Ionic liquids confined for solid-state devices.

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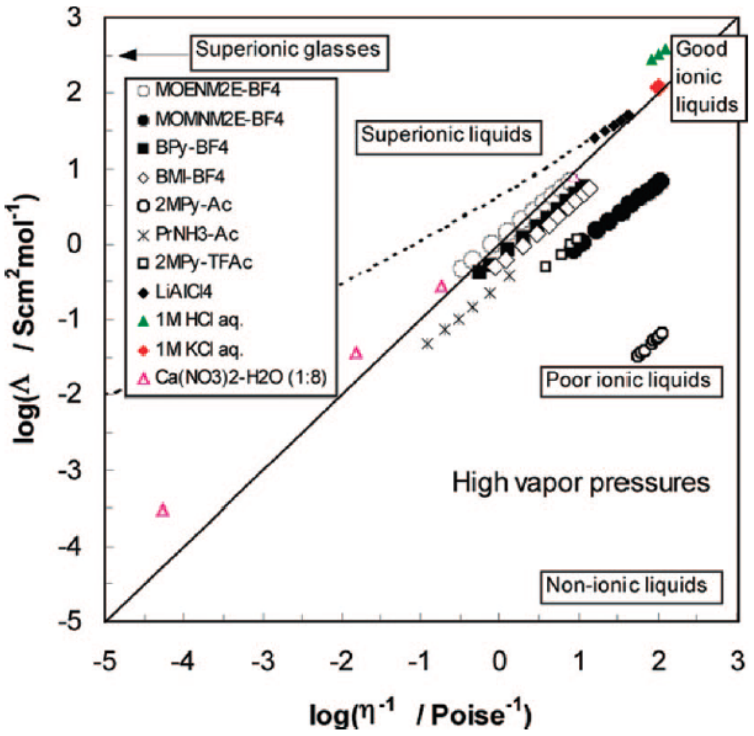
Few intensive properties of ILs

« This Account covers research dating from the early 1960s in the field of low-melting molten salts and hydrates, which has recently become popular under the rubric of “ionic liquids”. »

A. Angell, *Acc. Chem. Res.* 2007, *40,* 1228–1236



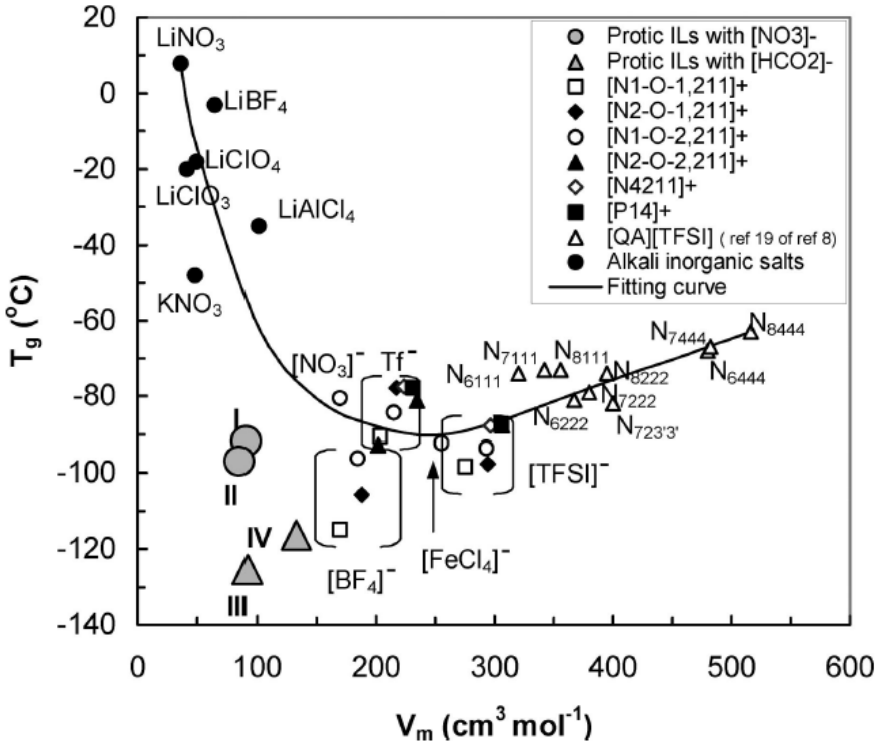
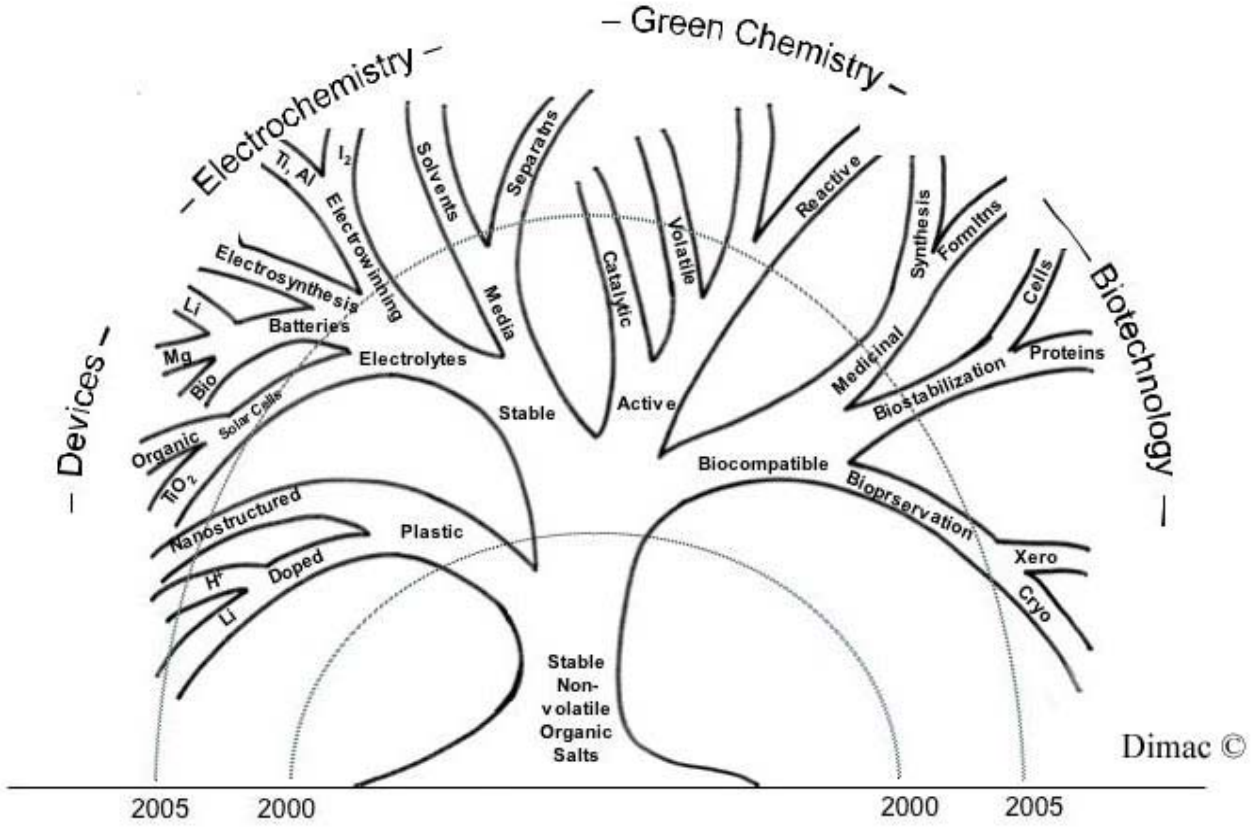
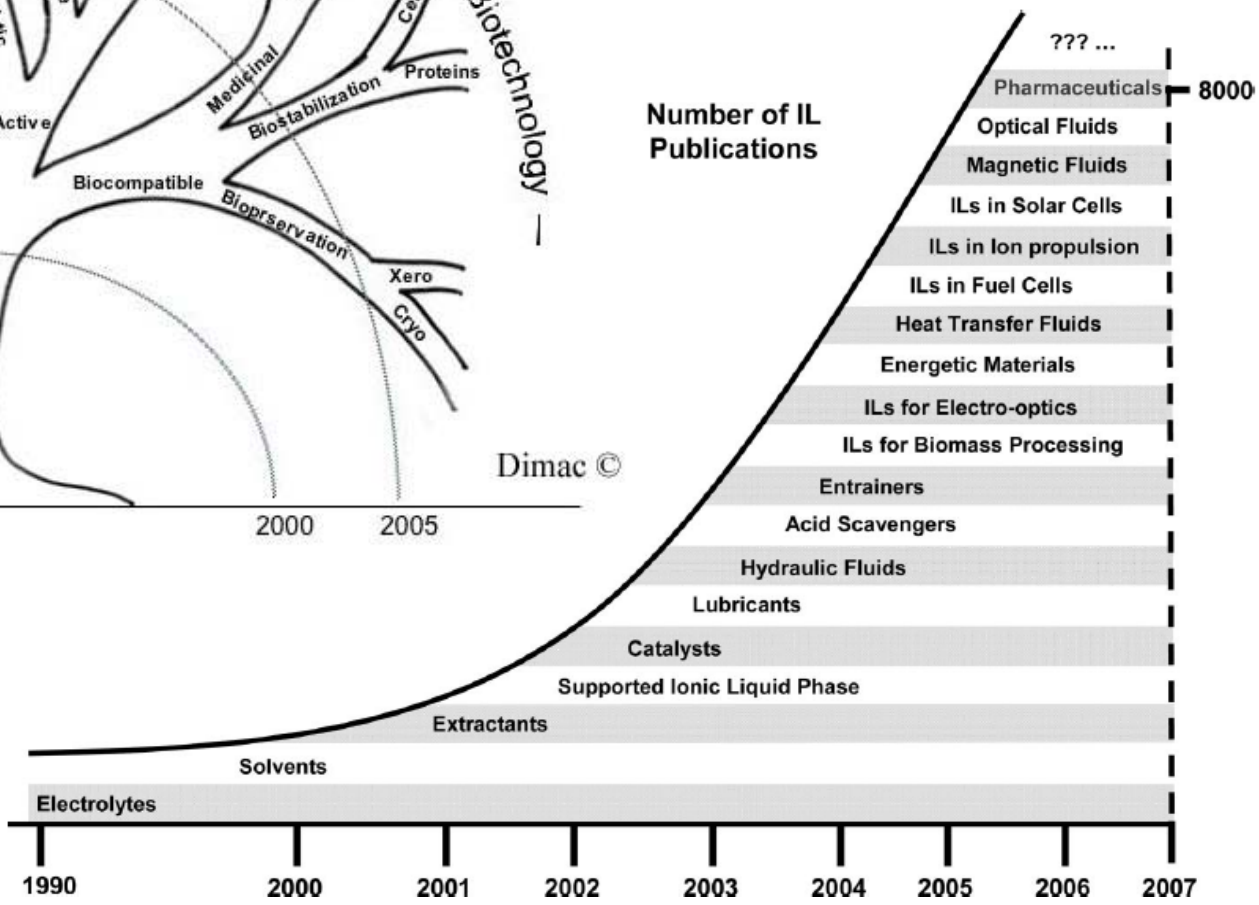


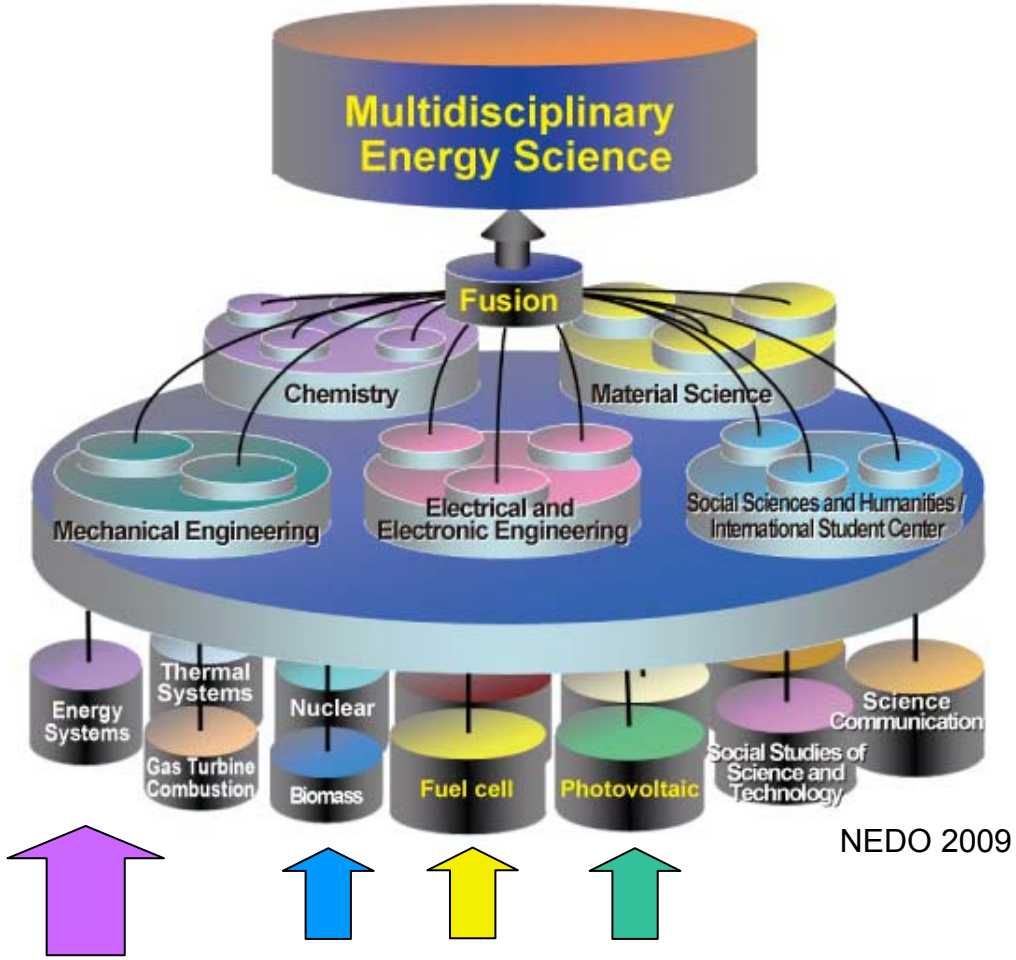
FIGURE 5. Walden Plot for ionic liquids and other molten salt and hydrate systems. Position of ideal line is fixed by data for KCl in 1 M aqueous solution. “Good” ionic liquids cluster on the ideal line.

Fields for ionic liquids …





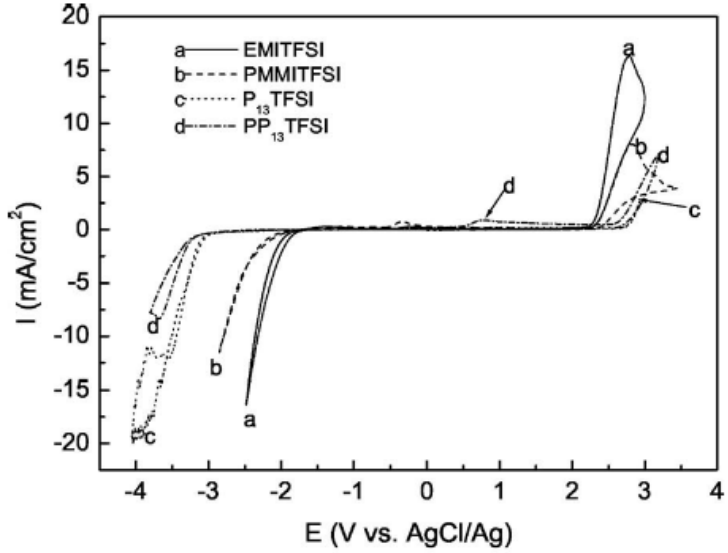
… and needs for solid-state devices



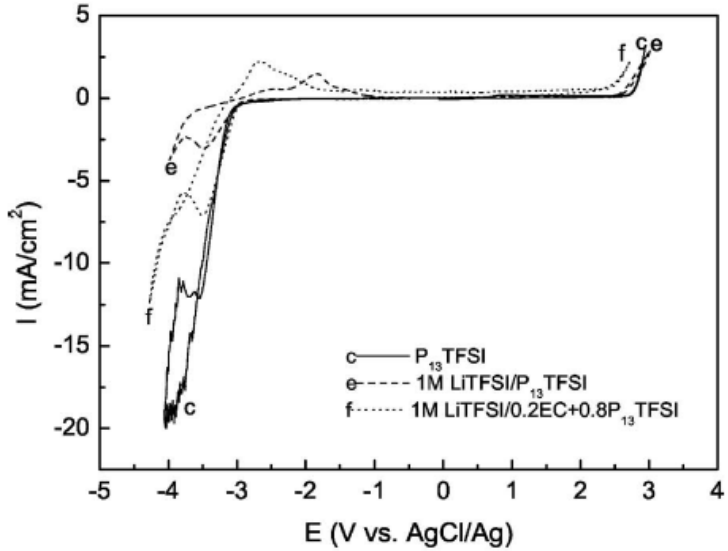
NEDO 2009

Immobilization of ILs within polymers : PVDF-HFP / P13TFSI / LiTFSI / EC

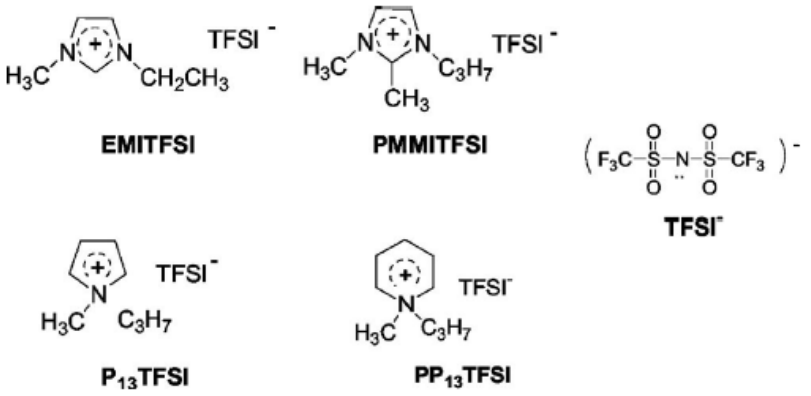
H. Ye et al., *J. Electrochem. Soc.*, 2007, **154,** 11, A1048



(a)



(b)



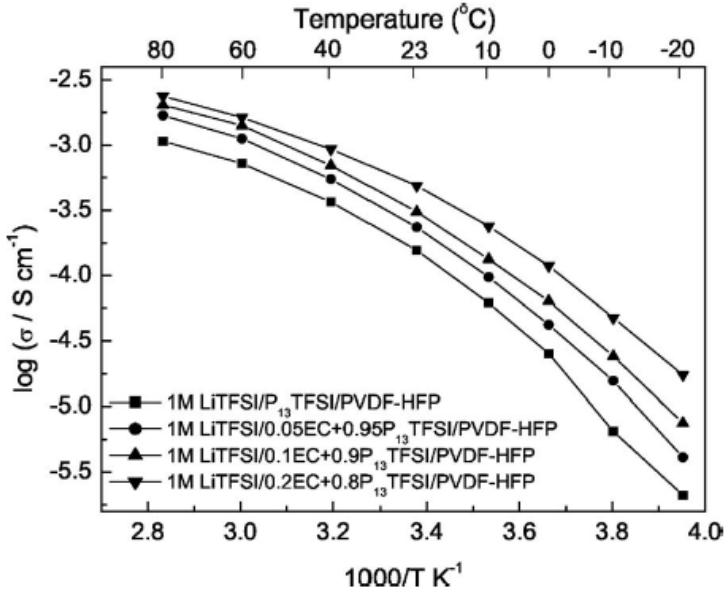
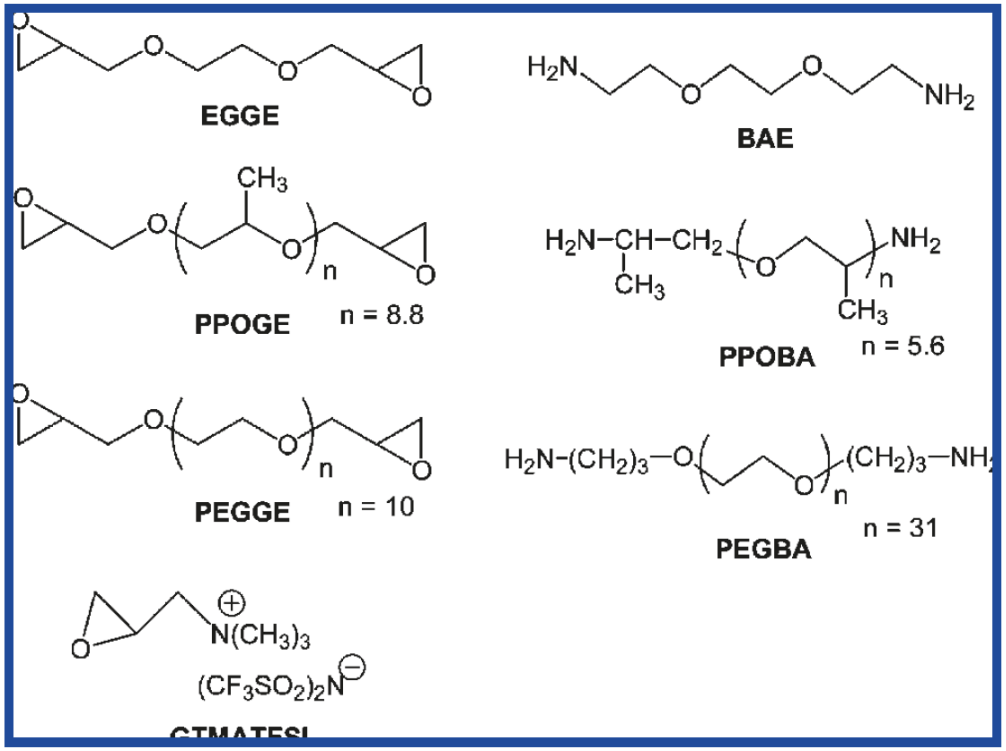
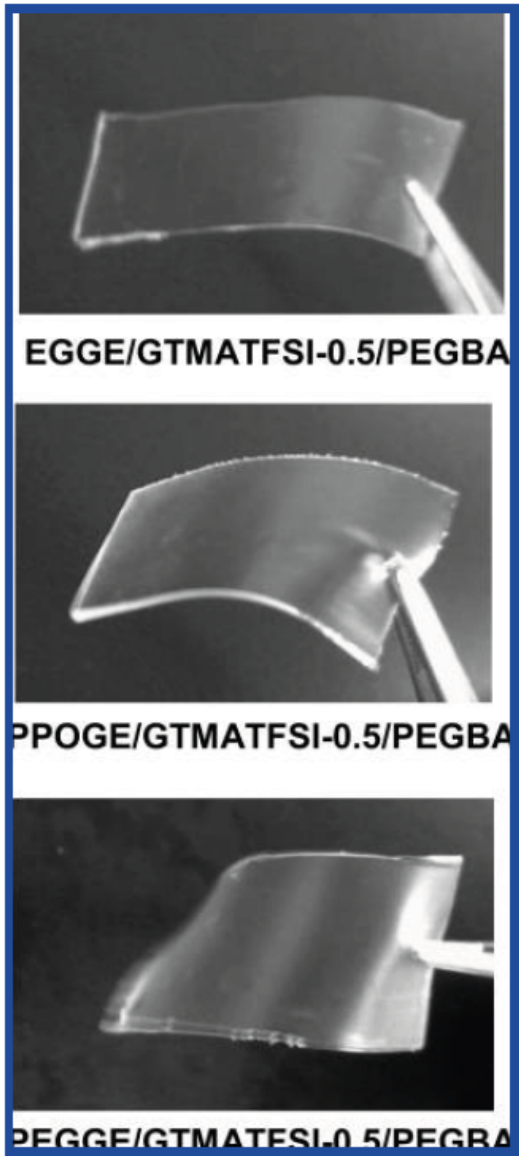


Figure 6. Temperature dependence of the ionic conductivity of 1 M LiTFSI/xEC + $(1 - x)$ P_{13}TFSI/PVDF-HFP (x = 0, 0.05, 0.1, and 0.2) membranes.

In situ polymerisation with IL entrapment

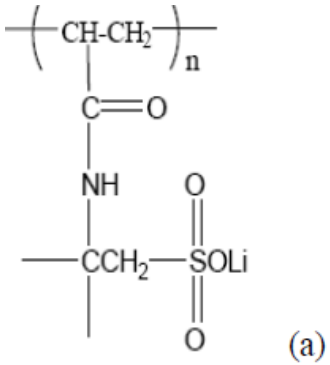


samples	GTMATFSI content (wt%)	ionic conductivity (S/m)
EGGE/GTMATFSI-0.5/BAE	43	$< 1.0 \times 10^{-5}$
EGGE/GTMATFSI-0.5/PPOBA	32	$< 1.0 \times 10^{-5}$
EGGE/GTMATFSI-0.5/PEGBA	15	1.5×10^{-3}
PPOGE/GTMATFSI-0.5/BAE	21	$< 1.0 \times 10^{-5}$
PPOGE/GTMATFSI-0.5/PPOBA	18	1.4×10^{-5}
PPOGE/GTMATFSI-0.5/PEGBA	11	1.2×10^{-3}
PEGGE/GTMATFSI-0.5/BAE	24	2.2×10^{-4}
PEGGE/GTMATFSI-0.5/PPOBA	20	2.3×10^{-4}

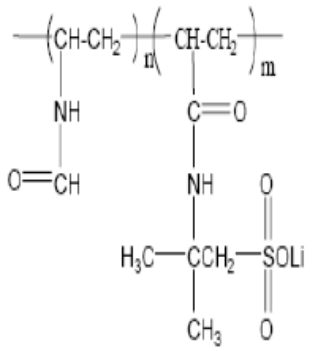


T. Endo et al., *Macromolecules* 2009, 42, 4580–4584

ILs confined in polymers



(a)



(b)

Poly (lithium2-acrylamido-2-methyl-propanesulfonate – vinyl formamide) mixed with 90wt% ionic liquid with ethanol, stirred over night and then dried.

E.H. Cha et al., *J. Power Sources*, 2007

Laser printing of nanocomposite solid-state electrolyte membranes for Li micro-batteries

M. Ollinger et al., *Appl. Surf. Sci.*, 252 (2006) 8212

6.4 wt.% DMBITFSI
3.6 wt.% PVdF-HFP
1.1 wt.% nc-TiO2
88.9 wt.%DBE

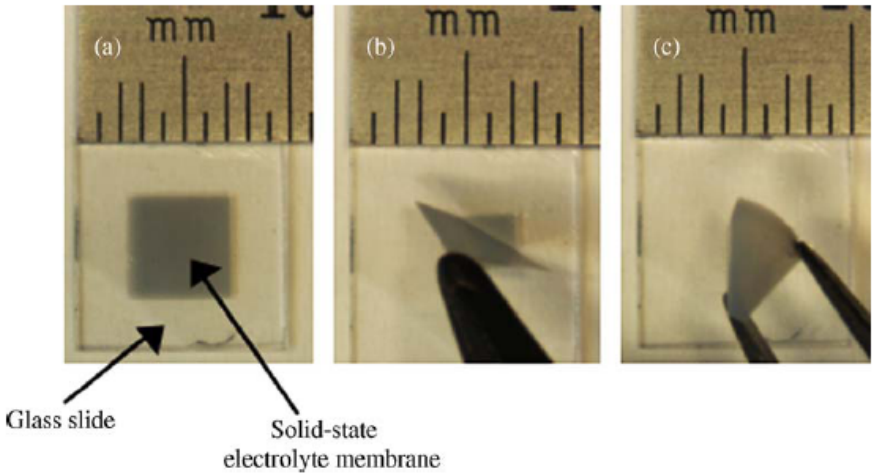
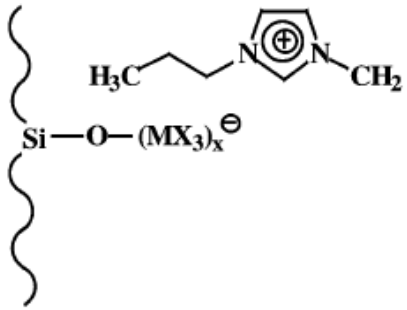
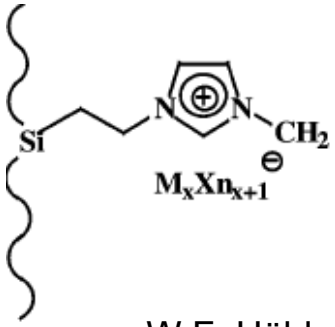


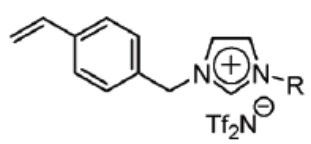
Fig. 3. Optical micrographs showing the strength and flexibility of the nanocomposite solid-state electrolyte membranes laser printed on a glass slide. (a) Membrane laser printed on a glass slide, (b) membrane partially lifted off from glass slide, and (c) membrane held using tweezers.

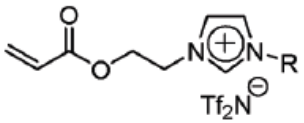
Covalent cation or anion self-polymerisation or covalent grafting : regularity



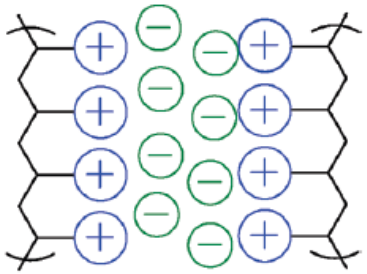


W.F. Hölderich, *Green Chem.*, 2002, 4, 88–93

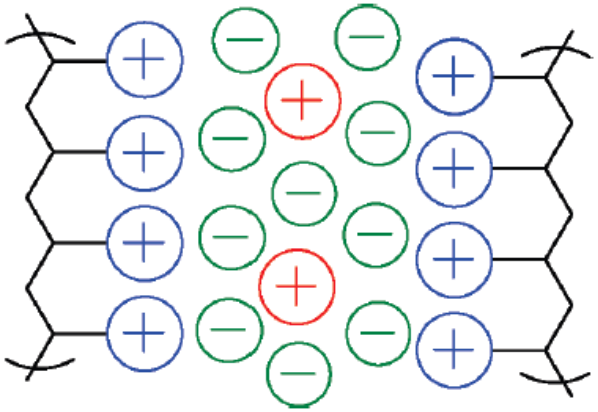




(a) R = $-(CH_2)_nCH_3$, n = 0, 3, 5



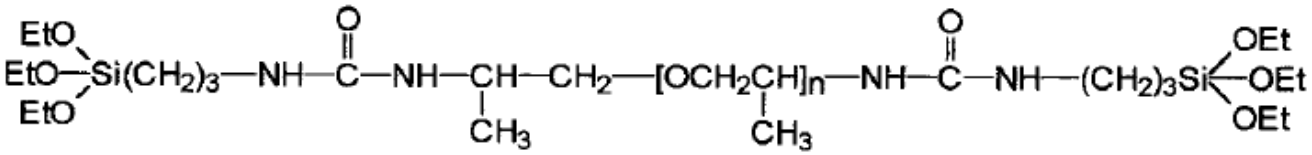
(b)



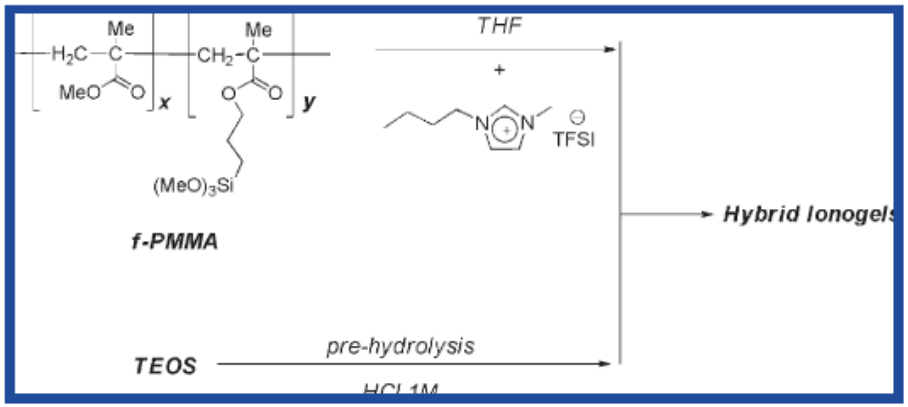
Representation of a poly(RTIL)–RTIL composite

R. Noble et al., *Acc. Chem. Res.* 152-159 2010 Vol. 43, No. 1

Polymer-Inorganic Hybrids : *in situ* polycondensation.



J. Le Bideau, J.-B. Ducros, D. Guyomard, D. Brevet, A. Vioux, ANR LISSIL, 2007-2009



A. Vioux, L. Viau et al. *Chem. Mater.* 2009, 21, 5575–5577

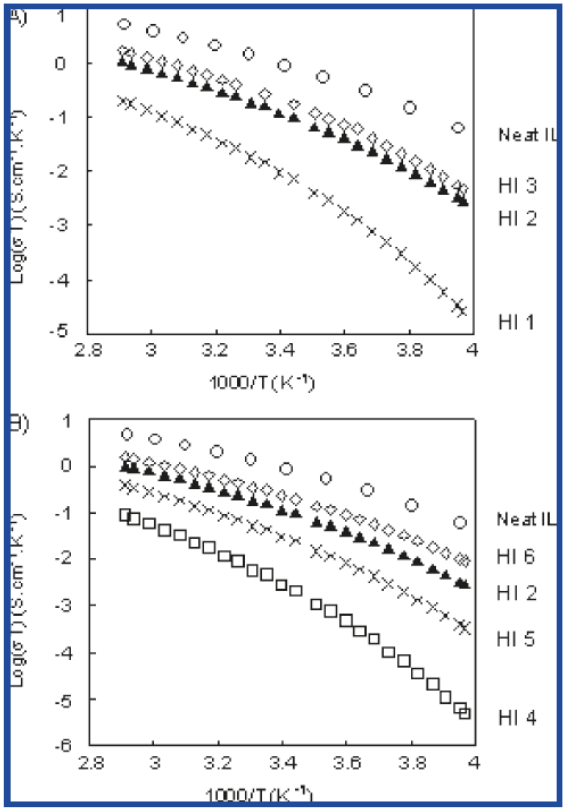
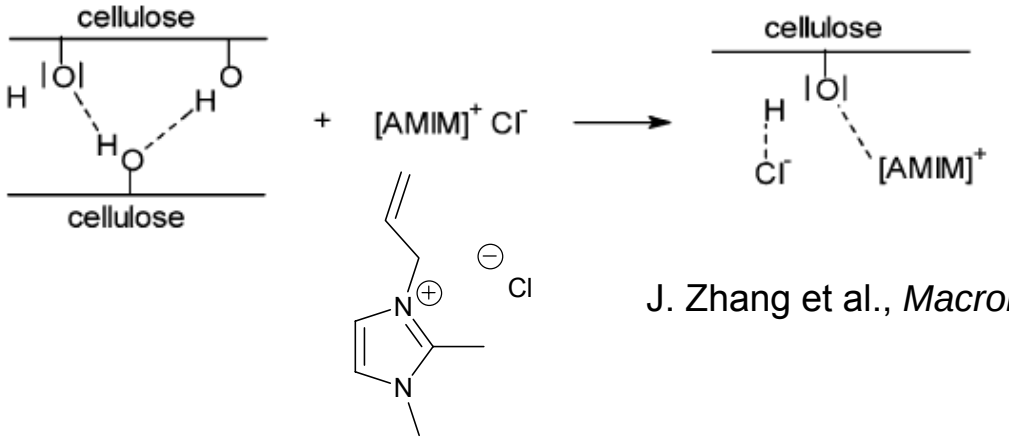


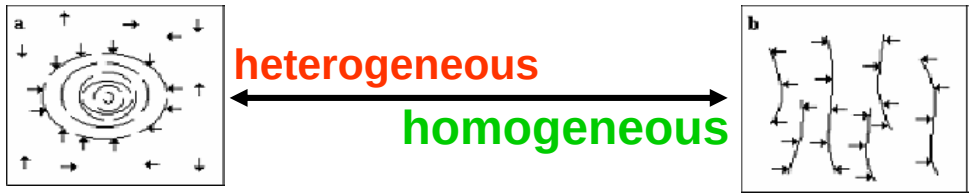
Figure 1. Conductivity plots for hybrid ionogels (A) f-PMMA/TEOS 60/40 with various n (**HI 1**−**3**), (B) n = 2, various proportions of f-PMMA/TEOS (**HI 2**, **4**−**6**).

Biopolymers

Cellulose solubilisation by inter-chains hydrogen bonds breaking



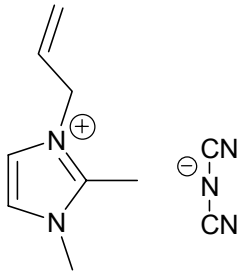
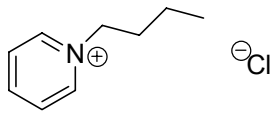
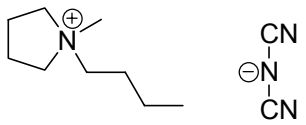
J. Zhang et al., *Macromolecules* 38 (2005) 8272-8277



Biopolymers

Homogeneous IL route to hybrid inorganic derivatives of polysaccharides : increase of the Si content

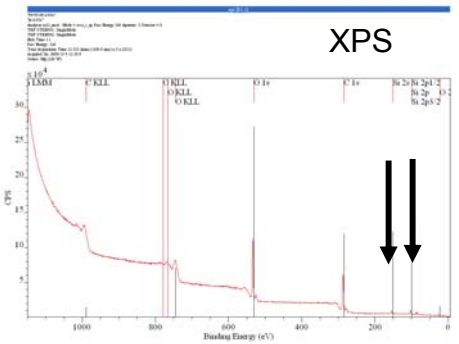
J. Le Bideau, J. Recho, P. Weiss, A. Fatimi, J. Guicheux, *Patent*, **2008,** FR08/05473, PCT 2010

Ionic liquid	Si content in HPMC-Si
	0.85 < Si wt% < 0.90
	1.56 < Si wt% < 1.61
	3.08 < Si wt% < 3.20

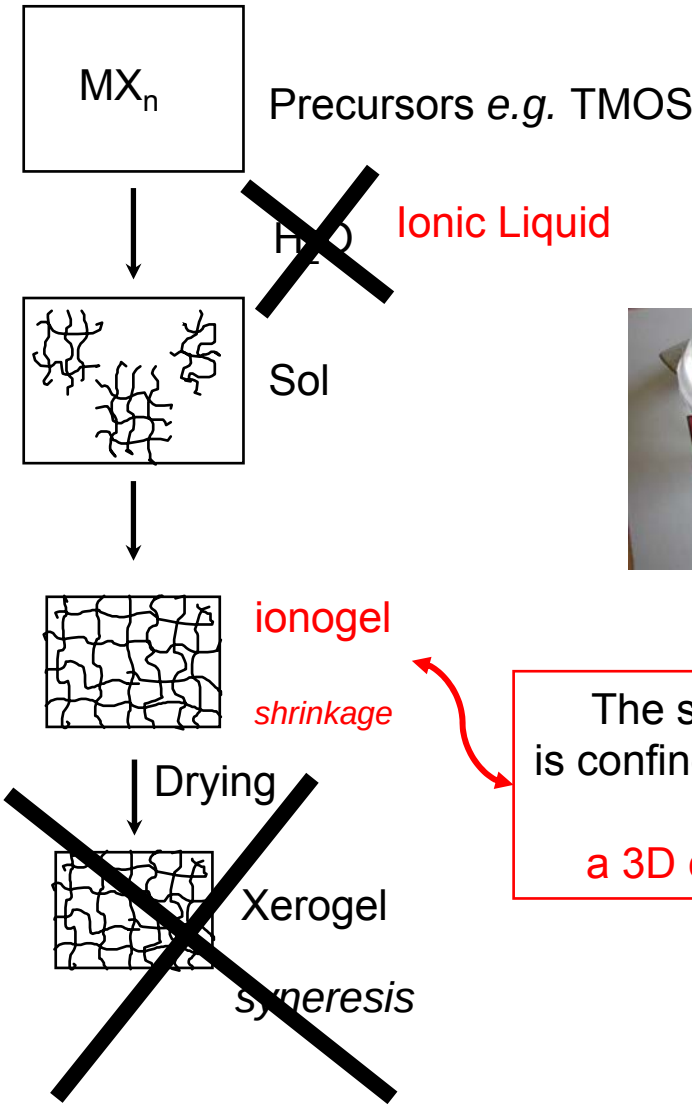
increasing Si content

Previous heterogeneous route : maxi. 0.6 Si wt%

EDX & XPS :
Si presence confirmed



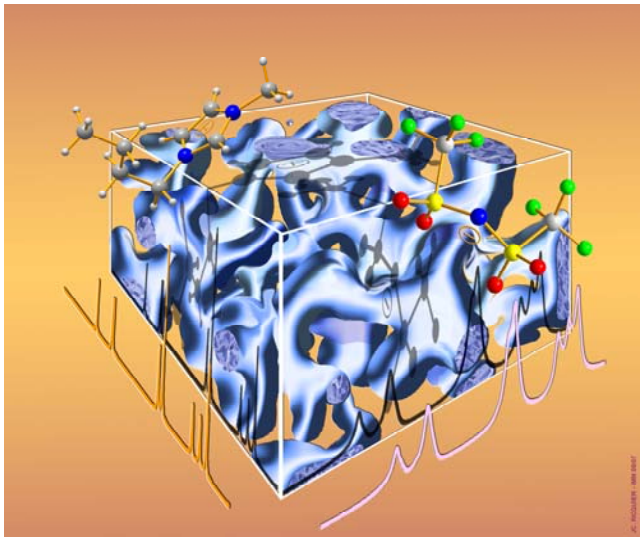
Another route for ionic liquid based “all-solid” devices : sol-gel route in ionic liquid to first generation monolithic *ionogels* (IL @ mesoporous silica)



The solvent (ionic liquid) is confined in the final material as a 3D continuous network

Carboxylation		
$HCOOH+Si(OMe)_4$	$\rightleftharpoons$	$(MeO)_3SiOOCH+MeOH$
$HCOOH+SiOH$	$\rightleftharpoons$	$SiOOCH+H_2O$
Esterification		
$MeOH+HCOOH$	$\rightleftharpoons$	$MeOOCH+H_2O$
Hydrolysis		
	H^+	
$SiOMe+H_2O$	$\rightleftharpoons$	$SiOH+MeOH$
$SiOOCH+H_2O$	$\rightleftharpoons$	$HCOOH+SiOH$
Condensation		
$2SiOH$	$\longrightarrow$	$SiOSi+H_2O$
$SiOH+SiOMe$	$\longrightarrow$	$SiOSi+MeOH$
$SiOH+SiOOCH$	$\longrightarrow$	$SiOSi+HCOOH$
$SiOOCH+SiOMe$	$\longrightarrow$	$SiOSi+MeOOCH$
$SiOMe+HCOOCH$	$\longrightarrow$	$SiOSi+MeCOOCH$

Sharp, K.G., J. Sol-Gel Sc. Tech. 2 (1994) 35

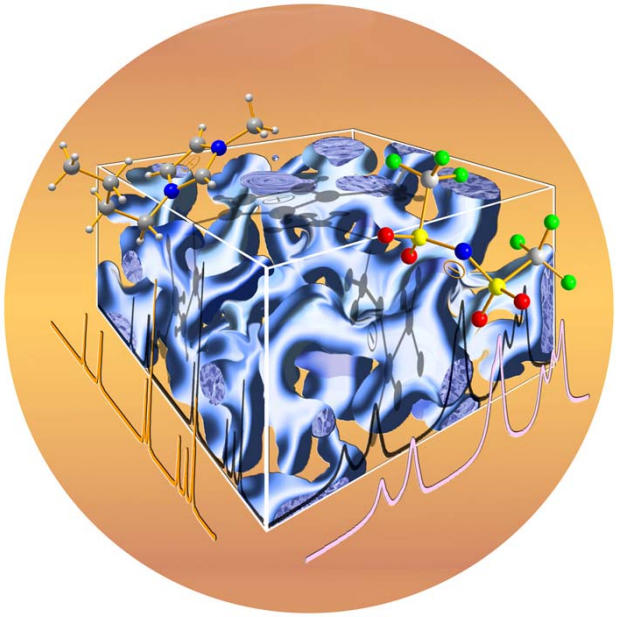


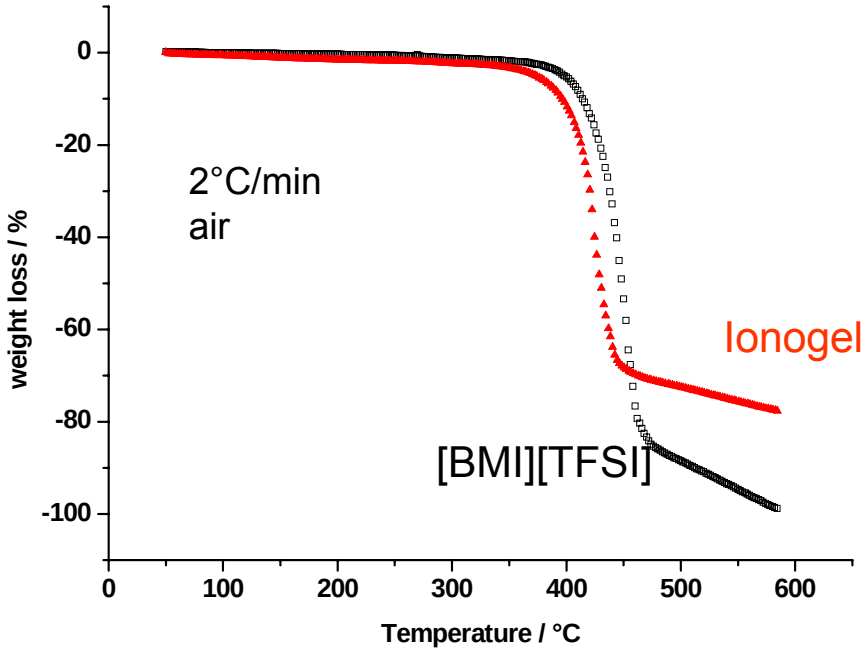
A. Vioux, J. Le Bideau et al., *Patent* FR 2004 - 2857004
Patent WO 2005 - 007746

J. Le Bideau, A. Vioux et al., *Chem. Commun. (2005) 1082 & Prog. Solid State Chem.*, 2005, 33, 217

Ionogels : transparent monolithic solids

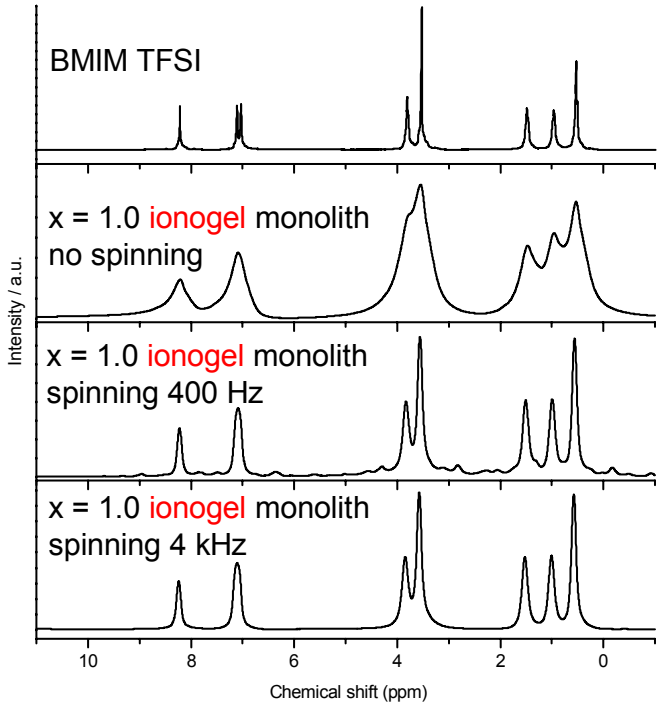
- One step *chimie douce* route
- Typically : silicon alkoxyde / formic acid / ionic liquid
  = 1 / 7.8 / 0.5 mol
- Gelification time at RT : 1h to 36h (composition dependent)
- Aging at RT : 6 to 9 days, or 1 day with ultra sounds
- Young modulus ≈ 60 MPa
- Stable up to 370 °C
- 6-20 nm pores diameter
- ~ 800 $m^2.g^{-1}$





Direct evidence of the liquid state of the confined IL @ monolithic mesoporous silica *ionogel*

NMR ^{1}H / 9.4 T / T = 293 K



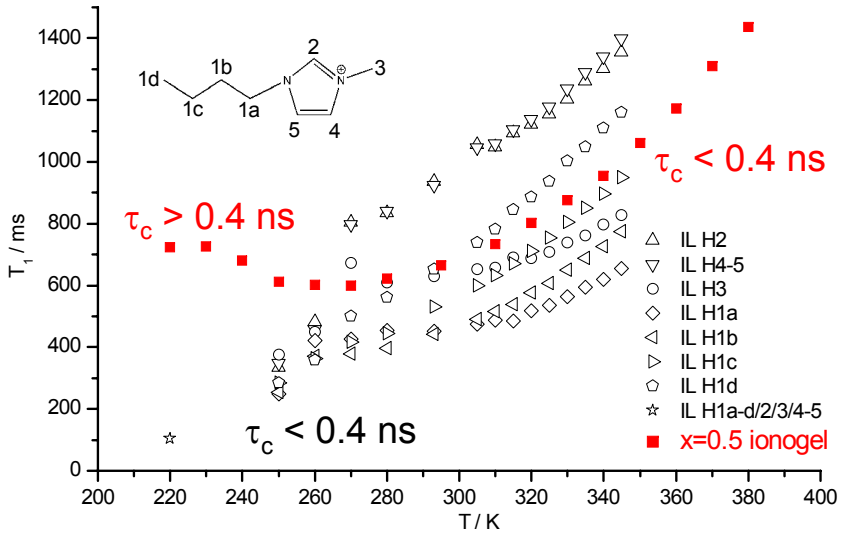
• Without rotation : dipole-dipole and *csa* partially averaged :

only small decrease of the dynamics of the confined IL.

• Above 400 Hz, the resolution stays lower than that of the instrument :

distribution of chemical shifts due to silica walls neighbouring.

T_1 variation *vs.* confinement ^{1}H / 9.4 T

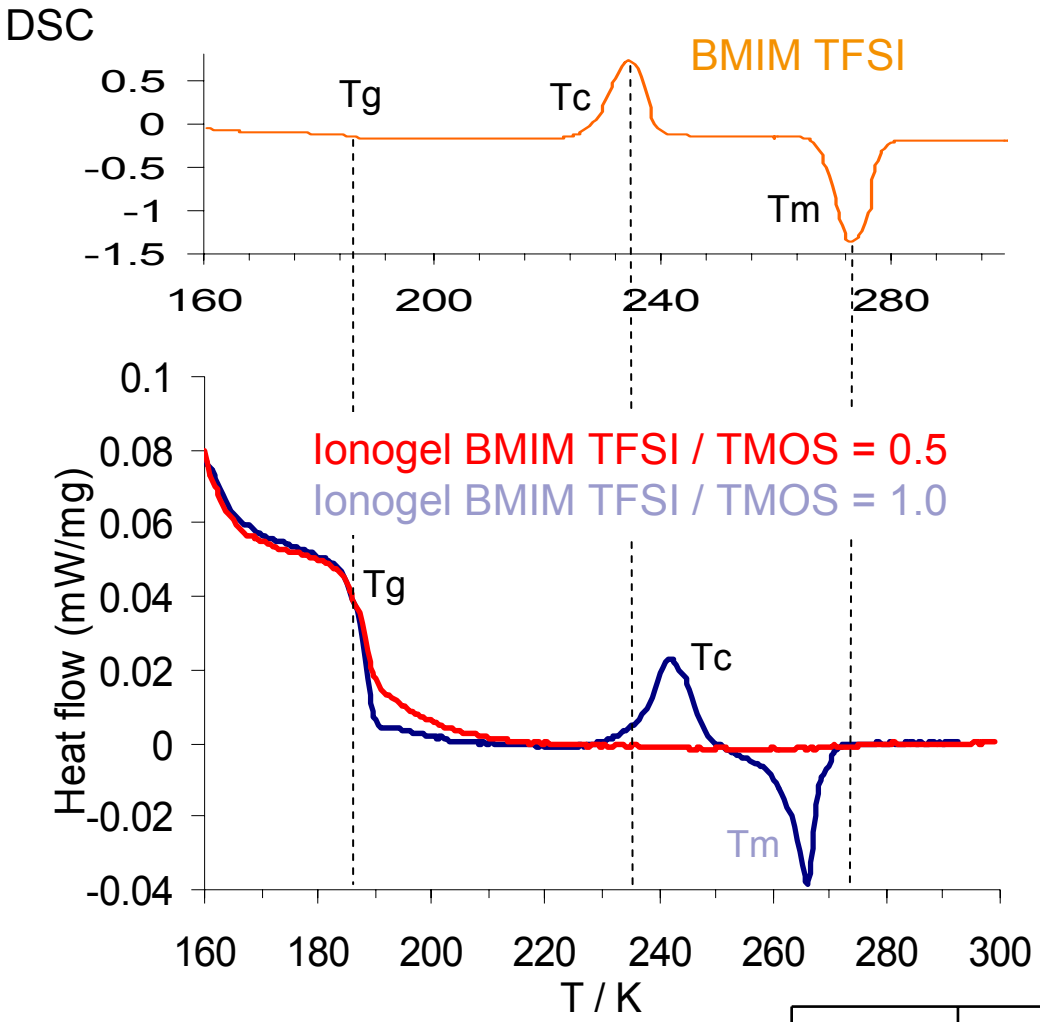


➢ T_1 for confined IL within ionogel similar to T_1 for genuine IL

➢ IL shows a solid-liquid transition around 270 K in opposition to ionogel

J. Le Bideau, P. Gaveau, S. Bellayer, M.-A. Néouze, A. Vioux, *Phys. Chem. Chem. Phys*., 2007, 9, 5419-5422

IL @ mesoporous silica *ionogel* : phase transition



x = 1.0 → x = 0.5
decrease of the relative quantity of IL
⇔
decrease of the pore size
⇔
disappearance of crystallisation
for the confined IL.

x=0.5 ionogel does not exhibit any transition around 270 K

	Tc / K	Tm / K	Hc / J.mol^{-1}	Hm / J.mol^{-1}	
BMIM TFSI	232.7	272.2	17800	21800	mol ratio
x=1.0 ionogel	240.9	266.2	656	532	**~ 3 %**

M.-A. Néouze, J. Le Bideau, P. Gaveau, S. Bellayer, A. Vioux, *Chem. Mater.* 2006, *18,* 3931-3936

Polymer gels obtained by the polymerization of MMA in EMITFSI

higher thermal stability than plain polymer
higher confinement effect

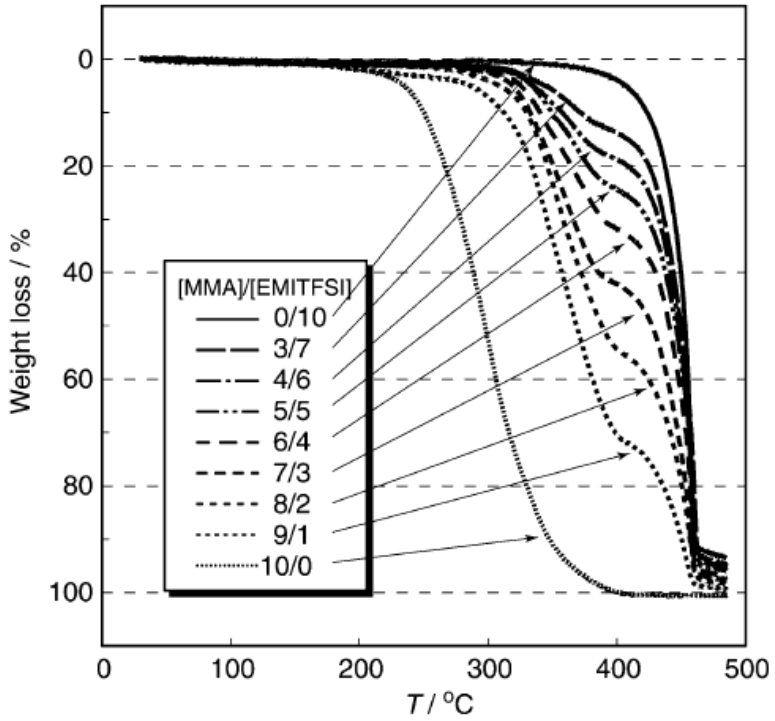


Figure 1. TG curves for MMA network polymers with different mole fractions of dissolved EMITFSI and EMITFSI bulk at a heating rate of 10 °C min^{-1}.

M. Watanabe et al., *J. Am. Chem. Soc.*, 2005, *127*, 4976

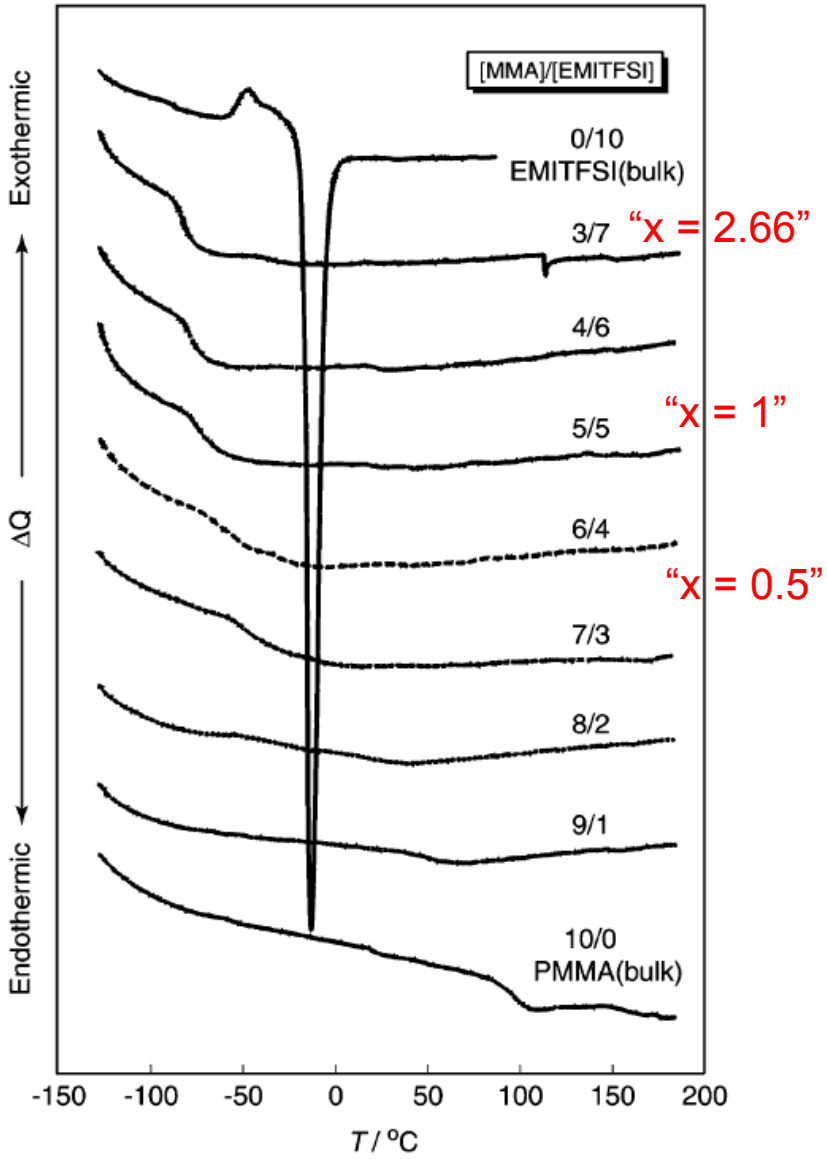


Figure 2. DSC thermograms for MMA network polymers with different mole fractions of dissolved EMITFSI and EMITFSI bulk at a heating rate of 10 °C min^{-1}.

IL @ mesoporous silica *ionogel* : NMR Pulsed-Gradient Spin-Echo : microscale

Time and space scales probed

$R_{Dif}(\Delta) \sim (D\,\Delta)^{1/2}$

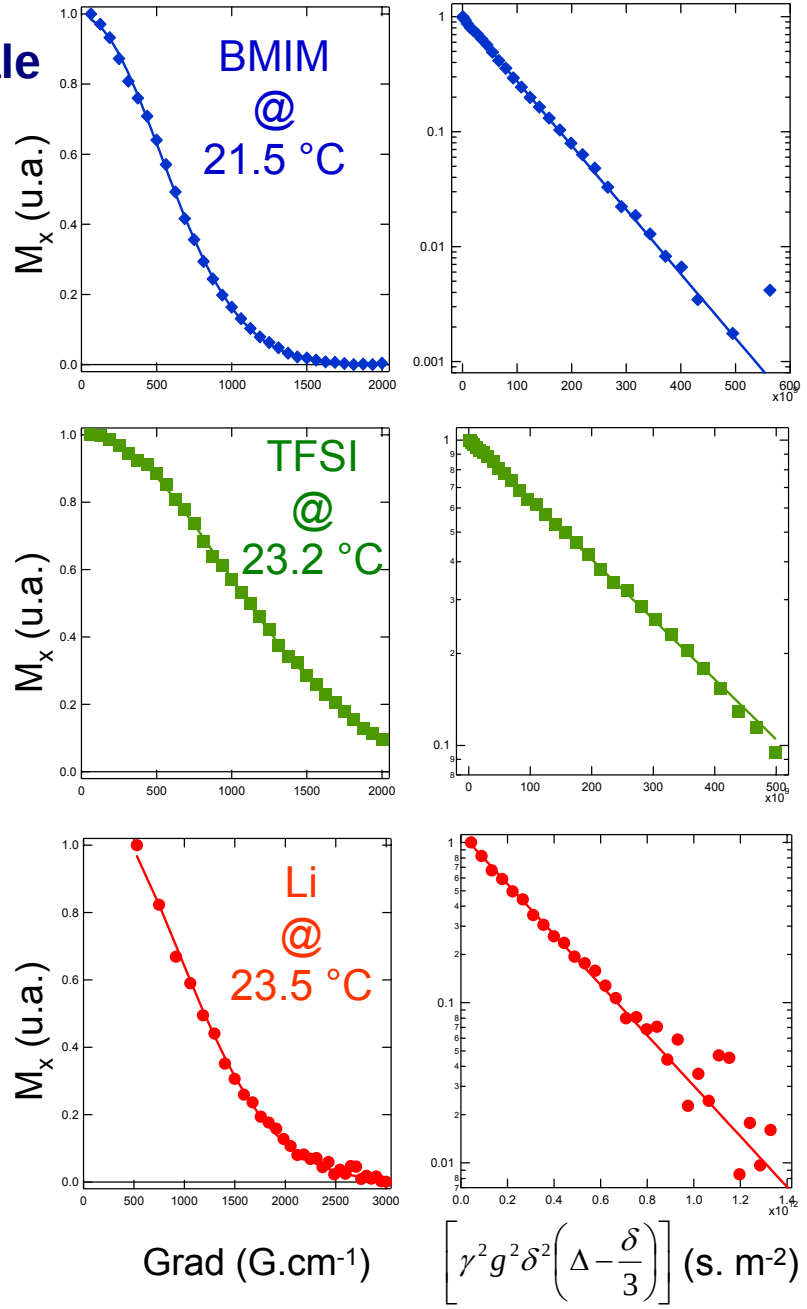
	D_{PGSE}	$R_{Dif}(\Delta=20ms)$
H_2O	2.3×10^{-5} cm^2.s^{-1}	6.78 µm
BMIM	**1.3×10^{-7} cm^2.s^{-1}**	**0.51 µm**
TFSI	4.5×10^{-8} cm^2.s^{-1}	0.30 µm
Li	3.6×10^{-8} cm^2.s^{-1}	0.27 µm

- Single slope : single regime
- Lower motion of Li vs. BMIM and TFSI

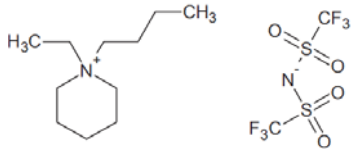
D. Petit et al., *ANR LISSIL* 2009

	diffusion coefficients D /(10^{-12} m^{2}s^{-1})			
sample	$[BMIM]^+$	Li^+	Tf^-	BF_4^-
$[BMIM]BF_4$	11	–	–	11
$[BMIM]BF_4$/LiTf	4.5	1.5	1.9	2.5

L. van Wüllen et al., *Chem. Mater.*, 2009



PVDF-HFP / IL / Li : dynamics



0.1 molar fraction (0.2 mol LiTFSI/kg IL in PP24) / PVdF–HFP

weight ratios of the mixed salt to PVdF–HFP :
60:40, 70:30, 80:20 (resp. M60, M70, and M80)

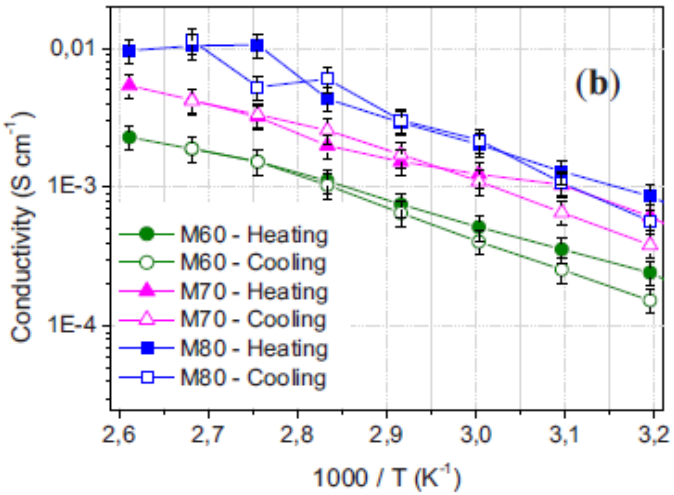


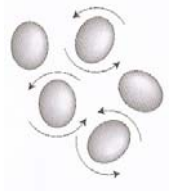
Table II. Self-diffusion coefficient values of ^{1}H, ^{19}F, and ^{7}Li nuclei, and related selected ratios. Representative values at 25°C. Multisample imaging.

	$D(^{1}H)^{a}$	$D(^{19}F)^{a}$	$[D(^{1}H)/D(^{19}F)]$	$D(^{7}Li)^{a}$	$[D(^{19}F)/D(^{7}Li)]$
Neat IL ($PP_{24}TFSI$)	0.67	0.63	1.06	–	–
Doped IL (0.2 M LiTFSI)	0.50	0.45	1.12	0.24	1.9
80% doped IL membrane	0.21	0.18	1.21	0.19	0.95

[a] ($\times 10^{-7}$ cm^2/sec) All data acquired nominally at 25°C

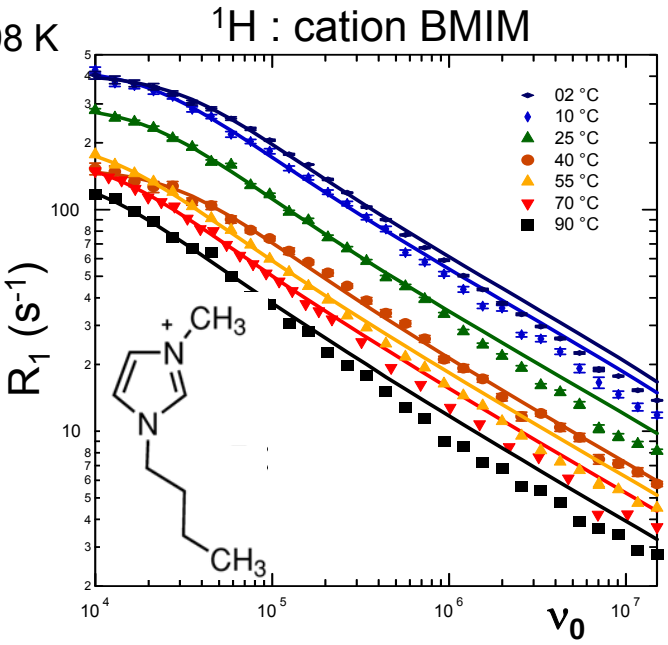
B. Scrosati et al., J. Electrochem. Soc., 2009, **156,** 7, A514

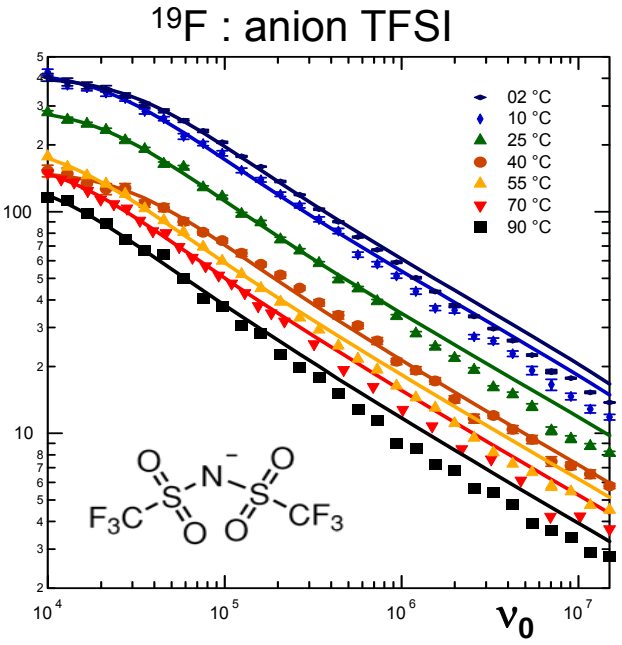
IL @ mesoporous silica *ionogel* : ^{1}H and ^{19}F NMR Relaxometry : nanoscale



Ex: isotrope rotation of water
(η = 1 cP at 293 K) :
τ_c = 3.5 ps,
D = 2.3x10^{-9} m^2.s^{-1}

T = 298 K





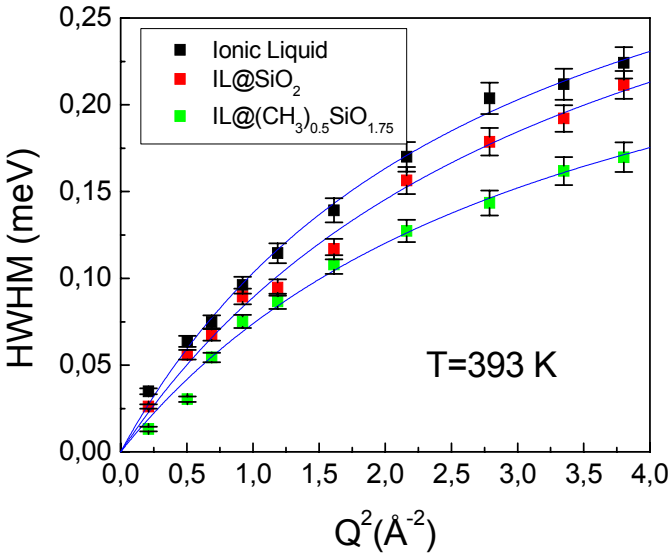
Local surface time	τ_m	62 ps	49 ps
Escape time	τ_s	4.1 µs	5.5 µs
Mini. neighbouring dist.	d	0.21 nm	0.22 nm
Diffusion coefficient	$D \sim d^2/\tau_m$	**1.2x10^{-6} cm^2.s^{-1}**	1.7x10^{-6} cm^2.s^{-1}
Mean displacement	$R \sim (D\tau_s)^{1/2}$	**22 nm**	30 nm

- Similar values for ^{1}H and ^{19}F : cation-anion pair behaviour
- High values : viscosity
- Mean displacement : order of pore size

D. Petit, J.-P. Korb, P. Levitz , D. Brevet, J. Le Bideau, *Diff. Fund.*, 2009, 10, 7.1 - 7.3.

IL @ mesoporous silica *ionogel* :

Quasi-Elastic Neutron Scattering : pico-second dynamics (ps-ns)



Slight increase of HWHM : only slight decrease of the short time dynamics upon confinement (BMIM only)

T = 300 K / λ = 5.2 Å

Characteristic residence time

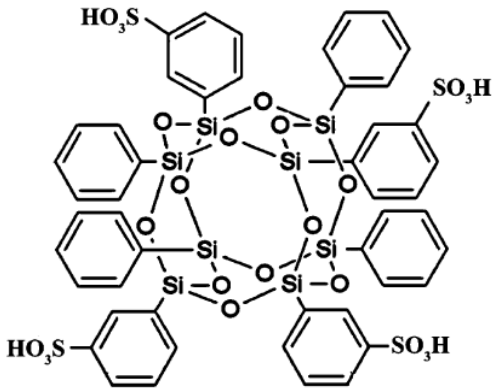
BMIM TFSI	D = 1.9 $\times 10^{-5}$ $cm^2.s^{-1}$	τ = 2 ps
BMIM TFSI + Li TFSI @ $(CH_3)_{0.5}SiO_{1.75}$	**D = 3.2$\times 10^{-5}$ $cm^2.s^{-1}$**	**τ = 2 ps**

Almost same diffusivity is obtained
in case of confined IL compared to pristine IL

S. Mitra, J.-M. Zanotti et al., *ANR LISSIL* 2009

Nafion / IL / filler Si-cluster

N.M. Choudhury et al., *Appl. Mater. Interf.*, 2009



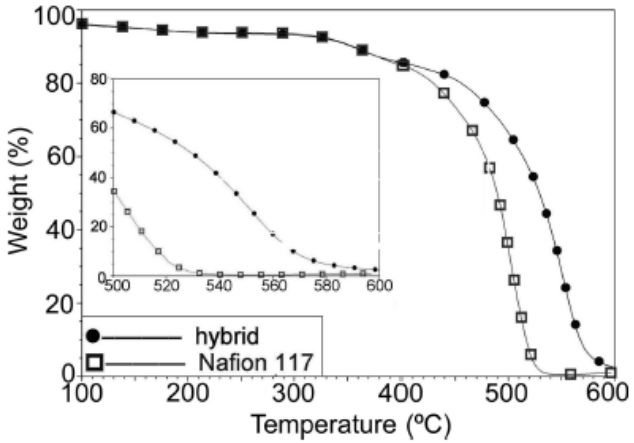


FIGURE 5. TGA comparison of Nafion 117 and the Nafion–POSS hybrid membranes.

- strong ionic interaction between Nafion and POSS;

- increased glass transition temperature and thermal stability;

-BMI-TFSI / POSS / Nafion 117 compared to a Nafion 117 and a Nafion-IL membrane:
higher proton conductivity
(5 mS/cm at 150 °C with 20% IL).

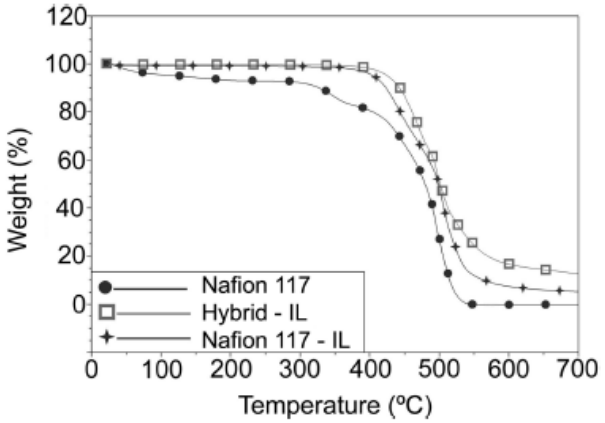
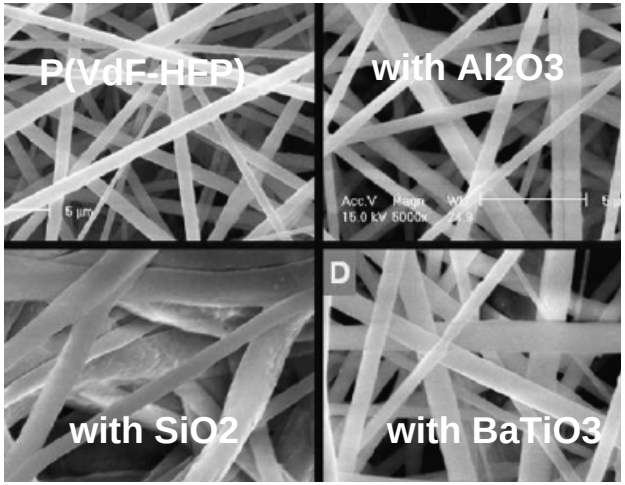


FIGURE 6. TGA of the IL-containing membranes compared to Nafion.

Nanocomposite polymer / IL / filler ceramic

J.-H. Ahn et al., *Electrochim. Acta, 2010,* 55, 1347



P(VdF-HFP)
6wt% of ceramic fillers
SiO2, Al2O3 or BaTiO3
14 nm, 40–47 nm, 30–50 nm, resp.
0.5M LiTFSI in BMITFSI

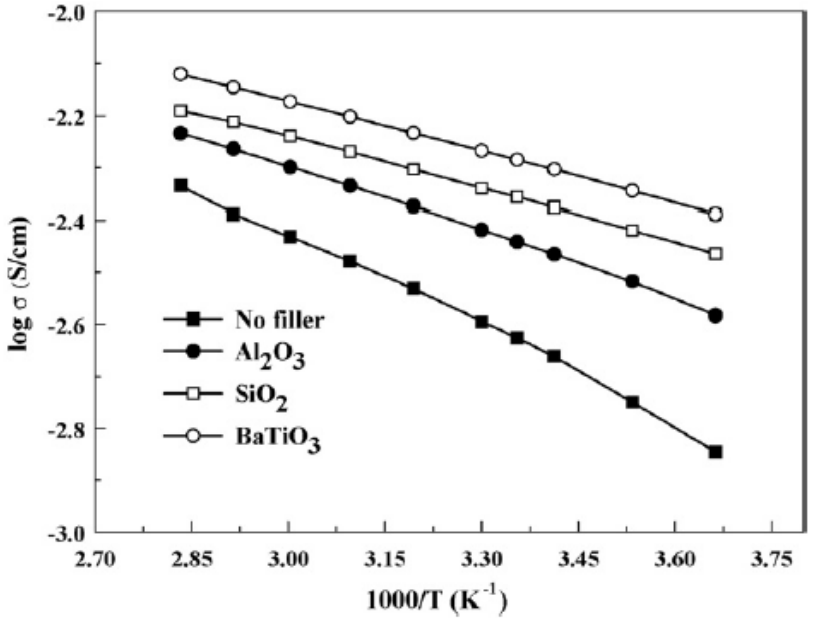


Fig. 4. Ionic conductivities of polymer electrolytes based on electrospun P(VdF-HFP) membranes with different ceramic fillers at different temperatures.

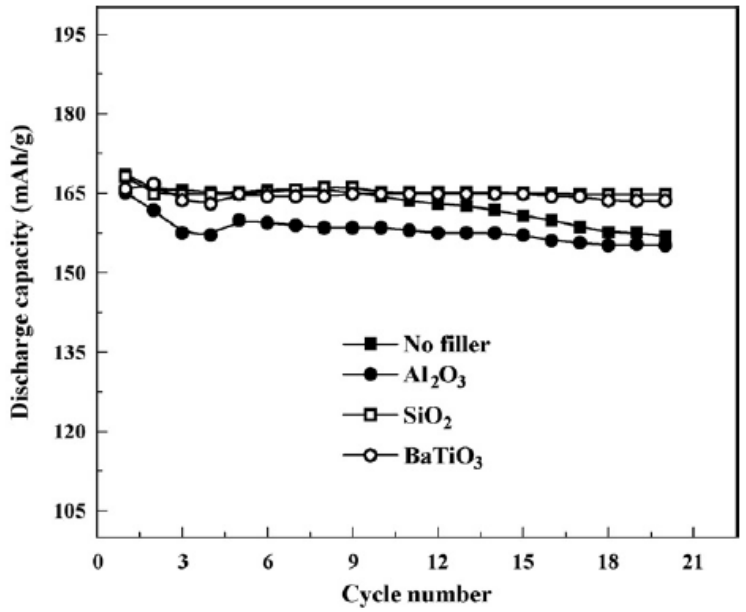


Fig. 9. Cycle performance (discharge capacities) of NCPEs based on electrospun P(VdF-HFP) membranes activated with 0.5 M LiTFSI in BMITFSI (Li/NCPE/$LiFePO_4$ cell, 0.1 C-rate, 25 °C).

Summary

- **Different routes to solid state devices for different purposes :**
- **ILs : a multi(but not all !)-purpose tool box ;**
- Aiming at really liquid ionic liquids for long standing devices owing to non volatility.

✓ **Real liquid state for IL confined in monolithic porous oxides ionogels ;**

✓ PGSE diffusion coefficients are smaller, and due to larger time and space scales would be influenced by the mesoporous silica network (walls and tortuosity) ;

✓ At shorter time and smaller space scales, no influence of the silica network.

✓ **Confinement of IL within polymers or oxides or composites appears promising for all-solid devices with ionic liquid properties.**

✓**Large potential progresses through additives and hybrid organic-inorganic assemblies.**

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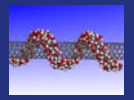
PMN [a] **Physique des matériaux et nanostructures**



ST2E [b] **Stockage et Transformation Electrochimiques de l'Energie**

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PMN — **Physique des matériaux et nanostructures**