Electrochemical Energy Storage Devices Based on Carbon-Dioxide as Electroactive Species

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WHY CONSIDERING CO2 FOR BATTERY DESIGN?

- **Highly efficient catalysts are available for both reduction and oxidation of CO2 with moderate overpotentials.**
- **CO2 is easy to compress to supercritical or liquid state.**
- **Supercritical/liquid CO2 is excellent "green" solvent.**
- **Ionic liquids based on reduced forms of CO2.**
- **Ionic liquids have anomalous melting point depression in CO2 atmosphere.**

CO_2 electrochemistries of primary consideration:

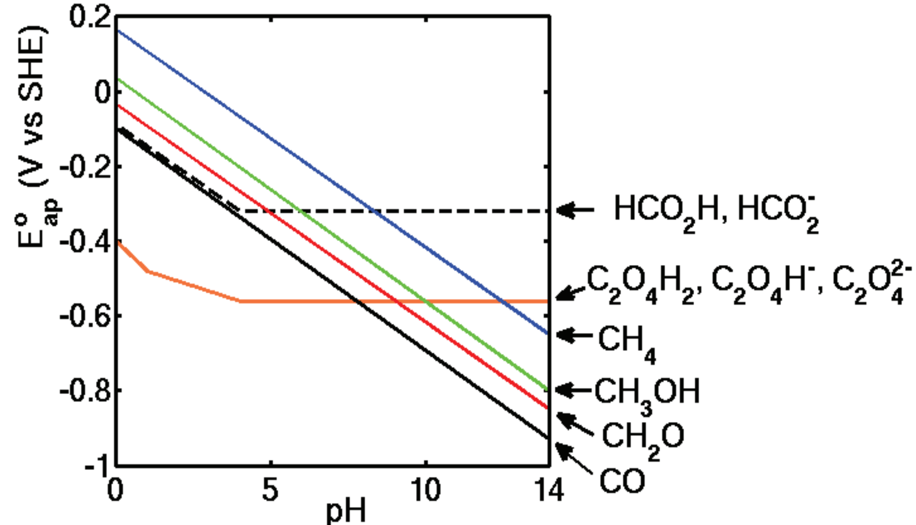


Figure from J-M. Saveant, Chem. Rev. 108, 2348 (2008).

In aprotic medium:

$$2CO_2 + 2e^- \rightarrow C_2O_4^{2-}$$

$$2CO_2 + 2e^- \rightarrow CO_3^{2-} + CO$$

Robust, easy to back-oxidize.

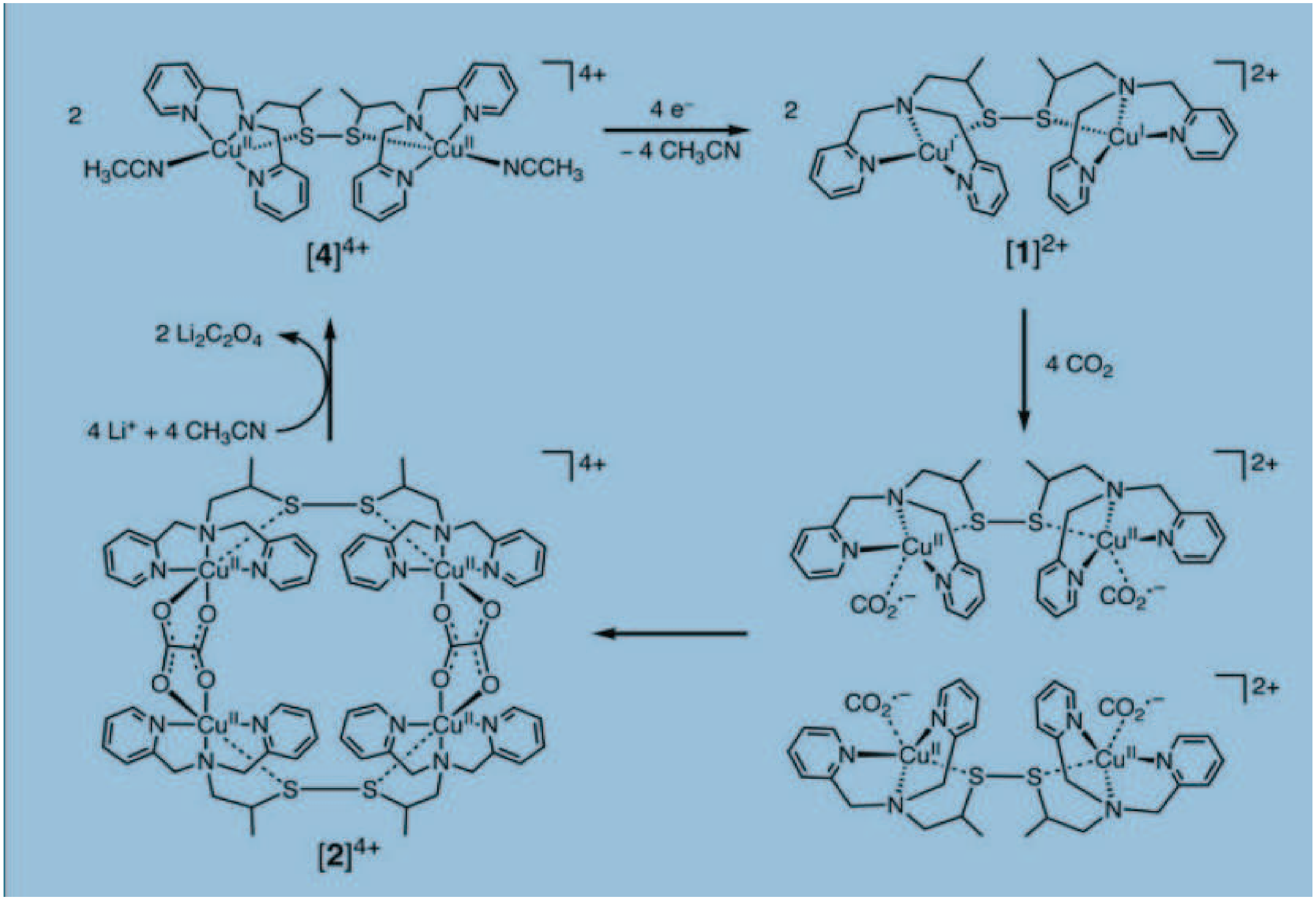
In protic medium:

$$CO_2 + H_2O + 2e^- \rightarrow HCOO^- + OH^-$$

$$4CO_2 + 2H_2O + 4e^- \rightarrow 2HCO_3^- + 2HCOO^-$$

Approximately pH neutral.

Catalyst for CO_2 reduction to oxalate:



100% oxalate yield, at -0.03V wrt SHE in acetonitryl.

Raja Angamuthu, et al. Science 327, 313 (2010).

Effect of electrolyte on CO2 reduction:

TABLE III

Run No.	Catholyte and anolyte [1]	Applied voltage (volts)	Maximum temp. (° C.)	Run time (hr.)	Current density (ma./cm.^{2})	Coulombic yield of (C_2O_4=), (percent)
6	{0.3 M TEPC/DMF {0.3 NaOH/H_2O	15	-------------	14	5.1	71.8
7	{0.3 M TEPC/DMF {0.3 M $NaHCO_3/H_{20}$	15	-------------	12	3.9	93.8
8	{0.3 M TEPC/DMF {Sat'd NaCl/H_2O	15	33	6	6.0	68.7
9	{0.3 M TEPC/DMF {Sat'd NaCl/H_2O	25	50	5½	17.7	72.2
10	{0.3 M TEPC/DMF {Sat'd NaCl/H_2O	35	61	1½	19.5	87.6
11	{0.3 M TEPC/DMF {Sat'd NaCl/H_2O	35	76.5	2½	30.6	97.8
12	{0.2 M TEBr/DMF {Sat'd NaCl/H_2O	35	59	2	15.0	77.9
13	{0.3 M TEPC/DMA {Sat'd NaCl/H_2O	35	74	2	25.8	83.5
14	{0.3 M TEPC/DMSO {Sat'd NaCl/H_2O	35	63.5	2	20.8	87.5

[1] See footnote at the end of Table II.

From US Patent 3720591 (1973)

Very high oxalate yield
Due to the use of
Tetraethyl-ammonium
Perclorate electrolyte in DMF.

Electrodes for oxalate oxidation to CO_2 :

1. Nobel metals.

2. Graphite

3. Highly boron doped diamond film

4. PbO2 (best for alkaline media).

etc.

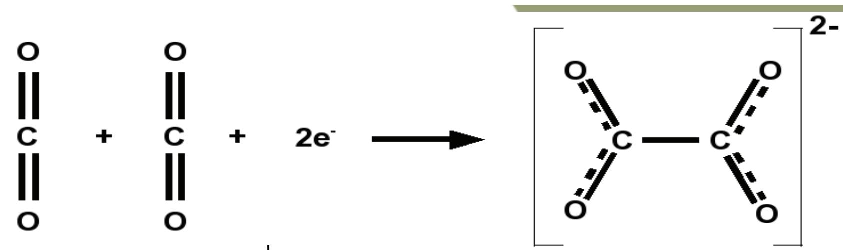
Electrochemical Liquid-to-Fluid or Liquid-to-Gas conversion

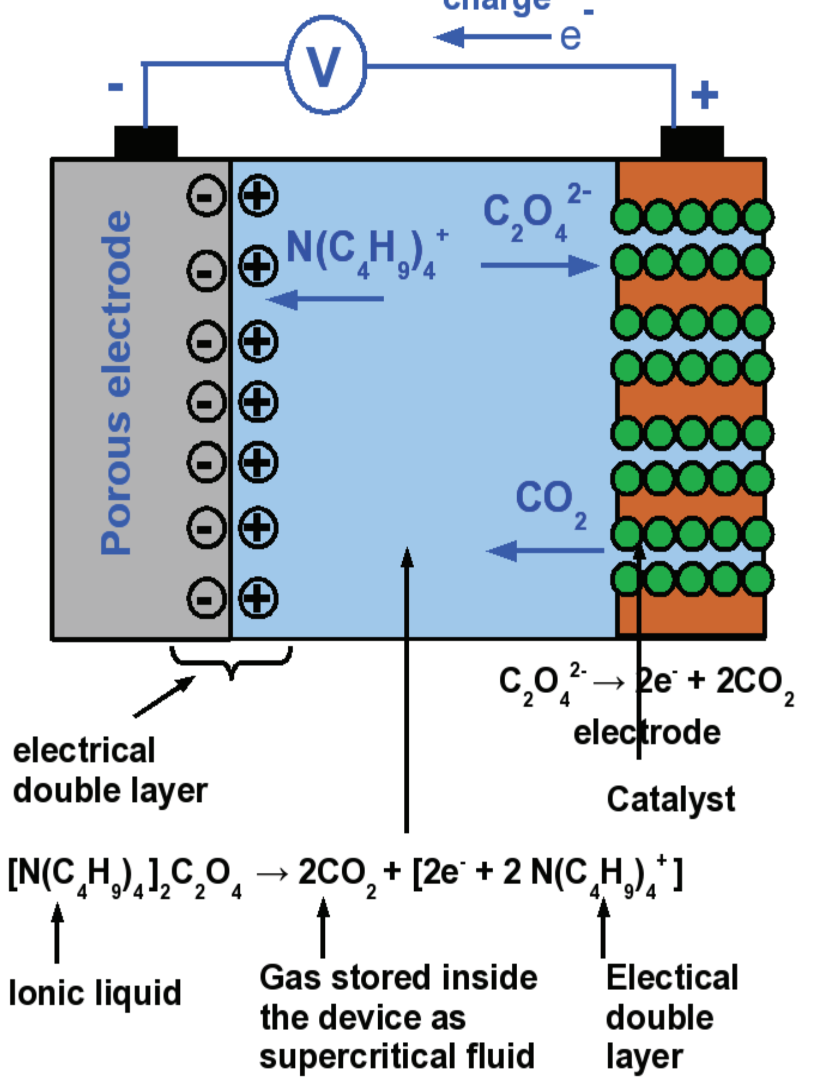
Supercritical or gas-phase carbon dioxide ↔ **an oxalate-ion containing ionic liquid.**

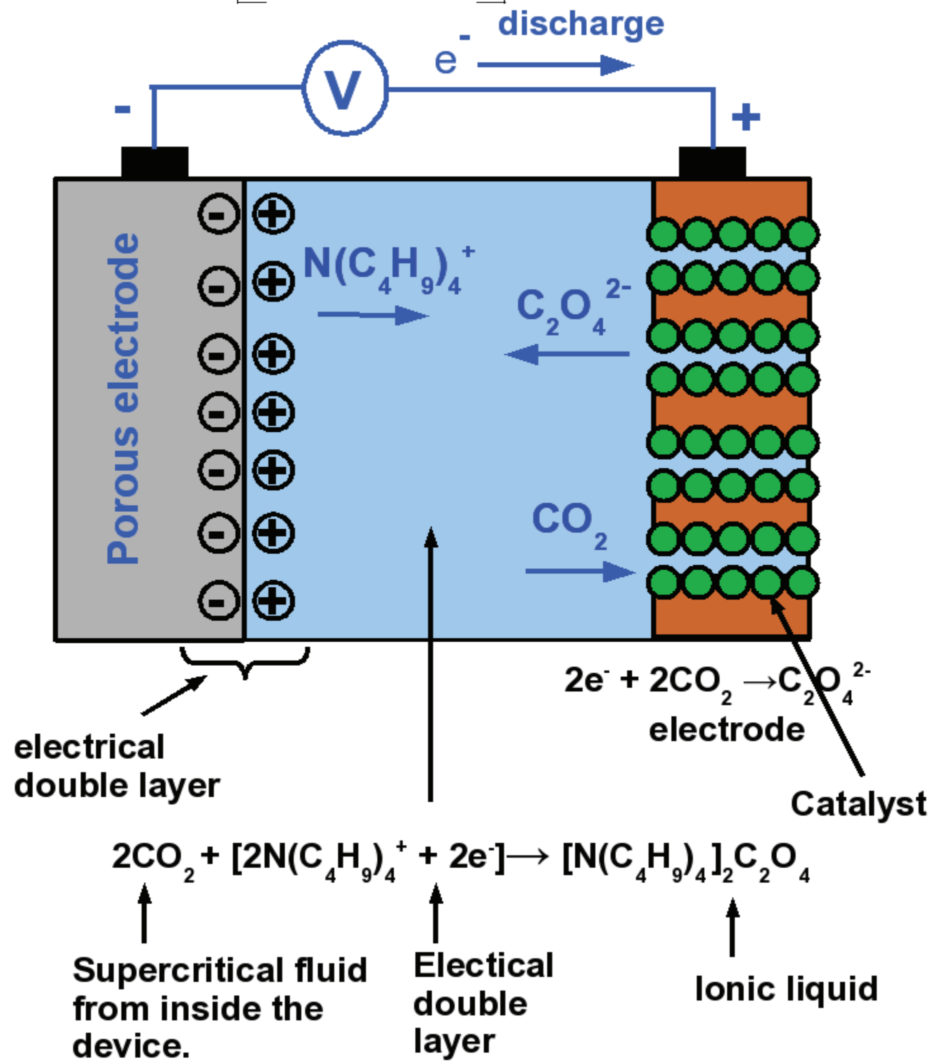
The cation of the ionic liquid is stored in electrical double layer (supercapacitor) on the negative electrode in the charged state.

The big picture

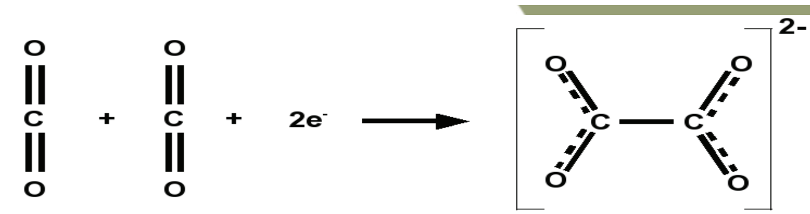
(CO_2 stored inside the device)

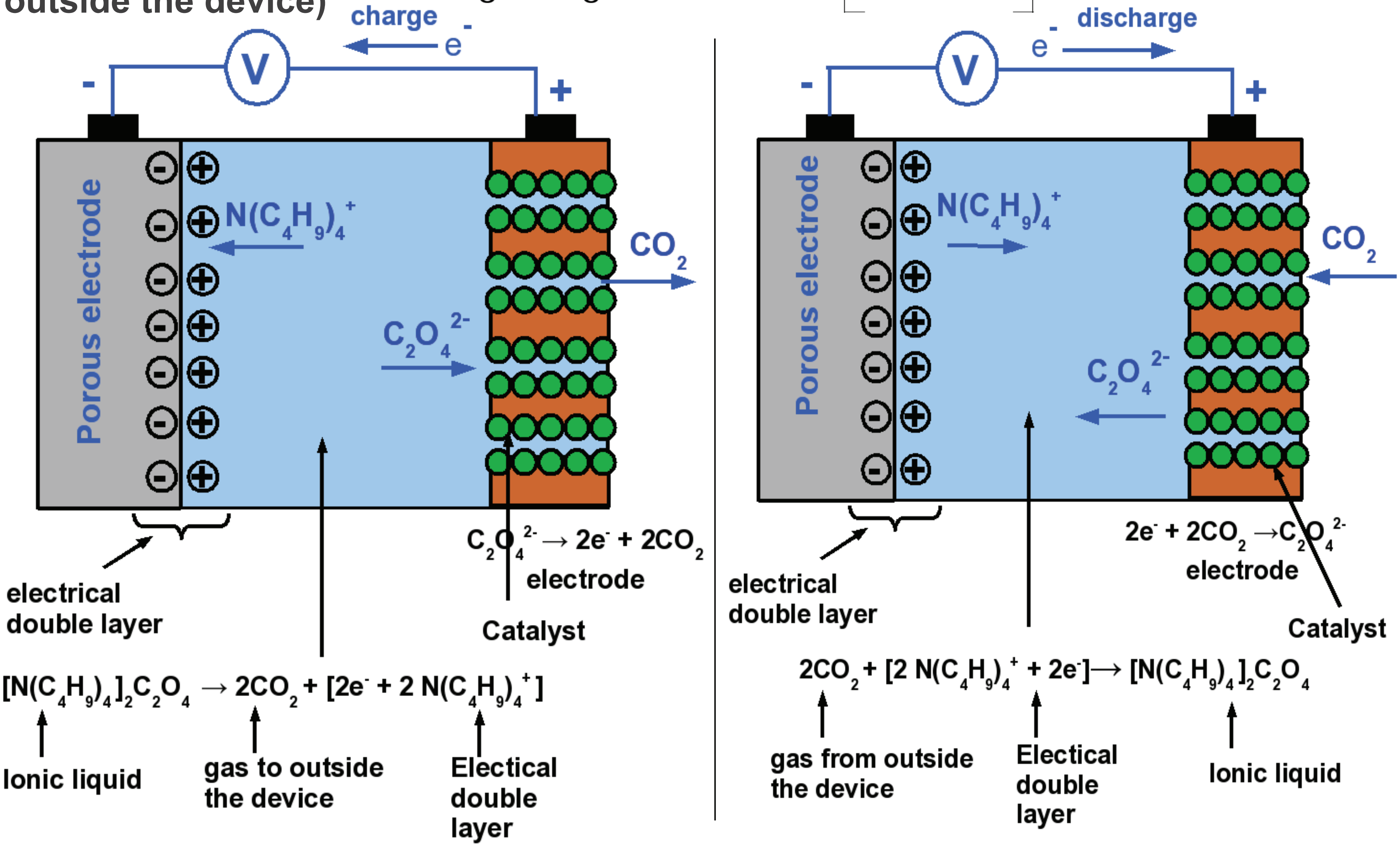






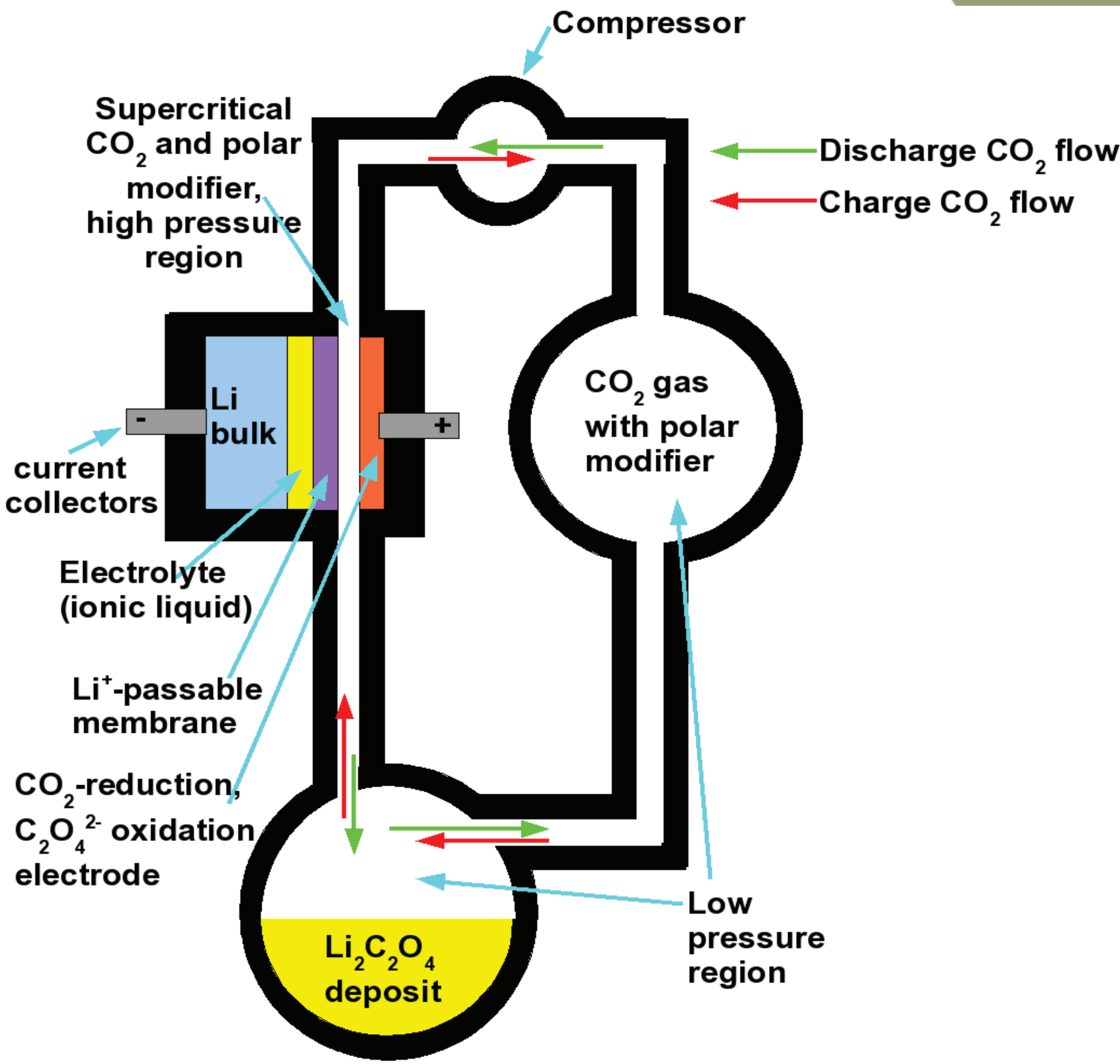
The big picture
(CO_2 stored
outside the device)





NO NEED FOR HIGH PRESSURE CONTAINER

Flow Battery based on CO_2 electrochemistry



Many different variants of electrochemical energy storage devices can be built on CO_2 electrochemistry:

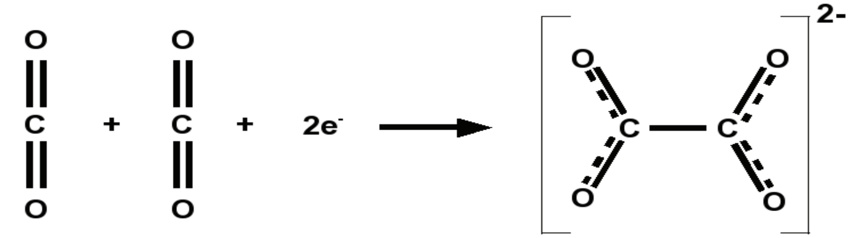
A whole overlooked platform of energy storage devices!

For more variants, see our patent application:

K. Németh, G. Srajer, M. van Veenendaal:
Electrochemical Energy Storage Device Based on Carbon Dioxide as Electroactive Species

http://www.freepatentsonline.com/y2010/0330435.html

Why using CO_2 instead of O_2 ?



1. CO_2 is less reactive than O_2: both disadvantage and advantage.
   Disadvantage: in discharging: less voltage
   Advantage: in recharging: instead of agressive O species environmentally benign CO_2 is produced: does not "eat up" electrolyte and electrode.

2. Reduction of CO_2 to Oxalate ($C_2O_4^{2-}$ preferred discharge product of CO_2): catalyst are available with ~100% Faradaic yield and selectivity for oxalate at a potential near 0V wrt SHE (see e.g. "Electrocatalytic CO_2 Conversion to Oxalate by a Copper Complex", Raja Angamuthu, et al. Science 327, 313 (2010);)

3. Oxidation of Oxalate ($C_2O_4^{2-}$ preferred discharge product of CO_2) during recharge is a well established process, goes with small overpotential and yields 100% CO_2. No desperate need for catalyst development for the recharge process.

Why using CO_2 instead of O_2 ?

4. CO2 is present in the air and can be collected very efficiently, thus it provides a potential fuel component available from the air.
   Besides O2, only CO2 is electrochemically useful from the air.

5. CO2 is uniquely well and easily compressable (supercritical point at ~70 bar and ~30 C). Supercritical CO2 has been known for long as an excellent green-chemistry solvent. CO2 can be both solvent of electrolyte and electroactive species.

6. CO_2 reduction product oxalate ($C_2O_4^{2-}$) can form ionic liquids with organic cations (e.g. quaternary ammonium and phosphonium cations).

7. A large number of ionic liquids have anomalous melting point depression in CO_2 atmosphere (Scurto AM, et.al, "Melting point depression of ionic liquids with CO_2: Phase equilibria", INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH Volume: 47 Issue: 3 Pages: 493-501).

Why using CO_2 instead of O_2 ?

8. In the CO2-based devices there would be much simpler phase-interfaces, than in Li-O2 batteries, since there are no solid reaction products.

Summary:

CO_2 electrochemistry may be more advantageous than O_2 electrochemistry for building efficient, “green” and economic electrochemical energy storage devices.