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Enhanced stability of hexacyanoferrate-based modified electrodes prepared under centrifugal fields

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Highly stable modified electrodes were fabricated by the deposition of electroactive films onto substrate electrode surfaces under centrifugal fields.

Centrifugal effects on electrochemical processes are of interest, although this is not usually reported in the literature due to the lack of suitable apparatus. According to the development of apparatus for centrifugal studies,[1,2] it is possible to study electrochemical systems under centrifugal forces. Atobe *et al.*[2] have studied electropolymerization of aniline under centrifugal field. Previously, we have reported that fractal dimension of gold electrodeposits decreases when stronger centrifugal fields are applied during the deposition process.[3] Moreover, preparation of more effective cathodes for using in secondary lithium batteries has also been described.[4]

Modification of electrode surfaces with transition metal hexacyanoferrates is an advancing and rapidly growing subject in modern electrochemistry.[5–8] Indeed, the fabrication of stable electrodes is desirable for technological applications due to interesting properties of chemically modified electrodes. Aluminium as an excellent substrate electrode for the deposition of highly stable electroactive films has been previously introduced for various modifier materials including hexacyanoferrates.[9–12] Here, the deposition of a thin film of cobalt hexacyanoferrate onto an Al substrate electrode under centrifugal fields is considered.

The film deposition was performed in a centrifugal cell similar to that described previously.[1,2] However, as the modification process was performed chemically (not electrochemically) the cell design was much simpler in comparison with the previous reports.[1,2] Indeed, simple chemical deposition was performed in a rotating tube (centrifugal cell).

The voltammetric studies were performed using a low-noise homemade potentiostat with a conventional three-electrode cell and the modified electrode as a working electrode. A saturated calomel electrode (SCE) and a platinum wire were used as reference and counter electrodes, respectively. The amperometric measurements were performed using a digital multimeter (Sanua, PC200) connected to a computer. All solutions were prepared using analytical grade chemicals (Merck) and twice-distilled and deionised water. The substrate electrode was prepared from an aluminium rod with a geometrical surface area of 0.9 cm^2. The working electrode was the cross section of the Al rod embedded in a Teflon cylinder, and the electrode prepared was used under stationary conditions throughout the experiments.

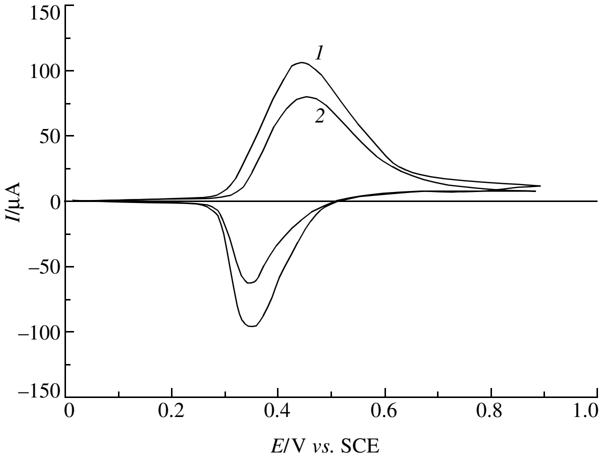

Figure 1 Cyclic voltammograms of the modified electrode prepared by the deposition of a CoHCF film onto an aluminium substrate electrode under (*1*) Earth's gravity and (*2*) a centrifugal field of 140*g*. The supporting electrolyte was 0.5 M KCl. The scan rate was 50 mV s^{-1}.

The preparation of an aluminium electrode modified with a CoHCF film includes two chemical steps. The first is chemical deposition of a thin film of cobalt on the surface of the aluminium electrode, which can be easily performed by immersing the Al electrode into a 0.5 M $CoCl_2$ solution containing 1.0 M KCl as the supporting electrolyte. This step is just a simple electroless deposition of a thin layer of metallic cobalt on the Al electrode. Note that this process is partly accompanied by metal oxidation; however, the cobalt oxides formed can also be transformed to CoHCF and this action does not make problem for the second step of the modification process. Indeed, the formation of such a passive layer can increase the stability of the electroactive film deposited on the Co electrode. Secondly, chemical transformation of the deposited film to cobalt hexacyanoferrate was carried out by dipping the deposited electrode in a solution of 5 mM $K_3Fe(CN)_6$ containing 0.1 M KCl as a supporting electrolyte.

The modification can be examined by cyclic voltammetry. A detailed mechanism of the aluminium passivation during the electroless process providing higher stability of the film deposited has been described previously.[11] Difference in the electrochemical behaviour (cyclic voltammetric characterization) of the Al substrate electrode, Co-deposited Al electrode and the electroactive film Al modified electrode has also been reported.[13]

Typical cyclic voltammetric characteristics of the modified electrodes based on hexacyanoferrate films is accompanied with a well-defined peaks couple corresponding to the redox of the surface-confined iron centres (Fe^{II}/Fe^{III}) in the hexacyanoferrate lattice). Electrochemical characteristics of cobalt hexacyanoferrate film modified electrodes have been extensively studied in the literature.[14–16] Electrochemical behaviours of cobalt hexacyanoferrate film modified electrodes are complex displaying different cyclic voltammetric characteristics depending on the synthesis method employed for the preparation and deposition of CoHCF. For example, two different types of the CoHCF films with one redox couple[17] and two redox couples[18] have been reported.

To the aim of this research, a simple method was applied just for the comparison of the CoHCF films deposited in the absence and presence of centrifugal fields. Thus, we do not study the electrochemical properties of the CoHCF films here and use its conventional voltammetric behaviour to investigate the stabilities of the electroactive films deposited. Figure 1 shows the voltammetric behaviours of the CoHCF modified electrodes prepared under Earth's gravity and a centrifugal field of 140*g*. As seen, general voltammetric characteristics of both electrodes are the same and the shapes of the voltammograms are similar. However, both anodic and cathodic peak currents are higher for the electrode prepared under centrifugal fields.

Under centrifugal fields, a greater amount of the electroactive material is deposited onto the electrode surface as a result of a squeezing process. In other words, the induced force of centrifugal field causes the deposition of a denser film. As the voltammetric characteristics of modified electrodes are directly related to the amount of electroactive materials attached to the electrode surfaces, stronger voltammetric behaviours with higher

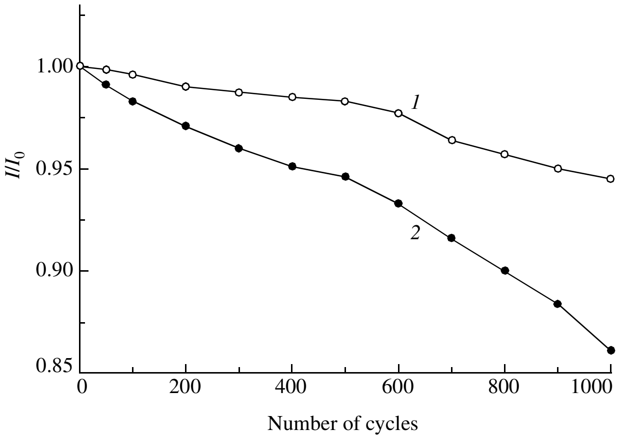

Figure 2 Electrochemical stability of the CoHCF film modified electrodes prepared under (*a*) Earth's gravity and (*b*) a centrifugal field of 140*g*.

peak currents are observed for the electrode prepared under centrifugal field. On the other hand, preparation of denser electroactive materials is of practical interest because of a more effective electrochemical behaviour.

As the main drawback of hexacyanoferrate-based modified electrodes is the gradual dissolution during potential cycling,[19,20] the deposition of electroactive materials with high chemical and electrochemical stabilities is very important to gain practical applications. Using aluminium as the substrate electrode increases stability of the electroactive film about 10 times higher than ordinary substrate electrodes, *e.g.*, glassy carbon.[9–12]

To investigate the centrifugal effects on the electrode stability, the electrochemical stabilities of the modified electrodes prepared under Earth's gravity and centrifugal field were compared. For this purpose, the voltammetric behaviours of the electrodes were examined during potential cycling, where the potential was scanned between 0.0 and 0.9 V *vs.* SCE with a potential scan rate of 50 mV s^{-1}. The results are presented in Figure 2. Although the CoHCF film deposited onto the aluminum substrate is very stable, the CoHCF film deposited under centrifugal field has higher stability. The electrode prepared under centrifugal field shows only a 6% decrease in the peak current after 1000 potential cycles. Whereas it has been reported that a CoHCF film formed on a glassy carbon electrode exhibits a 10% in the peak current after only 100 potential cycles and a 90% decrease after 1000 cycles.[20] The results indicate that the modified electrode prepared under centrifugal field has a significant stability.

As it has described previously,[11] the existence of more suitable sites on an aluminium substrate in comparison with ordinary substrates for the deposition of electroactive materials made it an excellent substrate electrode. For the modified electrode, as a centrifugal field is directly forced to the deposition process, the connection of the electroactive film is stronger. As the result of squeezing effect, the material deposited is settled on the substrate surface with strong (squeezed) connection. On the other hand, the electroactive material is orderly deposited onto the substrate surface under centrifugal field. This phenomenon was reported based on a fractal study of Au-electrodeposit surfaces.[3]

It was demonstrated that a highly stable modified electrode could be prepared by the deposition of the electroactive film under centrifugal field. Generally, centrifugal fields can be applied as a powerful tool for the effective deposition of different materials on surfaces to prepare highly stable solid films.

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