

“Nuevos Materiales para cátodos y electrolitos en Baterías de Ión-Litio”



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Materiales para Cátodo

Ión-Litio

1. LiFePO₄

Grupo Espacial: Pnma

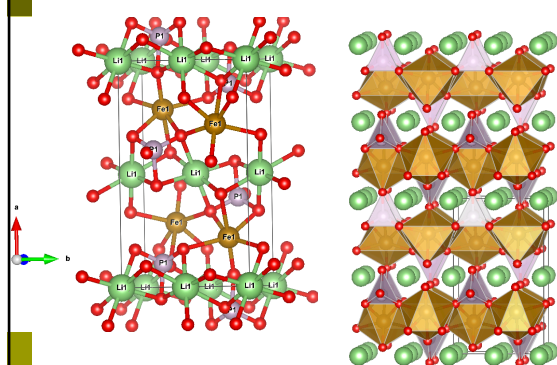


Table 1 Rietveld refinement structural parameters for LiFePO₄/C and LiFe_{0.99}Co_{0.01}PO₄/C samples. The fitting errors are displayed in parenthesis

Sample	a (Å)	b (Å)	c (Å)	V (Å ³)	D _c (nm)
LiFePO ₄ /C	6.0061 (2)	10.3263 (4)	4.6920 (2)	291.00 (2)	75 (2)
LiFe _{0.99} Co _{0.01} PO ₄ /C	6.0042 (2)	10.3221 (3)	4.6895 (1)	290.64 (2)	79 (2)

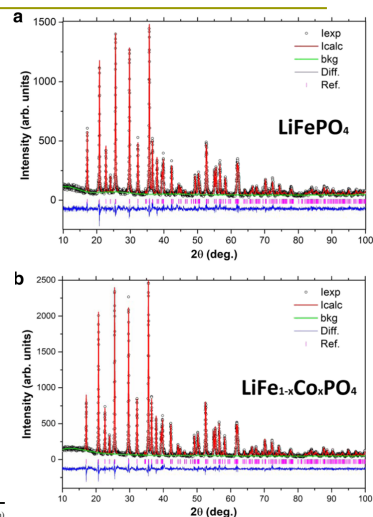
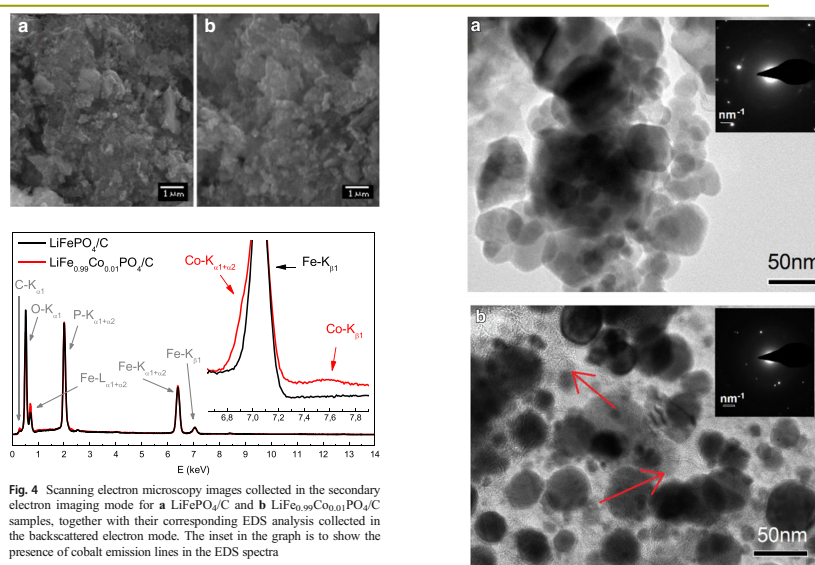


Fig. 2 Rietveld refinements of X-ray diffraction patterns for a LiFePO₄ and b LiFe_{0.99}Co_{0.01}PO₄ samples

2. SEM/EDX y TEM/SAED



3. SAXS y Ramn

$$I(q) = Ge^{-\frac{(qR_G)^2}{3}} + B \left[\operatorname{erf} \left(\frac{qR_G}{\sqrt{6}} \right) \right]^{3P} q^{-P}$$

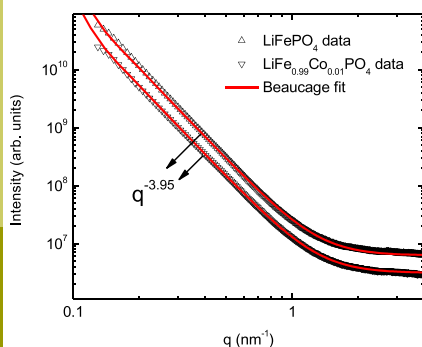


Fig. 3 Small-angle X-ray scattering patterns and Beaucage fittings of LiFePO_4 and $\text{LiFe}_{0.99}\text{Co}_{0.01}\text{PO}_4$ samples. The $I(q) \sim q^{-3.95}$ power law observed in both cases evidenced no drastic apartment from the Porod law. In the logarithmic scale displayed in the graph, the power law region appears as a linear trend whose slope corresponds to the Porod exponent (P), in this case $P = -3.95$

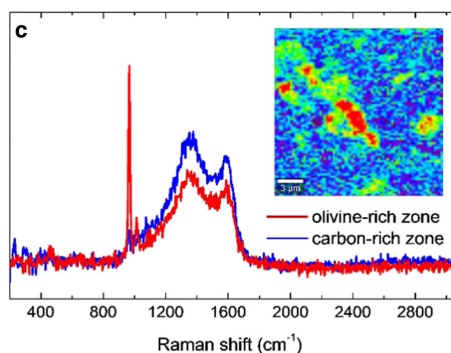


Fig. 5 Transmission electron microscopy images for a LiFePO_4/C and **b** $\text{LiFe}_{0.99}\text{Co}_{0.01}\text{PO}_4/\text{C}$ samples. The inset shows a selected area electron diffraction pattern for each case. **c** Raman microscopy spectra and image (inset) corresponding to the olivine-rich and carbon-rich zones in the samples

Ionics
<https://doi.org/10.1007/s11581-019-02908-7>

ORIGINAL PAPER



Insights of cobalt doping on carbon-coated LiFePO_4 olivine nanoparticles prepared by citric acid combustion route as cathodes for lithium batteries

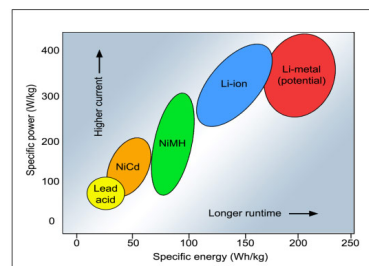
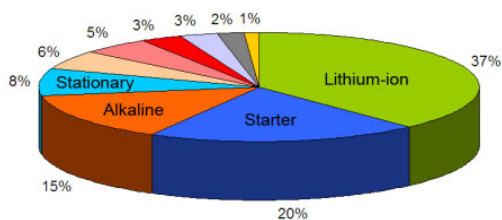
Fernando Pignanelli¹ · Mariano Romero¹ · Dominique Mombrú¹ · Erika Téliz² · Verónica Díaz³ · Jorge Castiglioni⁴ · Fernando Zinola² · Ricardo Faccio¹ · Álvaro W. Mombrú¹

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Materiales para Electrolito

Ión-Litio

1. Materiales para Almacenamiento de Energía: Baterías de Litio



Cátodo

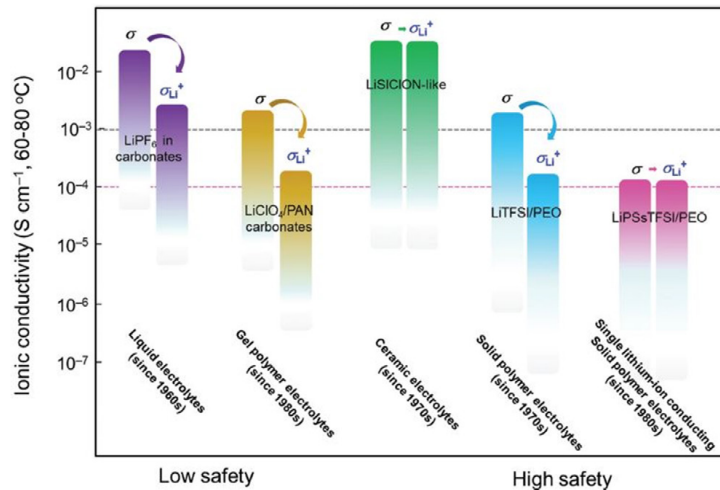
- Lithium cobalt oxide (LiCoO_2)
- Lithium nickel manganese cobalt oxide (LiMnCoO_2)
- Lithium iron phosphate (LiFePO_4)
- Lithium nickel cobalt aluminum oxide (LiNiCoAlO_2)

Aplicaciones

- cell phones, tablets, laptops, cameras
- Chevy Volt
- Electric vehicle
- Tesla

https://batteryuniversity.com/index.php/learn/article/global_battery_markets

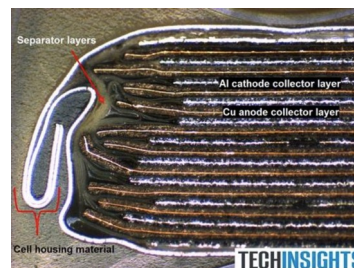
1. Materiales para Almacenamiento de Energía: Baterías de Litio



Anil Arya and A L Sharma 2017 *J. Phys. D: Appl. Phys.* **50** 443002

1. Electrolitos Sólidos:

Samsung Recall Note 7:
Uso de electrolitos líquidos



In the original run of devices, the battery, produced by a Samsung subsidiary, contained a design flaw that made electrodes on the top-right of the battery susceptible to bending. This weakened separation between positive and negative tabs of the battery, thus resulting in [thermal runaway](#) and [short circuits](#). Some batteries were also missing insulation tape entirely. Samsung reported that these oversights resulted from the vendor's push to ramp up production of batteries for the replacement phones in order to meet demand.

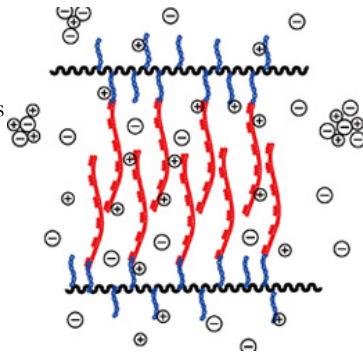
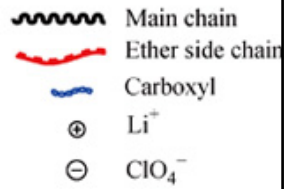
2. Estrategia y Metodología

Estrategia

- ▣ Disminuir la viscosidad intrínseca del polímero (Tg y Tm)
- ▣ Mejorar la afinidad entre el Li^+ y el polímero
- ▣ Mejorar conducción catiónica Li^+
- ▣ Bajar conducción aniónica (ej. ClO_4^-)

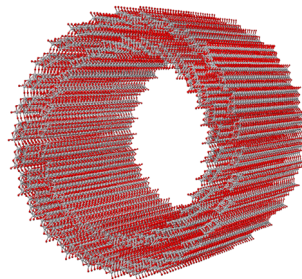
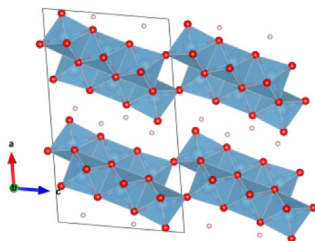
Metodología

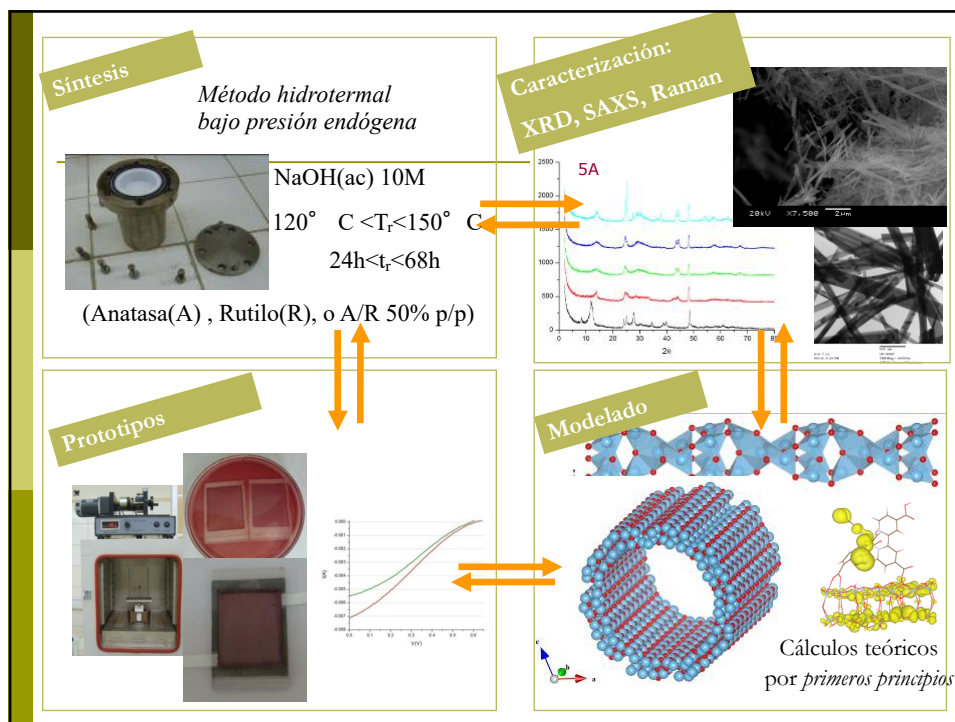
- ▣ Síntesis de nuevos Materiales y Nanomateriales
- ▣ Agregado de cargas (fillers):
 - Modificación del Tg/Tm del Polímero
 - Afinidad anión con la carga
- ▣ Caracterización Químico Estructural
- ▣ Caracterización y evaluación de desempeño Eléctrico



2. Nanotubos de HTNT como fillers

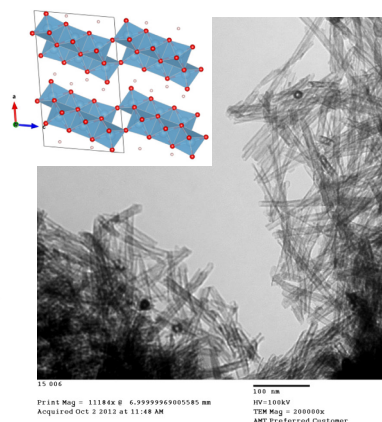
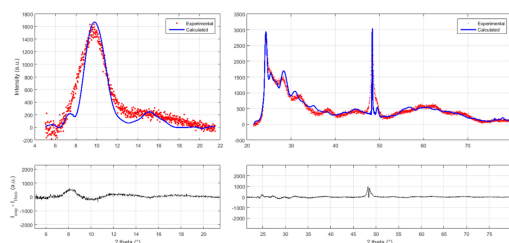
- ▣ ¿Por qué?
- ▣ Los nanotubos de HTNT poseen un área específica importante.
- ▣ Se conoce la morfología y estructura de los nanotubos (bloque de construcción)
- ▣ Tiene estructura bicapa, que permite alojar otros iones





2. Caracterización de HTNT:

- NT de $\text{H}_3\text{Ti}_2\text{O}_7$: Raman, BEM, TEM y XRD
- Espesor de 2 a 3 nm
- Diámetro medio de 9 nm
- Largo de 15 nm



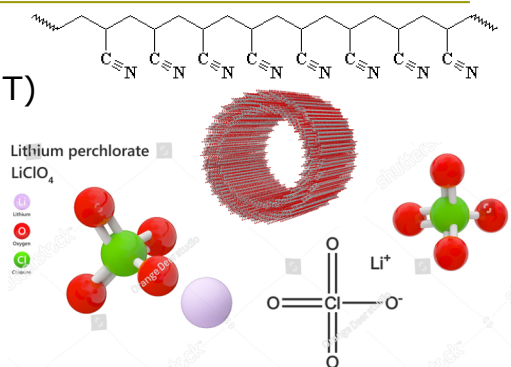
- [1] L. Fernández-Werner et al, Journal of Energy Storage, 12 (2017) 66-77.
 [2] F. Pignanelli et al, Mater. Res. Bull., 106 (2018) 40-48.

2. Selección del Sistema

- Polímero: PAN
- Carga: $\text{H}_3\text{Ti}_2\text{O}_7$ (HTNT)
- Sal: LiClO_4

Se espera:

- Disociar la sal
- Li^+ se asocie al PAN
- ClO_4^- limitado en su movimiento ¿asociado al HTNT?



3. Caracterización Estructural

- Small Angle X-ray Scattering (SAXS)
- XRD convencional
- DSC: calorímetro diferencial

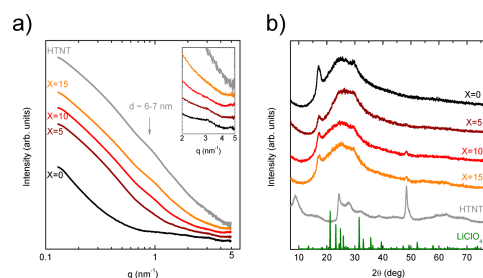


Figure 3. (a) Small angle X-ray scattering and (b) X-ray powder diffraction patterns for Li-PAN-HTNT-X with $X = 0, 5, 10, 15$, HTNT samples, and crystalline LiClO_4 reference.

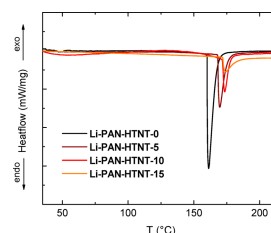


Figure 7. Differential scanning calorimetry profiles for Li-PAN-HTNT-X with $X = 0, 5, 10$, and 15° .

Table 2. DSC Analysis for Li-PAN-HTNT-X with $X = 0, 5, 10$, and 15°

	$X = 0$	$X = 5$	$X = 10$	$X = 15$
T_m ($^\circ\text{C}$)	161.2	169.7	173.4	173.9
ΔH_m (J/g)	159.03	74.74	35.26	34.69

^aMelting temperature (T_m) and heat (ΔH_m) were obtained from DSC analysis.

3. Caracterización Estructural

□ FTIR y Raman

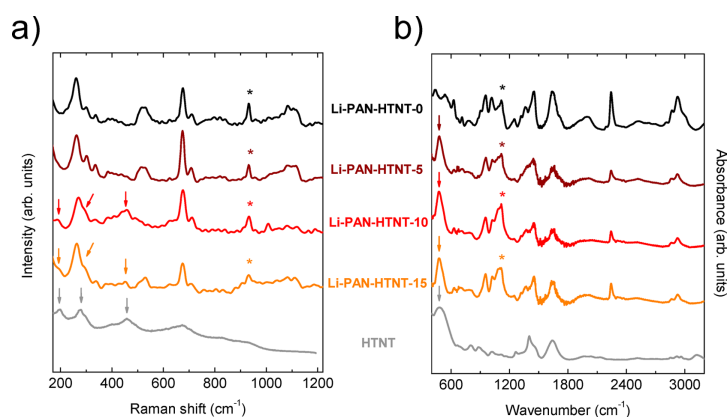


Figure 4. (a) Raman and (b) FT-IR spectra for Li-PAN-HTNT-X with X = 0, 5, 10, 15 and pure HTNT. The arrows and asterisks indicate the presence of HTNT and perchlorate modes, respectively.

3. Caracterización Estructural

□ Confocal Raman

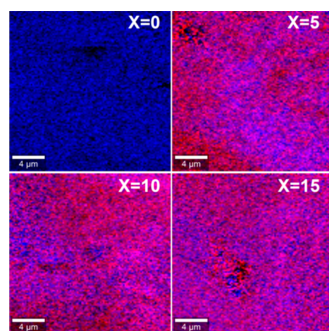


Figure 5. Confocal Raman microscopy images for Li-PAN-HTNT-X with X = 0, 5, 10, and 15. The HTNT-rich (red) and PAN-DMSO-rich (blue) zones in the image were obtained by filtering the peaks at 456 cm⁻¹ ascribed to Ti-O-Ti and at 670 cm⁻¹ ascribed to C-S-C stretching modes, respectively.

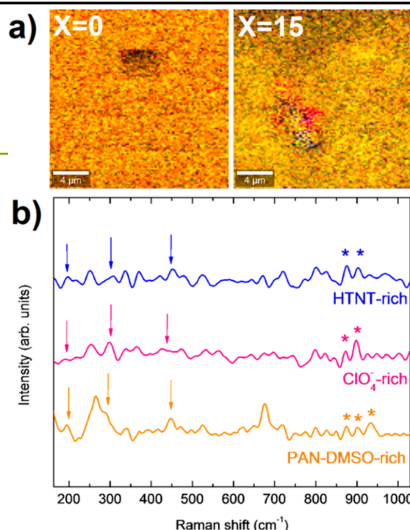
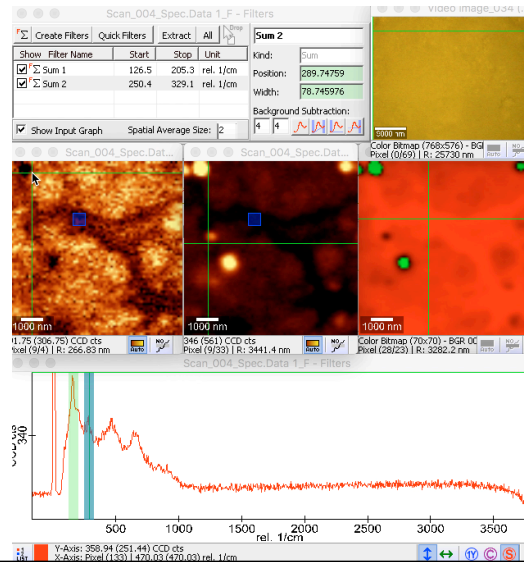


Figure 6. (a) Confocal Raman microscopy images and (b) selected area Raman spectra for Li-PAN-HTNT-X with X = 0 and 15. The HTNT-rich (blue), PAN-DMSO-rich (orange), and perchlorate-rich (pink) zones in the image were obtained by filtering the peaks at 456 cm⁻¹ ascribed to Ti-O-Ti stretching, 670 cm⁻¹ ascribed to C-S-C stretching, and 870–930 cm⁻¹ ascribed to ClO₄ stretching modes, respectively. The arrows and asterisks indicate the presence of HTNT and perchlorate modes, respectively.

3. Caracterización de NT: Microscopia Raman

Ejemplo de Funcionamiento:

- Muestra de NT calentados a $T=200^{\circ}\text{C}$.
- Presencia de Nanopartículas de Anatasa en muestra de NT.



3. Dinámica Molecular

Sistema Li-PAN-PEI
776 átomos, ensamble NVT 2ns
Seguido por DFT

$$I(q) = \sum_i \sum_j f_i f_j e^{-i(qr_{ij} \cos \gamma)} = \sum_i \sum_j \left(f_i f_j \frac{\sin(qr_{ij})}{qr_{ij}} \right)$$

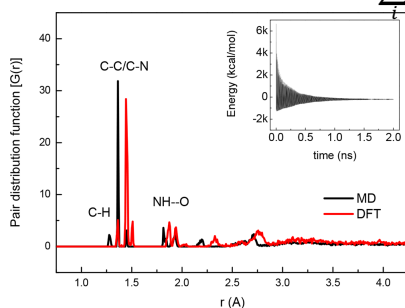


Figure 2. Theoretical PDF $[G(r)]$ for the Li-PEI-PAN model using MD and DFT. The energy convergence for MD simulation is shown in the inset.

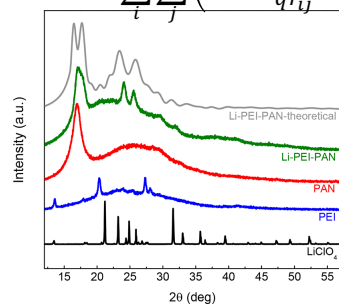
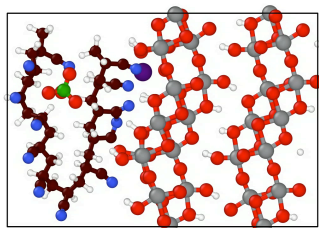


Figure 3. Experimental XRD patterns for LiClO_4 , PEI, PAN, and Li-PEI-PAN and theoretical simulation of XRD patterns for Li-PEI-PAN.

3. Dinámica Molecular

- NVT a 300 K (3 ps polímero + 500 fs DFT sistema total)
- $E_{\text{conf1}} - E_{\text{conf2}} = 5.0$ eV

Conf. 1



Conf. 2

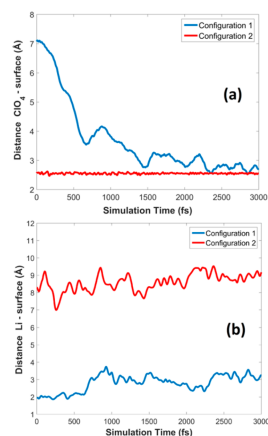
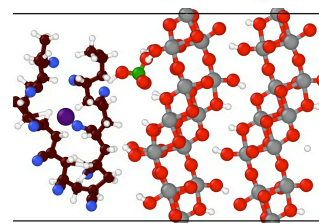


Figure 2. (a) Perchlorate and (b) lithium ions distance from HTNT surface in configurations 1 and 2 as a function of simulation time.

4. Caracterización Electroquímica

- Propiedades Eléctricas

$$\sigma_{\text{total}} \sim 3.95 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$$

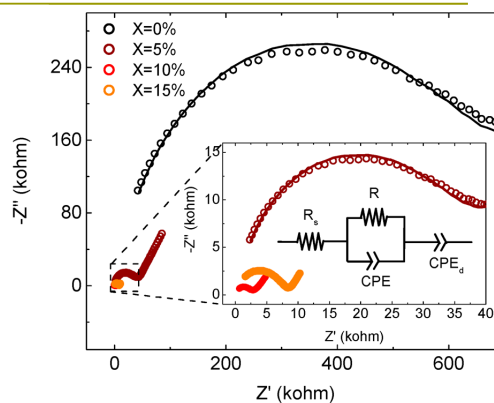


Table 3. Impedance Spectroscopy Analysis for Li-PAN-HTNT-X with X = 0, 5, 10, and 15^a

	X = 0	X = 5	X = 10	X = 15
R (ohm)	$(6.13 \pm 0.12) \times 10^5$	$(3.39 \pm 0.07) \times 10^4$	$(2.53 \pm 0.12) \times 10^3$	$(7.93 \pm 0.25) \times 10^3$
CPE Q ₀ (F)	$(1.37 \pm 0.20) \times 10^{-12}$	$(2.48 \pm 0.37) \times 10^{-11}$	$(2.09 \pm 0.62) \times 10^{-9}$	$(4.53 \pm 1.00) \times 10^{-10}$
CPE n	0.860 ± 0.011	0.860 ± 0.012	0.685 ± 0.023	0.717 ± 0.018
σ (S·cm ⁻¹)	$(1.63 \pm 0.08) \times 10^{-6}$	$(2.95 \pm 0.15) \times 10^{-5}$	$(3.95 \pm 0.20) \times 10^{-4}$	$(1.26 \pm 0.64) \times 10^{-4}$

^aResistance (R) and constant phase element (CPE) parameters were calculated from the circuit model fittings shown in Figure 8b, inset. The lithium conductivity (σ) was calculated using $\sigma = 1/\rho$ using $\rho = R(A/d)$ with $A = 0.1$ cm² as the electrode contact area and $d = 0.1$ cm as the pellet thickness. In all cases, the analysis was performed in triplicate.

5. Conclusiones Generales

- Se realizó la preparación de nanocompuestos polímero-nanopartícula
- Se caracterizaron de forma Químico-Estructural
- Se caracterizaron electroquímicamente, con valores en rangos aceptables, acorde al estado del arte. $\sigma_{total} \sim 3.95 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$

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Article
pubs.acs.org/JPCA

Enhancement of Lithium-Ion Transport in Poly(acrylonitrile) with Hydrogen Titanate Nanotube Fillers as Solid Polymer Electrolytes for Lithium-Ion Battery Applications

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ABSTRACT: In the present work, we report the enhancement of lithium-ion dissociation and transport in poly(acrylonitrile) host promoted by the addition of hydrogen titanate nanotube fillers for solid polymer electrolytes. We show experimental and theoretical evidence of lithium perchlorate dissociation due to the presence of the acidic hydrogen titanate nanotubes embedded in the polymer matrix. We performed confocal Raman microscopy analysis to reveal the presence of lithium perchlorate dissociation at the interface of polymer and nanotube fillers. The large affinity of perchlorate anions at the hydrogen titanate nanotube surface, as envisaged from the *ab initio* molecular dynamics simulations, could be responsible for the enhancement of more than 2 orders of magnitude in the lithium conductivity, reaching $\sim 4 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ for a certain amount of nanotube fillers addition.

