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Electrochemical studies on metal-hexacyanocobaltate(III) thin solid films in aqueous electrolytes

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Electrochemical behaviour of thin films of potassium/metal hexacyanocobaltate(III) (KMHCCo or $KM_{x-1}[Co(CN)_6]_y$ where M = Co, Fe, or Ru, in terms of reduction of small oxoanions was investigated. Glassy carbon electrodes modified with electrochemically prepared KMHCCo were used as the solid phase in the heterogeneous solid–liquid charge transfer process. The redox behaviours of the counter central ions of KMHCCo have been investigated in aqueous electrolytes using dynamic voltammetric techniques, and electrochemical impedance spectroscopy. The effect of supporting electrolyte components on the electrochemical behaviour was also investigated. Evidences for electrocatalytic capabilities for oxidation of glucose and for the reduction of BrO_3^- and IO_3^- were recorded.

Keywords: *hexacyanocobaltate; electocatalysis; modified electrode; micropores; thin film*

1. Introduction

The attention of many researchers [1–14] has been focused on the special properties of polynuclear hexacyanometalates (HCM) such as the possibility of forming solid films of conductor phases or semiconductor phases; simplicity of manipulation of structures; occurrence of multi-redox centres; magnetic and electrochromic behaviours and their resemblance to zeolitic materials. In particular, in electrocatalysis, one can see how it is possible to make full use of these properties in applications [15–19], especially in electrochromic [20], and reversibility modelling [21]. The combination of more than one HCM, to form multilayered assemblies of these compounds, has been found to have applications in sensor fabrication [22], display technologies [23], solid state batteries [24], chemical precipitation of radioactive caesium from waste solutions [25], and hydrogen storage [26], to name but a few. Very limited studies have been done on metal hexacyanocobaltate polynuclear solid films. The paper reports on the electrochemical behaviour of KMHCCo thin solid films having microporous struc-

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ture prepared using an electrochemical technique. The redox behaviour of the counter cations and those of the central atoms in $[Co(CN)_6]^{3-}$ in various supporting electrolytes was also studied. The question of whether these assemblies improve catalytic activity on the electrode surface is also explored.

2. Experimental

Materials. Reagent grade $K_3[Co(CN)_6]$, $FeCl_3$, $RuCl_3$, KCl and $KClO_4$, were obtained from Aldrich Chemical Co. All other reagents were of at least reagent grade and were used without further purification.

Instruments and methods. An electrochemical cell of three conventional electrode types in a small vial container was used. The reference electrode was a Ag/AgCl (saturated KCl) with the half-cell potential of –45 mV vs. saturated calomel electrode (SCE), the counter (auxiliary) electrode was a platinum (Pt) wire, and the working electrode was glassy carbon (GC, 0.071 cm^2 surface area, Bioanalytical Systems). The working electrode was cleaned by polishing with 1 μm α-Alumna paste and rinsed with water and acetone prior to use. A BAS 100B electrochemical analyzer (Bioanalytical Co.) was used to perform the electrochemical studies.

Electrochemical impedance spectroscopy (EIS) studies were carried out using a BAS impedance module. Faradic impedance measurements were carried out within a frequency range of 0.1 mHz to 1 kHz. The current response was monitored by a current transducer whose sensitivity range was automatically adjusted for each frequency range examined. The data were analyzed with a Fourier transform algorithm.

Films of MHCCO (M = Co, Fe, Ru) were electrodeposited on glassy carbon electrode (GCE) surfaces by repetitive potential cycling of a glassy carbon (GC) disk electrode between –0.20 and 1.0 V vs. Ag/AgCl, in freshly prepared aqueous solutions containing equi 5 mM of $K_3[Co(CN)_6]2H_2O$, and $FeCl_3$, or $RuCl_3$, or $CoCl_2$ and 0.1 M KCl (pH 2). Unless otherwise stated, scans were carried out at a sweep rate of 0.2 $V{\cdot}s^{-1}$. The electrodes were then rinsed thoroughly and transferred to a redox free electrolyte where their electrochemical responses were examined.

3. Results and discussion

3.1. Redox behaviour of FEHCCO films. Background

In hexacyanometalates (HCM) of the general formula $M_A^X[M_B^Y(CN)_6]_Z$, M_B^Y is the central atom, while M_A^X is the fixed counter cation. Both M_A^X and M_B^Y are generally transition metals. The reduction of the fixed counter cation of these compounds can take place via electron/cation addition, according to the following equation:

$$\mathrm{M}_\mathrm{A}^{X}\left[\mathrm{M}_\mathrm{B}^{Y}(\mathrm{CN})_6\right]_Z + \mathrm{e} + \mathrm{M}^{+} \longrightarrow \mathrm{MM}_\mathrm{A}^{X}\left[\mathrm{M}_\mathrm{B}^{Y}(\mathrm{CN})_6\right]_Z \tag{1}$$

Oxidation of the central atom can take place by electron loss followed by anion addition:

$$\mathrm{M}_\mathrm{A}^{X}\left[\mathrm{M}_\mathrm{B}^{Y}(\mathrm{CN})_6\right]_Z - \mathrm{e} + \mathrm{X}^{-} \longrightarrow \mathrm{M}_\mathrm{A}^{X}\left[\mathrm{M}_\mathrm{B}^{Y+1}(\mathrm{CN})_6\right]_Z \tag{2}$$

Reduction of the counter cation, according to Eq. (1), produces the reduced form, while oxidation of the central atom in the anion complex, according to Eq. (2), produces the oxidized form. The colour of the reduced or the oxidized forms depends on $\mathrm{M}_\mathrm{A}^{X}$ and $\mathrm{M}_\mathrm{B}^{Y}$. The *CV* for HCM may show redox waves corresponding to the reduction of the counter ion and oxidation of the central atom. In some cases, the redox waves (if any) of the excess counter ions occupying interstitial sites of the octahedrally shaped metal cyanide complex may be detectable. Previous studies [8, 24] indicated that the redox wave at a lower positive potential corresponds to the reduction of the counter ion, while that at a higher positive potential it represents the oxidation of the central atom. Some of these studies [10] indicated that the counter ion affects the formal potential of the central atom.

3.2. Electrodeposition of $\mathrm{KCo}_{x-1}[\mathrm{Co(CN)}_6]_y$

Repetitive cycling of a glassy carbon (GC) disk electrode potential between –0.20 and 1.0 V vs. Ag/AgCl in aqueous solutions containing equi 5 mM of $\mathrm{K_3[Co(CN)_6]\cdot 2H_2O}$, $\mathrm{CoCl_2}$ and 0.1 M KCl (pH 2) is shown in Fig. 1a. The growth of the redox wave with successive scanning is an evidence for the buildup of the $\mathrm{KCo}_{x-1}[\mathrm{Co(CN)}_6]_y$ film. The redox behaviour of the deposited film was investigated by cycling the potential of the modified electrode in redox-free electrolytes. The results are shown in Fig. 1b. To understand the *CV* behaviour of the electrode we consider the effects of the electrolytes used in this study. The dissociation of the counter Co^{2+} ions from $\mathrm{KCo}_{x-1}[\mathrm{Co(CN)}_6]_y$ would result in formation of $[\mathrm{Co(H_2O)_6}]^{2+}$ in neutral $\mathrm{KClO_4}$ or CoCl_4^{2-} in KCl solution. In Figure 1b, the *CV* characteristics of $\mathrm{KCo}_{x-1}[\mathrm{Co(CN)}_6]_y$ are shown in neutral KCl electrolyte, in KCl at pH = 2, and in $\mathrm{KClO_4}$. The redox behaviour of either CoCl_4^{2-} or $[\mathrm{Co(H_2O)_6}]^{2+}$ cannot be identified under the adopted experimental conditions, or within the studied potential range. This suggests that the observed redox waves in Fig. 1b are due to the central Co atom in $[\mathrm{Co(CN)_6}]^{3-}$. It can be noticed that increasing the acidity not only results in an upward shift in the formal potential by about 100 mV, but it also lowers both the cathodic and anodic redox currents. This can be attributed to the large ionic size of $\mathrm{H_3O^+}$ (900 pm) in acidic electrolyte. On the other hand, in Fig. 1b a decrease of the redox wave formal potential in of $\mathrm{KCo}_{x-1}[\mathrm{Co(CN)}_6]_y$ in $\mathrm{KClO_4}$ electrolyte approximately by 100 mV, with an increase of the cathodic and anodic currents. The lower reduction potential and larger current than that reported in KCl electrolytes suggests that the electron transfer process is thermodynamically and kinetically favoured in aqueous $\mathrm{KClO_4}$.

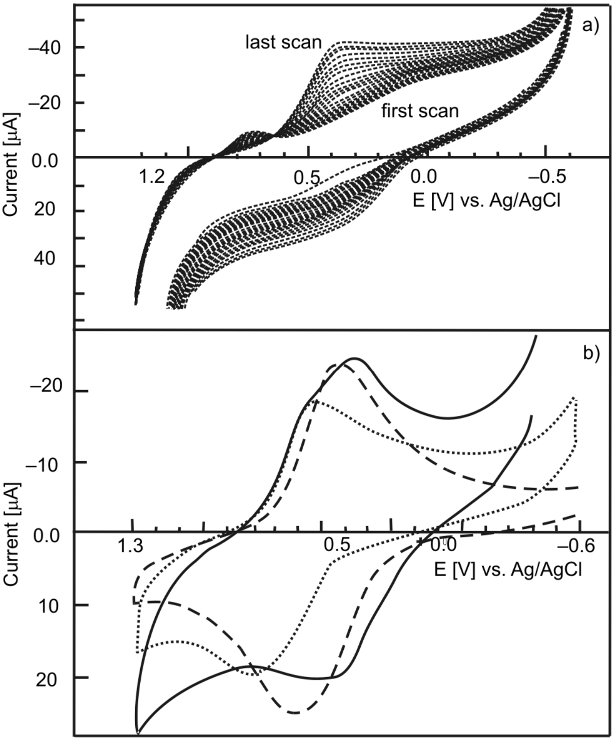

Fig. 1. Repetitive *CV* characteristics at 0.2 V·s^{-1} of GCE a) in equi 5 mM of $K_3[Co(CN)_6]$ and $CoCl_2$ in 0.1 M KCl/HCl (pH = 2), scan started at –0.20 V vs. Ag/AgCl, b) modified with $KCo_x[Co(CN)_6]_y$ in 0.1 M KCl (dashed line), 0.1 M KCl/HCl (pH = 2) (dotted line), and $KClO_4$ (solid line)

3.3. Electrodeposition of $KFe_{x-1}Ru[Co(CN)_6]_y$

Thin films of $KM[Co(CN)_6]_y$ where M = Fe or Ru were deposited, following the same procedure used in the electrodeposition of $KCo_{x-1}[Co(CN)_6]_y$. Figure 2 displays the *CV*s recorded for GCE in 0.1 M KCl/HCl (pH = 2) containing $K_3[Co(CN)_6]$, $FeCl_3$, (Fig. 2a), and $K_3[Co(CN)_6]$, $FeCl_3$, $RuCl_3$ (Fig. 2b). The film deposited with $FeCl_3$ gives poor stability and adherence to the surface of GCE. On the other hand, when both $FeCl_3$ and $RuCl_3$ are used (Fig. 2b), a steady growth of a robust film is observed, as indicated by the symmetric rise of both cathodic and anodic peak currents. This is not the case for the *CV* displayed in Fig. 2a. The obvious effect of $RuCl_3$ can be clearly identified from the *CV*s displayed in Fig. 3. This figure shows that the solid film of $KFe_{x-1}[Co(CN)_6]_y$ gives an ill defined *CV* in supporting electrolyte only (Fig. 3a) with a large capacitive current, while $KFe_xRu[Co(CN)_6]_y$ (Fig. 3b) shows three surface redox waves with formal potentials $E_f^{o\prime}$ at 0.2 V, 0.85 V and 1.230 V with a very low capacitive current. These well defined surface redox waves displayed in Fig. 3b along with the film stability support the reported studies [1, 12] that ruthenium provides a stability factor to the polynuclear hexacyano metal films.

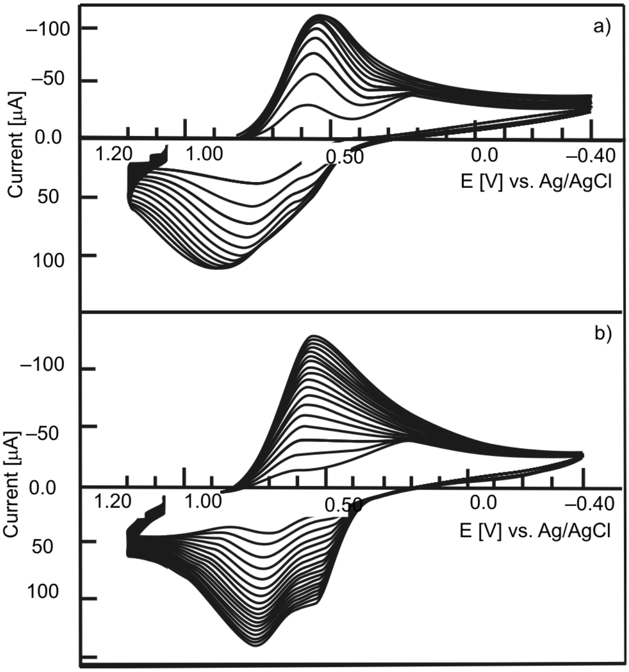

Fig. 2. Repetitive *CV* characteristics at 0.2 V·s^{-1} of GCE in equi 5mM of each of: a) $K_3[Co(CN)_6]$,$FeCl_3$, $RuCl_3$, b) $K_3[Co(CN)_6]$, $FeCl_3$, in 0.1 M KCl/HCl (pH = 2). Scan started at –0.20 V vs. Ag/AgCl

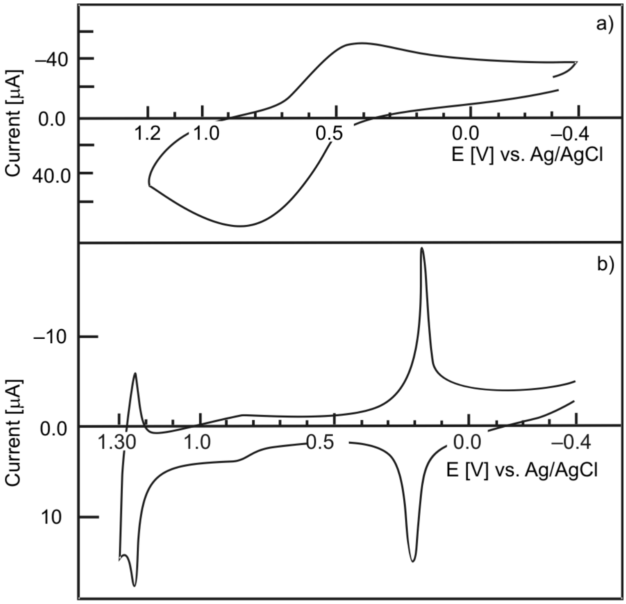

Fig. 3. *CV* characteristics in 0.1 M $KClO_4$/HCl (pH = 2) at 0.2 V·s^{-1} of GCE modified with: a) $KFe_x[Co(CN)_6]$, b) $KRu_xFe_y[Co(CN)_6]$

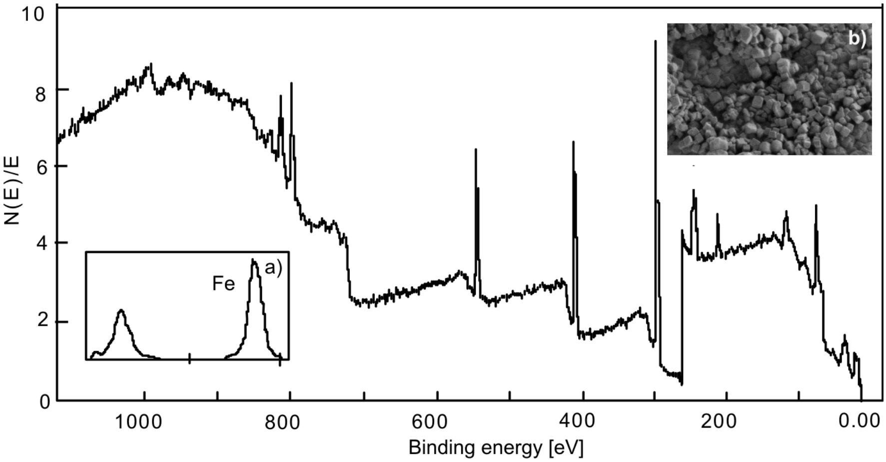

Fig. 4. XPS for the thin solid film of $KRu_xFe_y[Co(CN)_6]_z$.
Insets: a) Fe peaks, b) SEM of the deposited film

Figure 4 shows the **X**-ray photoelectron **s**pectrum (XPS) for $KFe_xRu[Co(CN)_6]_y$ film, the inset a) shows Fe peaks while Co peaks are clearly indentified, Ru 3d is being obscured by C 1s, and Ru 3p are covered by noise between 400 and 500 eV. Inset 4b is the scanning electron micrograph of the film $KFe_xRu[Co(CN)_6]_y$ deposited on GCE film. Although spectroscopic evidence of Ru with Fe in hexacyanocobaltate film is not as strong as the electrochemical evidence displayed in Fig. 3b, both are supporting evidences of deposition of $KFe_x Ru[Co(CN)_6]$. The redox wave with $E_f^{o\prime}$ at 1.235 V vs. Ag/AgCl is a strong indication of Ru existence in the film. The redox wave at 0.85 V, shown in Fig. 3, indicates that the formation of higher oxidation states of ruthenium (oxoruthenium) does not depend on the position of Ru atoms in the network of the polymer. Furthermore, studies show that the redox waves are independent of each other and are not affected by oxygen reduction (Fig. 2b).

3.4. Effect of the supporting electrolyte on the redox potentials of MHCCO

3.4.1. Cation effect

The influence of cations on the electrochemical behaviour of MHCCo was investigated by cycling the potential of GCE modified with $KFe_x Ru[Co(CN)_6]_y$ at 0.2 $V\cdot s^{-1}$ in 0.1 M $KClO_4$, 0.1 M $NaClO_4$, and 0.1 M $LiClO_4$. The results are shown in Fig. 5a. Similar studies were performed on CoHCCo film in 0.1 M KCl, 0.1 M $MgCl_2$, 0.1 M $BaCl_2$ or in 0.1 M $AlCl_3$ (Fig. 5b).

Reaction (1) indicates that the reduction process of the counter metal involves gaining electron/s and the addition of a supporting electrolyte cation. The change in the shape of the redox wave and potential can be used as an indicator for the cation effect. Recalling that the hydrated ionic sizes (in pm) are: H_3O^+ – 900, Li^+ – 600, Na^+

– 450, K^+ – 300, Mg^{2+} – 800, Ba^{2+} – 500, and Al^{3+} – 900. Replacing K^+ with a larger size cation leads to sluggish electron transfer and poor or ill defined redox peaks. This can be noticed in Fig. 5a, as the peak current of the redox waves with $E_f^{o\prime}$ at 0.180 V and that at 1.235 V decreases in the order $Li^+ > Na^+ > K^+$. On the other hand, the effects of multivalent cations such as Mg^{2+}, Ba^{2+}, and Al^{3+} on the redox wave of $[Co(CN)_6]^{3-}$ in $KCo_x[Co(CN)_6]_y$ were consistent with their ionic sizes, and were similar to that observed for monovalent cations.

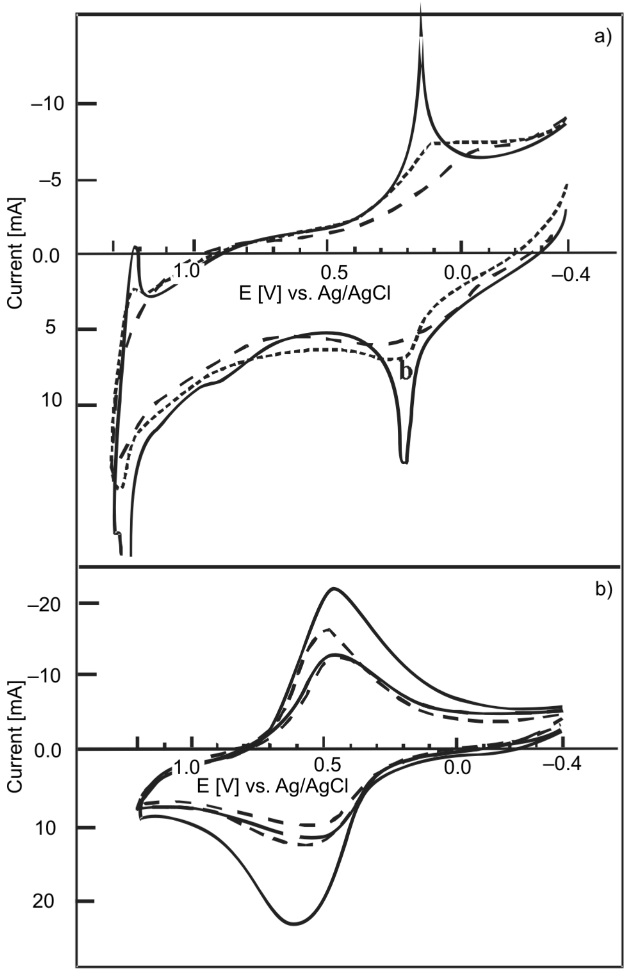

Fig. 5. *CV* characteristics at 0.2 $V \cdot s^{-1}$ of GCE modified with a) RuFeHCCo in: 0.1 M $KClO_4$ (solid line), 0.1 M $NaClO_4$ (dashed line), c) 0.1 M $LiClO_4$ (dotted line), b) $KCo_x[Co(CN)_6]_y$ in: 0.1 M KCl (thick solid line), 0.1 M $MgCl_2$ (thick dashed line), 0.1 M $BaCl_2$ solid line), 0.1 M $AlCl_3$ (dashed line)

The results displayed in Fig. 5b, illustrates such an effect. However, Ba^{2+} shows inconsistent effect with its ionic size. Such behaviour in the presence of barium can be explained by the fact that Ba^{2+} can make a contact-pair with $[Co(CN)_{6}]^{3-}$ with the displacement of some of the water molecules from its hydrous complex. This contact-ion pair adopts an inner sphere mechanism during the charge transfer process. This phenomenon has been studied [27] with $[Fe(CN)_6]^{3-}$. Magnesium cations cannot form contact pairs but rather solvent separate pairs with hexacyanometalate unit without displacement any of any their hydrous complex water molecules. This keeps the outer sphere charge transfer mechanism unchanged. It is worthwhile mentioning that hexacyanocobaltate is very selective to some alkali metals ions such as Cs. This selectivity has its applications in chemical precipitation of radioactive caesium from waste solutions with iron(II) hexacyanocobaltate(III) and triphenylcyanoborate [25].

3.4.2. Anion effect

Reaction (2) involves the incorporation of supporting electrolyte anions. Studies show that changing the supporting electrolyte from KCl to $KClO_4$ does not cause a tangible difference in the formal redox potential (Fig. 1b). Such behaviour is anticipated, since there is no large difference in the hydrodynamic radii of Cl^- and ClO_4^- ions as they are 300 and 350 pm, respectively. Such results indicate that the anion size has little or no effect on reaction (2).

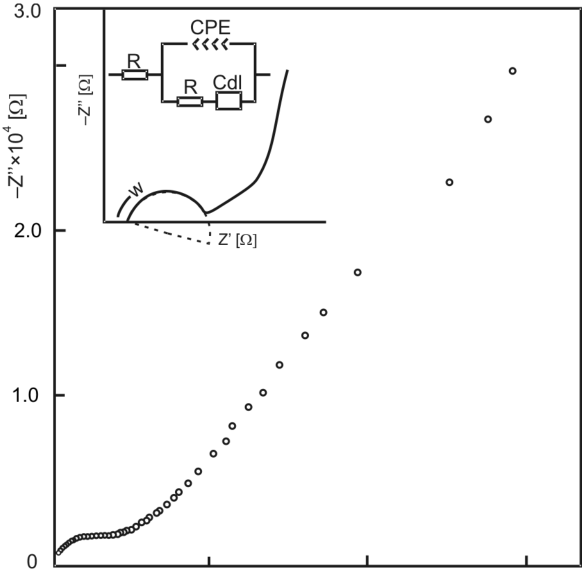

Fig. 6. Nyquest plot for GCE modified with $RuFe_x[Co(CN)_6]_3$ at 0.150 V vs. Ag/AgCl in 0.1 M $KClO_4$

In Figure 6, the Nyquest plot is shown for GCE modified with $RuFe_x[Co(CN)_6]_3$ at 0.150 V vs. Ag/AgCl in 0.1 M $KClO_4$. A case of overlapping kinetic/diffusional controlled regions of impedance behaviour can be noticed. At high frequencies, $\omega > 50$, an ill-defined semicircular plot was obtained, while at very low frequencies, 1< ω < 0.01, the impedance plot reflected a diffusional control. When measurements were extended to a very small *ω* (0.001 Hz), an indication of charge saturation behaviour was observed, however, Fig. 6 also can fit the modified Randles-type equivalent circuit with constant phase element (CPE), which acts as a capacitor. The permeability of the deposited film to aqueous K^+, which was confirmed by *CV* studies, indicates the porous nature of this film. This porosity is further confirmation for the equivalent circuit type of this electrochemical system.

3.5. Catalytic behaviour of K $Fe_x Ru[Co(CN)_6]_y$

Thin films of $KFe_x Ru[Co(CN)_6]_y$ on the surface of GCE exhibited some electrocatalytic activities towards the reduction of small oxoanions such as bromates and chlorates, and the oxidation of glucose.

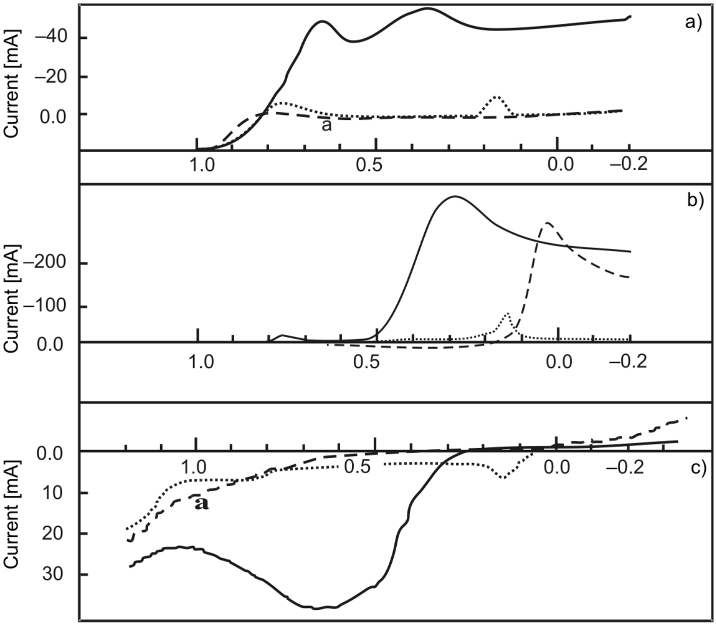

Fig. 7. Linear sweep voltammetry at 0.02 $V \cdot s^{-1}$ of: a) native GCE in KCl/HCl (pH = 2) containing 0.05M $KBrO_3$ (dashed line), GCE modified with RuFeHCCo in KCl/HCl (pH = 2) (dotted line) and GCE modified with RuFeHCCo in KCl/HCl (pH = 2) containing 0.05M $KBrO_3$ (solid line); b) native GCE in KCl/HCl (pH = 2) containing 0.05M $KClO_3$ (dashed line), GCE modified with RuFeHCCo in KCl/HCl (pH = 2) (dotted line) and c) GCE modified with RuFeHCCo in KCl/HCl (pH = 2) containing 0.05M $KClO_3$ (solid line); c) native GCE in KCl/HCl (pH = 2) containing 0.05 M glucose (dashed line), GCE modified with RuFeHCCo in KCl/HCl (pH = 2) (dotted line), GCE modified with RuFeHCCo in KCl/HCl (pH = 2) containing 0.05M glucose (solid line)

Evidence for such catalytic behaviour can be noticed in the linear scan voltammetry obtained in selected electrolytes. Figure 7a (solid line) shows a great increase in the cathodic current starting at 0.815 V in the presence of BrO_3^-, thereby indicating the catalytic activities of the hexacyanometalate films. Similar results are shown in Fig. 7b (solid line) in the presence of ClO_3^-. The catalytic reduction of chlorates and bromates is evident by the rise of cathodic current at the reduction potential that is more positive than that recorded at native electrode. Figure 7 also shows that the reduction of bromates (Fig. 7a, solid line) took place at more positive potentials than those of chlorates (Fig. 7b, solid line). Such observations can be attributed to the electron configuration and hence the energy level diagram of the central chlorine and bromine atoms in the studied oxoanions. Reduction of Cl in ClO_3^- took place at 0.280 V while that for Br in BrO_3^- took place at 0.700 V. Br atom in bromate ion uses an expanded 4d orbital which occupies a larger volume with less orientation than that of 3d in the Cl atom of chlorate anions. Furthermore, the first of the two reduction peaks shown in Fig. 7a, solid line is due to the interaction between Br 4d and Ru 4d orbitals in the monooxoruthenium species incorporated in the film. The closer energy levels of these two atoms facilitate the charge transfer process. This is not the case with chlorates, due to the difference in Cl 3d and Ru 4d evident by oxoruthenium small cathodic peak shown in Fig. 7b at 0.780 V. The studies also show that hexacyanometalates catalyze the oxidation of glucose (Fig. 7c, solid line). This catalytic oxidation behaviour can be attributed to the inclusion of some oxoruthenium compound within the FEHCCO network structure [28] .

4. Conclusions

The electrochemical behaviour of KMHCCo thin solid films fabricated using electrochemical technique in aqueous electrolytes indicates only one redox wave for $KCo[Co(CN)_6]$, corresponding to the central Co atom in the $[Co(CN)_6]^{3-}$ anion . When Ru coexists among counter ions in the KMHCCo, the redox behaviour of the film shows multi one-electron *CV* waves. KMHCCo films show size-discrimination behaviour towards supporting electrolyte cations. Like other hexacyanometalates, KMHCCo posses catalytic activities towards both electro-oxidation of biologically active molecules such as glucose, and electro-reduction of some small oxoanions. Studies also demonstrated the possibility of seeding a variety of redox centres in hexacyanometalates inorganic polymers and manipulating these structures to perform a desired function now is possible.

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