

Electrochemical Charging of Indium Hexacyanoferrate Films in DMSO and Acetonitrile Water Mixtures Containing Alkali Metal Cations

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(Received June 5th, 2001)

Indium hexacyanoferrate films were investigated in water-acetonitrile and water-dimethylsulfoxide mixtures containing various alkali metal cations. The films, which were electrodeposited from the supporting electrolytes containing lithium cations, occurred to have fairly open structure permitting the transport of alkali metal cations in the solutions (mixtures) rich in nonaqueous solvents. The slopes of dependencies of formal potentials on the logarithms of concentrations of alkali metal cations were consistent with the predominant involvement of counteranions in the redox reactions. But in the cases when the content of nonaqueous solvent was relatively high, the slopes were definitely lower than Nernstian (60 mV per cation activity decade), thus implying a more complex mechanism of the reaction.

Key words: indium hexacyanoferrate, films, alkali metal counteranions, zeolitic structure, cyclic voltammetry, DMSO, acetonitrile-water mixtures

Prussian Blue type metal hexacyanoferrates [1–4] belong to a class of mixed-valence inorganic materials, which are capable to form rigid polymeric films on electrode surfaces that are of potential importance to such applications as energy storage [5], ion exchange and sensing [6,7], molecular electronics and magnetism [8,9], and construction of electrochromic display devices [10]. From structural viewpoint, metal hexacyanoferrates have approximately cubic lattice structures, in which a metal (*e.g.* Fe^{III}, Co^{II}, Cu^{II}, or In^{III}) is typically hexacoordinated by N atoms, and the low-spin iron(II) is hexacoordinated by C atoms of bridging cyanide ligands. The materials resemble redox organic polymers [11] in a sense that they contain three-dimensionally distributed hexacyanoferrate redox sites between which fast electron transfer is feasible. Metal hexacyanoferrates feature lattice defects (in the form of vacancies) and interstitial sites, which are spacious enough to easily accommodate alkali metal cations. It is believed that these counteranions are inserted during reduction but they are excluded during oxidation [12–30] and their flux provides charge balance during redox reactions. The actual degree of hydration (solvation) of the mobile, structural, cations is unclear. When investigated in potassium electrolytes, metal hexacyanoferrate films show reversible electrochemical behavior and they are characterized by fairly fast dynamics of charge propagation. Although, some reports concern the role of electrolyte anions during electrochemical charging

[31–33], no substantial contribution from anions to charge propagation in metal hexacyanoferrates has been typically found.

There has been still a limited information available on the electrochemical behavior and charge propagation mechanisms in metal hexacyanoferrate films in non-aqueous solutions. It has been reported that the electrochemical charging of Prussian Blue is kinetically controlled by the transport of potassium, sodium and lithium electrolyte cations in propylene carbonate solutions [34]. Some data have been reported on the electrochemical characteristics of Prussian Blue films in such nonaqueous solvents as acetonitrile, dimethylformamide, tetrahydrofuran [35] also in the context of potential applications of the system as a cathode for lithium batteries [36].

The major objective of this research is to correlate the electrochemical behavior of such a model system as indium(III) hexacyanoferrate(II,III), InHCNFe, with the nature of the nonaqueous solvent and alkali metal cation during redox reactions. Because indium(III) is not electroactive in the investigated range of potentials, InHCNFe shows, in potassium electrolyte, a single set of cyclic voltammetric peaks related to electron transfer between hexacyanoferrate(II,III) groups. Since the voltammetric response is reversible, and the peaks are narrow and well-defined, InHCNFe can be considered as a good probe for studying hexacyanoferrate(II,III) redox reactions in cyanometalates formed with trivalent metals. InHCNFe films have been found to be more selective to the flux of alkali metal countercations in comparison to the hexacyanoferrates formed with divalent metals (*e.g.* of nickel) [21]. We also address the importance of the film preparation method, and we produce a more “open” zeolitic structure by electrodepositing InHCNFe in the presence of large lithium (hydrated), rather than smaller potassium (hydrated), countercations. As representative nonaqueous solvents (for the preparation of mixtures with water), we have chosen two different examples, characterized by distinct basicities or donor abilities, *i.e.* donor numbers (DN), dimethylsulfoxide, DMSO (DN = 27.8) and acetonitrile, AN (DN = 14.1), (with respect to water, DN = 18). It has been established that the rates of electrode reactions, kinetics and thermodynamics of complexation reactions in mixed water-nonaqueous solvents reflect the donicity difference between solvents or the preferential solvation by a nonaqueous solvent [37–40].

EXPERIMENTAL

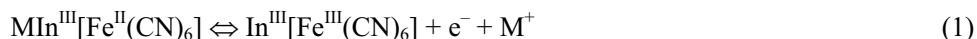
All chemicals were of analytical grade quality and were used without further purification. Metal hexacyanoferrate films were typically fabricated on glassy carbon substrates. Thin films of indium hexacyanoferrate (InHCNFe) were electrodeposited by cycling the potential of working electrode in the freshly prepared solution of 25 cm³ 1.0 mol dm⁻³ KCl, 20 cm³ H₂O, 4 cm³ 1×10⁻² mol dm⁻³ K₃Fe(CN)₆ and 4 cm³ 1×10⁻² mol dm⁻³ In(NO₃)₃. Typically, the procedure of potential cycling was performed at 50 mV s⁻¹ for 25 min in the potential range from 0.9 to 0 V.

Alternatively, the films were fabricated in lithium salt electrolytes. Then, the electrodeposition was done in the solution containing 25 cm³ 1.0 mol dm⁻³ LiCl, 19 cm³ H₂O, 3 cm³ 1×10⁻² mol dm⁻³ K₃Fe(CN)₆ and 3 cm³ 1×10⁻² mol dm⁻³ In(NO₃)₃, and it involved 160 full voltammetric cycles at 50 mV s⁻¹ in the potential range from 1.1 to 0 V. Such modified electrodes were subsequently conditioned in distilled water

for 1 h. In general, the resulting layers were characterized by an excellent stability, permitting a series of measurements to be done with a single electrode prepared. Experiments were carried out at room temperature. All potentials were expressed *versus* the saturated calomel electrode (SCE) reference. Electrochemical measurements were done with an Autolab (ECO CHEMIE) model PGSTAT 20 analyzer. Glassy carbon disks (6 mm, diameter) were typically used as electrode substrates. In the figures of cyclic voltammograms, cathodic and anodic currents are negative and positive, respectively.

RESULTS AND DISCUSSION

Fig. 1A shows cyclic voltammetric responses of indium(III) hexacyanoferrate(III,II), InHCNFe, in aqueous KCl solutions. With the decreasing concentration of K^+ ions, the cyclic voltammetric mid-peak potentials of InHCNFe shift toward more negative values. In the investigated range of concentrations, 0.1–0.001 mol dm^{-3} , this shift is approximately 49 mV per decade change of potassium ion activity. Although this value is lower than that (60 mV) expected from the Nernst dependence, the result is still consistent with the direct participation of potassium counterions in the system's redox process. It can be expected that the predominant reaction mechanism involves a flux of K^+ ions accompanied by electron transfers in such a way that potassium ions are incorporated into InHCNFe during reduction and excluded from the film during oxidation. Thus, the predominant, reversible redox reaction of InHCNFe can be described using the general equation proposed earlier [25,33]:



where M^+ stands for alkali metal counterion (K^+ , Na^+). When concentration of K^+ was below 0.03 mol dm^{-3} (Fig. 1A, Curves 1 and 2), the flux of potassium ions became insufficient to penetrate fully the film and to provide charge balance for complete electrolysis of InHCNFe (at 100 mVs^{-1}). Consequently, the shape of the respective voltammetric peaks was drawn out and the peaks were lower (in comparison to Curves 3 and 4 in Fig. 1A).

Addition of acetonitrile (AN) to the supporting electrolyte led to the decrease of voltammetric peak currents, resulted in some peak broadening, and it caused a shift of the potentials of voltammetric peaks towards more positive values. Fig. 1B shows the behavior of InHCNFe in the most concentrated mixture studied, *i.e.* containing 80% (vol.) AN in water, where the influence of the nonaqueous solvent was the most pronounced. Apparently, the mobility of potassium cations, which were partially solvated by AN molecules [41–43] and therefore presumably larger in comparison to hydrated K^+ , was somewhat lower. Despite some shift of the potential, we do not expect any significant reorganisation of InHCNFe structure. The potential shift effect shall be attributed to liquid junction potential existing between investigated water-organic mixtures and aqueous SCE reference electrode.

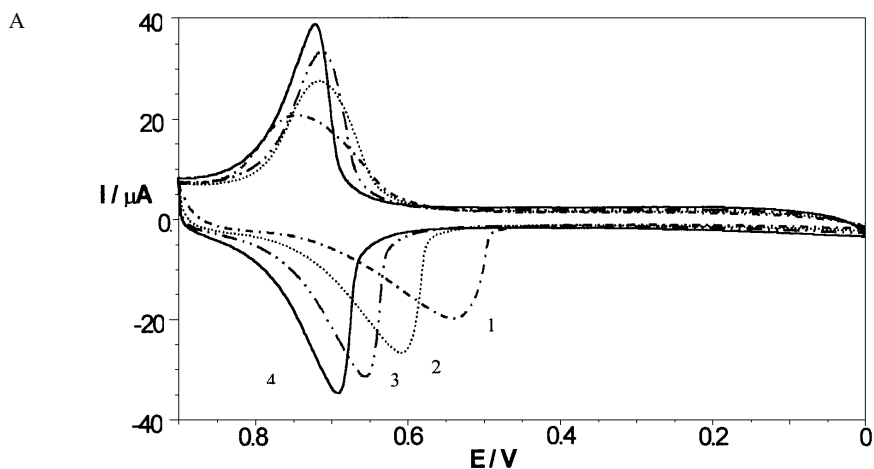


Figure 1A. Cyclic voltammograms of InHCNFe film in aqueous solution containing varying amounts of KCl: (1) 3.0×10^{-3} , (2) 1.0×10^{-2} , (3) 3.0×10^{-2} and (4) 1.0×10^{-1} M. Scan rate 0.05 V s^{-1} .

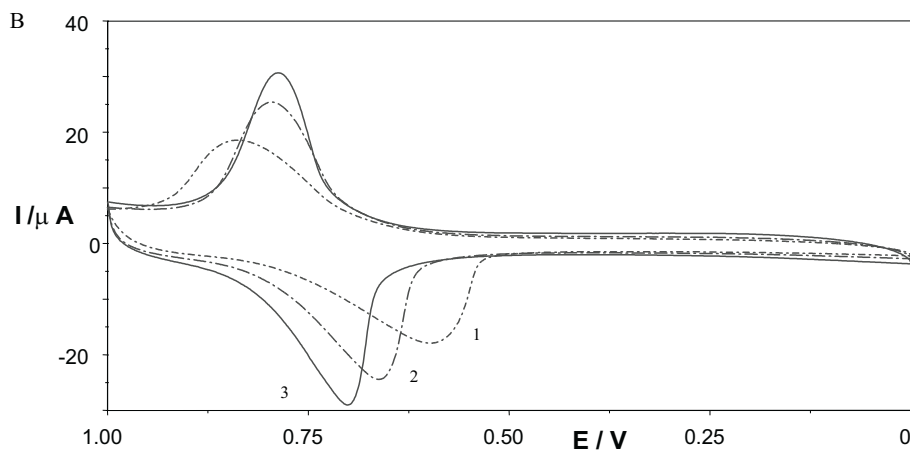


Figure 1B. Cyclic voltammograms of InHCNFe film in water-AN mixtures containing 80% acetonitrile and KCl at concentration: (1) 3.0×10^{-3} , (2) 1.0×10^{-2} and (3) 3.0×10^{-2} M. Scan rate 0.05 V s^{-1} .

In the above experiments, InHCNFe films were prepared from the solution for modification containing potassium salt electrolyte. Unfortunately, such films did not show any reasonable electroactivity in water-AN mixtures containing sodium salt electrolyte and AN at more than 50% (vol.). Apparently, sodium counterions were largely in form of sodium salt associates [41–43], which are too large to be transported within the zeolitic structure of InHCNFe. We hypothesized that the zeolitic channels of InHCNFe shall be larger or the film possesses a high degree of disorder when electrodeposited in the presence of fairly large hydrated lithium counterions. Therefore, in the further work, we considered InHCNFe films prepared from the solution for modification containing lithium salt electrolyte (InHCNFe/Li).

Fig. 2 shows the voltammetric responses of InHCNFe/Li film recorded in (A) potassium, (B) sodium, and (C) cesium salt electrolytes containing the respective cations at different concentrations. In the presence of potassium cations at the same concentration, the voltammetric peaks of InHCNFe/Li (Fig. 2A) are comparable to those of InHCNFe (Fig. 1A). It is noteworthy that fairly well defined peaks (but lower) have been observed in sodium salt electrolyte (Fig. 2B). But upon transfer of the InHCNFe/Li modified electrode to the solution containing Cs^+ cations, the system of voltammetric responses has become very poorly developed (Fig. 2C). In view of the lower mobility of hydrated Na^+ (in comparison to smaller hydrated K^+), it is easy to explain the appearance of lower voltammetric peaks in NaCl (than in KCl). But in the presence of cesium ions, which while hydrated shall be smaller than hydrated K^+ , the redox reaction of InHCNFe/Li is almost blocked. The same blocking effect (for simplicity not shown in Fig. 2) was observed in RbCl. It should be mentioned that the blocking effect might be caused by some contraction of the channels during the oxidation of the hexacyanoferrate [26]. Apparently, cesium and rubidium ions enter the system lattice in mostly dehydrated form and, once they have entered, they tend to stay due to their fairly large ionic (dehydrated) radii.

We have also performed experiments in water-AN mixtures containing various alkali metal cations at different concentrations. Fig. 3 shows the cyclic voltammetric responses of InHCNFe/Li recorded in (A) potassium, (B) sodium, and (C) cesium salt electrolytes. It comes from the comparison of the data of Fig. 3 with Fig. 2 that, in the presence of large amounts of AN (80–90%), the voltammetric peaks are still developed (for potassium and sodium salt electrolytes), though, they tend to be more drawn out. This phenomenon presumably reflects a lower mobility of alkali metal cations, due to a partial solvation by AN molecules and/or as result of association of the salts in water-AN mixtures and to some extent a higher ohmic resistance of the water-AN mixtures [41–43]. As before (Fig. 2C), the voltammetric responses are largely

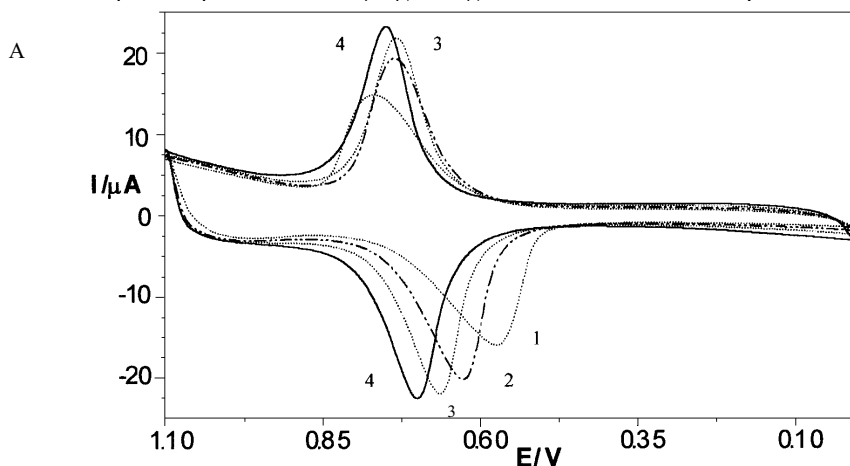


Figure 2A. Cyclic voltammograms of InHCNFe/Li film in aqueous solution containing varying amounts of KCl: (1) 3.0×10^{-3} , (2) 1.0×10^{-2} , (3) 3.0×10^{-2} and (4) 1.0×10^{-1} M. Scan rate 0.05 V s^{-1} .

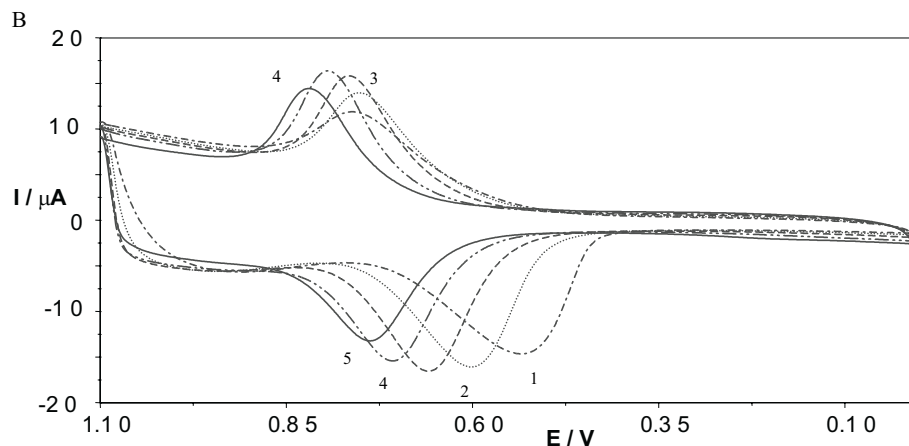


Figure 2B. Cyclic voltammograms of InHCNFe/Li film in aqueous solution containing varying amounts of Na^+ : (1) 1.0×10^{-3} , (2) 3.0×10^{-3} , (3) 1.0×10^{-2} , (4) 3.0×10^{-2} and (5) 1.0×10^{-1} M. Scan rate 0.05 V s^{-1} .

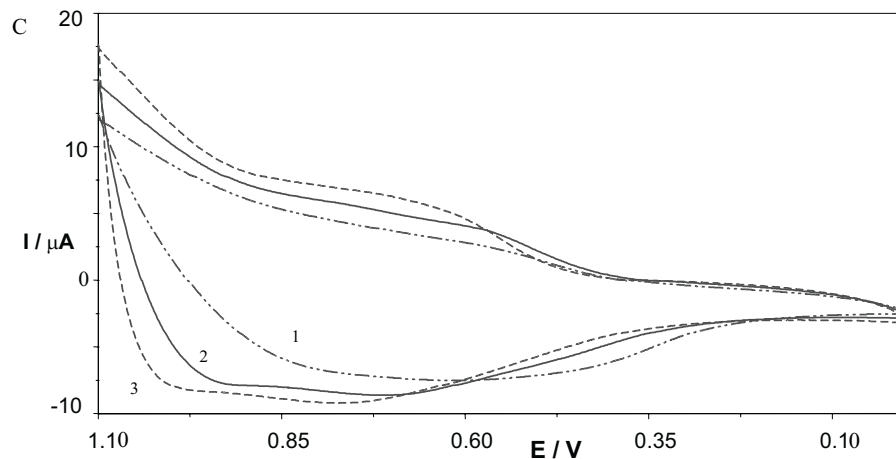


Figure 2C. Cyclic voltammograms of InHCNFe/Li film in aqueous solution containing varying amounts of Cs^+ : (1) 1.0×10^{-3} , (2) 3.0×10^{-3} and (3) 1.0×10^{-2} M. Scan rate 0.05 V s^{-1} .

blocked by cesium ions (Fig. 3C). The electroactivity of the latter system can be restored by exposure to sodium salt electrolytes (Fig. 4). It is likely that the trapped Cs^+ ions are removed then by more mobile Na^+ ions. The currents of cathodic and anodic peaks increase with Na^+ concentration in the solution, but the peaks potentials are basically unchanged. This effect can be used for determination of Na^+ concentration in the presence of a concentrated cesium salt.

The InHCNFe/Li system is characterized by defined (though drawn out) voltammetric peaks in water-DMSO mixtures containing (A) potassium and (B) sodium cations (Fig. 5). In the above experiments, the content of DMSO was on the 40–60% (vol.) level; larger amounts of DMSO would limit solubility of the respective alkali

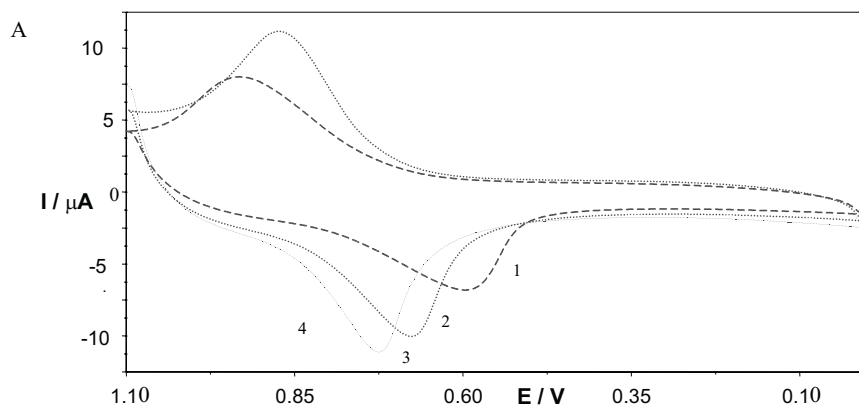


Figure 3A. Cyclic voltammograms of InHCNFe/Li film in water-AN mixtures containing 90% acetonitrile and K^+ at concentration: (1) 1.0×10^{-3} , (2) 3.0×10^{-3} , (3) 1.0×10^{-2} and (4) 3.0×10^{-2} M. Scan rate 0.05 V s^{-1} .

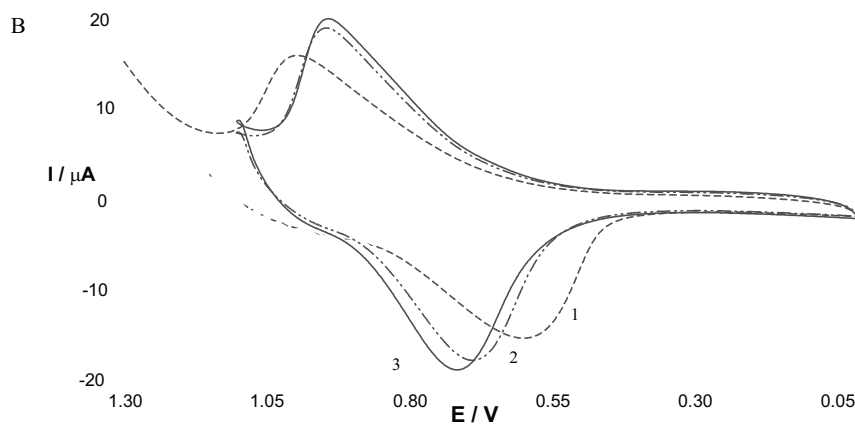


Figure 3B. Cyclic voltammograms of InHCNFe/Li film in water-AN mixtures containing 90% acetonitrile and Na^+ at concentration: (1) 3.0×10^{-3} , (2) 1.0×10^{-2} and (3) 3.0×10^{-2} M. Scan rate 0.05 V s^{-1} .

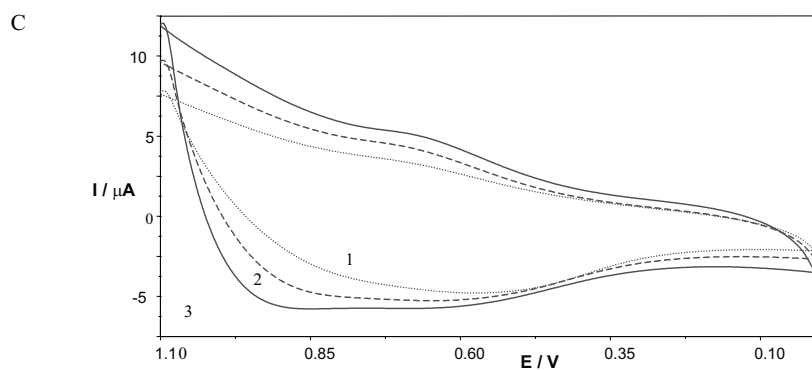


Figure 3C. Cyclic voltammograms of InHCNFe/Li film in water-AN mixtures containing 80% acetonitrile and Cs^+ at concentration: (1) 1.0×10^{-3} , (2) 3.0×10^{-3} and (3) 1.0×10^{-2} M. Scan rate 0.05 V s^{-1} .

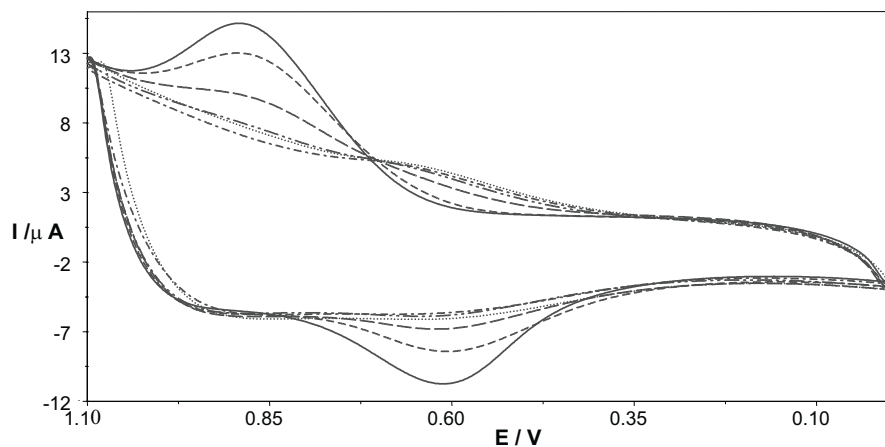


Figure 4. Cyclic voltammograms of InHCNFe/Li film in water-AN mixtures containing 80% acetonitrile and Cs^+ at concentration $1.0 \times 10^{-2} \text{ M}$ and different amounts of Na^+ : (---) 0, (.....) 2.5×10^{-5} , (- · - ·) 5.0×10^{-5} , (- - -) 1.0×10^{-4} , (- -) 3.0×10^{-4} , and (—) $6.0 \times 10^{-3} \text{ M}$. Scan rate 0.05 V s^{-1} .

metal cations. In the case of water-DMSO mixtures (Fig. 5), the mobility of alkali metal cations, which are likely to be preferentially solvated with DMSO [41–43], seems to be lower when compared with aqueous solutions. Finally, the voltammetric peaks were most poorly developed in the presence of cesium ions in water-DMSO mixture (Fig. 5C).

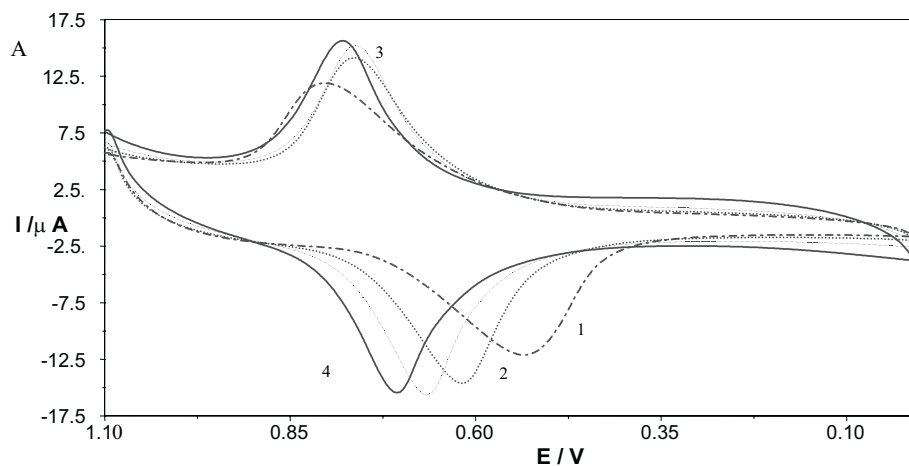


Figure 5A. Cyclic voltammograms of InHCNFe/Li film in water-DMSO mixtures containing 40% acetonitrile and K^+ at concentrations: (1) 3.0×10^{-3} , (2) 1.0×10^{-2} , (3) 3.0×10^{-2} and (4) $1.0 \times 10^{-1} \text{ M}$. Scan rate 0.05 V s^{-1} .

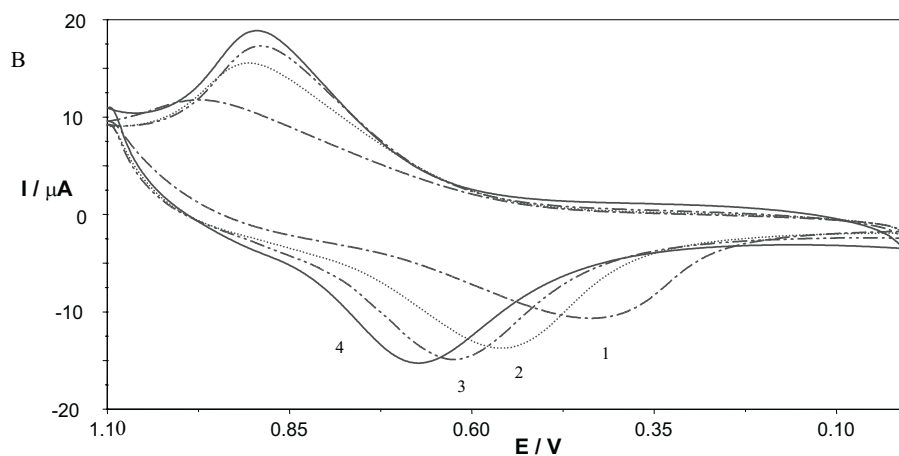


Figure 5B. Cyclic voltammograms of InHCNFe/Li film in water-DMSO mixtures containing 60% acetonitrile and Na^+ at concentration: (1) -3.0×10^{-3} , (2) -1.0×10^{-2} , (3) -3.0×10^{-2} and (4) -1.0×10^{-1} M. Scan rate 0.05 V s^{-1} .

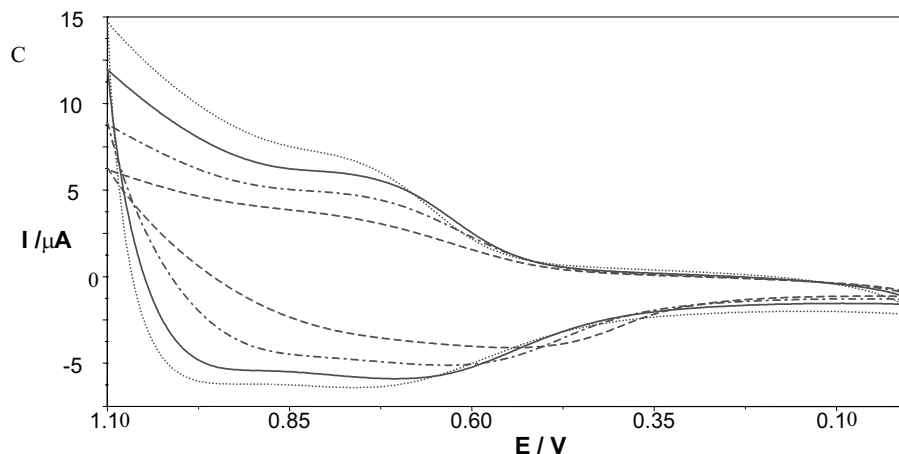


Figure 5C. Cyclic voltammograms of InHCNFe/Li film in water-DMSO mixtures containing 60% acetonitrile and Cs^+ at concentration: (---) -1.0×10^{-3} , (- · -) -3.0×10^{-3} , (—) -1.0×10^{-2} and (····) -3.0×10^{-2} M. Scan rate 0.05 V s^{-1} .

Some attention was also paid to the dependencies of formal (E_f), namely mid-peak, potentials on the logarithms of activity of alkali metal cations studied in water-AN (Fig. 6) and water-DMSO mixtures (Fig. 8). The activity coefficients, which refer to infinite dilution in the solvent discussed, were calculated according to Davies equation [44], ϵ values for the water-AN and water-DMSO mixtures were taken from literature [42]. It is apparent from the data of Figs. 6 and 8 that, in the presence of K^+ ions, the slopes of the dependencies are close or somewhat lower (30–55 mV per activity decade) than the Nernstian value (60 mV). The slope decreases with increasing of the acetonitrile and DMSO content in the mixtures investigated. Thus, it can be concluded that, despite the addition of a nonaqueous solvent, the mechanism of

charge propagation is predominantly controlled by the motion of electrolyte cations (according to (1)). In water-AN mixtures, the potential of the GC electrode modified by InHCNFe/Li in presence of K^+ ions increases with the rise of the AN content in the mixtures. This observation can be attributed to liquid junction potentials existing between investigated water-organic mixtures and aqueous SCE reference electrode. When the potentials are expressed vs. Fic^+/Foc , solvent independent electrode [38] (see. Fig. 6B), the electrode potential dependencies lie within 10 mV from one another when moving from water to the water-AN mixtures containing 90% (vol.) AN. In general, the slopes were closer to Nernstian, when the InHCNFe/Li system was investigated in sodium salt (Fig. 7 and Fig. 8 B) in the solution containing from 0 to 60% (vol.) acetonitrile. Also, the slopes were closer to Nernstian in water-DMSO mixtures when investigated in the same concentration range. Further increase of content of a nonaqueous solvent tended to cause a decrease of the slope (below 50 mV per activity decade), thus implying the possibility of a more complex charge propagation mecha-

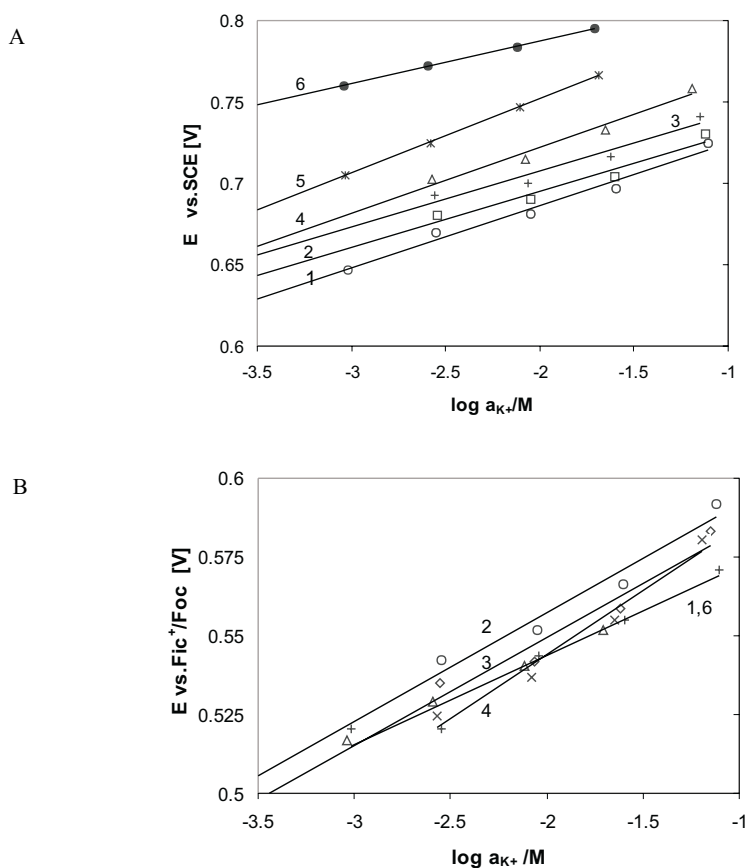


Figure 6. The formal potential of the GC electrode modified by InHCNFe/Li film as a function of K^+ ion activity in water-AN mixtures containing following amounts of acetonitrile: (1) – 0, (2) – 20, (3) – 40, (4) – 60, (5) – 80 and (6) – 90% (vol.). The potentials are expressed *versus*: A – SCE (saturated aqueous calomel electrode), B – Fic^+/Foc (ferrocene electrode).

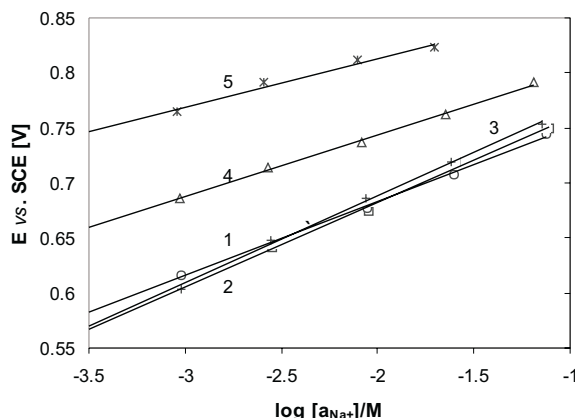


Figure 7. The formal potential of the GC electrode modified by InHCNFe/Li film as a function of Na^+ ion activity in water-AN mixtures containing acetonitrile: (1)–0, (2)–20, (3)–40, (4)–60, and (5)–90% (vol.).

nism. It is difficult to draw any definite conclusion at this stage but, in this context, recent works postulating some secondary involvement of electrolyte anions shall be mentioned [31–33]. It is likely that, in the situations where the mobility of counter-cation is lower, the anions may play some role. Further research is in progress along this line.

CONCLUSIONS

We demonstrate that the formal potentials of InHCNFe (which was electrodeposited on glassy carbon support and prepared in the presence of potassium salt) change nearly theoretically with the logarithm of potassium ion activity ($\Delta E_f/\Delta \log a_{\text{K}^+} \approx 50$ mV). Experiments performed with a similar InHCNFe modified electrode, but prepared in the presence of lithium salt (instead of potassium ions) are consistent with the view that the latter system has an even more open “zeolitic” structure because the flux of all alkali metal cations is feasible during redox reactions.

Formal potentials measured for this electrode in aqueous solutions exhibited linear dependencies *versus* the logarithms of potassium and sodium ions activities with the slopes slightly lower than the theoretical (59 mV per decade of activity).

In the mixtures of acetonitrile with water, and dimethylsulfoxide with water, formal potentials were barely dependent on the $\log a_{\text{K}^+}$, *i.e.* the slopes of dependencies were practically independent of the content of organic component in the mixtures up to 80% (vol.). When the experiments were carried out in the presence of sodium in water-DMSO mixtures, the E_f^0 vs. $\log a_{\text{Na}^+}$ dependencies were also linear and they yielded the Nernstian slopes within the limits of experimental error. Such dependencies were also linear in water-AN mixtures. Further, at least up to 40% (vol.) of AN they were practically overlapping.

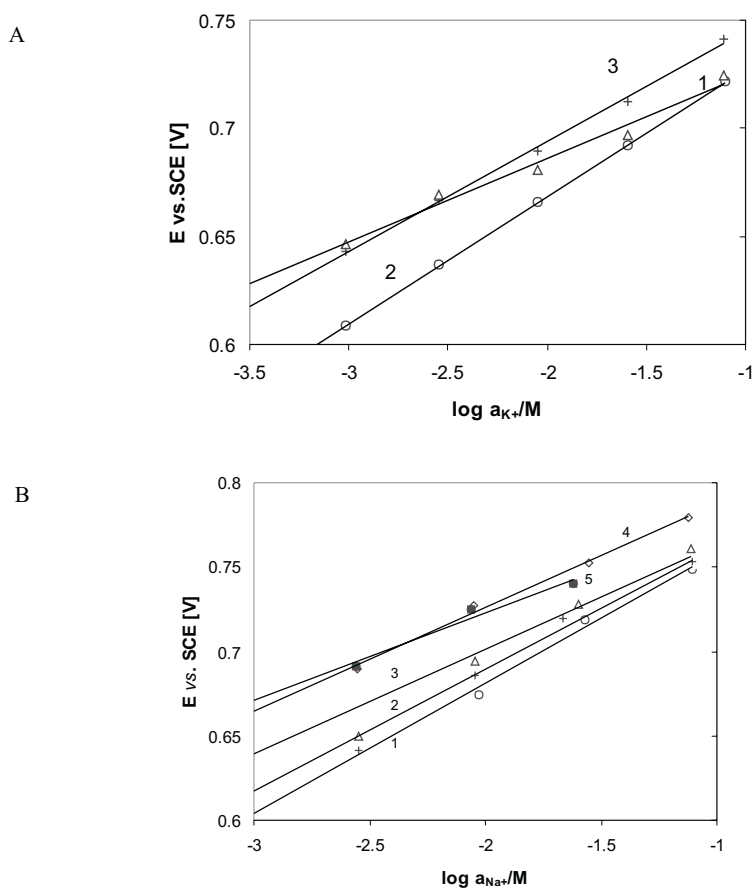


Figure 8. The formal potential of the GC electrode modified by InHCNFe/Li film as a function of A – K⁺, B – Na⁺ ion activity in water-DMSO mixtures containing DMSO: (1) – 0, (2) – 20, (3) – 40, (4) – 60 and 5 – 90% (vol.).

In the presence of Cs⁺ ions, the redox processes of the studied system were in general largely inhibited. In the case of mixtures of water with DMSO, and in the presence of Cs⁺ ions with concentrations ranging from 10⁻³ mol dm⁻³ to 3 × 10⁻² mol dm⁻³, the electrode reactions were also practically blocked.

The fact that, the system's redox behaviour and positions of peaks (formal potentials) are strongly dependent on the choice and the concentration of alkali metal counterions, makes INHCNFe for potential interest for analytical determinations and separations, especially in mixed solvents, where the use of traditional ion selective electrodes is difficult.

Acknowledgments

This work was supported by the Polish State Committee for Scientific Research, under Grant 3T09A 09313.

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