

# Diffusion of Silver Ions in Zeolite Y Preceded by a Coupled Chemical Reaction: Electrochemical Observation and Modeling

Mark D Baker,\* Michael McBrien, and Ian Burgess

Department of Chemistry and Biochemistry, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

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It is the goal of this work to show that the complex chronoamperometry of partially silver ion exchanged  $\text{Ag}_{3.1}\text{Na}_{52.9}\text{Y}$  can be understood by treating the passage of silver cations to the electrode solution interface as a diffusion-controlled reaction preceded by a feeding chemical step. This is achieved via the solution of a CE (chemical followed by electrochemical) process using simulation methods adopting a finite difference approach whereupon the zeolite is divided into a set of discrete volume elements corresponding to the large and small channels of zeolite Y. The fit with the experimentally recorded chronoamperometry of a monograin  $\text{Ag}_{3.1}\text{Na}_{52.9}\text{Y}$ -modified electrode covers 30 s after the application of the pulse. Using this approach, accurate determinations of intrazeolite diffusion coefficients will be possible only when exact equilibrium cation locations are known.

## Introduction

Electrochemical processes occurring in the presence of zeolites have evoked some interest due to possible applications in electroanalytical chemistry<sup>1–4</sup> and electrocatalysis.<sup>5,6</sup> To date cyclic voltammetry has been the principal characterizational technique. A useful alternative is chronoamperometry (CA). In CA the current is recorded as a function of time, but the potential bias is maintained at a constant value. The CA of zeolite-modified electrodes (ZMEs) has been studied in our research group for several years. Thus far we have focused attention largely on partially ion exchanged  $\text{Ag}_{56-x}\text{Na}_x\text{Y}$  ( $0 \leq x \leq 56$ ). The predominant placement of silver cations within the small channel system (i.e., outside of the supercages) is possible, serving as a useful model system in assessing zeolite extraframework cation occupancy on electrochemical response. Chronoamperometry of  $\text{Ag}_{56-x}\text{Na}_x\text{Y}$  has shown both diffusion and nondiffusion control.<sup>7,8</sup> The chronoamperometry of  $\text{Ag}_{3.1}\text{Na}_{52.9}\text{Y}$  has been modeled by describing the release of silver cations from the zeolite in terms of a rate-limiting pseudo-first-order process.<sup>7</sup> The data were however fit at very short time. In this paper we present a model that fits the current response of  $\text{Ag}_{3.1}\text{Na}_{52.9}\text{Y}$ , over 30 s of the current decay.

## Experimental Section

**Materials and Electrochemistry.** Zeolite Y (LZY 52) was donated by UOP. Ion exchange was effected in 0.01 M or more dilute solutions of silver nitrate to produce the desired ion-exchange level. Typically 1 g of zeolite was exchanged in 250 mL of solution. The ion-exchange reaction was performed in the dark, and following an overnight exchange, the zeolite sample was carefully washed, air-dried, ground to a fine powder, and stored in the dark. X-ray diffraction patterns remained unchanged after this procedure. The level of ion-exchange ( $\pm 5\%$ ) was determined by atomic absorption. The unit cell composition of the sample was determined to be  $\text{Ag}_{3.1}\text{Na}_{52.9}\text{Y}$ .

A one-compartment three-electrode electrochemical cell was used with a platinum flag counter electrode and a platinum wire

quasi-reference electrode. The latter was employed in order to completely eliminate chloride ion interference and also to improve signal-to-noise. Monograin zeolite layers were fabricated by adapting the procedure developed by Calzaferri and co-workers.<sup>9</sup> In this method, an ethanolic slurry containing 5 mg of zeolite/mL was prepared. Aliquots of 15  $\mu\text{L}$  of this were then withdrawn and applied to the conductive surface of the tin oxide (TO) on the glass electrode (donated by Libby Owens Ford, Toledo, OH). Upon evaporation of the ethanol an approximately 1  $\text{cm}^2$  film of mass 75  $\mu\text{g}$  of zeolite resulted. This film was then overcoated with 10  $\mu\text{L}$  of a 50  $\mu\text{g/mL}$  polystyrene (MW 32 600) in THF to improve the mechanical stability of the film. SEM showed that this method produced compact zeolite films one to two particles thick as reported by Li et al.<sup>9</sup> Electrodes were stored in the dark until required for use. Electrochemical measurements were recorded with a PAR 273A (EG&G) potentiostat. Chronoamperometry was carried out in aqueous solutions of 1 M  $\text{NaNO}_3$  (Aldrich). Prior to measurements, the electrolyte solution was purged with oxygen-free nitrogen. During chronoamperometry, the zeolite-modified electrodes were biased at a cathodic potential of  $-900$  mV with respect to the Pt wire quasi-reference electrode. To collect chronoamperometric decays, each electrode was subjected to one pulse program immediately following immersion in the electrolyte solution. Current decays were directly collected in digital form. The data were then processed using Origin 4 (Microcal Software, Northampton MA) and then either fit to eq 3 (see text) or directly compared to the output of the simulation program (vide infra).

**Simulation.** Using the finite difference method<sup>10</sup> to simulate the cation motion in zeolite Y, the flux from small to large channels was calculated from

$$-d[\text{Ag}^+(\text{sc})]/dt = k_f[\text{Ag}^+(\text{sc})][\text{Na}^+(\text{lc})] - k_b[\text{Ag}^+(\text{lc})][\text{Na}^+(\text{sc})] \quad (1)$$

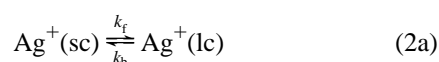
where sc and lc refer to small and large channels, respectively. Note that  $k_f[\text{Na}^+(\text{lc})]$ , the pseudo-first-order rate constant ( $k'_f$ )

has been previously determined in our laboratory as  $0.87 \text{ s}^{-1}$ ,<sup>7</sup> and this value is used in the simulation below.

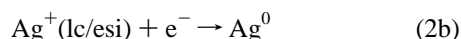
Dissection of the zeolite particle into discrete volume elements in the simulation was based on the connection between the large and small channels in zeolite Y. The unit cell was treated as a cubic box of side  $24.7 \text{ \AA}$ , with an attached "small" box. X-ray diffraction techniques have not detected large channel silver in low loading silver zeolite Y,<sup>11,12</sup> so for the purposes of the simulation, the equilibrium between silver cations was taken to lie far toward the small channel species using  $([\text{Ag}^+(\text{lc})]/[\text{Ag}^+(\text{sc})]) = 1/20$ . The concentration of sodium in the small and large channels was set constant during the potential bias, which is reasonable at the low silver ion exchange levels used, in going from 52.9 to 56  $\text{Na}^+$  per unit cell, for a fully depleted silver ZME. This is upheld by the XRD data.<sup>11</sup> In Table 1 of this reference the ratio of located small to large channel sodium cations is 1.8 for  $\text{NaY}$  and 1.6 for  $\text{Ag}_2\text{Y}$ . The flux of silver cations at the electrode surface will actually be the sum of the fluxes from the outermost supercage and the outermost sodalite cage. For simplicity, the diffusion coefficient for small channel silver was set to zero in the simulation since the ratio  $D(\text{large channel})/D(\text{small channel})$  is extremely large.

### Theory: CE Reactions and ZMEs

Redox via extrazeolite electron transport necessitates the passage of intrazeolite  $\text{Ag}^+$  through the zeolite pores together with coupled counteremotion of electrolyte cations, as in binary ion-exchange. For  $\text{AgY}$  this can be treated using the formalism first developed by Brown, Sherry, and Krambeck,<sup>13,14</sup> which has also been applied to ZMEs.<sup>8</sup> Silver cations placed in the small channel system must undergo coupled first-order and diffusive processes in order to exit the zeolite, or reach the electrode solution interface as shown in eqs 2a and 2b.



and



where esi is the electrode–solution interface. Step 2b above indicates that the supply of silver cations at the esi is via diffusion through the supercages. Small channel silver cations can be considered to be diffusionally immobile (within the small channels) due to the steric constraints of the hexagonal prisms that join adjacent sodalite cages. However they can enter the large channels via a common six-ring, whereupon diffusion is facile.

The electrochemical process described in eq 2 (i.e., an electrochemical reaction preceded by a chemical reaction) is referred to as a CE reaction. A solution has been given by Koutecký and Brdička.<sup>15</sup> For equal diffusion coefficients of small and large channel silver cations, the instantaneous current is given by

$$i = i_0 \exp[\beta^2 t] (1 - \text{erf}[\beta t^{1/2}]) \quad (3)$$

where  $\beta = (Kk_f)^{1/2}$ ,  $i_0 = nFAD^{1/2}C\beta$ .  $C$  is the total  $\text{Ag}^+$  concentration.

This solution pertains only when semi-infinite diffusion occurs. Thus in the case of the ZME the diffusion layer must not cross the zeolite particle.

It is unusual in a CE process for the interchanging species to have substantially different diffusion coefficients. The solution

was afforded by Eddowes and Grätzel.<sup>16</sup> Here an effective diffusion coefficient ( $D_{\text{eff}}$ ) replaces  $D$  in eq 3 such that

$$D_{\text{eff}} = \frac{D(\text{sc})[\text{Ag}^+(\text{sc})] + D(\text{lc})[\text{Ag}^+(\text{lc})]}{[\text{Ag}^+(\text{sc})] + [\text{Ag}^+(\text{lc})]} \quad (4)$$

where  $D(\text{sc})$  and  $D(\text{lc})$  are diffusion coefficients for small and large channels, respectively.

When the rate of the chemical reaction is fast enough compared to diffusion to maintain the equilibrium concentrations of  $\text{Ag}^+(\text{sc})$  and  $\text{Ag}^+(\text{lc})$ , this reduces to

$$D_{\text{eff}} = \frac{D(\text{sc})K + D(\text{lc})}{1 + K} = D(\text{lc})/(1 + K) \quad \text{as } D(\text{sc}) \rightarrow 0 \quad (5)$$

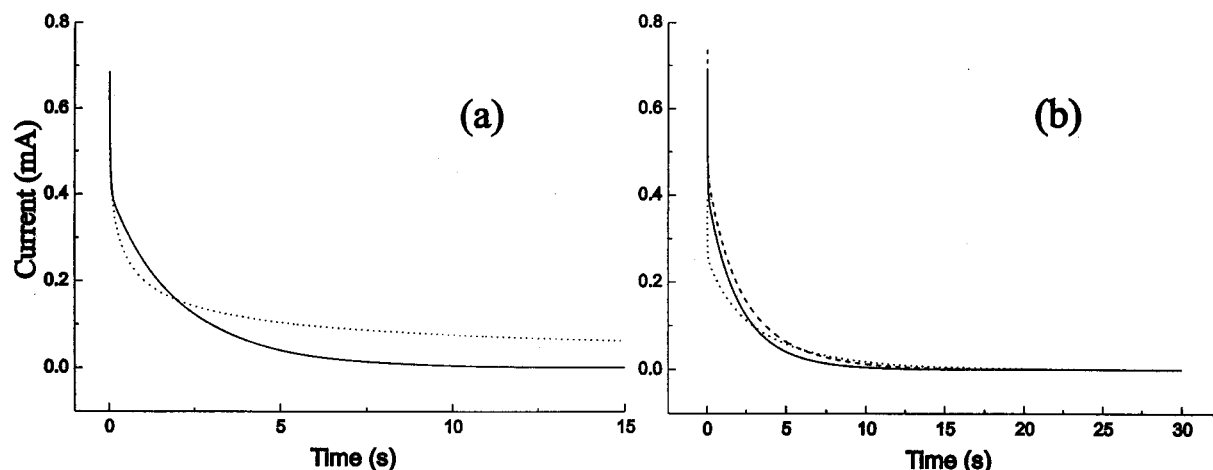
This expression can hold for the ZME only at short times (before semi-infinite diffusion stops). Also the cation distribution must be at equilibrium at all times. Otherwise the effective diffusion coefficient will be space and/or time dependent and no analytical solution will exist.<sup>16</sup>

### Results and Modeling: Chronoamperometry of $\text{Ag}_{3.1}\text{Y}$

Assuming that small and large channel silver maintain equilibrium concentrations throughout the CA experiment is invalid. A comparison of the ZME chronoamperometry with the analytical CE solution (eq 3) is shown in Figure 1a. The fit is poor at short and long times.

The charge passed during the 30 s following the potential bias to the  $\text{AgY}$  sample shown in Figure 1 is equal to 1.4 mC. Using the known cation exchange capacity for zeolite Y and the mass of zeolite per electrode, this indicates that 100% of the silver present in the coating is reduced during the potential bias. The diffusion layer of the silver cation thus extends completely across the zeolite particles which have a mean diameter of  $1 \mu\text{m}$  from SEM measurements. Using the diffusion layer length,  $\delta$ , as given by Galus<sup>17</sup> (i.e.,  $\delta = \sqrt{D\pi t}$ ), we can estimate  $D$  by approximating  $\delta$  to the particle diameter and estimating the time taken for 50% of the silver cation to react. This gives  $D$  as approximately  $10^{-8} \text{ cm}^2/\text{s}$ , which is in reasonable agreement with the simulated value. Several fits with experiment are shown in Figure 1b, for  $k_f' = 0.87 \text{ s}^{-1}$  and  $K = 1/20$ . Since the value of  $K$  is not known accurately, the fits were not refined by allowing  $K$  and  $D$  to vary. Rather, the fits were judged visually for a fixed value of  $K$ , only varying  $D$ . Representative fits for  $D = 2 \times 10^{-8}$  and  $4 \times 10^{-8} \text{ cm}^2/\text{s}$  are given. The fit for the larger diffusion coefficient gave a standard deviation of the residuals (i.e., the difference between experimental and simulated curves of 0.012 mA). Note that the fit is very sensitive to the simulation diffusion coefficient. As the value of  $D$  is increased, the initial current is larger (i.e., the flux of silver at the esi is increased); however this depletes the particles of silver, resulting in smaller currents (compared to simulations with smaller values of  $D$ ) at longer times. The fits were not judged at times longer than 30 s since the zeolite is essentially fully depleted of silver. Note that semi-infinite diffusion is not occurring for a significant portion of the current decay since the diffusion layer crosses the zeolite particles in a few seconds (the exact time will of course depend on the magnitude of the diffusion coefficient).

In the analytical solution given by eqs 3 and 4, the measured diffusion coefficient is smaller than the true diffusion coefficient. In the case where the diffusion coefficient of  $\text{Ag}^+(\text{sc})$  is zero, then  $D_{\text{eff}} = D(\text{lc})/(1 + K)$ . Measurements of diffusion coef-



**Figure 1.** (a) Experimental chronoamperometry for Ag<sub>3.1</sub>Na<sub>52.9</sub>Y (—) and analytical (···) (i.e., using eqs 3 and 4)  $i$  vs  $t$  curve for a solution-phase CE reaction. The poor fit at longer times is caused by the violation of the semi-infinite diffusion condition and nonequilibrium of the zeolite cation composition during the electrochemical bias. (b) Experimental chronoamperometry for Ag<sub>3.1</sub>Na<sub>52.9</sub>Y (—) and simulated  $i$  vs  $t$  curves for ZME CE reaction. Simulation parameters:  $K = (k_f/k_b) = 1/20$ ,  $k_f' = 0.87 \text{ s}^{-1}$  (see ref 7). Experimental conditions: electrolyte solution 1 M NaNO<sub>3</sub>, bias potential  $-900 \text{ mV}$ . Simulation diffusion coefficients:  $4 \times 10^{-8} \text{ cm}^2/\text{s}$  (---) and  $2 \times 10^{-8} \text{ cm}^2/\text{s}$  (···).

ficients by fitting experimental data to eq 3 therefore result in the determination of an effective diffusion coefficient. Unless  $K$  is known, the true diffusion coefficient cannot be determined.<sup>18</sup> The diffusion coefficient that can be determined from the simulation is the true intrazeolite silver–sodium counter diffusion coefficient. The exact magnitude cannot be assessed unless  $K$  is known exactly, which will require more accurate XRD determinations.

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