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SHORT COMMUNICATION

A well-defined reference electrode in acetonitrile

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1. Introduction

A reference electrode should have two principal qualities: first, *a well defined potential*; and second, *stability*, in terms of drift and fluctuation. In contrast to aqueous systems, it is difficult to find an appropriate electrode for non-aqueous solvents such as acetonitrile. Many authors [1-4] use the saturated calomel electrode (SCE) even though most textbooks [5, 6, 7] point out that the SCE has an unknown and unreproducible potential shift, resulting from the liquid junction between water and the nonaqueous solvent. In fact potential drifts of up to 100 mV could be observed. This may be one of the reasons why experimental data in the literature for the energy level of bands in Si measured with SCE differ by up to 0.5 V [3, 4, 8]. As a result of these problems textbooks recommend the use of a metal/metal ion system such as $Ag/AgClO_4$ (0.01 M). We found, however, poor stability. In addition, contamination of the test solution is possible, a severe problem in experiments carried out in the absence of a redox pair such as capacitance measurements at semiconductor–electrolyte contacts. To avoid contamination, some authors [9] have used quasi-reference-electrodes (QRE), i.e. a metal wire (Pt or Ag) immersed directly in the test solution. This type of electrode attains a moderately stable, but irreproducible, potential after some hours. The exact potential must be determined by means of a redox pair of known potential. Although such systems are quite easy to handle, they cannot be recommended, because stability is not guaranteed. Peerce and Bard [9] proposed a reference electrode consisting of an electrodeposited polyvinylferrocene film on a platinum electrode. This system appears to perform well; however, it requires intricate experimental preparation.

Coetzee and Gardner [10, 11] recommended a new system working with the redox couple I_3^-/I^-. It is surprising that this reference system, despite its advantages, is not used more frequently. In order to provide additional information on this system, we improved its design and made further investigations to demonstrate its performance.

2. Experimental details

As solvent acetonitrile was used (Fluka puriss. p.a.). The redox pair was I_3^-/I^- in equimolar concentrations of 0.05 M, prepared by sodium iodide (Fluka puriss. p.a.); and iodine (Fluka puriss. p.a.). In order to eliminate diffusion potentials. 1 M $LiClO_4$ (Fuka puriss. p.a.) was added as supporting electrolyte. If an absolute medium is required, $LiClO_4$ has either to be dried or substituted by tetrabuylammonium perchlorate.

All experiments were carried out in two-electrode cells of different shapes. Potentials were measured by an electronic pH/voltmeter (Knick 10) with an impedance of $2 \times 10^{12}\,\Omega$. Pt wires were used as electrodes, cleaned in nitric acid (Fluka puriss. p.a.) and washed with double distilled water and acetone (Fluka puriss. p.a.). Because of the equilibrium.

$$I_3^- \rightleftharpoons I_2 + I^-$$

there is a possibility for I_2 to evaporate and then to diffuse into the gas space. This leads to a potential drift of some millivolts over several hours. In order to suppress the escape of iodine, the space above the electrolyte inside the maintube was filled by a glass-body as shown in Fig. 1. I_2 can also diffuse through plastic materials (such as PTFE). Therefore the electrode was entirely made of glass, in contrast to the proposition in [11]. The junction of the reference electrolyte and cell electrolyte consisted of a glass frit (1 mm diameter, leakage rate ca $10^{-3}\,cm^3\,h^{-1}$).

In experiments without a redox couple in the cell electrolyte, the level of the cell electrolyte was set above the level of the reference electrolyte in order to generate a slight flow into the reference electrode. This prevented the contamination of the cell electrolyte by diffusion of the iodine redox pair.

3. Results

3.1. *Stability*

In order to acquire information on the behaviour of the redox system I_3^-/I^-, a first series of experiments in a cell without junctions and diaphragms was carried out, the two platinum wires being immersed in the same electrolyte solution. This allowed the elimination of all possible sources of potential drops. As expected from theory, we measured a potential of 0 mV in a range of less than 0.1 mV. A similar experiment, carried out with the redox pair Ag/Ag^+, showed stability only in the range of some millivolts. This can probably be explained by the fact that the exchange current density of the couple I_3^-/I^- is 100 times higher than that of the couple Ag/Ag^+ [10]. The half cells were then separated by placing one of the platinum wire electrodes in a glass tube with a frit. The electrolyte on both sides of the frit was the same. In this cell an offset of 0 mV was initially measured. An increase in the

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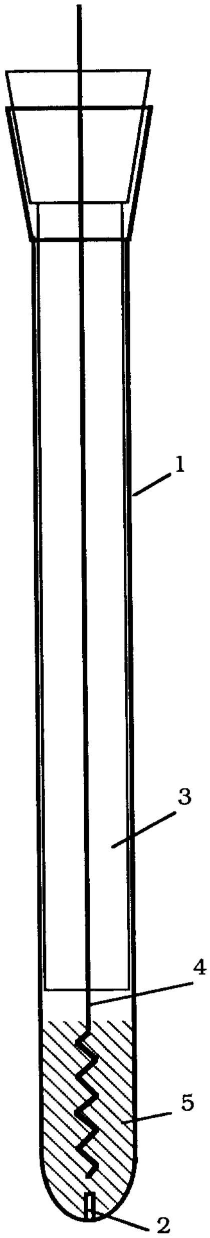

Fig. 1. Schematic of optimized reference electrode. (1) Glass tube, (2) glass frit, (3) glass body, (4) Pt-electrode, and (5) electrolyte.

offset potential may be attributed to the loss of I_2 by diffusion and was eliminated by the particular cell construction described above. The optimized cell had a long time stability in the range of 1 mV over one week. The potential oscillated over the range 0.1 mV.

3.2. *Nernstian behaviour*

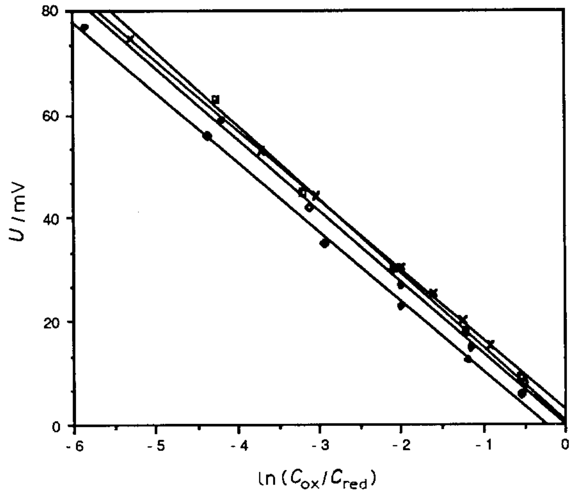

Fig. 2. Nernstian behaviour of the redox system I_3^-/I^-. Concentrations: I^- 0.05 M, I_3^- 0.0007 to 0.03 M.

The concentration dependence of the electrode potential was measured in a two electrode cell with a burette. The concentration ratio of the reduced and the oxidized species was changed by titration. A platinum wire was used as indicator electrode. The potential of this half cell was measured against the new reference electrode. Initial concentrations were 0.05 M NaI and 0.00007 M I_3^-. The concentration of I_3^- was increased continuously up to 0.03 M in logarithmic steps by adding I_2, whereas the concentration of NaI remained constant. This experiment was repeated as shown in Fig. 2. According to the Nernst equation

$$\Phi_0 = \Phi_{00} + \frac{RT}{nF}\ln\left(\frac{c_{ox}}{c_{red}}\right)$$

where Φ_{00} is the standard redox potential of the redox pair and Φ_0 is the potential of the half cell, the experimentally measured potential V of an electrode can be represented as a linear function of the logarithm of the concentration ratio of the two species. For a two electron reaction such as

$$3I^- \rightleftharpoons I_3^- + 2e^-$$

the slope of the linear function is 13 mV at room temperature. Because the I_3^-/I^- system was used as reference, the value of the intercept should be 0 mV.

Values for slope and intercept were calculated by regression for each experiment. (Fig. 2) The results of the regressions are given in Table 1. The calculated slopes fit the theory well. The theoretical values for the slope and the intercept lie in the confidence interval calculated by the Student-t-distribution. All potentials of the reference electrode can be expected within an interval of 10 mV. The error between data in one experiment is much smaller than between all potentials measured at the same concentration, therefore an offset potential of some mV is significant. An F-test for first order regression revealed no arguments against the model.

Although statistics support the theory, it is believed that the difference between the value of the slope

Table 1. Analysis of redox titration data to show Nernstian behaviour

Exp no.	Slope/mV	Intercept/mV	Correlation
1	– 13.47	3.27	1.00
2	– 13.49	– 3.05	0.998
3	– 14.32	0.72	0.998
4	– 13.87	– 0.26	0.997
Mean	– 13.79	0.17	
Conf. interval	± 0.94	± 5.7	(95%)
All data	– 13.96	0.31	0.987

calculated by theory and that determined by experimental data is significant and is a consequence of the assumption of ideal solutions. This appears likely in view of a small trend towards a flatter curve in the region of small concentrations.

3.3. *Relation to the redox system in water*

As mentioned above, the redox potential in relation to the aqueous system is difficult to define experimentally. Data given in standard tables are not reliable. For I_3^-/I^- in acetonitrile redox, potentials from $-0.124\,V$ [11] up to $+1.79\,V$ [12] are published. This is very doubtful as the redox potential of I_3^-/I^- in aqueous systems is $+0.536\,V$. Due to solvation effects, the potential is expected to be more negative in acetonitrile than in water. To estimate an approximate redox potential, Pleskow [14] recommends correcting the value for aqueous systems with the solvation effect for I_3^-/I^- in

$$I_3^- + 2e^- \rightleftharpoons 3I^- \qquad E_0 = +0.256\,V \pm 10\,mV$$

This coincides with the first experiments we conducted to determine the flatband potential of p-Si by Mott-Schottky plots.

4. Conclusions

The redox electrode described above appears to be a favourable, easily managed alternative to the known redox electrodes in acetonitrile. It is stable and shows Nernstian behaviour over a wide concentration range. Although its redox potential against a redox system in water cannot be measured, an approximate value can nevertheless be given.

Acknowledgement

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