

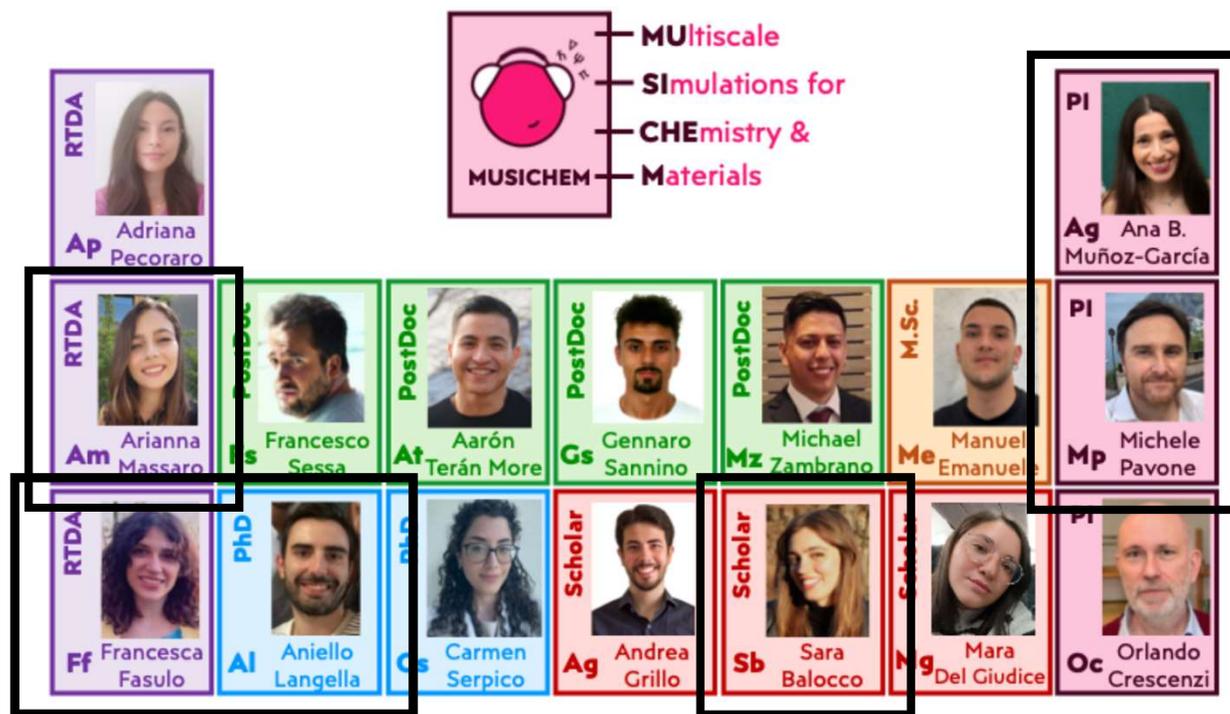


Physico-chemical processes at the electrode-electrolyte interfaces

Arianna Massaro

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University of Naples Federico II



<http://www.musicchem.unina.it>



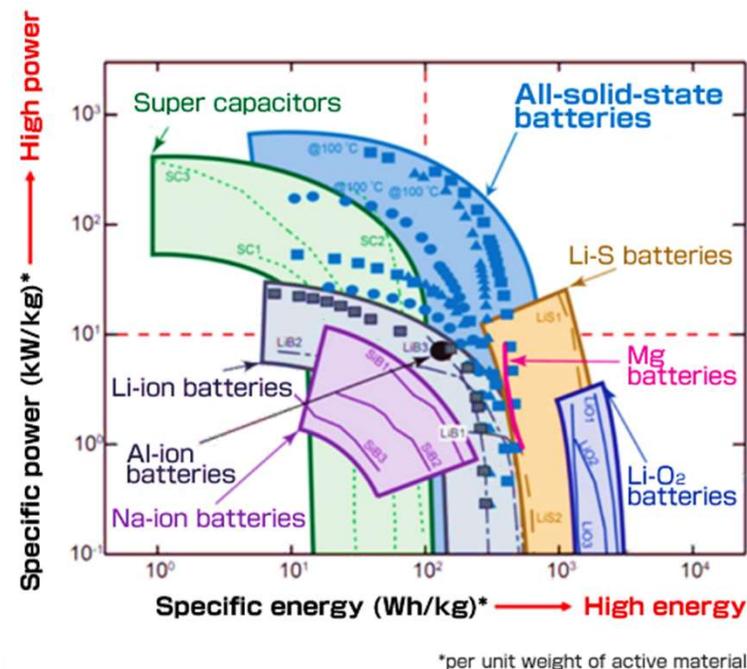
Lithium Metal: The Most Attractive Anode Material for Rechargeable Batteries

Advantages:

- ✓ low electrochemical potential: -3.04 V vs SHE ;
- ✓ ultrahigh theoretical specific capacity: 3860 mAh g^{-1}
- ✓ low density vs other present anode materials: 0.53 g cm^{-3}

Challenges:

- ❑ long-term stability, safety and cyclability
- ❑ aggressive dendritic growth of Li Metal
- ❑ short-circuit due to penetration through the battery separator
- ❑ decrease of Coulombic Efficiency owing to formation of electrically isolated / “dead” Li



all-solid-state batteries combine features of batteries and capacitors

Nat Energy 2016, 1, 16030

- high specific energy batteries: Li-Sulfur, Li-air(O₂)
- high specific power batteries: Solid-state batteries



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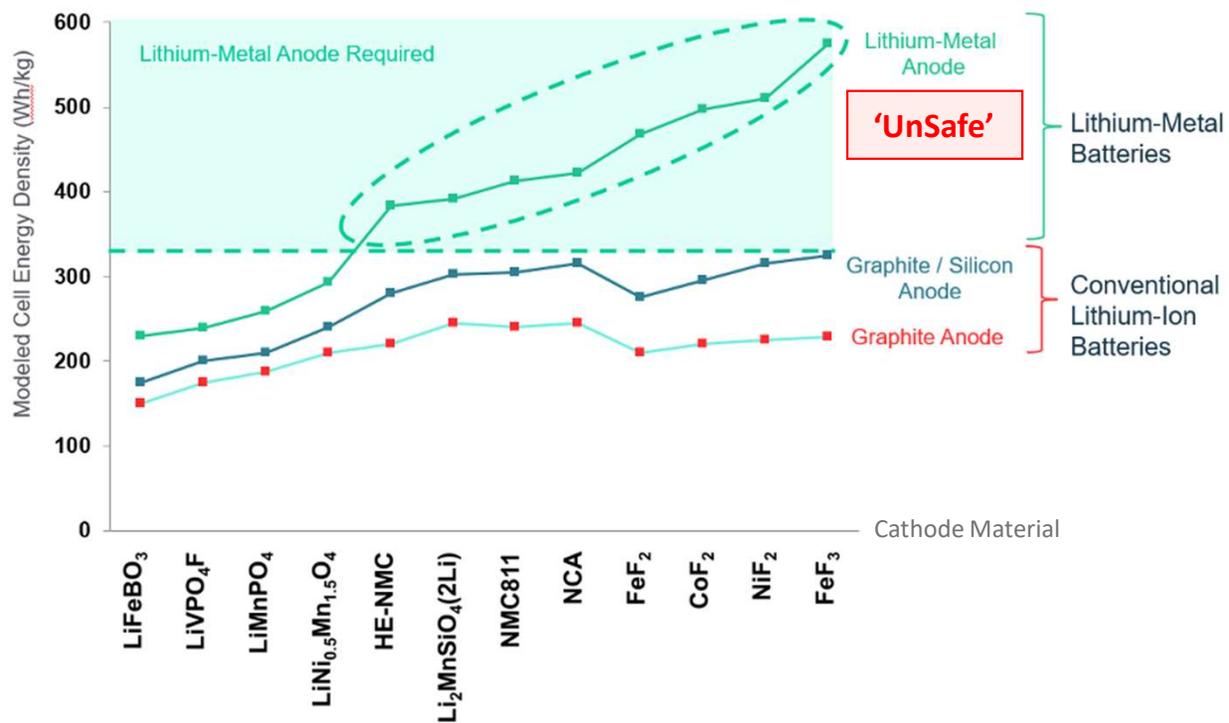
Physico-chemical processes at the electrode-electrolyte interfaces

Lithium Metal: The Most Attractive Anode Material for Rechargeable Batteries

Low Electrochemical Potential:
-3.04 V vs SHE

Low Density:
0.53 g cm⁻³

Ultrahigh Theoretical Specific Capacity:
3860 mAh g⁻¹



QuantumScape's solid-state lithium-metal battery technology results in December 2020

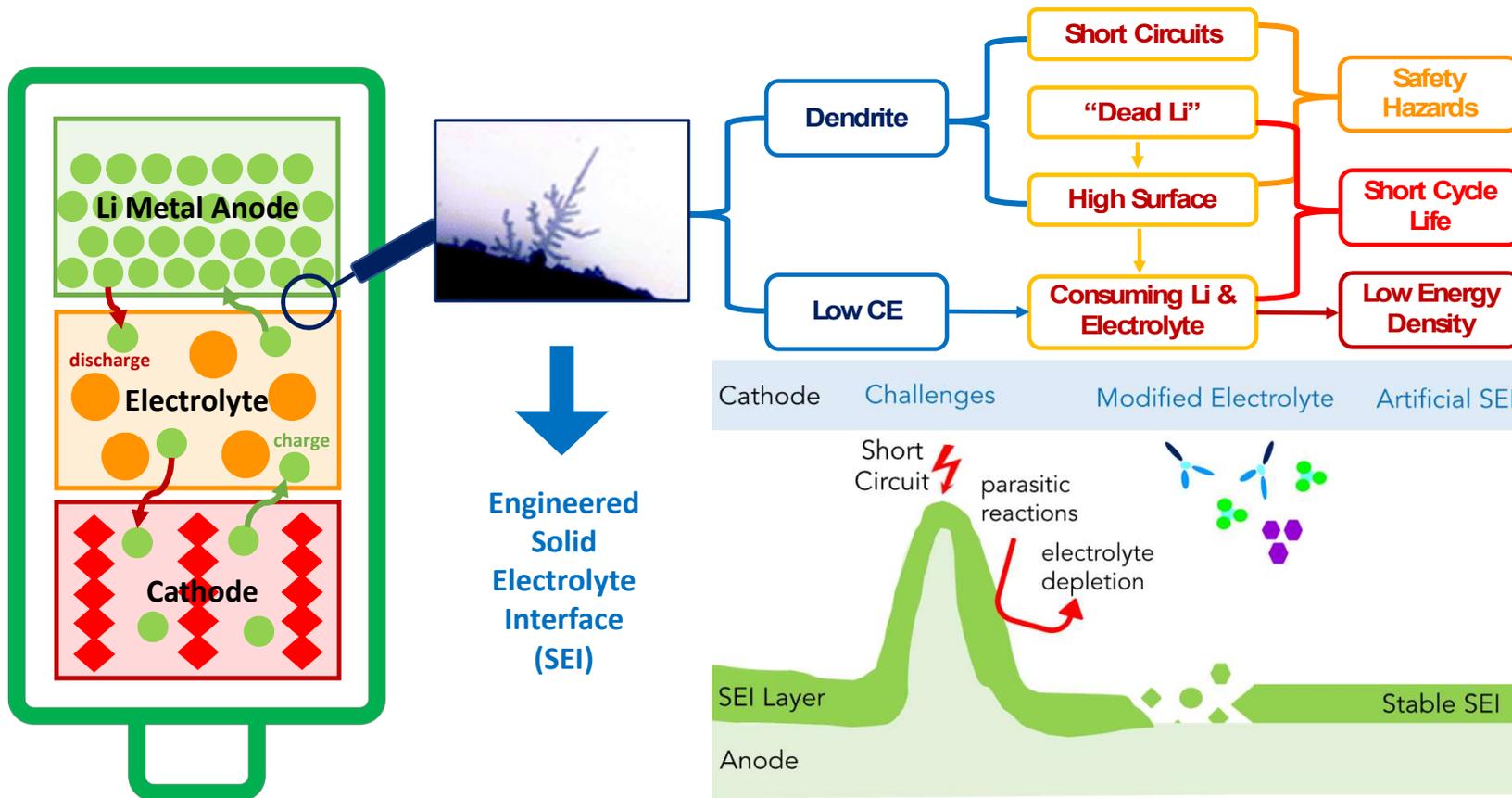
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Physico-chemical processes at the electrode-electrolyte interfaces



Lithium Metal: The Most Attractive Anode Material for Rechargeable Batteries



[1] J. Crystal Growth, 1976, 34, 239; [2] Energy Environ. Sci., 2014, 7, 513; [3] J. Mater. Chem. A, 2021,9, 10012

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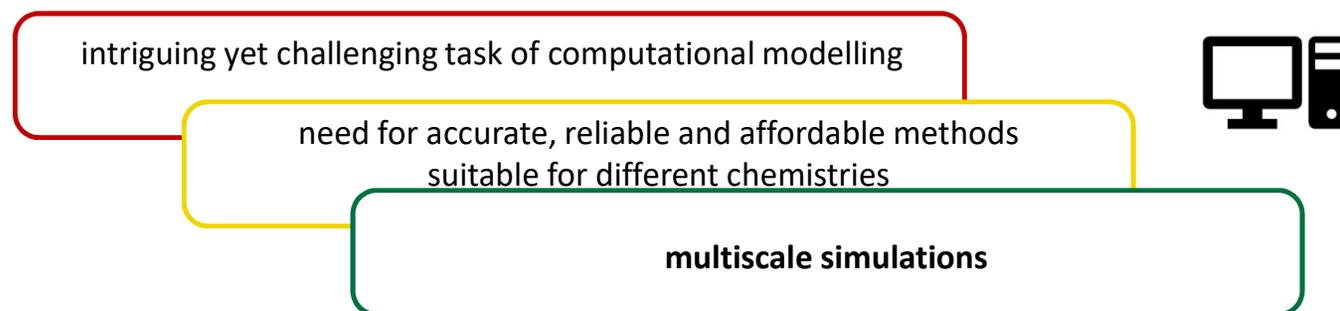
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Physico-chemical processes at the electrode-electrolyte interfaces



Our Activity Within the Project

- SEI is usually composed by high variety of components with very different chemical nature
- heterogeneity even more intricated at boundary with metal



1. vinylene carbonate (VC) reactivity on Li(001) surface

- common additive to conventional electrolytes for promoting the formation of stable and protective SEI
- tangled decomposition and polymerization processes *via* reductive ring-opening reactions
- developing embedding method for molecular reactivity at metal surface

2. structuring and dynamics of electrolytes on Li surface terminations

- polyethylene oxide (PEO): good Li⁺ conductive polymer, sustainability and flexibility requirements, unclear decomposition pathways across SEI formation
- theoretical description of reaction mechanism

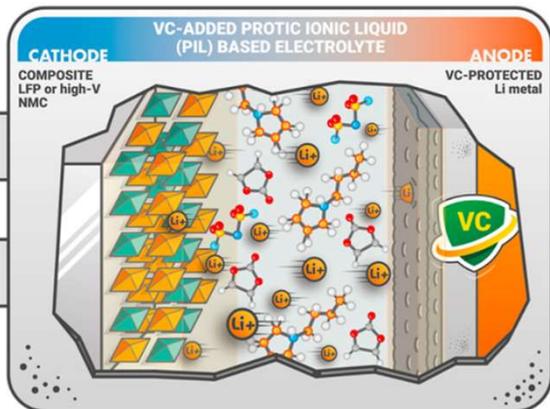


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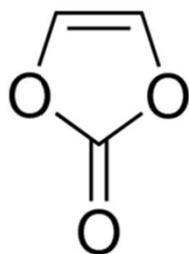
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Solid Electrolyte Interface: An Effective Electrochemical Barrier for Li Metal Anode



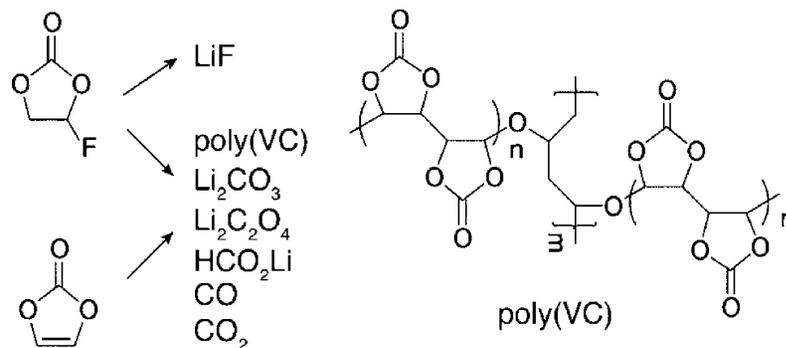
J. Power Sources 2021, 481, 228979



Vinylene Carbonate (VC) - 1,3-Dioxol-2-one

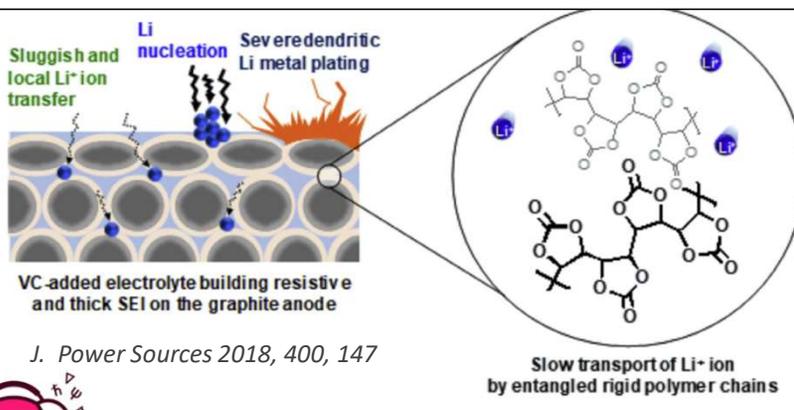
adding VC increases the stability of Li metal-electrolyte interface

Polymerization vs Decomposition ?



Chem. Mater. 2016, 28, 8149

Nano Lett. 2020, 20, 418–425



J. Power Sources 2018, 400, 147



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Physico-chemical processes at the electrode-electrolyte interfaces

Density Functional Embedding Theory (DFET)

Prof Chen Huang

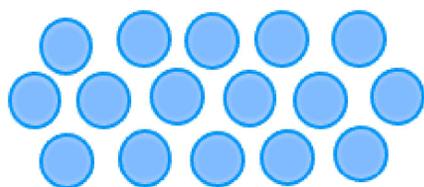


High-Level Description of Possible VC Dissociation Pathways and Interaction with Li-Surface

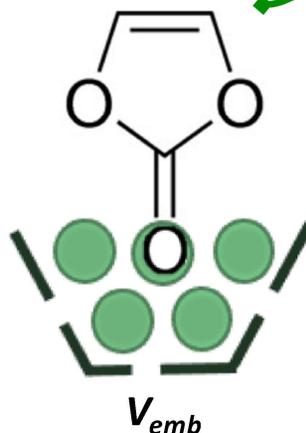
decoupling the complex electronic structure of the reacting electrolyte molecule from that of the metallic background

$$E_{\text{tot}}[n_{\text{tot}}] = E_{\text{clu}}[n_{\text{clu}}] + E_{\text{env}}[n_{\text{env}}] + E_{\text{int}}[n_{\text{clu}}, n_{\text{env}}]$$

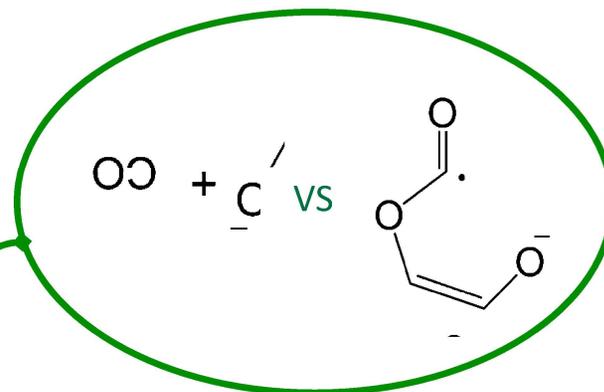
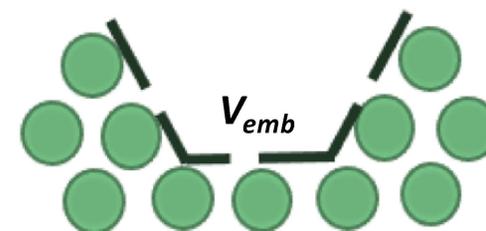
Total System



=



+



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Density Functional Embedding Theory (DFET)

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High-Level Description of Possible VC Dissociation Pathways and Interaction with Li-Surface

decoupling the complex electronic structure of the reacting electrolyte molecule from that of the metallic background

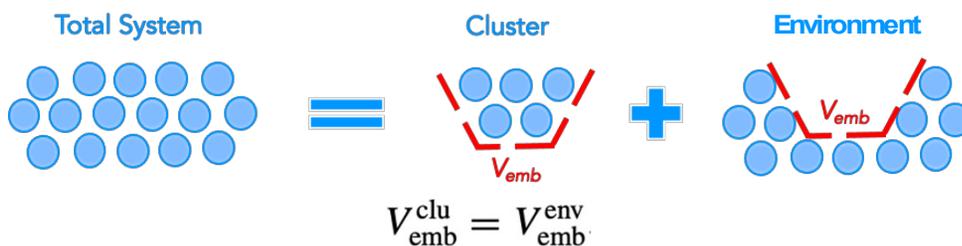
V_{emb} by maximizing an
extended Wu–Yang functional
known from OEP theory:

$$W[V_{\text{emb}}] = \tilde{E}_{\text{I}}[\rho_{\text{I}}, V_{\text{emb}}] + \tilde{E}_{\text{II}}[\rho_{\text{II}}, V_{\text{emb}}] - \int \rho_{\text{tot}}(\vec{r}) \cdot V_{\text{emb}}(\vec{r}) d\vec{r}$$

$$\tilde{E}_{\text{K}}[\rho_{\text{K}}, V_{\text{emb}}] = E_{\text{K}}[\rho_{\text{K}}] + \int \rho_{\text{K}}(\vec{r}) \cdot V_{\text{emb}}(\vec{r}) d\vec{r}$$

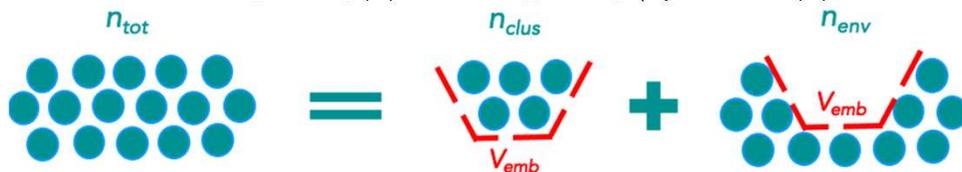
The optimized V_{emb} used within higher-level
electronic structure calculations on cluster

$$(\hat{H}_{\text{I}} + V_{\text{emb}}[\rho_{\text{I}}, \rho_{\text{tot}}])\Psi_{\text{I}} = E_{\text{I}}\Psi_{\text{I}}$$



The uniqueness of embedding potential

$$n_{\text{clu}}[V_{\text{emb}}](\mathcal{r}) + n_{\text{env}}[V_{\text{emb}}](\mathcal{r}) = n_{\text{tot}}(\mathcal{r})$$



C. Huang, M. Pavone, E. A. Carter, *J. Chem. Phys.* 2011, 134, 154110

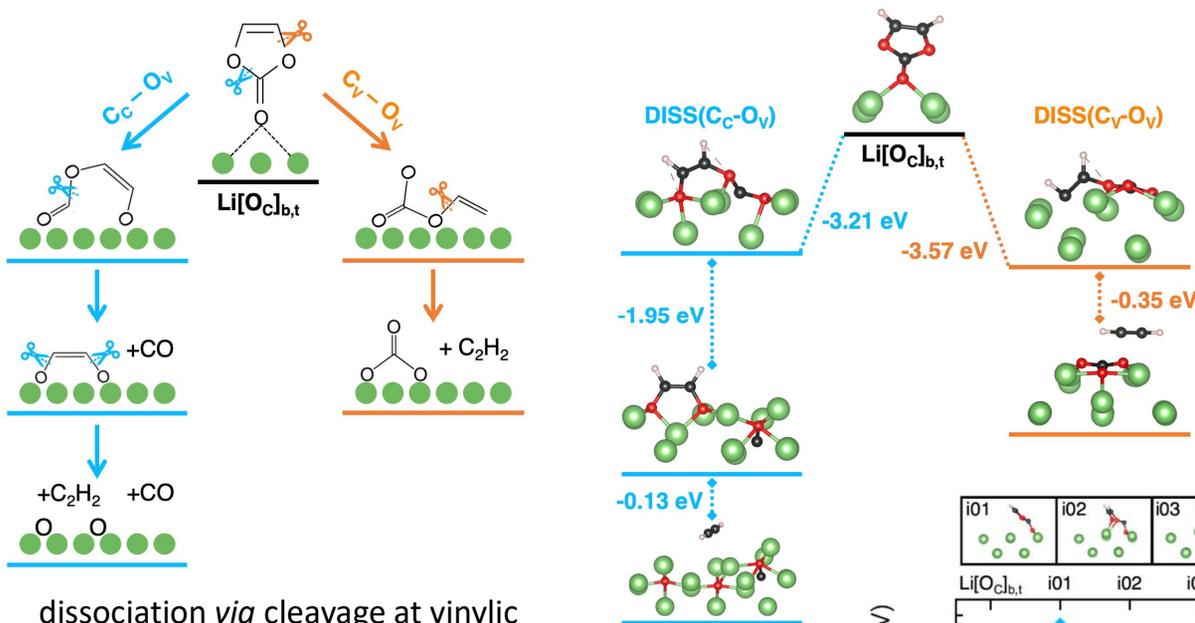
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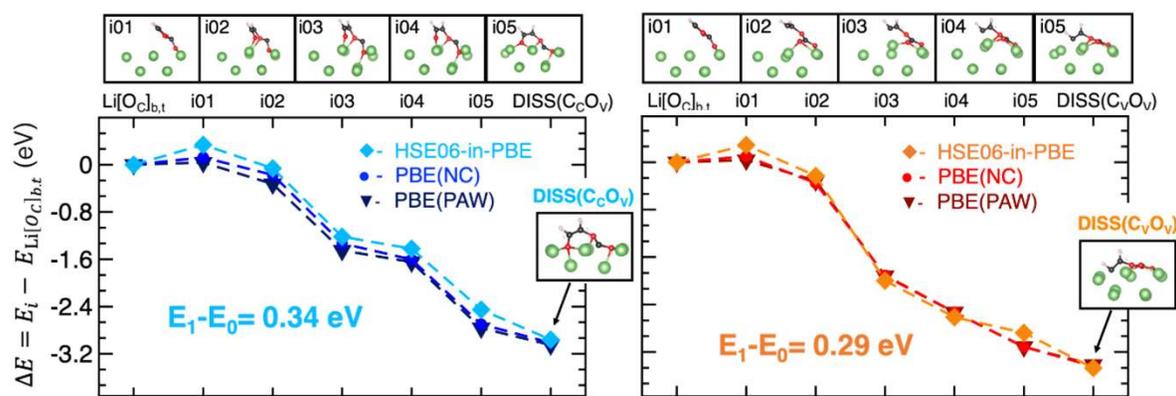


Ab-Initio Study on Li-VC Interaction: HSE06-in-PBE embedding



- thermodynamically accessible mechanisms for ring-opening reaction
- energy barriers in the range of 0.29-0.34 eV
- DFET HSE06-in-PBE predicts an energy barrier toward ring-opening reduction not detected by DFT-PBE

- dissociation *via* cleavage at vinylic sites more likely to occur
- dissociated VC as radical initiator : highly reactive intermediate undergo decomposition to C_2H_2 & Li_2CO_3 or polymerization
- explain low-release of C_2H_4 and SEI composition



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Physico-chemical processes at the electrode-electrolyte interfaces



Structuring and dynamics of electrolytes on Li metal surfaces

1. Model the PEO decomposition reaction on Li metal surface → key to understand & design functional SEI
2. Evaluate the reaction energetics and mechanism at different operating voltage

RESEARCH ARTICLE

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Increasing Ionic Conductivity of Poly(ethylene oxide) by Reaction with Metallic Li

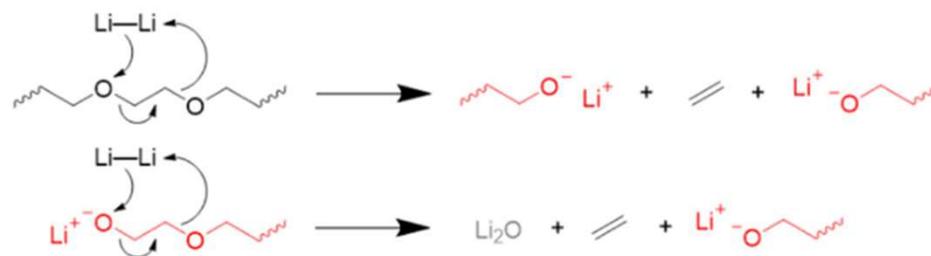
Pei Liu, Michael J. Coughlan, Yisi Zhu, Justin G. Connell, Daniel Sharon, Shrayesh N. Patel, Paul C. Redfern, Peter Zapol, Nenad M. Markovic, Paul F. Nealey, Larry A. Curtiss,* and Sanja Tepavcevic*

Poly(ethylene oxide) (PEO) was the first lithium-ion conducting polymer developed 50 years ago and is still the most popular electrolyte matrix for solid-state lithium metal batteries. While many studies focus on increasing PEO ionic conductivity through doping with Li salts, little work has addressed using PEO and Li directly to generate Li⁺-conducting species in situ. Reaction between PEO and Li leads to ionic conductivity largely from Li⁺, in contrast to the case of added salts where the anion contribution dominates. Herein, electrochemical impedance spectroscopy shows the ionic conductivity of PEO thin films increases up to three orders of magnitude (from 10⁻⁷ to 10⁻⁴ S cm⁻¹) when contacted with Li at elevated temperature. This is due to the reduction of ether bonds, which produces lithium alkoxides that are responsible for Li⁺ transport. Density functional theory analysis confirms this mechanism as thermodynamically favorable. X-ray photoelectron spectroscopy also shows the presence of organolithium species and Li₂O, which are responsible for propagating reactions with PEO and forming an electronically insulating layer at the PEO-Li interface that halts further reaction, respectively. The underlying mechanisms of Li-polymer electrolyte reactions is clarified and new pathways for in situ Li⁺ doping of polymer electrolytes is presented.

1. Introduction

One of the most important technological advances in sustainable energy harvesting and storage is the development of the Li-ion battery technology. In recent years, increasing demand for energy has revived development of sustainable storage technologies with Li metal as the anode due to the high theoretical specific capacity of Li metal (3860 mA h g⁻¹).¹⁻⁴ As a result, the focus of much research in the field of Li energy storage is centered on development of solid electrolyte materials that can replace flammable organic solvents and enable the use of Li metal anodes, required for high energy density batteries.^{5,6} To fully implement solid-solid Li-ion technology, many challenges need to be resolved, namely the stability of electrode materials and electrolytes and selectivity of electrochemical interfaces.⁷ Addressing these

For a system of PEO thin films and vacuum-deposited Li metal ...



... Li atoms on surface break the PEO ether bonds to form Li-OR and ethylene

Liu, et al., *Adv. Energy Sustainability Res.*, 3: 2100142, 2022

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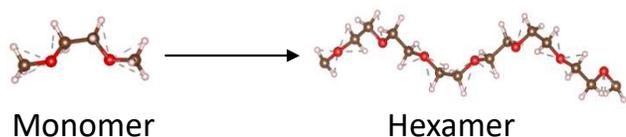
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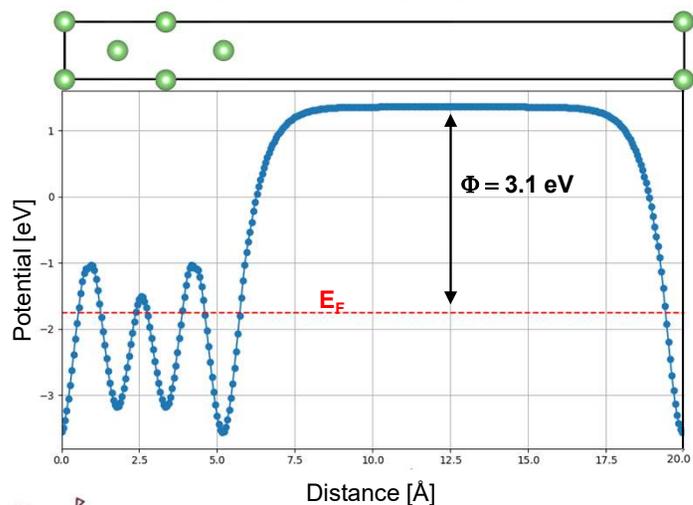


Structuring and dynamics of electrolytes on Li metal surfaces

How to model PEO chain?



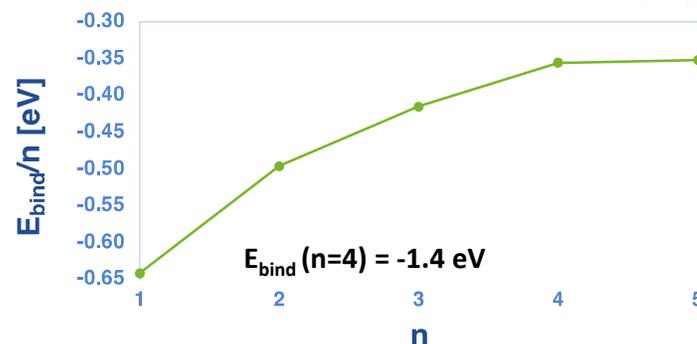
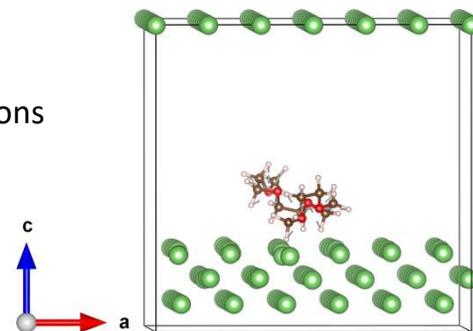
How to model Li metal surface?



How to model PEO/Li interface?

PEO parallel to **(010)** & **(100)** directions

$$E_{bind} = E_{Li-PEO} - E_{Li} - E_{PEO}$$



O. Borodin, *J. Phys. Chem. C*, 117, 17, 8661, 2013

M. Ebadi, *J. Mater. Chem. A*, 7, 8394, 2019



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Physico-chemical processes at the electrode-electrolyte interfaces

Structuring and dynamics of electrolytes on Li metal surfaces

1. Thermodynamics of PEO decomposition at 0V:
evaluation of free-energy reaction profiles, identification of TS & reaction products
2. Effect of voltage application & presence of Li salts:
towards realistic but more complex heterogeneous interfaces

Challenges from computational chemistry:

1. Are OK-calculations sufficient to describe the reaction barriers? → AIMD / MetaD approaches
2. How to model a complex interface? (PEO chain size, Li surface, decomposition products) → DFET method
3. Which is the influence of the salt? → ML-based force fields



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Structuring and dynamics of electrolytes on Li metal surfaces

Computational details



PBE-GGA/PAW potentials (-D3BJ)

E_{cutoff} : 600 eV

k_{pts} mesh 100 sup: 10 10 1

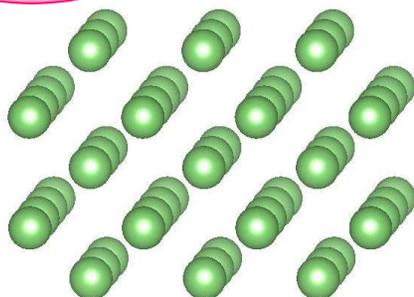
110 sup: 8 10 1

111 sup : 8 8 1

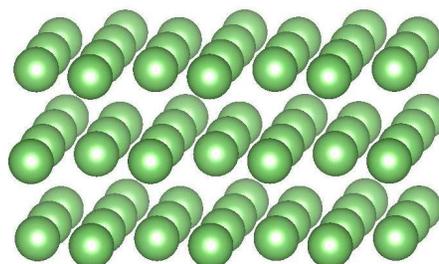
Vacuum: 10 Å

Surface	Cell parameters		Layers	γ [eV Å ⁻²]
	a [Å]	b [Å]		
1 0 0	3.311	3.311	4	0.0400
			6	0.0396
			8	0.0405
1 1 0	4.682	3.311	4	0.0439
			6	0.0441
			8	0.0440
1 1 1	4.682	4.682	4	0.0374
			6	0.0402
			8	0.0391

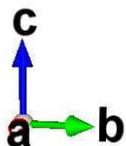
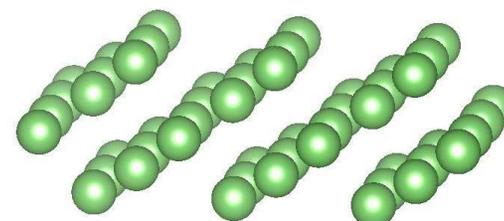
1 0 0



1 1 0



1 1 1



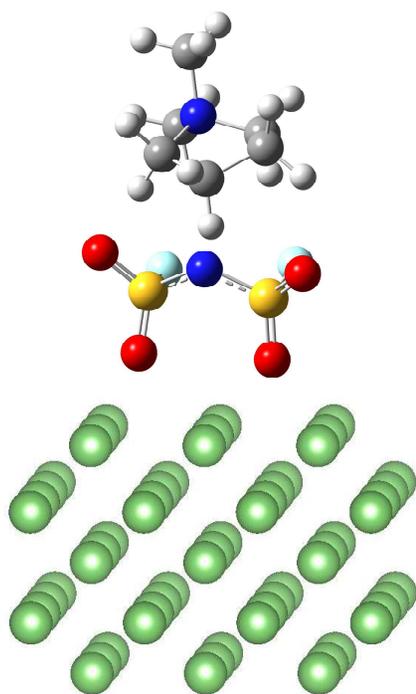
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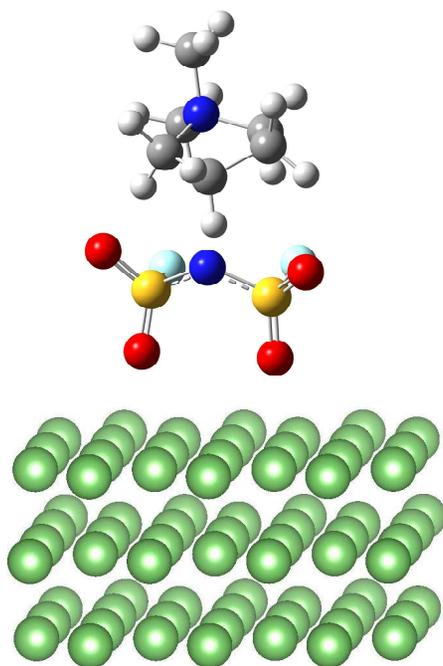
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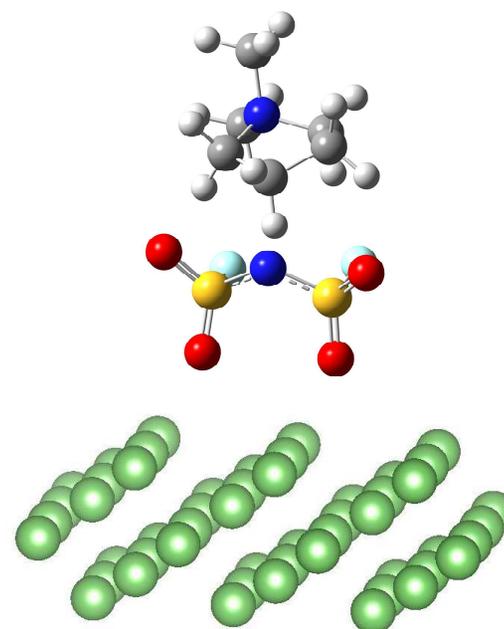
1 0 0



1 1 0



1 1 1



Ionic liquid Pyr₁₄ FSI

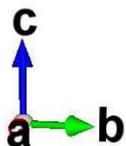
Color code: C grey

N blue

O red

S yellow

Li green



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Thank You!



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