Methyl Viologen–Zeolite Electrodes: Intrazeolite Charge Transfer

Gion Calzaferri,* Martin Lanz and Jian-wei Li

Institute for Inorganic and Physical Chemistry, University of Berne, Freiestrasse 3, CH-3000 Berne 9, Switzerland

Cyclic voltammograms of methyl viologen-exchanged zeolite Y as a monograin layer on glassy carbon electrodes in different aqueous alkali electrolyte solutions indicate efficient intrazeolite charge transfer.

It is still a matter of debate whether the electroreduction of methyl viologen (MV^{2+}) exchanged into zeolite Y is an intra- or an extra-zeolite process.[1,2] Walcarius *et al.* investigated the cyclic voltammetric behaviour of a pressed mixture of zeolite and carbon with paraffin oil in aqueous electrolyte and concluded that the MV^{2+} is first ion-exchanged out of the zeolite and then reduced within the bulk of the carbon paste electrode.[3] The results of Gemborys and Shaw in acetonitrile electrolyte, however, are compatible with an intrazeolite process.[4] They used carbon-free MV^{2+}–Y-zeolite modified electrodes where the zeolite grains were pasted on the electrode with polystyrene. Applying a new method for preparing mechanically stable dense zeolite monograin layers on substrate electrodes,[5] we have been able to distinguish between an intrazeolite ion transport in Cu^{2+}–Y-zeolite[6] and an intrazeolite electron transport mechanism in Ag^+–A-zeolite.[5,7] The same method has been successful in studying intra- *versus* extra-zeolite charge-transfer at MV^{2+}–Y-zeolite electrodes in different aqueous alkali electrolytes.

Samples with different degrees of MV^{2+} exchange were prepared by the following procedure: 1 g of Na^+–Y-zeolite (Union Carbide, LZY-52) was suspended in doubly distilled water (200 ml) containing an appropriate amount of *N,N′*-dimethyl-4,4′-bipyridyl dichloride ($MVCl_2$; Fluka, purum >98%) and stirred overnight. The exchanged zeolite was separated from the solution by centrifugation and decantation of the liquid. It was then washed three times with doubly distilled water and centrifuged. The thus obtained samples were dried at 60 °C for 3 hours. Weighed amounts of the modified zeolites were dissolved in 2 mol dm^{-3} HCl solution (20 ml) for several days to determine the degree of exchange. Dissolution of zeolite Y was not complete, but use of a large excess of protons in the solution ensured that all the MV^{2+} was exchanged out of the zeolite. The MV^{2+} content of the solutions was determined photometrically. As a reference a standard solution of $MVCl_2$ (dried in vacuum at 70 °C for 3 hours) was prepared and the absorption coefficient of MV^{2+} was determined as 2×10^4 dm^3 mol^{-1} cm^{-1} at λ_{max} 258 nm. MV^{2+}–Y-zeolites with exchange degrees ranging from 4 to 56% were investigated.† The maximum degree of exchange reported in the literature is about 2 MV^{2+} molecules per supercage or 16 molecules per unit cell, respectively, which corresponds to 57% of all cations exchanged.[8] The zeolite monograin layer electrode preparation technique has been described previously,[6] and glassy carbon discs (diameter 3 mm) with Teflon sheathing were used as substrate electrodes. Before they were coated with zeolite, they were polished under rotation at 3000 rpm with 0.3 µm Al_2O_3 and washed ultrasonically. The exchanged zeolite (60 mg) was dispersed ultrasonically in water (15 ml) and 5 µl of this dispersion was dropped on the surface of the pretreated glassy carbon electrode and allowed to dry very slowly in a covered beaker at room temperature. On to the dried zeolite layer, 5 µl of polystyrene solution (0.75 mg polystyrene in 20 ml tetrahydrofuran) was added and allowed to evaporate. The coatings prepared in this way contained 20 µg of zeolite and 0.2 µg of polystyrene.

Cyclic voltammograms were performed in 0.05 mol dm^{-3} aqueous electrolytes of LiCl, NaCl, KCl and CsCl.‡ Fig. 1 shows voltammograms of 17% ion-exchanged MV^{2+}–Y-zeolite for the different supporting electrolytes and the voltammogram of a 3.5 mmol dm^{-3} $MVCl_2$ solution in 0.05 mol dm^{-3} NaCl at a blank glassy carbon electrode. Scans were recorded from 0 to −1.3 V and back to 0 V *vs.* SCE with a scan rate of 20 mV s^{-1}. The first two sweeps measured immediately after immersing the electrode into the solution are shown. Voltammograms obtained with MV^{2+}–Y-zeolites of higher or lower exchange degrees were similar to those in Fig. 1.

The reductive sweep of the $MVCl_2$ solution at the blank glassy carbon electrode shows two waves at −0.71 and −1.04 V which correspond to the reactions $MV^{2+} + e^- \rightarrow MV^{\cdot+}$ and $MV^{\cdot+} + e^- \rightarrow MV^0$, respectively. There is a significant difference of the cyclic voltammograms of the MV^{2+}–Y-zeolite with respect to this reference; both reduction waves are observed, but their size strongly depends on the electrolyte cation, and the first reductive peak potential appears at more negative values (Table 1). The first reductive wave is small in LiCl and increases in the series $Li^+ < Na^+ < K^+$. The second reductive wave shows the opposite behaviour. It is large in LiCl and decreases in the order $Li^+ > Na^+ > K^+ > Cs^+$. This trend is well reflected in the current and charge values listed in Table 1.

In the LiCl electrolyte, the small current and charge passed during the first wave can be understood considering the large hydrated radius of Li^+, which hinders its movement into the zeolite. Reduction is coupled to the movement of electrolyte cations from the solution into the zeolite to compensate for the change in charge. Cation movement immediately follows the electroreduction step in the case of an intrazeolite reduction process, whereas in an extrazeolite process the ion-exchange of cations in solution with the zeolite-exchanged redox species precedes the electroreduction.[1] The hydrated radius and the absolute value of the standard hydration enthalpy decrease in the order $Li^+ > Na^+ > K^+ > Cs^+$. Higher cationic mobility leads to faster leaching of the methyl viologen out of the zeolite, which, at monograin modified electrodes, reduces the amount of the available electroactive methyl viologen. The decrease of the

Table 1 Peak potential *E vs.* SCE, peak current *I* and charge *Q* of the first (P1) and second (P2) reduction waves of 17% ion-exchanged MV^{2+}– Y-zeolite monograin layers on glassy carbon in different electrolytes and at blank glassy carbon in 0.05 mol dm^{-3} NaCl + 3.5 mmol dm^{-3} $MVCl_2$. The values in parentheses give the percentage of reduced MV^{2+} based on the total amount present

Electrolyte	*E* (P1)/V	*I* (P1)/µA	*Q* (P1)[a]/µC	*Q* (P1)[b]/µC	*E* (P2)/V	*I* (P2)/µA	*Q* (P1 + P2)[c]/µC	*Q* (P1 + P2)[d]/µC
LiCl	−0.83	7.4	106 (20%)	49 (9%)	−1.05	86.1	455 (44%)	630 (60%)
NaCl	−0.79	18.8	182 (35%)	103 (20%)	−1.03	69.5	498 (48%)	545 (52%)
KCl	−0.78	34.7	390 (75%)	298 (57%)	−1.05	45.3	435 (42%)	752 (72%)
CsCl	−0.76	27.0	232 (44%)	151 (29%)	−1.05	30.8	355 (34%)	425 (41%)
MV^{2+}[e]	−0.71	35.3	213		−1.04	60.8	437	

[a] Uncorrected values. [b] Values after subtraction of a baseline-scan obtained with viologen-free zeolite. [c] Values after subtraction of a linear baseline. [d] Values after subtraction of a baseline-scan obtained with viologen-free zeolite. [e] 3.5 mmol dm^{-3}.

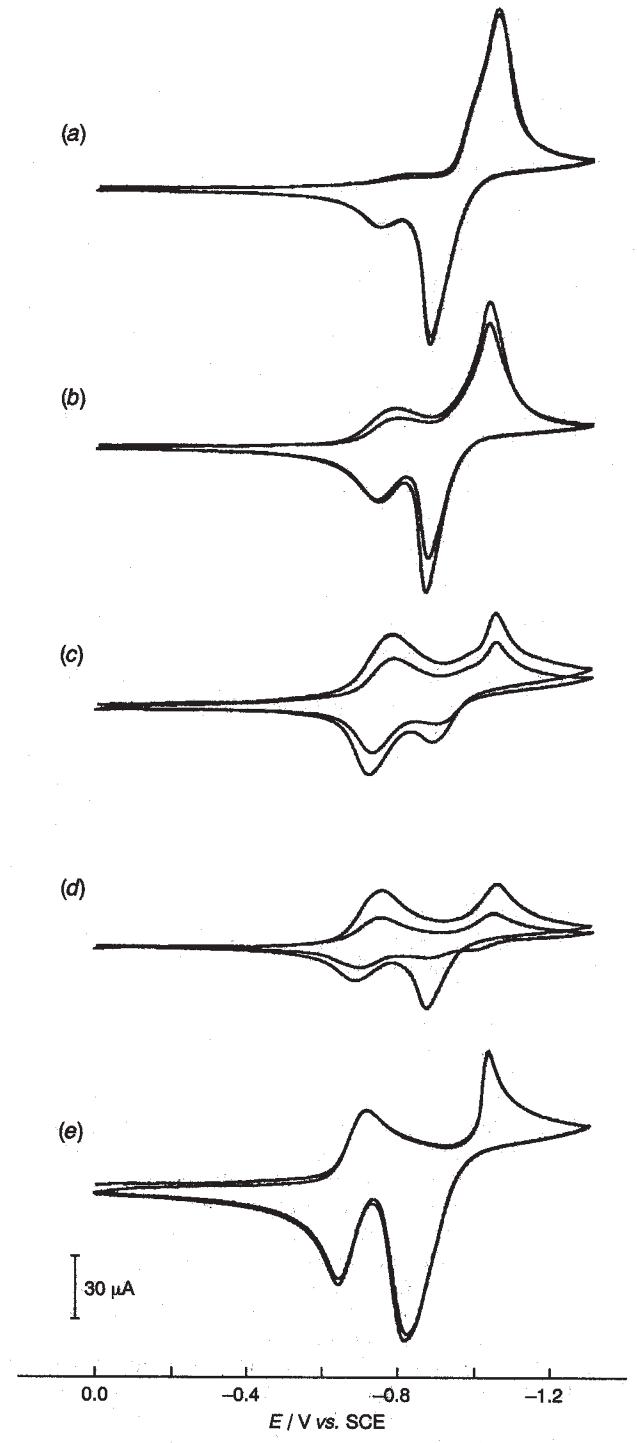

Fig. 1 Cyclic voltammograms of 17% ion-exchanged MV^{2+}–Y-zeolite monograin layers on glassy carbon in different 0.05 mol dm^{-3} electrolyte solutions at 20 °C at a scan rate of 20 mV s^{-1}. The initial potential is 0 V and the switching potential is −1.3 V. The upper half of traces are the cathodic currents. The first and second sweep just after immersion of the electrode into the electrolyte are shown. Electrolytes from top to bottom: (*a*) LiCl, (*b*) NaCl, (*c*) KCl and (*d*) CsCl, (*e*) blank glassy carbon electrode in 0.05 mol dm^{-3} NaCl + 3.5 mmol dm^{-3} $MVCl_2$.

current of the second voltammetric sweep compared to the first sweep is a measure for this leaching rate which is slow in LiCl electrolyte and increases in the order $Li^+ < Na^+ < K^+ < Cs^+$, see Fig. 1. The increase of the current of the first cathodic peak in the series $Li^+ < Na^+ < K^+$ is due to increasing higher cation mobility, while the decrease from K^+ to Cs^+ (see Table 1) is due to leaching. A similar behaviour has been found in copper–zeolite modified electrodes.[6]

Discussing more fully the LiCl electrolyte; the first reduction step involves reduction of 9% of the MV^{2+} molecules to the radical cation $MV^{\cdot+}$. However, the second reduction wave is much larger than the first and a total of 60% of the MV^{2+} ions are reduced to MV^0 after both reduction waves. Within the second reduction step the MV^0 produced conproportionates with MV^{2+}, according to $MV^{2+} + MV^0 \rightleftarrows 2\,MV^{\cdot+}$, to give 2 $MV^{\cdot+}$, which can be further reduced to MV^0.[9] The occurrence of the conproportionation reaction shows that the methyl viologen is constrained within the zeolite and does not diffuse away and confirms the intrazeolite nature of the reduction mechanism. In an extrazeolite process the methyl viologen molecules would diffuse away from the monograin modified electrode and would not undergo further redox processes. This is, however, not compatible with out data. The decrease of the current in the second voltammetric sweep compared to the first one is small. In the second sweep, a total of 57% of the MV^{2+} ions are reduced to MV^0, almost the same proportion as in the first sweep. These data are only compatible with the assumption of an intrazeolite charge-transfer. We further observed an anodic shift of the first reduction peak potential of viologen-exchanged zeolite when the electrolyte concentration was increased.[6]

For the NaCl electrolyte, the observed behaviour is almost the same. The degree of leaching is small and the amount of electroactive viologen is high. In addition, we observed an approximately linear dependence of the reductive peak current on the degree of exchange. A variation of the scan rate yielded a square-root dependence of the peak current on the scan rate. This conforms to the semi-infinite linear diffusion model for cyclic voltammetry.[10] In the case of the KCl and CsCl electrolyte solutions the degree of leaching is larger but the total reductive current in the first sweep is still high.

We acknowledge financial support by the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung, grant No. 20-040598.94/1 and by the Swiss Federal Office of Energy BEW, grant No. (93)034.

Received, 23rd February 1995; Com. 5/01113B

Footnotes

† The different amounts of $MVCl_2$ added to the suspensions and the corresponding MV^{2+} exchange degrees were 20.6 (4), 41.8 (10), 62.7 (14), 82.2 (17), 143.9 (31), 205.6 (42), 328.9 (52) and 417.2 mg (56%)

‡ A one-compartment, three-electrode cell with a water jacket connected to a constant-temperature circulator (20 °C) was employed; argon-purged supporting electrolyte; Pt sheet counter electrode and SCE reference electrode with a KCl bridge electrolyte solution with Vycor frit; EG&G model 273 potentiostat and model 270 electrochemical analysis system; no *IR* compensation.

References

1 B. R. Shaw, K. E. Creasy, C. J. Lanczycki, J. A. Sargeant and M. Tirhado, *J. Electrochem. Soc.*, 1988, **135**, 869.
2 D. R. Rolison, in *Advanced Zeolite Science and Applications*, ed. J. C. Jansen, M. Stöcker, H. G. Karge and J. Weitkamp, *Stud. Surf. Sci. Catal.*, 1994, **85**, 543.
3 A. Walcarius, L. Lamberts and E. G. Derouane, *Electrochim. Acta*, 1993, **38**, 2257, 2267.
4 H. A. Gemborys and B. R. Shaw, *J. Electroanal. Chem. Interfacial Electrochem.*, 1986, **208**, 95.
5 J. Li and G. Calzaferri, *J. Chem. Soc., Chem. Commun.*, 1993, 1430.
6 J. Li and G. Calzaferri, *J. Electroanal. Chem.*, 1994, **377**, 163.
7 J. Li, K. Pfanner and G. Calzaferri, *J. Phys. Chem.*, 1995, **99**, 2119.
8 K. B. Yoon and J. K. Kochi, *J. Phys. Chem.*, 1991, **95**, 3780.
9 C. L. Bird and A. T. Kuhn, *Chem. Soc. Rev.*, 1981, **10**, 49.
10 A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, Wiley, New York, 1980, p. 213.