V CONGRESO COLOMBIANO DE ELECTROQUÍMICA
VIII SEMINARIO INTERNACIONAL DE QUÍMICA APLICADA
III Escuela Andino-Amazónica de Química
WORKSHOP QUÍMICA Y BIOLOGÍA DE HONGOS CON POTENCIAL BIOTECNOLÓGICO

Synthesis and characterization of the V-doped $Li_{0.3}La_{0.57}Ti_{1-x}V_xO_3$ solid electrolyte for all-solid state lithium-ion batteries.

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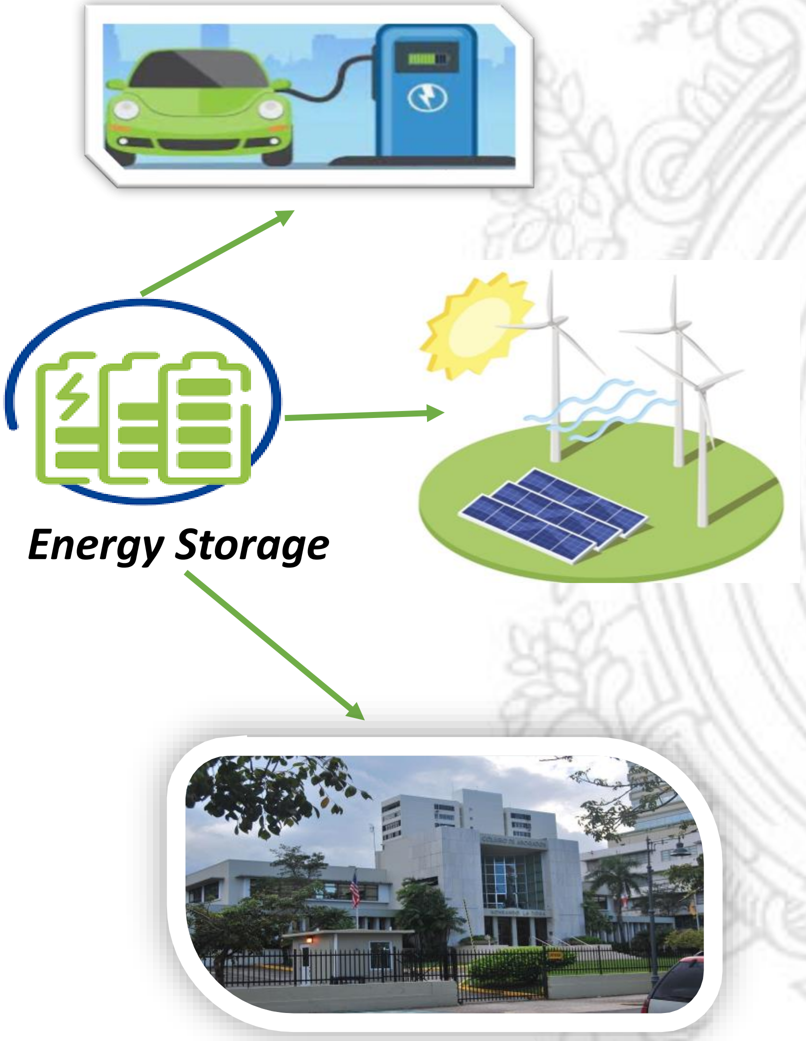
Energías Renovables del Chocó

OUTLINE

- ***Introduction***
- ***Solid electrolyte.***
- ***Methology***
- ***Result.***
- ***Concluison***



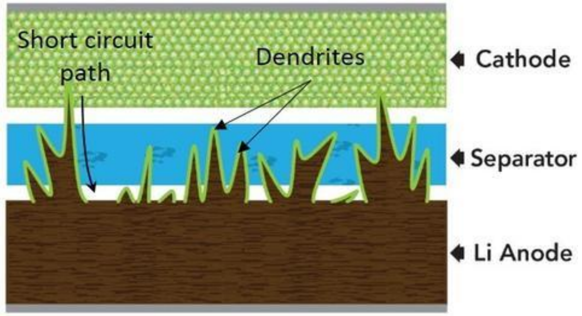
Introduction

Li-ion batteries

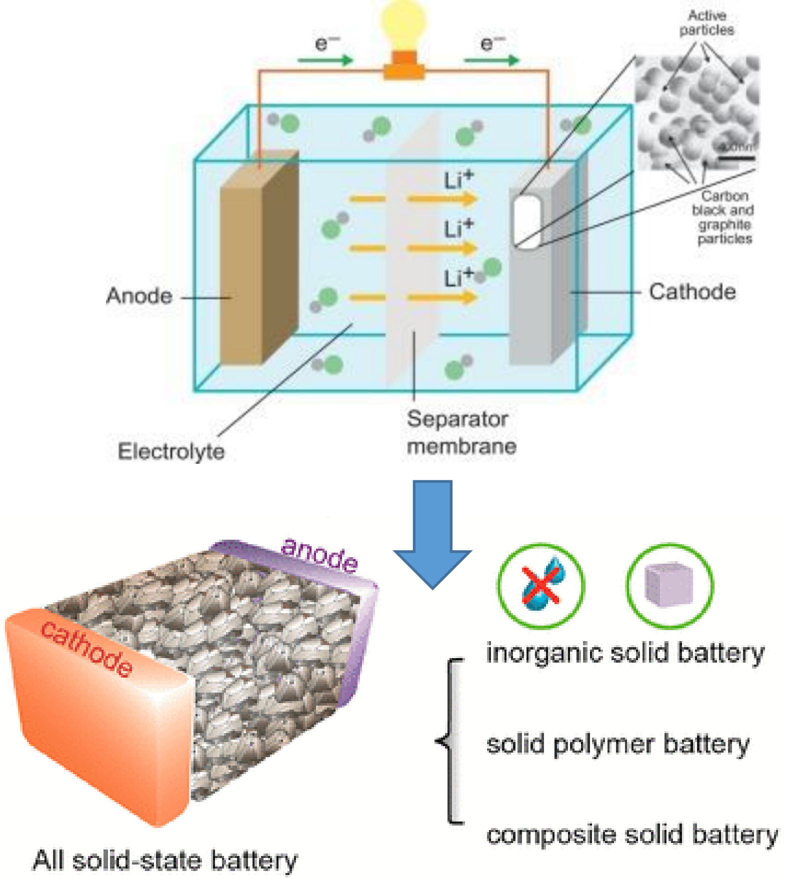
Problems

Thermally unstable electrolyte

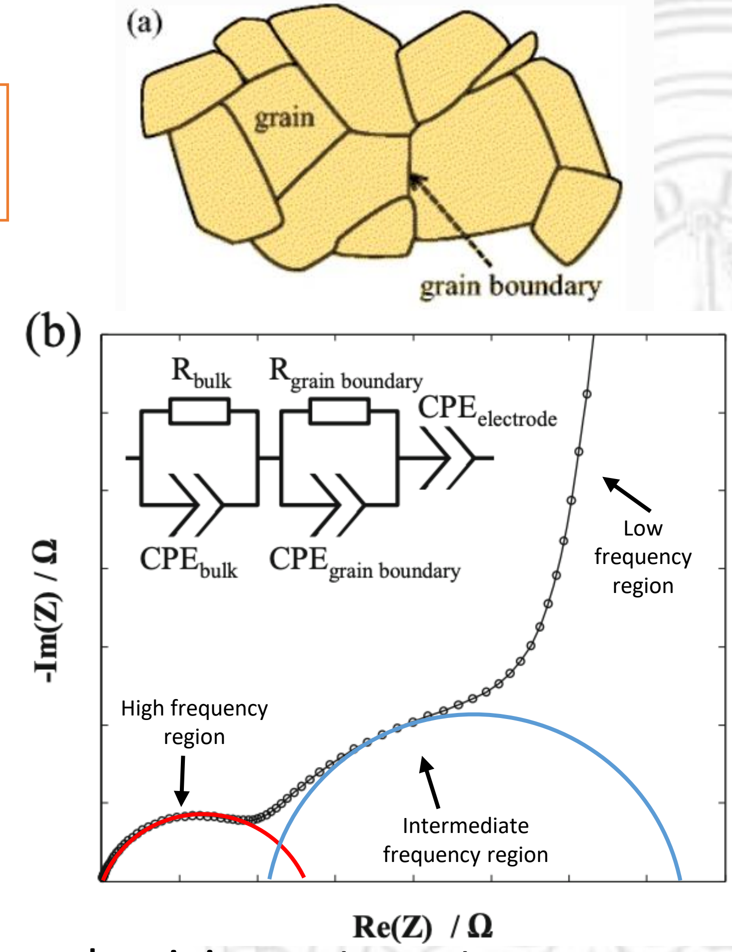
Dendrite growth during charging



Important difference between solid and liquid electrolytes: ion transport mechanism.



All-solid state Li-ion batteries (ASSB).



Ionic conductivity

$$\sigma = \frac{1}{R} \times \frac{d}{S}$$

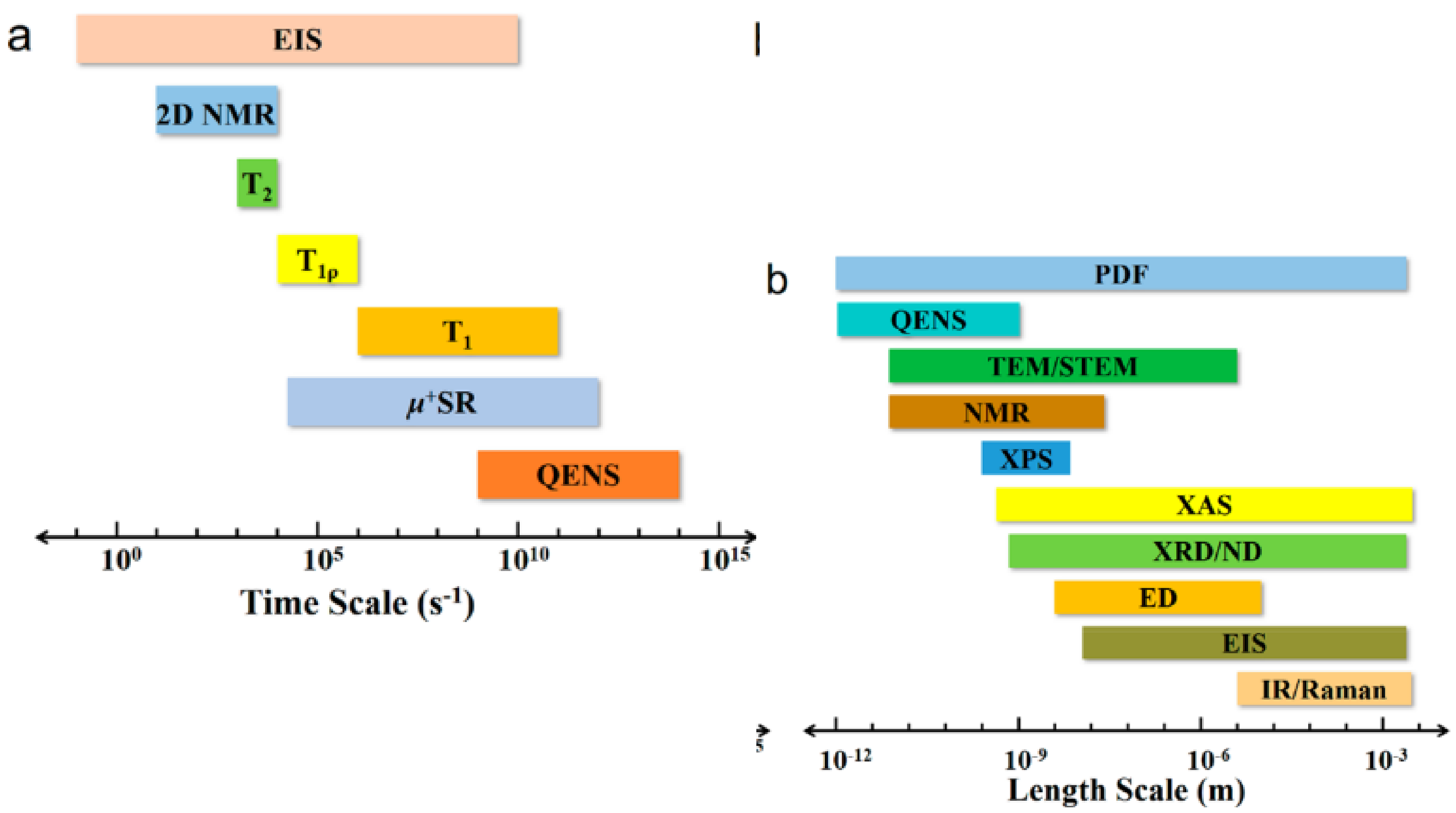
The Arrhenius equation

$$\sigma(T) = \sigma_o \, e^{-E_a / K_b T}$$

R. Chen, Q. Li, X. Yu, L. Chen, y H. Li, *Chem. Rev.*, nov. 2019.
Braun, P., Uhlmann, C., Weber, A. *et al.* *J Electroceram* **38,** 157–167 (2017)

Introduction

Ion diffusion processes in solids occur microscopically and macroscopically.



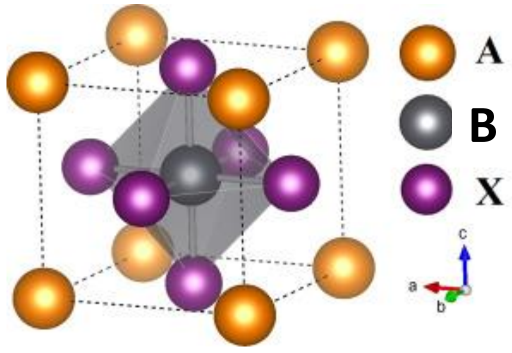
- To measure ionic conductivity by EIS it is assumed that:
- Measurements are supposed to be made at steady state.
- It is assumed that there is linearity between the perturbation and its response. For example, a small potential difference is applied, so that its response is linear.
- It is assumed that in the frequency range studied the process of ion transport in grains, grain limits and diffusion in electrodes occur.
- The brick layer model is widely used to separate the contributions of grain conductivity and grain boundary, which are assumed to be uniform and identical grain boundaries.

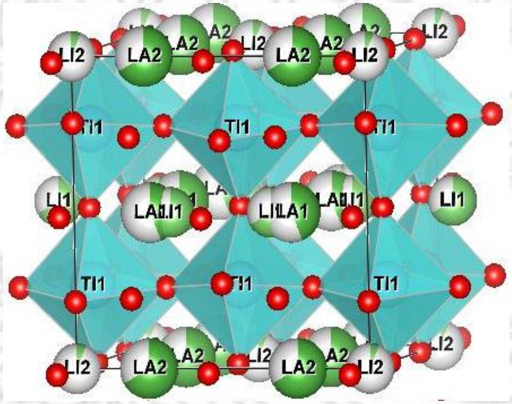
Chemical Reviews, (2020) *120*(13), 5954-6008.

Introduction

Electrolyte	Li-ion conductivity (10^{-3} S/cm)	Electrochemical Stability window (V vs Li/Li^+)
Carbonate liqued electrolyte	5 - 10	1.1 - 4.7
Solid polymer at (80°C)	1 – 4	0.3 – 4
Solid polymer at RT	0.0003 – 0.08	0.2 – 4
Sulfides	0.1 – 10	1.5 – 2.5
Anti-perovskite	0.3 – 9	0.2 – 3
NASICON	0.5 - 1	2.2 – 4.3
Amorphous LiPON	0.0003 - 0.003	0.6 – 2.6
Perovskite	0.008 - 0.5	1.7 – 4.4

Oxide $Li_{0.34}La_{0.51}TiO_{2.94}$ (LLTO) with perovskite structure (ABO_3) has an ionic conductivity of grain of 1.0×10^{-3} S / cm.
However, it has an ionic conductivity of grain boundary of 2.0×10^{-5} S / cm and it is unstable at potentials lower than 1.7V.





Tolerance factor or Goldschmidt

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$ where $0.75 < t < 1.0$

Chemical reviews, 2019, vol. 120, no 14, p. 6820-6877.

Mathodology

Synthesis: The sol-gel method was used to obtain the solid electrolytes.

Starting precursors
- **$La(CH_3CO_2)_3{\cdot}xH_2O$**
- **$LiC_2H_3O_2{\cdot}2H_2O$**

- **C3H8O**
- **$Ti\{OCH(CH_3)_2\}_4$**

- **VOC_2O_4**

90ºC vacuum

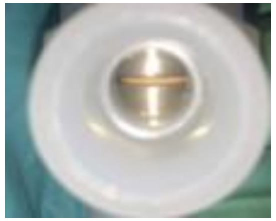
900ºC 12 hour

1200ºC 12 hour

St. 1

St. 2

St. 3

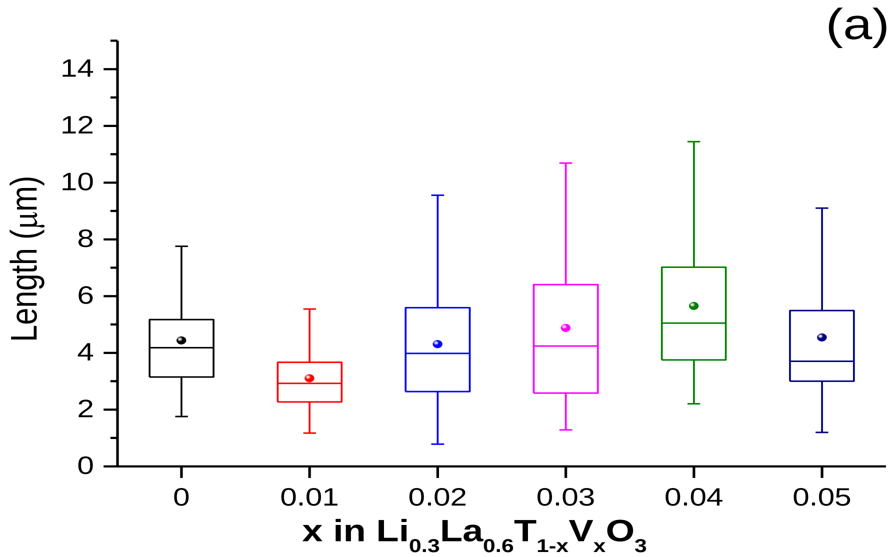


St. 4

Caracterization:
- SEM
- RAMAN
- XRD

- **EIS**
- **Chronoamperometry**

Results



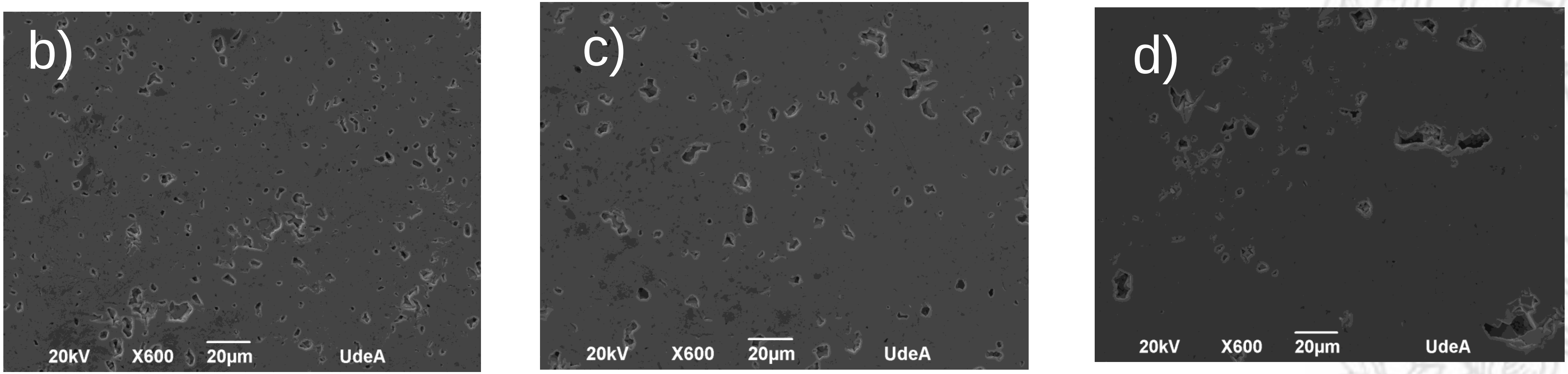


Figure 1 (a) Particle size distribution (St. 2) for the solid electrolyte $Li_{0.3}La_{0.57}Ti_{1-x}V_xO_3$ (b-d) the cross-section of solid electrolyte for x=0; 0.02 and 0.05, respectively.

Results

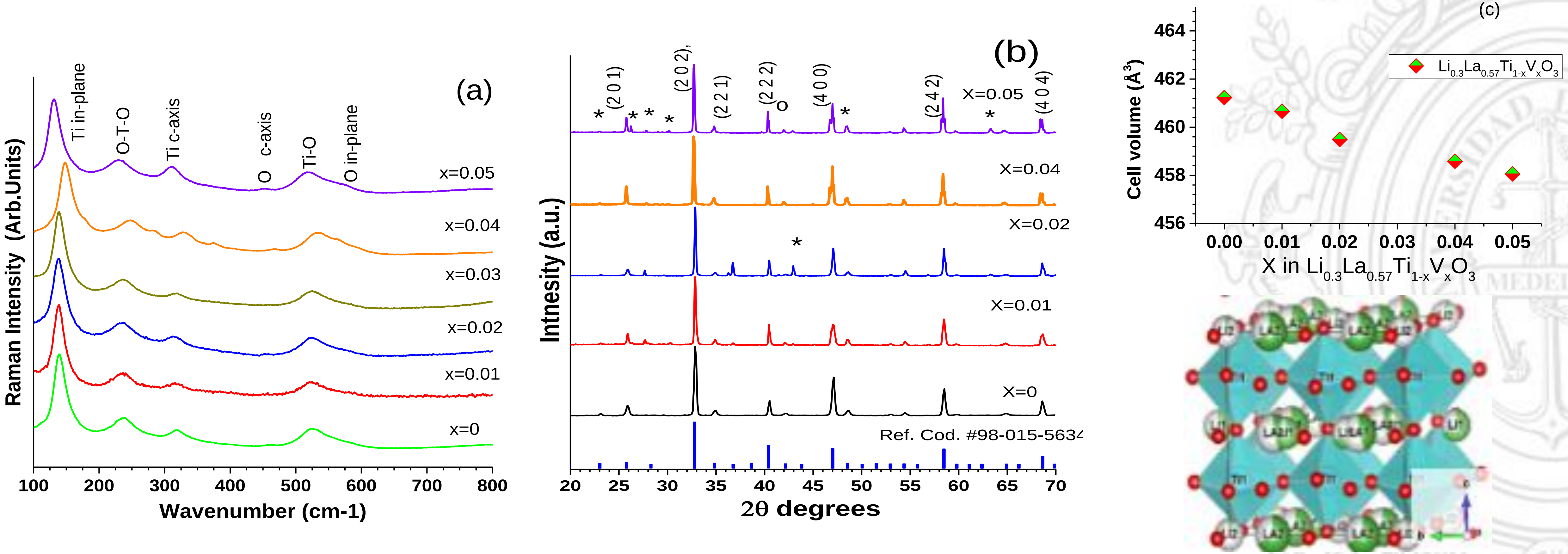


Figure 2 RAMAN spectra (a) and x-ray diffraction patterns (c) and unit cell volume for the solid electrolyte at $Li_{0.3}La_{0.57}Ti_{1-x}V_xO_3$ with x = 0, 0.1, 0.02, 0.03, 0.04 and 0.05.

Results

Calculation of lithium-ion ionic conductivities.

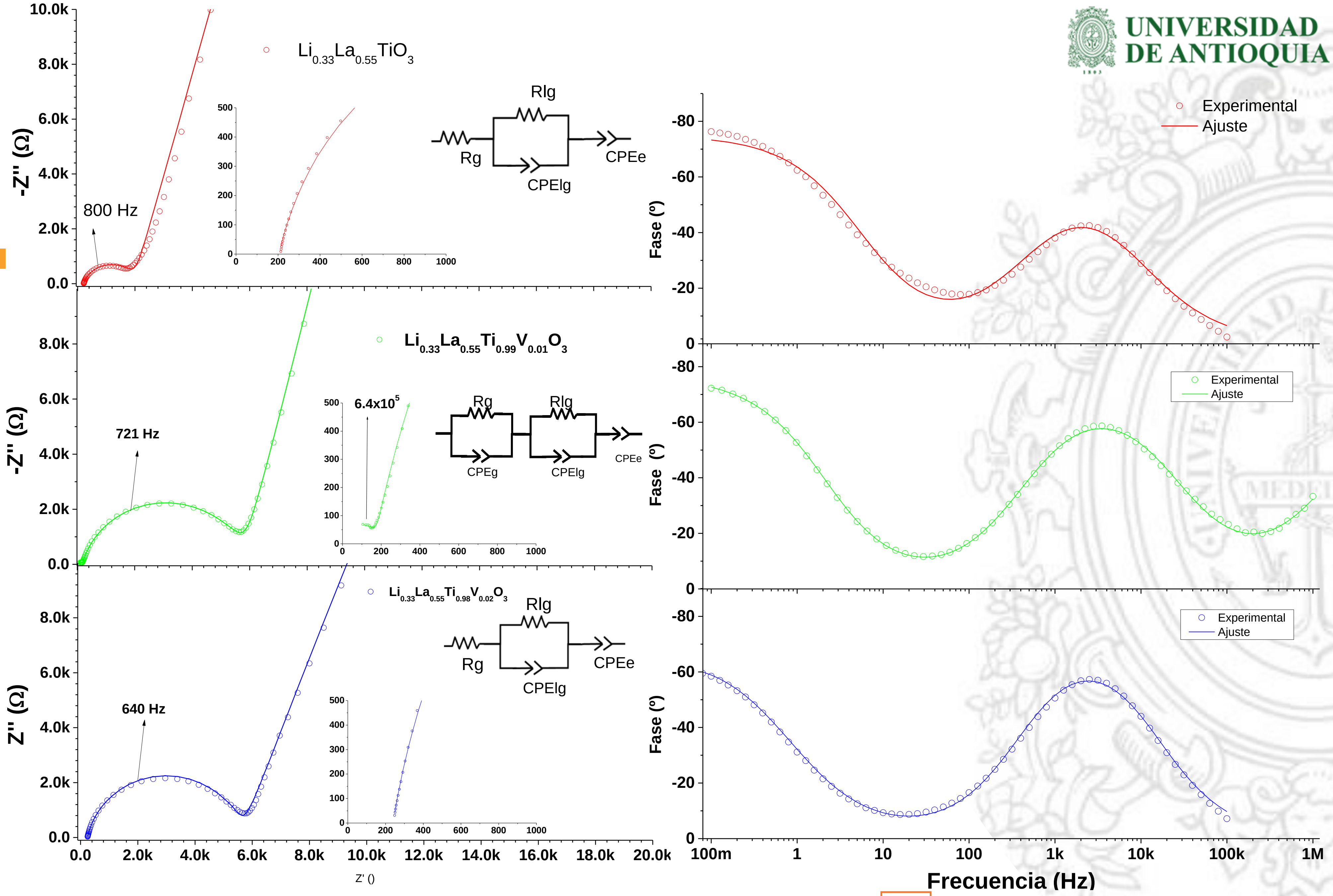


Figure 3 a) Nyquist and Bode diagram of $Li_{0.3}La_{0.57}Ti_{1-x}V_xO_3$ (x= 0.01, 0.02 and 0.03).

Results

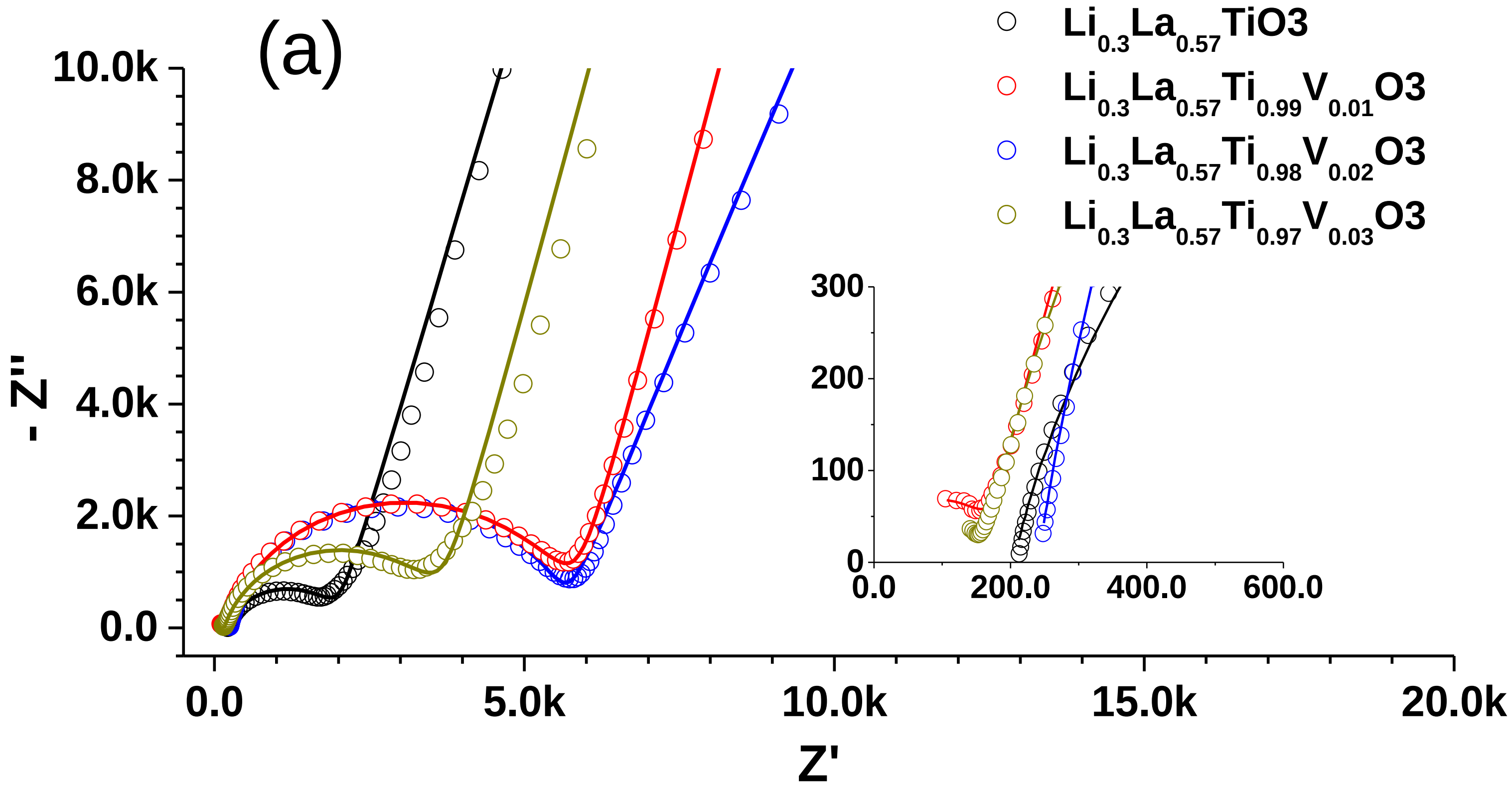


Figure 4 a) Nyquist diagram of $Li_{0.3}La_{0.57}Ti_{1-x}V_xO_3$ (x= 0, 0.1, 0.02 and 0.03).

Calculation of ionic conductivity (σ)

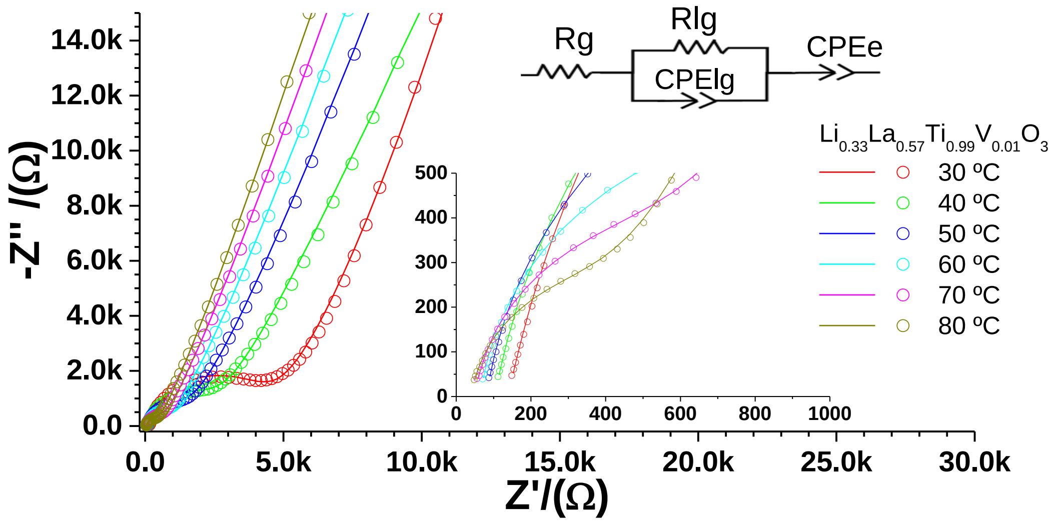
$$\sigma = \frac{L}{RA}$$

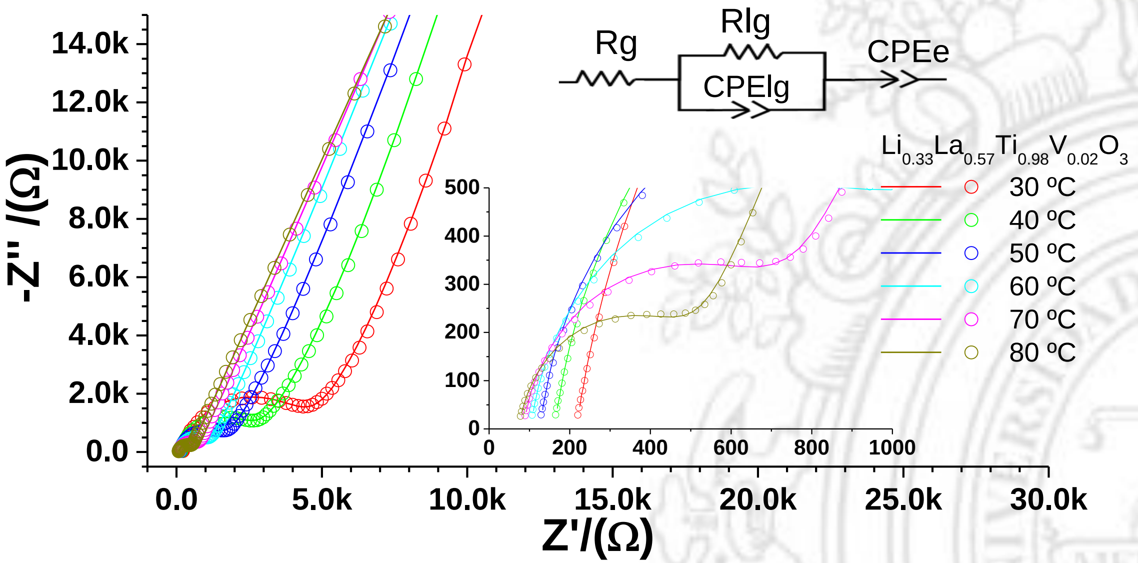
L: Thickness

A: Area

A: Resistance

Results





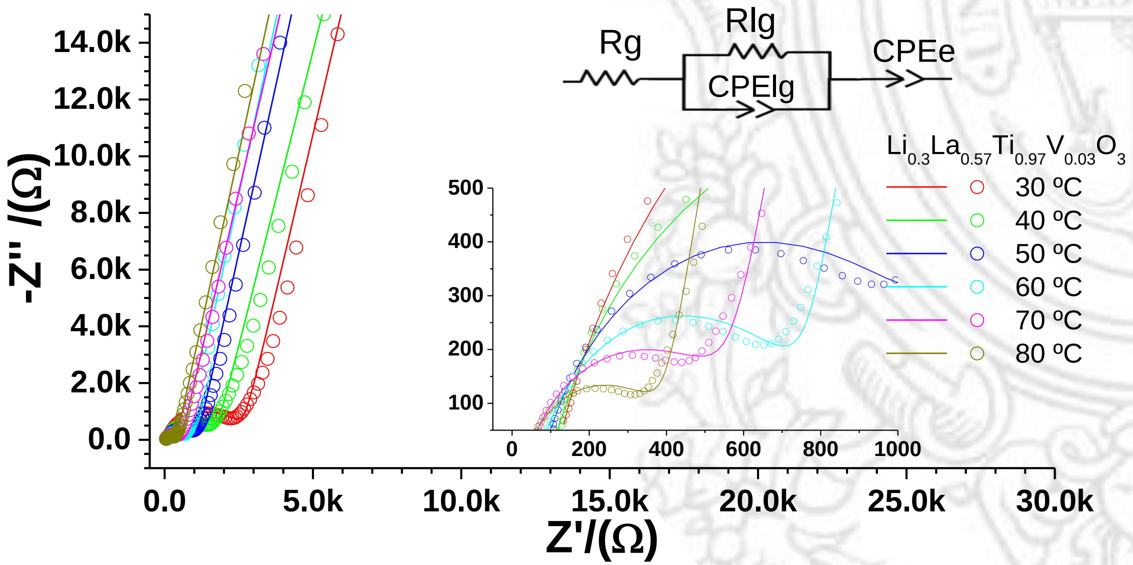


Figure 5 a) Nyquist diagram as a function of the temperature of $Li_{0.3}La_{0.57}Ti_{1-x}V_xO_3$ (x= 0, 0.1, 0.02 and 0.03).

Results

The activation energy is obtained from the Arrhenius equation.

$$\sigma(T) = \sigma_o e^{-\frac{Ea}{k_B T}}$$

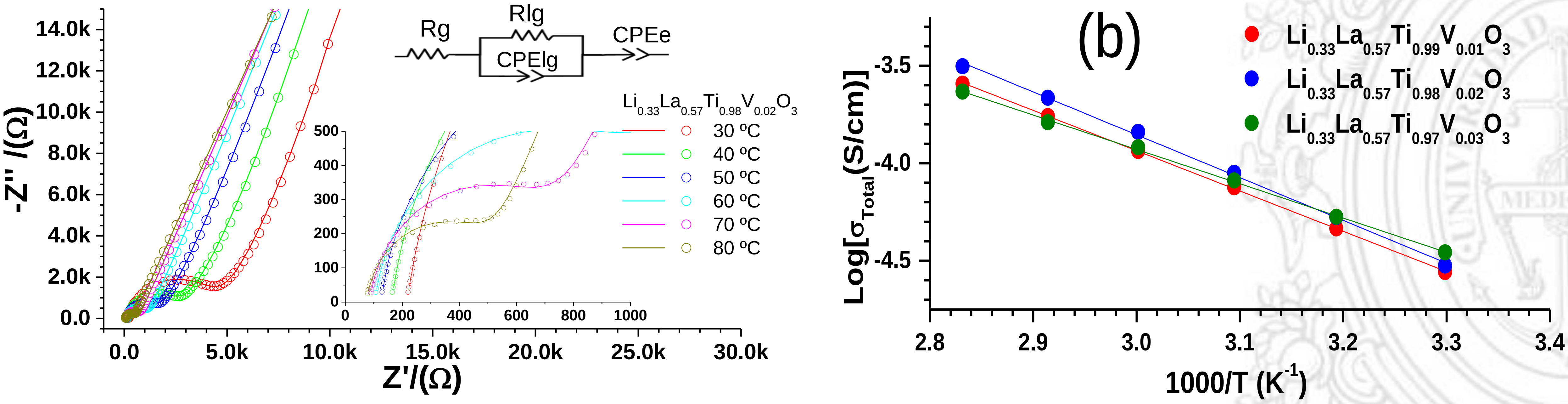


Figure 6 a) Nyquist diagram and (b) Arrhenius plot of $Li_{0.3}La_{0.57}Ti_{1-x}V_xO_3$ (x= 0, 0.1, 0.02 and 0.03).

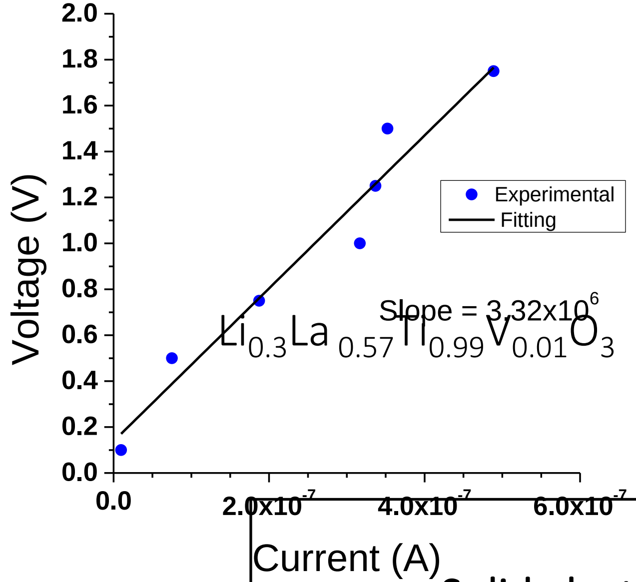
Results

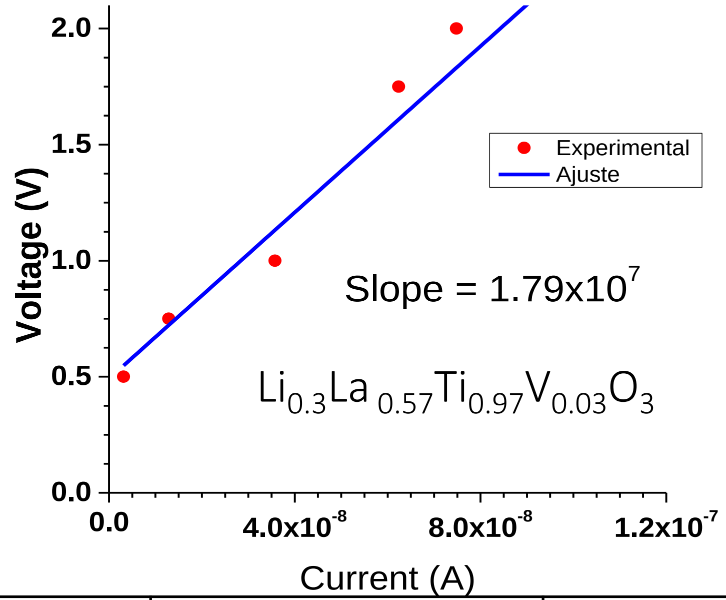
Table 1. Ionic conductivity Summary,activation energy and electronic conductivity for the electrolyte $Li_{0.3}La_{0.57}Ti_{1-x}V_xO_3$.

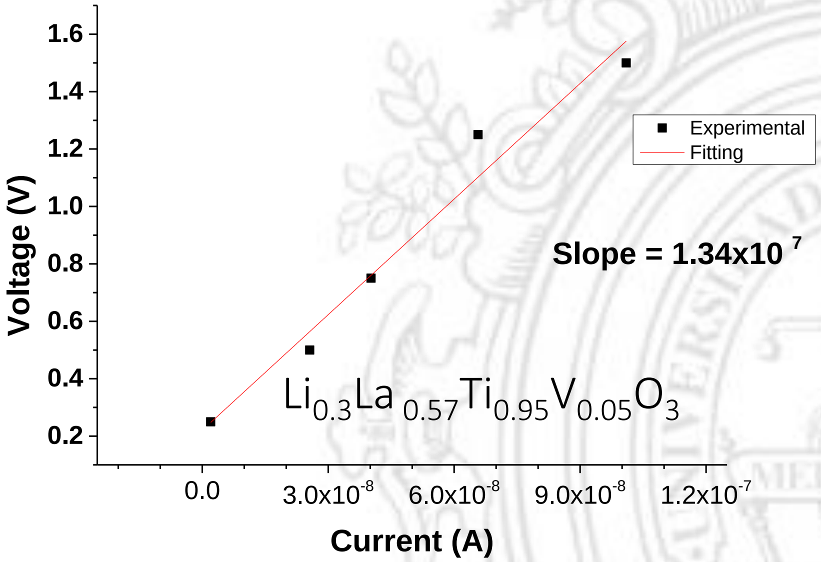
Solid electrolyte	σ_g (S/cm)	σ_{gb} (S/cm)	σ_{Total} (S/cm)	$Ea\ (eV)$
$Li_{0.34}La_{0.51}TiO_3$	-	-	$2x10^{-5}$ [3]	-
x = 0	$4.38x10^{-4}$	$5.07x10^{-5}$	$4.54x10^{-5}$	0.45
x = 0.01	$6.17x10^{-4}$	$3.75x10^{-5}$	$3.53x10^{-5}$	0.410
x = 0.02	$7.43\ x10^{-4}$	$2.25x10^{-5}$	$2.18x10^{-5}$	0.436
x = 0.03	$5.73\ x10^{-4}$	$2.63\ x10^{-5}$	$2.51\ x10^{-5}$	0.349

Results

Calculation of electrical conductivity by chronoamperometry







Solid electrolyte	Resistence (Ω)	Electronic conductivity (S/cm)
$Li_{0.3}La_{0.57}Ti_{0.99}V_{0.01}O_3$	$3.32x10^6$	$2.93x10^{-8}$
$Li_{0.3}La_{0.57}Ti_{0.98}V_{0.02}O_3$	$1.79x10^7$	$6.07x10^{-9}$
$Li_{0.3}La_{0.57}Ti_{0.97}V_{0.03}O_3$	$1.79x10^7$	$5.10x10^{-9}$
$Li_{0.3}La_{0.57}Ti_{0.96}V_{0.04}O_3$	$3.95 x10^6$	$2.30x10^{-8}$
$Li_{0.3}La_{0.57}Ti_{0.95}V_{0.05}O_3$	$1.34 x10^7$	$8.21x10^{-9}$

Conclusion

The XRD pattern shows the formation of $Li_{0.3}La_{0.57}Ti_{1-x}V_xO_3$ with perovskite structure in the orthorhombic crystalline system (space group Cmmm), showing a decrease of unit cell with the vanadium amount, which can be attributed V^{+5} insertion of ionic radius (0.54 Å) lower than Ti^{+4} (0.605 Å) in B site of perovskite structure.

The solid electrolyte $Li_{0.3}La_{0.57}TiO_3$ without vanadium exhibits the highest total ionic conductivity $4.54x10^{-5}$ S/cm, and the $Li_{0.3}La_{0.57}Ti_{0.98}V_{0.02}O_3$ exhibits the best grain conductivity ($7.43x10^{-4}$ S/cm).

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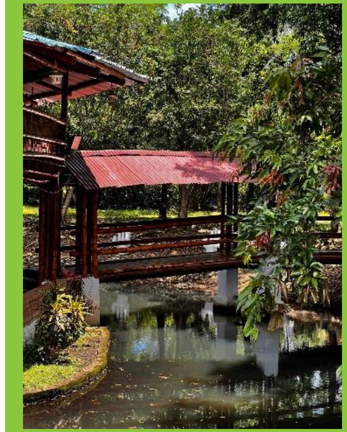

Gracias por la atención

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Energías Renovables del Chocó

Coeficientes de difusión.

Coeficiente de difusión aleatoria **Dr** en procesos microscópicos.

$$D_r = \frac{\langle R_n^2 \rangle}{b t_n} = \frac{a^2 \nu}{b}$$

Donde Rn es desplazamiento total de un ion en movimiento en n pasos, tn es la duración completa en n pasos, a es la distancia de salto entre dos sitio vecinos, b es un factor geométrico de 2, 4 , 6 dimensiones, y v es un la frecuencia de salto la cual se puede expresar como.

$$\nu = \nu_0 \exp\left(-\frac{\Delta G}{k_B T}\right) = \nu_0 \exp\left(\frac{\Delta S}{k_B}\right) \exp\left(-\frac{\Delta H}{k_B T}\right)$$

Luego

$$D_r = \frac{1}{b} a^2 \nu_0 \exp\left(\frac{\Delta S}{k_B}\right) \exp\left(-\frac{\Delta H}{k_B T}\right)$$

Coeficiente de difusión aleatoria se relacionas con procesos macroscópicos por. coeficiente de difusión de largo alcance Dσ a través del coeficiente de difusión del trazador D*, relación de Haven HR y factor de correlación f, según la ecuación de Nernst−Einstein

$$D_\sigma = \frac{\sigma k_B T}{c q^2}$$

Donde $H_R = D^*/D_\sigma$ y $f = D^*/D_r$.

De lo anterior, se puede expresar la conductividad iónica como:

$$\sigma = \frac{1}{6} \frac{f}{H_R} \frac{c q^2}{k_B T} a^2 \nu_0 \exp\left(\frac{\Delta S}{k_B}\right) \exp\left(-\frac{\Delta H}{k_B T}\right)$$