

Alkali Ion Sensor Based on Prussian Blue-covered Interdigitated Array Electrodes

M. HARTMANN and E. W. GRABNER

Institute of Physical and Theoretical Chemistry, University of Frankfurt, Niederurseler Hang, D-6000 Frankfurt am Main 50 (F.R.G.)

P. BERGVELD

Biomedical Engineering Division, Twente University of Technology, NL-7500 AE Enschede (The Netherlands)

Abstract

Thin films of ferric ferrocyanide (Prussian Blue) were electrochemically deposited on interdigitated array (IDA) electrodes yielding systems which can be considered as chemiresistors in sensing alkali ion concentrations in an adjacent electrolyte. From the dependence of the steady-state current on the electrode (bias) potential at variable cation concentrations for different alkali ions and for mixtures of alkali ions, the possibilities of analytical application are elucidated. It is concluded that Prussian Blue-coated IDA electrodes are, in principle, suitable as chemiresistors for the determination of alkali ion concentrations with increasing selectivity in the series $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$.

Introduction

Prussian Blue (PB) has attracted much interest from electrochemists because of its electroanalytic [1], electrochromic [2], charge storage [3, 4] and membrane [5] properties. Wrighton and coworkers pioneered the use of microlithographically defined microarray electrodes for the study of electroactive films [6, 7]. The deposition of PB on an interdigitated array electrode was performed for the first time by Murray and coworkers [8, 9]. In this paper the possibility of application of PB-covered IDA electrodes to the analysis of alkali ions is studied.

Experimental

The interdigitated array consists of two fingered electrodes (Pt), with 50 fingers each, being deposited on a $1 \text{ mm} \times 1 \text{ mm}$ area of an insulating substrate (Si/SiO_2). The microstructures were patterned by means of ion beam etching (Fig. 1).

After rinsing the IDA electrodes for several minutes in concentrated HCl and subsequent washing with water, PB films were potentiostatically deposited from an aqueous solution of 20 mM FeCl_3 , 20 mM $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.01 M HCl at 0.5 V versus Ag/AgCl for 2.5 min. The films were about 300 nm thick. All chemicals used (Merck, Fluka) were of purissimum quality, and the water was triply distilled. The solutions were degassed by Ar bubbling throughout. Typical IDA electrode measurements were performed with a voltage, ΔE , of 10–50 mV applied between the two fingered electrodes, meanwhile potentiostatically controlling the bias potential, E_b , of the film with respect to an Ag/AgCl reference electrode. This electrode served at the same time as the counter electrode. The electronic equipment for this kind of measurement was a home-made current amplifier with a sensitivity up to 10^{-12} A. The measurement data were stored and processed by a computer (Commodore model 4032) via an A/D converter. All experiments were performed at room temperature 22 ± 1 °C).

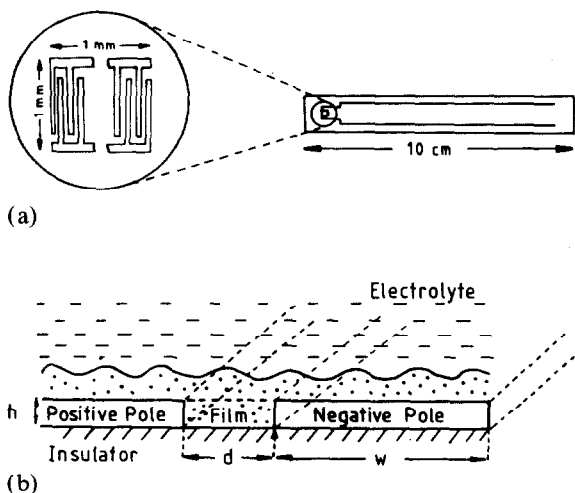


Fig. 1. Geometric arrangement (a) and cross section (b) of an interdigitated array electrode: width of a finger $w = 7 \mu\text{m}$; gap between two fingers $d = 3 \mu\text{m}$; finger height $h = 0.3 \mu\text{m}$.

Results and Discussion

General Considerations

In using a PB-coated IDA electrode as a chemiresistor, the following assumptions are made [13]:

(i) The PB film is in thermodynamic equilibrium throughout while measuring the steady-state (diffusion) current, i_d ;

(ii) The reduction of the high-spin Fe redox centres within the film occurs reversibly and is accompanied by reversible insertion of cations from the electrolyte, without interaction of the latter with the host lattice.

Corresponding to the reaction



the Nernst equation

$$E = E^0 + (RT/F) \ln \left\{ \frac{x}{(1-x)} \left(\frac{c}{c^0} \right) \right\} \quad (2)$$

holds, where ox_f and red_f denote the high-spin Fe redox centres in the oxidized and reduced states, respectively, C^+ denotes the cations in the electrolyte with concentration c . c^0 is the standard concentration (1 mol dm^{-3}), and $x = c_{\text{ox}}/c_f$ is the mole fraction of oxidized redox centres with $c_f = c_{\text{ox}} + c_{\text{red}}$ denoting the total concentration of the high-spin Fe redox centres.

(iii) The geometric arrangement of the PB-coated IDA electrode (see Fig. 1(b)) is simplified by neglecting those portions of the film above the fingers.

Dependence of the Steady-state Current, i_d , on the Bias Potential, E_b

A small voltage ΔE is applied between the two fingered electrodes and E_b is stepped by increments of 25 mV from 0 V to 0.375 V, i.e., from the reduced state of PB (Prussian White or Everitt's salt) to the oxidized state (PB). Within 2–3 min the current, $i(t)$, reaches a steady-state value, i_d . In Fig. 2, i_d normalized with respect to the maximum value, $i_{d,m}$, is plotted as a function of E_b for three different concentrations of RbCl. For $c = 1 \text{ M}$ a nearly ideal bell-shaped curve is obtained. However, the width at half-height, $\Delta E_{1/2}$, is remarkably larger (about 160 mV) than the value of 90 mV predicted by theoretical considerations on the basis of an ideal insertion electrode [10]. It is therefore concluded that the insertion of Rb^+ into PB occurs with some repulsive interaction with the host lattice, resulting in a broadened width of half-height [10, 11].

Figure 2 reveals, in addition, that the potential of the maximum steady-state current,

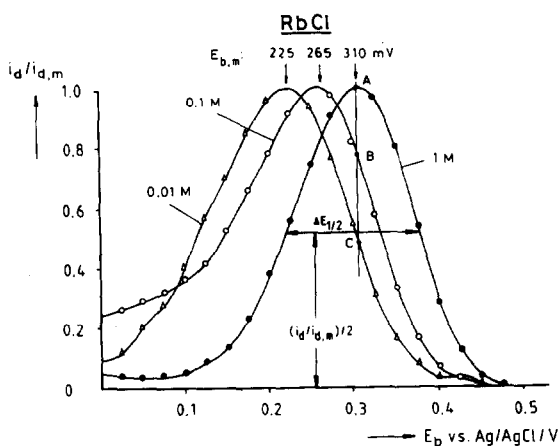


Fig. 2. Normalized digit current, $i_d/i_{d,m}$, as a function of the bias potential, E_b , at three different concentrations of RbCl. $\Delta E = 50 \text{ mV}$; $E_{b,m}$, potential of maximum digit current, $i_{d,m}$; $i_{d,m} = 405 \text{ nA}$ (1 M), 300 nA (0.1 M), 590 nA (0.01 M).

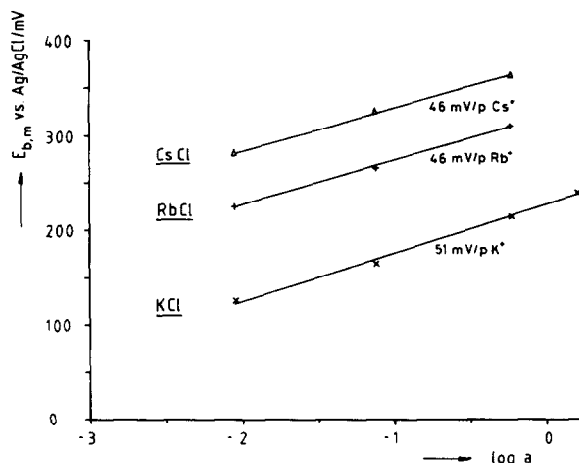


Fig. 3. Bias potential of maximum digit current, $E_{b,m}$, as a function of the cation activity, a . Electrolytes: KCl, RbCl, and CsCl, respectively. Numbers indicate the slopes of the straight lines.

$E_{b,m}$, depends on the concentration in a nearly Nernstian way as predicted by eqn (2). This is shown in Fig. 3. The $E_{b,m}$ values for CsCl are shifted to more positive potentials and for KCl to more negative potentials. Thus at a concentration of 0.1 M, $E_{b,m}$ is 165 mV for K⁺, 265 mV for Rb⁺, and 325 mV for Cs⁺ (all values versus Ag/AgCl).

Dependence of the Steady-state Current, i_d , on the Concentration, c

At a given reference concentration c' , the maximum value of the steady-state current, $i'_{d,m}$, is measured at the bias potential, $E'_{b,m}$. Thereafter the electrolyte of the reference concentration is replaced by an electrolyte of unknown concentration, c . This corresponds to a transition of point A in Fig. 2 to points B and C, respectively. A steady-state current, i_d , results, which is related to c by [13]

$$i_d/i'_{d,m} = (4c/c')/[1 + (c/c')]^2 \quad (3)$$

This equation can be approximated by

$$\log(i'_{d,m}/i_d) \approx -0.6 \pm \log(c/c') \quad (4)$$

For $c < 0.1c'$ and $c > 10c'$ linear relationships between i_d and $1/i_d$, respectively, on one hand and c on the other are obtained:

$$i_d \approx (4i'_{d,m}/c')c \text{ and } 1/i_d \approx [1/(4i'_{d,m}c')]c \quad (4a)$$

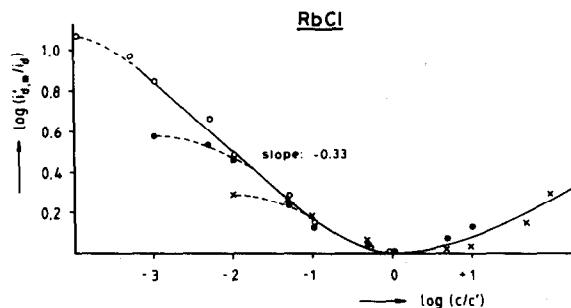


Fig. 4. Logarithmic plot of inverse normalized digit current, $i_{d,m}/i_d$, vs. normalized concentration, c/c' . Electrolyte RbCl. Reference concentration, c' : 1 M (O), 0.1 M (●), and 0.01 M (x); $E_{b,m}$: 310 mV (O), 265 mV (●), and 225 mV (x).

The results for different values of c' are shown in Fig. 4. The slope of the curve obtained experimentally (-0.33) is smaller than the theoretical value (-1) by a factor of three. This follows immediately from the fact that the $\Delta E_{1/2}$ value increases with decreasing concentration, leading to i_d values larger than expected for an ideal $\Delta E_{1/2}$ of 90 mV. Larger i_d values, however, cause a smaller slope (see Fig. 4).

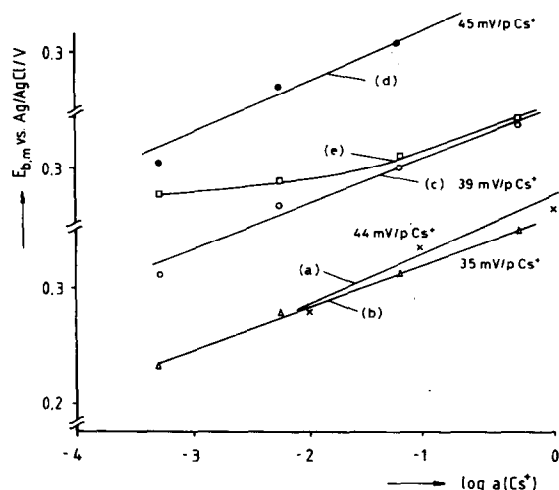


Fig. 5. Bias potential of maximum digit current, $E_{b,m}$, as a function of the activity of Cs⁺ in 0.5 M solutions of LiCl (b), NaCl (c), KCl (d), and RbCl (e). Curve (a) is obtained from pure CsCl solutions. Numbers indicate slopes. (The curves are shifted on the potential axis for clarity.)

Selectivity Measurements

The selectivity of PB-coated IDA electrodes with respect to different alkali ions has been studied by taking $i_d/i_{d,m} - E_b$ curves for mixtures of alkali ions with variable concentrations. The potential, $E_{b,m}$, of the maximum steady-state current depends on the Cs^+ concentration in a nearly Nernstian fashion, as demonstrated in Fig. 5. The straight lines demonstrate that, except for Rb^+ (curve e), the linear dependence of $E_{b,m}$ on $\log a(\text{Cs}^+)$ is not altered in the presence of 0.5 M solutions of Li^+ , Na^+ , and K^+ ions, resulting in approximate selectivity coefficients [12] smaller than 10^{-3} . For Cs^+ with respect to Rb^+ , an approximate selectivity coefficient $K_{\text{CsRb}} \approx 10^{-2}$ can be estimated.

Conclusions

It has been demonstrated that PB-coated IDA electrodes can be considered as chemiresistors, the conductivity of which depends on the concentration of alkali ions in an adjacent electrolyte. Thus such systems, in principle, can be used as alkali ion sensors. For the non-optimized PB-coated IDA electrodes, an approximate detection limit of about 10^{-4} can be assumed. They show selectivity behaviour in the series $\text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li}$.

Acknowledgements

The authors are greatly indebted to the Deutsche Forschungsgemeinschaft for financial support and to Johan Bomer for preparing the IDA electrodes.

References

- 1 K. Itaya, N. Shoji and J. Uchida, Catalysis of the reduction of molecular oxygen to water at Prussian-Blue-modified electrodes, *J. Am. Chem. Soc.*, **106** (1984) 3423–3429.
- 2 D. Ellis, M. Eckhoff and V. D. Neff, Electrochromism in the mixed-valence hexacyanides, *J. Phys. Chem.*, **85** (1981) 1225–1231; K. Itaya, K. Shibayama, H. Akahoshi and S. Toshima, Prussian-Blue-modified electrodes: an application for a stable electrochromic display device, *J. Appl. Phys.*, **53** (1982) 804–805.
- 3 V. D. Neff, Some performance characteristics of Prussian Blue battery, *J. Electrochem. Soc.*, **132** (1985) 1382–1384.
- 4 E. W. Grabner and S. Kalwellis-Mohn, Hexacyanoferrate layers as electrodes for secondary cells, *J. Appl. Electrochem.*, **17** (1987) 653–656.
- 5 P. J. Kulesza and K. Doblhofer, The membrane properties of Prussian Blue films on electrodes, *J. Electroanal. Chem.*, **274** (1989) 95–109.
- 6 H. S. White, G. P. Kittlesen and M. S. Wrighton, Chemical derivatization of an array of three gold microelectrodes with polypyrrole, *J. Am. Chem. Soc.*, **106** (1984) 5375–5377.
- 7 M. S. Wrighton, Prospects for a new kind of synthesis: assembly of molecular components to achieve functions, *Comments Inorg. Chem.*, **4** (1985) 269–294.
- 8 C. E. Chidsey, B. J. Feldman, C. A. Lundgren and R. W. Murray, Micrometer-spaced platinum interdigitated array electrodes: fabrication, theory, and initial use, *Anal. Chem.*, **58** (1986) 601–607.
- 9 B. J. Feldman and R. W. Murray, Electron diffusion in wet and dry Prussian Blue films on interdigitated array electrodes, *Inorg. Chem.*, **26** (1987) 1702–1708.
- 10 W. R. McKinnon and R. R. Haering in J. O'M. Bockris and A. Conway (eds.), *Modern Aspects of Electrochemistry*, Vol. 15, Plenum Press, New York, 1983, p. 235.
- 11 D. Engel and E. W. Grabner, Charge transfer at a copperhexacyanoferrate-modified glassy carbon electrode, *Z. Phys. Chem., N. F.*, **160** (1988) 151–168.
- 12 G. J. Moody and J. D. R. Thomas, *Selective Ion Sensitive Electrodes*, Merrow, Shildon, 1971, p. 14.
- 13 M. Hartmann, E. W. Grabner and P. Bergveld, Prussian Blue-coated interdigitated array electrodes for possible analytical application, *Anal. Chim. Acta*, **242** (1991) 249–257.