

As shown, the esterase preparation from porcine pancreas§ gave the highest selectivity among several enzymes which have been examined. It should be noted that this enzyme is distinct from porcine pancreatic cholesterol esterase which exhibited a lower degree of stereoselectivity ( $E = 5$ ).

Nonetheless, one valid argument may arise regarding the rate enhancement, *i.e.*, it may be caused by the electron-withdrawing nature of the methoxy moiety rather than the steric relaxation effect. To clarify this speculation, activated esters such as the *N,O*-bis(chloroacetyl) and *N,O*-bis(trichloroacetyl) derivatives **5** and **6**, respectively were also examined. Both compounds were similar to **2** with regard to energy-minimized conformation and degree of steric congestion (not shown). However, after being exposed to the enzymes, **5** and **6** did not show any sign of hydrolysis. This result thus confirmed the conclusion derived from our molecular-modelling study. In addition to **3**, several other

analogues have also been suggested as potential substrates, and are currently under investigation.

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§ Porcine pancreas acetone powder (Sigma, 10 g) was suspended in 30 ml of 50 mmol dm<sup>-3</sup> potassium phosphate buffer (pH 7.0), and subjected to homogenization. The tissue debris was removed by centrifugation at 12000 × g for 20 min, and the supernatant was applied to a DEAE-Sepharose CL-6B column (5 × 10 cm) equilibrated with 10 mmol dm<sup>-3</sup> potassium phosphate buffer (pH 7.0). The column was first washed with 360 ml of the equilibrating buffer, and then eluted with a linear gradient (600 ml) consisting of 0 to 0.5 mol dm<sup>-3</sup> NaCl in the same buffer. Fractions of 8 ml were collected. The esterase activity was assayed using *p*-nitrophenyl acetate as the substrate. Fractions 94 to 124, which contained the esterase, were collected, and the pooled solution was used directly for the enzymatic reaction. The synthetic utility of this enzyme is currently under investigation.

## Quasi-reversible Silver Zeolite Electrode Prepared by Photochemical Modification

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By linking 1 μm-size zeolite A particles as a dense monograin layer onto a Pt electrode and subsequent ion-exchange, a silver zeolite electrode can be prepared which shows the silver reduction and oxidation steps in the zeolite to be quasi-reversible.

The sustained interest in zeolite-modified electrodes has been comprehensively explored in a recent review article by Rolinson.<sup>1</sup> The route chosen by Mallouk and coworkers<sup>2</sup> for the chemical modification of electrode surfaces with aluminosilicates is appealing, since it apparently leads to reproducible and durable coatings while avoiding the use of complex materials like composites containing, besides zeolites, conductive powders and polymers or inert oils. Reasoning along similar lines we have developed a simple and fast technique for the preparation of monograin-zeolite-modified electrodes.

Zeolite Na<sub>12</sub>-A (Linde 4A, Baylith T, Bayer, 2.0 g) was conditioned at 150 °C at reduced pressure in an atmosphere of 20 mbar H<sub>2</sub>O for 4 h. From this zeolite powder a suspension was prepared by adding dry MeCN (80 ml) and sonication for 5 min. After addition of triethoxyvinylsilane (Merck, synthesis grade, 1 ml), modification took place during 4 days of continuous stirring at room temperature. The suspension was filtered, and the residue washed with MeCN and dried at 100 °C at reduced pressure. The integrity of this surface-functionalized zeolite lattice was determined by FTIR transmission spectroscopy<sup>3</sup> and X-ray powder diffraction. A 4 mm diameter Pt disk electrode with PTFE sheathing, polished with 0.3 μm Al<sub>2</sub>O<sub>3</sub> and surface-oxidized in HNO<sub>3</sub> (conc.) for 5 min, was coated with 5 μl of a zeolite dispersion (15 mg

modified zeolite per 2 ml dry MeCN, 10 min sonication, 2 min sedimentation) and illuminated with an 8 W 254 nm UV lamp for 10 min to induce polymerisation of the surface vinyl groups and to evaporate the solvent. The thickness and density of a sample of about 35 μg of the resulting zeolite layer was analysed by SEM. As shown in Fig. 1(a) the coating achieved by our technique consists of one to two monograin layers of zeolite particles of an average size of about 1 μm<sup>3</sup>; its mechanical stability is high, for example it may be carefully peeled off as a film as done for this figure in its upper right corner. Before use in cyclic voltammetry,<sup>†</sup> the modified electrode was ion-exchanged by immersion in a AgNO<sub>3</sub> (0.1 mol dm<sup>-3</sup>) solution for 5 min and washed in deoxygenated water for another 5 min. Fig. 2(a) shows cycles 1–4 and Fig. 2(b) cycles 6–8 of the electrode's voltammogram measured immediately after contact with the electrolyte. The observed continuous decrease of the cathodic and anodic peak currents is primarily a consequence of concurrent ion-exchange of

† One-compartment, three-electrode cell; Pt sheet counter and (Hg–HgSO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub> sat.) reference electrode; EG&G mod. 173 potentiostat and mod. 175 universal programmer; LiClO<sub>4</sub> (1 mol dm<sup>-3</sup>) (Merck, p.a.) Ar-purged supporting electrolyte; no IR compensation.

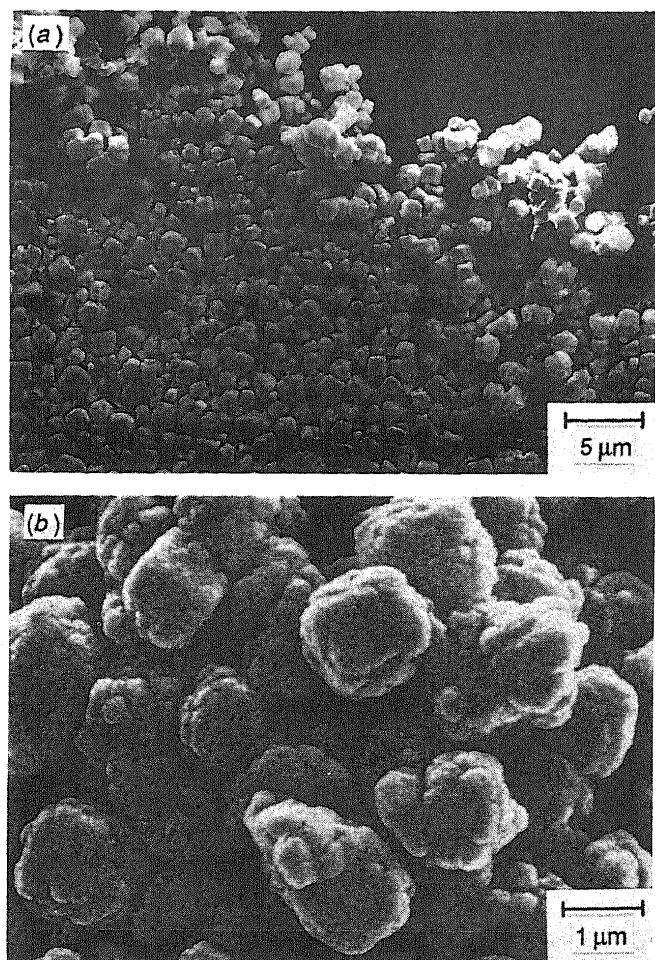


Fig. 1 SEM micrographs of zeolite  $\text{Na}_{12}\text{-A}$  modified Pt electrode after ion-exchange in  $\text{AgNO}_3$ ; (a) before cyclic voltammetry; (b) after 20 voltammetric cycles. (For details see text).

$\text{Ag}^+$  zeolite by  $\text{Li}^+$  electrolyte which complicates the interpretation of any coulometric measurements as long as the silver concentration in the zeolite is not stationary. Time-independence of the voltammetric waves is reached after about 20 cycles. If, after this treatment the electrode is removed from the electrolyte, washed, dried and re-examined by SEM, the previously clean surface of the zeolite particles is found to be covered by excrescences similar in morphology to metallic deposits encountered in other zeolite studies<sup>4</sup> [Fig. 1(b)]. The identification of these outgrowths as silver crystallites is supported by earlier XRD measurements showing specific Ag diffraction lines indicative of crystallite sizes in the range of 200–2000 Å. Using the replica technique the zeolite carrier crystals could be dissolved such that in the transmission electron microscope only the remaining silver particles were observed.<sup>5</sup> This finding of course raises the question as to the electrochemical properties of the excrescences. The shoulder observed in the cathodic peak of the first sweep is in agreement with the results of a recent study on silver exchanged zeolite Y modified-electrodes by Baker *et al.*<sup>6</sup> who attributed the phenomenon of two distinct cathodic waves to the response of two electrochemically distinguishable silver species occupying sites I and I' of zeolite Y. The explanation of our observation in terms of the zeolite AgA structure<sup>7</sup> suggested further experiments. The peak potential of the small second anodic wave developing with time and first evident from cycle no. 6 [Fig. 2(b)] matches exactly the peak potential of the  $\text{Ag}^0$  reoxidation as measured by cyclic voltammetry of  $\text{AgNO}_3$  on the same blank Pt electrode under otherwise identical conditions. We therefore conclude that the observation is due to oxidation of a silver phase similar to that generated by deposition of  $\text{Ag}^0$  monolayers on Pt; since the zeolite coating produced by our technique is permeable to

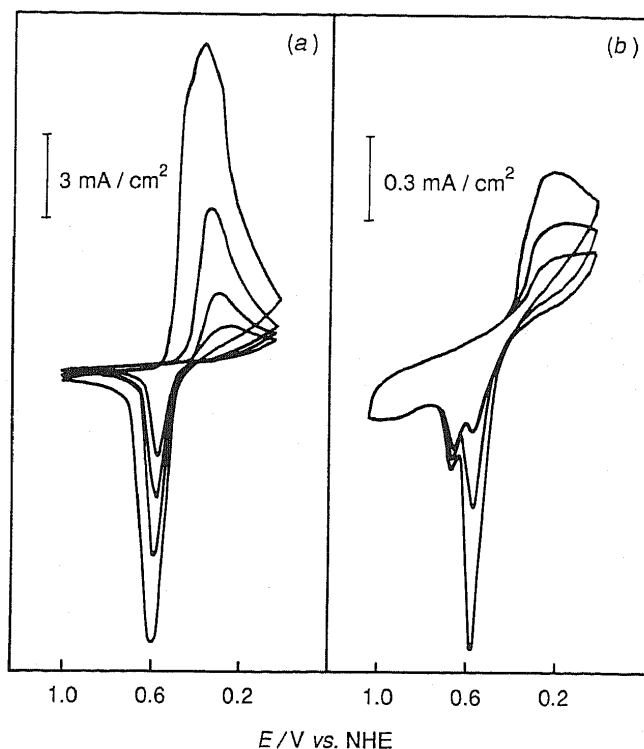


Fig. 2 Cyclic voltammogram of silver zeolite modified electrode;  $\text{LiClO}_4$  ( $1 \text{ mol dm}^{-3}$ ),  $22^\circ\text{C}$ ,  $50 \text{ mV/s}$ ; upper half of traces are cathodic currents; current densities are normalized to Pt disk area; (a) cycles 1–4; (b) cycles 6–8.

$\text{Ag}^+$ , the deposition of silver directly on the supporting electrode cannot be excluded with certainty, but it is definitely not a dominating process.

In Fig. 2 the shift of both cathodic and anodic peak potentials towards negative values with decreasing  $\text{Ag}^+$  zeolite concentration is significant; the potentials eventually stabilize, as do the corresponding currents. At present the exact nature of the silver species formed during electrochemical reduction of the zeolite modified electrode has not been determined, but the formation of  $\text{Ag}_n^{m+}$ , where  $m < n$ , in the zeolite is possible. With decreasing silver concentration smaller values of  $n$  (cluster size) are expected to be favoured. From the work of Henglein<sup>8</sup> the electrochemical potential of small silver clusters in aqueous environments is known to be a pronounced function of cluster size with the two extremes of  $-1.8 \text{ V vs. NHE}$  for  $n = 1$  and the value of  $+0.799 \text{ V}$  for the conventional bulk electrode. The extent and direction of our observed potential shifts suggest that the shifts are a manifestation of different silver cluster size.

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