

## Supporting Information

### **Advanced *In-Situ* Technology for Li/Na Metal Anodes: An In-Depth Mechanism Understanding**

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**Summary of Li/Na metal anodes with different *in-situ* technologies:**

**Table S1.** Performance and parameters of Li/Na anodes with functional solvents or Li/Na salts.

Solvents or Li/Na salts	Half cells test				Symmetrical cells test			Ref.
	Current (mA cm <sup>-2</sup> )	Capacity (mAh cm <sup>-2</sup> )	CE	Cycle	Current (mA cm <sup>-2</sup> )	Capacity (mA cm <sup>-2</sup> )	Cycle	
FEC solvent	--	--	--	--	2	3.3	~1100	1
VEC solvent	0.5	0.5	98.1%	1400	1	1	500	2
FFS solvent	0.5	0.5	99%	400	0.5	0.5	550	3
LiTFPFB salt	--	--	--	--	0.5	0.5	250	4
LiHFDF salt	--	--	--	--	0.5 2	1 4	250 ~90	5
NaDFOB salt	--	--	--	--	1.5	0.1	515	6

Annotations:

1. FEC: fluoroethylene carbonate

VEC: vinylethylene carbonate

FFS: “full fluorosulfonyl” electrolyte

LiTFPFB: lithium trifluoro(perfluoro-tert-butyloxy)borate

LiHFDF: lithium 1, 1, 2, 2, 3, 3-hexafluoropropane-1, 3-disulfonimide

NaDFOB: sodium-difluoro(oxalato)borate

2. “--” means that no information is provided in the literature.

**Table S2.** Performance and parameters of Li/Na anodes with different additives.

Additives	Half cells test				Symmetrical cells test			Ref.
	Current (mA cm <sup>-2</sup> )	Capacity (mAh cm <sup>-2</sup> )	CE	Cycle	Current (mA cm <sup>-2</sup> )	Capacity (mAh cm <sup>-2</sup> )	Cycle	
Li <sub>2</sub> S <sub>8</sub>	0.5	0.5	~97%	~120	10	10	2000	7
PSD	2	1	99.1%	420				8
	2	2	99%	250	--	--	--	
	2	3	98.9%	250				
PST	2	1	99%	400				9
	2	2	98.9%	220	--	--	--	
	2	3	98.6%	220				
LiPO <sub>2</sub> F <sub>2</sub>	--	--	--	--	0.5	0.5	250	10
					1	1	100	
LiDFOB	0.5	1	98.5%	200	1	1	300	11
					2	1	180	
KPF <sub>6</sub>	--	--	--	--	0.5	0.5	216	12
SbF <sub>3</sub>	--	--	--	--	0.5	0.5	~500	13
HFAA	--	--	--	--	1	0.5	200	14
					2	1	100	
TCBQ	--	--	--	--	5	2	~22	15
					3	1	~150	
AlCl <sub>3</sub>	0.5	2	99%	150	0.5	1	~237	16
SiCl <sub>4</sub>	--	--	--	--	3	1	~500	17
SO <sub>2</sub> Cl <sub>2</sub>	0.5	0.5	95%	150	0.5	1	500	18
					1	1	600	

Annotations:

1. PSD: poly(sulfur-random-1,3-diisopropenylbenzene)

PST: poly(sulfur-random-triallylamine)

LiDFOB: lithium difluoro(oxalate)borate

HFAA: hexafluoroacetylacetone

TCBQ: tetrachloro-1,4-benzoquinone

2. "--" means that no information is provided in the literature.

**Table S3.** Performance and parameters of Li/Na anodes with high concentration electrolytes.

Additives	Half cells test				Symmetrical cells test			Ref.
	Current (mA cm <sup>-2</sup> )	Capacity (mAh cm <sup>-2</sup> )	CE	Cycle	Current (mA cm <sup>-2</sup> )	Capacity (mAh cm <sup>-2</sup> )	Cycle	
4 M LiFSI-DME	4 10	1 1	98.4% 97%	1000 500	10	0.5	6000	19
2.1 M NaFSI/DME- BTfE	1	1	~99%	400	1 2	1 1	500 ~960	20
3 M LiCF <sub>3</sub> SO <sub>3</sub> - DOL/DME	1	3	98.6%	100	1	3	~135	21
4 M LiTFSI- LiDFOB-FEC/DMC	0.5	1	>98%	800	0.5	0.5	500	22
10 M LiFSI- EC/DMC	0.5	1	98.8%	150	--	--	--	23

Annotations:

1. "--" means that no information is provided in the literature.

**Table S4.** Performance and parameters of Li/Na anodes with *in-situ* protective layers.

Additives	Half cells test				Symmetrical cells test			Ref.
	Current (mA cm <sup>-2</sup> )	Capacity (mAh cm <sup>-2</sup> )	CE	Cycle	Current (mA cm <sup>-2</sup> )	Capacity (mAh cm <sup>-2</sup> )	Cycle	
COF layer	--	--	--	--	1	1	200	24
	--	--	--	--	2	2	200	
PPy@Ni foam	1	2	99%	250				25
	1	5	98%	90	--	--	--	
	1	10	--	60				
PDA@3D Cu	0.5	1	97.3%	200				26
	1	1	96.2%	150	1	1	500	
	2	2	96.4%	150				
CAM layer	3	1	99%	400	0.5	1.5	~258	27
LiECHFP layer	--	--	--	--	1	1		28
	--	--	--	--	2	2	100	
	--	--	--	--	5	5		
CPLi	--	--	--	--	3	2	~750	29
LiF layer	--	--	--	--	1	1	350	30
	--	--	--	--	2	1	400	
	--	--	--	--	5	1	240	
LPS layer	--	--	--	--	1	1	200	31
	--	--	--	--	4	1	800	
Li <sub>3</sub> PS <sub>4</sub> layer	--	--	--	--	0.5	1	400	32
Na <sub>3</sub> PS <sub>4</sub> layer	--	--	--	--	1	1	~135	33
	--	--	--	--	3	1	~210	
[LiNBH] <sub>n</sub> layer	--	--	--	--	1	1	550	34
	--	--	--	--	3	1	~1050	
Li-Al layer	--	--	--	--	0.5	1	800	35
	--	--	--	--	5	1	~1125	
LiF/Cu layer	--	--	--	--	2.5	0.5	~2000	36

O-I hybrid layer	--	--	--	--	1 2	1 1	1500 1100	37
3D LiF-Li layer	--	--	--	--	1	1	800	38
LiF layer (G-S)	--	--	--	--	1 3 5	1 1 1	300 180 300	39
C-Li <sub>2</sub> S-LiI layer	--	--	--	--	1 2 3	1 1 1	300 200 200	40
Al <sub>2</sub> O <sub>3</sub> layer	--	--	--	--	0.25 0.25 0.5	0.125 1 1	900 50 30	41

Annotations:

1. COF: covalent organic framework

PPy: polymerizing polypyrrole

PDA: polydopamine

CAM: cyanuric acid and melamine

LiECHFP: lithium 2-((ethoxycarbonyl)oxy)-1,1,1,3,3,3-hexafluoro-propan-2-olate

CPLi: carboxylate-protected Li

LPS: Li<sub>3</sub>PS<sub>4</sub>

O-I: organic-inorganic

G-S: gas-solid reaction

2. "--" means that no information is provided in the literature.

**Table S5.** Performance and parameters of Li/Na anodes with *in-situ* polymer electrolytes.

Additives	Half cells test				Symmetrical cells test			Ref.
	Current (mA cm <sup>-2</sup> )	Capacity (mAh cm <sup>-2</sup> )	CE	Cycle	Current (mA cm <sup>-2</sup> )	Capacity (mAh cm <sup>-2</sup> )	Cycle	
Quasi SSGPE	--	--	--	--	1	1	220	42
PEGA+PFE	--	--	--	--	2	4	1000	43

Annotations:

1. SSGPE: solid state gel polymer electrolyte

PEGA+PFE: poly(ethylene glycol) methyl ether methacrylate + 2,2,3,3,3-pentafluoropropyl acrylate

2. "--" means that no information is provided in the literature.

**Table S6.** Performance and parameters of Li/Na anodes with *in-situ* growth techniques.

Additives	Half cells test				Symmetrical cells test			Ref.
	Current (mA cm <sup>-2</sup> )	Capacity (mAh cm <sup>-2</sup> )	CE	Cycle	Current (mA cm <sup>-2</sup> )	Capacity (mAh cm <sup>-2</sup> )	Cycle	
Au NPs@C	0.5	1	>98%	300	--	--	--	44
Sn-C	2	1	99.7%	500				
	2	3	99.5%	250	--	--	--	45
	2	5	99.3%	250				
NaF@SnO <sub>2</sub> -RGO	1	0.5	99.7%	3000	0.5	1	900	46

Annotations:

1. "--" means that no information is provided in the literature.



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