

# Reductive Reactions via Li excess in Mixture Electrolytes of Li Ion Battery: *Ab-initio* Molecular Dynamics Study

Woon Ih Choi\*, Min Sik Park, Youngseon Shim, Hyosug Lee, Dong Young Kim, Yoon-Sok Kang, Meiten Koh

Samsung Advanced Institute of Technology, Samsung Electronics, 130 Samsung-ro, Suwon, Gyeonggi-do 16678, Republic of Korea

Supporting Information

**Table S1. Reaction Products of EC+DMC+LiPF<sub>6</sub> electrolytes after 5 ps of molecular dynamics run.**

Electrolyte Composition				Gas molecules			PF <sub>6</sub> <sup>-</sup>		Inorganic Salt		Organic Salt	
EC	DMC	LiPF <sub>6</sub>	Li Excess	CO	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	PF <sub>3</sub>	PF <sub>2</sub> <sup>-</sup>	LiF (F <sup>-</sup> )	CO <sub>3</sub> <sup>2-</sup>	Anion Radical (ch × #)	Merged (ch × #)
			4			1				1		1 (-2×1)
			8			2	1		3	1		3 (-2×1, -1×2)
25	25	4	12	1		1	1		3	1	3 (-2×2, -1×1)	1 (-3×1)
			16	1		3	2	1	10	3	1 (-2×1)	
			20	3		1	3		9	1	8 (-1×6, -2×2)	1 (-2×1)
			4			2				2		
			8			2				2	1 (-2×1)	1 (-2×1)
40	10	4	12			4	1		3	4		1 (-2×1)
			16			6	1		3	6		1 (-2×1)
			20	1		5				5	4 (-2×3, -1×1)	2 (-2×1, -1×1)

**Table S2. Reaction Products of FEC+DMC+LiPF<sub>6</sub> electrolytes after 5 ps of molecular dynamics run.**

Electrolyte Composition				Gas molecules			PF <sub>6</sub> <sup>-</sup>	Inorganic Salt		Organic Salt	
FEC	DMC	LiPF <sub>6</sub>	Excess Li	CO	CO <sub>2</sub>	C <sub>2</sub> H <sub>3</sub> F	PF <sub>3</sub>	LiF (F <sup>-</sup> )	CO <sub>3</sub> <sup>2-</sup>	Anion Radical (ch × #)	Merged (ch × #)
25	25	4	4	2				2		1 (-1×1)	1 (-1×1)
			8	4			3		5 (-1×5)		
			12	6			6		6 (-1×6)		
			16	6	1		7	1	7 (-1×7)		
			20	4	1	1	12	1	6 (-1×6)	1 (-1×1)	
40	10	4	4	2				1		3 (-1×3)	
			8	1	1		3	1	2 (-1×2)	1 (-1×1)	
			12	3	1	1	6	1	4 (-1×4)	1 (0×1)	
			16	2		2	12		5 (-1×5)	1 (-1×1)	
			20	4	1	1	2	13	1	7 (-1×7)	1 (0×1)

**Table S3. Reaction Products of EC+DMC+LiPF<sub>6</sub> electrolytes after 5 ps of molecular dynamics run. Reactions with Li<sup>+</sup> excess are compared with excess electron only case.**

Electrolyte Composition				Gas molecules			PF <sub>6</sub> <sup>-</sup>		Inorganic Salt		Organic Salt	
EC	DMC	LiPF <sub>6</sub>	Li Excess	CO	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	PF <sub>3</sub>	PF <sub>2</sub> <sup>-</sup>	LiF (F <sup>-</sup> )	CO <sub>3</sub> <sup>2-</sup>	Anion Radical (ch <sub>1</sub> ×# <sub>1</sub> , ch <sub>2</sub> ×# <sub>2</sub> )	Merged (ch <sub>1</sub> ×# <sub>1</sub> , ch <sub>2</sub> ×# <sub>2</sub> )
			4			2				2		
			8			2				2	1 (-2×1)	1 (-2×1)
40	10	4	12			4	1		3	4		1 (-2×1)
			16			6	1		3	6		1 (-2×1)
			20	1		5				5	4 (-2×3, -1×1)	2 (-2×1, -1×1)
			4e			1				1	1 (-2×1)	
			8e			2				2	1 (-2×1)	1 (-2×1)
40	10	4	12e	2		2				2	4 (-2×4)	
			16e			6				6		2 (-2×2)
			20e	1		5				4	2 (-2×1, -1×1)	5 (-2×4, -1×1)
Electrolyte Composition				Gas molecules			PF <sub>6</sub> <sup>-</sup>		Inorganic Salt		Organic Salt	
EC	DMC	LiPF <sub>6</sub>	Li Excess	CO	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	PF <sub>3</sub>	PF <sub>2</sub> <sup>-</sup>	LiF (F <sup>-</sup> )	CO <sub>3</sub> <sup>2-</sup>	Anion Radical (ch <sub>1</sub> ×# <sub>1</sub> , ch <sub>2</sub> ×# <sub>2</sub> )	Merged (ch <sub>1</sub> ×# <sub>1</sub> , ch <sub>2</sub> ×# <sub>2</sub> )
			4			1				1		1 (-2×1)
			8			2	1		3	1		3 (-2×1, -1×2)
25	25	4	12	1		1	1		3	1	3 (-2×2, -1×1)	1 (-3×1)
			16	1		3	2	1	10	3	1 (-2×1)	
			20	3		1	3		9	1	8 (-2×2, -1×6)	1 (-2×1)
			4e			1						2 (-2×2)
			8e	2		1				1	3 (-2×3)	
25	25	4	12e	2		3				3	2 (-2×2)	1 (-2×1)
			16e			5	1		3	5	2 (-2×2)	
			20e	1		7	1		3	7	3 (-1×2, -2×1)	

**Table S4. Reaction Products of FEC+DMC+LiPF<sub>6</sub> electrolytes after 5 ps of molecular dynamics run.**

Reactions with Li<sup>+</sup> excess are compared with excess electron only case.

Electrolyte Composition				Gas molecules			PF <sub>6</sub> <sup>-</sup>	Inorganic Salt		Organic Salt	
FEC	DMC	LiPF <sub>6</sub>	Excess Li	CO	CO <sub>2</sub>	C <sub>2</sub> H <sub>3</sub> F	PF <sub>3</sub>	LiF (F <sup>-</sup> )	CO <sub>3</sub> <sup>2-</sup>	Anion Radical	Merged
			4	2				1		3 (-1×3)	
			8	1		1		3	1	2 (-1×2)	1 (-1×1)
40	10	4	12	3	1	1		6	1	4 (-1×4)	1 (0×1)
			16	2			2	12		5 (-1×5)	1 (-1×1)
			20	4	1	1	2	13	1	7 (-1×7)	1 (0×1)
			4e			1		1	1	1 (-1×1)	
			8e	4				3		3 (-1×3)	1 (-1×1)
40	10	4	12e	5				6		6 (-1×6)	
			16e	7				7		9 (-1×9)	
			20e	7				10		10 (-1×10)	1 (0×1)
Electrolyte Composition				Gas molecules			PF <sub>6</sub> <sup>-</sup>	Inorganic Salt		Organic Salt	
FEC	DMC	LiPF <sub>6</sub>	Excess Li	CO	CO <sub>2</sub>	C <sub>2</sub> H <sub>3</sub> F	PF <sub>3</sub>	LiF (F <sup>-</sup> )	CO <sub>3</sub> <sup>2-</sup>	Anion Radical	Merged
			4	2				2		1 (-1×1)	1 (-1×1)
			8	4				3		5 (-1×5)	
25	25	4	12	6				6		6 (-1×6)	
			16	6		1		7	1	7 (-1×7)	
			20	4		1	1	12	1	6 (-1×6)	1 (-1×1)
			4e			1		1	1	1 (-1×1)	
			8e	3		1		3	1	3 (-1×3)	
25	25	4	12e	3		1		5		7(-1×7)	
			16e	5		1		6	1	8(-1×8)	
			20e	4		1		8	1	9(-1×9)	1 (-1×1)

**Table S5. Reaction Products of EC+DMC+LiPF<sub>6</sub> electrolytes after 5 ps of molecular dynamics run. Instead of dumping 12 electrons, various electron transfer rate is examined. Boldfaced cases indicate solvated electrons that do not participate bond breaking reaction yet.**

Electrolyte Composition				Gas molecules			PF <sub>6</sub> <sup>-</sup>		Inorganic Salt		Organic Salt		
EC	DMC	LiPF <sub>6</sub>	$\Delta n_e \times N$	CO	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	PF <sub>3</sub>	PF <sub>4</sub> <sup>-</sup>	LiF (F <sup>-</sup> )	CO <sub>3</sub> <sup>2-</sup>	Anion Radical (ch <sub>1</sub> ×# <sub>1</sub> , ch <sub>2</sub> ×# <sub>2</sub> )	Merged (ch <sub>1</sub> ×# <sub>1</sub> , ch <sub>2</sub> ×# <sub>2</sub> )	
25	25	4	+2e×6			4				4	3 (-1×3)	1 (-1×1)	
			<b>+4e×3</b>					<b>1</b>	<b>2</b>	<b>2</b>	<b>1 (-2×1)</b>	<b>1 (-2×1)</b>	
			<b>+6e×2</b>			2					<b>2</b>	<b>2 (-1×2)</b>	<b>2 (-2×2)</b>
			+12e×1	1		1		1	2	1	3(-2×2, -1×1)	1 (-3×1)	
40	10	4	<b>+2e×6</b>			<b>3</b>				<b>2</b>	<b>1 (-2×1)</b>	<b>1 (-2×1)</b>	
			+4e×3			5				5		1 (-2×1)	
			+6e×2			3	1		3	3		2 (-2×2)	
			+12e×1			4		1	2	4		1 (-2×1)	

**Table S6. Reaction Products of FEC+DMC+LiPF<sub>6</sub> electrolytes after 5 ps of molecular dynamics run. Instead of dumping 12 electrons, various electron transfer rate is examined. Boldfaced cases indicate that there exist solvated electrons that do not participate bond breaking reaction yet.**

Electrolyte Composition				Gas molecules			PF <sub>6</sub> <sup>-</sup>		Inorganic Salt		Organic Salt		
FEC	DMC	LiPF <sub>6</sub>	$\Delta n_e \times N$	CO	CO <sub>2</sub>	C <sub>2</sub> H <sub>3</sub> F	PF <sub>3</sub>	PF <sub>2</sub> <sup>-</sup>	LiF (F <sup>-</sup> )	CO <sub>3</sub> <sup>2-</sup>	Anion Radical (ch <sub>1</sub> ×# <sub>1</sub> , ch <sub>2</sub> ×# <sub>2</sub> )	Merged (ch <sub>1</sub> ×# <sub>1</sub> , ch <sub>2</sub> ×# <sub>2</sub> )	
25	25	4	<b>+2e×6</b>	<b>2</b>					<b>5</b>		<b>4 (-1×4)</b>	<b>1 (-1×1)</b>	
			+4e×3	1					6		6 (-1×6)		
			+6e×2	2						6		5 (-1×5)	1 (-1×1)
			+12e×1	6						6		6 (-1×6)	
40	10	4	<b>+2e×6</b>	3					4		4 (-1×4)	2 (-2×2)	
			+4e×3	1			1		7		5 (-1×4, -2×1)		
			+6e×2	3						5		7(-1×7)	
			+12e×1	2		1				5	1	4 (-1×4)	1 (-1×1)

**Table S7. Reaction products when mass of hydrogen is used instead of tritium. FEC/DMC(25/25)+ Li<sup>+</sup>(20) case.**

Electrolyte Composition				Gas molecules			PF <sub>6</sub> <sup>-</sup>	Inorganic Salt		Organic Salt	
FEC	DMC	LiPF <sub>6</sub>	Excess Li	CO	CO <sub>2</sub>	C <sub>2</sub> H <sub>3</sub> F	PF <sub>3</sub>	LiF (F <sup>-</sup> )	CO <sub>3</sub> <sup>2-</sup>	Anion Radical (ch × #)	Merged (ch × #)
			Tritium mass	4		1	1	12	1	6 (-1×6)	1 (-1×1)
			Hydrogen mass	6		1	1	11	1	6 (-1×8)	

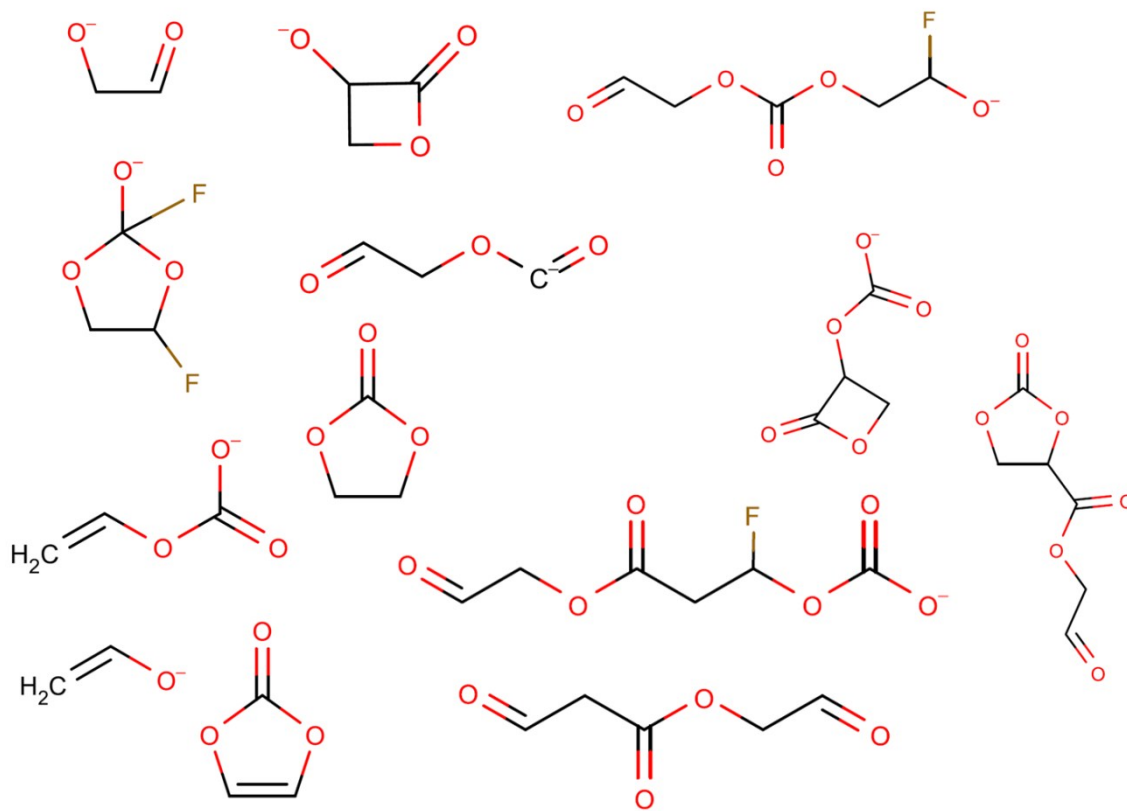


Figure S1. newly generated organic species out of FEC+DMC electrolyte.

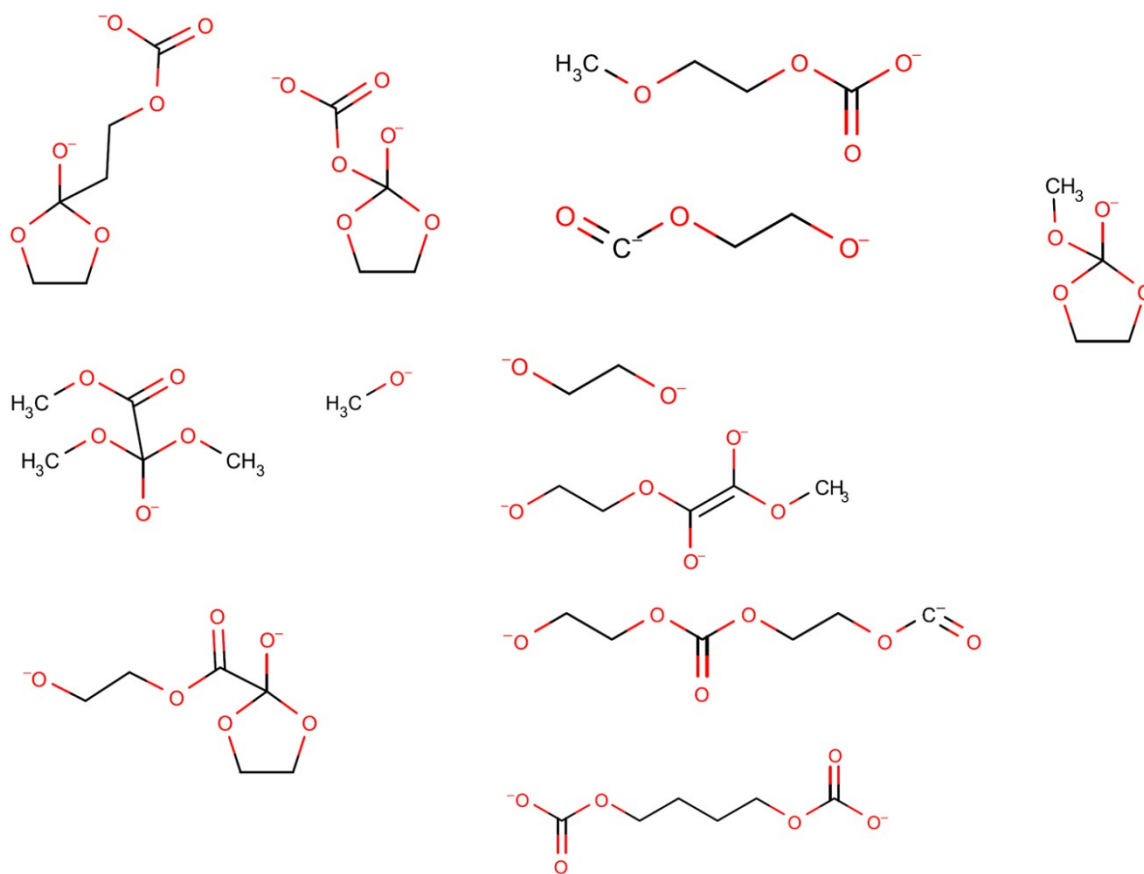


Figure S2. Newly generated organic species from EC+DMC electrolyte