

# Materials Design Approaches for High Energy and High Power Density Batteries

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I.

## CO<sub>2</sub>/oxalate cathodes as safe and efficient alternatives in high energy density metal–air type rechargeable batteries

**Objective:** Compare CO<sub>2</sub>/oxalate cathodes ( $2\text{CO}_2 + 2\text{e}^- \rightarrow \text{C}_2\text{O}_4^{2-}$ ) as potential alternatives to O<sub>2</sub>/peroxide ones ( $\text{O}_2 + 2\text{e}^- \rightarrow \text{O}_2^{2-}$ ).

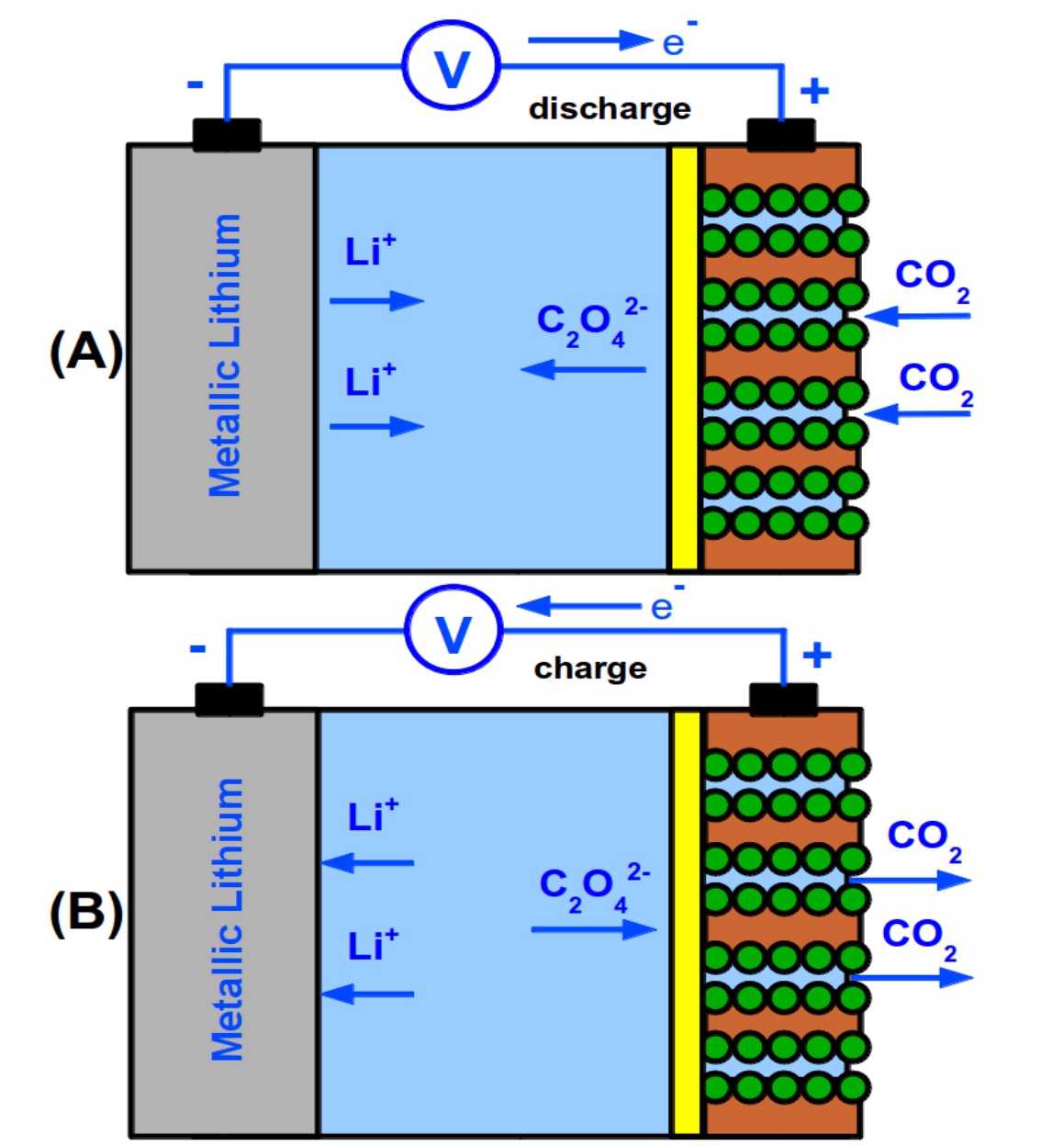
	CO <sub>2</sub>	O <sub>2</sub>
Cathode/discharge:	$2\text{CO}_2 + 2\text{e}^- \rightarrow \text{C}_2\text{O}_4^{2-}$	$\text{O}_2 + 2\text{e}^- \rightarrow \text{O}_2^{2-}$
Voltage: (vs. Li/Li <sup>+</sup> )	~3 V (copper-complex catalyst)	~3 V (without catalyst)
Rechargeability:	Yes (small overpot., at ~3.8V)	Yes (high overpot. at ~4.2V)
Storage tank:	Light (easy to compress)	Heavy (difficult to compress)
Supply from air:	Yes (via CO <sub>2</sub> selective membrane)	Yes (via H <sub>2</sub> O, N <sub>2</sub> and CO <sub>2</sub> filter)
Hybrid battery/supercapacitor (negating mass):	Possible	Likely Not Possible
Tunability of diffusion-speed via CO <sub>2</sub> or O <sub>2</sub> pressure:	Yes (supercritical CO <sub>2</sub> )	None known
Theoretical Specific Energy and Rate Capacity:	High (1577 Wh/kg) (easier to realize)	High (3448 Wh/kg) (difficult to realize)
SAFETY (Robust Design)	THERMALLY STABLE / FIRE-RETARDANT	THERMAL RUNAWAY (EXPLOSION) HAZARD
Opportunity for multifunctionality	Air-conditioning, battery temperature control, CO <sub>2</sub> /oxalate cathode	None known

Table 2 Standard reaction enthalpies ( $\Delta_r H^\ominus$ ) and Gibbs free energies ( $\Delta_r G^\ominus$ ) of energy storage reactions discussed in the present study, as calculated from  $\Delta_r H^\ominus$  and  $\Delta_r H^\ominus$  data of Table 1. Data of the LiCoO<sub>2</sub>-based Li-ion battery are from ref. 21–23

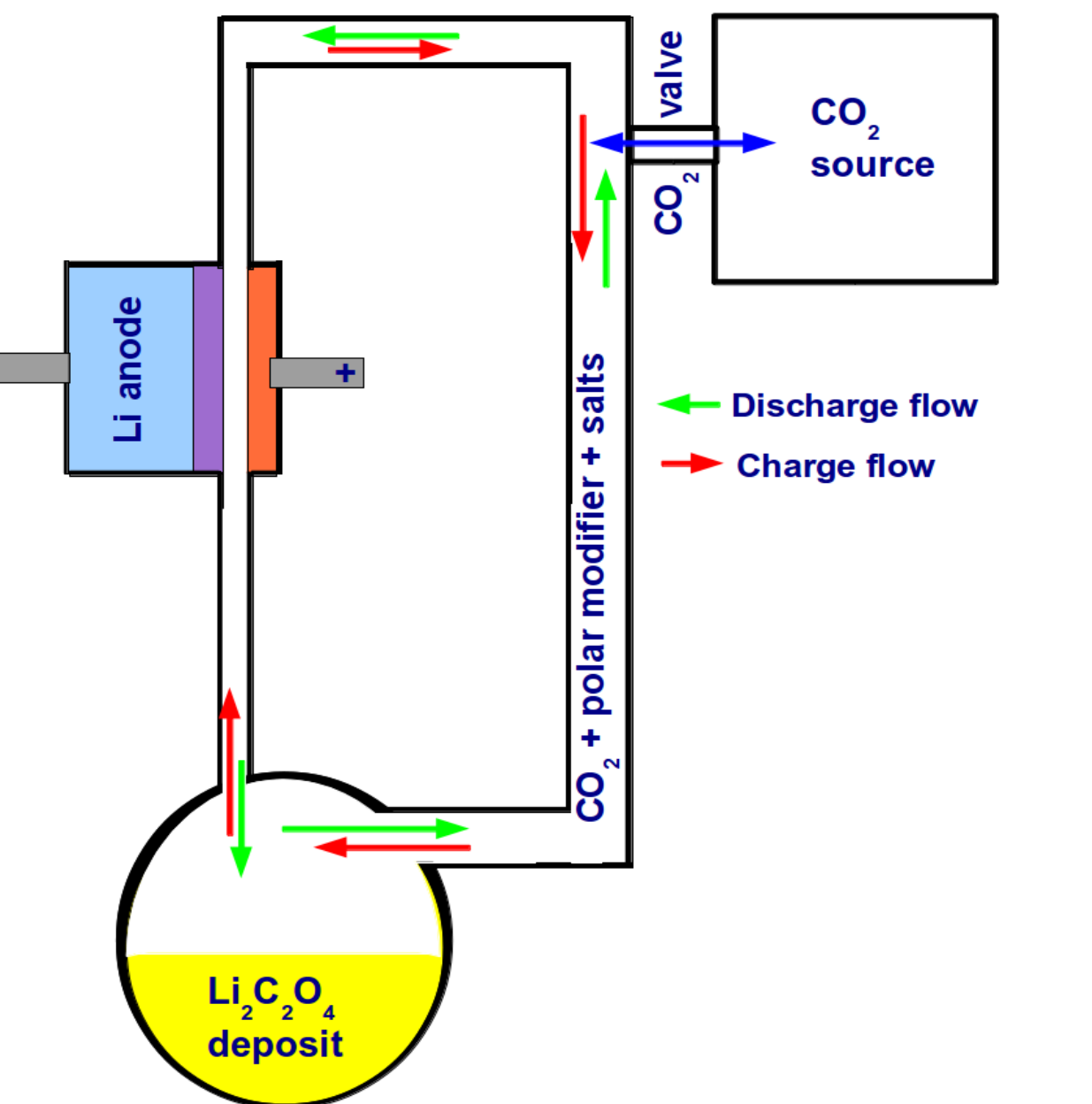
System	Reaction	$\Delta_r H^\ominus$ (kJ mol <sup>-1</sup> )	$\Delta_r G^\ominus$ (kJ mol <sup>-1</sup> )
n-Octane	$\text{C}_8\text{H}_{18}(\text{g}) + 12.5\text{O}_2(\text{g}) \rightarrow 8\text{CO}_2(\text{g}) + 9\text{H}_2\text{O}(\text{g})$	–5116	–5259
Li-ion (LiCoO <sub>2</sub> )	$\text{Li}_x\text{C}_6(\text{s}) + \text{Li}_{1-x}\text{CoO}_2(\text{s}) \rightarrow \text{C}_6(\text{s}) + \text{LiCoO}_2(\text{s})$	—	–213
Li–O <sub>2</sub> /oxide	$2\text{Li}(\text{s}) + 1/2\text{O}_2(\text{g}) \rightarrow \text{Li}_2\text{O}(\text{s})$	–599	–562
Li–O <sub>2</sub> /peroxide	$2\text{Li}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{Li}_2\text{O}_2(\text{s})$	–633	–571
Li–[O <sub>2</sub> + CO <sub>2</sub> ]/carbonate	$2\text{Li}(\text{s}) + \text{CO}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \rightarrow \text{Li}_2\text{CO}_3(\text{s})$	–823	–738
Li–O <sub>2</sub> /oxalate	$2\text{Li}(\text{s}) + 2\text{CO}_2(\text{g}) \rightarrow \text{Li}_2\text{C}_2\text{O}_4(\text{s})$	–590	–579

Table 3 Theoretical gravimetric and volumetric energy ( $\Delta_r H^\ominus$ ) densities and capacities of energy storage reactions, as well as open circuit voltages (OCV), densities of products and rechargeabilities.  $\Delta_r H^\ominus$  values have been taken from Table 2. Note that the OCV for the Li–CO<sub>2</sub>/oxalate cell is based on the standard electrode potential of  $\text{U}_3(\text{CO}_2)_3/\text{C}_2\text{O}_4^{2-} = -0.03$  V from ref. 16 and on  $\text{U}_3(\text{Li}/\text{s})/\text{Li}^+ = -3.04$  V from ref. 17. OCV-s of the other cells are based on ref. 6 and 21–23. The OCV of the Li–(O<sub>2</sub> + CO<sub>2</sub>)/carbonate cell is identical to that of the Li–O<sub>2</sub>/peroxide one, as of ref. 13, i.e. the addition of CO<sub>2</sub> to a Li–O<sub>2</sub>/peroxide cell produces extra heat instead of electrical energy, while its rechargeability is debated.<sup>10,22,23</sup> O<sub>2</sub> or CO<sub>2</sub> may be supplied from air or from a gas tank carried on the vehicle leading to different energy densities. Discharge capacities are referenced to bulk lithium and are identical for all Li–air type systems (3830 mA h kg<sup>-1</sup> and 2045 mA h cm<sup>-3</sup>), while charge capacities are referenced to solid discharge products. Densities of solids are based on crystal structures at standard state

System	OCV (V)	Density of product (kg L <sup>−1</sup> )	Energy density		Charge capacity		Rechargeability		
			Gravimetric (W h kg <sup>−1</sup> )		Volumetric (W h L <sup>−1</sup> )				
			(Air)	(Tank)	(Air)	(Tank)			
n-Octane	—	—	12 814	—	9008	—	—	N	
Li-ion (LiCoO <sub>2</sub> )	3.6	5.05	—	568	—	2868	273	1379	Y
Li–O <sub>2</sub> /oxide	2.9	2.02	11 151	5204	5955	10 512	1787	3610	N
Li–O <sub>2</sub> /peroxide	3.0	2.25	11 329	3448	6050	7758	1165	2621	Y
Li–[O <sub>2</sub> + CO <sub>2</sub> ]/carbonate	3.0	2.10	11 329	2143	6049	4500	724	1520	Y/N
			+ 3313	+ 627	+ 1769	+ 1316			
Li–CO <sub>2</sub> /oxalate	3.0	2.14	11 488	1577	6134	3375	525	1125	Y



A simple implementation of a Li–CO<sub>2</sub>/oxalate battery. The electrolyte may be based on glymes, ionic liquids, etc. Both cation or anion selective membranes may be used. The green circles denote the catalysts (such as copper complexes) in the porous positive electrode. Panel (A) is for discharge, panel (B) for charge.



A flow battery, utilizing a supercritical mixture of CO<sub>2</sub> and polar modifiers (glymes, propylene carbonate, etc). The mixture allows for the dissolution of the discharge product and for very fast ion transport, therefore allows for high charge/discharge rates. The orange stripe refers to the catalytic CO<sub>2</sub>/oxalate positive electrode. The purple stripe is the cation selective membrane.

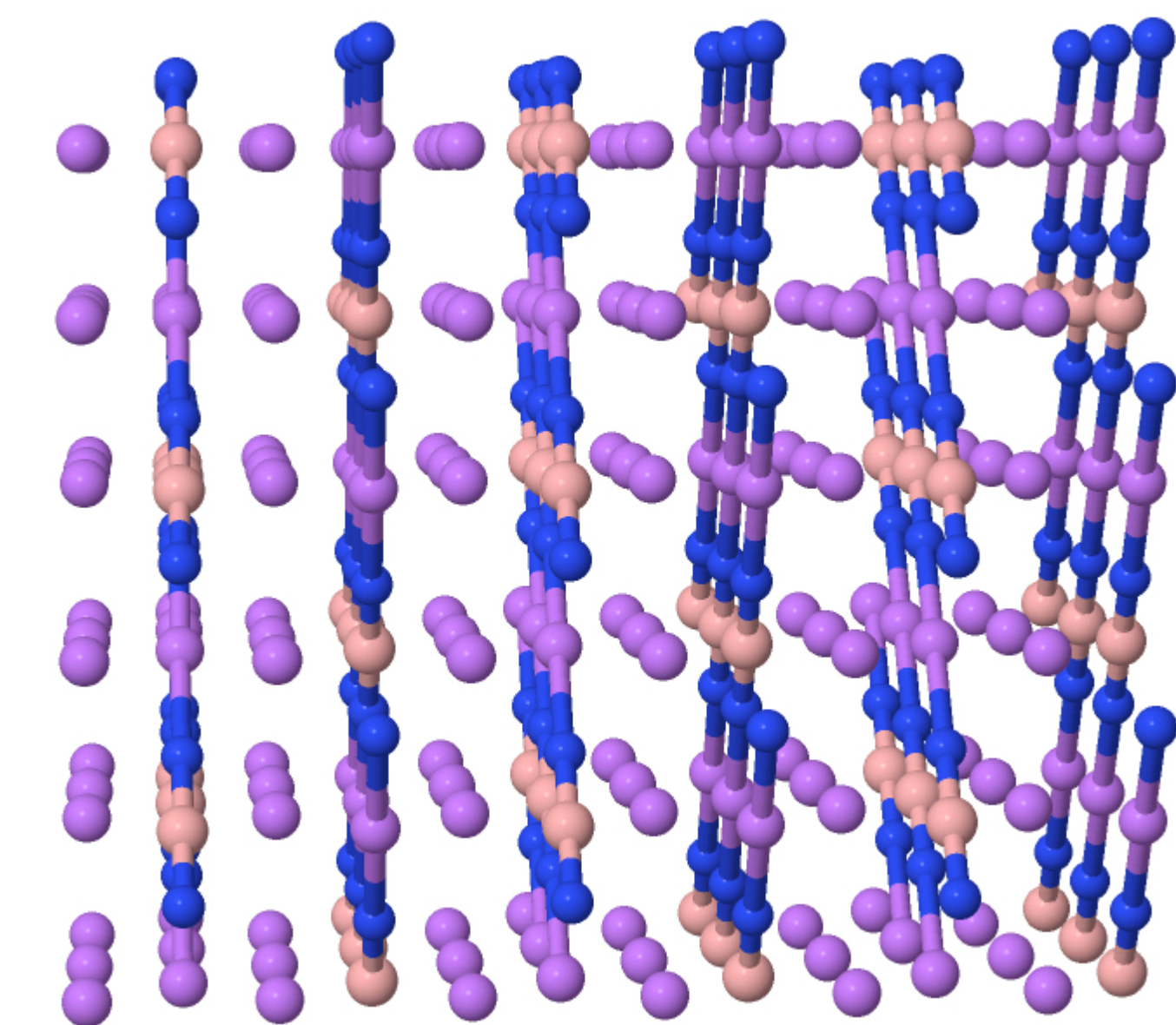
**References:**  
1.a.) K. Németh, G. Srajer: CO<sub>2</sub>/oxalate Cathodes as Safe and Efficient Alternatives in High Energy Density Metal-Air Type Rechargeable Batteries, RSC Advances, 2014, 4, 1879.

1.b.) K. Németh, M. van Veenendaal, G. Srajer: Electrochemical Energy Storage Device Based on Carbon Dioxide as Electroactive Species. US Patent 8389178, issued on March 5, 2013.

II.

## Ultrahigh Energy Density Li-ion Batteries Based on $\alpha\text{-Li}_x\text{BN}_2$ ( $1 \leq x \leq 3$ )

**Objective:** Utilize  $\alpha\text{-Li}_3\text{BN}_2$ , an existing material, as intercalation cathode electroactive species in the discharge reaction  $2\text{Li} + \text{LiBN}_2 \rightarrow \text{Li}_3\text{BN}_2$ . It is the oxidation number of N that changes during the charge/discharge cycles.



The layered structure of  $\alpha\text{-Li}_3\text{BN}_2$ .

Color code: Li – violet, B – magenta, N – blue.

Polymeric strands of -Li-N-B-N- repeating units form planes and two additional Li<sup>+</sup> ions per formula unit are located between these planes.

Li<sup>+</sup> ions between the polymeric planes can reversibly intercalate.

In the polymers of  $\alpha\text{-Li}_3\text{BN}_2$  (discharged form), [N-B-N]<sup>3-</sup> anions are linearly coordinated to Li<sup>+</sup> ions. In the charged form, LiBN<sub>2</sub>, there are [N-B-N]<sup>-</sup> anions, the oxidized form of [N-B-N]<sup>3-</sup>.

### Energy Storage Characteristics of $\alpha\text{-Li}_3\text{BN}_2$ As predicted by Density Functional Theory

Cell reaction for discharge:  $2\text{Li} + \text{LiBN}_2 \rightarrow \text{Li}_3\text{BN}_2$

Cell reaction energy:  $\Delta E = -7.22$  eV .

Cell voltage:  $U = -\Delta E / 2$  electrons = **3.61 V** (vs Li/Li<sup>+</sup>) .

Mass-density:  $\rho_M(\text{Li}_3\text{BN}_2) = 1.823$  kg/L .

Gravimetric energy density:  $\rho_{EG}(\text{Li}_3\text{BN}_2) = \mathbf{3247}$  Wh/kg .

Volumetric energy density:  $\rho_{EV}(\text{Li}_3\text{BN}_2) = 5919$  Wh/L .

Gravimetric capacity density:  $\rho_{CG}(\text{Li}_3\text{BN}_2) = 899$  mAh/g.

Volumetric capacity density:  $\rho_{CV}(\text{Li}_3\text{BN}_2) = 1638$  mAh/cm<sup>3</sup>.

Volume change per 2-electron transfer: **2.8%**

#### Experimental data:

Ionic conductivity: 3 mS/cm (T=400 K)

Activation energy of ionic conduction: 78 kJ/mol (~0.8 eV)

#### Comparison:

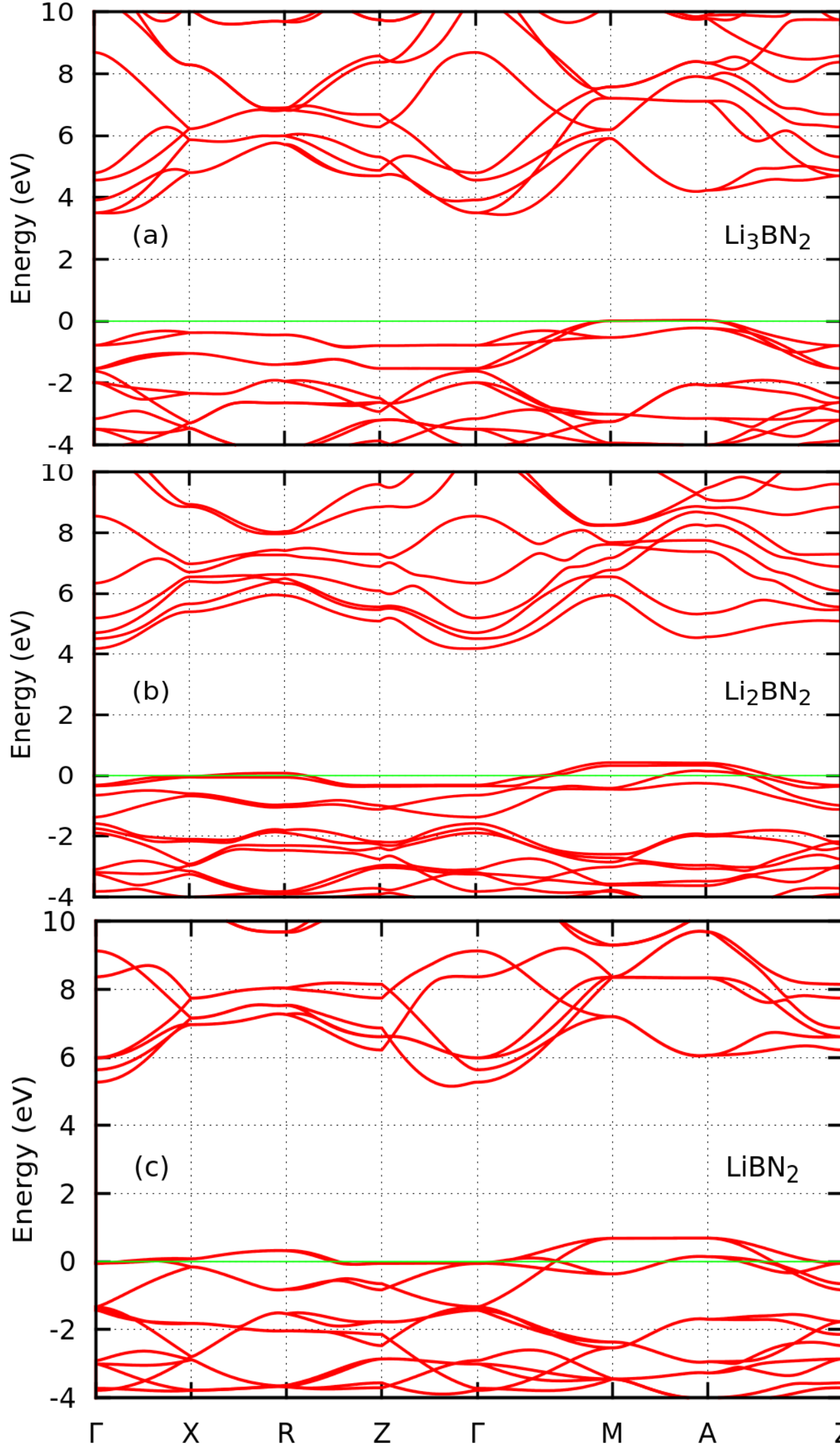
$\rho_{EG}(\text{Li-air}) = 3450$  Wh/kg (including the weight of O<sub>2</sub>)

$\rho_{EG}(\text{Li}_2\text{S}) = 2600$  Wh/kg (conversion based)

$\rho_{EG}(\text{Li-FeF}_3) = 1950$  Wh/kg (conversion based)

$\rho_{EG}(\text{Li}_3\text{Cr}(\text{BO}_3)(\text{PO}_4)) = 1700$  Wh/kg (intercalation based, best design of Ceder group at MIT)

$\rho_{EG}(\text{LiCoO}_2) = 600$  Wh/kg (intercalation based)



**Figure 2:** Band structures of Li<sub>3</sub>BN<sub>2</sub> and its de-lithiated derivatives. Li<sub>3</sub>BN<sub>2</sub> is insulator, while its de-lithiated derivatives are metallic conductors.

#### References:

[2a] K. Németh: Materials Design by Quantum-Chemical and Other Theoretical/Computational Means: Applications to Energy Storage and Photoemissive Materials, International Journal of Quantum Chemistry 2014, in press, DOI: 10.1002/qua.24616

[2b] K. Németh: Ultrahigh Energy Density Li-ion Batteries Based on Cathodes of 1D Metals with -Li-N-B-N- Repeating Units in alpha-LixBN2 (1≤x≤3), submitted for publication, <http://arxiv.org/abs/1404.0412> .

III.

## Functionalized (h-)BN Species for High Energy and High Power Density Batteries

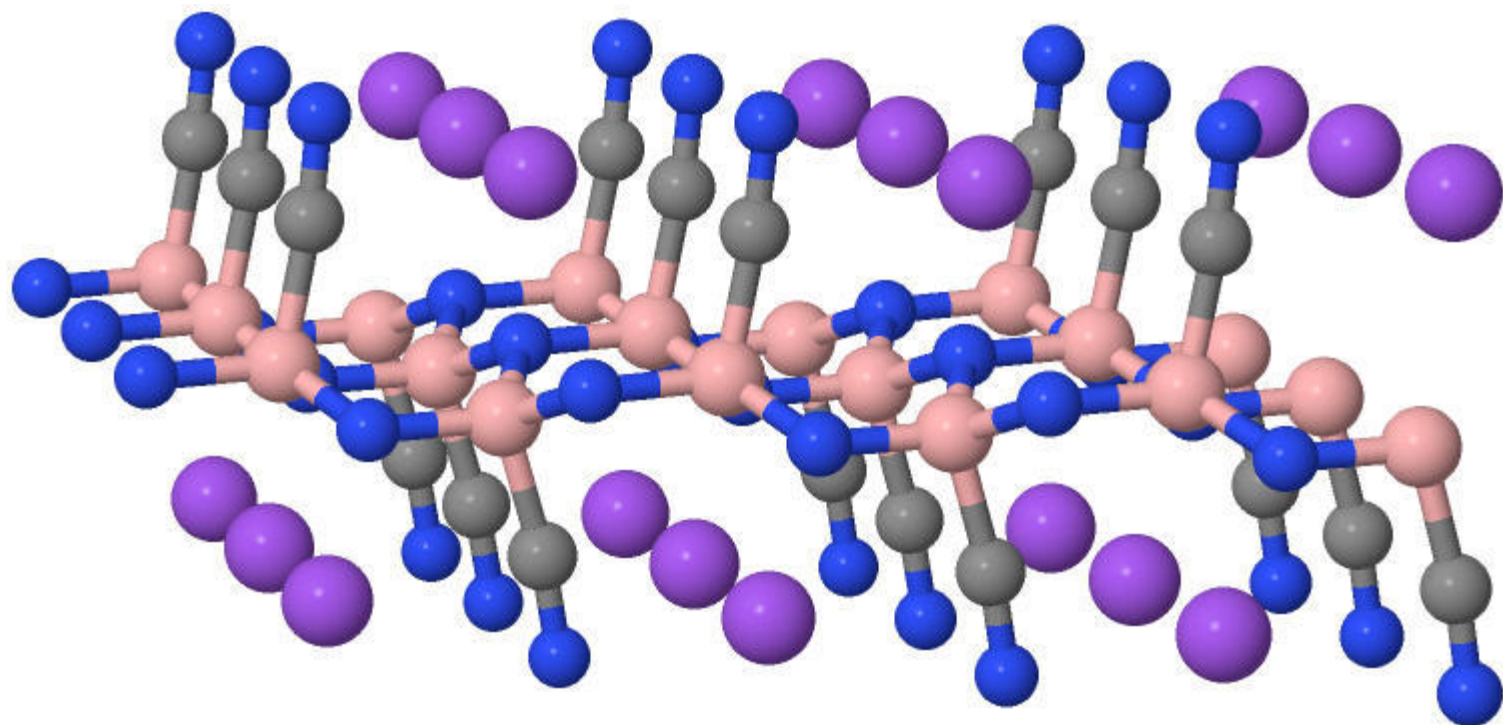
**Objective:** Functionalization of the surface of monolayer h-BN or BN-nanotubes is a way to tune the electrochemical potential and to create intercalation/conversion sites on the surface.

➤ **Functionalized BNs (FBNs) are a very rich field and present an [entirely new platform](#) for energy storage applications.**

➤ **They are [universal intercalation](#) materials and can intercalate Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Al<sup>3+</sup> cations.**

➤ **These materials are [very light](#) because they totally eliminate the use of transition metals, leading to large specific capacities and high energy densities.**

➤ **The majority of FBNs are monolayer (or nanotube) materials and thus have [fast charging and discharging rates](#) because intercalation does not require diffusion within a crystal; it is just one step directly from the electrolyte.**



**Figure 3:** A monolayer of cyano (-CN) functionalized h-BN, with intercalated Na<sup>+</sup> ions (3x3 supercell). Color code: Na – violet, B – magenta, N – blue, C – gray . Note that -CN groups are attached only to B atoms in the h-BN surface. The Na-deintercalated species are metallic conductors, the Na intercalated ones are semiconductors.

Cell reaction for discharge: **Na + BN(CN) → BN(CN)Na**

Cell reaction energy:  $\Delta E = -2.87$  eV

Cell voltage:  $U = -\Delta E / 1$  electrons = **2.87 V** (vs Na/Na<sup>+</sup>) .

Mass-density:  $\rho_M(\text{BN(CN)Na}) \approx 3.406$  kg/L .

Gravimetric energy density:  $\rho_{EG}(\text{BN(CN)Na}) = \mathbf{1042}$  Wh/kg.

Volumetric energy density:  $\rho_{EV}(\text{BN(CN)Na}) = 3547$  Wh/L.

Gravimetric capacity density:  $\rho_{CG}(\text{BN(CN)Na}) = 363$  mAh/g.

Volumetric capacity density:  $\rho_{CV}(\text{BN(CN)Na}) = 1236$  mAh/cm<sup>3</sup>.

#### Energy density depends on the functional group!

#### Comparison:

$\rho_{EG}(\text{NaFe}_{0.5}\text{Co}_{0.5}\text{O}_2) = 425$  Wh/kg (intercalation based)

$\rho_{EG}(\text{Na}_{1.5}\text{V(PO}_{4.8}\text{)F}_{0.7}) = 521$  Wh/kg (intercalation based)

#### Synthesis of functionalized (h-)BN-s:

Many possibilities exist, such as nucleophilic or electrophilic attack by functionalization agents, or radicals based functionalization. Nucleophilic attack based functionalization attaches functional groups to the B atoms only, while electrophilic ones link groups to the N atoms. The known radicals based functionalizations attach groups to the B atoms. Many functionalized (h-)BN-s already exist but have not been tested as electroactive species in batteries yet.

#### Other examples of functionalized (h-)BN-s:

It is possible to achieve an energy density of 1532 Wh/kg (6130 Wh/L) using Al<sup>3+</sup> cations, at an OCV of 1.72 V (vs Al/Al<sup>3+</sup>) with a specific functionalized h-BN. [3b]

#### Why BN monolayer, instead of graphene or doped graphene?

The BN monolayer is uniquely well suited for functionalization as:

1. It contains highly polarized atoms with +/- 0.5 partial charges → good target for nucleophile/electrophile attack based functionalization.
2. The high electronegativity of N in B-functionalized BN helps to store electrons on the monolayer. The N in B-functionalized BN also helps to complex the intercalated cation.
3. Either only the B or the N sites are typically functionalized, leaving space for ion intercalation in the surface.
4. h-BN or BN-nanotubes allow for maximum density surface intercalation, as the patterned BN surface is optimal for both functionalization and intercalation site densities.

#### Selection of functional groups:

For cathode materials, the functionalization should make the FBN a strong electron acceptor, for anode materials a strong electron donor. Such functional groups are well known in organic chemistry, for example in aromatic functionalization and in organic charge transfer complexes (Bechgaard salts).

#### References:

[3a] K. Németh: Materials Design by Quantum-Chemical and Other Theoretical/Computational Means: Applications to Energy Storage and Photoemissive Materials, International Journal of Quantum Chemistry 2014, in press, DOI: 10.1002/qua.24616

[3b] K. Németh, Functionalized Boron Nitride Materials as Electroactive Species in Electrochemical Energy Storage Devices, patent pending, 2013.