Electronic Supplementary Material (ESI) for Chemical Society Reviews.

Combining Theories and Experiments to Understand the Sodium Nucleation Behavior Towards Safe Sodium Metal Batteries

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Table S1. The reported strategies that cannot be compatible between Na and Li metal battery systems.[1-9]

Strategy	method	Na	Li
Electrolyte components	Nitrate salt + Polysulfides in ether (1, 2)	No	Yes
Artificial SEI	Graphene films (3-5)	Yes	No
3D matrix	Pristine 3D Cu foam (6, 7)	No	Yes
	Porous Al (8)	Yes	No
Surface energy	Au film (9)		Better
	Ti foil (9)	Better	

Table S2. Reported works on constructing artificial SEI to suppress Na dendrite growth.[10-19]

Work	Artificial SEI	Method	Electrolyte	Current density (mA cm^{-2})	Capacity (mAh cm^{-2})	Overpotential
10	Al_2O_3	Atomic layer deposition (ALD)	Ether	3	1	~20 mV over 500 h
11	PVDF	Blade-coating method	Ether	5	2	~150 mV over 550 h
12	NaF-rich with Na_3Sb alloy	React with SbF_3 in the solution	Ether	5	5	~50 mV over 800 h
13	Multi-layer Graphene film	Chemical vapor deposition and dry-transfer	Carbonate	2	3	~300 mV over 300 h
14	Inorganic−organic MLD-alucone	Molecular layer deposition	Carbonate	3	1	~200-400 mV over 120 h
15	NaF	React with BF_3 in the solution	Carbonate	2	1	~250 mV over 90 h
16	NaBr	React with 1-Bromopropane in the solution	Carbonate	1	1	~150 mV over 250 h
17	Na_3PS_4	React with P_4S_{16} in the solution	Carbonate	1	3	~300 mV over 250 h
18	NaI	React with 1-Iodopropane in the solution	Carbonate With FEC	0.25	0.75	~50 mV over 500 h
19	Al_2O_3	ALD	Carbonate	0.5	1	~200 mV over 120 h

Table S3. The difference of nucleation and growth behavior between Li and Na metal.[20-24]

Influence factor	**Differences in nucleation and growth behavior between Na and Li**
Electrolyte	1) The de-solvation energy of Na^+ is lower than Li^+ in organic electrolytes,[20] hence the charge transfer overpotential (η_t) in Na nucleation is lower than Li, ultimately affecting overall nucleation overpotential. 2) In carbonate electrolytes, it is more challenging to form uniform SEI on Na metals due to higher solubility of Na-SEI compared to Li counterpart.[21] In this case, Na^+ distribution is more inhomogeneous, making it difficult to achieve uniform Na nucleation sites compared to Li system.
SEI	The SEI components and structures can significantly impact ion transport and diffusion pathways and therefore affect the nucleation behavior. For example, ion transport barriers for halogenated SEI salt layers in Na system are lower than that in Li system, leading to a lower diffusion overpotential (η_d) for Na nucleation compared to Li.[22]
Wettability	A good wettability leads to a smaller contact angle and lower nucleation overpotential for uniform nucleation and deposition. Li and Na can have different wettability behaviors on the same substrate due to the differences in chemical reactivity. Examples: the wettability of molten Na on a bare titanium (Ti) foil is much better than molten Li; in contrast, gold (Au) film coated substrate exhibits a better wettability with Li than Na.[23]
Dendrite	The formation of Li dendrites is commonly described by standard nucleation theory that needle-like Li dendrites grow without branches, or moss-like dendrites that show 3D omnidirectional growth. Meanwhile, needle-like Na dendrite is described by the granular nucleation of Na at a pit on a Na-metal and the continuous linear growth of Na.[24]

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