# **Research in** Chemical Energy **Storage**

**Susana I. Córdoba Torresi**

Instituto de Química – USP. São Paulo (SP), Brasil

# SÃO PAULO

## Materials for energy conversion

# Hydrogen Lab – IFGW – University of Campinas UNICAMP)



The Hydrogen Laboratory investigates power generation systems from renewable and non-renewable sources, especially for the production of hydrogen and its use in fuel cells.

*Reformer (Ethanol)  for hydrogen production*


*Vega-2, the hydrogen fuel cell electric car built by the group*

# FUEL CELL AND HYDROGEN CENTER (CCCH/IPEN-SP)



Three main areas were developed: PEMFC (Proton Exchange Membrane Fuel Cell); SOFC (Solid Oxide Fuel Cell); REFORM ($H_2$ production from ethanol reforming) and lately, in 2007, the group of NUCLEAR AND NON-CARBOGENIC HYDROGEN PRODUCTION.

# Electrocatalysis in metals and alloys.

The electrocatalysis is one of the most important areas of modern electrochemistry, being related to current fundamental problems such as electrochemical energy conversion and environmental protection. The research in electrocatalysis has been approached from various points of view, but the main ones are:

i) Determining the mechanism and kinetics of electrochemical reactions of interest;

ii) To identify the nature and properties of the species (including intermediaries) that participate in the reaction, and

iii) The influence of the characteristics of the interface (including adsorbed species) on the reaction kinetics and mechanism;

iv) The correlation of kinetics and reaction mechanism with physical and structural properties of electrocatalytic substrates.

# Systems for electrochemical energy conversion.

These activities are divided between the fuel cell and nickel-hydride batteries. Several small prototypes ( 50-200 W ) to give reached build a 600 W 50 W were built. A prototype come to operate for 5000 hours compared to those produced by international companies performance have been developed . In recent years the Group has been dedicated to researching and developing cells of solid polymer electrolyte ( PEFC , polymer electrolyte fuel cell ) . One of the most important achievements is the development of technology to fabricate gas diffusion electrodes for phosphoric acid cells and solid polymer electrolyte. The Group has also developed and successfully tested a module 100W of solid polymer cell. Currently , efforts are being made in the search for electrocatalytic systems of high surface activity , including ways to reduce catalyst deactivation at acceptable levels when the operation of the system involves hydrogen produced by reforming or the direct oxidation of methanol . Other studies of basic research has been done in several component modules of PEFC , involving : ( a) basic studies of development and improvement of electrocatalysts and gas diffusion electrodes; ( b ) study of water balance in the polymer membrane , which is a crucial point in this system; ( c ) design of gas distributors ( " flow field " ) , Intercalation of Li - carbon nanotechnology and research in the area of production and physico- chemical characterization of materials for electrochemical devices (V2O5 , LiMn2O4 , LiAxByO2 , a = Ni , Ga B = Co , amorphous carbons obtained from bagasse , natural graphite); single and multiple wall carbon nanotubes. This lab has the infrastructure to preparation of the above materials and composite electrodes for Li ion batteries , thin films by spin-coating and electrochemical methods. Also has reactors for the production of SWNT and MWNT ( arc reactors and CVD ) buit by the group . currently , we are conducting studies on olivine $LiFePO_4$ doped with transition metals and developing projects for production of NTC which include mechanistic studies of growth. The group also engaged in studies of their functionalization with groups OH and S.

## Organic and Hybrid Solar Cells

• Study of new or modified organic materials such as conducting polymers derived from polythiophene, poly (p-phenylene vinylene) and polyfluorene, porphyrins & phthalocyanines, carbon nanotubes, fullerenes and more recently graphene.

• Synthesis and application of inorganic semiconductors as electron transport/absorber materials in hybrid solar cells. The inorganic semiconductor nanoparticles are comprised of metal oxides such as $TiO_2$ and ZnO, as well as CdS and CdSe (in the form of spherical nanoparticles, nanotubes, and/or nanorods, etc)

## Dye Sensitized Solar Cells

•Preparation and characterization of new polymeric and gel electrolytes as substitutes for the existing liquid electrolytes.

•Synthesis of new Ru(II) dyes based on polypyridine compounds and polymer conductors for hole transport.

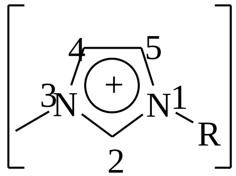
•Synthesis and characterization of new coordination polymers.

## Photocatalysis

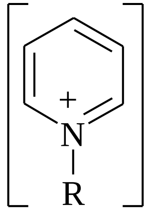
•We aim to investigate the photocatalytic properties of several nanocomposites based on inorganic semiconductors towards photocatalytic reduction of $CO_2$ and water splitting.

# Ionic liquids

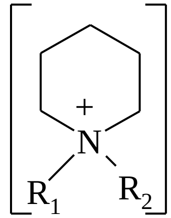
Most commonly used cations:



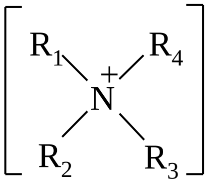
1-alkyl-3-methyl-imidazolium



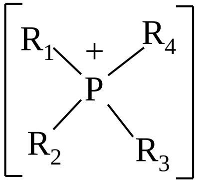
*N*-alkyl-pyridinium



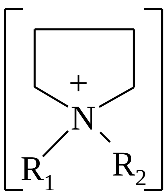
*N*-alkyl-*N*-methyl-piperidinium



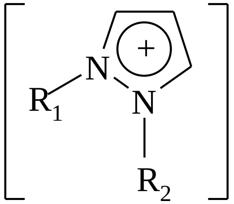
Tetraalkyl-ammonium



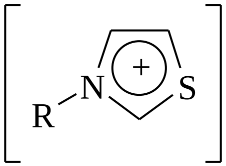
Tetraalkyl-phosphonium



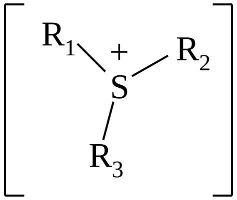
*N*-alkyl-*N*-methyl-pyrrolidinium



1,2-dialkyl-pyrazolium



*N*-alkyl-thiazolium



Trialkyl-sufonium

$R_{1,2,3,4} = CH_3(CH_2)_n$, *(n* = 1, 3, 5, 7, 9); aryl; *etc*.

Some possible anions:

water-immiscible ⟶ water-miscible

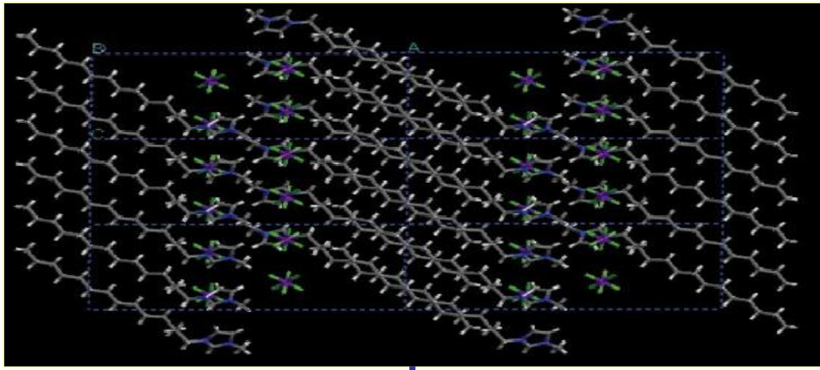
| | | |
|---|---|---|
| $[PF_6]^-$ | $[BF_4]^-$ | $[CH_3CO_2]^-$ |
| $[NTf_2]^-$ | $[OTf]^-$ | $[CF_3CO_2]^-$, $[NO_3]^-$ |
| $[BR_1R_2R_3R_4]^-$ | $[N(CN)_2]^-$ | $Br^-$, $Cl^-$, $I^-$ |
| | | $[Al_2Cl_7]^-$, $[AlCl_4]^-$ (decomp.) |

# Properties



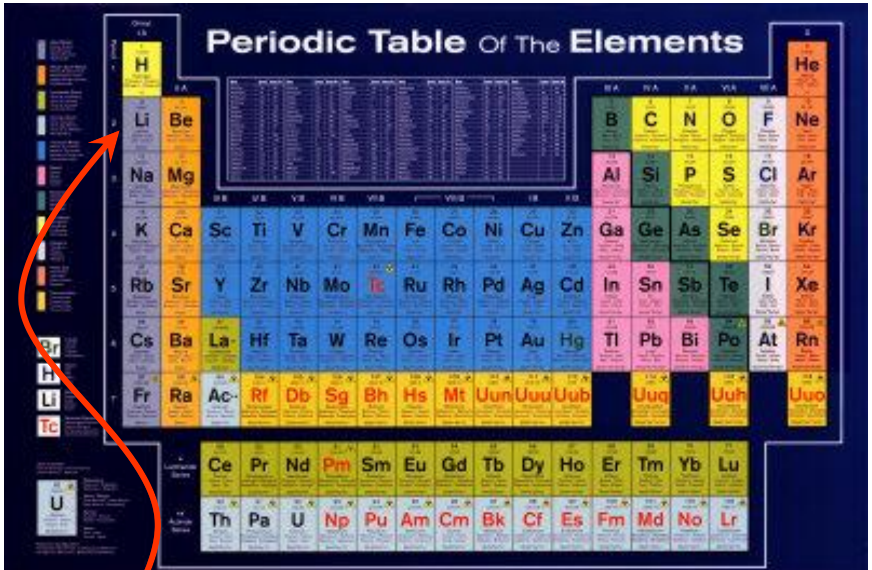
**Ionic liquid**

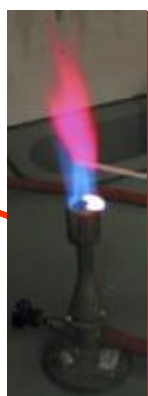
- Thermal stability
- Very low vapor pressure
- Ionic conductivity
- Tuning properties
  - Electrochemical window
    - Cation → Negative potential limit
    - Anion → Positive potential limit
  - Viscosity
  - Hydrophobic degree
    - Mainly depends on the anion used
  - Structural characteristics
    - Polar/non-polar characteristics of the substituents



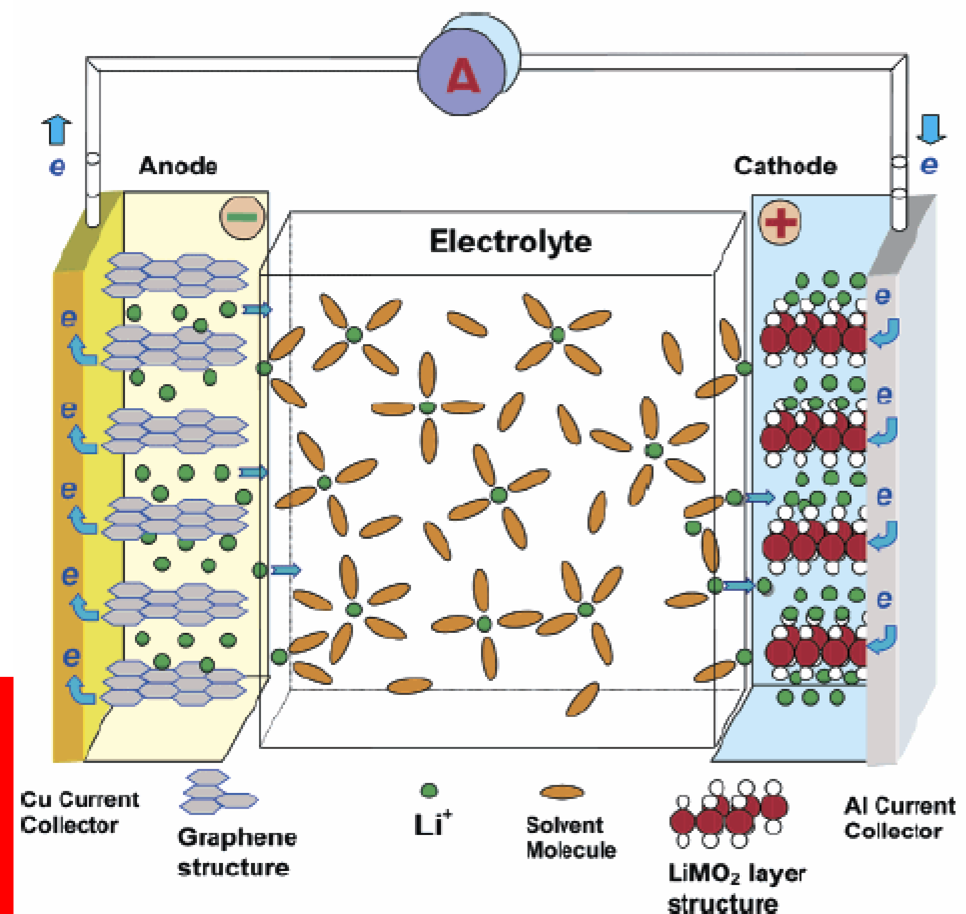
# Lithium-ion battery



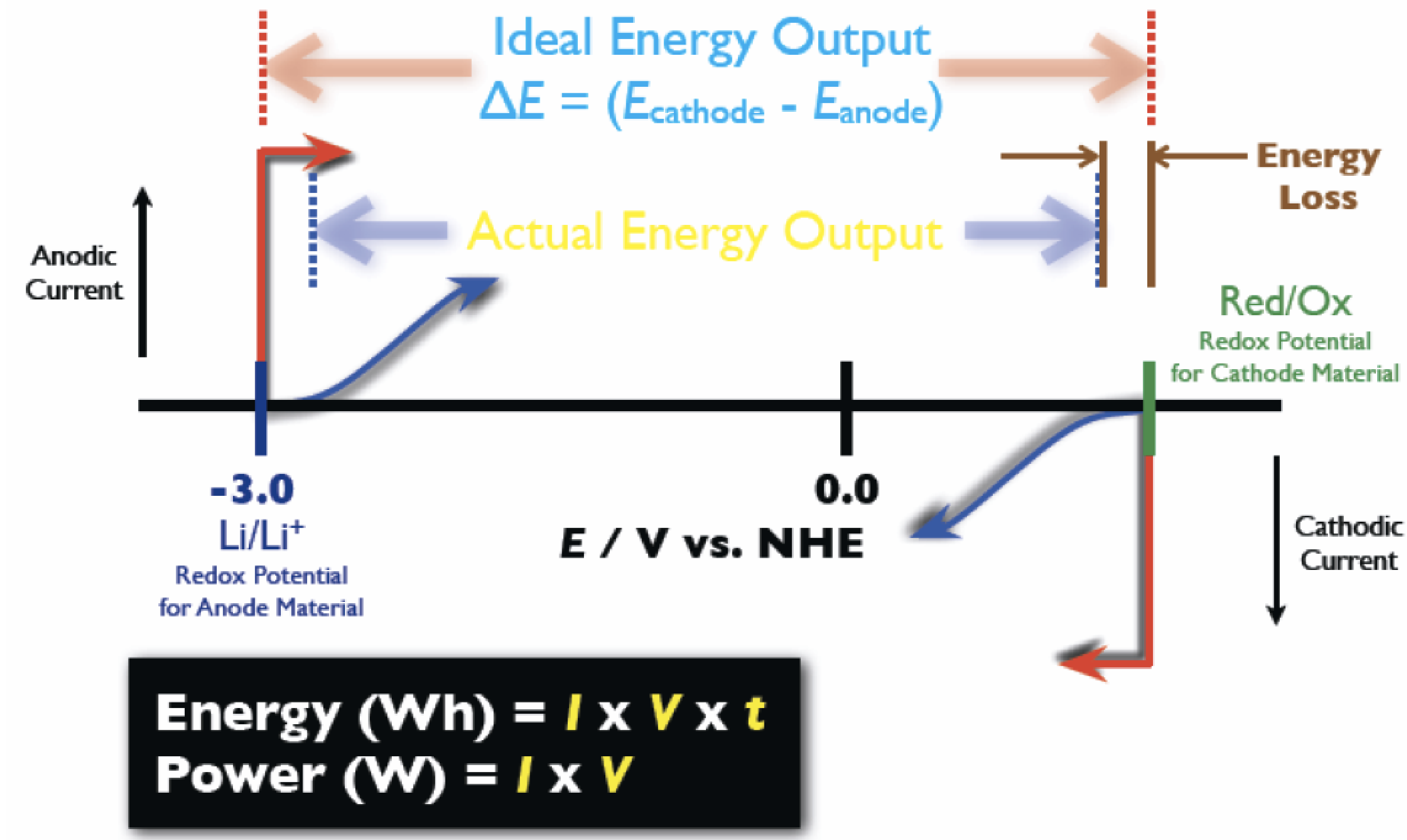


**Li**
Atomic number: 3
Molar mass: 6.939
δ= 3.88 g $cm^{-3}$
Capacity: 3863.03 A h $kg^{-1}$
Potential: -3.05 V vs NHE



# Lithium-ion battery



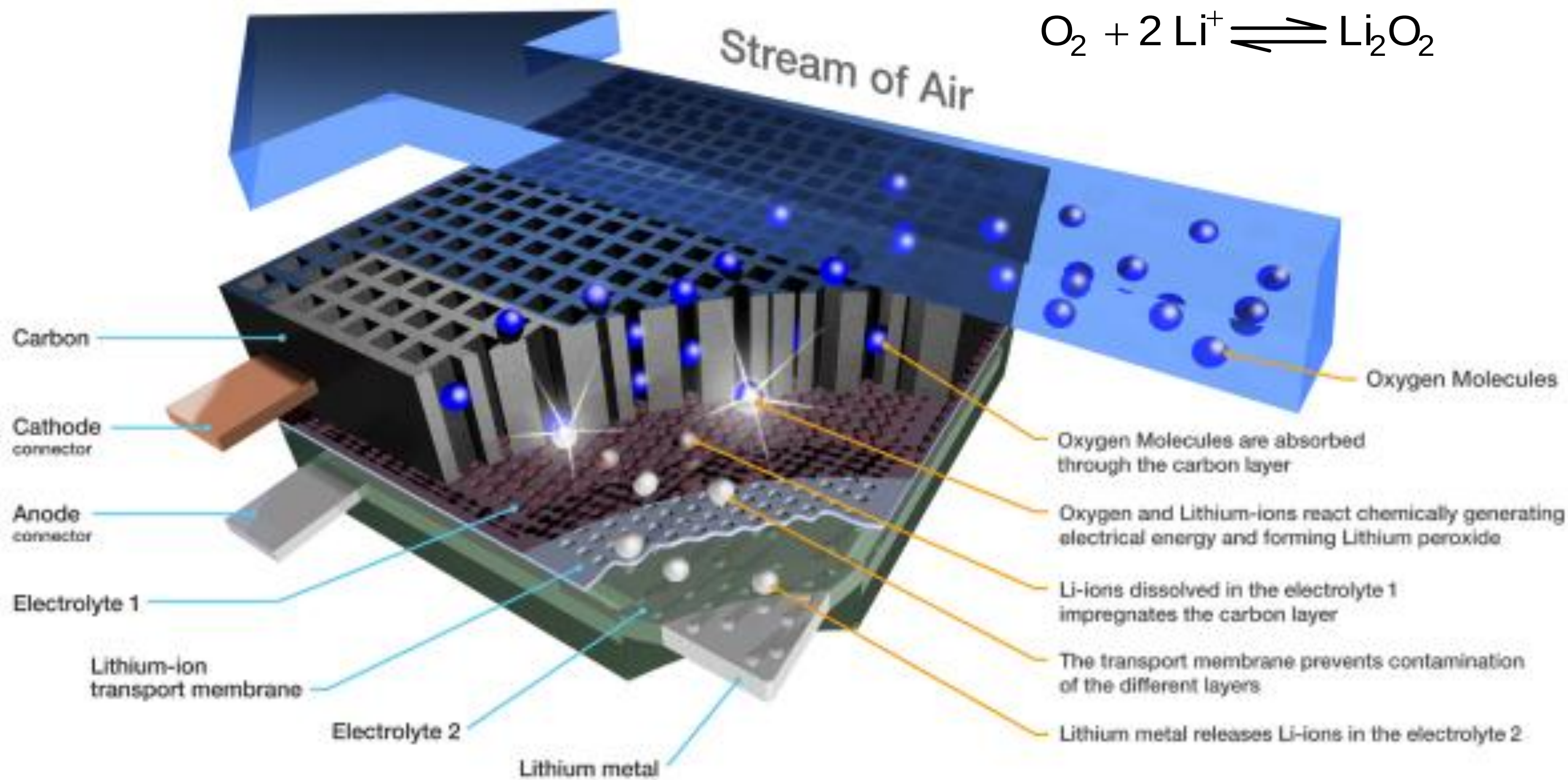

The design of the battery is a compromise between the available energy and the ability to extract this energy producing the smallest possible loss (internal resistance).

# Lithium-air battery

$$2\,Li \rightleftharpoons 2\,Li^{+} + 2\,e^{-}$$

$$O_2 + 2\,e^{-} \rightleftharpoons O_2^{2-}$$

$$O_2 + 2\,Li^{+} \rightleftharpoons Li_2O_2$$




http://www.ibm.com/smarterplanet/us/en/smart_grid/article/battery500.html

# Lithium-air battery

**Anode** (-): lithium electro-deposition.

**Cathode** (+): thin porous carbon film, where $O_2$ can permeate.

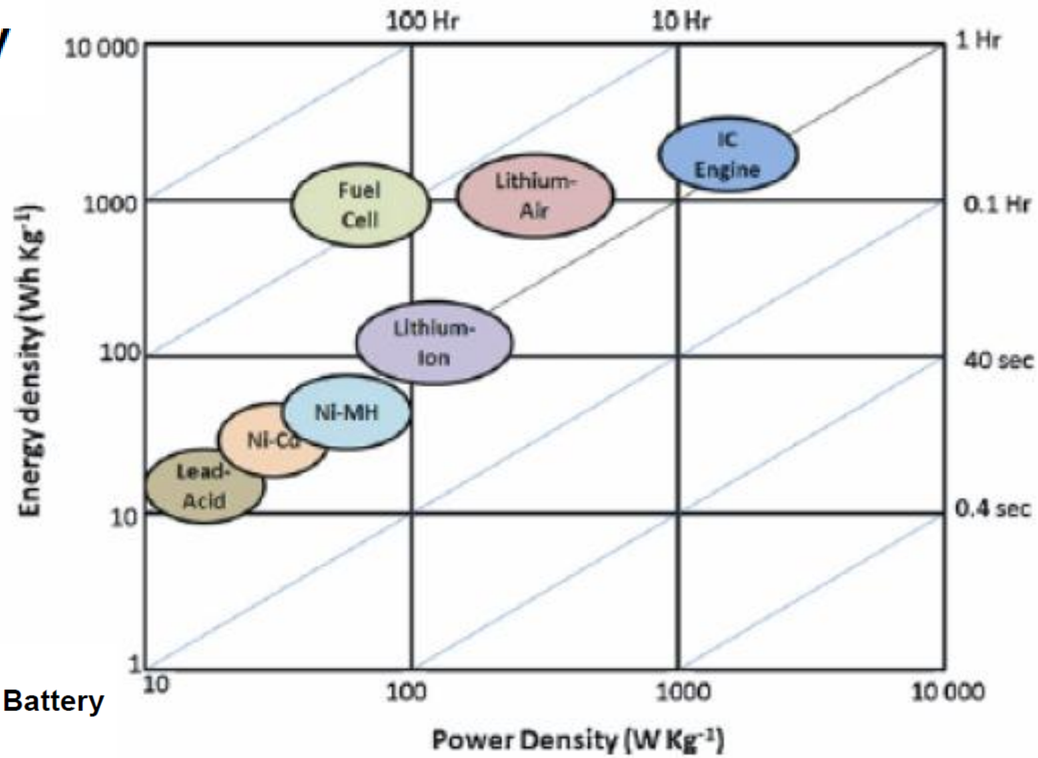
**Electrolyte**: cation lithium conducting gel or polymer .

$$4Li + O_2 = 2Li_2O \quad 3,1\ V$$

$$2\ Li + O_2 = Li_2O_2 \quad 2,9\ V$$

**12.583 vs.**

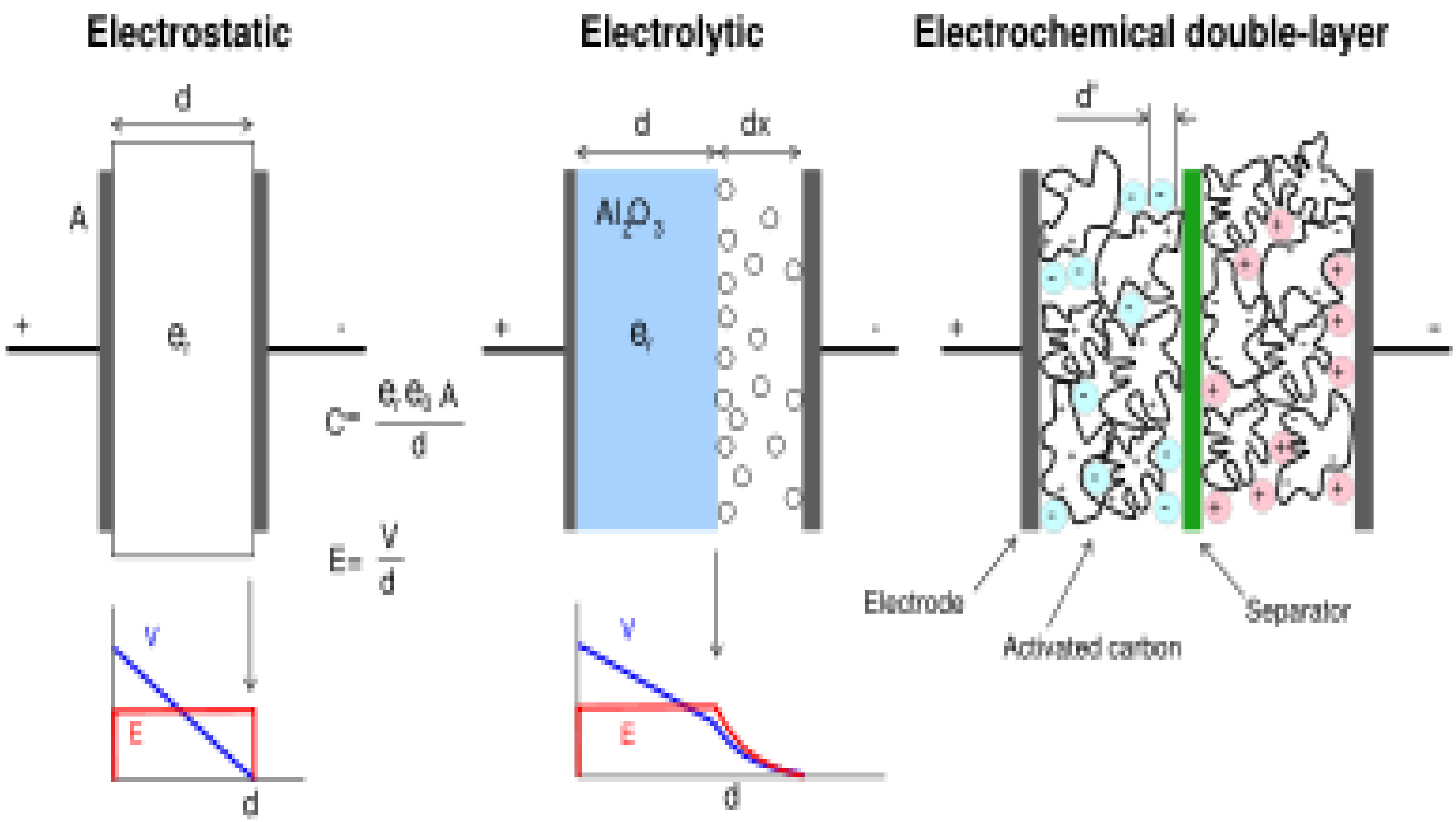
**12.222 A h V kg$^{-1}$ for gas**




K. M. Abraham and Z. Jiang
A Polymer Electrolyte-Based Rechargeable Lithium/Oxygen Battery
J. Electrochem. Soc., Volume 143, Issue 1, pp. 1-5 (1996)

# Electrochemical Capacitors

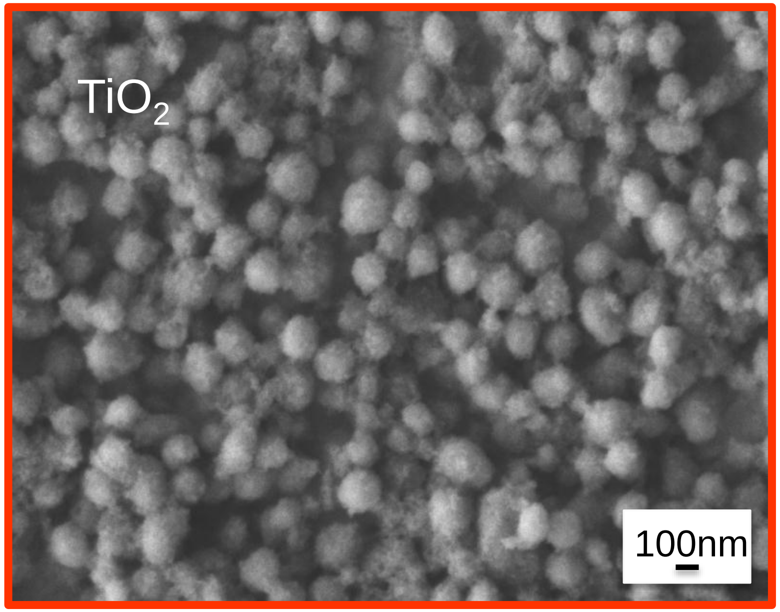


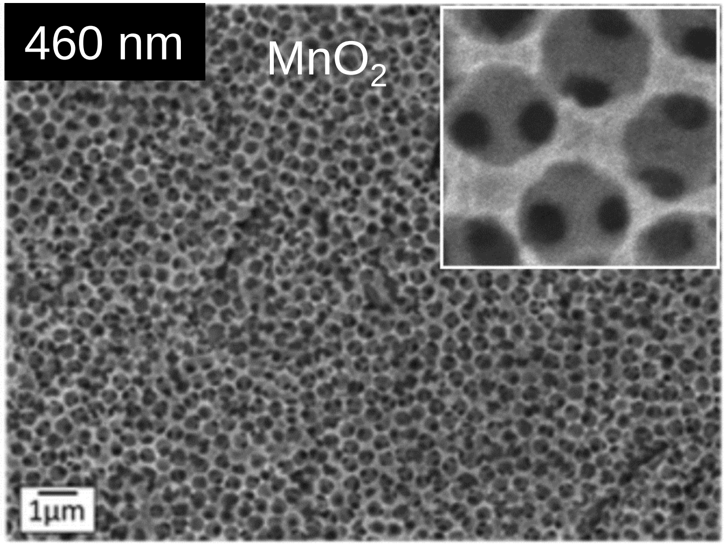


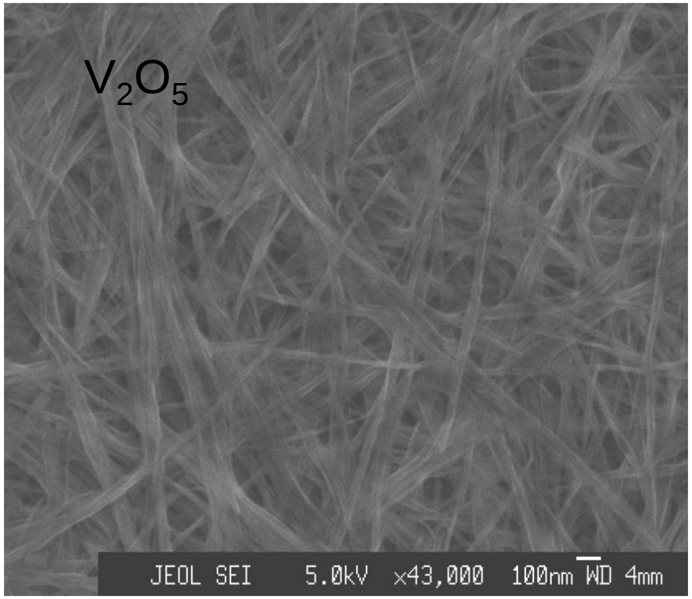
# Nano-structured materials



$TiO_2$, $MnO_2$, graphenes, $V_2O_5$

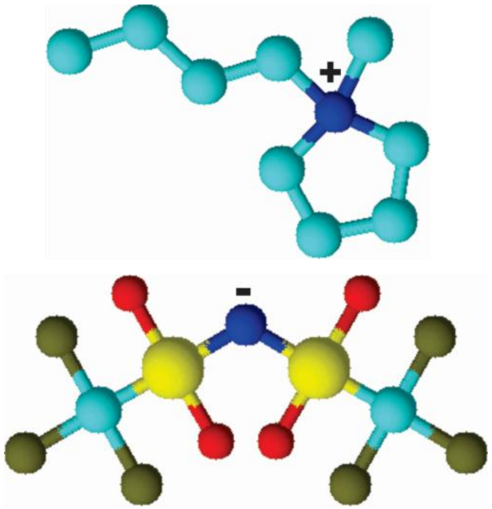


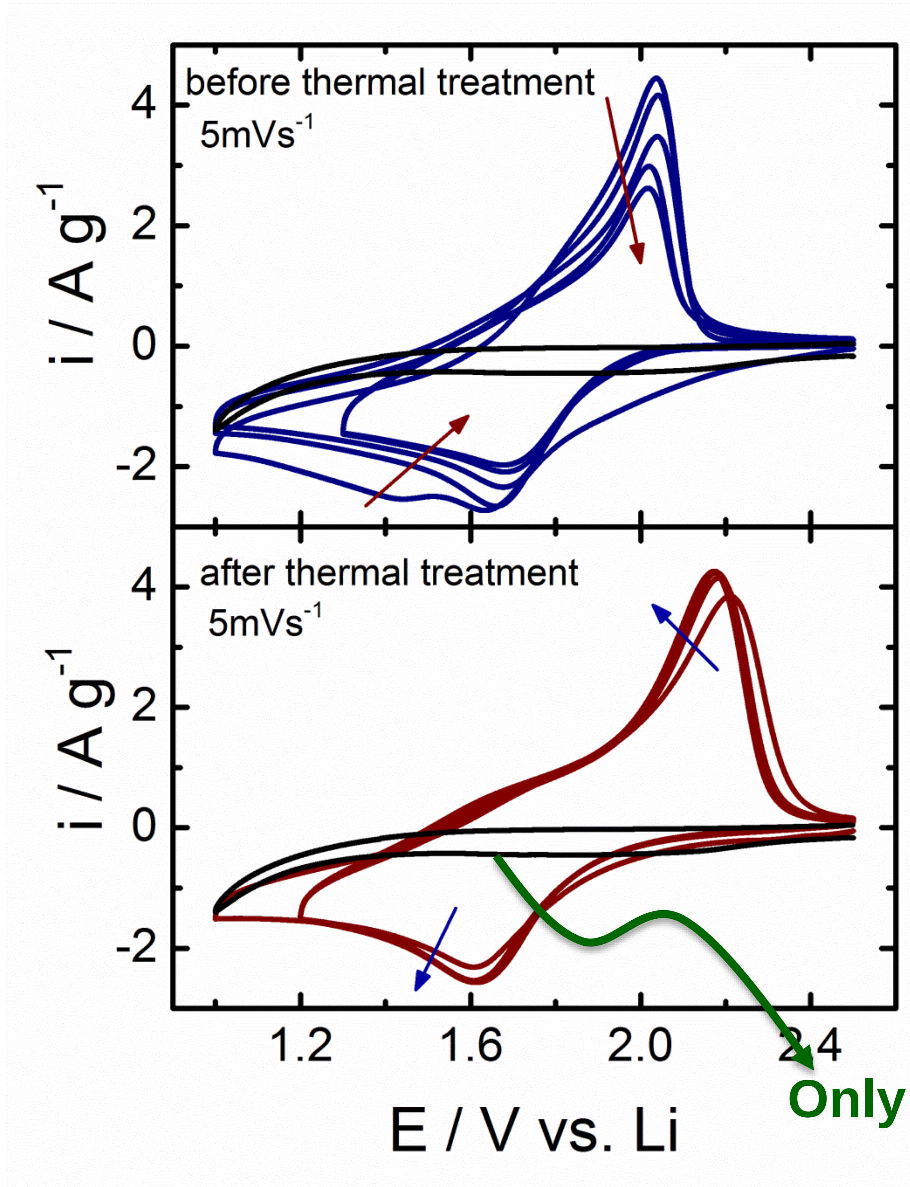
# Cyclic voltammetry in $Pyr_{1.4}Tf_2N$





$Pyr_{1.4}Tf_2N$

Nanoparticles of $TiO_2$




$LiTf_2N$ 0.03 mol $L^{-1}$ in $Pyr_{1.4}Tf_2N$

# Summary and Contacts