

4<sup>èmes</sup> Réunions plénières de la Fédération H<sub>2</sub>  
La Grande Motte | 7-11 Octobre 2024

## S06 : Réactivité redox de surface d'oxydes envisagés comme cathode de piles à combustibles à oxyde solide

Elise Berrier, Valerie Theuns, Siavash Alizadeh, Donovan  
Ledru, Marie-Hélène Chambrier



# Contexte: Le projet KNOWSKITE-X

Consortium: 10 partenaires



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**KNOWSKITE-X**  
Knowledge-driven fine-tuning of perovskite-based electrode materials for reversible Chemicals-to-Power devices



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- ▶ Industriels: FIAXELL (SW), C2C Newcap (PT)

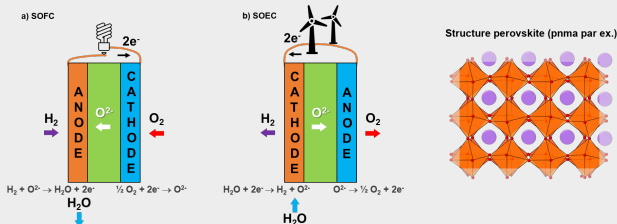


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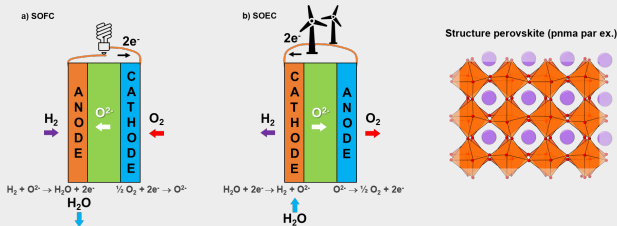
# KNOWSKITE-X: Les matériaux

## Des oxydes mixtes comme électrodes SOC



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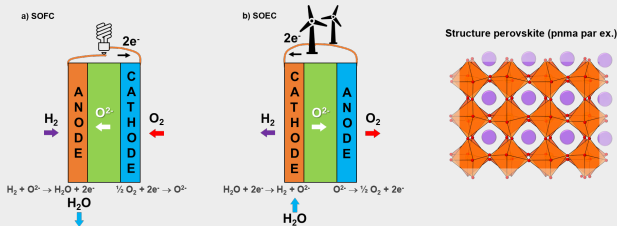
## Des oxydes mixtes comme électrodes SOC



► formulations  $\text{A}_{\alpha-x}\text{A}'_x\text{B}_{1-y}\text{B}'_y\text{O}_{3\pm\delta}$ ;  $0.7 < \alpha < 1$

# KNOWSKITE-X: Les matériaux

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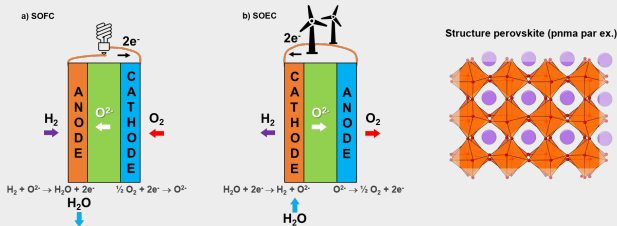


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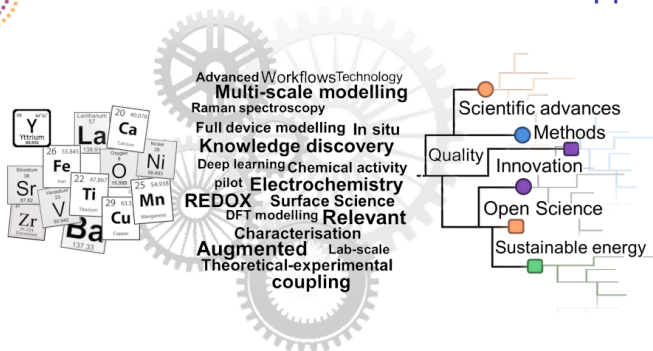
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- ▶ A / A': Ba, Bi, Ca, K, La, Li, Na, Pb, Pr, Sr, Nd, Pr, Tb ...
- ▶ B / B': Na, Te, Fe, Ti, Co, Ru, Mo, Mn, Bi, Nb, Te, Mg, W, Ta, Sb, Al, V, Zn, Hf ...



# KNOWSKITE-X: Approche



Elements d'anatomie d'une électrode performante

LSCF + NiO = LSFN

Le système BCTF



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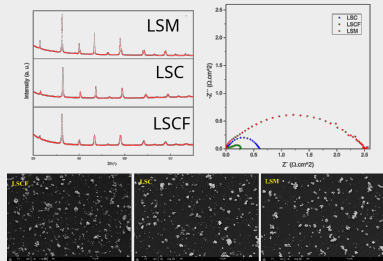
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# LSCF, LSM, NiO...

## Quelques propriétés physico-chimiques

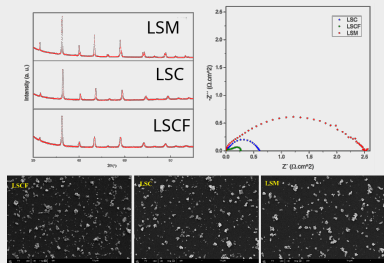
### Structure & Morphologie



# LSCF, LSM, NiO...

## Quelques propriétés physico-chimiques

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▶ perovskite majoritaire



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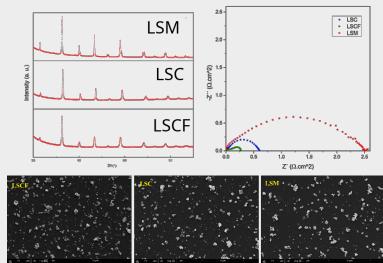


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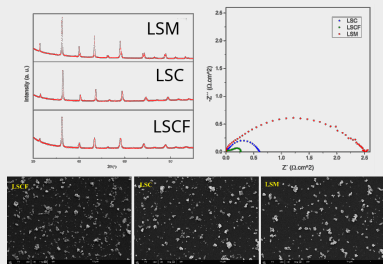
- ▶ perovskite majoritaire
- ▶ morphologies comparables



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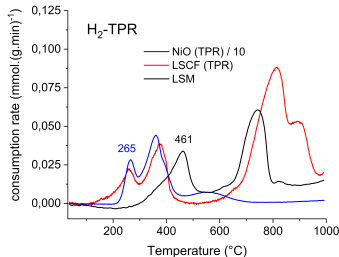
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### réactivité redox



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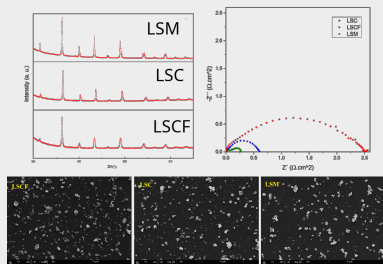
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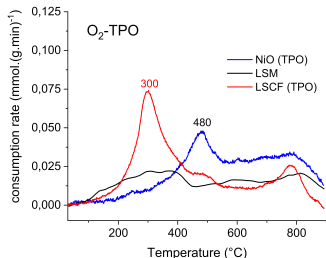
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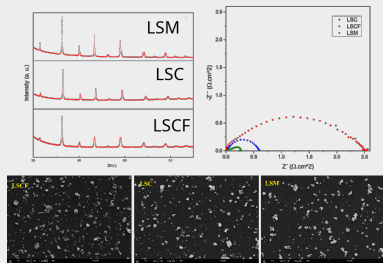
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#### TPR-TPO

- ▶ NiO réductible sous H<sub>2</sub> (HOR)
- ▶ LSCF re-oxidable sous O<sub>2</sub> (ORR)



## Elements d'anatomie d'une électrode performante

LSCF + NiO = LSFN

## Le système BCTF



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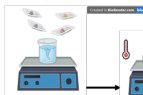
**KNOWSKITE-X**

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# Exploration dans le système LSFN

Mixing starting materials in deionized water at room temperature



$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$   
 $\text{Sr}(\text{NO}_3)_2$   
 $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$   
 $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$   
 Citric Acid  
 Glycine

Drying the solution on hot plate until the combustion



The resulting ash-like powder



Grinding with an Agate Pestle

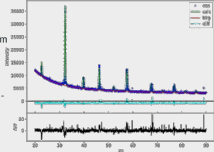


## Structure



### Rietveld refinement data:

Crystallite size: 176 nm  
 $a = 5.5528 \text{ \AA}$   
 $b = 5.5288 \text{ \AA}$   
 $c = 7.8276 \text{ \AA}$   
 Density: 6.725  
 Space group: P b n m -  
 Orthorhombic



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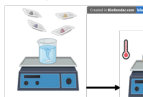


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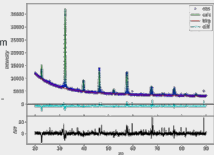


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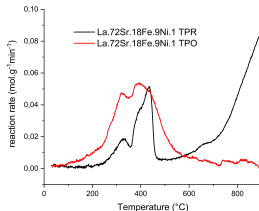


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## activité redox



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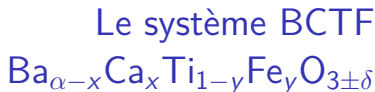
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## Motivation et Approche

cation	rayon ionique
$\text{Ba}^{2+}$	1.61 Å
$\text{Ca}^{2+}$	1.34 Å
$\text{Ti}^{2+}$	0.605 Å
$\text{Fe}^{3+}$	0.645 Å

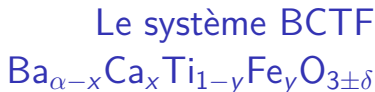


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## Motivation et Approche

- ▶ Métaux abondants, non toxiques et non critiques

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$\text{Ba}^{2+}$	1.61 Å
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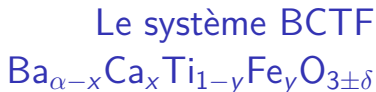


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## Motivation et Approche

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- ▶ Couple redox  $\text{Fe}^{3+} / \text{Fe}^{2+}$

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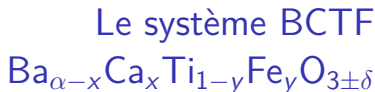
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## Motivation et Approche

- ▶ Métaux abondants, non toxiques et non critiques
- ▶ Couple redox  $\text{Fe}^{3+} / \text{Fe}^{2+}$
- ▶ Perovskite de base:  $\text{BaTiO}_3$

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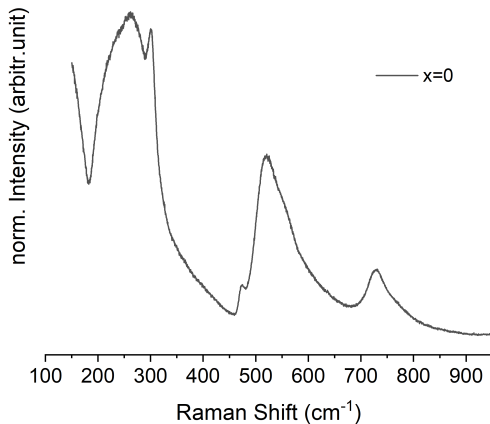
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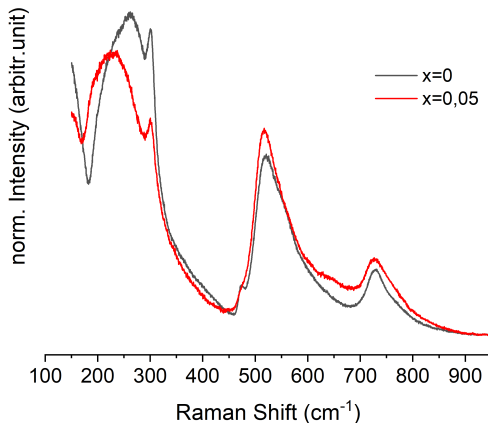


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# Structure des B85CTF0-20



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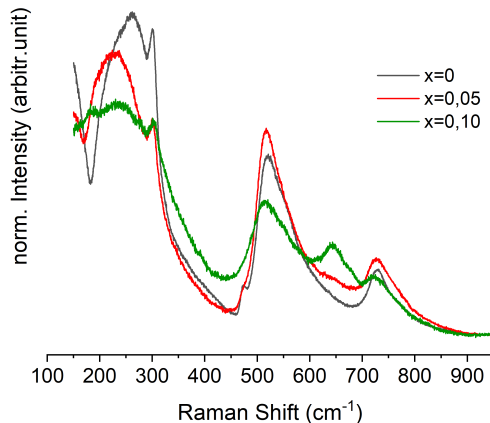


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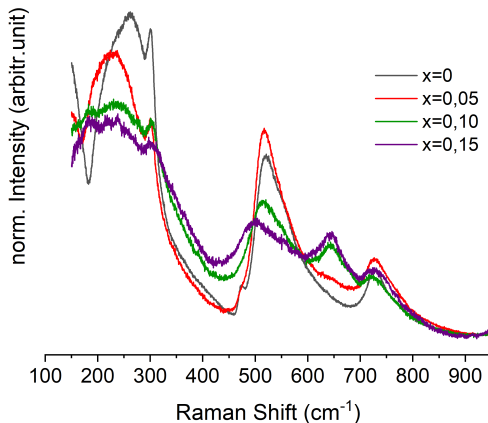


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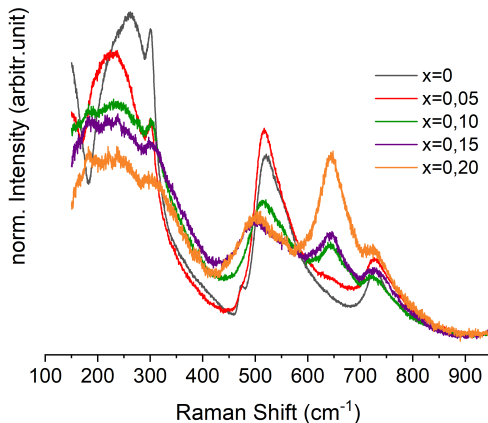
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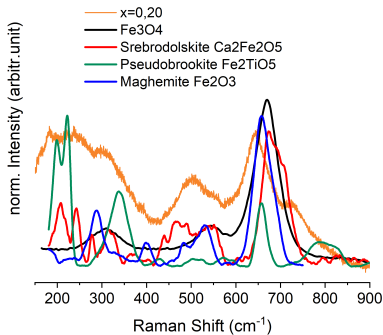
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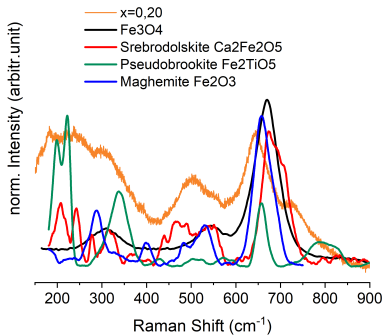


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## Structure

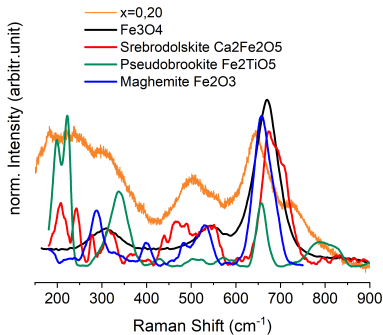




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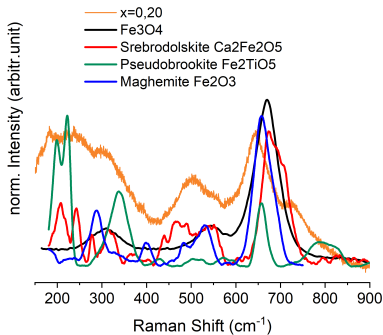
▶ Fe en solution?





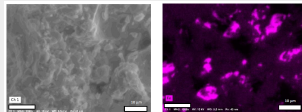
## Structure

- ▶ Fe en solution?
- ▶ DRX accord



## Structure

- ▶ Fe en solution?
- ▶ DRX accord
- ▶ EDS (15kV, x2000):


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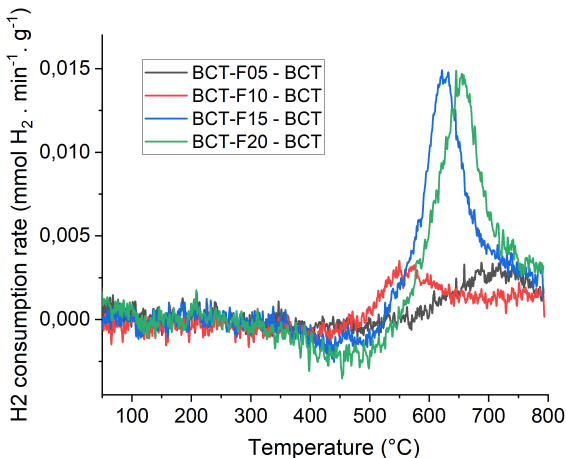
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# Réductibilité des B85CTF-5 à 20



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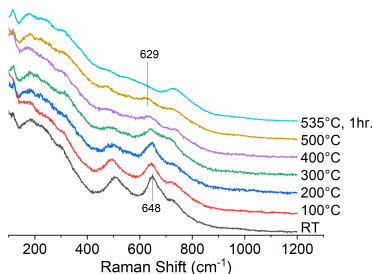


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# Cyclage redox de B85CTF-20

## exploration structurale de la réduction (HOR)

Spectro. Raman *in situ*  
pendant la RPT

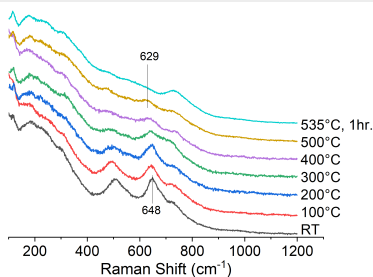




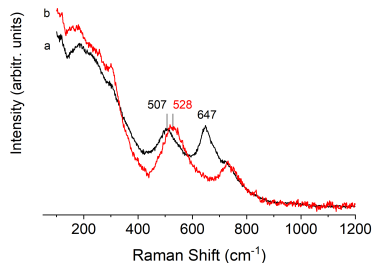
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### Retour à Tamb.



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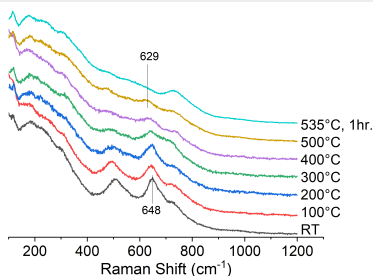
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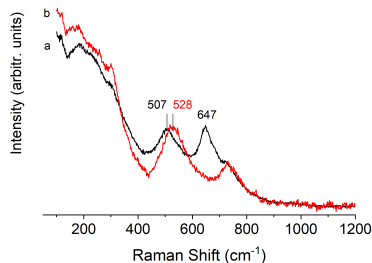
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### Retour à Tamb.



### post-TPR

La phase "Fe" est réduite



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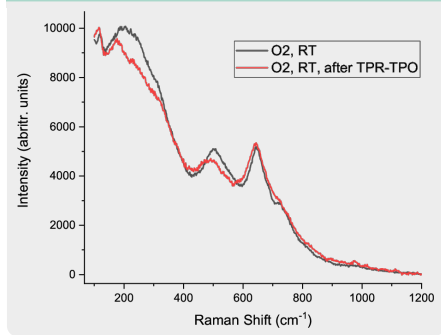
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# Cyclage redox de B85CTF-20

## exploration structurale de la ré-oxydation (ORR)

### Spectro. Raman *in situ* après la TPO



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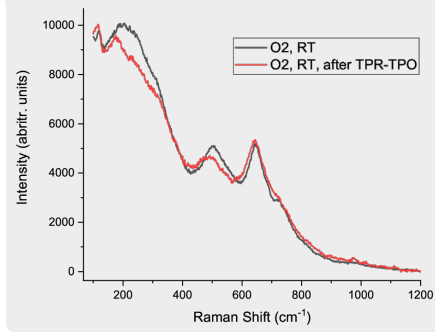
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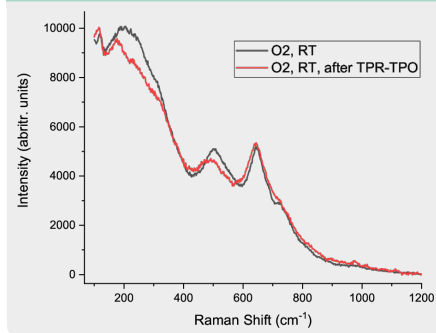




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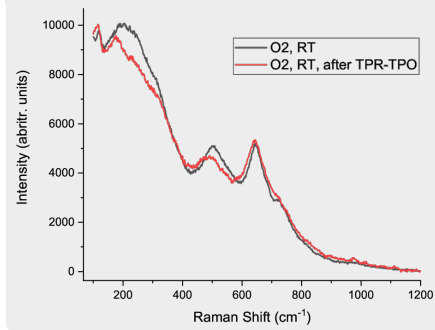
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## Quelques Conclusions

- ▶ Approche "catalyse hétérogène" des matériaux d'électrode:
  - ▶ surface: quantitatif-qualitatif
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  - ▶ *operando*
  - ▶ réactions modèles (eg. réactivité méthanol, NH<sub>3</sub>, CO<sub>2</sub>...)



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Merci pour votre attention



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