

Short communication

Organic esters of phosphoric acid as electrolytes for a protonic photoelectrochromic window

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Abstract

The paper deals with phosphoric acid organic esters such as commercially available diphenylphosphate and custom made cyclic phosphoric ester of oligo(propylene oxide). The *N,N*-dimethylformamide and propylene carbonate solutions of these compounds were tested for potential application as electrolytes in a protonic electrochromic cell with tungsten trioxide as an active compound. As a reference, a solution of phosphoric acid of identical concentration was used. Cyclic chronovoltamperometry studies were used to test both the stability window of the electrolytes on a platinum electrode and the stability of indium tin oxide and tungsten trioxide electrodes against the electrolyte solution. The proton intercalation process was also studied. The experiments were performed both for dry solutions (vacuum drying of compounds) and for ones, which were on purpose contaminated with water. Additionally, the dc conductivity of the studied systems was measured for the whole possible operational temperature range. Generally, it was observed that the ester solutions give a better photochromic response of the WO₃ electrode but are more aggressive to its surface. This observation is valid especially for the water-contaminated systems.

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1. Introduction

The photoelectrochromic phenomenon is widely known for transition metal oxides (WO₃, MoO₃, NiO₂) for a long period of time [1,2]. The optical properties are modulated when ions are inserted into (intercalation) or extracted from (deintercalation) an oxide film upon the application of a voltage of the order of few volts between the outer electrodes. Anhydrous systems based on lithium ion intercalation have been widely tested [3,4] and introduced into practical applications (auto-dimming rear windows for cars, smart windows [5]). To overcome the disadvantages of lithium electrolytes, a protonic system can be used [2]. The proton mobility in the electrolyte is much higher in comparison with that of the lithium cation. Additionally, the intercalation/deintercalation processes of protons into and out of the oxide layer are quicker than in the case of lithium ions. The potential range needed for an effective device operation is in this case narrower, which additionally

leads to the diminishing of the danger of the electrode deterioration in the case of moisture intake by the cell. Some designs of laminated devices incorporating a proton polymeric electrolyte were presented in [6,7]. Poly(2-acrylamido-2-methyl-1-propane sulfonic acid) (PAMPS), branched polyethyleneimine (BPEI), poly(methyl methacrylate) (PMMA), poly(vinyl butyral) (PVB) and others were used in combination with different oxide materials. An electrochemical and optical response of the WO₃|PEO,H₃PO₄|ITO (Indium Tin Oxide) was studied in [8], to determine the intercalation mechanism in this system. The authors use a model of superficial diffusion assuming homogeneous diffusion of absorbed hydrogen in the electrode material to explain the obtained data. This model is limited to short time scale processes only. A similar system plasticized by the addition of MeCN was studied in [9]. The electrochemical redox behaviors and electrochromic characteristics of WO₃ and Prussian blue have been examined in two- and three-electrode systems with polymeric gels as electrolyte [10]. They were based on copolymers of 2-hydroxyethylmethacrylate and neopentylglycoldimethacrylate with lithium perchlorate and a solvent mixture of propylene carbonate–butylene carbonate. With the conductivity of the material equal to 10^{−3} S cm^{−1} at 303 K, a reversible

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coloration/bleaching was observed for more than 10^5 cycles. The problem of the residual water content in protonic polymeric electrolytes was studied in [11]. The WO_3 electrode is stable against the polymeric electrolytes if they contain only bound water. An excess of moisture leads to electrode deterioration. The PAMPS containing system is reported to be the most promising.

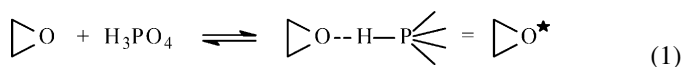
Nonaqueous protonic gels incorporating H_3PO_4 have been synthesized [12] with the use of different solvents such as propylene carbonate (PC), *N,N*-dimethylformamide (DMF), 1-methyl-2-pyrrolidone, ethylene glycol and several polyglycols. The highest conductivity was obtained for gels containing DMF in a network based on glycidyl methacrylate and PC in a network based on methyl methacrylate. It is observed that due to the dilution effect for PC based gels their conductivity is lower than that observed for the solution of the same acid concentration. In the case of DMF, the effect of gelation on conductivity depends on the sample composition. Proton conducting gel electrolytes containing poly(vinylidene fluoride) (PVdF) matrix, DMF and H_3PO_4 were characterized in [13]. Highly conductive ($5 \times 10^{-4} \text{ S cm}^{-1}$) visible light transparent systems were obtained over a narrow concentration range (78–85 mass% of H_3PO_4 in DMF). The systems obtained were stable up to 70–120 °C. Gels containing H_3PO_4 as a proton donor and various combinations of polymer matrix and solvent were described in [14]. The highest conductivities are achieved for polymers based on glycidyl methacrylate while those based on methyl methacrylate gave the lowest results. PVdF based gels are placed in the middle of the obtained conductivities range. The electrochemical stability window of the tested systems allows them to be applied in a WO_3 Ni(O)OH electrochromic cell.

In [15] it has been shown that in H_3PO_4 doped polymer gels containing poly(glycidyl methacrylate) (PGMA) matrix most of the glycidyl groups of the polymer react with the acid. The presence of various phosphate species including *ortho*- and *pyro*-phosphoric acid and organic phosphates was confirmed. Solvent protonation increases with increasing acid concentration. Selective deuteration was used in [16] to study the DMF– D_3PO_4 –PGMA system. It is shown that the Grotthus mechanism involving the hopping of the proton from one molecular site to another one, as well as the vehicular mechanism due to the motion of the D_2PO_4^- and D_4PO_4^+ ions are responsible for the motion of the proton in these electrolytes.

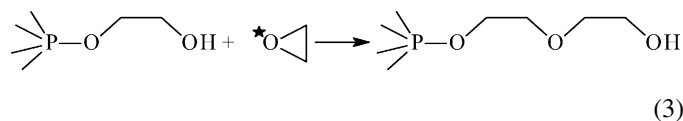
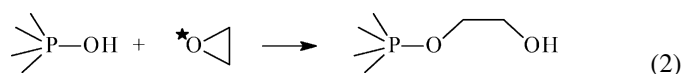
A comparison between PVdF based gels containing pure phosphoric acid and some esters including phenylphosphate, diphenylphosphate and *t*-butylphenylphosphate is presented in [17]. The incorporation of organophosphorous compounds into trapped DMF leads to an about one order of magnitude increase of conductivity over the whole temperature range in comparison with analogous samples containing H_3PO_4 solution. The conductivity changes are explained by the fact that esters are stronger acids in comparison with the H_3PO_4 itself. The $\text{p}K_\alpha$ (negative logarithm of the acidity constant) values for these compounds reported in [18] can suggest that the dissociation degree is higher. The conductivity is higher for monoesters in comparison with diesters and decreases with an increase in the size of the ester group. The last observation is in contrast with the $\text{p}K_\alpha$ data, which can be explained by changes of the charge car-

rier mobility. Similar systems incorporating both DMF and PC, phosphoric acid, different esters including phosphorylated calix [4] arenes were studied in [19]. Among all gel compositions, the best results have been achieved for the PMMA–PC–DMF–ester system combining high conductivity with thermal stability and optical transparency. Higher conductivities obtained for gels containing protophilic (DMF or DMF–PC) in comparison with protophobic (PC) solvents as well as measured proton diffusion coefficient values prove that the mechanism of conduction changes from Grotthus-type to vehicular with an increase in the protophobic character of the solvent. Phosphoric acid alkyl and alkylaryl diesters have been reported as materials modifying polyaniline. In such a system they play the role of a protonating agent and plastifier. Thus, electron-conducting polymers processable by thermal methods have been obtained [19]. Due to the fact that mono- and diesters of phosphoric acid have a higher value of the first ionization constant than the parent acid, they are useful for application as a source of protons in polymer gel electrolytes doped with several types of phosphoric acid esters [20].

Oligomeric phosphoric esters can be obtained in the reaction of phosphoric acid and oxiranes [21]. They result from the oxirane addition to the P–OH and C–OH groups, catalyzed by acidic groups, according to the activated monomer mechanism (1):



Further elementary steps involve the addition of the activated monomer to the P–OH (2) and consequently C–OH bonds (3):



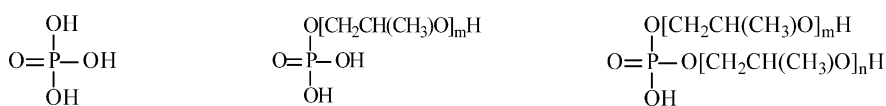
The mechanism of oxiranes addition to the acids of phosphorus in anhydrous non-polar media was described in [21]. Depending on the reaction conditions, first of all, on the reactant molar ratio, products of various degrees of POH groups' conversion and degree of oxirane oligomerization are formed.

As phosphoric acid esters give promising conductivity, stability and gel formation results, they can be potentially applied to the WO_3 electrochromic cell. However, the problem of the electrochemical stability window of these compounds must also be investigated. The behavior of the electrodes (WO_3 and ITO) in so strongly acidic solutions must be also tested. In this paper we want to compare the H_3PO_4 , diphenylphosphate and an adduct of propylene oxide and H_3PO_4 [22,23] solutions in DMF and PC in terms of their conductivity and applicability in electrochromic systems. Additionally, the influence of water traces on the electrochemical properties of studied systems will be tested to simulate the realistic conditions of the electrochromic window exploitation.

2. Experimental

All compounds used for the electrolytes synthesis were carefully dried prior to use. Solvents (*N,N*-dimethylformamide and propylene carbonate Aldrich, HPLC grade) were purified (mainly dried) by double vacuum distillation over molecular sieves. Anhydrous phosphoric acid was obtained by the reaction of 85% orthophosphoric acid with phosphorus pentoxide. Later, vacuum drying (8 h, 110 °C) was applied. Similar drying conditions were used for diphenylphosphate (ES1) (Aldrich synthesis grade).

Oligomeric mono- and diester mixtures (ES2) were formed in the reaction of phosphoric acid with propylene oxide (PO). The reactions with anhydrous phosphoric acid were carried out in a 100 ml three-neck flask, equipped with a magnetic stirrer and a dry ice condenser, to which a weighed amount of phosphoric acid was first introduced and, then, PO by means of a dropping funnel. The reaction is highly exothermic and, therefore, cooling with a mixture of acetone and dry ice was applied to maintain room temperature. The product composition was determined by means of NMR and MALDI-TOF mass spectrometry. When using a two-fold molar excess of PO with respect to phosphoric acid, a mixture composed of mono and diesters of average oxypropylene sequence length equal 4 and about 50% of unreacted acid are obtained (4). The product is of the form of a viscous liquid. At a five-fold PO excess, a mixture of mono, di- and triesters is present in the products and no free phosphoric acid was found. The obtained compound was dried in vacuum (16 h, 50 °C) prior to use.



All processes with the reagents and solutions (mixing, drying, etc.) were carried out under vacuum or in a nitrogen filled dry-box (<5 ppm H₂O) to avoid water vapor absorption in the samples. Concentration of all acidic compounds in the tested solutions was equal to 5 mg ml⁻¹. The electrochemical experiments were performed in a vacuum cell with an Ag/AgCl reference electrode and Pt grid as a counter electrode. Pt wire, ITO covered glass (20 Ohm cm⁻²) and WO₃/ITO glass (vacuum deposited) were used as working electrodes. An EG&G PAR 273A potentiostat/galvanostat was used for all chronovoltamperometrical experiments. Impedance spectroscopy experiments used for the conductivity evaluation were performed in a two-electrode cell with blocking electrodes made of pure titanium. An Atlas 98HI Frequency Response Analyzer was used in 1 Hz–100 kHz frequency range. The cell was immersed in a HAAKE cryostat to control the measurement temperature in the 223–333 K range.

3. Results and discussion

In the first step, a set of conductivity data was collected for all the electrolytes studied for a temperature range corresponding to the practical application of the photoelectrochromic cell

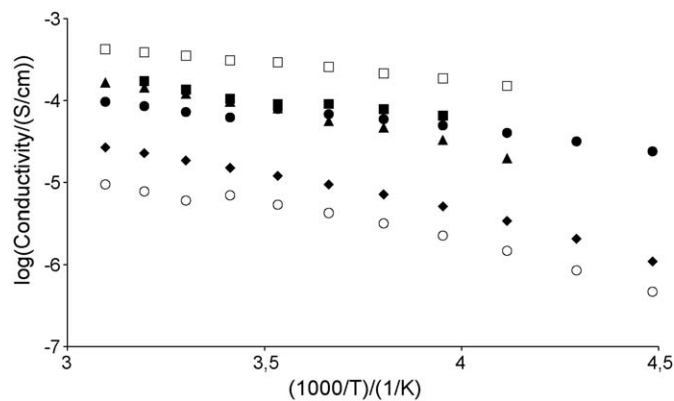


Fig. 1. Dependence of conductivity of the studied electrolytes as a function of temperature. \blacklozenge : H₃PO₄ in PC, \blacksquare : H₃PO₄ in DMF, \blacktriangle : ES1 in PC, \square : ES1 in DMF, \circ : ES2 in PC, \bullet : ES2 in DMF.

(223–323 K). From the point of view of the response time the limiting value of the conductivity is in order of 10⁻⁴ S cm⁻¹. Fig. 1 shows that only one of the studied systems (ES1 in DMF) exhibits so high conductivity values. Both electrolytes incorporating the ES2 compound give significantly lower conductivity values. The conductivity of the other systems lies in range 10⁻⁵–10⁻⁴ S cm⁻¹. Taking into consideration the low concentration of the studied solutions one can expect that apart from the ES2 compounds, the rest of the studied systems in the practically applied range of concentrations may also fulfill the conductivity threshold (compare with [12,13]).

Next, the electrochemical stability window was tested for all the studied systems. For this purpose cyclic voltammograms were collected with a platinum-working electrode. For H₃PO₄ in PC the system was stable between -0.7 and +1.2 V versus Ag/AgCl reference. The influence of water addition (about 0.1 wt.%) on the system behavior was also tested. The stability range is here narrowed to -0.4 to +0.8 V. Additionally, the observed capacitance current is two times higher in comparison with the dry system. The results for a DMF based system are generally similar. The window for a dry system is equal to -0.6 to 1.4 V, while water addition limits the upper value to 1.1 V. The obtained results are consistent with the data presented in the literature [14,24].

The results obtained for the solutions of esters are ambiguous. For ES1 in PC the stability window is limited to -0.7 to +0.8 V. Contamination with water leads to additional narrowing of the lower voltage limit to -0.3 V. The appearance of a pair of redox peaks in this range of potential (see Fig. 2a) can be observed. The current values are here one order of magnitude higher when compared to the pure system with consequent electrolyte decomposition. On the contrary, the DMF/ES1 system reveals a wide stability window -0.6 to +1.7 V (Fig. 2b) with visibly higher currents than for any other dry system. This can

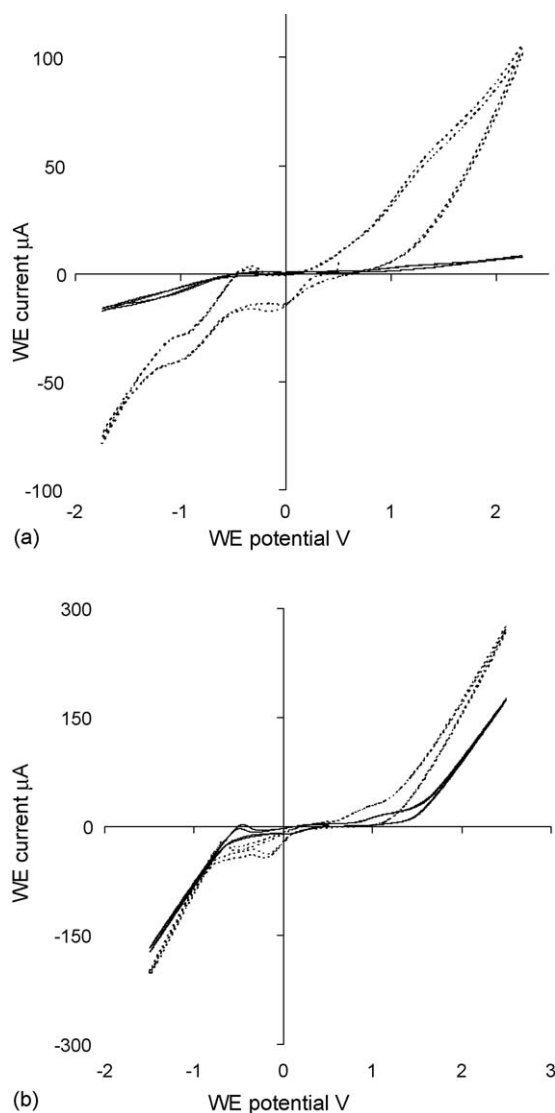


Fig. 2. Cyclic voltammogram registered for (a) ES1 PC solution on Pt working electrode with scanning rate 5 mV s^{-1} and (b) for ES1 DMF solution on Pt working electrode with scanning rate 5 mV s^{-1} . Solid line – dry electrolyte, dashed line – water contaminated one.

be attributed to a significantly higher conductivity value for this electrolyte. In this case water addition does not lead to a current increase while the upper stability limit is decreased to $+1.2 \text{ V}$ with small additional redox peaks within the window.

ES2 solutions in both PC and DMF show the smallest observed current densities. The stability window is in range -1.0 $+1.3 \text{ V}$ and is slightly narrowed by water addition. The measured curves are mainly of a capacitance character with no significant peaks observed. An about two-fold current increase is observed for water-contaminated systems.

The third stage of the research was based on the study of the interaction of ITO electrode (supporting material for most of electrochromic devices) with the studied electrolytes in both dry and water-contaminated state. For H_3PO_4 -PC and H_3PO_4 -DMF electrolytes the ITO electrode behaves almost identically to the Pt one. A very slow deterioration of the electrode surface can be observed (mainly in the case of DMF) for

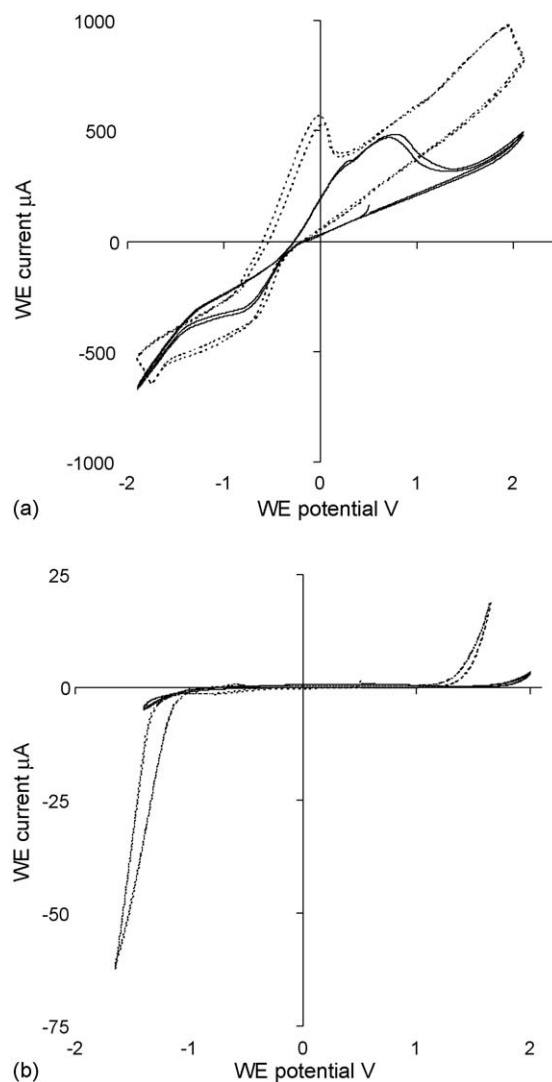


Fig. 3. Cyclic voltammogram registered for (a) ES2 DMF solution on ITO working electrode with scanning rate 5 mV s^{-1} and (b) for ES2 DMF solution on ITO working electrode with scanning rate 5 mV s^{-1} . Solid line – dry electrolyte, dashed line – water contaminated one.

a long time (10 h) at a relatively high positive potential. This phenomenon should not prove to be of practical importance. Contrary to these observations, both solutions of ES1 seem to be extremely aggressive to the ITO surface. A pair of red-ox peaks is observed at -0.7 and $+0.7 \text{ V}$, respectively for DMF solution (see Fig. 3a – solid line). For water-containing electrolytes a quick radical deterioration of the ITO layer (up to complete dissolution) can be observed in a few voltammetric cycles. In this case the water content leads not only to a significant current density increase but decreases the potential of the oxidation peak to 0 V not influencing the reduction peak (see Fig. 3a – dashed line). A less pronounced but also important degradation process is observed for the PC solutions of ES1.

In contrast, ES2 solutions in both DMF and PC are significantly more stable against the ITO electrode. For the DMF solution (Fig. 3b) a flat curve containing no peaks within the stability window (-1.1 $+1.6 \text{ V}$) is observed. Water addition

does not change the observed behavior leading only to the narrowing of the window (-1.1 to $+1.2$ V) and to some increase of the observed current. For dry ES2/PC solutions the situation is similar. The observed curve has an almost identical shape with an identical stability window. The addition of water has even a smaller influence in comparison with the DMF/ES2 system. In this case the stability window remains the same as for the dry system. The current increase is also not so significant.

The observed promising stability of the ES2 solutions against ITO electrode encouraged us to check the possibility of the long-term work of the tested solution. A multi-cycle experiment with a low scan rate (2.5 mV s^{-1}) was thus performed. For this experiment the ES2/DMF system was chosen because of the very low conductivity of the ES2/PC solution. The results gathered in Fig. 4 show that an important decrease of the current is observed between the first and 10th cycle (a) for water containing ES2/DMF electrolyte while an analogous change for the dry solution (b) is significantly less pronounced (curves almost overlap).

Finally, the interaction between electrolytes and the WO_3 electrode was tested. In the case of H_3PO_4 -PC solution a typ-

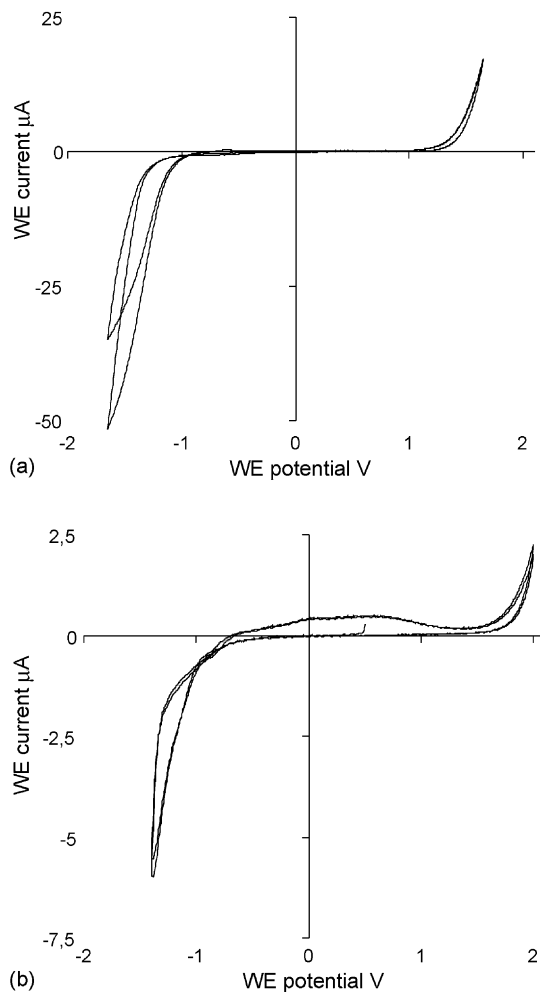


Fig. 4. Cyclic voltammogram registered for ES2 DMF solution on ITO working electrode with scanning rate 2.5 mV s^{-1} (1st and 10th cycle). (a) Wet electrolyte; (b) dry one.

ical intercalation curve is observed. Water addition does not affect significantly the peak potentials, but increases the peak current about twenty times. An electrode coloration can be easily observed for scanning rates lower than 25 mV s^{-1} . The only difference between PC and DMF solutions is the 1.5 times higher current density for the second solvent used. Similar observations are valid also for ES1 solutions. In comparison with the H_3PO_4 system an additional pair of red-ox peaks can be observed at -0.5 and -0.3 V. The coloration process is quicker and more intensive but, unfortunately, the electrode slowly dissolves in the electrolyte. The addition of water to this electrolyte leads to a current increase by the factor of 2. The coloration process is more intensive and the shape of the curve changes (see Fig. 5a). The wet electrolyte is also more aggressive against the WO_3 surface in comparison with the dry one.

The ES1 PC-based systems are more aggressive towards the WO_3 surface in comparison with the ones containing DMF. In

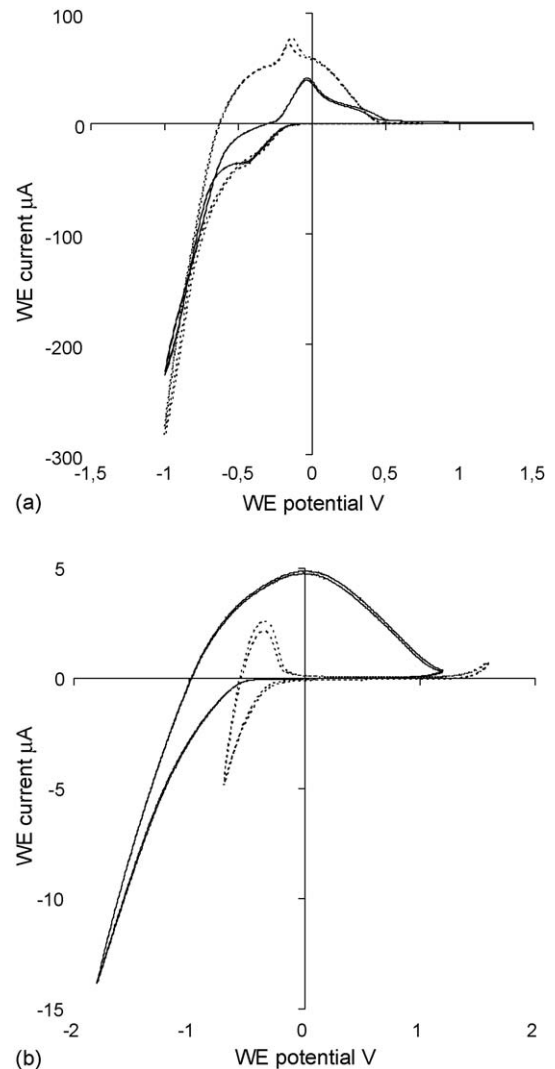


Fig. 5. Cyclic voltammogram registered for (a) ES1 DMF solution on WO_3 working electrode with scanning rate 5 mV s^{-1} and (b) for ES2 PC solution on WO_3 working electrode with scanning rate 5 mV s^{-1} . Solid line – dry electrolyte, dashed line – water contaminated one.

this case they reveal a tendency opposite to the one observed for the ITO electrode where the DMF solutions were extremely corrosive. The observed shape of the curve is similar to the one observed for the DMF/ES1 wet system for both PC/ES1 dry and wet electrolytes. Contamination with water leads this time to a significant current increase (one order of magnitude) and to the intensification of the coloration process.

ES2/DMF solutions reveal significantly lower current densities in comparison with the ES1/DMF system with the dominant factor of the capacitance currents. The addition of water does not lead to a current density change. On the contrary, the PC/ES2 solution reveals a typical shape of the curve for the intercalation process [9] (Fig. 5b) with a very broad anodic peak related to the deintercalation. The addition of water makes the anodic peak narrower and shifts the intercalation potential to more positive values (Fig. 5b). Unfortunately, a change of the optical properties due to the intercalation process for all system containing ES2 can be observed only for the slowest scanning rate (2.5 mV s^{-1}). This observation can be related to the significantly lower conductivity of these systems. On the other hand, the electrode is in this case stable against the electrolyte.

4. Conclusions

The studied solutions of phosphoric acidesters reveal some interesting properties as potential electrolytes for photoelectrochromic devices. Unfortunately, systems with relatively good conductivity and coloration seems to be strongly aggressive against ITO, which is the supporting material for most of the electrochromic electrodes, and slightly against WO_3 – a typical representative of active materials. A correlation between conductivity and electrochemical properties can be observed. ES1 solutions revealing the highest conductivity yield a quick and strong coloration/decoloration effect with high current densities. On the other hand, the ES2 based systems exhibiting low conductivity (particularly ES2–PC) give a weak and slow response being also slightly corrosive against ITO but not against WO_3 . Generally, the strong corrosive properties of the ES1 compound can be attributed rather to its properties such as the highest $\text{p}K_\alpha$ and possibility of complex formation between the phenyl rings of the ester and the metal ion coming from the deteriorating oxide surface. If the technical question of sealing the ITO surface from electrolyte could be solved, the DMF/ES1 system would be most promising for further investigation. The long-term working device should be also carefully protected against humidity intake as water presence in the electrolyte increases its corrosive properties. Other organic esters of phosphoric acid could be also tested.

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