



Electrochemical Behavior of Gallium Hexacyanoferrate Film Directly Modified Electrode in a Cool Environment

Ali Eftekhari*^z

Electrochemical Research Center, Tehran, Iran

Electrochemistry of gallium hexacyanoferrate (GaHCF) as an analogue of prussian blue having a high-potential redox system was studied. A thin film of GaHCF was directly generated on a Ga substrate surface to fabricate a modified electrode. Electrochemical behavior of the modified electrode was studied at a typical cool environment of *ca.* 5°C. Although electrochemical activity of the electroactive film for ion insertion/extraction at this temperature is weaker than that at ambient temperature, the GaHCF film, however, showed excellent electrochemical activities. The redox potential of GaHCF was found to be higher than other transition metal hexacyanoferrates. The electroactive film formed on the electrode surface had an acceptable stability during both potential cycling and long-term usage. The results were indicative of the fact that GaHCF is a suitable modifier for the modification of electrode surfaces. On the other hand, the present work reports electrochemistry of an electroactive solid film with high-potential redox, and also well-defined electrochemical behavior of such systems, in a cool environment.
© 2004 The Electrochemical Society. [DOI: 10.1149/1.1773111] All rights reserved.

Manuscript submitted November 3, 2003; revised manuscript received January 14, 2004. Available electronically August 11, 2004.

Since the Neff report¹ regarding electrodeposition of a thin film of prussian blue (PB) on an electrode surface, much research has been devoted to the modification of electrode surfaces with PB and its analogues. Preparation of thin films of different transition metal hexacyanoferrates has been described in the literature. Interestingly, this era was synchronized with the development of chemically modified electrodes (CMEs). Because of the numerous applications of CMEs, considerable attention has been paid to the modification of electrode surfaces with various modifier materials. After Neff's report and the works which followed, PB and its analogues were introduced as desirable candidates for the fabrication of CMEs. Due to the importance of this subject, fabrication of CMEs based on powders or solid films of different modifier materials including PB analogues has been extensively reviewed in the literature.²⁻⁷

Although the electrochemistry of solid indium hexacyanoferrate has been well documented in the literature,⁸⁻¹⁵ however, no report has been made about the hexacyanoferrate salt of its similar element, gallium. Whereas both of them are in the same group in the periodic table and have similar properties from the inorganic chemistry point of view. The properties of the bottom elements of group IIIA of the periodic table are similar to transition metals, and they have been used for various applications as well as transition metals. Indeed, the chemistry of gallium hexacyanoferrate is not well studied even in the inorganic chemistry literature. In the present research, we studied the electrochemical behavior of a solid film of gallium hexacyanoferrate (GaHCF) film modified electrode for the first time. To this aim, the electroactive film was directly generated onto a Ga electrode surface based on a direct modification method. More recently, direct modification has been described as an efficient method for the preparation of highly stable modified electrodes.¹⁶⁻¹⁸

Experimental

All chemicals were of analytical grade without further purification, as obtained from Fluka. Doubly distilled water was used for the preparation of solutions. The Ga electrode was obtained from pure gallium with purity better than 99.99%. The Ga electrode was constructed from a gallium wire (diameter 2 mm, outer length 20 mm) inserted into a glass tube. Both ends of the glass tube were sealed with epoxy resin with 2 cm extending out of the tube. All potentials were referenced to a saturated calomel electrode (SCE). The voltammetric measurements were performed at the supporting electrolyte of KCl or other alkali metal chlorides with $a(M^+) = 1$, unless otherwise noted. For the investigation of the effect of the supporting electrolyte concentration, different solutions of KCl with different

potassium ion activities were used. The simple Debye-Huckel approximation was used for the calculation of activities of potassium ions in dilute solutions. The electrochemical experiments were carried out using a low-noise homemade potentiostat and the data were recorded by a computer running CorrView software. The experimental environment was kept cool to avoid gallium melting, and the experiments were performed at a room-cooled temperature (5°C).

The modification of the Ga electrode surface was carried out by a one-step electroless deposition. GaHCF film was generated on the electrode surface by dipping the Ga electrode in the modifier solution, which was an aqueous solution of 5 mM $K_3Fe(CN)_6$ in 0.1 M KCl as the supporting electrolyte for a limited period of time. The modification process proceeds via a chemical oxidation reaction of the metallic gallium to Ga^{3+} in the aqueous solution. Then, the Ga^{3+} formed on the electrode surface participates in a reaction with hexacyanoferrate ions to generate GaHCF. The film thickness is strongly dependent on the modification time. For this study, a typical modification time of 15 min was chosen to reach an acceptable thickness of the electroactive film. After the modification process, the modified electrode was conditioned in the same supporting electrolyte for 1 h.

As the modification was carried out by a simple chemical process, generation of GaHCF on the Ga electrode surface can be expected to be indispensable. However, to prove the formation of GaHCF, spectroscopic analysis was employed. It is well known that absorption spectroscopic characteristics of hexacyanoferrates are accompanied by an absorption peak at about 2100 cm^{-1} due to the stretching vibration of the CN group.¹⁹ The material generated on the electrode surface has a formula structure of $Ga^{III}[Fe^{III}(CN)_6]$, as the infrared spectra absorption was obtained at 2076 cm^{-1} accompanied by two absorption peaks in the range of $450\text{--}650\text{ cm}^{-1}$ corresponding to the binding modes of the Fe-C or the binding of the Fe-CN-Ga.²⁰ Chemical analysis of the compound also suggests similar results. Although spectroscopic measurements were a preliminary investigation and detailed spectroelectrochemical studies of the GaHCF are to be reported elsewhere, however, the obtained results provide strong evidence for the formation of gallium hexacyanoferrate. Indeed, due to the simplicity of the preparation method, such spectroscopic results are satisfactory, as have been widely cited in the literature.

Results and Discussion

Electrochemistry of gallium in different aqueous media has been extensively studied as noted in the literature.²¹⁻²⁴ Although, metallic gallium is strongly subject of corrosion, modification of its surface with GaHCF protects it from further corrosion. Therefore, the fabricated modified electrode can be used in different media like the other hexacyanoferrate-based modified electrodes. Figure 1 shows

* Electrochemical Society Active Member.

^z E-mail: eftekhari@elchem.org

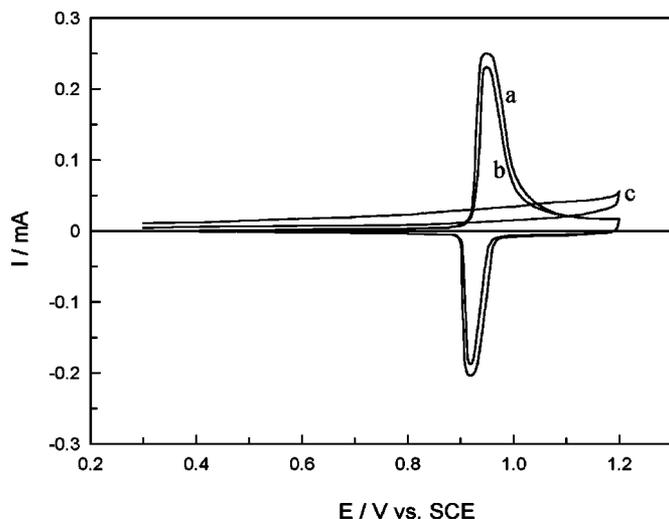


Figure 1. Typical cyclic voltammogram of the GaHCF film directly formed on a Ga electrode surface in the supporting electrolyte of KCl solution with $\alpha(\text{K}^+) = 1$ at the first (a) and 1000th (b) cycles ($v = 100 \text{ mV s}^{-1}$). (c) A typical cyclic voltammogram of the metallic Ga electrode (unmodified electrode) in the same experimental condition.

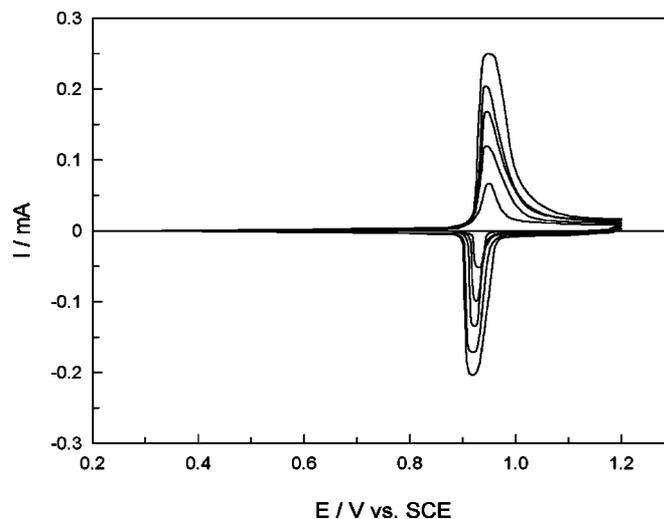
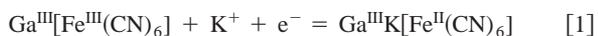
cyclic voltammetric characteristics of the GaHCF film directly formed on the Ga substrate. It is a typical cyclic voltammogram (CV) of the modified electrode recorded in the potential range located between 0.3 and 1.2 V vs. SCE. A typical CV of a bare Ga electrode is also presented in Fig. 1. It is obvious that the metallic gallium is electrochemically active at high potentials even in the neutral supporting electrolyte of KCl.

As can be seen, the CV has a well-defined shape, which can be attributed to the cool environment employed for the electrochemical measurements. The CVs reported in Fig. 1 indicate that the amounts of anodic and cathodic charges are not exactly the same for the GaHCF film modified electrode. This is indeed common in the electrochemical behavior of intercalating systems, and such behavior has been widely reported in the literature devoted to the electrochemistry of transition metal hexacyanoferrates (cf., Ref. 25-31).

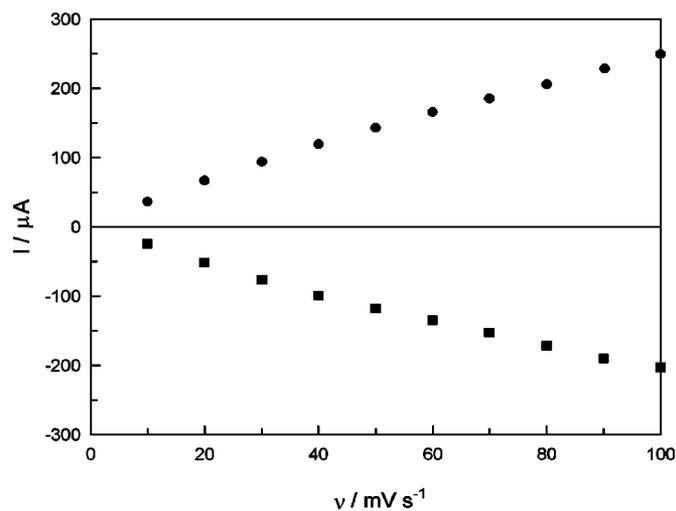
Since the diffusion during the insertion process is different from that during the extraction process, a completely reversible behavior cannot be expected. For instance, it has been demonstrated, based on a geometrical model, that the influences of the film structure are different on the insertion and extraction processes.³² In other words, the diffusion through a solid film with a complicated structure may proceed differently in the course of insertion and extraction. This asymmetric shape of CVs is more obvious for the insertion/extraction of other alkali metal ions such as Li^+ , in which the corresponding diffusion process is weaker.^{30,31}

It can be concluded that this behavior is stronger for the present case, which was investigated in a cool environment, since diffusion is highly temperature-dependent. However, the similarity of the CVs of the fresh GaHCF film modified electrode and the cycled electrode suggests that the difference of the anodic and cathodic charges is not due to irreversible insertion of the electroactive species (*i.e.*, known as capacity fading due to the decrease of active sites on the electroactive film for subsequent insertion/extraction processes).

Although the voltammogram is similar to those reported for other hexacyanoferrates (particularly indium hexacyanoferrate), the redox couple is observed at a relatively higher potential. The redox couple, corresponding to the surface-confined iron centers ($\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$), has the formal potential of $E^{0'} = 0.931 \text{ V vs. SCE}$. It is indeed due to the following redox system



(A)

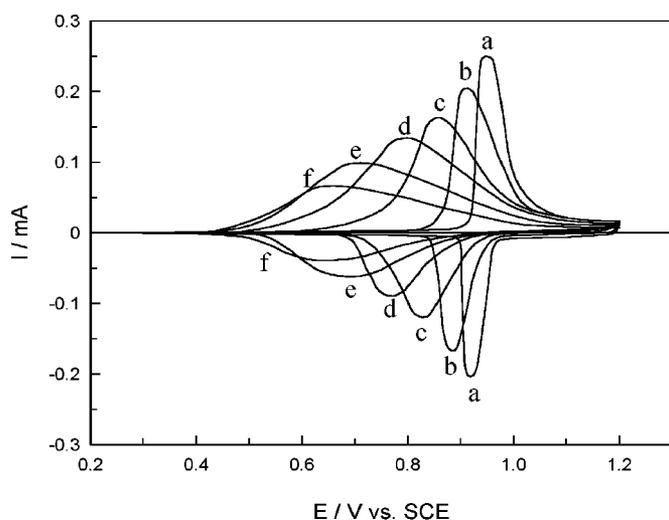


(B)

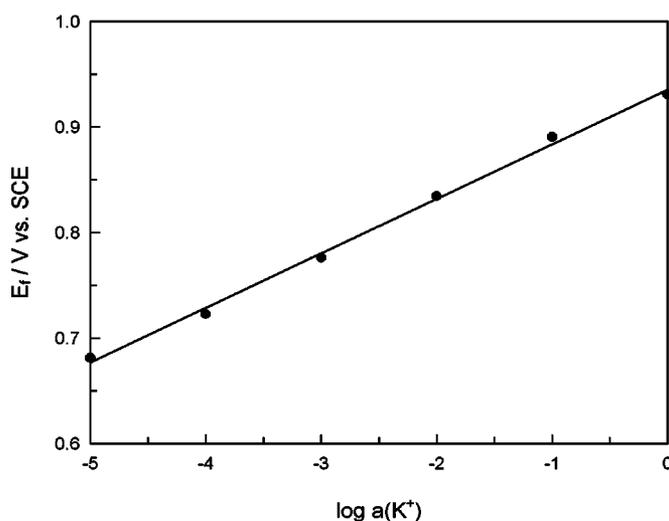
Figure 2. (A) Cyclic voltammetric characteristics of the GaHCF film directly modified electrode in the supporting electrolyte of KCl solution with $\alpha(\text{K}^+) = 1$ recorded at different scan rates (20, 40, 60, 80, and 100 mV s^{-1}). (B) Scan rate dependency of both anodic (●) and cathodic (■) peak currents of the GaHCF film directly modified electrode.

Scan rate dependencies of both anodic and cathodic peak currents are illustrated in Fig. 2. The curve is directly proportional for potential scan rates lower than 100 mV s^{-1} , indicating a surface reaction. The deviation from the linear relationship at higher scan rates is indicative of the mass-transport limitation within the electroactive film. At higher scan rates, the peak current is proportional to the square root of the scan rate, which indicates diffusional behavior in charge transport.

Similar to other hexacyanoferrates, the voltammetric behavior of the GaHCF film directly modified electrode is highly dependent on the concentration of the supporting electrolyte. In fact, a linear relationship can be found at different ion activity of the supporting electrolyte instead of its concentration. Figure 3 presents this dependence, as the formal potential of the modified electrode was calculated from CVs recorded at different potassium ion activities. This indicates a slope of 51.7 mV/decade for this dependence. According to the discussion made on the thermodynamic behavior for the redox system of PB and its analogues,² the alkali metal ion of the supporting electrolyte is involved in the redox reaction of the electroactive material according to the Nernst equation



(A)



(B)

Figure 3. (A) Cyclic voltammetric behaviors of the GaHCF film directly modified electrode in the supporting electrolytes made from KCl solutions with different potassium ion activities: 1 (a), 10^{-1} (b), 10^{-2} (c), 10^{-3} (d), 10^{-4} (e), and 10^{-5} (f). (B) Effect of potassium ion activity on the voltammetric characteristics of the modified electrode.

$$E = E^0 + RT/F \ln[a(\text{GaHCF})a(\text{K}^+)/a(\text{GaKHCF})] \quad [2]$$

where $a(\text{GaHCF})$ and $a(\text{GaKHCF})$ refer to the activities of the gallium hexacyanoferrate and potassium salt of the gallium hexacyanoferrate in the solid solution. As can be seen, the electrochemical response of the GaHCF film directly modified electrode properly obeys the Nernst equation, as the curve (Fig. 3) has a slope close to the theoretical slope of the Nernst equation (55.4 mV/decade at 5°C).

In addition to the supporting electrolyte concentration, the type of the alkali metal ion has a significant effect on the voltammetric characteristic of the modified electrode (Fig. 4). As can be seen, the curves have significant differences in comparison with the results reported for PB analogues with well-defined electrochemical properties. Moreover, as the current research was performed in a cool environment, a significant difference is expected between the results obtained here and those reported in the literature, because the diffusion process is strongly temperature-dependent. However, the results are comparable and partially similar to those obtained in the ideal

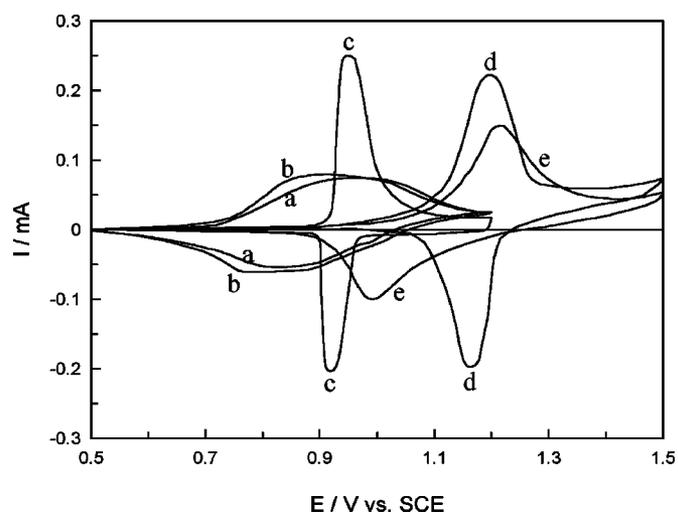


Figure 4. Cyclic voltammetric characteristics of the GaHCF film directly modified electrode in the supporting electrolytes [with $a(\text{M}^+) = 1$] of different alkali metal chlorides: LiCl (a), NaCl (b), KCl (c), RbCl (d), and CsCl (e). Scan rate, 100 mV s^{-1} .

condition of solid-state cell by Scholz and Dostal.³³ The formal potentials of the modified electrode in the presence of different supporting electrolytes are listed in Table I. The standard free energy of hydration of the alkali metal ions and the diameter of the naked cations are also noted for comparison.³³

It has been described that the main drawback for CMEs based on transition metal hexacyanoferrates is the gradual dissolution during potential cycling.³⁴ Some devices have been reported for improving the stability of electroactive films formed on the electrode surfaces. Two reasons are responsible for reaching highly stable films, (i) stability of the electroactive material and (ii) stable connection (deposition) of the electroactive film on the substrate surface.

The first reason can be resolved by improving the stability of the hexacyanoferrate lattice. Kulesza *et al.*³⁵ 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 lower solubility of the relevant silver-containing film. Cataldi *et al.*^{34,36-38} have reported that the incorporation of ruthenium into the lattice of indium hexacyanoferrate improves the stability of the film formed on a glassy carbon electrode.

The second reason, connection of the electroactive film to the substrate surface, is related to the deposition conditions and the substrate electrode employed. Indeed, the deposition manner is very important for gaining a stable connection between the electroactive film and the substrate surface. For instance, it is possible to strengthen the connection of the depositing electroactive film to the substrate surface by forcing the deposition process by an external mechanical force. This approach has been used for the preparation

Table I. Effect of the type of supporting electrolyte on the formal potential of the GaHCF film directly modified electrode, where $a(\text{M}^+) = 1$ and $v = 100 \text{ mV s}^{-1}$.

Alkali metal ion	Cation diameter/pm	E_f/V vs. SCE	$\Delta G/kJ \text{ mol}^{-1}$
Li ⁺	148	0.897	-114.6
Na ⁺	204	0.843	-89.7
K ⁺	276	0.931	-73.5
Rb ⁺	298	1.179	-67.5
Cs ⁺	340	1.108	-60.8

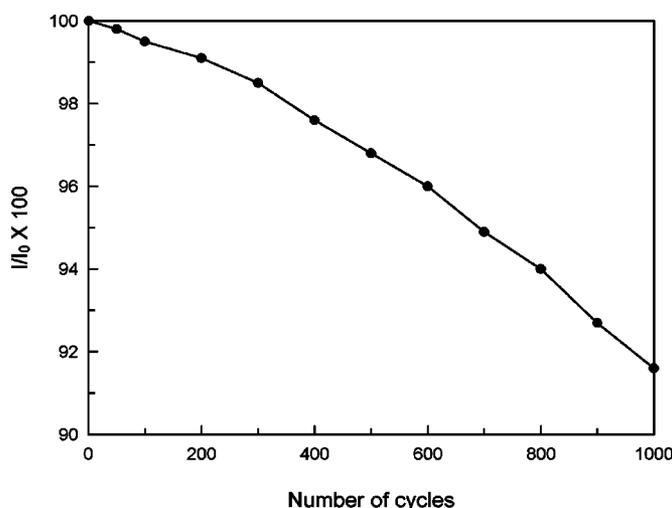


Figure 5. Normalized anodic peak height of the GaHCF film directly modified electrode as a function of the number of potential cycles.

of similar electrodes modified by PB and its analogues with an applied mechanical force induced in the presence of a centrifugal field³⁹ or a magnetic field.⁴⁰

Using a different strategy, it is possible to strengthen this connection by using suitable substrate electrodes. For example, aluminum is a suitable substrate electrode for the preparation of chemically modified electrodes to deposit highly stable electroactive films.⁴¹⁻⁴⁴ This is due to the well-known behavior of aluminum in an 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 film deposited on the passive substrate is more stable in comparison with conventional electrodes.⁴¹ A detailed mechanism of the formation of the initial metallic layer and its transformation to the corresponding transition metal hexacyanoferrate has been described for the deposition of palladium hexacyanoferrate on a silicon substrate.⁴⁵ In a sense the second stage of deposition of transition metal hexacyanoferrate on aluminum or silicon substrates [*i.e.*, chemical (electroless) transformation of the metallic films formed on the substrate surface to the corresponding transition metal hexacyanoferrates] is a kind of direct modification. Indeed, as the Ga passivation occurred during the deposition of the first layers of the electroactive material, the Ga passivated surface assists the electroactive film to establish better contact with the substrate electrode.

The electrochemical stability of the GaHCF film directly formed on the Ga substrate surface was investigated as an important factor for the fabrication of modified electrodes. The repetitive cyclic voltammograms were recorded in the supporting electrolyte by scanning the potential in the range of 0.3-1.2 V vs. SCE with a scan rate of 100 mV s⁻¹. As presented in Fig. 1, only a negligible decrease appears in the film activity after 1000 cycles. The electroactive film is highly stable and shows only about an 8% decrease during 1000 potential cycles (Fig. 5). Whereas, for the most similar polynuclear cyanide complex, indium hexacyanoferrate (InHCF) films, growth on glassy carbon, a 90% decrease after the same number of potential cycles has been reported.³⁴

In addition to the enhanced stability of the GaHCF film directly modified electrode during potential cycling, the film has significant stability during long-term usage (Fig. 6). The common problem regarding the investigation of long-term stability of modified electrodes due to the role of electrochemical experiments has been discussed previously. Thus, to avoid this failure, the electrode was freely stored and only every 10 days was a cyclic voltammetric experiment performed. By this approach, it is possible to be assured that the electrochemical experiments are not responsible for the loss

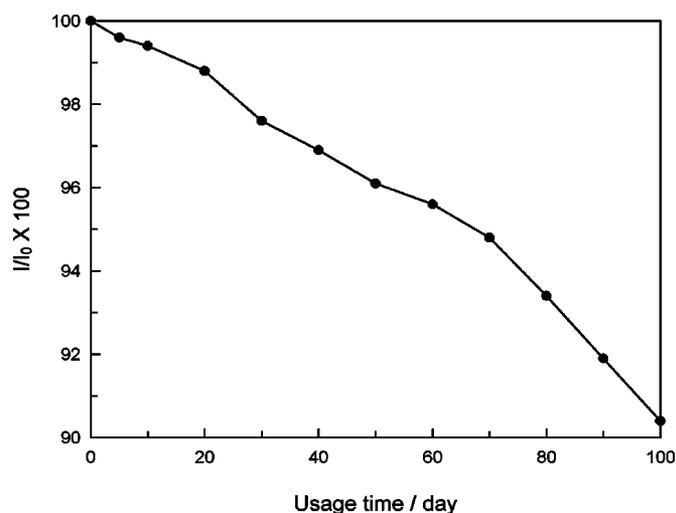


Figure 6. Normalized anodic peak height of the GaHCF film directly modified electrode as a function of time during long-term storage. The electrode was stored in the supporting electrolyte at 5°C, and the electrochemical measurements were performed in the short times, at which the electrode was taken from the supporting electrolyte.

of electrochemical activity. The results obtained (Fig. 6) suggest that the GaHCF film directly modified electrode shows less than a 10% decrease in the peak current after 100 days of usage. This indicates that the electroactive film is also stable in the course of long-term storage.

This electrochemical behavior of GaHCF suggests that it is an interesting electroactive material for the systems which need high-redox potentials. For example, hexacyanoferrate-based batteries are one of the types of rechargeable batteries with excellent cycleability,⁴⁶⁻⁴⁸ and due to the recent developments in hexacyanomethylate-based anodes with negative redox potentials,^{49,50} finding suitable cathodes with high redox potentials is of interest for practical applications of this type of secondary battery. Interestingly, it has been reported that PB and its analogues can be successfully used as cathode materials for lithium secondary batteries.⁵¹ Therefore, for instance, the high redox potential of GaHCF can be used to design high-voltage secondary cells (used on available anodes with sufficient negative potentials).

It should also be noted that electrochemical behavior of GaHCF at ambient temperature is similar to other PB analogues, but the results are not well-defined in comparison with those reported for a cool environment. In other words, the well-defined behavior of the results reported here is due to the cool environment employed. Although, such a cool environment was chosen due to limitations of the GaHCF directly modified electrode for high temperatures, however, the results reported reflect the electrochemical behavior of PB analogues in a cool environment. The detailed electrochemistry of GaHCF (not in the form of directly modified electrode) is being investigated and will be reported elsewhere.

Conclusions

The possibility of forming a thin GaHCF film on an electrode surface was studied. In addition to the first study of GaHCF, as a PB analogue, and reporting a modifier material for the preparation of modified electrodes, the present paper described the electrochemical behavior and properties of a transition metal hexacyanoferrate with high formal potential, which is very desirable for energy storage purposes. The present research introduced a high-potential redox system. Well-defined electrochemical behavior of a hexacyanoferrate-based modified electrode in a cool environment was shown.

References

1. V. D. Neff, *J. Electrochem. Soc.*, **125**, 886 (1978).
2. K. Itaya, I. Uchida, and V. D. Neff, *Acc. Chem. Res.*, **19**, 162 (1986).
3. F. Scholz and B. Meyer, *Chem. Soc. Rev.*, **23**, 341 (1994).
4. K. R. Dunbar and R. A. Heintz, in *Progress in Inorganic Chemistry*, Vol. 45, K. D. Karlin, Editor, p. 283, Wiley, New York (1997).
5. F. Scholz and B. Meyer, in *Electroanalytical Chemistry*, Vol. 20, A. J. Bard and I. Rubinstein, Editors, p. 1, Marcel Dekker, New York (1998).
6. R. W. Murray, in *Molecular Design of Electrode Surfaces, Techniques of Chemistry Series*, Vol. XXII, R. W. Murray, Editor, Wiley, Chichester (1992).
7. N. R. de Tacconi, K. Rajeshwar, and R. O. Lozna, *Chem. Mater.*, **15**, 3046 (2003).
8. P. J. Kulesza and M. Faszynska, *J. Electroanal. Chem.*, **252**, 461 (1988).
9. P. J. Kulesza and M. Faszynska, *Electrochim. Acta*, **34**, 1749 (1989).
10. S. Dong and Z. Jin, *Electrochim. Acta*, **34**, 963 (1989).
11. E. Czirok, J. Bacska, P. J. Kulesza, G. Inzelt, A. Wolkiewicz, K. Mielcznikowski, and M. A. Malik, *J. Electroanal. Chem.*, **405**, 205 (1996).
12. M. A. Malik, G. Horanyi, P. J. Kulesza, G. Inzelt, V. Kertesz, R. Schmidt, and E. Czirok, *J. Electroanal. Chem.*, **452**, 57 (1998).
13. E. Csahck, E. Vieil, and G. Inzelt, *J. Electroanal. Chem.*, **457**, 251 (1998).
14. P. J. Kulesza, M. A. Malik, M. Berrettoni, M. Giorgetti, S. Zamponi, R. Schmidt, and R. Marassi, *J. Phys. Chem. B*, **102**, 1870 (1998).
15. N. R. de Tacconi, K. Rajeshwar, and R. O. Lozna, *J. Electroanal. Chem.*, **500**, 270 (2001).
16. A. Eftekhari, *Anal. Lett.*, **33**, 2873 (2000).
17. A. Eftekhari, *Anal. Lett.*, **34**, 541 (2001).
18. A. Eftekhari, *J. Electroanal. Chem.*, **537**, 68 (2002).
19. J. B. Ayers and W. H. Piggs, *J. Inorg. Nucl. Chem.*, **33**, 721 (1971).
20. K. Itaya and I. Uchida, *Inorg. Chem.*, **25**, 389 (1986).
21. R. D. Armstrong, W. P. Race, and H. R. Thirsk, *Electrochim. Acta*, **31**, 45 (1971).
22. R. S. Perkins, *J. Electroanal. Chem.*, **101**, 47 (1979).
23. R. M. Manevich, L. A. Sokolova, and G. T. Kryuchkova, *Russ. J. Electrochem.*, **37**, 1072 (2001).
24. V. N. Korshunov and V. A. Safonov, *Russ. J. Electrochem.*, **38**, 768 (2002).
25. S. B. Moon, A. Xidis, and V. D. Neff, *J. Phys. Chem.*, **97**, 1634 (1993).
26. S. Moon and J. D. Moon, *Bull Korean Chem. Soc.*, **15**, 1042 (1994).
27. U. Schroder and F. Scholz, *Inorg. Chem.*, **39**, 1006 (2000).
28. A. Widmann, H. Kahlert, I. Petrovic-Prelevic, H. Wulff, J. V. Yakhmi, N. Bagkar, and F. Scholz, *Inorg. Chem.*, **41**, 5706 (2002).
29. S. Dong and Z. Jin, *J. Electroanal. Chem.*, **256**, 193 (1988).
30. S.-M. Chen, *J. Electroanal. Chem.*, **521**, 29 (2002).
31. S.-M. Chen and C.-M. Chan, *J. Electroanal. Chem.*, **543**, 161 (2003).
32. A. Eftekhari, *Solid State Ionics*, **141**, 41 (2003).
33. F. Scholz and A. Dostal, *Anal. Chem.*, **34**, 2685 (1995).
34. T. R. I. Cataldi and G. E. De Benedetto, *J. Electroanal. Chem.*, **458**, 149 (1998).
35. P. J. Kulesza, T. Jedral, and Z. Galus, *Electrochim. Acta*, **34**, 851 (1989).
36. G. E. De Benedetto and T. R. I. Cataldi, *Langmuir*, **14**, 6274 (1998).
37. T. R. I. Cataldi and G. E. De Benedetto, *Electroanalysis*, **10**, 1163 (1998).
38. T. R. I. Cataldi, G. E. De Benedetto, and A. Bianchini, *J. Electroanal. Chem.*, **448**, 111 (1998).
39. A. Eftekhari, *Mendeleev Commun.*, **12**, 206 (2002).
40. A. Eftekhari, *Z. Phys. Chem. (Munich)*, **217**, 1369 (2003).
41. A. Eftekhari, *Talanta*, **55**, 395 (2001).
42. A. Eftekhari, *Synth. Met.*, **125**, 295 (2001).
43. A. Eftekhari, *Sens. Actuators B*, **80**, 283 (2001).
44. A. Eftekhari, *Mikrochim. Acta*, **141**, 15 (2003).
45. A. Eftekhari, *J. Electroanal. Chem.*, **558**, 75 (2003).
46. V. D. Neff, *J. Electrochem. Soc.*, **132**, 1382 (1985).
47. K. Kuwabara, J. Nunome, and K. Sugiyama, *Solid State Ionics*, **48**, 303 (1991).
48. M. Jayalakshmi and F. Scholz, *J. Power Sources*, **91**, 217 (2000).
49. A. Eftekhari, *J. Power Sources*, **117**, 249 (2003).
50. A. Eftekhari, *J. Mater. Sci. Lett.*, **22**, 1251 (2003).
51. A. Eftekhari, *J. Power Sources*, **126**, 221 (2003).