Preparation and Characterization of Electrically Switched Ion Exchange Films

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Abstract

Wastewater treatment by conventional methods as ion exchange, coagulation and precipitation is very important. A relatively new method for wastewater treatment is introduced; this method is known as electrically switched ion exchange (ESIX). ESIX can be used to separate metal ion contaminants from industrial wastewater. The ESIX method involves sequential application of reduction and oxidation potentials to an ion exchange film to induce the respective loading and unloading of Cs^+. The metal ion separated from the wastewater and unloaded from the electrode by modulating the potential applied to the film. This technology is superior to conventional methods (e.g conventional ion exchange) as it requires very little energy for ionic separation. In this study, two films of nickel hexacyanoferrate were prepared on nickel electrodes with different preparation procedures. Each film shows different performance in Cs^+ separation. Scanning electron microscopy was used to characterize the modified film surfaces. Cyclic voltammetry was used to investigate the ion exchange capacity and stability. These two films show a high capacity and stability for Cs^+ separation.

Keywords: Electrically switched ion exchange (ESIX), Nickel, ion separation, selectivity to cesium, nickel hexacyanoferrate, electroactive films.

1. Introduction:

Cesium ion (Cs^+) in radioactive waste is of particular concern as it is of high radioactivity and its half life time is almost 30 years [1, 2]. Cs^+ separation from the radioactive fission products is of great importance, as its removal reduces the waste radioactivity. Recovered radioactive cesium can then be repurposed as a radioactive source for gamma irradiation in nuclear research facilities or used in medical equipment sterilization [3-6].

Electrically switched ion exchange (ESIX) combines the ion exchange process with electrode reactions for a reversible and selective separation of Cs^+, and has the added benefit of generating relatively small amounts of secondary wastes [7]. The ESIX process was noticed to be selective to Cs^+ and K^+ than Na^+. Further, the ESIX process is highly energy efficient, with small voltages required (< 2 V) for the uptake and elution of ions [8].

The ESIX system consists of an electroactive ion exchange film that is electrochemically deposited onto a nickel electrode (Figure 1). The deposition of the ion exchange film is regulated using applied electric potential [9-12].
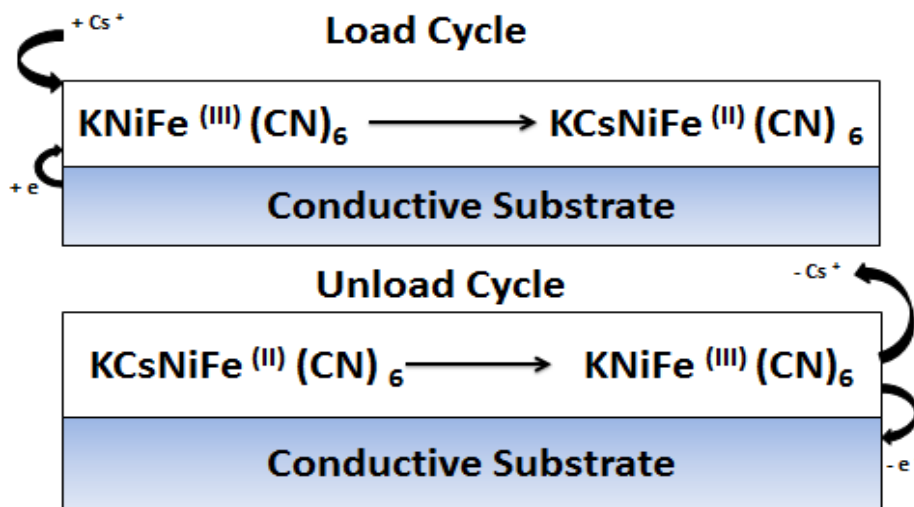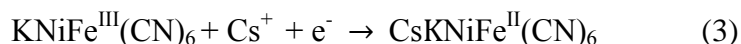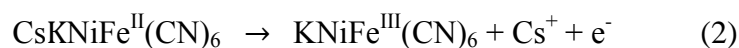

Figure (1) conductive substrate covered with Nickel hexacyanoferrate film [7].

Nickel electrode is subjected to an applied potential in a solution containing $K_3Fe(CN)_6$, the nickel on the surface is oxidized to Ni^{2+} on the electrode surface and reacts with the $Fe(CN)_6$ anion in solution, causing the formation and precipitation of insoluble nickel hexacyanoferrate on the exposed portion of the electrode. The reaction is shown in equation 1 [8].

$$Ni^{+2} + K_3Fe(CN)_6 \longrightarrow KNiFe(CN)_6 + 2K^+ + 2e^- \quad (1)$$
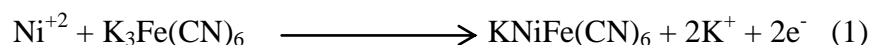
The reduction of the ferricyanide film requires the uptake of Cs^+ from waste solution. While the oxidation requires a release of the same ion back into concentration solution in order to maintain electro neutrality of the film, the oxidation of ferrocyanide film to the ferricyanide form, equation 2, and the reduction of the ferricyanide film to the ferrocyanide form, equation 3, are the main driving forces behind the ion exchange [9,13].

$$CsKNiFe^{II}(CN)_6 \ \rightarrow \ KNiFe^{III}(CN)_6 + Cs^+ + e^- \qquad (2)$$

$$KNiFe^{III}(CN)_6 + Cs^+ + e^- \rightarrow CsKNiFe^{II}(CN)_6 \qquad (3)$$

2 Experimental methods

2.1 General and electrochemical

A Potentiostat (Wave Driver 10, Pine Research Instrumentation) was used to deposit and characterize films. The software that was used to control the Potentiostat (Aftermath 2.0) was provided by Pine Research Instrumentation. A standard three-electrode system was used in the preparation and characterization of electroactive films. A saturated calomel electrode (SCE) was used as a reference electrode for the potential measurements. A platinum counter electrode with a surface area of 5 cm^2 was employed in all experiments. The reference and the counter electrode were located less than two cm from the working electrode. The working electrode was composed of nickel and its composition and preparation is further described in Section 2.2.

The chemicals which were used, $K_3Fe(CN)_6$, KNO_3, and $CsNO_3$, were all reagent-grade with greater than 99% purity and were used without further purification. Deionized water (18.2 MΩ cm^{-1}) was used in all salt solution preparations and cleaning of electrochemical cell components.

2.2 Surface preparation

Nickel disks (99.99% pure) were used as the working electrodes. A nickel disk was embedded in a Teflon holder suspended in the test solution. The portion of the disk exposed to test solution has a diameter of 0.5 cm and an area 0.2 cm^2.

2.3 Film preparation

The nickel hexacyanoferrate films preparation methodology was adapted from the method described by Bocarsly et al. [14, 15] In their work, nickel was first oxidized at an anodic potential of 0.6 V – 1 V relative to SCE for approximately 30 min. in a solution containing 10 mM $M_3Fe(CN)_6$ and a supporting electrolyte 0.1 M MNO_3, and an insoluble, stable alkali $MNiFe^{III}(CN)_6$ was formed on the electrode surface, where M was K, Na, or Cs.

In this work, a solution containing 30 mM $K_3Fe(CN)_6$ and 0.5 M KNO_3 was used for the film preparation. The solution had oxygen stripped from it by bubbling nitrogen gas through the solution before starting the deposition procedure. Table 1 represents the different parameters for film preparation.

Table 1: film preparation voltage

Film number	1st step (20 min)	2nd step (20 min)
A	0.25 V	1.1 V
B	0.3 V	1.15 V

Two ESIX films were prepared by submerging a nickel electrode in a solution of 30 mM $K_3Fe(CN)_6$ and 0.5 M KNO_3 and then applying the electrical potential for the initial phase of the film deposition. For film (A) a potential of 0.25 V was applied for 20 minutes and then a potential of 1.1 V was applied for a further 20 minutes. While in film (B) a potential of 0.3 V was applied for 20 minutes and then a potential of 1.15 V for further 20 minutes was applied. The purpose of using low voltage for the first step was to form a very thin mononuclear layer on the ESIX film to act as a nucleation sites for the other layers of the ESIX film, which were deposited under the higher voltage in the second step.

2.4 Film characterization

The film was characterized in multiple ways. First, the surface morphology for the prepared films was imaged using scanning electron microscopy conducted using a JOEL 7000 electron microscope to examine the film morphology.

The film's capability for repeated cycling of ESIX was characterized using cyclic voltammetry, which was conducted in a 1 M $CsNO_3$ solution. The applied potential started at 0.2 V and was scanned anodically to 0.9 V then catholically to -0.2 V then back to 0.2 V at a scan rate of   100 mV s^{-1}.

3 Results and discussion

3.1 Film morphology by SEM

Figure 2 is the SEM image of the two films. The surface of the nickel electrode coated with hexacyanoferrate is displayed at a magnification of 30,000 X.
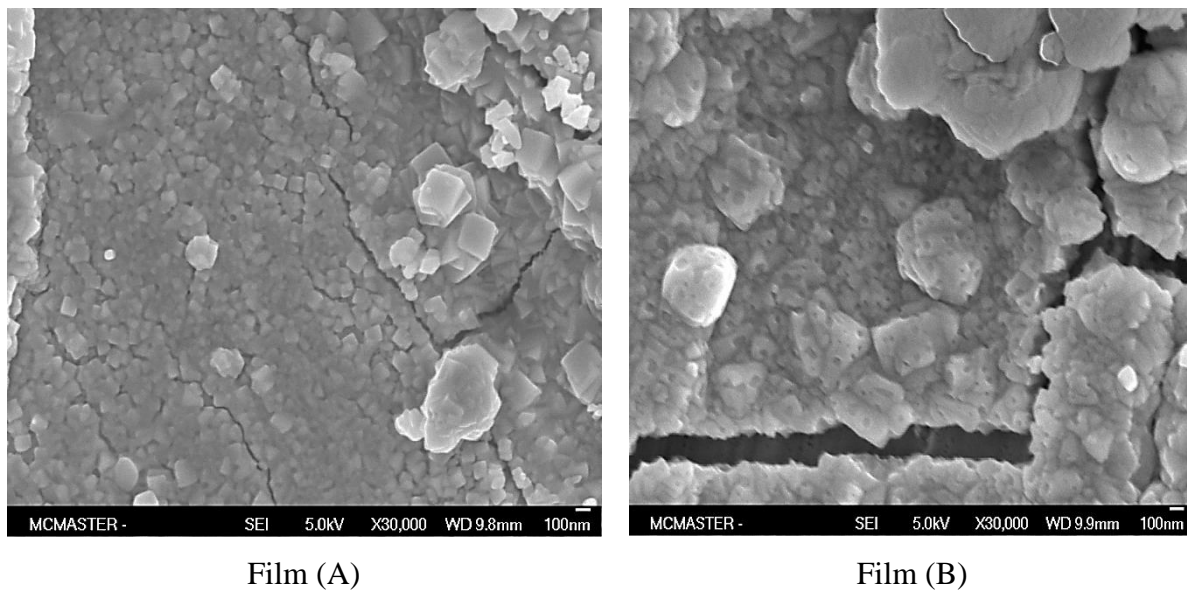
| Film (A) | Film (B) |

Figure 2: SEM images of the two films

Film (A) image shows a uniform layer of the prepared film. However this film seems to be more uniform than film (B) with few cracks. These cracks are believed to be happened due to the drying process before SEM imaging. We believe that these cracks don't exist in the film used to load and unload Cs^+. This uniform layer is believed to be formed due to the initial low applied voltage in the first step (0.25 V) followed by the 2nd step (1.1 V).

The image of Film (B) shows a denser layer of the prepared film than Film (A). However it have one big crack which is also believed to happened due to the drying process before SEM imaging, also it shows that the surface of the film is full of pitting. The 1st step applied potential (0.3 V) leads to the formation of a strong monolayer of nickel hexacyanoferrate while The higher voltage for the 2nd step in the film preparation (1.15 V) causes more layers of nickel hexacyanoferrate to be built up, forming this more densely layered film and leads to the formation of more pitting causing the increase of the film surface area.

3.2 Film characterization (Cyclic Voltammogram)

Voltammogram curves are shown for each film which represents the electrical behavior of the films for cycles 1 and 1000. From this measurement, it is possible to determine how the capacity diminishes during repetitive Cs^+ loading and unloading.

Also shown is the integration of the current signal obtained from the voltammogram. This was measured in order to calculate the maximum charge capacity of each film as well as its surface coverage. The maximum charge capacity is simply the total amount of charge that the film is able to retain per unit area, while the surface coverage is calculated by dividing the maximum charge capacity by Faraday's Constant to obtain the number of redox species that

contribute to the current. These calculations give insight to the number of active site per unit area [16].
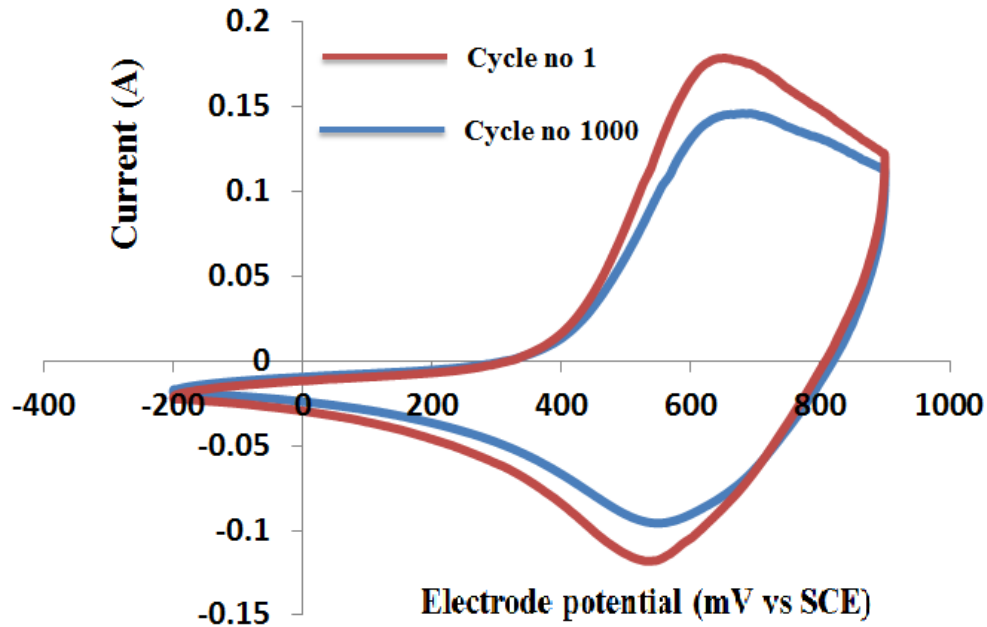
3.2.1 Film A (0.25 V then 1.1 V)

Figure 3: Cyclic voltammogram for Film A in 1 M CsNO$_3$

Figure (3) shows the cyclic voltammogram for Film A in a 1 M CsNO$_3$ solution. The shape of the cyclic voltammogram in the figure confirms that the loading and unloading of Cs$^+$ is occurring. The curves represent the voltammogram for cycles 1 and 1000. The peak current during the reduction cycle occurred at an applied potential of approximately 570 mV, where Cs$^+$ was loaded and the current approached 0 mA at 300 mV as the reduction of ferricyanide to ferrocyanide neared completion and terminated the uptake of Cs$^+$. The oxidation of ferrocyanide to ferricyanide begins with the unloading of Cs$^+$ from the film, which occurred at 800 mV, and the peak current during the release of Cs$^+$ from the cyclic voltammogram occurred at 650 mV. The peak current was reduced in cycle 1000, which indicates that the film loses its capacity during the Cs$^+$ removal process. The film capacity was reduced by approximately 35% after 1000 cycles of loading and unloading Cs$^+$.
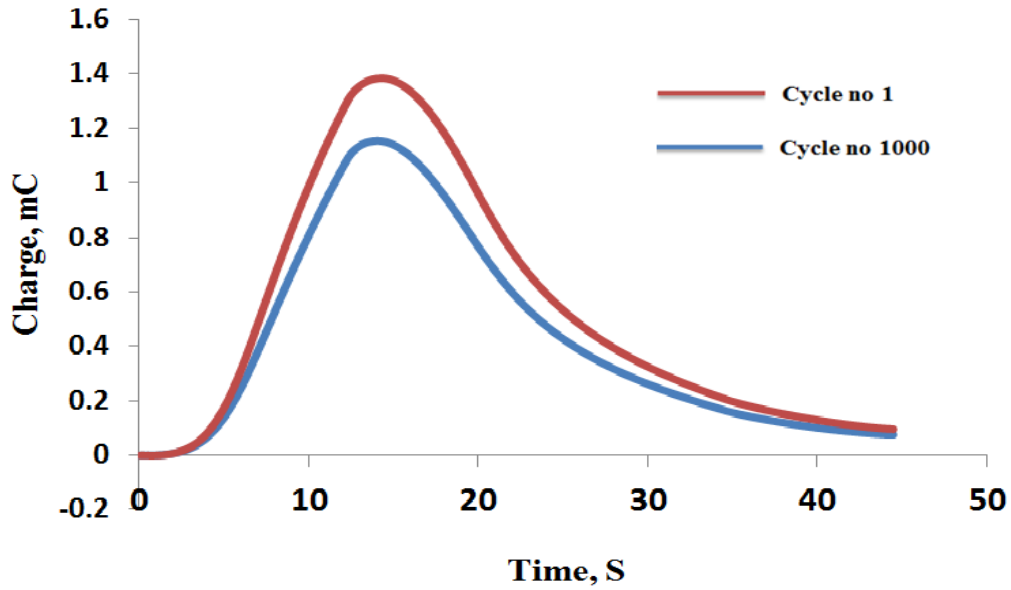
Figure 4: Integration of the current over the 1st and 1000th voltammetry sweeps for Film A

Figure 4 shows the capacity of Film A by integrating the current over the course of cycles 1 and 1000 from the voltammetry sweeps with respect to time. The maximum charge capacity of the film at cycles 1 and 1000 is summarized in Table 3.

Table 3: Film A characterization after cycles 1 and 1000

Cycles	Maximum charge capacity	Surface coverage
1	12×10^{-3} C cm^{-2}	1.2×10^{-7} mol cm^{-2}
1000	7.5×10^{-3} C cm^{-2}	7×10^{-8} mol cm^{-2}

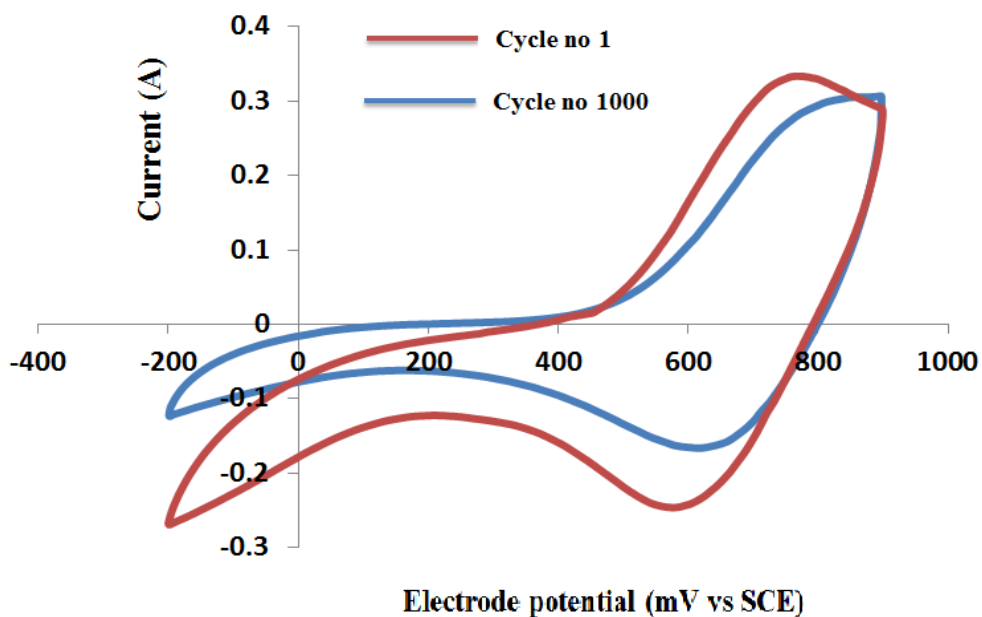**3.2.2 Film B (0.3 V then 1.15 V)**

Figure 5: Cyclic voltammogram for Film B in 1 M $CsNO_3$

Figure 5 shows the behavior of Film B under cyclic voltammetry in a 1 M $CsNO_3$ solution. During Cs^+ loading, the peak current occurred at an applied potential of approximately 600 mV, and the current approached zero at 350 mV as the maximum amount of Cs^+ was removed from solution. The oxidation of ferrocyanide to ferricyanide occurs as Cs^+ is unloaded, and the peak current achieved was 750 mV. There was a 10% decrease in the peak current between cycle 1 and cycle 1000.
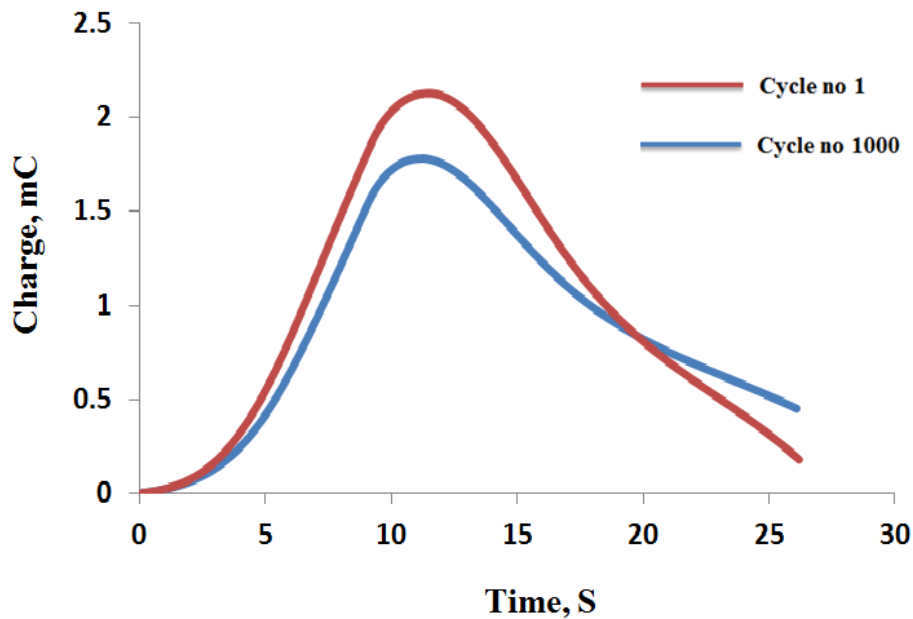

Figure 6: Integration of the current from cycles (1 and 1000) of Film B.

Figure 6 shows the capacity of the film. The maximum charge capacity of the film at cycles 1, and 1000 is summarized in table 4.

Table 4: Film B characterization after cycles 1, 500 and 1000.

Cycles	Maximum charge capacity	Surface coverage
1	13×10^{-3} C cm^{-2}	1.23×10^{-7} mol cm^{-2}
1000	10.2×10^{-3} C cm^{-2}	9.8×10^{-8} mol cm^{-2}

4 Conclusion

Two hexacyanoferrate films were prepared on nickel electrodes using different applied potentials in order to examine their capability for the electronically switched ion exchange of the Cs^+ ion from an aqueous solution. These films were compared by examining the surface morphology using SEM and their performance through cyclic voltammetry. The results show that there is a significant difference in the performance of the prepared films with regard to

Cs^+ loading and unloading, and that each film performance depends on the applied potentials used during the preparation of the film. In this instance, a film which was prepared by depositing nickel hexacyanoferrate using an initial voltage of 0.3 V relative to a SCE for 20 minutes in the initiation stage, followed by a voltage of 1.15 V relative to SCE for 20 minutes for film growth, demonstrates the best performance, as it demonstrated the lowest reduction in capacity with repeated cycling; which gives evidence that it would be a good candidate for electrically switched ion exchange film for the removal of Cs^+ from solution.

5 Acknowledgements

6 References

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