International Conference "Global/Local Innovations for Next Generation Automobiles"
Sendai International Center, Sendai, Miyagi (October 27, 2015)

A metal-free organic crystalline electrode for high energy density batteries

Applications

- Large Scale electricity storage devices

Itaru HONMA

(Tohoku University)

"Green Energy/ Nanotechnology researches" @ HONMA lab., IMRAM

Advanced secondary batteries for EV/HEV, Robots and iPhones

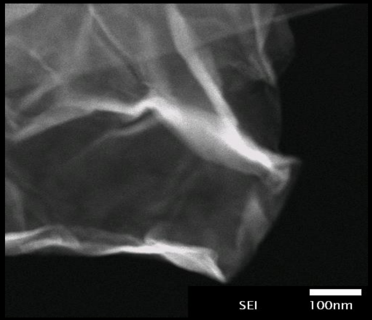
- high power lithium ion battery
- all solid state LIB
- Mg (multi-valence ion) secondary battery

Super-capacitor for winds & solar renewable energy storage

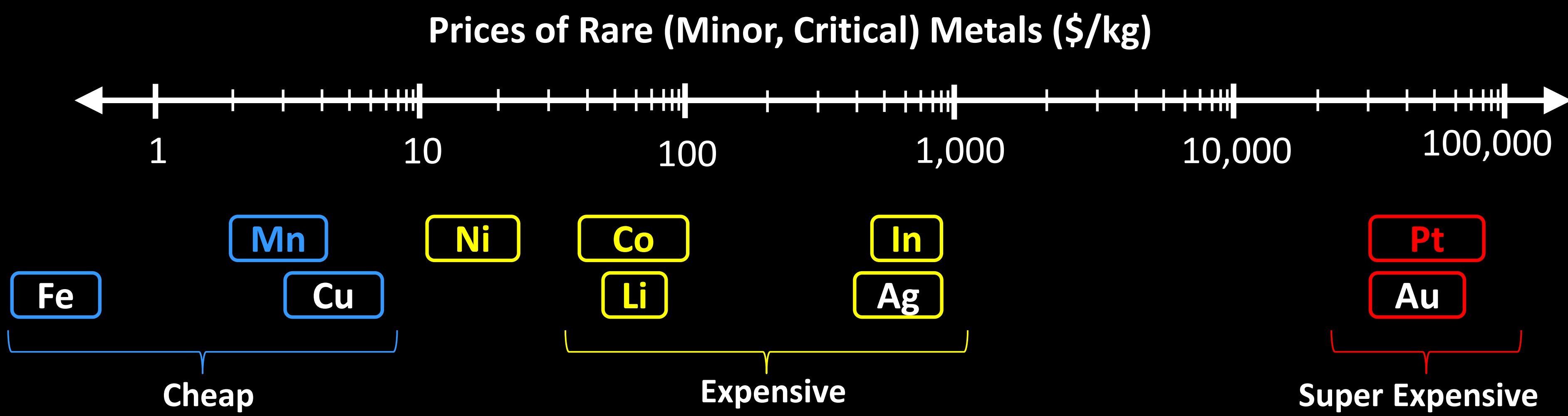
- <u>aqueous proton capacitor</u>
- redox flow capacitor

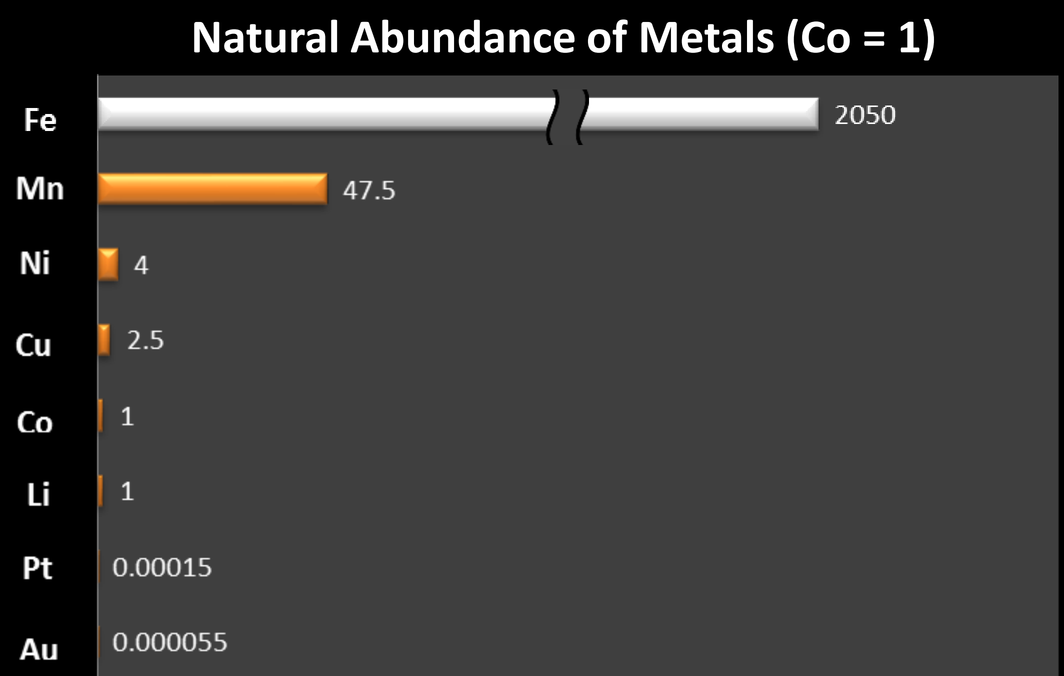
Nanotechnology for advanced energy materials

- nanoparticles/ ionic liquids
- graphene & nanoporous carbons
- supercritical fluid processing for nanoelectrodes



Rare metal's price and resources limitation are critical





Rare metal news; 2008-2010

Barbalace, Kenneth; "Periodic Table of Elements"

Organic Crystal as "Green Nanotechnology of Electrode"

TCNQ crystals

(Tetracyano- quinodimethane)

TTF-TCNQ (organic metals)

L.B.Coleman et al., ***Solid State Commun***. 12, 1125 (1973)

J. Ferraris et al., ***J.Am.Chem.Soc***., 95, 948 (1973)

$(TMTSF)_2PF_6$ (organic superconductor)

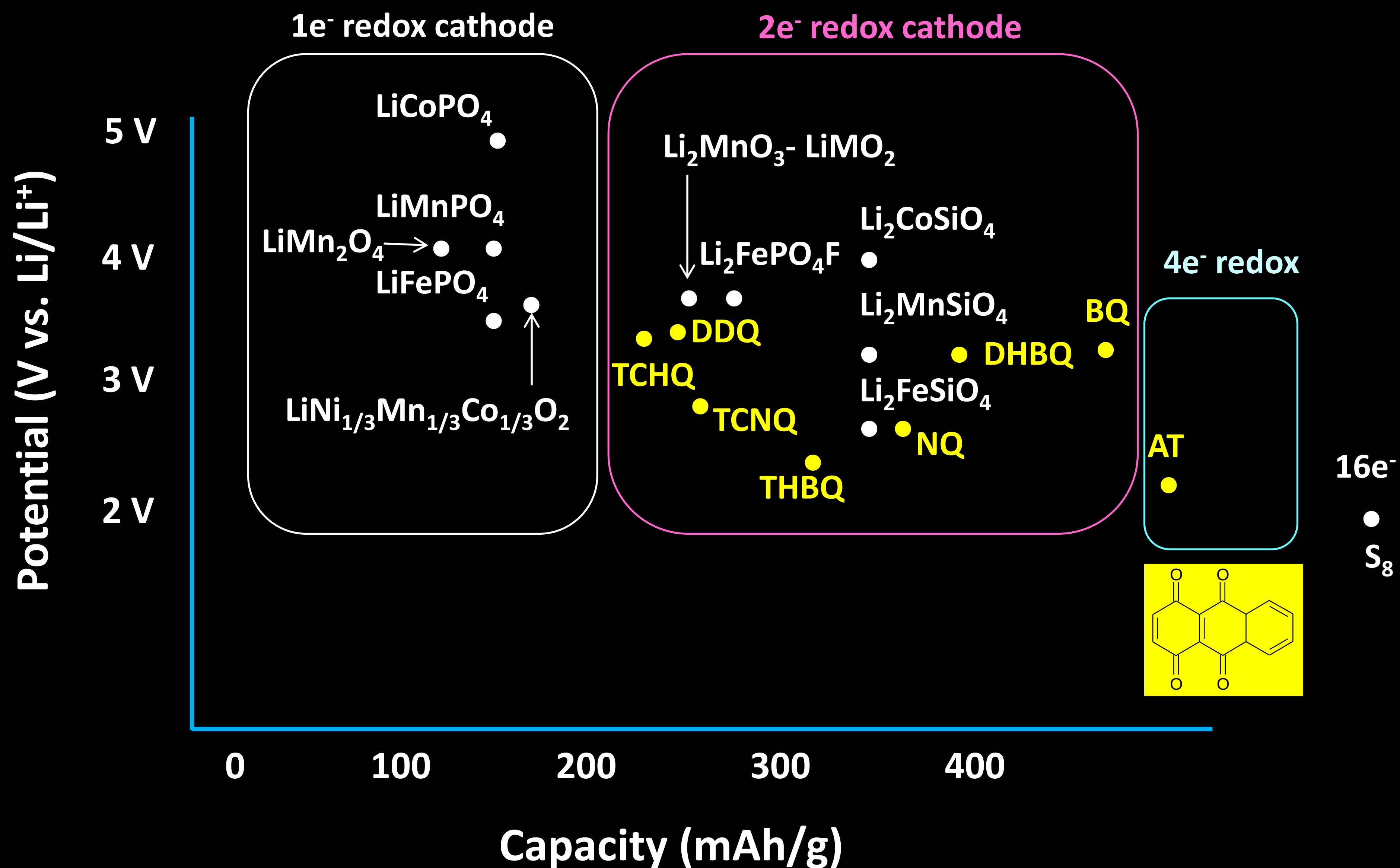
D.Jerome et al., ***J.Physique Lett***. 41, L95 (1980)

- **Metal free electrodes**
- **Natural abundance**
- **Environmentally friendly**
- **Safety & recyclability**
- **Cost effective**
- **No high temperature process**

↓

Exploration of rare-metal free, low cost & high energy density electrodes

High Capacity Cathode Candidates of Organic & Inorganic Materials



January 16th, 2013, B787 flight emergency by LIB burst

http://news.goo.ne.jp/photo/kyodo/nation/PN2013011901001640.html

Accident shows the weakness of B787 "Electric airplane"

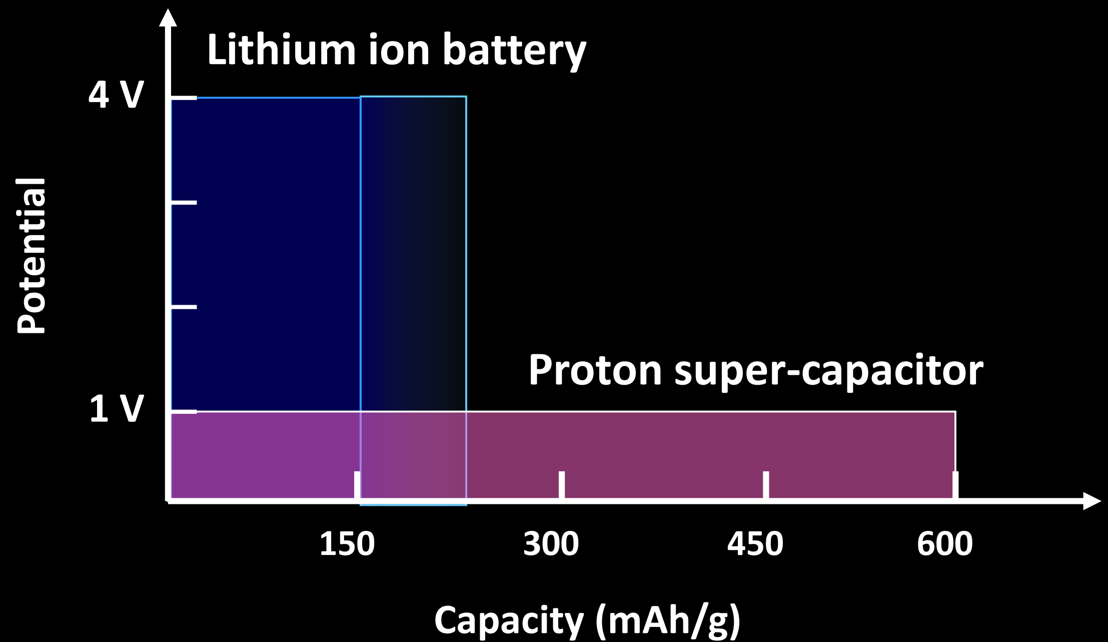
http://www.asahi.com/business/reuters/RTR201301160063.html

More safe, low cost, high energy density battery ?

Aqueous electrolyte in spite of organic

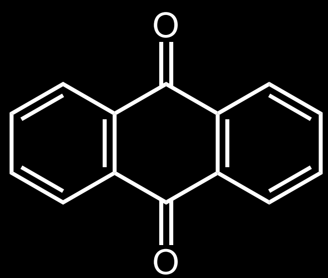
H^+ in stead of Li^+

Absolutely metal-free battery
(employing only 5 elements of H, C, O, Cl, S)

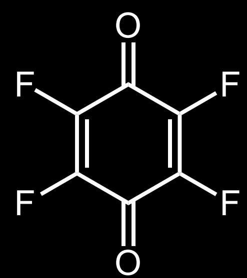


Large Redox Capacity of Organic Molecular Crystals

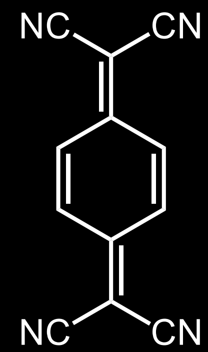
(Quinone)



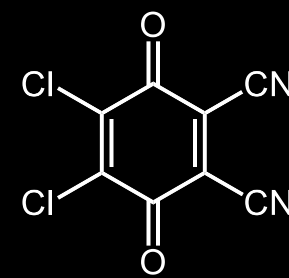
257 mAh/g
AQ
Anthraquinone



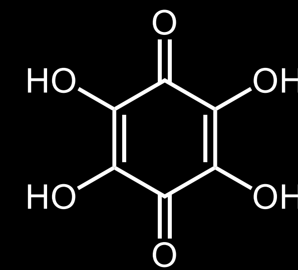
295 mAh/g
TFBQ
Tetrafluoro-benzoquinone



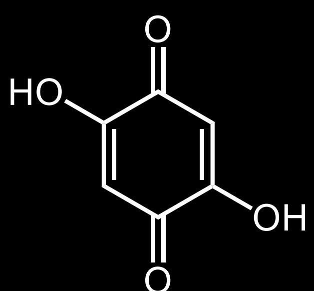
262 mAh/g
TCNQ
Tetracyano-quinodimethane



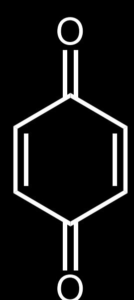
237 mAh/g
DDQ
Dichlorodicyano benzoquinone



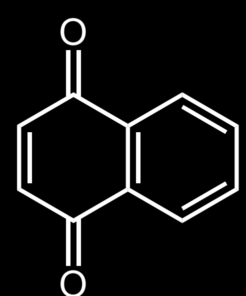
310 mAh/g
THBQ
Tetrahydroxy-benzoquinone



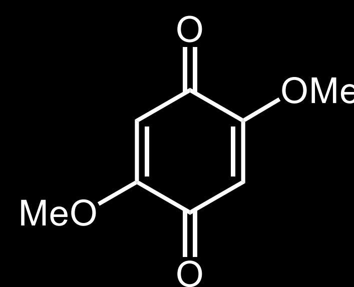
383 mAh/g
DHBQ
Dihydroxy-benzoquinone



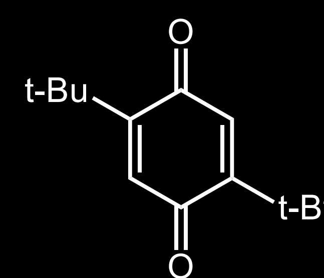
496mAh/g
BQ
Benzoquinone



339mAh/g
NQ
Naphthoquinone

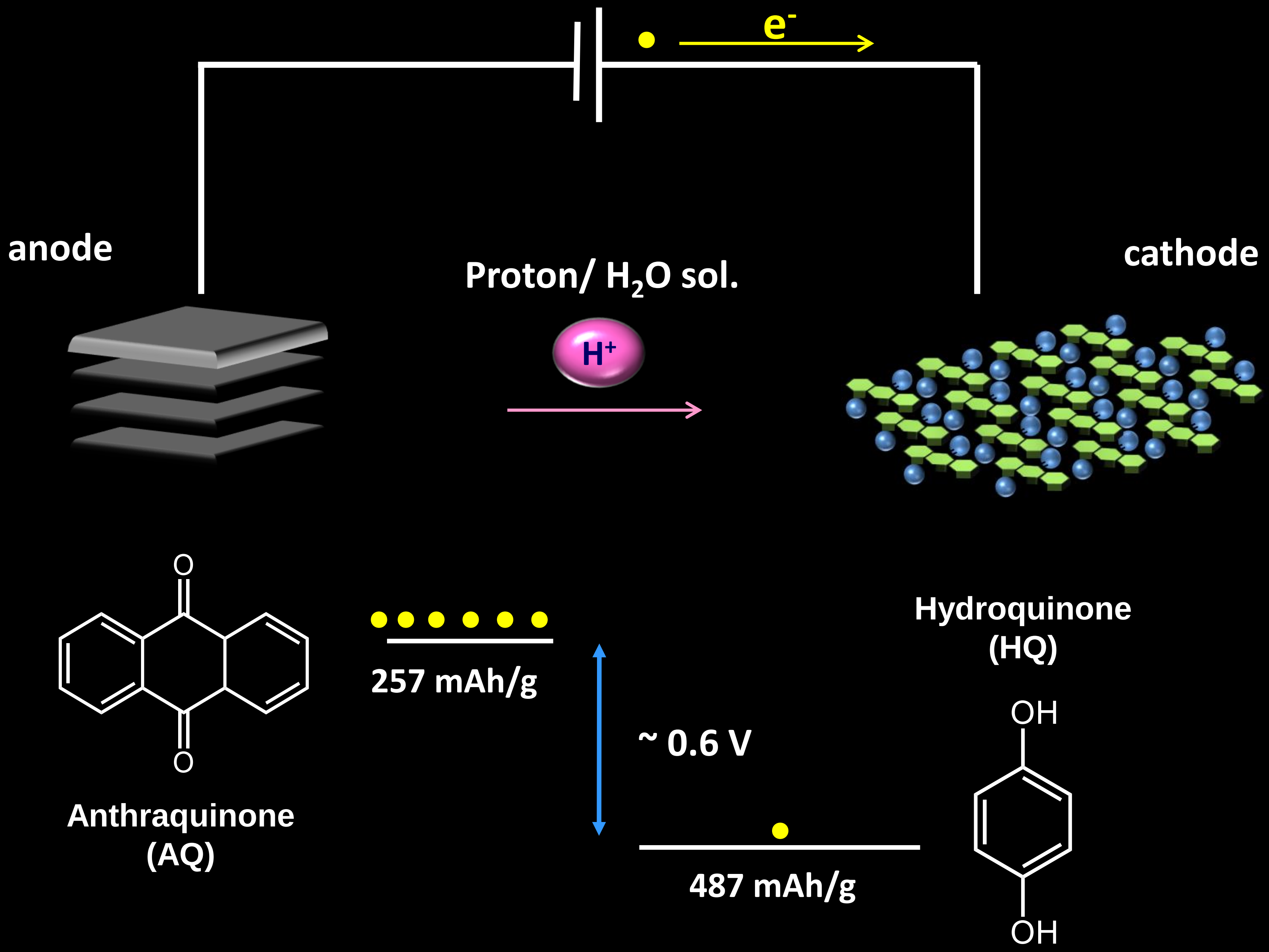


319mAh/g
DMBQ
Dimethoxy-benzoquinone



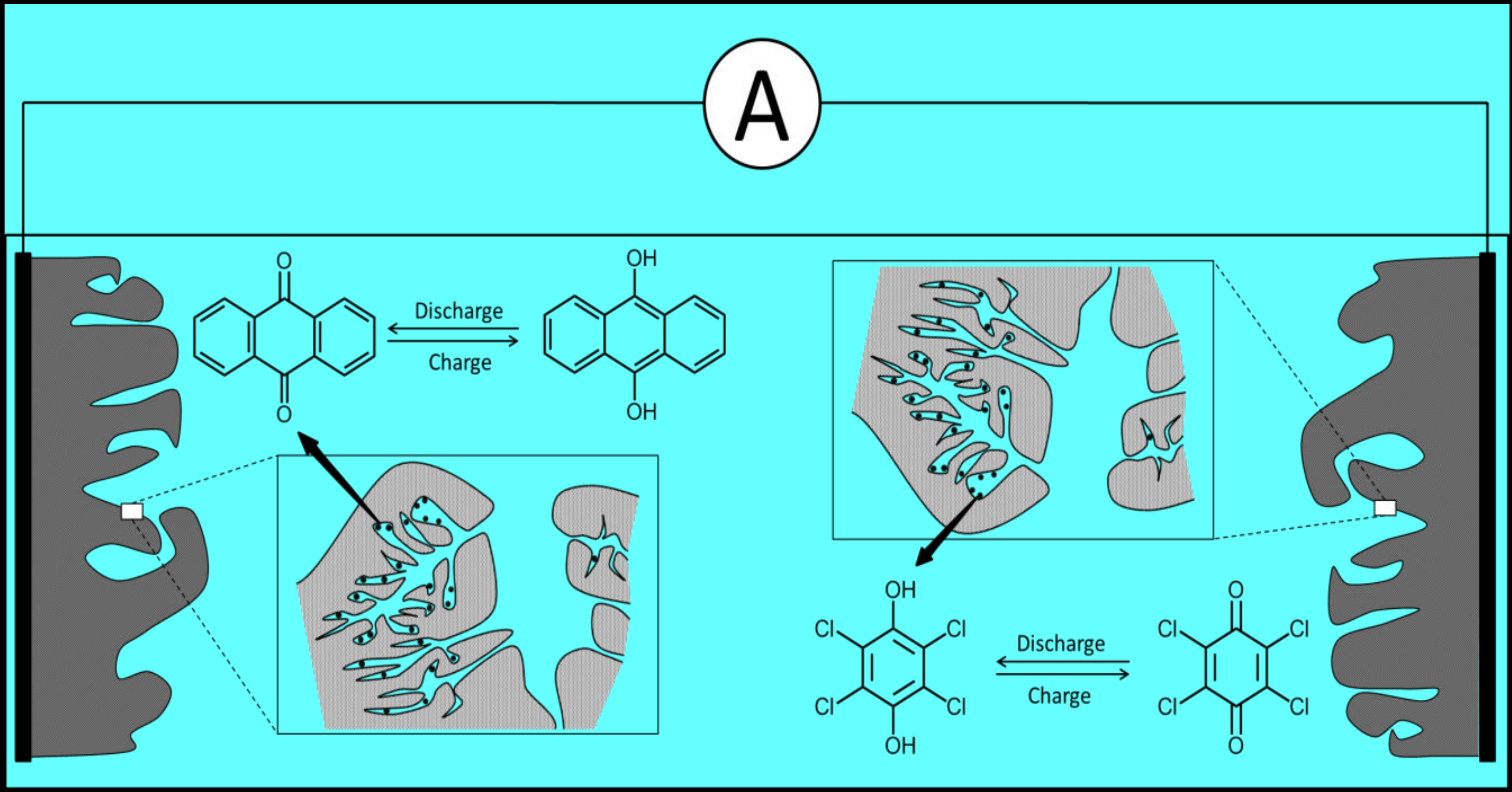
243mAh/g
DtBu-BQ
Di-t-Butyl-benzoquinone

Proton shuttle redox-capacitor



Organic nanocrystals in Nanoporous carbon electrodes

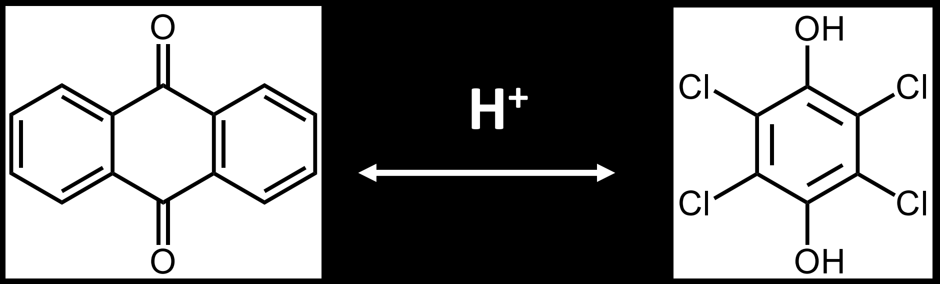
AQ (27wt.%)/Maxsorb /PTFE **TCHQ (27wt.%)/Maxsorb /PTFE**

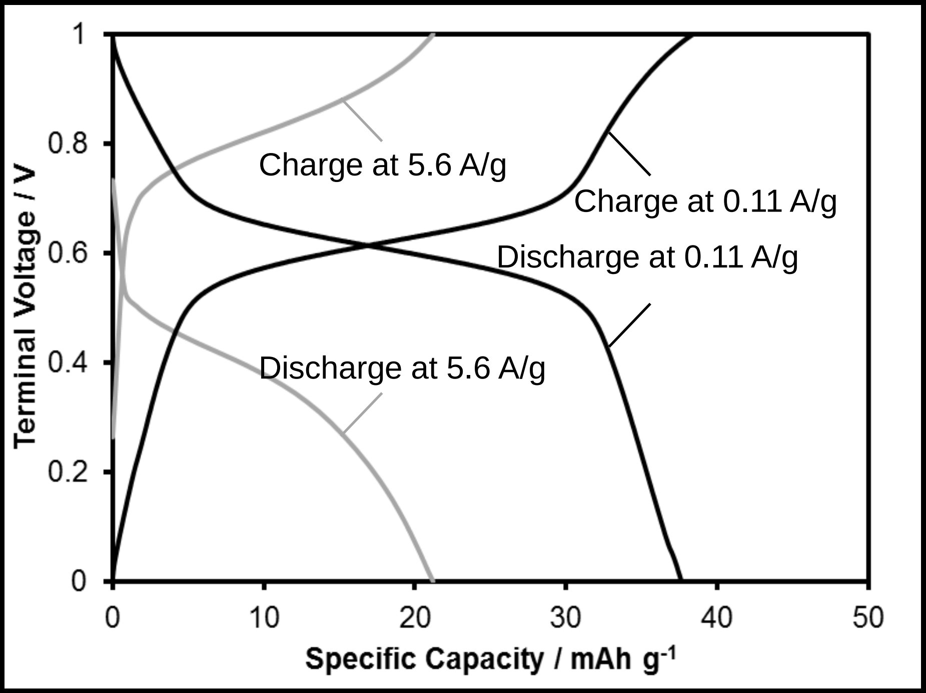


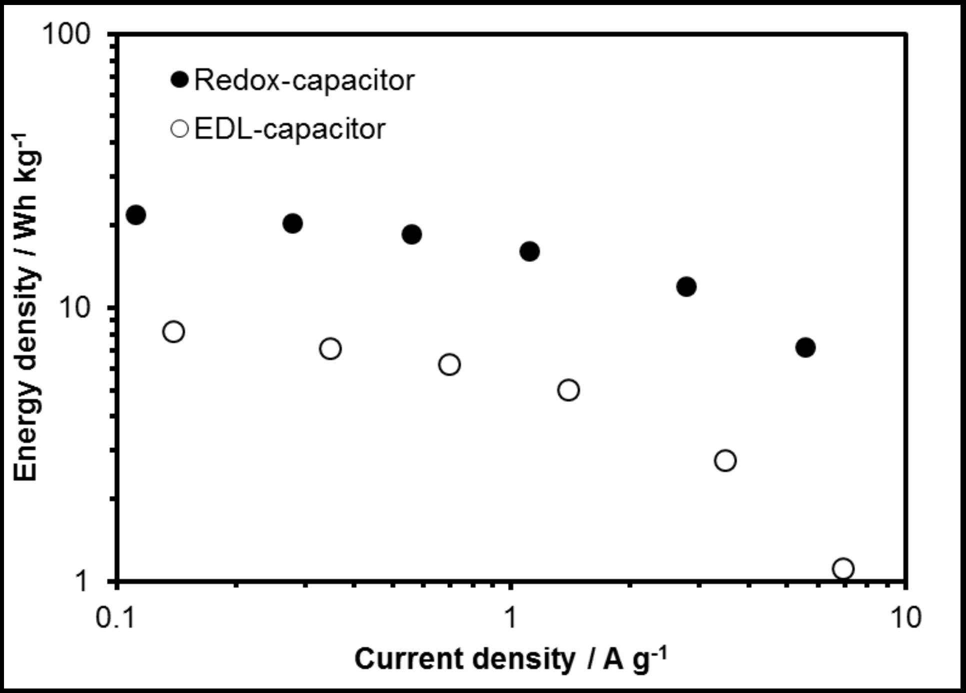
Organic nanocrystals are supported within 1-10nm sized Nanopores of carbon electrodes to suppress dissolution into the electrolyte solution

Rate capability of proton shuttle redox-capacitor

AQ(anode) – TCHQ(cathode)







Energy density and power density is larger than that of EDLC capacitor

Device potential of proton super-capacitor
(Proton shuttle redox-capacitor)

Battery device	Energy density	price	Cycle life	safety
EDLC	< 5 Wh kg^{-1}	◎	> 10000	◎
proton super-capacitor	10-20 Wh kg^{-1}	◎	> 1000	◎
Pb-acid	20-30 Wh kg^{-1}	○	< 1000	◎
Lithium ion capacitor	10-30 Wh kg^{-1}	△	> 10000	△
Lithium ion battery (LIB)	100-150 Wh kg^{-1}	△	~ 1000	△

The proton super-capacitor device in this work (only 5 elements of H, C, O, Cl, S are employed) is low cost, long cycle life and safety, however, has as same energy density as that of Pb-acid

➡ **Applications to stationary electricity storage for the smart grid, renewable energy (solar & wind power)**