Impact of Interface Electrochemistry on Li-Battery Performance:

A first-step study towards multi-scale modeling

Anne-Laure DALVERNY, Rémi KHATIB, Jean-Sébastien FILHOL, Marie-Liesse DOUBLET

Institut Charles Gerhardt – CNRS and Université Montpellier 2
doublet@univ-montp2.fr

ENERGY RS2E
The french network on electrochemical energy storage

UNIVERSITÉ MONTPELLIER 2
SCIENCES ET TECHNIQUES

OUTLINE

- Introduction to Li-Ion Batteries
- QM strategy / methodology for interface electrochemistry
- Results on multi-phased / nanosized conversion electrodes
- Conclusions / Challenges for multi-scale modeling in Li-ion batteries

Li-Ion Batteries

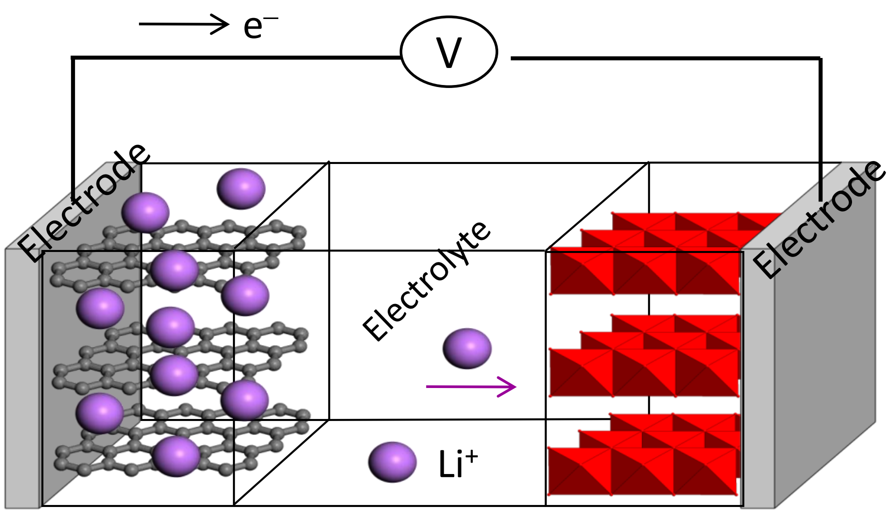
✓ Secondary (rechargeable) electrochemical devices

DISCHARGE

Negative

Low-potential vs. Li^+/Li^0

$0 < V \leq 1$ volt



Positive

High-potential vs. Li^+/Li^0

$4 \leq V < 5$ volts

Two simultaneous reversible electrochemical reactions

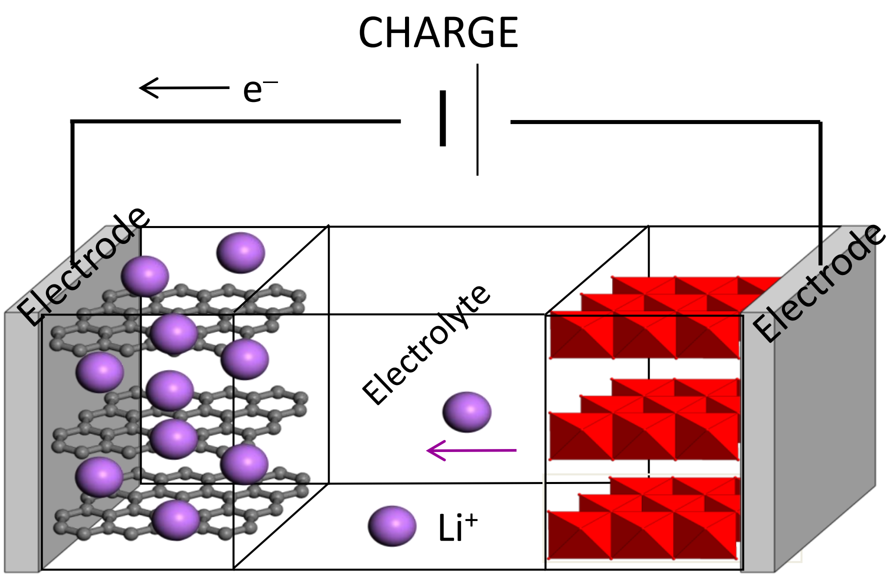
Working voltage $$V = -\frac{\Delta_r G}{nF}$$ G : Gibbs energy

✓ Secondary (rechargeable) electrochemical devices

<u>Negative</u>

Low-potential vs. Li^+/Li^0

$0 < V \leq 1$ volt



<u>Positive</u>

High-potential vs. Li^+/Li^0

$4 \leq V < 5$ volts

Two simultaneous reversible electrochemical reactions

Working voltage

$$V = -\frac{\Delta_r G}{nF}$$

G : Gibbs energy

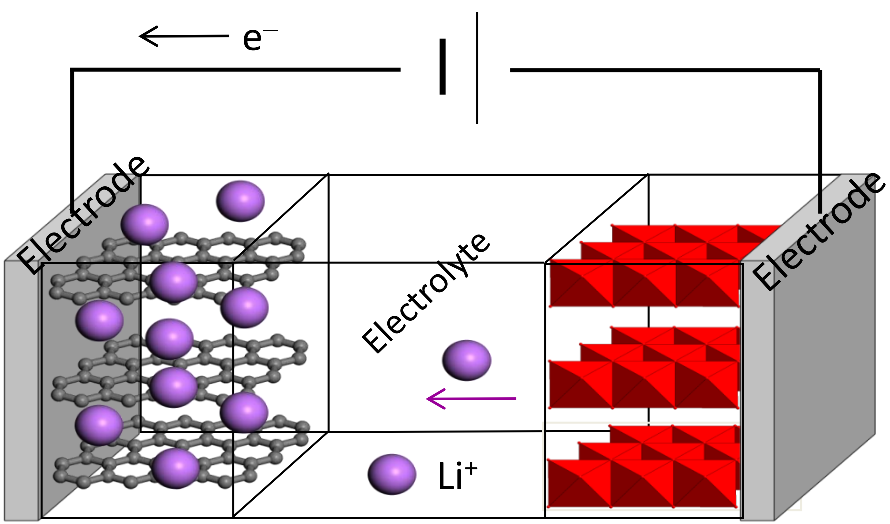
✓ Secondary (rechargeable) electrochemical devices

✓ Industrial specifications : $\Delta V \approx 4$ Volts

<u>Negative</u>

Low-potential vs. Li^+/Li^0

$0 < V \leq 1$ volt



<u>Positive</u>

High-potential vs. Li^+/Li^0

$4 \leq V < 5$ volts

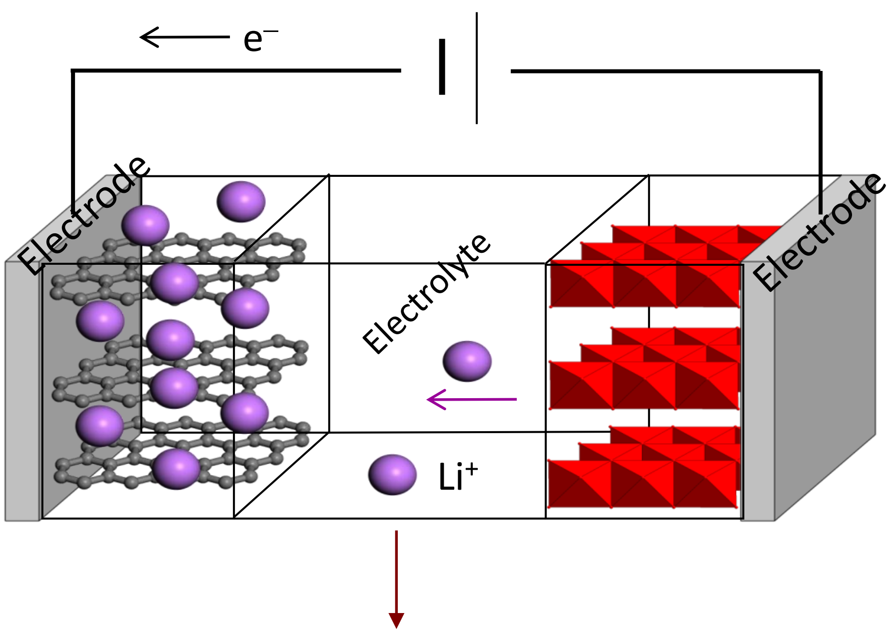
Two simultaneous reversible electrochemical reactions

Increase the energy density → Thermodynamics (V . Capacity)

Increase the efficiency → Kinetics (fast reactions)

Li-Ion Batteries

- ✓ Secondary (rechargeable) electrochemical devices
- ✓ Industrial specifications : $\Delta V \approx 4$ Volts
- ✓ Solving the related issues



Li+ PF_6^-
EC-DMC
Organic solvent

Surface Electrolyte Interphase (SEI)

Negative

Graphite (≈0 V)

Safety issues !

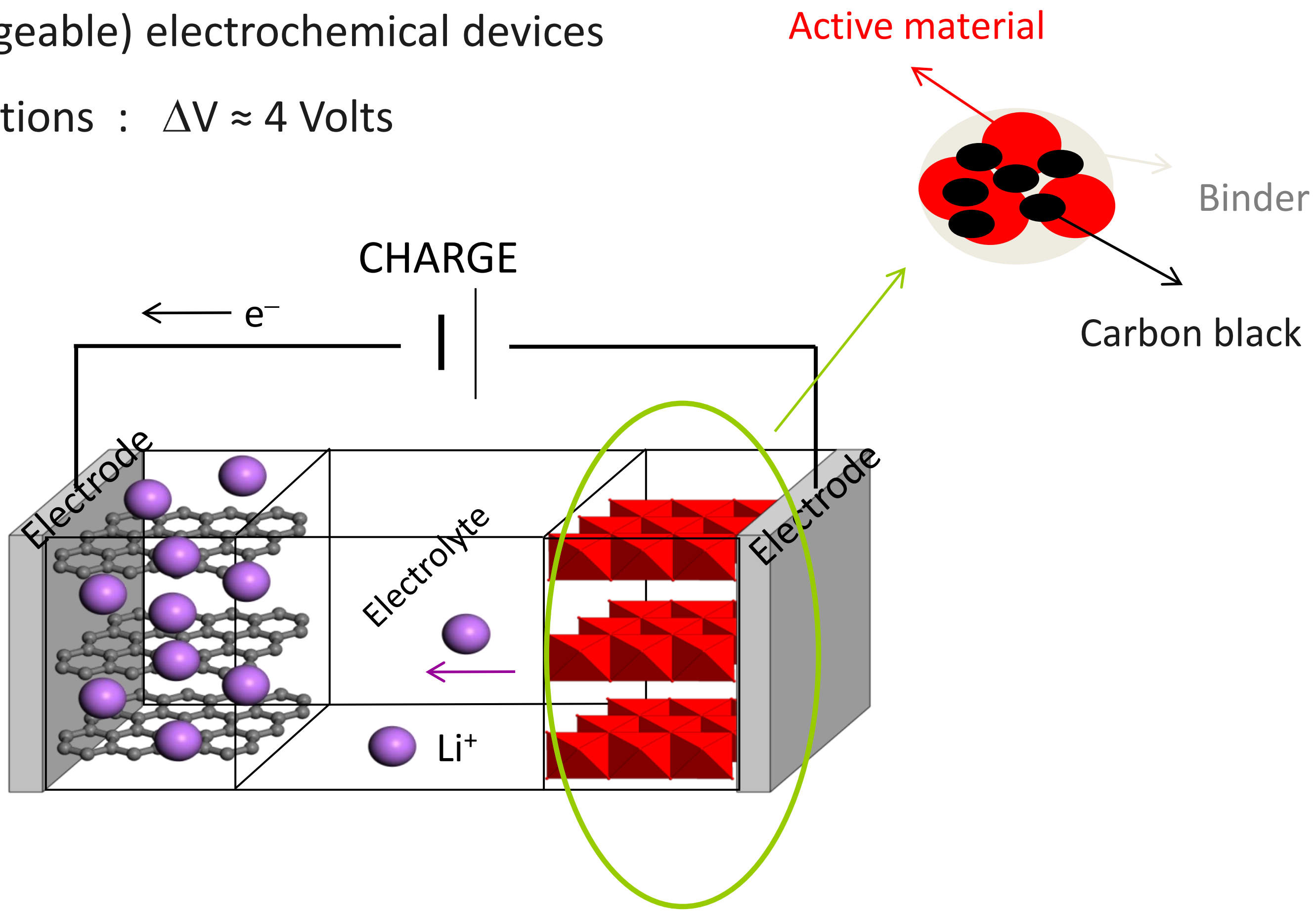
Positive

$LiCoO_2$ (2.7 V)
$LiFePO_4$ (3.5 V)

Stability issues !

ENERGY RS2E

- ✓ Secondary (rechargeable) electrochemical devices
- ✓ Industrial specifications : $\Delta V \approx 4$ Volts



Electrode reactivity **itself** is a challenge !!

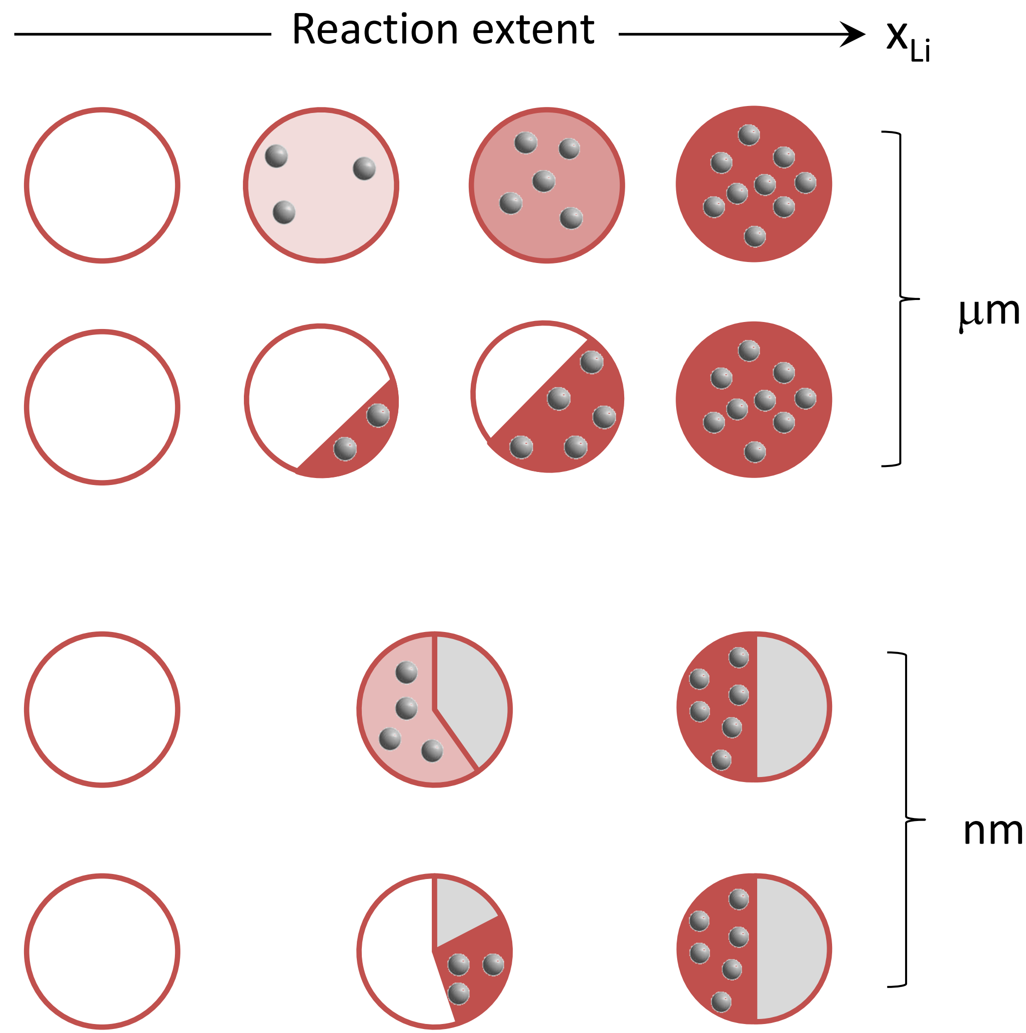
Electrode Reactions

Insertion

$MX + xLi \rightleftarrows Li_xMX$

Single phase

Two-phase



Displacement

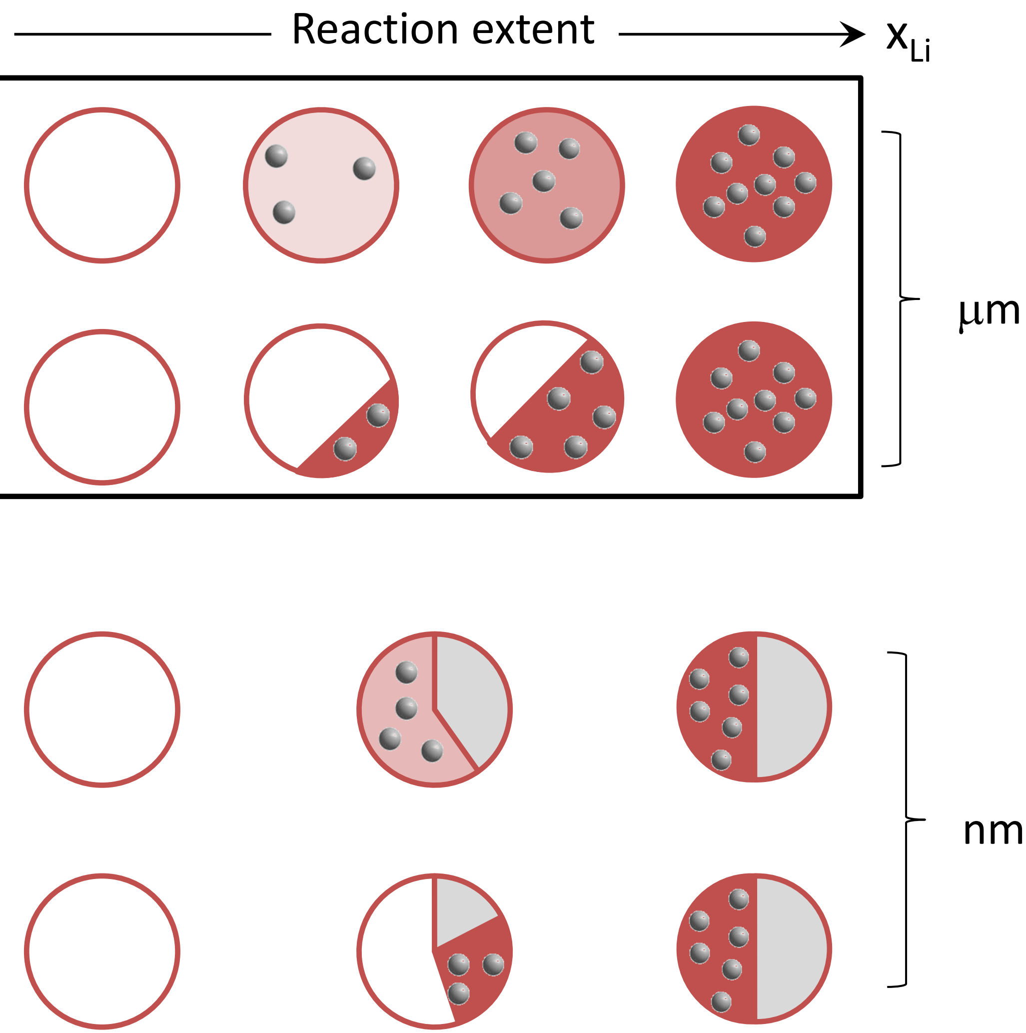
$MX + xLi \rightleftarrows M^0 + M_{(1-x)}Li_xX$

Conversion

$MX + xLi \rightleftarrows M^0 + LiX$

Very different Thermodynamics AND Kinetics

Electrode Reactions



Insertion

$MX + xLi \rightleftarrows Li_xMX$

Single phase

Two-phase

Displacement

$MX + xLi \rightleftarrows M^0 + M_{(1-x)}Li_xX$

Conversion

$MX + xLi \rightleftarrows M^0 + LiX$

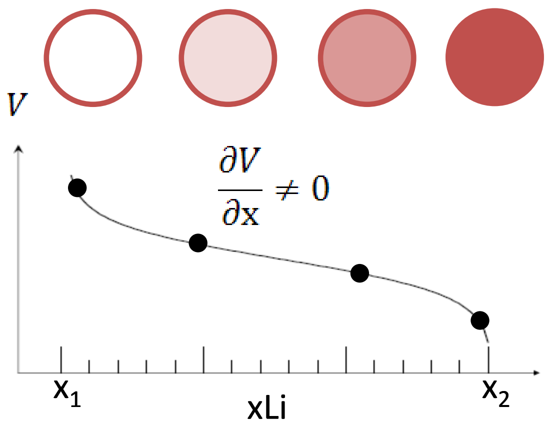
Very different Thermodynamics AND Kinetics

Electrode Reactions

$$Li_{x_1}H + (x_2 - x_1)Li \longrightarrow Li_{x_2}H$$

$$V = -\frac{\Delta_r G}{nF}$$

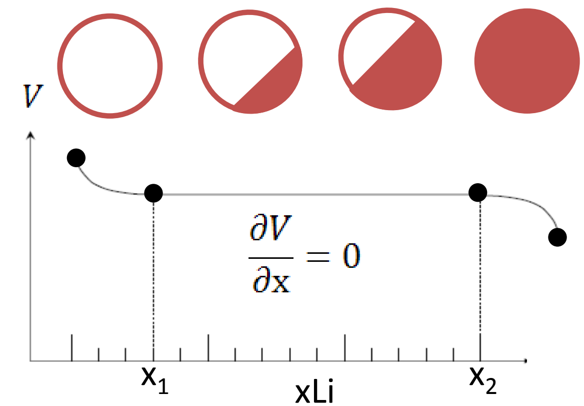
Single-Phase process



Nernst law

Kinetically limited by Li diffusion

Multi-phase process



Potential plateau

Kinetically limited by front-phase migration

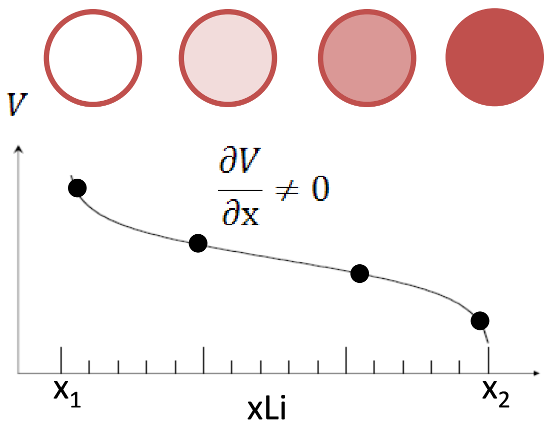
Electrode Reactions

$$Li_{x_1}H + (x_2 - x_1)Li \longrightarrow Li_{x_2}H$$

$$V = -\frac{\Delta_r G}{nF}$$

Methodological challenge !

Single-Phase process



Nernst law

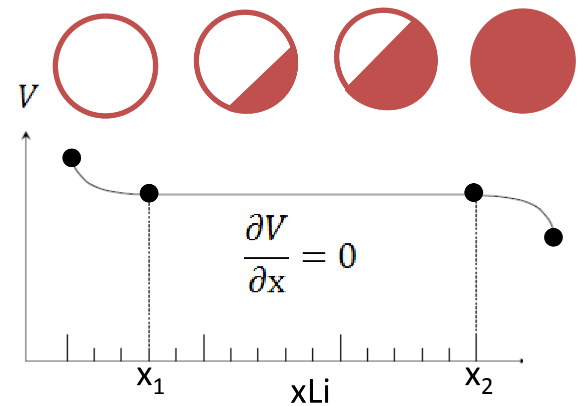
Kinetically limited by Li diffusion

$$V(x) = -\frac{1}{F}\left\{\frac{\partial G(x)}{\partial x} - G\left(Li^0\right)\right\}$$

Infinite number of phases to compute + entropy

Numerical challenge !

Multi-phase process



Potential plateau

Kinetically limited by front-phase migration

$$V(x) = -\frac{1}{F}\left\{\frac{G(x_2) - G(x_1)}{x_2 - x_1} - G\left(Li^0\right)\right\}$$

“Easy” to compute if one neglects

Surface / Interface effects !

AVERAGE VOLTAGES CALCULATIONS

Treated as (successive) two-phase processes

$$Li_{x_1}H + (x_2 - x_1)Li \longrightarrow Li_{x_2}H$$

$$V = -\frac{\Delta_r G}{nF}$$

$$V(\mathrm{x}) = -\frac{1}{F}\left\{\frac{G(\mathrm{x}_2) - G(\mathrm{x}_1)}{\mathrm{x}_2 - \mathrm{x}_1} - G\left(\mathrm{Li}^0\right)\right\}$$

Aydinol et. al PRB. 56 (1997) ; Zhou et al. PRB 70 (2004)

AVERAGE VOLTAGES CALCULATIONS

Treated as (successive) two-phase processes

$$Li_{x_1}H + (x_2 - x_1)Li \longrightarrow Li_{x_2}H$$

$$V = -\frac{\Delta_r G}{nF}$$

$$V(\mathrm{x}) = -\frac{1}{F}\left\{\frac{G(\mathrm{x}_2) - G(\mathrm{x}_1)}{\mathrm{x}_2 - \mathrm{x}_1} - G(\mathrm{Li}^0)\right\}$$

$$\Delta_r G = \Delta_r E + P\Delta_r V - T\Delta_r S \qquad \approx \Delta_r E$$

negligible neglected

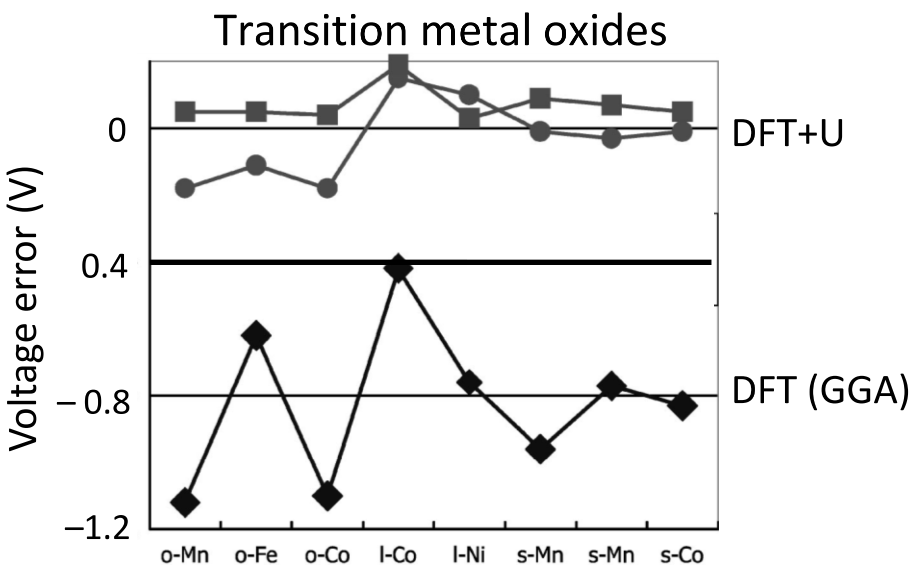
Average Voltages Calculations

Treated as (successive) two-phase processes

$$Li_{x_1}H + (x_2 - x_1)Li \longrightarrow Li_{x_2}H$$

$$V = -\frac{\Delta_r G}{nF}$$

$$V(x) = -\frac{1}{F}\left\{\frac{G(x_2) - G(x_1)}{x_2 - x_1} - G(Li^0)\right\}$$



F. Zhou et al. *PRB* **70** (2004) 235121

DFT, DFT+U, DFT Hybride ….

$$\Delta_r G = \Delta_r E + P\Delta_r V - T\Delta_r S \quad \approx \Delta_r E$$

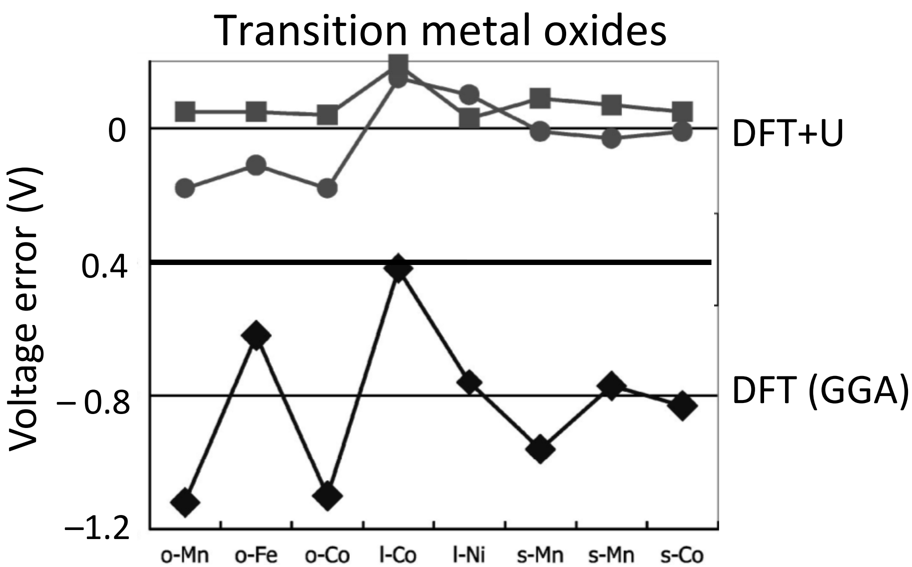
negligible neglected

Method generally used to “extract” the effective U value for any given system

AVERAGE VOLTAGES CALCULATIONS

Treated as (successive) two-phase processes

$$Li_{x_1}H + (x_2 - x_1)Li \longrightarrow Li_{x_2}H$$



F. Zhou et al. *PRB* **70** (2004) 235121

$$V = -\frac{\Delta_r G}{nF}$$

$$V(\mathrm{x}) = -\frac{1}{F}\left\{\frac{G(\mathrm{x}_2) - G(\mathrm{x}_1)}{\mathrm{x}_2 - \mathrm{x}_1} - G(\mathrm{Li}^0)\right\}$$

DFT, DFT+U, DFT Hybride ....

$$\Delta_r G = \Delta_r E + P\Delta_r V - T\Delta_r S \approx \Delta_r E$$

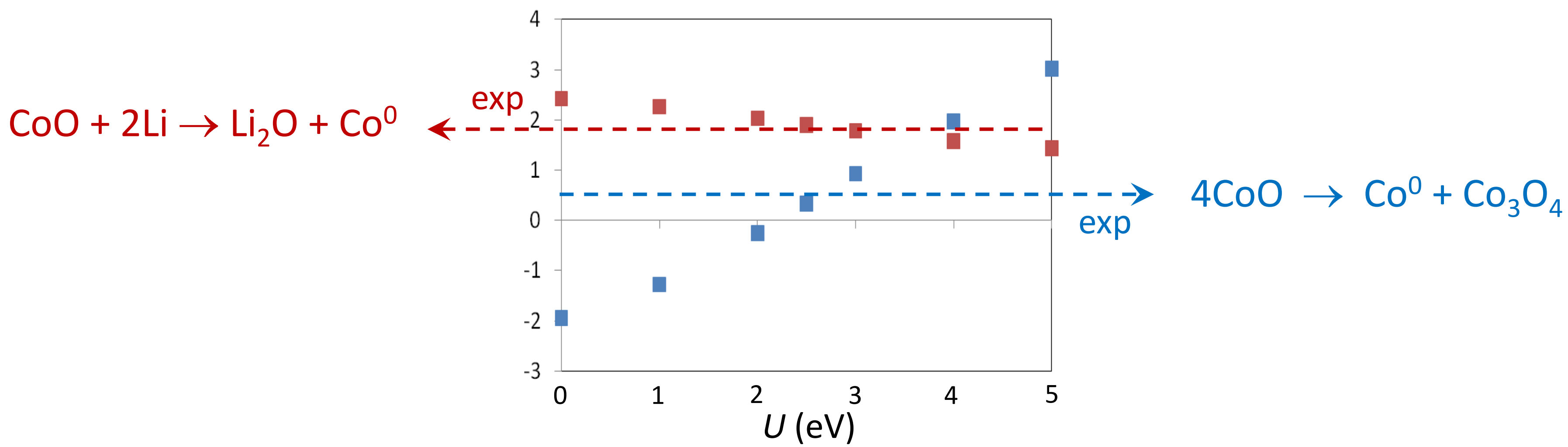
negligible neglected

Method generally used to “extract” the effective U value for any given system

⟶ Can be very dangerous !

AVERAGE VOLTAGES CALCULATIONS

$\Delta_r E$ (eV) and V (volt) computed within the DFT+U framework

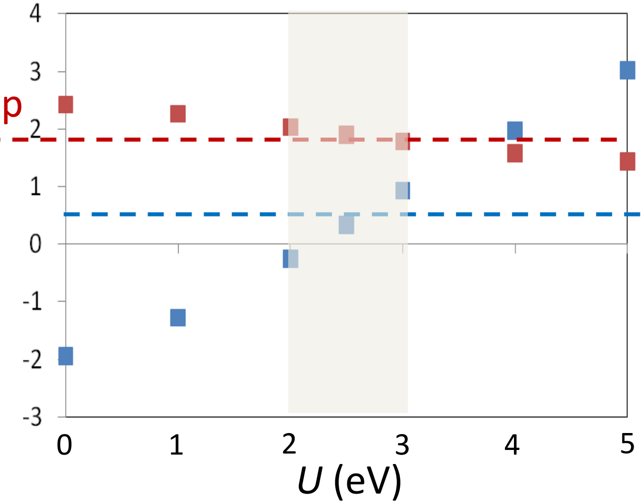


A.L. Dalverny et al. *J. Phys. Chem.* C 2010

AVERAGE VOLTAGES CALCULATIONS

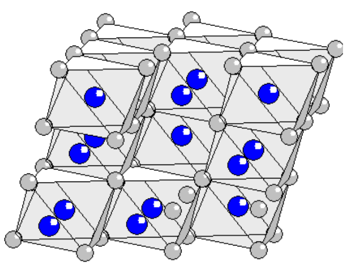
$\Delta_r E$ (eV) and V (volt) computed within the DFT+*U* framework

$CoO + 2Li \rightarrow Li_2O + Co^0$



$4CoO \rightarrow Co^0 + Co_3O_4$

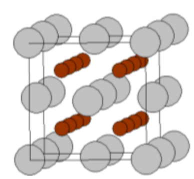
CoO



Strongly correlated AntiFerromagnet

DFT+*U* : *U*(Co) = 5eV !

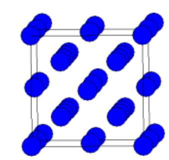
Li_2O



Band gap Insulator

DFT

Co^0



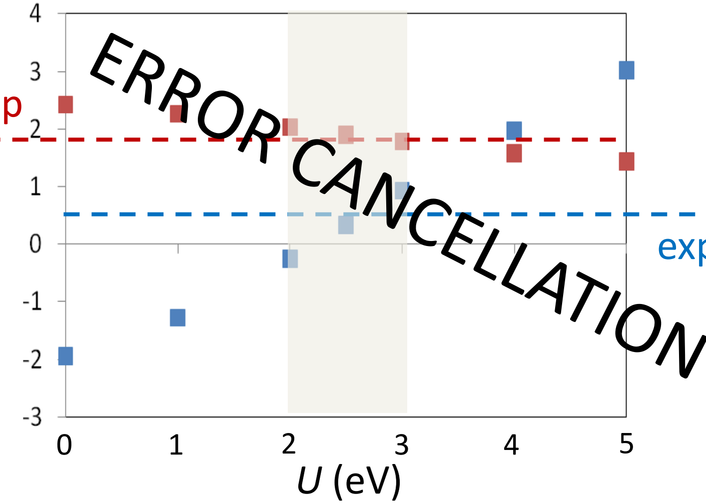
Ferromagnetic metal

DFT *U*(Co) = 0 eV

Average Voltages Calculations

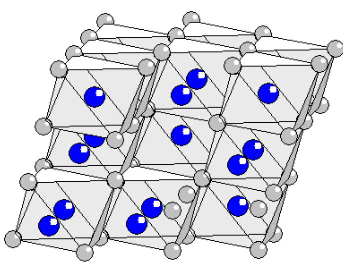
$\Delta_r E$ (eV) and V (volt) computed within the DFT+*U* framework

$CoO + 2Li \rightarrow Li_2O + Co^0$

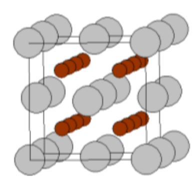


$4CoO \rightarrow Co^0 + Co_3O_4$

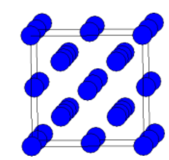
CoO



Li_2O



Co^0



Strongly correlated AntiFerromagnet

Band gap Insulator

Ferromagnetic metal

DFT+*U* : *U*(Co) = 5eV !

DFT

DFT *U*(Co) = 0 eV

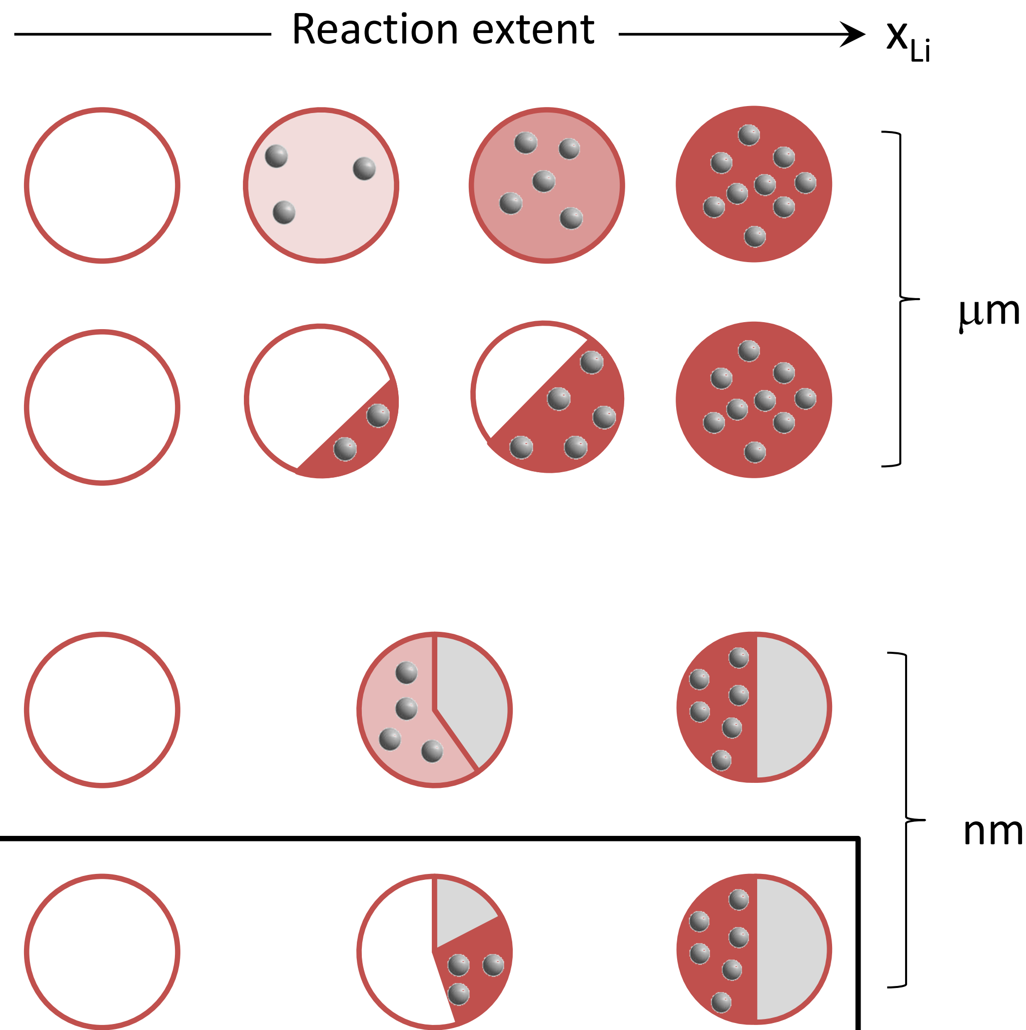
Electrode Reactions

Insertion

$MX + xLi \rightleftarrows Li_xMX$

Single phase

Two-phase



Displacement

$MX + xLi \rightleftarrows M^0 + M_{(1-x)}Li_xX$

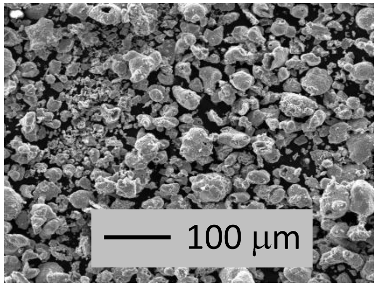
Conversion

$MX + xLi \rightleftarrows M^0 + LiX$

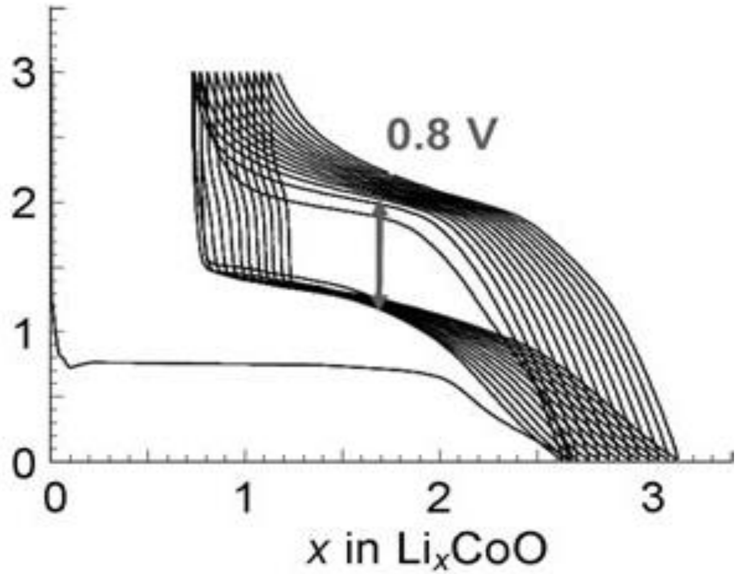
Prototypes for Surface / Interface Electrochemistry and Multi-Scale Modeling

Conversion Reactions

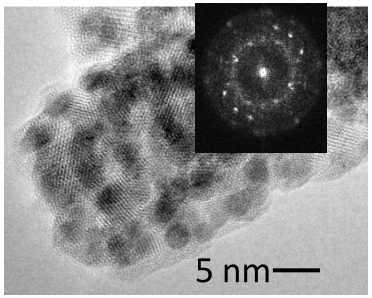
μm-sized electrode



$CoO + 2Li \rightleftarrows Li_2O + Co^0$



Nano-composite electrode



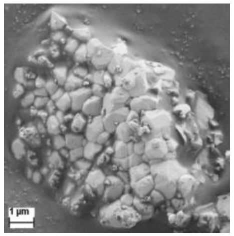
☺ Higher capacity than insertion

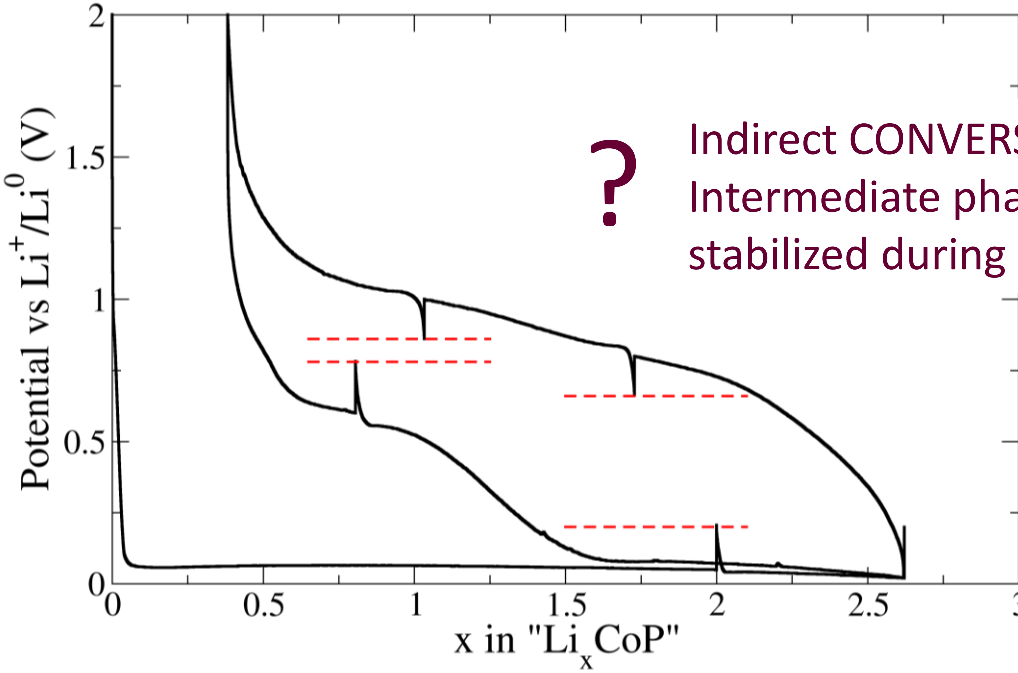
☹ Lower efficiency than insertion

CONVERSION REACTIONS

?

CoP + 3Li ⇆ ? ⇆ Li_3P + Co^0





? Indirect CONVERSION
Intermediate phases
stabilized during the process

☺ Higher capacity than insertion

☹ Lower efficiency than insertion

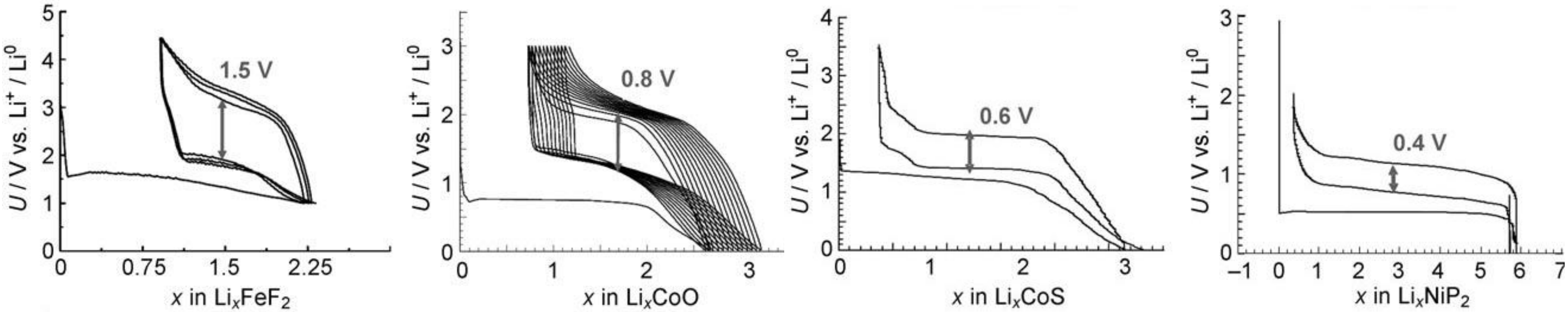
→ Voltage polarization ?

→ Voltage hysteresis ?

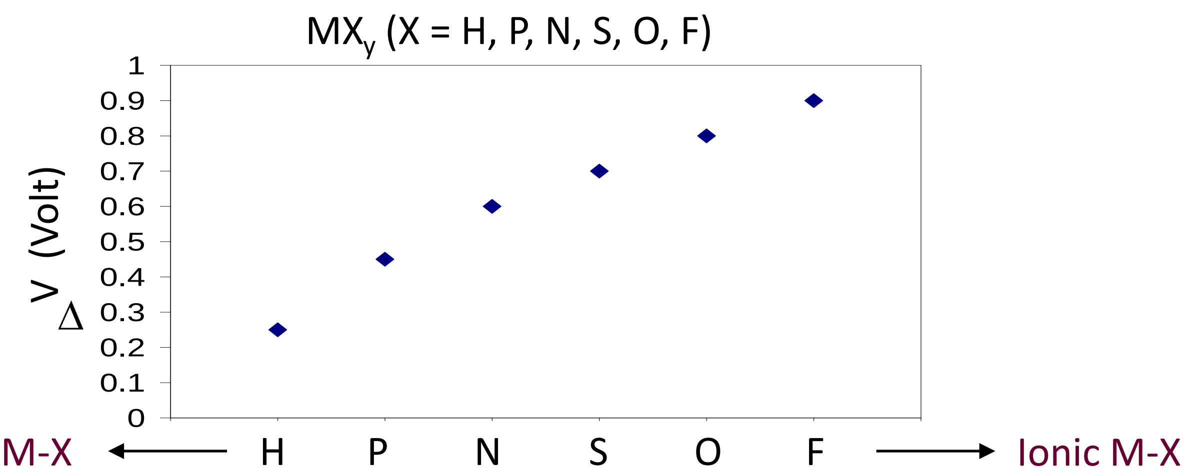
Thermodynamics
vs.
Kinetics

Conversion Reactions

$$MX_y + n.y\,Li \rightleftharpoons y\,Li_nX + M^0$$

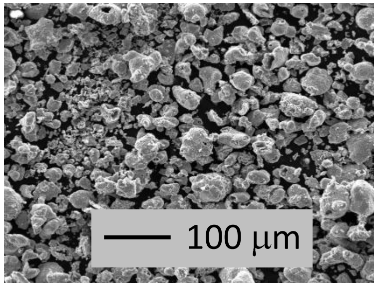


Bruce *et al. Angew. Chem. Int. Ed.* **2008**, 47, 2930 – 2946

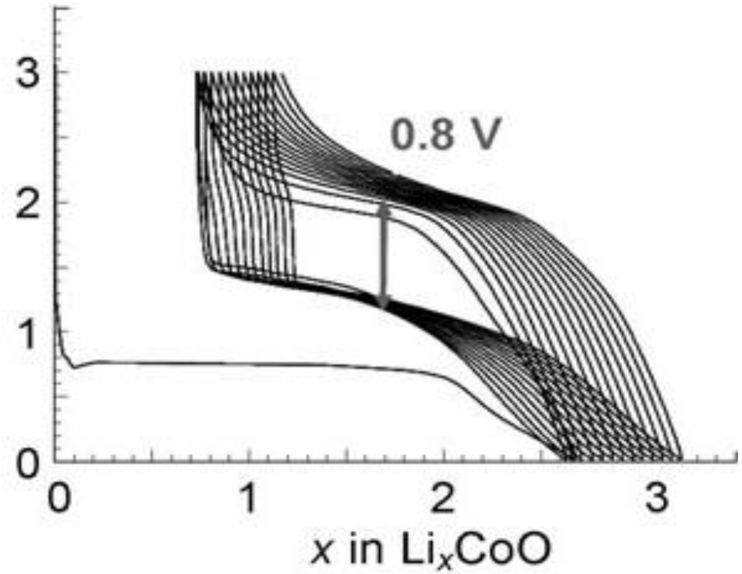


Conversion Reactions

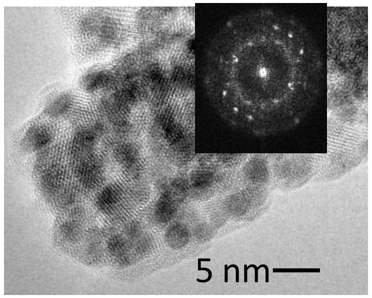
µm-sized electrode



$$MX + Li \rightleftarrows LiX + M^0$$



Nano-composite electrode



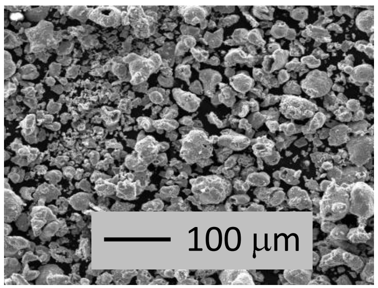
☺ Higher capacity than insertion

☹ Lower efficiency than insertion

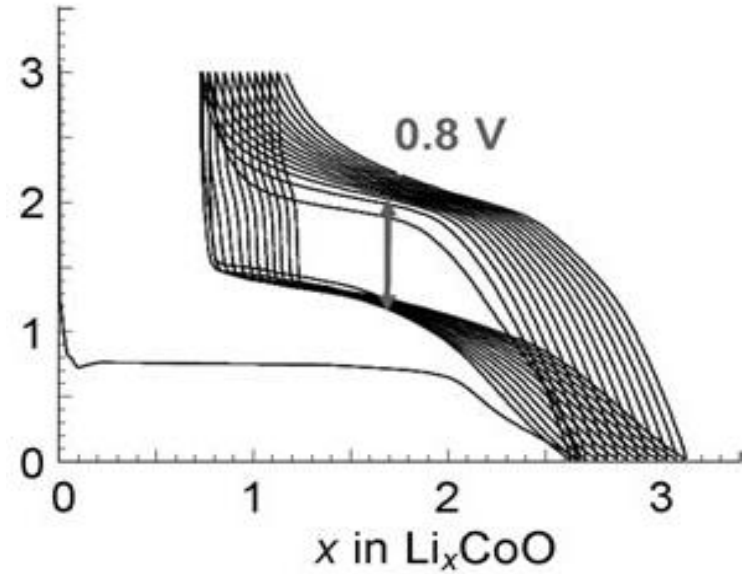
Surface / Interface effects

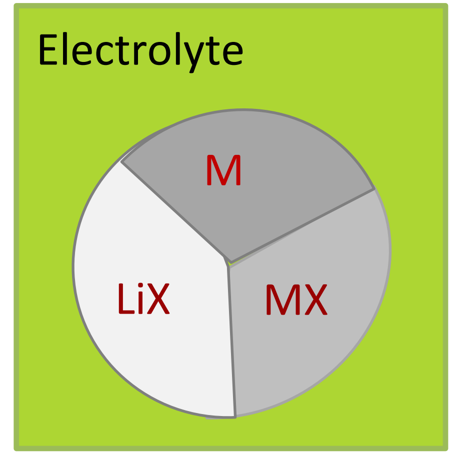
Conversion Reactions

μm-sized electrode

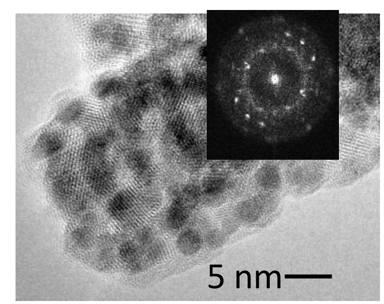


$$CoO + 2Li \rightleftarrows Li_2O + Co^0$$





Nano-composite electrode



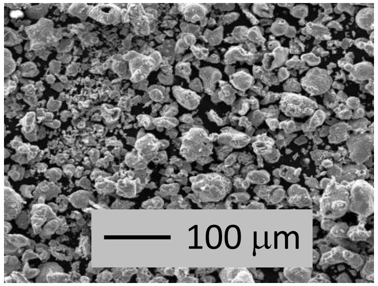
Higher capacity than insertion

Lower efficiency than insertion

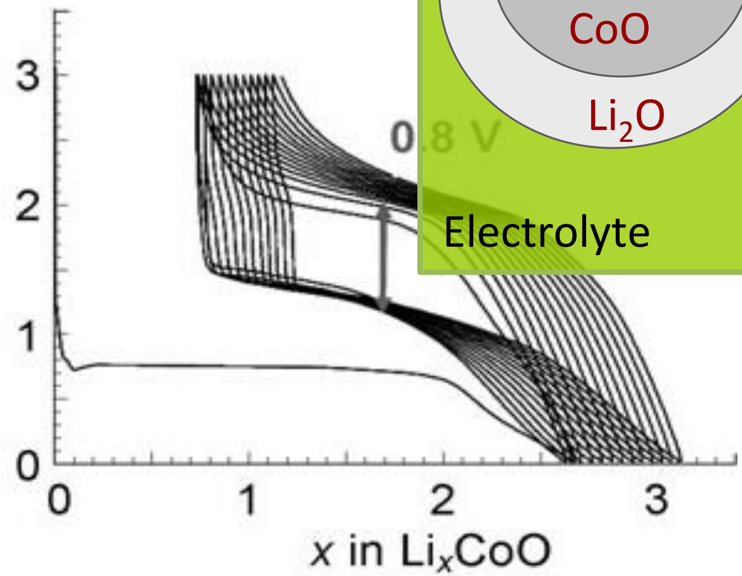
Surface / Interface effects

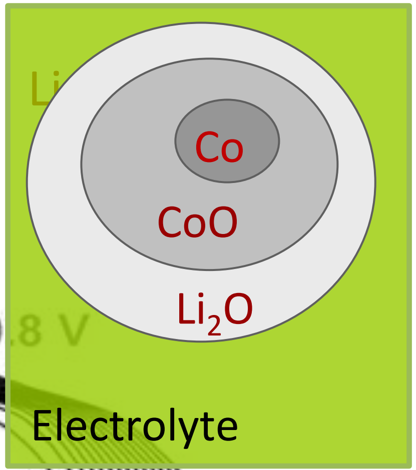
CONVERSION REACTIONS

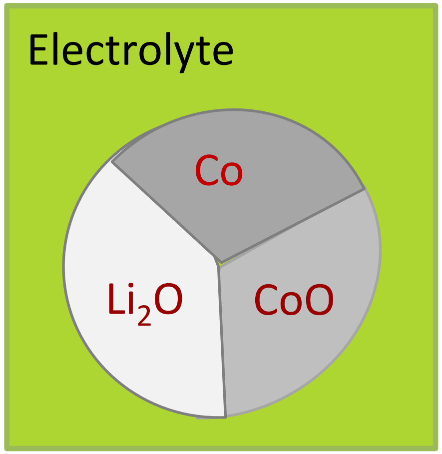
μm-sized electrode



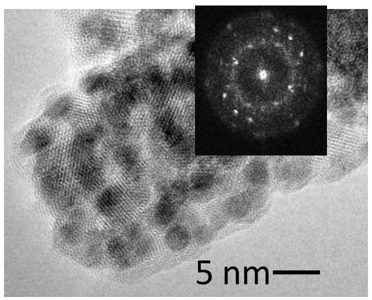
$CoO + 2Li \rightleftarrows$ Li







Nano-composite electrode



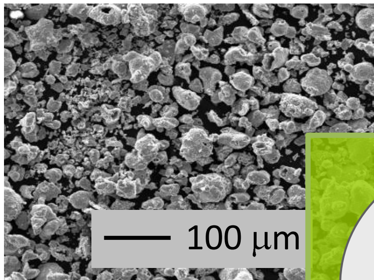
☺ Higher capacity than insertion

☹ Lower efficiency than insertion

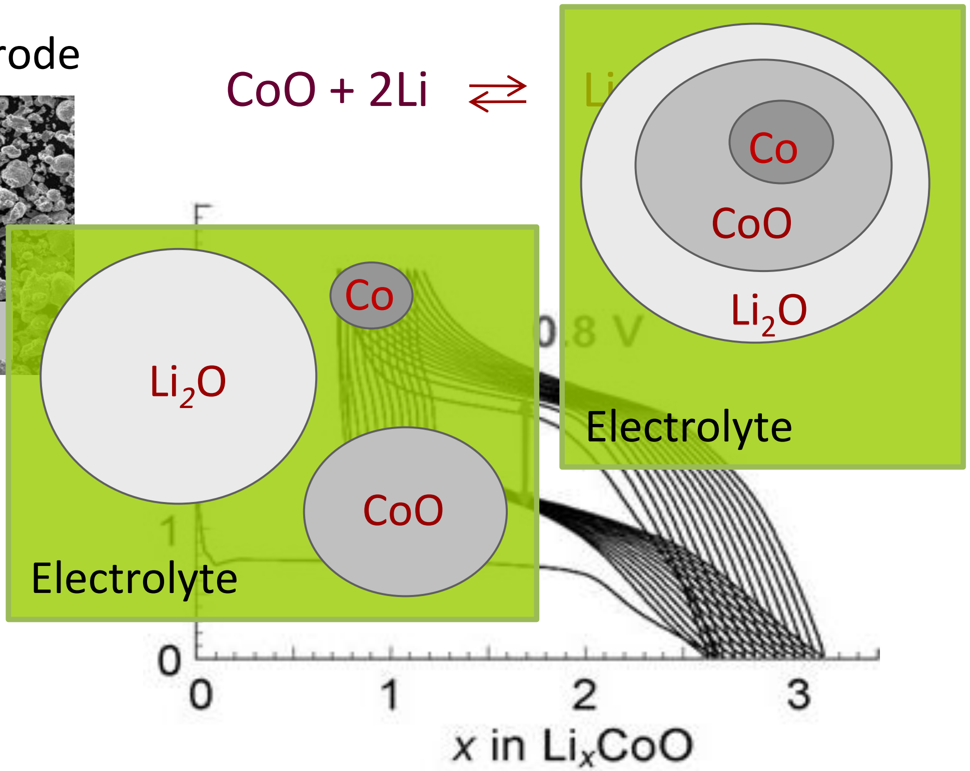
Surface / Interface effects

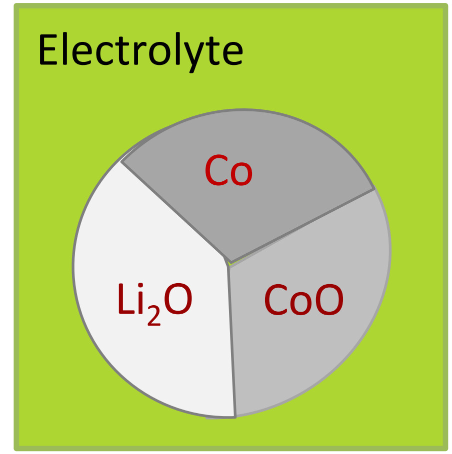
Conversion Reactions

μm-sized electrode

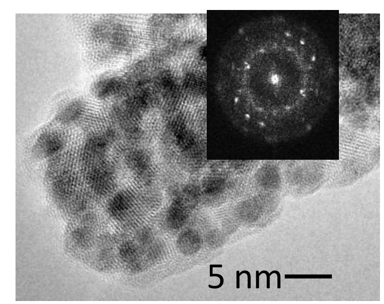


CoO + 2Li ⇄





Nano-composite electrode



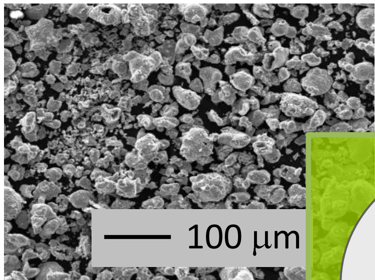
☺ Higher capacity than insertion

☹ Lower efficiency than insertion

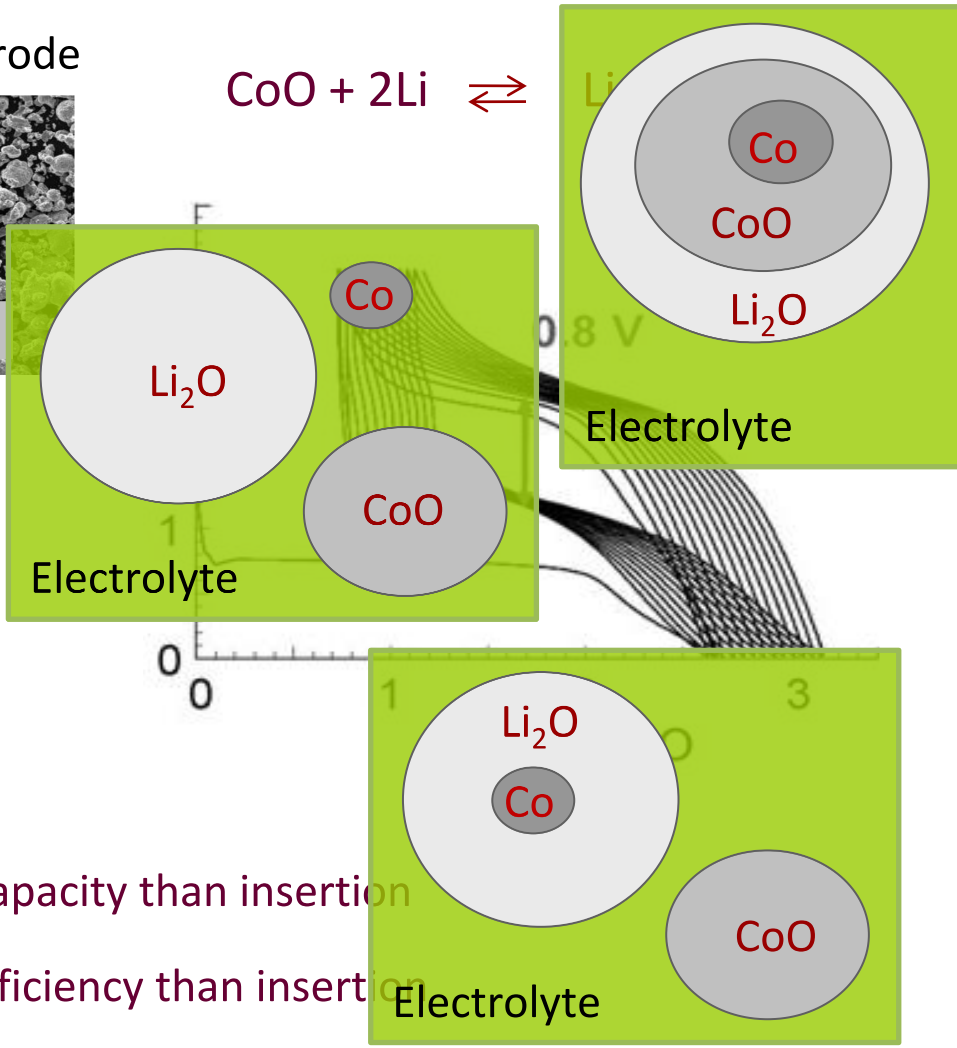
Surface / Interface effects

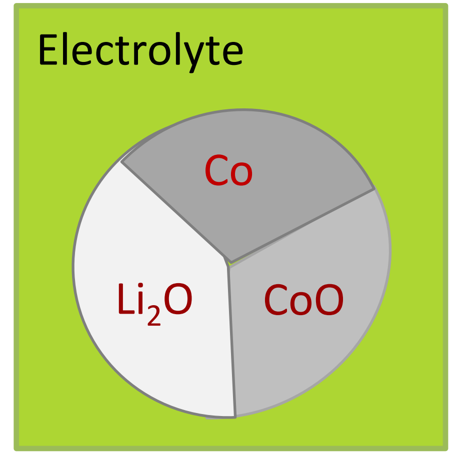
Conversion Reactions

µm-sized electrode

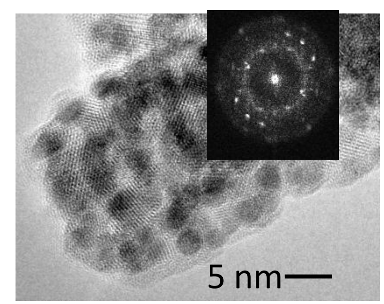


$CoO + 2Li \rightleftarrows$





Nano-composite electrode



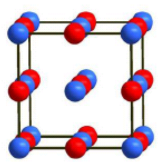
- ☺ Higher capacity than insertion
- ☹ Lower efficiency than insertion

Surface / Interface effects

NEW METHODOLOGY

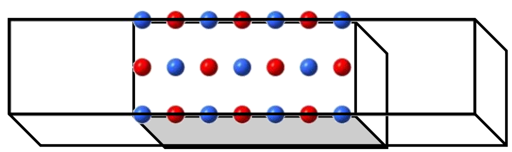
1. Based on first-principles (DFT) periodic calculations

Bulk



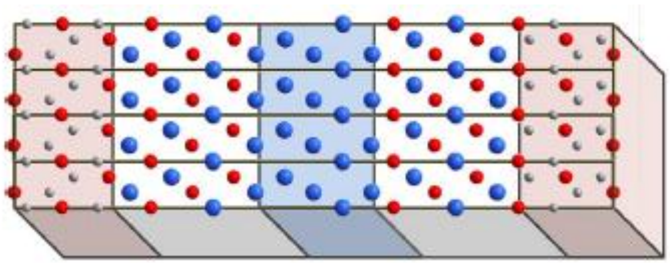
Intrinsic properties

Surface



Particle size

Interface



Texture / Morphology

2. Transferable to any type of electrochemical reaction

3. Easy handling

STRATEGY

<u>STEP</u> 1
THE INTERFACES

<u>STEP</u> 2
THE ELECTRODE

<u>STEP</u> 3
THE REACTION

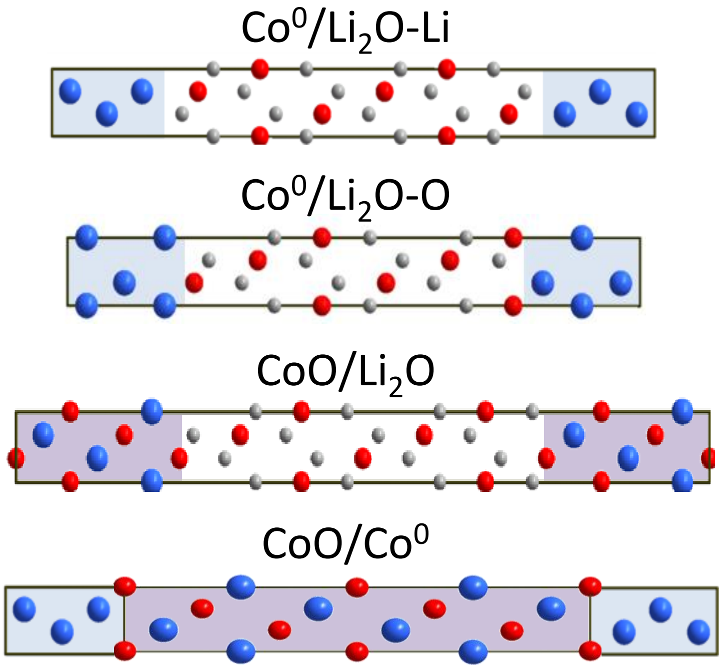
STRATEGY

STEP 1
THE INTERFACES

STEP 2
THE ELECTRODE

STEP 3
THE REACTION

Interface energies γ (J/m^2)

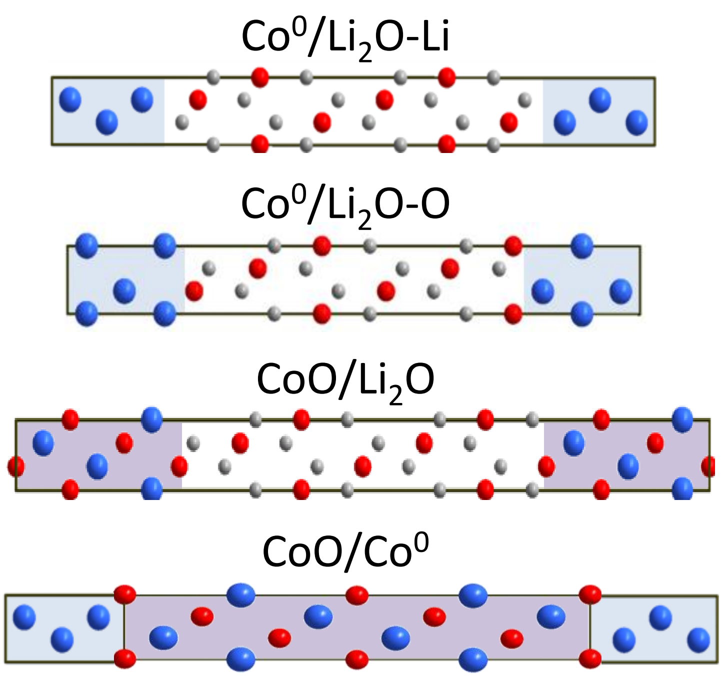


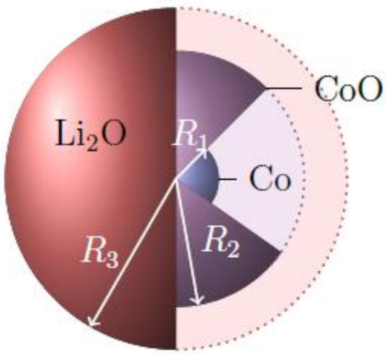
QM calculations

STEP 1	STEP 2	STEP 3
THE INTERFACES	THE ELECTRODE	THE REACTION

Interface energies γ (J/m²)

Electrode morphology





QM calculations

Wulff-like approach

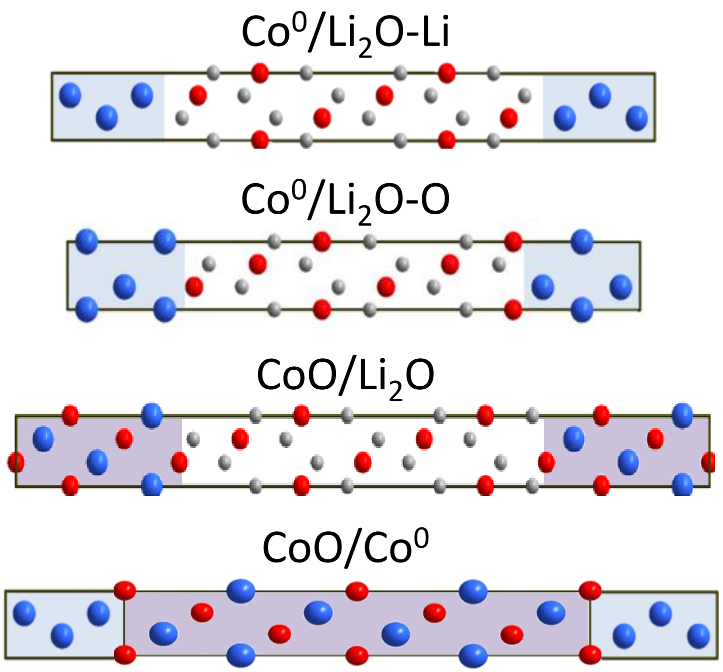
Dalverny *J. Mater. Chem.* 21 (2011) *10134*

Khatib et al. *J. Phys. Chem.* C submitted

STRATEGY

STEP 1
THE INTERFACES

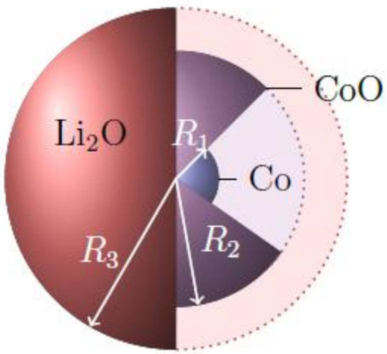
Interface energies γ (J/m²)



QM calculations

STEP 2
THE ELECTRODE

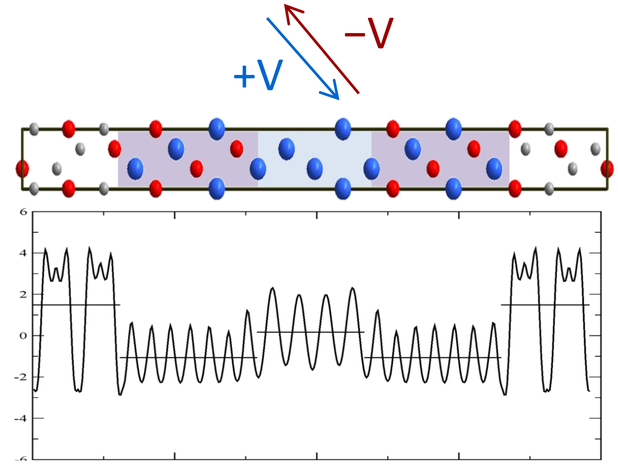
Electrode morphology



Wulff-like approach

STEP 3
THE REACTION

Electrochemistry



+ External field

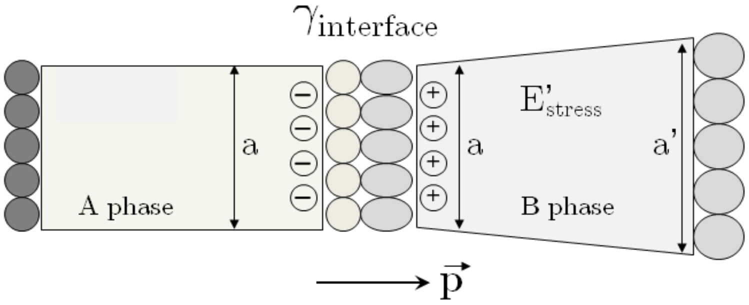
RESULTS

✓ What do you learn from this 3-step analysis ?

1. The **chemistry** governs the **interface stability** (morphology)
2. The **mechanical strain** drastically affects the **voltage**
3. The **interface electric dipole** is crucial for the **mechanism**

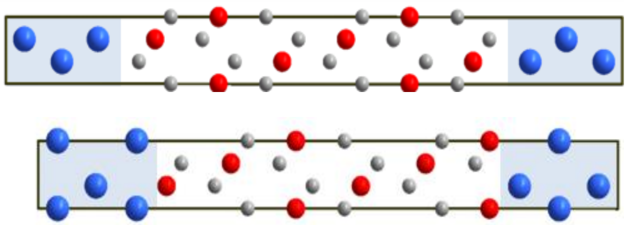
✓ An interface is described by 3 inter-dependent descriptors

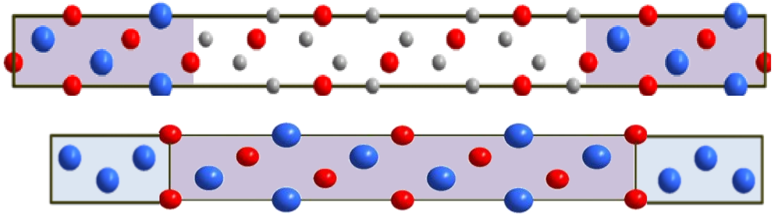
Chemical
Mechanical
Electrical



STEP 1: INTERFACES

CHEMICAL DESCRIPTOR



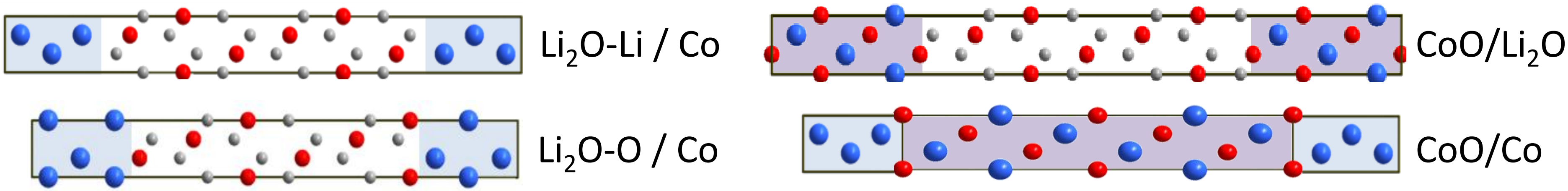


$$2\gamma A = 2\gamma^* A + \sum_i n_i \delta_i$$

Chemical contribution

Mechanical contribution

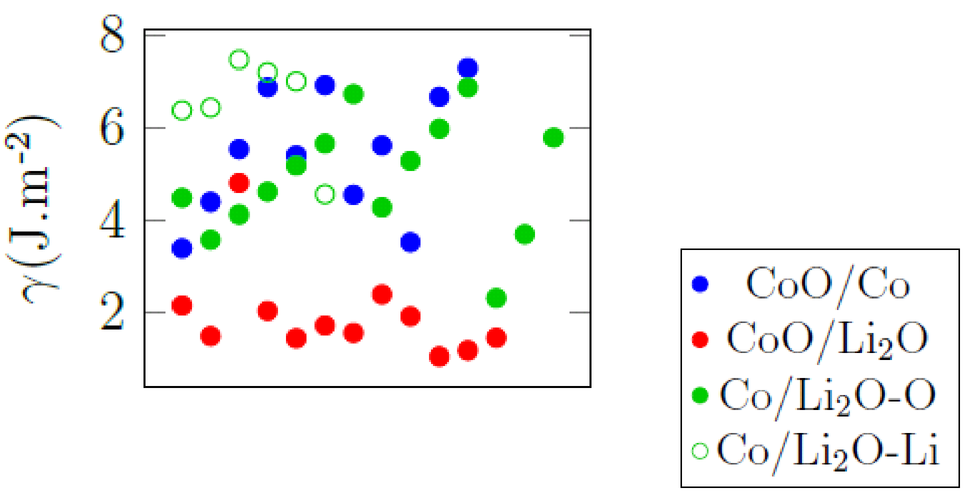
CHEMICAL DESCRIPTOR



$$2\gamma A = 2\gamma^* A + \sum_i n_i \delta_i$$

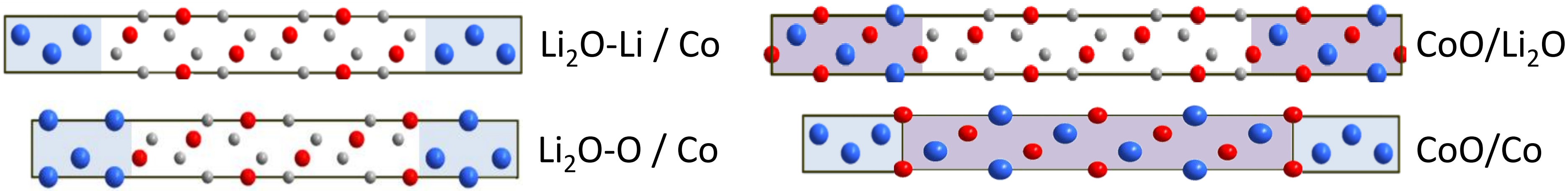
Chemical contribution

Mechanical contribution

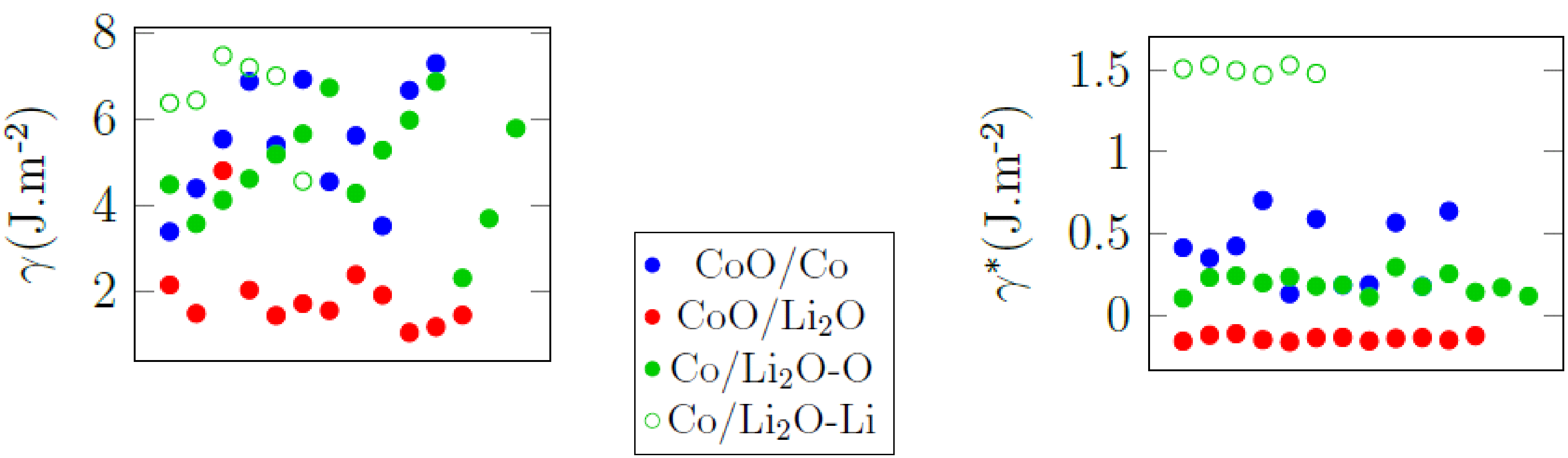


Step 1: Interfaces

Chemical Descriptor



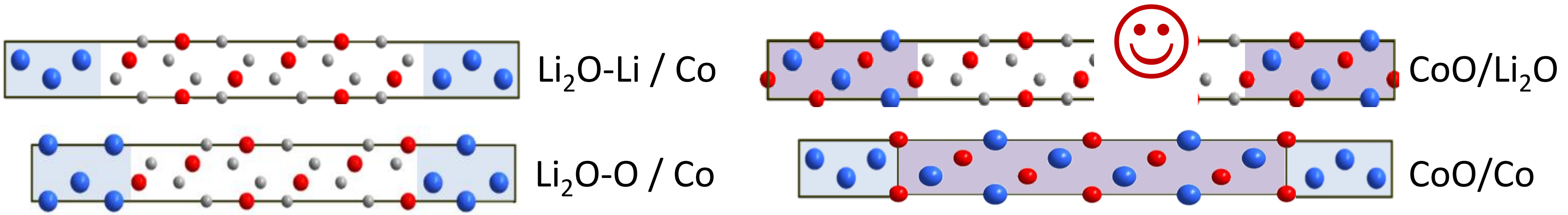
$$2\gamma A = 2\gamma^* A + \sum_i n_i\delta_i$$

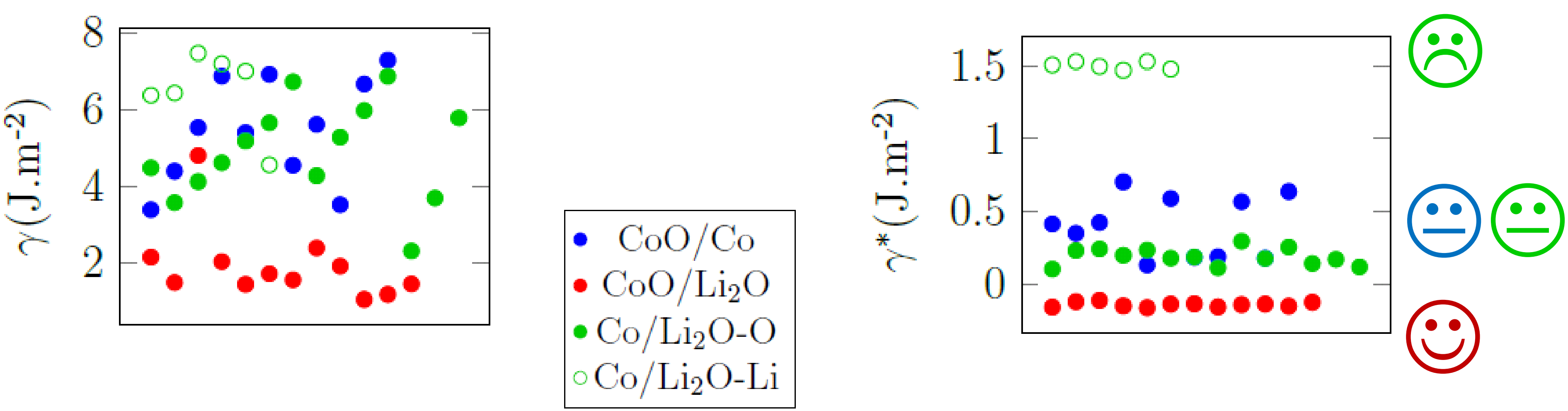


STEP 1: INTERFACES

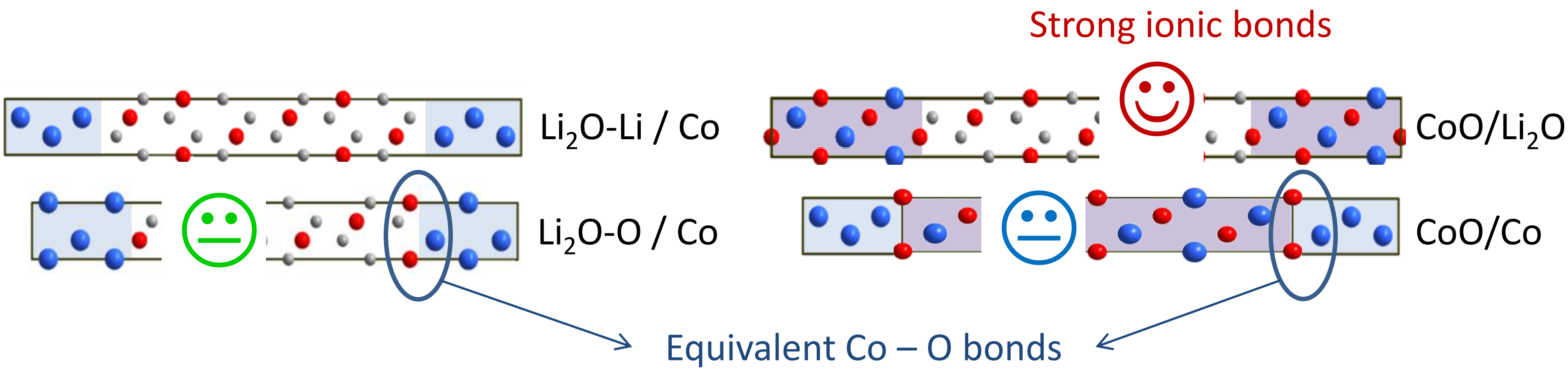
CHEMICAL DESCRIPTOR

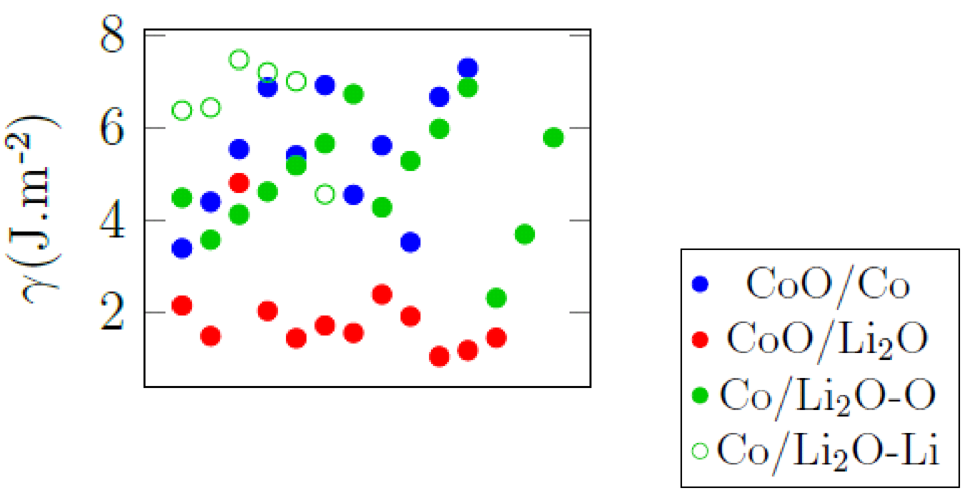
Strong ionic bonds

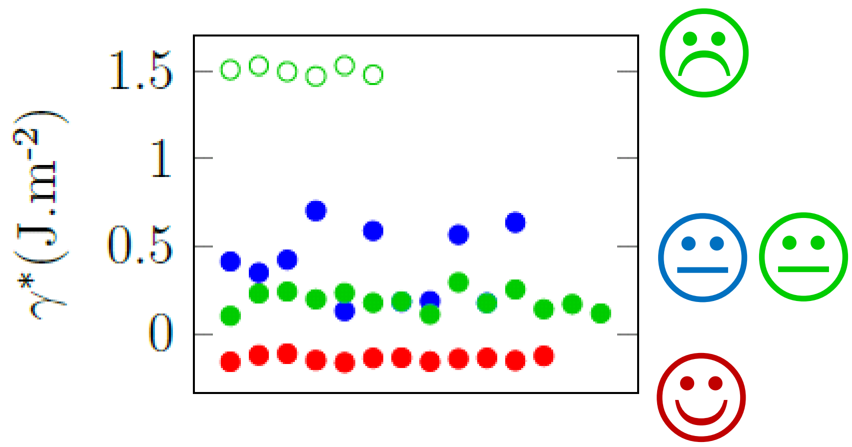




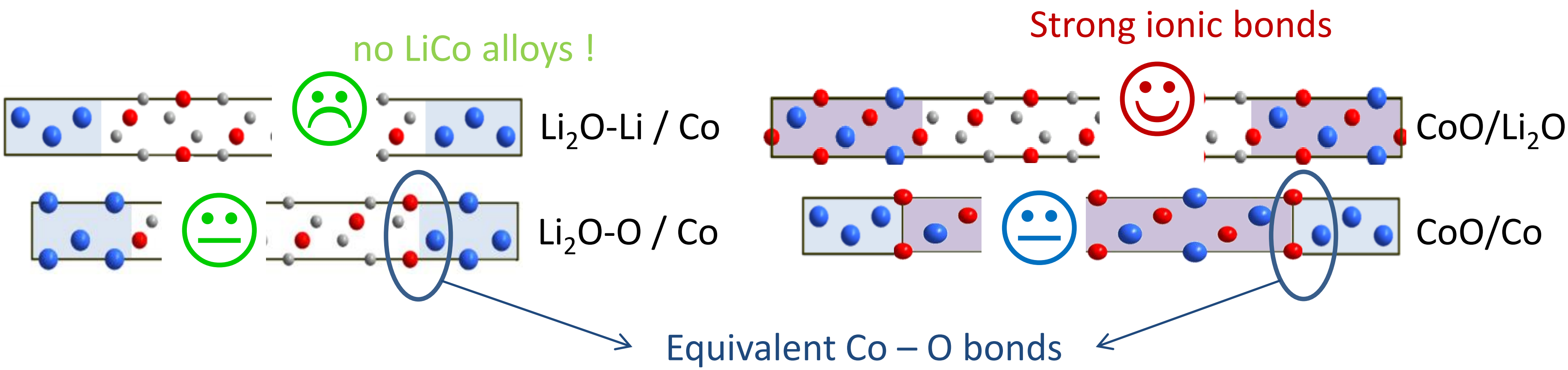
CHEMICAL DESCRIPTOR

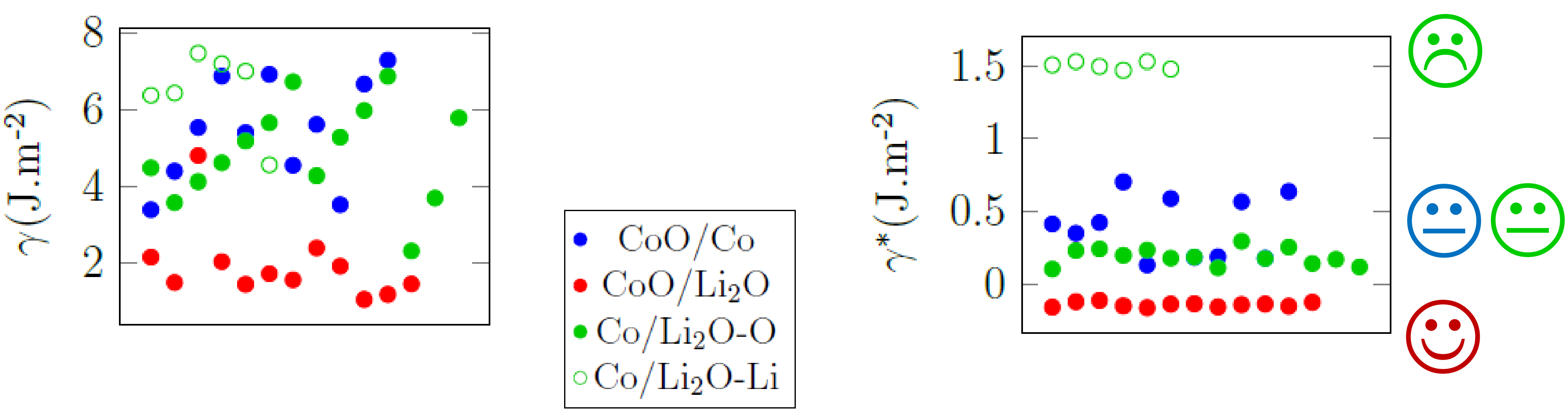






CHEMICAL DESCRIPTOR





STEP 2: ELECTRODE MORHPOLOGY

✓ Wulff-like approach to determine the electrode morphology

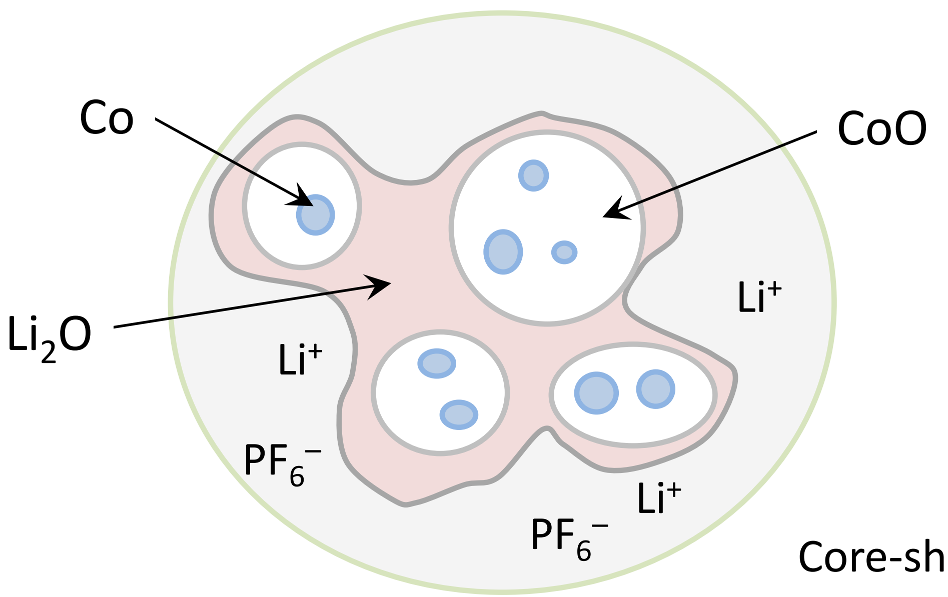
- **Maximizing** contact area of ☺ interfaces $Li_2$0 / electrolyte
  CoO / Li_2O

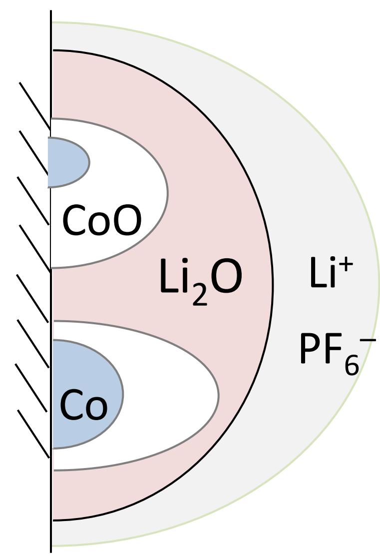
- **Minimizing** contact area of ☹ interfaces Co^0 / Li_2O-Li
- **Avoiding elastic stress**

Step 2: Electrode Morhpology

✓ Wulff-like approach to determine the electrode morphology

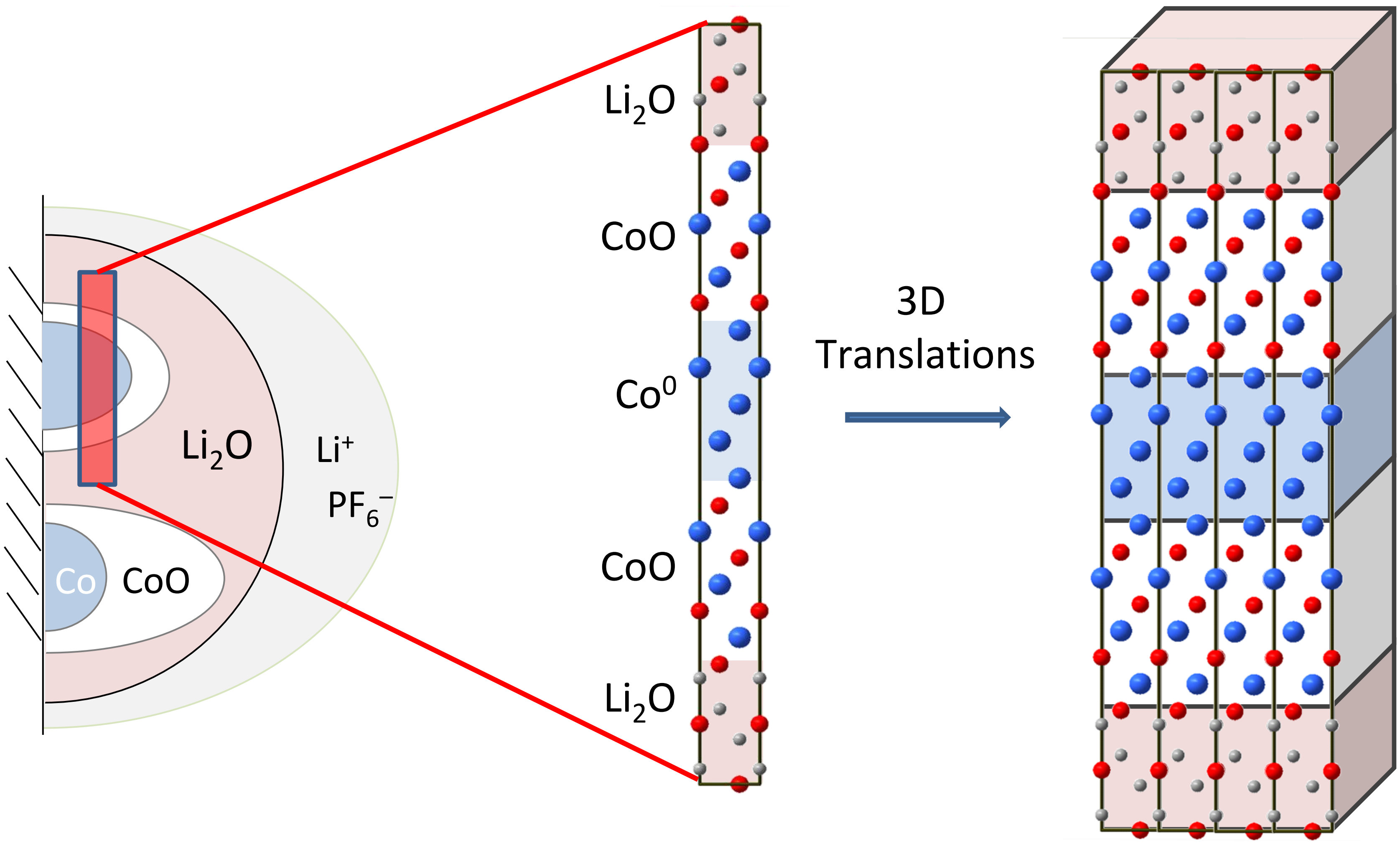
- **Maximizing** contact area of ☺ interfaces Li_20 / electrolyte
  CoO / Li_2O
- **Minimizing** contact area of ☹ interfaces Co^0 / Li_2O-Li
- **Avoiding elastic stress**





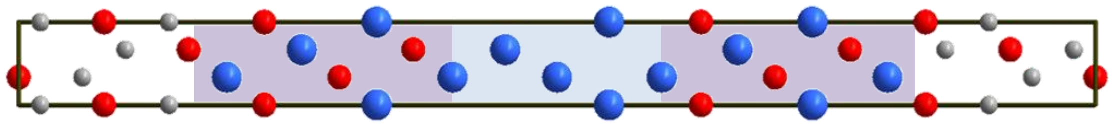
Core-shell morphology

Step 2: Electrode Morhpology



STEP 2: ELECTRODE MORHPOLOGY

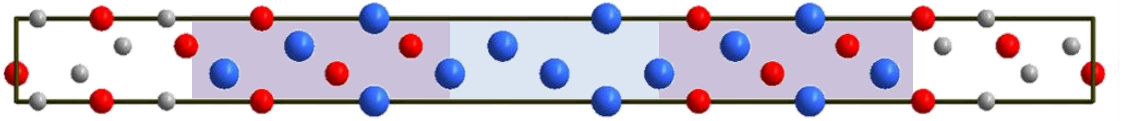
MECHANICAL DESCRIPTOR



- Unit cell symmetric with respect to Co^0 to avoid unphysical electric dipole

STEP 2: ELECTRODE MORHPOLOGY

MECHANICAL DESCRIPTOR



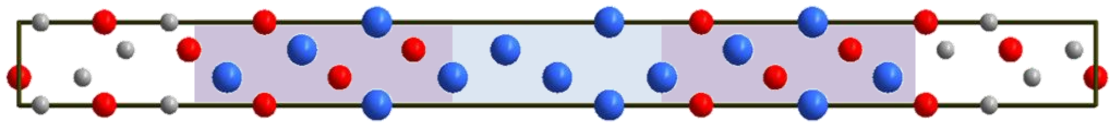
- Unit cell symmetric with respect to Co^0 to avoid unphysical electric dipole

- The relative layer thickness is directly related to the reaction extent through the relation:

$$(1\text{-}x)\ CoO + x\ (Co^0 + Li_2O)$$

STEP 2: ELECTRODE MORHPOLOGY

MECHANICAL DESCRIPTOR



- Unit cell symmetric with respect to Co^0 to avoid unphysical electric dipole

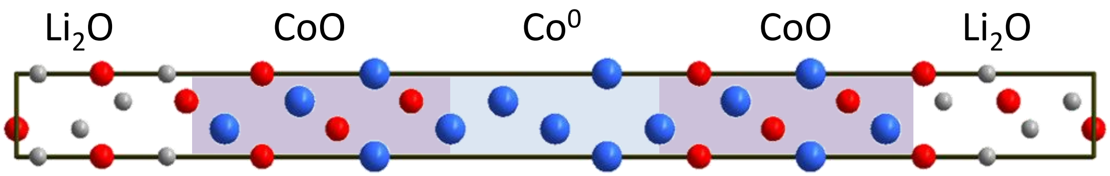
- The <u>relative layer thickness</u> is directly related to the <u>reaction extent</u> through the relation:

$$(1-x)\ CoO + x\ (Co^0 + Li_2O)$$

	Superlattices					Bulk
x	0.17	0.33	0.50	0.67	0.83	equilibrium
V (Volt)	1.84	**1.80**	**1.78**	**1.77**	1.90	2.18

STEP 2: ELECTRODE MORHPOLOGY

MECHANICAL DESCRIPTOR



- Unit cell symmetric with respect to Co^0 to avoid unphysical electric dipole

- The relative layer thickness is directly related to the reaction extent through the relation:

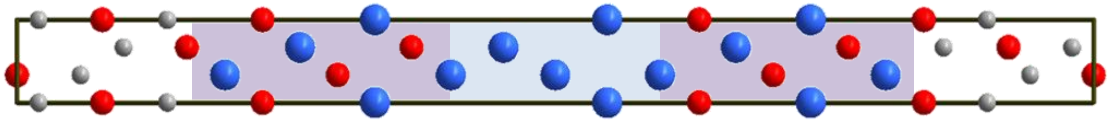
$$(1-x)\ CoO + x\ (Co^0 + Li_2O)$$

	Superlattices					Bulk	
x	0.17	0.33	0.50	0.67	0.83	equilibrium	strained
V (Volt)	1.84	**1.80**	**1.78**	**1.77**	1.90	2.18	**1.79**

Electrochemical potential (V) depends on the interface strain !

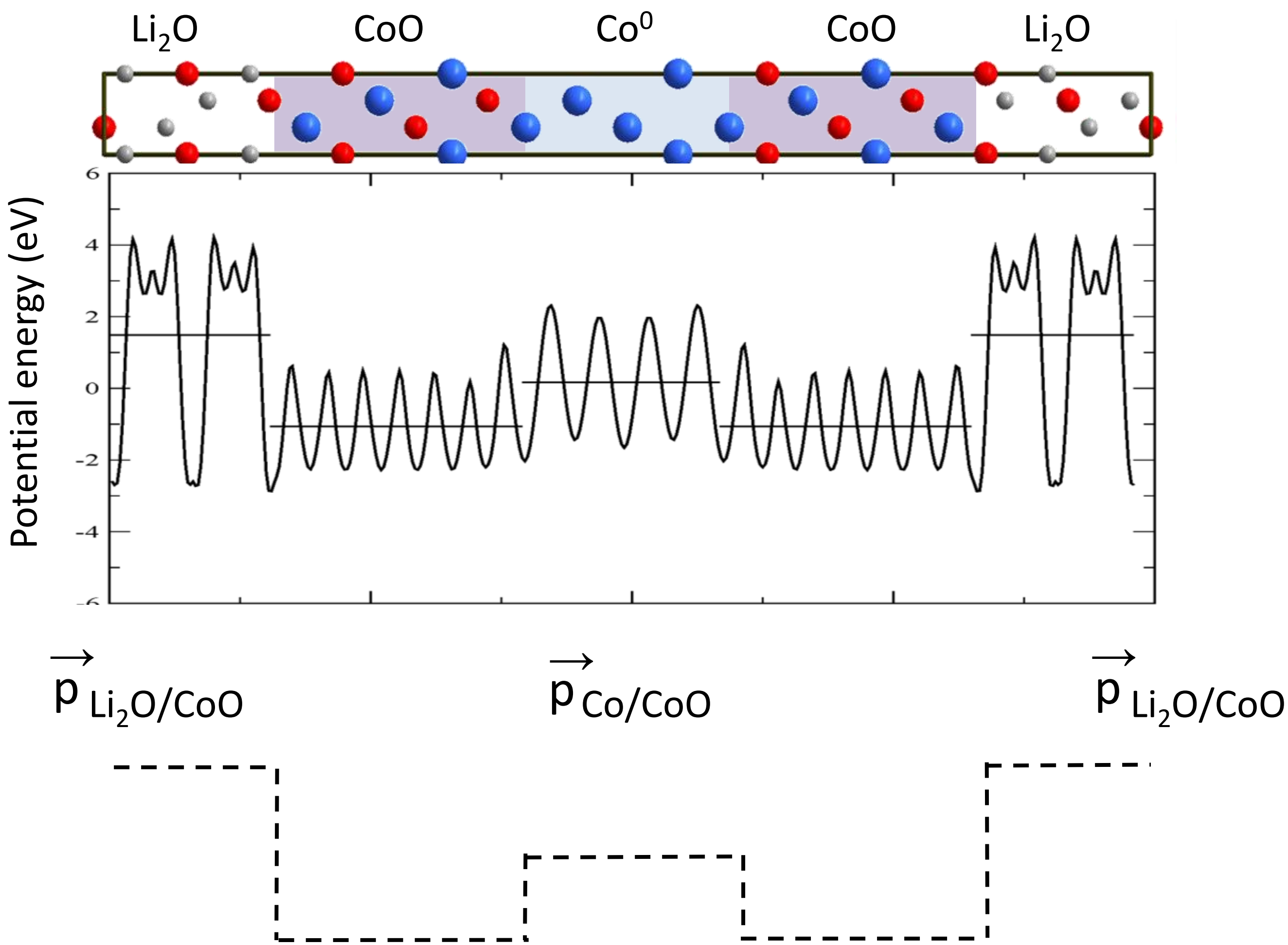
Step 3: The Reaction

Electrical Descriptor



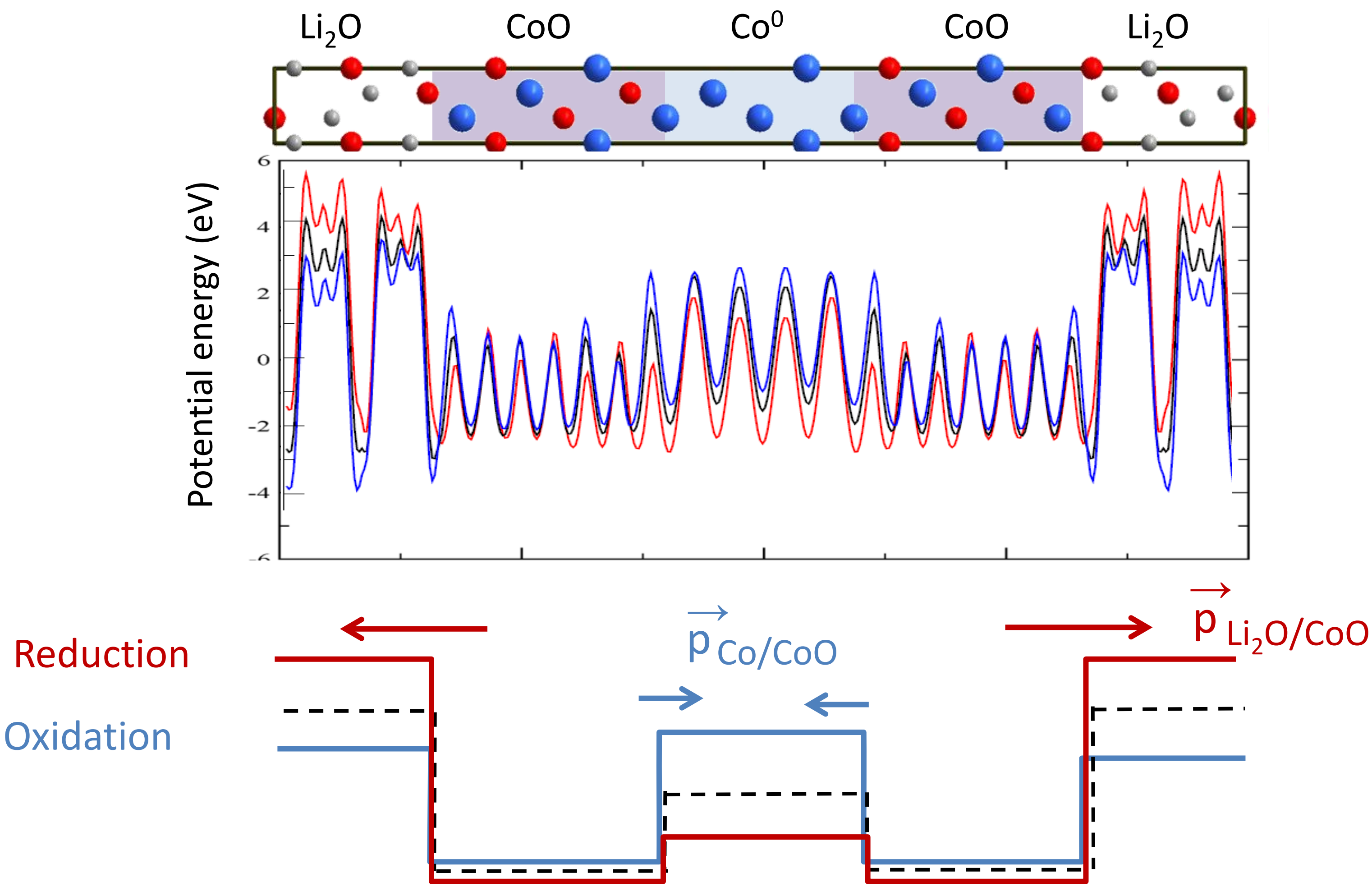
STEP 3: THE REACTION

ELECTRICAL DESCRIPTOR



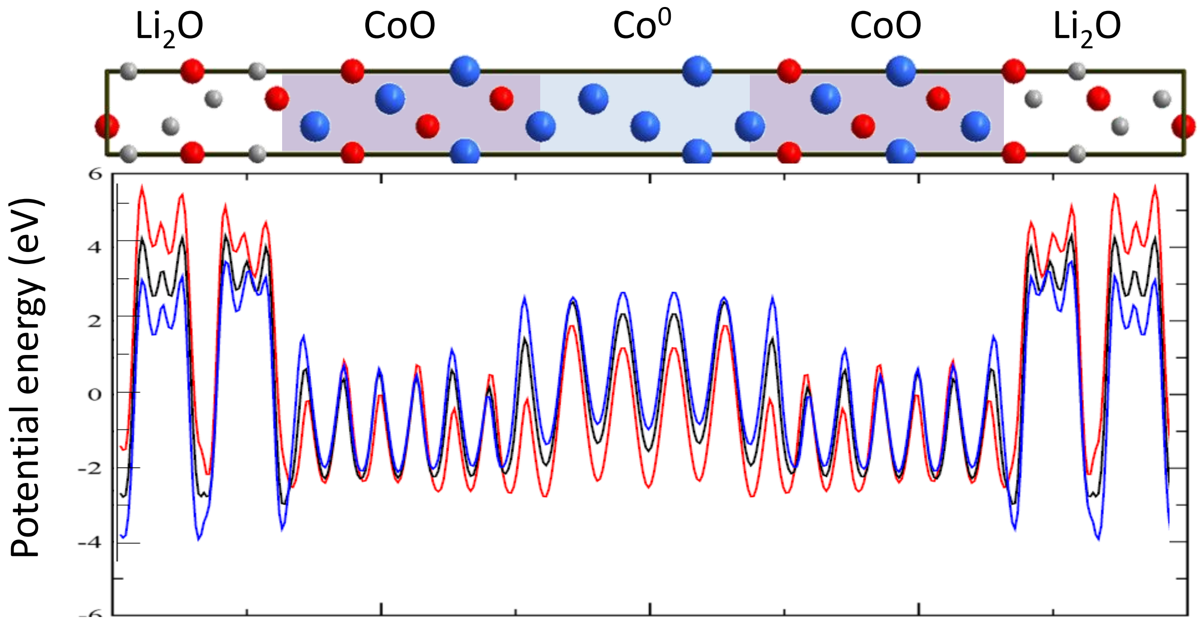
STEP 3: THE REACTION

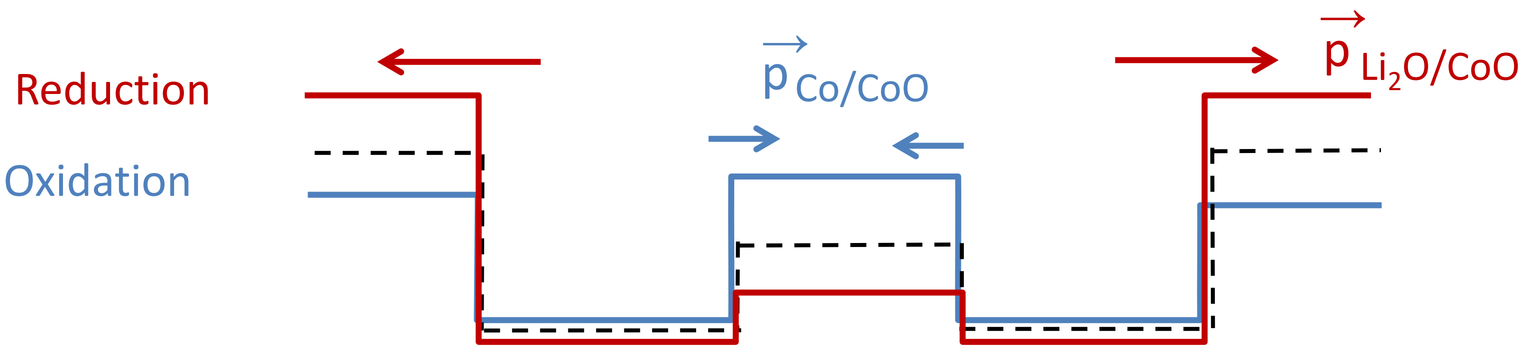
ELECTRICAL DESCRIPTOR



STEP 3: THE REACTION

ELECTRICAL DESCRIPTOR

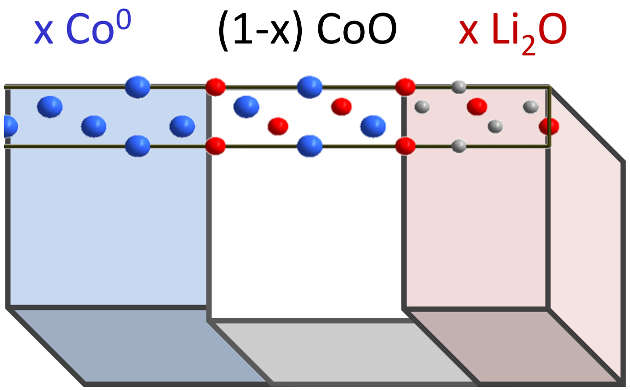


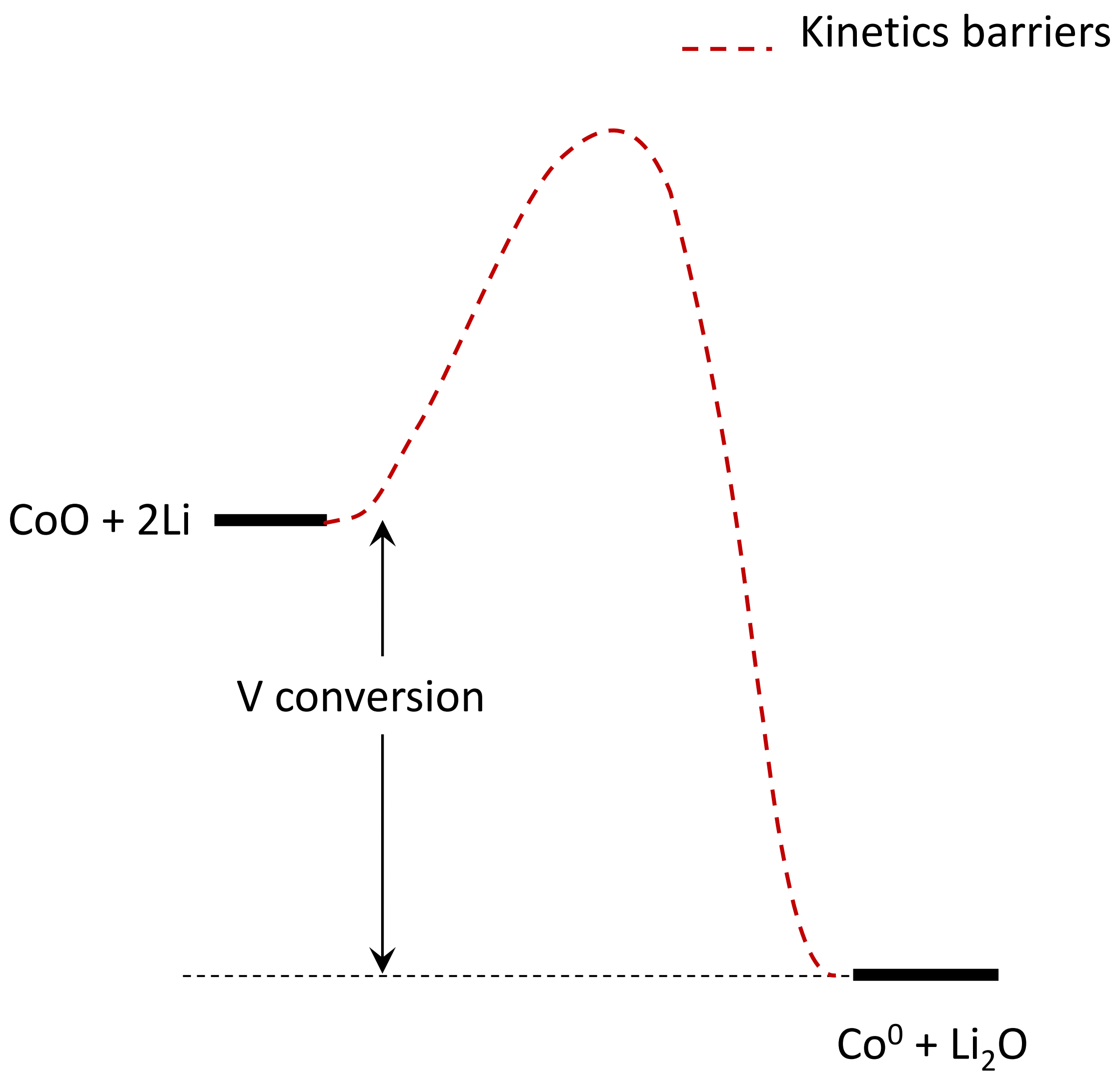


1. Different responses of the two interfaces

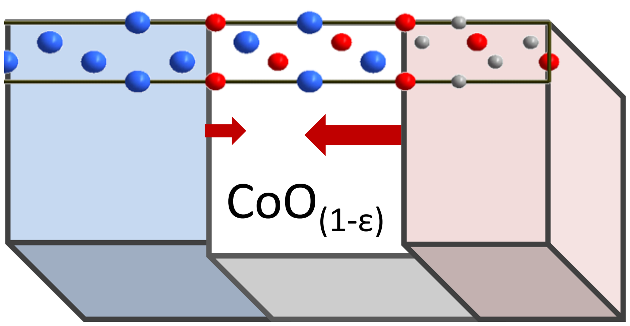
2. Asymmetric responses in charge/discharge

CONVERSION MECHANISM

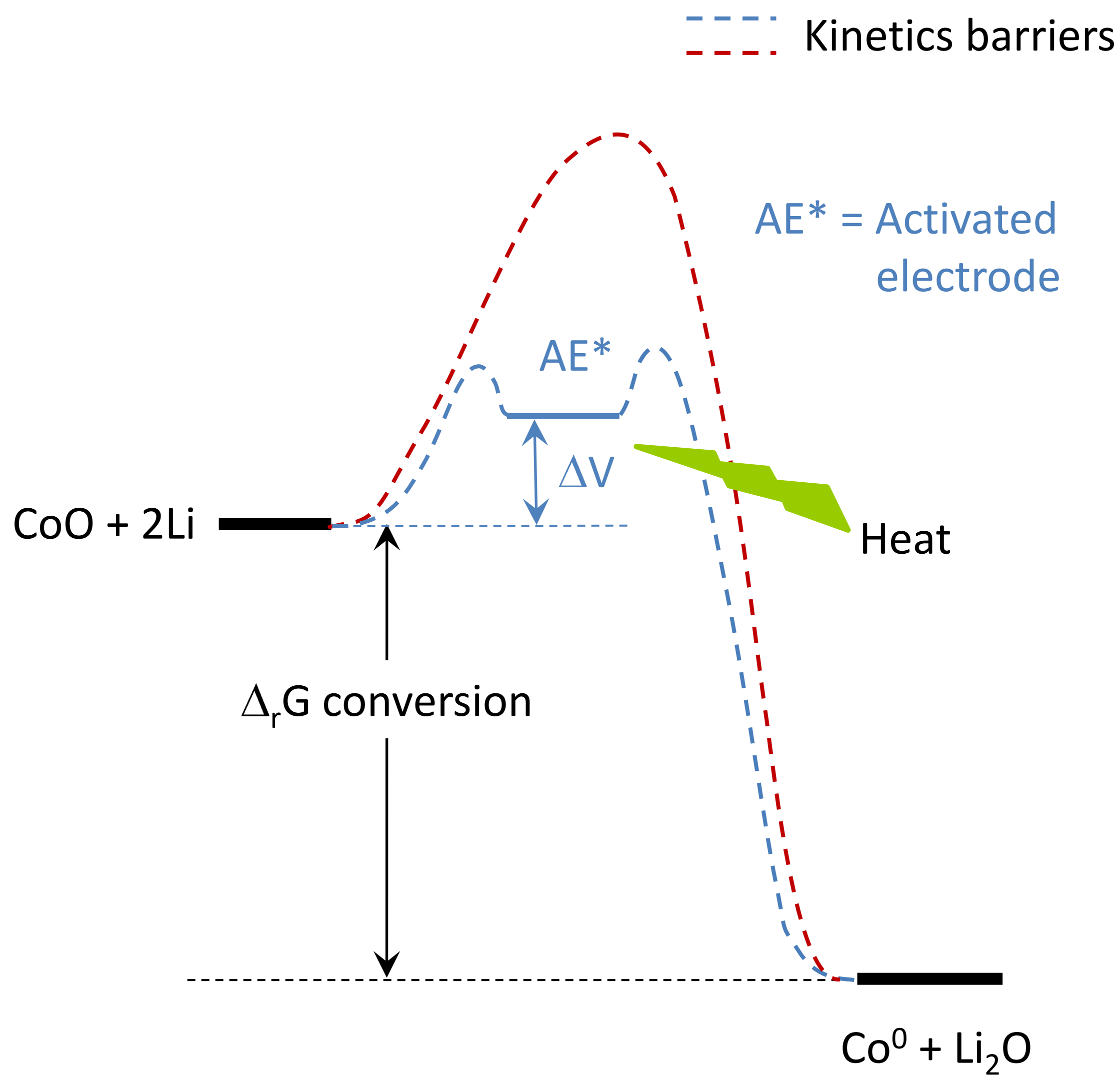




Conversion Mechanism



Electric field gradients affect the interfaces migration



SUMMARY

✓ What did you learn from this 3-step analysis ?

1. The **chemistry** governs the **interface stability**

   → Different morphologies (Kinetics)

2. The **mechanical strain** drastically affects the **voltage**

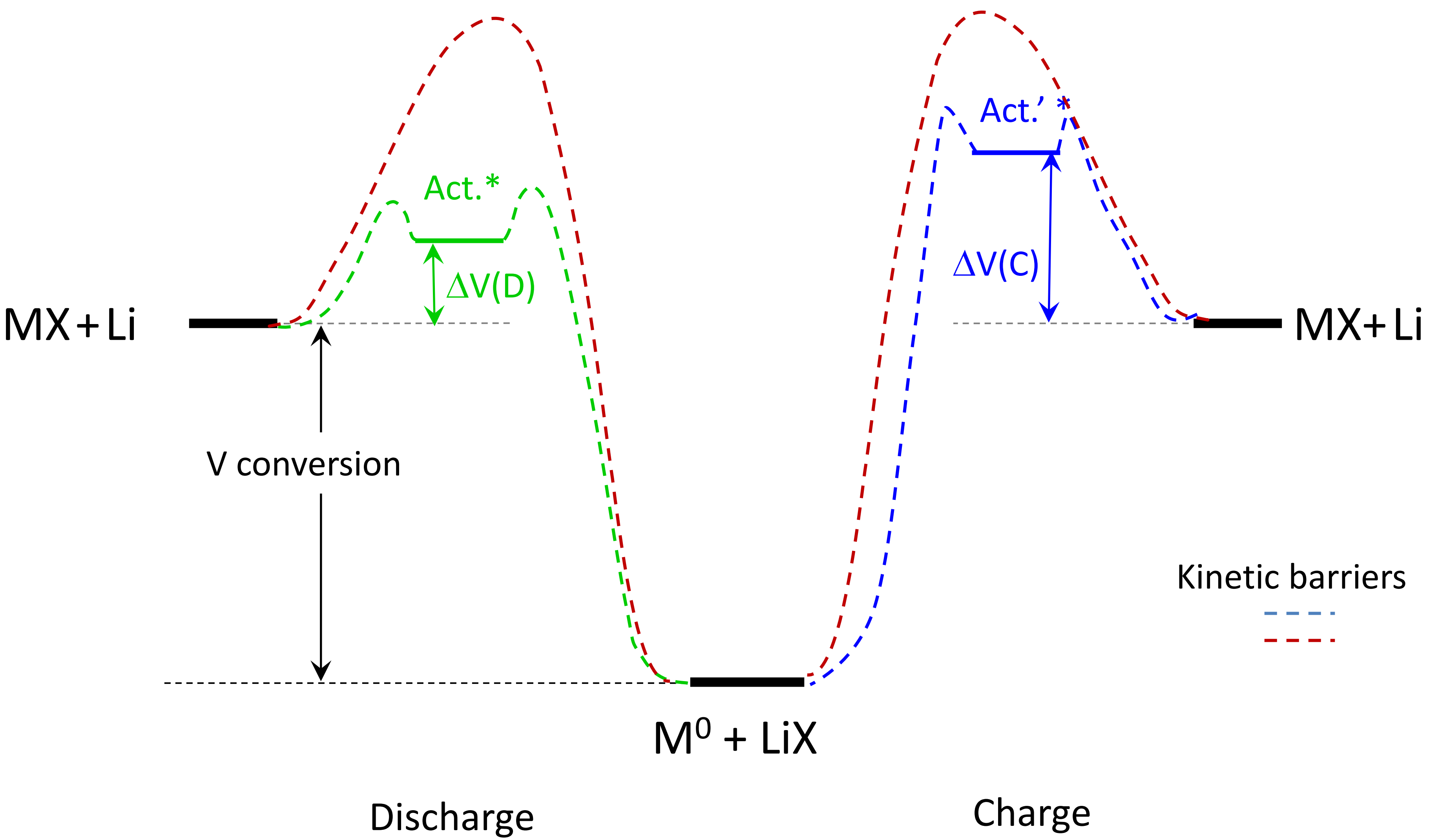
   → Different stress depending on the SOC / SOD

3. The **interface electric dipole** is crucial for the **mechanism**

   → Different mechanisms (Thermodynamics)

ORIGIN OF THE VOLTAGE HYSTERESIS

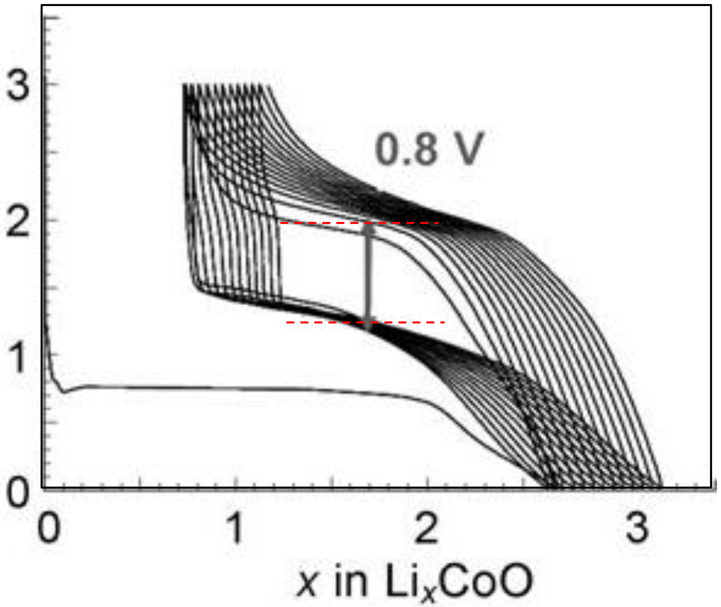
Defect Chemistry = Crucial to Initiate Conversion Reactions



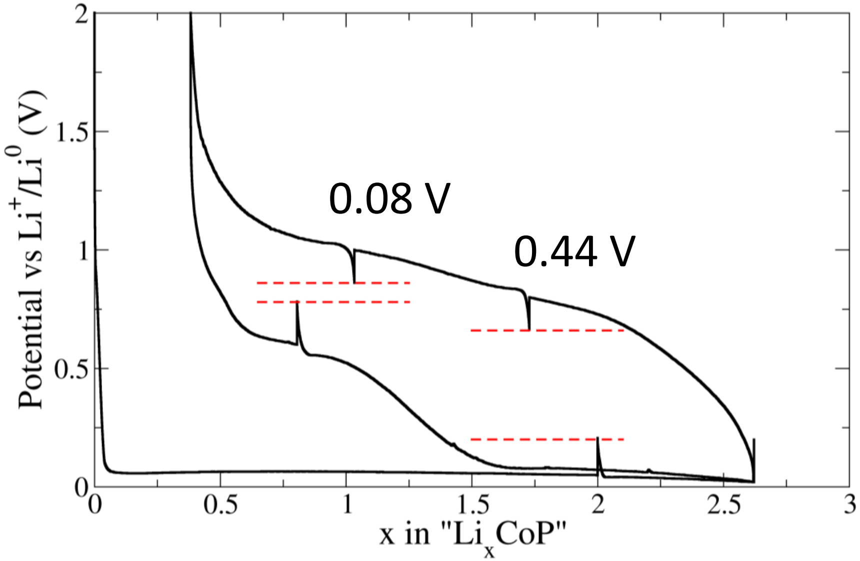
LAST BUT NOT LEAST QUESTION ?

✓ Can we be predictive and quantitative on
Mechanism + Voltage Hysteresis ?

$CoO + 2Li \rightleftarrows Li_2O + Co^0$

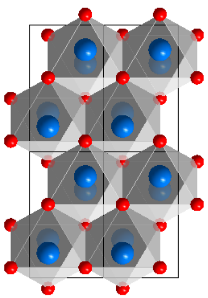


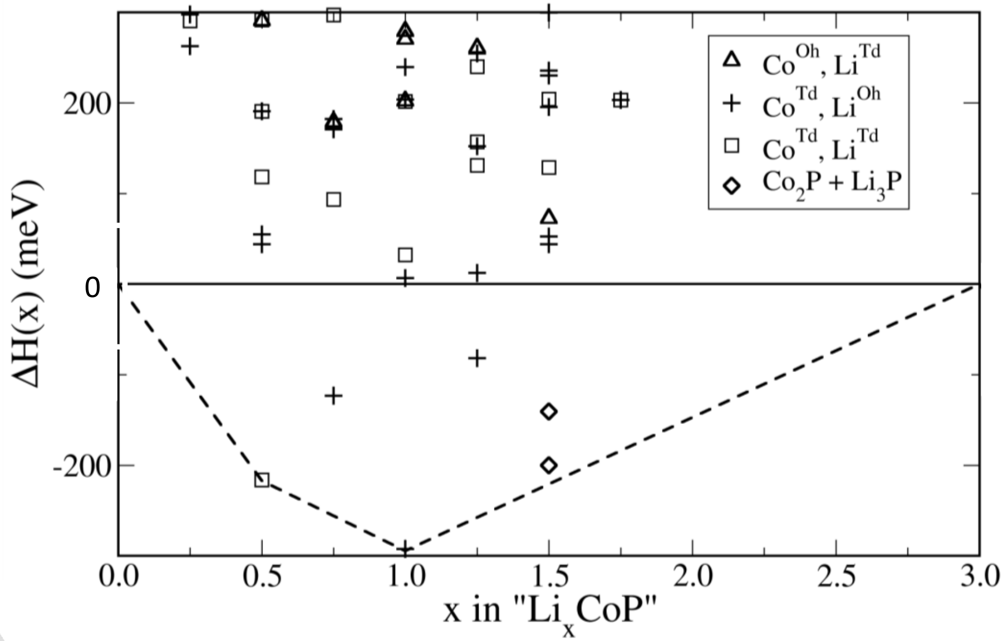
$CoP + 3Li \rightleftarrows Li_3P + Co^0$



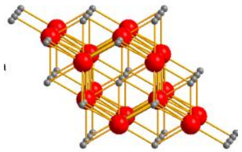
T = 0K Bulk Phase Diagram

CoP

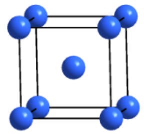


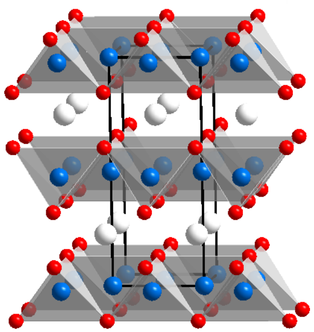


Li_3P

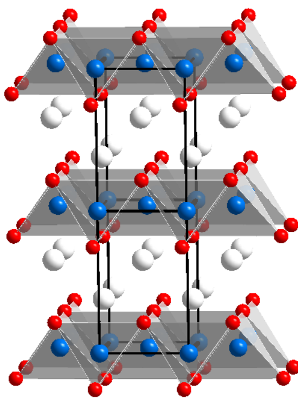


Co^0





$Li_{0.5}CoP$



LiCoP

2-step Insertion / Conversion mechanism

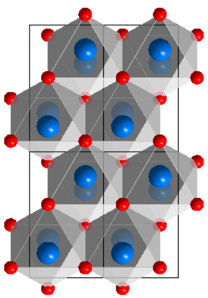
$CoP + ½ Li \rightarrow Li_{½}CoP$

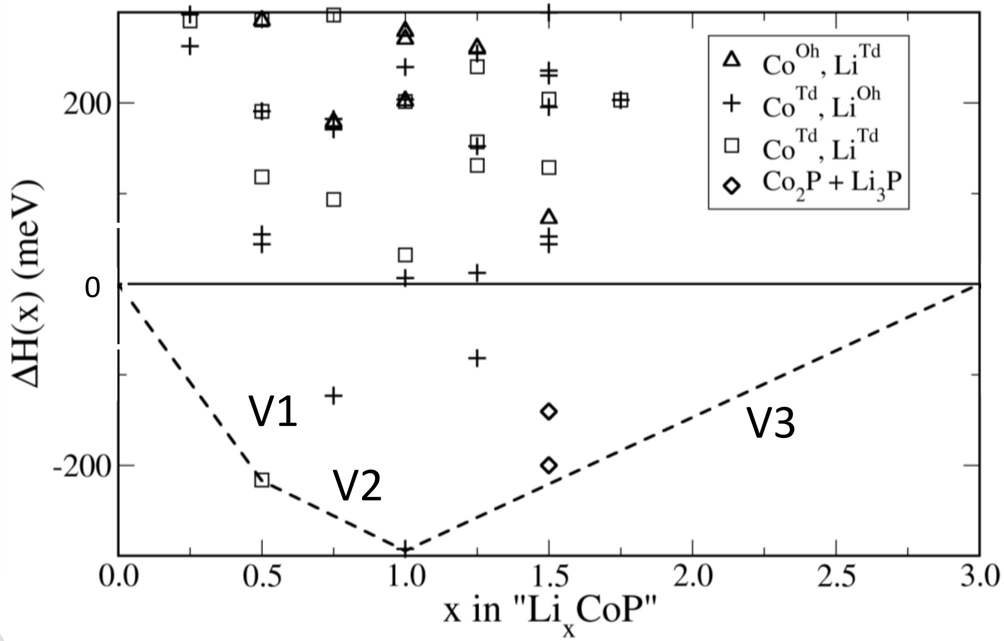
$Li_{½}CoP + ½ Li \rightarrow LiCoP$

$LiCoP + 2Li \rightarrow Li_3P + Co^0$

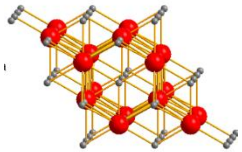
T = 0K BULK PHASE DIAGRAM

CoP

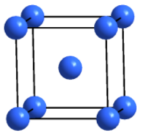


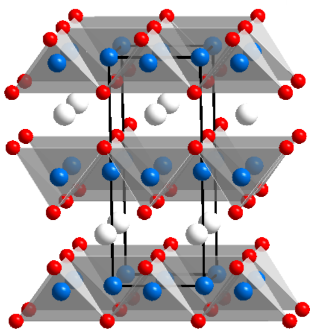


Li_3P

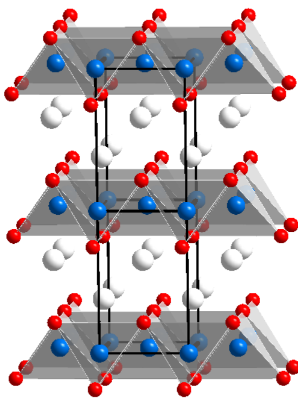


Co^0





$Li_{0.5}CoP$



LiCoP

2-step Insertion / Conversion mechanism

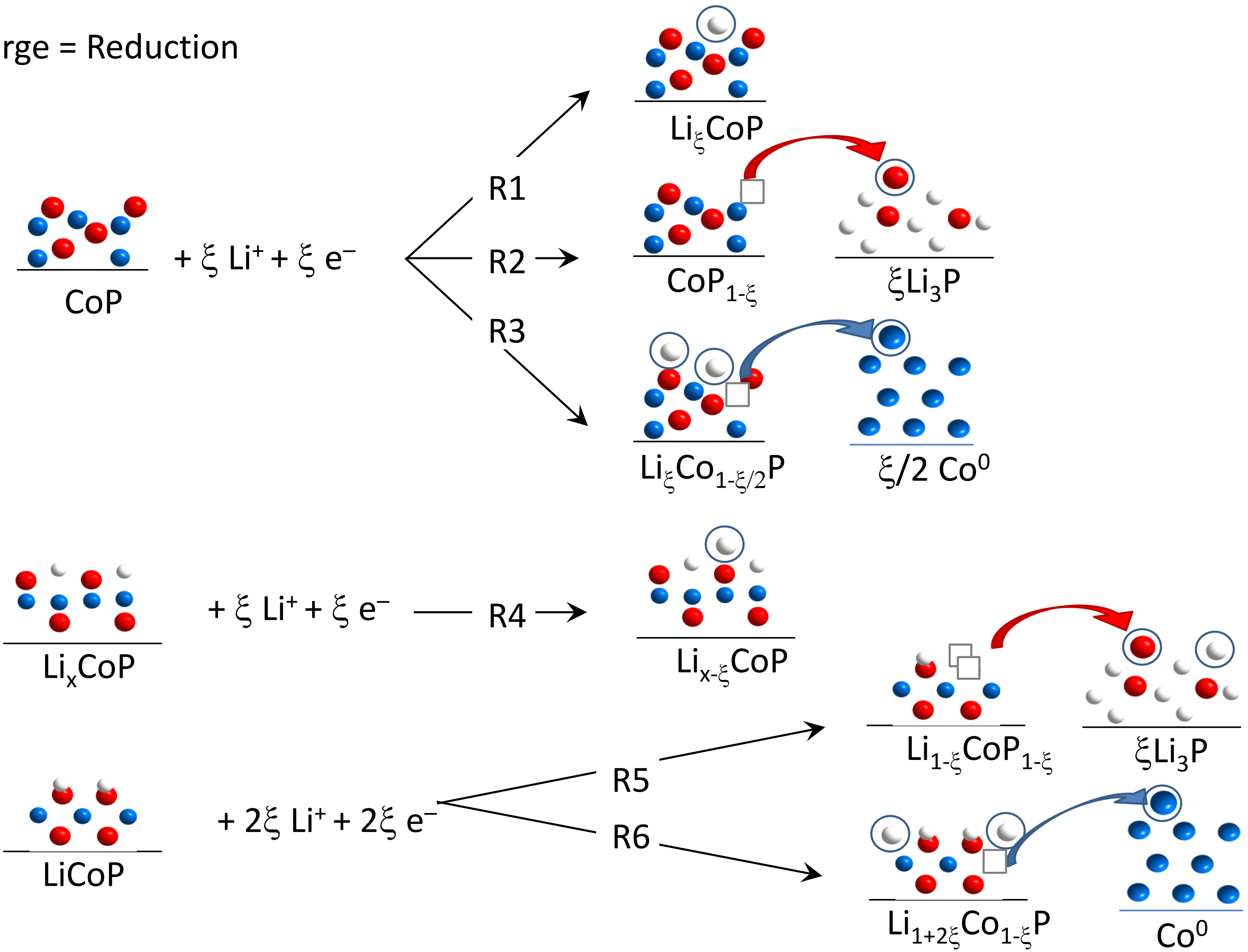
CoP + ½ Li → $Li_{½}CoP$

$Li_{½}CoP$ + ½ Li → LiCoP

LiCoP + 2Li → Li_3P + Co^0

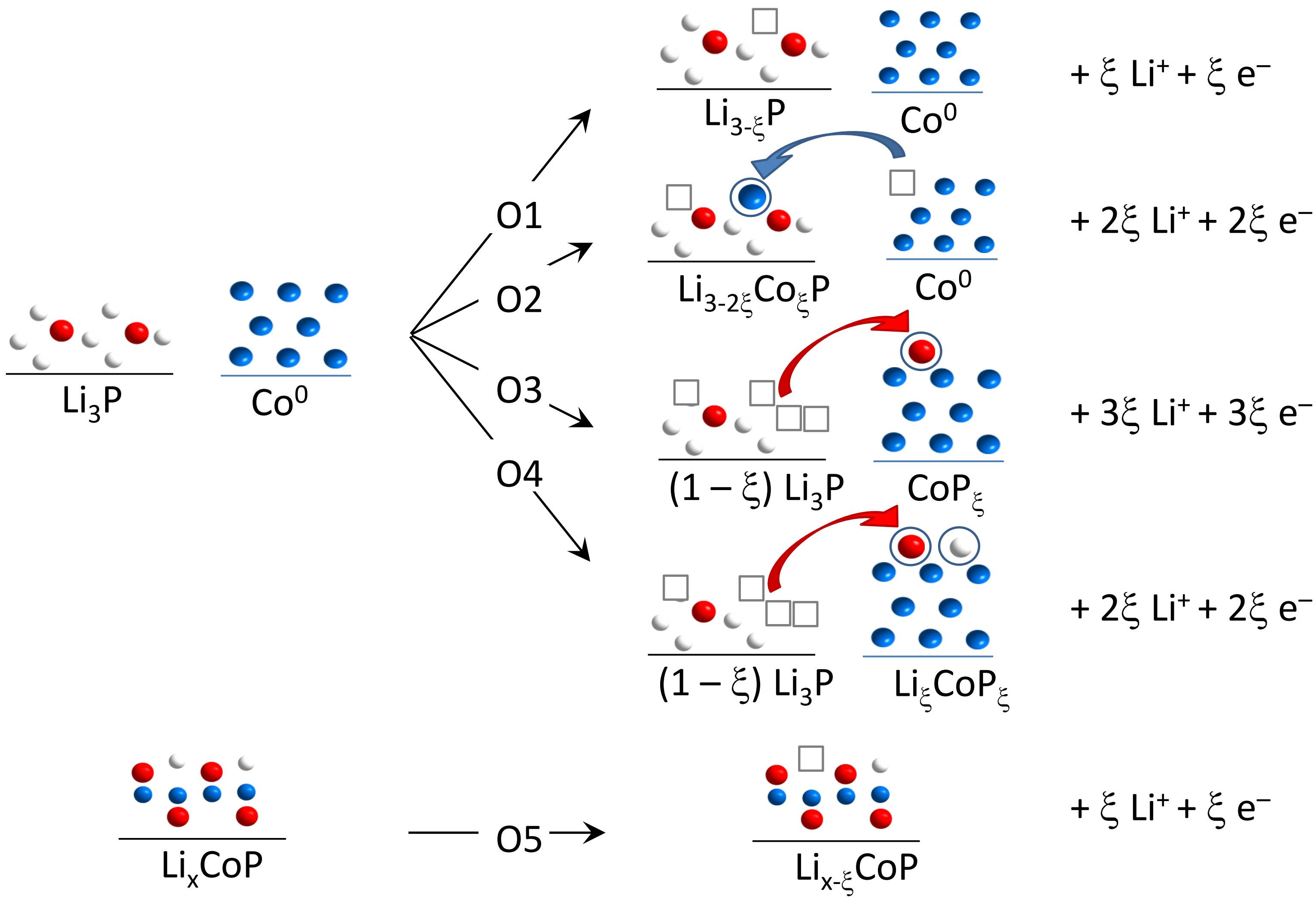
SURFACE REACTIVITY

Discharge = Reduction



SURFACE REACTIVITY

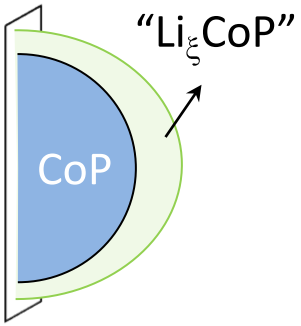
Charge = Oxidation



SURFACE REACTIVITY

DISCHARGE: Elementary reactions			ξ coverage	V (V)
Li-adsorption on the CoP surface to form a Li_xCoP interface				
	R1	$(CoP)\text{-}CoP + \xi Li \rightarrow (Li_\xi CoP)\text{-}CoP$	¼ Li per CoP	1.12
			½ Li per CoP	1.09
			¾ Li per CoP	0.87
			1 Li per CoP	0.86

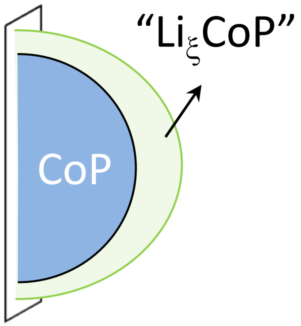
R1



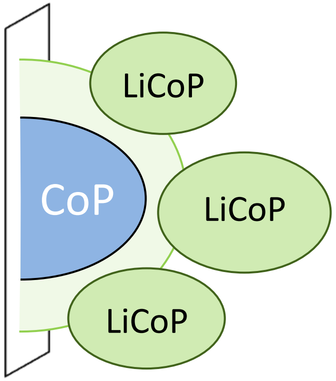
SURFACE REACTIVITY

DISCHARGE: Elementary reactions			ξ coverage	V (V)
Li-adsorption on the CoP surface to form a Li_xCoP interface				
	R1	(CoP)-CoP + ξLi → (Li_ξCoP)-CoP	¼ Li per CoP	1.12
			½ Li per CoP	1.09
			¾ Li per CoP	0.87
			1 Li per CoP	0.86
Nucleation of Li_xCoP “nanoparticles” from CoP “nanoparticles”				
	R1’	(CoP)-CoP + ξLi → (Li_ξCoP)-Li_ξCoP	½ Li per CoP	1.09
			1 Li per CoP	0.86

R1

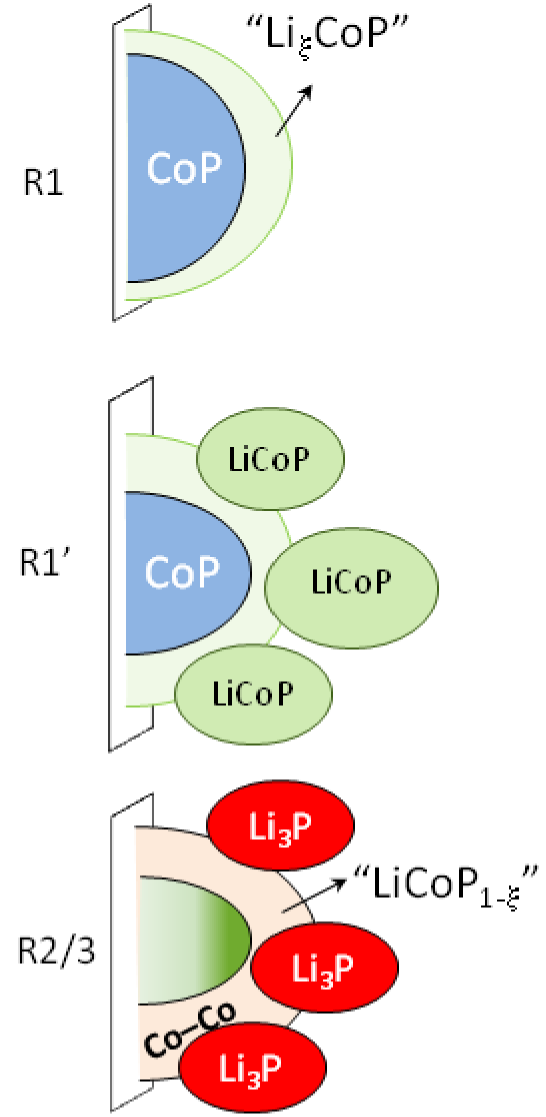


R1’

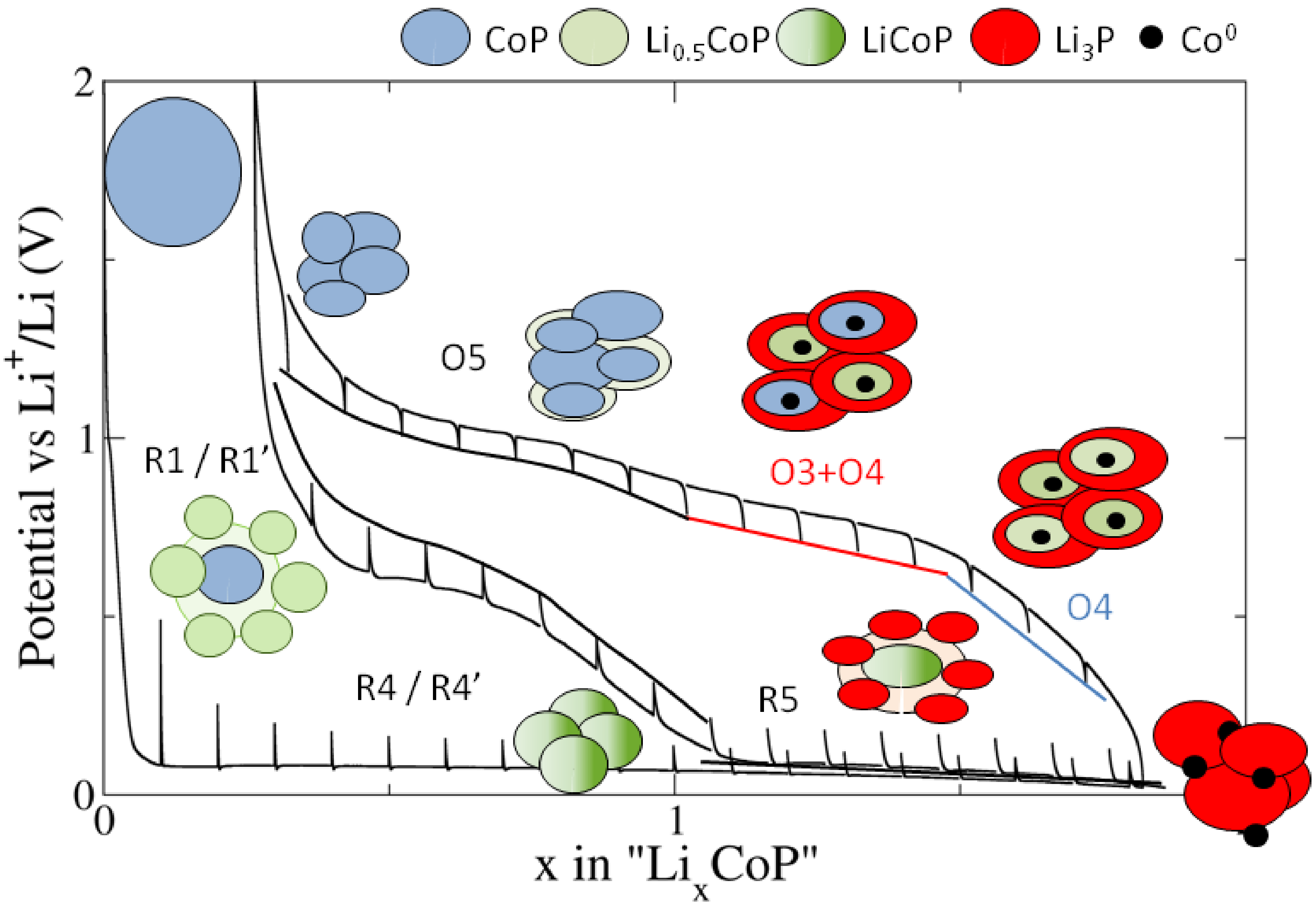


SURFACE REACTIVITY

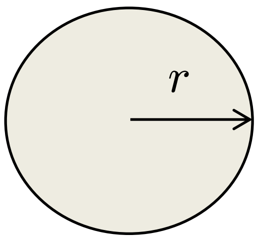
DISCHARGE: Elementary reactions			ξ coverage	V (V)
Li-adsorption on the CoP surface to form a Li_xCoP interface				
	R1	(CoP)-CoP + ξLi → (Li_ξCoP)-CoP	¼ Li per CoP	1.12
			½ Li per CoP	1.09
			¾ Li per CoP	0.87
			1 Li per CoP	0.86
Nucleation of Li_xCoP "nanoparticles" from CoP "nanoparticles"				
	R1'	(CoP)-CoP + 0.5Li → ($Li_{0.5}$CoP)-$Li_{0.5}$CoP		1.09
		(CoP)-CoP + 0.5Li → (LiCoP)-LiCoP		0.86
Creation of P-vacancies on the surface of CoP to form Li_3P				
	R2	(CoP)-CoP + 3ξLi → ($CoP_{1-\xi}$)-CoP + ξLi_3P	¼ P per Co	0.60
			½ P per Co	0.48
			¾ P per Co	0.44
			1 P per Co	0.33
Li-substitution for Co at the surface of CoP to form Co^0				
	R3	(CoP)-CoP + 3ξLi → ($Li_{3\xi}Co_{1-\xi}P$)-CoP + ξCo^0	¼ Co per CoP	0.37



ELECTROCHEMICAL PROCESS



SURFACE VS. BULK REACTIVITY



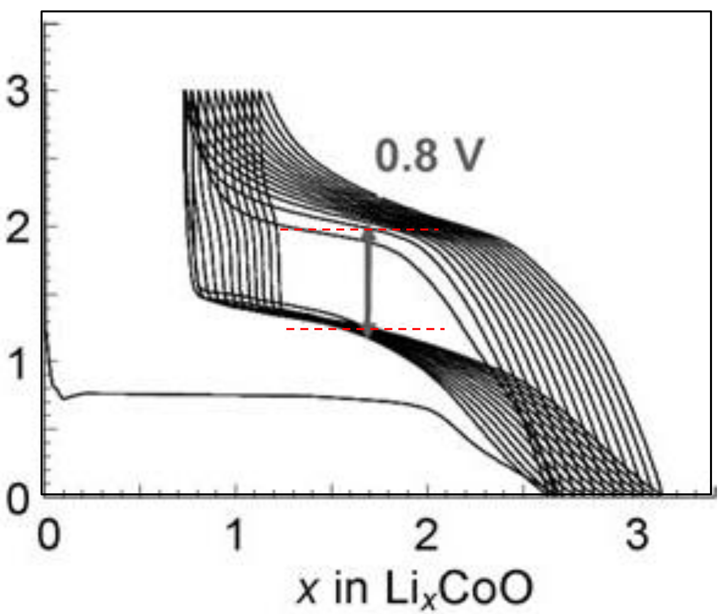
n_b : number of bulk atoms

n_s : number of surface atoms

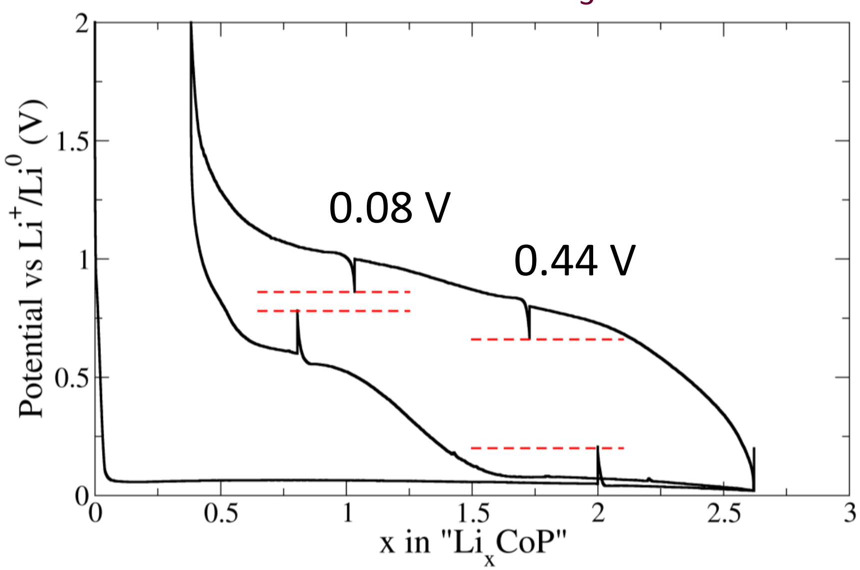
$n_b + n_s = n_T$

$$V(r) = \frac{n_s}{n_T} V_s + \frac{n_b}{n_T} V_b = \frac{3}{3+r} V_s + \frac{r}{3+r} V_b$$

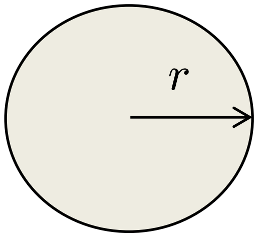
$CoO + 2Li \rightleftarrows Li_2O + Co^0$



$CoP + 3Li \rightleftarrows Li_3P + Co^0$



Surface vs. Bulk Reactivity



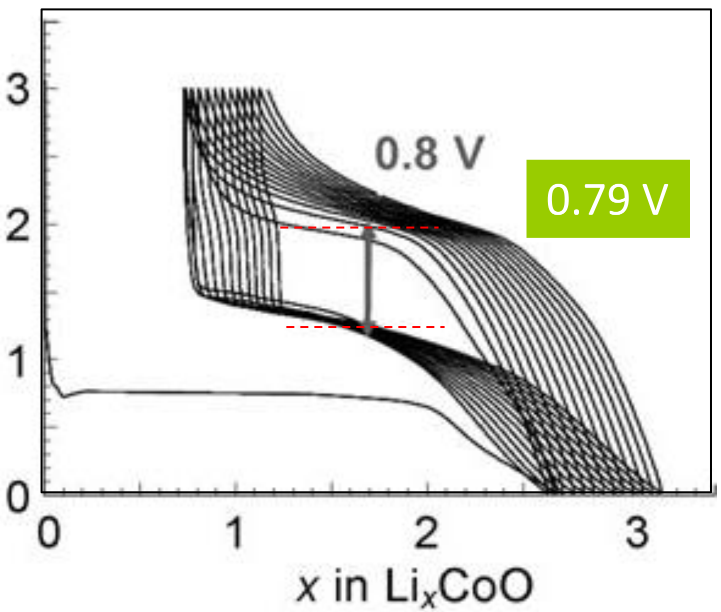
n_b : number of bulk atoms

n_s : number of surface atoms

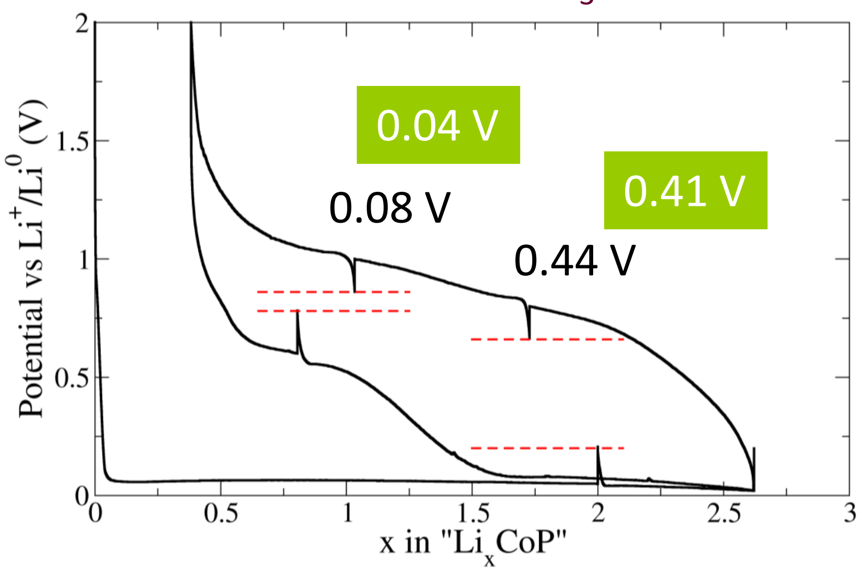
$n_b + n_s = n_T$

$$V(r) = \frac{n_s}{n_T} V_s + \frac{n_b}{n_T} V_b = \frac{3}{3+r} V_s + \frac{r}{3+r} V_b$$

$CoO + 2Li \rightleftarrows Li_2O + Co^0$



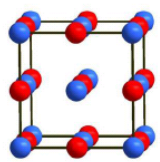
$CoP + 3Li \rightleftarrows Li_3P + Co^0$



Excellent Agreement between Experiment and Theory

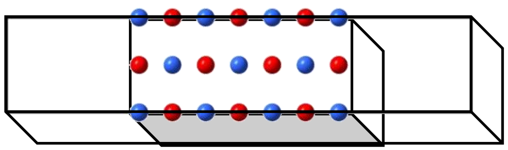
Conclusions / Perspectives ?

Bulk



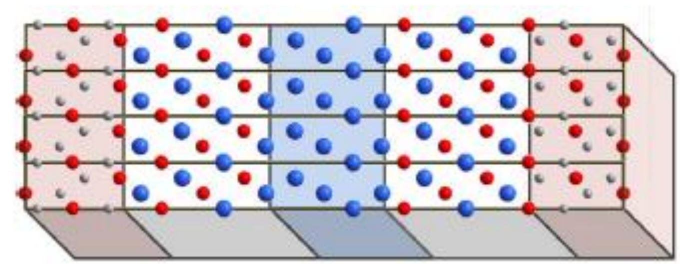
Intrinsic properties

Surface



Particle size

Interface



Texture / Morphology

✓ Efficient, easy-handling and powerful tool for bulk, surface and interface electrochemistry of **multi-phased & nano-sized electrodes** for Li-ion batteries

Conclusions / Perspectives ?

Much work still to be done …

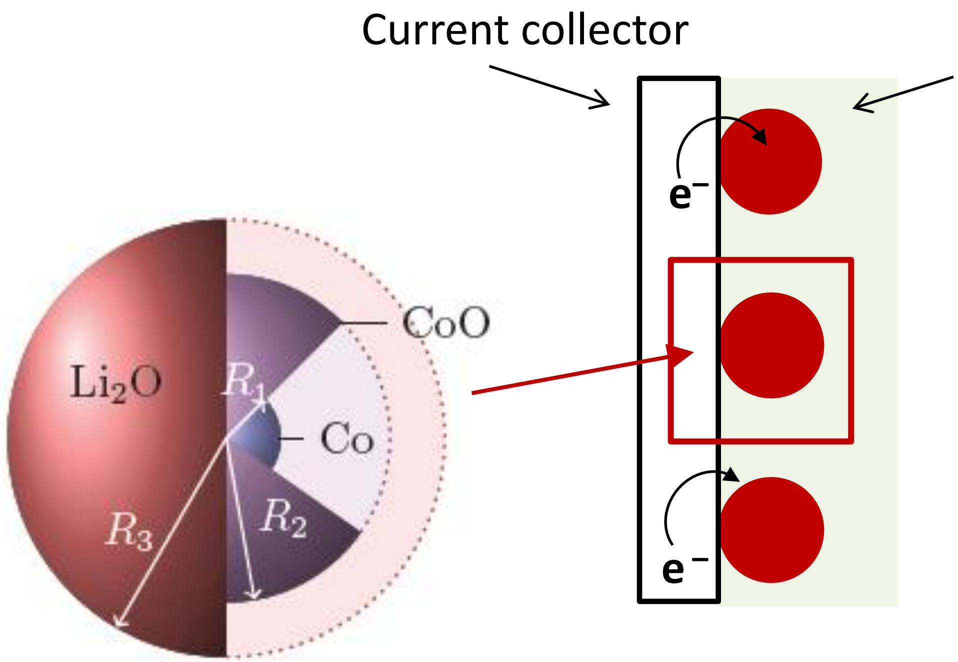
✓ Electrode / Binder / Carbon black
→ Impact on the interface reactivity

✓ Electrode / Electrolyte interfaces
→ Li-dendrites
→ SEI
→ Other electrolyte reduction processes

✓ Aging phenomena are being investigated through surface reactivity

✓ Development of bottum-up multi-scale models to simulate Charge / Discharge voltage profiles depending on operating conditions … (Collaboration with A. Franco)

PERSPECTIVES



Assumptions:
- constant C_{Li+}
- constant double layer capacity C_{dl}

Reaction rate coefficients

$$k_i = \frac{k_B T}{h} \exp\left(\frac{-\Delta G_i^{\ddagger}}{RT}\right)$$

Gibbs activation energy non constant
Depends on SOC / SOD, elastic stress, morphology ….

ACKNOWLEDGEMENTS

2 smart PhD students (co-authors)

Anne-Laure Dalverny
Rémi Khatib

Wolfgang, Vlasis, Yvan and Sassa for the very nice organisation and perfect accommodation

Dominique LARCHER
Experiments on CoO

Alejandro A. FRANCO
Multiscale approaches

... AND YOU ALL FOR YOUR ATTENTION