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Authors	Geaney, Hugh;O'Connell, John;Holmes, Justin D.;O'Dwyer, Colm
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# On the use of gas diffusion layers as current collectors in Li-O<sub>2</sub> battery cathodes

Hugh Geaney<sup>1,2</sup>, John O'Connell<sup>1,2,3</sup>, Justin D. Holmes<sup>1,2,3</sup> and Colm O'Dwyer<sup>1,2\*</sup>

<sup>1</sup>*Department of Chemistry, University College Cork, Cork, Ireland*

<sup>2</sup>*Tyndall National Institute, Lee Maltings, Cork, Ireland*

<sup>3</sup>*Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN), Trinity College Dublin, Dublin, Ireland*

## Abstract

We investigate the impact of using a carbon based gas diffusion layer (GDL) as the current collector for Li-O<sub>2</sub> batteries. It is shown that the GDL actively participates in ORR during discharge conditions and, if its mass is not accounted for, can lead to inflated discharge capacity figures compared to inert cathode supports. SEM and XRD analyses show that Li<sub>2</sub>O<sub>2</sub> discharge products form on cathodes composed of as-received GDL in a similar manner to that observed for carbon on stainless steel (SS) current collectors (at applied currents of 100  $\mu\text{A cm}^{-2}$  or less). The relative activity of the GDL, carbon on GDL and carbon-on-stainless steel current collectors from voltammetric measurements confirmed ORR and OER processes to be similar at all carbon-based surfaces. When heated above 300 °C, degradation of the binder in the GDL and associated loss of carbon from the substrate surface leads to reduced discharge times compared to the pristine GDL substrates. The data highlight the importance of the contribution to ORR/OER in carbon-based active current collector substrates when determining gravimetric capacities of Li-O<sub>2</sub> batteries.

\* **Corresponding author:** Colm O'Dwyer, Tel: +353 (0)21 4902732; Fax: +353 (0)21 4274097; email: [c.odwyer@ucc.ie](mailto:c.odwyer@ucc.ie)

## Introduction

Li-O<sub>2</sub> batteries are attracting ever increasing research attention due to their promise as high capacity energy storage devices.<sup>1-7</sup> These high capacities stem from a fundamentally different battery chemistry compared to conventional Li-ion systems. Li-O<sub>2</sub> batteries rely on the reversible formation and decomposition of a solid discharge product (Li<sub>2</sub>O<sub>2</sub>), nucleating from the electrolyte and/or on the cathode surface.<sup>8-13</sup> The formation of this discharge product requires the presence of O<sub>2</sub> meaning (at least conceptually) that this reagent can be provided directly from the atmosphere at an 'air breathing' cathode. The majority of cathode systems to date have consisted of carbon supported catalyst materials (e.g. Co<sub>3</sub>O<sub>4</sub>,<sup>14</sup> MnO<sub>2</sub>,<sup>15-17</sup> noble metals<sup>18, 19</sup> etc.), aimed at reducing the potentials for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) associated with discharge and charge processes respectively.<sup>20, 21</sup> While Li-O<sub>2</sub> batteries offer theoretical capacities which may be multiples of conventional Li-ion batteries, several issues related to the complex battery chemistry including large overpotentials (particularly on charging),<sup>22</sup> poor rate capability,<sup>23</sup> cathode and electrolyte instabilities,<sup>24-29</sup> reduced conductivities of Li<sub>2</sub>O<sub>2</sub><sup>30, 31</sup> and device level issues such as the provision of pure, dry O<sub>2</sub> must be addressed if these systems are to be realized as practical devices.<sup>32, 33</sup>

The issue of capacity determination in Li-O<sub>2</sub> batteries is a crucial one. Many reports calculate capacities based solely on the amount of carbon contained in the cathode. Commonly, the weights of catalysts and binders (which may be up to 50% of the total electrode mass) are ignored when determining specific capacities making some reported capacity figures difficult to truly assess with respect to the innovation in some aspect of the cell. To date, only carbon-free cathodes have shown true rechargeability (i.e. without curtailing the depth of discharge)<sup>34-36</sup> with the majority of long term cycling experiments for carbon-based cathodes conducted at a limited depth of discharge (typically 1000 mAhg<sup>-1</sup>) in an effort to minimize by-product formation and improve cycle life.<sup>37, 38</sup> An often

neglected issue in the development of Li-O<sub>2</sub> systems is the cathode current collector.<sup>39</sup> The vast majority of reports to date have examined the use of three types of cathode supports namely: i) metal meshes<sup>34, 35, 40-42</sup> ii) Ni foams<sup>43-45</sup> and iii) carbon based cathodes.<sup>46-49</sup> Carbon based cathodes such as commercial gas diffusion layers (GDL) are an interesting class of current collector (due to their low cost and low density in comparison to metal alternatives) but require further study if they are to be viable supports for Li-O<sub>2</sub> batteries.<sup>50-53</sup>

Here, we investigate the impact of using a carbon based GDL as the current collector for Li-O<sub>2</sub> batteries. It is shown through voltammetric analysis that the GDL actively participates in ORR during discharge conditions and, if its mass is not accounted for, can lead to inflated gravimetric capacity figures compared to inert cathode supports. SEM and XRD analyses show that Li<sub>2</sub>O<sub>2</sub> forms on the pristine GDL cathodes after a single discharge in a similar manner to that observed for conventional carbon on stainless steel (SS) current collectors from identical electrolytes. In contrast, stainless steel current collector substrates are shown to be truly inert and allow easy determination of the true gravimetric capacities of added active materials.

## **Experimental:**

### **Cathode preparation:**

GDL cathodes (SIGRACET GDL 24 BC) were made by cutting 1.75 cm<sup>2</sup> disks or 0.75 cm<sup>2</sup> rectangles from larger sheets. GDL cathodes were either analysed as received (room temperature (RT)) or heated in air to various temperatures (100 °C, 300 °C and 450 °C) overnight. GDL cathodes referred to 'as received' throughout the text do not contain any added active material. For the cathodes with added Super P carbon, slurries of Super P carbon (MTI corporation) and PVDF (average Mw ~534,000 from Sigma Aldrich) (weight ratio of 4.5:1) in NMP (99.5% anhydrous also from Sigma Aldrich) were prepared. These slurries were mechanically stirred before being dip coated on stainless steel mesh

current collectors or GDL discs. The meshes/GDL cathodes were dried overnight at 100 °C to remove the solvent and transferred immediately to an Ar glovebox before testing. The final mass loading of added active material (combined added carbon and PVDF weight) on both the 1.75 cm<sup>2</sup> GDL (with added Super P carbon) and SS cathodes was found to be 1 ±0.4 mg per 1.75 cm<sup>2</sup>. A similar mass loading was applied to the 0.75 cm<sup>2</sup> cathodes with added carbon. This active mass loading is comparable to the vast majority of previous reports for Li-O<sub>2</sub> batteries. The final weight ratio of the Super P/GDL used this study for the Super P on GDL cathodes is thus ~1:10. All cathodes were stored in the same Ar-filled drybox prior to testing.

### **Electrochemical testing**

Electrochemical tests were performed using an EI-Cell split cell. All cells were constructed within an Ar filled glovebox (O<sub>2</sub> and H<sub>2</sub>O < 0.1 ppm). The cathodes were first placed on the metal separator. A glass fiber filter paper was used as separator upon which 100 µl of electrolyte (1M LiClO<sub>4</sub> (battery grade, dry, 99.99% trace metals basis) in ≥ 99% Tetraethylene glycol dimethyl ether (TEGDME)) (both from Sigma Aldrich) was placed. A Li chip (MTI) was scraped on both sides and used as the anode. The cell was tightened and removed from the glovebox where it was immediately connected to an O<sub>2</sub> line and was purged with 0.25 bar O<sub>2</sub> for 60 minutes at open circuit voltage (OCV). Following this period, electrochemical measurements were conducted using a VSP Biologic galvanostat. All measurements were conducted using fixed applied currents rather than currents calculated based on the mass. All voltages quoted are vs Li/Li<sup>+</sup>. Where discharge capacities are presented in the text, they are calculated based on the mass of the components listed in the subscript of mAhg<sup>-1</sup><sub>x</sub>. Cyclic voltammetry measurements were conducted using a 3-electrode configuration with Li metal as both counter and reference electrodes. Voltammograms were recorded at a scan rate of 1 mV/s.

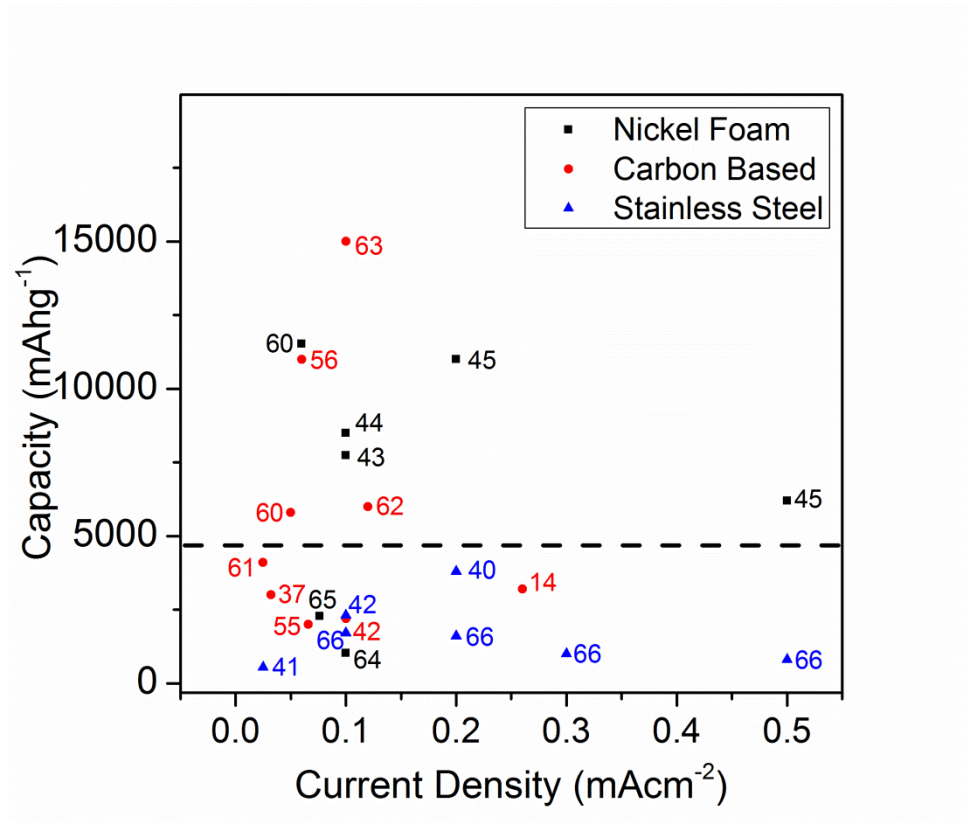
### **Materials characterization**

SEM analysis was performed on a FEI Quanta 650 FEG high resolution SEM equipped with an Oxford Instruments X-MAX 20 large area Si diffused EDX detector. Images were collected at operating voltages of 10-20 kV. All cathodes for SEM analysis were stored in an Ar-filled glovebox and transferred in closed containers with 0.1 ppm H<sub>2</sub>O and O<sub>2</sub>. Samples were loaded into the SEM as rapidly as possible and the SEM chamber was evacuated. XRD analysis was performed using a Phillips Xpert PW3719 diffractometer using Cu K $\alpha$  radiation (40 kV and 40 mA).

## Results and discussion

A wide range of reports have investigated the use of SS, Ni mesh and carbon based cathodes.<sup>54</sup> In Figure 1 the reported gravimetric capacities (mAhg<sup>-1</sup>) are plotted against the applied current density (mAcm<sup>-2</sup>) for a range of cathode systems. In each case, the discharge capacities (mAhg<sup>-1</sup>) have been calculated based on the added active material on the cathode surface (in the case of interwoven carbon cathodes the entire mass is considered). Looking at the discharge capacities reported for many of these cathode current collectors, it can be seen that SS based cathodes consistently show lower capacities than Ni foams and carbon-based cathodes. The dotted line in Figure 1 shows that gravimetric capacities for SS based cathodes are consistently below 5000 mAhg<sup>-1</sup> while those for carbon and Ni-based cathodes are regularly above this value. When considering the high discharge capacities reported for tests conducted using Ni foam cathodes it should be noted these current collectors have previously shown instability within typical Li-O<sub>2</sub> battery voltage windows (with contributions to the discharge time/charge due to parasitic side reactions).<sup>39, 54</sup> These previous investigations were conducted using a EC/DMC electrolyte which is unsuitable for practical Li-O<sub>2</sub> systems and thus the stability of Ni foam cathodes requires further study in more practical electrolytes (ether based, DMSO etc.). In terms of carbon based cathodes there are two possible reasons for the high capacity figures. For pure carbon cathodes made from interwoven carbon fibers, the lower density of the carbon compared to SS can account for the increased discharge

gravimetric capacities, particularly if the accumulated charge relates to a similar overall process of predominantly  $\text{Li}_2\text{O}_2$  formation.<sup>46, 47, 55</sup> The alternative explanation for the high capacity figures presented for the GDL based cathodes is the possible participation of the GDL in the ORR reaction during discharge. In this case, the longer discharge times are misconstrued as additional capacity from solely the added active material.<sup>56-58</sup>



**Figure 1:** Plot of gravimetric capacity vs applied current density for a variety of materials on different current collector substrates. The numbers beside each point correspond to the reference for each data point.<sup>14, 37, 40-45, 55, 56, 59-66</sup>

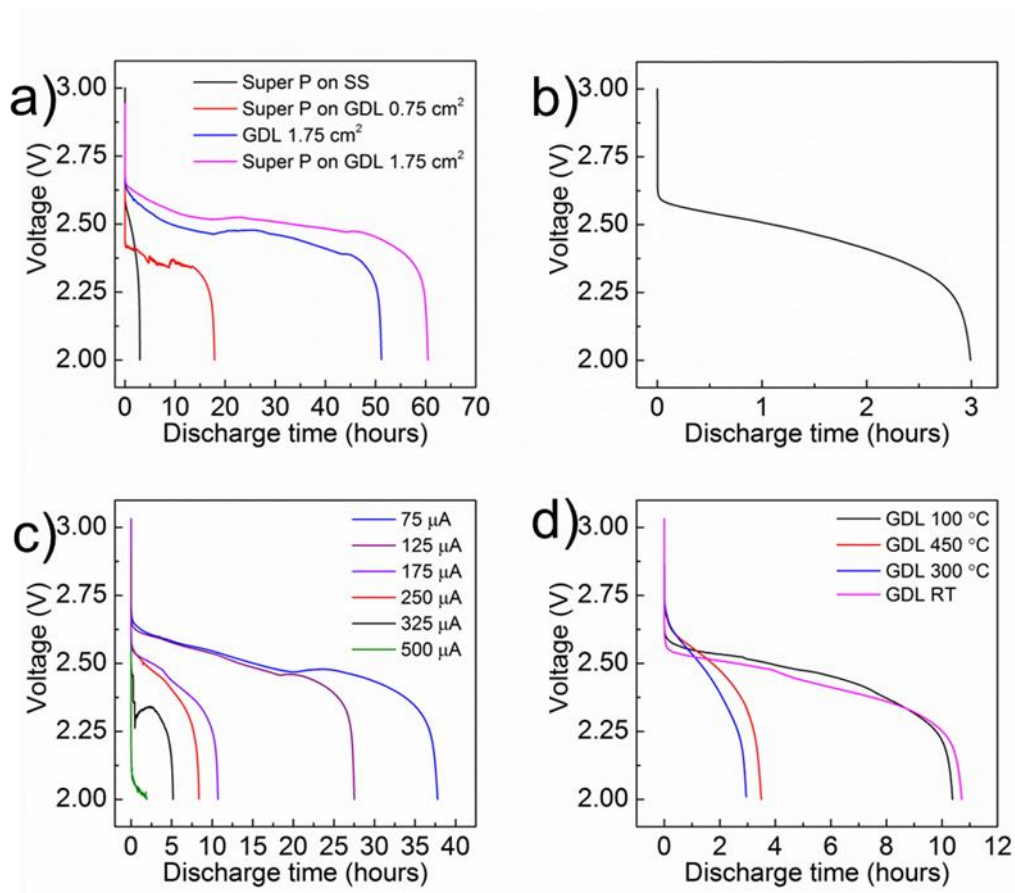
To quantify the contribution of active GDL cathode substrates to the overall discharge capacity estimate, different cathodes were compared at a fixed applied current (175  $\mu\text{A}$ ). In Figure 2 a), the first discharge profiles for i) Super P carbon on 1.75  $\text{cm}^2$  SS mesh, ii) Super P carbon on GDL cathode with an area of 0.75  $\text{cm}^2$ , iii) 1.75  $\text{cm}^2$  as received GDL, and iv) Super P carbon on 1.75  $\text{cm}^2$  GDL are presented. For the 1.75  $\text{cm}^2$  GDL cathode with added Super P carbon, identical applied

currents and similar mass loadings of carbon were investigated compared to the SS cathode. The mass loading on the GDL and SS were controlled to ensure accurate comparison given the key role of carbon mass loading in determining capacities.<sup>67</sup> Firstly, it can be seen that the 1.75 cm<sup>2</sup> as received GDL cathode (i.e. without any added carbon) presented a large discharge time of 50 hours. The smaller GDL cathode with added Super P carbon (0.75 cm<sup>2</sup>) showed a smaller discharge time of circa 18 hours due to the reduced cathode area for electrochemical reactions. There is a marked difference between the discharge behaviour of the 1.75 cm<sup>2</sup> cathodes composed of Super P on SS and the Super P on GDL. The two cathodes show a large difference in their discharge times. The Super P on SS cathode discharge to 2 V in just 3 hours (Figure 2 b) compared to over 60 hours for Super P on GDL. This strongly suggests that the GDL support actively participates in the overall discharge process.

The calculated capacities for each cathode formulation give a clearer insight into the role of the GDL as the current collector. The gravimetric capacities in this section will be presented as mAhg<sup>-1</sup><sub>x</sub> where x in each case represents the cathode materials considered in the calculation. For the as-received GDL cathode, the initial discharge capacity is 481.50 mAhg<sup>-1</sup><sub>GDL</sub> based on the entire cathode mass. The capacity for the cathode consisting of Super P carbon on GDL is either 5480.58 mAhg<sup>-1</sup><sub>Super P</sub> or 513.97 mAhg<sup>-1</sup><sub>GDL+Super P</sub> depending on the components factored into the calculation. The large discrepancy in these capacity figures is a direct consequence of the low mass loading of carbon used (and also widely in the literature) compared to the significantly larger comparative weight of the GDL current collector. When these capacity figures are compared with the Super P cathode discharged on SS (388.88 mAhg<sup>-1</sup><sub>Super P</sub>), it is clear that the vast majority of the apparent 5480.58 mAhg<sup>-1</sup><sub>Super P</sub> capacity for the Super P carbon on GDL is caused by an active GDL cathode. This data clearly shows that the contribution of the GDL to the discharge time should not be neglected. While the actual gravimetric capacity of the as-received GDL in terms of mAhg<sup>-1</sup><sub>GDL</sub> is quite low, the fact that it is much heavier than the added active material means that it dominates the discharge time of cathodes using GDL as the current collector, and will be the case for many carbon-based current collectors and



GDLs that are not passive during discharge. In future reports, the added discharge time due to the GDL should be ascertained to ensure that capacity figures are not artificially inflated. It should also be noted that other commercial GDL cathodes may contribute to the discharge times differently and that careful control experiments are required to ensure that artificially high capacities are not reported for other GDL systems. In fact, Adams et al. have shown that another commonly used GDL support (Toray carbon paper (TGP-H-030)) exhibits negligible discharge capacity.<sup>12</sup> This further confirms that different GDL supports must be carefully examined to assess their contribution to discharge capacities for each system in which they are employed.



**Figure 2:** a) Discharge curves for various cathodes with applied current of 175  $\mu\text{A}$ . b) Discharge of Super P on SS shown in a). c) As received GDL (0.75  $\text{cm}^2$ ) discharged with the indicated applied currents. d) Impact of thermal treatment on the discharge of as received GDL (0.75  $\text{cm}^2$ ) at 175  $\mu\text{A}$  applied current.

Single discharge tests were also conducted with different applied currents on 0.75 cm<sup>2</sup> as received GDL cathodes (Figure 2 c). It can be seen that the tests conducted at 75 and 125  $\mu$ A exhibited similar onset voltages for discharge (circa 2.625 V) as did those at 175 and 250  $\mu$ A (~2.55 V). The discharge times to 2 V for the GDL cathodes discharged at 325 and 500  $\mu$ A (5 and 2.5 hours respectively) were markedly lower, however, it is worth noting that these discharge times have a significant contribution to discharge capacity similar to Figure 2 (i.e. if gravimetric capacities were calculated based solely on the added mass of an active material on a GDL cathode). The reduction in gravimetric capacity and also discharge voltage is consistent with previous studies for carbon based cathodes which have shown poor rate capability for Li-O<sub>2</sub> systems.<sup>23, 58</sup> Additionally, the profiles for the tests conducted at high currents (i.e. 325 and 500  $\mu$ A) show increasingly noisy discharges. This is again consistent with the poor rate capability of Li-O<sub>2</sub> batteries noted by others.<sup>23</sup>

The thermal stability of the as-received GDL cathode was also assessed (Figure 2 d). 0.75 cm<sup>2</sup> GDL substrates were used i) as received, and after thermal treatment for 12 hours at ii) 100 °C, iii) 300 °C, and iv) 450 °C. It was found that the as-received GDL at RT and GDL heated at 100 °C exhibited near identical discharge behaviours while those heated above 300 °C showed markedly reduced discharge times. The GDL cathodes showed ~25 % mass loss after heating to 300 °C or higher. As shown next, elimination of polymer binder and some carbon at T > 300 °C reduces mass and so influence the discharge time, as expected from an active cathode material.

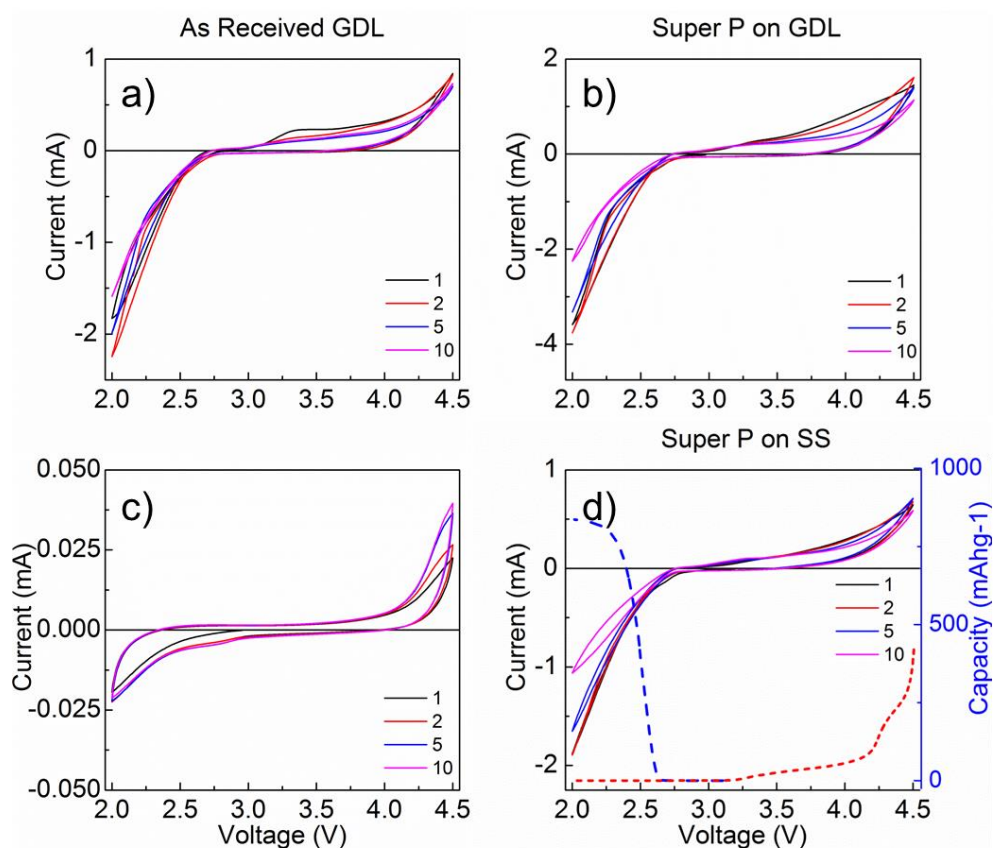
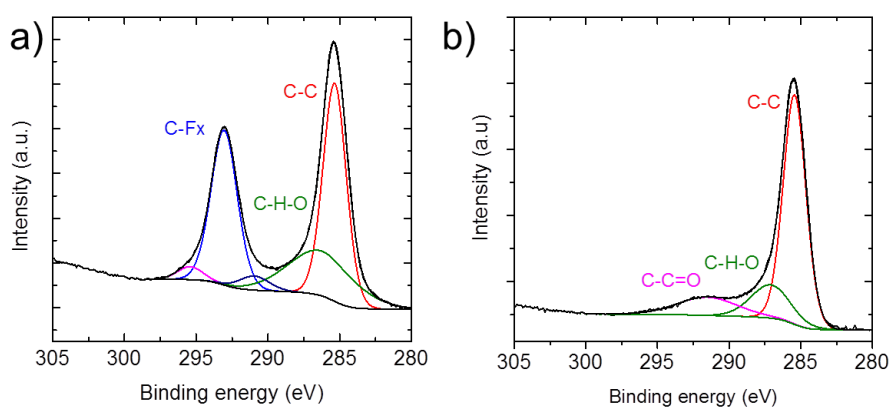


Figure 3: CV analysis conducted at 1 mV/s for different cathodes. a) 1.75 cm<sup>2</sup> as received GDL, b) Super P carbon on 1.75 cm<sup>2</sup> GDL, c) 1.75 cm<sup>2</sup> SS mesh control, and d) Super P carbon on 1.75 cm<sup>2</sup> SS. The dashed lines superimposed on the CV in d) are the discharge (blue) and charge (red) profiles taken from a constant current test (100  $\mu$ A applied) on a SS based cathode.

Cyclic voltammetry was used to compare the activity of SS with that of GDL as current collectors. In Figure 3 a), a CV of an as received GDL cathode was found to exhibit high current values of  $\approx 2$  mA on ORR and  $\approx 1$  mA on OER, and remained consistent over 10 cycles. When contrasting the control GDL with the Super P carbon on GDL (Figure 3 b) cathode, it can be seen that the voltammetric profiles are similar in shape. The anodic oxidation exhibits similar overpotentials for OER activation. An additional current is noted for Super P on GDL from a greater quantity of carbon and surface area; the exchange current density is increased over pure GDL. In contrast, the CV analysis of the control SS current collector in Figure 3 c) showed a marked reduction in current values for both ORR and OER compared to the GDL substrate. The only appreciable current is noted below 2.25 V and above 4.25 V, suggesting that the SS does not participating in ORR/OER.<sup>68</sup> The CVs

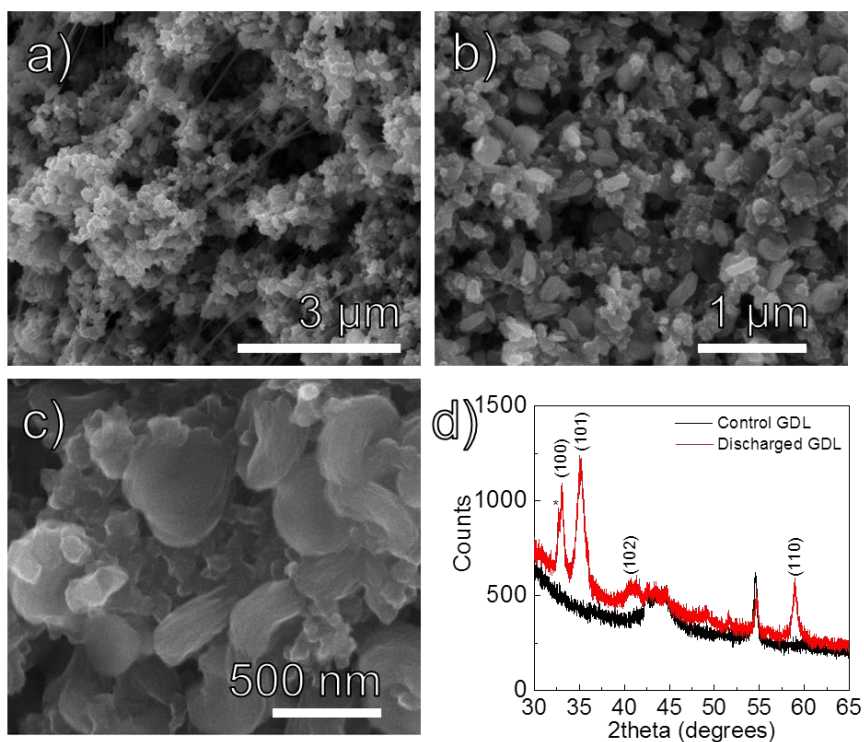
for the Super P carbon on SS cathode (Figure 3 d) show a similar profile to that seen for the Super P on GDL but with a marked reduction in ORR and OER currents. Reduced current and larger ORR/OER voltage windows in anodic oxidation stem from increased electrode resistance caused by a limited quantity of Super P as the only active material (rather than the current collector also participating in discharge/charge). The discharge and charge profiles taken from a constant current test (100  $\mu$ A applied current) conducted on a Super P on SS cathode are superimposed on the CV in Figure 3 d) and show similar onsets in the ORR and OER processes to those observed in the CV measurement.

XPS analysis was used to investigate whether the reduced discharge times for the heated GDL samples could be attributed to a weight loss of active carbon from the GDL surface. High resolution analysis of the C 1s core-levels for the pristine GDL substrate (Figure 4 a) showed the presence of peaks consistent with C-C, C-H-O. The analysis also confirmed the presence of C-F<sub>x</sub> species, consistent with a PTFE binder in the pristine GDL substrate. In contrast, the C-F<sub>x</sub> core-level emission is non-existent for the heated GDL substrate consistent with the degradation of PTFE binder present on the pristine GDL substrate heated at 450 °C for 12 h. It thus seems likely that the reduction in discharge time for the heated GDL cathode is due to a combination of the loss of active carbon and an elimination of parasitic by-product formed between the PTFE binder and Li<sub>2</sub>O<sub>2</sub> and its intermediates during discharge.<sup>69</sup>

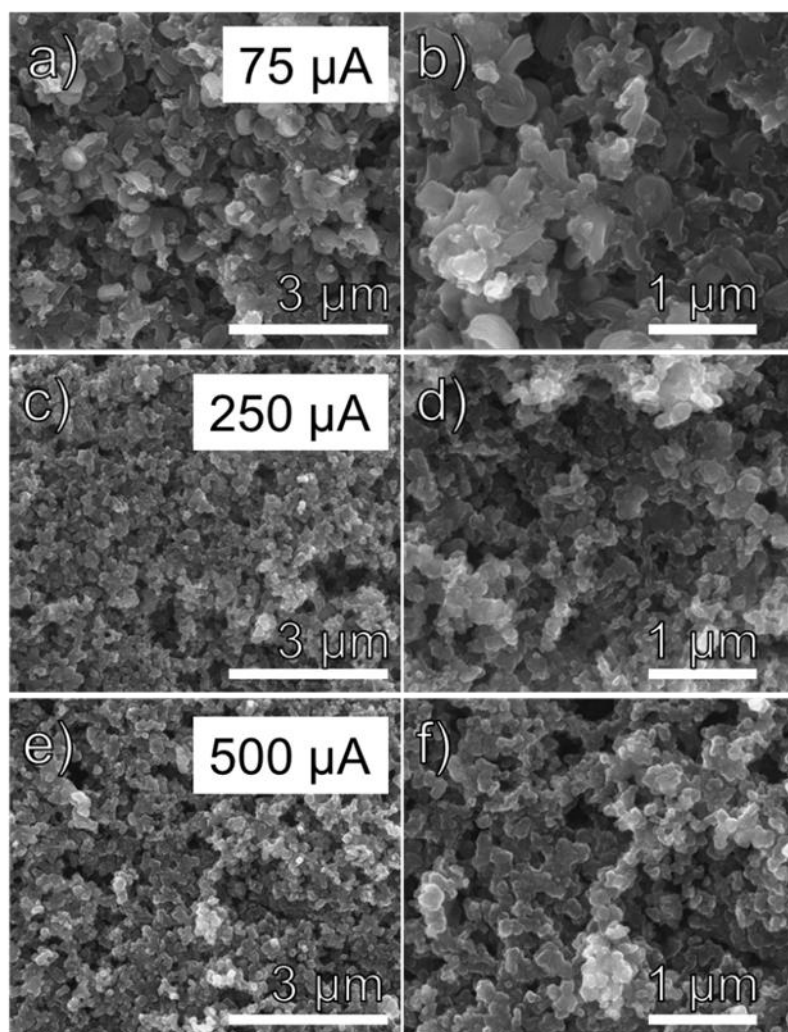


**Figure 4:** XPS analysis of GDL substrate before a) and after b) heating to 450 °C.

Given the large observed contribution of the GDL to the discharge time of the Li-O<sub>2</sub> cells presented above, SEM (Figure 5 a,b) and XRD (Figure 5 c) analyses were used to characterize an as-received GDL cathode after a single discharge at an applied current of 75  $\mu$ A (the corresponding discharge profile is shown in Figure 2 c)). From SEM analysis of the cathode (Figure 5 a,b), it is clear that the GDL surface is densely covered by characteristic Li<sub>2</sub>O<sub>2</sub> toroids after discharge. These sub-micron sized toroids have been widely reported as characteristic for carbon based cathodes<sup>12, 40</sup> with ether electrolytes. Their appearance on the GDL in this case over the long discharge times and applied current reported in Figure 2 is evidence of a similar process. Recent investigations suggest that the growth of these characteristic Li<sub>2</sub>O<sub>2</sub> toroids occurs predominantly in the electrolyte solution rather than on the cathode surface in H<sub>2</sub>O containing electrolytes with their size and morphology largely dependent on the level of water contained in the electrolyte.<sup>13</sup> The existence of sub 500 nm toroids in Figure 5 a-c) here can thus be explained by the relatively low applied current (0.1 mA/cm<sup>2</sup>) used and the H<sub>2</sub>O content of  $\approx$  500 ppm in the electrolyte. Given the similarity of the toroids formed on the GDL cathode to those previously noted for carbon based cathodes,<sup>12, 70</sup> it appears that the nature of the cathode is only one factor in determining the morphology of the Li<sub>2</sub>O<sub>2</sub> formed. Further studies will focus on investigating the morphology of Li<sub>2</sub>O<sub>2</sub> on carbon-free cathodes given that the report by Aetukuri et al. has already shown that the formation of Li<sub>2</sub>O<sub>2</sub> toroids on TiC is also dependent on the water content of the electrolyte. Confirmation of the appearance of crystalline Li<sub>2</sub>O<sub>2</sub> on the cathode is also provided by the XRD analysis shown in Figure 5 d) with reflections consistent with the formation of hexagonal phase Li<sub>2</sub>O<sub>2</sub> (JCPDS ref 74-0115).<sup>71-73</sup> A small shoulder peak (marked with an asterisk) consistent with the formation of crystalline LiOH was also noted. This data conclusively shows that the GDL actively contributes to the mass of the electrode involved in the entire ORR during battery operation.



**Figure 5:** a)-c) SEM images of as received GDL cathode after discharge at 75  $\mu\text{A}$  applied current showing characteristic  $\text{Li}_2\text{O}_2$  toroids formed on the different structures in the GDL. d) XRD analysis of control and same cathode in a) and b) with reflections indexed for the crystalline  $\text{Li}_2\text{O}_2$  formed on the cathode surface. The reflection with an asterisk is due to the formation of  $\text{LiOH}$  on the cathode surface.



**Figure 6:** SEM images of as received GDL cathodes discharged at applied currents of 75 (a,b), 250 (c,d) and 500  $\mu\text{A}$  (e,f). The discharge profiles have been shown in Figure 1 a).

SEM images of the as received GDL cathodes discharged at various applied currents shows behaviour similar to that observed for Super P on SS cathodes discharged in our studies<sup>74</sup> and similar to those presented by others in a TEGDME based electrolyte.<sup>12</sup> At low applied currents (Figure 6 (a,b), 75  $\mu\text{A}$ ), sub-micron toroidal shaped  $\text{Li}_2\text{O}_2$  discharge products formed across the surface of the carbon based GDL surface. These toroids were noted at currents below 100  $\mu\text{A}$  and were densely distributed across the entire GDL surface. In contrast, at higher applied currents (Figure 6 c,d: 250  $\mu\text{A}$  and Figure 6 e,f: 500  $\mu\text{A}$ ), no obvious  $\text{Li}_2\text{O}_2$  toroids were observed with the  $\text{Li}_2\text{O}_2$  discharge products likely forming as quasi amorphous thin films which are difficult to visualize with SEM analysis.<sup>12</sup>

Overall, the measurements confirm that discharge electrochemistry that results in  $\text{Li}_2\text{O}_2$  formation (among other species) occurs on GDLs as it does with other carbon-based and some carbon-free cathodes in Li- $\text{O}_2$  batteries. Electrochemical and structural examination of GDLs during discharges can be quantitatively accounted for during discharge processes (with defined electrolyte and discharge conditions) when determining the true gravimetric capacities and energy densities of Li- $\text{O}_2$  batteries.

### **Conclusions:**

This report has investigated the use of carbon based GDLs as cathode current collectors in Li- $\text{O}_2$  batteries. It has been shown that GDL current collectors actively participate in ORR during discharge and require careful consideration when calculating the gravimetric capacities of any added active material. XRD and SEM analysis confirmed the presence of crystalline  $\text{Li}_2\text{O}_2$  on as received GDL cathodes after discharge consistent with ORR during discharge at the current collector substrate, confirmed by voltammetric measurements. The thermal stability of the GDL cathodes (which is relevant to the high temperature growth of active materials on the GDL) was investigated and it was also found that the GDL lost active carbon and also showed binder degradation when heated above 300 °C, leading to reduced discharge times compared to the pristine GDL substrates. It was also found that characteristic  $\text{Li}_2\text{O}_2$  toroids only formed on the GDL substrates at lower current densities (typically below circa 100  $\mu\text{A cm}^{-2}$ ). The data highlight the importance of factoring the contribution of ORR/OER active current collector substrates when determining gravimetric capacities of Li- $\text{O}_2$  batteries.

### **Acknowledgements:**

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