

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.¹ The route chosen by Mallouk and coworkers² 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 Na₁₂-A (Linde 4A, Baylith T, Bayer, 2.0 g) was conditioned at 150 °C at reduced pressure in an atmosphere of 20 mbar H₂O 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 spectroscopy³ and X-ray powder diffraction. A 4 mm diameter Pt disk electrode with PTFE sheathing, polished with 0.3 μm Al₂O₃ and surface-oxidized in HNO₃ (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 ³; 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,[†] the modified electrode was ion-exchanged by immersion in a AgNO₃ (0.1 mol dm⁻³) 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–HgSO₄, K₂SO₄ sat.) reference electrode; EG&G mod. 173 potentiostat and mod. 175 universal programmer; LiClO₄ (1 mol dm⁻³) (Merck, p.a.) Ar-purged supporting electrolyte; no IR compensation.

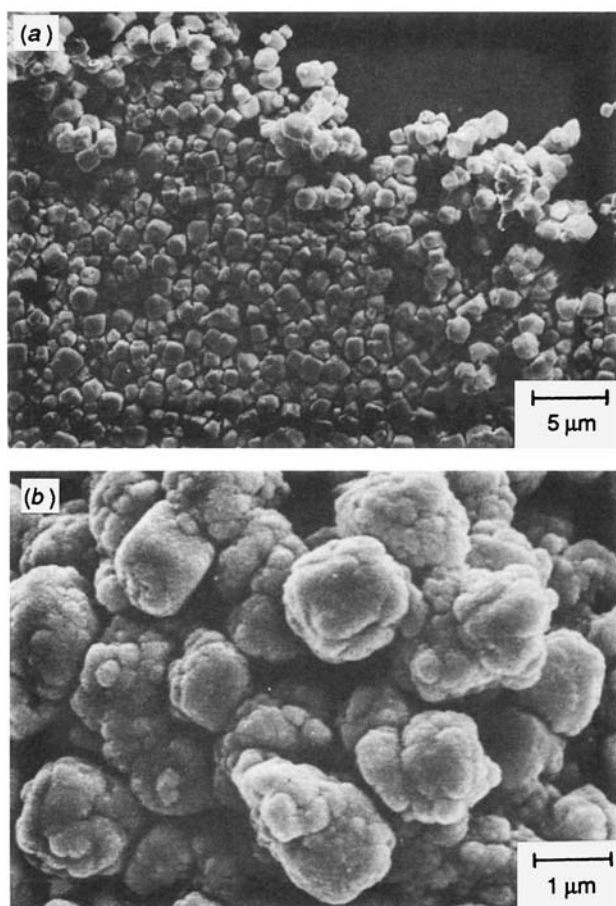


Fig. 1 SEM micrographs of zeolite Na₁₂-A modified Pt electrode after ion-exchange in AgNO₃; (a) before cyclic voltammetry; (b) after 20 voltammetric cycles. (For details see text).

Ag⁺_{zeolite} by 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 studies⁴ [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.⁵ 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.*⁶ 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 structure⁷ 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 Ag⁰ reoxidation as measured by cyclic voltammetry of AgNO₃ 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 Ag⁰ monolayers on Pt; since the zeolite coating produced by our technique is permeable to

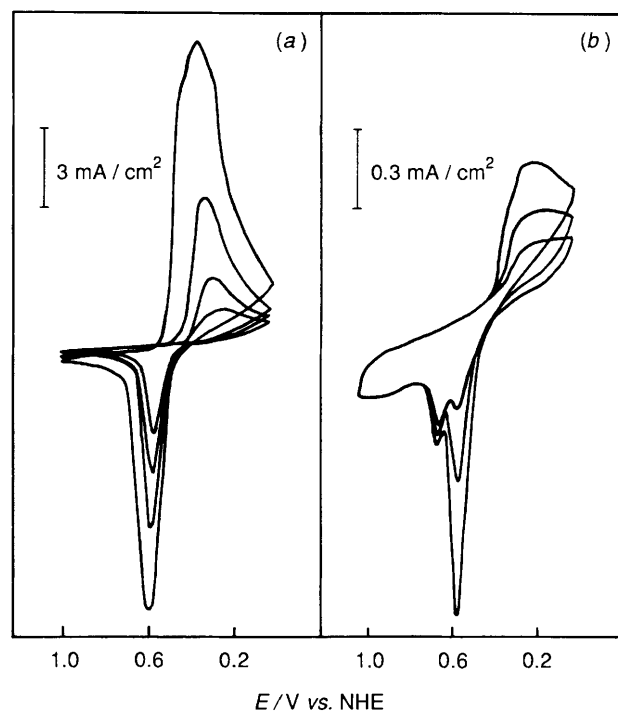


Fig. 2 Cyclic voltammogram of silver zeolite modified electrode; LiClO₄ (1 mol dm⁻³), 22 °C, 50 mV/s; upper half of traces are cathodic currents; current densities are normalized to Pt disk area; (a) cycles 1–4; (b) cycles 6–8.

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 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 Ag_mⁿ⁺, 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 Henglein⁸ 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 V vs. normal hydrogen electrode (NHE) for $n = 1$ and the value of $+0.799$ 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.

We thank Professor R. Giovanoli and his staff of the Electron Microscopy Laboratory, University of Berne, for invaluable SEM and XRD measurements and helpful discussions, and we acknowledge financial support by the Schweizerische Bundesamt für Energiewirtschaft through grant BEW-EPA 217.307.

Received, 14th January; Com. 1/00190F

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