Organic Ionic Plastic Crystals – Novel Ionic Electrolytes For Alkali Metal Electrodes

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Context: Need for cheap, reliable and safe energy storage

- Metal/air batteries (Zinc, Magnesium, oxygen reduction)
- Sodium-ion batteries
- Lithium Batteries
- Synthetic Energy Systems (ACES)
  - Flow batteries
  - Air cathodes
  - Thermal Energy Harvesting
- 3D Electromaterials
- Solid-State Electrolytes

 ➢ Developing materials and electrolytes to control safety, reliability and maximise energy density
Prototyping Facility to be established by mid 2016

Emulate Battery prototype line at Argonne National Laboratory

Up-scaling of electrode materials production
Nanostructured electrode materials

Draw-down electrode coater
Blister forming
Tab cut & weld
Bio-logic battery test station
Final pouch cell

Draw-down electrode coater
Pouch case sealing
Degas & seal unit

ARC Centre of Excellence in Electromagnetics Science
Market Size & Growth Projections Show Significant Growth For Advanced Batteries Over The Next 5-10 Years

Sources: Lux Research 2015, Navigant Research 2015, Panasonic Corporation presentation 2015

* Bubble size is not to scale
Common Li-ion Modules And Balance-of-system Are Beginning To Be Used To Address Both EV And Stationary Storage Markets

- Tesla-Panasonic and Daimler are building volume/scale and reducing cell and system cost by standardising battery components and architecture across products for both the EV and stationary storage markets.
Safety Is Increasingly A Critical Parameter For Advanced Batteries As More EV And Stationary Applications Are Commercialised

Safety standards for battery storage ‘critical to industry integrity’

After 3 Fires, Safety Agency Opens Inquiry Into Tesla Model S

Boeing issues lithium-ion battery warning

How Lithium Ion Batteries Grounded the Dreamliner

Safety worries lead US airline to ban battery shipments

FAA Backs Ban on Shipping Lithium Batteries on Commercial Airlines
Fundamental Materials Research – Ionic Liquids, Plastic Crystals, Ionomer Membranes

Research strength in electromaterials materials design and characterisation

(Australian Laureate Fellowship and Australian Center of Excellence in Electromaterials Science (ACES))

- Ionic Liquids – ‘liquid salts’ i.e., low melting point by design
- Plastic Crystals – ‘plastic salts’ i.e., pliable, ‘soft’ salts
- Ionomers – single ion conducting polymers

Advantages - Thermal & Chemical stability, non-volatile, non-flammable

i.e., intrinsically safe & durable batteries based on ionic electrolytes
What are Organic Ionic Plastic Crystals (OIPCs)?

- Cation-Anion pairs – analogous to Ionic Liquids
- ✓ Solid at room temperature → High reliability
- ✓ Electrochemical and thermal stability → Safe electrolytes
- ✓ Ease of processing (vs. ceramic electrolytes)

Ions have orientational or rotational disorder

But… still maintain long range order crystalline structure

But… ionic conductivity typically too low for device applications
Undergo one or a series of phase transformations up to the melting point
- Transport mechanism associated with: \(^1,^2\)
  - disorder modes in matrix ions
  - formation of secondary phases
  - presence of structural defects

- Conductivity can be enhanced;
  - Addition of ‘impurities’ – in this case Li salt \(^3\)
  - Addition of nanoparticles \(^4\)

Phosphonium OIPCs

- N-based OIPCs (e.g. ammonium, pyrrolidinium) often have Phase I at higher than ambient temperature
- Phosphonium ILs possess higher thermal and electrochemical stability than their ammonium counterparts
Variable Temperature Synchrotron - XRD

Pure & 4 mol% $P_{1444}$ FSI

- Phase III (0 °C) and Phase II (17 °C)
  - large differences between pure and doped samples
- Suggests at least 2 phases present in 4 mol% sample at lower temperatures (e.g. pure & lithium enriched phases)
- Phase I (30 °C) are very similar
- Similarity of XRD patterns at 30 °C suggests Li enriched phase has melted – consistent with DSC
  - Gel like solid in Phase I
Conductivity

Phase III & II – 3.5 order of magnitude increase of $\sigma$ with Li addition
- Li enriched phase?
- Amorphous phase?

4 mol% & 8 mol% similar $\sigma$

Phase I – likely existence of liquid component percolating at grain boundaries\textsuperscript{1} – lower $E_a$ - still exhibits soft-solid character

**Li | LiFePO$_4$ Cell Cycling at 30 °C**

i.e. Phase I

- 50 cycles at 0.3C (1.5 – 2 mg.cm$^{-2}$ cathode loading) – 160 mAh.g$^{-1}$
- SEI formation in initial cycling
- Cell polarisation decrease;
  - ‘preconditioning’ process$^1$
  - melting at interface
- Retained 130 mAh.g$^{-1}$ at 1C

Li | LiFePO$_4$ Cell Cycling at 20 °C

i.e. Phase II

• Reached 155 mAh.g$^{-1}$ at 0.1 C after the 10$^{th}$ cycle
• Large decrease in interfacial impedance with cycling – SEI formation & preconditioning
• Retained 118 mAh.g$^{-1}$ at 1 C
Li | C₆mpyrBF₄ 10 mol % LiBF₄ PVdF | LiFePO₄ Cell

Current rate : C/15 (nominal time for full discharge of capacity is 15hrs)

- Reduced interfacial impedance with cycling - preconditioning
- Approached theoretical capacity after 10 cycles at 80 °C
- Charge-discharge at 50 °C

OIPC conductivity @ 50 °C $3.3 \times 10^{-7}$ Scm⁻¹.
Thermal analysis & Conductivity

10% Li - C₂mpyrBF₄ + PVdF

C₂mpyrBF₄ + PVdF

10% Li - C₂mpyrBF₄

C₂mpyrBF₄

$^7$Li Solid-state NMR

LiBF$_4$ - C$_2$mpyrBF$_4$

LiBF$_4$ - C$_2$mpyrBF$_4$-PVdF

T (°C)

LiBF$_4$ - C$_2$mpyrBF$_4$-PVdF

70
60
50
40
30
10
0

200 100 0 -100 -200

7Li (ppm)

200 100 0 -100 -200

7Li (ppm)
Synchrotron Powder XRD

- $2^{\text{nd}}$ Li-rich phase evident in Phase II & IV – not evident in composite
- Li doped composite attains cubic structure in Phase II
- Broader peak widths indicating smaller crystallite sizes or higher lattice strain
- PALS measurements indicate increased average free volume size (pure OIPC)

![Graph showing XRD patterns of different compositions](image-url)
More ‘plastic’ systems…

Triethyl(methyl)phosphonium bis (fluorosulfonyl)imide

$[\text{P}_{1222}][\text{FSI}]$

Triethyl(methyl)phosphonium bis(trifluoromethanesulfonyl)imide

$[\text{P}_{1222}][\text{TFSI}]$
Li addition

Li plus fibres
Can we avoid Li ‘trapping’?

Poly(diallyl methylammonium)TFSI
Poly(DADMA)

Prof David Mecerreyes
SUMMARY

Lithium batteries are expected to become the dominant technology for EV and stationary energy storage in the coming decade.

OIPCs possess ‘ideal’ properties for application as electrolytes in high energy electrochemical devices.

- ‘Pre-conditioning’ is a key aspect in achieving good cell performance with OIPCs.
- Stable cycling performance of (Li | LiFePO₄) OIPC based demonstrated at practical rates at 30 °C and 20 °C.
- Flexible OIPC – electrospun polymer nanofibre composites with enhanced transport and mechanical properties were described.
- Functional nanofibres can modify OIPC phase nucleation and ion transport properties.
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