SYNTHESIS OF SUPER-NANOPOROUS CARBON ALLOY BY ELECTROOXIDATION OF A ZEOLITE TEMPLATED CARBON

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Strategic Japanese-Spanish Cooperative Program (FY2011)

"UNIQUE SUPER-POROUS CARBON ALLOYS FOR ASYMMETRIC HYBRID SUPERCAPACITORS"

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Japan Science and Technology Agency

PRI-PIBJP-2011-0766

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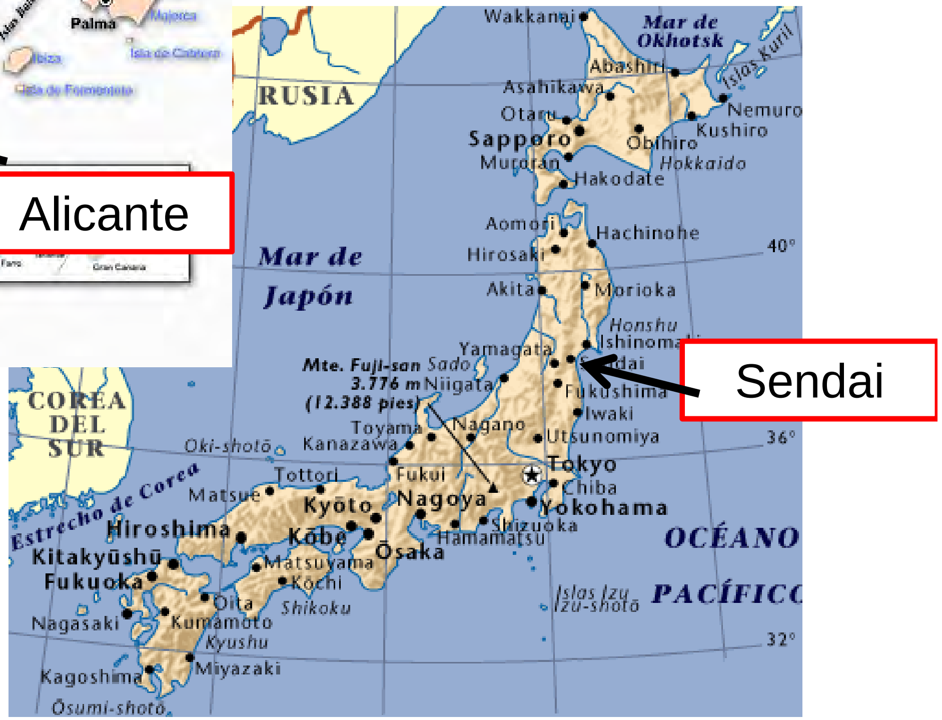

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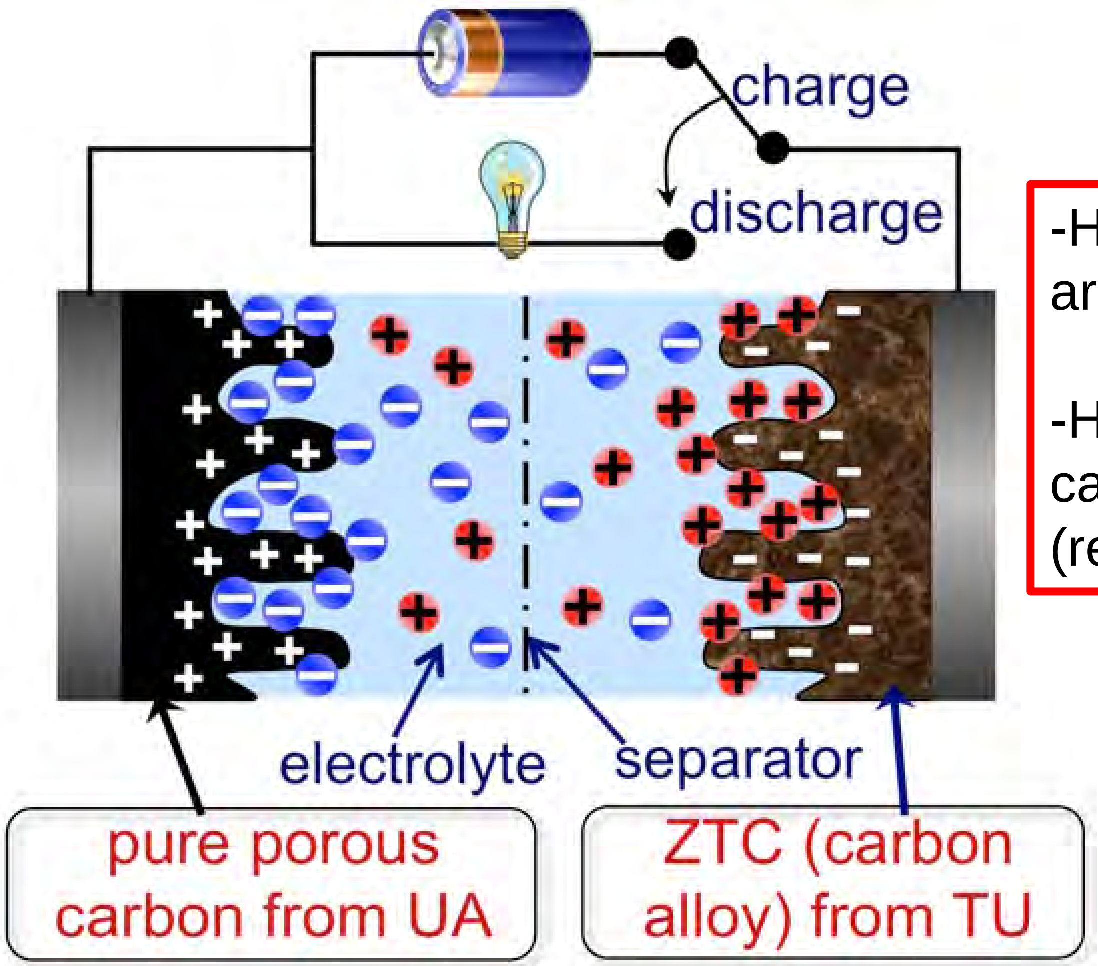
Izu-shotō
Nagasaki
Kumamoto
Kyushu
Miyazaki
Kagoshima
Ōsumi-shotō
40°
36°
32°
Sendai

Project Title:

"Unique super-porous carbon alloys for asymmetric hybrid supercapacitors"

Objective:

The aim of this project is to synthesize unique porous carbon alloy and to develop a carbon-based asymmetric hybrid supercapacitor using the carbon alloy as a positive electrode.



-High surface area → DLC

-High pseudo-capacitance (redox rxn.)

Concept of Carbon Alloy:

Carbon materials can be developed with a wide range of structures, textures and properties. This led to **the Japanese Carbon Group** to propose in 1992:

"Carbon alloys are materials mainly composed of carbon atoms in multi-component systems, in which each component has physical and/or chemical interactions with each other. Here carbons with different hybrid orbitals account as different components"

(Carbon alloys, E Yasuda et al Editors, Elsevier, 2003, p.9).

Concept of Carbon Alloy:

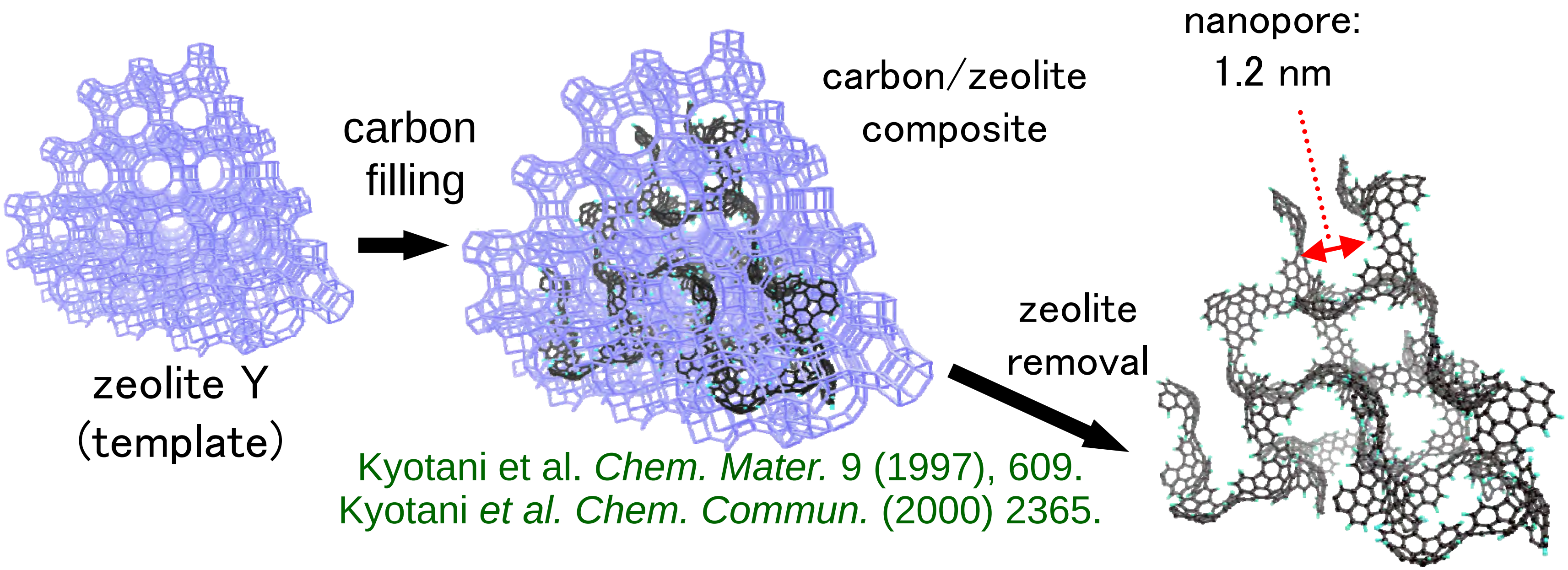
Carbon materials can be developed with a wide range of structures, textures and properties. This lead to **the Japanese Carbon Group** to propose in 1992:

TO SYNTHESIZE A SUPER-NANOPOROUS CARBON ALLOY BASED ON ZEOLITE TEMPLATED CARBON (ZTC)

“C ... osed
of ... ems, in
w ... or
ch ... re
carbons with different hybrid orbitals account as different components”

(Carbon alloys, E Yasuda et al Editors, Elsevier, 2003, p.9).

What is ZTC? Nano-sized carbon material with taylored and ordered pore network prepared using zeolite as template



Kyotani et al. *Chem. Mater.* 9 (1997), 609.
Kyotani *et al. Chem. Commun.* (2000) 2365.

Nishihara et al. *Carbon*, 47 (2009) 1220.

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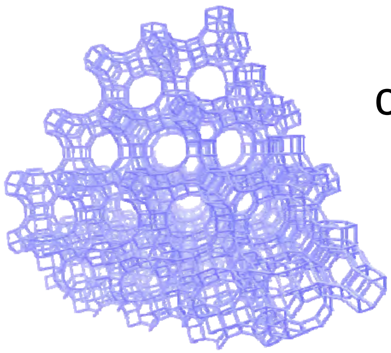
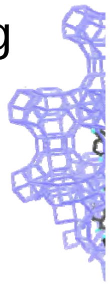
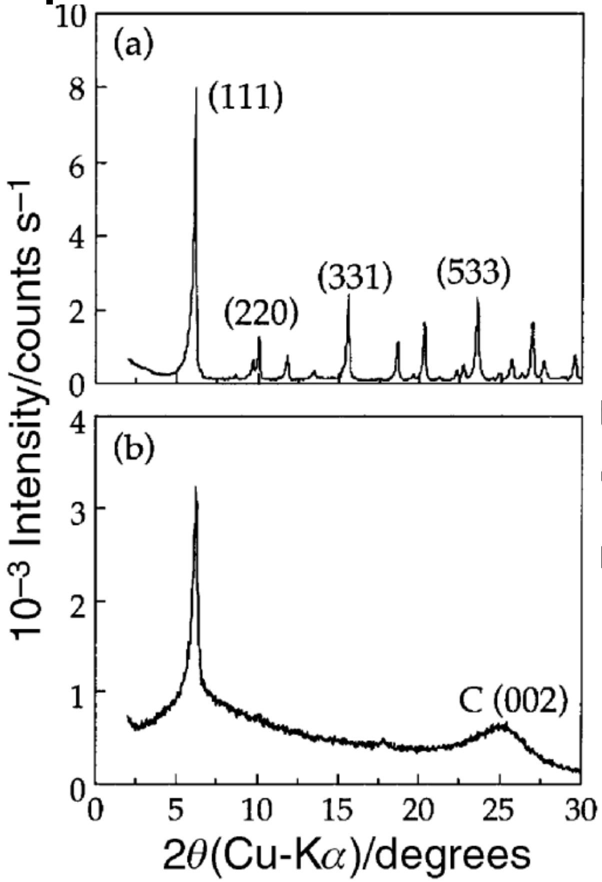


zeolite Y
(template)

carbon
filling



Kyotani et a
Kyotani *et al*



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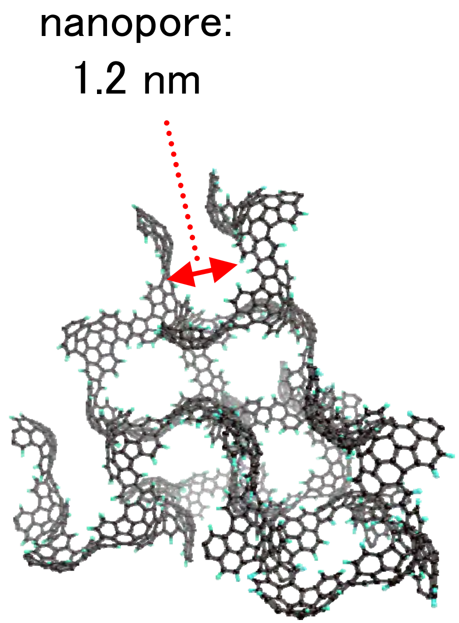
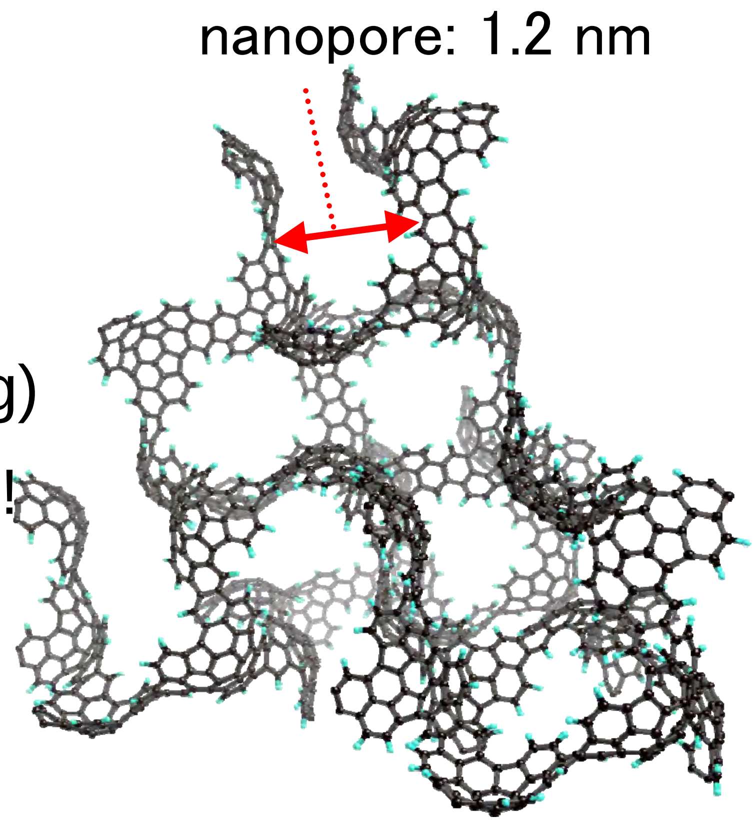


Nishihara et al. *Carbon*, 47 (2009) 1220.

Unique features ZTC

- 3D-nanographene network
- uniform nanopore size (1.2 nm)
- high surface area (up to 4000 m^2/g)
- large amount of carbon edge sites!
- all edge sites and graphene surface are fully exposed!

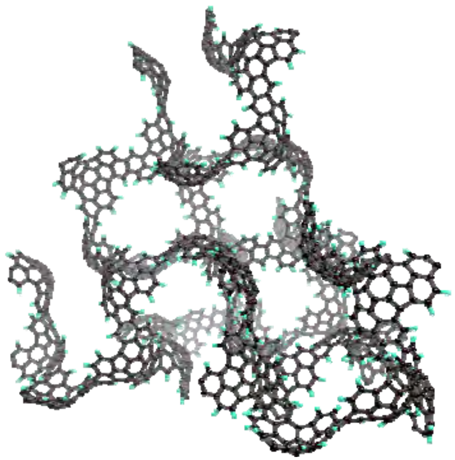
These features are beneficial to use ZTC as an electrode for electrochemical capacitors



Unique features ZTC

These features are beneficial to the use ZTC as an electrode for electrochemical capacitors

- Adequate electrolyte accessibility
- High mass transfer rate
- High surface area (high double layer capacitance)
- Formation of large amount of functional groups (redox properties, pseudocapacitance)



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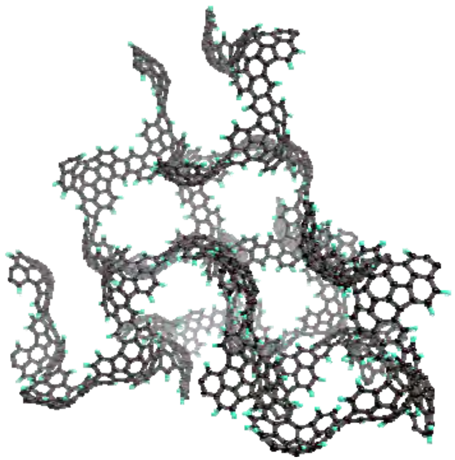
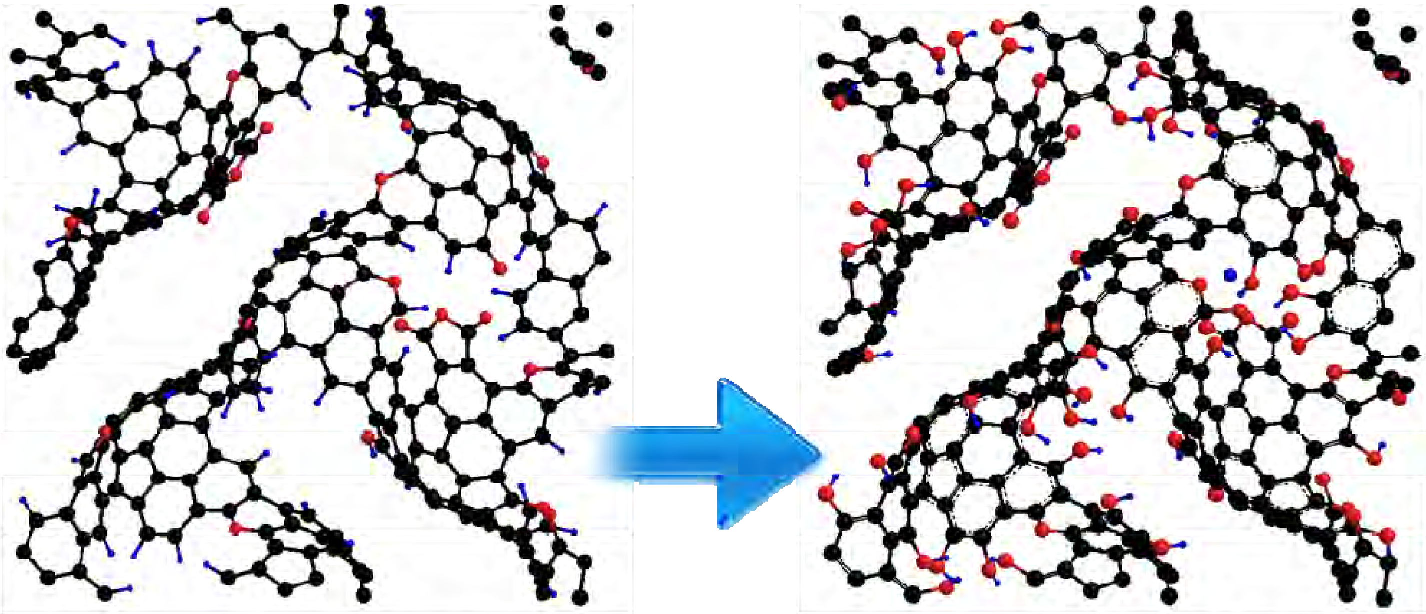


Unique features ZTC

EDGE SITES (C–H) | **HYDROXYL (C –OH)**



PRISTINE ZTC

S_{BET} = 3600 m²/g

Oxygen = 8.9 %

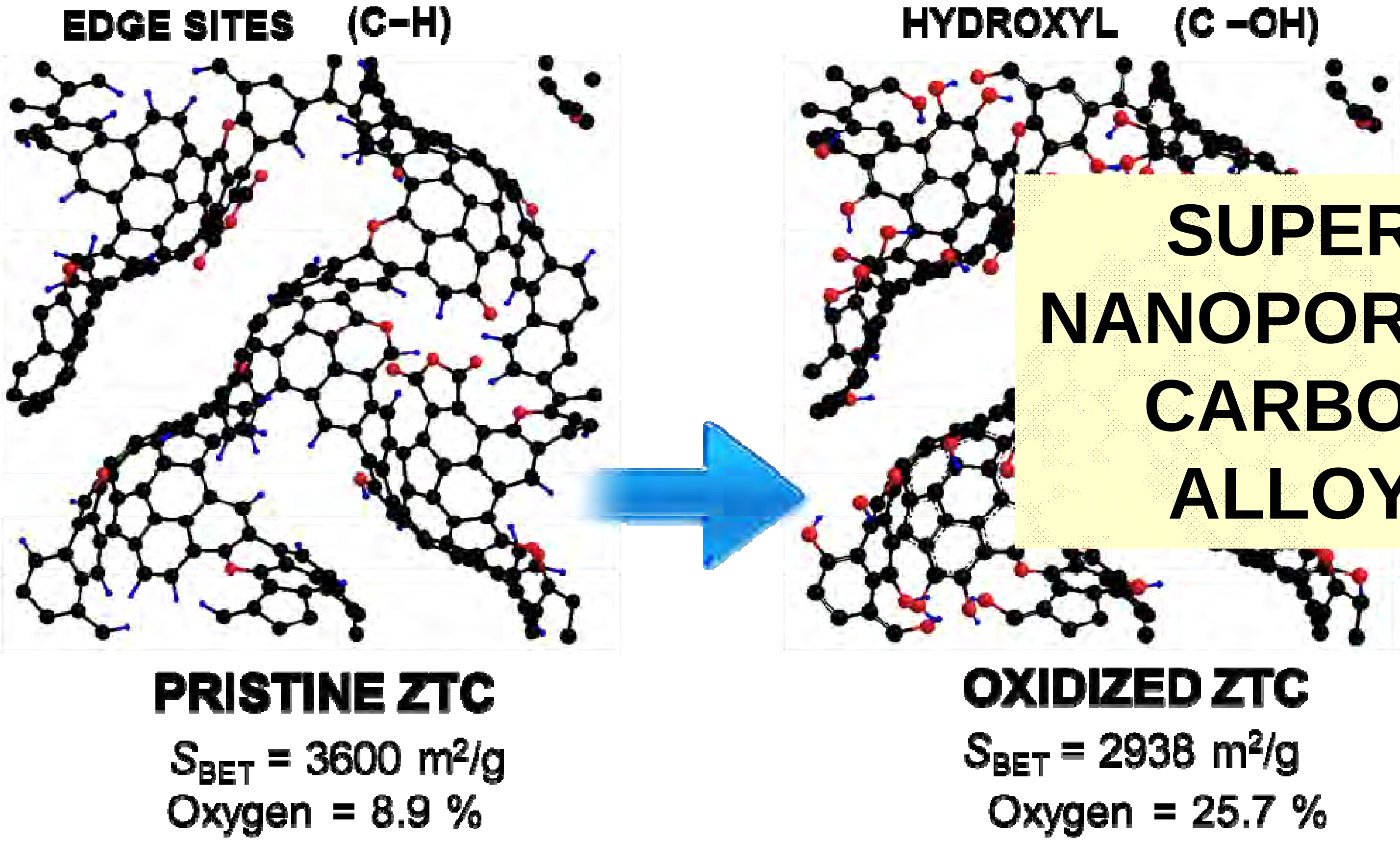
OXIDIZED ZTC

S_{BET} = 2938 m²/g

Oxygen = 25.7 %

Hypothetical oxidation process of ZTC and the modelled molecular structure of fully-oxidized ZTC.

Unique features ZTC

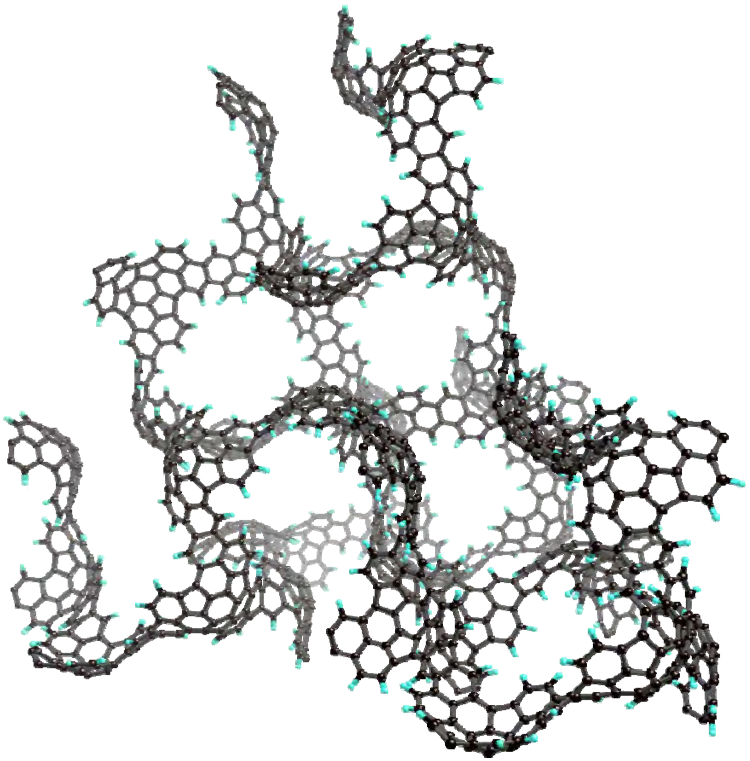


SUPER-NANOPOROUS CARBON ALLOY!

Hypothetical oxidation process of ZTC and the modelled molecular structure of fully-oxidized ZTC.

Main problems to achieve the objective

-ZTC has a quite fragile structure
-ZTC is very reactive
-Easy structure degradation



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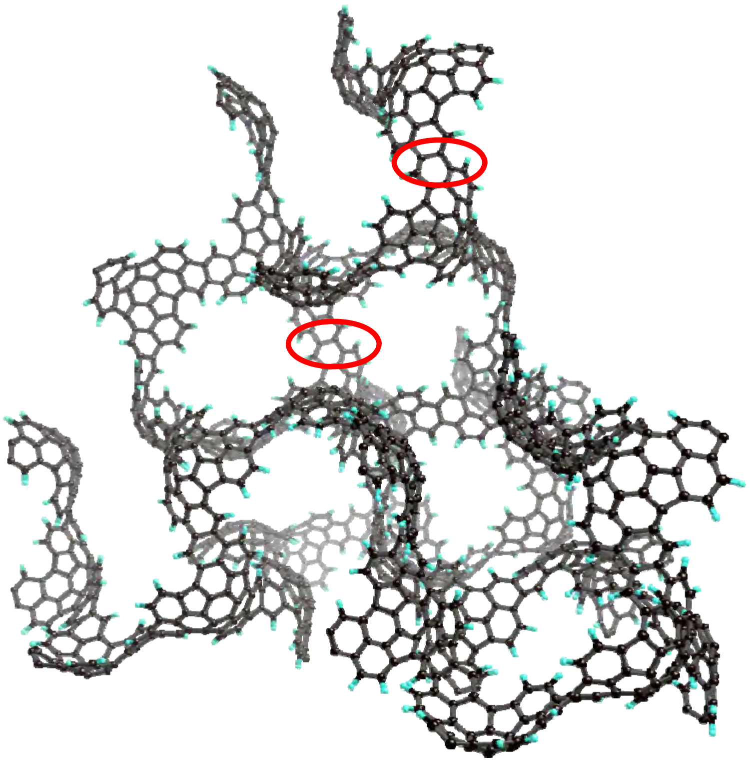

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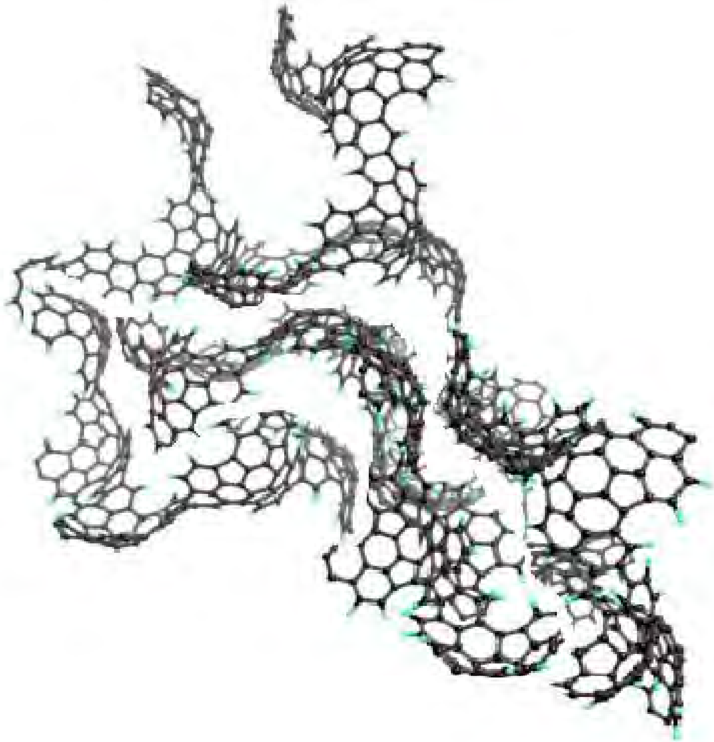
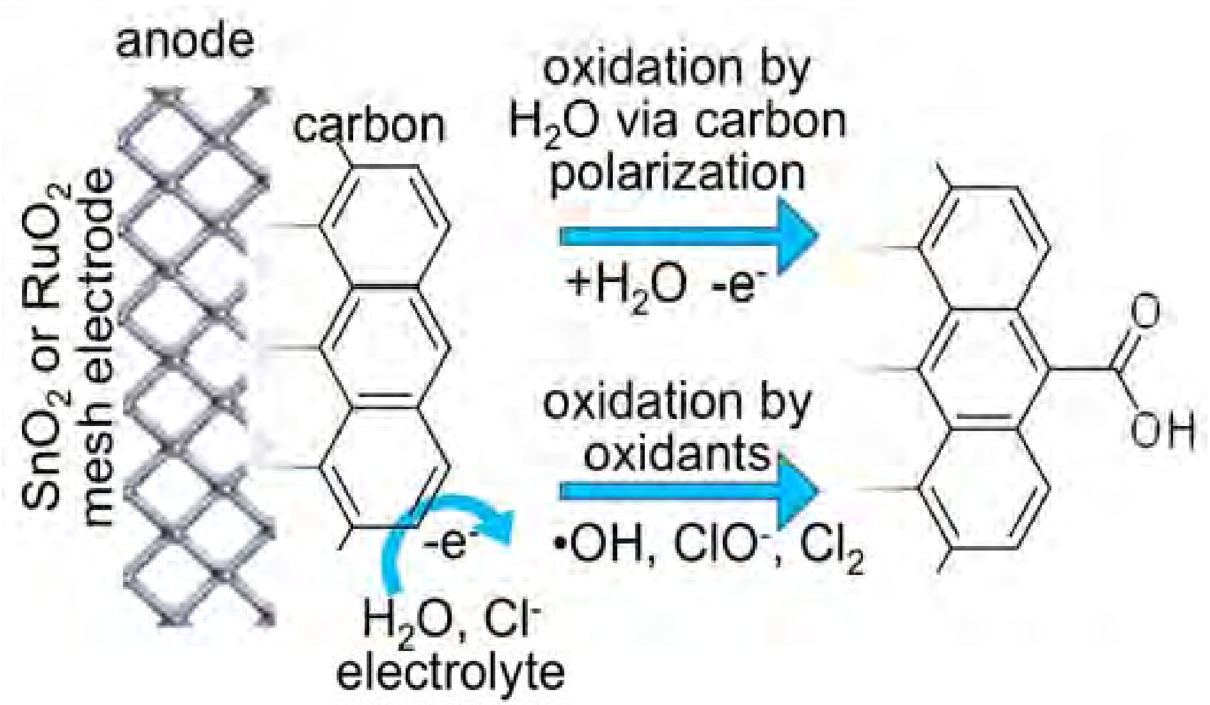


Objective of this work:

To make a detailed study of the ZTC electrooxidation to get large concentration of surface oxygen groups and high surface area



Experimental section

Electrochemical oxidation:

-Galvanostatic oxidation: I= 2-50 mA, t= 1-15h, T= 25ºC; Electrolytes: 1.0M NaOH, 1.0M H_2SO_4, 2wt% NaCl

- Cyclic voltammetry: ΔE= -0.1-1.2 V, v= 1 mV/s, 1.0M H_2SO_4

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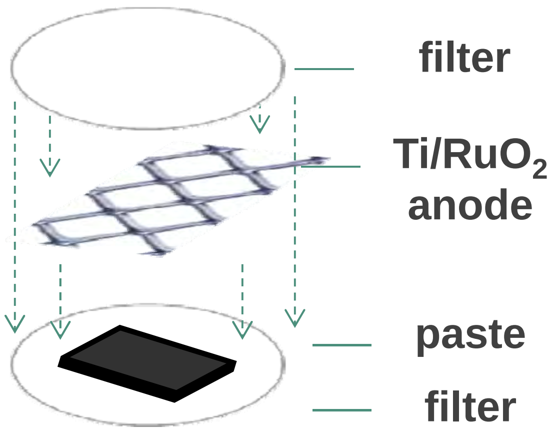
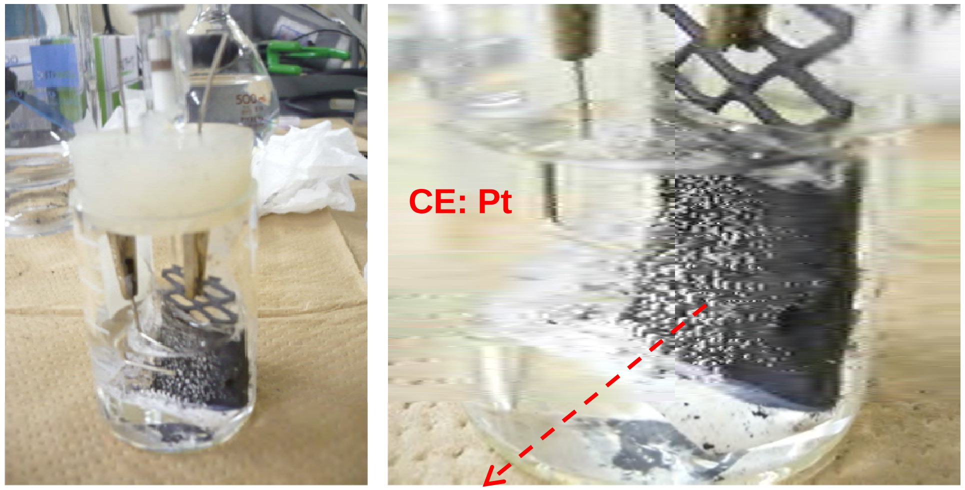


mass = 100 mg

area = 2.25 cm^2

thickness = 2 mm

3-electrode cell



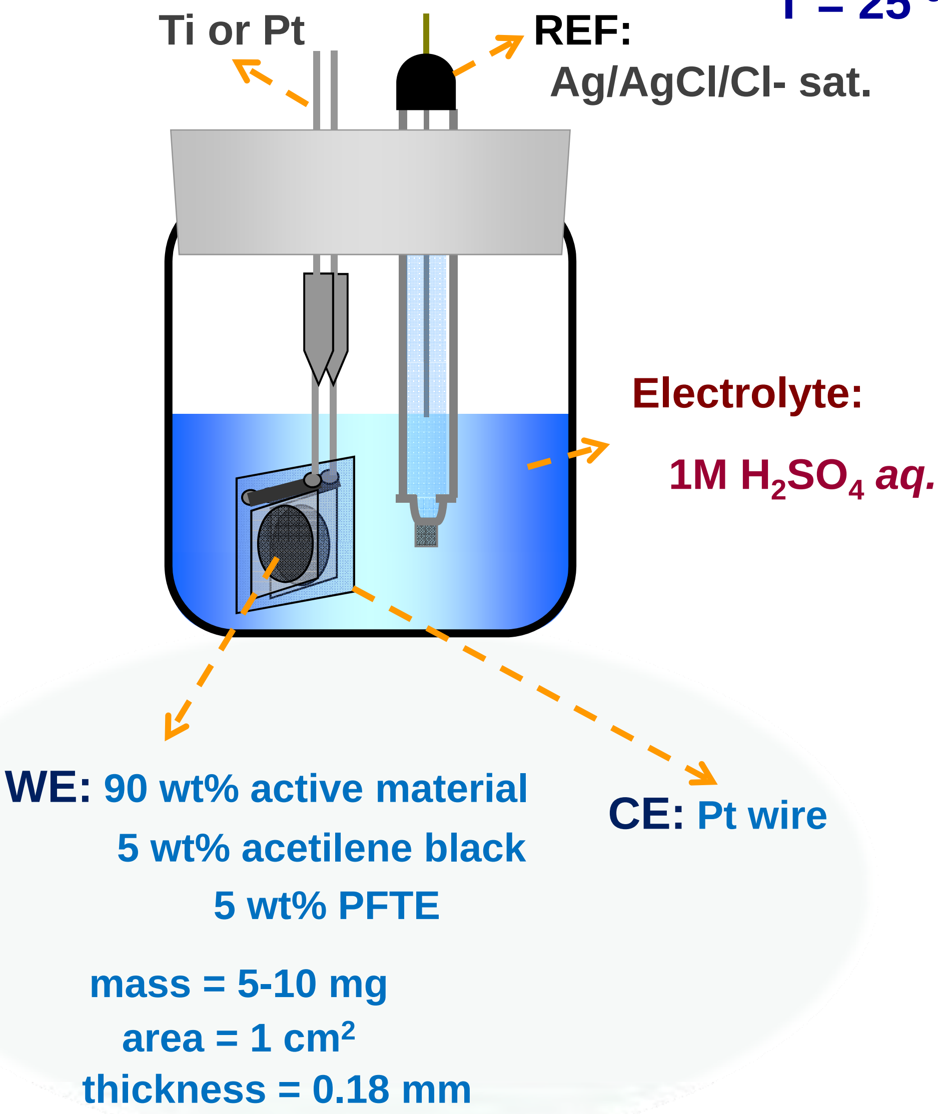
WE: (Ti/RuO$_2$ + ZTC paste)

3-electrode cell

Electrochemical oxidation:

-Cyclic voltammetry: ΔE= -0.1-1.2 V, v= 1 mV/s, 1.0M H_2SO_4

T = 25 ºC



Chemical oxidation:

- Oxidation by HNO_3 at different temperatures (45ºC, 80 ºC) and times (from 15 min to 15h). Oxidation by H_2O_2 was also done.

Characterization

Structural-Textural

- N_2 adsorption (-196 ºC)
- CO_2 adsorption (0 ºC)
- X-ray diffraction (XRD)

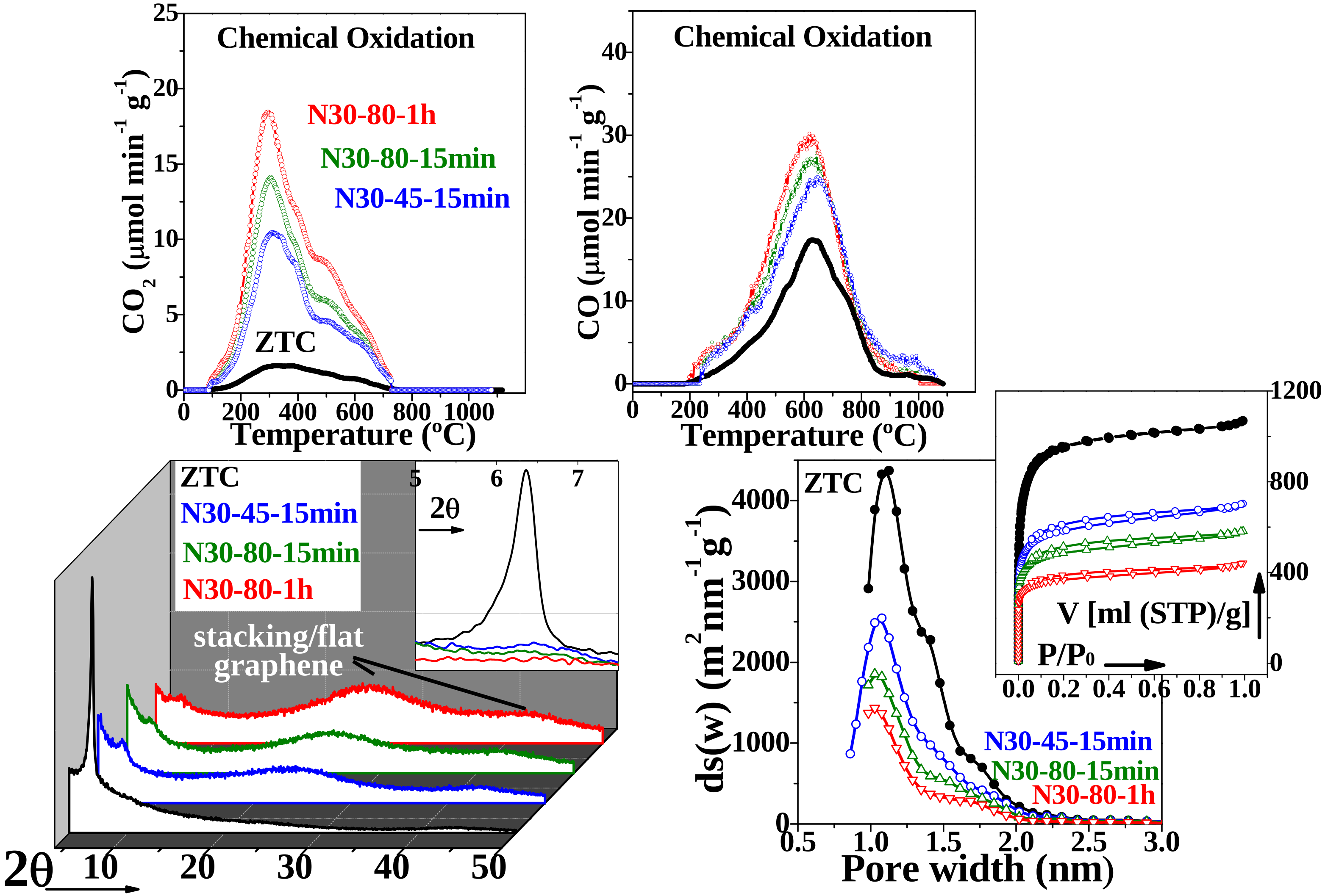
Surface Chemistry

- Temperature-programmed desorption (TPD)
- X-ray photoelectron spectroscopy (XPS)

Results and discussion.

Results and discussion.

Chemical oxidation



Chemical Oxidation
CO_2 (μmol min^{-1} g^{-1})
N30-80-1h
N30-80-15min
N30-45-15min
ZTC
Temperature (ºC)
Chemical Oxidation
CO (μmol min^{-1} g^{-1})
Temperature (ºC)
ZTC
N30-45-15min
N30-80-15min
N30-80-1h
stacking/flat graphene
2θ
ds(w) (m^2 nm^{-1} g^{-1})
Pore width (nm)
V [ml (STP)/g]
P/P₀

Sample	TPD					N_2 adsorption		
	CO µmol/g	CO_2 µmol/g	O µmol/g	ΔO* µmol/g	$\frac{CO}{CO_2}$	S_{BET} (m^2/g)	$V_T(N_2)$ (cm^3/g)	%S_{BET}
ZTC	2644	286	3216	0	9.24	3650	1.63	100
ZTC N30-45-15min	4181	1506	7193	3977	2.78	2230	1.07	61
ZTC N30-80-15min	4327	1923	8173	4957	2.25	1870	0.88	51
ZTC N30-80-1h	4676	2555	9786	6570	1.83	1420	0.66	39
ZTC N30-80-2h	4708	2864	10436	7220	1.64	1140	0.52	31

SUMMARY ABOUT CHEMICAL OXIDATION:

-Chemical oxidation is a fast process that easily destroys the unique structure of ZTC.

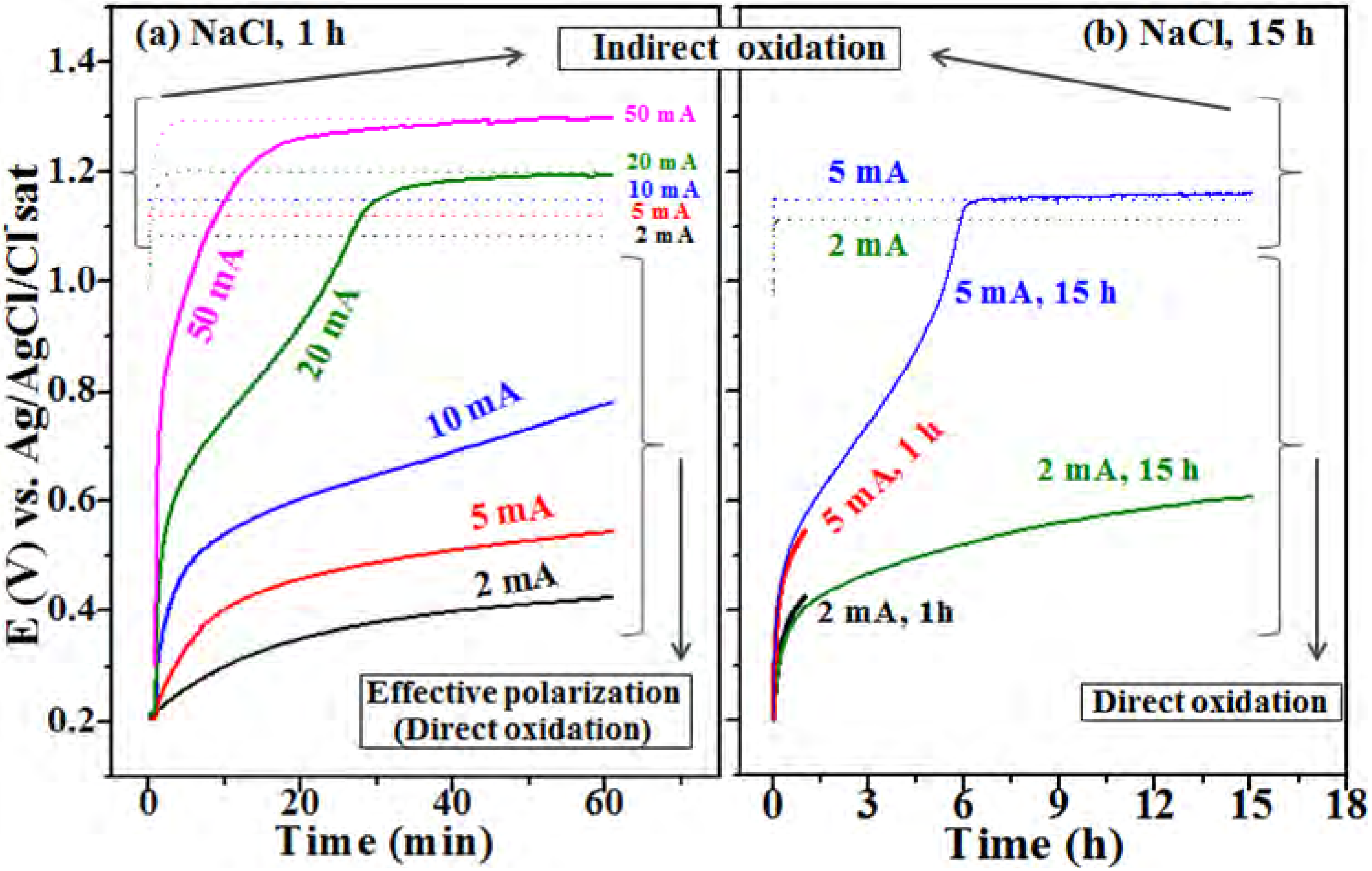
-It produces a very important decrease in porosity and structural order.

-High selectivity to CO_2-type groups, since it favours the oxidation of surface-oxidized sites.

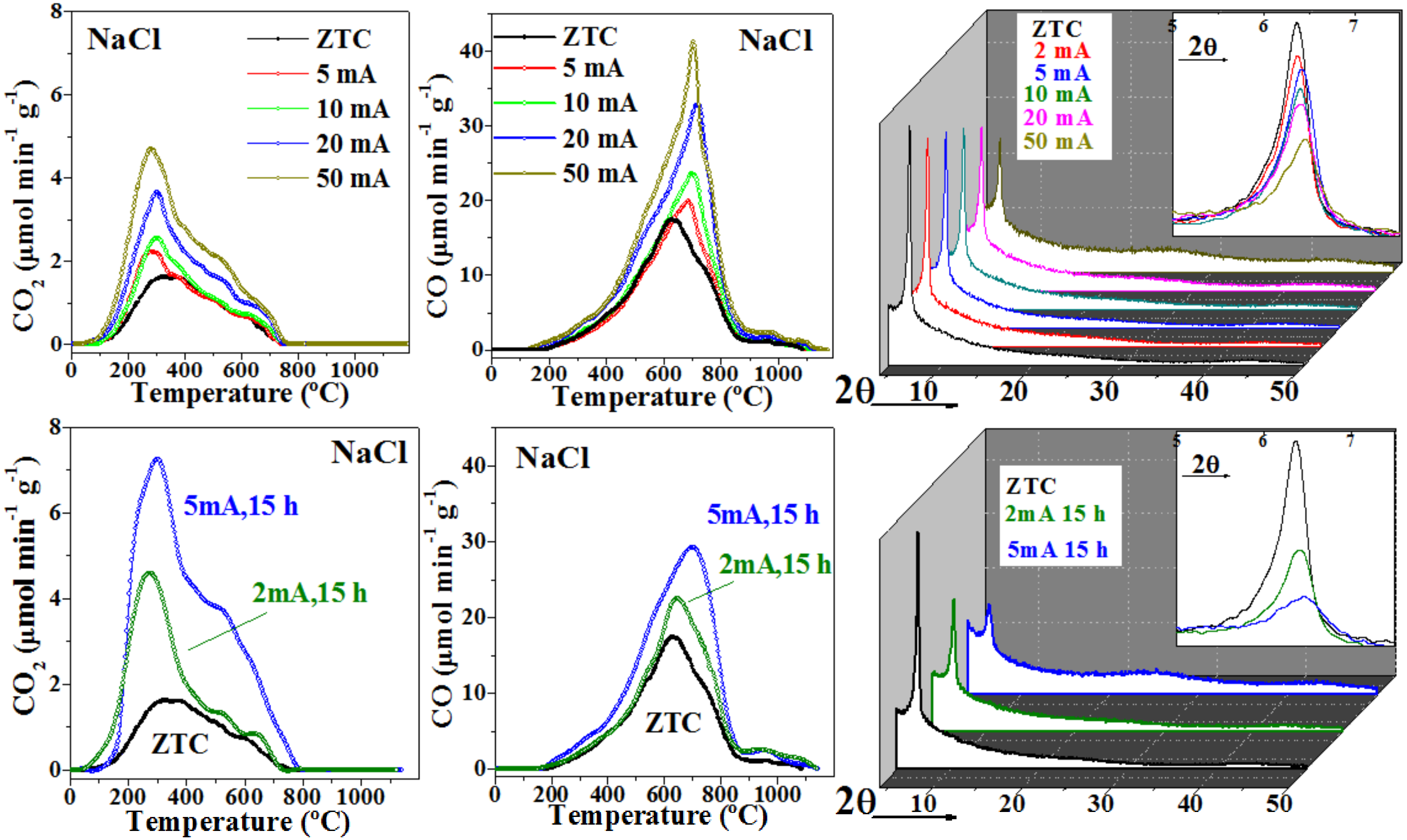
Results and discussion.

Electrochemical oxidation

Electrochemical oxidation: Galvanostatic oxidation



Electrochemical oxidation: Galvanostatic oxidation



Electrochemical oxidation: Galvanostatic oxidation

Sample	TPD					N_2 adsorption		
	CO µmol/g	CO_2 µmol/g	O µmol/g	ΔO^* µmol/g	$\frac{CO}{CO_2}$	S_{BET} (m^2/g)	$V_{DR}(N_2)$ (cm^3/g)	$\%S_{BET}$
ZTC	2644	286	3216	0	9.24	3650	1.54	100
ZTC 20Cl^- 1h	4398	529	5456	2240	8.31	2780	1.21	76
ZTC 50Cl^- 1h	5083	709	6501	3285	7.17	2680	1.16	73
ZTC 5Cl^- 15h	4669	1146	6961	3745	4.07	2430	1.01	67
ZTC 50Cl^- 3h	5880	1760	9400	6184	3.34	1210	0.50	33
ZTC 50Cl^- 10h	4849	4002	12853	9637	1.21	150	0.06	4
ZTC 50H^+ 1h	3442	435	4312	1096	7.91	3100	1.31	85
ZTC 5H^+ 15h	6095	1090	8275	5059	5.59	2290	0.89	63
ZTC 2H^+ 36 h (1.2V)	7159	1966	11091	7875	3.64	1863	0.77	51

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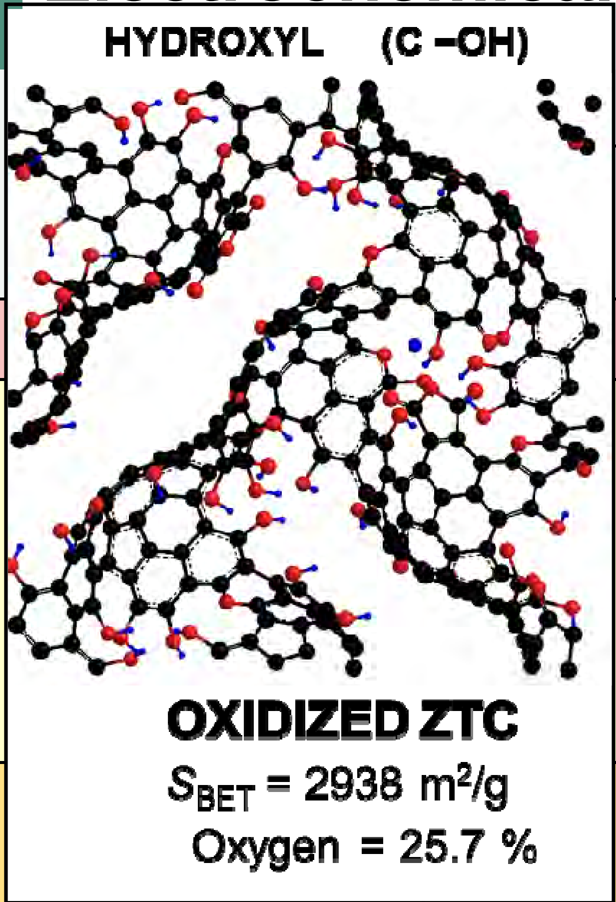

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		435	4[illegible]12	1096	7.91	3100	1.31	85
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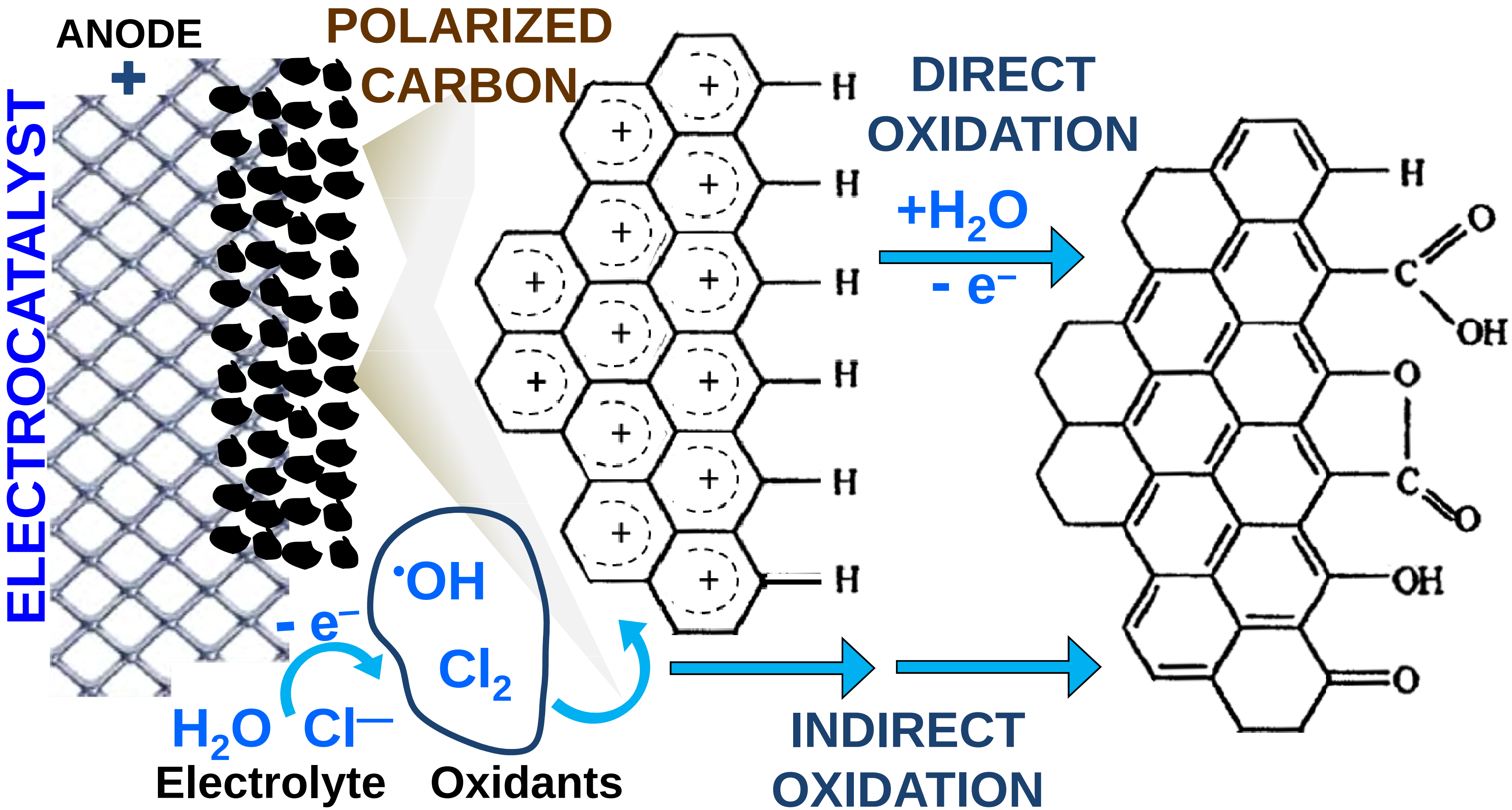
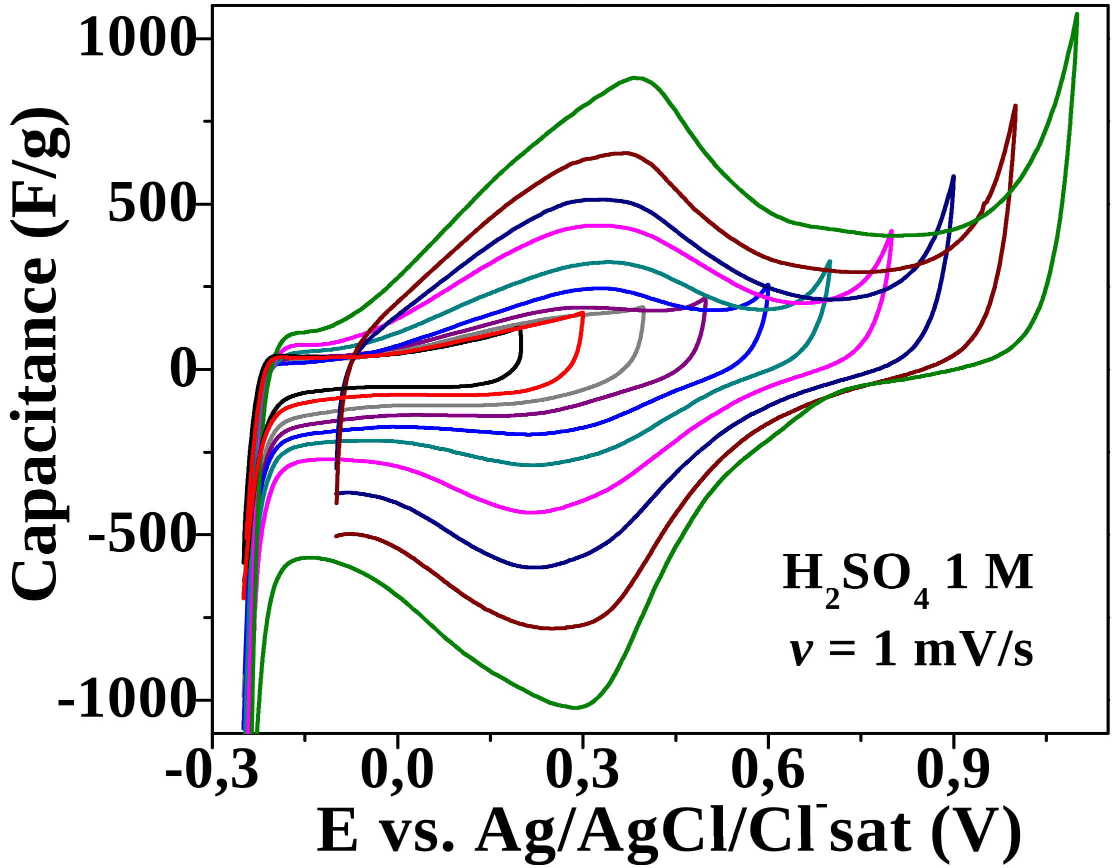
ZTC $2H^+$ 36 h (1.2V)	7159	1966	11091	7875	3.64	1863	0.77	51

Total oxygen content 18 wt%!

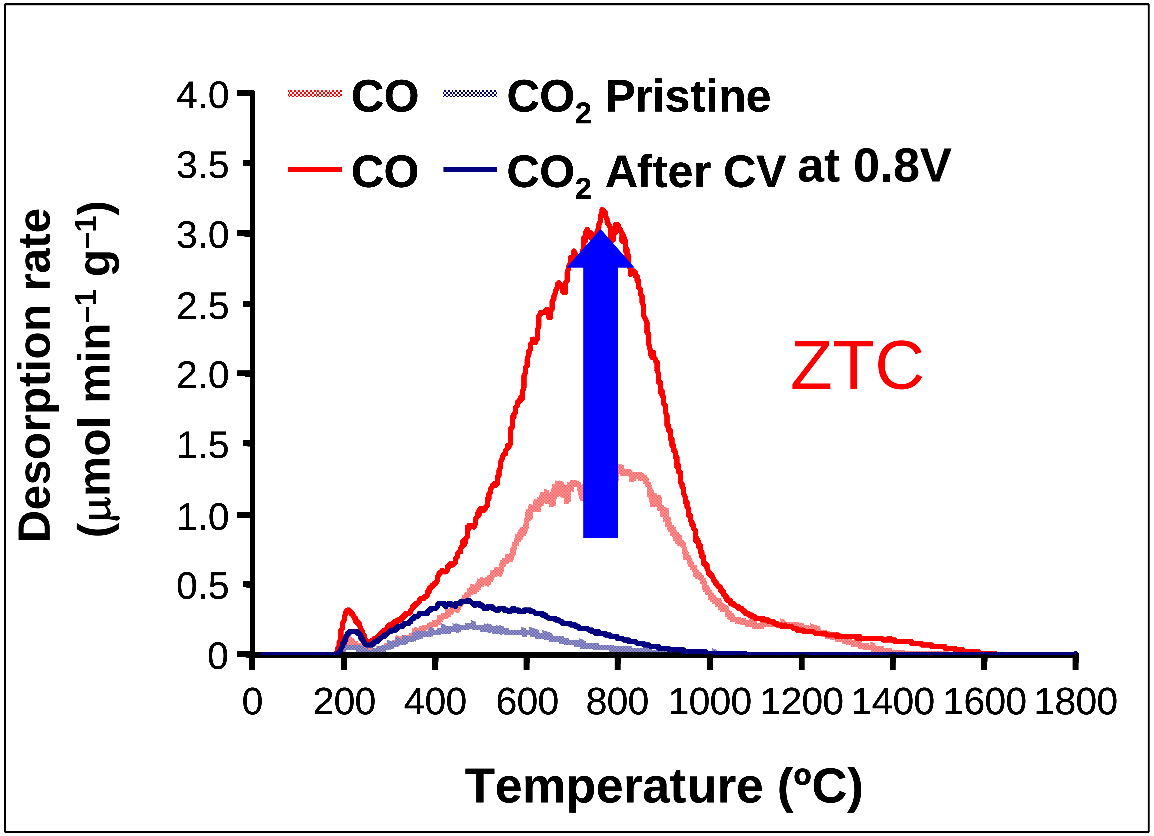
Electroxidation Mechanism



Electrochemical oxidation: Cyclic voltammetry

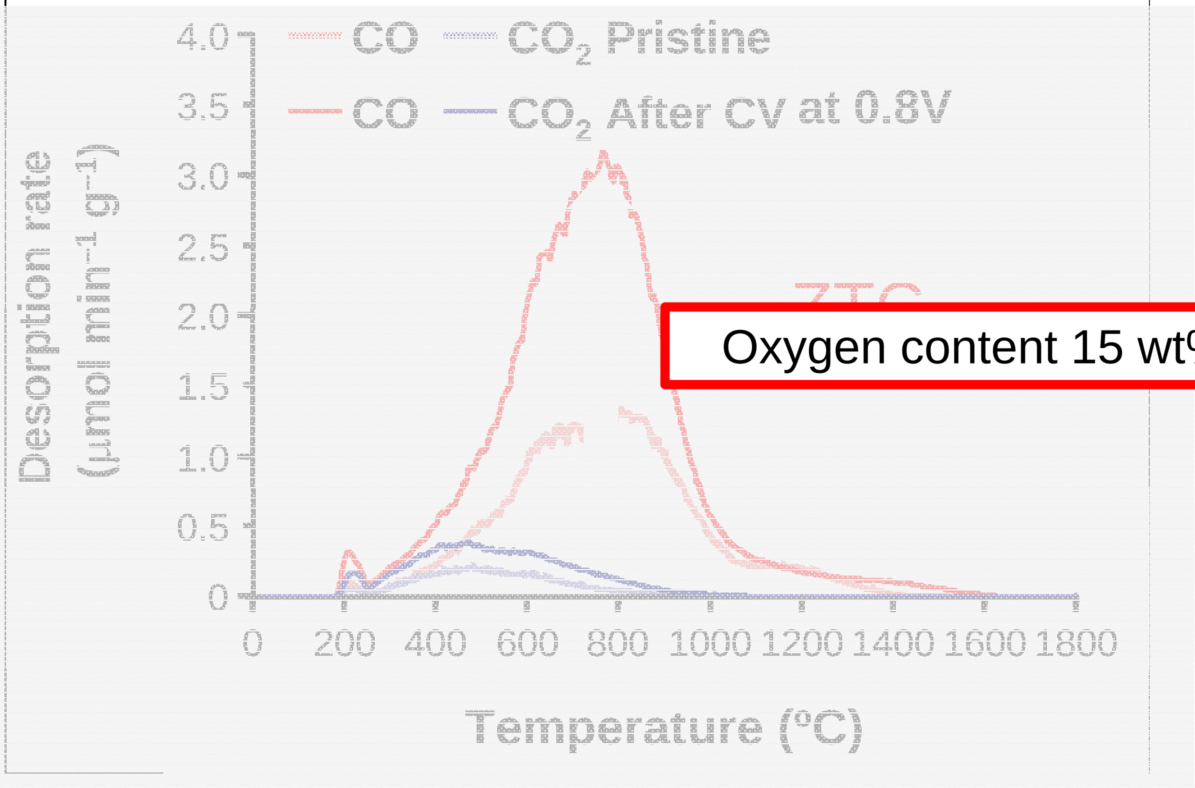


Electrochemical oxidation: Cyclic voltammetry



	TPD
Sample	**CO/CO_2**
ZTC	9.24
0.8 V	7.88
0.9 V	5.21
1.0 V	4.68
1.1 V	3.29

Electrochemical oxidation: Cyclic voltammetry



Oxygen content 15 wt%

	TPD
Sample	**CO/CO_2**
ZTC	9.24
0.8 V	7.88
0.9 V	5.21
1.0 V	4.68
1.1 V	3.29

Electrochemical oxidation: Cyclic voltammetry

Total capacitance (from charge-discharge at 50 mA/g in H_2SO_4):

-After CV oxidation up to 0.8 V, C = 500 F/g

-After CV oxidation up to 1.1 V, C = 700 F/g

Very close to conducting polymers (Pani nanobelts 873 F/g) or ruthenium oxide (720 F/g)*

(*)JN Tiwari, RN Tiwari, KS Kim, Progress in Materials Sci, 57 (2012) 724

Conclusions

CONCLUSIONS

- Synthesis of ZTC alloy has been studied by chemical and electrochemical oxidations.

- Chemical oxidation easily destroys the ZTC. Reaction rate is high at the beginning of the oxidation.

- Electrochemical oxidation permits a better control of the kinetics of the process.

-ZTC alloy with BET surface area close to 1900 m^2/g and oxygen content of 18 wt% has been successfully synthesised.

- ZTC alloy by cyclic voltammetry has a capacitance as high as 700 F/g.

Thank you very much for your attention