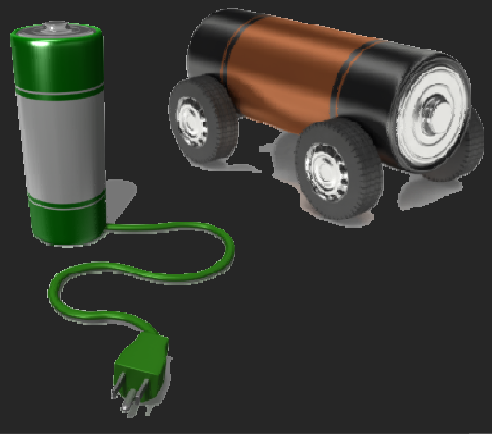
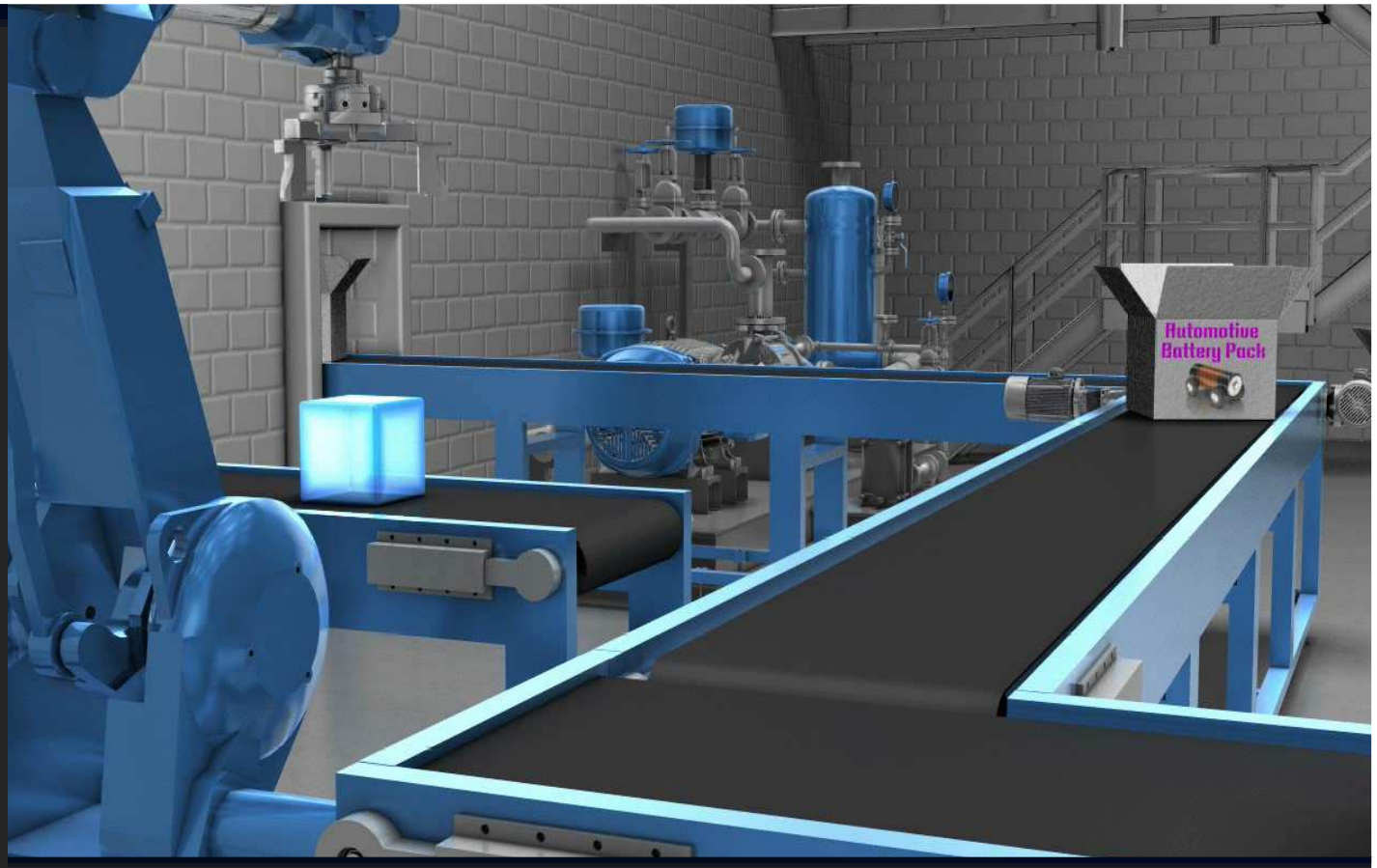
College on Multiscale Computational Modeling of Materials for Energy Applications

ICTP, Trieste, Italy
July 11, 2016





Engineering the Next Generation Rechargeable Batteries: A Multiscale Modeling Perspective I

Prof. Alejandro A. Franco

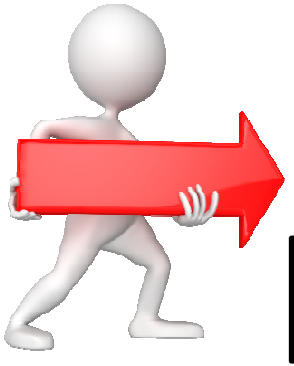
LRCS, Université de Picardie Jules Verne & CNRS – Amiens, France
Réseau sur le Stockage Electrochimique de l'Energie (RS2E)
ALISTORE European Research Institute

LABORATOIRE DE REACTIVITE ET CHIMIE DE SOLIDES

LRCS (UMR UPJV/CNRS 7314) ≅ 80 people

(Director: M. Morcrette)

- ***Electrochemical conversion and storage***
- Solid state materials chemistry
- Nanostructured materials
- Advanced characterization techniques
- Theory



➔ **LRCS** (Prof. J.M. Tarascon): lead the foundation of the national **RS2E** network and of the **ALISTORE** European Research Institute.

LRCS

Prof. Alejandro A. Franco

Engineering the Next Generation Rechargeable Batteries: a Multiscale Modeling Perspective I

College on Multiscale Computational Modeling of Materials for Energy

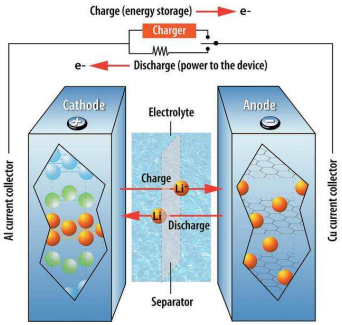
ICTP, Trieste, Italy - July 11, 2016

www.cnrs.fr

COMPUTATIONAL MULTISCALE MODELING @ LRCS

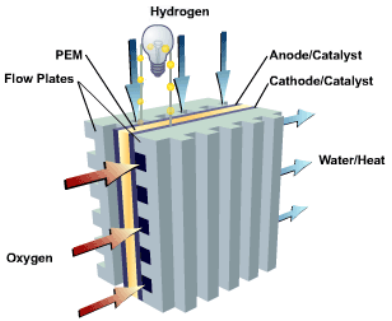
GENERAL GOAL
multiscale modeling for
understanding, predicting and improving

www.modeling-electrochemistry.com

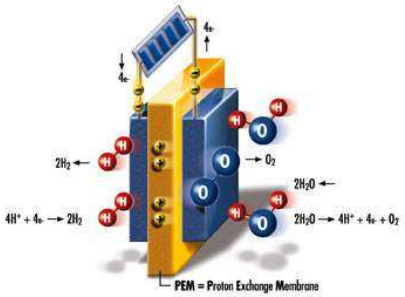


Rechargeable batteries

- Li-Ion
- Li-Air
- Li-Sulfur
- Redox Flow



PEM Fuel Cells



PEM Electrolyzers

From left to right: R. Zhao, Dr. M. Quiroga, A. Torayev, G. Shukla, Y. Yin, A. Geng, Prof. A..A Franco, M. Maiza, V. Thangavel, R. Andersson, C. Gaya, A. Shodiyev.

OUTLINE

MULTISCALE MODELING:
DEFINITIONS & CONCEPTS

LITHIUM-O_2 BATTERIES:
TECHNICAL CHALLENGES

KINETIC MONTE CARLO
MODELING APPROACH

CONTINUUM
MODELING APPROACH

THOUGHTS ON
THEORY VS. EXPERIMENT

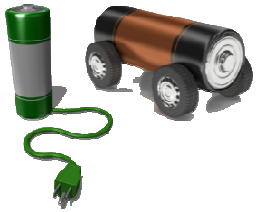
MULTISCALE MODELING: DEFINITIONS & CONCEPTS

LITHIUM-O_2 BATTERIES: TECHNICAL CHALLENGES

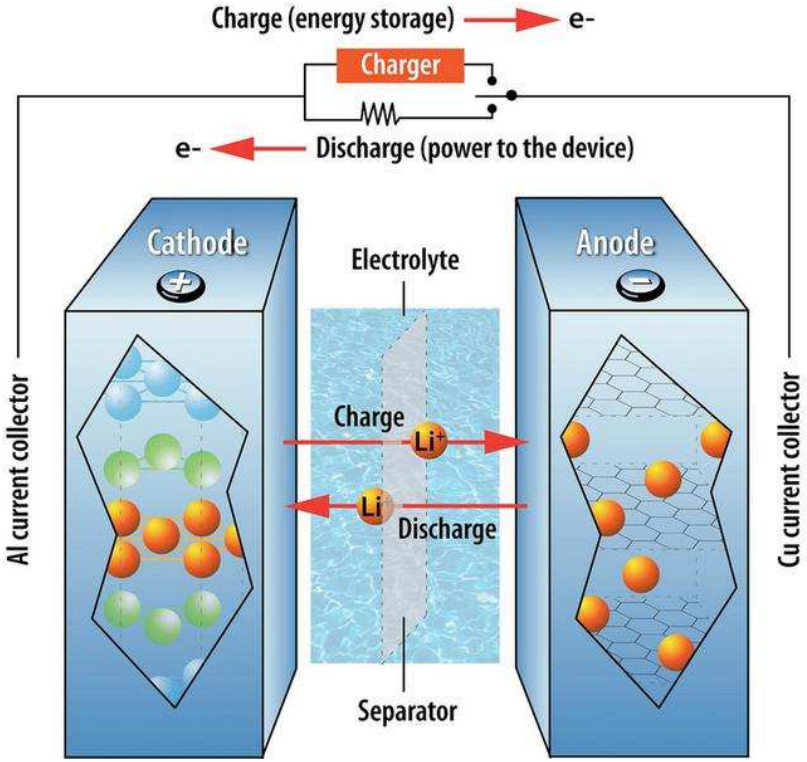
KINETIC MONTE CARLO MODELING APPROACH

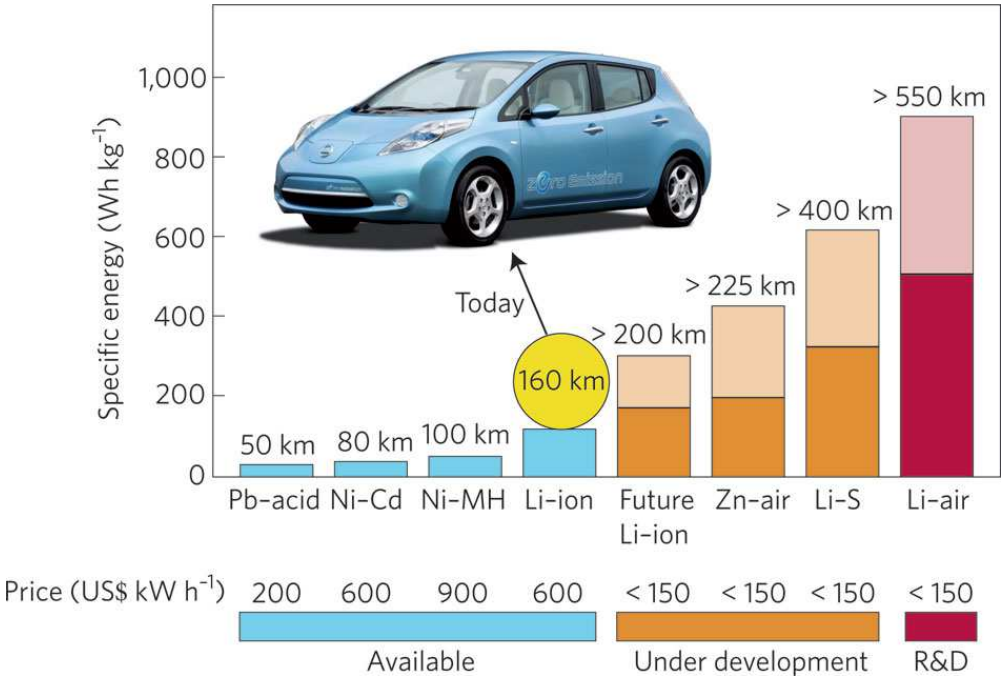
CONTINUUM MODELING APPROACH

THOUGHTS ON THEORY VS. EXPERIMENT



BATTERIES FOR AUTOMOTIVE APPLICATIONS





P.G. Bruce, S.A. Freunberger, L.G. Hardwick, J.M. Tarascon, *Nature Materials* **11** (2012) 19 .

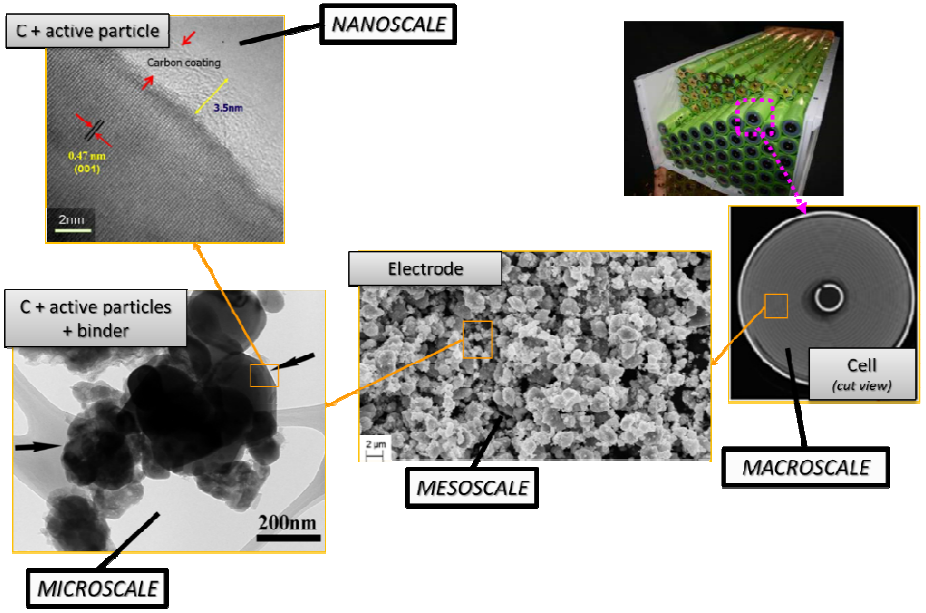
Prof. Alejandro A. Franco

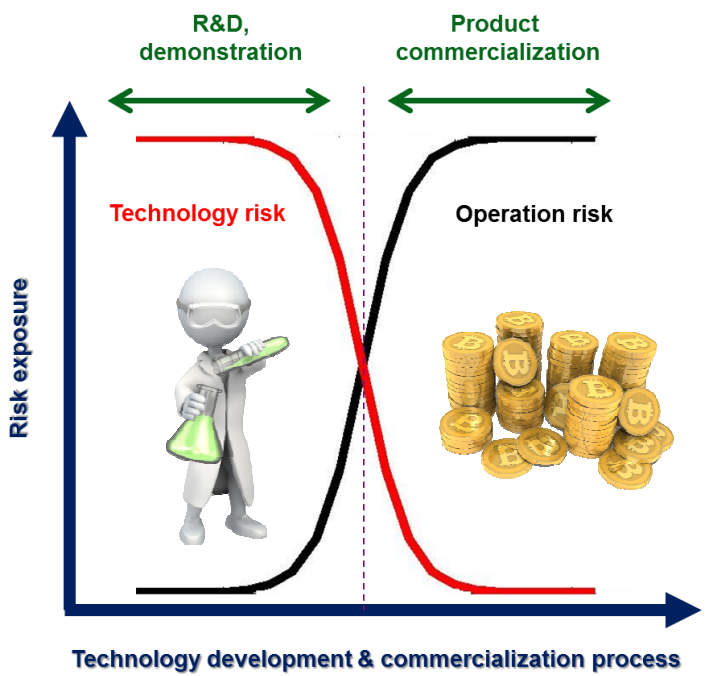
Engineering the Next Generation Rechargeable Batteries: a Multiscale Modeling Perspective I
College on Multiscale Computational Modeling of Materials for Energy
ICTP, Trieste, Italy - July 11, 2016

www.cnrs.fr

BATTERY FUNCTIONAL COMPLEXITY

Example: lithium ion battery





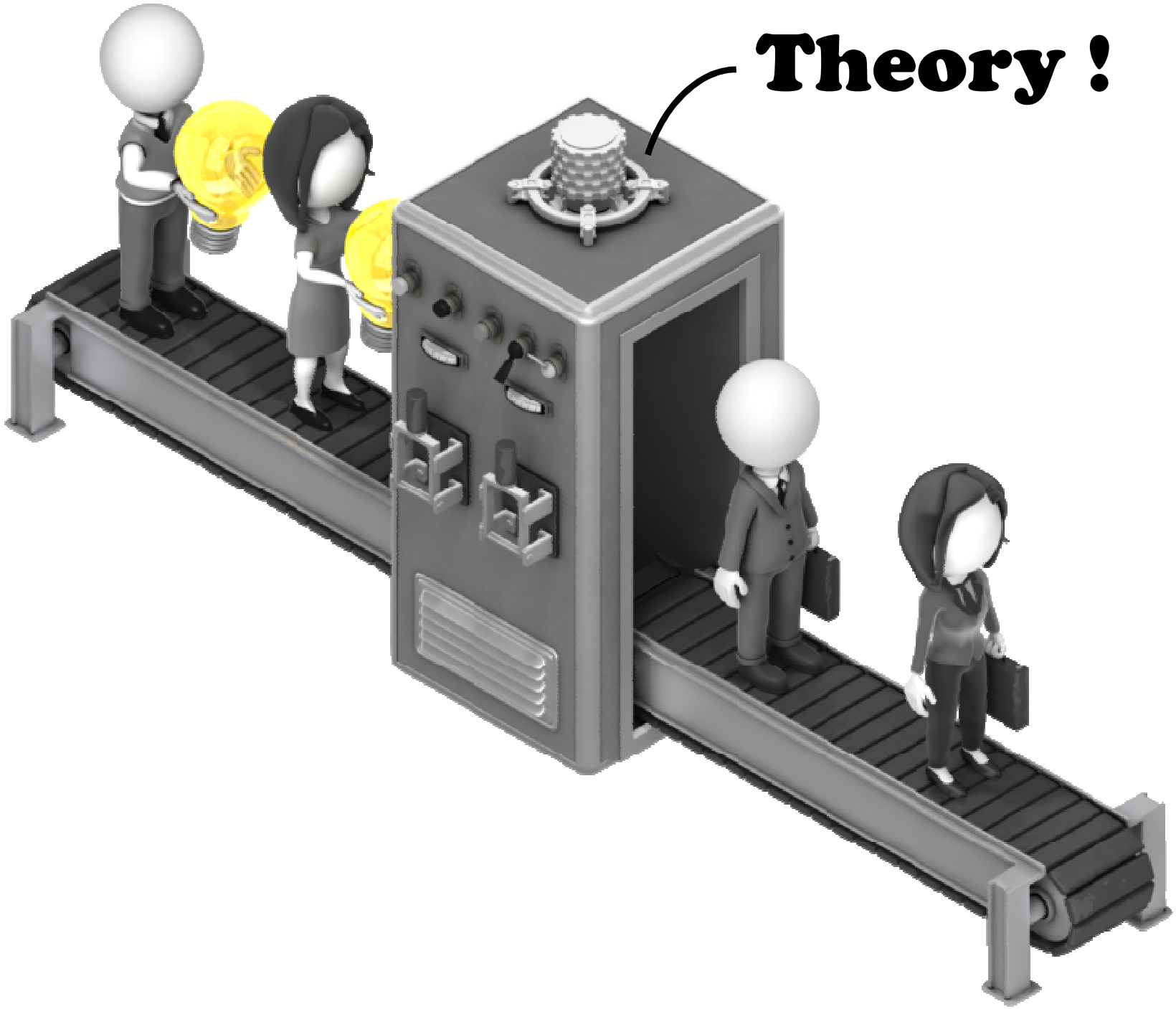
➔ **ELECTROCHEMISTRY, TRANSPORT, THERMO-MECHANICS**

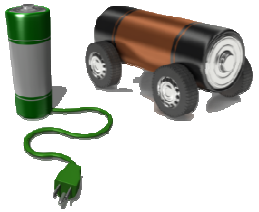
A.A. Franco, *RSC Adv.* **3** (2013) 13027.
A.A. Franco in: Encyclopedia of Applied Electrochemistry, G. Kreysa, K. Ota, R. F. Savinell (Eds.), Springer, New York (2014).

Prof. Alejandro A. Franco

Engineering the Next Generation Rechargeable Batteries: a Multiscale Modeling Perspective I
College on Multiscale Computational Modeling of Materials for Energy
ICTP, Trieste, Italy - July 11, 2016

www.cnrs.fr


Theory !

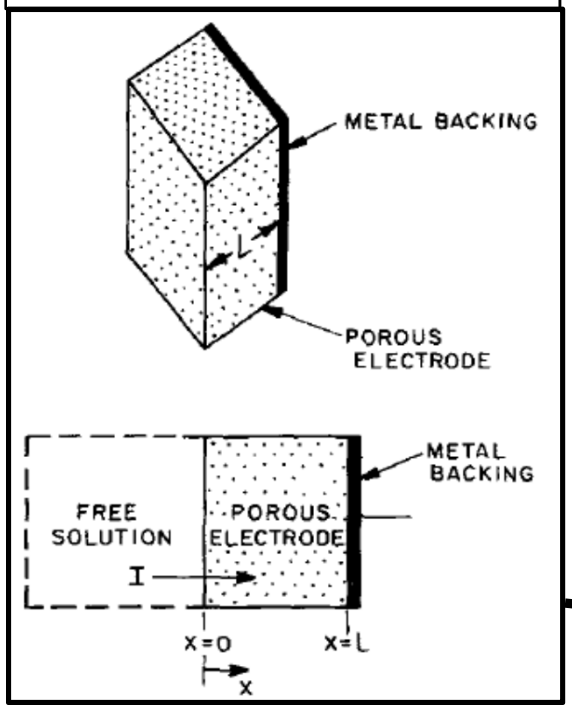


BATTERY MODELING OVER THE LAST 60 YEARS

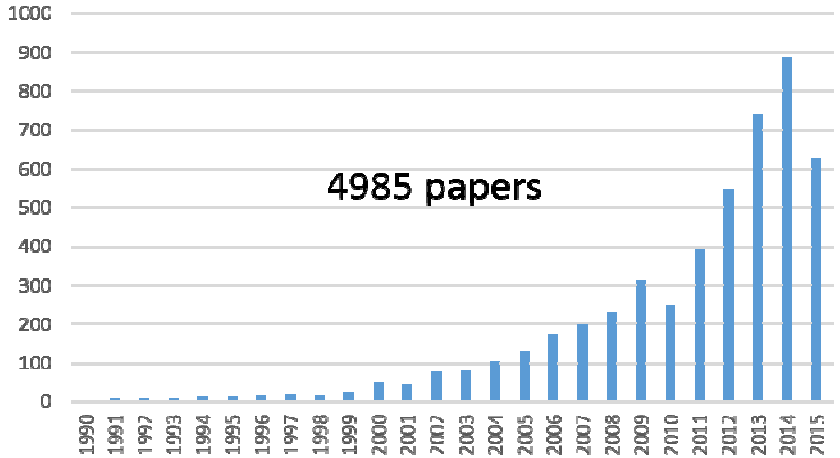
- Growing very significantly since the **early 1990s**.

POROUS ELECTRODE THEORY

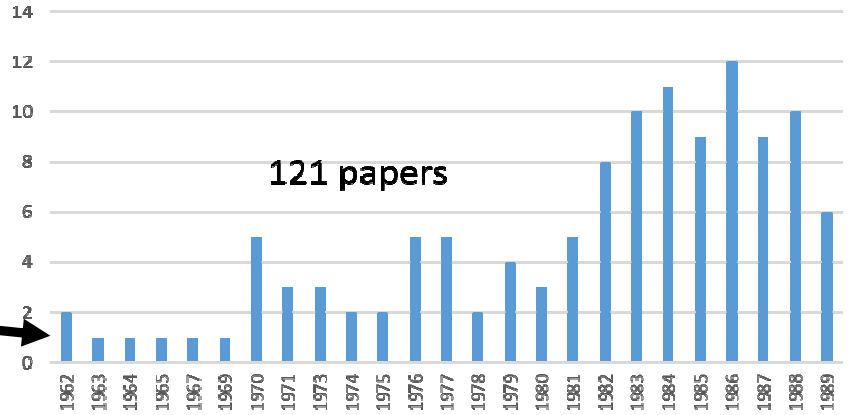
J. S. Newman, C. W. Tobias, *J. Electrochem. Soc.*, **109** (12) (1962) 1183.



1990-2015



1960-1989



LRCS

Prof. Alejandro A. Franco

Engineering the Next Generation Rechargeable Batteries: a Multiscale Modeling Perspective I

College on Multiscale Computational Modeling of Materials for Energy

ICTP, Trieste, Italy - July 11, 2016

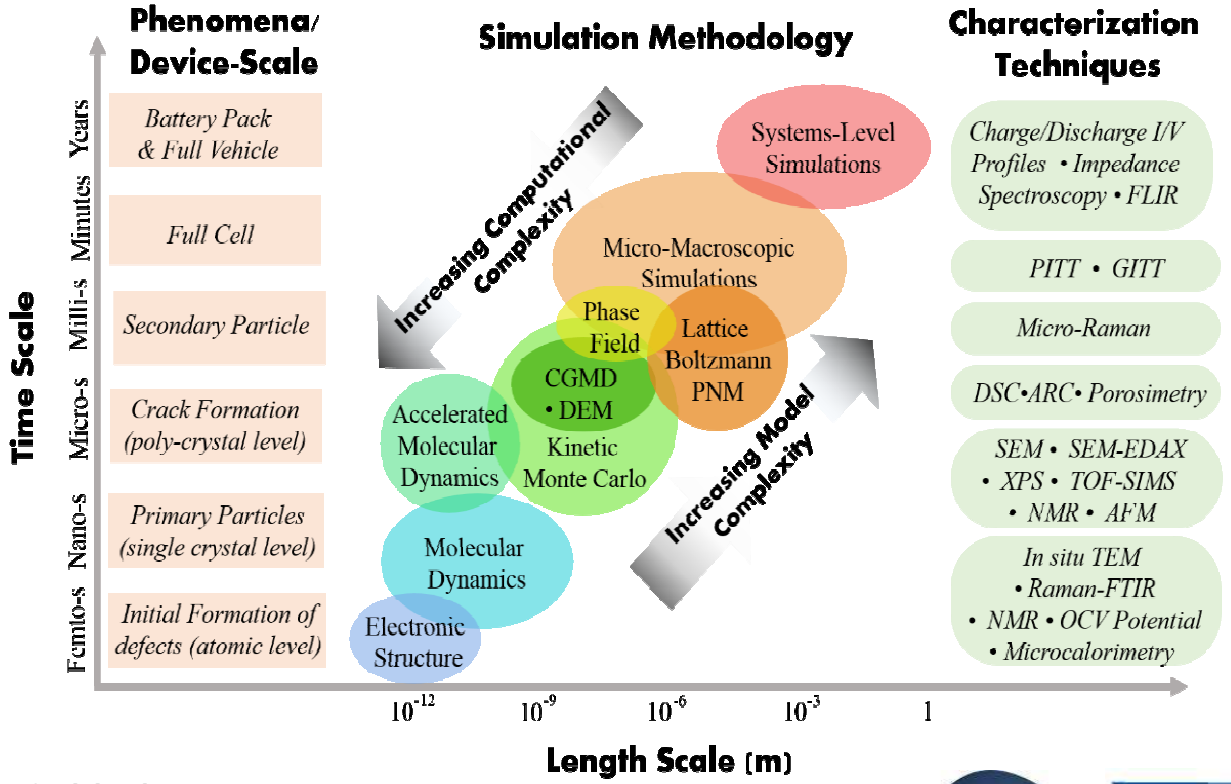
cnrs www.cnrs.fr

UNIVERSITÉ de Picardie Jules Verne

COMPUTATIONAL MODELING: OVERALL PICTURE

Method(s) choice

- ↳ Compromise between computational & model complexity;
- ↳ Easiness to compare model outputs with experimental data.



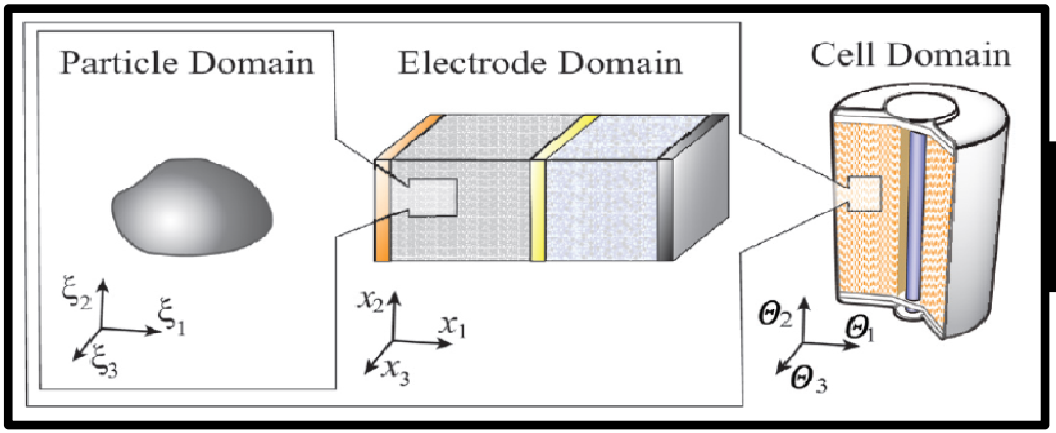
Prof. Alejandro A. Franco

Engineering the Next Generation Rechargeable Batteries: a Multiscale Modeling Perspective I

College on Multiscale Computational Modeling of Materials for Energy
ICTP, Trieste, Italy - July 11, 2016

www.cnrs.fr

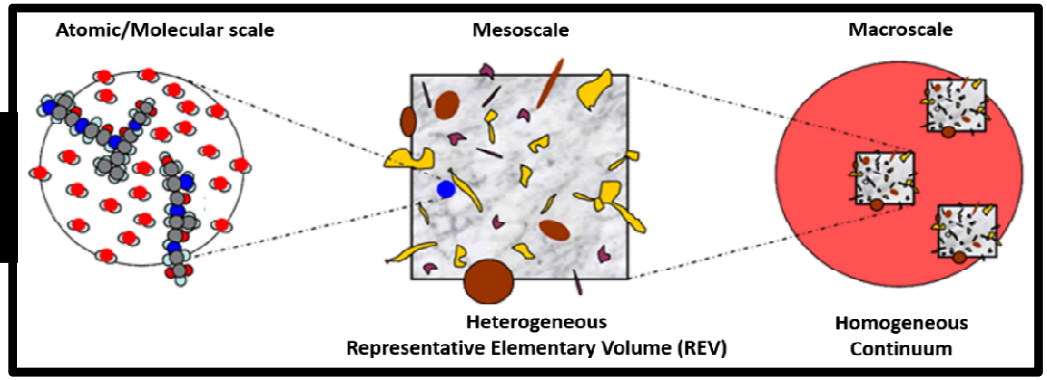
"MULTI-SCALE" MODELS OF BATTERIES



Scales seggregation

K. Kim et al., *J. Electrochem. Soc.*, **158** (8) (2011) A955.

Scales homogenization

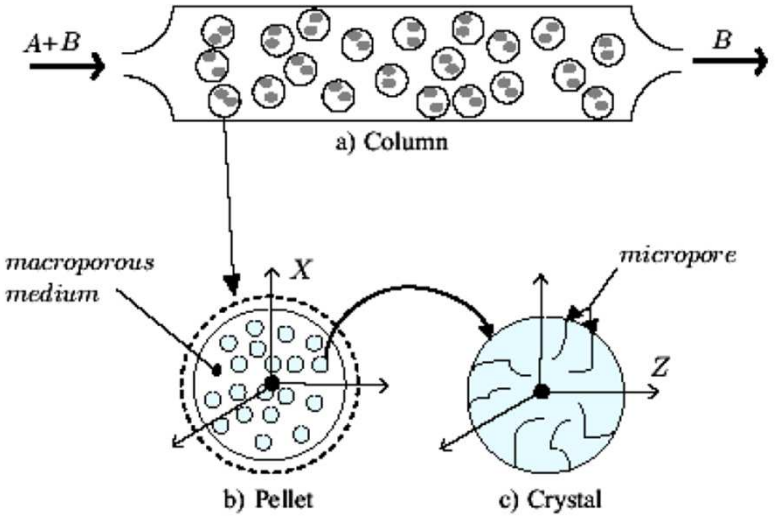


Prof. Alejandro A. Franco

Engineering the Next Generation Rechargeable Batteries: a Multiscale Modeling Perspective I
College on Multiscale Computational Modeling of Materials for Energy
ICTP, Trieste, Italy - July 11, 2016

www.cnrs.fr

AN EXAMPLE OF A MULTISCALE MODEL (FULLY CONTINUUM)



Example: diffusion in multiple scales and volume reactions within the crystal

$$\frac{\partial C_i^{Column}}{\partial t} + \nabla_y . J_i^{Column} = S_i^{Column/Macrop} = \gamma J_i^{Macrop}$$

$$\frac{\partial C_i^{Macropor}}{\partial t} + \nabla_x . J_i^{Macropor} = S_i^{Macrop/Microp} = \gamma' J_i^{Microp}$$

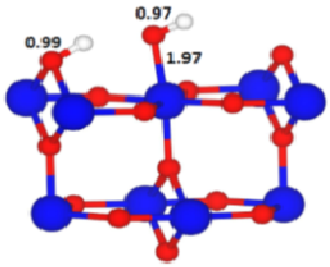
$$\frac{\partial C_i^{Microp}}{\partial t} + \nabla_z . J_i^{Microp} = \sum_i v_i$$

$$v_i = k_i \prod_j C_j^{Microp} - k_{-i} \prod_{j'} C_{j'}^{Microp}$$

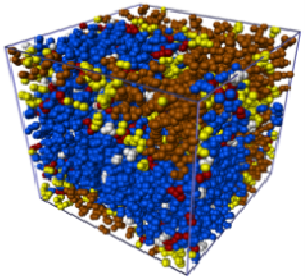
Single paradigm multiscale model

MULTI-PARADIGM MULTI-SCALE MODELS (MMM): WORKFLOWS

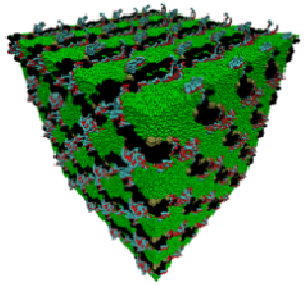
DFT



MD



CGMD



MATERIALS PROPERTIES

Transport = f (structure) → *E.g. via stochastic modeling*
Structure = f (chemistry) → *E.g. via CGMD, MC*

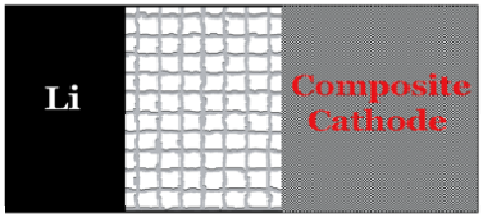
Activity = f (structure) → *Via ab initio, DFT*
Structure = f (chemistry) → *E.g. via MC*

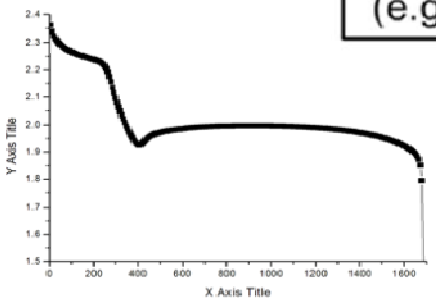
Continuum

Device model

Observables
(e.g. $U_{cell}(I)$)

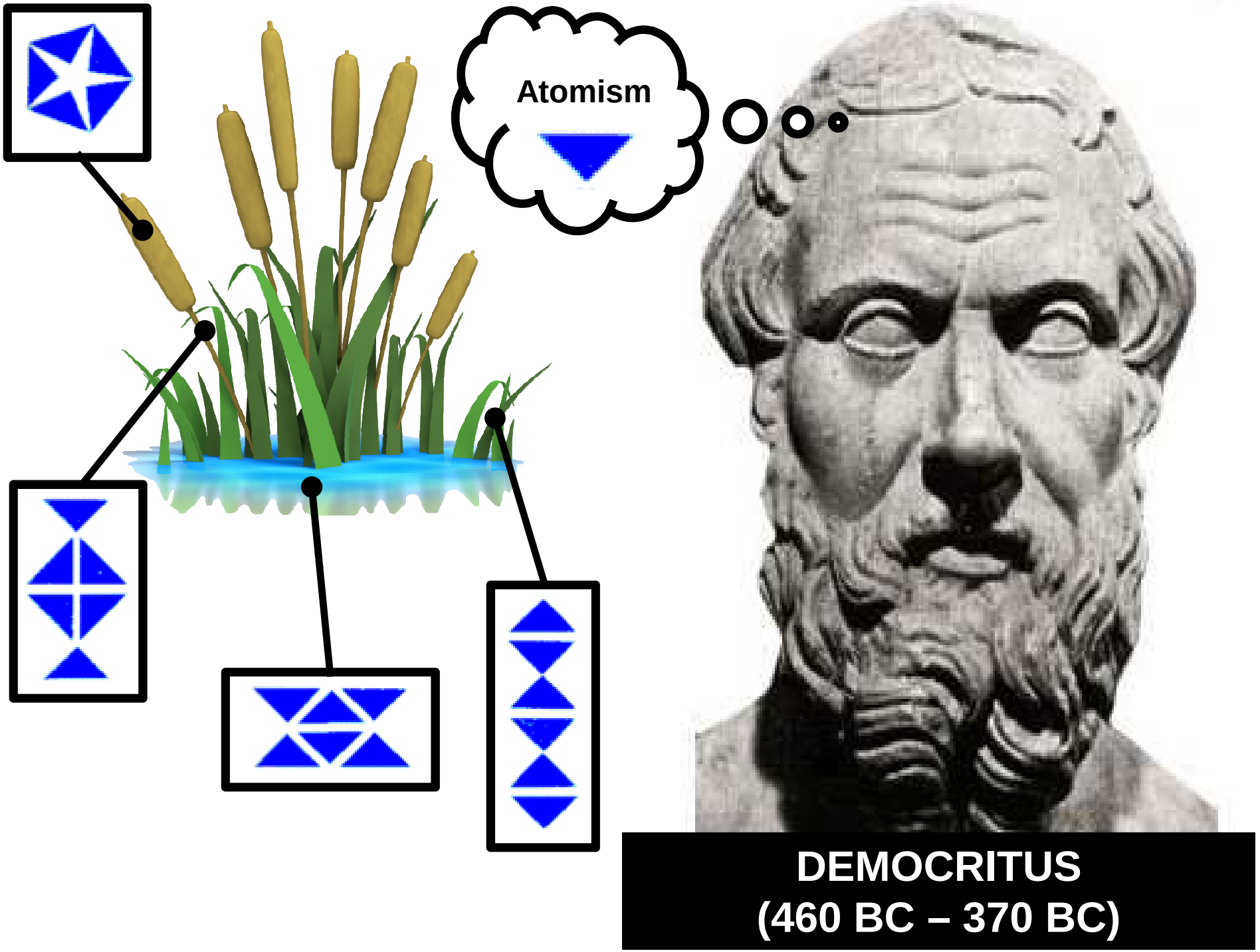
Separator





DATABASES

ON-THE-FLY COUPLING

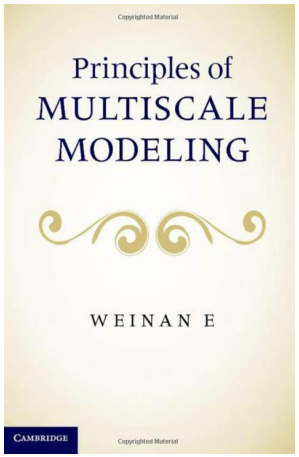

Atomism
DEMOCRITUS
(460 BC – 370 BC)

MULTI-SCALE MODELING IN PRACTICE

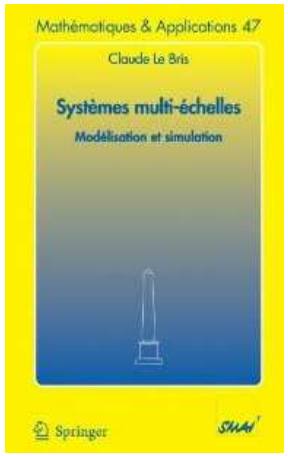
Multi-scale Modeling.

- ↳ It attracted a growing interest since beginning of the 2000s.
- ↳ Applications: weather forecasting, nuclear energy, geology, biology…

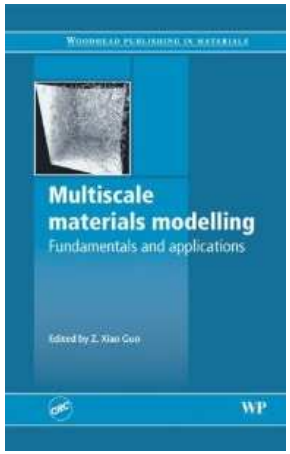
2003



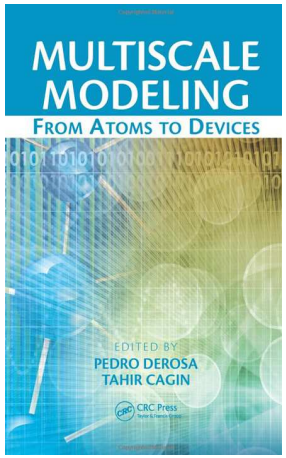
2005



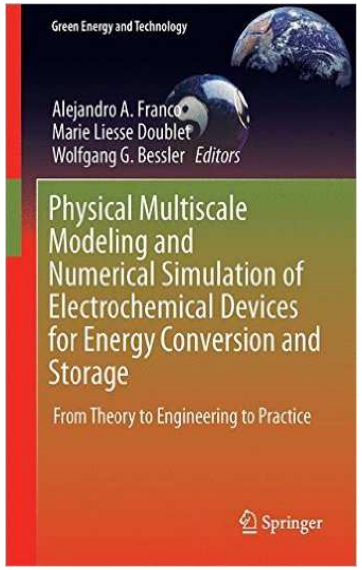
2007



2011



2015



First full book on battery applications!

LRCS

Prof. Alejandro A. Franco

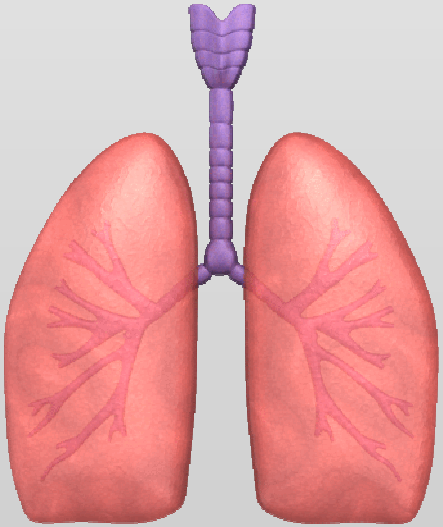
Engineering the Next Generation Rechargeable Batteries: a Multiscale Modeling Perspective I

College on Multiscale Computational Modeling of Materials for Energy

ICTP, Trieste, Italy - July 11, 2016

cnrs
www.cnrs.fr

UNIVERSITÉ de Picardie Jules Verne



MULTISCALE MODELING:
DEFINITIONS & CONCEPTS

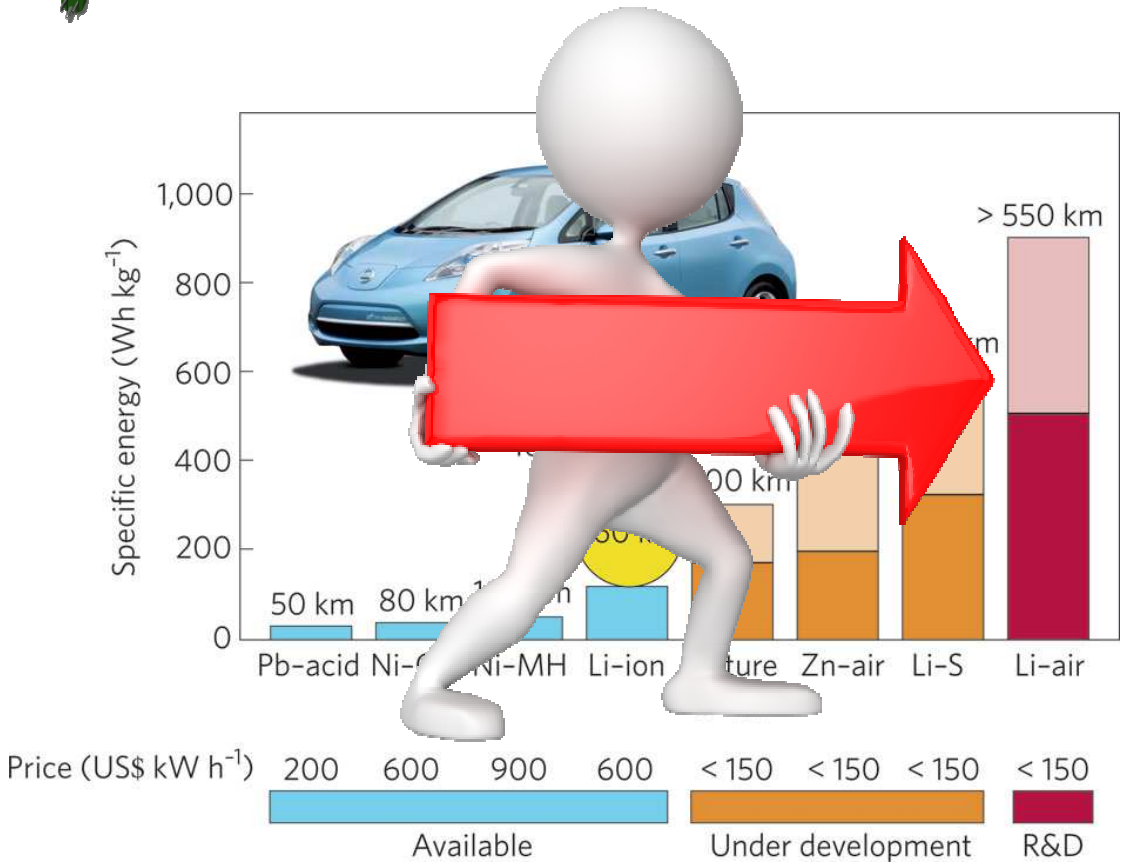
LITHIUM-O_2 BATTERIES:
TECHNICAL CHALLENGES

KINETIC MONTE CARLO
MODELING APPROACH

CONTINUUM
MODELING APPROACH

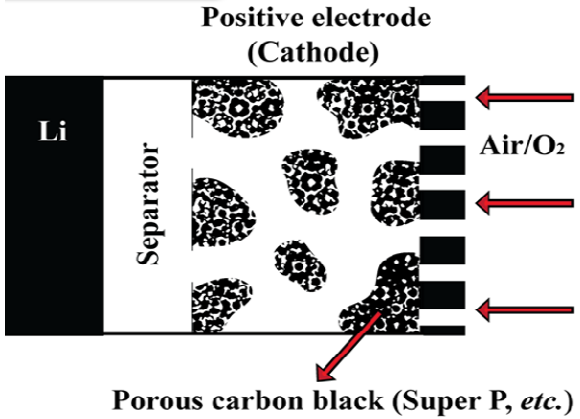
THOUGHTS ON
THEORY VS. EXPERIMENT

LITHIUM AIR BATTERIES (LAB) FOR AUTOMOTIVE APPLICATIONS?

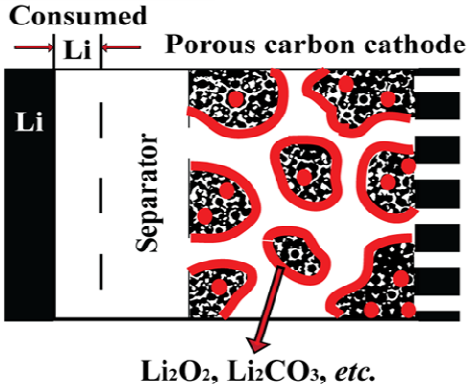


P.G. Bruce, S.A. Freunberger, L.G. Hardwick, J.M. Tarascon, *Nature Materials* **11** (2012) 19 .

CHARGED



DISCHARGED $O_2 + 2Li^+ + 2e^- \rightarrow Li_2O_2$ (solid)



Prof. Alejandro A. Franco
Engineering the Next Generation Rechargeable Batteries: a Multiscale Modeling Perspective I

College on Multiscale Computational Modeling of Materials for Energy
ICTP, Trieste, Italy - July 11, 2016

www.cnrs.fr

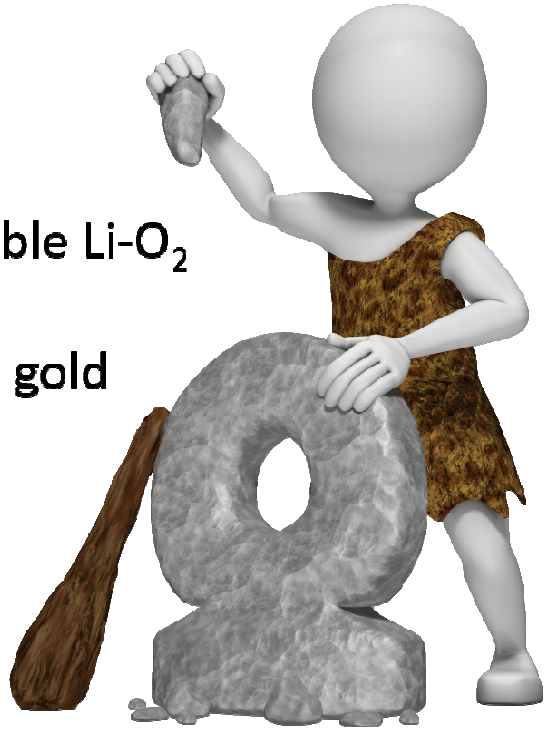
LAB: A BRIEF HISTORY

K.M.Abraham	1996	First introduction of Li-air battery with polymer electrolyte
J. Read	2002	Employ organic electrolytes O_2 solubility and transport
P.G.Bruce	2006	Successful operation of rechargeable Li-O_2 battery
	2012	Good cyclability with porous gold electrode

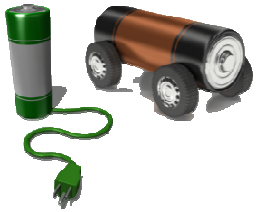
S.H. Yang	O_2 reduction mechanism
A.C. Luntz	Li_2O_2 morphology dependence Li_2O_2 conductivity Stability of electrolyte
…	…..

LAB: A BRIEF PREHISTORY

K.M.Abraham	1996	First introduction of Li-air battery with polymer electrolyte
J. Read	2002	Employ organic electrolytes O_2 solubility and transport
P.G.Bruce	2006	Successful operation of rechargeable Li-O_2 battery
	2012	Good cyclability with porous gold electrode
S.H. Yang		O_2 reduction mechanism
A.C. Luntz		Li_2O_2 morphology dependence Li_2O_2 conductivity Stability of electrolyte
...		.....



CHALLENGES…

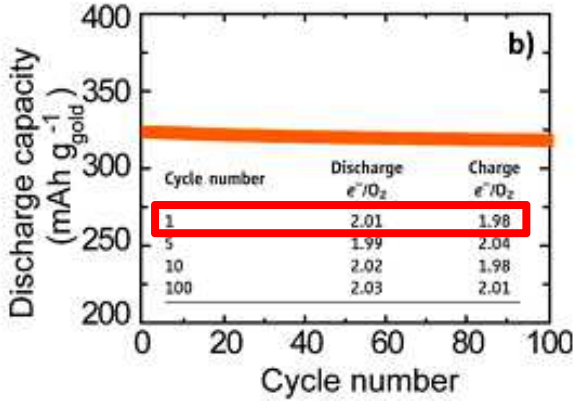


CHALLENGE I: REPRODUCIBILITY BETWEEN GROUPS

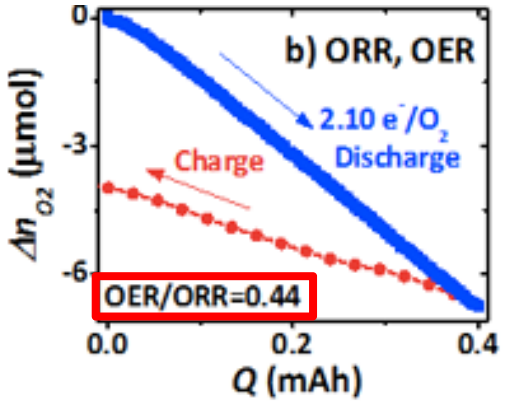
Inspired by Peng et al. and Thotiyl et al.'s results, ~~we have~~ tried to duplicate these experiments as closely as possible, i.e., with a Li metal anode, a thick 15 μm NPG cathode, or a TiC cathode similar to the one by Thotiyl et al., and LiTFSI/DMSO as the electrolyte. Figure 22 presents our results for oxygen reduction and evolution during the first galvanostatic cycle on the NPG and TiC cathodes. Unfortunately, these studies were unable to reproduce the spectacular results obtained by Peng et al. and Thotiyl et al. for reasons that remain unclear. Using

A.C. Luntz, B.D. McCloskey, *Chem. Rev.* **114** (2014) 11721.

➔ **Ratio of the number of electrons to oxygen molecules upon discharge and charge.**



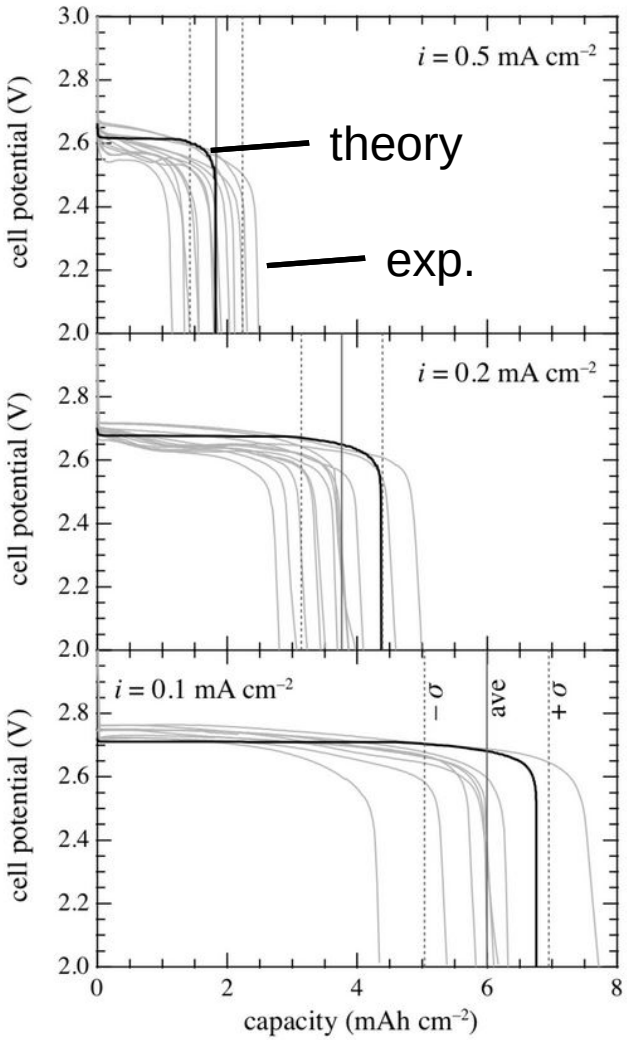
V.S.



Z. Peng *et al. Science* **337** (2012) 563.

A.C. Luntz, B.D. McCloskey, *Chem. Rev.* **114** (2014) 11721.

CHALLENGE II: REPRODUCIBILITY WITHIN ONE GROUP



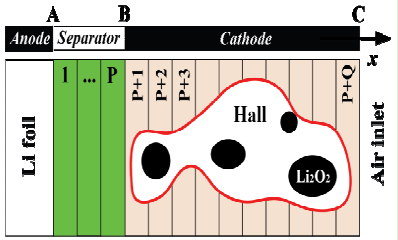
➔ **Even under same operation conditions, the obtained results could have some dispersion !**

J. Liu *et al.* *Abstract 581* , Conference on Electrochemical Energy Conversion & Storage with SOFC-XIV (July 26-31, 2015)

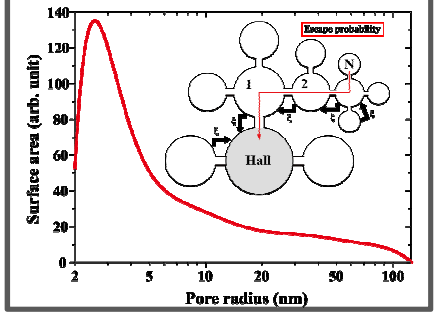
OUR MULTISCALE MODELING APPROACH

A.A. Franco, *RSC Adv.* **3** (2013) 13027.
A.A. Franco, in: Encyclopedia of Applied Electrochemistry, G. Kreysa, K. Ota, R. F. Savinell (Eds.), Springer, New York (2014).
A.A. Franco in: A.A. Franco, M.L. Doublet, W. Bessler, Eds., *Physical Multiscale Modeling and Numerical Simulation of Electrochemical Devices for Energy Conversion and Storage*, Springer London (2016).

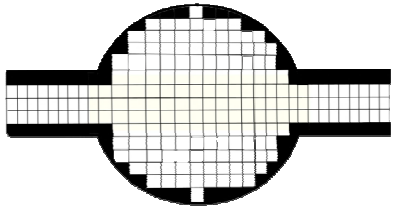
Continuum Model



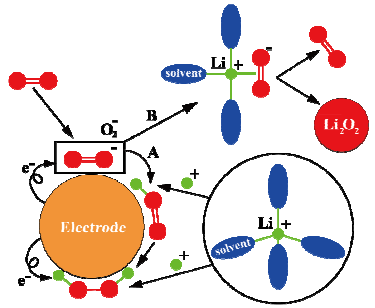
Pore Network Model



Monte Carlo Model



DFT Model



10^{-3} m **10^{-7} m** **10^{-8} m** **10^{-10} m**

Cell **Electrode Microstructure** **Reaction**

Prof. Alejandro A. Franco

Engineering the Next Generation Rechargeable Batteries: a Multiscale Modeling Perspective I
College on Multiscale Computational Modeling of Materials for Energy
ICTP, Trieste, Italy - July 11, 2016

www.cnrs.fr

MULTISCALE MODELING:
DEFINITIONS & CONCEPTS

LITHIUM-O_2 BATTERIES:
TECHNICAL CHALLENGES

KINETIC MONTE CARLO MODELING APPROACH

CONTINUUM
MODELING APPROACH

THOUGHTS ON
THEORY VS. EXPERIMENT

KINETIC MONTE CARLO: MESOSCOPIC VIEWPOINT

➔ **Mesoscopic viewpoint:** between the size of a quantity of atoms and some micrometers.

ATOMISTIC
Quantum properties

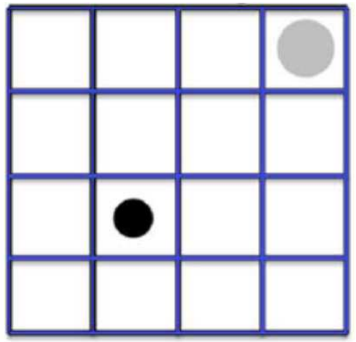
MESOSCOPIC
Properties affected by fluctuations around an average

STATISTICAL MECHANICS

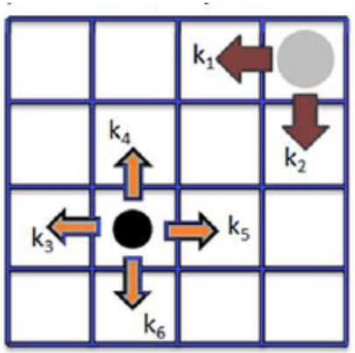
CONTINUUM
Average properties
(laws of classical physics)

KINETIC MONTE CARLO: VARIABLE STEP SIZE METHOD

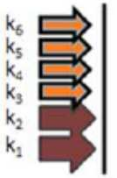
INITIAL CONFIGURATION



IDENTIFICATION OF POSSIBLE EVENTS



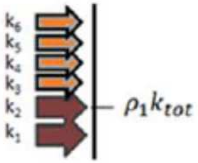
CALCULATION OF THE TOTAL RATE



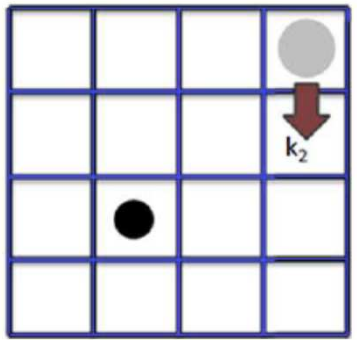
$$k_{tot} = \sum_{i=1}^{M=6} k_i$$

GENERATION OF RANDOM NUMBER TO FIND EVENT N

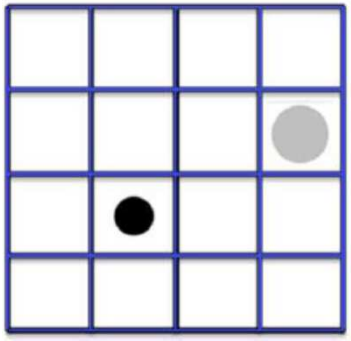
$$\sum_{i=1}^{N} k_i \geq \rho_1 k_{tot} \geq \sum_{i=1}^{N-1} k_i$$



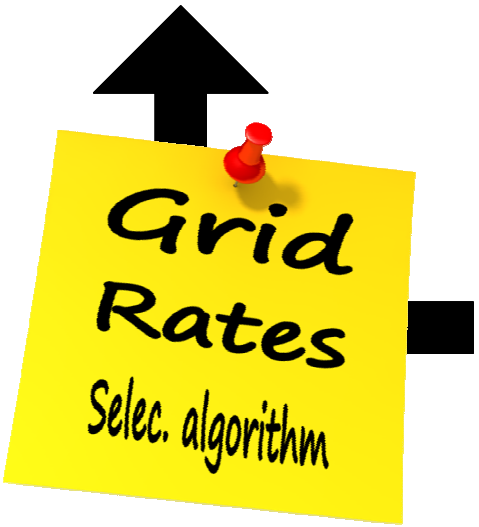
EXECUTION OF EVENT N



GENERATION OF RANDOM NUMBER & CLOCK UPDATE

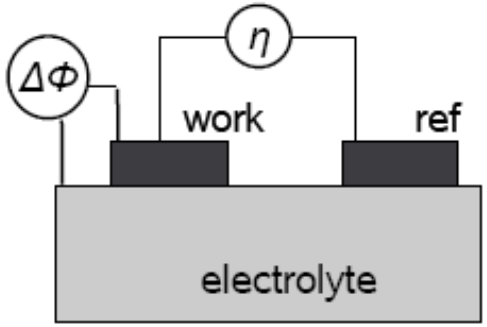


$$t \rightarrow t - \frac{ln(\rho_2)}{k_{tot}}$$



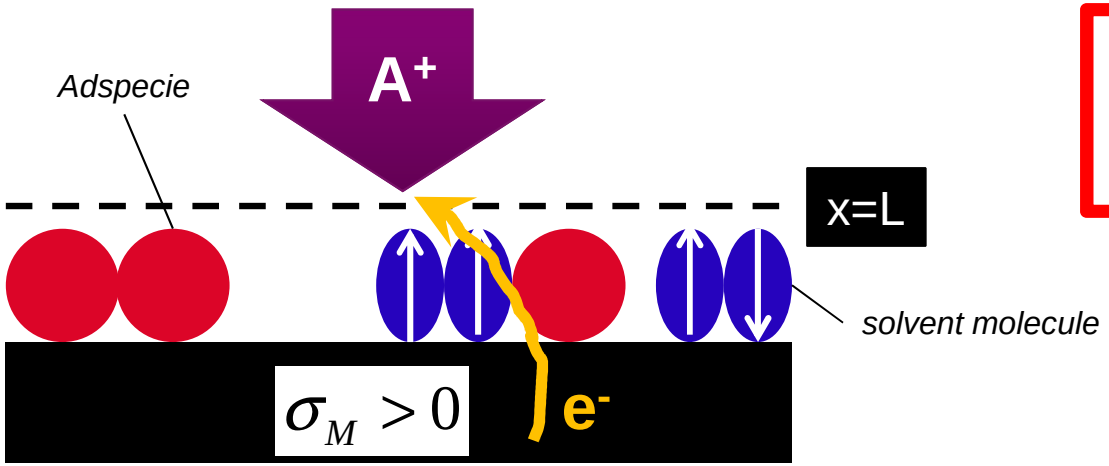
D.T. Gillespie, *Journal of Computational Physics*, **22**(4) (1976) 403.

ELECTROCHEMISTRY CONDITIONS (1/2)



$$k_i \approx \exp\left(\frac{-E_{act} + f(\Delta\Phi)}{RT}\right)$$

$$f(\Delta\Phi) \approx \beta\,\Delta\Phi = \frac{d}{\varepsilon_0}\left(\sigma_{free} - \left|\vec{P}\right|\right)$$



- $\sigma_{free} = \sigma_M + Fn_{\max} \sum_{ad-ions} z_j \theta_j$
- $\left|\vec{P}\right| = \sum_{dipoles} \mu_{i_\perp}\left(\vec{\theta}_i - \overleftarrow{\theta}_i\right)$

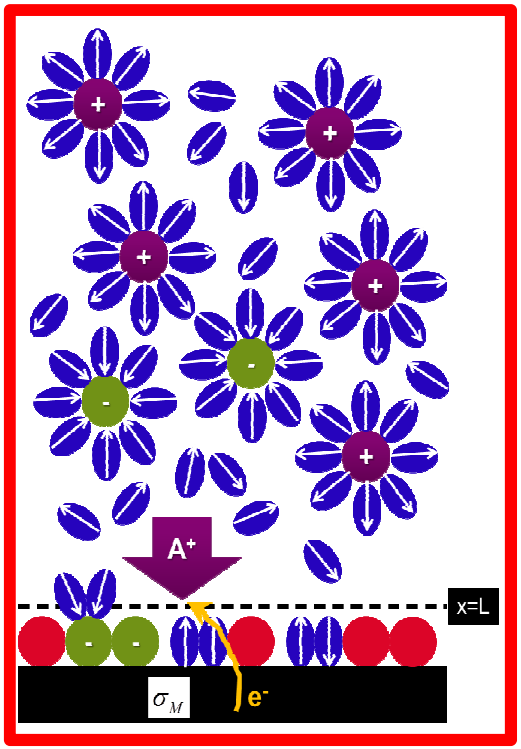
$$\left(J - J_{Far}\right)dt_{kMC} = d\sigma_M$$

M.A. Quiroga, A.A. Franco, *J. Electrochem. Soc.*, **162** (7) (2015) E73.

ELECTROCHEMISTRY CONDITIONS (2/2)

DIFFUSION **QUANTUM INTERACTIONS** **ELECTROMIGRATION** **SOLVENT SCREENING** **FINITE SIZE**

$$\frac{\partial c_i}{\partial t} = B_i \nabla^2 c_i + \frac{B_i}{k_B T} \vec{\nabla} \cdot \left(c_i \vec{\nabla} a_i^j c_i c_j \right) + \frac{B_i}{k_B T} z F \vec{\nabla} \cdot \left(c_i \vec{\nabla} \varphi \right) + F \nabla \left(c_i \vec{p} \cdot \vec{\nabla} \varphi \right) + f_1(\beta_l, c_l) + f_2(\beta_l, c_l)$$

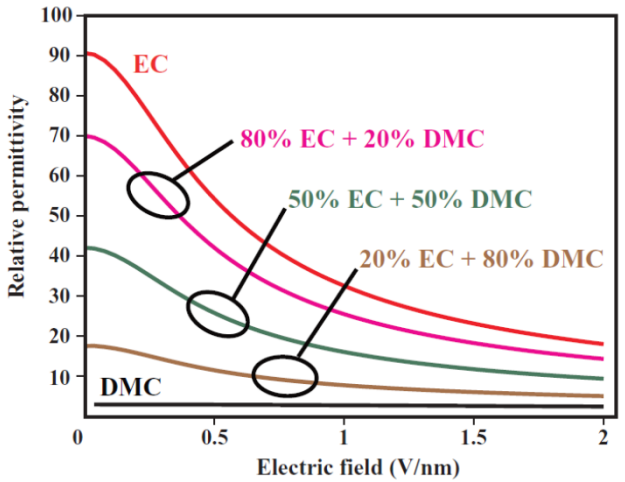


CLASSICAL POISSON'S EQUATION **SOLVENT POLARIZATION EFFECT**

$$\varepsilon_0 \nabla . (-\nabla \varphi) = F \sum_i z_i C_i - F \sum_s \left[\left(\vec{\nabla} . \vec{p}_s \right) c_s + \vec{p}_s . \vec{\nabla} c_s \right]$$

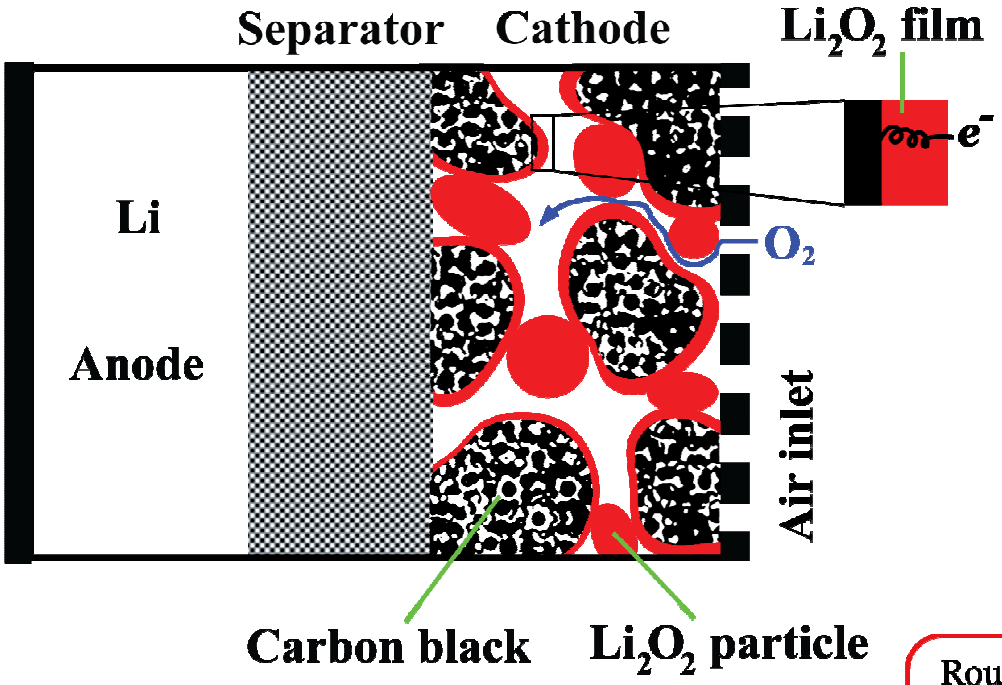
LANGEVIN FUNCTION

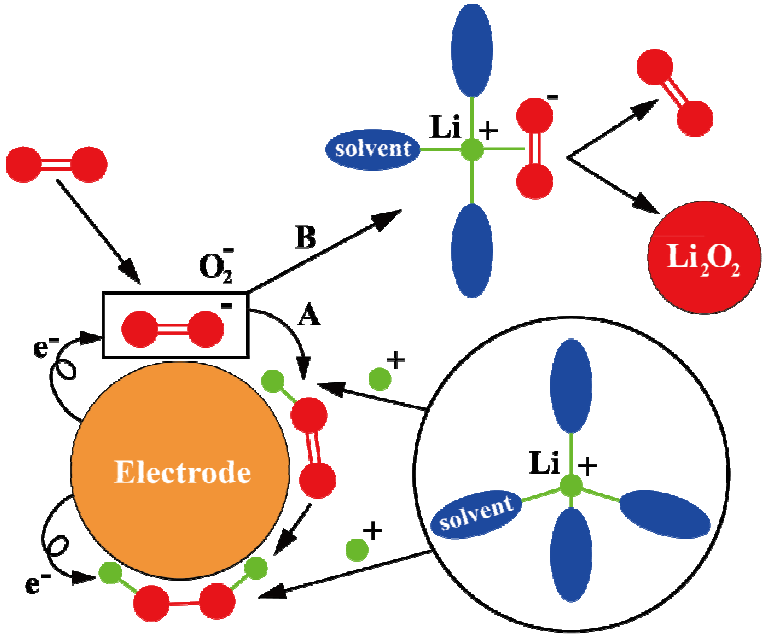
$$\vec{p}_s = p_s^0 \Im \left(\frac{p_s^0 |E|}{k_B T} \right) \frac{E}{|E|}$$



- A.A. Franco et al., *J. Electrochem. Soc.*, **153** (6) (2006) A1053.
- M. A. Quiroga, K.H. Xue, T.K. Nguyen, M. Tulodziecki, H. Huang, A.A. Franco, *J. Electrochem. Soc.*., **161** (8) (2014) E3302.

OXYGEN REDUCTION REACTION (ORR) @ LI-O_2 BATTERIES





$O_2 + 2Li^+ + 2e^- \rightarrow Li_2O_2$ (solid)

Route A: Insulating thin film formation on the active surface

Consequence	Decrease of oxygen diffusion coefficient:	Yes
	Comsumption of active surface area:	Yes

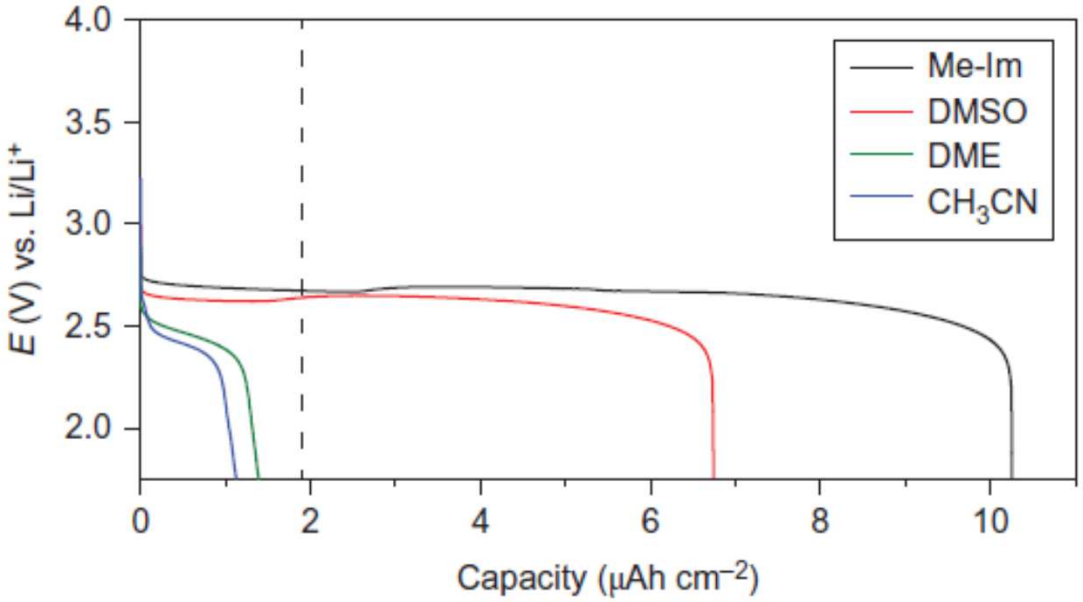
Route B: Solution phase nucleation-growth of Li_2O_2 particles

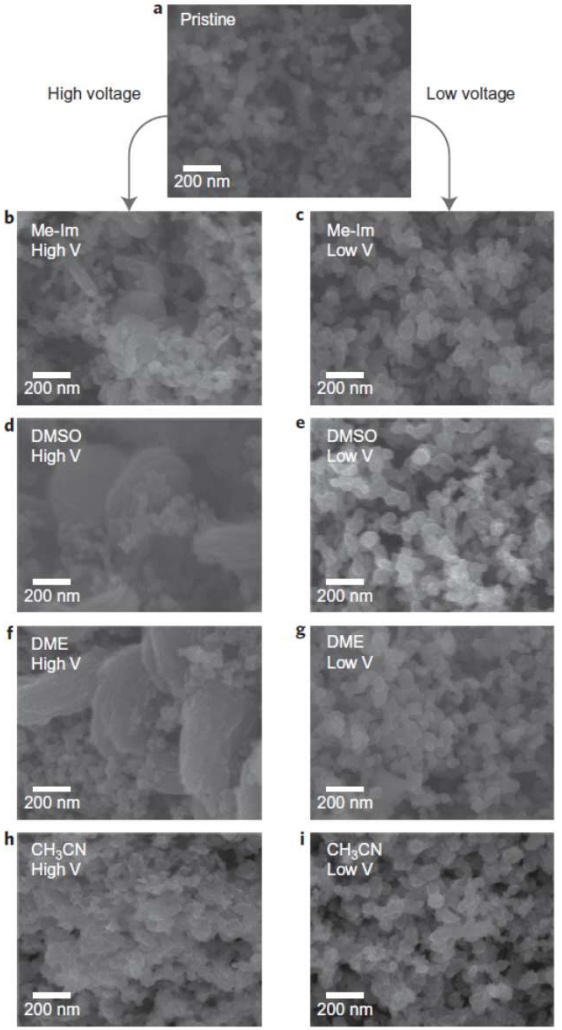
Consequence	Decrease of oxygen diffusion coefficient:	Yes
	Comsumption of active surface area:	No

A.A. Franco, K.H. Xue, *ECS J. Solid State Science and Tech.*, **2** (10) (2013) M3084.
L. Johnson, C. Li, Z. Liu, Y. Chen, S. A. Freunberger, P. C. Ashok, B. B. Praveen, K. Dholakia, J.-M. Tarascon, and P. G. Bruce, *Nature Chemistry* **6** (2014) 1091.

SOLUTION PHASE VS. THIN FILM ORR MECHANISMS

➔ Solvent influences the capacity and the Li_2O_2 deposit morphology.





L. Johnson, C. Li, Z. Liu, Y. Chen, S. A. Freunberger, P. C. Ashok, B. B. Praveen, K. Dholakia, J.-M. Tarascon, and P. G. Bruce, *Nature Chemistry* **6** (2014) 1091.

Prof. Alejandro A. Franco

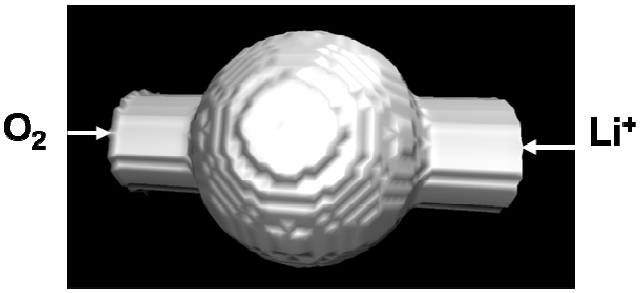
Engineering the Next Generation Rechargeable Batteries: a Multiscale Modeling Perspective I
College on Multiscale Computational Modeling of Materials for Energy
ICTP, Trieste, Italy - July 11, 2016

www.cnrs.fr

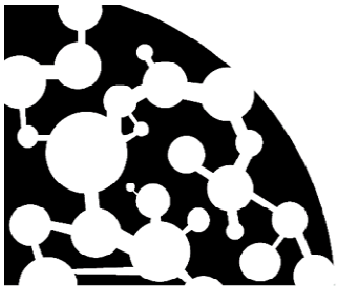
KINETIC MONTE CARLO MODELING OF THE ORR (1/3)

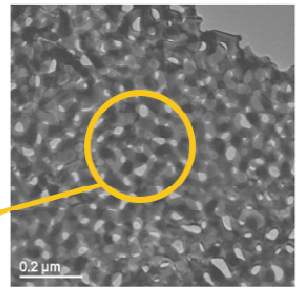
GEOMETRICAL CONSIDERATIONS

Pore size: 10-30 nm



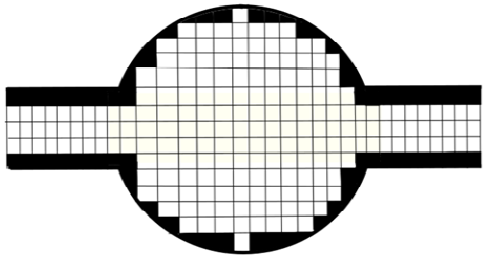
NanoPorous Gold Electrode





Z.Peng *et al*. *Science* **337**, 563–566 (2012)

Grid size: 5 Å



$$Li^+ + O_{2(sol)} + e^- \xrightarrow{k_1} LiO_2^* \quad (1)$$

$$LiO_2^* \underset{k_{-2}}{\overset{k_2}{\longleftrightarrow}} LiO_{2(sol)} \quad (2)$$

$$LiO_2^* + Li^+ + e^- \xrightarrow{k_3} Li_2O_2^* \quad (3)$$

$$LiO_{2(sol)} \xrightarrow{k_4} \frac{1}{2}Li_2O_2 + \frac{1}{2}O_2 \quad (4)$$

REACTIONS

G. Blanquer, Y. Yin, M.A. Quiroga, A.A. Franco, *J. Electrochem. Soc*, **163** (3) (2016) A329.

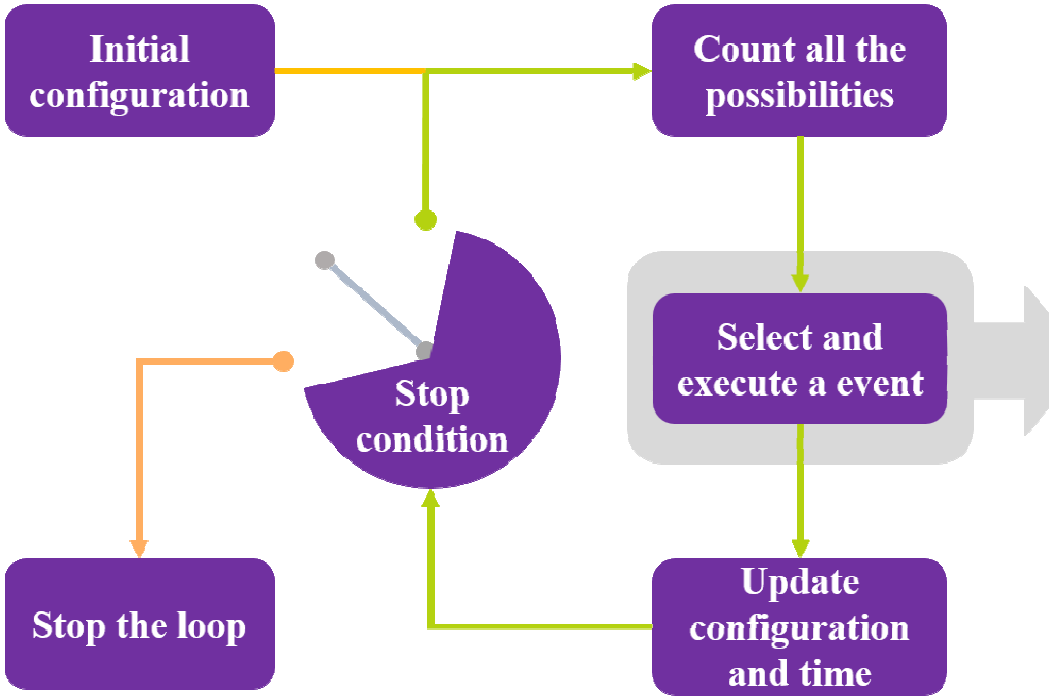
Prof. Alejandro A. Franco

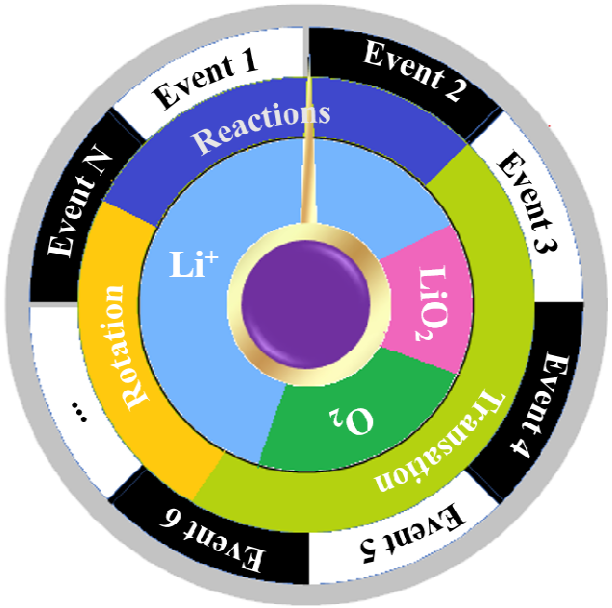
Engineering the Next Generation Rechargeable Batteries: a Multiscale Modeling Perspective I
College on Multiscale Computational Modeling of Materials for Energy
ICTP, Trieste, Italy - July 11, 2016

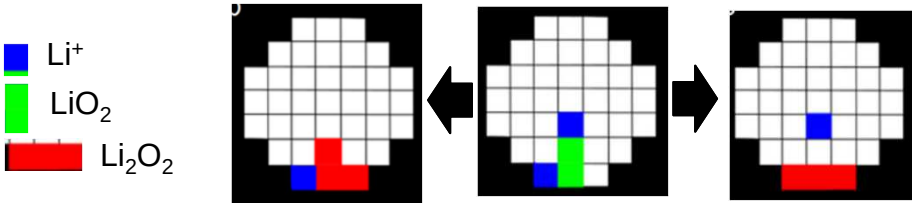
www.cnrs.fr

KINETIC MONTE CARLO MODELING OF THE ORR (2/3)

Electrochemical **Variable Step Size Method (VSSM):** description, within the on lattice approach, of diffusion, reactions between species and adsorption/desorption.



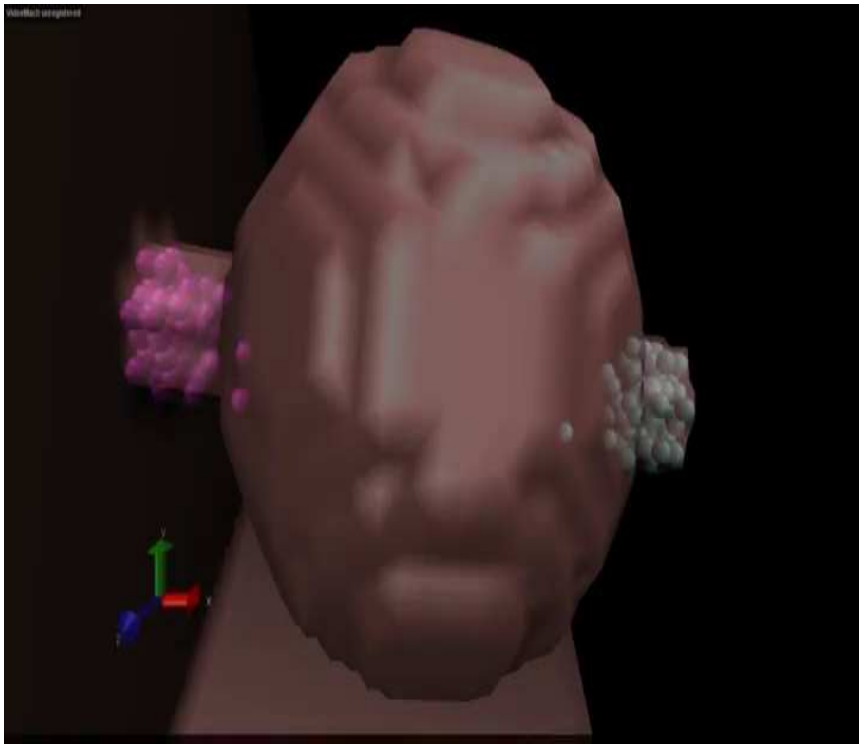




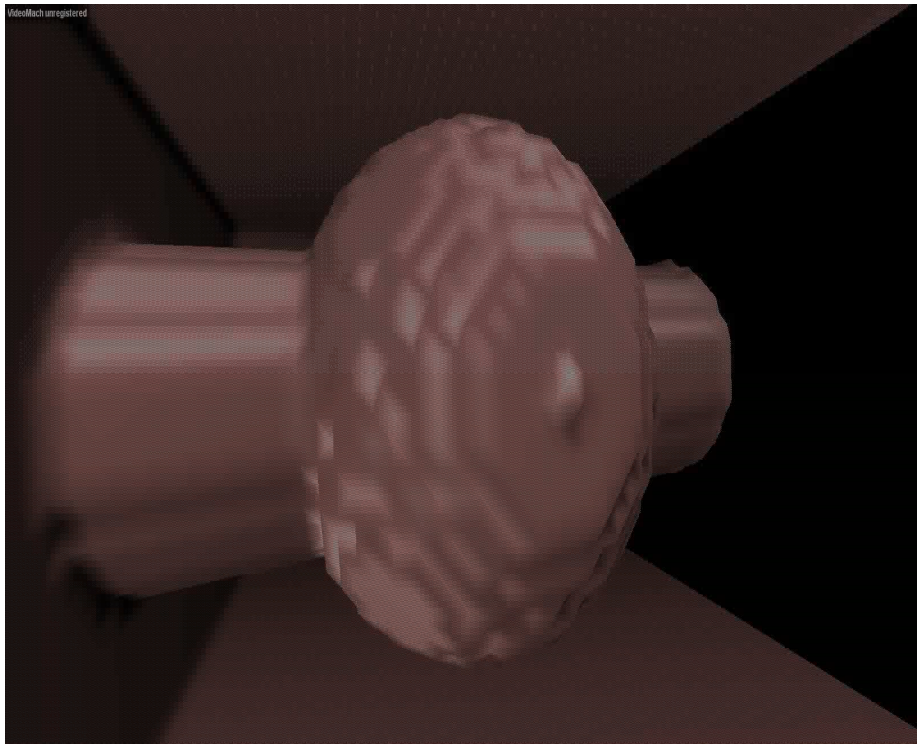
G. Blanquer, Y. Yin, M.A. Quiroga, A.A. Franco, *J. Electrochem. Soc*, **163** (3) (2016) A329.
M.A. Quiroga, A.A. Franco, *J. Electrochem. Soc.*, **162** (7) (2015) E73.

KINETIC MONTE CARLO MODELING OF THE ORR (3/3)

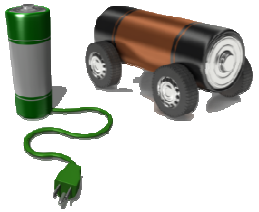
Li^+ and O_2 transport



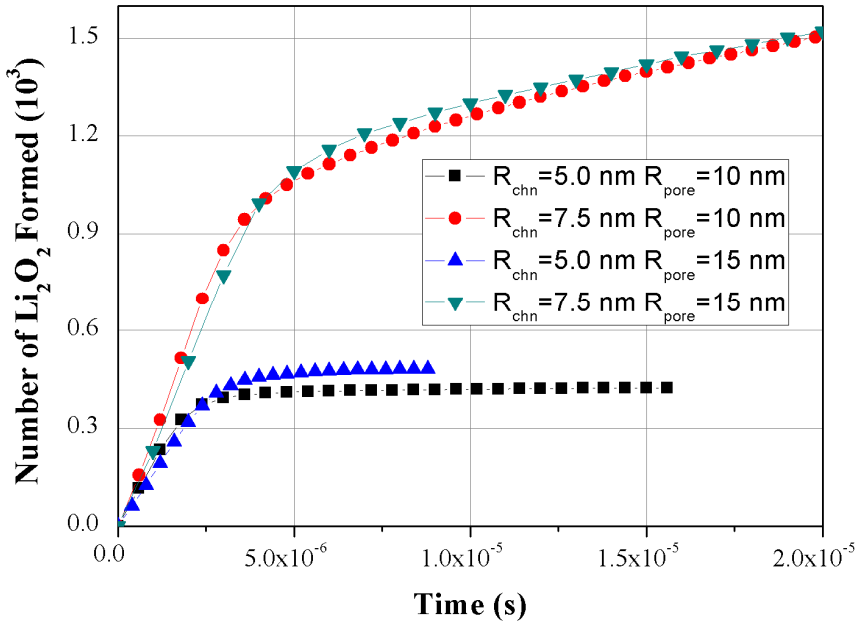
Li_2O_2 formation

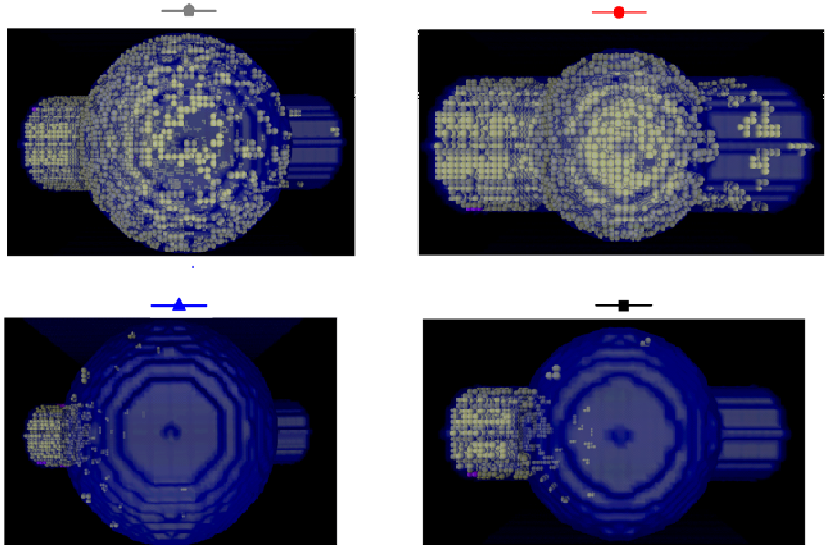


G. Blanquer, Y. Yin, M. Quiroga, A.A. Franco, *J. Electrochem. Soc*, **163** (3) (2016) A329.



CALCULATED IMPACT OF THE PORE GEOMETRY





Discharge process is limited by channel clogging

Increase the capacity by enlarging the channel size

G. Blanquer, Y. Yin, M.A. Quiroga, A.A. Franco, *J. Electrochem. Soc*, **163** (3) (2016) A329.

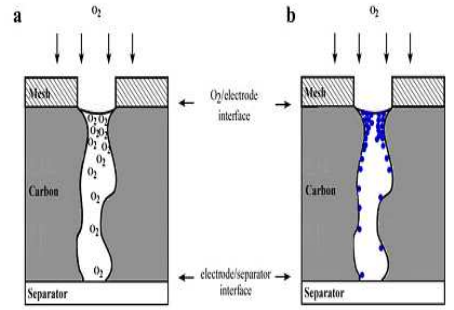
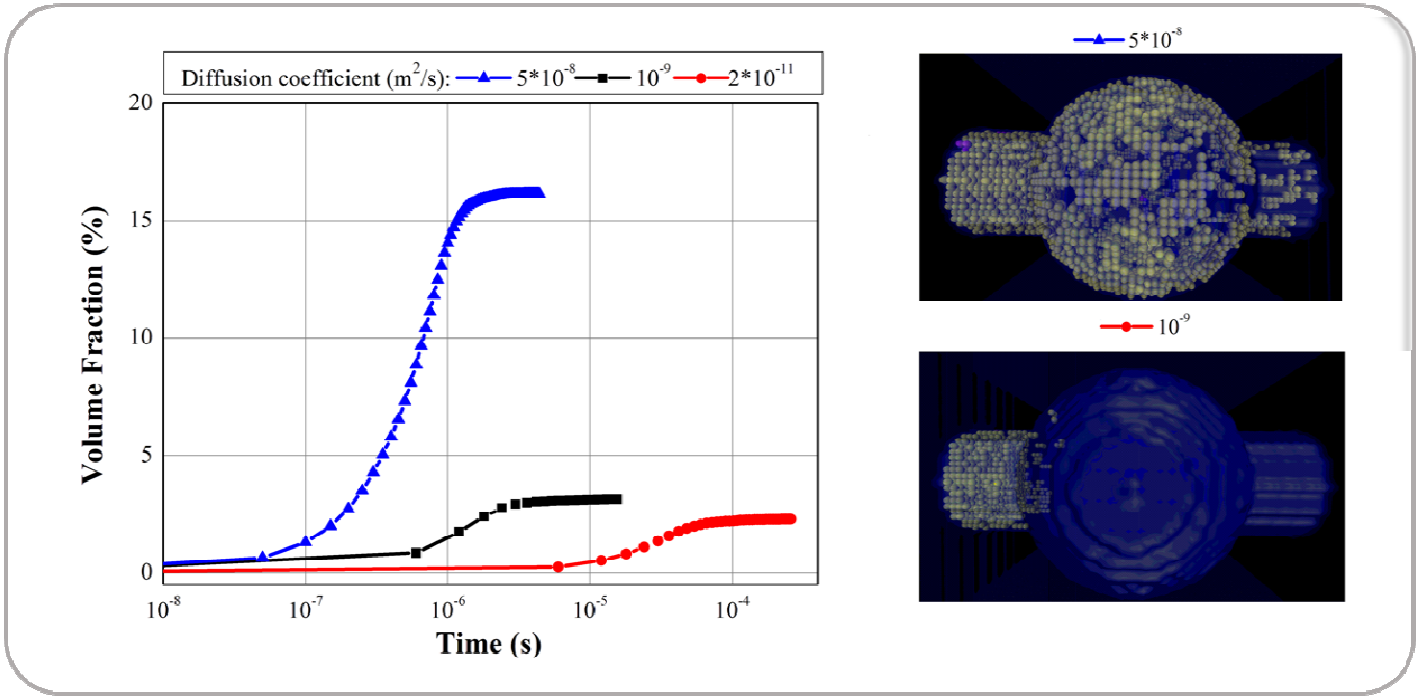


Figure 2. Schematic representation of the oxygen electrode a) before discharge and b) after discharge.

I. Landa-Medrano *et al.*, *J. Electrochem. Soc.*, **162** (2015) A3126.

CALCUMATED IMPACT OF THE O_2 DIFUSSION COEFFICIENT



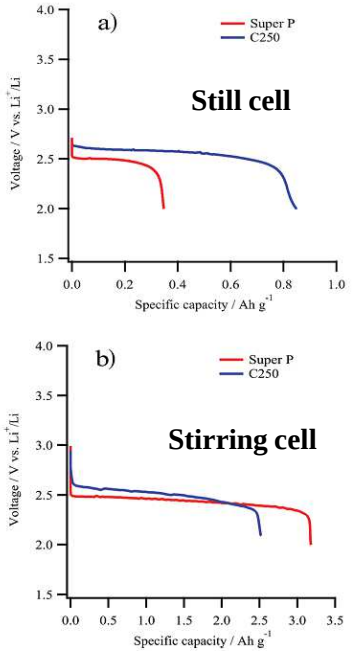


Figure 1. Discharge profiles of Super P and C250 electrodes at 60 °C under a current density of 0.1 mA cm^{-2} in a (a) still- and (b) stirred-electrolyte cell.

M. Aklalouch *et al.*, *ChemSusChem.* (2015).

Higher diffusion coefficient
Higher capacity

→ **Decrease viscosity of electrolyte**

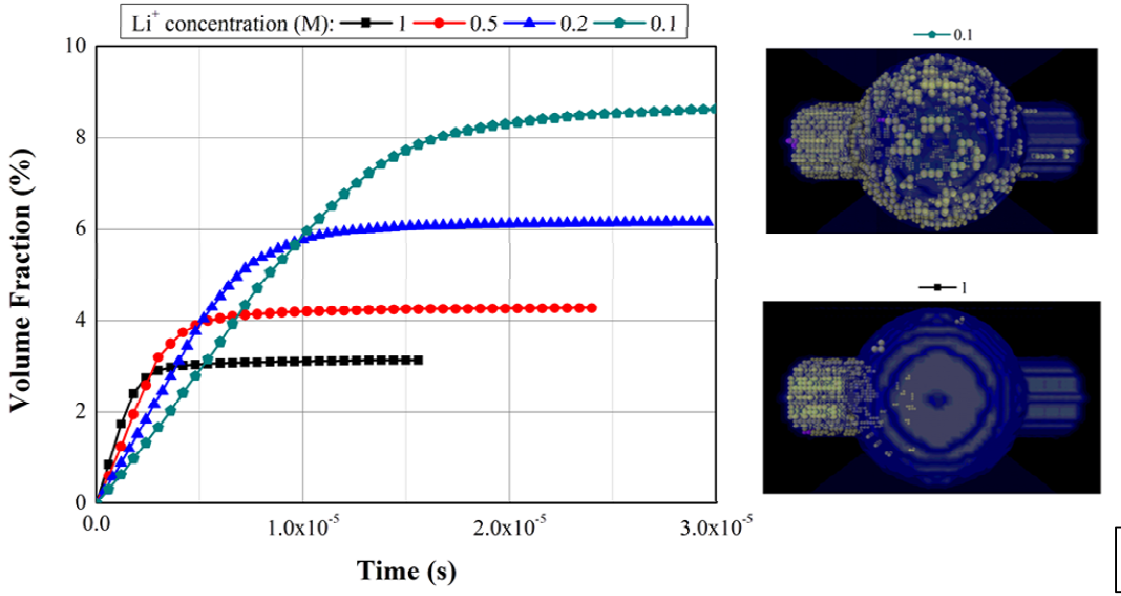
G. Blanquer, Y. Yin, M.A. Quiroga, A.A. Franco, *J. Electrochem. Soc*, **163** (3) (2016) A329.

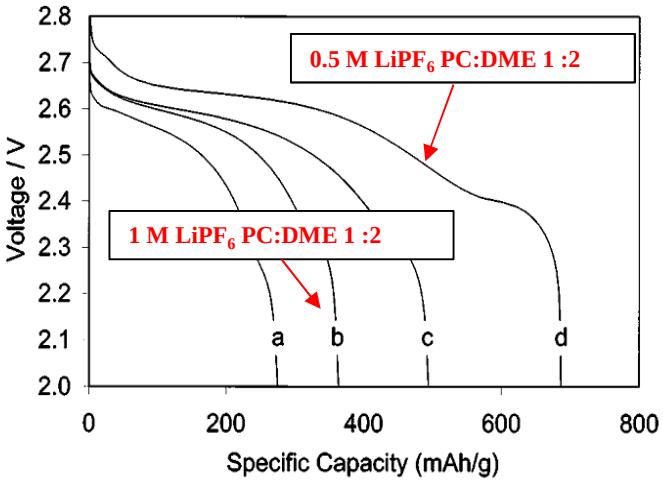
Prof. Alejandro A. Franco

Engineering the Next Generation Rechargeable Batteries: a Multiscale Modeling Perspective I
College on Multiscale Computational Modeling of Materials for Energy
ICTP, Trieste, Italy - July 11, 2016

www.cnrs.fr

CALCULATED IMPACT OF SALT CONCENTRATION





J. Read *et al.*, *J. Electrochem. Soc.*, **150** (2003) A1351.

Higher Li^+ concentration accelerates pore clogging due to more hindrance for O_2 transport

Lower ionic strength of electrolyte enhances capacity

G. Blanquer, Y. Yin, M.A. Quiroga, A.A. Franco, *J. Electrochem. Soc*, **163** (3) (2016) A329.

Prof. Alejandro A. Franco

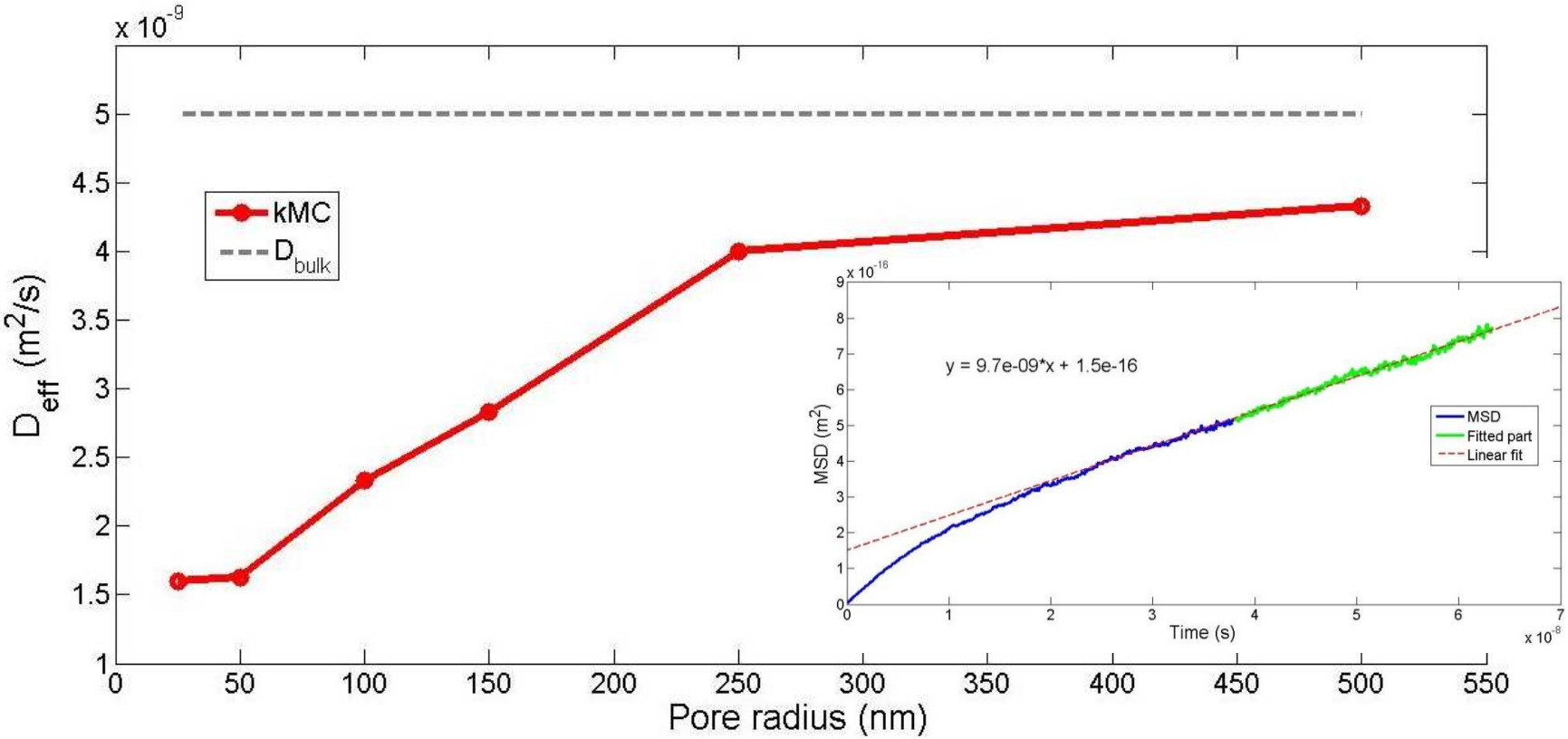
Engineering the Next Generation Rechargeable Batteries: a Multiscale Modeling Perspective I
College on Multiscale Computational Modeling of Materials for Energy
ICTP, Trieste, Italy - July 11, 2016

www.cnrs.fr

MEAN SQUARE DISPLACEMENT METHOD: EFFECTIVE DIFFUSION COEFFICIENTS

$$< \Delta r_t > = \frac{1}{N} \sum_{i=1}^{N} < [\overrightarrow{R_{i,t}} - \overrightarrow{R_{i,t_0}}]^2 >$$

$$D = \left[\frac{1}{6t} < \Delta r_t > \right]_{t \gg t_c}$$



Prof. Alejandro A. Franco

Engineering the Next Generation Rechargeable Batteries: a Multiscale Modeling Perspective I

College on Multiscale Computational Modeling of Materials for Energy
ICTP, Trieste, Italy - July 11, 2016

www.cnrs.fr


Monte Carlo Electrochemistry
Simulation Software for Innovation
MESSI
Tomorrow:
Hands-On Session!

MULTISCALE MODELING:
DEFINITIONS & CONCEPTS

LITHIUM-O_2 BATTERIES:
TECHNICAL CHALLENGES

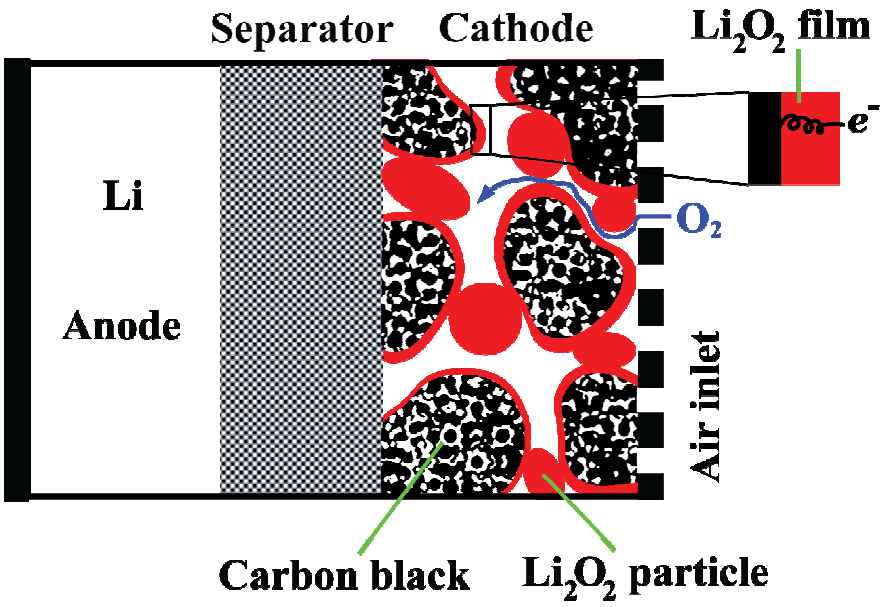
KINETIC MONTE CARLO
MODELING APPROACH

**CONTINUUM
MODELING APPROACH**

THOUGHTS ON
THEORY VS. EXPERIMENT

POROUS ELECTRODES IN LITHIUM O_2 BATTERIES

Lithium O_2 Battery at discharge

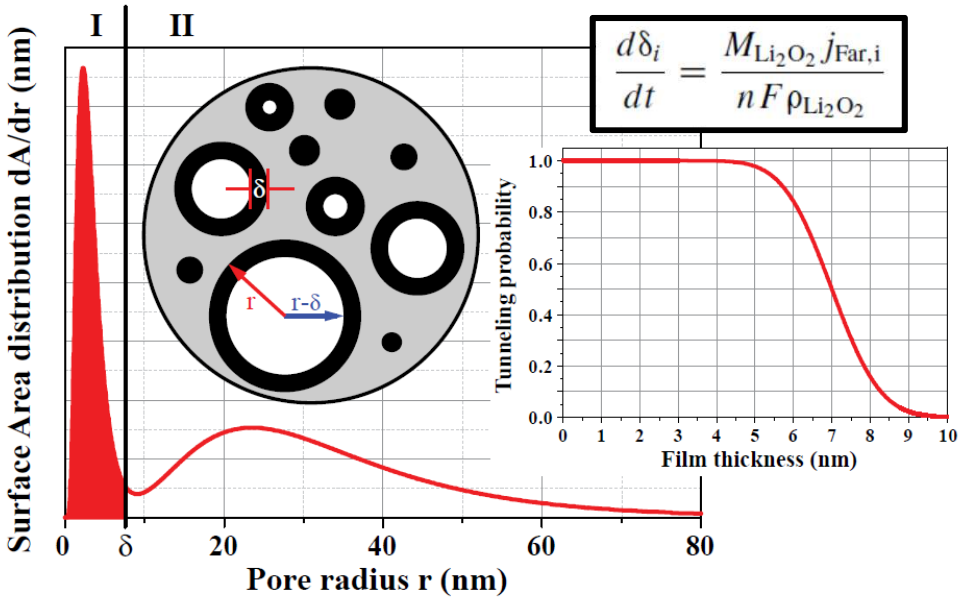


$O_2 + 2Li^+ + 2e^- \rightarrow Li_2O_2$ (solid)

Thin film mechanism

$$a_i = \left[\frac{1 - erf(\delta - 7)}{2}\right] a_i^0$$

$$\frac{d\delta_i}{dt} = \frac{M_{Li_2O_2}\, j_{Far,i}}{n F \rho_{Li_2O_2}}$$



➔ Porosity vs. Electronic tunneling probability vs. Reactive surface area.

A.A. Franco, K.H. Xue, *ECS J. Solid State Science and Tech.*, **2** (10) (2013) M3084.
K.H. Xue, T.K. Nguyen, A.A. Franco, *J. Electrochem. Soc.*, **161** (8) (2014) E3028.

Prof. Alejandro A. Franco

Engineering the Next Generation Rechargeable Batteries: a Multiscale Modeling Perspective I
College on Multiscale Computational Modeling of Materials for Energy
ICTP, Trieste, Italy - July 11, 2016

www.cnrs.fr

MICROSTRUCTURALLY-RESOLVED MODEL

O_2 diffusion

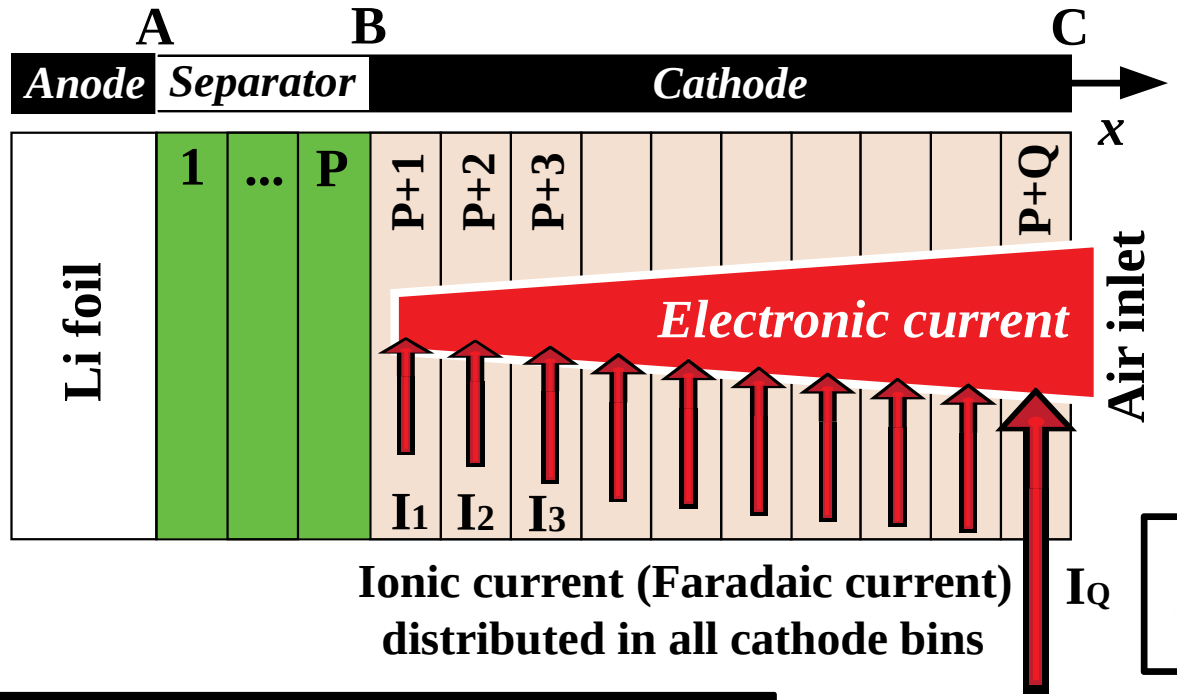
$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D\left(\frac{\partial c}{\partial x}\right)\right] - \frac{a j_{Far}}{nF}$$

$$D = \left(\frac{\epsilon}{\tau}\right) D_0 = \epsilon^{1.5} D_0$$

$$\epsilon = (1 - s)\,\epsilon_0$$

$$s = \frac{M_{Li_2O_2}}{\epsilon_0 n F \rho_{Li_2O_2}} \int a j_{Far} dt$$

$$j_{Far} = nFkc^{1-\beta} \exp\left(-\frac{\beta n F \eta}{RT}\right)$$



Finite difference method

Prof. Alejandro A. Franco

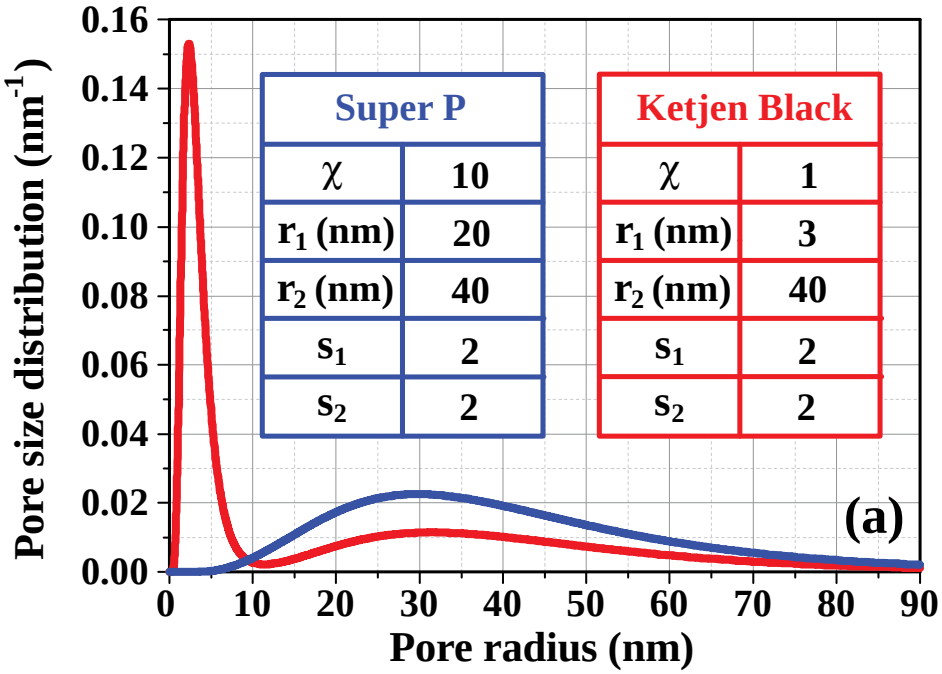
Engineering the Next Generation Rechargeable Batteries: a Multiscale Modeling Perspective I

College on Multiscale Computational Modeling of Materials for Energy
ICTP, Trieste, Italy - July 11, 2016

www.cnrs.fr

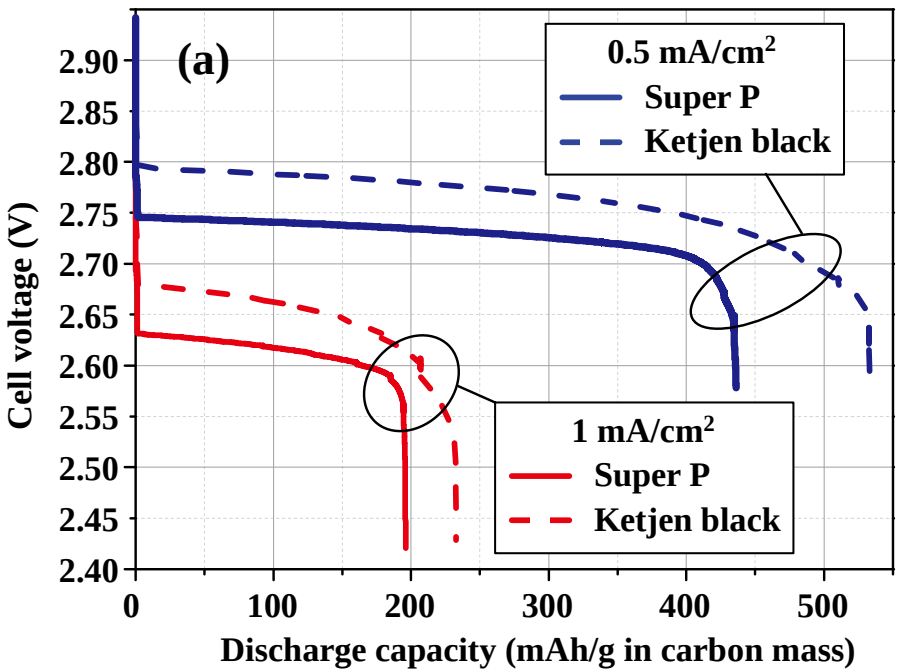
IMPACT OF THE PSD ON THE DISCHARGE CURVE

➔ For intermediate and high current densities, KB provides lower overpotential and higher capacity than SP.



Super P	
χ	10
r_1 (nm)	20
r_2 (nm)	40
s_1	2
s_2	2

Ketjen Black	
χ	1
r_1 (nm)	3
r_2 (nm)	40
s_1	2
s_2	2



- A.A. Franco, K.H. Xue, *ECS J. Solid State Science and Tech.*, **2** (10) (2013) M3084.
- K.H. Xue, T.K. Nguyen, A.A. Franco, *J. Electrochem. Soc.*, **161** (8) (2014) E3028.

Prof. Alejandro A. Franco

Engineering the Next Generation Rechargeable Batteries: a Multiscale Modeling Perspective I
College on Multiscale Computational Modeling of Materials for Energy
ICTP, Trieste, Italy - July 11, 2016

www.cnrs.fr

SOLUTION PHASE: O_2^- ESCAPE PROBABILITY

First reduction

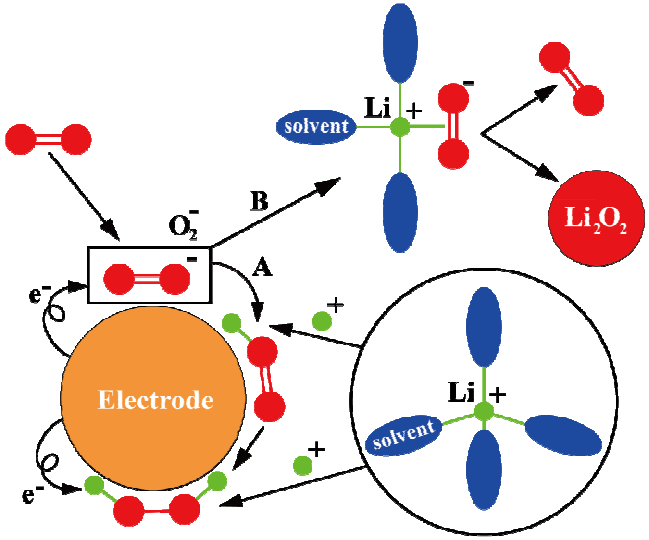
$$O_{2\,(sol)} + e^- \xrightarrow{\text{surface}} O_{2\,(sol)}^-$$

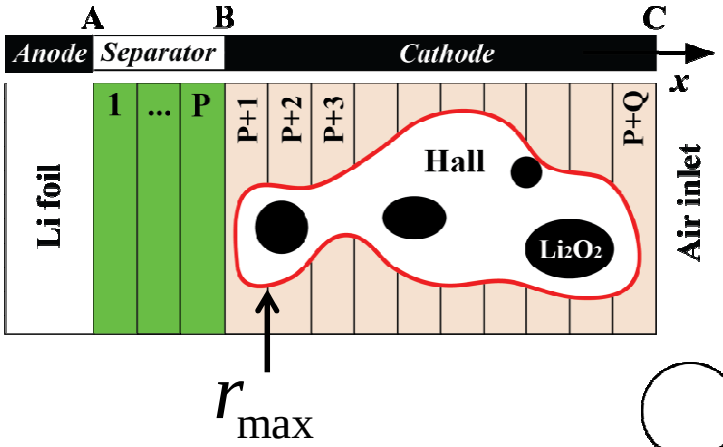
Second reduction

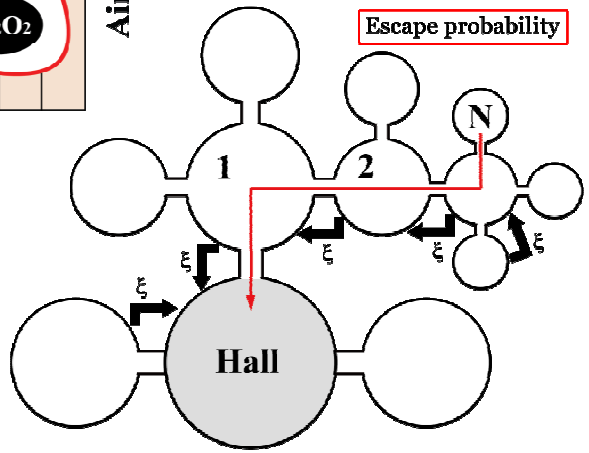
$$O_{2\,(sol)}^- \longrightarrow \chi(r)\, O_{2\,(sol)}^- + [1-\chi(r)]\, O_2^*$$

Route A: $[1-\chi(r)]\, O_2^* + 2[1-\chi(r)]\, Li^{+\,*} + [1-\chi(r)]\, e^- \xrightarrow{\text{surface}} [1-\chi(r)]\, Li_2O_{2\,(film)}$

Route B: $\chi(r)\, O_{2\,(sol)}^- + \chi(r)\, Li^+_{(sol)} \longrightarrow \left[\frac{\chi(r)}{2}\right] Li_2O_{2\,(particle)} + \left[\frac{\chi(r)}{2}\right] O_2 \uparrow$







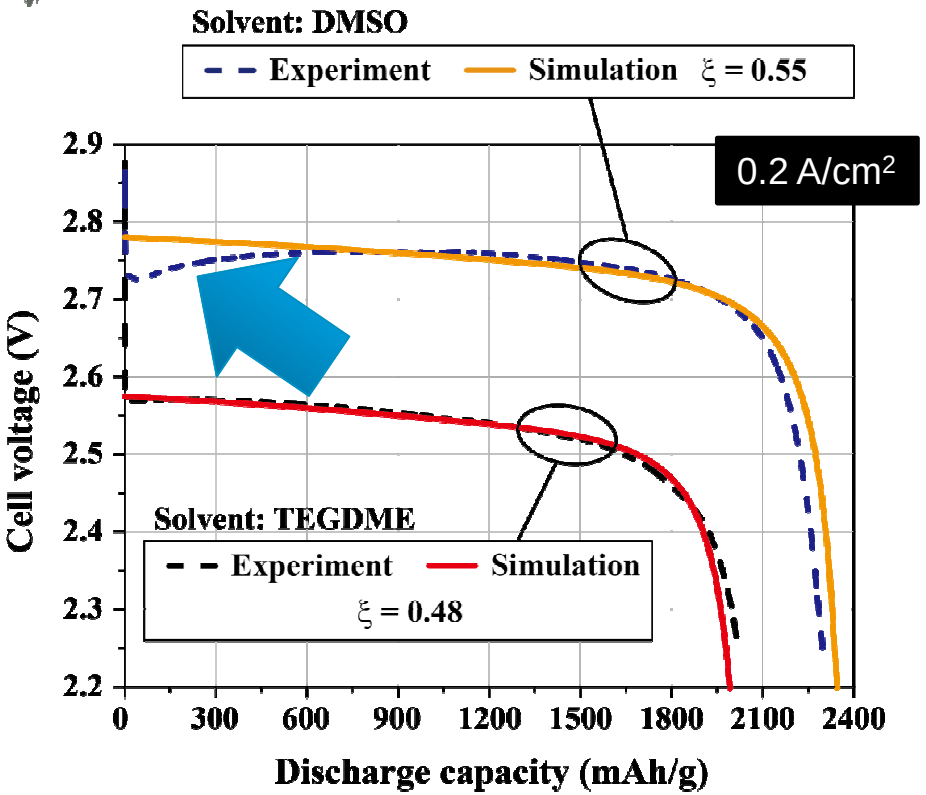
Escape function

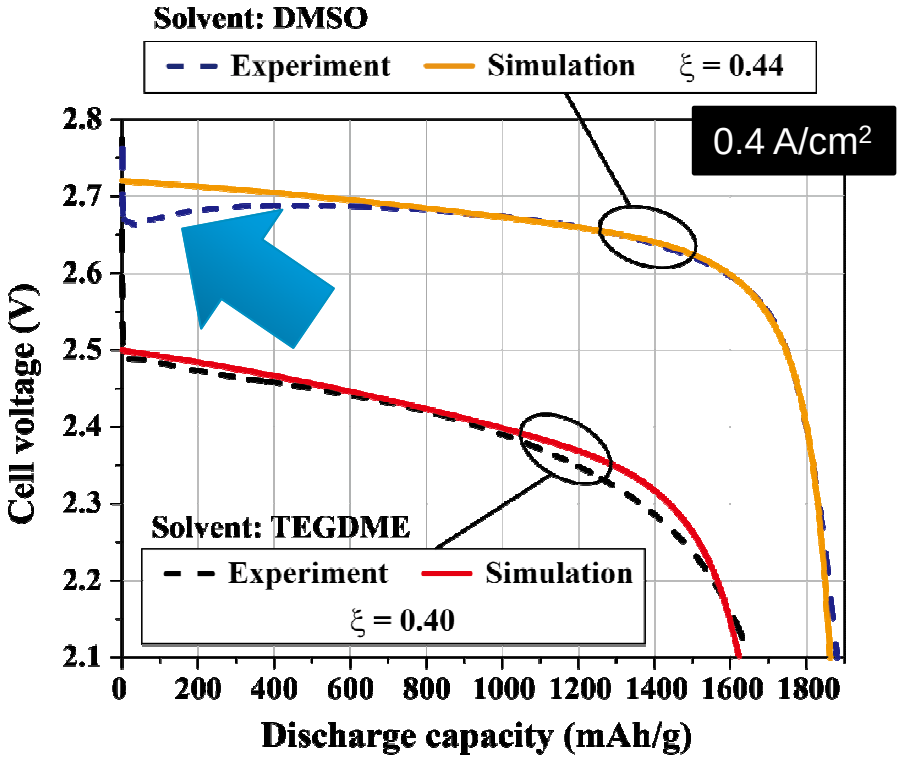
$$\chi(r) = \xi^N = \xi^{\frac{r_{max}-r}{r_{max}}}$$

ξ increases with the donor number

K.-H. Xue, E. McTurk, L. Johnson, P. G. Bruce, and A. A. Franco, *Journal of the Electrochemical Society*, **162** (4) (2015) A614.

IMPACT OF SOLVENT ON DISCHARGE

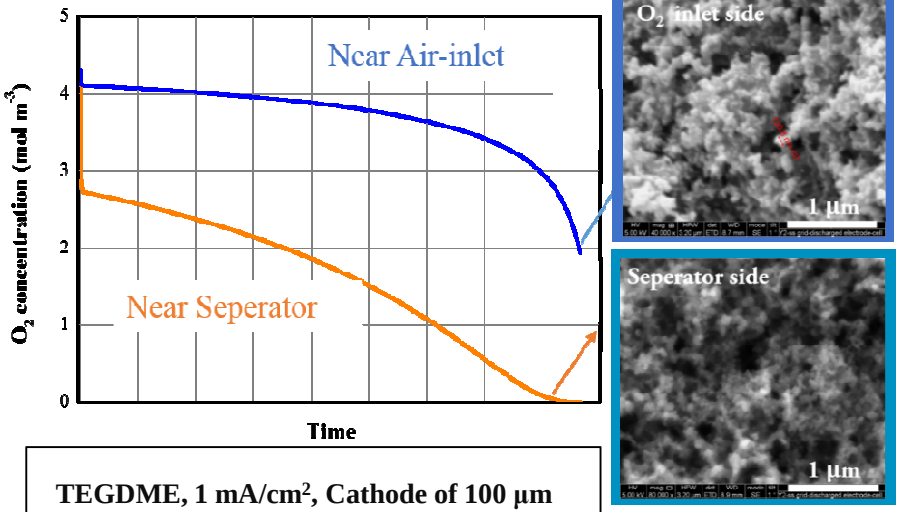




- High donor number (DN) solvent → high O_2^- lifetime in the solution.
  - ξ is larger in DMSO (DN: 29.8) than TEGDME (DN: 16.6).
  - ξ decreases with the discharge rate.
- Max. capacity and overpotential dependent on the PSD, O_2 solubility and solvent viscosity.

K.-H. Xue, E. McTurk, L. Johnson, P. G. Bruce, and A. A. Franco, *Journal of the Electrochemical Society*, **162** (4) (2015) A614.

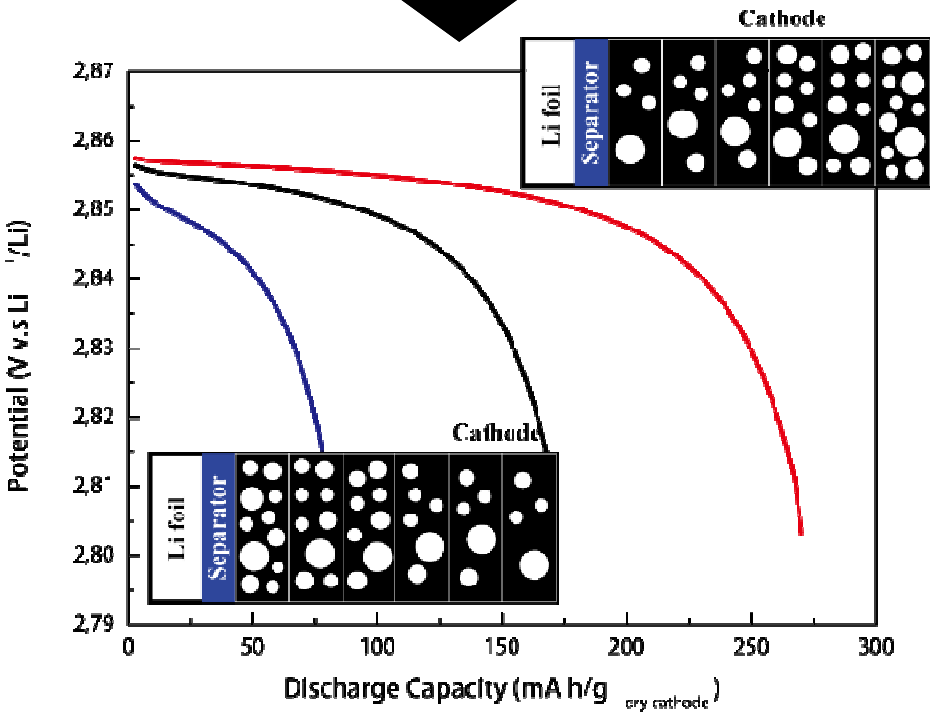
CALCULATED Li_2O_2 PRODUCT HETEROGENEITY



TEGDME, 1 mA/cm^2, Cathode of 100 µm

More Li_2O_2 formed close to the O_2 inlet. Insufficent discharge of inner part mainly due to poor O_2 transport.

Implementing porosity gradient



TEGDME
1 mA/cm^2
100 µm
ε – 75%

A.A. Franco, K.H. Xue, *ECS J. Solid State Science and Tech.*, **2** (10) (2013) M3084.
K.H. Xue, T.K. Nguyen, A.A. Franco, *J. Electrochem. Soc.*, **161** (8) (2014) E3028.

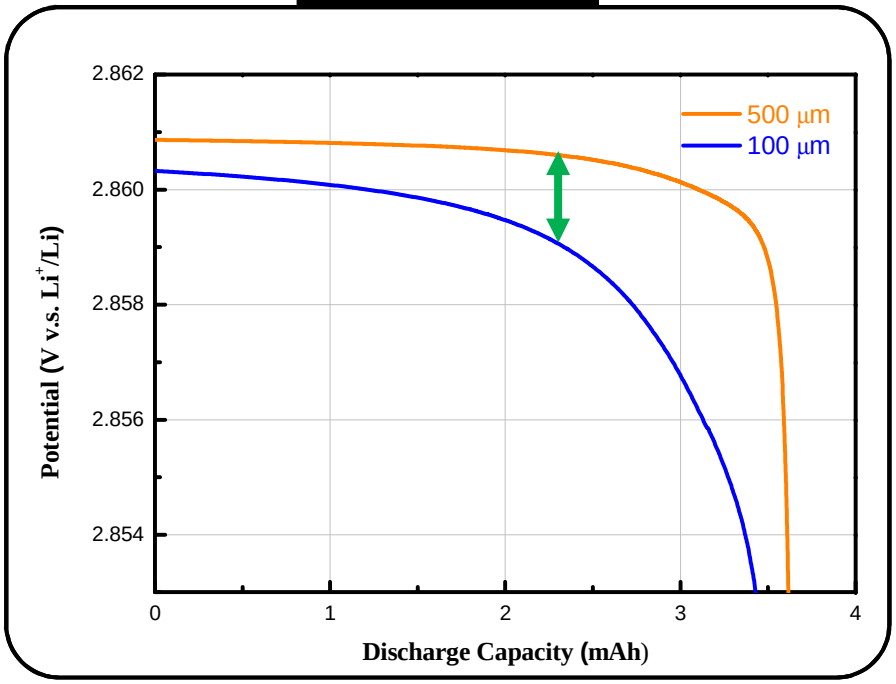
Prof. Alejandro A. Franco

Engineering the Next Generation Rechargeable Batteries: a Multiscale Modeling Perspective I
College on Multiscale Computational Modeling of Materials for Energy
ICTP, Trieste, Italy - July 11, 2016

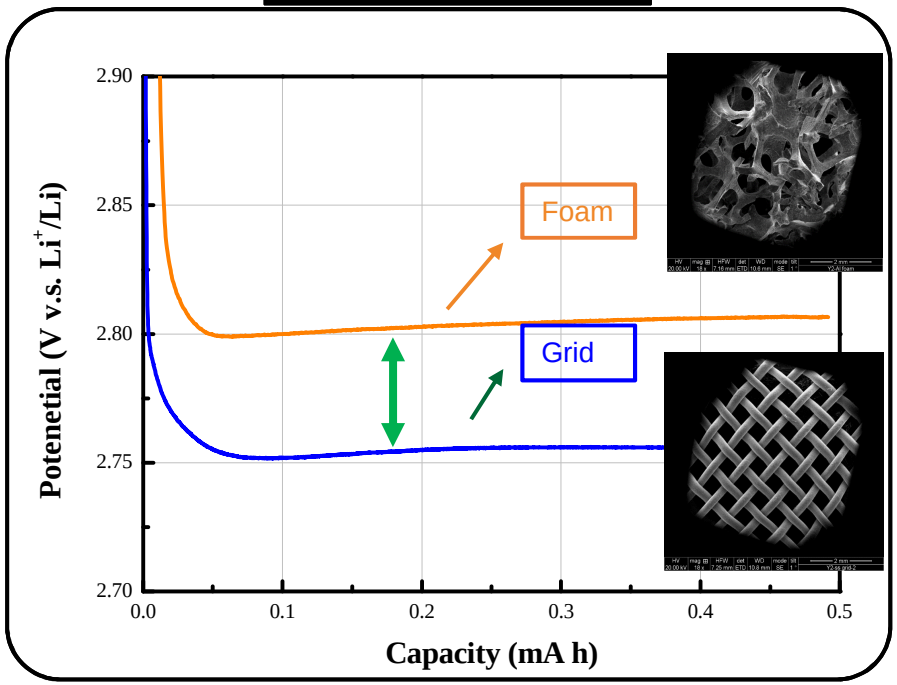
www.cnrs.fr

CALCULATED LOCAL CURRENT DENSITY IMPACT

MODELING



EXPERIMENTS



Overpotential decreases as the local current density increases.

90%C_{sp} + 10% PVdF – 5,7 mg, 5.9 mg – 1 bar O_2
100 µA/cm² – 2.2-4.5 V – 1 M $LiClO_4$ in DMSO
Cycling with capacity limitation of 0.5 mAh

Prof. Alejandro A. Franco

Engineering the Next Generation Rechargeable Batteries: a Multiscale Modeling Perspective I
College on Multiscale Computational Modeling of Materials for Energy
ICTP, Trieste, Italy - July 11, 2016

www.cnrs.fr

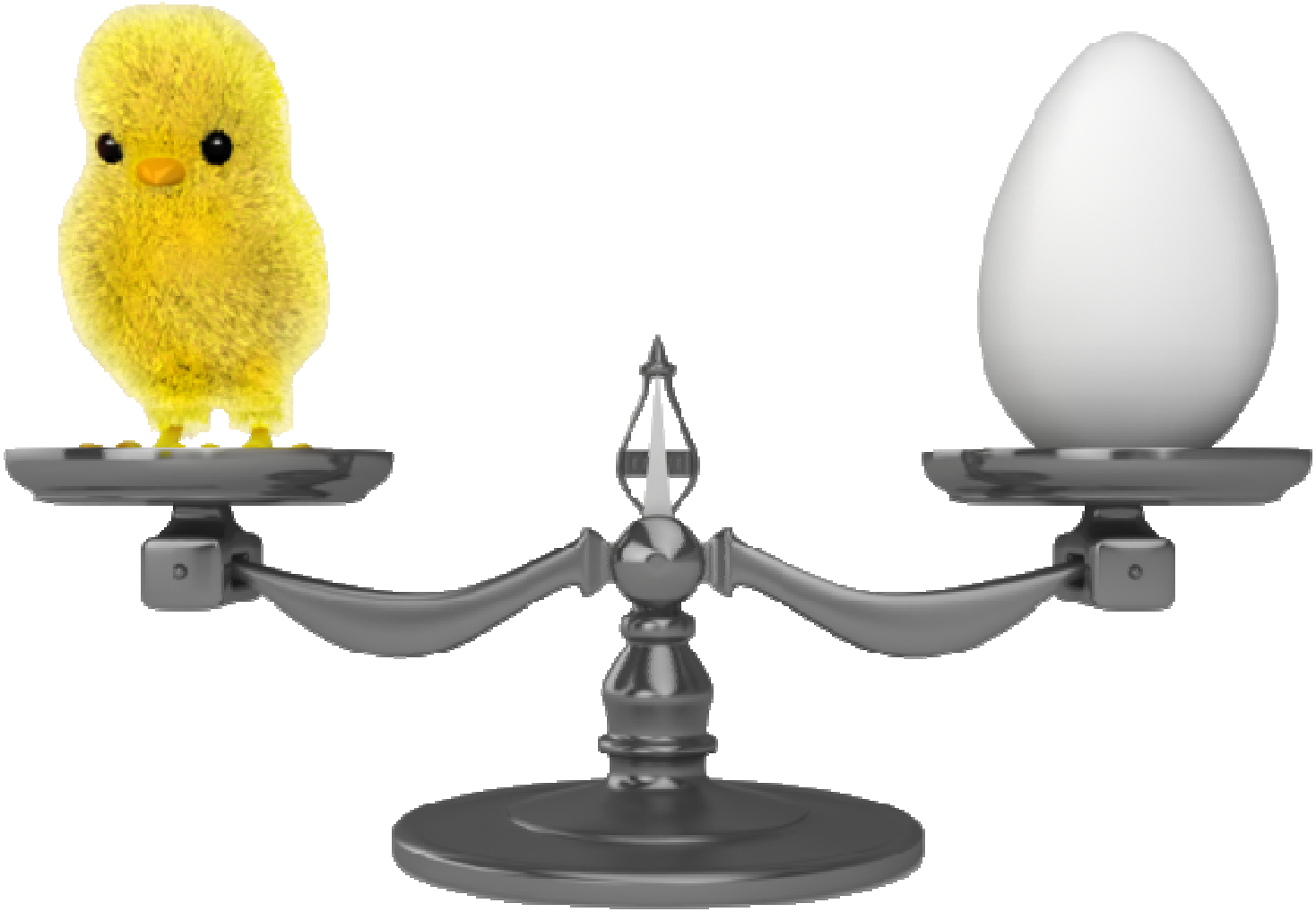
MULTISCALE MODELING:
DEFINITIONS & CONCEPTS

LITHIUM-O_2 BATTERIES:
TECHNICAL CHALLENGES

KINETIC MONTE CARLO
MODELING APPROACH

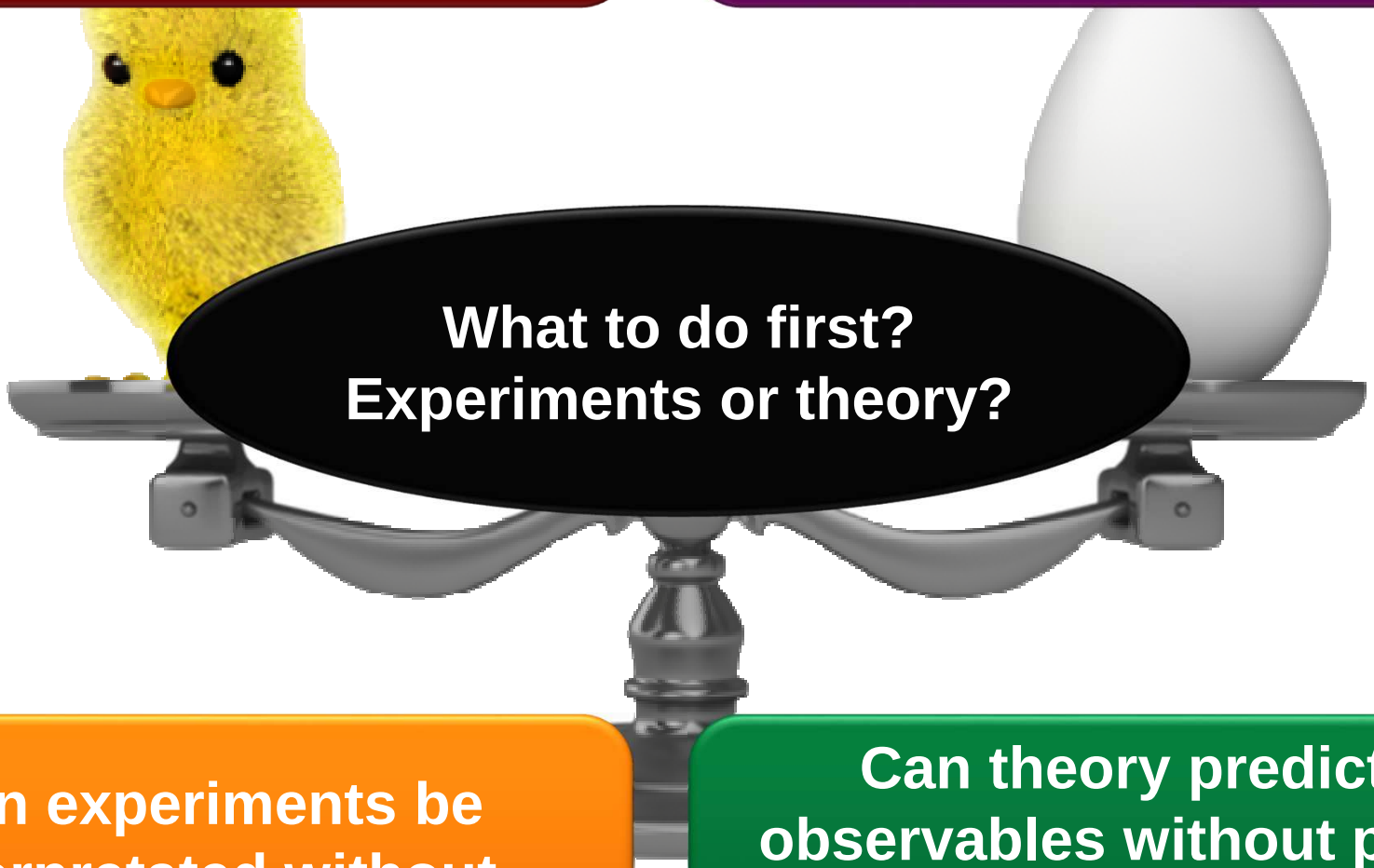
CONTINUUM
MODELING APPROACH

THOUGHTS ON
THEORY VS. EXPERIMENT



Do experiments validate theory?

Does theory explains experiments?



What to do first?
Experiments or theory?

Can experiments be interpretated without theory?

Can theory predict observables without prior calibration with experiments?

ACTIVE MATERIALS DATA MINING

Opportunities and challenges for first-principles materials design and applications to Li battery materials

Gerbrand Ceder

This article is based on the MRS Medal presentation given by Gerbrand Ceder (Massachusetts Institute of Technology) on December 1, 2009, at the Materials Research Society Fall Meeting in Boston. Ceder was awarded the Medal "for pioneering the high-impact field of first-principles thermodynamics of batteries materials and for the development of high-power density Li battery compounds."

The idea of first-principles methods is to determine the properties of materials by solving the basic equations of quantum mechanics and statistical mechanics. With such an approach, one can, in principle, predict the behavior of novel materials without the need to synthesize them and create a virtual design laboratory. By showing several examples of new electrode materials that have been computationally designed, synthesized, and tested, the impact of first-principles methods in the field of Li battery electrode materials will be demonstrated. A significant advantage of computational property prediction is its scalability, which is currently being implemented into the Materials Genome Project at the Massachusetts Institute of Technology. Using a high-throughput computational environment, coupled to a database of all known inorganic materials, basic information on all known inorganic materials and a large number of novel "designed" materials is being computed. Scalability of high-throughput computing can easily be extended to reach across the complete universe of inorganic compounds, although challenges need to be overcome to further enable the impact of first-principles methods.

MRS BULLETIN • VOLUME 35 • SEPTEMBER 2010 • www.mrs.org/bulletin ■ 693

Voltage calculation

$$\Delta x\ \mathrm{Li} + \mathrm{Li}_x\mathrm{MO}_y \Leftrightarrow \mathrm{Li}_{x+\Delta x}\mathrm{MO}_y \qquad V(x) = -\frac{\mu_{\mathrm{Li}(x)}^{\mathrm{cathode}} - \mu_{\mathrm{Li}}^{\mathrm{anode}}}{F}$$

$$\langle V \rangle = \frac{-\left[E(\mathrm{Li}_{x_2}\mathrm{MO}_y) - E(\mathrm{Li}_{x_1}\mathrm{MO}_y) - (x_2 - x_1)E(\mathrm{Li\ metal})\right]}{(x_2 - x_1)F}.$$

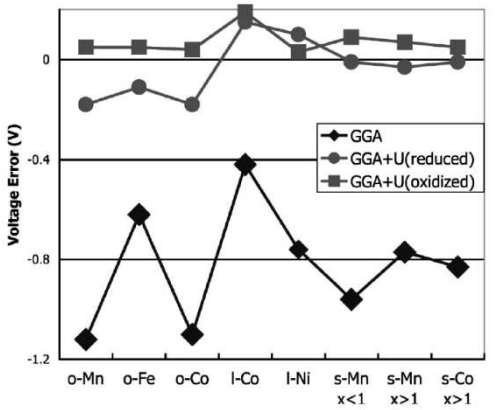


FIG. 6. Difference between calculated and experimental voltage (Refs. 5–9), for GGA and GGA+U, at the calculated U of the oxidized (delithiated) and reduced (lithiated) states, respectively (l =layered, s=spinel). For the spinel structures two voltage values for the $0<x<1$ and $1<x<2$ plateaus are calculated separately. Olivine $LiNiPO_4$ is not shown here because the voltage is unknown.

Ceder *et al.*, *Phys. Rev. B*, **70** (2004) 235121.

Prof. Alejandro A. Franco

Engineering the Next Generation Rechargeable Batteries: a Multiscale Modeling Perspective I

College on Multiscale Computational Modeling of Materials for Energy

ICTP, Trieste, Italy - July 11, 2016

www.cnrs.fr

ACTIVE MATERIALS DATA MINING

Log in

Page | Discussion | Read | View source | View history | Go | Search

GGA+U calculations

It is well-known that first principles calculations within the local density approximation (LDA) or generalized gradient approximation (GGA) lead to considerable error in calculated redox reaction energies of many transition metal compounds. This error arises from the self-interaction error in LDA and GGA, which is not canceled out in redox reactions where an electron is transferred between significantly different environments, such as between a metal and a transition metal or between a transition metal and oxygen. Extensive discussion of this issue can be found in the following works.[1][2][3][4]

In the Materials Project, we have calibrated U values for many transition metals of interest using the approach outlined in Wang et al.'s work[3]. At the present moment, U values have been calibrated for transition metal oxide systems only. The choice of systems to which we apply U was largely determined by our experience and by systematic benchmarking. It is very likely that we will expand calibration of U values to more chemical systems in the future.

Navigation

- Wiki home
- Recent changes
- Random page
- Help
- Materials Project portal

Toolbox

- What links here
- Related changes
- Special pages
- Printable version
- Permanent link

Contents [hide]

Calibration of U values

The U values were obtained by fitting to experimental binary formation enthalpies as described in Wang et al.'s work, which is simple and accurately reproduces phase stabilities. A least squares method of obtaining the correct U value was used, as follows:

1. For each non-overlapping formation energy reaction considered, we find the region where the formation energy error passes zero. For the V-O system, this includes the following:
    1. $2\ V_2O_3 + O_2 \rightarrow 4\ VO_2$
    2. $4VO_2 + O_2 \rightarrow 2\ V_2O_5$
2. For each formation energy region identified, we fit the linear equation $\mathrm{Error/redox} = mU + c$ to the final U range. In the case of V, we will have two sets of (m,c).
3. We find the U value that minimizes the sum of square Error / Redox.
4. In the case of V, we get a U value of 3.25.

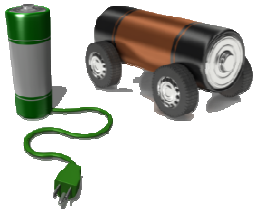
Prof. Alejandro A. Franco

Engineering the Next Generation Rechargeable Batteries: a Multiscale Modeling Perspective I

College on Multiscale Computational Modeling of Materials for Energy

ICTP, Trieste, Italy - July 11, 2016

www.cnrs.fr



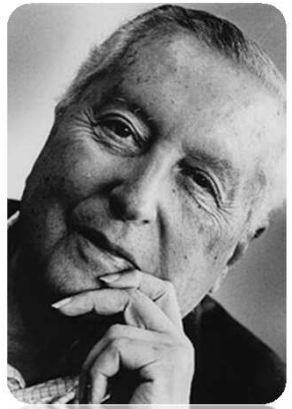
NON-EQUILIBRIUM THERMODYNAMICS: PRINCIPLES

➔ **POSTULATE:** the thermodynamic flux densities are functions of the thermodynamic efforts.

$$J = f(X_\alpha, X_\beta, X_\chi \ldots)$$

$$J = f(X_\alpha)$$

Osanger (1903-1976)



Prigogine (1917-2003)

$$J_i = J_i(X_\alpha) = J_i(X_\alpha = 0) + \frac{1}{1!}\frac{\partial J_i}{\partial X_\alpha}(X_\alpha = 0)X_\alpha + \frac{1}{2!}\frac{\partial^2 J_i}{\partial X_\alpha^{\,2}}(X_\alpha = 0)X_\alpha^{\,2} + \frac{1}{3!}\frac{\partial^3 J_i}{\partial X_\alpha^{\,3}}(X_\alpha = 0)X_\alpha^{\,3} \ldots$$

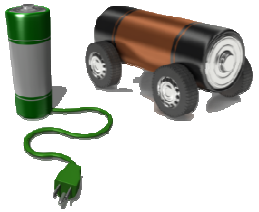
➔ **1st order N.E.T.:** linear functions.

$$J_i = \sum_j L_{ij} X_j$$

IONIC TRANSPORT IN ELECTROLYTES

$$J = -L_1 \nabla\mu - L_2 \nabla\phi$$

- ionic current
- chemical potential
- electrostatic potential



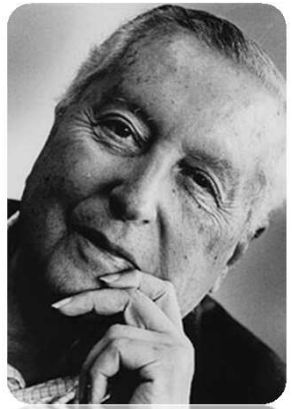
NON-EQUILIBRIUM THERMODYNAMICS: PRINCIPLES

➔ **POSTULATE:** the thermodynamic flux densities are functions of the thermodynamic efforts.

$$J = f(X_\alpha, X_\beta, X_\chi \ldots)$$

$$J = f(X_\alpha)$$

Osanger (1903-1976)



Prigogine (1917-2003)

$$J_i = J_i(X_\alpha) = J_i(X_\alpha = 0) + \frac{1}{1!}\frac{\partial J_i}{\partial X_\alpha}(X_\alpha = 0)X_\alpha + \frac{1}{2!}\frac{\partial^2 J_i}{\partial X_\alpha^2}(X_\alpha = 0)X_\alpha^2 + \frac{1}{3!}\frac{\partial^3 J_i}{\partial X_\alpha^3}(X_\alpha = 0)X_\alpha^3 \ldots$$

➔ **1st order N.E.T.:** linear functions.

$$J_i = \sum_j L_{ij} X_j$$

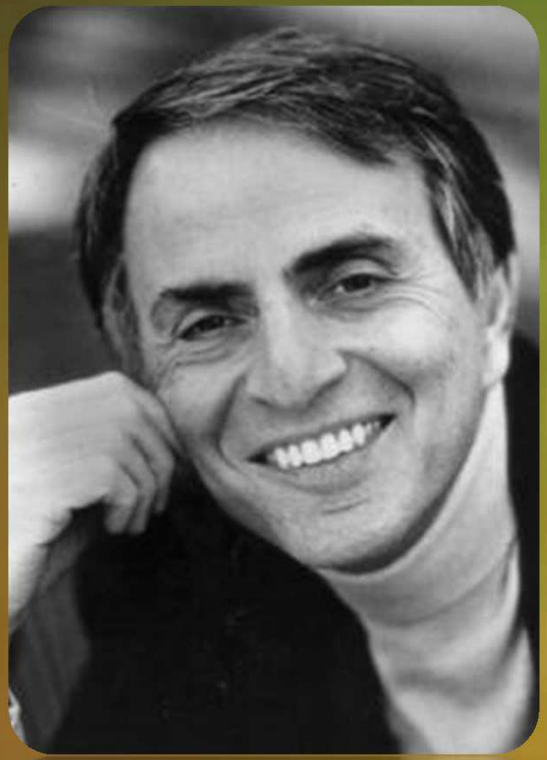
IONIC TRANSPORT I

$$J = -L_1 \nabla \mu$$

ionic current

chemical potential

Parameters are always model dependent!



Carl Sagan

"Modern science has been a voyage into the unknown, with a lesson in humility waiting at every stop.
Many passengers would rather have stayed home."

Amiens cathedral by night

TO BE CONTINUED…

www.modeling-electrochemistry.com
alejandro.franco@u-picardie.fr