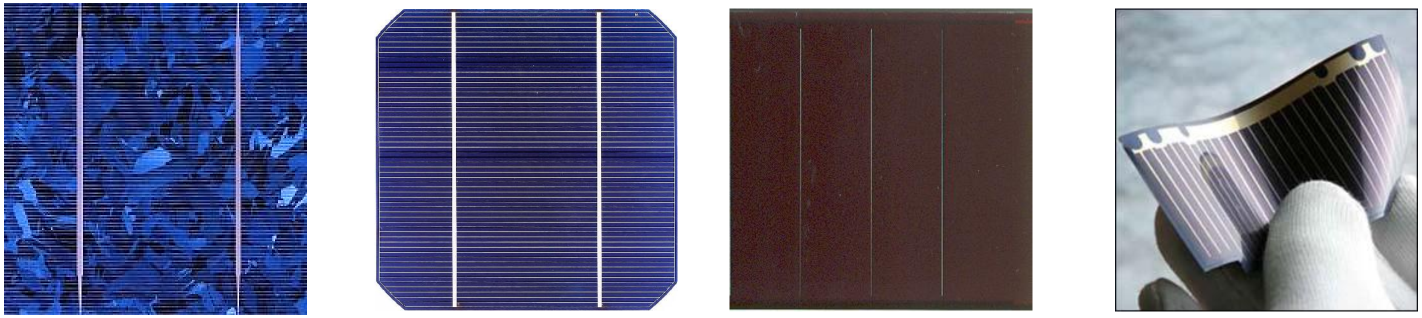
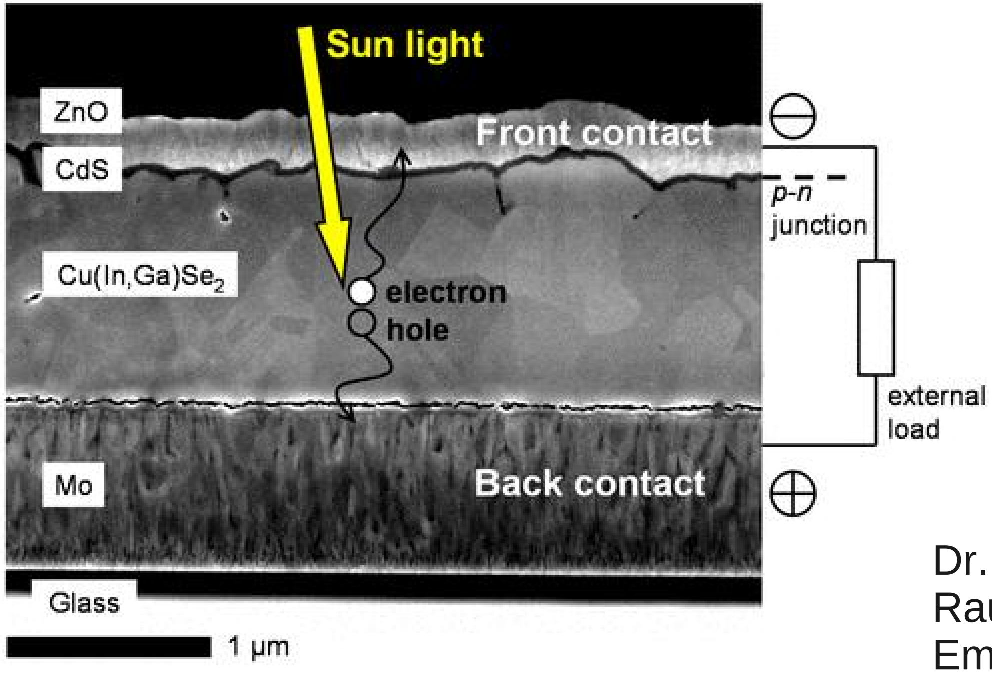
Dye Sensitized Solar Cells (27027-01)

(Dienstag, 8:00-10:00 Departement Physik, Seminarzimmer 3.12)





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Übersicht der Vorlesung

22.02.2011	allg. Einführung in die Solarenergie
01.03.2011	Physikalische Grundlagen der Photovoltaik I
08.03.2011	Physikalische Grundlagen der Photovoltaik II
15.03.2011	(Fastnachtsferien)
22.03.2011	Photochemische und photoelektrische Methoden der Energiewandlung
29.03.2011	Aufbau der Farbstoffsolarzelle, vgl. org. Solarzelle
05.04.2011	TiO_2 Nanopartikel als Substrat der Frabstoffsolarzelle
12.04.2011	Geeignete molekulare Farbstoffe zur Sensibilisierung
→ **19.04.2011**	Funktionsweise und Alternativen für den Elektrolyten
26.04.2011	(Osterferien)
03.05.2011	(FANAS meeting)
10.05.2011	Experimentelle Methoden zur Solarzellen-Charakterisierung
17.05.2011	Experimentelle Methoden zur Solarzellen-Charakterisierung
24.05.2011	Bau und Charakterisierung eigener Solarzellen
31.05.2011	

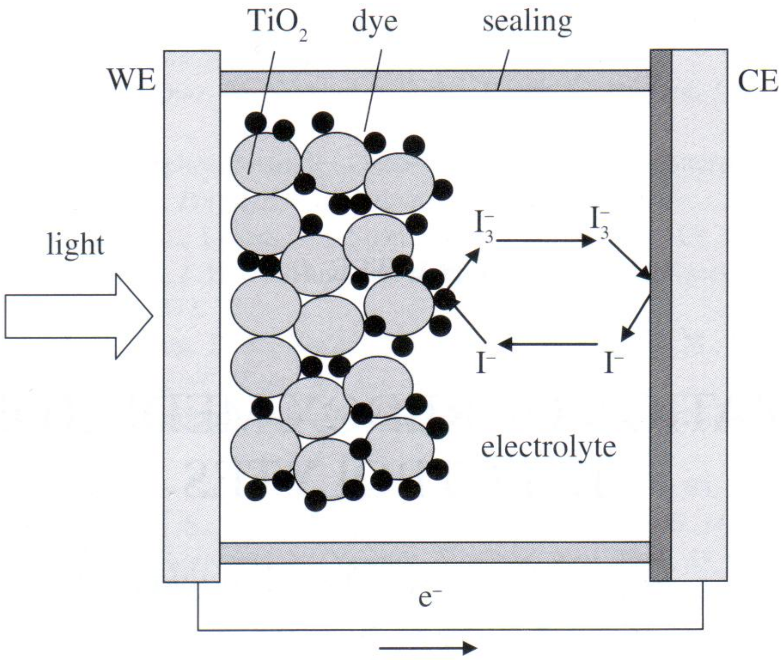
Funktionsweise und Alternativen für den Elektrolyten

Redox Mediators and Electrolytes

- Liquid Electrolytes
  - Organic solvents
  - Cations
  - Additives
  - Electron Mediators

- Ionic Liquid Electrolytes
- Quasi- and Solid State Electrolytes

Standard Setup

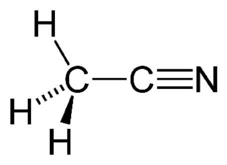


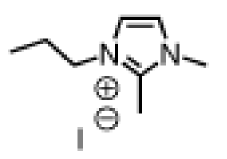
- Liquid electrolytes
  - Organic solvent-based
  - Ionic liquid-based
- Quasi-solid state electrolytes
- Solid state electrolytes

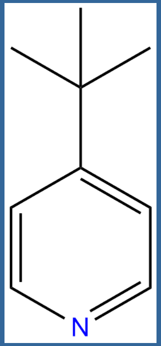
Typical electron mediator: iodide/triiodide redox couple
Function: reduce dye cation by electron injection, charge transport
Additives: e.g. lithium salt, tert-butylpyridine

Liquid Electrolytes

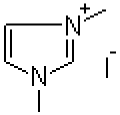
- Organic solvent-based electrolytes (OLEs)
  - Mainly based on acetonitrile (CH_3CN)
  - Dissolves wide range of organic and inorganic compounds
  - Record cell (11.1%) consisting:
    - Dimethyl propyl imidazolium iodide (0.6 M) $C_8H_{15}N_2I$
    - lithium iodide (0.1 M)
    - iodine (0.05 M)
    - tert-butylpryidine (0.5 M)

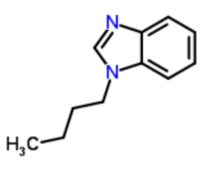


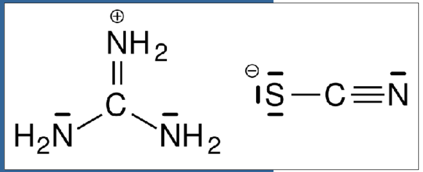


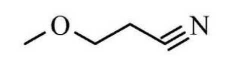


Liquid Electrolytes





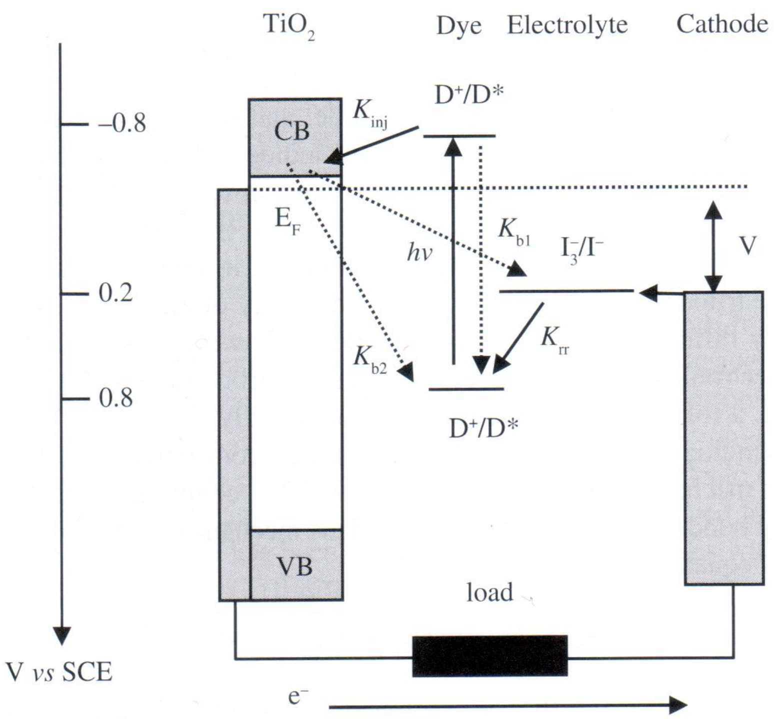




- Ionic liquid-based electrolytes (ILEs)
  - Better long-term stability
  - Non-volatile
  - Efficiency of 8.5-9.5% is reached:
    - 1,3-dimethyl imidazolium iodide (DMII) (1.0 M)
    - Iodine I_2 (0.15 M)
    - N-butylbenzoimidazole (NBB) (0.5 M)
    - guanidinium thiocyanate (GNCS) (0.1 M)
    - in 3-methoxypropionitrile (MPN)

Further improvements by adding gelling agents:
Inorganic nanoparticles, low molecular weight and polymer gelators

Charge Transfer Processes



- $S^*|TiO_2 \rightarrow S^+|TiO_2 + e_{cb}^-(TiO_2)$
- $S^+|TiO_2 + 3/2I^- \rightarrow S|TiO_2 + 1/2I_3^-$
- $S^+|TiO_2 + e_{cb}^-(TiO_2) \rightarrow S|TiO_2$
- $2e^-|TiO_2 + I_3^- \rightarrow 3I^-$
- $I_3^- + 2e^-|Pt \rightarrow 3I^-$

- Oxidation of I^-
- I_3^- migration
- Reduction of I_3^-
- I^- back diffusion
- Recombination processes

Iodide is depleted at the photoanode and triiodide at the cathode
Typically sufficient excess of iodide (10x)
The diffusion coefficient of iodide is higher -> current limitations due to I_3^-

Organic Solvents

- The flatband potential V_{fb} of the TiO_2 is sensitive to the solvent
  - Water and nonaqueous protic solvents shift V_{fb} to positive values, are independent of other cations (Li^+), and enhance desorption of dye molecules (alcoholic solvents)
  - Optimal organic solvents are nitrile and ester based
    - Acetonitrile
    - 3-methoxypropionitrile
    - Valeronitrile
    - Ethylene carbonate
    - Propylene carbonate

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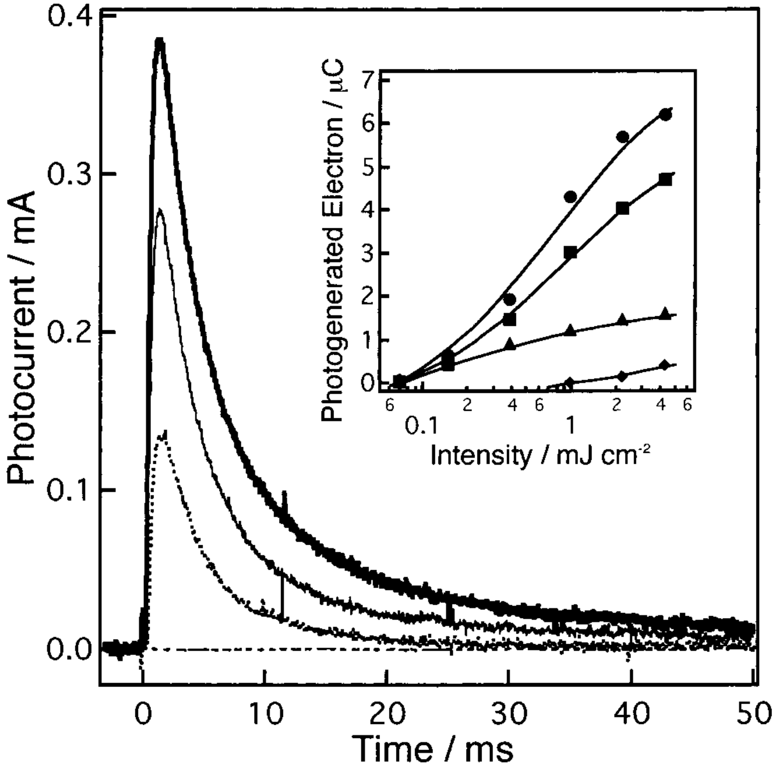
Cations

- Screening of the photo-injected electrons in the TiO_2 network
- Various cations were analyzed LiI, NaI, KI, RbI, CsI
  decreasing J_{sc} and increasing V_{oc} with increasing cation radius
- Injected electrons accumulate in the conduction band of TiO_2, cations compensate the charge by adsorption or intercalation, V_{fb} moves to positive values and the drop depends on type of cation
- Small cations adsorb easily on TiO_2 and increase the photocurrent while decreasing the V_{oc}
- The effect depends strongly on the cation density

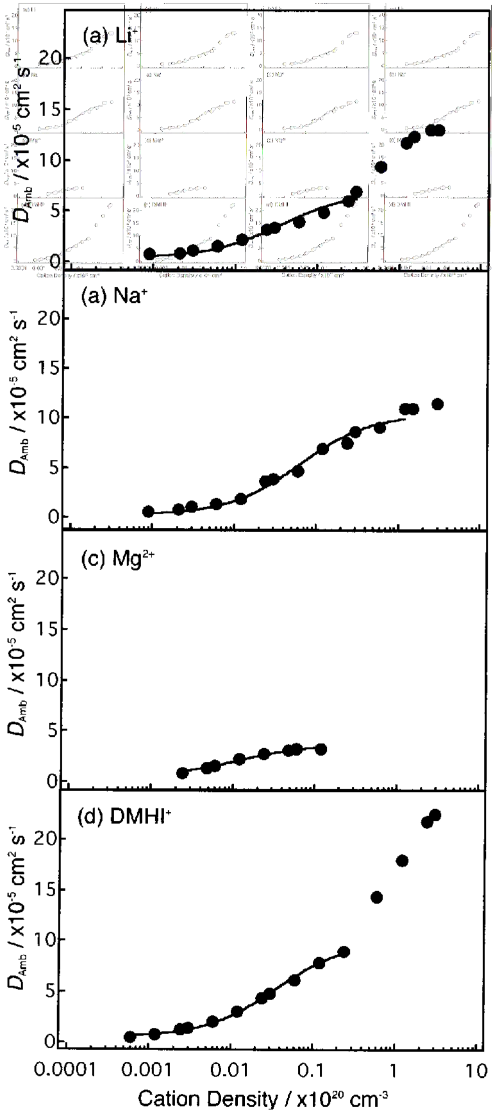
Photocurrent transients



- Photocurrent transients induced by pulsed UV irradiation for 7.2 µm thick TiO_2 mesoporous electrodes in ethanol with 0.5 M of salts.
- Salts used are $LiClO_4$ (bold line), $NaClO_4$ (solid line), $TBA^+ClO_4^-$(dotted line), and $DMHI^+Br^-$ (broken line).
- Inset shows amounts of photo-generated electron as a function of the pulse intensity in the presence of Li^+ (circles), Na^+ (squares), TBA^+ (triangles), and $DMHI^+$ (diamonds).

S. Kambe et al., J. Phys. Chem. B 106, 2967, (2002).

Diffusion coefficients



- Diffusion coefficients as a function of cation density of
- $LiClO_4$ (a), $NaClO_4$ (b), $Mg(ClO_4)_2$ (c), and $DMHI^+ClO_4^-$ (d) in acetonitrile.
- Description by the ambipolar diffusion model

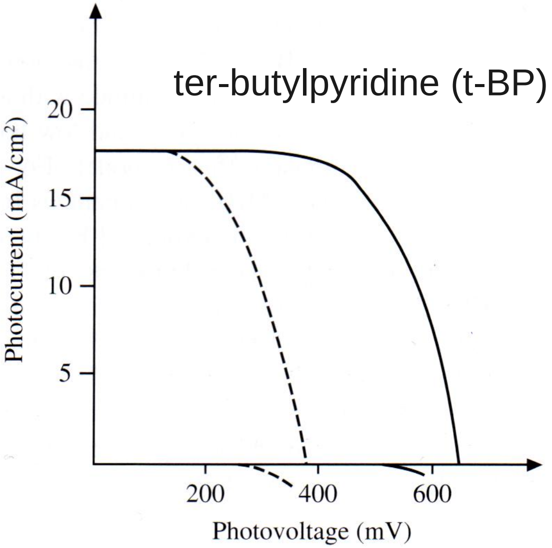
$$D_{amb} = \frac{(n+p)}{(n/D_p) + (p/D_n)}$$

n and D_n are the negative charge density and diffusion coefficients
p and D_p are their negative counter parts

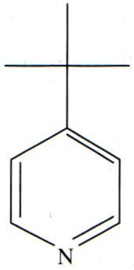
S. Kambe et al., J. Phys. Chem. B 106, 2967, (2002).

Addetives

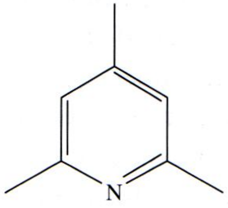
Enhanced performance by nitrogen-containing heterocyclic compounds



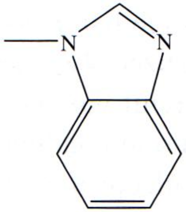
- Suppression of back electron transfer (K_{b2})
- Free surface areas after sensitization are covered by additives
- Smaller additives higher V_{oc}
- Negative shift of V_{fb}
- Formation of charge transfer complexes with I_3^-



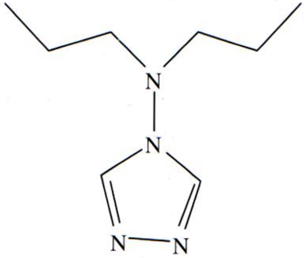
4-*ter*-butylpyridine



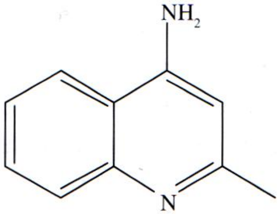
2,4,6-trimethylpyridine



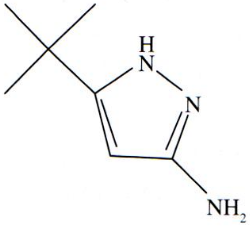
N-methylbenzimidazole



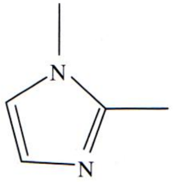
N,N-dipropyl-4*H*-1,2,4-triazol-4-amine



2-methylquinolin-4-amine

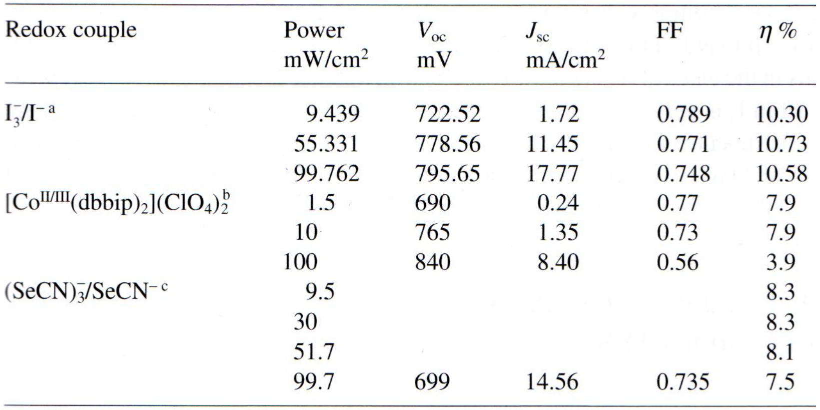


5-*tert*-butyl-1*H*-pyrazol-3-amine



1,2-dimethyl-1*H*-imidazole

Electron Mediators

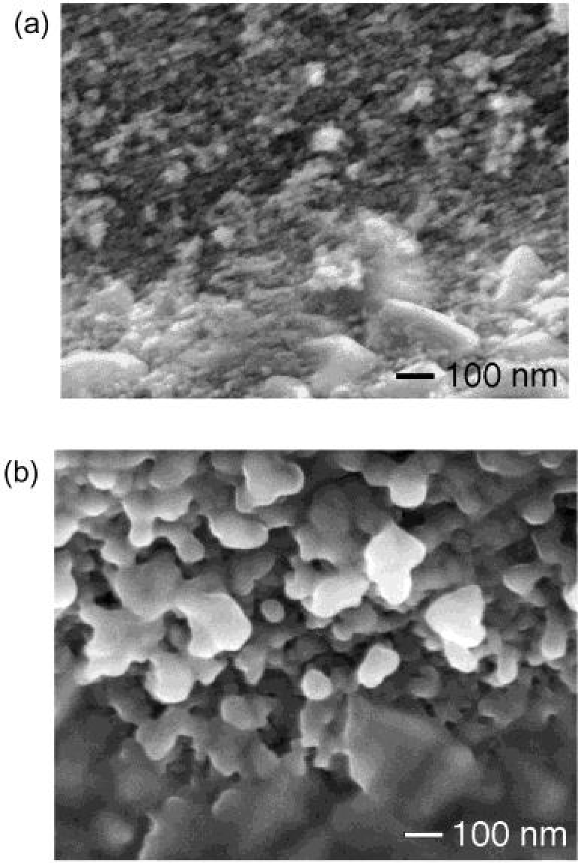


Redox couple	Power mW/cm^2	V_{oc} mV	J_{sc} mA/cm^2	FF	η %
I_3^-/I^- [a]	9.439	722.52	1.72	0.789	10.30
	55.331	778.56	11.45	0.771	10.73
	99.762	795.65	17.77	0.748	10.58
$[Co^{II/III}(dbbip)_2](ClO_4)_2$ [b]	1.5	690	0.24	0.77	7.9
	10	765	1.35	0.73	7.9
	100	840	8.40	0.56	3.9
$(SeCN)_3^-/SeCN^-$ [c]	9.5				8.3
	30				8.3
	51.7				8.1
	99.7	699	14.56	0.735	7.5

- Limits of the I_3^-/I^- redox couple:
  - Light screening due to adsorption on TiO_2
  - Low redox potential (limits V_{oc})
  - Corrosivity on most metals
- Other electron mediators give mainly poor conversion efficiencies due to mass transport limitations and unsuitable chemical kinetics
- Most promising:
  - Polypyridyl cobalt complexes
  - $(SeCN)_3^-/SeCN^-$ redox couples

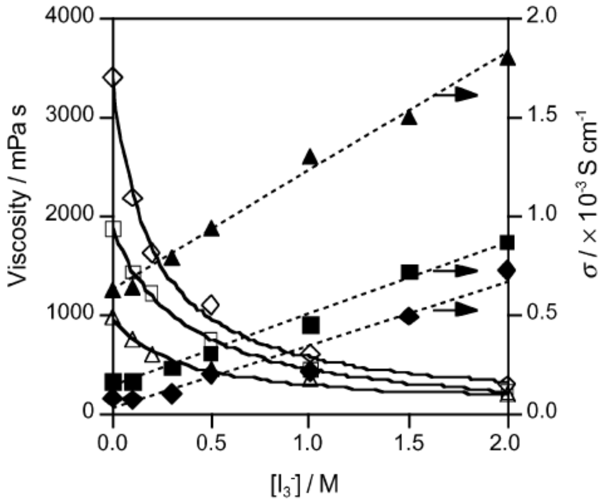
Ionic Liquid Electrolytes

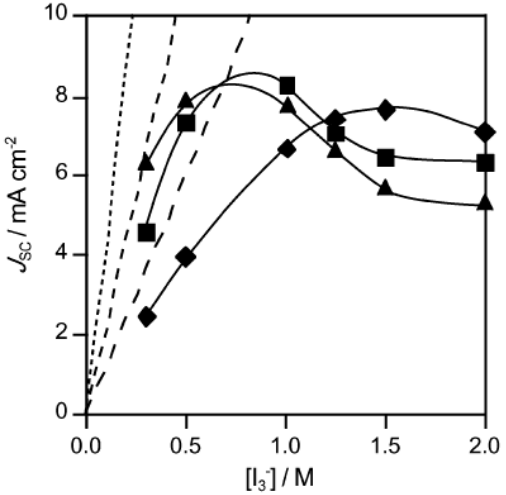
- Advantages:
  - Low melting point
  - Thermal and chemical stability
  - Negligible vapor pressure
  - Non-flammability
  - Wide electrochemical parameter set
  - High ionic conductivity and solubility for most organic and inorganic materials
- Disadvantages
  - High viscosity....low diffusion...higher I_3^- concentration necessary
  - Light absorption due to I_3^-



W. Kubo et al., J. Phys. Chem. B 107, 4374, (2003).

Ionic Liquid Electrolytes

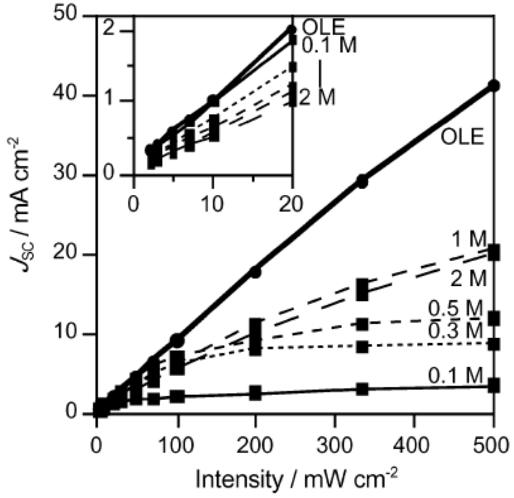


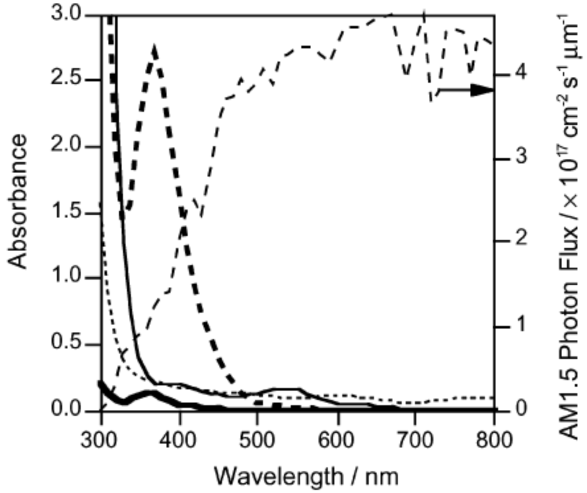


- Effect of I_3^- concentration in ILE
- on **viscosity** left axis: open triangle, PMImI; open square, HMImI; open diamond, NMImI and
- on **conductivity** right axis: closed triangle, PMImI; closed square, HMImI; closed diamond, NMImI
- The **diffusion coefficient** in ILEs is 1-2 orders of magnitude lower than that in OLEs -> I_3^- concentration gradient
- Due to higher concentration also **higher light absorption**

W. Kubo et al., J. Phys. Chem. B 107, 4374, (2003).

Ionic Liquid Electrolytes





- Effect of incident light intensity on J_{SC} using OLE (circles) and ILE (HMImI, squares) with various I_3^- concentrations
- Absorption spectra of OLE $[I_3^-] = 0.05$ M (bold curve), ILE $[I_3^-] = 1$ M (bold dashed curve), and dye adsorbed TiO_2 film (solid curve) normalized to 1 µm thick, conducting glass (dotted curve); and AM1.5 photon flux density (dashed curve, right axis).
- Essential to improve the charge transfer of I_3^-, not only by increasing concentration but by decreasing the viscosity and increasing the conductivity.

W. Kubo et al., J. Phys. Chem. B 107, 4374, (2003).