Influence of synthesis parameters on g-C3N4 polysulfides trapping: A systematic study

Original
Influence of synthesis parameters on g-C3N4 polysulfides trapping: A systematic study / Versaci, D., Cozzarin, M., Amici, J., Francia, C., Leiva, E.P.M., Visintin, A., Bodoardo, S.. - In: APPLIED MATERIALS TODAY. - ISSN 2352-9407. - ELETTRONICO. - 25:(2021), p. 101169. [10.1016/j.apmt.2021.101169]

Publisher:
ELSEVIER

Published
DOI:10.1016/j.apmt.2021.101169

Influence of synthesis parameters on g-C_3N_4 polysulfides trapping: a systematic study.

Daniele Versaci[a], Melina Cozzarin[c], Julia Amici[a], Carlotta Francia [a], Ezequiel P. M. Leiva[d], Arnaldo Visintin[b] and Silvia Bodoardo[a]*

[a] Electrochemistry Group, Department of Applied Science and Technology (DISAT), Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129 Torino (Italy)

[b] Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, CCT La Plata-CONICET, La Plata, Argentina

[c] YPF Tecnología S.A., Av. Del Petroleo s/n - (Entre 129 y 143), Berisso, Buenos Aires, Argentina

[d] INFIQC, CONICET and Departamento de Química Teórica y Computacional, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Córdoba, Argentina

*Corresponding authors:

Daniele Versaci, Tel.: +39 011 090 4789; E-mail address: daniele.versaci@polito.it;

KEYWORDS: lithium sulfur battery, double-layer, carbon nitride, polysulfides trapping

ABSTRACT

Beyond Li-ion batteries, one of the most promising technology is the Lithium-Sulphur (Li-S) not only for its higher theoretical energy density (about 2600 Wh kg^{-1}) but because sulfur is relatively inexpensive and non-toxic. However, the Li-S battery suffers from "shuttle effect" of polysulfides. Thus, restricting shuttling means increasing cell performance and durability. DFT calculations showed that graphitic carbon nitride (g-C_3N_4) exhibits strong interactions with Li_2S (*e.g.* superior to graphene-like carbon) and acts as polysulfides trapping agent. In this work, the role of g-C_3N_4, synthetized from different precursor and at different polycondensation temperatures was systematically studied, using a double layer approach for the electrode preparation, which ensures direct interaction between g-C_3N_4 and soluble lithium-polysulfides.

This systematic study confirms the importance of the morphological and superficial properties of the material. In particular, carbon nitride from urea precursor remarkably improves the performance of the sulphur cathode, increasing the specific capacity of the cell by 25% and improving its useful life over 500 cycles. According to the morphological characterization and the XPS analysis, benefits are achieved from polycondensation of urea at 550 °C. The obtained g-C_3N_4 shows the highest proportion of -NH_2 species on the surface, which favours the interaction with polysulfides.

1. INTRODUCTION

Lithium-ion batteries (LIBs) are well established energy storage devices for electronic, transportation and renewable-energy applications. Unfortunately, the current Li-ion technology is reaching its intrinsic limits in terms of energy density and specific capacity as a consequence of the intercalation/insertion-compounds chemistry [1]. At the same time, to meet the ever-increasing energy storage demand for electrical mobility and smart grids, future batteries have also to guarantee sustainable and cheaper solutions. Alternative systems that can deliver higher capacities and energy densities need to be developed and implemented [2].

Beyond Li-ion battery, one of the most promising next-generation energy storage system is the lithium-sulphur (Li-S) battery. Sulphur offers many advantages compared to traditional LIBs active materials at the cathode. From a commercial perspective, sulphur is earthly abundant, geographically well-distributed, non-toxic and can be produced from desulphurization processes from oil and gas industries. This means that the overall battery price and the environmental impact can also be reduced [3][4]. From the electrochemical point of view, Li-S technology is expected to achieve 2-3 times higher (about 2600 Wh kg^{-1}) energy density than the actual LIBs, thanks to the particular chemistry of the system, which involves the reaction of sulphur (α-S_8) to Li_2S, through the formation of lithium polysulfides (LiPSs) intermediates [5]. The peculiarity of Li-S system is that the discharge products have different physical properties. Typically, S_8 and Li_2S are solid and insoluble in the common electrolytes, while the intermediate LiPSs are soluble in organic solvents. As a matter of fact, the huge number of intermediate species and the complex reaction mechanism are responsible for the drawbacks of the system. Indeed, commercialization of the lithium-sulphur technology is still limited by some key challenges that have to be addressed [6]. Elemental sulphur has very low electronic conductivity (5×10^{-30} S cm^{-1} at 25 °C.) [7]. The insulator nature of both sulphur and Li_2S results in large polarization and slow kinetic processes, limiting sulphur utilization. For this reason, sulphur needs to be intimately mixed with a conductive additive such as carbon, which inevitably reduces the energy density of the system. At the same time a huge volume expansion occurs during the solid-liquid-solid transition process, causing structural and morphological changes of the cathode [7][8][5].

However, the most important issue of Li-S system is related to LiPSs dissolution. On one hand, dissolution of LiPSs is beneficial to achieve full active-material utilization because new bulk sulphur can be continuously exposed to the electrolyte and participate to the reaction [4]. On the other hand, the dissolved long chain polysulfides can diffuse out of the cathode and migrate towards the anode, where they directly react with metallic lithium creating nonconductive and insoluble Li_2S precipitate on its surface. This process is known as “polysulfides shuttle effect”, which results in both anode corrosion and irreversible loss of active material, with consequent low capacity retention and low Coulombic efficiency [7]. Moreover, during cell resting, sulphur reacts directly with lithium ions in the electrolyte producing soluble lithium polysulfides with consequent self-discharge of the cell [5][7][8].

In the last years, different approaches and methods have been adopted to solve these issues with the purpose to achieve a widespread introduction of this technology in the market [8].

Research attempted to design and develop suitable cathode nanocomposites, with conductive carbon scaffolds and/or conducting polymers in order to increase the electrical conductivity and provide structural integrity of the S cathode [5]. Moreover, novel electrolyte formulations have been implemented with the aim of creating a passivating and protective film on metallic lithium anode, limiting polysulfide shuttle effect [3][4][8]. Another important strategy is LiPSs confinement. In general, this is realized by immobilizing LiPSs species within the cathode via physical or chemical adsorption [9][10][11][12]. However, physical adsorption cannot confine polysulfides completely, while materials that carry out chemical bonding have the general disadvantage of low specific surface area, thus low sulphur loadings can be achieved. Therefore, physical or chemical processes taken individually show limited improvements, while their combination creates synergies and is the most promising strategy to address shuttle effect [9].

In the last five years, g-C_3N_4 has been studied as suitable polysulfides trapping agent in Li-S battery. Many investigations have been focused on understanding the origin of the strong interaction between carbon nitride and lithium polysulfides [13]. The existence of a strong electrostatic affinity between carbon nitride and LiPSs was confirmed and validated [14][15][16] both by density functional theory (DFT) simulations and experimental data. These studies pointed out a strong contribution of g-C_3N_4 in the kinetics of LiPSs redox reactions due to the high surface polarization of carbon nitride, which alters the molecular configurations of the adsorbed LiPSs, affecting the electron transport and increasing the rate of the redox conversion reaction. The combination of DFT calculations and spectroscopic studies highlighted that the binding energy between Li_2S_2 (or Li_2S_4) and g-C_3N_4 increases by increasing the concentration of doped N in g-C_3N_4. This means that accessible pyridinic nitrogen adsorption sites are the key factor for the improvement of electrochemical performance. [17][18][19].

Starting from theoretical predictions, many different strategies were adopted to properly exploit the g-C_3N_4 properties as LiPSs trapping agent. Carbon nitride was largely investigated as sulphur host, often coupled with graphene to increase the conductivity. Alternatively, many studies were oriented to modify polyolefin-based separators with g-C_3N_4 or create novel interlayer architectures [18][19]. Recently, a selective double layer structure of the cathode was investigated to mitigate LiPSs diffusion. This was obtained by simply coating the surface of a S/C cathode with a thin laminated graphene-based or polymer-based interlayer [20][21][22]. Following the same strategy Qu *et al.* [23] developed a 2D laminated composite of graphene and g-C_3N_4 nanosheets (g-C_3N_4/GS), directly spread on the sulphur cathode surface.

As a matter of fact, many types of doping, morphologies, and different precursors of carbon nitride were reported in various studies. To date though, no systematic study comparing the role of different carbon nitride precursors as well as the different synthesis temperatures was carried out. In fact, most of the reported investigations are difficult to compare, because of the different adopted strategies and test parameters (*e.g.* sulphur mass loading, electrolyte uptake *etc.*) employed.

For this reason, this work investigates the role of g-C_3N_4, synthetized from different precursors and at different temperatures, using a double layer cathode approach. The designed double layer cathode guarantees good interaction between LiPSs and the carbon nitride, since the carbon nitride, which has neither an optimal mesoporosity nor an optimal electronic conductivity, is not directly mixed with sulphur. Hence the cathode is composed of two layers. In the first layer, sulphur is intimately mixed with the conductive carbon, which is a good electron conductor for the electrochemical reaction. In the second layer the good distribution of carbon nitride allows the material to better exert its trapping action towards LiPSs.

2. EXPERIMENTAL SECTION

2.1. Material preparation

In order to investigate the effects of different physicochemical properties of g-C_3N_4 towards LiPSs trapping, three different carbon nitride materials were prepared starting from urea (≥ 98 % Sigma Aldrich), dicyandiamide (DCDA, ≥ 99.0 % Sigma Aldrich) and melamine (MLM, ≥ 99 % Sigma Aldrich), respectively. It is important to note that urea, dicyandiamide and melamine are nontoxic, cheap and easily available precursors [24] .

In a typical condensation process 6 g of urea, dicyandiamide or melamine were put into a semi-closed alumina boat and heated to 550 °C in a tubular furnace for 3 h with a heating rate of 2.5 °C min^{-1}. After the reaction, the furnace was cooled to room temperature and the resultant g-C_3N_4 samples were grounded into powder, washed several times with water and ethanol and centrifuged at 10000 - 12000 RPM for 15 minutes. The different g-C_3N_4 powders prepared starting from urea, dicyandiamide, melamine, were named as: CN-U, CN-D, CN-M, respectively.

In the second part of the work, urea was treated at three different annealing temperatures: 450, 550, and 650 °C, respectively. All the obtained samples discussed in this section were labelled as CN-U-x, where x refers to the specific annealing temperature~~s~~.

2.2. Material characterization

XRD analysis was carried out by a PANalytical X'Pert (Cu Ka radiation) diffractometer. Data were collected with a 2D solid state detector (PIXcel) from 10 to 80° 2θ with a step size of 0.026 2θ and a wavelength of 1.54187 Å.

Fourier Transform Infrared Spectroscopy (FTIR) was measured with a Nicolet™ iS50 FTIR spectrometer (Thermo Scientific™) equipped with ATR tool. 32 scans were collected with a resolution of 4 cm^{-1} from 4000 to 400 cm^{-1}.

Thermogravimetric analysis was performed on a Linseis TGA PT 1600 instrument by heating the composite at 10 °C min^{-1} from room temperature to 800 °C in air.

FESEM analysis was carried out by Zeiss SUPRA™ 40 with Gemini column and Schottky field emission tip (tungsten at 1800 K). Acquisitions were made at acceleration voltage of 3 kV and working distance (WD) between 2.1 - 8.5 mm, with magnification up to 1000 KX.

The Brunauer-Emmett-Teller specific surface area (SSA) was determined by nitrogen physisorption at 77 K using a Micrometrics ASAP 2020 instrument. The specific surface area was calculated with the BET model in the relative pressure range of 0.07 - 0.30 by assuming 0.162 nm^2/molecule as the molecular area of nitrogen.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a PHI Model 5000 electron spectrometer equipped with an aluminium anode (1486 eV) monochromatic source, with a power of 25.0 W, and high-resolution scan with 11.75 eV pass energy. The instrument typically operates at pressures below 5×10^{-8} mbar.

For polysulfides adsorption tests, a solution 0.1 M of Li_2S_6 was prepared directly reacting Li_2S and S_8 (in the weight ratio 1:5) into a mixture of DME and DIOX (1:1 by volume) for 72 h at 70 °C, under continuous stirring in argon atmosphere. Li_2S_6 was chosen as representative soluble long-chain polysulfide species. The resulting brownish-red Li_2S_6 solution was then diluted to 1.0 mM for the polysulfide adsorption test. Then, a quantity of different carbon nitride equivalent to 0.5 m^2 surface area was added to 20 μL of 1.0 mM of Li_2S_6 solution diluted in 2 mL of DME:DIOX 1:1 v/v mixture and left to interact for 12 hours [25].

The UV-Vis absorption spectra were detected by a UV–vis spectrophotometer (JENWAY, 6850 UV/Vis. Spectrophotometer) within the spectral range of 200 - 500 nm.

2.3. Electrochemical measurements

All the working electrodes were prepared by solvent tape casting method. The so called “standard” sulphur cathode electrode (STD) was prepared using pure sulphur (≥ 99.5 % Sigma Aldrich) as active material, Ketjenblack® (KjB, EC-300J, AkzoNobel), as conductive carbon additive and poly(vinylidenedifluoride) (PVdF, Solvay; 10 wt.% in N-methyl-2-pyrrolidinone solution) as polymeric binder. The “standard” electrode composition (STD) was set up 60:30:10 wt.%, respectively for (S:KjB:PVdF), in all experiments. This ratio was chosen with the aim to obtain a cathode with reproducible sulphur loading, using a simple mixing procedure and taking into account that this is a simple and easily scalable procedure. The final mixture was mechanically deposited on the aluminium current collector by Doctor Blade technique. The blade was adjusted for a 200 µm deposition using an automatic film applicator (Sheen 1133N) with a speed of 50 mm s^{-1}. After the slurry deposition the coated aluminium foil was dried at 50 °C in air. A similar procedure was used to obtain the double layer cathode. The dried standard electrode was first obtained following the previously mentioned procedure and was subsequently coated by a second layer containing carbon nitride. The ratio between CN, KjB and PVDF, contained in the second layer slurry was 80:10:10, with a blade thickness of 200 µm. In the DL electrodes containing CN-U-550, the carbon nitride mass loading was about 0.9 mg cm^{-2}. For all the DL electrodes the S/CN ratio was kept in the range of 0.9 – 1.0, in order to have a comparable S/CN ratio.

After solvent evaporation in air, disks of 2.54 cm^2 were punched out, vacuum dried at 40 °C (in a Büchi Glass Oven B-585) for 4 h, then transferred into an Argon filled dry glove-box (MBraum Labstar, H_2O and O_2 content < 1 ppm) for cell assembly. The active material loading of the “standard” sulphur cathode (STD) was ~ 1 – 1.2 mg cm^{-2}. It is worth noting that the obtained electrodes have been carefully selected according to their weight and morphology.

The electrodes were assembled in 2032 coin-type cells with lithium disk (Chemetall Foote Corporation, Ø 16 mm) as counter electrode and PP polymeric membrane (Celgard 2500, 25 µm thickness, Ø 19 mm) as separator. The electrolyte was a solution of 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DIOX) 1:1 (v/v) with 1.0 M lithium bis(trifluoromethanesulfonyl)imide ($CF_3SO_2NLiSO_2CF_3$, LiTFSI) and 0.25 M lithium nitrate ($LiNO_3$, ≥ 99.9 % Sigma Aldrich). The solution was stored in argon filled glove box for at least 12 h before the use. The electrolyte amount for each kind of experiment never exceeded 20 μL, corresponding to ~ 10 - 11 μL mg^{-1} (referred to S quantity).

The cycling performances of the cathodes were investigated by means of galvanostatic discharge-charge cycling (GC) using an Arbin LBT-21084 battery tester at room temperature. Galvanostatic discharge-charge tests were carried out in the potential interval 1.8 - 2.6 V vs. Li^+/Li^0 at different current rates. The C-rate was calculated using the theoretical capacity of sulphur (1672 mAh g^{-1}). For cyclic voltammetry (CV), the electrode potential was reversibly scanned between an extended range of potential from 1.7 to 2.8 V vs. Li^+/Li^0 at 0.1 mV s^{-1}.

Electrochemical Impedance Spectroscopy tests (EIS) were performed with Bio-Logic® VSP-3e multichannel potentiostat, equipped with impedance modules. Each spectrum was recorded in the frequency range of 100 kHz to 10 mHz, with an excitation potential of 5 mV and 10 points per decade.

3. RESULTS AND DISCUSSION

3.1. Morphological characterization

Graphitic carbon nitride can be easily prepared by the direct pyrolysis of various organic precursors (Figure 1a). The intrinsic physicochemical properties of g-C_3N_4, including morphology, thermal stability, surface area, pore volume, and yield are closely related to the precursor [24].

The morphological characterization of the prepared samples was performed by FE-SEM investigation. The FE-SEM images of g-C_3N_4 samples are depicted in Figure 1. All the g-C_3N_4

particles exhibit wrinkles and irregular shapes. In particular, CN-D and CN-M consist of large amounts of dense and thick nanosheets with irregular shape assembled together, resulting in a condensed morphology (Figure 1a, d and b, e). On the contrary, CN-U shows dispersed smooth and thin irregular flakes with characteristic higher porous morphology (Figure 1c, f), respect to the other two. The typical higher porous structure is due to the different reaction pathway of urea respect to melamine and dicyandiamide, as discussed below [26][27].

Please insert here Figure 1

Elemental analysis was carried out to evaluate the C/N ratio for the different samples (Table S1). The three carbon nitride samples showed a C/N ratio of 0.57 - 0.58, which is less than the theoretical value of 0.75 and less than the average value usually reported in literature (*e.g.* 0.70) [28]. The similar C/N ratio of the different carbon nitride confirms the excess of nitrogen in all samples, if compared to theoretical values. These observations are attributed to the incomplete condensation of amino groups, which is related to the small, but significant, amounts of hydrogen that is still present in the compounds [29]. This explains why the general formula $C_xN_yH_z$ is usually assigned to carbon nitride [28]. In some cases, determination of C:N:H ratios is affected by the presence of other elements *i.e* exposure to air or moisture, which can be incorporated into the samples [28]. For example, the evident missing amount reported for CN-U in Table S1 can be attributed to oxygen or moisture, which is still present in the sample.

XRD patterns (Figure 2b) of the three g-C_3N_4 samples clearly show two peaks at 27.6° and 13.5°, which are assigned to (002) and (100) planes, respectively. The main peak at 27.6 ° (002) is attributed to the strong interplanar stacking of the conjugated aromatic systems while the less pronounced peak at 13.5° is due to the in-plane tri-s-triazine units, which form one-dimensional (1D) melon units [24]. These two diffraction peaks are consistent with the XRD patterns of g-C_3N_4 (JCPDS 87-1526). No particular difference is seen in the position of XRD peaks for g-C_3N_4 powders prepared from different precursors, confirming identical crystal structures [26]. The interplanar d-spacing was calculated considering the strong peak at 27.6° and was around 3.26 Å for all samples. In the XRD spectra of CN-U, the two main peaks are broader and have lower intensity as a consequence of smaller crystalline domains [27]. The possible explanation for the different peak shapes in CN-U can be attributed to the alternative polycondensation route [26]. In fact, during the thermal condensation of urea, the heptazine-based structure might not be completely formed and some structural defects can be present in the final product [27]. The FWHM of the Bragg lines of g-C_3N_4 powders, was calculated in order to compare the size of the crystallites. The average crystallites sizes are 13.18, 40.94 and 31.02 nm for CN-U, CN-D and CN-M, respectively. To summarize, the XRD patterns all belong to g-C_3N_4 structure but both the intensity and breadth of the peaks are strictly related to the different nanostructures and morphologies of the as-prepared g-C_3N_4 samples [24].

The FT-IR spectra of g-C_3N_4 are shown in Figure 2c. All samples showed some evident groups of signals centred in three different regions of the spectra: at 3000 – 3500 cm^{-1}, 1200 – 1700 cm^{-1} and 700 – 800 cm^{-1}. The absorption peaks in the 700 – 800 cm^{-1} region are typically assigned to the bending vibration mode of carbon nitride heterocycles, in particular the band at 801 cm^{-1} is characteristic of out of plane bending vibration mode of the triazine units [24]. The bands in the 1200 – 1650 cm^{-1} region correspond to the typical stretching vibration modes of the heptazine heterocyclic ring (conjugated C=N). The 2172 cm^{-1} peak is only observable in the CN-U spectra and is assigned to C≡N triple bond. The presence of this peak indicates that the aromatic unit of g-C_3N_4 was partly broken and defected [30]. Another interesting difference among the samples is seen in the 3000 – 3500 cm^{-1} region. The absorption band at 3170 cm^{-1} is assigned to the stretching mode of O-H while the band at 3336 cm^{-1} belongs to the N-H vibration mode [30]. This indicates the existence of uncondensed amino groups and absorbed H_2O molecules in all samples. However, the peaks intensity of CN-U is stronger than that of CN-D and CN-M, indicating that urea improves the polycondensation of g-C_3N_4 [24]. Nonetheless, all samples basically retain the carbon nitride structure.

All the synthetized samples have similar nitrogen adsorption-desorption isotherms (Figure 2d), which belong to the Type IV isotherm with H3 loop corresponding to monolayer coverage and multilayer adsorption, typical of non-rigid aggregates of plate-like particles [31]. The specific surface areas were 4.5, 5.1 and 44.8 m^2 g^{-1} for CN-D, CN-M and CN-U, respectively while the pore volume lets us suppose that all samples have negligible microporosity and some disordered interparticle mesoporosity (Figure 2e). CN-U has the highest specific surface area and highest porosity, confirming its different morphology.

More precisely, both the specific surface area~~s~~ and pore volume~~s~~ of CN-U are one order of magnitude higher than those of CN-D and CN-M, as reported in Table S2. The different morphological characteristics for CN-U are due to the particular synthetic route of carbon nitride from urea, which induces the formation of large amount of gas such as NH_3 and H_2O, favouring the expansion of the packing layers and higher porous structures. In particular, the presence of oxygen heteroatom in urea affects the thermal condensation process, originating water vapour, which can act as "soft template" producing porous structures and inducing the expansion of carbon nitride layers [27]. As previously observed, higher porosity specific surface area of the urea-derived g-C_3N_4 can enhance the electrochemical properties of the carbon nitride [27]. In particular, the high surface area facilitates the mass transfer providing more active sites for surface-dependent reactions. At the same time structural defects resulting from the lack of a proper s-triazine structure can generate more catalytic active sites for LiPSs interaction [27].

Please insert here Figure 2

To better investigate the chemical state of the different elements and the surface composition and functionalization, samples were analysed by X-ray photoelectron spectroscopy (Figure 3). The comparison of the survey spectra reveals that all samples predominantly contain C, N and O elements (Figure S1). No significant shift in the binding energy of C1s, N1s and O1s signals is detected, showing that the chemical state on the surface of the g-C_3N_4 is almost the same in the various samples. Moreover, the similar intensity of C1s and N1s peaks suggests that the amount of C and N is almost the same in each sample. Table 1 reports the relative percentage of C and N for CN-D, CN-M and CN-N calculated by high resolution XPS spectra deconvolution. Unfortunately, the quantitative XPS analysis of C is hindered by the presence of ‘‘adventitious’’ C1s signals deriving from the carbon tape used to mount the samples. However, a small signal of silicon was also detected and used to evaluate the contribution of the carbon tape in the C1s spectra. For samples CN-M and CN-U, the C1s core level spectra (Figure 3a, b, c) was deconvoluted into four components: sp^2 hybridized C atoms (284.8 eV), C–O (286.2 eV), N–C=N (288.0 eV) and C=O (288.9 eV). The C1s spectrum of CN-D (Figure 3a), was deconvoluted in five components. The additional peak centred at 290.2 eV is ascribed to O=C–O. As previously mentioned, the carbon tape signals can interfere in the analysis, these peaks are located at 284.8 eV for main C–C interaction, at 286.1 eV (C–O) and at 288.7 eV (O–C=O) due to surface oxidation of the carbon film [28]. For this reason, the high resolution N1s spectrum (Figure 3d, e, f) helps to obtain more information on the carbon nitride surface chemistry. The N1s spectra were deconvoluted into three main components. In particular, the peak at 398.5 eV was attributed to hybridized nitrogen in C–N bonds (C=N–C) of triazine rings, which is consistent with the peak at 288 eV of sp2 bonded C atoms in the C1s spectrum. The peak at 399.6 eV refers to the central N atoms bridging between three heptazine rings (N–$(C)_3$). The peak at 401.1 eV is indicative of C–N–H uncondensed amino groups (H–N–$(C)_2$) [28]. No signals were detected at 403 eV due to N–O species.

As reported in Table 1, the different surface functionalities of CN-U, respect to CN-D and CN-M is particularly evident. In fact, the surface of carbon nitride obtained from urea is particularly rich of pyridinic nitrogen, which is the major adsorption sites of LiPSs. This is in good agreement with similar conclusions achieved by other studies, combining theoretical calculations with experimental analysis [17][18][19][32].

Please insert here Figure 3

Please insert here Table 1

To further evaluate the polysulfide adsorption capability of the various carbon nitrides, a visual adsorption test under argon atmosphere was performed. After adding g-C_3N_4 to the Li_2S_6 solutions the colour appears yellow for all samples, as depicted in Figure 4a. The solution containing CN-U appears paler, due to the intrinsic colour of carbon nitride obtained from urea, which is closer to pale yellow. After resting for 12 hours without stirring, only the solution containing CN-U is transparent (Figure 4a). On the contrary, the solution containing CN-M shows no colour fading, while the one with CN-D shows only a mild discolouration. Accordingly, the interaction between CN-U and LiPSs is the strongest one. The consistent colour fading, clearly observable after 12 hours, confirms the strong interaction between lithium polysulfides and carbon nitride, especially for CN-U. According to SSA analysis, it is worth noting that, the added amount of 0.5 m^2 for CN-U is definitely lower in comparison to the others, so the active sites accessibility is particularly important for a good physico-chemical interaction. We also show a comparison at 0 hours and after 12 hours among the pure Li_2S_6

reference solution, the Li_2S_6 solution with 0.5 m^2 of KjB and the Li_2S_6 solution with 0.5 m^2 of CN-U (Figure 4b). The LiPSs solution with CN-U showed an evident discoloration after 12 hours, confirming that carbon nitride has relevant adsorption capability for LiPS. On the contrary no discoloration is seen with KjB, confirming that the interaction of KjB is weak and not sufficient for high sulphur loadings.

Regarding the electrochemical characterization of the double-layer electrodes, cyclic voltammetry and galvanostatic cycling were performed for all the samples.

Figure 4c shows the cyclic voltammetry profiles at a scan rate of 0.1 mV s^{-1}, within the cut-off potentials of 1.6 - 2.8 V. All the CV curves demonstrate typical sulphur cathode behaviour. As expected, the two peaks detected during the initial cathodic reduction, correspond to two different redox processes. The first reduction peak at 2.23 V refers to the reduction of sulphur (S_8) to soluble long-chain lithium polysulfide (Li_2S_x, $4 < x < 8$), while the second reduction peak centred at 1.95 V is assigned to the further conversion of long-chain LiPSs to insoluble short-chain lithium polysulfides (Li_2S_2 or Li_2S). By contrast, during the oxidation process, two overlapping anodic peaks at 2.45 V and 2.55 V are observed. These peaks represent the formation of both higher order polysulfides and elemental sulphur, by the oxidation of low order LiPSs. The peaks potential of the double layer electrodes are shifted if compared to the peaks positions of the single layer electrode (STD). Precisely, in double-layer electrodes the two reduction peaks are shifted toward lower potentials while the oxidation peaks move towards higher potentials if compared with STD cathode.

Generally, the broader shape observed for the DL electrodes is attributable to the presence of the second layer, and due to the consequent smaller ion diffusion typical for thicker electrodes, as already observed in previous work [33][34]. Secondly, the initial higher polarization can be related to the semiconducting nature of carbon nitride, which is widely distributed in the second layer. In fact, as possible to see in the FE-SEM micrographs (Figure S5), DL electrode containing CN-U shows a wide distribution of carbon nitride into the top-layer. While the electrodes with CN-D and CN-M present a less homogeneous distribution of dense and thick agglomerates.

Carefully observing the voltammograms of DL cathodes, some accentuated anodic and cathodic peaks shoulders are detectable. The presence of different peaks/shoulders are attributable to the different reduction reactions involved in the Li-S discharge process. The presence of evident and well-defined shoulders for the DL electrodes, lets us suppose that carbon nitride shifts some polysulfides conversion reactions. In fact, the broader profile can, also, indicate the presence of numerous species undergoing the anodic reaction, over a wide range of potentials. Similar CV voltammograms were also reported by Yao *et al.* [35].

The galvanostatic charging and discharging behaviour of the cathodes was compared at C/5 for 200 cycles, after three activation cycles at C/10.

Figure 4e shows the first-cycle galvanostatic voltage profiles at C/10 of the STD and of the double-layer electrodes, which all exhibit the typical two plateau discharge curves. The first plateau at 2.3 V is related to the reduction of sulphur to long-chain LiPSs, and the second, at 2.1 V, corresponds to the reduction into short-chain LiPSs. The four cathodes delivered an initial discharge capacity at C/10 of about 780, 870, 1010 and 1150 mAh g^{-1} for STD and double layer STD+CN-D, STD+CN-M, STD+CN-U electrodes, respectively. The initial higher capacity of STD+CN-x electrodes can be due to the additional contribution to the discharge capacity of about 93.6 mAh g^{-1} due to g-C_3N_4 [23]. A second explanation can be a partial rearrangement of the active sulphur material after the initial charge-discharge cycle. In particular, the g-C_3N_4 layer can reduce the capacity loss originating from the rearrangement of sulphur during the first cycles [23].

After 200 cycles (Figure 4d), the discharge capacity at C/5 was 340 mAh g^{-1} for STD electrode and 406, 609 and 740 mAh g^{-1} for STD+CN-D, STD+CN-M, and STD+CN-U, respectively. The capacity retention (for the 1st and the 200th cycles at C/5) is higher for the double-layer electrodes, resulting 88.1 % for STD+CN-U and 73.9 %, 58.0 %, 52.6 % for STD+CN-M, STD+CN-D and STD, respectively. This means that the capacity fade of the STD+CN-U is only 0.06 % per cycle. The Coulombic efficiency at the 200th cycle is higher than 99 % for all samples (Figure S6, Table S3).

The overpotential of the electrodes was calculated measuring the voltage hysteresis (ΔE) between charge and discharge curves at 50 % of the total discharge capacity (Q1/2) at the 1st cycle (Figure S7a). The STD cathode showed an initial polarization of 0.17 V, whereas in the double layer cathode the polarization was 0.23 V. The large overpotential observed in first cycles should be ascribed to the initial wetting process between the cathode and the electrolyte, and this is particularly true for the double-layer electrode, where sulphur is confined in the bottom layer, thus the electrolyte needs more time to reach it. Moreover, the layer of g-C_3N_4 decreases the conductivity of the cathode and increases the overpotential. At the 1st cycle, for STD the capacity of the upper (Q1) and the lower (Q2) plateaux were 269 and 510 mAh g^{-1} respectively, corresponding to a total discharge capacity of about 779 mAh g^{-1}, which is definitely lower than sulphur theoretical value of 1675 mAh g^{-1}. On the contrary, for the double-layer cathode Q1 was 374 mAh g^{-1} and Q2 was around 808 mAh g^{-1}, which summed together correspond to a total discharge capacity of 1182 mAh g^{-1}, that is 34 % higher capacity than that of STD. The corresponding Q1 and Q2 values of the single-layer electrode are approximately 35 and 65 %, respectively, while they are 32 and 68 % for the double-layer, which means that the percentage contribution of upper-plateau discharge, due to long-chain LiPSs, is lower for the cathode containing carbon nitride.

Considering the charge/discharge curves from the 1st to 200th cycle (Figure S7b, c), for STD and STD-CN-U, the polarizations increase with the increase of the current density from C/10 to C/5. Larger polarization of double-layer electrodes is seen at higher C-rate, while the overpotential of ~~STD~~ cathode is quite constant at C/5. As depicted in Figure S7c, the polarization of STD + CN-U increases from C/10 to C/5 (3rd to 5th cycle) but decreases from 5th to 200th cycle at constant C/5-rate. This means that after some "activation" cycles, the initial polarization effect is mitigated, due to the presence of carbon nitride. The decrease of specific capacity (ΔQ) related to the upper plateau, between the 1st and 200th cycle, is around 147 mAh g^{-1} for the STD and 115 mAh g^{-1} for the STD + CN-U electrode. As known, the region of the upper discharge plateau is ascribable to the formation of soluble long-chain polysulfides. Therefore, it is possible to assume that the decrease of specific capacity (ΔQ) related to the upper plateau, is mainly due to the formation and diffusion of soluble polysulfides into the electrolyte, which induces the irreversible loss of active sulphur. For this reason, the values of ΔQ can be directly correlated to the suppression of polysulfide diffusion [36]. The lower ΔQ observed for double layer cathode means a lower irreversible loss of active sulphur and consequently an effective lower LiPSs dissolution, thanks to the presence of carbon nitride. These results indicate that the carbon nitride layer not only enhances the specific capacity of the cell but also reduces the capacity loss originating from rearrangement of active sulphur during cycling.

To evaluate the self-discharge of the battery the STD cell and the STD+CN-U cell were cycled at C/10 for one cycle and then rested for 20 days (Figure 4f). During the rest phase, the open circuit potential (OCV) of the cells were measured once per minute then two charge/discharge cycles were performed at the end of the rest time. The measurement was performed to evaluate the static stabilization of Li-S cells and the decay of the open-circuit voltage due to polysulfides diffusion, which is related to the self-discharge of the cell with consequent irreversible capacity fading. Both the OCV and the capacity retention after the rest time were used to evaluate the effect of carbon nitride on the discharge behaviour of the cell. The STD electrode delivered an initial capacity of 780 mAh g^{-1} (at C/10), while the STD + CN-U delivered an initial capacity of 980 mAh g^{-1}. After 20 days-rest, the specific capacity of STD was 650 mAh g^{-1} with capacity retention of 83 %, while the STD +

CN-U successfully recovered up to 910 mAh g^{-1} with capacity retention of 93 %. After the long-time rest the STD cell exhibited severe capacity fading, 10 % higher than that of STD + CN-U.

Both cells demonstrated an initial voltage of 2.37 V after the first cycle at C/10. After resting for 20 days, the STD cell voltage showed an OCV of about 2.227 V, indicating a voltage decay of 145 mV. After the same rest time, the STD + CN-U cell showed a final voltage of 2.314 V, with a voltage decay of about 61 mV, which is consistently lower than the OCV decay of the STD. These results can be reasonably attributed to the polysulfides trapping action and the consequent self-discharge inhibition due to g-C_3N_4 in the double-layer cathode.

Please insert here Figure 4

Thus, carbon nitride obtained from urea is the best candidate for lithium polysulfides trapping. The reason is twofold. First, we observed that morphology is a key factor, since the SSA of CN-U is one order of magnitude higher than that of the other samples. This increases the presence of active sites able to interact with LiPSs. Second, the different surface chemistry of CN-U, being particularly rich of pyridinic nitrogen, allows specific interactions with LiPSs species.

To better investigate and discriminate the role of surface chemistry and material morphology on LiPSs adsorption ability, the influence of the synthesis temperature was examined. Three different g-C_3N_4 samples were synthesized by thermal condensation process, starting from urea, at the annealing temperatures of: 450°, 550° and 650 °C, respectively. The samples were labelled as CN-U-x, where x refers to the specific annealing temperature.

The FESEM micrographs of the prepared samples are shown in Figure 5a. At the process temperature of 450 °C, g-C_3N_4 shows a regular morphology composed of wavy and smooth flakes with a low presence of visible pores. Increasing the temperature to 550 °C, the typical flakes are still present, but some rolled and conical structures start to appear, originating a visible porosity into the sample. The thermal degradation is particularly evident at 650 °C, where the original large flakes are seriously degraded, and highly porous structure is visible.

The structural characteristics of the samples are further analysed by X-ray diffraction and FT-IR spectroscopy (Figure 5b). The XRD pattern indicates that g-C_3N_4 was already formed even at low annealing temperature of 450 °C and is still present 650 °C. This is consistent with the two typical diffraction peaks at around 13° and 27.5° corresponding to (001) and (002) planes, respectively (JCPDS file no. 87–1526). The main peak results slightly shifted from 27.26° to 27.52° in CN-U-550, if compared to CN-U-450, but it is around 27.36° for CN-U-650 sample. However, the interplanar d-spacing of the interlayer stacking of conjugated aromatic system is 3.25 Å and quite similar for all the samples.

The FT-IR analysis of the samples shows the typical absorption bands of carbon nitride, confirming the formation of g-C_3N_4 at all temperatures (Figure 5c). The obtained spectra are similar to the ones previously described (Figure 2c) however, the peaks in the range of 3000 - 3700 cm^{-1} are sharper for CN-U-650, indicating that more C–NH_2 groups and C–NH–C bridges between heptazine units are present in the structure [37]. This results in a greater fraction of small polymer segments containing only few heptazine units with -NH/NH_2 groups at the ends [37] and suggests that the higher temperature of polymerization promotes the planarization of the g-C_3N_4 layers, weakening the interactions between two adjacent atoms, which are respectively located in two adjacent tri-s-triazine rings [38].

To confirm the different porosity and surface area of the synthetized samples, the nitrogen adsorption-desorption isotherms and pore size distribution (PSD) were evaluated by BET method. The pore size distribution denotes the mesoporous structure for all g-C_3N_4 (Figure 5 d, e) [39][40]. In particular, CN-U-450 and CN-U-550 have small mesopores at about 3-5 nm and some larger mesopores at about 35 - 45 nm. Interestingly, the CN-U-650 pore distribution is wider and more heterogeneous, presenting huge amount of mesopores of about 35-45 nm. Additionally, mesopores at 3 - 5 nm and micropores at 2 nm, are present. This porosity is due to the splitting of the nanosheets layers during the thermal condensation and exfoliation process of carbon nitride. Particularly, small mesopores may be originated by the nanosheets splitting, while larger mesopores can be prevalently formed by the packing process of g-C_3N_4 layers [39][40]. The characteristic PSS of CN-U-650 is the result of the thermal exfoliation occurring at high temperature and the consequent structure degradation, which originates a higher number of pores. The generation of higher porous structure allows a significant enhancement of specific surface area, which increases as the process temperature rises. The specific surface areas of CN-U-450 is about 42 m^2 g^{-1}, similar to the one at 550 °C (48 m^2 g^{-1}). In contrast, the specific surface area is twice for CN-U-650, which is about 84 m^2 g^{-1}. In general, the BET surface area of g-C_3N_4 increases with the polycondensation temperature, because the temperature increment promotes the separation of layers in g-C_3N_4. Over 600 °C, the decomposition of carbon nitride layer networks occurs, which creates additional pores in the structure and a characteristic “sponge-like” morphology.

Please insert here Figure 5

The surface chemical composition of the synthetized samples was also evaluated by XPS analysis (Figure 6). The survey spectra for all g-C_3N_4 samples revealed three main peaks, at 288, 400, and 532 eV belonging to carbon, nitrogen and oxygen, respectively (Figure S8). The presence of oxygen is more pronounced in CN-U-550 and CN-U-650 samples due to some adsorbed moisture and/or air.

For all samples, the C1s spectra (Figure 6a, b, c) were deconvoluted in four main peaks, as previously reported. In particular, the peak at 284.8 eV arises from the adventitious carbon of the carbon tape (Csp2, Csp3) [41], while the weak peak at 286.2 eV is due to nitrogen-related defects of g-C_3N_4 (N–CH=N or C–O bonding). The intense peak around 288.1 eV was identified as the typical sp^2-hybridized carbon (N–C=N) in the aromatic s-heptazine ring and the other peaks at 289 - 290.1 eV are assigned to C=O or O=C–O species. The high-resolution N1s spectra (Figure 6d, e, f) were deconvoluted into three peaks, centred at 398.5, 399.6, and 401.1 eV, respectively. The peak at 398.5 eV corresponds to sp^2-hybridized nitrogen in triazine rings (C–N=C), while the peak at 399.6 eV is due to tertiary nitrogen N–$(C)_3$ groups. The weaker peak at 401.1 eV can be attributed to quaternary N (H-N–$(C)_2$) [39][42].

Please insert here Figure 6

The ratio between C=N–C and N–$(C)_3$ was calculated in order to evaluate the influence of synthesis temperature on the surface chemical composition, and reported in Table 2. The CN-U-550 sample presents higher percentage of secondary nitrogen species (C=N–C ~ 47-56 %) and lower percentage of tertiary nitrogen species (N–$(C)_3$ ~ 25 – 38 %), while CN-U-450 shows similar percentage of both species. CN-U-650 shows higher amounts of N–$(C)_3$ compared to C=N–C and H–N–$(C)_2$ species (about 30 %). A ratio of 0.99, 1.3, and 0.6 for CN-U-450, 550, and 650, respectively, was measured.

A low value of the C=N–C/N–(C)$_3$ ratio indicates the presence of nitrogen vacancy in the triazine rings site. The relative intensity of the two main peaks reveals that more tertiary nitrogen (N–(C)$_3$), instead of pyridinic nitrogen (C=N–C), is formed as the synthesis temperature increases [39][41]. Therefore, XPS analysis indicates that, by increasing the temperature up to 650 °C, a chemical transition from pyridinic nitrogen to tertiary nitrogen occurs with consequent degradation of g-C_3N_4 sheets.

Please insert here Table 2

Since substantial differences were noticed between CN-U-450 and CN-U-650, we expect differences in LiPS trapping capabilities.

To evaluate the LiPSs adsorption capability 20 µL of 1.0 mM of Li_2S_6 solution diluted in 2 mL of DME:DIOX 1:1 v/v mixture were directly added to a quantity equivalent to 0.5 m^2 surface area of CN 450, 550, and 650 (Figure 7a). After resting the samples for 12 hours, both solutions with CN-U-550 and CN-U-650 showed colour fading, although the latter is of lower intensity. CN-U-450 still showed a yellowish coloration, demonstrating lower interaction with Li_2S_6.

The UV-Vis absorption test of carbon nitride obtained from urea at 550 °C is reported in Figure S9. It is well recognized that LiPSs “Li_2S_x” ($2 < x < 16$) present three main absorption regions at 400 nm, 300 nm, and 200 nm [43][44][45]. In particular, Li_2S_4, Li_2S_6 and Li_2S_8 species produce characteristic peaks in the region above 300 nm, respectively at 400, 430, and around 500 nm [46], while elemental sulphur exhibits strong absorption below 300 nm [46]. More in general, the large absorption band between 300 and 400 nm can be assigned to a mixture of Li_2S_x ($1 < x < 8$) species and/or radicals [45]. Observing the UV-Vis spectra, the absorbance of the solution containing CN-U-550 is much lower than pure polysulfides solution, which is consistent with the colour fading observed in the solution after 12 h. The remarkable absorption intensity decrease, in the range between 350 – 500 nm, suggests the effective LiPSs entrapment capability of carbon nitride.

To further verify the nature of the chemical interaction between g-C_3N_4 and LiPSs, XPS analysis was performed on the carbon nitride powder after the LiPSs adsorption test Figure S10. Concerning high resolution XPS spectra of nitrogen (N1s), the peak attributable to pyridinic bond (C=N−C) shifted slightly from 398.5 to 398.9 eV, indicating the existence of a chemical interaction between g-C_3N_4 and polysulfides species [47]. This was confirmed also by the amount reduction of this functional group passing from 47.9 to 25 %. At the same time the peaks of high-resolution spectra of C1s are shifted at lower binding energy, this can be due to the strong chemical interaction between g-C_3N_4 and LiPSs [48][49]. In addition, a peak centred at 285.4 eV was detected, which can be assigned to C−S bond [48]. In the high resolution XPS spectra of sulphur, the peak centred at 162.8 is associable to Li−S bonds of LiPSs or, according to Fan *et. al*, it may also be ascribed to C−S binding between g-C_3N_4 and LiPSs [47]. The peak centred at 169.1 V could be attributed to SO_x species derived from sulphur oxidation in air [48]. It is important to note that, in the range of 166 - 170 eV, are generally detectable the peaks corresponding to the formation of thiosulfate and/or polythionate, which are considered effective polysulfide mediators to limit the diffusion of polysulfides [25][50]. Lastly, the symmetric peak at 55.45 eV in all Li1s spectra is attributed to Li–S bond. Therefore, XPS analysis demonstrates that g-C_3N_4 obtained from urea at 550 °C can effectively adsorb LiPSs, thus enhancing the cycling stability of the batteries.

In Figure 7b the specific charge and discharge capacities were compared for each sample, for the first 10 cycles. The cells were cycled at C/10 for the initial 3 cycles and then cycled at C/5. All the double-layer (STD + CN-U-x) cathodes displayed higher specific capacities than the STD electrode.

The initial specific capacity of the STD cathode was 800 mAh g^{-1} at C/10, which is significantly lower if compared to STD + CN-U-x cathodes, which is more than 1000 mAh g^{-1} for all samples. On the contrary, increasing the current at C/5, the specific capacity of STD + CN-U-650 rapidly decreases to lower values than the STD. At the same time, as shown in Figure 7c, the specific capacity of STD + CN-U-450 decreases after 30 cycles, reaching a value comparable to the STD.

Figure 7d depicts and compares the charge/discharge curves at the first cycle (at C/10). The characteristic plateaus are well discernible, and the polarization is similar for all the samples. All STD + CN-U-x electrodes show slightly higher polarization than STD. This behaviour is due to the intrinsic nature of carbon nitride double-layer, as previously explained.

After 200 cycles (Figure 7c), the STD + CN-U-550 cathode delivered 750 mAh g^{-1}, which is significantly higher than that of STD (345 mAh g^{-1}). Both STD+CN-U-450 and STD+CN-U-650 showed very low specific capacities after long-cycling test. In particular, STD+CN-U-450 cell failed after 195 cycles, while STD+CN-U-650 cell delivered a specific capacity of 250 - 300 mAh g^{-1} after 200 cycles at C/5.

To understand the real behaviour of the double-layer in STD+CN-U-x electrodes and discern the contribution of the different g-C_3N_4 structures, the specific capacity at 5th and 200th cycles are reported in Table S4, with the corresponding capacity loss (% per cycle) at C/5. The capacity loss between the 5th and the 200th cycle is 0.23 % per cycle for STD cathode. A similar capacity loss is observed for STD + CN-U-450, while for STD + CN-U-550 it is about a third of that of the STD. The low capacity loss observed for both STD+CN-U-450 and STD+CN-U-550 reflects their good capacity retention. The capacity trend of STD + CN-U-650 is highly instable, which means that the capacity decrease is not constant during cycling, making it more difficult to determine the capacity retention.

Figure S11 compares the Coulombic efficiencies (CE) of the cathodes. The CEs of STD and STD + CN-U-550 are close to 100 %, reflecting good charge and discharge efficiency in each cycle. The unsteady CE values for STD + CN-U-650 can be assigned either to parasitic reactions or to the occurrence of shuttle mechanism responsible for longer charge.

All cells were cycled for more than 500 cycles at C/5, in order to evaluate both the long cycling stability and the capacity retention (Figure 7e). The final capacity of STD + CN-U-550 was 570 mAh g^{-1}, meaning 55 % of the initial capacity at C/5 and corresponding to 0.9 mAh g^{-1} loss per cycle.

Please insert here Figure 7

EIS measurements were performed at OCV, after three formation cycles at C/10 for both STD and STD+CN-U-550.

The EIS spectra consist of a depressed semicircle at high to medium frequency regions and a bended line in the low-frequency region (Figure 8). In general, the depressed semicircles result from the superposition of many semicircles, corresponding to several parallel contributions [51]. Typically, the Nyquist plot of a Li-S cell can be described by an equivalent electrical circuit consisting of an initial ohmic resistance (R_{el}) in series with one or more R//CPE elements (connected in parallel). R_{el} is the bulk electrolyte resistance, which can be strongly influenced by polysulfides dissolution. CPEs and R_s can be attributed to the surface double layer capacity and surface resistance of lithium and sulphur electrodes, respectively. While CPE_{ct} and R_{ct} are assigned to the pore double layer capacity and the charge transfer resistance, respectively. W is the Warburg impedance due to the diffusion of the polysulfides within the cathode [52].

The initial R_{el} and R_{ct} values are comparable in both electrodes, confirming a good filling and diffusion in the double-layer by the electrolyte. Therefore, despite of the second layer, g-C_3N_4 with high surface area guarantees fast electrolyte permeation. A lower value of Rs was calculated for the double-layer electrode, meaning a lower surface resistance for this electrode. The higher Rs observed for the single-layer standard cathode, after only three cycles, can be attributable to a more pronounced passivation layer formed on both the anode and cathode surfaces, and to a higher amount of Li_2S.

Please insert here Figure 8

These results confirm that the differences in terms of specific surface area, pore distribution and general morphology can inevitably contribute to the final electrochemical performances. However, the different surface chemistry, in particular the amount of nitrogen species, is reasonably the major factor affecting the electrochemical behaviour. The huge amount of tertiary nitrogen in CN-U-650 and the concomitant low amount of pyridinic nitrogen is probably one of the most relevant cause of the low electrochemical performance.

4. CONCLUSIONS

To limit the shuttle effect, a double-layer approach based on carbon nitride-was investigated in this work. The adoption of the double-layer approach allows carbon nitride to directly interact with lithium polysulfides while the interaction between sulphur and conductive mesoporous carbon black is guaranteed. The double-layer electrodes showed good cycle performances, suggesting enhanced interaction between the polysulfides and carbon nitride. In particular, the electrode containing carbon nitride synthetized from urea showed the best performances in terms of specific capacity, capacity retention and coulombic efficiency. This suggested that urea improves the chemical and morphological features of g-C_3N_4 towards LiPSs trapping compared to dicyandiamide and melamine.

We also discussed how the different temperatures of polycondensation of urea affect the specific surface area and the surface functionalities of the final g-C_3N_4. In particular, the greater amount of pyridinic nitrogen is a basic parameter for achieving excellent electrochemical performances since it is recognised as active site for the interaction with polysulfides. Carbon nitride obtained at 550 °C showed the best electrochemical results, increasing the cell specific capacity by 25% and improving its useful life over 500 cycles.

In summary, a layer of carbon nitride, directly coated on the cathode surface is a successful strategy to increase the electrochemical performances of sulphur-based electrodes. Moreover, the shuttle effect can be effectively restricted inserting carbon nitride with optimized morphological properties and surface functionalities. Finally, the double-layer strategy resulted a versatile technique for future optimizations and industrial scale-up of S-based cathodes.

Acknowledgments

The authors wish to thank Mauro Raimondo and Marta Gallo from Politecnico di Torino for FE-SEM and N_2 adsorption/desorption analyses, and Antonela Cánneva and Andrés Donadelli from YPF Tecnología S.A. Buenos Aires, for XPS analyses.

Authors kindly acknowledge Polar project (progetto per l’internazionalizzazione della ricerca tra Politecnico di Torino e Argentina, prof Silvia Bodoardo) for funding.

The processed data required to reproduce these findings will be provided upon request to the corresponding authors.

Table 1. Relative percentage of C and N species area of CN-D, CN-M and CN-N calculated by high resolution XPS spectra deconvolution.

		CN-D		***CN-M***		***CN-U***	
BINDING ENERGY (EV)	**Specie**	**Area %**	**Area relative%**	**Area %**	**Area relative%**	**Area %**	**Area relative%**
398.5	C=N–C	38.25	10.74	37.37	10.82	60.14	22.36
399.6	N– (C)$_3$	40.04	11.24	47.74	13.82	29.75	11.06
401.1	H–N(C)$_2$	21.71	6.10	12.65	3.66	7.47	2.78
403.0	N–O	-	-	-	-	-	-
284.8	Csp^2 Csp^3 Cadv	49.32	35.47	50.31	35.75	37.79	23.74
286.3	C–O	12.32	8.87	9.56	6.79	13.71	8.61
288.1	N–C=N	10.35	7.44	14.06	9.99	39.54	24.84
288.9	C=O	22.37	16.09	26.07	18.53	8.96	5.63
290.1	CO$_3^{-2}$	5.62	4.04	-	-	60.14	22.36
	%N	32.48		35.25		37.18	
	%C*	67.52		64.75		62.82	
	N/C	**0.48**		**0.54**		**0.59**	

Table 2. Relative percentage of C and N species area of CN-U obtained at different temperatures, calculated by high resolution XPS spectra deconvolution.

		CN-U-450		***CN-U-550***		***CN-U-650***	
BINDING ENERGY (EV)	**Specie**	**Area %**	**Area rel %**	**Area %**	**Area rel %**	**Area %**	**Area rel %**
398.5	C=N-C	16.07	41.81	16.32	47.91	8.03	27.25
399.6	N-(C)3	16.26	42.31	12.86	37.77	12.56	42.66
401.1	H-N(C)2	5.44	14.17	3.96	11.64	8.54	29.01
403.0	N-O	16.07	41.81	1,32	47.91	8.03	27.25

Captions to Figures

Fig. 1. FESEM micrographs of STD+CN-D (a, d), STD+CN-M (b, e) and STD+CN-U (c, f) at 25 and 50 KX respectively.

Fig. 2. Synthesis scheme (a), XRD patterns (b), FT-IR/ATR spectra (c) N_2 adsorption-desorption isotherms (d) and pore-size distribution with specific surface area (inset) (e) comparison for the g-C_3N_4 samples prepared starting from different precursors.

Fig. 3. XPS high resolution C1s of CN-D (a), CN-M (b) and CN-U (c) and high resolution N1s of CN-D (d), CN-M (e) and CN-U (f).

Fig. 4. Lithium polysulfides adsorption test (a, b), cyclic voltammetry comparison at 0.1 mVs-1 (c), galvanostatic charge/discharge cycling comparison (d), first cycle galvanostatic charge/discharge

profiles comparison at C/10 (e) between single-layer cathode and double-layer cathodes and self-discharge comparison of single-layer standard electrode and CN-U based double-layer electrode (f).

Fig. 5. FESEM micrographs at 50 KX (a), XRD patterns (b), FT-IR/ATR spectra (c) N2 adsorption-desorption isotherms (d) and pore-size distribution (e), comparison of carbon nitride powder obtained at different temperatures.

Fig. 6. XPS high resolution C1s of CN-U-450 (a), CN-U-550 (b) and CN-U-650 (c) and high resolution N1s of CN-U-450 (d), CN-U-550 (e) and CN-U-650 (f).

Fig. 7. Lithium polysulfides adsorption test (a), galvanostatic charge/discharge cycling for the first 10 cycles (b) and for 200 cycles (c), first cycle galvanostatic charge/discharge profiles at C/10 (d), comparison for double-layer cathodes with g-C3N4 obtained at different temperatures. Galvanostatic charge/discharge long cycling for double-layer containing CN-U-550 (e).

Fig. 8. Nyquist plot comparison of single-layer and double-layer cathode and adopted equivalent circuits.

References:

[1] A.A. Review, A. Fotouhi, Lithium-Sulfur Battery Technology Readiness, (2017). https://doi.org/10.3390/en10121937.

[2] G. Ganas, G. Kastrinaki, D. Zarvalis, G. Karagiannakis, A.G. Konstandopoulos, D. Versaci, S. Bodoardo, Synthesis and characterization of LNMO cathode materials for lithium-ion batteries, Mater. Today Proc. 5 (2018) 27416–27424. https://doi.org/10.1016/j.matpr.2018.09.059.

[3] A. Rosenman, E. Markevich, G. Salitra, D. Aurbach, A. Garsuch, F.F. Chesneau, Review on Li-Sulfur Battery Systems: An Integral Perspective, Adv. Energy Mater. 5 (2015) 1–21. https://doi.org/10.1002/aenm.201500212.

[4] G. Li, S. Wang, Y. Zhang, M. Li, Z. Chen, J. Lu, Revisiting the Role of Polysulfides in Lithium–Sulfur Batteries, Adv. Mater. 30 (2018) 1–19. https://doi.org/10.1002/adma.201705590.

[5] L. Borchardt, M. Oschatz, S. Kaskel, Carbon Materials for Lithium Sulfur Batteries - Ten Critical Questions, Chem. - A Eur. J. 22 (2016) 7324–7351. https://doi.org/10.1002/chem.201600040.

[6] S. Evers, L.F. Nazar, New approaches for high energy density lithium-sulfur battery cathodes, Acc. Chem. Res. 46 (2013) 1135–1143. https://doi.org/10.1021/ar3001348.

[7] R. Xu, J. Lu, K. Amine, Progress in Mechanistic Understanding and Characterization Techniques of Li-S Batteries, Adv. Energy Mater. 5 (2015) 1–22. https://doi.org/10.1002/aenm.201500408.

[8] T. Li, X. Bai, U. Gulzar, Y.J. Bai, C. Capiglia, W. Deng, X. Zhou, Z. Liu, Z. Feng, R. Proietti Zaccaria, A Comprehensive Understanding of Lithium–Sulfur Battery Technology, Adv. Funct. Mater. 29 (2019) 1–56. https://doi.org/10.1002/adfm.201901730.

[9] S.Y. Li, W.P. Wang, H. Duan, Y.G. Guo, Recent progress on confinement of polysulfides through physical and chemical methods, J. Energy Chem. 27 (2018) 1555–1565. https://doi.org/10.1016/j.jechem.2018.04.014.

[10] J. Zheng, J. Tian, D. Wu, M. Gu, W. Xu, C. Wang, F. Gao, M.H. Engelhard, J.-G. Zhang, J. Liu, J. Xiao, Lewis Acid–Base Interactions between Polysulfides and Metal Organic Framework in Lithium Sulfur Batteries, Nano Lett. 14 (2014) 2345–2352. https://doi.org/10.1021/nl404721h.

[11] X. Hong, R. Wang, Y. Liu, J. Fu, J. Liang, S. Dou, Recent advances in chemical adsorption and catalytic conversion materials for Li–S batteries, J. Energy Chem. 42 (2020) 144–168. https://doi.org/10.1016/j.jechem.2019.07.001.

[12] J.J. Velasco, P. Vélez, M.E. Zoloff Michoff, A. Visintín, D. Versaci, S. Bodoardo, G.L. Luque, E.P.M. Leiva, Role of the solvent in the activation of Li 2 S as cathode material: a DFT study, J. Phys. Condens. Matter. 33 (2021) 344003. https://doi.org/10.1088/1361-648X/ac08b9.

[13] P. Vélez, M. del C. Rojas, J. Velasco, M.L. Para, D. Barraco, E.P.M. Leiva, G.L. Luque, On the role of oxidized graphene interfaces in lithium sulfur batteries: Thermodynamic and kinetic aspects using density functional theory, Appl. Surf. Sci. 550 (2021) 149358. https://doi.org/10.1016/j.apsusc.2021.149358.

[14] J. Liang, L. Yin, X. Tang, H. Yang, W. Yan, L. Song, H.M. Cheng, F. Li, Kinetically Enhanced Electrochemical Redox of Polysulfides on Polymeric Carbon Nitrides for Improved Lithium-Sulfur Batteries, ACS Appl. Mater. Interfaces. 8 (2016) 25193–25201. https://doi.org/10.1021/acsami.6b05647.

[15] Q. Pang, L.F. Nazar, Long-Life and High-Areal-Capacity Li–S Batteries Enabled by a Light-Weight Polar Host with Intrinsic Polysulfide Adsorption, ACS Nano. 10 (2016) 4111–4118. https://doi.org/10.1021/acsnano.5b07347.

[16] Y. Zheng, H. Li, H. Yuan, H. Fan, W. Li, J. Zhang, Understanding the anchoring effect of Graphene, BN, C 2 N and C 3 N 4 monolayers for lithium−polysulfides in Li−S batteries, Appl. Surf. Sci. 434 (2018) 596–603. https://doi.org/10.1016/j.apsusc.2017.10.230.

[17] C.-Y. Fan, H.-Y. Yuan, H.-H. Li, H.-F. Wang, W.-L. Li, H.-Z. Sun, X.-L. Wu, J.-P. Zhang, The Effective Design of a Polysulfide-Trapped Separator at the Molecular Level for High Energy Density Li–S Batteries, ACS Appl. Mater. Interfaces. 8 (2016) 16108–16115. https://doi.org/10.1021/acsami.6b04578.

[18] K. Liao, P. Mao, N. Li, M. Han, J. Yi, P. He, Y. Sun, H. Zhou, Stabilization of polysulfides

via lithium bonds for Li-S batteries, J. Mater. Chem. A. 4 (2016) 5406–5409. https://doi.org/10.1039/c6ta00054a.

[19] J. Wutthiprom, N. Phattharasupakun, J. Khuntilo, T. Maihom, J. Limtrakul, M. Sawangphruk, Collaborative design of Li-S batteries using 3D N-doped graphene aerogel as a sulfur host and graphitic carbon nitride paper as an interlayer, Sustain. Energy Fuels. 1 (2017) 1759–1765. https://doi.org/10.1039/C7SE00291B.

[20] Z. Xiao, Z. Yang, L. Wang, H. Nie, M. Zhong, Q. Lai, X. Xu, L. Zhang, S. Huang, A lightweight TiO2/Graphene interlayer, applied as a highly effective polysulfide absorbent for fast, long-life lithium-sulfur batteries, Adv. Mater. 27 (2015) 2891–2898. https://doi.org/10.1002/adma.201405637.

[21] J. Fang, F. Qin, J. Li, K. Zhang, W. Liu, M. Wang, F. Yu, L. Zhang, Improved performance of sulfur cathode by an easy and scale-up coating strategy, J. Power Sources. 297 (2015) 265–270. https://doi.org/10.1016/j.jpowsour.2015.06.153.

[22] W. Sun, X. Ou, X. Yue, Y. Yang, Z. Wang, D. Rooney, K. Sun, A simply effective double-coating cathode with MnO2 nanosheets/graphene as functionalized interlayer for high performance lithium-sulfur batteries, Electrochim. Acta. 207 (2016) 198–206. https://doi.org/10.1016/j.electacta.2016.04.135.

[23] L. Qu, P. Liu, Y. Yi, T. Wang, P. Yang, X. Tian, M. Li, B. Yang, S. Dai, Enhanced Cycling Performance for Lithium–Sulfur Batteries by a Laminated 2D g-C 3 N 4 /Graphene Cathode Interlayer, ChemSusChem. 12 (2019) 213–223. https://doi.org/10.1002/cssc.201802449.

[24] W. Zhang, Q. Zhang, F. Dong, Z. Zhao, The multiple effects of precursors on the properties of polymeric carbon nitride, Int. J. Photoenergy. 2013 (2013). https://doi.org/10.1155/2013/685038.

[25] D.S. Wu, F. Shi, G. Zhou, C. Zu, C. Liu, K. Liu, Y. Liu, J. Wang, Y. Peng, Y. Cui, Quantitative investigation of polysulfide adsorption capability of candidate materials for Li-S batteries, Energy Storage Mater. 13 (2018) 241–246. https://doi.org/10.1016/j.ensm.2018.01.020.

[26] H.Y. Xu, L.C. Wu, H. Zhao, L.G. Jin, S.Y. Qi, Synergic Effect between Adsorption and Photocatalysis of Metal-Free g-C3N4 Derived from Different Precursors, PLoS One. 10 (2015) 1–20. https://doi.org/10.1371/journal.pone.0142616.

[27] M. Ismael, Y. Wu, D.H. Taffa, P. Bottke, M. Wark, Graphitic carbon nitride synthesized by simple pyrolysis: Role of precursor in photocatalytic hydrogen production, New J. Chem. 43 (2019) 6909–6920. https://doi.org/10.1039/c9nj00859d.

[28] T.S. Miller, A.B. Jorge, T.M. Suter, A. Sella, F. Corà, P.F. McMillan, Carbon nitrides: Synthesis and characterization of a new class of functional materials, Phys. Chem. Chem. Phys. 19 (2017) 15613–15638. https://doi.org/10.1039/c7cp02711g.

[29] A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J.O. Müller, R. Schlögl, J.M. Carlsson, Graphitic carbon nitride materials: Variation of structure and morphology and their use as metal-free catalysts, J. Mater. Chem. 18 (2008) 4893–4908. https://doi.org/10.1039/b800274f.

[30] H. Dong, X. Guo, C. Yang, Z. Ouyang, Synthesis of g-C3N4 by different precursors under burning explosion effect and its photocatalytic degradation for tylosin, Appl. Catal. B Environ. 230 (2018) 65–76. https://doi.org/10.1016/j.apcatb.2018.02.044.

[31] M. Thommes, K. Kaneko, A. V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K.S.W. Sing, Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), Pure Appl. Chem. 87 (2015) 1051–1069. https://doi.org/10.1515/pac-2014-1117.

[32] J. Xu, D. Su, W. Zhang, W. Bao, G. Wang, A nitrogen–sulfur co-doped porous graphene matrix as a sulfur immobilizer for high performance lithium–sulfur batteries, J. Mater. Chem. A. 4 (2016) 17381–17393. https://doi.org/10.1039/C6TA05878G.

[33] J. Ma, M. Yu, H. Ye, H. Song, D. Wang, Y. Zhao, W. Gong, H. Qiu, A 2D/2D graphitic carbon nitride/N-doped graphene hybrid as an effective polysulfide mediator in lithium-sulfur batteries, Mater. Chem. Front. 3 (2019) 1807–1815. https://doi.org/10.1039/c9qm00228f.

[34] X. Huang, Z. Wang, R. Knibbe, B. Luo, S.A. Ahad, D. Sun, L. Wang, Cyclic Voltammetry in Lithium–Sulfur Batteries—Challenges and Opportunities, Energy Technol. 7 (2019) 1–13. https://doi.org/10.1002/ente.201801001.

[35] S. Yao, S. Xue, S. Peng, M. Jing, X. Qian, X. Shen, T. Li, Synthesis of graphitic carbon nitride at different thermal-pyrolysis temperature of urea and it application in lithium – sulfur batteries, J. Mater. Sci. Mater. Electron. 0 (2018) 0. https://doi.org/10.1007/s10854-018-9906-2.

[36] E.T. Kim, J. Park, C. Kim, A.G. Simmonds, Y.E. Sung, J. Pyun, K. Char, Conformal Polymeric Multilayer Coatings on Sulfur Cathodes via the Layer-by-Layer Deposition for High Capacity Retention in Li-S Batteries, ACS Macro Lett. 5 (2016) 471–475. https://doi.org/10.1021/acsmacrolett.6b00144.

[37] L.T. Mai Oanh, L.T. Hang, N.D. Lai, N.T. Phuong, D.V. Thang, N.M. Hung, D. Danh Bich, N. Van Minh, Influence of annealing temperature on physical properties and photocatalytic ability of g-C 3 N 4 nanosheets synthesized through urea polymerization in Ar atmosphere, Phys. B Condens. Matter. 532 (2018) 48–53. https://doi.org/10.1016/j.physb.2017.05.026.

[38] X. Fan, Z. Xing, Z. Shu, L. Zhang, L. Wang, J. Shi, Improved photocatalytic activity of g-C3N4 derived from cyanamide-urea solution, RSC Adv. 5 (2015) 8323–8328. https://doi.org/10.1039/c4ra16362a.

[39] I. Papailias, T. Giannakopoulou, N. Todorova, D. Demotikali, T. Vaimakis, C. Trapalis, Effect of processing temperature on structure and photocatalytic properties of g-C 3 N 4, Appl. Surf. Sci. 358 (2015) 278–286. https://doi.org/10.1016/j.apsusc.2015.08.097.

[40] F. Dong, Y. Li, Z. Wang, W.K. Ho, Enhanced visible light photocatalytic activity and oxidation ability of porous graphene-like g-C 3 N 4 nanosheets via thermal exfoliation, in: Appl. Surf. Sci., Elsevier B.V., 2015: pp. 393–403. https://doi.org/10.1016/j.apsusc.2015.04.034.

[41] B. Choudhury, K.K. Paul, D. Sanyal, A. Hazarika, P.K. Giri, Evolution of Nitrogen-Related Defects in Graphitic Carbon Nitride Nanosheets Probed by Positron Annihilation and Photoluminescence Spectroscopy, J. Phys. Chem. C. 122 (2018) 9209–9219. https://doi.org/10.1021/acs.jpcc.8b01388.

[42] J. Liu, T. Zhang, Z. Wang, G. Dawson, W. Chen, Simple pyrolysis of urea into graphitic carbon nitride with recyclable adsorption and photocatalytic activity, J. Mater. Chem. 21 (2011) 14398–14401. https://doi.org/10.1039/c1jm12620b.

[43] A. Gupta, A. Bhargav, A. Manthiram, Highly Solvating Electrolytes for Lithium–Sulfur Batteries, Adv. Energy Mater. 9 (2019) 1803096. https://doi.org/10.1002/aenm.201803096.

[44] Q. He, A.T.S. Freiberg, M.U.M. Patel, S. Qian, H.A. Gasteiger, Operando Identification of Liquid Intermediates in Lithium–Sulfur Batteries via Transmission UV–vis Spectroscopy, J. Electrochem. Soc. 167 (2020) 080508. https://doi.org/10.1149/1945-7111/ab8645.

[45] A. Kawase, S. Shirai, Y. Yamoto, R. Arakawa, T. Takata, Electrochemical reactions of lithium–sulfur batteries: an analytical study using the organic conversion technique, Phys. Chem. Chem. Phys. 16 (2014) 9344–9350. https://doi.org/10.1039/C4CP00958D.

[46] J. Zheng, X. Fan, G. Ji, H. Wang, S. Hou, K.C. DeMella, S.R. Raghavan, J. Wang, K. Xu, C. Wang, Manipulating electrolyte and solid electrolyte interphase to enable safe and efficient Li-S batteries, Nano Energy. 50 (2018) 431–440. https://doi.org/10.1016/j.nanoen.2018.05.065.

[47] C.Y. Fan, H.Y. Yuan, H.H. Li, H.F. Wang, W.L. Li, H.Z. Sun, X.L. Wu, J.P. Zhang, The Effective Design of a Polysulfide-Trapped Separator at the Molecular Level for High Energy Density Li-S Batteries, ACS Appl. Mater. Interfaces. 8 (2016) 16108–16115. https://doi.org/10.1021/acsami.6b04578.

[48] X. Guo, X. Liu, H. Yu, Y. Lu, Q. Liu, Z. Li, Designable Hierarchical Cathode for a High-Efficiency Polysulfide Trapper Toward High-Performance Lithium–Sulfur Batteries, J. Electron. Mater. 48 (2019) 551–559. https://doi.org/10.1007/s11664-018-6754-z.

[49] Q. Pang, D. Kundu, M. Cuisinier, L.F. Nazar, Surface-enhanced redox chemistry of polysulphides on a metallic and polar host for lithium-sulphur batteries, Nat. Commun. 5 (2014) 4759. https://doi.org/10.1038/ncomms5759.

[50] H. Qu, J. Zhang, A. Du, B. Chen, J. Chai, N. Xue, L. Wang, L. Qiao, C. Wang, X. Zang, J. Yang, X. Wang, G. Cui, Multifunctional Sandwich-Structured Electrolyte for High-Performance Lithium–Sulfur Batteries, Adv. Sci. 5 (2018) 1700503. https://doi.org/10.1002/advs.201700503.

[51] N.A. Cañas, K. Hirose, B. Pascucci, N. Wagner, K.A. Friedrich, R. Hiesgen, Investigations of lithium-sulfur batteries using electrochemical impedance spectroscopy, Electrochim. Acta. 97 (2013) 42–51. https://doi.org/10.1016/j.electacta.2013.02.101.

[52] M. Hagen, G. Feisthammel, P. Fanz, H.T. Grossmann, S. Dörfler, J. Tübke, M.J. Hoffmann, D. Börner, M. Joos, H. Althues, S. Kaskel, Sulfur Cathodes with Carbon Current Collector for Li-S cells, J. Electrochem. Soc. 160 (2013) A996–A1002. https://doi.org/10.1149/2.149306jes.