

MATERIALS SCIENCE PRINCIPLES RELATED TO ALLOYS OF POTENTIAL USE IN RECHARGEABLE LITHIUM CELLS

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Summary

The rechargeability of electrochemical cells is often limited by negative electrode problems. The fundamental reasons for some of these problems when using elemental electrodes, as well as the basic principles involved in the different behaviors of alloys that undergo either insertion or reconstitution reactions at reactant species activities less than unity, will be briefly discussed.

Thermodynamic and kinetic properties of a number of alloys that might be used as electrodes in lithium systems are now known. Several of these have quite rapid kinetics and attractive capacities, with relatively small voltage losses and weight penalties, even down to ambient temperatures.

The all-solid, mixed-conductor matrix concept, in which two different binary alloy systems can be combined to produce dense, all-solid electrodes with the kinetic properties of fine particle dispersions, as well as attractive microstructural reversibility upon cycling, will also be discussed.

Introduction

The cycling behavior of electrochemical cells, especially at lower temperatures, is often limited by negative electrode problems. These may include gradually increasing impedance, which is observed as increased electrode overvoltage. In some cases there is macroscopic shape change. If elemental electrodes are used (below their melting points), there may be dendrite growth, or a tendency for filamentary or whisker growth. This may lead to disconnection and electrical isolation of active material, resulting in loss of capacity. It may also result in electrical shorting between electrodes.

In the absence of a significant nucleation barrier, deposition of a species will tend to occur anywhere at which the electric potential is such that the element's chemical potential is at, or above, that corresponding to unit activity. This means that electrodeposition may take place upon current collectors and other parts of an electrochemical cell that are at the same potential as the negative electrode, as well as upon the electrode structure where it is actually desired. This was a significant problem during the period

in which attempts were being made to use pure (molten) lithium as the negative electrode in high-temperature, molten salt cells. Another problem was the fact that alkali metals dissolve in their halides at elevated temperatures, leading to electronic conduction and self discharge.

In addition to these problems, the electrodeposition of a pure elemental negative electrode upon recharge can be inherently unstable on a microscopic scale, even in the presence of a chemically clean interface. It has been shown that electrodeposition can lead to an electrochemical analog of the constitutional supercooling that occurs during thermally-driven solidification [1, 2]. This will be the case if the current density is such that solute depletion in the electrolyte near the electrode surface causes the local gradient of the element's chemical potential in the electrolyte immediately adjacent to the solid surface to be positive. Under such a condition, there will be a tendency for any protuberance upon the surface to grow at a faster rate than the rest of the interface. This leads to exaggerated surface roughness, and eventually to the formation of stable dendrites. In more extreme cases, it leads to the nucleation of solid particles in the liquid electrolyte ahead of the growing solid interface.

Further, the interface between the negative electrode and the adjacent electrolyte is often not clean. Instead, reaction between the electrode and species in the electrolyte can lead to the formation of reaction product layers. The properties of these layers can have significant effects upon the resultant behavior of the electrode. In some cases they may be useful solid electrolytes, and allow electrodeposition through them. But in many others they are ionically blocking, and thus can greatly increase the interfacial impedance. The presence of such layers, and the local nature of their electrical breakdown, generally related to defects in their structure that lead to spots of locally reduced impedance, often causes the formation of deleterious filamentary growths upon recharge. This is an endemic problem with the use of organic solvent electrolytes with lithium electrodes at ambient temperatures.

These problems can often be alleviated by the use of alloys that undergo either topotactic or reconstitution reactions, instead of elements, as negative electrode reactants. If the diffusion of the depositing species, *e.g.*, Li, in the alloy is sufficiently fast that the activity at the surface remains less than unity, dendrite formation can be avoided. Deposition also occurs preferentially upon the desired electrode structure, rather than at other locations in the cell. In favorable cases, the formation of deleterious surface films may also be avoided.

However, the use of alloys with reduced activities implies reduced cell voltages, as well as increased weight. Therefore, possible increases in reversibility and cycle life of such electrodes are accompanied by reductions in the associated specific energy and energy density of cells in which they are employed.

Another potential problem in the use of alloy electrodes relates to the fact that there may be a significant volume or shape change involved in the

electrode reaction. In some cases this will lead to mechanical deterioration of the electrode structure. In other cases, it is negligible.

Principles determining the potential and capacity of alloy electrodes

The theoretical basis for understanding and predicting the potentials and capacities of both binary and ternary lithium alloys has now been established. These important practical parameters are directly related to the thermodynamic properties and compositional ranges of the pertinent phases in the respective phase diagrams.

There are two different types of reactions that can occur in electrodes [3]. One type includes topotactic reactions, in which a mobile guest species is inserted into, or extracted from, a static host crystal lattice, whose basic structural configuration remains essentially unchanged. The other, called reconstitution reactions, involves major structural rearrangements, with some phases being formed, and others being consumed, during the reaction. Topotactic reactions relevant to battery electrodes are often called insertion, or in the 2-dimensional case, intercalation, reactions. Reconstitution reactions are generally of the formation reaction or displacement reaction types. If the number of phases present is equal to the number of components (under isothermal and isobaric conditions), according to the Gibbs Phase Rule, all of the intensive parameters are independent of overall composition. This means that the electrode potential, under equilibrium or near-equilibrium conditions, is essentially constant. This leads to generally-desirable plateaux in discharge curves.

The lengths of these plateaux are determined by the extent of the two-phase regions in the related phase diagrams in the case of binary alloys. In the ternary case, it is determined by the width of the three-phase, constant-potential triangles.

Whereas, as pointed out above, it is possible to have topotactic reactions in alloys, it has been found that these do not generally extend over appreciable compositional ranges in lithium-based alloy systems. For this reason, as well as the fact that such solid solution reactions produce potentials that vary with composition rather than exhibiting constant-voltage plateaux, the bulk of the work to-date has focussed upon materials that undergo reconstitution reactions.

For illustration, we shall look at a few examples relating to these reactions.

Let us consider the schematic phase diagram shown in Fig. 1 [4] for a binary system Li-M. Suppose that this alloy system were to be used as an electrode in a lithium-based battery system at temperature T_0 . Reaction with lithium results in the overall composition moving horizontally across this phase diagram, as shown by the dotted line. In doing so, it would alternately cross single-phase and two-phase regions. When in a single-phase region, the lithium activity varies continually with composition, in

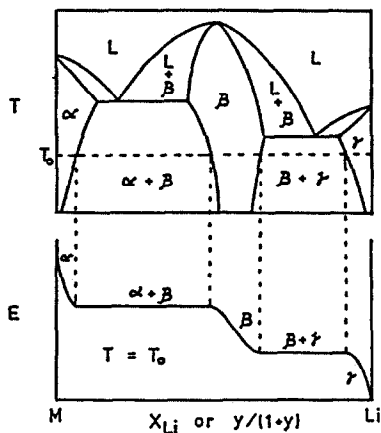


Fig. 1. Hypothetical phase diagram and related equilibrium titration curve.

accordance with the Gibbs Phase Rule. Correspondingly, in two-phase regions, it is composition-independent.

The lower part of the Figure shows how the electrode potential, E , which is determined by the lithium activity, varies with electrode composition, and thus with the state of charge, in this hypothetical binary system. We see that such an electrode can give either a charge-dependent potential, or a voltage plateau, depending upon the number of phases present.

A more complicated example, with actual data for lithium-tin alloys, is shown in Fig. 2 [5]. We see that this phase diagram contains six relatively-narrow intermediate phases at 415 °C. As a result, the equilibrium potential-composition data, called the equilibrium titration curve, show six, two-phase plateaux, separated by single-phase regions. The Figure also shows that the titration curve is somewhat different at 150 °C, in accordance with the changes in the phase diagram at that temperature.

If the Gibbs free energies of formation of the relevant phases are known, the values of the plateau potentials can be calculated, as they are directly related to the appropriate reactions in each part of the phase diagram and titration curve. Likewise, the lengths of the various constant-potential plateaux are determined by the extent of the two-phase regions in the phase diagram.

Ternary systems

The same general principles can be used to understand and predict potentials and capacities of ternary electrode materials. In this case, one uses isothermal sections of ternary phase diagrams, the so-called Gibbs triangles, upon which to plot compositions. In ternary systems, the Gibbs Phase Rule tells us that three-phase equilibria will have composition-dependent intensive properties, *i.e.*, activities and potentials. Thus compositional ranges that span three-phase regions will lead to potential plateaux.

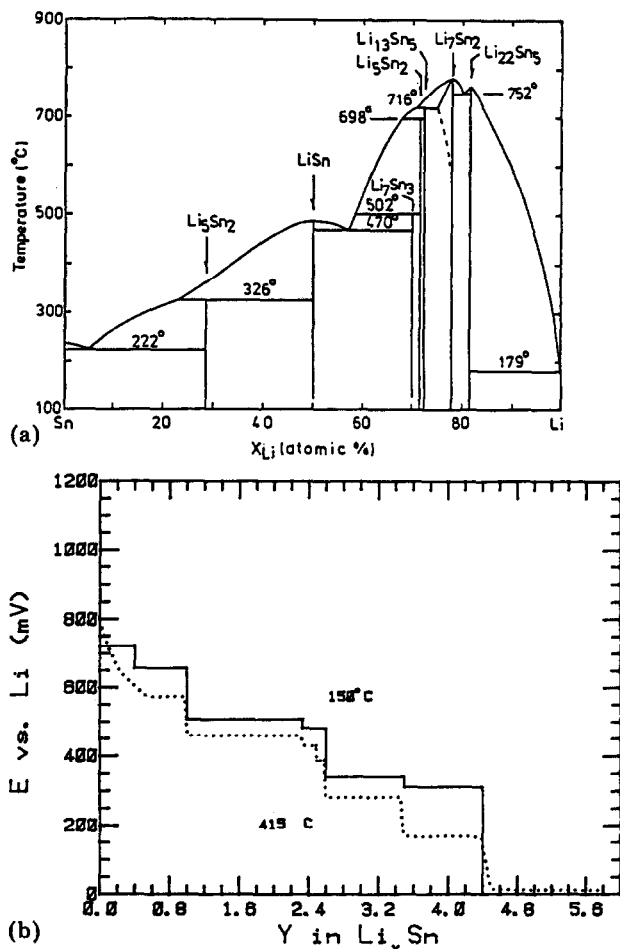


Fig. 2. Phase diagram (a) and titration curves (b) at 415 and 150 °C for the lithium-tin system.

Therefore, if the ternary phase diagram and the initial electrode composition are known, the compositional ranges of individual plateaux can be predicted, and with the relevant thermodynamic data, the potentials of each plateau can be calculated.

Experimental results on lithium alloys

An experimental arrangement employing the LiCl-KCl eutectic molten salt has been used in our laboratory, at temperatures near 400 °C, to study the phase diagrams and thermodynamic properties of alloys in the Li-Al, Li-Si, Li-Sb, Li-Bi, Li-Sn, Li-Pb, Li-In, Li-Ga and Li-Cd binary systems. The equilibrium potentials, as well as the stoichiometric ranges over which they are found, are presented in Table 1.

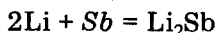
TABLE 1

Thermodynamic data for a number of binary alloys

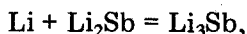
Voltage vs. Li	System	Range of y	Temp. (°C)	Ref.
0.047	Li _y Si	3.25 - 4.4	400	24 - 27
0.058	Li _y Cd	1.65 - 2.33	400	28
0.080	Li _y In	2.08 - 2.67	400	29
0.089	Li _y Pb	3.8 - 4.4	400	30
0.091	Li _y Ga	1.53 - 1.93	400	31
0.122	Li _y Ga	1.28 - 1.48	400	31
0.145	Li _y In	1.74 - 1.92	400	29
0.156	Li _y Si	2.67 - 3.25	400	24 - 27
0.170	Li _y Sn	3.5 - 4.4	400	32
0.237	Li _y Pb	3.0 - 3.5	400	30
0.271	Li _y Pb	2.67 - 3.0	400	30
0.283	Li _y Si	2 - 2.67	400	24 - 27
0.283	Li _y Sn	2.6 - 3.5	400	32
0.300	Li _y Al	0.08 - 0.9	400	33
0.332	Li _y Si	0 - 2	400	24 - 27
0.373	Li _y Cd	0.33 - 0.45	400	28
0.375	Li _y Pb	1.1 - 2.67	400	30
0.387	Li _y Sn	2.5 - 2.6	400	32
0.430	Li _y Sn	2.33 - 2.5	400	32
0.455	Li _y Sn	1.0 - 2.33	400	32
0.495	Li _y In	1.2 - 0.86	400	29
0.507	Li _y Pb	0 - 1.0	400	30
0.558	Li _y Cd	0.12 - 0.21	400	28
0.565	Li _y Ga	0.15 - 0.82	400	31
0.570	Li _y Sn	0.57 - 1.0	400	32
0.750	Li _y Bi	1.0 - 2.82	400	34
0.875	Li _y Sb	2.0 - 3.0	400	34
0.910	Li _y Sb	0 - 2.0	400	34

More recently, attention has been turned to the evaluation of such properties at lower temperatures. This has involved measurements [6] using LiNO₃-KNO₃ molten salts at about 150 °C, as well as experiments with organic-solvent-based electrolytes at ambient temperatures [7, 8].

Coulometric titration data were obtained over this wide temperature range for two alloy systems, Li-Sb and Li-Bi, each of which has two intermediate phases, in order to illustrate relevant principles. The temperature dependence of the potentials of the two-phase equilibria in the Li-Sb system fell upon two straight lines, corresponding to the reactions

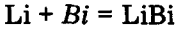


and



where *Sb* indicates the lithium-saturated terminal phase.

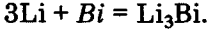
In the Li-Bi case, however, where the comparable reactions are



and



the temperature dependence is different. The data for the two reactions converge at high temperatures. Above about 420 °C, the LiBi phase is no longer stable, and there is only a single reaction,



In addition, the potentials of the second reaction fall along two straight line segments, depending upon the temperature range. There is a significant change in slope at about 210 °C, resulting in a negligible temperature dependence of the potential at low temperatures, due to the melting of bismuth.

From these temperature dependences, one can obtain values of the molar entropies of these several reactions. They are given in Table 2.

TABLE 2

Thermodynamic data for the Li-Sb and Li-Bi systems

Reaction	Molar entropy of reaction (J/K mol)	Temp. range (°C)
$2\text{Li} + \text{Sb} \longrightarrow \text{Li}_2\text{Sb}$	-31.9	0 - 500
$\text{Li} + \text{Li}_2\text{Sb} \longrightarrow \text{Li}_3\text{Sb}$	-46.5	0 - 600
$\text{Li} + \text{Bi} \longrightarrow \text{LiBi}$	0	0 - 200
$2\text{Li} + \text{LiBi} \longrightarrow \text{Li}_3\text{Bi}$	-36.4	0 - 400

In addition to the investigations at elevated temperatures, attention has been given to the ambient temperature properties of several alloy systems. Data on the potentials and stoichiometric ranges of the plateaux in the Li-Sb, Li-Bi, Li-Sn, Li-Pb, Li-Zn and Li-Cd systems at 25 °C are shown in Table 3.

The Li-Cd system is especially interesting, for it has a long plateau, spanning about 1.5 Li per mole, at a potential only about 50 mV above pure lithium.

Kinetic properties

Whereas thermodynamic considerations control the potentials and capacities of electrode reactants, their kinetic behavior is determined by other parameters.

TABLE 3

Plateau potentials and composition ranges in lithium alloys at low temperatures

Voltage vs. Li	System	Range of y	Temp. (°C)	Ref.
0.005	Li _y Zn	1 - 1.5	25	8
0.055	Li _y Cd	1.5 - 2.9	25	8
0.157	Li _y Zn	0.67 - 1	25	8
0.219	Li _y Zn	0.5 - 0.67	25	8
0.256	Li _y Zn	0.4 - 0.5	25	8
0.292	Li _y Pb	3.2 - 4.5	25	8
0.352	Li _y Cd	0.3 - 0.6	25	8
0.374	Li _y Pb	3.0 - 3.2	25	8
0.380	Li _y Sn	3.5 - 4.4	25	7
0.420	Li _y Sn	2.6 - 3.5	25	7
0.449	Li _y Pb	1 - 3.0	25	8
0.485	Li _y Sn	2.33 - 2.63	25	7
0.530	Li _y Sn	0.7 - 2.33	25	7
0.601	Li _y Pb	0 - 1	25	8
0.660	Li _y Sn	0.4 - 0.7	25	7
0.680	Li _y Cd	0 - 0.3	25	8
0.810	Li _y Bi	1 - 3	25	7
0.828	Li _y Bi	0 - 1	25	7
0.948	Li _y Sb	2 - 3	25	7
0.956	Li _y Sb	1 - 2	25	7

The kinetic properties of alloy electrodes are often determined by the rate at which solid state diffusion can occur through the outer phase of a two-phase microstructure. The pertinent basic parameter is therefore the chemical diffusion coefficient.

Some intermediate phases in lithium alloy systems have crystal structures that result in a very high rate of lithium diffusion, indicating that they are good candidates for high rate cells.

Several techniques have been developed whereby precise and reliable values of the chemical diffusion coefficient can be obtained by the use of molten salt electrochemical cell techniques [9 - 13]. The physical arrangement can be closely related to that used for the thermodynamic measurements mentioned above.

The principles underlying the application of transient or relaxation electrochemical methods for the determination of the chemical diffusion coefficient in solids have been reviewed in a number of the places cited above, and thus will not be discussed here. One of the especially attractive features of this approach, compared with conventional methods, is the relative ease with which one can obtain data of high precision.

In addition to these methods, it was shown a few years ago [13 - 17] that a steady state a.c. method can also be used to obtain chemical diffusion data.

Using a combination of kinetic measurements and coulometric titration, which provides great compositional resolution, the variation of the diffusion coefficient with composition within phases, even if they have very narrow ranges of composition, can be readily obtained. This is particularly important in understanding the kinetics of polyphase electrode reactions.

As pointed out by Wagner in an important paper [18] in 1953, the chemical diffusion coefficient can be very much greater than the self-diffusion coefficient in some materials. It is the latter quantity that has generally been measured in conventional radiotracer studies of diffusion in metals and alloys. This relationship is simply

$$D_c = D_s W,$$

where the quantity W is an enhancement factor, which can be written

$$W = d \ln a_i / d \ln c_i,$$

where a_i and c_i are the activity and concentration of electrically neutral species i , respectively. This enhancement factor has been discussed by Wagner [18, 19], and was expressed in a somewhat different form by Darken [20], who called it the "thermodynamic factor". A general discussion of this factor, and its evaluation under various conditions relevant to electrochemical systems appeared [9] in 1977. By the use of the coulometric titration technique, the compositional variation of W can be experimentally determined.

These various techniques have been used to investigate chemical diffusion in a number of binary lithium alloys at elevated temperatures, and more recently, at ambient temperatures. Some of these data are included in Table 4. It can be seen that the value of W can be very large in some cases, and that this can lead to unusually high values of the chemical diffusion coefficient. This is indeed a fortunate circumstance, for it permits much faster electrode kinetics than would otherwise be the case.

The mixed-conductor matrix concept

In order to provide a high reactant surface area, and thus be able to achieve appreciable macroscopic current densities while maintaining low local microscopic charge and particle flux densities, many battery electrodes that are used in conjunction with liquid electrolytes are produced with porous microstructures containing very fine particles of the solid reactant materials. This porous structure is permeated with the electrolyte.

The porous, fine-particle approach has several characteristic disadvantages. Among these are difficulties in producing uniform and reproducible microstructures, and limited mechanical strength when highly porous. In addition, they often suffer time-dependent changes in both microstructure and properties during cyclic operation.

TABLE 4

Data on chemical diffusion in lithium alloy phases

Nominal comp.	Range of composition (% Li)	Max. value of D_c ($\text{cm}^2 \text{s}^{-1}$)	Max. value of W	Temp. ($^{\circ}\text{C}$)	Ref.
LiAl	16.4	1.2×10^{-4}	70	415	13, 33
Li ₃ Sb	0.05	7.0×10^{-5}	70000	360	9
Li ₃ Bi	1.37	2.0×10^{-4}	370	380	35
Li ₁₂ Si ₇	0.54	8.1×10^{-5}	160	415	27
Li ₇ Si ₃	3.0	4.4×10^{-5}	111	415	27
Li ₁₃ Si ₄	1.0	9.3×10^{-5}	325	415	27
Li ₂₂ Si ₅	0.4	7.2×10^{-5}	232	415	27
LiSn	1.9	4.1×10^{-6}	185	415	36
Li ₇ Sn ₃	0.5	4.1×10^{-5}	110	415	36
Li ₅ Sn ₂	1.0	5.9×10^{-5}	99	415	36
Li ₁₃ Sn ₅	0.5	7.6×10^{-4}	1150	415	36
Li ₇ Sn ₂	1.4	7.8×10^{-5}	196	415	36
Li ₂₂ Sn ₅	1.2	1.9×10^{-4}	335	415	36
LiGa	22.0	6.8×10^{-5}	56	415	31
LiIn	33.0	4.0×10^{-5}	52	415	29
LiCd	63.0	3.0×10^{-6}	7	415	28
Li ₃ Sn ₄		$6 - 8 \times 10^{-8}$		25	7
Li ₇ Sn ₃		$3 - 5 \times 10^{-7}$		25	7

A quite different approach was introduced a few years ago [21 - 23], whereby a dense, solid electrode was fabricated which had a composite microstructure in which particles of the reactant phase were finely dispersed within a solid, mixed-conducting, metallic matrix. This provides a large internal reactant/matrix interfacial area. If the matrix material has a high chemical diffusion rate for the electroactive species, it can be rapidly transported through the solid matrix to this interfacial region, where it undergoes the chemical part of the electrode reaction. If the matrix material is also an electronic conductor, it acts as the electrode's current collector, and the electrochemical part of the reaction takes place on the outer surface of the composite electrode.

Upon discharge of such an electrode by deletion of the electroactive species, if a residual reactant particle does not interact with the surrounding matrix, it remains as a relic in the microstructure. This provides a fixed, permanent location for the reaction to take place during following cycles. This provides a mechanism for the achievement of true microstructural reversibility.

There are several features of this situation that serve to illustrate and expand upon some of the principles discussed above. There are both thermodynamic and kinetic requirements that must be met.

The matrix and the reactant phase must be thermodynamically stable in contact with each other. One can evaluate this possibility if one has informa-

tion about the relevant phase diagram — which typically involves a ternary system — as well as the titration curves of the component binary systems. In a ternary system, two materials must lie at the corners of the same constant-potential tie triangle in the isothermal ternary phase diagram in order not to interact. The potential of the tie triangle determines the electrode reaction potential. Therefore, an additional requirement is that the reactant material has two phases present in the tie triangle, but the matrix phase only one. This is another way of saying that the stability window of the matrix phase must span the reaction potential, and that the binary titration curve of the reactant material has a plateau at the tie triangle potential. One can evaluate the possibility that these conditions are met from knowledge of the binary titration curves, without having to do a large number of ternary experiments.

The kinetic requirements for a successful application of these concepts are also understandable. The primary issue is the chemical diffusion rate of the electroactive species in the matrix phase. That can be determined by the various techniques discussed above.

An example has been demonstrated [21 - 23] that meets all of these requirements: the use of the phase with the nominal composition $\text{Li}_{13}\text{Sn}_5$ as the matrix, in conjunction with reactant phases in the lithium-silicon system at temperatures near 400 °C. This is an especially favorable case, due to the high chemical diffusion coefficient of lithium in the $\text{Li}_{13}\text{Sn}_5$ phase. There are surely other examples. We are currently investigating some possible combinations that might be useful at ambient temperatures in lithium systems.

One other obvious requirement is that the microstructure must have the ability to accommodate any volume changes that might result from the reaction that takes place internally. This can surely be taken care of by clever microstructural design and fabrication techniques.

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