Electrochemically assisted metal uptake by cation exchange based chemically modified electrodes

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Carbon paste electrodes containing powdered cation exchange resin (Amberlite IR120) have been fabricated and applied to the uptake of copper ion in aqueous solution. The copper uptake reaction was carried out at open circuit and at different cathodic potentials. Linear potential sweep voltammetry was used to quantify the accumulated ions. With the application of an optimum cathodic potential, the amount of copper absorbed increased four to nine-fold in comparison with similar uptake at open circuit conditions. The effect of different resin size employed in the chemically modified electrodes, on the sensitivity of the electrode response was also studied as a function of peak current.

1. Introduction

In recent years, ion exchange technology has become one of the most widely employed techniques in the treatment of industrial effluents, process water demineralization and in the manufacturing of ultra-pure water for electronic industries. There are many reasons for this widespread use, foremost of which are the possibility of resin regeneration and the ease of process operation. A major drawback of the conventional ion exchanger is the difficulty in altering the inherent rate of chemical absorption. One possible way of overcoming this is to incorporate ion exchanger into an electrode. This has resulted in the development of chemically modified electrodes [1-3].

There have been new developments in the ion exchangers usage, in the form of ion exchange membrane, electrodialysis, powdered ion exchange resins, and electrochemical ion exchange reactions for waste water treatment. Much interest has been focused recently on electrochemical ion exchange over conventional ion exchange process [4-6]. In electrochemical ion exchange, an electrode is chemically modified by incorporating an ion exchange material into the electrode structure. Ion exchange reactions are controlled by application of an electrode potential between the composite ion exchange working electrode and the counter electrode. Elution or regeneration of the exhausted ion exchanger is achieved by simple polarity reversal. Thus this process can eliminate the use of regenerative chemicals, furthermore it is also possible to reduce the volume of waste produced during regeneration.

Electrochemical ion exchange has good potential for water-softening (Ca, Mg removal), industrial effluent processing (Pb, Cd, Hg, and other heavy metals removal), and precious metal recovery (Ag, Au). However, so far the research work has been focused more on removal of radioactive ions from nuclear waste [4, 5]. Waste waters from metal processing industries (printed circuit board and plating baths) contain large amount of copper ions. Ion exchange is commonly employed for metal recovery at low concentration [7]. The present study was carried out on electrochemical absorption of copper using powdered Amberlite IR120 hydrogen from cation exchange resin added to a mixture of graphite powder and binder. The resulting electrode is termed chemically modified carbon paste electrode (CMCPE).

The CMCPE fabrication method allows flexibility in different ion exchanger loading and convenient renewal of the surface. These attractive features permit repetitive measurements. By using electrodes containing different resin loading and different ratios of various components, the optimum electrode composition can be obtained. These data can thus be used to compare and classify other commercially available cation exchangers.

2. Experimental details

2.1. Apparatus and reagents

Three 50 ml cells were used, namely, the preconcentration cell containing the copper solution, the measurement cell containing the supporting electrolyte solution, and the cleaning cell containing 10% hydrochloric acid. Copper(II) stock solution of 0.158 M was prepared by dissolving copper sulphate in deionized water; working standard solutions were prepared by dilution as required.

The supporting electrolyte was 0.5 M potassium nitrate solution. The electrode cleaning solution was 10% hydrochloric acid. All reagents were of analytical grade. Amberlite strong cation sulphonated acid resin IR120 in the H^+ form was obtained from

Rohm and Haas. Linear voltammograms were recorded with a EG&G Model 362. The experimental setting for the scan rate was $20\,mV\,s^{-1}$. A platinum foil auxiliary electrode and a saturated calomel reference electrode (SCE) were used for all the voltammetric experiments. All the potentials reported in this paper were referred to the SCE.

2.2. Electrode preparation

The CMCPEs were prepared by mixing in a mortar 1.5 g of graphite powder (Johnson Matthey, 99% pure, < 325 mesh or 45 μm) with 1.0 g of commercial vaseline (Chasebrough Ponds) and 0.06 to 1.05 g of IR120 wet protonated resin (Rohm & Haas, 350–850 μm), which corresponds to 2.0–35.0 wt % resin electrode. Before the above mixing, the resin beads were powdered to a size in the range 75–150 μm and cleaned in hydrochloric acid. Subsequently, after the mixing, the carbon paste was packed into a syringe (2 mm i.d., 4 mm o.d.), and a nickel wire was inserted into the syringe for electrical contact.

2.3. Procedure

The study was conducted to characterize the uptake of copper(II) with CMCPE of 2 to 35 wt % resin, with and without the application of cathodic potential during the preconcentration step (i.e. metal uptake). The procedure consisted of three main steps, namely, preconcentration, voltammetric measurement and electrode cleaning [1–3].

To ascertain the background current levels, a cyclic voltammogram of the deaerated supporting electrolyte (0.5 M KNO_3) was first obtained. Then the CMCPE was immersed in the preconcentration cell containing the copper ions of known concentration for a fixed period of 2 min at open circuit conditions and at various fixed cathodic potential from −0.5 to −3.0 V vs SCE, at a fixed magnetic stirrer setting. Then the electrode was rinsed with deionized water and placed in another cell containing the supporting

Fig. 1. Linear voltammograms obtained with CMCPE of 10% resin, in a copper solution of 200 p.p.m. Contact time: 2 min; scan rate: $20\,mV\,s^{-1}$. (a) With an applied voltage of −0.5 V, (b) without applied voltage, (c) background scan.

electrolyte. The potential of the working electrode was scanned from −0.5 to +1.50 V vs SCE, and the resulting peak current was measured (Fig. 1). Different scan rates were tried in order to find the best peak response with respect to the background current. The scan rate of $20\,mV\,s^{-1}$ [3] was found to yield a well defined stripping peak.
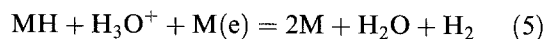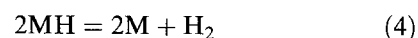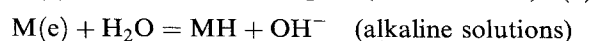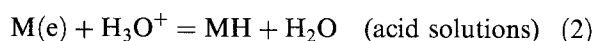
Once the scan was completed, a thin layer of the electrode material on the surface was physically removed and the electrode with new surface was reconditioned in a 10% hydrochloric acid solution for 10 min, the solution was stirred by a magnetic stirrer. The electrode was then rinsed thoroughly with deionized water and the supporting electrolyte. The removal of copper from the electrode was monitored by the same scanning procedure as in the voltammetric measurement step. The residual current should be of the same order as the initial scan, otherwise, the cleaning step should be repeated.

4. Results and discussion

4.1. Effect of cathodic potential on copper uptake

During the preconcentration step, the applied cathodic potential was varied, in order to select the optimum potential for the absorption of copper. When the cathodic potential applied on the working electrode is low, there will be no enhancement of copper uptake, as in the case of open circuit condition i.e. no potential applied on the working electrode. At a very high working electrode potential, hydrogen evolution will occur. This may either enhance or interfere with the copper absorption at the electrode according to the degree of hydrogen evolution. Figure 2 shows the individual stripping peak current data obtained during the preconcentration step, when the applied cathodic potential was set at 0, −0.5, −1.0, −1.5, −2.0, −2.5 and −3.0 V vs SCE. It can be seen that the optimum potential for the peak current is around −0.5 V vs SCE. The peak currents decreased as the applied potential increased from the peak potential to −3.0 V vs SCE. At the applied potential between −2.5 to −3.0 V vs SCE, the peak currents measured were either the same as the zero volt condition or even lower, as in the case of the 2% resin electrode.

The following reactions are known to occur during the preconcentration step when a cathodic potential is applied to the CMCPE, in a copper solution.

$$2RSO_3H + Cu^{2+} = (RSO_3)_2Cu + 2H^+ \qquad (1)$$

$$M(e) + H_3O^+ = MH + H_2O \quad \text{(acid solutions)} \qquad (2)$$

$$M(e) + H_2O = MH + OH^- \quad \text{(alkaline solutions)} \qquad (3)$$

$$2MH = 2M + H_2 \qquad (4)$$

$$MH + H_3O^+ + M(e) = 2M + H_2O + H_2 \qquad (5)$$

Equation 1 depicts the uptake of copper ions by the ion exchanger. Equations 2 and 3 describe the reduc-
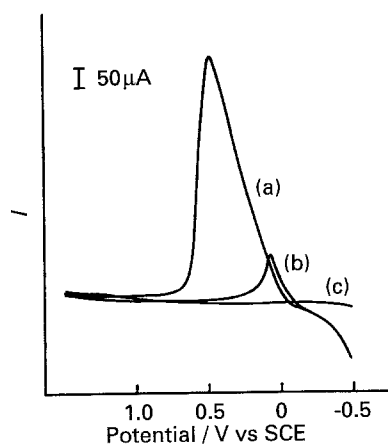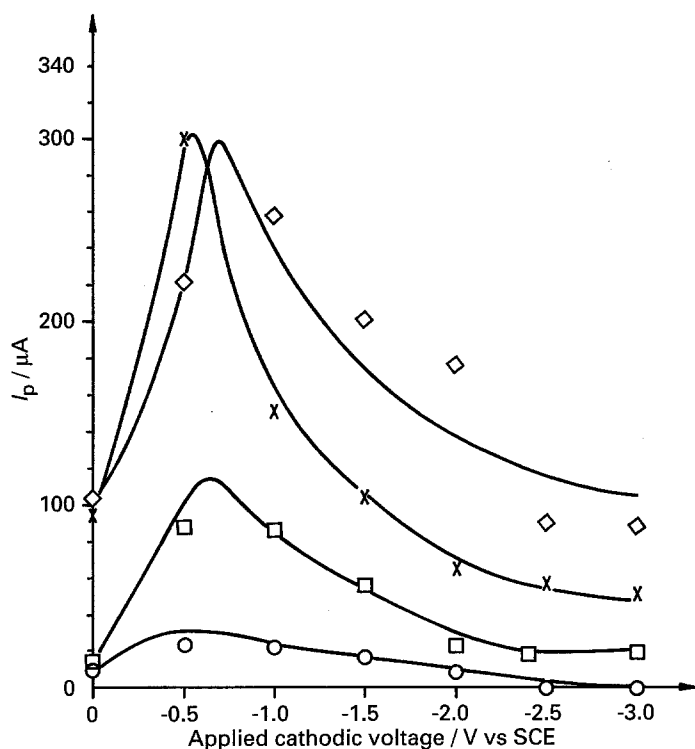
Fig. 2. Effect of applied cathodic potential on peak current. Conditions: 2 min contact time from a 200 p.p.m. $(3.1 \times 10^{-4} \text{ M})$ copper solution; scan rate 20 mV s^{-1}. Resin: (O) 2%, (□) 10%, (×) 25% and (◇) 35%.

tion of water in acid and alkaline media on the electrode M [8]. The adsorbed hydrogen ions i.e. MH, are desorbed via either Equation 4 or 5. Thus, the pertinent hydrogen evolution path is a function of electrode material, the operating pH and the potential of the working electrode. Figure 3 is obtained from linear scan voltammograms of different weight % resin in the CMCPE electrodes. At −1.5 V and beyond, it can be seen that the residual current increases significantly, while at lower voltage the residual current is small. It can be deduced that the main component of the residual current is caused by hydrogen evolution. Thus the reduction of the stripping peak current, which increases from the peak potential (Fig. 2), is mainly due to the increase of hydrogen evolution as the applied voltage increases during the preconcentration step.

Besides the hydrogen evolution reactions described above, it is also suggested [9] that the hydroxyl ions from Equation 3 deprotonate the weak cation exchanger, as shown in Equation 6, and the liberated

carboxylic ions then undergo an exchange reaction as shown in Equation 7. Thus the reactions in Equations 6 and 7 enhance the uptake of cation ions (M^+).

$$RCOOH + OH^- = RCOO^- + H_2O \tag{6}$$

$$RCOO^- + M^+ = RCOOM \tag{7}$$

$$RSO_3H + OH^- = RSO_3^- + H_2O \tag{8}$$

$$RSO_3^- + M^+ = RSO_3M \tag{9}$$

Equations 8 and 9 depict the plausible similar reactions when strong acid cation exchangers are used. Under only slight acidic to neutral conditions, which is true for the present system i.e. $CuSO_4$ pH 5; both Equations 2 and 3 may be applied. From the results obtained (Fig. 2), it seems that the effect of hydrogen evolution on the peak current is potential dependent. At around −0.5 V vs SCE, hydrogen evolution enhances the uptake of copper, while at the much higher potentials above −1.5 V vs SCE, there is excessive hydrogen evolution. In this case, a layer of very small hydrogen gas bubbles may form on the electrode surface, hindering the diffusion of copper ions to the electrode surface and thus decreasing the adsorption efficiency.

During the measurement phase, the potential on the working electrode was set at −0.5 V vs SCE, and was then scanned to +1.5 V vs SCE. At −0.5 V vs SCE, the cations (i.e. copper) retained by the ion exchanger are reduced (i.e. Equations 10 and 11). The reduced material is reoxidized during the anodic scan (Equation 12); a copper stripping peak is thus formed (Fig. 1).

$$RSO_3M + e^- = RSO_3^- + M^0 \tag{10}$$

$$RSO_3^- + H^+ = RSO_3H \tag{11}$$
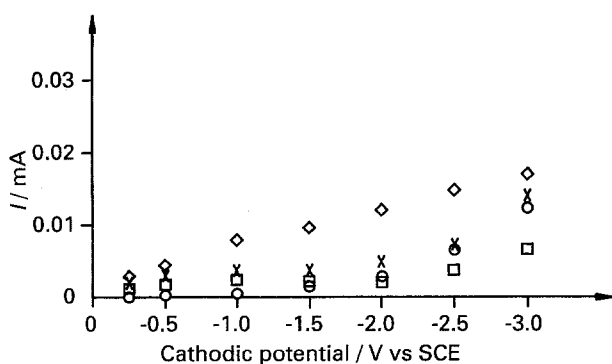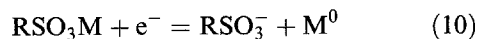
$$M^0 - e^- = M^+ \tag{12}$$

Fig. 3. Linear scan voltammograms obtained with different wt % resin in CMCPE electrodes. Conditions: diluted sulphuric acid solution with pH 5; scan rate 10 mV s^{-1}. Resin: (O) 2%, (□) 10%, (×) 25% and (◇) 35%.

From Fig. 1, it can be seen that there is an anodic shift of peak current potential for copper oxidation when a cathodic potential is applied to the CMCPE during the preconcentration step. Under open circuit conditions, as there is less copper being retained by the ion exchanger, copper ions are reduced and oxidized near the graphite surface. When −0.5 V vs SCE was applied to the working electrode during the preconcentration step, there was a significant increase in the diffusion of copper ions into the working electrode and the uptake of copper ions by the resin was enhanced. After the occurrence of copper reduction, due to the high concentration of copper in the electrode mixture, some copper invariably deposits on other copper particles adjacent to the graphite surface. Thus, the oxidation reaction on copper occurs at different surfaces; this resulted in the shift of potential at the oxidation peak current. Another contributing factor could be due to the larger quantity of copper ions being oxidized in Fig. 1(a) than in Fig. 1(b), and hence leading to an apparent shift in peak potential.

4.2. Effect of copper concentration on peak current

The effect of copper concentration on peak current was first investigated under open circuit conditions. Figure 4 illustrates the average peak current data as a function of increased copper concentration from 200 to 10 000 p.p.m. (0.0032 to 0.158 M). The average peak current in general increases with increasing copper concentration up to 1200 p.p.m. (0.019 M), except for the 2% resin electrode. For the 10% electrode, the current reaches a plateau beyond this concentration, this indicates that the active surface sites are saturated at around 1200 p.p.m. in the present experimental conditions. The onset of saturation means that all the active sites used to collect the anolyte i.e. copper ions, have been occupied; after this point the analytical signal i.e. peak cur-

rent, will not increase in spite of increasing the anolyte concentration. For the 25% electrode at 1200 p.p.m. saturation did not occur and the signals continue to increase even after 1200 p.p.m., but the gradient obtained was of a lower value. As for the 35% electrode the linear voltammetry obtained were mostly in the form of double peaks, and there was also a significant increase in the residual current, due to the increase in electrode resistance as a result of the increase in resin content [10]. The occurrence of the double peaks cannot be explained at present. Thus no peak current was recorded for copper solution higher than 800 p.p.m. for the 35% electrode.

The gradients of the peak currents as a function of copper concentration up to 1200 p.p.m. for the 10, 25 and 35% electrodes are found to be 0.1913, 0.2276 and 0.2990 μA (p.p.m.)$^{-1}$, respectively. Thus, the peak current increases with increasing resin content in the CMCPE. For copper concentrations of 1200 p.p.m. and above, the gradient for the 25% electrode was reduced from 0.2276 to 0.0245, this indicates the concentration range where transition occurs. In the transition phase, the linear relation between the peak current and the solution concentration is slowly changed to a saturation condition. It is thus expected that the saturation plateau will be reached if the copper concentration in the solution increases further.

Figure 5 depicts the average peak current obtained with an applied cathodic voltage of −0.5 V vs SCE during the preconcentration stage. The data presented can be evaluated as follows:
(i) In all cases, there is a significant enhancement in the plateau current when a potential of −0.5 V vs SCE is applied during preconcentration.
(ii) For the low resin content electrode (i.e. 2%), the plateau current occurs at around 400 p.p.m. copper solution.
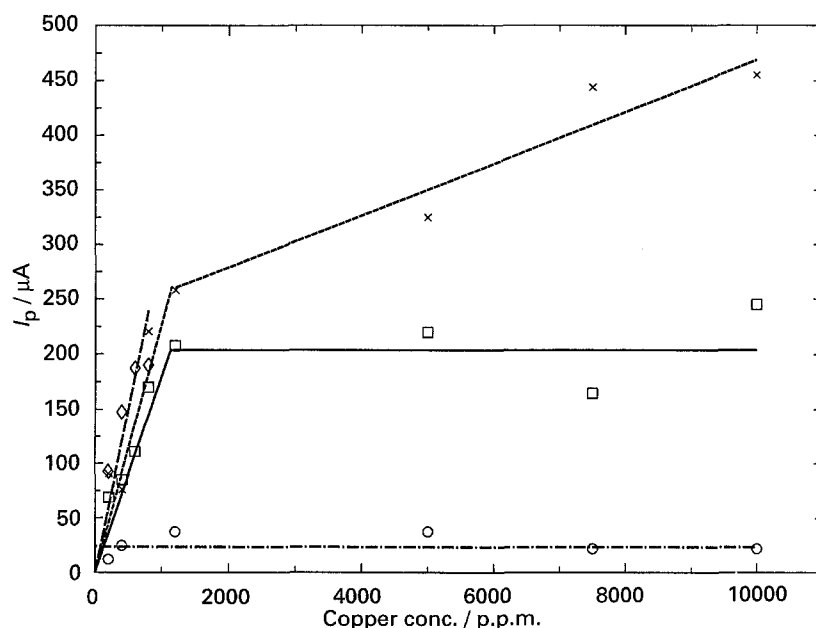(iii) Up to 1200 p.p.m. of copper solution, the peak current values for all the remaining electrodes are

Fig. 4. Effect of copper solution concentration on peak current, with no applied voltage, scan rate 20 mV s^{-1}. Resin: (O) — · — 2%, (□) —— 10%, (×) — — − 25% and (◇) — — 35%.
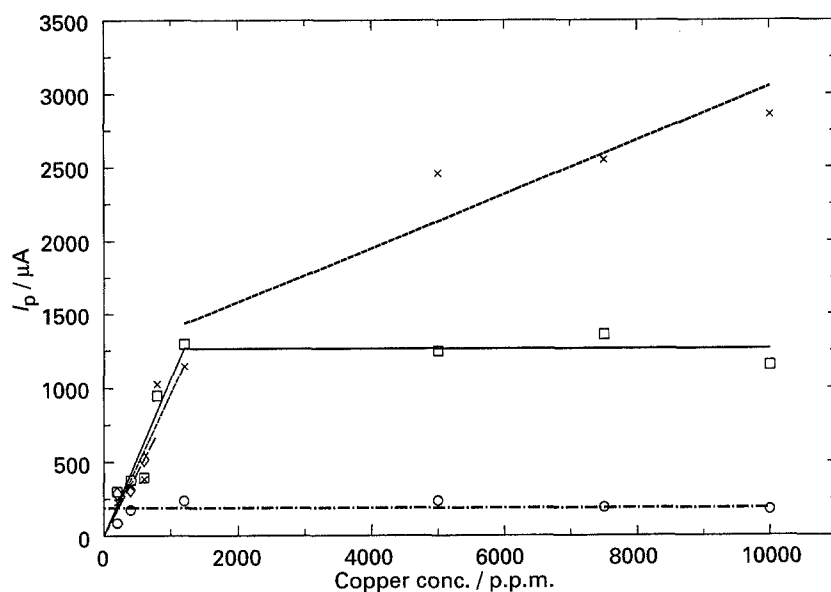
Fig. 5. Effect of copper solution concentration on peak current, with an applied voltage of $-0.5\,V$ vs SCE to the CMCPEs; scan rate $20\,mV\,s^{-1}$. Resin: (○) $-\cdot-\cdot$ 2%, (□) —— 10%, (×) $---$ 25% and (◇) $--$ 35%.

mostly clustered together, the gradients are found to be 1.05, 0.96 and 0.87 for 10, 25 and 35% resin electrodes, respectively. In view of some fluctuation in the data measured, the calculated average gradients is $0.96 \pm 0.09\,\mu A\,(p.p.m.)^{-1}$.

(iv) For 10% resin electrode at copper concentration higher than 1200 p.p.m., there is no detectable increase in the peak current as the concentration increases from 1200 p.p.m. to 10 000 p.p.m. This indicates that the CMCPE is saturated at around 1200 p.p.m.

(v) For the 25% resin electrode, the gradient decreases from 0.96 to 0.18 in the copper concentration rate 1200 to 10 000 p.p.m. This situation is similar to that at open circuit conditions, where a transition phase was observed before the onset of saturation.

Table 1 compares the saturated peak currents obtained under open circuit (I_{p1}) and applied cathodic potential of $-0.5\,V$ (I_{p2}) at saturation. It can be seen that with the application of an optimum cathodic potential to the CMCPE, the amount of copper absorbed increased four to nine-fold at the saturation condition, under the influence of electrostatic migration. This significant enhancement in the uptake of metal ions in a solution has tremendous application in aqueous waste treatment. Further work is in progress in the direction of employing an anodic potential to desorb the attached ions from the CMCPEs; such an elution method, if successful, would significantly reduce the usage of regeneration chemicals and deionized water for backwashing in a normal ion exchange operation.

4.3. Effect of resin size on peak current

Figure 6 shows the dependence of peak currents on resin size used in the CMCPEs, under the conditions of open circuit and an applied voltage of $-0.5\,V$ vs SCE, in a 200 p.p.m. copper solution operating under the same procedures as before. In both conditions, CMCPEs with resin size in the range 75–150 μm recorded a much higher peak current than electrodes with resin size less than 75 μm or size in the range 150–315 μm. The electrode diameter was 2000 μm and the graphite powder was $< 45\,\mu$m. The effect of different resin size on the sensitivity of CMCPEs, expressed in terms of peak current in the present studies, has not been evaluated in similar work [1, 2, 9, 10].

It is known that by reducing the size of resin, the metal uptake reaction should be more rapid and there is a greater utilization of the exchange capacity. As a substantial portion of the total exchange capacity is located within the resin particle, diffusion becomes a controlling factor in practical ion
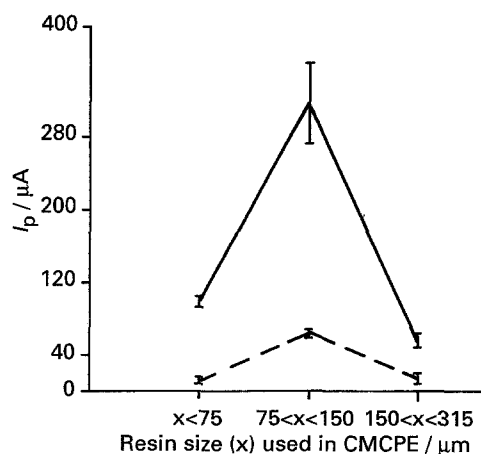
Table 1. Saturated peak current at different resin electrodes

Electrode/ wt % resin	Saturation Cu solution conc./ p.p.m.	Saturated peak current/μA		
		0 V, I_{p1}	−0.5 V, I_{p2}	I_{p2}/I_{p1}
2	1 200	20	190	9.5
10	1 200	204	1264	6.2
25	1 200	258	1142	4.4
25	10 000	470	3000	6.4

Fig. 6. Effect of resin size on peak current. Conditions: 200 p.p.m. copper solution, scan rate $20\,mV\,s^{-1}$, CMCPE with 10% resin. Dotted line: open circuit conditions; full line: applied $-0.5\,V$ vs SCE to the CMCPE.

exchange operation. It has been reported that the commercial ion exchange resins utilize only 50% of the ultimate exchange capacity [11]. Thus ultrafine resin smaller than 45 μm have been employed in condensate polishing for water/steam quality control in boilers for electricity generation [12]. The experimental results of CMCPE with resin size in the range 75–150 μm gives a higher sensitivity compared with data for resin size less than 75 μm or size in the range 150–315 μm. This indicates that the texture, physical and chemical properties of the resin have been altered and its activity has been reduced. A study on the total exchange capacity of different resin sizes was conducted. It was found that the total exchange capacities of the hydrogen form resins with sodium ions for uncrushed resin (i.e. sizes < 75 μm, 75–150 μm, 150–315 μm) were 4.43, 5.32, 9.29 and 5.22 m (equiv.) g^{-1} dry resin, respectively. These data show that the resin with dimensions in the range 75–150 μm yields a higher exchange capacity than the rest of the samples and thus increases the peak current response of the CMCPE (i.e. Fig. 6).

Ready made ultrafine ion exchange resin can be purchased from resin suppliers. These resins are widely employed in the field of chromatography. The resins are produced initially as extremely fine beads of 40 to 300 μm in size. They are generally uniform in texture and, unlike the powdered resin, which is obtained by grinding the usual bead resins, these chromatography resins are normally without any cracks. A comparison of the ready made powdered resin with that from grinding would be an interesting study.

Acknowledgements

References

[1] J. Wang, B. Greene and C. Morgan, Anal. Chim. Acta 158 (1984) 15.
[2] G. T. Cheek and R. F. Nelson, Anal. Lett. 5 (1978) 393.
[3] W. S. Wu, M. S. Uddin and H. Chi, Bull. Electrochem., (in press) 1994.
[4] N. J. Bridger, C. P. Jones and M. D. Neville, J. Chem. Tech. Biotechnol. 50 (1991) 469.
[5] P. M. Allen, N. J. Bridger, C. P. Jones, M. D. Neville and A. D. Turner, in 'Recent Developments in Ion Exchange', Vol. 2, (edited by P. A. Williams and M. J. Hudson), Elsevier, Barking, UK (1990) p. 213.
[6] R. J. W. Adams and J. Hudson, in 'Recent Developments in Ion Exchange, Vol. 2, (edited by P. A. Williams and M. J. Hudson), Elsevier, Barking, UK (1990) p. 231.
[7] C. J. Saieva, US Patent 4 652 352, 24 March 1987.
[8] J. O'M. Bockris and A. K. N. Reddy, 'Modern Electrochemistry', Vol. 2, Plenum Press, New York (1973).
[9] S. Evan, M. A. Accomazzo and J. E. Accomazzo, J. Electrochem. Soc. Vol. 116(2) (1969) 309.
[10] L. Hernandez, P. Hernandez, M. H. Blanco and M. Sanchez, Analyst 113 (1988) 41.
[11] J. H. Duff and J. A. Levendusky, Proc. Amer. Power Conference 26 (1962) 739.
[12] K. Dorfner (Ed.), 'Ion Exchange' Walter de Gruyter, Berlin and New York (1991) p. 791.