

Silver Zeolite 4A Modified Electrodes: Intrazeolite Effect

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The cyclic voltammograms of Ag⁺-exchanged zeolite A as a monograin layer on glassy carbon electrodes show a dramatic dependence on the degree of exchange and indicate that the silver ions in the zeolite are electrochemically 'active'.

All kinds of spectroscopic techniques have been applied for characterizing silver zeolites but only a few studies have been devoted to electrochemical characteristics of zeolite-modified electrodes containing silver ions.¹⁻³ We have found recently that electrodes modified with a dense monograin zeolite layer are well suited for electrochemical studies⁴ and we now describe the voltammetric behaviour of silver zeolite A, Ag_xNa_{12-x}(AlO₂)₁₂(SiO₂)₁₂, for different degrees of exchange *x*. To understand the operation of zeolite electrodes, it is important to distinguish between responses originating from the surface and the interior of the zeolite. For this reason extra- and intra-zeolite electrochemical processes will be discussed.

A 3 mm diameter glassy carbon disk electrode with Teflon sheathing was polished with 0.3 μm Al₂O₃, washed ultrasonically in water three times and electrolysed in 0.1 mol l⁻¹ LiClO₄ at a rotation frequency of 3000 rpm by holding the potential at 0.9 V vs. saturated calomel electrode (SCE) for 5 min, and then washed thoroughly with doubly distilled water. 5 μl of zeolite dispersion [60 mg of zeolite Na₁₂-A (Linde 4A, Baylith T, Bayer) in 15 ml of H₂O, 1 h sonication before use] was dropped on the surface of the electrode. After slowly drying at room temp., 5 μl of polystyrene solution [3 mg of polystyrene in 25 ml of tetrahydrofuran (THF)] was dropped on the zeolite layer and evaporated at room temp. The coating obtained contains 20 μg of zeolite and 0.6 μg of

polystyrene and consists of one monograin layer as analysed by scanning electron microscopy (SEM). The mechanical stability of this layer is high; no apparent loss of zeolite from the surface of the glassy carbon electrode rotating at 3000 rpm in aqueous solution has been observed. Before use in cyclic voltammetry,[†] the modified electrodes were cleaned with rotation at 500 rpm in 0.1 mol l⁻¹ NaNO₃ for 10 min, then ion-exchanged in the dark with rotation at 500 rpm in NaNO₃ + AgNO₃ solutions with different Ag⁺/Na⁺ ratios for different Ag⁺-exchange degrees, and finally washed thoroughly in doubly distilled water. Cyclic voltammograms were measured at different scan rates immediately after immersion of the electrodes into the electrolyte. The cyclic voltammograms measured at 5 mV s⁻¹ for electrodes with different degrees of exchange x of 2.6, 4.0, 6.5 and 12 are shown in Fig. 1. The reproducibility of these results was checked by carrying out all experiments three times. The integrated area of the first cathodic wave was the same within $\pm 5\%$. This indicates that the experimental procedure is reproducible and that the zeolite layer on the glassy carbon electrode is stable.

About 85% of the silver ions in the zeolite are electrochemically reduced at this scan rate during the first cathodic scan for all degrees of exchange investigated. A dramatic dependence of the peaks and shoulders on the degree of exchange x is apparent in Fig. 1. This indicates the presence of eight electrochemically distinct silver species, which we denote as A, B, C, D, E, F, G and H, respectively. We first note that the peak potential of the peak H matches exactly the peak potential of reduction of silver ions on the same blank glassy carbon electrode under otherwise identical conditions. It is caused by diffusion of Ag⁺ ions from the zeolite to the surface of the glassy carbon electrode and reduction during the cathodic scan. Because the degree and the rate of this process depend on the initial Ag⁺-exchange degree x , this peak appears only in the fully Ag⁺-exchanged sample, $x = 12$. Baker and Zhang³ have explained the voltammetric behaviour of their silver zeolite Y modified electrodes by assuming that Ag⁺ ions located at two different sites in zeolite Y possess different redox abilities. In fully hydrated silver zeolite A, the Ag⁺ ions are located at four different sites. It was reported that the least strongly coordinated silver ions are reduced first.⁵

We have observed seven electrochemically distinct species (A–G) in addition to H, however, and found that the appearance of them strongly depends on x , a fact that has not hitherto been reported. To explain these observations, further assumptions have to be made. First, the silver ions prefer the sites in the zeolite to which they are most strongly coordinated. Secondly, the reduced Ag⁰ atoms react with each other and with unreduced Ag⁺ ions to form uncharged and charged silver clusters, Ag_{*n*}^{*m*+} ($m < n$), the sizes of which are limited by the sizes of the zeolite cages. These clusters possess different redox abilities.^{6,7}

We conclude that at low Ag⁺-exchange degrees, the Ag⁺ ions are mainly located at sites at which it is more difficult for them to be reduced and smaller clusters are formed as compared with high Ag⁺-exchange degrees. The electrodes respond in the more negative potential region in this case. With increasing Ag⁺ concentration, more and more Ag⁺ ions occupy sites at which they are easily reduced and larger clusters are formed as compared with low Ag⁺-exchange degrees. As a result, the electrode responds in the more

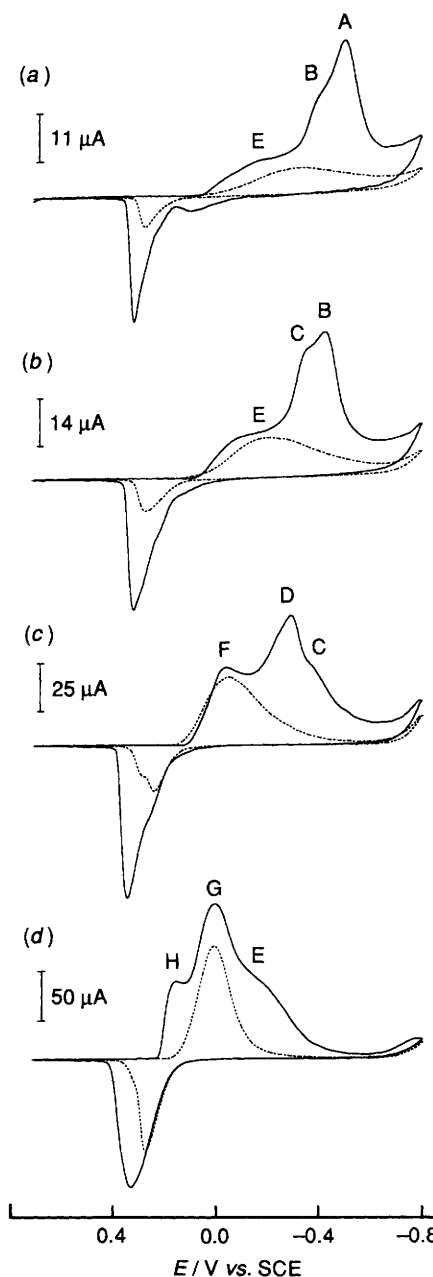


Fig. 1 Cyclic voltammograms of silver zeolite 4A modified electrodes in 0.1 mol l⁻¹ LiClO₄ at 20 °C at a scan rate of 5 mV s⁻¹. The initial potential is 0.7 V and the switching potential is -0.8 V. The upper half of traces are the cathodic currents. (a), (b), (c) and (d) illustrate measurements at different degrees of silver ion-exchange, namely $x = 2.6, 4.0, 6.5$ and 12. Solid lines are the first cycles and dashed lines are the second cycles. SCE = saturated calomel electrode.

positive potential region. This means that the seven peaks and shoulders (A–G) are caused not only by site-effects, but also by the formation of silver clusters of different size which depends on the initial concentration of Ag⁺ ions in the zeolite.

What is the reason for the dramatic decreases of the current in the second cycles? This decreases faster at low x than at high x , and, as mentioned above, nearly the same percentage (about 85%) of Ag⁺ ions in the zeolite are reduced during the first cathodic scan for all degrees of exchange. This can be explained by assuming that the decrease of the current during the second cycle is mainly caused by migration of uncharged silver clusters out of the zeolite framework and growth on the surface of the zeolite to form electrochemically 'silent' silver particles.^{4,9} Provided that the smaller uncharged silver clusters migrate faster than the larger ones,⁸ the current of the second cycle is expected to decrease faster at low exchange degree.

[†] One-compartment, three-electrode cell with a water jacket for connection to a constant-temperature circulator; Pt sheet counter electrode and saturated calomel reference electrode with a 1 mol l⁻¹ NaNO₃ bridge electrolyte solution with Vycor frit to avoid the influence of Cl⁻ ions; EG&G model 273 potentiostat and model 270 electrochemical analysis system; LiClO₄ (0.1 mol l⁻¹) (Merck, p.a.) Ar-purged supporting electrolyte solution; no IR compensation.

All explanations given in this paper are also supported by the observed influence of the scan rate (0.5 to 50 mV s⁻¹) on cyclic voltammograms. We conclude that the cathodic reduction of silver ions in the zeolite A is dominated by intrazeolite processes.

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