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Derivative voltammetry: a simple tool to probe reaction selectivity in photoelectrochemical cell

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We demonstrate the use of derivative voltammogram method to predict the selectivity of the photo-driven oxidation of 5hydroxymethylfurfural (HFM) on WO₃ photoanode as a function of applied potential using only information obtained from linear sweep voltammogram (LSV). This method can be a simple tool to gain an insight into reaction selectivity in

photoelectrochemical cells. Photoelectrochemical (PEC) cells have received much attention as promising devices to convert renewable solar energy into hydrogen through the water splitting reaction.¹⁻³ Overall water splitting constitutes two half reactions, the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). In a PEC device these reactions occur at a semiconductor-liquid junction and are driven by photopotential developed in a photocathode and/or photoanode. Since the product of the OER, oxygen, has low economic importance, researchers are currently exploring alternative oxidation reactions that produce value-added products—both in PEC systems and in the dark electrolysis configuration.^{4–9} In the most commonly-used aqueous systems, an alternative oxidation reaction must compete with the OER, and enhancing the selectivity of the oxidation to the desired alternate product is an important goal. Many parameters such as solvent choice,¹⁰ electrode material,¹¹ and the waveform of the applied potential¹² have been shown to influence oxidative selectivity. Among these parameters, the controlling the working potential of the anode holds a key influence.^{13–18} Since the standard halfcell potential and any kinetic barriers are different for each reaction, one can expect separate reactions to proceed at different rates at a given applied potential. Hence, the applied potential can greatly affect the selectivity of the reaction. Furthermore, since Faradaic current is proportional to the rate of the redox reaction on the electrode surface, linear sweep

voltammetry (LSV) can be used to gain some insight into the relationship between the rate of the reaction and the applied potential. In practice, when multiple reactions take place on the electrode, the current measured is convoluted, making the interpretation of the voltammogram challenging. Performing mathematical derivation of the voltammogram with respect to the applied potential can help to resolve a current densityapplied potential (J-E) curve that is convoluted due to multiple reactions.¹⁹ The derivative voltammogram can reveal buried features in the J-E curve and allows one to gain more insight into the reactions that takes place on the electrode surface at a different applied potentials.²⁰ Derivative voltammograms (also called $\partial J/\partial E$ analysis) have been demonstrated to aid the analysis of complex systems consisting of many redox-active substrates,^{21,22} however, to the best of our knowledge, the dJ/dE analysis approach has not been applied to PEC systems with photoanodes where alternative oxidation reactions are sought to be optimized over the OER, despite the added information one can obtain with no additional experimental setup requirement. In this work, we demonstrate the use of dJ/dE analysis to guide the optimal applied potential to afford highest selectivity for the oxidation the of 5hydroxymethylfurfural (HMF) over the OER in aqueous electrolyte with a WO3 photoanode. The oxidation of HMF is an interesting alternative reaction to OER for water splitting. The final product, 2,5-furandicarboxylic acid (FDCA), is a monomer for polyethylene furanoate (PEF), a bioplastic with much fossil-oil-derived polyethylene potential to replace terephthalate (PET).²³ The interest in using PEF has led to attention to the development of the HMF oxidation reaction in the biomass valorisation community in the past few years.²⁴ Many hydrothermal routes to oxidize HMF to FDCA have been shown in the literature, but high pressure and temperature are usually required.^{25,26} HMF oxidation can also be driven by PEC systems under ambient conditions⁵ and we recently reported the direct, solar driven oxidation of HMF to FDCA on WO₃-based photoanodes in aqueous electrode at pH 4.2727 We found only moderate yields of FDCA due to competition from water

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oxidation and other by-product formation. Hence, we are motivated to improve the selectivity of HMF oxidation in this system using $\partial J/\partial E$ analysis as a simple tool to gain insight into the relationship between reaction selectivity and the applied potential.

Typical WO₃ photoanodes (prepared by a sol-gel method on transparent conducting glass substrate) were used for our investigation. The morphology of the WO3 layer, and basic characterization by Raman spectroscopy and X-ray diffraction are shown in the Electronic supplementary information (ESI) as Figure S1, Figure S2 and Figure S3, respectively. The J-E curves of a typical WO₃ photoanode in sodium phosphate buffer electrolyte (NaP_i) with and without and 5 mM HMF are shown in Figure 1A. The J-E curve of WO₃ in both electrolytes are the same in the dark, no significant current is observed in the potential range scanned versus the reversible hydrogen electrode (RHE). With simulated solar illumination (1-Sun), the J-E curve in the HMF/NaPi solution shows a shift in photocurrent onset potential of -0.18 V and a higher saturated photocurrent density by 0.37 mA cm⁻² in comparison to the J-E curve in the NaPi electrolyte. The derivative of the J-E curve (with respect to the applied potential, $\partial J/\partial E$) was approximated numerically and is shown for the NaPi electrolyte in Figure 1B where a single peak at +0.95 V vs. RHE is observed. In contrast, the dJ/dE curve of the photoanode in HMF/NaPi electrolyte (Figure 1C) shows a broad, two-humped peak from approximately +0.65 to +0.95 V vs. RHE. To gain more insight into the obtained derivative voltammogram, we fit the derivative photocurrent to a mathematical model as described in the ESI (Mathematical foundation section). In brief, the model takes a basis from Gericher's equation with a Gaussian density of states and accounts for the increasing photocurrent in the plateau region of the J-E curve due to the additional band-bending at higher applied potentials, which drives additional carriers to the semiconductor liquid junction in low-carrier-mobility semiconductors like oxides.²⁷ The model fitting parameters are shown in Table S1 (ESI), and graphically the fit reveals one peak at +0.96 V vs. RHE in the NaP_i electrolyte case (red line in Figure 1B). For the HMF/NaPi electrolyte, the best fit (red line in Figure 1C) shows two peaks at +0.66 V vs. RHE (∂J/∂E-peak1) and +0.96 V vs. RHE ($\partial J/\partial E$ -peak2). The attempt to fit the $\partial J/\partial E$ of the HMF/NaPi electrolyte with only one Gaussian density of states does not yield a good fit (see Figure S4, ESI). We suggest that

each peak in the derivative voltammogram corresponds to a different reaction taking place on the electrode surface, thus there is at least one reaction taking place in the NaP_i electrolyte while for the HMF/NaP_i solution there are at least two reactions. Since the peak at +0.66 V vs. RHE is only found when HMF is present in the system, we assign this peak to the photo-oxidation of HMF. Since the peak at +0.96 V vs. RHE is found in both cases, it is reasonable to assign this to the water photo-oxidation reaction.

Numerical integration of the mathematical fit of the $\partial J/\partial E$ yields a simulated J-E curve. The simulated J-E curves in the NaP_i electrolyte and the HMF/NaPi solution are depicted in Figure 2A and Figure 2B, respectively, in comparison to the experimental data. The simulated J-E curves (red solid lines) match the experimental value (blue solid lines) well in both cases. As our observation that the $\partial J/\partial E$ -peak1 and $\partial J/\partial E$ -peak2 in the $\partial J/\partial E$ analysis of the HMF/NaPi solution are correlated with the oxidation of HMF and water, respectively, we propose that the separate numerical integration of these two Gaussian densities of states (corresponding to J_{sim}-peak1 and J_{sim}-peak2) represent the decoupled photocurrent densities associated with HMF oxidation and water oxidation, respectively. These decoupled J-E curves are also shown in Figure 2B. We can see that the ratio of the photogenerated charges (total photocurrent) attributed to either HMF oxidation or water oxidation is dependent on the applied potential. With the information on this deconstructed photocurrent, we can predict the selectivity for HMF oxidation as the function of the applied potential from Equation 1.

Selectivity _{HMF oxidation} =
$$\frac{J_{sim}-peak1}{J_{sim}-Sum} \times 100\%$$
 (1)

Where J_{sim}-Sum represents the sum of the two decoupled J-E curves. We tested this prediction by performing photoelectrolysis of HMF at +0.65 V, 0.85 V and 1.20 V vs. RHE. The concentration of HMF (as measured by high performance liquid chromatography) as a function of the passed charge is shown in Figure 2C. It should be noted that the oxidation of HMF to its final product FDCA is a multistep reaction with each of the steps proceeding through a two-electron oxidation and leading to an intermediate species (see Figure S5, ESI). Therefore, we calculate the selectivity for HMF oxidation based on the assumption that HMF undergoes a two-electron oxidation.



Figure 1 (A) Linear sweep voltammograms of WO₃ in NaP_i and HMF/NaP_i solution with and without illumination. The $\partial J/\partial E$ analysis of WO₃ in **(B)** NaP_i electrolyte and **(C)** HMF/NaP_i solution.

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Moreover, it is important to note that the J-E curves of the pure intermediate species in aqueous electrolyte are very similar to that of HMF²⁸ due to their similar redox potentials. This makes resolving peaks in the $\partial J/\partial E$ analysis of the electrolyte containing multiple intermediates challenging. We demonstrate this by performing the $\partial J/\partial E$ analysis of 2,5diformylfuran (DFF), the intermediate that was found to appear in the highest concentration in HMF oxidation on WO₃.²⁸ The LSVs of illuminated WO3 in HMF/NaPi, DFF/NaPi and blank (NaPi) electrolyte are shown in Figure S6, ESI. The J-E curve of both HMF/NaP_i and DFF/NaP_i are very similar. Indeed, the $\partial J/\partial E$ analysis can be applied to the J-E curve of the DFF/ NaPi solution (see Figure S6B, ESI), but the similarity of the J-E curve makes the $\partial J/\partial E$ fit of both solutions to be very similar. Therefore, the estimation of selectivity of HMF oxidation over the OER from the data in Figure 2C was performed using the initial rate of HMF consumption when the concentration of intermediated was small (i.e., by considering the slope of the initial time points from each of the runs) to ensure minimal deviation from the condition used to perform the $\partial J/\partial E$ analysis. The extrapolated initial rate of HMF consumption for the different potentials is shown as the broken lines in Figure 2C. The predicted selectivity (calculated from Equation 1) and the experimental values obtained from the HMF consumption rate (the calculation for the experimental selectivity is shown in the ESI) are compared

in Figure 2D and Table 1. The prediction is very accurate at the low applied potential (+0.65 V vs. RHE) but deviates from the experimental values at the higher applied potentials (+0.85 and 1.20 V vs. RHE). This difference between the predicted and the experimental-determined selectivity could be the result of mass transport limitations. The number of available photogenerated holes is higher at the more positive applied potential. If the concentration of HMF at the WO₃/electrolyte is not sufficient, the excess holes may react with other species in the solution, resulting in a lower selectivity. We addressed this possibility by performing photoelectrolysis of HMF at a higher initial HMF concentration of 100 mM at +0.65 V and 1.20 V vs. RHE (see Figure S7, ESI). We found that the selectivity is lower at 1.2 V vs. RHE than at 0.65 V vs. RHE in both initial concentrations. This suggests that the decrease in the selectivity is not due to mass transport limitations. Alternatively, the observed deviation can be attributed to the absence of kinetic considerations in the ∂J/∂E analysis. Indeed, at higher applied bias, if the kinetics of water oxidation were faster than that of HMF oxidation we would expect the observed deviation. It has been shown in the literature that water oxidation on WO₃ proceeds through the formation of peroxo species and not directly O₂ via the fourhole OER.^{29,30} The kinetics of this reactions may be faster than HMF oxidation.



Figure 2 Experimental and simulated photocurrent in (**A**) NaP_i electrolyte and in (**B**) HMF/NaP_i solution. (**C**) The concentration of HMF as a function of passed charge at 0.65 V, 0.85 V and 1.20 V vs. RHE with the fitted selectivity for HMF oxidation. (**D**) Predicted and the experimental-determined selectivity for HMF oxidation at different applied potential.

To gain more insight, and provided with an ability to probe the relationship between the applied potential and the selectivity of the reaction demonstrated earlier, we next aimed to describe and provide the physical meaning of the peaks in the derivative voltammogram. Chemical reactions on photoanodes utilize the photoexcited minority charge carriers (holes) to perform redox reactions. Typically, the photogenerated holes are energetically localized in the valence band edge at the semiconductor/liquid interface, due to the induced bandbending at this junction. Nevertheless, some electronic states with energy levels that lie within the bandgap of semiconductors can be present. These electronics states can have diverse origins ranging from any features that break the

Table 1 Predicted and the experimental-determined selectivity

 for HMF oxidation

Applied Potential	Selectivity for HMF oxidation (%)	
(V vs. RHE)	Experimental	Predicted
0.65	72.0	68.2
0.85	27.5	47.7
1.20	13.7	28.8

symmetry of the bulk semiconductors such as vacancies and dangling bonds to the chemical states between the semiconductor surface and the chemical species in the electrolyte. These latter electronics states are known as surface states.^{31,32} The minority charge carriers can accumulate within the surface states and then react with the redox-active species in the electrolyte, hence performing the redox reaction. Alternatively, the accumulated charge carriers can also recombine with the majority charge carriers. The surface states that promote the reactions can be called intermediate surface states (i-SS) while the ones that promote recombination can be labelled as recombining surface states (r-SS).³¹

One probable physical meaning of the derivative voltammogram was proposed by Can Li and co-workers³³ who suggested that $\partial J/\partial E$ is proportional to the density of intermediate states on the surface of semiconductors as a function of the applied potential (DOS(E)). Using a set of surface modified hematite photoanodes and comparing the DOS(E) as probed by the derivative voltammogram to electrochemical impedance spectroscopy (EIS) and fast cyclic voltammetry (the common methods for detecting intermediate states), the authors found a similar trend, which supported their view.³³

To verify if this postulation applies to our system with competing oxidation reactions, we first investigate the DOS(E) in our system by EIS (See Figures S8 and S9, ESI, for the raw EIS data and the results of the fitting to the circuit model in Figure 3). For EIS, the accumulation of charges in the surface states is assumed to contribute to the surface capacitance (C_{ss}) with the relationship $C_{ss} = q \cdot DOS(E)$, where q is the electron charge.³⁴

The analysis of the WO₃ photoanode with and without HMF in the electrolyte show very similar results with one surface capacitive (C_{ss}) peak at +0.95 V vs. RHE with relatively the same magnitude. The capacitance greatly increases at applied potentials below +0.6 V vs. RHE (see Figure S10, ESI). When comparing the DOS(E) as found by EIS to the $\partial J/\partial E$, we found the DOS(E) peak observed by EIS overlaps well with the $\partial J/\partial E$ peak2 (Figure S11). This supports the view that the $\partial J/\partial E$ -peak2 can represent the distribution of the intermediate states (i-SS) which are associated with water oxidation on WO₃. As for the $\partial J/\partial E$ -peak1, since the EIS analysis does not show any surface states around +0.60 V vs. RHE, we cannot directly link the $\partial J/\partial E$ peak1 to the intermediate states. This demonstrates that the $\partial J/\partial E$ analysis can give additional and complimentary information to EIS.

Regarding the origin of the $\partial J/\partial E$ -peak1, it may come from a short-lived i-SS or an i-SS that does not involve charge accumulation at the surface. Since probing EIS relies on the charge accumulation at the steady-state, such i-SSs may not be detectable by EIS. Heidary and co-workers studied the interaction between HMF and NiOOH thin film using surfaceenhanced Raman spectroscopy and found that HMF can be adsorbed onto the surface of NiOOH.³⁵ The interaction was found to be a non-covalent bond, as the team only observed a slight shift in the Raman signal. It is thus reasonable to think that HMF may have certain non-covalent interactions with WO₃, and this adsorbed HMF may be the i-SS that is responsible for $\partial J/\partial E$ peak1. Nevertheless, we cannot discount the possibility of an outer sphere charge transfer mechanism between HMF and WO3 where HMF directly inject electrons into WO3 without being adsorbed onto the WO₃ surface.



Figure 3 DOS(E) as probed by EIS analysis of WO_3 in NaP_i electrolyte and HMF/NaP_i solution.

Conclusions

In conclusion, we demonstrated the use of an $\partial J/\partial E$ analysis of linear scanning voltammograms from a photoanode in a system with competing oxidation reactions in predicting selectivity. We applied this analysis to study the selectivity between HMF oxidation and water oxidation on WO₃ photoanode and found that the $\partial J/\partial E$ analysis can predict the selectivity trend of HMF oxidation over the OER. The prediction is accurate at low applied potential and showed a deviation from the experimental value at the higher applied potential. We attributed this deviation to the kinetics of the reaction that should have a more profound effect at the higher bias. By comparing the $\partial J/\partial E$ curves to EIS analysis, we conclude that $\partial J/\partial E$ provides additional information that helps to give insight about the nature of surface states. Overall, we believe that this method could be used to give a quick estimation of the selectivity of the reaction as the function of applied potential for other photoelectrosynthesis systems.

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Conflicts of interest

There are no conflicts to declare

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