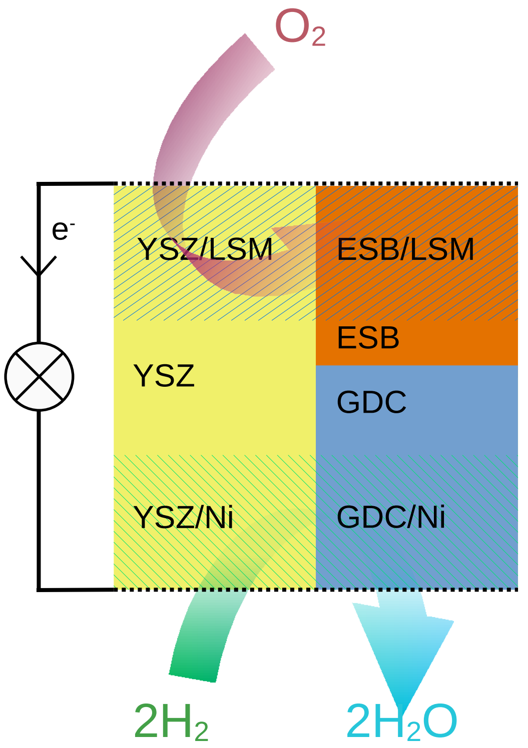
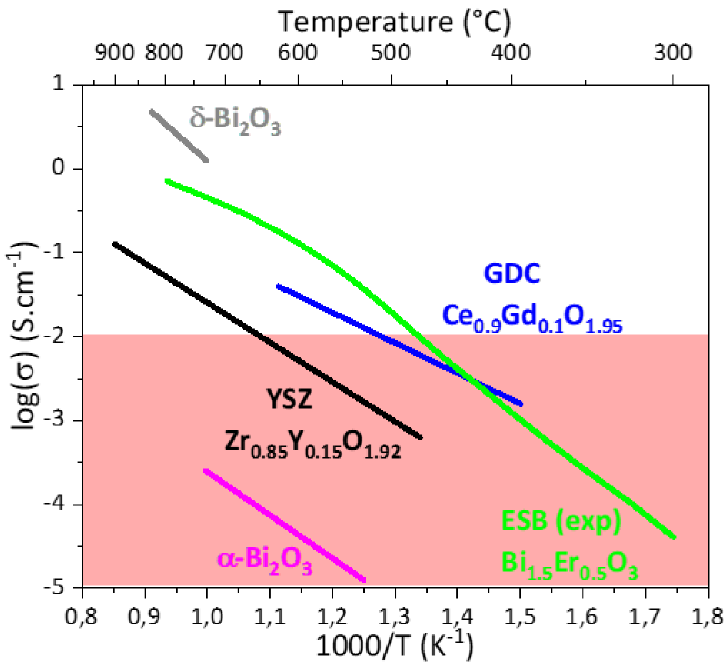
Victor Duffort, Martin Pajot, Soukaina Mountadir, Edouard Capoen,
Anne-Sophie Mamede, Rose-Noëlle Vannier

Influence de la teneur en strontium sur les performances des électrodes composites $Bi_{1.5}Er_{0.5}O_3/La_{1-x}Sr_xMnO_3$ pour SOFC basse température

1ère REUNION PLENIERES de la Fédération HYDROGENE (FRH2) du CNRS
1er juin 2021

Bi-layered electrolytes for LT-SOFC





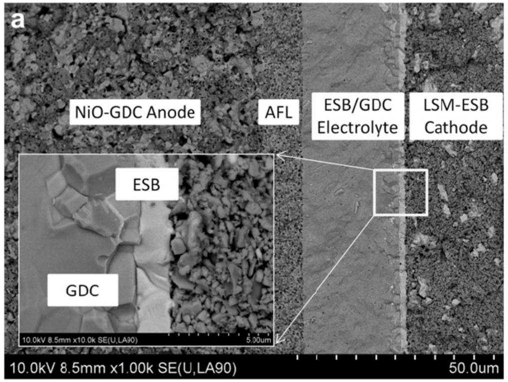
YSZ based SOFC ⇒ 800 °C

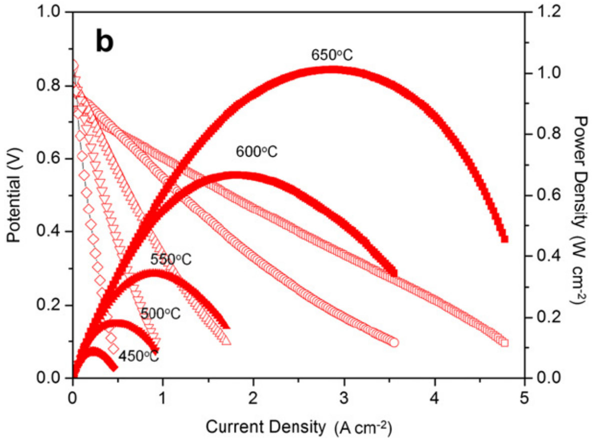
- ➔ Aging
- ➔ Materials compatibility

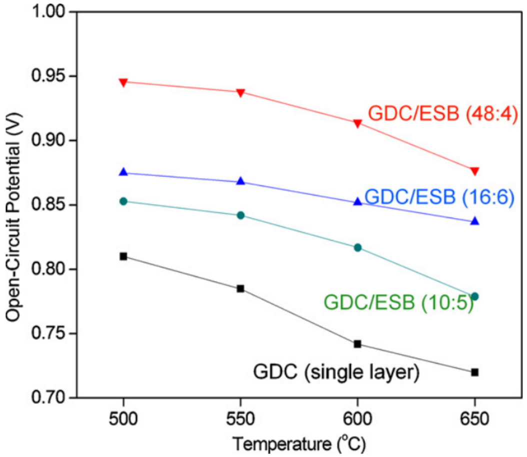
YSZ substitution by better ionic conductors

- ➔ Cathodic compartment $Bi_{2-x}Er_xO_3$ (ESB), minimizes electronic leakage from GDC.
- ➔ Anodic compartment $Ce_{1-x}Gd_xO_{3-\delta}$ (GDC), protects ESB from reduction

Ni/GDC|GDC|ESB|LSM/ESB







~1 W cm^{-2} @ 650 °C[1]

Cell optimization with fixed LSM composition[2-3].

➔ LSM = $La_{0.8}Sr_{0.2}MnO_3$, *i.e.* high temperature material

SrO segregation 1000 °C[4]

What is the optimum composition of $La_{1-x}Sr_xMnO_3$ for low temperature applications?

1 – M. Camaratta *et al.*, *J. Electrochem. Soc.*, ***2008***, *155, B135*
2 – S. J. Jim *et al.*, *J. Power Sources*, ***2017***, *344, 218*
3 – J. W. Park *et al.*, *J. Hydrogen Energy*, ***2017***, *42, 6332*
4 – J. Druce, *Energy Environ. Sci.*, **2014**, 7, 3593

Structure and synthesis of $La_{1-x}Sr_xMnO_{3+\delta}$

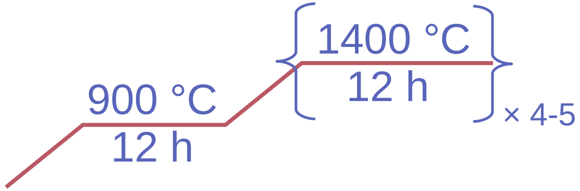
Solid state synthesis

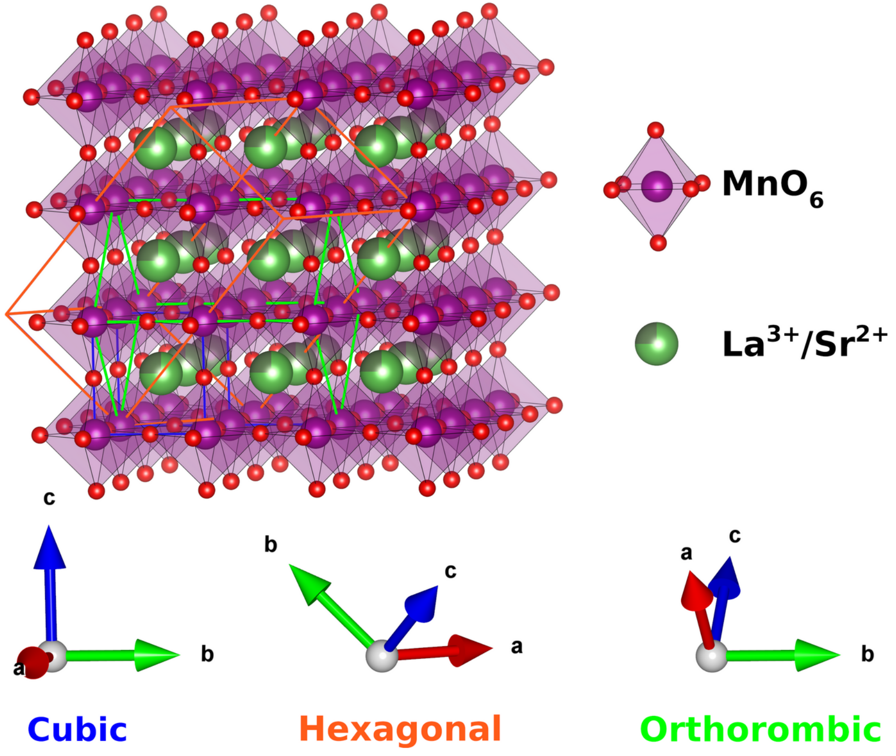
Starting materials

➔ La_2O_3, $SrCO_3$, MnO

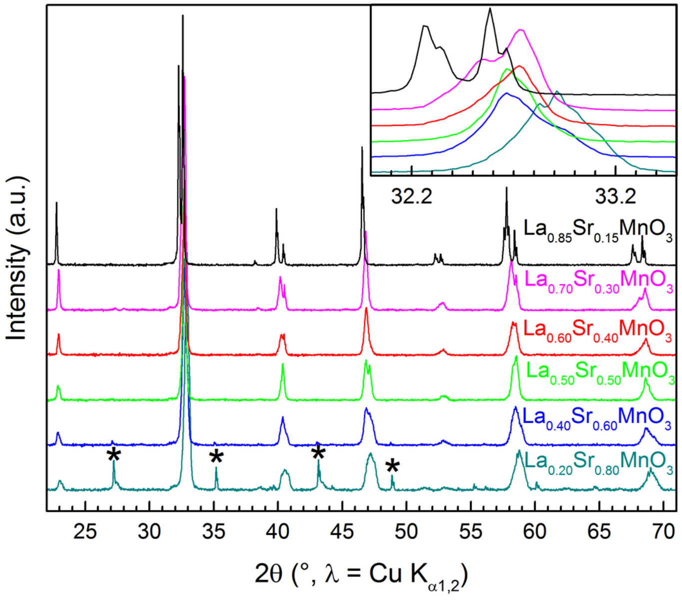
Six compositions
x = 0.15, 0.3, 0.4, 0.5, 0.6, 0.8

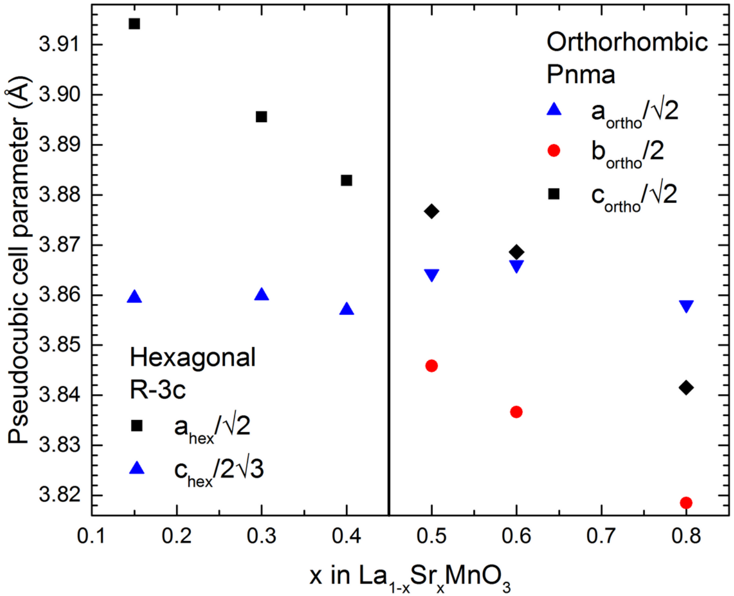
Heat treatment





Structural characterization





Goldschmidt tolerance factor

- ➔ $LaMnO_3 \Rightarrow t = 0.95$
- ➔ $SrMnO_3 \Rightarrow t = 1.04$

4H-hexagonal perovskite impurity for $x > 0.6$

Small overall distortion from cubic structure

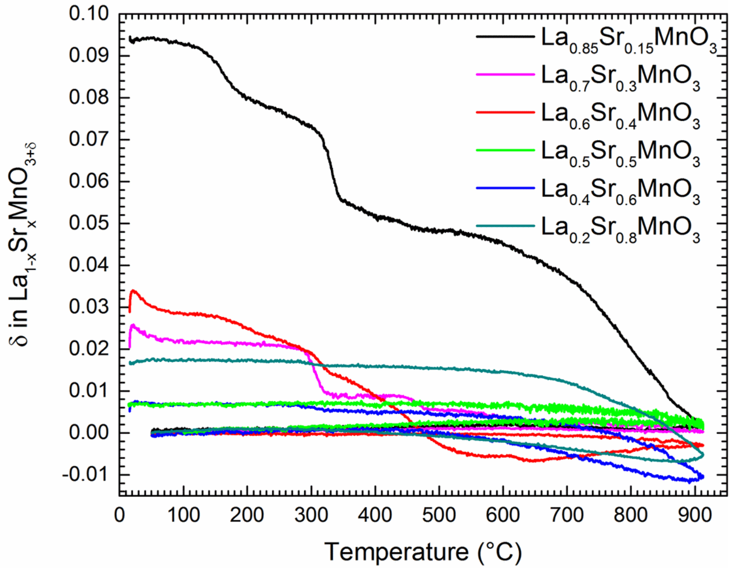
Hexagonal to orthorhombic transition for $x > 0.4$

Transition related to oxygen stoichiometry

M. Pajot *et al.*, *J. Power Sources*, ***2020***, *450, 227649*

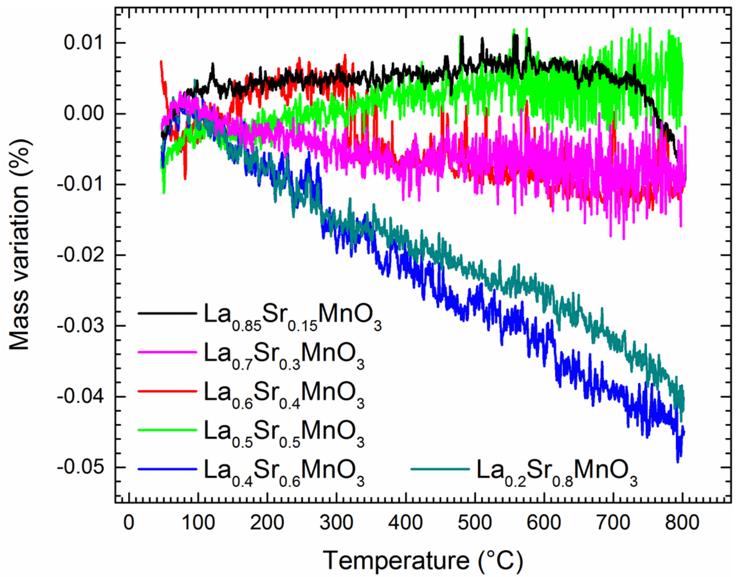
Oxygen stoichiometry in $La_{1-x}Sr_xMnO_{3+\delta}$

Evaluation of the oxygen stoichiometry by TGA under argon



- ➔ 900 °C annealing under Ar yields $\delta = 0$
- ➔ oxygen content proportional to Mn^{3+} content

Evaluation of the oxygen stoichiometry stability in air

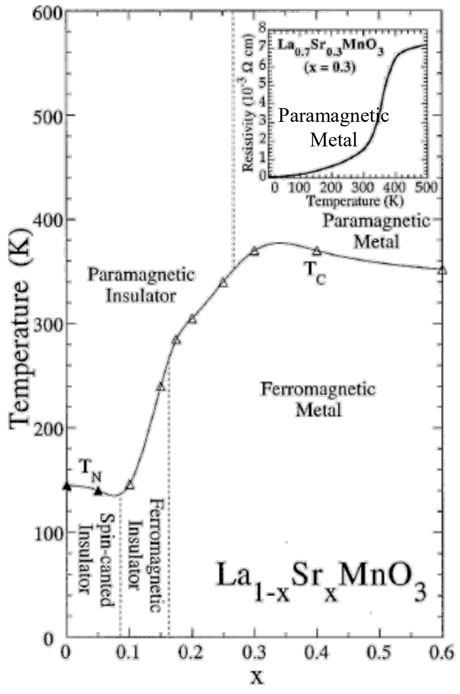


- ➔ Over-stoichiometry is stable in the temperature range of interest RT – 800 °C
- ➔ Oxygen uptake during synthesis

M. Pajot *et al.*, *J. Power Sources*, ***2020***, *450, 227649*

Electronic transport characterization

Magneto transport properties are well studied but high temperature not so much.

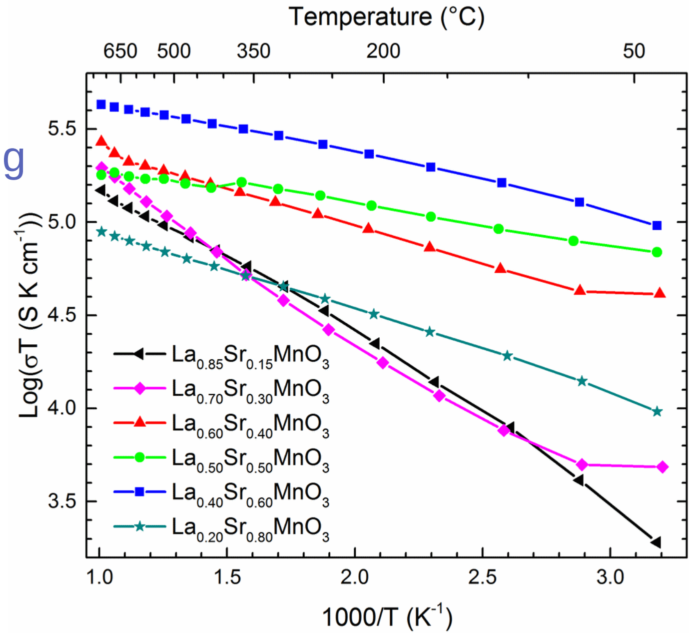


All compositions are semi-conducting in the paramagnetic state

Activation energy decreases with increasing Sr^{2+} substitution

Maximum conductivities are obtained for $0.4 < x < 0.6$

High temperature electronic conductivity in air

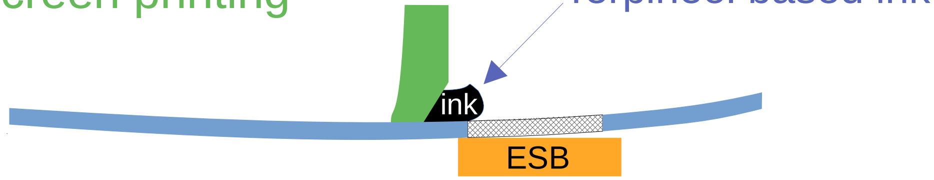


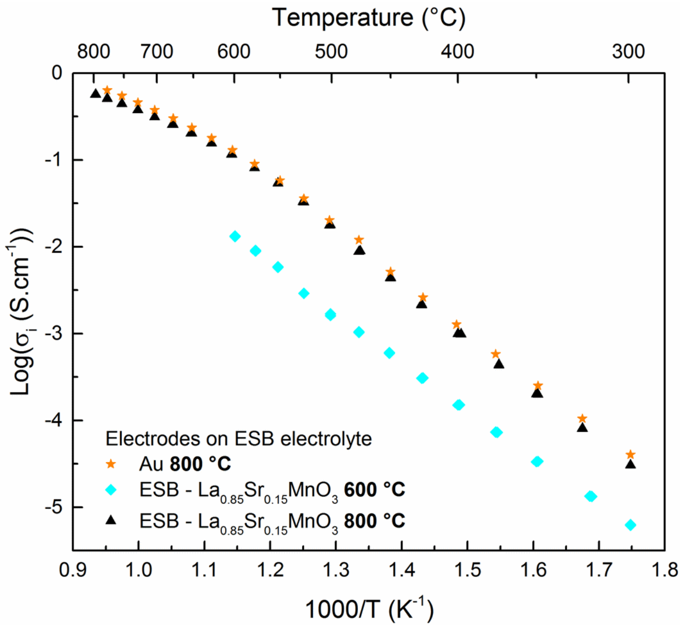
M.C. Martin *et al.*, *Phys. Rev. B*, ***1995***, *53*, *14285*

M. Pajot *et al.*, *J. Power Sources*, ***2020***, *450*, *227649*

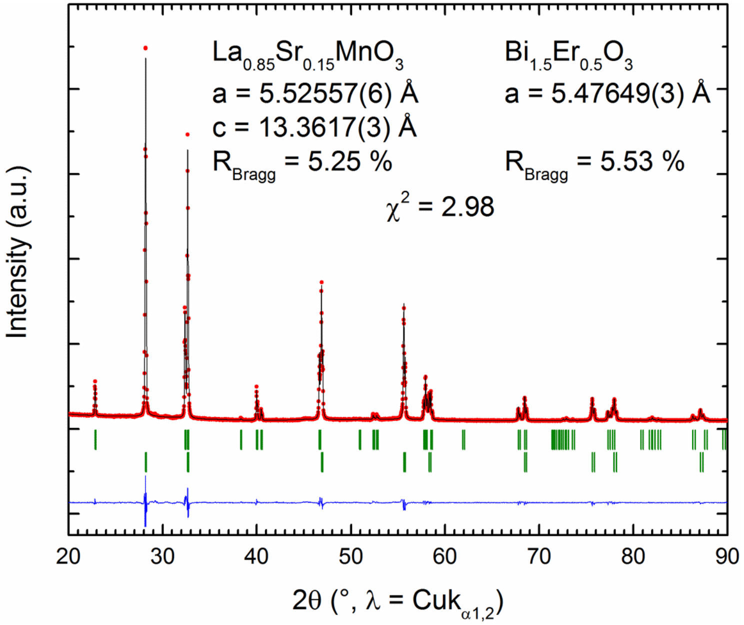
Electrode sintering

Screen printing

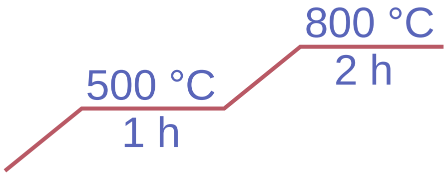


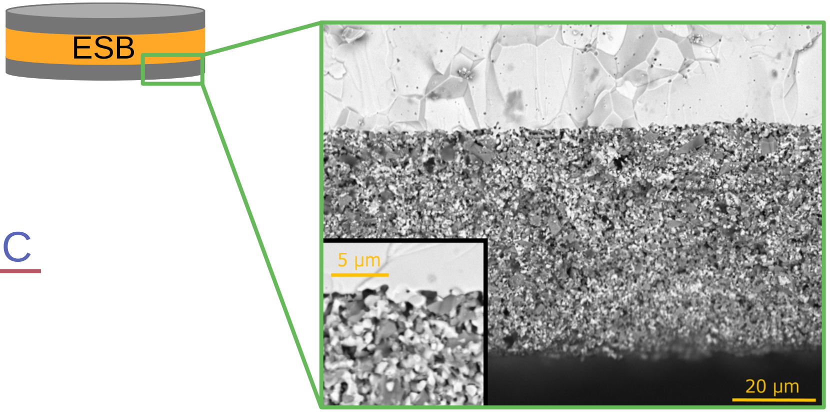


No reactivity up to 800 °C

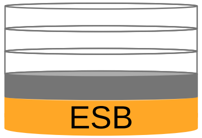


Heat treatment



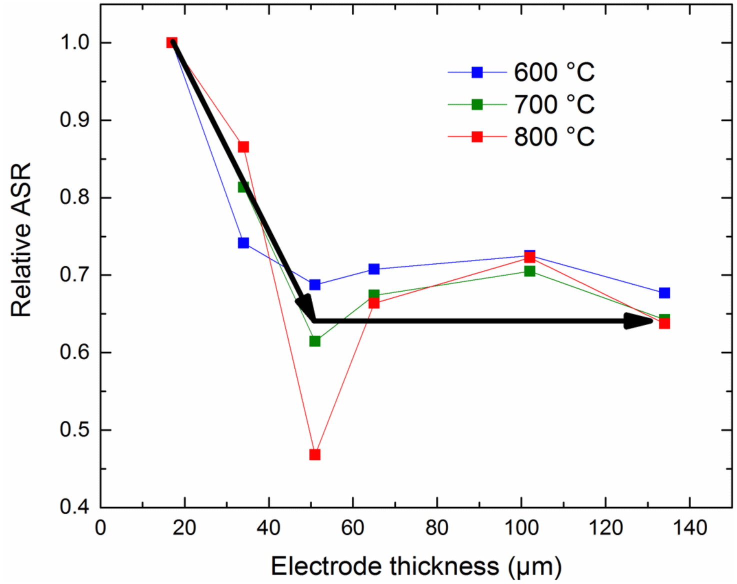


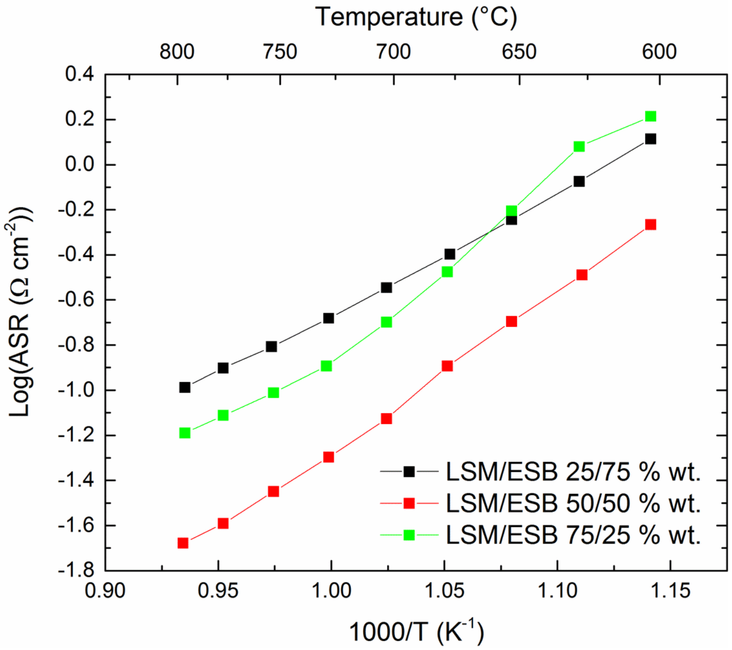
Electrode optimization

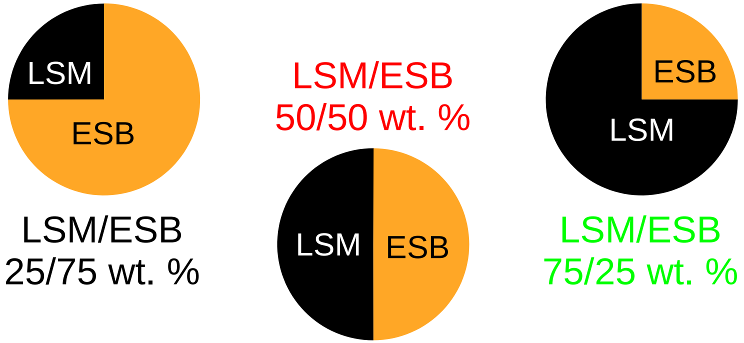


~ 17 µm per layer

3 layers, *i.e.* ~45 µm is best

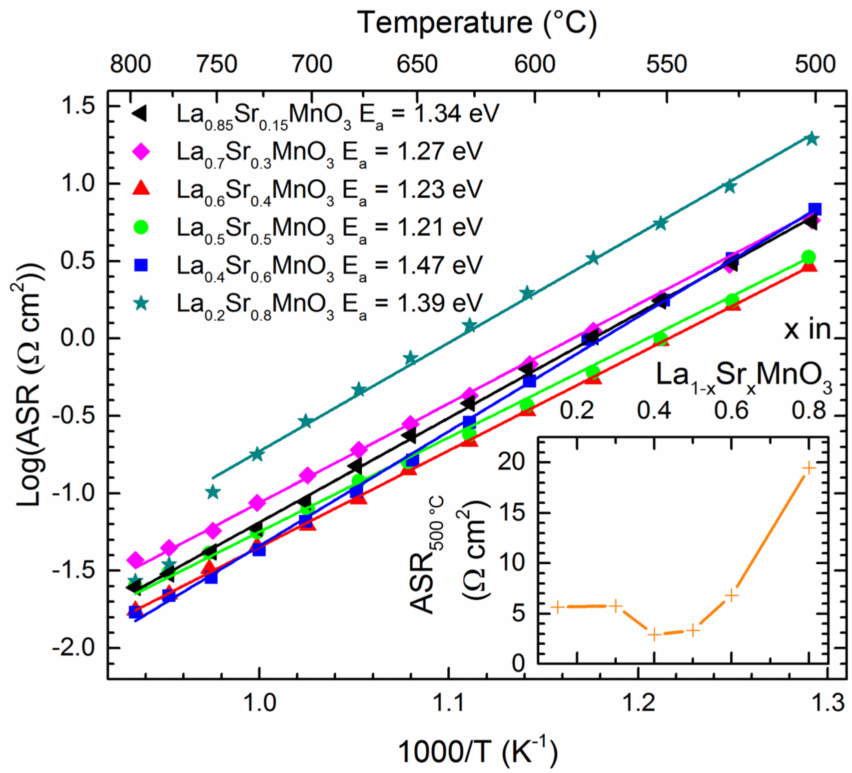






Catalytic activity

Composition	δ	Spc. Grp.	a (Å)	b (Å)	c (Å)	σ@500 °C (S cm^{-1})	Avg. Mn Ox. Sate
$La_{0.85}Sr_{0.15}MnO_{3+\delta}$	0.09	$R\bar{3}c$	5.53551(5)		13.3694(2)	117	3.3
$La_{0.7}Sr_{0.3}MnO_{3+\delta}$	0.02	$R\bar{3}c$	5.5092(5)		13.371(1)	131	3.3
$La_{0.6}Sr_{0.4}MnO_{3+\delta}$	0.03	$R\bar{3}c$	5.4912(4)		13.361(1)	235	3.5
$La_{0.5}Sr_{0.5}MnO_{3+\delta}$	< 0.01	*Pnma*	5.4650(3)	7.6917(4)	5.4825(3)	215	3.5
$La_{0.4}Sr_{0.6}MnO_{3+\delta}$	<0.01	*Pnma*	5.4670(2)	7.6732(1)	5.471(2)	474	3.6
$La_{0.2}Sr_{0.8}MnO_{3+\delta}$	<0.01	*Pnma*	5.4561(1)	7.6369(1)	5.4327(1)	86	3.8



Best results for x ~ 0.4 – 0.5

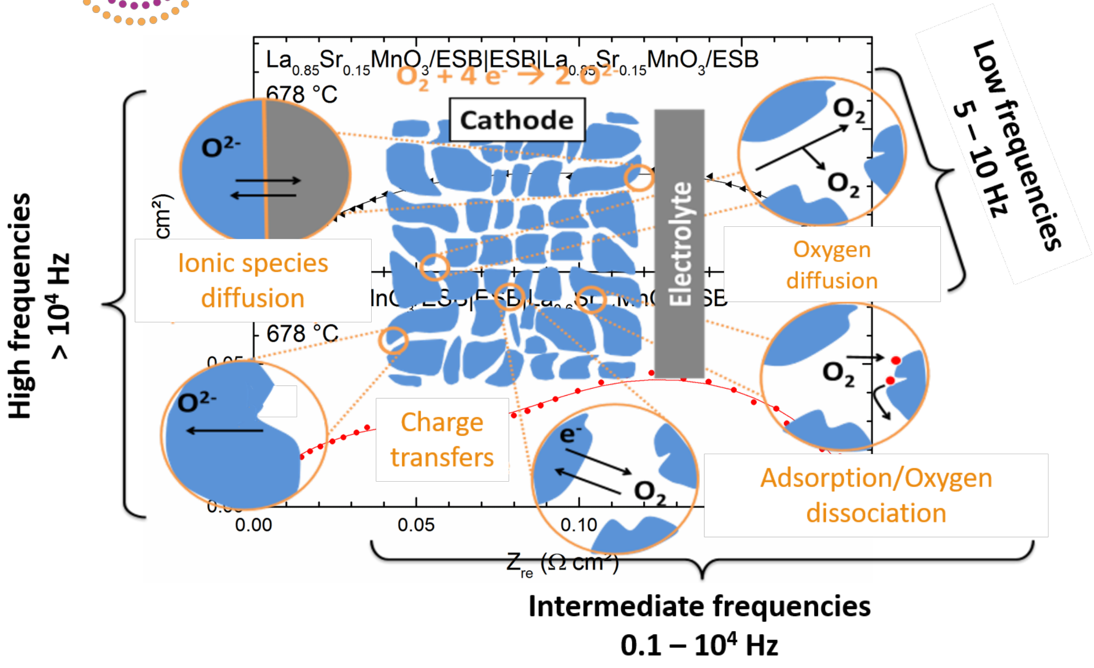
➔ Not related to the crystal structure

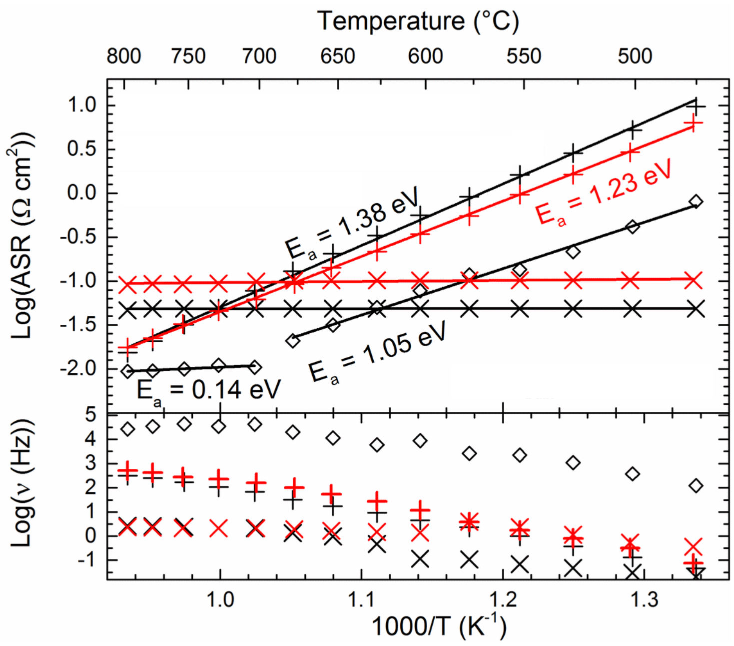
➔ Not directly related to the conductivity

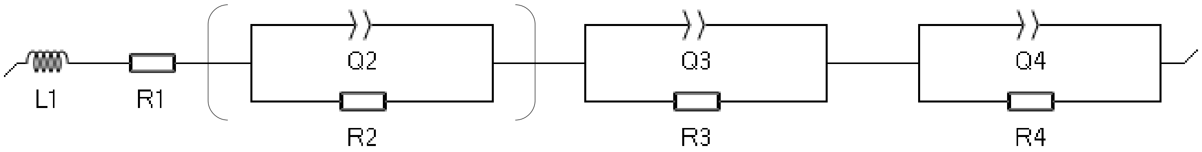
Comparative study of $La_{0.85}Sr_{0.15}MnO_3$ and $La_{0.6}Sr_{0.4}MnO_3$

M. Pajot *et al.*, *J. Power Sources*, ***2020***, *450*, 227649

ORR mechanism







Bulk incorporation

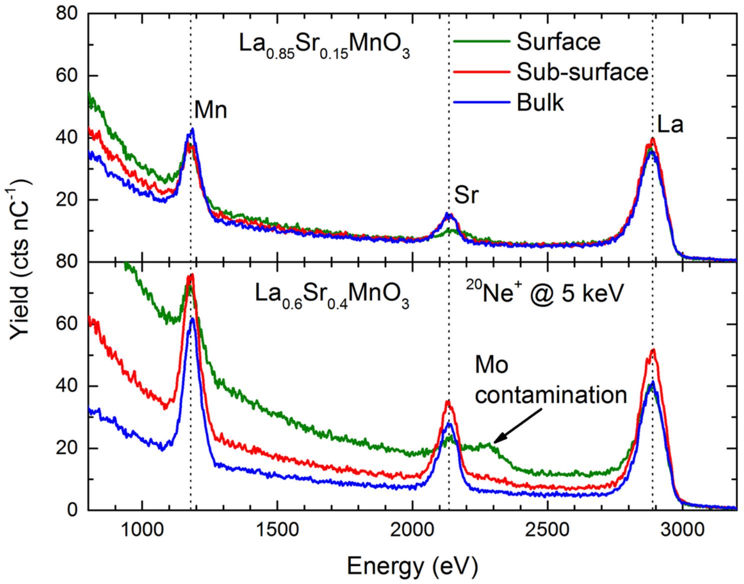
O_2 gas diffusion

Dissociative adsorption

M. Pajot *et al.*, *J. Power Sources*, ***2020***, *450, 227649*

Surface composition

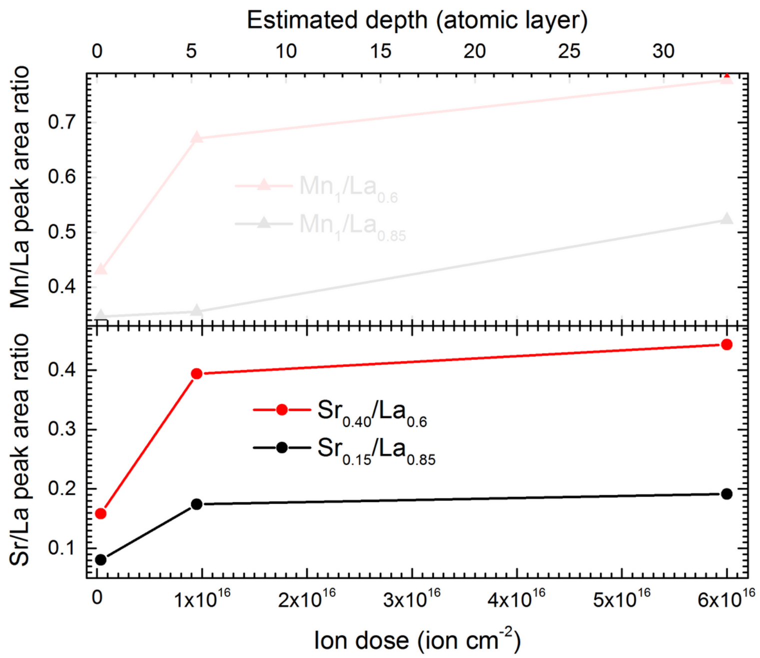
LEIS spectra of samples annealed at 800 °C



No evidence of SrO segregation at 800 °C

Rapid equilibrium of A-site vacancy concentration

Mn surface depletion in $La_{0.85}Sr_{0.15}MnO_{3+\delta}$



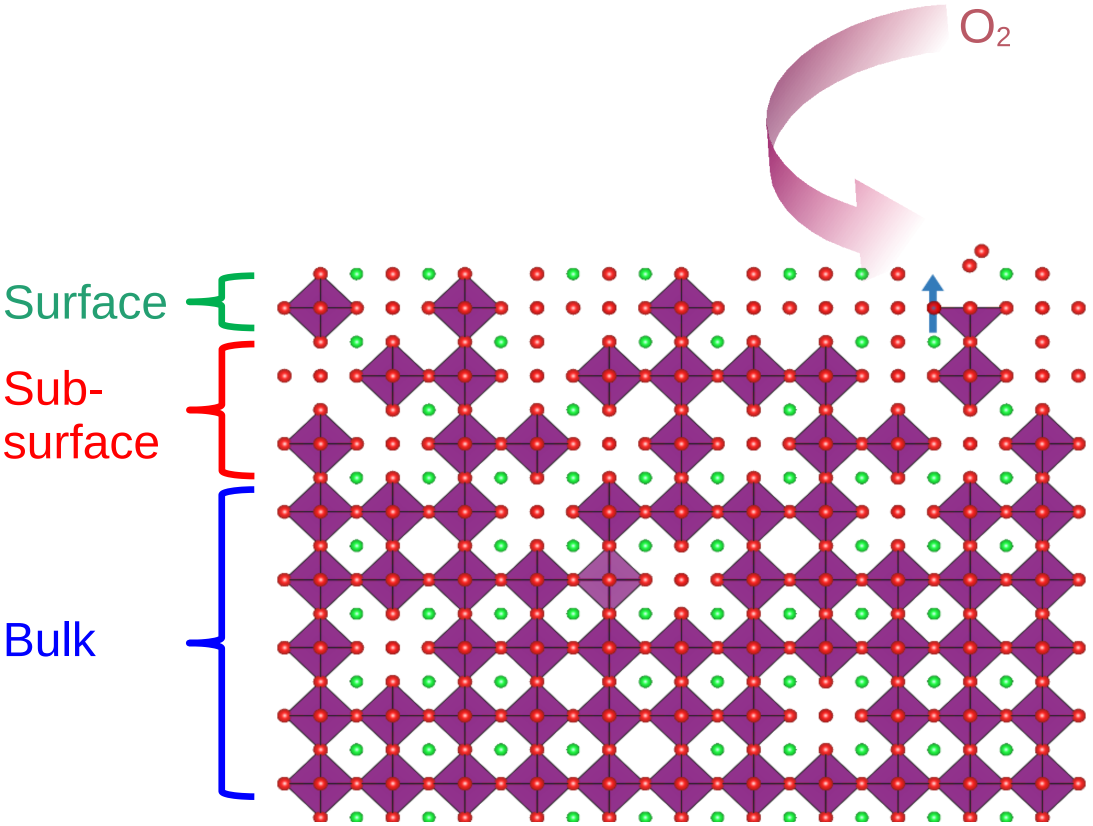
M. Pajot *et al., J. Power Sources*, ***2020***, *450, 227649*

Oxidation mechanism

$La_{1-x}Sr_xMnO_{3+\delta}$

⇕

$(La_{1-x}Sr_xMn)_{1-y}O_3$



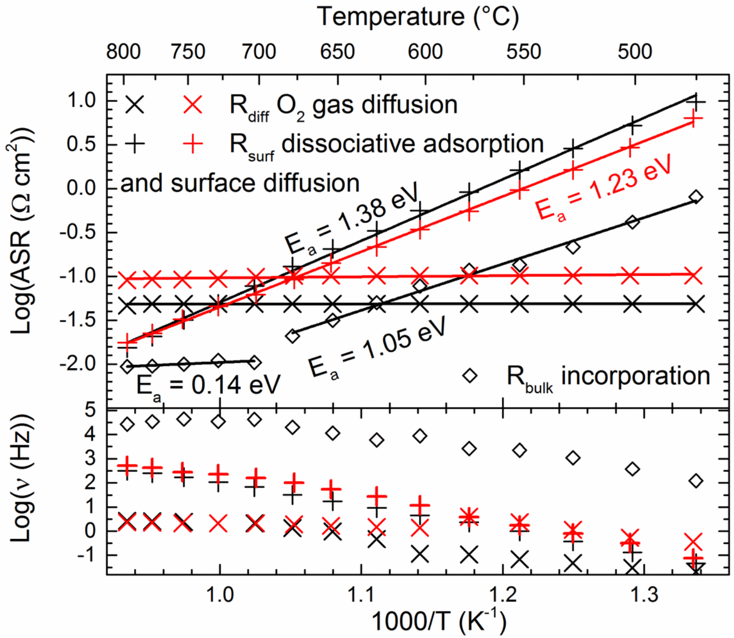
$x = 0.15 \Rightarrow \delta = 0.09$ // $y = 0.03$
$x = 0.40 \Rightarrow \delta = 0.03$ // $y = 0.01$

High mobility on A-site ⇒ vacancy diffusion
Low mobility on B-site ⇒ surface vacancies

J.F. Mitchell *et al.*, *Phys. Rev. B*, ***1996***, *54*, *6172*

Conclusion

Improved ORR



Faster surface and bulk kinetics

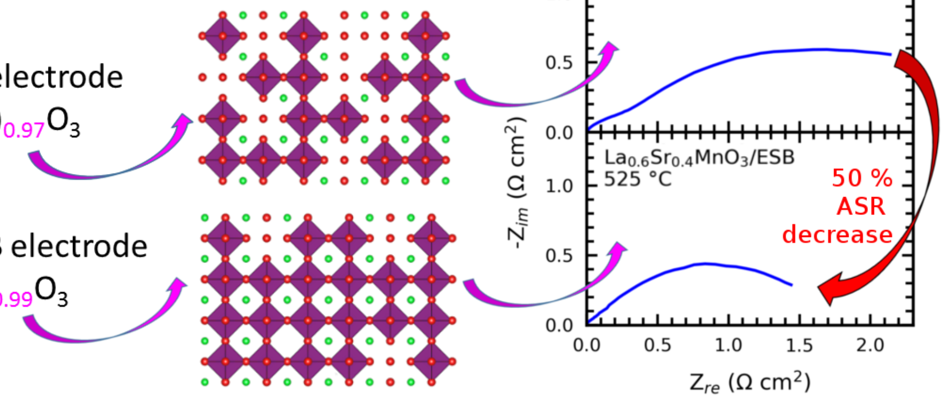
Electrode composition optimization

$(La_{1-x}Sr_xMn)_{1-y}O_3$/ESB composite electrodes

Cationic vacancy distribution

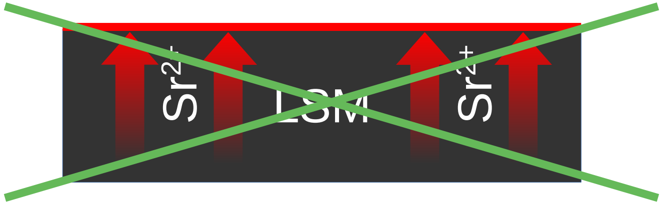
Typical LSM/ESB electrode $(La_{0.85}Sr_{0.15}Mn)_{0.97}O_3$

Optimized LSM/ESB electrode $(La_{0.6}Sr_{0.4}Mn)_{0.99}O_3$



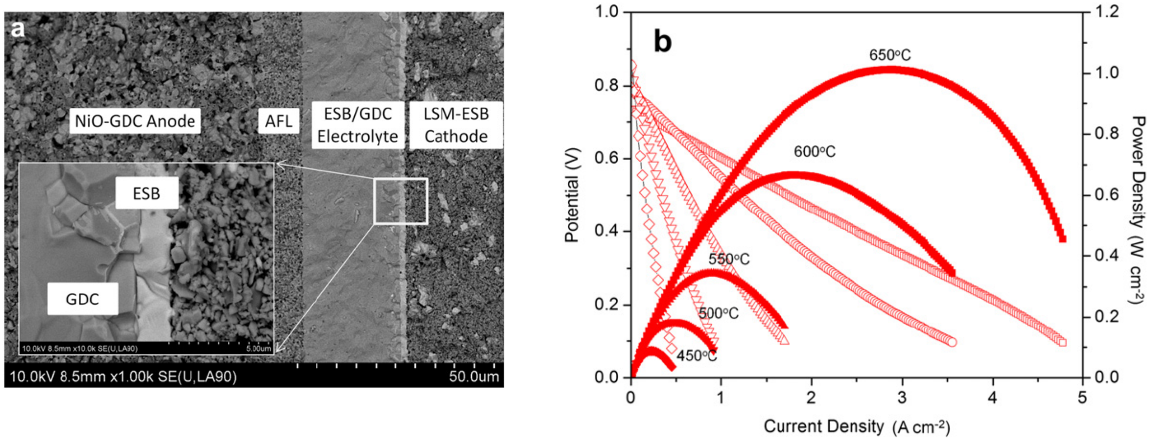
Surface behavior of LSM at reduced temperature

No SrO segregation at the surface of LSM up to 800 °C



Perspectives // Acknowledgments

Full cell test with GDC/ESB electrolyte



Finer understanding of the ORR kinetics

- ➔ dissociation coefficients
- ➔ surface composition

Ph.D students
M. Pajot
S. Mountadir

Experimentalists
A.-S. Mamede (LEIS)
R. Jooris (EIS)
E. Capoen (EIS)

Team Member
R.-N. Vannier

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AGENCE NATIONALE DE LA RECHERCHE ANR

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Région Hauts-de-France

M. Camaratta *et al., J. Electrochem. Soc.*, ***2008***, *155, B135*