Ion–selective sensors based on molybdenum bronzes

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Abstract New pH- and sodium ion-sensitive metal-oxide-type sensors have been developed and tested with a direct solid state contact method. Performance was demonstrated at ambient temperature with single crystals of several molybdenum bronzes (i.e. $Na_{0.9}Mo_6O_{17}$, $Li_{0.9}Mo_6O_{17}$, $Li_{0.33}MoO_3$ and $K_{0.3}MoO_3$). The pH sensors with Na-molybdenum-oxide bronzes show near ideal Nernstian behavior in the pH range 3–9. The response is not affected by the direction of the pH change. The response time of most molybdenum bronze pH sensors is less than 5 s for 90% response. The sodium molybdenum bronze sensor responded reproducibly and fast to changes of Na^+ concentration in the range $1–10^{-4}$ mol dm^{-3}. Cross sensitivity tests to other ions such as H^+ or K^+ have shown that the new sodium ion sensor may be used when the concentration of other ions is an order of magnitude smaller than the Na^+ concentration. pH sensors with single crystals of molybdenum oxide bronzes can be used to follow pH titrations.

Keywords Molybdenum oxide bronzes · Solid state ion-selective sensor

Introduction

In recent years the glass pH electrode has tended to supplant all other types of sensing electrodes for pH measurement [1, 2]. The hydrogen/platinum electrode nowadays is used only for thermodynamic investigations or for the accurate determination of the pH values of non-reducible buffer solutions. For in-line pH sensing, although the glass electrode is by far the most attractive choice of chemists, it is not suitable for some special applications (i.e. clinical and food applications) for obvious reasons such as mechanical fragility, high impedance, and dehydration/alkali errors at low/high pH conditions. Some of the problems of glass electrodes could be reduced by eliminating the internal reference buffer between the inner glass membrane surface and the Ag/AgCl electrode immersed in this buffer [3]. The problem consists in developing a stable contact that provides a reversible transition from the ionic to the electronic part of the sensor. In view of these problems, emphasis in recent years has shifted to the development of an all-solid-state sensor alternative for the glass electrode.

Glass electrodes for sodium ion sensing, first developed by Lengyel and Blum [4], have been studied systematically for interferences and other limitations by Eisenman et al. [5]. Modern ATI Orion sodium electrodes are glass electrodes with an internal system eliminating temperature-dependent drift. These electrodes are very stable and have relatively fast response times, but also have a number of disadvantages: they are affected by fouling of glass, or higher temperature, have a limited pH application range (7–11), and cannot be used for some special applications (e.g. food industry) [2].

Several tungsten oxide bronzes $A_xM_yWO_3$ (A = Na, K, Rb, Li, Co, Tl, etc.; M = K, Li, NH_4) in polycrystalline form have been proposed for application as ion-selective electrodes by Dobson et al. [6, 7]. These investigations, as well as earlier reports on the tungsten and other bronzes as pH sensors [8, 9, 10, 11], and the application of Na_xWO_3 for Na^+ sensing [12], prompted us to investigate the application of some of molybdenum oxide bronzes as pH sensors. Ternary molybdenum bronzes have been of interest in recent years owing to their interesting physical properties such as highly anisotropic transport properties [13, 14] and superconductivity [15, 16], and have been reviewed by Hagenmuller [17] and in more detail recently by Greenblatt

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[18]. In contrast to the tungsten bronzes, the molybdenum bronzes are stoichiometric and more stable. In addition, good quality single crystals of the Mo bronzes used as sensors have clear advantages compared to polycrystalline samples. Recently we reported preliminary investigations of some of the molybdenum bronze single crystals as pH and sodium ion sensors [19, 20, 21]. We have found that the sodium molybdenum bronze ($Na_{0.9}Mo_6O_{17}$) electrode is sensitive to changes of hydrogen ion concentration, but also shows significant cross sensitivity to other ions, e.g. Li^+, Na^+, K^+.

In this paper we review the results of studies on molybdenum bronze single-crystal electrodes for pH and sodium ion sensing and try to correlate them to the cation exchange reaction in the subsurface layer of the molybdenum bronze.

Experimental

Single crystals of the molybdenum oxide bronzes $A_xMo_yO_z$ (A = Li, Na, K) used in this work were prepared by a temperature gradient flux technique as described elsewhere [22, 23].

The cation-sensitive electrodes were fabricated by attaching conducting leads, such as a platinum wire, to the molybdenum oxide bronze single crystals with a graphite conductive adhesive (Master Bond, NJ) and coating the entire assembly with a resin. A small area of the crystal surface was exposed (i.e. not coated) and used for the sensing (Fig. 1).

The pH sensing characteristics of the membranes were evaluated by measuring their e.m.f. against a standard Ag/AgCl reference electrode with a Fisher Accumet 15 high-impedance pH meter. The pH response of the electrodes was monitored in commercially available buffer solutions, hydrochloric acid, and different bases, as well as in some titration systems.

The sodium ion sensing characteristics of the crystal membranes were evaluated by measuring their e.m.f. against a standard Ag/AgCl reference electrode. Aqueous solutions of sodium nitrate or chloride of varying pH were prepared by the addition of hydrochloric acid or sodium hydroxide solutions. The K^+ concentration was varied by the addition of potassium nitrate solutions. A fresh solution was used for each sodium ion concentration measurement. The electrode was rinsed between each measurement with sodium electrode rinse solution (0.01 M $NaNO_3$) to maintain an Na^+ sensing film on the surface of the molybdenum bronze crystal.

Results and discussion

Theoretical considerations

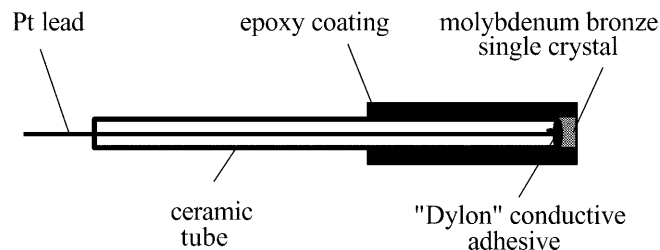It is assumed that the pH and other ion-sensing properties of molybdenum oxide bronze electrodes depend on cation-exchange reactions similar to those proposed for the tungsten bronze electrodes [24, 25]; therefore the structure of molybdenum oxide bronzes has to be considered. The A_xWO_3 phases are wide-range non-stoichiometric compounds ($0 < x < 1$); all form with perovskite-like structures. The molybdenum oxide bronzes are stoichiometric or nearly so [18]; however, there are three different classes of the ternary phases, based on stoichiometry and structure.

The structure of the hexagonal, purple bronze, $K_{0.9}Mo_6O_{17}$, can be described in terms of slabs of Mo-O corner-sharing polyhedra. The idealized structure of $K_{0.9}Mo_6O_{17}$, viewed in Fig. 2 along the a axis, shows the infinite layers of corner-sharing molybdenum-oxygen polyhedra stacked along the c axis and held together by K^+ ions in a KO_{12} icosahedral environment of oxygens.

The structure of $K_{0.3}MoO_3$ is built of ReO_3-type infinite sheets of distorted MoO_6 octahedra held together by K^+ cations (Fig. 3). The unit of the structure is 10 edge- and corner-sharing MoO_6 octahedra, which corner share to form infinite sheets along the [010] and [102] directions.

The crystal structures of the Li-Mo-O bronzes are unique. Because of the small size of the Li^+ ion, three-dimensional (3D) interconnected network structures form instead of the layer-like structures favored by the $A_{0.3}MoO_3$ (A = K, Rb, Tl) blue and $A_{0.9}Mo_6O_{17}$ (A = Na, K, Tl) purple bronzes discussed above. The structure of $Li_{0.33}MoO_3$ can be viewed as derived from an ReO_3-type shear structure of V_2O_5-like layers in the ac plane, with every fourth octahedron in the edge-shared zigzag chains being a LiO_6 octahedron [26].

The structure of the Mo bronzes is relatively open for cation-insertion or ion-exchange reactions, similar to other oxide bronzes (i.e. tungsten or vanadium oxide bronzes [27, 28]). Owing to the complex geometry of the crystal lattice of the molybdenum oxide bronzes, a distribution of ion-exchange site enthalpies and
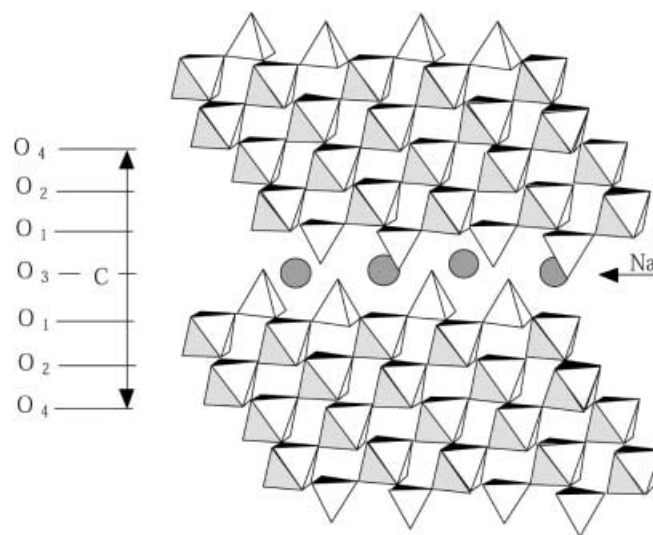
Fig. 1 Scheme of the ion-selective molybdenum bronze electrode

Fig. 2 Crystal structure of $K_{0.9}Mo_6O_{17}$
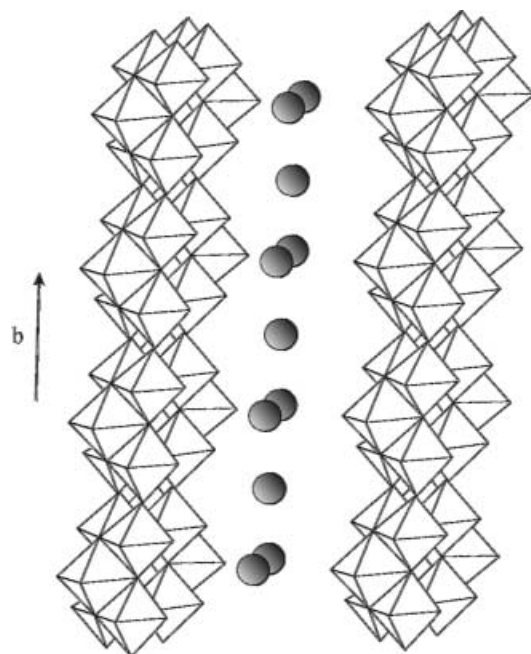
Fig. 3 Crystal structure of $K_{0.3}MoO_3$

$$I= H^+, Na^+, K^+... \qquad B= Mo_yO_z$$
$$A=Na^+, K^+, Li^+$$

Fig. 4 Schematic view of ion exchange at an interface of the molybdenum ion-selective electrode

consequently of complex ion-exchange processes would be expected. Furthermore, the structure of the molybdenum oxide bronze electrode subsurface, which determines the sensing properties, will be significantly different from that of the bulk structure.

Ion-exchange properties of the bronzes

The ideal ion-sensitive sensor should be structurally stable over a wide temperature range and provide uniform ion-exchange capacity in the measured ion-activity range [25]. In the case of layered oxides such as MoO_3, the hydrated alkali metal and hydrogen species can be replaced and interchanged by ion exchange from aqueous electrolyte solutions [29]. Similarly, when the molybdenum oxide bronze electrode contacts a solution, surface hydrolysis may occur and a proton (or other ions) exchange process establishes an interfacial potential between the solution and the bronze electrode surface (Fig. 4). The measured potential difference depends on the pH (or the concentration of other ions), when the solution/electrode interface is reversible with respect to ion (i.e. proton) exchange and the electrode/substrate (connector) is electronically reversible. At the ion-sensitive electrode surface, ions may enter in various steps. An ion from solution can cross the interface and exchange (Fig. 4a). If the ion approaches the electrode surface at an inactive site, back diffusion to the bulk of the solution may occur (Fig. 4b) or the ion from solution could diffuse on the surface of the sensor to an active site (Fig. 4c). The charge transfer is the next step in the electrode reaction, when the primary ion crosses
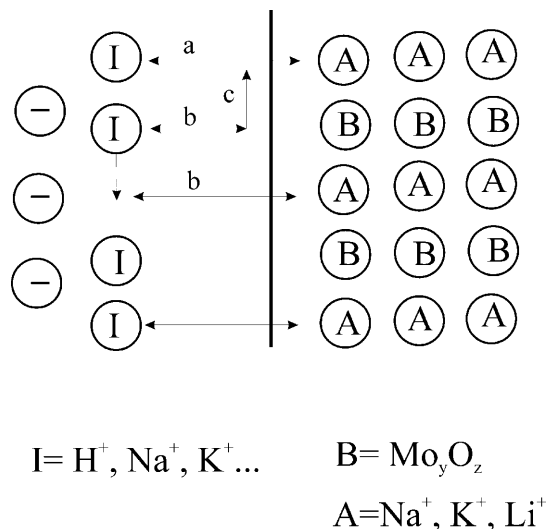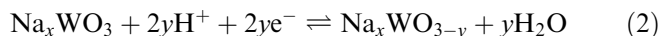
the interface to participate in the ion-exchange process. The rate-determining step in the ion exchange is the counter diffusion of ions within the solid, provided the concentration of in-going ions at the surface is high enough and stirring does not allow undue concentrations of the out-going ions to accumulate at the surface of the exchange electrode. Small particle size and a large interdiffusion coefficient favor rapid ion exchange [30]. The hydration of the ions, prior adsorption of the ion complex (e.g. $[H(H_2O)_n]^+$) on surface oxygens, and/or formation of hydroxyl groups on the surface and surface diffusion of the exchanging species, are expected to take place.

Na_xWO_3

The composition of the surface layer of the electrode during the electrochemical reaction is believed to change according to Randin et al. [24] and Fog and Buck [25]:

$$Na_xWO_3 + yH^+ + ye^- \rightleftharpoons Na_xH_yWO_3 \qquad (1)$$

In contrast, reaction (2):

$$Na_xWO_3 + 2yH^+ + 2ye^- \rightleftharpoons Na_xWO_{3-y} + yH_2O \qquad (2)$$

is less likely to be the equilibrium process involved in pH sensing, because it requires the breaking of a tungsten-oxygen bond, which is expected to be energetically less probable than the diffusion of a hydrogen ion and an electron transfer required to adjust the oxidation state of tungsten. $Na_{0.9}Mo_6O_{17}$ and $Li_{0.33}MoO_3$ show semiconducting behavior with resistivities of 0.0028–0.21 Ω cm and ~5 Ω cm, respectively, at room temperature [18]. Then, if $Na_xH_yWO_3$ is regarded as a solid solution of hydrogen atoms in the oxide network, the electrode potential for reaction (1) is given by:

Fig. 5 pH response of various single crystals of molybdenum oxide bronzes as sensors
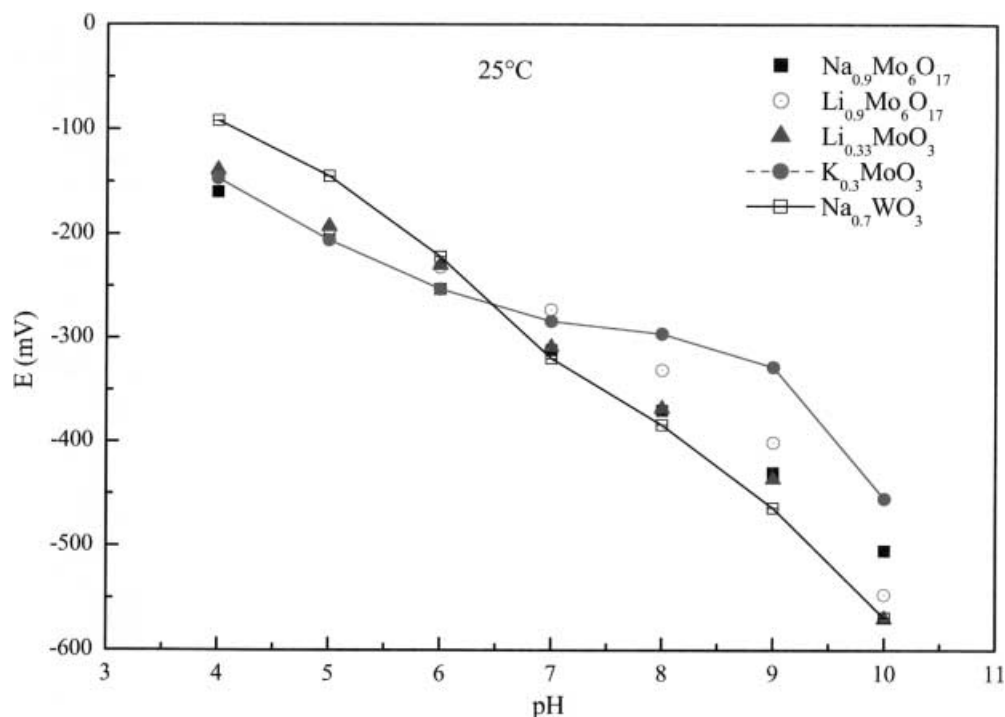
Fig. 6 Temperature-dependent pH response of a $Na_{0.9}Mo_6O_{17}$ sensor
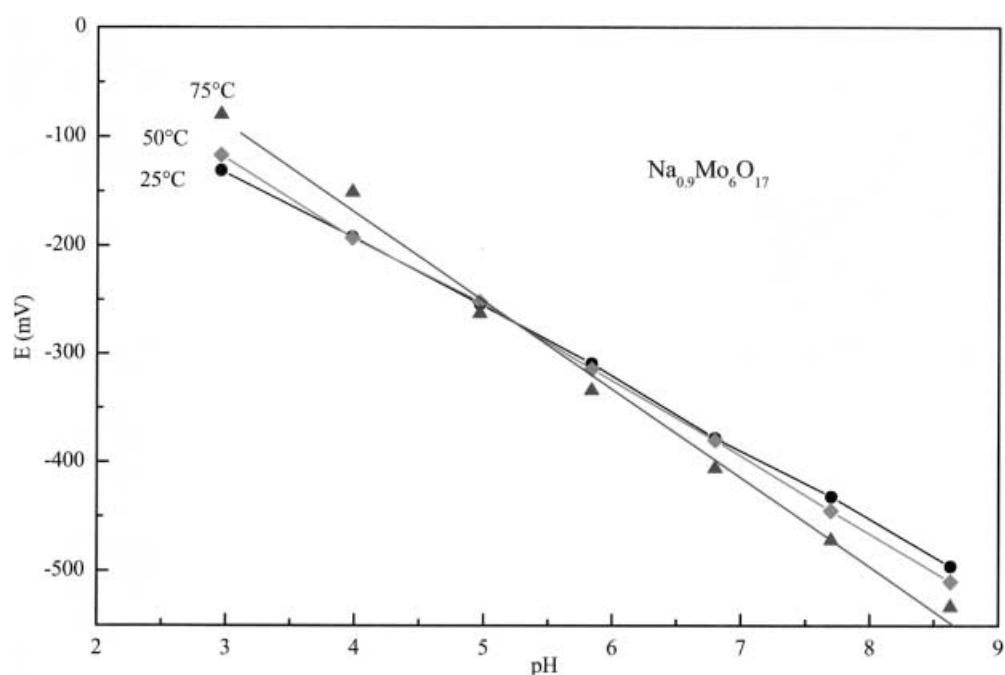
$$\Delta\phi = \frac{1}{F}\left(\mu_{H^+} + \mu_{e^-}^s - \mu_H^s\right) = \text{const.} + \frac{RT}{F}\ln(a_{H^+})$$
$$-\frac{RT}{F}\ln\left(a_H^s\right) \qquad (3)$$

where μ_H^s and a_H^s are respectively the chemical potential and the activity of hydrogen in the solid solution phase (subsurface layer of the oxide bronze).

Thus the electrode responds to hydrogen ions in the solution (a_{H^+}) as well as to hydrogen activity (a_H) in the solid-solution phase. The insertion process (Eq. 1) is probably limited to the subsurface region of the bronze electrode [25].

$A_xMo_yO_z$

The exact mechanism by which the molybdenum oxide bronze electrodes respond to changing pH conditions is not clear at present. However, because the ion-exchange-

Fig. 7 Dynamic pH response of $Li_{0.33}MoO_3$ (**a**) and $Na_{0.9}$-Mo_6O_{17} (**b**) single crystal sensors
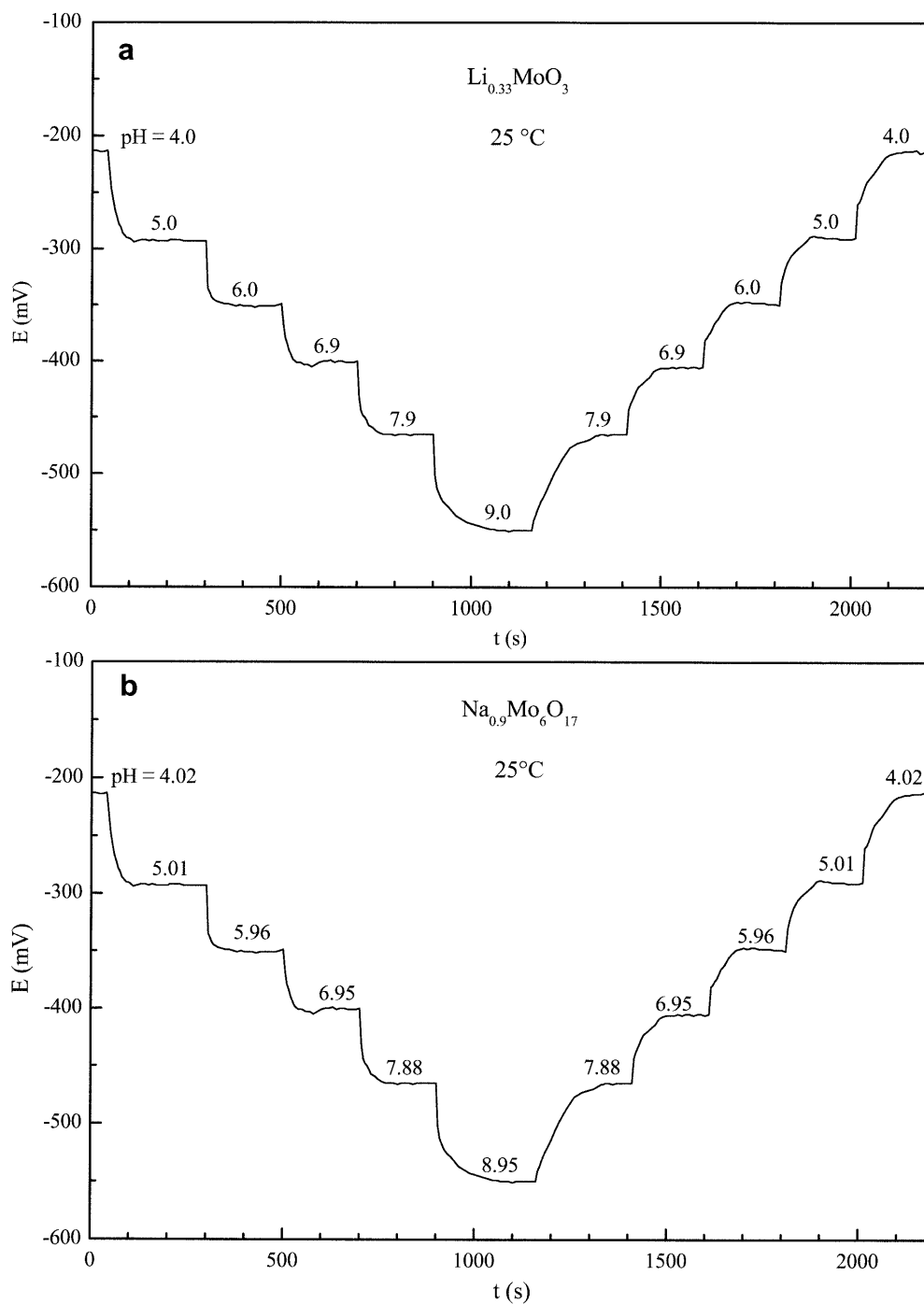
type pH sensors involve bulk and/or surface ion conductivity, two possible mechanisms can be proposed:

$$A_xMo_yO_z + \delta H^+ + \delta e^- \rightleftharpoons A_xH_\delta Mo_yO_z \qquad (4)$$

or:

$$A_xMo_yO_z + \delta H^+ \rightleftharpoons A_{x-\delta}H_\delta Mo_yO_z + \delta A^+ \qquad (5)$$

where proton insertion (4) or exchange (5) is taking place, similar to that suggested for the tungsten bronze pH sensors by Fog and Buck [25]. In the case of

molybdenum bronzes, oxygen deficiency and the formation of an oxygen-deficient phase $(A_xMo_yO_{z-\delta})$ is also unlikely. Thus, similar to the tungsten bronze electrode, if $A_xH_\delta Mo_yO_z$ is considered as a solid solution of hydrogen atoms in the oxide, the electrode potential for reaction (4) or (5) may be given by:

$$\Delta\phi = \frac{1}{F}\left(\mu_{H^+} + \mu_{e^-}^s - \mu_H^s\right) = \text{const.} + \frac{RT}{F}\ln(a_{H^+})$$
$$- \frac{RT}{F}\ln\left(a_H^s\right) \qquad (6)$$

Fig. 8 Titration of 110 mL of 0.0017 M HCl with 0.1 M NaOH with various molybdenum oxide bronze pH sensors
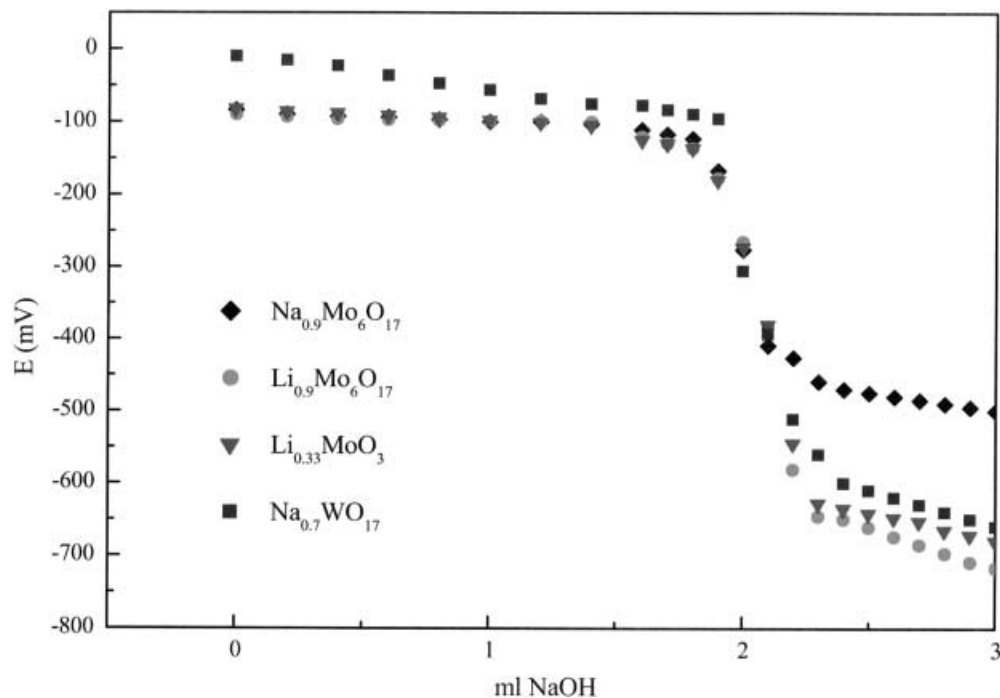
Fig. 9 Cross-sensitivity tests of $Na_{0.9}Mo_6O_{17}$ pH electrodes to Li^+, Na^+ and K^+ ions
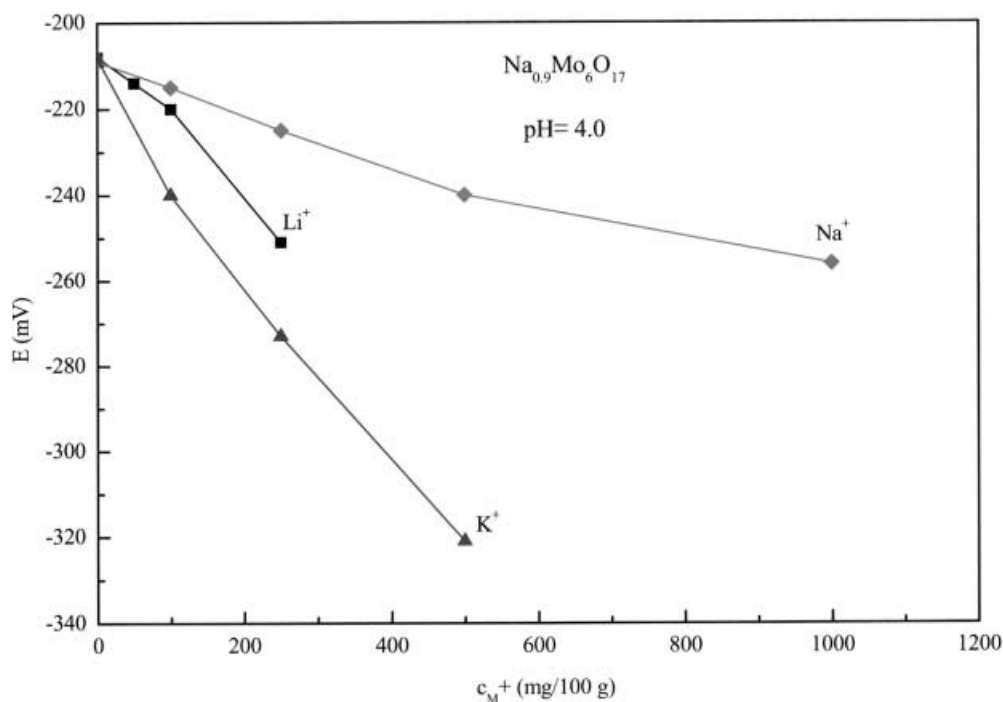
or:

$$\Delta\phi = \frac{1}{F}\left(\mu_{H^+} - \mu_H^s - \mu_{A^+}\right) = \text{const.} + \frac{RT}{F}\ln(a_{H^+})$$
$$- \frac{RT}{F}\ln\left(a_H^s\right) - \frac{RT}{F}\ln(a_{A^+}) \qquad (7)$$

respectively. $\Delta\phi$ depends on the hydrogen ion (a_H^+) or A-ion (a_A^+) activity in solutions as well as on hydrogen

activity in the solid phase. Calculations based on idealized model cation-exchange systems are difficult to apply to molybdenum oxide bronze systems. It is the cation-exchanged surface film (or subsurface layer) of the molybdenum oxide bronze that determines the electrode properties rather than the bulk composition of the molybdenum bronze single crystal. The composition of this film (or layer) is undoubtedly substantially different from that in the interior of the crystal, and is, in

Fig. 10 Potentials of $A_xMo_yO_z$ electrodes versus Ag/AgCl reference electrode as a function of Na^+ concentration in NaCl solutions
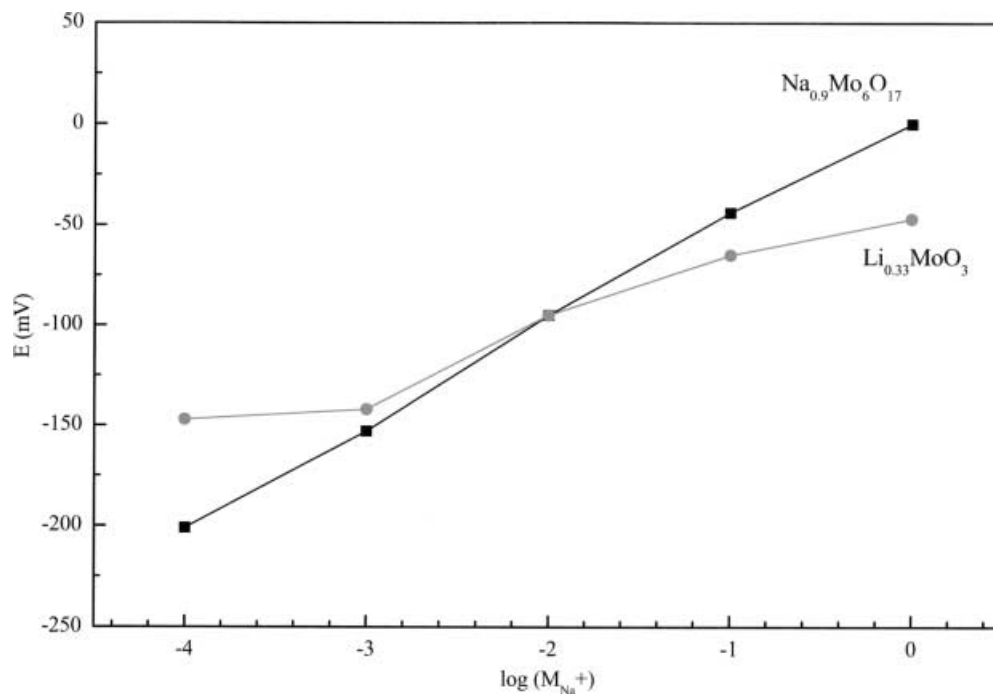
Fig. 11 Potentials of different $Na_{0.9}Mo_6O_{17}$ electrodes versus Ag/AgCl reference electrode as a function of $NaNO_3$ concentration
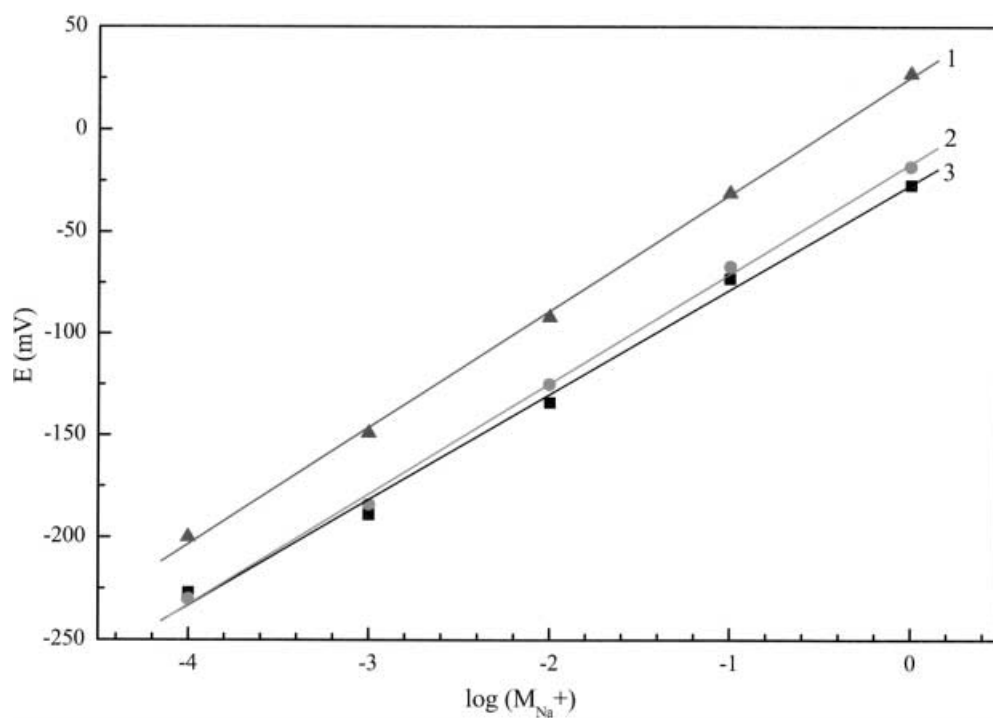
general, in real systems unknown and/or cannot be controlled.

The plot of measured e.m.f. (E) versus pH (or $pA = -\log a_A^+$, where $A = Li$, Na, K) should yield a straight line with a slope ~59 mV/pH at 25 °C, when the activity of protons (or other ions) in the subsurface layer of the molybdenum bronze is assumed constant at the conditions of the measurement and the interference of other ions is not significant.
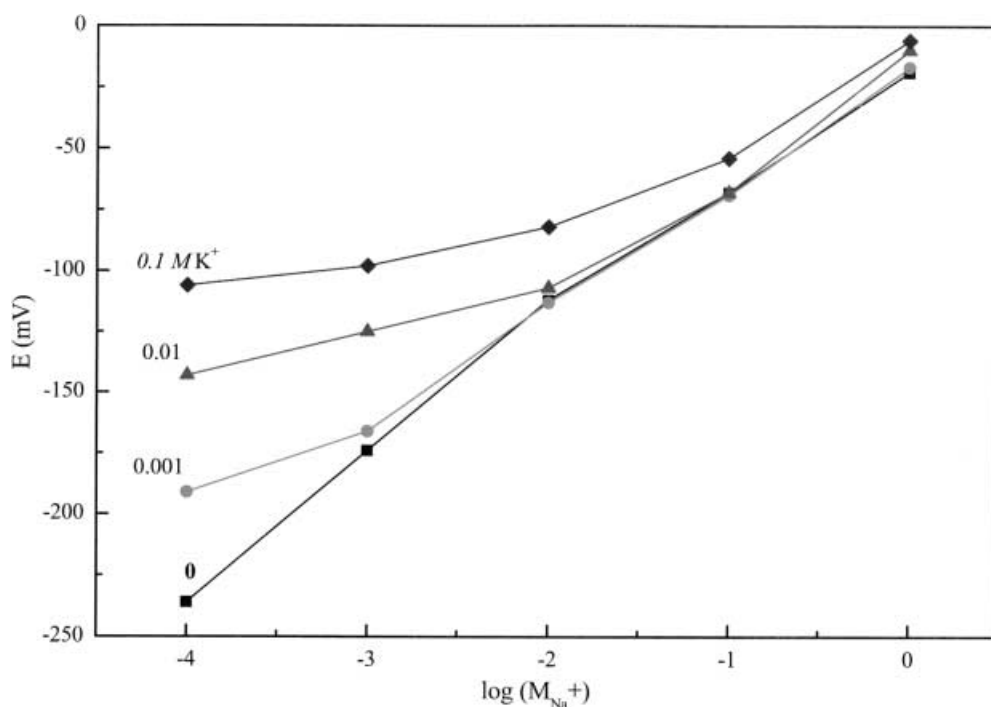
pH sensing

It is seen from Fig. 5 that pH sensors with Li- and Na-molybdenum oxide bronze single crystals as the sensitive electrode show linear behavior in the range 3–9 at room temperature with a slope of ca. –59 to –60 mV/pH. Thus we can assume that the hydrogen activity in these molybdenum bronzes at the conditions of the measurement is nearly constant. The response was unaffected by the

Fig. 12 Dynamic pNa response of the $Na_{0.9}Mo_6O_{17}$ sensor in $NaNO_3$ solutions ($-\log c_{Na}^+$)
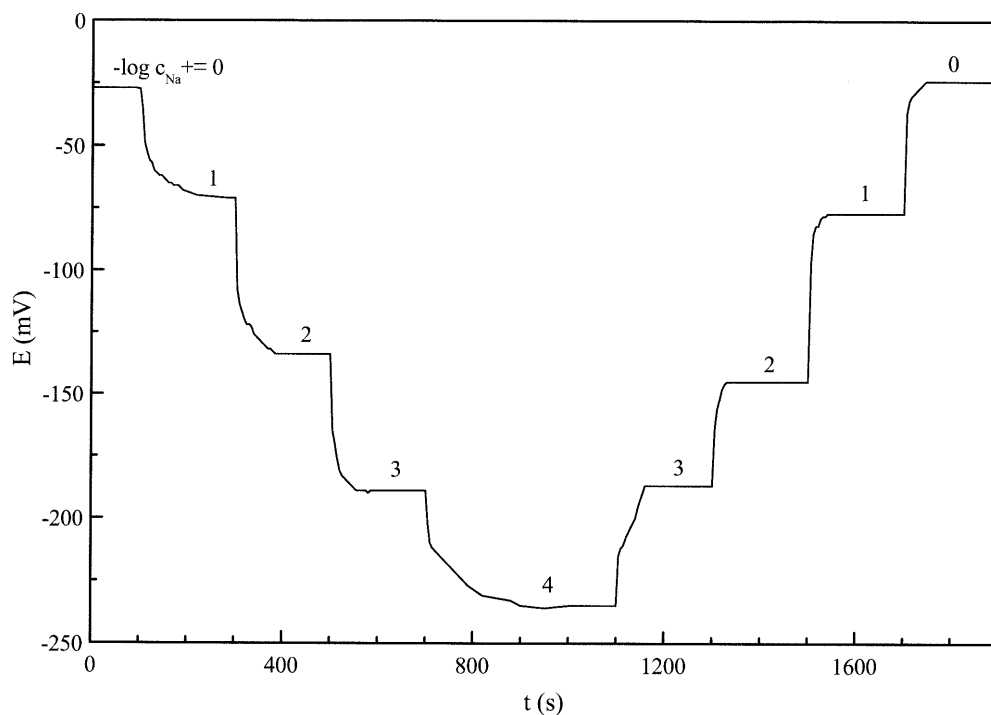
Fig. 13 Cross-sensitivity tests of the $Na_{0.9}Mo_6O_{17}$ sensor to K^+ ions in $NaNO_3$ solutions containing constant K^+ concentrations (marked K^+-ion concentrations in mol dm^{-3})


direction of the pH change. In contrast, the pH sensor with a Na-tungsten bronze sensitive electrode shows deviation from linearity, as well as Nernstian behavior with a slope –76.3 mV/pH at 25 °C (Fig. 5). It has also been established reproducibly that strong acids or strong bases suppress the sensitivity of the Mo-bronze pH sensors investigated here. When the temperature of the analyte solution is increased the molybdenum oxide bronze pH electrodes also show Nernstian response with

–64 mV/pH and –69 mV/pH slopes at 50 °C and 75 °C, respectively (Fig. 6).

The Na- or Li-molybdenum bronze sensors are extremely sensitive to changes of pH of the analyte (Fig. 7). Figure 7b represents typical dynamic behavior of the molybdenum bronze pH sensors with $Na_{0.9}Mo_6O_{17}$ as the sensitive electrode. The response time of the $Na_{0.9}Mo_6O_{17}$ sensor to pH changes over a wide pH range is less than 5 s for 90% response, except

Fig. 14 Cross-sensitivity tests of the $Na_{0.9}Mo_6O_{17}$ sensor to H^+ ions in $NaNO_3$ solutions (marked sodium ion concentrations in mol dm^{-3})
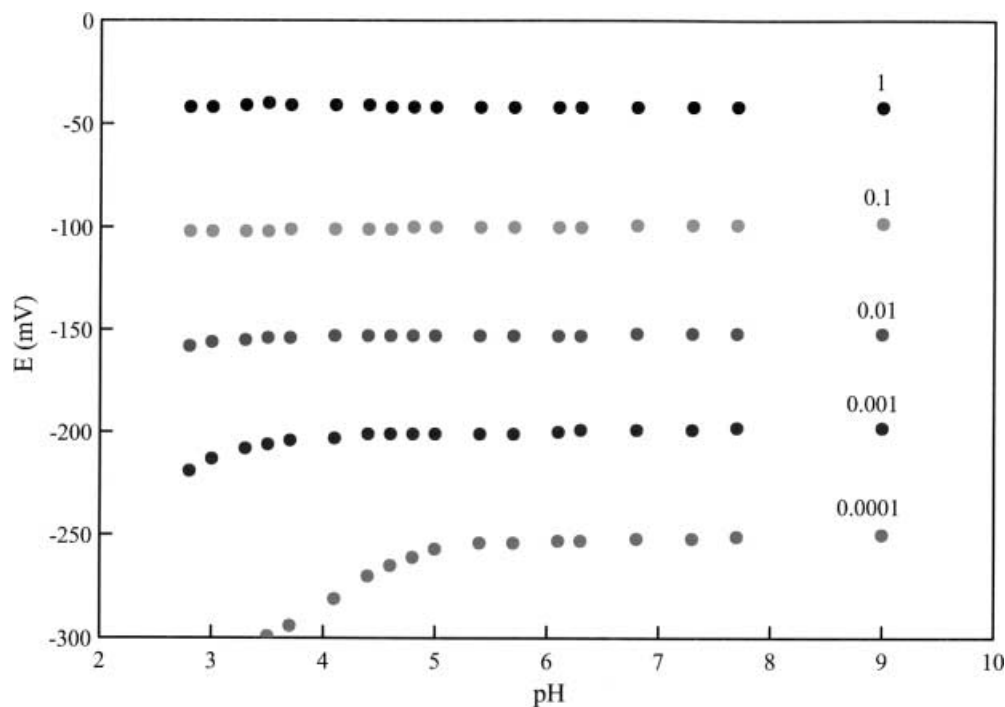
Table 1 pH tests in liquid foods at 25 °C

Food product	Glass pH electrode pH	$Li_{0.33}MoO_3$ sensor		$Na_{0.9}Mo_6O_{17}$ sensor 1		$Na_{0.9}Mo_6O_{17}$ sensor 2	
		pH	E (mV)	pH	E (mV)	pH	E (mV)
Apple juice	3.69	3.65	−118	3.74	−145	3.80	−148
Milk	6.56	5.84	−249	6.10	−274	6.19	−279

at high and low proton concentrations. In the latter case, proton exchange or insertion is probably the limiting factor. Similar response behavior is observed with other molybdenum bronze pH sensors. Tests with tungsten bronze (Na_xWO_3) sensors showed unstable responses in the 4–9 pH range.

A number of titrations have been performed in aqueous media. The pH sensor consisted of a molybdenum (or tungsten) oxide bronze single crystal, which functioned as the sensing electrode, and saturated Ag/AgCl, which served as a reference electrode. Some of these titrations were also performed with glass electrodes. The titration curves with bronze sensing electrodes closely resembled those of the glass electrode (Fig. 8).

No ion-selective electrode is entirely selective towards the ion specified. The presence of other ions can seriously impair sensing performance. Such interferences can take several forms, depending on the type of electrode material [31, 32]. Cross-sensitivity tests of pH sensors with single crystals of $Na_{0.9}Mo_6O_{17}$ show significant selectivity error in solutions containing K^+, Na^+ or Li^+ (Fig. 9). Further, these electrodes were reduced and/or complexed on the surface by iodide ions. We found potential increases of some 10 mV with

$Na_{0.9}Mo_6O_{17}$ as the pH sensor in buffer solutions by changing the Na^+ or K^+ concentration in the range 0–1000 mg/100 g and 0–500 mg/100 g, respectively; typical concentration ranges of these ions are present in different liquid foods [33]. However, the Li-molybdenum bronze electrode, $Li_{0.33}MoO_3$, appears to be highly selective to H^+ ions, consistent with the 3D structure, the smaller size of the interstitial cavities, and the more tightly bound Li^+ ions.

pNa sensors

It is seen from Fig. 10 that sodium ion sensors with a Li- or Na-molybdenum bronze single crystal as the sensitive electrode show quite different behavior. The sodium molybdenum bronze sensor has linear behavior between sodium ion concentrations of 10^{-4} and 1 mol dm^{-3}, with a slope of −50 to −57 mV/pNa for different sensor samples (Fig. 11). The lithium molybdenum bronze sensor shows deviation from linearity at low and high $[Na^+]$. Based on the response tests of several sensors, it is reasonable to assume that the sodium ion activity in the subsurface layer of sodium molybdenum bronze is nearly constant at the conditions of the measurements.

The sodium ion sensors with the Na-molybdenum-oxide bronze are extremely sensitive to changes of Na^+ concentration of the analyte. Figure 12 presents typical dynamic behavior of $Na_{0.9}Mo_6O_{17}$ sensors as a function of the Na^+ concentration in the analyte. The response time of the $Na_{0.9}Mo_6O_{17}$ sensor to changes of $[Na^+]$ over a wide concentration range was less than 10 s for 90% response, except at low sodium ion concentration (i.e. 10^{-4} mol dm^{-3}). In the latter case, sodium ion exchange was probably the limiting factor. Potentials of sodium ion sensors show relatively good stability over a wide range of sodium ion concentrations.

Cross-sensitivity tests of sodium ion sensors with single crystals of $Na_{0.9}Mo_6O_{17}$ show significant selectivity error in solutions containing K^+ or H^+ (Figs. 13 and 14). For comparison, the curve (0) shown in Fig. 13 gives data for the sodium molybdenum bronze electrode behavior in a solution containing only sodium nitrate. Clearly, the molybdenum bronze electrode has an appreciable cross sensitivity to potassium ions, particularly when the potassium ion concentration is comparable or higher than that of the sodium ion. A marked response to changes in proton concentration at low pH was noted in dilute sodium nitrate solutions, <0.01 mol dm^{-3} (Fig. 14). As might be expected, the higher the sodium ion concentration, the less is the effect of pH, even at low pH values. An increase in sodium concentration by a factor of 10 decreases the lower limit of the pH-independent sodium response of the sensor by one pH unit. This corresponds to the pH dependence of the sodium error of glass electrodes. In the pH range 3–9 the solution pH appears to have little effect on the $[Na^+]$ sensing properties of the sodium molybdenum bronze electrode when the $[Na^+]$ is over 0.01 mol dm^{-3}.

pH measurements in liquid foods with a prototype molybdenum oxide bronze sensor show relatively good agreement with pH glass electrode measurements (Table 1).

Conclusions

We have demonstrated that single crystals of Li- and Na-molybdenum bronzes, $Li_{0.33}MoO_3$ and $Na_{0.9}Mo_6O_{17}$, fabricated into electrodes by direct solid state contact, are new metal-oxide-type pH ion-sensitive electrodes and $Na_{0.9}Mo_6O_{17}$ is also a new sodium-ion-selective electrode. These sensors respond to changing pH and/or sodium ion concentration in the analyte rapidly and show relatively good reproducibility in the pH range 4–9 or sodium ion concentration of 1–10^{-4} mol dm^{-3} and near-Nerstian behavior.

The sodium molybdenum bronze electrode is suitable for the determination of sodium ion content, particularly when the interfering ions (i.e. K^+ or H^+) are present in a concentration range at least an order of magnitude smaller than the $[Na^+]$ to be determined.

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