CH5715
Energy Conversion and Storage

Electrolytes

For lecture notes:  http://jtsigroup.wp.st-andrews.ac.uk/ch5715-energy-conversion-and-storage/

Textbook
Solid State Electrochemistry  Cambridge - P. G. Bruce
Electrolytes

- Solution
- Polymer
- Ceramic – Solid electrolyte
- Physical aspects of solid electrolytes
Solution Electrolytes

salt + solvent $\rightarrow$ solution

$\Delta G$ negative

$\Delta G = \Delta H - T \Delta S$

$\Delta S$ of salt increases, $\Delta S$ of solvent decreases

Overall $\Delta S$ positive but still small

Dissolution depends on enthalpy changes

NaCl does not dissolve in hexane
Water as a solvent - is it unique?

1. Strong H-bonding - a network

2. Large dielectric constant $\varepsilon=80$

3. Both cations and anions are solvated

$$\text{Li}^+(\text{OH}_2)_6 \quad \text{F}^-(\text{H}_2\text{O})_4$$

LiF highly soluble, both Li$^+$ and F$^-$ stabilised in water

In water, solubility depends on the enthalpy of cation and anion solvation being larger than the lattice energy

$$|\Delta H_{\text{sol}}| > |\Delta H_{\text{latt}}|$$

LiF soluble

MgO insoluble
Non-Hydrogen Bonded Solvents

Contrast with H₂O Aprotic

1. Only weakly associated - easy to create vacancies for ions.

2. Anions barely solvated - LiF insoluble
   Br⁻, I⁻ or better still ClO₄⁻, BF₄⁻, BPh₄⁻ are all soluble.

3. Dissolution depends on the strength of the cation - solvent bond vs. the lattice energy i.e. only the cations promote dissolution.

4. ε low 5-40 stabilisation of ions by dipole interactions less important.

Examples
   acetonitrile CH₃CN propylene carbonate
Dissolution depends on local ion-solvent molecule interactions → solvation enthalpy.

Water - both cation and anion solvation competes with lattice energy.

Non-aqueous → only cation competes with lattice

<table>
<thead>
<tr>
<th>LiF</th>
<th>LiClO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insoluble</td>
<td>soluble</td>
</tr>
</tbody>
</table>
Anions less strongly solvated; barely solvated in non-aqueous solvents.

First: ions interact with the solvent molecules immediately surrounding them
ion-solvent interactions

Second: ions interact with each other. Around any ion there will be an atmosphere of oppositely charged ions. Net negative charge around each cation will interact electrostatically with it
→ lower energy.

This is termed Debye-Hückel ion atmosphere ion-ion interactions
If ions highly charged and/or solvent has low dielectric constant, \( \varepsilon \), then

**ION PAIRING**

\[
M^+ + X^- + (MX)^0
\]

e.g. LiClO\(_4\) in THF
Electrolytes

Polymer electrolytes are particularly promising-safety

However, liquids now widely commercialised in solid state batteries.

Organic electrolyte encapsulated in polymer mesh
Solid Polymer Electrolytes

Many salts can be dissolved in organic solvents.

e.g. LiClO₄ in CH₃O-[CH₂-CH₂-O]₂-CH₃
    (linear chain ether)

instead of [CH₂-CH₂-O]₂ we can have [CH₂-CH₂-O]ₙ where n=100, 1000, etc
⇒ organic polymer - polyethylene oxide

When n is large → polymer is a solid at room temperature.

But salts may still be dissolved in the high m.wt. polymers by e.g. melting polymer

Films may be prepared 100nm thick of polymeric solids with dissolved salts
The cations and anions are mobile within the solid polymer film

LiClO$_4$ in polyethylene oxide (1 million molecular weight) has a conductivity of

$10^{-3} \ \Omega^{-1} \text{cm}^{-1}$ at $\sim$100$^\circ$C

equal to 1M LiClO$_4$ in diethylether at RT

Polymer electrolytes with this conductivity at room temperature are now known

e.g.

```
  CH       CH       CH
   \     /       /       /
   CH$_2$ CH$_2$ CH$_2$
   \   \   \       /
   O    O    O       /
   CH$_3$ CH$_3$ CH$_3$
```

Flexible back-bone with ethylene oxide side chains $\Rightarrow$ high conductivity
Table 1. Nonaqueous Electrolytes for Li-Ion Batteries

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>Example of classical electrolytes</th>
<th>Ionic conductivity ($\times 10^{-3}$ s/cm) at room temp</th>
<th>Electrochemical window (V) vs Li$^+/Li^0$</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid organic</td>
<td>1M LiPF$_6$ in EC:DEC (1:1)</td>
<td>7$^3$</td>
<td>1.3$^7$</td>
<td>4.5$^6$</td>
</tr>
<tr>
<td></td>
<td>1M LiPF$_6$ in EC:DMC (1:1)</td>
<td>10$^3$</td>
<td>1.3$^7$</td>
<td>&gt;5.0$^3$</td>
</tr>
<tr>
<td>Ionic liquids</td>
<td>1M LiTFSI in EMI-TFSI</td>
<td>2.0$^{15}$</td>
<td>1.0$^{15}$</td>
<td>5.3$^{15}$</td>
</tr>
<tr>
<td></td>
<td>1M LiBF$_4$ in EMI-BF$_4$</td>
<td>8.0$^{15}$</td>
<td>0.9$^{16}$</td>
<td>5.3$^{16}$</td>
</tr>
<tr>
<td>Polymer</td>
<td>LiTFSI-P(EO/MEEGE)</td>
<td>0.1$^{24}$</td>
<td>&lt;0.0$^{24}$</td>
<td>4.7$^{24}$</td>
</tr>
<tr>
<td></td>
<td>LiClO$_4$–PEO$_8$ + 10 wt % TiO$_2$</td>
<td>0.02$^{26}$</td>
<td>&lt;0.0$^{26}$</td>
<td>5.0$^{26}$</td>
</tr>
<tr>
<td>Inorganic solid</td>
<td>Li$<em>{4-x}$Ge$</em>{1-x}$P$_x$S$_4$ ($x = 0.75$)</td>
<td>2.2$^{28}$</td>
<td>&lt;0.0$^{28}$</td>
<td>&gt;5.0$^{28}$</td>
</tr>
<tr>
<td></td>
<td>0.05Li$_4$SiO$_4$ + 0.57Li$_2$S + 0.38Si$_2$</td>
<td>1.0$^{30}$</td>
<td>&lt;0.0$^{30}$</td>
<td>&gt;8.0$^{30}$</td>
</tr>
<tr>
<td>Inorganic liquid</td>
<td>LiAlCl$_4$ + SO$_2$</td>
<td>70$^{20}$</td>
<td>-</td>
<td>4.4$^{20}$</td>
</tr>
<tr>
<td>Liquid organic + Polymer</td>
<td>0.04LiPF$_6$ + 0.2EC + 0.62DMC + 0.14PAN</td>
<td>4.2$^{38}$</td>
<td>-</td>
<td>4.4$^{38}$</td>
</tr>
<tr>
<td></td>
<td>LiClO$_4$ + EC + PC + PVdF</td>
<td>3.0$^{39}$</td>
<td>-</td>
<td>5.0$^{39}$</td>
</tr>
</tbody>
</table>
Electrolyte characteristics for Batteries

1) Large electrolyte potential window $E_g$ so does not decompose across potential range:
2) Retention of the electrode/electrolyte interface during cycling when the electrode particles are changing their volume.
3) A Li-ion conductivity $\sigma_{\text{Li}} > 10^{-4}$ S/cm over the temperature range of battery operation.
4) An electronic conductivity $\sigma_e < 10^{-10}$ S/cm.
5) A transference number $\sigma_{\text{Li}} / \sigma_{\text{total}} \sim 1$
6) Chemical stability over ambient temperature ranges and temperatures in the battery under high power.
7) Chemical stability with respect to the electrodes, including the ability to form rapidly a passivating solid/electrolyte-interface (SEI) layer.
8) Safe materials, i.e., preferably nonflammable and nonexplosive if short-circuited.
9) Low toxicity and low cost.
Schematic representations of polymer electrolyte networks.

a, Pure (dry) polymer consisting of entangled chains, through which the Li ions (red points) move assisted by the motion of polymer chains.

b, A hybrid (gel) network consisting of a semicrystalline polymer, whose amorphous regions are swollen in a liquid electrolyte, while the crystalline regions enhance the mechanical stability.

c, A poly-olefin membrane (Celgard for instance) in which the liquid electrolyte is held by capillaries.
1 PEO-LiCF$_3$SO$_3$;
2 new solutes with high-dissociation PEO-Li [(CF$_3$SO$_2$)$_2$N] bis(trifluoromethanesulfone)imide (TFSI)
3 low-Tg combination polymer;
4 plasticized polymer electrolyte PEO-Li[(CF$_3$SO$_2$)$_2$N] +25% w/w PEG-dimethylether (mol wt, 250)
5,6 liquid crystalline polymer electrolytes
7 gel-type polymer (X-linked PEO-dimethacrylate- Li [(CF$_3$SO$_2$)$_2$N]-PC 70%);
8 liquid electrolyte PC/DME LiCF$_3$SO$_3$; trifluoromethanesulfonate
9 liquid electrolyte EC/DMC-LiPF$_6$ at low temperature ;
10 gel electrolyte P(VDF-HFP)/EC/DMC-LiPF$_6$. 
Local Coordination

(b) Crystal structure of the \(\text{(PEO)}_3: \text{NaClO}_4\) complex.
Crab-like motion assisted by chains

Fig. 5.5 Cartoon of ion motion in a polymer.

Solid State Electrochemistry Bruce
Crystalline vs Amorphous Polymer Electrolytes

Fig. 5.3 Comparison of the temperature-dependent conductivities for amorphous PEO:NH$_4$SCN (circles) and crystalline PEO:NH$_4$SCN (squares).
Polymer Electrolytes do form Crystalline Phases with salts

Fig. 5.10 Phase diagram of the PEO–LiClO₄ system. From Vallée et al. (1992).
Crystal Structure

Fig. 5.11 (a) Crystal structure of the \((\text{PEO})_3\):NaI complex.
Crystalline polymer electrolytes

P. G. Bruce *et al.* *Nature* **412**, 520 (2001);
Figure 2 Ionic conductivity $\sigma$ (S cm$^{-1}$) of amorphous (open circles) and crystalline (filled circles) PEO$_6$:LiSbF$_6$ as a function of temperature.

Note
MWt 1000 Xlline vs 100,000 Amorphous
Putting together a lithium battery

Figure 4: Schematic drawing showing the shape and components of various Li-ion battery configurations. **a.** Cylindrical; **b.** coin; **c.** prismatic; and **d.** thin and flat. Note the unique flexibility of the thin and flat plastic LiION configuration; in contrast to the other configurations, the PLiION technology does not contain free electrolyte.
CH5715
Energy Conversion and Storage

Ionic Conduction 2

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Electrolytes

Polymer electrolytes are particularly promising-safety

However, liquids now widely commercialised in solid state batteries.

Organic electrolyte encapsulated in polymer mesh

Solid electrolytes not widely used now

Considerable interest in incorporating batteries into printed circuit boards - crystalline electrolytes

LiI formed in situ has been used, similar to AgI
Ion-Conducting Membranes

Ionic Conductivity \((\text{Scm}^{-1})\)

Ionic crystals \(< 10^{-13} - 10^{-4}\)
Solid Electrolytes \(10^{-4} - 10\) - ceramic membranes
Ion-conducting polymers \(10^{-4} - 10^{-2}\)
Strong liquid electrolytes \(10^{-3} - 10^{1}\)

\[ \sigma = ne\mu \]

\[ \mu = f(T) \quad \text{Nernst Einstein relation} \quad \mu = qD/kT. \]
SOLID ELECTROLYTES

![Graph showing the logarithm of conductivity (σ) versus reciprocal temperature (1000/T) for various solid electrolytes. The graph includes lines for α-AgI, conc. H₂SO₄, RbAg₄I₅, Na β-alumina, ZrO₂, CaF₂, AgCl, Na₃Zr₂PSi₂O₁₂, and β-AgI.]}
Ionic Radii

Covalent Radius 100 picometres

H⁺: 0.0 Å
[OH⁻]: 95 Å
H⁻: 145 Å
[NH₄⁺]: 1.48 Å
[N⁻]: 1.71 Å
[O⁻]: 1.40 Å
[F⁻]: 0.72 Å

Li⁺: 68 Å
Na⁺: 97 Å
K⁺: 133 Å
Rb⁺: 147 Å
Cs⁺: 167 Å
Be²⁺: 35 Å
Mg²⁺: 66 Å
Ca²⁺: 99 Å
Sr²⁺: 122 Å
Ba²⁺: 134 Å

Al³⁺: 61 Å
Ga³⁺: 62 Å
In²⁺: 81 Å
Tl⁺: 147 Å
Tl³⁺: 95 Å

P³⁻: 212 Å
S²⁻: 184 Å
Se²⁻: 198 Å
Te²⁻: 221 Å
I⁻: 216 Å

Sc³⁺: 81 Å
Ti³⁺: 76 Å
V³⁺: 88 Å
Cr³⁺: 74 Å
Mn³⁺: 80 Å
Fe³⁺: 74 Å
Co³⁺: 63 Å
Ni²⁺: 69 Å
Cu²⁺: 96 Å
Zn²⁺: 74 Å

Pd²⁺: 80 Å
Ag⁺: 126 Å
Cd²⁺: 97 Å
Pt²⁺: 80 Å
Au⁺: 137 Å
Hg²⁺: 110 Å
- Verbraeken Nature Materials 2015
CRYSTALLINE IONIC CONDUCTORS

- Defects in solids
- Ionic migration in solids
- Fast ion conductors
- Examples of Solid Electrolytes
How do ions move in solid electrolytes?

General requirements

1. Mobile ions must partially occupy a set of energetically equivalent or near equivalent sites.

2. The sites must be interconnected by continuous pathways.

1. Partial occupancy
A perfect crystal of NaCl would not support ionic conductivity. Schottky defects → a few Na\(^+\) and Cl\(^-\) vacancies → ions can move.

Solid electrolytes are good conductors - contain many ions and many vacancies i.e. occupancies of 10% to 90%.
Schottky Vacancies
Point defects and cation migration

(a) Vacancies (vacant lattice site) [Schottky defect is $V_M^*$ plus $V_X^*$]

(b) Interstitials (atom on an interstitial site)

Frenkel defects (vacancy plus interstitials)
Intrinsic Conductivity

\[ K = \frac{[V_{Na}][V_{Cl}]}{[Na^+][Cl^-]} \approx \frac{N_N^2}{N^2} \]

\( E_f = \) Energy of formation for \( V_{Na} \) and \( V_{Cl} \)

\[ K = C \exp(-E_f / kT) \]

\( \therefore N_N = N \sqrt{C \exp(-E_f / kT)} \]

\( = C \exp(-E_f / 2kT) \)
Extrinsic conductivity

Aliovalent doping

\[ \text{eg } \text{NaCl} \quad 2 \text{Na}^+ \rightarrow \text{Cd}^{2+} + \text{V}_{\text{Na}}^- \]

\[ \text{ZrO}_2 \quad 2 \text{Zr}^{4+} \rightarrow 2 \text{Y}^{3+} + \text{V}_{\text{O}}^{2+} \]

\[ \text{CaF}_2 \quad \text{Ca}^{2+} \rightarrow \text{Y}^{3+} + \text{F}_i^- \]
Jump mechanism in 3d space

Influence of dopants on conductivity behaviour in NaCl
Vacancy and Interstitial Conduction Mechanisms

Interstitialcy mechanism
Ionic Migration/Ionic Conductivity

Ionic Conductivity (Scm\textsuperscript{-1})

Ionic crystals < 10\textsuperscript{-13} - 10\textsuperscript{-4}
Solid Electrolytes 10\textsuperscript{-4} - 10
Strong liquid electrolytes 10\textsuperscript{-3} - 10\textsuperscript{1}

\[ \sigma = ne \mu \]

\[ \mu = f(T) \] Nernst Einstein relation \[ \mu = qD/kT. \]
2. Pathways
e.g. move between two tetrahedral sites

through a narrow bottleneck.
Potential Energy Profile

ion vibrates in its site, $v^o = 10^{13} \text{ s}^{-1}$

Boltzmann distribution of energies

Each second a proportion, $v$, of the $10^{13}$ vibrations ($v^o$) will have enough energy to escape the site (i.e. $\geq E$)

$v =$ no. of successful jumps

hopping mechanism
\( \mu \) s function of \((v,d)\)

where \( \mu \) - mobility of the ion
\( d \) - jump distance between sites

\[
\mu = \mu^\circ \exp\left(-\frac{E}{RT}\right) \\
\sigma = c(1-c)q\mu^\circ \exp\left(-\frac{E}{RT}\right) \\
\]
c - concentration
q - charge

\[\text{In}c(1-c)q\mu^\circ \text{In}\sigma \quad \text{vs} \quad \frac{1}{T}\]
Ionic hopping model

Arrhenius equation

\[ \sigma T = A \exp\left(-\frac{E_a}{kT}\right) \]

A - relates to number of carriers per unit volume,
\[ a_0^2, \]
jump frequency
\[ E_a = \text{Activation Energy} \]
Equation for conductivity contains number of vacancies plus a term which indicates how easily they move through the crystal lattice.

\[ \sigma = N \frac{q^2}{kT} \gamma \left[ V_o \right]_s \left( 1 - \left[ V_o \right]_s \right) a_0^2 \nu_0 \exp \left\{ \frac{-\Delta H_m}{kT} \right\} \]

\( \Delta H_m \) is “migration enthalpy”

- Ions jump from site to site
- Requires a vacant site to jump into
- Jumps biased by electric field
- Jumps require thermal energy to get over energy barrier.
- Need low \( \Delta H_m \) for high ionic conductivity
Electrolytic domain

Electrons and holes have higher mobilities than ions
Variable valence metal ions (e.g. transition metals) are bad for solid oxide electrolytes
LaGaO$_3$ Oxide ion electrolyte

La$_{0.8}$Sr$_{0.2}$Ga$_{0.9}$Mg$_{0.1}$O$_x$

$V_O^{••}$ oxide ion conduction

$2V_O^{••} + \frac{1}{2}O_2 \rightarrow O_O^x + 2h^+$

Below 300°C in air electronic
Ionic transference number

\[ t_{\text{ion}} = \frac{\sigma_{\text{ion}}}{\sigma_{\text{ion}} + \sigma_{\text{el}}} \]

For a SOFC electrolyte working over a range of \( P_{O_2} \)

\[
\langle t_{\text{ion}} \rangle = \frac{\int_{\text{cathode}}^{\text{anode}} t_{\text{ion}} d(\ln(P_{O_2}))}{\ln(P_{O_2}^{\text{cathode}}) - \ln(P_{O_2}^{\text{anode}})}
\]

Need \( \langle t_{\text{ion}} \rangle \) to be close to 1 e.g. >0.99
In proton conductors there is a temperature gap where proton conduction is too low → The Norby Gap

*T. Norby, Solid State Ionics 125 (1999) 1*
SOLID ELECTROLYTES
Structure of Beta-Alumina

β

β’’
**β-Alumina**

\[ M_2O.nX_2O_3 \text{ - } M \text{ - Alkali, Cu, Ag, H}_3O, \]
\[ X \text{ - Al, Ga, Fe} \]

NaAl\(_{11}O_{17}\) ideal
Na - β (8-11), β"(5-7)

Structure consists of spinel blocks separated by less dense layers - conduction planes.

2 dimensional Na conductor

\[ E_a \sim 0.16 \text{ eV} \]
Beta battery

Na/S operates at 300-350°C

CELL REACTION: $2\text{Na} + \text{S} \rightleftharpoons \text{Na}_2\text{S}_5$ $2.08\text{V}$

The sodium–sulphur cell
Phase diagram for the sodium–sulphur system

practical sodium–sulphur cells. (By courtesy of British Railways Board)
Zebra Battery

ZEBRA Batteries are designed for electric and hybrid vehicles. They use salt and nickel for electrode materials with a ceramic electrolyte.

<table>
<thead>
<tr>
<th>Technical data</th>
<th>ZEBRA Battery</th>
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</thead>
<tbody>
<tr>
<td>Type</td>
<td>Z23</td>
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<tr>
<td>Z23-332-ML3X-76</td>
<td>30x6691</td>
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<tr>
<td>Capacity</td>
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<td>Rated Energy</td>
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<tr>
<td>Open circuit voltage</td>
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<td>0 - 16% DOD</td>
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<tr>
<td>Max. regen. voltage</td>
<td>V</td>
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<td>0 - 16% DOD</td>
<td>279</td>
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<td>Min. op. voltage</td>
<td>V</td>
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<td>Max. discharge current</td>
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<td>0 - 16% DOD</td>
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<td>Max. discharge current</td>
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<td>Cell Type / No. of cells</td>
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<td>Weight with BMI</td>
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<tr>
<td>Specific energy without BMI</td>
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<tr>
<td>Energy density without BMI</td>
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<td>Energy 2 h discharge</td>
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<td>Power density</td>
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<td>Peak power</td>
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<td>70% DOD, 23°C, 35°C</td>
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<td>Ambient temperature</td>
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<tr>
<td>Thermal loss</td>
<td>W</td>
</tr>
<tr>
<td>at 270°C internal temperature</td>
<td>&lt; 90</td>
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<tr>
<td>Cooling</td>
<td>air</td>
</tr>
<tr>
<td>Heating time</td>
<td>h</td>
</tr>
<tr>
<td>Periphery</td>
<td>24 h at 230 VAC</td>
</tr>
<tr>
<td>Fast charge</td>
<td>no fast charge</td>
</tr>
</tbody>
</table>

System design recommendation:
- MES-DEA Charger
- Min. discharging time: 120 min.
- Max. degree of discharge: 80%

The information contained herein is subject to change without notice

Components for Electric Vehicles

ZEBRA

Via Laveggio, 16 CH - 6866 Stabio - Switzerland
TEL +41 (0)91 6415211 FAX +41 (0)91 6415233 E-mail: info@mes-dea.ch internet: http://www.mes-dea.ch

Zebra battery
Li ion Conductors

Best are 1-2 orders of magnitude less conductive than Na β- alumina, ie $10^{-3} - 10^{-4}$ Scm$^{-1}$

Li$_3$N - layered structure Li, LiN$_2$
Li β alumina
Li$_{0.5}$La$_{0.5}$TiO$_3$
Various Li silicate frameworks - LISICON

Li polymer electrolytes are good alternative.
ANION CONDUCTORS

Fluorite anion conductors

PbF$_2$, SnPbF$_4$ $10^{-1}$ Scm$^{-1}$ at room temperature

La$_x$Sr$_{1-x}$F$_2$

ZrO$_2$ based ion conductors, Y$_2$O$_3$ and CaO doping

Conductivities $10^{-2}$ Scm$^{-1}$ at 1000°C
The ionic resistance of 1% CdCl₂ doped NaCl decreases with temperature according to Arrhenius behaviour, with an increase in activation energy for conduction from 0.7 eV to 1.3 eV at 500°C as temperature increases. Sketch this on a schematic Arrhenius type plot and suggest why this change occurs. Also add to this diagram a plot showing how the traces for 2% and 3% doping of NaCl with CdCl₂ would appear.