Introduction to the Materials Science of

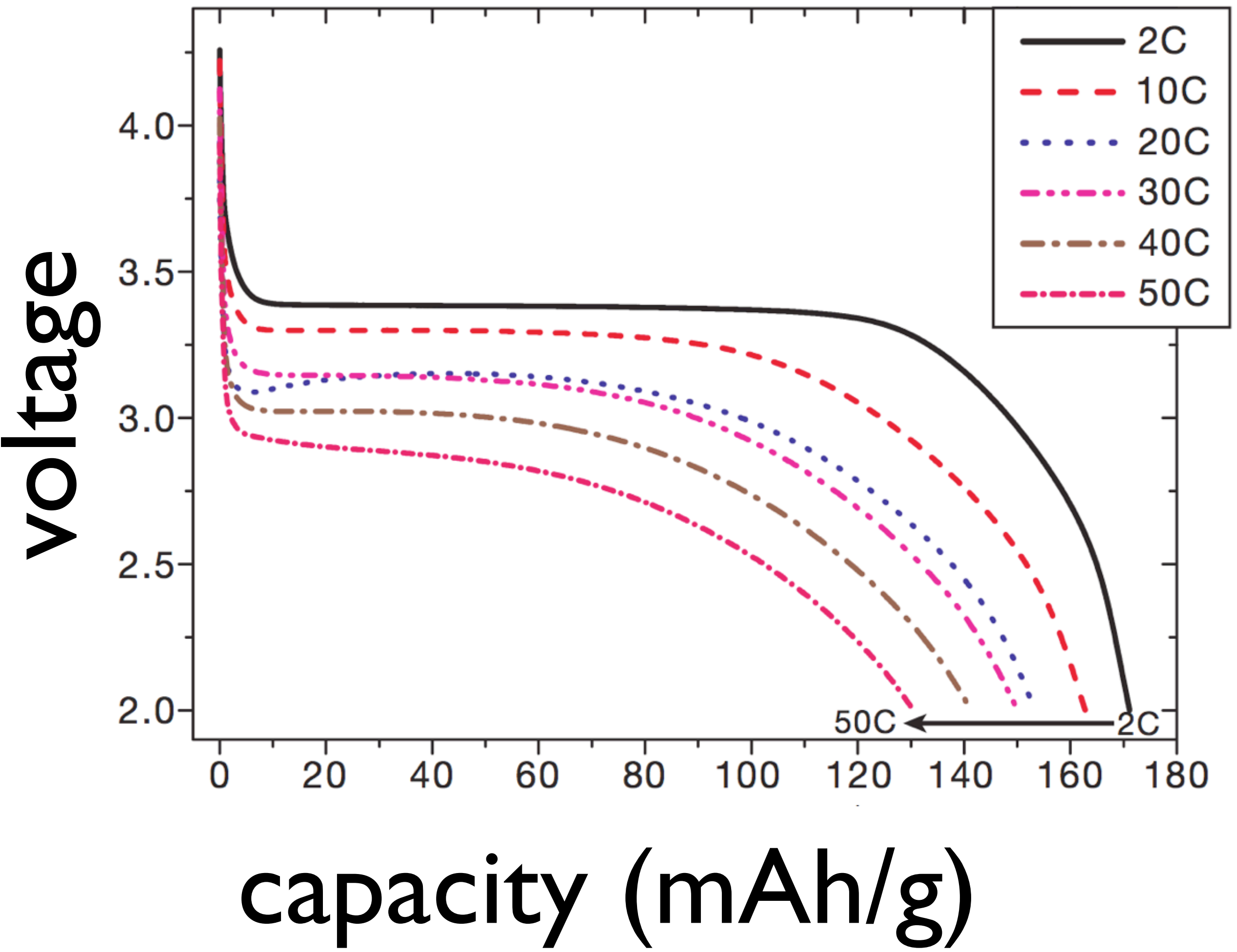
Rechargeable Batteries

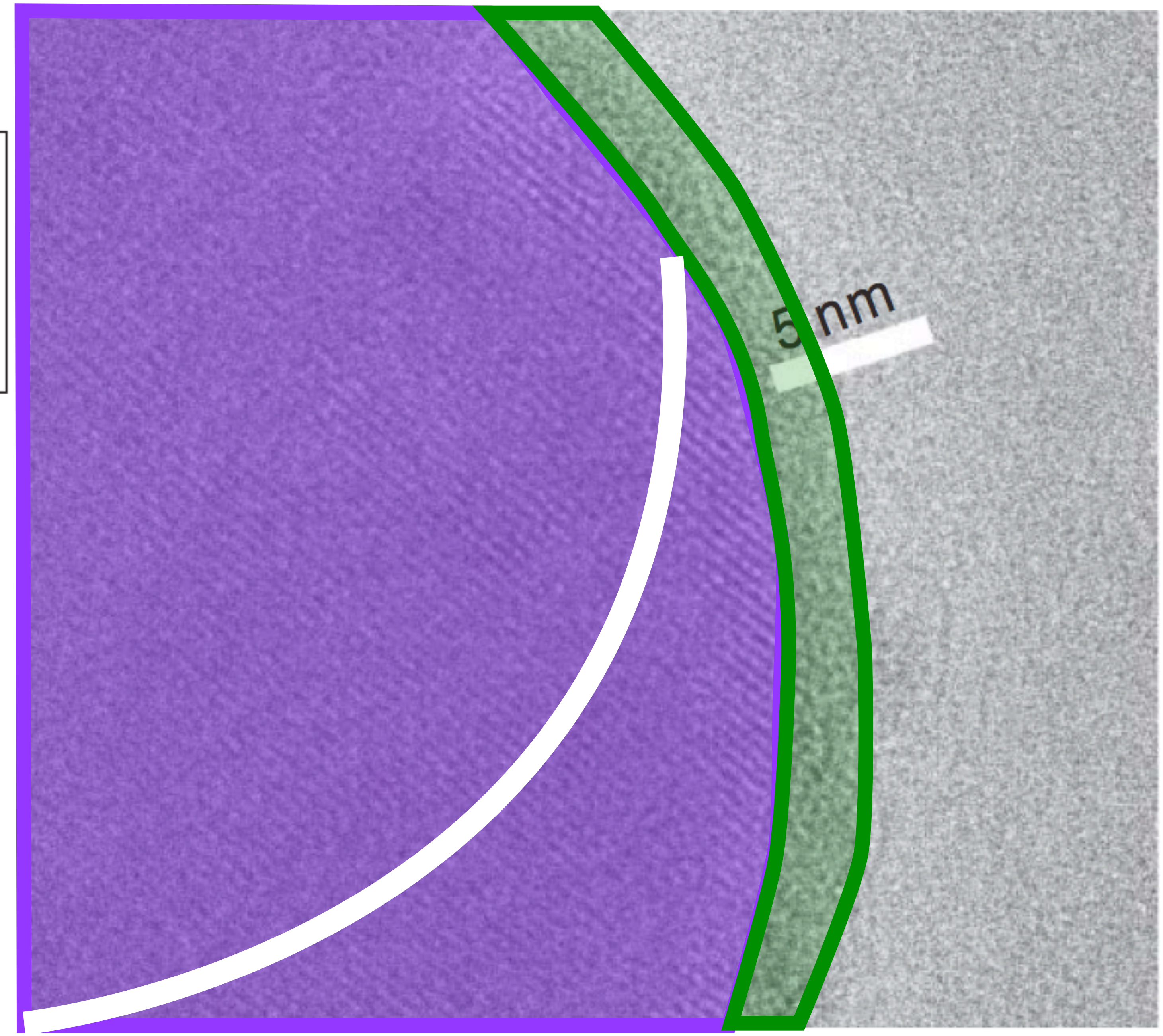
Week 4: Reversible and Irreversible Interfacial Reactions

Lecture 4.2: Interface Related Reactions

By R. Edwin Garcia
Associate Professor of Materials Engineering
Purdue University

Engineering the Kinetics at the Interface





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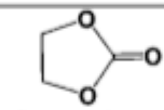
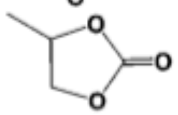
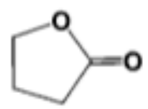
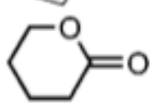
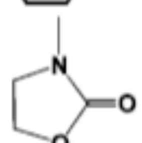
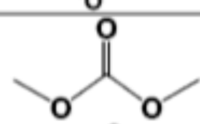
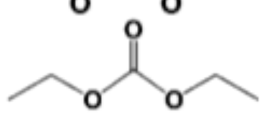
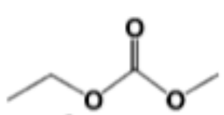
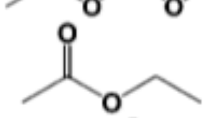
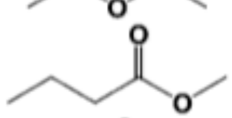
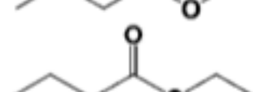
B. Kang and G. Ceder "Battery Materials for Ultra Fast Charging and Discharging." Nature (458) p.190-193,2009.

Summary of Organic Electrolytes

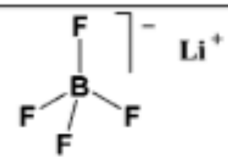
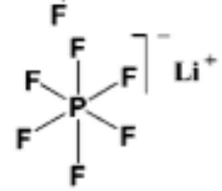
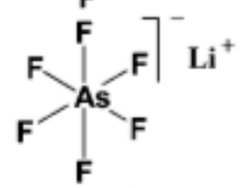
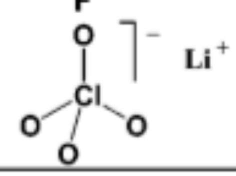
Organic Carbonates and Esters as Electrolyte Solvents

Solvent	Structure	M. Wt	T_m/ °C	T_b/ °C	η/cP 25 °C	ε 25 °C	Dipole Moment/debye	T_f/ °C	d/gcm^{-3}, 25 °C
EC		88	36.4	248	1.90, (40 °C)	89.78	4.61	160	1.321
PC		102	-48.8	242	2.53	64.92	4.81	132	1.200
BC		116	-53	240	3.2	53			
γBL		86	-43.5	204	1.73	39	4.23	97	1.199
γVL		100	-31	208	2.0	34	4.29	81	1.057
NMO		101	15	270	2.5	78	4.52	110	1.17
DMC		90	4.6	91	0.59 (20 °C)	3.107	0.76	18	1.063
DEC		118	-74.3 [a]	126	0.75	2.805	0.96	31	0.969
EMC		104	-53	110	0.65	2.958	0.89		1.006
EA		88	-84	77	0.45	6.02		-3	0.902
MB		102	-84	102	0.6			11	0.898
EB		116	-93	120	0.71			19	0.878

Kang Xu "Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries." Chem. Rev. 2004, 104, 4303–4417.

Summary of Salts

Lithium Salts as Electrolyte Solutes

Salt	Structure	M. Wt	T_m/ °C	$T_{decomp.}$, / °C in solution	Al-corrosion	σ /mScm^{-1} (1.0 M, 25 ° C) in PC	σ /mScm^{-1} (1.0 M, 25 ° C) in EC/DMC
$LiBF_4$		93.9	293 (d)	> 100	N	3.4 [a]	4.9 [c]
$LiPF_6$		151.9	200 (d)	~ 80 (EC/DMC)	N	5.8 [a]	10.7 [d]
$LiAsF_6$		195.9	340	> 100	N	5.7 [a]	11.1 [e]
$LiClO_4$		106.4	236	>100	N	5.6 [a]	8.4 [d]
Li Triflate	$Li^+ CF_3SO_3^-$	155.9	>300	>100	Y	1.7 [a]	
Li Imide	$Li^+ [N(SO_2CF_3)_2]^-$	286.9	234 [b]	>100	Y	5.1 [a]	9.0 [e]
Li Beti	$Li^+ [N(SO_2CF_2CF_3)_2]^-$				N		

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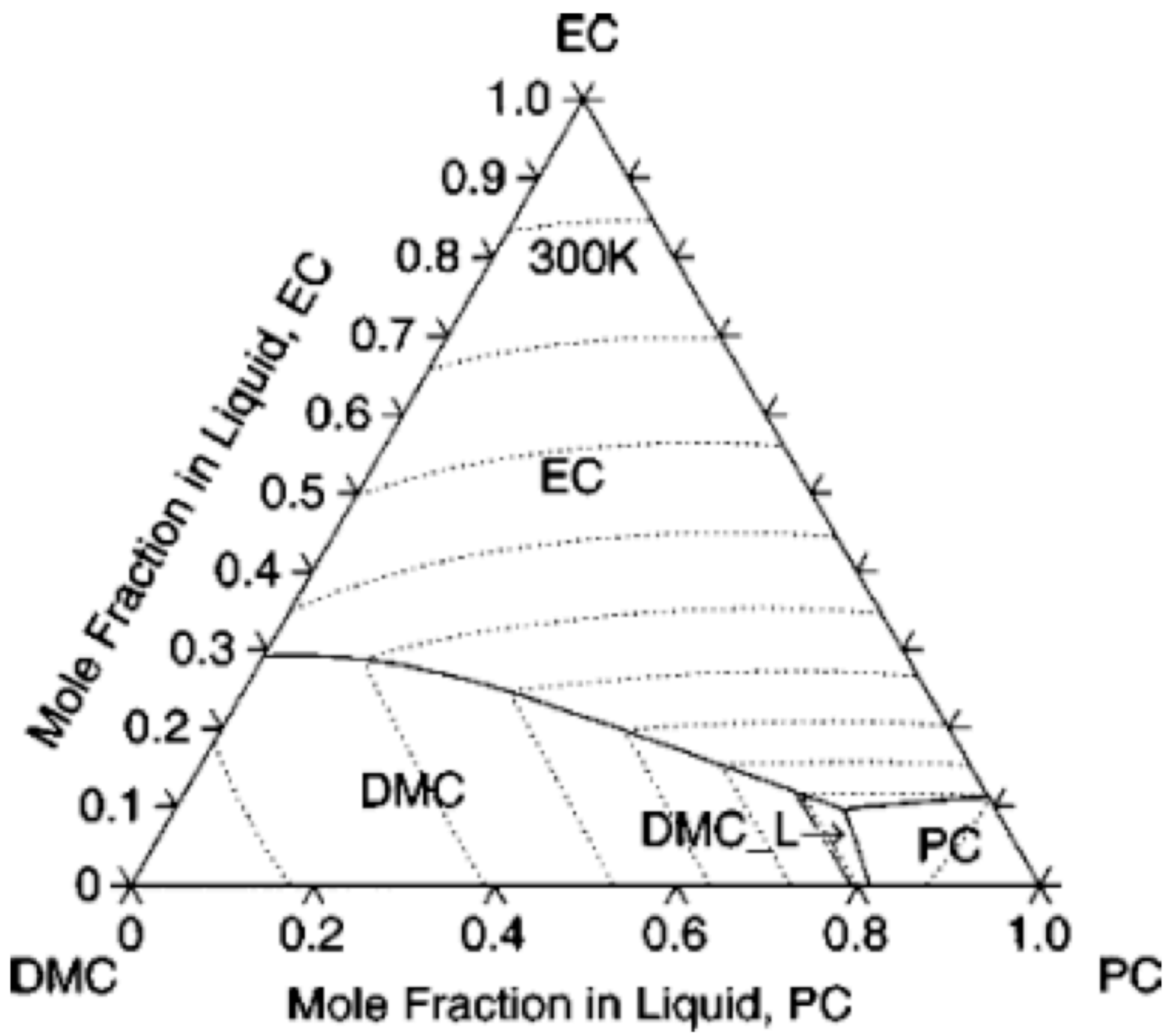
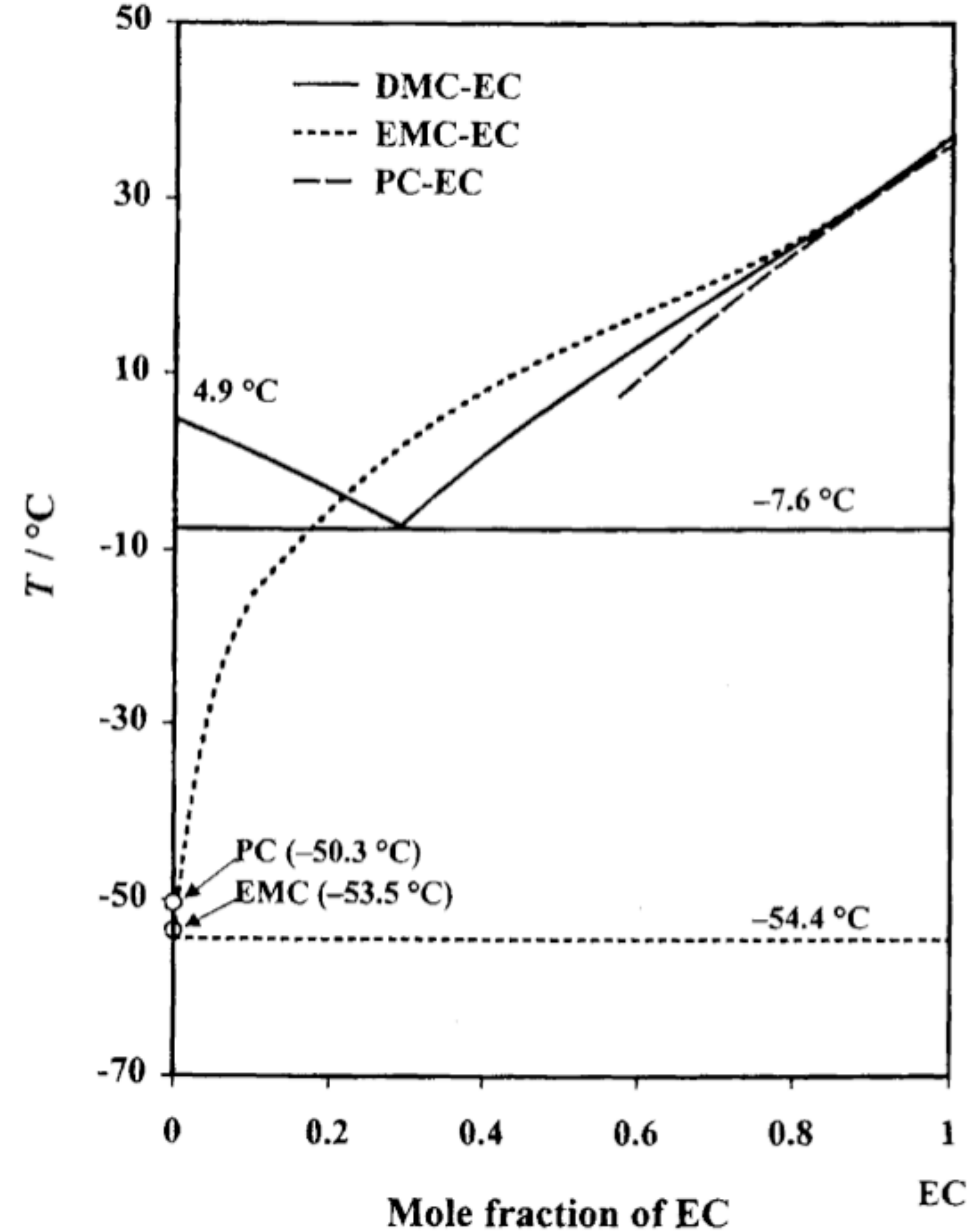
Electrolyte Mixtures





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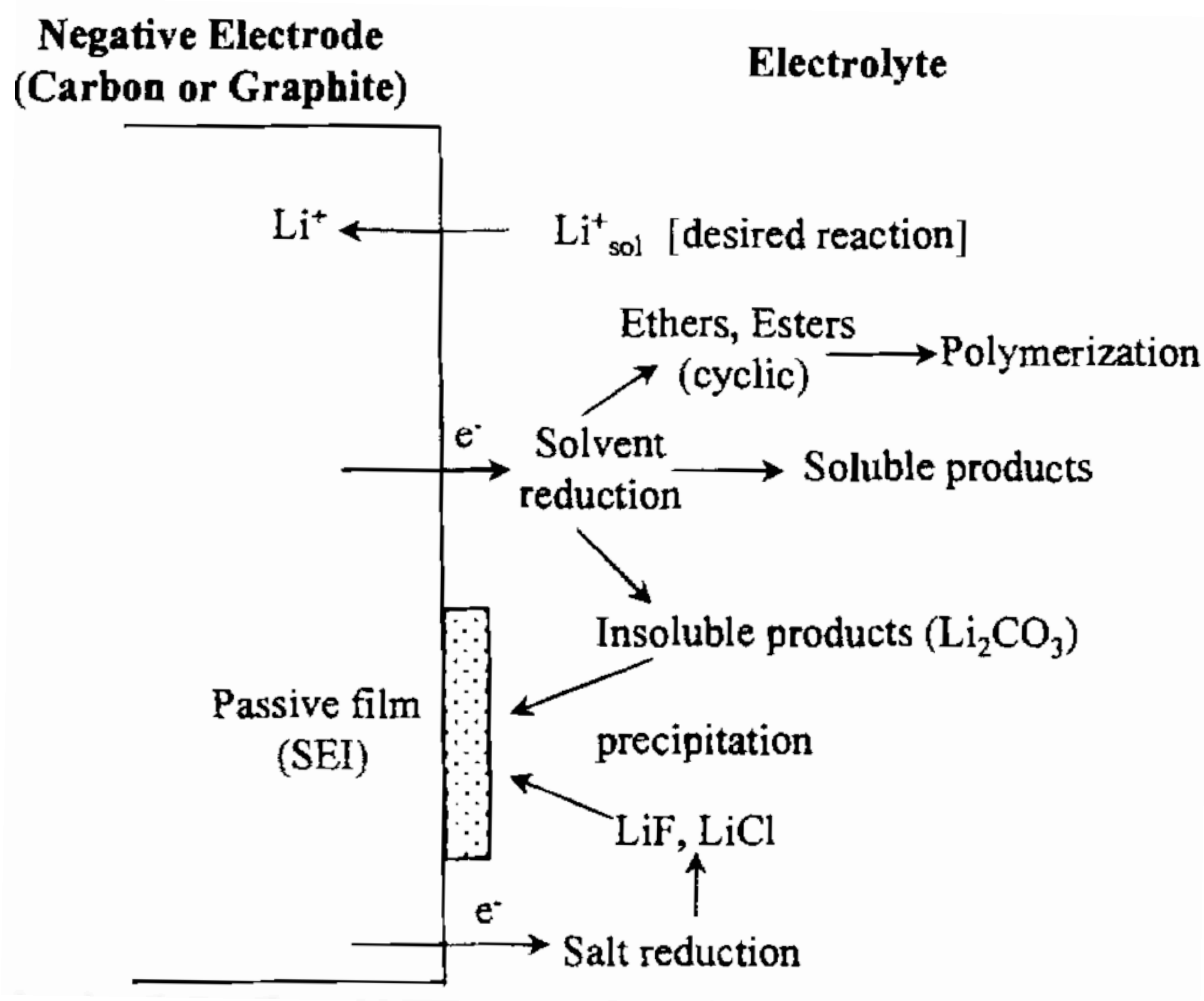
Interface-Related Reactions



P. Arora R. E. White, and M. Doyle"Capacity Fade Mechanisms and Side Reactions in Lithium –Ion Batteries" J. Electrochem. Soc. 1998, Volume 145, Issue 10, Pages 3647-3667.

SEI Chemistry

Table 1
Contents of the SEI as reported in the literature.

Component	Present	Not present	Notes
$(CH_2OCO_2Li)_2$	[11,15,28–30]		Being a two electron reduction product of ethylene carbonate (EC); it is found mostly in the SEI of the EC based electrolytes.
$ROCO_2Li$	[11,15,19,29,31]		They are present in the outer layer of the SEI and are absent near Li [32]. They occur in most propylene carbonate (PC) containing electrolytes, especially when the concentration of PC in the electrolyte is high.
Li_2CO_3	[11,31–33]	[16,27,34,35]	Not always present [18]. Normally present in the SEI formed in EC or PC based electrolytes. It may also appear as a reaction product of semicarbonates with HF or water or CO_2.
ROLi	[15,16,35–39]		Most commonly found in the SEI formed in ether electrolytes like tetrahydrofuran (THF), but may also appear as dimethyl carbonate (DMC) or ethyl methyl carbonate (EMC) reduction product [40]. It is soluble and may thus undergo further reactions [41].
LiF	[27,32,34]		Mostly found in electrolytes comprising of fluorinated salts like $LiAsF_6$, $LiPF_6$, $LiBF_4$. It is a major salt reduction product. HF contaminant also reacts with semi carbonates to give LiF byproduct. Amount of LiF increases during storage [42].
Li_2O	[34,43,44]	[18,26,27]	It may be a degradation product of Li_2CO_3 during Ar^+ sputtering in the XPS experiment.
Polycarbonates	[27,45]		Present in the outermost layer of the SEI, close to the electrolyte phase. This part imparts flexibility to the SEI.
LiOH	[30,46,47]	[27,43]	It is mainly formed due to water contamination [48,49]. It may also result from reaction of Li_2O with water or with ageing [35].
$Li_2C_2O_4$	[35,39]		It is found to be present in 18650 cells assembled in Argonne National Labs containing 1.2 M $LiPF_6$ in EC:EMC (3:7) electrolyte. Li carboxylate and Li methoxide were also found in their SEI [35].
HCOLi	[19]		It is present when methyl formate is used as co-solvent or additive.

P. Verma, P. Maire, P. Novák "A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries." Electrochimica Acta 55 (2010) 6332–6341.

Spatial Distribution of SEI Components

3 min of Cu-surface on EC:DEC (1:2)+1M of $LiBF_4$

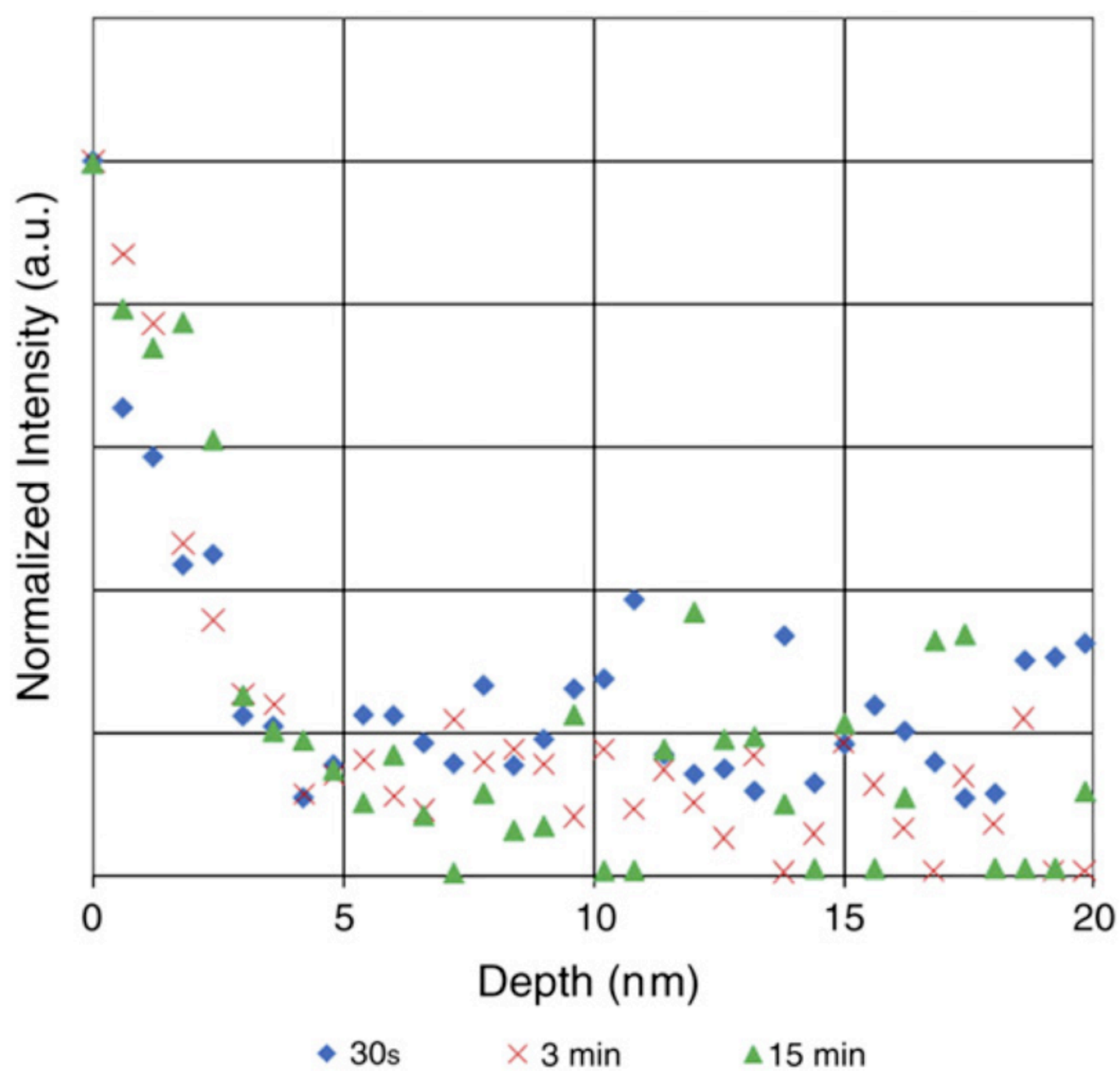


Fig. 1. SIMS $^{11}B^+$ depth profile through $^7LiClO_4$ SEI after immersion in $^6LiBF_4$ electrolyte. $^{11}B^+$ intensity normalized to total ion counts.

time of flight secondary ion mass spectrometry

P. Lu, S.J. Harris "Lithium transport within the solid electrolyte interphase." Electrochemistry Communications 13 (2011) 1035–1037.

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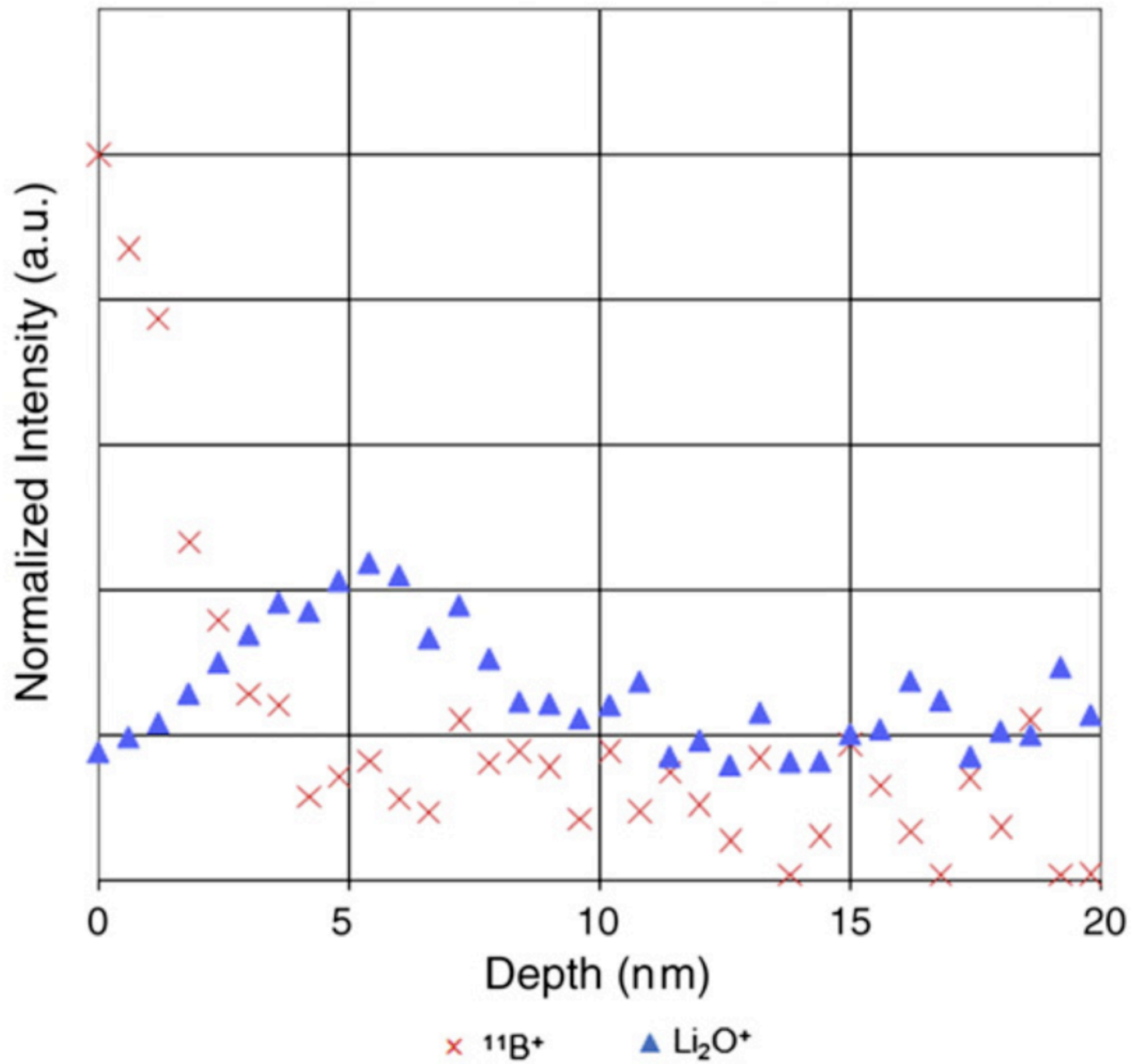

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Fig. 2. SIMS $^{11}B^+$ and $^7Li_2O^+$ depth profiles through $^7LiClO_4$ SEI after immersion in $^6LiBF_4$ electrolyte for 3 min. $^{11}B^+$ and $^7Li_2O^+$ intensities normalized to total ion counts.

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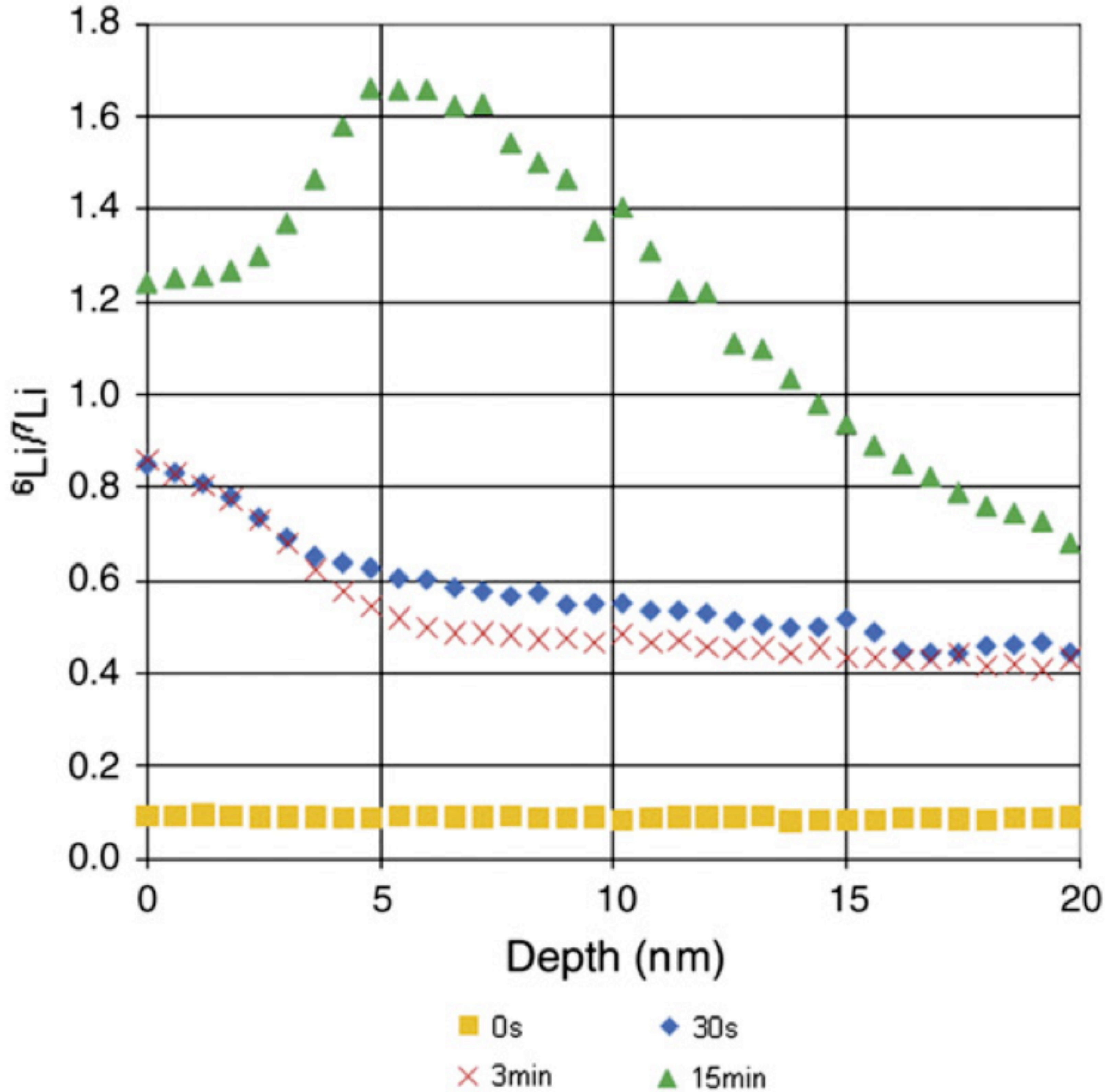

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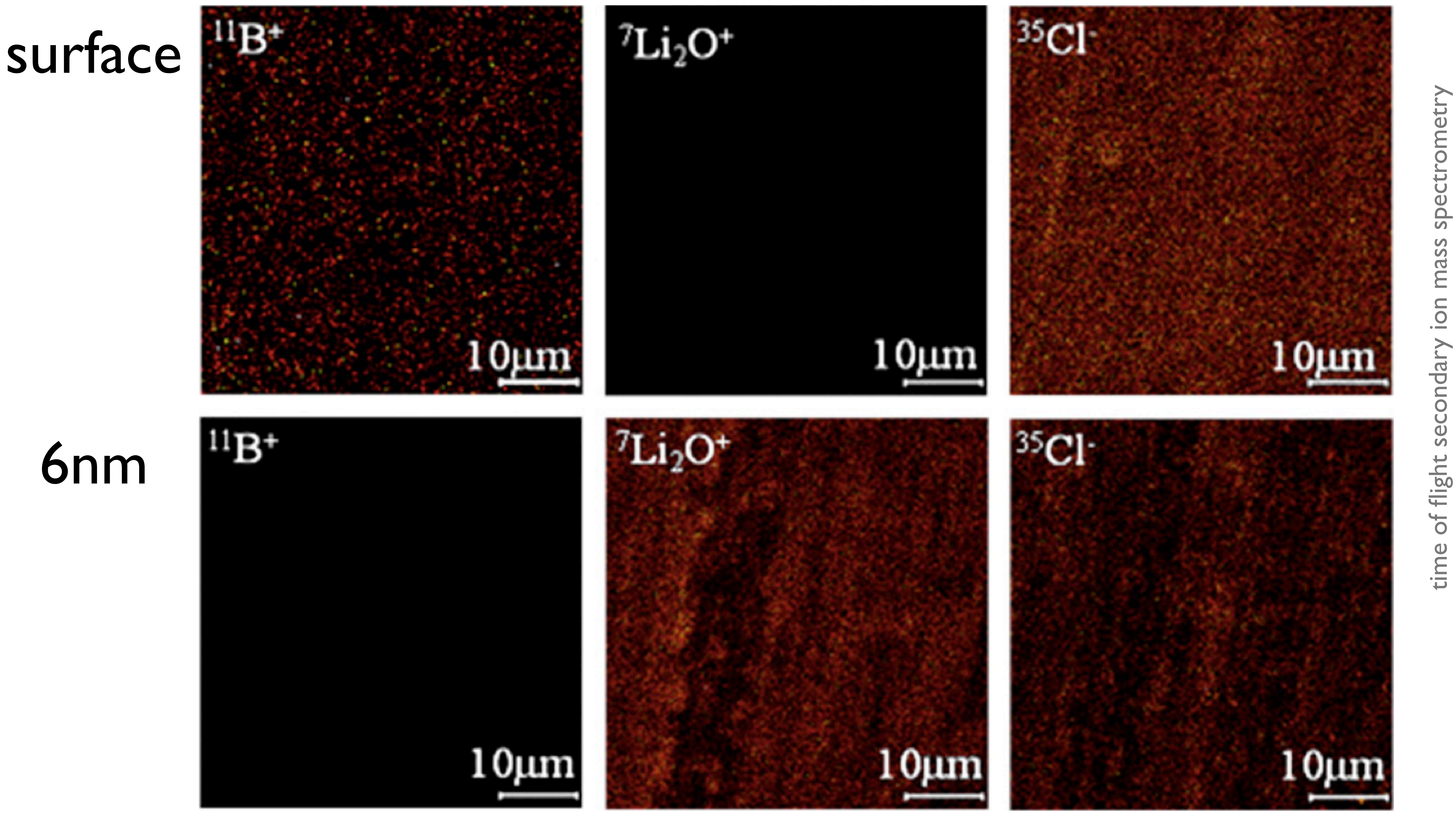


P. Lu, S.J. Harris "Lithium transport within the solid electrolyte interphase." Electrochemistry Communications 13 (2011) 1035–1037.

AFM-Determined SEI Morphology

($EC{:}DMC/LiPF_6$)

$2EC + 2e^- + 2Li^+ \longrightarrow (CH_2OCO_2Li)_2\downarrow + CH_2{=}CH_2\uparrow.$

$EC + 2e^- + 2Li^+ \longrightarrow LiCH_2CH_2OCO_2Li\downarrow.$

$DMC + e^- + Li^+ \longrightarrow CH_3\bullet + CH_3OCO_2Li\downarrow$ and/or $CH_3OLi\downarrow + CH_3OCO\bullet.$

Trace $H_2O + e^- + Li^+ \longrightarrow LiOH\downarrow + \frac{1}{2}H_2\uparrow.$

$LiOH + e^- + Li^+ \longrightarrow Li_2O\downarrow + \frac{1}{2}H_2\uparrow.$

$H_2O + (CH_2OCO_2Li)_2 \longrightarrow Li_2CO_3 + CO_2 + (CH_2OH)_2.$

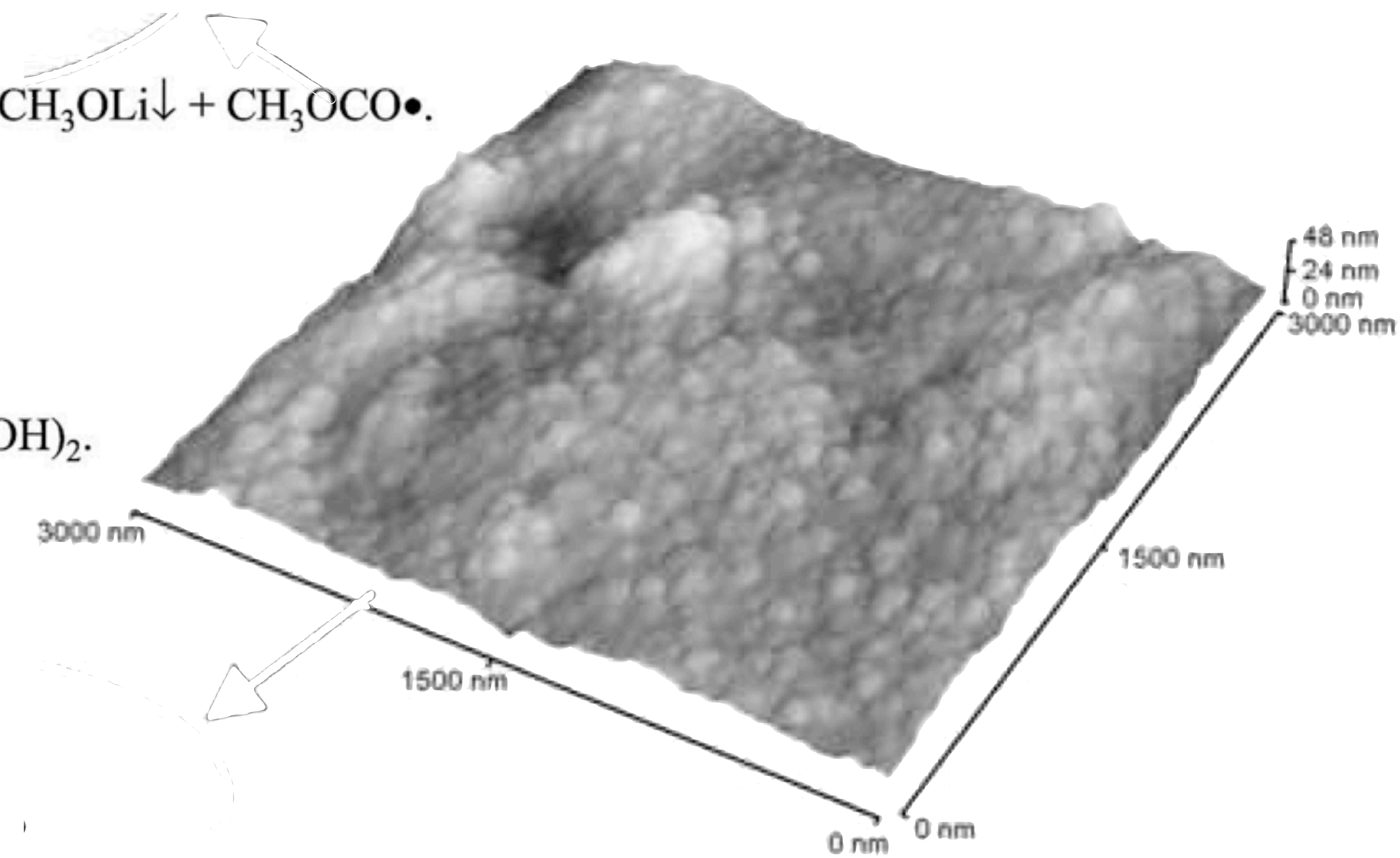
$2CO_2 + 2e^- + 2Li^+ \longrightarrow Li_2CO_3\downarrow + CO\uparrow.$

$LiPF_6 + H_2O \longrightarrow LiF + 2HF + PF_3O.$

$PF_6^- + ne^- + nLi^+ \longrightarrow LiF\downarrow + Li_xPF_y\downarrow.$

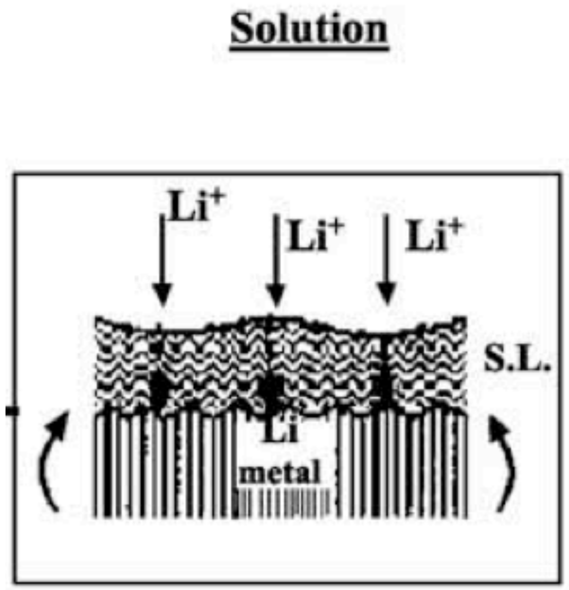
$PF_3O + ne^- + nLi^+ \longrightarrow LiF\downarrow + Li_xPOF_y\downarrow.$

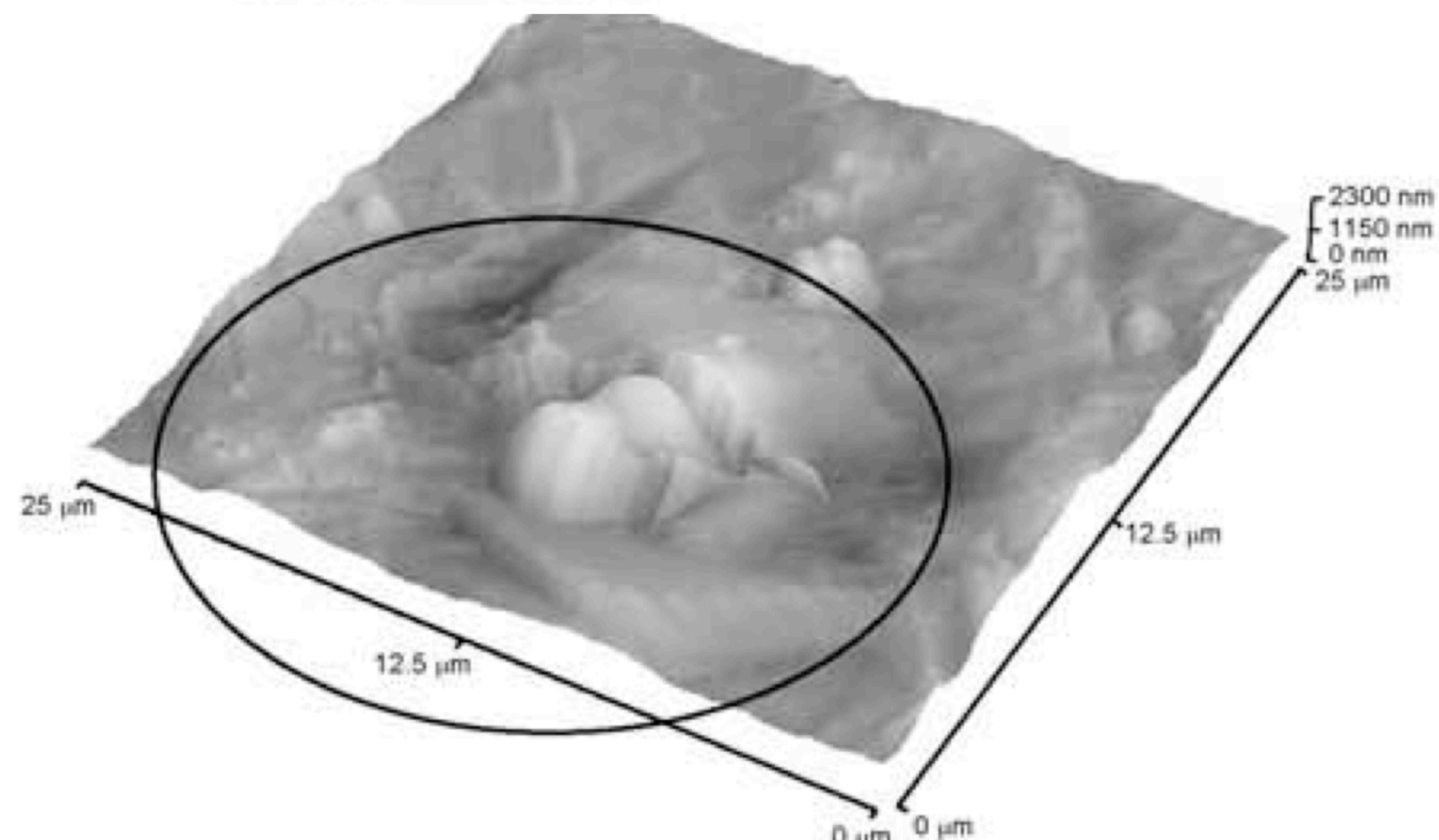
$HF + (CH_2OCO_2Li)_2\downarrow, Li_2CO_3\downarrow \longrightarrow LiF\downarrow + (CH_2COCO_2H)_2, H_2CO_3(sol.).$



D. Aurbach, E. Zinigrad, Y. Cohen, H. Teller "A short review of failure mechanisms of lithium metal and lithiated graphite anodes in liquid electrolyte solutions." Solid State Ionics 148 (2002) 405–416.

Surface Morphology During Recharge





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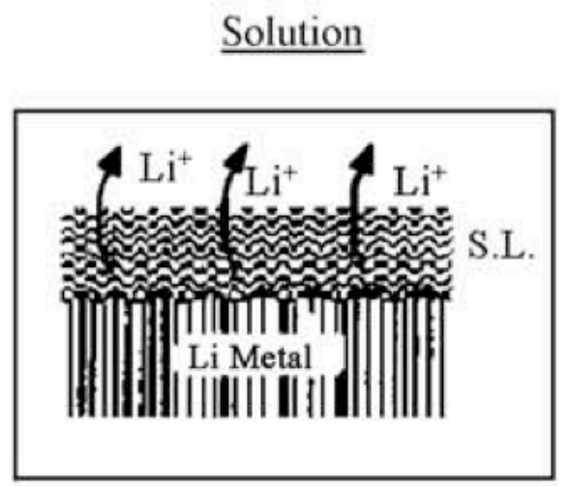
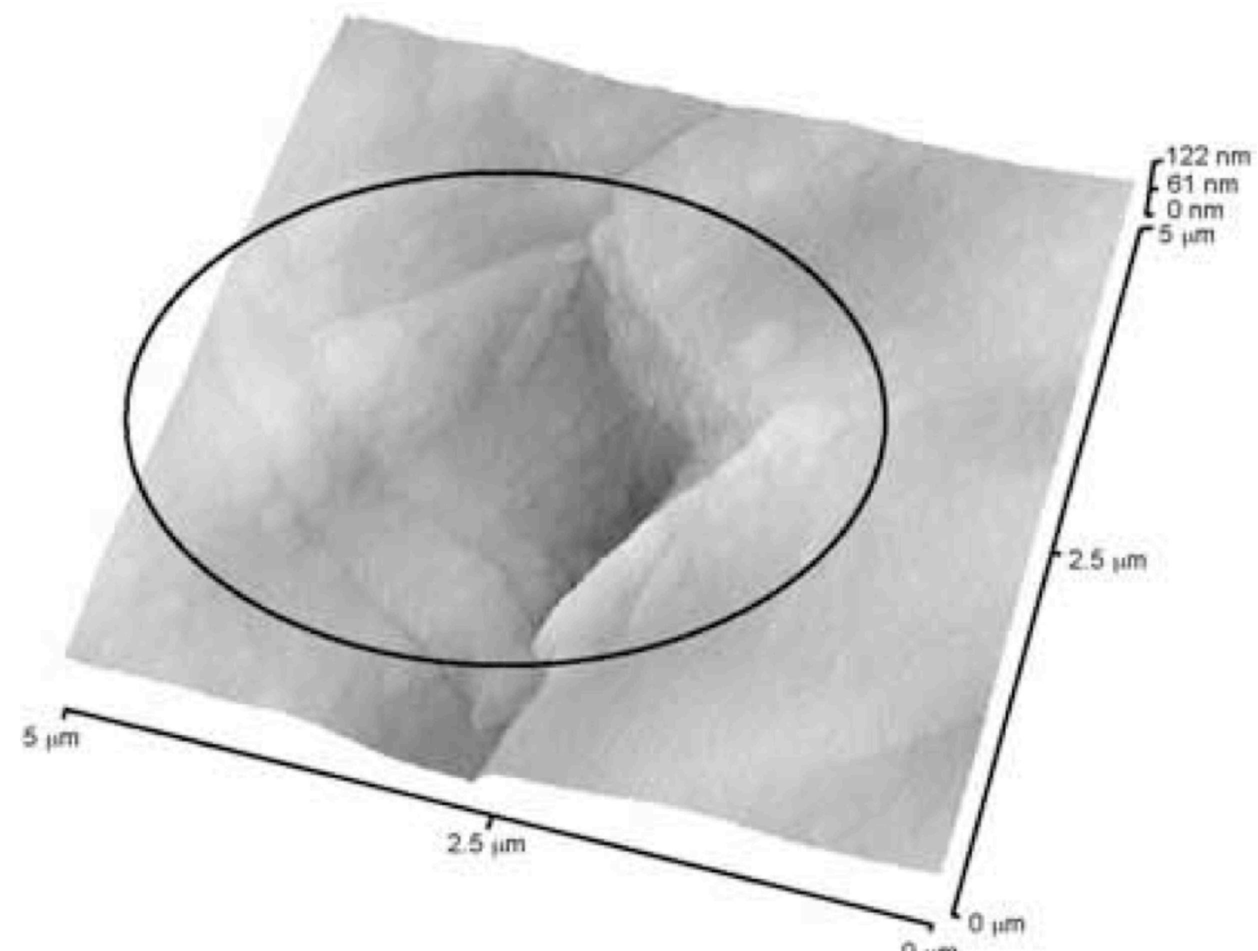
Surface Morphology During Discharge





D. Aurbach, E. Zinigrad, Y. Cohen, H. Teller "A short review of failure mechanisms of lithium metal and lithiated graphite anodes in liquid electrolyte solutions." Solid State Ionics 148 (2002) 405–416.

SEI-Induced Exfoliation

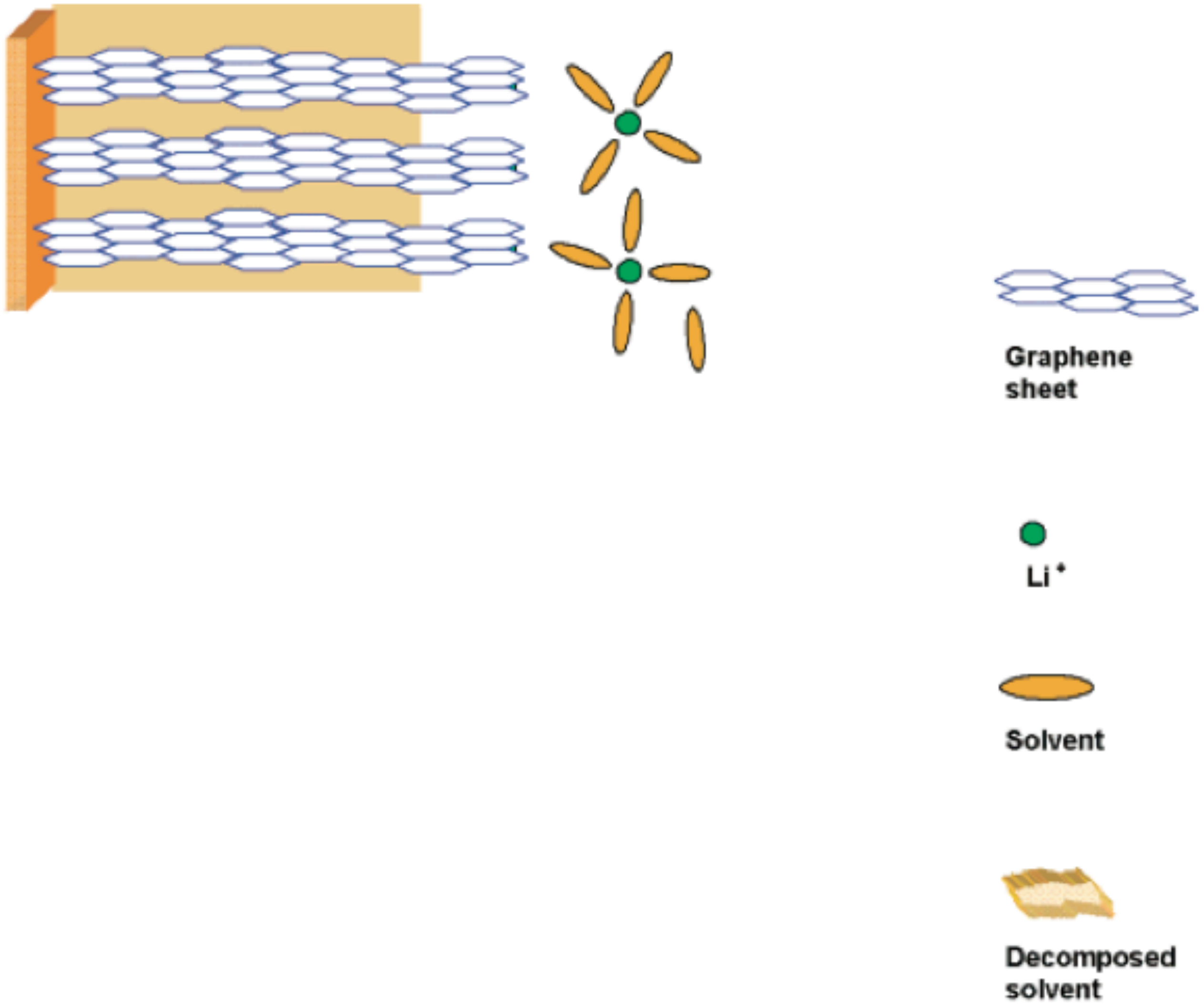


Figure 12. Schematic illustration of the SEI formation mechanism via the decomposition of $Li(solv)_xC_y$. Reconstructed based on ref 251.

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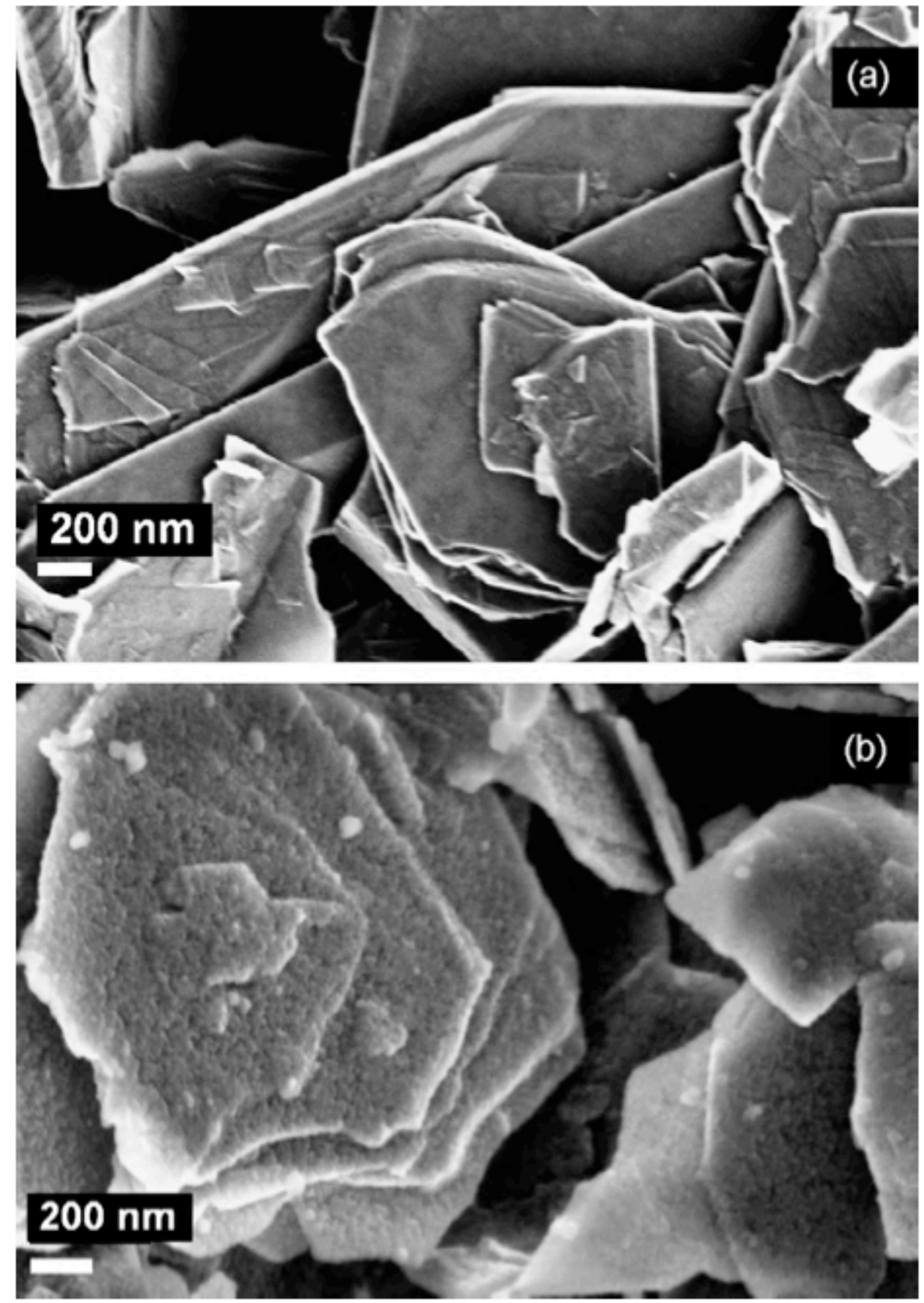
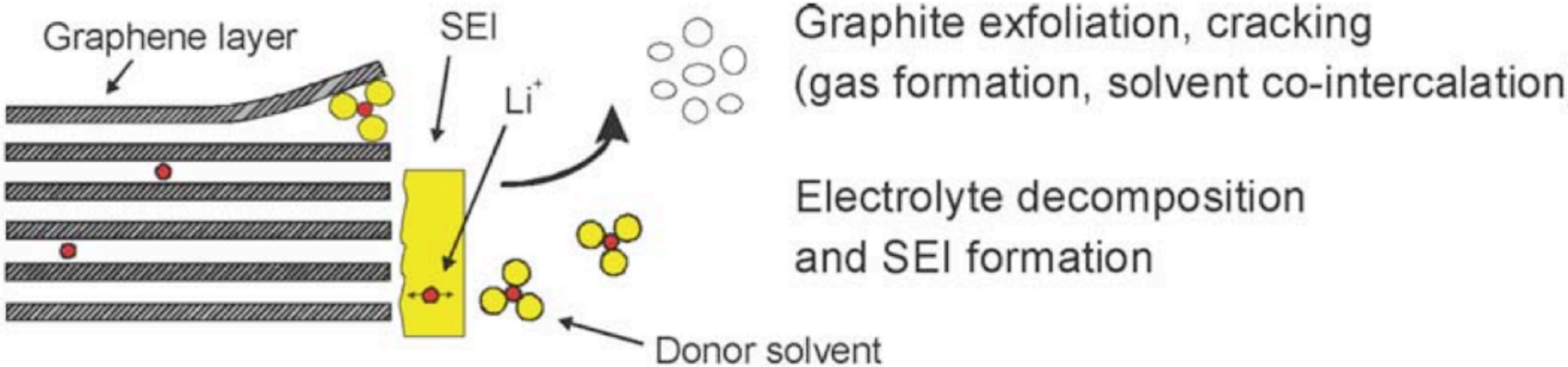


Fig. 3. SEM of composite SFG6 (TIMCAL®) graphite electrode (90% graphite and 10% PVDF-HFP binder): (a) pristine electrode and (b) electrode after one cycle vs. Li metal in 1 M $LiPF_6$ in EC:DMC (1:1) electrolyte at C/10 rate.

P. Verma, P. Maire, P. Novák "A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries." Electrochimica Acta 55 (2010) 6332–6341.

Summary of Anode Interfacial Reactions



J. Vetter et al. "Ageing mechanisms in lithium-ion batteries." Journal of Power Sources 147 (2005) 269–281

Summary of Anode Aging Mechanisms

Table 1
Lithium-ion anode ageing—causes, effects, and influences

Cause	Effect	Leads to	Reduced by	Enhanced by
Electrolyte decomposition (→SEI) (Continuous side reaction at low rate)	Loss of lithium Impedance rise	**Capacity fade** **Power fade**	Stable SEI (additives) Rate decreases with time	High temperatures High SOC (low potential)
Solvent co-intercalation, gas evolution and subsequent cracking formation in particles	Loss of active material (graphite exfoliation) Loss of lithium	Capacity fade	Stable SEI (additives) Carbon pre-treatment	Overcharge
Decrease of accessible surface area due to continuous SEI growth	Impedance rise	**Power fade**	Stable SEI (additives)	High temperatures High SOC (low potential)
Changes in porosity due to volume changes, SEI formation and growth	Impedance rise Overpotentials	Power fade	External pressure Stable SEI (additives)	High cycling rate High SOC (low potential)
Contact loss of active material particles due to volume changes during cycling	Loss of active material	**Capacity fade**	External pressure	High cycling rate High DOD
Decomposition of binder	Loss of lithium Loss of mechanical stability	Capacity fade	Proper binder choice	High SOC (low potential) High temperatures
Current collector corrosion	Overpotentials Impedance rise Inhomogeneous distribution of current and potential	Power fade Enhances other ageing mechanisms	Current collector pre-treatment (?)	Overdischarge Low SOC (high potential)
Metallic lithium plating and subsequent electrolyte decomposition by metallic Li	Loss of lithium (Loss of electrolyte)	Capacity fade (power fade)	Narrow potential window	Low temperature High cycling rates Poor cell balance Geometric misfits

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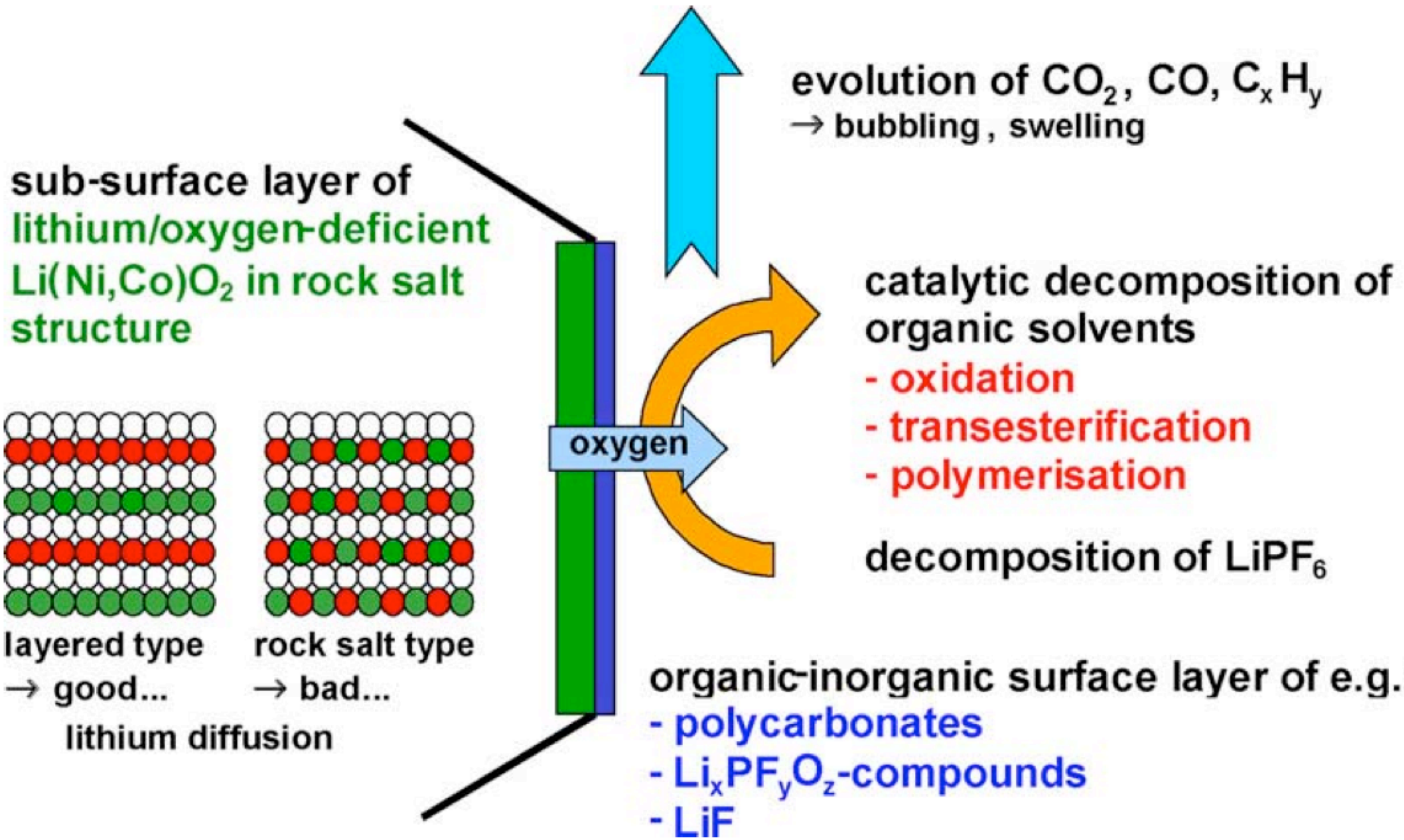
The Li(Co,Ni)O_2 System



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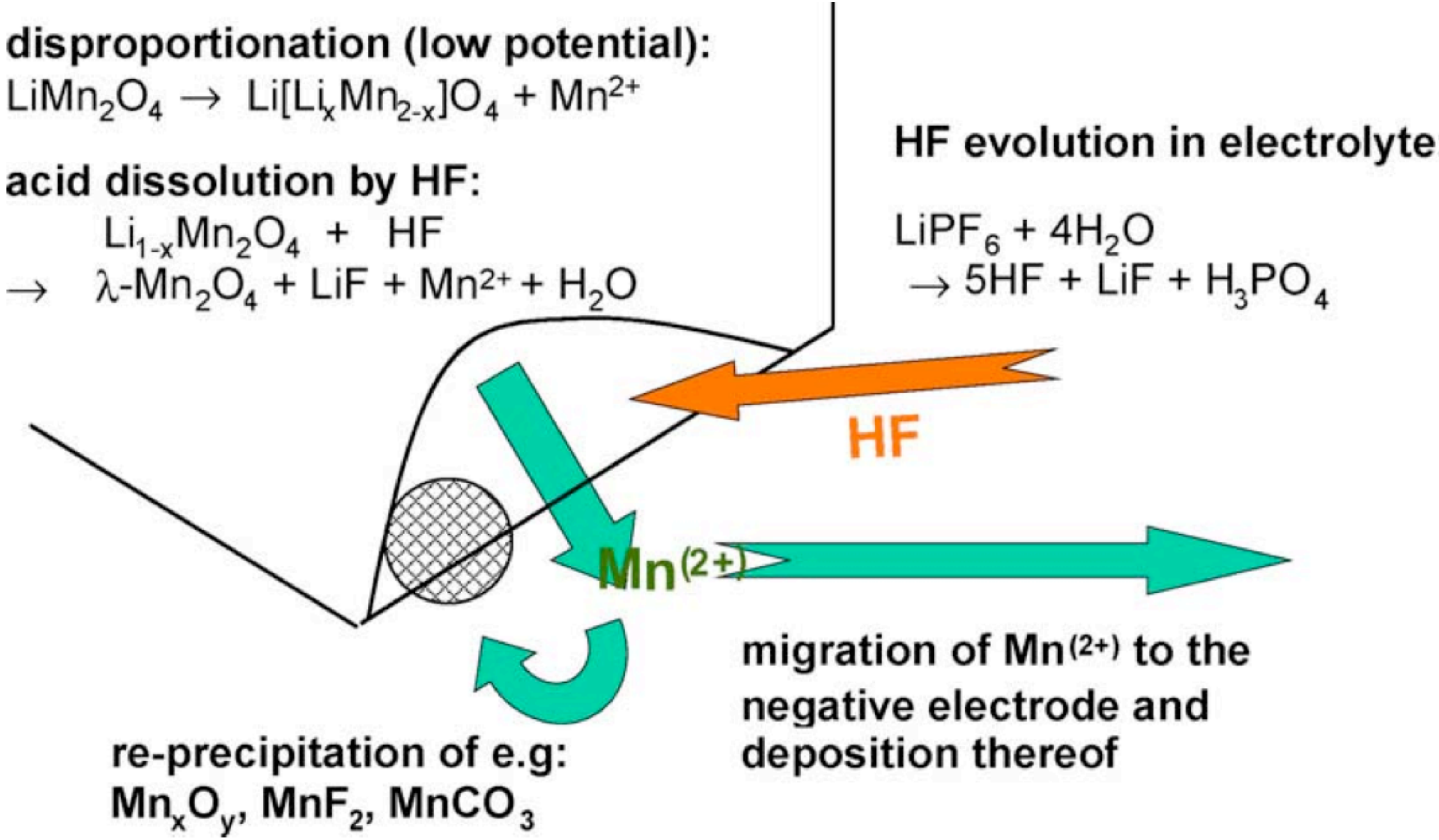
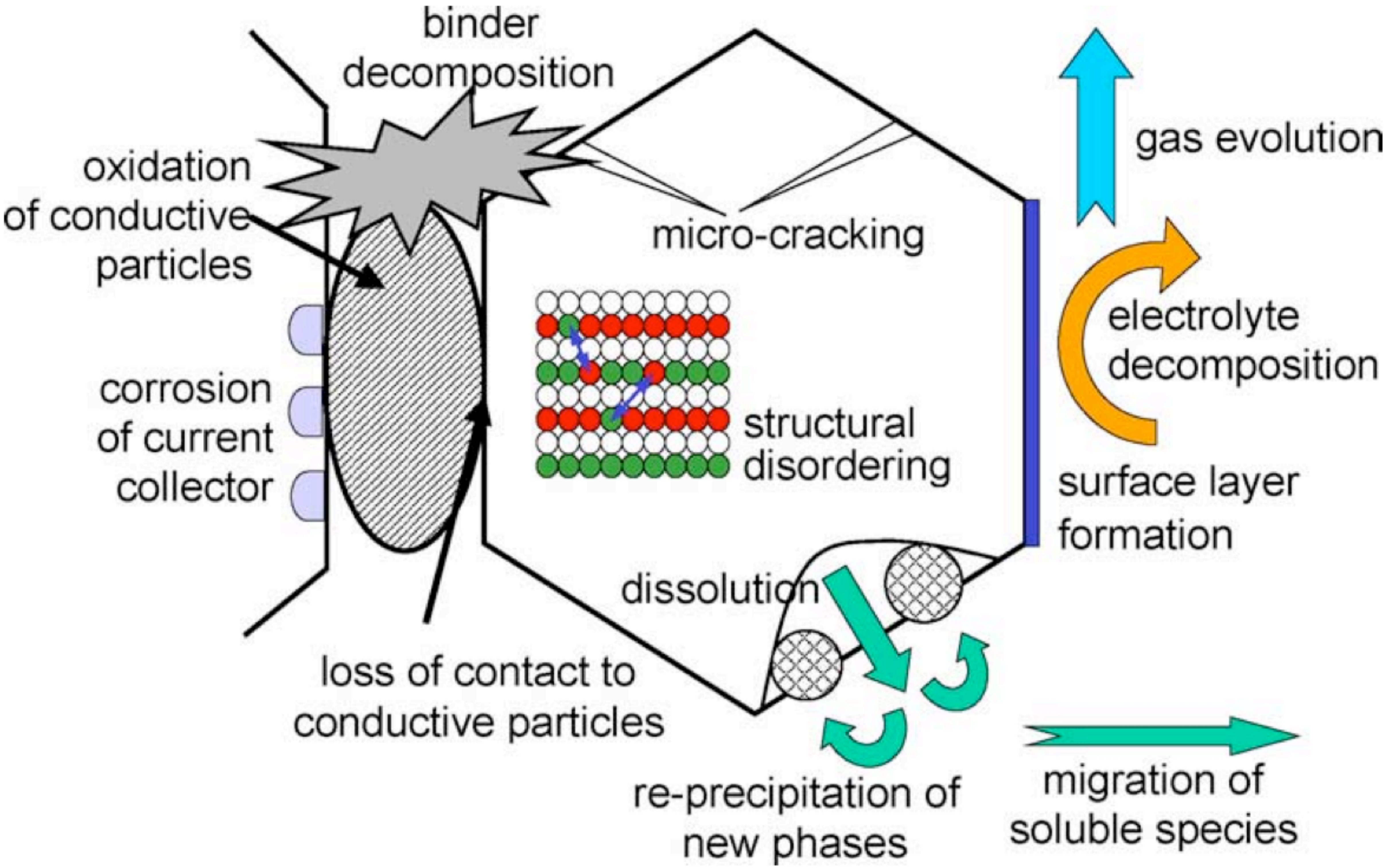
The $LiMn_2O_4$ System



J. Vetter et al. "Ageing mechanisms in lithium-ion batteries." Journal of Power Sources 147 (2005) 269–281

Summary of Cathode Interfacial Reactions



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