

# 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.

## ***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 takes advantage of the vastly increased path length and high spatial resolution provided by a stable optical cavity, has also been coupled with electrochemical methods.[17, 18]

Significant advantages can be gained in terms of spectral information and speed of data acquisition by coupling the above methods with broadband light sources. In this context, new supercontinuum radiation (SCR) sources with their high spectral brilliance and extremely broad wavelength coverage are of particular interest.[19, 20] SCR is generated through nonlinear processes upon intense pumping of optical materials. The nonlinear effects are enhanced in photonic crystal fibres (PCFs)[21] and broadband SCR from the blue to the near-infrared is readily generated in PCFs using short laser pulses.

There has been a recent surge in attempts to bring the cavity enhanced techniques such as cavity ringdown and cavity enhanced absorption spectroscopy (CEAS) developed in the gas phase, to bear on condensed phase problems.[15, 17, 22] Incoherent Broadband CEAS (IBBCEAS) has already been employed in conventional liquid cells using white diodes.[23, 24] We describe an evanescent wave variant of BBCEAS (EW-BBCEAS) using SCR[20, 25] to study electrochemical reactions using the properties of evanescent field. By way of demonstration, 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 510-570nm using EW-BBCEAS.

## **Experimental Section**

### **EW-BBCEAS apparatus**

Figure 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.[22] 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 fibre laser operating at 10 MHz (Fianium SC400). 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 fibre 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 1s.

### **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  $\text{KNO}_3(\text{aq})$  (as supporting electrolyte). Electrochemical generation of  $[\text{IrCl}_6]^{2-}$  was achieved by stepping the potential from 0.3 to 0.8 V vs. Ag/AgCl for various step times (typically 10 -120 s) or by sweeping the potential at various scan rates.

Figure 2 shows the UV-visible absorption spectra of 5 mM Ir(III) and Ir(IV) solutions. The spectral window for these experiments, limited by filters and mirrors available was 510-570nm. The reference spectrum required for CEAS was taken with pure Ir(III) solution.

## Results and discussion

Figure 3(a) shows the evolution of the evanescent field absorption spectra during a chronoamperometry experiment, as the working electrode was stepped for 120 s from 0.3 V to 0.8 V and back. The high absorbance below 530 nm matches the Ir(IV) absorption feature (Figure 2). The Ir(IV) concentration within the evanescent field reaches a maximum after ca. 50 s when all  $[\text{IrCl}_6]^{3-}$  within 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.

Figure 3(b) shows the interfacial spectrum recorded during a cyclic voltammogram in which the potential was swept from 0.3 V to 0.9 V (vs. Ag/AgCl) and back at  $5 \text{ mV s}^{-1}$ . 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, figure 4(a) shows the  $[\text{IrCl}_6]^{2-}$  concentration, derived from the absorbance at 520 nm, 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. 50s, once all  $[\text{IrCl}_6]^{3-}$  has been oxidized within the thin layer. Figure 4(b) shows the time evolution of the interfacial  $[\text{IrCl}_6]^{2-}$  concentration during the cyclic voltammogram (0.3 V to 0.8 V vs. Ag/AgCl at  $5 \text{ mV s}^{-1}$ ). Again, the simulated concentration and current transients are in good agreement with the experimental data.

In the present experimental arrangement the minimum detectable  $[\text{IrCl}_6]^{2-}$  concentration within the evanescent field was estimated to be 140  $\mu\text{M}$ . (Mikhail, surely this is only from a single wavelength – if we average all wavelengths recorded simultaneously it must improve significantly, no)



## ***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 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. 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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## Figure Captions:

*Figure 1:* The broadband evanescent-wave cavity enhanced spectrometer employing supercontinuum radiation for detection at the silica-water interface. Only the working electrode is shown in the cell for simplification

*Figure 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 ( $R > 0.999$ ).

*Figure 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.

*Figure 4:* Measured (black) and simulated (red) interfacial Ir(IV) concentration during (a) a 120 s chronoamperometry experiment (120 s at 0.8 V vs. Ag/AgCl), and (b) a cyclic voltammogram (5 mV s<sup>-1</sup>). The measured (blue) and simulated (green) current transients are also shown.



## Figures

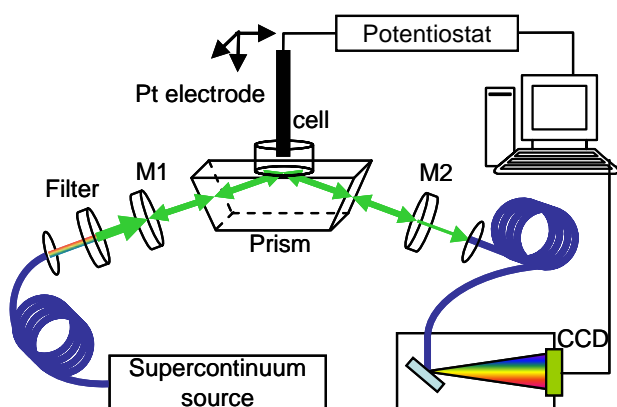


Figure 1

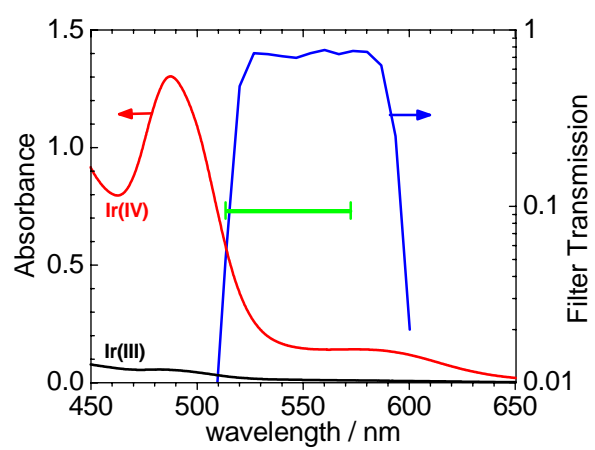


Figure 2

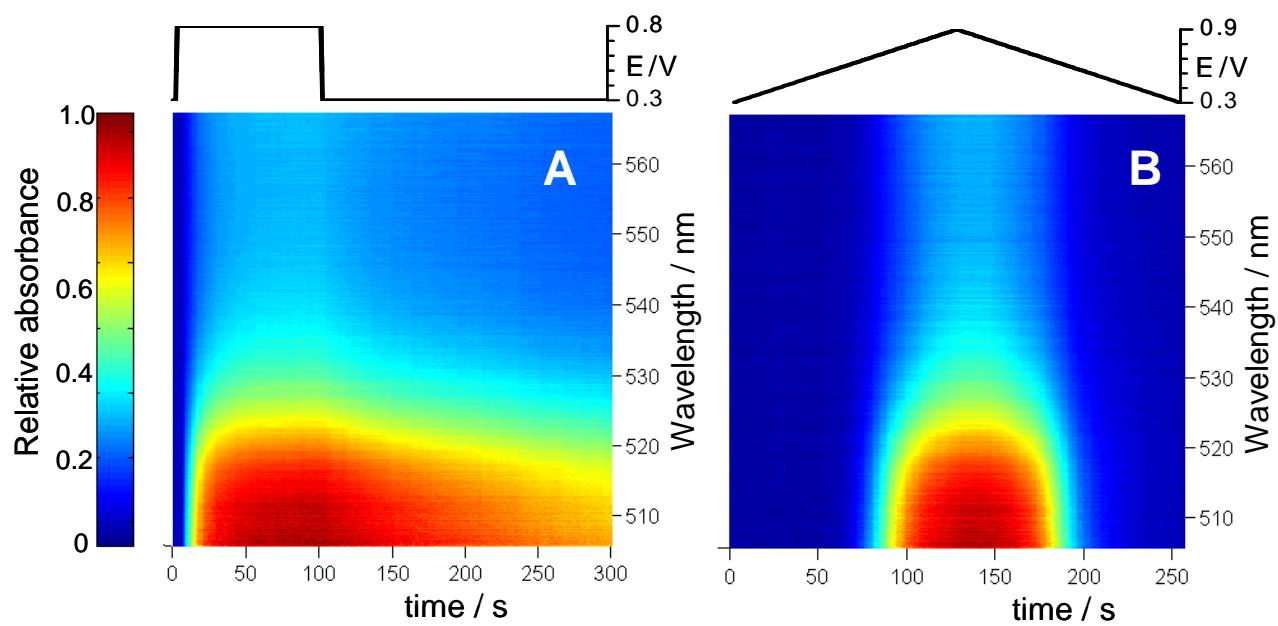


Figure 3

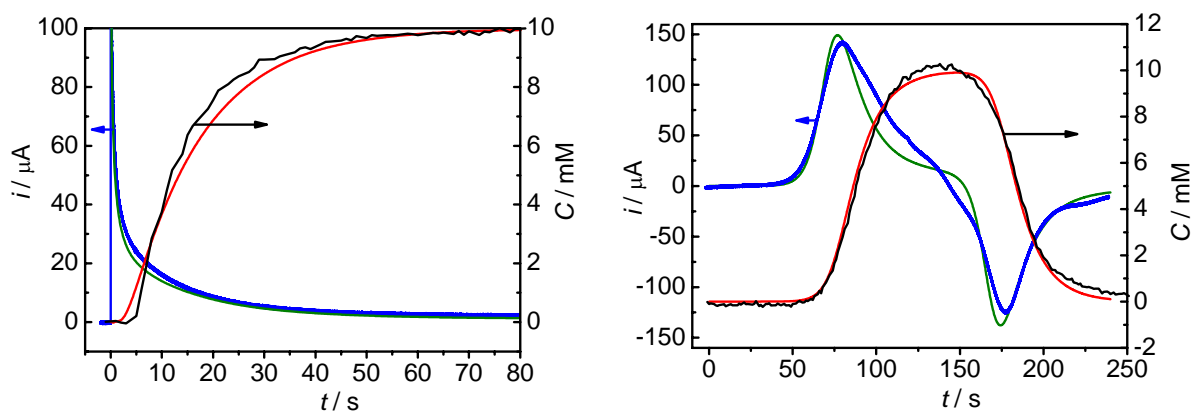


Figure 4

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