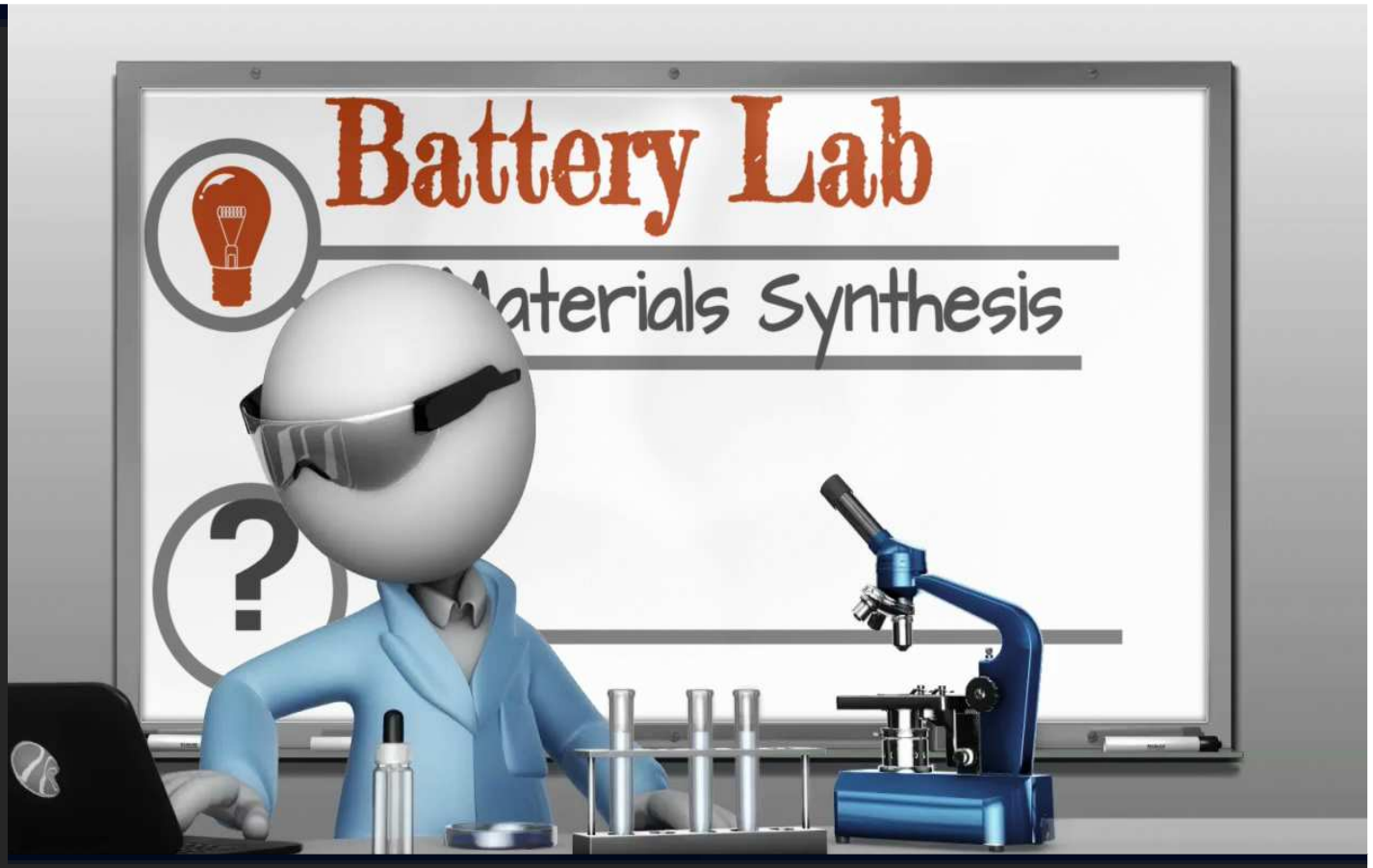
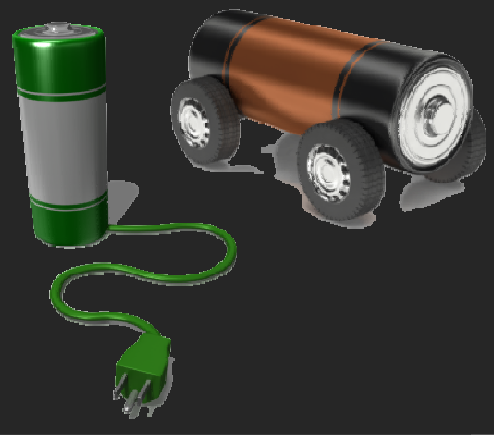
© Prof. Alejandro A. Franco – LRCS, UPJV, Amiens

College on Multiscale Computational Modeling of Materials for Energy Applications

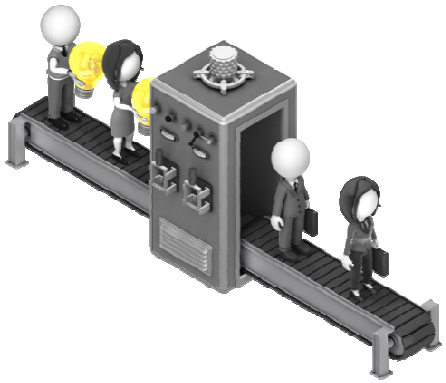
ICTP, Trieste, Italy
July 13, 2016

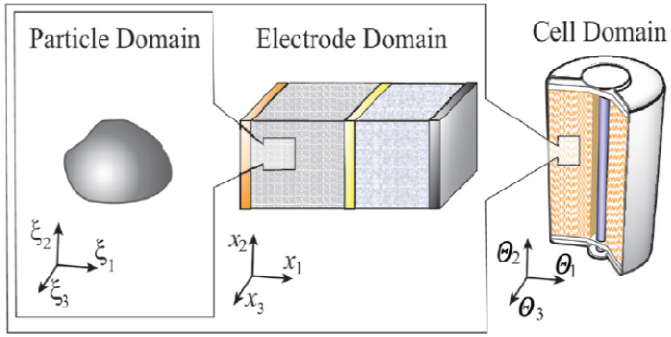


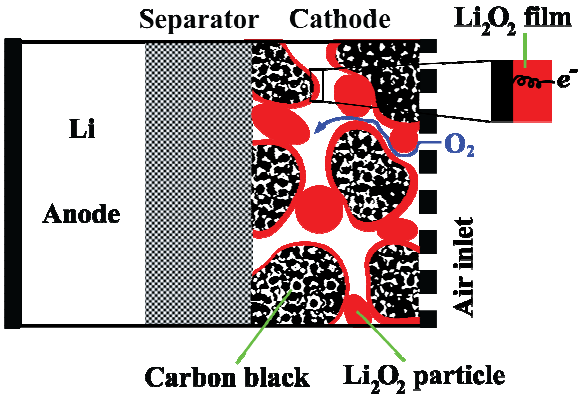
Engineering the Next Generation Rechargeable Batteries: A Multiscale Modeling Perspective II

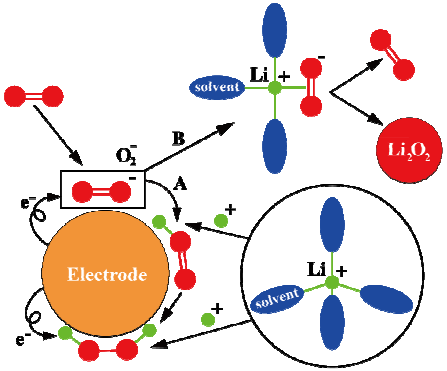


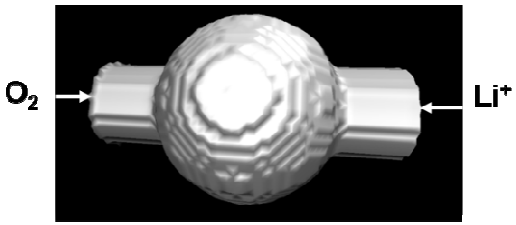
Prof. Alejandro A. Franco
LRCS, Université de Picardie Jules Verne & CNRS – Amiens, France
Réseau sur le Stockage Electrochimique de l'Energie (RS2E)
ALISTORE European Research Institute

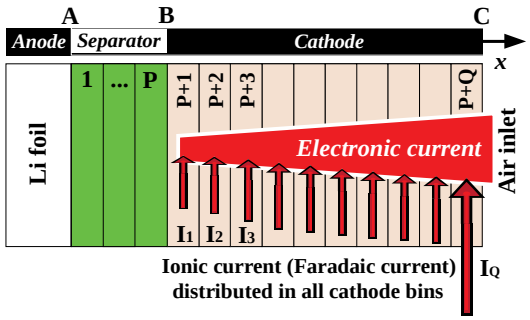



Particle Domain
Electrode Domain
Cell Domain


Separator
Cathode
Li_2O_2 film
Li
Anode
O_2
Air inlet
Carbon black
Li_2O_2 particle

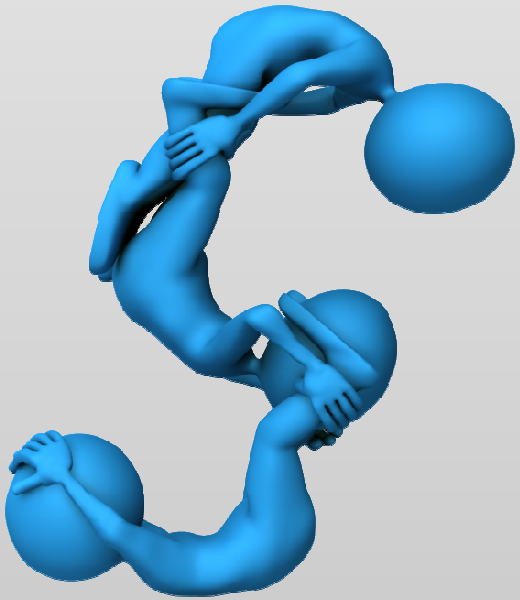

solvent
Li
Li_2O_2
Electrode
A
B


O_2
Li^+


A
B
C
Anode
Separator
Cathode
x
Li foil
1
...
P
P+1
P+2
P+3
P+Q
Electronic current
Air inlet
I_1
I_2
I_3
I_Q
Ionic current (Faradaic current)
distributed in all cathode bins

OUTLINE

- Li-S BATTERIES I: CONTINUUM
- Li-S BATTERIES II: kMC
- REDOX FLOW BATTERIES: kMC
- PEM FUEL CELLS: HYBRID
- CHALLENGES & OPPORTUNITIES



Li-S BATTERIES I: CONTINUUM

Li-S BATTERIES II: kMC

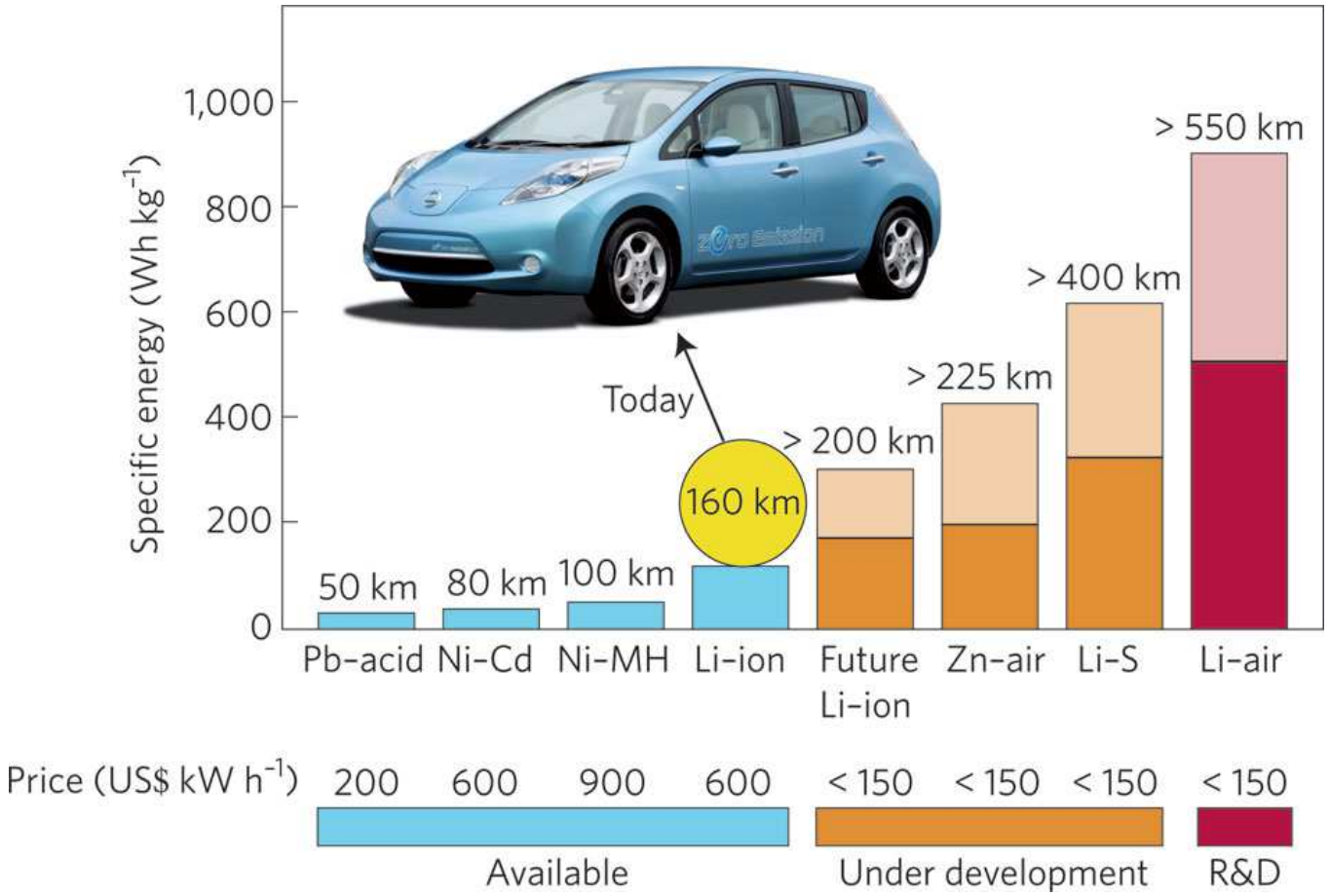
REDOX FLOW BATTERIES: kMC

PEM FUEL CELLS: HYBRID

CHALLENGES & OPPORTUNITIES

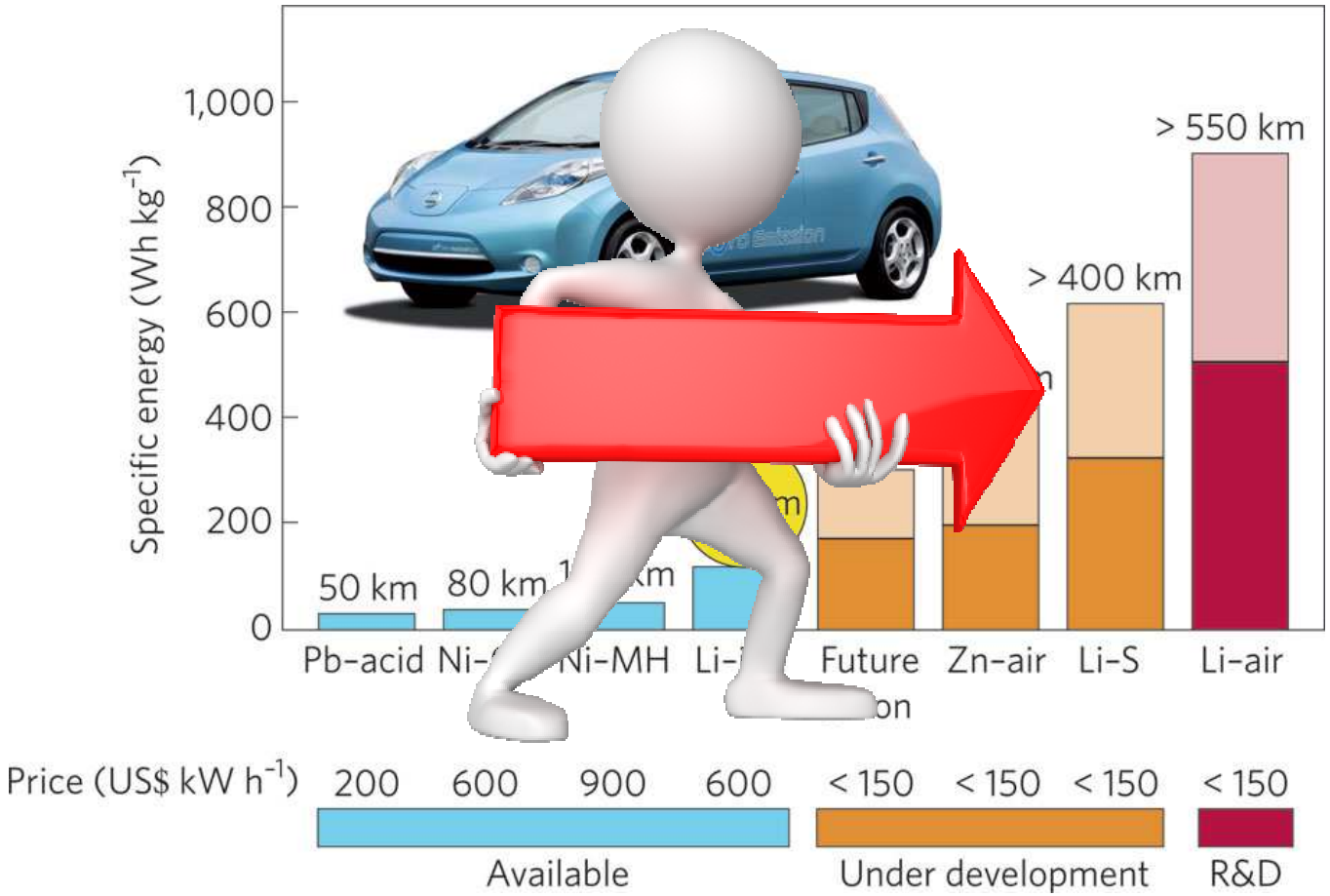
OIL

LITHIUM-SULFUR BATTERIES: INTRODUCTION (1/2)



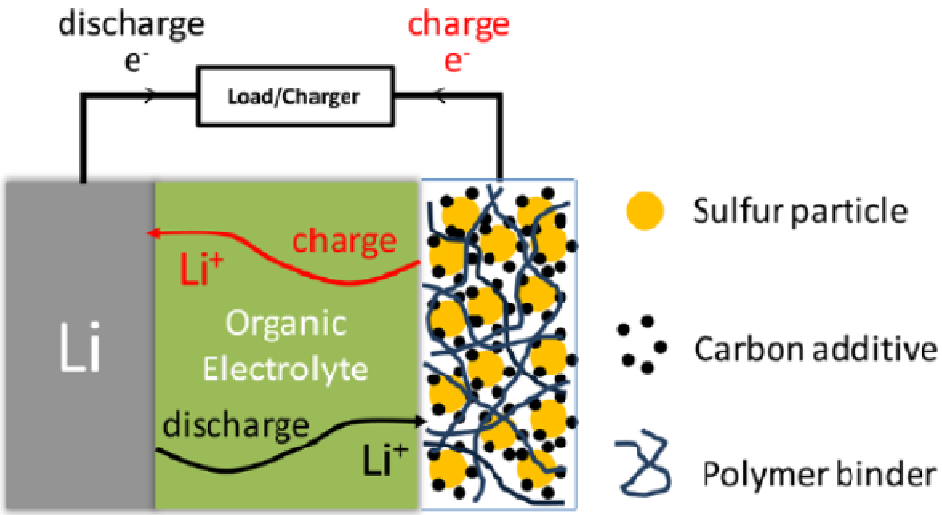
P.G. Bruce, S.A. Freunberger, L.G. Hardwick, J.M. Tarascon, *Nature Materials* **11** (2012) 19 .

LITHIUM-SULFUR BATTERIES: INTRODUCTION (1/2)



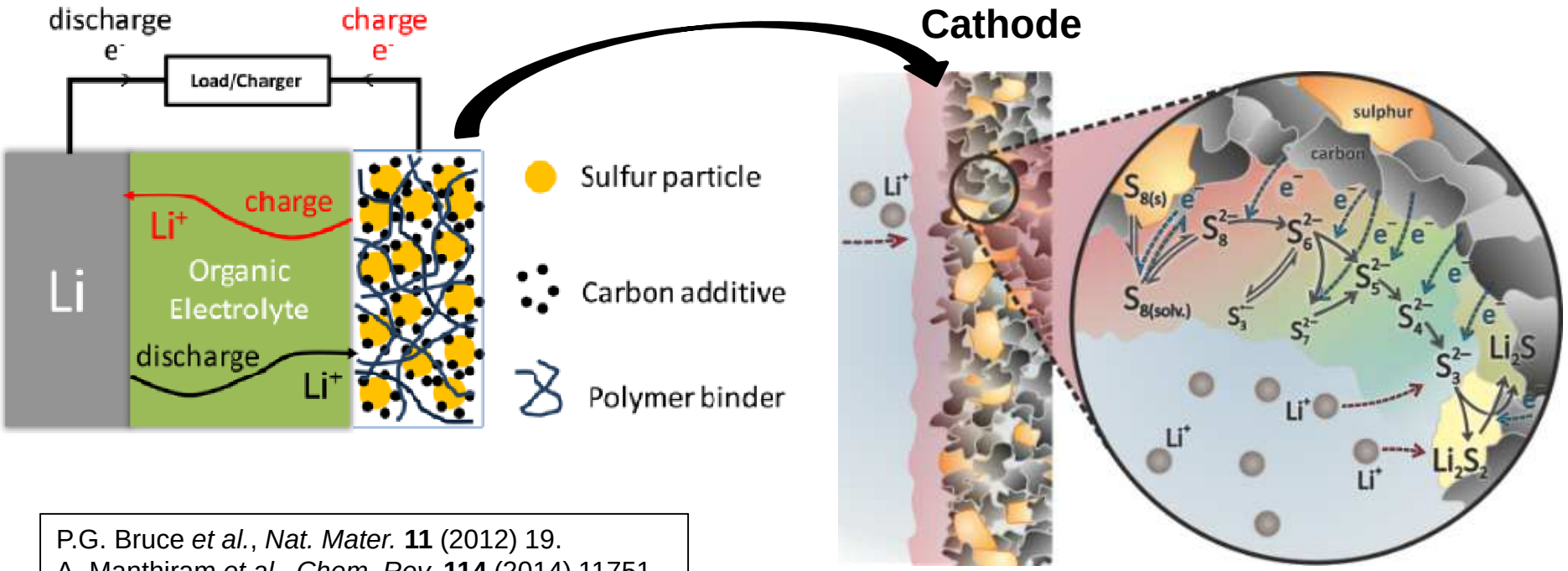
P.G. Bruce, S.A. Freunberger, L.G. Hardwick, J.M. Tarascon, *Nature Materials* **11** (2012) 19 .

LITHIUM-SULFUR BATTERIES: INTRODUCTION (2/2)



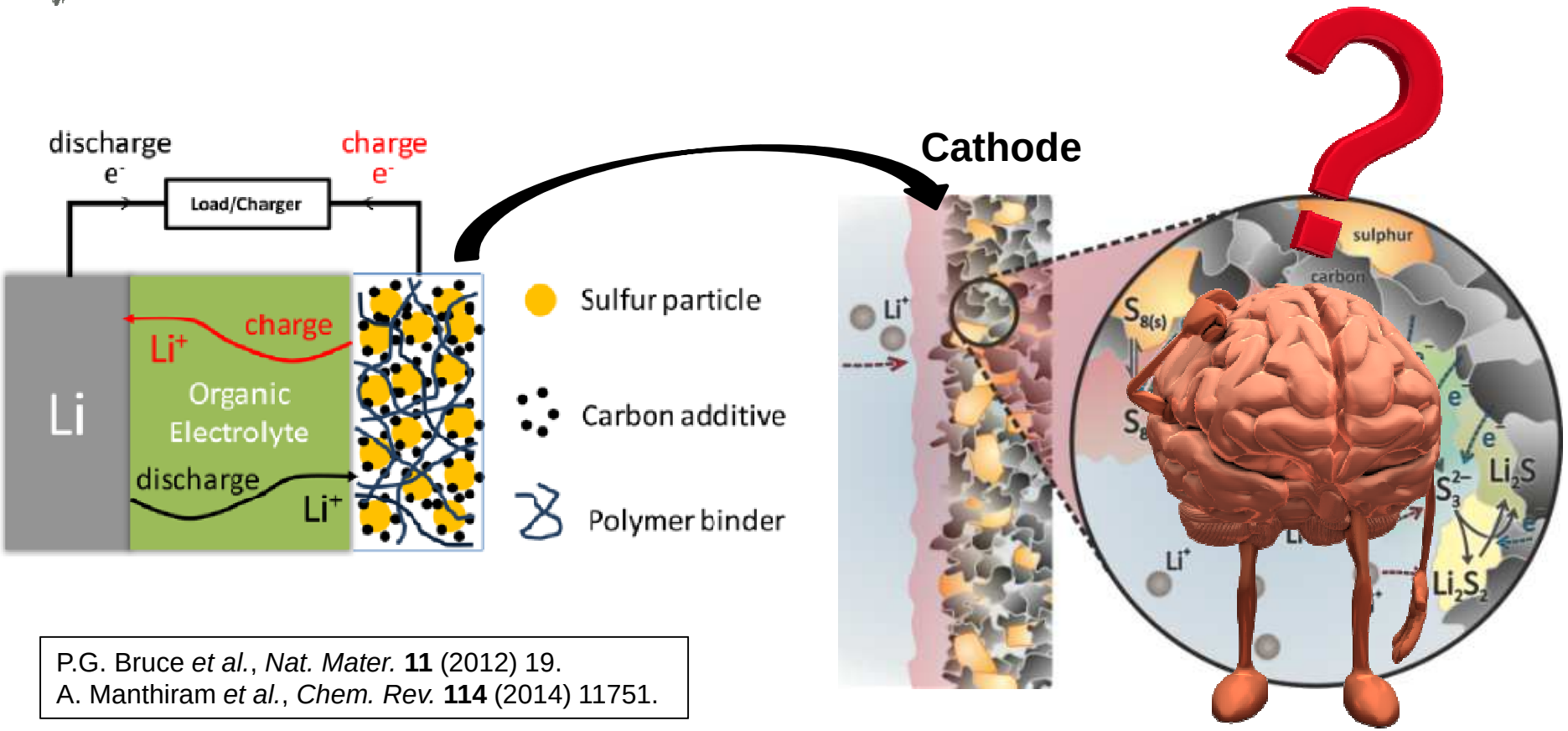
P.G. Bruce *et al.*, *Nat. Mater.* **11** (2012) 19.
A. Manthiram *et al.*, *Chem. Rev.* **114** (2014) 11751.

LITHIUM-SULFUR BATTERIES: INTRODUCTION (2/2)



P.G. Bruce *et al.*, *Nat. Mater.* **11** (2012) 19.
A. Manthiram *et al.*, *Chem. Rev.* **114** (2014) 11751.

LITHIUM-SULFUR BATTERIES: INTRODUCTION (2/2)



P.G. Bruce *et al.*, *Nat. Mater.* **11** (2012) 19.
A. Manthiram *et al.*, *Chem. Rev.* **114** (2014) 11751.

➔ **One key to enhance LiS batteries:** deeper insights about the porous electrode microstructure impact on the cell performance.

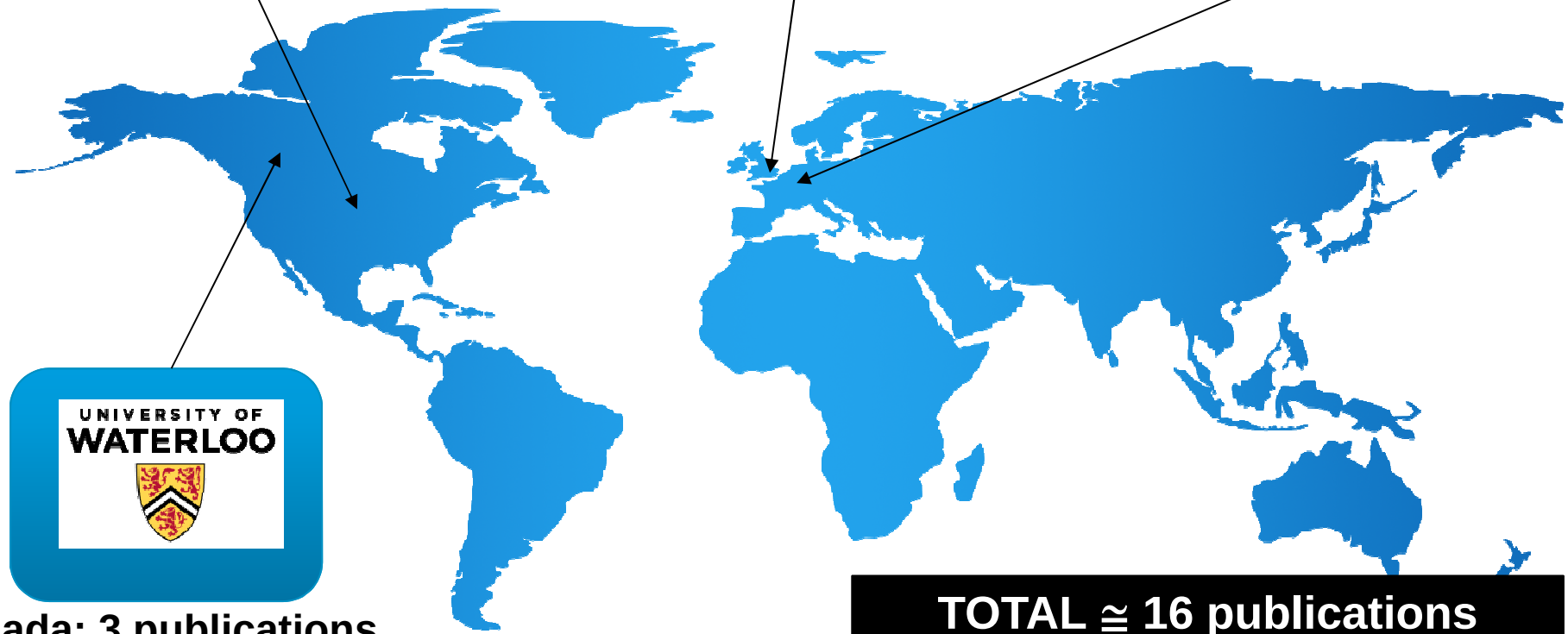
↳ e.g. sulfur repartition between different scales of porosity, Li_2S location…

GREAT OPPORTUNITIES FOR COMPUTATIONAL MODELING

USA: 8 publications

UK: 1 publication

Germany: 4 publications



Canada: 3 publications

TOTAL ≅ 16 publications

THE FIRST ENGINEERING (CONTINUUM) MODEL

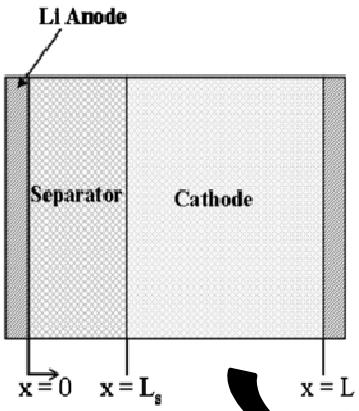
2008

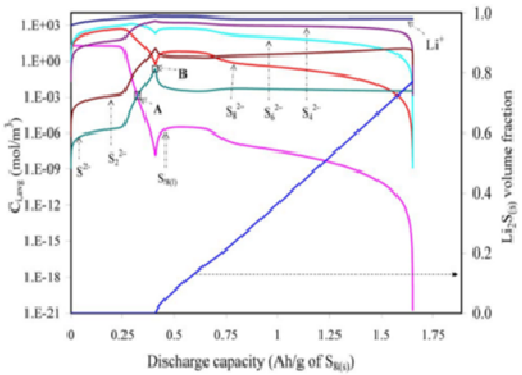
UNIVERSITY OF SOUTH CAROLINA

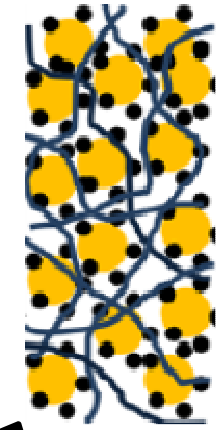
K. Kumaresan, Y. Mikhaylik, R.E. White, *J. Electrochem. Soc.* **155**(8) A576

↳ **Physical model:**

- Reduction and precipitation reactions.
- Lithium salt and polysulfides transport.
- ***Cathode (C:S) microstructure represented with an effective porosity.***
- ***Lack of comparison with experimental data.***







$$\frac{\partial C_i(x,t)}{\partial t} = -\nabla.\vec{J}_i(x,t) + \gamma.j(x,t)$$

$$\vec{J}_i(x,t) = -D_i \nabla C_i(x,t)$$

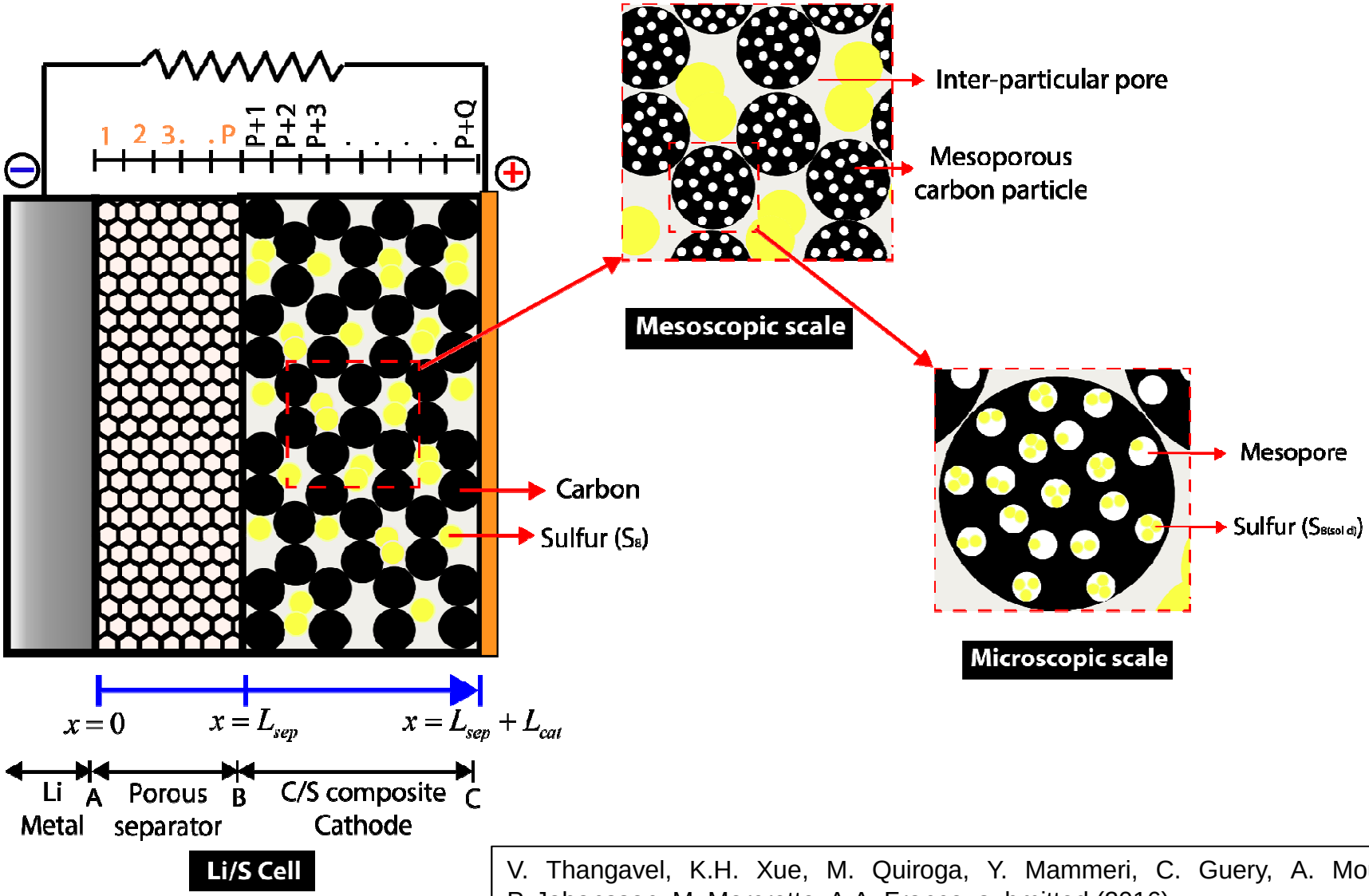
$$D_i = \frac{\varepsilon}{\tau} D_i^{bulk}$$

Specific surface area (m^2/m^3)

Porosity (m^3/m^3)
Tortuosity

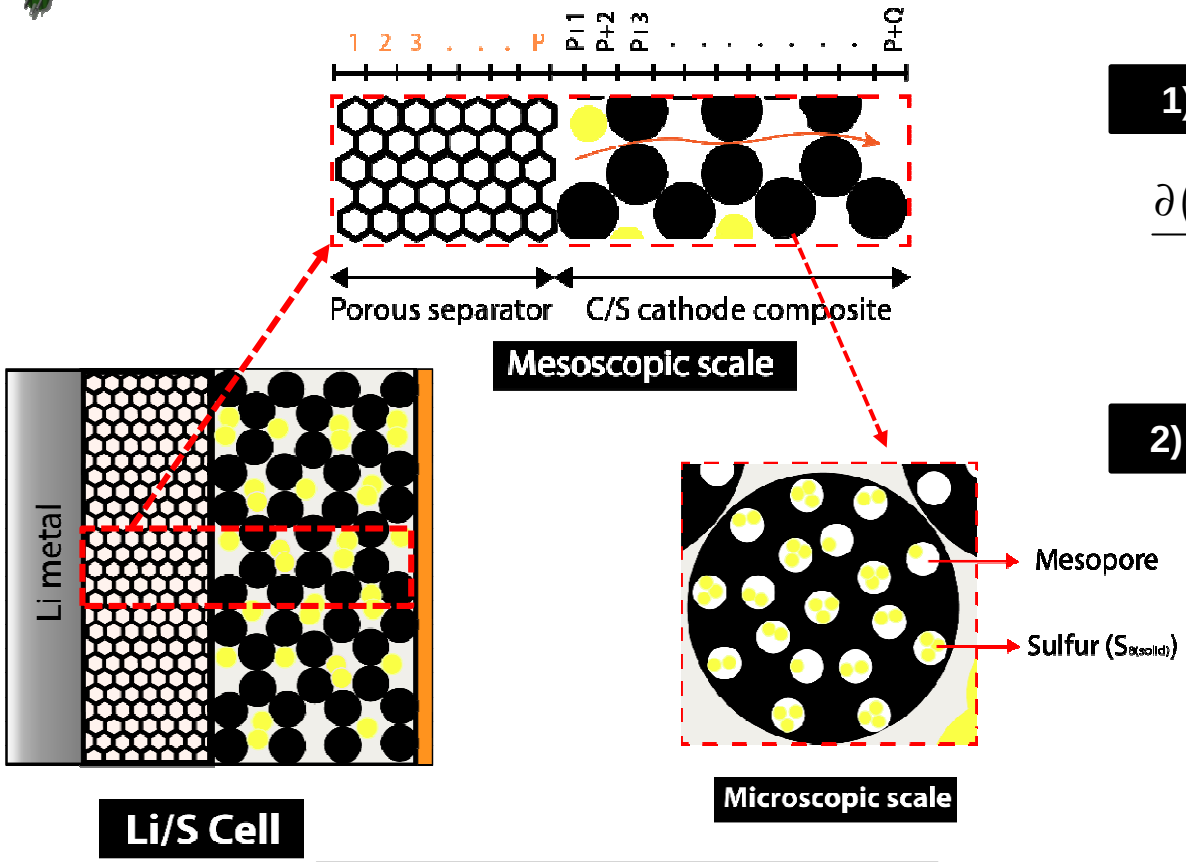
OUR APPROACH

1D-CONTINUUM CELL MODEL



V. Thangavel, K.H. Xue, M. Quiroga, Y. Mammeri, C. Guery, A. Moustari, P. Johansson, M. Morcrette, A.A. Franco, submitted (2016).

SULFUR-BASED SPECIES TRANSPORT

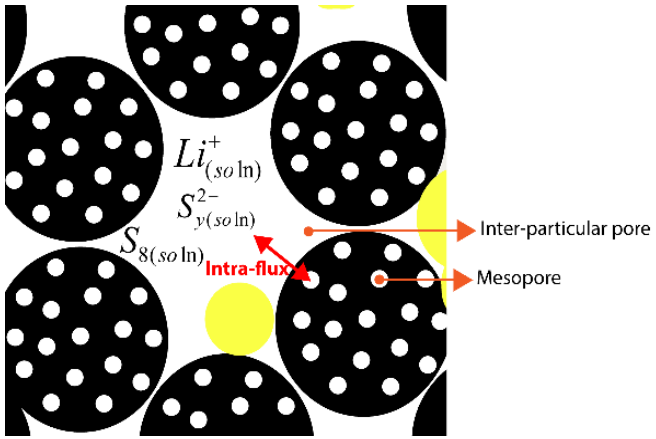


1) Mass conservation for mesoscale

$$\frac{\partial(\varepsilon_1 c_1)}{\partial t} = \frac{\partial}{\partial x}\left[(\varepsilon_1)^{1.5} D\left(\frac{\partial c_1}{\partial x}\right)\right] + r_1 - R_1 + f$$

2) Mass conservation for microscale

$$\frac{\partial(\varepsilon_2 c_2)}{\partial t} = r_2 - R_2 - f$$



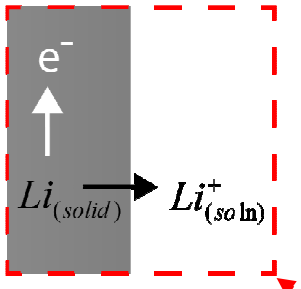
3) Intra-flux between two scales

$$f \propto K_{flux}(c_2 - c_1)\Xi(\delta_1)$$

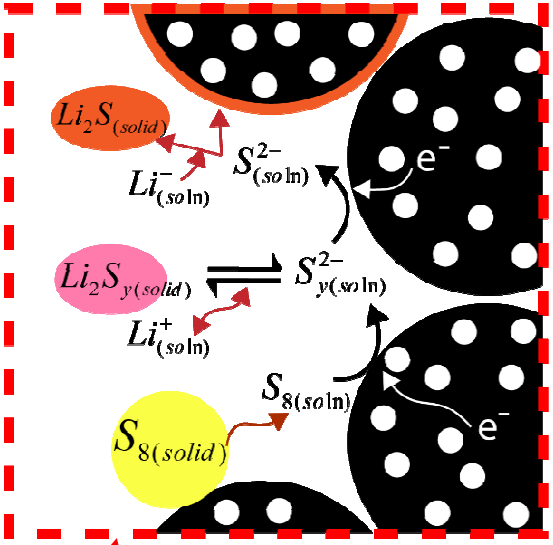
r : generation rate through electrochemical reactions
R : sink rate due to chemical dissolution/precipitation
f : species intra-flux between the two scales

ELECTROCHEMICAL & PRECIPITATION REACTIONS

↳ The dissolved sulfur ($S_{8(soln)}$) undergoes a series of elementary reduction reactions to produce $S^{2-}_{(soln)}$.

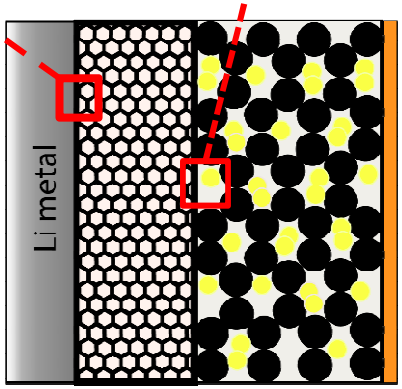


Anode side



Cathode side

y: 8, 6, 4 & 2

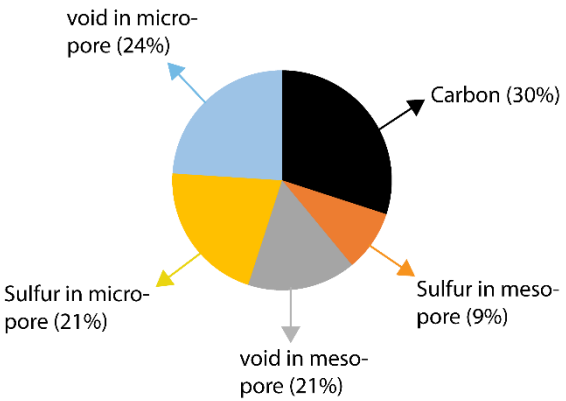


Li/S Cell

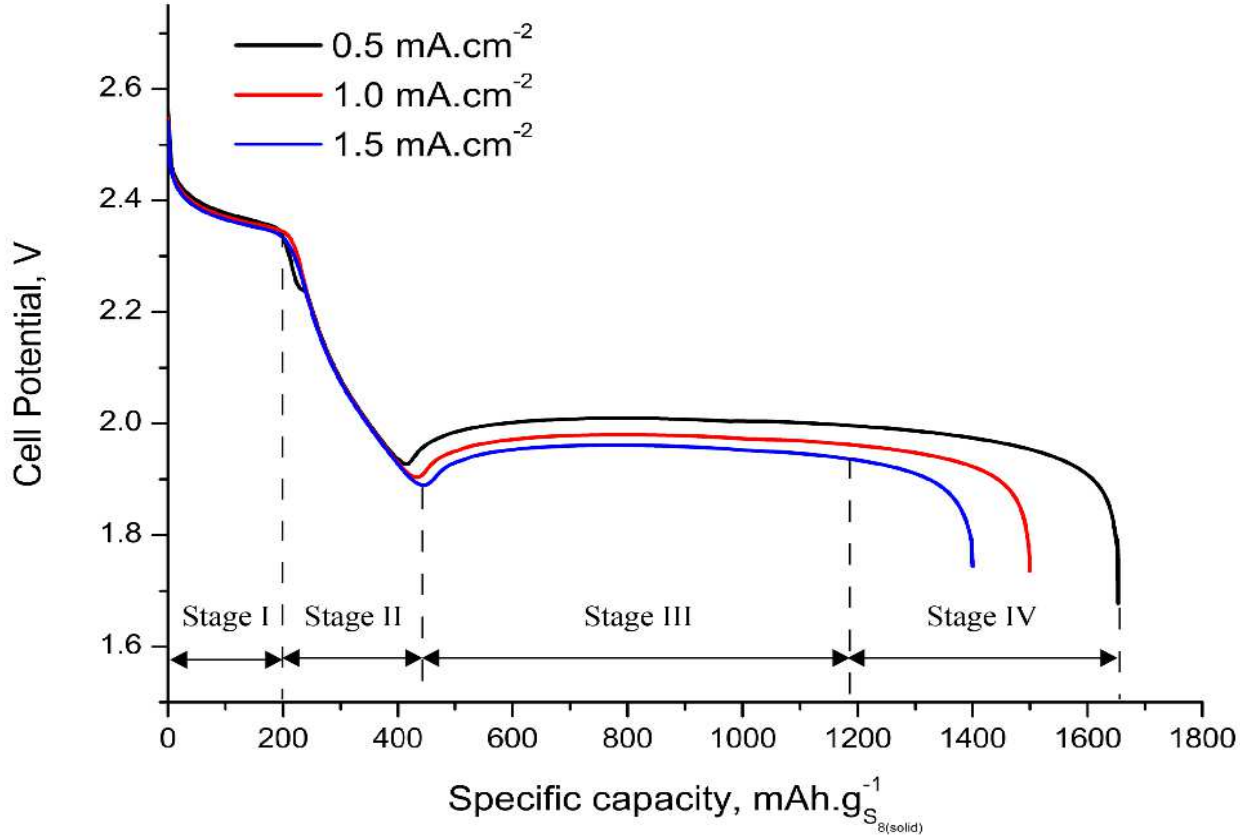
↳ Precipitation/dissolution of $Li_2S_{y(solid)}$.

↳ Li_2S precipitates both as film and particle.

CALCULATED RATE CAPABILITIES (1/3)

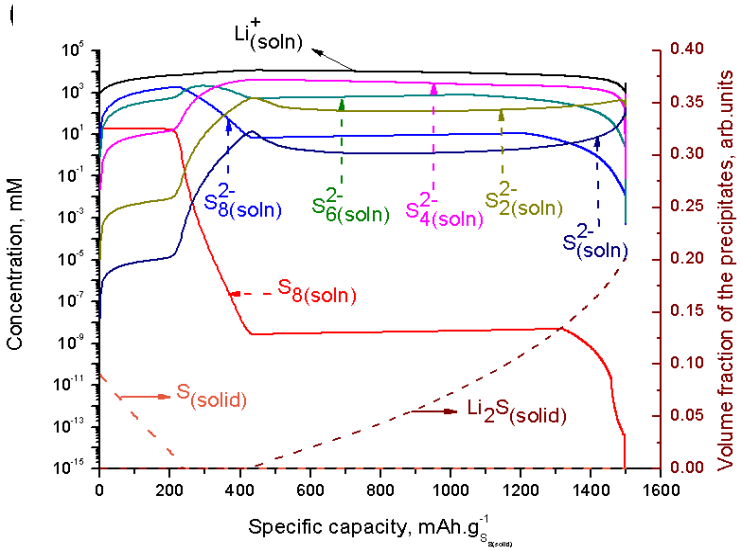


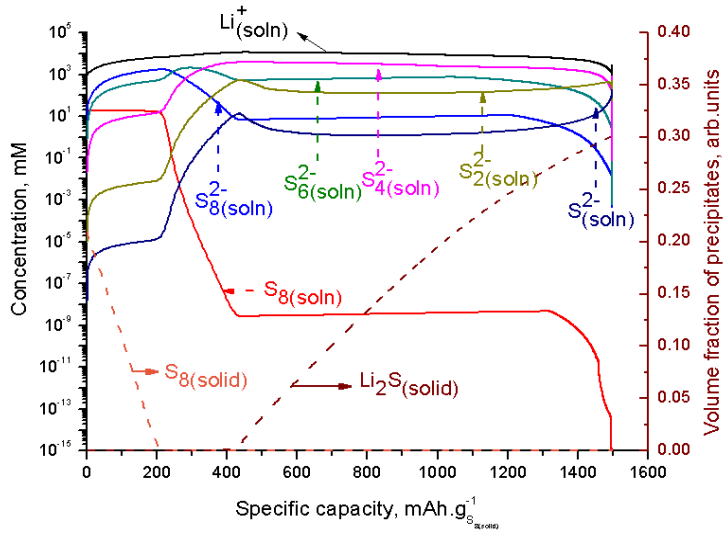
$S_{8(solid)}$ loading= 2.48 mg.cm^{-2}

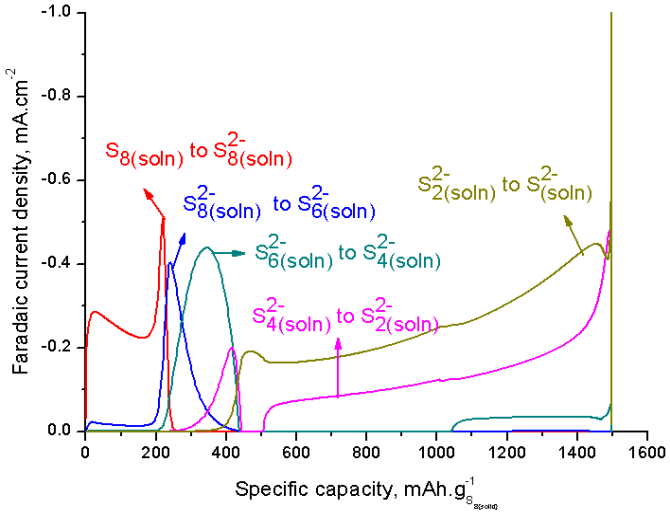


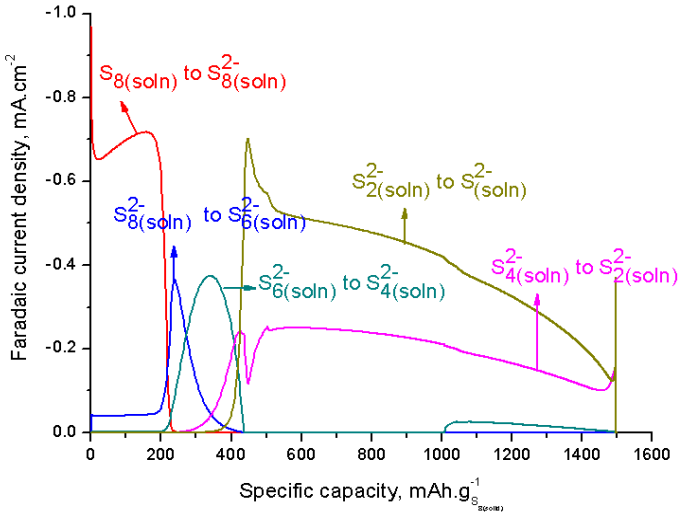
CALCULATED RATE CAPABILITIES (2/3)

Inter-particle region | **1.0 mA.cm^{-2}** | **Mesoporous region**



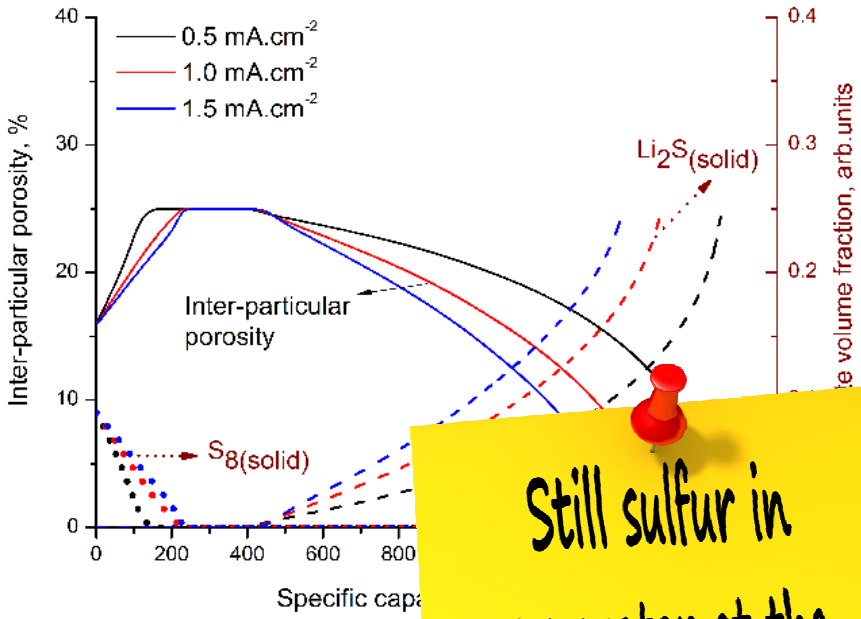






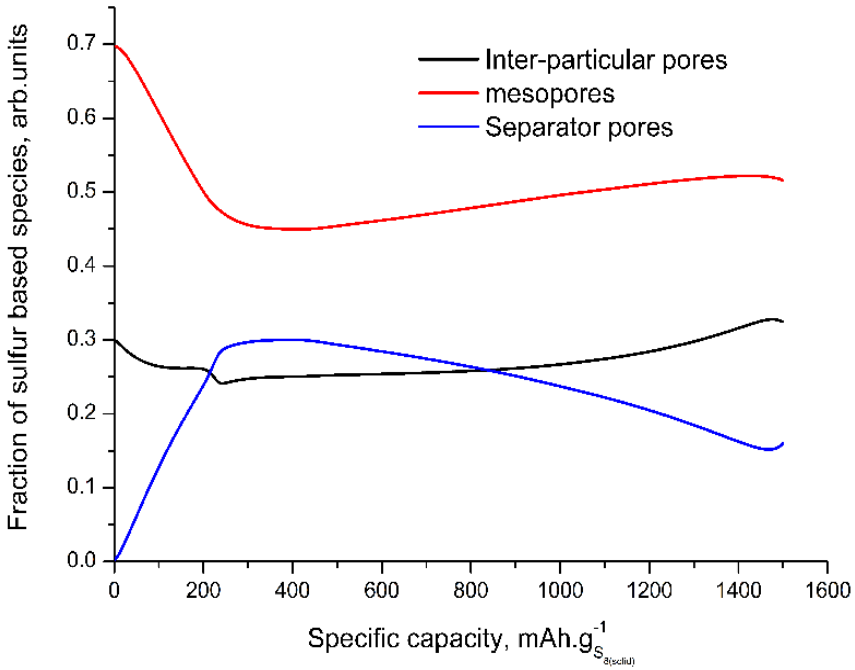
CALCULATED RATE CAPABILITIES (3/3)

Li_2S film growth near the separator
(tunneling distance: 10 nm)



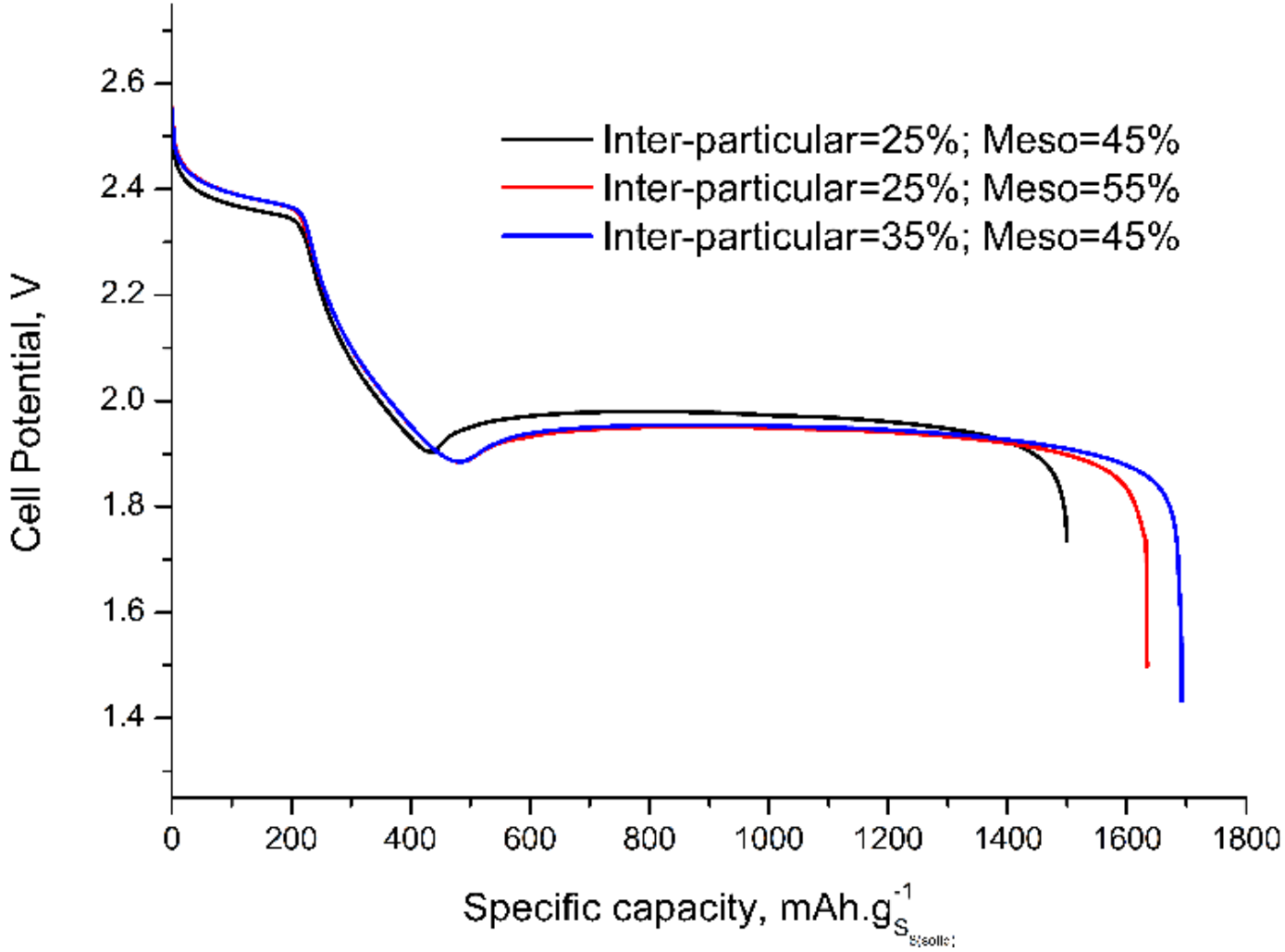
1.0 mA.cm^{-2}

Exchange of sulfur between various domains



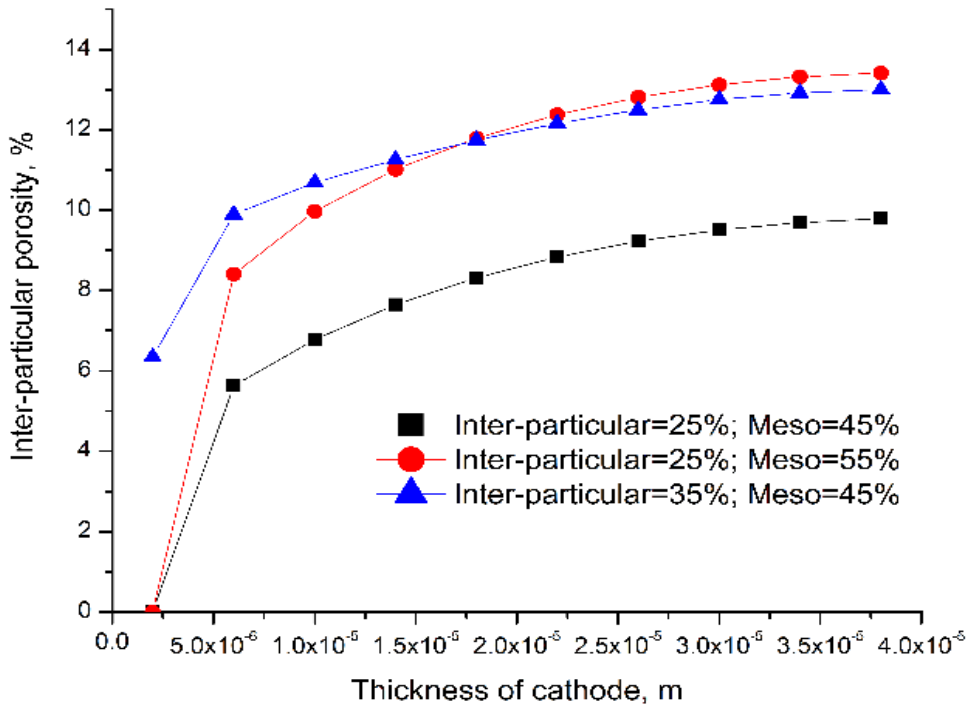
Still sulfur in separator at the end of discharge

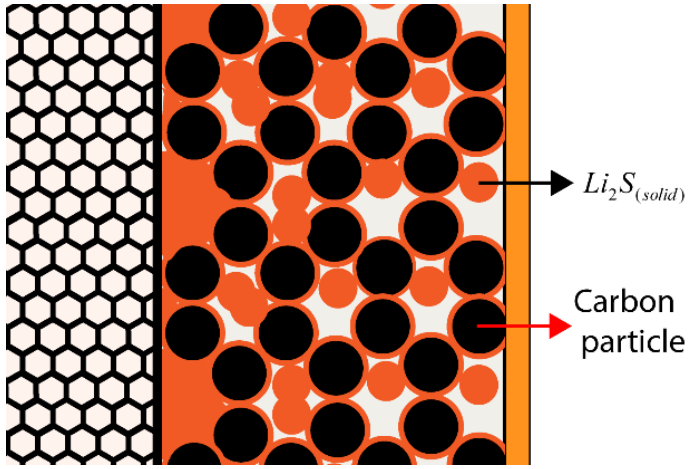
IMPACT OF CARBON POROSITY (1/2)



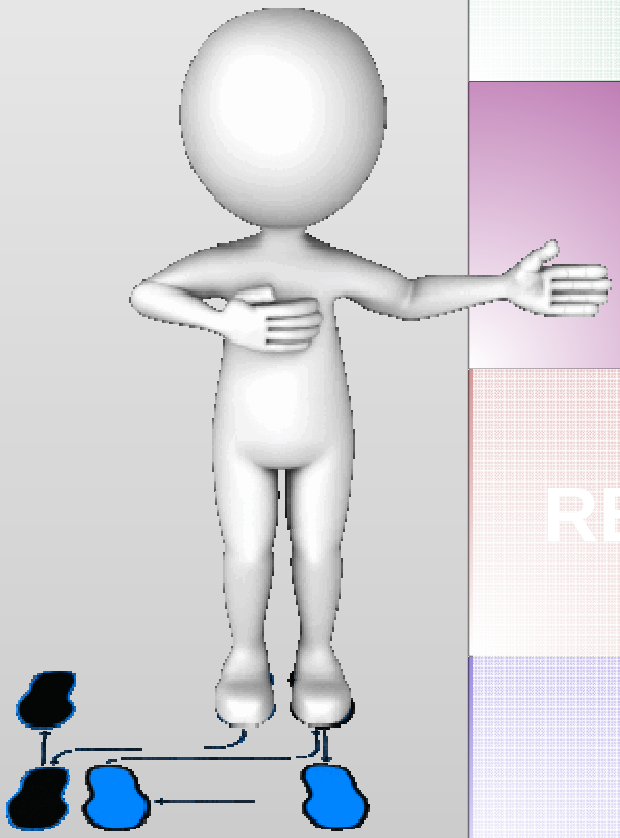
IMPACT OF CARBON POROSITY (2/2)

End of discharge





↳ For the cathodes containing 25% of carbon inter-particle porosity, discharge stops due to clogging of the inter-particle pores.



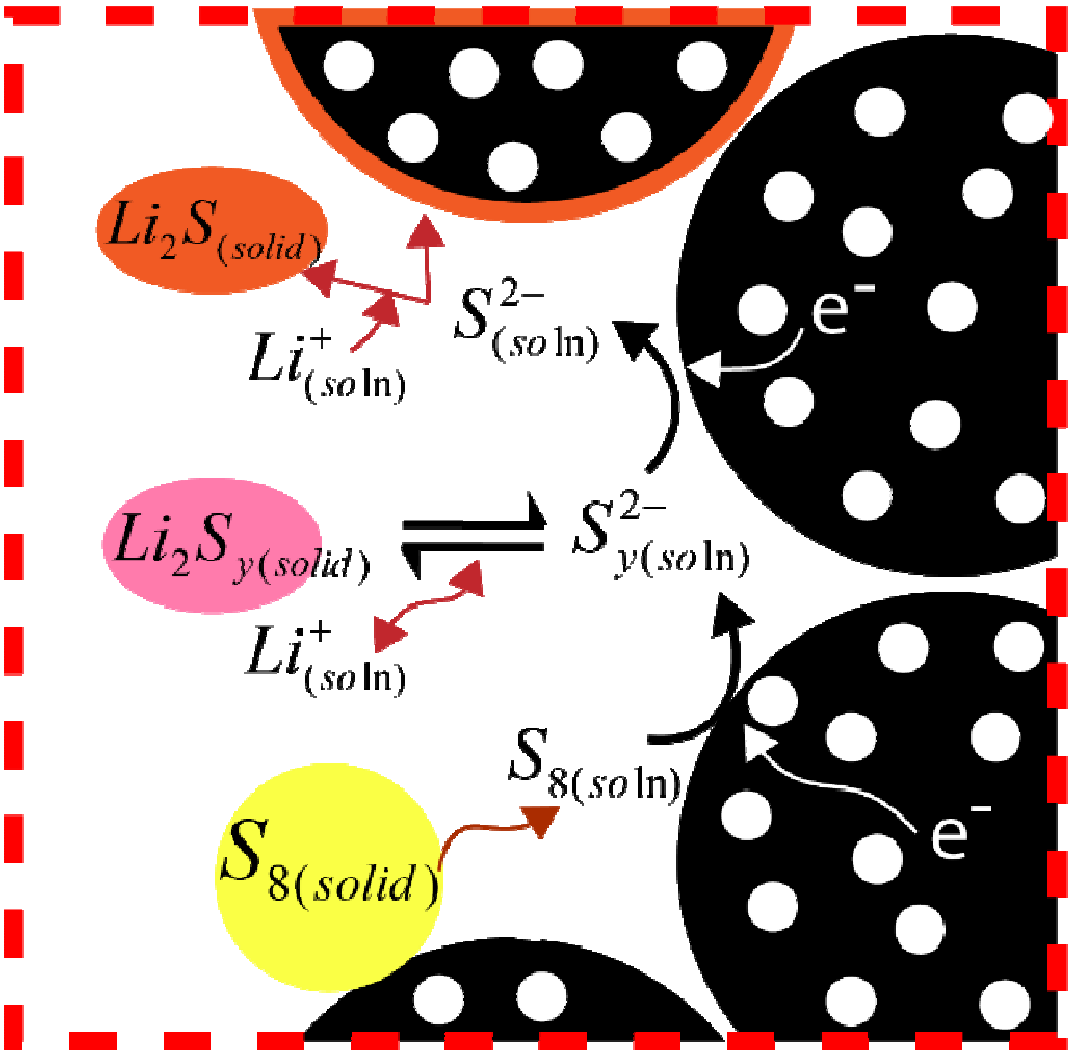
Li-S BATTERIES I: CONTINUUM

Li-S BATTERIES II: kMC

REDOX FLOW BATTERIES: kMC

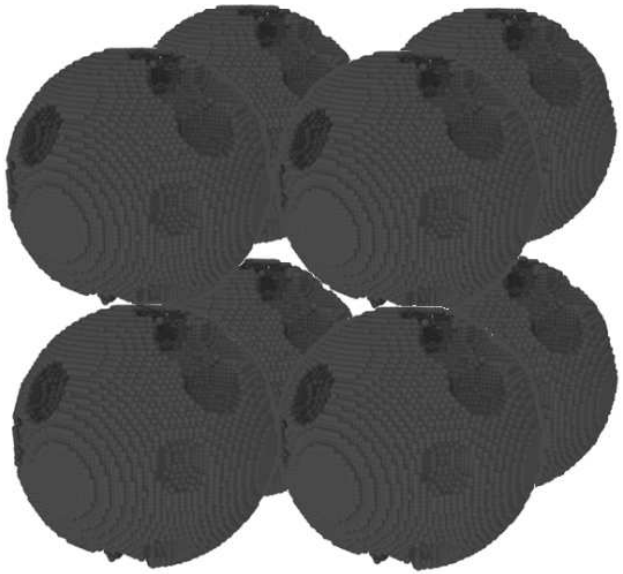
PEM FUEL CELLS: HYBRID

CHALLENGES & OPPORTUNITIES

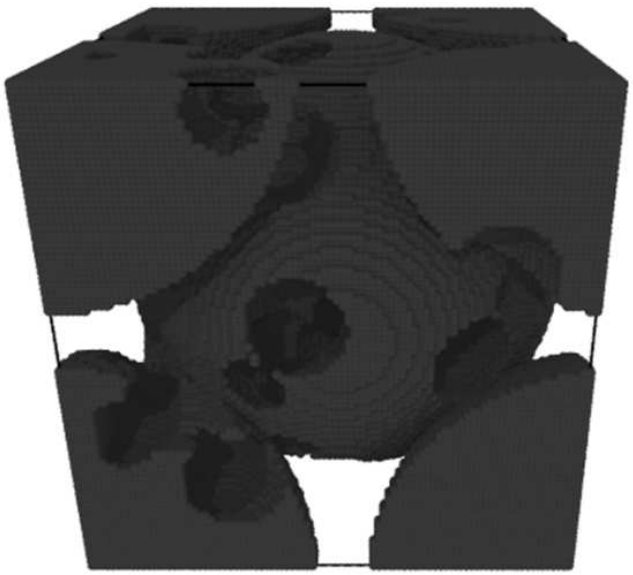


Cathode side

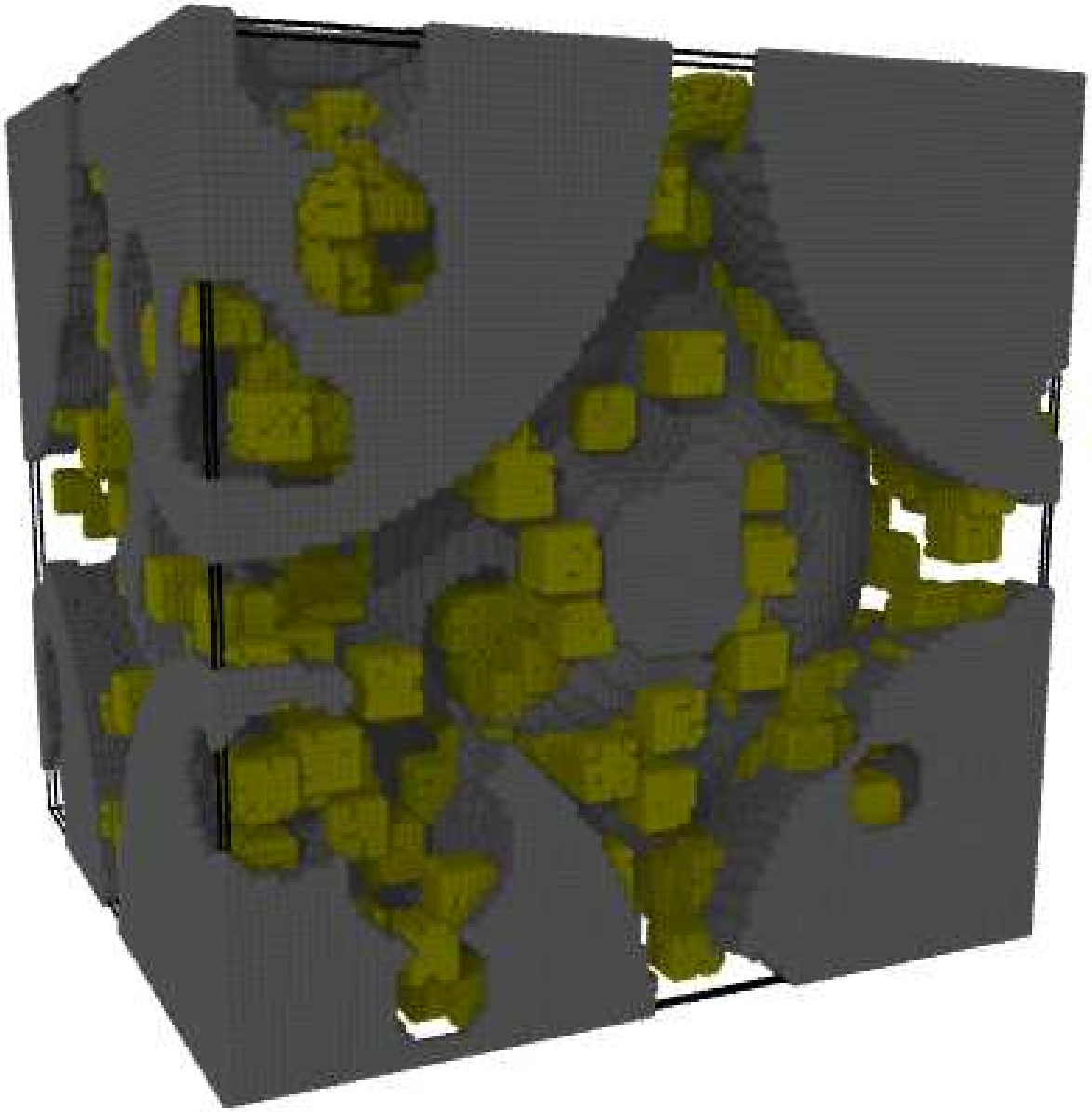
y: 8, 6, 4 & 2

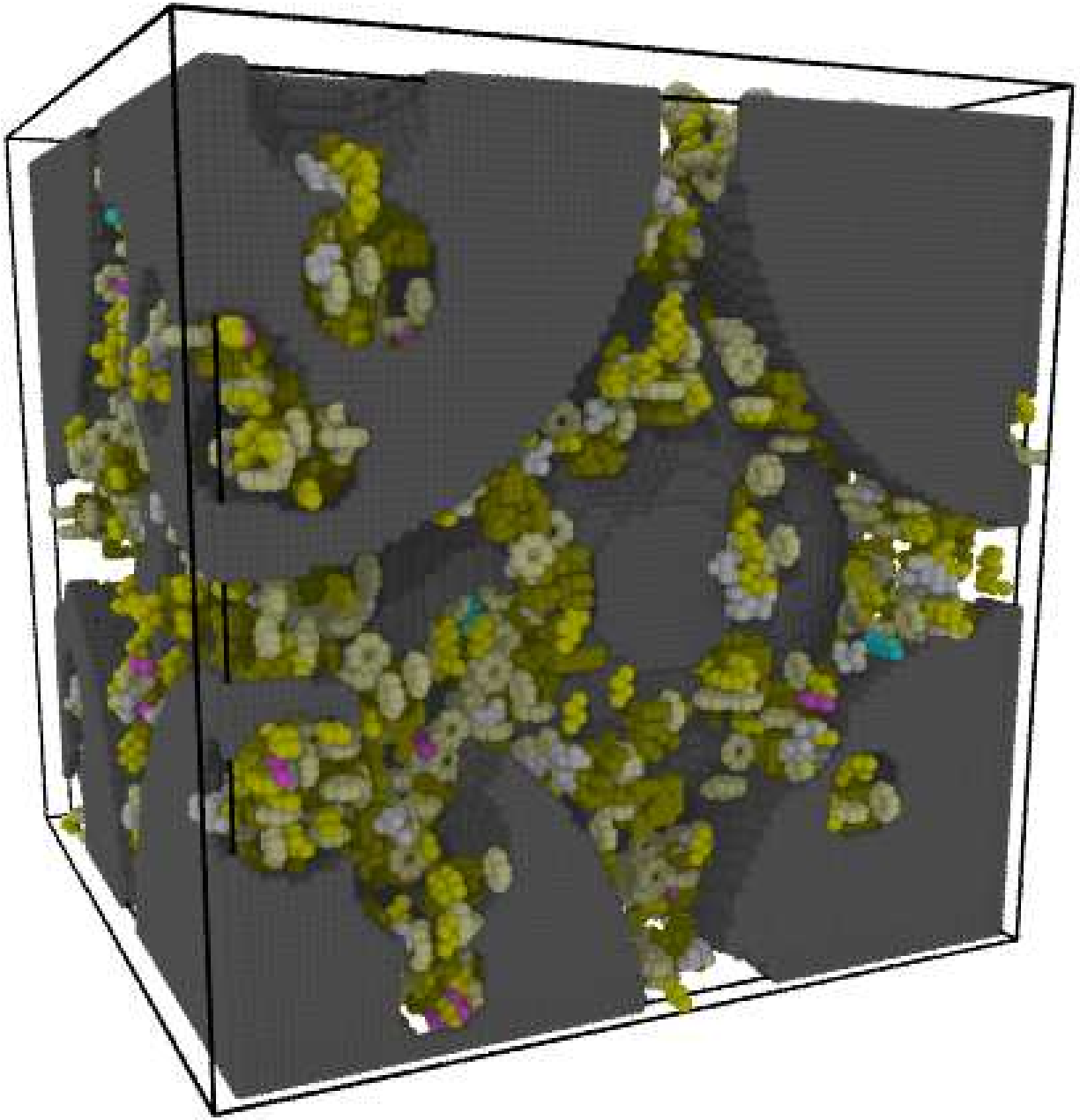


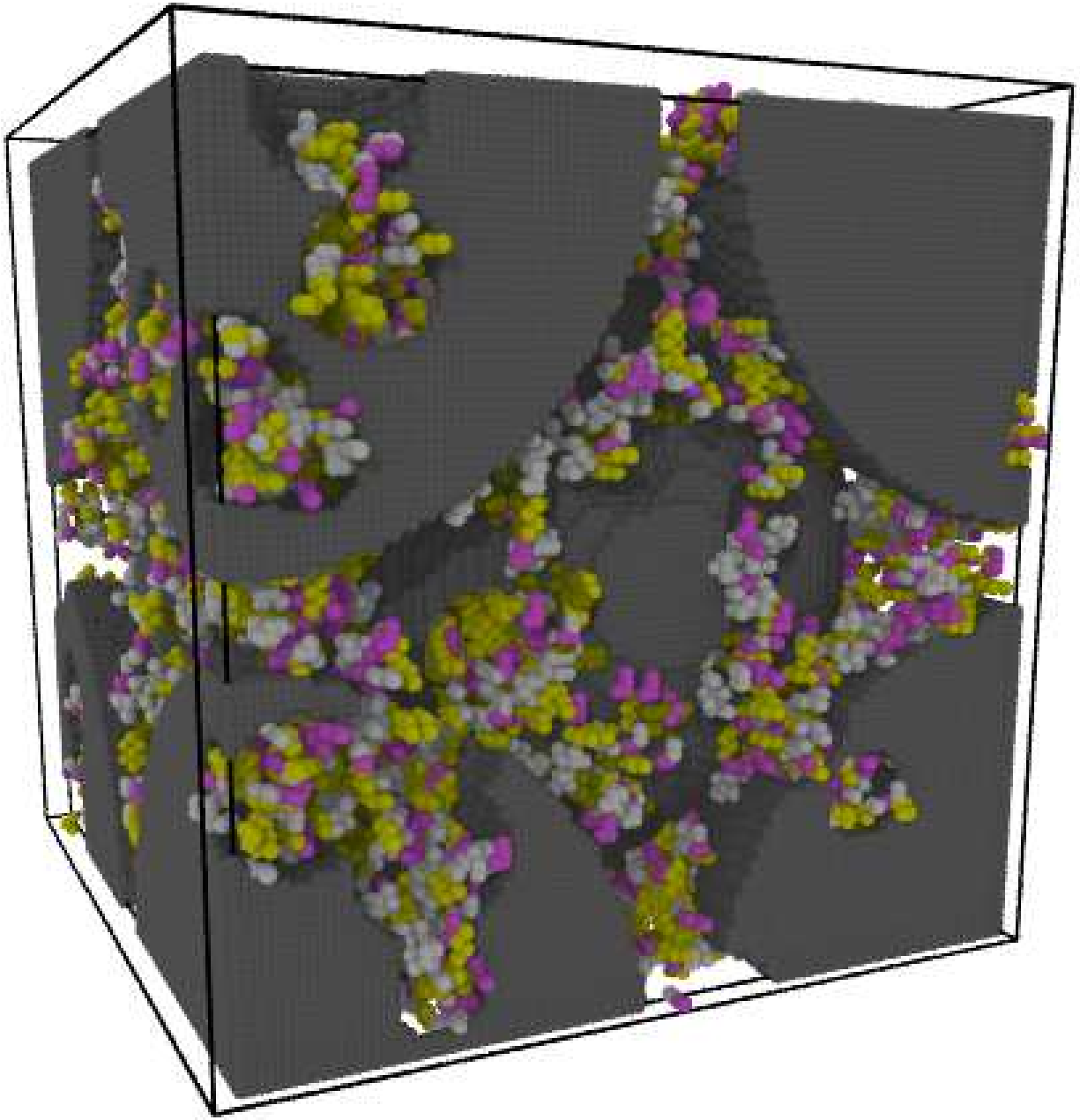
SC

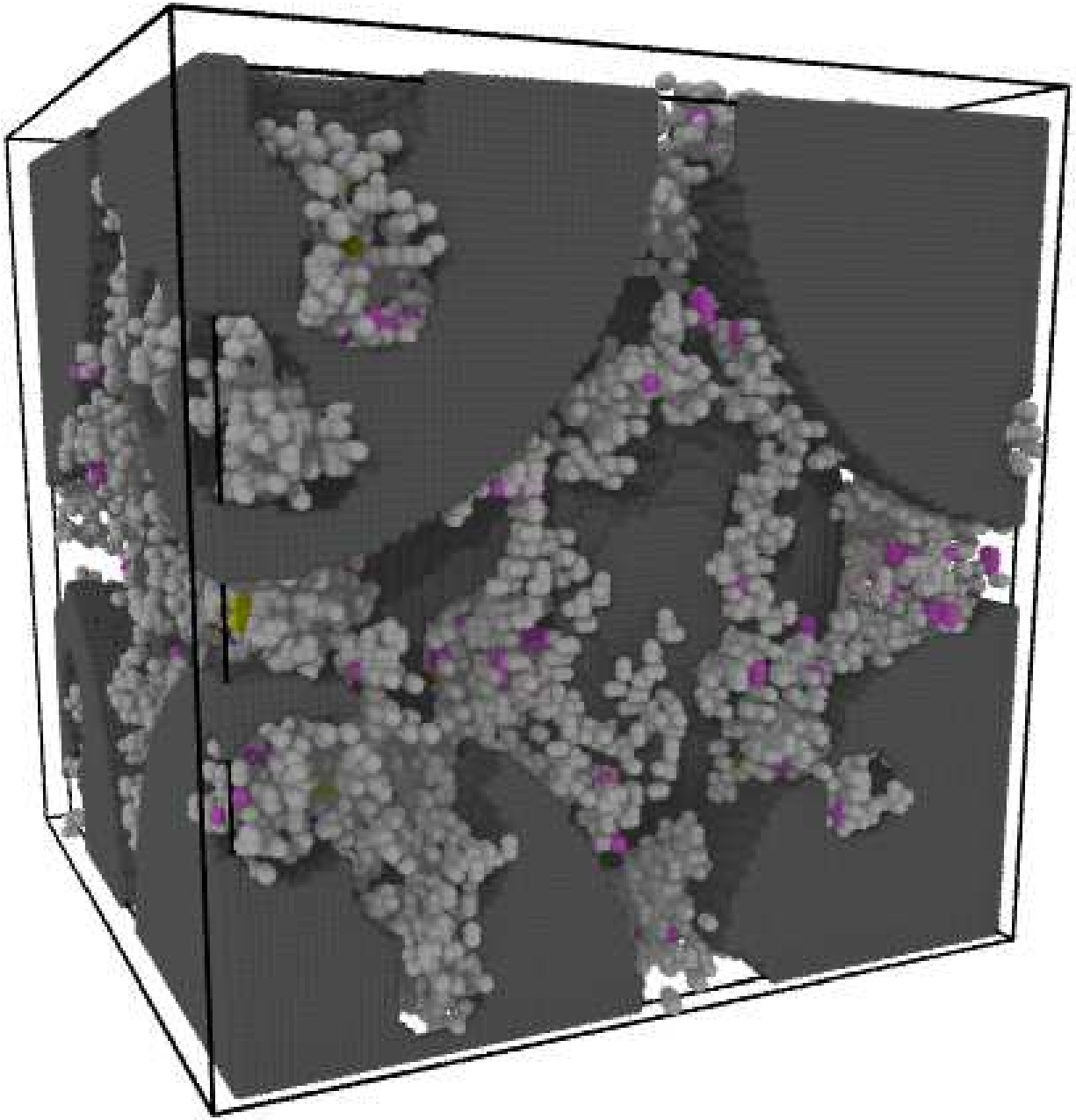


BCC



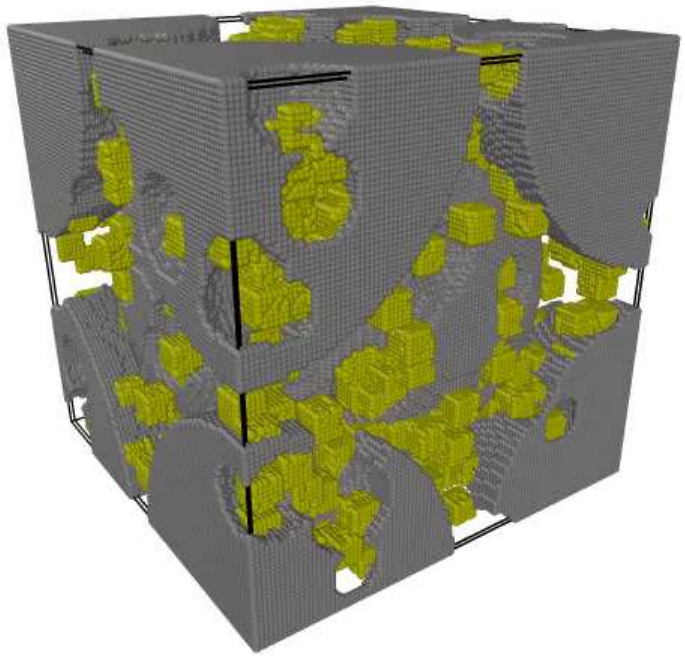


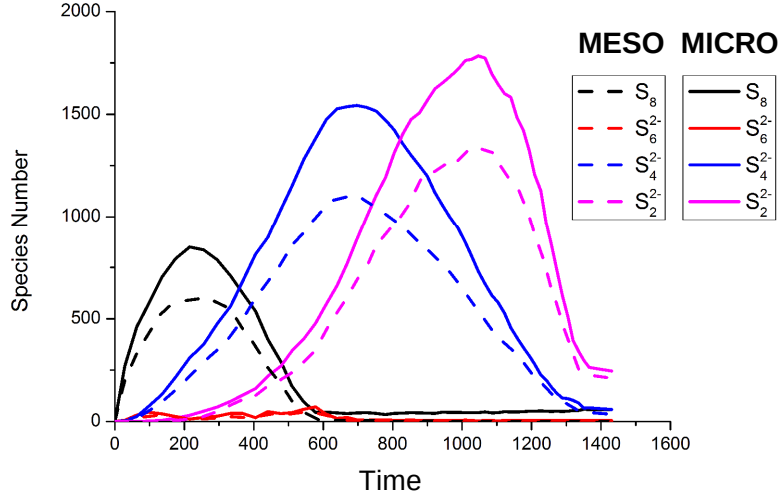


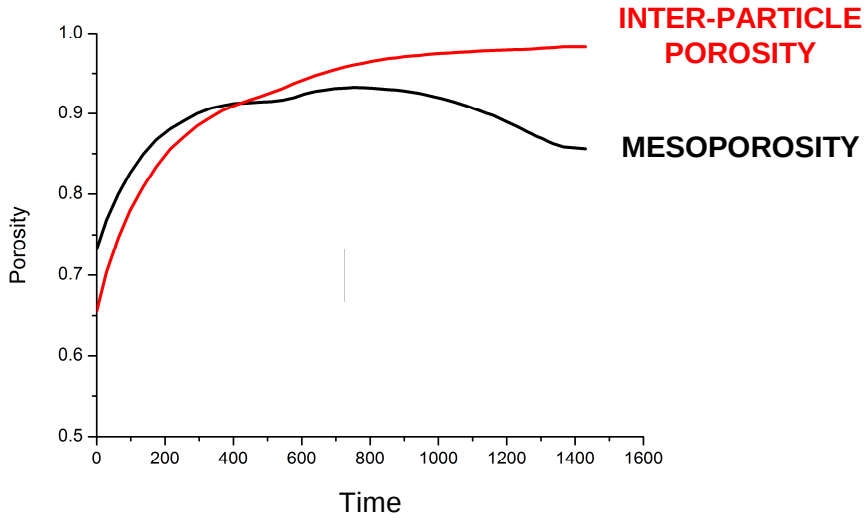


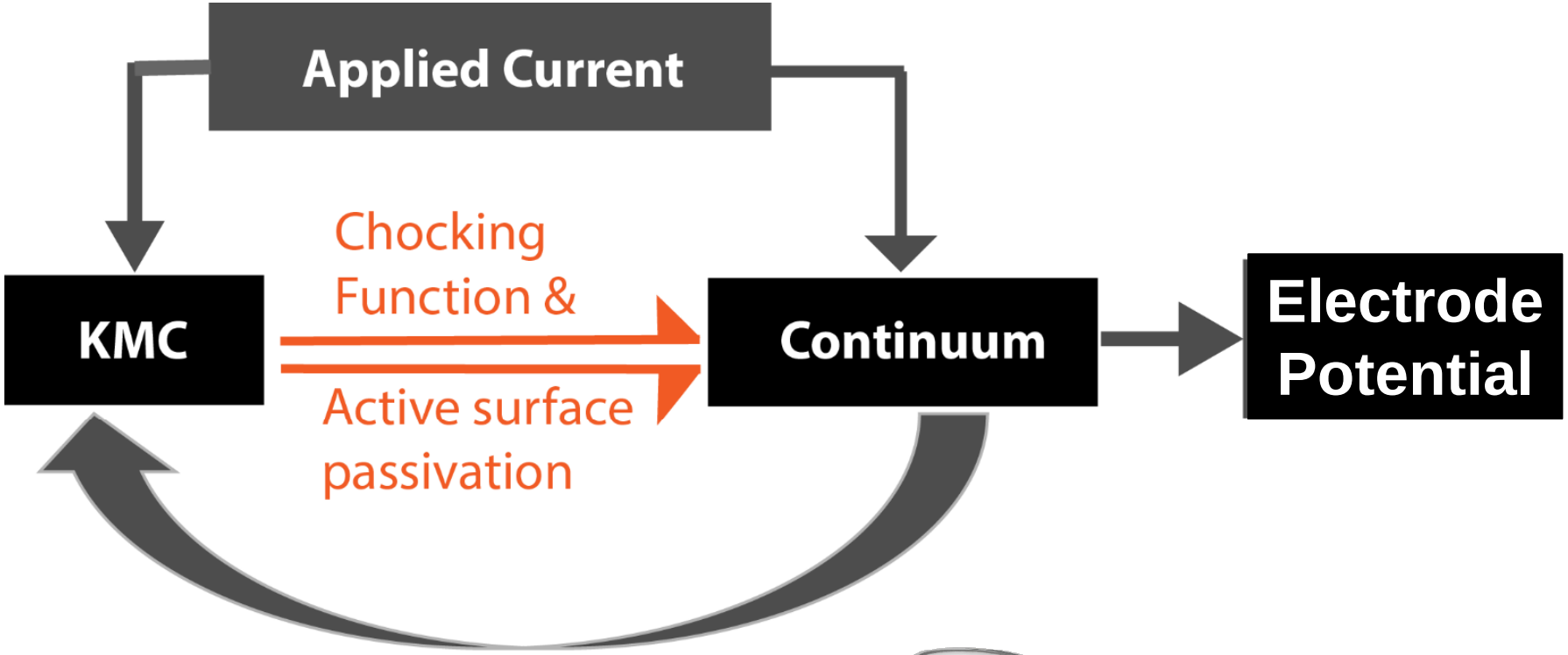
CALCULATED C/S SYSTEM EVOLUTION

- Porosity = 0.7
- Sulfur loading= 1/1 volume of carbon
- C-rate = 1.5 mA/cm^2








Applied Current
KMC
Chocking
Function &
Active surface
passivation
Continuum
Electrode
Potential
Carbon particles
packing & its
Porous structure

Li-S BATTERIES I: CONTINUUM

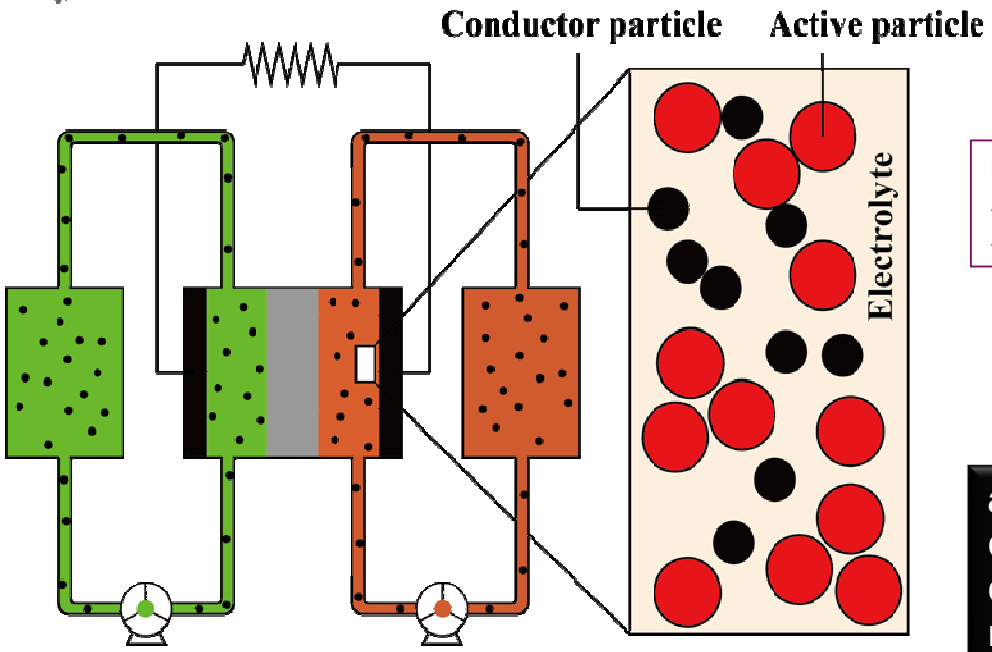
Li-S BATTERIES II: kMC

REDOX FLOW BATTERIES: kMC

PEM FUEL CELLS: HYBRID

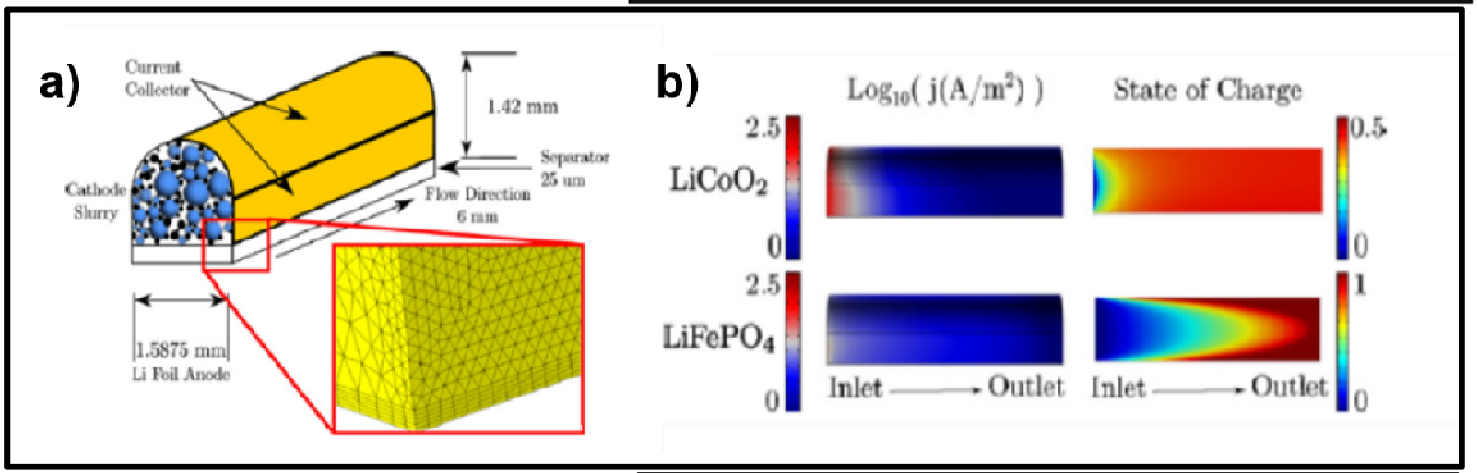
CHALLENGES & OPPORTUNITIES

SLURRY-BASED REDOX FLOW BATTERIES



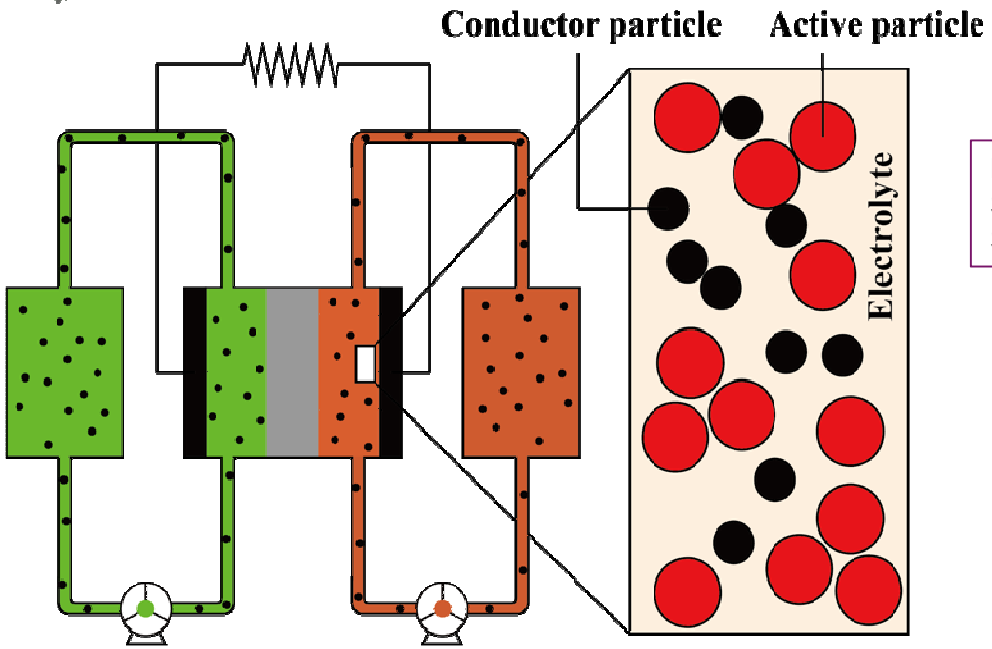
M. Duduta *et al.*, *Adv. Energy Mater.*, **1** (2011) 511.
S. Hamelet *et al.*, *J. Electrochem. Soc.*, **159** (8) (2012) A1360.
S. Hamelet *et al.*, *J. Electrochem. Soc.*, **160** (3) (2013) A516.

a) Continuum model of a SRFB; **b)** calculated current densities and states of charge along the cathode channel for two types of activation materials.



K.C. Smith *et al.*, *J. Electrochem. Soc.*, **161** (4) (2014) A486.

SLURRY-BASED REDOX FLOW BATTERIES



M. Duduta *et al.*, *Adv. Energy Mater.*, **1** (2011) 511.
S. Hamelet *et al.*, *J. Electrochem. Soc.*, **159** (8) (2012) A1360.
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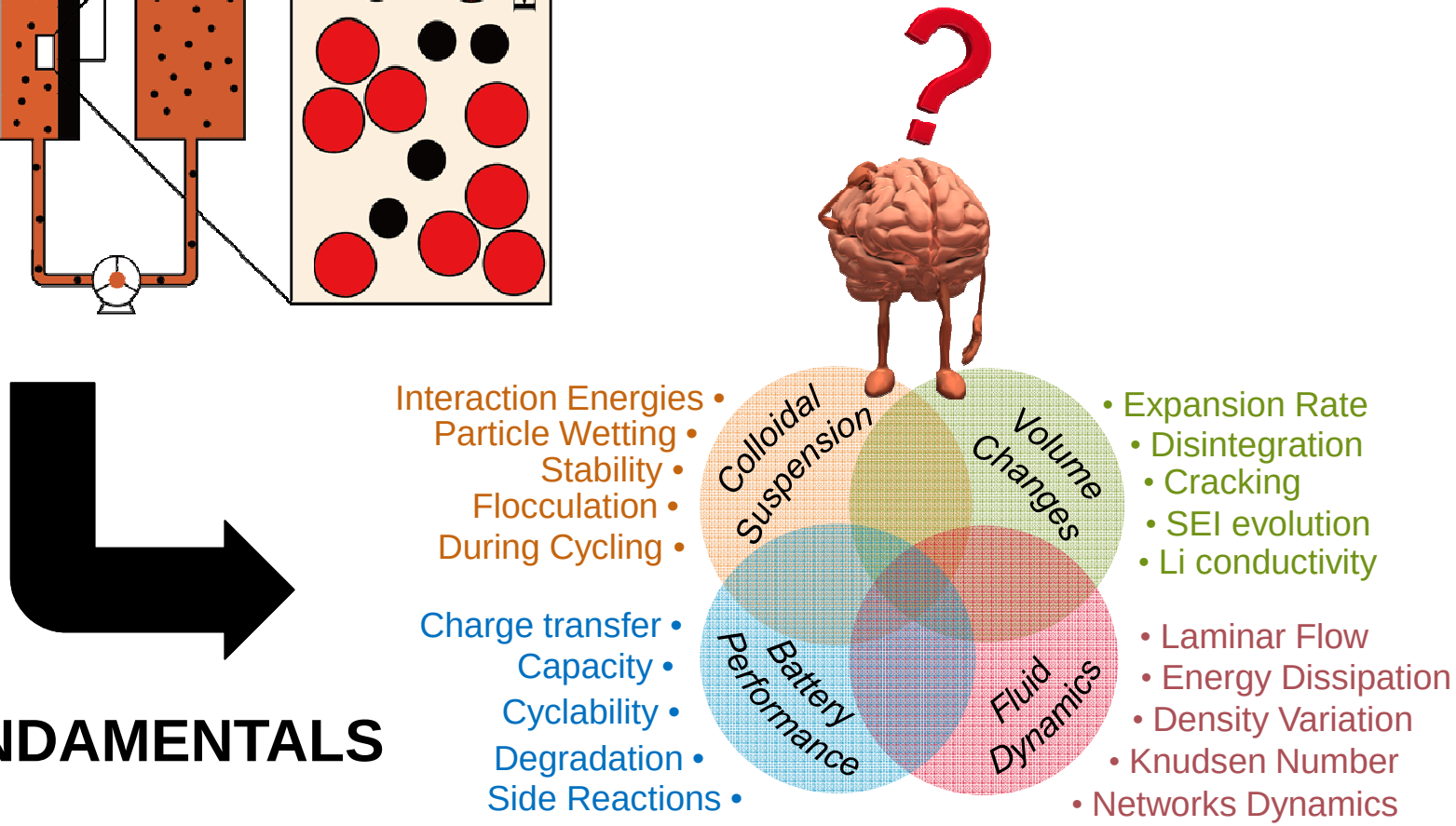
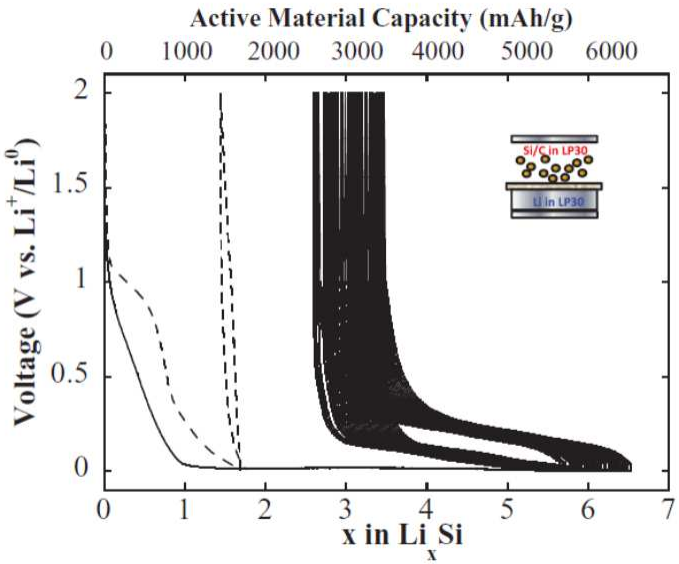


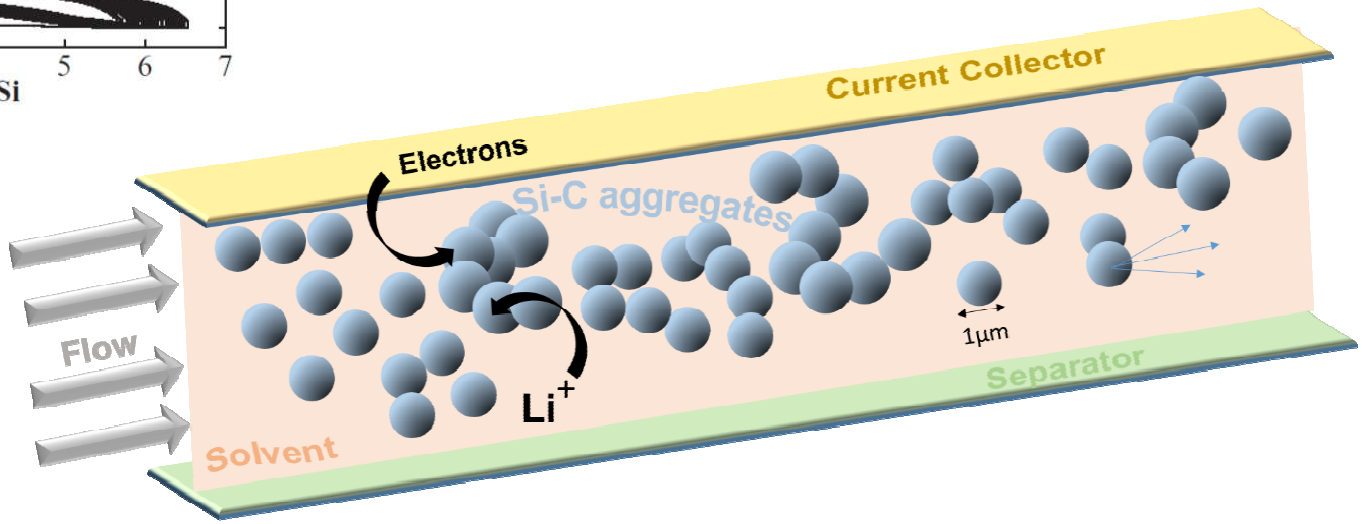
FUNDAMENTALS

SILICON/C SLURRY-BASED REDOX FLOW BATTERIES



S. Hamelet *et al.*, *J. Electrochem. Soc.*, **159** (8) (2012) A1360.
S. Hamelet *et al.*, *J. Electrochem. Soc.*, **160** (3) (2013) A516.

GOAL: develop a model describing the electrochemical behavior of the Si/C slurry under static and flow conditions.



Prof. Alejandro A. Franco

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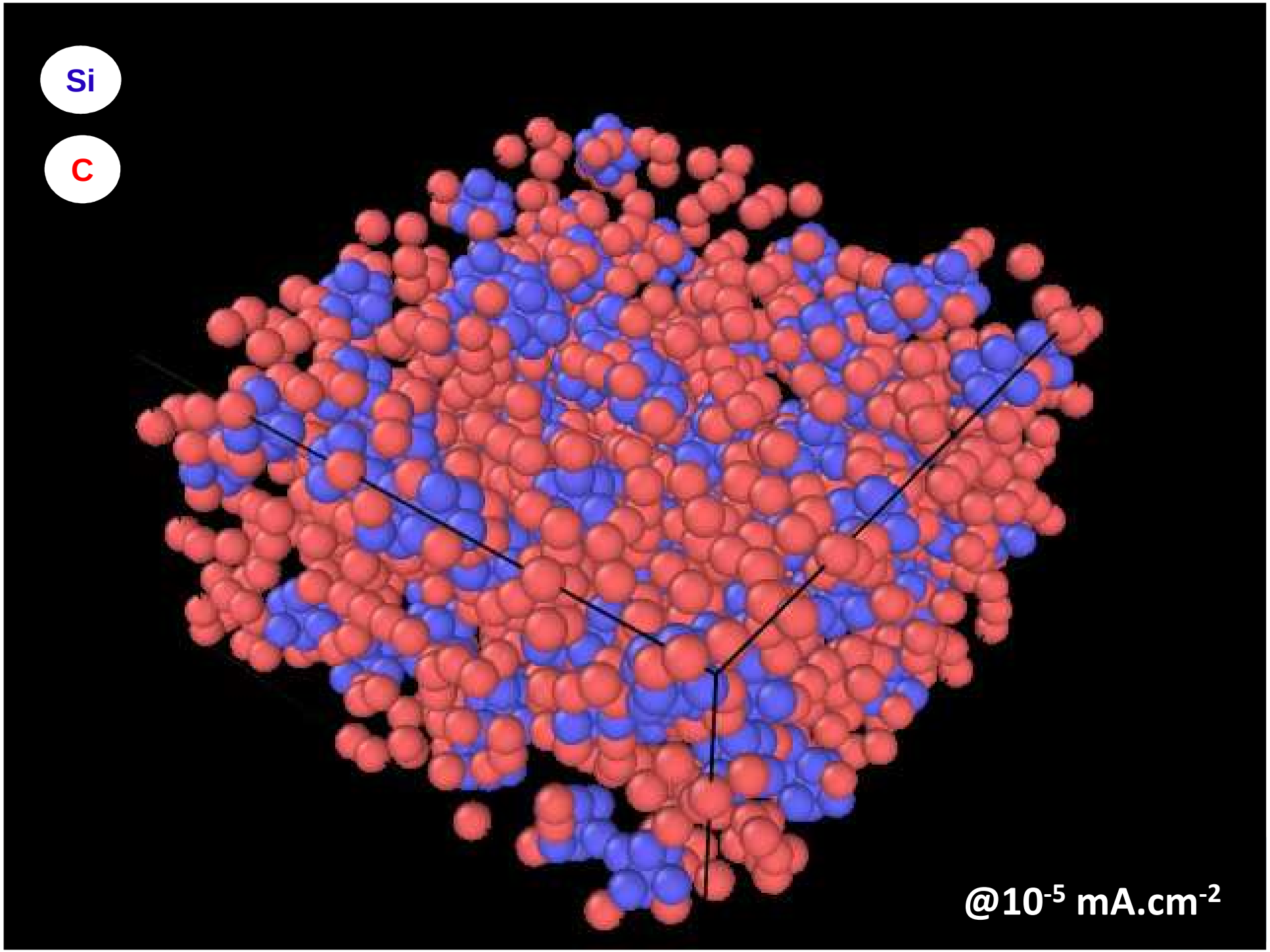
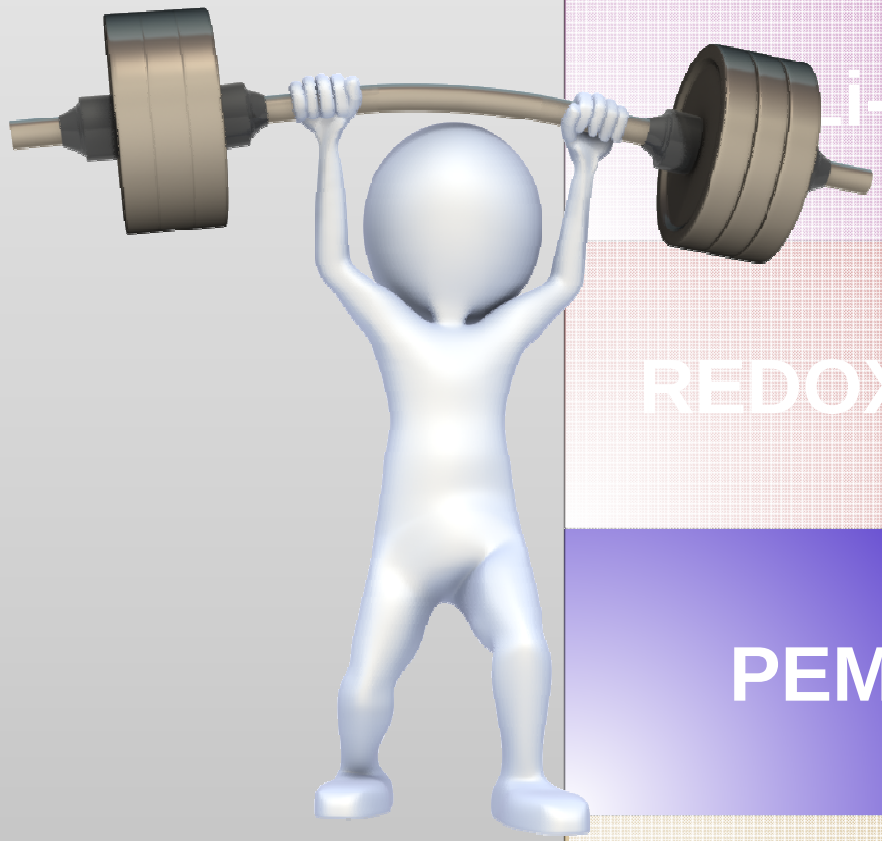

Si
C
@10-5 mA.cm-2



Li-S BATTERIES I: CONTINUUM

Li-S BATTERIES II: kMC

REDOX FLOW BATTERIES: kMC

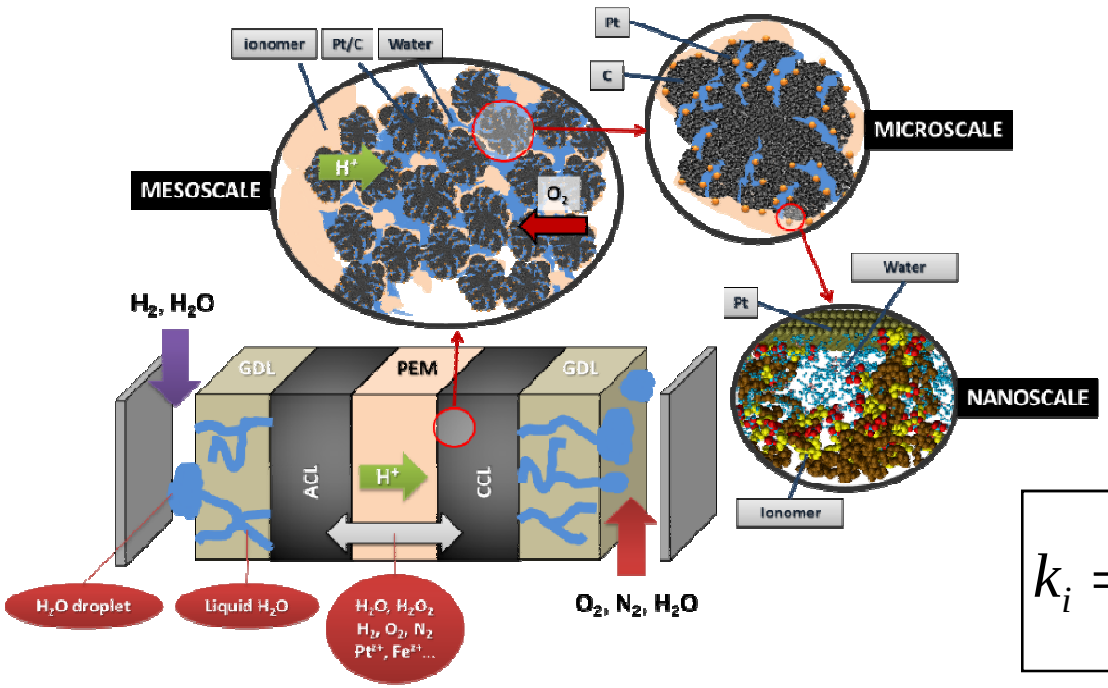
PEM FUEL CELLS: HYBRID

CHALLENGES & OPPORTUNITIES

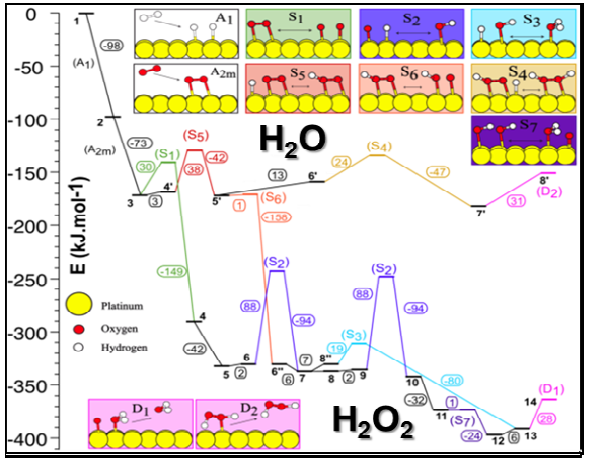
DFT

A 14-YEARS-OLD PEM FUEL CELL MODEL

Performance model



ORR DFT-calculated activation energies



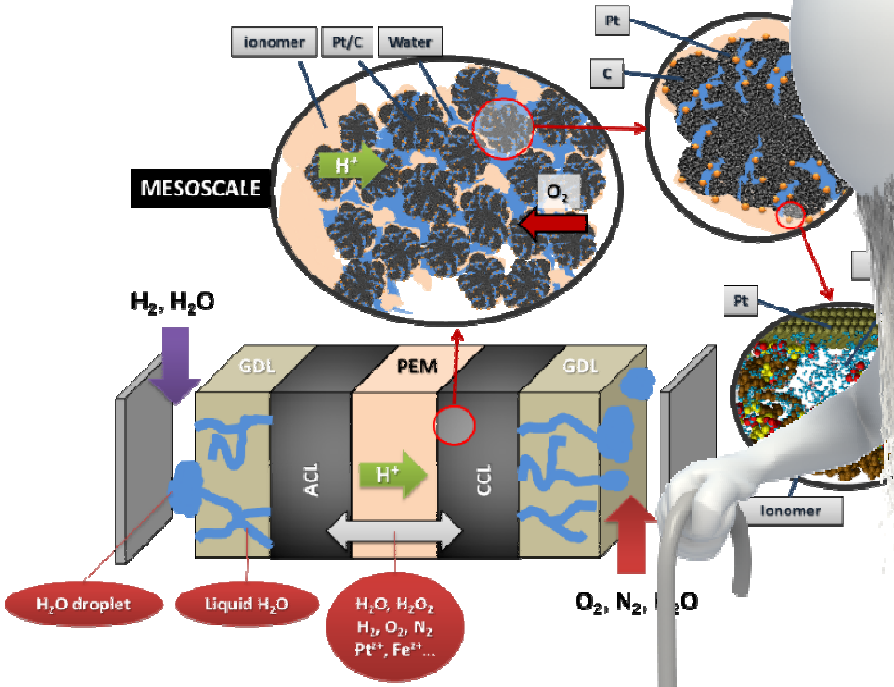
$$k_i = \nu \frac{k_B T}{h} \exp\left(\frac{-E_{act} + f(\sigma)}{RT}\right)$$

elementary act	E_{act}^{fwd} (kJ mol^{-1})				E_{act}^{bwd} (kJ mol^{-1})					ΔE_{reac} (kJ mol^{-1})		
θ_{OH} (ML)	0	1/6	1/3	1/2	0	1/6	1/3	1/2	0	1/6	1/3	1/2
(S1) $O_{2(ads)} \rightarrow 2O_{(ads)}$	30	31	44	51	149	137	150	150	−119	−106	−106	−99
(S6) $O_{2(ads)} + H_{(ads)} \rightarrow OOH_{(ads)}$	38	35	40	35	42	56	53	56	−3	−21	−13	−21
(S2) $O_{(ads)} + H_{(ads)} \rightarrow OH_{(ads)}$	88	90	84	80	94	100	108	115	−6	−10	−24	−34
(S3) $OH_{(ads)} + H_{(ads)} \rightarrow H_2O_{(ads)}$	19	16	15	23	80	85	94	157	−61	−69	−78	−133
(S9) $OOH_{(ads)} + H_{(ads)} \rightarrow H_2O_{2(ads)}$	24	33	23	–	46	52	57	–	−23	−18	−34	–
(S7) $OOH_{(ads)} \rightarrow OH_{(ads)} + O_{(ads)}$	0	5	4	–	158	156	199	–	−159	−152	−195	–
(S4) $2OH_{(ads)} \rightarrow H_2O_{(ads)} + O_{(ads)}$	1	5	5	–	24	25	26	–	−24	−20	−21	–

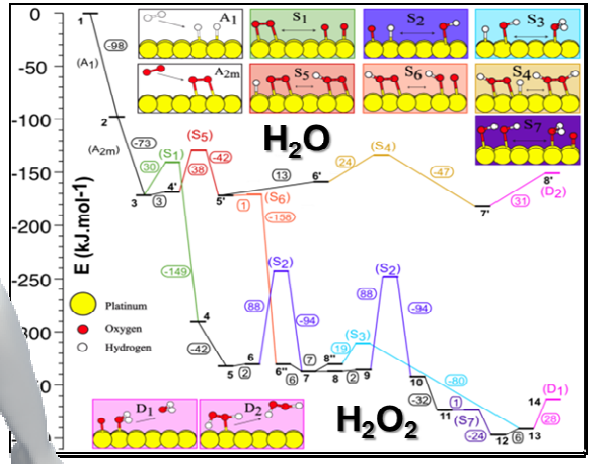
a) A.A. Franco et al., *J. Electrochem. Soc.* **153** (6) (2006) A1053; **b)** A.A. Franco et al., *Fuel Cells* **7** (2007) 99; **c)** R.F. de Morais, D. Loffreda, P. Sautet, A.A. Franco, *Electrochim. Acta*, **56**, (2011) 10842; **d)** R.F. de Morais, A.A. Franco, P. Sautet, D. Loffreda, *ACS Catalysis*, **5** (2015) 1068.

A 14-YEARS-OLD PEM FUEL CELL MODEL

Performance model



ORR DFT-calculated activation energies



$$\frac{k_B T}{h} \exp\left(\frac{-E_{act} + f(\sigma)}{RT}\right)$$

elementary act	E_{act}^{fwd} (kJ mol^{-1})				(kJ mol^{-1})				ΔE_{reac} (kJ mol^{-1})		
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(S1) $O_{2(ads)} \rightarrow 2O_{(ads)}$	30	31	44	51	13	150	150	−119	−106	−106	−99
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(S2) $O_{(ads)} + H_{(ads)} \rightarrow OH_{(ads)}$	88	90	84	80	100	108	115	−6	−10	−24	−34
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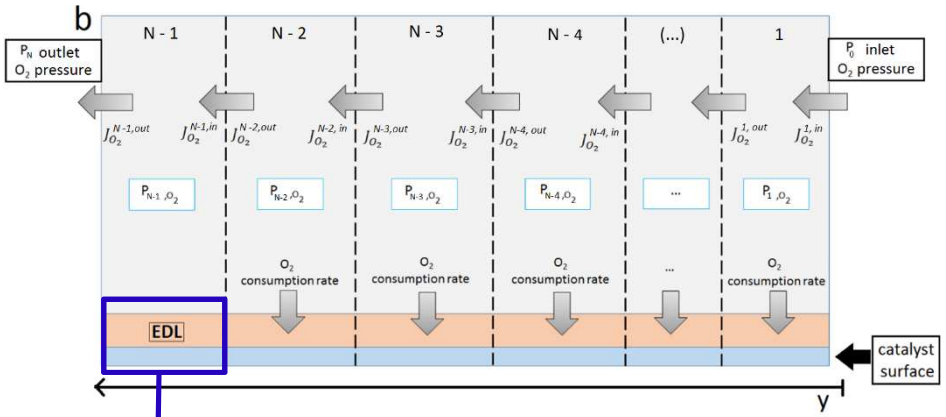
(S9) $OOH_{(ads)} + H_{(ads)} \rightarrow H_2O_{2(ads)}$	24	33	23	–			–	−23	−18	−34	–
(S7) $OOH_{(ads)} \rightarrow OH_{(ads)} + O_{(ads)}$	0	5	4	–		9	–	−159	−152	−195	–
(S4) $2OH_{(ads)} \rightarrow H_2O_{(ads)} + O_{(ads)}$	1	5	5	–		6	–	−24	−20	−21	–

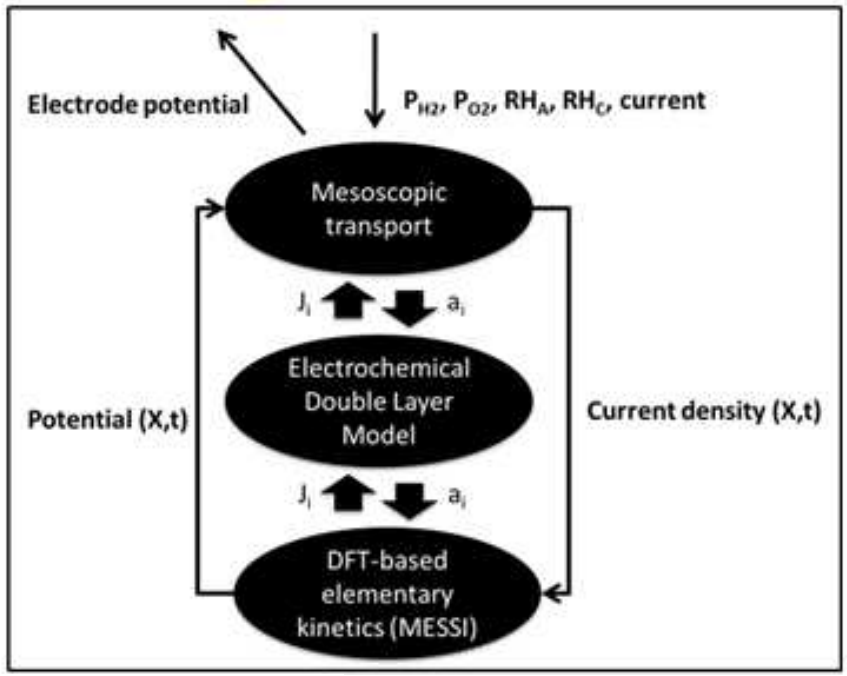
a) A.A. Franco et al., *J. Electrochem. Soc.* **153** (6) (2006) A1053; **b)** A.A. Franco et al., *Fuel Cells* **7** (2007) 99; **c)** R.F. de Morais, D. Loffreda, P. Sautet, A.A. Franco, *Electrochim. Acta*, **56**, (2011) 10842; **d)** R.F. de Morais, A.A. Franco, P. Sautet, D. Loffreda, *ACS Catalysis*, **5** (2015) 1068.

PEMFC CATHODE: COUPLING ON-THE-FLY KMC WITH CONTINUUM (1/2)

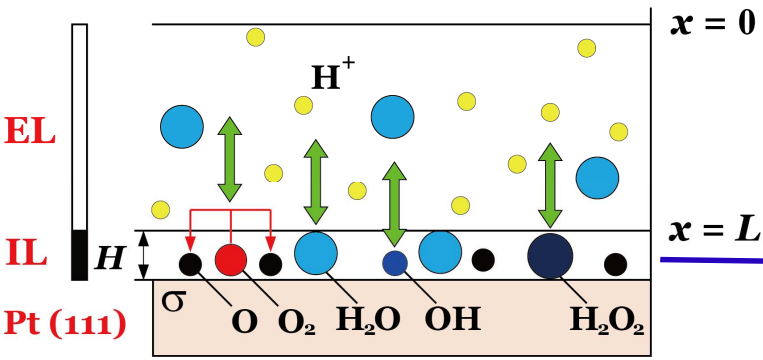
O_2 transport channel side view

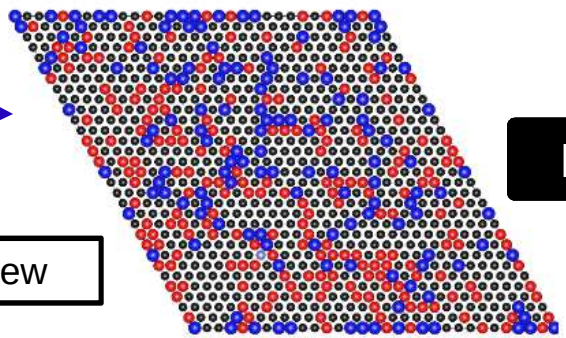


Overall algorithm



CONTINUUM





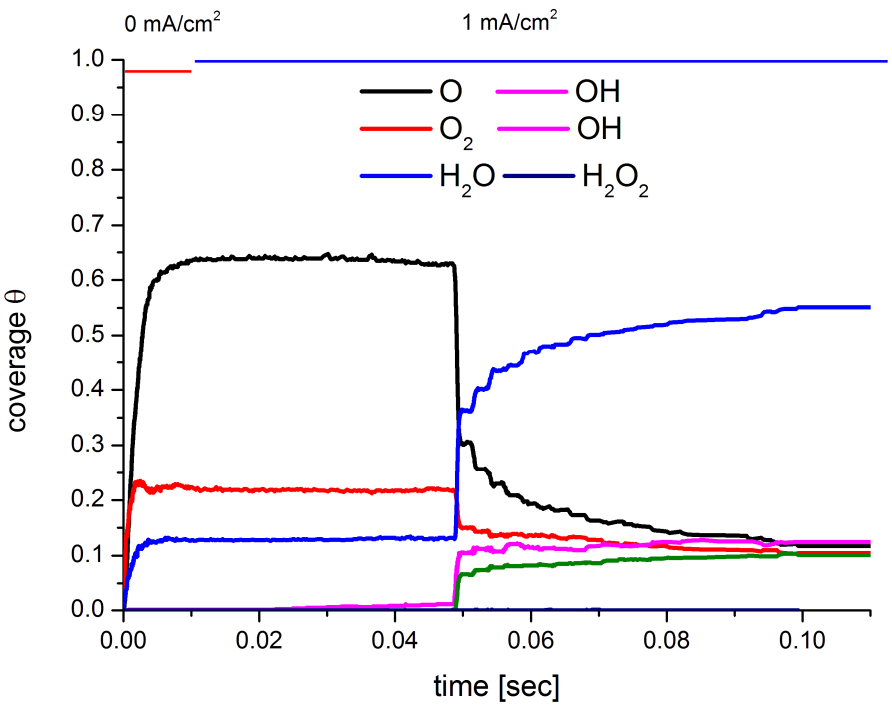
KMC

Catalyst top view

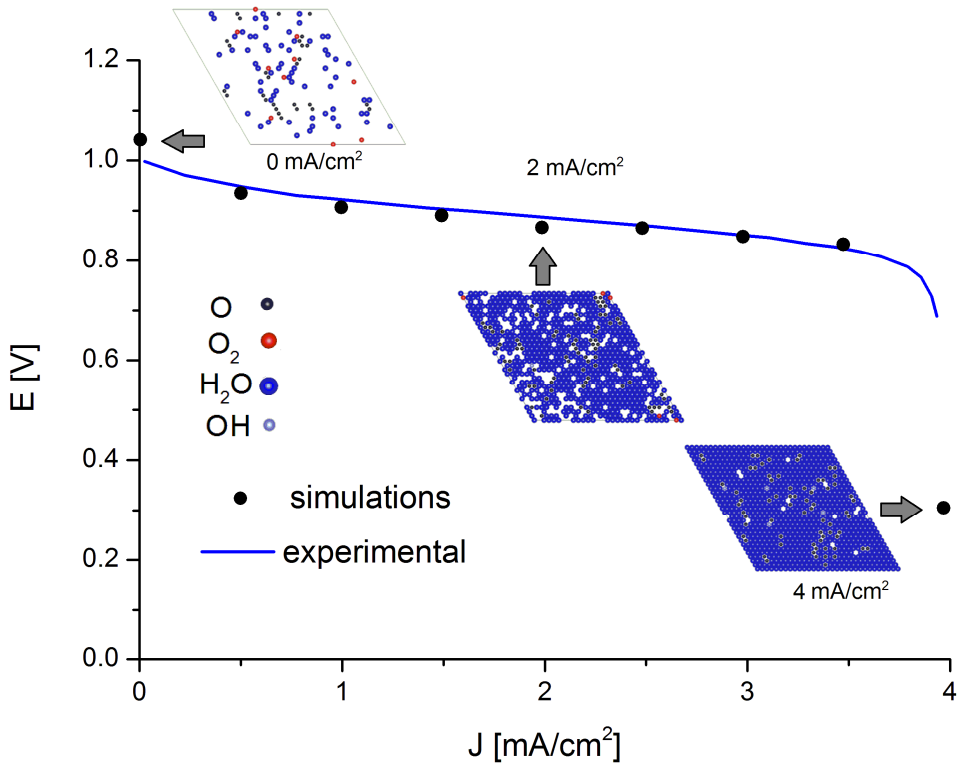
M.A. Quiroga, A.A. Franco, *J. Electrochem. Soc.*, **162** (7) (2015) E73.

PEMFC CATHODE: COUPLING ON-THE-FLY KMC WITH CONTINUUM (2/2)

COVERAGE EVOLUTION

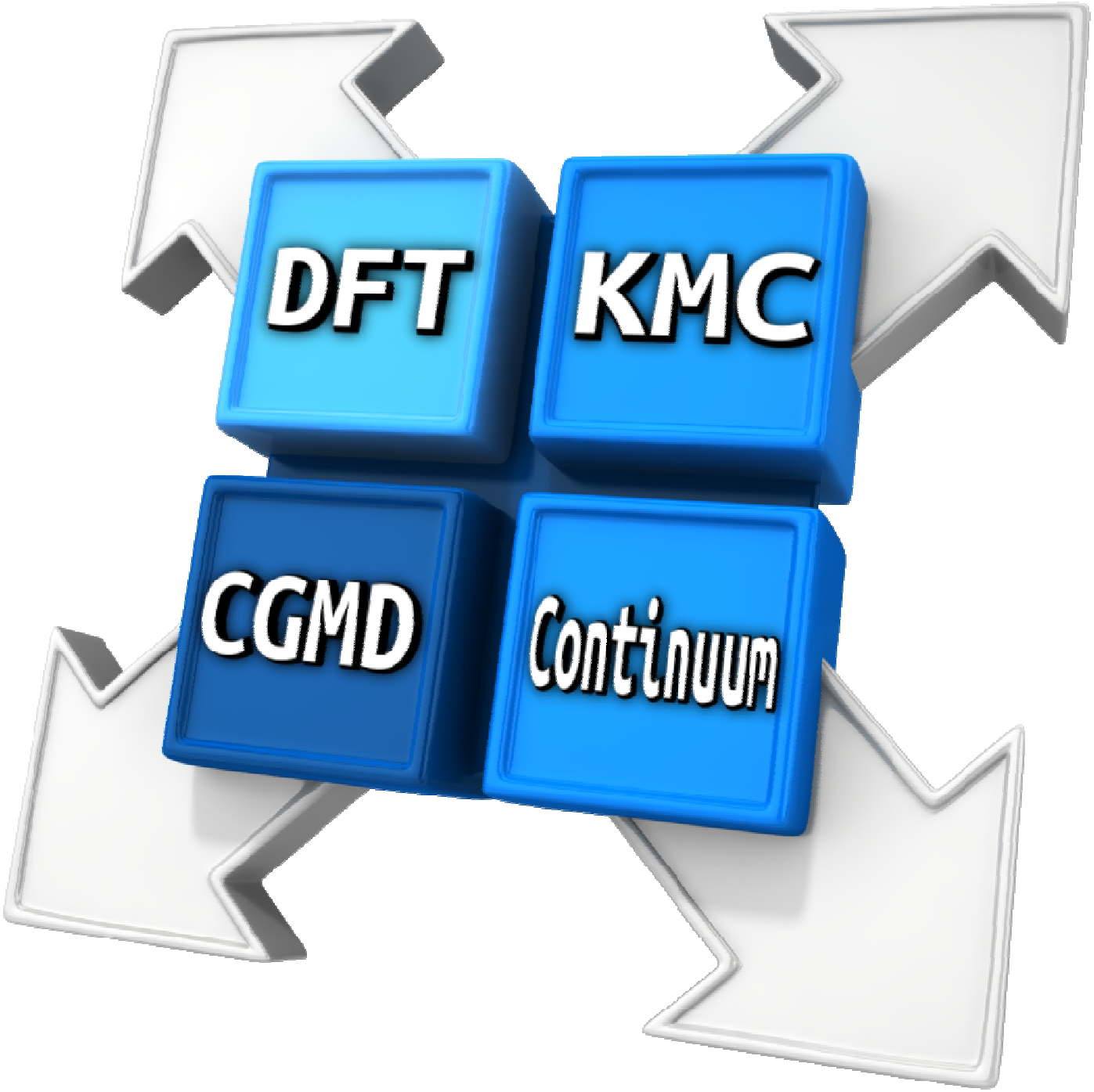


POLARIZATION CURVE



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

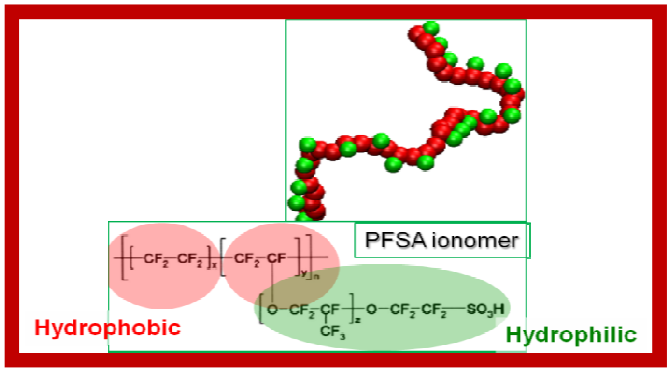
Experimental data from: Stamenkovic *et al.*, *Science* **315** (2007) 493.

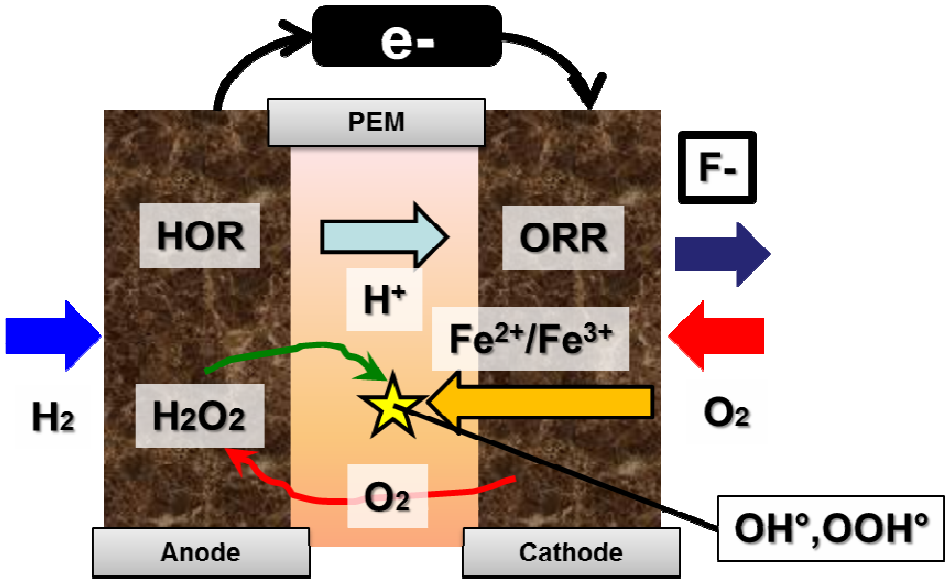

DFT
KMC
CGMD
Continuum

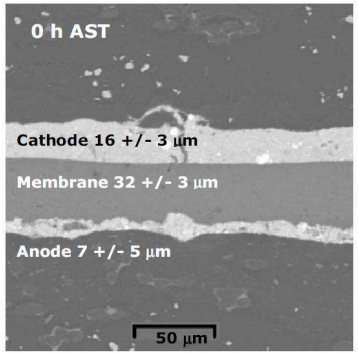
MEMBRANE DEGRADATION

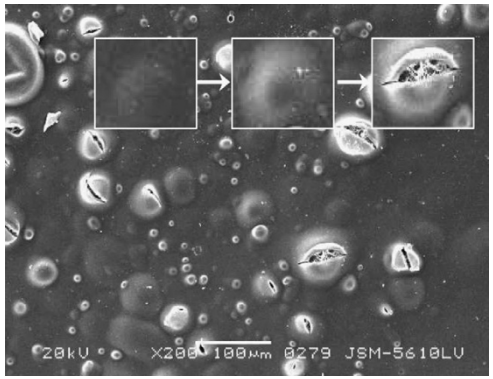
➔ **PFSA membrane degradation occurs during the PEMFC operation:**

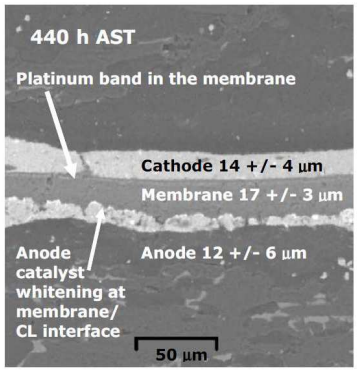
- ❑ **porosity increase**
- ❑ **thickness decrease**
- ❑ **pinhole formation**
- ❑ **fluoride ions release**

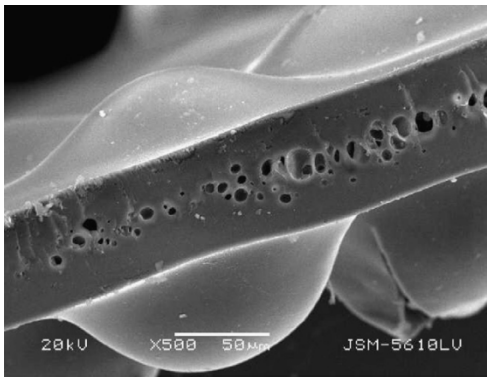






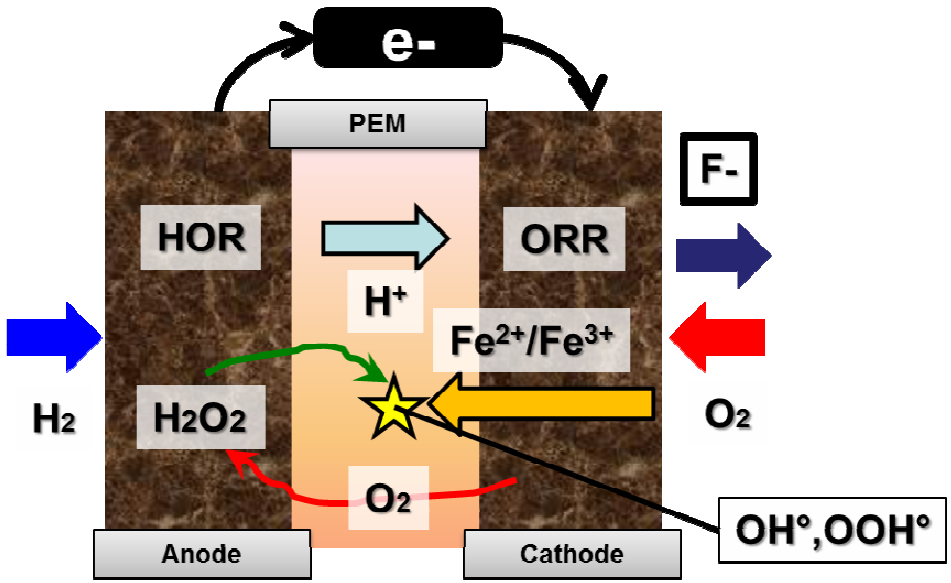




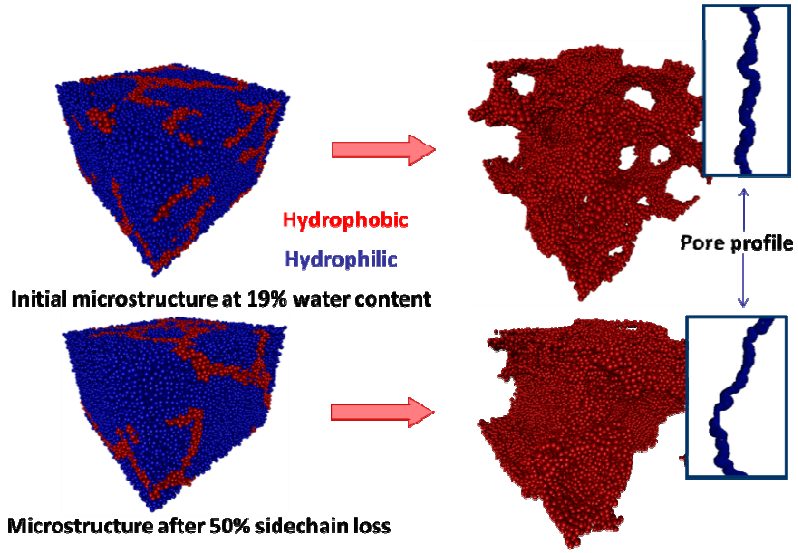


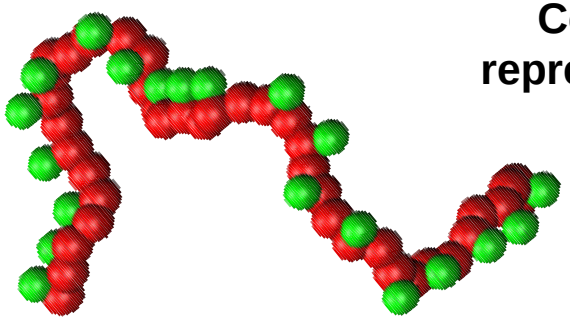
H. Tang *et al.*, *J. Power Sources.*, **170** (2007)

FULL PEMFC: COUPLING ON-THE-FLY KMC WITH CONTINUUM (1/4)



Coarse Grain MD databases



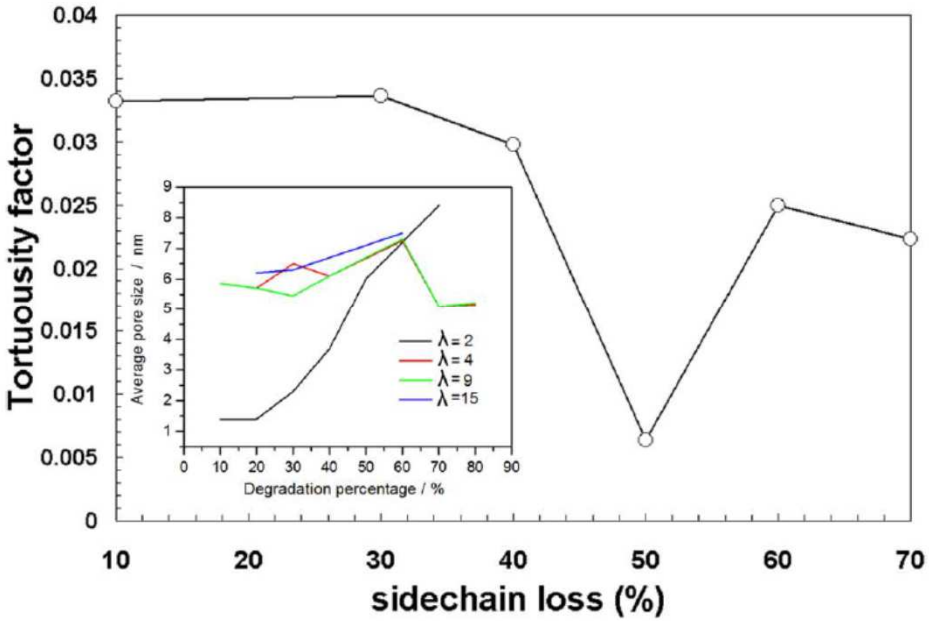


Coarse grained representation of the ionomer

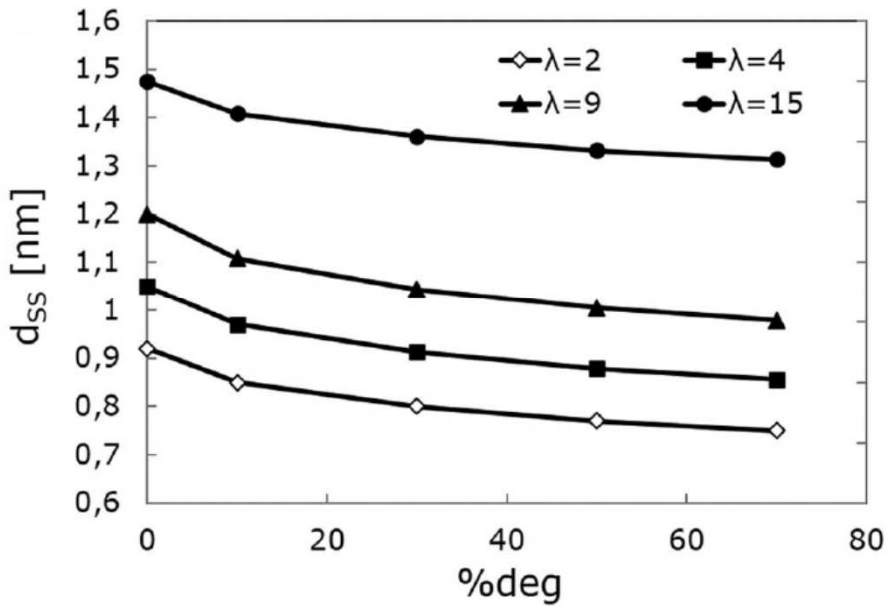
M.A. Quiroga, K. Malek, A.A. Franco, *J. Electrochem. Soc.*, **163** (2) (2016) F59.

FULL PEMFC: COUPLING ON-THE-FLY KMC WITH CONTINUUM (2/4)

Impact of degradation on the tortuosity and average pore size



Impact of degradation on the side-chain/side-chain distance



$$D_i^{eff} = \frac{\varepsilon}{\tau} D_i^0$$

$$\sigma_{H^+}^{eff} \approx D_{H^+} = \frac{l^2}{z\tau_D}$$

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ICTP, Trieste, Italy - July 13, 2016

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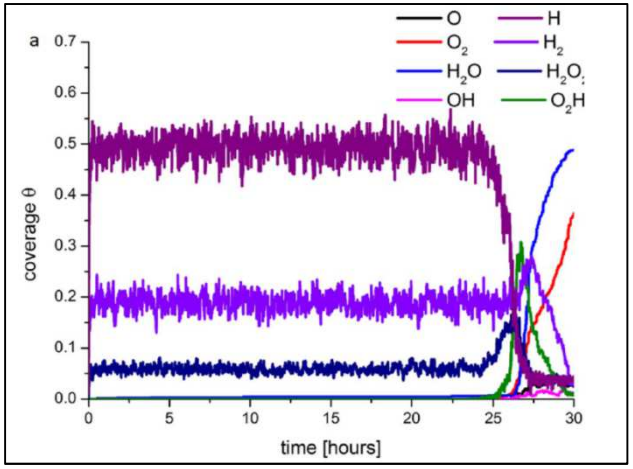
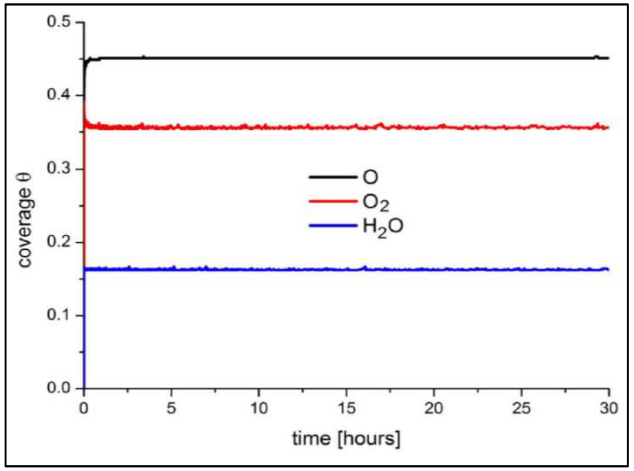
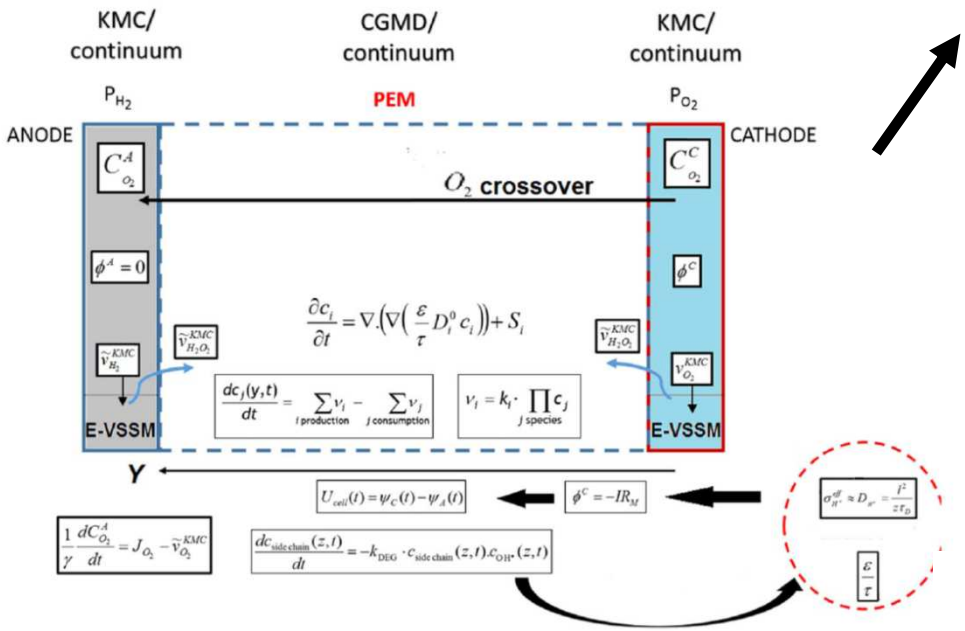
FULL PEMFC: COUPLING ON-THE-FLY KMC WITH CONTINUUM (3/4)



Open Circuit Conditions

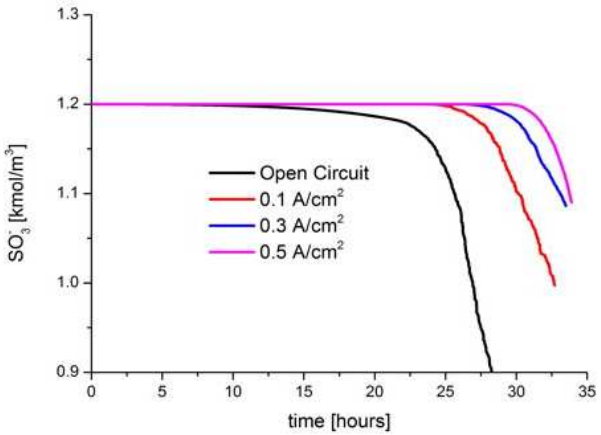




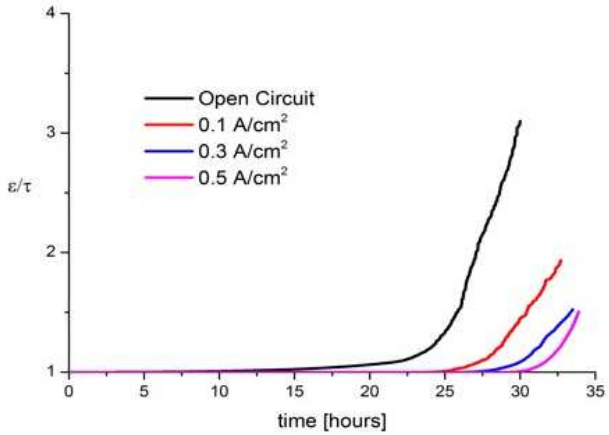
M.A. Quiroga, K. Malek, A.A. Franco, *J. Electrochem. Soc.*, **163** (2) (2016) F59.

FULL PEMFC: COUPLING ON-THE-FLY KMC WITH CONTINUUM (4/4)

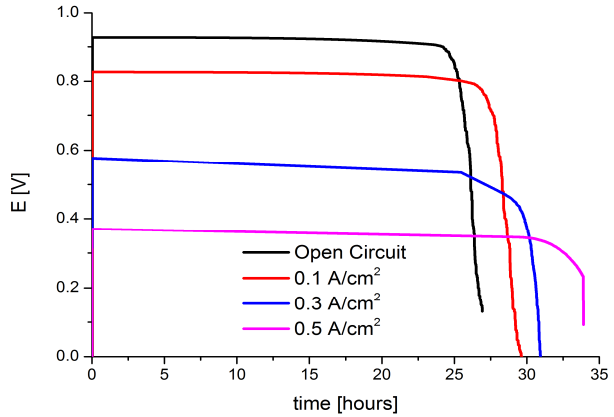
SO_3^- concentration



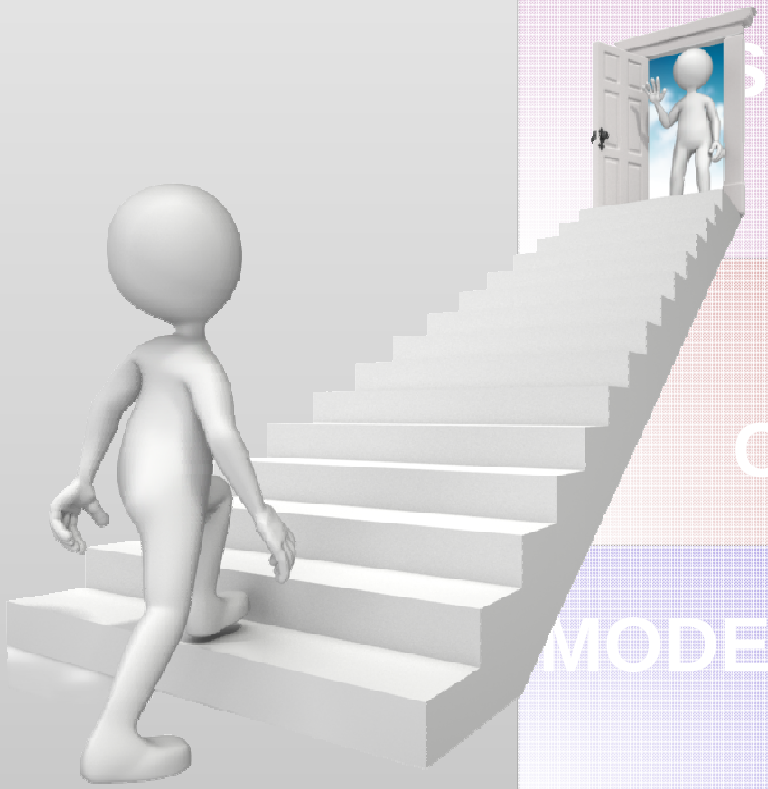
Porosity/ tortuosity



Cell potential



M.A. Quiroga, K. Malek, A.A. Franco, *J. Electrochem. Soc.*, **163** (2) (2016) F59.



Li-S BATTERIES:
CHALLENGING THE MODELING

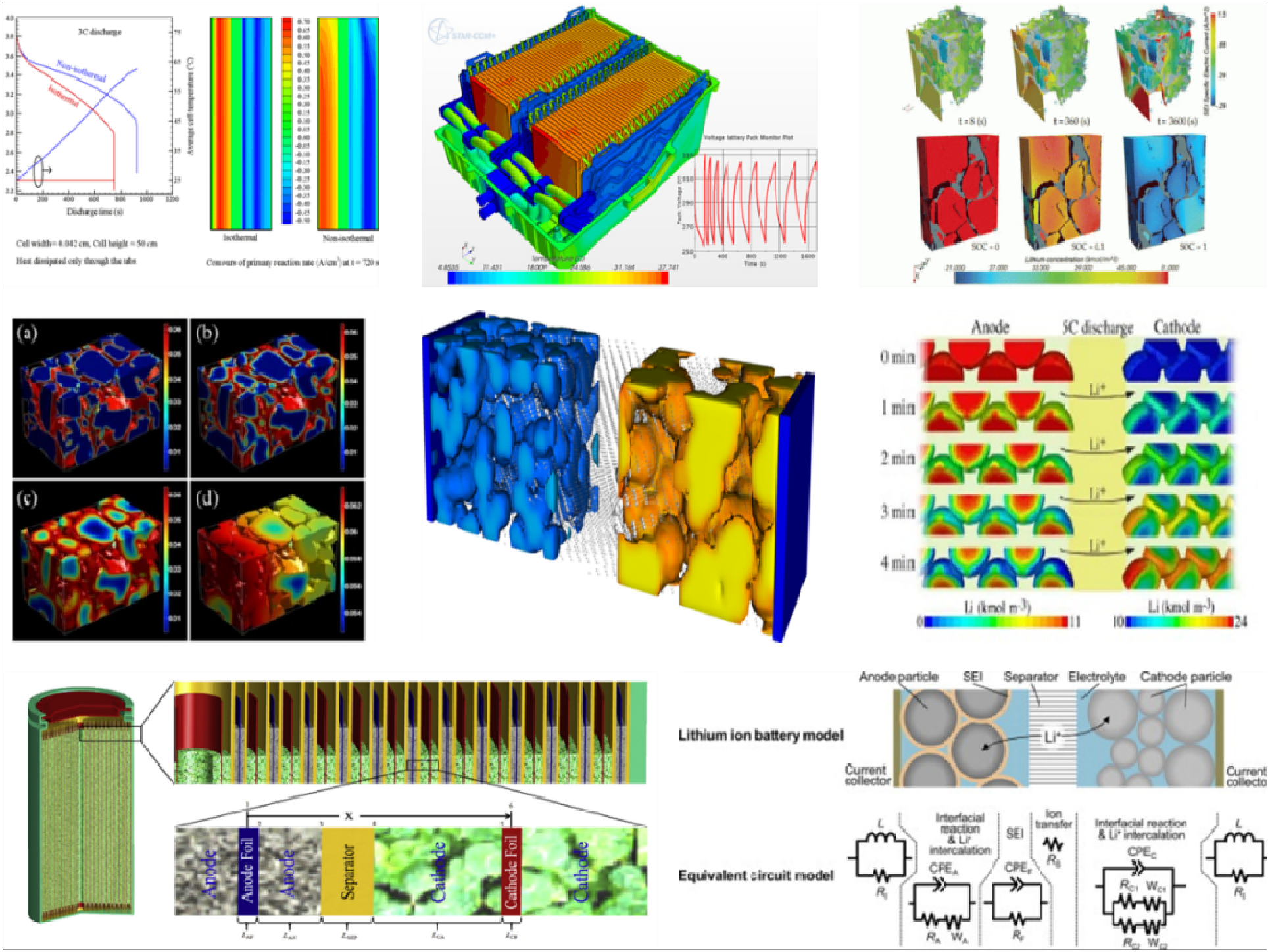
S REDUCTION REACTIONS:
KMC MODELING

Li-S CELLS:
CONTINUUM MODELING

MODELING SLURRY REDOX FLOW
BATTERIES

CHALLENGES & OPPORTUNITIES

CIVILIZATION'S LEVEL OF TECHNOLOGY ADVANCEMENT CORRELATED TO ITS CAPACITY TO STORE INFORMATION (The Cosmic Connection, 1973).


3C discharge
Non-isothermal
Isothermal
Discharge time (s)
Average cell temperature (°C)
Cell width = 0.042 cm, Cell height = 50 cm
Heat dissipated only through the tabs
Isothermal
Non-isothermal
Voltage battery Pack Monitor Plot
t = 8 (s)
t = 360 (s)
t = 3600 (s)
SOC = 0
SOC = 0.1
SOC = 1
(a)
(b)
(c)
(d)
Anode
5C discharge
Cathode
0 min
1 min
2 min
3 min
4 min
Li+
Li (kmol m-3)
Li (kmol m-3)
Anode Foil
Anode
Separator
Cathode
Cathode Foil
Cathode
x
Lithium ion battery model
Anode particle
SEI
Separator
Electrolyte
Cathode particle
Current collector
Current collecto
Equivalent circuit model
Interfacial reaction & Li+ intercalation
SEI
Ion transfer
Interfacial reaction & Li+ intercalation

EUROPEAN MATERIALS MODELING COUNCIL

EMMC goals:

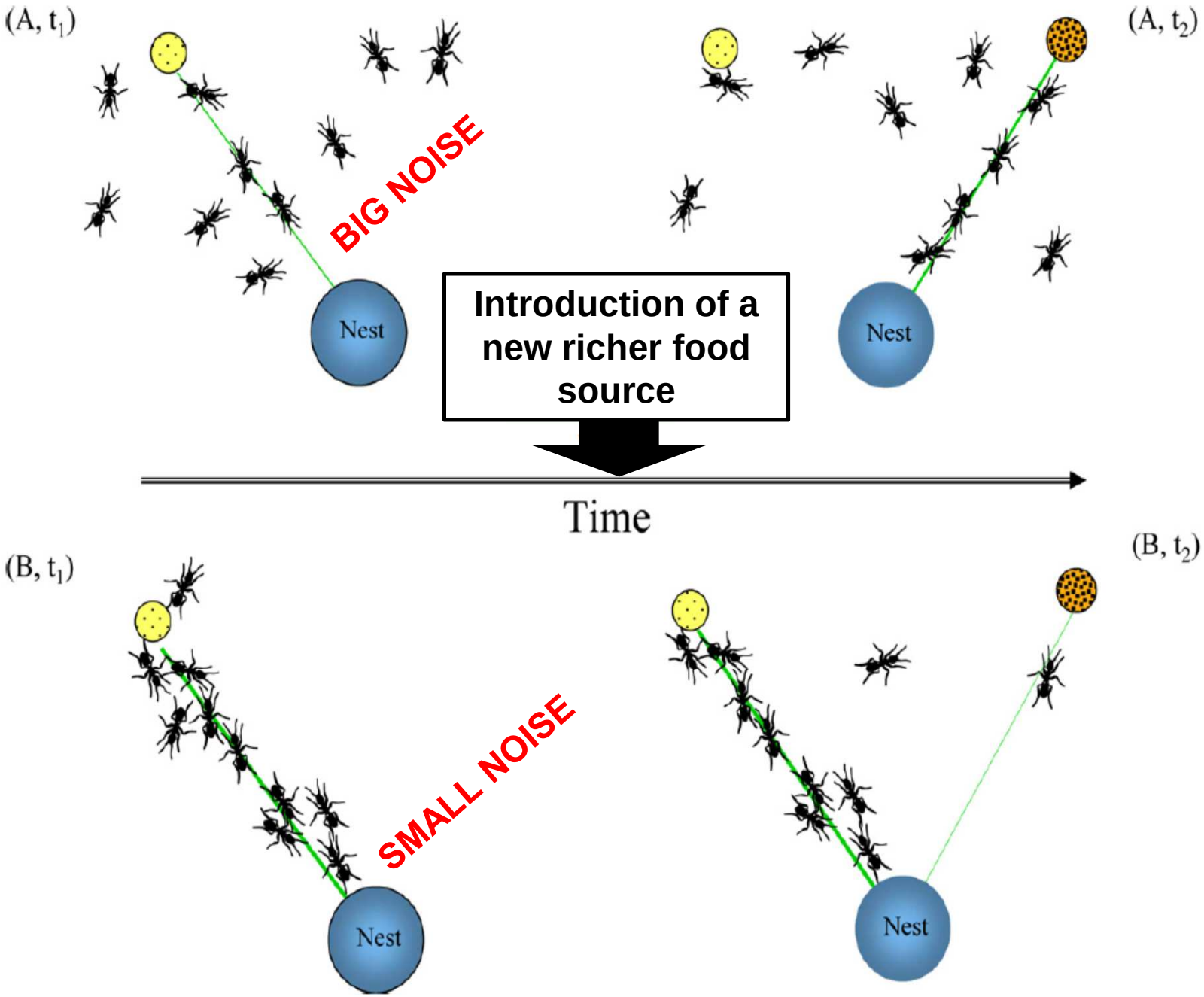
- ↳ Establishing **standards** for the transferability of data between different groups;
- ↳ Generation of a common multipurpose database;
- ↳ Improve the **tangibility** of the modeling work, **reusability** of models by industrials;
- ↳ Encouraging development of freeware.

https://emmc.info/

MODELS

INDUSTRY

CROSS-DISCIPLINARITY



D. J. T. Sumpter, The principles of collective animal behavior, *Phil. Trans. R. Soc. B,* **361** (2006) 5.

International Journal of Food Properties, 12: 252–260, 2009
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ISSN: 1094-2912 print / 1532-2386 online
DOI: 10.1080/10942910802322768

KINETIC MODELING OF TEXTURE PROPERTIES OF BOLOGNA SAUSAGE UNDER COOKING CONDITIONS

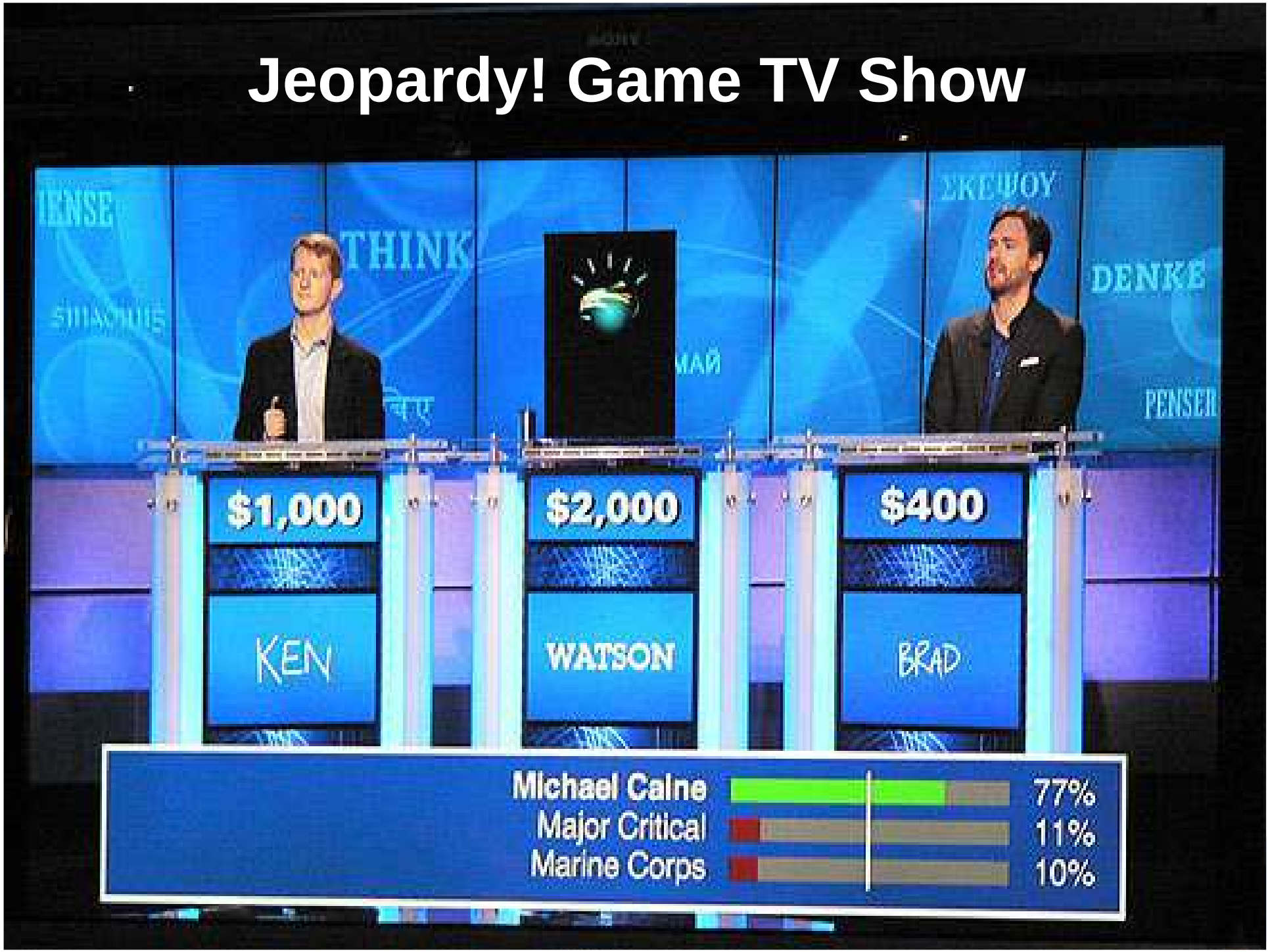
C.R. Chen, M. Marcotte, and A. Taherian
Agriculture and Agri-Food Canada's Food Research and Development Centre, Casavant Blvd West, St. Hyacinthe, QC, Canada

Texture properties are important indices for the evaluation of Bologna sausage quality. The objective of the study was to investigate the effect of cooking temperature and time on texture properties, to determine correlations between various texture properties (i.e., hardness, springiness, adhesiveness, cohesiveness, gumminess, chewiness, and resilience), and to develop kinetic models of selected texture properties as a function of cooking temperature and time. Cooking conditions were established at five levels of cooking temperature from 50–70°C, and at five levels of cooking time from 10 to 30 min. Results showed that cooking conditions (temperature and time) and their interactions significantly affected the texture properties except for the adhesiveness ($p < 0.01$). A significant correlation ($p < 0.01$) was found between gumminess and chewiness. The relationship between cooking temperature and time and texture properties can be well described by a second order polynomial equation. Statistical results showed that these kinetic models can be used ($R^2 > 0.92$) for the prediction of Bologna sausage texture properties within the range of experimental cooking conditions.

Keywords: ***Kinetics, Model, Texture, Bologna, Processed meat, Cooking process, Hardness, Springiness, Adhesiveness, Cohesiveness, Gumminess, Chewiness, Resilience.***

REVERSE-THINKING

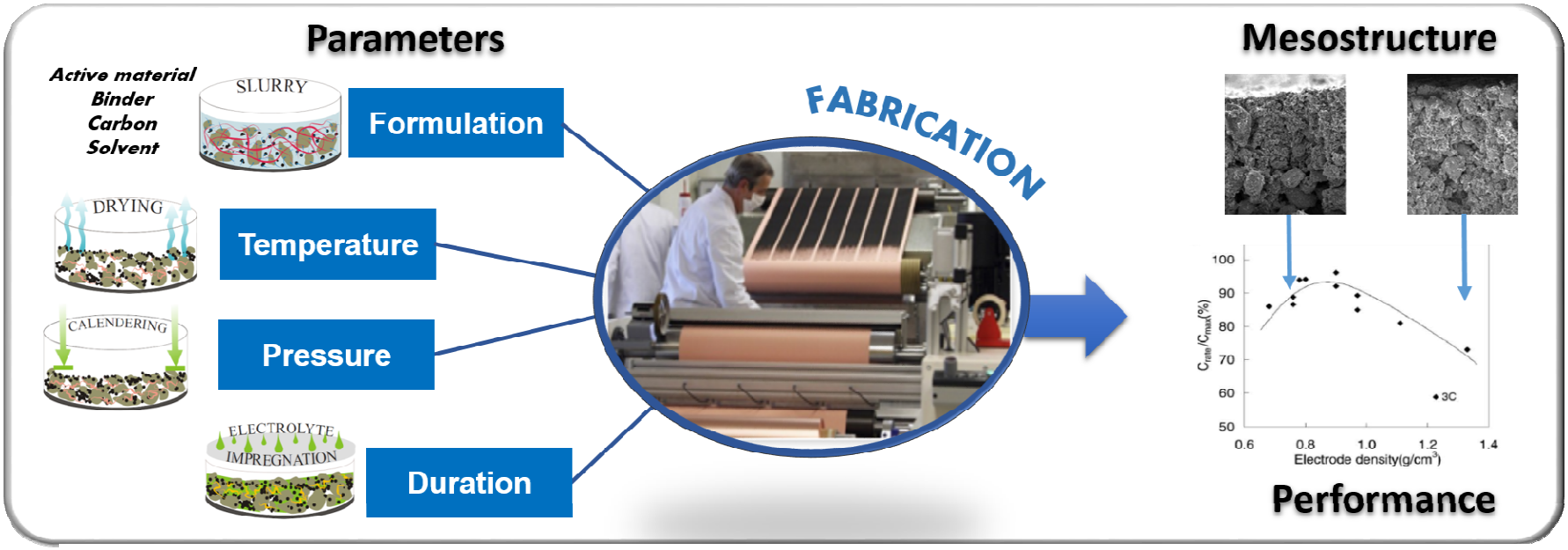
Jeopardy! Game TV Show



MODELING FOR REVERSE ENGINEERING…

Need of reverse engineering modeling approaches

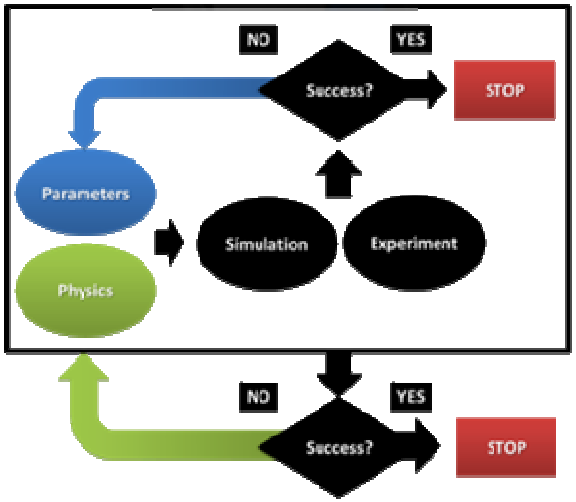
↳ For a given performance/durability/safety targets, use computations to discover how to achieve those targets.



A.A. Franco, Ed., *Rechargeable Lithium Batteries,* Woodhead/Elsevier, Cambridge, UK (2015).

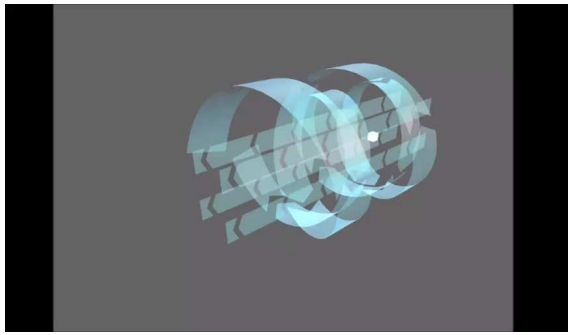
SOME CHALLENGES FOR MULTI-SCALE MODELING

AUTOMATAS FOR MODELS GENERATION



COUPLING WITH COST ANALYSIS

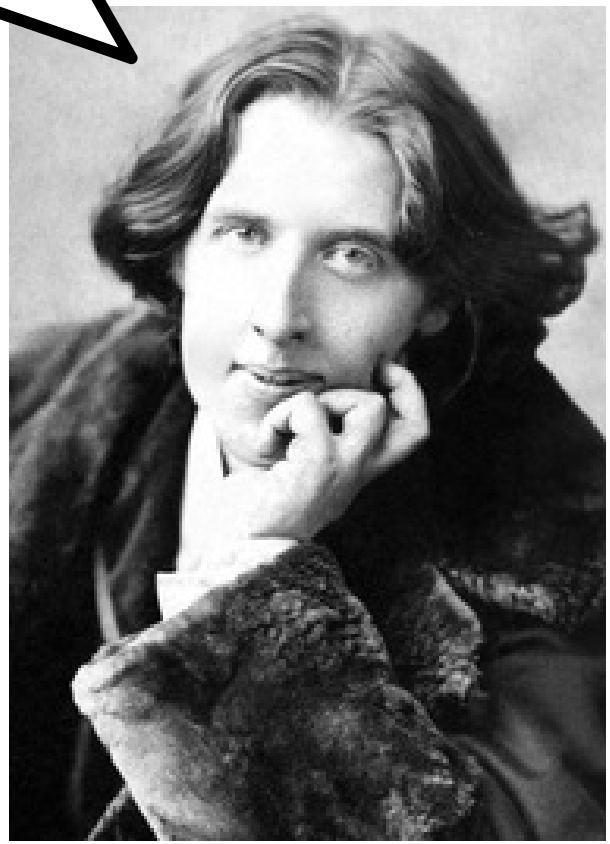
3D IMMERSIVE VISUALIZATION



Physical Multiscale Modeling and Numerical Simulation of Electrochemical Devices for Energy Conversion and Storage, A.A. Franco, M.L. Doublet, W. Bessler, Eds., Springer London (2016).

“BE YOURSELF,

everyone else is already taken”



Oscar Wilde (1854-1900)

Acknowledgements

- ICTP (Nicola, Ralph) for this opportunity
- M. Morcrette (LRCS)
- D. Larcher (LRCS)
- C. Guery, A. Mastouri (LRCS)
- L. Johnson, P. Bruce (Univ. Oxford, UK)
- C.P. Grey (Univ. Cambridge, UK)
- M.L. Doublet (ICG, France)
- J.P. Chehab, Y. Mammeri (LAMFA, France)
- P. Johansson (Chalmers, Sweden)
- Colleagues at LRCS, RS2E and ALISTORE
- My students and postdocs

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.

Amiens cathedral by night

THANK YOU

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alejandro.franco@u-picardie.fr