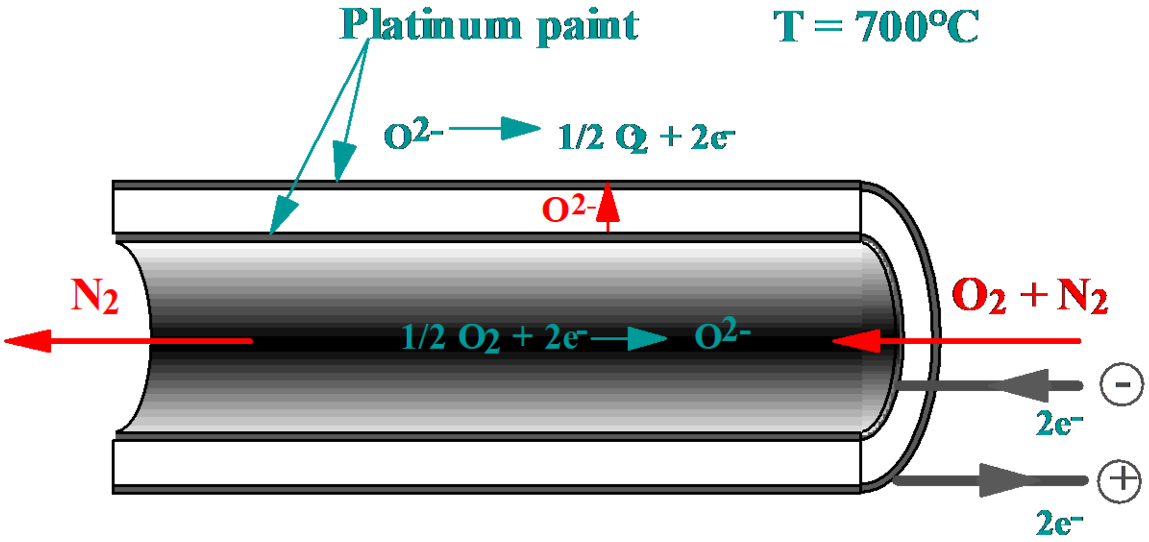
Quatrième partie :

Quelques applications dans le domaine des capteurs électrochimiques hautes températures

- **Oxygen electrochemical pump**



Platinum paint

T = 700°C

$O^{2-} \longrightarrow 1/2\ O_2 + 2e^-$

O^{2-}

N_2

$O_2 + N_2$

$1/2\ O_2 + 2e^- \longrightarrow O^{2-}$

⊖

$2e^-$

⊕

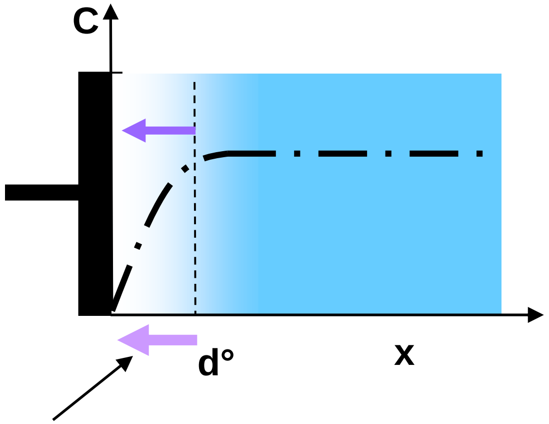
$2e^-$

Amperometric chemical sensors

Passive sensors: need an external source

Theory (electrochemistry) :

- **under current : species are consumed at the electrode: ex ox + ne$^-$ $\longrightarrow$ red**



from 0 to a distance x from the electrode: decrease of the concentration of oxidizer

d° is the thickness of the diffusion layer

- **The diffusion flux of the oxidizer and then the current intensity is limited and proportional to C and 1/d°**

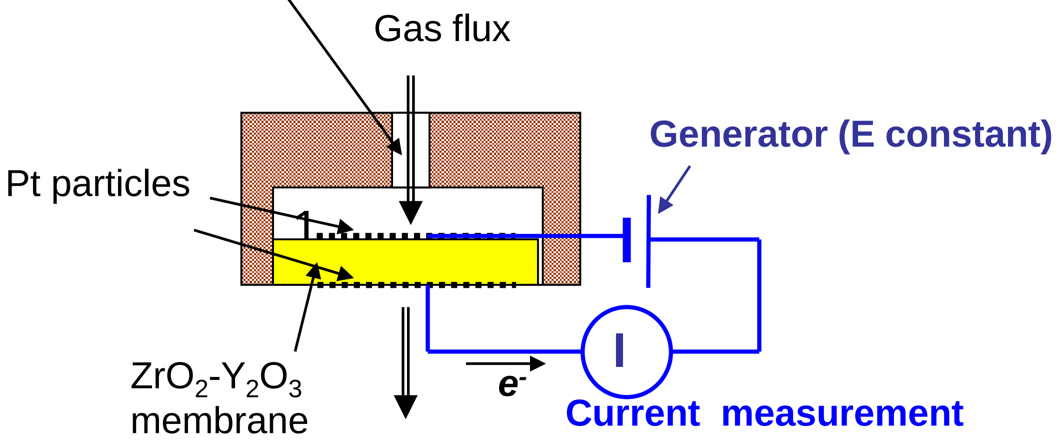
with d° fixed by:

- **the mobility of the specie**
- **a physical barrier**

First kind sensor (direct transduction)

Charge carrier in the conducting membrane is the analysed specie

Physical barrier to limit gas diffusion: micrometric hole



Fick law $\rightarrow I_{lim} \propto P_{O2}$

Reactions:

Interface 1(interior):
cathode

$$O_2 + 4\,e^{-}_{Pt} \rightarrow 2\,O^{2-}$$

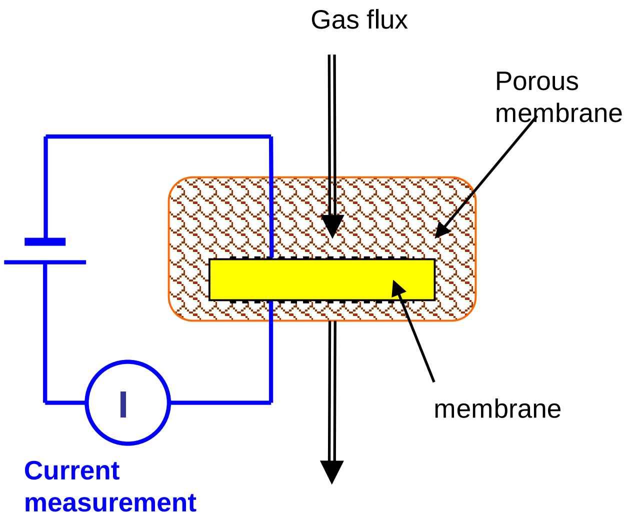
Interface 2 (exterior)
anode

$$2\,O^{2-} \rightarrow O_2 + 4\,e^{-}_{Pt}$$

Current value corresponding to an O_2 concentration equal to 0 at the cathode interface

Other configuration:

Porous membrane limiting gas diffusion



Current measurement

For:

$O_{2,}$, H_2O, NO_x, H_2 ….

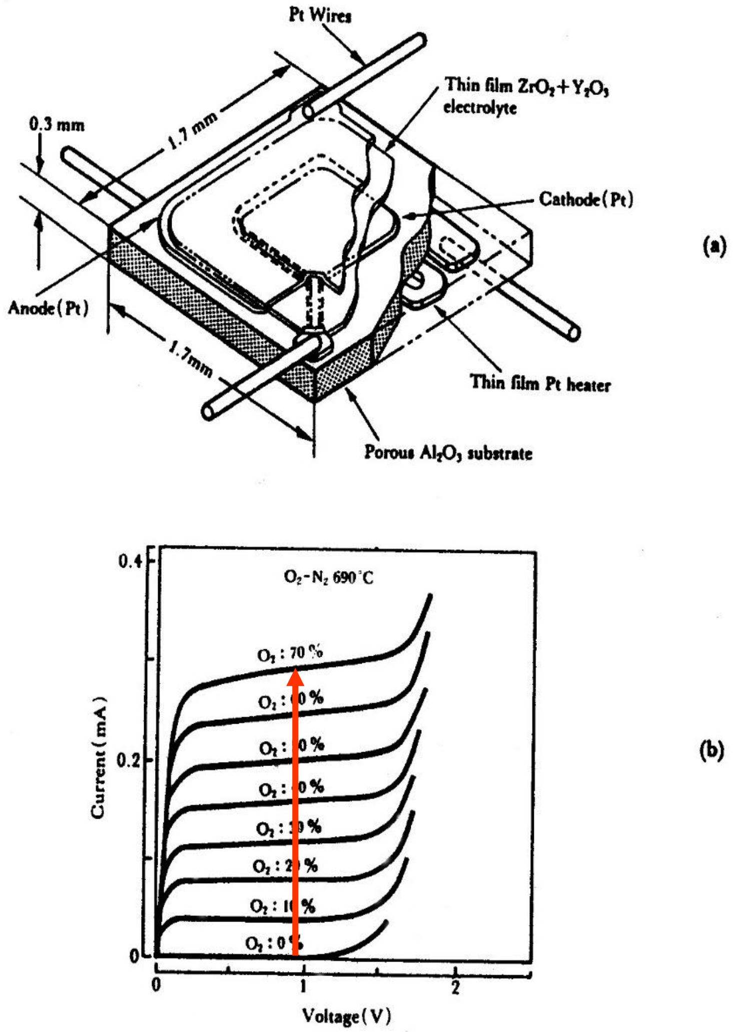
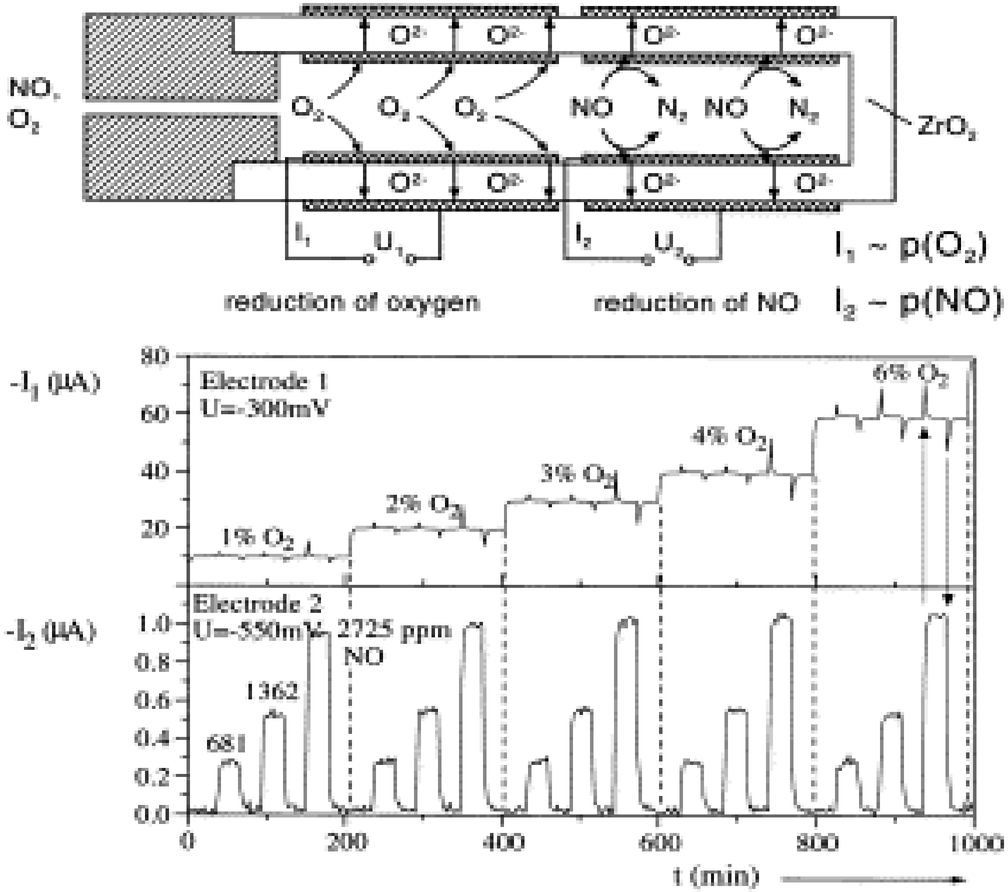


Fig. 4 Thin film limiting current type oxygen sensor.
(a) Structure
(b) Current *vs.* voltage characteristic at 690℃ for various oxygen concentrations (vol % O_2) in O_2-N_2 gas mixtures.

Presence of two pairs of electrodes



Development :

Optimization of

the electrode material

(catalytic effects)

Example of compounds :

$Ce_{0.8}Gd_{0.2}O_{1.9}$

to catalyse O_2 reduction

$Gd_{0.7}Ca_{0.3}CoO_{3-\delta}$

to catalyse NO reduction

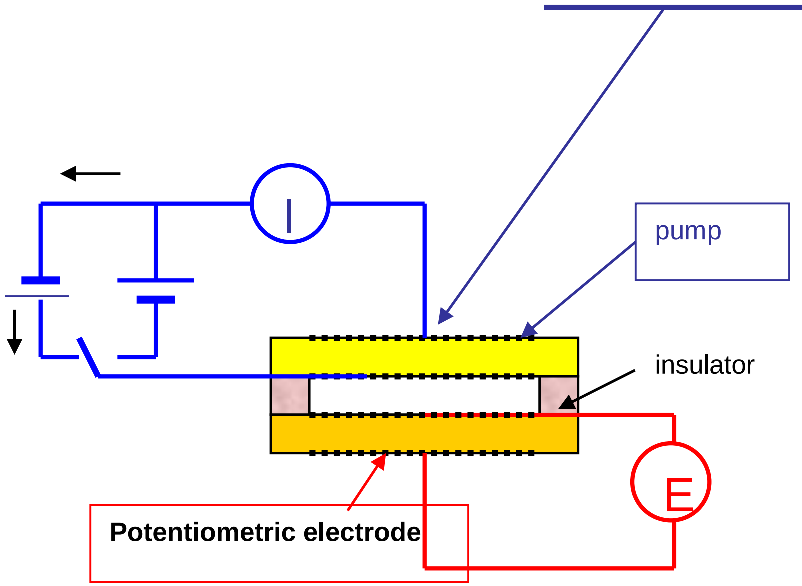
Miniaturisable system…

Coulometric chemical sensors

A combination of two zirconia based sensors:

1 - Electrochemical reaction:

$O_2 + 4\,e^- \rightarrow 2\,O^{2-}$ and $2\,O^{2-} \rightarrow O_2 + 4\,e^-$



2 – Potentiometric O_2 sensor

ΔP_{O2} indicator

2 stages :

1- the chamber is emptied

2- and filled up until $\Delta P_{O2} = 0$

Gas : $P = n\dfrac{RT}{V°}$

Faraday : $n = I\,t\,/4\,F$

Response :

$$P = I \times t\,\frac{RT}{4FV°}$$

Conclusion :

Amperometric gas sensors are based on

The measurement of an electronic current at a constant potential

The measured current is linked to electrochemical reactions:

Involving the analyzed specie
Controlled by the diffusion of the reactant

The principle is based on the used of ionic ceramic conductors

Stabilized (or doped) zirconia is also used and present a good life time

The response law is linear (type : $I = f(\text{activity}_{\text{analysed specie}})$

Example of the synthesis and the characterization of NASICON-type ceramics for environmental applications

The basic steps for the elaboration of the sensor :

1- Bibliographic study for the choice of the membrane material

Required properties:
* High water stability
* High ionic conductivity
* High selectivity

2- Synthesis of the ceramic compounds

Solid state reaction or sol-gel synthesis or….. ?

3- Physico-chemical characterization of the materials

To prepare an high quality ceramic
To optimise the detection and selectivity properties of the membrane

4- Fabrication of the sensor and evaluation of the performance in situation

Main advantages of the NASICONs:

- very **hard** material (ceramic !!!)

- oxide compound (chemically **# inert**)

- very good **ionic** conductor at low T which induced a **low impedance and a fast** transduction of the sensors

- structure (i.e. conductive sites) adaptable to the analysed cation

Compositions studied to optimize the conduction and the selectivity towards lithium ion:

$\mathbf{Li_{1+x}Al_xTi_{2-x}(PO_4)_3}$ **with** $\mathbf{0 \leq x \leq 0.7}$
$\mathbf{Li_{1+x}Al_xGe_{2-x}(PO_4)_3}$ **with** $\mathbf{0 \leq x \leq 0.7}$

For the preparation of dense pellets two synthesis routes have been tested:

the powders co-grinding

and the sol-gel method

Compositions $Li_{1+x}Al_xM_{2-x}(PO_4)_3$ with $0 \leq x \leq 0$ & M = Ti or Ge

Sol-gel method for powder synthesis

Characterization methods

Powder compacting & sintering

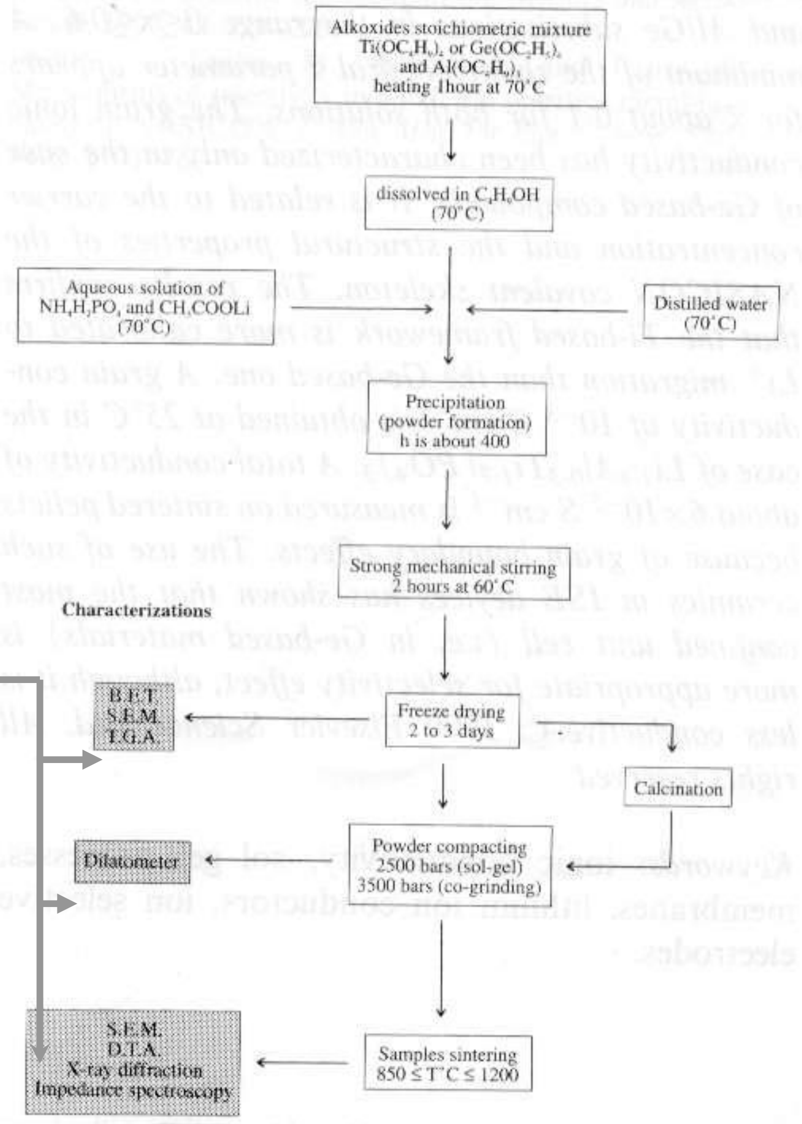


Fig. 1. Li^+-NASICON sol–gel synthesis flow diagram.

Powder synthesis by co-grinding:

Solid state reactions from Li_2CO_3, Al_2O_3, TiO_2 or GeO_2 and $(NH_4)_2HPO_4$

- **Stoichiometric mixtures were ground 100 h in ethanol (zirconia grinding balls)**
- **The dried powder was heated for 2h. at 900°C and ground again, before compacting and sintering**

Materials characterizations

Morphological properties: sintering properties as a function of:

Synthesis method

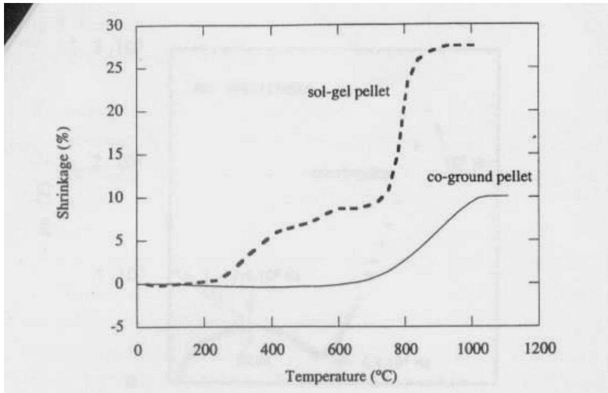


Fig. 3. Shrinkage study during the sintering of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ synthesized by the co-grinding and sol–gel processes.

Composition

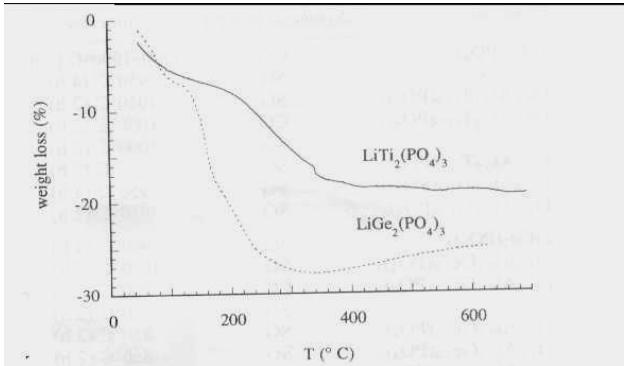


Fig. 4. Thermogravimetric analysis of $LiA_2(PO_4)_3$ (A = Ti and Ge) powders. The heating rate is 1°C min^{-1}.

ISEs applications need the use of high density membranes

Structural properties

Differential Thermal Analysis

(heating rate 10°C min^{-1})

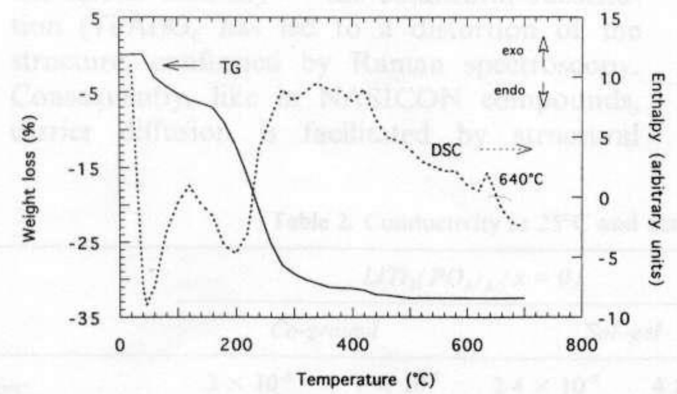


Fig. 4. Thermogravimetric and differential scanning calorimetry analysis of a doped powder synthesized by the sol–gel route.

Crystallisation temperature (°C) of sol-gels materials

	x					
$Li_{1+x}Al_xTi_{2-x}(PO_4)_3$	0	0.1	0.3	0.5	0.6	0.7
	720	685	655	650	640	630

Effect of the aluminium doping:

decrease of the crystallisation temperature
increase of the compacting (better sintering)

X-ray diffraction study

Solubility limit of Al in the Li$^+$-NASICON framework LiA$_2$(PO$_4$)$_3$ (A=Ti & Ge): 30 mol%

NASICON-type solid solution: $0 \leq x \leq 0.6$

Cell parameters of the NASICON hexagonal unit

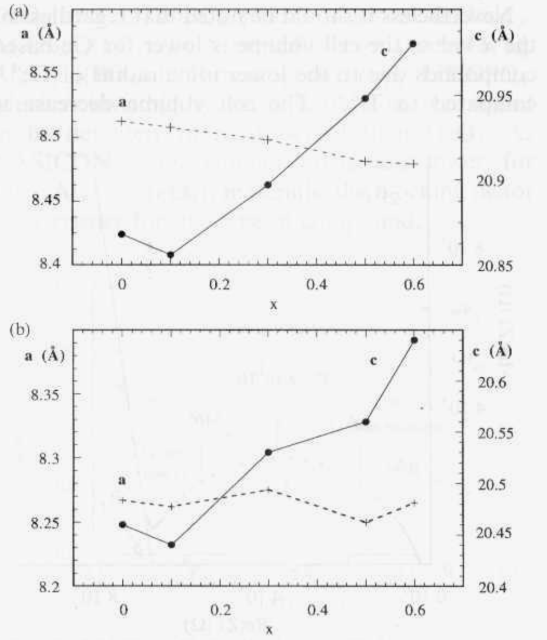


Fig. 6. Cell parameters (hexagonal unit) for: (a) Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$; (b) Li$_{1+x}$Al$_x$Ge$_{2-x}$(PO$_4$)$_3$.

"a" parameter evolutions: qualitative function of the ionic radius of the cation in the octahedrical site

Al/Ti substitution: decrease of "a"
Al/Ge substitution: "a" constant

	Ionic radius (Å)
Al^{3+}	**0.535**
Ti^{4+}	**0.605**
Ge^{4+}	**0.530**

"c" parameter evolutions: new occupancy of the conduction sites because Al/Ti or Ge substitutions increase charge carrier number (Li$^+$ doping)

Electrical properties

The ionic conductivity is determined by Electrochemical Impedance Spectroscopy (EIS)

Principle: the measurement of the resistance of the material

$$R = \Delta U/\Delta I$$

…and the resistance calculated

The current response is recorded

**A sinusoidal signal
in potential is applied
at different frequencies**

$$\boxed{\sigma = \frac{1}{R}\times\frac{l}{S}}$$

**with σ the conductivity ($S.cm^{-1}$)
R the resistance (Ω or S^{-1})
l the pellet thickness (cm)
S the pellet surface (cm^2)**

Experimental:

**Potential amplitude 100 mV
Frequency range 13MHz – 5 Hz
Pellets are coated with gold layers on each side which act as electrodes
Studied temperature 25°C – 400°C**

Electrical properties - Results

« Nyquist » plots

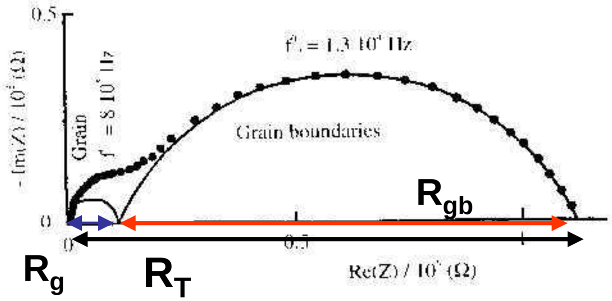


Fig. 9. Impedance diagram at 37°C for $Li_{1.1}Al_{0.1}Ge_{1.9}(PO_4)_3$ obtained with the sol gel process.

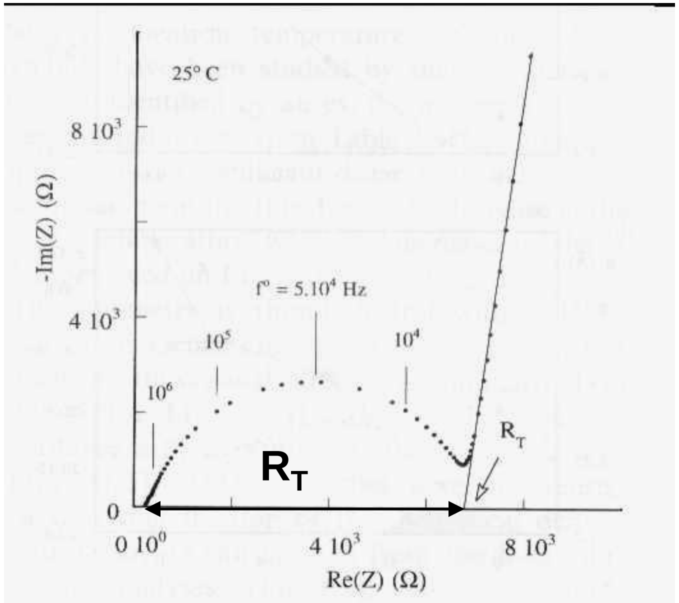
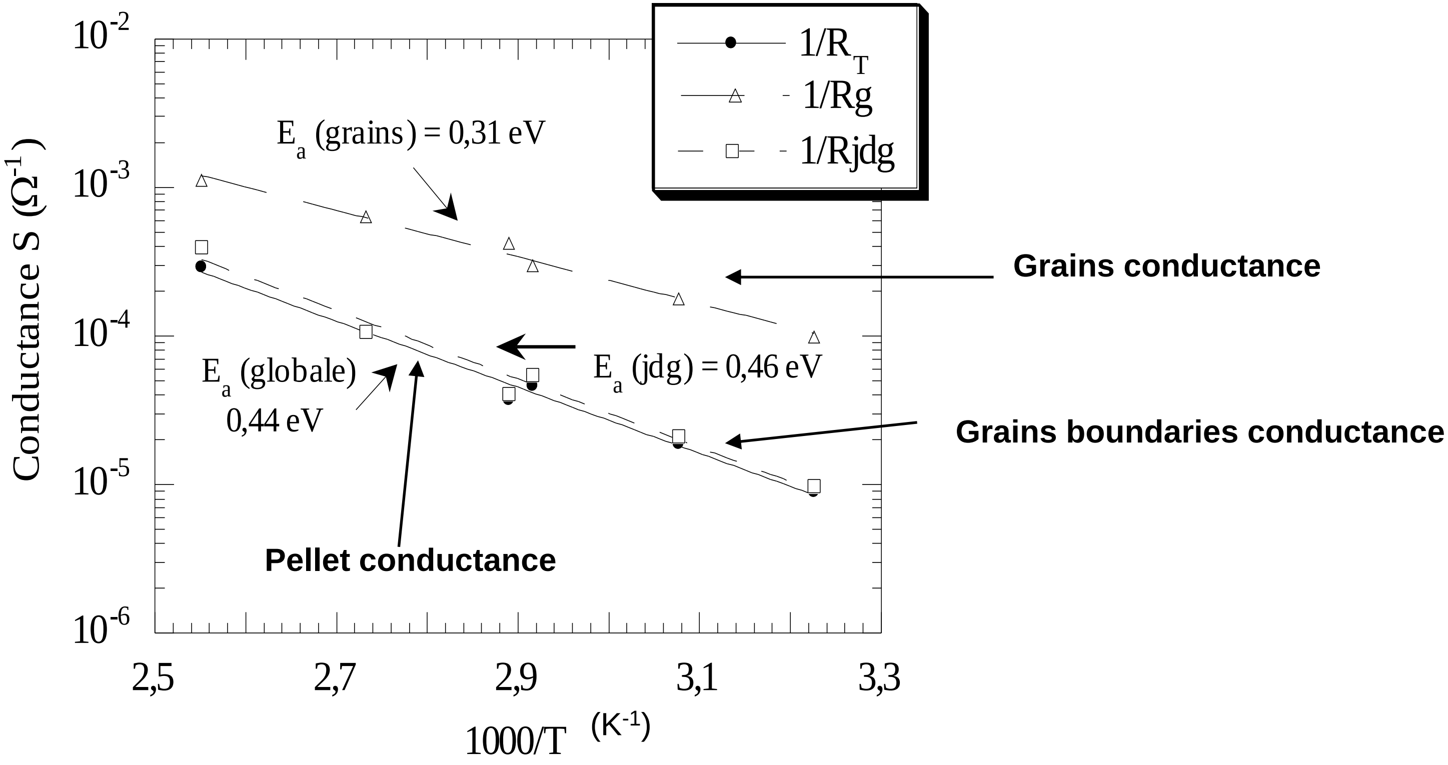


Fig. 7. Impedance diagram obtained at 25°C on a $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ pellet, using Au electrodes.

The frequency study allows us to distinguish different migration phenomena :

High frequency: migration of the charge carrier into the grain
Lower frequency: migration of the charge carrier in the grain boundary
Very low frequency: interfaces phenomena

Possible to determine the grain resistance R_g, the grain boundaries resistance R_{gb} and the pellet resistance R_T(macroscopic resistance…)



E_a (grains) = 0,31 eV

E_a (globale) 0,44 eV

E_a (jdg) = 0,46 eV

Grains conductance

Grains boundaries conductance

Pellet conductance

Conductivity of the grains boundaries is the limiting factor !

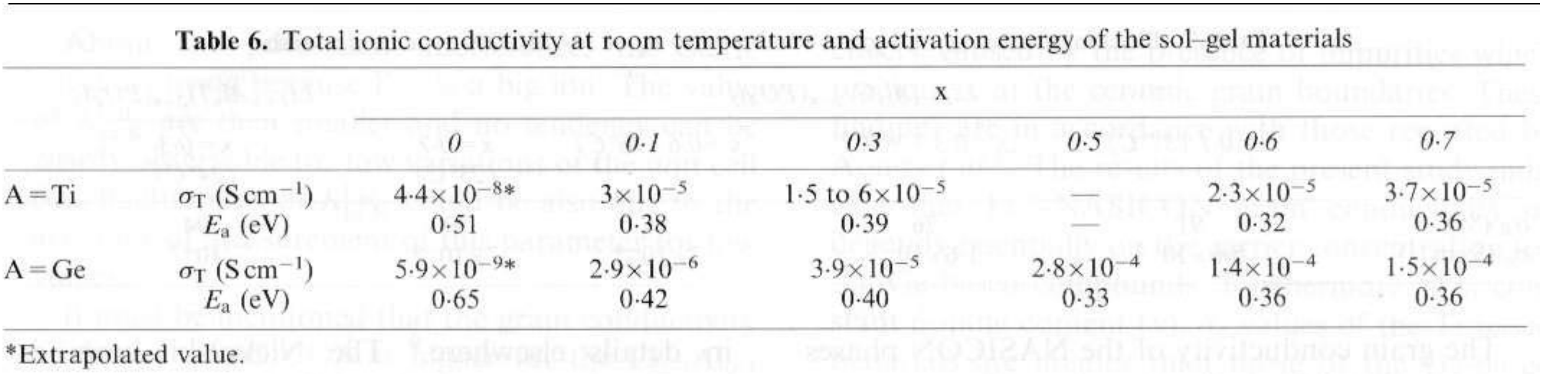


Table 6. Total ionic conductivity at room temperature and activation energy of the sol–gel materials

		x = 0	x = 0·1	x = 0·3	x = 0·5	x = 0·6	x = 0·7
A = Ti	σ_T (S cm^{-1})	$4{\cdot}4\times10^{-8}$*	3×10^{-5}	1·5 to 6×10^{-5}	—	$2{\cdot}3\times10^{-5}$	$3{\cdot}7\times10^{-5}$
	E_a (eV)	0·51	0·38	0·39	—	0·32	0·36
A = Ge	σ_T (S cm^{-1})	$5{\cdot}9\times10^{-9}$*	$2{\cdot}9\times10^{-6}$	$3{\cdot}9\times10^{-5}$	$2{\cdot}8\times10^{-4}$	$1{\cdot}4\times10^{-4}$	$1{\cdot}5\times10^{-4}$
	E_a (eV)	0·65	0·42	0·40	0·33	0·36	0·36

*Extrapolated value.

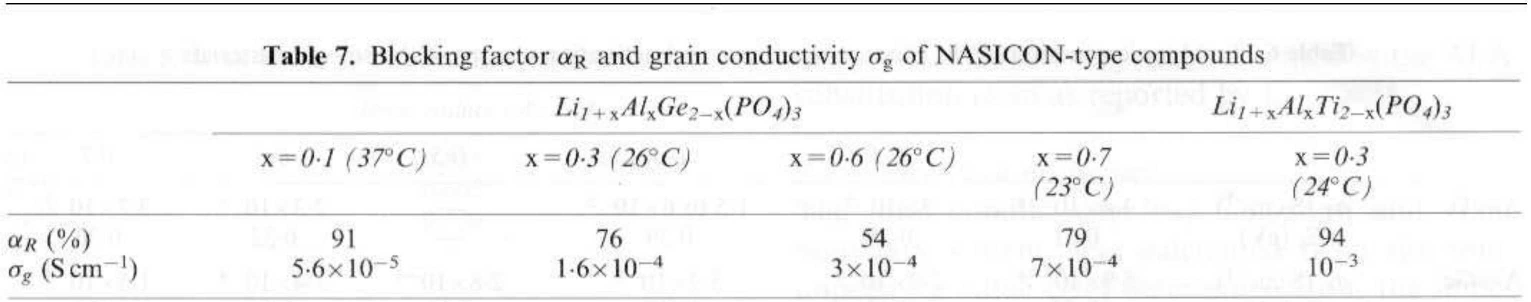


Table 7. Blocking factor α_R and grain conductivity σ_g of NASICON-type compounds

	$Li_{1+x}Al_xGe_{2-x}(PO_4)_3$				$Li_{1+x}Al_xTi_{2-x}(PO_4)_3$
	x = 0·1 (37°C)	x = 0·3 (26°C)	x = 0·6 (26°C)	x = 0·7 (23°C)	x = 0·3 (24°C)
α_R (%)	91	76	54	79	94
σ_g (S cm^{-1})	$5{\cdot}6\times10^{-5}$	$1{\cdot}6\times10^{-4}$	3×10^{-4}	7×10^{-4}	10^{-3}

σ_{grain} ($Li_{1+x}Al_xTi_{2-x}(PO_4)_3$) > σ_{grain} ($Li_{1+x}Al_xGe_{2-x}(PO_4)_3$)

$[Ti_2P_3O_{12}]^-$ covalent skeleton better calibrated to Li+ conduction that $[Ge_2P_3O_{12}]^-$