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Deposition of stable electroactive films of polynuclear cyanides onto silicon surface

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Abstract

The possibility of using silicon as the substrate electrode for the deposition of electroactive films of transition metal hexacyanoferrates was investigated. The silicon surface was successfully modified by the electroactive films based on a simple method. The studies of the electrochemical behavior and electrocatalytic properties of a palladium hexacyanoferrate (PdHCF) film-modified silicon electrode showed that the electrode fabricated had excellent properties and electrochemical activity. The possibility of the use of silicon substrate was also examined for the deposition of NiHCF and CoHCF films. The modification was carried out by electrodeposition of metals onto the substrate surface and chemical transformation of the metallic films deposited into their hexacyanoferrate salts. The results obtained from electrochemical studies indicate clearly that the electroactive films have excellent electrochemical activities compared with conventional hexacyanoferrate-based modified electrodes. In addition, deposition of electroactive films onto silicon surface provides an enhanced stability of the electroactive films during potential cycling and long-term storage.

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Keywords: Silicon substrate; Electroactive film; Hexacyanoferrates; PdHCF; Enhanced stability; Electroless deposition

1. Introduction

Modification of electrode surfaces with electroactive films has had considerable attention in both scientific and technological research due to its practical significance. Deposition of thin films of conducting materials onto semiconductor surfaces has particular technological importance. Among semiconductors, silicon is one of the most interesting and important materials due to its vast range of applications, e.g. microelectronics, solar cells, etc. Thus, deposition on a silicon surface is a rapidly growing and advancing area of research. Metallization of the silicon surface using the technology of ultralarge-scale integrated (ULSI) devices is of importance due to advancing microelectronic technology in deep subquarter-micrometer and increasing number of electronic devices on a small chip [1–7].

Studies of chemically modified electrodes (CMEs) are an important area of research in modern electrochemistry. Several modifier materials have been proposed for the preparation of CMEs. Among modifier materials, Prussian blue (PB) and its analogues are very interesting inorganic materials for the modification of electrode surfaces. Due to their interesting properties, they have been widely used for different practical performances such as electrochromic devices [8], sensors [9], electrocatalysis [10], intelligent overlayer design [11], oxidation inhibitors in solar cells [12], battery purposes [13], photochargeable device [14], etc. Thus, it is very important to deposit thin films of electroactive materials on different substrates, for practical applications. In addition to conventional substrate electrodes (e.g. Pt, Au, glassy carbon, etc), other substrates have also been employed for the preparation of CMEs. For example, superior properties of aluminum as an excellent substrate for the deposition of highly stable films of various electroactive materials have been reported [15–18].

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Although, a variety of materials have been deposited on silicon substrates for microelectronic application, to our knowledge, no research has been devoted to studies of the deposition of transition metal hexacyanoferrate on silicon electrodes. Kulesza and coworkers have studied the solid-state voltammetric behavior of PB encapsulated within silica in a different context [19]. Deposition of electroactive materials on silicon provides an opportunity for using CMEs in microelectronic systems. Of course, its practical aspect is beyond the aim of the present research, as we wish to show this possibility as a preliminary investigation. For this purpose, deposition of palladium hexacyanoferrate (PdHCF) onto a silicon surface is studied. PdHCF is a PB analogue with excellent electrochemical properties; however, less attention has been given to this compound for the modification of electrode surfaces [20,21]. In addition, these two papers relate to the electrochemical behavior of PdHCF, and its stability and electrocatalytic properties are studied here for the first time. The approach proposed in Refs. [20,21] was also investigated for the deposition of two well-known analogues of PB, namely nickel hexacyanoferrate (NiHCF) [22–24] and cobalt hexacyanoferrate (CoHCF) [25–27] on Si substrate surface. However, the present paper has a general interest as the results presented can be used typically for the preparation of various CMEs, which have different applications.

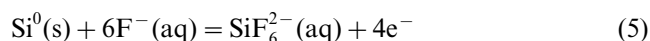
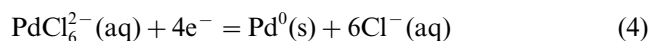
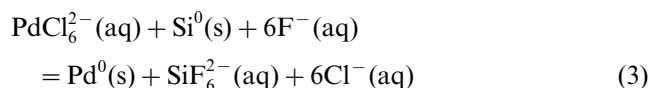
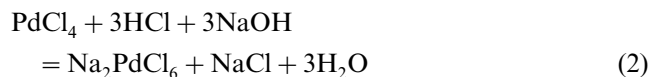
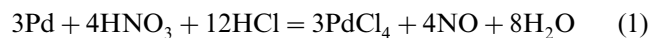
2. Experimental

The working electrode was prepared from a p-type silicon wafer thoroughly cleaned by degreasing in acetone and trichloroethylene, boiling in nitric acid to remove metallic impurities, and dipping in a solution of 10% HF (48%) The heavily doped p⁺ surface of the substrate electrode was prepared according to the available method reported in the literature [6]. This carefully polished p-type silicon wafer, which was doped by diffusing boron into the silicon, is susceptible for silicon metallization with strong adhesion of deposited metal. The modification of the silicon surface with electroactive films of metal hexacyanoferrates was performed in two different steps. In the first step, a thin metallic layer was deposited onto the silicon substrate surface, and the metallic film deposited was transformed into the corresponding hexacyanoferrate salt.

An aqueous solution of HF/H₂O (1:4) was used before the deposition process to remove the native silicon oxide. Then, the electrode was immediately conditioned in a solution of sodium chloropalladate dissolved in dilute HF. The problem is that conventional HF activator solutions (HF + metal chloride + HCl), which have been successfully used for the deposition

of metals (e.g. Ni), are not applicable for the case of Pd to deposit an adhesive metallic film. This problem can be overcome by using metal complexing agents. For example, ammonium hydroxide (NH₄OH), ammonium fluoride (NH₄F) and triammonium citrate ((NH₄)₃C₆H₅O₇) have been used successfully for Pd deposition [28,29]. NH₄OH, as a known and low-cost complexing agent, was used for this purpose.

The Pd metallization of the Si substrate can be described by the following reactions:



The chloropalladate complex was generated as a result of Pd dissolving in HCl in the presence of NH₄OH (Reaction 1). Then, sodium chloropalladate was precipitated as a result of the following reaction (Reaction 2). Finally, the salt was dissolved in an HF solution to prepare the plating solution.

By immersing the Si electrode into the complex bath generated as the result of reactions (1) and (2), the Si atoms are partly replaced by the metal atoms according to reaction (3). During this process, Pd ions act as the oxidizing agent of Si, and fluorine species act as the complexing agent of Si oxidation products to remove some Si atoms from the substrate surface, replacing these with Pd. Indeed, the cathodic reduction of Pd(IV) and the anodic oxidation of Si occur simultaneously as two half-cell electrochemical reactions (Reactions (4) and (5)), and the combined reaction is that noted in reaction (3). Fluoride ions have a critical role in the deposition process, as they prevent the creation of silicon oxide and dissolve the Si skeleton to a soluble complex of SiF₆²⁻.

In the case of basic complexing agents, in mixed solution plating, similar reactions occur and the existence of NH₄OH causes the generation of a Pd–ammine complex (probably Pd(NH₃)₂Cl₂) complex instead of [PdCl₄]²⁻; however, the exact mechanism of this process is still not well known [6]. Both the multi-step and mixed solution plating approaches are applicable for Pd deposition on the silicon substrate, but the latter, in the presence of basic complexing agents, provides Pd films with stronger adhesion. The plating solution was prepared from 0.04 g PdCl₂ dissolved in 1.2 ml of HCl (35%) and addition of 22 ml of HF (48%) and 40 ml of NH₄OH (25%). The deposition time was 10 min to obtain an acceptable thickness, as the substrate elec-

trode is completely covered with the metallic layer and is not very thick.

The second step of the surface modification can be easily carried out by dipping the prepared electrode in an acidic (ca. 0.1 M HNO₃) solution of 10 mM K₃Fe(CN)₆+1.0 M KCl. This deposition process was also performed for 10 min. In this step, the acidic medium causes the chemical oxidation of the metallic Pd to Pd²⁺, then, a complexation reaction between Pd²⁺ and hexacyanoferrate ions at the electrode surface causes the formation and deposition of PdHCF film onto the substrate surface. The infrared absorption curve of the compound was very similar to that reported in the literature [20], displaying a strong absorbance peak of the –CN functional group at 2058 cm⁻¹ and characteristic hexacyanoferrate peaks in the range 400–800 cm⁻¹.

A similar procedure was used for the deposition of metallic layers of Ni and Co on the silicon substrate. The first step (metallization of Si) was similar to that of Pd; however, as the latter metals are more active than Pd, a half-deposition time was used for the second step. Indeed, the chemical transformation of the deposited metallic (Co and Ni) films into their hexacyanoferrate salts was achieved in 5 min.

The electrochemical measurements were performed using a homemade potentiostat connected to a computer running CORVIEW software. The experiments were carried out at a three-electrode conventional cell containing the working electrode at room temperature. All potentials were referenced to a saturated calomel electrode (SCE). All of the reagents were of analytical grade without further purification.

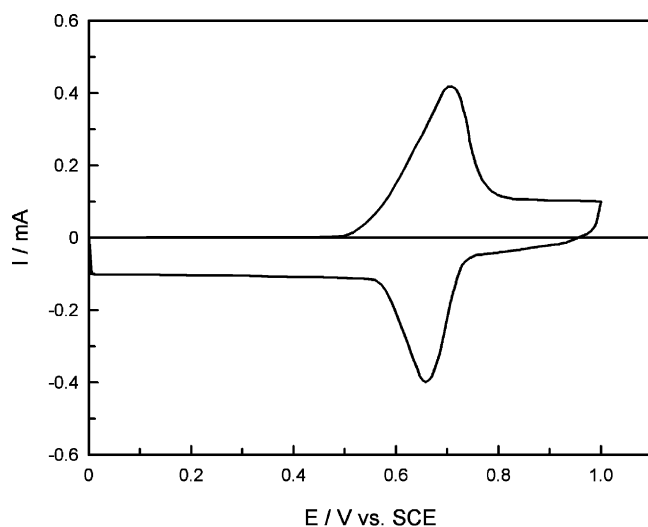
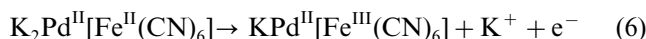


Fig. 1. Typical cyclic voltammogram of the PdHCF film-modified silicon electrode in the supporting electrolyte of 0.5 M KCl. Scan rate: 100 mV s⁻¹.

3. Results and discussion

3.1. Electrochemical characteristics of the PdHCF film-modified silicon electrode

Fig. 1 shows typical cyclic voltammetric behavior of the PdHCF film-modified silicon electrode in an aqueous supporting electrolyte. As expected, the curve shows a pair of redox peaks corresponding to the Fe²⁺/Fe³⁺ or Fe(CN)₆⁴⁻/Fe(CN)₆³⁻ redox couples. This is indicative of the fact that hexacyanoferrate ions are the only electroactive sites in the deposited film displaying one pair of redox peaks, and the peak current was controlled by a diffusion process. The redox couple of the system under investigation can be attributed to the following reaction:



3.2. Electrocatalytic activity of the PdHCF film-modified silicon electrode

One of the best-known electrochemical properties of CMEs is their electrocatalytic activity. However, electrocatalytic properties of PdHCF have not been reported in the literature. To investigate the electrocatalytic properties of PdHCF, the electrochemical oxidation of ascorbic acid was chosen as a typical example. The electrocatalytic oxidation of ascorbic acid at the PdHCF film-modified silicon electrode was investigated by the cyclic voltammetric technique, as presented in Fig. 2. A cyclic voltammogram was also

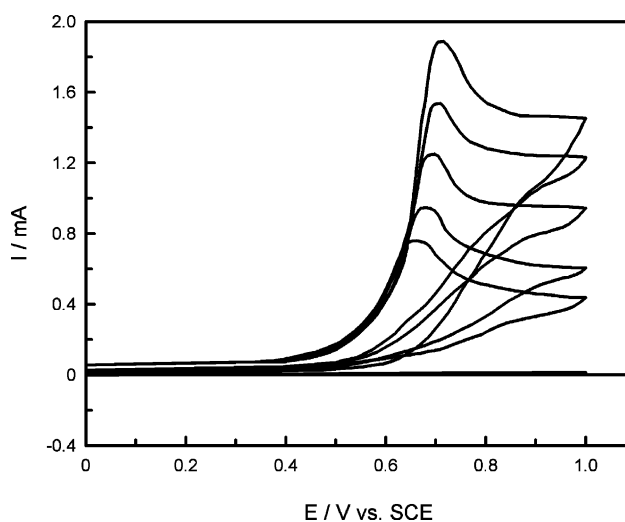


Fig. 2. A set of cyclic voltammograms featuring the electrocatalytic oxidation of ascorbic acid (with different concentrations: 3, 6, 9, 12 and 15 mM) in 0.25 M phosphate buffer (pH 7.2) at the PdHCF film-modified silicon electrode, and a featureless cyclic voltammogram showing the electrochemical behavior of an unmodified silicon electrode in a solution of 15 mM ascorbic acid. Scan rate: 100 mV s⁻¹.

recorded for an unmodified Si electrode (a featureless CV). The electrocatalytic activity of PdHCF with respect to ascorbic acid oxidation can be understood from the cyclic voltammeteric characteristics.

The voltammetric measurements at higher potential scan rates also reveal the catalytic reaction occurring at the PdHCF film-modified silicon electrode due to the considerable catalytic reaction rate. As expected, the peak currents appearing as the result of the ascorbic acid oxidation are proportional to the square root of the scan rate (Fig. 3(a)) suggesting that the reaction is mass

transfer controlled. Similar to the electrocatalytic properties of other PB analogues and CMEs, there is a shift towards more positive potentials in the peak potential with an increase of scan rate, which is due to a kinetic limitation in the reaction between the redox sites of the PdHCF film and ascorbic acid. As shown in Fig. 3(b), the scan rate normalized current ($I_p v^{-1/2}$) is independent of scan rate. Therefore, the oxidation is diffusion controlled which attests to a rapid but not rate limiting reaction between the redox sites in the PdHCF film and ascorbic acid. Moreover, the net reaction is not limited

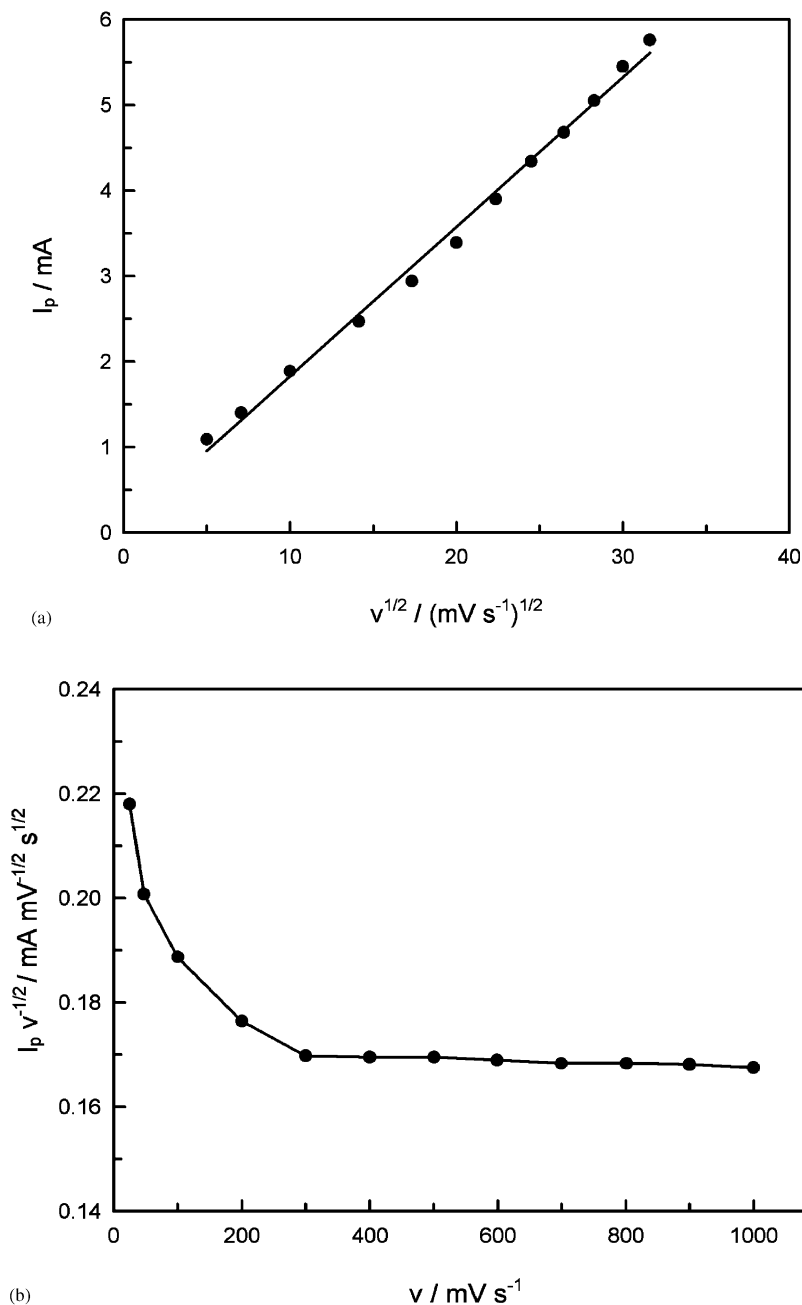
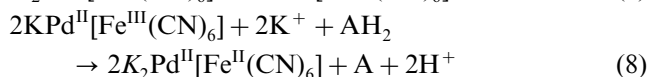
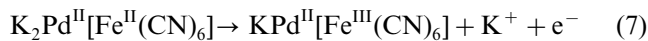


Fig. 3. The dependence of the peak current of ascorbic acid oxidation on the scan rate. Experimental conditions as in Fig. 2.

by the charge propagation through the thin film. In addition, the curve (Fig. 3(b)) shows a typical shape indicating an EC_{cat} process.

The results are indicative of the fact that the overall electrochemical oxidation of ascorbic acid at the PdHCF film-modified silicon electrode is controlled by the diffusion of ascorbic acid in the solution and the cross-exchange process between ascorbic acid and redox sites of the PdHCF film. According to the EC catalytic mechanism of ascorbic acid oxidation, the overall process can be expressed as follows:



Based on the above-mentioned results, it can be concluded that the PdHCF film and consequently, the PdHCF film-modified silicon electrode has excellent catalytic properties similar to other PB analogues. This provides strong evidence that the approach proposed (deposition of an electroactive film on a Si substrate) can be used for the preparation of electrocatalysts.

3.3. Electrochemical stability of the PdHCF film-modified silicon electrode

One of the main problems in the preparation of CMEs, which should be taken into account, is the stability of the electroactive film deposited on the substrate surface. In fact, it is the most important factor for practical performance. This feature is not usually recognizable in preliminary electrochemical studies of CMEs, as they do not contain repetitive cyclic voltammetric measurements. Fig. 1 shows only the voltammetric characterization of the modified electrode during the first potential scan. However, it has been reported that the main drawback for CMEs based on transition metal hexacyanoferrates is their gradual dissolution during potential cycling [30]. Some devices have been reported for improving the stability of electroactive films formed on electrode surfaces. Two factors are responsible for the stability of the electroactive films deposited: (i) the stability of the electroactive material, and (ii) stable connection (deposition) of the electroactive film on the substrate surface.

The first factor can be achieved by improving the stability of the hexacyanoferrate lattice. Kulesza et al. [31] have claimed a better stability of NiHCF films deposited in the presence of Ag(I) ions. It has been suggested that the incorporation of Ag(I) provides an augmented cross-linking between microparticles of NiHCF, probably due to the lower solubility of the relevant silver-containing film. Cataldi et al. [30,32–34] have reported that incorporation of ruthenium into the lattice of indium hexacyanoferrate film improves the

stability of the film formed on a glassy carbon electrode. However, this problem is inappropriate for the system under investigation, as PdHCF is a stable compound from the inorganic chemistry point of view and consequently, it has acceptable stability under electrochemical conditions.

The second factor, the connection of the electroactive film to the substrate surface, is related to the deposition conditions and the substrate electrode employed. Indeed, the deposition method is very important to obtain a stable connection between the electroactive film and the substrate surface. For example, aluminum is a suitable substrate electrode for the preparation of CMEs for the deposition of highly stable electroactive films [15–18]. This is due to the well-known behavior of aluminum in aqueous media and the occurrence of a passivation process. Formation of a passive film on the aluminum surface causes the generation of a more suitable surface for the deposition of electroactive films, and the deposited film on the passive substrate is more stable in comparison with conventional electrodes [15]. A similar phenomenon has also been reported for direct modification, as the electroactive metals are deposited onto the electrode surface in accordance with passivation of the metallic substrate [35–37].

On the other hand, if we believe that physical attachment of the electroactive material onto the substrate electrode is mainly responsible for the film stability, mechanical (physical) factors should have significant effects on the stability of electroactive films deposited on substrate surfaces. Interestingly, such effects have been studied in the literature for the deposition of hexacyanoferrate films on electrode surfaces. Significantly higher stability was achieved for the CoHCF film deposited under centrifugal forces [38]. Similarly, both chemical and electrochemical stabilities of PB deposited in the presence of magnetic fields were improved in comparison with those of PB deposited in the absence of an applied magnetic field [39].

For the electrodes prepared based on two chemical steps for the surface modification, the film stability is mainly related to the adhesion strength of the metallic layer first deposited on the substrate surface, and the second step is not responsible for the stability achieved as it is a simple chemical transformation of the metal to its hexacyanoferrate salt. Thus, the enhanced stability of PdHCF film deposited on the silicon substrate can be expected, as very strong adhesion of metallic films on silicon is well known and has been widely used for the metallization of silicon even for commercial applications [1–7]. For the case of deposition on an aluminum substrate, formation of aluminum oxide during the modification process is responsible for the enhanced stability of the deposited film, as it provides more suitable sites for the deposition of electroactive material. Similarly, pre-treatment of the silicon surface with HF

and its active reaction with Si during the modification process provide strong adhesion of the deposited metal layer with the silicon substrate. The electrochemical stability of the PdHCF film deposited on the silicon substrate during potential cycling is presented in Fig. 4. The decrease occurring in the peak current, as the result of potential cycling, was less than 10% after 2000 cycles.

As is seen, using a silicon substrate significantly improves the film stability as it shows a significant resistance in potential cycling. Interestingly, it can be observed that the stability of PdHCF itself is higher than that of other hexacyanoferrates, e.g. Ni and Co, as reported in the literature [23–27] and as is presented below. It can be concluded, by comparison of electroactive films similarly deposited on conventional glassy carbon substrate electrodes, that NiHCF and CoHCF (and also similar hexacyanoferrates) show about a 90% decrease after 1000 potential cycles whereas PdHCF shows a 50% decrease after the same number of cycles.

3.4. Chemical stability of the PdHCF film-modified silicon electrode

In addition to electrochemical stability during potential cycling, the electroactive film deposited on the substrate surface should have considerable chemical stability during long-term usage. The above-mentioned statements on the electrochemical stability of the electroactive film are also true for its chemical stability. In fact, the gradual dissolution of the electroactive film in the absence of an electrical force during long-term storage also occurs. Fig. 5 shows the chemical stability of the PdHCF film-modified silicon electrode compared with a conventional PdHCF film-modified glassy carbon electrode. The data were obtained from voltam-

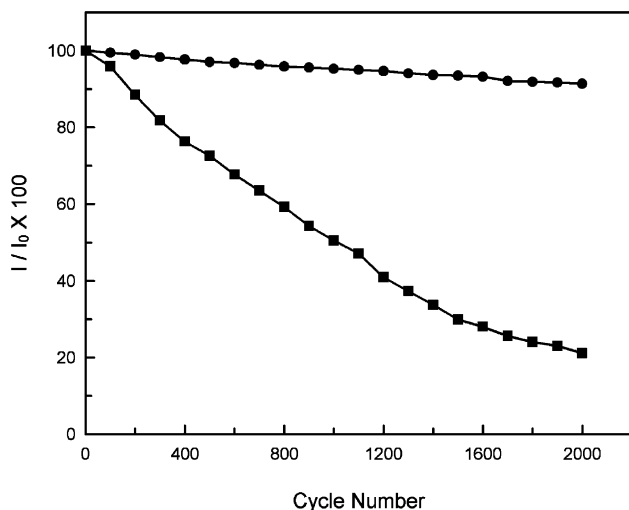


Fig. 4. The relationship of the peak current of the voltammetric characteristic of the PdHCF film-modified glassy carbon electrode (■) and the PdHCF film-modified silicon electrode (●) to the cycle number. Experimental conditions as in Fig. 1.

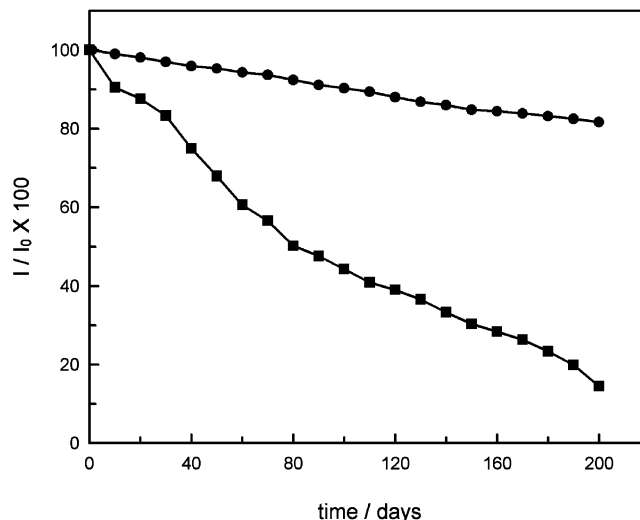


Fig. 5. Chemical stability of the PdHCF film-modified glassy carbon electrode (■) and the PdHCF film-modified silicon electrode (●).

metric measurements of the modified electrodes after different times of storage in the supporting electrolyte.

3.5. Electrochemical stability of the NiHCF and CoHCF films growth on silicon substrate

As presented above, a silicon substrate could be successfully used for the deposition of PdHCF film. Now, to examine the same substrate electrode for the deposition of other hexacyanoferrates, similar experiments were carried out for two common (widely used and well-known) hexacyanoferrates, namely NiHCF and CoHCF. Similar to the case of PdHCF, using a silicon substrate does not make any difference to the electrochemical behavior and properties of the NiHCF- and CoHCF-modified electrodes. The silicon substrate employed just enhances the stability of the electroactive films deposited. Therefore, the electrochemical behavior of the NiHCF and CoHCF film-modified silicon electrodes is not presented here as it has been reported in the literature [22–26]. The influences of the use of a silicon substrate on the stabilities of the electroactive films deposited are shown in Figs. 6 and 7. Due to the similar electrochemical properties of NiHCF and CoHCF compounds, the curves are similar. Although they have the same electrochemical stabilities, it seems that CoHCF has a higher stability than NiHCF in the first part of the experiment (initial cycles, ca. < 500), and vice versa for the second part of the experiment (total cycles, ca. > 500). This suggests that CoHCF itself has a higher stability in comparison with NiHCF; however, NiHCF was strongly attached to the substrate surface. Although, this is a simple speculation based on a very small difference between the experimental results obtained for two different compounds, such attention based on further in depth investigations would be very

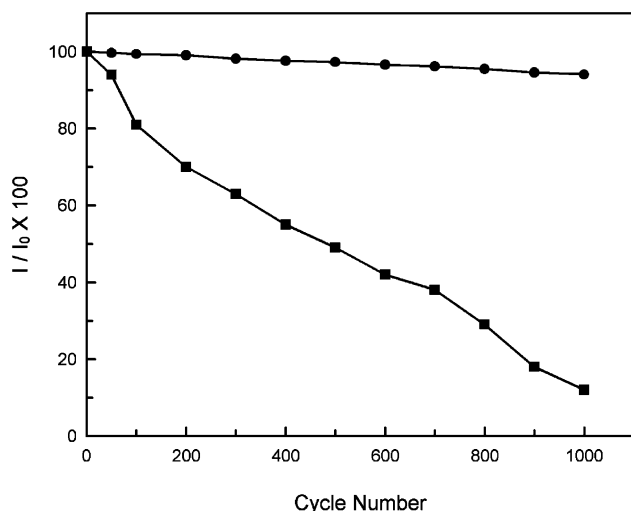


Fig. 6. Electrochemical stability of the NiHCF film formed on a glassy carbon substrate electrode (■) and a silicon substrate electrode (●) during potential cycling.

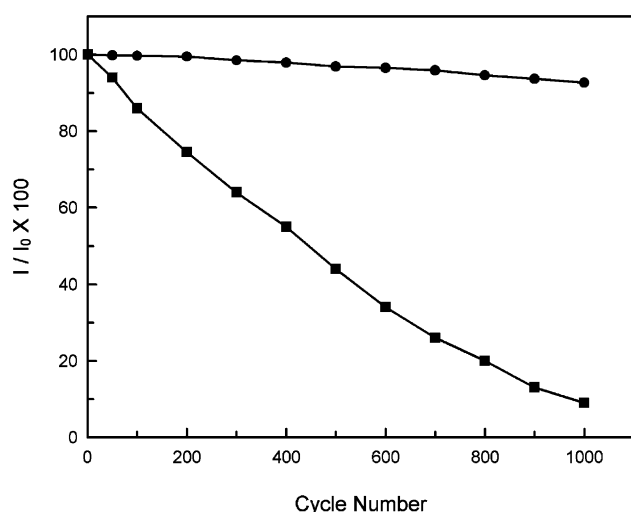


Fig. 7. Electrochemical stability of the CoHCF film formed on a glassy carbon substrate electrode (■) and a silicon substrate electrode (●) during potential cycling.

useful for practical applications of the use of suitable modifiers for the fabrication of CMEs for specified purposes.

4. Conclusions

It was demonstrated that a silicon substrate could be used for the deposition of various electroactive materials for the preparation of CMEs. The electrochemical studies of the PdHCF film-modified silicon electrode showed that the electroactive film was stably attached to the substrate surface, while the electrochemical properties of the electroactive material remained the same. In

addition, PdHCF was introduced as an interesting compound for the preparation of CMEs. In comparison with PB analogues, PdHCF shows electrochemical behavior similar to that of other hexacyanoferrates, e.g. it shows excellent electrocatalytic activity. However, the stability of the PdHCF compound itself under the electrochemical conditions is about twice that of other PB analogues, which is desirable for practical performances. The approach proposed was also examined for two other hexacyanoferrate salts, which are well known in solid-state electrochemistry. The results obtained from various investigations of the different systems provide strong evidence for the possibility of using silicon substrates for the deposition of insoluble salts of polynuclear cyanide complexes. Moreover, due to the vast number of applications of silicon in high-tech products, it provides a new opportunity for using such electroactive materials in microelectronics and similar technologies.

References

- [1] P.L. Pai, C.H. Ting, *IEEE Electron Device Lett.* EDL-10 (1989) 423.
- [2] H.A. Marzouk, J.S. Kim, P.J. Reucroft, R.J. Jacob, J.D. Robertson, C. Eloi, *Appl. Phys. A* 58 (1994) 607.
- [3] N. Awaya, T. Kobayashi, *Jpn. J. Appl. Phys.* 37 (1998) 1156.
- [4] A.A. Pasa, W. Schwarzacher, *Phys. Status Solidi A* 173 (1999) 73.
- [5] J.C. Ziegler, A. Reitzle, O. Bunk, J. Zegenhagen, D.M. Kolb, *Electrochim. Acta* 44 (1999) 4599.
- [6] S. Karmalkar, J. Banerjee, *J. Electrochem. Soc.* 146 (1999) 580.
- [7] A. Eftekhari, *Microelectron. Eng.* 69 (2003) 17.
- [8] S. Dong, F. Li, *J. Electroanal. Chem.* 210 (1986) 31.
- [9] K.-C. Ho, C.-L. Lin, *Sens. Actuators B* 76 (2001) 512.
- [10] S.-M. Chen, *J. Electroanal. Chem.* 417 (1996) 145.
- [11] L.J. Amos, M.H. Schmidt, S. Sinha, A.B. Bocarsly, *Langmuir* 2 (1986) 559.
- [12] G. Seshadri, J.K.M. Chun, A.B. Bocarsly, *Nature* 352 (1991) 508.
- [13] M. Jayalakshmi, F. Scholz, *J. Power Sources* 91 (2000) 217.
- [14] M. Kaneko, K. Takahashi, E. Tsuchida, *J. Electroanal. Chem.* 227 (1987) 255.
- [15] A. Eftekhari, *Talanta* 55 (2001) 395.
- [16] A. Eftekhari, *Synth. Met.* 125 (2001) 295.
- [17] A. Eftekhari, *Sens. Actuators B* 80 (2001) 283.
- [18] A. Eftekhari, *Mikrochim. Acta* 141 (2003) 15.
- [19] K. Miecznikowski, J.A. Cox, A. Lewera, P.J. Kulesza, *J. Solid State Electrochem.* 4 (2000) 199.
- [20] M. Jiang, Z. Zhao, *J. Electroanal. Chem.* 292 (1990) 281.
- [21] M.H. Pournaghi-Azar, H. Dastangoo, *J. Electroanal. Chem.* 523 (2002) 26.
- [22] A.B. Bocarsly, S. Sinha, *J. Electroanal. Chem.* 137 (1982) 157.
- [23] M.T. Kelly, G.A. Arbuckle-Keil, L.A. Johnson, E.Y. Su, L.J. Amos, J.K.M. Chun, A.B. Bocarsly, *J. Electroanal. Chem.* 500 (2001) 311.
- [24] Y. Tani, H. Eun, Y. Umezawa, *Electrochim. Acta* 43 (1998) 3431.
- [25] M. Jiang, Z. Zhou, Z. Zhao, *Ber. Bunsen-Ges. Phys. Chem.* 95 (1991) 720.
- [26] J. Joseph, H. Gomathi, G.P. Rao, *J. Electroanal. Chem.* 304 (1991) 263.
- [27] S.-M. Chen, *Electrochim. Acta* 43 (1998) 3359.

- [28] F.A. Lowenheim (Ed.), *Modern Electroplating*, Wiley, New York, 1974.
- [29] S. Karmalkar, D. Sridhar, J. Banerjee, *J. Electrochem. Soc.* 144 (1997) 1696.
- [30] T.R.I. Cataldi, G.E. De Benedetto, *J. Electroanal. Chem.* 458 (1998) 149.
- [31] P.J. Kulesza, T. Jedral, Z. Galus, *Electrochim. Acta* 34 (1989) 851.
- [32] G.E. De Benedetto, T.R.I. Cataldi, *Langmuir* 14 (1998) 6274.
- [33] T.R.I. Cataldi, G.E. De Benedetto, *Electroanalysis* 10 (1998) 1163.
- [34] T.R.I. Cataldi, G.E. De Benedetto, A. Bianchini, *J. Electroanal. Chem.* 448 (1998) 111.
- [35] A. Eftekhari, *Anal. Lett.* 33 (2000) 2873.
- [36] A. Eftekhari, *Anal. Lett.* 34 (2001) 541.
- [37] A. Eftekhari, *J. Electroanal. Chem.* 537 (2002) 59.
- [38] A. Eftekhari, *Mendeleev Commun.* 12 (2002) 206.
- [39] A. Eftekhari, *Z. Phys. Chem.*, submitted for publication.