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Evanescent wave broadband cavity enhanced absorption spectroscopy using supercontinuum radiation: A new probe of electrochemical processes

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ABSTRACT

An evanescent wave variant of broadband cavity enhanced absorption spectroscopy using a supercontinuum light source has been used to detect electrogenerated species at the silica-water interface. In proof-of-concept experiments $[\text{IrCl}_6]^{2-}$ was produced by electro-oxidation of $[\text{IrCl}_6]^{3-}$ in a thin layer electrochemical cell. Diffusion of the Ir(IV) across the cell to a silica interface was monitored yielding real-time concentrations within an evanescent field region at the interface. The optical response was compared with the electrochemical response during chronoamperometric step and cyclic voltammetric experiments and both were simulated by finite element modeling. The experiment is highly sensitive to interfacial processes and its wide spectral width and fast time resolution make it a potentially powerful tool for *in situ* spectroscopic monitoring of processes and intermediates in dynamical electrochemistry.

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1. Introduction

Spectroelectrochemistry has become an essential tool for the investigation of redox processes at electrodes with a diverse range of approaches used to obtain simultaneous spectral and electrochemical information. These approaches include the use of optically transparent electrodes (OTE) [1,2] optically transparent thin layer electrochemical cells (OTTLE) [3,4] long optical path length cells (LOPTLC) [5–8] and cells adapted for reflection spectroscopy [9,10]. The combination of electrochemical methods with infrared attenuated total internal reflection (ATR) spectroscopy has become a standard tool for investigating dynamics at electrodes [11–13]. Recently, evanescent wave cavity ringdown spectroscopy (EW-CRDS), [14–16] which combines the increased path length and high spatial resolution provided by a stable optical cavity, has also been coupled with electrochemical methods [17,18].

There has been a recent surge in efforts to bring the cavity enhanced techniques developed in the gas-phase to bear on condensed phase problems [15,17,19]. One method capable of providing wide spectral information is broadband cavity enhanced absorption spectroscopy (BBCEAS). In its simplest incarnation, CEAS involves injection of light into a high finesse optical cavity.

The time integrated intensity of light passing through the cavity provides a measure of inherent cavity losses and intracavity absorptions. The sensitivity is enhanced by the use of highly reflective cavity mirrors which vastly increases the effective path length (up to several km in gas-phase applications). Although mainly applied to gas-phase problems, BBCEAS has been employed in conventional bulk liquid cells using incoherent sources such as xenon lamps and white diodes [20,21].

This communication describes an evanescent wave variant of BBCEAS (EW-BBCEAS) developed to study electrochemical reactions at a silica-solution interface. The technique is sensitive to absorbing or scattering species present in the 200–500 nm deep evanescent field established beyond the interface whenever light is totally internally reflected. Typically, the time resolution of BBCEAS is limited by the accumulation times required to establish high signal to noise. For these experiments, the speed of data acquisition was increased by incorporating a supercontinuum radiation (SCR) source, providing both high spectral brilliance and extremely broadband wavelength coverage [22–24]. SCR is generated through nonlinear processes upon intense pumping of optical materials. The nonlinear effects are enhanced in photonic crystal fibres (PCFs) [25] and broadband SCR from the blue to the near-infrared is readily generated in PCFs using short laser pulses. The new instrument provides a powerful combination of broadband spectral information coupled with high sensitivity, high spatial resolution and high time resolution.

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By way of demonstration of the EW-BBCEAS technique for electrochemical applications, we report the monitoring of $[\text{IrCl}_6]^{2-}$ generated by electrochemical oxidation of $[\text{IrCl}_6]^{3-}$ in a thin layer cell arrangement [17]. Both potential step (chronoamperometric) and cyclic voltammetric experiments have been performed during which the absorption spectrum within the evanescent field was continuously measured in the region 510–570 nm using EW-BBCEAS.

2. Experimental section

2.1. EW-BBCEAS apparatus

Fig. 1 shows the experimental arrangement. Two highly reflective concave mirrors (M1, M2 Layertec. $R_{550\text{ nm}} > 99.99\%$, 1 m radius of curvature) and a custom fused silica prism are arranged in a folded cavity [19]. The total internal reflection angle is 75 degrees, slightly greater than the silica-water critical angle. A liquid cell within which electrochemical experiments were performed was mounted above the prism.

The optical cavity was filled with broadband light from a commercial SCR source: 5 ps pulselength fiber laser operating at 10 MHz (Fianium SC400) [24]. The output power was 2 W with bandwidth 400–2500 nm. For our purposes, it was spectrally filtered to a bandwidth of 70 nm centered around 535 nm, to match the mirror reflectivities and to avoid saturation of the detector. After filtering, the total optical power was 9 mW. Light escaping through the back mirror (M2) was coupled via an optical multimode fiber into a grating spectrometer (PI Acton SP2300) equipped with a 1340×400 pixel CCD camera (PI Acton Pixis 400B). The signal was typically integrated for 0.5 s.

2.2. Electrochemical measurements

Experiments were performed in a thin layer electrochemical cell arrangement with a circular 2 mm diameter platinum working electrode. The electrode was aligned $150 \pm 10 \mu\text{m}$ above the evanescent field as described previously [17]. To permit cyclic voltammetric and chronoamperometric step experiments, a platinum wire counter electrode was employed with a chlorinated silver wire acting as a quasi reference electrode. The cell contained a solution of 10 mM $[\text{IrCl}_6]^{3-}$ in 0.1 M KNO_3 (aq) (as supporting electrolyte). Electrochemical generation of $[\text{IrCl}_6]^{2-}$ was achieved by stepping the potential from 0.3 to 0.8 V versus Ag/AgCl for various step times (typically 10–120 s) or by sweeping the potential at various scan rates.

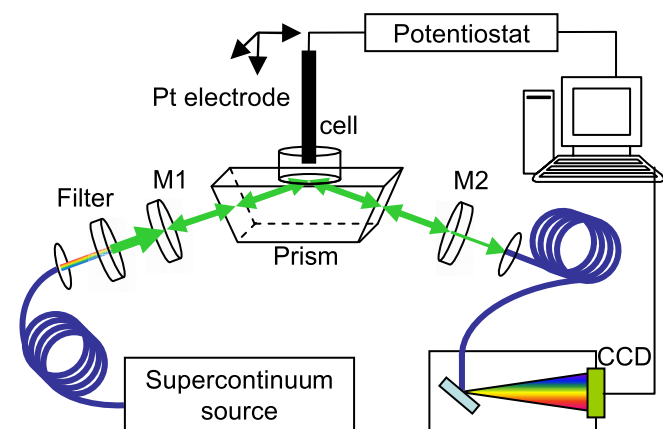


Fig. 1. The broadband evanescent wave cavity enhanced spectrometer employing supercontinuum radiation for detection at the silica-water interface. For clarity only the working electrode is shown.

Fig. 2 shows the UV–vis absorption spectra of 0.5 mM Ir(III) and Ir(IV) solutions. The spectral window for these experiments, limited by filters and mirrors available, was 510–570 nm. The necessary reference spectrum required for CEAS was obtained with pure water and the spectrum of the Ir(III) solution in the cell was recorded before and after each electrochemical experiment to compensate for any drift in the intensity or spectrum of the SCR source.

3. Results and discussion

Fig. 3a shows the evolution of the interfacial absorption spectrum during a chronoamperometry experiment, as the working electrode was stepped for 120 s from 0.3 V to 0.8 V and then to open circuit. The high absorbance below 540 nm matches the Ir(IV) absorption feature (Fig. 2). The Ir(IV) concentration within the evanescent field reaches a maximum after ca. 50 s when all $[\text{IrCl}_6]^{3-}$ in the thin layer cell has been oxidised. After 120 s, the potential was stepped to open circuit and $[\text{IrCl}_6]^{2-}$ diffuses out of the thin layer cell resulting in a slow decay of the interfacial absorbance.

Fig. 3b shows the interfacial spectrum recorded during a cyclic voltammogram in which the potential was swept from 0.3 V to 0.9 V (versus Ag/AgCl) and back at 5 mV s^{-1} . Again, the absorbance increases as the electrode potential is taken in the anodic direction but decreases on the return sweep as the Ir(IV) is actively reduced at the electrode. The optical response trails the electrode potential by a few seconds as the electrochemically generated $[\text{IrCl}_6]^{2-}$ diffuses across the cell into the evanescent field.

To illustrate the quantitative nature of these measurements, Fig. 4a shows the $[\text{IrCl}_6]^{2-}$ concentration, derived from the $\lambda = 520 \text{ nm}$ data, as a function of time during a 120 s potential step experiment. The current was measured simultaneously with the EW-BBCEAS signal and gives information on the mass transport of $[\text{IrCl}_6]^{3-}$ to the electrode. Finite element simulations, performed as described previously [17] were carried out in order to treat mass transport (diffusion) in the thin layer cell arrangement and are in good agreement with the experimental data. The absorbance reaches a plateau after ca. 50 s, once all $[\text{IrCl}_6]^{3-}$ has been oxidized within the thin layer. Fig. 4b shows the time evolution of the interfacial $[\text{IrCl}_6]^{2-}$ concentration during the cyclic voltammogram (0.3–0.8 V versus Ag/AgCl at 5 mV s^{-1}). Again, the simulated transients are in good agreement with the experimental data.

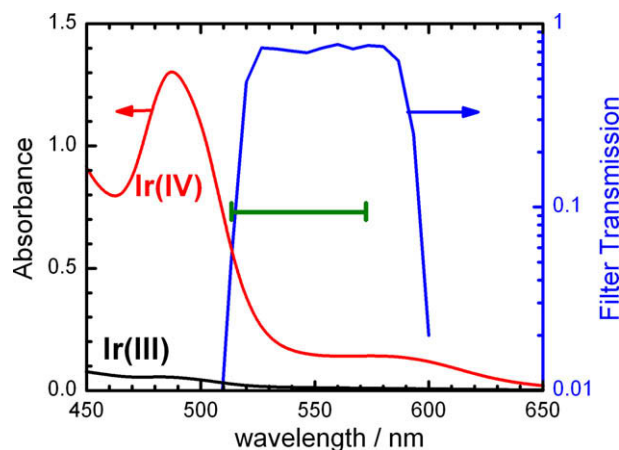


Fig. 2. UV–vis spectra of 0.5 mM $[\text{IrCl}_6]^{3-}$ (black) and $[\text{IrCl}_6]^{2-}$ (red) solutions. The blue curve indicates the spectrum of the filtered supercontinuum radiation and the green line the region of high mirror reflectivity ($R > 0.999$).

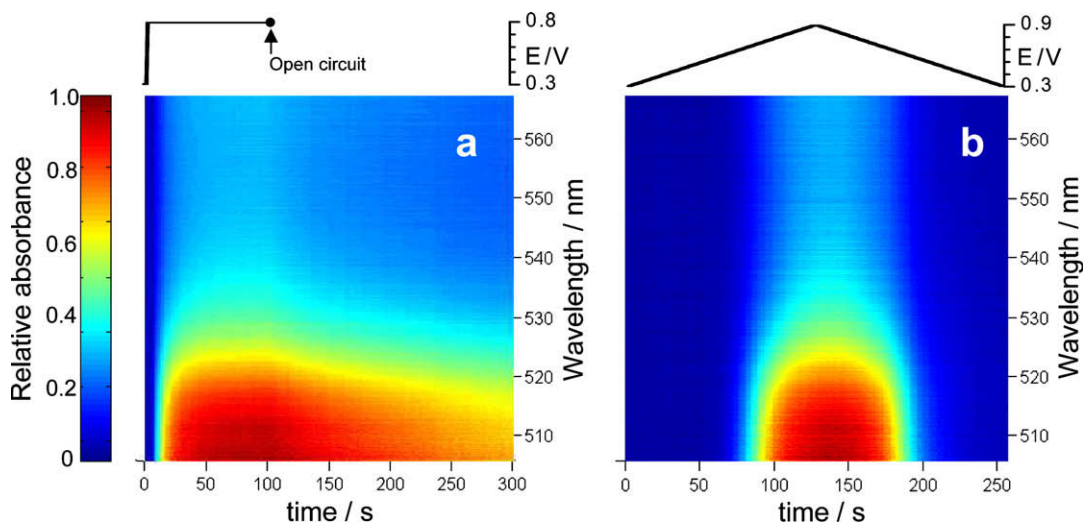


Fig. 3. Contour plots of the interfacial absorption spectra of electrogenerated $[\text{IrCl}_6]^{2-}$ as a function of time during (a) a chronoamperometric step experiment and (b) a cyclic voltammetric experiment.

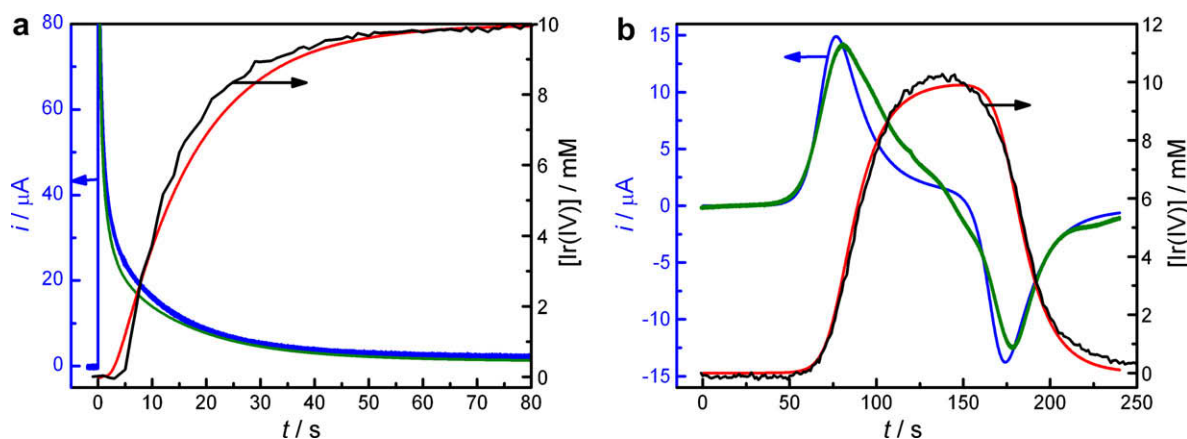


Fig. 4. Measured (black) and simulated (red) interfacial Ir(IV) concentration during (a) a 120 s chronoamperometry experiment (120 s at 0.8 V versus Ag/AgCl), and (b) a cyclic voltammogram (5 mV s^{-1}). The measured (blue) and simulated (green) current transients are also shown.

A detailed analysis of the sensitivity of this method will follow but in this initial demonstration, depending on the wavelength the light undergoes 60–95 round trips of the cavity before the intensity falls by a factor $1/e$. The sensitivity can be estimated [20] in terms of the minimal detectable extinction coefficient, $(\alpha l)_{\text{min}}$, which averages 1.4×10^{-5} over our spectral range with a peak of 6.8×10^{-6} . In our effective path length of ca. $1 \mu\text{m}$ [17] our minimum detectable Ir(IV) concentration for a 0.5 s acquisition is $57 \mu\text{M}$ – equivalent to detecting 5.7 nM Ir(IV) in a conventional 1 cm cuvette in the same time. As with EW-CRDS, the technique will be a particularly sensitive probe of interfacial processes such as adsorption and related phenomena [14,18].

4. Conclusions

We have demonstrated an evanescent wave variant of broadband cavity enhanced spectroscopy which proves to be a sensitive technique for detecting electrogenerated species within a thin layer cell, specifically at interfaces. Use of a supercontinuum radiation source provides a significant multiplex advantage over narrow spectral linewidth experiments by enabling the whole absorption spectrum of species within the evanescent field to be recorded essentially continuously. The high spectral brilliance of

the SCR source yielded acceptable signal to noise ($>100:1$) with 0.5 s accumulation. In turn, the cavity enhancement increases the sensitivity of the instrument through the multiple passes it induces. This powerful combination of broadband spectral information coupled with high spatial and temporal resolution will find a myriad of applications in monitoring surface reactions such as nucleation, dissolution and interfacial charge propagation.

The spectral window accessible in this study was limited to 70 nm by convenient mirrors and filters but we anticipate extension of the wavelength range to the whole of the visible region will be straightforward. In this case it will be necessary to take account of the wavelength dependence of the penetration depth. This will open up many more possibilities of new applications not only in electrochemistry but also in the fields of physics, material sciences and chemical biology.

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