J Mater Sci (2006) 41:4749–4754
DOI 10.1007/s10853-006-0029-4

Solution route synthesis of dendrite Cu_6Sn_5 powders, anode material for lithium-ion batteries

**T. Sarakonsri · T. Apirattanawan · S. Tungprasurt ·
T. Tunkasiri**

Received: 21 March 2005 / Accepted: 19 September 2005 / Published online: 6 May 2006

Abstract Intermetallic dendrite particles, such as Cu_6Sn_5 compound, possible anode materials for high power lithium-ion batteries, can be synthesized by using solution technique. Solution route method can induce the formation of the compound by performing a redox reaction between metal chloride salts and metallic reducing powder in a suitable solvent. The morphological features and single-phase formation corresponding to different processing conditions including solvent type, reducing agent particle size, and reaction temperature, were determined. The X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) results illustrate the dendritic morphology of Cu_6Sn_5 particles with small amount of impurities, which can be synthesized by using ethylene glycol as solvent and zinc powder as reducing agent. Reducing agent particle size and reaction temperature have a very small effect on the formation of the Cu_6Sn_5 dendrite powder.

Introduction

Rechargeable lithium battery has long been known as a state of the art because of its high energy density in a portable size. The microstructure properties of a positive and a negative electrode material make this type of battery outstanding among other types of battery. Commercially rechargeable lithium battery is composed of $LiCoO_2$ as a positive electrode and graphite as a negative electrode. These electrodes were considered as intercalation electrodes because they act as a host lattice structure for lithium insertion/extraction without significant change in lattice parameters. Graphite electrode delivers about 360 mAh/g or about 700 mAh/cc. The outstanding feature of this electrode is that the volume expansion of the alloy phase is only about 6% [1]. However, there is concern about the safety of this cell because of the fact that lithiated graphite electrodes, Li_xC_6, reach the lithium potential when cells approach a fully charged state, as well as the presence of a highly oxidizing $Li_{1-x}CoO_2$ electrode and a flammable organic electrolyte [2]. Recently, alternative negative electrodes with the zinc-blende structure that operate a few hundred millivolts above lithiated graphite have been proposed [3]. Like the $LiCoO_2$ structure, the zinc-blende compounds contain vacant interstitial sites for lithium ions to be inserted reversibly without dramatic volume expansion. Recently the idea of an intermetallic compound MM′ was introduced by M.M. Thackeray group [3–5], where M is an active alloying element and M′ is an inactive element (or elements). η-Cu_6Sn_5 (space group $P6_3/mmc$), which has NiAs and Ni_2In structures (similar to zinc-blende), was considered as an intermetallic insertion electrode [3]. The electrochemical investigation of this intermetallic compound electrode shows that it has excellent properties (about 275 mAh/g or about 1900 mAh/cc) and is potentially safer over graphite electrode [2, 3, 6].

Mechanically alloying or ball milling process was reported [6] for the preparation of Cu_6Sn_5 compound. Small particle sizes are usually obtained by this method.

T. Sarakonsri (✉) · T. Apirattanawan · S. Tungprasurt
Department of Chemistry, Chiang Mai University, Chiang Mai 50200, Thailand
e-mail: scchi017@chiangmai.ac.th

T. Tunkasiri
Department of Physics, Chiang Mai University, Chiang Mai 50200, Thailand

However, due to high pressure applied during the process, this may introduce some disordered or amorphous phase in the product as well as particle agglomeration due to high reactivity surfaces [7], which will result in poor cycle ability. Smaller particles with relatively low crystal defects may be required to improve the cell performance. Solution route method was introduced here as an alternative way of making crystalline intermetallic compounds at ambient temperature with size approaching nanometer scale. Initial experiment [8, 9] showed that the precipitate was formed in a specific morphology with dendrite structure, which is composed of very fine particles. The reaction conditions are considered to have an influence on the dendrite formation. This research will explore the effect of processing parameter, such as solvent, reducing agent particle size, and reaction temperature, to the dendrite formation of Cu_6Sn_5 compound.

Experimental

The general idea of solution route method may be represented as an oxidation–reduction reaction between metal chloride salts and a reducing agent in a non-aqueous solution. Processing parameters such as solvent, reducing agent particle size, and reaction temperature were varied in order to examine the effect of the processing parameters to the dendrite formation (shown in Table 1). Polar solvents with various viscosities such as ethylene glycol (EG, JT. Baker, purity 99.0%), dimethyl sulfoxide (DMSO, Sigma Chemical) and dimethyl formamide (DMF, Labscan Asia, 99.8% v/v) were chosen. Size of reducing agent particle (Fluka, 10 and 45 μ particle size) may be involved in kinetic process and affect the size of the dendrite particles. However, due to an exothermic reaction, some oxide compounds may be introduced in the product. The reaction temperature was then controlled at 0°. In contrast, a reaction above room temperature may introduce the driving force for the phase transformation to occur as more intermetallic phase will be obtained. In this experiment, the reaction temperature of zero, ambient, and 50° will be investigated.

Table 1 Processing parameters for the synthesis of Cu_6Sn_5 compound

Reaction	Solvent types	Particle size of Zn (μ)	Temp (°C)
EGZn45TR	EG	45	Room
EGZn45T0	EG	45	0
EGZn10TR	EG	10	Room
EGZn45T50	EG	45	50
DMSOZn45TR	DMSO	45	Room
DMFZn45TR	DMF	45	Room

The preparation of Cu_6Sn_5 was conducted and coded according to the processing parameters as shown in Table 1. The detail of the preparation for the first experimental condition is described as follows. Stoichiometric amounts (Eq. (1)) of $CuCl_2$ (Sigma-Aldrich, purity 99.0%) and $SnCl_2{\cdot}2H_2O$ (Sigma-Aldrich, purity 99.99%) were dissolved in ethylene glycol (EG, JT. Baker, purity 99.0%) at room temperature. Zinc powder, a reducing agent, was gradually added to the solution. The reaction was continuously stirred for over 1 h before it was filtered and washed by methanol (Merck, commercial grade). Finally, it was dried in an oven at 65 °C for 30 min.

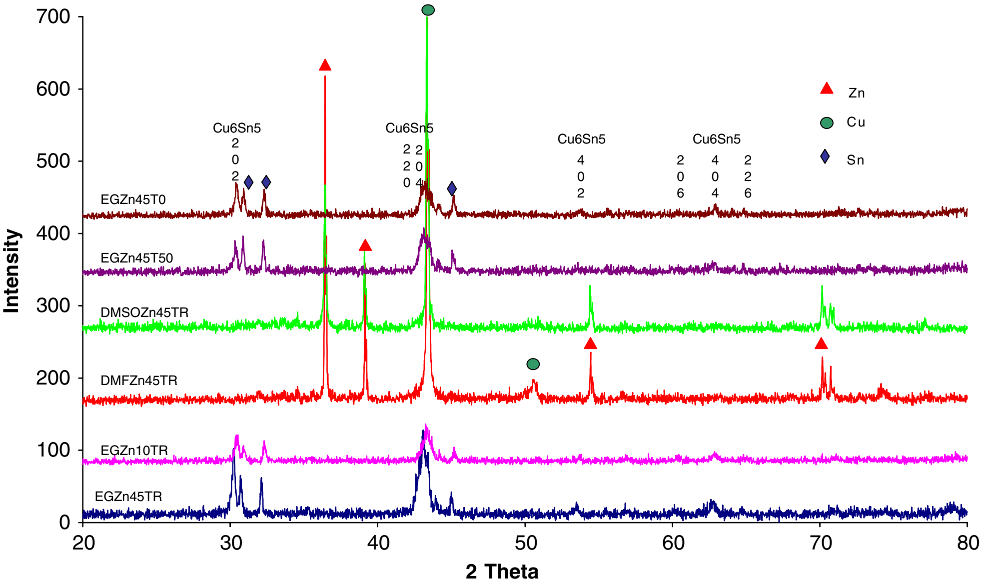
$$6CuCl_2+5SnCl_2+11Zn + Cu_6Sn_5+11ZnCl_2 \tag{1}$$

Phases present were examined by powder X-ray diffraction (XRD, siemen D500/D501, CuK_α (λ1.54) Ni filter, 2θ = 10–80°) technique, as well as by quantitative analyses. Secondary electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS) (JEOL JSM-6335F) technique was used to observe the morphology of the product powders. Finally, the nanometer scale morphology directly related to the crystallography of the phase present was determined by transmission electron microscopy (TEM, JEOL JEM-2010) technique.

Results and discussion

Powder XRD patterns (Fig. 1) from the preparation of Cu_6Sn_5 indicated the occurrence of Cu_6Sn_5 hexagonal structure (JCPDS card no 02–0713) in all conditions using ethylene glycol (EG) as solvent, although it is varied in concentration (Table 2) due to the presence of Sn metal as impurity. The concentration of Cu_6Sn_5 and Sn phases were calculated as percentage volume fraction by direct comparison method using the integrated intensities of Cu_6Sn_5 (101) and Sn (101) peaks [10]. The calculated volume fractions of Cu_6Sn_5 phase were slightly different in the four conditions (EGZn45T0, EGZn10TR, EGZn45T50, and EGZn45TR). However, these small differences may not be significantly counted as the effect of processing parameters. It is remarkable that alloy, such as Cu_6Sn_5 can thermodynamically be produced at ambient temperature with a short period of time by this method, an impossibility according to the phase diagram at this temperature. However, as the contaminated Sn phase exists, annealing in inert gas atmosphere at about 400 °C may be required to improve intermetallic purity. For other observations, only Zn and Cu metals were detected in XRD patterns in the conditions using dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) solvents. The disappearance of Cu_6Sn_5 compound in DMSO and DMF conditions can be

Fig. 1 Powder XRD patterns from the synthesized of Cu_6Sn_5 with conditions EGZn45TR, EGZn10TR, DMFZn45TR, DMSOZn45TR, EGZn45T50, and EGZn45T50



explained by the possibility of Sn^{2+} ion preferably coordinating with these solvent molecules, which act as ligands through their oxygen atoms to form stable coordinated ions, $[(CH_3)_4S_2Cl_4O_2Sn]^{4+}$ [11–13]. The formation of these coordinated ions hindered the reduction Sn^{2+} ion to a metal form. Thus, unreacted Zn powder remained after the reaction had finished.

After the XRD data had been obtained, the SEM technique for morphological study was employed. The SEM micrographs of product powders synthesized from all conditions for Cu_6Sn_5 are revealed in Fig. 2. Dendrite particles are found in conditions using EG as solvent. Plate-shape particles were obtained with conditions using DMF and DMSO solvents corresponding to Cu metal, identified by EDS spectrum. The SEM result, which was in consistency with XRD data, indicated the appearance of the remained Zn metal as equiax white particles located on top of the Cu plates. It should be noted that the reactions in DMF and DMSO solvents could not be used to stimulate dendrite intermetallic phase. Due to large distribution of dendrite particle sizes in both conditions (EGZn45TR and EGZn10TR) as illustrated in Fig. 2, the effect of reducing particle size to dendrite formation is not diverse enough to be measured.

The microstructure of the dendrite particles was confirmed by TEM technique. Figure 3 shows the TEM micrographs of dendrite particles synthesized from condition EGZn45TR, EGZn10TR, EGZn45T0, and EGZn45T50. The inserted figures are the consequent selected area diffraction pattern from the dendrite area, which gives diffraction spots correspond to the crystallographic planes of Cu_6Sn_5 hexagonal structure. The SAD patterns of both single and polycrystalline crystals suggest crystalline dendritic morphology of Cu_6Sn_5 phase obtained. The previous SEM results illustrate dendrite morphology observed in all conditions using EG as solvent, which was verified by TEM images associated with SAD patterns as Cu_6Sn_5 compound. Therefore, it can be summarized that the intermetallic Cu_6Sn_5 compound prepared by this method is considered to appear as dendritic configuration.

Table 2 Percentage calculated volume fraction of Cu_6Sn_5 and Sn phases from XRD data using integrated intensities of Cu_6Sn_5 (101) and Sn (101) peaks

Reaction	Volume fraction (%) Cu_6Sn_5:Sn
EGZn45TR	97.48:2.52
EGZn10TR	99.66:0.34
EGZn45T0	99.73:0.27
EGZn45T50	99.50:0.50

The dendritic growth morphology is of particular importance to the application of the compound materials as a component in the Li ion negative electrode. The high surface area to volume ratio inherent in the dendrite morphology acts to reduce the interface overpotential by reducing the current density. It is not obvious, however, why a dendritic morphology is stabilized in this method of synthesis. The 'point efffsect of diffusion' is the mechanism that has been considered for the stabilizing of the dendrite morphology during solidification. However, when electric potentials are involved, there is also a contribution from the point effect of the electric field. The proposal put forth here is that the compound dendrites nucleate on the Zn powder, acting as electrodes for the reduction of the Sn and Cu ions. The proposed mechanism is illustrated in Fig. 4. The electrochemical overpotential at the solution/precipitate interface will produce an electric field acting to focus the ionic current to the dendrite tip. This idea has been considered previously as a rationalization for dendrite formation during electroplating [14].

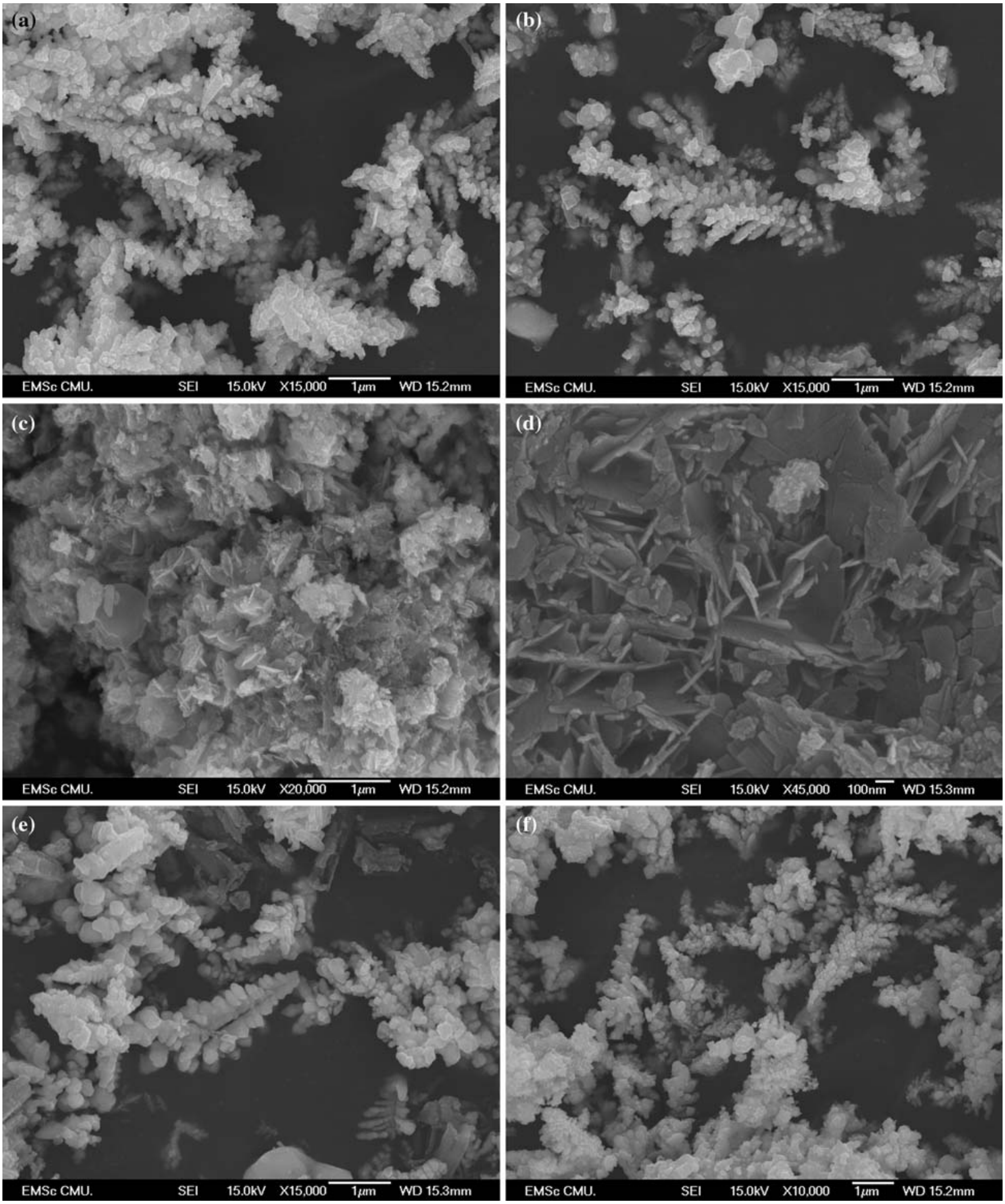


Fig. 2 SEM micrographs from the synthesis of Cu_6Sn_5 with conditions (**a**) EGZn45TR, (**b**) EGZn10TR, (**c**) DMFZn45TR, (**d**) DMSOZn45TR, (**e**) EGZn45T50, and (**f**) EGZn45T0

Conclusion

The nanometer crystalline dendrite Cu_6Sn_5 powder was successfully synthesized by reacting copper and tin chloride salts with zinc powder in an inert polar non-aqueous solvent such as ethylene glycol. Particle size of zinc powder, a reducing agent, did not affect the size of dendrite particles, nor the reaction temperatures in the range of 0–50 °C has

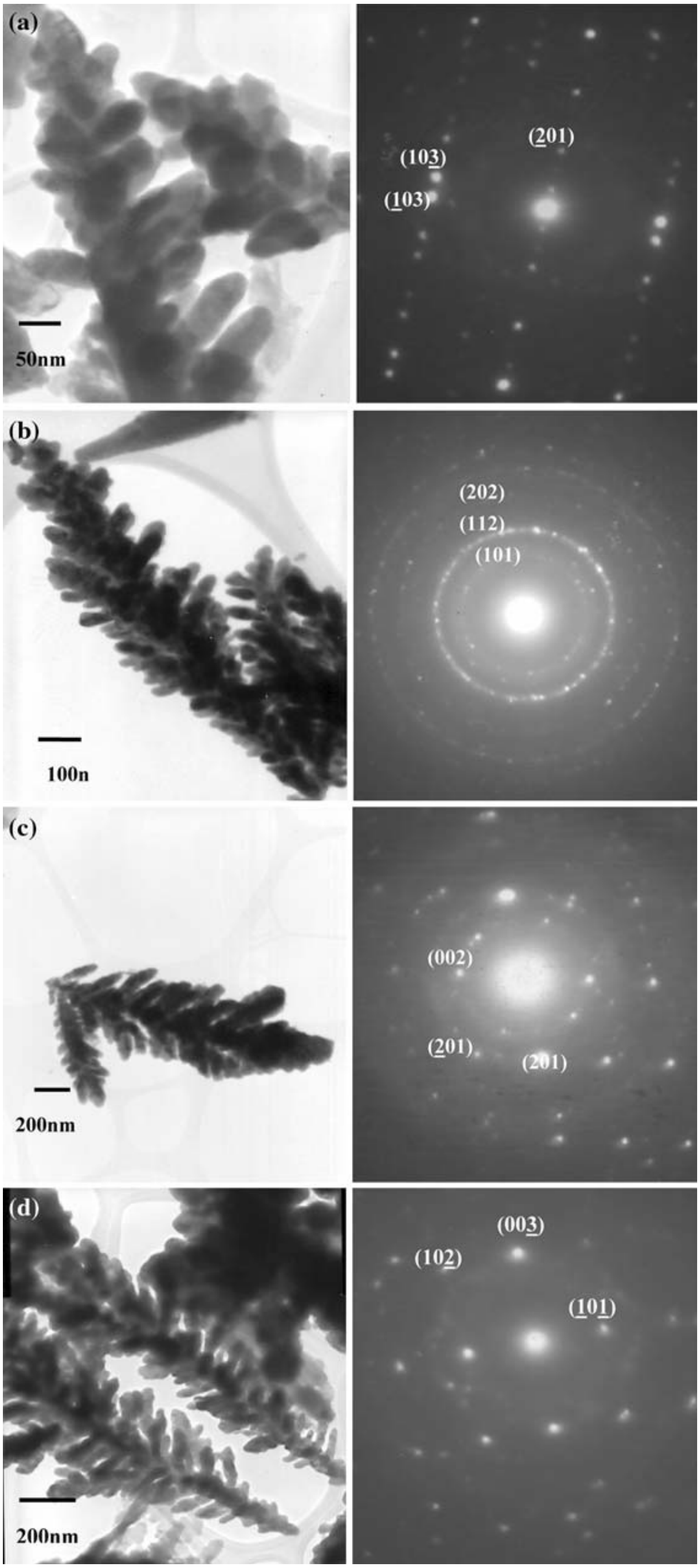


Fig. 3 TEM micrographs and the corresponding diffraction patterns from the synthesis of Cu_6Sn_5 with conditions (**a**) EGZn45TR, (**b**) EGZn10TR, (**c**) EGZn45T0, and (**d**) EGZn45T50

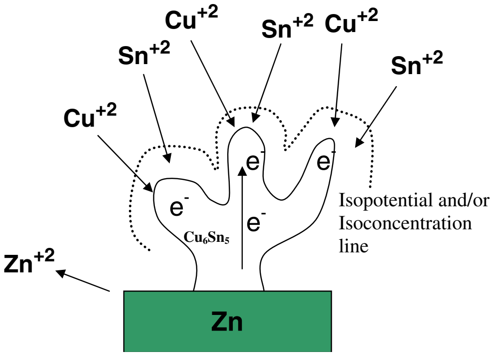


Fig. 4 Schematic diagram of the mechanism of the dendrite nucleation

significant effect on the formation of the intermetallic phase. Thus, the solution route method is an economic, convenient, and powerful technique for making dendritic morphology intermetallic compounds.

Acknowledgements The CMU electron microscopy research and service center is thanked for sample testing. Supports for this work from the Thailand Research Fund (TRF) and The Commission on Higher Education, contract no MRG4680166, are gratefully acknowledged.

References

1. Thackeray MM, Vaughey JT, Kahaian AJ, Kepler KD, Benedek R (1999) Electrochem Comm 1:111
2. Kepler D, Vaughey JT, Thackeray MM (1999) Electrochem Solid-State Letts 2(7):307
3. Thackeray MM, Johnson CS, Kahaian AJ, Kepler KD, Vaughey JT, Shao-Horn Y, Hackney SA (1999) ITE Battery Letts, vol 1, no 1
4. Yang J, Winter M, Besenhard JO (1996) Solid-State Ion 90:281
5. Besenhard JO, Yang J, Winter MJ (1997) J Power Sour 68:87
6. Kepler D, Vaughey JT, Thackeray MM (1999) J Power Sour 81–82:383
7. Janot R, Guérard D (2005) Progr Mater Sci 50:1
8. Sarakonsri T (2002) Ph.D. Thesis, Michigan Technological University, Houghton
9. Sarakonsri T, Johnson CS, Hackney SA, Thackeray MM (in Press) J Power Sour
10. Cullity BD (1977) Elements of X-ray diffraction, 2nd edn. Addison-Wesley, Massachusetts
11. Davanzo CU, Yoshitaka G (1981) J Chem Soc Dalton Trans Inorg Chem 3:843
12. Davanzo CU, Yoshitaka G (1982) Inorg Chim Acta 60:219
13. Coghi L, Pelizzi C, Pelizzi G (1976) J Organometal Chem 114:53
14. Modern Electrochemistry: an introduction to an interdisciplinary area. Plenum Press, New York, 1970