CIC energiGUNE
energy cooperative research centre

Project scope and definition

Vitoria, 12 de mayode2014

2014

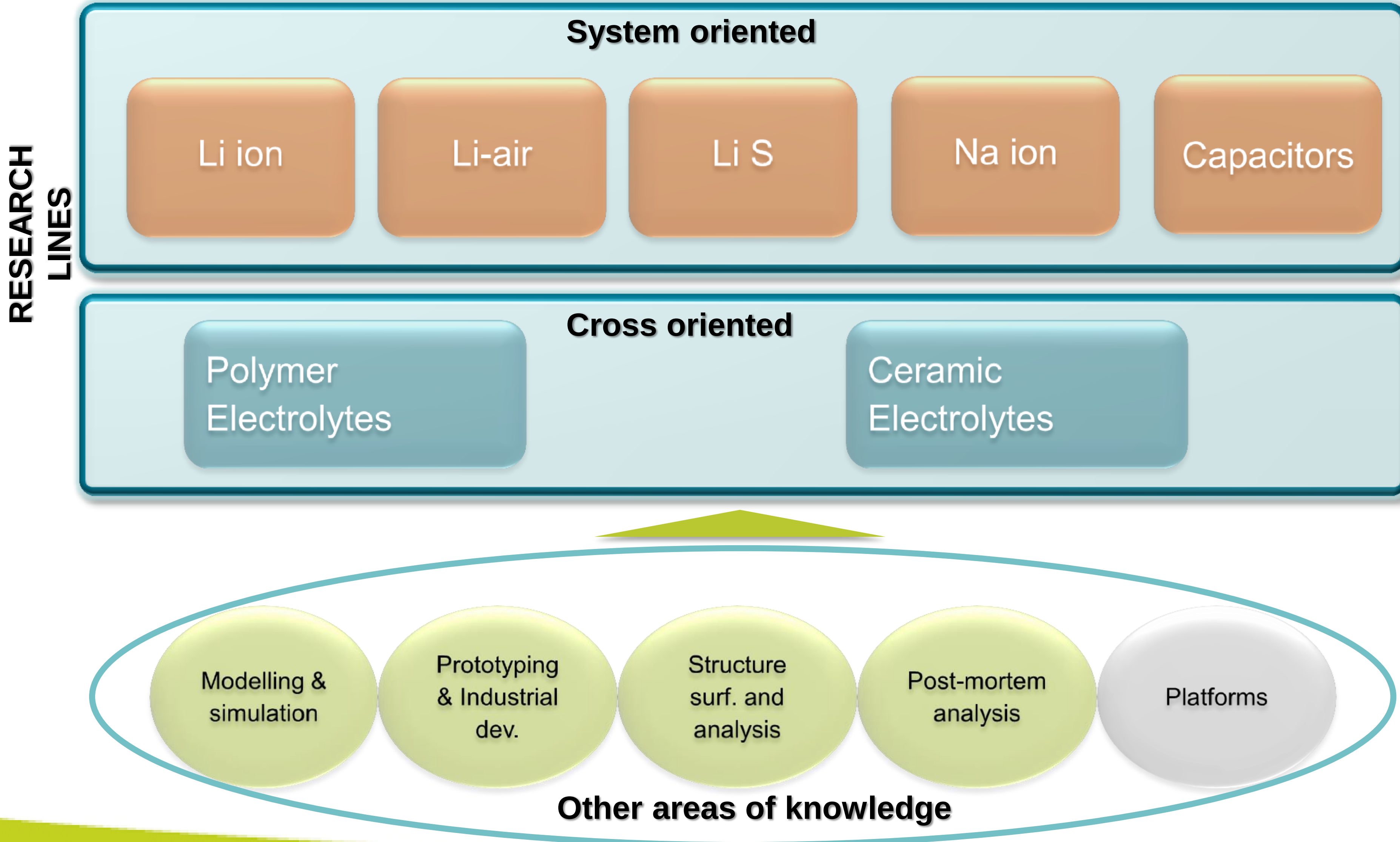
1. CIC Research Areas

Electrochemical Storage:

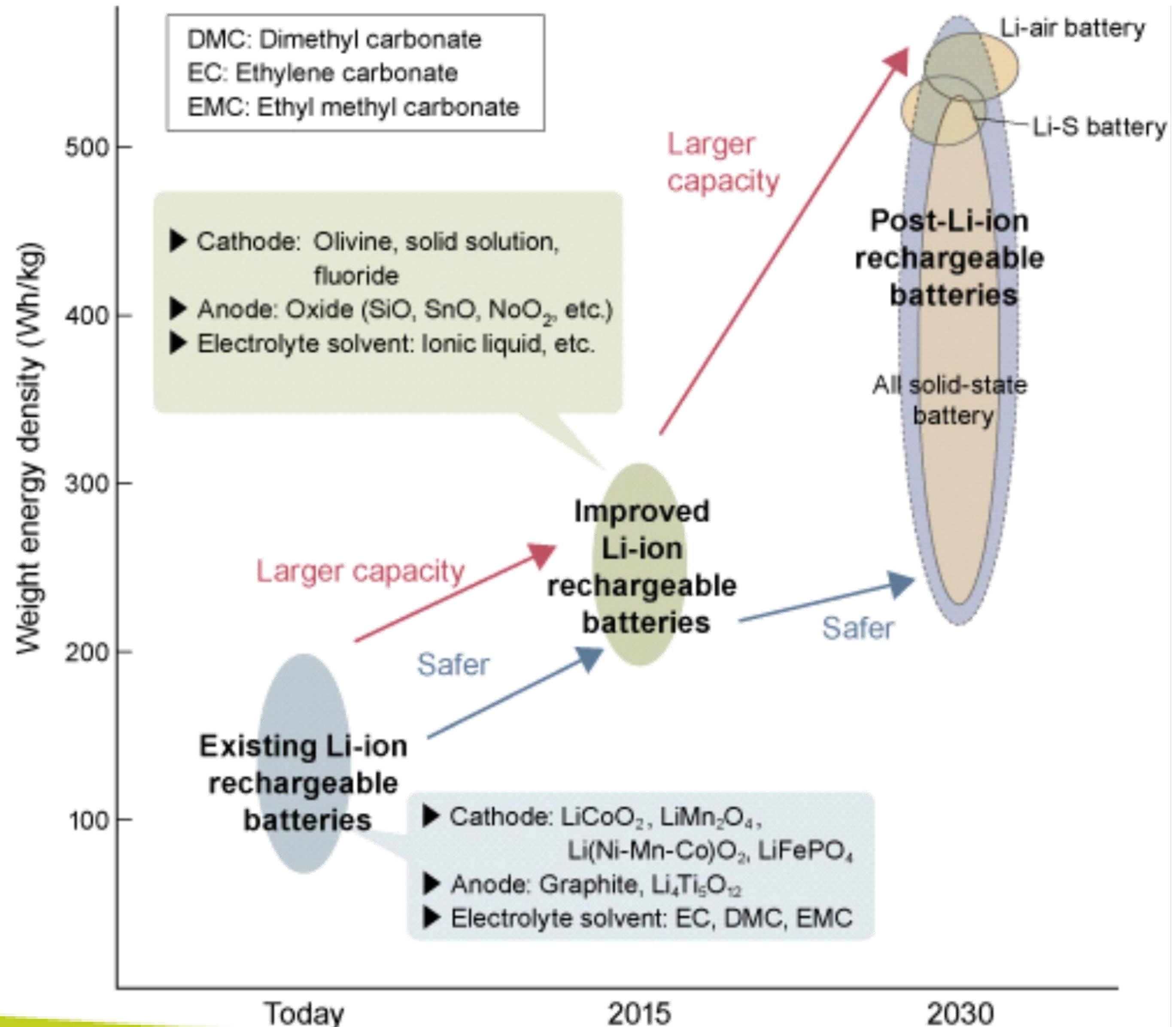
"Batterie and Supercaps

CIC Research Areas: EES

Research Lines



Li-based Batteries: Status and Trend



http://techon.nikkeibp.co.jp/article/HONSHI/20100127/179674/

Li-ion Research Line Background

Goals

- **Increase of energy density (350 Wh/kg)**:
  - Increase of cell voltage
  - Increase of capacity
- **Reduction of cost (< 200 € kWh):**
  - use of cheap TM-based compounds
  - replacement of Cu current collectors
  - Binder-free electrodes
- **Reduced environmental impact**
- **Cycleability (5000 cycles)**
- **High energy efficiency**
- **Reduce degradation and increase lifetime**

Technical Approach

- Develop and improve high energy density materials based on **intercalation reactions**:
  - High voltage materials
  - High capacity materials (>2e^-/TM)
- Overcome limitations of **conversion reactions**:
  - Reduce voltage hysteresis through a materials approach
  - Develop positive and negative electrodes with improved performance and cost
  - Use of optimized electrolyte formulation with ionic carriers
- Search for an optimized electrolyte formulation for Li-ion batteries through the study of electrode/electrolyte **interfaces**.
- Elucidate **reaction mechanisms** through the development of novel in-situ analytical tools

Post lithium-ion batteries

To satisfy the industrial needs developing of new batteries is required:

- High energy density batteries: Metal-oxygen/air batteries
- Low cost batteries : Sodium-ion batteries.
- Other types of batteries that have attracted much attention:

    Magnesium-ion

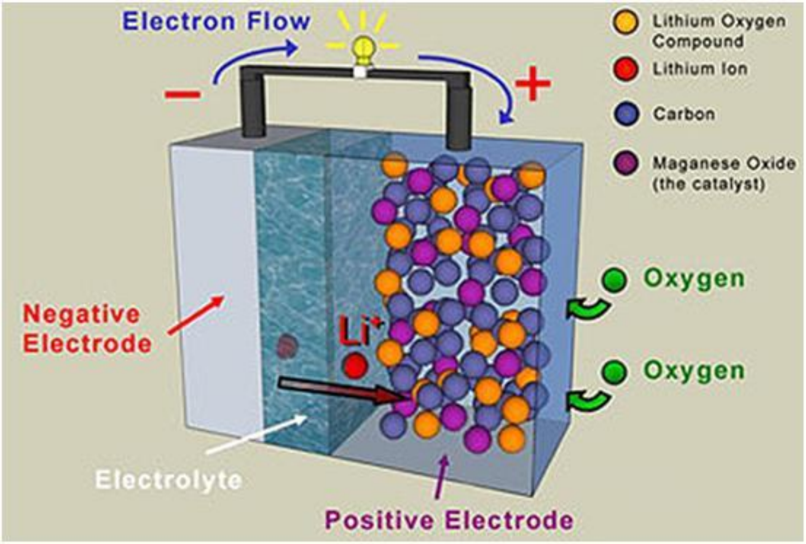
    Organic electrode batteries

H.Zhou , *Energy & Environ. Sci.* (2013) DOI:10.1039/c3ee90024j

Li-air Batteries

Starting with the knowledge acquired from Li-ion batteries, to obtain batteries with higher energy density, up to 10 fold increase in gravimetric energy density.

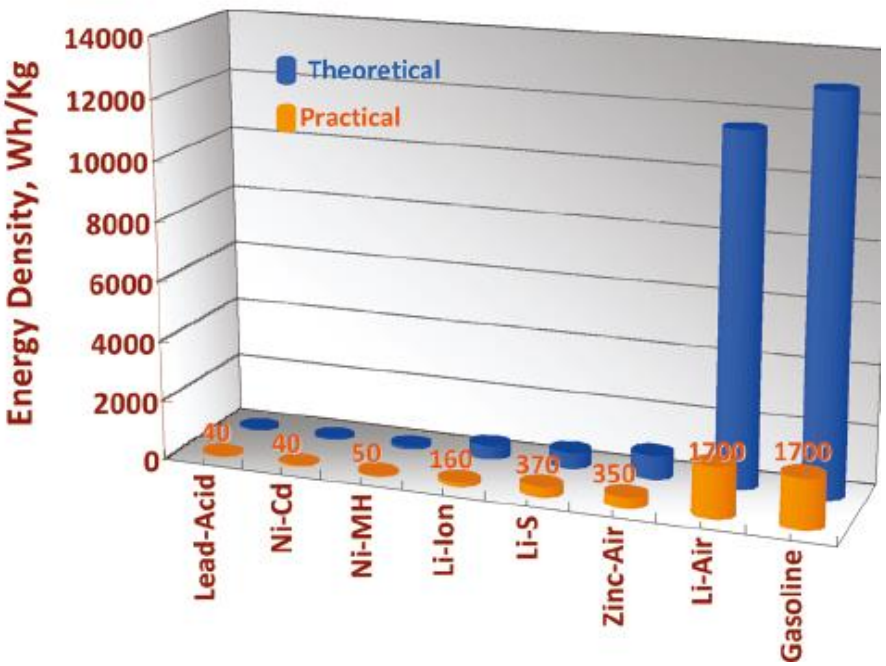
Li-Air BATTERIES



$Li^{(s)} \leftrightarrow Li^{+} + e^{-}$ (anode)

$Li^{+} + 1/2O_2 + e^{-} \leftrightarrow 1/2Li_2O_2$ (cathode)

$Li^{+} + 1/4O_2 + e^{-} \leftrightarrow 1/2Li_2O$ (cathode)



- Discharge voltage of 2.7 V
- Theoretically energy density: >11500 Wh/kg based on Li only

Question: practically, can it really compete with Li-ion and what are main issues?

Li-air Research Line Background

The goal of this work is to develop a working prototype for a ***rechargeable*** Li-air battery with the following figures of merit :

- Cycle life ≥ 5000 cycles at 80-90% DoD
- Specific energy density 4000 Wh/kg
- Operating temperature range -25 to 60 ˚C
- The time frame: medium term range (i.e. 5-10 years)

Strategy

- Development of a reliable ***cell baseline***
- Synthesis, characterization and electrochemical testing of ***alternative anode materials***
- Synthesis, characterization and electrochemical testing of nanostructured cathode materials:
  - Carbonaceous ***cathode supports*** (*nanocarbons, metal-nanocarbon hybrids, etc.*)
  - ***Electrocatalysts*** for the oxygen evolution reaction (OER) and for the oxygen reduction reaction (ORR). (Task developed at the University of the Basque Country –UPV/EHU)

EES
(Batteries & Supercaps)

Project with industry

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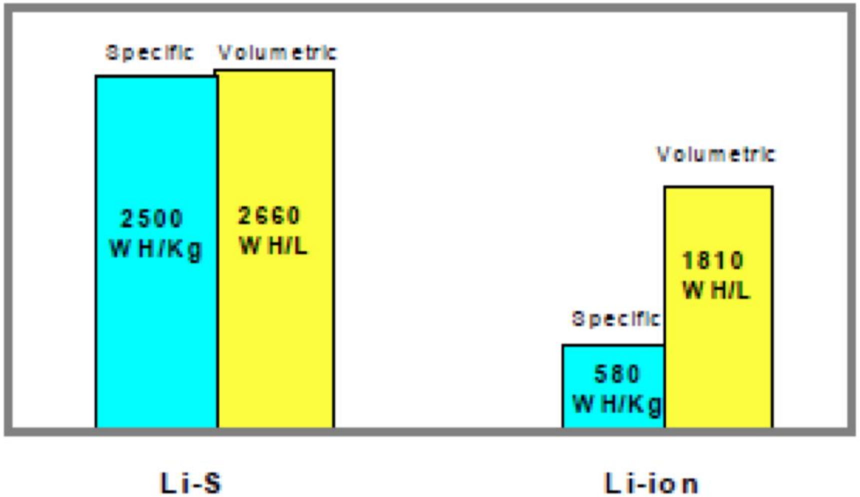
Title:	Advanced materials and new technologies for Li-S batteries
Goal:	To develop a working prototype Li-S battery with the following target : - specific energy density > 500 Wh/kg, - driving autonomy >400km, - cost < 250 $/kWh.
Objectives:	• Research of **anodic materials** focused on avoiding dendrite formation in the Li negative electrode, or replacing it by an alloy with higher chemical stability towards sulfides. • Study of **cathodic materials** based on redox polymers with disulfide (S-S) bonds to eliminate capacity fading associated with solubility of polysulfide specii. • Substitution of liquid electrolytes with **polymer electrolytes** in order to minimize the dissolution of polysulfides. • **Simulation techniques** to complement the interpretation of the experimental studies, to investigate atomic-scale features and to predict the improvements of materials.

Results:	New Project	Collaborators:	Agreement with industry to be drawn

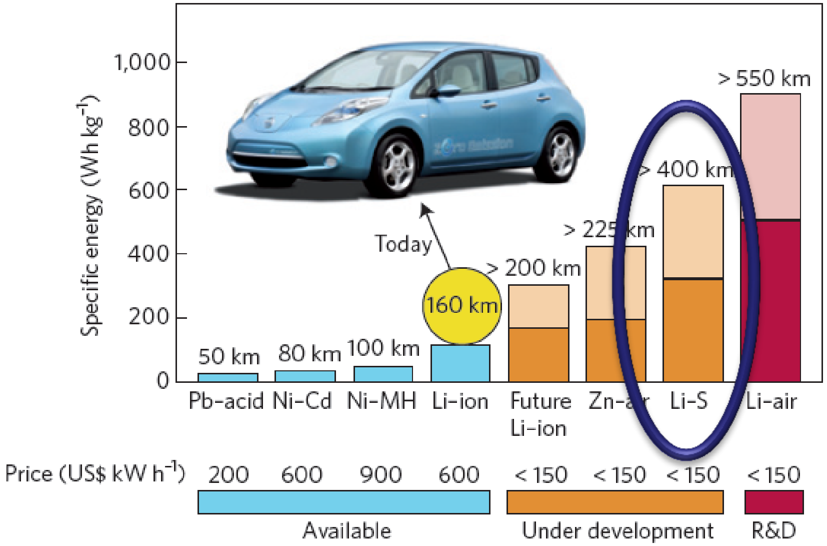
Why Li-S Batteries?

Potential impact of the innovation: *Li-S batteries are of great interest because:*

- **High energy density (3 times compared to Li-ion batteries)**
- **High capacity**
- **High rate capability**
- **Low cost**
- **Safety**

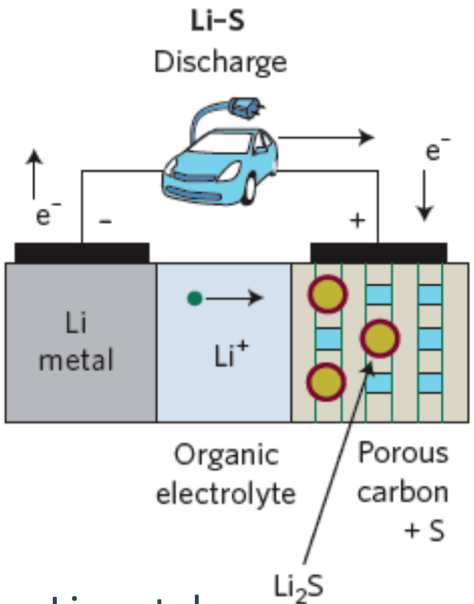


Theoretical energy density comparison
(Tudron F.B. *et al. Sion Power Corporation, 2004*).



Specific energies for rechargeable batteries
(Bruce P.G *et al. Nature Materials,* 11,19 (2012)).

How does a Li-S battery work?



Anode: Li metal

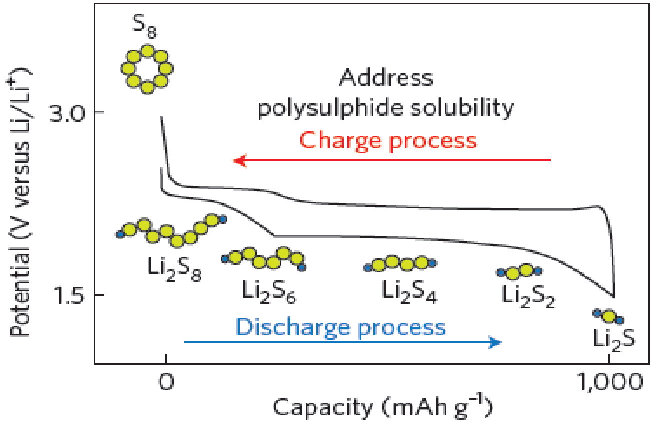
Electrolyte: Organic electrolyte

Cathode: Porous Carbon + S

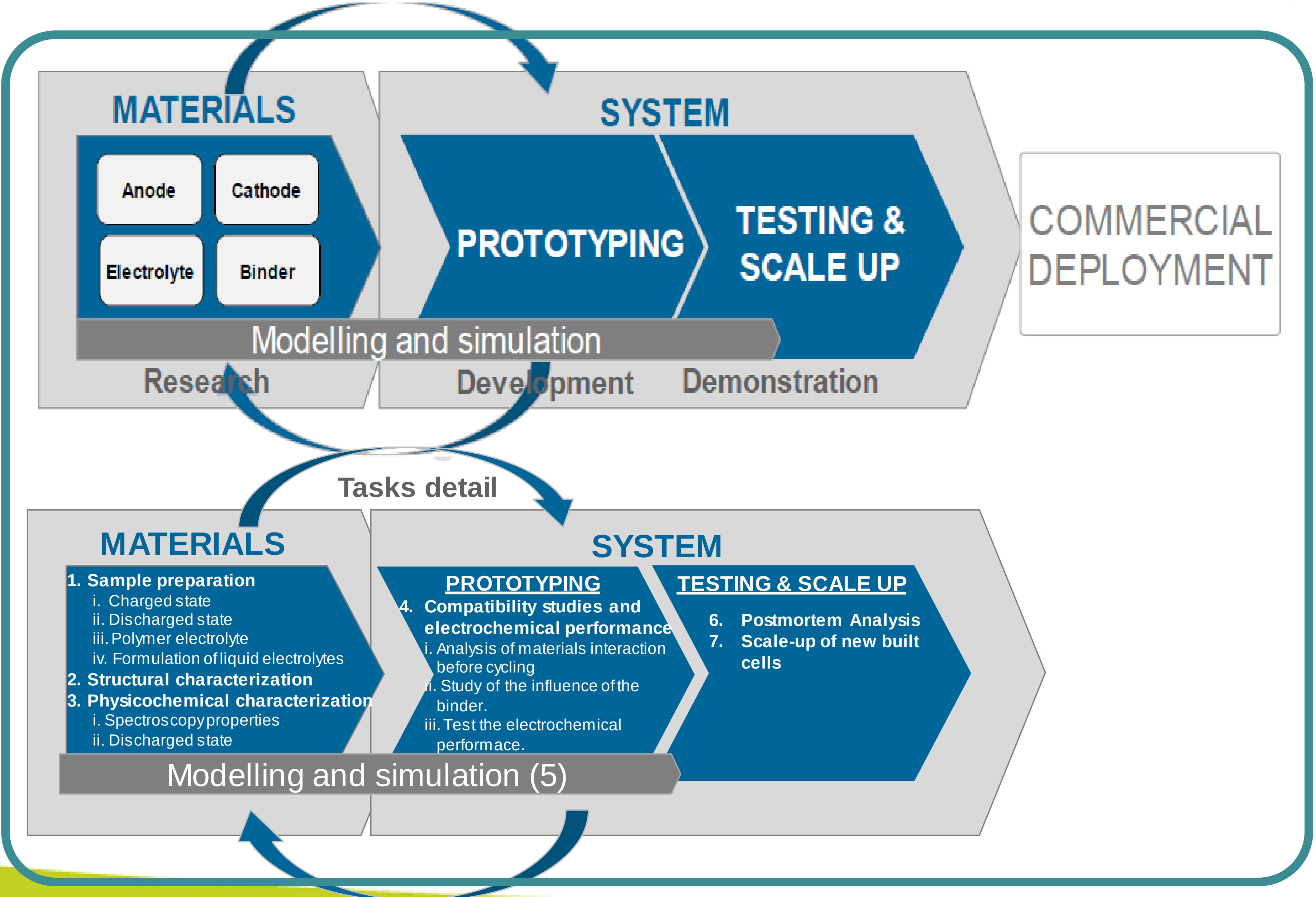
Electrochemical reaction:

$S_8 + 16Li \Leftrightarrow 8Li_2S$ $E^o = 2.15V$

Issues



- The solid sulfur is reduced to form polysulfides.
- The high-voltage plateau (2.4-2.1V) is related to the reduction of elemental sulfur to the higher order lithium polysulfides (Li_2S_n, $8 \geq n \geq 4$).
- Further reduction of high-order polysulfides (Li_2S_n, $n \geq 4$) to lower-order (Li_2S_n, $n<4$) occurs at the low-voltage plateau (<2.1V).


MATERIALS
Anode
Cathode
Electrolyte
Binder
SYSTEM
PROTOTYPING
TESTING &
SCALE UP
COMMERCIAL
DEPLOYMENT
Modelling and simulation
Research
Development
Demonstration
Tasks detail
MATERIALS
1. Sample preparation
i. Charged state
ii. Discharged state
iii. Polymer electrolyte
iv. Formulation of liquid electrolytes
2. Structural characterization
3. Physicochemical characterization
i. Spectroscopy properties
ii. Discharged state
SYSTEM
PROTOTYPING
4. Compatibility studies and electrochemical performance
i. Analysis of materials interaction before cycling
ii. Study of the influence of the binder.
iii. Test the electrochemical performace.
TESTING & SCALE UP
6. Postmortem Analysis
7. Scale-up of new built cells
Modelling and simulation (5)

EES (Batteries & Supercaps)

ETORTEK Jan'10 – Dec'12
ETORTEK Jan'11 – Dec'13

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Title:	**Development of Viable Na-ion Battery Technology**
Goal:	Development of a low cost high energy sodium ion battery for **stationary storage applications** with target values of: - cycle life ≥ 2000 cycles at 85% capacity retention, - specific energy density >130 KWh/kg (current Li technology),
Objectives:	To produce a complete battery based on the intercalation of Na ions at room and close to room temperature. Composed of: -high voltage cathode (>3.5V vs. Na) -medium voltage anode (<1.5V) which should show high stability. Electrolyte formulations will be developed in parallel for the chosen electrode materials. Once we have both candidates, we will perform nanostructuration of the active materials on both electrodes for improved electrochemical performance.

Results:

- Patent: 1 requested
- Papers: 3published + 2 submitted
- Review:Top Ten most-read (May '12)
- Conferences: 2 presentations

Collaborators:

Universidad del País Vasco / Euskal Herriko Unibertsitatea
BERKELEY LAB
The University of Michigan

Research Line Background

Energy &
Environmental Science

Dynamic Article Links

Cite this: *Energy Environ. Sci.*, 2012, **5**, 5884

www.rsc.org/ees

REVIEW

Na-ion batteries, recent advances and present challenges to become low cost energy storage systems

Verónica Palomares,[a] Paula Serras,[a] Irune Villaluenga,[a] Karina B. Hueso,[a] Javier Carretero-González[b] and Teófilo Rojo*[ab]

First review on Na-ion batteries

- **Cited >180 times**

In the Top 10 most-read articles in 2013

Energy &
Environmental Science

RSC Publishing

REVIEW

View Article Online
View Journal | View Issue

Cite this: *Energy Environ. Sci.*, 2013, **6**, 2312

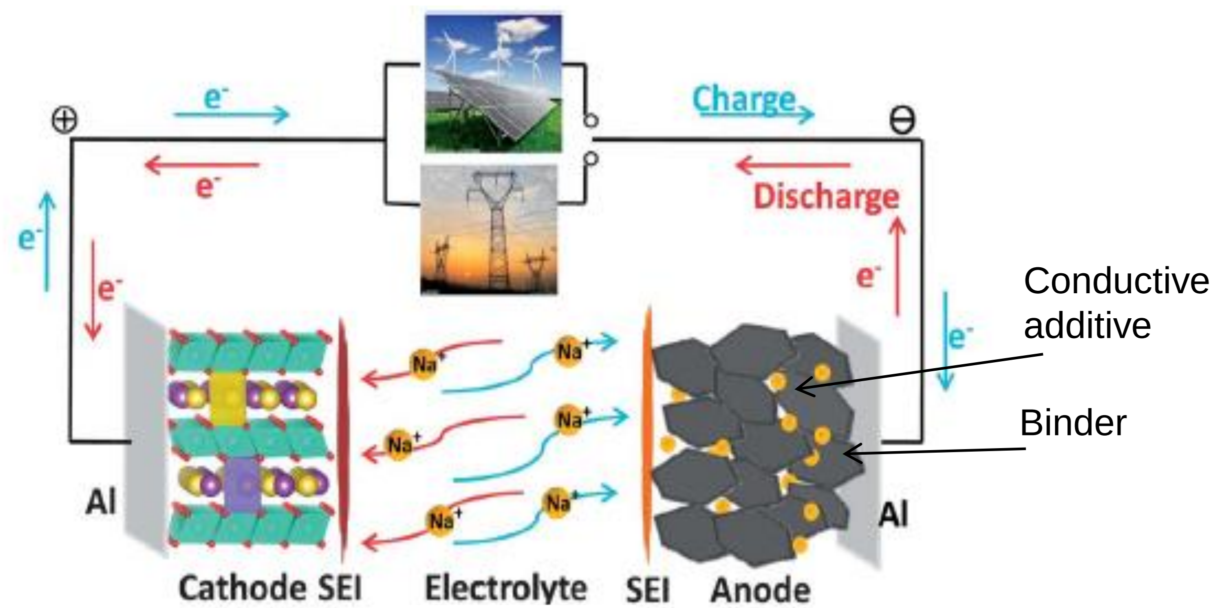
Update on Na-based battery materials. A growing research path

Verónica Palomares,[a] Montse Casas-Cabanas,[b] Elizabeth Castillo-Martínez,[b] Man H. Han[b] and Teófilo Rojo*[ab]

Recent advances in:

- **Na-ion batteries**
  - ✓ **Aqueous**
  - ✓ **Non-aqueous**
- **Na-air batteries**

Schematic of a typical Na-ion cell



$Na_{2/3}MO_2 \rightarrow Na_{2/3-x}MO_2 + xNa^+ + xe^-$

1M $NaPF_6$
EC:DMC

$Na_2Ti_3O_7 + 2Na^+ + 2e^- + \rightarrow Na_4Ti_3O_7$

Ideal Battery

- *High cell voltage and specific capacity*
- *High energy density*
- *Safety*
- *Low-cost*
- *Long cycle life.*

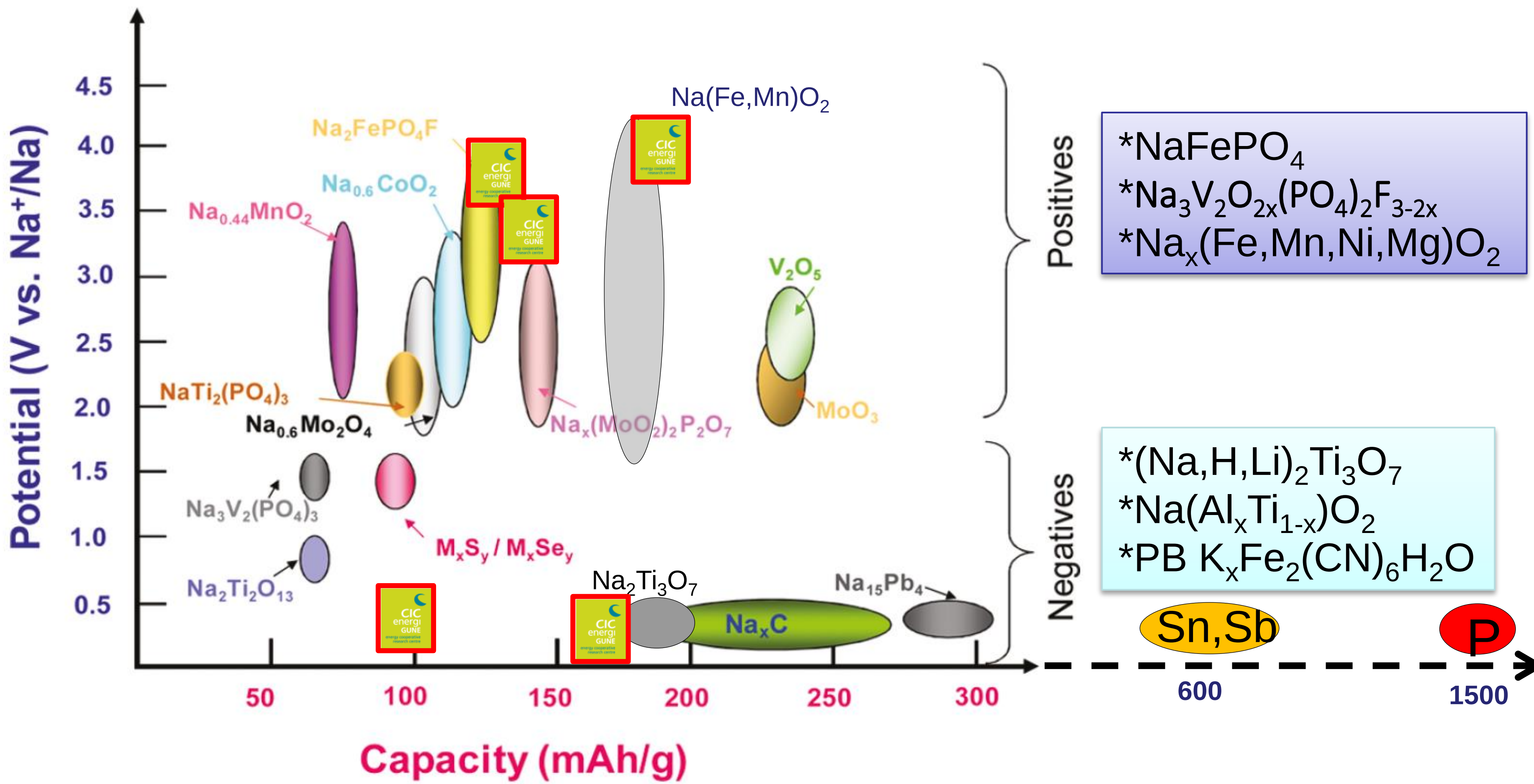
Modeling Calculations

- Energy Density : 210 $Whkg^{-1}$

With:

- Cathode capacity of 200 $mAhg^{-1}$
- Anode : 500 $mAhg^{-1}$
- *Average Cell Potential: 3.3V*

Current research of Na-ion electrode materials



Modified from P. Seguntuvan, *Chem. Mater.* (2011)

Solid Electrolytes

EES
(Batteries & Supercaps)

Internal Project

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energy cooperative research centre

Title:	**Solid Electrolytes for Na & Li batteries**
Goal:	To develop more **secure and reliable solid electrolytes** with high ionic conductivity, through the replacement of currently used liquid organic solvents.
Objectives:	**Polymer Electrolytes** -Preparation hybrid nanoparticles grafted either with polymer stands or/and plasticizer (such as ionic liquid, organic compounds with high dielectric constant, etc.). **Ceramic Electrolytes** -Use of ceramic ionic conductors to increase the safety and chemical and electrochemical stability of the systems with the advantage that ceramic materials can be obtained with a wide variety of stoichiometries, crystal structures and microstructures which lead to a controlled range of electrochemical properties with applicability in these devices.
Results:	• Papers: 1 under preparation • Conferences: 1 presenations

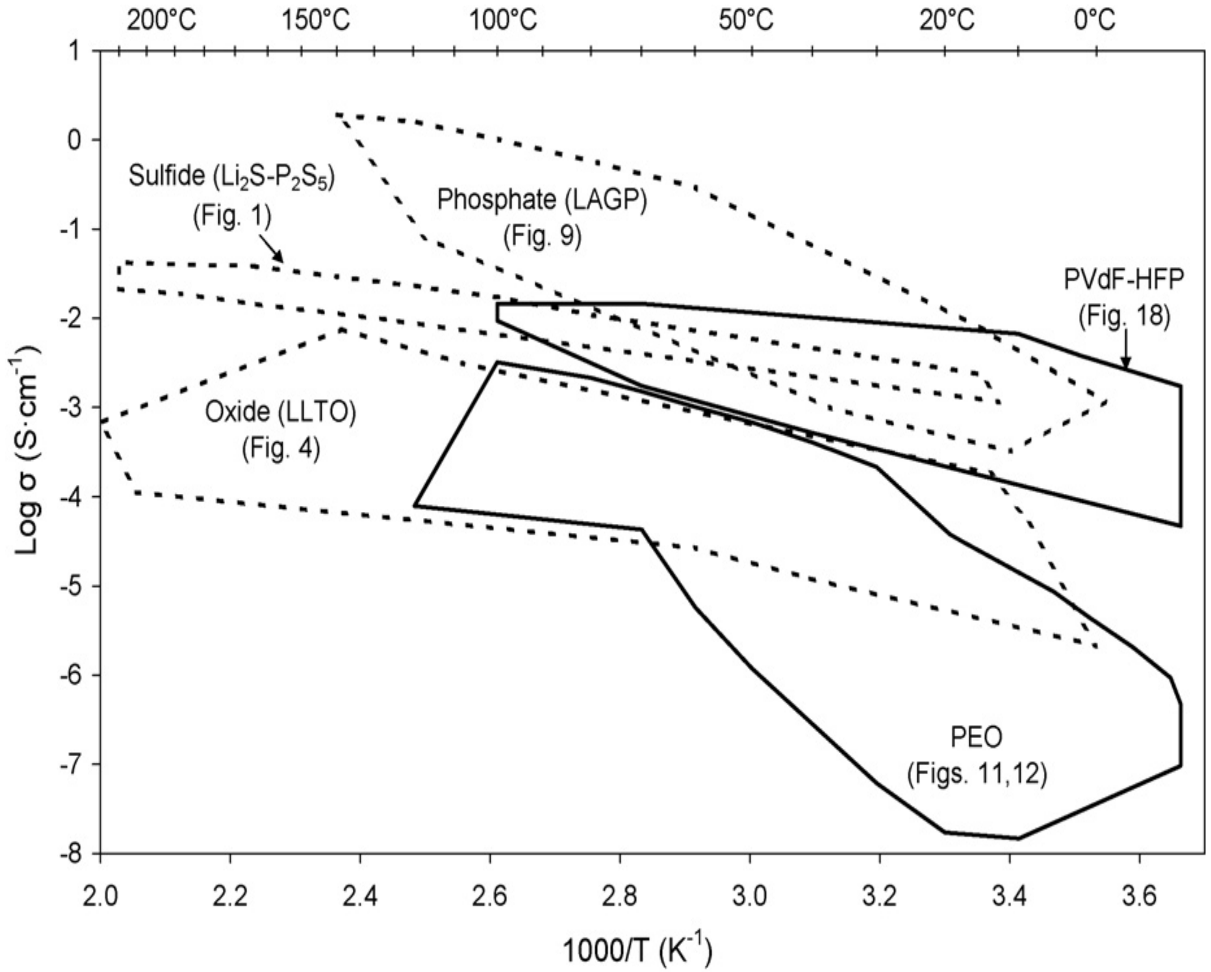
Collaborators: Imperial College London

Solid Electrolytes

Two types
- Inorganic ceramic electrolyte
  -Sulfides, phosphates, oxides. glasses
- Organic polymer electrolyte
  -Solid polymer (PEO)
  -Polymer gel

Advantages
- Safer and more reliable than conventional solvent based liquid electrolytes
- Potentially being able to simplify battery design and manufacturing process

Major issues
- Low conductivity, especially at low temperatures
- Poor mechanical strength
- Compatibility with electrode materials
- Stability of the interface



Fergus, Journal of Power Sources 195 (2010) 4554–4569

1. Research Line Background

❑ Research Line Goals:

Goal:

To develop more secure and reliable solid electrolytes with high ionic conductivity (>10^{-5} S/cm at room temperature with a transport number $t^+ \rightarrow 1$) through the replacement of currently used liquid organic solvents.

Objectives:

- **Ceramic Electrolytes**

➢ Wide variety of stoichiometries, crystal structures and microstructures for high diffusion.

➢ Increase the safety and chemical and electrochemical stability of the systems.

- **Polymer Electrolytes**

Preparation of hybrid nanoparticles grafted either with polymer stands or/and plasticizer (such as ionic liquid, organic compounds with high dielectric constant, etc.).

Global Aims

- Development of stable ceramic electrolytes with high conductivity.
  - Air insensitive
  - Wide electrochemical window
- Investigation of ion transport in oxide matrices both in bulk and grain boundaries.
  - Control of microstructure - processing
  - Development of thin film electrolytes

  } Minimisation of Grain Boundary

  - Modelling (bulk)
  - SIMS/LEIS IEDP

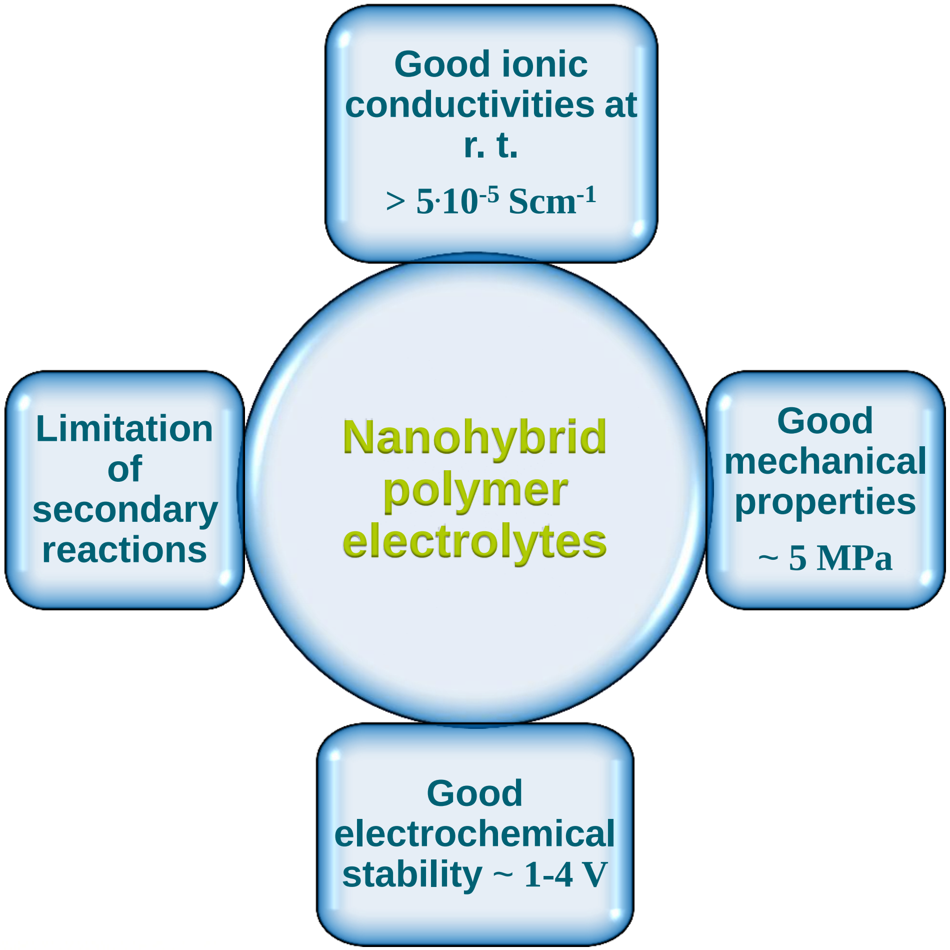
  } At Imperial

- Systems
  - $La_{2/3-x}Li_{3x}TiO_3$ (LLTO)
  - $Li_7La_3Zr_2O_{12}$ Garnets

Polymer Electrolytes

Objectives:

To develop more secure and reliable solid electrolytes with high ionic conductivity through the replacement of currently used liquid organic solvents.

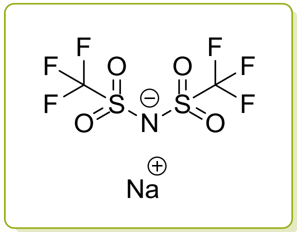


Nanohybrid polymer electrolytes

➢ Solvent-free, hybrid electrolytes based on nanoscale organic/silica hybrid materials (NOHMs) have been recently prepared with Li salts.

➢ In the Na salts such as sodium bis(trifluoromethanesulfonyl)imide (NaTFSI) ≈ 2/3 of the current is carried by anions that generate:

- high concentration polarization
- internal resistance
- voltage loss



➢ The anchoring of the anion could avoid concentration gradients, with only Na^+ mobile, yet keeping relatively good ionic conductivities.

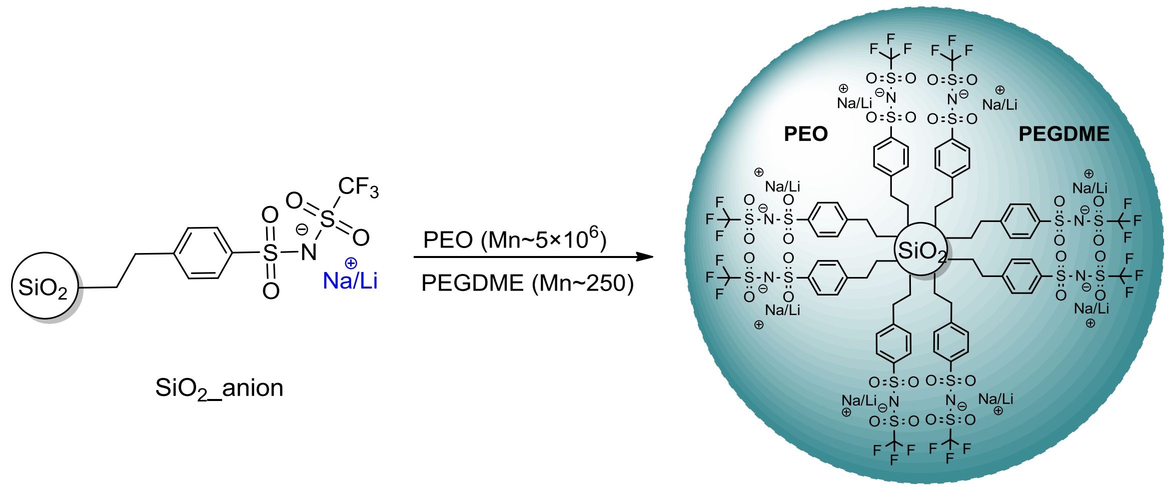
HOW?

Nanoparticles grafted with the anions of Na^+ salts

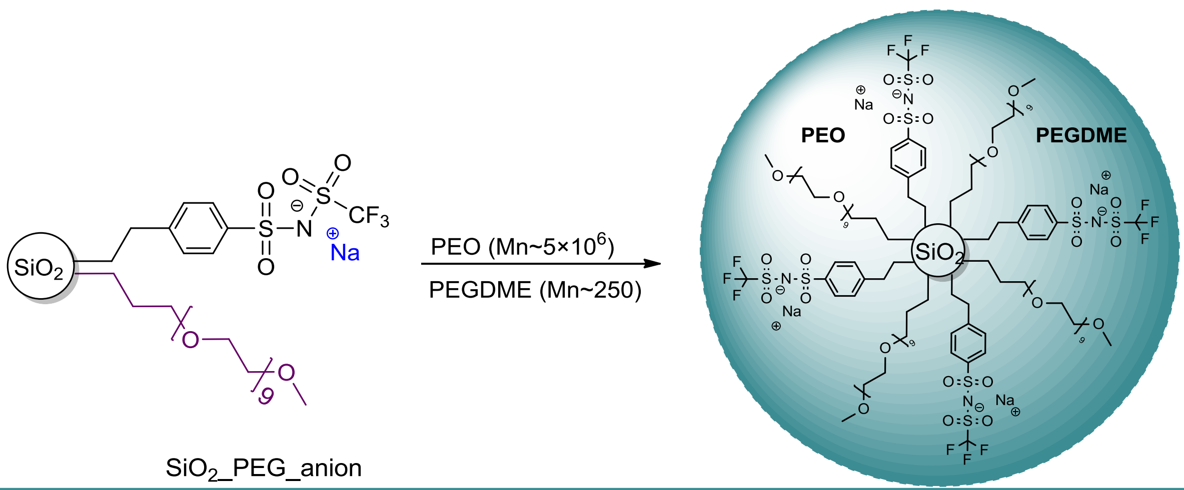
J.L. Schaefer, S.S. Moganty, D.A. Yanga, L. A. Archer, *J. Mater.Chem*. 21 (2011) 10094.

Nanohybrids electrolytes

New polymer electrolytes with nanoSiO_2 grafted with PEG and/or anion.



SiO2_anion



SiO2_PEG_anion

EES
(Batteries & Supercaps)

ETORTEK Jan'12 – Dec'15
Project with industry

CIC energiGUNE
energy cooperative research centre

Title:	Development of Capacitors
Goal:	To optimise the synthesis of **carbon materials** and **transitional metals oxide/nitrides** to obtain high energy and power of supercapacitors in both gravimetric and volumetric terms.
Objectives:	Synthesis of novel electrode materials for electrochemical capacitor application with easier production and less costly than the best electrochemical capacitor electrode materials known to date. -Optimised synthesis of nanoporous carbons from different precursors. -Exploration of pseudocapacitive materials based on the oxides/nitrides of transitional metals.

Results:

- Industrial collaboration
- Papers: 0
- Conference presentations: 6

Collaborators:

Université Paul Sabatier TOULOUSE III
eika
MONDRAGON UNIBERTSITATEA

1. Research Line Background - Materials & Systems

Electrochemical Capacitors
or
Supercapacitors

EDLCs
(Carbon materials)

Non-Faradaic
(no charge transfer)

CIC works on:

- Activated carbons from renewable inexpensive biomass precursors
- Soft-template ordered mesoporous carbons for high-rate supercapacitors

Pseudocapacitors
(Oxides and conducting polymers)

Pseudocapacitance
Charge transfer through surface faradaic reactions

CIC works on:

- Transitional metal oxides (e.g., MoO_3)
- Transitional metals nitrides/oxinitrides (VNx)

CIC's Research Areas

Batteries & Supercaps
Post-mortem Analysis

EES
(Batteries & Supercaps)

MAT4BAT
Project with industry

CIC energiGUNE
energy cooperative research centre

Title:	**Batteries & Supercaps Post-mortem Analysis**
Goal:	The aim of this work generate extensive knowledge on failure roots and a better understanding of critical ageing mechanisms occurring in different electrochemical devices (batteries, supercapacitors…) in order to propose behavioral and predictive models for battery performance and lifetime under various practical operating conditions (charge, discharge, rest time). Strong interactions with industrial partners and international technological centers are expected.
Objectives:	• A complete literature survey about ageing mechanisms of Li-ion batteries and supercapacitors • Cell opening. • Defining protocols for opening pouch-cells and cylindrical cells (safe state of charge, controlled atmosphere…) and samples collection • Chemical characterization: ICP, surface characterization (XPS, EDS) • Physical characterization: electron microscopy • Electrochemical characterization: potentiostatic tests, galvanostatic tests and impedance spectroscopy

Results:

- Industrial collaborations

Collaborators: CEGASA GROUP, IK4 IKERLAN Research Alliance, Argonne NATIONAL LABORATORY, CAF, Orona

Why Prototype ?

CIC energiGUNE
energy cooperative research centre

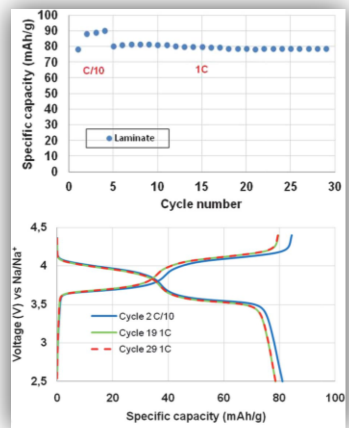
- ❑ Fill up the gap between basic Research and Advanced Engineering

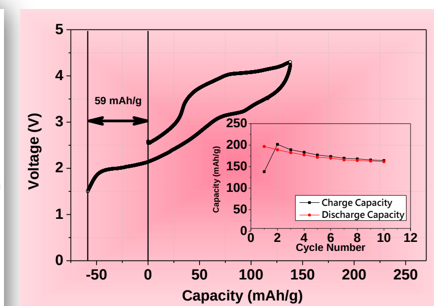
Basic Research → Best Results / RL Output → Prototyping → Advanced Engineering || Feasibility Studies → Other Intermediate Steps / Management → Final Production **Industry**

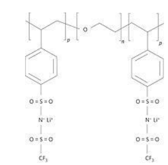
Various Research Lines at CIC

- ❑ *Lithium Ion Batteries*
- ❑ *Sodium Ion Batteries*
- ❑ *Li – S Batteries*
- ❑ *Supercapacitors*
- ❑ *Solid Electrolytes*

Some results possess challenge for future advancement

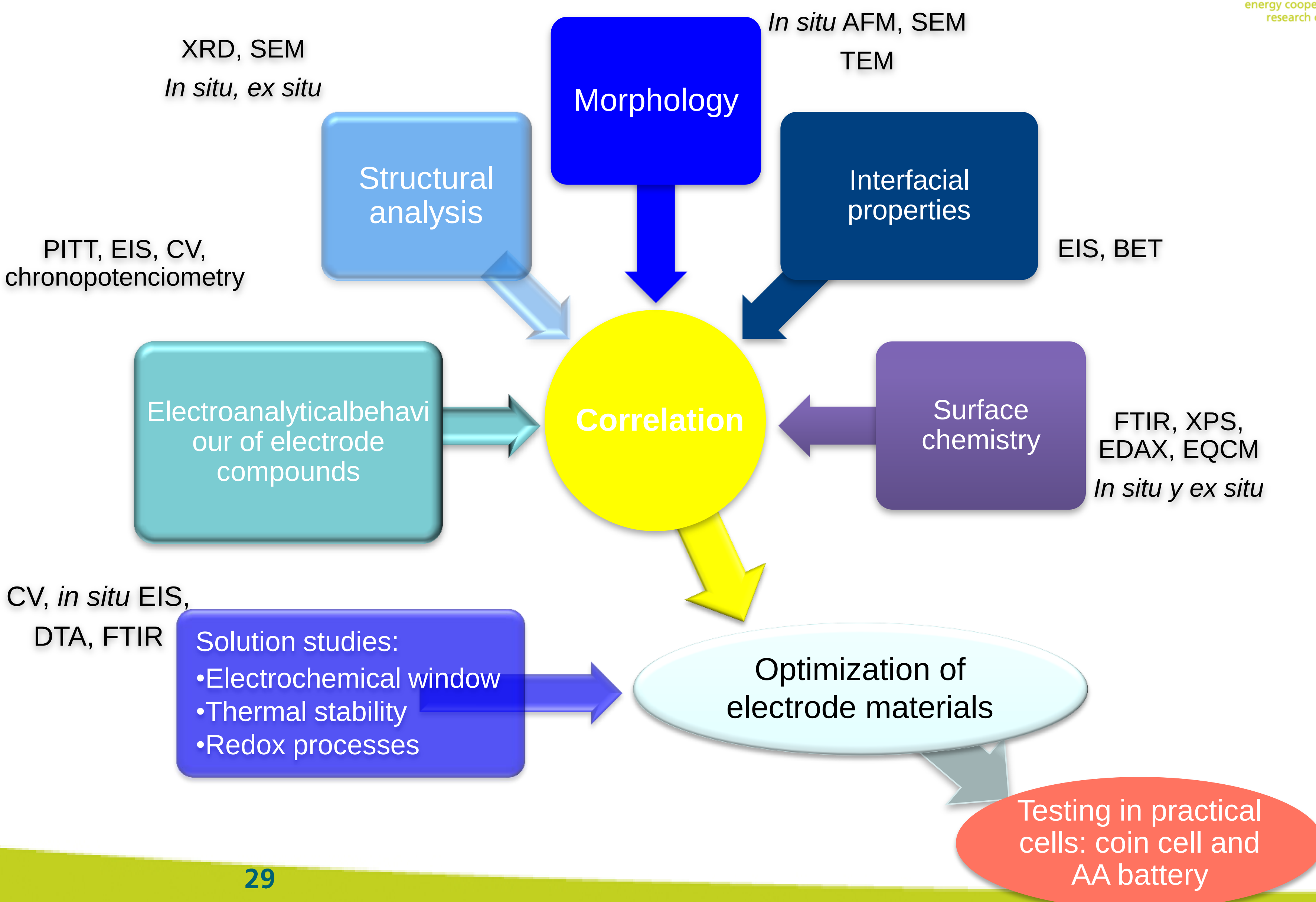






- ❑ Gives an opportunity focus on critical parameters at device level
- ❑ Allignment of the research output with the market needs

Strategy for R&D on batteries



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THANK YOU FOR YOUR ATTENTION

2013