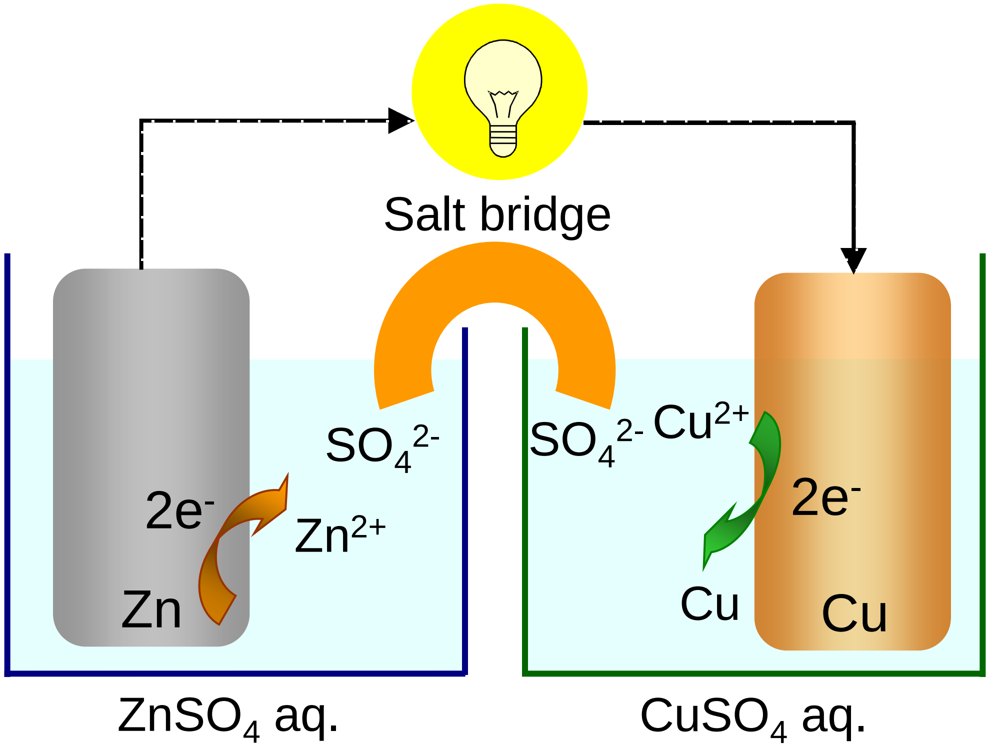
Organic Batteries

Hiro Nishide
Waseda University, Tokyo, Japan
Gwangju Institute of Science and Technology, Korea

Zinc-Copper Battery (Daniell Cell)




A Daniell Cell 1855

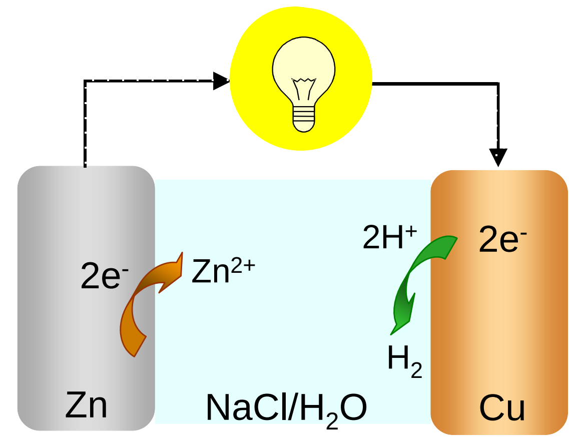
[Anode]

$Zn \rightarrow Zn^{2+} + 2e^-$

[Cathode]

$Cu^{2+} + 2e^- \rightarrow Cu$

Volta Cell



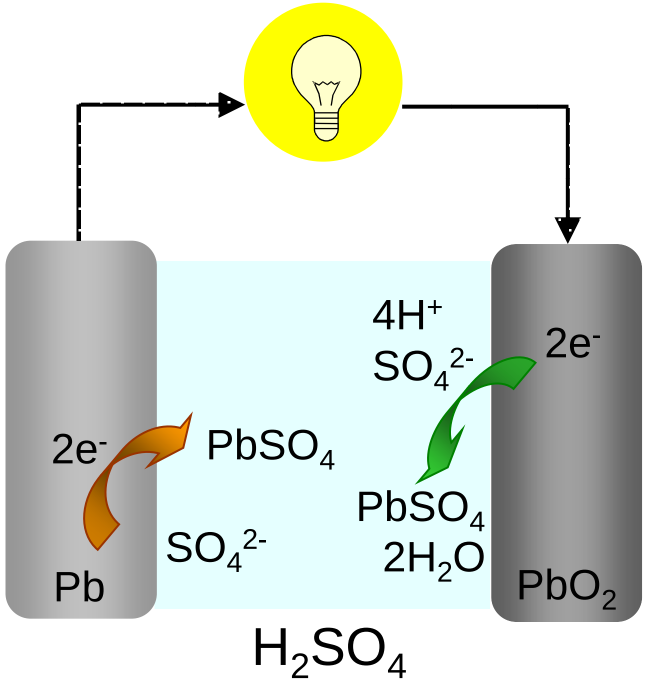
[Cathode]

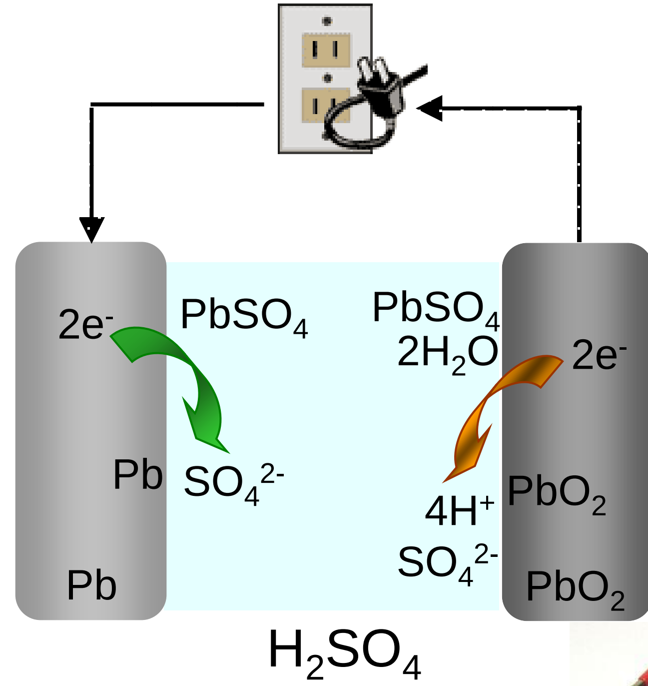
$2H^+ + 2e^- \rightarrow H_2$

Standard Redox Potential (Ionization Tendency)

(-) Li < K < Na < Zn < Fe < Co < Cu < Ag < Pt < Au (+)

Lead-acid Battery: Rechargeable/Secondary Battery





Discharging

[Anode]

$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

[Cathode]

$PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$

$\rightarrow PbSO_4 + 2H_2O$

Charging

[Anode]

$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$

[Cathode]

$PbSO_4 + 2H_2O$

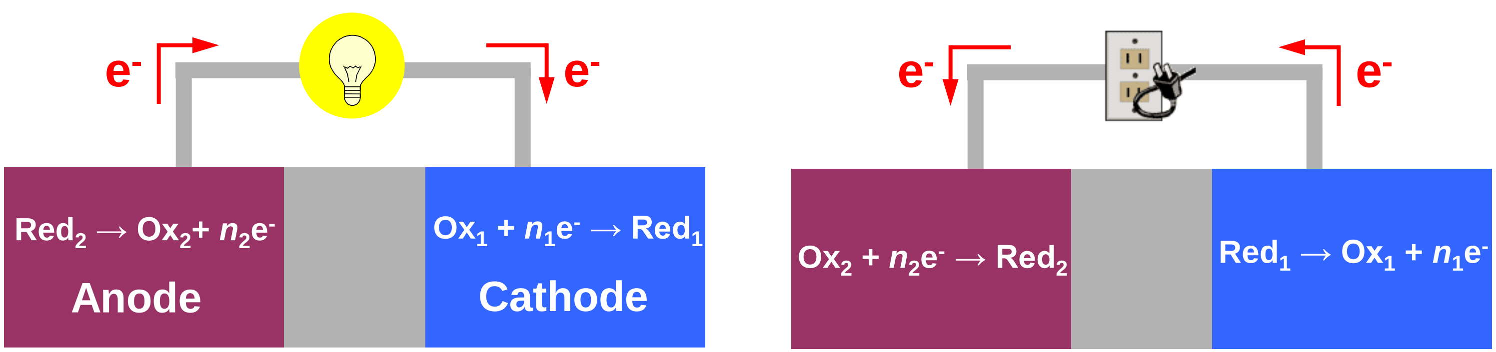
$\rightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$

Rechargeable/Secondary Battery

Definition: A rechargeable battery is a cell for the generation of electrical energy in which the cell, after being discharged, is restored to its original charged condition *reversibly* by an electric current flowing in the direction opposite to the flow of current when the cell was discharged.

Cell Configuration

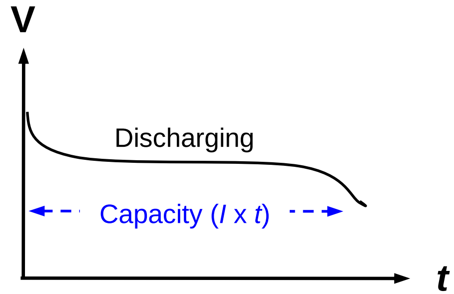
⊖ Negative Electrode	| Anode-active Material (= Reducing Agent)	| Electrolyte (Separator)	| Cathode-active Material (= Oxidizing Agent) |	⊕ Positive Electrode



Reversible Conversion Cell for "Chemical Reaction Energy ⇄ Electrical Energy"

Technical Terms in Battery (1)

Capacity: The quantity of electricity (Ah) that can be obtained by discharging until the cell reaches the end of life.



Electricity for 1 mol of e- = 1 Faraday (F) = 96485 C = 26.8 Ah.

Electrochemical Equivalent: The mass of element or molecule (in g) transported by 1 C of electricity.

Li (6.94 g/mol): $Li \rightarrow Li^+ + e^-$, 6.94/96485 = 7.19×10^{-5} g

PbO_2 (239 g/mol): $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$
239/(96485 x 2) = 1.24×10^{-3} g

Specific Capacity (in mAh/g or Ah/kg)
= 1000/(electrochemical equivalent x 3600)

Li: 1000/(7.19×10^{-5} x 3600) = 3860 mAh/g

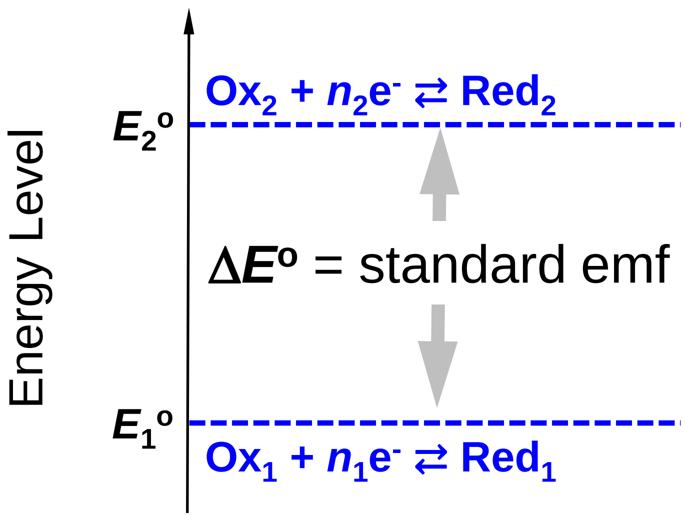
PbO_2: 1000/(1.24×10^{-3} x 3600) = 224 mAh/g

Technical Terms in Battery (2)

Electromotive Force (emf): A difference in electric potential that tends to give rise to electric current.

⊖ Anode | $Red_2 \rightleftarrows Ox_2$ | Electrolyte | $Ox_1 \rightleftarrows Red_1$ | Cathode ⊕

<u>*Overall:*</u> $\boldsymbol{n_2 Ox_1 + n_1 Red_2 \rightleftarrows n_2 Red_1 + n_1 Ox_2}$



$E_2 = E_2^o - RT/(n_2F)\ \ln(a_{Red_2}/(a_{Ox_2})$

⇨ Anode

$E_1 = E_1^o - RT/(n_1F)\ \ln(a_{Red_1}/(a_{Ox_1})$

⇨ Cathode

emf: $E = \boldsymbol{E_1} - \boldsymbol{E_2} = \Delta E^o - RT/(n_1 n_2 F)\ \ln\{(a_{Red_1}{}^{n_2} a_{Ox_2}{}^{n_1})/(a_{Ox_1}{}^{n_2} a_{Red_2}{}^{n_1})\}$

Cell Voltage: $V = E$ (emf) $- IR$

Technical Terms in Battery (3)

Power: P (W) = current I (A) x cell voltage V (V)

C Rate: 1C (or 1 I_t) Discharging corresponds to the constant-current discharging of rated capacity at 1 h.

For example, the 1 C discharging of a lead acid battery with a rated capacity of 12 Ah corresponds to the discharging at 12 A, and 2 C corresponds to the discharging at 24 A. The C rate is also used to show the charging current.

Faraday Efficiency (Coulomb Efficiency):
Efficiency of active mass (=electrode-active material)
= (actual capacity) / (theoretical capacity)

Self Discharge: The loss of performance when a battery is not in use.

Li−MnO_2 primary battery will deliver 90% of their energy even after 8 years on the shelf; that is, its self-discharge is low. Rechargeable batteries are generally have more rapid loss of capacity on storage. The rechargeable Ni−MH cell, for instance, will lose up to 30% of its capacity in a month.

Technical Terms in Battery (4)

Cyclability: Capability of charging/discharging cycles without loss of capacity.

A commercial cell must be capable of completely discharging and then fully recharging for >300 times and not lose >20% of its capacity, which requires a robust system and reversible electrode reactions. There can be no side reactions that result in the loss of the active materials during the cycle. High cyclability secondary batteries reduce their environmental load.

Electrode-Active Materials: An electrode-active material (or active mass) is the material that generates electrical current by means of a chemical reaction within the battery.

- The *anode*-active material is used in the negative electrode associated with oxidative chemical reactions that release electrons into the external circuit during discharging.
- The *cathode*–active material is used in the positive electrode associated with reductive chemical reactions that gain electrons from the external circuit during discharging.

Requisites for Electrode-Active Materials

Energetically**,**

✓The standard potentials (E^o) for the anode and cathode active materials must be largely different to produce a large emf.

✓The specific capacity (in mAh/g) must be large for high energy density.

Kinetically**,**

✓The redox reaction must be rapid, to allow excellent rate performance.

✓The electrode-active layer must be substantially conductive for small *IR* drop.

✓When ion inclusion/exclusion is involved in the electrode reaction, the mass transfer must be rapid.

Other Requisites:

✓Redox cyclability.

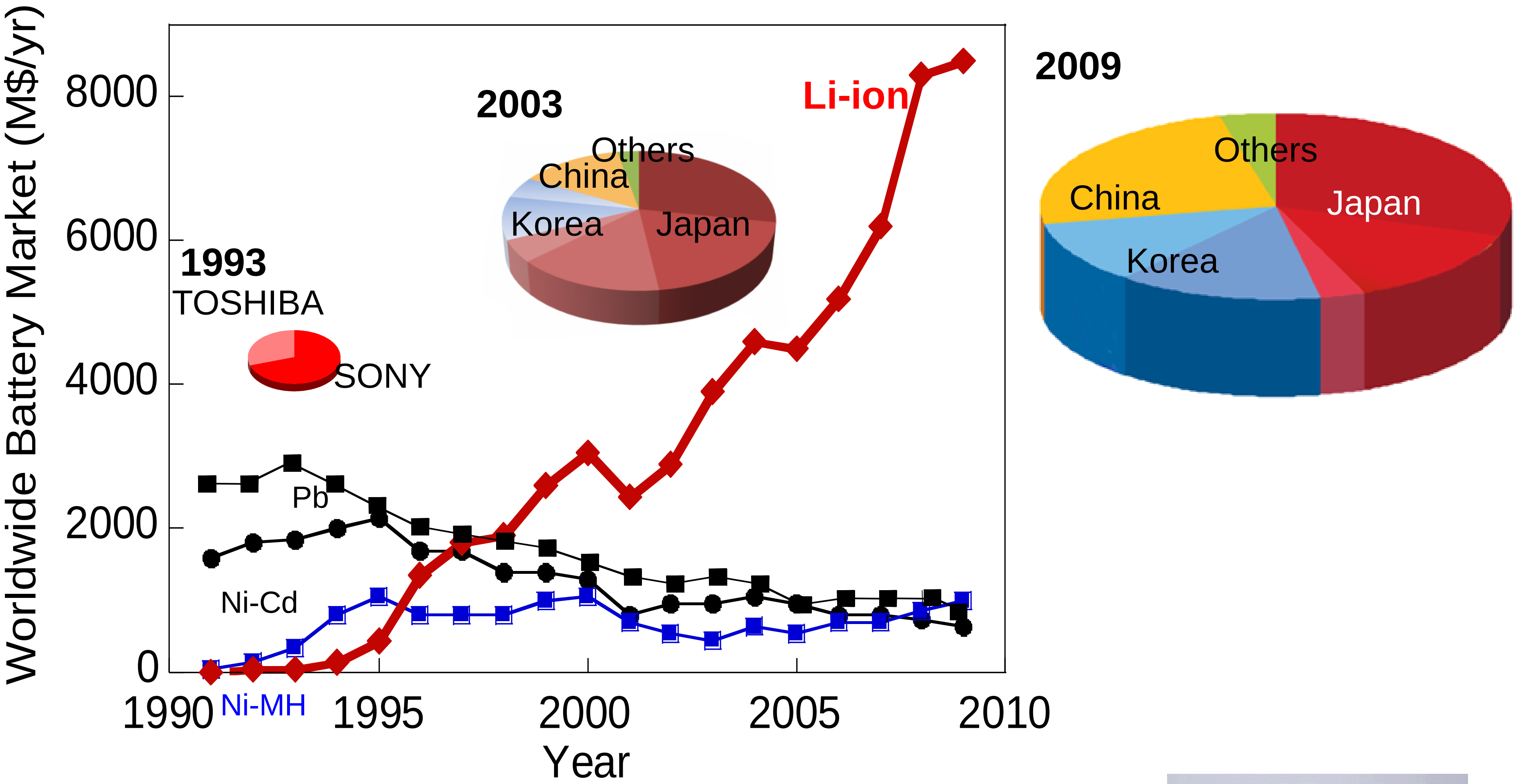
✓Insolubility in electrolyte solutions, to avoid self-discharge.

Organic batteries use organic redox-active molecules, which are typically polymers, for the electrode-active materials.

Sustainable Battery

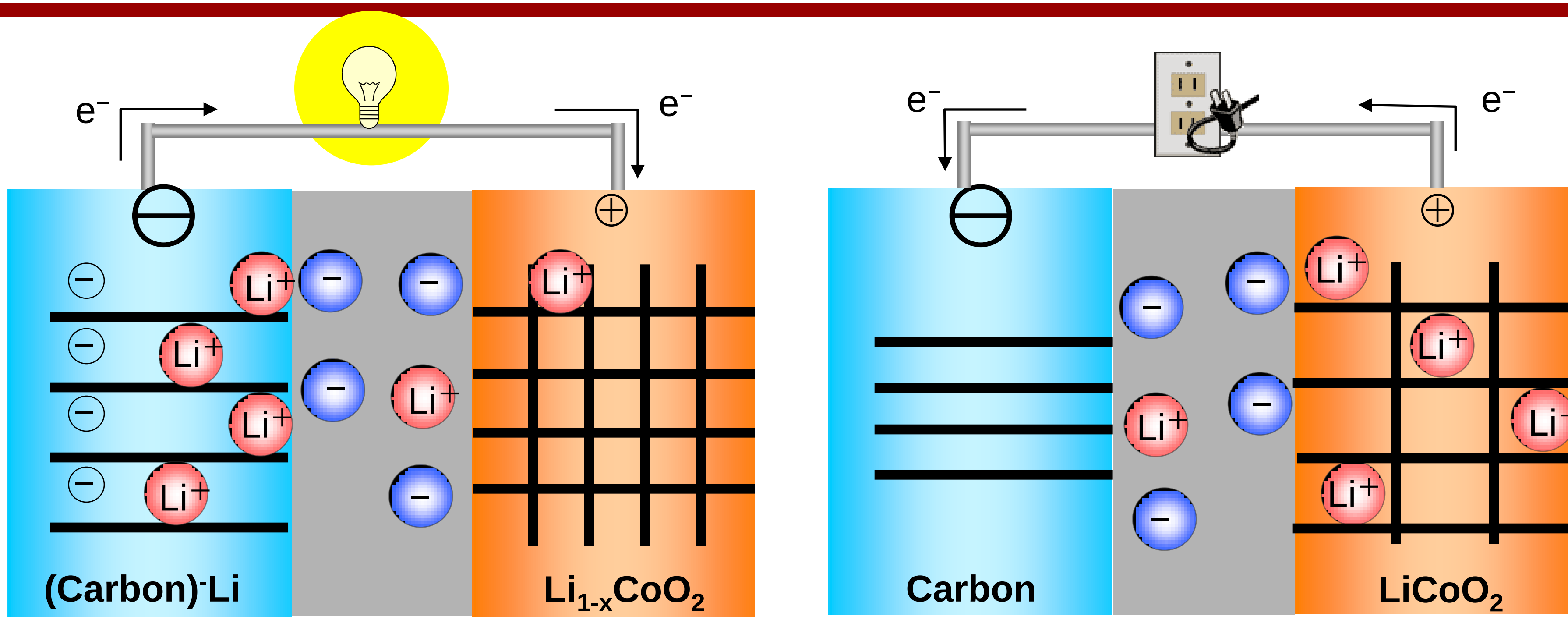
Energy devices designed to store and supply electric power, characterized by clean and reduced CO_2 emission, effective utilization of alternative fuels, low environmental load, and safety, for a sustainable society. Organic batteries are inherently sustainable, owing to the environmentally benign fabrication and disposing processes, low toxicity and safety, based on the use of organic, resource-unlimited, and heavy metal-free materials.

Global Production of Li-ion Batteries in 2009



Source: Calculated from data of Japanese Battery Industry Association (2010)

Li-Ion Battery



Lithium-ion Intercalation Materials

Discharging

[Cathode]

$2Li_{0.5}CoO_2 + Li^+ + e^- \rightarrow 2LiCoO_2$

[Anode]

$C_6Li \rightarrow C_6 + Li^+ + e^-$

Charging

[Cathode]

$2LiCoO_2 \rightarrow 2Li_{0.5}CoO_2 + Li^+ + e^-$

[Anode]

$C_6 + Li^+ + e^- \rightarrow C_6Li$

[Overall Reaction] $0.5C_6Li + Li_{0.5}CoO_2 \underset{\text{Charging}}{\overset{\text{Discharging}}{\rightleftarrows}} C_3 + LiCoO_2$: 100 mAh/g

Why Li Ion Battery ?

Why intercalation of Li ion ?

✓Li ion is separated from each other, to suppress metallic Li (dendrite) formation.

Why Li ion?

✓The highest voltage ($0.5C_6Li + Li_{0.5}CoO_2 \rightleftarrows C_3 + LiCoO_2$: 3.6 V)
✓Large anode capacity ($Li_xC \rightarrow xLi^+ + xe^- + C$: 372 mAh/g)
✓Large specific capacity (3860 mAh/g)
✓The highest energy density (360 mWh/g)
✓Light weight (high energy density)

Why Li ion is unstable?

✓Slow kinetics on the Li-ion diffusion into electrodes
✓Heat generation (lattice transformation of $LiCoO_2$, short circuit formation by metallic impurities)
✓Ignition, explosion (metallic Li formation by overcharging, side reaction of Li_xC and $Li_{1-x}CoO_2$ with electrolytes)

Conventional Primary and Secondary Batteries

Batteries	Cathode	Anode	Voltage (V)
Manganese oxide battery	MnO_2	Zn	1.5
Alkaline battery	MnO_2	Zn	1.5
Silver oxide battery	Ag_2O	Zn	1.6
Air battery	O_2	Zn	1.4
Lead acid battery	PbO_2	Pb	2
Nickel-cadmium battery	NiOOH	Cd	1.2
Nickel metal-hydride battery	NiOOH	MH(H)	1.2
Vanadium-lithium battery	V_2O_5	Li-Al	3
Lithium-ion battery	$LiCoO_2$	C	4

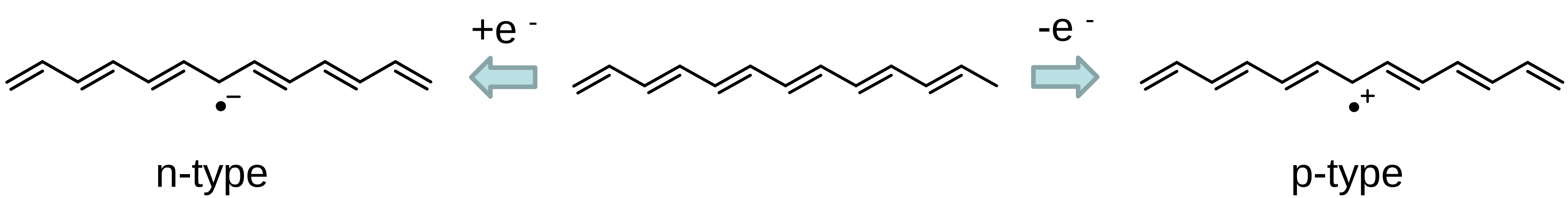
All of the conventional batteries are made up of HEAVY METALS !

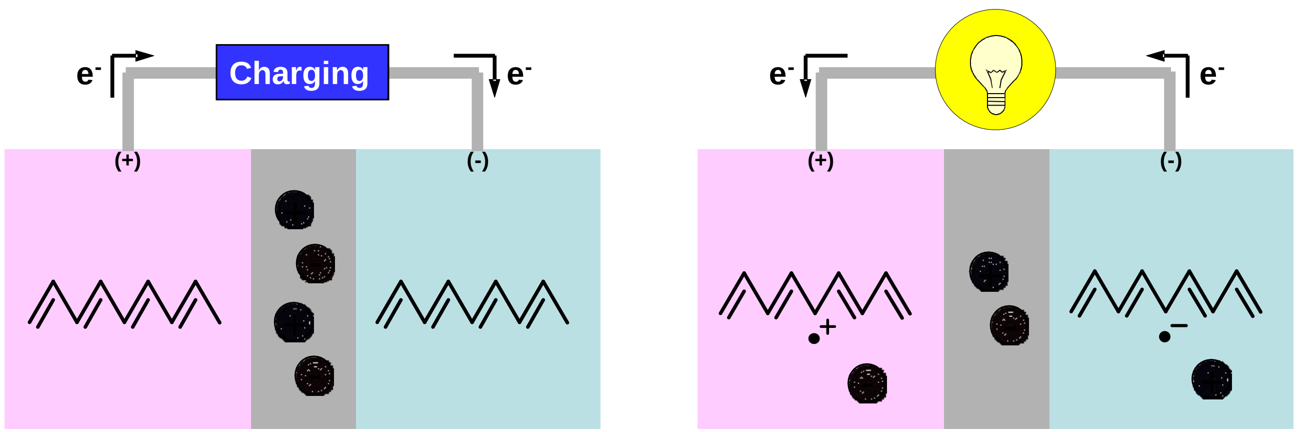
- *Given voltage is automatically governed by the coupling metal and metal oxide species.*
- *Limited metal resources / Tedious wasting processes / Non-safety such as ignition.*

Reversible n- and p-Type Electrochemical Doping of Polyacetylene:an Organic Battery

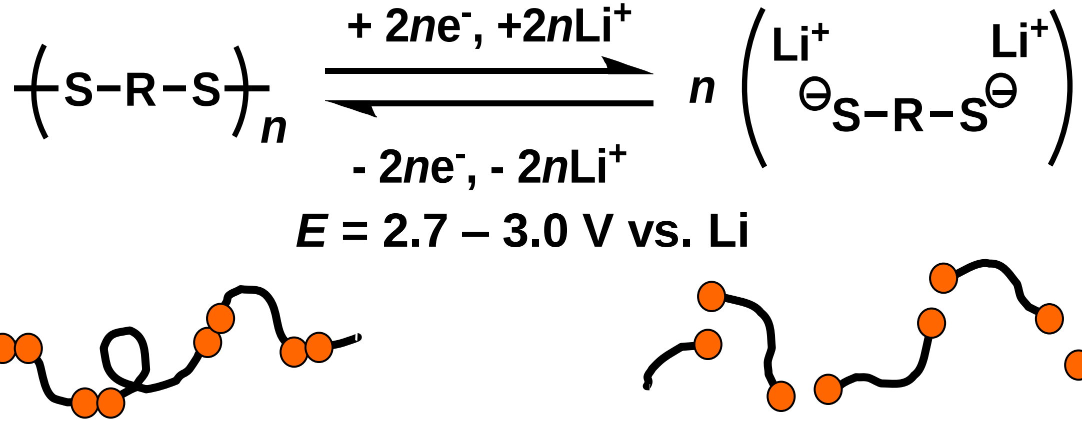
A. G. MacDiarmid and A. J. Heeger, *Chem. Commun.*, 317 (1981)

Films of polyacetylene, $(CH)_x$ are electrochemically and reversibly doped n-type and p-type, which may be utilized as the anode- and/or cathode-active material in a rechargeable battery.



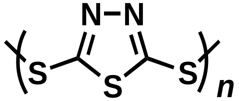


Organo-disulfide/dithiol Redox Polymers

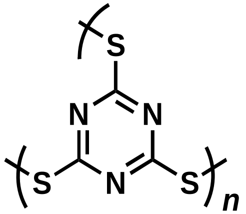


Disulfide

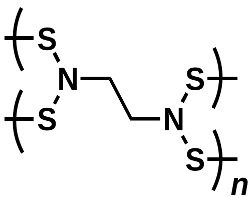
Dithiolate salt



362 mAh/g



461 mAh/g



723 mAh/g

<u>Advantage</u>

High theoretical charge capacity

<u>Limitation</u>

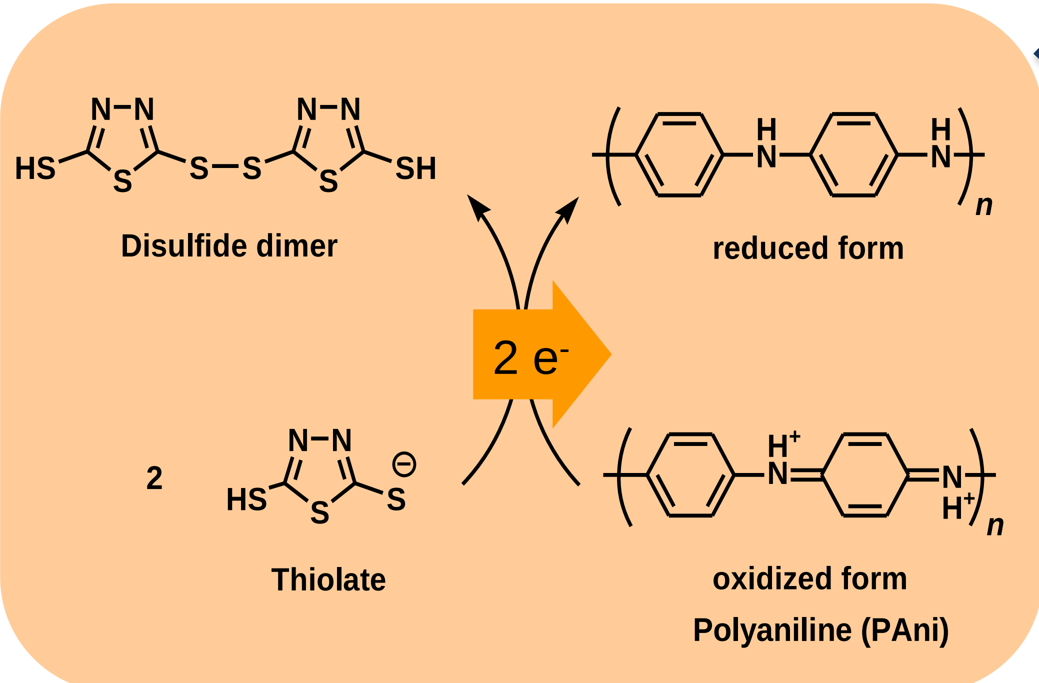
Bond chain formation/scission (slow kinetics)

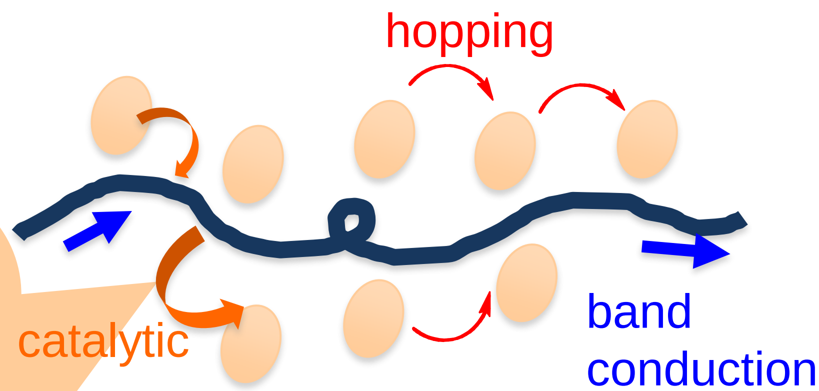
Possible nasty oder

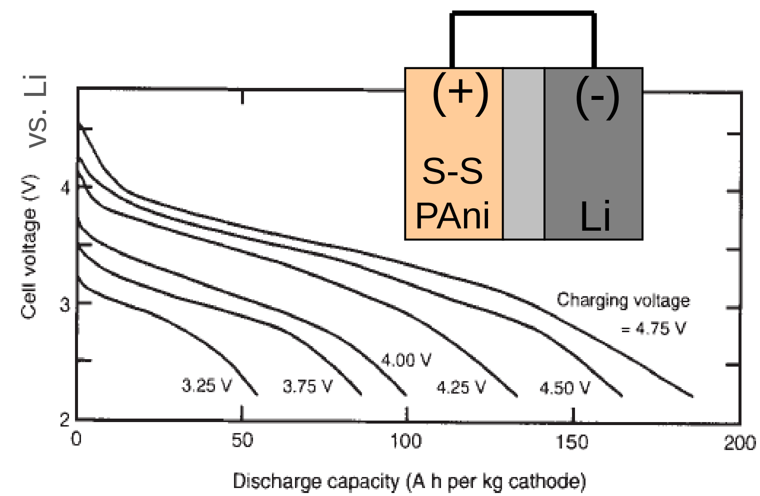
S. J. Visco, *J. Electrochem. Soc.*, **138**, 1891 (1991)

Organosulfur Materials + Conducting Polymer

Blending with Conducting Polymer





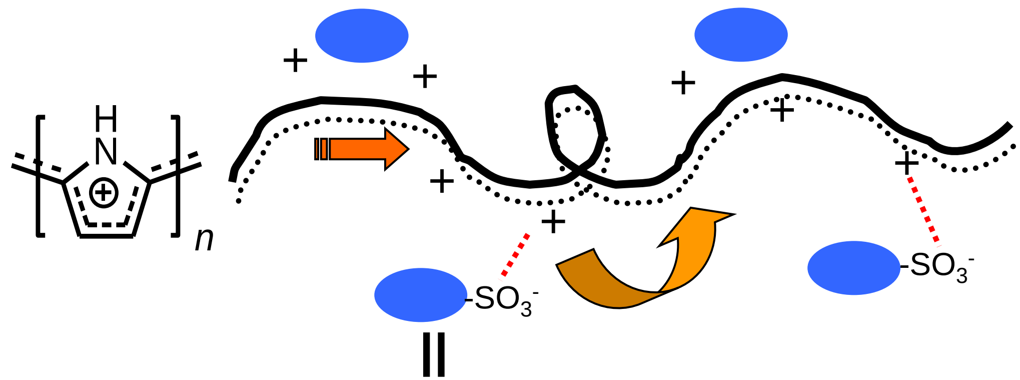


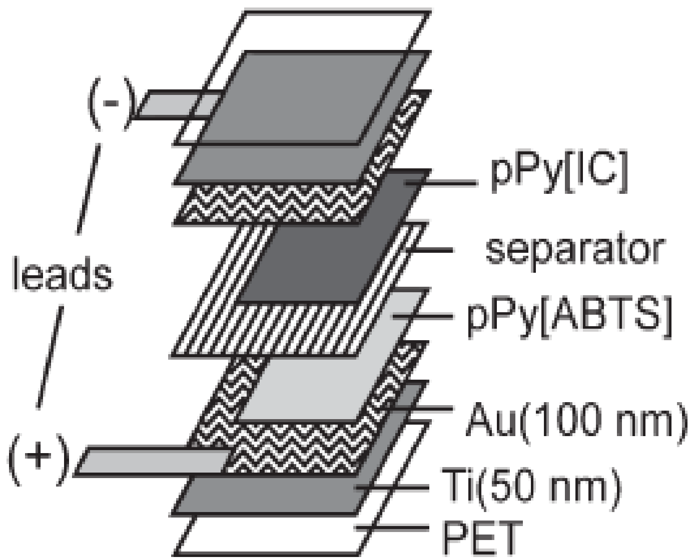
Polyaniline serves as a conducting pathway.

N. Oyama, *Nature*, **373**, 599 (1995)

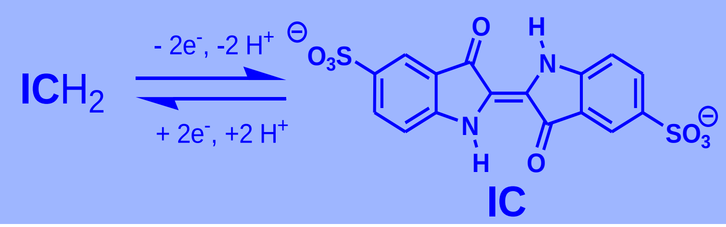
Conducting Polymer Doped with Redox-Active Dopant

Redox-active dopant was incorporated into p-doped polypyrrole (pPy) by electrostatic interaction.

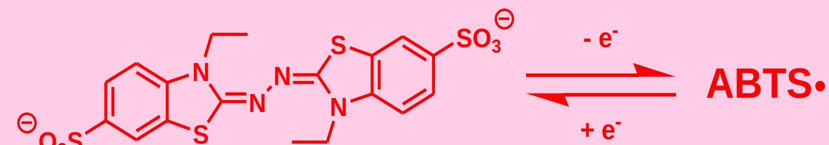




Redox-active Dopant (n-type)



Redox-active Dopant (p-type)



ABTS

<u>Limitation</u>

・Limited loading amount of redox-active dopants due to the low doping degree

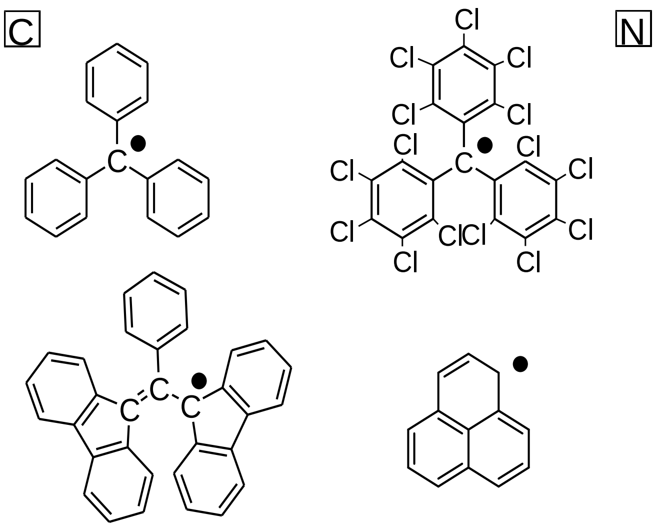
・Lack of long-term stability out of the dopant

G. T. R. Palmore, *Adv. Mater.*, **18**, 1764 (2006)

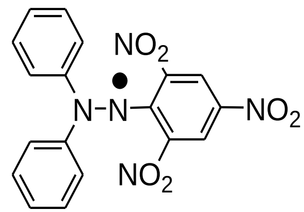
Robust Organic Radicals

- sterically protected structure
- resonanced structure

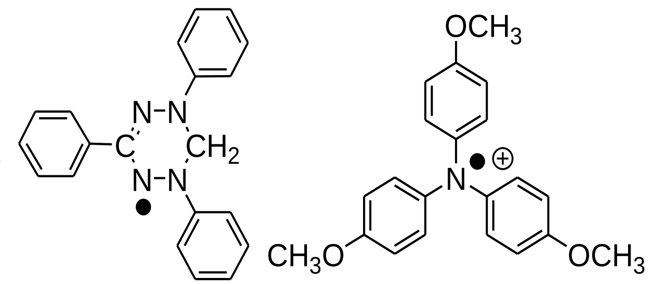
C

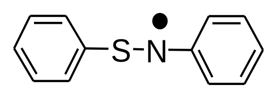


N

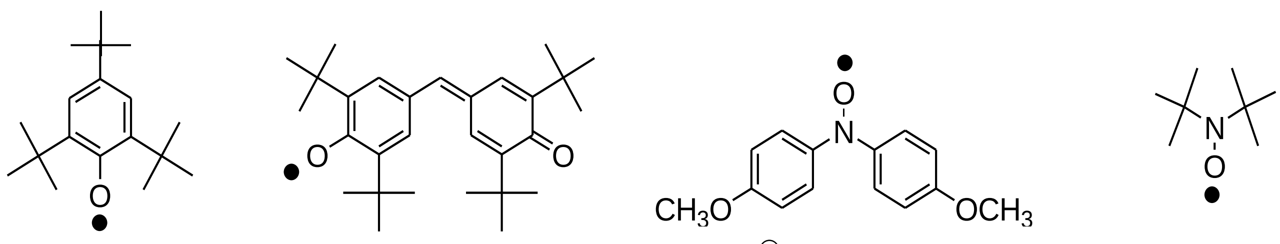


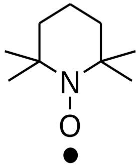
DPPH



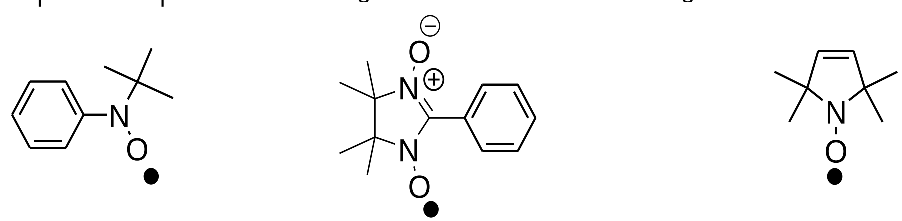


O

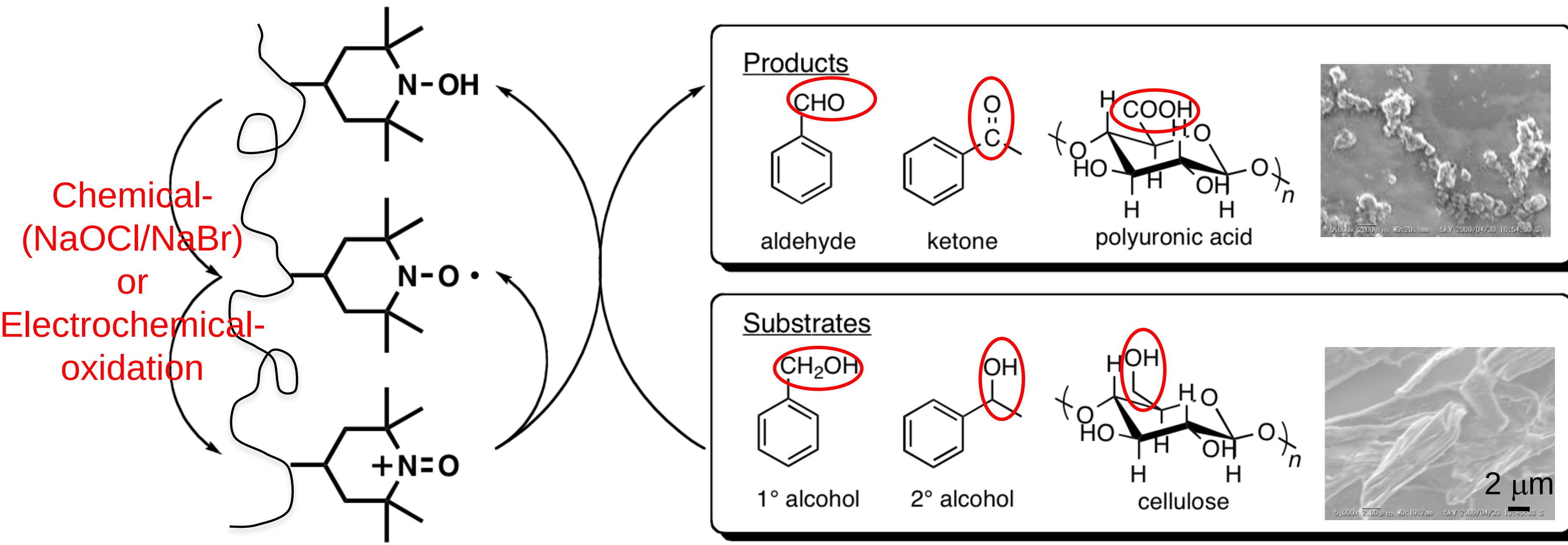




TEMPO

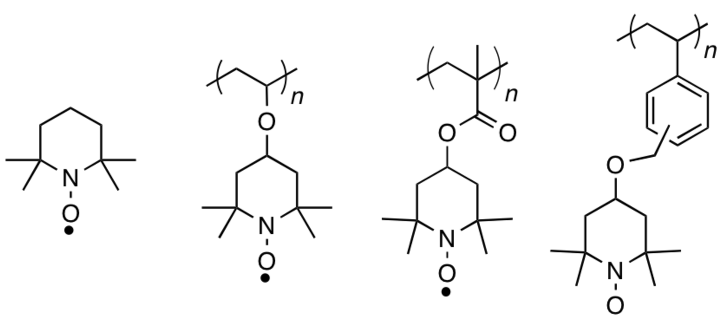


TEMPO-Mediated Oxidation: Green Catalyst



Nitroxide Polymer

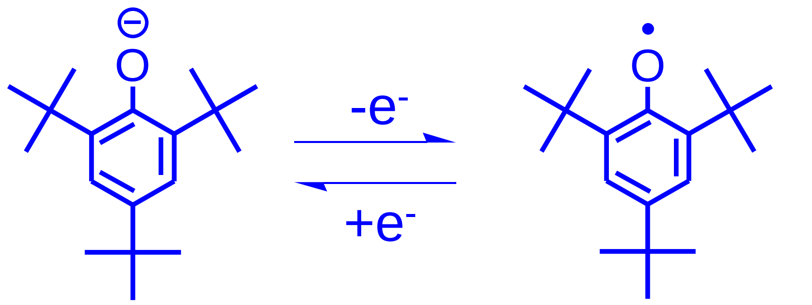
Room temp., 1 day.



Polymer-supported catalysts
-Facile removal by simple filtration
-Metal-free / Environmental-benign

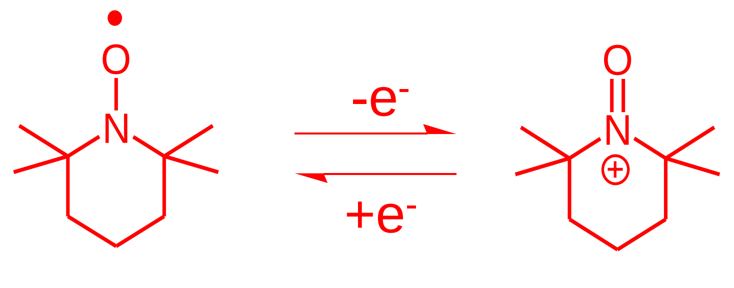
p- and n-type Redox Couples of Organic Radicals

n-type: anode-active

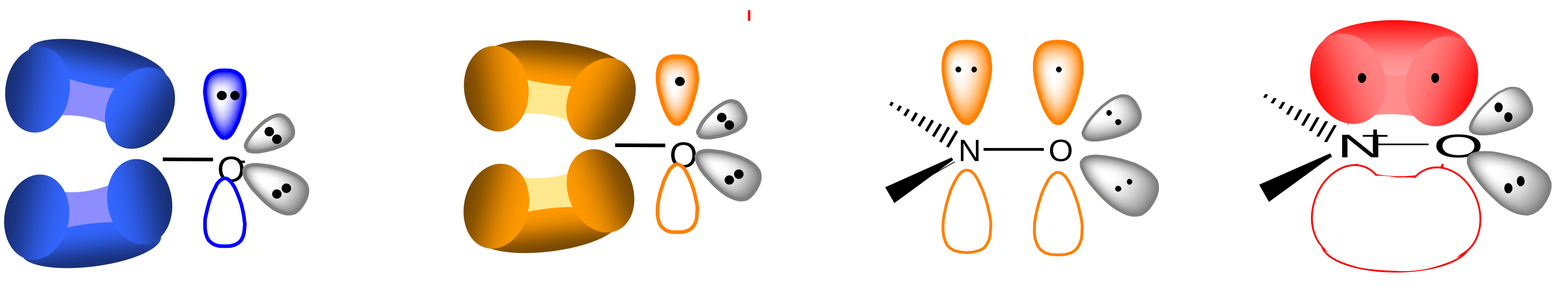


phenolate anion phenoxyl radical

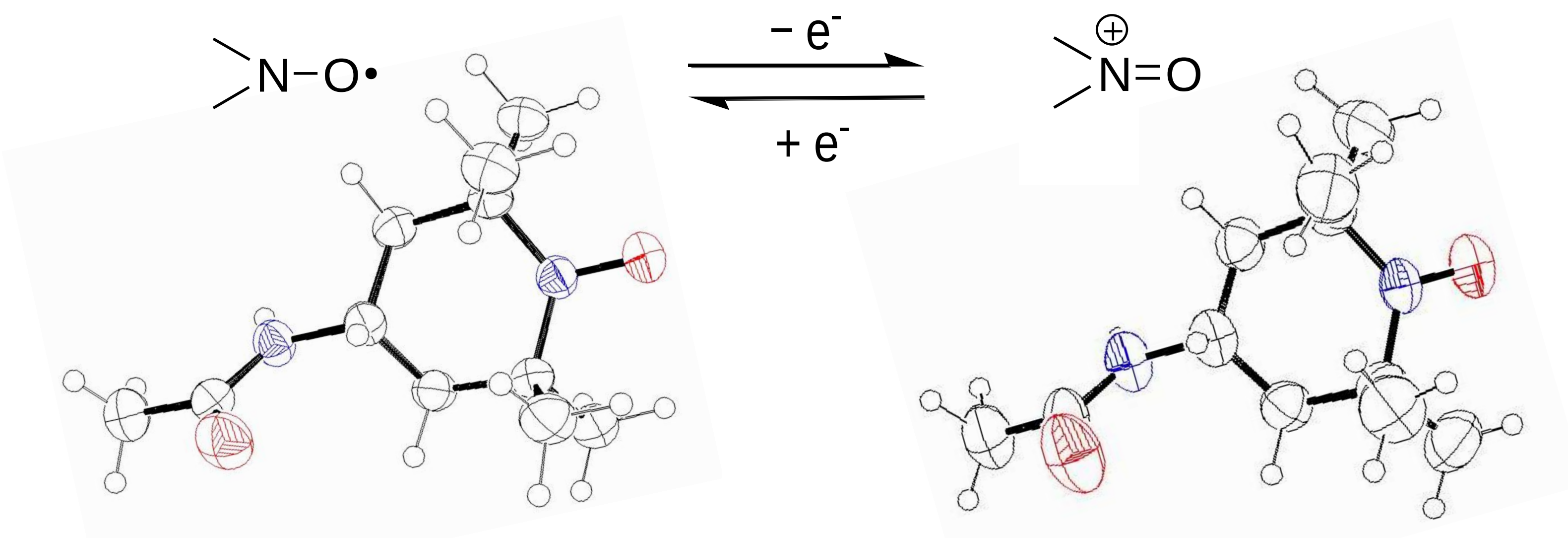
p-type: cathode-active



nitroxide radical oxoammonium cation

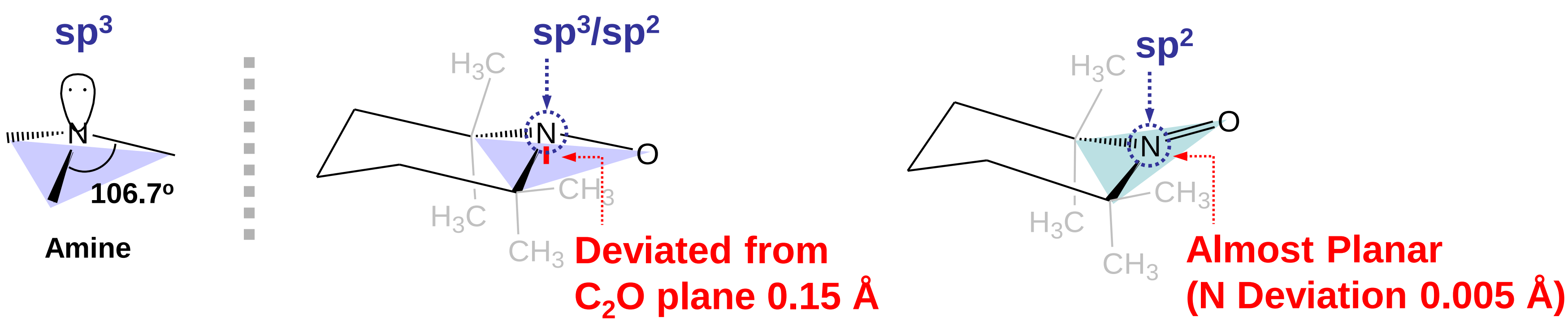


Nitroxide Radical and Oxoammonium Cation



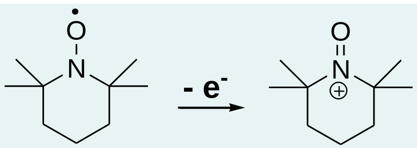
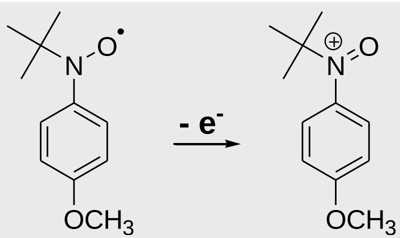
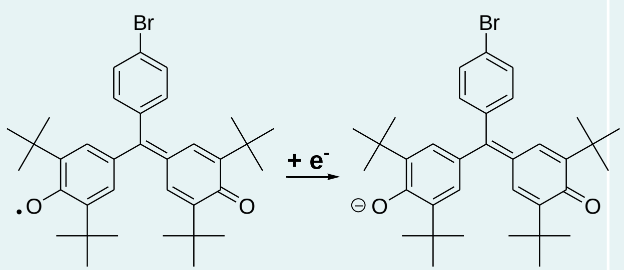
N-O	1.28 Å
IR $\nu_{N\text{-}O}$	1467 cm^{-1}
∠O-N-C	112°

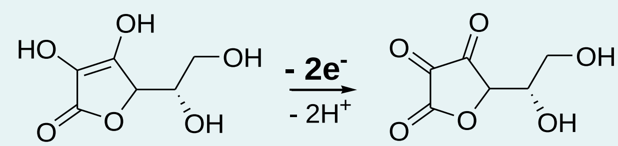
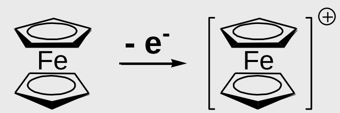
N-O	1.18 Å
IR $\nu_{N\text{-}O}$	1626 cm^{-1}
∠O-N-C	122°



Chem. Lett., **36**, 866 (2007).

Electron Transfer Rate Constant k_0 for Radical Molecules in Solution

Redox Reaction	k_0 (cm/s)
	1.0×10^{-1}
	1.7×10^{-1}
	0.38×10^{-1}

Redox Reaction	k_0 (cm/s)
	$\sim 10^{-4}$
	$\sim 10^{-2}$
$2\ C_4H_9SH \xrightarrow[-\ 2H^+]{-\ 2e^-} C_4H_9S\text{-}SC_4H_9$	$\sim 10^{-8}$
$Cu \xrightarrow{-\ e^-} Cu^+$	$\sim 10^{-1}$

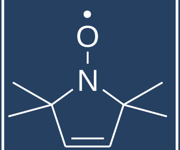
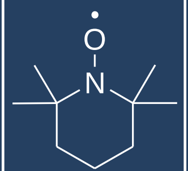
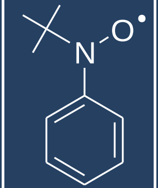
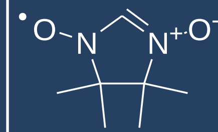
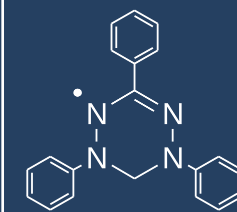
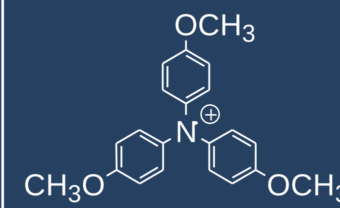
Radical Molecules: $k_0 = 10^{-1}$—10^{-2} cm/s

➡ ***Very Rapid 1e⁻ Transfer***

Bull. Chem. Soc. Jpn., **77**, 2203 (2004).

Molecular Designing of Radical Groups

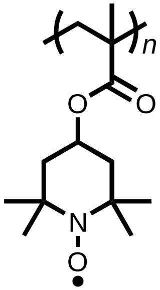
for High-Performance Charge Transport/Storage

Radical								
Capacity (Mol. Wt.) ($mAhg^{-1}$)	186	191	172	163	171	64	86	80
Electron Transfer Rate Const. k_0 ($cm\ s^{-1}$)	10^{-2}	10^{-2}	10^{-1}	10^{-2}	p: 10^{-1} n: 10^{-2}	10^{-2}	p: 10^{-2} n: 10^{-2}	10^{-3}
Electron Exchange Rate Constant k_{ex} ($M^{-1}s^{-1}$)	10^9	10^9	10^9	10^7	10^7	10^9	p: 10^7 n: 10^6	10^8
Durability $\tau_{half\ life}$	3 d	6 m	6 m	3 d	2 m	1 m	6 m	1 m

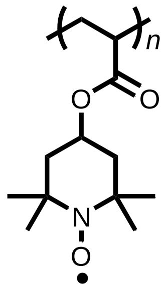
K. Oyaizu, H. Nishide, in “Handbook of Radical Chemistry and Biology”, Ed. A. Studer, Wiley (2011)

Nitroxide Radical Polymers Based on Various Polymer Backbones

(1) poly(meth)acrylate

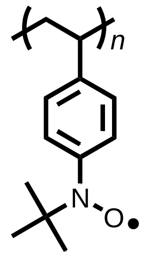


111 mAh/g

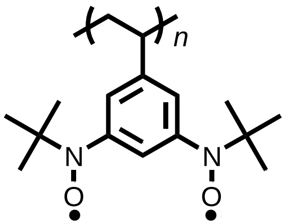


118 mAh/g

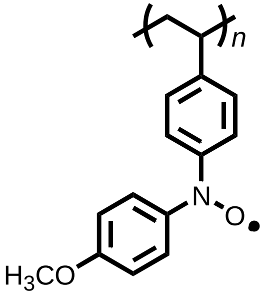
(2) polystyrene



141 mAh/g

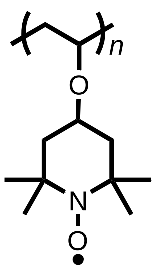


193 mAh/g



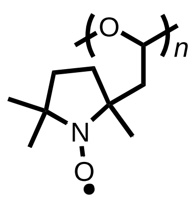
112 mAh/g

(3) poly(vinyl ether)

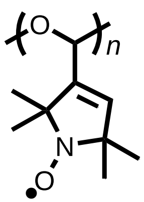


135 mAh/g

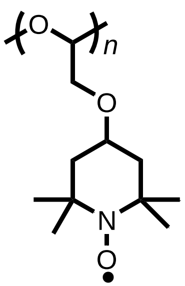
(4) polyether



145 mAh/g

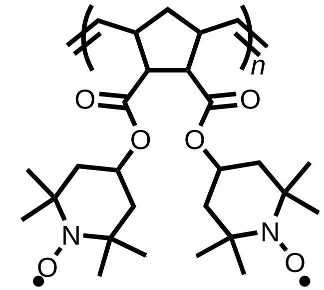


147 mAh/g



118 mAh/g

(5) polynorbornene



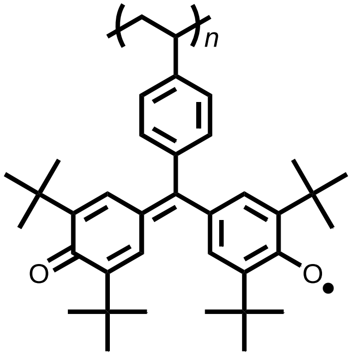
109 mAh/g

Electrochim. Acta, **50**, 827 (2004); *Macromolecules,* **40**, 3167 (2007);*Chem. Commun.*, 1730 (2007); *Macromolecules*, **41**, 6646 (2008); *J. Phys. Chem.*, **B144**, 8335 (2010); *Chem. Lett.*, **40**, 222 (2011)

n-Type Radical Polymers

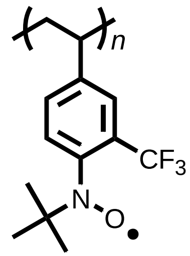
$$R\cdot + e^{-} \rightleftharpoons R^{\ominus}$$

(1) Galvinoxyl radical

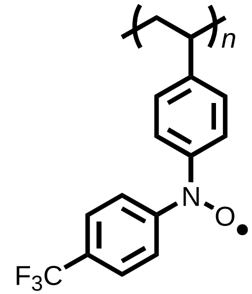


51 mAh/g

(2) CF_3-substituted nitroxides

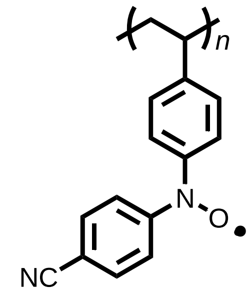


141 mAh/g



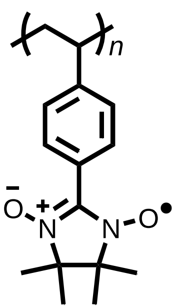
96 mAh/g

(3) CN-substituted nitroxides



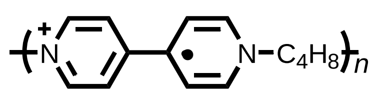
114 mAh/g

(4) Nitronyl nitroxides



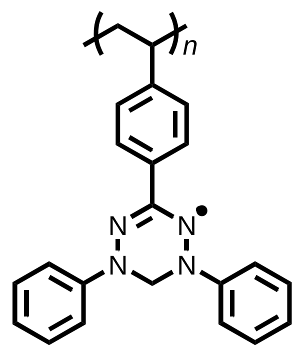
103 mAh/g

(5) Viologen



126 mAh/g

(6) Verdazyl

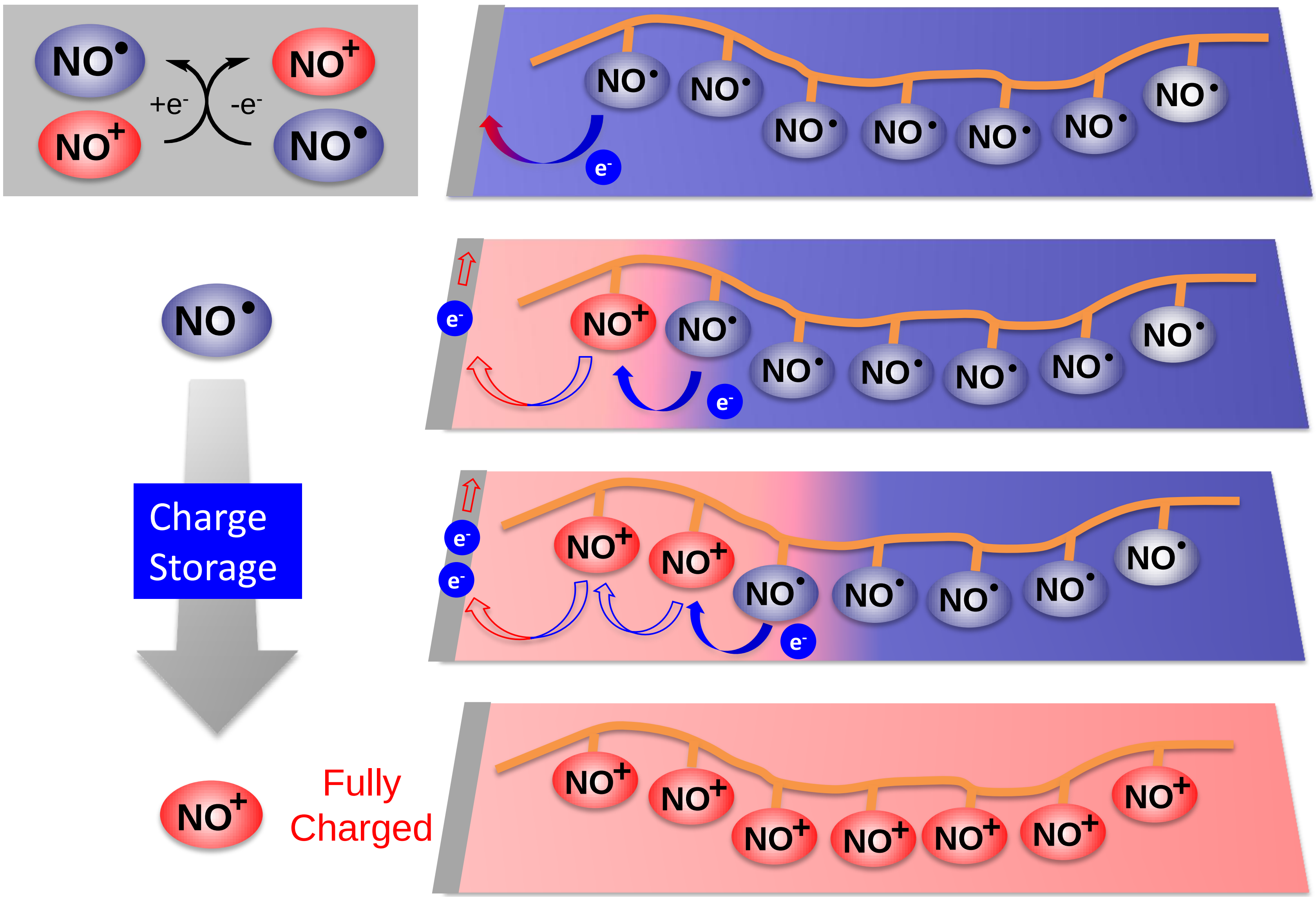


79 mAh/g

Macromolecules, **40**, 3167 (2007); *Adv. Mater.*, **21**, 1627 (2009); *Chem. Lett.*, **40** 184 (2011); *Adv. Mater.*, **23**, 751 (2011).

Charge-Transport and -Storage on Radical Polymer

Electron-Transfer (Charge-Transport) through Self Electron-Exchange Reaction

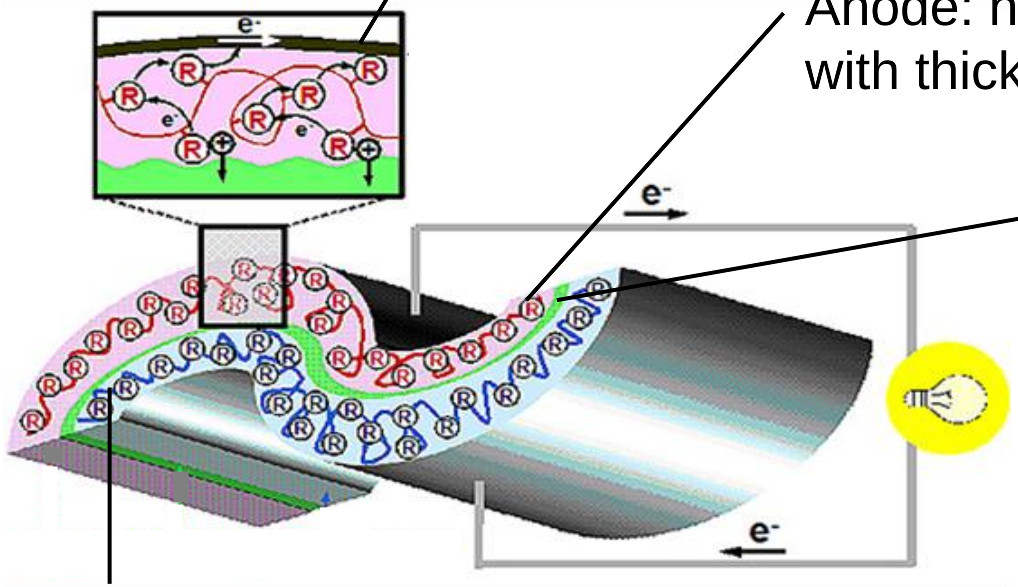


Configuration of Radical Polymer Battery

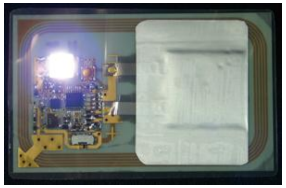
Current Collector (Ex: ITO-PET with 100 μm thickness)

Anode: n-Type radical polymer layer with thickness of 1–10 μm

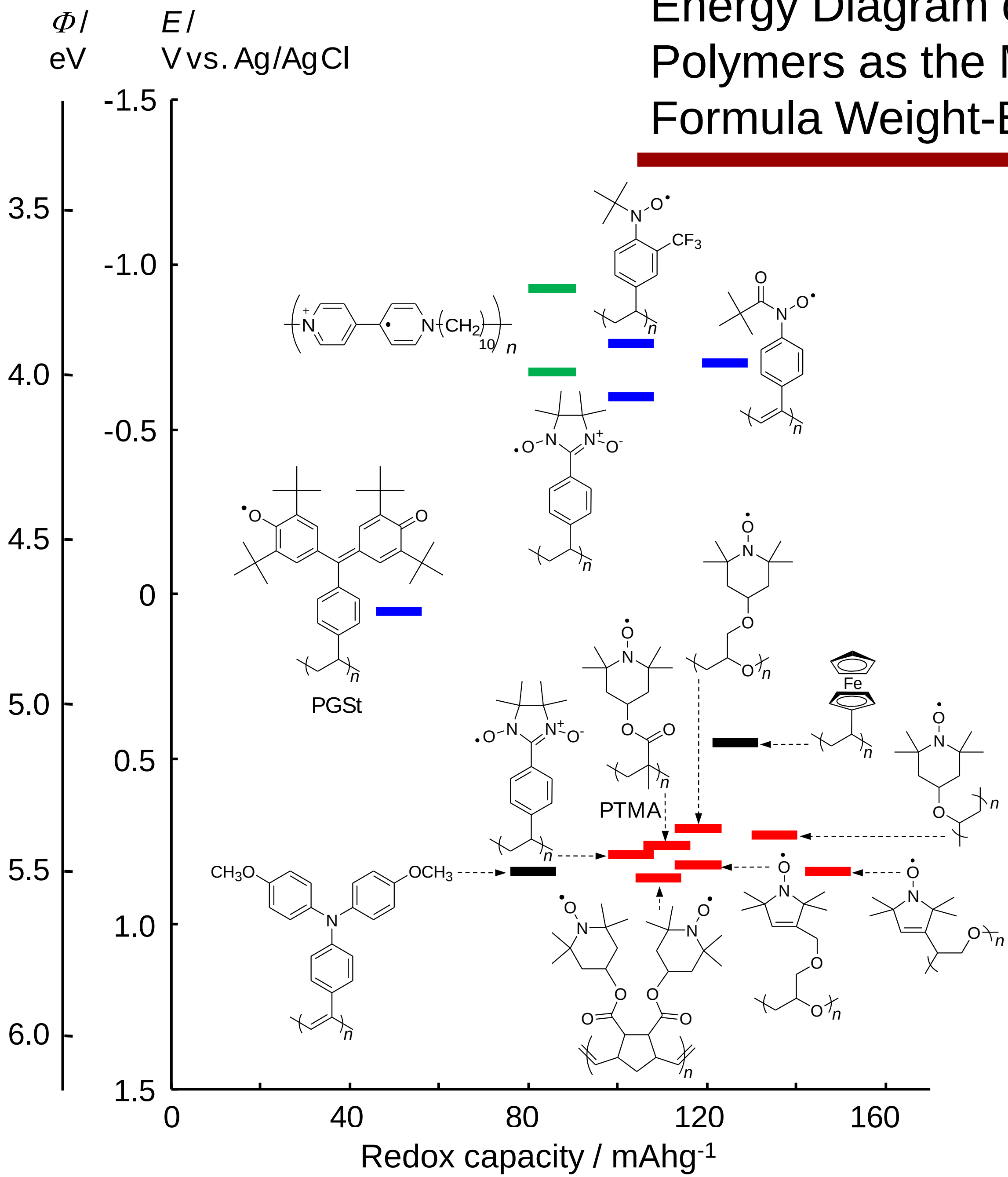
Electrolyte/Separator = Microporous film (Ex: polyethylene film with 200 nm pore and 20 μm thickness) holding electrolyte (Ex: propylene carbonate or oligo ethyleneoxide containing ammonium salt)



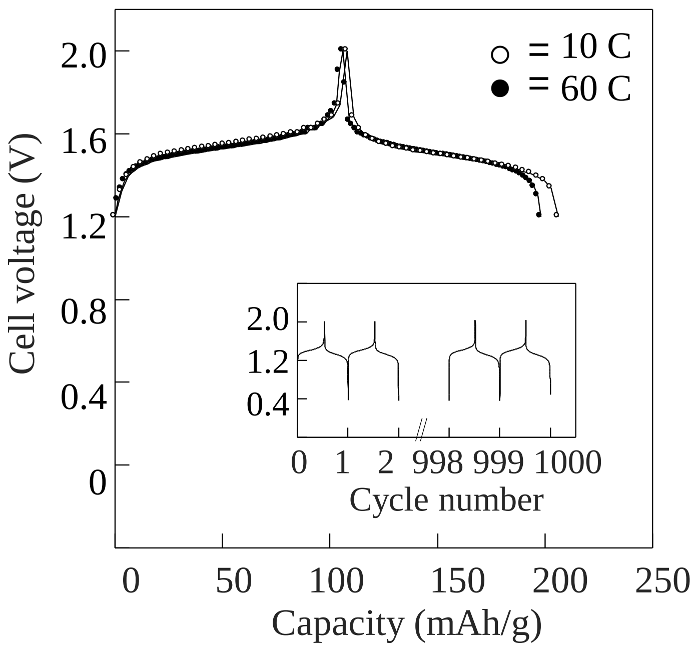
Cathode: p-Type radical polymer layer with thickness of 1–10 μm



Energy Diagram of p-Type and n-Type Radical Polymers as the Map of Redox Potentials vs Formula Weight-Based Capacities

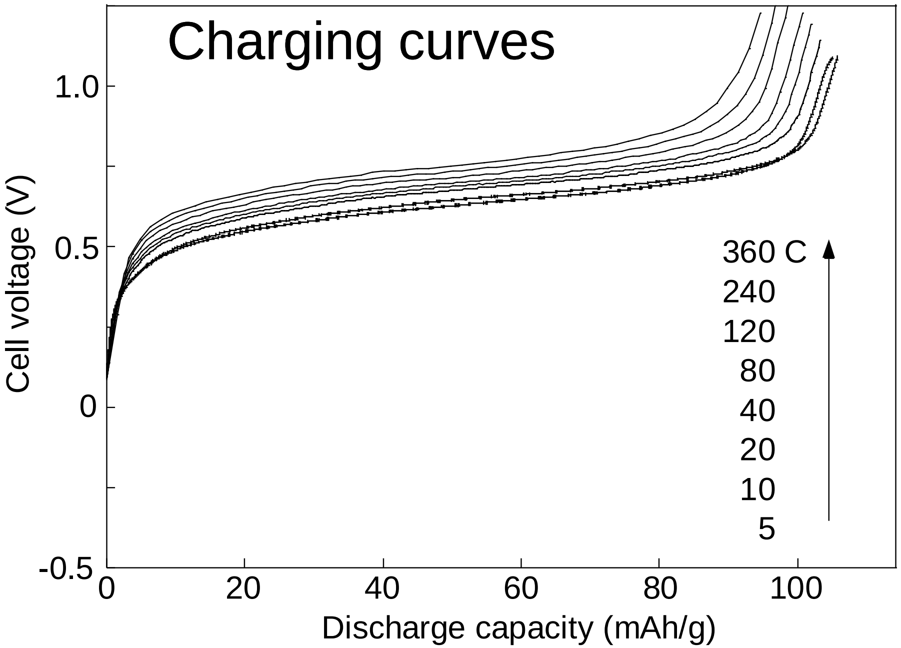


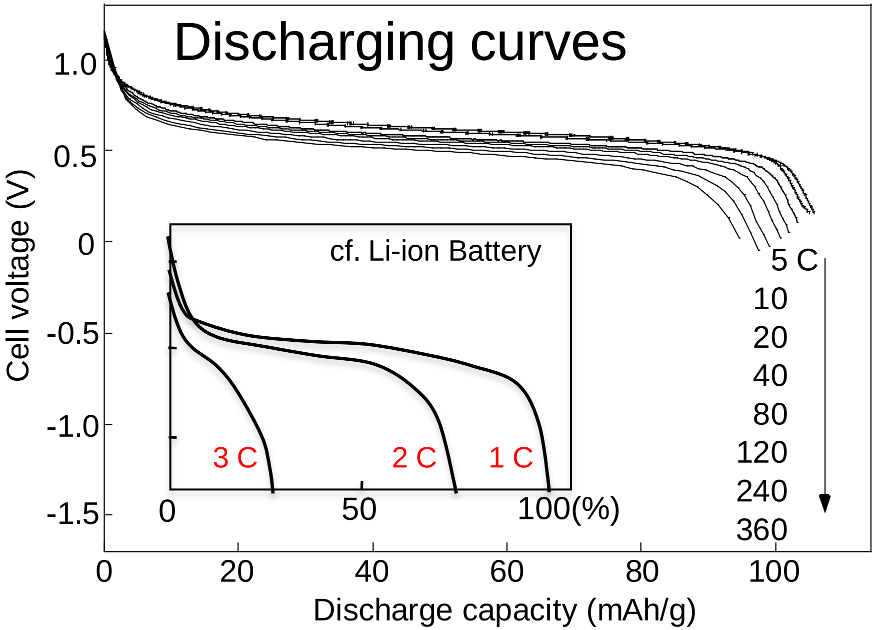
Both current efficiency and Faraday efficiency are almost 100%.



Current Rate Performance

Super rapid charging, High power discharge: Rapid electron-transfer in radical molecules / Amorphous morphology





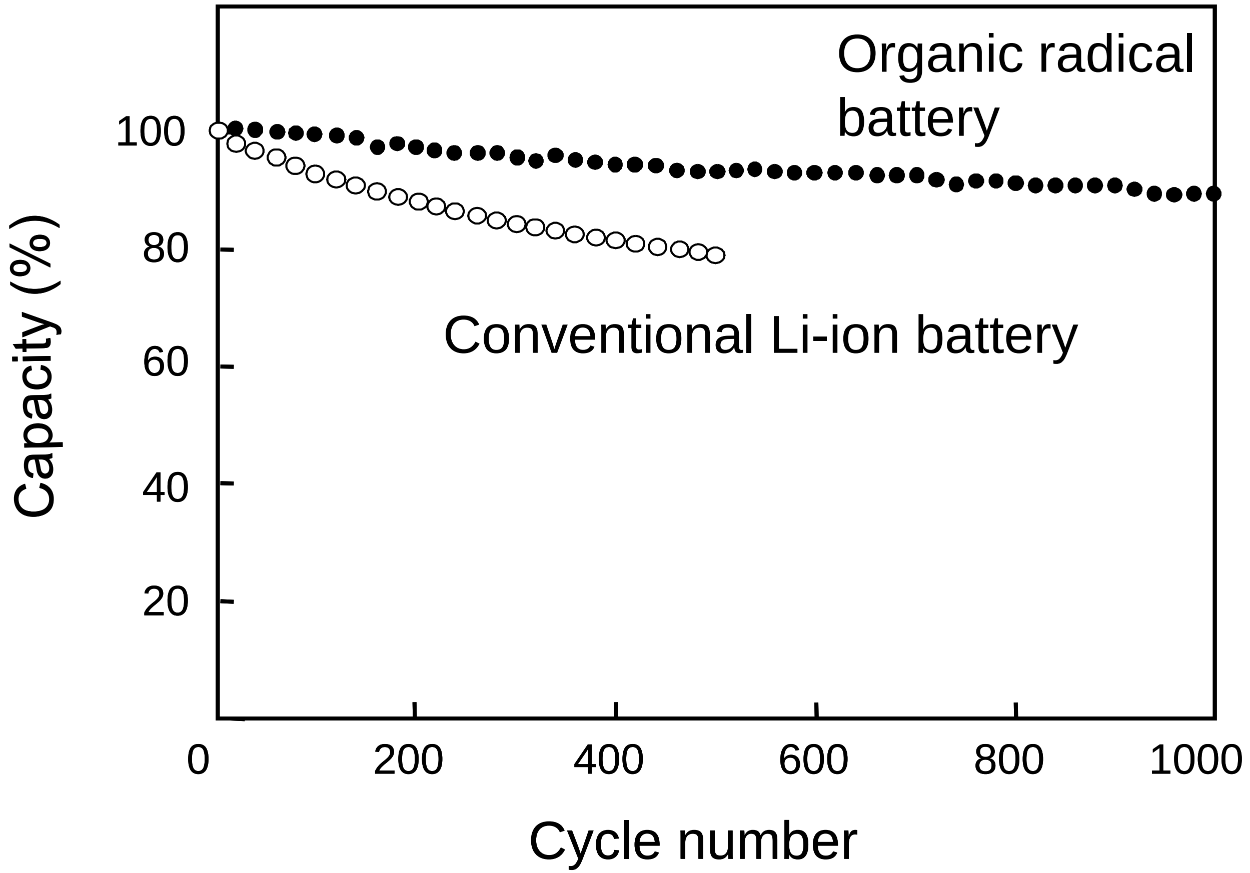
Charging time: < 5 sec

No voltage drop at any discharging rate

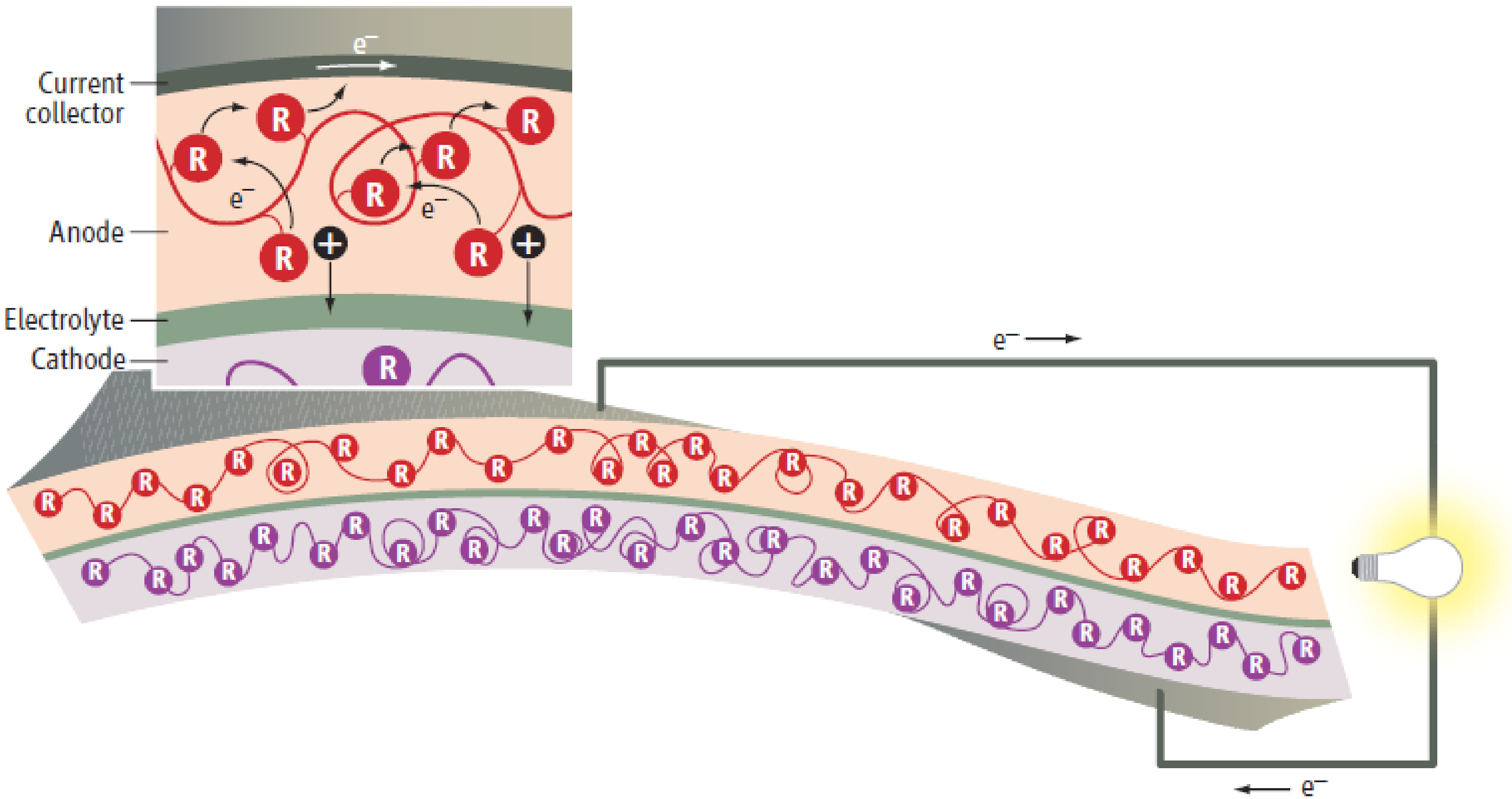
Unit C = Total capacity of the cell is (dis)charged for 1 hr.

Charge/Dischage Cycle-ability

Surprisingly long cycle life



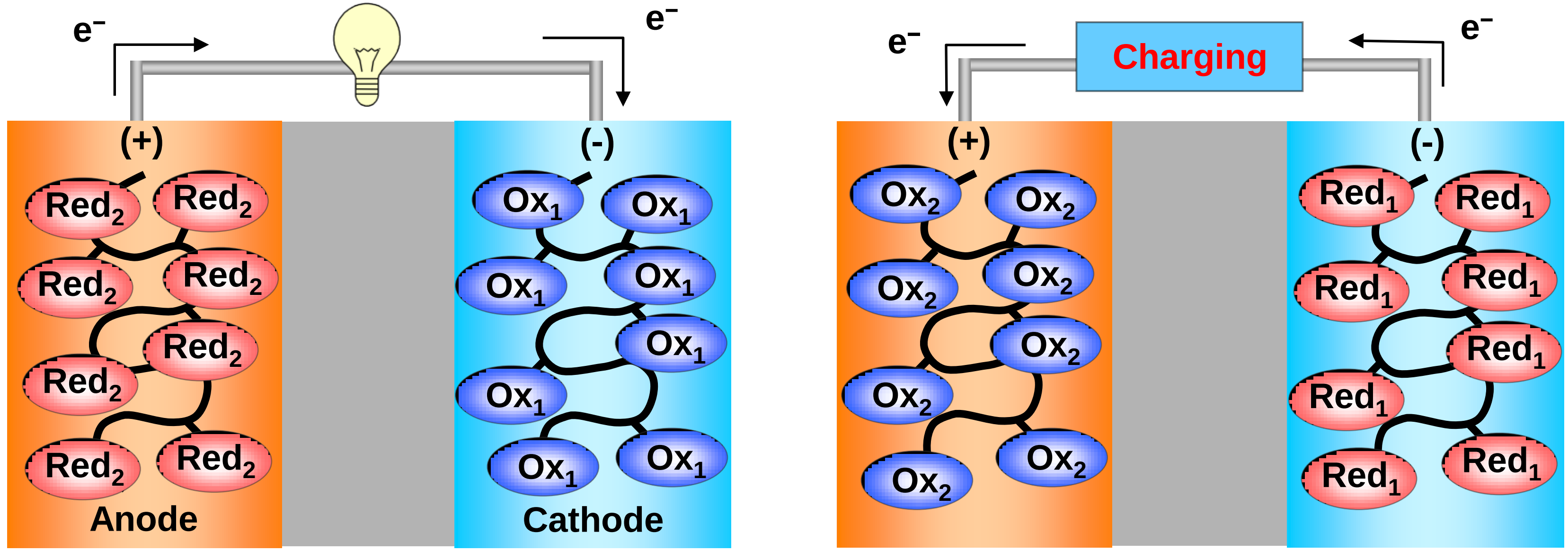
Charge/discharging process without any structural change of the electrode
Stability of the radical: shelf life of the battery > 5 years



Example of a flexible plastic battery. The R groups in the cathode and in the anode have different redox potentials. During the charging process, charge is stored by oxidizing R groups at the cathode and reducing R groups at the anode. The output voltage of the battery corresponds to the gap between the redox potentials. The curves connecting the R groups are polymer chains, which give flexibility. Many R groups are attached to the polymer chain, so that electrons can hop between neighboring R groups to produce the output current.

Nishide and Oyaizu, *Science*, **319**, 737 (2008).

Polymer Electrode-Based Battery



Why a “polymer”?

・Immobilization of the redox site in the electrode, to exclude elution of the redox site into the electrolyte and to avoid self-discharge.

・The redox site with a very high density, for high capacity and high rate charge propagation.

・Appropriate mobility of counter ions

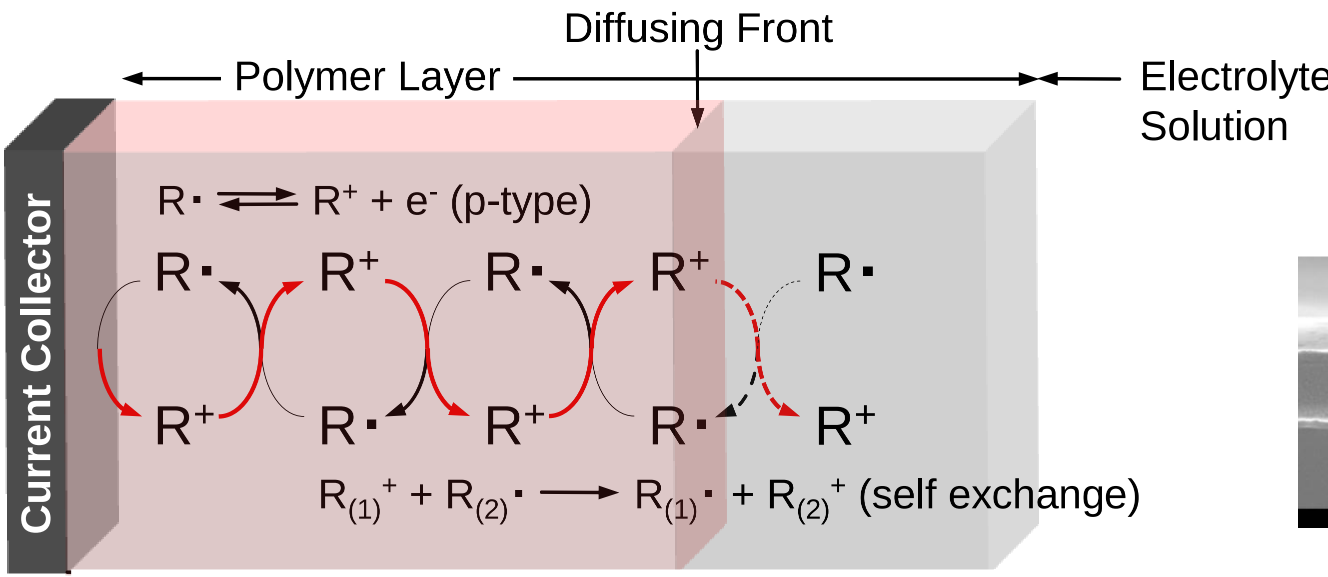
・Amorphous and plastisized, to avoid deformation and heat-generation during charging and discharging.

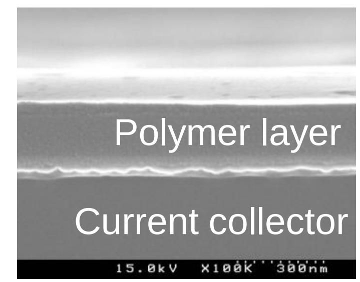
・Molding of electrode

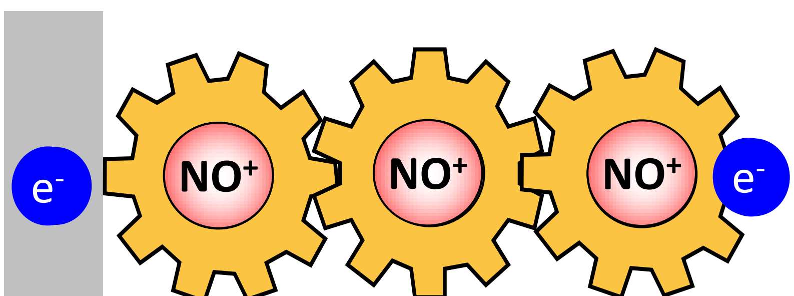
・Flexibility

・Wet fabrication process

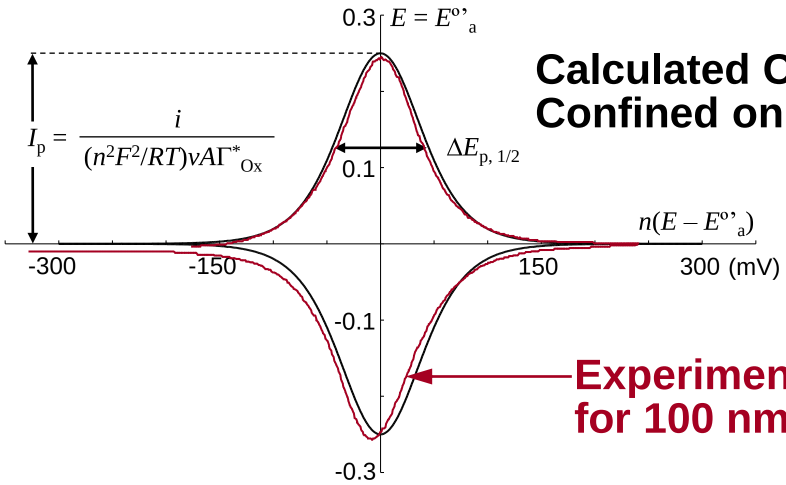
Charge Propagation in the Radical Polymer Layer Equilibrated with an Electrolyte Solution







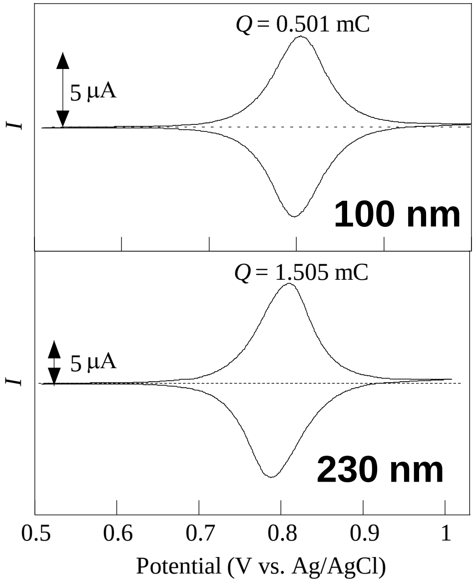
Surface-Confined Nernstian Wave for the Radical Polymer Layer

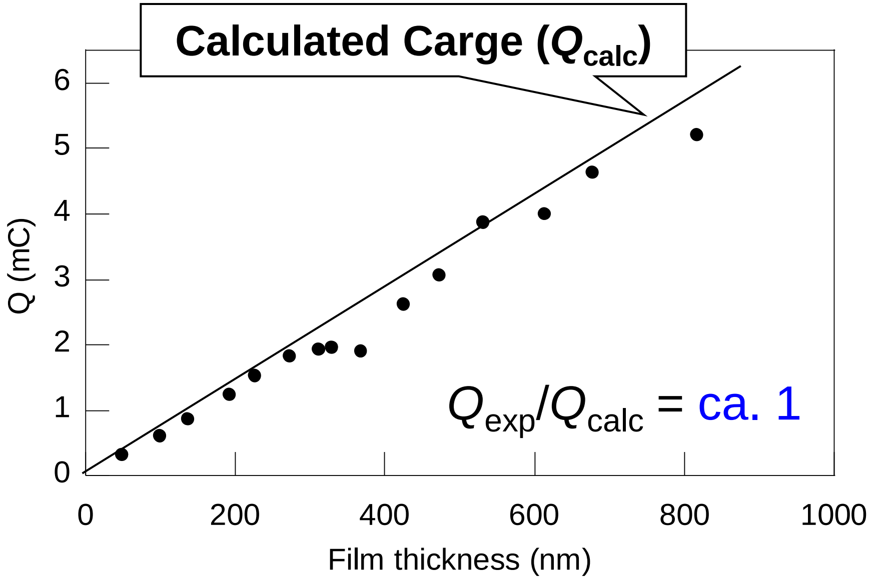


Calculated CV for Redox Species Confined on Electrodes

Experimental CV Trace for 100 nm-thick Polymer Layer

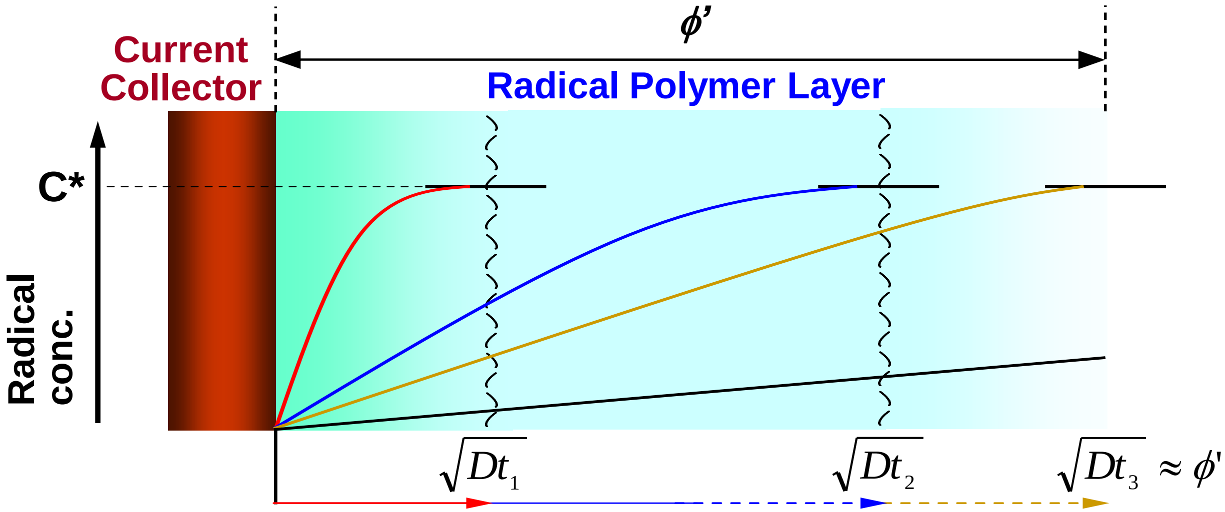
Scanned at 1 mV/s



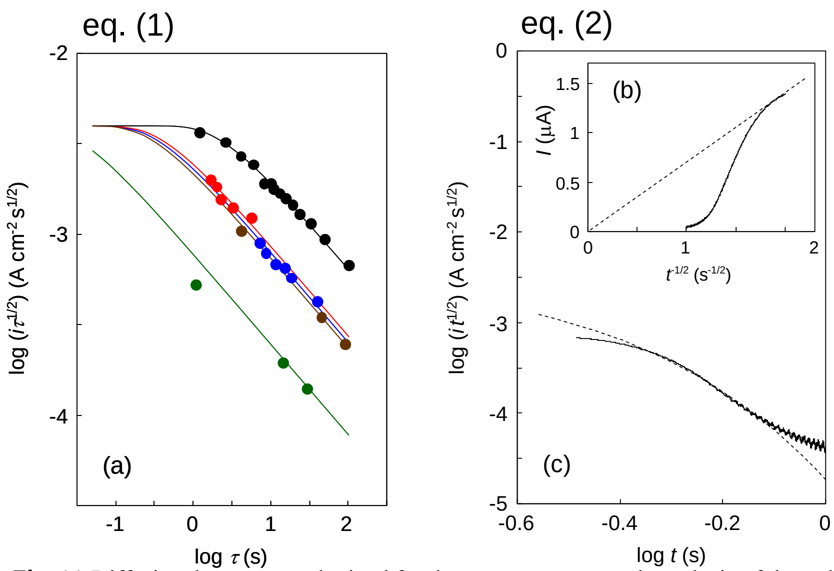


- The electron-transfer (charge propagation) is not accompanied with any diffusion of the redox-site (The redox-site is immobilized).
- Almost 100% of the redox site in the polymer layer contributes to the charge-storage up to 1 μm thickness.

Finite Diffusion throughout Polymer Layer



Homogeneous Layer
Thickness Uniformity



Sand plots for finite diffusion processes

$$i\tau^{1/2} = \frac{nF(\pi D)^{1/2}C^*}{2}\left[1 + 2\sum_{m=1}^{\infty}\left\{\exp\frac{-m^2\phi'^2}{D\tau} - \frac{m\phi'\pi^{1/2}}{(D\tau)^{1/2}}\,\mathrm{erfc}\frac{m\phi'}{(D\tau)^{1/2}}\right\}\right]^{-1} \quad (1)$$

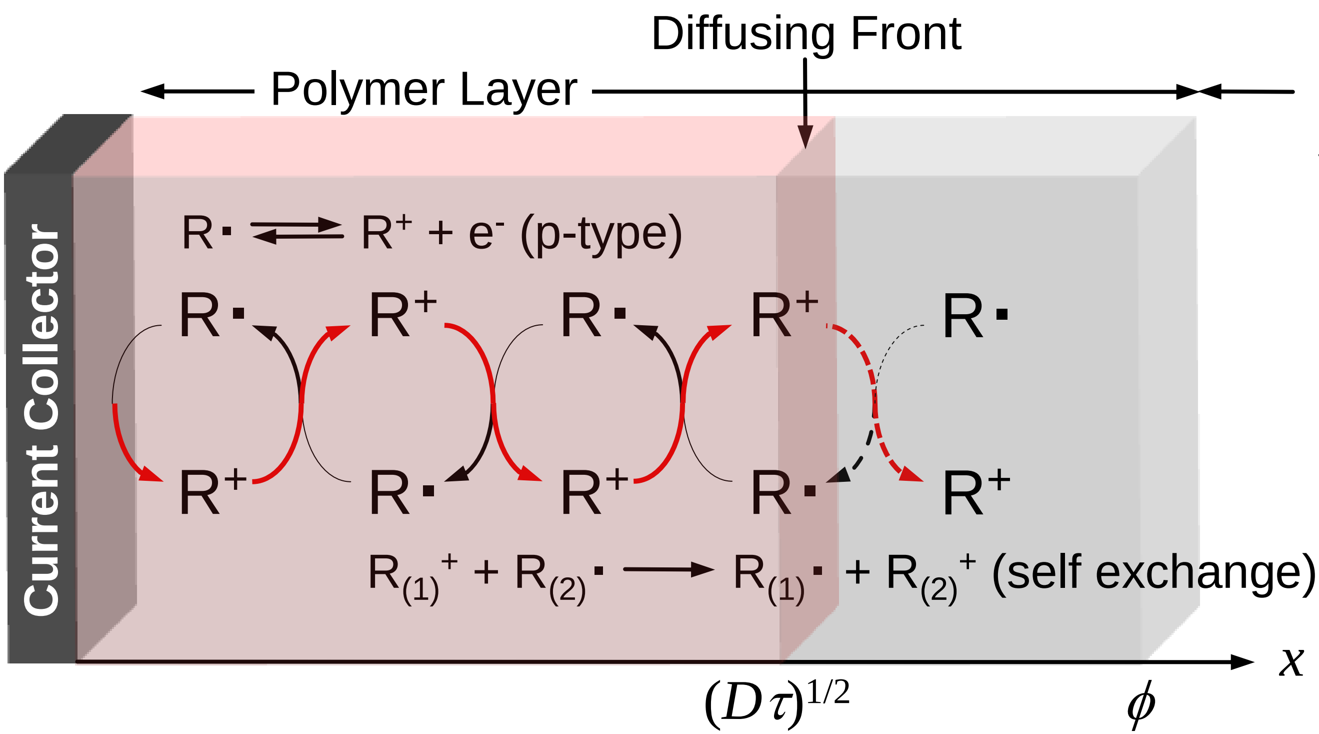
ϕ' = 330, 140, 130, 120, and 40 nm, respectioely

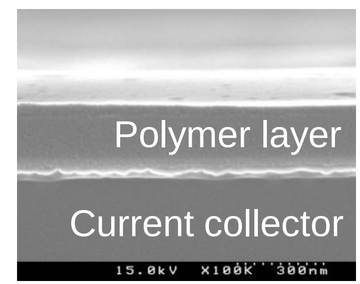
Cottrell plots for a finite diffusion process

$$\log(it^{1/2}) = \log\left[\frac{nFD^{1/2}C^*}{\pi^{1/2}}\left\{1 + 2\sum_{m=1}^{\infty}(-1)^m \exp\frac{-m^2\phi'^2}{Dt}\right\}\right] \quad (2)$$

Fig. (a) Diffusional responses obtained for the constant-current electrolysis of the polymer layer. Curves calculated from eq 1 were fitted to τ at different current densities of i = 3.3 – 0.067 mA cm^{-2} in chronopotentiometry using a thickness of ϕ' = 330 (black), 140 (red), 130 (blue), 120 (brown), and 40 nm (green) in the swollen state. (b) Cottrell plots for chronoamperometry after applying a potential pulse of 0 to 1.2 V vs. Ag/AgCl. The dashed line corresponds to a semiinfinite diffusion process. (c) Diffusional responses obtained for the chronoamperometry. Solid curve was obtained experimentally in (a). Dashed curve was calculated from eq 2 using a thickness of ϕ' = 140 nm.

Charge Propagation during the Oxidation of a p-Type Radical Polymer Confined at a Current Collector Surface and Equilibrated in an Electrolyte Solution





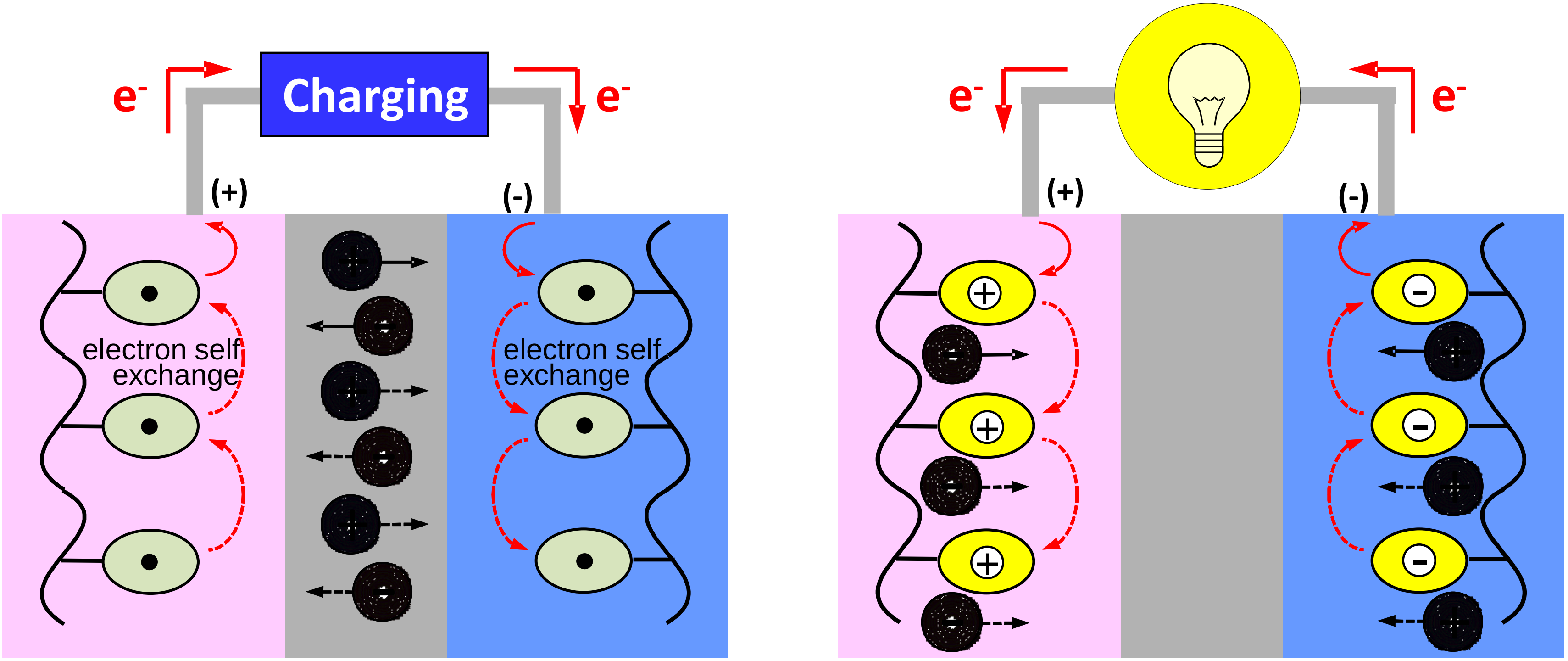
Mean distance between the unpaired electrons (δ) ＜ 10 Å

Rate const for electron self-exchange reaction (k_{ex}) = 10^{5-8} $M^{-1}s^{-1}$

Diffusion coeff for charge propagation (D) = 10^{-7} - 10^{-9} cm^2s^{-1}

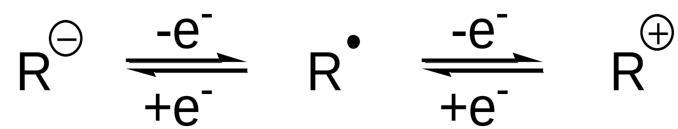
J. Am. Chem. Soc., **130**, 14459 (2008).

Charging/Discharging Process: Electron Transport and Storage

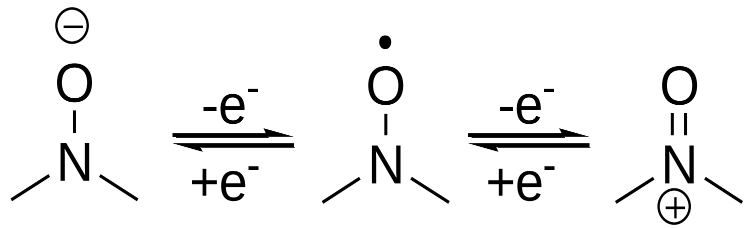


Reversible Electron-transfer Reaction of Organic Robust and Electroactive Radicals (a) and Electron-transfer Reaction of Organic Molecules Coupled to Irreversible Chemical Reactions (b)

(a)

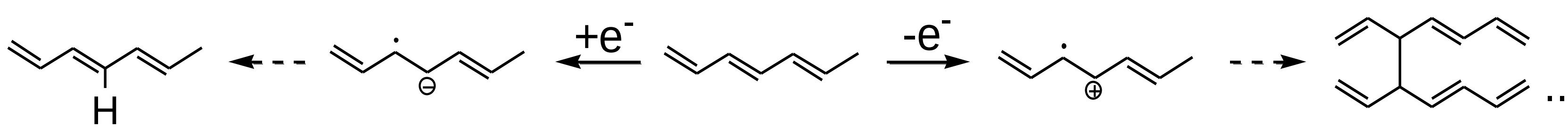


Organic Robust Radical (Open Shell)

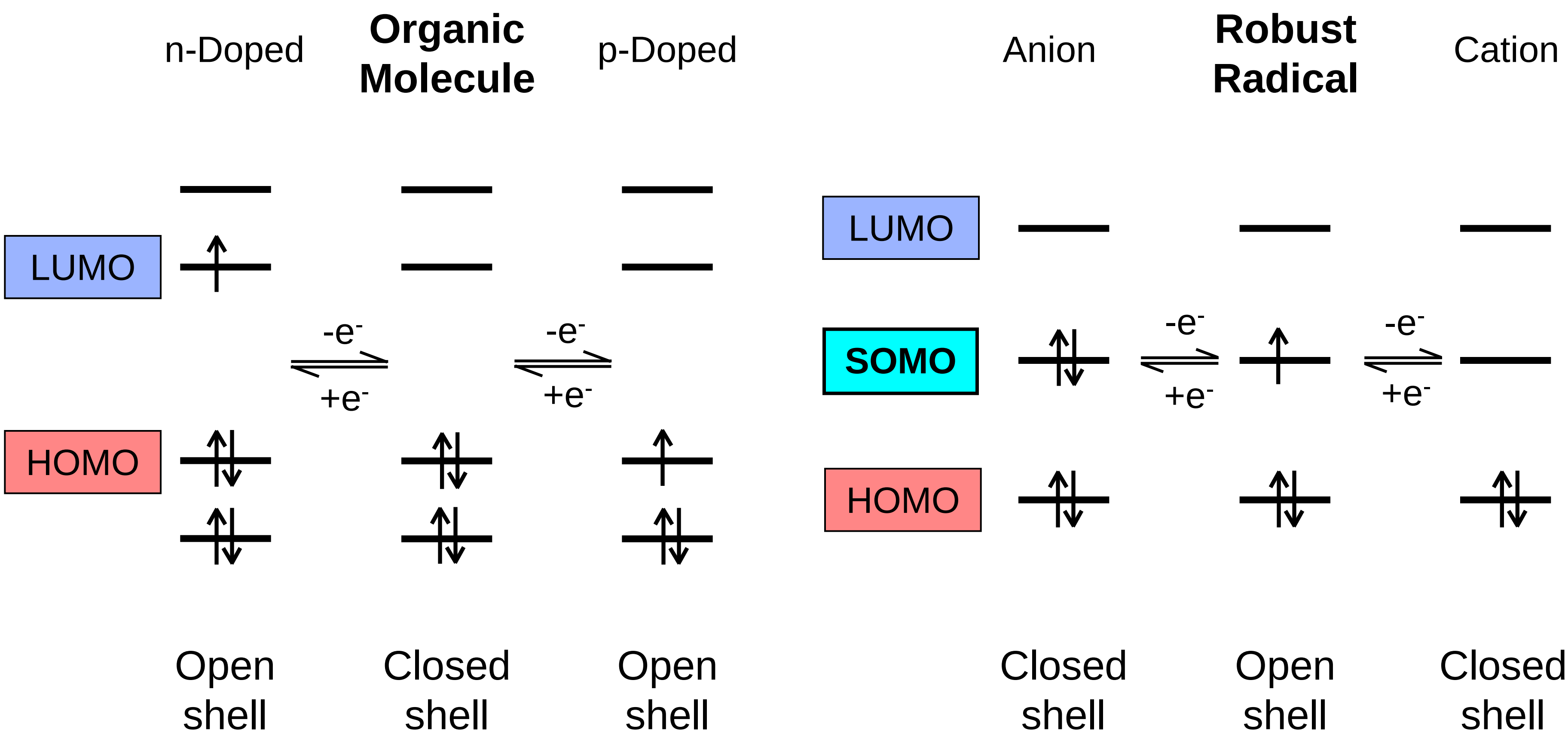


(b)

Organic Molecules (Closed Shell)

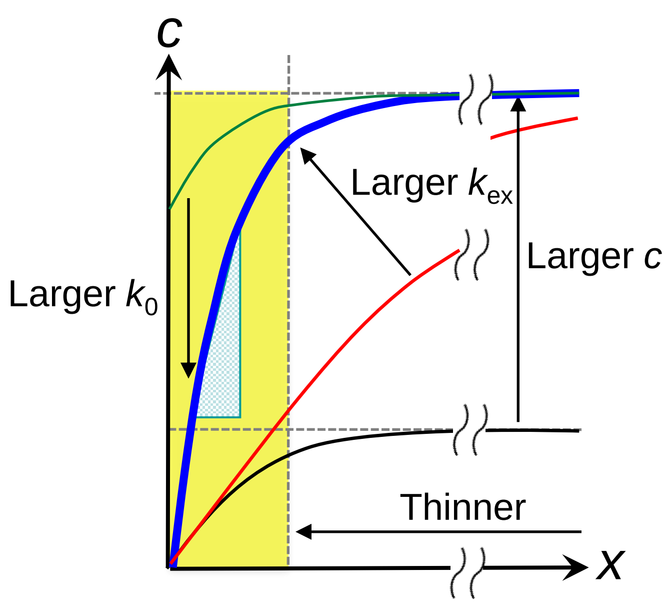


Reversible Electron-transfer of Organic Robust / Electroactive Radicals vs Doping of Organic Molecules



Large Flux of Charge Mediated through Radical Polymer

The redox gradient-driven charge transport by the enhanced exchange reaction among the densely populated radical redox sites accomplishes substantial flux of electron with **very-high current density of 0.1–100 mA/cm^2 .**

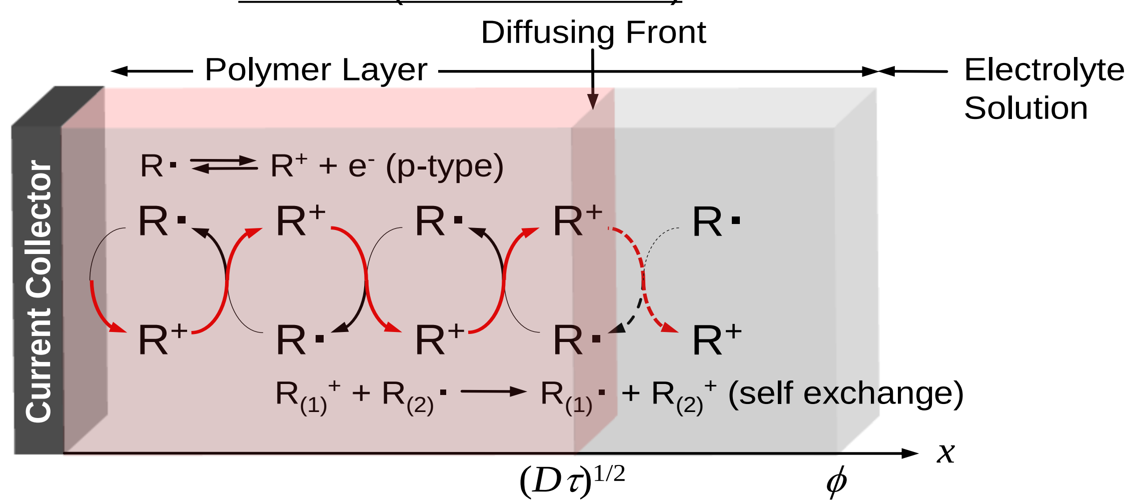


Thin Layer of the Radical Polymer Equilibrated with Electrolyte

$$J = -nFD\,\frac{dc}{dx}$$

$$= -nF\left(\frac{1}{6}k_{ex}\delta^2 c\right)\frac{dc}{dx}$$

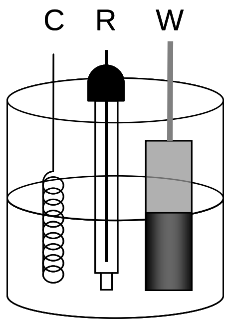
$10^{-8\sim-10}$ (cm^2/s) × $10^{-2\sim-3}$ (mol/cm^3)
÷ $10^{-4\sim-5}$ (cm) × 96485 (C/mol)
≈ $10^{-4}\sim 1$ (C/s·cm^2 = A/cm^2)

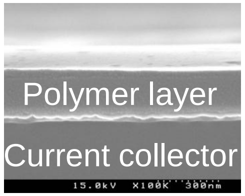


If you make a Radical Polymer Battery: Beaker Cell Test

Half-Cell

Working: Polymer coated on Pt, Al, ITO/PET, etc

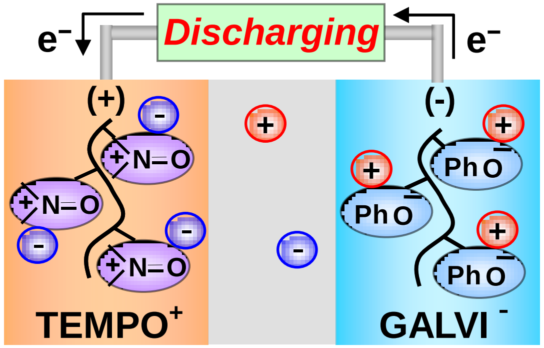


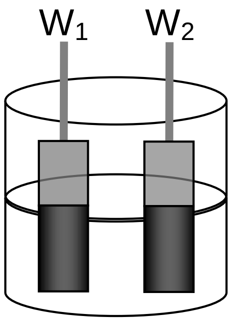


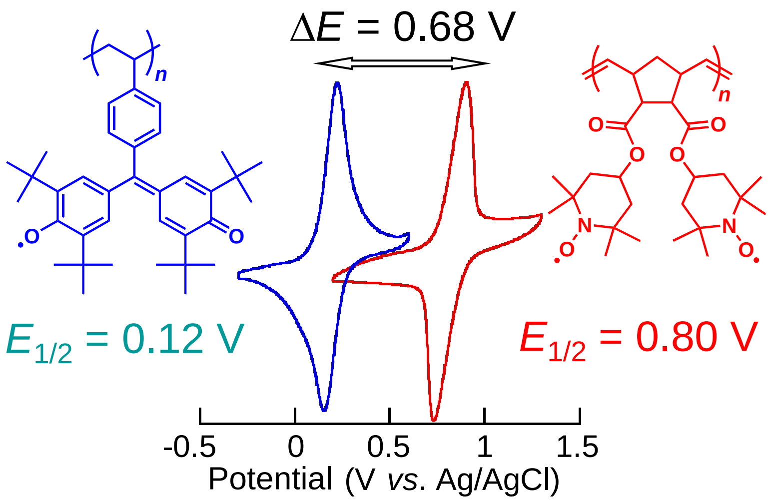
Counter: Pt wire

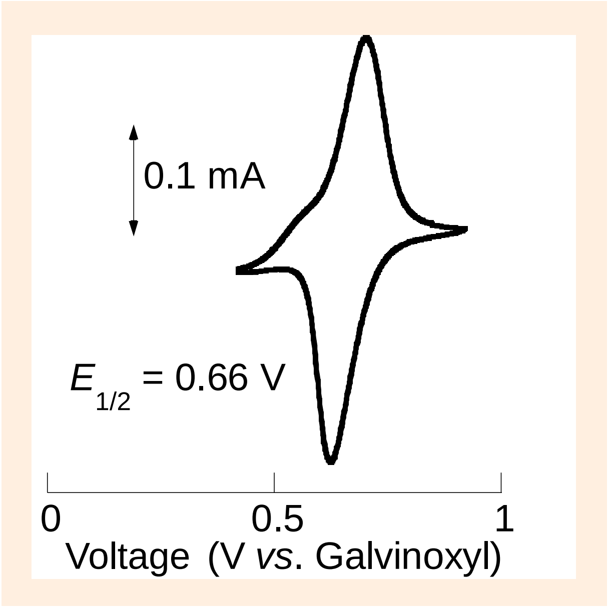
Reference: Ag/AgCl

Electrolyte: 1 M $LiPF_6$ in Ethylene carbonate/diethyl carbonate (v/v = 1/1)



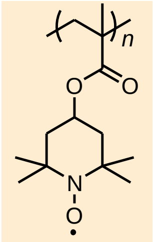




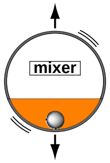


Electrode/Cell Preparation Process

Polymer



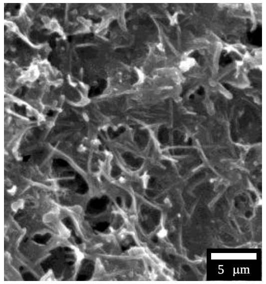
Mixing



Carbon: Vapor Grown Carbon Fiber (0.15ϕx10-20 μm: Showa Denko Co.)
Binder: Polyvinylidene fluoride
Solvent: N-Methylpyrrolidone

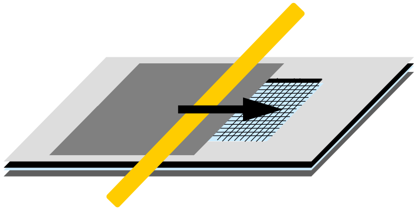
Polymer/Carbon/Binder/Solvent

Slurry



Coating

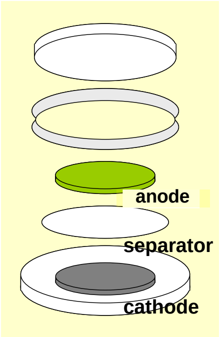
Electrode



Bar Coater

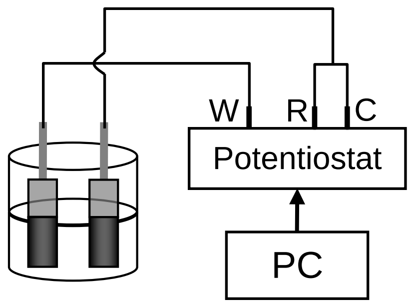
Aluminium foil

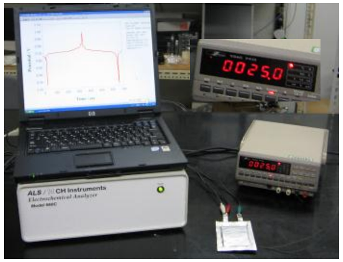
Coin Cell

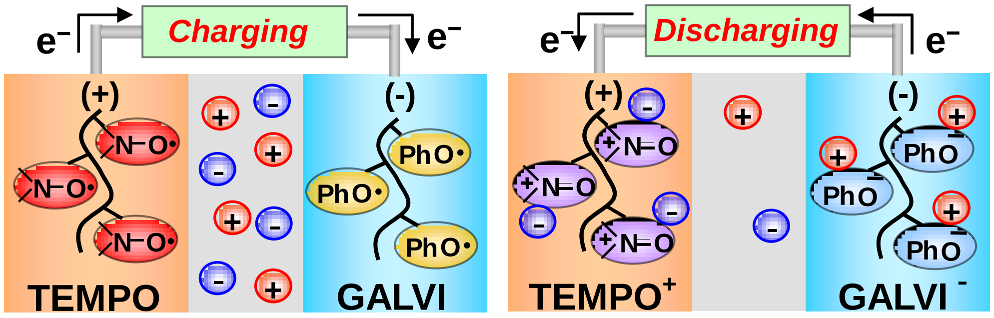


Chronopotentiometry and Charging/Discharging Curves

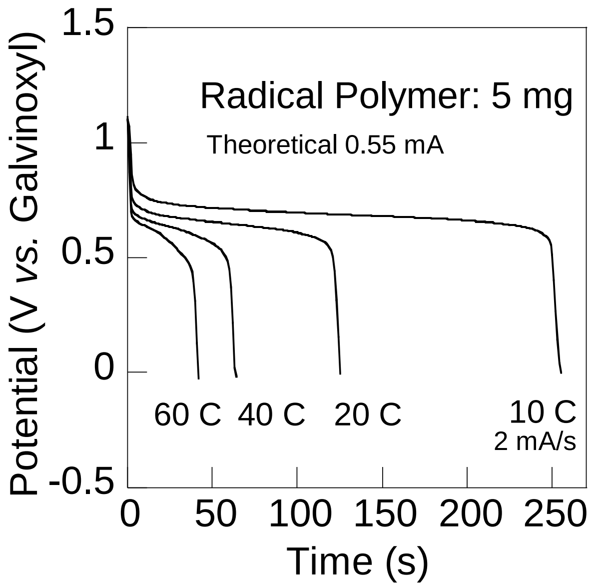
Chronopotentiometry



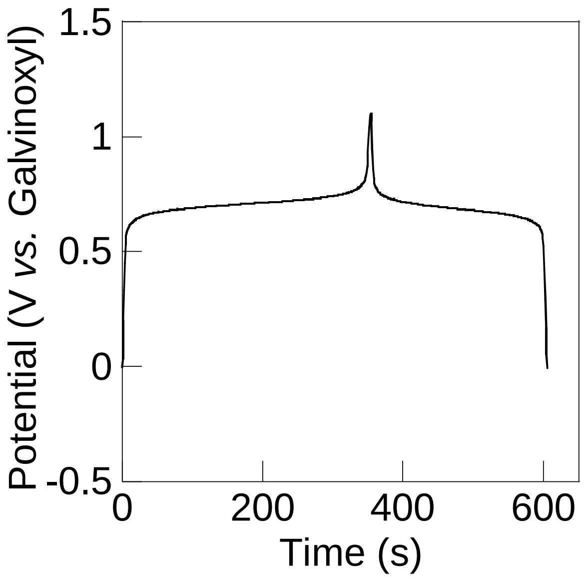




Rate performance



Charging/Discharging curve



Mass Specific Capacity

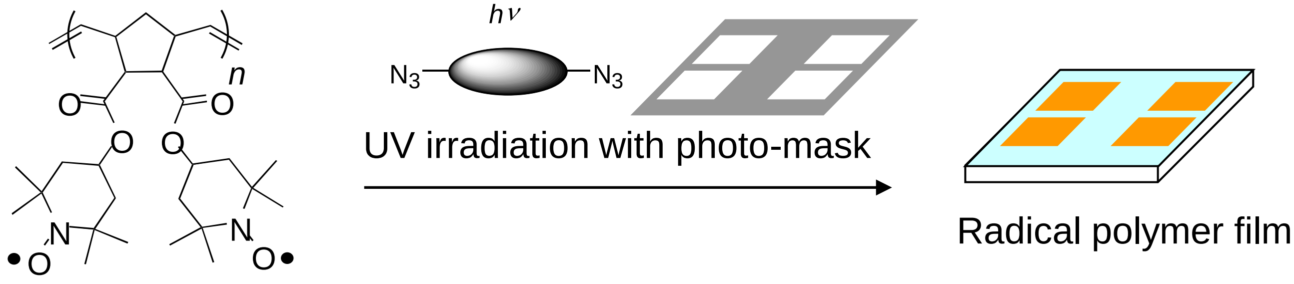
⇩

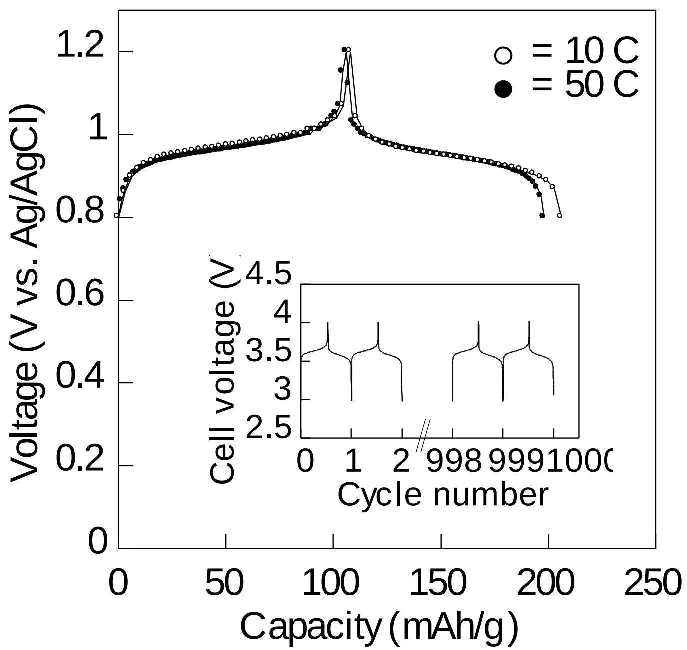
$$109\ [\text{mA/g}] \times \frac{\text{Time [s]}}{3600\ [\text{s}] \times \frac{1}{\text{rate}}}$$

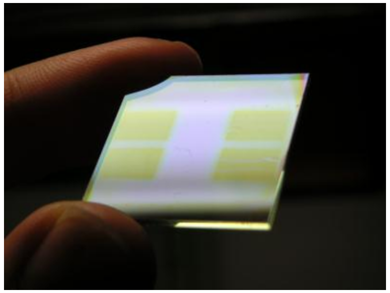
$$= \frac{\text{Capacity [mAh/g]}}{\text{(Experimental)}}$$

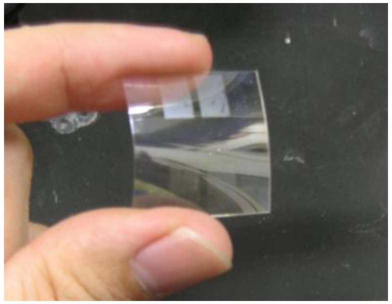
Preparation of Electrode-Active Thin film

Radical polymer / bisazide (10/1) in ethyl lactate







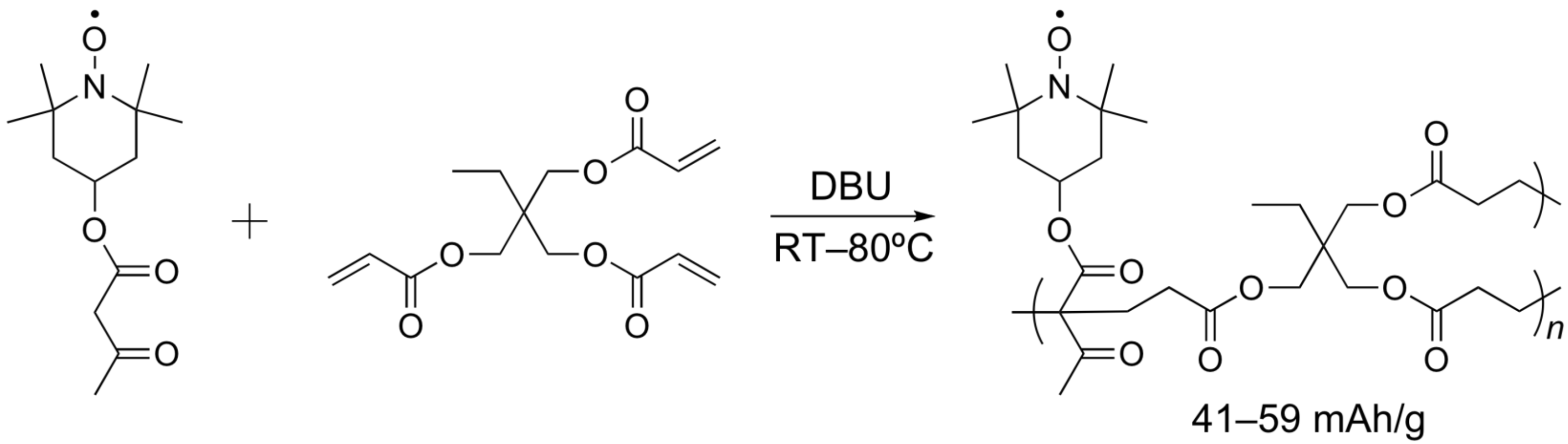


Polymer layer (50 ~ 500 nm)
Roughness < 4 nm

Photo-crosslinking provides an electro-active thin film.
Good processability, Bendable, Transparent

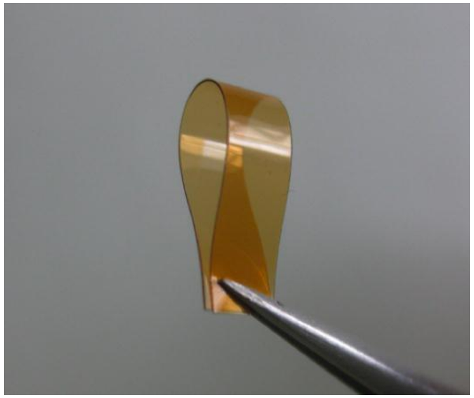
Chem. Commun., 1730 (2007).

Thermal-Cured TEMPO Polymer



Michael reaction of TEMPO-acetoacetate and triacrylate to yield TEMPO-bearing networked polyester:

- Click-chemistry
- No radical quenching
- Tunable swellability
- Flexible and tough

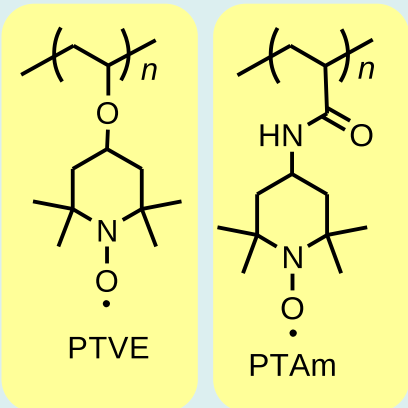


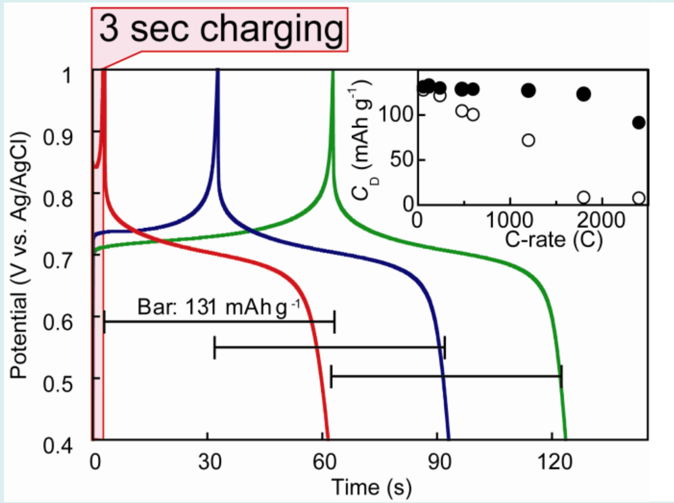
A Self-standing film of the thermal-cured TEMPO polymer

Chem. Comm., 3475 (2010)

Aqueous Electrolyte-type Radical Polymer Battery

Hydrophilic radical polymers

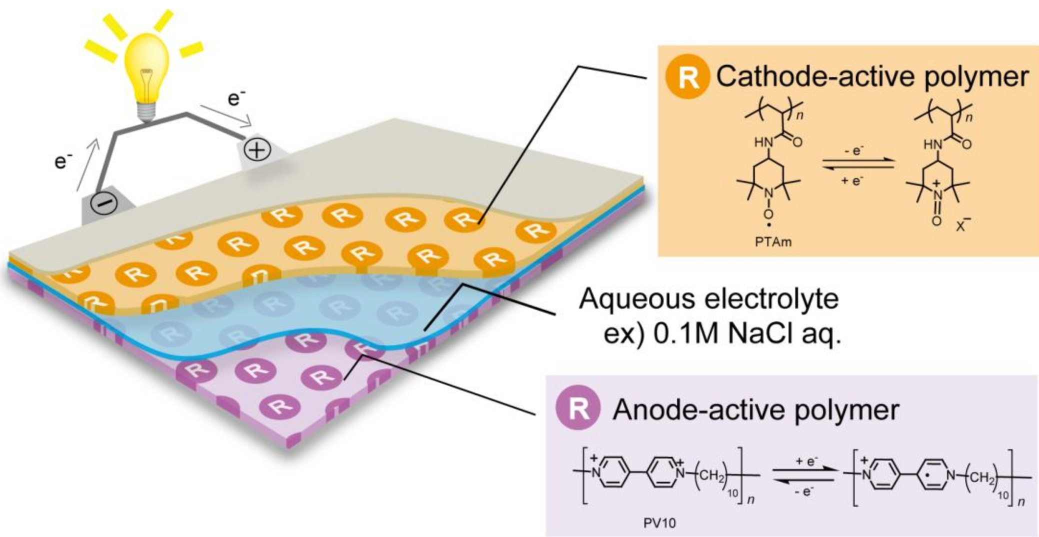


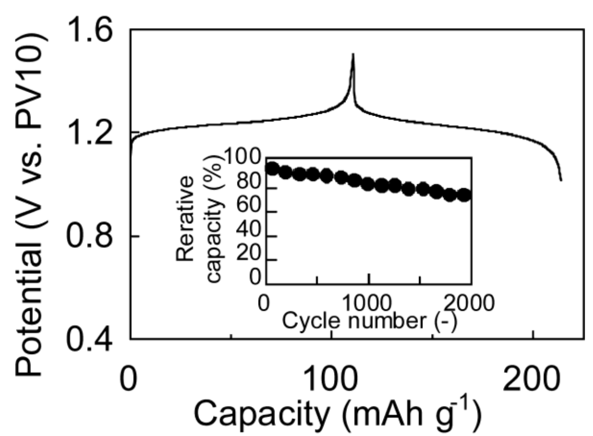


Advantages

- ✓High equivalent electrical conductivity: 10^{-2} m^2 S mol^{-1}
  - ⇨ Ultra fast full chargy in as short as 3s.
- ✓High recycability
- ✓Eco-friendly
- ✓Low ignition risk

Battery configuration and performance

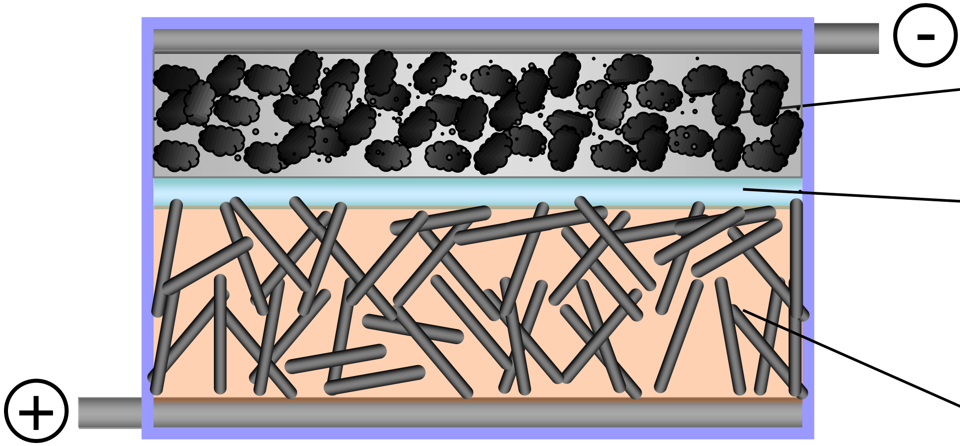




Chem. Commun., 836 (2009)

Proto-type Radical Battery: Radical Polymer Composite Cathode

Energy Density: 120 Wh/L, Power Density: 11 kW/L, Cell Thick: 100 μm



Graphite Anode (10 μm)

Separator + Electrolyte (20 μm):
(1.5 M $LiPF_6$ EC/DEC)

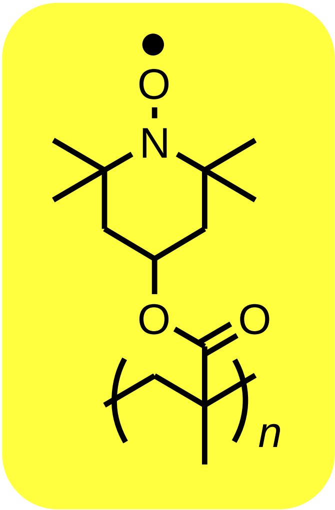
Radical Polymer
Composite Cathode (70 μm):

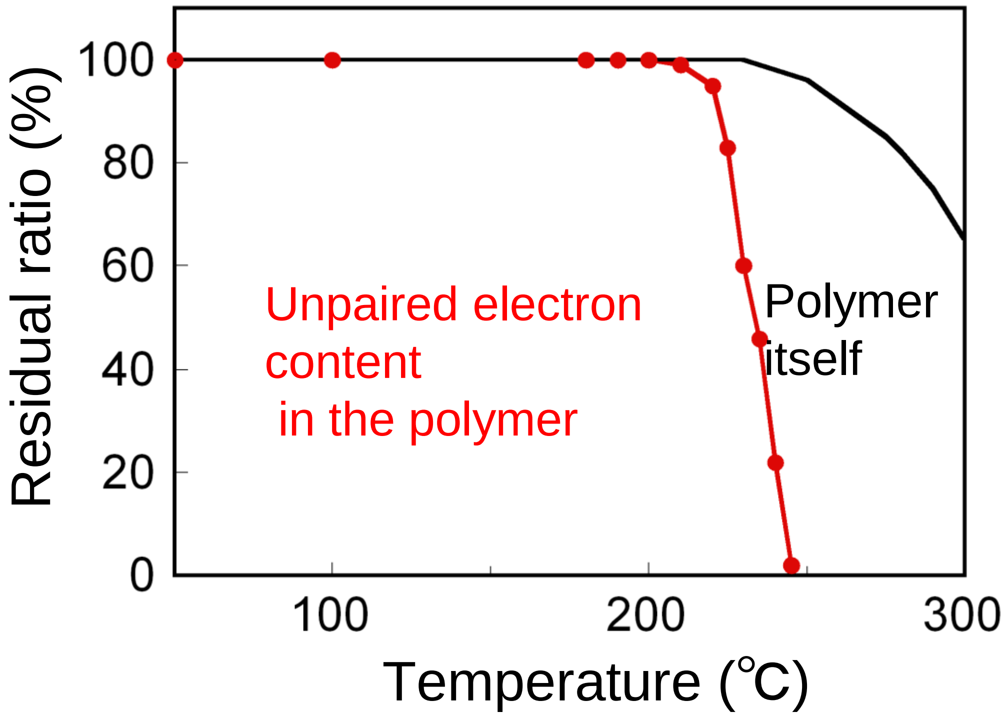
PTMA with Mol. Wt. 200K + 20%
Graphite fiber 150 nm ϕ × 5 μm)

NEDO Projects on "Radical Battery for Ubiquitous Power"

a member of the DIC group

Thermal Stability of Nitroxide Radical Polymer





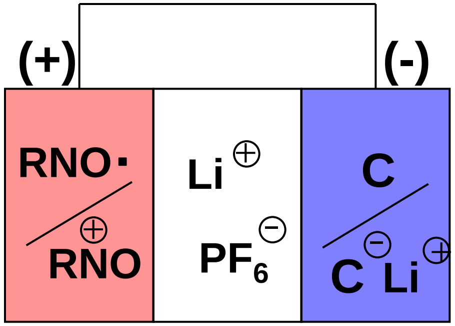
Glass Transition Temp. T_g = 153°C
Decomposed at > 220°C

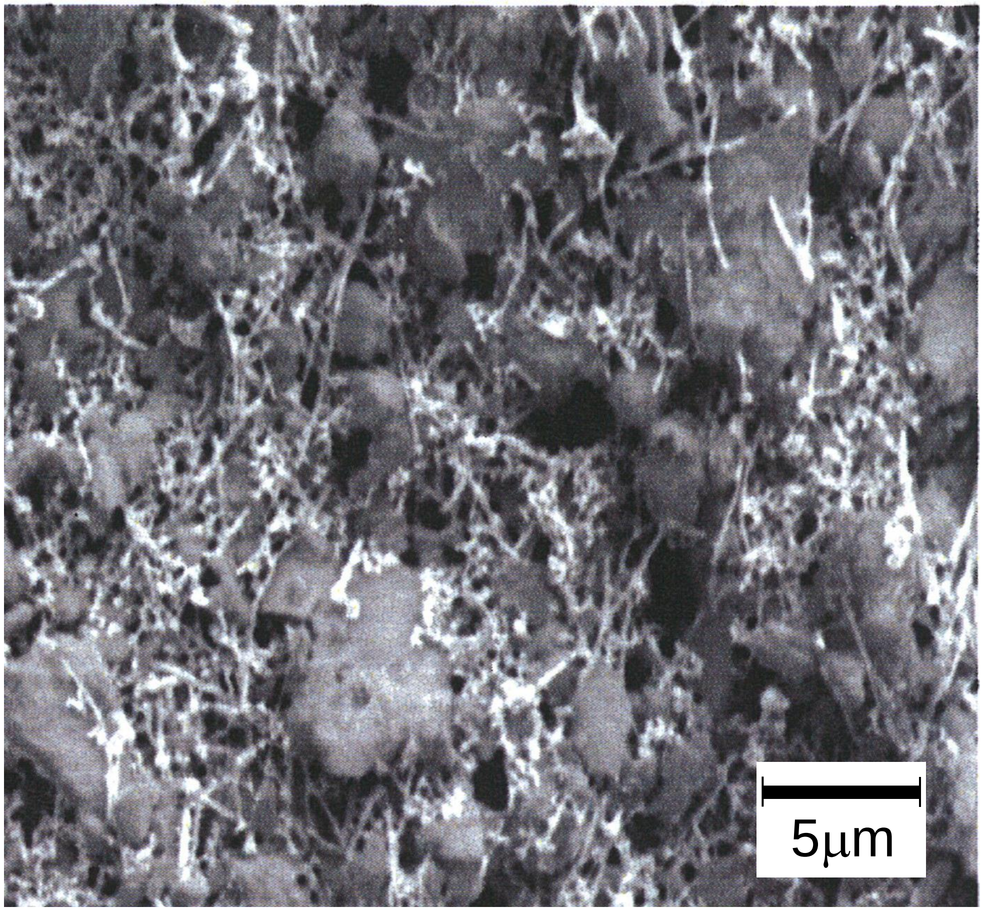
Half life under Ambient Conditions > 1 year
(under heated (165°C) air ~ 2 days)

Electrochim. Acta, **50**, 827 (2004).

Radical Polymer as the Composite Electrode

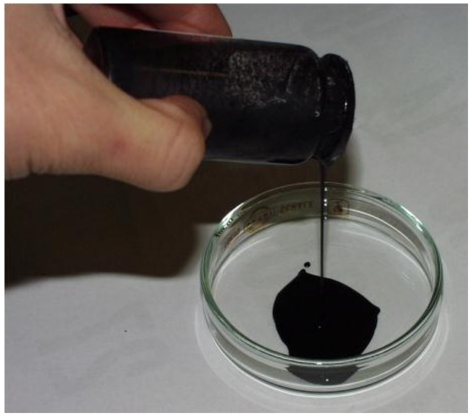
Proto-type Radical Battery



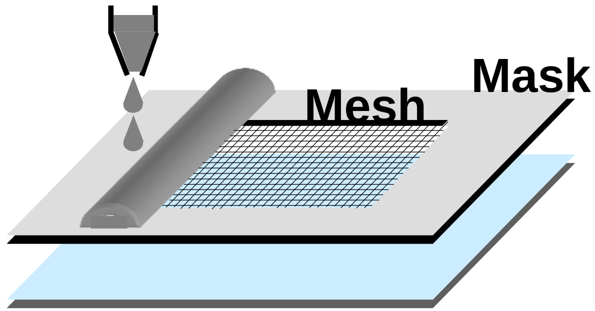


PTMA (Crosslink 1%, Mol. Wt. 200K) = 70%, Graphite fiber (VGCF) = 14%, Carbon particle (Super P) = 7%, Binder (CMC+PTFE) = 9%

Screen Printing Process for Electrode Fabrication

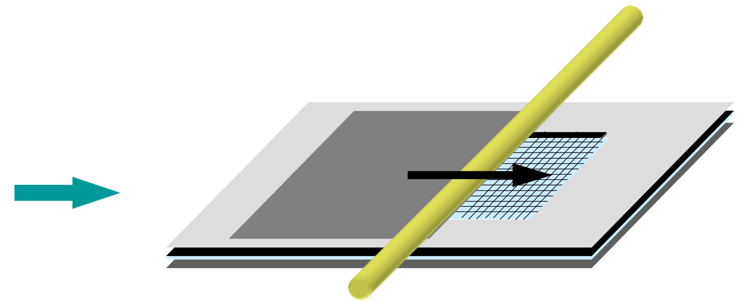


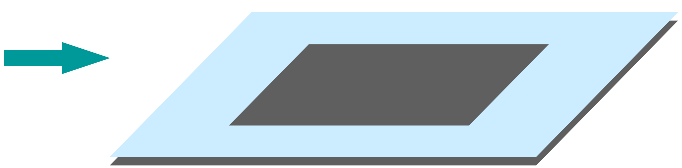
Radical Polymer/C
Composite Ink

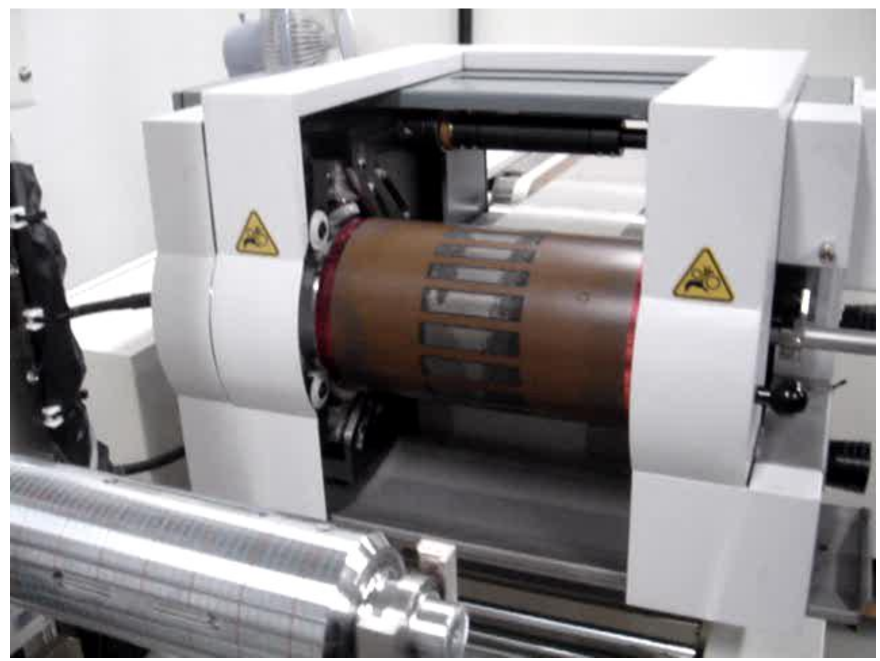


Al Current Collector

"Printable Power"

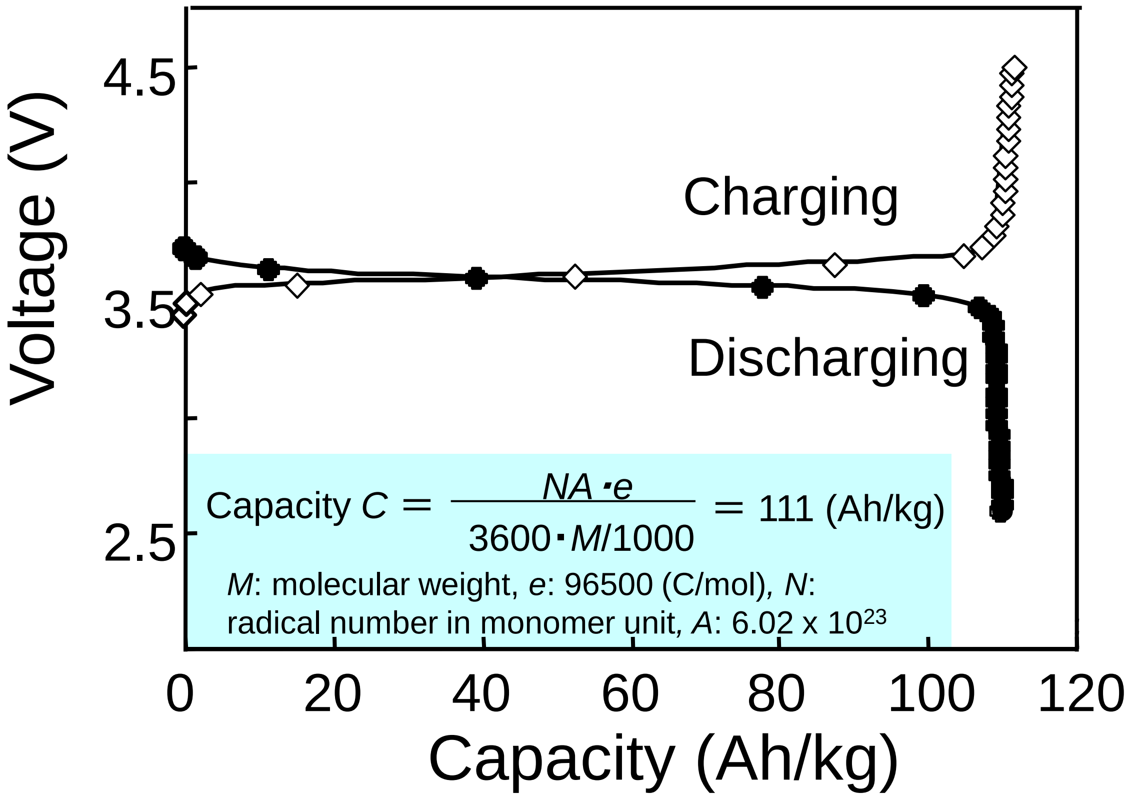






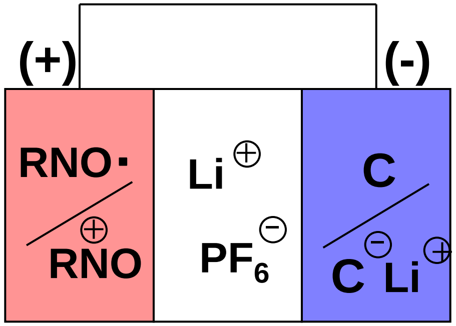
Charge/discharge curves

High current efficiency: Simple one electron-transfer,
nm-Sized, amorphous morphology



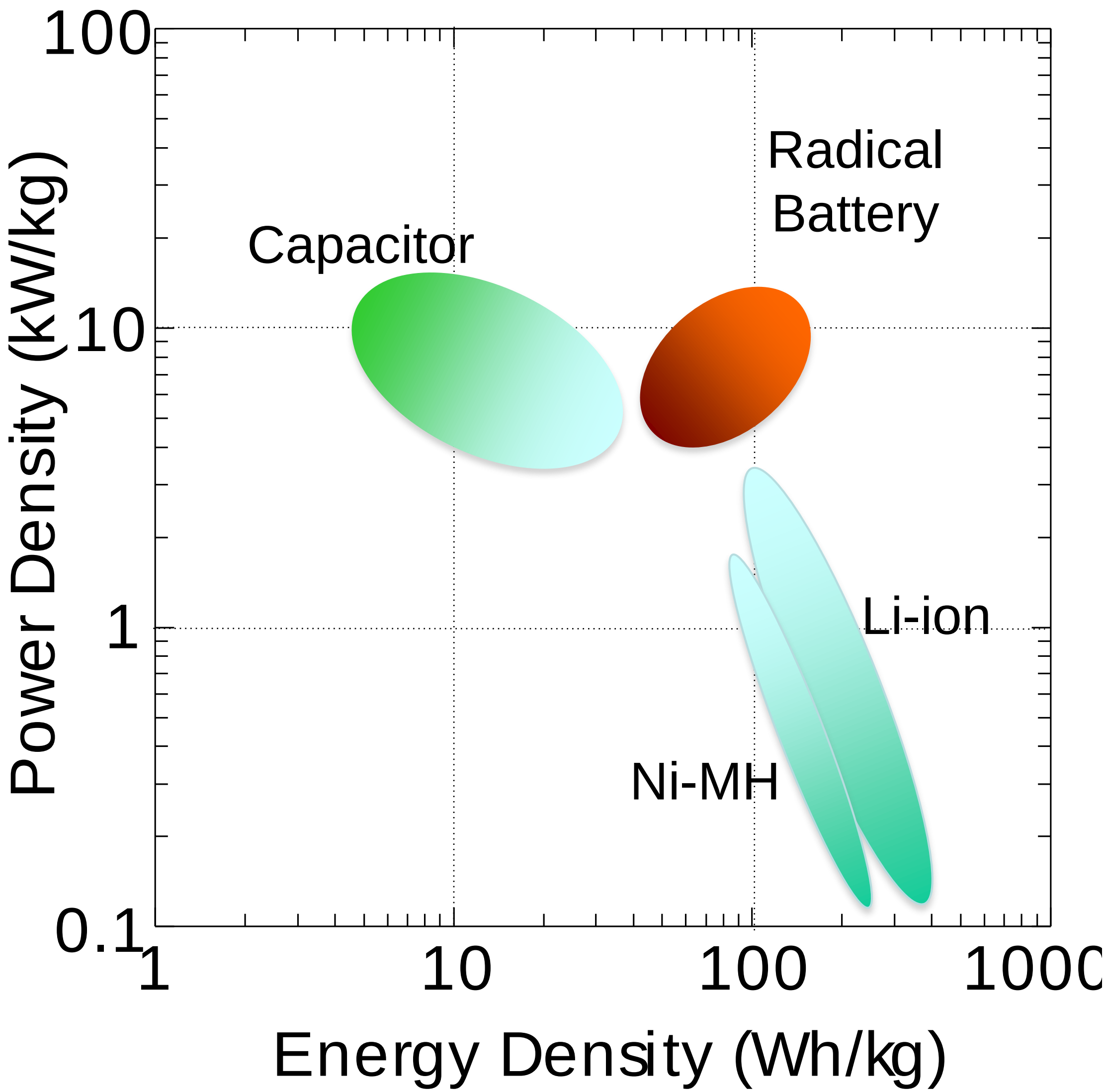
$$\text{Capacity } C = \frac{NA \cdot e}{3600 \cdot M/1000} = 111 \text{ (Ah/kg)}$$

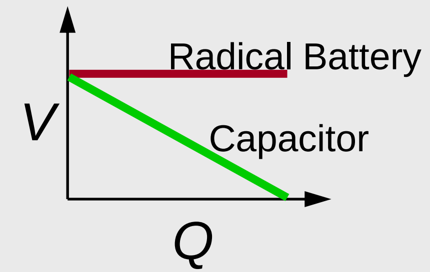
M: molecular weight, *e*: 96500 (C/mol), *N*: radical number in monomer unit, *A*: 6.02×10^{23}



Capacity: Almost 100% of the loaded radical polymer was electrode-active.
Current efficiency: 100%

Ragone Plot





Radical Battery vs. Capacitor

- Constant Output Voltage
- Free from Self-discharge

Organic Radical Battery

Fabricated in the smart cards and RFID tags

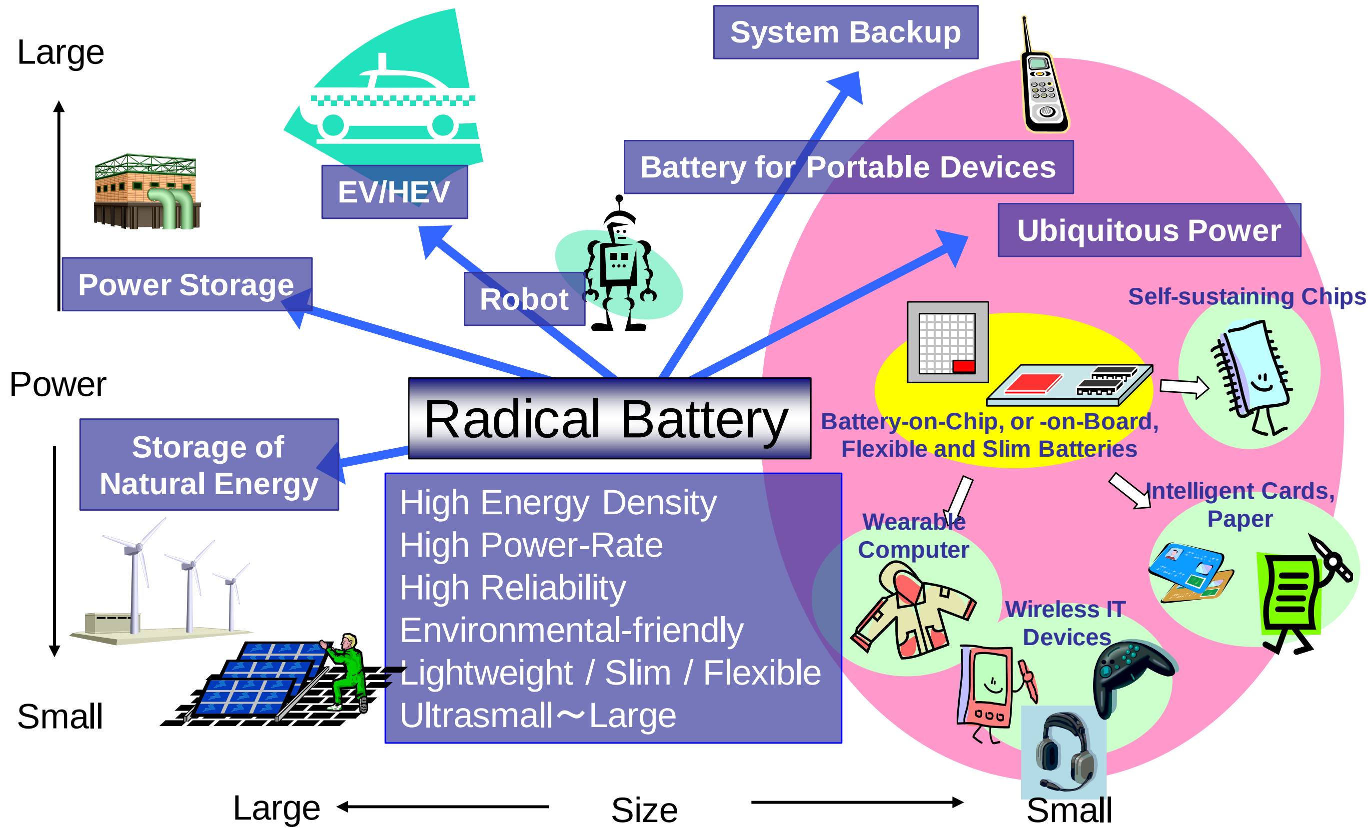
Flexible, paper-like battery

http://www.nec.co.jp/press/ja/0902/1302.html

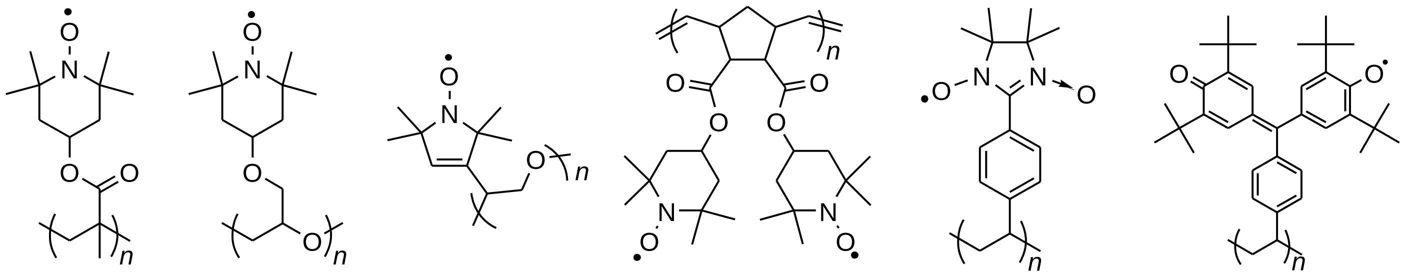
Radical Polymer Battery

- Light-weight, Flexible, Thin-film
- Less Energy-consuming Wet Fabrication Process
- Less-limited Organic Resources
- Easy Disposability: Burned away without toxic gas and ash formation
- Less-toxic Organic Materials: No-ignition, Non-fuming

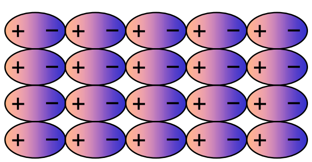
Safe & Environmentally-Benign (^_^)



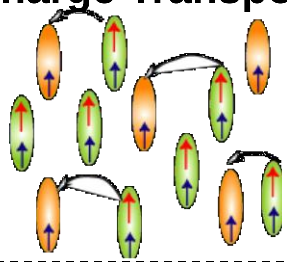
Ultimately Enriched Unpaired Electrons Placed on Non-Conjugated Polymer Scaffolds



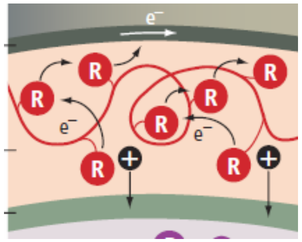
Charge Separation



Charge Transport

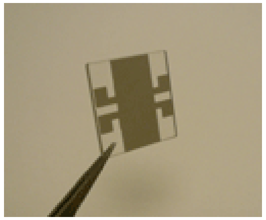


Charge Storage

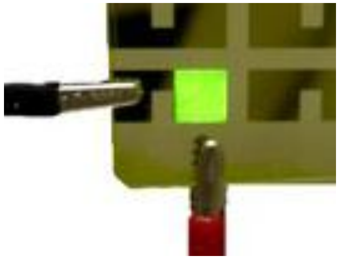


Rechargeable Batteries

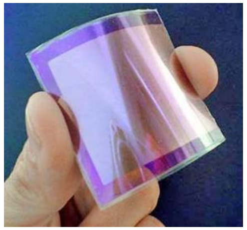
Polymer Memory



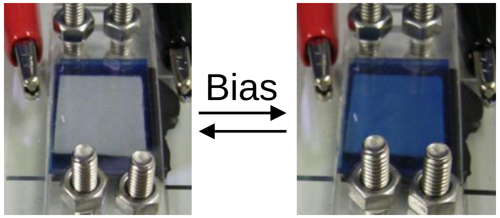
Hole-Transporting Layer



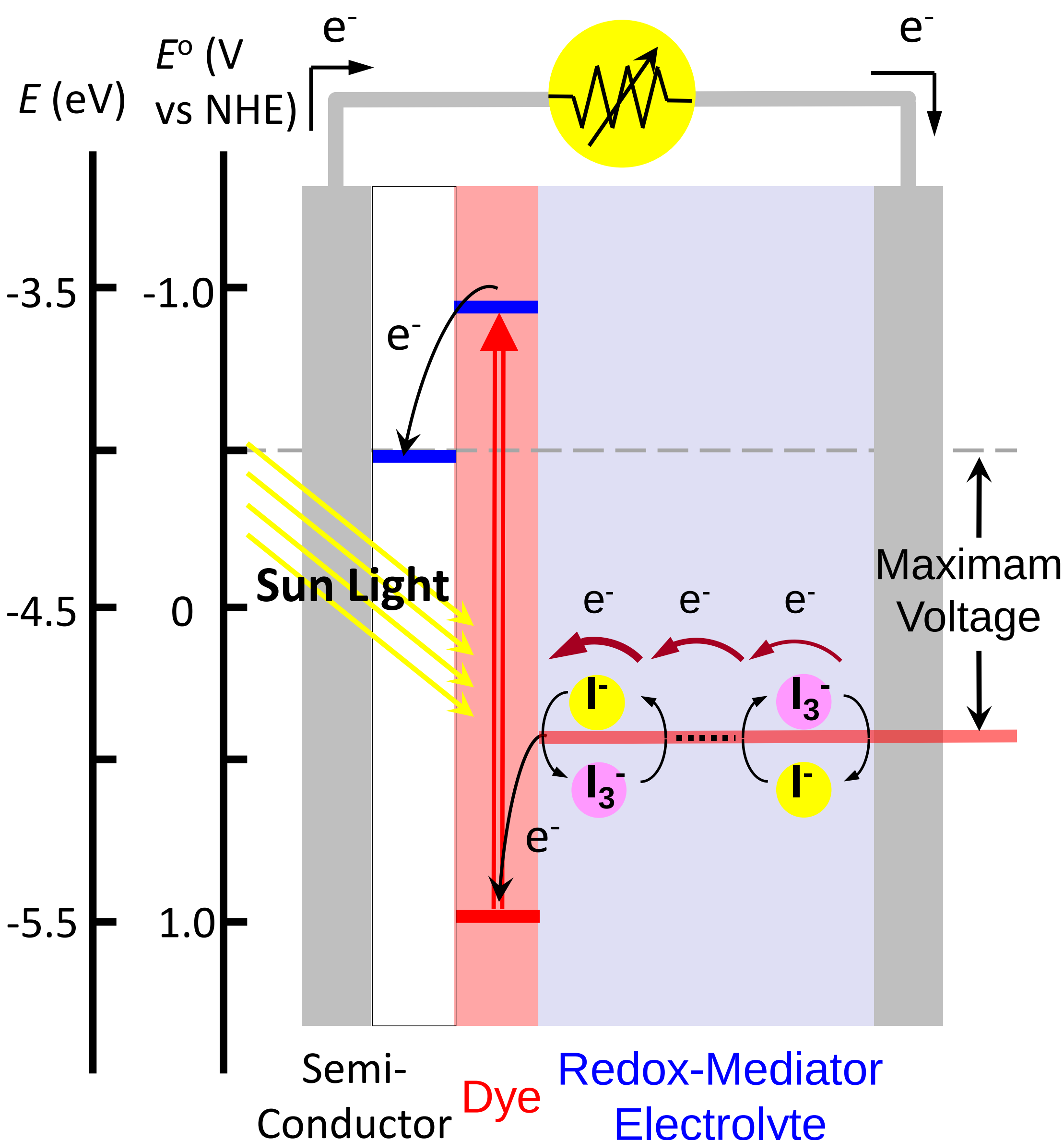
Photovoltaic Cell



Electrochromic Display



Dye-Sensitized Solar Cell (Grätzel Cell)



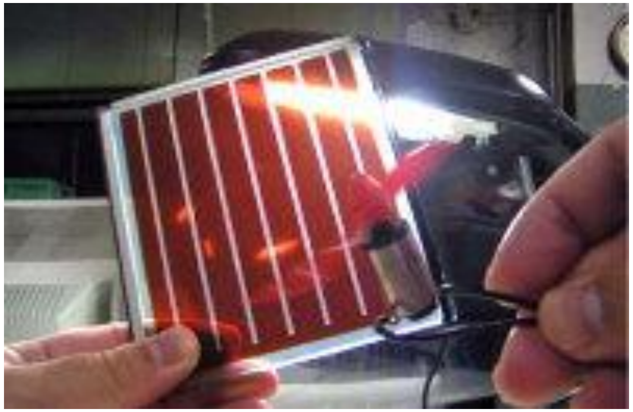
(1) Photo-excitation of dye-sensitizer

(2) Electron injection into metal oxide semi-conductor

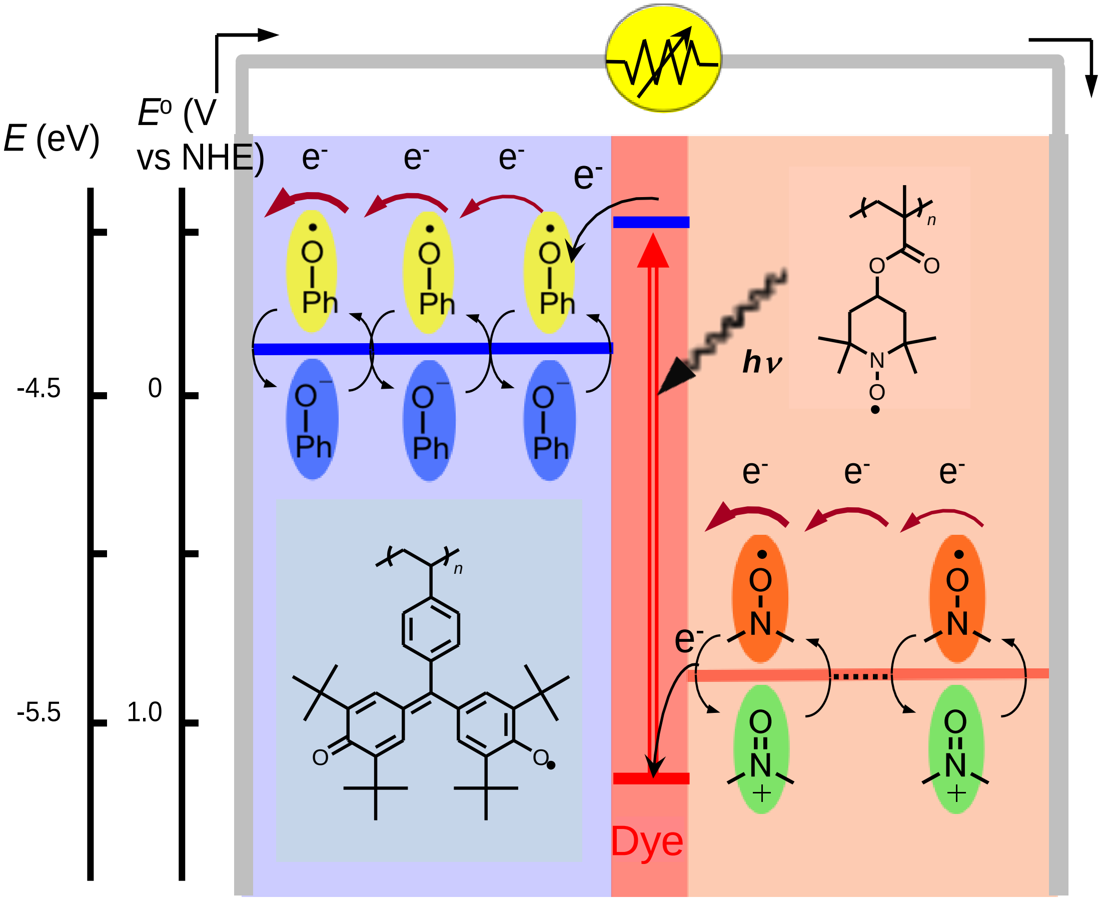
(3) Transport of electron

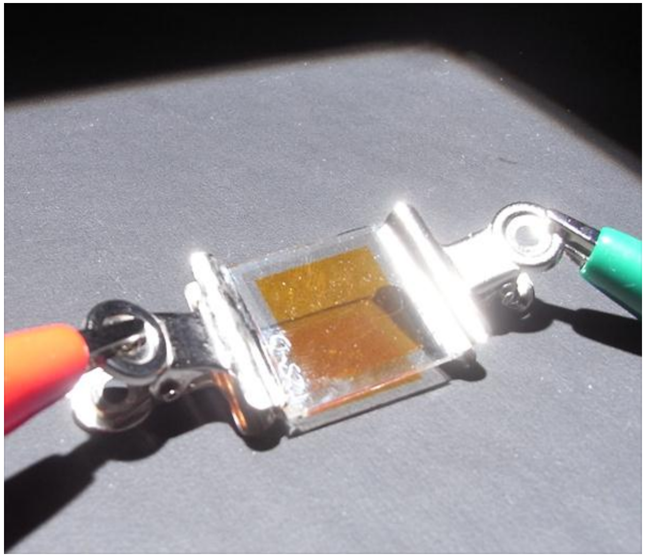
(4) Regeneration of the dye by redox-mediator

(5) Diffusion of the mediator and its regeneration

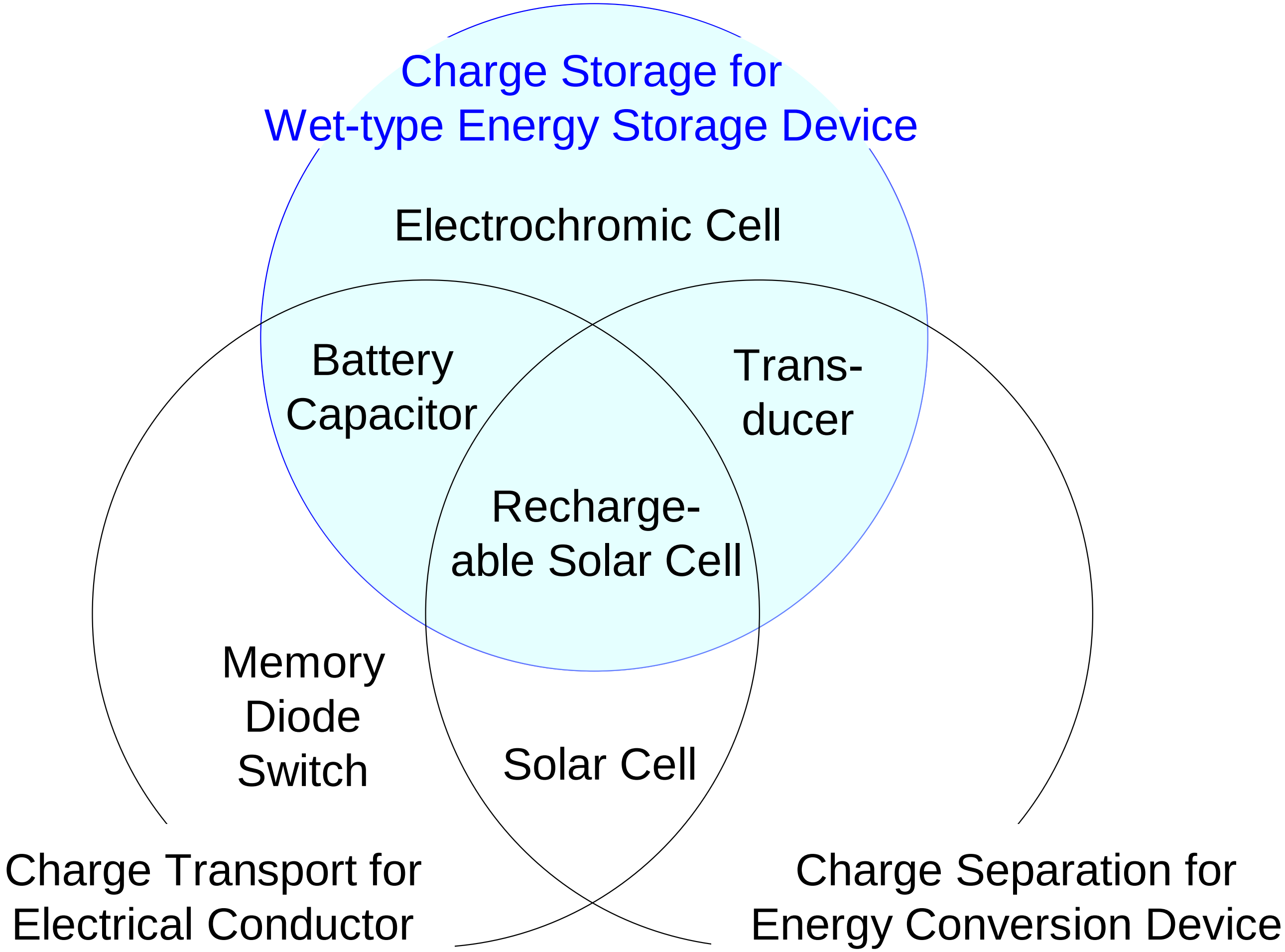


Totally Organic-Based Dye-Sensitized Solar Cell



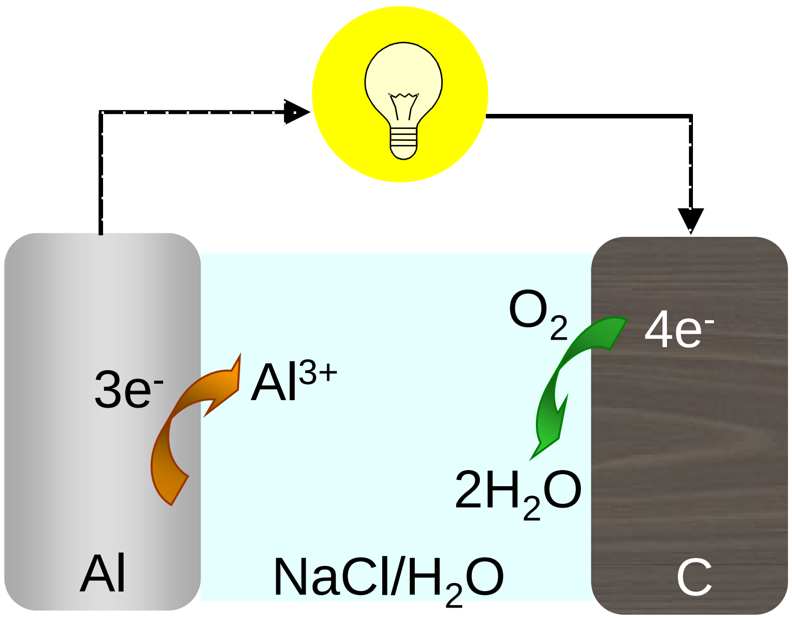


Radical Polymers as a New Class of Electroactive Materials: Their Electronic Functionalities Leading to Organic Devices



Adv. Mater., **21**, 2339 (2009).

Charcoal-Aluminium Battery



[Anode]

$$Al \rightarrow Al^{3+} + 3e^-$$

$$Al^{3+} + 6H_2O \rightarrow [Al(OH)_6]^{3-} + 6H^+$$

[Cathode]

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$