9. Positive electrodes in lithium systems (Huggins, ch. 9)

1. Insertion reaction electrodes
2. Interstitial site or redox species
3. Cell assembled in the discharged state
    A. Solid positive electrodes in lithium systems
    B. Liquid positive electrode reactants
    C. Hydrogen & water in positive electrode materials

1. Insertion reaction electrodes

-1976 Whittingham, xLi + $TiS_2 \rightarrow Li_xTiS_2$, x: 0~1

→ insertion-driven solid solution redox process

→ reversible over many cycles

-Insertion of Li into other materials, V_2O_5, LiV_3O_8, V_6O_{13}

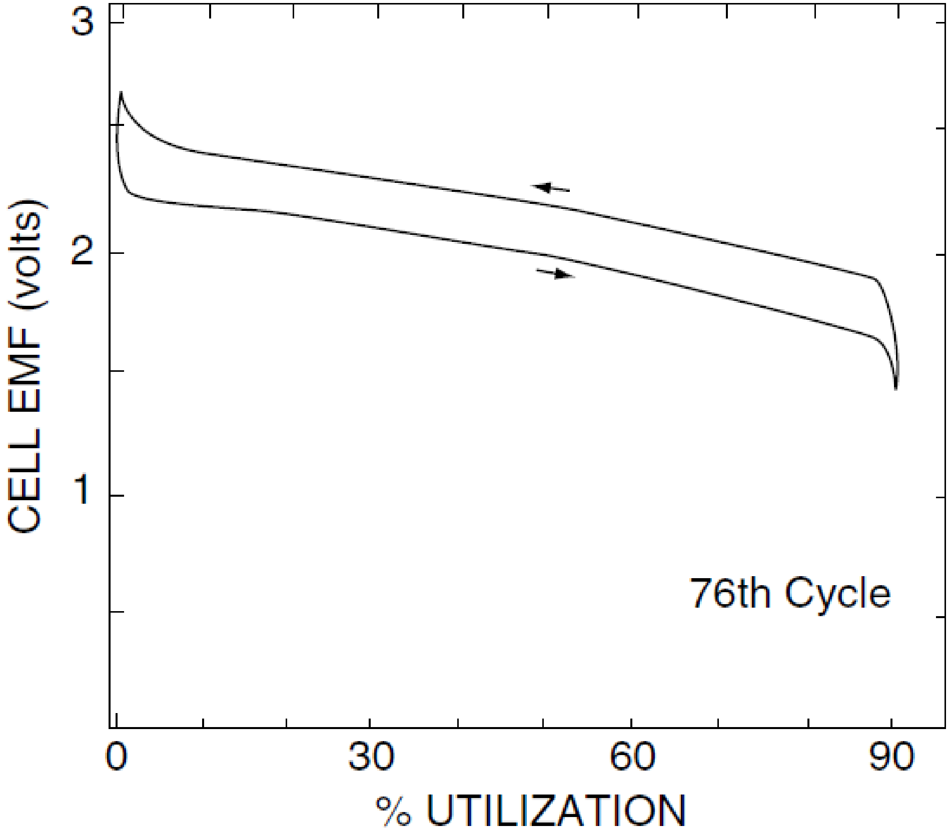


Fig. 9.1 Charge/discharge behavior of a Li/TiS_2 cell after 76 cycles

2. More than one type of interstitial site or more than one type of redox species

-more than one plateau in voltage-composition curve,

e.g. Li → V_2O_5

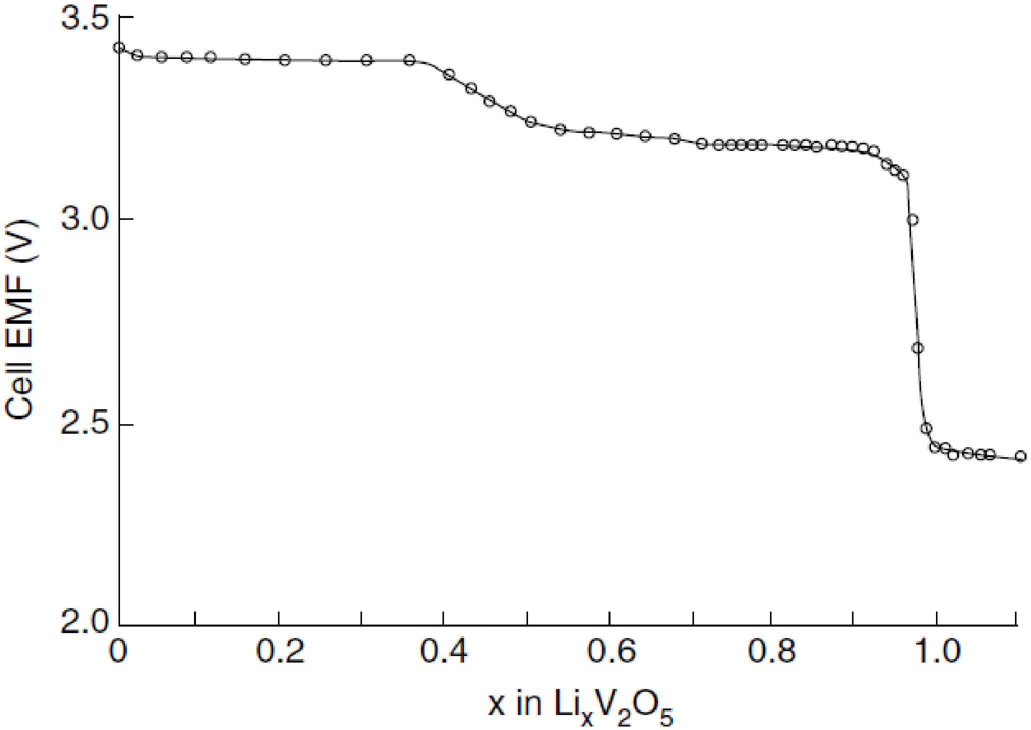


Fig. 9.2 Variation of the potential with the concentration of lithium guest species in the V_2O_5 host structure

3. Cell assembled in the discharges state

-if a positive electrode initially contains lithium, and some or all Li is deleted, the potential goes up, rather than down, as it does upon the insertion of lithium

→ Therefore, it is possible to have positive electrode materials that react with lithium at potentials above about 3V, if they already contain lithium, and this lithium can be electrochemically extracted

If starting in charged state → glove box needed because of no/small Li in positive electrode + pure Li or Li_xC negative → electrode oxidizing condition, operation at low potential (lower than 3 V) → As Li↑, positive electrode potential goes down toward that of pure lithium

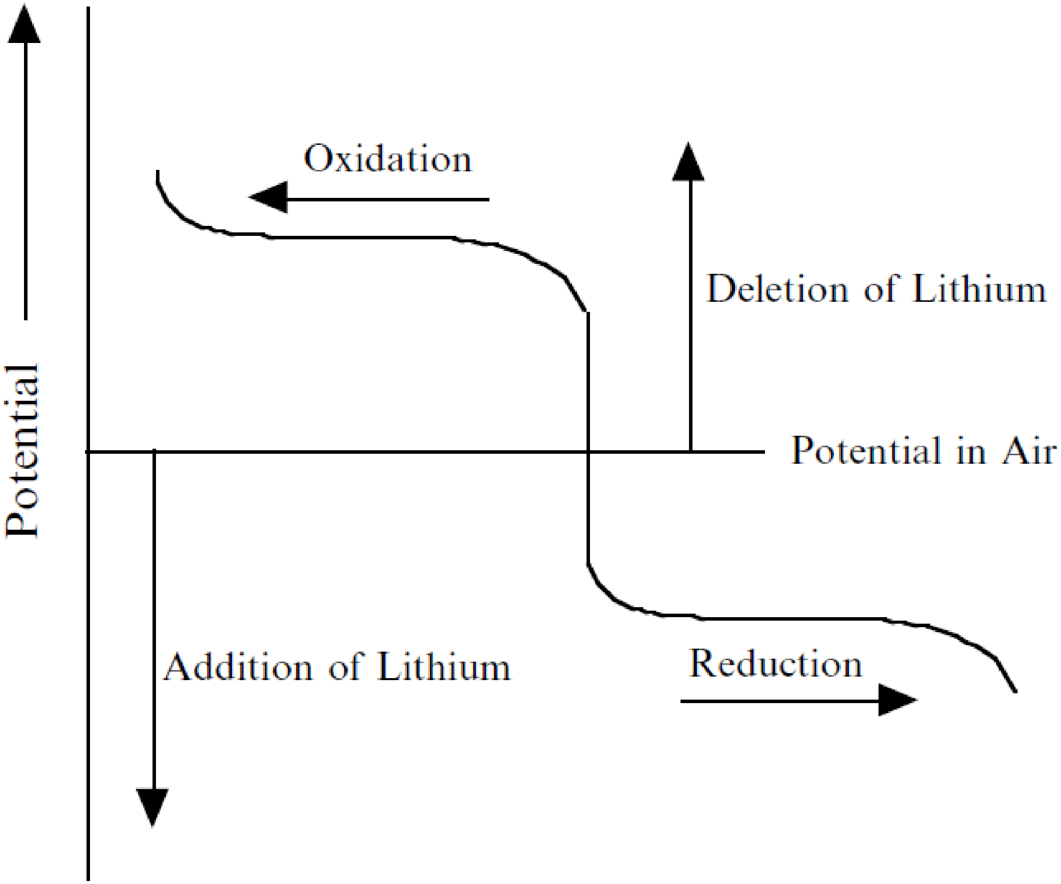


Fig. 9.3 Schematic of the behavior of a material that is amphoteric, i.e, that can be both electrochemically oxidized at high potentials by the deletion of lithium, and electrochemically reduced at lower potentials by the addition of lithium

-This approach, involving the use of materials in which lithium is already present, was first demonstrated in Prof. Goodenough's laboratory in Oxford. The first examples of materials initially containing lithium, and electrochemically deleting lithium from them, were the work on $\mathrm{Li}_{1-x}\mathrm{CoO}_2$ [12] and $\mathrm{Li}_{1-x}\mathrm{NiO}_2$ [13] in 1980. They showed that it is possible in this way to obtain high reaction potentials, up to over 4V.

[12] K. Mizushima, P.C. Jones, P.J. Wiseman and J.B. Goodenough, Mater. Res. Bull. 15, 783 (1980).

[13] J.B. Goodenough, K. Mizushima and T. Takada, Jpn. J. Appl. Phys. 19 (Suppl. 19-3), 305 (1980).

→ SONY of a lithium battery containing a carbon negative electrode and a $LiCoO_2$ positive electrode that became commercially available in 1990

→ assembled in the discharged state. They were activated by charging, whereby lithium left the positive electrode material, raising its potential, and moved to the carbon negative electrode, whose potential was concurrently reduced.
This cell can be represented as

$$Li_xC/\text{organic solvent electrolyte}/Li_{1-x}CoO_2$$

and the cell reaction can be written as

$$C + LiCoO_2 = Li_xC + Li_{1-x}CoO_2$$

A. Solid positive electrodes in lithium systems

A1. Introduction

-As the insertion of lithium causes the potential to decrease, and those positive electrodes necessarily operated at potentials lower than that of air, the voltage of such cells was limited to about 3V

→ air-stable positive electrode materials that already contained lithium, and their operation by the deletion of lithium, led to the possibility of batteries with significantly higher voltages

→ this also required a different strategy for the negative electrodes, for they must be initially devoid of lithium

-Cells can be assembled in air in the discharged state. To be put into operation, they must be charged, the lithium initially in the positive electrode being transferred to the negative electrode

Li_xC/organic solvent electrolyte/$Li_{1-x}CoO_2$

-charge/discharge curve of Li_xCoO_2
-0.5Li per mole of $LiCoO_2$ can be reversibly deleted and reinserted → the charge involved in the transfer of lithium ions is balanced by Co^{3+}/Co^{4+} redox reaction

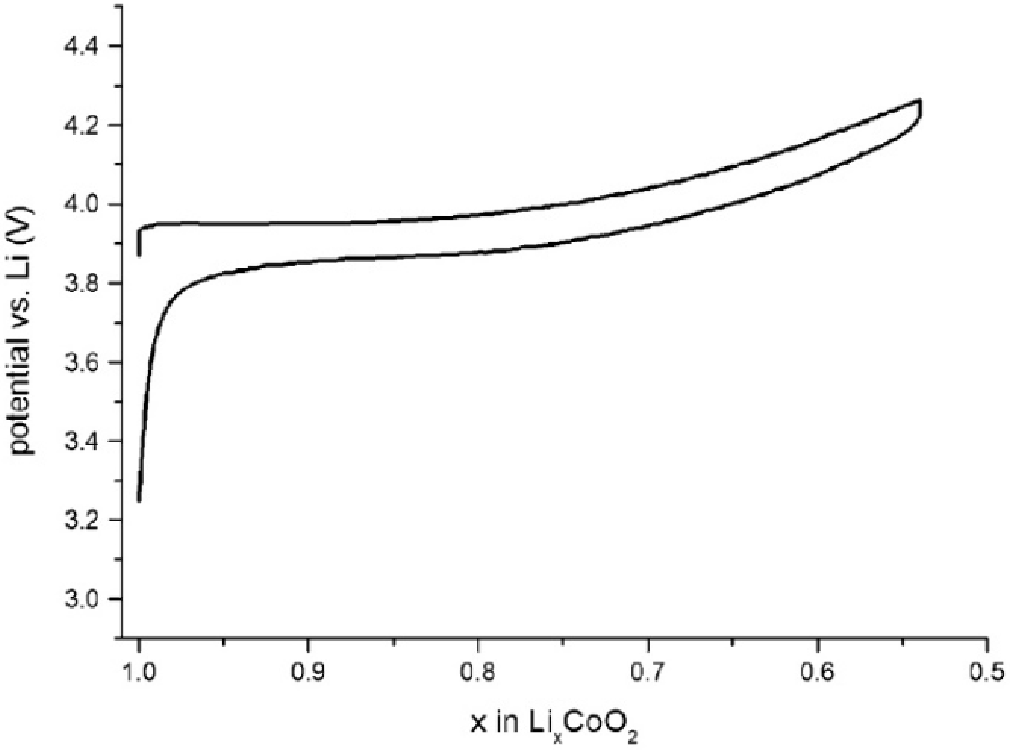


Fig. 9A.1 Charge/discharge behavior of Li_xCoO_2

-Quite a number of materials for positive electrode

face-centered cubic packing of oxide ions: *spinel* structure($LiMn_2O_4$), *ordered cation distribution(layered structures* ($LiCoO_2$ and $LiNiO_2$)

hexagonal close-packed oxide ion packing: ordered *olivine-related structures* (e.g. $LiFePO_4$)

more open crystal structures, sometimes called *framework* or *skeleton* structures. These are sometimes described as containing *polyanions:* sulfates, sulfates, molybdates, tungstates, phosphates, as well as Nasicon, Nasicon-related materials (e.g., $Li_3V_2(PO_4)_3$ and $LiFe_2(SO_4)_3$) → In these materials lithium ions can occupy more than one type of interstitial position

Table 9A.1 Common valences of redox ions in solids

Element	Valences	Valence range	Comments
Ti	2, 3, 4	2	
V	2, 3, 4, 5	3	
Cr	2, 3, 6	1	6 is poisonous
Mn	2, 3, 4, 6, 7	2	6, 7 usable?
Fe	2, 3	1	
Co	2, 3	1	
Ni	2, 3, 4	2	
Cu	1, 2	1	

An example of the reaction of lithium with an electrode material containing two redox ions, a Li−Mn−Fe phosphate with the olivine structure

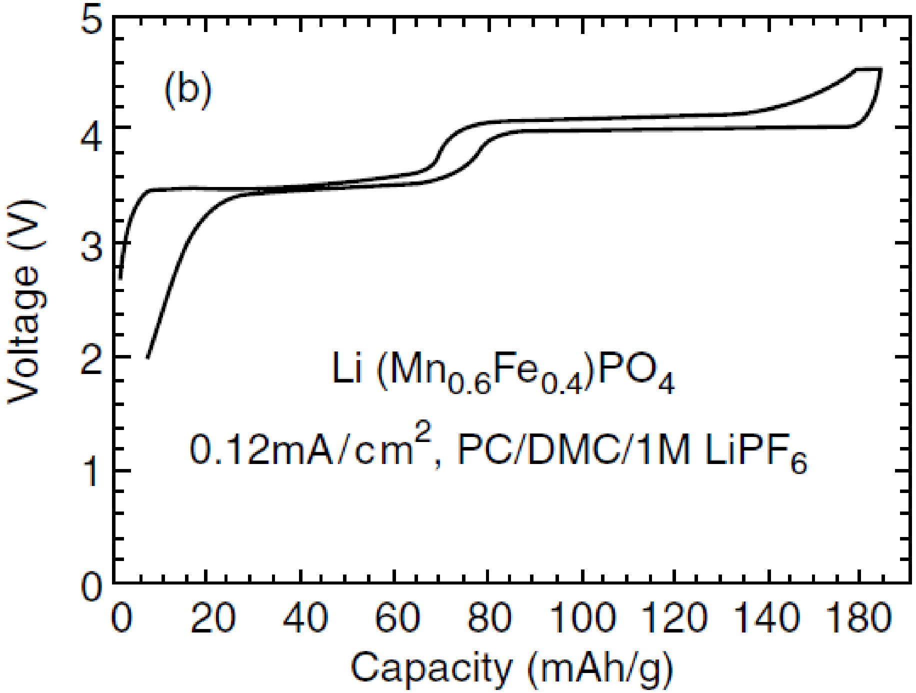


Fig. 9A.2 Charge–discharge curve of the reaction of lithium with an example of a double-cation olivine material

Not all redox reactions are of practical value in electrode materials, and in some cases, their potentials depend upon their environments within the crystal structure

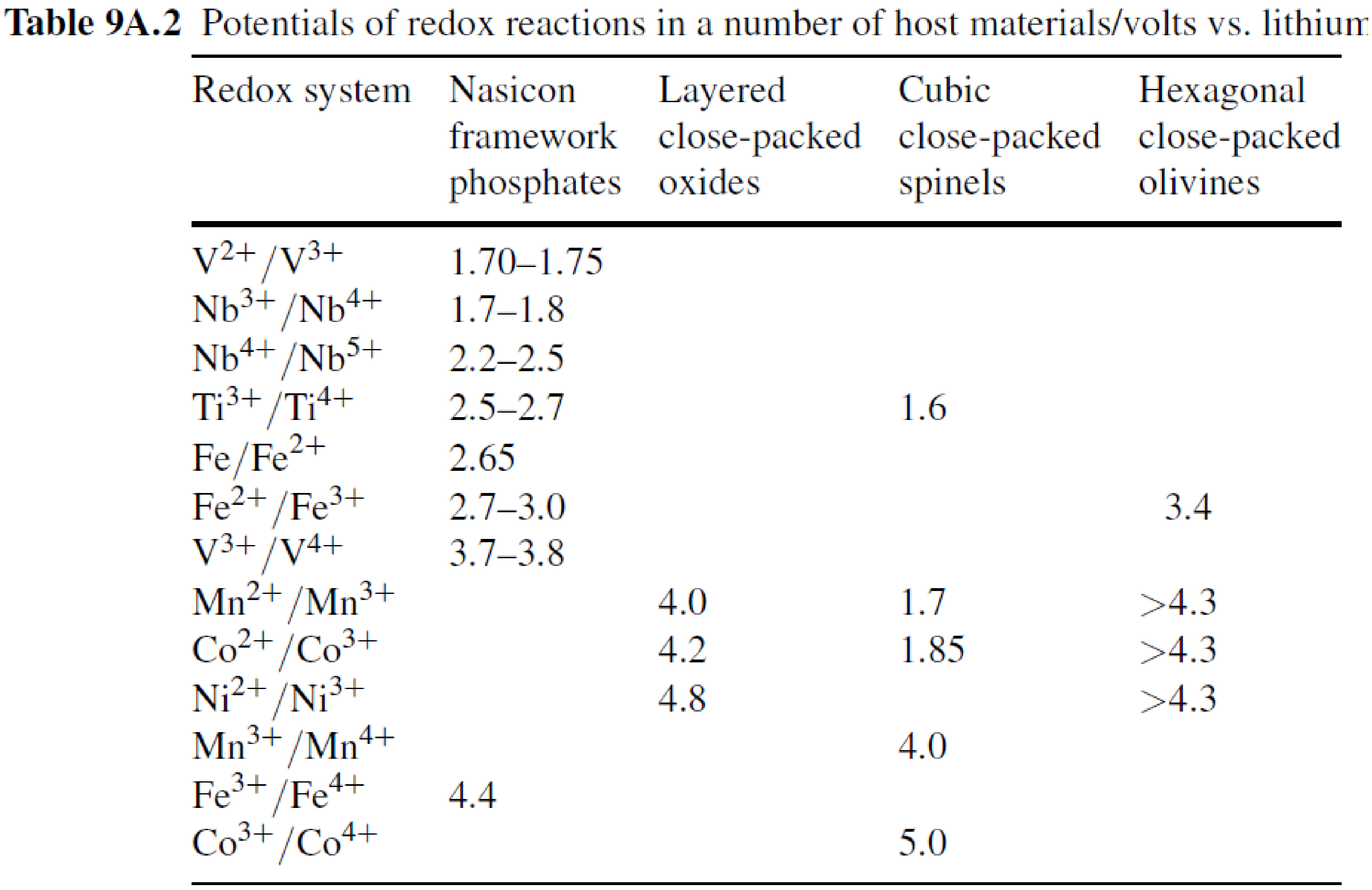


Table 9A.2 Potentials of redox reactions in a number of host materials/volts vs. lithium

Redox system	Nasicon framework phosphates	Layered close-packed oxides	Cubic close-packed spinels	Hexagonal close-packed olivines
V^{2+}/V^{3+}	1.70–1.75			
Nb^{3+}/Nb^{4+}	1.7–1.8			
Nb^{4+}/Nb^{5+}	2.2–2.5			
Ti^{3+}/Ti^{4+}	2.5–2.7		1.6	
Fe/Fe^{2+}	2.65			
Fe^{2+}/Fe^{3+}	2.7–3.0			3.4
V^{3+}/V^{4+}	3.7–3.8			
Mn^{2+}/Mn^{3+}		4.0	1.7	>4.3
Co^{2+}/Co^{3+}		4.2	1.85	>4.3
Ni^{2+}/Ni^{3+}		4.8		>4.3
Mn^{3+}/Mn^{4+}			4.0	
Fe^{3+}/Fe^{4+}	4.4			
Co^{3+}/Co^{4+}			5.0	

When lithium or other charged mobile guest ions are inserted into the crystal structure, their electrostatic charge is balanced by a change in the oxidation state of one or more of the redox ions contained in the structure of the host material
→ the reaction potential of the material is determined by the potential at which this oxidation or reduction of these ions occurs in the host material
→ In some cases, this redox potential is rather narrowly defined, whereas in others redox occurs over a range of potential, due to the variation of the configurational entropy with the guest species concentration, as well as the site distribution

A2.Influence of the crystallographic environment on the potential

-a given redox reaction takes place can affect the value of its potential

-redox ion is octahedrally surrounded by oxide ions, and the oxide ions also have cations with a different charge in tetrahedral environments on the other side. The electron clouds around the oxide ions are displaced by the presence of adjacent cations with different charges

e.g. $Fe_2(SO_4)_3$
two Li's per formula
Unit flat discharge curve indicating a reconstitution reaction at 3.6V vs. Li/Li

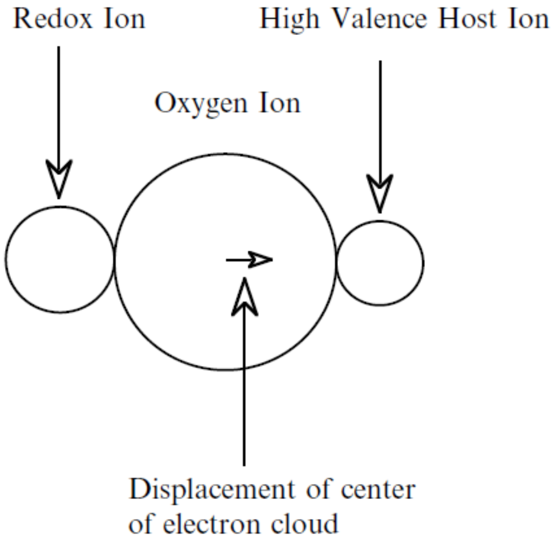
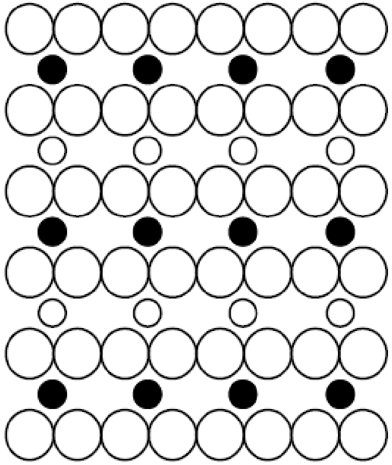


Fig. 9A.3 Schematic of the displacement of the electron cloud around an oxide ion by the charge upon nearby cations

A3. Oxides with Structures in Which the Oxygen Anions Are in a Face-Centered Cubic Array

A3.1 Materials with Layered Structures

Li_xCoO_2, stable in air, with x=1: close-packed face-centered cubic of oxide ions, with Li^+ and Co^{3+} cations occupying octahedrally coordinated positions in between layers of oxide ions → cation positions are ordered such that the lithium ions and the transition metal ions occupy alternate layers between close-packed (111) planes of oxide ions → layered, rather than simple cubic, structures



Layered Structure

Fig. 9A.4 Simplified schematic of a layered structure in which there is alternate occupation of the cation layers between the close-packed oxide ion layers. The solid and open small circles represent two different types of cations. The larger circles are oxide ions

-When lithium ions move between octahedral sites within the layers of this structure, they must go through nearby tetrahedral sites that lie along the jump path (simple minimum energy path model). Li_xCoO_2 can be cycled many times over the range $1 > x > 0.5$, but there is a change in the structure and a loss of capacity if more Li^+ ions are deleted.

-lower cost and less poisonous → $LiNiO_2$ → Li_xNiO_2 is difficult to prepare with the right stoichiometry. This results in a loss of capacity. Also $LiNiO_2$ readily loses oxygen at high potentials, destroying its layer structure, and tending to lead to safety problems because of an exothermic reaction with the organic solvent electrolyte

modification of Li_xNiO_2 by the substitution of other cations for some of the Ni^{3+} ions → replacement of 20–30% of the Ni^{3+} ions by Co^{3+} ions will impart sufficient stability. Other introduction of Mg^{2+}, Al^{3+} or Ti^{4+} ions

-$LiMnO_2$: alpha $NaFeO_2$ structure. If more than 50% of the lithium ions are removed during charging, conversion
to the spinel structure. About 25% of the Mn ions move from octahedral sites in their normal layers into the alkali metal layers, and lithium is displaced into tetrahedral sites. → this conversion to the spinel structure can be avoided by the replacement of half of the Mn ions by chromium

-$Li_xMn_{0.5}Ni_{0.5}O_2$ → good electrochemical properties, with indications of a solid solution insertion reaction in the potential range 3.5–4.5V vs. Li (redox reaction from Ni^{2+} to Ni^{4+}, whereas the Mn remains as Mn^{4+}) → no problem with Jahn-Teller distortions (related to the presence of Mn^{3+}) At higher Mn → reconstitution reactions

-$LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$: Co ions evidently stabilizes the layer structure against conversion to the spinel structure → limited electronic conductivity. When fully lithiated, Ni^{2+}(major electrochemically active species), Co^{3+}(active at high potential), Mn^{4+}(no active role, reduce cost)

A3.2 Materials with the spinel structure

-AB_2O_4 : close-packed face-centered cubic arrangement of oxide ions (parallel layers of oxide ions on (111) planes), both octahedrally coordinated sites and tetrahedrally coordinated sites between the oxide ion planes

-In *normal spinels*, the A (typically monovalent or divalent) cations occupy 1/8 of the available tetrahedral sites, and the B (typically trivalent or quadrivalent) cations 1/2 of the B sites.

-In *inverse spinels*, the distribution is reversed

-spinel structure is quite common in nature, indicating a large degree of stability→ a tendency for the materials with the layer structures to convert to the closely related spinel structure (Fig. 9A.5)

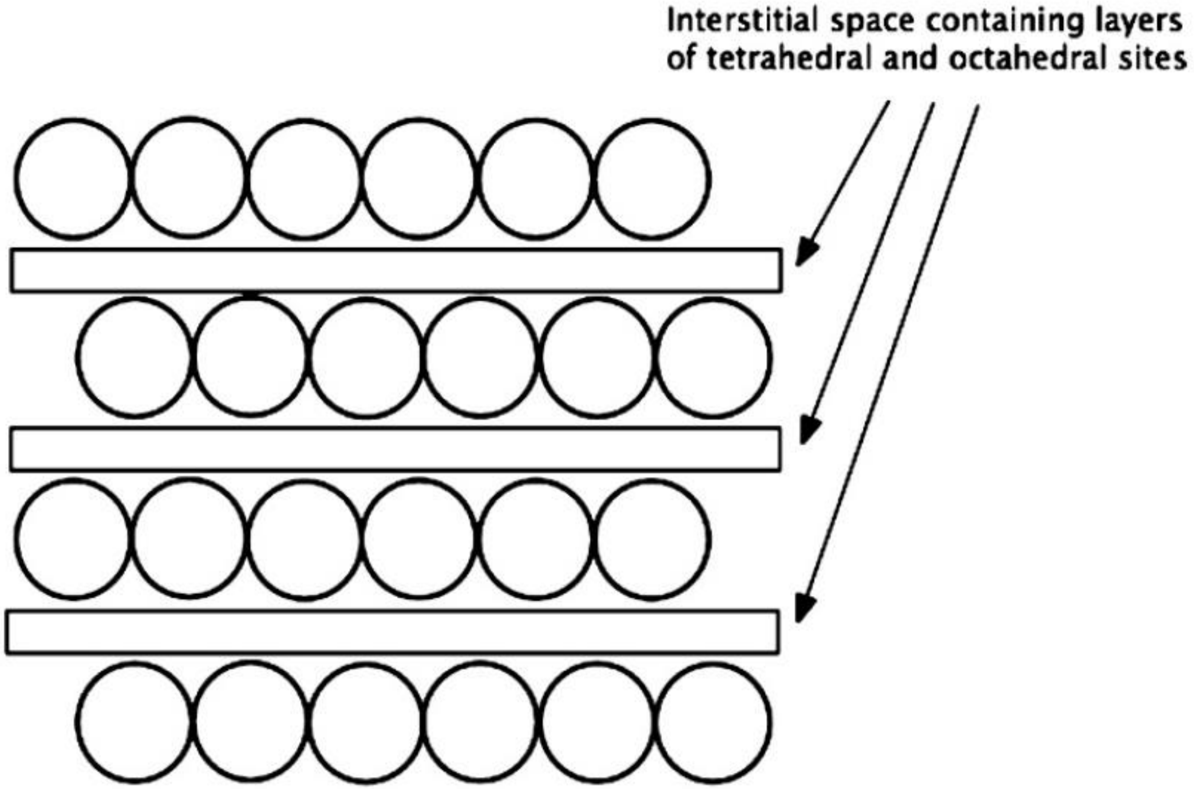


Fig. 9A.5 Schematic of the spinel structure in which the cations between the close-packed (111) planes of oxide ions are distributed among both tetrahedral and octahedral sites

-$Li_xMn_2O_4$ (for x = 1, 10% loss of capacity than Li_xCoO_2), but better kinetics and does not have a great tendency to evolve oxygen

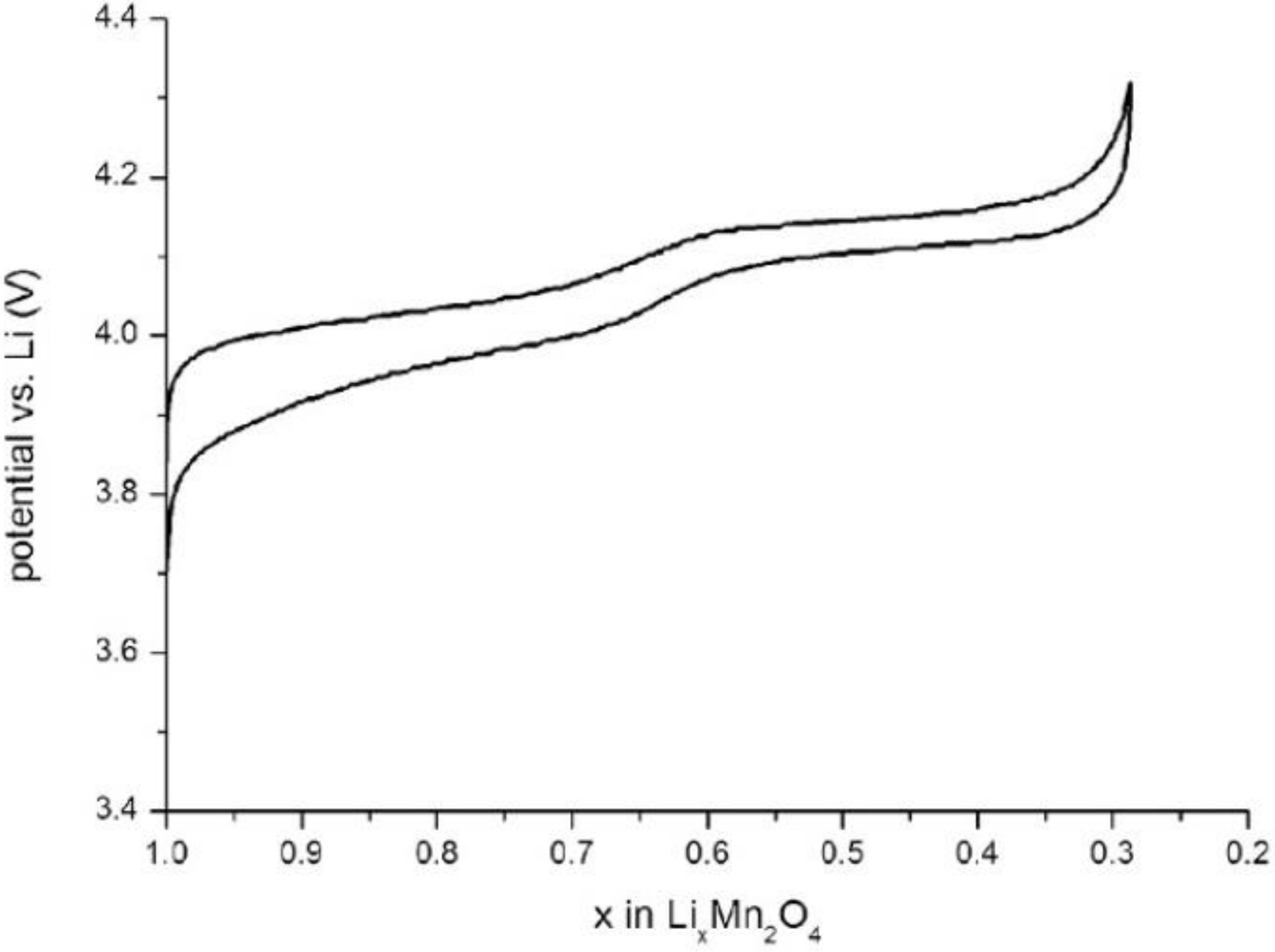


Fig. 9A.6 Charge/discharge behavior of $Li_xMn_2O_4$

-two plateaus → ordering reaction of lithium ions on the tetrahedral sites when x is about 0.5.

Low cost, good kinetics, nonpoisonous

-problems

(1) loss of Mn^{2+} into the organic solvent electrolyte as the result of a disproportionation reaction when the potential is low near the end of discharge.

$$2Mn^{3+} = Mn^{4+} + Mn^{2+}$$

→ these ions travel to the carbon negative electrode, with the result that a layer of manganese metal is deposited that acts to block lithium ion transport

(2) at low potentials, local onset of Jahn-Teller distortion that can cause mechanical damage to the crystal structure. On the other hand, if the electrode potential becomes too high as the result of the extraction of too much lithium, oxygen can escape and react with the organic solvent electrolyte .

-These problems are reduced by modification of the composition of the electrode by the presence of additional lithium and a reduction of the manganese: theoretical capacity of $LiMn_2O_4$ is 148mAh g^{-1}, this modification results in a capacity of only 128mAh g^{-1}

-substitution of some of the Mn^{2+} ions in Li_xMnO_2 by Cr^{3+} ions → capacity upon the 3.8-V plateau was decreased in proportion to the concentration of the replaced Mn ions. But when the potential was raised to higher values, it was found that this missing capacity at about 4V reappeared at potentials about 4.9V that was obviously related to the oxidation of the Cr ions

-replacement of copper ions: $LiCu_xMn_{2-x}O_4$ → a second plateau appears at 4.8–5.0V due to Cu^{2+}/Cu^{3+} reaction, in addition to the normal behavior of Li-Mn spinel in the range 3.9~4.3 V that is related to Mn^{3+}/ Mn^{4+} reaction → overall capacity↓ (Fig. 9A.7)

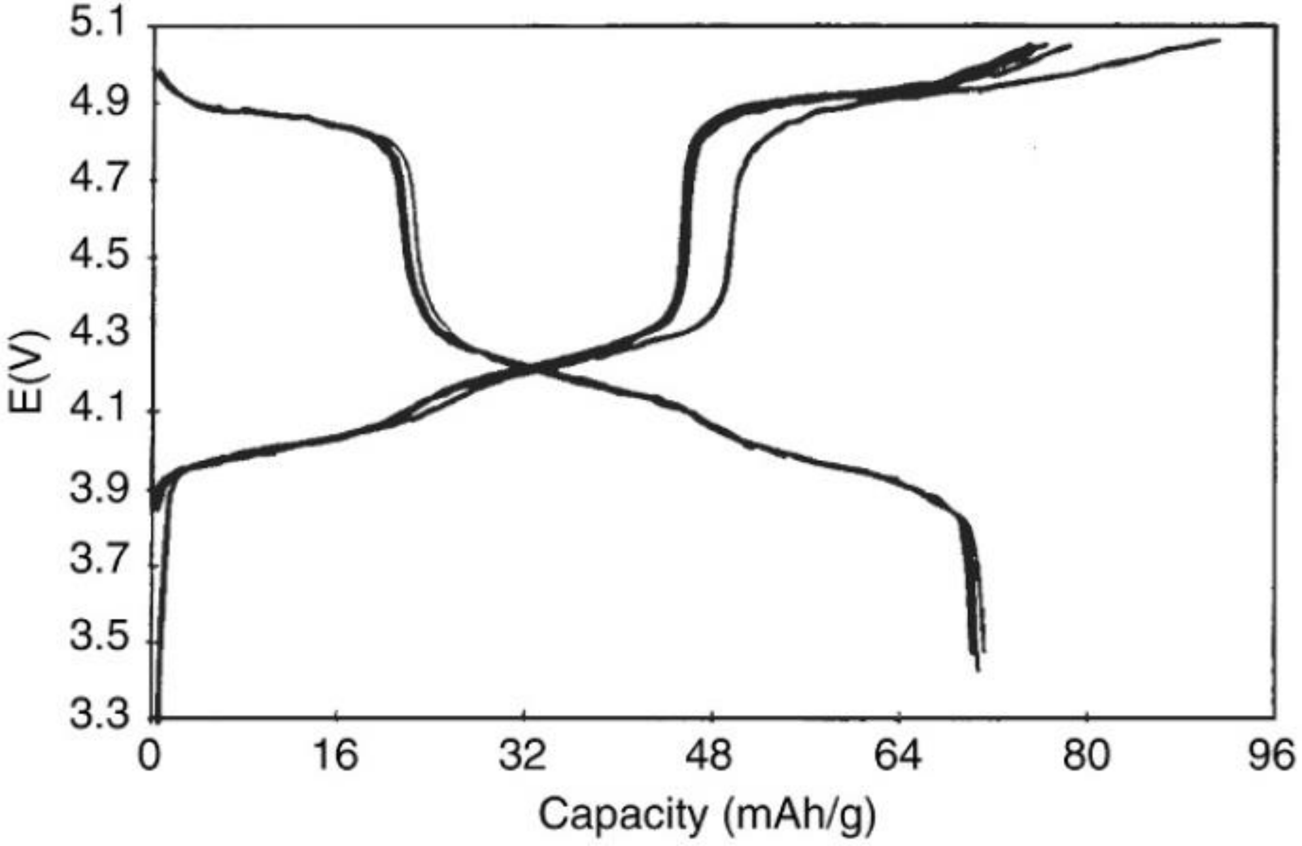


Fig. 9A.7 Potential–composition curves for $LiCu_{0.5}Mn_{1.5}O4$

-Various elements are substituted

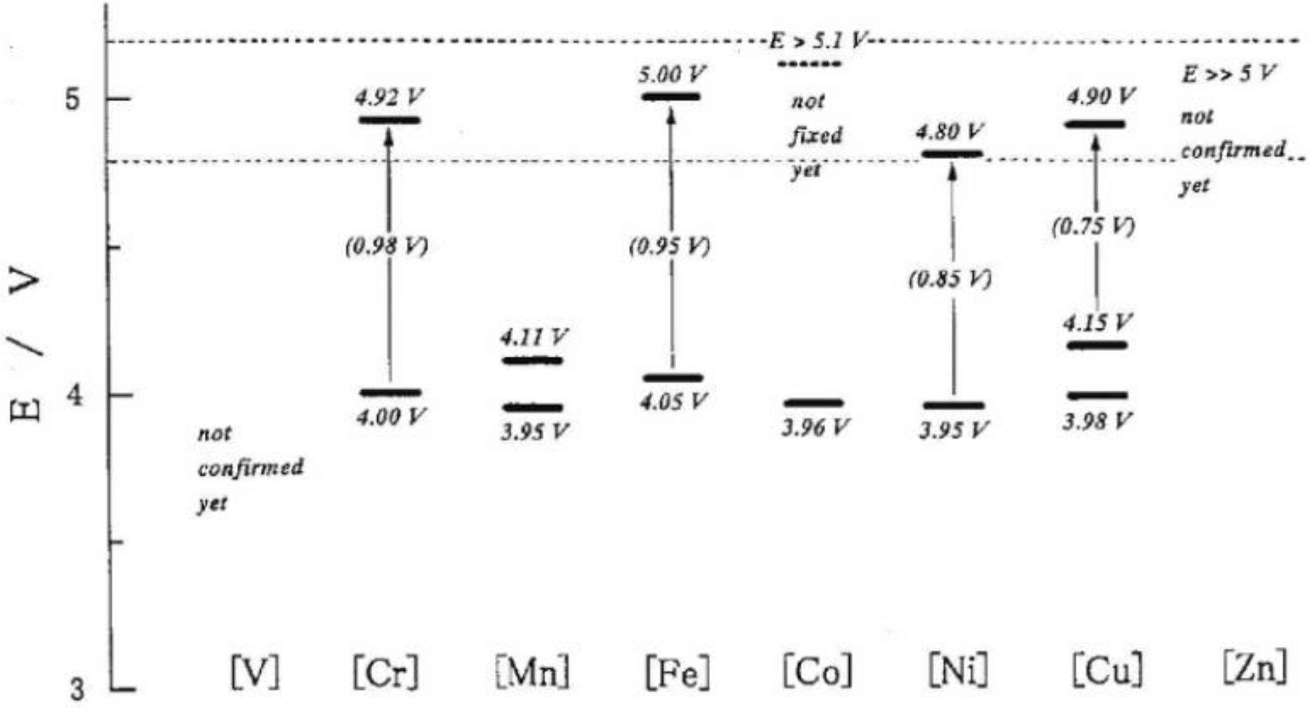


Fig. 9A.8 Potential ranges, vs. Li, of redox potentials found as the result of the introduction of a number of cations into lithium manganese spinels. The operating potential range of lithium manganese spinel itself is also shown

-Li$_x$Ni$_{0.5}$Mn$_{1.5}$O$_4$: two reconstitution reactions, rather than solid solution behavior (two reactions with potential separation of only 20 mV)

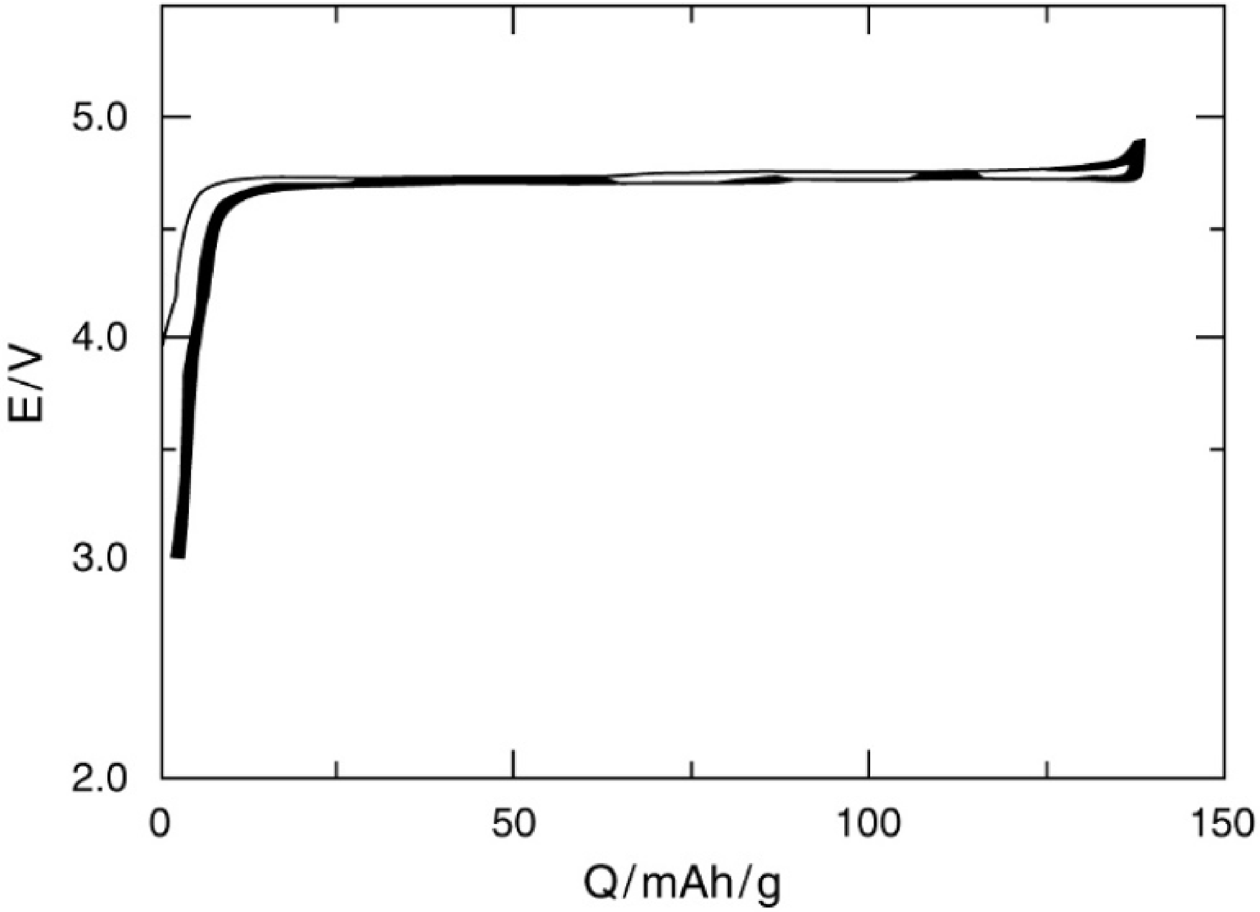


Fig. 9A.9 Charge/discharge curves for Li$_x$Ni$_{0.5}$Mn$_{1.5}$O$_4$

Also a reconstitution reaction with a capacity of one Li per mole at 2.8 V, as well as further Li uptake via a single phase reaction below 1.9 V → higher potentials relate to nickel, the lower one to manganese

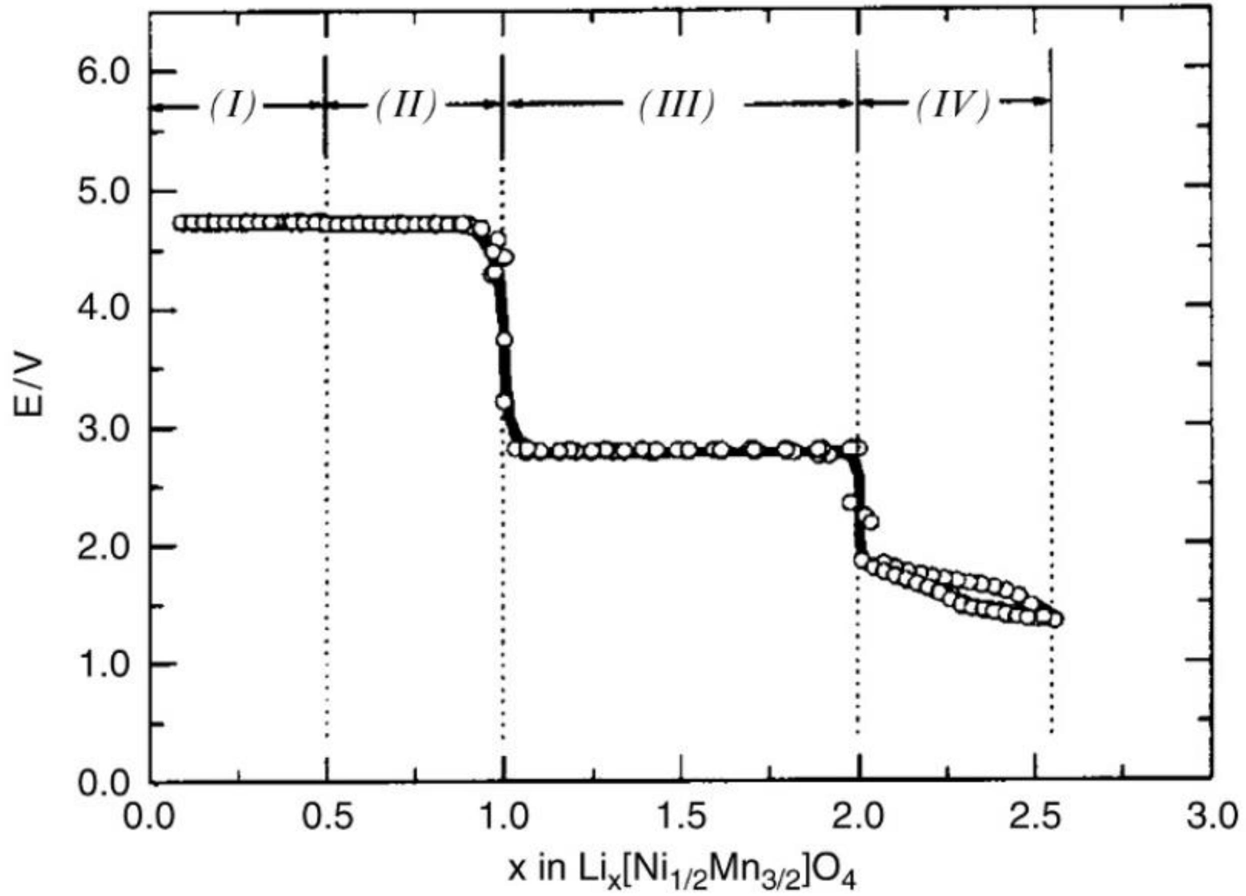


Fig. 9A.10 Coulometric titration curve for the reaction of lithium with $Li_xNi_{0.5}Mn_{1.5}O_4$

A3.3 Lower potential spinel materials with reconstitution reactions

-example: spinel-structure material that has a reconstitution reaction at 1.55V vs. Li. This is $Li_{1.33}Ti_{1.67}O_4$ that can also be written as $Li_x[Li_{0.33}Ti_{1.67}O_4]$, for some of the lithium ions share the octahedral sites in an ordered arrangement with the titanium ions. It also sometimes appears in the literature as $Li_4Ti_5O_{12}$
→ this spinel-structure material is unusual in that there is essentially no change in the lattice dimensions with variation of the amount of lithium in the crystal structure, and it has been described as undergoing a *zero-strain insertion reaction*. This is an advantage in that there is almost no volume change-related hysteresis, leading to very good reversibility upon cycling → this can be used negative electrode or positive electrode

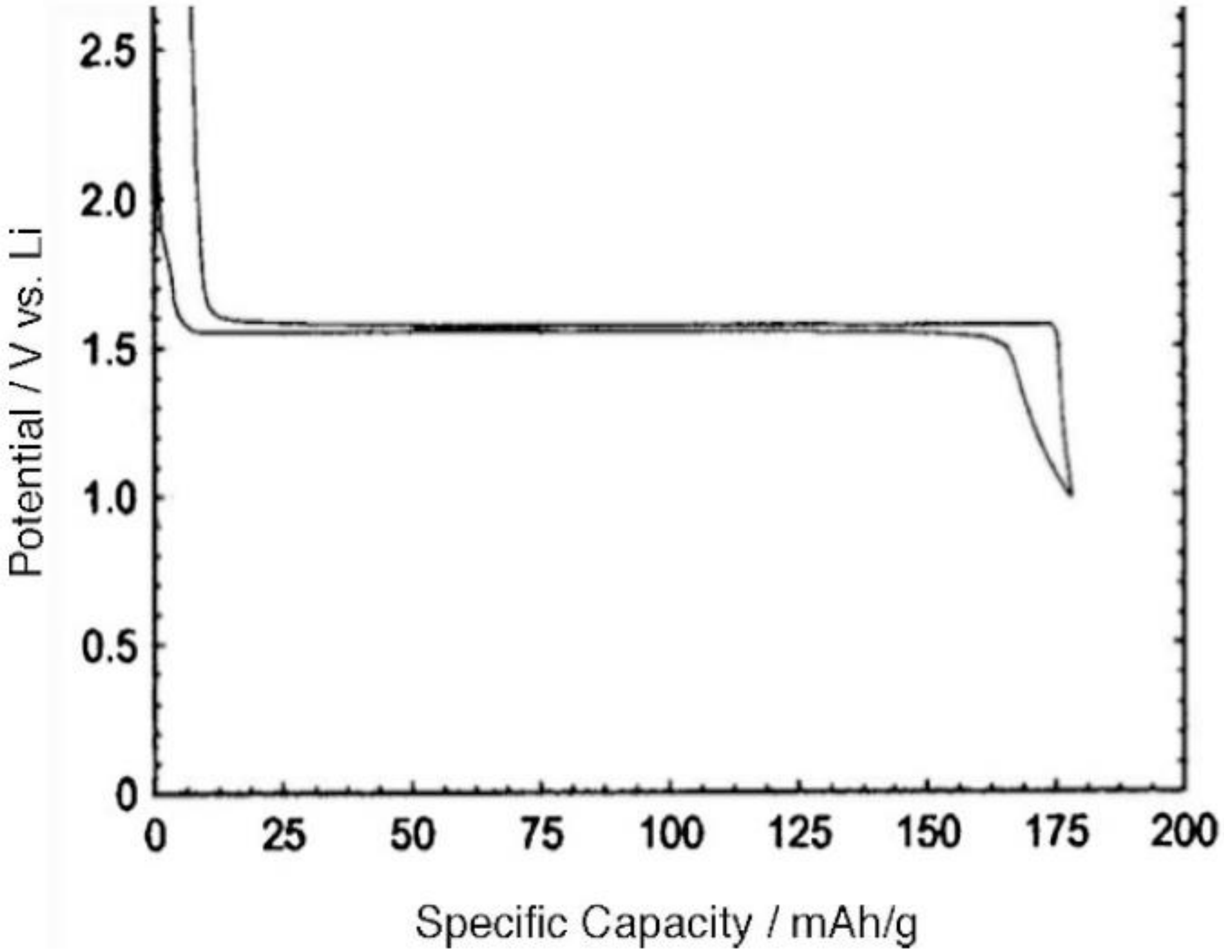


Fig. 9A.11 Charge/discharge curve for $Li_4Ti_5O_{12}$

A4 Materials in which the oxide ions are in a close-packed hexagonal array

Whereas in the spinel and the related layered materials such as Li_xCoO_2, Li_xNiO_2, and Li_xMnO_2 the oxide ions are in a cubic close-packed array, there are also many materials in which the oxide ions are in a hexagonal close-packed configuration. Some of these are currently of great interest for use as positive electrode reactants in lithium batteries, but are generally described as having *framework structures*. They are sometimes also called *scaffold, skeleton, network*, or *polyanion* structures.

A4.1 The Nasicon structure

-First attention due to be found to be very good solid electrolyte for sodium ions, $Na_3Zr_2Si_2PO_{12}$ → monoclinic symmetry: MO_6 octahedra sharing corner oxide ions with adjacent XO_4 tetrahedra. Each octahedron is surrounded by six tetrahedra, and each tetrahedron by four octahedra. These are assembled as a three-dimensional network of M_2X_3 groups. Between these units is three-dimensional interconnected interstitial space, through which small cations can readily move

-by using M cations whose ionic charge can be varies, it is possible to make materials with this same structure that undergo redox reactions upon the insertion or deletion of lithium within the interstitial species

→ positive electrode

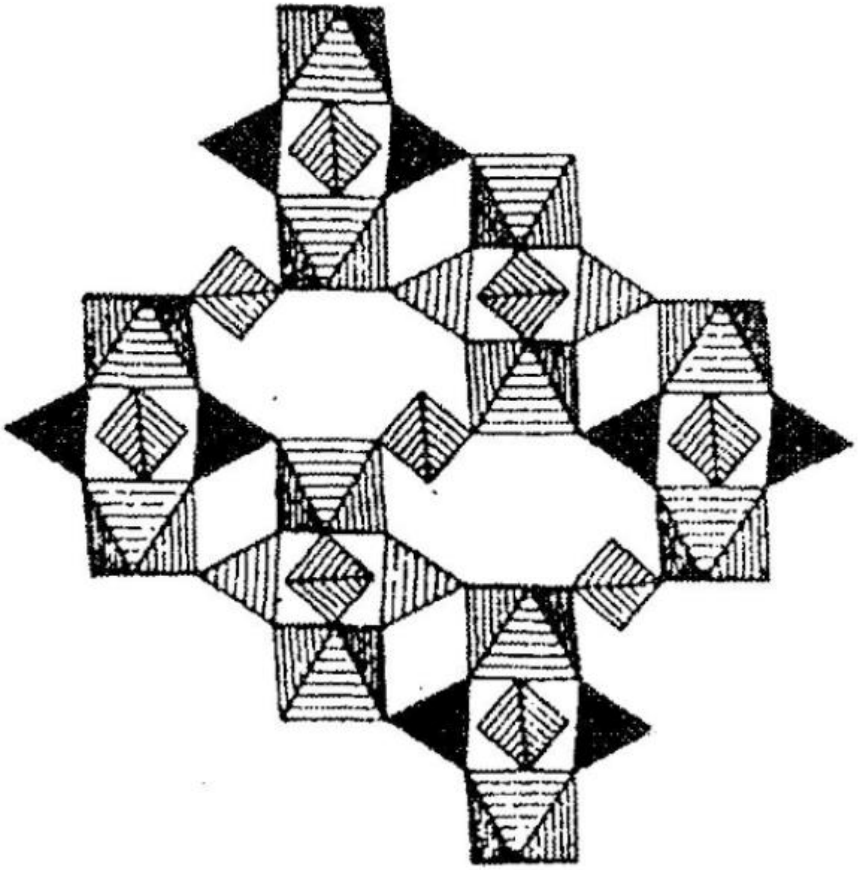


Fig. 9A.12 Schematic representation of the Nasicon structure e.g. $Li_3V_2(PO_4)_3$: three two-phase plateaus, corresponding to the the extraction of two of the lithium ions in the initial structure. The first two plateaus indicate that there are two slightly different configurations for one of the two lithium ions. The potential must be increased substantially, to over 4V, for the deletion of the second.

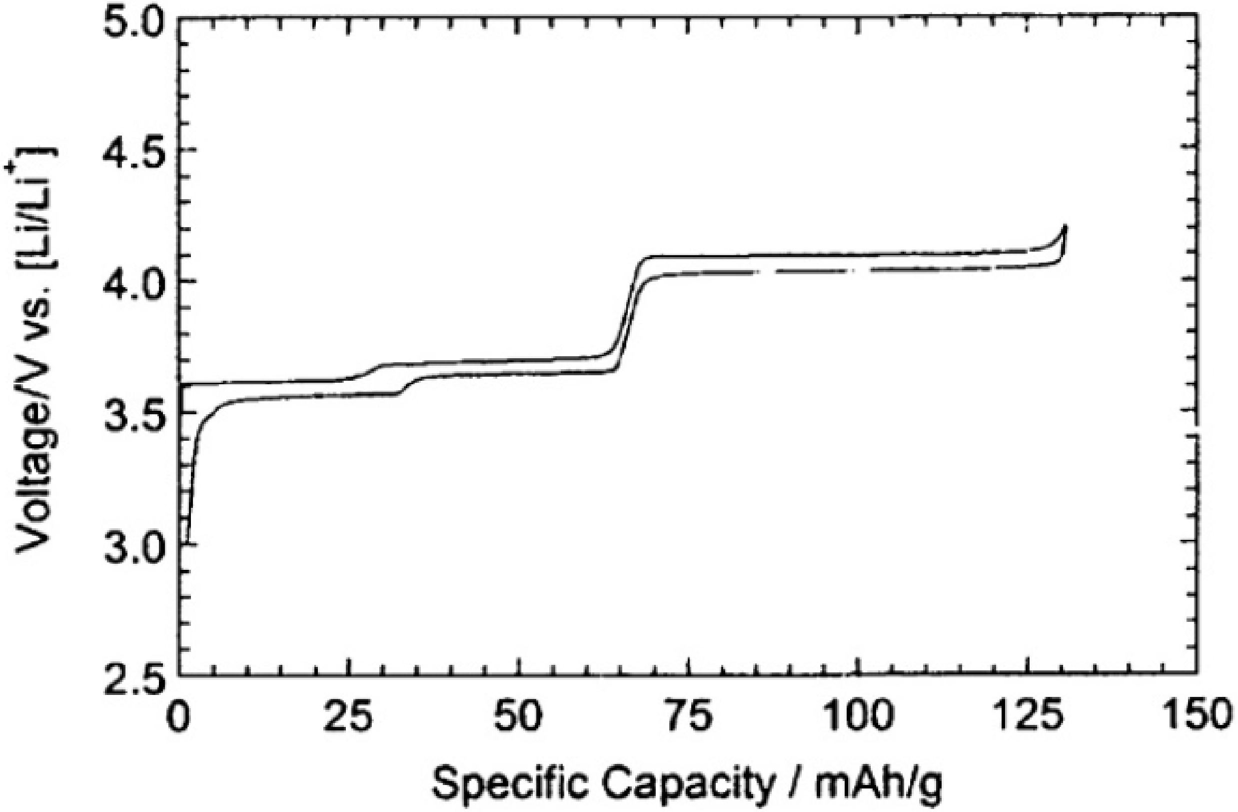


Fig. 9A.13 Charge/discharge curve for $Li_3V_2(PO_4)_3$ that has the Nasicon structure

Experiments showed that it is possible to extract the third lithium from this material by going up to about 5V, but that this process is not readily reversible, whereas the insertion/extraction of the first two lithium ions is highly reversible

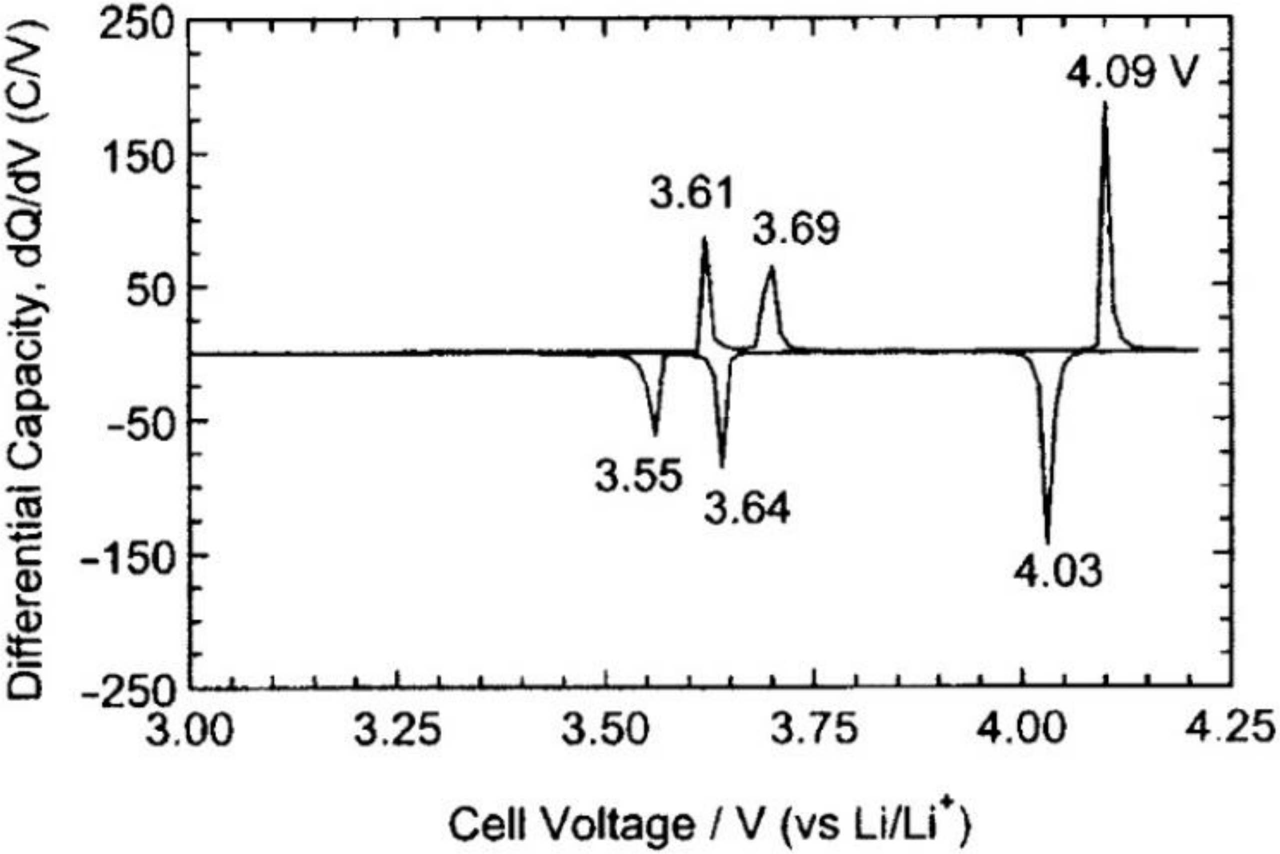


Fig. 9A.14 Differential capacity plot corresponding to the charge/discharge data for $Li_3V_2(PO_4)_3$ shown in Fig. 9A.13

A4.2 Materials with the Olivine Structure

-Another group of materials that have a hexagonal stacking of oxide ions : Olivine structure, $LiFePO_4$

-olivine structure, M_2XO_4, M ions are in half of the available sites of the close-packed hexagonal oxygen array. X ions occupy one-eighth of the tetrahedral sites→ two octahedral sites in olivine are crystallographically distinct, and have different sizes.

e.g. $LiFePO_4$: lithium and transition metal cations have an ordered cation distribution. The M1 sites containing lithium are in linear chains of edge-shared octahedral. M2 sites are in a zigzag arrangement of corner-shared octahedral → the result is that lithium transport is highly directional in this structure. Deletion of lithium occurs by a reconstitution reaction with a moving two-phase interface in which $FePO_4$ is formed at a potential of 3.43V vs. Li→ theoretical specific capacity of 170mAh g^{-1}, which is higher than that obtained with $LiCoO_2$. Lower electronic conductivity (R & D topic)

A5 Materials containing fluride ions

-replacement of some of oxide ions in lithium transition metal oxides by fluoride ions

e.g. lithium vanadium fluorophosphates, $LiVPO_4F$ → triclinic structure ($LiFePO_4 \cdot OH$) → redox reaction V^{3+}/V^{4+}

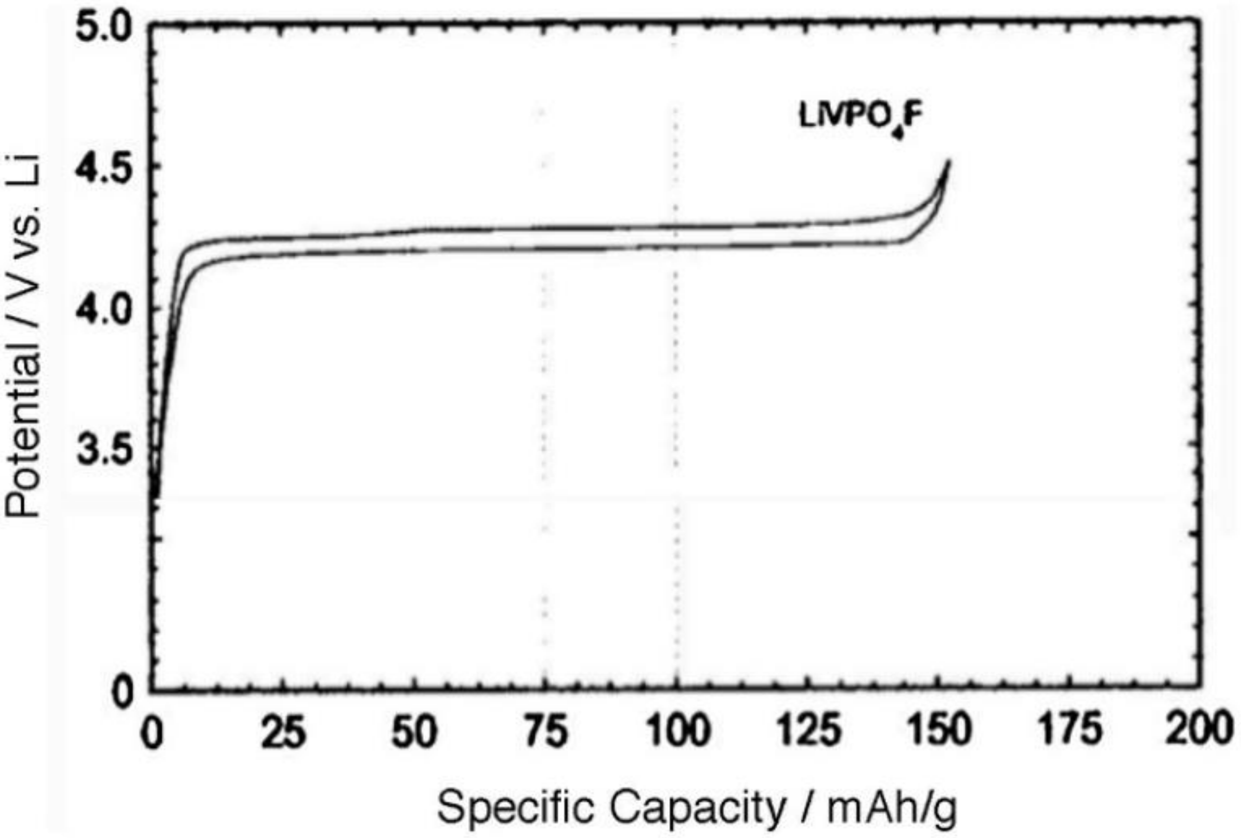


Fig. 9A.15 Charge/discharge behavior of $LiVPO_4F$

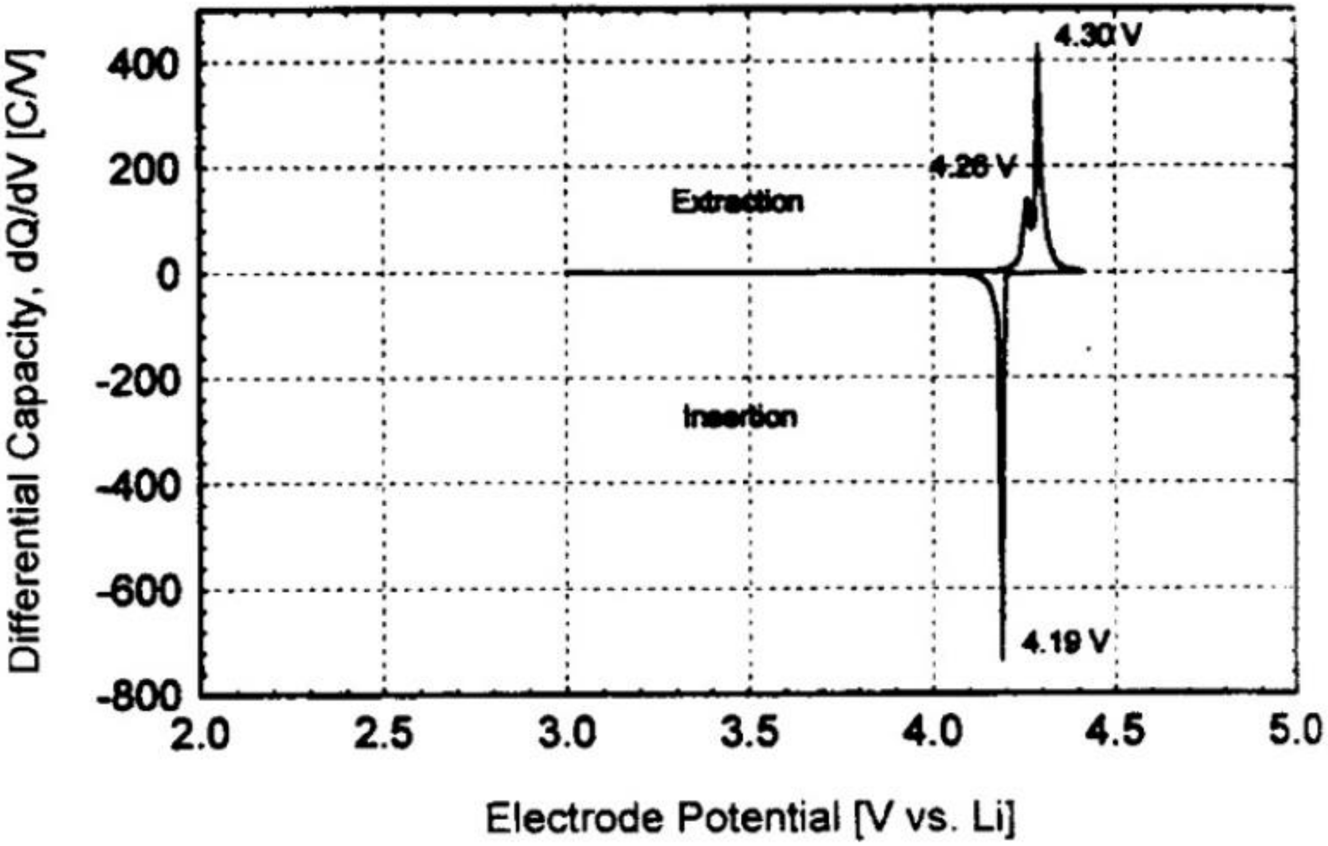


Fig. 9A.16 Differential capacity plot corresponding to the charge/discharge data for $LiVPO_4F$ shown in Fig. 9A.15

B. Liquid Positive Electrode Reactants

B1 Introduction

-there are two types of primary batteries that have been available commercially, in which the reactant is a liquid: the Li/SO_2 and Li/$SOCl_2$ (thionyl chloride) systems → very high specific energies. But because of safety considerations these batteries are not in general use, and are being produced for military and space purposes

B2 The Li/SO_2 system

-positive side: large surface area carbon electrode → $Li_2S_2O_4$ is formed upon discharge → very flat at 3.0 V (Fig. 9B.1), reconstitution reaction

$$2Li + 2SO_2 = Li_2S_2O_4$$

The theoretical specific energy of this cell can be calculated to be 4,080kWh kg^{-1},a high value

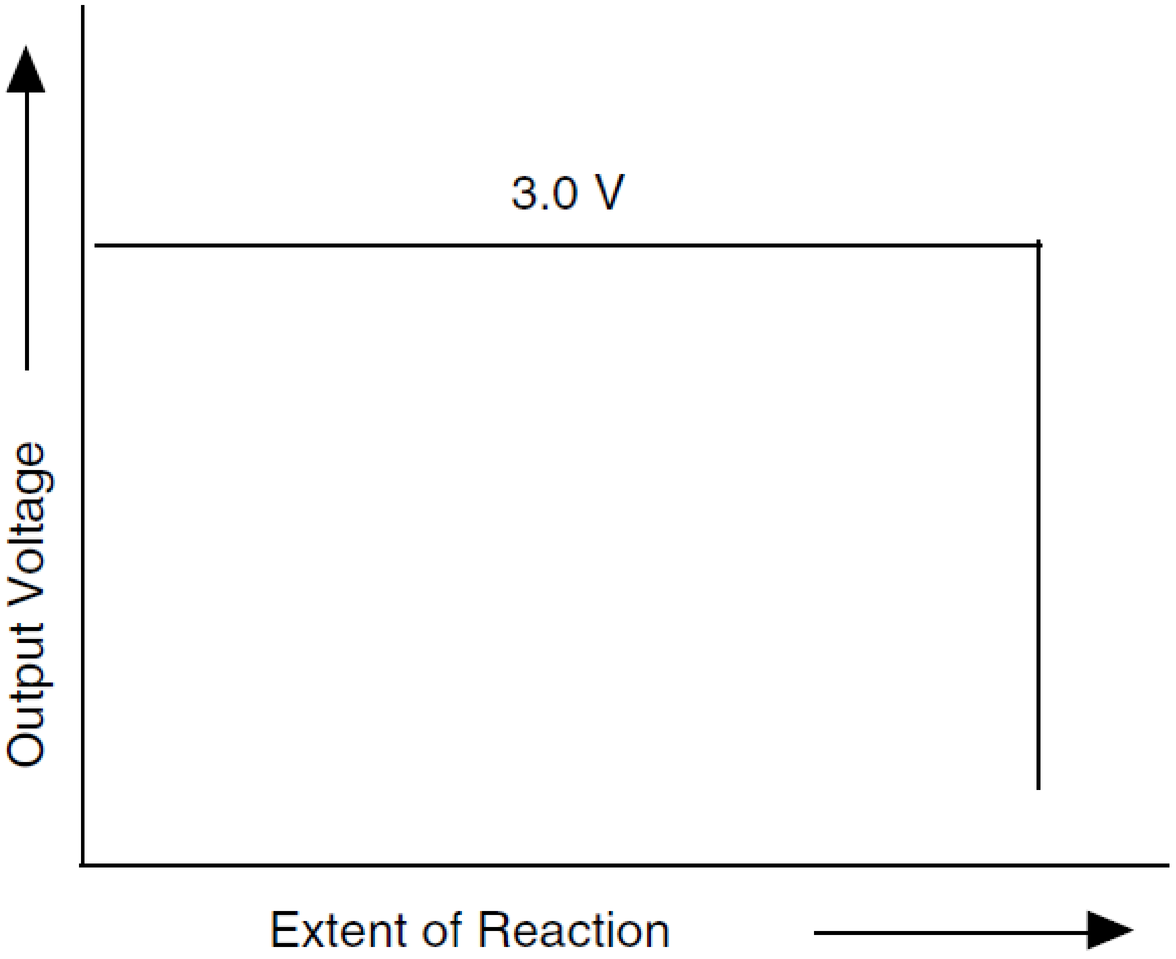


Fig. 9B.1 Discharge curve for a Li/SO_2 cell

Table 9B.1 Gibbs free energies of formation of phases in the Li–S–O system at 25°C

Phase	Gibbs free energy of formation ($kJ\ mol^{-1}$)
Li_2O	−562.1
SO_2	−300.1
Li_2S	−439.1
$Li_2S_2O_4$	−1,179.2

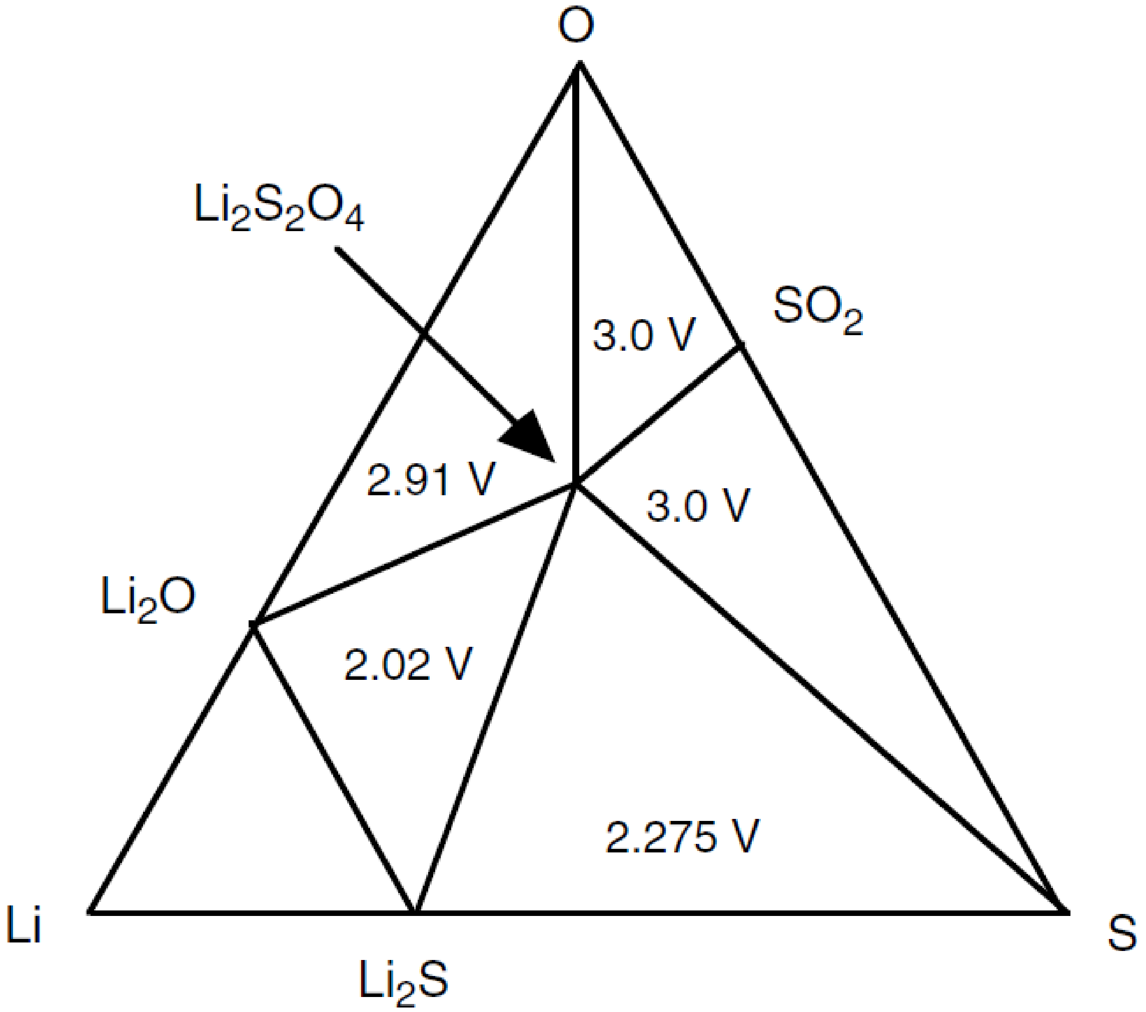


Fig. 9B.2 Phase stability diagram for the ternary Li–S–O system at ambient temperature

B3 The Li/SOCl$_3$ system

-higher constant voltage plateau at 3.66 V

$$4Li + 2SOCl_2 = 4LiCl + S + SO_2$$

The theoretical specific energy: 7250 kWh kg^{-1}

C. Hydrogen and water in positive electrode materials

-electrochemical insertion/deletion of hydrogen is a major feature in some types of aqueous batteries

metal hydrides as negative electrode

-it is generally known that alkali metals react vigorously with water, with the evolution of hydrogen. In addition, materials containing lithium are sensitive to air and/or water. It has been known that hydrogen (protons) can be present in oxides, and that water can be absorbed into some selective cases.

C2 Ion exchange

-Na^+ by Li^+, Li^+ by H^+

-the presence of anions in the solution that react with lithium ions to form stable products, such as LiCl (can either remain in solution or precipitate as a solid product)

$$HCl + LiMO_2 = HMO_2 + LiCl$$

C3 Simple addition methods

-hydrogen can be simply added to a solid in the form of interstitial protons

-simultaneous introduction of hydrogen component and oxygen component of water, i.e., both protons and oxide ions.

C4 Thermodynamics of the Li-H-O system

-considers an electrochemical cell with pure lithium at the negative electrode, the potential of water that is saturated with $LiOH \cdot H_2O$ will be 2.23V when hydrogen is present at 1 atm.

On the other hand, water saturated with LiOH $\cdot H_2O$ will have a potential of 3.46V vs. Li if 1 atm of oxygen is present. It can be seen that under these conditions water has a stability window of 1.23V, as is the case in the binary hydrogen–oxygen system

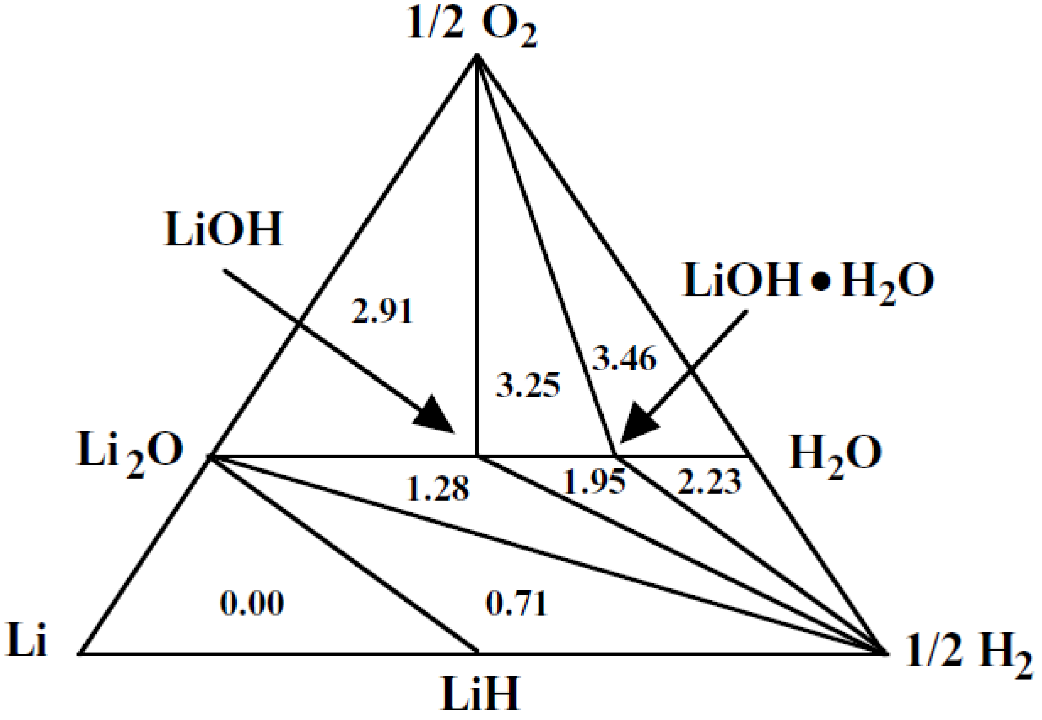


Fig. 9C.1 Calculated phase stability diagram for the Li–H–O system at 298 K, assuming unit activities of all phases. The numbers within the triangles are their respective potentials vs. pure lithium