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Deep Eutectic Solvents

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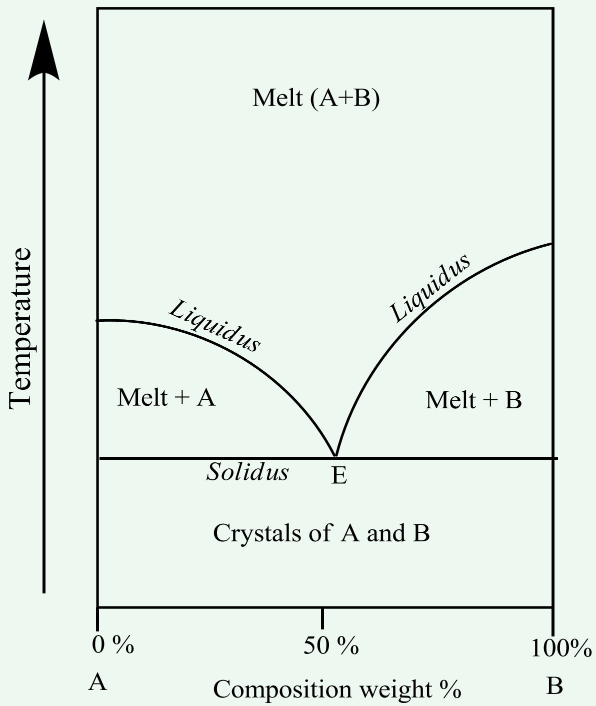
Contents

- Definitions
- Physical Properties
- Applications – synthesis, electrochemistry, metal processing

Eutectics

- Mixture of 2 compounds that has the lowest melting point (E)
- Depression of freezing point related to the strength of interaction between the two components



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First vs. Second generation ILs

- cation + anion + complexing agent ↔ cation + complex anion

or potentially

- cation + anion + complexing agent ↔ complex cation + anion

- $Cat^+ F^- + BF_3 \leftrightarrow Cat^+ + BF_4^-$
- $Cat^+ Cl^- + AlCl_3 \leftrightarrow Cat^+ + AlCl_4^-$
- $Cat^+ Cl^-$ + urea ↔ $Cat^+ + Cl^-$.urea
- $LiClO_4 + 3.5\ H_2O \leftrightarrow Li^+.xH_2O + ClO_4^-.yH_2O$

<u>All that changes is the value of the equilibrium constant</u>

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Key Requirements for a New Solvent

- Low cost
- High solute solubility
- Wide potential window
- Environmental compatibility
- No registration requirements

To satisfy these criteria it is necessary to use eutectic based ionic liquids

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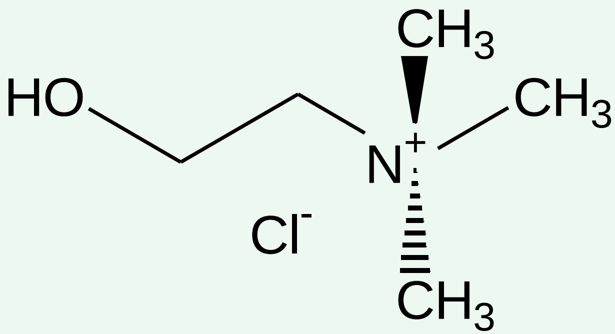
Why choline chloride?

- Non-toxic (vitamin B4 RDA – 550mg)
- Produced on Mt scale (chicken feed additive) hence costs about <u>2 Euro/kg</u>
- Non-toxic and biodegradable

$(CH_3)_3N$ + HCl + ethylene oxide

E factor = 0



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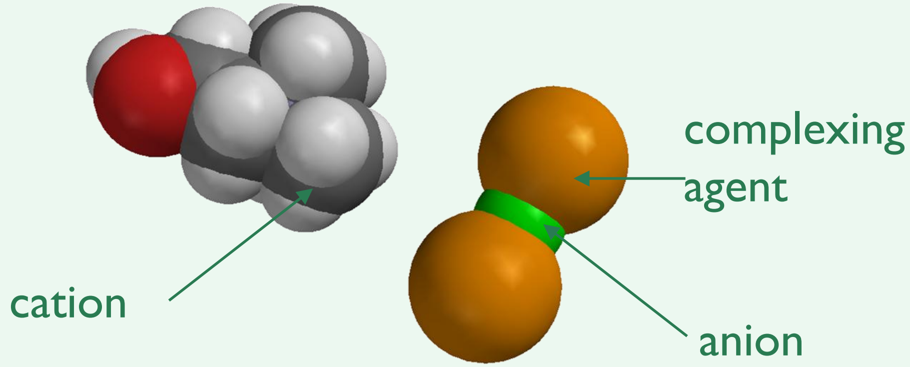
Ionic Liquids

Choline like cations with various complexing agents

$R_1R_2R_3R_4N^+ X. zY$



- Type I — $Y = MCl_x$, M = Zn, Sn, Fe
- Type 2 — $Y = MCl_x.yH_2O$
- Type 3 — Y = RZ, Z = $CONH_2$, COOH, OH

Studied far less than imidazolium based liquids
but already over 70 publications

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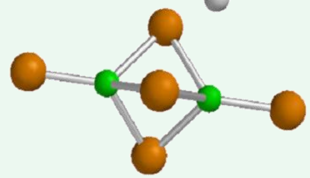
Type 1: Metal Salts

$R_1R_2R_3R_4N^+$ X. zY Y = MCl_x, M = Zn, Sn, Fe

Metal containing ionic liquids

- Aluminium based ionic liquids well known
- Ionic liquids can also be formed with $ZnCl_2$, $SnCl_2$ and $FeCl_3$
- Easy to make
- Do not react with water
- $ChCl + 2ZnCl_2 \rightarrow Ch^+ \, Zn_2Cl_5^-$

$HOC_2H_4N^+(CH_3)_3$



$Zn_2Cl_5^-$

Table 1. Freezing Points for 1:2 QAS/Metal Halide Ionic Liquids

R_1	R_2	R_3	R_4	anion	metal halide	T_f/°C
Me	Me	Me	C_2H_4OH	Cl^-	$ZnBr_2$	38
Me	Me	Me	C_2H_4OH	Cl^-	$FeCl_3$	65
Me	Me	Me	C_2H_4OH	Cl^-	$SnCl_2$	37
Me	Me	Me	$C_2H_4OC(O)Me$	Cl^-	$ZnBr_2$	48
Me	Me	Me	$C_2H_4OC(O)Me$	Cl^-	$SnCl_2$	20
Me	Me	Me	C_2H_4Cl	Cl^-	$SnCl_2$	63
Me	Me	benz	C_2H_4OH	Cl^-	$SnCl_2$	17
Me	Me	benz	C_2H_4OH	Cl^-	$FeCl_3$	21

Abbott et al. Inorg. Chem. 2004, 3447

ZnCl$_2$ and SnCl$_2$ do not form Lewis basic liquids

Physical Properties

Very viscous

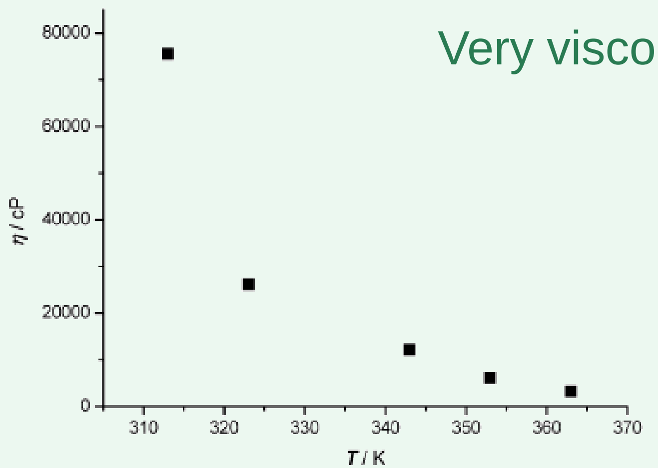


Figure 4. Viscosity of a 2 ZnCl$_2$/1 ChCl mixture as a function of temperature.

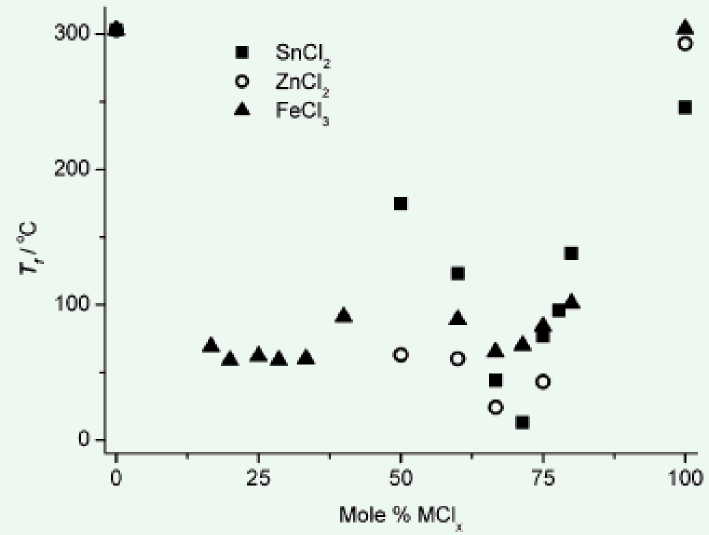


Figure 1. Freezing point for the ZnCl$_2$/ChCl and SnCl$_2$/ChCl systems as a function of composition.

Mono and di-metallic species dominate

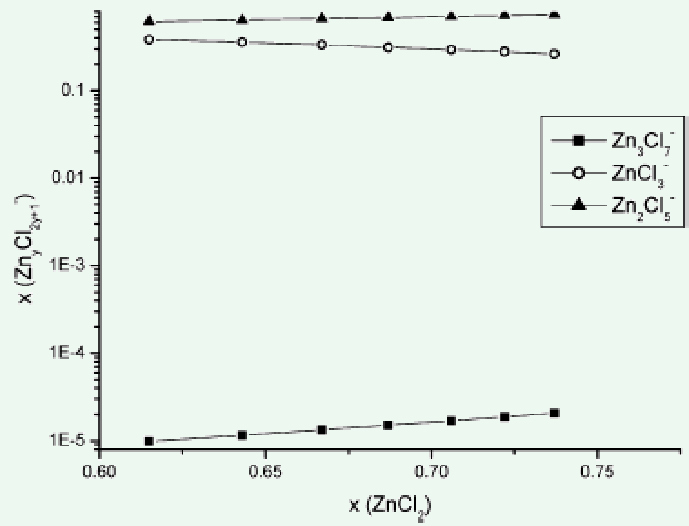


Figure 3. Mole fraction of chlorozincate anions in a choline chloride/zinc chloride ionic liquid as a function of composition at 60 °C.

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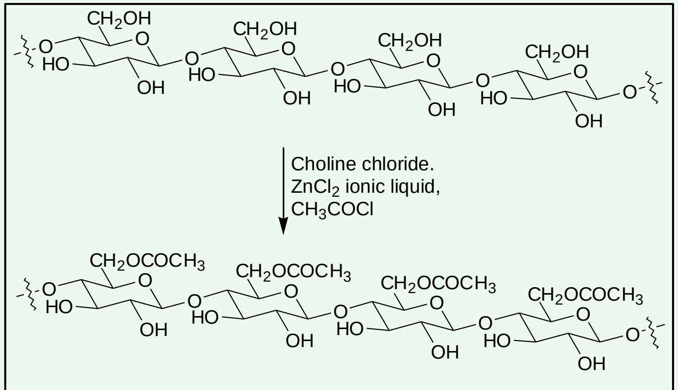
Lewis Acid Catalysed Reactions

- Friedel Crafts
- Diels Alder
- Fisher Indole
- Acetylation of cellulose



Scheme 1

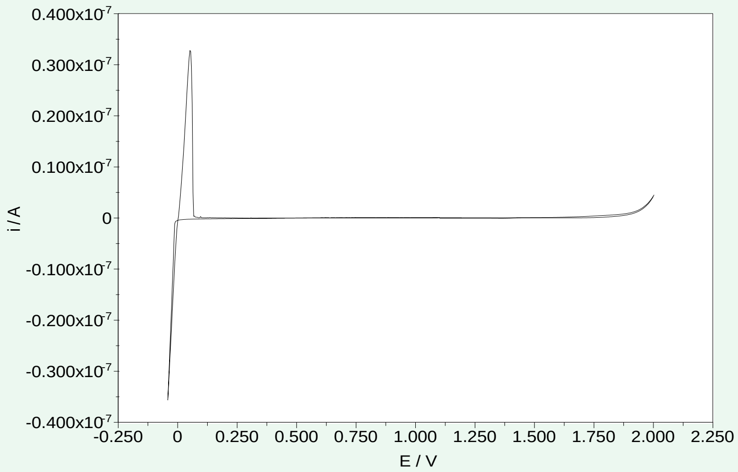
Advantages:

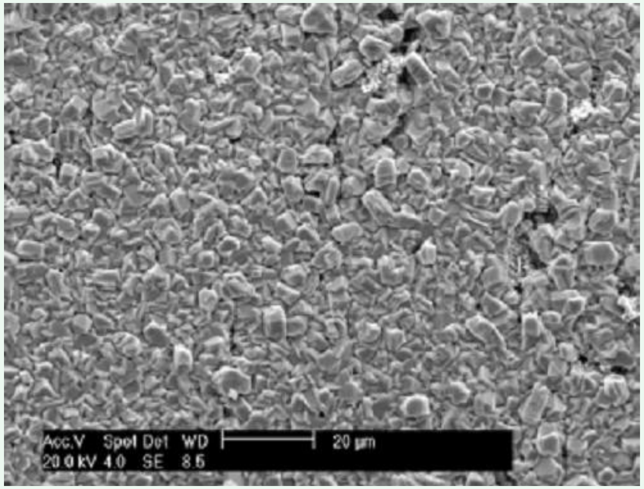
- Products form separate phase - can be decanted/ distilled from the ionic liquid
- No solvent residues
- High yields
- High regioselectivity

Abbott et al. Green Chem., 2002, 4, 24.
Abbott et al. Green Chem., 2005, 7, 705.
Morales et al. Chem. Commun., 2004 158

Zinc Deposition - IL

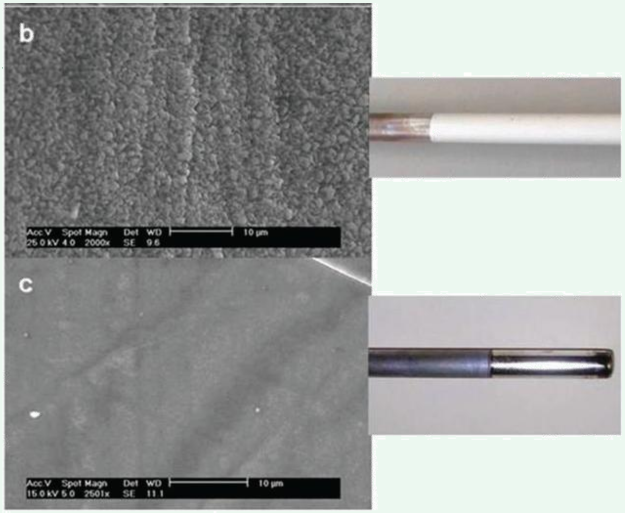
- High current efficiency (>99%) (no $H_2\uparrow$)
- Zinc deposition almost totally reversible (soluble anodes)
- Deposition of alloys possible
- Non-microcracked deposit
- High corrosion resistance





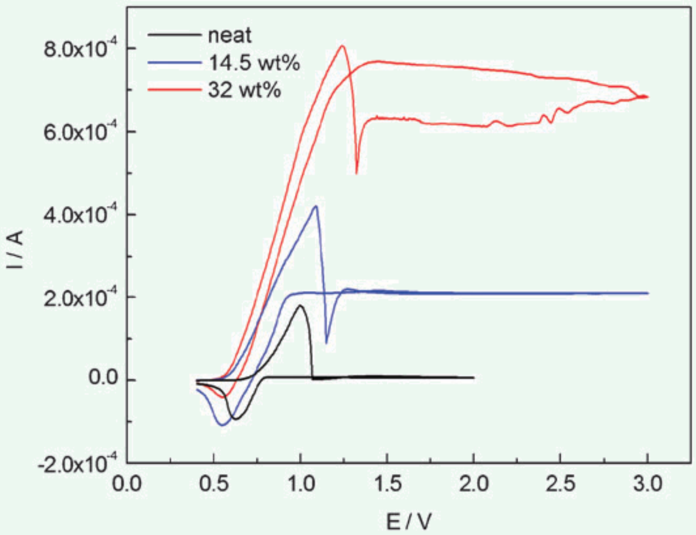
Abbott et al. Trans IMF, 2001 79,204.

Chloroaluminate systems still being



System affected by;

- Mass transport
- Added electrolyte
- Speciation
- Anode material



Phys. Chem. Chem. Phys., 2010, 12, 1862

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Aluminium Deposition

- Mirror finish can be obtained
- 35 L Pilot plant now being operated
- New IP uses no QAS

Abbott et al. PCCP (2010), 12, 1862

Type 2: Hydrated Metal Salts

$R_1R_2R_3R_4N^+$ X. zY Y = $MCl_x.yH_2O$

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Hydrated Salt Mixtures

- Developed to incorporate other metals into ionic liquids
- Mixture of quaternary ammonium salts with a hydrated metal salt
- Does not form liquid with all salts
- No ‘free’ water molecules
- A lot less viscous than Type I

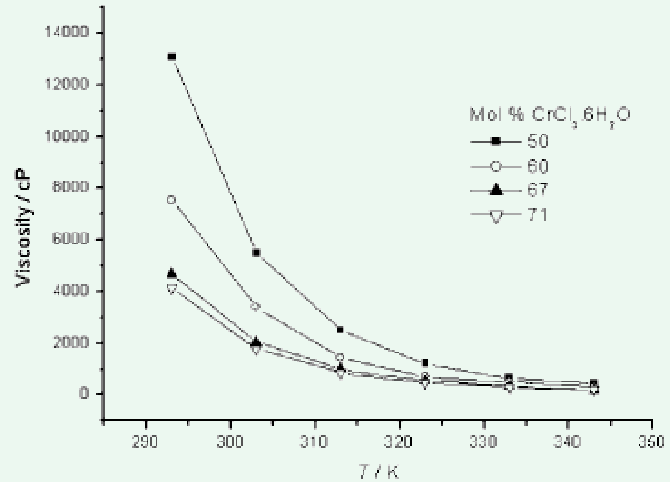

Figure 1. Viscosity of $ChCl/CrCl_3{\cdot}6\,H_2O$ mixtures as a function of temperature and composition

Abbott et al., Chem. Eur. J. 2004, 10, 3769

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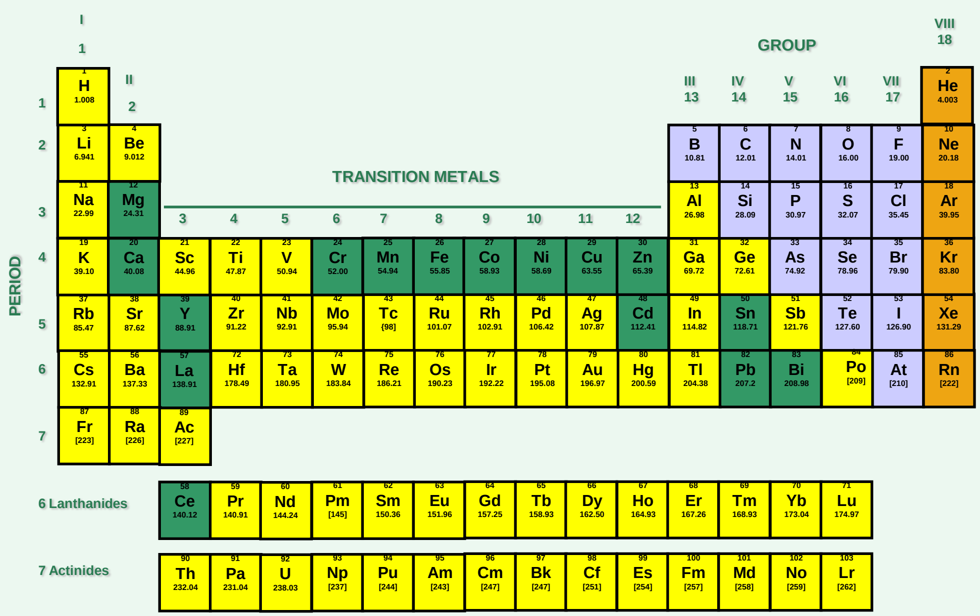
Hydrated Salt Mixtures

- Applicable to a wide range of other metals in various oxidation states



Hydrated Salt	f.p / ^{o}C
$CrCl_3.6H_2O$	4
$CaCl_2.6H_2O$	5
$MgCl_2.6H_2O$	10
$CoCl_2.6H_2O$	16
$LaCl_3.6H_2O$	6
$CuCl_2.2H_2O$	48

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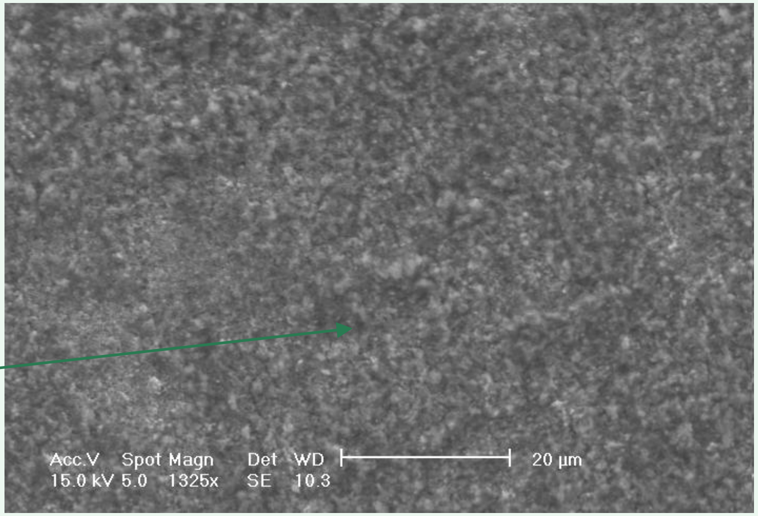
Chromium Plating

- Negligible hydrogen evolution
- High current efficiency (>90%)
- Uses Cr(III) (less toxic, less e^-)
- Non microcracked deposit
- Soluble anodes



SEM image of the deposit formed following the electrolysis of the ChCl: $2CrCl_3.6H_2O$ system containing 10 wt% LiCl at 60 ^oC for 2 hours onto a nickel electrode at a current density of 0.345 $mAcm^{-2}$.

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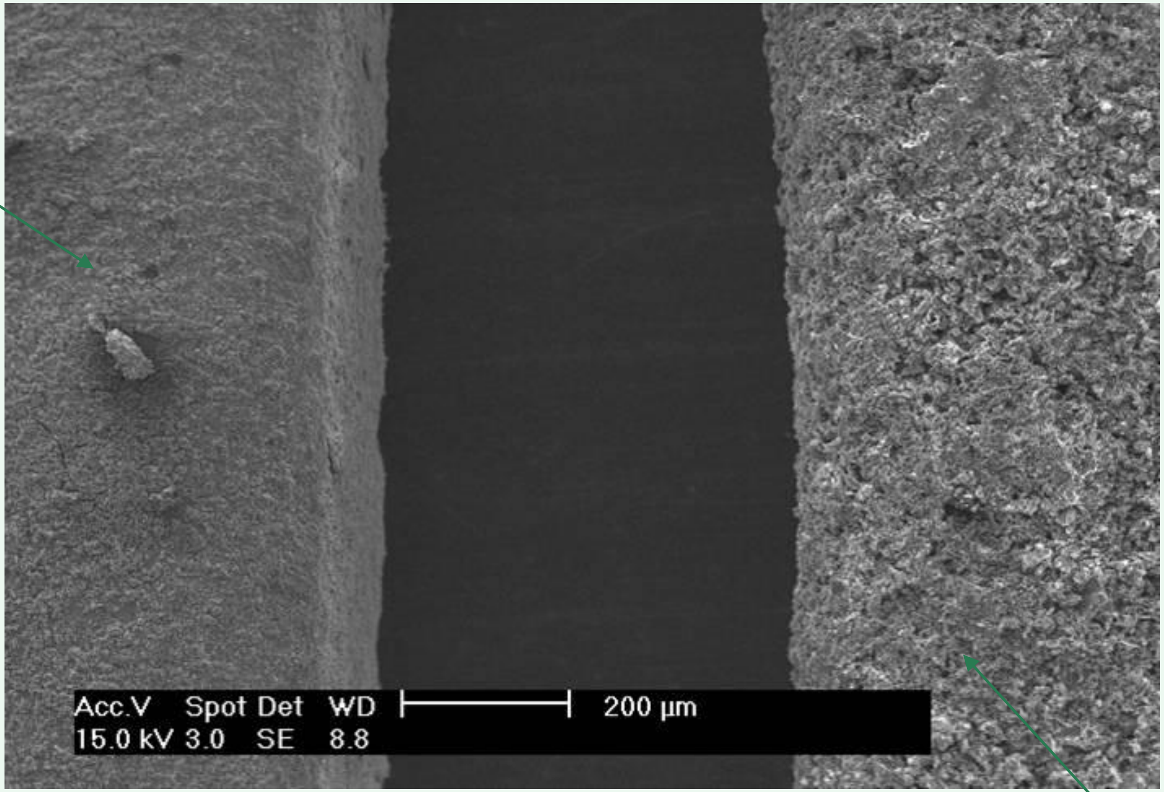
Composite Materials

- Stable colloidal suspensions can be made and these can be incorporated into metallic coatings

Cr



Cr + 0.1 µm Al_2O_3

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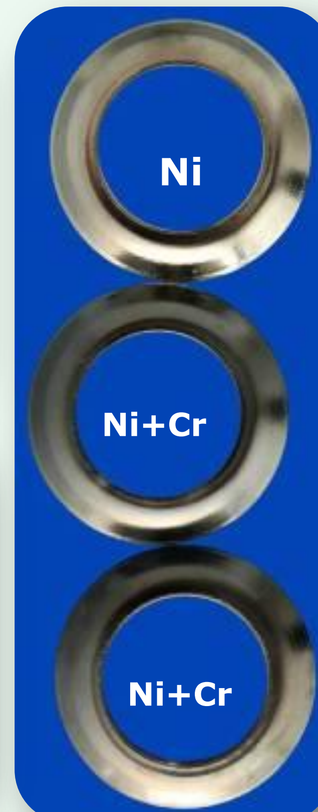
Chromium Plating

- New formulations have led to bright Cr deposits.
- Surfaces can be ground – good adhesion



Chromium Plating

- Improved current efficiency (economic benefit)
- Less toxic components – non-corrosive (social benefit)
- Improved product (market benefit)
- Recyclable bath (environmental benefit)
- More versatile substrates (larger market)

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Type 3: Hydrogen Bond Donors

$R_1R_2R_3R_4N^+ X. zY$ $Y = RZ$, $Z = CONH_2$, $COOH$, OH

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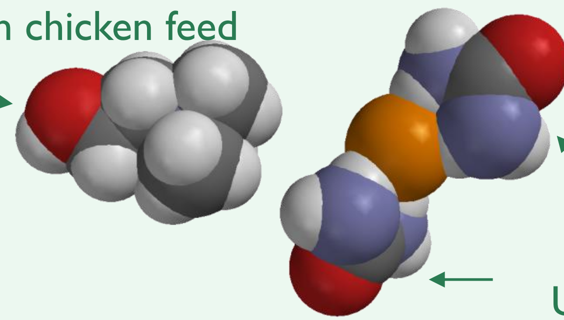
Deep Eutectic Solvents

- Many HBDs are INEXPENSIVE (c.a. £1/kg), Non-toxic, Non-flammable, Biodegradable, Versatile (>10^5 liquids), Unusual solvent properties.

Choline chloride – A vitamin in chicken feed



Urea – A common fertiliser

HO_2C-R_1	Acids
$H_2N-C=O-R_2$	Amides
$HO-R_3$	Alcohols

- Dissolve a wide range of solutes e.g. salts, polar organics, metal oxides, amino acids, enzymes and surfactants.

Abbott et al. Chem. Comm., 2003, 70

Abbott et al. JACS 2004, 126, 9142

Deep Eutectic Solvents

Hydrogen bond donor	Fr Pt. /^{o}C
Amides	
Urea, NH_2CONH_2	12
Acetamide, CH_3CONH_2	51
Thiourea, NH_2CSNH_2	69
Acids	
Trichloroacetic acid Cl_3CCO_2H	-24
Phenlyacetic acid $C_6H_5CH_2CO_2H$	-5
Malonic acid, $HO_2CCH_2CO_2H$	3
Oxalic Acid, HO_2CCO_2H	13
p -Toluene sulfonic acid $CH_3C_6H_4SO_3H$	27
Alcohols	
m – Cresol, $CH_3C_6H_4OH$	< –35
Phenol C_6H_5OH	–30
Ethylene glycol	–10
Glycerol	–20
D (-) Fructose, $C_6H_{12}O_6$	5

Solvent properties can be markedly changed by altering the HBD

Freezing points of mixtures of hydrogen bond donors with choline chloride in a 2:1 ratio.

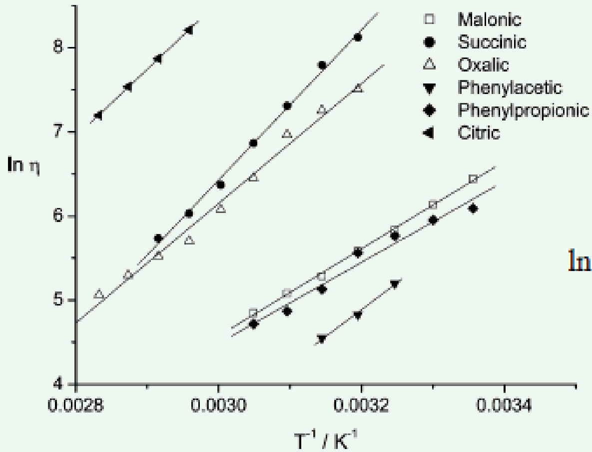


Figure 4. Plot of log viscosity vs. reciprocal of temperature for a variety of DES.

$$\ln\eta = \ln\eta_0 + \frac{E_\eta}{RT}$$

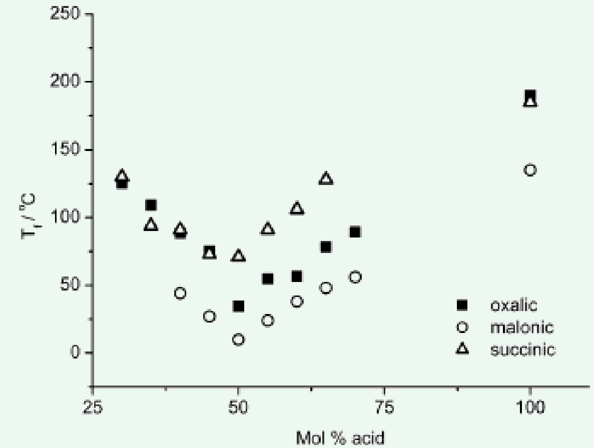


Figure 2. Freezing points of choline chloride with oxalic, malonic, and succinic acids as a function of composition.

Eutectic point occurs at 1:1 composition for bifunctional molecules

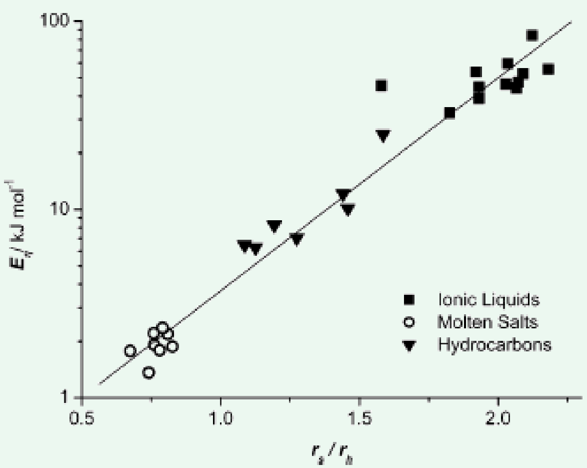


Figure 6. Energy for activation of viscous flow as a function solvent to hole radius ratio.

Activation energy for viscous flow related to size of the ion and void volume

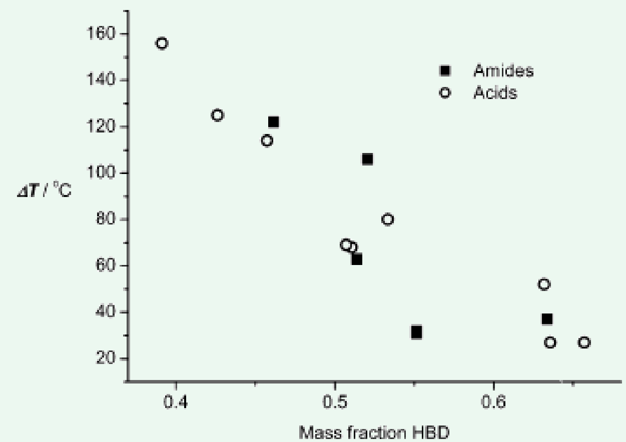


Figure 3. Freezing point depression for the eutectic mixtures listed in Table 1 and reported in the literature[10] as a function of mass fraction of HBD.

Depression of freezing point related to the amount of HBD

Product	Complexing agent
Reline	Urea
Maline	Malonic acid
Oxaline	Oxalic acid
Glyceline	Glycerol
Ethaline	Ethylene Glycol
Chromeline	$CrCl_3.6H_2O$

Many products require a mixture of complexing agents to get the right properties.

Can be made easily on a large scale.

1.3 tonnes of Ethaline

Metal Deposition

- A range of metals and alloys have been deposited from these ionic liquids

1																	18
H	2											13	14	15	16	17	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

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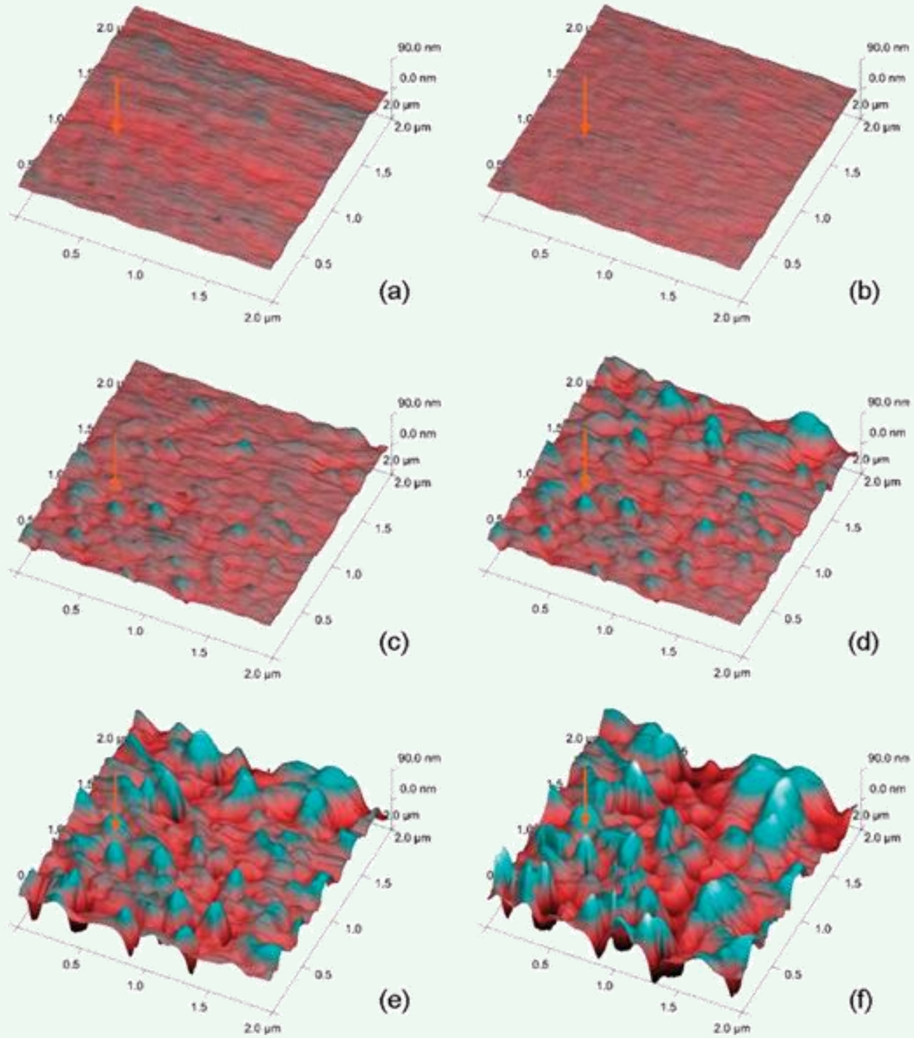
Nucleation mechanism

- Mechanistic study using in situ AFM/QCM
- Now using DHM to improve time resolution
- Studied Ag, Cu, Zn and Ni



Smith et al. Anal. Chem. (2009), 81, 8466

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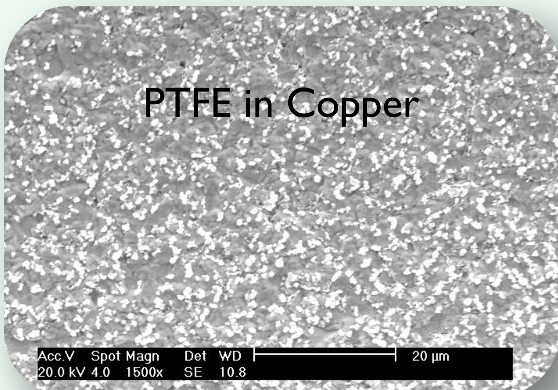
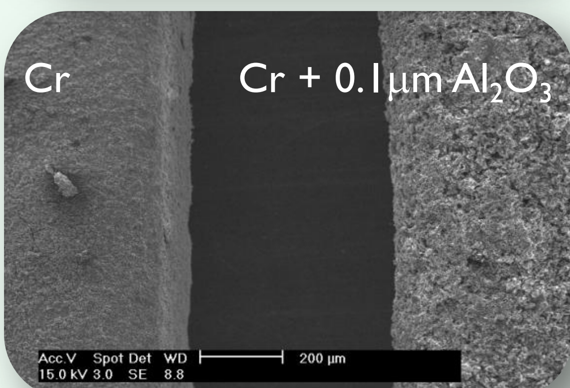
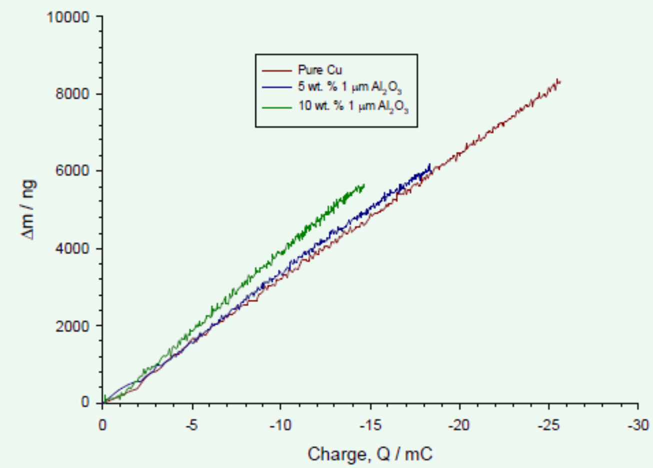
Composite Materials

- Stable colloidal suspensions can be made and these can be incorporated into metallic coatings





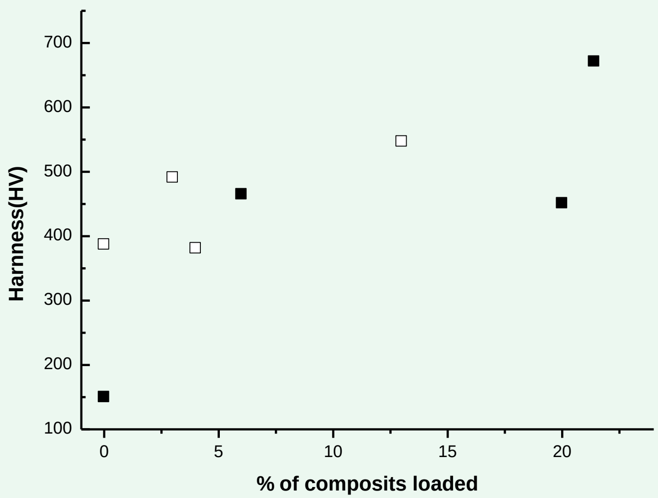


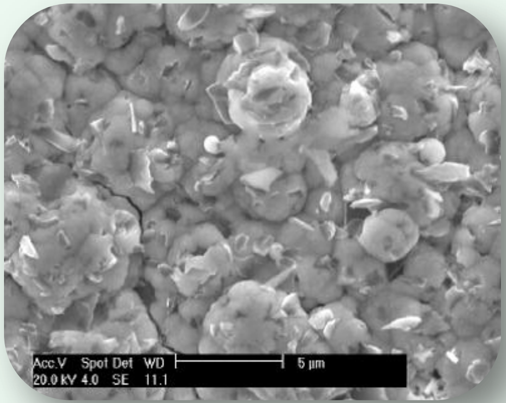
Wt % Al_2O_3 in solution	Wt % Al_2O_3 in coating	
	0.05 µm particles	1 µm particles
0.5	0.7	2.0
5	3.3	3.5
10	27.3	23.0

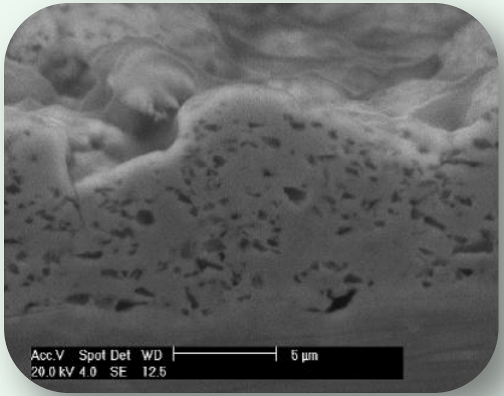
Abbott et al. Phys. Chem. Chem. Phys., 2009, 11, 4269
Martis, et al Electrochim. Acta 2010, 55, 5407

Nickel composite deposition

- Deposition of composites
- Even distribution of particulates
- Increase in material hardness and wear resistance







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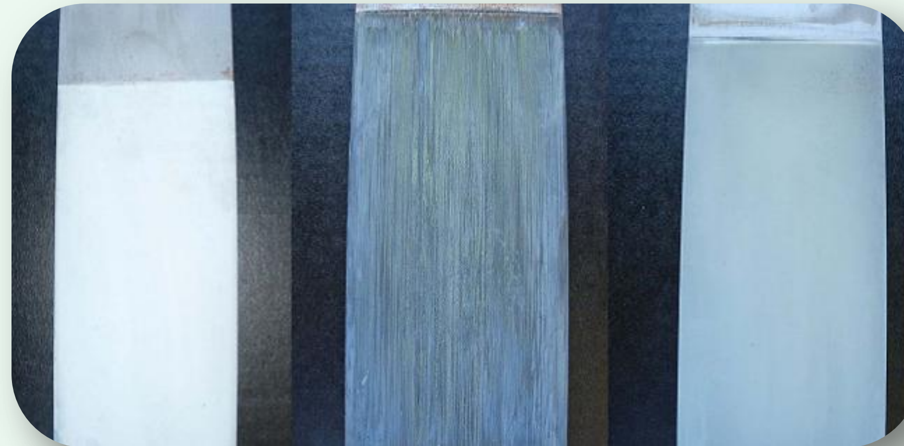
Alloy deposition

- Zn and a range of Zn alloys (Cu, Fe, Ni and Sn) were successfully deposited and the systems characterised
- Scale up the processes to a large laboratory scale, real parts coated and post treatment finishes applied
- Major focus on **ZnSn** alloys due to their potential for Cd replacement

Abbott et al. Trans. I. M. F. 87, 2009, 201-207
Abbott et al. Trans. I. M. F. 86, 2008, 234-238

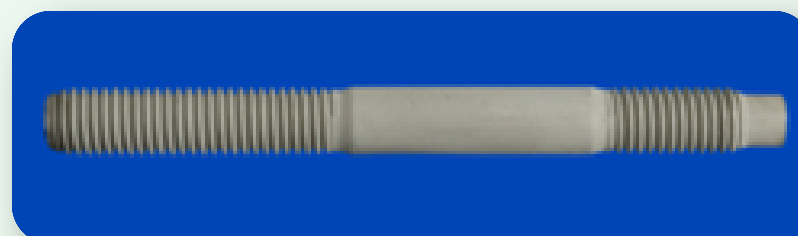
Zn Alloys

ZnSn on 10 mm rods



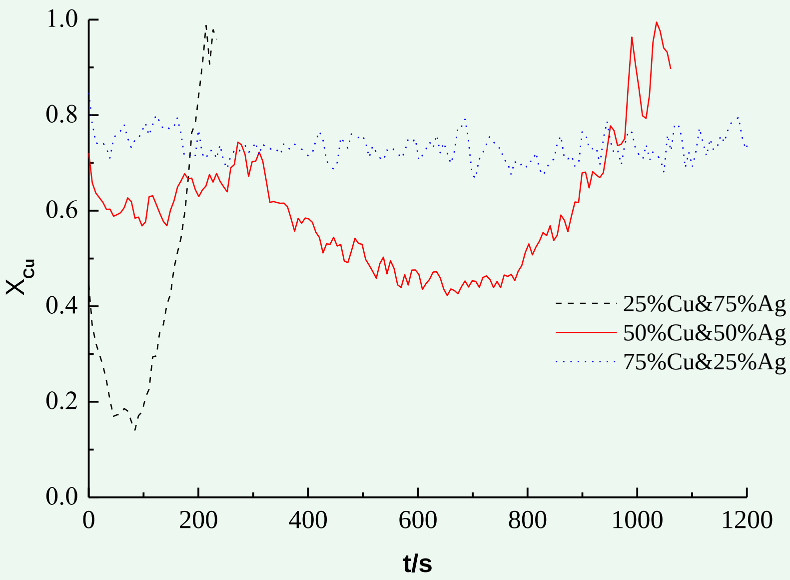
Zn, ZnNi and ZnSn on plates 150x80 mm

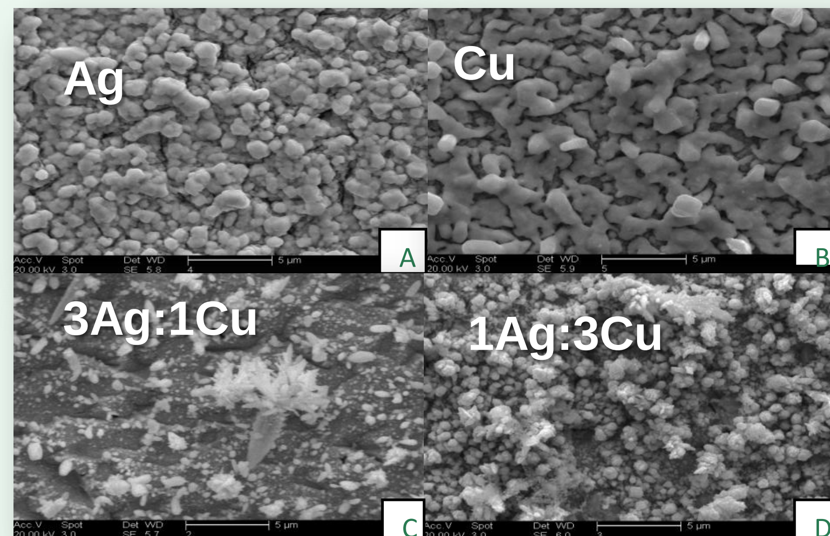
ZnSn on real parts



Copper Alloys

- Real time monitoring achieved using EQCM
- Currently studying mechanism of nucleation





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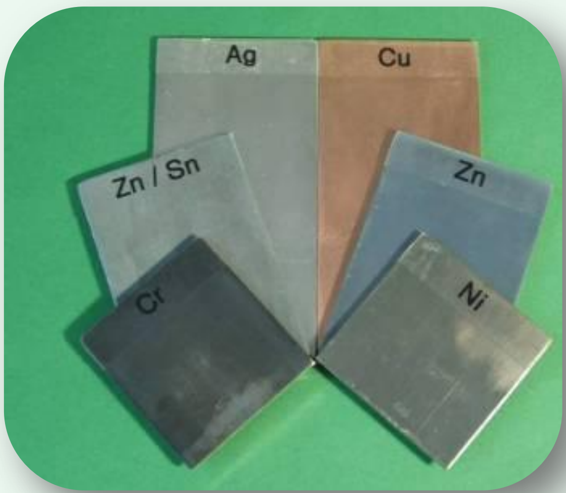
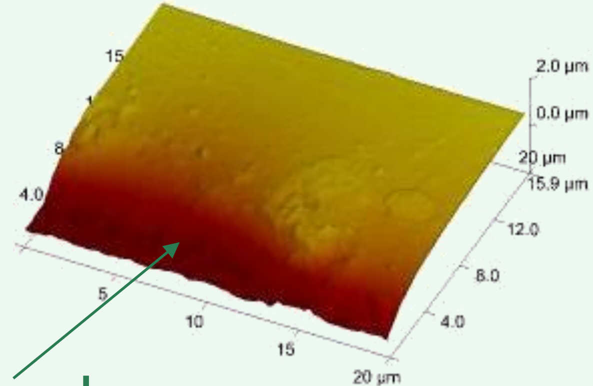
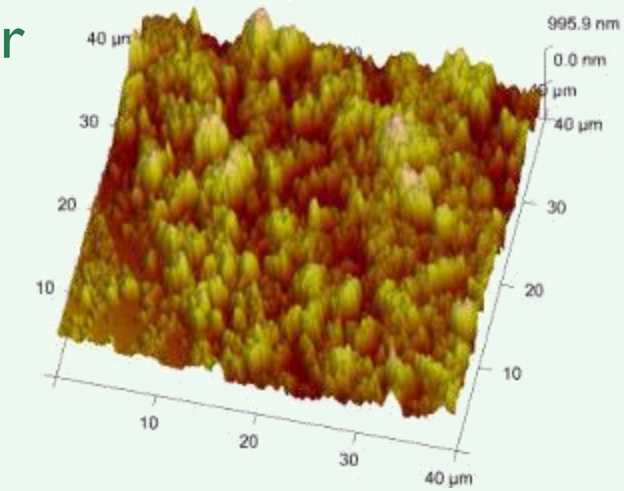
Brighteners

- Brighteners have been developed for a variety of metals



Cu deposited with and without brightener





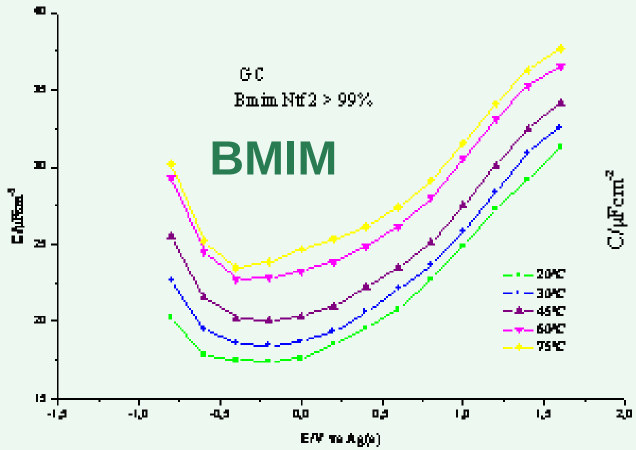
Mechanism is different for each metal and additive

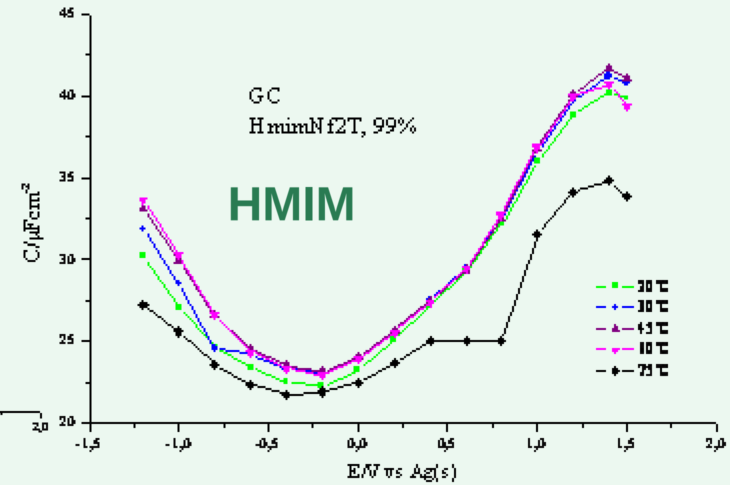
- Some work by changing double layer properties
- Others change speciation and redox potentials

Abbott et al. Phys.Chem.Chem.Phys. 2006, 8, 4265

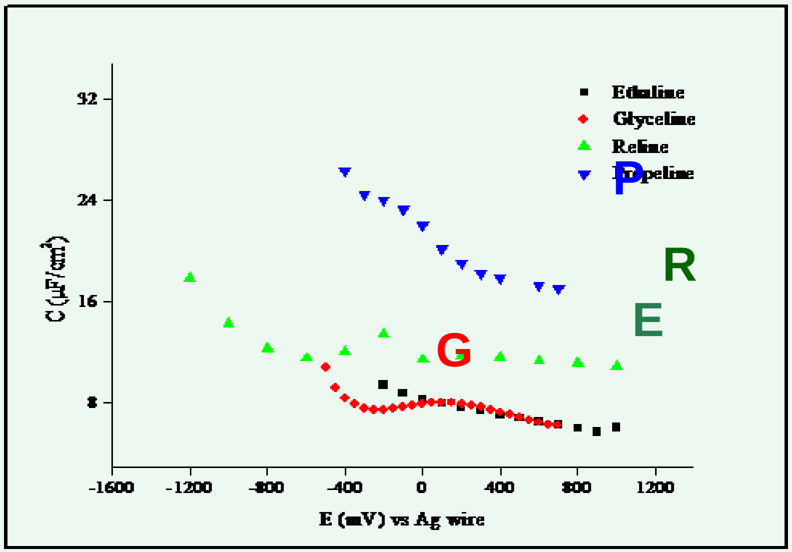
Double layer

Imidazolium based ionic liquids





Nucleation depends upon complex charge and reduction potential



Capacitance – potential curves for different liquids

Speciation

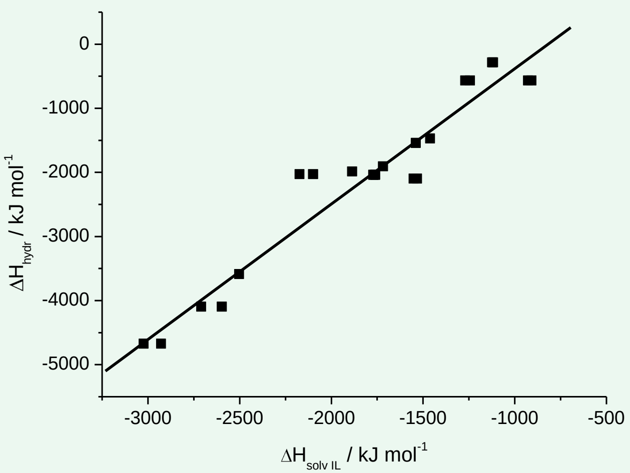
- Speciation affects redox potentials
- Recently studies EXAFS of Zn, Ni and Cu in Reline and Ethaline
- Unusual results

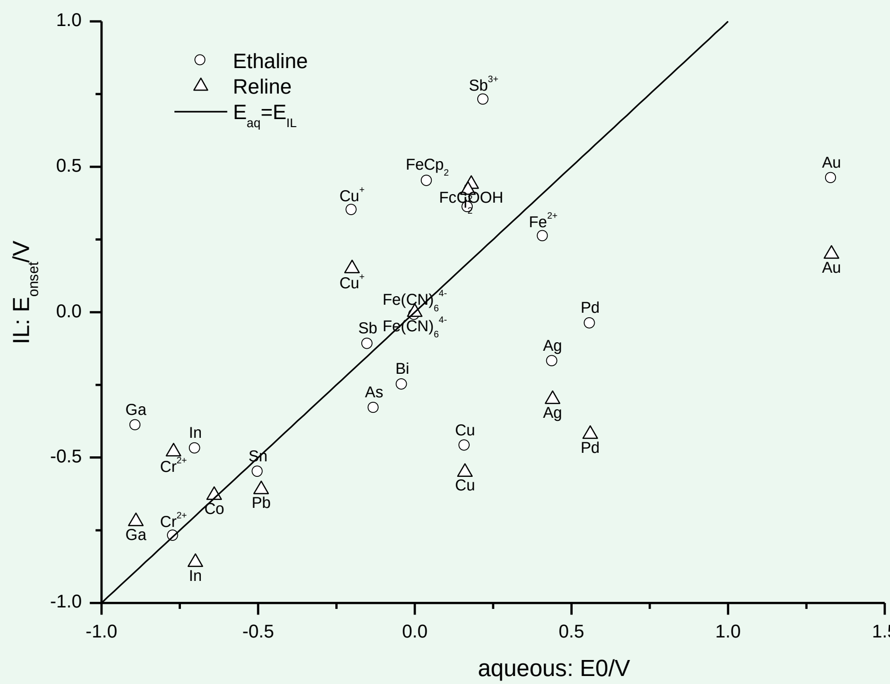
Cu^{2+} in various ionic liquids and Deep Eutectic Solvents.

Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem., ***2008***, *102, 21-45*

Comparison of $E_{1/2}$ values

- Electrochemical series constructed
- Enthalpies of solvation calculated
- Good correlation with enthalpy of hydration





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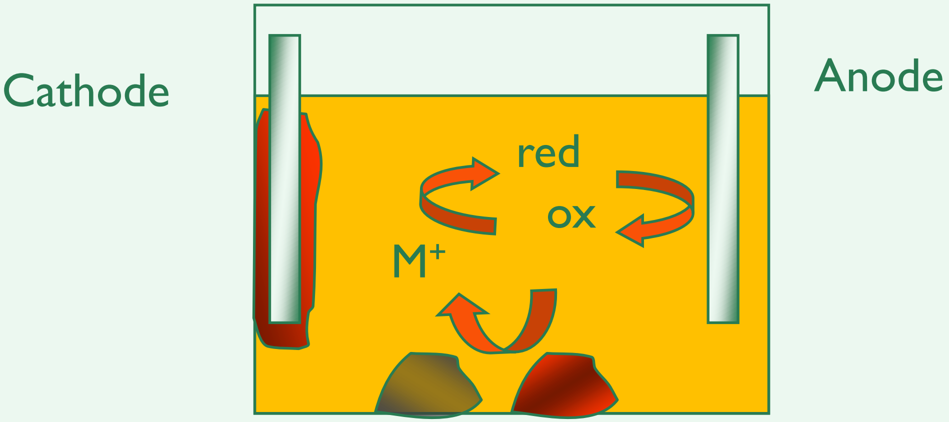
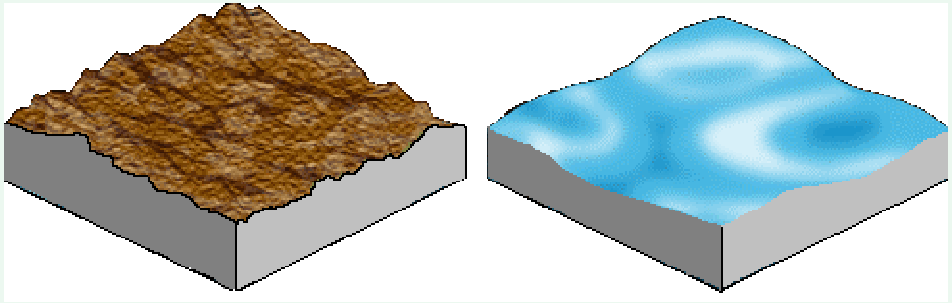
Electrocatalysis

- New methodology developed for oxidation of metals from native state.
- Has been applied to mixtures of metals
- Electrocatalytic oxidation of metals has been achieved
- Quantitative separation of Cu from Zn has been demonstrated.



Electropolishing

- Large worldwide industry - mostly stainless steel
- Opposite to electroplating i.e. dissolves metal off
- Decreases wear and improves corrosion resistance
- Uses sulphuric and phosphoric acids (HF + CrO_3)
- Low current efficiency (10 – 20%)



Before　　　　After

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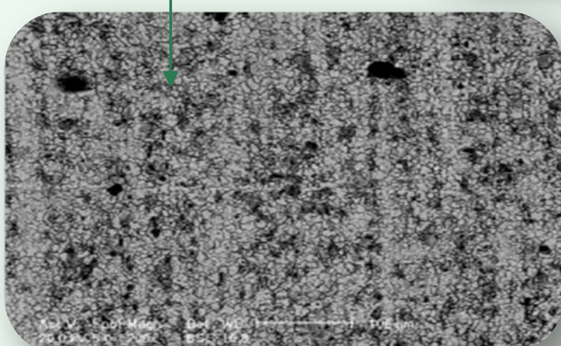
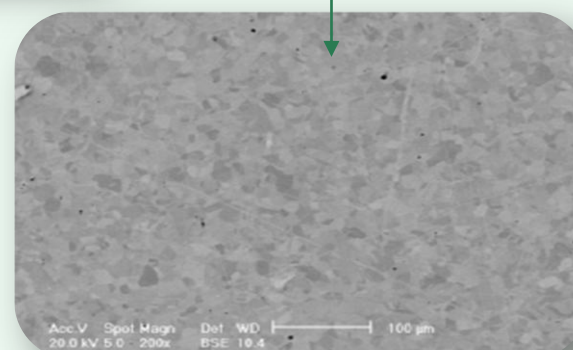
Pre-polished

Electropolished





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Scale-up

Standard tank, pump and fittings (PE, PP and nylon)

Stainless steel cathodes

Titanium anode jig

Negligible gassing at anode

anopol

Currently operating on 1300 kg at Anopol in Birmingham

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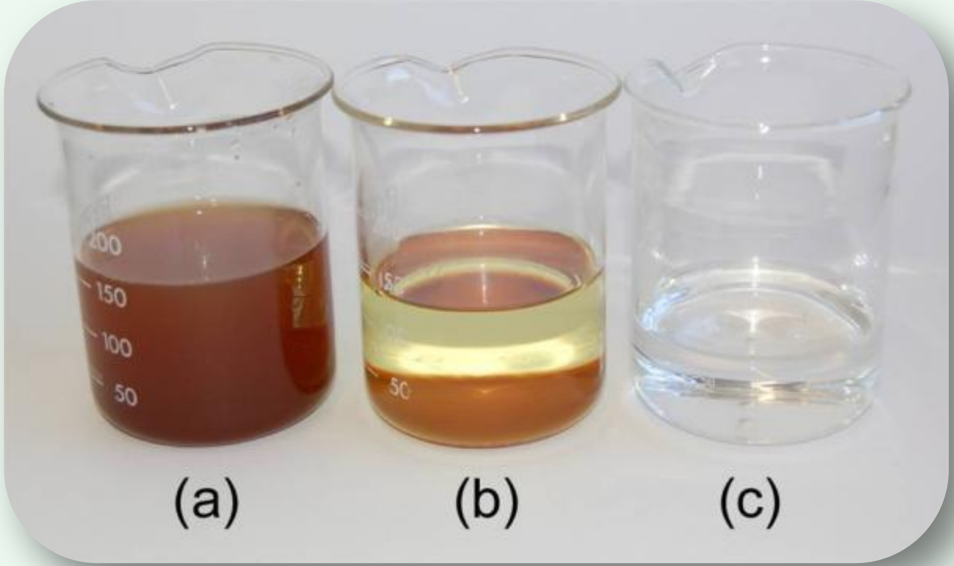
Recycling

- Liquid fully recyclable
- Spent Ethaline from the electropolishing process
- Equal volumes of water added (b) and then distilled off (c)

Metal	Saturation conc. / ppm
Iron	66746
Chromium	9150
Nickel	3135



Electropolishing

- Better surface finish (market)
- Non-corrosive (social)
- Benign liquid – ChCl/glycol (social)
- Improved current efficiency (>80%) (economic)
- Less gas evolution (environmental)
- Metal recoverable (environmental)
- Costs comparable with aqueous processes (0.17 Euro/ m^{-2})

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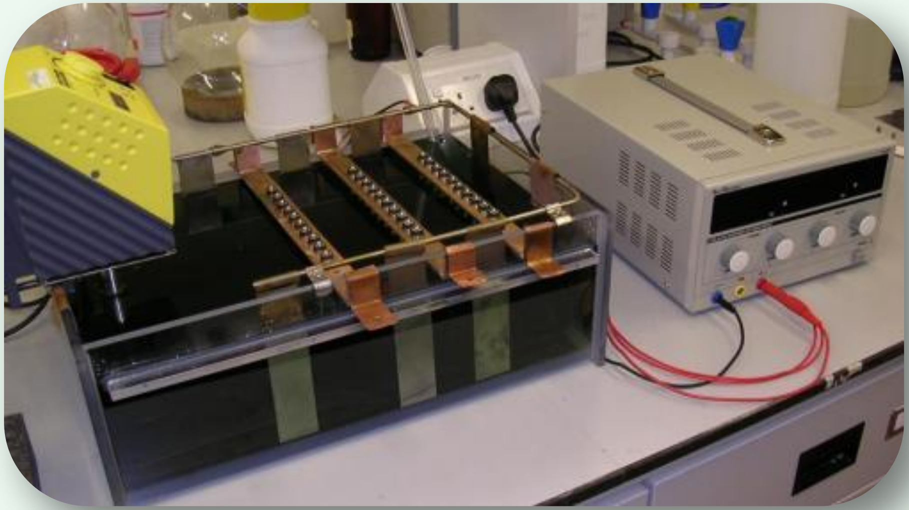
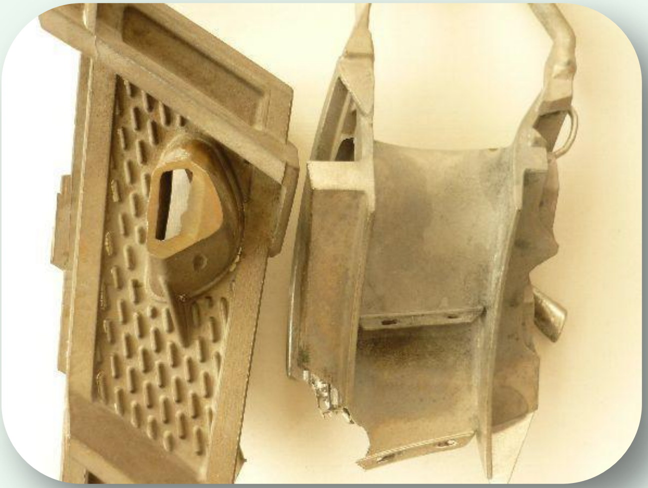
Electropolishing

- New market developed for super-alloy polishing





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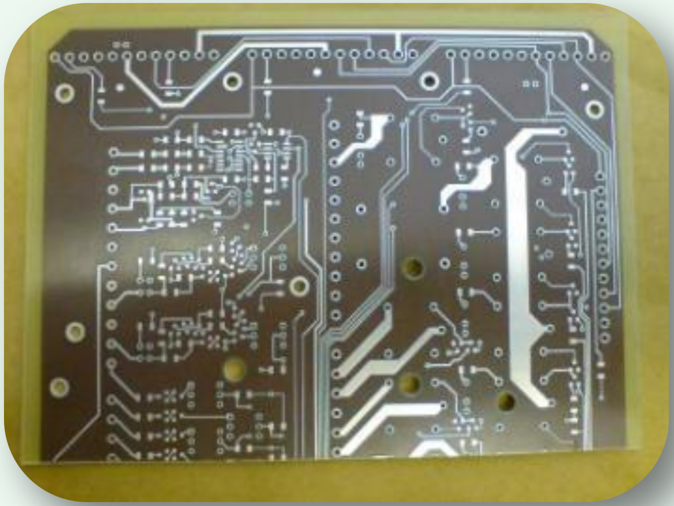
Automatic polishing line at Anopol.

Polishing line at UoL.

Batch polished steering wheel encoder disks

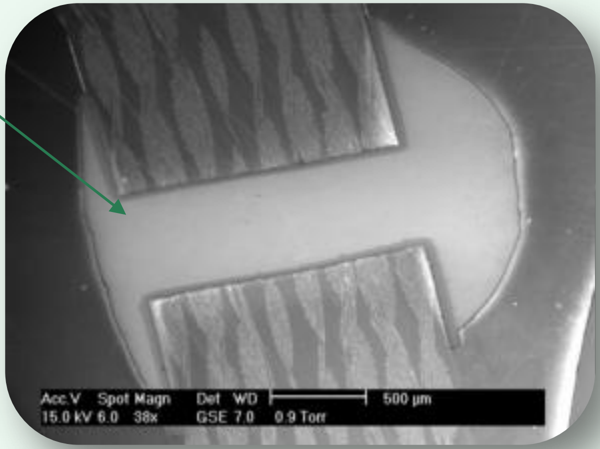
Electroless Silver

- Can also be used for electroless plating – Silver deposition



P.W. CIRCUITS LTD

Soldering Ag coated Cu interconnects



Currently being commercialised in Leicester

Electroless Silver

- Silver deposition process currently being scaled up
- PCB line now installed in Leicester

Abbott et al. PhysChemChemPhys 2007, 9, 3735
Smith et al. Circuit World 2010, 36, 3

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LEICESTER SHIRE economic partnership

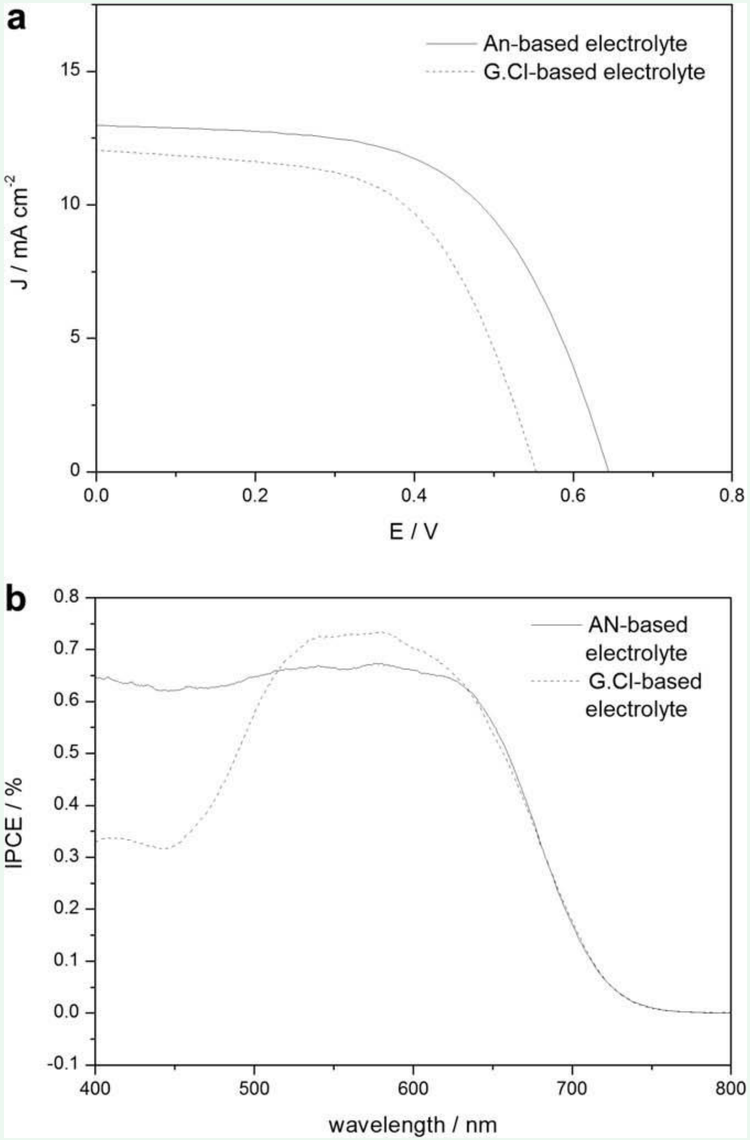
ild
ionic liquid demonstrator

IONMET

Dye Sensitise solar Cell

Uses ChI and glycerol in a Graetzel cell

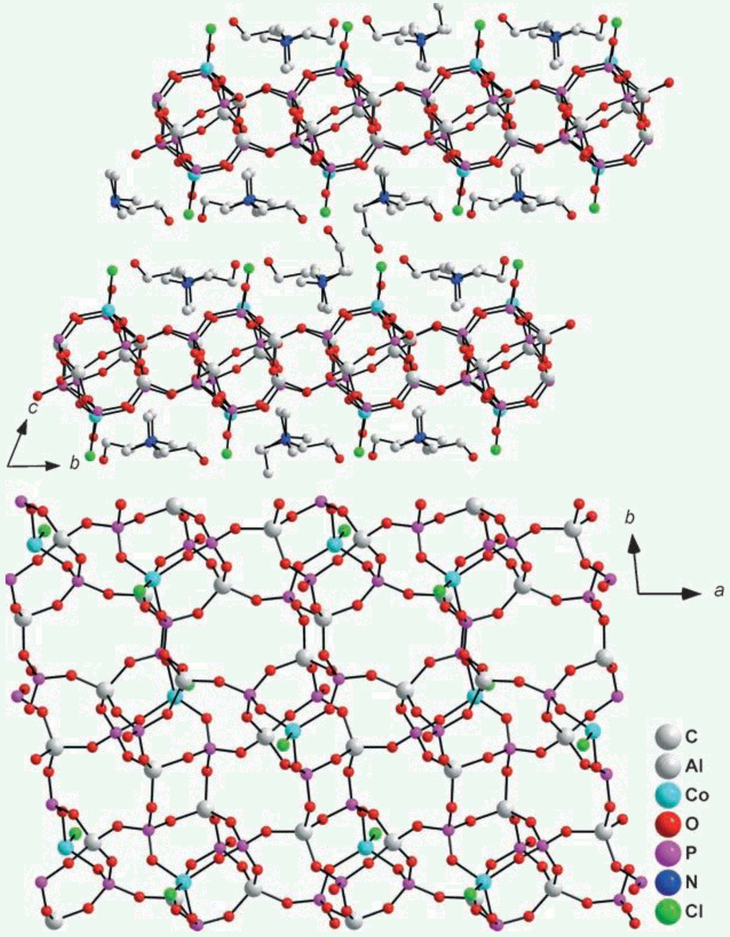
Results compare well with acetonitrile based electrolyte



Jhong et al. Electrochem. Comm. (2009), 11, 209

Ionothermal synthesis of zeolites

Cation of the DES acts as the structure-directing template



Synthesis of SIZ-14:
The ChCl: succinic acid (4 g),
aluminum isopropoxide (0.22 g), phosphoric acid (0.32 g, 85 wt% in water,) cobalt acetate tetrahydrate (0.21 g)
cyclam (0.15 g)
teflon-lined autoclave.
Mixture was heated at 180^{o}C for 3 days.

Parnham et al. Angew. Chem. Int. Ed. (2006), 45, 4962

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Urea Choline Chloride

Wide range of solutes show high solubilities

In general those capable of forming H bonds show the highest solubilities.

Solute	Solubility / mol/l
Lithium chloride	>2.5
Silver Chloride	>0.66
D-alanine	>0.38
benzoic acid	>0.82
Copper (I) oxide	>0.11
Calcium carbonate	>0.21
SDS	>0.36

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Urea Choline Chloride

Wide range of solutes show high solubilities e.g. metal oxides

Dissolved oxides can be recovered electrochemically

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High solubility demonstrated for a range of metal oxides

Metal Oxide	M.pt. / °C	Solubility / ppm
Al_2O_3	2045	<1
CaO	2580	6
CuO	1326	470
Cu_2O	1235	8725
Fe_2O_3	1565	49
Fe_3O_4	1538	40
MnO_2	535	493
NiO	1990	325
PbO_2	888	9157
ZnO	1975	8466

Solubility of metal oxides in a 2:1 urea: choline chloride eutectic at 60 °C.

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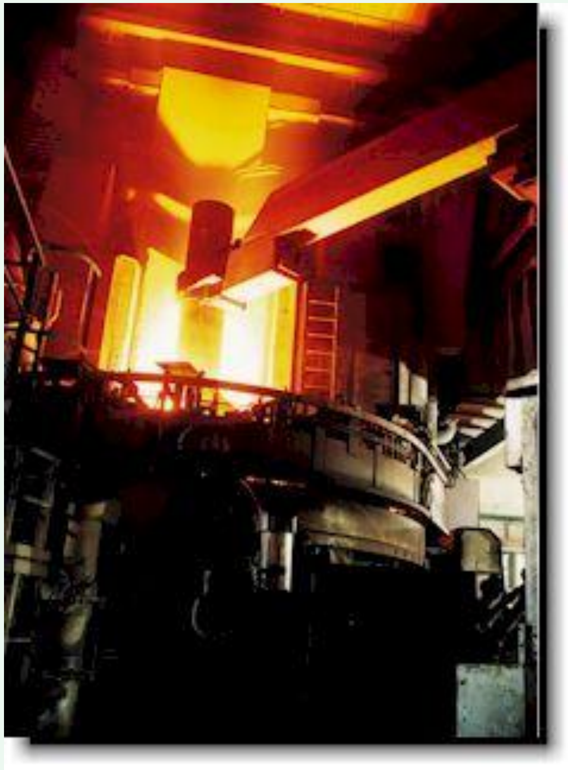
Tunable Metal Oxide Solubility

	Solubility / mol dm^{-3}		
	CuO	Fe_3O_4	ZnO
1 Malonic acid: 1ChCl	0.246	0.071	0.554
1 Oxalic acid: 1ChCl	0.071	0.341	0.491
2Phenylpropionic acid: 1ChCl	0.473	0.014	>0.491

EAF Dust

- EAF produces c.a. 15 - 20 kg of dust per tonne of steel.
- The dust is classed as a toxic waste because of the high heavy metal content.
- Several million tonnes of dust are produced per annum.
- Dust forms when volatile metals, e.g. Pb and Zn vaporise at the high operating T and are oxidized in the airflow through the furnace.



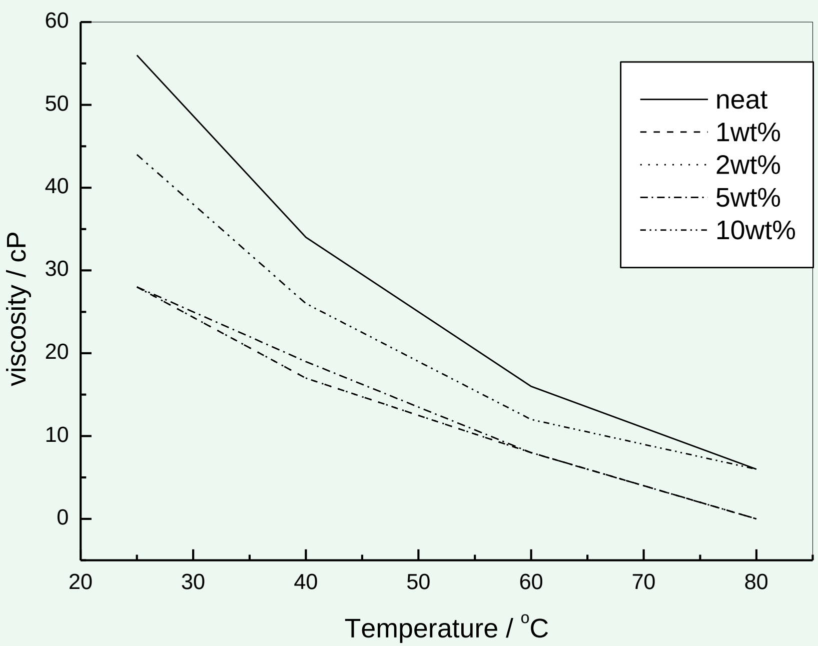
EAF Dust

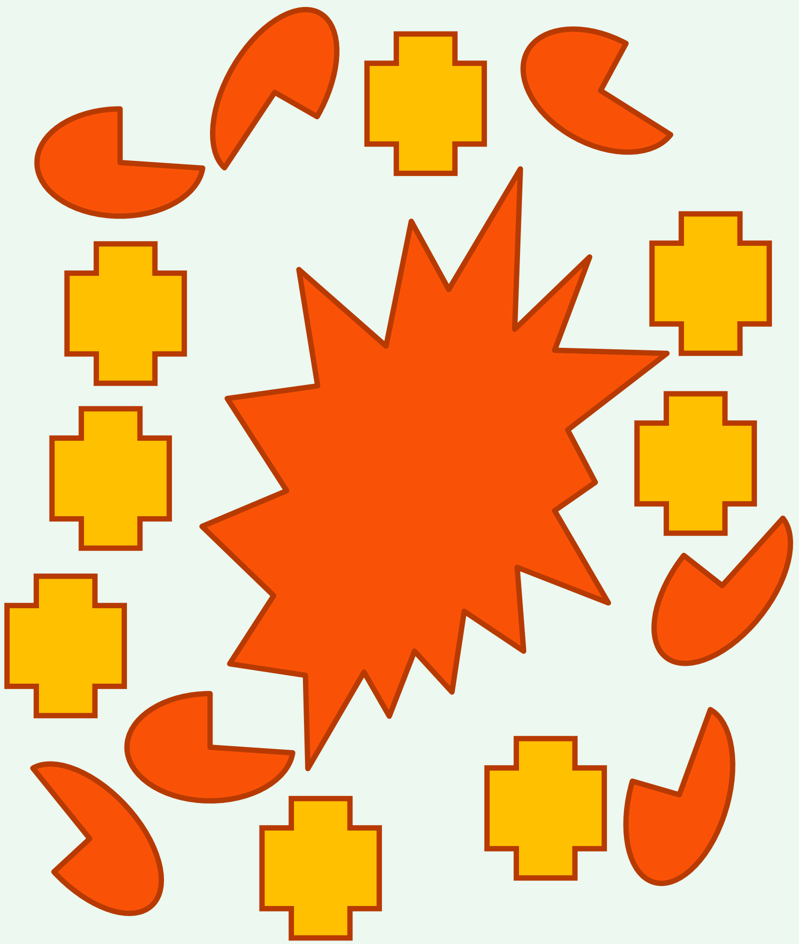
Composition of EAF dust sample

Metal	Content in EAF dust /wt %	Solubility of metal oxide /ppm	Solubility from EAF dust /ppm
Al	12	Al_2O_3 – < 1	<1
Cu	1	CuO - 470 Cu_2O - 8725	5
Fe	38	Fe_2O_3 - 89 Fe_3O_4 – 40	16
Mn	4.5	MnO_2 – 493	-
Pb	4	PbO_2 _ 9157	113
Si	4	SiO_2 - < 1	<1
Zn	33	ZnO – 8466	4288

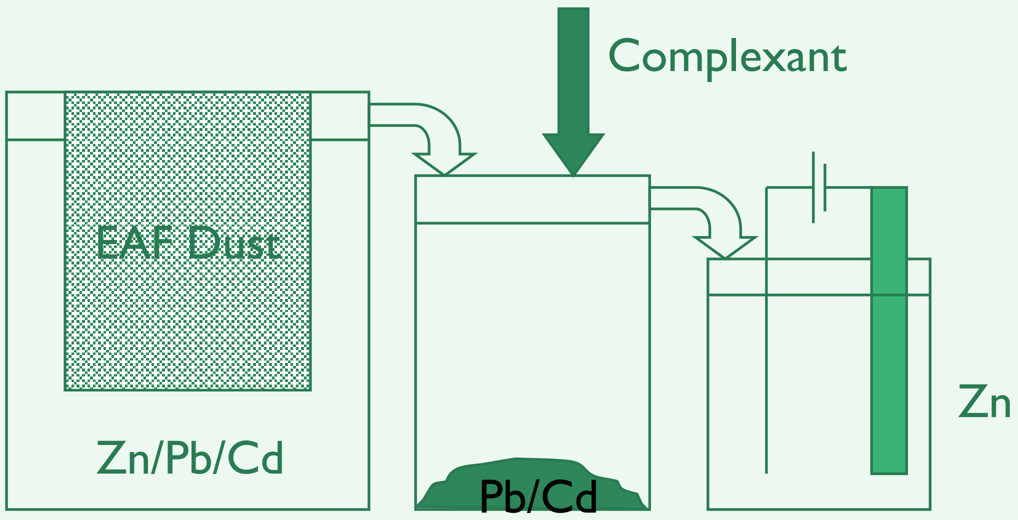
Colloids

- Colloidal particles decrease viscosity
- Increase free volume





Electric Arc Furnace Dust



Dust contains 38% Fe, 33% Zn, 4% Pb and 1% Cd

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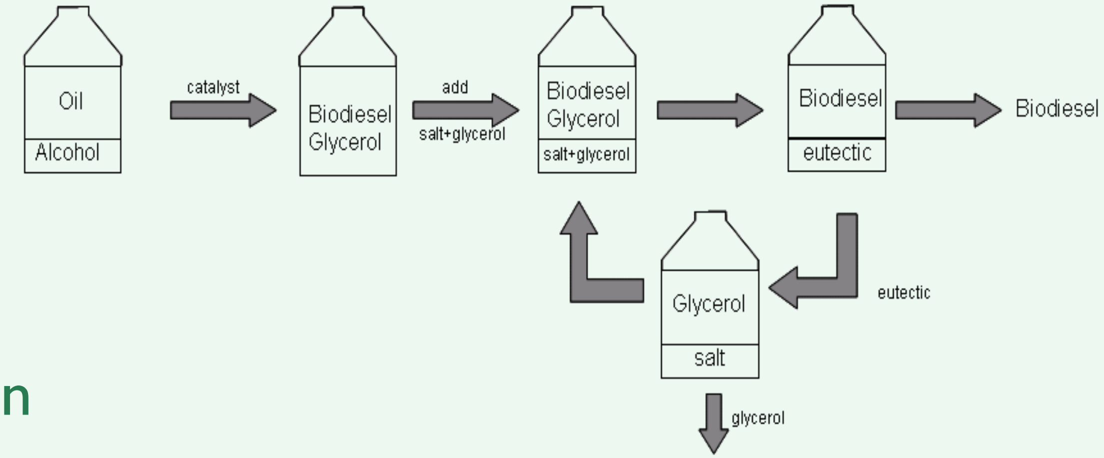

Other applications

- Biodiesel purification
- Cleaning – Hard surface cleaners, surfactant delivery systems, antifungal/antimicrobial action, wipe delivery systems.
- Modification of cellulose with anionic/ cation functionalities
- Batteries – rechargeable zinc cells
- Antistatics, refractive index matches

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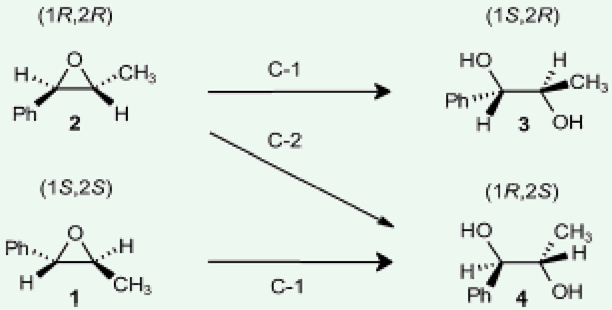
Biocatalysis

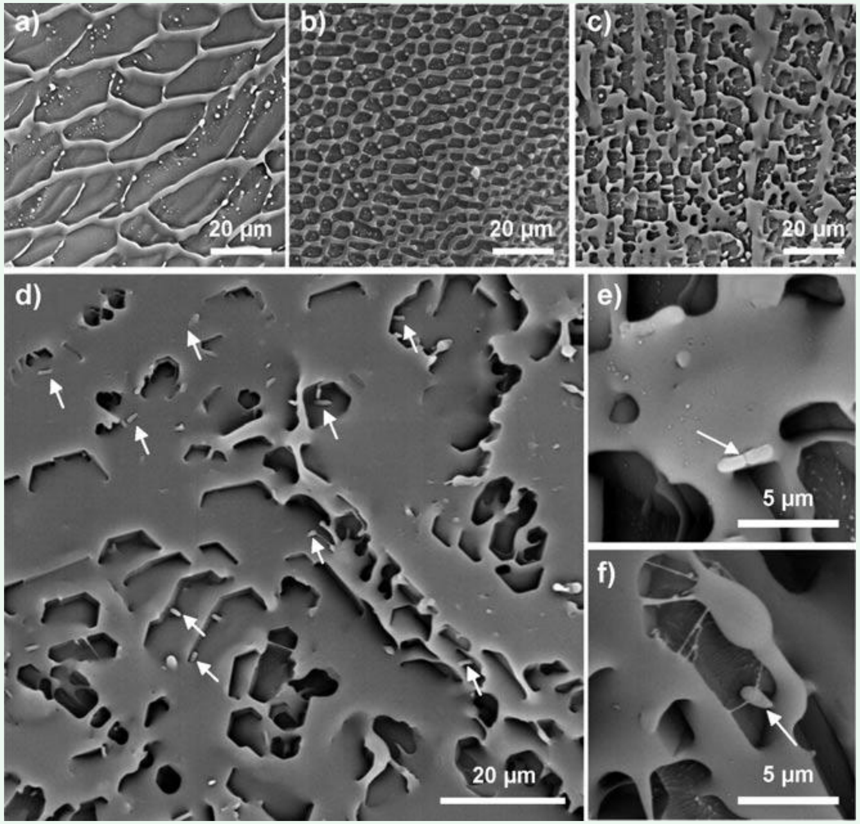


potato epoxide hydrolase StEH1
DESs improve product yield and product distribution. Used as mixtures with co-solvents.

Table 2
Steady state kinetic parameters for StEH1 catalyzed hydrolysis of (1S,1S)-2-MeSO, at different DES concentrations[a].

Solvent	Conc. (%)	k_{cat} (s^{-1})	K_M (mM)	k_{cat}/K_M ($s\ \mu M)^{-1}$
Buffer	–	63 ± 3	0.077 ± 0.01	0.82 ± 0.1
GLY	20	51 ± 2	0.12 ± 0.01	0.42 ± 0.05
	40	57 ± 5	0.25 ± 0.04	0.23 ± 0.04
	60	44 ± 5	0.53 ± 0.09	0.082 ± 0.02
ET	20	63 ± 2	0.24 ± 0.02	0.26 ± 0.03
	40	61 ± 6	0.49 ± 0.08	0.12 ± 0.02
	60	31 ± 6	1.2 ± 0.3	0.026 ± 0.008
REL	20	65 ± 4	0.36 ± 0.04	0.18 ± 0.02
	40	92 ± 10	1.5 ± 0.3	0.060 ± 0.01

Lindberg et al., J. Biotech. (2010), 147, 169

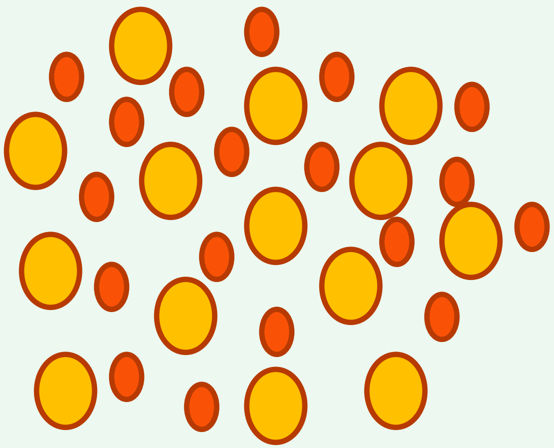


Tapping of E-coli bacteria in ChCl: glycerol

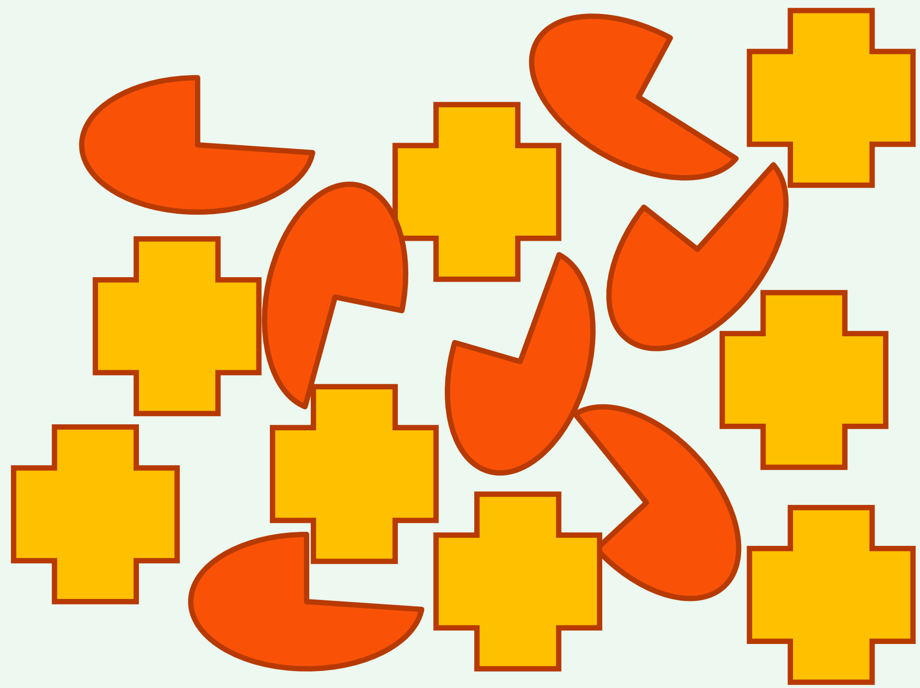
Gutierrez *et al. Angew. Chem., Int. Ed. (2010), 49, 2158*

Molten salts vs. ionic liquids

- Ionic liquids are different from molten salts because of their ionic size and the temperature of the system.



Molten Salt



Ionic Liquid

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Why are ionic liquids viscous?

- Because they have large ions and a small void volume

- Assume that an ionic liquid behaves like this slide puzzle – ions can only move if there are spaces next to them.

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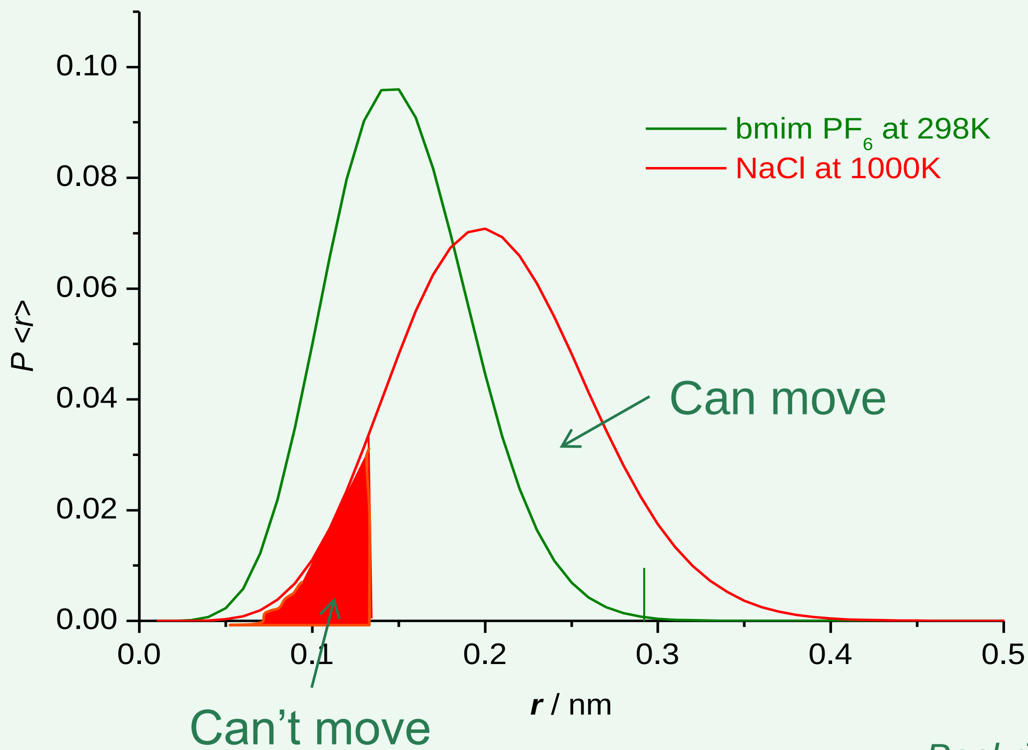
The model

The ions are large c.a. 0.4 nm

The holes are small c.a. 0.2 nm

One in a million ions has a hole next to it that is big enough to move into



$$Pdr = \frac{16}{15\sqrt{\pi}} a^{7/2} r^6 e^{-ar^2} dr$$

hole size

$$a = 4\pi\gamma / kT$$

surface tension

Bockris, Disc. Faraday Soc., 1961,32, 218-236

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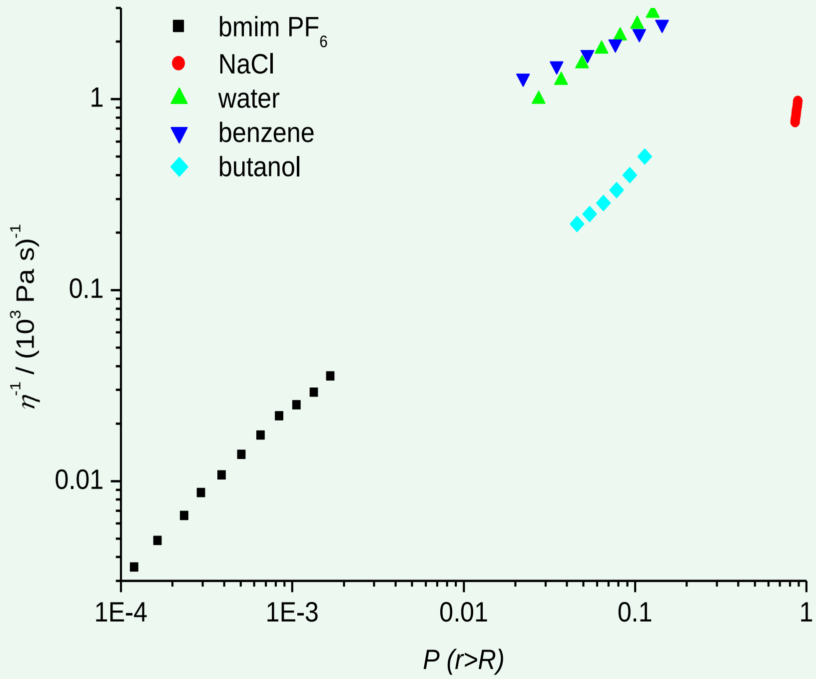
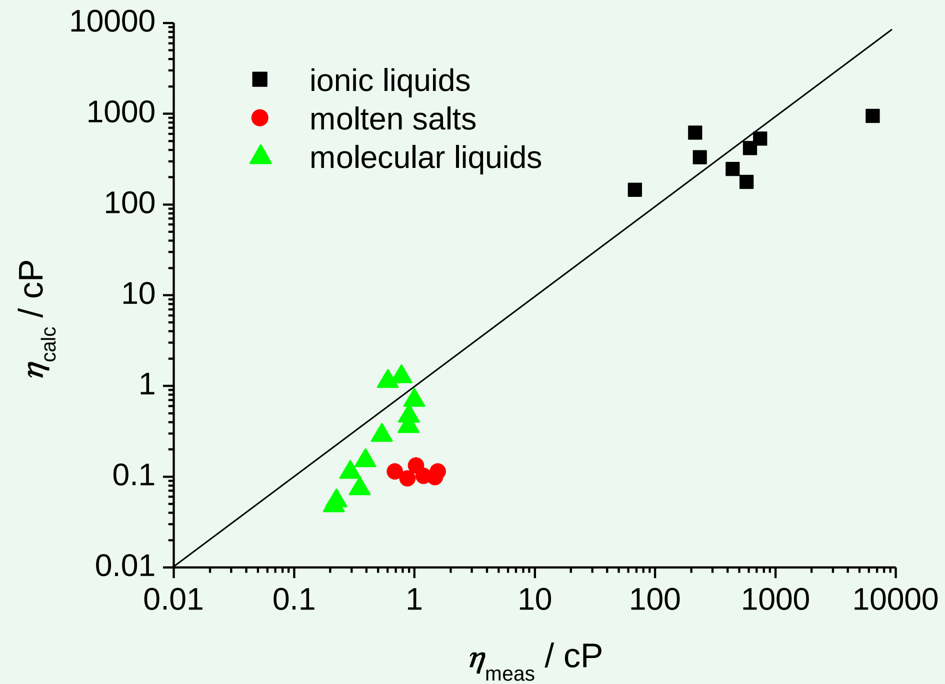
- Fluidity is proportional to hole probability



What is the constant of proportionality?

Hole Theory



If P(r>R) = 1 (ideal gas)

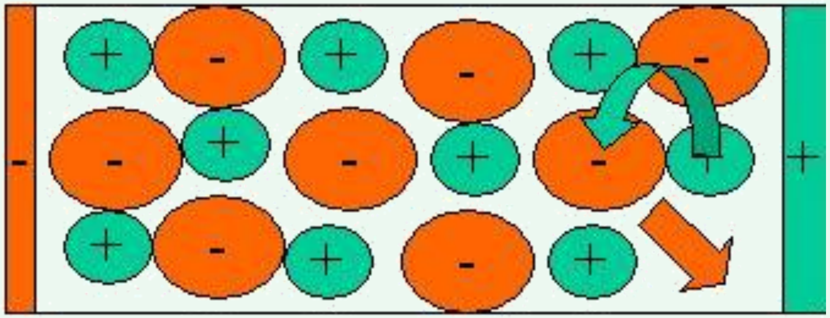
Viscosity mass speed area

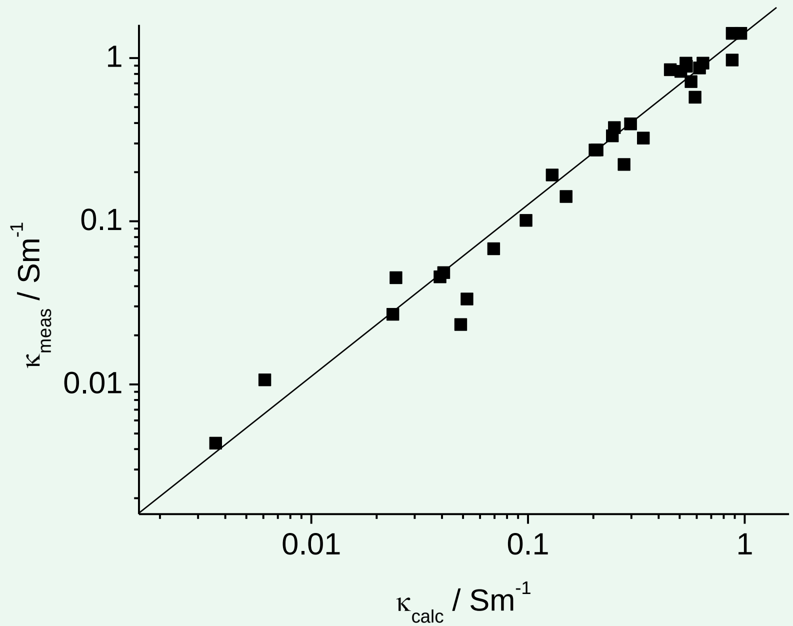
$$\eta = \frac{m\bar{c}/2.12\sigma}{P(r > R)}$$

Limitation

- For molten salts the anion and cation have different sizes and therefore different transport numbers
- For ionic liquids transport numbers are more similar.

Conductivity – Hole Theory



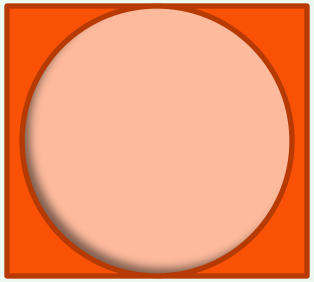


- If hole concentration is very low hole migration must limit charge transport
- Hence conductivity is described by Nernst Einstein Equation
- $\lambda_+° = z^2 F e / 6 \pi \eta R_+$
- Hence derive an equation for conductivity

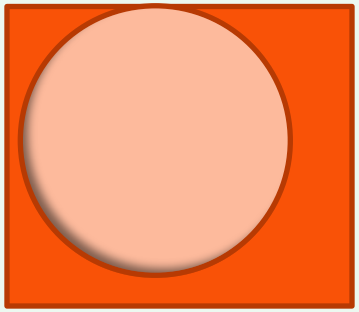
$$\kappa = \frac{z^2 Fe}{6\pi\eta}\left(\frac{1}{R_+} + \frac{1}{R_-}\right)\frac{\rho}{M_w}$$

Limitations

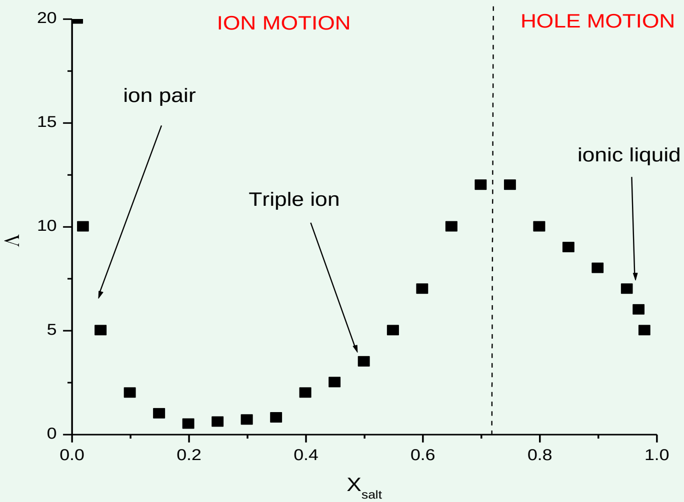
- Most cations are definitely not spherical
- The model is flawed because the ion does not need a similar sized hole to move into – It is the hole that moves.



Ion <u>cannot</u> move



Ion <u>can</u> move



Conclusions

- Ionic liquids based on choline chloride are useful for large-scale applications
- Versatile range of liquids possible
- Offer numerous social, environmental and economic advantages

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Background Reading

- A. P. Abbott *Phys. Chem. Chem. Phys.* 2006, 8, 4265-4279
- A. P. Abbott, *Trans. I. M. F.* 86, 2008, 196-204
- F. Endres, A. P. Abbott and D. MacFarlane, Electrodeposition using Ionic Liquids, Wiley VCH, Weinheim, 2008

More information from

- www.ionmet.eu
- www.scionix.co.uk
- www.leicester-ils.co.uk/