Zeolitic rectification of electrochemical ion transfer ☆

Robert A.W. Dryfe [a],*, Stuart M. Holmes [b]

[a] *Department of Chemistry, UMIST, PO Box 88, Manchester M60 1QD, UK*
[b] *UMIST Centre for Microporous Materials, Department of Chemistry, PO Box 88, Manchester M60 1QD, UK*

Abstract

The modification of the water | 1,2-dichloroethane interface with a zeolite membrane is reported: application of a potential difference across the modified interface allows the selective transfer of ionic species on the basis of the applied interfacial potential difference and the dimensions of the transferring ion with respect to those of the zeolite pores. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Modified electrodes; Liquid/liquid electrochemistry; Zeolites; Ion-selective electrodes

1. Introduction

The modification of electrode surfaces with mediating layers such as polymers or self-assembled monolayers (SAMs) has been the subject of intense research activity in recent years [1]. Incorporation of groups such as cyclic peptides within a SAM, supported on a gold electrode, has been shown to form nanotubes that allow size-specific sensing of molecules small enough to enter the tubules [2]. There have been various studies of the behaviour of metallic electrodes, which have been modified with porous solid films, such as clays and zeolites [3,4]. Experimental results have been generally interpreted in terms of an electron transfer to/from species located initially within the zeolite [5], however the difficulties associated with the formation of a continuous, adherent zeolite film on a metallic substrate and the characterisation of the modified substrate have restricted such studies. An alternative approach has been recently reported by Hupp and co-workers, whereby a cavity-containing, molecular square assembly was deposited on a glassy carbon or gold electrode surface: molecules were transported to the electrode surface by way of the central intramolecular nanometre-scale cavities, however a residual response from pinhole defects was also observed [6]. Meanwhile, there has been an upsurge in activity relating to the electrochemistry of the liquid | liquid interface: polarisation of the interface between two immiscible electrolyte solutions (ITIES) can lead to the potential-dependent transfer of ions [7]. The active ITIES has been miniaturised through the use of individual micro-holes [8], microhole arrays [9] and polymeric membrane materials [10]. The ITIES has also been modified by the adsorption of lipids to form monolayer films [11,12], in studies of charge transfer across the liquid | liquid interface. However, to date there have not been any reports of the modification of the ITIES with solid films such as zeolites, or other inorganic materials. This communication reports the voltammetric behaviour observed at the ITIES, where the interface has been modified by a membrane of silicalite, a zeolite with a non-polar (uncharged) framework.

2. Experimental

A silicalite membrane was prepared using a previously reported method involving growth of a film on a mercury surface [13]. The membrane was grown from a clear solution, yielding a film with an approximate thickness of 50 μm. The membrane was then calcined in

a flow of air at 450°C to remove the tetrapropylammonium cations from the silicalite pores: these cations act as structure-directing agents during the growth of the film. Silicalite has the MFI structure and is the all-silica analogue of ZSM-5 (Zeolite SOCONY Mobil-5). ZSM-5 was first synthesised by the Mobil Corporation [14] and has a three dimensional pore structure consisting of both straight and sinusoidal 10 (Si) ring channels. The sinusoidal channels are elliptical with pore dimensions of 0.55×0.51 nm while the straight channels are also slightly elliptical, their dimensions being 0.56×0.53 nm. The absence of aluminium in the zeolite framework means that Brønsted acidity is eliminated. The hydrophobic nature of the all-silica structure has meant that silicalite has found widespread use in the separation of small organic molecules from water [15]. Furthermore, the neutral framework structure minimises electrostatic effects on the subsequent electrochemical processes. Scanning electron microscopy (SEM) of the silicalite membranes was performed using a Hitachi S520 microscope. Water was obtained from a Milli-Q purification system (Millipore, Watford, UK). The organic solvent (1,2-dichloroethane 99% +, DCE) was supplied by Lancaster Synthesis (Morecambe, UK). Bis(triphenylphosphoranylidene) ammonium tetraphenyl borate (BTPPA TPB) was prepared by metathesis of bis(triphenylphosphoranylidene) ammonium chloride (BTPPA Cl, 97%, supplied by Aldrich Co., Gillingham, UK) and sodium tetraphenylborate (99%, Lancaster) [16]. Lithium sulphate (99% +), lithium chloride, tetramethylammonium (TMA) sulphate and tetraethylammonium (TEA) hydroxide were purchased from Aldrich. A membrane of 6-mm diameter was attached to a glass tube using a silicone rubber compound. Once cured, the tube was filled with an aqueous lithium sulphate solution (0.020 M) and left to stand. The electrochemical cell design was similar to the arrangement used by Campbell and Girault for voltammetry at the micro-ITIES [8]. The glass tube was immersed subsequently in a DCE solution containing 0.021 M BTPPA TPB, as the supporting electrolyte. The organic solution was covered with an appropriate aqueous reference electrolyte (a solution containing 1 mM BTPPA Cl, along with 0.012 M lithium chloride). The silicalite-modified water | DCE interface was then polarised using a four-electrode potentiostat (Autolab PGSTAT 20, from Eco-chemie, Utrecht, the Netherlands), capable of providing positive-feedback compensation for the resistance associated with the organic phase and the zeolite membrane itself. Voltammograms recorded in the presence of transferring ions were recorded at least 2 h after the addition of the aliquot of solution containing the ion of interest, to allow the composition of the cell (including the membrane) to re-equilibrate. Silver | silver chloride and silver | silver sulphate wires were used as reference electrodes in the organic and aqueous phases, respectively. Platinum gauze was used as the counter electrode in both phases. All experiments were performed at room temperature (293 ± 3 K).

3. Results and discussion

The cell employed throughout this study can be written as:

Ag(s)|AgCl(s)|BTPPA Cl (1 mM)

+ LiCl (0.012 M) (aq)|BTPPA TPB (0.021 M)

(DCE)‖silicalite|Li$_2$SO$_4$ (0.020 M) + X

+ (aq)|Ag$_2$SO$_4$(s)|Ag(s)
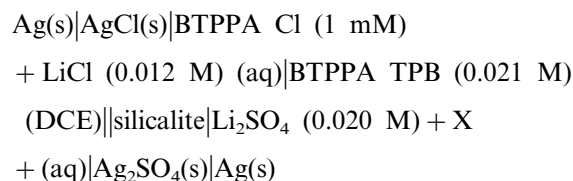
(where X^+ is the ion to be transferred, which is either TMA or TEA, added to the aqueous phase as sulphate and hydroxide salts, respectively, and the double bar denotes the polarised interface).

SEM images of a portion of the silicalite membrane used for the electrochemical study are shown in Fig. 1. The images show clearly the elongated crystals, characteristic of silicalite [17]. The membrane consisted of randomly orientated crystals, inter-grown to form a coherent structure. The pores of the zeolite created an
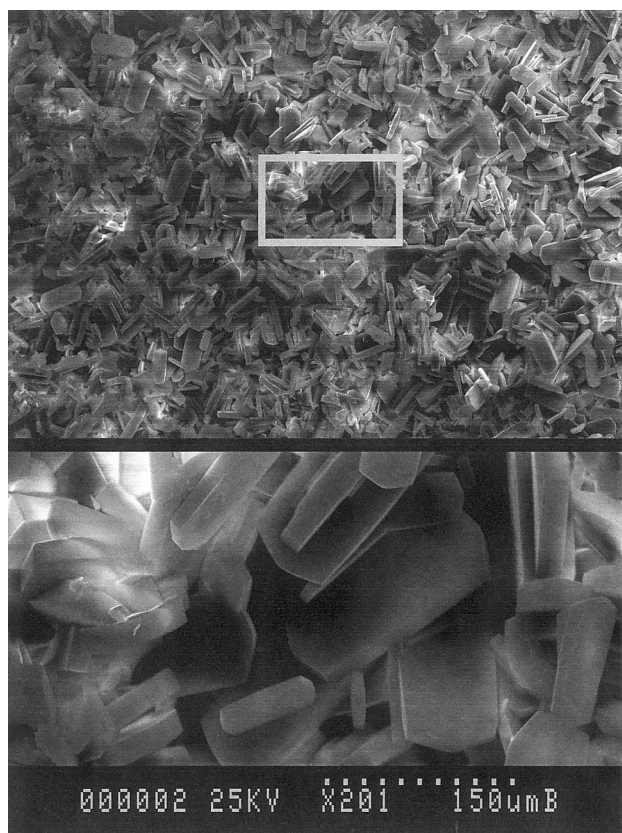

Fig. 1. SEM images of the silicalite membrane used at the modified ITIES. A scale is shown on the lower image (150 μm).
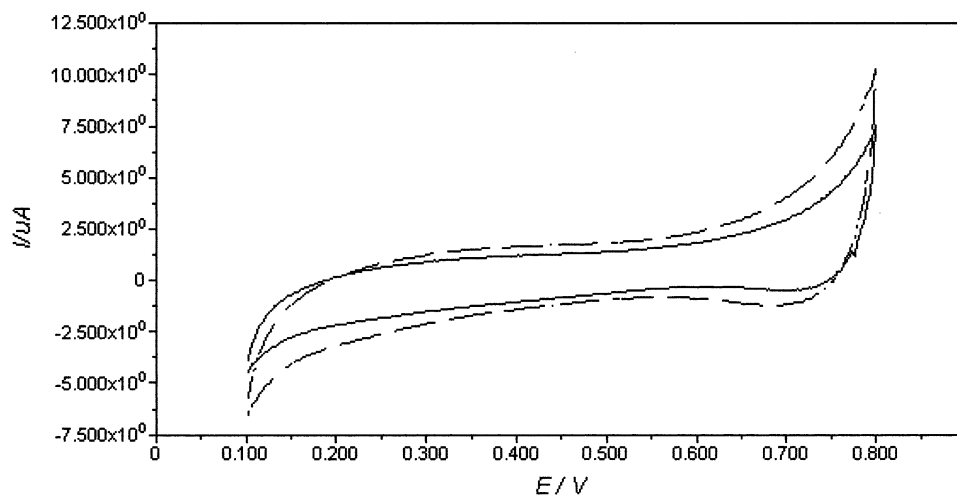
Fig. 2. The background cyclic voltammetric response of the water | DCE interface using the cell described in the text in the absence of a transferring ion (X$^+$). The potential difference was swept at a rate of 0.05 V s^{-1} (solid line) and 0.10 V s^{-1} (broken line).
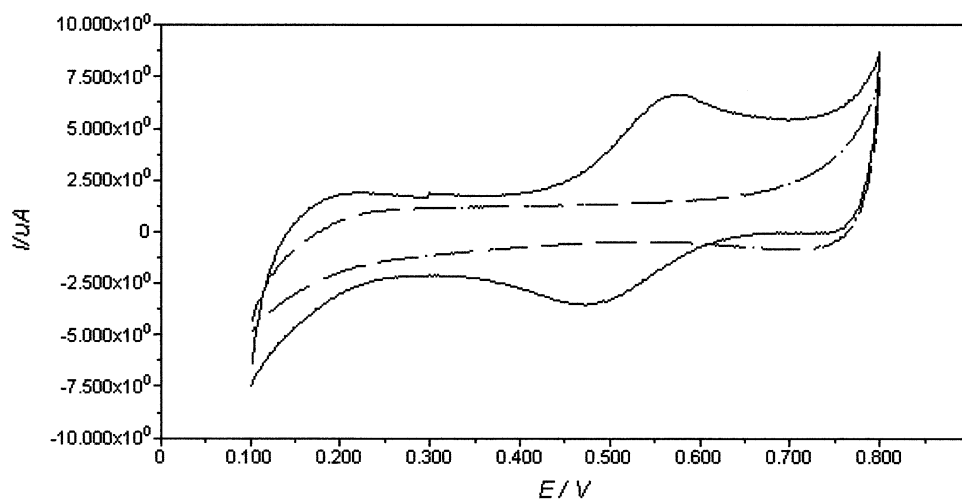

Fig. 3. The cyclic voltammetric response of the water | DCE interface using the cell described in the text with X$^+$ = TMA (solid line, bulk aqueous phase concentration of 2.50 mM). The response of the cell before the addition of TMA is given by the broken line. The potential difference was swept at a rate of 0.05 V s^{-1} in both cases.

array of nanometre scale water | DCE interfaces. Polarisation of the interfacial array by the application of a triangular potential waveform gave the response shown in Fig. 2 where a relatively flat region corresponding to the capacitive charging of the interfacial array is limited at both ends by a Faradaic current, corresponding to the transfer of supporting electrolyte ions. This background response was entirely reproducible and was qualitatively similar to the background response observed at the unmodified ITIES [16,18]. The addition of a species such as TMA to the aqueous phase of the cell, which is known to undergo a reversible transfer from water to DCE within the window defined by the supporting electrolyte ions [19], led to the appearance of a peak in the voltammogram on sweeping the aqueous phase to positive potentials with respect to the oil phase. Fig. 3 shows the cyclic voltammogram obtained

for the transfer of TMA cations from the aqueous phase to DCE and vice versa, along with the background response obtained from the same cell before the addition of the TMA sulphate solution. The peak currents (I_p) of the forward and reverse scans were located at applied potential differences (E) of approximately + 0.57 and + 0.48 V, respectively. The background subtracted voltammogram is given in Fig. 4. The ratio of the forward to reverse I_p values was considerably greater than unity, i.e. the flux of TMA out of the aqueous phase was larger than the flux of returning species. This observation is in marked contrast to the reversible voltammetry reported at the unmodified ITIES [19]. Subsequent voltammograms were characterised by a reduction of the Faradaic current, although this reduction was less pronounced if a considerable time (tens of minutes) elapsed between voltammograms.

TMA transfer at two different sweep rate (v) values is shown in Fig. 5 I_p appeared to depend linearly on $v^{1/2}$, as predicted for a diffusion-controlled process [20], for v values in the range 0.02 to 0.20 V s^{-1}. The analysis of the I_p values was complicated by the dependence of the voltammetric response on the number of voltammograms recorded previously (q.v.). However, the linear I_p versus $v^{1/2}$ dependence observed suggested that the current was controlled by linear, rather than radial, diffusion [9]. Fig. 6 shows the cyclic voltammograms obtained on the addition of an aliquot of tetraethylammonium (TEA) hydroxide solution to a cell containing only background electrolyte. No Faradaic current is observed within the potential window. By contrast, the transfer of the TMA ion (added after the addition of TEA) is seen clearly. The voltammetric transfer of TEA across the unmodified ITIES has been widely studied: the process is chemically reversible and the reported

standard Gibbs energies of transfer from water to DCE are lower than the values reported for TMA [21].

The background response obtained in the absence of a transferring ion, X, can be interpreted in terms of the transfer of the aqueous phase supporting electrolyte ions. The ionic diameters reported for these ions are less than or equal to the dimensions of the silicalite pores: the crystallographic diameter of the lithium ion is 0.15 nm [22], whilst that of the sulphate ion has been quoted as 0.51 nm [23]. By contrast, the ions used as the organic phase supporting electrolyte were considerably larger and thus would not transfer across the ITIES if an intact silicalite membrane were present between the two solutions. For example, the crystallographic diameter of TPB is 0.84 nm [22]. This exclusion phenomenon may be responsible for the slight increase in the size of the potential window observed, relative to those reported using identical electrolytes at the un-
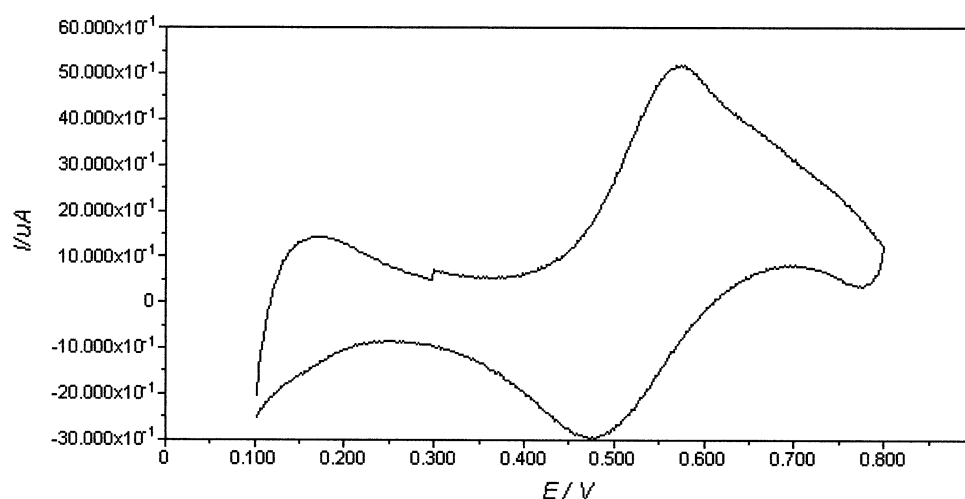

Fig. 4. The cyclic voltammetric data for TMA transfer shown in Fig. 3, with the background response of the cell (also shown in Fig. 3) subtracted.
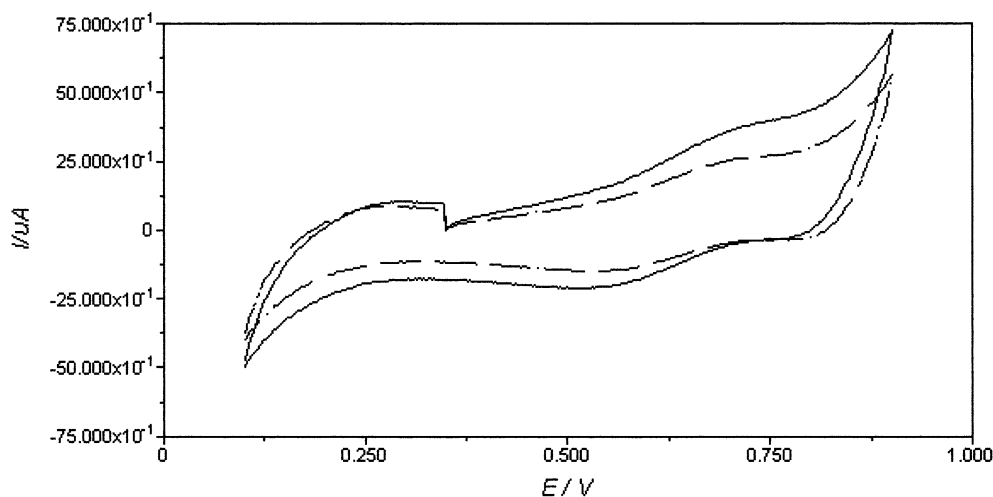

Fig. 5. The cyclic voltammetric response of the water | DCE interface using the cell described in the text with X$^+$ = TMA (solid line, bulk aqueous phase concentration of 2.00 mM). The potential difference was swept at a rate of 0.10 V s^{-1} (broken line) and 0.20 V s^{-1} (solid line).
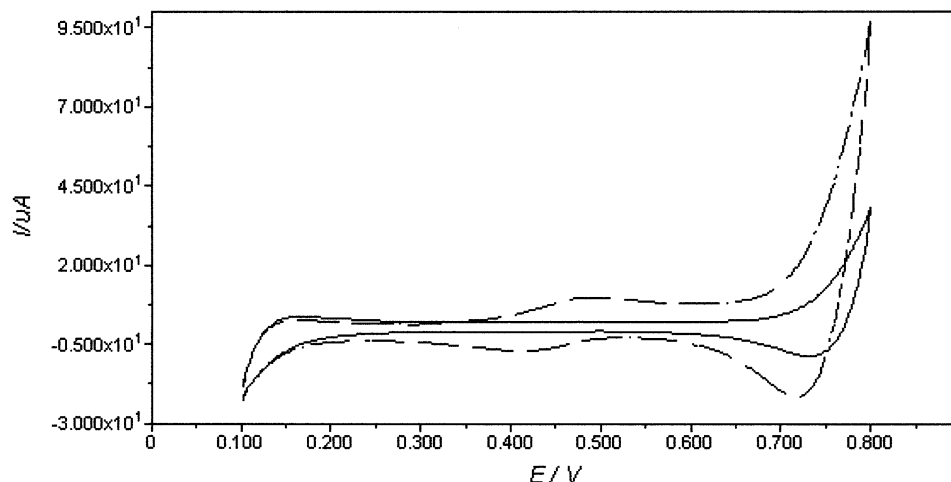
Fig. 6. The cyclic voltammetric response of the water | DCE interface using the cell described in the text with $X^+ =$ TMA (broken line, bulk aqueous phase concentration of 0.83 mM) and $X^+ =$ TEA (solid line, bulk aqueous phase concentration of 0.39 mM). The sweep rate employed was 0.06 V s^{-1} in both cases.

modified ITIES [16,18]. The hydrophobic nature of silicalite suggests that the internal surface would be preferentially wetted by DCE; any DCE entering the pores would not contain supporting electrolyte, thus implying that an ion-free layer would exist within the membrane. The filling procedure adopted was intended to counteract this phenomenon, by giving the aqueous solution time to percolate into the pores of the zeolite before immersion in the DCE phase. This implies that an asymmetric diffusion field would have arisen at the liquid | liquid interface since a linear diffusive flux through the pores of the membrane would be expected (to a first approximation) on the aqueous side of the interface, whereas a radial diffusive flux to the membrane surface may be established on the DCE side of the interface [8]. This effect may be responsible for the steady-state current response seen particularly at the negative end of the potential window. It should be noted that the hydrated diameters for both of the aqueous supporting electrolyte ions are larger than the diameter of the silicalite pores, for example the value reported [22] for lithium is 0.70 nm: this indicates that these ions must lose at least part of their hydration shells on entering the silicalite pores. The voltammetric behaviour observed in the presence of the TMA cation indicated that this ion was able to transfer across the water | DCE interface, via the pores of the silicalite membrane. The diameter reported for the TMA cation (0.56 nm) is comparable to the dimensions of the silicalite pores. It has also been assumed previously that TMA transfers from water to an organic solvent (nitrobenzene) with no hydration shell [22]. The similarity between the diameter of the cation and those of the silicalite pores suggested that the transfer observed in this case could occur only for the bare TMA ion, whilst the partial loss of reversibility and the decline in the

current, recorded over subsequent scans, could be attributed to the adsorption of a proportion of the transferred TMA on the portion of the silicalite surface exposed to the organic solvent.

It can be deduced that the electrochemically driven transfer of the TEA cation has been suppressed by the presence of the zeolite membrane, although at the unmodified ITIES it should be favoured thermodynamically (relative to TMA). The diameter of the TEA cation has been quoted as 0.67 nm in recent theoretical work on the Gibbs energies of ion transfer at the ITIES, which (as with TMA) concluded that this ion would be transferred to nitrobenzene without any associated water molecules [22]. It should be noted that slightly smaller values have been reported for the diameters of the TMA and TEA ions (0.52 and 0.62 nm, respectively) [24]. The findings detailed here have demonstrated the size-selective principle, since the dimensions quoted for TEA should prevent its transfer across the silicalite-modified water | DCE interface. This type of molecular-sieving behaviour is characteristic of zeolite materials such as silicalite. A cut-off in the uptake of molecules with critical diameters exceeding 0.6 nm has been observed in sorption measurements using silicalite [15]. Further, the integrity of the silicalite membrane (and the non-occurrence of transport via pinhole defects) is demonstrated by the absence of a peak due to TEA.

4. Conclusions

It has been shown that the complete exclusion of certain ions from microporous materials at the liquid | liquid interface can be achieved — the crucial parameter being the size of the transferring species.

Consequently, selective transfer of ions across the modified ITIES on the basis of potential and size is demonstrated. Analysis of the resultant ion-transfer voltammetry allows some quantification of the transfer process, whilst comparison with the voltammetry of the bare liquid | liquid interfaces gives information on the role of the zeolite in modifying ion transfer. Quantitative analysis of the results presented in this study should allow conclusions to be drawn about the transport and adsorption of ions within zeolite structures.

References

[1] M.P. Soriaga (Ed.), Electrochemical Surface Science, ACS Symposium Series, vol. 378, ACS, Washington DC, 1988.
[2] K. Motesharei, M.R. Ghadiri, J. Am. Chem. Soc. 119 (1997) 11306.
[3] P.K. Ghosh, A.J. Bard, J. Am. Chem. Soc. 105 (1983) 5691.
[4] D.R. Rolison, Chem. Rev. 90 (1990) 867.
[5] M.D. Baker, M. McBrien, I. Burgess, J. Phys. Chem. B 102 (1998) 2905.
[6] S. Bélanger, J.T. Hupp, C.L. Stern, R.V. Slone, D.F. Watson, T.G. Carrell, J. Am. Chem. Soc. 121 (1999) 557.
[7] H.H. Girault, in: J.O. Bockris (Ed.), Modern Aspects of Electrochemistry, vol. 25, Plenum, New York, 1993, p. 1.
[8] J.A. Campbell, H.H. Girault, J. Electroanal. Chem. 266 (1989) 465.
[9] S. Wilke, M.D. Osborne, H.H. Girault, J. Electroanal. Chem. 436 (1997) 53.
[10] B. Hundhammer, S.K. Dhawan, A. Bekele, H.J. Seidlitz, J. Electroanal. Chem. 217 (1987) 253.
[11] J. Koryta, L.Q. Hung, A. Hofmanova, Stud. Biophys. 90 (1982) 25.
[12] A.-K. Kontturi, K. Kontturi, L. Murtomäki, B. Quinn, V.J. Cunnane, J. Electroanal. Chem. 424 (1997) 69.
[13] Y. Kiyozumi, F. Mizukami, K. Maeda, T. Kodzasa, M. Toba, S. Niwa, Progress in Zeolites and Microporous Materials: Studies in Surface Science and Catalysis, vol. 105, Elsevier, Amsterdam, 1997, p. 2225.
[14] G.T. Kokotailo, S.L. Lawton, D.H. Olson, W.M. Meir, Nature 272 (1978) 437.
[15] J. Kärger, D.M. Ruthven, Diffusion in Zeolites and Other Microporous Solids, Wiley, New York, 1992 Ch. 14.
[16] Y. Shao, A.A. Stewart, H.H. Girault, J. Chem. Soc. Faraday Trans. 87 (1991) 2593.
[17] C.S. Cundy, B.M. Lowe, D.M. Sinclair, Faraday Discuss. 95 (1993) 235.
[18] A.A. Stewart, Y. Shao, C.M. Pereira, H.H. Girault, J. Electroanal. Chem. 305 (1991) 135.
[19] V. Mareček, Z. Samec, J. Koryta, Adv. Colloid Interface Sci. 29 (1988) 1.
[20] A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications, Wiley, New York, 1980 Ch. 6.
[21] T. Wandlowski, V. Mareček, Z. Samec, Electrochim. Acta 35 (1990) 1173.
[22] T. Osakai, K. Ebina, J. Phys. Chem. B 102 (1998) 5691.
[23] H.D.B. Jenkins, K.P. Thakur, J. Chem. Ed. 56 (1979) 576.
[24] M. Abraham, J. Liszi, J. Inorg. Nucl. Chem. 43 (1981) 143.