Appendix   For Setup Pourbaix Diagrams

A.1 Pourbaix diagrams and MALT/CHD

At present, the thermodynamic database MALT does not contain any aqueous species in its main database. Even so, the thermodynamic data for some aqueous species are available at 298.15 K and those data can be utilized in constructing the Pourbaix diagram. On the other hand, the present CHD for windows can provide a basis of constructing such Pourbaix diagrams, although this has been developed originally for constructing high temperature chemical potential diagrams.

Here, a method of constructing Pourbaix diagrams will be explained by using the user's data file, "FeSAqueous.txt" which store the thermodynamic data for aqueous species in the Fe-S-H-O system. This appendix is based on the following paper:

H. Yokokawa, N. Sakai, T. Kawada, and M. Dokiya, "Generalized Electrochemical Potential Diagrams for Complex Aqueous ($M-X-H-O-e^-$) Systems," J. Electrochem. Soc. 137(2)**, 388 (1990).**

Another example is the Li-Mn-O-H system which appears as the important system for the positive electrode for lithium batteries. This will be based on the user's data file, "LiMnOHAqueous.txt."

User's DataBase: FeSAqueous.udb

In this appendix, the compounds and aqueous species listed in Table A. 1 are used in constructing Pourbaix diagrams. The condensed compounds are those retrieved from the thermodynamic database MALT. Data source "udb" means the FeSAqous.udb which are compiled from the user data file "FeSAqueous.txt." The data source of the aqueous species are the NBS thermodynamic properties published in 1982 which are the main parts of the MALT database so that the consistency of the data in the FeSAqueous.udb with the Main Database is obvious.

In the NBS tables, some data are lack in the absence of the experimental data. For the construction of chemical potential diagram, only the Gibbs energy data are used. On the other hand, the Gibbs energy in MALT Direct is calculated from the enthalpy data and the entropy data. When enthalpy and entropy are lack but Gibbs energy is available in the NBS table, the NBS data could not be used directly. In such a case, user data are treated as follows as a convenient method although this has no physical meaning, that is, the enthalpy value is assumed to be the same as the Gibbs energy and the entropy is calculated to reproduce the Gibbs energy value from thus assumed enthalpy.

In addition, the heat capacity of all aqueous species is assumed to be zero. Apparently, this is not correct.

Thus, please note that the present data set of the aqueous species are not valid at temperatures other than 298.15 K.

Table A.1 Gibbs energy change for formation of compounds and their data sources

Compound	state	$\Delta_f G^o/RT$	source
H_2S	g	-13.53	MALT
SO_2	g	-121.14	MALT
Fe^{2+}	ao	-31.84	udb
Fe^{3+}	ao	-1.90	udb
$HFeO_2^-$	ao	-176.82	udb
S^{2-}	ao	34.63	udb
SO_4^{2-}	ao	-300.49	udb
HS^-	ao	4.87	udb
HSO_4^-	ao	-305.11	udb
$FeSO_4^-$	ao	-311.91	udb
H_2S	ao	-11.24	udb
H_2O	l	-95.72	MALT
H_2O_2	l	-48.69	MALT
$H_2SO_4*6.5H_2O$	l	-922.66	MALT
Fe	c	0.00	MALT
Fe_2O_3	c	-299.55	MALT
Fe_3O_4	c	-409.85	MALT
FeS	c	-40.52	MALT
FeS_2	c	-67.36	MALT
$FeSO_4$	c	-331.31	MALT
$Fe_2(SO_4)_3$	c	-909.78	MALT
$FeSO_4*7H_2O$	c	-1012.99	MALT

What are Pourbaix Diagrams

Usually, the Pourbaix diagrams can be used for different types of diagrams.

One is the predominance area diagram, in which the dominant aqueous species will be given as a function of pH and pE, where pH means $-\log a(H^+)$ and pE is the corresponding variable for electrical potential. Resulting area of each aqueous species can be expressed in terms of convex polygons.

The second, important diagram is the normal diagram in which the equilibria between the aqueous species and the condensed phases are shown as chemical potential diagrams.

Here, these two types of diagrams will be reproduced using the CHD for Windows.

Fe-O-H-e$^-$ system

In the MALT for Windows, the thermodynamic data should be retrieved in the following manner.

1) User data file, FeSAqueous.txt, should be selected and compiled (menu Tool/User data/compile user data text file).
2) In the menu of Tool/MALT options, check should be made on the option for including aqueous species in the options in searching.
3) In the menu of "Get compounds by elements", "Compounds consisting of combinations of elements" should be selected as the mode of searching compounds. When the element sets of O,H, Fe will be selected, the compounds and aqueous species in the Fe-O-H-e$^-$ system will be retrieved.

In CHD for Windows, these thermodynamic data will be transferred from MALT by means of MALT Direct.

Note again here that the present thermodynamic data for aqueous species stored in the user database: FeSAqeous.udb does not include the high temperature heat capacity data. Calculation at temperatures other than 298.15 K leads to serious errors so that this should never be attempted.
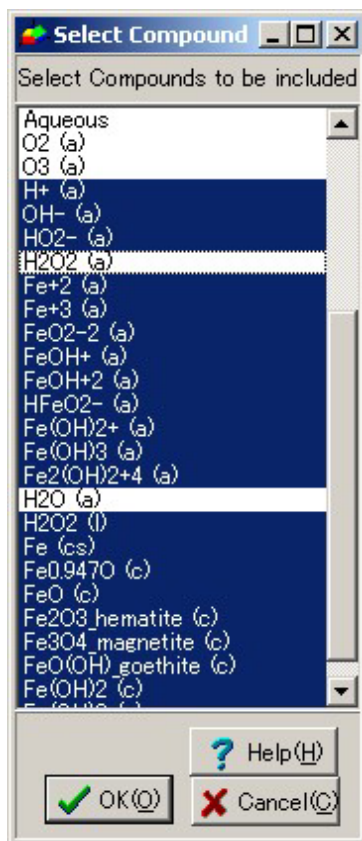
Fig. A1.1 Selection of Species to be included in the chemical potential diagram.

Chemical System

The first diagram to be constructed is the Pourbaix diagram for the Fe-O-H-e⁻ system. Species to be included are determined as followed:

1) Menu Chemical System is selected:

   Selection of compounds is made by "selection by Default" with checking on the "Condensed phases" and "Aqueous species."

2) Then, "Reselection" button is clicked.

3) Among the listed species, the following species are excluded.

   O2(a), O3(a), H2O2(a)

Fig. A1.1 shows the resulting form for selecting compounds. The focused species and compounds are to be included in the diagram construction.

Diagram Specification

Dimension Selection :

No further specification is needed; that is, 298.15 K is selected.

Fixation

Since the Pourbaix diagram is constructed under the condition of $a(H_2O) = 1$. For this purpose, the following is made:

1) Select the species, H2O a, in the list of species and compounds.
2) Select the coefficient of 1.

Diagram Selection

Here, the three dimension surface diagram is selected as diagram type.

As Coordinates, the followings are listed:

(D:O)

(D:Fe)

(D:pE)

Here, (D:pE) is the coordinate corresponding to the electric charge. In the present treatment of CHD, the charge is treated as pseudo element. As a result, working variable for the electrical potential is defined as follows,

$$pE = \phi / 2.303 \, kT \qquad\qquad (A1.1)$$

where ϕ is the electrical potential. This is well related with the pH defined as

$$pH = -\mu(H^+) / 2.303 \, kT = -\log a(H^+) \qquad\qquad (A1.2)$$

To modify the coordinates appropriate for the Pourbaix diagram,

1) pH is selected as X axis. For this purpose, first focus is moved on the first line of (D:O) and double click on this line. A species, H+ (a), is first selected and the coefficient of –1 is selected in the Coefficient Fom.
2) pE is selected as Y axis. For this purpose, focus is moved on the (D:pE) and then click the upward arrow to move the (D:pE) to the second line.
3) The coordinate (D:Fe) is not changed.

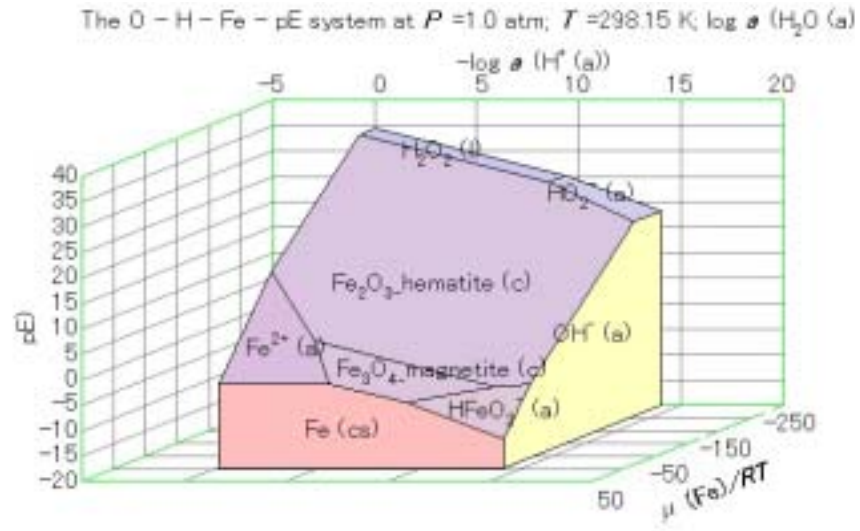**Equilibria between condensed phases and aqueous species I generalized diagram**

The 0 – H – Fe – pE system at P =1.0 atm; T =298.15 K; log a (H$_2$O (a)

$-$log a (H$^+$ (a))

Fig. A1.2 The generalized electrochemical potential diagram for the Fe-O-H-e$^-$ system at 298.15 K under the condition of a(H$_2$O) = 1.

Fig. A1.2 shows the generalized electrochemical potential diagram for the Fe-O-H-e$^-$ system at 298.15 K under the condition of a(H$_2$O) = 1. The important point as the generalized diagram is that the chemical potential or the activity of Fe is explicitly expressed in the diagram. In this diagram, the condensed phase and the aqueous species are respectively shown as stable polygon.

There are several points to be noted here:

1) Aqueous species are presented as the condition that their activity is equal to unity.

2) On the other hand, those species or compounds which do not contain the iron component form the frame within which the iron compounds can be displayed as stable compounds; namely, H$^+$, H$_2$O$_2$(l), HO$_2^-$, and OH$^-$ form such a frame as shown in Fig. A1.2.

Equilibria between condensed phases and aqueous species II Pourbaix diagram

Fig. A1. 3(a) and 3(b) are the diagram to reproduce the Pourbaix diagram.

Fig. A3(a) is the two dimensional chemical potential diagram which is constructed under the same calculation conditions as Fig. A1.2. When compared with the normal Pourbaix diagram, the regions beyond pH=0 or 14 are lacked. This is because the H$^+$ and OH$^-$ species are explicitly included as
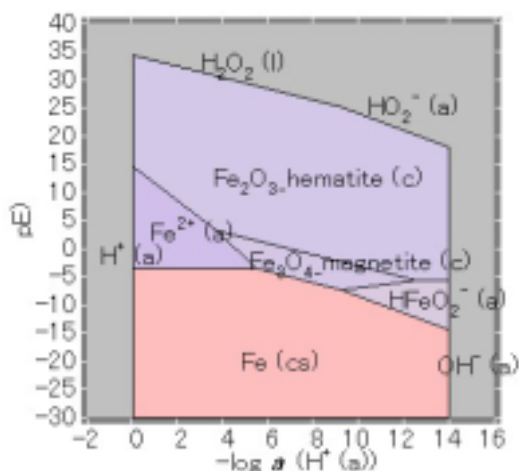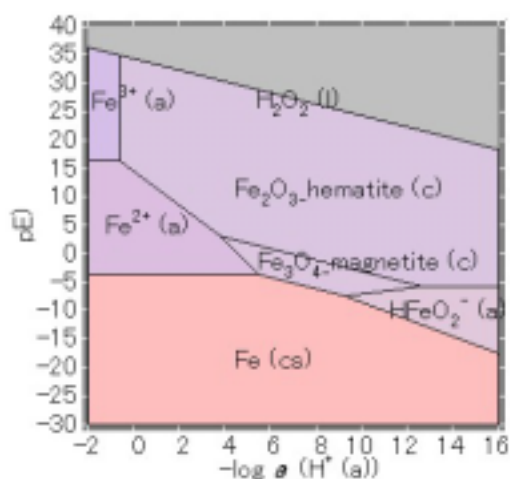
Fig. A1.3 The generalized electrochemical potential diagram for the Fe-O-H-e$^-$ system at 298.15 K under the condition of $a(H_2O) = 1$. (a) with and (b) without H^+, HO_2^-, and OH^- species.

target compounds to be included as stable species and their activity is defined as unity.

To reproduce the Pourbaix diagram which shows the equilibria beyond these limits, the following can be made.

1) In the menu of "Chemical System / Selection of compounds," "ReSelection" button is clicked and the species, H^+, HO_2^- and OH^-, are excluded.

2) Other conditions are the same as before.

Resulting diagram is shown in Fig. A1. 3(b). The species, Fe^{3+}, appears as stable species.

Predominant area diagram

Pourbaix also proposed to use the predominant area diagram which indicate what aqueous species is predominant in the given thermodynamic conditions in terms of pH and pE.

To reproduce the predominant area diagram, the following setting can be made:

1) In the menu of "Chemical System / Selection of Compounds, the default setting is made only on the aqueous species.

2) Then, "ReSelection" button is clicked and those species which do not contain the iron component will be excluded; namely, O_2, O_3, H^+, HO_2^-, OH^-, H_2O_2 will be excluded.

Fig. A1. 4 shows the predominant area diagram in which only the iron containing aqueous species are presented as predominant species.
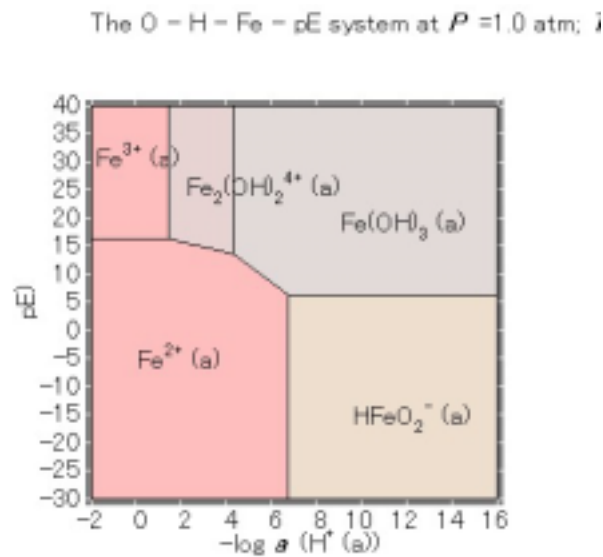

Fig. A1.4 The predominant area diagram for the Fe-containing species at 298.15 K.

S-O-H-e⁻ System

Chemical System:

The same user database is used to retrieve the thermodynamic data for the S-O-H-e⁻ system.

The Pourbaix diagram and the predominant area diagram for the S-O-H-e⁻ system can be constructed in the same procedures as those in the Fe-O-H-e⁻
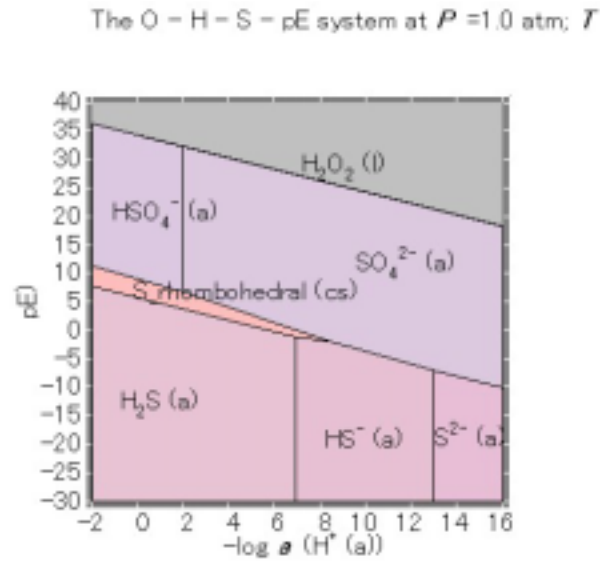
The O − H − S − pE system at P =1.0 atm; T

Fig. A1.5 The Pourbaix diagram for the S-O-H-e⁻ system at 298.15 K.

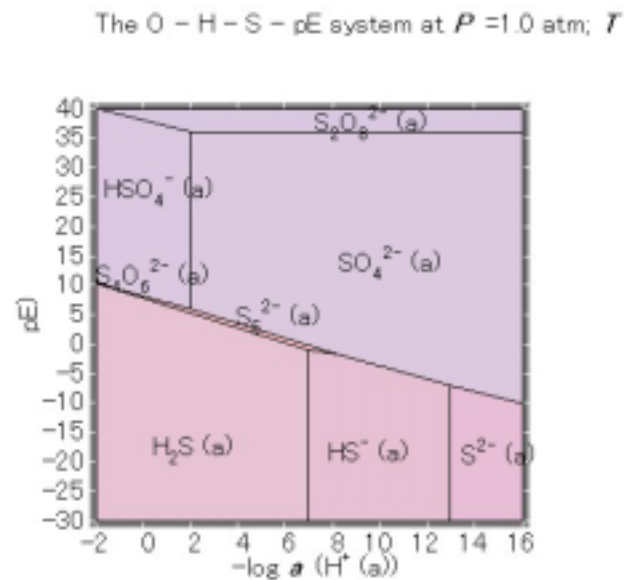The O − H − S − pE system at P =1.0 atm; T

Fig. A1.6 The predominant area diagram for the S-containing species at 298.15 K.

system.

Fig. A1.5 shows the two dimensional chemical potential diagram for the S-O-H-e⁻ system. As sulfur compounds, only S appears as stable compounds.

Fig. A1. 6 shows the predominant area diagram for the sulfur aqueous species. This is very similar to Fig. A1. 5 where except S, aqueous species are the stable ones.

Fe-S-O-H-e⁻ System

The most powerful point of the present CHD program is to construct the Pourbaix diagram for the multicomponent system without any difficulty. As described above, we do not need to have any other algorithms for constructing the Pourbaix diagram or the predominant area diagram. What is needed in constructing such diagrams is only the following:

1) Select the species to be included in construction of diagram.
2) Specify the condition that $a(H_2O) = 1$.
3) Select the coordinates appropriate for the Pourbaix diagrams. Particularly, pH and pE should be correctly selected.

The same procedures will be adopted below to construct the Pourbaix diagram for the Fe-S-O-H-e⁻ multicomponent system.

Chemical System
    The thermodynamic data for the Fe-S-O-H-e⁻ system are retrieved from the MALT main database and the user database: FeSAqueous.udb.

Three Dimensional Chemical Potential Diagram

Selection of Compounds
    Condensed phases and also aqueous species are included, although species in the O-H-e⁻ system are excluded to eliminate the limits derived from H^+ etc.

Fixation
  Only the activity of water is fixed at unity.

Diagram Coordinates
     $-\log a(H^+)$ (=pH)

pE

log a(Fe) – log a(S)

(D:Fe)

After execute the command Run, the range limits are modified as follows:

	-log a(H$^+$)	pE	log a(Fe)-log a(S)
min	-2	-40	-100
max	16	40	150
step	2	10	50
factor	1	0.25	0.125

Fig. A1.7 shows the three dimensional Pourbaix diagram for the Fe-S-O-H-e$^-$ system ate 298.15 K under a(H$_2$O)=1. As the third axis, we select the valuable of log a(Fe) – log a(S). The type of axis variable is convenient for treating two metals in equivalent manner. Here, we are treating two elements, iron and sulfur.

In Fig. A1.7, the phase equilibrium information for the Fe-O-H-e$^-$ subsystem appears in front of the diagram. On the right hand side, the dissection at pH=16 appears as a function of log a(Fe)-log a(S).

Conventional diagram for the Fe-S-H$_2$O system

Traditionally, the Pourbaix diagram for the Fe-S-H$_2$O system has been constructed under the assumption that the redox element of the target diagram is Fe so that only species which contain the iron component will appears in the diagram.

To reproduce such a diagram in CHD, the following should be made:

1) the third axis is changed to – log a(Fe) + log a(S). This is to present the sulfur containing compounds before the iron containing compounds which do not include sulfur.

2) In the menu of rotation of 3D diagram, the conversion matrix is changed to as follows;

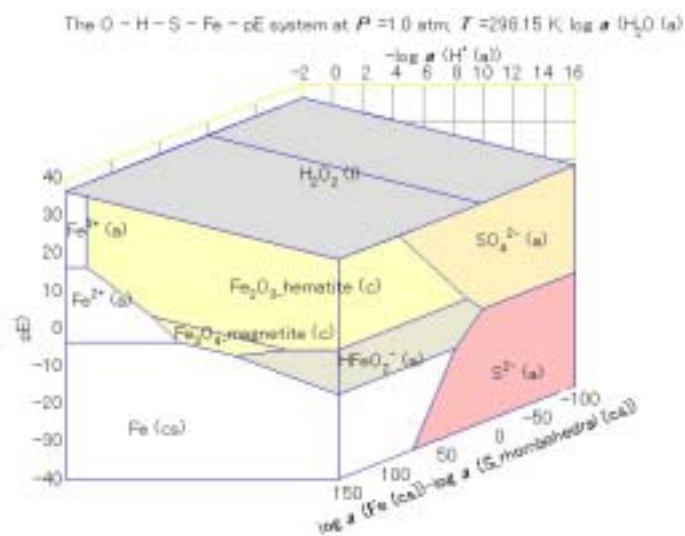|	X-axis	Y-axis	Z-axis
Horizontal	1.0	0.0	0.0
Vertical	0.0	1.0	0.0
Depth	0.0	0.0	1.0

Fig. A1.7 The Three Dimensional Pourbaix diagram for the Fe-S-O-H-e⁻ system at 298.15 K.
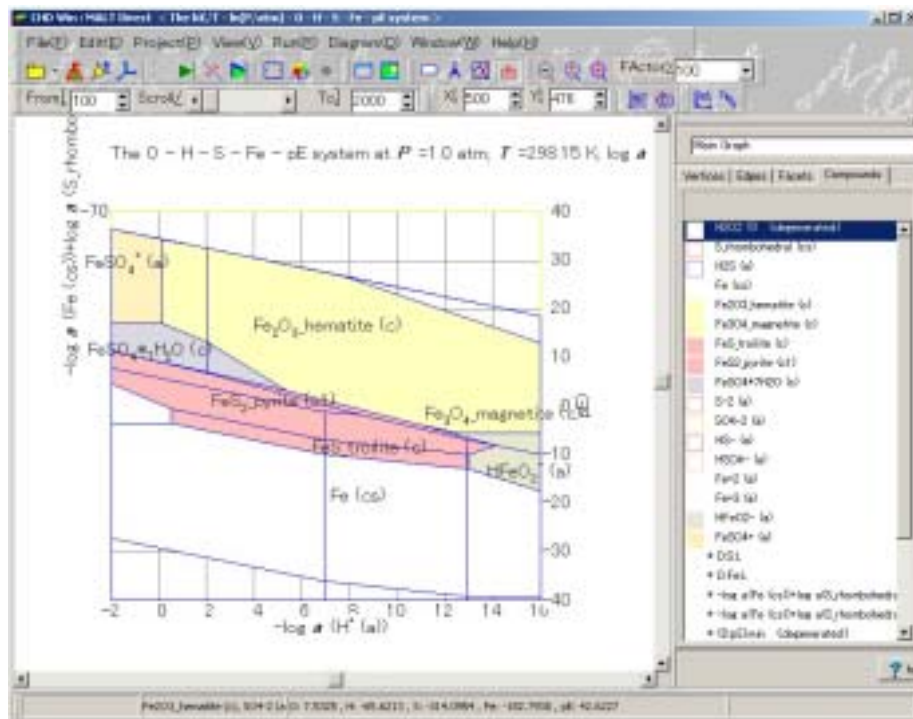

Fig. A1.8 The Three Dimensional Pourbaix Diagram projected on the pH-pE plane.

3) In the menu of Graph Inspector / "Compounds" page, the transparency of

the displayed compounds is changed in the following compounds:

H2O2 (l)

S_Rhombohedral (cs)

H2S (a)

S-2(a)

SO4- (a)

HS-(a)

HSO4- (a)

Fig. A1. 8 shows the three dimensional diagram which is rotated so as to give the normal two dimensional Pourbaix diagram. There are several blue lines which are not related with the stable polygons of the species. These are borderlines for species which are converted to be transparent.

The phase equilibria become complicated so that it is not easy to distinguish the respective stable area. For example, in Fig. A1. 8, it is not easy where the stability region of Fe_3O_4. To make clear the relative relations among the stability areas, the option of zoom can be used. Fig. A1.9 shows the enlarged diagram; here, the stability region can be well recognized in relations to other stability areas.
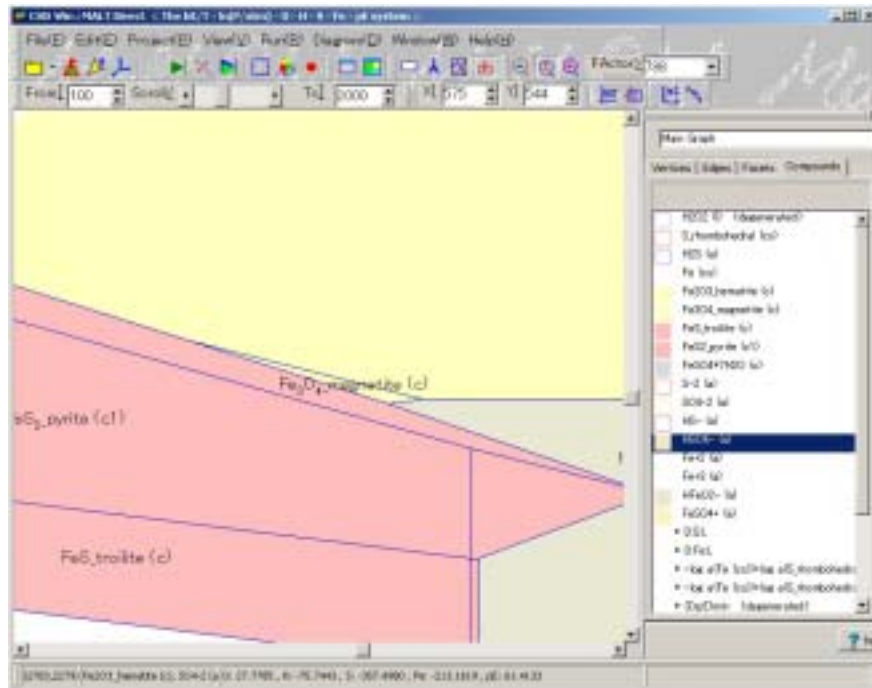

Fig. A1.9 The Three Dimensional Pourbaix Diagram projected on the pH-pE plane. This is enlarged diagram to show clearly the stability area of Fe_3O_4.

Dissections

There are many ways to specify another fixation to obtain the two dimensional diagram or the three dimensional surface diagram. One of the most attractive ways is to make a dissection on the three dimensional diagram.

Fig. 1A.10 shows the dissection diagram which was constructed on the basis of the previously constructed three dimensional diagram (Fig.A1. 8,9).

The menu of Run / Dissection is selected. The dissection plane is defined by selecting the variable of pH, that is, H^+ is selected and the coefficient of –1 is selected.

"Dissection Swing" should be checked.

"Profile Diagram" should be also checked. The diagram type is specified as dissected diagram(2D). The coordinates are selected as follows;
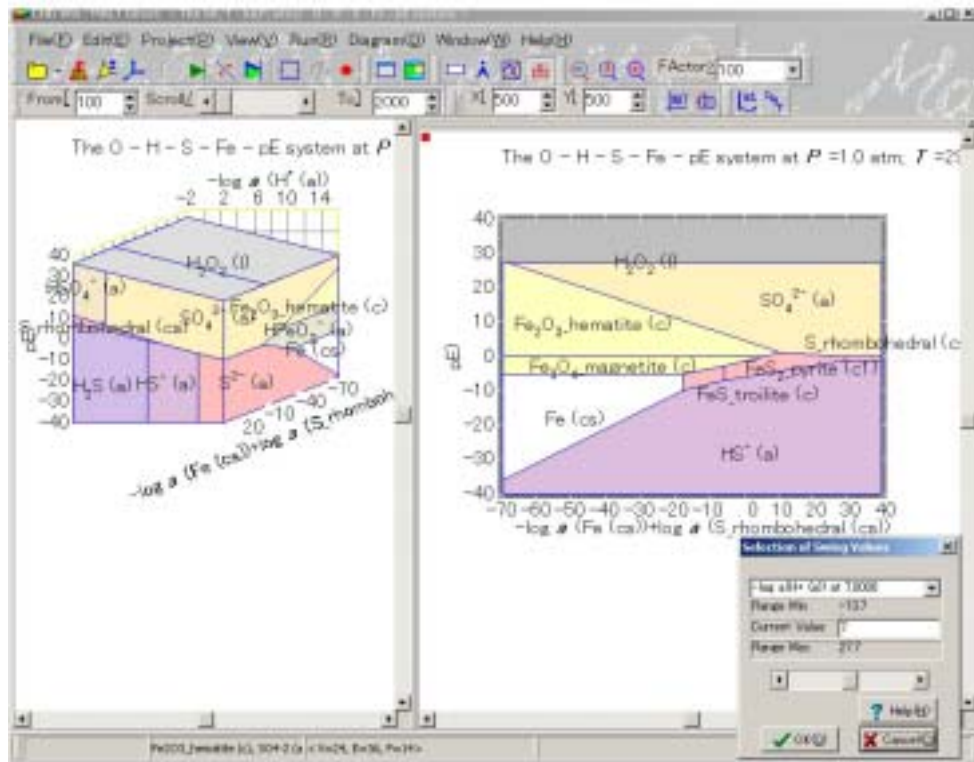

Fig. A1.10 The dissection diagram at pH=7 for the three Dimensional Pourbaix Diagram at 298.at K.

1) The axis variable, $-\log a(Fe) + \log a(S)$, is moved to the x-axis.
2) The axis variable, pE, is moved to the y-axis.
3) As a result, the working variable pH is moved to the z-axis that will not be used in 2D dissection diagram.
4) When the Selection of Swing Values appears, the range limits are changed by right-hand-mouse click; the new values should be changed from -2 to 16.

Fig. A1. 10 shows the dissection at pH=7. In the left hand side, the phase relations in the Fe-O-H-e$^-$ system are presented, whereas the phase relations in the corresponding sulfur system are shown in the right hand side. In between, those species which contain both iron and sulfur appear.

Relation among diagrams for dry, hydrated and wet systems

Since the chemical potential diagram for the Fe-S-O system and the electrochemical potential diagram for the Fe-S-O-H-e$^-$ system can be constructed by the same algorithm and the same program, it is very easy to compare those diagrams under the same conditions. One interesting comparison from the chemical point of view is the construction of diagrams with the same coordinates for the dry, the hydrated and the wet systems. By hydrated system, the diagram is constructed for the Fe-S-O-H system without any aqueous species. Even so, the activity of water is fixed at unity in the system, some hydrated compounds can be formed. By wet system, the diagram can contain the aqueous species in addition to the compounds appearing in the hydrated system.

Fig.A1.11 compares three diagrams for the Fe-S-O (-H-e$^-$) systems. As wet systems, pH=7 is adopted.

In the hydrated system, $FeSO_4$ disappears and instead, $FeSO_4 \cdot 7H_2O$ appears. In addition, $H_2SO_4 \cdot H_2O$ appear in the upper-right corner.

In the aqueous system, the aqueous species, $SO_4(a)$, appears instead of $FeSO_4$, $FeSO_4 \cdot 7H_2O$ or $H_2SO_4 + H_2O$. In addition, the aqueous species, HS^-, appears in the left hand side. This diagram should be compared with the Pourbaix-type dissection diagram in Fig. A2.10.
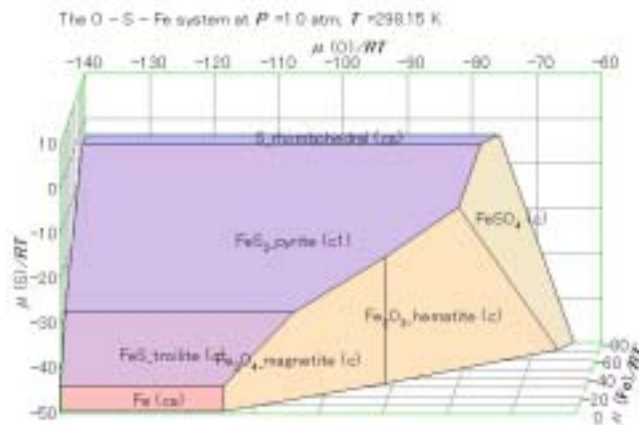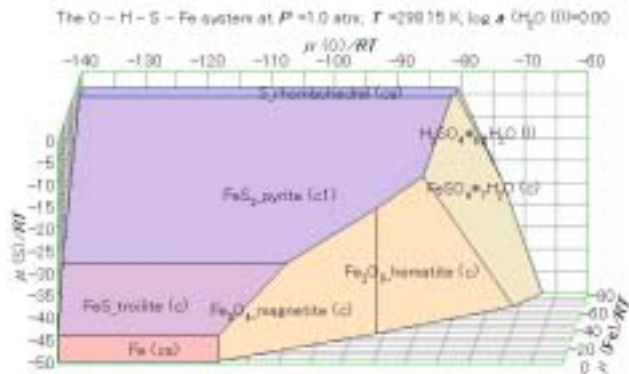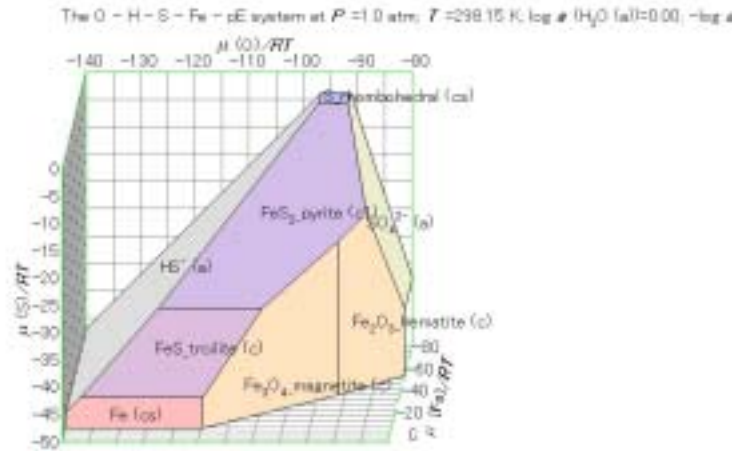
Fig. A1.11 The chemical potential diagrams for the Fe-S-O system: (a) wet system, (b) hydrated system (c) dry system

A2 Electrochemical potential diagrams for Li-Mn-O-H-e⁻ system

The present electrochemical potential diagram can be applied to many materials issues associated with the electrochemical devices. One of such applications is the lithium batteries.

Here, an attempt will be made to construct the electrochemical potential diagram for the Li-Mn-O-H-e⁻ system. Although the electrolyte for lithium battery does not contain water in it, it will be interesting to know the phase equilibria associated with the Li-Mn-O-H system because it has been already pointed out that the presence of a small amount of acidic water that is caused by the oxidation of the electrolyte may enhance the manganese dissolution.

Chemical System

The thermodynamic data for the Li-Mn-O-H-e⁻ system can be completed when the user database, LiMnOHAqueous.txt is used.

Pourbaix diagram for the Mn-O-H-e⁻ system

The thermodynamic data for the Mn-O-H-e⁻ system are retrieved as follows:

1) user database "LiMnOHAqueous.udb" is loaded in the menu "Options / User data /load user database."
2) In the menu "Tools / Customize MALT Setting ," check should be made for the "including Aqueous species" in the Options for Search in "General" page.
3) In the menu "Search Compounds," "Get compounds" with "Search by Elements" is selected. In the form of "Search Compounds by Elements," the mode of "Compounds consisting of combination of the elements" is checked and then "Mn," "O," and "H" are selected.
4) After preparing the thermodynamic data in MALT with above procedures , the "MALT Direct" is used to transfer the data to CHD.

In a similar manner described in Appendix 1, the two dimensional Pourbaix diagram for the Mn-O-H-e⁻ system can be constructed as in Fig. A2.1.

5) In the chemical system, the selection of compounds is made by first selecting the "Select by Default" with check on the condensed phases and the aqueous species and then by clicking "ReSelction" button to remove the species of O2(a), O3(a), H⁺(a), OH⁻(a), HO2⁻(a), H2O2(a).
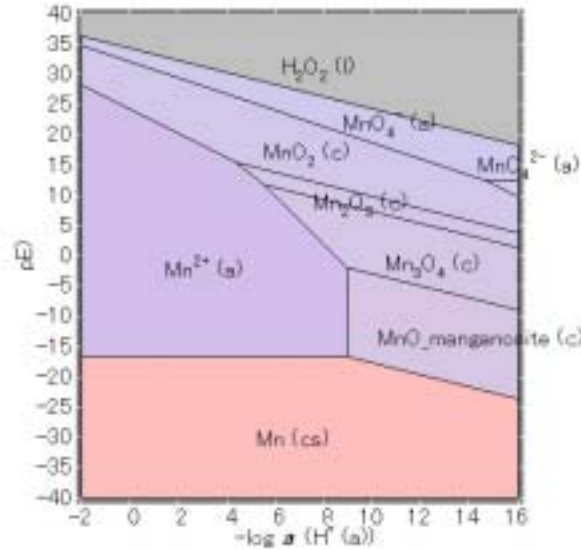
Fig. A2.1 The Two Dimensional Pourbaix Diagram for the Mn-O-H-e⁻ system at 298.15 K.

6) In the menu "Project / Specify Diagram," the fixation is made to select the water, H2O(a), with the fixed value at unity and the diagram type of 2D chemical potential diagram with the coordinates of -log $a(H^+)$ as the x axis and the (D:pE) as the y axis and (D:Mn) as the z-axis.

7) Since the resulting diagram has a display range wider than the normal, the display range of diagram should be changed by selecting the menu "Diagram / Range." The proper range for the x- and the y-axes are the followings

	-log $a(H^+)$	pE
min	-2	-40
max	16	40
step	2	10
factor	1	0.25

The chemical feature of the Pourbaix diagram for Mn is that the aqueous species Mn^{2+} as well as MnO_4^- and MnO_4^{-2} are present.

Pourbaix Diagram for the Li-O-H-e⁻ system

In the same manner, the Pourbaix diagram for the Li-O-H-e⁻ system can be constructed as given in Fig. A2.2. In this system, only Li⁺ species apears as the

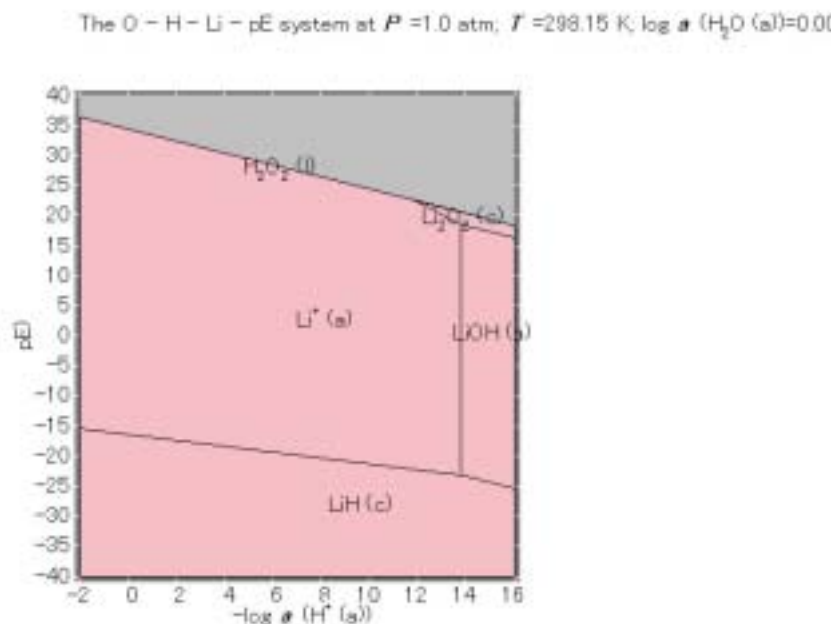The O⁻ – H – Li – pE system at P =1.0 atm; T =298.15 K; log a (H₂O (a))=0.0(

Fig. A2.2 The Two Dimensional Pourbaix Diagram for the Li-O-H-e⁻ system at 298.15 K.

stable species. However, the stability region of Li⁺ is quite wide compared with the corresponding species in the Mn-O-H system.

Three dimensional Pourbaix diagram for the Li-Mn-O-H e⁻ system

The three dimensional Pourbaix diagram can be set up by the following procedures:

1) Data retrieval for the Li-Mn-O-H-e⁻ system from the MALT main database and the user database: LiMnOHAqueous.udb.
2) Remove of aqueous species which do not include Li or Mn.
3) Fixation of water, H2O, at the activity of unity
4) The diagram type of 3D chemical potential diagram
5) Change of the coordinates as follows:

    X axis : -log a(H⁺)   (=pH)

    Y-axis : pE

- 114 -

Z-axis : log a(Mn) – log a(Li)

6) Diagram Range is defined as

	-log a(H$^+$)	pE	log a(Mn)-log a(Li)
min	-2	-40	-90
max	16	40	60
step	2	10	10
factor	1	0.25	0.125

Fig. A2.3 shows the resulting diagram. Phase equilibria in the Mn-O-H-e⁻ subsystem shown in Fig. A2.1 appears in the front plane in Fig. A2.3, whereas in the right hand side plane, the phase equilibria at *pH=16* appear.

Since this is the three dimensional diagram so that some additional procedures are needed to know more detailed information of the target chemical equilibria.

The followings are the possible procedures
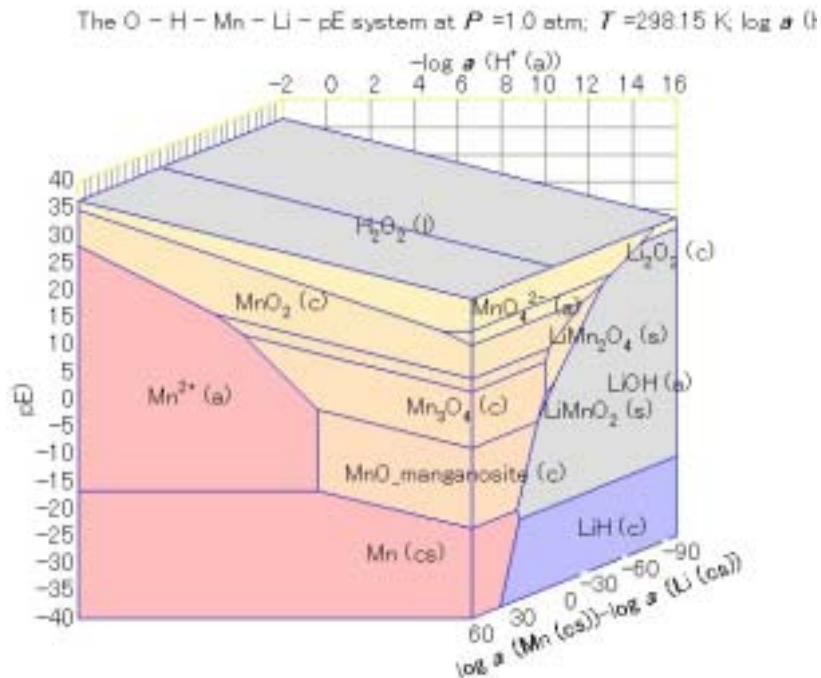
1) To make some compounds transparent.

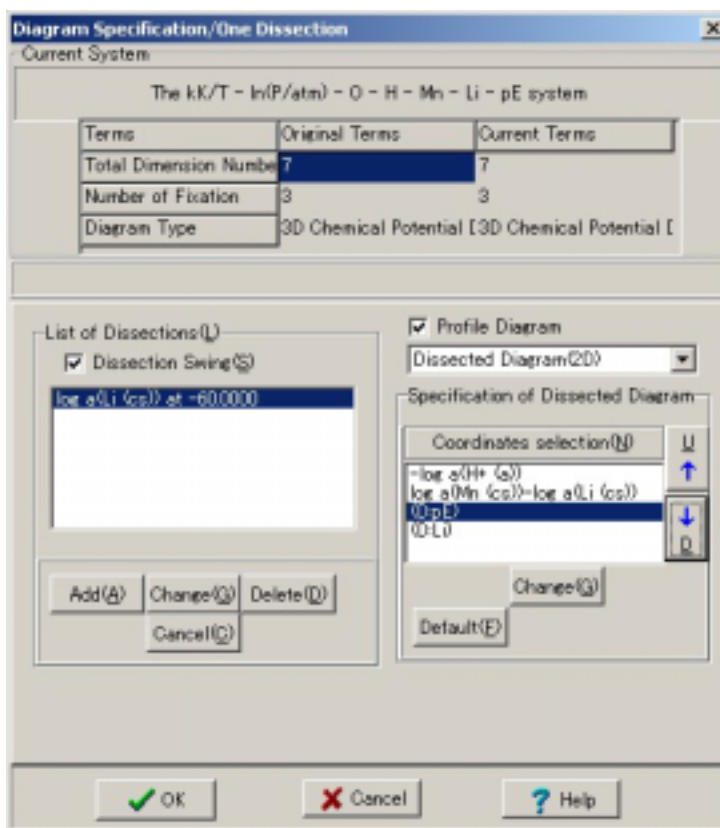Fig. A2.3   The Three Dimensional Pourbaix Diagram for the Li-Mn-O-H-e⁻ system at 298.15 K.

Fig. A2.4   The Diagram Specification / One Dissection for the three
Dimensional Pourbaix Diagram for the Li-Mn-O-H-e⁻ system at 298.15 K.

2) To make one dissection and to swing the dissection value.

3) To make a series of dissections

One dissection at log a(Li) = -60

Here, an attempt is made to make a dissection by fixing the lithium activity.

The menu "Dissection" is selected.   Thus, the dialog for the Diagram
Specification / One Dissection page will appear as Fig. A2.4.   One dissection
plane is selected by clicking the Add button and the Li(cs) is selected among
the Compound candidate.   At this time, the fixed value is input as –60.

When profile diagram is checked, the diagram can be selected between the
dissected diagram (2D)or the dissected diagram (3D).   Here, the dissected
diagram (2D) is selected.   In Fig. A2.4, the X-axis for the 2D dissection
diagram is defined as –log a(H⁺), the Y-axis being log a(Mn) – log a(Li).

A resulting dissection diagram is shown in Fig. A2.5.   In this diagram, the

display form for the dissection diagram is docked in the right-hand side docking panel.

The CHD Main form has the two docking panels; that is, the right-hand panel and the bottom-side panel. When the top frame of the display form is dragged by putting the control key and left click of mouse, the position of cursor appearing with the dragging square frame can be adjusted between the Right-hand frame of the Main Form and the scroll bar of the Main Display Panel. Then, the Dissection Display Form will be docked to the panel as shown in Fig. A2.5. The relative size of the main display panel and the additional display panel can be adjusted by manipulating the position of splitting bar adjacent to the vertical scroll bar of the main display panel.
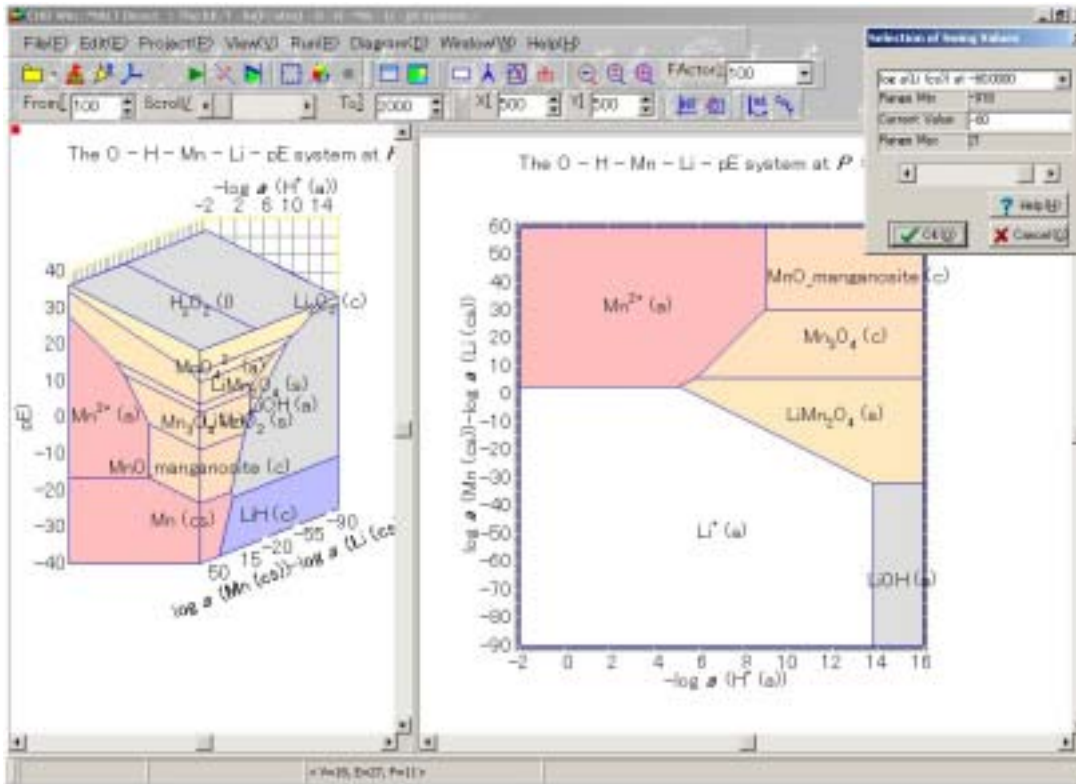

Fig. A2.5 The Three Dimensional Pourbaix Diagram for the Li-Mn-O-H-e⁻ system at 298.15 K with the dissected diagram (2D) at log a(Li)=-60. In the upper right corner, the Form for Selection of Swing values appears. The dissected value can be changed by manipulating the scroll bar.
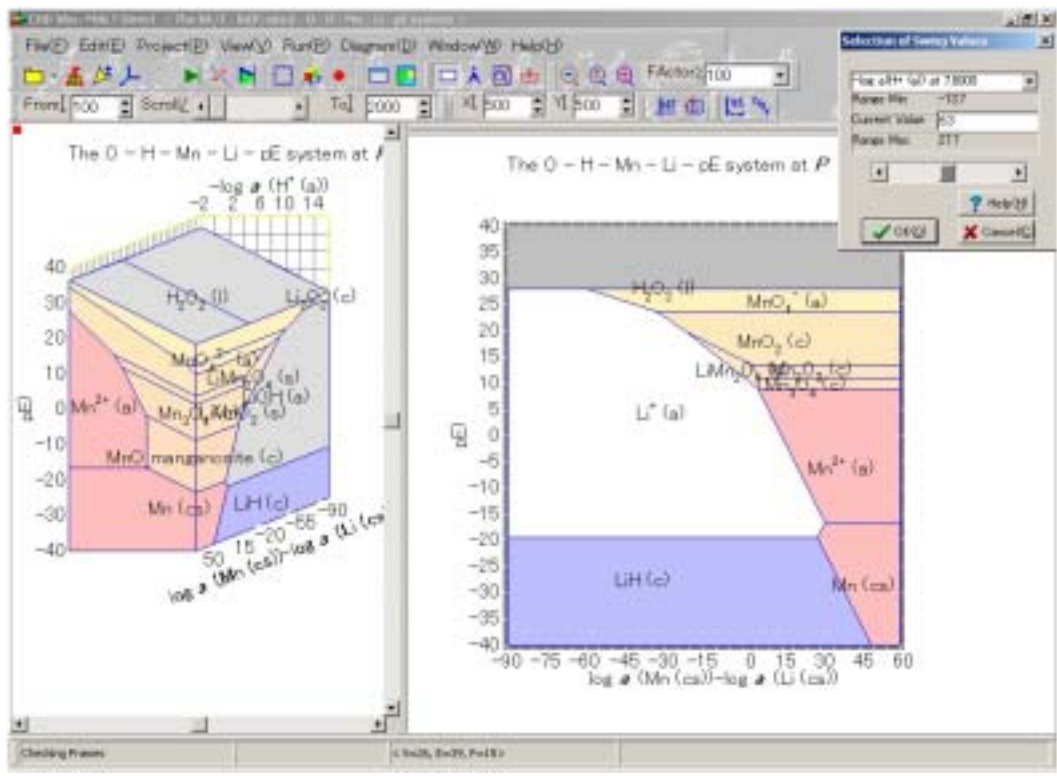
Fig. A2.6 The Three Dimensional Pourbaix Diagram for the Li-Mn-O-H-e$^-$ system at 298.15 K with the dissected diagram (2D) at -log $a(H^+)$=6.3.

When the Dissection Swing option is checked, the small form for selecting the swing value appears as in Fig. A2.5. Whenever the dissection value is changed, a new diagram is constructed and updated in the same display panel.

Fig. A2. 6 shows the dissection diagram for another dissection. Here, the pH, that is, -log$a(H^+)$, is defined as a dissection at 6.3. As the X-axis, the logarithmic activity difference, log a(Mn)-log a(Li), is adopted. The equilibria in the manganese system appear in the right-hand side, whereas those in the lithium system are given in the left-hand side.

In the chemical potential diagrams shown in Figs. A2.5 and 6, the chemical stability of LiMn$_2$O$_4$ against the dissolution into aqueous solutions can be discussed by using the following considerations.

First, the electrode reaction of LiMn$_2$O$_4$ can be written as follows;

$$LiMn_2O_4 = Li^+(a) + Mn_2O_4 + e^- \tag{A2.1}$$

The right-hand side direction is the charging process and the left-hand side direction is the discharging process. In Fig. A2.5, the lithium activity is fixed at log a(Li)=-60, and the equilibria between $LiMn_2O_4$ and Li^+(a) is shown.

> **Since $E/V = -(2.303\ RT\ /\ F)\ \log a(Li)$, log $a(Li)$=-60 corresponds to E=3.55 V**

This indicates that this lithium activity corresponds to the discharging process where Li^+(a) is inserted into Mn_2O_4 phase. In Fig. A2.6, the three phase combination of Li^+(a) / $LiMn_2O_4$/Mn_2O_4 corresponds well the above electrode reaction.

In addition to the normal electrode reaction, there is some possibility that side reactions can occur during the charge/discharge processes. The manganese dissolution is one of the most important side reactions. It has been pointed out that the manganese dissolution is enhanced by the acidic environments caused from the oxidation of electrolyte component. Since $LiMn_2O_4$ is dissolved into Li^+ and Mn^{2+}, this reaction can be written as follows:

$$LiMn_2O_4 + 8H^+ + 3e^- = Li^+(a) + 2Mn^{2+}(a) + 4\ H_2O(a) \tag{A2.2}$$
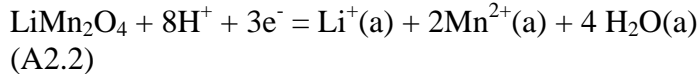
In Fig.A2.5, the stability regions of Li^+ and Mn^{2+} appear in the low values of pH=–log $a(H^+)$, whereas $LiMn_2O_4$ appears in the high pH region. This well corresponds to the fact that $LiMn_2O_4$ is dissolved under the acidic condition.

This is the reaction that consumes the electron so that this can be regarded as discharge-process-enhancing reaction. Actually, during the discharge process, the lithium activity increases (the electrode potential value decreases); In Fig. A2.5, the dissection value can be changed from –60 to –58. This corresponds to a change in lithium activity on discharge. On this change in the lithium activity, the stability area of $LiMn_2O_4$ becomes small. In other wards, the three-phase point of Li^+/$LiMn_2O_4$/Mn^{2+} shifts to the more basic side; that is, the manganese dissolution is enhanced.
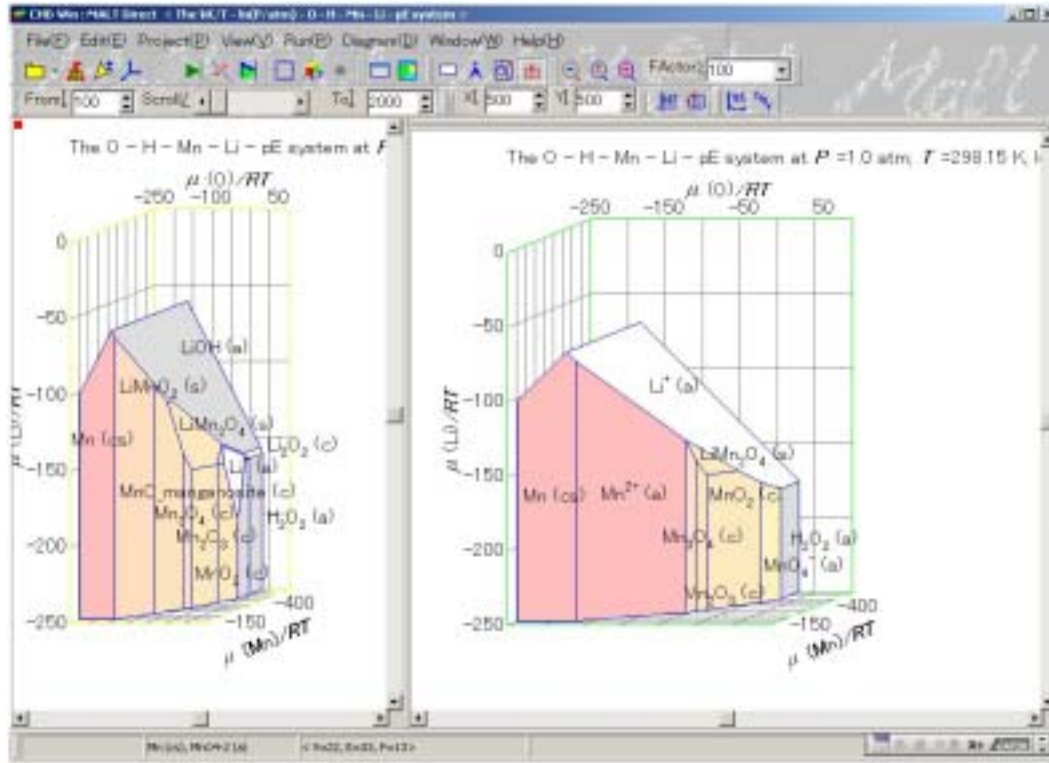
Fig. A2.7 The Three Dimensional Pourbaix Diagram for the Li-Mn-O-H-e[-] system at 298.15 K in the normal high temperature coordinates for the Li-Mn-O systems.

In Fig. A2. 6, the interesting phase equilibria are plotted. Here, three-phase point of $Li^+/LiMn_2O_4/Mn^{2+}$ is represented as the vertex point of their stability polygons. There is however, a new feature appearing in this diagram. That is, the spinel phase, Mn_3O_4, becomes very close to that three-phase point. This thermodynamically implies that the dissolved manganese ions, Mn^{2+}, can be precipitated as the spinel phase. Since the $LiMn_2O_4$ itself has the spinel structure, it is suggested that there is no kinetic barrier for Mn_3O_4 to be precipitated.

$$3Mn^{2+} + 4H_2O = Mn_3O_4 + 8H^+ + 2e^- \tag{A2.3}$$
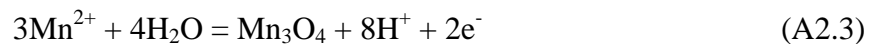
By combining with (A2.1), the following reaction can be written:

$$3LiMn_2O_4 + 8H^+ + 5e^- = 3Li^+ + 2Mn_3O_4 + 4H_2O \tag{A2.4}$$

By comparing Eqa. (A2.4) and (A2.1), the following is obvious: The

manganese ions remain without change in the ionic configuration after the lithium ion is removed in (A2.1), whereas the manganese ions in (A2.4) can be regarded as reconstructed from aqueous solution; in such a case, there are no lithium sites in the new spinel precipitate.

Thus, these diagrams can give the reasonable explanation for the following facts in the lithium batteries.

1) Manganese dissolution is enhanced in the acidic situation after the oxidation of electrolyte component.
2) Manganese dissolution becomes more severe on discharge process.
3) Even so, the manganese dissolution tends to be mild on heavily discharge state.
4) The capacity loss is also associated with the manganese dissolution. The loss of the lithium site due to the occupation of manganese ions should be the reason for the capacity fading.

Relation among the Pourbaix diagram for the multi-component system and the high temperature chemical potential diagram.

Since the Li-Mn-O system is one part of the subsystems of the Li-Mn-O-H-e$^-$ system, it can be possible to compare the phase relation appears in Fig. A2. 5 and 6 with those chemical potential diagrams proposed for high temperature use.

The main chemical potential diagram in Fig. A2.7shows the three dimensional diagram for Li-Mn-O-H-e$^-$ system at $a(H_2O)=1.0$. Although the aqueous species are shown in this diagram, they are not well shown because the axis of pH now disappears. In other wards, the phase equilibria developing along the pH axis are degenerated into the non-pH axis. Actually, there should be many species at one point in the three chemical potential diagram.

To display the diagram in Fig.A2.7, the species of MnO_4^- and MnO_4^{2-} are changed to be transparent.

The comparison is made in Fig. A2. 7 where the same phase equilibria as in Fig. A2. 6 are plotted in the normal three dimensional diagram. In this diagram, the stable polygons for Li^+ and Mn^{2+} appear in addition to the non-aqueous species. This clearly shows how the aqueous species affect on the normal phase equilibria.