Spatiotemporal Mapping of Diffusion Layers Using Synchrotron Infrared Radiation

Michael J. Lardner a, Kaiyang Tu a, Scott M. Rosendahl a,b,c, Ferenc Borondics b, Ian J. Burgess a,*

a Department of Chemistry, University of Saskatchewan, S7N 5C9, Saskatoon, Saskatchewan, Canada
b Canadian Light Source, S7N 0X4, Saskatoon, Saskatchewan, Canada
c Department of Chemistry and Chemical Biology, McMaster University, L8S 4M1, Hamilton, Ontario, Canada

A R T I C L E I N F O

Article history:
Received 10 July 2014
Received in revised form 23 October 2014
Accepted 28 October 2014
Available online 30 October 2014

This work is dedicated to Professor Jacek Lipkowski on the occasion of his 70th birthday and in recognition of his many contributions to electrochemistry.

Keywords:
synchrotron infrared radiation
diffusion layers
diffusion coefficients
errocyanide/ferrocyanide
thin-layer cell diffusion
finite element simulation

A B S T R A C T

Synchrotron infrared (SIR) radiation has been employed to map the diffusion layer surrounding a platinum working electrode. A thin-cavity transmission cell containing a raised, 12 μm platinum working electrode is employed to generate a two-dimensional diffusion space. The use of a prototypical redox system, i.e. the diffusion controlled reduction of ferricyanide (Ox) and concurrent production of ferrocyanide (Red), allows for a proof of principle evaluation of the viability of SIR for simultaneous mapping (in time and space) of the concentrations of species in the diffusion layer. Diffusion coefficients for the two species in the redox couple are extracted by comparing the experimental results with numerical simulations using finite elements. Absolute values of $D_{\text{Ox}} = 4.3 \times 10^{-6}$ cm$^2$ s$^{-1}$ and $D_{\text{Red}} = 3.6 \times 10^{-6}$ cm$^2$ s$^{-1}$ have been obtained which are systematically lower by about 30% than those independently determined from electrochemical measurements in the 0.1 M NaF supporting electrolyte. However, their ratio is in excellent agreement with accepted values. Deviations are attributed to heterogeneity in the SIR beam’s intensity profile as well as difficulties in accurately accounting for the working electrode’s pronounced edge effects. Implications for future IR spectrotlectrochemical studies of chemical reactions in electrochemically generated diffusion layers are discussed.

1. Introduction

The high brilliance of mid-infrared radiation generated from a synchrotron provides a unique opportunity to map vibrational modes with near diffraction limited resolution [1–3]. Applications of synchrotron infrared radiation (SIR) are primarily motivated by spatially resolved mapping of materials and surfaces, with subcellular imaging of biological systems being a particularly noteworthy example [4–6]. In recent years, this group has used SIR to explore the temporal evolution of diffusion controlled electrochemical reactions [7,8] using a customized transflectance spectroelectrochemical cell [9]. Critically, we have shown in proof of principle studies that SIR provides sufficient photon throughput to allow the measurement of femtosecond quantities of electro-generated species produced/consumed at an ultramicroelectrode with microsecond time resolution [7]. Concurrent with our ongoing efforts to perform SIR spectroelectrochemistry at the RC time constant limit of an ultramicroelectrode, new strategies are being developed to use SIR to extract diffusion coefficients and rate constants for homogenous chemical reactions occurring in the diffusion layer created by a preceding electrochemical step. Pruiksma and McCreery first reported the use of optical absorption spectroscopy to map the spatiotemporal changes near an ultramicroelectrode nearly 35 years ago [10]. More sensitive spectroscopic and probe techniques have been developed since then. Amatore and co-workers have previously demonstrated that mechanistic insights into chemical reactions preceded by an electrochemical conversion can be obtained using confocal Raman microspectroscopy [11] and fluorescence spectroscopy [12] to map dynamic concentration profiles of reactants, intermediates and products. The high spatial resolution and sensitivity of scanning electrochemical microscopy (SECM) has also been applied for similar purposes [13,14]. However, these techniques are limited by the fact that they are only sensitive to a small class of redox molecules i.e. optical methods such as absorption or fluorescence

http://dx.doi.org/10.1016/j.electacta.2014.10.145
0013-4686/$ - see front matter © 2014 Elsevier Ltd. All rights reserved.
spectroscopy require that the species being interrogated contain a suitable chromophore and away from mettal surfaces, high sensitivity Raman spectroscopy can only be achieved if the probe molecule has an electronic transition resonant with the high power excitation source (resonant Raman effect). Similarly, SEC requires the formation of redox-active intermediates and products. IR spectroscopy is much more universal, requiring neither extended delocalization of electrons nor redox activity, and SIR microspectroscopy can provide comparable spatial resolution to SEC measurements. The recognition that spatiotemporal mapping of active catalysts provides new information on heterogeneous surfaces has sparked increasing interest in using spectroscopic techniques to follow reaction kinetics with spatial resolution exceeding the length scale of the active catalyst [15]. For example, synchrotron sourced soft x-ray imaging and spectromicroscopy techniques have been used to follow temporal changes during metal deposition [16,17], reactions within electrodeposited polyners [18,19] and mass-transport phenomena in fuel-cells [20,21]. Recently, vibrational imaging of heterogeneous catalysts such as zeolites [22,23] and even microreactors under operating conditions [24] have been reported demonstrating that synchrotron infrared radiation is a powerful tool for mapping the spatiotemporal dependence of chemical reactions.

In this work we report upon our initial efforts to use a modified spectroelectrochemical cell to perform transmission SIR measurements of an evolving diffusion front produced by the reduction of solution-based ferricyanide at a platinum electrode. Particular emphasis is placed on the effect of the beam profile, geometry of the cell, and the influence of aperture settings on the quality of the IR signal. Numerical modelling (finite element in space and finite differences in time) of the diffusion controlled reaction allows for comparison of experimental data to the predicted response and offers insight into the optimization of future design parameters.

2. Experimental

2.1. Reagents and Solutions

Potassium ferricyanide (K₃Fe(CN)₆ ≥ 99.0% trace metals basis) and potassium ferrocyanide (K₄Fe(CN)₆ · 3H₂O, ≥ 99.95% trace metals basis) and sodium fluoride (NaF ≥ 99.98%) were purchased from Sigma–Aldrich and used as received. All solutions were prepared using Milli-Q water (≥ 18.2 MΩ cm⁻¹). All electrolytes used in the IR spectroelectrochemical studies were composed of 10 mM K₃Fe(CN)₆ and 0.1 M NaF.

2.2. In-situ spectroelectrochemistry

The three electrode flow-through in situ spectroelectrochemical (SEC) cell was modified from our previous transfectance SEC cell [9] to allow for use in transmission mode. The main body of the cell is composed of PVC with an inlaid 1 cm x 1 cm x 0.2 cm CaF₂ window (Crystran, UK). A conventional three electrode arrangement consisting of a 12 μm thick Pt foil working electrode (WE), a 0.6 mm Pt wire counter electrode and a 0.25 mm silver wire was used as the reference electrode. As shown in Fig. 1, the Pt foil covered half of the lower CaF₂ window and both its edge and top surface were electroactive. Transmission IR measurements were made at varying distances from the electrode’s raised edge. A thin cavity was produced by sandwiching a nominally 25 μm thick PTFE gasket between the cell and an upper CaF₂ window (25 mm diameter, 1 mm thickness). The actual window-to-window and Pt-to-window thicknesses were determined from the interference fringes observed in the empty cell.

Cyclic voltammetry and double-step chronoamperometry experiments were performed using custom software written in LabView (National Instruments, USA) and a HEKA PG 590 potentiostat. Precise synchronization of the potential step and the time-resolved IR collection was achieved using a National Instruments USB 6351 X-series multifunction data acquisition card.

2.3. FT-IR Measurements

Fourier-transform infrared measurements were collected using the 01B1 mid-IR beamline facilities at the Canadian Light Source. The end station consists of a Bruker 70 V spectrometer coupled to a Hyperion 3000 IR microscope. The IR light was focused using a 15x objective and measured either with a narrowband 100 μm mercury cadmium telluride (MCT) detector or a 64 x 64 pixel focal plane array with a pixel resolution of 2.7 μm. All time-resolved measurements were collected with a mirror velocity of 80 kHz and a resolution of 4 cm⁻¹ resulting in a minimum time resolution of ~0.25 sec. Each rapid scan experiment consisted of 10 interferograms collected at the reference potential of +0.50 V, which were averaged and used as the reference spectra, followed by the collection of 40 individual interferograms after the potential step to -0.50 V. For each beam position, IR measurements over 256 replicate double-potential step sequences were collected and averaged.

2.4. Linear Sweep Voltammetry

CV studies of ferricyanide and ferrocyanide were performed using a HEKA PG590 potentiostat and its independently calibrated voltage scan generator. Measurements were made in an all glass cell, with a gold counter electrode and an external Ag/AgCl in saturated KCl reference electrode connected to the main cell via a salt bridge. The working electrode (BASI) was a 3 mm diameter gold wire embedded in a polymer resin. The electrode was mechanically polished, washed with Milli-Q water, and then electrochemically cleaned in a separate cell containing 0.5 M H₂SO₄. To ensure a constant working electrode area, this cleaning procedure was not repeated when switching between the 0.10 M NaF and 0.10 M KCl electrolytes. Independent measurements were made for each supporting electrolyte and each half of the ferri/ ferrocyanide redox couple. The concentration of the redox species was 1.0 mM. Electrolytes were extensively degassed with argon and a very weak overpressure of argon was maintained above the electrolyte during the voltammetry to minimize oxygen reduction currents without causing convection. The initial potential was biased positive (negative) of the formal potential when the redox active species in the electrolyte was ferricyanide (ferrocyanide). After a single linear sweep, the potential was stepped back to the initial value and the electrolyte was stirred and allowed to return to a quiescent state before the measurement was repeated. Triplicate
measurements of the peak currents were made for each sweep rate.

3. Results and Discussion

3.1. Numerical Simulations

Upon the application of a significantly large enough overpotential, and in the absence of convection and migration, a diffusion controlled flux of redox species is generated at the electrode surface. As the thickness of the diffusion layer is a function of both time and space, time-resolved SIR mapping of the solution volume around the working electrode provides a means of characterizing an evolving diffusion profile. The IR transmission cell described above allows an aperture-defined IR beam to interrogate the volume of solution at variable distances from the edge of the working electrode. An optimal geometry would also provide a simple diffusion space, readily amenable to known solutions of Fick’s second law, so that experimental results could be compared to theoretical concentration profiles of the diffusing species. However, optical requirements preponderate and in the current design force a cell geometry that mandates the use of numerical methods to model the temporal evolution of the two-dimensional diffusion space in the vicinity of the Pt electrode. The diffusion problem was simulated using commercial software (FlexPDE) that applies finite elements to model space and finite differences to model time. The system used to numerically solve the diffusion problem consisted of a two-dimensional Cartesian coordinate geometry, with the modeled spatial dimensions being normal to the top (z) and edge (x) surfaces of the platinum working electrode. Dimensionless variables were used with the following definitions

\[ C_{\text{OX}} = \frac{c_{\text{OX}}}{c_{\text{OX}}^*} \]  
\[ C_{\text{RED}} = \frac{c_{\text{RED}}}{c_{\text{OX}}^*} \]  
\[ T = tD_{\text{OX}}/h^2 \]  
\[ X = x/h \]  
\[ Z = z/h \]  
\[ W = w/h \]  
\[ D = D_{\text{RED}}/D_{\text{OX}} \]

where subscripts OX and RED refer to the oxidized and reduced species and \( t, D, c, w, \) and \( h \) are the time, diffusion coefficient, concentration, width of the electrode along the x-direction, and the thin-layer cavity thickness, respectively. Concentrations are normalized by the initial concentration of the oxidized species, \( c_{\text{OX}}^* \). As the known diffusion coefficients of the ferricyanide and ferrocyanide ions differ by roughly 15%, two reduced variable diffusion equations are necessary:

\[ D \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial z^2} \right) C_{\text{OX}} = \frac{\partial C_{\text{OX}}}{\partial T} \]  
\[ D \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial z^2} \right) C_{\text{RED}} = \frac{\partial C_{\text{RED}}}{\partial T} \]

The imposed boundary conditions are summarized in Table 1. The modeled space is presented in Fig. 2 and extended to \( X = 150 \) to ensure semi-infinite conditions were maintained. Empirically, it was found that the reduced width, \( W, \) of the Pt electrode used in the numerical solution did not change the numerical solution as long as \( W \geq 2. \) The distribution of the supporting electrolyte ions was not modelled as it was assumed that their concentration gradients affected neither the evolving diffusion profiles of the redox pair, nor the IR beam path (vide infra).

Fig. 3 shows the distribution of electrogenerated \( \text{Fe(CN)}_{6}^{4-} \) (normalized concentrations determined by numerical simulation) in a cross-section of the cell in the near electrode vicinity at three different times after the step to negative potentials. The diffusion layer growth in the Z direction initially dominates (Fig. 3a). With increasing time, the volume of electrolyte above the platinum working electrode becomes increasingly exhausted of \( \text{Fe(CN)}_{6}^{4-} \) and the isconcentration lines ‘wrap around’ the electrode’s edge and begin to extend further along the X-direction (Fig. 3b). After approximately two seconds, the diffusion zone is essentially invariant with time above the working electrode but continues to grow in the direction orthogonal to the electrode’s edge. At this stage, the diffusion is largely linear in nature as evidenced by the concentration distribution shown in Fig. 3c. The dotted outlines in Fig. 3 represents the cross-section of the SIR beam focused to a 10 \( \mu \text{m} \) spot [25] at a variable distance from the Pt edge.

3.2. Influence of Beam Profile and Aperture Settings

Fig. 3 reveals that the evolving diffusion layers are heterogeneous in both the X and Z directions. As the intensity distribution of IR light within the volume of electrolyte being interrogated may significantly affect the measured experimental response it is useful to measure the focused SIR beam itself. As reported by May et al., the radiation at 01B1 at the CLS is actually composed of two, closely spaced beams each with a roughly Gaussian intensity profile [26,27]. The focal spot size of SIR is frequency dependent due to diffraction effects and it is more convenient to work with a slightly defocused beam. The beam profile used for these experiments at 2000 cm\(^{-1}\) was acquired using a focal plane array after transmission through the electrolyte filled electrochemical cell and is shown in Fig. 4. This image is a map of the maximum transmission beam intensity as the solution did not contain either half of the

<table>
<thead>
<tr>
<th>Boundary/region in Fig. 2</th>
<th>Description</th>
<th>Boundary/Initial conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Electroactive edge of Pt electrode</td>
<td>for ( T &gt; 0 ) ( c_{\text{OX}} = 0 ) ( nA\left[Dc_{\text{OX}}\right]_R = 0 )</td>
</tr>
<tr>
<td>b</td>
<td>Electroactive edge of Pt electrode</td>
<td>for ( T &gt; 0 ) ( c_{\text{OX}} = 0 ) ( nA\left[Dc_{\text{OX}}\right]_R = 0 )</td>
</tr>
<tr>
<td>c</td>
<td>Bottom CaF2 window</td>
<td>( nA\left[Dc_{\text{OX}}\right]<em>R = 0 ) ( nA\left[Dc</em>{\text{OX}}\right]_R = 0 )</td>
</tr>
<tr>
<td>d</td>
<td>Far edge of diffusion space</td>
<td>( c_{\text{OX}} = 1 ) ( c_{\text{OX}} = 0 )</td>
</tr>
<tr>
<td>e</td>
<td>Top CaF2 window</td>
<td>( nA\left[Dc_{\text{OX}}\right]<em>R = 0 ) ( nA\left[Dc</em>{\text{OX}}\right]_R = 0 )</td>
</tr>
<tr>
<td>f</td>
<td>Vertical line above the electrode</td>
<td>( nA\left[Dc_{\text{OX}}\right]<em>R = 0 ) ( nA\left[Dc</em>{\text{OX}}\right]_R = 0 )</td>
</tr>
<tr>
<td>g</td>
<td>Body of electrolyte</td>
<td>for ( T &gt; 0 ) ( c_{\text{OX}} = 1 ) ( c_{\text{OX}} = 0 )</td>
</tr>
</tbody>
</table>
redox couple. The profile is highly asymmetric and cannot be described by a simple mathematical function. However, Fig. 4 also shows that blade apertures can be used to select the most intense portion of the profile and limit its heterogeneity. Furthermore, the two dimensional nature of the current problem means that heterogeneity parallel to the electrode’s edge (y-direction) is immaterial but heterogeneity perpendicular to the electrode’s edge (i.e. along the x-direction) causes the reported IR signal to be dominated by subareas of the beam’s projection with “hotter” photon flux. The focused nature of the IR beam means that there is also intensity heterogeneity along the vertical (z-direction) which generates a weighted response that will depend on the beam’s exact focal point and its depth of focus. Superposition of the simulated diffusion space and the apertured IR beam profile reveals that the resulting IR spectra will report on a distribution of concentrations and quantitatively accurate agreement between experimental and simulated results would require complex spatial convolution of the beam’s intensity profile with the diffusion space. While such a rigorous procedure is conceivable, it is beyond the scope of this proof-of-principle study. For our current purposes the IR photon intensity defined by the blade apertures was assumed to be homogenously distributed within the beam profile depicted in Fig. 3c. The error associated with this simplification is highest when the breadth of concentration distribution in both the horizontal and vertical directions is greatest. Fig. 3 reveals that this occurs at early times and small distances from the electrode. However, the error should be significantly less problematic at larger distances due to the increasing linearity of the diffusion front.

![Fig. 2. The caption for this Figure was accidentally omitted from the final manuscript. Thus, all the following figure captions are wrong. I will indicate the correct captions for the figures as annotations to the galleys.](image1.png)

Fig. 2. The simulated diffusion space for the IR spectroelectrochemical cell.

![Fig. 3. Simulated normalized concentration profiles of ferricyanide (Ox) in the thin cavity cell a) 0.1s, b) 1s and c) 10s after a potential step to -0.50V. The vertical (z-direction) dimension is normalized by the window to window distance (40 μm). The full width of the Pt electrode along the x-direction is not shown.](image2.png)

![Fig. 4. Simulated normalized concentration profiles of ferricyanide (Ox) in the thin cavity cell a) 0.1s, b) 1s and c) 10s after a potential step to -0.50V. The vertical (z-direction) dimension is normalized by the window to window distance (40 μm). The full width of the Pt electrode along the x-direction is not shown.](image3.png)
3.3. Time and spatial resolved studies

The infrared signatures of the ferri/ferrocyanide redox couple provide an excellent handle for measuring speciation as the CN stretching vibration blue shifts by ~75 cm⁻¹ upon reduction of the iron(III) complex [28–30]. Fig. 5 shows time-resolved SIR spectra taken after the potential applied to the electrode was stepped from +0.50 V to -0.50 V. Blade apertures were used to isolate a 10 µm x 40 µm spot of the SIR beam with the closest edge of its longer dimension positioned 15 µm from the electrode. The spectra in Fig. 5 are reported as relative changes in absorbance with a reference spectrum taken at the positive potential. The more intense signal arising from the increasing ferrocyanide (Red) signal at 2040 cm⁻¹, compared to the decreasing ferricyanide (Ox) signal at 2115 cm⁻¹, is explained by their well-known differences in molar absorptivity [31]. The signal-to-noise ratio for the 2040 cm⁻¹ band at the longest time is over 400 even though no more than ~200 femtomoles are interrogated by the beam. Additional time resolved experiments were repeated at distances of 30 µm, 45 µm and 60 µm in an effort to map the diffusion space. To compare the experimental data to our numerical modeling, the measured IR signal needs to be converted from a change in absorbance, ΔA, to a change in the normalized concentrations defined by Eqs. (1) and (2) above. The change in absorbance is related to a change in concentration, c, through Beer’s law

\[ \Delta A_{i,t} = \varepsilon_i b [c_{i,t} - c_{i,t-0}] = -\log \frac{I_{\text{step}}}{I_{\text{ref}}} \]

where \( \varepsilon_i \) is the molar absorptivity of species i (i = Red or Ox) at either 2041 cm⁻¹ or 2115 cm⁻¹ respectively, b is the transmission cell path length, \( I_{\text{step}} \) is the time-varying single-beam intensity at -0.50 V and \( I_{\text{ref}} \) is the single beam intensity at +0.50 V. The maximum change in the absorbance of the oxidized species, \( \Delta A_{\text{Ox,max}} \), occurs when the ferricyanide in the volume interrogated by the IR beam has been exhaustively electrolyzed, hence

\[ \Delta A_{\text{Ox,max}} = -\varepsilon_{\text{Ox}} b c_{\text{Ox}}^* \]

Normalized concentrations can be derived by dividing the change in the absorbance for both species by \( \Delta A_{\text{Ox,max}} \)

\[ \frac{\Delta A_{\text{Ox,t}}}{\Delta A_{\text{Ox,max}}} = 1 - \frac{c_{\text{Ox,t}}}{c_{\text{Ox}}} = 1 - C_{\text{Ox,t}} \]

\[ \frac{\Delta A_{\text{Red,t}}}{\Delta A_{\text{Ox,max}}} = \frac{c_{\text{Red,t}}}{c_{\text{Ox}}} = \frac{C_{\text{Red,t}}}{C_{\text{Ox}}} \]

(12)

\( \Delta A_{\text{Ox,max}} \) was determined in a separate static experiment with the beam 15 µm from the electrode edge and the potential was held at the step and reference potentials for several minutes prior to the acquisition of the single-beam spectra. The values of \( \varepsilon_{\text{Ox}} \) and \( \varepsilon_{\text{Red}} \) were taken from our previous SIR studies of the ferri/ferrocyanide redox couple [7].

The concentration transients extracted from the IR are shown in Fig. 6a and b and qualitatively behave as expected, with more rapid and extensive changes in the species’ concentrations occurring for absorption measurements closer to the electrode. More quantitatively this was confirmed through the numerical simulations. The parameters that control the simulated concentration transients are the window to window thickness of the cell, the thickness of the Pt working electrode, the diffusion coefficients of both redox species, and the beam profile. The first two parameters were determined from optical fringes in the empty cell to be 38 µm and 12 µm although the latter value varied for different positions on the Pt surface. Rather than imposing a complicated beam profile, a uniform distribution of photons within a cross-section of the 10 x 40 µm beam was assumed. To illustrate the dependence of the vertical position of the focal point and the depth of focus, the beam profile was divided into five, 10 µm thick (in the Z-direction) slabs. Numerically determined concentrations of Red and Ox within each slab were integrated and averaged resulting in a family of simulated curves (solid lines in Fig. 6) at each beam position.

![Fig. 5. Time-resolved changes in the IR absorbance of ferrocyanide (Red) (peak maximum at 2040 cm⁻¹) and ferricyanide (Ox) (peak maximum at 2115 cm⁻¹) following a potential step to -0.50V. The 10 µm wide beam was positioned 15 µm from the electrode’s edge.](image)

![Fig. 6. Experimental (points) and simulated (lines) concentration transients for a) ferricyanide (Ox) and b) ferrocyanide (Red). Concentrations have been normalized by the initial concentration of Ox. Experiments were performed with the closest edge of the beam 15 µm (squares), 30 µm (circles), 45 µm (up triangles) and 60 µm (down triangles) from the electrode’s edge.](image)
The spread in the family of curves is significant at the 15 um spot but negligible at larger distances.

Our strategy was to adjust the diffusion coefficients of Ox and Red until reasonably good agreement with the experimental transients at 60 μm was reached. The furthest distance from the electrode was chosen for this purpose as convolution of the beam intensity profile with the expanding diffusion layer is much less pronounced at large distances. These diffusion coefficients were then fixed for the simulations for the six other transients. As shown in Fig. 6 a and b good agreement between experiment and simulation for the larger beam-electrode separations were obtained for \( D_{\text{Ox}} = 4.5 \times 10^{-6} \text{ cm}^2 \text{s}^{-1} \) and \( D_{\text{Red}} = 3.6 \times 10^{-6} \text{ cm}^2 \text{s}^{-1} \). Fig. 6 shows that these apparent diffusion coefficients have the poorest fits when the beam is only 15 μm from the electrode edge. However, there is much better agreement for the larger distances. Large deviations from expected concentration profiles close to the electrode have been previously reported when spectroscopic methods were employed for diffusion layer mapping [12] and can be partially explained by the fact that large, electrochemically driven concentration gradients in the electrolyte produce refractive index gradients that cause the beam path to exhibit an angular divergence. However, as this angular divergence is also directly proportional to the path length [32] we expect it to be minimal in the present case. In addition, as anisotropic diffraction effects we suspect that the deviations from the simulated profiles are caused by convolution of the beam intensity profile with the non-linear and rapidly evolving diffusion zone that exists at the working electrode immediately after the potential step. In any event, the experimentally obtained values of the diffusion coefficients are about 40% smaller than the values typically reported for ferrocyanide and ferricyanide in 0.10 M KCl electrolytes [33]. It is well-known that diffusion coefficients display a dependence on temperature and the concentration of the supporting electrolyte but the water-structure breaking or forming nature of the electrolyte can also significantly perturb the transport properties of tracer ions [34]. For example, the diffusion coefficient of ferrocyanide in a strongly water-structure forming electrolyte such as 0.5 M MgSO4 has been reported to be less than 60% of its value in a weakly water-structure breaking electrolyte (0.5 M KNO3) [35]. To determine whether or not 0.10 M NaF perturbs the diffusion coefficients of Fe(CN)64– and Fe(CN)63– from their known values in 0.10 M KCl, a simple voltammetry study was performed in the two electrolytes. According to the Randles–Sevcik equation, the slope of the peak current plotted versus the square root of the scan rate is directly proportional to the diffusion coefficient. Furthermore, if the experiments are performed in the two different 0.10 M supporting electrolytes with identical concentrations of the redox-active species and the same electrode area, the ratio of the slopes will give the ratio of the diffusion coefficients in the two electrolytes. The relative diffusion coefficients, \( D_{\text{NaF}} / D_{\text{KCl}} \) were determined in this fashion and found to be 0.843 ± 0.015 for ferricyanide and 0.861 ± 0.045 for ferrocyanide. Both diffusion coefficients are attenuated by approximately the same extent in 0.10 M NaF but the factor is no more than 17% which cannot fully explain the unexpected sluggish diffusion in our spatiotemporal SIR experiments.

Although the absolute values of the diffusion coefficients obtained herein are systematically low, it is encouraging that the measured ratio, \( D_{\text{NaF}} / D_{\text{KCl}} \), is almost identical to that of both the known values in 0.10 M KCl and the results of our own electrochemical measurements in 0.10 M NaF. The fundamental reason for the measured error in \( D_{\text{NaF}} \) and \( D_{\text{KCl}} \) is not immediately obvious. The fact that the Pt foil working electrode is raised above the CaF2 is particularly problematic as it creates a significant edge effect [36] that may not be accurately modelled in the simulations. It was also not possible to polish the top of the Pt resulting in a slightly corrugated surface and a non-uniform thickness in the electrolyte layer above the working electrode. As a final comment we note that the cyclic voltammetry in the thin-cavity cell was distorted and the CVs seemed less reversible than our previous work with ferro/ferricyanide in similar cells. It is possible that the larger surface area of the electrode and the resistive thin cavity electrolyte results in too large a cell time constant which would hinder the charging of the electrode and significantly perturb the initial temporal development of the diffusion layer. Efforts are currently under way to construct a transmission cell with a smaller working electrode with a geometry more amenable for SIR experiments and numerical simulations.

4. Conclusions

The diffusion zone around a 12 μm thick platinum foil working electrode in a thin-cavity cell has been mapped in space and time using synchrotron infrared radiation. Unlike a conventional source, the high brilliance of SIR allows for excellent signal to noise ratios even when the spot size of the beam approaches the diffraction limit. Simulation of the diffusion problem has been performed with finite element/finite differences software and compared to the experimental data. We have assumed a simple, homogeneous distribution of incident photons within the beam in our simulations even though the beam’s intensity profile is actually irregular. This simplification leads to short time errors when the beam is closest to the electrode edge due to convolution of the rapidly evolving diffusion layer and the true heterogeneity in the beam’s intensity in the direction perpendicular to the electrode’s long axis. The experimental results indicate that the diffusion layers for both the ferrocyanide and ferricyanide species develop more slowly than predicted and reasonable agreement between experiment and simulation could only be obtained by using diffusion coefficients with values smaller than previously reported. This discrepancy is likely caused by geometric factors associated with the Pt working electrode. Nevertheless the ratio of the diffusion coefficients obtained herein is very close to the expected value and reveal that the iron (II) species has more hindered mass transport in the electrolyte. Efforts are currently underway to employ an embedded band electrode and a higher magnification microscope objective to further decrease the spot size of the beam. Although the current case has been limited to a simple redox couple it has been demonstrated that SIR is an excellent probe of the diffusion layer. Unlike competing methods, infrared spectroscopy does not require the electrogenerated species to be resonant Raman active, contain a chromophore, or be electroactive. With planned improvements to the methodology this technique should be suitable to follow fast chemical reactions involving irreversibly electrogenerated species.

Acknowledgments

This work was supported by a grant from the Natural Sciences and Engineering Research Council of Canada (NSERC). The authors would like to acknowledge the expertise of the Physics Machine Shop at the University of Saskatchewan. Research described in this paper was performed at the Mid-IR beamline of the Canadian Light Source, which is supported by the Natural Sciences and Engineering Research Council of Canada, the National Research Council Canada, the Canadian Institutes of Health Research, the Province of Saskatchewan, Western Economic Diversification Canada, and the University of Saskatchewan.
References


[25] The optical aperture of the focusing objective means that the beam is actually convergent with an an angle of incidence of 24°. The beam has a trapezoidal cross section with a bottom width of 10mm.


