

NEW REFERENCE ELECTRODE BASED ON PMMA POLYMER ELECTROLYTES

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The research on the field of polymer gel electrolytes is at the border between solid and liquid phase [1]. Common equipment and methods are used, but in some cases it is necessary to modify them even to develop new ones.

Electrochemical measurements in the medium of polymethylmethacrylate (PMMA) gel electrolytes require a new reference system, which does not contain liquid electrolyte. H. Sung [2] used electrode system Li/Li⁺ for the voltammetric measurements in the medium of polyvinylchloride (PVC) gel electrolytes. The electrode is realised by a metal lithium foil inserted between two sheets of PVC gel containing lithium perchlorate. The disadvantage is sensitivity to the aerial moisture.

Experimental

We have developed a reference system Cd/Cd²⁺ incorporated in PMMA polymer [3, 4]. The PMMA-Cd electrode is realised by a cadmium wire ($\varnothing = 1$ mm) inserted into a PMMA gel electrolyte containing 0.31 M solution of cadmium perchlorate in anhydrous propylencarbonate (PC). The gel electrolyte with Cd(ClO₄)₂ was prepared by *in-situ* polymerisation [3 – 5] of a mixture of methylmethacrylate (MMA) monomer, MMA oligomer and solution of Cd(ClO₄)₂ in PC.

The gel can be placed into a special cell for voltammetric studies (Figure 1). Behaviour of ferrocene/ferricinium system and cadmium ions in PMMA gel electrolytes was studied [3].

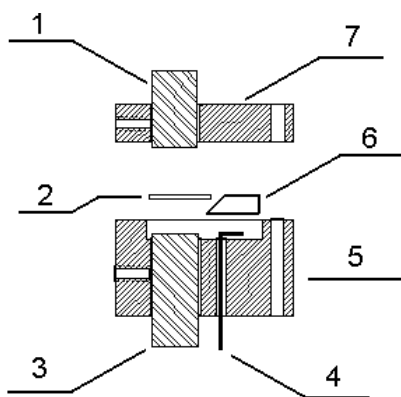


Fig.1. Three-electrode vessel for voltammetric measurements in the medium of PMMA gel electrolytes: 1 – Cd rod ($\varnothing = 13$ mm), 2 – PMMA gel with sample (e.g. ferrocene), 3 – work electrode (glassy carbon), 4 – cadmium wire of reference electrode ($\varnothing = 1$ mm), 5 – PTFE vessel, 6 – Cd/Cd²⁺ reference electrode, 7 – PTFE cover.

The PMMA gel with cadmium perchlorate was also tested as an electrode material for electrochemical measurements in non-aqueous solvents. Figure 2 shows scheme of the reference electrode used in liquid systems.

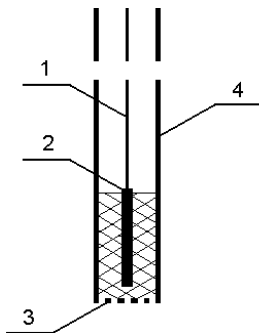


Fig.2. PMMA-Cd electrode for measurements in non-aqueous solvents: 1 – copper wire, 2 – cadmium wire inserted into PMMA gel electrolyte with $\text{Cd}(\text{ClO}_4)_2$, 3 – sintered glass, 4 – glassy tube (internal diameter 6 mm, length 10 cm).

The electrochemical experiments were performed at temperature 20°C using the potentiostat AUTOLAB (Eco Chemie, The Netherlands).

It is impossible to compare the values of half-wave potentials of definite electrochemical system in various solvents using the same of different reference electrodes. Therefore we have chosen an electrochemical system, whose solvation energy is not changed with substituting a solvent [6].

Cyclic voltammetry of ferrocen/ferricinium was used for determination of the PMMA-Cd electrode potential in common non-aqueous solvents: propylencarbonate, acetonitrile, *N,N*-dimethylformamide, dimethylsulfoxide and methanol. Saturated calomel electrode (SCE) with methanolic solution of KCl was chosen as the second reference electrode. Voltammograms of ferrocene were measured with the scan rate $10 \text{ mV}\cdot\text{s}^{-1}$, platinum was used as the work and auxiliary electrode. As a reference electrode figured either methanolic SCE or PMMA-Cd electrode. 0.1M lithium perchlorate was used as the supporting electrolyte.

Stability of the electrode potential in mentioned solvents for 70 – 80 hours was studied using zero-current chronopotentiometry with methanolic SCE in two-electrode arrangement.

Results and discussion

Five voltammetric scans of ferrocene were measured with methanolic SCE and PMMA-Cd electrode in a suitable potential range. Figure 3 presents voltammograms measured in dimethylformamide. Scan measured PMMA-Cd electrode is shifted to more positive potentials in comparison with methanolic SCE.

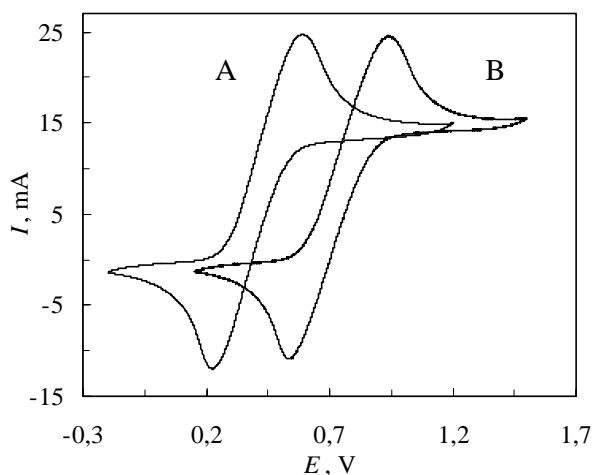


Fig.3. Voltammograms of 0.01M ferrocene in *N,N*-dimethylformamide: A – measured vs. methanolic SCE, B – measured vs. PMMA-Cd electrode ($10 \text{ mV}\cdot\text{s}^{-1}$ scan rate, work and auxiliary electrode platinum, supporting electrolyte 0.1 lithium perchlorate).

Half-wave potentials of ferrocene were determined in various solvents and the potentials of PMMA-Cd electrode were calculated following this equation:

$$E(\text{PMMA-Cd}) = \Delta E_{P/2} = E_{P/2}(\text{SCE}) - E_{P/2}(\text{PMMA-Cd}) \quad (1)$$

The results are summarised in Table 1 including relative standard deviation.

Table 1. Half-wave potentials of ferrocene (medians) measured vs. methanolic SCE or PMMA-Cd electrode, their difference computed according to the eq. 1 and relative standard deviation.

Solvent	$E_{P/2}(\text{SCE})$ [V]	$E_{P/2}(\text{PMMA-Cd})$ [V]	$\Delta E_{P/2}$ [V]	SD [%]
acetonitrile	0,332	0,802	-0,470	1,2
N,N-dimethylformamide	0,409	0,737	-0,329	0,8
dimethylsulfoxide	0,367	0,679	-0,312	1,5
methanol	0,431	0,800	-0,369	1,4
propylencarbonate	0,317	0,679	-0,362	1,6

Chronopotentiometrical measurements indicate that the potential of PMMA-Cd is stabilised within 50 minutes after placing into a solvent. After that is potential stable for next 72 hours with difference less than 5 mV from the mean value. In dimethylformamide was the fluctuation higher – 20 mV at maximum.

The potential stability improved with increasing age of the electrode. It is caused by ageing of the polymer gel electrolyte [1, 4].

It is necessary to keep the electrode for 60 hours after preparation in pure propylencarbonate to prevent later leaking of Cd^{2+} ions to the solution.

Applicability of the results

The PMMA-Cd electrode can be used as a reference electrode in non-aqueous solvents and in electrochemical measurements in the medium of polymer gel electrolytes and solid-state sensors. The electrode does not work in aqueous solutions.

Acknowledgements

This work was supported by the Grant Agency of the Academy of Sciences of Czech Republic (grant No. A4032002), by the Grant Agency of Czech Republic (grant No. 104/02/0731 and Junior grant No. B4813302) and by Ministry of Education of Czech Republic (grants No. Me-216/96 and CEZ J22/98:2622 00010).

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