Development of cross-linked polymer electrolytes for lithium batteries: an overview

Helmholtz Institute Münster (HI MS) ionics in energy storage, Germany

18.07.2018 / Dr. Jijeesh Ravi Nair

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NiPS Summer School 2018
Perugia (Italy): July 17 - 20, 2018

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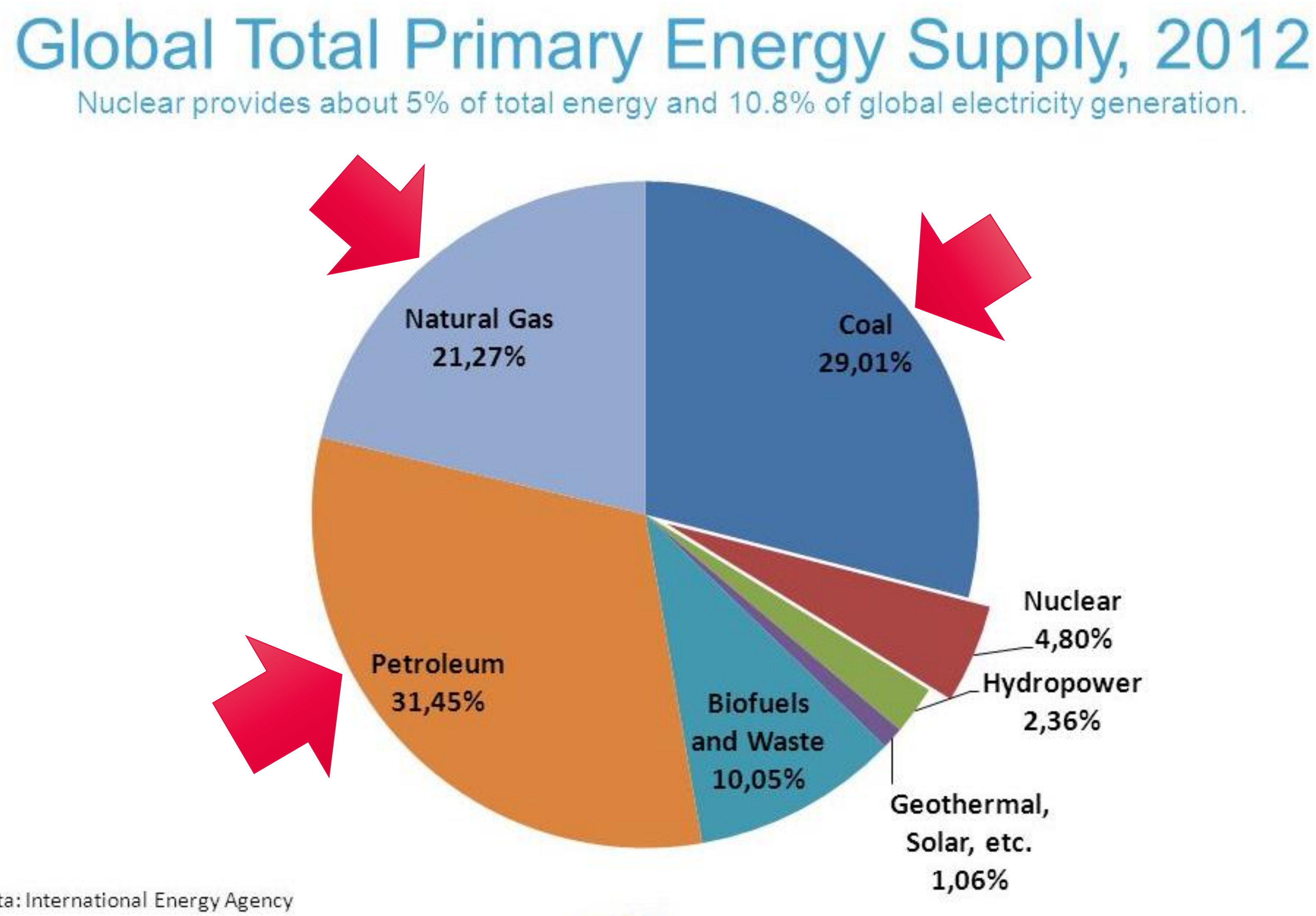
ENERGY

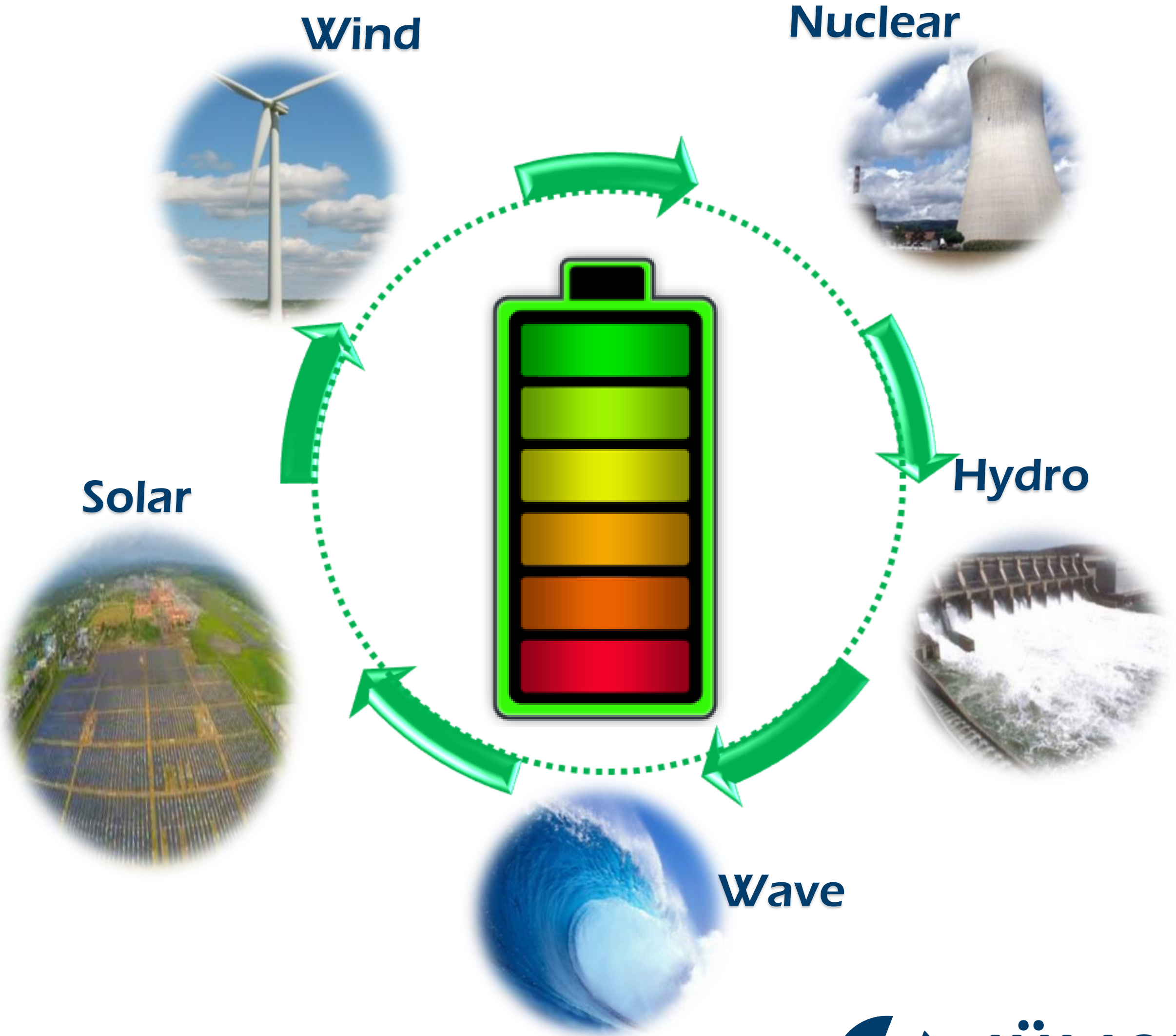

Global Total Primary Energy Supply, 2012
Nuclear provides about 5% of total energy and 10.8% of global electricity generation.
Natural Gas 21,27%
Coal 29,01%
Nuclear 4,80%
Hydropower 2,36%
Petroleum 31,45%
Biofuels and Waste 10,05%
Geothermal, Solar, etc. 1,06%
Data: International Energy Agency

THE ENERGY SCENARIO

Fluctuating price and limited resources

Crude Oil Price History Chart

Pollution



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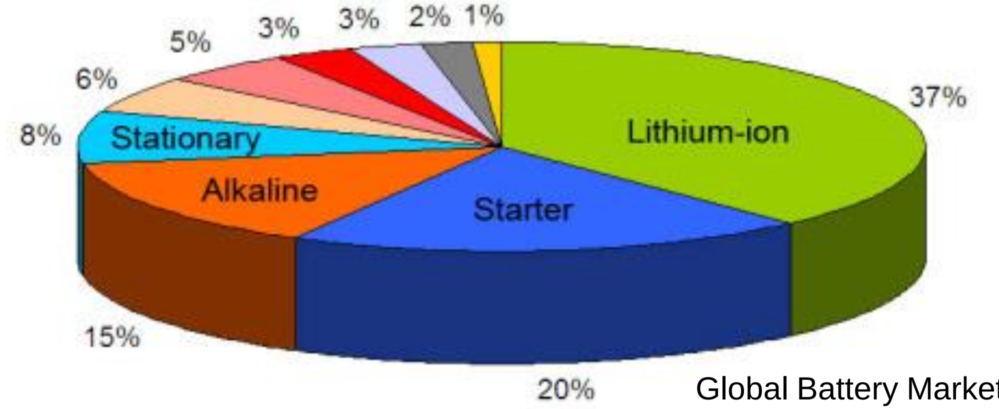
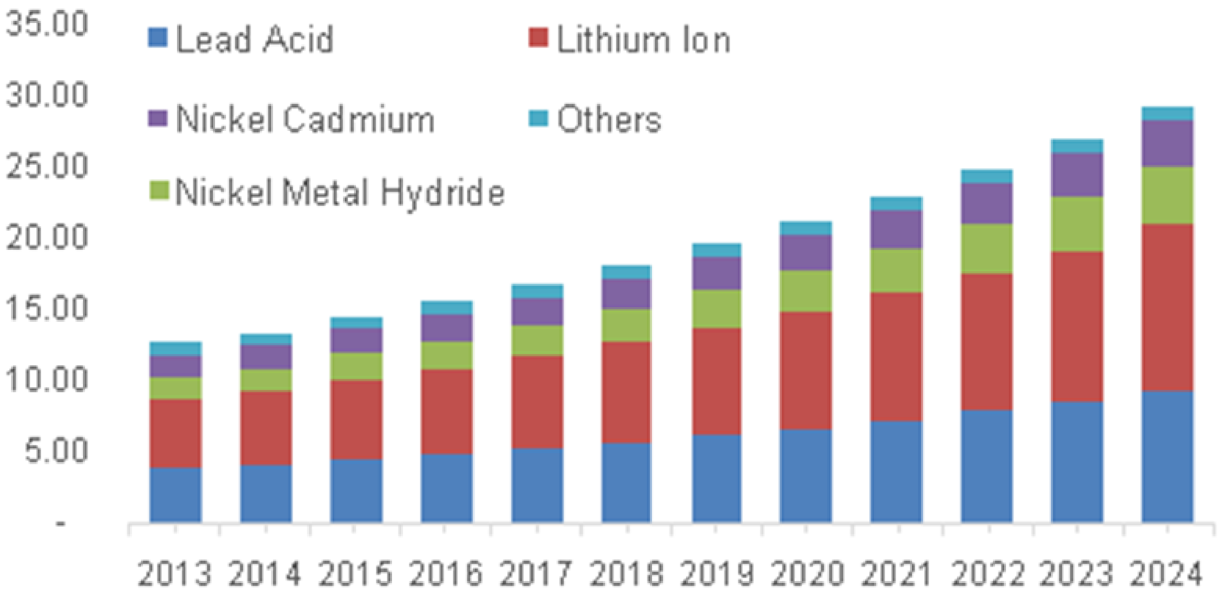
THE PRESENT BATTERY SCENARIO



Global Battery Market 2009

Market research and consulting services



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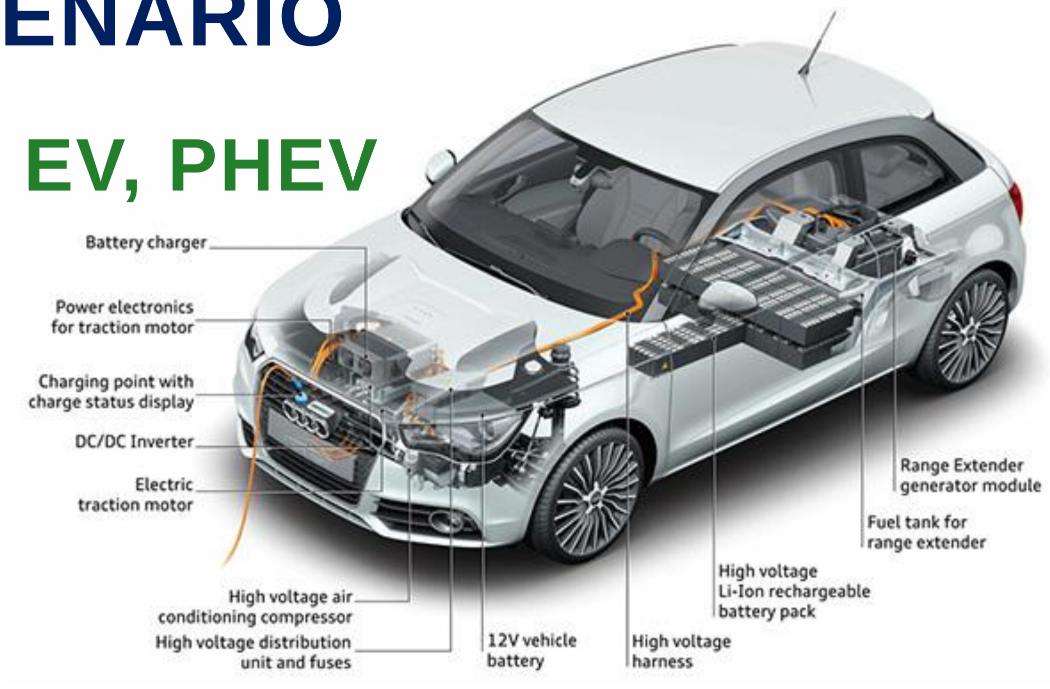
THE ENERGY SCENARIO

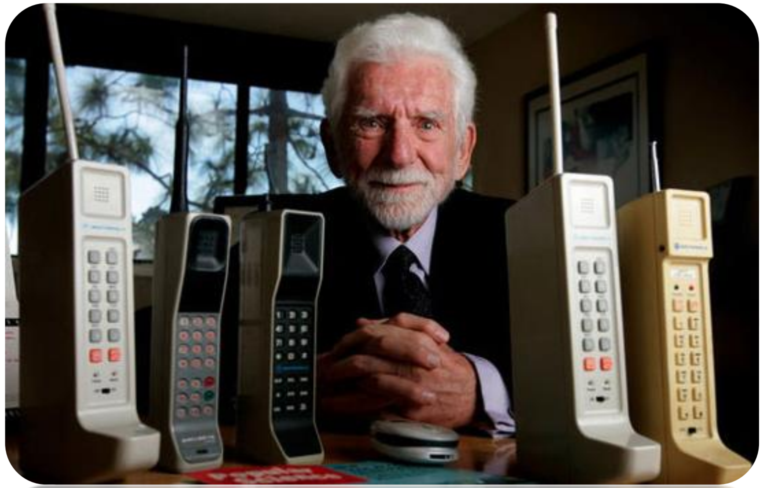
EV, PHEV



Consumer Electronics

Smart Grid

PRESENT MOBILE BATTERY



Martin Cooper
Motorola
DynaTAC 8000X
$3995
(Ni-Cd) battery
10 hours to Recharge

Today:

8GB RAM

256 GB Hard disk

Octa core processor

No Display to OLED

4-6 Ah Batteries

Fast Charging

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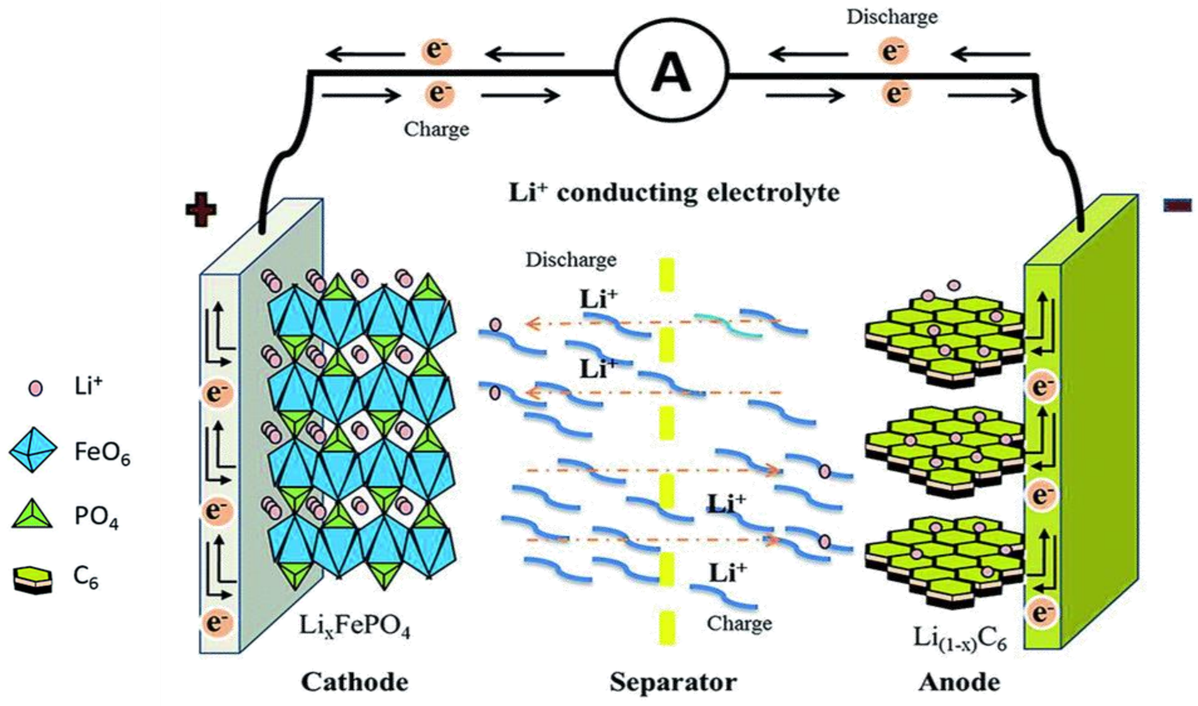
LI-ION CELLS: Working principle and characteristics

Li-ion batteries are based on fully mature technology with a wide range of applications



SONY 1990s

TYPICAL SETUP:

Cathode: Li-TMOs supported on Al metal

Separator: synthetic glass-fiber or Celgard®

Electrolyte: liquid solutions (organic solvents + Li-salt)

Anode: C-based compounds supported on Cu

Li^+ ions migrate back & forth in the electrolyte between the negative and positive electrodes upon discharge or charge. The electron flow counterbalances the ion flow within the electrode materials and externally through the outer electrical circuit. The potential difference between the positive and negative electrodes defines the cell potential.

LI-ION BATTERIES

DRAWBACKS:

- expensive/toxic materials (materials, solvents, binders)
- **Safety issues (liquid electrolyte)**
- Design adaptability (metal foils)
- Expensive to manufacture
- End-of-life treatment

SOLUTIONS:

✓Inventive, Innovative, Relevant and **eco-friendly materials**

✓Optimisation of existing chemistries

✓Reliable and low-cost synthesis

✓Easier/faster processes

✓**Switching to all-solid-state…**

KEYWORDS

eco-friendly

Top Notch performing

low-cost

up-scalable

safe





Better Batteries

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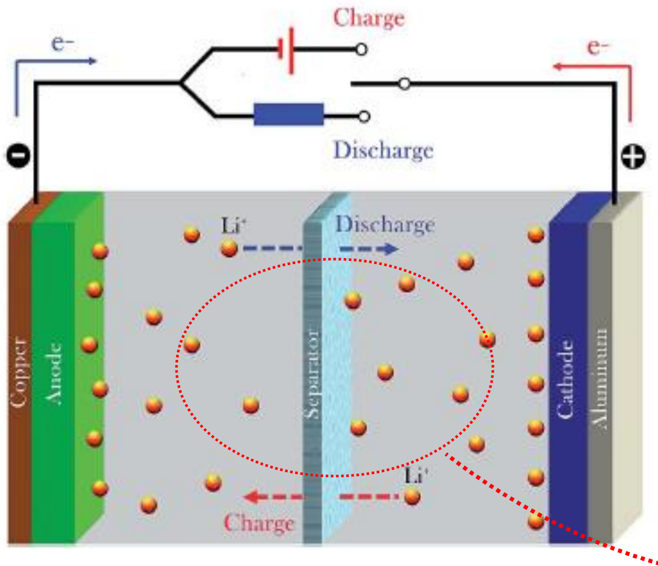
LITHIUM ION BATTERY



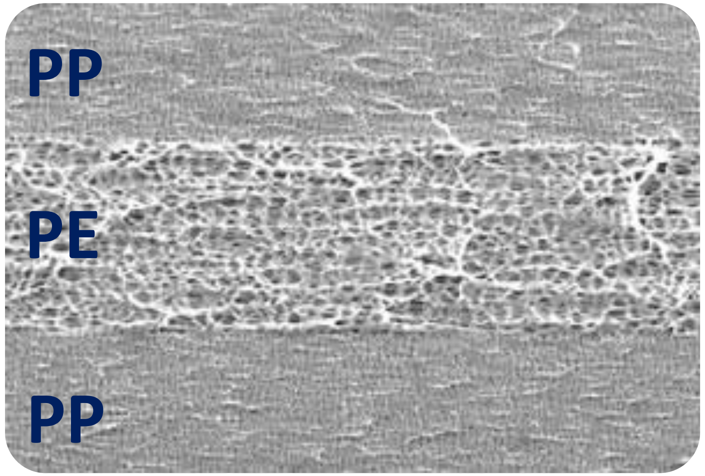
J Mater Chem A 2016, 4, 10038–69

Organic carbonates

Additives

Salts

Celgard as separator

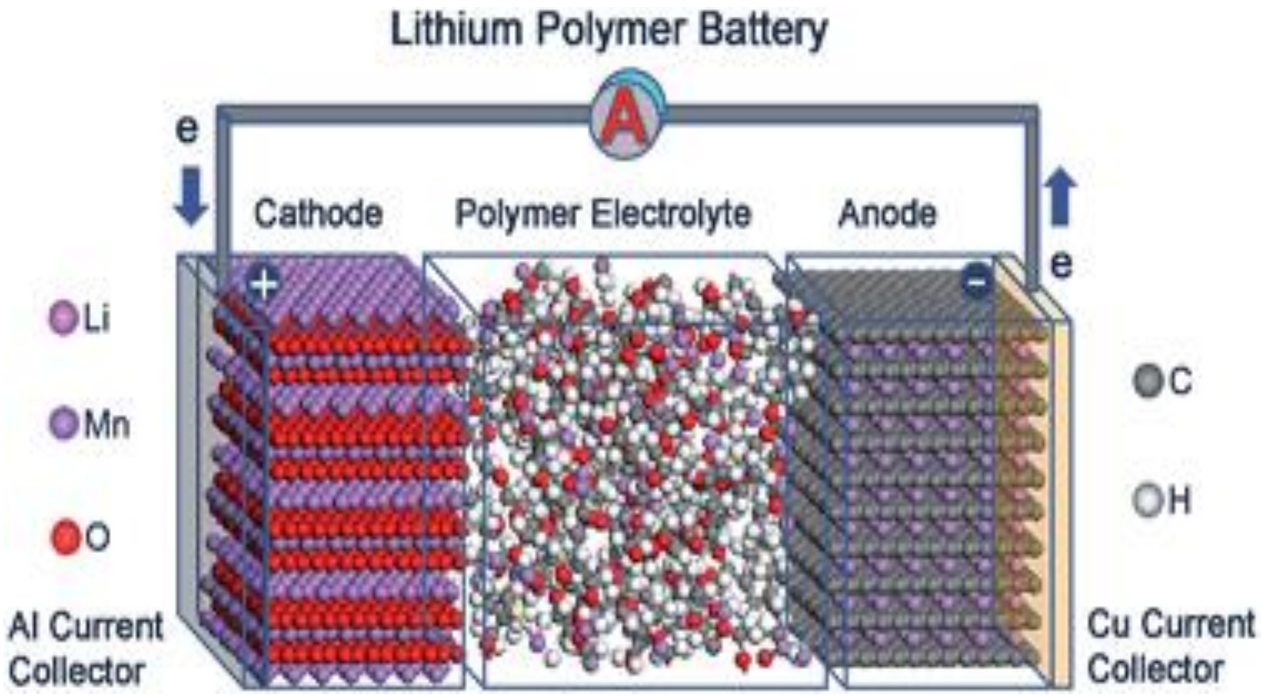


Fire

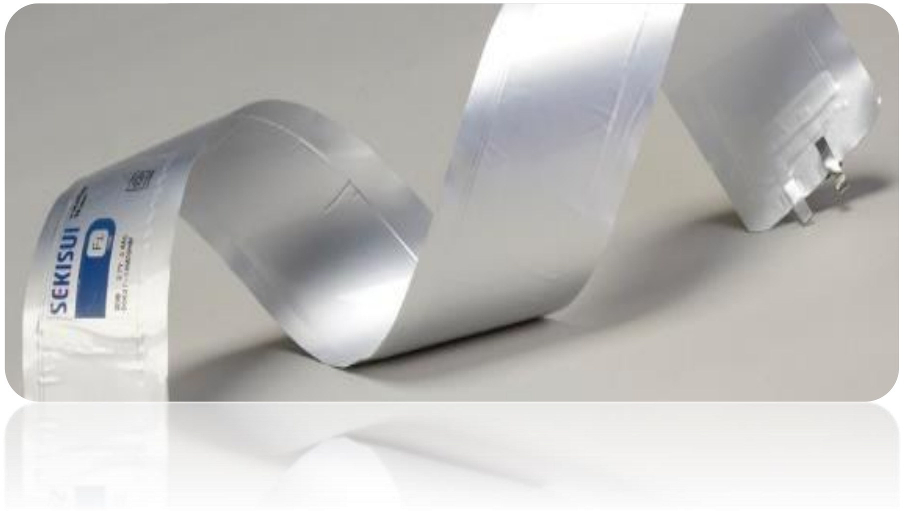
Leaking

Gas Evolution

LITHIUM POLYMER BATTERY



J. Mater. Chem. A, 2016,**4**, 10038-10069



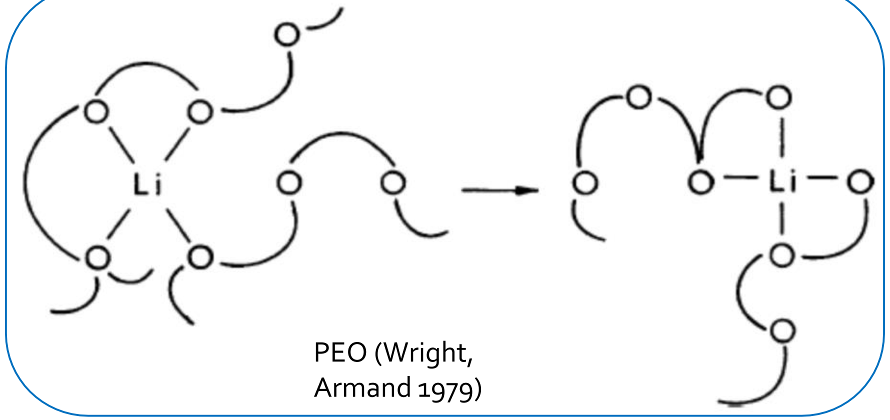
- Safety
- High energy

- Thin
- Flexible
- Leak-free

POLYMER CELLS

D. E. Fenton, J. M. Parker,
P. V. Wright,
Polymer, 1973,14, 589.

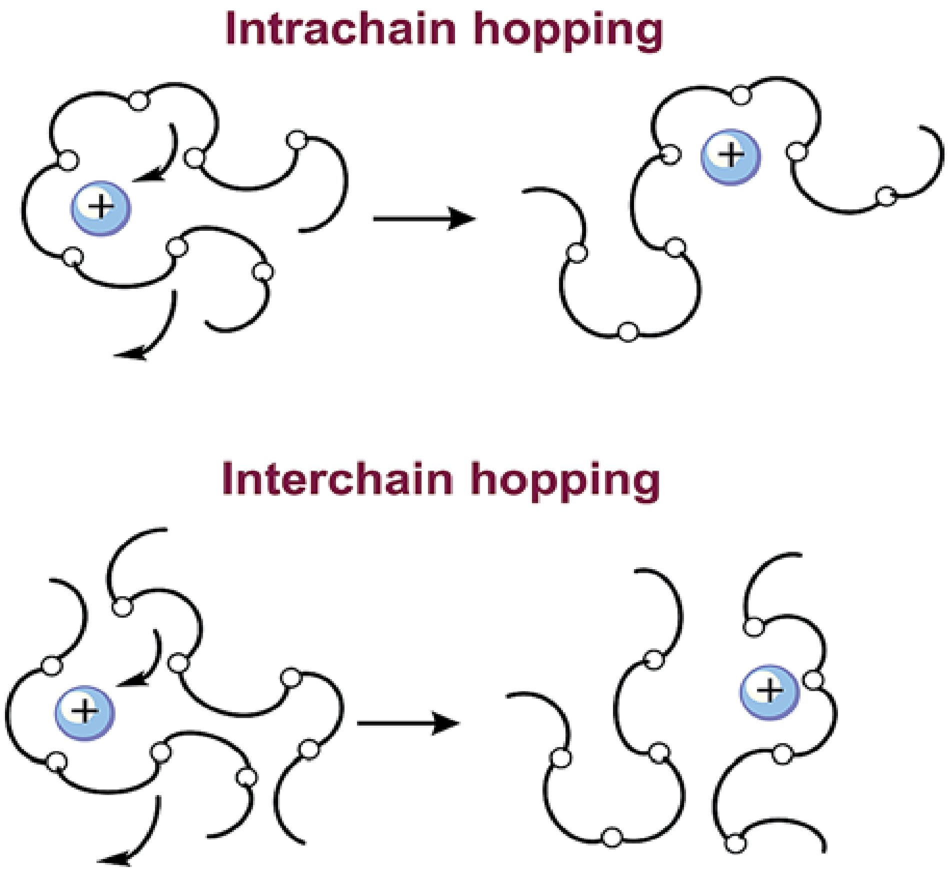
Wright and co-workers were the first to discover that the ether-based polymer, poly(ethylene oxide) (PEO) was able to dissolve inorganic salts and exhibit ion conduction at room temperature.



PEO (Wright, Armand 1979)

The microscopic environment remains liquid like for Li^+-ion, and the conductivity is "coupled" to the local segmental motion of the polymer, often characterized by T_g of the polymer.

ION CONDUCTION IN POLYMER ELECTROLYTE



J. Mater. Chem. A,2015, 3,19218–19253

- ion transport occurs by intrachain or interchain hopping
- the continuous segmental rearrangement results in a long-range displacement of lithium ions

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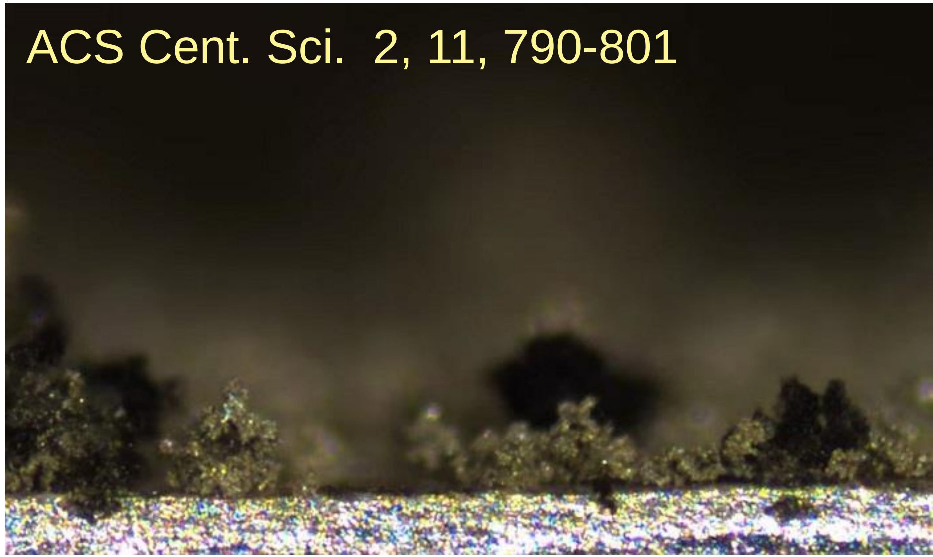
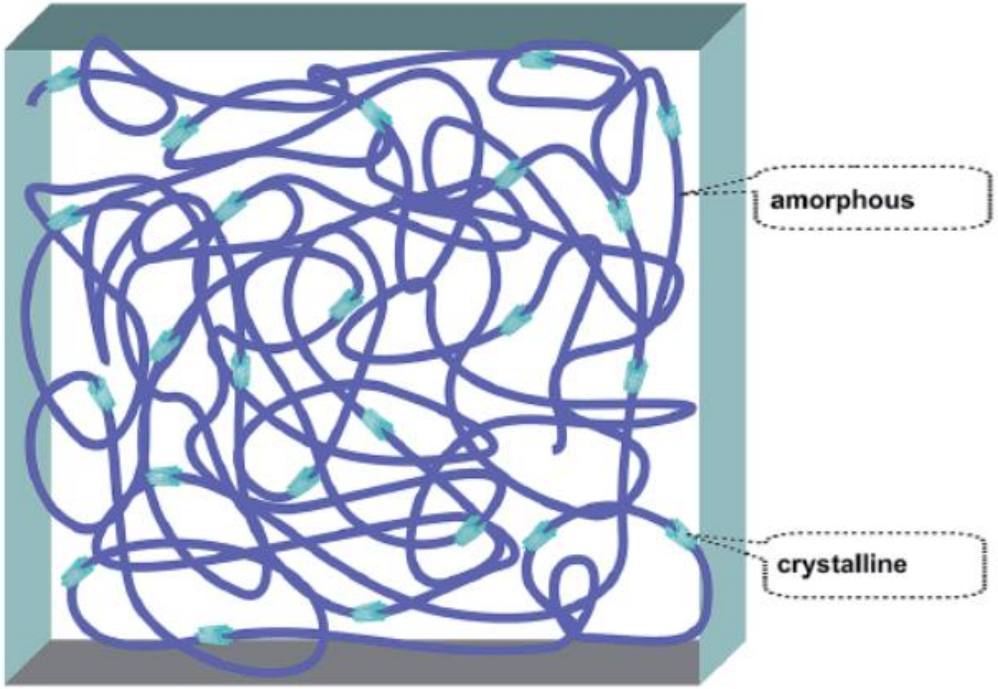
REQUIREMENTS OF POLYMER ELECTROLYTE

- High ionic conductivity (>1 mS.cm^{-1});
- Li^+ transference number (~1);
- Good mechanical strength (Mpa - GPa);
- Wide electrochemical stability window (> 5 V vs Li/Li^+);
- Excellent chemical and thermal stability;
- Processability;
- Availability & Cost;
- Eco-friendly.



PHYSICAL PROPERTIES OF POLYMERS



J. Mater. Chem. A,2015, 3,19218–19253

- Polymers are semi-crystalline;
- Crystallization (slow chain dynamics) is detrimental for ion transport;
- Amorphous phase (segmental mobility) aids ion transportation;

Crystallinity suppression is achieved by:

Addition of *plasticizer*, *nanofiller*, *polymer blends*, *grafting* onto polymer backbones, *cross-linking*, designing of block copolymers etc…

POLYMER ELECTROLYTE SYSTEMS

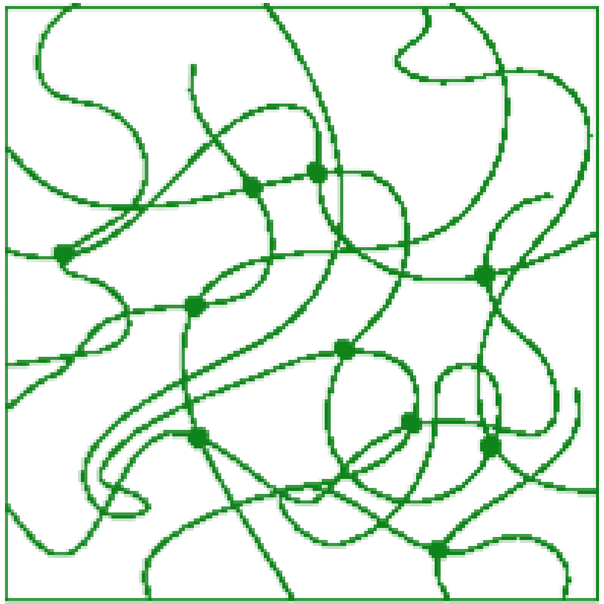
- Solid Polymer Electrolyte
- Gel Polymer Electrolyte
- Polymer Composite Electrolyte
- Single-ion Conductor
- Hybrid Electrolyte
- Cross-linked Polymer Electrolyte etc…

- **Lithium ion conductivity**
- **Mechanical property**
- **Li^+ ion transport number**

SOLVENT FREE POLYMERIZATION

Monomer
Oligomer
Salt
Additives
Initiator

Deposition
Polymerisation



Crosslinked network

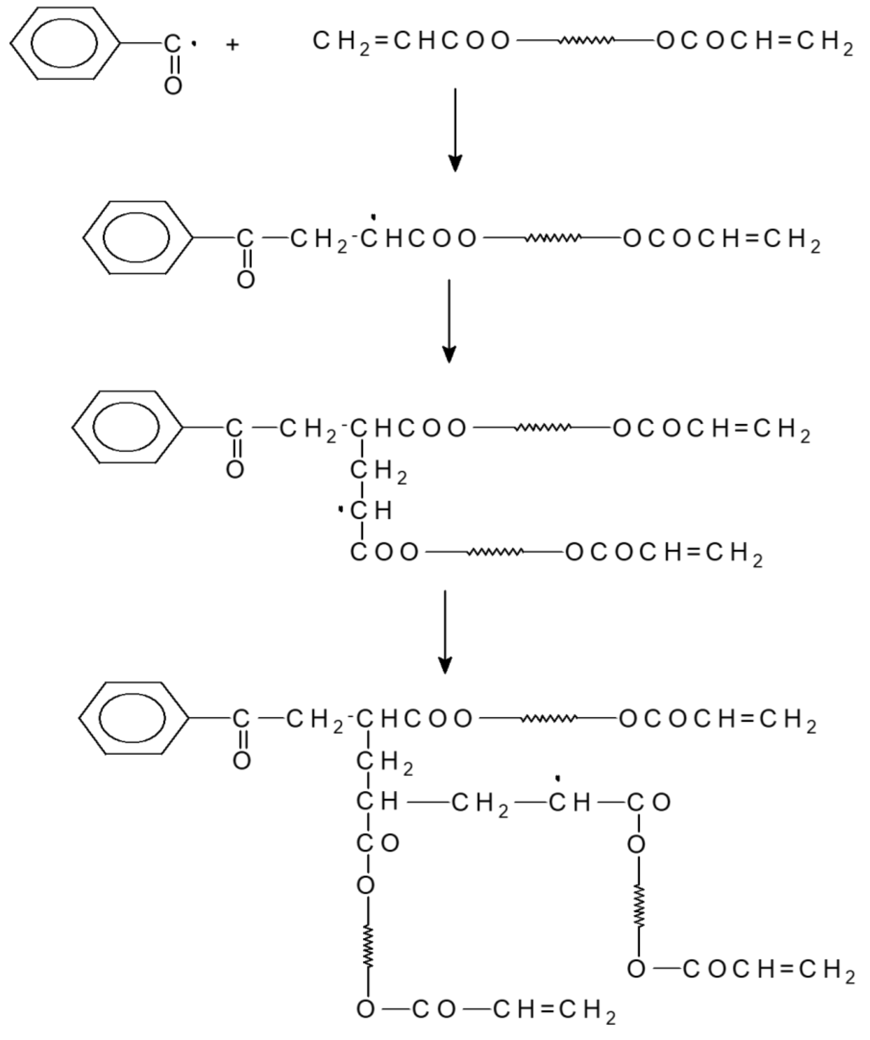
- Electrolyte components can reach to active materials;
- Good contact between the electrode and the electrolyte;
- Use existing state of the art manufacturing facility;
- No solvents needed.

GREEN PROCESS

16

UV INDUCED FREE RADICAL POLYMERIZATION

Initiation is triggered by UV irradiation: liquid precursor mix is transformed into a solid polymer (glassy or rubbery state).



Applications

Coatings, Adhesives

Inks, Electronics

Dental Materials

... Electrolyte Membranes ???

Advantages

- ✓ Rapid
- ✓ Cost effective
- ✓ No solvents
- ✓ No catalysts
- ✓ Single step preparation
- ✓ Transferable to the industrial scale

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POLYMER ELECTROLYTE TYPES

- **Gel Polymer Electrolyte - GPE**

  (all kinds of polymers – Thermoplastic / Thermoset)

  → POLYMER, PLASTICISERS, Li-X, ADDITIVES

- **Solid Polymer Electrolyte - SPE**

  (w/o Plasticizers – Thermoplastic / Thermoset - Block-co-polymers ….)

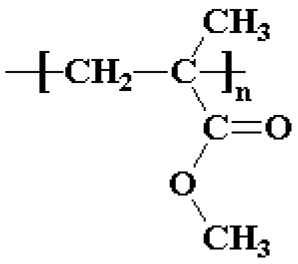
- **Composite/Hybrid Polymer Electrolyte - CPE**

  (ceramics, Al_2O_3, SiO_2 etc., MOFs, Cellulose)

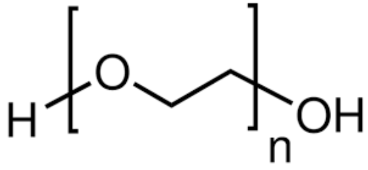
- **Crystalline Polymer electrolytes**

  (very few, PEO crystallites)

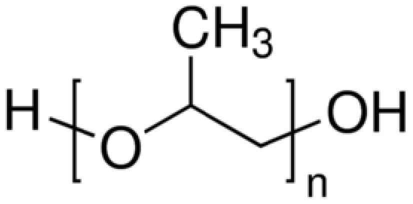
POLYMER MATRICES



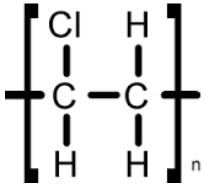
PMMA



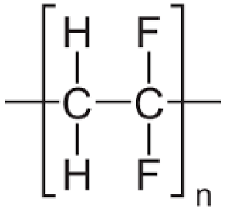
PEO



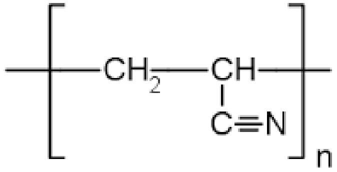
PPO



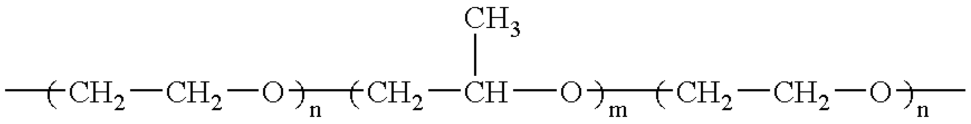
PVC



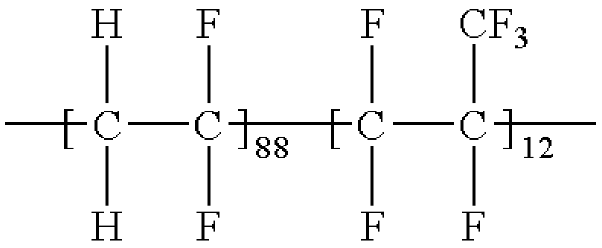
PVDF



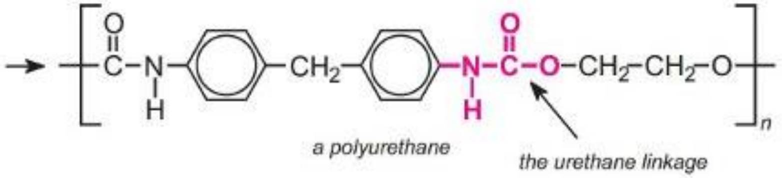
PAN



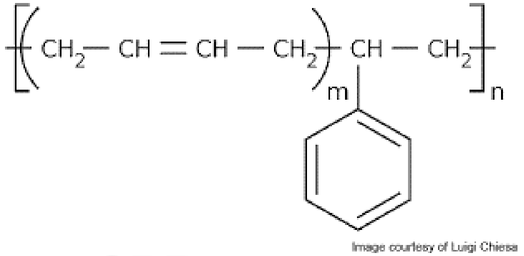
PEO-PPO



PVDF-HFP



PU



SBR

PEO-PMMA-PEO

PEO-PS-PEO

Block copolymers

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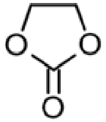
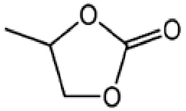
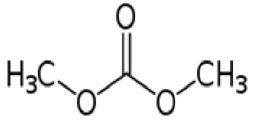
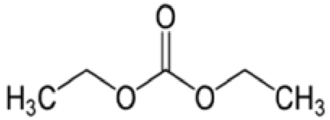
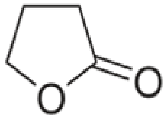
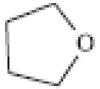
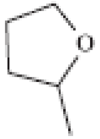
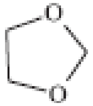
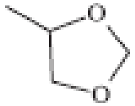
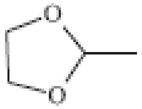
GPE

ELECTROLYTES – Organic Carbonates - Plasticizers

Solvent name	Structural formula	Boiling point /°C	Melting point, T_m/°C	Dielectric constant, ε
Ethylene carbonate, EC		248	39 - 40	89.6 at 40°C
Propylene carbonate, PC		241.5	-49	64.4
Dimethyl carbonate, DMC		91	4.2	3.12
Diethyl carbonate, DEC		127	-42.1	2.82
γ-Butyro Lactone, γ-BL		202	-43	39.1

M. Marcinek et al. / Solid State Ionics 276 (2015) 107–126

ELECTROLYTES – Organic Ethers - Plasticizers

Solvent	Structure	M. Wt	T_m/°C	T_b/°C	η/cP 25 °C	ε 25 °C
DMM		76	−105	41	0.33	2.7
DME		90	−58	84	0.46	7.2
DEE		118	−74	121		
THF		72	−109	66	0.46	7.4
2-Me-THF		86	−137	80	0.47	6.2
1,3-DL		74	−95	78	0.59	7.1
4-Me-1,3-DL		88	−125	85	0.60	6.8
2-Me-1,3-DL		88			0.54	4.39

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ELECTROLYTES – Li Salt

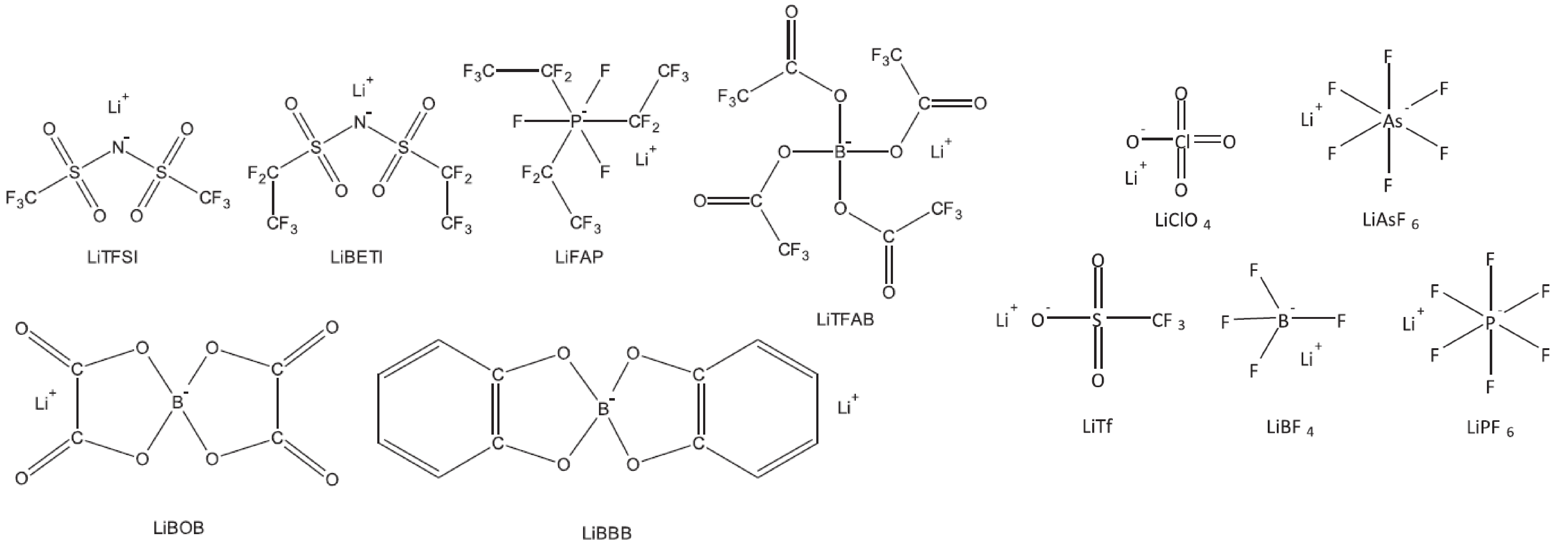


Fig. 2. New lithium conductive salts created for application in lithium-ion batteries. LiTFSI – $Li[N(SO_2CF_3)_2]$ – lithium bis(trifluoromethane sulfone)imide; LiBETI – $Li[N(SO_2CF_2CF_3)_2]$ – lithium bis(pentafluoroethane sulfone)imide; LiFAP – $Li[PF_3(CF_2CF_3)_3]$ – lithium fluoroalkylphosphate; LiTFAB – $Li[B(OCOCF_3)_4]$ – lithium tetrakis(trifluoroacetoxy)borate; LiBOB – $Li[B(C_2O_4)_2]$ – lithium bis(oxalato)borate; LBBB – $Li[B(C_6O_2)_2]$ – lithium bis (1,2-benzenediolato(2-)-O,O′) borate.

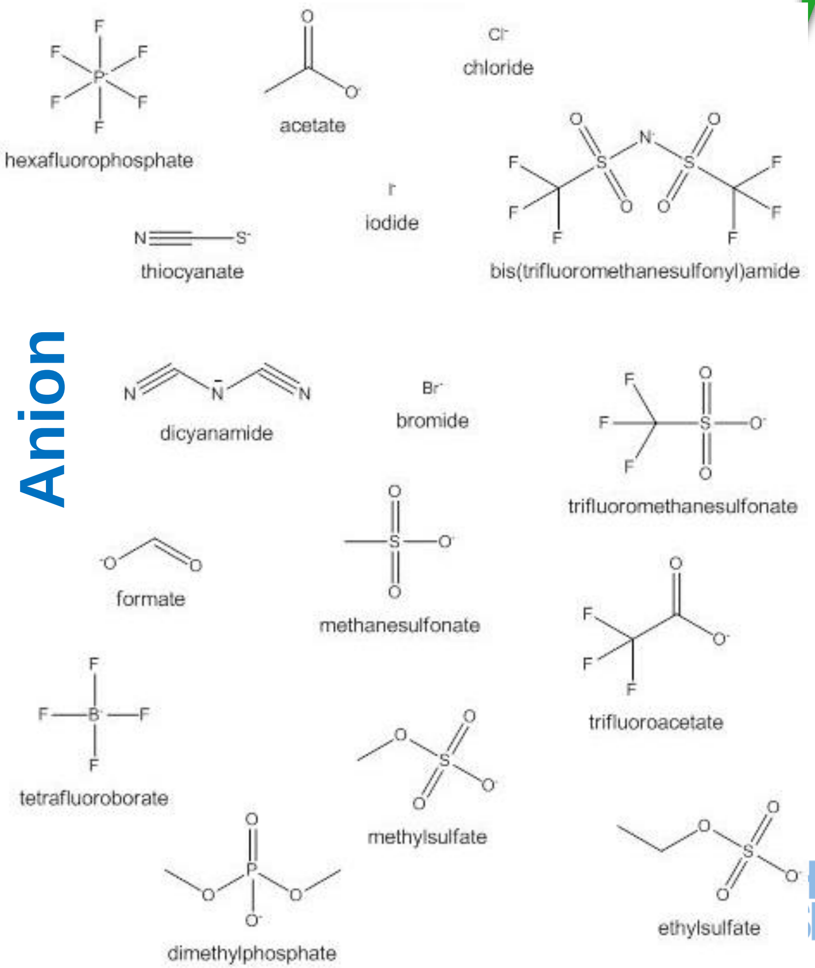
POLYMER ELECTROLYTES – RTILs - Plasticizers

ROOM TEMPERATURE IONIC LIQUIDS - RTILs

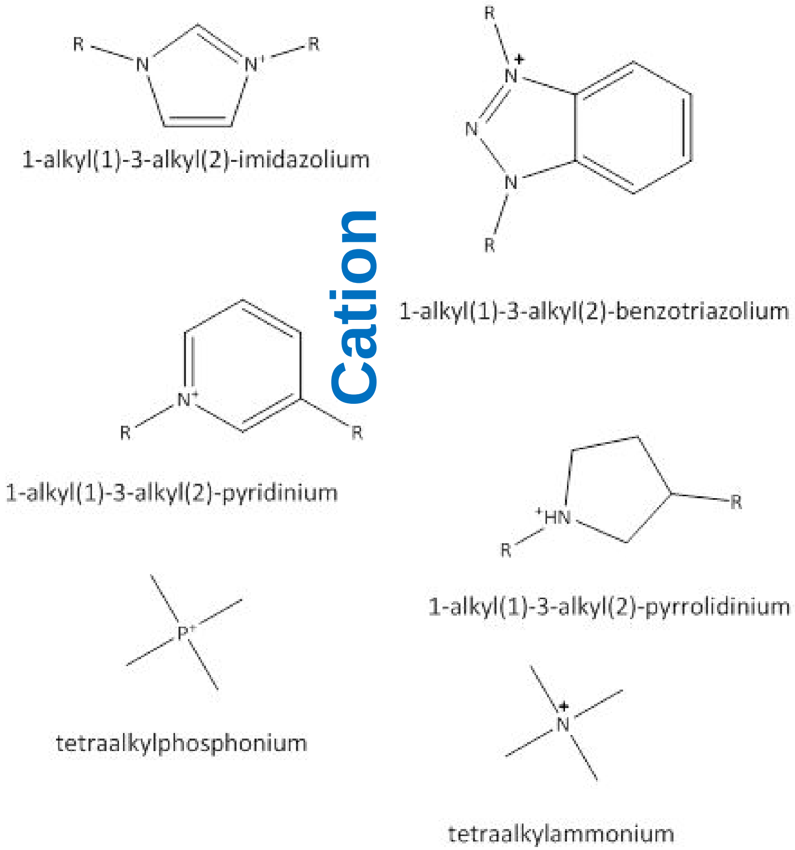
ORGANIC CATION
ORGANIC ANION

- High ionic conductivity
- High Boiling Point
- Low Vapor Pressure
- Fire resistant
- Recycled and Reused
- Green Solvent

Anion



Cation



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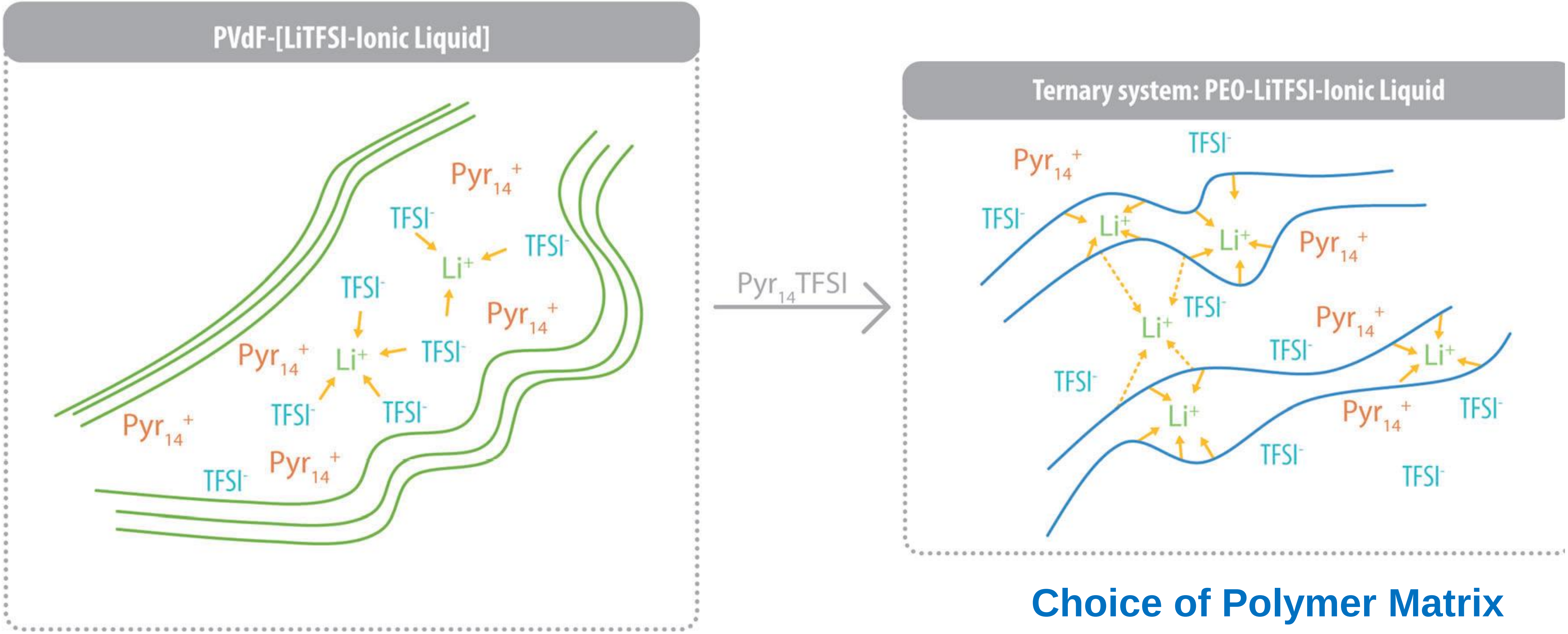
POLYMER ELECTROLYTES – RTIL



Choice of Polymer Matrix

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POLYMER ELECTROLYTES – RTILs

GPE

Year	Electrolyte composition	Am.	T_g/°C	σ at 20 °C/mS cm^{-1}	σ at 60 °C/mS cm^{-1}
1996	$PAN_4[TEMAB_7LiOAc_2LiTFSI_1]_6$	–	–	1.0×10^{-6}	3.0×10^{-5}
2003	$PEO_{20}LiTFSI\ [Pyr_{13}TFSI]_{2.15}$	no	−60	3.0×10^{-4}	1.5×10^{-3}
2003	$PPEGDA_{15\%}[LiBF_4Im_{12}BF_4]_{85\%}$	–	−81	1.2×10^{-4}	1.8×10^{-4}
2004	$[PPyr_{11}TFSI]_{50\%}[Li(G4)]TFSI_{50\%}$	yes	−55	1.0×10^{-4}	8.0×10^{-4}
2005	$[PEO_{50\%}[Im_{1.1.8}Tf]_{50\%}]LiTf_{0.5M}$	no	–	2.0×10^{-6}	2.0×10^{-4}
2005	$P(P[PEO\text{-}PPO]Acr_3)_{0.84}\ LiTFSA\text{-}30_{0.16}$	yes	−60	4.0×10^{-5}	2.0×10^{-4}
2007	$PEO_{20}LiTFSI_2\ [Pyr_{14}TFSI]_{1.92}$	yes	–	1.1×10^{-4}	1.0×10^{-3}
2007	$PEO_{20}LiTFSI_1[Py_{4.1}TFSI]_1$	no	−51	–	6.0×10^{-4}
2008	$P([AMPS\text{-}Li]_1\text{-}VF_9)_{10\%}\ [Im_{12}TCM]_{90\%}$	yes	−81	5.0×10^{-3}	2.0×10^{-2}
2008	$PEO_{20}LiTFSI_1[Pip_{13}TFSI]_1$	no	−49	–	1.2×10^{-3}
2008	$PEO_{20}LiTFSI_2\ [Pyr_{14}TFSI]_2$	yes	−65	1.0×10^{-4}	2.0×10^{-4}
2009	$[PPyr_{11}TFSI]_{36\%}LiTFSI_{14\%}\ [Pyr_{14}TFSI]_{50\%}$	–	–	1.0×10^{-4}	1.5×10^{-3}
2010	$[PPyr_{11}TFSI]_{28\%}LiTFSI_{12\%}\ [Pyr_{14}TFSI]_{60\%}$	no	−67	1.6×10^{-6}	1.0×10^{-3}
2010	$PEO_{20}LiTFSI_1\ [Pyr_{1.2O1}TFSI]_{1.5}$	no	−73	7.0×10^{-5}	1.4×10^{-3}
2011	$[P(Gua_{33\%}\text{-}MMA_{67\%})TFSI]_{70\%}\ LiTFSI_{30\%}$	–	−60	–	1.8×10^{-4}
2011	$[P(Gua\text{-}MMA)]_{59\%}LiTFSI_{12\%}\ [Gua_{13}TFSI]_{23\%}\ [SiO_2]_{6\%}$	yes	−60	–	2.3×10^{-5}
2011	$PEO_{20}LiTFSI_1\ [S_{2.2.2}TFSI]_1$	no	–	5.0×10^{-4}	2.0×10^{-2}

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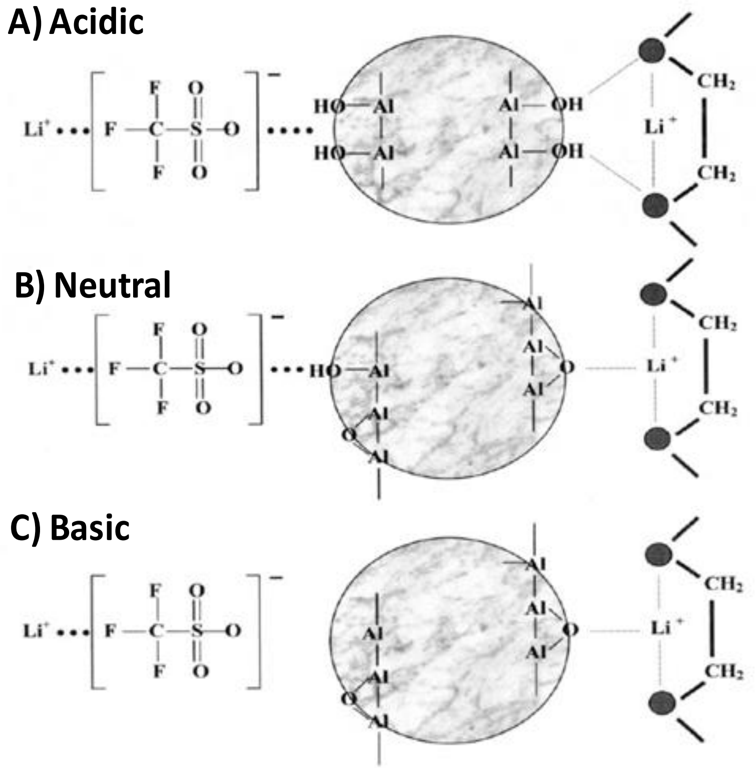
Composite Polymer Electrolytes



CPE

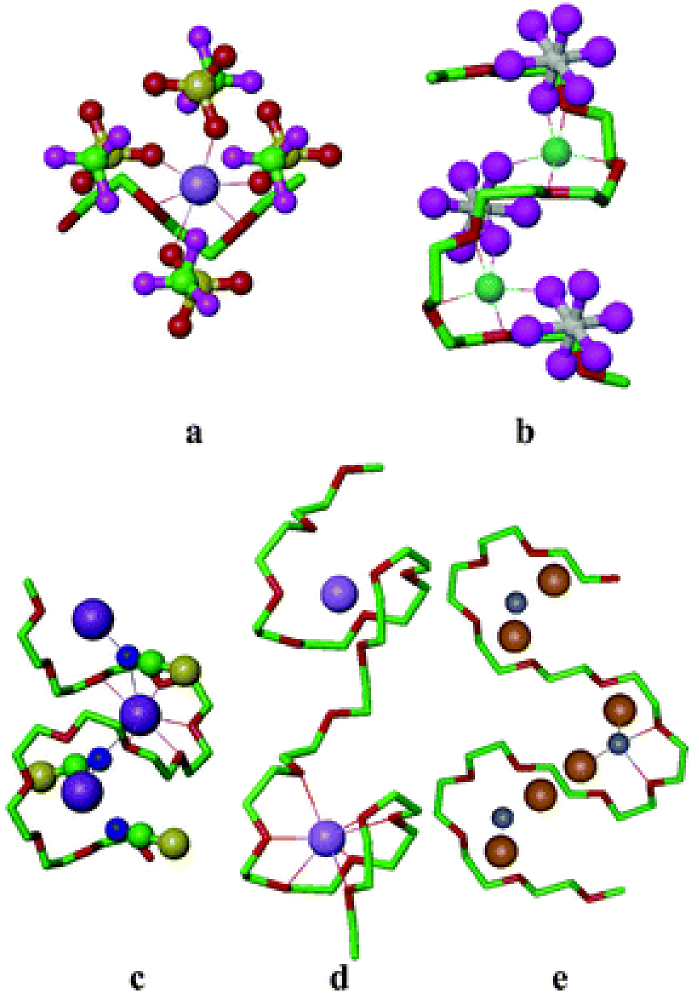
PEO
LiX
Al2O3

Solvent Processing

CPE: High surface area fillers such as ZrO_2, TiO_2, Al_2 O_3 and hydrophobic fumed silica were incorporated into the polymer matrices and are called "composite polymer electrolytes" or "composite ceramic electrolytes"

Electrochimica Acta 46; 2001; 2457

Crystalline Polymer Electrolytes



PEO_6:$LiXF_6$

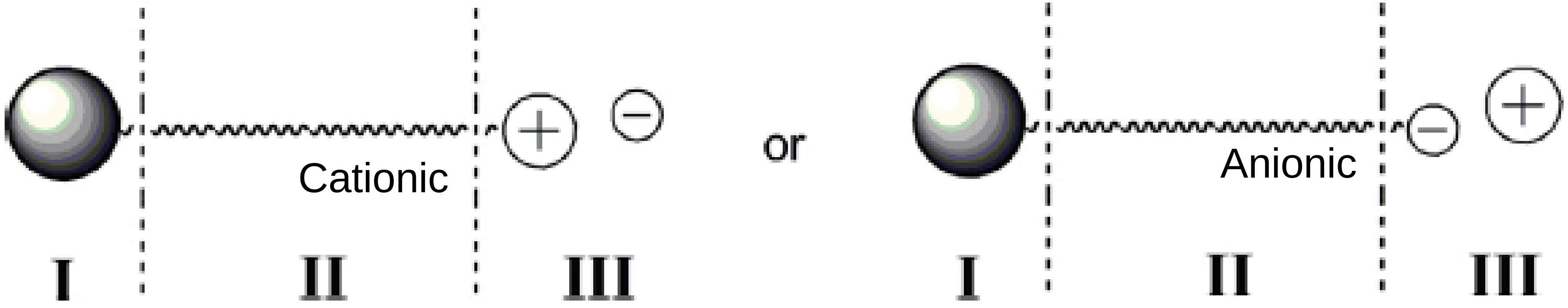
(X=P, As, Sb)

10^{-7}/10^{-9} Scm^{-1}

The polymer film is composed of many grains each of which is composed of many such crystallites.

P.G. BRUCE - Dalton Trans., 2006, 1365-1369

POLYELECTROLYTES – PIL

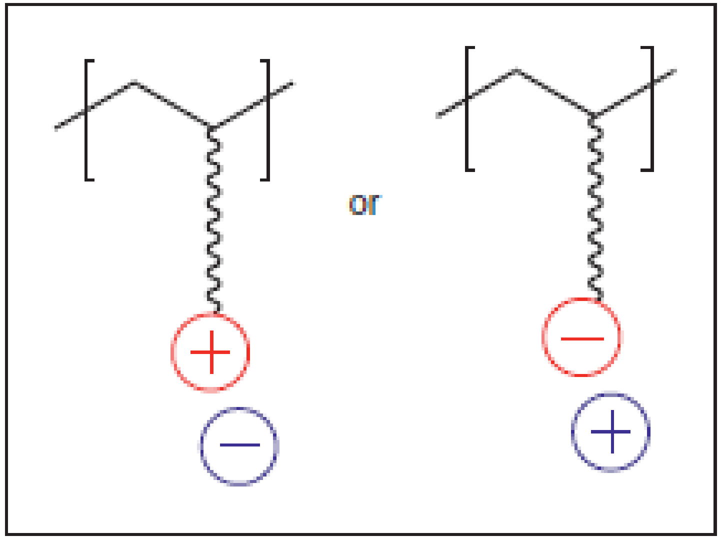


Single ION conductors

. A schematic representation of ionic liquid like monomer: I – reactive group, II – spacer, III – ion species.

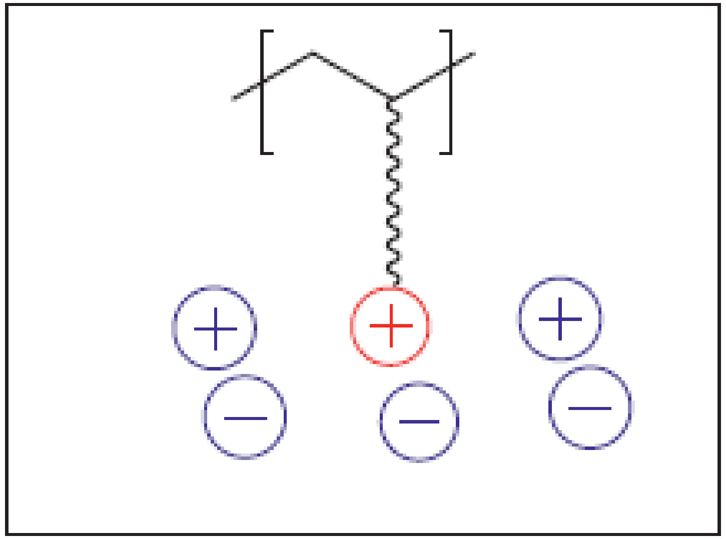
Solid Polymer Electrolytes (SPE)s

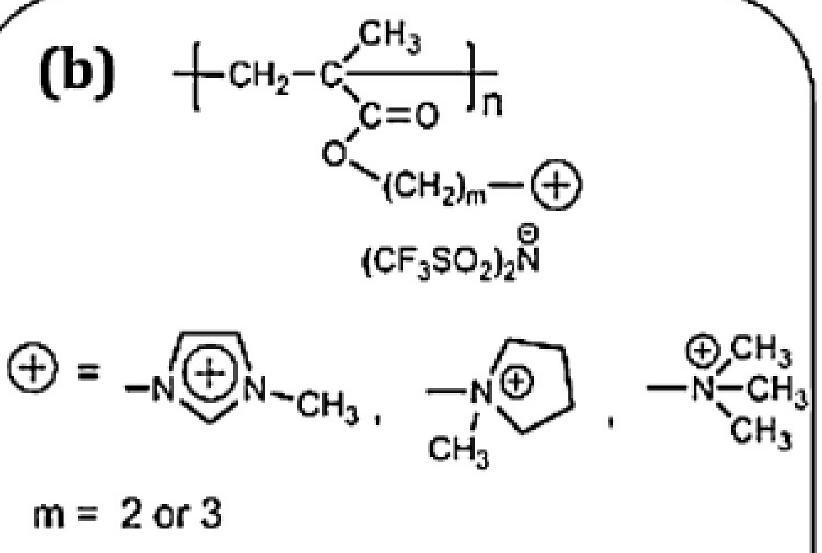
POLY(IONIC LIQUID)S



Gel Polymer Electrolytes

IONGELS

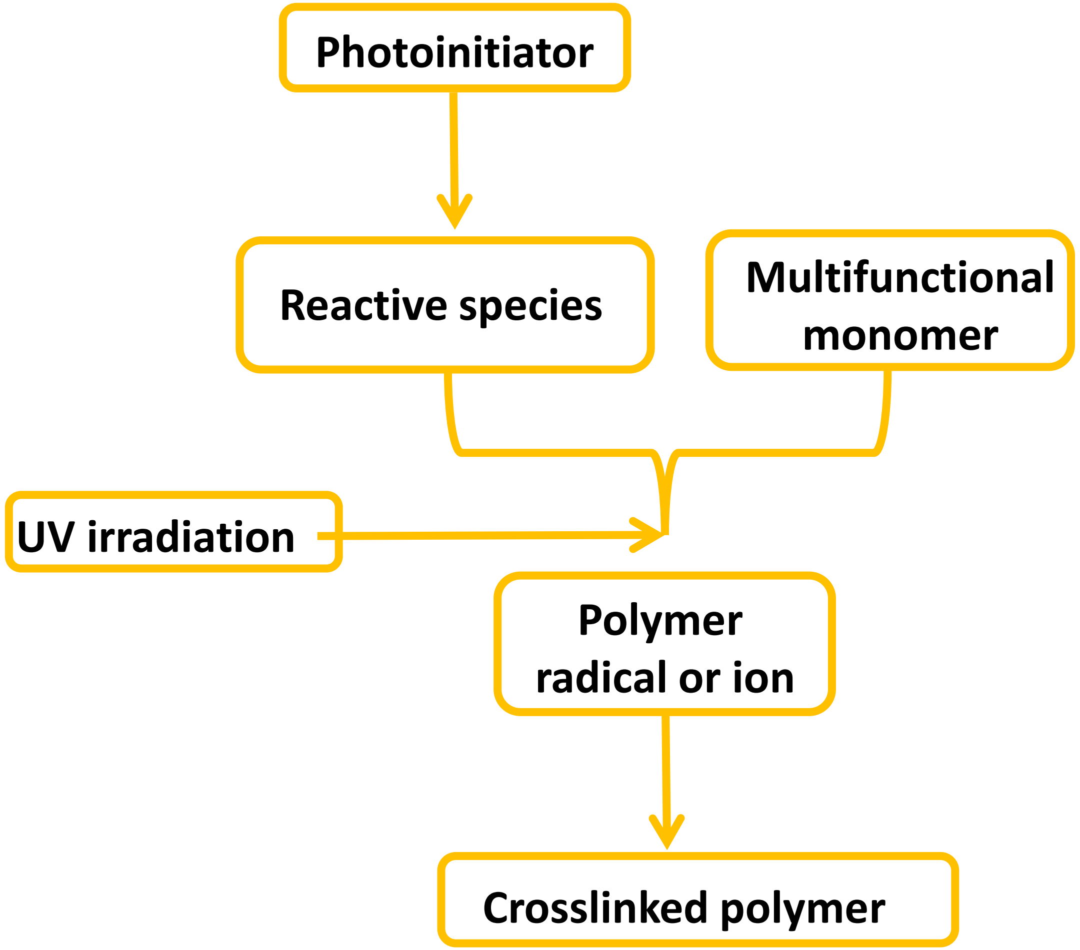




Shaplov et al. / Electrochim. Acta 175 (2015) 18–34

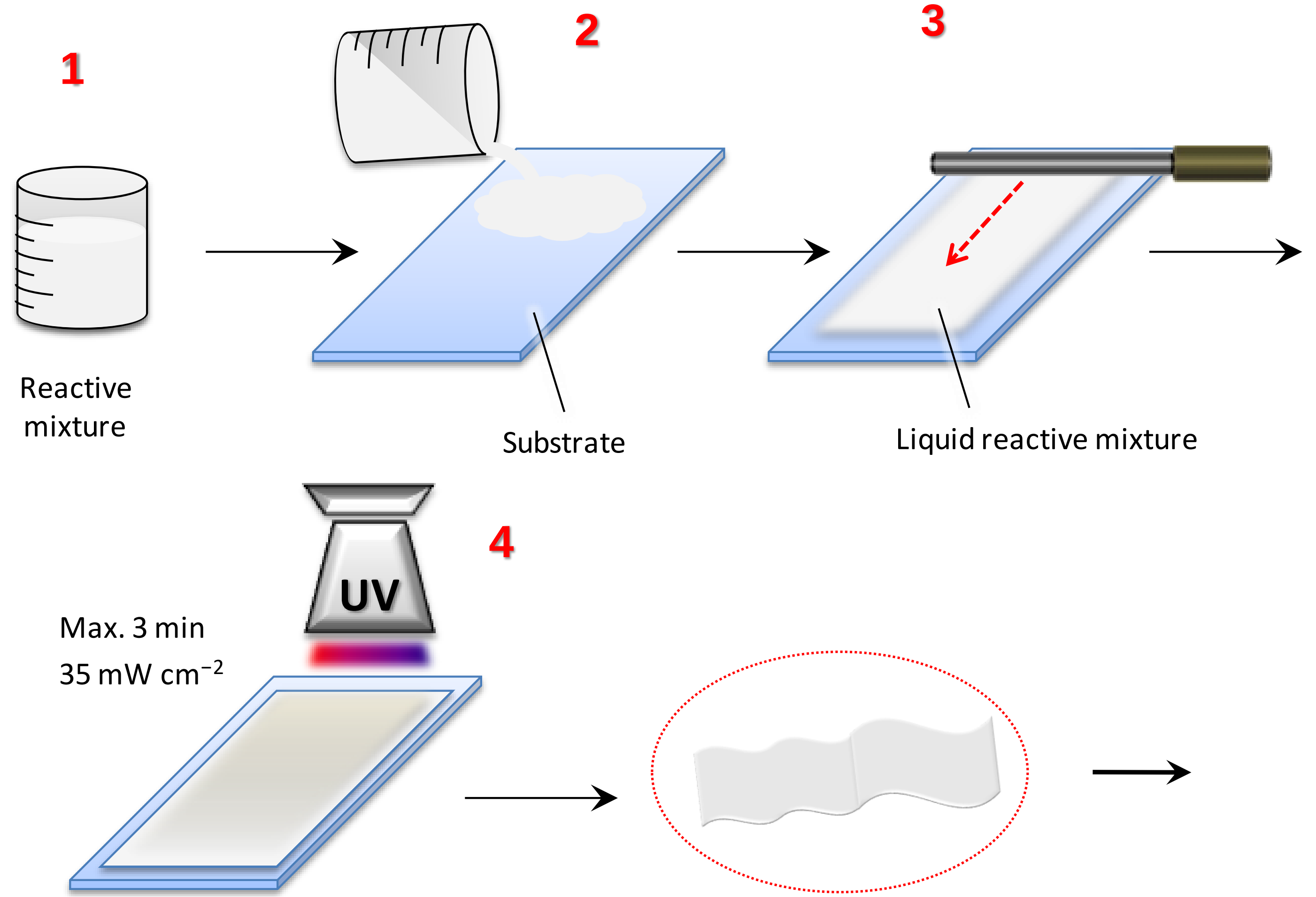
PHOTO-POLYMERIZATION: UV-CURING

A polymerization reaction where initiation is triggered by a UV radiation



- **Rapid**
- **Inexpensive**
- **Single step preparation**
- **No solvents**
- **No catalysts**
- **Transferable to the industrial scale**

POLYMER ELECTROLYTES PREPARATION



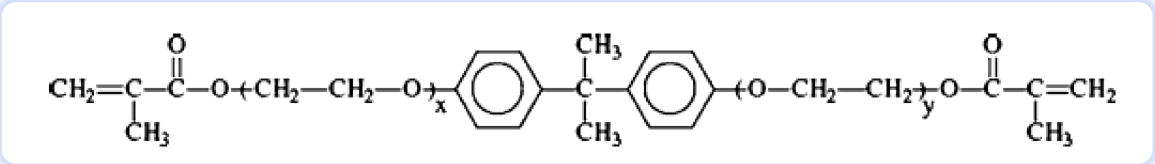
1. Mixing of reactive ingredients
2. Pour it over substrate
3. Draw down over substrate
4. UV exposure

CROSSLINKED GEL POLYMER ELECTROLYTES

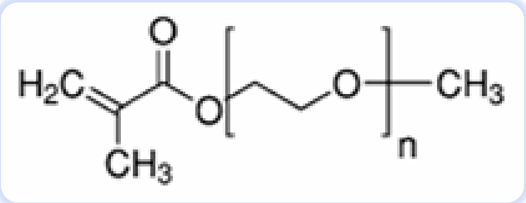
GPE

Methacrylate based polymer backbone

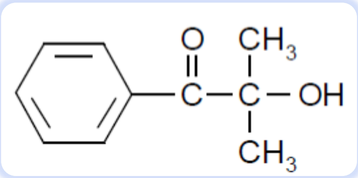
BEMA – Bisphenol-A-ethoxylate dimethacrylate



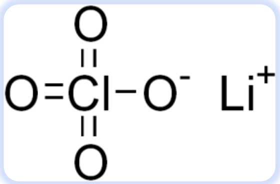
PEGMA



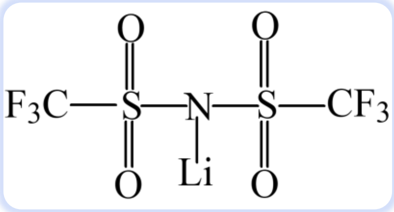
Darocur 1173, (D1173)



$LiClO_4$

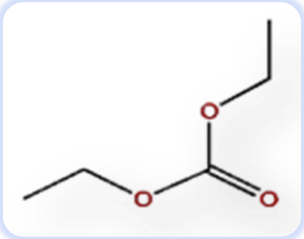


LiTFSI

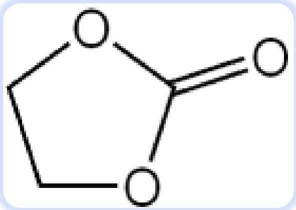


Organic Carbonates

Diethyl (DEC), Dimethyl (DMC) carbonate



Ethylene (EC), Propylene (PC) carbonate



Excellent conductivity

J.Power Sources 178 (2008) 751–757

POLYMER ELECTROLYTES (SILOXANE) – Surface Modification

Acrylated Silicone Polyether Copolymers

Key Features & Typical Benefits:

Thermal resistance

Chemical resistance

Low T_g polymers

NO UV-induced degradation

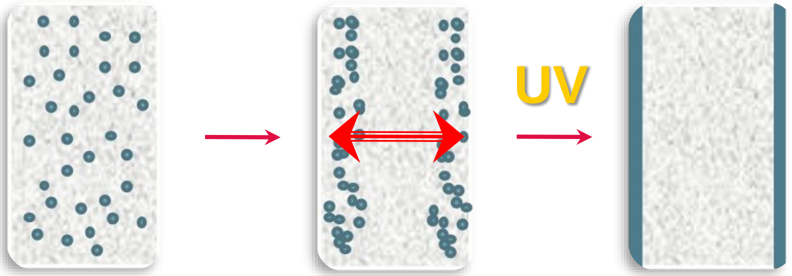
Improved substrate wetting

Large variety of choices - **Self migrating**

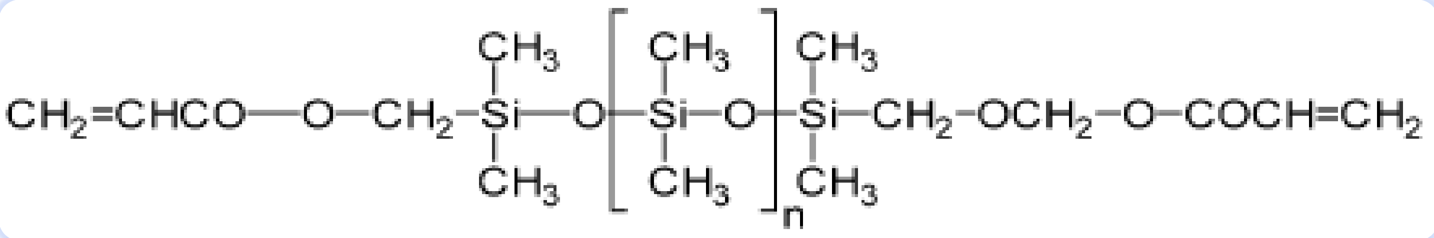
↓ **Surface Tension**

↑ **Contact Angle**

Surface enriched with –Si-O– groups: increase hydrophobicity, separating layer at the surface of the film



Structure of Coatosil-3509 (SAC, Mn: 2700)



Oxidation Stability

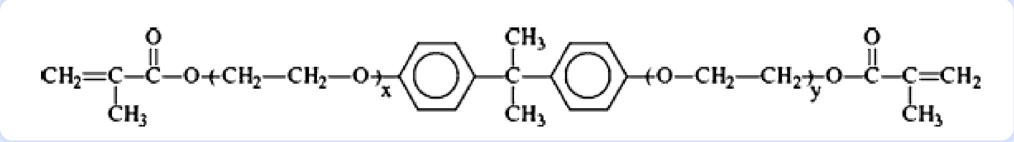
Li Interface

Electrochim Acta 55 (2010) 1460

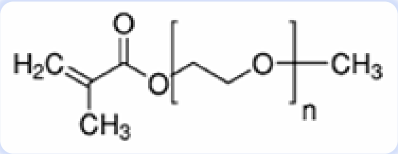
CROSSLINKED GEL POLYMER ELECTROLYTES

Methacrylate based polymer backbone

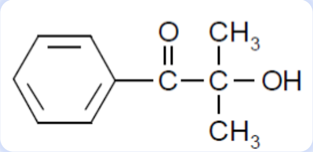
BEMA – Bisphenol-A-ethoxylate dimethacrylate



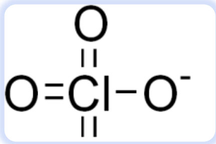
PEGMA



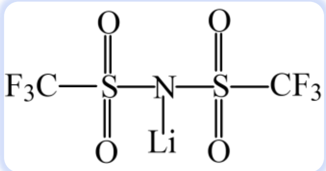
Darocur 1173, (D1173)



$LiClO_4$

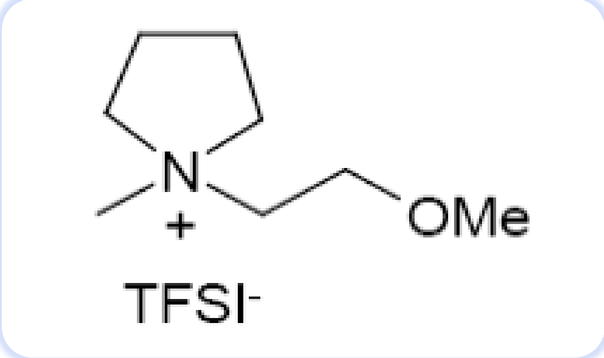


LiTFSI

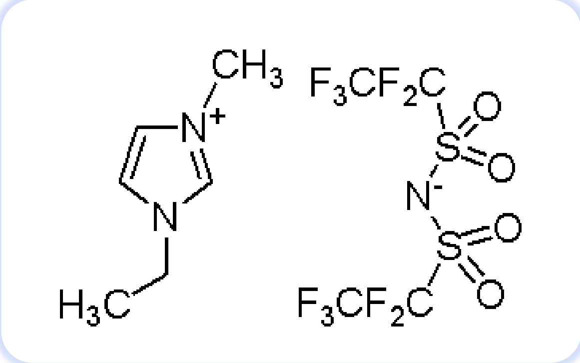


Low volatile RTILs

Structure of PYRA-TFSI

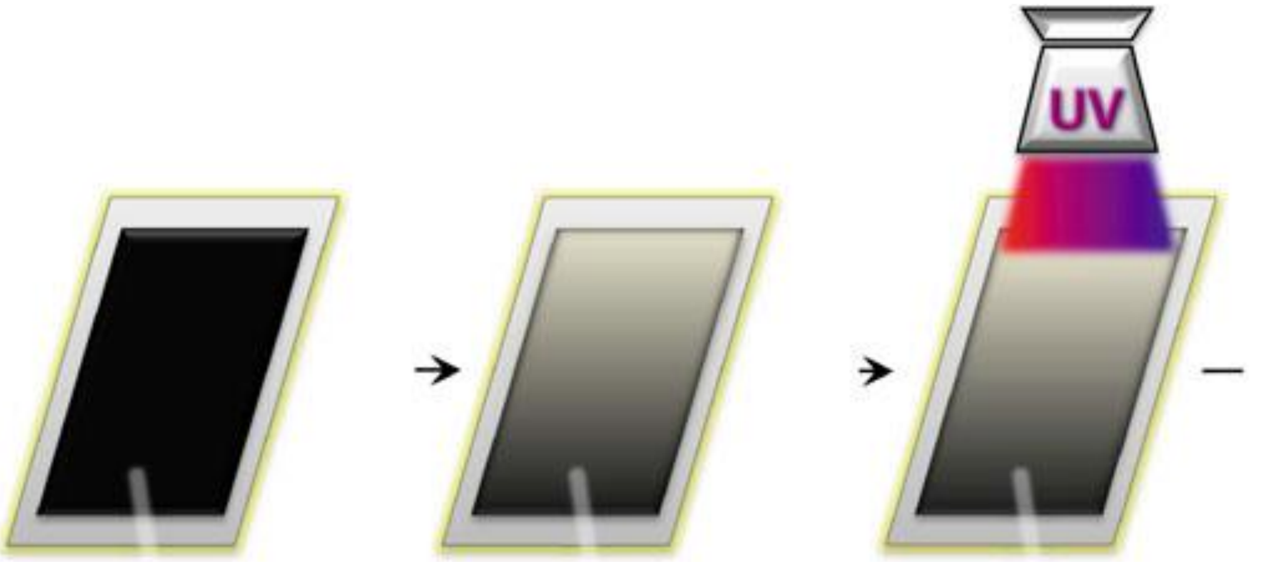


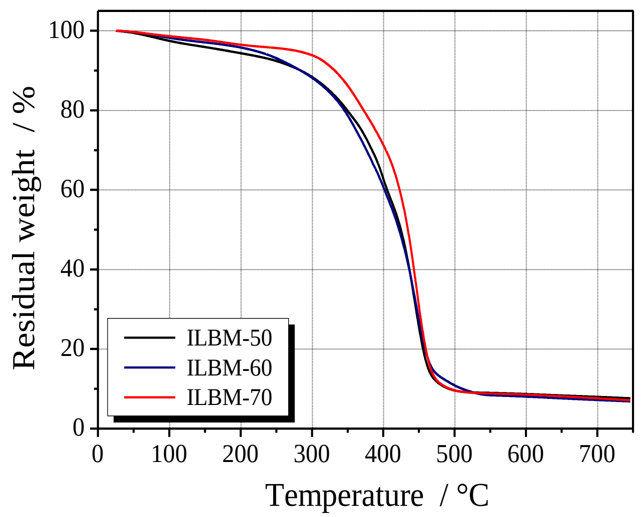
Structure of EMI - PFSI

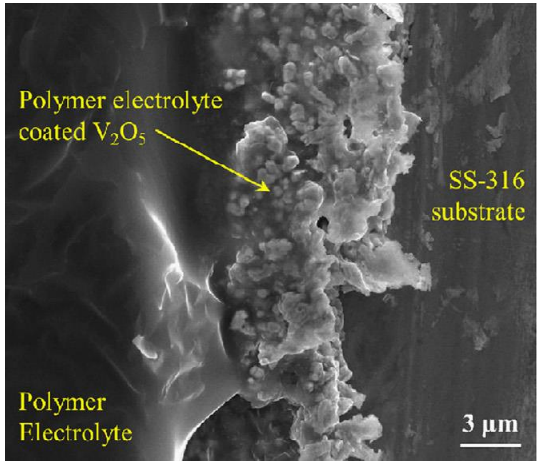


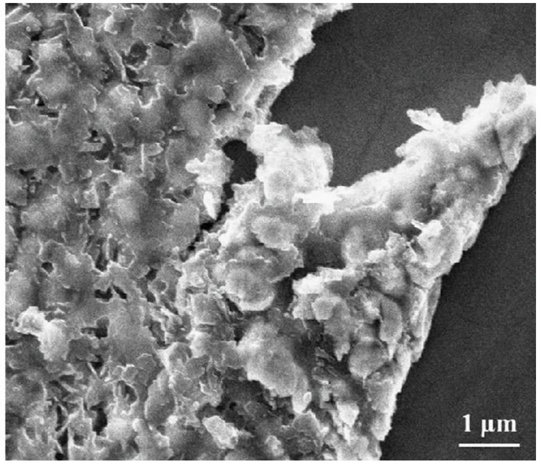
J. Memb. Sci. 423–424 (2012) 459

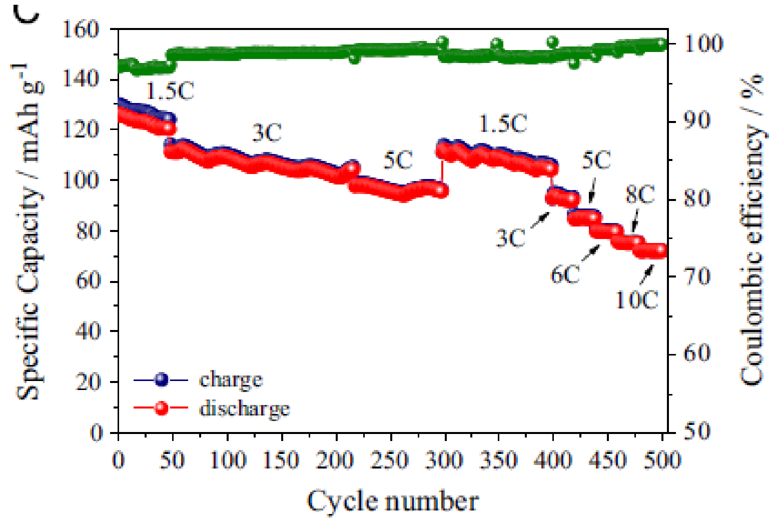
POLYMER ELECTROLYTE MEMBRANES (RTIL)











Nano Energy (2013) 2, 1279-1286

POLYMER ELECTROLYTES – Reinforcement

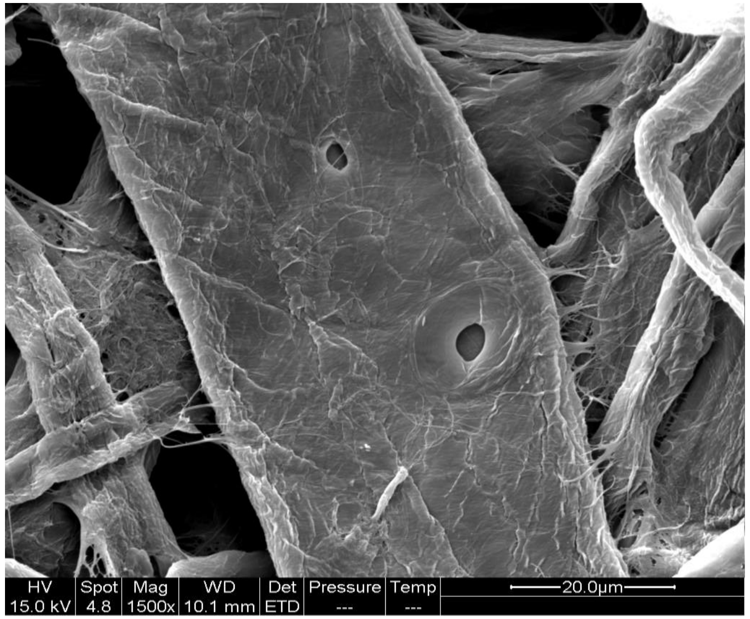
Group for Applied Materials and Electrochemistry

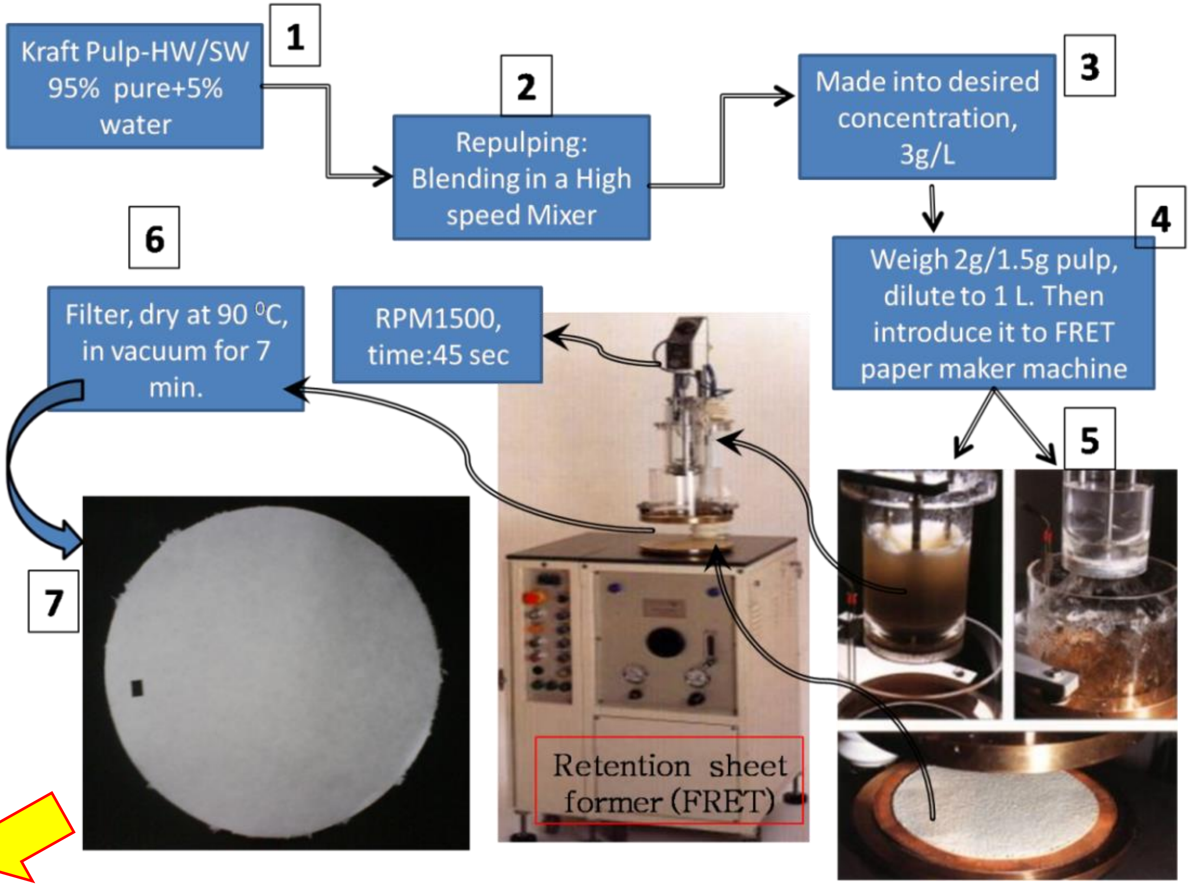
UV-cured methacrylic membranes with cellulose hand-sheets for Li-based battery electrolyte.

Hand sheet Preparation

Hard Wood (HW)	Soft Wood (SW)
Soft material	Hard material
Short fibres	Long fibres
Low porosity	High porosity

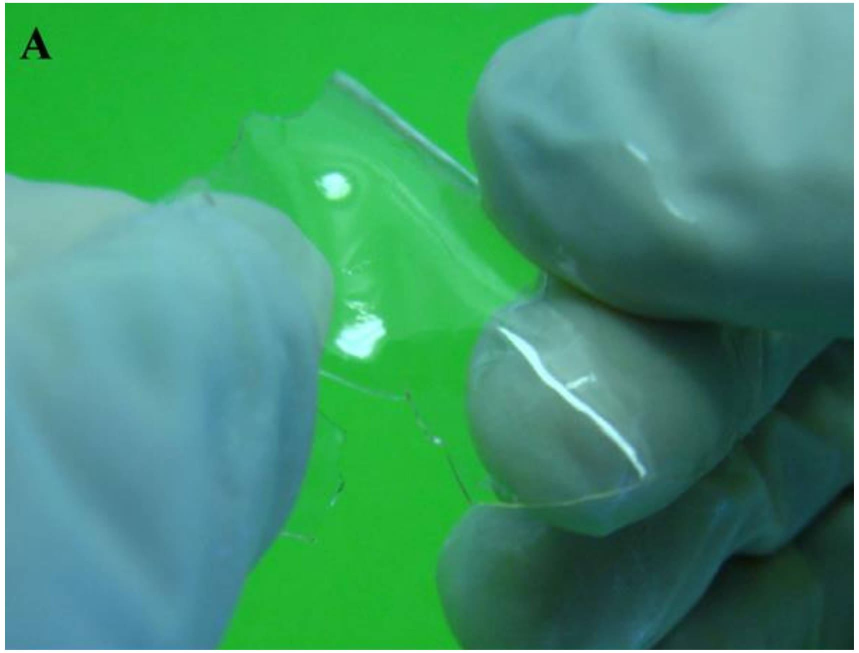
HW:SW = 60:40

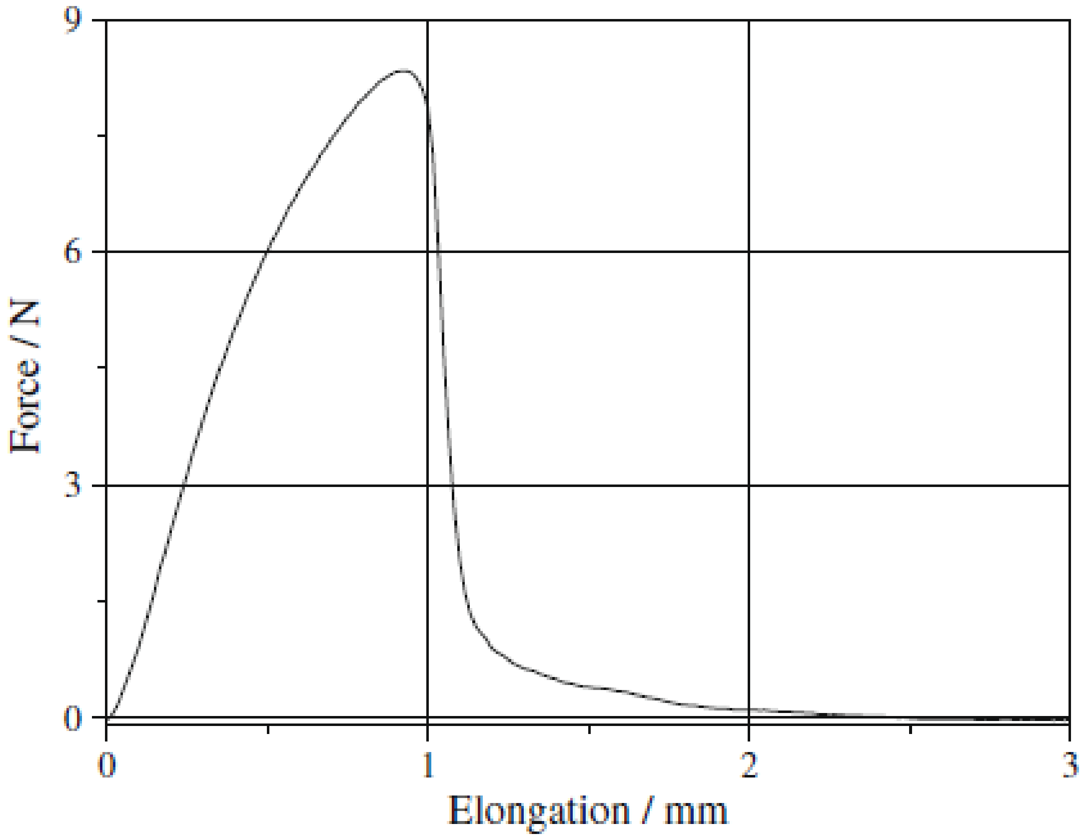




Electrochem. Commun. 11 (2009) 1796

POLYMER ELECTROLYTE MEMBRANES (Cellulose)



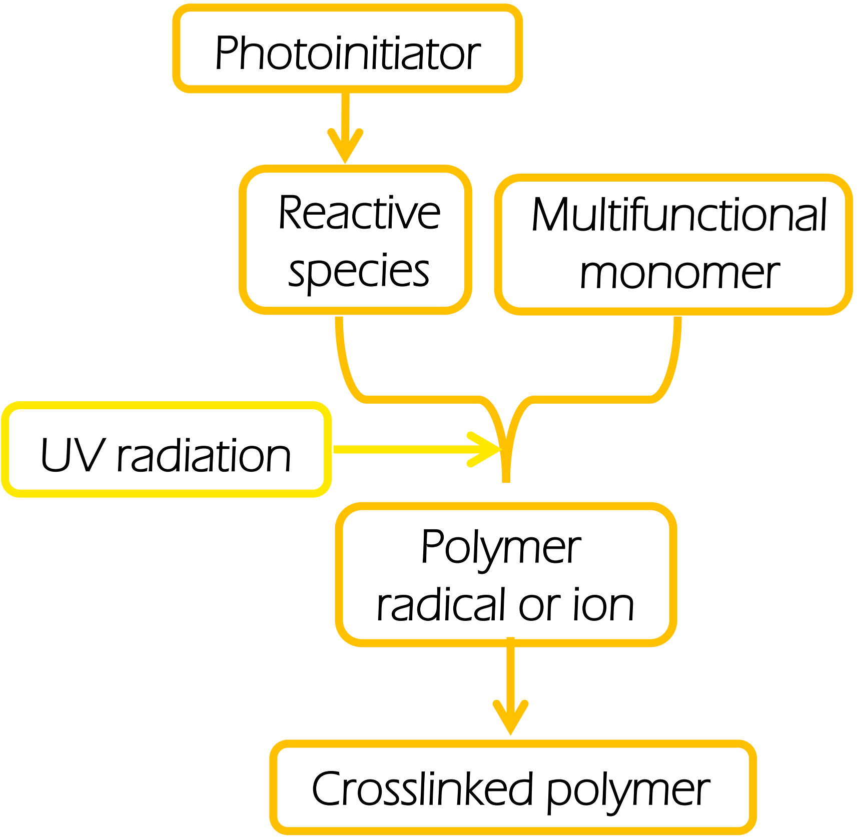


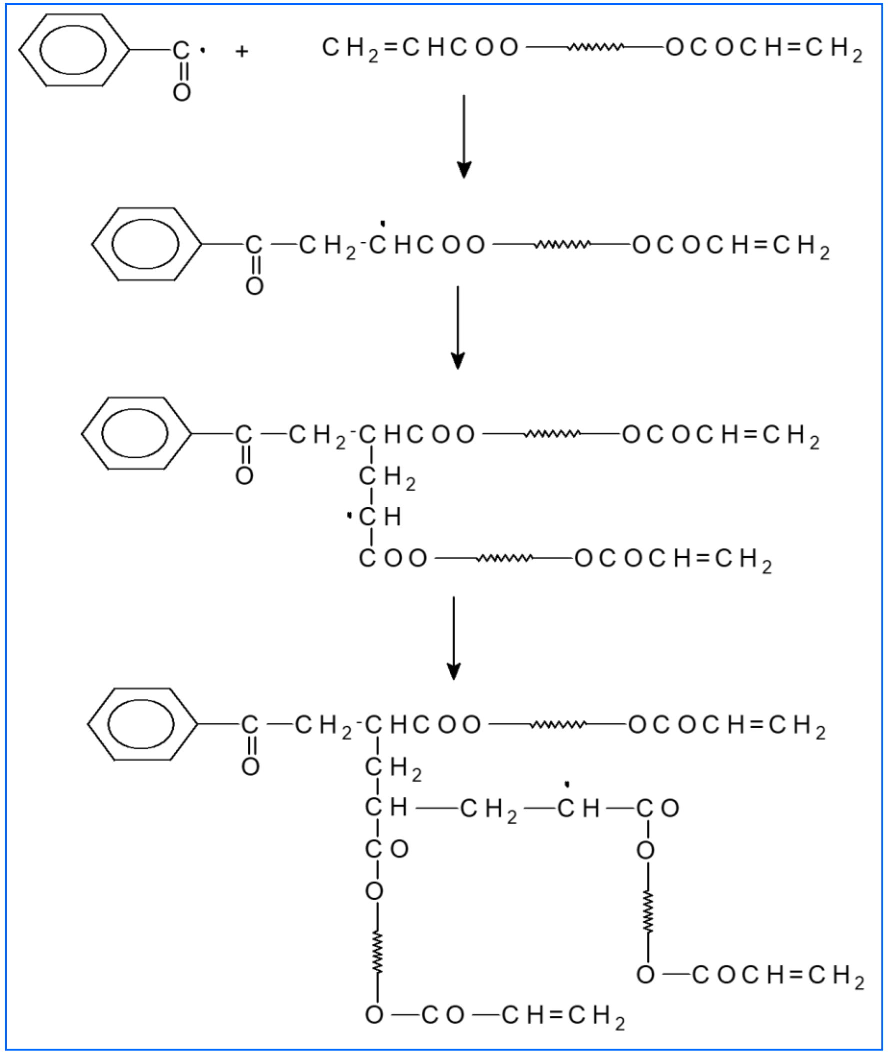
σ > 0.5mS/cm

Liquid >50%

Young's modulus - 417 Mpa
Tensile strength - 2.7 MPa

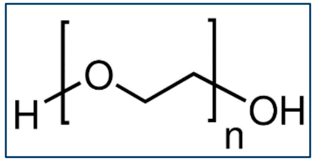
PHOTO-POLYMERIZATION: UV-CURING



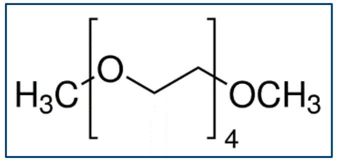


ALL-SOLID STATE BATTERIES FOR LOW TEMPERATURE

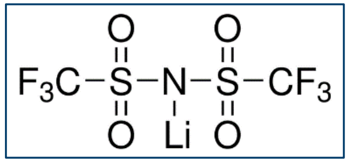
MATERIALS and PROCESS



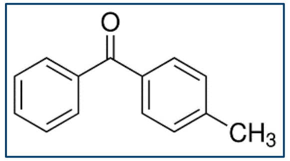
PEO



TEGDME



LiTFSI



ME-BENZOPHENONE

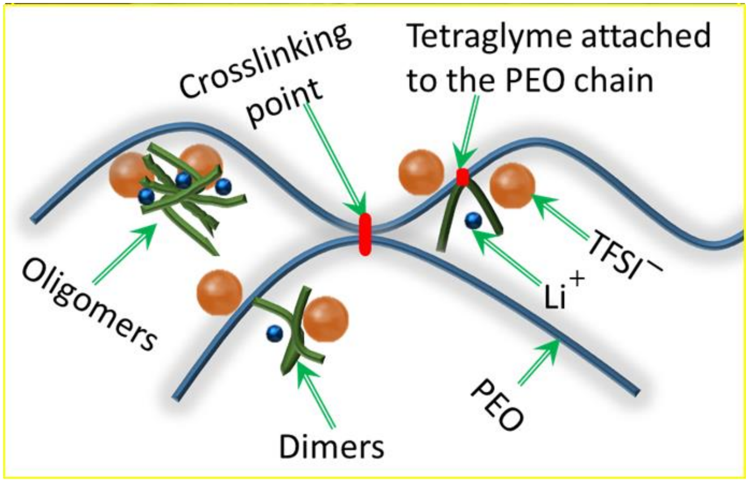
RTILs

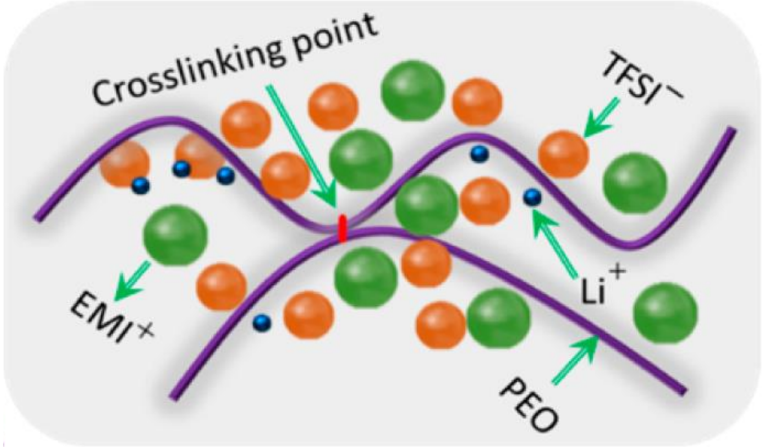
MIX @60°C

Hot Press

TEGDME

RTILs





Hydrogen Abstraction Mechanism

Inter-connected PEO chains with plausible branched clusters of TEGDME oligomers or RTILs

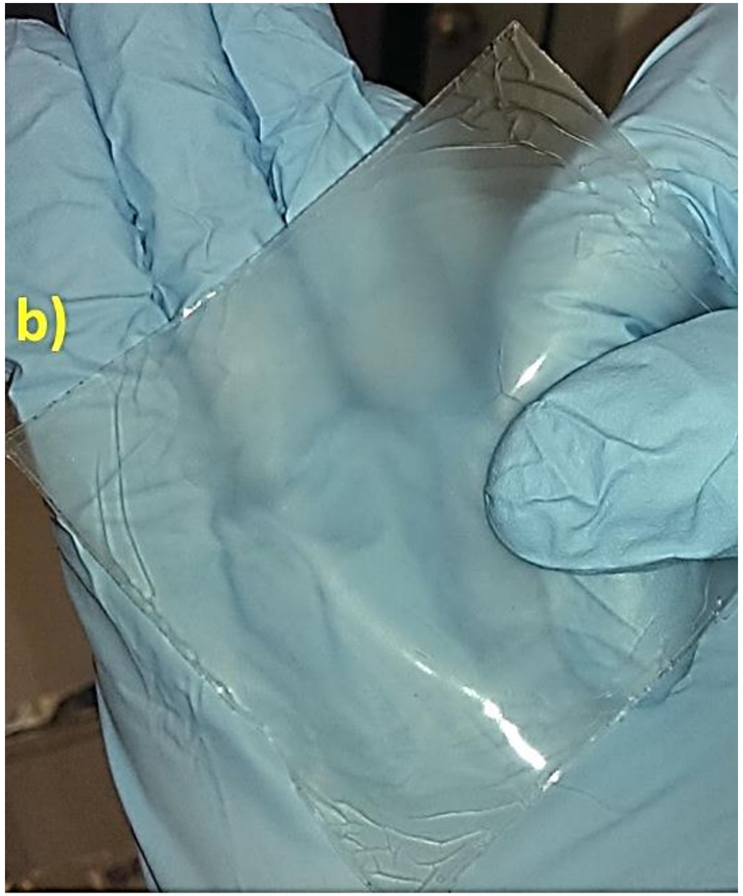
WWU MÜNSTER

RWTH AACHEN UNIVERSITY

Group for applied Materials and Electrochemistry

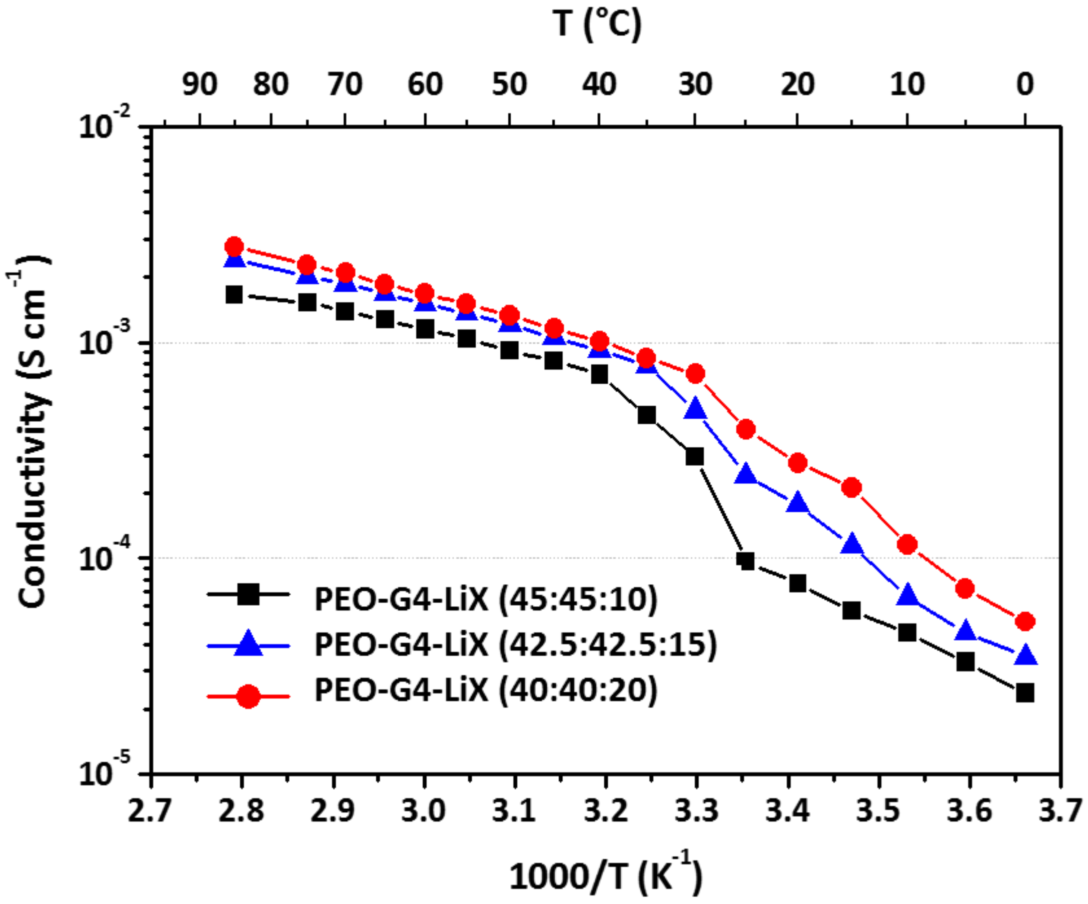
JÜLICH Forschungszentrum

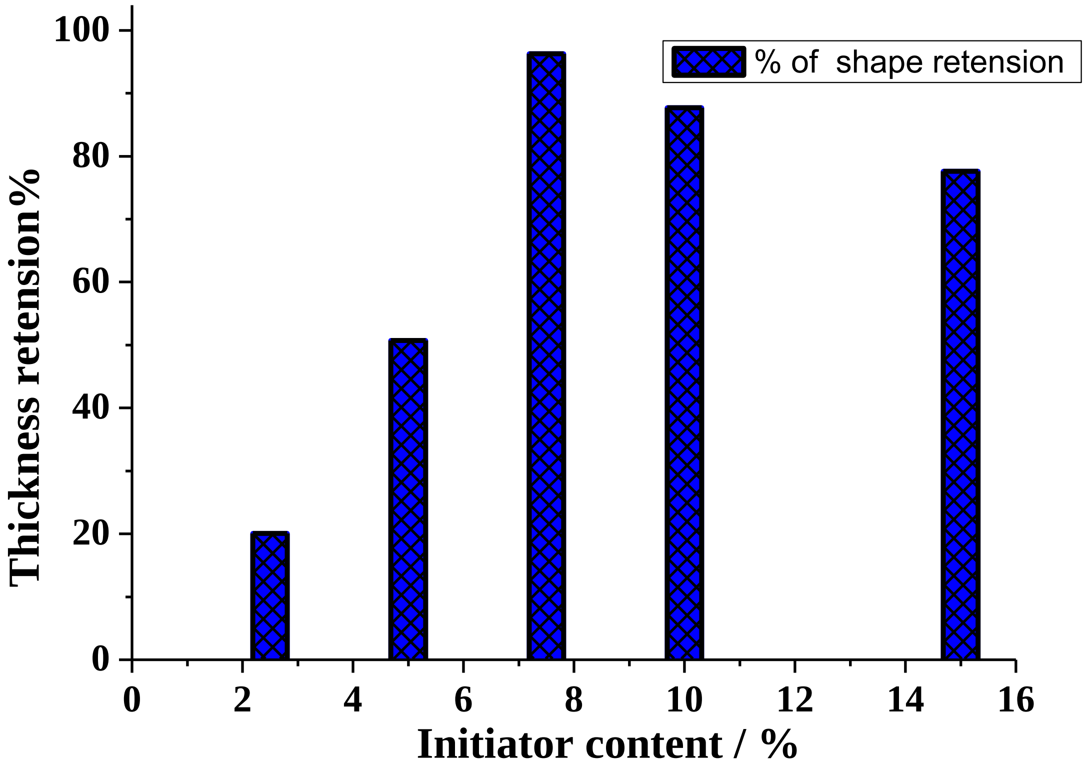
CROSSLINKED MEMBRANES



FLEXIBLE

IONIC CONDUCTIVITY & SHAPE RETENSION

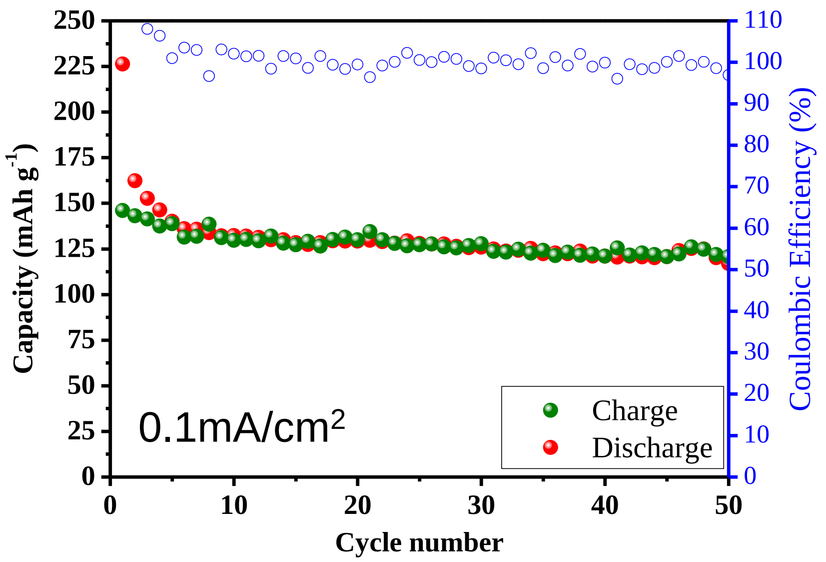


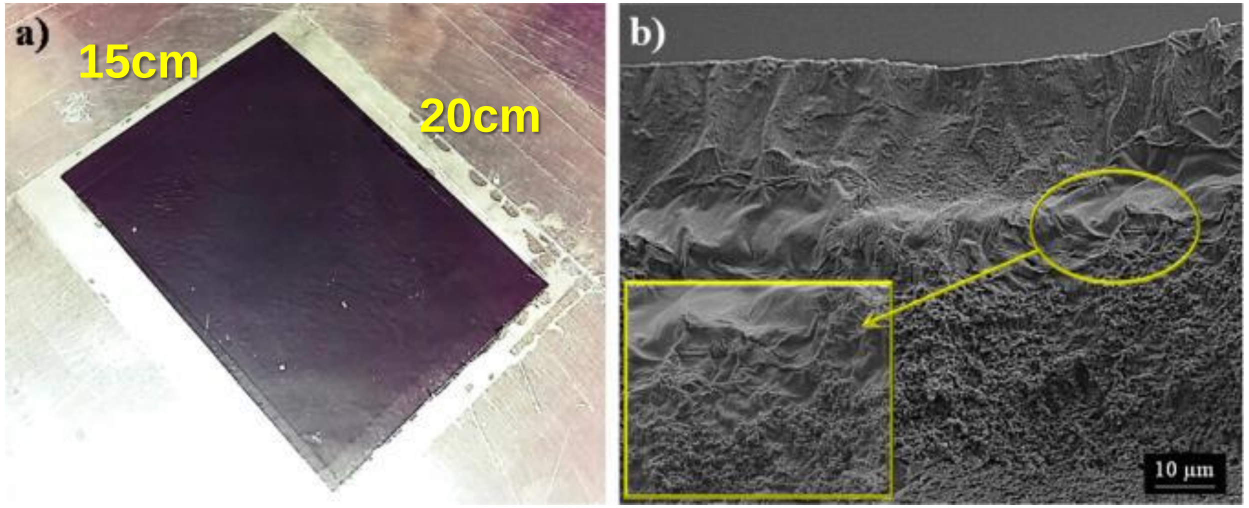


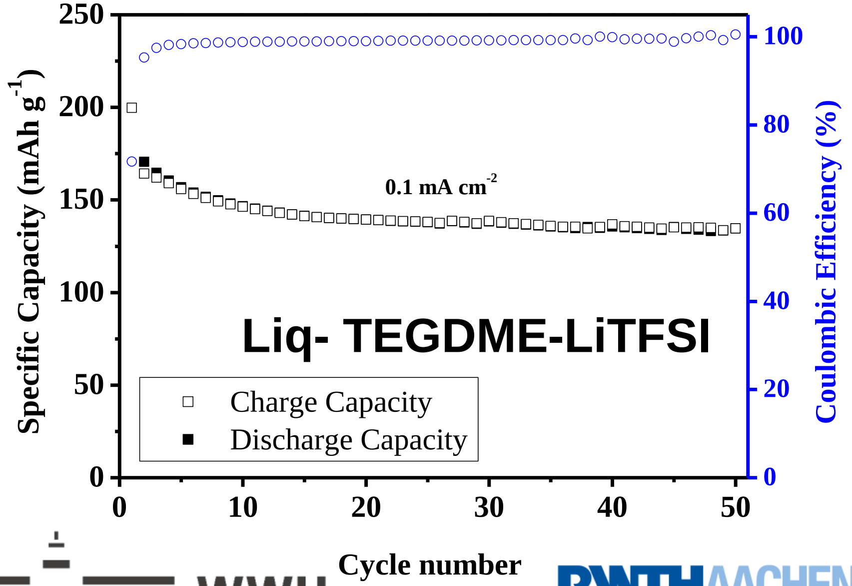
Conductivity ≥ 0.2 mS cm^{-1} @20°C

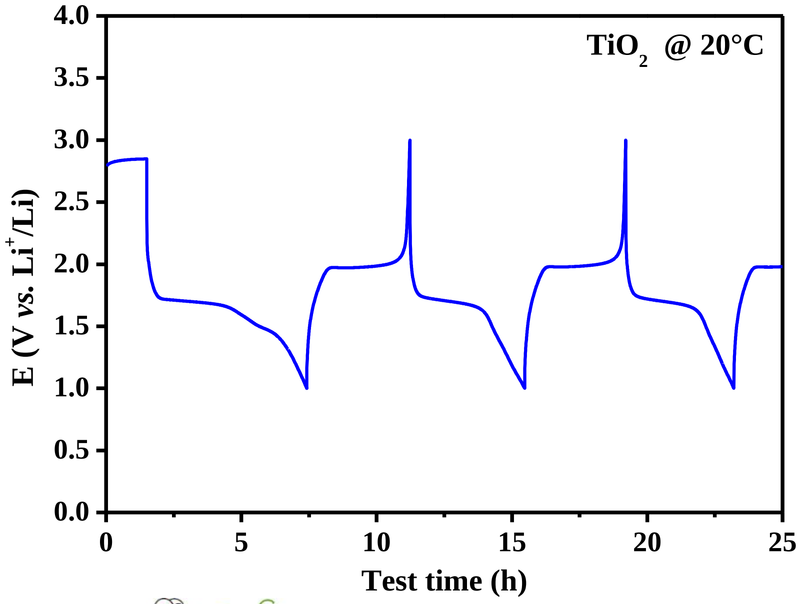
Volume change ≈ 3%

GALVANOSTATIC CYCLING @ 20°C – TiO_2 / PEM / Li









Stable cycling

High efficiency

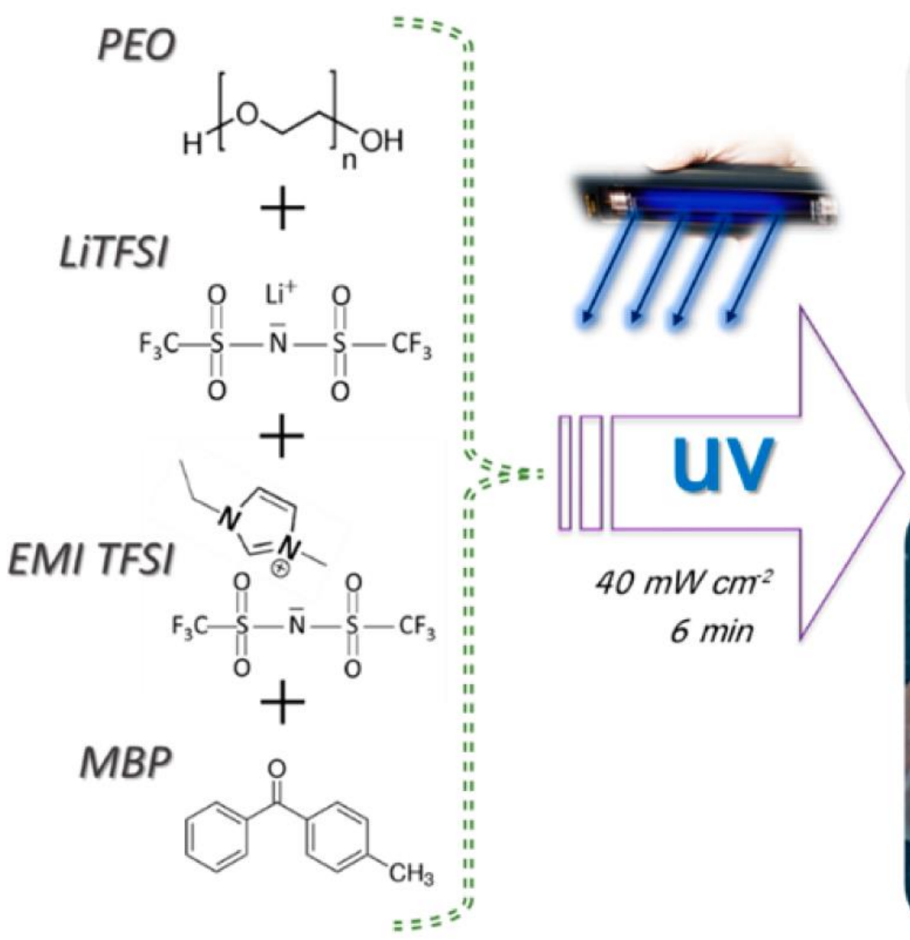
WWU MÜNSTER

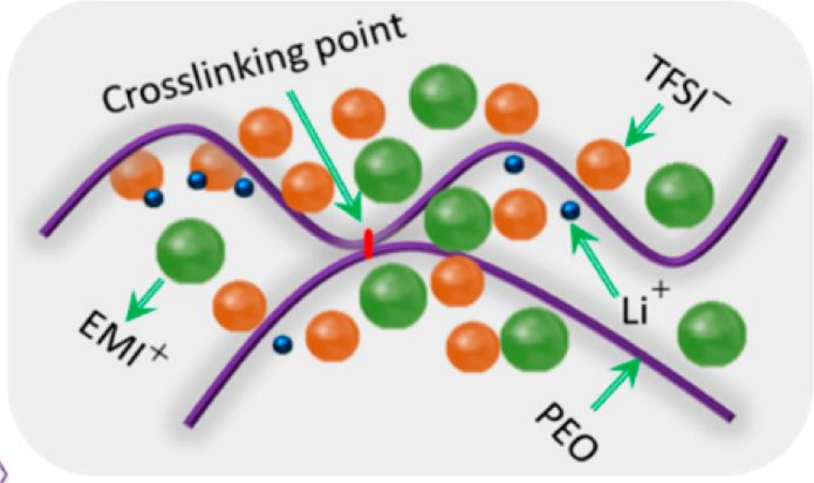
RWTH AACHEN UNIVERSITY

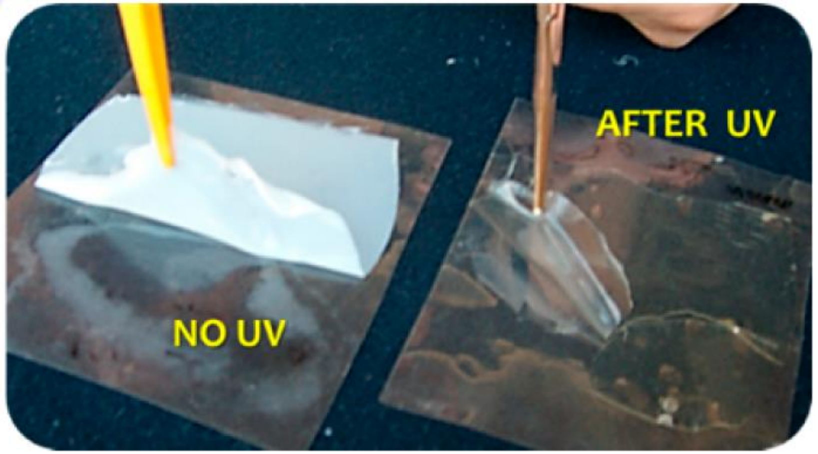
Group applied Materials and Electrochemistry

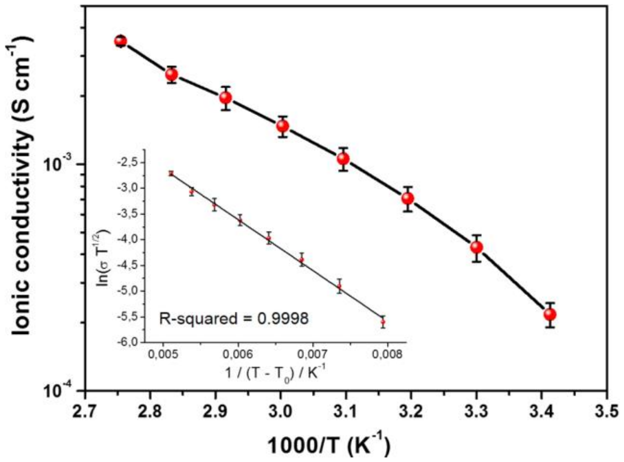
JÜLICH Forschungszentrum

CROSSLINKED POLYMER ELECTROLYTE (RTIL)









Crystallinity Inhibition

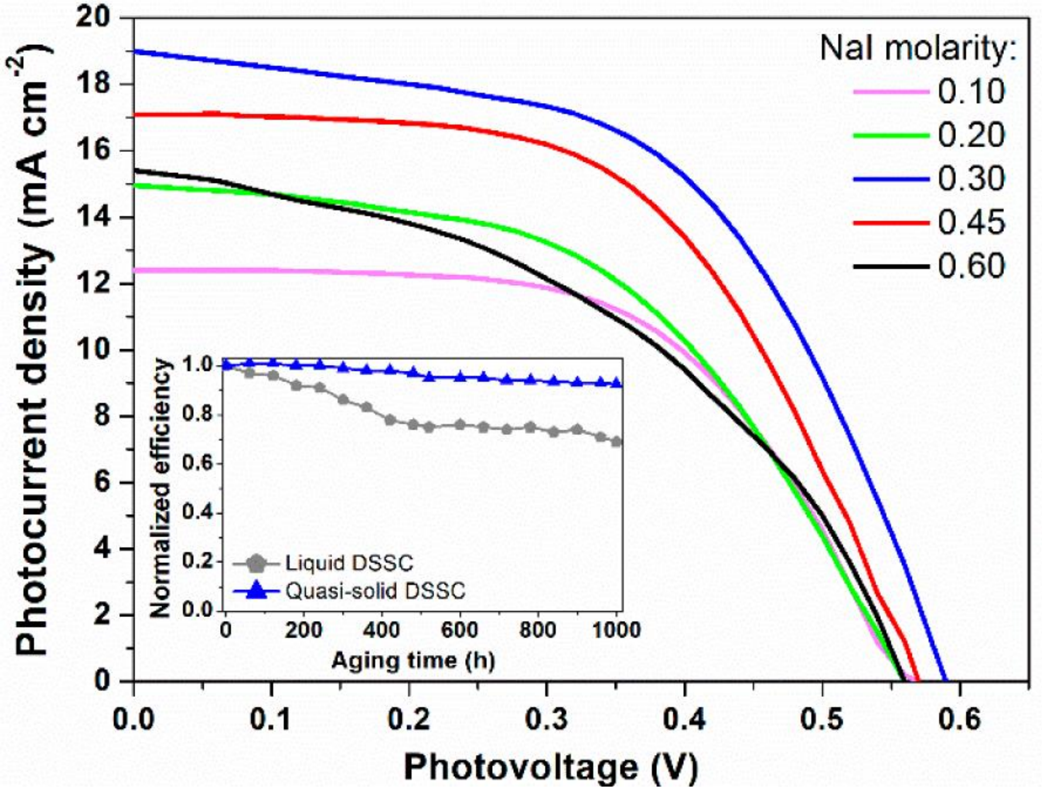
Mechanical stability

Flexibility

Ionic conductivity

QUASI-SOLID DYE-SENSITIZED SOLAR CELL

I^- (M)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	Efficiency (%)
0.1	0.57	12.40	0.52	3.70
0.2	0.56	14.95	0.53	4.42
0.3	0.59	19.00	0.55	***6.10***
0.45	0.57	17.1	0.54	5.22



J-V characterization @15' swelling

The versatility of these membranes in applications such as electrochromic devices (ECD) & DSSCs make this process a strong tool to prepare universal membranes with multi-utility.

SEMI-INTERPENETRATING ELECTROLYTE NETWORKS

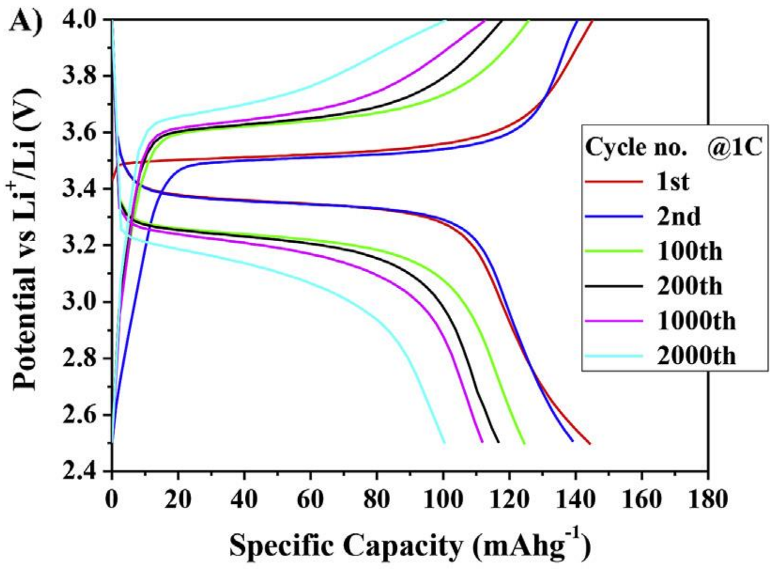
Materials

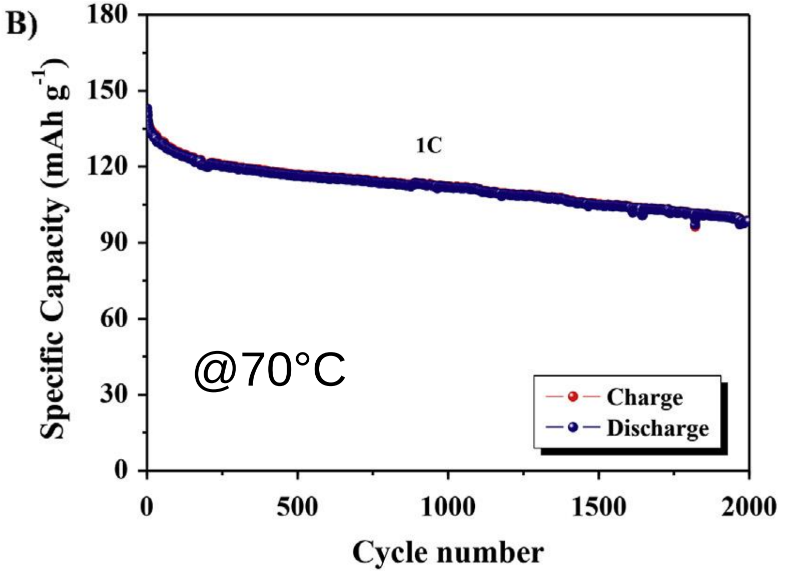
BEMA 30 wt%

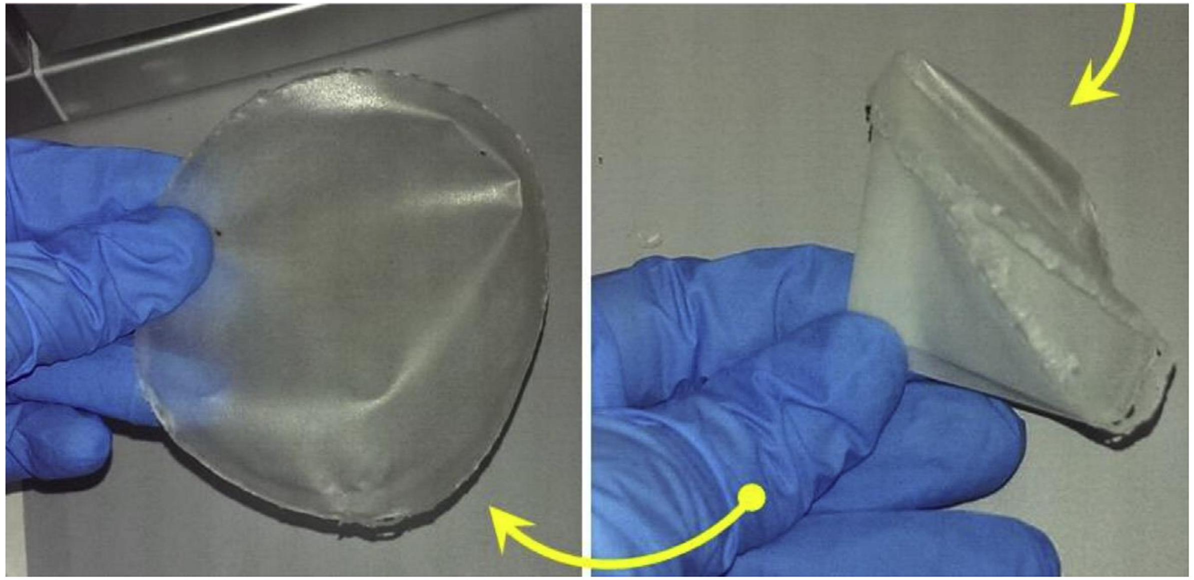
PEO 50 wt%

LiTFSI 20wt. %

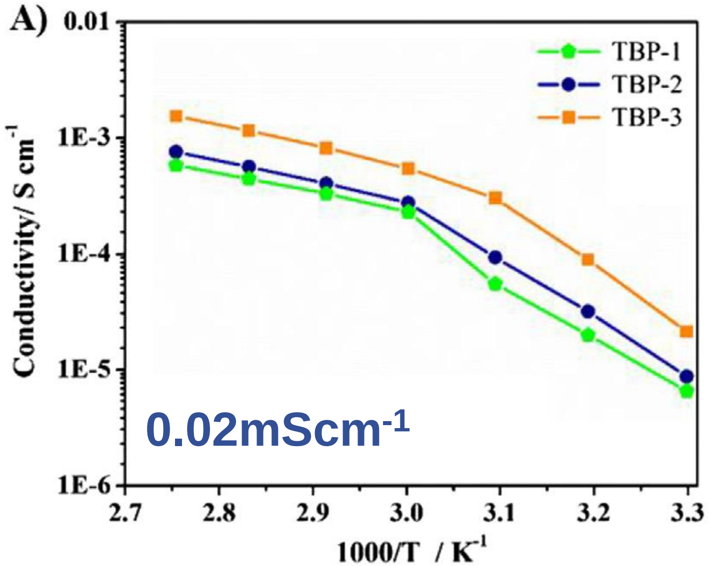
AIBN (ACN)







Dimensional stability after the thermal abuse

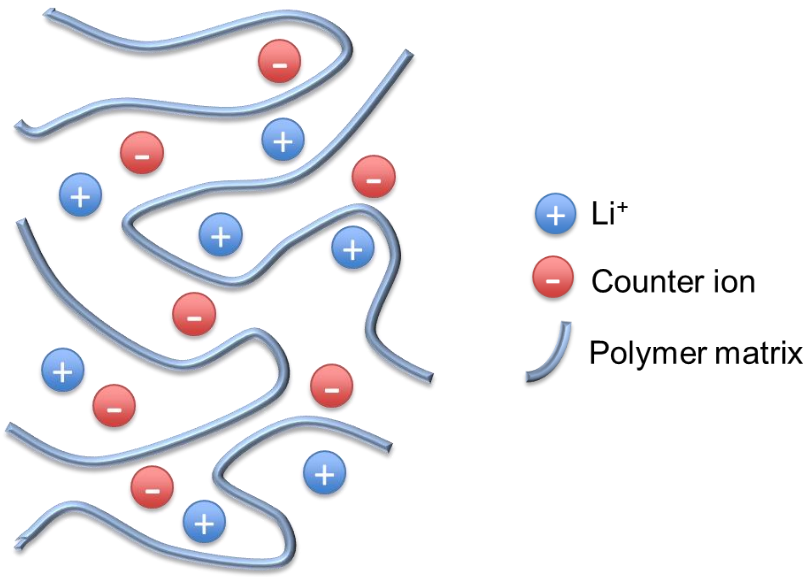


Group for Applied Materials and Electrochemistry

CROSSLINKED SINGLE-ION CONDUCTORS

POLYMER ELECTROLYTES: Polymer Matrix + Lithium Salt

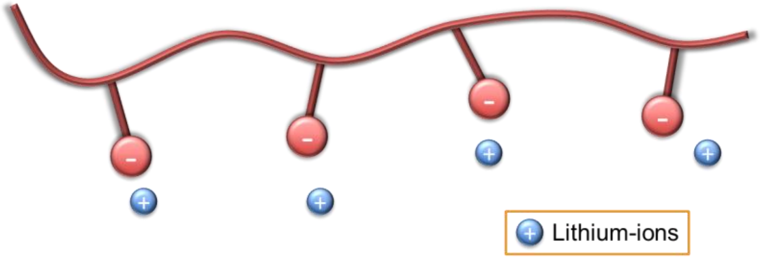
Neutral Polymer Matrix



Polyelectrolytes

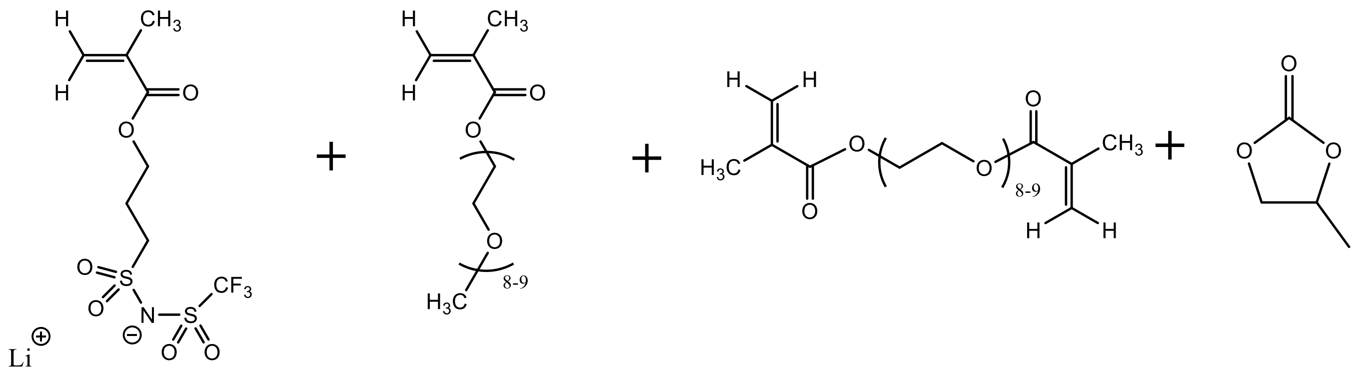
Cationic **Anionic**

Lithium Single-ion Conductors



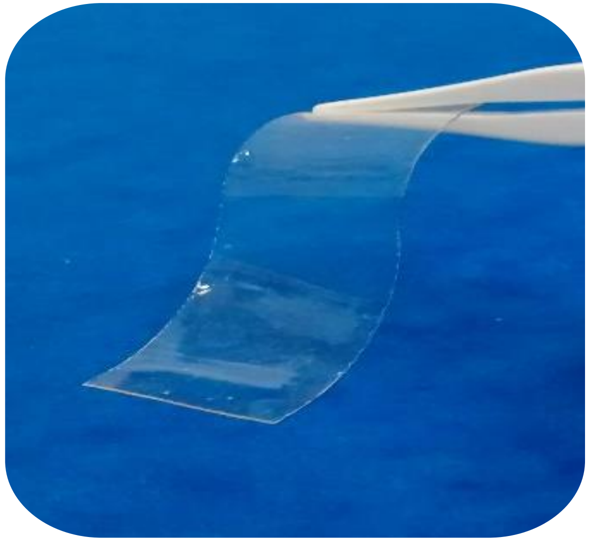
The lithium transport number ~1

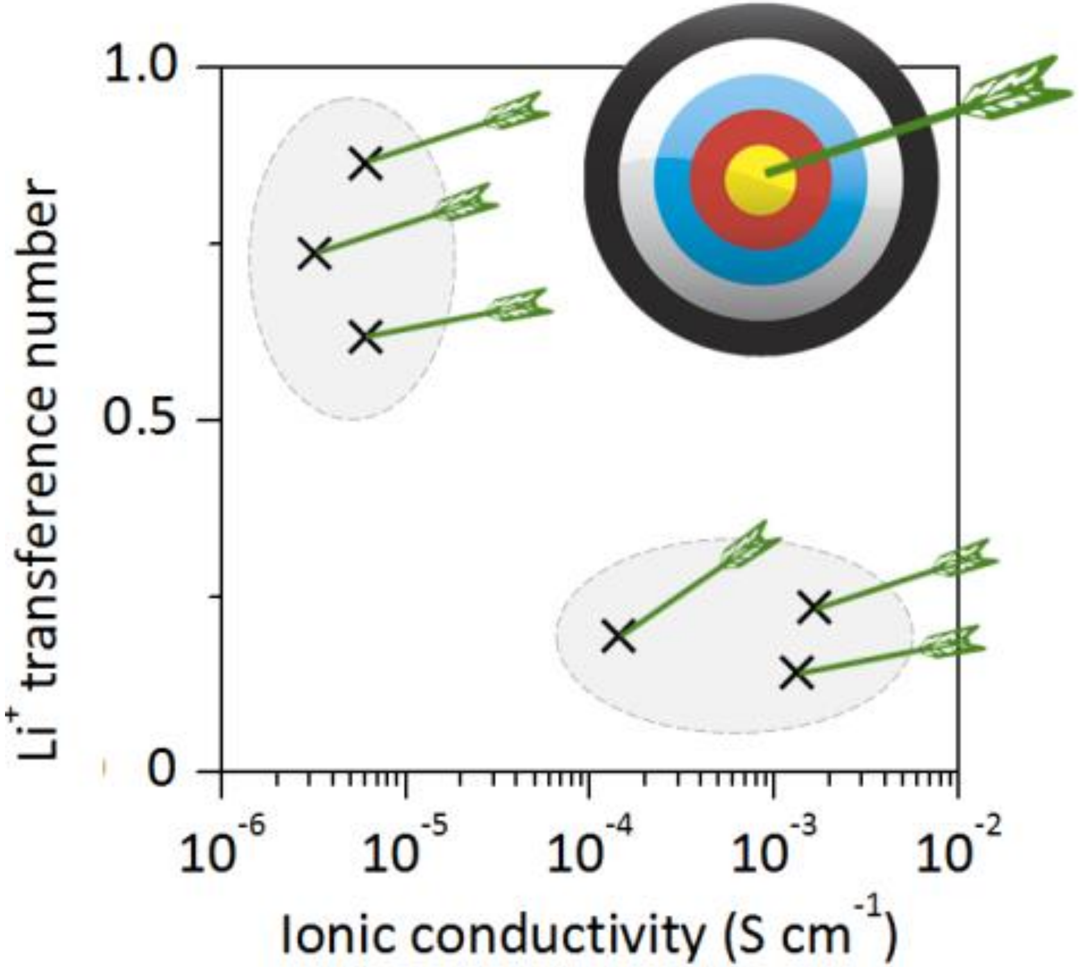
CROSSLINKED SINGLE-ION CONDUCTORS



LiMTFSI PEGM PEGDM PC

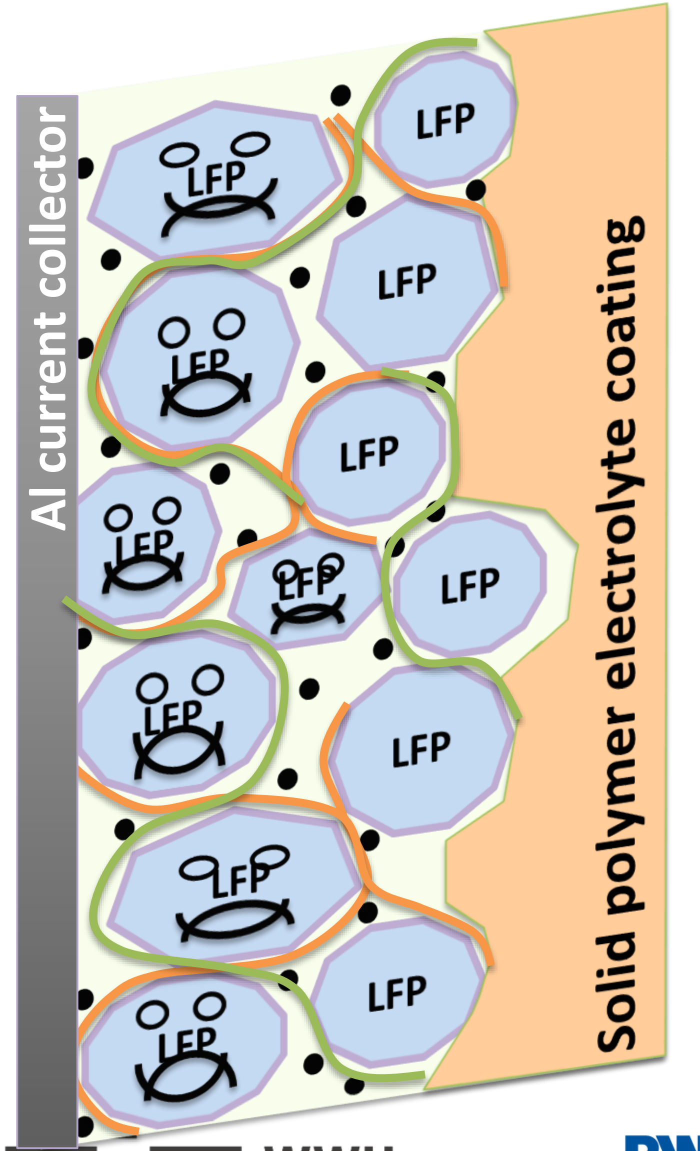
Curing 4 h 70 °C

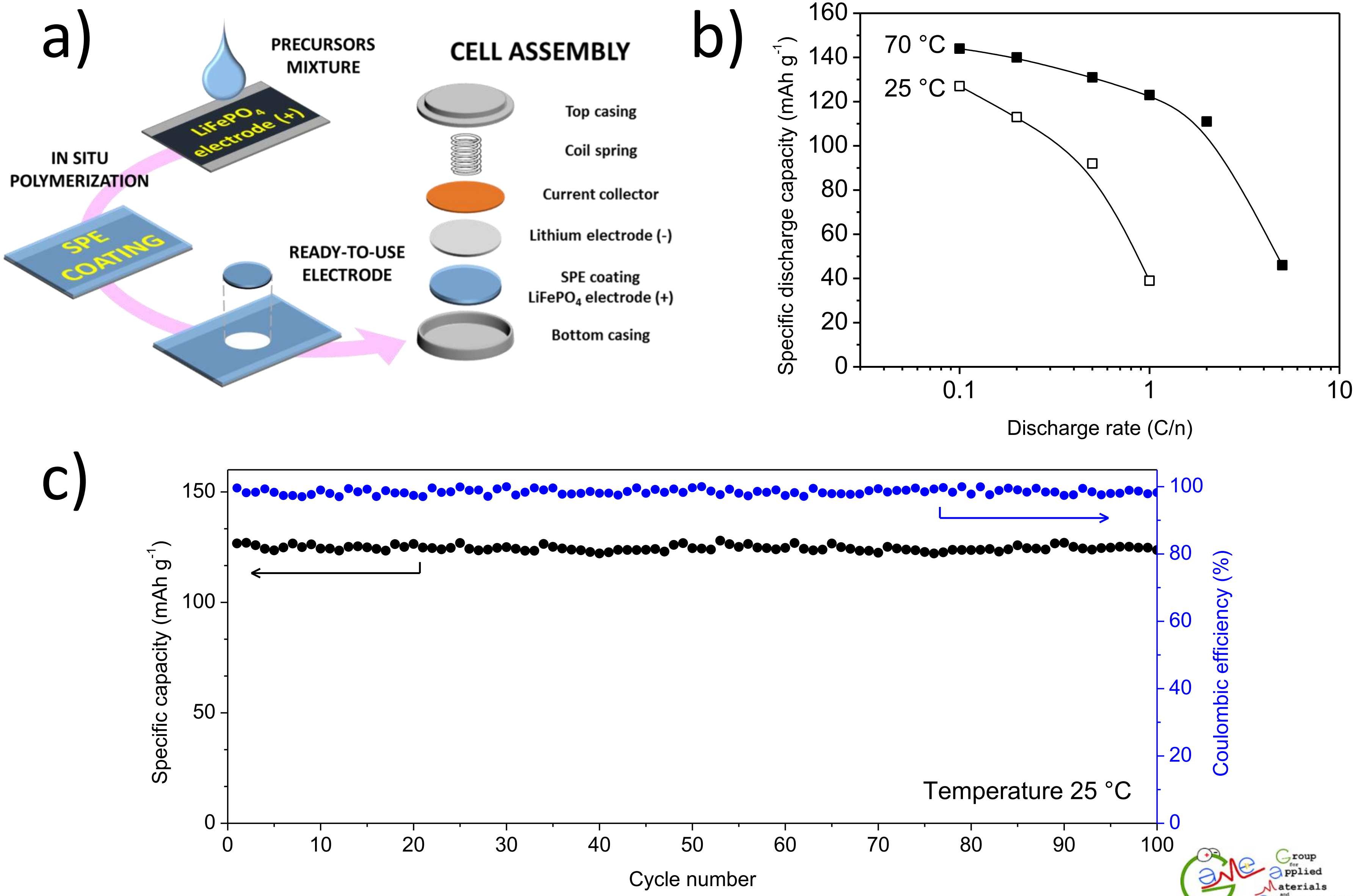




SINGLE-ION CONDUCTORS

POLYMAT





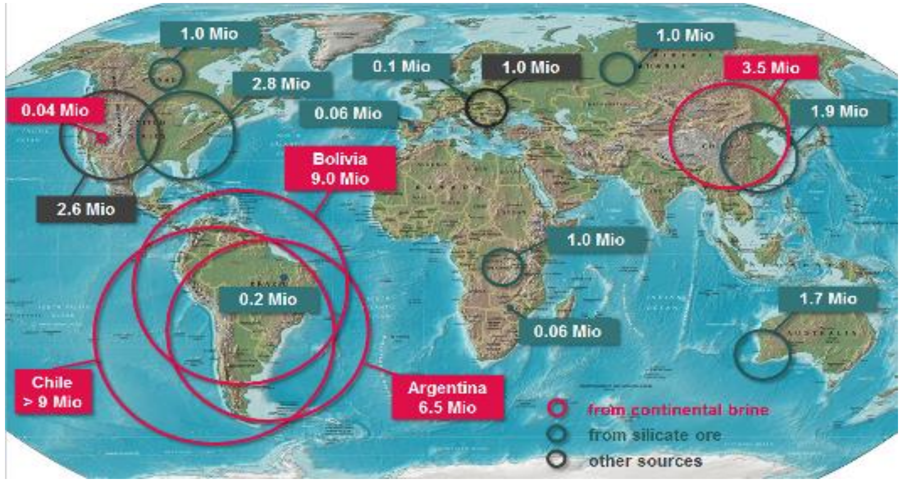
WWU MÜNSTER

RWTH

Group for Applied Materials and Electrochemistry

LITHIUM: THE NEW "GOLD" ?

Accessible global Li reserves are in remote or in politically sensitive areas. Increasing utilization of Li in energy storage applications with a higher "price point" will ultimately escalate the price of Li compounds even with extensive battery recycling programs, thereby making large-scale storage based on this element less affordable.

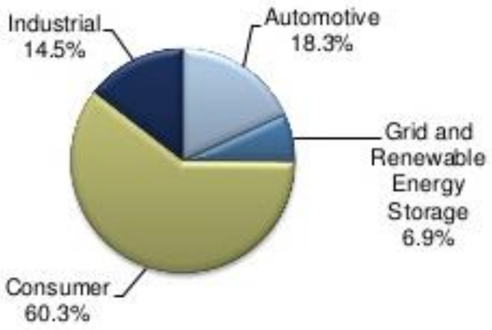


Market segmentation by application

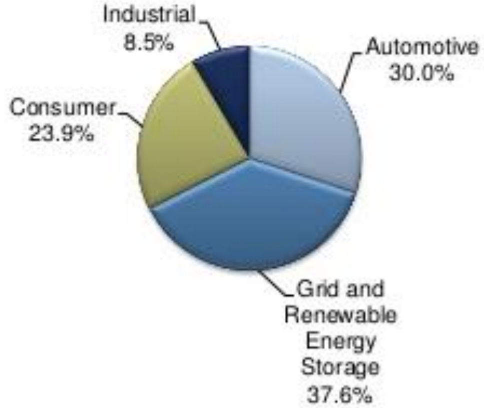
Key Takeaway: The consumer segment dominates the global lithium-ion battery market with increased use in laptops, smart phones, power tools, and other applications.

Key Takeaway: The utility segment dominates the market as utilities are seeking smart grid solutions that utilize lithium-ion batteries to improve operational efficiency and effectiveness.

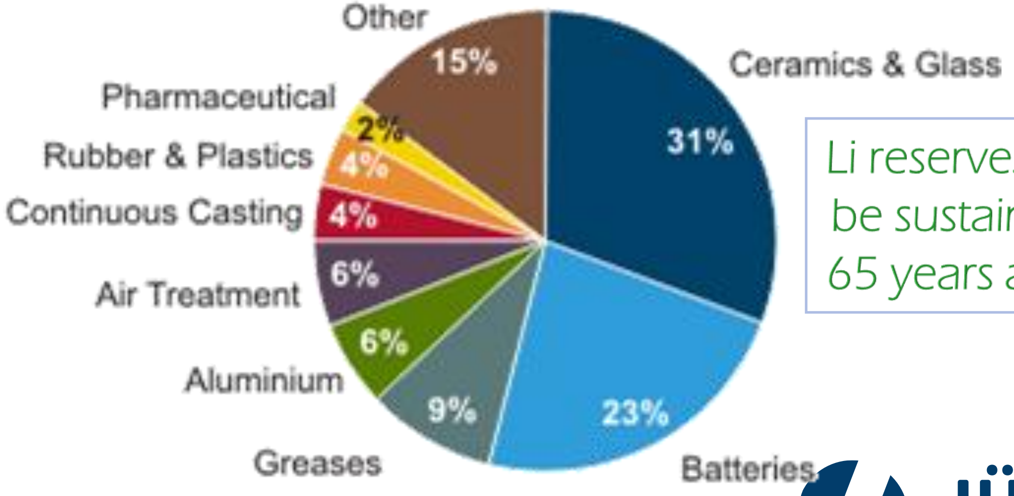
Total Lithium-ion Battery Market: Percent Revenue Breakdown by Application, Global, 2013



Total Lithium-ion Battery Market: Percent Revenue Breakdown by Application, Global, 2020



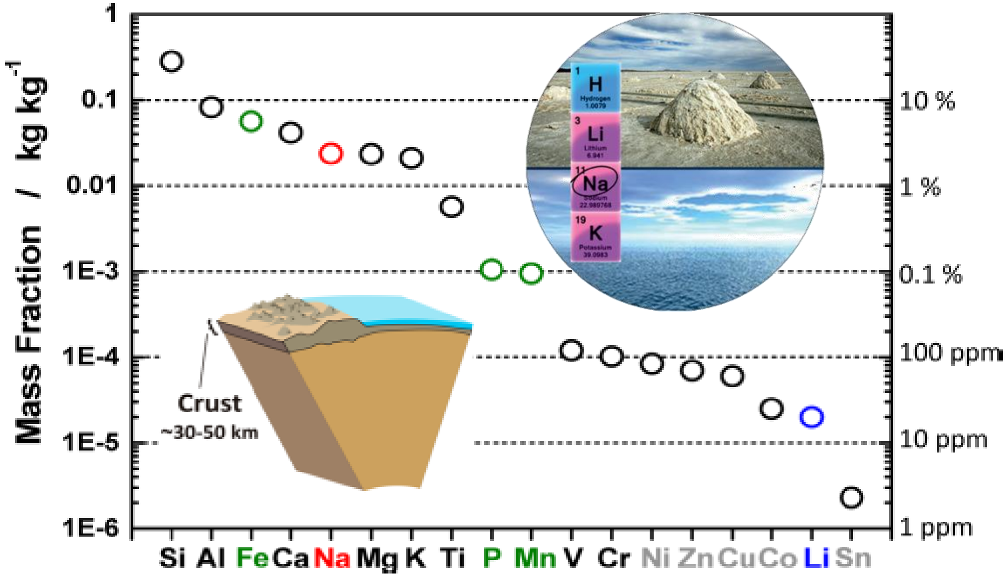
Current lithium by end user

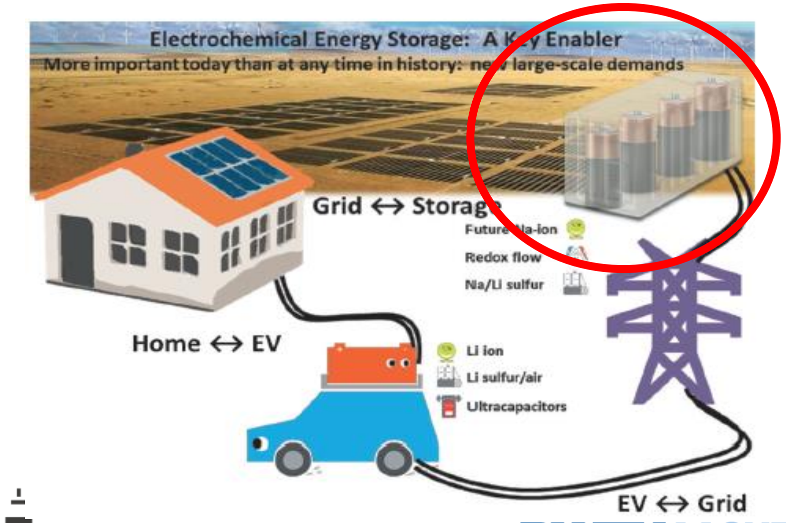


Li reserves could be sustained for 65 years at most

JÜLICH Forschungszentrum

SODIUM-ION BATTERIES: Large-scale Energy Storage





- **Sodium resources are "unlimited", attainable at low cost and geographically distributed.**
- **Very suitable redox potential (–2.71 V versus SHE), only a small energy penalty to pay vs. lithium.**
- **Same working principle as Li-ion batteries, similar materials.**
- **Gravimetric and volumetric energy densities of Na-ion battery would not exceed those of its Li analogue because of the relatively heavier and larger Na atom and less-reducing potential of Na. However, energy density is not a critical issue in large-scale energy storage.**
- **Sodium-based batteries offer a higher energy density than aqueous batteries and lower cost than Li-ion batteries, with some now approaching the energy density of the latter.**

L. F. Nazar & co, *Angew. Chem. Int. Ed.* 54 (2015) 3431
P. Johansson & co., *J. Mater. Chem. A* 3 (2015) 22
Y. S. Hu & co., *Energy Environ. Sci.* 6 (2013) 2338
S. Komaba & co., *Chem. Rev.* 114 (2014) 11636

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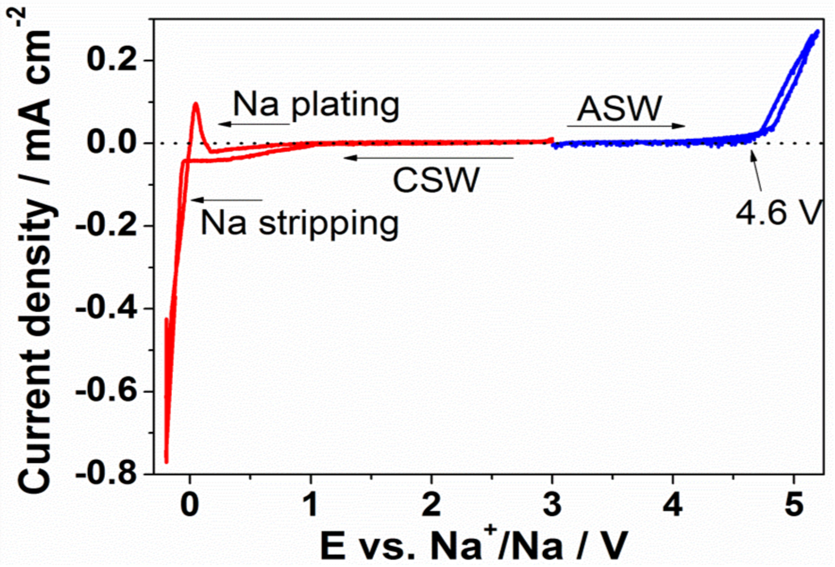
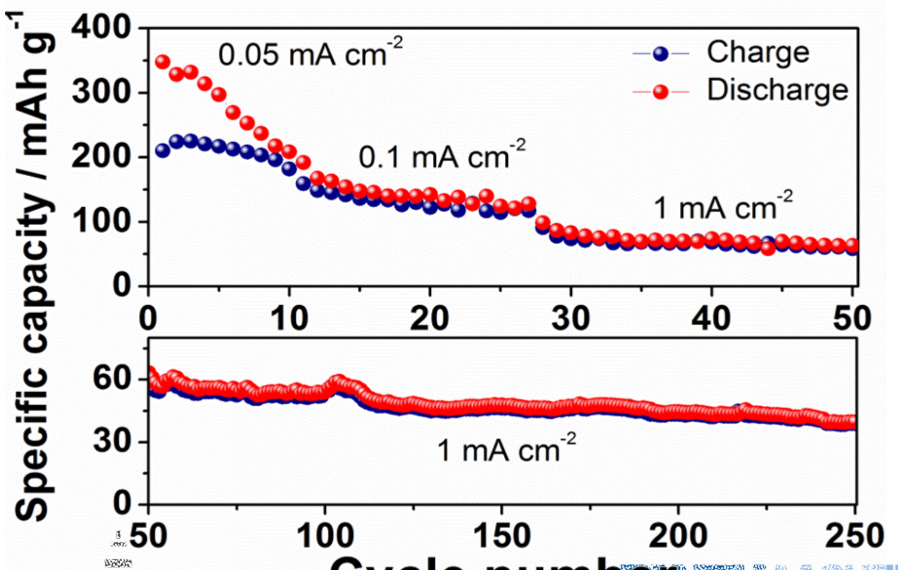
Na-POLYMER CELL TESTING

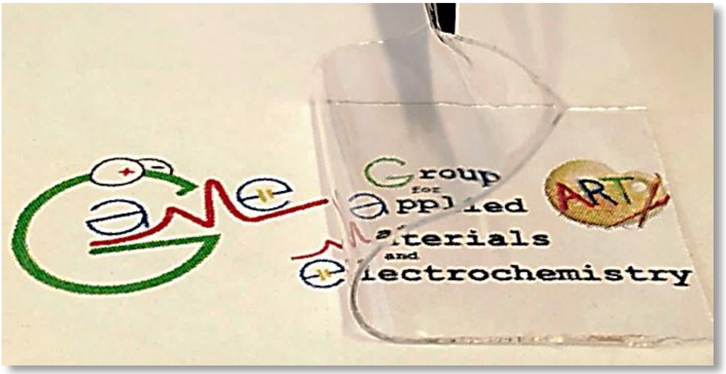


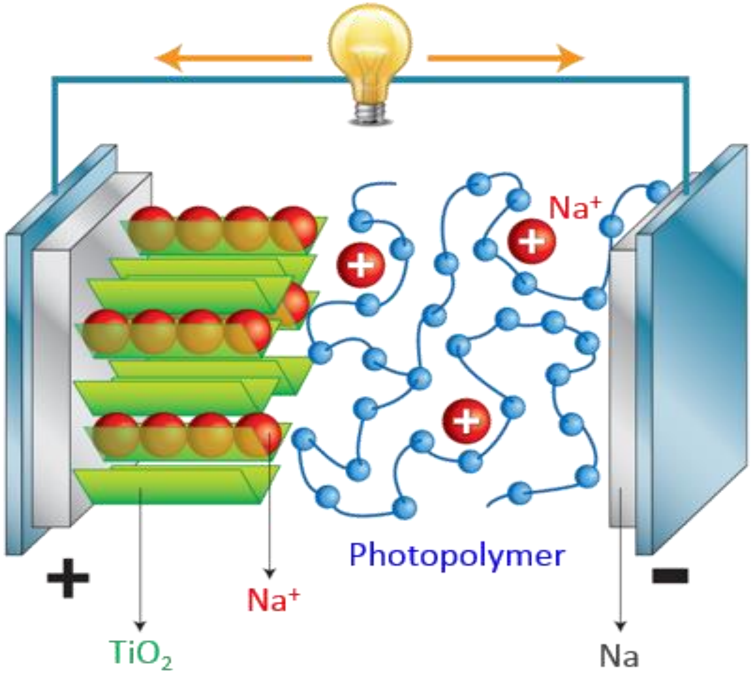


- **Electrochemical stability window** (ESW) between OCV and 5.2 V vs. Na/Na^+ (anodic scan) and between OCV and –0.2 V vs. Na/Na^+ (cathodic).
- **No noticeable electrochemical reactions** occurred at positive potentials ranging from the sodium reversible plating/stripping process below 0.2 V to above 4.7 V vs. Na/Na^+ where the current started flowing.
- The polymer electrolyte is suitable for practical application even in NIBs with **high working potential**.

Working electrode: TiO_2 anatase: Na-CMC:C (74:8:18); **Counter**: Na.

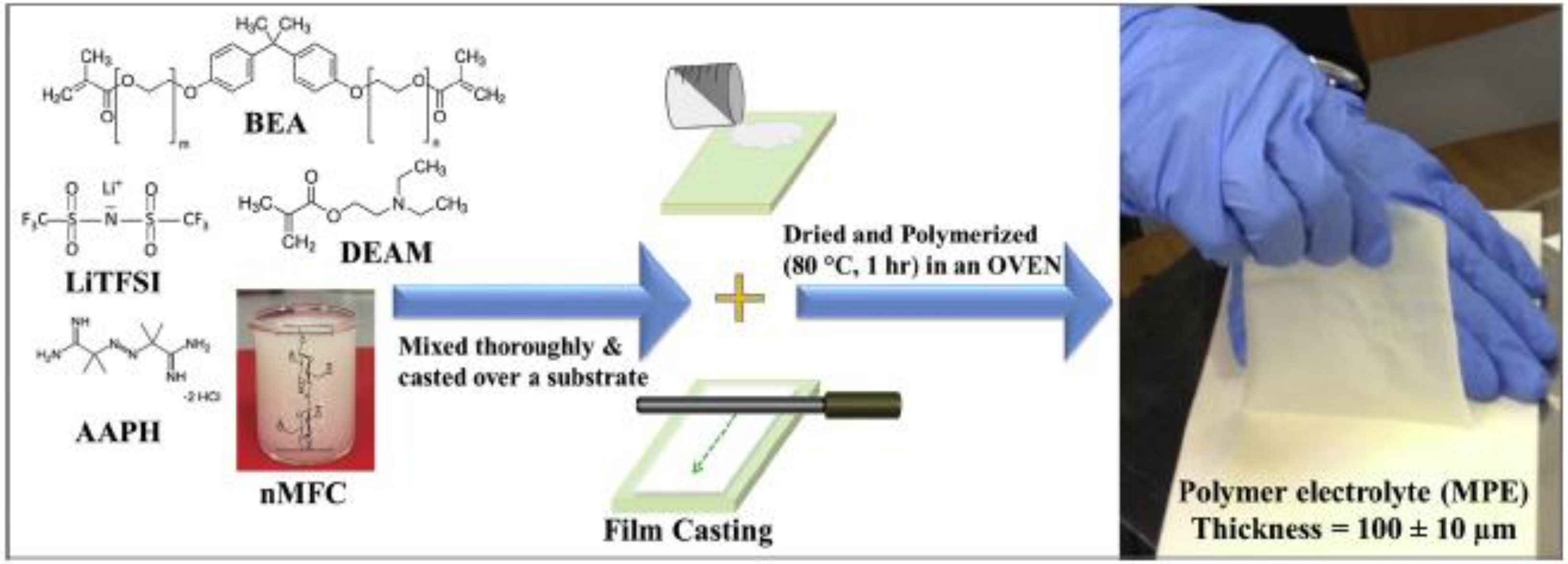
Initial specific capacity: **350 mAh g^{-1}**.

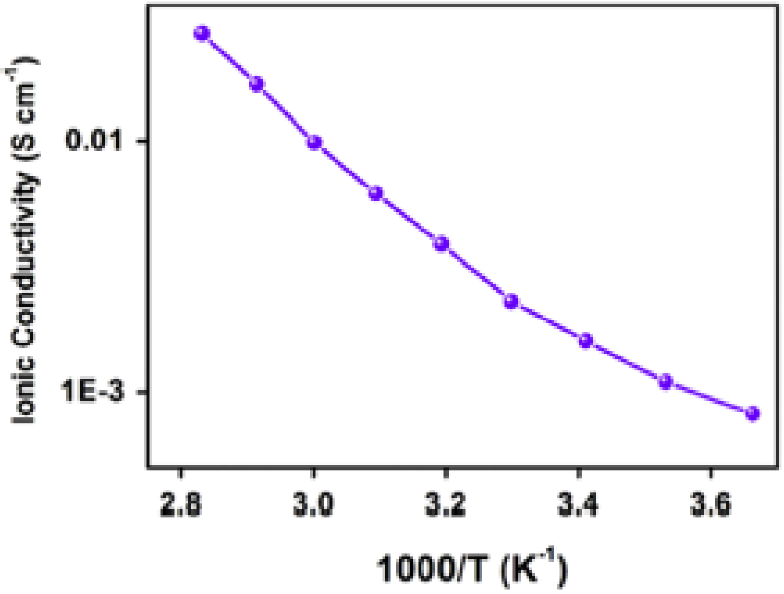




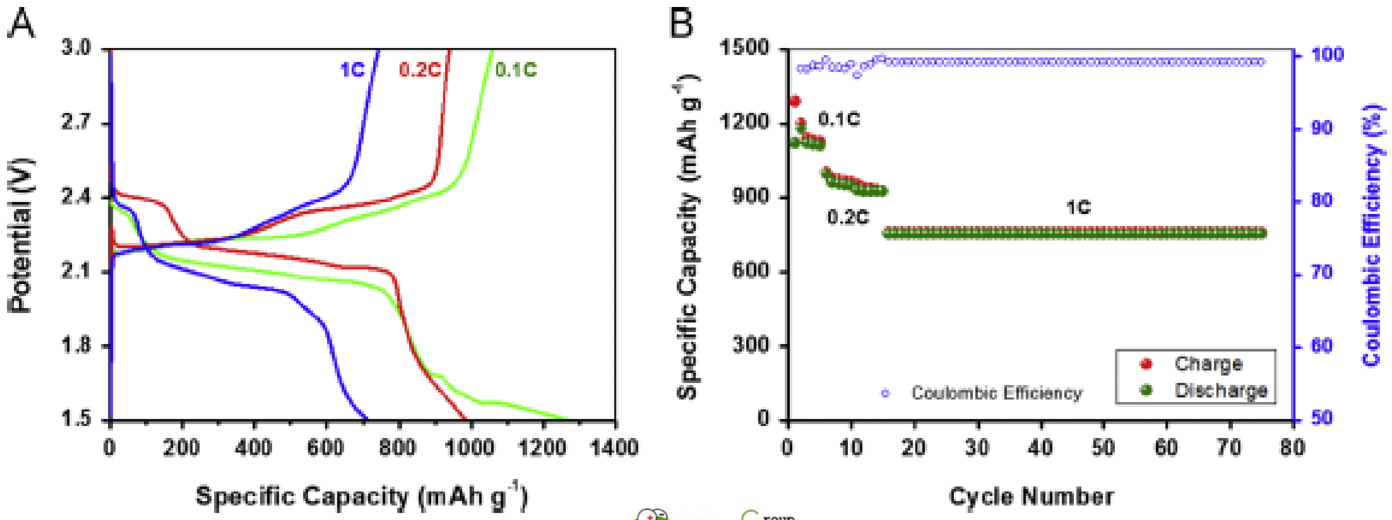
ChemSusChem 8 (15) 3668

Li-Sulfur: Nano cellulose-laden composite polymer electrolytes





Then liquid electrolyte: 0.75 M solution of LiTFSI in a 1:1(v/v) mixture of tetraethylene glycol Dimethylether (TEGDME) and 1,3-dioxolane + Lithium Nitrate ($LiNO_3$, 0.5M),



Towards paper-based energy storage devices

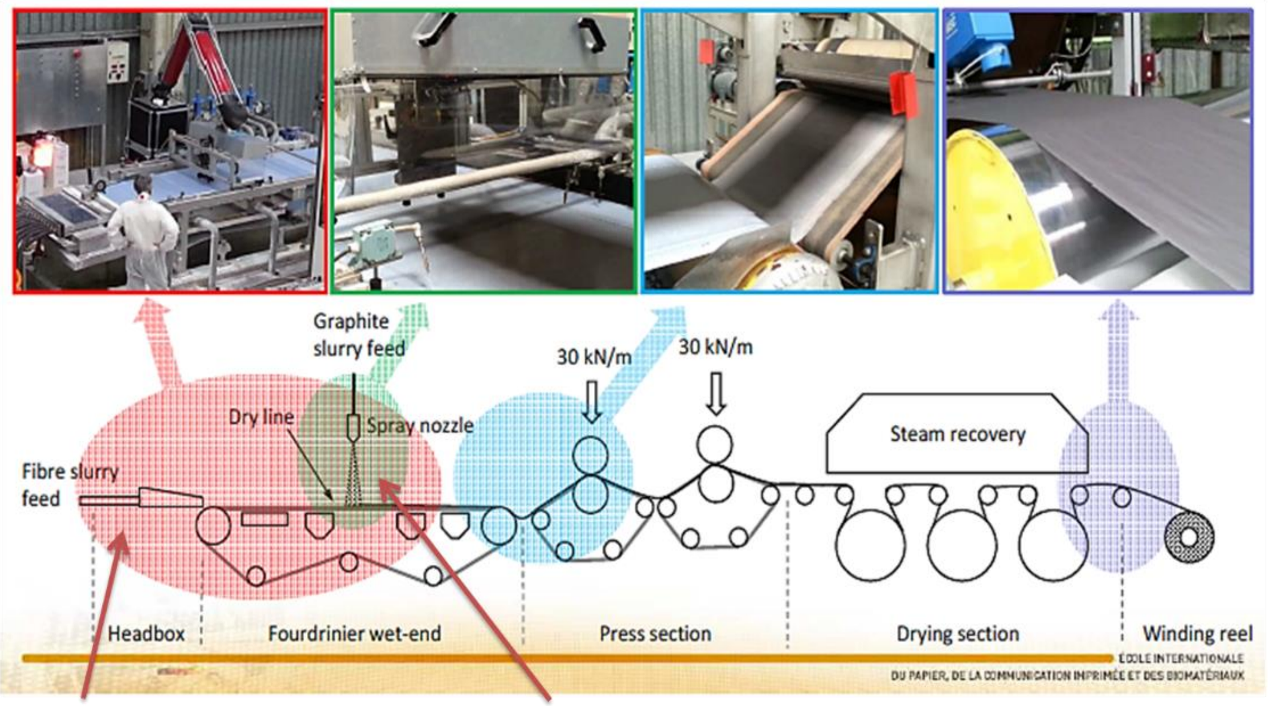
Spray coating and papermaking technologies were implemented on a pilot line for the large-scale production of battery electrodes coupling the use of water based electrode formulations and bio-sourced binders with flexible and high production capacity technologies.

Electrode manufacturing vs. papermaking

- **Materials:**
  - *Fluorinated binders* (or CMC)
  - Active materials
  - Polymeric additives
- **Coating technologies**
  - *Organic slurries* (or aqueous)
  - Slurry coating on metal substrate
  - *Solvent evaporation in oven*
- **Typical production rates:**
  - Machine speed: 10-100 m/min
  - Machine width: 0.5-1 m
  - *Throughput: 5-100 m^2/min*

- **Materials:**
  - *Cellulose fibres*
  - Active materials
  - Mineral fillers
- **Papermaking technologies**
  - Processing of fibre *aqueous slurries*
  - Slurry dewatering for sheet formation
  - Sheet coating with minerals/polymers
- **Typical production rates:**
  - Machine speed: 200-1000 m/min
  - Machine width: 2-7 m
  - *Throughput: 400-4000 m^2/min*

Pre-industrial paper electrodes by spray deposition



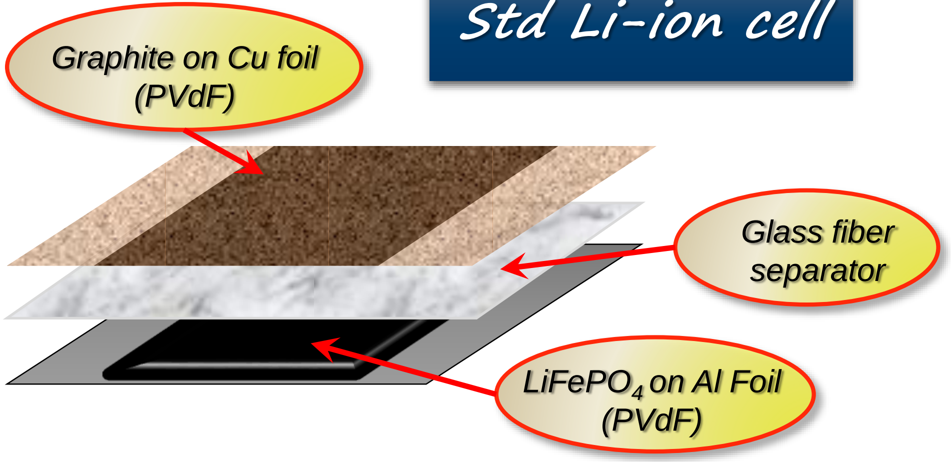
Paper sheet:
pre-separator, beaten cellulose fibres

Electrode aqueous slurry:
MFC binder, carbon black, graphite

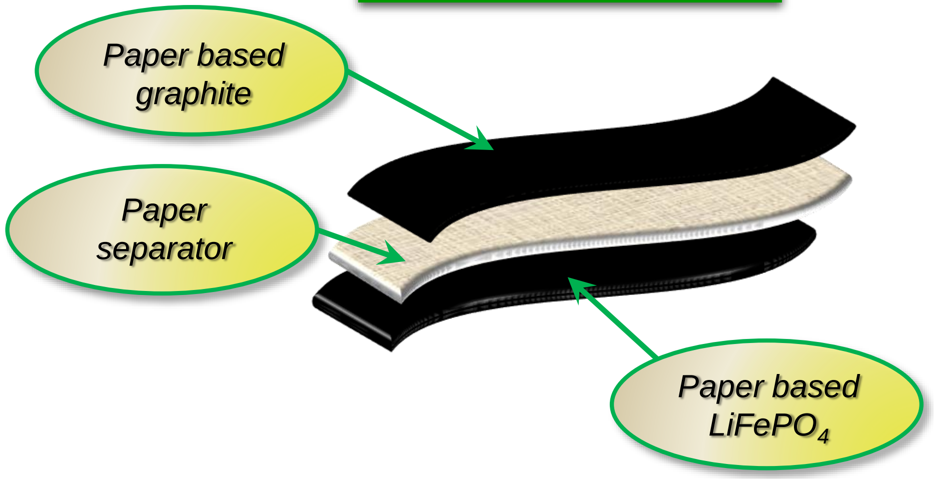
Chem. Eng. J. 243 (2014) 372; *Patent WO 2013/050713 A1*

Cellulose-based flexible Li/Na-ion paper cells

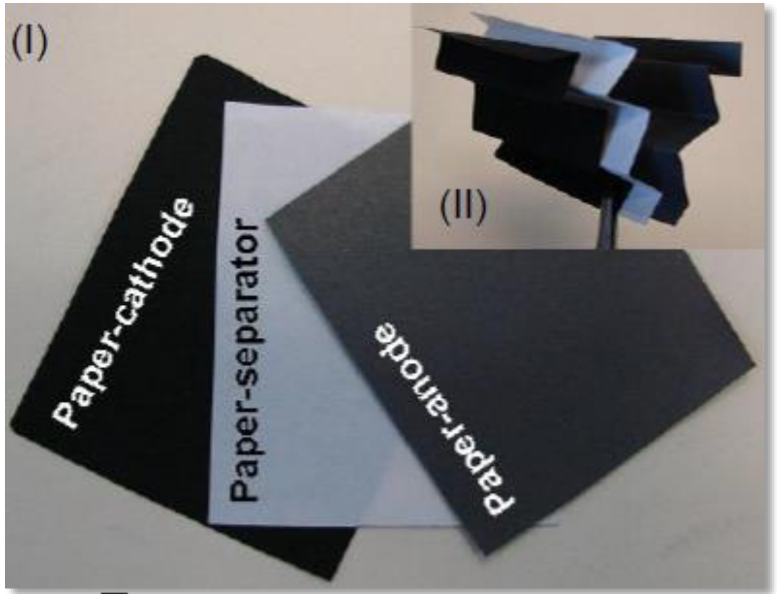
Std Li-ion cell



All-paper cell



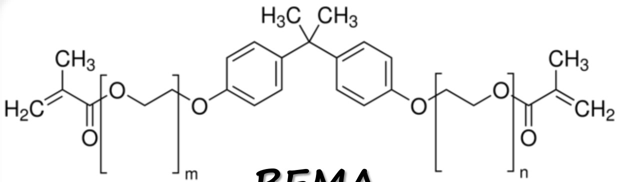
- No metal-foils
- No synthetic binders
- No synthetic separator



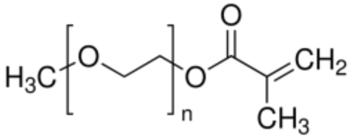
95 % recyclable !!!

J. Mater. Chem. 20 (2010) 7344; Cellulose 20 (2013) 1523; Cellulose 20 (2013) 571; ACS Ind. Eng. Chem. Res. 53 (2014) 10982; J. Mater. Chem. A 3 (2015) 14894

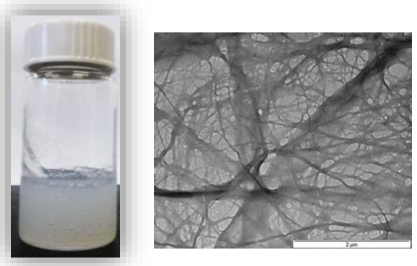
MFC-reinforced quasi-solid polymer electrolytes



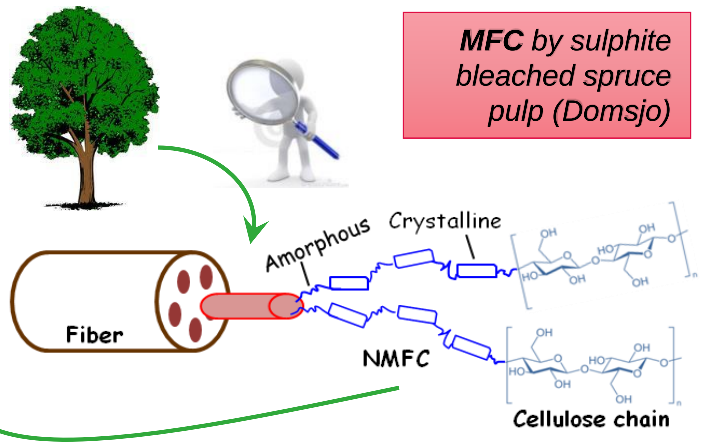
BEMA



PEGMA

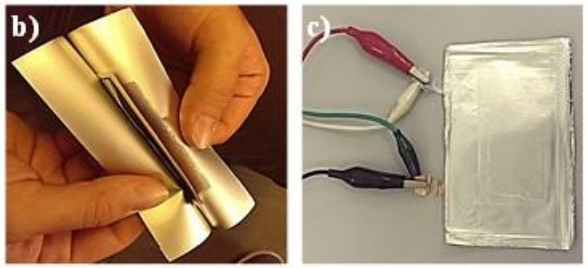


MFC
in water suspension

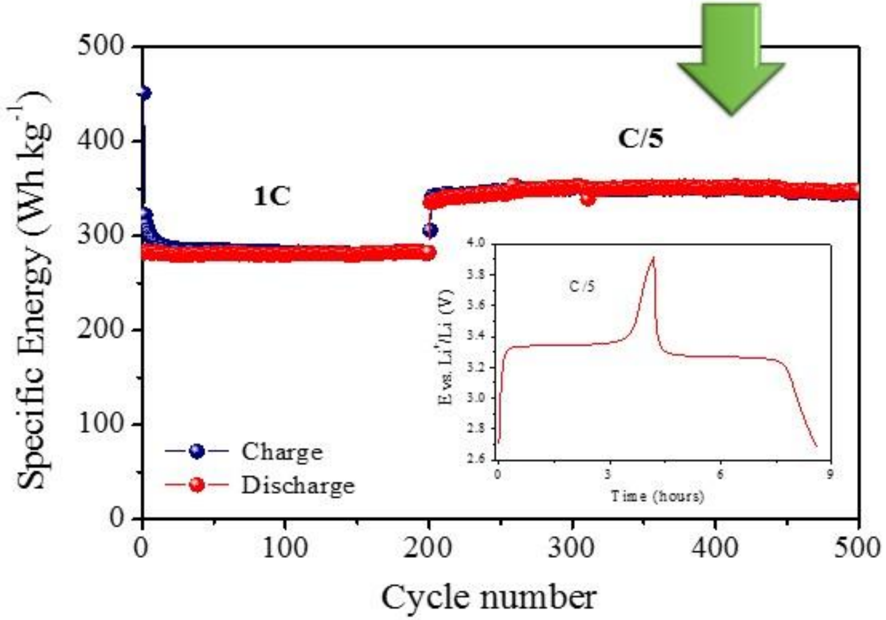


***MFC** by sulphite bleached spruce pulp (Domsjo)*

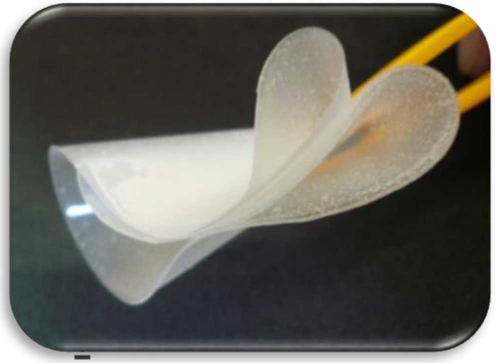
coffee bag "pouch cell"

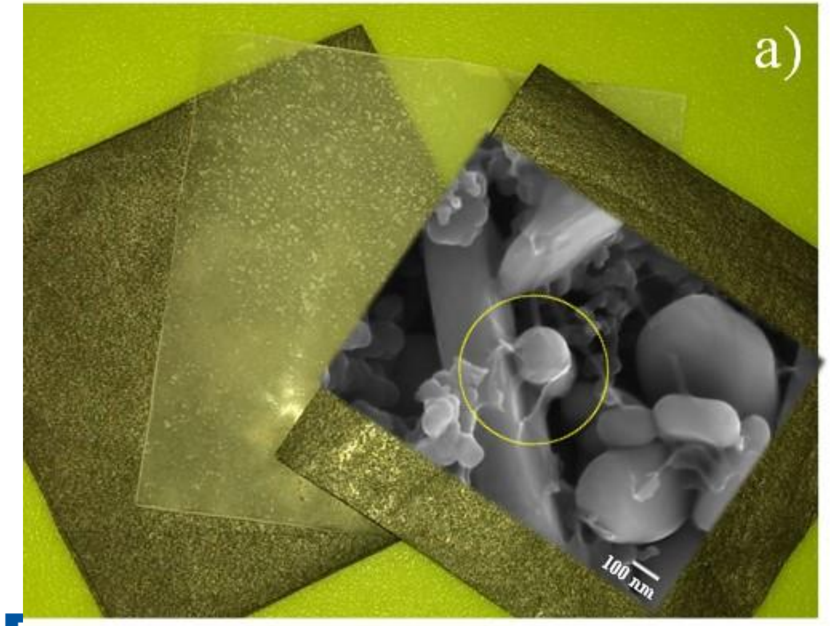


assembly / sealing **testing**



COMPOSITE MFC-POLYMER ELECTROLYTE





Carbon (2016) Carbon 2016

SUMMARY

- Suitable polymer matrix selection is very important
- Crosslinking can be used as an effective tool to modulate the physical properties of polymer electrolytes
- UV induced crosslinking is effective in indusctrially upscaling the polymer electrolyte process
- Cross-linked polymer electrolytes are versatile and can be applied in Li/Na batteries, Lithium-Sulfur batteries, DSSCs, Supercapacitors, FETs, Memristors, and so on..

Thank you ....

Organizing Committee, NiPS Summer School 2018

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POLYMAT

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