# ELECTROCHEMICAL ION EXCHANGE

**J. P. H. Sukamto, S. D. Rassat, R. J. Orth and M. A. Lilga**, Pacific Northwest National Laboratory, Richland, WA, USA

## Introduction

Electrochemical ion exchange (EIX) is a process where electrochemistry and ion exchange (IX) are combined to effect the separation of ions more efficiently than the use of either technique alone, especially in minimizing secondary waste generation. The varieties of EIX, beginning with those using electrochemically inactive IX materials and proceeding to those using electrochemically active ion exchange (EaIX) materials, are discussed here.

## EIX Processes Using Electrochemically Inactive Ion Exchange Materials

Some materials used in the EIX process are not active electrochemically, that is, they do not contain functional groups that can be reduced or oxidized. Examples of commonly used separation techniques of this type include *electrodialysis* and *electrophoresis/electrochromatography*. In electrodialysis, the permselectivity of IX membranes is used in combination with an electric field to separate anions and cations. In a variation of conventional electrodialysis called *electrodiaresis polishing*, IX materials are packed between the IX membranes; the IX material serves as an immobile electrolyte. The schematic of the process shown in **Figure 1** shows that the water is processed through the IX materials. Due to the high concentration of ionic sites in the IX material, fairly resistive (up to 15 MΩ) water can be produced at the outlet. In electrophoresis/electrochromatography where IX packing materials are used, IX interactions between the analyte and the column material enhance the separation capability over that available if differences in electrophoretic mobilities alone were used.

Another process in this category, a process termed *EIX* by the original researchers (Allen *et al.*), uses an assembly consisting of an electrochemically inactive IX material attached to an electrode as the separation agent. This approach, for the separation of cations, is shown in **Figure 2**. (It should be noted that the term 'EIX' is used more broadly here to denote a set of separation techniques that use electrochemistry and IX, not just the process shown in **Figure 2**.) Here, a cathodic potential is applied to the electrode material assembly for the uptake of cations. The applied potential serves to generate an electric field that increases the transport rate of cations toward the electrode material assembly and to electrolyse water to produce hydroxyl ions that activate the IX material. To elute the sorbed cations, an anodic potential is applied to the electrode/cationic ion exchange material assembly. This results in the local

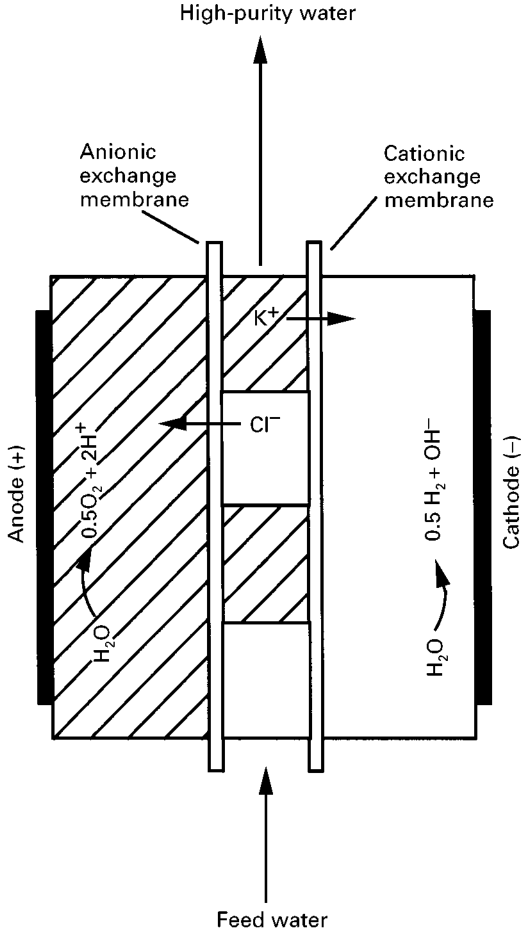

**Figure 1** Cationic and anionic IX resins are depicted as hatched and open areas, respectively. Only cations are mobile in the cationic IX material, and only anions are mobile in the anionic IX material. Cations in the feed water are expelled from the water while flowing through the cationic IX material. Similarly, anions are expelled from the feed water while flowing through the anionic IX material.

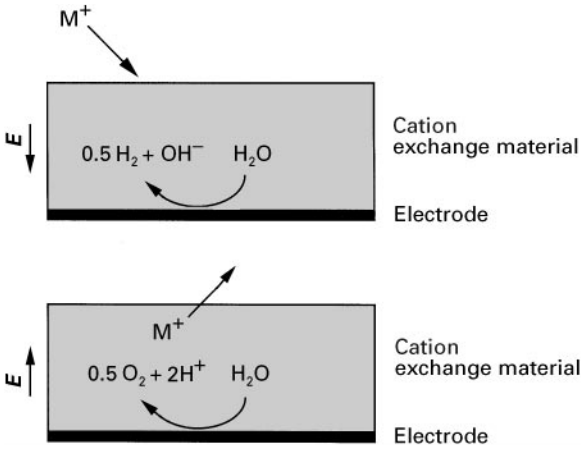

**Figure 2** Cation uptake (top) and elution (bottom) at the EIX electrodes. Water reduction leads to production of hydroxyl ions resulting in the de-protonation of sites in the cationic IX resin. In turn, the IX resin will uptake cations to maintain electroneutrality. The electric field, ***E***, present during the water-reduction process, serves to enhance cation transport to/within the cationic IX resin. The reverse reactions occur during cation elution.

production of hydrogen ions from the splitting of water, which in turn displaces the sorbed cations as in conventional IX processes. In addition, an electric field is generated which accelerates the transport rate of cations. For anions, anionic IX materials are used; an anodic potential is applied to the assembly during uptake and a cathodic potential is applied during elution. The advantages of this approach over conventional IX processes are increased uptake rate due to the applied electric field and more efficient use of hydrogen or hydroxyl ions for both uptake and elution. Although the thermodynamics of the elution process have not changed as compared to conventional IX, the close mity of the generated hydrogen or hydroxyl ions to the exchange sites increases the overall process rate by reducing the time required for uptake and elution. In addition, fewer excess hydrogen or hydroxyl ions are required.

## EIX Processes Using Electroactive Ion Exchange Materials

**Figures** 3(A) to (D) show conceptually the electroactive ion exchange (EaIX) approach, a subset of EIX techniques. Here, EIX processes, where EaIX materials are used, will be denoted as EIX/EaIX. **Figure** 3(A) and (B) illustrate cation separation. The reduction of a generic EaIX material, X, results in a net negative charge that has to be compensated by a cation (see **Figure** 3A). Provided that X is selective

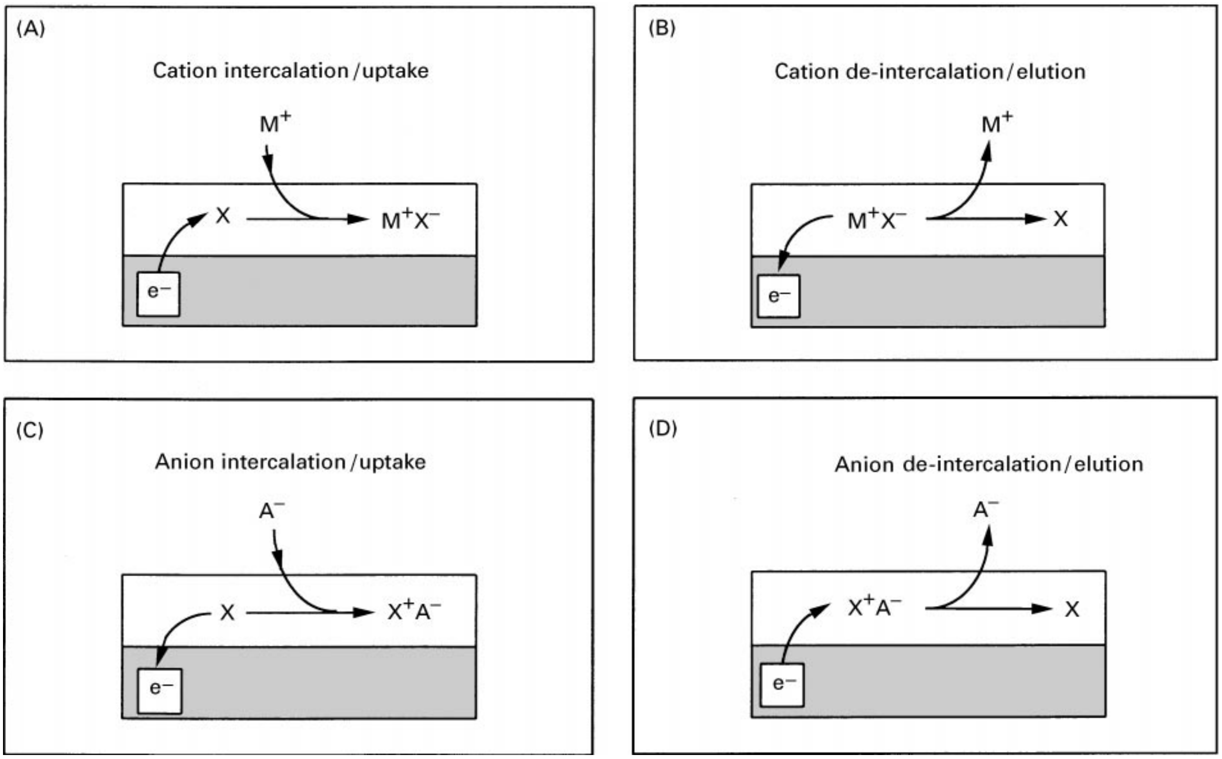

**Figure 3** (A) Cation intercalation/uptake during film reduction. (B) Cation de-intercalation/elution during film oxidation. (C) Anion intercalation/uptake during film oxidation. (D) Anion de-intercalation/elution during film reduction.

for a specific cation, then the cation uptake shown in **Figure** 3(A) results in the selective separation of a cation, $M_1^+$, from, say $M_2^+$. Elution of $M_1^+$ is simply achieved by oxidizing $X^-$ back to X, which is necessarily accompanied by the expulsion of $M_1^+$ (see **Figure** 3B). The analogous uptake and elution of anions are shown in **Figure** 3(C) and (D), respectively. For anions, uptake occurs during oxidation, and elution accompanies reduction. It should be noted that the same sequence of oxidation and reduction is used for the EIX/EaIX approach and the process shown in **Figure** 2. More importantly, however, the two approaches are very different with respect to the specific electrochemical reactions that take place during oxidation and reduction. In the process shown in **Figure** 2, both oxidation and reduction reactions are water-splitting. The reductive water-splitting results in hydrogen gas and hydroxyl ion production, whereas the oxidative water-splitting results in oxygen gas and hydrogen ion production. While this approach results in relatively efficient use of the protons and hydroxyls, the exchange ratio is not one to one. That is, more than one equivalent of protons is required to displace one equivalent of cations (or uptake one equivalent of anions). In addition, in the processing of radioactive materials, hydrogen gas generation is undesirable because of safety issues. On the other hand, with the use of EaIX materials (as shown in **Figure** 3A to D), only one equivalent of electrons is needed to elute one equivalent of ions. Therefore, using EaIX materials further reduces the amount of secondary waste generated. The electric field generated within EaIX materials has two functions: firstly to increase the transport rate of ions through the EaIX material and secondly to attract (or expel) the ions to the binding sites since the electric field is strongest near an oxidized or reduced site. The last point is particularly noteworthy since it implies that highly selective materials can be used. Although the requirements of high selectivity and ease of elution are typically in conflict, the two requirements are not mutually exclusive if the elution is purely electrostatic in nature.

EaIX materials have been applied for analytical-scale separation in a process called *electrochemical chromatography*. This process is very similar to conventional liquid chromatography except that the stationary phase is electroactive. As in conventional chromatographic processes, the retention times for different ions are largely controlled by interactions with the stationary phase. However, the redox state of the stationary phase allows additional control of the interactions between the analytes and the stationary phase. For example, anions can be easily separated from cations by applying a positive or anodic potential to the stationary phase. Separation of the different anions, however, still relies on the specific interactions between the stationary phase and the ions.

EaIX materials may also be used for preparative-scale separations. Two modes of operation are possible: packed bed and membrane. The sequence of operational events in the packed bed mode in EIX/EaIX is a combination of the sequences used in electrochemical chromatography and conventional IX processes: firstly, analyte is sorbed into the EaIX material during the uptake cycle (with or without the application of a potential) and secondly the sorbed ions are eluted from the EaIX material by the application of a potential (see **Figure 4**). It should be noted that EaIX materials can be used as conventional IX materials during the sorption cycle; the distinguishing feature of the EaIX material is the ability to elute sorbed ions by simply applying the appropriate potential (**Figure** 3B and D). In the second mode of operation, the EaIX materials are made as membranes (see **Figure** 5). This mode of operation is superior to the packed-bed approach since solution switching is not required. This in turn implies that continuous operation is possible and that neither the process nor waste stream will be diluted, which necessarily occurs when solution switching takes place in the packed-bed mode. On the other hand, the packed-bed mode is more advantageous in treating very

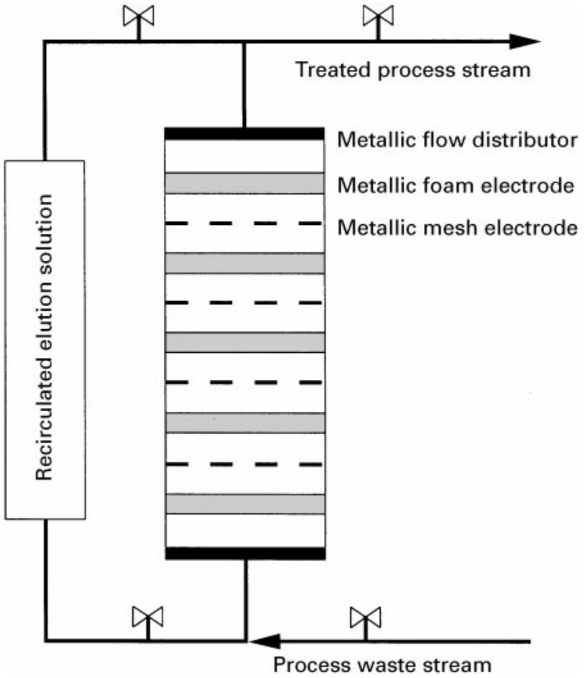

**Figure 4** EIX/EaIX columns consist of the EaIX electrodes and counterelectrodes. Connections to the elution solutions are closed during sorption of target ions from the process waste stream. Sorption can be with or without an applied potential (see eqns [2] and [3] in the text). Elution is achieved by applying a potential (see **Figure** 3B and D) and flowing the elution solution.

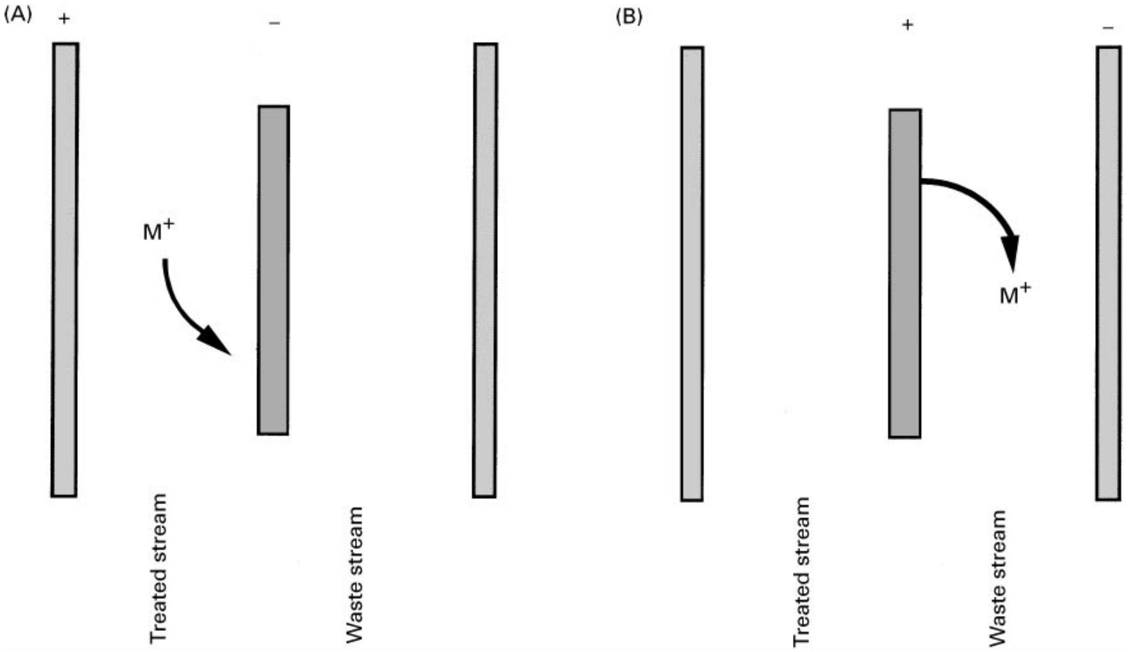

**Figure 5** The EaIX membrane is always an electrode when used in the membrane mode. (A) Reduction of EaIX membrane (negative electrode) results in uptake of cations from the treated stream. (B) Oxidation of EaIX membrane (positive electrode) results in elution of cations to the waste stream. The treated and waste streams never come in contact.

dilute streams since more intimate contact between the process stream and the EaIX materials is possible. In addition, there are possibly more difficulties associated with preparing EaIX materials as membranes than as packed-bed materials.

## Characterization of EaIX Materials

In the development and testing of an EIX/EaIX process, the ion-loading capacity and specific ion selectivity of the EaIX materials are of particular interest. Selectivity is defined in terms of a separation factor $\alpha_1^2$, which describes the selectivity for species '2' over species '1':

$$\alpha_1^2 = \frac{x_2'/x_1'}{x_2/x_1} \qquad [1]$$

The numerator is the ratio of ion mole fractions within the EaIX material, and the denominator is the mole fraction (or concentration) ratio in the bulk binary solution contacting the EaIX material. The separation factor is especially useful for estimating process performance. For example, **Figure 6** shows the fraction of $Na^+$ recovered as a function of $K^+$ removed for various values of $\alpha_{Na}^K$. The plots show that if a minimum of 90% $Na^+$ recovery is required while expelling $>70\%$ of the $K^+$, then an $\alpha_{Na}^K$ of approximately 30 is needed.

### Electrochemical Methods

In addition to standard bulk contact methods typically used to characterize IX materials, electrochemical methods are well suited for evaluating EaIX materials, especially for evaluating their expected performance when an applied potential is used in the uptake cycle. Two conventional electrochemical methods – *cyclic voltammetry* and *chronoamperometry* – are particularly useful in evaluating the ion-loading capacity of EaIX materials. Cyclic voltammetry is best suited for a planar geometry since

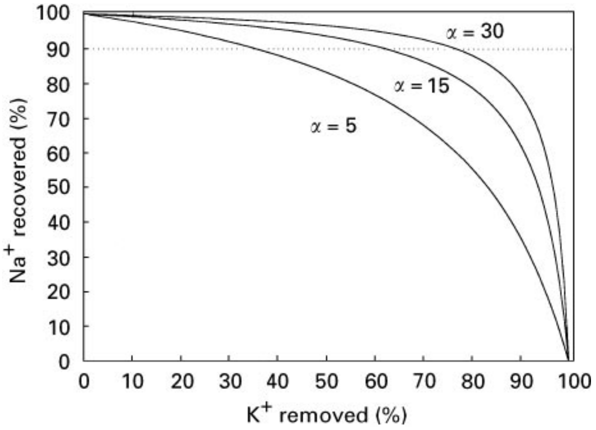

**Figure 6** Fraction of $Na^+$ recovered as a function of $K^+$ removed for various separation factor, $\alpha_K^{Na}$.

the slowly ramped applied potential is less intrusive on the samples. Chronoamperometry, on the other hand, is more suitable for determining the capacity of EaIX materials deposited on a high-surface area electrode because mass transfer limitations affect measured cyclic voltammograms (CVs).

A CV is obtained by measuring the current passed at the electrode as the applied potential is swept linearly at a fixed scan rate between two potential limits. When a suitable potential window is selected, cations (anions) are loaded into the EaIX material during the cathodic (anodic) sweep and the ions are eluted during the reverse sweep. The total charge passes in a load or unload cycle, as determined by integrating the current over any linear sweep, is a direct measure of the ion-loading capacity when the charge transfer is only a result of a known electrochemical reaction (see eqn [2] below). In chronoamperometry, the potential is stepped from one potential limit to the other. The current is measured while the potential is held at a limit for a fixed period of time, and again, the integrated charge passed is a measure of the ions loaded into or eluted from an EaIX electrode assembly.

### Electrochemical and Gravimetric Methods

The two electrochemical methods described above yield only the ion-loading capacity. In order to determine the separation factor, an additional independent measurement is required. This is accomplished by combining the electrochemical measurements with gravimetric measurements. A common term for this combined method is electrochemical quartz crystal microgravimetry (EQCM). As the name suggests, mass accumulation within the EaIX material is monitored in addition to the total charge passed. Typically, quartz crystals are coated with an electrode on which a layer of an EaIX material is deposited. The fundamental frequency of the crystal is very sensitive to the mass loaded in the EaIX material; monitoring this fundamental frequency, the mass loaded during uptake and elution can be determined. For a crystal oscillating at 5.9 MHz, a 1 Hz decrease in the frequency corresponds to a mass increase of $\sim 4.0 \times 10^{-9}$ g. In EQCM, the oscillation frequency is monitored at the same time that the potential is swept to obtain a CV. This combination of measurements gives simultaneous information on electrochemical (ion) capacity and mass changes during load and elution cycles. Since mass change differs according to the molecular weight of the ions transported in and out of the EaIX film, the selectivity of the EaIX material for an ion in a binary mixture of known composition can be determined using EQCM. The analysis is complicated, but not prohibitively, by the simultaneous transport of solvent (e.g., hydration water) and other species with the ions of interest.

### Flow Cell Methods

Flow cell methods for EIX/EaIX characterization differ from conventional IX methodologies only in the material preparation. To achieve high volumetric ion-loading capacity, EaIX materials are typically coated on high surface-area electrodes (e.g., porous metal foam or mesh). These EaIX electrodes can be used in any of the modes represented in eqns [2] and [3]. To create an EaIX bed, multiple porous electrodes are used in series (see **Figure** 7A and B). When used in the conventional mode in the uptake cycle, the process stream simply flows through the electrodes. The effluent solution composition is analysed and breakthrough curves are obtained.

## Properties of EaIX Materials

Functional requirements of EaIX materials are electronic conductivity, ionic conductivity, selectivity for the ion of interest, and reasonable stability (physical and chemical). Of the numerous inorganic and organic materials that fulfil all or some of the listed requirements, discussions will be limited to nickel hexacyanoferrate (NiHCF) as an example of a cationic EaIX material and polyvinylferrocene (PVF) as an example for an anionic EaIX material.

Hexacyanoferrate materials (including NiHCF) are known to be selective for alkali metals and, in

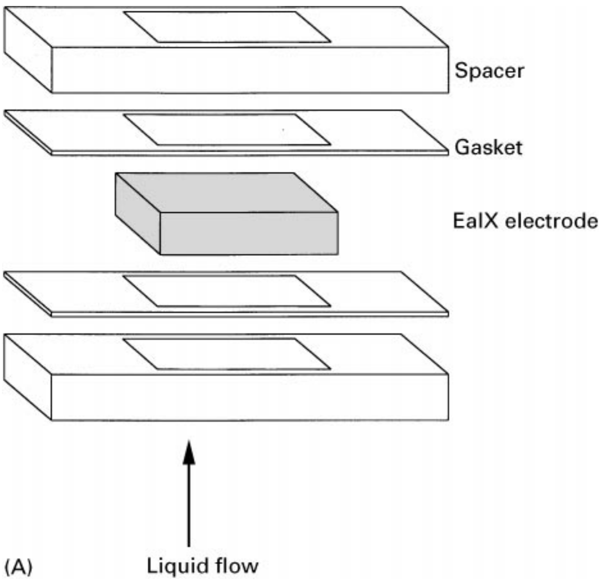

**Figure 7** (A) Single electrode with the associated spacers and gaskets. (B) Eight-stack cell used for flow-through studies.

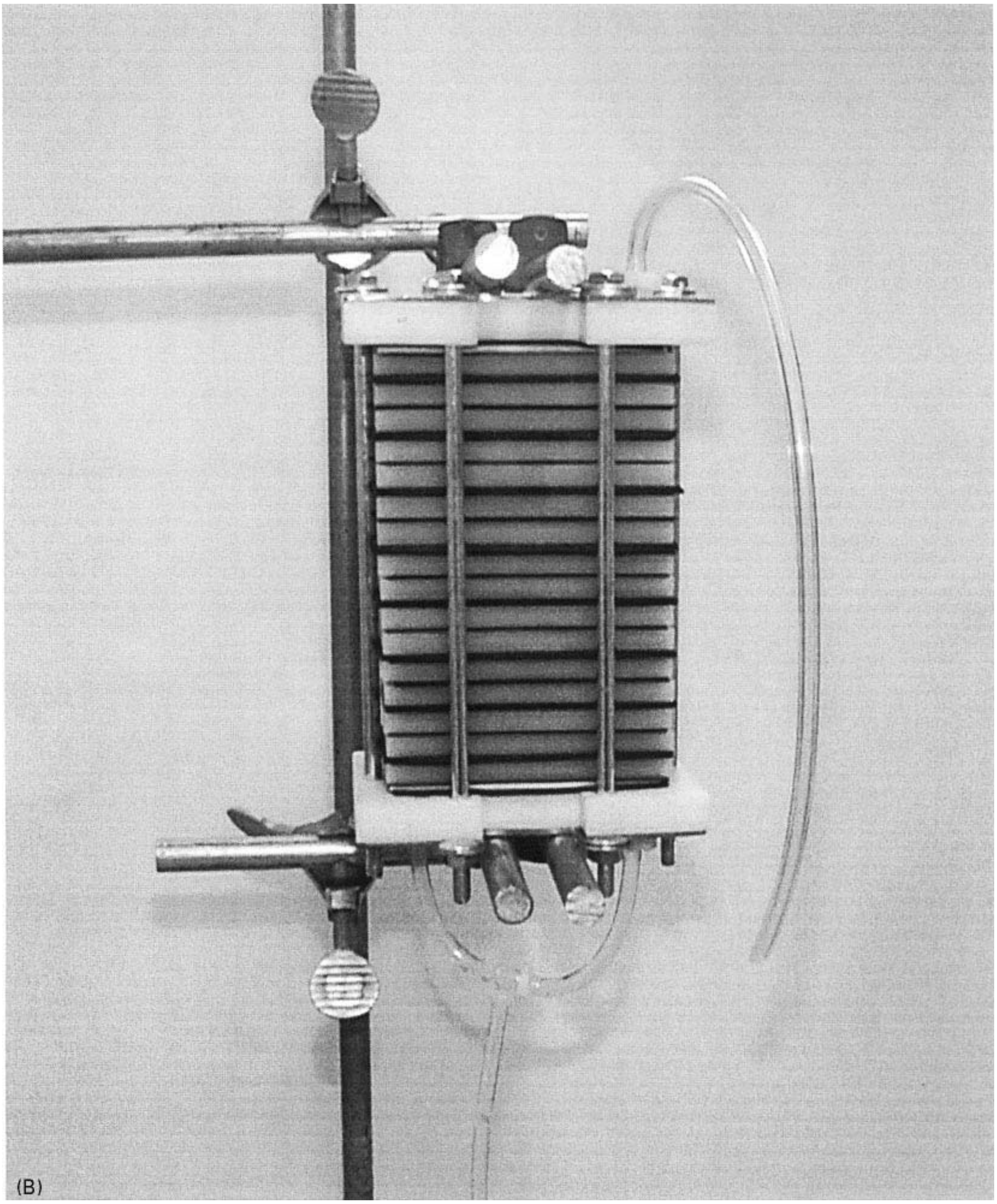

**Figure 7** *Continued*

particular, are extremely selective for cesium ($Cs^+$) over sodium ($Na^+$) and potassium ($K^+$). More recently, the preference of polyvinylferrocene for perrhenate (nonradioactive chemical analogue of pertechnetate) anions over nitrate anions has been demonstrated.

### Nickel Hexacyanoferrate

Nickel hexacyanoferrate $[Ni^{II}Fe^{II/III}(CN)_6^{2-/-}]$ (NiHCF), an electroactive material, is known to complex reversibly with the alkali metal cations such as $Na^+$, $K^+$, and $Cs^+$. Upon reduction of the iron ($Fe^{III}$) centre in NiHCF, an alkali cation associates with the ferrocyanide moiety to maintain charge neutrality through the following reaction, where $M^+$ is an alkali metal cation:

$$MNi^{II}Fe^{III}(CN)_6 + M^+ + e^- \leftrightarrow M_2Ni^{II}Fe^{II}(CN)_6 \quad [2]$$

The reverse reaction, upon oxidation of the $Fe^{II}$ centre, results in the dissociation of a single alkali metal cation per molecule of hexacyanoferrate. Oxidation of NiHCF film deposited on a substrate electrode, therefore, leads to the expulsion or deintercalation of alkali cations from the film into a contacting solution, while the reduction of deposited NiHCF film leads to the uptake or intercalation of alkali cations from solution into the film (see **Figure** 3B and A, respectively). The selectivity for alkali cations $M^+$ by NiHCF increases with molecular weights, $Cs^+ \gg K^+ > Na^+$. Therefore, $K^+$ or/and $Na^+$ is readily exchanged for $Cs^+$; for example:

$$Na_2Ni^{II}Fe^{II}(CN)_6 + 2Cs^+ \leftrightarrow Cs_2Ni^{II}Fe^{II}(CN)_6 + 2Na^+ \qquad [3]$$

Equation [3] shows that the EaIX material can be used in conventional IX. The $Cs^+$ is bound so strongly that elution is only possible through oxidation of the Fe centre from II to III. Chemical oxidation has been demonstrated with NiHCF as well as for the copper and zinc analogues. Approximately five column volumes of 8 mol $L^{-1}$ nitric acid are required for effective elution of all the sorbed $Cs^+$. The cost and hazard associated with this eluent are significant. Use of the EIX/EaIX approach, therefore, provides an attractive alternative since the oxidation can be done more efficiently via the electrochemical approach.

It is imperative for the EIX/EaIX process that there is intimate contact between the EaIX material and the electronically conducting substrate. NiHCF can be conveniently deposited onto a conducting substrate electrochemically. A nickel surface corroded in a solution containing hexacyanoferrate ions results in the precipitation/deposition of NiHCF on the surface. The electrochemical route is particularly advantageous over other methods (e.g., precipitation and sol-gel) since deposition within the pores of a porous electrode can be carried out readily.

**Applications** The selectivity of NiHCF for alkali cations with an affinity order $Cs^+ \gg K^+ > Na^+$ is attributed to the relative sizes of the ions, both hydrated and not, and the NiHCF cubic lattice structure that the ions must penetrate and then occupy. Because NiHCF is both electronically and ion conducting, is readily deposited as a film on conductive electrode substrates, and is alkali cation-specific, it is an ideal EaIX material for $K^+$ and $Cs^+$ separation applications.

*Potassium separation* The forest products industry requires selective removal of $K^+$ and recovery of $Na^+$. As the plots in Figure 6 show, the separation factor is critical in determining the extent to which $Na^+$ can be recovered for a required removal of $K^+$. Therefore, quantification of $\alpha^{K}_{Na}$ is essential for scale-up purposes and capital cost estimation. Because equipment capital costs scale roughly with the electrode costs, it is necessary to minimize electrode area to make the EaIX process financially attractive. The larger the separation factor $\alpha^{K}_{Na}$, the smaller the EaIX electrode area necessary to remove a given amount of $K^+$. Electrode area is also reduced if the ion capacity of the EaIX material per unit electrode area is increased.

The selectivity of NiHCF for $K^+$ in preference to $Na^+$ was quantified by EQCM and by bulk-contact experiments. Separation factors $\alpha^{K}_{Na}$ ranged from about 5 using EQCM to a maximum of 24 in bulk-contact tests; these differences will be discussed further below. **Figure** 8(A) and (B) show the results of EQCM experiments for a NiHCF-coated quartz crystal in contact with potassium and sodium sulfate solutions and mixtures. The CVs in **Figure** 8(A) show

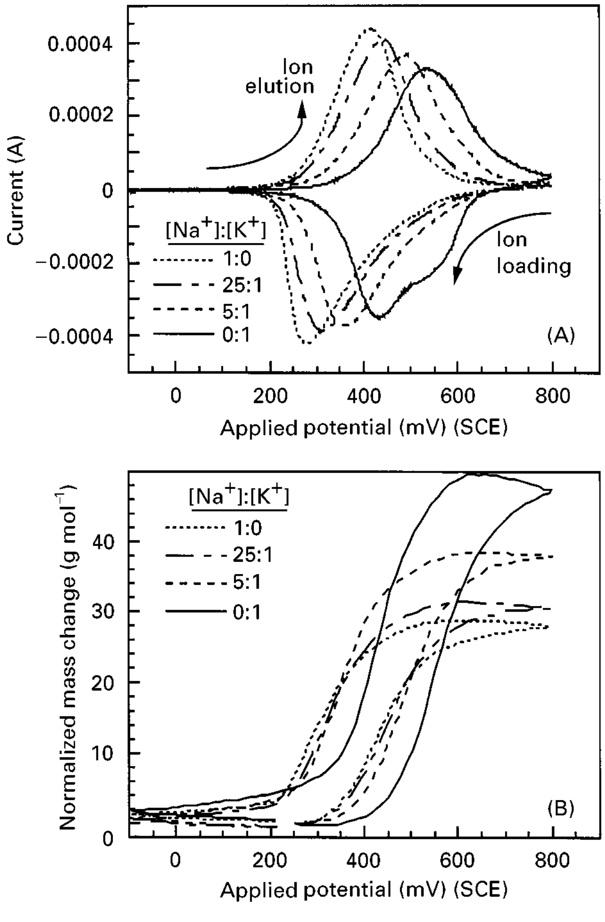

**Figure 8** EQCM results for a series of 0.5 mol $L^{-1}$ $Na_2SO_4$ and 0.5 mol $L^{-1}$ $K_2SO_4$ solution mixtures demonstrating selectivity of a NiHCF film for $K^+$ over $Na^+$: (A) Cyclic voltammograms indicate sensitivity to $K^+$ in solutions > 25 times more concentrated in $Na^+$; and (B) QCM mass data, normalized by the ion-loading capacity and converted to units of apparent molar weight, indicate greater mass changes as solutions become more concentrated in $K^+$ and relatively more $K^+$ is loaded into the film. (Adapted, with permission from Rassat *et al.* (1999), Elsevier Science.)

**Table 1** Apparent molar masses and separation factors in mixtures of 0.5 mol $L^{-1}$ sodium and potassium sulfate solutions. (Adapted, with permission from Rassat *et al.* (1999), Elsevier Science)

| *Solution* $x_{Na} : x_K$ | *Experiment 1* | | *Experiment 2* | | *Experiment 3* | |
|---|---|---|---|---|---|---|
| | *M′ (g mol⁻¹)* | $\alpha_{Na}^{K}$ | *M′ (g mol⁻¹)* | $\alpha_{Na}^{K}$ | *M′ (g mol⁻¹)* | $\alpha_{Na}^{K}$ |
| 1 : 0 | 29.0 ± 0.5 | | 25.3 ± 0.4 | | 22.8 ± 0.4 | |
| 25 : 1 | 31.7 ± 0.5 | 3.8 ± 1.1 | 30.2 ± 0.6 | 5.3 ± 0.8 | 28.4 ± 0.4 | 5.9 ± 0.7 |
| 10 : 1 | 35.4 ± 0.5 | 4.6 ± 0.6 | 35.2 ± 0.6 | 5.6 ± 0.5 | 32.7 ± 0.5 | 5.1 ± 0.4 |
| 5 : 1 | 39.2 ± 0.6 | 5.0 ± 0.7 | 39.4 ± 0.6 | 5.2 ± 0.5 | 36.9 ± 0.6 | 4.6 ± 0.4 |
| 0 : 1 | 49.4 ± 0.9 | | 53.0 ± 0.9 | | 52.3 ± 0.8 | |

the reversibility of the cation uptake (negative currents) and elution (positive currents). In addition, the area between the abscissa and either the negative or positive currents is proportional to the net ionic loading. Combined with the apparent molar weights shown in **Figure** 8(B), separation factors ranging from 3.8 to 5.9 were calculated (see **Table 1**). In addition to providing quantitative estimates of the separation factors, **Figure** 8(A) and (B) qualitatively show the preference of $K^+$ over $Na^+$. As the mixtures become more concentrated in $K^+$, the peaks shift to higher potential, more in line with that of pure $K_2SO_4$ solution. Even in solutions five times more concentrated in $Na^+$, the peaks shift substantially toward those for pure $K_2SO_4$ solution, indicating the relative selectivity of NiHCF for $K^+$. The shift towards higher apparent molecular weights in the mixtures also indicates the preference for $K^+$.

Bulk-contact tests of NiHCF, a more direct measure of selectivity, resulted in separation factors ranging from 14 to 24. Representative experimental details and results are shown in **Table 2**. In all the tests shown in Table 2, the $Na^+ : K^+$ molar concentration ratio was ~12, which is the approximate ratio of the ions in pulp mill application. The amount of $K^+$ taken up by the NiHCF without any applied potential (IX mode, eqn [3]) was determined from the total solution volume and the difference in $K^+$ concentration before and after contact. The separation factor, $\alpha_{Na}^{K}$, determined by this bulk-contact method, is very sensitive to the total capacity value. Since there are more uncertainties in determining the total capacity for the foam electrodes (in comparison to the small planar EQCM electrodes), the variability and uncertainty of bulk-contact separation factors obtained are greater. Despite the uncertainties associated with the total capacity, the batch-contact tests are in agreement with the EQCM results in that NiHCF materials are selective for $K^+$ over $Na^+$. The reason for the difference in the magnitude of the separation factors determined by the two techniques is presently unclear. Three possibilities are (1) differences in NiHCF film preparations resulting from differences in the electrode substrate on which they were deposited, (2) differences in solution ionic strengths (~1 mol $L^{-1}$ alkali for EQCM and < 0.1 mol $L^{-1}$ alkali for bulk contacting), and (3) the potential was applied to NiHCF in the EQCM experiments but not in the bulk-contact tests.

**Table 2** NiHCF bulk-contact separation factors and experimental conditions. (NiHCF-coated circular disc electrodes ~5-cm diameter by ~0.6-cm thick, 80 pores inch$^{-1}$ porosity, and ~60 cm$^2$ cm$^{-3}$ specific volume contacted with 18 mL of mixed ion solution)

| *Test* | *[K⁺] (mM)* | | *[Na⁺] (mM)* | | *Capacity (C)* | $\alpha_{Na}^{K}$ |
|---|---|---|---|---|---|---|
| | *Initial* | *Final* | *Initial* | *Final* | | |
| 1 | 2.19 | 1.30 | 28.0 | 29.1 | 2.06 | 14 |
| 2 | 0.97 | 0.30 | 13.0 | 13.7 | 2.31 | 15 |
| 3 | 4.81 | 3.44 | 56.8 | 54.1 | 1.97 | 24 |

*Cesium separation* The radioactive isotope $^{137}Cs$, a fission product of nuclear fuel processing and corrosion of fuel rods in commercial nuclear reactors, is a trace component of several process and waste streams in the nuclear industry. Because of the strong affinity of NiHCF for $Cs^+$, separation of this ion by EIX/EaIX is ideal. **Figure** 9(A) and (B) show the EQCM results for dilute $Cs^+$ in competition with excess $Na^+$. The experiments are analogous to those described for $K^+$ separation above, but the shifts toward pure $Cs^+$ solutions observed in the mixtures are more pronounced.

**Table 3** summarizes the apparent molar masses and separation factors $\alpha_{Na}^{Cs}$ for a series of $Na^+ : Cs^+$ mixtures. The separation factors range from 178 to 593, clearly demonstrating the enhanced selectivity of NiHCF for $Cs^+$ relative to $Na^+$ and $K^+$ (compare to **Table 1**). Neglecting the results for the 81 $Na^+ : 1\ Cs^+$ mixture, which had a higher estimated uncertainty, there appears to be a trend of increasing $Cs^+$ selectivity with decreasing $Cs^+$ concentration.

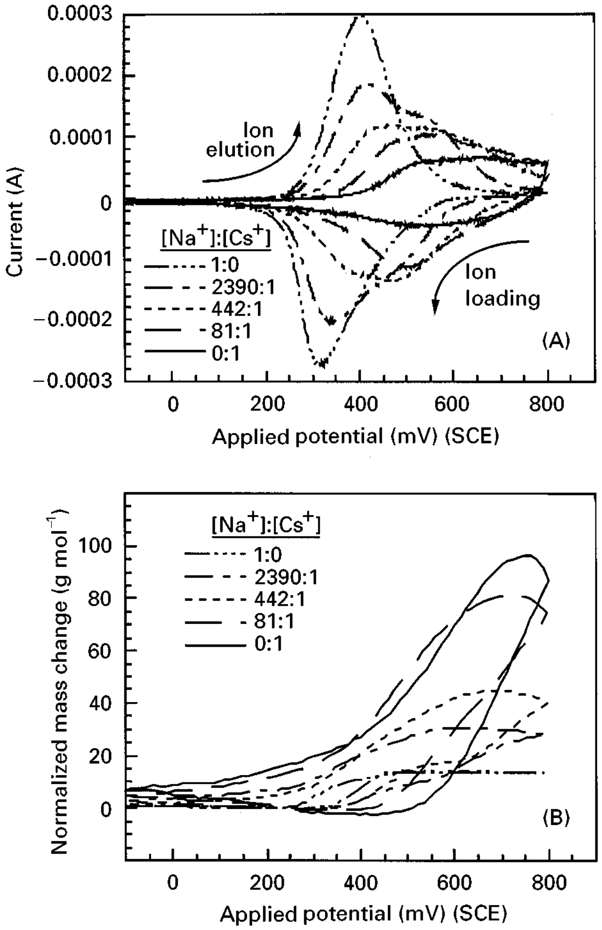

**Figure 9** EQCM results for a series of 1.0 mol L$^{-1}$ NaNO$_3$ and 1.0 mol L$^{-1}$ CsNO$_3$ solution mixtures demonstrating selectivity of NiHCF film for Cs$^+$ over Na$^+$: (A) cyclic voltammograms indicate sensitivity to Cs$^+$ in solutions ~2400 times more concentrated in Na$^+$; and (B) QCM mass data, normalized by the ion-loading capacity and converted to units of apparent molar weight, indicate greater mass changes as solutions become more concentrated in Cs$^+$ and relatively more Cs$^+$ is loaded into the film. (Adapted, with permission from Rassat *et al.* (1999), Elsevier Science.)

In the limited range of K$^+$ and Na$^+$ mixtures tested, such a trend was not detected.

Flow-through EIX/EaIX experiments demonstrate the regenerability of the EaIX material without the use of highly oxidizing solutions. Breakthrough curves for a 0.2-ppm Cs$^+$ feed stream are shown in **Figure 10**. Here, the EIX/EaIX system was operated in the conventional IX mode in the uptake cycle. The breakthrough curve for the first flow test shows that the breakthrough point (where the concentration of Cs$^+$ in the effluent stream is one-half the feed concentration) occurs after ~110 bed volumes were passed in the first flow test. In subsequent flow tests, each following regeneration of the NiHCF electrodes, the breakthrough capacity was reduced to ~40 bed volumes and the breakthrough profiles were consistent.

**Table 3** Apparent molar masses and separation factors in mixtures of 1.0 mol L$^{-1}$ sodium and cesium nitrate solutions. Rassat *et al.* (1999), courtesy of Elsevier Scientific.

| *Solution* $x_{Na}$ : $x_{Cs}$ | *M′ (g mol$^{-1}$)* | $\alpha^{Cs}_{Na}$ |
|---|---|---|
| 1 : 0 | 14.4 ± 0.2 | |
| *2390 : 1 | 31.1 ± 0.9 | 593 ± 40 |
| *910 : 1 | 37.3 ± 2.1 | 341 ± 36 |
| 442 : 1 | 46.1 ± 1.0 | 268 ± 15 |
| 155 : 1 | 59.3 ± 1.0 | 178 ± 12 |
| 81 : 1 | 83.0 ± 1.3 | 361 ± 60 |
| 0 : 1 | 98.4 ± 2.2 | |

*Gravimetric and/or electrochemical measurements not at steady state.

Regeneration cycles were carried out by potential cycling in a solution of sodium nitrate. The reasons for the diminished breakthrough volume after the first cycle are presently unclear. It is speculated that this is a ‘plugging’ issue. One hypothesis is that because of the great affinity of NiHCF for Cs$^+$ and strong binding in the cubic lattice, migration of Cs$^+$ to all sites within the film is hindered, and therefore, some Cs$^+$ are permanently bound in the NiHCF. The most noteworthy point is that regeneration of the EaIX material is reversible (starting with the second cycle) without the need for strong oxidiz-

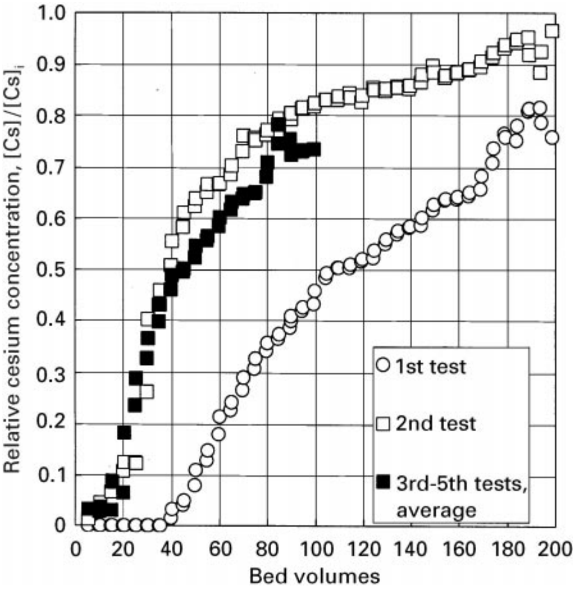

**Figure 10** Breakthrough curves for a feed stream of 0.2-ppm Cs in a EaIX bed consisting of eight NiHCF-coated porous nickel foam electrodes operated in IX mode. The electrodes were regenerated electrochemically in concentrated NaNO$_3$ solution between each test. Experimental conditions: 80 pores inch$^{-1}$ or ~60 cm$^2$ cm$^{-3}$ nickel foam; CsNO$_3$ solution flowed at 24 mL min$^{-1}$; bed volume of ~39 mL; and maximum ion capacity ~2.0 C.

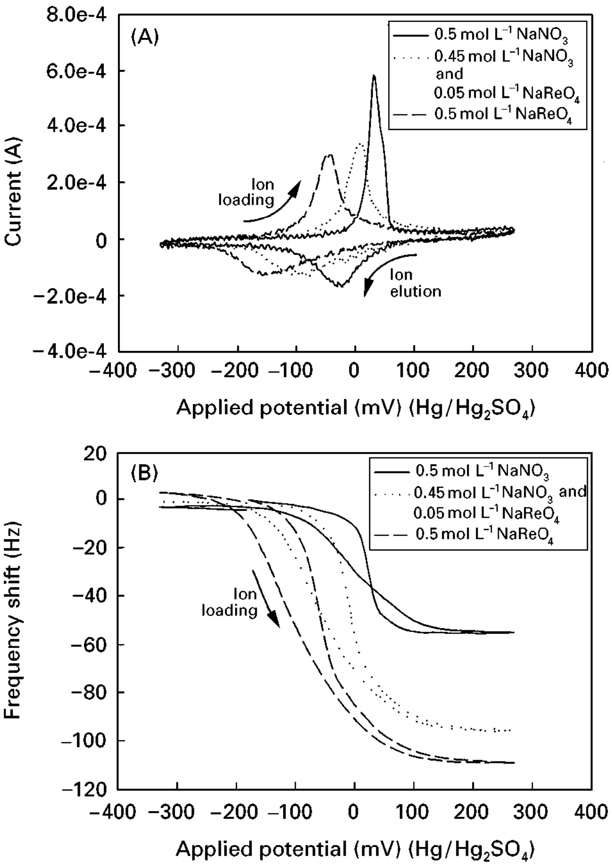

**Figure 11** EQCM results for a series of 0.5 mol $L^{-1}$ $NaNO_3$ and 0.5 mol $L^{-1}$ $NaReO_4$ solution mixtures demonstrating selectivity of a PVF film for $ReO_4^-$ over $NO_3^-$: (A) cyclic voltammograms indicate sensitivity to $ReO_4^-$ in solutions nine times more concentrated in $NO_3^-$; and (B) QCM frequency shifts indicate greater mass changes as solutions become more concentrated in $ReO_4^-$ and relatively more $ReO_4^-$ is loaded into the film.

ing solutions (i.e., 8 mol $L^{-1}$ nitric acid used by previous researchers).

### Polyvinylferrocene

Polyvinylferrocene $[-(Fe^{II/III}(C_5H_5)(C_5H_4CH_2CH_2)^{1+/0})-]$, or PVF, is a well-studied organometallic polymer. In contrast to NiHCF, oxidation of PVF to the 1+ state requires the uptake of anions to maintain electroneutrality (see **Figure** 3C), making PVF a suitable anionic EaIX material candidate. Recently, the preference of PVF for perrhenate ($ReO_4^-$) over nitrate ($NO_3^-$) was demonstrated. The uptake and elution reactions are analogues to that shown in eqn [2]. As with NiHCF, PVF can also be used as conventional IX materials. Specifically, the $NO_3^-$ in $(PVF^+)(NO_3^-)$ is readily exchanged for $ReO_4^-$. Other possible applications for PVF include the extraction of arsenates and chromates.

PVF has been prepared through chemical, electrochemical, and plasma polymerization. Both plasma and electrochemical polymerizations should be suitable for depositing PVF within porous substrate.

**Applications** The preference of polyvinylferrocene for perrhenate (nonradioactive chemical analogue of pertechnetate) anions over nitrate anions has been demonstrated. Nitrates are the main competing anions for separation of pertechnetate in radioactive tank wastes. The current and the frequency responses of a PVF-coated EQCM as a function of a cyclic potential scan are shown in **Figure 11**(A) and (B). (The frequency response is shown rather than the normalized mass change because of complications due to the less rigid PVF films compared to the NiHCF films.) The more negative (cathodic) potential peaks observed in the pure $ReO_4^-$ solution and in the mixture, compared to a pure $NO_3^-$ solution, indicate the preference of $ReO_4^-$ over $NO_3^-$. In addition, the frequency responses shown in **Figure 11**(B) indicate a substantial mass gained in the PVF film upon oxidation in a solution containing both $NO_3^-$ and $ReO_4^-$, more mass than can be attributed to $NO_3^-$ alone. This supports the contention that $ReO_4^-$ ions (which are heavier than $NO_3^-$) are preferentially taken up by the PVF. The data shown in **Figure 11**(A) and (B) correspond to a separation factor of 30.

## Future Developments

EIX processes (using EaIX and nonelectroactive IX materials) are very promising methods for ion separation due to the potential savings resulting from minimization of secondary waste generation. Better understanding of system performance through large-scale (e.g., pilot-scale) studies still needs to be carried out as well as the development of new materials. For example, EaIX materials selective for strontium ($Sr^{2+}$) are of interest to the nuclear industry. Calcium ($Ca^{2+}$) selective materials are valuable for preventing scale formation in many industries. Finally, effective removal of $NO_3^-$ and arsenate anions is critical for safe drinking water.

*See also:* **II/Ion Exchange:** Historical Development; Inorganic Ion Exchangers; Organic Ion Exchangers; Theory of Ion Exchange.

## Further Reading

Genders D and Weinberg NL (eds) (1992) *Electrochemistry for a Cleaner Environment*. East Amherst, NY: The Electrosynthesis Company Inc.

Krishnan R and Ibanez J (1997) *Environmental Electrochemistry. Fundamentals and Applications in Pollution Abatement*. San Diego: Academic Press.

Lewis TM, Wallace GG and Smyth MR (1999) Electrofunctional polymers: their role in the development of new analytical systems. *Analyst* 124: 213.

Rassat SD, Sukamto JH, Orth RJ, Lilga MA and Hallen RT (1999) Development of an electrically switched ion exchange process for selective ion separations. *Separation and Purification Technology* 15: 207.

Rose TL, Rudd E, Murphy O and Conway BE (eds) (1994) *Proceedings of the Symposium on Water Purification by Photocatalytic, Photoelectrochemical, and Electrochemical Processes*. Pennington, NJ: The Electrochemical Society.

Tsuda T (ed.) (1995) *Electric Field Applications in Chromatography, Industrial and Chemical Processes*. Weinheim: VCH.

# ELECTRODIALYSIS: ION EXCHANGE

**G. Pourcelly**, Laboratory of Materials and Membrane Processes, Montpellier, France

## Introduction

Separations with synthetic membranes have become increasingly important; today membrane processes are used in a wide range of applications and their number will certainly increase.

A membrane is a permselective polymer, inorganic or metal phase which restricts the motion of certain species. By controlling the relative rates of transport of various species it gives one product depleted in certain components and a second product concentrated in these components. Membrane performance is characterized by two terms: flux and selectivity. Flux (or permeation rate) is the volumetric mass flow of fluid passing through the membrane per unit area of membrane and unit mass time. Selectivity is a measure of the relative permeation rates of different components through the membrane.

Processes may be classified according to the driving force used: (1) a pressure differential leads to micro-, ultra- and nanofiltration and reverse osmosis; (2) a concentration difference across the membrane leads to diffusion of a species between two solutions (dialysis); (3) a potential field applied to an ion exchange membrane leads to migration of ions through the membrane (electrodialysis, membrane electrolysis and electrochemical devices). This last category and more specifically electrodialysis is the subject of this section. This electrically driven process uses ion exchange membranes, a description of which follows.

## Ion Exchange Membranes

Electrodialysis (ED) uses membranes containing fixed charged groups attached to the polymer backbone of its membrane. Two kinds of ion exchange membranes (IEMs) are used in ED: *homopolar membranes* bearing fixed charges of the same sign and *bipolar membranes* bearing positive and negative fixed charges located on each side of the membrane.

IEMs are sheet-shaped materials through which a selective ion transport can be established under a driving force, generally an electric field and/or a concentration gradient.

Most of them are of a polymeric nature. They are constituted of reticulated macromolecular chains forming a tridimensional structure. In this network, ionizable functionalized groups are attached to the polymeric matrix and are at the origin of the membrane selectivity. For example cation exchange membranes (CEMs) contain fixed negative charges and mobile cations which can be exchanged with other cations present in an external phase in contact with the membrane. The ions balancing the fixed exchange sites are called counterions. The concentration of counterions is relatively high and therefore counterions carry most of the electric current through the membrane. The fixed charges attached to the polymer matrix repel ions of the same charges (co-ions). This exclusion, which is a result of electrostatic repulsion, is called Donnan exclusion, named after F. G. Donnan, who first reported the phenomenon in 1910. However, as the membrane selectivity is never ideal, the membrane material can be penetrated by a non-negligible amount of electrolyte. A schematic structure of such a homopolar CEM is depicted in **Figure 1**. Under an applied electric field, the CEM bearing sulfonic exchange groups ($-SO_3^-$) mainly allows the transport of counterions.

A bipolar membrane (BPM) is composed of two layers of ion exchangers joined by a hydrophilic junction. The diffusion of water from both sides of the BPM allows it to dissociate under the electrical field to generate protons and hydroxyl ions, which further migrate from the junction layer through the cation exchange and anion exchange layers of the bipolar membrane. Generally, the cation exchange groups are sulfonic and the anions are trimethyl quaternary