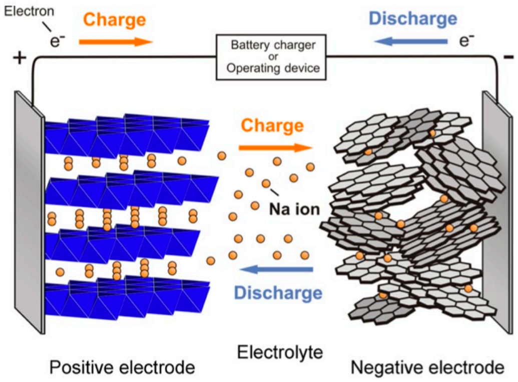
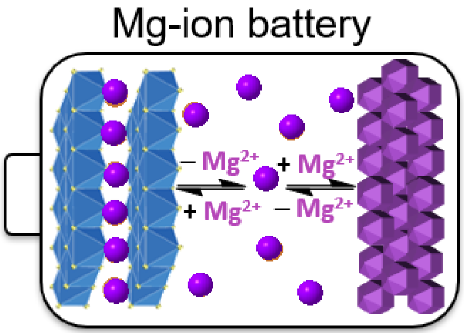
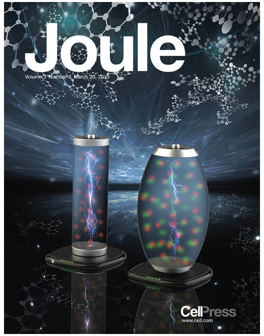
Substitutes for Li-ion Batteries in Motive Applications:
Sodium and Magnesium-based Batteries







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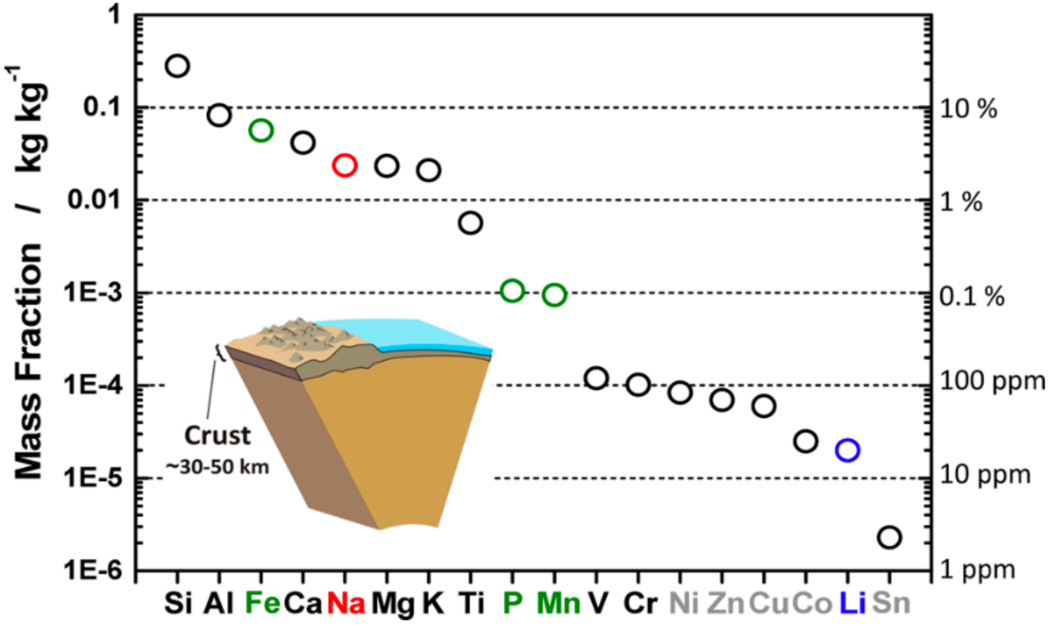
NAATBatt INTERNATIONAL

UNIVERSITY of HOUSTON

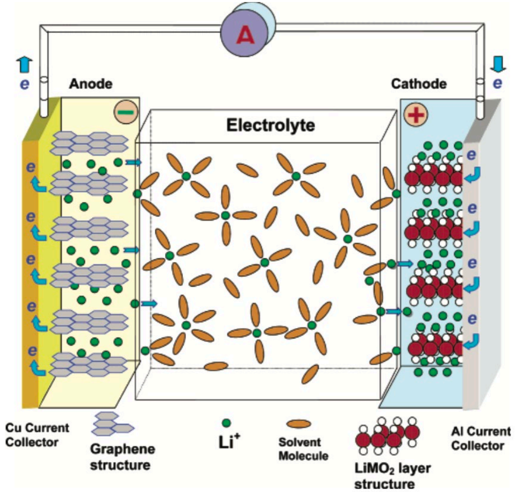
Why Need a Substitute - Materials Availability and Cost



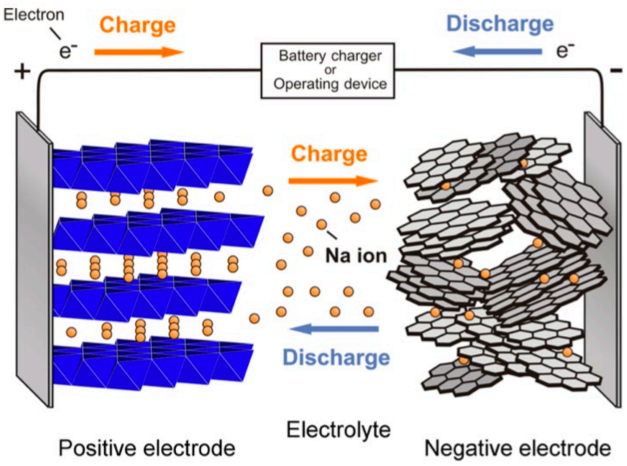
Johnson, C. S. et al. Adv. Funct. Mater. 2013, 23, 947.

- Li resource is 20 ppm in the Earth's crust and is unevenly distributed.
- Na, Mg, Ca, and Al are top 10 most abundant elements.
- NIBs remove the need to use Cu foils because no Al-Na alloy formation.
- Mg foils can be used directly as anode.

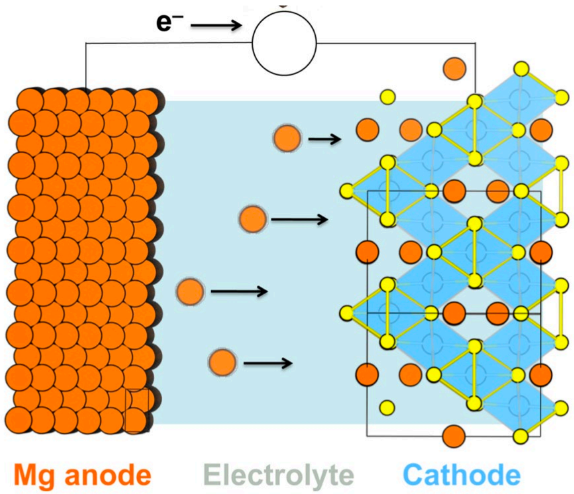
Li-ion vs. Na-ion vs. Mg-ion Batteries



Li-ion battery



Na-ion battery



Mg-ion battery

- ➢ Na^+ and Mg^{2+} serve as charge carriers in a “rocking-chair” mechanism, meaning no net change of electrolyte composition.
- ➢ Knowledge of LIBs and manufacturing knowhows can be adopted for Na and Mg battery chemistries.
- ➢ NIBs and MIBs are better viewed as alternative solutions for large-scale energy storage rather than a direct competitor of LIBs for motive applications.

Physical Properties of Charge Carriers

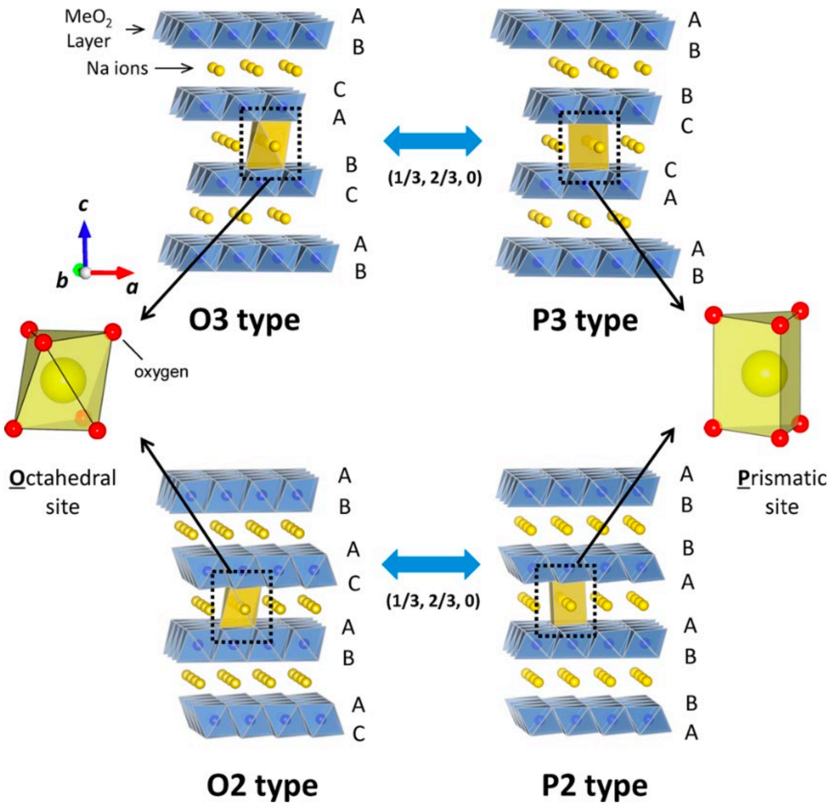
Table 1. Comparison of the Physical Properties of Li^+, Na^+, K^+, and Other Candidates as Charge Carriers for Rechargeable Batteries

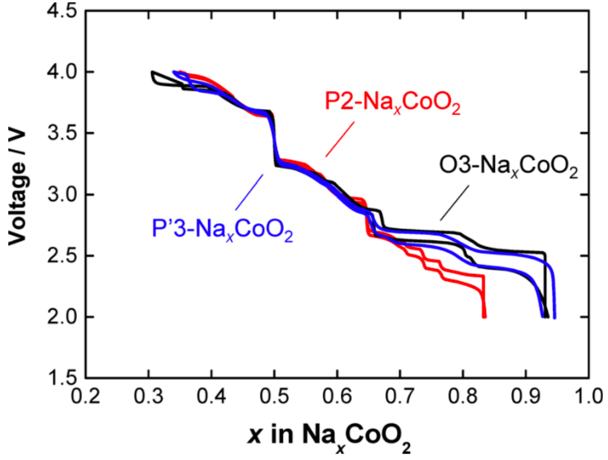
	Li^+	Na^+	K^+	Mg^{2+}	Al^{3+}	Ca^{2+}
relative atomic mass	6.94	23.00	39.10	24.31	26.58	40.08
mass-to-charge ratio	6.94	23.00	39.10	12.16	8.86	20.04
theoretical gravimetric capacity of $ACoO_2$[a] (mAh g^{-1})	274	235	206	260	268	242
theoretical volumetric capacity of $ACoO_2$[a] (mAh cm^{-3})	1378	1193	906			
E^0 (A/A^+_{aq}) (V vs SHE)	−3.04	−2.71	−2.93	−2.4	−1.7	−2.9
E^0 (A/A^+_{PC}) V vs Li/Li^+_{PC}[14]	0	0.23	−0.09			
Shannon's ionic radii (Å)[27]	0.76	1.02	1.38	0.72	0.54	1.06
Stokes radii in water (Å)[28]	2.38	1.84	1.25	3.47	4.39	3.10
Stokes radii in PC (Å)[29]	4.8	4.6	3.6			
limiting molar ionic conductivity in PC (S cm^2 mol^{-1})[29]	8.3	9.1	15.2			
desolvation energy in PC (kJ mol^{-1})[30]	215.8	158.2	119.2	569.4		
melting point (°C)	180.5	97.8	63.4	650	660	842

[a]Theoretical capacities of $ACoO_2$ with the multivalent ions are estimated based on $Mg_{0.5}CoO_2$, $Al_{1/3}CoO_2$, and $Ca_{0.5}CoO_2$.

Komaba, S. et al. Chem. Rev. 2020, ASAP.

Cathodes of NIBs

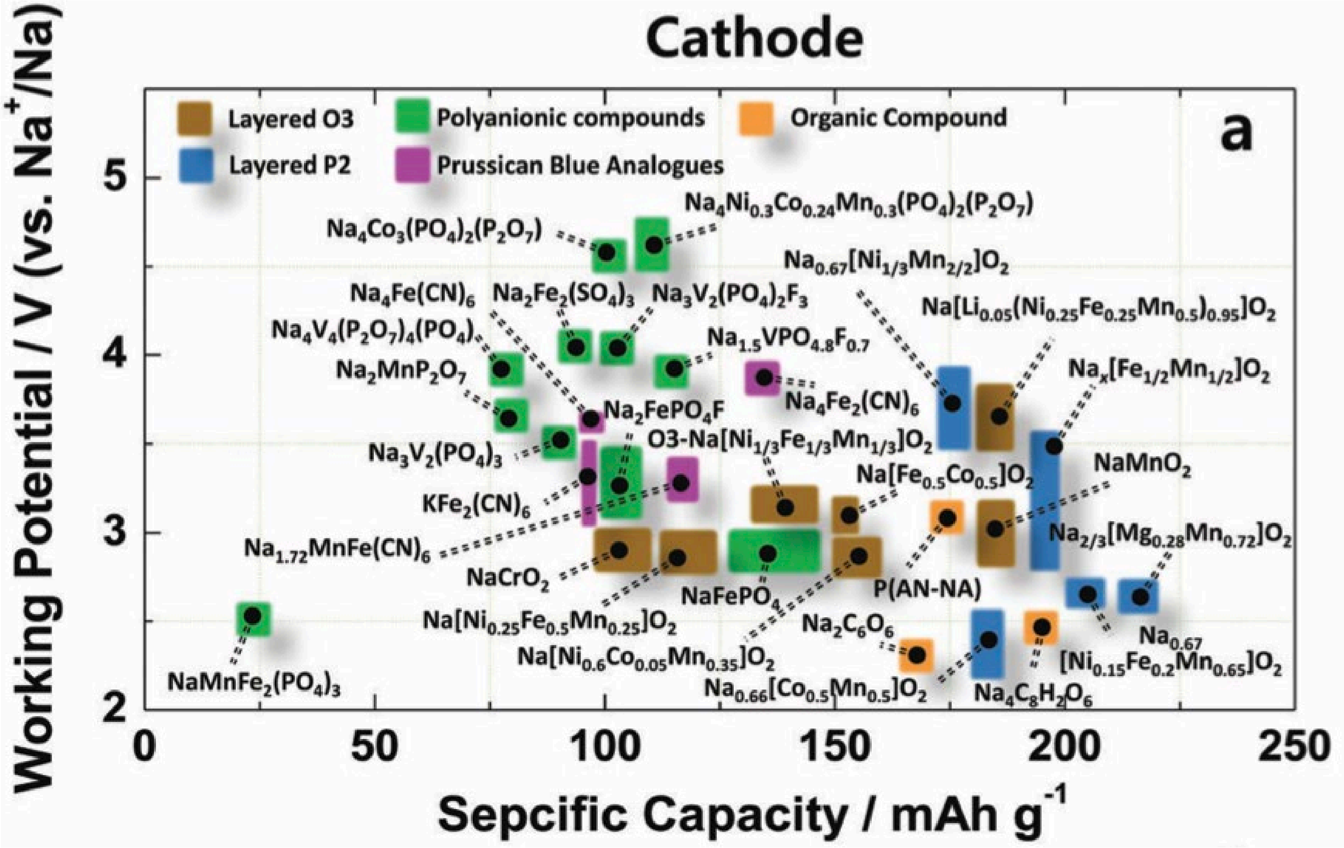




- O3-type (Octahedral site) vs P2-type (Prismatic site) layered oxide
- Na-extraction induces phase transitions: O3->P3, P2->O2.

Komaba, S. et al. Chem. Rev. 2014, 14, 11636.

Cathodes of NIBs



Sun, Y-K. et al. Chem. Soc. Rev. 2017, 46, 3529.

Anodes of NIBs

Na+ insertion into non-graphitic carbon (hard carbon)

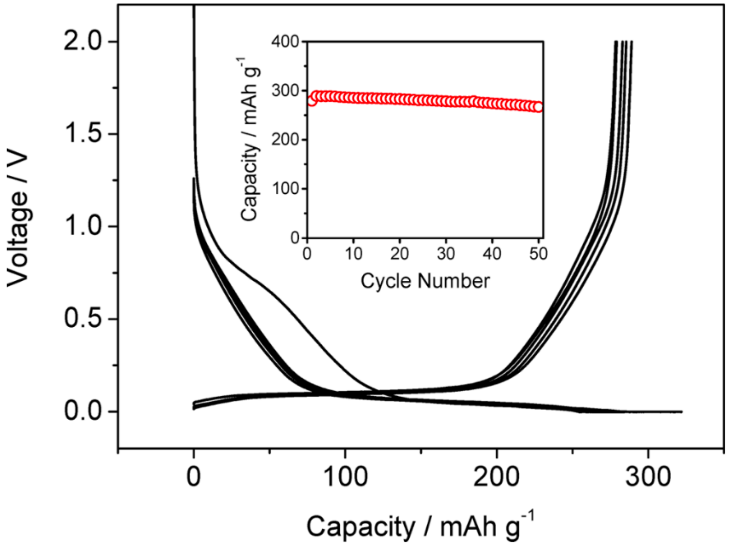
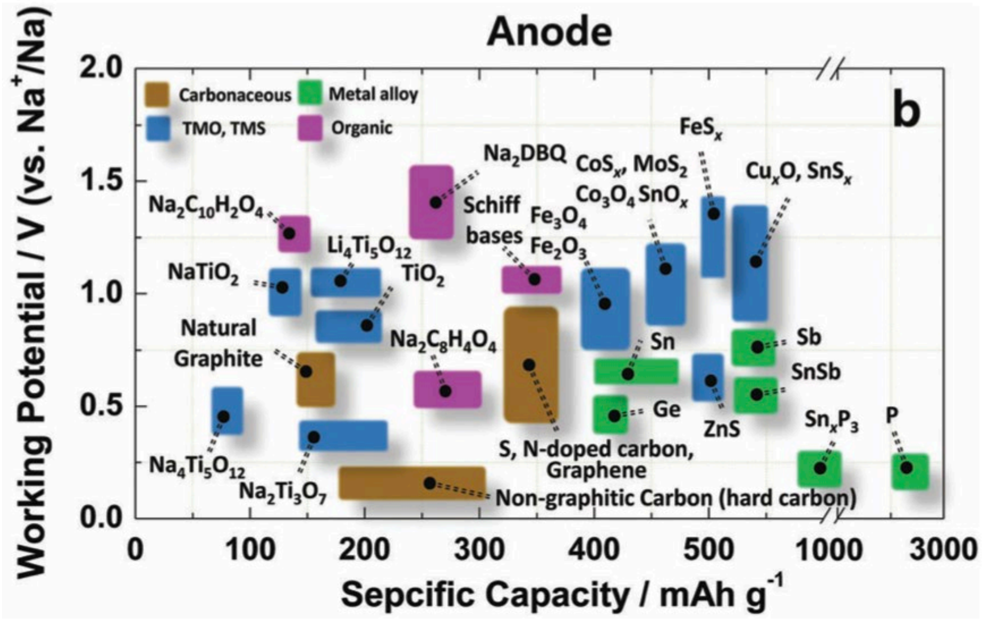


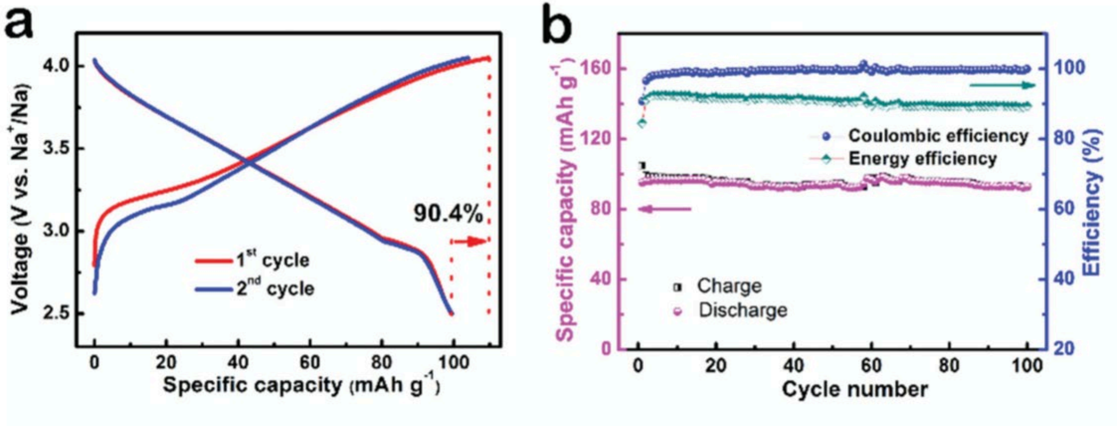
Figure 27. Charge/discharge curves of hard-carbon electrodes, derived from sucrose carbonized at 1300 °C, at a rate of 25 mA g^{-1} in 1 mol dm^{-3} $NaClO_4$ dissolved in PC:FEC (98:2 in vol %), and its capacity retention is also shown in the inset. Reprinted with permission from

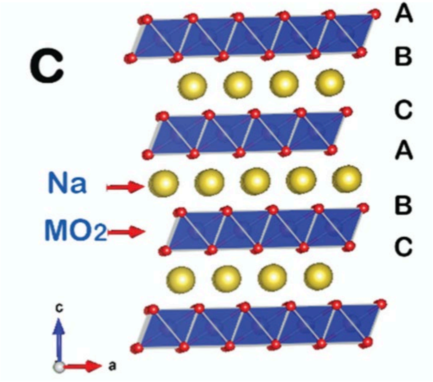
Komaba, S. et al. Chem. Rev. 2014, 14, 11636.



Sun, Y-K. et al. Chem. Soc. Rev. 2017, 46, 3529.

NIB Full Cells

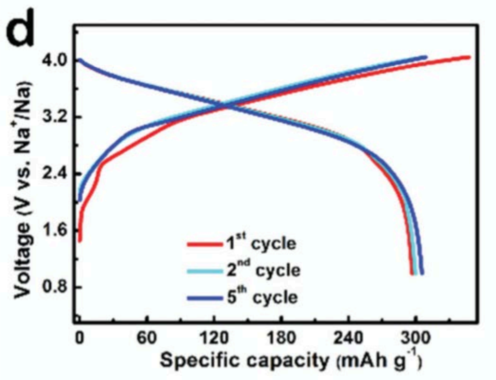


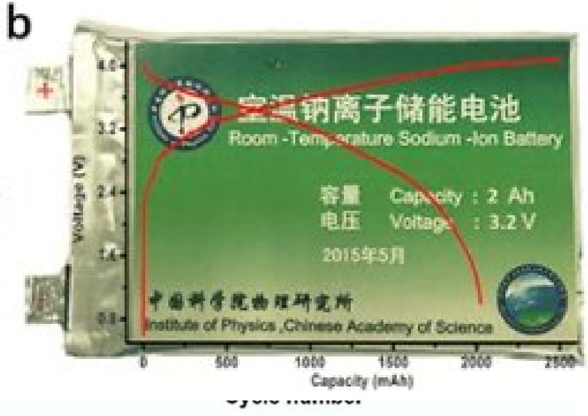


$O3\text{-}Na_{0.9}[Cu_{0.22}Fe_{0.30}Mn_{0.48}]O_2$

Y.S.Hu (IOP CAS) Adv. Mater., 2015, 27

Anthracite carbon anode



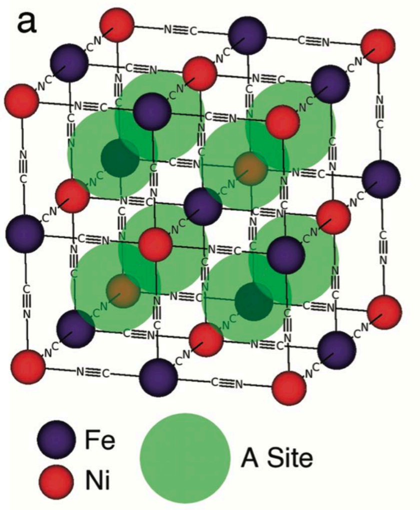


135 Wh/kg, >2000 cycles, $100/kWh

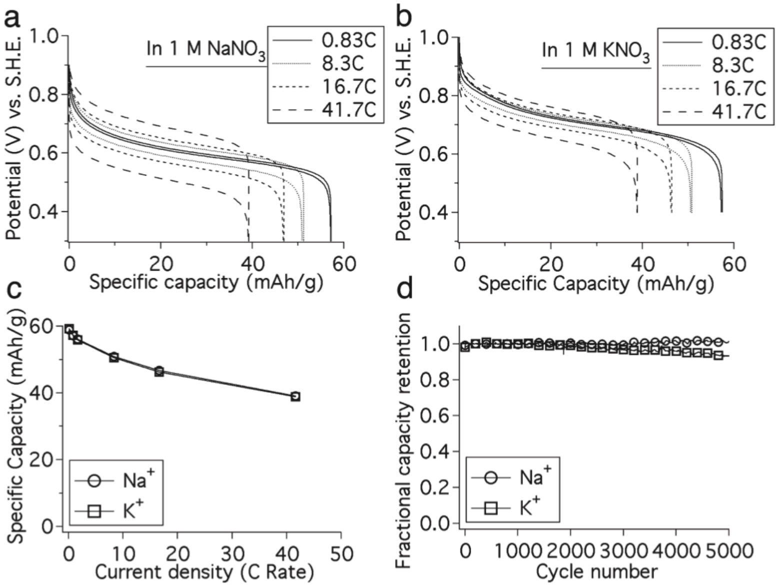
30 kW/100kWh

中科海钠 HiNa BATTERY

Aqueous NIBs



Prussian Blue Analog
Based electrode

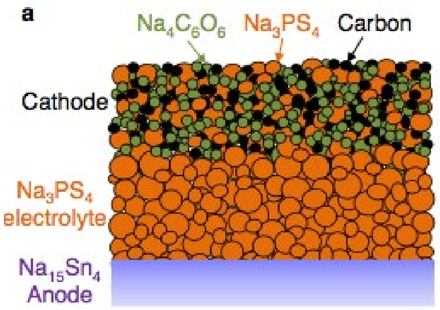


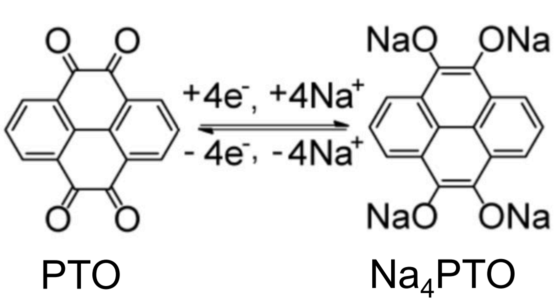
Aqueous electrolyte increases safety but reduces energy density

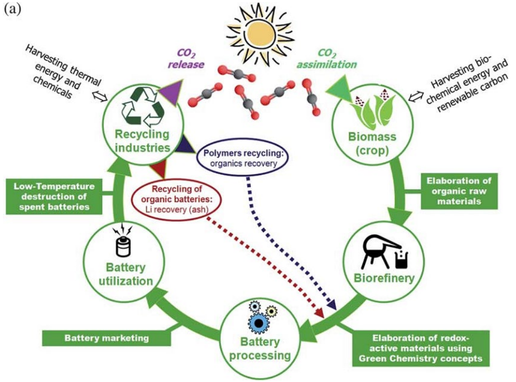
Natron Energy
Energy Storage Innovations

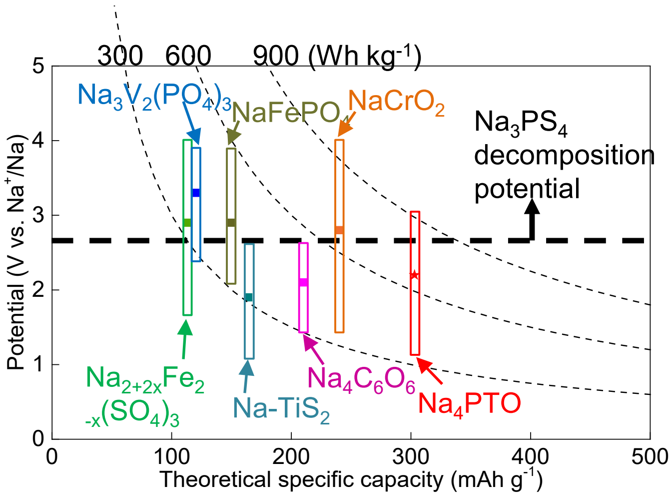
Cui Y. *et al.* Nano Lett. 2011, 11, 5421–5425

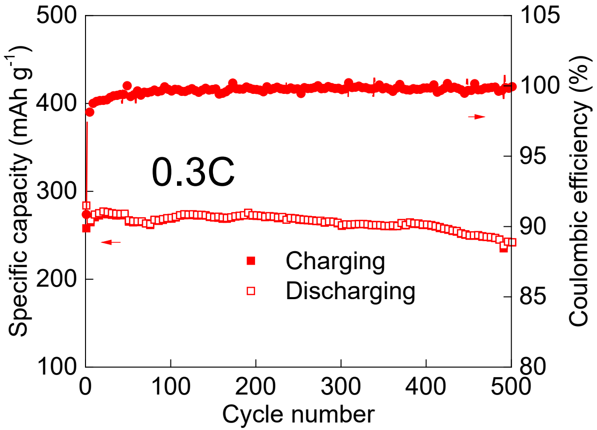
First All-solid-state NIB using Organic Electrode Materials

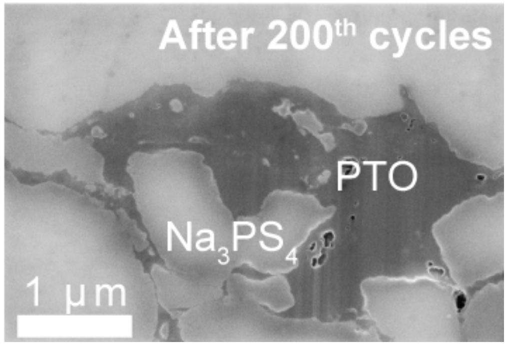








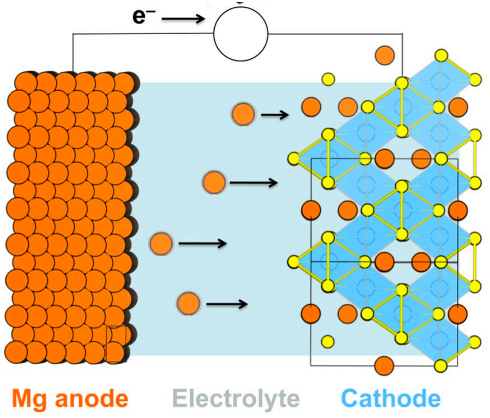


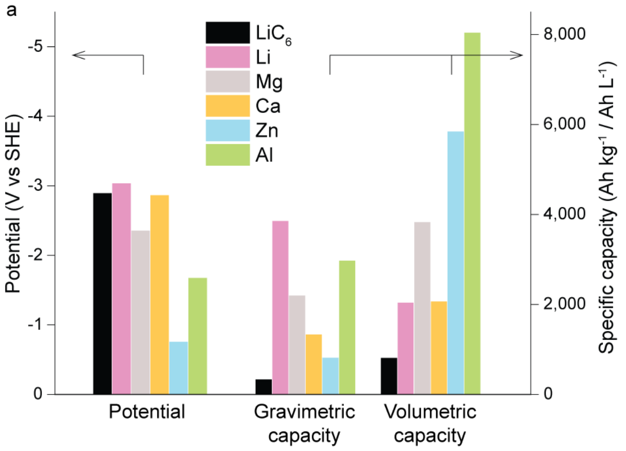


No crack at interface

Yao *et al*, *Joule*, **2019**, *DOI: 10.1016/j.joule.2019.03.017*

MV battery – A Less Mature Technology



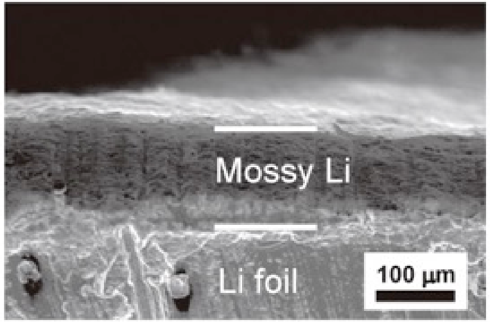


- A common assessment simply looks at the anode side. Metal thickness for 5 mAh cm^{-2}:

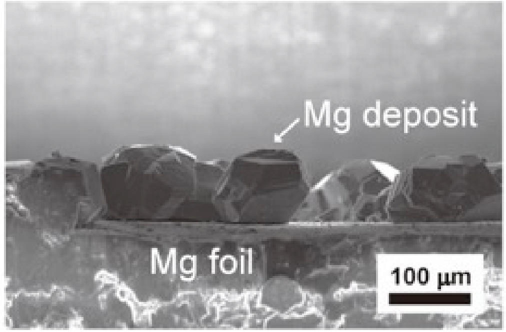
Li	**24 um**
Mg	**13 um**
Ca	**24 um**
Zn	**8 um**
Al	**6 um**

- This assessment does not consider less negative redox potential of MV. Also energy density is governed by both anode and cathode.

MV Battery Anode: Dendrite-free Plating



- Mg has been widely reported to show densely packed crystals, in contrast to Li dendrites.
- Mg dendrites are only reported in electrolyte solutions that show poor reversibility.
- The dendritic deposits are characterized by complicated composition instead of being pure Mg.

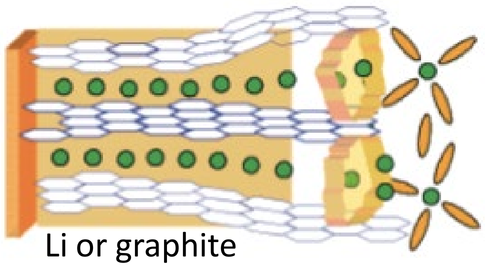


Yoo, Yao, *ACS App. Mat. Int.*, 2015, **7**, 7001.

R. Davidson, S. Banerjee, *ACS Energy Lett.* 2019, 4, 375.

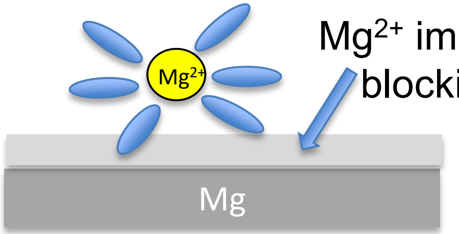
MV Battery: Electrolyte Challenge

Li System – SEI formation

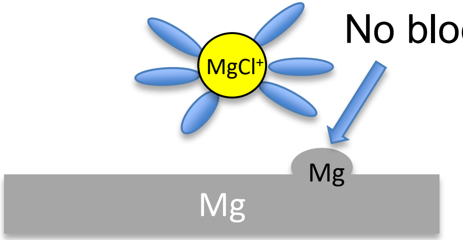


Mg System

Anions: ClO_4^-, $TFSI^-$, BF_4^-
Solvents: carbonate, nitrile, sulfoxide



Corrosive Mg electrolyte



APC 3.3V (Solvent: THF, ether)

$PhMgCl + AlCl_3 \rightarrow [MgCl^+][Ph_xAlCl_{4-x}]$
(x= 0 - 4)

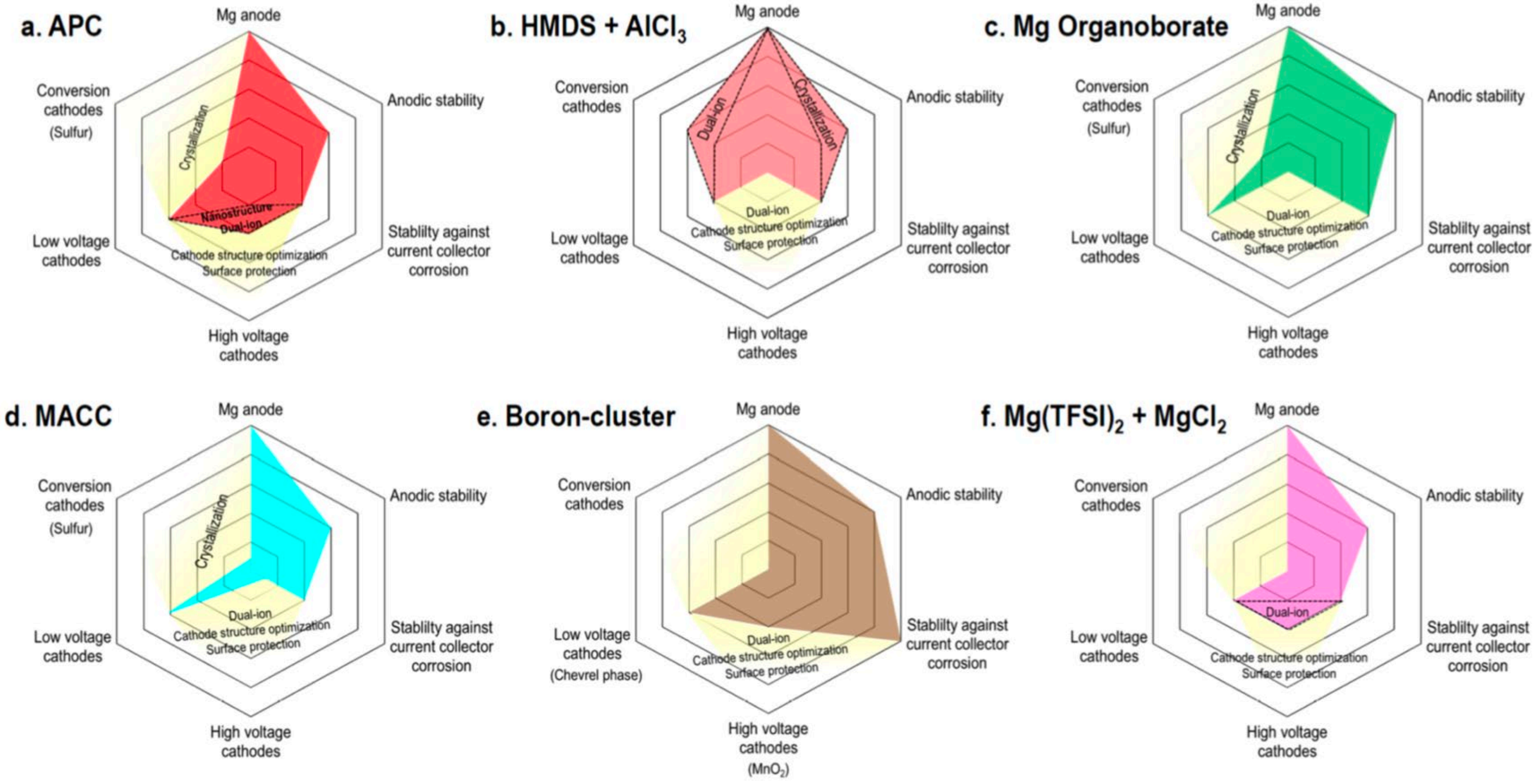
MACC 3.3V

$MgCl_2 + AlCl_3 \rightarrow [MgCl^+][AlCl_4^-]$

Non-corrosive Mg Electrolyte

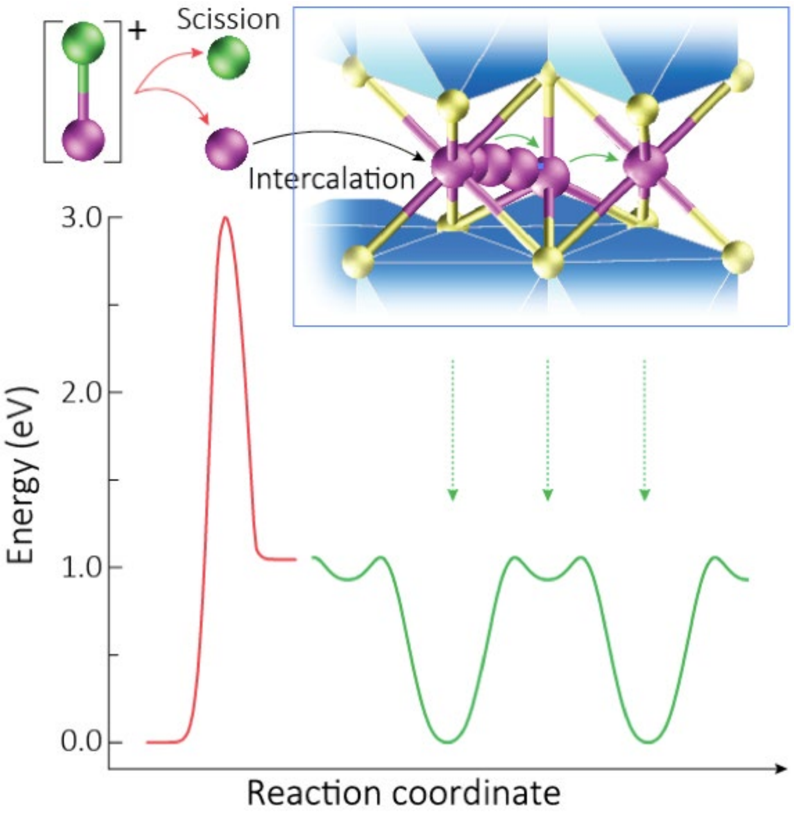
Halogen-free $Mg(TFSI)_2$ and Mg carborane for Mg reversible deposition/stripping

MV Battery: Electrolyte Challenge



Ceder, G. et al. Chem. Rev. 2017, 117, 4287.

MV battery – Cathode Challenges



High energy to break Mg-Cl ion pair:

- Energy cost to break Mg-Cl is calculated to be ~ 3 eV.
- Surface atoms of Mo_6S_8 catalyze interfacial cation dissociation.

Mg^{2+} diffusion is sluggish due to high charge density

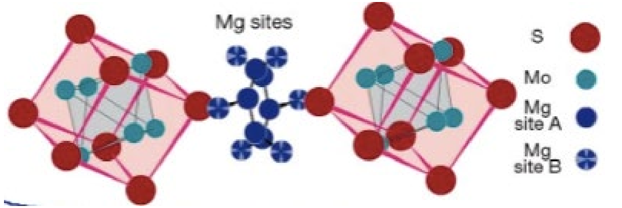
- Ionic radius is similar: 0.68 Å (Li^+) vs 0.74 Å (Mg^{2+})
- Polarization strength: 21.6 (Li^+) vs 47.3 (Mg^{2+}) $10^3/pm^2$

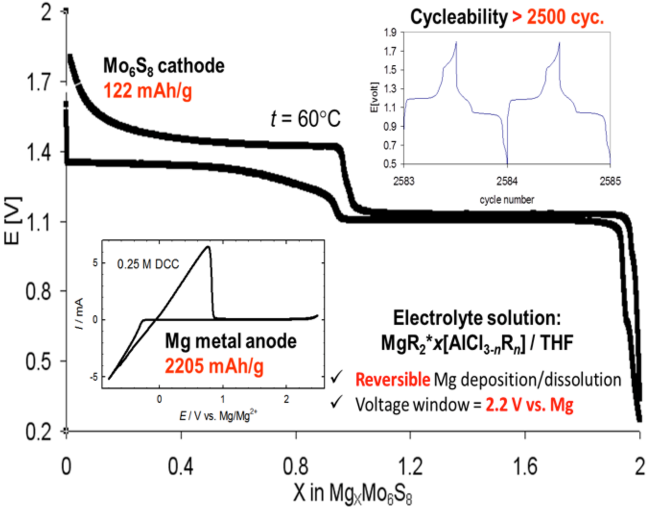
H. D. Yoo, Y. Yao, *Nat. Commun*, 2017, **8**, 339.

L.F. Wan et al. *Chem. Mater*. 27, 5932 (2015)

State-of-art MIBs

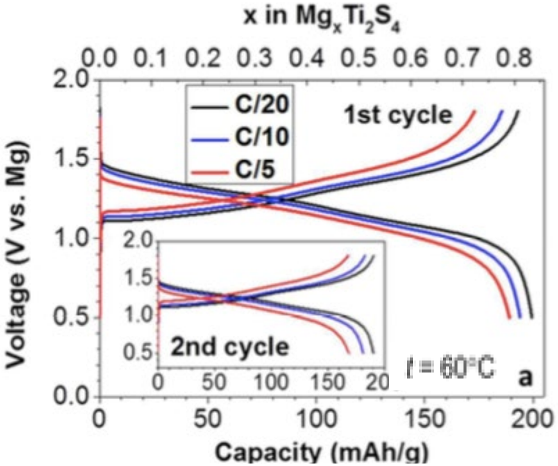
Chevrel Phase



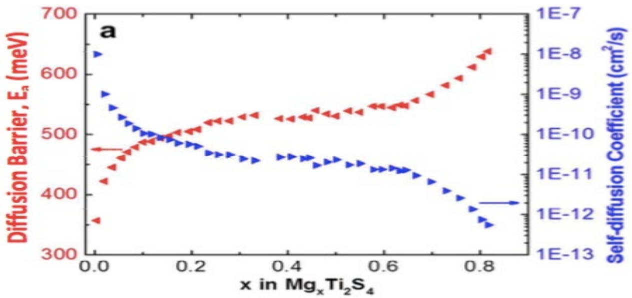


D. Aurbach et al., *Nature*, **407** (2000) 724.

Thiospinel



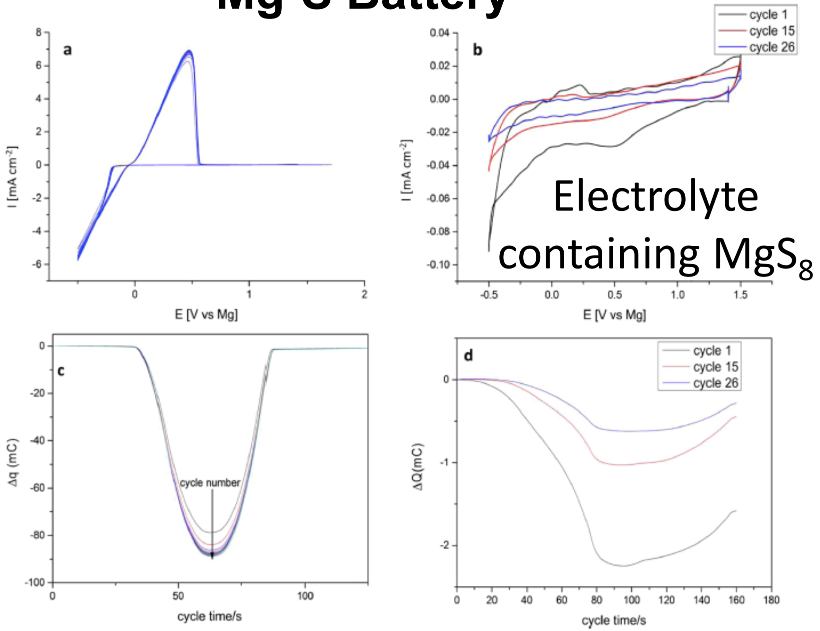
at 60 ℃



L.F. Nazar ***Energy Environ. Sci.***, **9** (2016) 2273

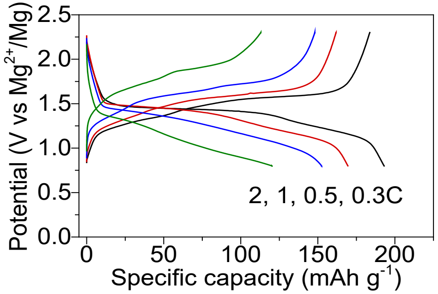
Bypass Solid-state Mg Diffusion

Mg-S Battery

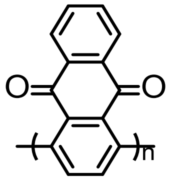


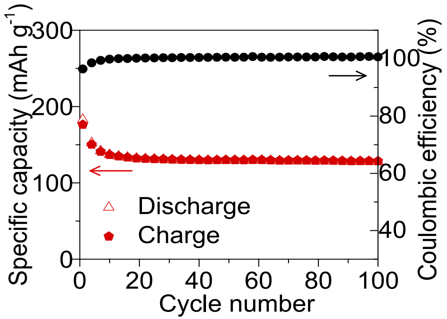
Aurbach, *ACS Applied Mater. Interfaces* 2018, 10, 36910

Mg-Polymer Battery



P14AQ–Mg^{2+}





Y. Yao *et al.*, Joule, 2019, 3, 782.

- Polysulfide migrate to anode may passivate Mg anode.

Organic polymers delivere high specific energy and power.

Conclusions and Outlook

- Na, Mg-ion batteries use much more abundant elements as charge carriers.
- Both non-aqueous and aqueous NIBs are under commercialization development. Cost is expected to be lower than LIBs.
- Mg anodes show dendrite-free plating behavior. MV cathodes remain a major challenge.
- Novel electrolyte solutions with compositions vastly different should be invented without compromising the metallic anode performance.
- NIBs or MIBs may not compete for motive application due to lower energy density, but may substitute LIBs in large-scale energy storage.