

Evidence for diffusional coupling in electrochemical thin layers: implications for surface coverage calibration via electrochemical infrared spectroscopy

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Received: 24 July 2006 / Revised: 16 January 2007 / Accepted: 19 January 2007 / Published online: 23 May 2007
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Abstract The time dependence of the concentration of CO₂ in an electrochemical thin layer cavity is studied with Fourier transform infrared spectroscopy (FTIR) in order to evaluate the extent to which the thin layer cavity is diffusionaly decoupled from the surrounding bulk electrolyte. For the model system of CO on Pt(111) in 0.1 M HClO₄, it is found that the concentration of CO₂, formed by electro-oxidation of CO, equilibrates rapidly with the surrounding bulk electrolyte. This rapid equilibration indicates that there is diffusion out of the thin layer, even on the short time scales of typical infrared experiments (1–3 min). However, since the measured CO₂ absorbance intensity as a function of time is reproducible to within 10%, a new time-dependent method for surface coverage calibration using solution-phase species is proposed.

Keywords Electrochemical infrared spectroscopy · Platinum · Carbon Monoxide · Diffusion

Introduction

Infrared absorbance spectroscopy sheds light on the identity of adsorbed molecules, the nature and site of the adsorbate/surface bond, and even the symmetry of the adsorbed species [1]. When the infrared spectrum of an adsorbed layer is analyzed as a function of adsorbate coverage,

additional insight regarding overlayer structure and inter-adsorbate coupling can be gained [1]. In the past 20 years, this powerful tool of infrared surface spectroscopy has also been applied in electrochemical environments. Infrared spectroscopy at the solid–liquid interface can provide all the above information about adsorbate identity and bonding as well as a wealth of information about the electrochemical double layer and the Stark tuning effect [2].

In electrochemical infrared spectroscopy, it is crucial to minimize the amount of bulk electrolyte in the infrared beam path so as to avoid masking surface features with solvent peaks. One key to minimizing the solvent effect is to perform the experiment with the electrode as close as possible to the infrared transparent window, effectively forming only a very thin layer cavity of solvent between the window and the electrode [3]. This thin layer cavity is believed to be 1–10 μm thick [2]. Early in the development of the electrochemical infrared spectroscopy technique, the mass transport characteristics of ions in the thin layer cavity were explored in order to evaluate how ion migration might affect spectra obtained via electrochemical infrared spectroscopy [3–7]. It was agreed that ion migration was the dominant form of mass transport into and out of the thin layer cavity and that diffusion of dissolved species was negligible on the time scale of the infrared experiments, ~1–3 min [3–7].

The assumption of diffusional decoupling of the thin layer cavity was applied to the problem of estimating the coverage of adsorbed CO on Pt(111) [8, 9]. The adsorbed CO was electro-oxidized to solution-phase CO₂ at which point the absorbance intensity of the $\nu_{as}(\text{CO}_2)$ band was used as a proxy for the original CO coverage. Given that the thin layer cavity was said to be diffusionaly decoupled from the bulk of the solution, there was no concern about changes in the $\nu_{as}(\text{CO}_2)$ band intensity as the experiment progressed (generally ~3 min) [10, 11]. Recently, difficulties in applying

Dedicated to Prof. Dr. Teresa Iwasita on the occasion of her 65th birthday in recognition of her numerous contributions to interfacial electrochemistry.

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the method of CO coverage calculation using the $\nu_{\text{as}}(\text{CO}_2)$ have been noted for a moderate size Pd-covered Pt(111) electrode (4.5 mm) [12]. The rate of diffusion of the CO_2 out of the thin layer cavity was sufficiently rapid such that the intensity of the $\nu_{\text{as}}(\text{CO}_2)$ continually decreased even during very short time intervals [12].

Though it is currently possible to calibrate the CO coverage using highly accurate coulometric procedures and cyclic voltammetry [13–15], these methods are not as convenient as the simple measurement of the $\nu_{\text{as}}(\text{CO}_2)$ of solution-phase CO_2 formed by electro-oxidation of adsorbed CO. In this work, we revisit the question of diffusional decoupling between the thin layer cavity and the bulk electrolyte in order to determine if it is possible to use the solution-phase signal of an electro-oxidized molecule to accurately calibrate the surface coverage of its redox partner. We show that while there is significant short time scale (<3 min) equilibration between species in the thin layer and those in the bulk, if the time dependence of the concentration of the dissolved species is accounted for, it is still possible to calculate surface species coverage with a precision of $\pm 10\%$.

Materials and methods

All experiments were performed at room temperature in a standard electrochemical cell, as described previously [2]. Potentials were measured and reported vs a reversible hydrogen electrode (RHE). The Pt(111) electrode was 10 mm in diameter and ~ 3 mm thick. Prior to each experiment, the Pt(111) electrode was annealed for 10 min in a hydrogen flame and then quickly transferred to a controlled $\text{H}_2(\text{g})/\text{Ar}(\text{g})$ atmosphere where it was allowed to cool for 15 min. The ratio of $\text{H}_2(\text{g})$ to $\text{Ar}(\text{g})$ in the cooling atmosphere was approximately 8:1. After cooling, the Pt(111) electrode was protected with a drop of Milli-Q water in equilibrium with the $\text{H}_2(\text{g})/\text{Ar}(\text{g})$ atmosphere and transferred to the electrochemical cell. This procedure is known to yield a clean, defect-free surface [16].

All spectroscopy experiments were performed in a 0.1 M HClO_4 solution prepared from perchloric acid (Alfa Aesar, 99.9985%) and Milli-Q water. Except during measurements, argon gas (White Martins, 99.9999%) was used to purge the solution of oxygen. A dilute gas mixture of carbon monoxide and nitrogen (White Martins, 5.08% CO , balance N_2) was bubbled into the cell to create the carbon monoxide overlayer. Depending on the rate of bubbling, saturation coverage could be achieved in 3 to 10 min. After exposure to CO , the electrolyte was purged for 10 min with argon before beginning infrared spectroscopy measurements.

The infrared spectroscopy experiments were performed using a Nicolet spectrometer (Model 870, FTIR ESP) and a

liquid nitrogen cooled mercury cadmium telluride (MCT) detector. A prismatic CaF_2 window beveled at $\sim 65^\circ$ was attached to the bottom of the electrochemical cell, and a thin layer was created by pressing the electrode against the window. Spectra were collected at 4 cm^{-1} resolution using the single potential alteration infrared reflectance spectroscopy (SPAIRS) method [17].

The sequence of procedures for the diffusion experiment was as follows: Using the dosing procedure outlined above, a full monolayer of CO was formed on the surface with the electrode potential held at 50 mV. The excess CO was purged from the solution with $\text{Ar}(\text{g})$. The electrode was then lowered to the infrared window forming a thin layer of solution between the electrode and the window. Next, the infrared beam was aligned, and the entire configuration was permitted to equilibrate for 20 min. After this equilibration period, an infrared spectrum was taken with the crystal held at 50 mV. Subsequently, the electrode potential was increased to 1,000 mV for 5 s, a procedure known to oxidize all CO to CO_2 (data not shown). Immediately afterwards, the electrode potential was returned to 50 mV, and another infrared spectrum was taken. Subsequently, a spectrum was taken every minute after the initiation of the first spectrum for a total of 10 min.

Results

The absorbance intensity of the $\nu_{\text{as}}(\text{CO}_2)$ of solution-phase CO_2 , a well-defined peak at $2,343 \text{ cm}^{-1}$, decreases steadily as a function of time after electro-oxidation of a saturated CO overlayer on Pt(111) (Figs. 1 and 2). According to

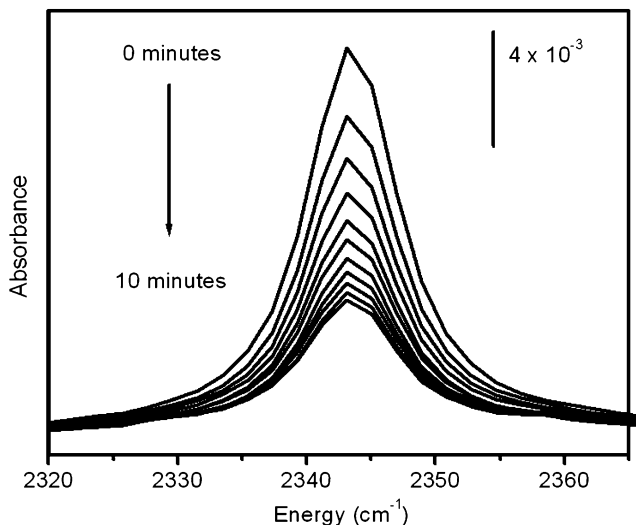


Fig. 1 The $\nu_{\text{as}}(\text{CO}_2)$ region of ten infrared spectra taken after electro-oxidation of a saturated overlayer of CO on Pt(111). The CO dosing voltage was 50 mV vs RHE. Spectra were recorded one per minute after electro-oxidation and were ratioed against the infrared spectrum taken before electro-oxidation

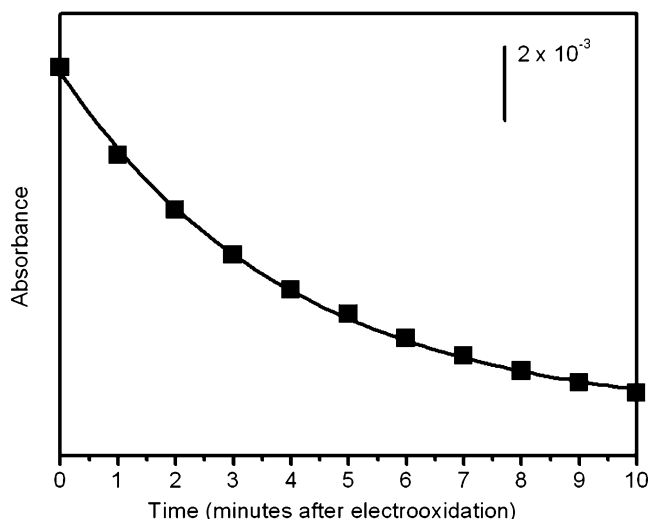


Fig. 2 The absorbance intensity of the $\nu_{as}(\text{CO}_2)$ as a function of time after electro-oxidation of a saturated overlayer of CO on Pt(111)

Beer’s law, the decrease in the absorbance intensity of the $\nu_{as}(\text{CO}_2)$ must correspond to a diminution in the amount of solution-phase CO_2 in the infrared beam path.

In order to confirm that diffusion and not CO_2 reduction to CO accounts for the decrease in CO_2 concentration observed during the present experiment, the infrared spectrum taken immediately after electro-oxidation was ratioed to the infrared spectrum taken 10 min after electro-oxidation (Fig. 3). Since no change was observed in the $\nu(\text{CO})$ region from $2,000\text{ cm}^{-1}$ to $2,100\text{ cm}^{-1}$, reduction is ruled out as a possible explanation for the decrease in the CO_2 concentration. Indeed, while CO_2 can be reduced to CO on polycrystalline platinum at low potentials in acidic media [18], the rate of CO_2 reduction to CO on Pt(111) is over ten times slower than that found for Pt(110) [19].

Since adsorption of CO_2 on platinum surfaces occurs only weakly at 80 K [20], adsorption of CO_2 is also not believed to account for the reduction in the concentration of CO_2 in the thin layer cavity. Reaction of gaseous CO_2 with water to form carbonic acid was also considered as a mechanism by which the amount of CO_2 in the thin layer cavity could decrease. However, the equilibrium constant for formation of carbonic acid from CO_2 and water is only 1.7×10^{-3} [21], meaning that reaction can account for at most a 1% reduction in the amount of CO_2 in the thin layer cavity. Hence, given the absence of reduction, adsorption, and significant chemical reaction, diffusion from the thin layer cavity is the most likely mechanism for the decrease in the absorbance intensity of the $\nu_{as}(\text{CO}_2)$ band.

To confirm that the time-dependent decrease in the concentration of CO_2 in the thin layer cavity is consistent with the concentration decrease expected from diffusion, calculations were performed to simulate diffusion under the conditions of the experiment. Specifically, diffusion from the thin layer cavity was modeled as radial diffusion from a

cylinder. The equation corresponding to the solution of Fick’s laws for diffusion into or out of a cylinder is [22]:

$$\frac{C_{av} - C_f}{C_i - C_f} = \sum_{\nu=1}^{\infty} \frac{4}{\zeta_{\nu}^2} \exp \left[-\zeta_{\nu}^2 D t / r_0^2 \right] \quad (1)$$

where C_{av} is the average concentration at time t . C_i and C_f are the initial and final concentrations in the cylinder, respectively. D is the diffusion coefficient and r the cylinder radius. The ζ_{ν} are the roots of the Bessel function of zero order.

The infinite series solution was truncated at $\nu=6$, and numerical simulations were performed for a cylinder of radius 0.5 cm and heights varying from 1 to 10 μm (note that the dependence of the diffusion on the height of the cylinder is reflected through the initial concentration). The value of the diffusion coefficient was allowed to vary from $1 \times 10^{-5}\text{ cm}^2/\text{s}$ to $1 \times 10^{-4}\text{ cm}^2/\text{s}$. Since $C_f \ll C_i$, it was approximated that C_f can be neglected such that the RHS of Eq. 1 provides an estimate of the time-dependent concentration of CO_2 in the cylinder as normalized by division by the initial concentration. This normalization is important as it allows for direct comparison of the calculated values with the normalized experimental values. For a diffusion coefficient of $5 \times 10^{-5}\text{ cm}^2/\text{s}$, the calculated values of the time dependence of the normalized concentration (C_{av}/C_i) show good agreement with the measured values (Fig. 4). Although $5 \times 10^{-5}\text{ cm}^2/\text{s}$ is somewhat higher than the measured diffusion coefficient for aqueous diffusion of CO_2 , $\sim 1.9 \times 10^{-5}\text{ cm}^2/\text{s}$ [23], the agreement is considered adequate in light of the well-known difficulty of measuring diffusion coefficients [23].

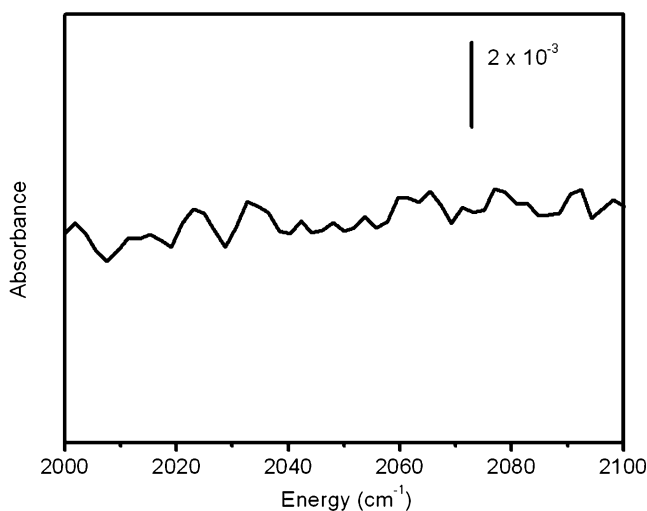


Fig. 3 The $\nu(\text{CO})$ region of the infrared spectrum of a saturated overlayer of CO on Pt(111) taken at 10 min after electro-oxidation ratioed against the infrared spectrum taken immediately after electro-oxidation

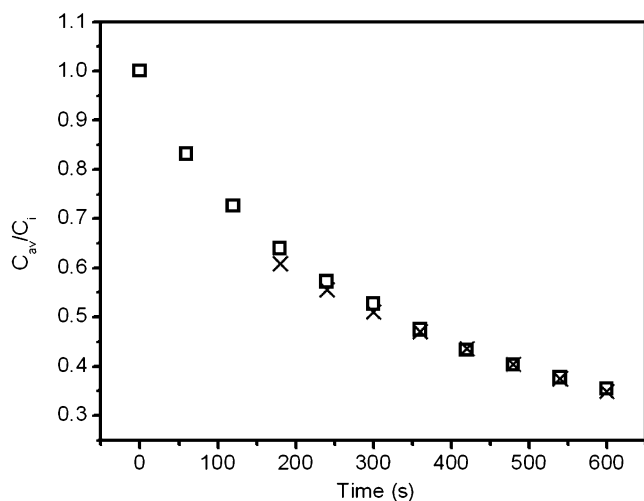


Fig. 4 A comparison of the experimentally observed (*open squares*) and numerically calculated (*crosses*) normalized concentrations of dissolved CO_2 ($C_{\text{average}}/C_{\text{initial}}$) in the thin layer cavity as a function of time after electro-oxidation. Note that for the numerically calculated values, truncation of the infinite series solution at the sixth Bessel root results in underestimation of the normalized concentration for smaller values of time. As such, calculated values are only shown for $t > 180$ s

The amount of CO_2 measured at a given time after electro-oxidation varies slightly from experiment to experiment. This variation may be due to small changes in the timing of the data collection. In all experiments performed, the value of the absorbance intensity recorded 1 min after the initiation of electro-oxidation varies by no more than 10% from the average absorbance intensity recorded at the same time (Fig. 5).

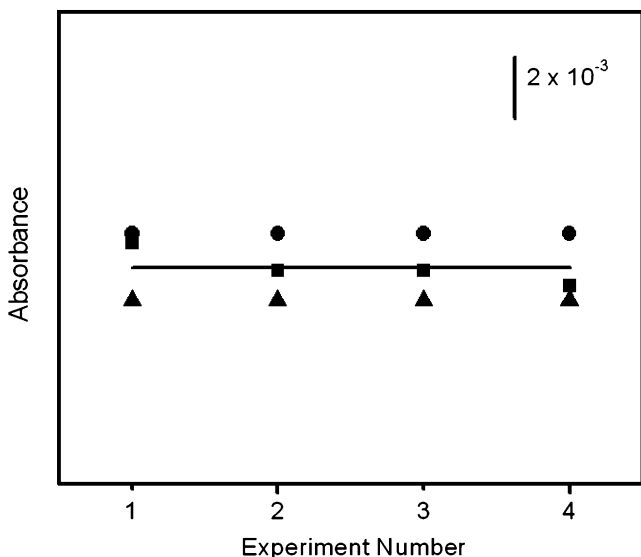


Fig. 5 Four separate measurements of the absorbance intensity of $\nu_{\text{as}}(\text{CO}_2)$ peak recorded at 1 min after electro-oxidation of a saturated overlayer of CO on Pt(111) (*black squares*) as compared to the average of the experimental values (*solid line*) and +10% (*black circles*) and -10% (*black triangles*) of the average experimental value

Discussion

The marked decrease in the $\nu_{\text{as}}(\text{CO}_2)$ as a function of time indicates that the assumption of diffusional decoupling of the thin layer cavity does not hold even for an electrode as large as 10 mm in diameter. Despite the observation that the intensity of the $\nu_{\text{as}}(\text{CO}_2)$ changes over short time scales, it is still possible to use the absorbance intensity of this species to calibrate the relative surface coverage of CO. Given that the value of the $\nu_{\text{as}}(\text{CO}_2)$ absorbance at 1 min varies by no more than 10% of the average 1-min absorbance, a linear coverage calibration curve will associate any given absorbance intensity with a relative CO coverage precise to within 10% (Fig. 6).

It is important to note that a separate calibration curve must be derived for each unique combination of solution-phase species and electrode radius. According to the numerical simulations for diffusion from thin layer cavities, the time-dependent concentration profile will vary markedly as a function of diffusion coefficient and radius size (Fig. 7). However, even for a small electrode ($r=0.2$ cm) and rapid diffusion rate (1×10^{-4} cm^2/s), there is always at least 30% of the original solution-phase species remaining after 1 min, indicating that the coverage calibration method is still possible for these systems.

Though the present observation of significant equilibration between the thin layer cavity and the bulk electrode is in accord with a recent study of CO on a smaller (4.5 mm) electrode [12], it contradicts earlier assertions [3–6] that the thin layer cavity is diffusively decoupled for short time scales. It is not likely that the slower mass transport

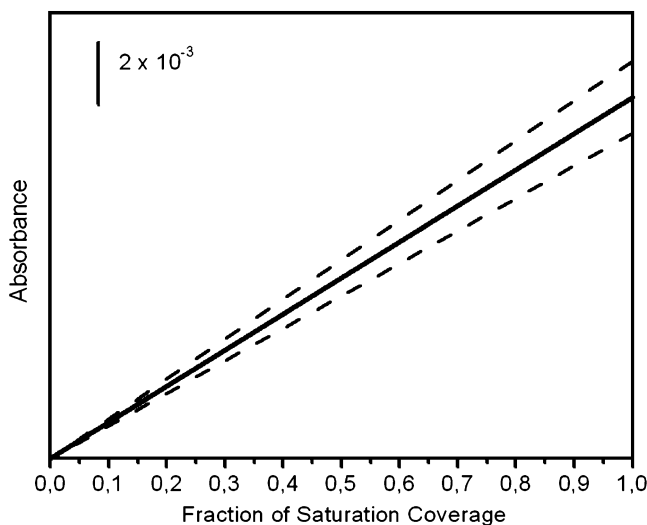


Fig. 6 The coverage calibration curve relating the absorbance intensity of the $\nu_{\text{as}}(\text{CO}_2)$ peak recorded at 1 min after electro-oxidation of CO on Pt(111) to the fraction of CO saturation coverage present before the electro-oxidation. The *dashed lines* represent error bars of $\pm 10\%$

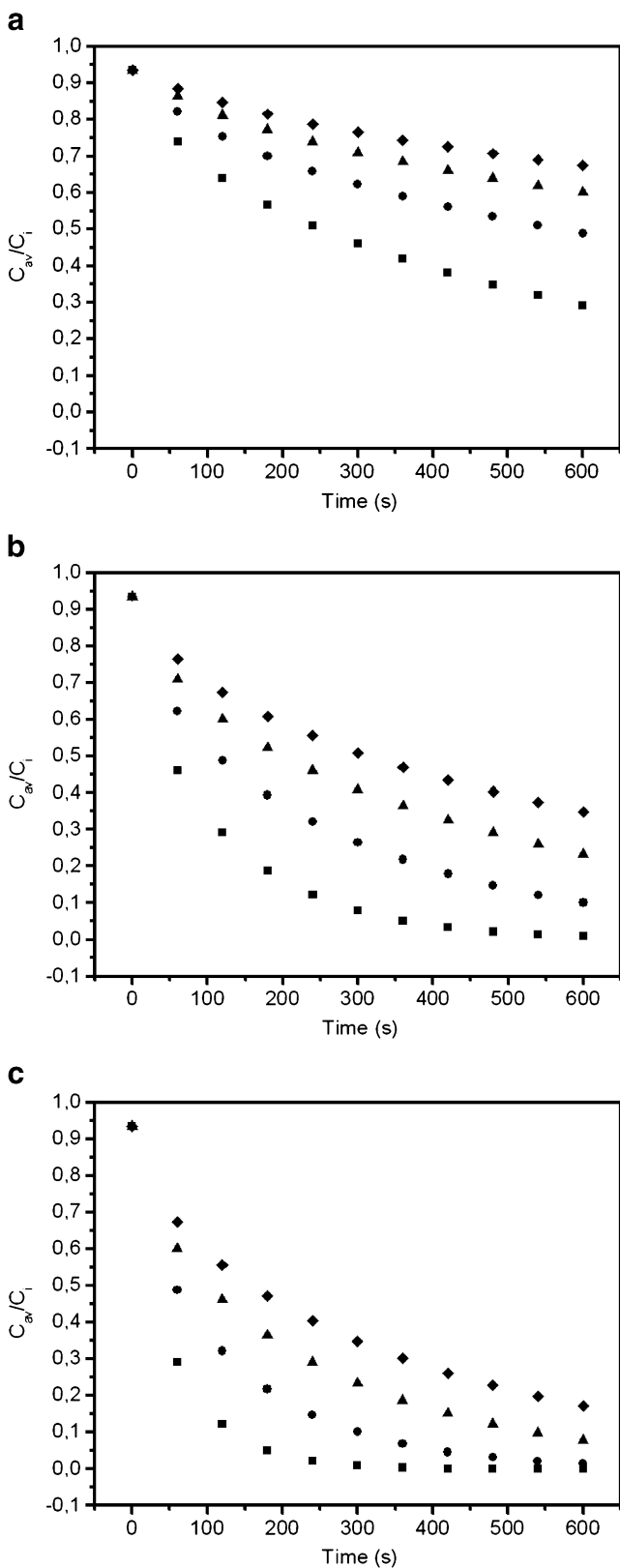


Fig. 7 a–c Time dependence of the calculated values of the normalized concentration ($C_{average}/C_{initial}$) of a dissolved species in a cylinder of radius 0.5 cm (black diamonds), 0.4 cm (black triangles), 0.3 cm (black circles), and 0.2 cm (black squares) assuming that the diffusion coefficient of the species is **a** 1×10^{-5} cm²/s, **b** 5×10^{-5} cm²/s, and **c** 1×10^{-4} cm²/s. Note that the analytical solution of the problem of diffusion out of a cylinder is an infinite series. Truncation of the infinite series results in underestimation of the values of the normalized concentration. This underestimation is negligible for large values of time ($t > 200$ s)

previously [4] observed is due to differences in cavity geometries. The radius of the electrode used in this work was 0.5 cm, comparable in size or larger than the majority of electrodes used in electrochemical infrared studies. The relatively large size of the electrode would favor slower diffusion in this study, not faster (Fig. 7). Further, the numerical model shows that while the height of the cavity will significantly affect the actual concentration of a species in the cavity, it will not significantly affect the rate at which the species diffuses out of the cavity. For a given electrode radius and diffusion constant, the half life of the species in the thin layer cavity is largely invariant to cavity heights from 1 to 20 μm. For an electrode with a radius of 0.5 cm and a species with a diffusion constant of 5×10^{-5} cm²/s, the time required for the concentration of the species in the thin layer cavity to decrease to half its original concentration is approximately 6 min, irrespective of cavity height.

A more likely reason for the relatively rapid equilibration between the thin layer cavity and bulk solution observed in this work is that the present experiment probes the motion of a neutral molecule rather than that of an ion [3–7]. Since the mass transport of an ion depends on both migration and diffusion, it may be that the slower equilibration observed in previous work [4] is due to the retarding effect of an electric field rather than to geometrically hindered diffusion. CO₂ and the ions previously studied (azide, cyanate, and thiocyanate [4]) all have aqueous diffusion coefficients on the order of 2×10^{-5} cm²/s [24]. Thus, CO₂ and the ions previously studied are expected to have the same diffusion characteristics but different ionic migration characteristics.

Conclusions

The assumption of diffusional decoupling of the thin layer cavity from the bulk electrolyte does not hold even for large electrodes and short time scales. The equilibration between the thin layer cavity and the solution-phase species can be modeled numerically by radial diffusion out of a cylinder. The diffusion coefficient calculated by the numerical model is in reasonable agreement with the measured diffusion coefficient for CO₂. Despite the marked time dependence of the solution-phase species concentration in the thin layer

cavity, it is still possible to use the absorbance intensity of the solution-phase species to measure coverage precise to within 10%. The key to reproducible coverage determination is to measure the absorbance of the solution-phase species at a fixed time after electro-oxidation.

Acknowledgments The authors gratefully acknowledge the support of the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP). LJD wishes to thank FAPESP for a postdoctoral fellowship grant under process number 04/03051-6.

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