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Supplementary information

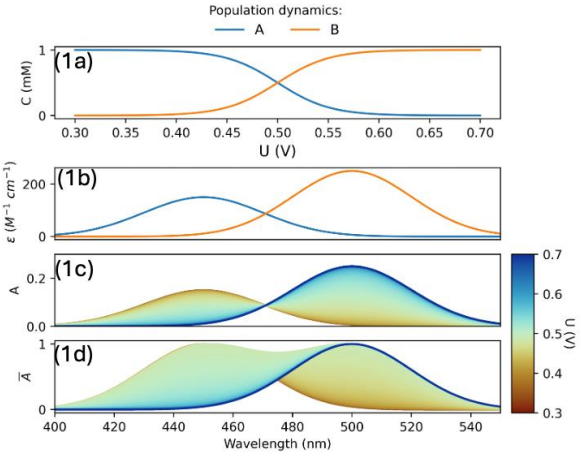
Operando ultraviolet–visible optical spectroelectrochemistry of surfaces

In the format provided by the authors and unedited

Supplementary Box 1. Absolute absorbance, relative absorbance and coulometric properties in spectroelectrochemistry

Consider a simple redox reaction at equilibrium with no mass transport limitation:

$$A \rightleftharpoons B + e^-$$



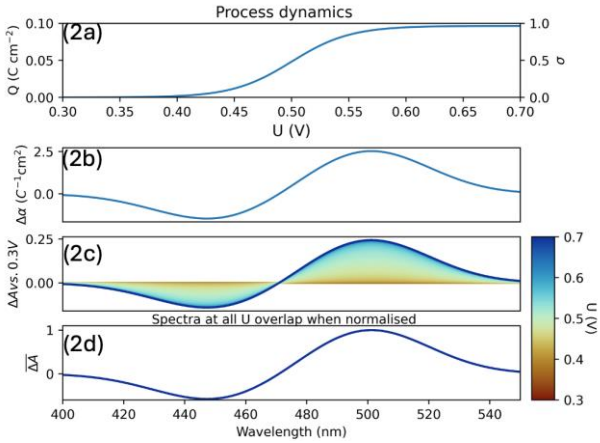
Classic presentation of SEC – Absolute absorbance

A common goal in SEC is to extract concentration dynamics (B1-1a) and the standard potential of a reaction from absorbance. Here, each species has a simple Gaussian molar absorptivity extinction spectra (B1-1b). Absorbance evolves (B1-1c) according to the Beer-Lambert Law:

$$A(\lambda, U) = l(\varepsilon_A(\lambda)C_A(U) + \varepsilon_B(\lambda)C_B(U))$$

If the extinction spectra are known, $C_A(U)$ and $C_B(U)$ can be found by fitting $A(\lambda, U)$ to a linear combination of $\varepsilon_A(\lambda)$ and $\varepsilon_B(\lambda)$ spectra.

If extinction spectra are unknown then no simple process can resolve concentration dynamics. Features like **isobestic points** (B1-1c, 470 nm) suggest (but do not prove) interconversion, and are not guaranteed to exist. No simple mathematical treatment generally allows us to generally extract the concentration dynamics (e.g. normalising each spectrum $A(\lambda, U)$ by its maximum, $\bar{A}(\lambda, U)$, gives a confusing result (B1-1d).



Simplifying SEC data – relative absorbance

The change in absorbance relative to the start of the reaction (0.3 V) is:

$$\Delta A(\lambda, U) = l\boldsymbol{C}(U)(\varepsilon_B - \varepsilon_A) = l\boldsymbol{C}(U)\Delta\varepsilon(\lambda)$$

Where **C** here is interconverting concentration (A lost, B generated). As this is a one electron process, **C** and charge (Q) related by: $\frac{Q}{lF} = C$, where F is Faraday's constant:

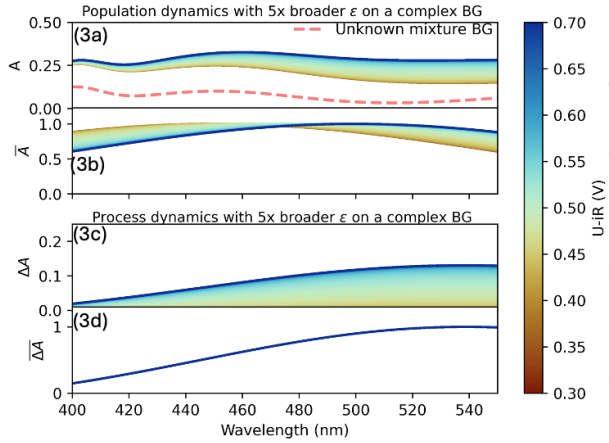
$$\Delta A(\lambda, U) = Q(U)\Delta\alpha(\lambda)$$

F is subsumed into $\Delta\varepsilon$ to give $\Delta\alpha$ and l into C, using common length units. As there must be a charge corresponding to the complete reaction (Q_T), the degree of completion of the rxn can simply be expressed as $\sigma = Q/Q_T$ (B1-2a). This contacts thermodynamic standard potentials for a process ($U^{\ominus}$) via the Nernst equation:

$$U = U^{\ominus} + \frac{RT}{F}\mathrm{Ln}(\frac{\sigma}{1-\sigma}).$$

As the charge passed increases (B1-2a), a single spectral shape – that of $\Delta\alpha(\lambda)$ (B1-2b) grows (B1-2c). This greatly simplifies analysis as spectra now monitor processes rather than individual species. Data about individual concentrations is not generally recoverable without additional assumptions or information. Because a single spectral shape grows, normalising that spectrum by its maximum value will always give the same result (B1-2d). This provides a simple test to show if a single process or if a mixture of process is occurring.

Advantages of monitoring processes not populations



In this example, identical concentration dynamics occur but now the extinction spectra have been broadened 5x to simulate the broad spectra occurring in solids. In addition, a background spectrum (B1-3a orange dashed line) has been added to simulate a background absorbance by an unreactive bulk whose absorbance cannot be isolated from the absorbance the species undergoing interconversion.

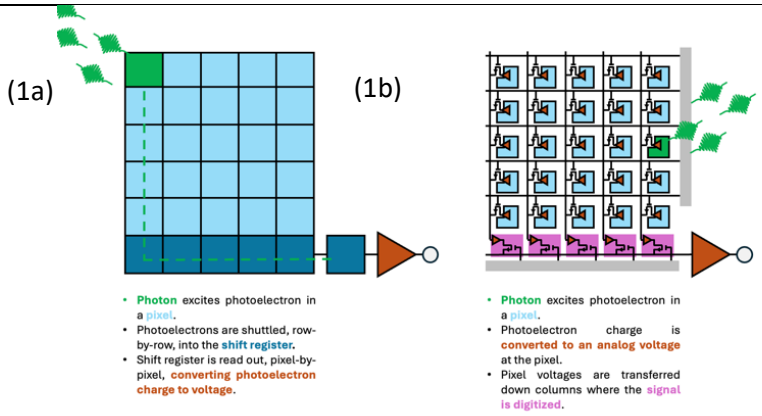
Absorbance evolution now lacks an isosbestic point despite interconversion occurring because of the broadening of the extinction spectra, leading to monotonically increasing absorbance dynamics (B1-3a). Normalisation of absorbance (B1-3b) is uninformative. Plotting $\Delta A(\lambda, U)$ cancels the unknown background shows a single process spectrum growing monotonically (B1-3c). As the evolution scales a single differential coulometric absorbtivity spectrum, process dynamics can easily be resolved through fitting:

$$\Delta A(\lambda, U) = \beta(U)\overline{\Delta\alpha}(\lambda)$$

Where $\overline{\Delta\alpha}(\lambda) = \frac{\Delta\alpha(\lambda)}{\Delta\alpha(\lambda_{max})}$, λ_{max} is the wavelength where the spectrum (B1-3d) is maximal. β is a fitting coefficient $\beta(U) = \Delta\alpha(\lambda_{max})Q(\mathrm{U})$. The dynamics of the fitting are directly proportional to Q and can be used to directly calculate θ as $\theta = \beta/\max(\beta)$. The partial charge can be extracted if $\Delta\alpha(\lambda_{max})$ is known. This advantage is magnified in situations where multiple reactions occur over the potentials studied (see examples).

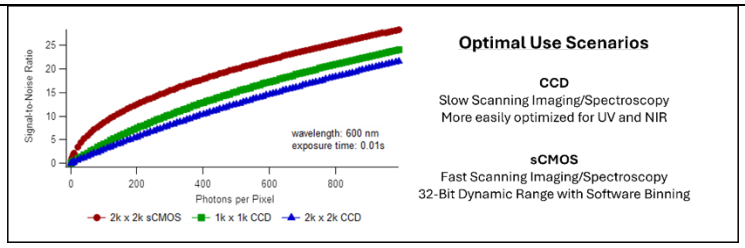
Supplementary Box 2. Principles of operation and possible pitfalls 2D detectors

(1a) (1b)

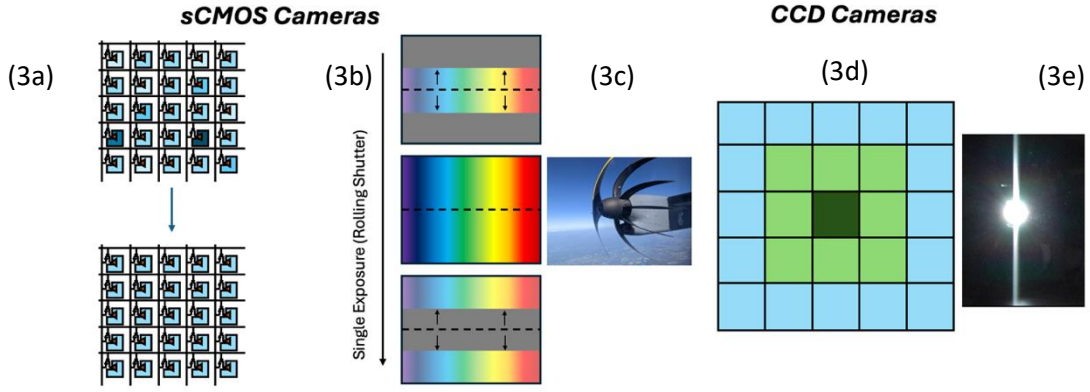


CCD (B2-1a) and sCMOS (B2-1b) cameras enable broadband spectral measurements by dispersing light across the sensor array. For SEC, sCMOS holds several advantages originating from differences in the readout architecture. Photon generated signals (photoelectrons) on a CCD camera are read out serially, having been shuttled row-by-row into a shift register where they are shifted pixel-by-pixel through a common readout node. Photoelectrons in sCMOS are converted to voltages at the pixel level with columns then being readout in parallel.

(2)



Representative signal-to-noise plots for a 2k x 2k sCMOS camera (ZL41 4.2, Oxford Instruments Andor) and two CCDs matching the sensor size (iKon-M, Oxford Instruments Andor) and pixel array size (iKon-L, Oxford Instruments Andor). All curves were calculated using the read noise for the camera's fastest readout rates, with 10 ms exposures, and have been normalized to pixel size to provide a proper comparison. For data rich SEC measurements, the sCMOS holds a clear advantage because it maintains a low noise floor while operating with a readout rate 100x faster than comparable CCD cameras (500 MHz vs. 5 MHz). CCDs, on the other hand, will excel for long exposure spectroscopies where their superior thermal properties limits contributions of thermal noise and slower readout rates (*i.e.* lower read noise) can be used.



sCMOS improve spectral quality through on-camera image processing provides correction maps to resolve noisy, hot and variable responsive pixels to improve sCMOS cameras' quantitative performance (B2-3a). This also enables a "software binning", post readout, that can extend the digitization bit depth to 32 bit, from 16 bit, which is attractive for SEC where small and large differences in absorption can be resolved in the same spectrum. However, rolling shutter operation (B2-3b), which provides the lowest noise and fastest frame rates comes at the expense of a temporal blur (B2-3c) between spectra as the readout time differs at the top/bottom and center of the sensor. Pixel saturation (B2-3d) induced blooming artifacts (B2-3d) that occur in CCDs are minimized in sCMOS cameras, minimizing artificial spectral broadening under bright conditions (Credit from artefact photographs: Wikipedia)

Supplementary Table 1. Optimisations and limitations for SpEC techniques

Limitation:	Solution
Changes in the UV-visible region not guaranteed	Use of complementary techniques
Similar differential attenuation spectra suspected to be from two processes with one process being reactive	Time resolve the two processes using PD-SpEC. Use of complementary techniques
Redox processes are bulk penetrating	Use thinner samples, nanostructure, reduce porosity by annealing at elevated temperature. Check that spectra do not increase in magnitude if the sample is made thicker but surface area is held approximately constant.
Insulating or overly thick materials	Detect using SW-SpEC. Reduce thickness or improve conductivity
Processes overlap in potential range studied	Use of complementary techniques
Optimization:	
Interpreting spectra from intensities commensurate to dark noise	Check raw intensity spectra – be aware of the lower bound of the instrument dynamic range and ensure that intensity spectra are at least a factor of five larger than this value. Any spectral regions where intensity is below this value should be removed during data analysis. Subtracting the dark counts from all spectra may be possible but can increase noise.
Interpreting spectra arising from saturated pixels/inducing blooming on a CCD	Check the raw intensity image on the detector. Be aware of the saturation threshold on the pixel level and ensure that all counts are below this value. **Do not analyse spectra if any pixel is saturated. Introduce an attenuating filter and repeat the measurement.**
Choosing a starting potential significantly below/above the open circuit potential for an anode/cathode.	Check fitting – if the rise of a component is truncated choose an earlier starting potential in CV SEC. Starting too far below the resting potential of an oxygen evolution catalyst can destroy it, resulting in irreversible spectra. Consider the resulting potential and the stable redox processes for your material.
Interpreting spectra as absolute concentrations	Interpret spectra as the fingerprint electrochemical process quantified by partial charge with unknown stoichiometry.
Interpreting spectra as reactions with 1:1 stoichiometry.	Assume attenuation spectra provide no information about stoichiometry without additional evidence or explicit reasoning.
Interpreting sequential spectra as sequential reactions	Avoid assuming sequential (A→B→C) reactions without additional evidence or explicit reasoning.
Not iR compensating spectra	Measure cell/solution resistance, perform iR compensation.
Misinterpreting time resolution of a CMOS cameras in overlap mode	Be aware spectra at adjacent times may share characteristics – the last readout of a row in a CMOS image is most similar to the first row readout of the subsequent image.