Assessing the performance of reactant transport layers and flow fields towards oxygen transport: A new imaging method based on chemiluminescence

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HIGHLIGHTS

- Direct imaging of the effect of flow fields and transport media on oxygen distribution.
- Light generation visible to unaided eye showing regions of high oxygen transport.
- 20 μm and 40 ms spatial and time resolution achieved.
- Flow field effects and pressure driven convection processes identified.

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ABSTRACT

A new, simple and precise ex-situ optical imaging method is developed which allows indirect measurement of the partial pressure of oxygen (as ozone) within fuel cell components. Images of oxygen distribution are recorded with higher spatial (~20 μm) and time (40 ms) resolutions. This approach is applied to assess oxygen concentration across the face of a pseudo polymer electrolyte fuel cell (PEFC), with a serpentine design flow field. We show that the amount of light produced is directly proportional to the partial pressure of ozone, in the same way as the local current density in a PEFC is proportional to the partial pressure of bimolecular oxygen. Hence the simulated system provides information relevant to a PEFC with the same geometry operating at the same stoichiometric ratio. This new approach allows direct imaging of flow under lands due to pressure gradients between the adjacent channels and non-laminar flow effects due to secondary flow around U-turns. These are major discoveries of fundamental importance in guiding materials development and in validating modelling studies. We find that contrary to many simulation papers, advection is an important mechanism in both the gas diffusion layer (more properly “reactant transport layer”) and the microporous layer. Models which do not include these effects may underestimate reactant transport to the catalyst layer.

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1. Introduction

Several challenges remain to improving the performance and reducing the cost of polymer electrolyte fuel cells (PEFC), e.g. (i)
cost competitive oxygen reduction reaction (ORR) catalysts with high enough activity and durability; and (ii) cathode electrodes (reactant transport layer — “GDL”, catalyst layer etc) and flow field designs for managing the delicate mass transport phenomena. These key factors play a crucial role in reducing (or eliminating) the amount of platinum required within a PEFC and in maximising the partial pressure of oxygen at the catalyst layer region, respectively. The latter is related to the first-order dependence of the rate of the ORR on the oxygen partial pressure in actual PEFC catalysts [1–3].

The partial pressure of oxygen in the cathode compartment, most importantly in the catalyst layer, must be provided at a sufficiently high level to prevent significant mass transport losses and therefore for sustaining a high total system efficiency. During operation of a PEFC, the oxygen concentration at the cathode catalyst layer is locally lowered by unbalanced oxidant flow distribution and/or unsatisfactory water management within the reactant transport medium and/or catalyst layer. Hence, an important PEFC research area is the development of new reactant transport media and flow field designs. The main objective is to maximize the partial pressure of oxygen at the catalyst layer interface whilst preventing deleterious effects (large pressure drops, flooding etc.) and thus optimising overall PEFC system performance and efficiency. Modelling has played a crucial role in such developmental work. However, there are few experimental methods available for confirming such modelling results [4–6], particularly the distribution of oxygen at the catalyst layer interface. This lack of experimental verification hampers further theoretical and PEFC system developments, e.g. new gas transport media.

Measurement of local oxygen concentration at different points in a fuel cell may be indirectly estimated from the local current density [4,6,7], although spatial resolution is only on the ~mm scale. An alternative method for measuring the concentration of oxygen at the cathode of a PEFC utilises fluorophore molecules, which are sensitive to quenching by oxygen [8]. However, this fluorescence quenching technique provides relatively low spatial and time resolutions of 300 μm and 500 ms, respectively.

A method for determining the flux of oxygen within PEFC electrodes should present high spatial (few micrometres) and time (few milliseconds) resolutions. These distance and time scales correspond to the feature size existing in PEFC components (catalyst layer/microporous layer being ~μm's and characteristic flow rates through channels being ~ms⁻¹, which imply mm flow distance in 1 ms). Therefore, the present authors have chosen to use chemiluminescence, in parts, due to the high intensity of the emitted light in special cases.

Chemiluminescence techniques have been successfully used for quantifying ozone (O₃), an allotrope of oxygen, in the Earth’s atmosphere [9,10]. These optical sensors quantify ozone via monitoring photons emitted in the chemiluminescent reaction between O₃ and an appropriate dye molecule. The instantaneous heterogeneous reaction between ozone and the dye molecule yield emission of photons (usually in the visible wavelength range), with high enough light intensity that detection of ppb concentrations are possible [10]. The present authors appropriately used these features as baselines to propose a new and powerful approach for estimating the pattern of the flux and the local mass transport of oxygen at the experimentally and theoretically desired catalyst layer interface.

As an allotrope of oxygen, ozone has served to indirectly measure the distribution of bimolecular oxygen, which is appropriate due to the similar binary diffusion coefficients in nitrogen (0.175 cm² s⁻¹ and 0.16 cm² s⁻¹ for bimolecular oxygen and ozone respectively and at 1 atm) [11,12]. Utilising rather inexpensive equipment, compared to previous research [4], the approach described in this paper achieves a higher spatial resolution of...
~20 μm and a higher time resolution of ~40 ms. It is noteworthy to quote that the sensor developed here could allow spatial and time resolutions of 1 μm and 1 ms. Another advantage of the presently proposed method is that the flux of the reactive gas is imaged at the desired reactant transport layer/catalyst layer interface in a simulated PEFC. It is noteworthy mentioning that here the membrane is mimicked by an appropriate glass sheet. The high resolutions achieved in the present work are of great importance in developing new gas transport media for PEFCs and in validating models of gas transport in flow fields/gas transport media. For instance, it has been predicted by modelling works that flow is non-uniform in gas transport media [13], and such non-uniformity is proved to indeed be the case through this work.

2. Experimental methods

2.1. Construction of the simulated fuel cell hardware

A simulated fuel cell was constructed from glass-reinforced epoxy laminate sheets (FR4) and precisely machined with a CNC machine (Bungard CCD/ATC). The advantages of using this material are many, as flexibility in design and machining, inertness and stiffness, along with the feature that it is much cheaper and simpler to work with than actual PEFC graphite plates.

The cell was constructed from 100 × 100 × 4 mm thick FR4 sheets, as illustrated in Fig. 1. Multiple FR4 boards were laminated together utilising low-flow prepregs to make up the cell construction illustrated in Fig. 1. The flow fields were machined to 1 mm depth and 0.8 mm in width, with 1.6 mm lands in a single serpentine style with a total of ten parallel channels (22.4 mm in width and height). This configuration was chosen as replica of an actual 5 cm² PEFC single cells.

2.2. Data acquisition apparatus and procedure

An ozone enriched air stream of constant concentration was generated via flowing air through an ozone generator (BMT Sestechnik, Berlin, Germany, model: BMT-801), which had the capability of quantitatively varying the concentration of ozone produced (at a fixed flow rate). Gas flow rates were controlled by a mass flow controller (Omega Engineering Limited, model: FMA 3706). For quantifying the concentration of ozone, the outlet flow stream from the ozone generator was passed through a quartz flow cell (Kromatek Ltd UK, masked flow cell - ES Quartz Glass 190 nm–2500 nm PL 10 mm, Vol 0.24 mL), which was placed into a benchtop UV–Vis Spectrophotometer (Perkin Elmer Lambda 25). Quantification occurred at the known ozone UV absorption peak ($\lambda_{\text{max}} = 253.7; \varepsilon = 3000 ± 30 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) [14].

Fig. 2 displays the experimental setup utilized in this work for imaging the oxygen flux. The bottom cartoon illustrates the experimental apparatus, where after enrichment with ozone the gas stream could either, (a) be directly fed to the UV–Vis spectrophotometer for concentration determination without any chemiluminescent reaction (bypass mode), or (b) directed through the cell and then to the spectrophotometer. The amount of ozone consumed in the chemiluminescent reaction was calculated based on the difference between these UV–Vis absorption signals for ozone (bypass minus through cell). This allowed the exact
and without different gas transport media, highlighting the time necessary to “vent” the cell or the flow field channels and gas lines. Symbols stand for: – FR4 board based measurement cell only; – cell with carbon paper; – cell with teflonated carbon paper; – cell with teflonated carbon paper having a microporous layer. Inset: production of CO2 from a fuel cell electrode with lint-free paper (Kimberly-Clark medical wipes) before being placed into an oven at 60 °C for 30 min. The as-dried ozone sensor plates were then employed as indirect oxygen sensors within 24 h, hence preventing any small though possible deleterious effect due to dye photo-degradation.

The amount of dye deposited was assessed through weighing the sensor plates before and after the deposition. The typical determination of light produced per ozone consumed, and also the stoichiometric coefficient for the operating point. It is noteworthy that the consumption of ozone by the gas transport media was measured when no dye layer was present. A blank experiment was also carried out where only the cell and sealing gasket were present. It was confirmed that, within the precision of the UV–Vis measurements, no ozone is consumed by the FR4 boards utilized in this work (Fig. 3).

The top cartoon in Fig. 2 illustrates the measurement cell used during experiments. As in an actual single PEFC, the cell is assembled with a gasket (from PAR Group Ltd, product: ~140 μm thick PTFE Coated Glass Cloth) for sealing purposes.

At a gas flow rate of 200 sccm, i.e. the flow velocity within the cell is estimated at 4.2 m s⁻¹ (assuming only the channels), the Reynolds number is 240 (assuming the gas transport medium acts as a solid wall). This suggests that the flow is in the laminar regime. Hence, we might expect replacement of the initial air by ozone to be very quick. However, replacement or “degassing” of the gas entrained in the gas transport media, which is a porous carbon paper in this work, might be expected to take a little longer depending on the degree of advection within the gas transport layer. According to the data in Fig. 3, once an ozone rich gas stream is switched (via three way valves shown in Fig. 2) to flow through a flow field, the necessary time to “vent” the flow field channels, the transport media and the gas line is ~10 s. Therefore, analysis performed in this work have taken images collected 10 s after directing the ozone stream to the cell.

The interaction of ozone with the gas transport media used in this work was tested as shown in Fig. 3. According to the data in Fig. 3 (inset) and within the precision of the mass spectrometer used to look for CO2 production, ozone does not react with the test components at room temperature to produce CO2, even at the increased levels used in this test. There is a small amount of ozone consumed when in the through cell mode (Fig 3, main diagram). Under a pseudo-steady state condition, the carbon layer consumed 30 ± 5 ppm ozone, the teflonated carbon layer consumed 14 ± 3 ppm ozone and the teflonated carbon layer with a microporous layer consumed 41 ± 8 ppm ozone. These represent approximately 2.5%, 1.1% and 3.4% in regards to the total ozone in the inlet gas stream, which is acceptably small. The lack of CO2 production suggests that ozone loss is associated with either self-decomposition of the ozone (ozone is unstable and spontaneously decomposes to O₂), or partial oxidation of cell components which does not lead to the formation of CO2.

2.3. Preparation of the indirect oxygen imaging sensors

The oxygen imaging sensors were prepared in a similar way to that mentioned in the literature of chemiluminescent ozone analysers [10], using 7-Diethylamino-4-methylcoumarin (Coumarin 1, Sigma Aldrich, 99%) as dye and ethanol as solvent. It is noteworthy to mention that gallic acid (from Sigma Aldrich, ≥98.0%) was later incorporated into the dye solution, to act as an energy transfer and anti-oxidizing agent (Section 3.2.2). The material employed for supporting the dye was silica gel (Sigma Aldrich Nano Silica Gel on TLC Plates). Briefly, 5 cm × 5 cm ozone sensor plates were immersed for 10 s into an ethanolic solution of coumarin 1. On removal, excess liquid was removed at the edges of the glass sheet with lint-free paper (Kimberly–Clark medical wipes) before being placed into an oven at 60 °C for 30 min. The as-dried ozone sensor plates were then employed as indirect oxygen sensors within 24 h, hence preventing any small though possible deleterious effect due to dye photo-degradation.

Fig. 3. Ozone concentration during bypass mode (Fig. 2) and after switching gas stream to the measurement cell with and without different gas transport media, highlighting the time necessary to “vent” the cell or the flow field channels and gas lines. Symbols stand for: – FR4 board based measurement cell only; – cell with carbon paper; – cell with teflonated carbon paper; – cell with teflonated carbon paper having a microporous layer. Inset: production of CO2 from a fuel cell electrode with lint-free paper (Kimberly-Clark medical wipes) before being placed into an oven at 60 °C for 30 min. The as-dried ozone sensor plates were then employed as indirect oxygen sensors within 24 h, hence preventing any small though possible deleterious effect due to dye photo-degradation.

Fig. 4. Light generation through interaction with ozone. (a) Direct reaction of ozone with 7-diethylamino-4-methylcoumarin leading to dye consumption; (b) reaction of ozone with gallic acid followed by Förster energy transfer to 7-diethylamino-4-methylcoumarin.
average weight of coumarin deposited on a 25 cm² sensor plate by immersion in a 50 g dm⁻³ (0.22 mol dm⁻³) dye solution in ethanol was 684 ± 32 μg cm⁻² (2.96 ± 0.14 μmol cm⁻²). This small standard deviation illustrates the reproducibility of the technique.

The ozone sensor plates as bought had a 200 μm thick silica gel layer, the thickness of which was varied in order to assess different support thicknesses, as illustrated in Fig. 5. A film applicator (Sheen, model1117 Micrometer Adjustable Film Applicator) was utilized in order to precisely and gradually thin the silica gel layer until a desired thickness was reached. The required thickness was verified by a digital micrometer (Mitutoyo Digimatic Micrometer). This procedure proved to be quick, simple and precise with a deviation of ±3 μm.

2.4. Procedure for image analysis and corresponding correlation to the on-line ozone concentration

Videos were collected with an inexpensive CCD camera utilising a Sony Super HAD CCD sensor, which possess appropriate low light performance and a linear response (Abus WDR 3D DNR Day/Night 650 TVL). Frames were extracted from the videos making use of a free software package FFmpeg [15]. These frames were then analysed with the public domain Java image processing program, Image [16]. This programme allows for integration of light intensity along all pixels of an image, cropping of regions with subsequent integration of light intensity of the pixels, consistent subtraction of backgrounds etc.

The UV–Vis Spectrophotometer results allowed for the direct correlation of light intensity produced by the chemiluminescent reaction to the amount of ozone consumed by this process. The integration of light intensity across all pixels in an image was compared to the reduction in the amount of ozone consumed as measured using the UV–Vis Spectrophotometer, in order to generate calibration curves.

3. Results and discussion

3.1. Determination of the reactant flux at the catalyst layer interface

Light generation in the active layer occurs due to a reaction between ozone and the coumarin dye. As it has been discussed in the literature [10], ozone directly reacts with the dye (Fig. 4(a)) to generate photons in the visible region. The coumarin dye is therefore consumed in this reaction, and care must be taken to limit the ozone concentration and contact time, as discussed further below. An alternative path utilises an energy transfer agent [10], Fig. 4(b). In this case, the reaction proceeds via the Forster-resonant energy transfer mechanism, where the energy transfer reactant, upon reaction with ozone, generates products in an excited state, whose excess energy is transferred to the dye, which then luminesces. In this case the dye is considered not to be consumed, although the energy transfer material is.

Fig. 5. Example of result of the present gas transport imaging technique. The top diagram illustrates a cross-section of the serpentine flow field and how reactant generates light when it has traversed across the gas diffusion layer. The bottom six images show experimental images of light generation, highlighting those regions in which reactant permeation through the gas transport medium is enhanced. Secondary flow near flow field corners enhances light generation. Air flow rates are specified in the figure along with the measured ozone stoichiometry. For comparison, the equivalent current density for a PEFC at that stoichiometry and air flow rate is also shown. Pixel intensity integrated for 40 ms (single frame). Ozone concentration in the inlet air stream is 1300 ppm. Sensor plates composed of a 150 μm silica layer. Dye treatment utilised 2.2 mol dm⁻³ coumarin and 2.2 mol dm⁻³ gallic in ethanol. Gas transport medium is a carbon paper from Toray, type TGP-H-60. No back pressures. Dry air at room temperature (25 °C ± 2 °C).
Fig. 5 provides some striking images generated using the new technique presently proposed. Images in Fig. 5 display light generation associated with the transport of ozone through a flow field, and then through the subsequent gas transport layer before impinging on the sensor plate (illustrated in Fig. 2). Sufficient light is produced to see with the naked eye. Each image shows the flow rate used and the effective stoichiometric coefficient for the consumption of ozone under those conditions. Also shown is the equivalent current density for a PEFC running at the same air flow rate and cathode stoichiometry. Those areas with high mass transport of gas due to increased advection in the channel and gas transport layer show up brighter. The amount of light generated (and thus the ease of gas transport with the flow rate) increases as the volumetric gas flow is increased. Furthermore, secondary flow is apparently predominant at and after U-turns and the effective flow area increases with flow rate. This later fact explains one of the reasons for applying high fixed stoichiometric flows for comparing standard PEFC results. For instance, the US Department of Energy specifies a cathode stoichiometry of 9.5 for testing the mass activity of new ORR electrocatalysts.

Cross flow of gas to neighbouring channels through the gas transport media has been modelled [17] to happen due to pressure gradients between channels. Due to the high spatial resolution achieved by the presently proposed technique, this is proven to be the case by data shown in Fig. 5. The magnitude of the pressure drop is greatest at the points where the neighbouring channels are furthest from the U-bend. Hence, convective flow under the land through the gas transport layer is expected to be higher in this region, and hence higher luminous intensity. This phenomenon is demonstrated in Fig. 5 and is more prominent moving from upstream to downstream. According to data in Fig. 5 at higher flow rates, gas also diffuses towards the previous channel at the U-turns. This is attributed to the formation of vortexes at the U-turns. Inspection of data suggests a gradual decrease in the light intensity from the inlet to the outlet of the serpentine flow field. As shown later in the paper, this is due to the consumption of ozone moving downstream through the flow field—i.e. it is due to a reduction in the ozone concentration in the channel from inlet to outlet. It is noteworthy mentioning that this would represent the scenario at the cathode of an PEFC operating under oxygen mass transport limited conditions (disregarding effects of water).

Pressure and velocity fields within a PEFC has been modelled [13], predicting the existence of a maximum pressure gradient on the corner between the flow field land and the gas transport layer (as illustrated by the top zoomed region in Fig. 5). This effect would cause convective flow to come up underneath the lands increasing with the flow rate of gas. This is apparently observed in Fig. 5, whereas the enlargement caused by secondary flow at the U-turns is much more prominent and clear. Yang et al. [18] have modelled the distribution of the local membrane current density predicting this to be much larger under the flow channel area, owing to the faster access of the reactants. It was also shown that from channel inlet to outlet, the concentration of reactant species decreases due to consumption of reactants. These are also demonstrated in Fig. 5, while the images also show that the flow underneath the lands or ribs is clearly not equidistantly distributed.

It can also be observed in Fig. 5 that the light generation areas are wider at the beginning of each channel segment, narrowing towards each end. This narrowing does not appear purely due to the depletion of the reactant in the channel as there is a clear enhancement at the beginning of the next segment. This effect can be rationalized as secondary flow upon the change in gas momentum at the U-turns, which is then gradually directed towards a more-laminar flow at the end of each channel segment, as illustrated by the bottom-zoomed cartoon in Fig. 5. This explanation is also constructed based upon the magnitude of the local pressure along the channel segments (Fig. 11), where the partial pressure of reactant gas remains similar at the first four-five U-turns (further details in Section 3.3). It is important to consider that compression of the gas could also contribute to similar effects, however under the present flow velocities (4.17 m s⁻¹–9.38 m s⁻¹), this would not be expected to be a major factor. We also observe from Fig. 5, that at higher flow rates, gas is more prone to flow over the edges of the 5 cm² active area, which highlights the importance of gaskets surrounding the electrodes.

For most practical applications of PEFCs, air is utilized rather than pure oxygen. Therefore mass transport due to the diminished oxidant partial pressure critically affects the overall cell performance. This limitation can be addressed by operation at stoichiometries significantly higher than unity, as mentioned above and markedly shown in Fig. 5. However, this approach results in an increased parasitic power loss and reduces PEFC system efficiency. Therefore, for a fuel cell design to effectively tackle oxygen transport, flow distribution at the reactant transport medium/catalyst layer interface must be rigorously defined and evenly distributed throughout the reaction field or electrode area, towards increasing catalyst utilisation. Indeed, the effectiveness of platinum utilization...
back pressures. Dry air at room temperature (25 °C; 1300 ppm. Gas transport medium is a carbon paper from Toray, type TGP-H-60. No back pressures. Dry air at room temperature (25 °C ± 2 °C).

has been estimated to be as low as 10% in regions with ineffective mass transport [19]. These points have led to modelling and experimental studies of flow distribution within PEFCs. Despite the number of modelling works [13,18,20], there are few experimental studies in this field and the majority focus in the flow field region [6,18]. This might reflect the lack of experimental approaches/techniques capable of probing the catalyst layer interface region, as remarkably illustrated by Fig. 5.

Data in Fig. 5 also provide indirect evidence of the augmentation of the total partial pressure of oxygen towards the catalyst layer with increasing gas flow rate, i.e. provides evidence of improved catalyst utilization at higher stoichiometries. More direct evidence of this effect is seen in Fig. 6(a), where the total pixel intensity with flow rate is plotted along with the contribution of the convective flow to the total pressure drop along the hardware. For comparison, the equivalent Reynolds number for the system (80 °C) is also displayed. For the lower five flow rates tested a direct linear relationship between integrated pixel intensity and the flow rate is observed (linear fit, \( r^2 = 0.999 \)). The non-zero intercept of the line is associated with background pixel noise, and incomplete light shielding of the cell. At higher flow rates the light intensity falls short of that which would be expected. Evidently, beyond a certain point an increase in the flow rate does not give an added improvement in reactant distribution/total partial pressure, which is tentatively assigned with the contribution of the convective flow at the GDL to the pressure drop along the cell, Fig. 6(b). Hence, this value apparently represents an optimum gas distribution towards the reactant transport layer/catalyst layer interface of a routinely utilized single serpentine flow field design — that is further increases in gas flow rate will not lead to significant improvements in performance, once contributions due to convective flow reaches a steady state. These also evidence the utilization of high stoichiometric flows for comparing and testing new ORR catalysts in PEFCs.

### 3.2. Physical chemistry of the reactive gas imaging sensor

Ozone is a highly reactive gas that promptly reacts with a range of chemical compounds. Organic dyes are an example of such, however with a striking feature of producing light upon this reaction. Heterogeneous solid phase chemiluminescence ozone sensors have been developed taking advantage of this feature [10,21]. These sensors are used to detect atmospheric ozone at ppm and ppb levels. The physical chemistry behind these sensors rely on the gas molecules diffusing through a porous support, followed by reaction with the dye molecules adsorbed on the surface of the support (Fig. 5) to emit photons. These photons are then collected by, for instance, a photomultiplier, and this allows the quantification of ozone concentrations in the gas stream. It is noteworthy to mention that the binary diffusion coefficient (at 1 atm pressure) of \( O_3 \) in nitrogen and that of ozone in nitrogen are 0.175 cm\(^2\) s\(^{-1}\) and...
0.16 cm$^2$ s$^{-1}$ respectively, a 9% difference [11,12] which suggests that ozone is a reasonably good mimic for O$_2$ in fuel cell systems. Under realistic operating conditions of a fuel cell (\(P = 150 \text{ kPa}\), \(T = 80 \degree \text{C}\), and 50% RH), the binary diffusion coefficient of oxygen in nitrogen at 50% RH can be calculated as 0.22 cm$^2$ s$^{-1}$ using the generalized FSG theory [22]. Hence, compared to operation in a PEFC, the diffusive flux of ozone at room temperature in our experiment is a little low although still within a regime in which useful information can be obtained, especially as advection also appears to be an important transport mechanism (see below). Furthermore, operation of our experimental approach at a temperature of 70 \degree \text{C} would increase the bimolecular diffusion coefficient of ozone to 0.22 cm$^2$ s$^{-1}$ [23] i.e. the same as oxygen under the PEFC conditions mentioned above.

In developing this new approach, the present authors have used the approach previously developed for a single point ozone sensor (a zero-dimensional measurement), and expanded it to produce a two dimensional sensor imaged using a CCD camera. The amount of light generated is clearly visible to the naked eye, allowing us to use rather unsophisticated and inexpensive hardware.

### 3.2.1. The effect of the silica layer thickness and dye loading

By correlating the amount of light generated during the reaction with the amount of ozone consumed, it is possible to determine the luminous efficiency of the indirect oxygen imaging chemiluminescence sensor as a function of the different operational variables, for instance the concentration of dye in the deposition solution. This is also important in assessing the linearity and stability of light production. Displayed in Fig. 7 is the relative luminous efficiency, \(\eta_{rel}\), of light generation for a range of different sensor plates. The relative luminous efficiency is calculated as the total integrated pixel intensity for one frame (40 ms) divided by the amount of ozone consumed during the chemiluminescent reaction between Coumarin and ozone during the reference period of time. It is noteworthy that the total amount of ozone consumed during the chemiluminescent reaction is measured synchronously to the imaging by use of an UV–Vis Spectrophotometer, which is coupled to the outlet gas stream, Fig. 2. The inset in Fig. 7 shows the \(\eta_{rel}\) divided by the mean value for the appropriate dataset. Data in Fig. 7 suggest that a thick layer of silica gel, although producing more light per ozone consumed also shows relatively unstable light production — the light production seems to increase over time, and the standard deviation is high (514). By contrast, use of a thinner layer of dye results in an adequate response. Of the two samples made with 150 \(\mu\)m silica layers, the one made using 2.2 M coumarin solution shows a light output with the smallest standard deviation (73) and no long term bias, whereas that made with the 4.4 M coumarin solution shows a slight decrease over time, with a larger standard deviation (134). The higher overall efficiency of the thicker silica layer is probably due to the greater average separation of coumarin molecules in the silica, which would reduce self-quenching [24]. This is confirmed by the effect of increasing the dye concentration on the 150 \(\mu\)m layers, which almost halves the luminous efficiency for doubling of coumarin dye content (Section 3.2.2). The poor stability of the thicker silica layer can be interpreted as indicating an issue with the diffusion of ozone through thick layers. Furthermore, non-uniform light intensities may be due to light being absorbed by the dye and the thick silica layer.
over time, light is generated closer to the glass interface (verified during experiments), which causes an increase in light/ozone detected (not the amount produced). By tuning both the thickness and dye loading on the silica, an optimum sensor can be produced with appropriate light production efficiency and stability (150 μm, 2.2 M coumarin).

3.2.2. The addition of an energy transfer agent: gallic acid

According to the data in Figs. 7 and 8, increasing the concentration of dye deposited on the support causes a decrease in the amount of light generated, suggesting self-quenching, as also suggested in Section 3.2.1 for thicker silica layer. In order to reduce quenching, it is necessary to increase the average dye molecule separation i.e. reduce the volumetric loading of the dye. However, this leads to lower absolute light intensities. One approach for mitigating this lower light intensity is to use an energy transfer reagent, a common example of which is gallic acid [10]. This molecule acts as an antioxidant and energy transfer reagent, where ozone reacts with gallic acid to produce an excited reaction product. This transfers energy to the dye, which then fluoresces, Fig 4(b) [10]. The gallic acid does not act to significantly quench the dye.

Evidence for this is the two-fold contribution of gallic acid to the total light intensity generated, Fig. 8. Data in Fig. 8 evidences the energy transfer reactant promotes an approximately 50% increase in light generation, at the optimum dye concentration, and secondly it reduces the effect of self-quenching at higher concentration. The latter advantage is illustrated by the evident suppression in the reduction of light generation at higher dye loadings. Therefore, gallic acid was incorporated into the dye solution for preparing the indirect oxygen imaging sensors.

It is noteworthy mentioning that utilizing an energy transfer/anti-oxidizing reagent enhances the longevity of the optical ozone sensor, i.e. the rate of degradation of the dye is significantly reduced. This in turn renders an expanded linear region for accurately correlating light intensity to the partial pressure of the reactive gas (Section 3.2.4).

3.2.3. Linearity of light generation to ozone partial pressure

The light intensity generated by the chemiluminescent reaction is linearly correlated to the partial pressure of ozone, i.e. Light Intensity ≈ PO3, Fig. 9. The partial pressure of ozone was calculated based on Appendix XI of ASTM Standard D4574-09 [25]. It is also
noteworthy mentioning that the concentration of ozone was varied by tuning the ozone generator, with a constant flow rate of gas. This quantification is of fundamental importance on indirectly quantifying the local partial pressure of the reactive gas along the reactant transport layer/catalyst layer interface, as illustrated in Fig. 11.

Data plotted in Fig. 9 evidence that the ozone sensor system presently developed works under mass transport limited conditions, where the diffusion of ozone through the gas transport media limits the amount of light generated. This scenario is appropriate for indirectly studying the impact that the constituents of a gas transport media has over the transport of oxygen towards the reactant transport layer/catalyst layer interface of a PEFC (no electrochemical reaction and dry gas, Section 3.3).

3.2.4. Time variation of ozone response

In order to establish the time variation of the chemiluminescent response, the total integrated pixel light intensity was plotted as a function of the experimental time for cropped regions along the flow field length, Fig 10. In this diagram, the integrated light intensity is assessed as a function of time at three different regions of the flow field under three different flow rates of air. The data show a characteristic structure — after an initial plateau, the light production starts to fall away. Light production is initially always greatest at the inlet, and least at the outlet. The light intensity of the plateau region is proportional to the reactant flow rate. The inflection points correspond to the appearance of dead spots in the images corresponding to total consumption of dye at that region. The inflection point occurs sooner for regions where more light is being produced, as might be expected. The difference in absolute value of light production at different positions in the flow field at short time is due to the greater ozone concentration at the inlet compared to the outlet (i.e. ozone consumption along the channel). For the sampled points at the middle and outlet, there is a slight increase in intensity during the plateau region, probably due to a slow increase in local ozone concentration as the upstream regions reduce their ozone consumption. During the plateau region, it would appear that the light production is independent of the coumarin coverage on the silica, i.e. Light Intensity $\propto P_0 J (C_{\text{coumarin}})^{10.5}$, where $C_{\text{coumarin}}$ is the coverage of coumarin on the silica (mol cm$^{-2}$). In a follow up work, the kinetics of this process is extensively explored. It is noteworthy highlighting that this zero order dependence of light generated on $C_{\text{coumarin}}$ evidences that the presently developed indirect oxygen imaging system works under ozone mass transport conditions. This scenario is well appropriate for studying the impact that the constituents of a gas transport media has over the transport of oxygen towards the reactant transport layer/catalyst layer interface of a PEFC (dry gas, Section 3.3).

In this set of experiments, a low cost hardware (e.g. an off-the-shelf camera) with only moderate low light performance was utilized. By shifting to a camera with much better low light performance, it would be possible to increase the length of the plateau significantly e.g. by shifting to a camera with improved low light performance and at the same time dropping ozone concentration, the length of the plateau could be increased by a factor of 100–1000.

3.3. Comparison of light intensity generation with current production in a PEFC

In order for this ex-situ approach to be a viable representation of what happens within a fuel cell, it is necessary for the light generation process to accurately mimic the current generation processes within the cathode of a PEFC. For this to happen, at a minimum, the following must occur:

a) The components used should be the same as those used within a PEFC;

b) The current generation process should be dominated by processes occurring withing the cathode and not by anode processes (e.g. hydrogen starvation) or membrane issues (e.g. low conductivity);

c) The reaction process should be first order with respect to the reactant;

d) The reaction process should show no time variation, i.e. light generation process produces same amount of light over time under steady state conditions (as occurs with current in a PEFC);

e) The reactant should not react with the material of the PEFC, only the “catalyst layer”;

f) The reactant should show transport properties similar to bimolecular oxygen;

Ideally one would also have a system which showed:

g) Product water being produced at the same rate as in a PEFC and being transported in the same way;

h) Enthalpy of the reaction is similar to oxygen reduction so heating effects are approximately similar.

Common components available for fuel cells have been used in the presently developed system. The catalyst layer have been replaced by an ozone detection layer, which under the right conditions detects every ozone molecule reaching this layer (Fig 7, plateau region in Fig. 10) – i.e. we are operating under the condition that electrokinetics are fast, and performance is limited by local reactant transport. This situation exists when the fuel cell is being operated at high power density. The present study explicitly set out to study oxygen transport through the reactant transport layer and MPL of the cathode. Therefore, the operational region is defined as not being limited by “the cathode electrokinetics or electrolyte”. As shown in Fig. 9, the light generation process is first order with ozone concentration. Therefore, this reliably replicates the electrokinetics of oxygen reduction for which there is a first order dependence on bimolecular oxygen concentration. By carefully tailoring the light generation layer, the present authors have been able to generate a layer which shows light output independent from time (for a defined period – plateau in Fig. 10). Data in Fig. 3 clearly shows that there is visually no reaction between ozone and the fuel cell components studied in the present investigation. Finally, the probe molecule used for this study has a similar diffusion coefficient to bimolecular oxygen, although as described above the diffusion coefficient may be a little lower than that seen for oxygen under fuel cell operating conditions. Operation of our system at a temperature of 70 °C would increase the diffusion coefficient of ozone to the same value as oxygen under realistic fuel cell operating conditions ($P = 150$ kPa, $T = 80$ °C, and 50% RH, see earlier). Hence the requirements for (a–f) are met. Comparison of these results with an operating fuel cell would ideally occur under conditions in which the fuel cell geometry is the same, the gas flow rates are the same, and the stoichiometry for oxygen consumption are the same as for ozone consumption (Fig. 5).

With regard to water, this is a product of the reaction of ozone with the coumarin dye, though the rate of water production is likely to be smaller than that within a PEFC. The present authors are looking into the rate of water production during this reaction to measure the magnitude of this difference. The Enthalpy of the reaction between ozone and the coumarin dye is much greater than that of the oxygen reduction in a PEFC. However, the total heat produced is liable to be much smaller here, due to the rate of
reaction between ozone and the coumarin dye being much lower than that at the cathode of a PEFC.

These appropriately selected features of the presently proposed approach evidence that our imaging technique can provide useful information about reactant transport through reactant transport and microporous layers within a PEFC environment (as shown in Fig. 11).

3.4. The impact of PTFE and a microporous layer of a GDL on the distribution of a reactive gas at the reactant transport layer/catalyst layer interface of a simulated-PEFC

Based on the above results, and making sure that we are operating in the plateau region of Fig. 10, it is possible to directly correlate the ozone partial pressure to the amount of light locally produced (Fig. 9, Light Intensity \( \propto p_{O_3}(\text{coumarin})^3 \)). Hence, a local map of ozone partial pressures can be generated, mimicking that of oxygen on the cathode of a PEFC (operating under mass transport limited conditions and disregarding effects of water).

The reactant transport layer is an important constituent of PEFCs, where these provides mechanical support for the catalyst layer, electronic pathway for electrons and a flow channel for the reacting gases and product water towards and from the three-phase-boundary interface [26]. With regards to the later characteristic, the transport layer is commonly complimented by a microporous layer (MPL) on one of its faces. This is composed of carbon black powder and a hydrophobic agent such as PTFE. The resulting pores in the MPL are primarily between 0.1 and 0.5 \( \mu m \) in diameter, which is smaller than the pore size of the gas transport layer, 10–50 \( \mu m \) [27]. Under this conventional configuration, the gas transport media is composed of two layers, a macroporous carbon substrate and a microporous composite layer. The impact of these components on the distribution of a reactive gas at the catalyst layer interface is illustrated in Fig. 11, i.e. the macroporous carbon layer without and with TeflonTM, and the latter without and with a microporous layer. Data in Fig. 11 shows that when TeflonTM is added to the macroporous layer (c.a. refloated carbon paper), this causes a reduction of ~3.0% in the total partial pressure of the reactive gas at the catalyst layer interface, i.e. the PTFE “obstructs the flux of reactive gas”. Similarly, when a microporous layer is added on one face of the teflonated carbon paper an additional loss of -3.5% is seen. This results in a cumulative loss in reactant partial pressure of ~6.5% at the heart of a PEFC, or at the catalyst layer interface. Even though the hydrophobic agent and the microporous layer are important for, e.g. water management, catalyst ink distribution etc, these benefits come at the expense of a lower partial pressure of reactive gas at the catalyst layer interface. These results highlight that even at such an advanced stage of development, PEFCs have much room for further development and that new diagnostic tools, such as the one presented here can play a crucial role in this aspect.

4. Conclusions

The present work has developed a new, inexpensive, simple and effective methodology for indirectly determining the profile of a reactive gas at the catalyst layer interface of the cathode of a simulated PEFC. By selecting the proper operating regime, it is possible to directly image the reactant partial pressure across the entire face of an electrode at ~20 \( \mu m \) spatial resolution and 40 ms time resolution.

It has been shown that higher flow rates lead to better distribution of the reactive gas throughout the reaction field or electrode area, which is highly desirable towards maximizing the utilization of catalysts in the catalyst layer. The present work has also provided evidence for secondary flow of gas near flow field corners, bringing to light an “unexpected” parameter to the “expected” laminar PEFC fluid dynamics. The importance that cut to size gaskets may play on preventing gas cross over the edge of the electrodes is presented to be critical at high flows.

The impact of the components of a reactant transport medium, namely hydrophobic agent and microporous layer, on the distribution of a reactive gas at the catalyst layer interface is shown to be detrimental. Both components diminish the flux of reactive gas, which would be seen in an operating PEFC as increased gas mass transport losses. This highlights that there is scope for further development of gas transport media. Future advances to this technique should attempt to increase operating temperature in order to better match the binary diffusion coefficient of ozone with that of oxygen under fuel cell operating conditions; incorporate the effect of condensed water distribution in the reactant transport layers; and measure how this influences reactant transport. Incorporation of the technique in an operating fuel cell would give even more benefits.

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