The World Conference on Carbon: Common fundamentals, remarkably versatile applications

CARBON 2016 July 10–15

The Penn Stater Conference Center Hotel, State College, Pennsylvania, USA

Program at a Glance

Sunday workshop/tutorial:
Confirmed plenary speakers: M. Dresselhaus, P. Ajayan, M. Endo, R. Ruoff, H. Terrones, T. Kyotani

Monday evening student mixer (pizza party)

Conference plenary lectures: A. Ferrari (**Monday**), J. Dahn (**Tuesday**), K. Novoselov (**Wednesday**), M. Strano (**Thursday**), D. Zhao (**Friday**)

Medalists Roundtable:

Donald Bethune, Robert Curl, Mildred Dresselhaus, Morinobu Endo, Konstantin Novoselov
(moderated by P. Thrower, Editor-Emeritus of *CARBON*, and R. Hurt, Editor-in-Chief of *CARBON*)

Legend for Codes Below

Legend			
S1: Carbons for Health and Medicine	S2: Carbon Blacks and Flame-Formed Carbons	S3: Catalysts and Electrocatalysts	S4: Cokes and Graphite
S5: Electrochemical Carbons	S6: Fibers and Composites	S7: Fullerenes, Nanotubes, and Other Curved Nanostructures	S8: Graphene
S9: Modeling and Simulation	S10: Porous Carbons		

Schedule for 2016 Carbon Conference

TIMES	MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY
08:30–09:40	Opening Plenary *Ferrari*	Oral Presentations 5 S4, S5, S6, S8, S10	Oral Presentations 9 S5, S6, S7, S8, S10	Oral Presentations 13 S3, S5, S8, S9, S10	Closing Plenary *Zhao*
09:40–10:00	Snacks	Snacks	Snacks	Snacks	Snacks

10:05–11:15	**Oral Presentations 1** **S1, S2, S4, S5, S6**	**Plenary** ***Dahn***	**Plenary** ***Novoselov***	**Plenary** ***Strano***	**Oral Presentations 17** **S3, S5, S7, S10**
11:20–12:40	**Oral Presentations 2** **S1, S2, S4, S5, S6**	**Oral Presentations 6** **S5, S6, S8, S9, S10**	**Oral Presentations 10** **S3, S5, S7, S8, S10**	**Oral Presentations 14** **S3, S5, S8, S9, S10**	**Oral Presentations 18** **S3, S5, S7, S9, S10**
12:45–14:00	**Lunch**	**Lunch**	**Lunch**	**Lunch** **(American Carbon Society Business Meeting)**	**Lunch**
14:05–15:35	**Oral Presentations 3** **S1, S2, S4, S5, S6**	**Oral Presentations 7** **S3, S5, S6, S8, S10**	**Oral Presentations 11** **S3, S5, S7, S8, S10**	**Oral Presentations 15** **S3, S5, S7, S8, S10**	**N/A**
15:40–16:40	**Oral Presentations 4** **S1, S4, S5, S6, S10**	**Oral Presentations 8** **S3, S5, S6, S8, S10**	**Oral Presentations 12** **S3, S5, S7, S8, S10**	**Oral Presentations 16** **S3, S5, S7, S8, S10**	**N/A**
16:40–18:40	**Poster Presentations 1 and Snacks**	**Poster Presentations 2** **and Appetizers**	**Medalists Roundtable**	**Poster Presentations 4** **and Appetizers**	**N/A**
19:00–21:00	**Student Mixer**	**Picnic**	**Poster Presentations 3** **and Snacks**	**Banquet (19:00–22:00)**	**N/A**

O8-3
(tbd)

S3: Electrocatalysis - 1
(L Dai, presiding)

O10-1
DESIGN PRINCIPLES OF HETEROATOM-DOPED NANOCARBON ELECTROCATALYSTS FOR FUEL CELLS AND METAL-AIR BATTERIES
Zhenghang Zhao[1], Mingtao Li[2], Lipeng Zhang[1], Liming Dai[3], Zhenhai Xia[1]
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O10-2
ABOUT THE EFFECT OF MICROPOROSITY IN THE OXYGEN REDUCTION REACTION
Ramiro Ruiz-Rosas[1], Carolina González-Gaitán[2], María José Valero-Romero[3], José Rodríguez-Mirasol[3], Tomás Cordero[3], Emilia Morallón[2], and Diego Cazorla-Amorós[1]
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O10-3
INSIGHTS INTO THE METAL-SUPPORT INTERACTION OF PT SUPPORTED ON N-DOPED CARBON NANOTUBES: EFFECT OF ELECTRON TRANSFER ON CATALYSIS
Xiaomei Ning, Yuhang Li, Hao Yu, Hongjuan Wang, and Feng Peng
School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510640, China.

O10-4
DESIGNING POROUS STRUCTURES IN CARBON-BASED ELECTROCATALYSTS
Xinliang Feng
Department of Chemistry and Food Chemistry & Center for Advancing Electronics Dresden (cfaed), Technische Universität Dresden, 01062 Dresden, Germany.

S3: Green Catalysis - 1
(M Titirici and R White, presiding)

O11-1 (Keynote)
BOTTOM-UP DESIGN OF METAL-FREE CARBOCATALYSTS FOR THE CONVERSION OF BIOMASS UNDER HYDROTHERMAL CONDITIONS
Jack Carraher and Jean-Philippe Tessonnier*
Department of Chemical and Biological Engineering, Iowa State University and NSF Engineering Research Center for Biorenewable Chemicals (CBiRC), Ames, Iowa, USA.

O11-2

NOVEL DESIGN OF ANCIENT MATERIALS FOR A NEW GENERATION OF CATALYSTS WITH TUNABLE SELECTIVITY

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O11-3

LIGNIN-DERIVED CARBON MATERIALS AS CATALYSTS FOR WET PEROXIDE OXIDATION

Maria Martin-Martinez[1], Maria Filomena F. Barreiro[1], Adrián M.T. Silva[2], José L. Figueiredo[2], Joaquim L. Faria[2] and Helder T. Gomes[1]

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O11-4

NANOPOROUS CARBON AND CARBIDE MATERIALS AS SUPPORTS FOR THE SUSTAINABLE PRODUCTION OF LOWER OLEFINS FROM SYNTHESIS GAS WITH IRON-BASED CATALYSTS

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S3: Electrocatalysis - 2

(X Feng, presiding)

O12-1

LARGE-SIZE GRAPHENE TUBES: OXYGEN ELECTROCATALYSTS FOR ENERGY CONVERSION

Gang Wu

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O12-2

SYNTHESIS OF AMORPHOUS MoSX ANCHORED GRAPHENE FOR HIGHLY STABLE ELECTROCHEMICAL HER CATALYST

Cheol-Ho Lee[1,2], Jin-Mun Yun[3], Sungho Lee[1], Seong-Mu Jo[1], Doh C. Lee[2], Han-Ik Joh[1]

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LIGNIN-DERIVED CARBON MATERIALS AS CATALYSTS FOR WET PEROXIDE OXIDATION

Maria Martin-Martinez[1*], Maria Filomena F. Barreiro[1], Adrián M.T. Silva[2], José L. Figueiredo[2], Joaquim L. Faria[2] and Helder T. Gomes[1]

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INTRODUCTION

Lignin is one of the most abundant organic polymers in the nature, and is obtained in large amounts as a residue in paper and cellulosic bio-ethanol production industries (5-36x10^8 T/year) [1,2]. A major part of this industrial lignin is incinerated for energy production [3]. Nevertheless, the utilization of lignin as a fuel is not economically rational [3], and the development of alternative uses for lignin has been increasing in interest over the recent years. Due to its high carbon content and to a structure similar to that of bituminous carbon [2], it seems to be an adequate precursor for the production of activated carbon materials. Several examples can be found in the scientific literature regarding the preparation of activated carbons from lignin, using different procedures [4-6]. Highly porous materials have been developed, with specific surface areas (SSA) *ca.* 2000 m^2 g^{-1} and adsorbent capacities comparable to those reported for a number of commercial activated carbons [7].

Advanced oxidation processes, primarily based on the action of hydroxyl radicals ($HO^{\bullet}$) to oxidize organic pollutants, are regarded as promising solutions for the treatment of aqueous effluents containing recalcitrant and non-biodegradable compounds [8,9], typically found in wastewaters of several industries (pharmaceutical, petrochemical, dyes, paper…). These type of compounds are particularly difficult to remove by conventional biological processes, mainly when present at high concentrations (1-10 g L^{-1}) [10]. Among advanced oxidation processes, catalytic wet peroxide oxidation (CWPO) uses hydrogen peroxide (H_2O_2) and a suitable catalyst to promote the formation of the $HO^{\bullet}$, for the degradation of the organic species, under relatively mild operation conditions (0.1-0.2 MPa, 20-130 °C).

The classical heterogeneous catalysts employed in CWPO consist of a metallic active phase, mainly Fe-based, supported on a porous material (activated carbons, pillared clays, zeolites…). However, these catalysts usually suffer from severe deactivation during the oxidation due to the leaching of the metallic phase to the reaction solution, obliging to further steps in the global treatment process in order to remove or recover the metals from the treated waters. This has lead to the development of metal-free materials capable to catalyze the decomposition of H_2O_2 into radical species. Thus, since carbonaceous materials has been found as suitable metal-free catalysts

in the CWPO process, their use has been spread with promising results both in the activity shown and the stability evidenced [11].
In this context, in the present work, organic agro-industrial wastes are used as raw materials for the development of carbonaceous materials, evaluating for the first time the use of activated carbons produced from lignin as metal-free catalysts for the CWPO of wastewaters with high pollutant concentration. A 4-nitrophenol (4-NP) solution (with a concentration of 5 g L^{-1}) was used as model wastewater.

METHODOLOGY

A wheat and hemp lignin, obtained from a soda pulping-precipitation process (Sarkanda, Granit S.A.), was carbonized trough annealing under inert atmosphere (N_2, 100 cm^3 min^{-1}) at 120 °C, 400 °C, 600 °C (60 min at each temperature) and 800 °C (240 min), defining a heating ramp of 2 °C min^{-1}. The resulting carbon, ground to 0.10-0.25 mm, was named LG. The carbon material LG was further thermally activated under oxidative atmosphere (Air, 100 cm^3 min^{-1}, 60 min) at activation temperatures in the range 150 to 350 °C, to obtain materials with different textural properties and surface chemistry. The as prepared activated carbons were named LG followed by a number corresponding to the activation temperature used (*i.e.* LG-150, LG-200, LG-300 and LG-350).
The composition of the lignin used as starting raw material was determined by elemental analysis. N_2 adsorption-desorption isotherms (-196 ºC) were obtained to characterize the textural properties of the prepared materials. The surface chemistry of the activated carbons was characterized by (i) the determination of the pH of point of zero charge (pH_{PZC}) [12] and (ii) the estimation of the concentration of surface acidic and basic sites, using titration techniques [12].
The CWPO runs were conducted in a 250 mL magnetically stirred (600 rpm) glass reactor. In a typical experiment, the reactor was loaded with 50 mL of a 4-NP aqueous solution (5 g L^{-1}) and heated to 50 °C. The pH was adjusted to 3 (using H_2SO_4 and NaOH solutions) and the stoichiometric concentration of H_2O_2 needed to completely mineralize 4-NP was incorporated. Finally, 2.5 g L^{-1} of catalyst were loaded to the system.
Pure adsorption experiments were also carried out to assess the capacity of the different carbons to adsorb the 4-NP, and differentiate between pollutant removal due to adsorption and oxidation.
The concentrations of 4-NP and the intermediates and/or byproducts derived from its oxidation were quantified by high performance liquid chromatography. A colorimetric method was used to follow the concentration of H_2O_2 during the reaction [13], using a UV/VIS spectrophotometer. Finally, the total organic carbon (TOC) content was determined using a carbon analyzer, by the difference between total carbon and inorganic carbon.

RESULTS AND DISCUSSION

The results on the elemental analysis of the lignin Sarkanda are shown in **Table 1**, with a notorious presence of oxygen in its composition being found, which is in line with the available hydroxyl groups that characterize this type of raw materials. The N_2 adsorption-desorption analysis (results shown in **Table 2**) of LG reveals a non-porous material, with a SSA of 5 m^2 g^{-1}. Its thermal activation leads to a significant porosity generation, progressively developed when increasing the activation temperature used, showing LG-350 a SSA *ca.* 540 m^2 g^{-1}.
With regard to the surface chemistry of the activated carbons, **Table 3** summarizes the pH_{PZC} and the concentration of surface acidic and basic sites present in the prepared materials. As can be observed, in spite of the gradual increase of acidity with the increase of the activation temperature

used (probably due to the incorporation of oxygenated groups during the treatment under air atmosphere), all the activated carbons show higher concentration of basic groups than acidic groups, even though the ratio basicity/acidity decreases when increasing the activation temperature. This remarkable basic character is corroborated by the pH_{PZC} values obtained in all the materials. Basic carbon materials are known to be more active in the decomposition of H_2O_2 [14,15]. Therefore, all the prepared activated carbons are expected to be appropriate for the CWPO process.

In order to evaluate the ability of the prepared activated carbons to act as metal-free catalysts in the CWPO of high-concentrated 4-NP solutions, 24-hours runs were done at the experimental conditions described in the methodology section. The removal of 4-NP and the decomposition of H_2O_2 observed are shown in **Figure 1**. As can be seen, the catalysts prepared using the higher activation temperatures (300 °C and 350 °C) were able to remove around 70 % of 4-NP, with a moderate H_2O_2 decomposition rate being observed. On the other hand, in spite of the better H_2O_2 decomposition observed, the materials prepared at the lower activation temperatures (150 °C and 200 °C), and the carbon LG, removed less than 25 % of 4-NP.

The higher porosity development of LG-300 and LG-350 could explain their better 4-NP removal results, since a higher SSA favors the adsorbent capacity. In order to discriminate this hypothesis, pure adsorption runs were done using operation conditions equivalent to those of the CWPO tests, but without H_2O_2. **Figure 2** compares the results of 4-NP removal after 24 hours in the CWPO and adsorption runs. The H_2O_2 and TOC conversions are also shown, as well as the H_2O_2 consumption efficiency to mineralize the pollutant ($\eta_{H_2O_2}$), defined as the TOC removal per unit of H_2O_2 decomposed [11]:

$$\eta_{H_2O_2} = \frac{\%\ TOC\ removal}{\%\ H_2O_2\ decomposed} x100$$

As expected, the adsorbent capacity of the activated carbons increases with the activation temperature, in the same order as the SSA does. Nevertheless, the contribution of adsorption in the removal of 4-NP in all of them was insignificant, with 4-NP removals of only 5 and 8 % being respectively observed with LG-300 and LG-350. It is thus concluded that the better results obtained with these two catalysts in the CWPO of 4-NP are not exclusively due to a better adsorption capacity.

The H_2O_2 conversion also differs from one material to the others, with the materials showing the lower H_2O_2 decompositions surprisingly revealing the better performances in the CWPO of 4-NP. The higher 4-NP removals obtained with LG-300 and LG-350 suggest that the decomposition of H_2O_2, when catalyzed by these activated carbons, is highly efficient for the generation of $HO^{\bullet}$ radicals, responsible by the mineralization of 4-NP. This is confirmed by the values of $\eta_{H_2O_2}$, close to 100 % with both catalysts.

The activated carbons obtained at the lowest activation temperatures, LG-150 and LG-200, promoted a faster decomposition of H_2O_2, in agreement with the higher concentration of basic functionalities in these materials, which, as observed in **Table 3**, diminishes when increasing the activation temperature used. However, this faster decomposition of H_2O_2 seems to favor the formation of non-reactive species due to the recombination of the formed radicals, directly affecting the process efficiency, $\eta_{H_2O_2}$ dropping to *ca.* 50 %. This, joined to the low adsorbent capacity of these materials, which hinders the approximation of 4-NP to the sites responsible for

the generation of $HO^{\bullet}$ radicals, leads to a low 4-NP conversion, in spite of the better decomposition of H_2O_2 observed.

CONCLUSIONS

All the lignin-based carbon materials prepared in this work are active in the H_2O_2 decomposition and in the 4-NP removal by CWPO.

The temperature used in the carbon activation plays an important role in the porosity development and in the surface chemistry of the activated carbons generated. This dependence is particularly evident in the materials activated at the higher temperatures, which present superior SSA and lower basicity/acidity ratios.

The activated carbons prepared at the higher activation temperatures (300 ºC and 350 °C) promoted an efficient H_2O_2 decomposition, removing around 70 % of 4-NP. On the contrary, the materials prepared at the lower activation temperatures (150 ºC and 200 °C) promoted a faster but inefficient H_2O_2 decomposition, the 4-NP removal being lower than 25 % after 24 h in these cases. This low efficiency is mainly attributed to the formation of non-reactive species due to the recombination of the $HO^{\bullet}$ radicals generated from the decomposition of H_2O_2 at higher rates, as well as to the poor adsorption capacity of these materials.

ACKNOWLEDGMENTS

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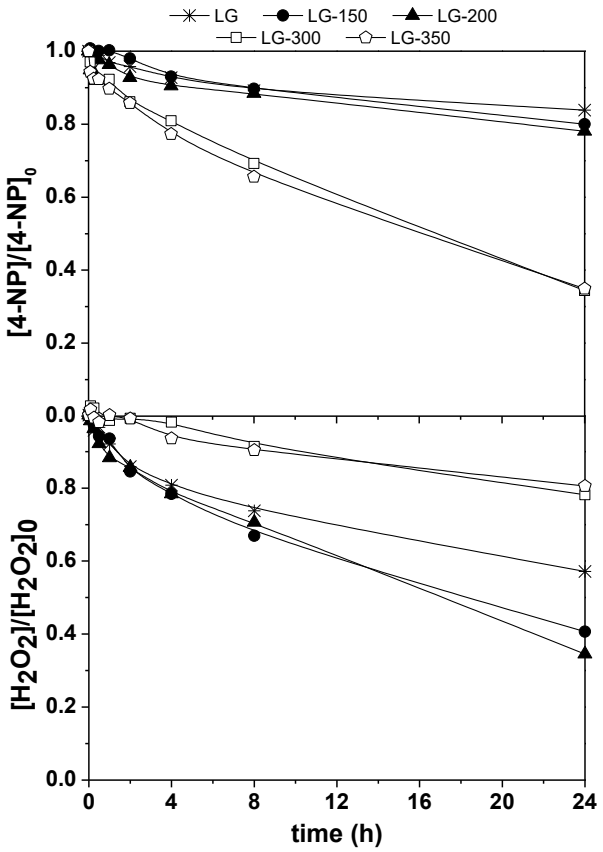

Figure 1. Evolution of 4-NP and H_2O_2 concentration with time in the CWPO experiments.

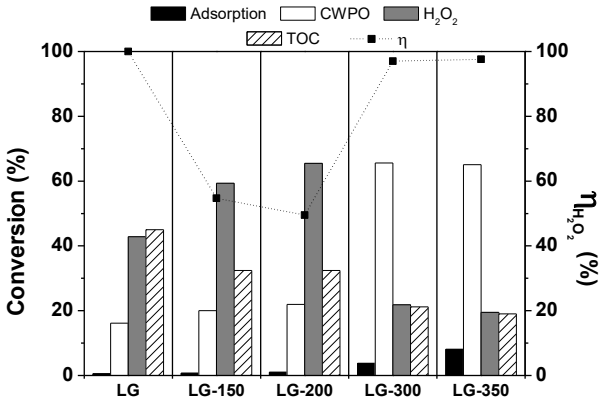

Figure 2. Removal of 4-NP by adsorption and by CWPO; TOC removal, H_2O_2 decomposition and $\eta_{H_2O_2}$ obtained in the CWPO experiments; results after 24 h.

Table 1

Composition of the ligning Sarkanda as determined by elemental analysis (w/w%).

C	H	N	S	O
58.84	5.86	1.14	1.01	29.89

Table 2

Specific surface area (S_{BET}), micropore volume (V_{micro}) and non-microporous surface area (S_{meso}) of the prepared activated carbons.

Catalyst	S_{BET} ($m^2\ g^{-1}$)	V_{micro} ($cm^3\ g^{-1}$)	S_{meso} ($m^2\ g^{-1}$)
LG	5	0.00	5
LG-150	12	0.00	12
LG-200	260	0.12	18
LG-300	395	0.21	29
LG-350	539	0.26	74

Table 3

pH_{PZC}, concentration of surface acidic and basic sites of the prepared activated carbons.

Catalyst	pH_{PZC}	acidity (μmol g^{-1})	basicity (μmol g^{-1})	bas/ac
LG	8.7	246	1193	4.85
LG-150	8.9	343	1383	4.03
LG-200	9.8	418	1288	3.08
LG-300	8.7	534	1020	1.91
LG-350	8.3	697	823	1.18