

I. CO₂/oxalate cathodes as safe and efficient alternatives in high energy density metal-air type rechargeable batteries

Objective: Compare CO₂/oxalate cathodes (2CO₂ + 2e⁻ → C₂O₄²⁻) as potential alternatives to O₂/peroxide ones (O₂ + 2e⁻ → O₂²⁻).

Table 1: Comparison of CO₂/oxalate and O₂/peroxide positive electrodes for energy storage.

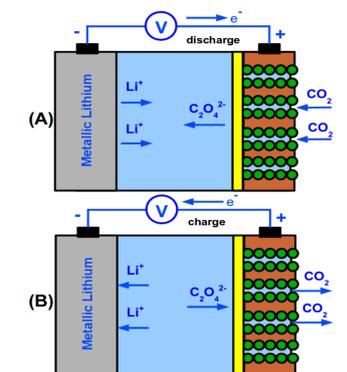
	CO ₂	O ₂
Cathode/discharge:	2CO ₂ + 2e ⁻ → C ₂ O ₄ ²⁻	O ₂ + 2e ⁻ → O ₂ ²⁻
Voltage: (vs. Li/Li⁺)	~3 V (copper-complex catalyst)	~3 V (without catalyst)
Rechargeability:	Yes (small overpot., at ~3.8V)	Yes (high overpot. at ~4.2V)
Storage tank:	Light (easy to compress)	Heavy (difficult to compress)
Supply from air:	Yes (via CO ₂ selective membrane)	Yes (via H ₂ O, N ₂ and CO ₂ filter)
Hybrid battery/supercapacitor (negating mass):	Possible	Likely Not Possible
Tunability of diffusion-speed via CO₂ or O₂ pressure:	Yes (supercritical CO ₂)	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 ₂ /oxalate cathode	None known

Table 2 Standard reaction enthalpies (Δ_rH⁰) and Gibbs free energies (Δ_rG⁰) of energy storage reactions discussed in the present study, as calculated from Δ_rH⁰ and Δ_rH⁰ data of Table 1. Data of the LiCoO₂-based Li-ion battery are from ref. 21–23

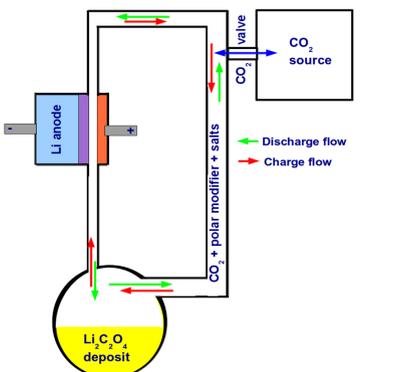
System	Reaction	Δ _r H ⁰ (kJ mol ⁻¹)	Δ _r G ⁰ (kJ mol ⁻¹)
n-Octane	C ₈ H ₁₈ (g) + 12.5O ₂ (g) → 8CO ₂ (g) + 9H ₂ O(g)	-5116	-5259
Li-ion (LiCoO ₂)	Li _{1-x} CoO ₂ (s) + Li _{1-x} CO ₂ (s) → C ₆ (s) + LiCoO ₂ (s)	-	-213
Li-O ₂ /oxide	2Li(s) + 1/2O ₂ (g) → Li ₂ O(s)	-599	-562
Li-O ₂ /peroxide	2Li(s) + O ₂ (g) → Li ₂ O ₂ (s)	-633	-571
Li-[O ₂ + CO ₂]/carbonate	2Li(s) + CO ₂ (g) + 1/2O ₂ (g) → Li ₂ CO ₃ (s)	-823	-738
Li-O ₂ /oxalate	2Li(s) + 2CO ₂ (g) → Li ₂ C ₂ O ₄ (s)	-590	-579

Table 3 Theoretical gravimetric and volumetric energy (Δ_rH⁰) densities and capacities of energy storage reactions, as well as open circuit voltages (OCV), densities of products and rechargeabilities. Δ_rH⁰ values have been taken from Table 2. Note that the OCV for the Li-CO₂/oxalate cell is based on the standard electrode potential of U₀₁(CO₂/C₂O₄²⁻) = -0.03 V from ref. 16 and on U₀₁(Li/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-(O₂ + CO₂)/carbonate cell is identical to that of the Li-O₂/peroxide one, as of ref. 13, i.e. the addition of CO₂ to a Li-O₂/peroxide cell produces extra heat instead of electrical energy, while its rechargeability is debated^{10,21,22}. O₂ or CO₂ 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⁻¹ and 2045 mA h cm⁻³), 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 ⁻¹)	Energy density		Charge capacity		Rechargeability		
			Gravimetric (W h kg ⁻¹)	Volumetric (W h L ⁻¹)	Gravimetric (mA h g ⁻¹)	Volumetric (mA h cm ⁻³)			
								(Air)	(Tank)
n-Octane	—	—	12 814	—	9008	—	—	N	
Li-ion (LiCoO ₂)	3.6	5.05	—	—	—	2868	273	1379	Y
Li-O ₂ /oxide	2.9	2.02	11 151	5204	5955	10 512	1787	3610	N
Li-O ₂ /peroxide	3.0	2.25	11 329	3448	6050	7758	1165	2621	Y
Li-[O ₂ + CO ₂]/carbonate	3.0	2.10	11 329	2143	6049	4500	724	1520	Y/N
Li-O ₂ /oxalate	3.0	2.14	+ 3313	+ 627	+ 1769	+ 1316	—	—	—
			11 488	1577	6134	3375	525	1125	Y



A simple implementation of a Li-CO₂/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 CO₂ 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 CO₂/oxalate positive electrode. The purple stripe is the cation selective membrane.

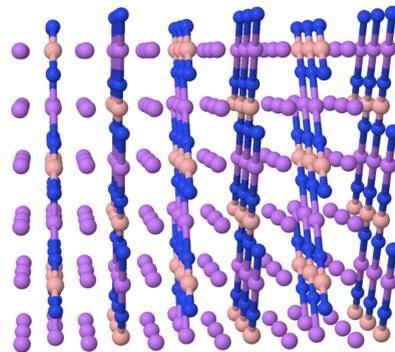
References:

1.a.) K. Németh, G. Srajer: CO₂/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 α-Li_xBN₂ (1 ≤ x ≤ 3)

Objective: Utilize α-Li₃BN₂, an existing material, as intercalation cathode electroactive species in the discharge reaction 2Li + LiBN₂ → Li₃BN₂. It is the oxidation number of N that changes during the charge/discharge cycles.



The layered structure of α-Li₃BN₂.

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

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

Li⁺ ions between the polymeric planes can reversibly intercalate.

In the polymers of α-Li₃BN₂ (discharged form), [N-B-N]³⁻ anions are linearly coordinated to Li⁺ ions. In the charged form, LiBN₂, there are [N-B-N]⁻ anions, the oxidized form of [N-B-N]³⁻.

Energy Storage Characteristics of α-Li₃BN₂ As predicted by Density Functional Theory

Cell reaction for discharge: 2Li + LiBN₂ → Li₃BN₂

Cell reaction energy: ΔE = -7.22 eV.

Cell voltage: U = -ΔE / 2 electrons = **3.61 V** (vs Li/Li⁺).

Mass-density: ρ_m(Li₃BN₂)=1.823 kg/L.

Gravimetric energy density: ρ_{EG}(Li₃BN₂) = **3247 Wh/kg**.

Volumetric energy density: ρ_{EV}(Li₃BN₂)=5919 Wh/L.

Gravimetric capacity density: ρ_{CG}(Li₃BN₂)=899 mAh/g.

Volumetric capacity density: ρ_{CV}(Li₃BN₂)=1638 mAh/cm³.

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:

ρ_{EG}(Li-air) = 3450 Wh/kg (including the weight of O₂)

ρ_{EG}(Li₂S) = 2600 Wh/kg (conversion based)

ρ_{EG}(Li-FeF₃) = 1950 Wh/kg (conversion based)

ρ_{EG}(Li₃Cr(BO₃)(PO₄)) = 1700 Wh/kg (intercalation based, best design of Ceder group at MIT)

ρ_{EG}(LiCoO₂) = 600 Wh/kg (intercalation based)

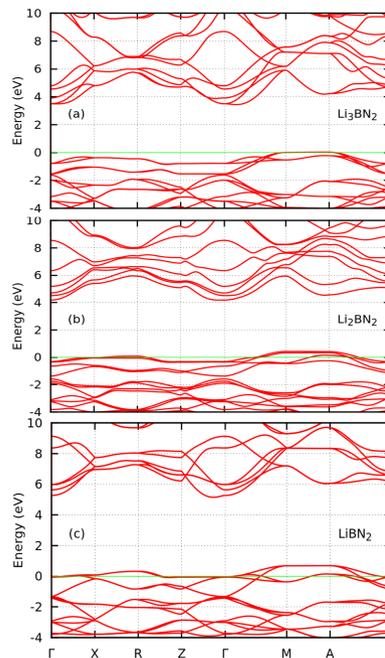


Figure 2: Band structures of Li₃BN₂ and its de-lithiated derivatives. Li₃BN₂ is insulator, while its de-lithiated derivatives are metallic conductors.

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⁺, Na⁺, K⁺, Mg²⁺, and Al³⁺ 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.**

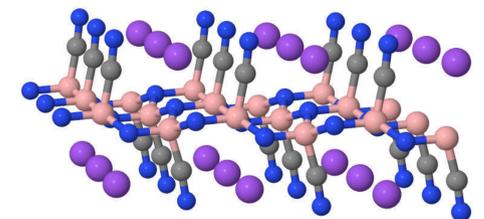


Figure 3: A monolayer of cyano (-CN) functionalized h-BN, with intercalated Na⁺ ions (3x3 supercell). Color code: Na – violet, B – magenta, N – blue, C – gray. Note that -CN groups are attached only to B atoms in the h-BN surface. The Na-deintercalated species are metallic conductors, the Na intercalated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

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

Cell reaction energy: ΔE = -2.87 eV

Cell voltage: U = -ΔE / 1 electrons = **2.87 V** (vs Na/Na⁺).

Mass-density: ρ_m(BN(CN)Na)≈3.406 kg/L.

Gravimetric energy density: ρ_{EG}(BN(CN)Na) = **1042 Wh/kg**.

Volumetric energy density: ρ_{EV}(BN(CN)Na)= 3547 Wh/L.

Gravimetric capacity density: ρ_{CG}(BN(CN)Na)=363 mAh/g.

Volumetric capacity density: ρ_{CV}(BN(CN)Na)=1236 mAh/cm³.

Energy density depends on the functional group!

Comparison:

ρ_{EG}(NaFe_{0.5}Co_{0.5}O₂) = 425 Wh/kg (intercalation based)

ρ_{EG}(Na_{1.5}V(PO₄)_{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 Al³⁺ cations, at an OCV of 1.72 V (vs Al/Al³⁺) 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.