

Lithium alloy negative electrodes

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Abstract

The 1996 announcement by Fuji Photo Film of the development of lithium batteries containing convertible metal oxides has caused a great deal of renewed interest in lithium alloys as alternative materials for use in the negative electrode of rechargeable lithium cells. The earlier work on lithium alloys, both at elevated and ambient temperatures is briefly reviewed. Basic principles relating thermodynamics, phase diagrams and electrochemical properties under near-equilibrium conditions are discussed, with the Li–Sn system as an example. Second-phase nucleation, and its hindrance under dynamic conditions plays an important role in determining deviations from equilibrium behavior. Two general types of composite microstructure electrodes, those with a mixed-conducting matrix, and those with a solid electrolyte matrix, are discussed. The Li–Sn–Si system at elevated temperatures, and the Li–Sn–Cd at ambient temperatures are shown to be examples of mixed-conducting matrix microstructures. The convertible oxides are an example of the solid electrolyte matrix type. Although the reversible capacity can be very large in this case, the first cycle irreversible capacity required to convert the oxides to alloys may be a significant handicap. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

There is a lot of interest in several different types of lithium-based rechargeable batteries, due to the expectation of high specific energies and energy densities. With only a few exceptions, elemental lithium is now generally replaced in the negative electrode of rechargeable consumer batteries by materials with a lower lithium activity because of potential problems with safety and loss of capacity upon cycling due to the instability of the lithium/electrolyte interface.

There are, however, two general disadvantages to this approach. One is that the lower lithium activity gives rise to an increase in the negative electrode potential, and thus a reduction in the cell voltage. The other is that the presence of additional components adds additional weight, and often, volume.

It was demonstrated in 1983 [1] that lithium can be reversibly inserted into graphite at room temperature when using an organic electrolyte and Sony introduced commercial rechargeable batteries containing negative electrodes

based upon carbon materials in 1989. Most of the presently produced rechargeable lithium cells use lithium-carbons in the negative electrode. However, these can also present problems, such as the loss of capacity during the first charge, due to irreversible lithium incorporation into the structure, as well as during subsequent cycling, and there is a potential safety hazard due to kinetic behavior limitations if the potential is too close to that of elemental lithium.

Attention has been given to the use of lithium alloys as an alternative to elemental lithium for an even longer time. Groups working on batteries with molten salt electrolytes that operate at temperatures above the melting point of lithium were especially interested in this possibility. Two major directions evolved during the period 1971–1977. The first involved the use of lithium–aluminum alloys [2–5], whereas another was concerned with lithium–silicon alloys [6–9].

In addition, a number of other binary alloy systems were investigated at temperatures around 400°C. These included the binaries Li–Sb [10,11], Li–Bi [10,12], Li–Sn [13,14], Li–Cd [15], Li–In [16], Li–Pb [17], and Li–Ga [18]. In addition, several ternary systems were also explored in that temperature range [19,20]. Binary alloy

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electrodes were also investigated at somewhat lower temperatures, using $\text{LiNO}_3\text{--KNO}_3$ molten salt electrolytes at about 150°C [21].

More recently, experiments were also undertaken on a number of binary systems, including Li–Sn, Li–Bi, Li–Sb, Li–Zn, Li–Cd, and Li–Pb, with organic solvent-based electrolytes at ambient temperatures [22–24]. There also has been some work on several ternary systems at ambient temperatures [25–29].

There was, however, no industrial interest in the possible use of alloys in the negative electrodes of commercial cells at that time. This situation suddenly changed when Fujifilm announced the development of lithium batteries that were constructed with amorphous metal oxides in the negative electrodes [30,31]. During the first charging cycle the oxides are converted to a composite microstructure containing both Li_2O and lithium–metal alloys by reaction with lithium. After this initial irreversible reaction, the electrochemical properties of these electrodes are essentially those of the resulting lithium alloys.

2. Basic concepts

In order to understand what is happening in these alloy and oxide systems it is useful to first consider equilibrium, or near-equilibrium, conditions. Under these conditions, the potentials and capacities of electrodes can be calculated by the use of thermodynamic principles if the relevant data are available. If experiments are done correctly, the resulting data are fully reproducible, and clearly show the limiting values of the important parameters.

Under dynamic conditions the behavior deviates from these equilibrium values. Unfortunately, however, quantitative results obtained under such conditions are often dependent upon details of both the electrode microstructure and the experimental parameters, and are not reproducible. Thus it is prudent to first look at what can be learned by considering the equilibrium situation.

Phase diagrams are very useful tools for presenting and understanding thermodynamic information. They are figures that show the phases present as a function of temperature (plotted on the abscissa) and the overall composition (along the ordinate) of a material system. As most electrochemical experiments involve changes in composition of the electrode materials at constant temperature, what happens under near-equilibrium conditions can be understood by following a horizontal line across the phase diagram at the appropriate temperature.

According to the Gibbs Phase Rule, if the temperature and the total pressure are kept constant all the intensive parameters, such as the chemical potentials of the various species present and the electrical potential, are independent of the overall composition when two phases are present in a two-component (binary) system. On the other hand, they vary with composition within a single-phase region of the

phase diagram. This is reflected in the electrochemical behavior, i.e., in the shape of charge–discharge curves. Simply stated, when two phases are present there is a plateau in these curves, independent of the state of charge, and thus of the relative amounts of the two phases. On the other hand, if the overall composition remains within a single phase region, the potential will depend upon the state of charge.

If we consider a binary alloy system that has intermediate (intermetallic) phases, their compositional regimes must always be separated by two-phase regions. Therefore, if the overall composition of the alloy is changed as the result of an electrochemical reaction, the electrode potential will go through a series of two-phase-region plateaus, separated by single-phase-region changes if near-equilibrium conditions are maintained. Such a situation is illustrated schematically in Fig. 1a.

If the state of charge changes such that the overall composition enters a two-phase region of the relevant phase diagram a reconstitution reaction takes place. Such reactions generally occur by the nucleation and growth of a new phase from the prior phase. The microstructure gradually changes as the relative volumes of the two phases vary as the reaction proceeds. When the initial phase has been completely consumed there is again only one phase present, and the potential no longer remains at the plateau value.

The necessary rearrangement of the constituent atoms to nucleate a new phase, which typically has a different crystal structure, and generally a different specific volume,

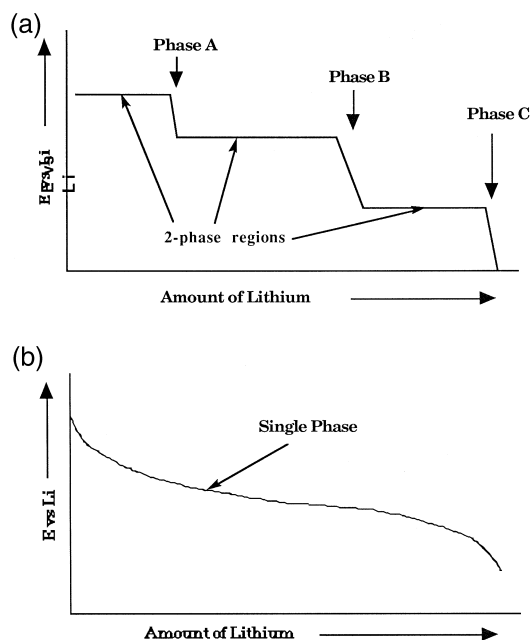


Fig. 1. (a) Schematic representation of titration curve of alloy system with three intermediate phases if equilibrium is attained. (b) Schematic representation of titration curve of alloy system if there is only selective equilibrium in the mobile species sublattice so nucleation of other phases does not occur.

can be a complicated and relatively slow process, requiring a significant amount of activation energy. As a result, it is often found that the nucleation process is kinetically hindered at low temperatures.

When the overall composition of the material is caused to change as the result of the passage of current through an electrochemical cell and the nucleation of the next equilibrium phase is impeded, further compositional changes can only occur within the crystal structure of the initial phase. Thus the composition of this phase is dynamically extended into a regime in which it is not actually thermodynamically stable. Under these conditions, the equilibrium plateau sequence is not obtained in charge and discharge curves. Instead, the material behaves as though it were composed of a single phase over a wide range of composition. This can be described as selective equilibrium. Equilibrium is attained in the mobile species (i.e., lithium) sublattice, but not in the host structure lattice. This type of behavior is shown schematically in Fig. 1b.

3. The Li–Sn alloy system

Because of the great current interest in Li–Sn alloys as the result of the Fuji development, that system will be used as an example of these principles. The equilibrium phase diagram of the Li–Sn system is shown in Fig. 2.

The experimentally measured equilibrium titration curve (potential versus composition plot) is shown in Fig. 3 for two temperatures, 400°C and 25°C [14,22]. To improve the clarity, the many data points measured at the higher temperature are not shown. Experiments reported by others under dynamic electrochemical conditions [32,33] do not show the one-phase, two-phase differentiation so clearly, but look more like Fig. 1b, indicating that under those experimental conditions only selective equilibrium in the lithium sublattice was obtained, without the reconstitution

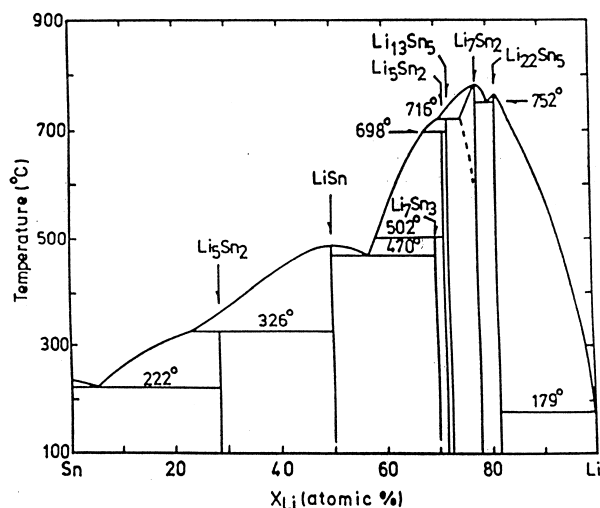


Fig. 2. Li–Sn phase diagram.

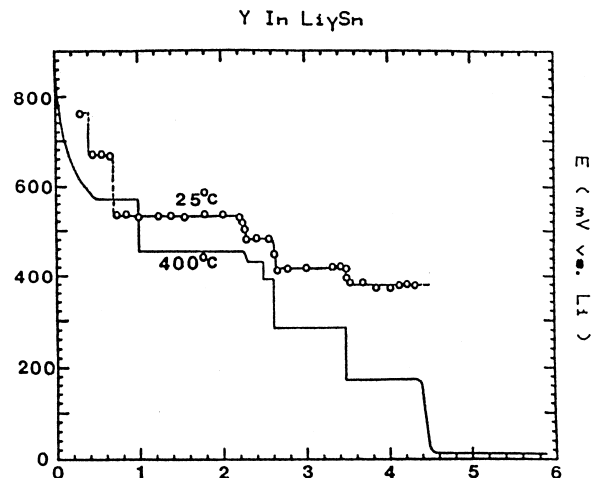


Fig. 3. Titration curves in the Li–Sn system at two temperatures.

reactions that would change the crystal lattice of the host material.

4. Other alloy systems at ambient temperature

As mentioned earlier, the equilibrium properties of a number of binary lithium alloy systems have been experimentally studied at ambient temperature. The potentials and composition ranges of the respective potential plateaus are given in Table 1 [22,23].

Table 1

Plateau potentials and composition ranges in lithium alloys at low temperatures

Voltage vs. Li	System	Range of y	Temperature (°C)	Reference
0.005	Li_yZn	1–1.5	25	[23]
0.055	Li_yCd	1.5–2.9	25	[23]
0.157	Li_yZn	0.67–1	25	[23]
0.219	Li_yZn	0.5–0.67	25	[23]
0.256	Li_yZn	0.4–0.5	25	[23]
0.292	Li_yPb	3.2–4.5	25	[23]
0.352	Li_yCd	0.3–0.6	25	[23]
0.374	Li_yPb	3.0–3.2	25	[23]
0.380	Li_ySn	3.5–4.4	25	[22]
0.420	Li_ySn	2.6–3.5	25	[22]
0.449	Li_yPb	1–3.0	25	[23]
0.485	Li_ySn	2.33–2.63	25	[22]
0.530	Li_ySn	0.7–2.33	25	[22]
0.601	Li_yPb	0–1	25	[23]
0.660	Li_ySn	0.4–0.7	25	[22]
0.680	Li_yCd	0–0.3	25	[23]
0.810	Li_yBi	1–3	25	[22]
0.828	Li_yBi	0–1	25	[22]
0.948	Li_ySb	2–3	25	[22]
0.956	Li_ySb	1–2	25	[22]

Table 2
Chemical diffusion coefficients of some lithium alloy phases

Phase	D (cm ² /s)
Li _{0.7} Sn	6×10^{-8} – 8×10^{-8}
Li _{2.33} Sn	3×10^{-7} – 5×10^{-7}
Li _{4.4} Sn	1.8×10^{-7} – 5.9×10^{-7}
LiZn	8.8×10^{-10} – 3.7×10^{-9}
LiCd	5.2×10^{-10} – 2.1×10^{-9}

The crystal structures of some of the intermetallic phases in lithium alloys are such that the chemical diffusion of lithium can be surprisingly rapid, even at ambient temperatures. Some examples are shown in Table 2 [22,24].

5. Composite microstructure electrodes

Practical electrodes generally have composite microstructures. Components are often added as binders for mechanical stability, or to enhance the electronic conduction within the structure. Others may be present to improve the ionic or atomic transport to or from the reactant phases. In the latter case, we can distinguish two different types of electrode structures, mixed-conductor matrix structures, and solid electrolyte matrix structures. In the case of mixed conductors, the matrix contributes to both the electronic conductivity and the transport of atomic species to the reactant sites. Solid electrolyte components, on the other hand, enhance the motion of ionic, but not electronic, species throughout the electrode structure.

6. Mixed-conductor matrix microstructures

In order to be able to achieve appreciable macroscopic currents 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 high reactant surface area porous structure is permeated by the electrolyte.

This porous fine-particle approach has several characteristic disadvantages. Among these are difficulties in producing uniform and reproducible microstructures, and limited mechanical strength when the structure is highly porous. In addition, such electrodes often suffer Ostwald ripening, sintering, or other time-dependent changes in both microstructure and properties during cyclic operation.

A quite different approach was introduced a few years ago [34–36] in which a dense solid electrode is fabricated which has a composite microstructure in which particles of the reactant phase are finely dispersed within a solid electronically conducting matrix in which atoms of the electroactive species are also mobile. There is thus a large internal reactant/mixed-conducting matrix interfacial area.

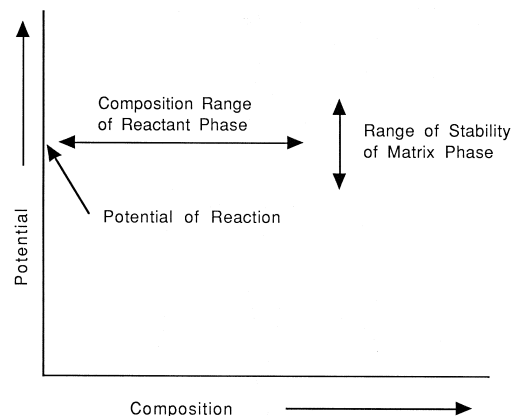


Fig. 4. Schematic representation of required potential and composition range requirement for matrix and reactant systems.

The electroactive species is transported by chemical diffusion through the solid matrix to this interfacial region, where it undergoes the chemical part of the electrode reaction. Since the matrix material is also an electronic conductor, it can also act as the electrode's current collector. The electrochemical part of the reaction is a simple conversion of lithium ions into lithium atoms, and takes place on the external surface of the electrode.

The general principles related to the desirable potential and capacity properties of the reactant and matrix materials in this composite microstructure are illustrated schematically in Fig. 4.

The matrix phase must have rapid diffusion of the electroactive species, and also must be stable over the potential range at which the reactant material reacts. It is not necessary that the matrix phase have appreciable capacity, as the capacity is primarily supplied by the reactant material.

An early example of this type of a mixed-conductor matrix hybrid microstructure was the use of a phase in the Li–Sn system as a matrix within which a Li–Si system

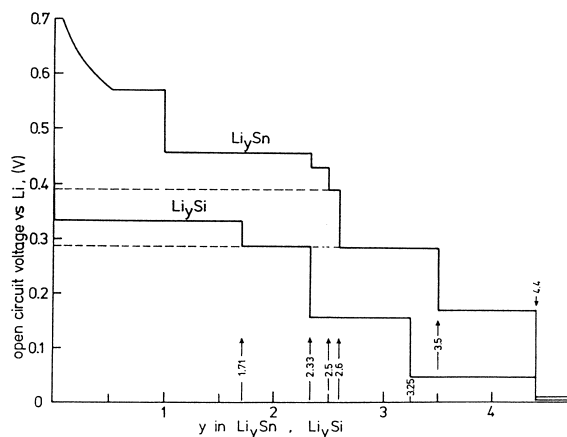


Fig. 5. Equilibrium titration curves of the Li–Sn and Li–Si systems at 415°C.

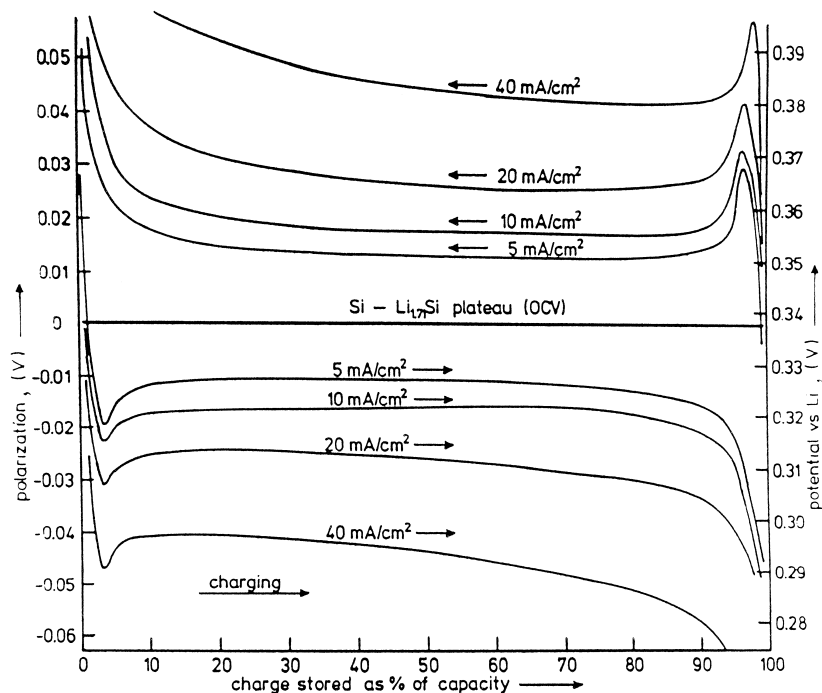


Fig. 6. Charge–discharge curves in the Li–Sn–Si system at several different current densities at 415°C.

reaction took place [34,35]. The equilibrium titration curves of the Li–Sn and Li–Si systems are shown superimposed in Fig. 5.

It can be seen that the phase $\text{Li}_{2.6}\text{Sn}$ is stable over a range of potential, including that at which the reaction $\text{Li} + \text{Si} = \text{Li}_{1.71}\text{Si}$ takes place, approximately 0.338 V vs. Li.

Fig. 6 shows a group of charge–discharge experiments at different current densities. It is seen that the electrode potential was determined primarily by the Li–Si reaction,

and that the amount of polarization was very small, only about 1 mV per mA/cm^2 current.

Another important feature that can be readily seen from these experiments is the existence of a nucleation barrier. At each end of the plateau, when there was only one phase present, the potential had to be overdriven in order to nucleate the second (product) phase when the current went in the reverse direction. It was clearly shown that if the reaction does not go to completion, and some of the required second phase is already present when the current

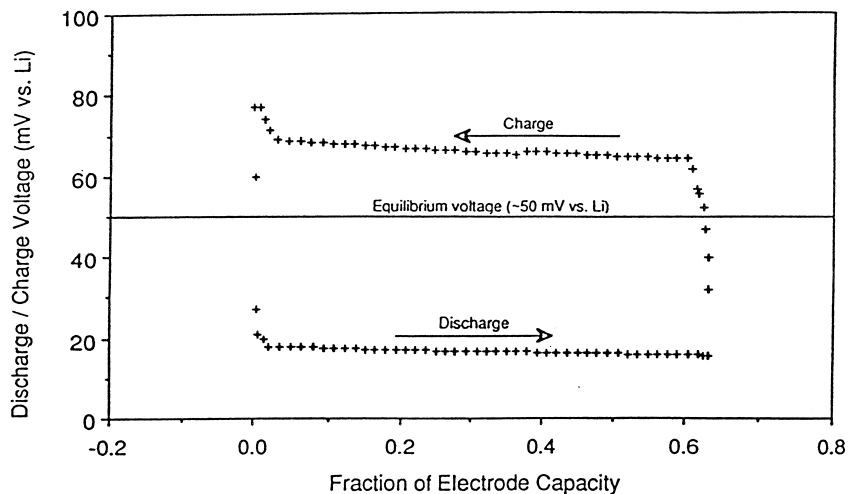


Fig. 7. Charge–discharge behavior in ternary Li–Sn–Cd system at ambient temperature.

is reversed, one can avoid the nucleation requirement, and the required potential overshoot disappears.

It has been demonstrated that these same principles can be applied at ambient temperatures [27]. In that case a different phase in the Li–Sn system was used as a mixed-conducting matrix for a reaction in the Li–Cd system. The reaction $\text{Li} + \text{LiCd} = \text{Li}_3\text{Cd}$ takes place at about 50 mV vs. pure Li. The phase $\text{LiSn}_{4.4}$, which has a high diffusion coefficient for Li, is stable in that range (see Table 2). The charge–discharge behavior at a current density of 0.1 mA/cm² of such an electrode at ambient temperature is illustrated in Fig. 7. In that case the capacity was restrained to avoid the second-phase nucleation problem.

7. Solid electrolyte matrix microstructures

The announcement by Fuji Photo Film [30,31] of the use of oxides in lithium cell electrodes called attention to the possibility of a different type of hybrid microstructure in which the matrix material is a solid electrolyte. In that case, the electrode initially contains a multicomponent oxide containing Sn. During the first charging cycle this oxide is converted into a composite microstructure containing lithium oxide (a solid electrolyte for Li) and tin alloys.

This approach has several potential advantages. One is that the oxides are stable in air, so the cell can be assembled in air in the discharged state. The conversion reaction can result in a composite microstructure that contains a stable and very fine dispersion of the alloy inside the oxide solid electrolyte.

In this case the electrochemical reaction takes place at the alloy/solid electrolyte interface inside the electrode structure, rather than on the outside of the electrode.

The formation of Li_2O is irreversible, and the lithium that is consumed in its formation represents an irreversible capacity loss. The residual Sn from the initial Sn-containing oxide can then react reversibly with additional Li, forming Li–Sn alloys.

Since one can, in principle, react 4.4 Li per Sn atom, this can lead to rather high reversible electrode capacities. These values are presented in Table 3, which also includes comparable data on three other oxide–alloy systems.

It is readily seen that the reversible capacities that may be attainable are very large. This is especially attractive for

applications in which the capacity density (capacity per unit volume) is more important than specific capacity (capacity per unit weight) because of the high density of some alloys.

On the other hand, the first cycle capacity loss is very high, and there must be Li available in the cell to accommodate it in addition to the amount that is required for the reversible behavior.

From experimental information that is available to date [32,33], it appears that this approach can often lead to apparent single-phase behavior, rather than polyphase reconstitution reactions that lead to well-defined plateaus in charge and discharge curves. Evidently the polyphase nucleation problem prevents the ready appearance of the equilibrium phases in this case. This may, indeed, be advantageous from a practical standpoint.

8. Final comments

Although current technology generally employs carbonaceous materials, there has been a large recent resurgence of interest in alloy systems as negative electrodes in lithium electrochemical systems. Although there has been an appreciable amount of work on lithium alloy systems, practical problems such as Ostwald ripening, sintering and the related loss of capacity have restricted their commercial use. Current interest is turning more toward materials with composite microstructures that contain alloy reactant materials combined with either mixed-conducting alloy phases or solid electrolytes. A number of the basic principles involved in these approaches have been discussed here. The matter of polyphase nucleation, and its avoidance or enhancement, is a very important feature of such materials.

It has been shown that there appears to be a significant advantage in the use of very small particles in cases in which there is a substantial change in specific volume upon charging and discharging electrode reactants [37]. Since the absolute magnitude of the local dimensional changes is proportional to the particle size, smaller particles lead to reduced problems with the decrepitation, or ‘crumbling’, of the electrode microstructure that often leads to loss of electrical contact, and thus capacity loss, as well as macroscopic dimensional problems. The use of

Table 3
Maximum theoretical capacity of electrodes containing simple oxides assuming complete equilibrium

Starting oxide	Reversible capacity (mA h/g oxide)	Irreversible capacity (mA h/g oxide)	Total capacity (mA h/g oxide)	Capacity ratio, reversible/total
SnO	875.36	397.89	1273.25	0.69
SnO ₂	782.43	711.30	1493.73	0.52
ZnO	493.92	658.56	1152.48	0.43
CdO	605.25	417.41	1022.66	0.59
PbO	540.32	240.14	780.47	0.69

composite microstructures can reduce this problem by reducing the opportunity for the growth of reactant particles by sintering or Ostwald ripening.

Whereas the Li–Sn alloy reactant system has received most attention to date, there are a number of other possibilities that will surely be explored in the future. It will certainly be interesting to see how these evolve in comparison to the carbon-based materials that are now of general current use.

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