Contents

- Motivation
- Electrochemical driving force
- Electrolytes-Briefly
Motivation

Society is undergoing a rapid and enormous change in energy production and use with electrification of transportation, communications and storage.

This "revolution" is creating an enormous demand for individuals trained in the design, production and assembly of all types of batteries and at all levels of expertise.

There are no simple, established mechanisms whereby entry level individuals (including students) can gain the expertise needed to become functioning workers in the battery field.

Our goal is to provide a detailed introduction to batteries beginning at the most basic levels, moving to more sophisticated learning opportunities as needs require.
Estimated U.S. Energy Consumption in 2017: 97.7 Quads

- **Electricity Generation**: 37.2 Quads
  - **Net Electricity Imports**: 0.06 Quads

- **Residential**: 10.7 Quads
- **Commercial**: 8.99 Quads
- **Industrial**: 26.2 Quads
- **Transportation**: 28.1 Quads
- **Energy Services**: 31.1 Quads
- **Rejected Energy**: 66.7 Quads

- **Natural Gas**: 28.0 Quads
- **Coal**: 14.0 Quads
- **Biomass**: 4.91 Quads
- **Petroleum**: 36.2 Quads
- **Hydro**: 2.77 Quads
- **Wind**: 2.35 Quads
- **Geothermal**: 0.211 Quads
- **Nuclear**: 8.42 Quads
- **Solar**: 0.775 Quads

Total Energy Consumption: 97.7 Quads

Source: Lawrence Livermore National Laboratory
What is driving vehicle electrification?

Fleet-Averaged Light-Duty Fuel Economy—Sales Weighted (UMTRI)
Frontiers of electrochemical energy storage

What is a battery = electrochemical storage device?

It provides a mechanism to store energy in chemical form that can be translated into an electric current.

This current can be used to power:

- Lighting, electric motors (for vehicles of all types),
- electronics (phones, computers, displays), heating, etc.

In order to be useful it must:

- Light weight
- Provide electrical energy rapidly and safely on demand.
- It must be easily restored to its original electrochemical form (rechargeable) easily and rapidly for repeated reuse.
Electrochemical storage devices

- Fuel cells
- Batteries
- Supercapacitors

LiCoO$_2$

Batteries

Definition

- A battery is a storage device used for the storage of chemical energy and for the transformation of chemical energy into electrical energy.
- Batteries consist of groups of two or more electric cells connected either serial for voltage or in parallel for current.

Two major types:

- Primary batteries
- Secondary batteries
Components of a typical battery

1. Cathode
2. Anode
3. Electrolyte

Primary Batteries

- **Definition**
  - In primary cells, the chemical reaction occurs only once
  - Source of direct current power

- **Voltage ranging from 1.25-1.50 V, used in torches, radios, watches etc.**

- **Low-cost, but short life**

- **Zn-MnO₂ cell (dry cell)**
  - Oxidation at anode: \( \text{Zn}(s) \rightarrow \text{Zn}^{+2}(aq) + 2\text{e}^- \)
  - Reduction at cathode: \( 2\text{MnO}_2(s) + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3(s) + 2\text{OH}^- \)
  - Voltage: 1.5 V
Secondary Batteries

- Definition
  - In secondary cells, the chemical reactions are reversible
  - These cells can be recharged by electric current

- Secondary cells are widely used in electric and hybrid vehicles, smart phones, digital cameras, laptops, etc.
Lead acid battery

- At anode: Pb (s) + $SO_4^{2-}$ (aq.) $\rightarrow$ PbSO$_4$ (s) + 2e$^-$
- At cathode: PbO$_2$ (s) + $SO_4^{2-}$ (aq.) + 4H$^+$ (aq.) + 2e$^-$ $\rightarrow$ PbSO$_4$ (s) + 2H$_2$O
- Voltage: 2 V, used for railways, power stations (stand-by supplies)

Advantages:
- Reliable - constant potential
- Inexpensive
- Rechargeable, portable

Drawbacks:
- Low life cycle
- Low energy density (30 ~ 40 Wh/Kg)
- Use of H$_2$SO$_4$ is dangerous

https://byjus.com/chemistry/lead-acid-battery/
Nickel–cadmium cell

- At Anode: Cd (s) + 2OH⁻ (aq) → Cd(OH)₂ (s) + 2e⁻
- At Cathode: NiO(OH) (s) + 2H₂O + 2e⁻ → 2 Ni(OH)₂ + OH⁻(aq)
- Voltage: 1.4V
- In small electronic calculators, electronic flash units, etc.

Advantages:
- Rechargeable
- High energy density

Drawbacks:
- Self discharge (20-30 % per month)
- Memory effect
- Toxicity of cadmium

https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_(Zumdahl_and_Decoste)/11%3A_Electrochemistry/11.5%3A_Batteries
Li Ion Battery

- At anode: \( x\text{Li}^+ + xe^- + 6\text{C} \leftrightarrow \text{Li}_x\text{C}_6 \)
- At cathode: \( \text{LiCoO}_2 \leftrightarrow \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^- \)
- Compared to Ni-Cd batteries:
  - No memory effect
  - Higher voltages (~3 ×)
  - Self discharge <5 % per month

What is the source of the electrochemical driving force that allow batteries to operate?
What is the source of the electrochemical driving force?

The chemical driving force across a battery, $\Delta G$ (Gibbs free energy), can be defined as:

The ease with which the anode material gives up electrons = ease of oxidation

Group I & II metals are easily oxidized to $M^+$ or $M^{2+}$

The ease with which the cathode material picks up electrons = ease of reduction

Group 16 & 17 most easily reduced to form $E^{1-}$ and $E^{2-}$

The mass of these elements defines their utility for battery applications, lower mass/e$^-$ means higher energy density.

Thus, Li, Na, Mg are the lightest and most easily oxidized metals

Oxygen and sulfur are the lightest and most easily reduced elements.

Halogens are easier…but not practical…
Relation of the Gibbs energy with chemical potential

Chemical driving force across battery is $\Delta G = \text{chemical potential between two electrodes}$. 

Expressed as the difference in standard Gibbs free energy/mol of reaction.

Basically $\Delta G_{\text{free energy}}$ of products and reactants that occur at neutral electrodes.

$$\Delta G_{\text{reaction}} = -zFE = \Delta \mu$$

$Z = \text{the charge number of mobile ion}$
$F = \text{Faraday's constant 96,500 coulomb/mol}$
$E = \text{Voltage between electrodes}$
$\Delta \mu = \text{chemical potential – ability to be oxidized/reduced}$

The $G_{\text{free energy}}$ depends on the battery chemistry which relies on the electrodes
Typical cathode materials

layered LiCoO$_2$

spinel LiMn$_2$O$_4$

olivine LiFePO$_4$

2D

3D

1D

Dimensionality of the Li$^{+}$-ions transport
Selection criteria for cathode

- High redox potential (values)
- High specific capacity (mAh/g values)
- Reversibility
- Mixed conductor ($\sigma_{m+} = \sigma_{e-}$)
- Good stability with respect to electrolyte system(s)
Typical anode materials

<table>
<thead>
<tr>
<th>Anode</th>
<th>Reversible Specific capacity (mAh/g)</th>
<th>Irreversible Specific capacity (mAh/g)</th>
<th>Average Voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>372</td>
<td>15-30</td>
<td>0.2-0.1</td>
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<tr>
<td>SnO₂</td>
<td>782</td>
<td>711</td>
<td>0.7-0.4</td>
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<tr>
<td>SnO</td>
<td>875</td>
<td>398</td>
<td>0.7-0.4</td>
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<tr>
<td>Sn</td>
<td>993(^\text{(*)})</td>
<td>-</td>
<td>0.7-0.4</td>
</tr>
<tr>
<td>Si</td>
<td>4,211(^\text{(*)})</td>
<td>-</td>
<td>0.4-0.1</td>
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<tr>
<td>Li</td>
<td>3,862</td>
<td>-</td>
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</tbody>
</table>

Define irreversible, asterisk?
Categories of anodes

- Intercalation
- Li metal
- Insertion
- Conversion (alloy)
Selection criteria for anode

- Low redox potential values
- High specific capacity (mAh/g values)
- Reversibility
- Mixed conductor ($\sigma_{m+} = \sigma_{e-}$)
- Constant voltage
Electrolytes
will be described in separate lectures

1. Liquids
2. Solids
3. Polymer
4. Composite or hybrid
Criteria for electrolytes

1. Wide potential window
2. High ionic conductivity
3. Chemically & electrochemically inert
4. Wide operating temperature range
5. Low volatility and flammability
6. Environmentally friendly

Traditional liquid electrolytes

- Low viscosity, polar liquids capable of dissolving $M^+/M^{2+}$ and anions.
- Operational window -40 °C to ≈ 60 °C.
- Typical Li$^+$ diffusion rates values
- Low flammability

# Traditional liquid electrolytes

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Structure</th>
<th>M. Wt</th>
<th>$T_m/^\circ C$</th>
<th>$T_b/^\circ C$</th>
<th>$\eta$/cP $25^\circ C$</th>
<th>$\varepsilon$ $25^\circ C$</th>
<th>Dipole Moment/debye</th>
<th>$T_p/^\circ C$</th>
<th>$d$/g/cm$^3$, $25^\circ C$</th>
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<td>1</td>
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<td>-125</td>
<td>85</td>
<td>0.60</td>
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<td>0.54</td>
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</table>

Polymeric electrolytes

- Multifunctional
- Flexible
- Good mechanical properties
- Moderate thermal stability
- Safe

Polymeric electrolytes

Solid polymer electrolytes (SPE)

- Polymer matrix + lithium salt

- Good safety, easy fabrication, low cost, high energy density, good electrochemical stability, and excellent compatibility with lithium salts

- But poor ionic conductivity at room temperature ($10^{-5}$-$10^{-1}$ mS cm$^{-1}$)
Polymeric electrolytes

Gel polymer electrolytes (GPE)

- Incorporate liquid plasticizer and/or solvent into a polymer–salt system.
- Conductivity can reach 1 mS cm\(^{-1}\), but poor mechanical strength and poor interfacial properties.
Progress with solid electrolytes

Advantages of solid-state electrolytes

details later in course

- Inorganic solid-state electrolytes enable robust cell chemistries
  - No electrolyte leakage
  - No organics to degrade
  - Improved safety – non-flammable
  - Could enable Li metal and high voltage cathodes (values)
  - Enhanced thermal stability
  - Could be fabricated in air
- High Li\textsuperscript{+} transference numbers values vs:
  - > 0.25 – liquid electrolyte these values are for liquids?
  - > 0.5 – polymer electrolyte
Introduction to Battery architecture
Lecture 2

Taylor Brandt, Mengjie Yu, Richard M. Laine, Eleni Temeche, Xinyu Zhang,
University of Michigan
Copyright: Laine Group, University of Michigan
Battery Architecture
  - Cell format

Components in:
  - Coin cell
  - Prismatic cell
  - Pouch cell

Solid state battery assembly
Cell formats

- Cylindrical cells
- Prismatic cells
- Pouch cells
- Coin cells

https://learn.sparkfun.com/tutorials/what-is-a-battery/all
Cylindrical Cells—Jelly Roll

**Definition**
- Cell with positive, negative electrodes, and separator in cylindrical container

Cylindrical Cells

- Advantages:
  - Good mechanical stability
  - High energy density
  - Lowest cost to manufacture
  - Mass produced in standard sizes
    - E.g. 18650 cell: 18 mm diameter, 65 mm length

- Challenges:
  - Low packaging efficiency
    - Relative heavy packing material

- Applications:
  - Traditional: power tools, medical instruments
  - New demands: military, drones and electric car

Cell formats prismatic cells

- **Definition**
  - Cell where positive, negative plates, and separator, stacking in prismatic container

M Zschornak et al., *Physical Sciences Reviews*, 2018, 20170111
https://www.vpwllc.com/prismatic-cells/
Prismatic Cells

Advantages:
- Hard case provides protection
- No standard size – advantage in design
  - Customizable packaging to meet cell/pack requirements

Challenges:
- No standard size – disadvantage in production
- Harder/more expensive to manufacture
  - Larger cells difficult for automated assembly
  - Often ineffective in high pressure situations

Applications:
- Mobile phones, tablets and laptops

M Zschornak et al., *Physical Sciences Reviews*, 2018, 20170111;
https://www.vpwllc.com/prismatic-cells/
Coin Cells

- **Definition**
  - Miniature battery w/circular cross-section
  - Overall height < diameter

- **Typical format for testing materials**

  - Top cap
  - Spring
  - Spacer
  - Anode
  - Electrolyte
  - Separator
  - Cathode
  - Bottom cap

Coin Cells

Advantages:
- Easy & cheap to manufacture
- Standardized sizes

Challenges:
- Usually single layer – limited capacity
- Often require slow charge rates
- Performance not scalable

Applications:
- Portable: cordless telephones, medical devices

https://en.wikipedia.org/wiki/Button_cell
Symmetric cell

- Uses 2 identical electrodes
  - One lithiated, the other delithiated
- Limits Li supply and Li foil reactions with electrolytes
- Differs from full cell
  - Only side reactions induced by the range of tested electrode’s potential can be observed

Half cell

- Using Li foil as reference/counter electrode
- Easy to make, can provide repeatable data
- Abundance of Li
  - Unable to observe problems with Li consumption

Pouch Cells

- **Definition**
  - Prismatic cell with metallic case replaced with flexible, heat-sealable foil package

Pouch Cells

- **Advantages:**
  - Lightweight packaging
    - Optimized packing efficiency >95%
  - Easily stackable

- **Challenges:**
  - No inherent protection against swelling
    - High temperature and humidity shorten cell life
    - Robust cell packaging required at pack level
  - Electrode delamination
    - Works best with pressure on stack

https://www.vpwllc.com/pouch-cells/
https://www.stockwell.com/blog/designing-battery-pad-for-li-ion-pouch/
Pouch Cells

- Commercial battery packs

- Applications:
  - Electric bikes, scooters
  - Consumer electronics
  - Electric tools

http://www.talgaresources.com/IRM/content/default.aspx
https://battery-system.com/product/3-7v-lipo-battery-pack-pouch-cell
Pouch vs coin cells--utility for research

- **Pouch cells:**
  - High area capacity cathode (3.8 mAh cm$^{-2}$)
  - Limited Li (N:P ratio of 2.6)
    - Areal capacity of anode to cathode
  - Lean electrolyte (E/C ratio of 3.0 g Ah$^{-1}$)
    - E/C ratio: electrolyte mass to capacity
  - Commercial Li$^+$ batteries: N/P ~1.1, E/C ~1.3 g Ah$^{-1}$

- **Typical Li metal coin cells (half cell):**
  - Low area capacity cathode (~1.0 mAh cm$^{-2}$)
  - Large excess Li (N:P ratio of 50)
  - Flooded electrolyte (E/C ratio >75 g Ah$^{-1}$)
  - Inconsistent results with practical batteries

---

Pouch cell processing Z-stacking

- Z-stacking is more commonly used in industry

<table>
<thead>
<tr>
<th>Electrodes</th>
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<td>discrete</td>
<td>continuous</td>
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<table>
<thead>
<tr>
<th>Separator</th>
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<tbody>
<tr>
<td>discrete</td>
<td>stacking</td>
</tr>
<tr>
<td>continuous</td>
<td>z-folding</td>
</tr>
</tbody>
</table>

Regular stacking: Stacked electrodes & stacked separators

Z-stacking: Stacked electrodes & Z-folded separators

Z-stacking: Z-folded electrodes & Z-folded separators

Pouch cell processing regular-stacking

(a) Cu and Al electron collectors  (b) Coat active materials  (c) Insert separators

(d) Stacking  (e) Electrode-to-tab joining  (f) Fill electrolyte and seal
Pouch cell case Al laminated film

- Punch Assembly

Materials:
- Nylon
- Al
- Polypropylene
- Adhesives

References:
- https://www.tvservice.basf.com/portal/basf/en/dt.jsp?setCursor=1_203919_492322&cursorPath=%7C492298%7C481768%7C492296%7C492298&setClientType=Desktop
- https://www.mtixtl.com/AluminumLaminatedFilm400mmWx7.5mL-EQ-alf-400-7.5M.aspx
Pouch cell case Al laminated film

- **Nylon:**
  - Keeps the shape of aluminum laminated film
  - Avoids deformation before manufacture

- **Aluminum:**
  - A layer of metal Al
    - **Al** reacts with oxygen to form a dense oxide film that prevents water and gas from penetrating
  - Blocks moisture infiltration (Nylon not waterproof)
  - Provides the plasticity for punching

- **Polypropylene:**
  - Heating PP layer causes melting/bonding to seal cells
    - Melting temperature ~ 100°C and PP is viscous

- **Thickness: 71 - 156 μm**
  - Different thickness for each layer in different models

https://www.targray.com/li-ion-battery/packaging-materials/aluminum-laminate-pouch
Pouch cell processing electrode-to-tab joining

- **Tab/terminal:**
  - Cathode: Al
  - Anode: Ni or Cu

- **Sealant:**
  - Usually contains PP
  - Bond with cell case (Al laminated film) under heating

- **Electrode-to-tab weld:**
  - Gather all the current collectors inside a cell
  - Join all current collectors to a tab which exits casing
  - Allow energy to be transferred to external sources

http://www.soteriabig.com
https://www.targray.com/li-ion-battery/packaging-materials/tabs
### Commonly used welding methods

- **Ultrasonic friction welding (UMW)**
  - Join substrate materials by high frequency ultrasonic vibration (>20 kHz) to under a clamping pressure

- **Resistance spot welding (RSW)**
  - Metal sheets welded together by electrical current and pressure between two electrodes

- **Laser Beam Welding (LBW)**
  - Materials fused together by concentrated heat generated by a laser beam

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**Working principles of**

- UMW
- RSW

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*J. Coignard et al., World Electr. Veh. J. 2018, 9(2), 22*

Seal--temporary seal

- Temporary seal:
  - Cell is completely sealed with an air receiver/air bag
  - Electrolyte wets/saturates electrodes

- Formation:
  - Cyclic charge/discharge, form SEI
  - Air receiver collects produced gas
Warm-pressing:
- Improve uniformity of cell flatness and thickness
- Drive air out into receiver
- Closely press separators and electrodes together
- Shorten Li$^+$ diffusion distance to reduce internal resistance

Final seal:
- Degas
  - Air receiver punctured 1st under vacuum to remove residual gases
- Cell vacuum-seal
  - An important step
- Remove air receiver
  - Last step in assembly
- Preferably limit time between formation and degassing

https://www.mtixtl.com/8mmWidthNickelTabasNegativeTerminalforPolymerLi-ionBattery50pcs.aspx
Challenges of Li$^+$ battery architecture

- Volume changes & structural degradation due to Li insertion/deinsertion
- Liquid electrolyte leakage
- Current collector corrosion
- High peripheral mass & housing package size
  Decreases the energy density

Development of SSBs could overcome these challenges
Solid state batteries architecture

Solid State
- current collector
- anode
SSE
- cathode
+ current collector

Active material
Solid state conductor
Carbon and binder

Hybrid
- current collector
- anode
SSE
- cathode
+ current collector

Active material
Carbon, binder, Li ion electrolyte (liquid/polymer)

Anode free- solid state batteries

Porous separator vs. solid electrolyte separators
2-D battery configuration

- 2D battery design compromise between energy density and power density because of the limitation in footprint area.

- Limited areal capacity 0.5 – 5 mAhcm\(^{-2}\)

- Making electrodes thicker in order to store more energy is not a viable approach
  - The mechanical integrity of the film decreases due to expansion and contraction of the active materials during cycling
  - Thicker films reduce the power density of the device

MCMB, mesocarbon microbeads.

3-D battery configuration

- 3D battery architectures takes advantage of the third dimension, height,
  - The amount of electrode material within a given footprint area is high
  - Areal capacity ~ 10 mAhcm\(^{-2}\)
  - Energy density and power density are effectively decoupled
  - Anode and cathode arrangements are unaffected by the additional thickness

Solid state batteries--micro batteries

3D micro batteries for MEMS devices

- Powering autonomous systems for applications e.g. medical implants, communications, & sensing
- 3D micro batteries use nanostructures to increase areal capacity; high surface area enables fast charging and discharging
  - Thin films deposited in trenches, pores, nanowires, or other structures to increase effective area within the same footprint.

Examples of 3-D battery configuration

Geometries to overcome material limitations

- Material properties at the nanoscale can differ from bulk properties
  - Nano and microscale geometry can result in different apparent properties

- Significantly higher surface to volume ratio - fast charge/discharge

In situ TEM tensile testing of Si nanowires

Si Nanowire Anodes

- Si volume changes drastically (400%) during Li insertion and removal
  - structural damage
  - Loss of electronic contact
- Nanowire morphology:
  - Leaves open space for expansion
  - Size dependent material properties
  - Direct electrical contact with current collector

Li plating: Textures Li Surface

- Mechanically stamped Li electrode
- Li plates in pits (where there is higher current density)
- Suppresses uncontrolled Li dendrite growth

Nano - Cu current collectors

- Inhomogeneities occur plating Li onto planar current collectors
  - Nucleation creates hotspots that grow into dendrites

- Microporous Cu current collectors
  - More uniform current density
  - Higher surface area - lower local current density
  - Li fills in the pores and dendrites are suppressed

- Scale and pore size matters
  - <5um pores performed significantly better than ~170um pores

Challenges for implementing 3D geometries

• SEI formation on high surface areas can be particularly detrimental
• SSBs require thin, conformal pinhole free films
  • Continued development of solid-state electrolytes
• In many cases, nano & micro-structures slow and costly to produce
  • Production scalability
  • Competitive market pricing
• Many approaches require further rigorous testing under a variety of conditions
  • Depth of charge/discharge
  • Rate of charge/discharge
Battery component design
Lecture 3

Taylor Brandt, Mengjie Yu, Richard M. Laine, Eleni Temeche, and Xinyu Zhang,
University of Michigan
Copyright: Laine Group, University of Michigan
Content

- Battery component design
  - Electrode
  - Electrolyte
  - Current collector
  - Binder
Battery management systems
Battery chemistries vs. energy density

Battery components

Electrode capacity: how much Li/mass (mAh/g)

Q. C. Horn and K. C. White. ECS meeting, 2007
Electrode design

Material loading to prepare electrodes

- **Active Material (AM) content**
  - Ideally maximizes AM content
  - Common cathode formulation - 94:3:3 (AM : Conductive Carbon : Binder)
  - Common anode formulation - 95:5 (AM : Binder)

- **High cell specific energy (Wh/kg) requires highest areal capacity**
  - Focus on ↑ AM wt.% and ↓ current collector mass
  - **Drawbacks:**
    - ↑ loading electrode ↓ power performance
    - Manufacture difficulties
Electrode Design

- **N:P Ratio**
  - Areal capacity [mAh cm\(^{-2}\)] of anode: cathode
  - Important to avoid overcharge
  - Capacity balancing: slight oversizing of anode capacity to avoid Li metal plating
    - Commercial N/P ratio \(\approx 1.1–1.2 : 1\)
    - Decrease in specific energy w/increase in unused material mass and volume

Graphite anode (MCMB, 314 mAhg\(^{-1}\)) & NMC (220 mAhg\(^{-1}\)) cathode potential profiles for different N/P ratios \(\rightarrow (N:P)Q -\) capacity used by active materials mass \((N:P)m \rightarrow\) capacity by active mass

\[314 \text{mAhg}^{-1} \times 0.7013\]

Anodes

- Graphite
- Metals
- Alloys
- Oxides
- Silicon-based

http://www.eai.in/blog/2018/12/research-status-of-anode/cathode-material.html
Anodes—graphite

- Industry standard
- Long cycle life
- Limited energy density
  - Theoretical capacity ≈ 372 mAh/g
- Layered structure
  - Intercalate/deintercalate Li to LiC₆
  - Rüdorff model
    - Stage III: LiC₃₆
    - Stage II: LiC₁₂
    - Stage I: LiC₆

↑ Galvanostatic intercalation/deintercalation of lithium in graphite anode

← Cross section of a graphite anode

S.E Trask et al., *J. Power Sources*, 2014, 259, 233-244
Beguin, Francois et al., “Surface properties, porosity, chemical and electrochemical applications.”, 2019, 677, 495-549
Ideal, have highest theoretical energy density

- Lithium: 3860 mAh/g
- Sodium: 1166 mAh/g
- Magnesium: 3833 mAh/g

Thickness varies

- For some large-scale Li is 40 um
- For coin cells 750 um is common

Volume change

No stable/metastable SEI forms on Li surface

↑ Thickness change of Li metal anode

**Anodes--alloys**

- Improved stability
  - Lower reactivity, less dendrite formation
- Theoretical capacity > graphite
  - $\text{Li}_{3.75}\text{Si}$ (3578 mAh/g);
  - $\text{Li}_{3.75}\text{Ge}$ (1385 mAh/g);
  - $\text{Li}_{4.4}\text{Sn}$ (993 mAh/g);
  - $\text{Li}_3\text{Sb}$ (660 mAh/g)
- Lower cost
- Volume change & particle agglomeration
- Example: $\text{Mo}_3\text{Sb}_7$–C
  - Discharge capacity (518 mAh/g and 907 mAh/cm³)
  - Exhibit capacity fade at ≈ 70 cycles

† Comparison of cyclability of $\text{Mo}_3\text{Sb}_7$, $\text{Mo}_3\text{Sb}_7$–C, & graphite (0–2 V vs Li/Li⁺, current 100 mA/g AM)

Anodes--oxides

- Transition metal oxides
- 2D layer or 3D network structure
  - Reversibly intercalate Li into lattice without destroying xtal structure
- Example: lithium titanate (LTO) $\text{Li}_4\text{Ti}_5\text{O}_{12}$

![Diagram of discharge process of $\text{Li}_{x+4}\text{Ti}_5\text{O}_{12}$]

Competition $x$ in $\text{Li}_{x+4}\text{Ti}_5\text{O}_{12}$

G. Jian et al., *Chinese Physics B*, 2016, 25(1), 018210
T. F. Yi et al., *J. Mater. Chem. A*, 2015, 3, 5750
Example: lithium titanate (LTO)
- Theoretical capacity: 175 mAh g\(^{-1}\)
- Negligible volume change
- Compared to graphite:
  - Improved cycle life and calendar life
  - Improved pulsing impedance

LTO/LMO and G/LMO pouch cells
Area specific impedance measurements (55 °C, 28 d) (left)
Cell discharge capacity (6C, 55 °C) (right)

L. Belharouak et al., *J. Power Sources*, 2011, 196, 10344–10350
Example: LTO vs graphite

- Lower heat generation (safer)

DSC of fully charged Graphite/LMO (left) LTO/LMO (right) pouch cells

M. Pfanzelt et al., *J. Power Sources*, 2011, 196, 6815–6821
Anodes--oxides

- Example: LTO
  - Compatibility with electrolytes
    - Avoids electrolyte deduction & SEI formation
  - Elevated temperature tolerance
  - Gas swelling
  - Applied in high-power-density fields
    - E.g. vehicles

Air bag volume changes in LTO/NCM pouch cells after ageing at 55 °C

W. Liu et al., *J. Power Sources*, 2017, 369, 103-110
Anodes--Silicon

- High theoretical energy density
  - Crystalline Si: 3579 mAh/g

- Drawback:
  - High volumetric expansion on lithiation (up to 400%)
    - Breaks electrode during cycling - mechanically unstable
    - Engineering of Si particle sizes to reduce expansion effects
  - High cost
  - Low coulombic efficiency (50–80%)
  - Most likely be used as a composite with carbon
    - Improves electrical conductivity and mechanical properties

S. Chae et al., Joule, 2017, 1, 47–60
Anodes--Silicon

- Example: nano graphene–nano Si
  - Si largely amorphous after 1st charge
  - Particles expand >2x after the 1st charge & crack after 1st discharge

  →
  a. XRDs & SEM surface morphologies of
  b. Si-graphene electrode
  c. before/after 1st lithiation,
  d. before/after 1st delithiation
  in full cell test (cathode: NCA)

KS. Eom et al., *J. Power Sources*, 2014, 249, 118-124
Anodes--Silicon

- Example: nano graphene–nano Si
  - Continuous capacity decrease
    - Continuous SEI formation & Si pulverization - cell performance affected significantly by anode

Capacity fade
(C/15 in 1st-5th, C/5 in 5th -10th, C/2 in 10th-50th )
(cathode: NCA, electrolyte: LiPF$_6$)

KS. Eom et al., *J. Power Sources*, 2014, 249, 118-124
Example: graphite–SiO\textsubscript{x} 

- Li alkyl carbonates (e.g. Li\textsubscript{2}CO\textsubscript{3}, ROCO\textsubscript{2}Li) form on anode surface at temps > 40 °C
- Graphite–SiO\textsubscript{x} electrodes failure mechanism

Anodes--Silicon

- Example: graphite–SiO$_x$
  - Capacity drops
    - Anode deterioration main cell degradation factor

Cycle performance of NCA/graphite–SiO$_x$ pouch cell

C. Liu et al., J. Mater. Chem. A, 2018, 6, 65-72
Cathodes

- Oxides
  - Commercial
  - Near-future
  - Future
- Non-oxides

http://www.eai.in/blog/2018/12/research-status-of-anode/cathode-material.html
Cathode - Oxides

- General characteristics of commercial oxides for Li$^+$ battery cathode

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure</th>
<th>Potential versus Li/Li$^+$, average V</th>
<th>Specific capacity, mAh/g</th>
<th>Specific energy, Wh/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO$_2$</td>
<td>Layered</td>
<td>3.9</td>
<td>140</td>
<td>546</td>
</tr>
<tr>
<td>LiNi$<em>{0.8}$Co$</em>{0.15}$Al$_{0.05}$O$_2$ (NCA)</td>
<td>Layered</td>
<td>3.8</td>
<td>180–200</td>
<td>680–760</td>
</tr>
<tr>
<td>LiNi$<em>{1/3}$Co$</em>{1/3}$Mn$_{1/3}$O$_2$ (NMC)</td>
<td>Layered</td>
<td>3.8</td>
<td>160–170</td>
<td>610–650</td>
</tr>
<tr>
<td>LiMn$_2$O$_4$ and variants (LMO)</td>
<td>Spinel</td>
<td>4.1</td>
<td>100–120</td>
<td>410–492</td>
</tr>
<tr>
<td>LiFePO$_4$ (LFP)</td>
<td>Olivine</td>
<td>3.45</td>
<td>150–170</td>
<td>518–587</td>
</tr>
</tbody>
</table>
Commercial oxides
- Nickel cobalt manganese oxide (NCM)
  - High capacity & operating voltage
  - Slow reaction with electrolytes
  - Moderate safety (oxygen release)
  - High cost of Ni and Co
- Available in different stoichiometries
Nickel cobalt manganese oxide (NCM)
- Available in different stoichiometries
  - $\text{Ni}_x\text{Co}_y\text{Mn}_z$, $X+Y+Z=1$
  - Common XYZ (increasing Ni%):
    - 111 (154 mAh/g)
    - 532 (164 mAh/g)
    - 622 (175 mAh/g)
    - 811 (>185 mAh/g)
Cathode - Oxides

- Lithium manganese oxide (LMO)
  - Low cost
  - Excellent high rate performance
  - High operating voltage
  - Mn dissolution issue, low capacity
    - Now blended with NMC as cathode to suppress Mn dissolution

Layer structure (NMC*)
- Lithium: Li
- Metal: Mn, Co
- Oxygen: O

Optimized storage of Lithium ions

Spinel structure (LMO**)
- Lithium: Li
- Metal: Mn
- Oxygen: O

↑ Voltage profile of LMO

← Layered NCM structure stores more Li⁺ (applied by NISSAN)

https://www.nissan-global.com/EN/TECHNOLOGY/OVERVIEW/li_ion_ev.html
Lithium Iron Phosphate (LFP) $\text{Li}_x\text{FePO}_4$

- Slow reaction with electrolyte
- Safe
  - No oxygen release
- No resource limitations
  - Moderate cost
- Low operating voltage
- Low capacity

Voltage profiles (versus Li) of LFP compared with LiCoO$_2$ and NCM →

R.J. Brodd (ed.), *Batteries for Sustainability: Selected Entries from the Encyclopedia of Sustainability Science and Technology*, 2013
Cathode - Oxides

- Lithium Iron Phosphate (LFP) $\text{Li}_x\text{FePO}_4$
  - $\text{Li}_x\text{FePO}_4$ discharge processes

---

**Cathode - Oxides**

- **Lithium cobalt oxide (LCO)**
  - Energy density: 180 Wt/kg, capacity = 274 mAh/g
  - Low self-discharge, high discharge voltage ≤ 4.45 V
  - Good cycling performance
  - Used in small electronics

- **Nickel cobalt aluminum oxide (NCA)**
  - Al in NCA improves thermal & electrochemical properties
  - High capacity
  - High operating voltage
  - Excellent high rate performance
  - Slow reaction with electrolytes
  - Potential resource limitations (high Ni & Co costs)

Voltage profiles of first charging of LCO, NCA and NMC

R.J. Brodd (ed.), *Batteries for Sustainability: Selected Entries from the Encyclopedia of Sustainability Science and Technology*, **2013**
Most oxides suffer from **thermal runaway**

- **Thermal runaway**: occurs when as cell reaches temperature where becomes self-sustaining as it creates $O_2$ (explosive and flammable)
- Especially severe when fully charged
- Usually, the higher the energy density, the worse safety performance
  - High nickel materials especially susceptible
  - Cathode and electrolyte are main factors for safety issues in a cell/pack

---

Li-Air configurations—Future cathode

Li-O₂ (non-aq)
Discharge

Li metal

O₂

Li⁺

Li₂O₂

Organic electrolyte

Porous carbon + catalyst

2Li⁺ + 2e⁻ + O₂ ⇌ Li₂O₂

Li-O₂ (aq)
Discharge

Li metal

O₂

Li⁺

LiOH

Aqueous electrolyte

Li⁺-conducting membrane

Porous carbon + catalyst

O₂-evolution electrode

2Li⁺ + 2e⁻ + ½ O₂ + H₂O ⇌ 2LiOH

Advantages:
• High specific energy density
• Air is everywhere

Disadvantages:
• Existing issues with Li-metal batteries
• Decomposition of active materials
• Poor rate capacity/power output
• High charging overpotential

High charging overpotential

- Voltages (vs. Li/Li$^+$)
  - Discharging: ~2.7 V
  - Charging: 4-4.5 V

Can this overpotential be mitigated with photocatalysis?

Routes for photon-assisted charging
- Mediated
- Unmediated

\[ 2\text{Li}^+ + 2e^- + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2 \]

Mediated charging

- **Discharging**
  - Normal Li-air configuration

- **Charging**
  - Li-metal connected to photoelectrode

- **Photoelectrode:** Dye-sensitized TiO$_2$

- **Mediator:** I$_3^{-}$/I$^{-}$
  - Redox potential: +3.55V

- **Electrolyte:** LiI and LiClO$_4$ in dimethylsulfoxide

Mediated charging configuration

Charging voltage: ~2.6 V
• Theoretical charging voltage: 2.96 V
• Li₂O₂ completely degraded

• Stability concerns
Mediators at Li-metal electrode

Unmediated charging

- Electrolyte: LiTFSI in tetraglyme(G4)
- Oxygen electrode also acts as photoelectrode
  - Graphic carbon nitride on carbon paper

Unmediated charging

- Charging voltage: 1.96V
- Theoretical charging voltage: 2.96V
- Electrical efficiency: 140%
- Oxidized Li$_2$O$_2$ completely

Stability - unmediated charging

- Stable after 70 cycles at 0.01 mA/cm²
- Not as stable at 0.03 and 0.05 mA/cm²
- Charge transport limitations

Unmediated charging-nanostructures

- Oxygen electrode acts as photoelectrode
  - Defective rutile TiO2 nanorod assembly on carbon textiles
- Electrolyte: 0.5 M LiClO₄ in TEGDME
- Discharge in the dark
- Charge in the light

Charging is challenge for Li-Air batteries
  - $\text{Li}_2\text{O}_2$ overpotential

This can be mitigated with photon-enhanced charging
  - Mediated and unmediated approaches are available

Stability could be improved using nanostructures

Current density enhancement is needed for practical applications
Li-Sulfur

Discharge

Advantage
• High specific energy - 2600 Wh/kg
• Cheap, abundant
• Light
• 2 Li for every S(Li$_2$S)

Disadvantage
- Cycling
- Sulfur conductivity
- Li metal anode stability

Challenges of Li-S battery

Challenges of Li-S battery

- Formation of insulating Li$_2$S on the Li anode

Challenges of Li-S battery

Sulfur cathode issue

• Formation of lithium polysulfide ($\text{Li}_2\text{S}_x$, $4 \leq x \leq 8$)
  • Side reaction with lithium anode
  Resulting in :-
  • Low energy efficiency
  • Self-discharge
  • Poor cyclic stability

Lithium anode issue

• Formation of lithium platting
  • Irreversible loss of Li$^+$ - capacity loss
  • Degradation of electrodes
  • Internal short circuit

**Li$_2$S as a cathode**

- The Li$_2$S cathode must overcome a huge potential (1V) barrier at beginning of delithiation.

- Polysulfide intermediates serving as redox mediators to facilitate the direct electrochemical oxidization of Li$_2$S.

---

**Polysulfide I**

- $4\text{Li}_2\text{S} \rightarrow \text{Li}_2\text{S}_4 + 2\text{Li}^+ + 2\text{e}^-$
- $2\text{Li}_2\text{S}_4 \rightarrow \text{Li}_2\text{S}_8 + 2\text{Li}^+ + 2\text{e}^-$

**Polysulfide II**

- $\text{Li}_2\text{S}_8 + 2\text{Li}_2\text{S} \rightarrow 2\text{Li}_2\text{S}_2 + \text{Li}_2\text{S}_6$
- $2\text{Li}_2\text{S}_2 + \text{Li}_2\text{S}_8 \rightarrow 3\text{Li}_2\text{S}_4$
- $2\text{Li}_2\text{S}_4 \rightarrow \text{Li}_2\text{S}_8 + 2\text{Li}^+ + 2\text{e}^-$
- $4\text{Li}_2\text{S}_6 \rightarrow 3\text{Li}_2\text{S}_8 + 2\text{Li}^+ + 2\text{e}^-$

---

Battery basics

Solvation

Lecture 4

Richard M. Laine, Eleni Temeche, Xinyu Zhang, Lisa Buch,
Taylor Brandt, Philyoung Kim
University of Michigan
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Content

- Diffusion in liquid electrolytes
- How to understand activity
- Diffusion in liquid, polymer and solid, electrolytes
- Summary
In liquid electrolytes $\text{Li}^+$ diffusion governed by:

- Chemical potential
- Solvent polarity (dielectric constant)
- Viscosity
- Solvation sphere
- Temperature
- Counterions
Mechanism of ionic transport in liquids

- Li\(^{+}\) transport in liquids involves diffusion of solvated Li\(^{+}\).

- \(\sigma_{\text{Li}^{+}}\) in aprotic electrolytes controlled/enhanced by:
  - Increasing salt/ion dissociation- e.g. \textit{by increasing dielectric constants}
  - Promoting mobility of solvated ions- \textit{lowering solvent viscosity}

\[
D_o = \frac{k_B T}{6\pi\eta R_o}
\]

\(\eta\) – Viscosity

\(R_o\) – Radius of solvating cation

\(k_B\) - Boltzmann constant

\(D_o\) - Diffusion coefficient

Traditional liquid electrolytes

• Are low viscosity, polar liquids capable of dissolving M\(^{+}\)/M\(^{2+}\) and anions.

• Operational windows from -40 °C to ≈ 60 °C.

• Typical Li\(^{+}\) diffusion rates

• Low flammability

# Traditional liquid electrolytes

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Structure</th>
<th>M. Wt</th>
<th>T&lt;sub&gt;m&lt;/sub&gt;/°C</th>
<th>T&lt;sub&gt;b&lt;/sub&gt;/°C</th>
<th>η/cP 25°C</th>
<th>ε 25°C</th>
<th>Dipole Moment/debye</th>
<th>T&lt;sub&gt;v&lt;/sub&gt;/°C</th>
<th>d/g·cm&lt;sup&gt;-3&lt;/sup&gt;, 25 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMM</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>76</td>
<td>-105</td>
<td>41</td>
<td>0.33</td>
<td>2.7</td>
<td>2.41</td>
<td>-17</td>
<td>0.86</td>
</tr>
<tr>
<td>DME</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>90</td>
<td>-58</td>
<td>84</td>
<td>0.46</td>
<td>7.2</td>
<td>1.15</td>
<td>0</td>
<td>0.86</td>
</tr>
<tr>
<td>DEE</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>118</td>
<td>-74</td>
<td>121</td>
<td>0.46</td>
<td>7.4</td>
<td>1.7</td>
<td>20</td>
<td>0.84</td>
</tr>
<tr>
<td>THF</td>
<td><img src="image4.png" alt="Structure" /></td>
<td>72</td>
<td>-109</td>
<td>66</td>
<td>0.46</td>
<td>7.4</td>
<td>1.7</td>
<td>-17</td>
<td>0.88</td>
</tr>
<tr>
<td>2-Me-THF</td>
<td><img src="image5.png" alt="Structure" /></td>
<td>86</td>
<td>-137</td>
<td>80</td>
<td>0.47</td>
<td>6.2</td>
<td>1.6</td>
<td>-11</td>
<td>0.85</td>
</tr>
<tr>
<td>1,3-DL</td>
<td><img src="image6.png" alt="Structure" /></td>
<td>74</td>
<td>-95</td>
<td>78</td>
<td>0.59</td>
<td>7.1</td>
<td>1.25</td>
<td>1</td>
<td>1.06</td>
</tr>
<tr>
<td>4-Me-1,3-DL</td>
<td><img src="image7.png" alt="Structure" /></td>
<td>88</td>
<td>-125</td>
<td>85</td>
<td>0.60</td>
<td>6.8</td>
<td>1.43</td>
<td>-2</td>
<td>0.983</td>
</tr>
<tr>
<td>2-Me-1,3-DL</td>
<td><img src="image8.png" alt="Structure" /></td>
<td>88</td>
<td></td>
<td></td>
<td>0.54</td>
<td>4.39</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

What creates the electrochemical driving force that allows batteries to function?

- Chemical driving force across battery is $\Delta$ in chemical potential between two electrodes.
  - Expressed as the standard Gibbs free energy/mol of reaction.
- Basically $\Delta G_{\text{free energy}}$ of products and reactants that occur at neutral electrodes.

$$\Delta G_{\text{reaction}} = -zFE = \Delta \mu$$

- $Z$ = the charge number of mobile ion
- $F$ = Faraday’s constant 96,500 coulomb/mol
- $E$ = Voltage between electrodes
- $\Delta \mu$ = chemical potential – ability to be oxidized/reduced
How to understand activity

The chemical potential of a system is \( \mu_i = \partial G_j / \partial n_i = \Delta G_j \)

mole fraction \( n \) of each phase \( j \) contributing to free energy

Free energy and chemical potential change as cell discharges charges

Moreover, chemical potential of each component \( j \) is not unity for that mole fraction. basically, \( \mu \) depends on activity of the species \( j \):

\[
\mu_i = \mu_i^* + RT \ln a_i \quad a \text{ is activity, what is it?}
\]

In order to understand why activity is not \( = 1 \), we can look at Li\(^+\) solvation in liquid electrolytes
Concentration vs activity

• In liquid electrolytes Li\(^+\) diffusion (activity) is governed by:
  
  • Solvent polarity (dielectric constant)
  
  • Viscosity
  
  • Solvation sphere
  
  • Temperature
  
  • Counterion
Solvation sphere—not just cation that moves
Solvation sphere vs. concentration

EC = ethylene carbonate
Activity as a function of solvation sphere
Solvation sphere probed using Raman
Activity as a function of solvation sphere and counterions.

Graphs showing density as a function of distance from Li⁺ and Mn²⁺. Diagrams of molecular structures of Li⁺ and Mn²⁺ complexes with different solvates.
Influence of FEC
Ionic conduction mechanism in polymer electrolytes
Polymer electrolytes

- Multifunctional
- Flexible
- Good mechanical properties
- Moderate thermal stability
- Safe

Solvation sphere w/polymers

Linear polymer electrolytes
- Salt-doped homopolymer
- Single-ion polymer
- Salt-doped block polymer

Nonlinear polymer electrolytes
- Salt-doped bottlebrush block polymer
- Salt-doped star block polymer
- Salt-doped cross-linked polymer

Universal design parameters

Polymer electrolytes with additives
- Salt-doped homopolymer with nanoparticles
- Salt-doped homopolymer with ionic liquids
- Salt-doped homopolymer with blended homopolymer
Solvation sphere w/polymers

Lewis-Basic Polymer

Strong Li$^+$ Coordination

Lewis-Acidic Polymer

Reduced Li$^+$ Coordination

Weak Anion Coordination

Strong Anion Coordination
Solvation sphere w/polymers
Solvation sphere w/polymers
PEO-based polymer electrolytes

- Flexible EO segments and ether oxygens:
- Strong donor character
- Readily complexes metal salts
- Commercially available, low cost

\( \text{M}^+ \) Ion diffusion mechanism in PEO

- \( \text{M}^+ \) coordinated by ether oxygens:
  - Similar to \( \text{M}^+ \) complexation by organic carbonates in liquid electrolytes.

- Ion transport occurs by breaking/forming M-O electrostatic interaction, either intrachain or interchain looping.

- Continuous segmental motion results in a long-range movement of \( \text{M}^+ \).

Reference 1,11
Anions

large diffuse anion
well solvated

Neutral solvent

charge dense anion
poorly solvated

charge dense anion
well solvated

large diffuse anion
poorly solvated

Ionic solvent
Anions
Diffuse anions—poorly coordinating

**A**

- \( \delta^+ \) donation from \( \delta^- \) acceptance
- \( K^+ \) coordination
- Scale: \( \delta^+ \) to \( \delta^- \)

**B**

- \( \text{O} = \text{Cl} - \text{O}^- \)
- DN: 35.31, AN: 225.94

**C**

- \( \text{F} - \text{S} - \text{O}^- \)
- DN: 70.71, AN: 155.23

**D**

- \( \text{F} - \text{S} - \text{O}^- - \text{S} - \text{O} - \text{F} \)
- DN: 21.08, AN: 111.01

**E**

- \( \text{F} - \text{P} - \text{F} \)
- DN: 10.46, AN: 48.78

**F**

- \( \text{O} - \text{S} \)
- DN: 124.68, AN: 80.75
Diffuse anions—poorly coordinating

\[
\begin{align*}
[MCl_4]^- & \quad [BF_4]^- & \quad [MF_6]^- & \quad [Sb_2F_{11}]^- & \quad [Sb_3F_{16}]^- & \quad [Sb_4F_{21}]^- \\
(M = Al, Ga) & & (M = As, Sb, Ir, Pt) & & & \\
\end{align*}
\]

\[
\begin{align*}
[OTT]^- & \quad [B(CF_3)_4]^- & \quad [M(C_6F_{13})_4]^-(M = B, Ga) & \quad [B(ArCF_3)_4]^- \text{ aka } “BArF” & \quad [HO(B(C_6F_{13})_3)_2]^-
\end{align*}
\]

\[
\begin{align*}
[CHB_{11}H_5Cl_6]^- & \quad [CHB_{11}H_5Br_6]^- & \quad [CHB_{11}Me_3Br_6]^- & \quad [CHB_{11}F_{11}]^- & \quad [CET(B_{11}F_{11})^- & \quad [B_{12}Cl_{11}NMe_3]^-
\end{align*}
\]

\[
\begin{align*}
[Al(OR_{pp})_4]^- & \quad [F(Al(OR_{pp})_2)_2]^- & \quad [Sb(OTeF_{5})_6]^-
\end{align*}
\]

\[
\begin{align*}
\text{Elements: } & H \quad B \quad C \quad N \quad O \quad F \\
& \quad Cl \quad Br \quad S \quad Sb \quad Te
\end{align*}
\]
Ionic conduction mechanism in solid electrolytes
Mechanism of ionic transport in solids

- Relies on concentration and distribution of defects
  - E.g. Schottky and Frenkel point defects
- Mobile species *must pass through periodic bottlenecks*
- Low migration energy ($E_m$) leads to high ionic mobility
Ion migration within a crystalline solid

- Schottky defects - random jumps between vacant sites

- Frenkel defects - direct interstitial jumps and migration

Activity in solid electrolytes

Li$^+$ diffusion in solids
Activity in solid electrolytes

Li\(^+\) diffusion in solids
Activity in solid electrolytes

- Li$^+$ diffusion in solids
- Size of channel for movement
- Distance ion has to hop
- Electrostatic repulsion of Al$^{3+}$, Ti$^{4+}$, Zr$^{4+}$, Si$^{4+}$, etc.
- All of these interfere, aid diffusion and control apparent activity

https://doi.org/10.1038/ncomms15893
Proposed Li$^+$ diffusion pathways in γ-LiAlO$_2$

Yellow: P1
Green: P2
Blue: P3
Gray: disfavored jumps
Dashed lines: possible

Li $\rightarrow$ A $\rightarrow$ A$'$ $\rightarrow$ Li$'$ (P1)
Li $\rightarrow$ B $\rightarrow$ Li$''$ (P2)
Li $\rightarrow$ A $\rightarrow$ B $\rightarrow$ Li$'''$ (P3)

Proposed lithium diffusion pathways in LiAl$_5$O$_8$
Li diffusion in solids
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**Diagram**

1. **Cathode** (LCO) → **Solid state electrolyte** (Garnet) → **Anode** (Li metal)

   - **I**: Li⁺ cations come out of the lattice structure of cathode;
   - **II**: pass through cathode/SSE interface;
   - **III**: cross SSE structure (crystalline or amorphous);
   - **IV**: move across the SSE/anode interface;
   - **V**: finally deposit onto the Li metal anode.
Li diffusion in solids—intercalation processes