8. Convertible reactant electrodes (Huggins, ch. 8)

1. Electrochemical formation of metals & alloys from oxides
2. Lithium-tin alloys
3. Lithium-tin oxide system
4. Irreversible and reversible capacities
5. Other possible convertible oxides

-Carbonaceous materials as negative electrode: commercialization of the camcorder battery by SONY in 1991.
-Continued consideration of the use of metallic and metal–metalloid alloys, due to the possibility of significant increases in specific capacity and capacity density
-Another alternative: oxides → high capacity

1. Electrochemical formation of metals & alloys from oxides

-Electrochemical conversion of oxides
-e.g. lithium–tin system
If an electrode initially containing SnO

$$2Li + SnO = Li_2O + Sn$$

(−562.1kJ mol^{-1} for Li_2O and −256.8kJ mol^{-1} in the case of SnO at 25°C) → 1.58V
Additional $Li + Sn = Li\text{-}Sn$
-if the formation of Li_2O is not reversible, the electrode will maintain a composite microstructure and behave as a binary Li-Sn alloy after the 1st cycle

2. Li-Sn alloys at ambient temperature

-number of plateau under equilibrium conditions

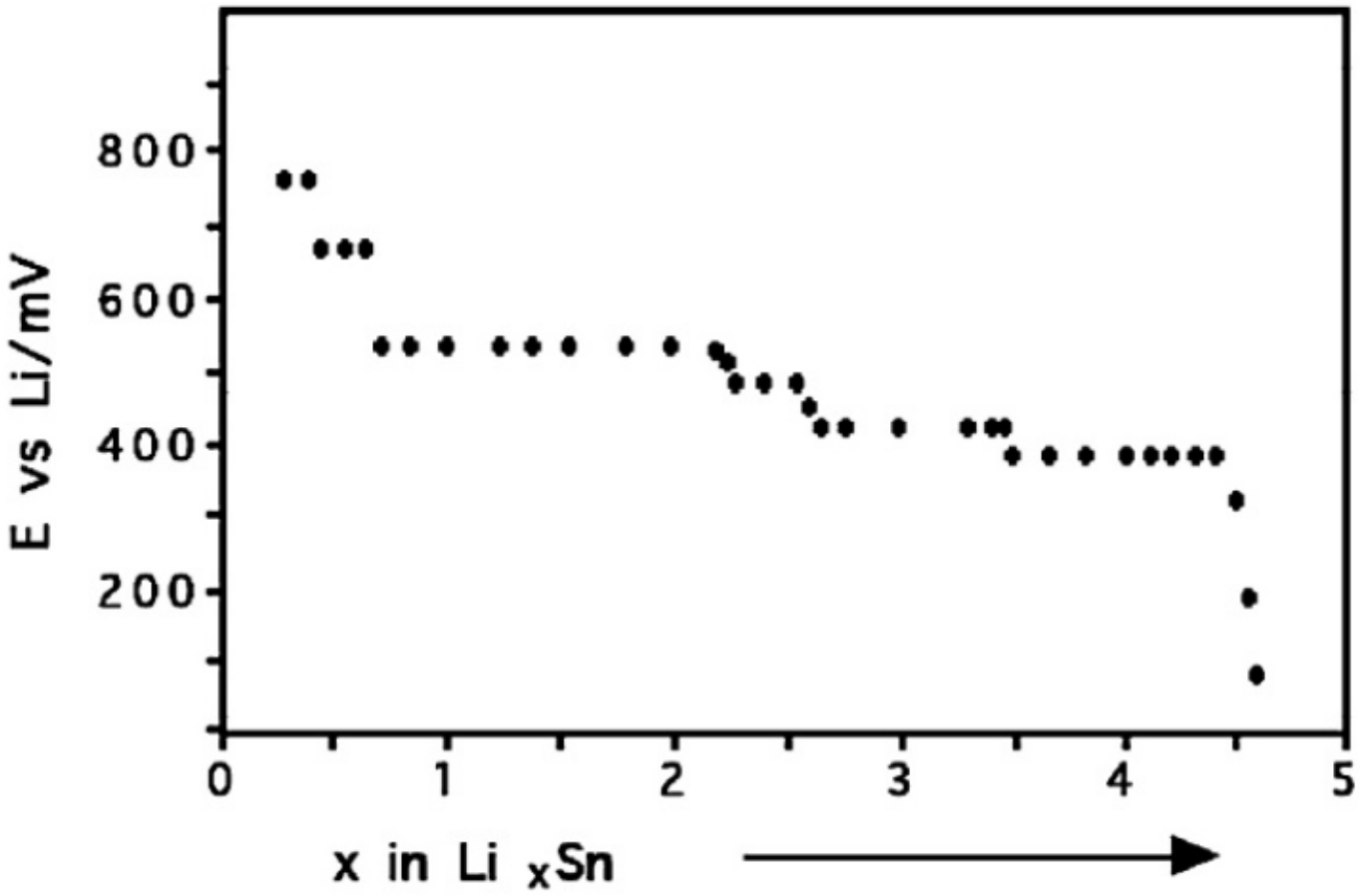

Fig. 8.1 Equilibrium titration curve for the reaction of lithium with tin at 25°C

Table 8.1 Plateau potentials and composition ranges of lithium–tin alloys at 25°C

Plateau Potential (voltage vs. Li)	Range of composition parameter x in Li_xSn
0.660	0.4–0.7
0.530	0.7–2.33
0.485	2.33–2.63
0.420	2.63–3.5
0.380	3.5–4.4

-the kinetics on the longest plateau, at 0.53V vs. Li and from x = 0.7–2.33 in Li_xSn, are quite favorable, even at quite high currents at ambient temperature. This is consistent with the results of measurements of the chemical diffusion coefficient in the two adjacent phases, $Li_{0.7}Sn$ and $Li_{2.33}Sn$, which were found to be quite high, 6–8 $\times 10^{-8}$ and 3–5 $\times 10^{-7}$ $cm^2\ s^{-1}$, respectively.

3. Li-tin oxide system

$$2Li + SnO \rightarrow Li_2O + Sn$$

-Li_2O: lithium-transporting solid electrolyte

Ionic conductivity at 25 ◦C

1.5 x 10^{-9}Scm^{-1}

→ composite microstructure with the reactant phase mixed with A solid electrolyte

-SnO & SnO_2

F = 3-3+2 = 2 (plateau)

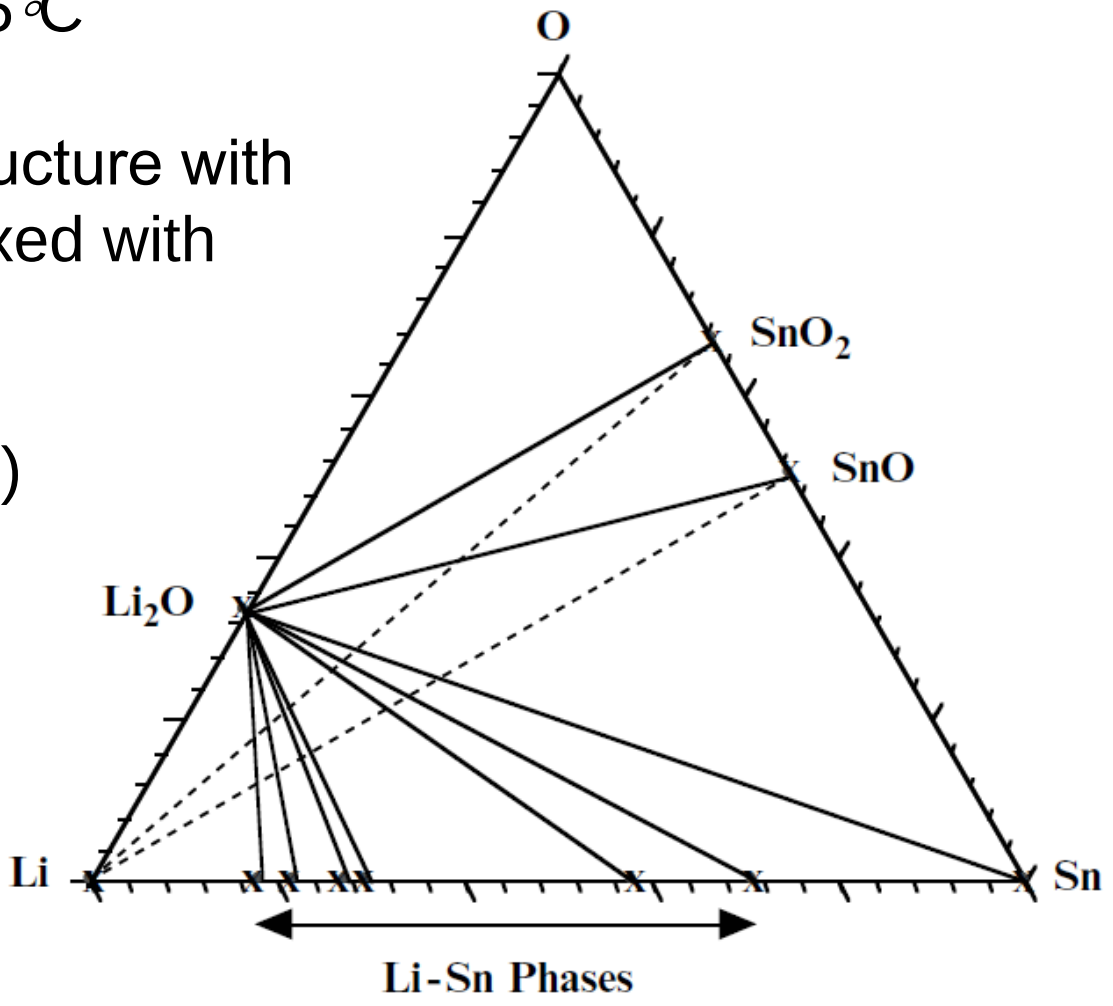

Fig. 8.2 Isothermal phase stability diagram for the Li–Sn–O system

Gibbs free energy of formation of SnO_2, SnO, and Li_2O,
it can be found that this reaction will take place at 1.88V vs. Li

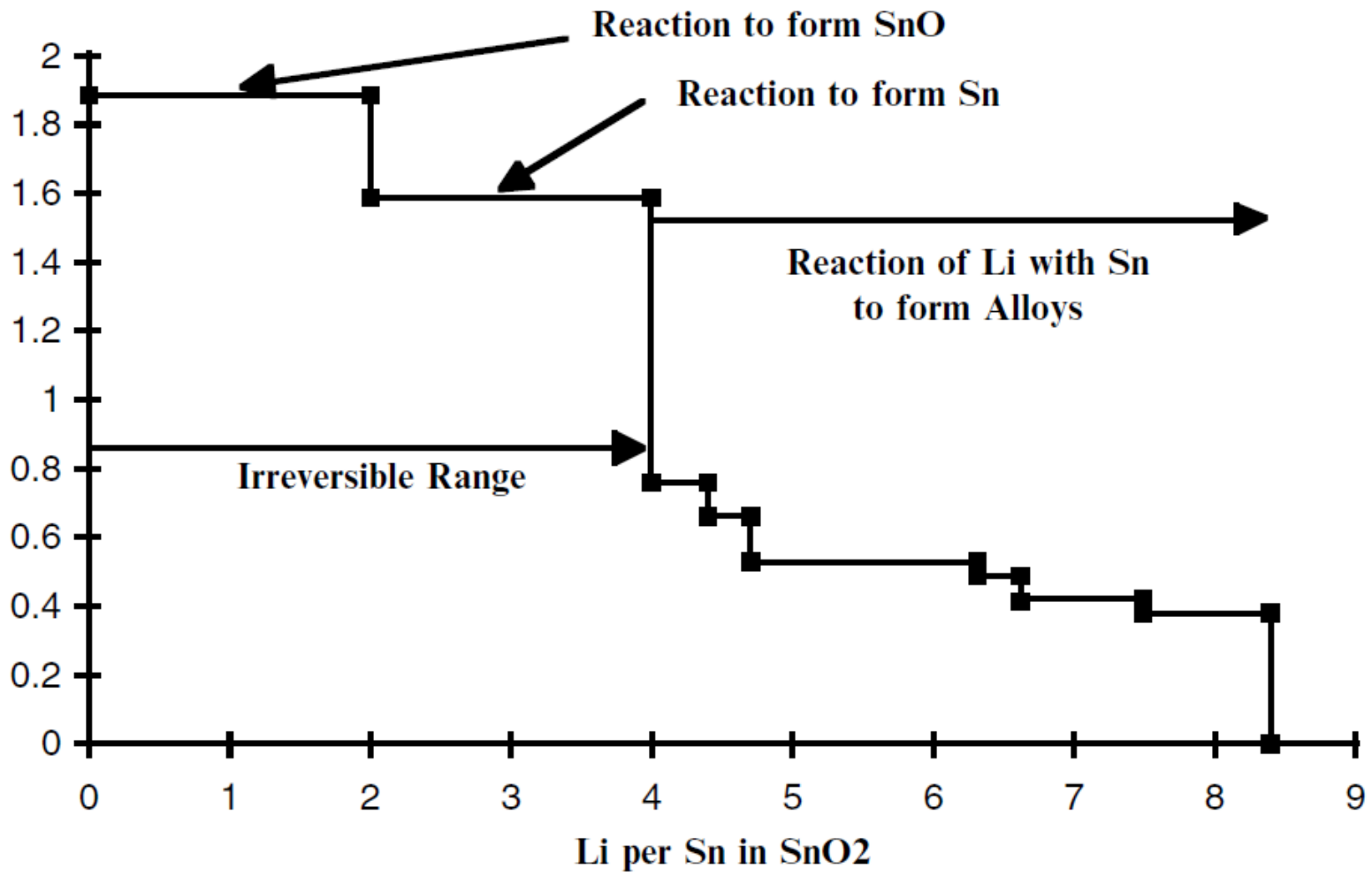

Fig. 8.3 Theoretical titration curve for the reaction of lithium with SnO_2 at 25°C

Initial SnO →1.58V vs. Li

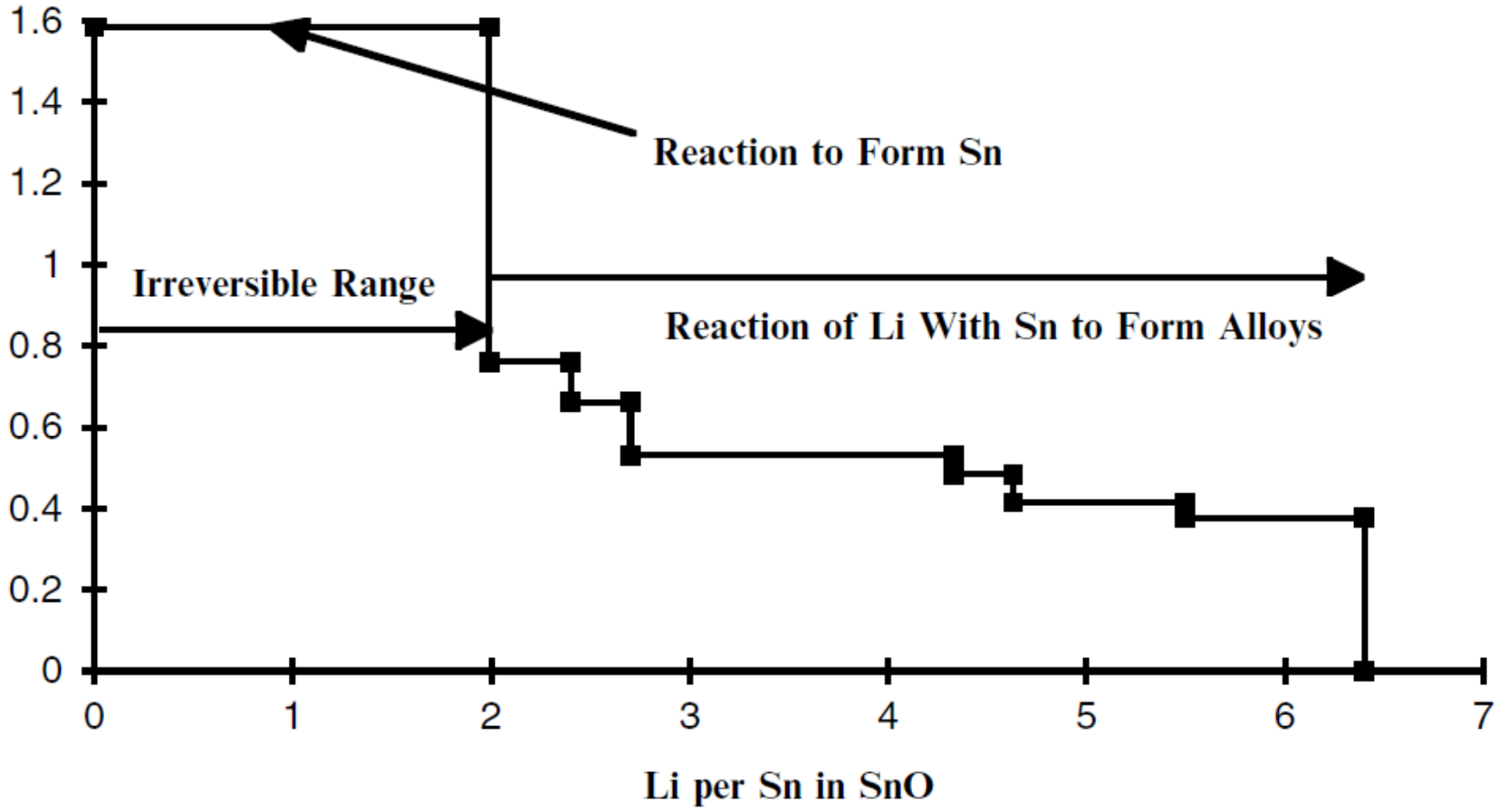

Fig. 8.4 Theoretical titration curve for the reaction of lithium with SnO at 25°C

Table 8.2 Equilibrium potentials of plateaus in three-phase regions in the Li−Sn−O ternary system at ambient temperature

Three-phase equilibrium	Potential
$Li_2O-O_2-SnO_2$	2.912
Li_2O-SnO_2-SnO	1.880
$Li_2O-SnO-Sn$	1.582
$Li_2O-Sn-Li_{0.4}Sn$	0.760
$Li_2O-Li_{0.4}Sn-Li_{0.714}Sn$	0.660
$Li_2O-Li_{0.714}Sn-Li_{2.33}Sn$	0.530
$Li_2O-Li_{2.33}Sn-Li_{2.6}Sn$	0.485
$Li_2O-Li_{2.6}Sn-Li_{3.5}Sn$	0.420
$Li_2O-Li_{3.5}Sn-Li_{4.4}Sn$	0.380

4. Irreversible and reversible capacities

5. Other possible convertible oxides

Table 8.3 Theoretical irreversible and reversible capacities of several convertible oxides

Starting oxide	Reversible capacity (mAh/g oxide)	Irreversible capacity (mAh/g oxide)	Total capacity (mAh/g oxide)	Ratio (Rev./total)
SnO	875.36	398	1273	0.69
SnO_2	782.43	711	1494	0.52
ZnO	493.92	659	1152	0.43
CdO	605.25	417	1023	0.59
PbO	540.32	240	780	0.69

Table 8.4 Theoretical data on other possible convertible oxides

Oxide	Stability of oxide (V)	Maximum E vs. Lithium (V)
Al_2O_3	2.73	0.18
B_2O_3	2.06	0.85
CdO	1.19	1.72
PbO	0.98	1.93
SiO_2	2.22	0.69
SnO	1.33	1.58
ZnO	1.66	1.25

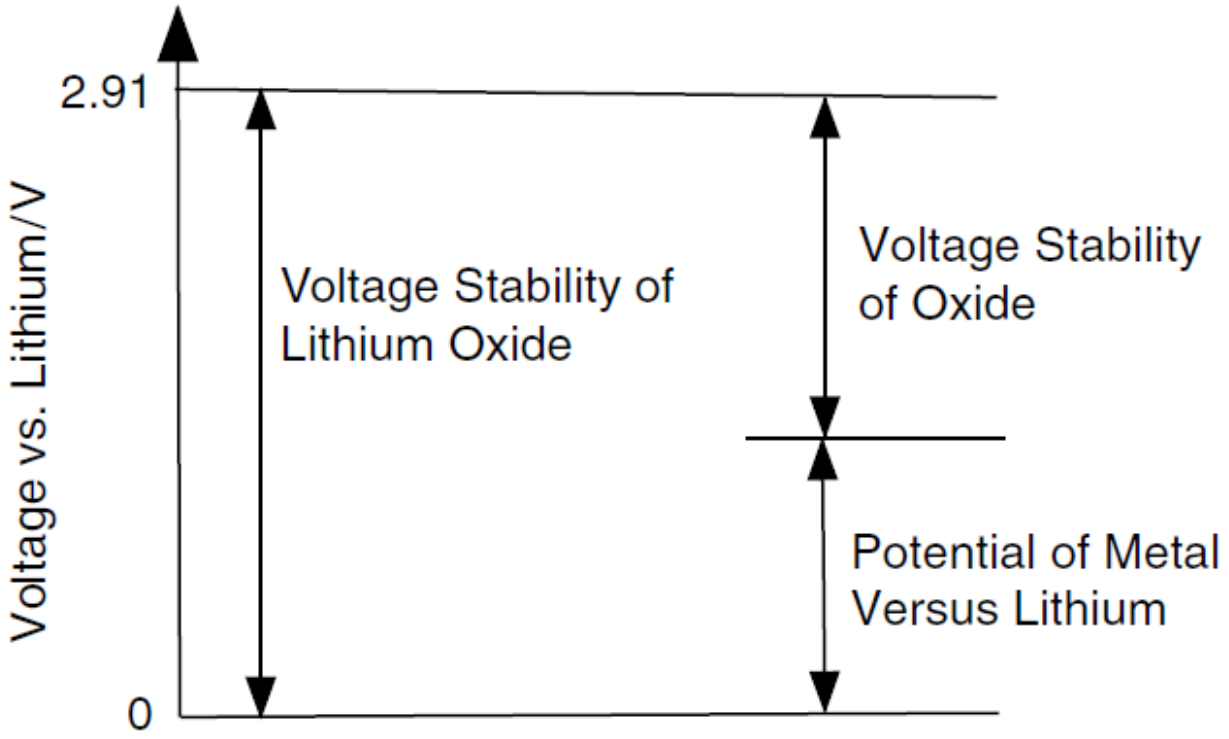

Fig. 8.5 Relative potentials in lithium–metal–oxygen systems