



## Research paper

New insights into electrocatalytic ozone generation via splitting of water over PbO<sub>2</sub> electrode: A DFT studyGregory Gibson<sup>a,b</sup>, Ashley Morgan<sup>b</sup>, P. Hu<sup>b</sup>, Wen-Feng Lin<sup>a,b,\*</sup><sup>a</sup> Department of Chemical Engineering, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK<sup>b</sup> Centre for the Theory and Application of Catalysis, School of Chemistry and Chemical Engineering, Queen's University of Belfast, Belfast BT9 5AG, UK

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## ABSTRACT

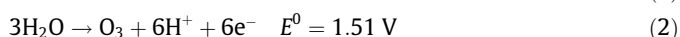
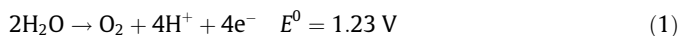
The viable mechanisms for O<sub>3</sub> generation via the electrocatalytic splitting of H<sub>2</sub>O over β-PbO<sub>2</sub> catalyst were identified through Density Functional Theory calculations. H<sub>2</sub>O adsorbed onto the surface was oxidized to form OH then O; the latter reacted with a surface bridging O to form O<sub>2</sub> which in turn reacted with another surface O to form O<sub>3</sub>. The final step of the mechanisms occurs via an Eley–Rideal style interaction where surface O<sub>2</sub> desorbs and then attacks the surface bridging oxygen, forming O<sub>3</sub>. A different reaction pathway via an O<sub>3</sub>H intermediate was found less favoured both thermodynamically and kinetically.

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## 1. Introduction

Ozone (O<sub>3</sub>) is a strong oxidant with wide applications across many disciplines related to advanced oxidation technologies. Due to its strong oxidizing nature O<sub>3</sub> is often used in disinfection processes at wastewater treatment facilities. It has relevance in removing unwanted odours, wood pulp bleaching and more recently in healthcare [1–6]. For practical uses, O<sub>3</sub> must be produced in an efficient and environmentally friendly manner, which to date has proven to be the greatest challenge. At present O<sub>3</sub> is produced industrially via the Cold Corona Discharge (CCD) method. This process involves two electrodes with alternating current, similar to an electric spark, with pure oxygen (O<sub>2</sub>) or dry air passing between them. Current efficiency (CE) values tend to be low at between 2 and 12 wt% depending on the source of O<sub>2</sub> [7,8].

Through the use of electrochemistry and in particular, electrocatalysis, a superior O<sub>3</sub> yield can be achieved via water splitting. In electrolysis, H<sub>2</sub>O undergoes decomposition at the anode through either a 4 or 6 electron process shown in reactions (1) and (2) [9]:



Reaction (1) shows the competing reaction, the formation of O<sub>2</sub> that can occur instead of the formation of O<sub>3</sub> in reaction (2). This can be quantified using thermodynamics. In comparison to O<sub>3</sub>, O<sub>2</sub> is thermodynamically superior in terms of stability and thus will readily form. To combat this, the inhibition of O<sub>2</sub>, and hence the formation of O<sub>3</sub> is of paramount importance. By running at a high onset potential with a large applied overpotential the thermodynamic barrier can be bypassed, resulting in O<sub>3</sub> formation. In selecting a suitable catalyst for the anode, the overpotential required for oxygen evolution reaction (OER) can be increased. During the production of O<sub>3</sub>, the increased overpotential required for OER results in partial inhibition of the oxygen evolution when compared to a material with a lower overpotential for OER [10,11]. Extensive research on catalyst suitability has been studied with varying degrees of success. Among the most common catalysts used are β-PbO<sub>2</sub> [10–12], Pt [13], dimensionally stable anodes (DSAs) [14], boron-doped diamond (BDD) [15,16] and SnO<sub>2</sub> based catalysts [17–19]. Foller et al., one of the pioneering groups in the study of electrochemical O<sub>3</sub> formation, used β-PbO<sub>2</sub> as the catalyst of choice. Using new and innovative methods O<sub>3</sub> was produced electrochemically. Foller summarised his research into four points:

- The anion must be resistant to further oxidation, or oxidize into a species that doesn't decrease the yield.
- The cation must undergo no cathodic reduction, nor be influenced by pH change.

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- Salt combinations must have sufficient solubility.
- No reactions with the ozone produced must occur.

Previous methods produced O<sub>3</sub> in low yield, resulting in low CEs. β-PbO<sub>2</sub> was the first to achieve a better CE than the CCD method, with values as high as 13% at room temperature [10]. Higher efficiencies were possible with the addition of a fluorinated anion; yielding CEs as high as 50%, although this occurred at 0 °C. As the goal is to produce highly efficient anodes whilst being as green as possible, the use of fluorine or other halogens are disapproved.

Although in these studies a significant amount of understanding has been gained there are still questions that need to be answered:

- Is the mechanism postulated correct or will it proceed via an alternative pathway?
- Are there any surface oxidants present?
- What role do these oxidants/adsorbents play?

The focus of this research is to address these questions within the parameters that can be studied using theoretical methods, with the aim to gain a reasonable yet computationally affordable approach to understanding the electrochemical O<sub>3</sub> production system, which has proven difficult to achieve in the past, and thus difficult to model. With this work being novel as a first theoretical study, simulations had to be run in order to determine the most stable facet of the PbO<sub>2</sub> anode, along with the optimal surface oxide coverage. From this a phase diagram can be constructed which aids in determining surface oxidant coverage, which in turn is important for modelling the reaction.

The main purpose of this research involved the modelling of a 4 step mechanism where water can be split to form O<sub>3</sub> under the suitable electrochemical conditions. The modelling was carried out using Density Functional Theory (DFT). β-PbO<sub>2</sub>, the experimentally approved catalyst of choice for this reaction, was chosen. It is a relatively simple system where the results gained could then be applied to more complex catalysts.

## 2. Theoretical methods

### 2.1. Surface adsorption calculations

The adsorption energy ( $E_{\text{ads}}$ ) was calculated using the following equation:

$$E_{\text{ads}}(\text{adsorbate}) = E(\text{adsorbate on surf.}) - E(\text{surf.}) - E(\text{free adsorbate in gas phase}) \quad (3)$$

Eq. (3) shows that the more negative the adsorption energy is, the greater the adsorption to the surface. In this instance it can be a clean surface or an oxide surface, depending upon the study. Each term in the equation must correspond to the same surface coverage, whether this is a pure metal or metal oxide.

Geometric optimization was obtained by performing electronic structure calculations using the *Vienna Ab-initio Simulation Package* (VASP), using plane wave basis set [20–22]. Electron exchange and correlation terms were described using the *Perdew–Burke–Ernzerhof* (PBE) functional [23]. Electron–ion interactions were modelled using the *projected augmented wave* (PAW) potential with system converging with cut-off energy of 500 eV [24].

The ground state was determined using Methfessel–Paxton smearing of 0.05 eV [25]. The most stable β-PbO<sub>2</sub> system was a (110) surface. This was modelled as a (2 × 2) unit cell on surface coverage's barring the 0.125 ML (ML = mono-layer) coverage. This coverage employed the use of a super cell modelled as a (4 × 2) unit cell. The *k*-points for the surfaces with (2 × 2) unit cell were

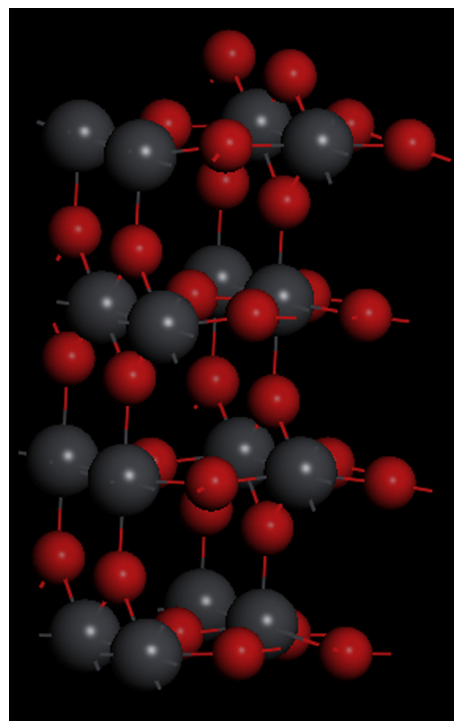
sampled using a 3 × 3 × 1 Monkhorst–Pack grid [26] with the super cell having *k*-points 1 × 3 × 1. A four-layered slab was employed, with the bottom two layers fixed in geometry, whereas top two layers were allowed to relax. Slab separation was provided normal to the surface by use of a 15 Å vacuum region. Transition state (TS) searching was implemented using a constrained minimisation method [27–29].

## 3. Results and discussion

### 3.1. Determination of the most stable facet of PbO<sub>2</sub>

PbO<sub>2</sub> can exist in two crystalline forms; the alpha version which is orthorhombic and the beta version which is tetragonal in shape. It has been suggested that the beta version is the more favoured structure for O<sub>3</sub> evolution. The alpha form is said to have better contact between particles, due to its more compact structure in comparison with the beta form. This compactness results in difficulty with discharge. For these reasons the beta form is often used when carrying out O<sub>3</sub> evolution [30].

Although studies on other surfaces were carried out, Foller and Tobias focused on exploring β-PbO<sub>2</sub> as their catalyst of choice for O<sub>3</sub> evolution. Other groups have also studied this system experimentally; however there are no examples in the literature studied on a theoretical level. Before modelling the reaction, the most stable surface facet had to be calculated. As this work is the first theoretical attempt, data on surface stability or morphology was lacking, so some common surface geometries were tested. The surface of β-PbO<sub>2</sub> is analogous to SnO<sub>2</sub>, which has been studied previously. The (110) facet is reported as the most stable for SnO<sub>2</sub>, so this was chosen as a sensible starting point. The four arrangements tested were (110), (111), (100) and (211) mono-atomic step edge facets.



**Fig. 1.** A diagram showing β-PbO<sub>2</sub> (110), the most stable surface facet, modelled as a four layer system. The grey atoms represent lead, and the red atoms represent oxygen. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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