

# State of the art of Li-ion Rechargeable Batteries and Solid Oxide Fuel Cells(SOFC)

By

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Institute of Physical Chemical Applied  
Research (IPCAR) UT.



*May 14, 2010*

# Cathode Materials for Li-ion Rechargeable Batteries

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# What is the IPCAR?



IPCAR: Institute of Physical Chemical Applied

Director: Dr  
Rolando Roque

→ **Energy Storage**  
Dr. Rolando Roque

→ **Rechargeable Lithium ion Batteries  
and Solid Oxide Fuel Cells (SOFC)**  
Dr. Santander Nieto

→ **Nanomaterials**  
Dr. Francisco Márquez and  
Dr. José Duconge

## Research Team

- María Cotto
- Carmen Bonilla
- Abraham García
- Carlos Neira
- Francisco Díaz
- Dr. Rolando Roque
- Dr. Francisco Márquez
- Dr. Santander Nieto
- Dr. José Duconge
- Dr. Agustín Ríos
- Ing. Ramón Polanco

## Important collaborations

- SPCLAB: Advanced Materials Research Laboratory, University of Puerto Rico, Río Piedras Campus.
- University of Puerto Rico, Cayey Campus
- Universidad Autónoma de Madrid

# Outline

- **Brief Introduction**

(Lithium ion Rechargeable Batteries)

- **Synthesis Method of cathode materials**

(Influence of Annealing Temp. and Annealing time, etc.)

- **Layered  $\text{Li}(\text{NiM})\text{O}_2$  Cathode** (M= Co, Al, etc)

Results and discussions

Summary

- **Lithium Manganese Spinel System**

Results and discussions

Nano-crystalline cathodes

Summary

- **Fuel Cells (SOFC)**

## Terminology : Li ion battery

*Capacity (C or Ah):* Total amount of charge involved in the electrochemical reaction

*Specific capacity (Ah/kg):* Capacity per unit mass.

Open Circuit voltage    Voltage with no load

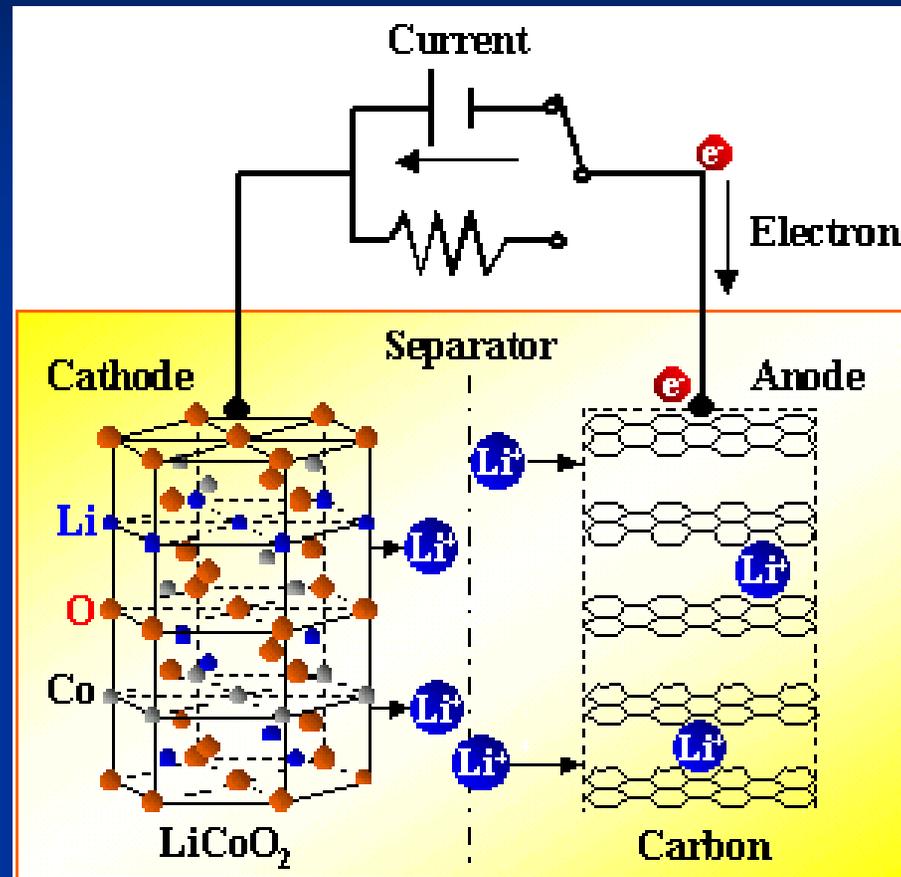
Theoretical capacity    26.8 Ah/(gm equivalent wt)

for  $\text{LiMn}_2\text{O}_4$   $(26.8/180.82) = 148 \text{ mAh/g}$

Measured capacity : (Current \* time) / (active material) mAh/gram

'C' rate : 1 C ~ 148 mA/g

# Working principles of a typical Li ion rechargeable battery



# The distinguishing features of today's commercial Li-ion batteries are:

**High operating voltage:** a single cell has an average operating potential of approx. 3.6 V

**Compact, lightweight, and high energy density** (1.5 times and spec.energy is about twice Ni-Cd batteries)

**Fast charging potential :** (80-90% of full capacity in one hour)

**High discharge rate:** up to 3C are attainable

**Wide range of operating temperature:** from  $-20$  to  $+60$  °C

**Superior cycle life:** service life of a battery exceeds 500 cycle

**Excellent safety**

**Low self-discharge:** only 8-12 % per month

**Long shelf-life:** no reconditioning required up to approx 5 years (Ni-Cd: 3 month)

**No memory effect:** can be recharged at any time

**Non-polluting:** does not use toxic heavy metals such as Pb, Cd or Hg.

## Cathode Materials Considerations

1. The transition metal ion should have a large work function (highly oxidizing) to maximize cell voltage.
2. The cathode material should allow an insertion/extraction of a large amount of lithium to maximize the capacity.

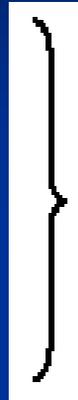
**High cell capacity + high cell voltage = high energy density**

3. The lithium insertion/extraction process should be reversible and should induce little or no structural changes. This prolongs the lifetime of the electrode.
4. The cathode material should have good electronic and Li<sup>+</sup> ionic conductivities. This enhances the speed with which the battery can be discharged.
5. The cathode should be chemically stable over the entire voltage range and not react with the electrolyte.
6. The cathode material should be inexpensive, environmentally friendly and lightweight.

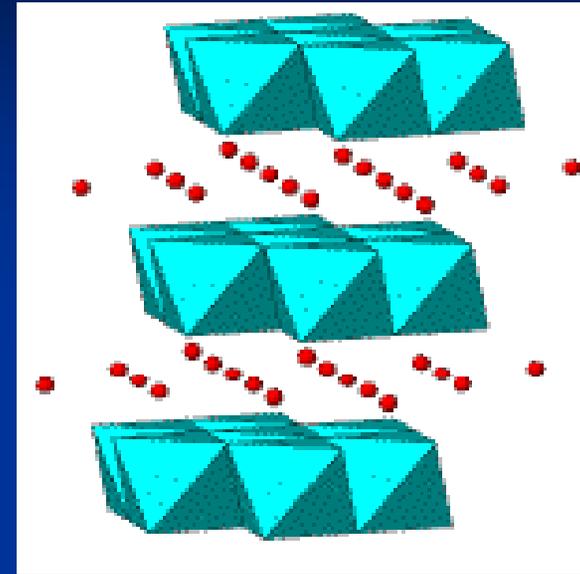
Taken from A. Manthiram &  
J. Kim, Chem. Mater. **10**,  
2895-2909 (1998).

# Materials for cathode

- $\text{LiNiO}_2$
- $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$
- $\text{LiMnO}_2$



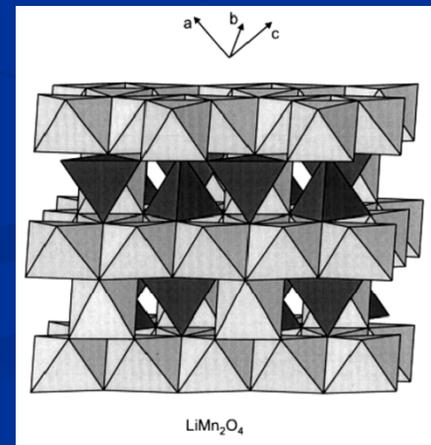
**Layered structures**



- $\text{LiMn}_2\text{O}_4$  (spinel structure)
- $\text{LiFePO}_4$  (olivine structure)



**3D structures**



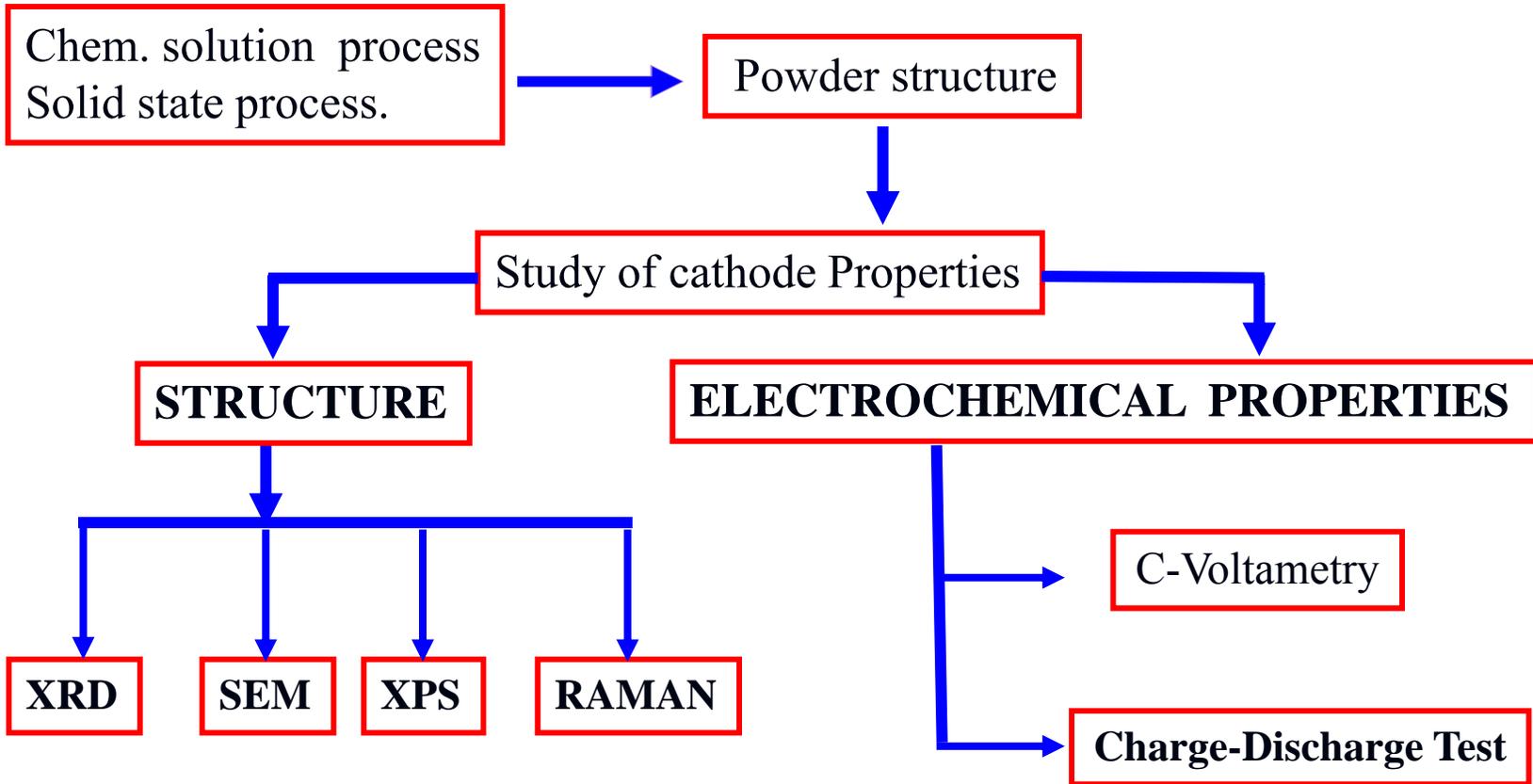
## *Comparison of battery system properties*

<b>Material</b>	<b>Pr. Cap. (mAh/g)</b>	<b>Density (g/cm<sup>3</sup>)</b>	<b>En. Dens. (mAh/cm<sup>3</sup>)</b>	<b>Shape of Discharge</b>	<b>Safety</b>	<b>Cost</b>	<b>Comment</b>
LiCoO <sub>2</sub>	160	5.05	808	Flat	Fair	High	Small-size LIB
LiNiO <sub>2</sub>	220	4.80	1056	Sloping	Poor	Fair	Very Difficult
LiMn <sub>2</sub> O <sub>4</sub>	148	4.20	462	Flat	Good	Low	HEV, EV
LiCo <sub>0.2</sub> Ni <sub>0.8</sub> O <sub>2</sub>	180	4.85	873	Sloping	Fair	Fair	LIP? Small Sca
LiMn <sub>0.5</sub> Ni <sub>0.5</sub> O <sub>2</sub>	160	4.70	752	Sloping	Good	Low	?
LiFePO <sub>4</sub>	160	3.70	592	Flat	Good	Low	Low Cond.

# Statement of The Research Problem

- Is it possible to reduce the annealing temperature of the cathode materials ?
- How to improve the capacity fade of the cathode materials without sacrificing the specific capacity?
- Influence of different metal ion dopants on structural and electrochemical properties of layered and spinel cathodes materials.
- Understanding of failure mechanism responsible for the capacity loss in layered compounds.
- Understanding the failure mechanism responsible for the capacity fade of nano-crystalline LMO using XPS analysis, XRD and micro-Raman spectroscopy.

# Method of Characterization

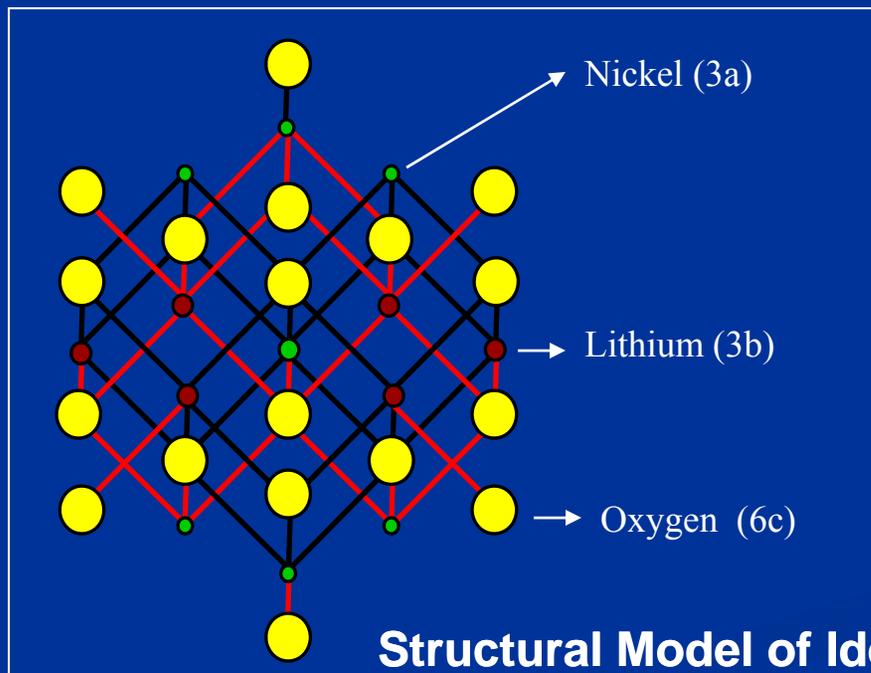


# Layered $\text{Li}(\text{Ni},\text{M})\text{O}_2$ Systems

# Current status

✓  $\text{LiCoO}_2$  is still the only commercialized cathode material due to its excellent electrochemical properties. However, cobalt is relatively expensive and toxic and only 50% of the theoretical capacity of  $\text{LiCoO}_2$  could be practically utilized.

✓  $\text{LiNiO}_2$  has been considered as a promising cathode material. It is extremely difficult, however, to synthesize stoichiometric  $\text{LiNiO}_2$  due to the high-temperature preparation conditions that lead to the formation of  $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ .

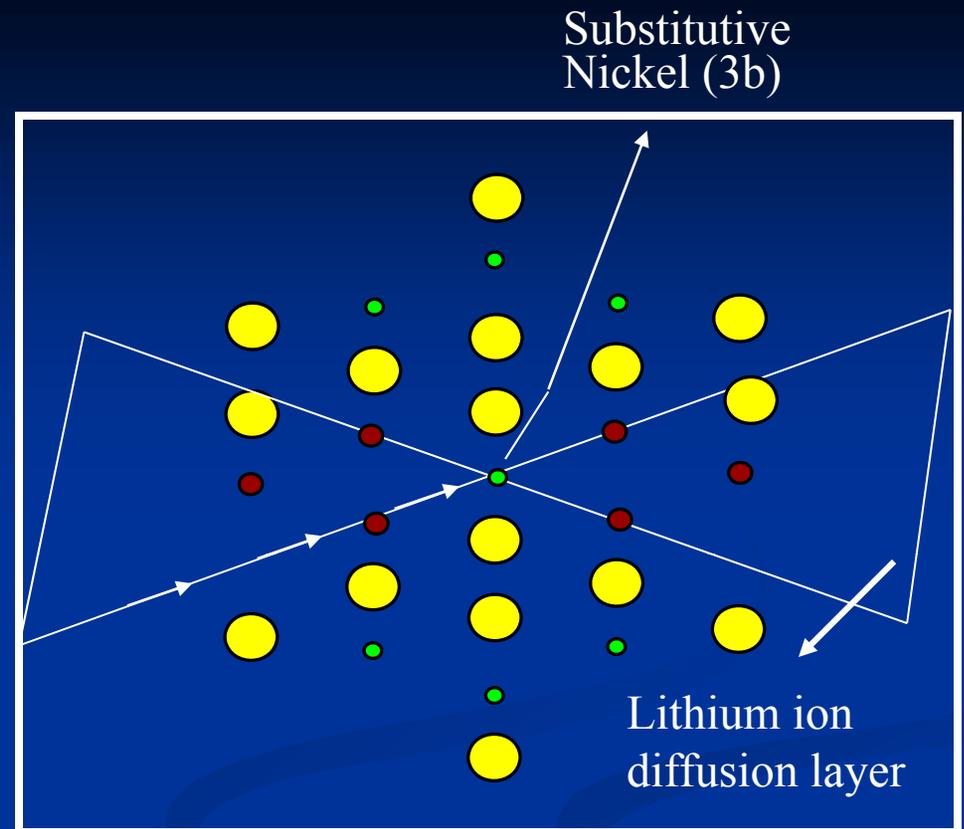


Due to the difficult oxidation of  $\text{Ni}^{2+}$  to  $\text{Ni}^{3+}$  and the volatility of the lithium compounds, nonstoichiometric oxides with  $0.005 < x < 0.2$  are usually obtained.

Structural Model of Ideal  $[\text{Li}]_{3b}[\text{Ni}]_{3a}[\text{O}]_{6c}$

## Current status (cont...)

The presence of nonstoichiometric  $\text{Ni}^{2+}$  ions in lithium-rich layers frustrates the long-range Li-Ni ordering, culminating at a critical lithium concentration of  $x = 0.38$  in a random distribution of  $\text{Li}^+$ ,  $\text{Ni}^{3+}$ , and  $\text{Ni}^{2+}$  ions within the cubic crystal structure



*Solid State Ionics 80 (1995)  
H. Arai, et al*

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Cationic substitutions have been found to improve the electrochemical properties in the case of layered nickel oxides

## Research approach

- Optimization of synthesis condition (of  $\text{Li}(\text{NiM})\text{O}_2$ ) and cell fabrication

Reaction time, reaction temperature

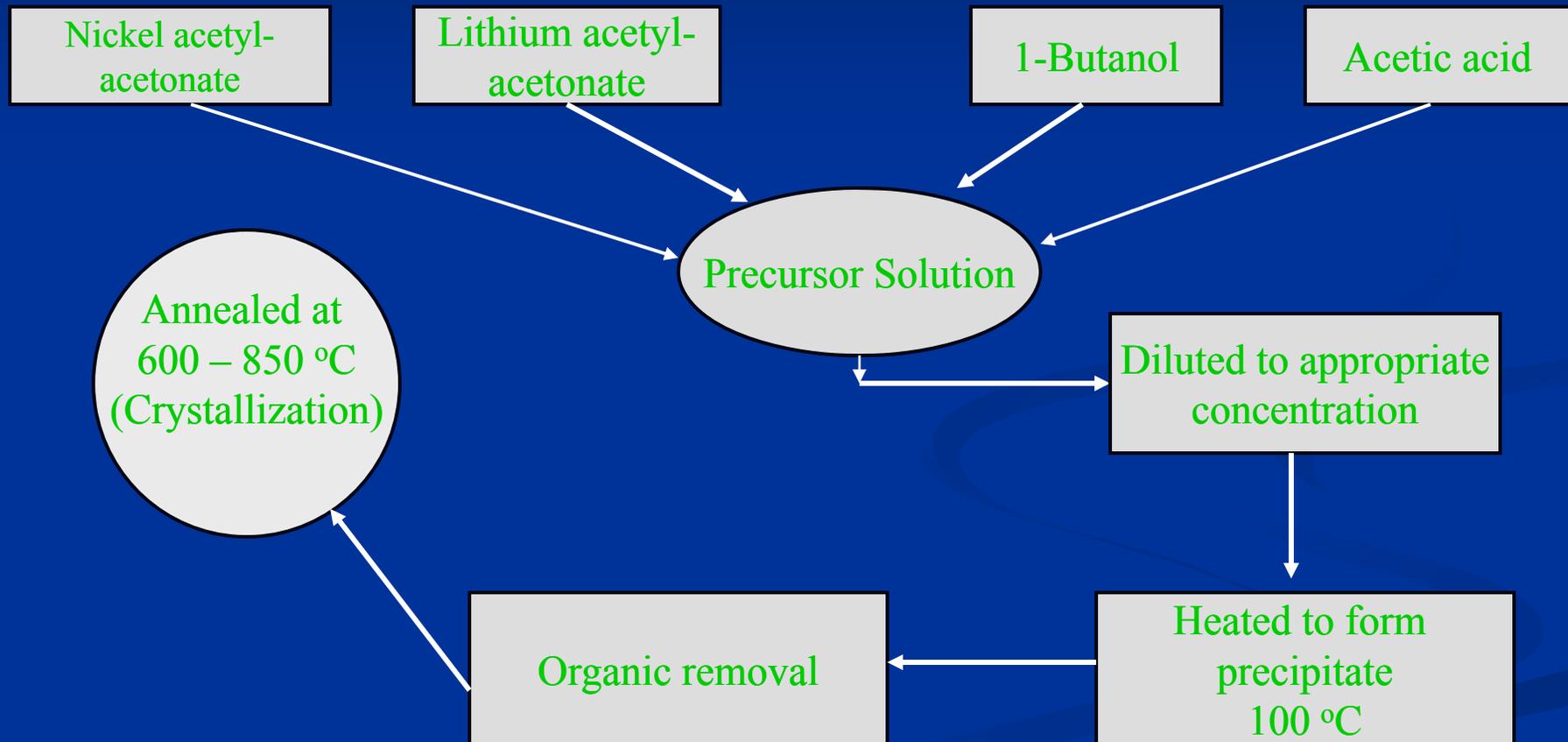
Formulation of composite cathode [Active material, C black, plasticizer and NMP (solvent)]

Formulation of electrolyte ( $\text{LiPF}_6$  salt, EC and DMC)

- Substitution of Ni ion with trivalent M Cation (M= Zr, Mo, Al, etc)

Partial substitution of nickel with other elements that leads to a reduction in the amount of Ni in the Li-type sites can be expected to improve the structural and electrochemical properties of lithium nickelate.

# Powder preparation



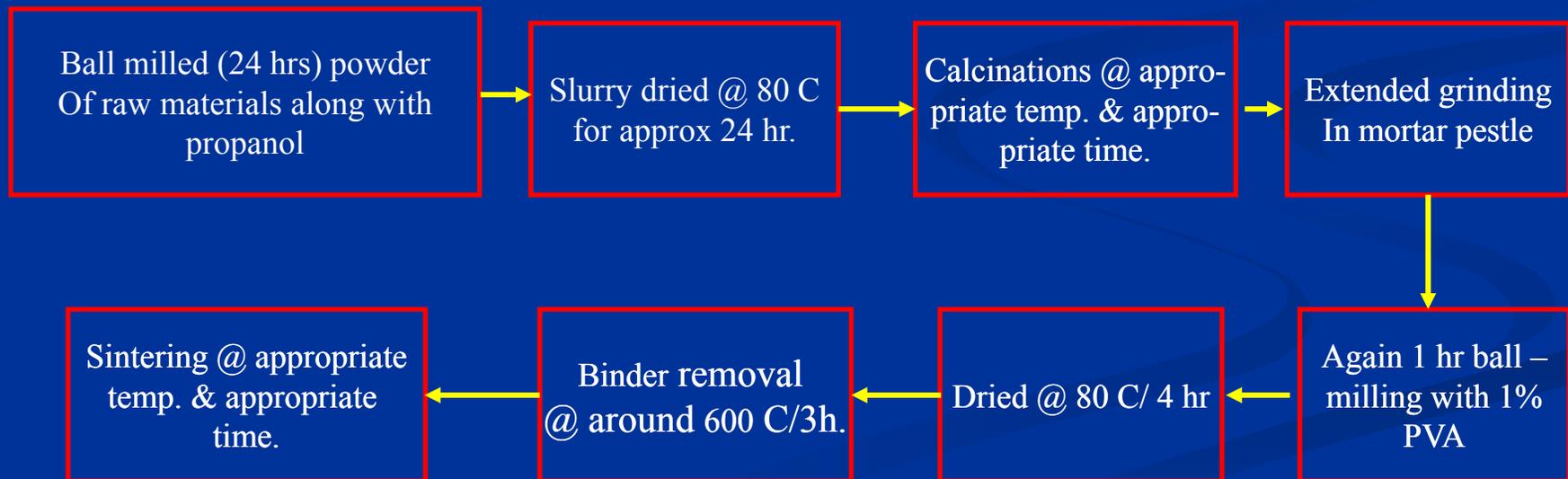
(Outline for Chem. solution derived  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  cathode )

# Powder Preparation

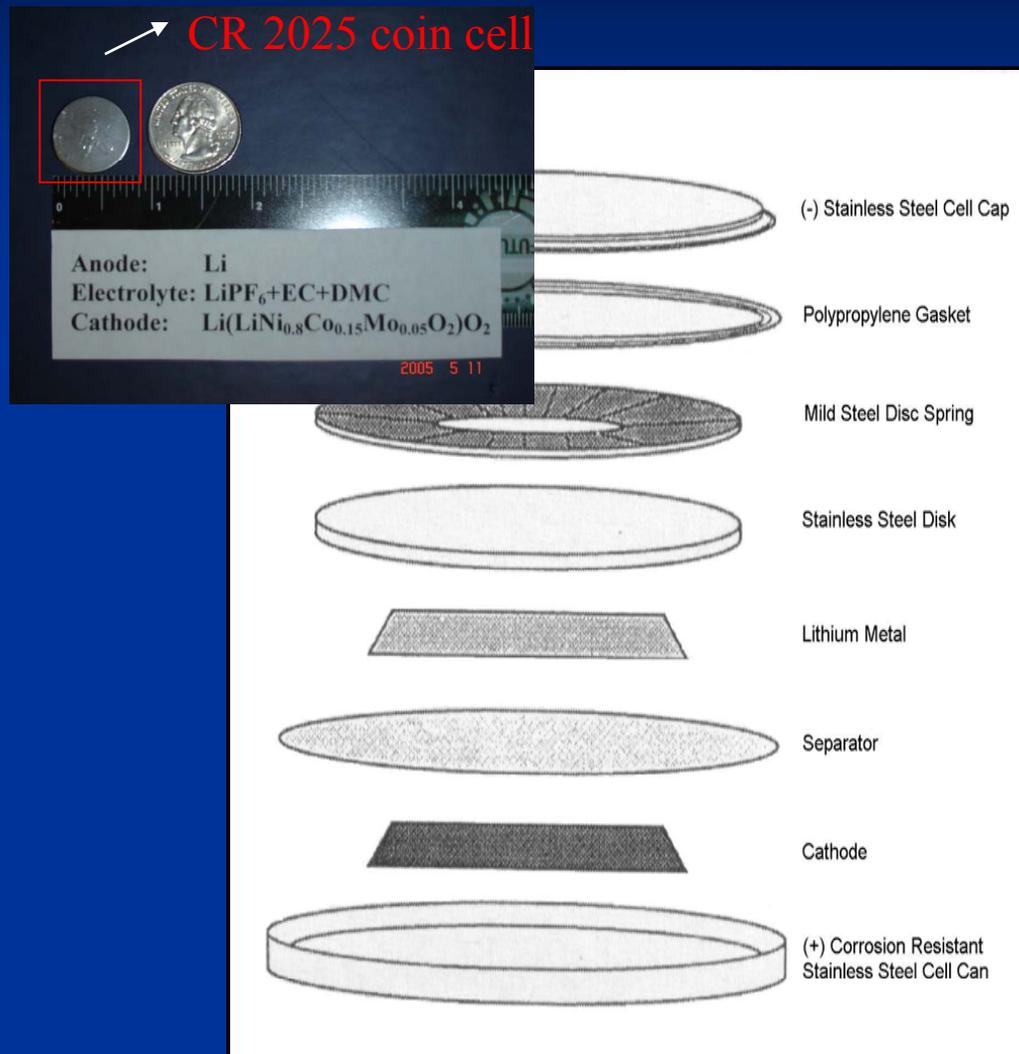
## Solid State Reaction:

$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  and  $\text{LiNi}_{0.25}\text{M}_{0.5}\text{Co}_{0.25}\text{O}_2$  were synthesized with the following processing route

Raw materials:  $\text{MO}_2$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{LiO}_2$  and  $\text{NiO}$  (99.9 % purity)



# Characterization of electrochemical properties



## Working electrode

Active powder – 80 wt%

Carbon black – 10 wt%

PVDF binder – 10 wt%

Solvent – NMP

Current collector- Al

## Electrolyte

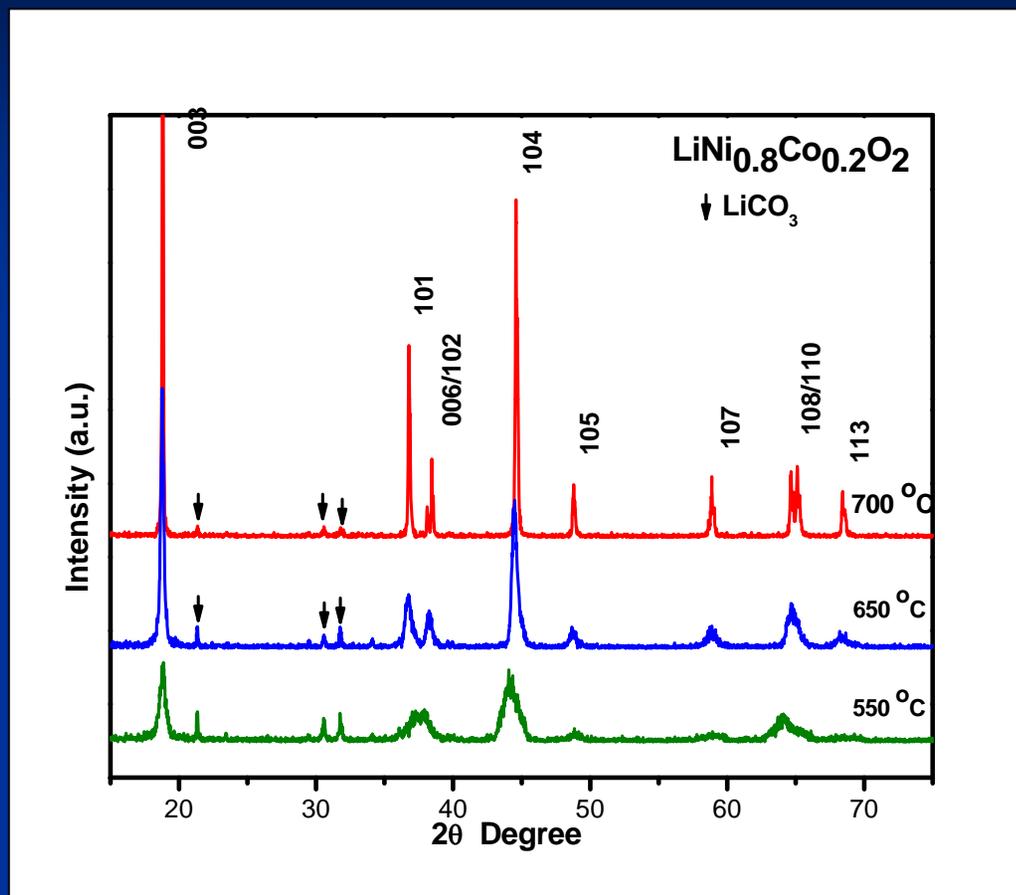
$\text{LiPF}_6$  – 1M

EC : DMC- 1:1

## Counter electrode

Li foil on copper

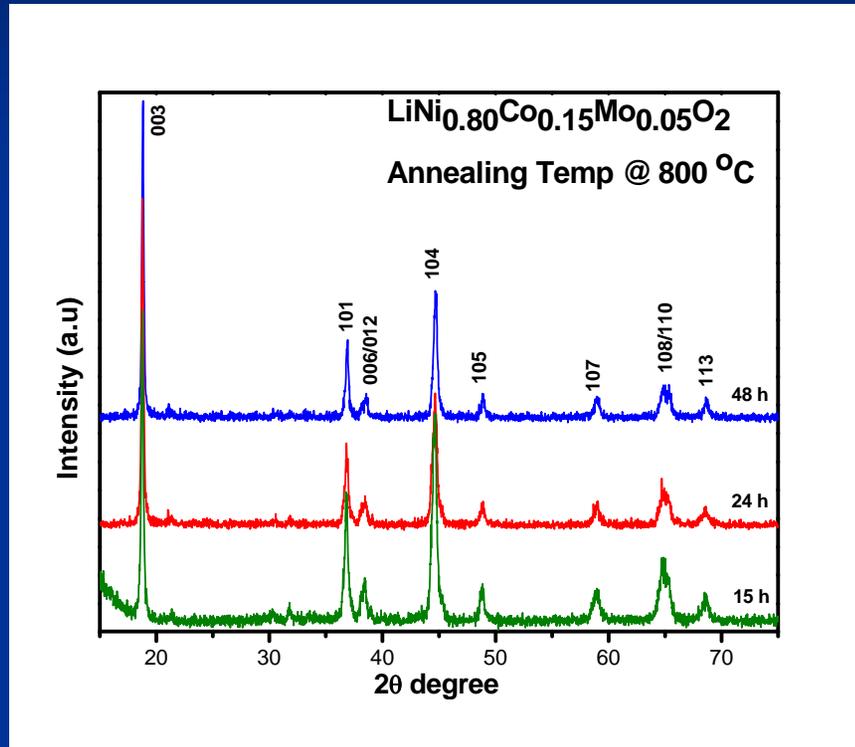
# X-ray diffraction analysis $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$



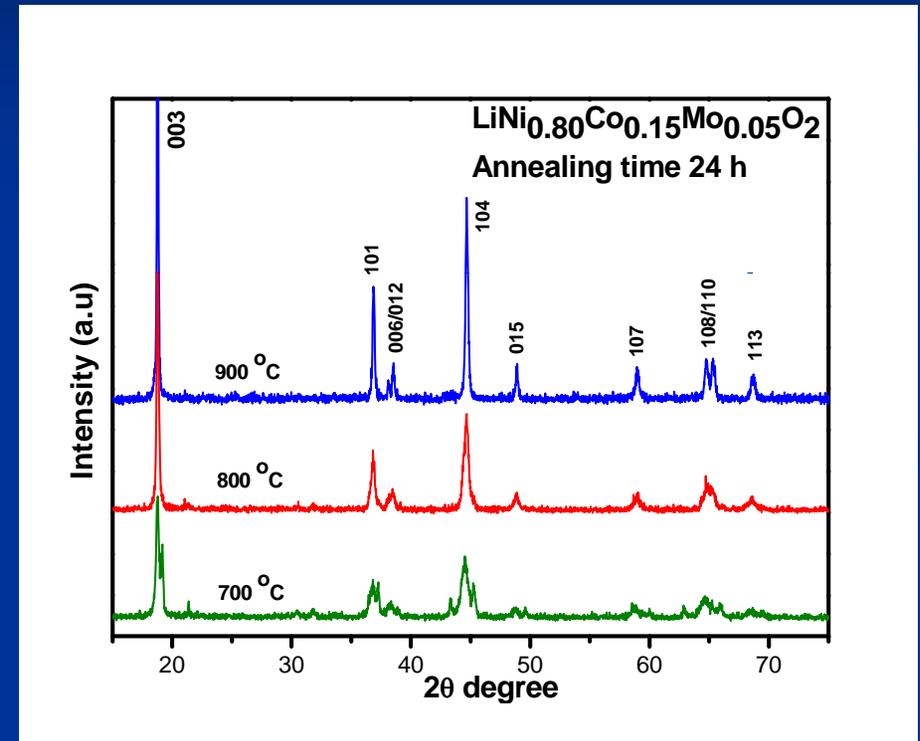
Hexagonal doublets (006/102) and (108/110) are splitted indicates reasonable hexagonal ordering

# X-ray diffraction analysis $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mo}_{0.05}\text{O}_2$

## Effect of reaction time



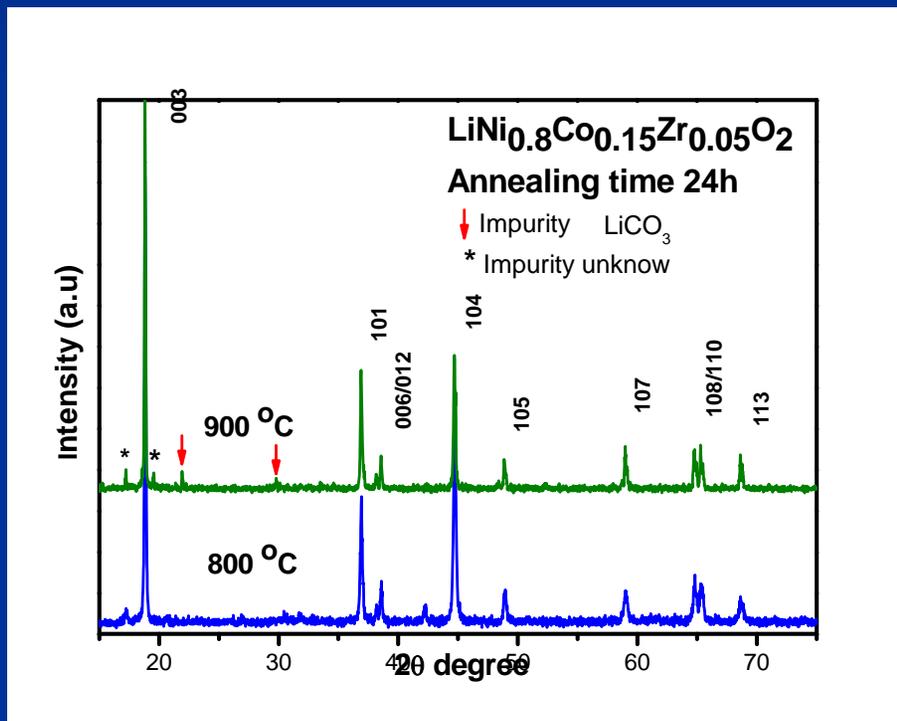
## Effect of reaction temperature



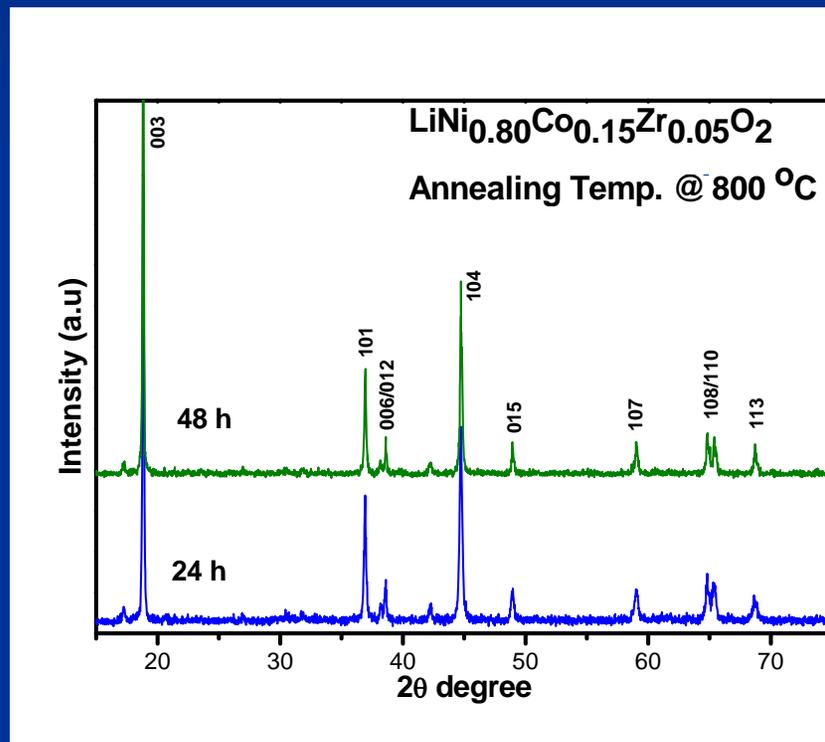
The data reveal that the structural stability increase with increase the temperature, and annealing time, as indicated by the separation between the (018) and (110) reflections

# X-ray diffraction analysis $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Zr}_{0.05}\text{O}_2$

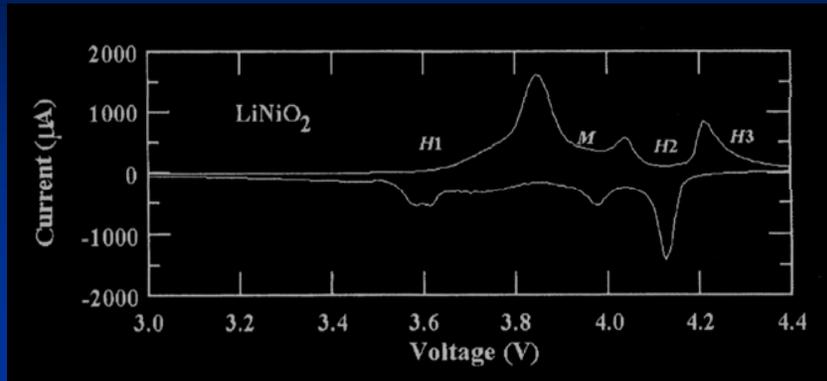
## Effect of reaction temperature



## Effect of reaction time

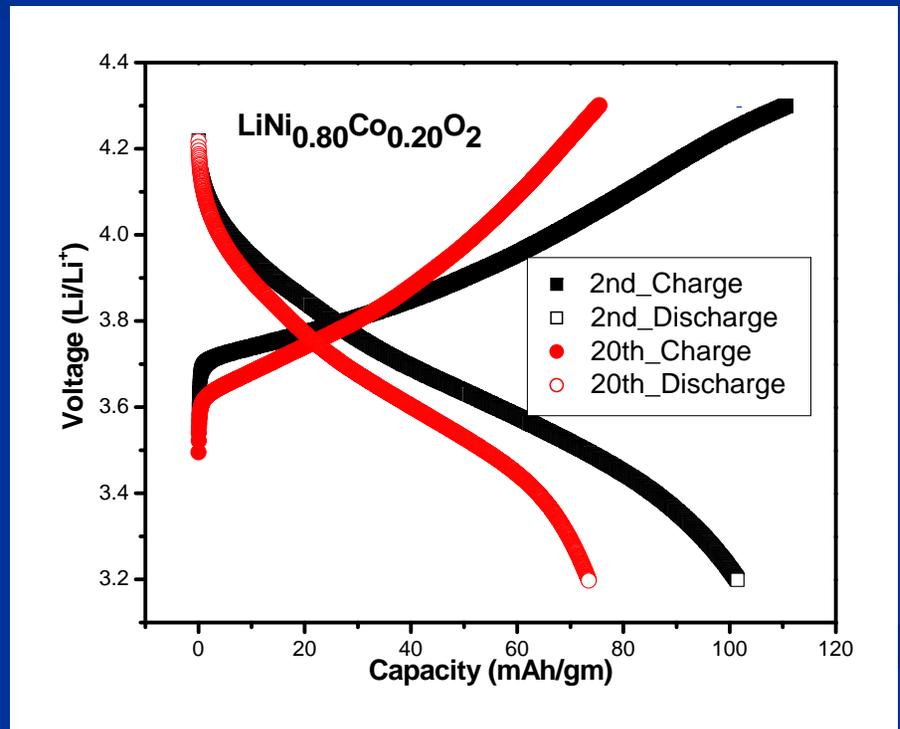
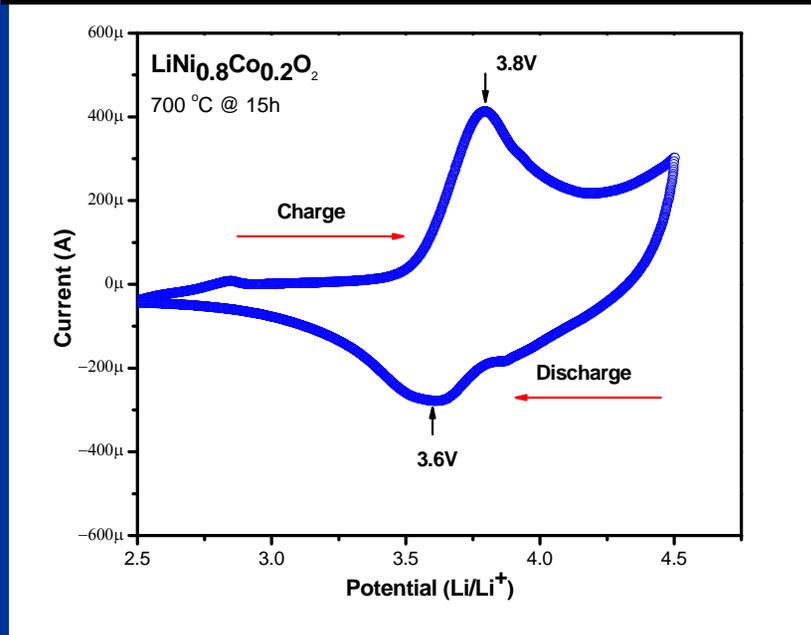


# Cycleability of $\text{LiNi}_{0.80}\text{Co}_{0.20}\text{O}_2$ cathode



Pure  $\text{LiNiO}_2$  was reported to exhibit three phase transitions during the Li extraction and insertion.

$\text{H1} \leftrightarrow \text{M} \leftrightarrow \text{H2} \leftrightarrow \text{H3}$  \*

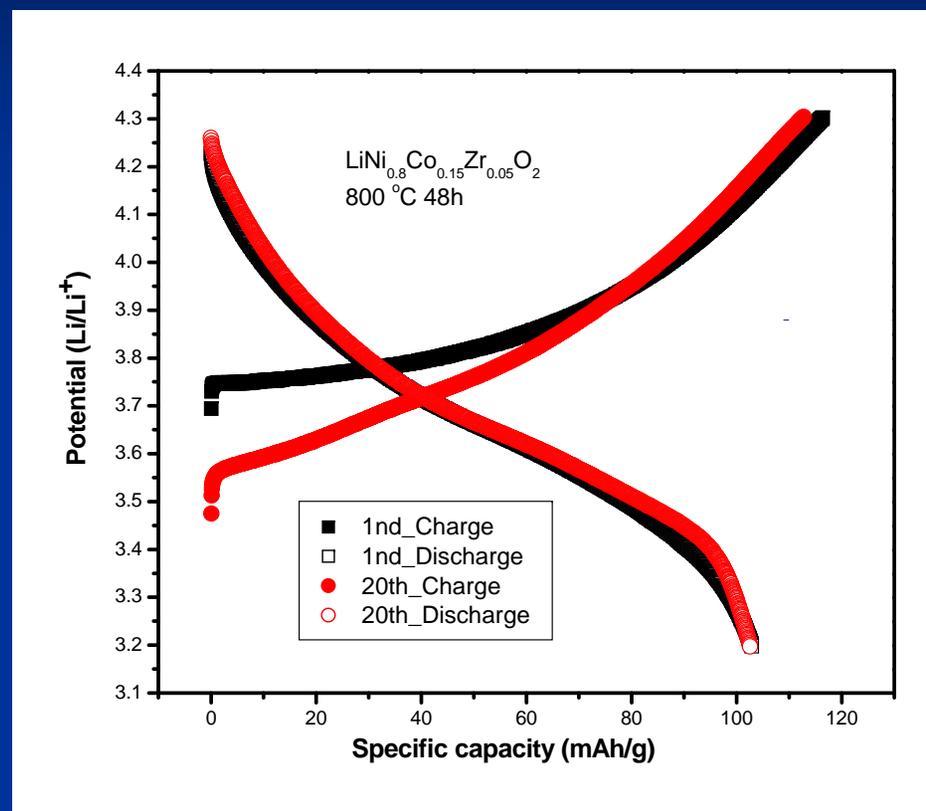
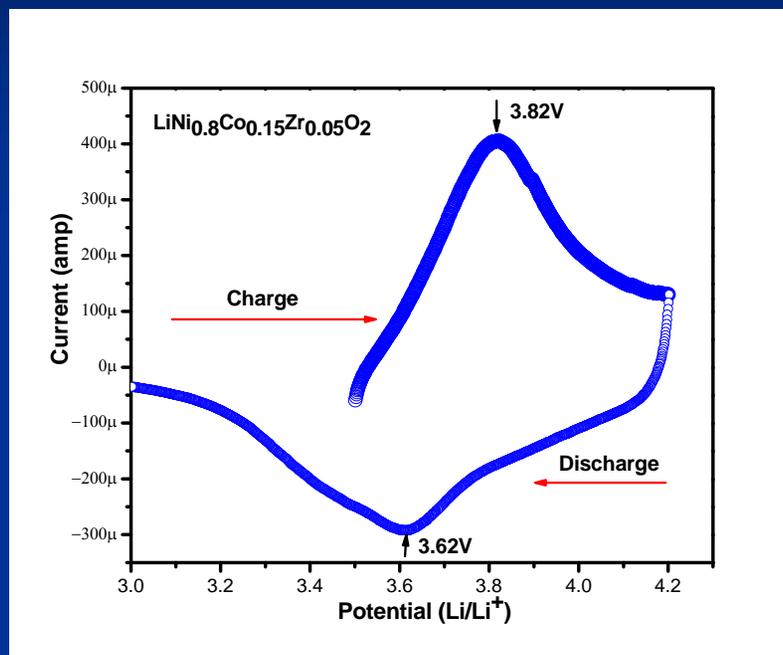


Single-phase reaction takes place during the charge and discharge cycling.

\* H. Arai, S. Okada, Y. Skurai, J.I. Yamaki, *Solid State Ionics* **95**, 275 (1997).

# Cycleability of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Zr}_{0.05}\text{O}_2$ cathode

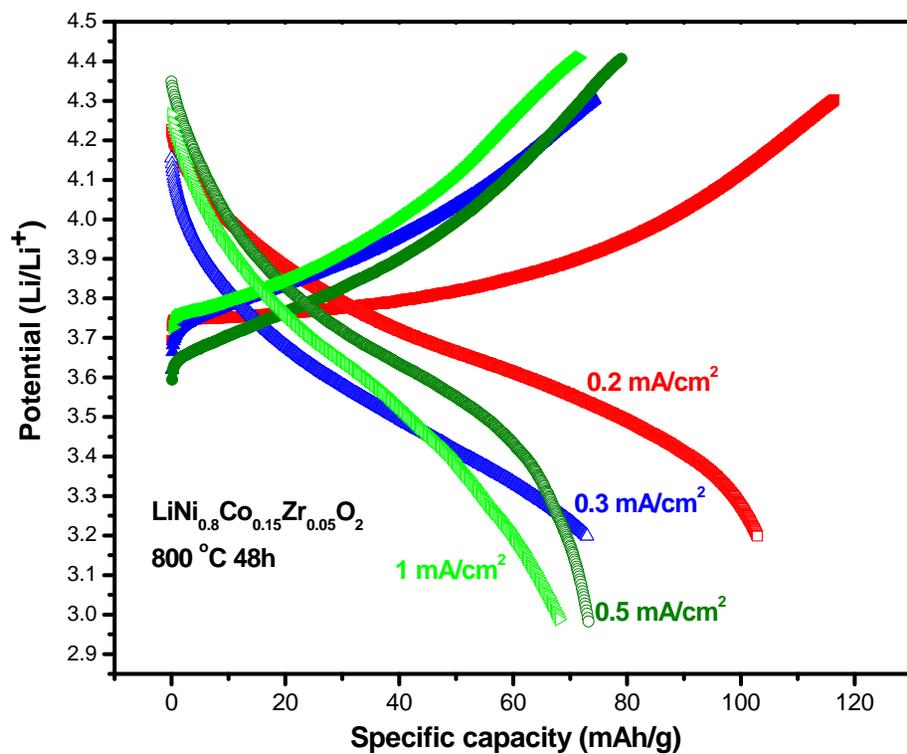
Load  $0.45\text{mA}/\text{cm}^2$



M doping could suppress the multi phase transition observed during the charge-discharge of  $\text{LiNiO}_2$  cathode materials

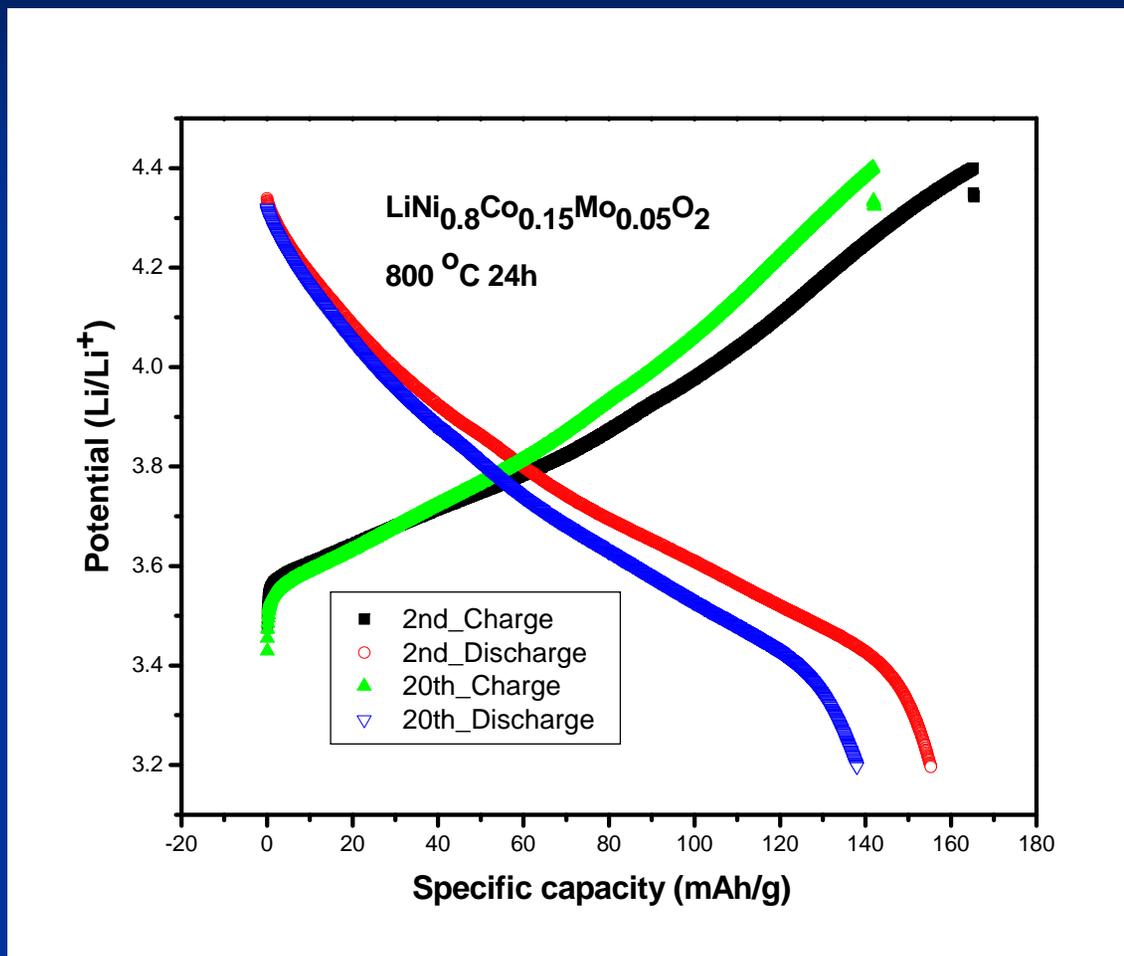
🏠 No capacity fading up to 20 cycles

# Cycleability of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Zr}_{0.05}\text{O}_2$ cathode



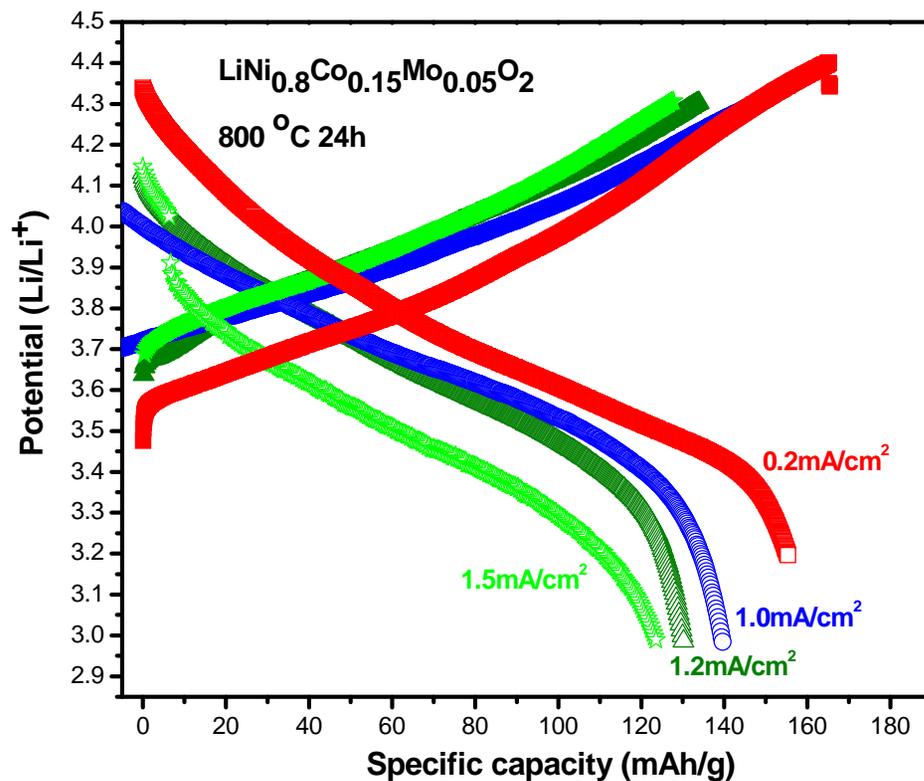
Rate (mA/cm <sup>2</sup> )	Discharge Capacity (mAh/gm)	% Capacity retention (No. of cycles)
0.2	100	100(20)
0.3	73	88(20)
0.5	73	74(20)
1.0	68	48(20)

# Cycleability of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mo}_{0.05}\text{O}_2$ cathode



High capacity and good capacity retention

# Cycleability of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mo}_{0.05}\text{O}_2$ cathode



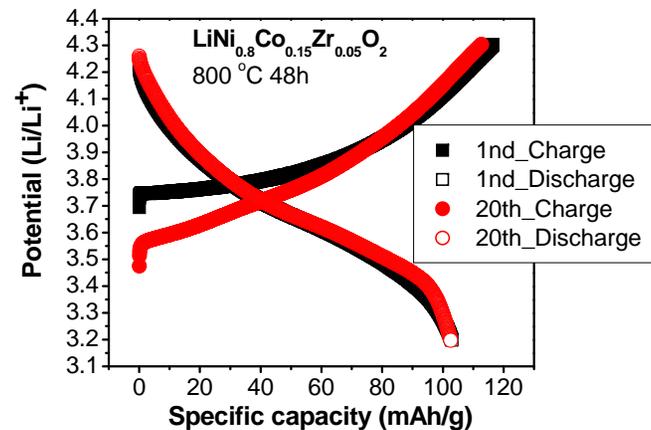
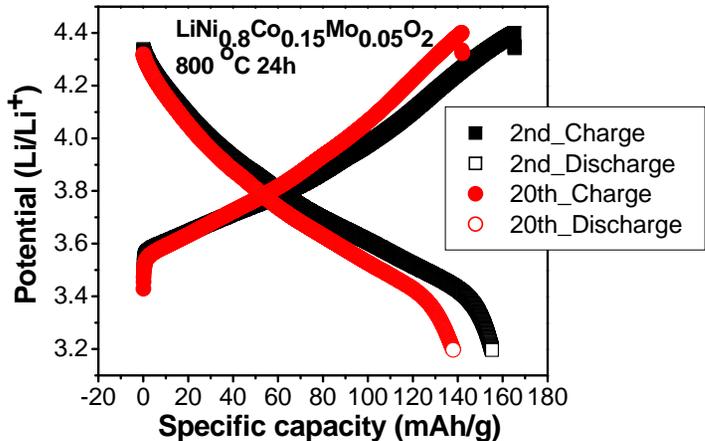
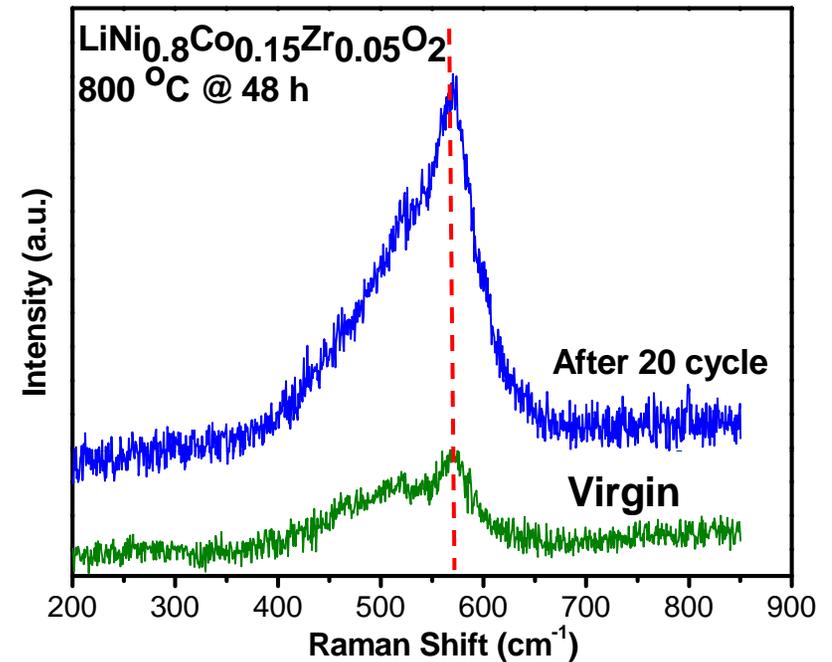
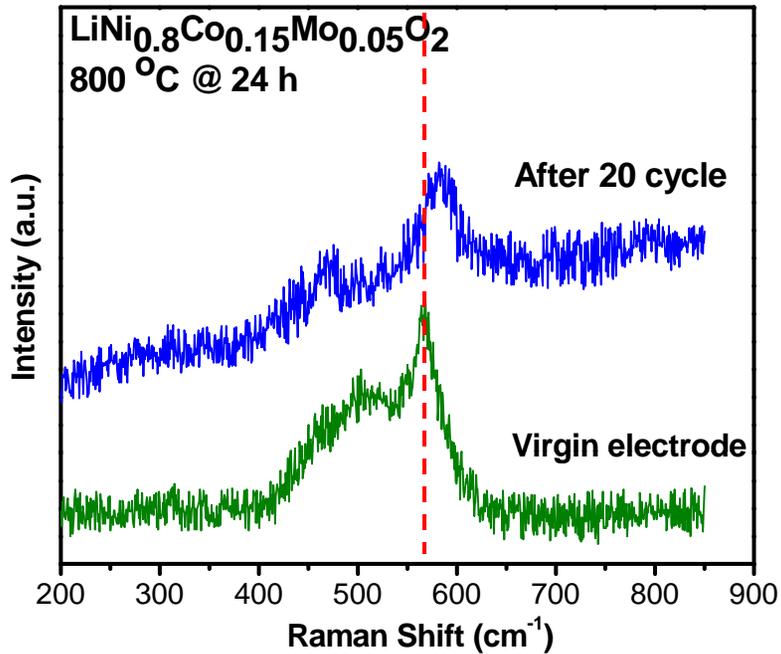
Rate (mA/cm <sup>2</sup> )	Discharge Capacity (mAh/gm)	% Capacity retention (No. of cycles)
0.2	155	89(20)
1.0	139	50(20)
1.2	130	55(20)
1.5	124	48(20)

## Comparison of the electrochemical characteristics of LNCMO based cathodes

Composition	Discharge Capacity (mAh/gm)	Rate	% Capacity retention (No. of cycles)
$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$	100	0.45 mA/cm <sup>2</sup>	72 (20)
$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mo}_{0.05}\text{O}_2$	155		89(20)
$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Zr}_{0.05}\text{O}_2$	102		100(20)

The electrochemical study on the metal oxide LNCMO resulted in good capacity retention than LNCO when the cell is cycled above 4 - 3.2V.

# Micro-Raman analysis : LNCMO



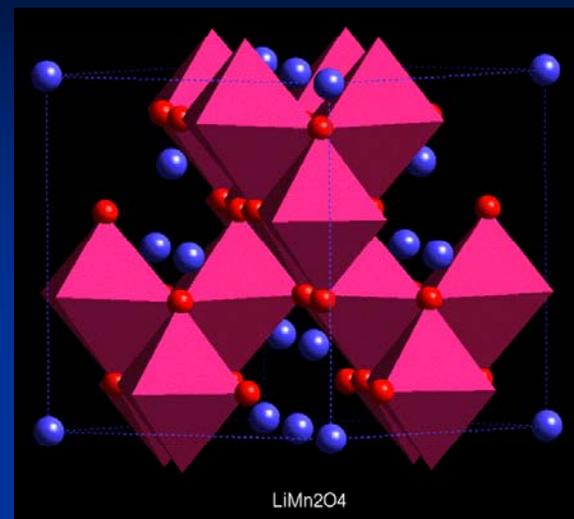
# Summary

- ✓ We have studied the electrochemical properties of solution route derived  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  and M doped  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  cathodes for Li ion rechargeable batteries.
- ✓  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  showed poor cycleability/ capacity fading.
- ✓ M doping ( $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{M}_{0.05}\text{O}_2$ ) produced good cycleability with less capacity fading.
- ✓ Micro Raman spectroscopy is very effective in examining the local structure change of lithium Nickelates oxide upon electrochemical or chemical cycling process and in estimating the phase stability of lithium Nickelates cathode materials.
- ✓ LNCMO can be considered as candidate for positive electrode in Li-ion batteries.

# ***3D Structure – Spinel Systems***

## LiMn<sub>2</sub>O<sub>4</sub> compounds:

- Advantages over other compounds:
- Theoretically all Li can be extracted
- Two voltage of operation
- Less expensive
- Environmentally much more benign



LiMn<sub>2</sub>O<sub>4</sub> compound has a cubic spinel structure, in which the Mn<sub>2</sub>O<sub>4</sub> framework is constructed of face sharing octahedra and tetrahedra which provide a conducting pathway for the lithium ions.

The structure remains intact for Li-insertion and extraction over the range  $-1 < x < 1$  composition range.

- **The high voltage (about 4V** with respect to Li) form of the spinel Li<sub>(1-x)</sub>Mn<sub>2</sub>O<sub>4</sub> is capable of releasing lithium ions. Removal of Li can be extended to x=1.
- **The low voltage (about 3V** with respect to Li) Li<sub>(1+x)</sub>Mn<sub>2</sub>O<sub>4</sub> form is capable of accepting lithium ions.

# Lithium manganate spinel

**Composition range  $0 \leq x \leq 1$  (~4V)**

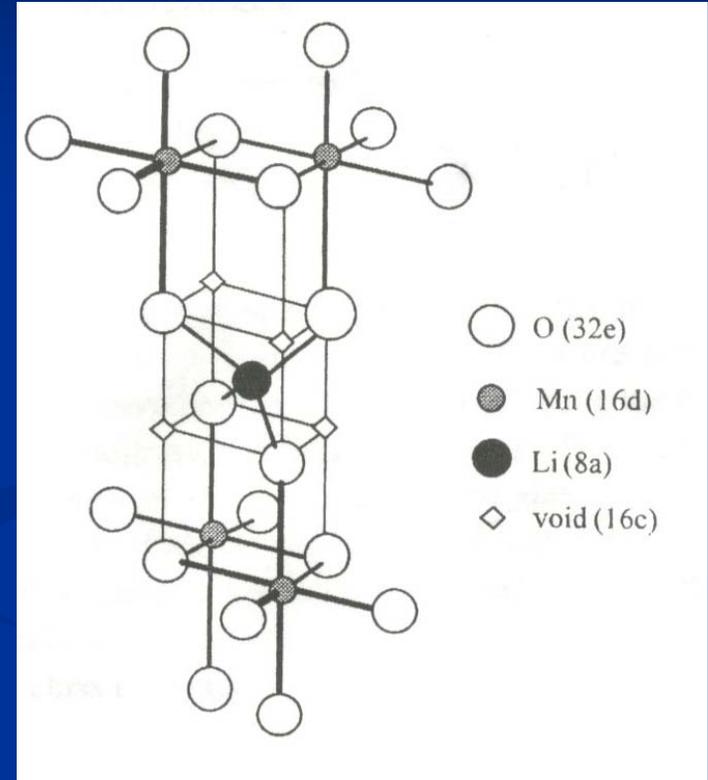


$\text{Li}^+$  extraction/insertion in **8a** sites occurs in two steps in the composition range of  $0 \leq x \leq 0.5$  and  $0.5 \leq x \leq 1$  respectively. Structure remains cubic spinel.

**Composition range  $1 \leq x \leq 2$  (~3V)**



$\text{Li}^+$  extraction/insertion occurs in **16d** sites and the cubic spinel ( $a = 8.248\text{\AA}$ ) transforms to a tetragonal rock salt structure ( $a=8.007\text{\AA}$ ,  $c=9.274\text{\AA}$ ).  
Structural distortion deteriorates properties.



*J.Phys:Condens.Matter 15 (2003)  
C.M Julien and M. Massot*

# Current status

**LiMn<sub>2</sub>O<sub>4</sub> spinel continue to show capacity fading and limited cycleability in the 4V region which is accentuated in the temperature range of 40-50°C**

**⚡ Normal spinel : 32 octahedral site, Mn<sup>3+</sup> 8 octahedral site, Mn<sup>4+</sup> 8 octahedral site, 16 remaining sites are vacant.**

**Mn<sup>4+</sup> (CN = 6) ionic radius 0.54 Å**

**Mn<sup>3+</sup> (CN = 6) ionic radius 0.58 Å (low spin)**

**Mn<sup>3+</sup> (CN = 6) ionic radius 0.65 Å (high spin)**

**Increase of Mn<sup>3+</sup>/ Mn<sup>4+</sup> ratio deteriorates the electrochemical properties. Ideally, it is required to maintain Mn<sup>3+</sup> concentration to less than one formula unit to suppress the distortion.**

**⚡ The onset of a damaging Jahn-Teller distortion at the particle surface of the spinel electrode at the end of discharge (above 3V) under dynamic non equilibrium condition**

# Research approach

- **Optimization of synthesis condition (of  $\text{LiMn}_2\text{O}_4$ ) and cell fabrication**

Reaction time, reaction temperature

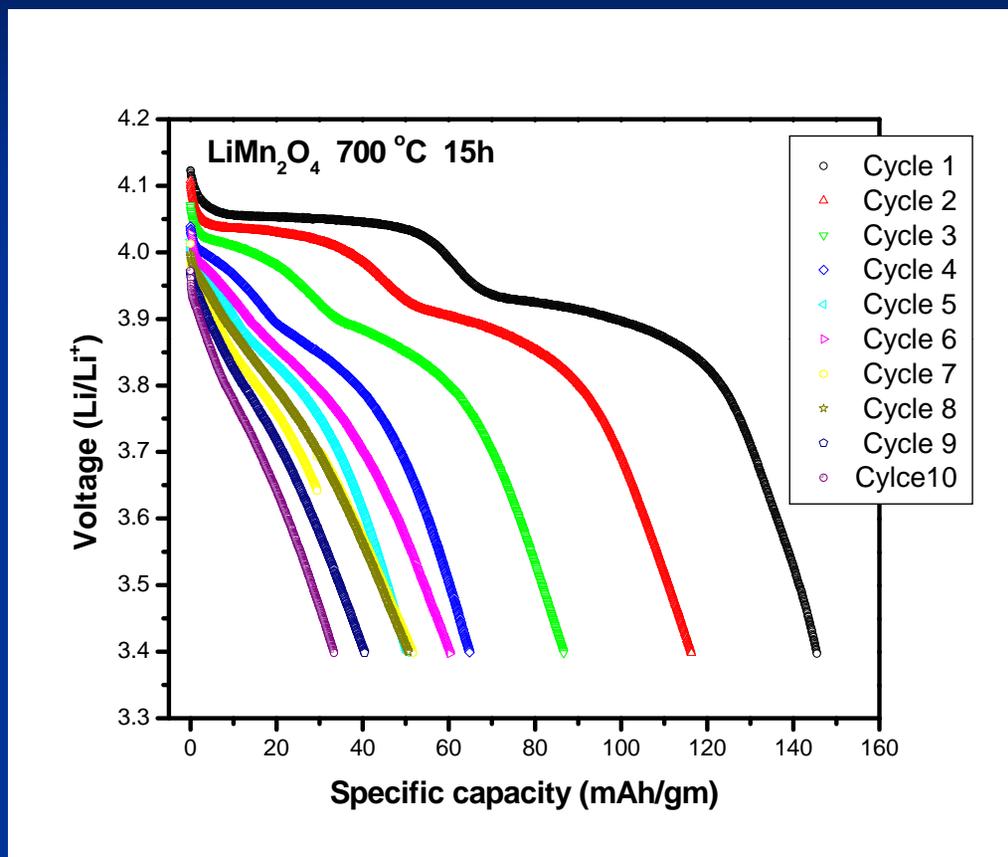
Formulation of composite cathode [Active material, C black, plasticizer and NMP (solvent)]

Formulation of electrolyte ( $\text{LiPF}_6$  salt, EC and DMC)

- **Substitution of Mn ion with trivalent Al and Cr**

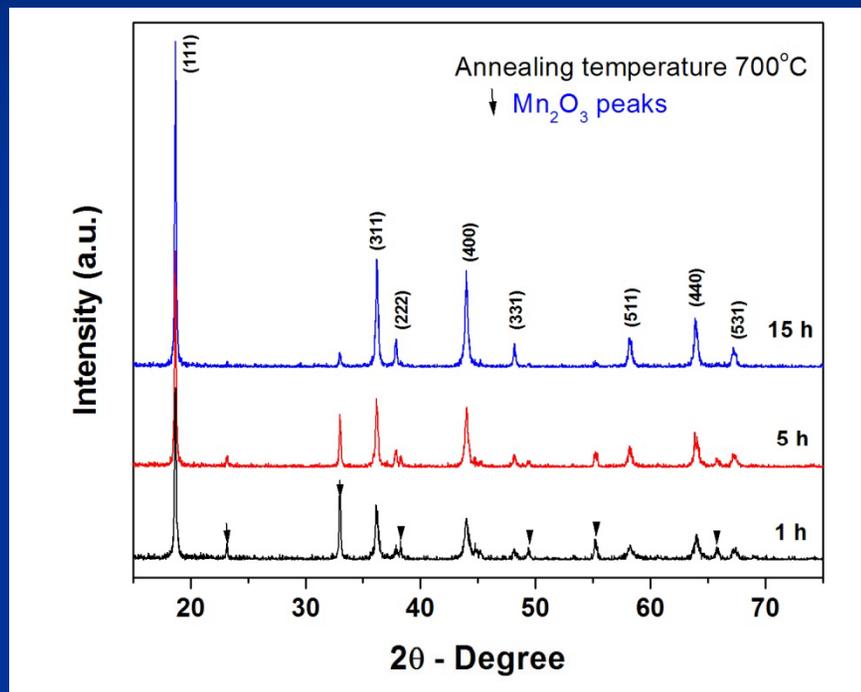
Increase the average oxidation state of Mn in the spinel framework

## Severe capacity fading! Our $\text{LiMn}_2\text{O}_4$



The fading is very severe in stoichiometric sample

# X-ray diffraction analysis



Effect of reaction time

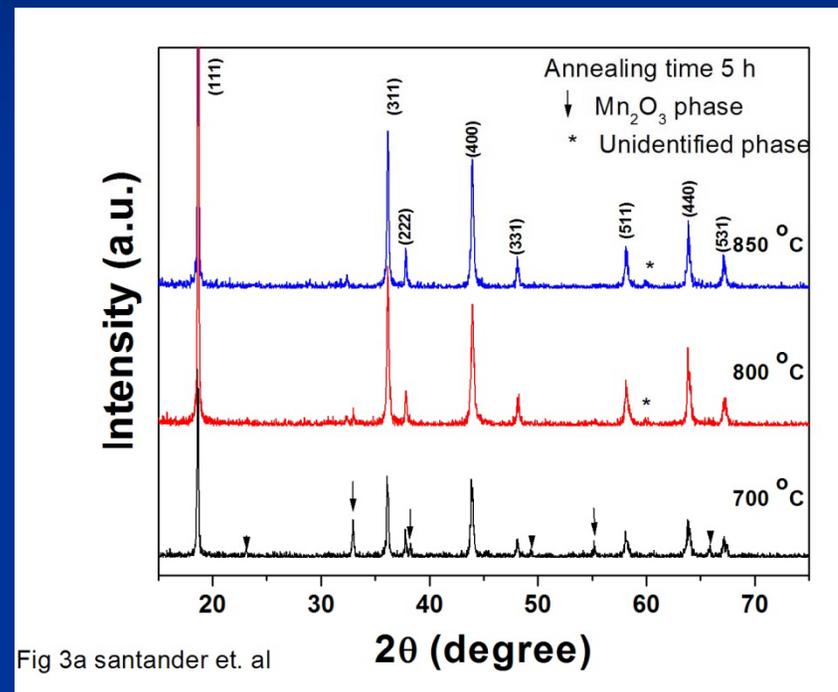
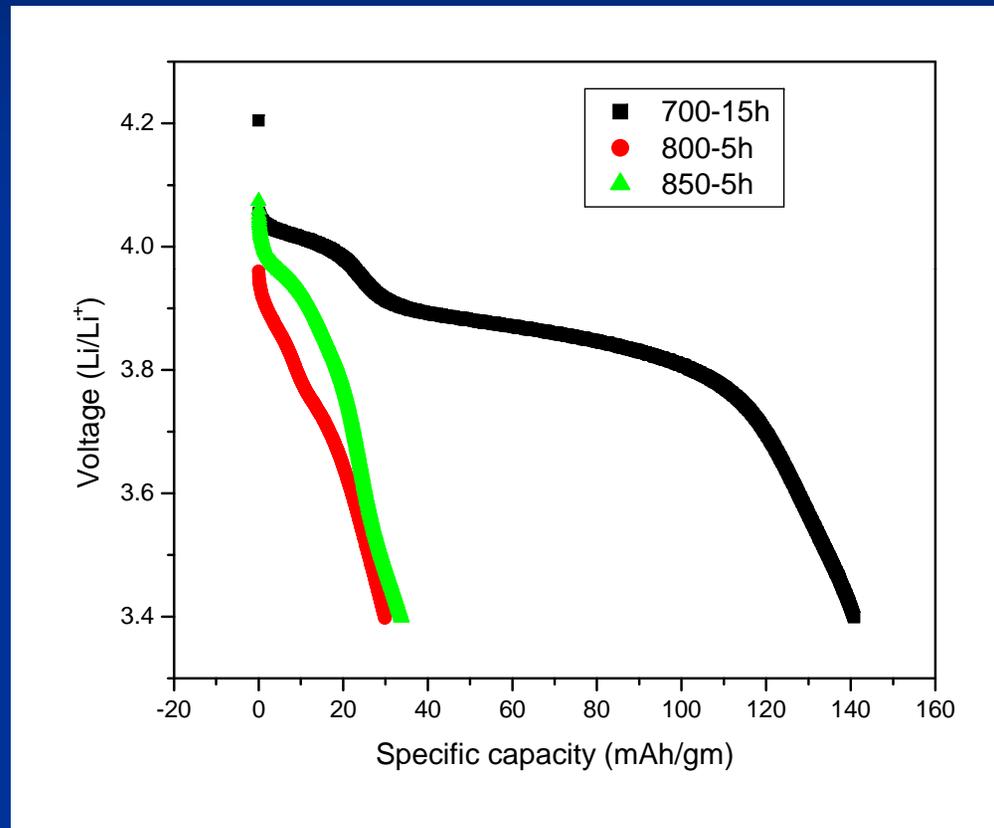


Fig 3a santander et. al

Effect of reaction temperature

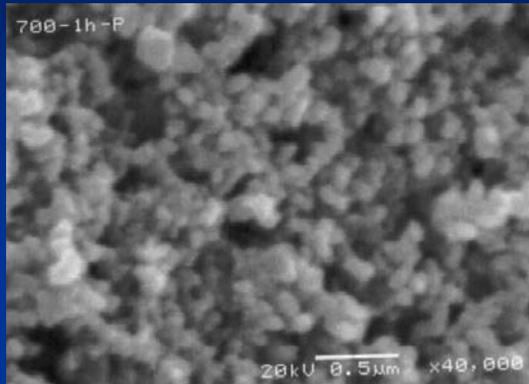
## Discharge capacity characteristics of $\text{LiMn}_2\text{O}_4$ for different reaction temperature



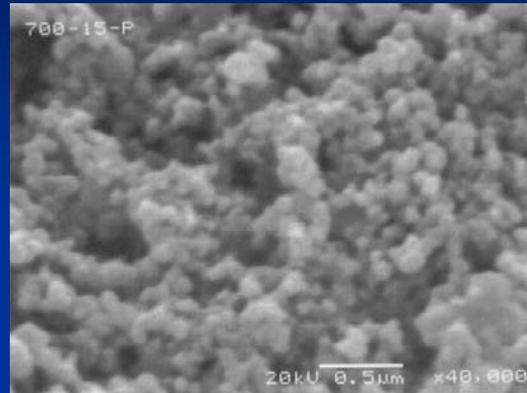
✓ Capacity is drastically reduced in case of cathode annealed at higher temperature

✓ Phase purity could not solve the cycleability fading problem

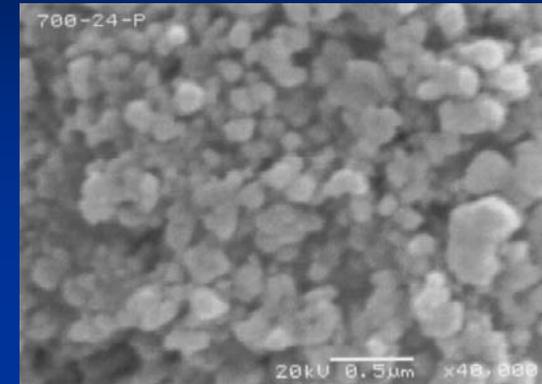
**solution synthesis route:** Limited growth, high nucleation density



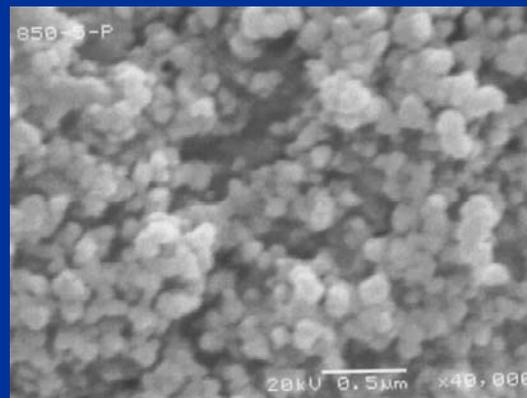
**700°C – 1h**



**700°C – 15h**



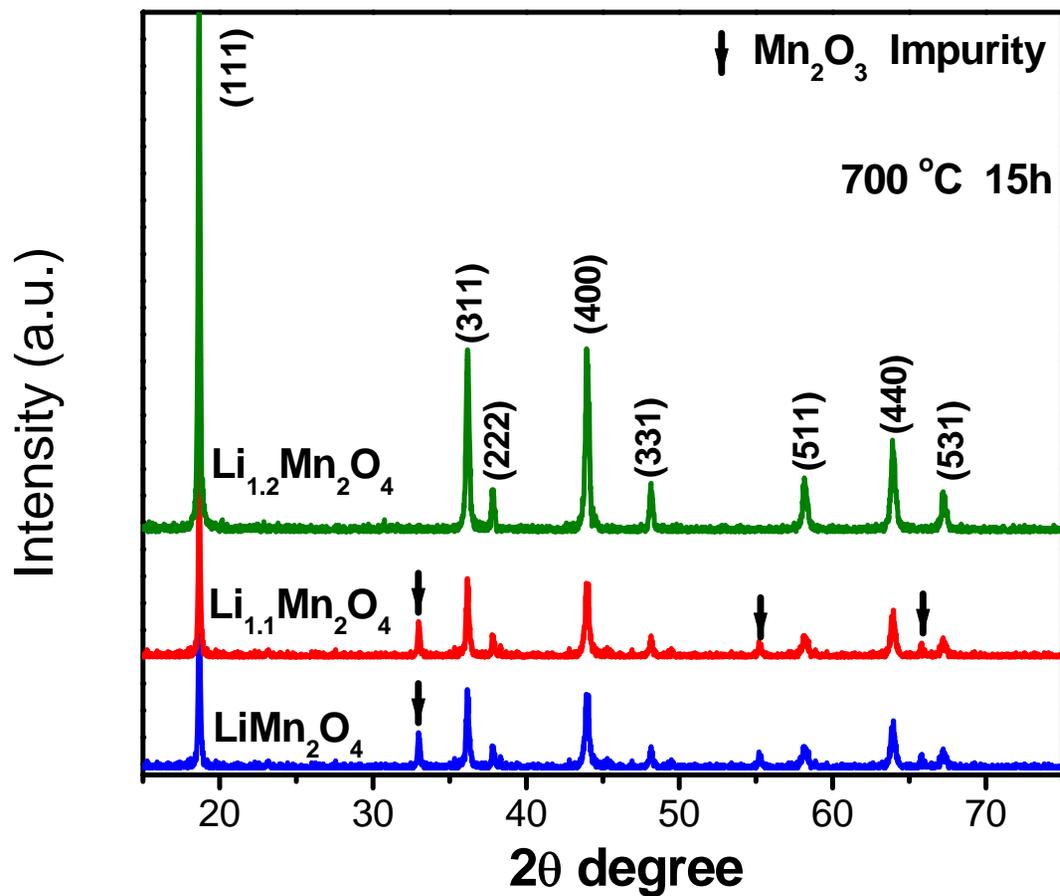
**700°C – 24 h**



**850°C – 5h**

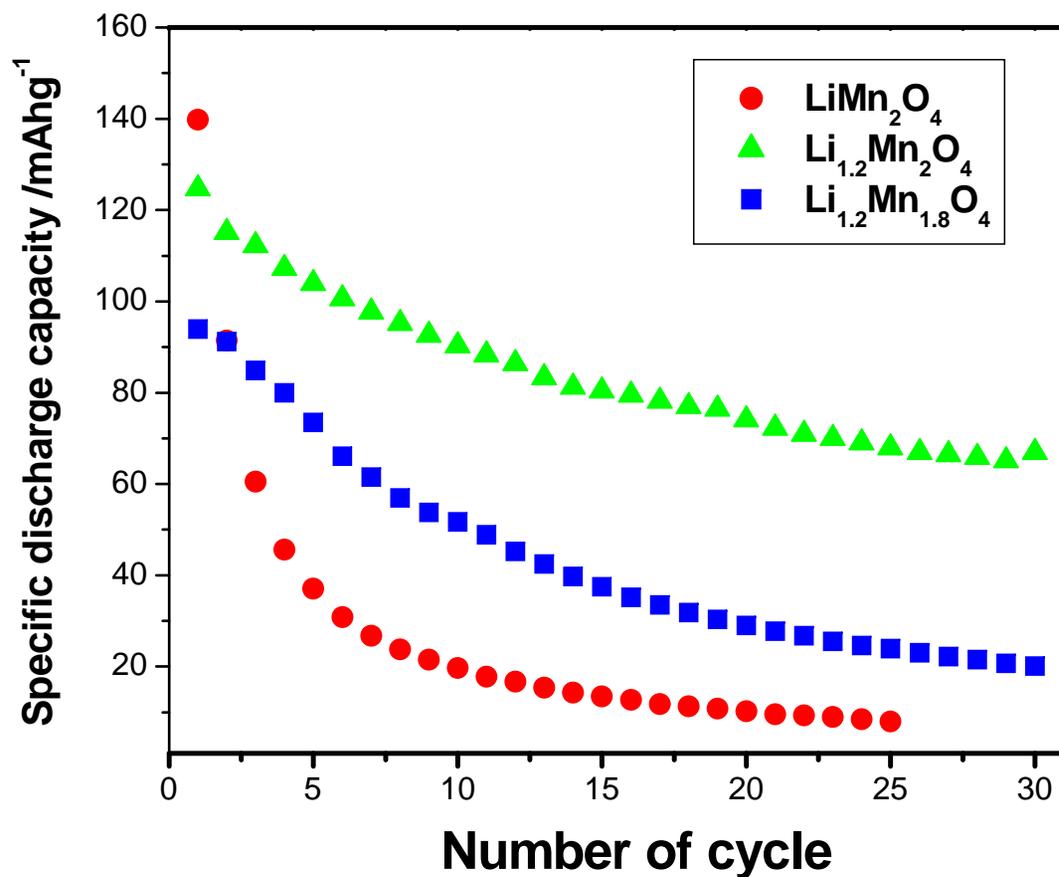
Effect of calcination time  
and temperature on the  
surface morphology

# X-ray diffraction analysis



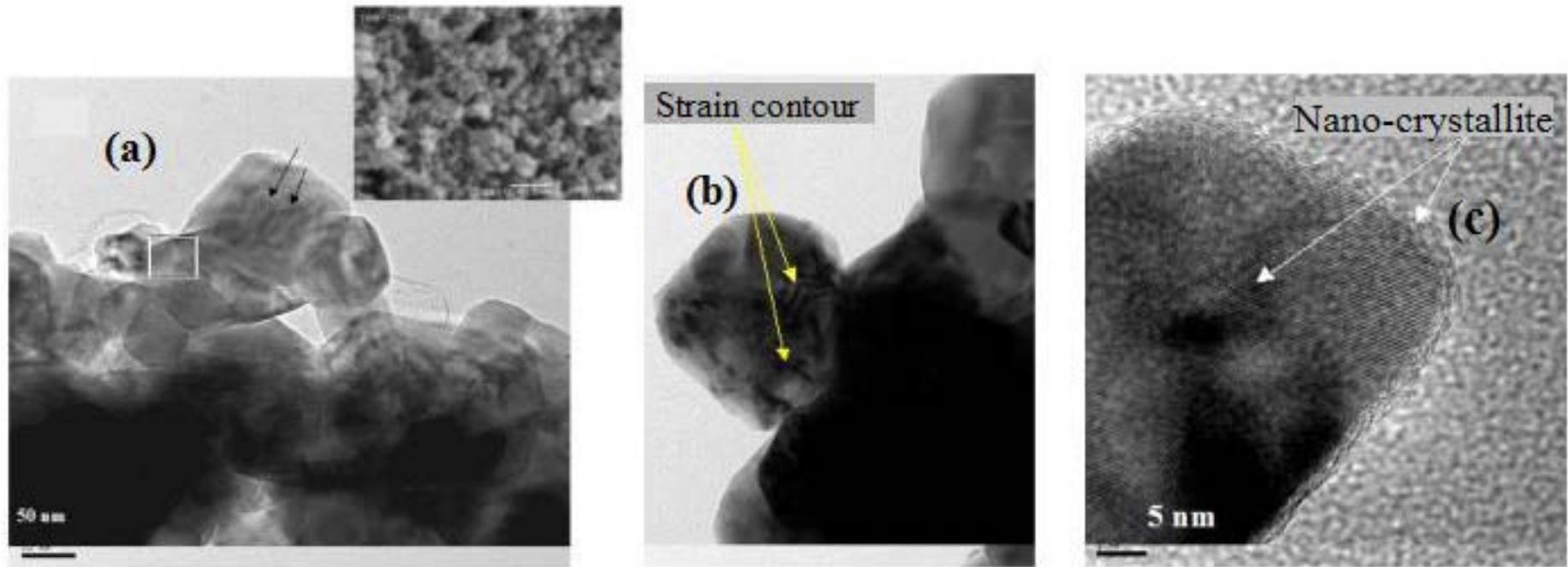
Extra 20% Li results in pure phase

# Comparison of cycleability of $\text{LiMn}_2\text{O}_4$ , $\text{Li}_{1.2}\text{Mn}_2\text{O}_4$ , and $\text{Li}_{1.2}\text{Mn}_{1.8}\text{O}_4$



- ✓ A small amount of excess lithium, it considerably reduce the capacity fade
- ✓ Fading problem is not fully solved

# Morphology of the synthesized $\text{LiMn}_2\text{O}_4$ cathode



**Particle size range – 60-100 nm**

**Black contours** appears due to retained strain

Each single particle constitutes **several nano-crystallites**

# Improvement of the capacity fading: Co-cation doping approach

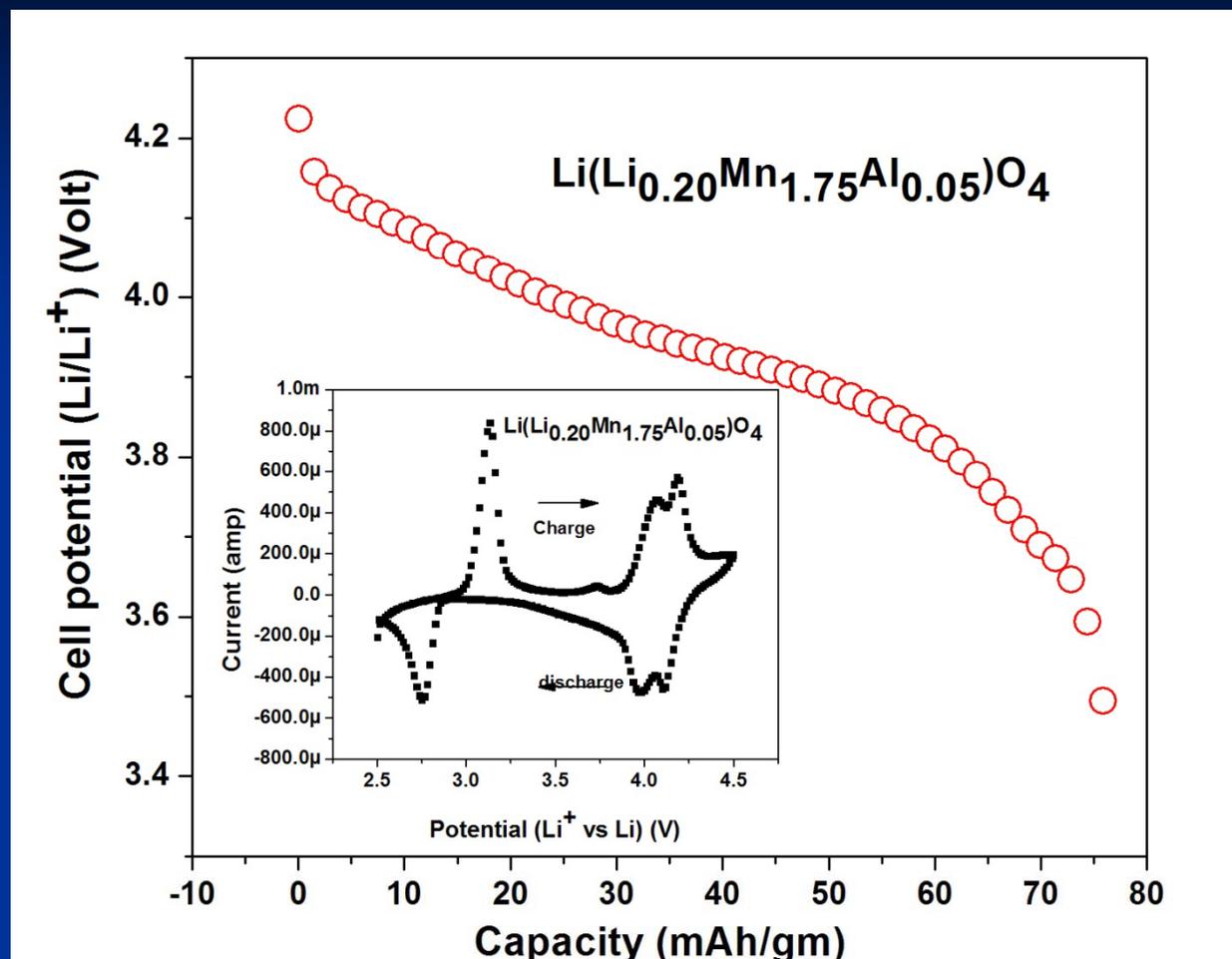
- Increase the average Mn oxidation state in the virgin electrode to delay the onset of JT distortion to lower voltage (Al<sup>+3</sup> doping replacing Mn ion)
  - Li<sup>+</sup> doping in Mn (16d) site, to retard the Li<sup>+</sup> diffusion in and out of the octahedral site during high rate discharge and charge respectively.
- 

Synthesized  $\text{Li}(\text{Li}_{0.20}\text{Al}_{0.05}\text{Mn}_{1.75})\text{O}_4$

Theoretically 0.35M Li<sup>+</sup> can be extracted yielding a capacity of **55 mAhgm<sup>-1</sup>**

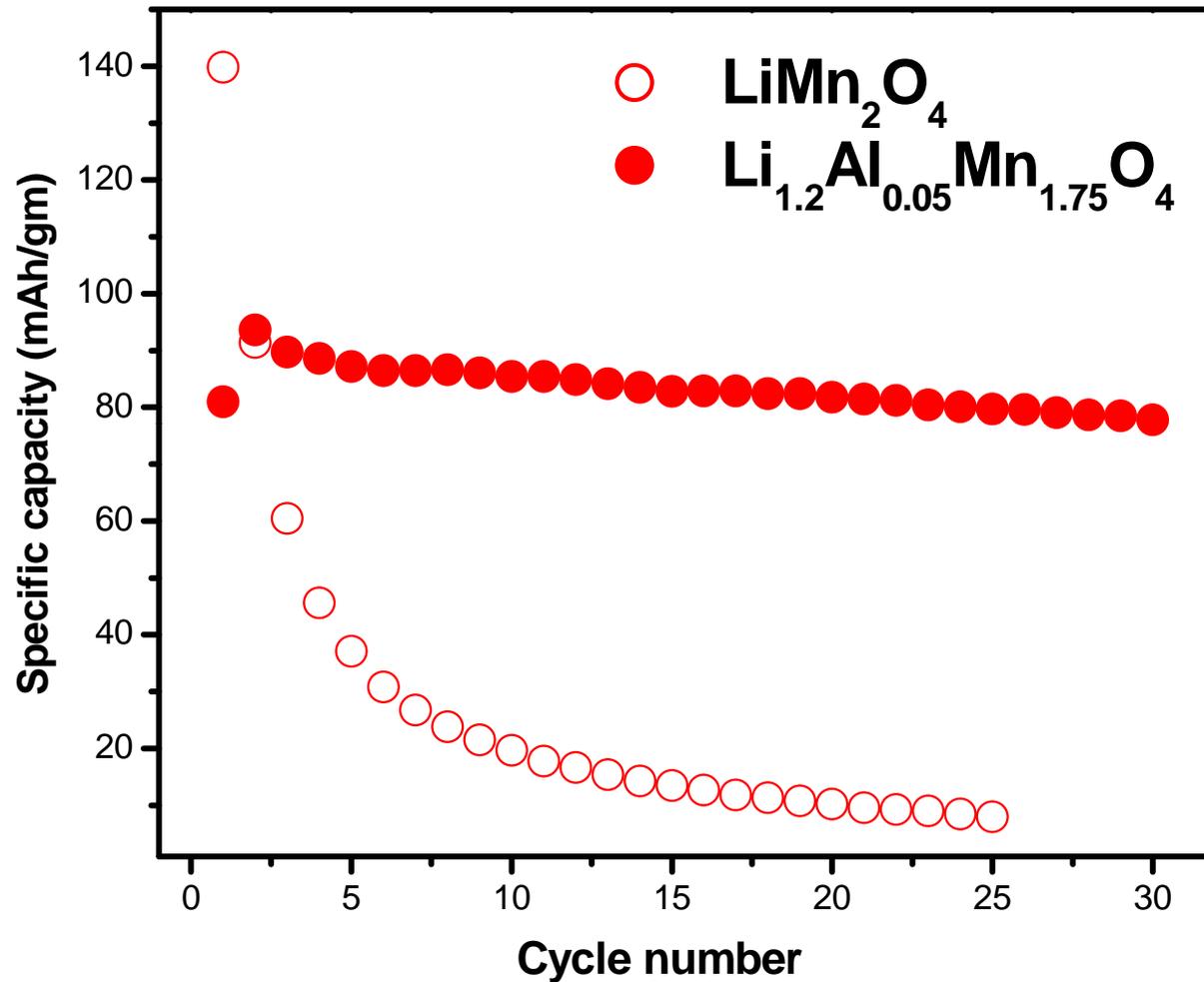
Average Mn valence state should be raised from +3.5 to **+3.8**

## Discharge profile of co-doped cathode

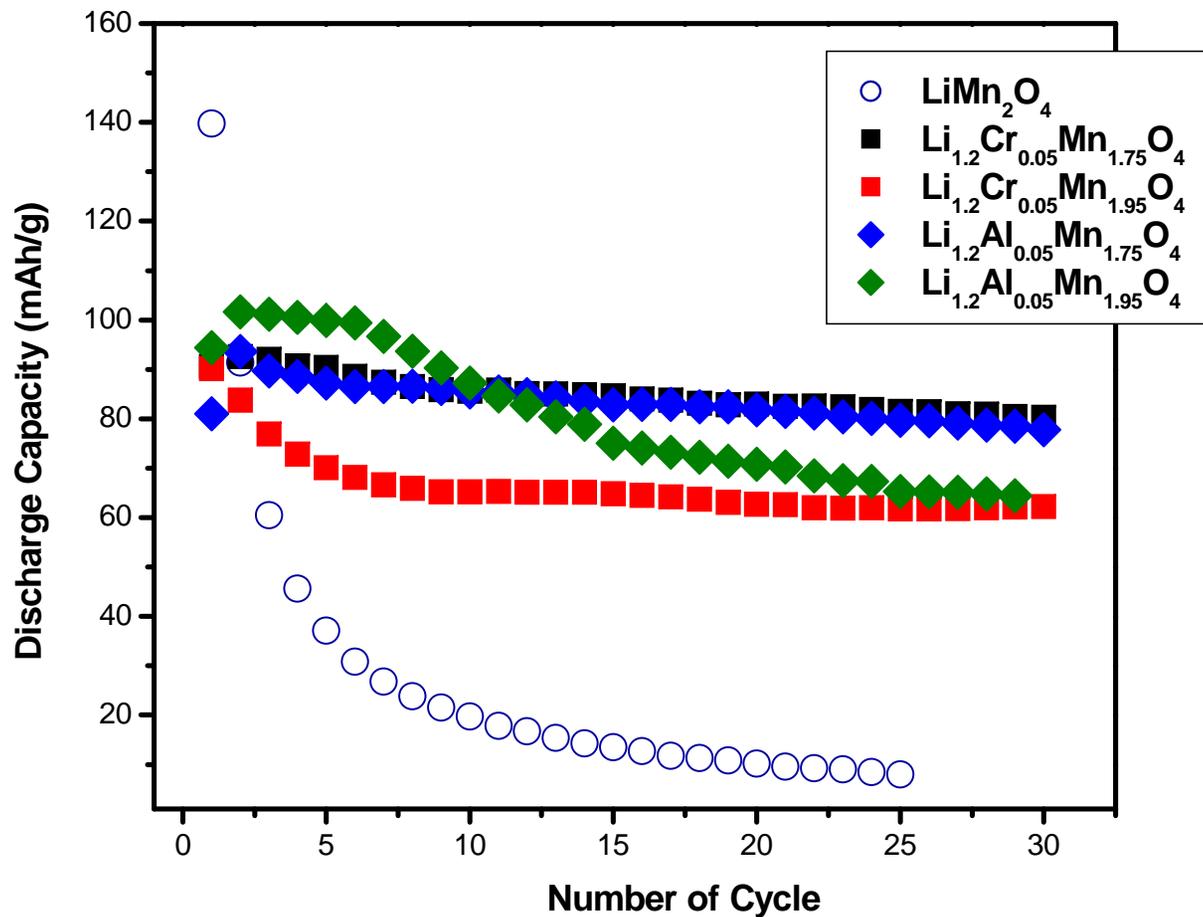


No distinct plateau is observed in the discharge profile which indicates that the long range cation ordering in the tetrahedral/octahedral sites are disturbed due to the insertion of dopants.

## Improved cycleability of the co-doped samples



# Improved cycleability of the co-doped samples



# Conclusions

In the 4V range severe capacity fading was observed in nano-size  $\text{LiMn}_2\text{O}_4$  particles

The XPS analyses in conjunction with the micro-Raman spectroscopy indicated that at the surface of LMO particles, the  $\text{Mn}^{+3}$  ion contents were increased after charge-discharge cycle.

The increase of  $\text{Mn}^{+3}$  ion contents as well as lattice strain could be related with the formation of tetragonal  $\text{Li}_2\text{Mn}_2\text{O}_4$  type compound at the surface of cubic lithium manganate.

The reason for the fading were believed to be due to the onset of the Jahn-Teller distortion towards the end of the discharge.

By simultaneous Li and Al doping (at 16d site) the average oxidation state of Mn ions in virgin LMO electrodes was increased and thereby the onset of cubic to tetragonal structural transition was delayed.

The discharge capacity of these co-cation doped lithium manganate was reduced, but their cycleability was improved.

# Future Directions

- Substitution of other transition metals into the Layered and spinel systems need to be investigated for further improvement of their electrochemical properties.
- To identify the cause of the impurity phase formation on layered compounds and find possible remedies to eliminate it, need to be investigated.
- The doping of Al and Li are needed to be further optimized to increase the discharge capacity of the nano-crystalline cathode materials.
- Surface modification with chemically more stable or inert materials and to study their effect on the cathodes of these coating.

# Las Celdas de Combustible: una forma eficiente y limpia de generación de energía.

*Santander Nieto, PhD.*

IPCAR: Institute of Physical Chemical Applied.



PREC: Puerto Rico Energy Center



Universidad del Turabo.



# Introducción

- Breve discusión sobre la situación energética actual
- Generalidades sobre las celdas de combustible
- Estado del arte en el área de celdas de combustible de óxido sólido (SOFCs)
- Materiales para SOFCs de temperatura intermedia (IT-SOFCs)

# Generación de energía - Situación actual

Las formas convencionales de generación de energía han llevado a problemas graves para la humanidad:

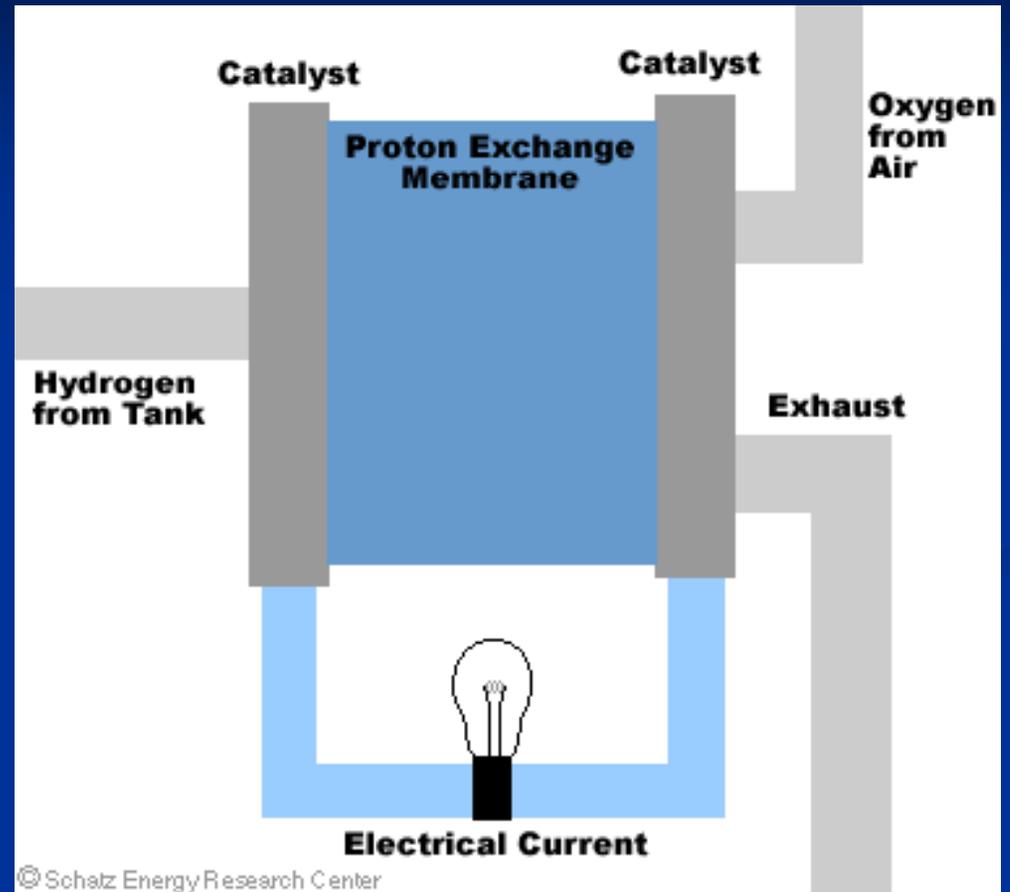
- Calentamiento global
- Contaminación ambiental (gases tóxicos, ruido, etc.)
- Crisis energética
- Distribución inadecuada (o injusta) de la energía
- Escasez de combustibles

En consecuencia, debemos buscar nuevas formas de generación de energía que sean más amigables con el medio ambiente y de alta eficiencia. Las **celdas de combustible**, en especial las de óxido sólido, son una importante alternativa.

# ¿Qué son las celdas de combustibles?

Son dispositivos electroquímicos que permiten la conversión de la energía de una reacción química en energía eléctrica.

En el caso más sencillo, la reacción que se aprovecha es la de formación de  $H_2O$  a partir de  $H_2(g)$  y  $O_2(g)$ .



**Animation of PEMFC**

## Ventajas de las celdas de combustible

- No tienen las limitaciones de las máquinas térmicas, de modo que teóricamente pueden alcanzar eficiencias cercanas al 95%. En la práctica se han obtenido eficiencias de hasta el 65%.
- No se emiten gases tóxicos y, si se utiliza hidrógeno como combustible, puede evitarse completamente la generación de gases de efecto invernadero.
- No tienen partes móviles, por lo que no producen ruidos.

¿Por qué todavía no se usan? El costo de esta tecnología es actualmente muy superior a las formas convencionales de generación de energía.

## Celdas de combustible vs. pilas convencionales

Ambas tienen un principio similar: generan energía eléctrica mediante un sistema electroquímico que no tiene las limitaciones termodinámicas de las máquinas térmicas y por ello tienen **alta eficiencia**.

- Las pilas convencionales son **sistemas cerrados**: los reactivos están en la propia pila y no es necesario contacto con el exterior. El problema de estos sistemas es que se agotan una vez consumidos los reactivos.
- Las celdas de combustible son **sistemas abiertos**: no se agotan mientras se provean los reactivos desde el exterior. Por ello tienen largas vidas útiles, sólo relacionados con problemas de degradación de los materiales empleados.

# Clasificación de las celdas de combustible

## Tipos de celdas

**PEMFC:** Celdas de membrana de intercambio protónico

**PAFC:** Celdas de ácido fosfórico

**MCFC:** Celdas de carbonato fundido

**SOFC:** Celdas de óxido sólido

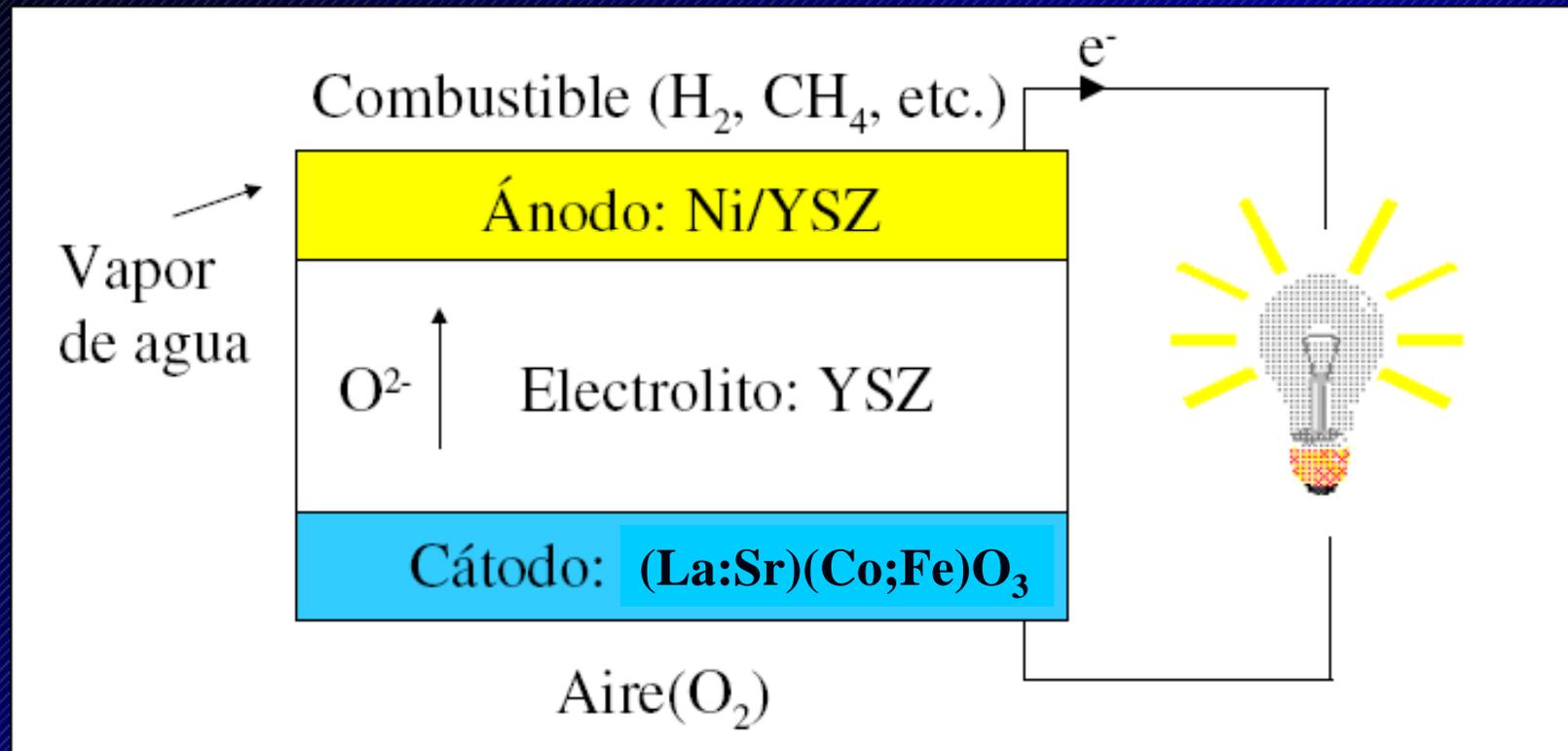
Celda	Temperatura	Ión móvil	Operación
<b>PEMFC</b>	80°C	H <sup>+</sup>	Reformado externo (CO < 10 ppm)
<b>PAFC</b>	200°C	H <sup>+</sup>	Reformado externo (CO < 5%)
<b>MCFC</b>	650°C	(CO <sub>3</sub> ) <sup>2-</sup>	Reformado interno
<b>SOFC</b>	500-1000°C	O <sup>2-</sup>	Reformado interno

# Aplicaciones más importantes

- Energía para la industria aeroespacial (ya fueron usadas en la misiones Gemini y Apollo)
- Transporte
- Energía domiciliaria
- Plantas de alta potencia
- Baterías para computadoras portátiles y dispositivos de baja potencia
- Generadores de energía en regiones alejadas de las redes de distribución

El tipo de celda a utilizar depende de la aplicación. En general, se propone las PEMFCs para transporte y las SOFCs para plantas de alta potencia.

# Celdas de combustible de óxido sólido (SOFCs)



- Tienen alta eficiencia (60-65%)
- No necesitan catalizadores de metales nobles
- No se degradan con CO y tienen alta tolerancia al S
- Gran flexibilidad en la elección del combustible: pueden operar con hidrocarburos (por ejemplo CH<sub>4</sub>)

## Conceptos generales

- Las celdas de combustibles de óxido sólido (SOFC) pueden operar en forma directa con hidrocarburos (en especial,  $\text{CH}_4$ ). No es necesario un reformado externo, sino que el mismo se produce en el propio ánodo de la celda en presencia de vapor de agua, gracias al empleo de catalizadores de níquel (“**reformado interno**”)
- La mayor dificultad de las SOFCs convencionales es su alta temperatura de operación. Por ello, actualmente se investigan nuevos materiales para electrolito y electrodo adecuados para operación a **temperaturas intermedias**. En el caso del cátodo, es necesario desarrollar nuevos conceptos
- Un importante objetivo a nivel mundial es el desarrollo de cátodos y ánodos adecuados para operación con diferentes combustibles, incluyendo **hidrocarburos, biogas e hidrógeno** a temperaturas intermedias

# Problemas tecnológicos a resolver

- **Reducción de la temperatura de operación**

Esto permitiría evitar problemas de degradación por difusión en las interfases o por ciclado térmico, a la vez que se pueden usar materiales de interconexión de bajo costo. Se requieren nuevos materiales para electrolito, cátodo y ánodo para SOFCs de temperatura intermedia (ITSOFCs).

- **Aumento de la eficiencia de las celdas**

- **Simplificación de los diseños**

- **Obtención de cátodos y ánodos adecuados para hidrocarburos, biogas e hidrógeno.**

- **Reducción de los costos de los materiales empleados**

# Materiales de interés actual para operación a temperaturas intermedias

## Electrolitos:

ZrO<sub>2</sub> dopada con Sc<sub>2</sub>O<sub>3</sub>

CeO<sub>2</sub> dopada con Sm<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub> o Y<sub>2</sub>O<sub>3</sub>

Perovskitas de (La;Sr)(Ga,Mg)O<sub>3</sub>

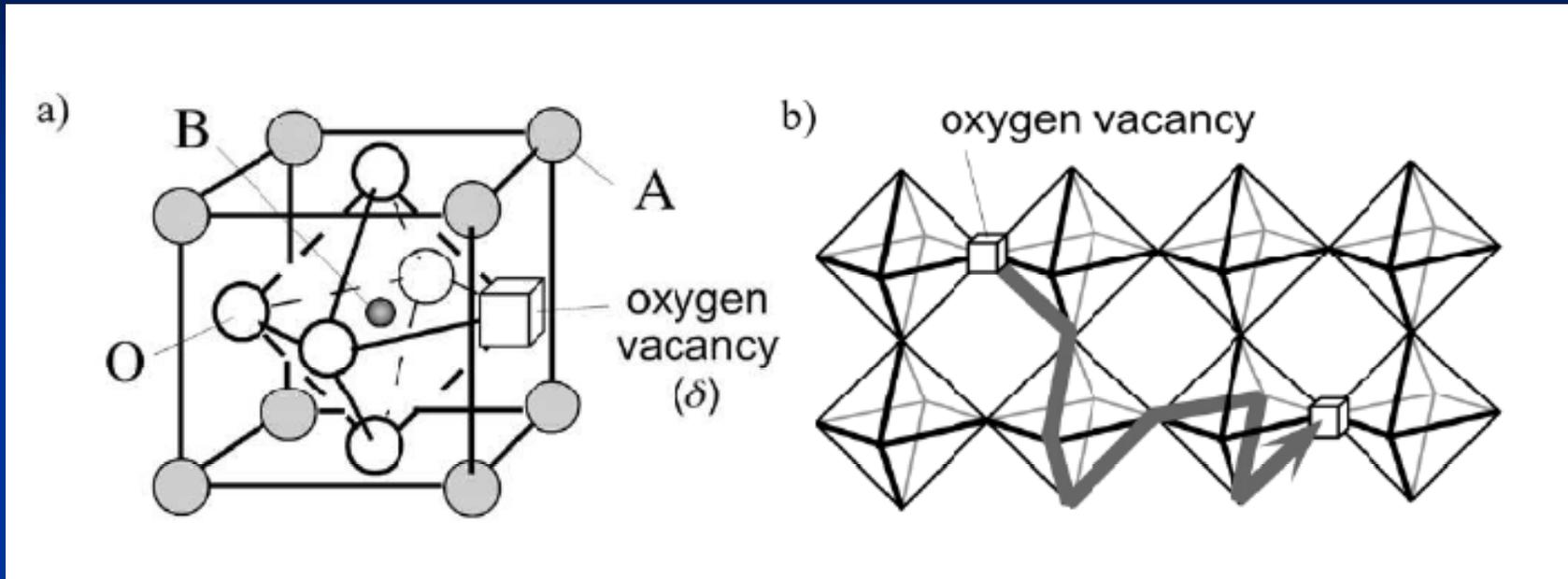
## Cátodos:

Éste es el tema de nuestra investigación. Se prueban materiales de base cobaltoferritas, como (La;Sr)<sub>1-x</sub>Ln<sub>x</sub>(Fe;Co)O<sub>3</sub>, y (Ba,Sr)<sub>1-x</sub>Ln<sub>x</sub>(Fe,Co)O<sub>3</sub> (Ln = Sm, Nd, Pr, 0.10 <x<0.20) que son conductores mixtos: materiales que conducen tanto por iones O<sub>2</sub> como por electrones.

## Ánodos:

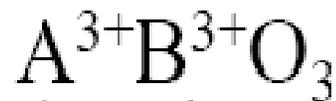
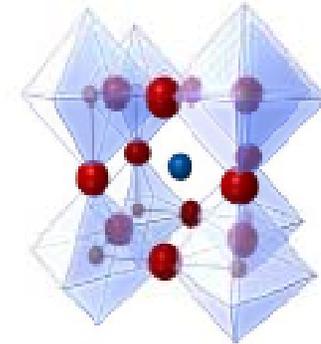
Generalmente se usan materiales de base CeO<sub>2</sub>.

## Conductores mixtos con estructura perovskita



Estructura cristalina de una perovskita  $ABO_3$  a posición de los iones en la estructura cubica; b) Camino seguido por medio de vacancias de oxígeno.

# Perovskite materials

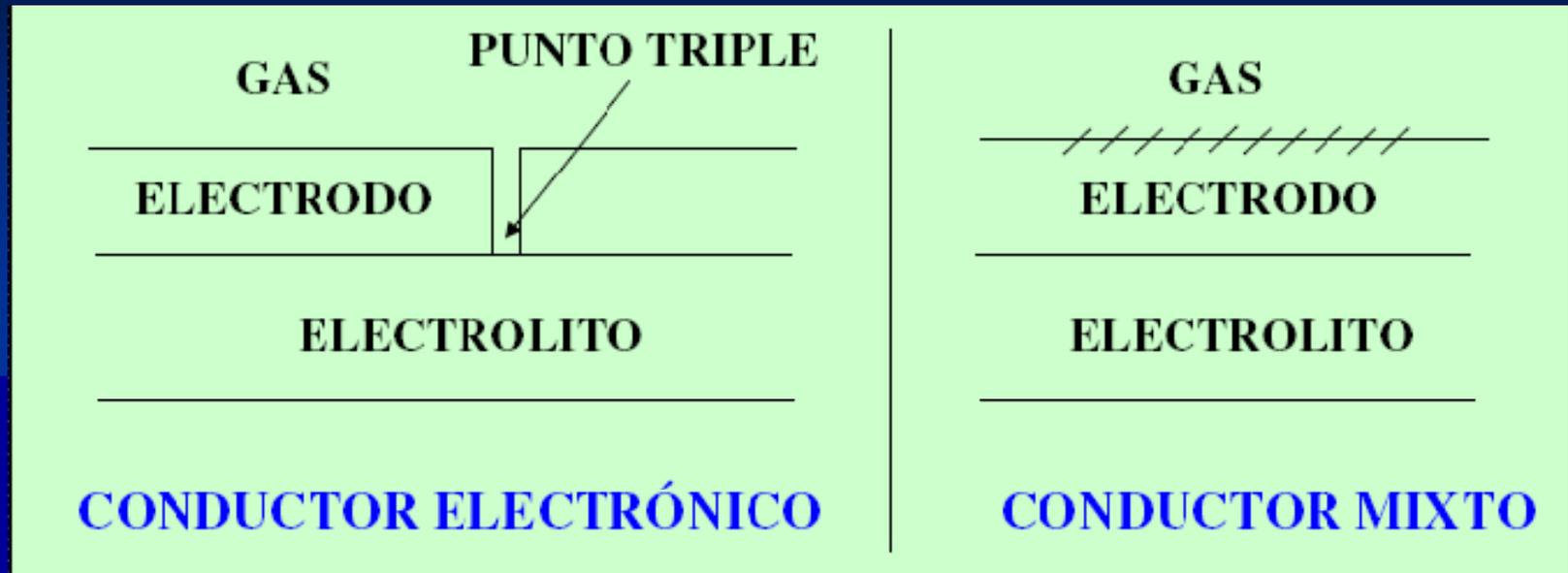


## Rare Earth ions

$La^{3+}$ ,  $Ce^{3+}$ ,  $Pr^{3+}$ ,  $Nd^{3+}$ ,  $Sm^{3+}$ ,  $Eu^{3+}$ ,  
 $Gd^{3+}$ ,  $Tb^{3+}$ ,  $Dy^{3+}$ ,  $Ho^{3+}$ ,  $Er^{3+}$ ,  $Yb^{3+}$ ,  
 $Lu^{3+}$

$Al^{3+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$ ,  $Ga^{3+}$ ,  
 $Co^{3+}$ ,  $Mn^{3+}$ ,  $In^{3+}$ ,  $Sc^{3+}$

# Electrodos basados en conductores mixtos



Los conductores mixtos son materiales que conducen simultáneamente por iones  $O^{2-}$  y  $e^-$ . Con estos materiales hay más puntos de reacción, ya que se da en toda la superficie del electrodo. En cambio, en los conductores electrónicos convencionales, la reacción se da sólo en los puntos triples electrolito/electrodo/gas.

**Cátodos:**  $(Ba;Sr)(Co;Fe)O_3$  y  $(La;Sr)(Co;Fe)O_3$

**Ánodos:** materiales basados en  $CeO_2$ , como  $ZrO_2CeO_2$

# Proyecto de IT-SOFCs del IPCAR

## Objetivos principales:

- **Obtención y caracterización de materiales adecuados para electrolito o electrodos de ITSOFCs operadas con hidrocarburos y biogas**
- **Desarrollo de cátodos para hidrocarburos y biogás**
- **Estudio de nuevas rutas de síntesis (sencillas y de bajo costo)**
- **Estudio de nuevos diseños (ej.: pilas de una cámara)**
- **Búsqueda de nuevos materiales o nuevas microestructuras para el electrolito o los electrodos**
- **Empleo de nanomateriales en IT-SOFCs**

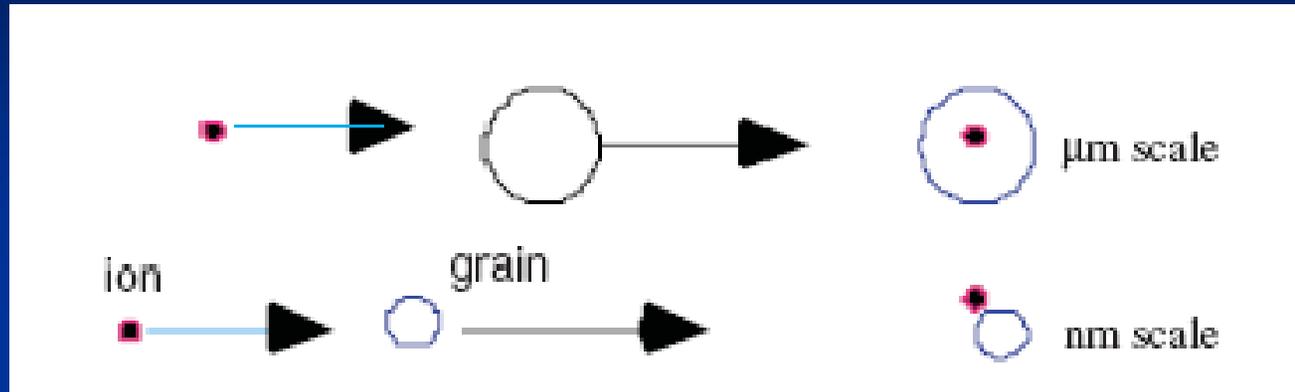
# ¿Podemos utilizar nanomateriales en pilas de combustible de óxido sólido?

Problema: Las temperaturas típicas de operación y de preparación de las SOFCs son muy altas!!

En principio, es posible emplearlos en IT-SOFCs, si la temperatura de preparación de todos los componentes de la celda es relativamente baja.

¿ Vale la pena intentarlo? ¿Qué ventajas podemos encontrar si usamos nanomateriales?

## Usando Nanomateriales se logra alta conductividad en materiales para SOFC



En el nivel microscopio, los iones  $O^{2-}$  pueden migrar a través de la estructura del grano; mientras que en la escala nano, la diferencia de tamaño entre el ion móvil y el grano es disminuida significativamente (ciento de veces menor que en el nivel micro), lo cual causa una fuerza enorme de expulsión a resistir la migración de  $O^{2-}$  cuando el ion se aproxima al grano, generando así un camino para que el ion pase alrededor del grano, es decir por su frontera o interfase.

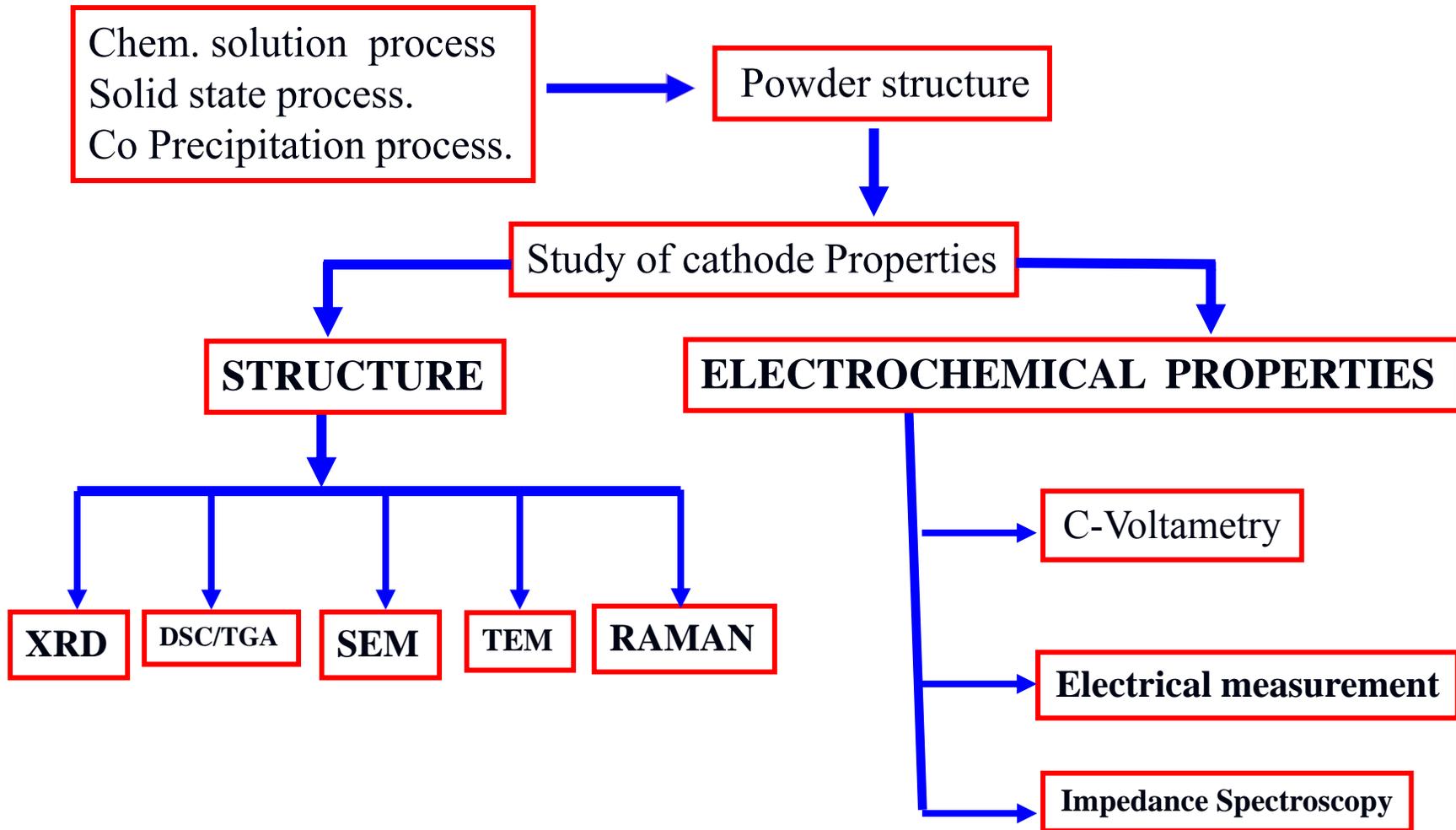
# Electrodos basados en conductores mixtos nanoestructurados de alta área específica

En el caso de electrodos de conductores mixtos, la reacción con el gas se produce en toda la interfaz electrodo/gas. Para electrodos nanoestructurados de alta área específica, la superficie de reacción aumenta significativamente.



Ej.: cátodos basados en cobaltitas, ánodos de  $\text{ZrO}_2\text{-CeO}_2$ , etc.

# Method of Characterization

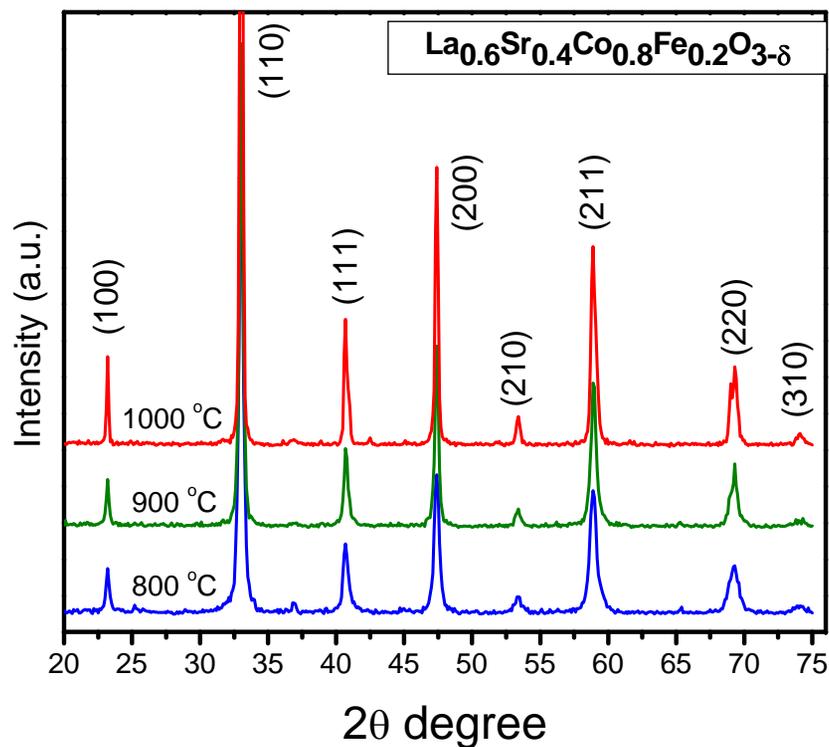


# Equipos

- Espectrómetro de absorción atómica
- Cromatógrafo de líquidos
- Cromatógrafo de gas
- TGA
- UV
- NMR
- FTIR
- CVD
- Prensa Hidráulica
- Molino de bolas
- Sping Coating
- Hornos de alta temperatura (1700°C)
- Estamos esperando un Difractómetro de Rayos X con cámara de alta temperatura

# Resultados recientes sobre materiales modernos para IT-SOFC

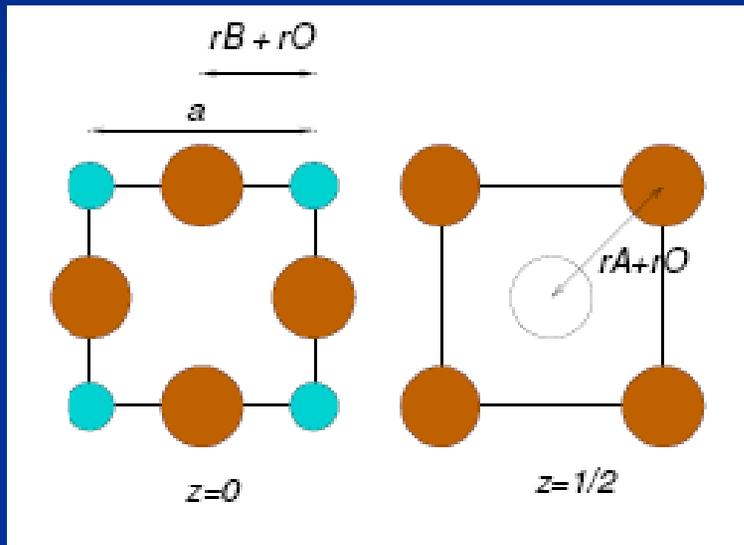
Difraccion de Rayos X de materiales para catodos



# El Factor de Tolerancia

En la perovskita cúbica tenemos:

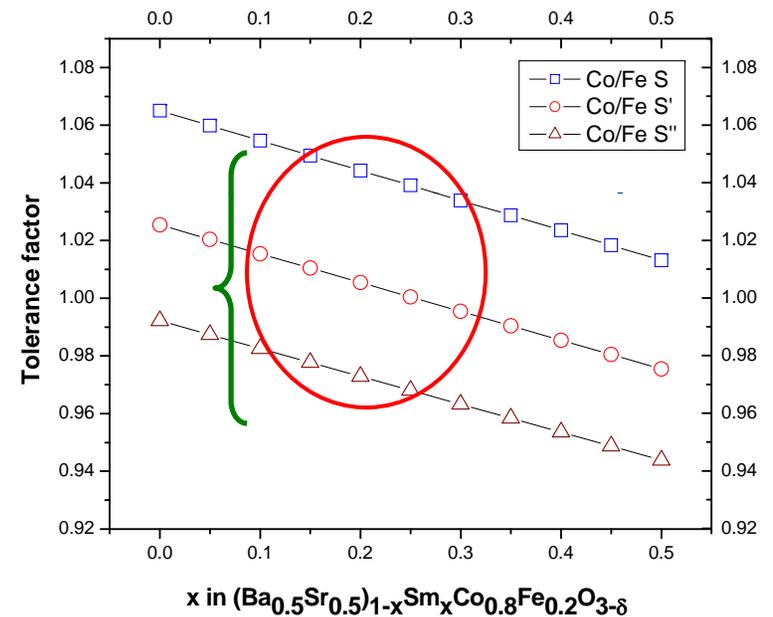
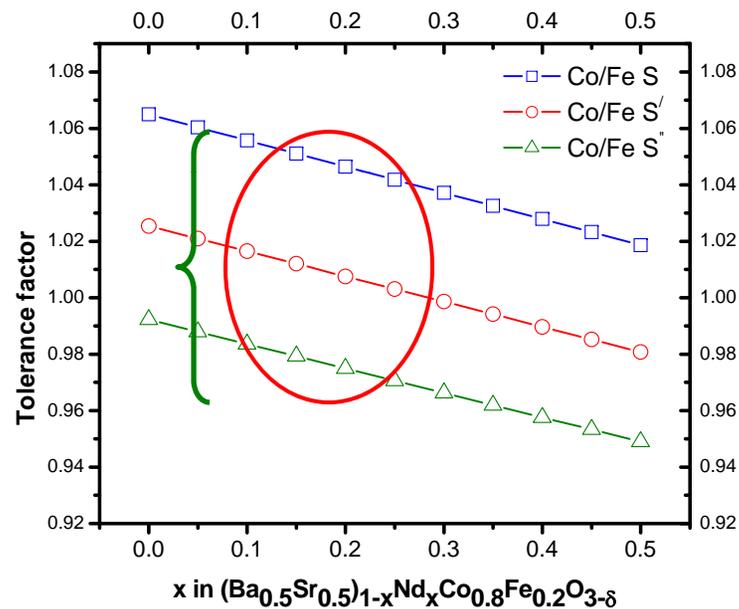
$$(r_A + r_O) = (\sqrt{2}/2)a = \sqrt{2}(r_B + r_O)$$



El factor de tolerancia de una perovskita está definido como:

$$t = \frac{(r_A + r_O)}{\sqrt{2}(r_B + r_O)}$$

# Factor de Tolerancia de materiales modernos para IT-SOFC



Si  $0.95 < t < 1$ , la simetría cúbica es estable

Si  $0.75 < t < 0.9$ , los compuestos poseen simetría ortorrómbica o rombohedral

# Resumen

- La principal dificultad de las SOFCs convencionales es su alta temperatura de operación. Por ello, se estudian materiales para electrolito y electrodo de temperatura intermedia.
- Para el caso del ánodo, cuando se utilizan hidrocarburos como combustibles, es necesario introducir nuevos conceptos que reemplacen al reformado interno: oxidación directa de hidrocarburos  
oxidación parcial de hidrocarburos: celdas de una cámara
- En el caso de SOFCs de temperatura intermedia, es posible emplear materiales nanoestructurados para electrolito y electrodo, los cuales pueden presentar mejores propiedades que los materiales convencionales.

## Futuros proyectos

- **Electrolitos sólidos nanoestructurados:** aumento de la conductividad iónica del electrolito
- **Electrodos de conductores mixtos nanoestructurados con alta área específica:** mayor eficiencia en las reacciones de electrodo (aplicable a cátodos y ánodos)
- Estudio de reducción del tamaño de partículas a nivel nano por medio de **cavitación**.
- Apoyar la investigación científica en la Universidad del Turabo
- Formación y entrenamiento de estudiantes subgraduados y graduados en el campo de almacenamiento de energía y celdas de combustibles.

*Thank you for your **ATTENTION***