



# Understanding how the oxygen evolution reaction kinetics influences electrochemical wastewater oxidation



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## ARTICLE INFO

### Article history:

Received 15 December 2017

Received in revised form

7 June 2018

Accepted 9 June 2018

Available online 13 June 2018

### Keywords:

Oxygen evolution reaction

Organic oxidation

Parallel reactions

Electrochemical wastewater treatment

Electrocatalysis

Microkinetic modelling

## ABSTRACT

The electrochemical oxidation of organic species in wastewater often occurs in parallel with the oxygen evolution reaction. At electrocatalytic anodes (e.g. IrO<sub>2</sub>), the organic species is oxidized by the surface bound oxygen species, S–O, an intermediate of the oxygen evolution reaction. Previously, the rate of organic oxidation by the S–O species has been assumed to be much faster than the combination of S–O to form O<sub>2</sub>, but here a model is developed without this assumption and solved numerically for a wide range of rate constants to determine steady-state polarisation curves for oxygen evolution and the rate of the oxidation of organics. Experimental oxygen evolution polarisation curves measured on IrO<sub>2</sub> anodes are fit to a model for the electrochemical oxide pathway to understand how the kinetics of the individual steps in the oxygen evolution reaction influence the rate of oxidation of organics. Multiple sets of rate constants describe the same steady-state polarisation curve with unique surface oxide coverage vs. potential behaviour. While this complicates the extraction of rate constants from oxygen evolution polarisation curves, it enables the study of influence of S–OH and S–O surface coverages on the organic oxidation rate while keeping the overall oxygen evolution kinetics constant. By comparing the organic oxidation over a range of kinetic parameters, it can be concluded that the organic oxidation reaction only alters the current density when the organic oxidation rate constant is many times larger than the rate constant for the competing step in the oxygen evolution reaction. Our model also shows that organics can be oxidized with by molecular O<sub>2</sub> via an S–O mediated process, although as this only occurs when the organic oxidation rate constant is very large and at low overpotentials where the specific oxidation rate is very low. The model also shows that organic oxidation reaction is almost entirely kinetically limited at low overpotentials and only becomes mass transport limited when the rate constant for the organic oxidation reaction is extremely large. The model is validated by comparing simulations against data for 4-nitrophenol oxidation at a 90 wt% SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>5</sub>- 10 wt% IrO<sub>2</sub> anode and is shown to correctly describe the potential dependence of the apparent first-order rate constant. From this, we conclude that only one type of surface coverage behaviour can describe the experimental results and that the specific rate constant for 4-nitrophenol oxidation on this anode is approximately  $2.3 \times 10^4 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

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## 1. Introduction

Electrochemical wastewater oxidation is promising way to treat wastewater with high chemical oxygen demand and chemicals toxic to most biological methods [1,2], including olive oil mill wastewater [3–6], herbicide residue [7], dyes [8,9], cyanide wastes [10,11] and phenolic compounds [4,12–17].

Despite the success of electrochemical oxidation in treating a

range of wastewaters, the high energy requirements of the process limits the industrial implementation of electrochemical wastewater treatment [18]. Part of the reason for the high energy requirements is the low current efficiency due to the unwanted parallel oxygen evolution reaction (OER) which occurs at the anode. To avoid this, anodes with very high overpotentials for the OER are often used [11,12,19,20] which oxidise the wastewater compounds via the hydroxyl radical formed at high potentials [17,21,22]. These anodes are often referred to as “non-active” anodes, and are exemplified by boron-doped diamond (BDD) anodes [1,2], although this approach inevitably leads to high energy requirements due to the high cell voltages applied. Furthermore, while BDD anodes can

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generate hydroxyl radicals at potential below the onset of the OER, complete mineralisation of the organic only occurs in parallel with the OER [23,24]. One solution to this problem is to develop electrocatalytic anodes with high activity for organic oxidation and low selectivity for the OER at low potentials. These anodes are normally called “active” anodes and the mechanism for organic oxidation involves an intermediate species of the OER [1,2,17,21]. In this case, it is clear that the inherent kinetics of these two reactions and the mass transport of the organic species to the anode surface will influence the overall process efficiency. In fact, in many examples [6,17,25–29] electrochemical wastewater treatment anodes contain noble metal oxides such as IrO<sub>2</sub> or RuO<sub>2</sub>, which are very active for the OER, and thus the selectivity of the electrode towards these parallel reactions must be a critical factor in determining the efficiency of the process. We also note that while these anodes can exhibit useful short-term performance, the long-term stability of such electrodes [30] should be considered if these anodes are to be used in industry.

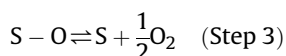
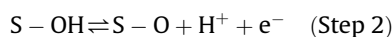
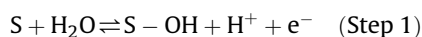
In order to understand and thus be in a position to minimise the energy requirements of electrochemical oxidation of wastewater, some mathematical models of the process have been proposed. In these models, the most common approach assumes that the organic oxidation reaction is much faster than the final step in the OER [19–21,31–33]. With this assumption, provided that there are no mass transfer limitations, these models predict the current efficiency of organic oxidation will be 100%. On boron-doped diamond anodes, this assumption appears to be valid as the reaction between the generated hydroxyl radical and the organic is very fast [21,31,33]. These models also suggest that if the applied current density is greater than the limiting current density, the overall rate of reaction should be controlled solely by mass transport and not by the nature of the anode. While these models provide simple analytical expressions capable of simulating electrochemical wastewater oxidation under mass transfer limiting conditions, experimental results show that the composition of oxygen evolving anodes can influence the kinetics of the organic oxidation rate, even when the applied current density is much greater than the limiting current [12] – an observation that clearly indicates that the organic oxidation reaction is under kinetic control with simultaneous oxygen evolution. There is also experimental evidence that the organic oxidation reaction occurs in parallel with the OER when the applied current is less than the limiting current [32] which confirms that the kinetics of the organic oxidation are not always much greater than the OER as assumed by these models. While this modelling approach is widely used to predict the bulk electrolysis vs. time behaviour, others have included the inherent kinetics of the competing reactions [32,34], however in these cases the OER mechanism was simplified to two step pathway involving the simultaneous transfer of two electrons, which seems unlikely to be physically realistic. Others have developed models incorporating both kinetic and mass transfer phenomena for when the oxidation of the organic species occurs via the electrochemically generated hydroxyl radical [21,31,33,35–37] with excellent agreement to experimental data. In particular, these models show that almost 100% current efficiency for organic oxidation can be achieved by balancing the rate of hydroxyl generation with the mass transport of organic towards the electrode, and highlight the importance of the ratio of applied current to the mass transport limiting current in determining the process performance.

In this paper, a model of the oxidation of organics in parallel with oxygen evolution at electrocatalytic anodes covering both the kinetic and mass transfer controlled regimes is developed and validated against experimental data. Our key hypothesis is that on “active” anodes, including the complete mechanism for the OER and accounting of the kinetics of the OER is required. Here we test

this hypothesis by simulating the organic oxidation reaction in parallel with the OER using kinetic parameters that fit experimental OER data. Finally, we compare our model with experimental data for the oxidation of 4-nitrophenol and show that our model can correctly describe the potential dependence of the 4-nitrophenol oxidation rate.

## 2. Mathematical model

While the anodic oxidation of organic molecules at electrodes have fairly complex reaction mechanisms, some useful insights can be gained by considering simple cases. As this paper is concerned with the oxidation of organics at an electrode capable of electrocatalytic oxygen evolution (e.g. IrO<sub>2</sub>), the organic oxidation will be assumed to follow the “active” electrode mechanism first proposed by Comninellis [17]. In this mechanism, the oxidation of the organic species is mediated by the higher-oxide (S–O, e.g. IrO<sub>3</sub>) formed on the anode surface at high potentials. Unlike boron-doped diamond or SnO<sub>2</sub> anodes, IrO<sub>2</sub> produce almost no hydroxyl radicals, ruling out the “non-active” oxidation mechanism [17]. To ensure that the overall process is consistent with proposed mechanisms for the OER, here the higher-oxide is formed as part of the electrochemical oxide pathway (Step 1–3) [38]:



where S is a free surface site. In the “active” electrode mechanism, the oxidation of an organic molecule completes (Step 4) with the generation of molecular oxygen gas (Step 3)



Importantly for the purposes of this investigation, the key factor which controls the current efficiency of the overall process are the relative rates of the Step 3 and Step 4 which compete for the same intermediate, S–O. This mechanism differs from the mechanisms proposed for “non-active” anodes such as boron-doped diamond, where the oxidation occurs via the hydroxyl radical which some assumed to be free within the diffusion layer [22,31,35–37] or physisorbed on the anode surface [21]. Here it is assumed that adsorption of organic species does not compete for active sites with the formation of adsorbed OH, although we note that others have suggested that organic adsorption can block the initial water discharge step on BDD anodes [24]. It is also assumed that the organic oxidation reaction is chemically irreversible, whereas all steps in the OER will be considered reversible. The reaction rates for each step are given by:

$$r_1 = k_1 c_{H_2O} N_{tot} (1 - \theta_{OH} - \theta_O) - k_{-1} c_{H^+} N_{tot} \theta_{OH} \quad (1)$$

$$r_2 = k_2 N_{tot} \theta_{OH} - k_{-2} c_{H^+} N_{tot} \theta_O \quad (2)$$

$$r_3 = k_3 N_{tot} \theta_O - k_{-3} c_{O_2}^{\frac{1}{2}} N_{tot} (1 - \theta_{OH} - \theta_O) \quad (3)$$

$$r_4 = k_{4f} N_{tot} \theta_O c_{R,surf} \quad (4)$$

where  $k_1$  and  $k_{-1}$  etc. are forward and back rate constants,  $c$  are concentrations and  $N_{tot}$  is the number of surface sites per unit electrode area.  $\theta_{OH}$  and  $\theta_O$  are the surface coverage of OH and O

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