^\circ=1.12$ V), which apparently occurs at the resulting Cl^- concentration (~ 50 mM) at a potential <1.5 V, affects the titration curve, resulting in a higher value for the equivalence time t_{eq} as compared with the experiment of Fig. 2.

In order to restrict the effect of Cl^- and other interfering redox couples, electroactive materials have been studied which can ex-

Fig. 3. Coulometric titration ($t_{eq}=1.46$ s) in a solution containing interfering Cl^- ions (2 mM KOH + 50 mM KCl + 0.1 M KNO_3). The actuator electrode current density was $20 \mu\text{A}/\text{mm}^2$.

change H^+ or OH^- ions at a lower potential than the potential where anodic electrolysis of water occurs (but higher than the potential of cathodic water electrolysis). Furthermore, the exchange of ions must be reversible, exclusive and fast as compared with the time taken to reach the equivalence point.

In this respect iridium oxide (Irox) and tungsten trioxide (WO_3) have been studied as possible new actuator materials. In this paper, however, the discussion is limited to WO_3 ; Irox will be discussed separately [3]. Only electrochemically grown WO_3 films will be discussed, because these WO_3 films are expected to have better properties (increased porosity, greater proton mobility) for the intended application than evaporated WO_3 films [15].

Electrochemistry of tungsten trioxide

In a solution containing small monovalent cations, e.g., H^+ , Na^+ , Li^+ , an electrochromic process can take place at a WO_3 electrode. Electrochromism is the property of a material in contact with an electrolyte whereby it changes colour reversibly in response to an applied potential.

Many studies on the electrochromic property of a WO_3 electrode have been published; these concern the fundamental nature of the colouration process and the practical aspects of interest in the construction of WO_3 -film display devices [e.g., 4, 5]. For the research

project described in this paper, the interest in WO_3 as an actuator material stems from the known exchange of protons during the electrochromic process [4, 5, 15].

The electrochromic process occurs according to the following reaction [5, 15]:

where M is usually a hydrogen ion, but may also be one of the other small cations mentioned. However, insertion of Li^+ and Na^+ ions occurs at relatively high potentials [4] (higher than the potential of anodic water electrolysis). Thus within the potential range determined by cathodic and anodic water electrolysis, M is exclusively a proton.

Insertion of protons reduces the W ion from W^{6+} in WO_3 to W^{5+} in H_xWO_3 [6]. Hitchman showed by analysing the equilibrium potentials involved that x in H_xWO_3 can reach a maximum of ~ 0.5 [7].

Thermodynamic properties

H^+ insertion into H_xWO_3 film electrodes causes a smooth decrease in the standard electrode potential with increasing x .

Crandall *et al.* [8] have reported the variation in the WO_3 standard electrode potential E° during H^+ insertion. They found an expression for E° , derived from their experimental electrode potential data, which is given here versus SCE:

$$E_{\text{H}_x\text{WO}_3}^\circ = -0.08 - 0.53x - 2 \frac{RT}{F} \ln\left(\frac{x}{1-x}\right) \quad (4)$$

Figure 4 shows a graphical representation of eqn. (4). The standard potential of H_xWO_3 at $x=0.36$ is equal to the standard potential

Fig. 4. Standard potential of a H_xWO_3 electrode as a function of x .

of cathodic electrolysis of water (i.e., -0.24 V). Values for x in excess of this may only be obtained by applying potentials at which H_2 evolution occurs simultaneously with H^+ insertion.

In a practical application of WO_3 as an actuator electrode in the coulometric sensor-actuator device, potentials at which electrolysis of water occurs must be avoided. As a result, x in H_xWO_3 will always be smaller than 0.36.

Kinetics

The insertion and release of protons at a WO_3 electrode occur according to two different mechanisms [9, 10] which will be described separately.

Proton insertion

During insertion of protons, the WO_3 electrolyte interface plays a critical role. Speed limitations due to diffusion of electrons or protons in the WO_3 film appear to be unimportant for practical applications.

After a cathodic potential step has been applied to the WO_3 electrode, the current density $j_i(t)$ due to insertion of protons in an infinitely thick WO_3 film can be written as [11]

$$j_i(t) = F \left[\frac{D_{\text{H}}}{\pi t} \right]^{1/2} (C_b - C_s(t)) \quad (5)$$

where D_{H} is the diffusion coefficient of H^+ in the aqueous phase ($9.3 \times 10^{-9} \text{ m}^2/\text{s}$), F is the Faraday constant ($96.5 \times 10^3 \text{ C/mol}$), C_b the H^+ bulk concentration and $C_s(t)$ the H^+ concentration at the surface of the WO_3 electrode.

$C_s(t)$ depends on the equilibrium of the reaction

If the equilibrium is totally shifted to the right-hand side (x has the maximum value of ~ 0.5), $C_s(t)$ will be zero. However, as previously described, in a practical application x must be smaller than 0.36 to avoid cathodic electrolysis of water. The equilibrium of the reaction thus results in a $C_s(t) > 0$.

After the potential step has been applied, the equilibrium of the reaction is established so fast that $C_s(t)$ can be supposed to be constant during the subsequent insertion of

protons. This means that the current density $j_i(t)$ is proportional to $t^{-1/2}$.

Proton release

During release of protons, the positive (protons) and negative (electrons) charges in the WO_3 film must be separated and exit from opposite sides of the film. Due to the large ratio of electron to proton mobility in the WO_3 film, the current density is fully determined by the space-charge-limited current flow of protons through the film. Hence, the voltage drop across the film entirely appears across the proton space-charge region.

After an anodic potential step has been applied to the WO_3 electrode, the current density $j_r(t)$ due to the release of protons can be written as [10]

$$j_r(t) = k \frac{V^{1/2}}{(4t)^{3/4}} \quad (6)$$

where k is a constant determined by WO_3 material properties and V is the potential across the film. As V and k are constant, the current density is thus proportional to $t^{-3/4}$.

Electronic transport properties

Insertion of protons in WO_3 films is accompanied by a large increase in electronic conductivity of the film. Crandall and Faughnan [12] have reported that the conductivity at 300 K of a thermally evaporated WO_3 film was increased from $\sim 1 \times 10^{-6} (\Omega \text{ cm})^{-1}$ for $x=0$ to $2 \times 10^{-3} (\Omega \text{ cm})^{-1}$ for $x=0.06$ and to $2 (\Omega \text{ cm})^{-1}$ for $x=0.24$.

However, because of the small film thickness of the actuator electrode and the use of current control, this change in conductivity will not affect the practical operation of the sensor-actuator device.

Experimental

For characterization experiments of the WO_3 films, small tungsten particles (99.9%, Micropure) were pulverized and evaporated ($2 \mu\text{m}$) on top of a Ti film (30 nm) that serves as an adhesion layer between the W film and the underlying tantalum oxide (Ta_2O_5) (which was deposited on top of an oxidized silicon wafer). After dicing, $5 \text{ mm} \times 5 \text{ mm}$ pieces were glued on a piece of printed

(b)

Fig. 5. (a) Top view of the actuator electrode as deposited on an ISFET. (b) Cross section of the ISFET- WO_3 sensor-actuator device.

circuit board and bonding wires were connected to the W film. The bonding wires and the edges of the chip were protected by epoxy, resulting in an area of $20\text{--}22 \text{ mm}^2$ which can be in contact with the solution.

Next, a WO_3 film was grown electrochemically by passing a current with a constant anodic current density of 6 mA/cm^2 for 4 min through the W film electrode with respect to a platinum counter electrode in a $1 \text{ M H}_2\text{SO}_4$ solution. This electrochemical oxide formation and the subsequent characterization experiments were carried out with a PAR (model 173/276) potentiostat/galvanostat.

The pH-sensitive ISFET in the sensor-actuator device was fabricated following the usual ISFET processing steps [13, 14]. For the actuator electrode a W film ($0.5 \mu\text{m}$) was evaporated around the gate, using a lift-off technique for patterning, on top of a Ti film (30 nm) for adhesion of the W film on

Fig. 6. Measurement set-up for the titration experiments.

the underlying tantalum oxide. A layer of polyimide was used to determine the active area (1 mm^2) of the actuator electrode to be in contact with the solution. The chip ($3 \text{ mm} \times 4 \text{ mm}$) was glued on a piece of printed circuit board and the bonding wires were protected by epoxy. On the active area of the actuator electrode a WO_3 film was grown electrochemically in a $1 \text{ M H}_2\text{SO}_4$ solution using a constant current density of 6 mA/cm^2 for 4 min. Figure 5 shows the resulting shape of the actuator electrode.

The measurement set-up for the titration experiments is shown in Fig. 6. After the (computer-controlled) current source is turned on, both the output signal of the ISFET amplifier and the actuator electrode potential are 250 times sampled by the multichannel A/D converter (Keithley system 570, typical input resistance $> 100 \text{ m}\Omega$) with an accuracy of 1.25 mV .

Results and discussion

Characterization of WO_3 films

WO_3 films grown with a constant anodic current density are porous and hydrated. Reichman and Bard [15] have undertaken a study correlating the differences in the rate of the electrochromic process and the differences in water content in WO_3 films. They demonstrated that an increase of the water content in a WO_3 film results in an increase in the rate of the electrochromic process.

The water content in the WO_3 film directly after the growing process can be increased by continuous potential cycling (scan rate 100 mV/s) between -0.25 and 0.75 V in a $1 \text{ M H}_2\text{SO}_4$ solution. Typical current-potential curves (i.e., cyclic voltammograms) during continuous cycling directly after growing are shown in Fig. 7.

Fig. 7. Cyclic voltammograms during continuous cycling (100 mV/s) in $1 \text{ M H}_2\text{SO}_4$. Curve 1, directly after growing; 2, after 135 cycles; 3, after 405 cycles; 4, after 945 cycles and 5 after 3825 cycles.

For potentials $> 0.3 \text{ V}$ the current is very small, which is in good agreement with the theory; for electrode potentials $> 0.3 \text{ V}$, x in H_xWO_3 is zero (see Fig. 4). If the potential is decreasing to a value $< 0.3 \text{ V}$, a cathodic current due to insertion of protons results. During the entire potential range from 0.3 to -0.25 V (where cathodic electrolysis of water begins) protons are inserted and x in H_xWO_3 increases to $x = 0.36$ at -0.25 V (see Fig. 4). After the scan reversal at -0.25 V , protons will be released and an anodic current results during the entire potential range until $x = 0$ at $\sim 0.3 \text{ V}$.

The area of the cyclic voltammogram is a measure for the amount of exchanged charge. During continuous cycling the area of the curves and thus the exchanged charge increases, which might indicate that an electrochromic process occurs in a larger volume of the film. The increase in the porosity and the water content enhances the diffusion process, since the film becomes a better ionic conductor (protons can be transported via H_3O^+ by exchange between adjacent water molecules). Figure 8 shows the increase in exchanged charge (i.e., the area of the cyclic voltammogram) during continuous cycling.

The cyclic voltammogram also becomes more featured during continuous cycling, indicating an increase in the rate of the redox process; the current response on the change in the electrode potential (according to the scan rate) becomes faster.

Fig. 8. Change in charge capacity of WO_3 during continuous cycling. The numbers correspond to the cyclic voltammograms in Fig. 7.

Fig. 9. Measured WO_3 electrode potential in open-circuit configuration in 1 $\text{M H}_2\text{SO}_4$. Curve 1, solution with dissolved oxygen; curve 2, deaerated solution.

The increase in the water content during cycling is a one-way process; after the cycling process the water content does not change any more even if the film is kept in a dry environment for several weeks. The cycling procedure can thus be seen as a preconditioning process for practical application of WO_3 actuator electrodes.

To determine the stability of the different oxidation states of WO_3 , the film was reduced to $\text{H}_{0.4}\text{WO}_3$ by a cathodic potential of -0.25 V in a 1 $\text{M H}_2\text{SO}_4$ solution. Afterwards the electrode potential was measured in an open-circuit configuration with the Keithley A/D converter connected to the computer system. The solution was stirred to avoid uncontrolled convection and possible concentration gradients.

The result is shown in Fig. 9, curve 1. At $t=t_0$, the reduced WO_3 electrode is disconnected from the potentiostat and the electrode

potential is measured. Within 2 min, the electrode potential has drastically increased. The $\text{H}_{0.4}\text{WO}_3$ film is now fully oxidized to WO_3 ($x=0$) due to the reaction with oxygen dissolved in the solution.

The same experiment was carried out in a solution which was deaerated by purging with nitrogen. The result is shown in Fig. 9, curve 2. Now the change in the electrode potential is much less because practically no oxidation takes place. The small increase in the electrode potential is probably due to a gas leak in the set-up, resulting in a small amount of oxygen in the solution.

To examine the kinetics of the electrochromic process, potential step experiments were carried out. In a 3 $\text{mM H}_2\text{SO}_4$ solution the electrode potential was stepped at $t=t_1$ from 0.4 to -0.35 V, which corresponds with an increase of x in H_xWO_3 from 0 to ~ 0.35 . At $t=t_2$ the potential was stepped to 0.4 V again. Figure 10 shows the current as a function of the time.

According to eqn. (5) the current due to insertion of protons is directly proportional to the bulk concentration. However, eqn. (5) is only valid if there is an unlimited amount of WO_3 to be reduced. If the bulk concentration is very high, the film totally reduces in a short time due to a large initial current. Thus eqn. (5) is only valid for a very short period of time. For bulk concentrations < 10 mM, the exchanged current after a few seconds (according to the integrated eqn. (5)) is comparable to the charge capacity of the film. For these concentrations eqn. (5) is a good theoretical description.

Fig. 10. Measured current response on potential steps. At $t=t_1$, $0.4 \rightarrow -0.35$ V; at $t=t_2$, $-0.35 \rightarrow 0.4$ V.

In order to investigate in more detail the current decay after $t=t_1$ and $t=t_2$ (Fig. 10) with respect to the theory (eqns. (5) and (6)), Fig. 11 shows the current after $t=t_1$ and $t=t_2$ as a function of $t^{-1/2}$ and $t^{-3/4}$, respectively.

In Fig. 11(a) the current due to insertion of protons after the cathodic potential step at $t=t_1$ is shown as a function of $t^{-1/2}$. The central part of the curve is linearly proportional to $t^{-1/2}$, which is in agreement with eqn. (5). The measured slope of the line is $1.0 \times 10^{-3} \text{ A s}^{1/2}$. According to eqn. (5), the theoretical slope of the line is $0.7 \times 10^{-3} \text{ A s}^{1/2}$ for an electrode surface of 21 mm^2 and assuming that $C_b - C_s \cong C_b$ ($=6 \text{ mM}$). Thus the measured slope is in fair agreement with the theory.

For small values of t (i.e., large values of $t^{-1/2}$) the current deviates from the linear behaviour. For these values of t , x in H_xWO_3 is still very small and thus the electric conductivity of the film is very small. The current is then limited by the resistance of the film.

(a)

(b)

Fig. 11. (a) Current due to the cathodic potential step at $t=t_1$ in Fig. 10 as a function of $t^{-1/2}$. (b) Current due to the anodic potential step at $t=t_2$ in Fig. 10 as a function of $t^{-3/4}$.

For large values of t (i.e., small values of $t^{-1/2}$) the current also deviates from the linear behaviour due to the saturation of the film with protons because all the WO_3 is reduced.

In Fig. 11(b) the current due to the release of protons after the anodic potential step at $t=t_2$ is shown as a function of $t^{-3/4}$. The central part of the curve has the expected linear behaviour according to eqn. (6). For very small and very large times the current deviates from the linear behaviour due to capacitive effects of the double layer at the electrode surface and the limited amount of protons available.

Titration experiments

Titration experiments were carried out in different alkaline solutions (in 20 ml 0.1 M KNO_3 supporting electrolyte) with an OH^- concentration ranging from 0.5 to 7 mM. Before the titration experiments were started, the solution was deaerated with nitrogen to reduce the effect of oxidation by dissolved oxygen.

A typical registration of a coulometric titration with a WO_3 actuator electrode is shown in Fig. 12. This titration was started 30 s after the WO_3 actuator electrode was totally charged with protons by reducing the film with a cathodic current until the electrode potential reached the value that corresponds with the totally reduced state in this solution.

The potential of the actuator electrode reaches $\sim 0.1 \text{ V}$, which is very auspicious regarding possible interfering redox couples. As compared with a platinum actuator elec-

Fig. 12. Typical coulometric titration ($t_{eq}=2.08 \text{ s}$) with an ISFET- WO_3 sensor-actuator device in a 2 mM $\text{KOH} + 0.1 \text{ M KNO}_3$ solution. The actuator electrode current density was $20 \mu\text{A}/\text{mm}^2$.

trode, whose potential reaches 1.5 V, WO₃ is thus a major improvement.

Adding 50 mM KCl and 2 mM KI did not affect the result of the titration at all. The reactions

and

did not occur at the WO₃ electrode, which was in agreement with our expectations.

Figure 13 shows the measured equivalence time t_{eq} as a function of the OH⁻ concentration (curve 1) as well as the equivalence time according to the theoretical model presented in ref. 2 (curve 2). The current density through the actuator electrode was 20 $\mu\text{A}/\text{mm}^2$.

The experimental curve has a constant time offset of 0.9 s as compared with the theoretical curve. This is due to the fact that the theoretical model describes the generation of protons at the surface of a noble metal actuator electrode and in reality protons are generated inside the WO₃ electrode and presumably need some time to reach the surface of the electrode. The slope of the measured curve is in good agreement with the theoretical model.

If the solution is not deaerated, the WO₃ actuator electrode potential remains sufficiently stable during the 30 s wait after charging the electrode with protons by a cathodic current. Therefore, the stability of the WO₃ actuator electrode, with respect to oxidation by dissolved oxygen, is satisfactory for the

determination of the OH⁻ concentration by a coulometric titration.

A problem for long-term practical application of WO₃ as an actuator material is the chemical stability of WO₃ in alkaline solutions [5, 16]. The dissolution rate of WO₃ in aqueous solutions increases with increasing pH. In a solution with an OH⁻ concentration of 1 to 10 mM, a WO₃ actuator electrode is visibly affected after intensive use for 4–6 h. Further research must be carried out to investigate whether the chemical stability can be improved or not. For iridium oxide it is known that a temperature treatment increases the chemical stability without increasing the response time [17].

Titration in an acidic solution by means of insertion of protons (as an indirect way of generating OH⁻ ions via the water equilibrium) in the WO₃ actuator electrode are not possible. Because the equilibrium of the reaction

is not totally shifted to the right-hand side, due to the necessary limitation of x to avoid cathodic water electrolysis, the H⁺ concentration at the electrode surface does not decrease sufficiently to reach the equivalence point in the titration curve.

Conclusions

The observed thermodynamic and kinetic behaviour of the redox process at an electrochemically grown WO₃ electrode is in good agreement with the theory described.

Electrochemically grown WO₃ can be used as an actuator material in the described sensor-actuator system to determine base concentrations. The measurements are in good agreement with the theoretical model described in ref. 2.

The major advantage of a WO₃ electrode as compared with a noble metal actuator electrode is the low potential at which protons are released in alkaline solutions. Hence the measurement is less sensitive to possibly interfering redox couples. A coulometric titration in the presence of Cl⁻ and of I⁻ ions, formerly not possible with the ISFET-platinum sensor-actuator device, is possible without any interference.

Fig. 13. Results of coulometric titration of KOH. Curve 1, measurement results; curve 2, results of the theoretical model.

Disadvantages are the slow dissolution of WO_3 and the restriction to alkaline solutions.

If the sensor-actuator device must operate in alkaline as well as in acidic solutions, another actuator material must be used (e.g., iridium oxide [3]). During insertion of protons, the equilibrium of the redox reaction at this actuator electrode must result in a proton surface concentration which is sufficiently small to reach the equivalence point.

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Biographies

Joost van Kerkhof was born in Wijk bij Duurstede, the Netherlands, on August 10, 1965. He received the M.S. degree in electrical engineering from the University of Twente, the Netherlands, in February 1990. The research described in this paper was part of his M.S. program. He will probably start Ph.D. research in the Biomedical Engineering Division of the Faculty of Electrical Engineering at the University of Twente.

Wouter Olthuis was born in Apeldoorn, the Netherlands, on October 23, 1960. He received the M.S. degree in electrical engineering from the University of Twente in 1986. By his work for the Centre for Micro-Electronics on solid-state electret materials for all-silicon microphones, he contacted the Biomedical Engineering Division of the Faculty of Electrical Engineering at the University of Twente, where he started his Ph.D. work on coulometric sensor-actuator systems in 1987.

Piet Bergveld was born in Oosterwolde, the Netherlands, on January 26, 1940. He received the M.S. degree in electrical engineering from

the University of Eindhoven, the Netherlands, in 1965 and the Ph.D. degree from the University of Twente, the Netherlands, in 1973. The subject of his dissertation was the development of ISFETs and related devices. Since 1965 he has been a member of the Biomedical Engineering Division of the Faculty of Electrical Engineering at the University of Twente and was appointed as full professor in biosensor technology. He is the chairman of the research unit Sensors and Actuators. His research subjects still concern the further

development of ISFETs and biosensors based on ISFET technology.

Martinus Bos received his M.S. degree in chemical technology at the Technical University of Delft, the Netherlands, in 1965. He received his Ph.D. degree in 1972 from the University of Twente for his work in analytical chemistry. He has been a staff member since 1972 of the Chemical Analysis group of the Faculty of Chemical Technology at the University of Twente. His research areas are electroanalysis and chemometrics.