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# Electrospun carbon fibers as air cathodes for aprotic Li-O<sub>2</sub> battery: towards cathode design for enhanced capacity

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*Key words:* Electrospun carbon fibers, Li-O<sub>2</sub> battery, aprotic, cathode

## ABSTRACT

This report investigates how the microstructures and chemical properties of carbon cathodes influence the discharge capacity of aprotic Li-O<sub>2</sub> batteries. For that, electrospun carbon fibers (CFs), Multi-wall carbon nanotubes (MWCNTs), carbon Super P and gas diffusion layer (GDL) were fully discharged at various applied current densities (0.05 - 0.5 mA.cm<sup>-2</sup><sub>(geom)</sub>) and characterized by means of ex-situ techniques such as XRD and FEG-SEM. The major discharge product for every carbon electrode was identified as Li<sub>2</sub>O<sub>2</sub> by both XRD and gas pressure analysis. The corresponding electrochemical results showed two different behaviors depending on the current density. At high current densities, all the carbon electrodes presented quite similar discharge capacities due to the most favored formation of Li<sub>2</sub>O<sub>2</sub> conformal film on the carbon surface. In contrast, at lower current densities, the morphology of the discharge product changed and Li<sub>2</sub>O<sub>2</sub> was preferably deposited as micrometer-sized toroids particles on all the carbon cathodes (except for GDL). In this particular regime, the specific capacity normalized by the active carbon surface area of the electrospun CFs cathode was surprisingly promoted compared to the other carbon materials. Interestingly, it was found that unlike for the other cathode materials, Li<sub>2</sub>O<sub>2</sub> homogeneously occupies the void volume of the electrospun carbon structure without any pores clogging, which was attributed to its particular macroporous architecture presumably facilitating a continuous O<sub>2</sub> diffusion through the electrode. The enhancement in discharge capacity might also be related to the presence of nitrogen active sites, as revealed by XPS analysis of the pristine carbon surface. All these features highlight that the carbon porosity and surface chemistry are key parameters to design efficient air cathodes for Li-O<sub>2</sub> batteries performing at low current density.

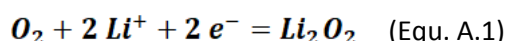
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## 1. Introduction

Non-aqueous Li-O<sub>2</sub> batteries have attracted significant attention over the past decade thanks to their high theoretical specific energy density around 2000 Wh.kg<sup>-1</sup><sub>(Li + carbon)</sub>. In comparison to other energy storage devices, including the conventional Li-ion batteries, they could be potentially suitable for electrical vehicles applications [1-3]. This enhancement in specific energy is related to the use of a gas to solid reaction in the pores of a conductive electrode, which is composed by cost effective carbon materials with low densities, and therefore facilitates high gravimetric capacities. During the discharge, O<sub>2</sub> gas is dissolved in the electrolyte and then electrochemically reduced to react with Li<sup>+</sup> ions to form Li<sub>2</sub>O<sub>2</sub> as the main product while the reverse reaction occurs during charge, decomposing Li<sub>2</sub>O<sub>2</sub> into Li<sup>+</sup> and O<sub>2</sub> (equation A.1).



Generally, the Li-O<sub>2</sub> reactions involved upon cycling were found to be dependent on the operating parameters of the cells (current density, oxygen pressure...), the nature and the concentration of electrolyte and the presence of electrocatalysts or redox mediators [4-17]. Previous studies have also demonstrated that the solubility of LiO<sub>2</sub> intermediate governs the discharge product morphology [18], varying from films to discs [19] and to toroids [20], which eventually impacts the battery performance. Besides the peculiar attention recently devoted to the understanding of the fundamental mechanisms controlling the Li-O<sub>2</sub> electrochemistry [21], there is an important consideration in the design and selection of effective porous air cathodes [22]. In fact, the real performance of Li-O<sub>2</sub> batteries including capacity fading, poor cycling and large discharge-charge voltage gap [23] is strongly attributed to the poor performance of the air electrodes because of the sluggish kinetics for oxygen reduction/evolution reactions and the inefficient air electrode design. Thus, one of the major challenge for Li-O<sub>2</sub> batteries is to design porous electrodes that must contain active carbon material providing abundant redox reaction sites and a large connected porous framework. It can be filled up by the Li<sub>2</sub>O<sub>2</sub> solid deposit during operation without clogging the pores [24] or passivating electrode surface [21,25], which are phenomena often suggested as the main factors limiting the cell capacity. Numerous carbon materials (e.g. activated carbon [26], Super P [27,28], GDL [29], carbon nanotubes (CNTs) [20], graphene [30], Vulcan XC72, Ketjen black [31,32], carbon paper [33], fibers [34]) were used as performant air cathodes for Li-O<sub>2</sub> applications, due to their low cost, high electrical conductivity, wide chemical and electrochemical stability and to their large specific surface area and high porosity. In addition to carbon materials, several cathode formulations required the use of binders, like PVDF and PTFE [35], which might also react during the discharge processes to form side products, leading to a decrease of the cell performance. One can imagine that playing on the carbon specifications including electronic conductivity, porosity, tortuosity and surface properties is the key strategy to improve the discharge capacity in Li-O<sub>2</sub> cells. However, no systematic investigation has clearly identified the critical carbon properties that impact effectively the Li-O<sub>2</sub> battery performance.

Hence, in this report our approach consists on comparing different carbon cathodes discharged at different rates to identify the key properties required to enhance the Li-O<sub>2</sub> battery electrochemical performance. Using carbon materials with different microstructures (size and porosity) and chemical properties (electrospun fibers (CFs), Multiwall carbon nanotubes (MWCNTs), carbon Super P and gas diffusion layer (GDL)), we systematically investigate the impact of carbon microstructure on the morphology/size and distribution of Li<sub>2</sub>O<sub>2</sub> discharge products and thus on the full discharge capacity

values reached at different rates. We employed ex-situ techniques including X-ray diffraction, Raman spectroscopy and FEG-SEM analysis for the structural and morphological characterizations of  $\text{Li}_2\text{O}_2$  products. The deposition process of  $\text{Li}_2\text{O}_2$  was found to be correlated with the current density as well as to the carbon nature. Then, we highlighted that at low discharge current densities, when compared with the other carbon materials, the self-standing and binder-free electrospun carbon electrodes composed of more than 90 percent void space and presenting a small surface area exposing active sites for the oxygen reduction reaction (ORR) is a very promising air cathodes as they can store homogeneously the solid  $\text{Li}_2\text{O}_2$  particles in the entire volume of the carbon. These findings contribute to a new understanding on how the carbon cathode design controls  $\text{Li}-\text{O}_2$  electrochemistry.

## 2. Experimental Section

### 2.1. Carbon electrodes

In this work, all the materials (except carbon Super P) are prepared in self-standing form with suitable mechanical strength. The four porous materials that were employed as cathodes to assemble the cells are:

The **Gas Diffusion Layer** (GDL, Freudenberg H2315), here used as cathode (200  $\mu\text{m}$  in thickness, 0.64  $\text{cm}^2$  disc) was obtained from Quintech. It consists of a macroporous and electrically conductive binder free carbon paper that is known to supply fuel cells with the reaction gas.

**Electrospun carbon fibers (CFs).** Self-standing fibrous carbon papers were prepared via electrospinning followed by heat treatment at high temperatures (Fig. S1). A solution of Polyacrylonitrile (PAN, Sigma Aldrich) with molecular weight of 150,000  $\text{g mol}^{-1}$ , one of the most commonly used precursors due to its high carbon content [36,37], is dissolved in dimethylformamide (DMF) solvent at 10 wt. % and extruded with a fixed 0.03  $\text{ml.min}^{-1}$  flow rate at 15–18 kV voltage in a sealed box under air flow to control the relative humidity in the atmosphere ( $\text{RH} \leq 20\%$ ). The distance between the needle tip and the grounded collector is fixed at 13 cm for all the preparation. The volume of the PAN / DMF solution was modulated leading to different membranes thicknesses (400–600  $\mu\text{m}$ ). Then, thermal steps are used to obtain carbon fibers from electrospun polymer fibers, following the procedure previously described [38]. Briefly, the polymer-based membranes are first dried at 70  $^\circ\text{C}$  under air to evaporate the residual DMF before to be stabilized at 280  $^\circ\text{C}$  under oxidizing atmosphere (i.e., air) to prevent further mass loss resulting from the fiber fusion / degradation at high temperatures in inert atmosphere. This step is critical to have fibers with good tensile strength. Finally, membranes are carbonized at 950  $^\circ\text{C}$  under argon to attain the graphitic structure and to produce conductive carbon, as confirmed by XRD and Raman studies (Fig. S2). After the carbonization process, the fibers diameter is reduced by 30 % due to the removal of non-carbon elements. The final electrospun carbon membrane is self-standing with very suitable mechanical resistance for use. The 600  $\mu\text{m}$  final electrospun carbon cathode denoted CF wt.% PAN was cut into a 0.64  $\text{cm}^2$  disc with the mass loading of 2  $\text{mg.cm}^{-2}$  approximately.

**Multi-Wall Carbon Nanotubes electrode.** First, 80 mg of MWCNTs (Nanocyl SA-NC7000,  $10 \pm 2$  nm in diameter) was dispersed in absolute ethanol and the resulting suspension was sonicated several times during 3 hours, increasing successively the volume of solvent. This latter was filtrated under vacuum on a PTFE membrane (Sartorius, pores diameter = 0.45  $\mu\text{m}$ ) and dried at room temperature (RT) overnight. MWCNT membrane is taken off from the PTFE surface to be self-standing and the carbon nanotube loading is 2.0  $\text{mg.cm}^{-2}$ . The as-prepared membrane with a thickness of 80  $\mu\text{m}$  was punched into a 0.64  $\text{cm}^2$  disc.

**Super P carbon.** Super P carbon electrode was prepared by the drop-casting method, as previously reported [39]. Briefly, 90 wt. % Carbon Super P (Csp, Timcal Ltd) and 10 wt. % polytetrafluorethylene (PTFE, 60 wt. % dispersion in water, Sigma-Aldrich) were mixed in a certain amount of isopropanol ( $\geq 99.9\%$ , Sigma-Aldrich) to prepare a slurry. This one was then deposited onto 11 mm diameter stainless steel meshes (AISI 316, 325 mesh, 0.036 mm diam wire, Alfa Aesar). After being dried in ambient air and washed with a water/ethanol ( $v/v = 1:2$ ) solution to remove the surfactants in the PTFE dispersion, these electrodes were further dried overnight at  $80\text{ }^{\circ}\text{C}$  under vacuum in BÜCHI oven and stored in glove box. Carbon Super P loading of the resulting electrodes is  $0.3 (\pm 0.02)$  mg with a surface area of  $0.4 (\pm 0.04)$   $\text{cm}^2$ .

## 2.2. Carbon electrode characterizations

X-ray diffraction (XRD) was used to investigate the crystallinity of the carbon cathodes and to identify the crystalline nature of the discharge products. A Bruker D8 Advance diffractometer with a  $\text{Cu K}\alpha$  radiation source ( $\lambda_1 = 1.5405\text{ \AA}$ ,  $\lambda_2 = 1.5443\text{ \AA}$ ) and a Lynxeye XE detector was used to collect the XRD patterns. The XRD patterns corresponding to the discharged electrodes were recorded for 40 min in the  $2\theta$  range of  $30 - 70\text{ }^{\circ}\text{C}$  at a continuous scan rate of  $1^{\circ}\text{ min}^{-1}$ , using an airtight sample holder with beryllium windows. Concerning the pristine electrodes, the XRD patterns were collected for 15 min with a scan rate of  $4^{\circ}\text{ min}^{-1}$ .

Raman spectra were recorded using a custom-built confocal Raman microscope with a  $50 \times 0.45$  NA objective (Nikon). The Raman system was equipped with a 473 nm diode laser (Sacher Lasertechnik) and a spectrometer (Shamrock SR-303i, Andor Technology) which employed a 400 lines/mm grating, blazed at 850 nm and was equipped with a deep depletion, back-illuminated, and thermoelectrically cooled CCD camera (Newton, Andor Technology) for the detection of the Raman signal. A silicon wafer was used for calibration.

The porous texture of the materials was analyzed by  $\text{N}_2$  adsorption at 77 K (Quadrasorb, Quantachrome, USA) and mercury intrusion porosimetry (Autopore IV, Micromeritics, USA). It is worthy to precise that the fibers are dense and the major porosity discussed in these materials is defined by the presence of inter-fiber spaces/voids. Prior to the  $\text{N}_2$  adsorption measurements, the samples were outgassed at  $120\text{ }^{\circ}\text{C}$  for 12 h under vacuum. The micropore and mesopore volumes and the pore size distribution were determined by a Non-Local Density Functional Theory method (NLDFT) with a slit shape pore model applied on  $\text{N}_2$  adsorption data. The meso- and macro-pore size distributions from mercury intrusion porosimetry were obtained from the pressure versus intrusion data using the Washburn equation.

Microscopic observations were performed by field emission gun-scanning electron microscopy (FEG-SEM) on a Hitachi SU-70 instrument which is provided with a Schottky Field Effect gun. Because of the extreme sensitivity of samples to electron beam, low accelerating voltage (1 kV) and low beam current conditions were selected to avoid any possible destruction of the discharge product. Conditions for secondary electron (SE) imaging were high resolution mode with the upper detector resulting in a narrow energy band filtering for out coming SE, as a consequence dielectrical properties of the different materials constituting the sample resulted in highlighted contrast. The SEM images of the pristine carbon electrodes are presented in Fig. S3 and the size distribution of the fibers was determined from these pictures using the ImageJ software. The discharged samples were transferred into the SEM under anaerobic conditions.

X-ray Photoelectron Spectroscopy (XPS) measurements were carried out to assess the surface chemical composition of the pristine carbon electrodes. The XPS spectra were collected on an

Omicron Argus X-ray photoelectron spectrometer, using a monochromated Al K $\alpha$  ( $h\nu = 1486.6$  eV) radiation. The emission of photoelectrons from the sample was analyzed at a take-off angle of 45° under ultrahigh vacuum conditions ( $1.10^{-9}$  Pa). XPS spectra were collected at pass energy of 20 eV for C1s, O1s, N1s, core XPS levels. The area of the sample analysis is approximately 1 mm<sup>2</sup>. All binding energy (BE) values were charge-corrected to the carbon C1s excitation set at 285.0 eV. The peak areas were determined after subtraction of a Shirley background. The atomic ratios calculations were performed after normalization using Scofield factors. Spectrum processing was carried out using the Casa XPS software package.

The contact angle experiments were carried out by dropping an electrolyte droplet on the carbon surfaces. Measurements were repeated three times. The electrolyte uptake which is one of the important characteristic properties for the carbon wettability behavior was estimated by soaking a precise volume of the electrolyte solution into the electrodes. The electrolyte excess was wiped off gently with a porous paper on both sides and the carbon materials were then weighted immediately. The electrolyte uptake (%) was calculated using the following equation [40].

$$\text{Electrolyte uptake} = [(W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}}] * 100\%$$

where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the weights of the electrolyte-swollen and dry carbon sample, respectively.

The electronic resistivity of the O<sub>2</sub> cathodes was measured by the four-probe technique (Jandel, Model RM3000). Additionally, they were also examined by electrochemical impedance spectroscopy (Solartron SI 1260, impedance/ Gain-phase analyzer) in Swagelok cells with an AC amplitude of 100 mV and a frequency ranging from 100 to 0.01 kHz.

### 2.3. Electrochemical characterization

**Li-O<sub>2</sub> cells assembling and testing.** Prior to use, Dimethoxyethane (DME) solvent was dried with freshly activated molecular sieves (4 Å) for two days. Lithium salt was dried under vacuum at 80 °C for 12 – 24 h. The 0.1 M electrolyte solution was prepared in an argon-filled glovebox (0.1 ppm of O<sub>2</sub>/0.1 ppm of H<sub>2</sub>O). The water content in the electrolyte solutions was analyzed by Karl Fischer titration and found to be below 10 ppm. Before electrochemical experiments, the carbon electrodes were dried under vacuum at 80 °C for 24 h. The pressure cells used in this work were previously described [39]. The cells were assembled in an Ar-filled glovebox (0.1 ppm of O<sub>2</sub>/0.1 ppm of H<sub>2</sub>O) using a Li metal foil anode (cut into a 0.64 cm<sup>2</sup> disc, 9 mm diameter), two Whatman porous glass fibers separators (dried under vacuum at 260 °C for 8 h), wetted with 300  $\mu$ L of the electrolyte (0.1 M LiPF<sub>6</sub> dissolved in DME) and a binder free air cathode consisting of self-standing carbon (electrospun fibers mat, MWCNT carpet, GDL, cut into a 0.64 cm<sup>2</sup> disc) or carbon Super P deposited on stainless steel mesh by drop casting. Stainless steel mesh was used as current collectors. The assembled cells were transferred from the glovebox, first evacuated before to be filled with dry and ultrapure gaseous O<sub>2</sub> (a pressure of ca. 1.6 bar has been set for all the tests). Cells are left at the open circuit voltage (OCV = 3.3 V) for 10 hours under temperature-controlled conditions (25 °C  $\pm$  0.1 °C fixed by an incubator) in order to ensure the homogeneity of the gas atmosphere and the full wetting of the electrode. The discharge measurements were carried out in galvanostatic conditions with cut off voltage of 2 V vs. E°<sub>Li/Li+</sub> using a Bio-Logic VMP3 potentiostat at different current densities in the range of 0.05–0.5 mA.cm<sup>-2</sup><sub>(geom)</sub>. The current density is estimated on the basis of the geometric surface of the electrode (0.64 cm<sup>2</sup>) fixed for every measurement. The total weight of the carbon electrodes ( $g_c$ ) before discharge was used for capacity normalization. Besides the electrochemical data, the pressure analysis and e<sup>-</sup>/O<sub>2</sub> ratios were calculated as described elsewhere [39]. The electrospun carbon fibers prepared from 10 wt.% PAN/DMF content were used in cells that are fully

discharged with a current density of  $0.05 \text{ mA}\cdot\text{cm}^{-2}_{(\text{geom})}$ . Each cell test was repeated three times to ensure the data reproducibility (example of CF–10 wt.% PAN discharged at  $0.05 \text{ mA}\cdot\text{cm}^{-2}_{(\text{geom})}$  are displayed in Figure S4). Generally, the standard deviation calculated from the capacities values obtained for three cells is approximately  $200 \text{ mA}\cdot\text{h}\cdot\text{g}_c^{-1}$ .

For post-mortem analysis (XRD, FEG–SEM) of carbon electrodes, the discharged Li–O<sub>2</sub> cells were first transferred without any exposure to ambient air to an Ar-filled glovebox and disassembled. Prior to the characterizations, the discharged cathodes were washed three times with dimethoxyethane (DME) to remove the electrolyte residues and dried in a vacuum chamber at RT for 15 min before analysis.

### 3. Results and discussion

To compare the electrochemical performances of the different carbon electrodes, discharges at different rates were made using a normalized current density by the geometrical surface area which is similar for every carbon (varying from  $0.05$  to  $0.5 \text{ mA}\cdot\text{cm}^{-2}_{(\text{geom})}$ ). Fig. 1a presents typical discharge voltage curves for Li–O<sub>2</sub> cells employing electrospun carbon cathodes at different rates. The electrochemical profiles of the other carbon cathodes were reported in Fig. S5. Whatever the nature of the carbon electrode, the discharge capacity and the discharge voltage decrease, when increasing the current density. At low current density, the discharge voltage is constant and closer to the thermodynamical potential for Li<sub>2</sub>O<sub>2</sub> (2.96 V vs. Li<sup>+</sup>/Li) [41]. The formation of Li<sub>2</sub>O<sub>2</sub> as a discharge product [42,43] was confirmed by post-mortem XRD patterns in which characteristic peaks for crystalline Li<sub>2</sub>O<sub>2</sub> could be observed for CFs, MWCNT and carbon Super P electrodes discharging at different rates (Fig. 2a). For GDL electrodes, no crystalline Li<sub>2</sub>O<sub>2</sub> could be identified as a discharge product, in agreement with the limited discharge capacity achieved with this type of carbon electrode.

**Fig. 1.** (a) Full discharge voltage profiles of the electrospun carbon electrode at different discharge rates. Variation of the full discharge capacities reached for the different carbon materials as a function of current density applied in Li–O<sub>2</sub> cells using 0.1 M LiPF<sub>6</sub> in DME. The capacities values were normalized by (b) the total carbon cathode weight ( $g_c$ ) or (c) the geometric cathode surface ( $0.64 \text{ cm}^2$ ) or (d) the active surface area ( $m_c^2$ ) calculated on the basis of the estimated surface area ( $\text{m}^2\cdot\text{g}^{-1}$ ) in table 1 and the carbon weight ( $g_c$ ).

Concomitantly, the cell pressure changes related to the O<sub>2</sub> consumption during the discharge process (Fig. S6) show for CFs, MWCNT and carbon Super P based cells a nearly  $2e^- / \text{O}_2$  ratio, consistent with the formation of Li<sub>2</sub>O<sub>2</sub> following equation (1) (Fig. 2b). In contrast, for the GDL cathode, a very low consumption of O<sub>2</sub> was detected, as expected from the poor performance observed for this electrode ( $\leq 10 \text{ mA}\cdot\text{h}\cdot\text{g}_c^{-1}$ ) at different discharge rates.

As can be seen in Fig. 1a and S5, the electrochemical behaviors of the cells at the different discharge rates are strongly dependent on the carbon electrodes, which require a deeper fundamental understanding of the intrinsic properties of each carbon. For that, the discharge capacities normalized by the geometric electrode surface, the mass of carbon and the active surface area of carbon (taking into account the specific surface area and the carbon mass) were compared (Fig. 1b, 1c, 1d). At low current densities corresponding to  $0.05 \text{ mA}/\text{cm}^2_{(\text{geom})}$ , carbon Super P electrodes exhibit the highest capacity value normalized by the geometric electrode surface or the mass of carbon. However, especially at high current densities the MWCNTs cathodes can be considered as the best performant carbon cathode as they deliver higher capacity normalized by the geometric electrode surface or the mass of carbon. Looking at the capacities normalized by the active carbon

surface area (Fig. 1d), two regimes are observed at low and large current densities. At low current densities, the electrospun carbon cathode delivered a capacity greater by a factor of 6 when compared to the other materials, which is not the case if we normalize by the geometric electrode surface or the mass of carbon. However, at large current densities  $\geq 0.2 \text{ mA}\cdot\text{cm}^{-2}_{(\text{geom})}$ , quite similar discharge capacities were obtained for all the carbon electrodes, which raised the question to know if in this regime only the surface of the electrode is used or the whole porosity available for electrochemical reactions. To explain this behavior, microscopic studies were performed on the discharged cathodes at the different rates across the whole carbon thickness to investigate the impact of the carbon microstructure on the  $\text{Li}_2\text{O}_2$  deposits in terms of their morphology, size and homogeneity of dispersion.

**Fig. 2.** (a) XRD patterns of the cathodes after full discharge at  $0.05 \text{ mA}\cdot\text{cm}^{-2}_{(\text{geom})}$ . (b) Gas evolution profiles of  $\text{Li}-\text{O}_2$  cells at low current density of  $0.05 \text{ mA}\cdot\text{cm}^{-2}_{(\text{geom})}$  using  $0.1 \text{ M LiPF}_6$  in DME, the ratio of number of electrons to oxygen is very close to 2.

~~In~~ Fig. 3 reported the FEG-SEM images of all the carbon materials at the  $\text{O}_2$  / cathode interface after full discharge at different current densities, whose corresponding discharge curves were presented in Fig.1. Two morphologies (toroids vs. film) for  $\text{Li}_2\text{O}_2$  particles were observed as a function of the current density. At high current densities, despite the formation of few small toroids shaped particles, one could observe a conformal film covering the entire surface of every carbon electrode (Fig. 3a). This morphology is in line with the quite similar discharge capacities obtained in this regime for these different electrodes. However, at low current densities, well-defined  $\text{Li}_2\text{O}_2$  toroids are formed on the carbon surfaces by stacking thin layers / platelets of  $\text{Li}_2\text{O}_2$  products during the course of the discharge process. These observations are in agreement with the reported morphology of  $\text{Li}_2\text{O}_2$  formed in ether-based electrolytes during discharge [20,44]. The formation of toroids with hundreds of nanometers is known to result from a solution mechanism and these particles could be more favorable for achieving high capacity cathodes as it was reported earlier [45,47]. For GDL electrode, regardless of the current density, a continuous amorphous thin film ( $\approx 10 \text{ nm}$ ) is homogeneously formed with some small agglomerates (Fig. 3b). Such a film formation, resulting from a surface mediated mechanism [42], indicates the electrical passivation of the GDL which is coherent with the rapid death of the cells exhibiting very low capacities and poor rate capability (Fig. 1).

**Fig. 3.** (a) Morphology of  $\text{Li}_2\text{O}_2$  products formed at the  $\text{O}_2$ /cathode interfaces during full discharge step of carbon materials in  $\text{Li}-\text{O}_2$  cells at different current densities using  $0.1 \text{ M LiPF}_6$  in DME. (b) Representative microscopic images of fully discharged GDL cathode regardless of the current density applied in the cell.

Based on these features, we can emphasize the effect of current density on the nucleation and growth kinetics of solid  $\text{Li}_2\text{O}_2$  onto the carbon electrodes. Indeed, when the current density is increased, the size of the toroids decreases which results in lower discharge capacities. For high current densities, independently of the carbon surface, the discharge takes place quickly and the nucleation from solvated precursors becomes faster than the growth, leading to the formation of conformal  $\text{Li}_2\text{O}_2$  films. Certainly, in this regime, we can suggest that the  $\text{Li}_2\text{O}_2$  morphology is the main parameter governing the capacity performance for all the carbon electrodes. At lower current densities, although the diffusion of the species should enhance the uniform growth of bigger particles, any subtle differences in the  $\text{Li}_2\text{O}_2$  morphology cannot justify the very important capacity



normalized by the active carbon surface area delivered by the electrospun carbon cathode when compared to the other carbon materials ( $\leq 0.1 \text{ mA}\cdot\text{cm}^{-2}_{(\text{geom})}$ ).

For further information, complementary FEG–SEM observations were carried out at the separator / cathode interfaces and through the carbon cathodes (cross section) discharged at  $0.05 \text{ mA}\cdot\text{cm}^{-2}_{(\text{geom})}$  (Fig. 4 and Fig. S7).

**Fig. 4.** Distribution of  $\text{Li}_2\text{O}_2$  products formed through the carbon cathode volume during full discharge step in Li- $\text{O}_2$  cells at low current density of  $0.05 \text{ mA}\cdot\text{cm}^{-2}_{(\text{geom})}$ .

The images confirm that any morphological differences between the different carbons are retained along the electrodes thickness and the formation of  $\text{Li}_2\text{O}_2$ , as conformal coatings or toroids occurs throughout the electrodes. This result implies that the Li– $\text{O}_2$  reactions are not limited to the carbon surface but all the carbon volume is participating as  $\text{Li}_2\text{O}_2$  deposits are present in the entire volume of the electrodes. Note that the utilization of the carbon volume was confirmed for all the current densities (Fig. S7). More interestingly, the  $\text{Li}_2\text{O}_2$  discharge product is uniformly distributed as toroids in the volume of the electrospun cathode with a constant particle size. However, for MWCNT at  $0.05 \text{ mA}\cdot\text{cm}^{-2}_{(\text{geom})}$ , the morphology of  $\text{Li}_2\text{O}_2$  deposit is not uniform:  $\text{Li}_2\text{O}_2$  toroids with  $1.2 \mu\text{m}$  in diameter are deposited on the top surface of MWCNT cathode, while smaller toroids with  $800 \text{ nm}$  in diameter were observed at the electrolyte/electrode interface. In the center of the electrode, the discharge product is a conformal film along the MWCNT sidewalls (Fig. 4). When considering carbon Super P cathode, similar tendencies as for MWCNT cathode are obtained. Hence, globally we notice that in MWCNT and carbon Super P cathodes the larger  $\text{Li}_2\text{O}_2$  particles are preferentially formed at the  $\text{O}_2$  interface rather than the electrolyte interface. All these observations suggest a diffusion limitation in the porosity of the MWCNT and carbon Super P cathodes, leading to heterogeneous distribution of  $\text{Li}_2\text{O}_2$  compared to electrospun carbon, which could be related to the inhomogeneous distribution of gaseous oxygen or  $\text{Li}^+$  in the electrode owing to the tortuosity of the conductive network. These features reveal that the size and distribution of  $\text{Li}_2\text{O}_2$  toroids formed in MWCNT and carbon Super P cathodes are highly dependent on the local concentration of reactant, either  $\text{O}_2$  or  $\text{Li}^+$ , suggesting that the whole carbon volume in these cathodes was not efficiently used to accommodate the discharge product in its porosity, in contrast to electrospun carbon cathode.

In order to reveal the effect of pores size and/or porosity volume on this limitation, mercury porosity experiments have been performed on the pristine carbon electrodes and the results are reported in Table 1.

#### **Table 1**

Surface and porosity characteristics of pristine carbon electrodes.

These experiments highlight that the electrospun carbon (CFs) electrode exhibits an open porous structure with large macropores volume ( $34.8 \text{ cm}^3\cdot\text{g}^{-1}$ ) and pore size (mean pore diameter of  $1\text{--}1.5 \mu\text{m}$ ). This result might explain the homogenous distribution of  $\text{Li}_2\text{O}_2$  resulting from a faster  $\text{O}_2$  diffusion from the oxygen side to the separator side in the entire electrode. Nevertheless, the narrower pore diameter for the other materials could impede the oxygen diffusion and lithium ion movement leading to pores clogging rather than a complete filling, alike previously reported for mesoporous gas diffusion electrodes (GDE) [48]. As a result, the discharge products are formed preferentially at the top and on the bottom of the electrode while the pore volume in the bulk was not used. The particular CF microstructure makes such a carbon paper a very interesting support for  $\text{Li}_2\text{O}_2$  discharge product. Furthermore, it is worthy to note that although the electrospun carbon

collected at the end of the full discharge presents a quite filled porosity with  $\text{Li}_2\text{O}_2$  particles, we can observe some empty voids which could mean that in contrast to what is assumed by the majority of studies, the pores clogging is not the main reason of the cell death. The limiting factor of this carbon material is probably due to other parameters such as the poor electronic conductivity of  $\text{Li}_2\text{O}_2$  [1,49,50] and not to the oxygen diffusion limitations since free space is still available and the diameter of  $\text{Li}_2\text{O}_2$  toroids is inferior to the pore size.

Since the oxygen seems to diffuse freely throughout the electrospun cathode volume, the impact of the CFs electrode thickness has then been tested, aiming to improve the discharge capacity. To do so, we adjusted the electrospinning parameters to fabricate thicker electrodes ranging from 400 to 600  $\mu\text{m}$ . Thicker electrospun carbon electrodes ( $> 600 \mu\text{m}$ ) were not investigated since they might present wettability issues with the electrolyte in the whole carbon volume. Fig. 5 shows that thicker cathode exhibits higher capacity and larger amounts of  $\text{Li}_2\text{O}_2$  toroids deposited in the entire carbon volume.

**Fig. 5.** (a) Full discharge voltage profiles of electrospun carbon fibers (CF\_10% PAN) with different thicknesses in Li-O<sub>2</sub> cells operating at  $0.05 \text{ mA}\cdot\text{cm}^{-2}_{(\text{geom})}$  using 0.1 M  $\text{LiPF}_6$  in DME. (b) FEG-SEM analyses of the fully discharged 600  $\mu\text{m}$ -CF cathode.

As the weight of the thicker cathode is not proportional to the thickness, the density is decreasing with the thickness and therefore the thicker electrode presents the most open porosity. Having more carbon active surface area associated with more available pores volume in thicker cathodes leads to the enhancement of the capacity (in  $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}_{\text{carbon}}$ ). The same trend was observed if we consider the capacity value normalized by the active carbon surface area (in  $\text{mA}\cdot\text{h}\cdot\text{m}_c^{-2}$ ) (Fig. S8).

Moreover, microscopic analysis confirmed this result as the  $\text{Li}_2\text{O}_2$  toroids were covering the entire thickness of the cathode (Fig. 5b). These experiments highlight that the electrospun carbon fibers acting as O<sub>2</sub> cathode without any binder or catalyst are good alternatives to improve the energy and power density of Li-O<sub>2</sub> batteries.

Aside from the carbon microstructure factor, other physico-chemical factors (wettability, the conductivity of the electrodes and the chemical composition of the carbon electrodes) might also influence the electrochemical behaviours. In one hand, the contact angle measurements (not shown here) revealed no notable differences between CF and the other cathodes, therefore, the contribution of the wettability factor can be excluded to explain the differences in the capacity performance.

On the other hand, the study of intensity ratio  $I_D/I_G$ , characteristic of the carbon structure and conventionally used to estimate the degree of the carbon materials graphitization, showed that GDL has the lowest  $I_D/I_G$  ratio indicating then a higher graphitic structure (Fig. S9) which is in line with its higher electronic conductivity value. According to the total electronic conductivity of the investigated carbon materials measured by four probe technique (surface) and impedance spectroscopy (bulk) (Table 2), it can be stated that GDL with good electronic conductivity properties presents the lowest discharge capacity. This finding reveals that the differences in performance cannot be directly related to the materials' conductivity properties.

## Table 2

Electronic conductivities values of carbon electrodes.

The chemical composition of the pristine carbon surfaces was finally evaluated by XPS (Fig. 6a). The data show mainly carbon (90–99%) and very small amounts of oxygen and nitrogen. Although the

amount of surface oxygen groups is quite similar for GDL, CF electrode and carbon Super P, MWCNT cathode exhibits a very limited concentration of this type of sites. Furthermore, the CF electrode exhibits the highest nitrogen content (7 %), suggesting that nitrogen functional groups remain at the surface (from polyacrylonitrile, PAN) due to the relatively low carbonization temperature (below 1300°C). Note that no traces of nitrogen groups were detected for MWCNT and carbon Super P samples.

**Fig. 6.** (a) XPS spectra of the different carbon electrodes with the related surface chemical composition. The binding energies for carbon, nitrogen and oxygen are 284.8, 389.32 and 533 eV, respectively. (b) XPS deconvolution of N1s peaks of carbon cathodes before discharge. N-1, N-2 and N-3 correspond to Pyridinic-N (BE = 398.3 eV), Pyrrolic-N (BE = 400.9 eV) and Graphitic-N (BE = 403.5 eV), respectively. (c) XPS analysis of the C1s region in carbon materials before discharge showing different chemical bonds  $sp^3$ ,  $sp^2$  and oxygen species present in different relative proportions. Carbon  $sp^2$  (BE= 284.8 eV), carbon  $sp^3$  (BE= 285.7 eV), C-O (BE=287.7 eV), C=O and/or C=N (BE= 289 eV) and shake up  $\pi-\pi^*$  (BE=290.7 eV). The peak lineshapes used were Voigt functions, i.e. Gaussian–Lorentzian convolutions, with an integral background subtracted prior to fitting. The peaks assignments were based on models discussed in [51].

Therefore, we can suggest that the increasing of nitrogen functional groups, known as active sites for ORR [52], could be also related to the performance enhancement. Nitrogen doped carbon materials for high performing lithium air batteries are already well outlined in the literature [53]. One can note that in the N1s spectra region (Fig. 6b), the relative amounts of pyridinic–N, and pyrrolic–N are different in CF–10%PAN and GDL electrodes. The electrospun CF has a higher amount of pyridinic–N than pyrrolic–N compared to GDL and presents also a supplementary contribution attributed to graphitic–N. Furthermore, the C speciation for the electrospun CF and GDL electrodes were determined (figure 6c). The C1s spectra reveal the presence of five peaks corresponding to carbon  $sp^2$ , carbon  $sp^3$ , C-O, C=O and/or C=N and shake up  $\pi-\pi^*$ . After deconvolution of the C1s spectra, we can notice that the relative amounts of carbon  $sp^2$  and carbon  $sp^3$  are different from one sample to another. The amount of the unsaturated carbon atoms is relatively higher in the electrospun carbon cathode which might be related to the presence of structural defects as introduced by the nitrogen atoms. One can hypothesize that the difference in the nature of the N sites and the related structural defects can explain the higher discharge capacity normalized by the active carbon surface area of the electrospun CFs compared to GDL electrode. Such hypothesis is supported by the recent strategy consisting in the N-doping of carbon materials to covalently anchor some electrocatalytically active sites serving to enhance the discharge capacity [12]. In our work, the presence of more nitrogen groups, associated with the suitable microstructure and porosity are revealed as the key parameters to explain why the CF electrode was more efficient when discharging at lower current density, [leaving aside the addition of electrocatalysts](#). Hence, we can conclude that the electrospinning is a simple and an efficient way to obtain a carbon electrode with an optimized pores volume and size required to balance the surface area and the diffusion of the reactants ( $Li^+$ ,  $O_2$ ), thus preventing the pores clogging by the discharge products. Besides, a further functionalization of the carbon surface via heat or acid treatments could be very useful to increase defects or reactive sites for the nucleation and growth of discharge products.

#### 4. Conclusions

In this work, the full discharge profiles and capacities of aprotic Li-O<sub>2</sub> batteries were discussed in relation with the intrinsic physico–chemical properties of various carbon materials (electrospun fibers, GDL, MWCNTs and carbon Super P) used as O<sub>2</sub> cathodes at different current densities. These

investigations aim at identifying the critical parameters controlling the electrochemical behaviors of the carbon cathodes discharged at different rates. The ex-situ XRD characterization and the gas pressure results confirmed crystalline  $\text{Li}_2\text{O}_2$  as the main discharge product which is consistent with a solution mechanism involved during the discharge process. Also, the ex-situ FEG-SEM observations evidenced that, as a function of the current density, the discharge capacities are dependent on the morphology (toroids / film) and/or the size distribution of the  $\text{Li}_2\text{O}_2$  particles in the carbon volume. At higher current densities, the formation of a  $\text{Li}_2\text{O}_2$  conformal film on all the carbon cathodes is more favored, leading to quite similar capacity. However, at low current densities, the self-standing and binder-free carbon fibers cathode (CF) prepared via electrospinning delivered the highest capacity normalized by the active carbon surface area. This was explained by the homogenous storage of crystalline  $\text{Li}_2\text{O}_2$  toroids in the entire carbon volume without any pore blocking probably due to a continuous oxygen diffusion in the 3D macroporous CF structure. In contrast, on the other carbon cathodes, the deposition of  $\text{Li}_2\text{O}_2$  toroids with larger diameters occurs preferably at the  $\text{O}_2$  rich interface rather than at the electrolyte rich interface. Furthermore, the significant enhancement of the discharge capacity for electrospun cathode at low rates was also found to be correlated to its chemical surface composition and more specifically to the presence of nitrogen species that can act as active sites for discharge and/or nucleation. Thus, the cumulative effect of a larger amount of surface active sites and the more advantageous microstructure of the carbon electrode is the cause of its better performance. This article highlights the importance of the electrospinning process for rational fabrication and engineering of binder-free macroporous carbon materials with higher capacity for battery systems and provides some enlightenment for the air electrode design.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at:..

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### Figures captions

**Fig. 1.** (a) Full discharge voltage profiles of the electrospun carbon electrode at different discharge rates. Variation of the full discharge capacities reached for the different carbon materials as a

function of current density applied in Li–O<sub>2</sub> cells using 0.1 M LiPF<sub>6</sub> in DME. The capacities values were normalized by (b) the total carbon cathode weight ( $g_c$ ) or (c) the geometric cathode surface (0.64 cm<sup>2</sup>) or (d) the active surface area ( $m_c^2$ ) calculated on the basis of the estimated surface area (m<sup>2</sup>.g<sup>-1</sup>) in table 1 and the carbon weight ( $g_c$ ).

**Fig. 2.** (a) XRD patterns of the cathodes after full discharge at 0.05 mA.cm<sup>-2</sup><sub>(geom)</sub>. (b) Gas evolution profiles of Li-O<sub>2</sub> cells at low current density of 0.05 mA.cm<sup>-2</sup><sub>(geom)</sub> using 0.1 M LiPF<sub>6</sub> in DME, the ratio of number of electrons to oxygen is very close to 2.

**Fig. 3.** (a) Morphology of Li<sub>2</sub>O<sub>2</sub> products formed at the O<sub>2</sub>/cathode interfaces during full discharge step of carbon materials in Li-O<sub>2</sub> cells at different current densities using 0.1 M LiPF<sub>6</sub> in DME. (b) Representative microscopic images of fully discharged GDL cathode regardless of the current density applied in the cell.

**Fig. 4.** Distribution of Li<sub>2</sub>O<sub>2</sub> products formed through the carbon cathode volume during full discharge step in Li-O<sub>2</sub> cells at low current density of 0.05 mA.cm<sup>-2</sup><sub>(geom)</sub>.

**Fig. 5.** (a) Full discharge voltage profiles of electrospun carbon fibers (CF\_10% PAN) with different thicknesses in Li-O<sub>2</sub> cells operating at 0.05 mA.cm<sup>-2</sup><sub>(geom)</sub> using 0.1 M LiPF<sub>6</sub> in DME. (b) FEG–SEM analyses of the fully discharged 600 μm-CF cathode.

**Fig. 6.** (a) XPS spectra of the different carbon electrodes with the related surface chemical composition. The binding energies for carbon, nitrogen and oxygen are 284.8, 389.32 and 533 eV, respectively. (b) XPS deconvolution of N1s peaks of carbon cathodes before discharge. N-1, N-2 and N-3 correspond to Pyridinic-N (BE = 398.3 eV), Pyrrolic-N (BE = 400.9 eV) and Graphitic–N (BE = 403.5 eV), respectively. (c) XPS analysis of the C1s region in carbon materials before discharge showing different chemical bonds sp<sup>3</sup>, sp<sup>2</sup> and oxygen species present in different relative proportions. Carbon sp<sup>2</sup> (BE= 284.8 eV), carbon sp<sup>3</sup> (BE= 285.7 eV), C-O (BE=287.7 eV), C=O and/or C=N (BE= 289 eV) and shake up π-π\* (BE=290.7 eV). The peak lineshapes used were Voigt functions, i.e. Gaussian–Lorentzian convolutions, with an integral background subtracted prior to fitting. The peaks assignments were based on models discussed in [51].

## Tables Captions

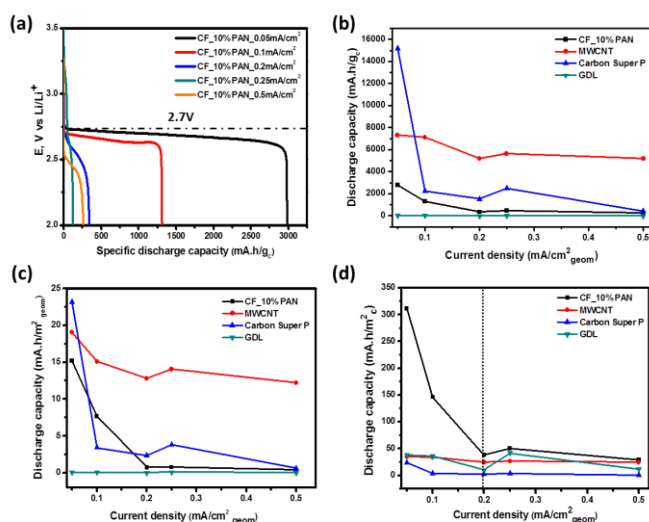
### Table 1

Surface and porosity characteristics of pristine carbon electrodes.

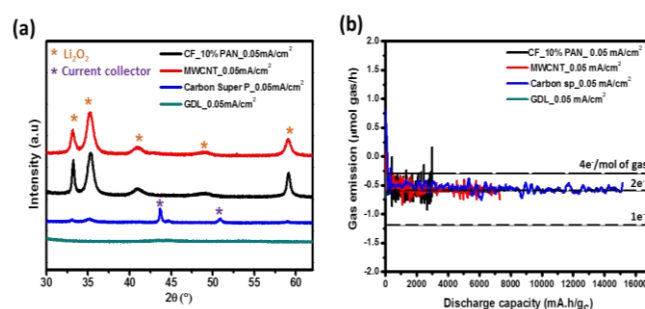
### Table 2

Electronic conductivities values of carbon electrodes.

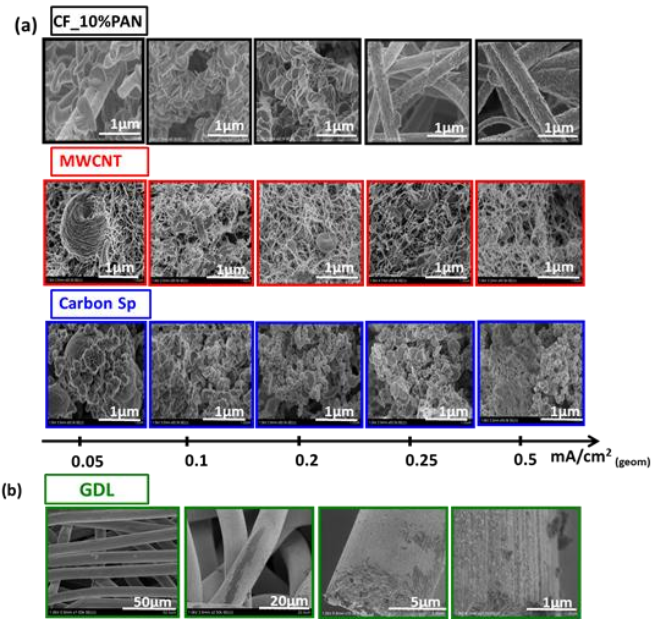




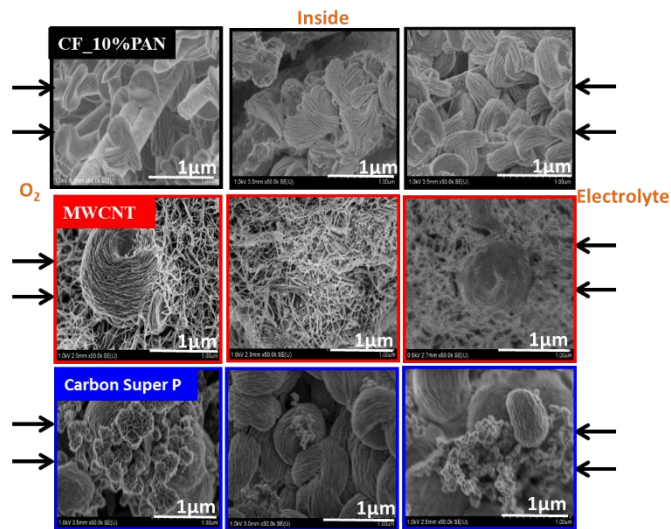
**Fig. 1.** (a) Full discharge voltage profiles of the electrospun carbon electrode at different discharge rates. Variation of the full discharge capacities reached for the different carbon materials as a function of current density applied in Li–O<sub>2</sub> cells using 0.1 M LiPF<sub>6</sub> in DME. The capacities values were normalized by (b) the total carbon cathode weight ( $g_c$ ) or (c) the geometric cathode surface (0.64 cm<sup>2</sup>) or (d) the active surface area ( $m^2.g^{-1}$ ) calculated on the basis of the estimated surface area ( $m^2.g^{-1}$ ) in table 1 and the carbon weight ( $g_c$ ).



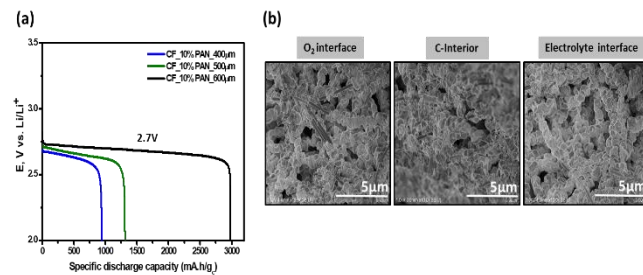
**Fig. 2.** (a) XRD patterns of the cathodes after full discharge at 0.05 mA.cm<sup>-2</sup><sub>(geom)</sub>. (b) Gas evolution profiles of Li–O<sub>2</sub> cells at low current density of 0.05 mA.cm<sup>-2</sup><sub>(geom)</sub> using 0.1 M LiPF<sub>6</sub> in DME, the ratio of number of electrons to oxygen is very close to 2.



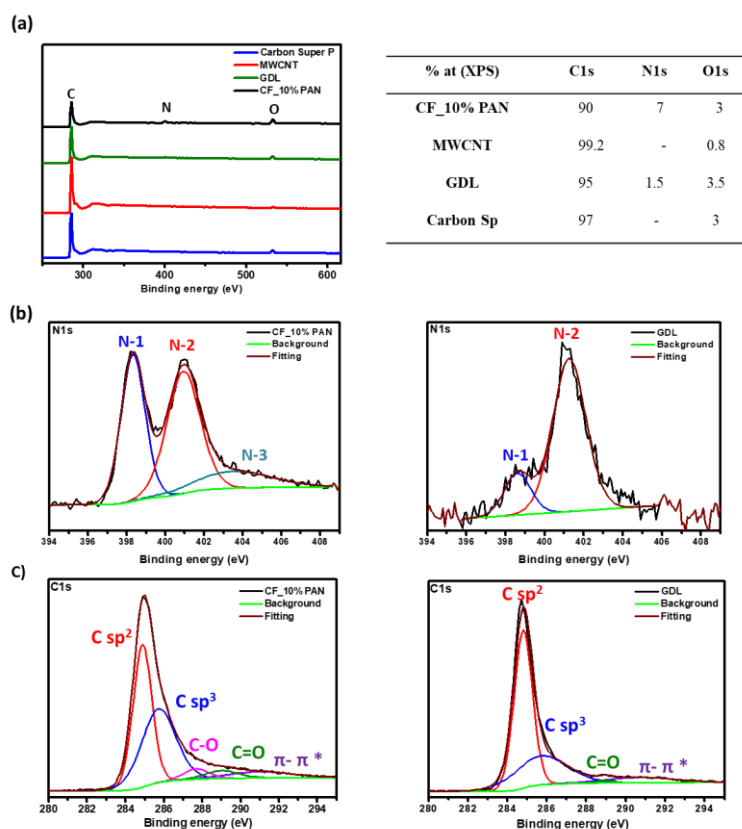
**Fig. 3.** (a) Morphology of  $\text{Li}_2\text{O}_2$  products formed at the  $\text{O}_2$ /cathode interfaces during full discharge step of carbon materials in  $\text{Li}-\text{O}_2$  cells at different current densities using 0.1 M  $\text{LiPF}_6$  in DME. (b) Representative microscopic images of fully discharged GDL cathode regardless of the current density applied in the cell.



**Fig. 4.** Distribution of  $\text{Li}_2\text{O}_2$  products formed through the carbon cathode volume during full discharge step in  $\text{Li}-\text{O}_2$  cells at low current density of  $0.05 \text{ mA}\cdot\text{cm}^{-2}$  (geom).



**Fig. 5.** (a) Full discharge voltage profiles of electrospun carbon fibers (CF\_10% PAN) with different thicknesses in Li-O<sub>2</sub> cells operating at 0.05 mA.cm<sup>-2</sup> (geom) using 0.1 M LiPF<sub>6</sub> in DME. (b) FEG-SEM analyses of the fully discharged 600 μm-CF cathode.



**Fig. 6.** (a) XPS spectra of the different carbon electrodes with the related surface chemical composition. The binding energies for carbon, nitrogen and oxygen are 284.8, 389.32 and 533 eV, respectively. (b) XPS deconvolution of N1s peaks of carbon cathodes before discharge. N-1, N-2 and N-3 correspond to Pyridinic-N (BE = 398.3 eV), Pyrrolic-N (BE = 400.9 eV) and Graphitic-N (BE = 403.5 eV), respectively. (c) XPS analysis of the C1s region in carbon materials before discharge showing different chemical bonds sp<sup>3</sup>, sp<sup>2</sup> and oxygen species present in different relative proportions. Carbon sp<sup>2</sup> (BE= 284.8 eV), carbon sp<sup>3</sup> (BE= 285.7 eV), C-O (BE=287.7 eV), C=O and/or C=N (BE= 289 eV) and shake up π-π\* (BE=290.7 eV). The peak lineshapes used were Voigt functions, i.e. Gaussian-Lorentzian convolutions, with an integral background subtracted prior to fitting. The peaks assignments were based on models discussed in [51].

**Table 1**

Surface and porosity characteristics of pristine carbon electrodes.

Carbon samples	Fibers size (nm) <sup>1</sup>	Surface area $\rho_c$ (m <sup>2</sup> .g <sup>-1</sup> ) <sup>2</sup>	Porosity $\epsilon_{theo}$ (%) <sup>3</sup>	V <sub>micro</sub> (d<2nm) (cm <sup>3</sup> .g <sup>-1</sup> ) <sup>4</sup>	V <sub>meso</sub> (2<d<50nm) (cm <sup>3</sup> .g <sup>-1</sup> ) <sup>4</sup>	V <sub>meso</sub> (50nm<d) (cm <sup>3</sup> .g <sup>-1</sup> ) <sup>5</sup>	V <sub>macro</sub> (50<d<100nm) (cm <sup>3</sup> .g <sup>-1</sup> ) <sup>5</sup>	V <sub>macro</sub> (50<d<200nm) (cm <sup>3</sup> .g <sup>-1</sup> ) <sup>5</sup>	V <sub>macro</sub> (d>200nm) (cm <sup>3</sup> .g <sup>-1</sup> ) <sup>5</sup>	Pores size (μm) <sup>5</sup>	Electrolyte uptake %
CF-10%PAN	260±30	9	96	0.06	0.05	0	0	0	34.8	1-1.5	550
GDL	10000±900	0.21	70	0	0.009	0	0	0.003	2.2	0.2-50	114
MWCNT	10±2	210	88	0.05	0.17	0.27	0.25	0.63	2.7	0.008-0.2	490
Carbon Super P (powder)	60±0.3	62	76	0.001	0.012	0.01	0.48	0.61	5.2	0.07-0.1	-

<sup>1</sup> Measured by SEM images using image J software

<sup>2</sup> Calculated from the fibers diameter observed from SEM images and the true density of carbon (2g.cm<sup>-3</sup>) assuming that all the fibers are uniform cylinders. Only the surface area of the carbon Super P bulk powder is estimated by BET measurements.

<sup>3</sup> Calculated by the equation  $\epsilon = 1 - (4m / \pi\rho_c d^2 L)$  ( $\epsilon$ : porosity, m: weight of the sample,  $\rho_c$ : true density of carbon = 2g.cm<sup>-3</sup>, d: diameter of the sample, L: thickness of the sample)[54] except for the Carbon Super P powder which porosity % is calculated by BET method.

<sup>4</sup> Obtained after applying the DFT method to the N<sub>2</sub> adsorption isotherm data

<sup>5</sup> Estimated by mercury porosimetry measurements.

**Table 2**

Electronic conductivities values of carbon electrodes.

Carbon samples	Resistivity R sheet (Ω.cm) <sup>1</sup>	Conductivity (S.cm <sup>-1</sup> ) <sup>2</sup>
CF-10%PAN-950°C	100-400	0.5 10 <sup>-2</sup>
GDL	2-5	5 10 <sup>-2</sup>
MWCNT	5-10	0.6 10 <sup>-2</sup>
Carbon Super P	-	-

<sup>1</sup> Results from four probe conductivity experiments.

<sup>2</sup> Calculated using Impedance measurements (see Fig. S10).