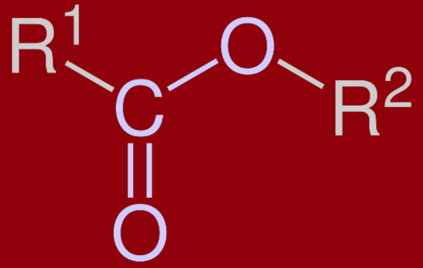
TASME 2024 Conference

July 7, 2024



Carboxylate ester-based electrolytes for Na-ion battery

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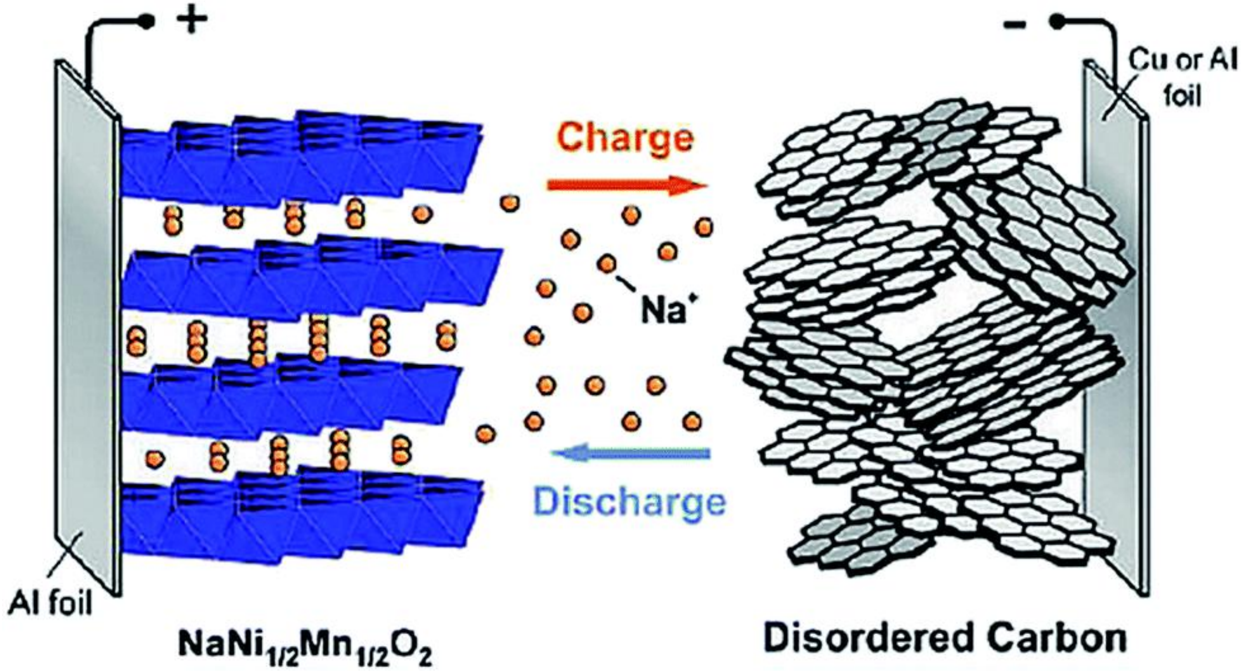
[1] Y. Qin, S. G. Choi, L. Mason, J. Liu, Z. Li, T. Gao, *Chem. Sci.* **2024**, 9224.

Content

Background: technological solution

➢ Sodium-ion batteries (SIBs)



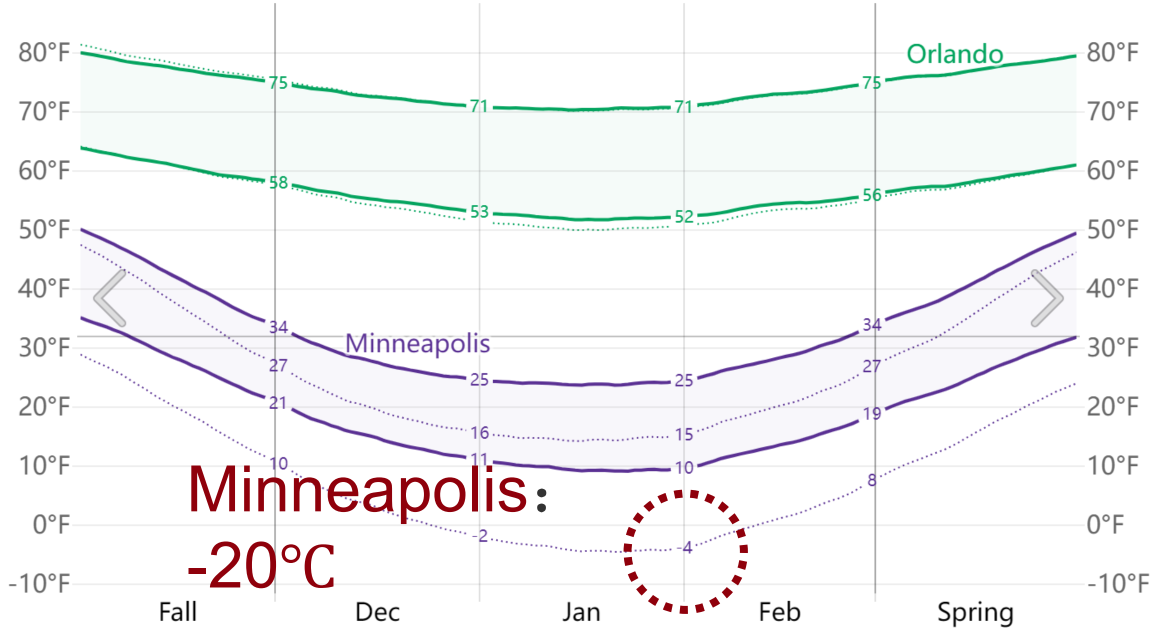
SOA electrolyte: 1M $NaPF_6$-EC/EMC(1:1 by vol)

Promising low-cost energy storage technology

RSC Adv. **2015**, *5* (65), 53129–53154.

Background: challenges of SIBs

1. Low first cycle Coulombic efficiency (30%–70%).
2. Inferior cycling stability (<1000 cycles).
3. Limited low-temperature (low-T) performance.



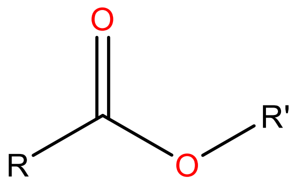
1M $NaPF_6$-EC/EMC(1:1 by vol)

- Conductivity reduces from **7.1** mS/cm at 25℃ to **1.4** mS/cm at -20℃.
- The charge transfer resistance increase by two orders of magnitude from **322 Ω** to **~31,000** Ω.

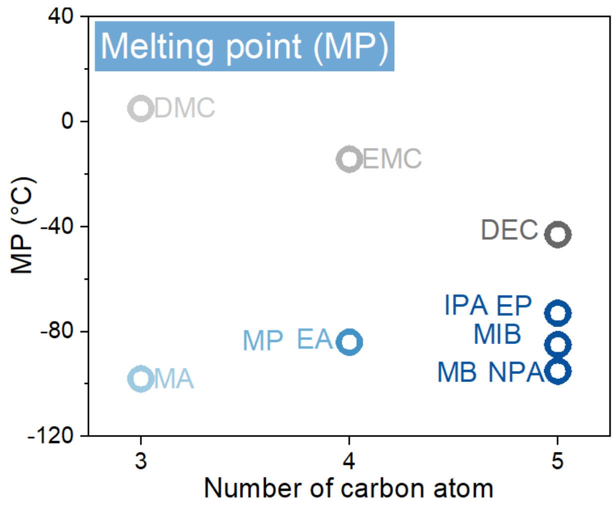
https://weatherspark.com/compare/s/3/23912~10405/Comparison-of-the-Average-Winter-Weather-in-New-York-City-and-Minneapolis; Nano Energy 2022, 103 (PA), 107746

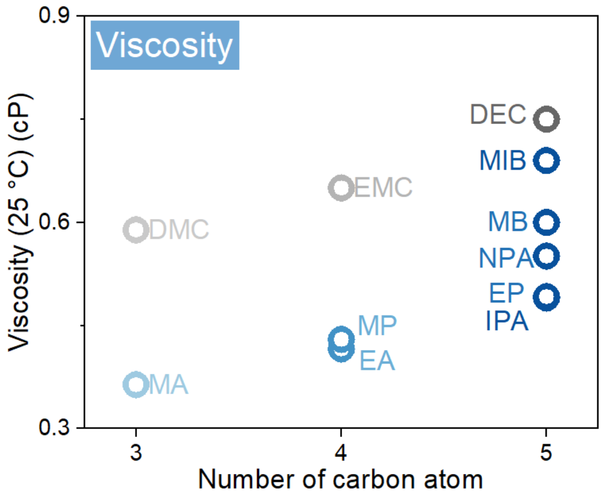
Hypothesis

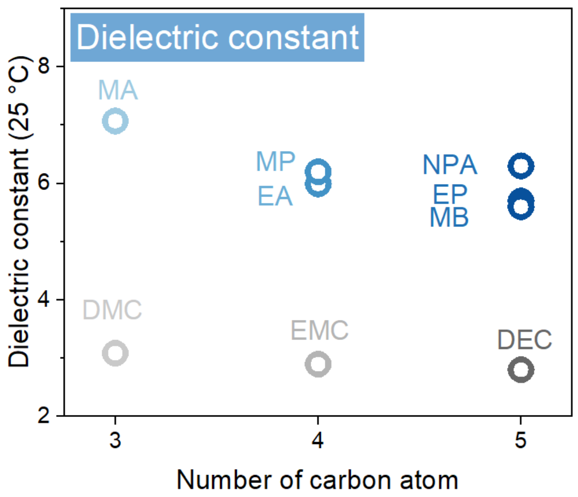
Carboxylate



- √ Low melting point (<-73 ℃)
- √ Low viscosity (<0.69 cP)
- √ High dielectric constant (>5.60)
- √ reasonable donor number (~16 kcal/mol)





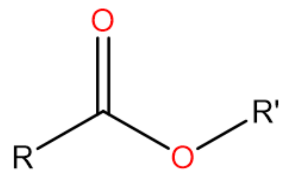


Carboxylate is a good solvent for low-T SIBs.

Scope

Chemistry

Carboxylate is a promising solvent for low temperature operation.

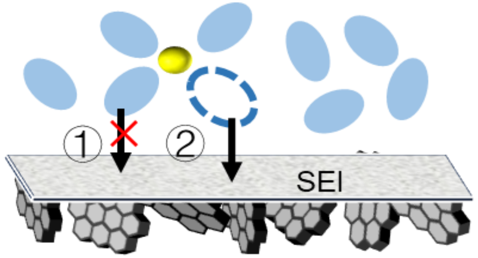


√ Low melting point (<-73 ℃)
√ Low viscosity (<0.69 cP)
√ High dielectric constant (>5.60)
√ Comparable donor number (~16 kcal/mol)

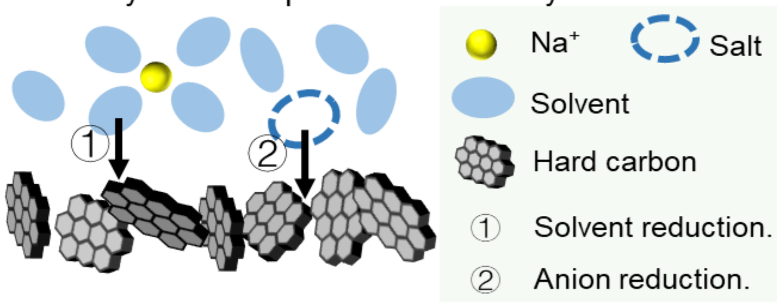
Property

Solvation	Transport	Interfacial
• Solvation number	• Conductivity	• SEI composition & Resistance

High concentration NaFSI-solvent: stable SEI formation.



Low concentration or use other salt: electrolyte decompose continuously.

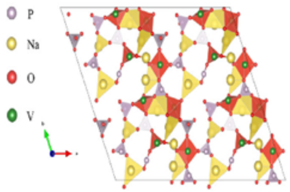


Performance

Hard carbon/Na, $Na_3V_2(PO_4)_3$/Na and low temperature performance were investigated.

Hard carbon

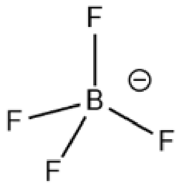
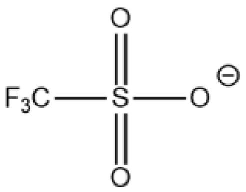
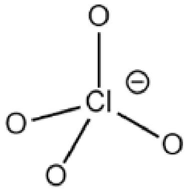
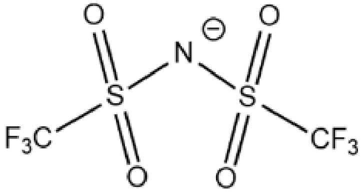
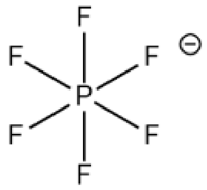
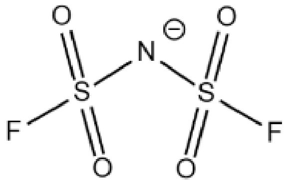
$Na_3V_2(PO_4)_3$



-20℃

Results: salt consideration

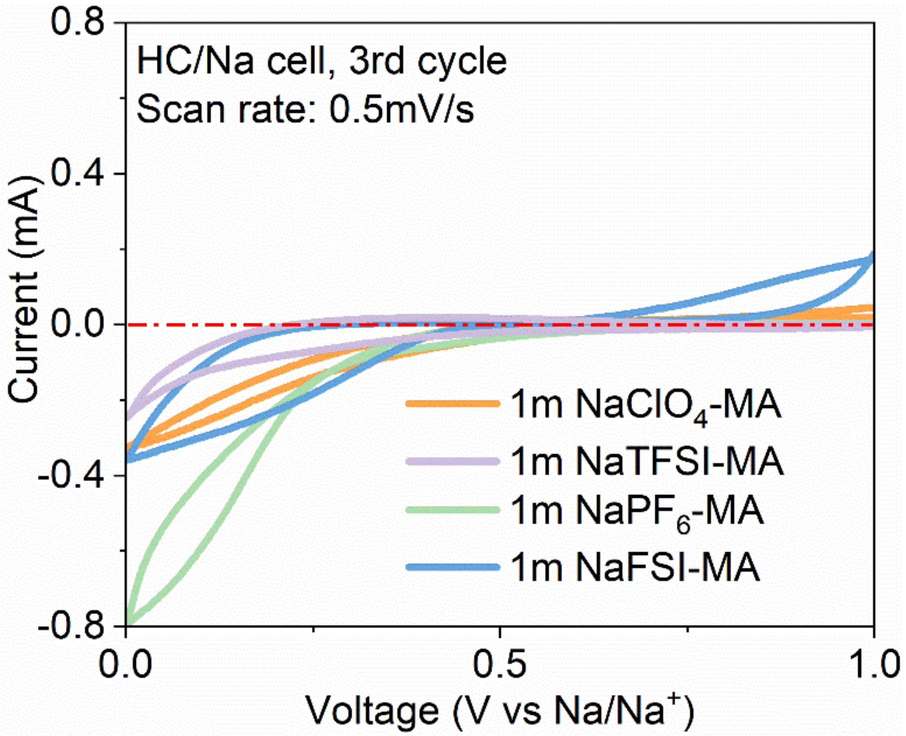
- Solubility (in MA).

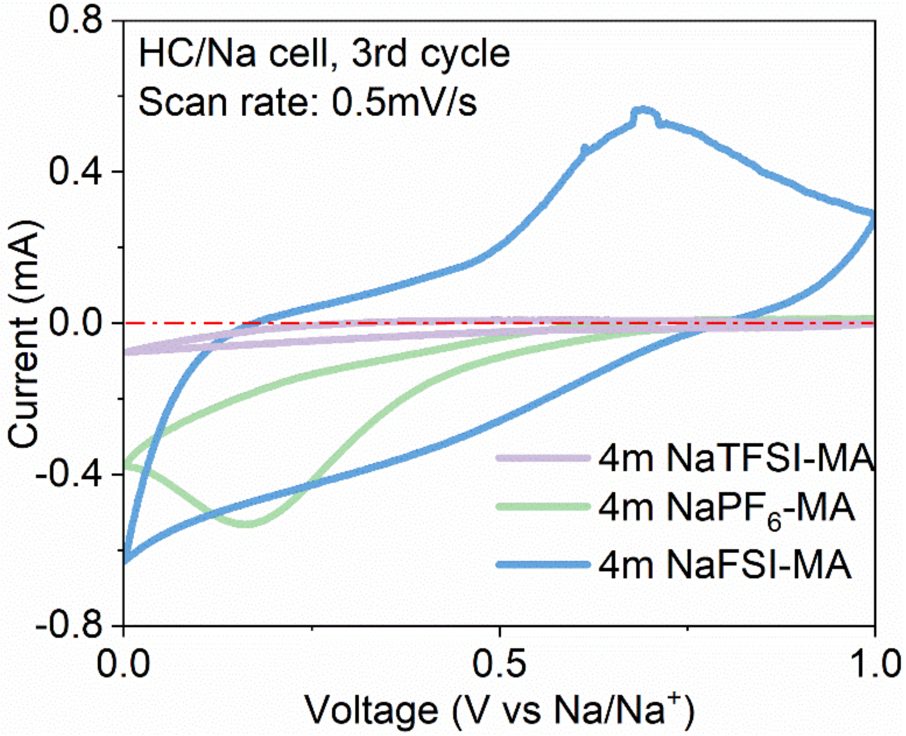
Salt		$NaBF_4$	NaOTf	$NaClO_4$	NaTFSI	$NaPF_6$	NaFSI
Chemical structure of anion							
Solubility in MA	Molality (m. mol/kg)	<0.01	0.1-0.2	1.6-1.8	5.2-6.0	6.0-7.0	11.0-11.8
	Molarity (m. mol/L)	<0.01	0.1-0.2	1.5-1.7	4.8-5.6	5.6-6.5	10.3-11.0

NaFSI stands out due to its highest solubility

Results: salt consideration

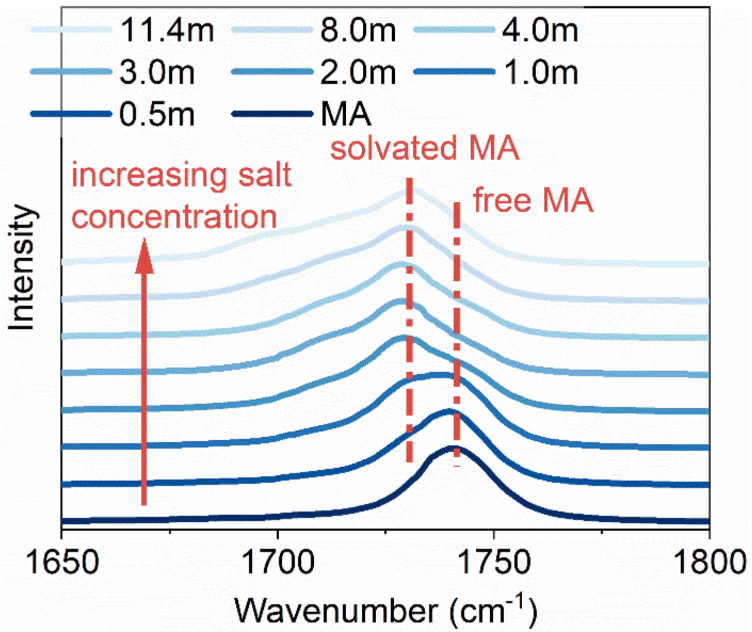
➢ Compatibility with HC anode.

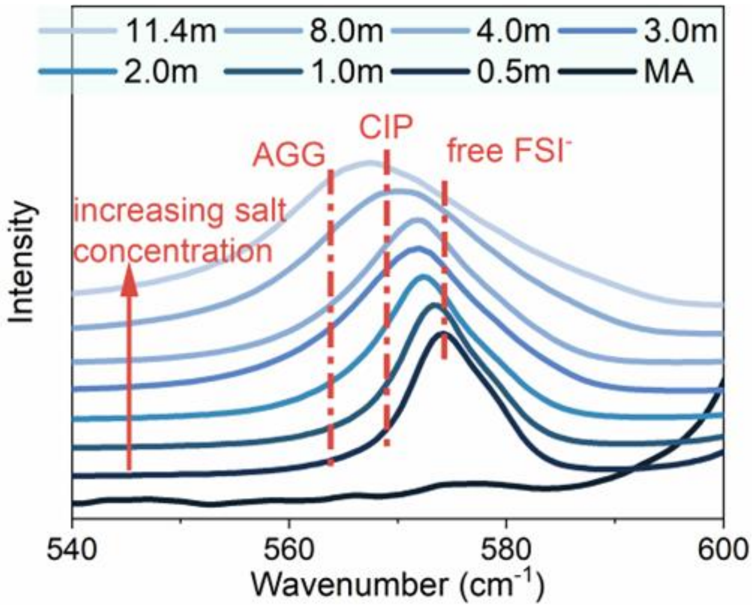




Only NaFSI is compatible with HC.

Electrolyte structure: FT-IR results

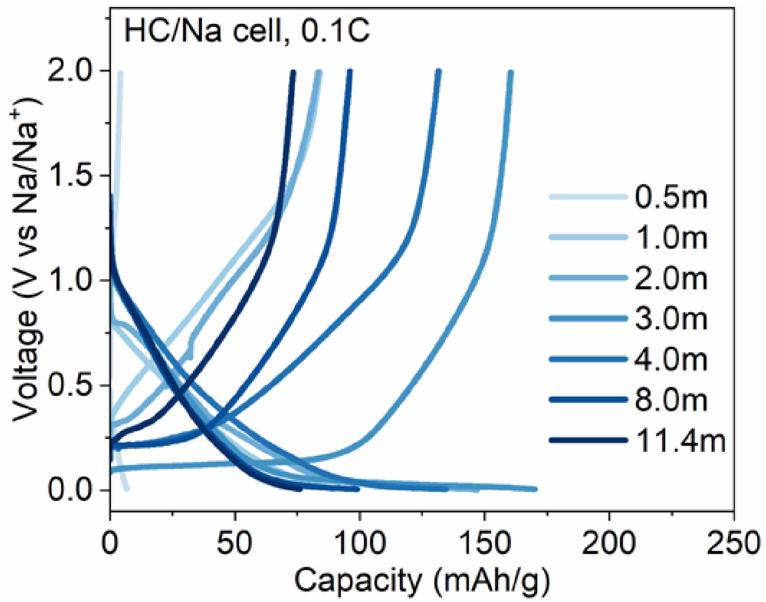


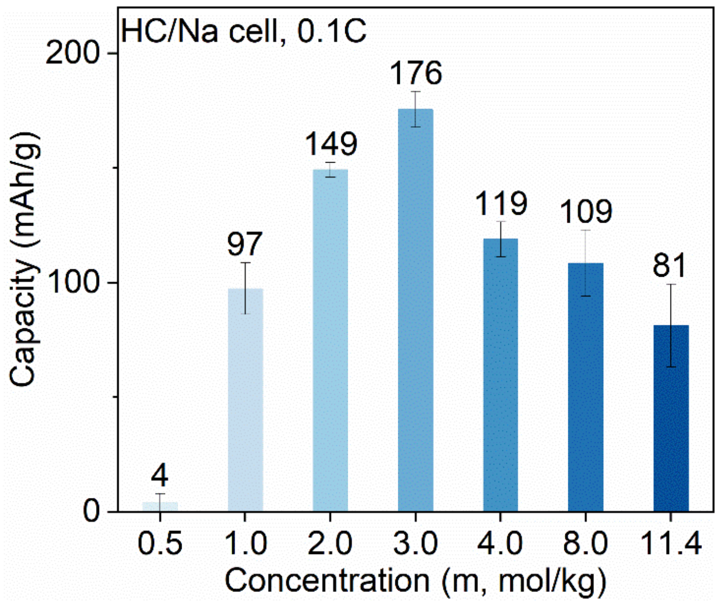


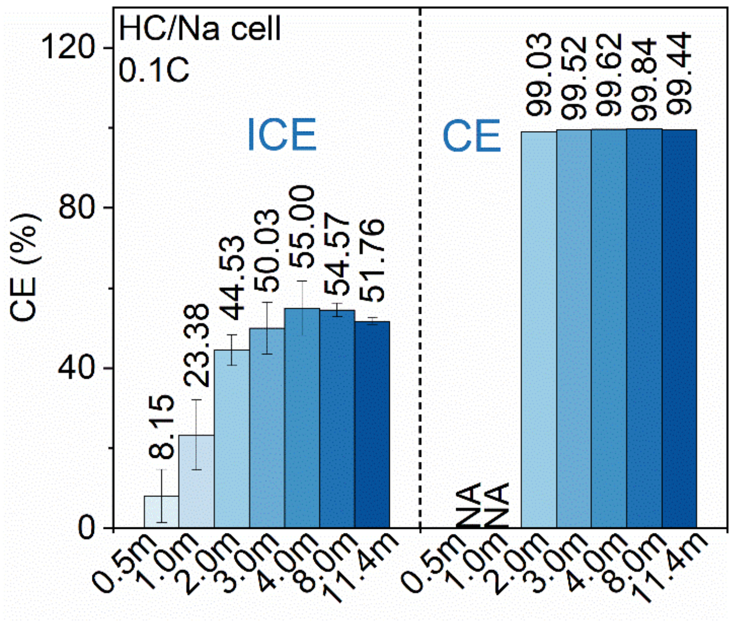
- Less free solvent in bulk with concentration increase.
- More anions enter Na solvation as concentration increase.

Results: salt concentration consideration

- Na/HC cell.



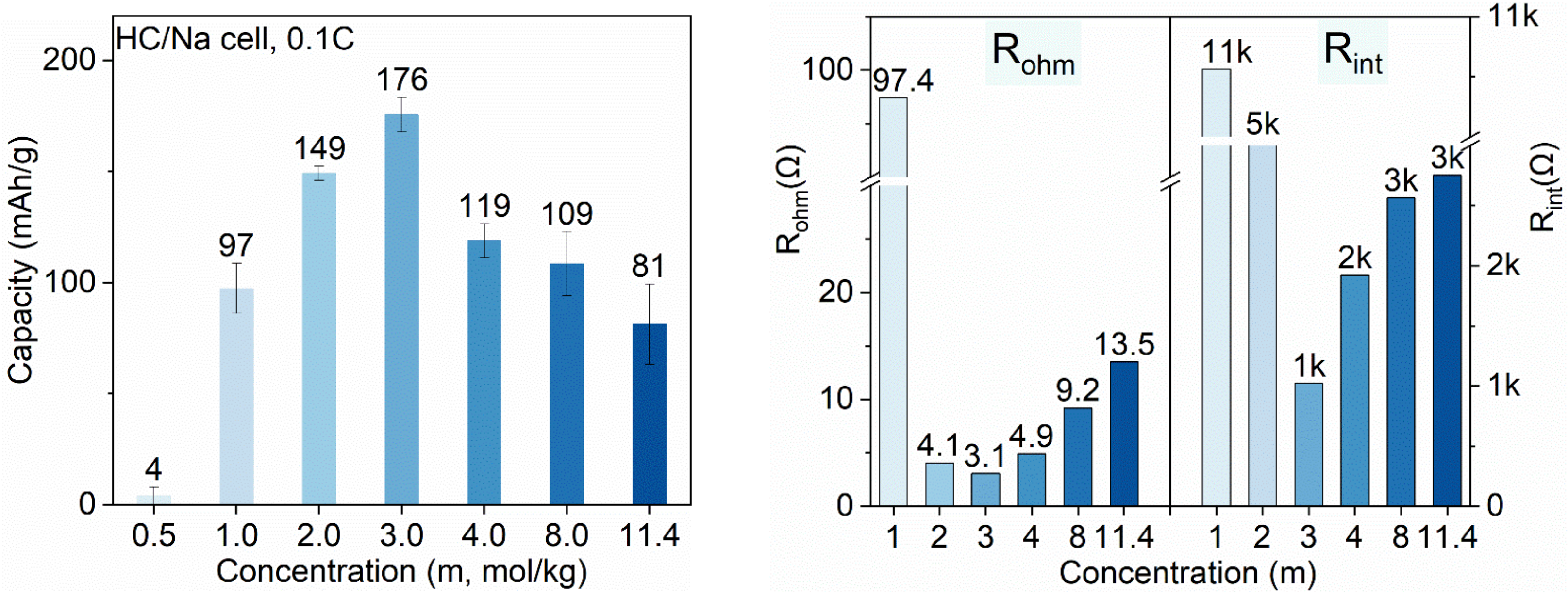




- 3m electrolyte shows the highest capacity.
- After SEI formation, 3m electrolyte shows comparable CE to SOA electrolyte.

Results: salt concentration consideration

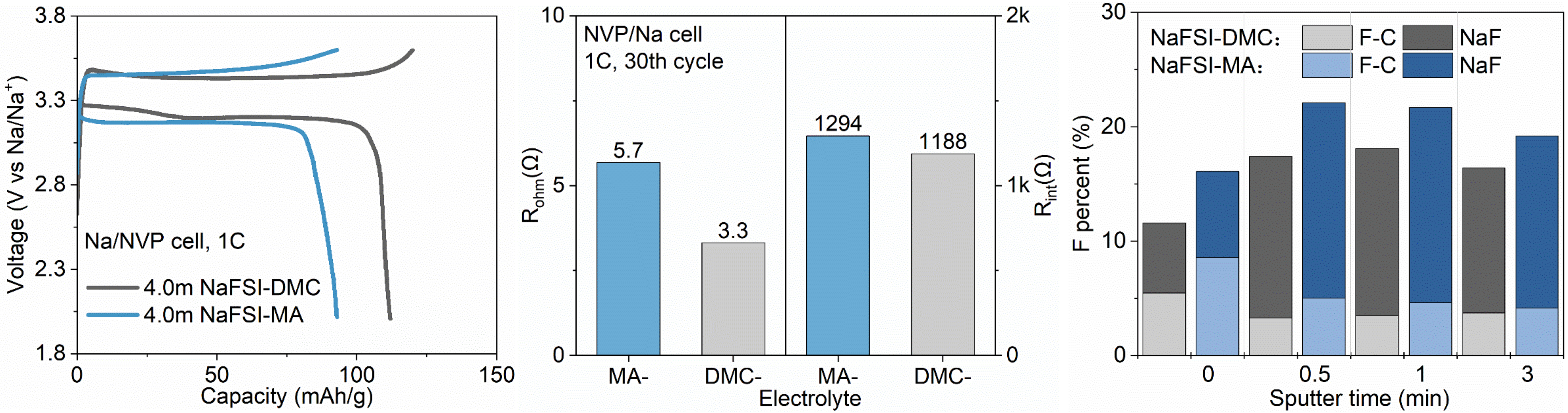
➢ Na/HC cell. EIS



- Both R_{ohm} and R_{int} reach a minimum at 3m.
- Internal resistance: Interfacial resistance is 2-3 orders higher than ohmic resistance
- Capacity inversely correlated with internal resistance

Results: carboxylate vs carbonate

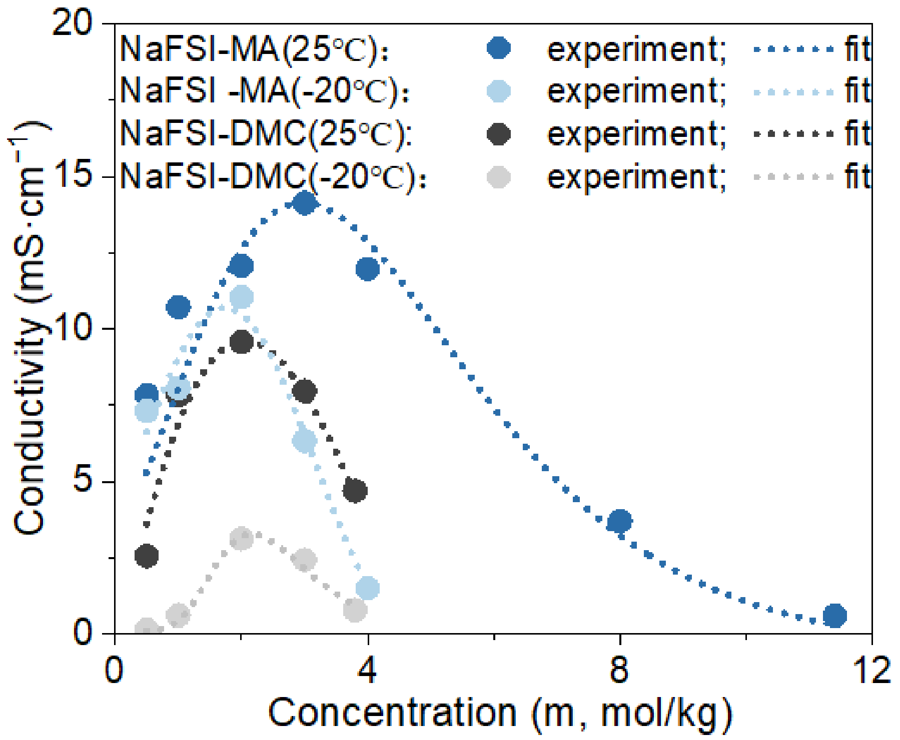
➢ Na/NVP cell

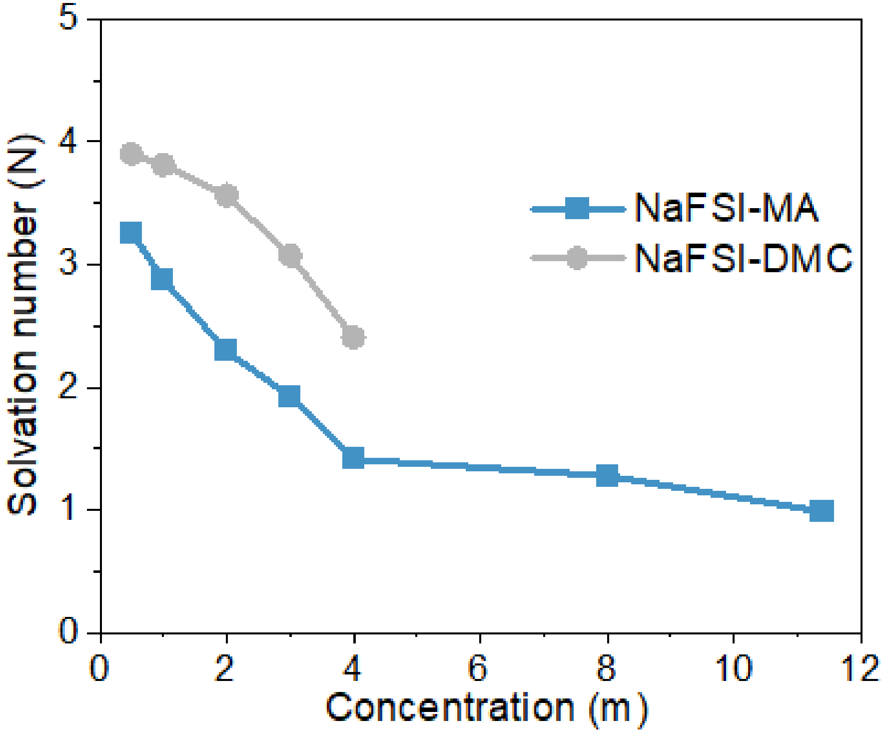


- **Carboxylate** have lower capacity due to the higher interfacial resistance.
- **Carboxylate** have higher NaF in CEI.

Results: carboxylate vs carbonate

➢ low-T performance: Conductivity.

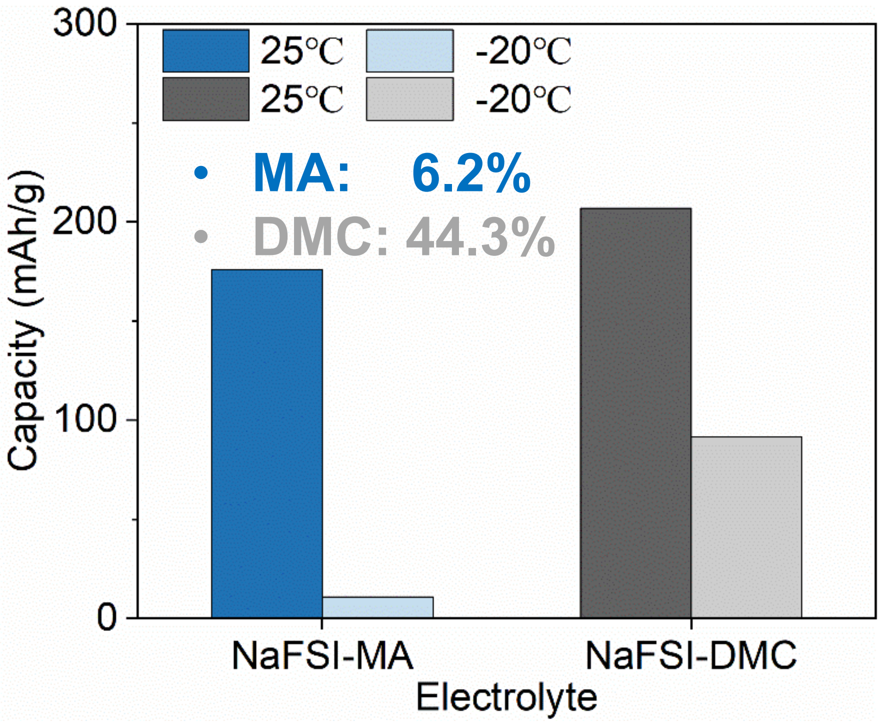


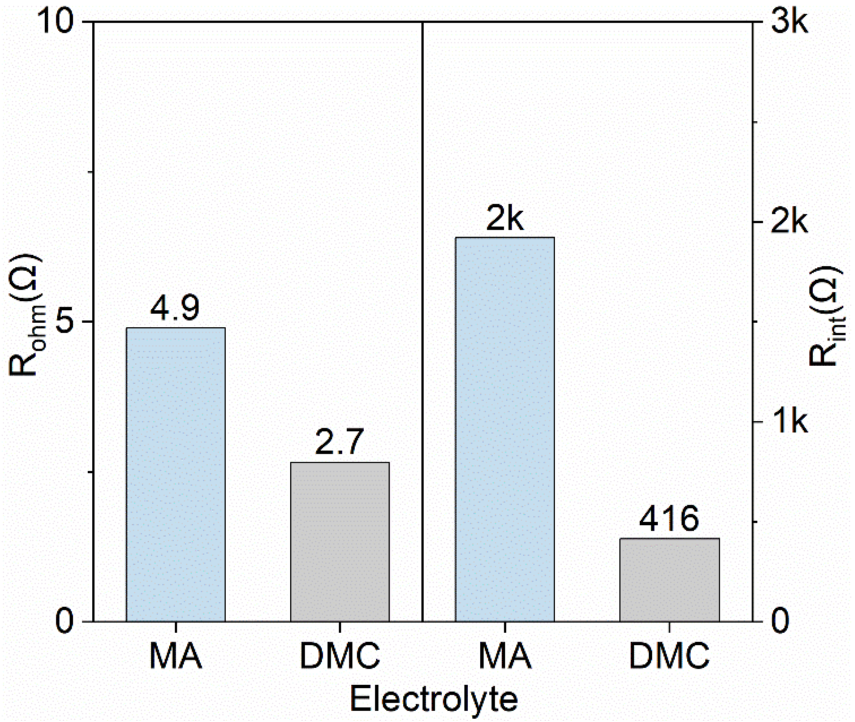


- **Carboxylate:** significantly higher conductivity than **carbonate at low T**
- **Carboxylate:** lower solvation number than **carbonate**

Results: carboxylate vs carbonate

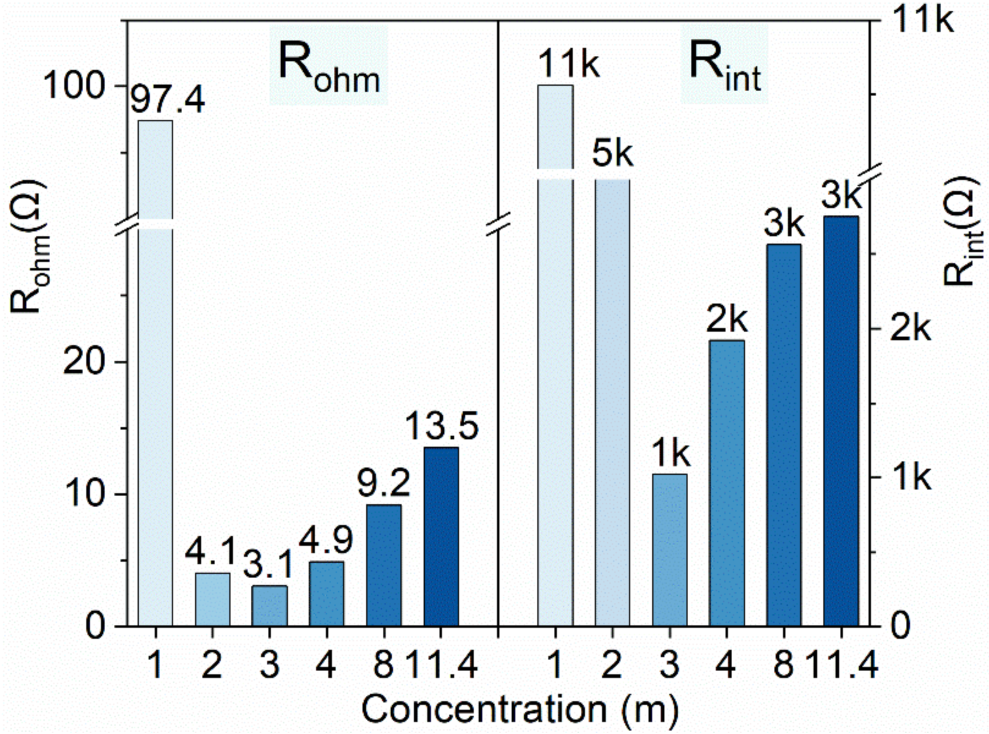
- low-T performance

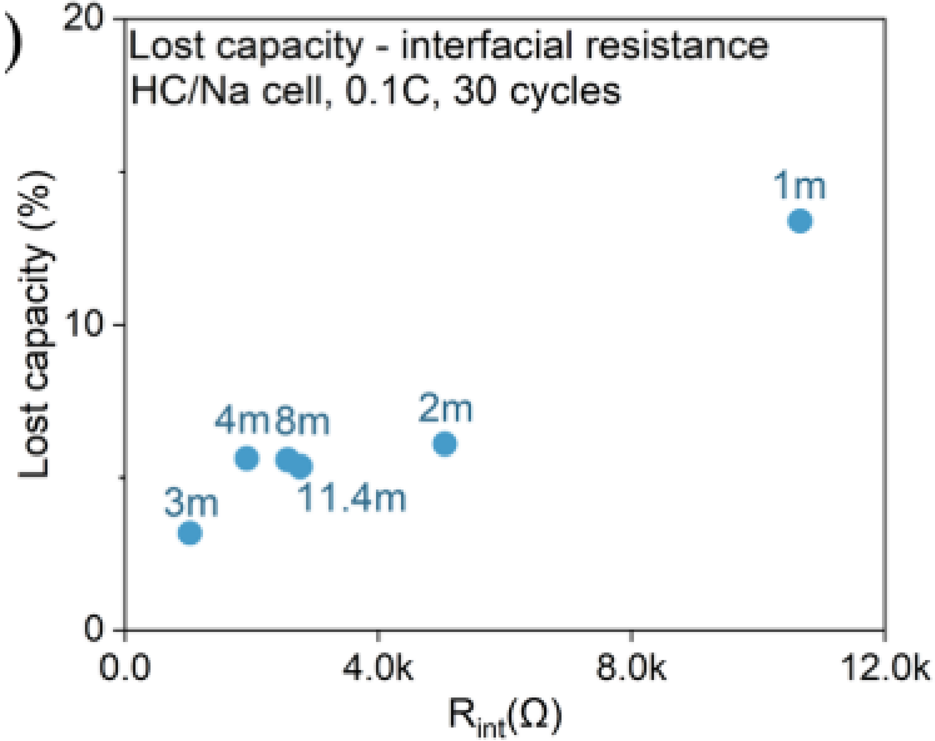




- **Carboxylate** electrolytes show much less capacity in Na/HC cell at low-T due to high interfacial resistance.

Why carboxylates have such high interfacial resistance?





- **Interfacial resistance is proportional to lost capacity due to electrolyte decomposition**
- **Carboxylate molecules are reactive and hard to form stable SEI**

Conclusion

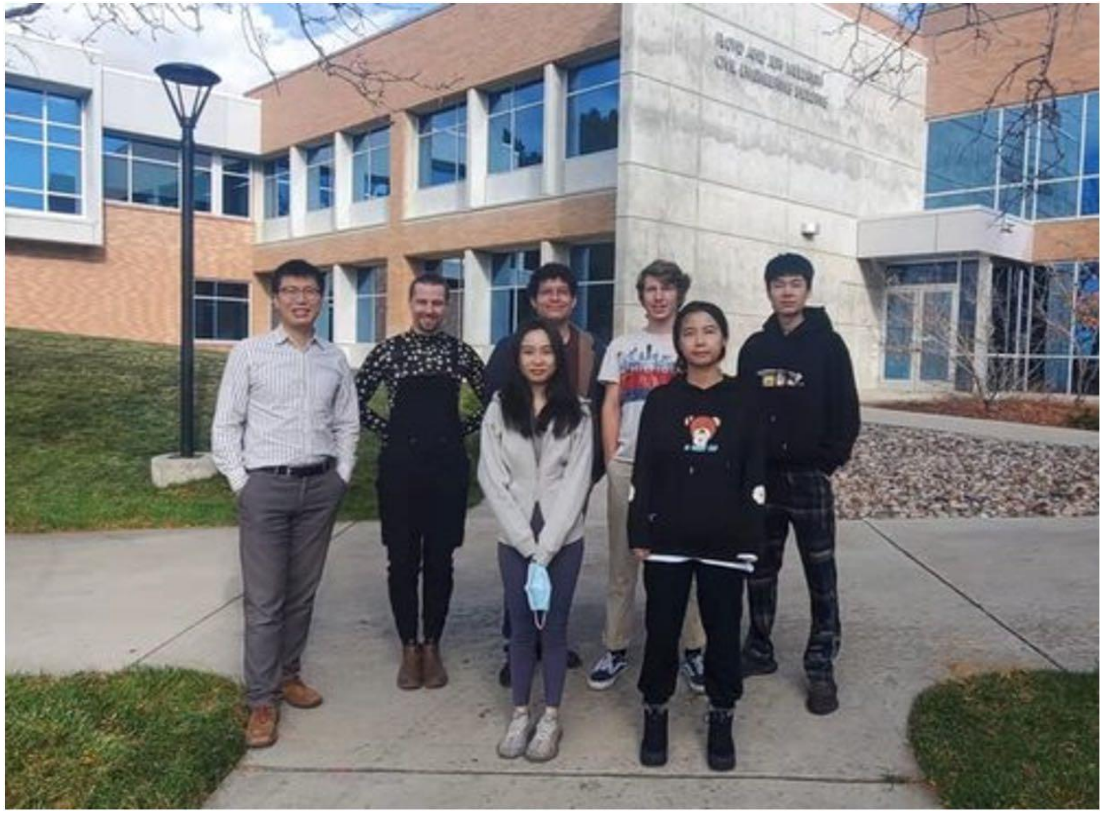
- **Findings:**
  - Carboxylate electrolyte shows better transport properties (conductivity) and comparable CE after SEI formation.
  - Anions help SEI formation in carboxylate electrolytes, and this phenomenon only applies to high-concentration NaFSI salt.
- **Challenge:**
  - carboxylate electrolytes are more reactive than their carbonate counterparts, which leads to low ICE, larger interfacial resistance, and lower capacity.
- **Future:**
  - Engineering co-solvent and additives to form stable SEI.

[1] Y. Qin, S. G. Choi, L. Mason, J. Liu, Z. Li, T. Gao, *Chem. Sci.* **2024**, 9224.

Acknowledgement

We acknowledge University of Utah for Prof. Gao's start-up funding and NSF award no. 2247407.

- Yunan Qin
- Seong Gyu Choi



Multi-scale Electrochemical Engineering Lab (ME2 Lab)

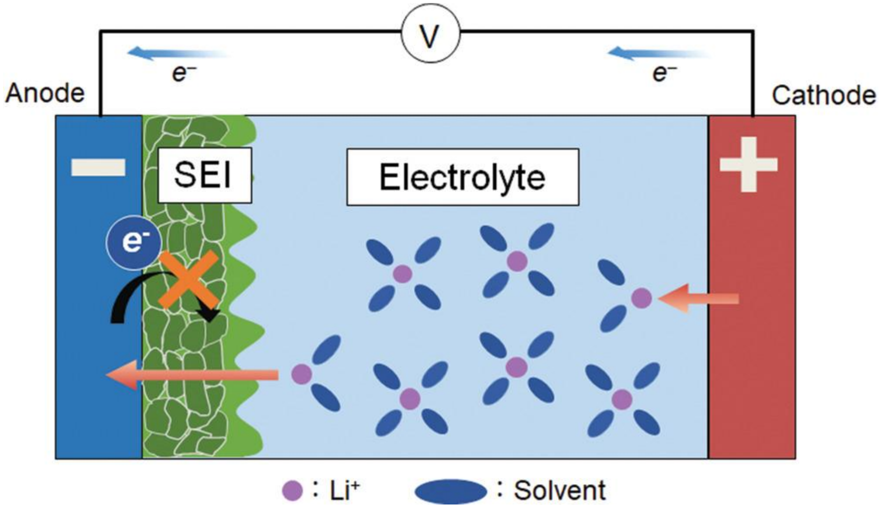
Group website:
https://www.taogao-echem.net/

Questions?

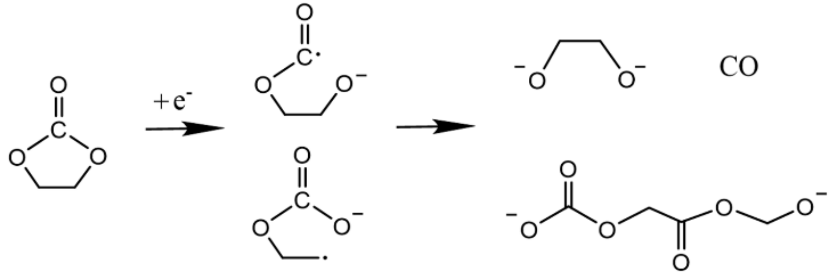
November 7, 2023

Why do few studies use carboxylates?

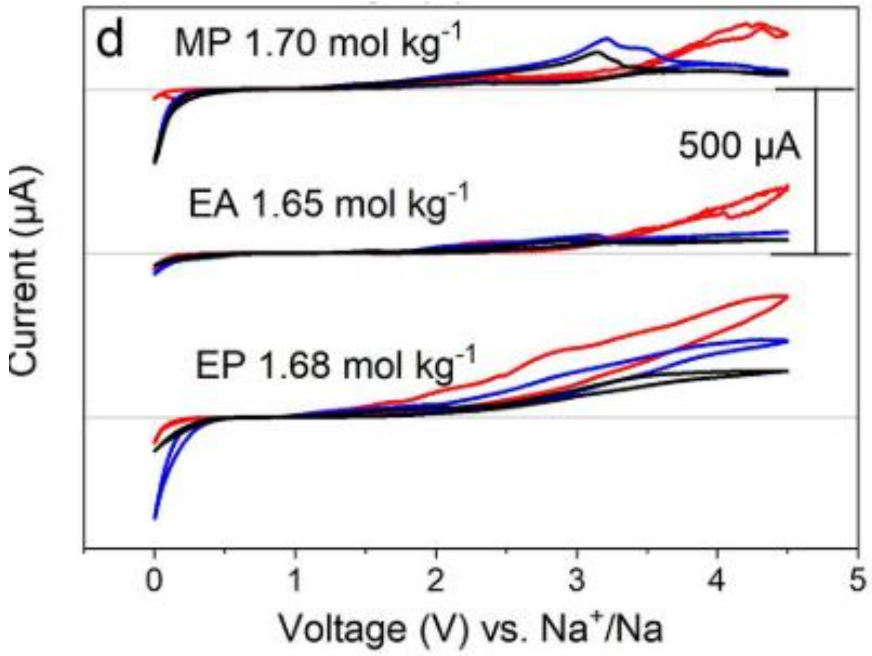
- Solid Electrolyte Interphase (SEI) .



1M $NaPF_6$-EC/EMC(1:1 by vol):



- No stable interphase in carboxylate.



Carboxylate is highly reactive and unable to form stable SEI.

Adv. Mater. **2021**, *33* (37), 1–15.   *Batter. Supercaps* **2021**, *4* (5), 791–814.

Background: low-T electrolytes

➢ Challenge for low-T electrolyte

- Freezing at low-T.
- Slowing down mass transport.
- Slowing down interfacial reaction

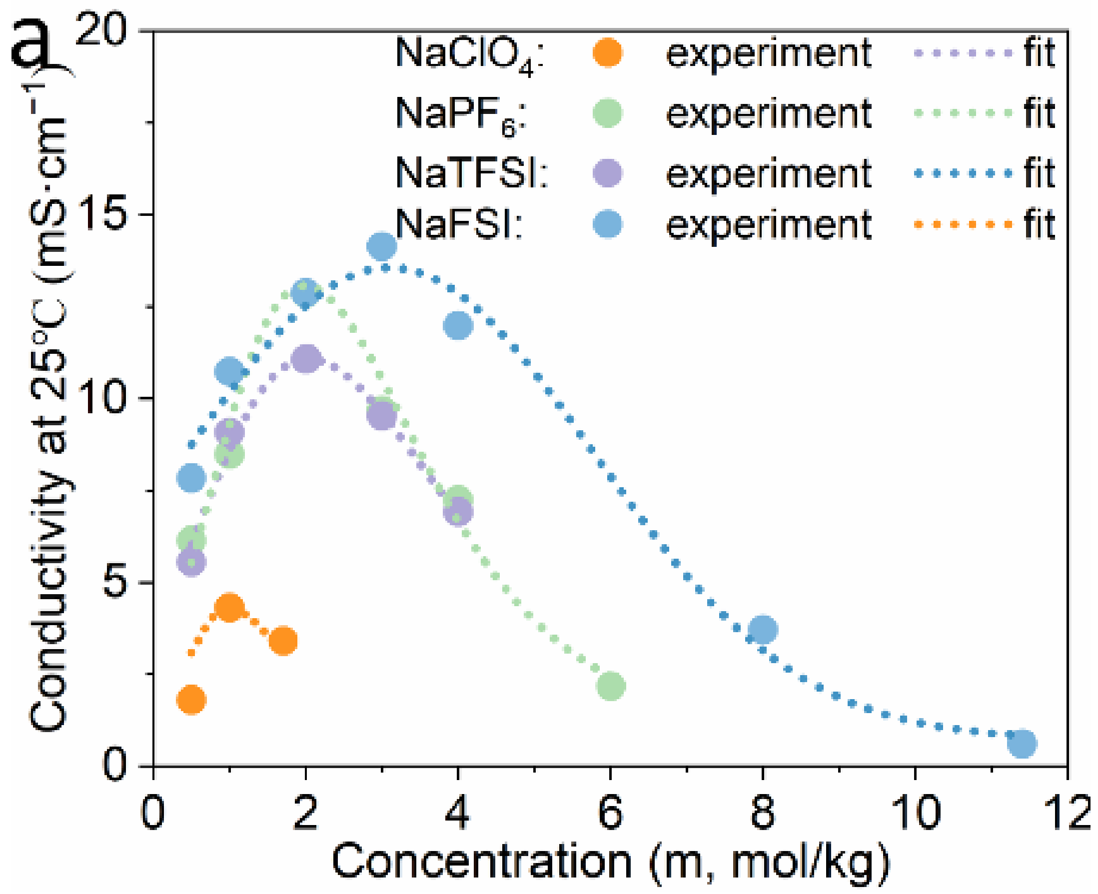
➢ Requirement

- Low melting point.
- High dielectric constant and low viscosity.
- Other requirements: chemical stability, low-cost, et.

Physicochemical properties of common carbonate solvents used in SIBs

Solvent	MP(℃)	BP(℃)	Viscosity (cP)	Dielectric constant
EC	36.4	248	1.9 (at 40°C)	90.1 (at 40°C)
PC	-48.8	242	2.48	64.9
DMC	4.6	91	0.589	3.087
EMC	-14.5	107.5	0.65	2.4/2.9/3.5
DEC	-43	126	0.75	2.805

➢ Conductivity.

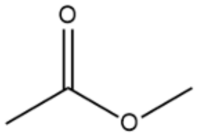
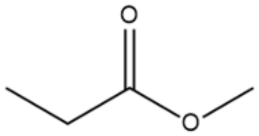
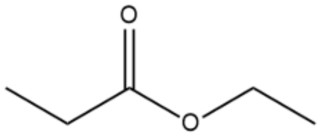
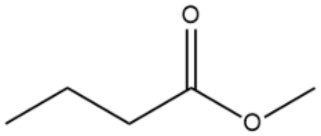
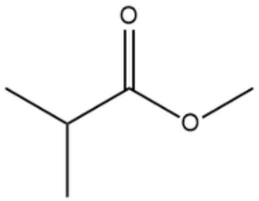
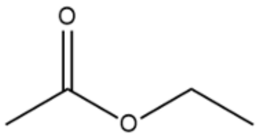
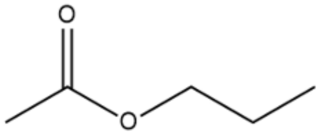
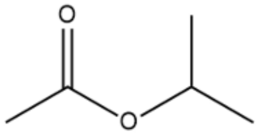
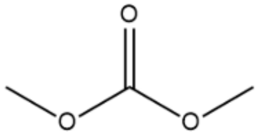
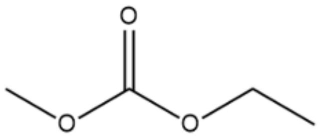
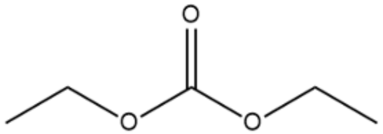


Results: carboxylate vs carbonate

THE UNIVERSITY OF UTAH

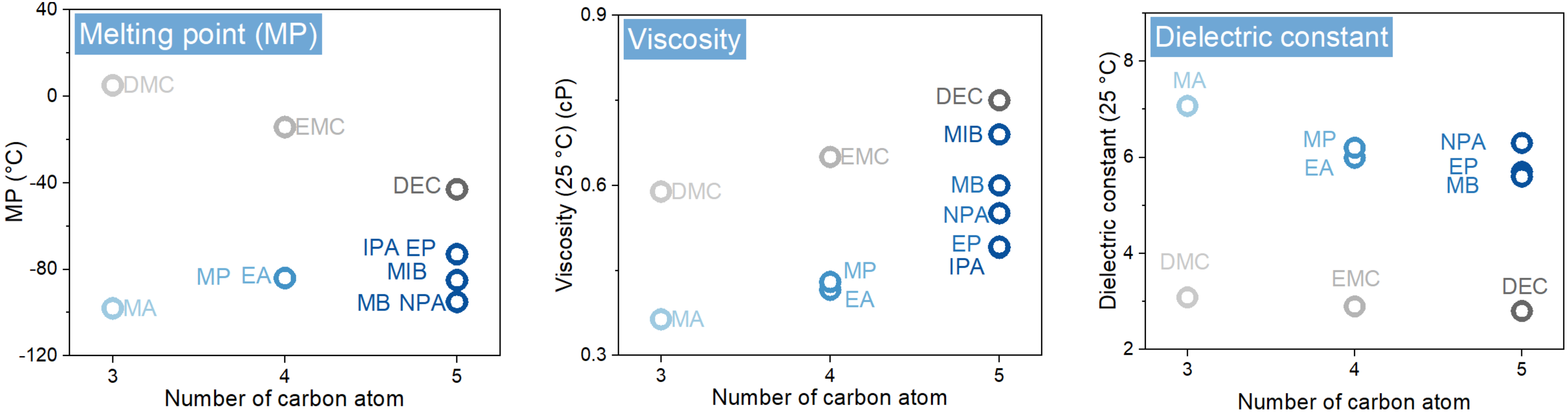
- Structure.

Comparation of chemical structure between carbonates and carboxylate

	3-carbon	4-carbon	5-carbon		
Carboxylate	 methyl acetate, MA	 methyl propionate, MP	 ethyl propionate, EP	 methyl butyrate, MB	 methyl isobutyrate, MIB
		 ethyl acetate, EA	 n-propyl acetate, NPA	 i-propyl acetate, IPA	
Carbonate	 dimethyl carbonate, DMC	 ethyl methyl carbonate, EMC	 diethyl carbonate, DEC		

Results: carboxylate vs carbonate

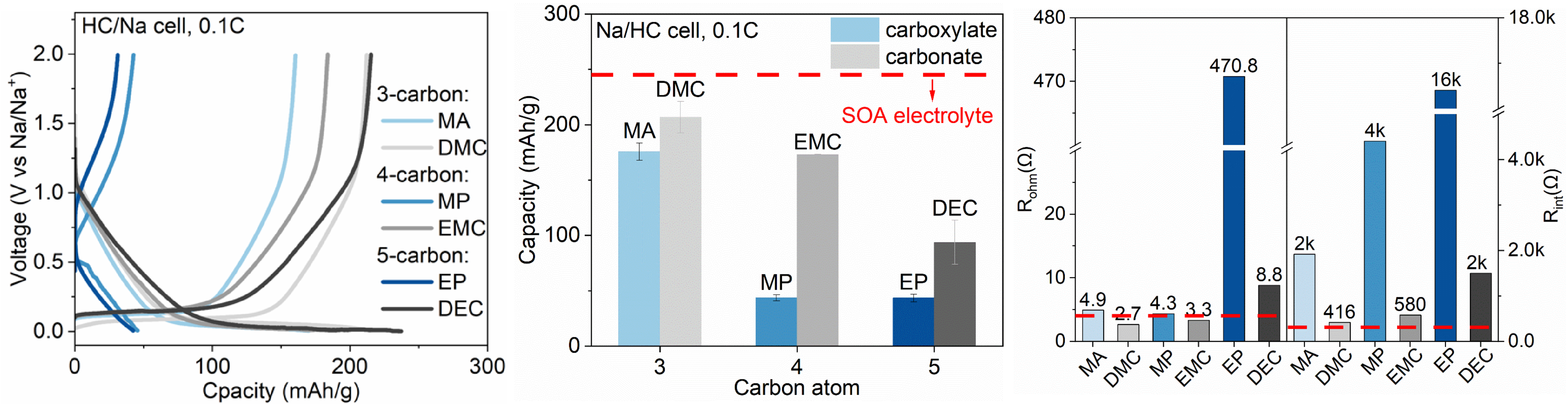
➢ Physical properties.



- **Carboxylate** have lower MP and viscosity, and higher dielectric constant.
- **MA** and **DMC** were selected as a representative of carboxylate and carbonate, respectively.

Results: carboxylate vs carbonate

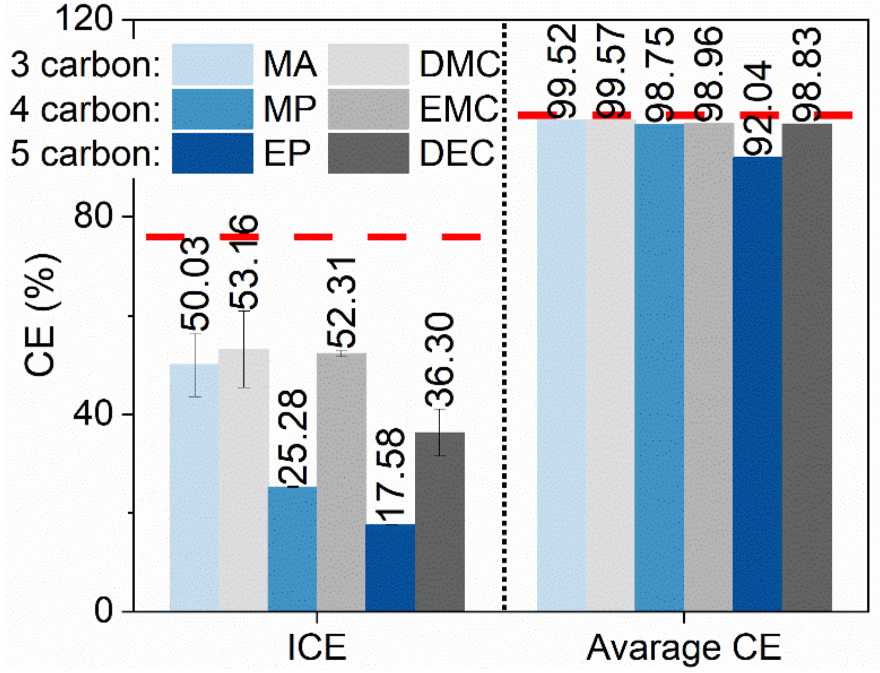
➢ Na/HC cell

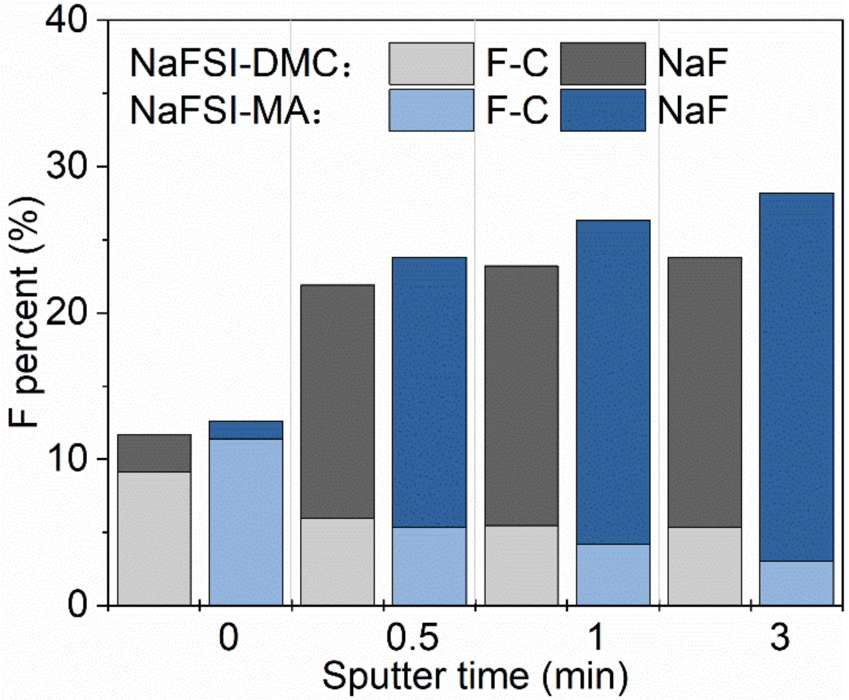


- **Carboxylate** have lower capacity due to the higher interfacial resistance.

Results: carboxylate vs carbonate

➢ Na/HC cell





- **Carboxylate** have lower ICE.
- **Carboxylate** have higher NaF in SEI.