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Tomoki Tsumura

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リチウム挿入／脱離反応に対する
遷移金属酸化物の結晶性の効果

Tomoki Tsumura

津村 朋樹

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Acknowledgments

Abstract

Recently, demand for high energy density batteries has increased with the spread of portable electronic equipment and for the development of electric vehicle. Lithium ion battery is one of the candidates, and some battery systems for portable phones and video cameras, such as LiCoO_2/C and $\text{LiMn}_2\text{O}_4/\text{C}$, have already been developed and put on the market. In the lithium ion batteries, lithium insertion/extraction with redox reaction of host is made use of as both cathode and anode reactions. Some transition metal oxides show reversible lithium insertion/extraction and have been studied for electrode materials. Because it is possible for these oxides to have a different crystal structure and to have a wide range of crystallinity, distinct electrochemical performances of these oxides have been reported.

The purpose of the present thesis is to study the effect of the crystallinity of transition metal oxides on lithium insertion/extraction. Five transition metal oxides, spinel type LiMn_2O_4 , ordered rock-salt type $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$, anatase type TiO_2 , crystalline V_2O_5 , and crystalline $\alpha\text{-MoO}_3$, were selected as cathode materials. In the first two lithium containing oxides, lithium ions situated in lattice sites (8a sites in LiMn_2O_4 and 3b sites in $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$) are extracted and inserted. For the rest of three samples, interstitial sites are used as diffusion pass and accommodation sites for lithium ions. LiMn_2O_4 and TiO_2 have three dimensional channels, $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ and $\alpha\text{-MoO}_3$ have two dimensional gaps, V_2O_5 has one dimensional channels for the diffusion of lithium ions.

In order to investigate electrochemical properties of these oxides, lithium cells using each oxide as cathode were fabricated and the potential change with time during charge-discharge was recorded. Sample powders were characterized by means of X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and UV-VIS absorption spectroscopy.

In order to get sample powders with different crystallinity, LiMn_2O_4 and $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ were prepared via dicarboxylate. For LiMn_2O_4 , structure and thermal decomposition of the precursor, lithium-manganese-dicarboxylate, were investigated. In oxalate and succinate systems, the precursor was suggested to have a chain-like structure, in which lithium and manganese ions were linked by dicarboxylate ions. For malonate and tartrate systems, mixtures of complex and manganese salt seemed to be formed. In the complex salt, manganese ion was connected with two dicarboxylate ions as bidentate to be

complex anion. Charge balance of the anion was achieved with lithium ion and proton. In all the four precursor systems, mixing on atomic scale of lithium and manganese ions was achieved, and these precursors decomposed at around 300 °C and changed to LiMn_2O_4 phase without any by-product.

For LiMn_2O_4 samples, crystallinity of the sample was characterized by lattice parameter, a_0 , and lattice strain, ϵ , which were determined by XRD measurements. Lattice parameter increases and lattice strain decreases with the increase in heating temperature and these changes seemed to be due to improvement of cation distribution in spinel structure and the decrease of mean oxidation state of manganese ion. The first discharge capacity above 3.5 V was found to increase linearly with the decrease of lattice strain and the increase of lattice parameter.

Crystallinity of $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ samples was evaluated by half width of XRD lines. The half widths of 003 and 104 lines, which corresponded to development of stacking thickness and extension of the layers, respectively, seemed to increase with the increase of distribution, or the increase of disorder rock-salt type cubic $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ domains. The first discharge capacity above 3.0 V increases with the improvement of crystallinity, or the decrease of disordered rock-salt type cubic $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ domains.

For lithium containing transition metal oxides, the decrease of crystallinity causes not only the decrease of the crystallite size but also imperfection of cation distribution. Thus the decrease of the crystallinity leads to change in the structural skeleton of host and the structural change seemed to be concerned with the decrease of the capacity.

On the other three transition metal oxides, TiO_2 , V_2O_5 , and MoO_3 , the first discharge capacity was independent from the crystallinity of the host. For MoO_3 powders, any effect of the crystallinity on electrochemical performance was not observed. At the beginning of the first discharge (at the plateau around 2.8 V), the spacing of the van der Waals gap in starting MoO_3 structure was widened irreversibly from 0.69 to 1.2 nm and the inner structure of the Mo-O octahedron layers was also changed by lithiation. So the effect of crystallinity of pristine MoO_3 did not affect to the electrochemical performance.

TiO_2 powders prepared by hydrothermal treatment of amorphous TiO_2 powders were proved to be comprised from amorphous and crystalline anatase parts, though they were reported to be a single phase of anatase type structure. The crystallinity of anatase parts decreased and the amount of amorphous part increased with the decrease in heating temperature. The first discharge curve of TiO_2 powders prepared under hydrothermal conditions showed gradual decrease of potential from 3.0 to 1.75 V and a plateau at 1.75 V,

which are corresponding to lithium insertion into amorphous and crystalline parts respectively. The capacity down to 1.6 V, or capacity of the gradual potential decrease plus that of plateau region, was almost the same among the samples used.

For V_2O_5 samples, the first discharge potential change up to $400 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ was strongly affected by host morphology, extension of VO_5 layer, but the total capacity down to 0.5 V was almost the same for samples with different crystallinity. The difference in discharge potential was due to slow diffusion of lithium ion in the V_2O_5 structure.

Electrochemical performance of the cathode of the five transition metal oxides is classified into two groups on the basis that whether the crystallinity of these oxides affects the capacity or does not. One shows a pronounced effect of crystallinity on the capacity of lithium insertion/extraction and the other shows no effect of the crystallinity on the capacity. LiMn_2O_4 and $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ belong to the former group and TiO_2 , V_2O_5 , and MoO_3 belong to the latter. In the latter group, potential change during discharge was affected by structure type. This classification is able to be extended to other electrode materials; graphite, LiCoO_2 and LiNiO_2 appertain to the former and almost all other electrode materials to the latter.

要旨

近年、各種のポータブル機器そして次世代型電気自動車のバッテリーとして、充放電可能な高エネルギー密度電池の研究開発が世界的規模で急速に進められている。リチウム二次電池は金属水素電池などと並んで最も有力な候補の一つであり、小型のものについては既に実用化され商業的に生産される段階に至っている電池系も存在する。リチウム二次電池の電極反応には電極活物質の構造中にリチウムイオンを可逆的に挿入/脱離する反応が利用されており、正極材として遷移金属酸化物、カルコゲン化合物および有機ポリマーが、負極材として黒鉛をはじめとした様々な炭素材料が研究されている。これらの化合物は調製法および調製条件により多種多様な結晶構造、結晶性、形態を持つことが知られており、それらはリチウムイオンの挿入/脱離反応に大きな影響を与えることが予想されるが、これらの要因を系統的に検討した例は少ない。

本研究では、遷移金属酸化物への電気化学的なリチウムイオンの挿入および脱離反応を行い、ホストの結晶性の効果について検討した。本研究でとりあげた電極活物質としての LiMn_2O_4 および $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ は格子サイトにおけるリチウムイオンの脱離/挿入反応を示し、 TiO_2 、 V_2O_5 および MoO_3 は格子間サイトへの挿入/脱離反応を示す。また、これらの酸化物はリチウムイオンの拡散パスとして LiMn_2O_4 および TiO_2 は三次元的に繋がるチャンネルを、 V_2O_5 は一次元的なチャンネルを、 $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ および MoO_3 は二次元的な広がりを持つ層間を有している。

広い範囲の結晶性を有するリチウム含有遷移金属酸化物サンプル (LiMn_2O_4 、 $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$) を合成するため、リチウム-遷移金属-ジカルボン酸塩を経由した合成法を開発した。この方法によりプリカーサーであるジカルボン酸塩の段階において金属イオンの原子オーダーの混合が可能となり、 300°C で目的の低結晶性酸化物が得られることを見いだした。 V_2O_5 、 MoO_3 はそれぞれのアンモニウム塩 (NH_4VO_3 、 $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$) の熱分解により合成し、 TiO_2 はアモルファスチタニアの水熱処理により合成した。これらのサンプルの結晶性は加熱温度を調節することにより変化させた。

得られた酸化物粉末のキャラクタリゼーション手段としてXRD、SEMおよびTEM、UV-VIS吸収スペクトル、XAS、XPSを用いた。また、電気化学的特性の評価は、酸化物粉末を正極に、そして負極にリチウムメタルを、電解液に1Mの過塩素酸リチウムを溶かしたエチレンカーボネート/ジエチルカーボネート混合溶液を用いた電池について行った。

格子サイトにおけるリチウム脱離/挿入反応を示す LiMn_2O_4 、 $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ において、その4V(vs. Li^+/Li)の放電プラトーにおける可逆的なリチウム脱離/挿入量は結晶性に強く依存していることが示された。 LiMn_2O_4 においては結晶性のパラメータとして格子定数およびXRD回折線の半価幅より格子歪を求めた。これらのパラメータに対し直線的に4Vのリチウム脱離/挿入量が増加することが確認された。そして、この結晶性の低下(格子定数の減少および格子歪の増大)は、カチオン分布の乱れ(マンガンイオンとリチウムイオンの置換やカチオン欠陥の生成)に起因すると推測された。 $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ においては、結晶性のパラメータとして層構造の積み重なるの厚さおよび層面の広がり度を反映すると考えられる003、104回折線の半価幅をとり可逆的な容量との関係を検討した。半価幅の増加すなわち結晶性の低下に伴い可逆容量は減少する傾向が見られた。この容量の減少も LiMn_2O_4 と同様、カチオン分布の乱れに起因すると推測された。

一方、格子間サイトへのリチウム挿入/脱離反応を示す TiO_2 、 V_2O_5 および MoO_3 においては、結晶性に対するリチウム挿入/脱離量の依存性は認められなかった。これらの酸化物ではアモルファス状態においてもリチウムイオンの挿入/脱離反応が確認されており、リチウム挿入/脱離反応に対して結晶構造は必要ないものと考えられる。

MoO_3 では結晶性の放電容量および放電電位に対する効果は全く見られなかった。 MoO_3 は放電初期において層間にリチウムイオンが挿入され、層構造は維持されるものの層間隔が0.69から1.24nmまで広げられるため、反応前のホスト構造の結晶性の効果が見られなかった。

水熱合成で得られた TiO_2 粉末はアナターゼ型構造の結晶子をアモルファスチタニアが被覆した形態を持ち、アモルファス領域へのリチウムの挿入反応は3.0~1.7Vの広い電位範囲で起

こり、結晶領域への挿入反応は1.7Vのプラトーで起こっていた。このアモルファス領域へのリチウムの挿入電位の広がり是非晶質化に伴う格子の乱れがリチウム挿入に対するサイトのエネルギー（ホスト中のリチウムのケミカルポテンシャル）に分布を生じさせたことに起因するものと考えられる。

V_2O_5 は3V以上の電位において LiV_2O_5 の組成までリチウムイオンが挿入されることが知られている。しかし、高結晶性の V_2O_5 層面の広がり大きなサンプルでは LiV_2O_5 の組成に達する前に放電電位が3V以下に降下することが確認された。この放電電位の変化はリチウムの拡散速度に対して回路を流れる電流密度が大きいため生ずる電位降下であった。 V_2O_5 へのリチウムイオンの挿入反応はホスト構造の変化を伴うため、その拡散速度は非常に遅いことが知られている。

本研究で用いた5種の遷移金属酸化物では、リチウム挿入／脱離反応に対する可逆容量が結晶性に強く依存するものとそうでないものの2つに分類されることが示された。そして、後者においては構造の種類により結晶性の変化や結晶成長に伴う粒子形態の変化が放電電位に大きな影響を与えることが確認された。この分類は他の電極活物質についても適応でき、前者に属するものとして $LiNiO_2$ 、 $LiCoO_2$ 等のリチウム含有遷移金属酸化物や層構造の発達した黒鉛材料が、後者にはその他のほとんどの遷移金属酸化物（ MnO_2 、 WO_3 および Nb_2O_5 等）および硫化物（ TiS_2 、 MoS_2 および FeS_2 等）が属すると考えられる。

本研究は、遷移金属酸化物の結晶性に着目することにより電気化学的リチウムイオンの挿入／脱離反応挙動を系統的にとらえ、上記のような分類を提案した。この結果は、最適な電極材の合成条件および新規な材料開発に対して重要な指針を与えることができるものと考えられる。

Chapter 1

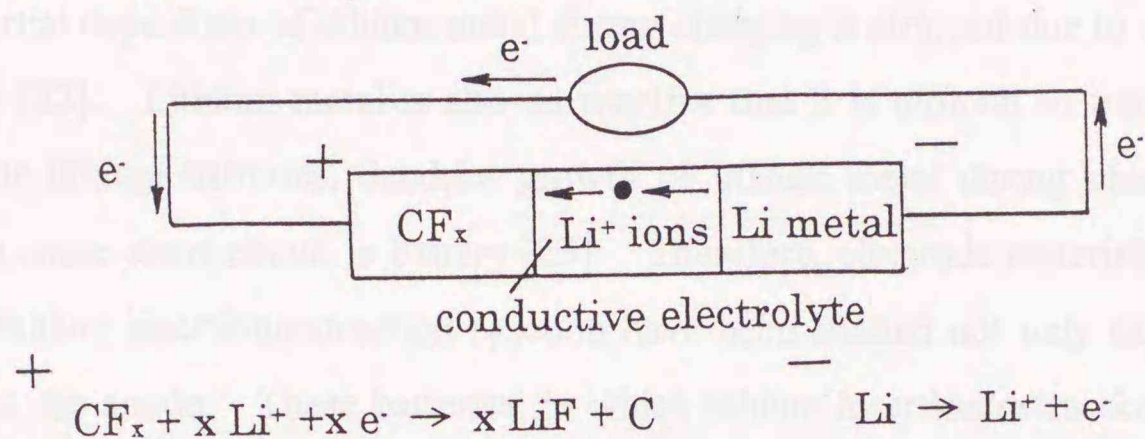
Introduction

1.1 Lithium batteries

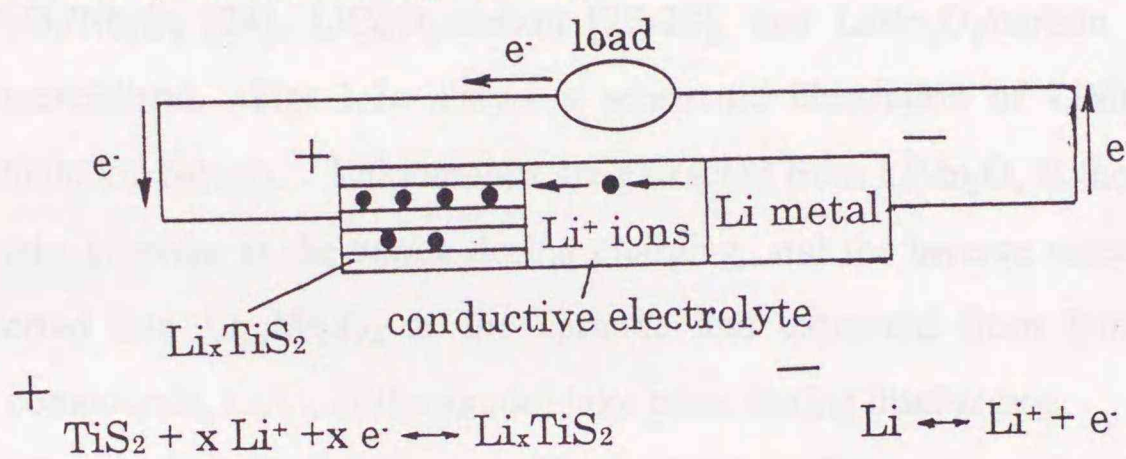
Lithium has been long time known to be a very attractive anode material for high energy density batteries because of its low equivalent weight of 6.941 and the most base standard potential of -3.045 V vs. SHE. From the ecological view point, lithium metal is thought to be suitable for anode material because it is harmless to environment compared to zinc and lead metals which have been extensively used as active electrode materials in various batteries. Lithium metal is stable in non-aqueous electrolytes, such as LiClO_4 dissolved propyrenecarbonate, because passivation layer is formed at the surface of lithium metal and the layer prevents the further chemical reaction between lithium metal and electrolyte, or hinders passing of electrons, but still allows for lithium diffusion during electrochemical reactions, such as discharging and charging [1-5]. According to the developments in the microelectronics industry, lithium battery technology has been developed since 1950's. Some of the primary lithium batteries with different cathode/anode combinations, such as lithium/sulfur dioxide (Li/SO_2) [6], lithium/manganese dioxides [7], lithium/graphite fluoride (Li/CF_x) [8], and lithium/iodine-polyvinylpyridine ($\text{Li}/\text{I}(\text{PVP})$) [9], are manufactured in commercial base. Fig. 1.1a shows the scheme of $\text{Li}/(\text{CF}_x)$ primary battery in non-aqueous electrolyte. During discharging, lithium metal dissolves into electrolyte giving electrons to the circuit (anode reaction) and graphite fluoride reacts with lithium ions and is reduced by electrons which are supplied from the anode through the circuit (cathode reaction). Resulting products of the cathode are lithium fluoride and carbon.

Recently rechargeable high power and high energy density lithium batteries (secondary lithium batteries) are demanded for portable equipment, such as video cameras and cordless phones and also for electric vehicles in order to reduce the atmosphere contamination. Research and development for the cathode materials which show reversible lithium insertion/extraction reaction have been made to improve charge-discharge cycle performance [10-13]. The rechargeable lithium batteries, such as Li/TiS_2 [14], Li/MoS_2 [15], Li/NbSe_3 [16], Li/MnO_2 [17], $\text{Li}/\text{vanadium oxides}$ [18-21], etc., have been proposed and demonstrated. Fig. 1.1b shows the scheme of Li/TiS_2 secondary battery. Lithium ions in the electrolyte are inserted into interlayer spacing of TiS_2 of the cathode during

a) CF_x / Li (primary cell)



b) TiS_2 / Li (secondary cell)



c) $\text{LiMn}_2\text{O}_4 / \text{C}$ (secondary cell)

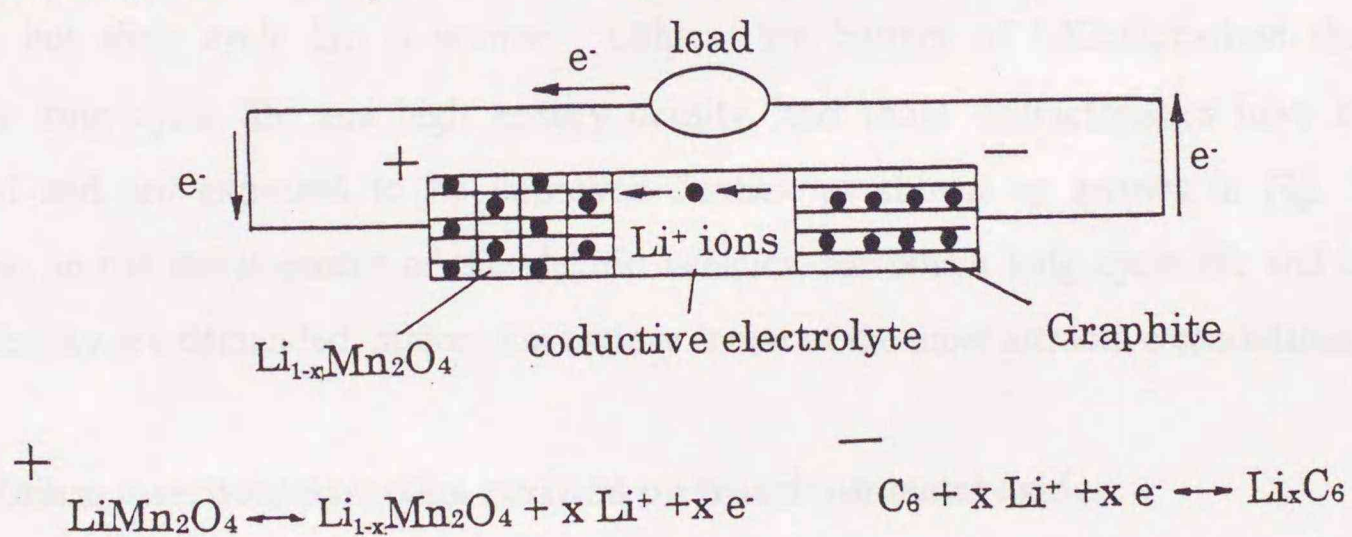


Fig. 1.1 Scheme of different lithium batteries.

discharging and extracted from there during charging. At the anode, dissolution and deposition of lithium metal occur during discharging and charging, respectively. But cycling of the metallic lithium anode in organic electrolyte was not completely reversible, because partial deposition of lithium metal during charging is stripped due to corrosion and passivation [22]. Lithium metal is also so reactive that it is difficult to treat in safety in rechargeable lithium batteries; dendrite growth of lithium metal during charge-discharge cycling can cause short-circuit in battery [23]. Therefore, electrode materials which show reversible lithium insertion/extraction reaction have been studied not only for the cathode but also for the anode. These batteries, in which lithium insertion/extraction compounds are used as electrode reactions at both electrodes, are named as lithium ion batteries. These are also called as rocking-chair type lithium batteries [10-13]; because lithium ions are transferred back and forth between anode and cathode. Some of the lithium ion batteries, such as $\text{LiV}_2\text{O}_5/\text{Nb}_2\text{O}_5$ [24], $\text{LiCoO}_2/\text{carbon}$ [25-28], and $\text{LiMn}_2\text{O}_4/\text{carbon}$ [29-32], are already commercialized. Fig. 1.1c shows a schematic illustration of $\text{LiMn}_2\text{O}_4/\text{graphite}$ secondary lithium ion battery. Lithium ions are extracted from LiMn_2O_4 at the cathode and are inserted into graphite at the anode during charging, and the inverse reactions (lithium ions are inserted into $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ at the cathode and extracted from lithium graphite intercalation compounds, Li_xC_6 , at the anode) take place during discharging.

Fig. 1.2 shows relationship between the cycle life and the energy density of various kinds of batteries commercialized in Japan [11]. The energy density of rechargeable lithium batteries of LiCoO_2/Li and MnO_2/Li systems is higher than that of other rechargeable systems, but their cycle life is poorer. Lithium ion battery of $\text{LiCoO}_2/\text{carbon}$ shows relatively long cycle life and high energy density, and those characteristics have been improved and are expected to be improved further, as shown by arrows in Fig. 1.2. Therefore, in the development of the electric vehicles, for which long cycle life and high energy density are demanded, lithium ion battery is one of the most attractive candidates.

1.2 Lithium insertion/extraction reaction on transition metal oxides

The possible electrode reactions in lithium batteries can be classified as shown in Fig. 1.3. The reactions are roughly divided into two groups, disproportionation and topochemical reactions [33]. In a disproportionation reaction, crystalline structure of the electrode materials is completely broken down during reaction. Materials such as CF_x , CuS , and CuO shows this type of reaction, which is revealed on CF_x as follows;

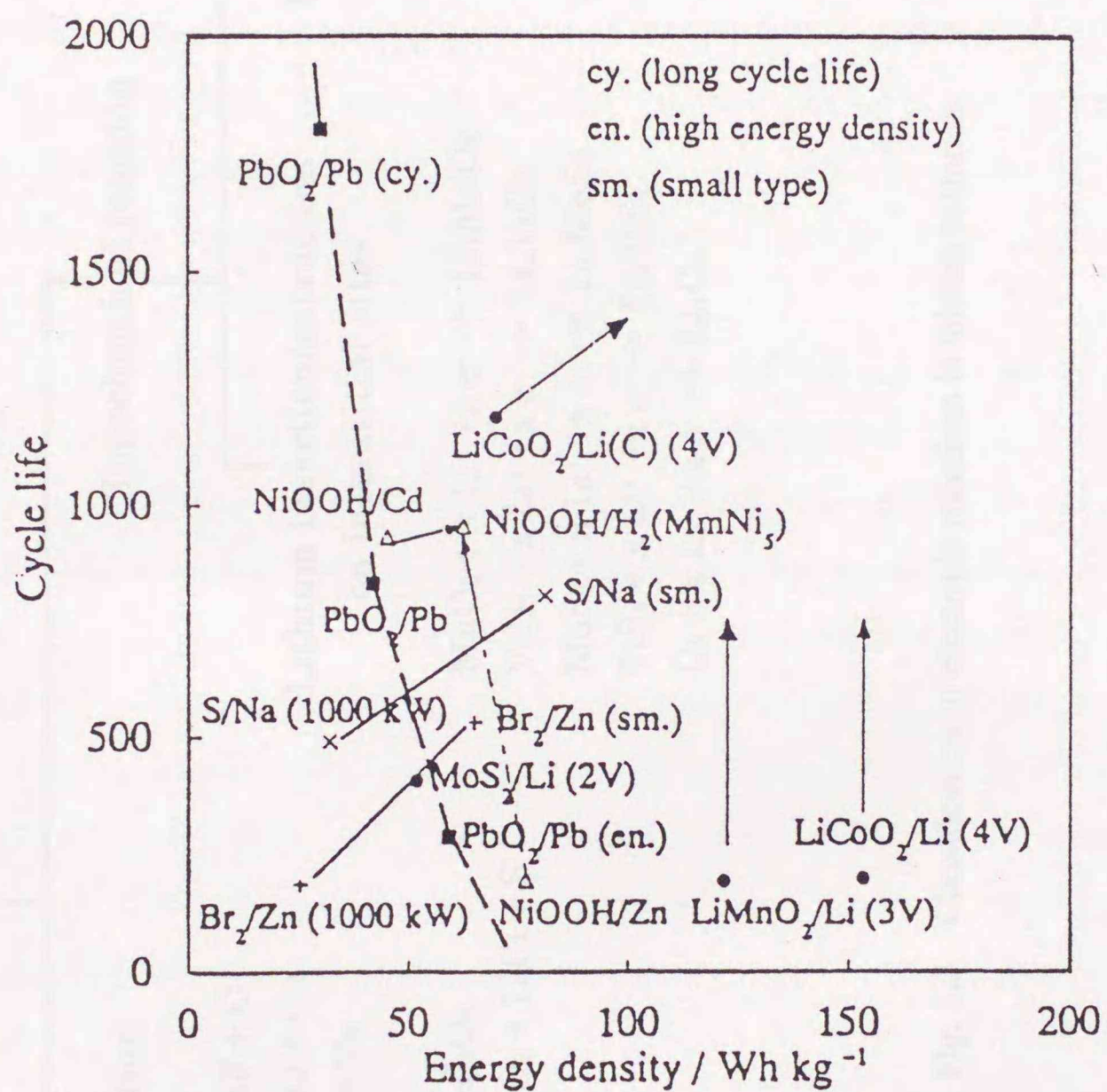
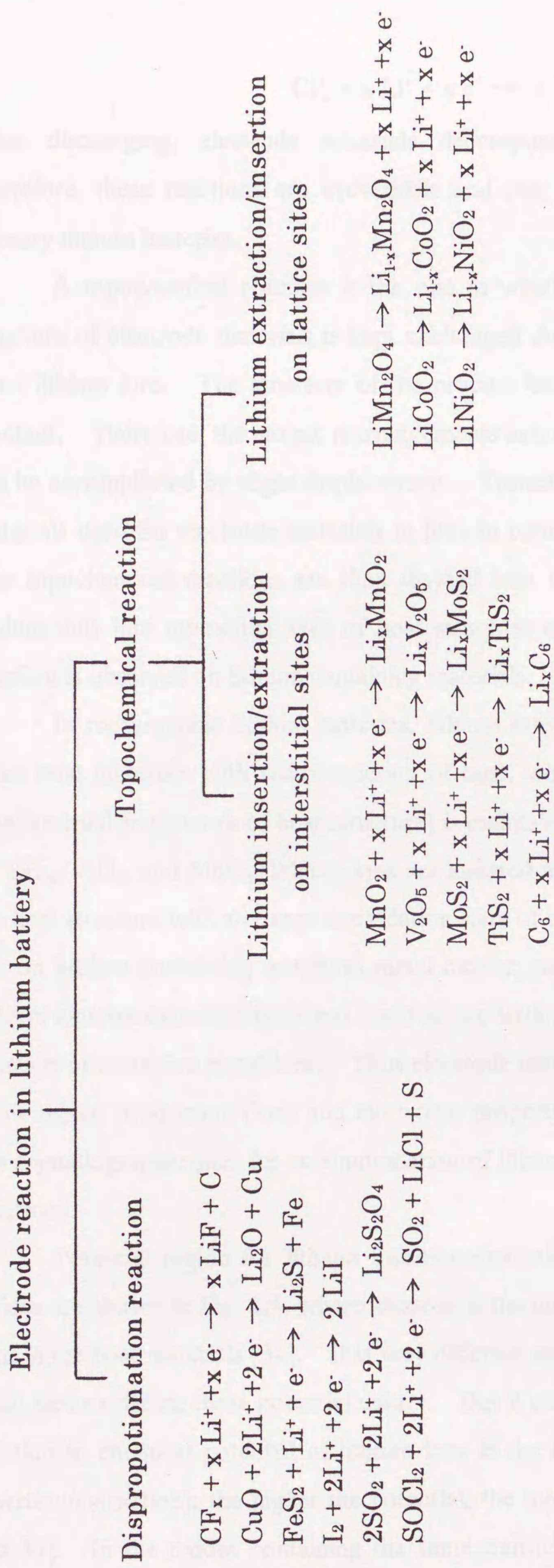
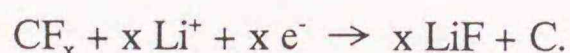


Fig. 1.2 Relation between the cycle life and the energy density of various kinds of batteries commercialized in Japan.





After discharging, electrode materials decompose to lithium fluoride and carbon. Therefore, these reactions are irreversible and can be used only in cathode reaction of primary lithium batteries.

A topochemical reaction is the one in which the fundamental framework of the structure of electrode materials is kept unchanged during the insertion/extraction of small-sized lithium ions. The structure of the product bears a close relationship to that of the reactant. Therefore, the atomic rearrangements associated with lithium insertion/extraction can be accomplished by slight displacement. Transition metal oxides, sulfides, and carbon materials used for electrode materials in lithium batteries show the topochemical reaction. The topochemical reactions are then divided into two reactions, insertion/extraction of lithium ions into interstitial sites of host structure and that into lattice sites. The latter reaction is observed on lithium containing materials.

In rechargeable lithium batteries, lithium ions are inserted into and extracted from these host materials with redox reaction of host, where chemical bonds of host structure (fundamental framework of host structure) is maintained. On transition metal oxides, such as TiO_2 , V_2O_5 , and MoO_3 , lithium ions are inserted into and extracted from vacant sites of the host structure with a change in oxidation state of transition metal ions in the host oxides, but on lithium containing transition metal oxides, such as LiCoO_2 , LiNiO_2 , and LiMn_2O_4 , lithium ions are extracted from and inserted into lattice sites of the host structure with redox reaction of transition metal ions. Thus electrode materials in rechargeable lithium batteries show mixed conduction (ions and electrons) property and, therefore, are required to have the crystallographic sites for accommodation of lithium ions and band structure for keeping electrons.

Potential region for lithium insertion/extraction reaction on some transition metal oxides are shown in Fig. 1.4, where abscissa is the number of d-electron of transition metal ions in the host materials [34]. It is very different among the oxides and it is still unknown what factors decide these potential values. But it can be said that the potential has a close relation to chemical potential of lithium ions in the host structure (site energy for lithium insertion/extraction); the higher the potential, the more stable lithium ion in host structure [35-37]. In the oxides containing the same transition metal ions, the potential tends to decrease with the decrease of the oxidation number of the metal ion.

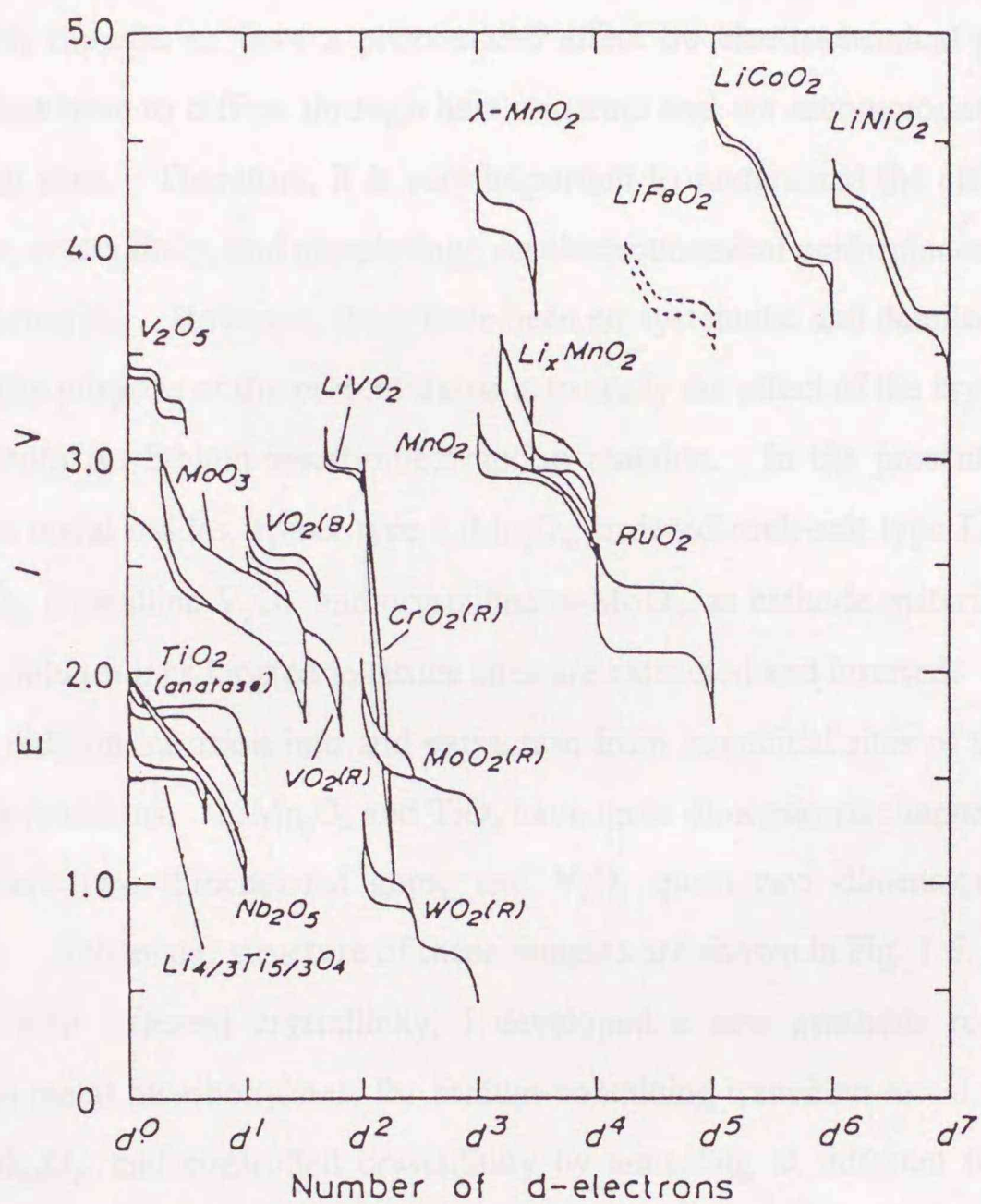


Fig. 1.4 Potential region for lithium insertion/extraction reaction on some transition metal oxides. The abscissa is the number of d-electron of transition metal ion in the host.

1.3 Purpose of the present thesis

Lithium insertion/extraction on many kinds of transition metal oxides have been studied by various authors and their distinct electrochemical performances have been reported. These oxides have a wide variety of structure, crystallinity, and morphology. These factors have been known to depend primarily on their synthesis methods and their conditions, particularly on ceramics to which transition metal oxides belong, and are reasonably thought to have a pronounced effect on electrochemical performance because lithium ions have to diffuse through host structure and are accommodated in either lattice or interstitial sites. Therefore, it is very important to understand the effects of these factors, structure, crystallinity, and morphology on electrochemical performance of these materials in lithium batteries. However, there have been no systematic and detailed studies so far.

The purpose of the present thesis is to study the effect of the crystallinity of transition metal oxides on lithium insertion/extraction reaction. In the present thesis, I chose five transition metal oxides, spinel type LiMn_2O_4 , ordered rock-salt type $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$, anatase type TiO_2 , crystalline V_2O_5 , and crystalline $\alpha\text{-MoO}_3$, as cathode materials. In the first two samples, lithium ions located in lattice sites are extracted and inserted. For the rest of three samples, lithium insertion into and extraction from interstitial sites of the host structure are electrode reactions. LiMn_2O_4 and TiO_2 have three dimensional channels, $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ and MoO_3 have two dimensional gaps, and V_2O_5 quasi two dimensional gaps for lithium diffusion. Schematic structure of these samples are shown in Fig. 1.5. In order to prepare samples with different crystallinity, I developed a new synthesis route, via lithium and transition metal dicarboxylates, for lithium containing transition metal oxides, LiMn_2O_4 and $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$, and controlled crystallinity by annealing at different temperatures [38,39]. V_2O_5 and MoO_3 samples were prepared by thermal decomposition of the corresponding ammonium salts, NH_4VO_3 and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$, respectively, at different temperatures. For preparation of TiO_2 samples, hydrothermal method with different conditions was applied [40]. Effect of the crystallinity of the host structure on electrochemical performance is expected to be distinct among the five samples because of the difference in their structure type.

1.4 Construction of the present thesis

The present thesis consists of eight chapters.

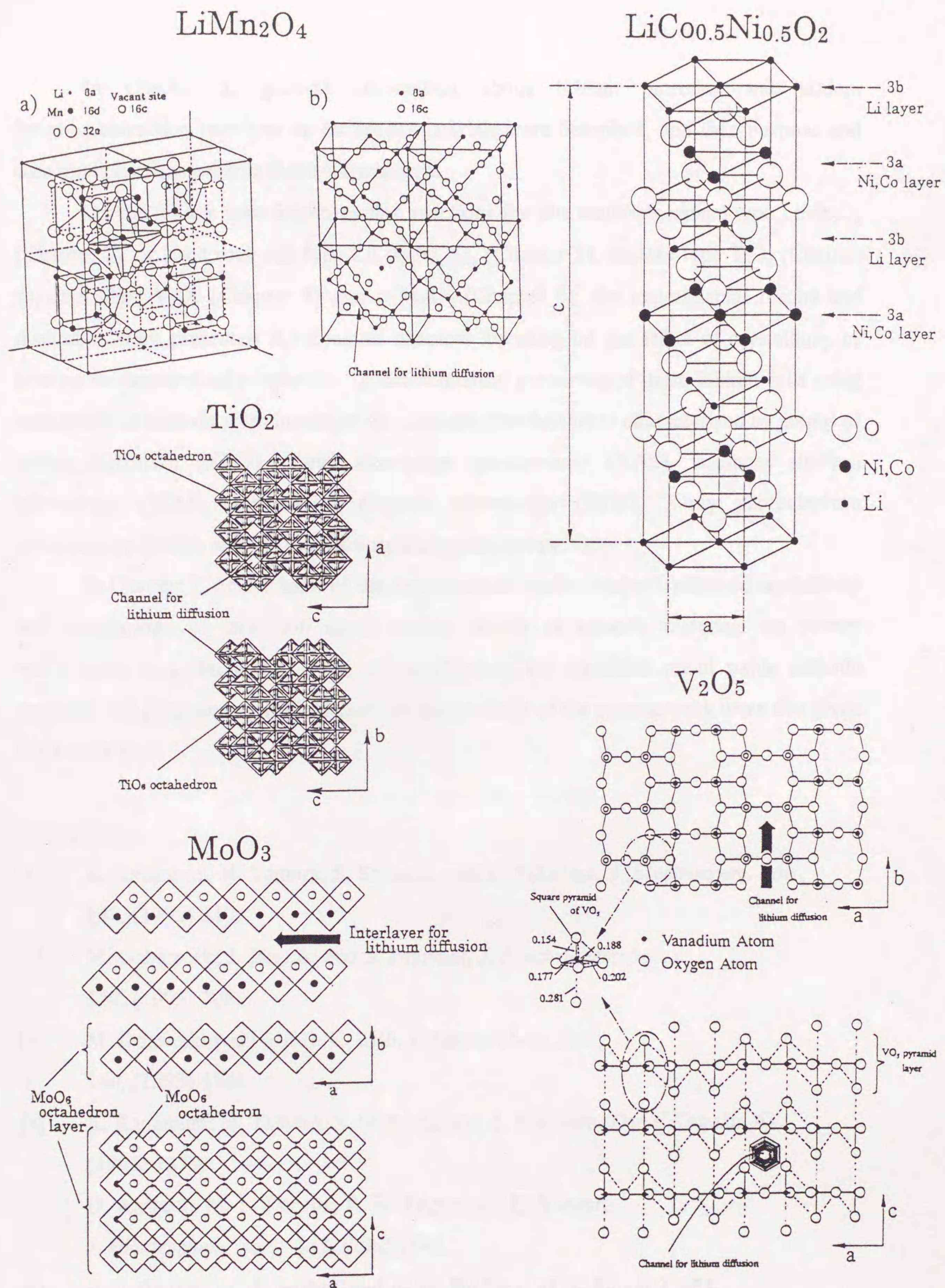


Fig. 1.5 Schematic structure of samples used.

In Chapter 1, general information about lithium batteries and lithium insertion/extraction reactions on electrode materials were described, and then purpose and construction of the present thesis were shown.

On the lithium insertion/extraction reactions for five materials, spinel type LiMn_2O_4 (Chapter 2), ordered rock-salt type $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ (Chapter 3), anatase type TiO_2 (Chapter 4), crystalline V_2O_5 (Chapter 5) and $\alpha\text{-MoO}_3$ (Chapter 6), the experimental results and discussion were presented in respective chapters, focusing on the effect of crystallinity of host on electrochemical properties. Electrochemical properties of those lithium cells using each oxide as cathode were investigated. Sample powders were characterized by means of X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and UV-VIS absorption spectroscopy.

In Chapter 7, on the basis of the experimental results obtained, effect of crystallinity and morphology of transition metal oxides (hosts) as cathode materials on battery performance was discussed. Idea of classification for transition metal oxide cathode materials was proposed. The conclusions and prospect of the present work were also given in Chapter 7.

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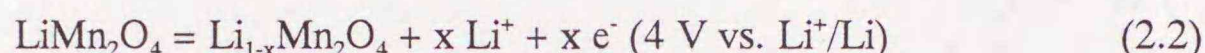
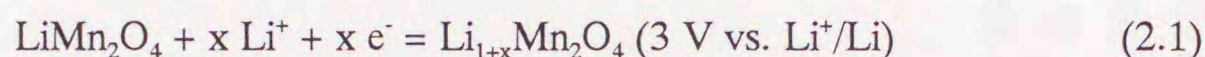
Chapter 2

Spinel type LiMn_2O_4

2.1 Introduction

Lithium manganate, LiMn_2O_4 , has a spinel structure with normal cation distribution, i.e. Li ions occupy 1/8 tetrahedral sites and Mn ions 1/2 octahedral sites of cubic close packed oxygen, belongs to the space group of $\text{Fd}3\text{m}$ [1-3]. Lithium, manganese, and oxygen atoms occupy 8a sites, 16d sites, and 32e sites, respectively. Three dimensional view of unit cell of the spinel structure and a linkage of 8a site, at which lithium ions locate, and also 16c sites, which are vacant, among four unit cells are shown in Figs. 2.1a and b, respectively.

Electrochemical lithium insertion into and extraction from LiMn_2O_4 takes place at a potential around 3 and 4 V (vs. Li^+/Li), respectively, and expressed as following reaction formulae [1-3];



The reaction (2.1) is the further insertion of lithium ions into spinel type LiMn_2O_4 , which occurs at 3 V and results in the formation of $\text{Li}_2\text{Mn}_2\text{O}_4$. During this reaction, lithium ions can diffuse through three dimensional network of 8a and 16c sites (Fig. 2.1b), and additional lithium ions are finally accommodated in half of 16c sites at 3 V and the resultant $\text{Li}_2\text{Mn}_2\text{O}_4$ crystal belongs to tetragonal. The reaction (2.2) is the extraction of lithium ions from 8a sites in spinel structure, which can occur at the potential of 4 V through the network of 8a and 16c sites and leave the same number of 8a sites vacant [1-3]. Schematic potential change curve on $\text{Li}_x\text{Mn}_2\text{O}_4$ from $x = 0$, i.e., cubic type Mn_2O_4 , to $x = 2.0$, i.e., tetragonal phase of $\text{Li}_2\text{Mn}_2\text{O}_4$, is shown in Fig. 2.2. At two plateaus around 4 V during the reaction (2.2), cubic symmetry of crystal structure is maintained during lithium extraction/insertion. In the range of $0.0 < x < 0.5$ two phases with different a_o -parameters, Mn_2O_4 and $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$, coexist, but in the range of $0.5 < x < 1.0$ a single phase existing where lattice parameter, a_o , changes continuously with x -value. Change in cell volume between Mn_2O_4 and LiMn_2O_4 is below 5.0 %. At the plateau of 3 V during the reaction (2.1), because of Jahn-Teller distortion caused by the increase in concentration of Mn^{3+} in octahedral site, $\text{Li}_2\text{Mn}_2\text{O}_4$ phase with tetragonal symmetry appears, and coexistence of cubic LiMn_2O_4 and tetragonal $\text{Li}_2\text{Mn}_2\text{O}_4$ phases is observed. In $\text{Li}_2\text{Mn}_2\text{O}_4$ phase, the c/a ratio of the unit cell increases by

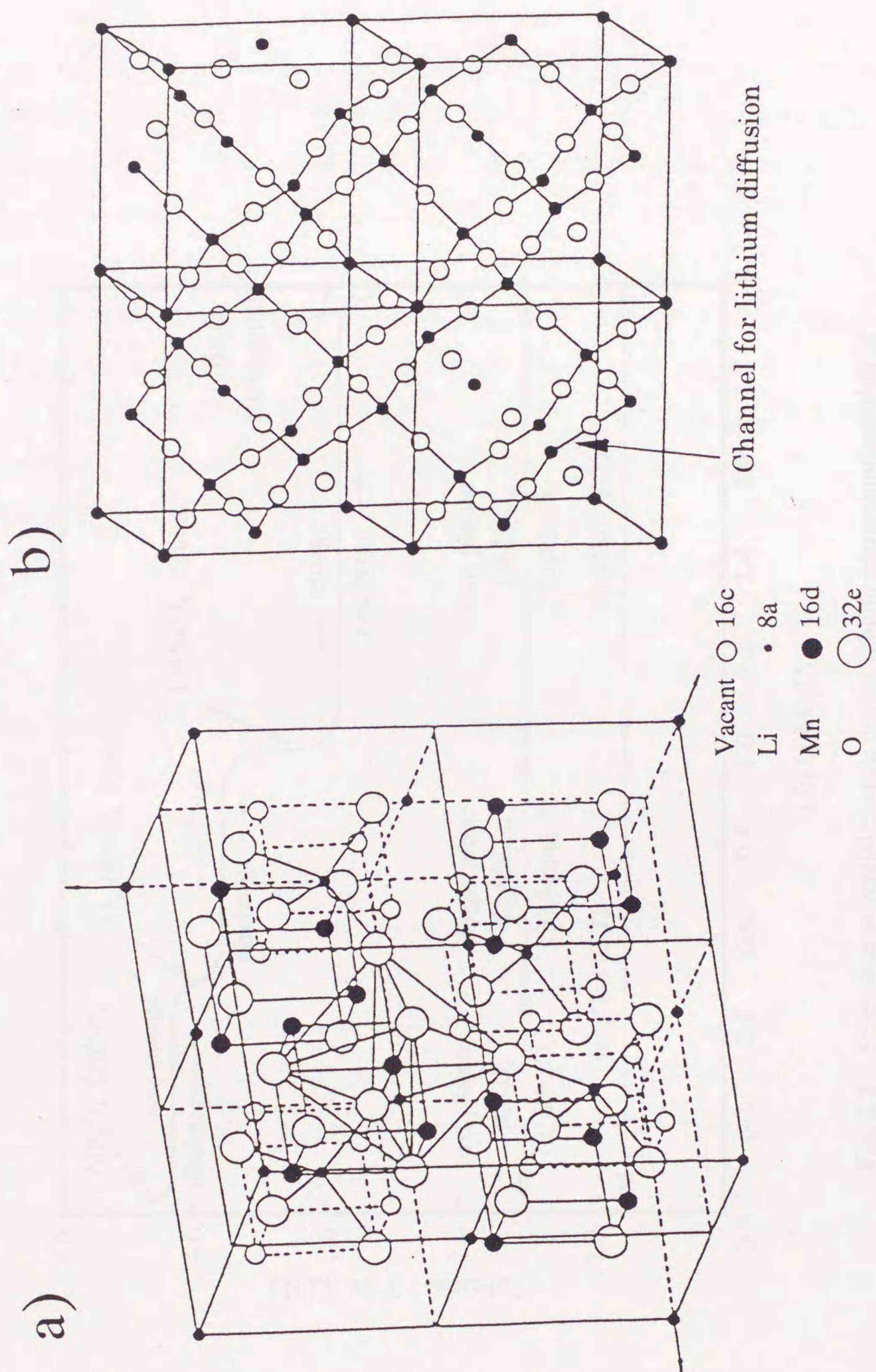


Fig. 2.1 Schematic view of a unit cell of LiMn_2O_4 structure a) and a linkage of 8a and 16c sites among the four unit cells b).

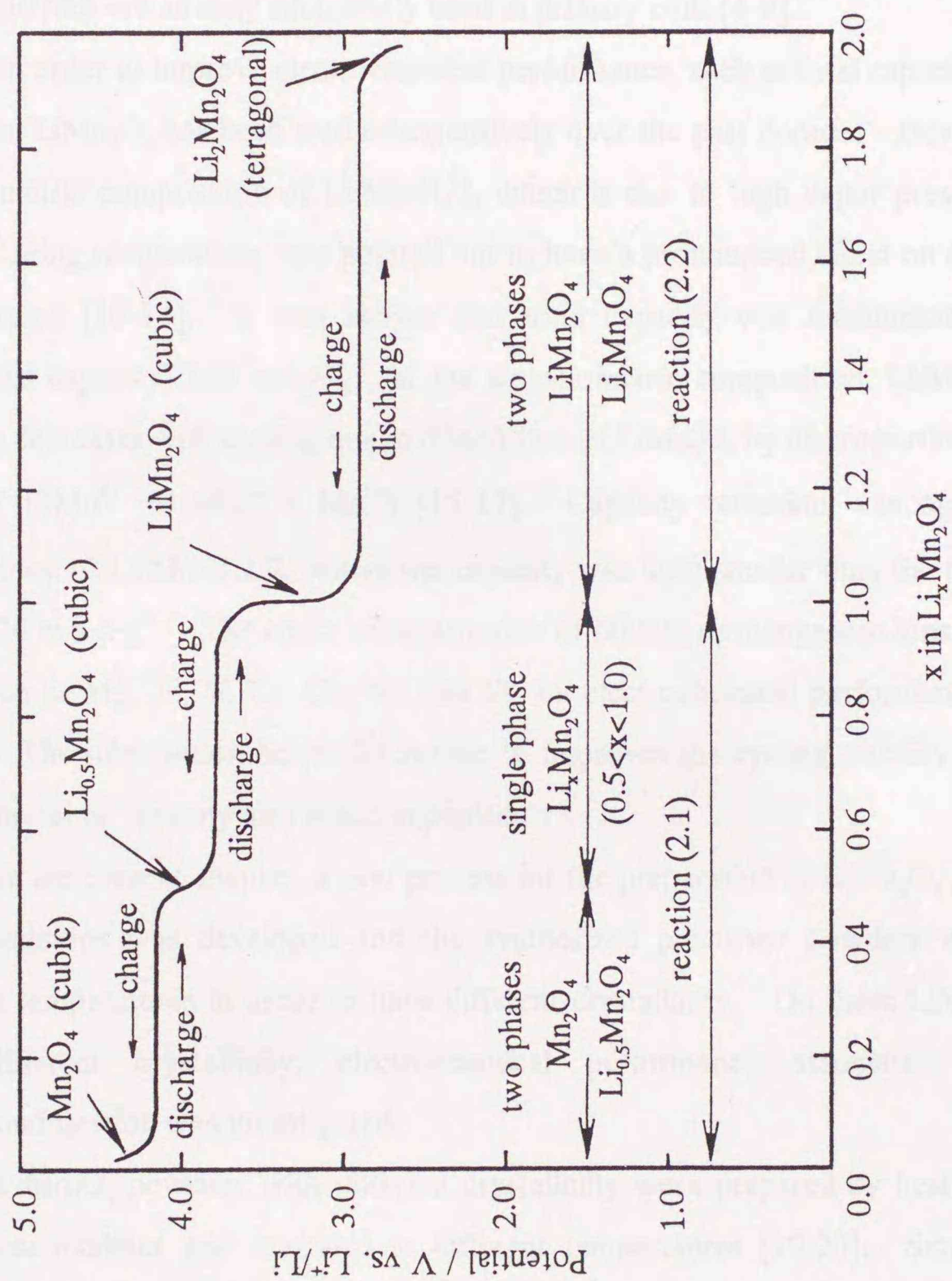


Fig. 2.2 Schematic potential change during lithium extraction/insertion of LiMn_2O_4 .

16 %, which is too large for the electrode to maintain its structural integrity on cycling. Therefore, LiMn_2O_4 can be one of the candidates as the cathode materials in 4 V lithium ion batteries similarly to LiCoO_2 and LiNiO_2 [4-9]. The cell based on lithium manganate as cathode is expected to exhibit following advantages: a) a low cost for electrode materials arising from an easier synthesis compared to LiNiO_2 and from the use of manganese which is more abundant and cheaper than cobalt, b) LiMn_2O_4 is stable in air, and c) the already well-known behavior with respect to toxicity (extremely low) and recycling, since manganese oxide materials are already extensively used in primary cells [4-9].

In order to improve electrochemical performance, such as total capacity and capacity retention, LiMn_2O_4 has been studied extensively over the past decade. Deviation from the stoichiometric composition of $\text{Li/Mn}=1/2$, which is due to high vapor pressure of lithium oxide at firing temperature, was pointed out to have a pronounced effect on electrochemical performance [10-14]. It was shown that total capacity was maximized, i.e. close to theoretical capacity, $148 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$, at the stoichiometric composition, $\text{Li/Mn}=1/2$, but the capacity decreases with cycling due to dissolution of LiMn_2O_4 by disproportionation reaction of Mn^{4+} ($2\text{Mn}^{4+} \rightarrow \text{Mn}^{3+} + \text{Mn}^{2+}$) [15-17]. Capacity retention was optimized at the composition of $\text{Li/Mn}=1.1/2$, where the capacity was little smaller than the theoretical one, about $120 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$. The effect of substitution of lithium or manganese ions by other metal ions, such as Mg, Ti, V, Cr, Co, Ni, and Fe, on electrochemical performance was studied [4,18]. The substitution below 20 atomic % improves the cycling stability even though a small amount of capacity loss is accompanied.

In the present chapter, a new process for the preparation of LiMn_2O_4 powders under mild conditions was developed and the synthesized precursor powders were heated at different temperatures in order to have different crystallinity. On these LiMn_2O_4 powders with different crystallinity, electrochemical performance associated with lithium extraction/insertion was investigated.

LiMn_2O_4 powders with different crystallinity were prepared by heating of lithium-manganese-oxalates and -tartrates at different temperatures [19,20]. Samples prepared were characterized by means of XRD, XAS, and XPS, and an effect of crystallinity of samples on electrochemical properties was studied. Capacity of the plateau at 4 V decreased linearly with the decrease of lattice parameter, a_o , and the increase of lattice strain, ϵ , both of which were measured by XRD. The decrease of lattice parameter, a_o , and the

increase of lattice strain, ϵ , with the decrease in heating temperature seemed to be due to imperfect cation distribution in spinel structure and the increase of mean oxidation state of manganese ions. For samples prepared via tartarates, capacity of plateau at 3 V was found to be independent of heating temperature, but the 3 V-capacity of samples prepared via oxalates decreased with the decrease in heating temperature.

2.2 Synthesis of LiMn_2O_4 via lithium-manganese-dicarboxylates

LiMn_2O_4 powders are mainly prepared by reacting a mixture of Li_2CO_3 and MnO_2 powders in air above 600 °C, followed by several successive grinding and annealing sequences [1-3]. It is difficult to control the stoichiometry and cation distribution in LiMn_2O_4 spinel in the solid state reaction, because some lithium oxides evaporate from the reaction system above 600 °C, which deteriorates the stoichiometry of resulting compounds. Therefore, it is important to develop a new process for synthesis of LiMn_2O_4 samples which can proceed under mild conditions.

Thermal decomposition of lithium-manganese-dicarboxylates to the LiMn_2O_4 was studied as one of the synthesis routes at low temperatures [19,20]. In order to determine the effects of dicarboxylate ions, four dicarboxylates, oxalates, malonates, succinates, and tartrates were selected.

The results of TG-DTA analysis and XRD measurements showed that LiMn_2O_4 phase was formed above 300 °C using the present method via all four dicarboxylates. That indicates the loss of the lithium component during heat treatment is thought to be slight and, therefore, the stoichiometry can be controlled at the stage of the precursor preparation. In addition, the formation of crystalline intermediate phase during decomposition via dicarboxylates was not observed. Because of the high possibility of obtaining powders with homogeneity in particle size, composition and structure, this method is promising.

2.2.1 Experimental

a) Preparation

The procedure for the preparation of LiMn_2O_4 spinel powder from lithium and manganese acetates through lithium-manganese-dicarboxylates is shown schematically in Fig. 2.3. Oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$), malonic acid ($\text{C}_3\text{H}_4\text{O}_4$) and succinic acid ($\text{C}_4\text{H}_6\text{O}_4$) differ only in the number of carbon atoms, but tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$) has two hydroxyl groups with the same carbon number as succinic acid. Lithium acetate dihydrate and manganese acetate

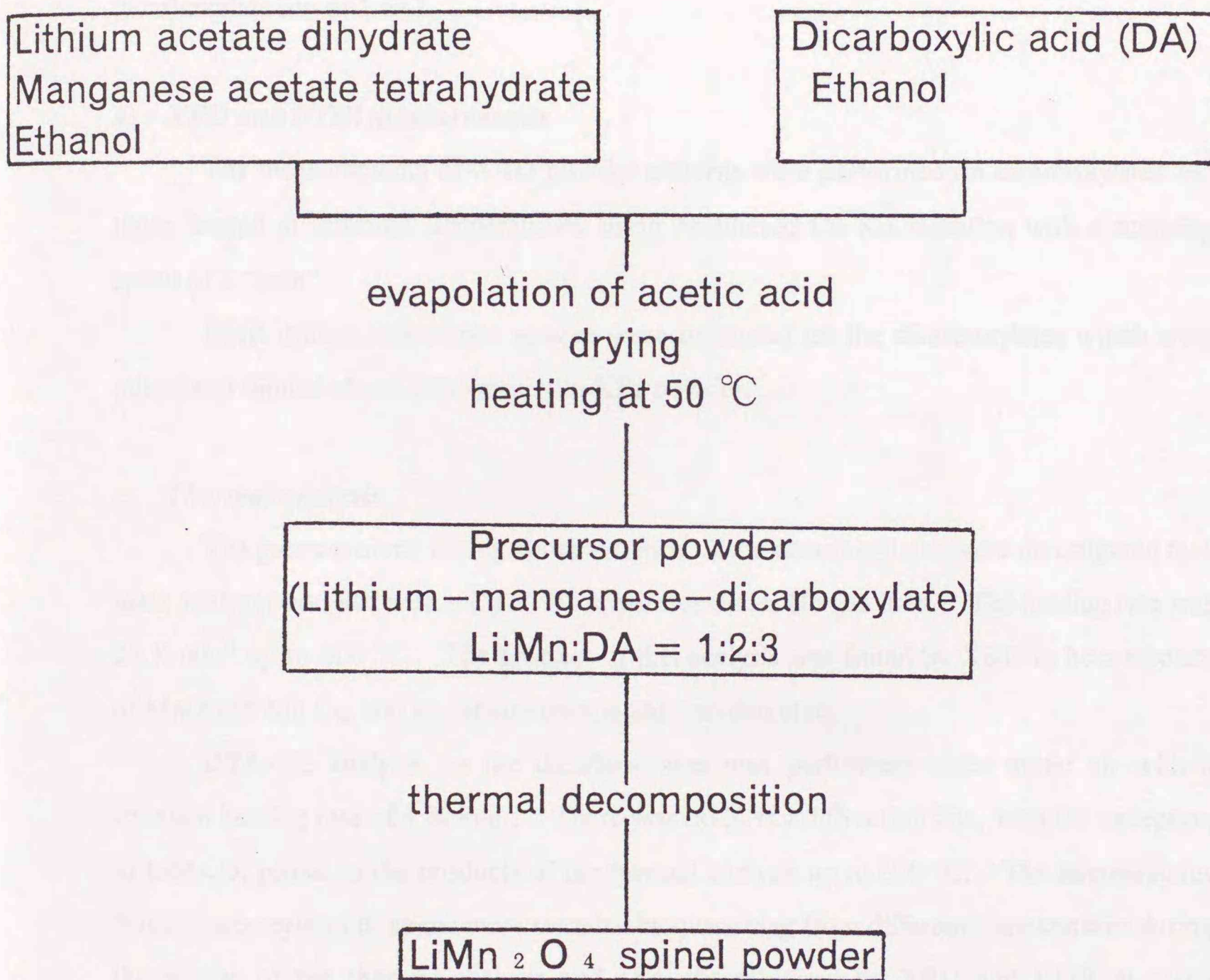


Fig. 2.3 Procedure for preparation of LiMn_2O_4 powders through lithium-manganese-dicarboxylates.

tetrahydrate (reagent grades) were dissolved in ethanol, the molar ratio of Li^+ to Mn^{2+} being 1 to 2. As soon as the solution was mixed with a dicarboxylic acid, the solution changed into a viscous sol. The molar concentration of dicarboxylic acid was the same as the total concentration of metal ions, i.e., lithium plus manganese ions. By heating the sol at above 50 °C, acetic acid and ethanol were evaporated, and a dry powder of lithium-manganese-dicarboxylates was obtained. For comparison, lithium and manganese dicarboxylates were prepared separately by the same procedure, using a molar ratio between metal ion and dicarboxylate ion of 1 to 1.

b) XRD and FTIR measurements

The measurements of XRD powder patterns were performed on dicarboxylates and those heated at different temperatures, using Ni-filtered $\text{Cu K}\alpha$ radiation with a scanning speed of $2^\circ \cdot \text{min}^{-1}$.

FTIR diffuse reflectance spectra were measured on the dicarboxylates which were mixed and diluted about 100 times with KBr powder.

c) Thermal analysis

The gases evolved during decomposition of the dicarboxylates were investigated by a mass analyzer coupled with a DTA-TG apparatus under He gas flow. The heating rate was $25 \text{ K} \cdot \text{min}^{-1}$ up to 600 °C. The product of this analysis was found by XRD to be a mixture of MnO and Mn_2O_3 , and no lithium compound was detected.

DTA-TG analysis on the dicarboxylates was performed under static air with a constant heating rate of $1 \text{ K} \cdot \text{min}^{-1}$. There was no X-ray diffraction line, with the exception of LiMn_2O_4 phase, in the products of the thermal analysis up to 600 °C. The intermediates from dicarboxylates to spinel were sampled by quenching from different temperatures during the course of the thermal analysis and also characterized by XRD and FTIR at room temperature.

2.2.2 Results

a) Tartrate system

Structure

The XRD pattern of lithium-manganese-tartrate (LMT), or the precursor, is shown in Fig. 2.4, where lithium tartrate (LT) and manganese tartrate (MT) are also presented.

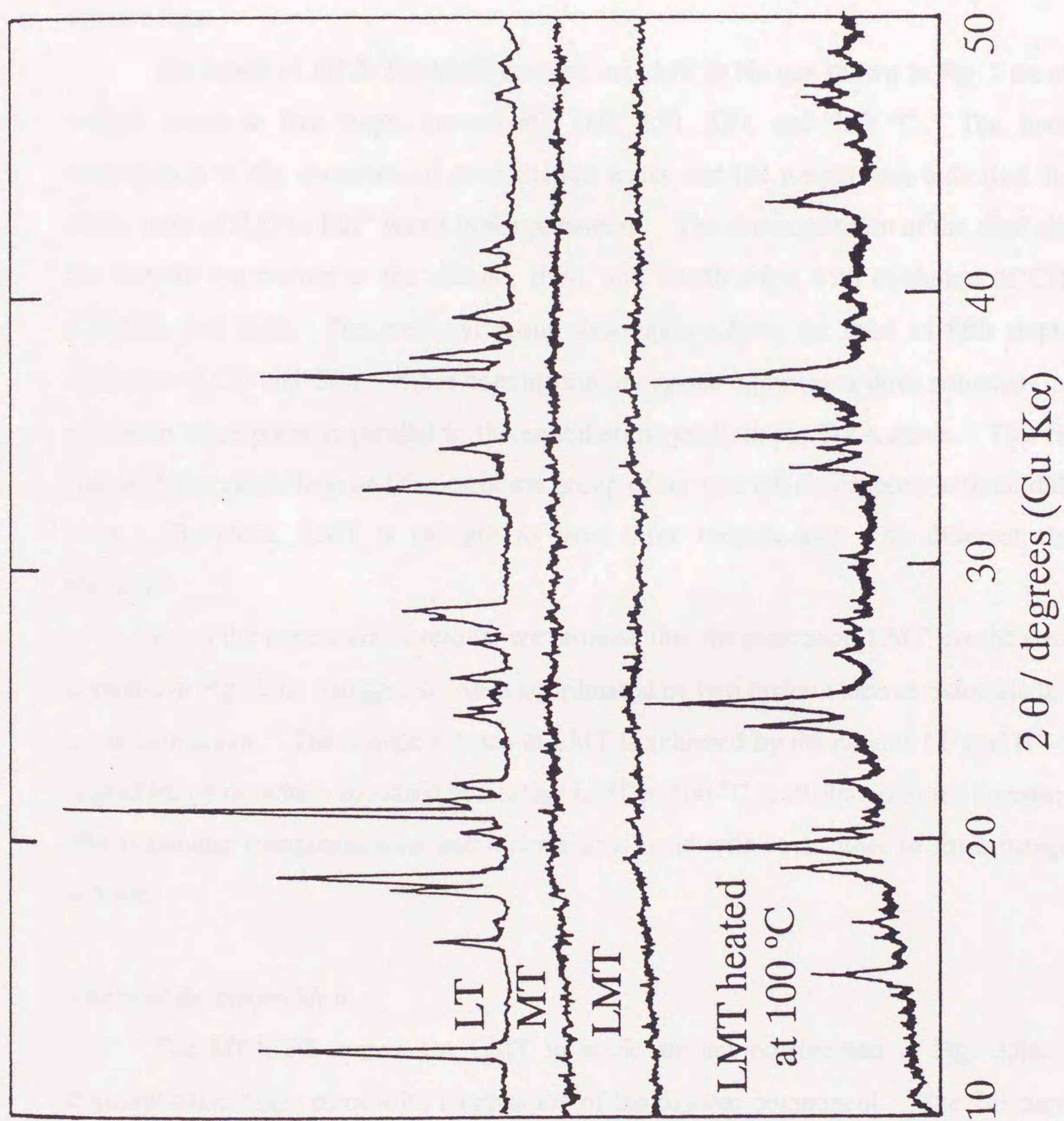


Fig. 2.4 XRD patterns of tartrates: lithium tartrate (LT); manganese tartrate (MT); lithium-manganese-tartrate (LMT); LMT heated at 100 °C for 24 h in static air with a constant heating rate of 1 K·min⁻¹.

LT has a crystalline structure whose diffraction pattern resembles with that of tartaric acid itself [21], but MT and LMT are in an amorphous state. After heating at 100 °C for 24 h in static air with a constant heating ratio of 1 K·min⁻¹, the sample LMT crystallized but its diffraction pattern could not be assigned to LT or MT.

The FTIR spectra of tartrates are shown in Fig. 2.5a. In the spectrum of LMT, there are no absorption peaks which are attributed to LT. It is rather similar to that of MT. This implies that, in the structure of LMT, lithium ions are not bound by carboxylic group of tartrate ions.

The result of DTA-TG-MAS analysis on LMT in He gas shown in Fig. 2.6a reveals weight losses in five steps, around 80, 160, 250, 320, and 380 °C. The first step corresponds to the evolution of coordination water and the weight loss indicated that the molar ratio of H₂O to Mn²⁺ was 1 in the precursor. The decomposition of the alkyl chain of the tartrate ion occurs at the second, third, and fourth steps with evolution of CH₂OH, C₂H₅OH, and H₂O. The carboxyl group decomposes from the third to fifth steps with evolution of CO and CO₂. Since combustion of organic component does not occur, all gas evolution takes place in parallel to the endothermic peak on the DTA curve. This reveals that both the alkyl chain and the carboxyl group of tartrate ion decompose in three different steps. Therefore, LMT is thought to have three tartrate ions with different thermal stability.

From the experimental results, we propose that the precursor, LMT has the structure depicted in Fig. 2.7a; manganese ion is coordinated by two tartrate ions as bidentate to form a complex anion. The charge balance in LMT is achieved by the cations Li⁺ and H⁺. The crystalline phase which appeared by heating LMT at 100 °C is attributed to the complex salt. The remaining manganese ions and tartrate ions bond with each other to form manganese tartrate.

Thermal decomposition

The DTA-TG curves for LMT in static air are represented in Fig. 2.8a. The decomposition takes place with combustion of the organic component. The TG curve for LMT shows that the weight loss occurs in three steps around 180, 250, and 290 °C, all of them being accompanied by exothermic peaks on the DTA curve. The XRD pattern of the sample recovered at point A did not show diffraction lines and its FTIR spectrum was identical with that of the starting materials, LMT. The sample recovered from point B did

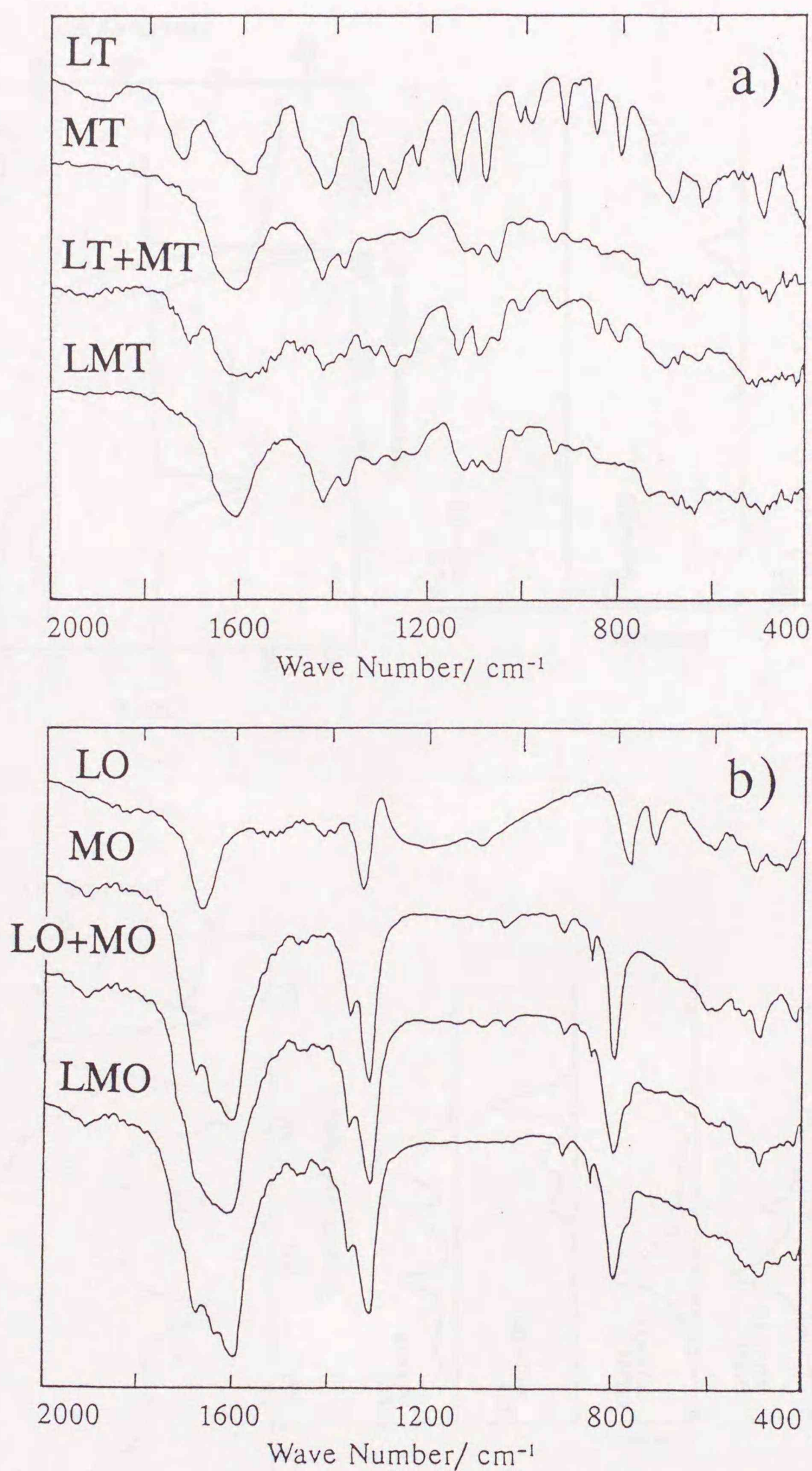


Fig. 2.5 FTIR spectra of tartrates (a) and oxalates (b):
 (a); lithium tartrate (LT); manganese tartrate (MT); mixtures of LT and MT, the molar ratio of these salts being 1 to 2; lithium-manganese-tartrate (LMT);
 (b); lithium oxalate (LO); manganese oxalate (MO); mixtures of LO and MO, the molar ratios of these salts being 1 to 2; lithium-manganese-oxalate (LMO).

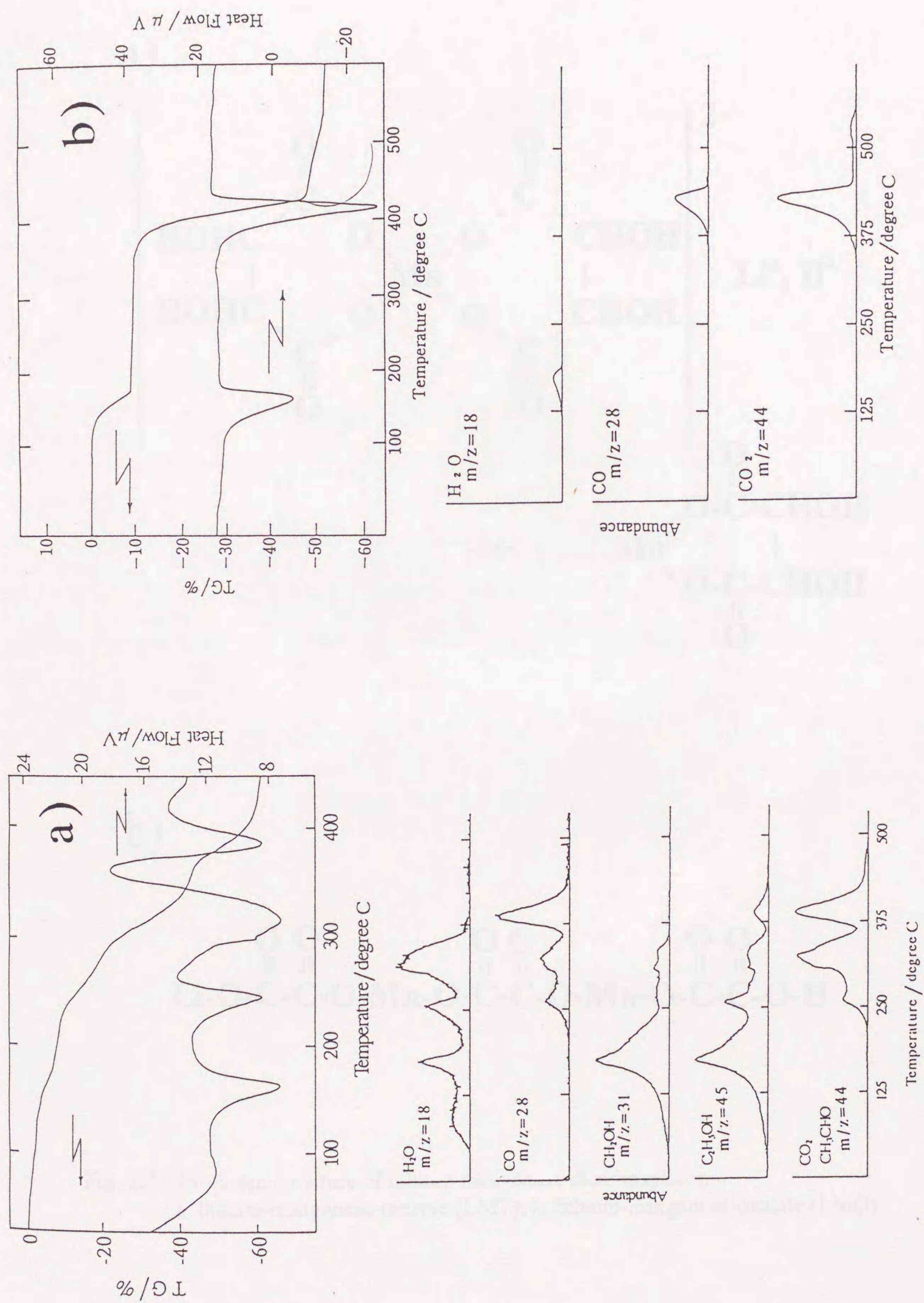


Fig. 2.6 DTA-TG curves and gaseous product in He gas: a, lithium-manganese-tartrate (LMT); b, lithium-manganese-oxalate (LMO).

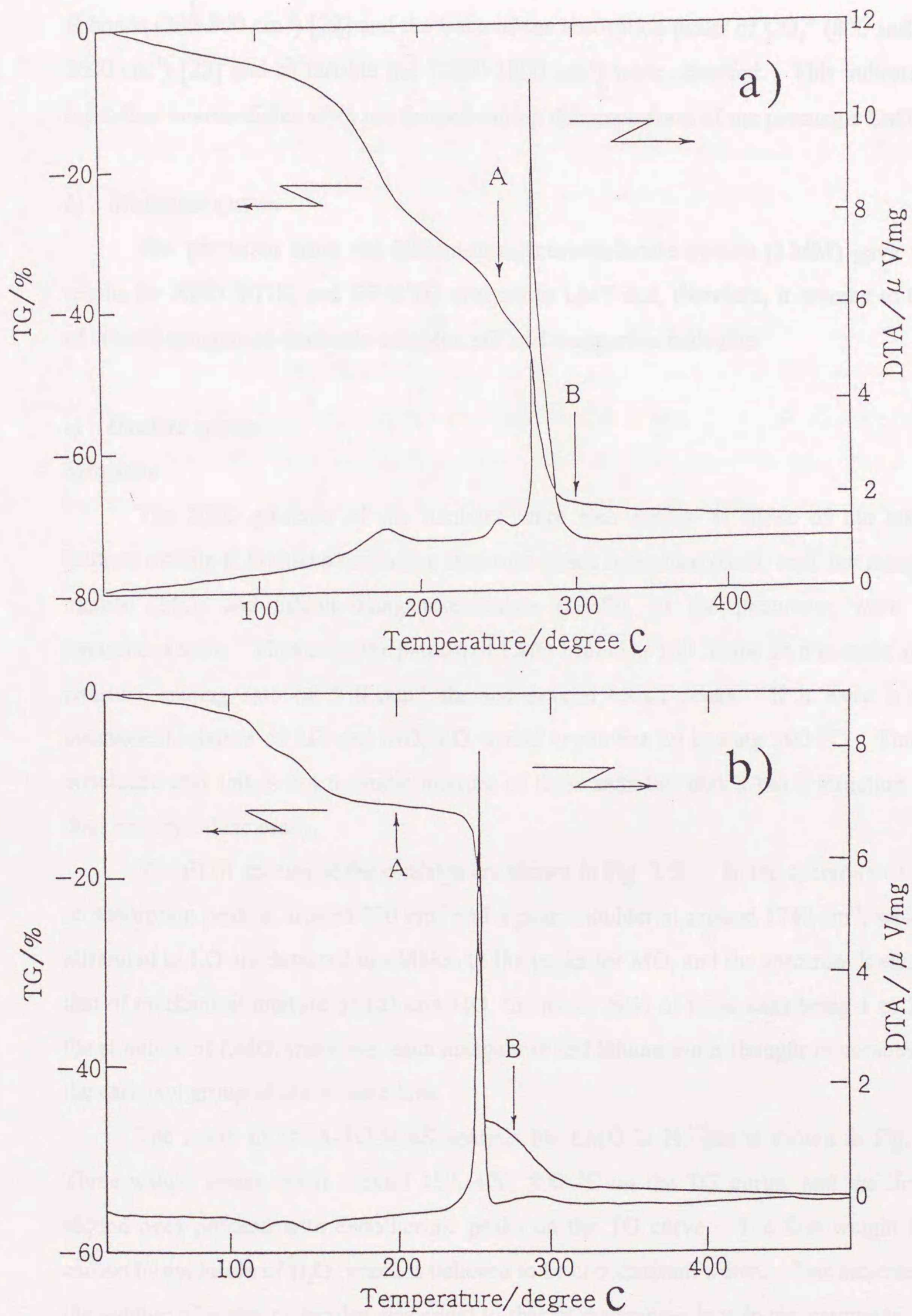


Fig. 2.8 DTA-TG curves in static air;
a, lithium-manganese-tartrate (LMT); b, lithium-manganese-oxalate (LMO).

not reveal XRD lines either and, in its FTIR spectrum, the absorption peak of Mn-O and Li-O bonds ($300\text{-}800\text{ cm}^{-1}$) [22] and the trace of the absorption peaks of CO_3^{2-} (800 and $1400\text{-}1600\text{ cm}^{-1}$) [23] and of tartrate ion ($1300\text{-}1800\text{ cm}^{-1}$) were observed. This indicates that crystalline intermediates were not formed during decomposition of the precursor LMT.

b) Malonate system

The precursor from the lithium-manganese-malonate system (LMM) gave similar results for XRD, FTIR, and DTA-TG analysis as LMT and, therefore, it seemed to consist of lithium-manganese-malonate complex salt and manganese malonate.

c) Oxalate system

Structure

The XRD patterns of the oxalates were also similar to those of the tartrates. Lithium oxalate (LO) had a crystalline structure which resembled oxalic acid, but manganese oxalate (MO) and lithium-manganese-oxalate (LMO), or the precursor, were in an amorphous state. However, the pattern of LMO heated at $100\text{ }^{\circ}\text{C}$ for 24 h in static air with constant heating rate of $1\text{ K}\cdot\text{min}^{-1}$ showed several broad peaks. If it were a simple mechanical mixture of LO and MO, LO would crystallize by heating $100\text{ }^{\circ}\text{C}$. Thus it is concluded that this is not a simple mixture of these salts but that it has a structure which does not crystallize easily.

The FTIR spectra of the oxalates are shown in Fig. 2.5b. In the spectrum of LMO, an absorption peak at around 770 cm^{-1} and a peak shoulder at around 1740 cm^{-1} , which are attributed to LO are detected in addition to the peaks for MO, and the spectrum is similar to that of mechanical mixture of LO and MO, the molar ratio of these salts being 1 to 2. In the structure of LMO, therefore, each manganese and lithium ion is thought to combine with the carboxyl group of the oxalate ions.

The result of DTA-TG-MAS analysis for LMO in He gas is shown in Fig. 2.6b. Three weight losses occur around 150 , 400 , $500\text{ }^{\circ}\text{C}$ on the TG curve, and the first and second ones proceed with endothermic peaks on the TG curve. The first weight loss is caused by evolution of H_2O , which is believed to be coordination water. This indicated that the number of water molecules was equal to that of manganese ions in the precursor. The large second weight loss and small third one correspond to CO and CO_2 gas evolution due to the decomposition of oxalate ions. The results indicates that oxalate ions in LMO

decomposed in one step, with no intermediate formed during its decomposition. Because the decomposition temperatures of LO and MO should be different, LMO was not a mixture of LO and MO. This suggests that every oxalate ions is attached to manganese ions in LMO.

From these results, a structure of LMO is proposed, as shown in Fig. 2.7b; lithium and manganese ions are linked by oxalate ions to form a chain-like structure.

Thermal decomposition

The DTA-TG curves for LMO in static air are shown in Fig. 2.8b. The TG curve for LMO shows weight losses in four steps, around 110, 140, 260, and 290 °C. Corresponding to these weight losses, two endothermic peaks are observed at the first and second steps, and sharp and broad exothermic peaks at the third and fourth steps, respectively. The XRD pattern of the sample at point A in the figure showed several broad peaks which were a little sharper than the peaks of the starting material, LMO. Its FTIR spectrum was identical with that of the starting material, LMO. The XRD pattern of the sample at point B showed no peaks. In the FTIR spectrum, Mn-O and Li-O bonds, CO_3^{2-} and oxalic acid ion (1300 and 1700 cm^{-1}) [24] were detected. A crystalline intermediate was not detected during the decomposition process.

d) Succinate system

Since lithium-manganese-succinate (LMS) revealed similar results as LMO, the structure of LMS is also proposed to be a chain-like structure.

2.2.3 Discussion

a) Structure of lithium-manganese-dicarboxylates

The experimental results indicate that the four lithium-manganese-dicarboxylate systems are classified into two groups from their structures: tartrate and malonate forming a mixture of the complex salt, in which two dicarboxylate ions are bound to manganese ion in bidentate state, and manganese salt; and oxalate and succinate having a chain-like structure.

The size of the ring which will be made if the dicarboxylate ion coordinates to manganese ion as bidentate may be related to the structure that the dicarboxylate has. The increasing order of size is: oxalic acid < malonic acid, tartaric acid < succinic acid.

Oxalate ions seemed to have difficulties making a ring with the metal ion because of the strain energy to form a small ring, while the ring of succinate ion was so large that it could not make a ring either because of the strain energy. Malonate and tartrate ions may be a suitable size to coordinate to manganese ion as bidentate, being free from strain energy. The geometrical issue might govern which structure type is taken by dicarboxylates.

b) Suitable precursor for LiMn_2O_4

As mentioned above, the lithium extraction/insertion reaction from LiMn_2O_4 in nonaqueous secondary lithium cells is influenced by its stoichiometry and particle size. Since LiMn_2O_4 powders were prepared above 300 °C using the present method via dicarboxylates, the loss of the lithium component during heat treatment is thought to be slight and, therefore, the stoichiometry can be controlled at the stage of the precursor preparation. The particle size of LiMn_2O_4 powders prepared were below 0.1 μm under SEM observation, larger particle size being easily obtained by high temperature annealing.

Avoiding the formation of crystalline intermediate phase during decomposition is an additional advantage for the present process via dicarboxylates, because of the high possibility of obtaining powders with homogeneity in particle size, composition and structure.

In particular of the four dicarboxylates investigated, the malonate may be the most suitable precursor for LiMn_2O_4 because it has the lowest decomposition temperature in air at the heating rate of 1 $\text{K}\cdot\text{min}^{-1}$, namely 260 °C.

Two precursors, oxalates and tartrates, with different structure were chosen in the present work in order to prepare LiMn_2O_4 powders for the following experiments to investigate the effect of precursor.

2.3 Lithium extraction/insertion on LiMn_2O_4

2.3.1 Sample preparation

Procedure for the preparation of samples is schematically shown in Fig. 2.3 [19,20]. Four series of LiMn_2O_4 samples were prepared via lithium-manganese-dicarboxylates. Series OX and 2OX were prepared by thermal decomposition of lithium-manganese-oxalates, and series TA and 2TA were prepared through lithium-manganese-tartrates. Stoichiometry of Li/Mn was controlled at the stage of preparation of the dicarboxylates, which are the precursor for LiMn_2O_4 powders, and the exact composition ratios of Li/Mn in

LiMn₂O₄ samples were determined by means of ICP-AES analysis. The precursors for LiMn₂O₄ were made as follows; lithium acetate dihydrates and manganese acetate tetrahydrates were dissolved in ethanol, the molar ratio of metal ion Li⁺/Mn²⁺ being about 1/2, and then the solution was mixed with ethanol solution of dicarboxylic acid. The mixed solution abruptly changed into viscous sol. Amount of dicarboxylic acid added was equal to the sum of metal ion, Li⁺+Mn²⁺. Precursor powders, lithium-manganese-dicarboxylates, were obtained by drying the sol. Each precursor was heated at different temperatures of 300, 600, and 800 °C for 24 hours with heating and cooling rates of 1 K·min⁻¹. These samples are referred to the codes, such as OX3, OX6, and OX8 using dicarboxylic acid and heating temperature, as shown in the first column of Table 2.1.

2.3.2 Characterization

XRD measurements were performed on the samples using Ni-filtered Cu K α radiation. The conditions for measuring overall XRD profiles, lattice parameter, half width of diffraction peaks are listed in Table 2.2.

Lattice parameter was calibrated by referring to an internal standard, crystalline silicon powder. From the observed value of half width of diffraction lines, 111, 311, 400, and 440 lines, lattice strain ϵ was calculated as follows. Broadening of diffraction line is assumed to be caused by crystallite size and lattice strain, and that observed half width of diffraction line observed, β_o , is expressed as a simple sum,

$$\beta_o = \beta_c + \beta_s, \quad (2.3)$$

where β_c and β_s are the broadening of diffraction line due to crystallite size and lattice strain, respectively. β_c is related to crystallite size, L , through so-called Scherrer's equation,

$$L = K \cdot \lambda \cdot (\beta_c \cdot \cos\theta)^{-1} \quad (2.4)$$

and β_s is defined as

$$\begin{aligned} \beta_s &= 2(\Delta d \cdot d^{-1}) \cdot \tan\theta \\ &= 2\tan\theta, \end{aligned} \quad (2.5)$$

by differentiating the Bragg equation, where K , λ , θ , and d are form factor, wave length of X-ray used, diffraction angle, and spacing for the line, respectively. From these equations,

$$\beta_o \cdot \cos\theta \cdot \lambda^{-1} = K \cdot L^{-1} + 2\epsilon \cdot \sin\theta \cdot \lambda^{-1} \quad (2.6)$$

Table 2.1 Composition ratio, XRD data, and electrochemical data of the samples.

Sample Code	Composition Ratio (2Li/Mn)	Lattice Parameter (nm)	Lattice Strain ($\times 10^{-2}$)	Capacity ($\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$)	Rest Potential (Volts vs. Li^+/Li)
OX3	0.94	0.816	3.76	8	3.432
OX6	0.94	0.823	0.0571	80	3.339
OX8	0.98	0.824	0.0356	114	3.247
2OX3	1.10	0.815	2.10	37	3.459
2OX6	1.09	0.821	1.09	82	3.529
2OX8	1.10	0.823	0.260	110	3.309
TA3	1.07	0.817	3.54	57	-
TA6	1.07	0.821	1.56	92	-
TA8	1.09	0.823	0.383	112	-
2TA3	0.92	0.819	3.31	64	3.428
2TA6	1.03	0.822	0.839	77	3.308
2TA8	0.97	0.825	0.0884	121	3.288

Table 2.2 Conditions for XRD measurements.

XRD measurements	Voltage (kV)	Current (mA)	Scan Speed (°/min)	Step (°)
Powder pattern	30	15	2	0.02
Lattice Parameter	40	20	0.25	0.01
Half Width	40	20	0.1	0.01

is derived. By plotting $\beta_0 \cdot \cos\theta \cdot \lambda^{-1}$ vs. $2\epsilon \cdot \sin\theta \cdot \lambda^{-1}$, applying by least-squares method and assuming $K = 1$, the lattice strain, ϵ , and crystallite size, L , are determined. This equation (2.6) has been called by Hall's equation.

Rietveld analysis was performed on the X-ray profile of samples OX3 and OX8. The profiles were measured by means of step scanning method using monochromated Cu $K\alpha$ radiation. Count time at each step was 5 and 0.5 seconds and interval of step was 0.05° and 0.015° in 2ϵ for samples OX3 and OX8, respectively. The EXAFS profile was also recorded for samples OX3 and OX8 using Mo $K\alpha$ radiation. The absorption edge of Mn $K\alpha$ was measured by one crystal transmission mode with spectroscopic crystal of Ge(220).

For 2OX and 2TA series samples, XPS spectra were recorded using Mg $K\alpha$ radiation. Sample powders were compacted to 5 mm diameter $\times$ 1 mm thick disc by handy press apparatus. Binding energy of electron was calibrated by referring to binding energy of C_{1s} electron

2.3.3 Electrochemical measurements

Composite cathode for electrochemical measurements was fabricated as follows; the LiMn_2O_4 sample powders were mixed with 10 wt.% carbon black and 10 wt.% PTFE molding powders. The mixture of 1 ± 0.03 mg was pressed on a stainless steel mesh and used as the cathode. The anode was lithium metal pressed on a nickel mesh. The electrolyte used was 1 M LiClO_4 dissolved in a 50/50 volume percent mixture of ethylenecarbonate (EC) / diethylcarbonate (DEC). Figs. 2.9a and b show construction of a conventional two electrode cell and a circuit used, respectively. Potential change with time during charge-discharge at a constant current of $10 \text{ mA} \cdot \text{g}^{-1}$ was recorded. Prior to electrochemical charge-discharge measurements, potential of the cathode was measured as a rest potential, after the composite cathode was immersed in the electrolyte for 12 hours. All electrochemical tests were carried out in the grove box filled with argon gas.

2.4 Results

2.4.1 Characterization

The composition ratios of 2Li/Mn are summarized in Table 2.1. Particular effect of heating temperature on the composition ratios is not observed. Series OX and 2TA

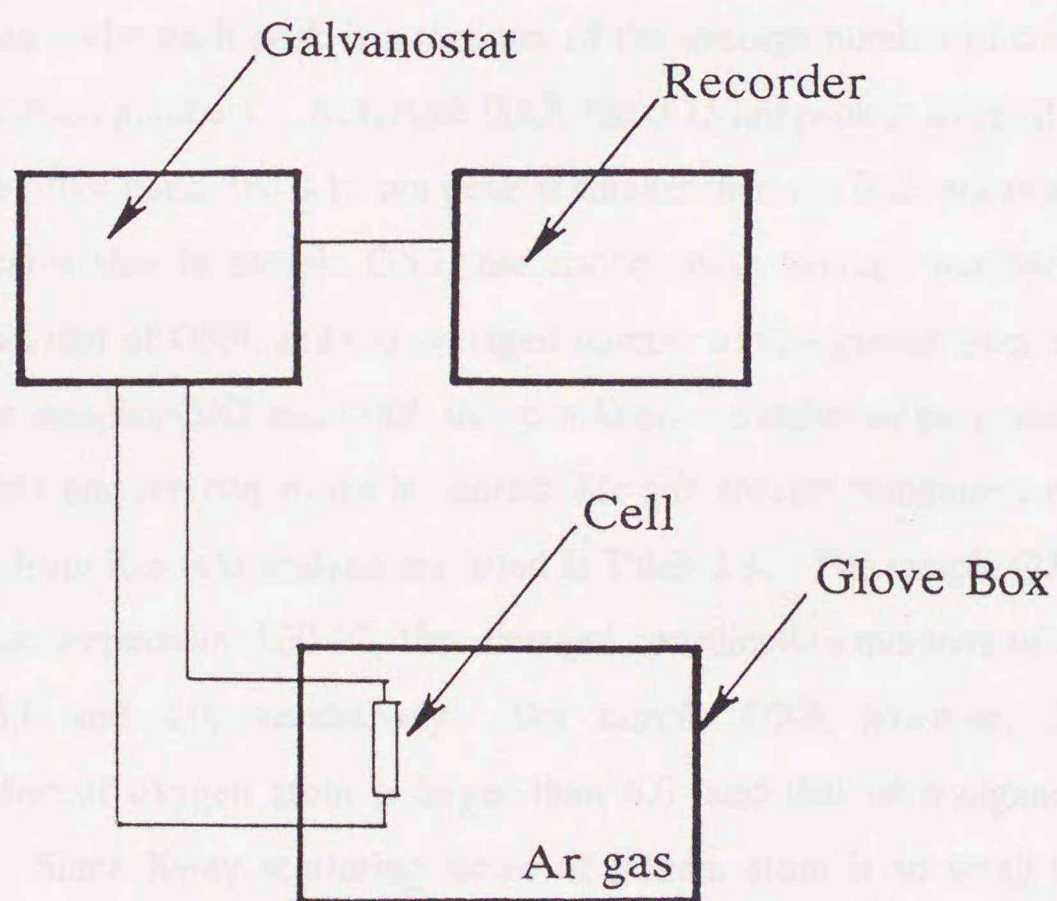
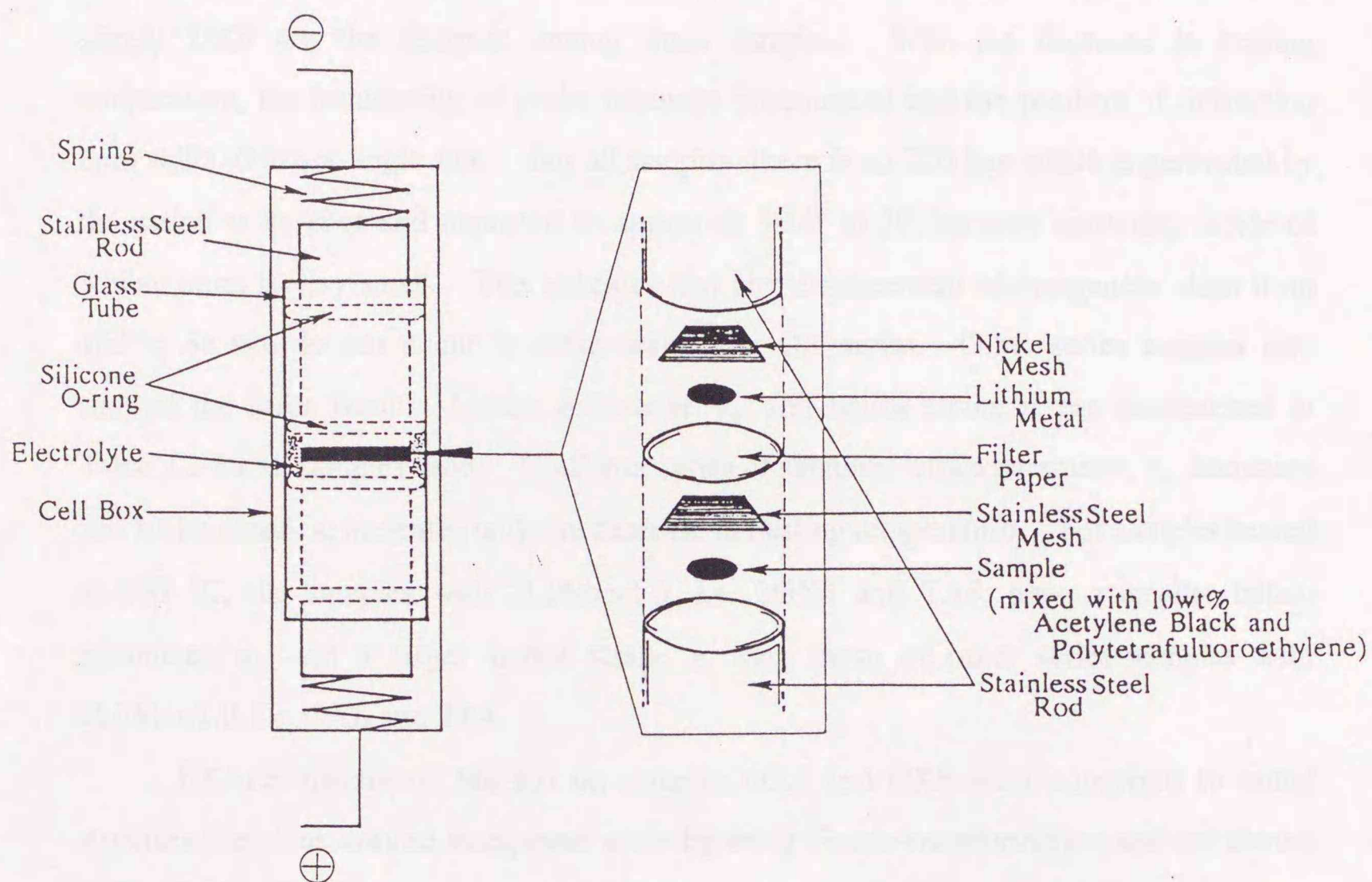


Fig. 2.9 Construction of the cell and the circuit used.

samples are lithium-deficient spinel ($2\text{Li}/\text{Mn} < 1$) and series 2OX and TA samples are lithium-excess spinel ($2\text{Li}/\text{Mn} > 1$).

The XRD patterns of OX series samples are shown in Fig. 2.10. The peaks of sample OX8 are the sharpest among three samples. With the decrease in heating temperature, the broadening of peaks becomes pronounced and the position of diffraction lines shifts to lower angle side. For all samples, there is no 220 line which is generated by the cation at 8a sites and expected to appear at 30.4° in 2θ , because scattering factor of lithium atom is very small. This indicates that any displacement of manganese atom from 16d to 8a site do not occur in these samples in OX series. Other series samples also showed the same result. Lattice parameter, a_0 , and lattice strain, ϵ , are summarized in Table 2.1 for all samples used. In all four series of samples, lattice parameter, a_0 , decreases and lattice strain, ϵ , increases with the decrease in heating temperature. For samples heated at 800°C , the samples with $2\text{Li}/\text{Mn} > 1.0$, i.e. 2OX8 and TA8, have a smaller lattice parameter, a_0 , and a larger lattice strain, ϵ , than those of other series samples with $2\text{Li}/\text{Mn} < 1.0$, i.e. OX8 and 2TA.

EXAFS spectra of Mn $K\alpha$ on samples OX3 and OX8 were converted to radial structure functions around manganese atom by using Fourier-transformation and are shown in Fig. 2.11. The peak at around 0.15 nm corresponds to the nearest neighboring oxygen atoms and the peak at around 0.25 nm is concerned with the nearest surrounding manganese atoms, and the area under each peak is a measure of the average number of corresponding atoms (i.e. coordination number). In sample OX3, the 0.15 nm peak is larger than the 0.25 nm peak. On the other hand, the 0.15 nm peak is smaller than the 0.25 nm peak in sample OX8. This indicates that in sample OX3, the coordination average number of oxygen atoms is larger than that of OX8, and the averaged number of manganese atom smaller than that of OX8. For samples OX3 and OX8, the coordination number of manganese atoms in neighboring 16d site and oxygen atoms in nearest 32e site around manganese atom in 16d site are calculated from Rietveld analysis are listed in Table 2.3. For sample OX8 annealed at, relatively higher temperature 800°C , the averaged coordination numbers of oxygen and manganese are 6.0 and 4.0, respectively. For sample OX3, however, the average coordination number of oxygen atom is larger than 6.0, and that of manganese atom is smaller than 4.0. Since X-ray scattering factor of lithium atom is so small that lithium atoms are hardly detected by X-ray measurements, the results on the average coordination

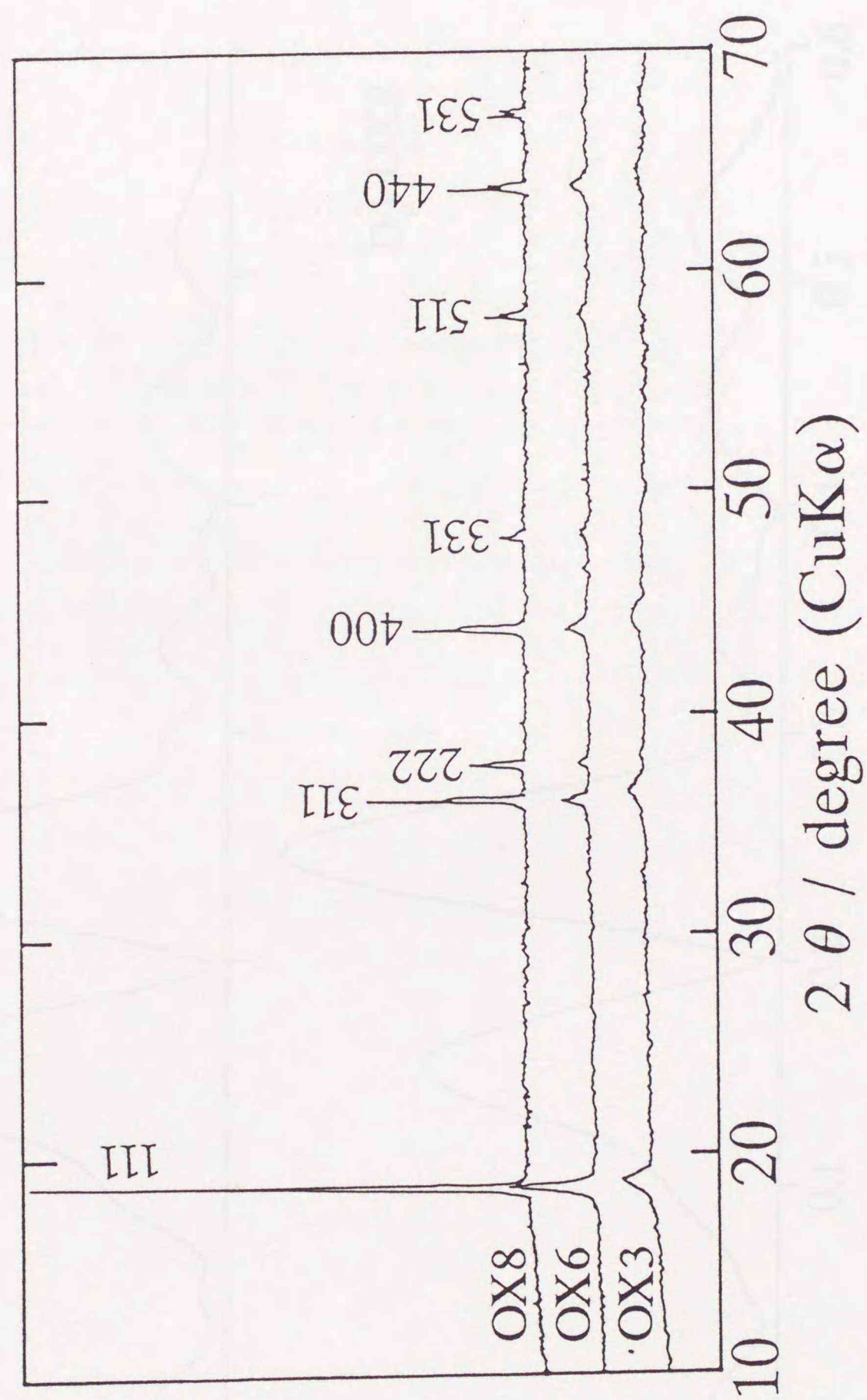


Fig. 2.10 XRD patterns of OX series samples.

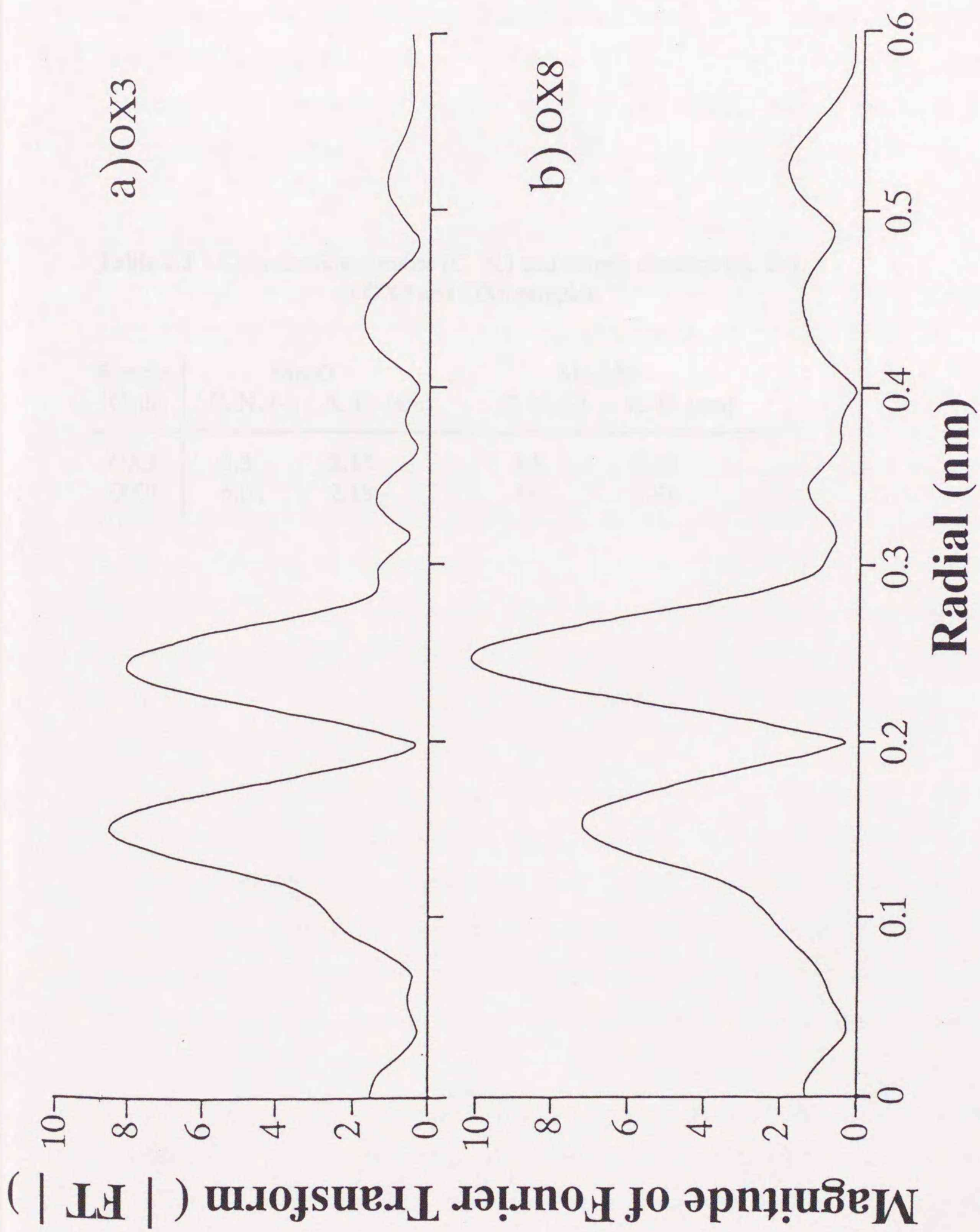


Fig. 2.11 Radial structure functions from manganese atom positions in LiMn_2O_4 .
a) OX3 and b) OX8.

Table 2.3 Coordination number (C. N.) and atomic distance (A. D.) of OX3 and OX8 samples.

Sample Code	Mn-O		Mn-Mn	
	C. N. (-)	A. D. (nm)	C. N. (-)	A. D. (nm)
OX3	6.3	2.15	3.8	2.88
OX8	6.0	2.18	4.0	2.91

number determined by EXAFS and Reitveld analysis indicate that vacancies of manganese atom in 16d site or displacement of lithium atoms from 8a to 16d sites are present in spinel structure of sample OX3.

Mn $2p_{3/2}$ peaks of 2OX and 2TA series samples are shown in Figs. 2.12a and b, respectively. For both series samples, a similar change of peak feature with heating temperature is observed. In samples heated at 300 °C, a peak at 642.2 eV and two shoulders at around 643.5 and 641.0 eV are observed. With the increase in heating temperature, the intensity of shoulder at 641.0 eV becomes higher, but there is no remarkable change in the peak at 642.2 eV and the shoulder at 643.5 eV.

2.4.2 *Electrochemical measurements*

Rest potential of the samples is summarized in Table 2.1. The lower the heating temperature, the higher the rest potential, except an inversion between 2OX3 and 2OX6 samples.

First charge-discharge curves of samples are shown on each series in Figs. 2.13a-d. The discharge curve of sample OX8 shows two plateaus at around 4 and 3 V, and the capacities for these two plateaus are about 120 mA·h·g⁻¹ each (Fig. 2.13a). For sample OX6, the discharge capacities at around 4 and 3 V are about 90 and 80 mA·h·g⁻¹, respectively (Fig. 2.13a). For sample OX3, there is no plateau in the charge-discharge curve and both the first discharge capacities above 3.5 V and that below 3.5 V are only about 30 mA·h·g⁻¹. Not only first discharge capacity at 4 V but also the capacity at 3 V decreases with the decrease in heating temperature.

In Fig. 2.13b, the discharge curve of sample 2OX8 has two flat plateau at around 3 and 4 V, whose capacities are about 130 and 120 mA·h·g⁻¹, respectively. With the decrease in heating temperature, both flatness and capacity of these two plateaus decrease. For sample 2OX3, discharge capacities above and that below 3.5 V are 50 and 60 mA·h·g⁻¹, respectively. A feature of the curve for sample 2OX6 is intermediate between samples 2OX8 and 2OX3, and discharge capacities at 3 and 4V are about 80 and 100 mA·h·g⁻¹, respectively.

In the first charge-discharge curves for TA series samples (Fig. 2.13c.), discharge curve of sample TA8 has flat two plateaus at around 4 and 3 V, whose capacities are 120 and 140 mA·h·g⁻¹, respectively. For TA series samples, both flatness and 4 V-capacity

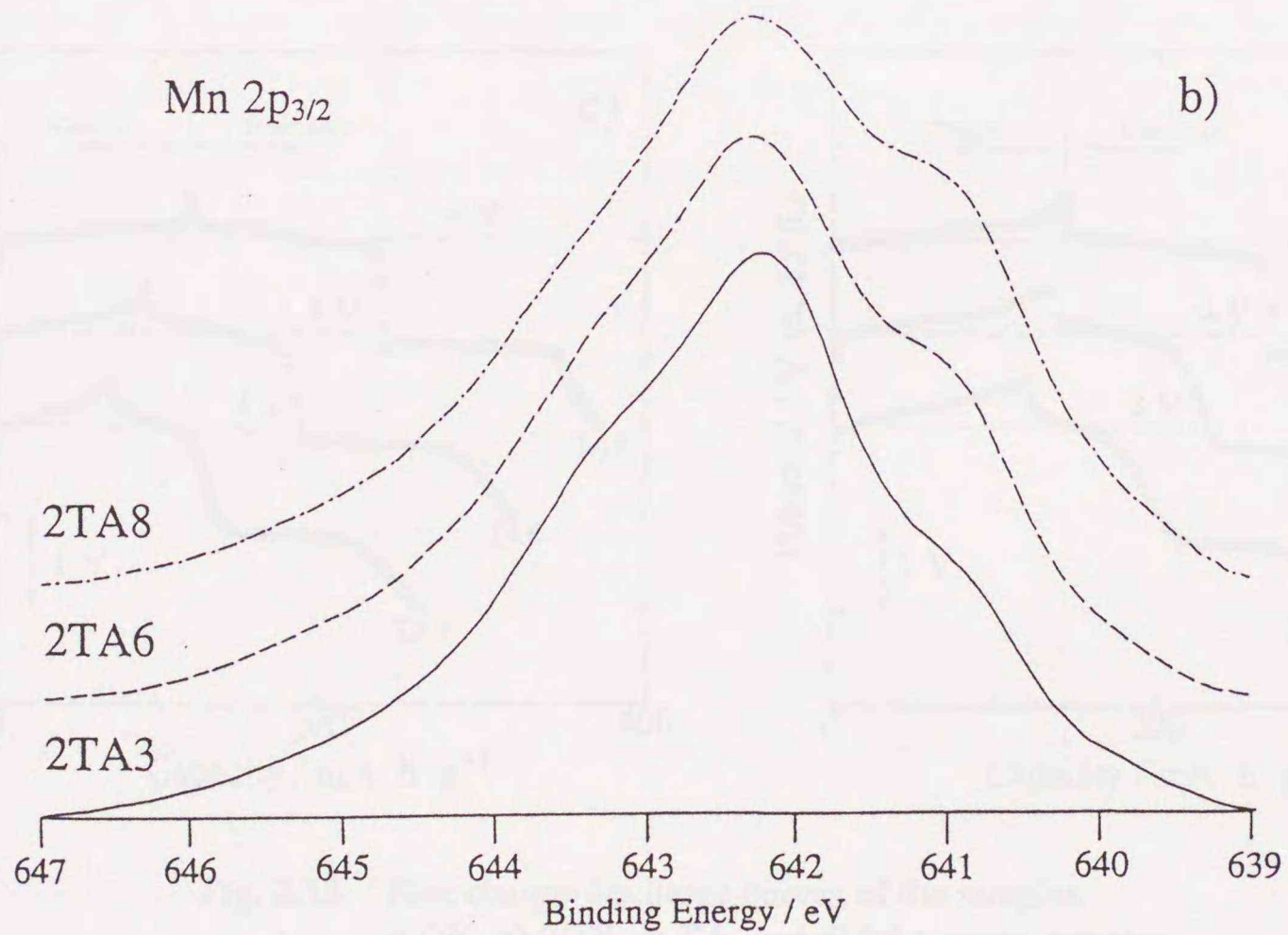
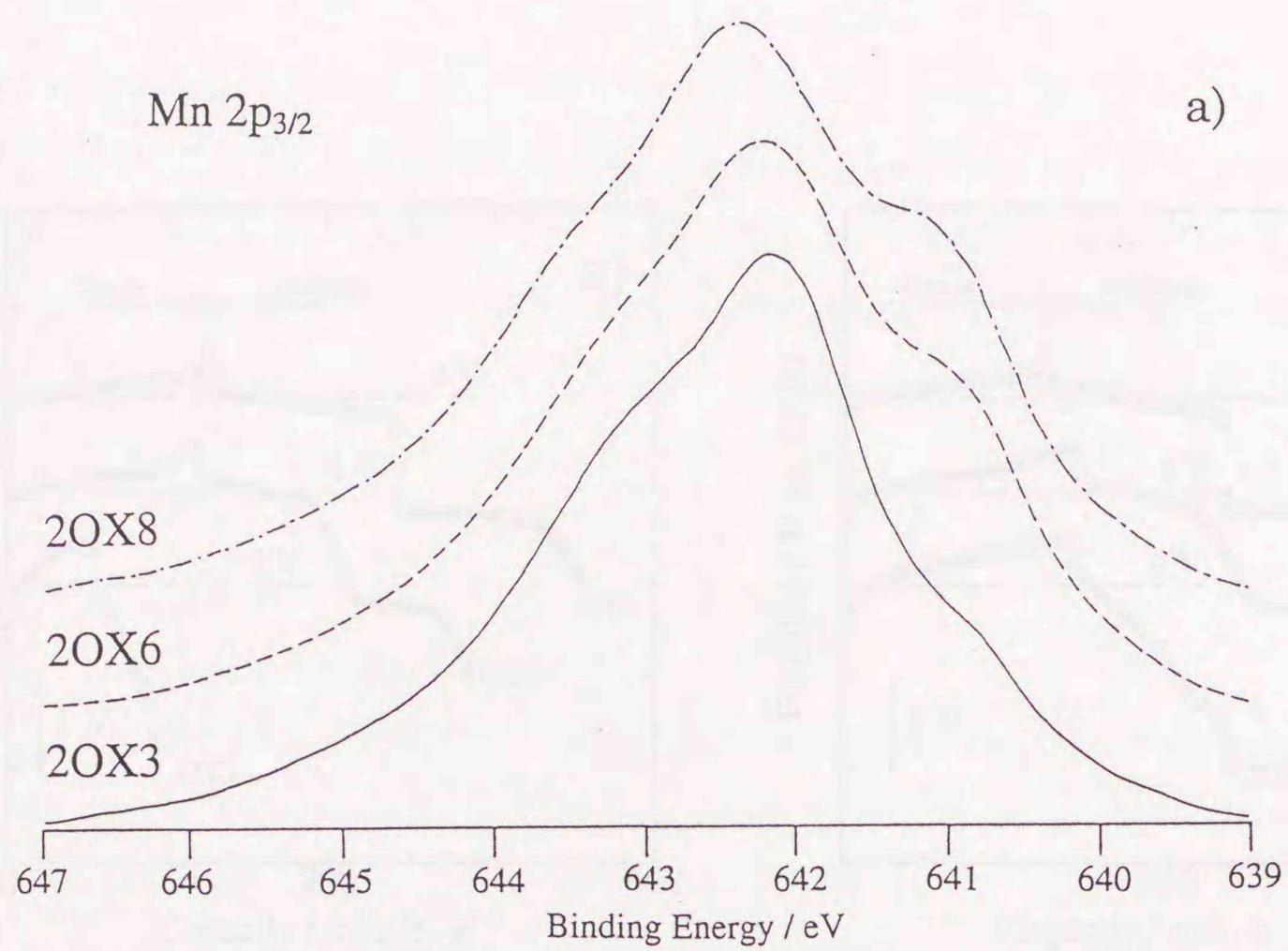


Fig. 2.12 Mn2p_{3/2} peaks in XPS spectra of 2OX and 2TA series samples.

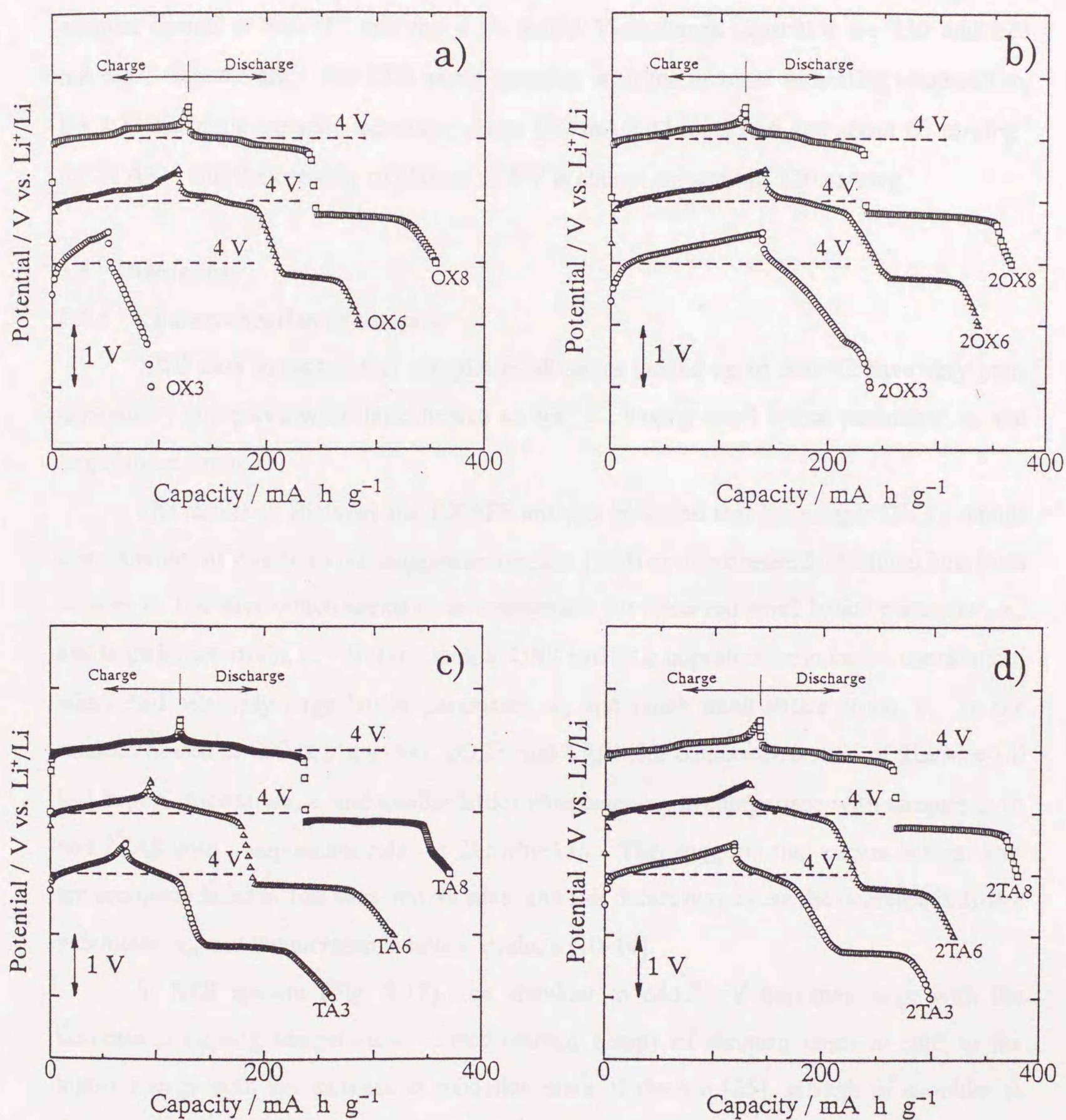


Fig. 2.13 First charge-discharge curves of the samples.
a) OX, b) 2OX, c) TA, and d) 2TA series samples.

decrease with the decrease in heating temperature and 4V-capacities of TA3 and TA6 are about 100 and 60 mA·h·g⁻¹, respectively, but the capacity of 3 V plateau is independent of heating temperature and about 140 mA·h·g⁻¹ for all the samples. In the curves of 2TA series samples (Fig. 2.13d), the curve of sample 2TA8 is similar to that of other three series samples heated at 800 °C, and the 4 V- and 3 V-discharge capacities are 130 and 120 mA·h·g⁻¹, respectively. For 2TA series samples, with the increase in heating temperature, the 4 V-discharge capacity increases; about 100 mA·h·g⁻¹ for 2TA6 and about 60 mA·h·g⁻¹ for 2TA3. But the capacity of plateau at 3 V is almost constant of 120 mA·h·g⁻¹.

2.5 Discussion

2.5.1 Characterization of samples

XRD data indicated that samples in all series heated up to 300 °C have very poor crystallinity compared with those heated to 800 °C, having small lattice parameter, a_0 , and large lattice strain, ϵ .

The results of Rietveld and EXAFS analysis indicated that the sample OX3 contains some amount of vacancies on manganese ion sites (16d) or displacement of lithium ions from 8a sites to 16d sites which seems to be responsible for observed small lattice parameter, a_0 , and large lattice strain, ϵ . But the sample OX8 had little imperfection in cation distribution; which had relatively large lattice parameter, a_0 , and much small lattice strain, ϵ . In the samples heated at 800 °C, however, 2OX8 and TA8 with composition ratio of 2Li/Mn > 1.0 had larger lattice strain, ϵ , and smaller lattice parameter, a_0 , in comparison with samples OX8 and 2TA8 with composition ratio of 2Li/Mn < 1.0. This suggests that excess lithium ions are accommodated in 16d sites, not 8a sites, and this defect may cause the decrease in lattice parameter, a_0 , and the increase in lattice strain, ϵ [10-14].

In XPS spectra (Fig. 2.12), the shoulder at 641.0 eV becomes large with the decrease in heating temperature. Since binding energy of electron tends to shift to the higher energy with the increase in oxidation state of the ion [25], growth of shoulder at 641.0 eV, which has the lowest binding energy among three peaks of Mn2p_{3/2}, is corresponding to the decrease in mean oxidation state of manganese ion at the surface. Therefore, with the increase in heating temperature, mean oxidation state of manganese ion decreases and sample heated at 300 °C has the highest mean oxidation state among three samples at the surface. Because displacement of lithium ion from 8a site to 16d one and

formation of cation vacancy lead to increase of mean oxidation state of manganese ion in order to keep electrical neutrality in the crystal, the increase of mean oxidation state of manganese ion seems to be due to defect in cation distribution in sample powders heated at lower temperature. Since ionic radius of Mn^{4+} (0.067 nm) is smaller than that of Mn^{3+} (0.072 nm), the increase of mean oxidation state of manganese ion is thought to cause small lattice parameter, a_0 , and large lattice strain, ϵ .

2.5.2 *Effect of crystallinity on electrochemical performance*

Rest potential tends to increase with the decrease of crystallinity. Rest potential is thought to be related to activity of lithium ion in host, which may be called site energy for lithium insertion/extraction. The higher the potential, the more stable lithium site is [26-31]. The decrease of crystallinity of LiMn_2O_4 host produces distortion of the structure which may make energy distribution of the sites for lithium insertion/extraction broad [30,31]. Therefore, the sample with the low crystallinity has the higher rest potential. Flatness of plateau is also related to the site energy [30,31]. If the activity of all lithium ions inserted into and extracted from the host structure, in other words, all site energies for lithium insertion/extraction are equal, charge-discharge curves have to show distinct plateau. Since the sample with low crystallinity has a larger distribution of site energy for lithium insertion/extraction compared to the sample with high crystallinity, flatness of plateau decreases with the decrease of crystallinity.

Relation between first discharge capacity above 3.5 V (4V-capacity) and lattice strain, ϵ , and lattice parameter, a_0 , are shown in Figs. 2.14a and b, respectively. First discharge capacity above 3.5 V increases linearly with the increase of lattice strain, ϵ , and the decrease of lattice parameter, a_0 . These changes in lattice strain, ϵ , and lattice parameter, a_0 , are reasonably supposed to be caused from the disturbance in cation distribution and the increase of mean oxidation state of manganese ion (the increase of the number of Mn^{4+} in LiMn_2O_4). Therefore, two explanations on the decrease of 4V-capacity can be considered. One explanation is that extraction/insertion of lithium ions around defect structure can not take place. Another one is as follows; since host LiMn_2O_4 is oxidized ($\text{Mn}^{3+} = \text{Mn}^{4+} + e^-$) with extraction of lithium, the decrease of the number of Mn^{3+} in host leads to the decrease of the 4V-capacity.

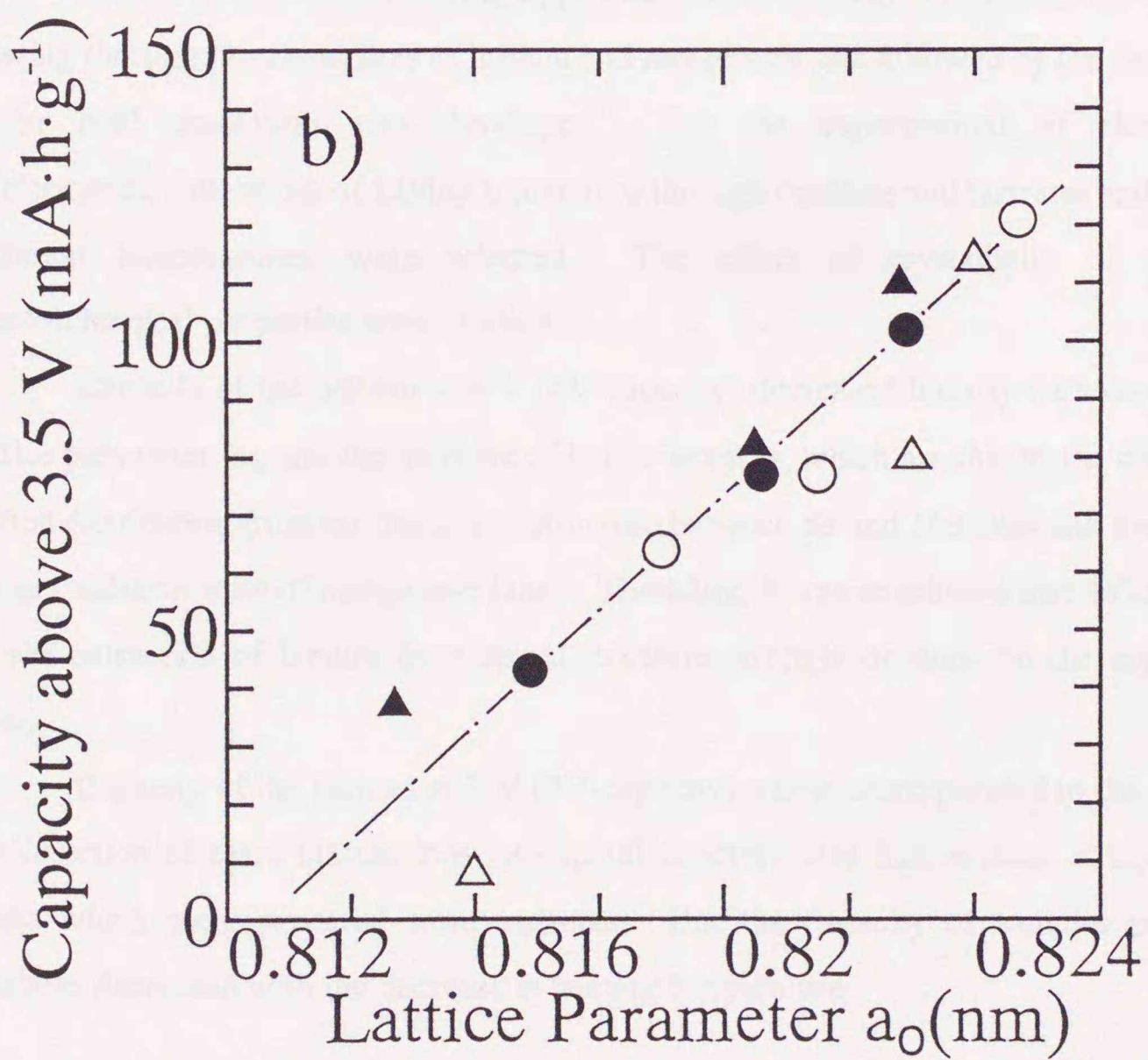
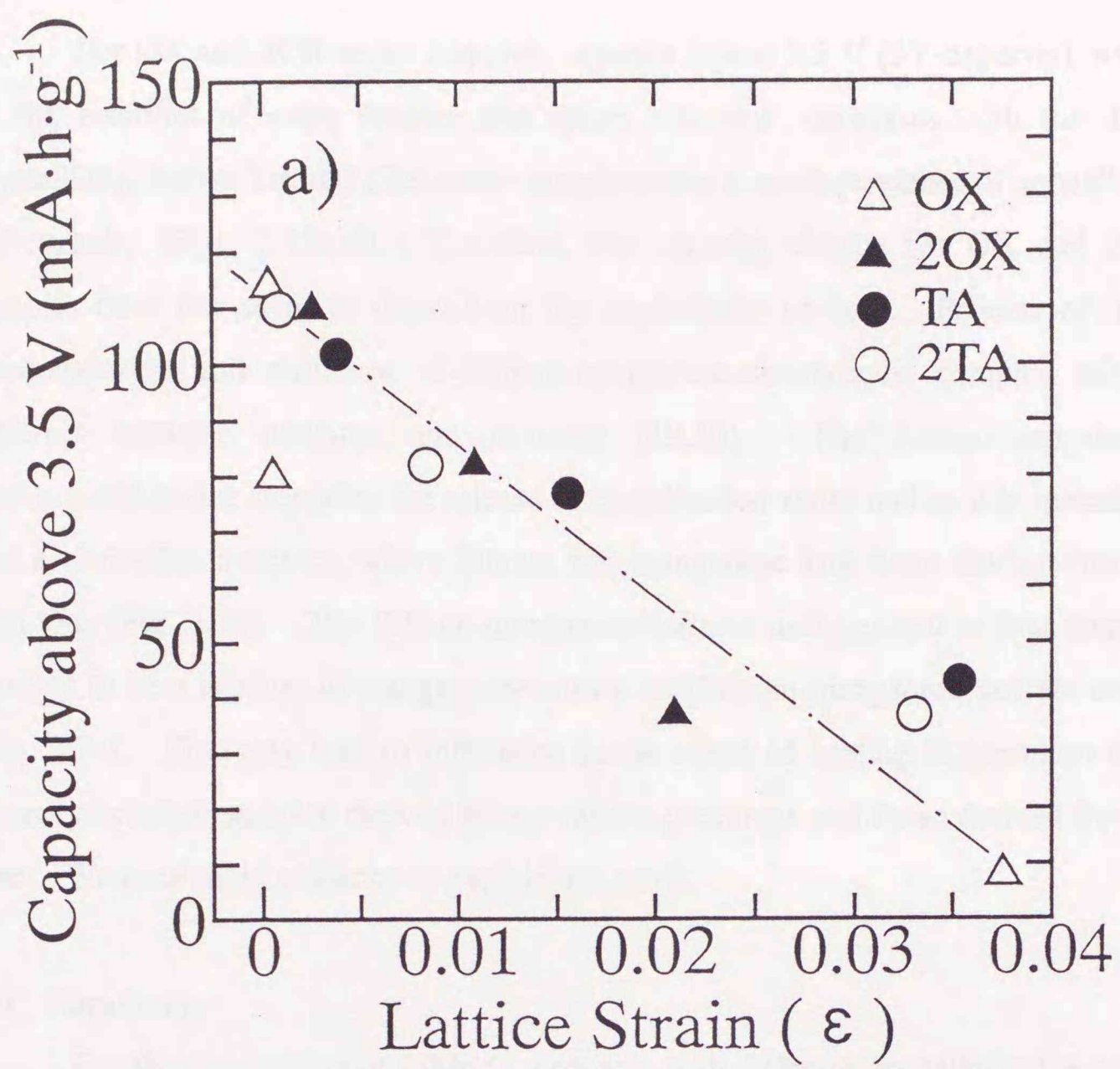


Fig. 2.14 Relation between first discharge capacity and lattice strain, ϵ , a) and lattice parameter, a_0 , b).

For OX and 2OX series samples, capacity below 3.5 V (3V-capacity), which is due to the insertion of extra lithium into spinel structure, decreases with the decrease of crystallinity, but on TA and 2TA series samples there is no dependence of crystallinity on the 3V-capacity (Figs. 2.13a-d). Therefore, the capacity change for OX and 2OX series samples does not seem to depend on the crystallinity of host. Process of the thermal decomposition and structure of lithium-manganese-dicarboxylic complex salt are very different between oxalates and tartrates [19,20]. The lithium-manganese-oxalate decomposed in one step after the release of coordination water and so it is speculated that it had a chain-like structure, where lithium and manganese ions were linking through oxalic acid ions (Fig. 2.7b). The lithium-manganese-tartrate decomposed in four steps and was thought to be a mixture of manganese-tartrate and lithium-manganese-tartrate complex salt (Fig. 2.7a). This may lead to difference in the effect of heating temperature on the 3V-capacity between samples derived from oxalates precursor and those derived from tartrates one. We need more evidence to explain the result.

2.6 Summary

For the preparation of LiMn_2O_4 powders with different crystallinity the new process passing through dicarboxylates of lithium and manganese and followed by the decomposition under mild conditions was developed. For the experimental of electrochemical performance, four series of LiMn_2O_4 prepared through oxalates and tartrates and annealed at different temperatures, were selected. The effect of crystallinity of samples on electrochemical properties were studied.

Capacity of the plateau at 4 V (4V-capacity) decreased linearly with the decrease of lattice parameter, a_0 , and the increase of lattice strain, ϵ , which are due to the disturbance of cation distribution from normal spinel structure between 8a and 16d sites and the increase of mean oxidation state of manganese ions. Therefore, it was concluded that 4V-capacity due to the extraction of lithium from spinel structure strongly depends on the crystallinity of host.

Capacity of the plateau at 3 V (3V-capacity) which corresponded to the reaction for the insertion of extra lithium ions into spinel structure was independent of crystallinity of hosts which were prepared from tartrates. But the capacity of samples prepared via oxalates decreased with the decrease in heating temperature.

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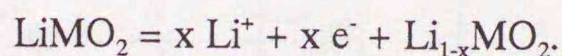
Chapter 3

Ordered rock-salt type $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$

3.1 Introduction

Ordered rock-salt type LiMO_2 ($\text{M} = \text{Co}$ and Ni) is isostructural with $\alpha\text{-NaFeO}_2$, in which transition metal and alkali metal ions are located at 3a and 3b sites, respectively, in a cubic close-packed oxygen array (Fig. 3.1.) and belongs to the space group $R\bar{3}m$. As seen from this figure, lithium ions and transition metal ions form respective layers between closed packed layers of oxygen. Therefore, lithium ions can diffuse along the two-dimensional linkage of 3b sites. As in $\alpha\text{-LiFeO}_2$, which has a random distribution of Li and Fe ions in octahedral site 3a and 3b, respectively in cubic system, LiMO_2 can have the cubic rock-salt type structure with disordered distribution of Li and M ions, in addition to ordered distribution. In the present chapter, a difference in electrochemical performance among the samples heated at different temperatures was found to be due to the relative amounts of these "ordered phase" and the "disordered phase".

Electrochemical lithium extraction/insertion reaction on LiMO_2 has been studied for cathode materials in 4 volt secondary lithium ion batteries because of its stable and high lithium insertion/extraction potential [1-3], which is expressed as,



For LiCoO_2 and LiNiO_2 , structural changes with lithium extraction and also with re-insertion of lithium have been reported by several authors [4-8]. Stability diagrams reported in different literature [6-8] and the changes of lattice parameters in monoclinic systems with x-value in $\text{Li}_{1-x}\text{NiO}_2$ are shown in Fig. 3.2, where the hexagonal cell was converted to monoclinic cell. With lithium extraction, the lattice parameters, a, b, c, and β , change discontinuously at four different x-values, associated with the change of crystal system in the order of hexagonal (H1), monoclinic (M), hexagonal (H2), and hexagonal (H3) phases, as shown in Fig. 3.2. For $\text{Li}_{1-x}\text{CoO}_2$, three different hexagonal and two different monoclinic phases are known to appear [4,5].

Ordered rock-salt type LiCoO_2 was prepared by heating the powder mixtures of lithium and cobalt carbonates at 900 °C for 20 hours followed by two further firings. By cycling of extraction/insertion of lithium ions, its structure was found to be kept [1]. Therefore, this material was used in commercial high-energy density lithium ion batteries as

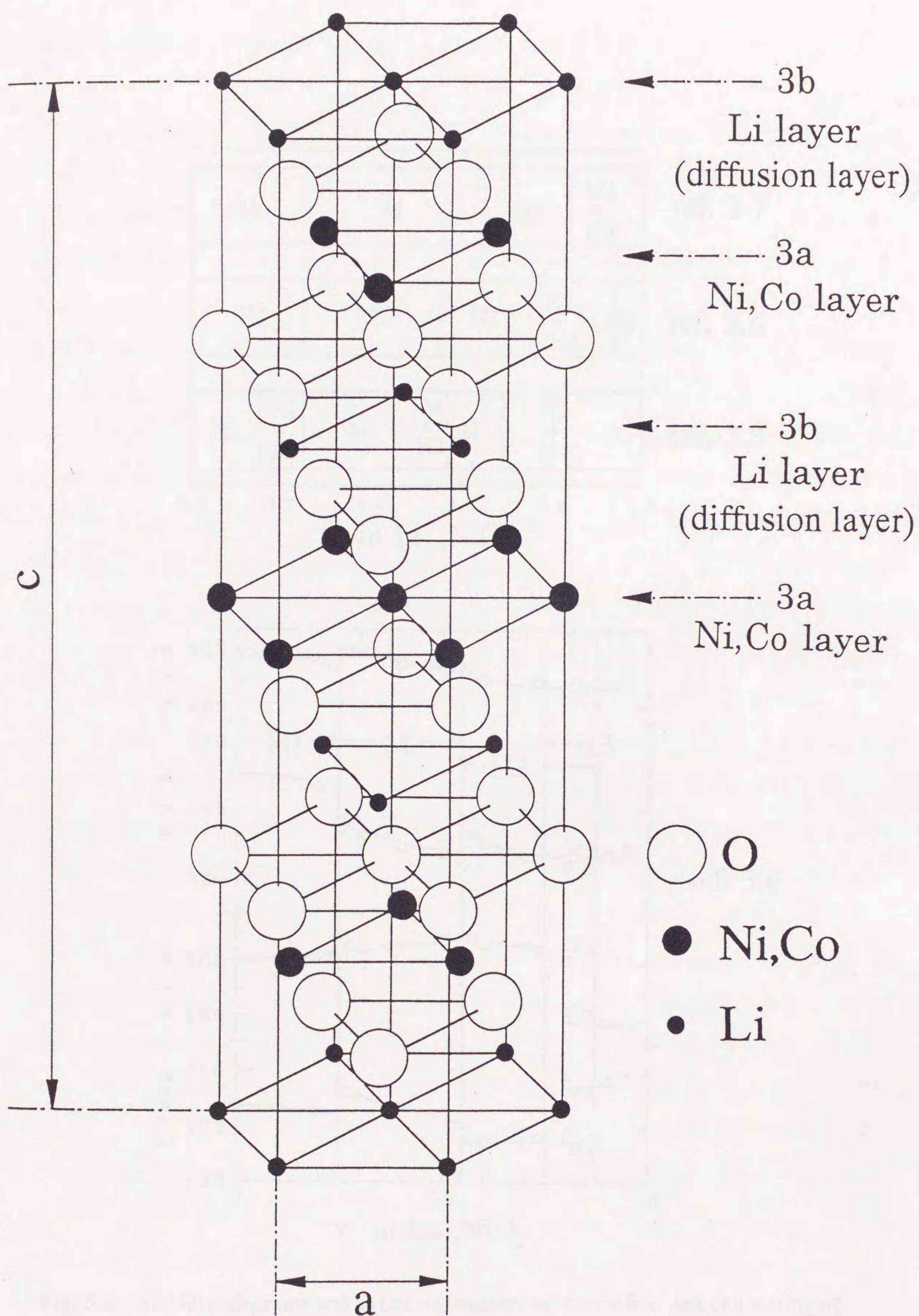


Fig. 3.1 Schematic view of ordered rock-salt $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ structure.

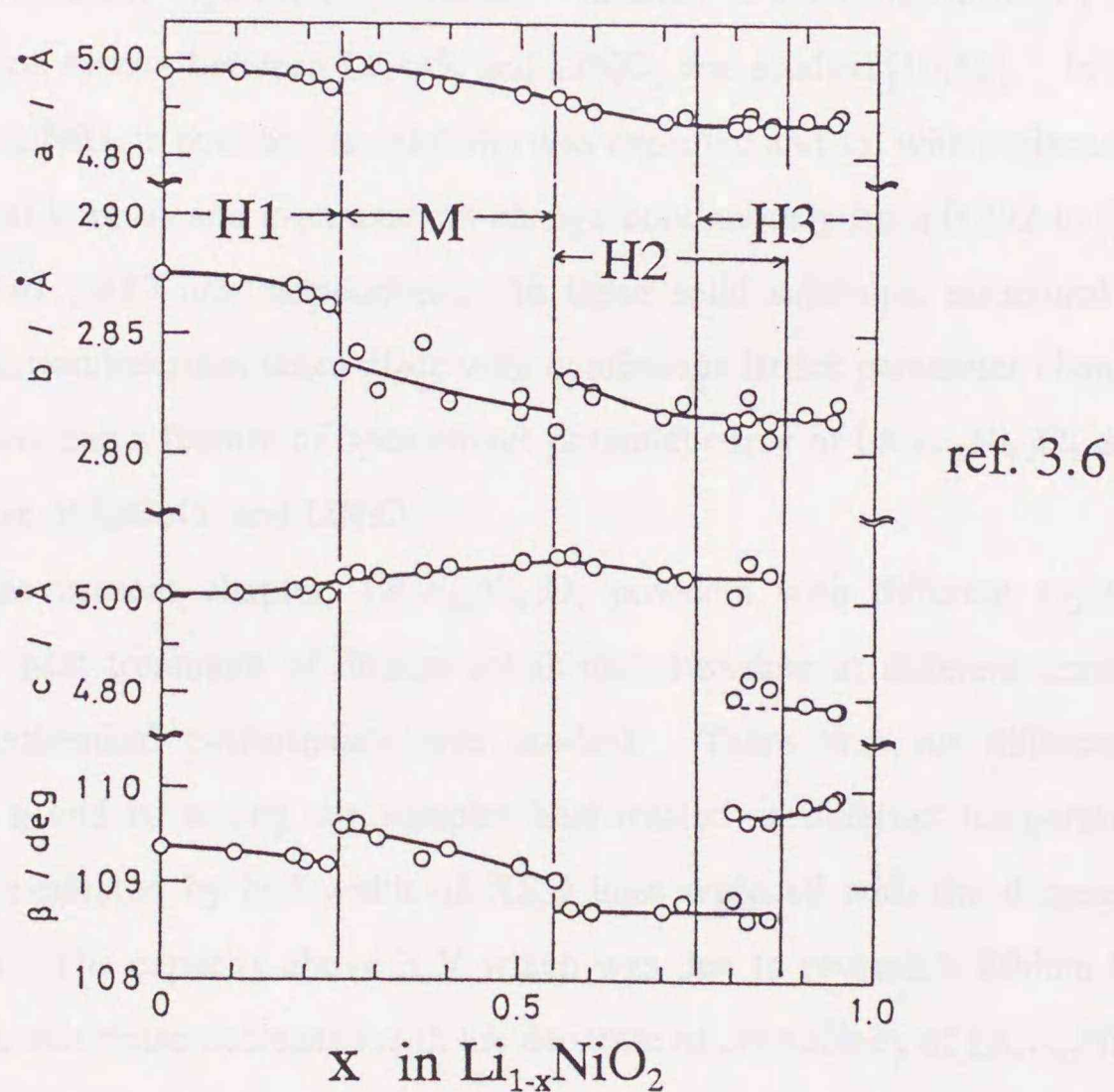
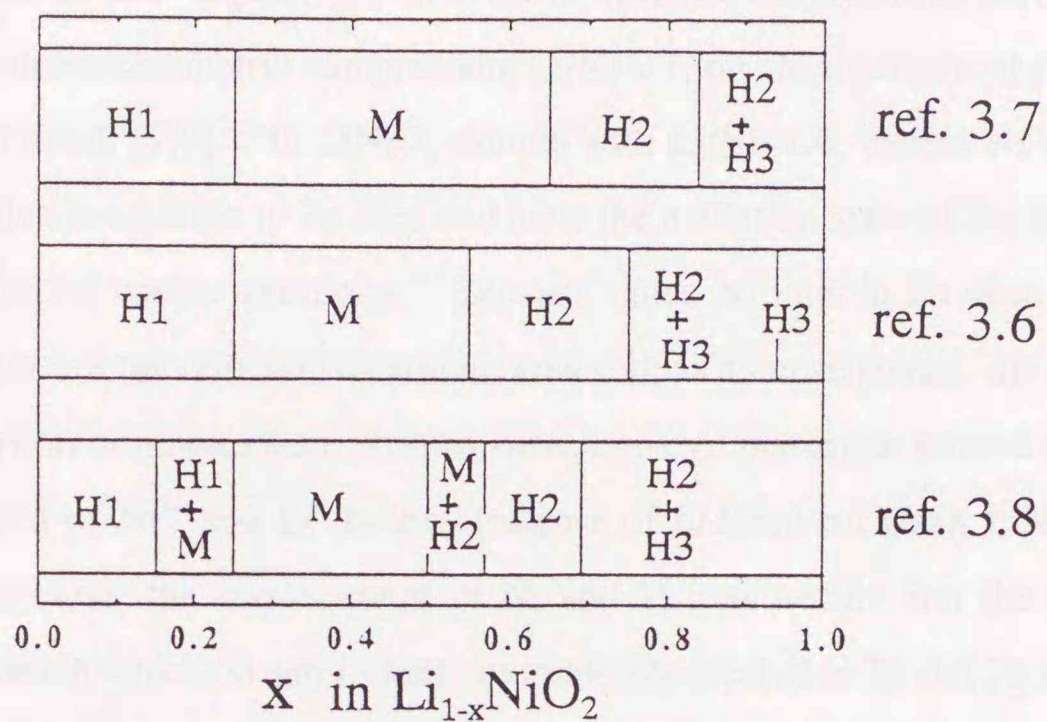


Fig. 3.2 Stability diagrams and lattice parameters of monoclinic unit cell setting of $\text{Li}_{1-x}\text{NiO}_2$ phase. In drawing figure hexagonal unit cell was converted to monoclinic unit cell.

cathode. The cobalt ions in this structure was designed to be replaced by either nickel or iron, if possible, because of economical reason. LiNiO_2 was prepared from stoichiometric mixtures of nickel compound and lithium one, such as NiO and Li_2O , $\text{Ni}(\text{NO}_3)_2$ and LiOH , and NiCO_3 and LiNO_3 . LiNiO_2 powders were obtained by heating these mixtures at ranging from 700 to 850 °C [6,7,9]. In order to optimize the electrode performance, effect of deviation from stoichiometric composition, $\text{Li/Ni} = 1$, on electrochemical performance has been studied in detail [7,9]. In LiNiO_2 sample with $\text{Li/Ni} < 1.0$, excess Ni ions have to be located in 3b sites in addition to 3a sites and have the oxidation state of 2+, accompanied by the same amount of cation vacancies. Because those Ni ions in 3b sites are reasonably supposed to interfere the diffusion of lithium ions and, as a consequence, the capacity due to extraction/insertion of lithium from 3b sites, which gives a plateau at around 4 V, decreased. Because ion radii of Ni^{3+} and Li^+ in the structure of ordered rock-salt LiNiO_2 with space group R3m are close, the displacement of Ni and Li ions occurs and the cubic rock-salt structure domains in which Ni and Li ions are randomly located in 3a and 3b sites are formed easily, in comparing with LiCoO_2 . This makes the preparation of battery-active LiNiO_2 , i.e., ordered rock-salt type LiNiO_2 , difficult. In order to avoid this difficulty in preparation a solid solution system between LiCoO_2 and LiNiO_2 was studied [10,11]. In this system of LiCoO_2 and LiNiO_2 , a continuous solubility was expected and so, with replacement of cobalt ions by nickel ions, a- and c-parameters change continuously from 0.282 to 0.288 nm and from 1.407 to 1.419 nm, respectively. In these solid solutions, structural change with lithium extraction/insertion takes place with continuous lattice parameter change, i.e. single phase reaction, and a feature of open circuit potential curve of $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ is intermediate between those of LiCoO_2 and LiNiO_2 .

In the present chapter, $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ powders with different crystallinity were prepared by heat treatment of lithium-cobalt-nickel-oxalate at different temperatures and their electrochemical performance was studied. There was no difference in lattice parameters, a and c, among the samples heat-treated at different temperatures, but the crystallinity evaluated by half width of XRD lines widened with the decrease in heating temperature. The capacity above 3 V which was due to reversible lithium insertion into ordered rock-salt phase decreased with the decrease of crystallinity of $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ cathode material, though total capacity down to 1.5 V for all the samples was the same; about 600 $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$.

3.2 Experimental

$\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ powder samples were obtained via lithium-nickel-cobalt-oxalate following exactly the same procedures as described in the previous chapter [12,13]. Procedure for sample preparation is shown in Fig. 3.3. Lithium acetate dihydrates, nickel tetrahydrates, and cobalt acetate tetrahydrates were dissolved in ethanol. Stoichiometric ratio between lithium ion and sum of transition metal ions ($\text{Ni}^{2+} + \text{Co}^{2+}$) and the ratio between two transition metal ions were controlled to be unity at this step. And then this solution was mixed with ethanol solution of oxalic acid. Amount of oxalic acid ions was equal to the sum of metal ions. Immediately after mixing of these solutions, the mixture changed into viscous sol. The sol was dried to obtain the precursor powder, which was thought to be lithium-cobalt-nickel-oxalate. From this precursor, $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ powders were prepared by thermal decomposition of the precursor at different temperatures of 500 to 800 °C for 24 hours under O_2 gas flow with a flow rate of $50 \text{ cm}^3 \cdot \text{min}^{-1}$. The heating and cooling rates were $1 \text{ K} \cdot \text{min}^{-1}$. These samples prepared at 500, 600, 700, and 800 °C were named as LNC5, LNC6, LNC7, and LNC8, respectively. Exact atomic ratio of metals in the samples, Li/Co/Ni, was determined by means of ICP-AES analysis and listed in Table 3.1.

The XRD patterns of the samples were recorded with Ni filtered Cu $\text{K}\alpha$ and Fe filtered Co $\text{K}\alpha$ radiation. From the XRD patterns, lattice parameters, a and c , and half widths of 003 and 104 peaks were measured. In the present study, half widths of diffraction lines are employed as a measure of crystallinity. Sharpening and intensity of 003 and 104 peaks are related to development of stacking and extension of layer structure, respectively. Lattice parameters were calibrated by referring to inner standard of crystalline Si powder.

Electrochemical two electrode cell with a composite cathode and an anode was fabricated, of which details were described in section 2.3.3. Charge-discharge curves in the range between 4.5 and 1.0 V vs. Li^+/Li were recorded at a constant current of $10 \text{ mA} \cdot \text{g}^{-1}$. All electrochemical tests were carried out in a grove box filled with argon gas.

3.3 Results

3.3.1 Characterization

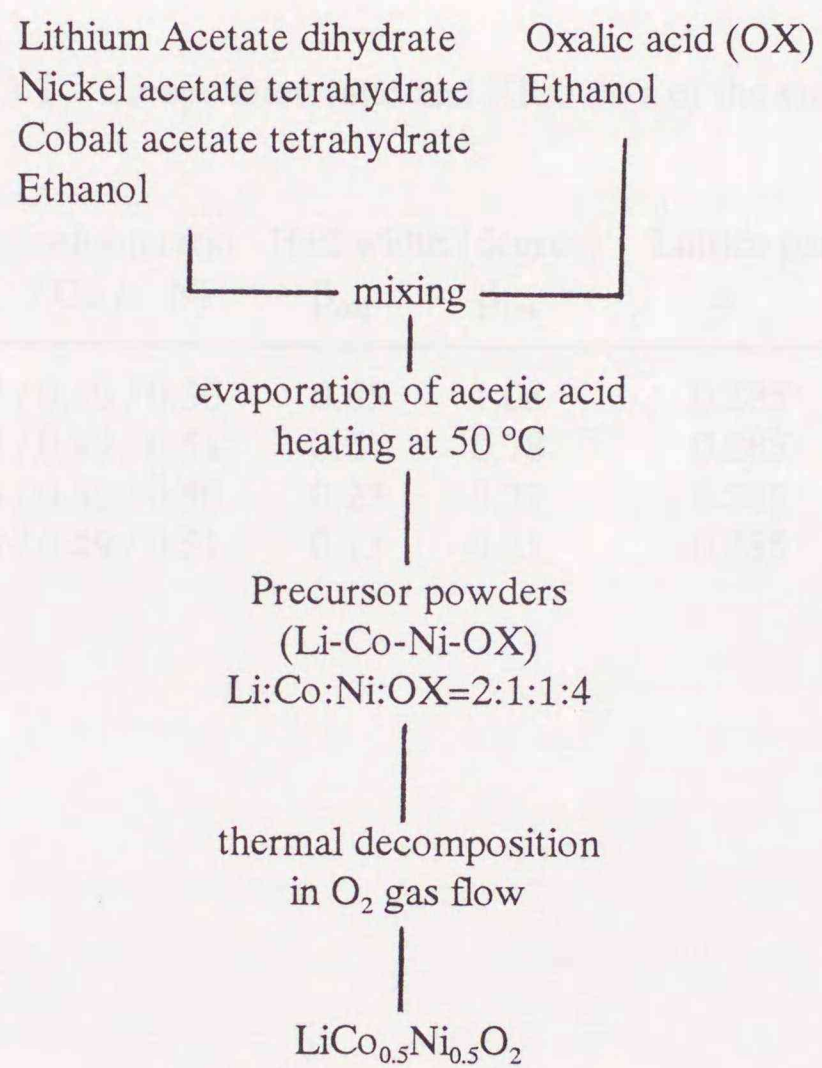


Fig. 3.3 Preparation procedure of $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ powders.

Table 3.1 Composition ratio and XRD data of the samples.

Sample Code	Composition ratio Li / Co / Ni	Half width (degree)		Lattice parameters (nm)	
		β_{003}	β_{104}	a	c
LNC5	0.87 / 0.50 / 0.50	0.85	1.08	0.285	1.41
LNC6	0.87 / 0.49 / 0.51	0.61	0.78	0.285	1.41
LNC7	0.93 / 0.50 / 0.50	0.23	0.31	0.285	1.41
LNC8	0.88 / 0.49 / 0.51	0.13	0.21	0.285	1.41

The XRD patterns of the samples are shown in Fig. 3.4. With the increase of heating temperature, all diffraction peaks become sharp and particularly the 003 line becomes strong in comparison with other peaks. This reveals the development of layered structure with the increase in heating temperature. Lattice parameters, a and c , and half widths of 003 and 104 lines are listed in Table 3.1. There is no difference of lattice parameters among the samples. Both half widths, β_{003} and β_{104} decrease with the increase in heating temperature.

3.3.2 Electrochemical performance

First charge-discharge curves of the samples down to 1.0 and 3.0 V are shown in Figs. 3.5a and b, respectively, where each curve was shifted upward sequentially by 1.0 V for easier view. Charge plateau begins from 3.8 V and its capacity is about $200 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ for all samples but the feature of these curves differs among the samples. Charge capacity of plateau below 4.0 V and gradual potential change region in the range between 4.0 and 4.5 V increases with the increase in heating temperature. Sample LNC5 shows a plateau at around 4.2 V. The lower the heating temperature, the larger potential drop by inverting of current direction from charge to discharge. In the discharge curves, two plateaus are observed at above 3.0 and around 1.5 V. The total capacity of the first discharge down to 1.0 V is about $600 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ for all the samples, but the capacity above 3V increases and that below 3 V decreases with the increase in heating temperature. Thus with the decrease in heating temperature, the first discharge capacity of the plateau at around 1.5 V increases with consuming the capacity above 3 V. Charge-discharge cycle above 3 V was almost reversible on all samples. However, once the cell was discharged down to 1.0 V, the cell was not rechargeable.

3.4 Discussion

With the increase in heating temperature, crystallinity of samples improves, the sample LNC8 having the highest crystallinity among the present samples.

In the low temperature crystallized LiCoO_2 , there is disordering of Co and Li sites, resulting in a cubic rock-salt type structure associated with distribution of Co and Li among the octahedral 3a and 3b sites of a cubic-close-packed array of oxygen [14,15]. In the $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ samples heated at low temperatures, the imperfection of cation distribution, or

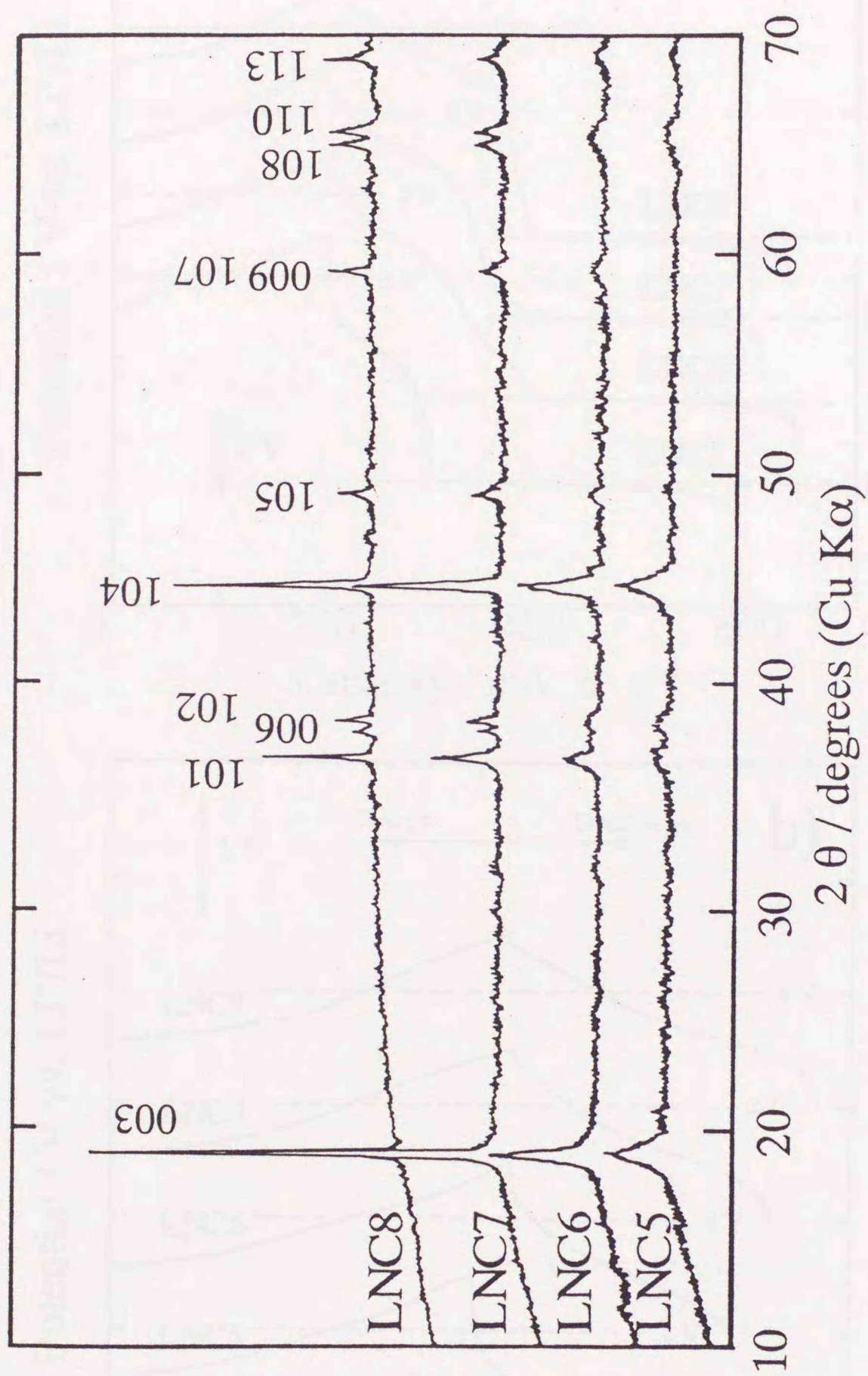


Fig. 3.4 XRD patterns of the samples.

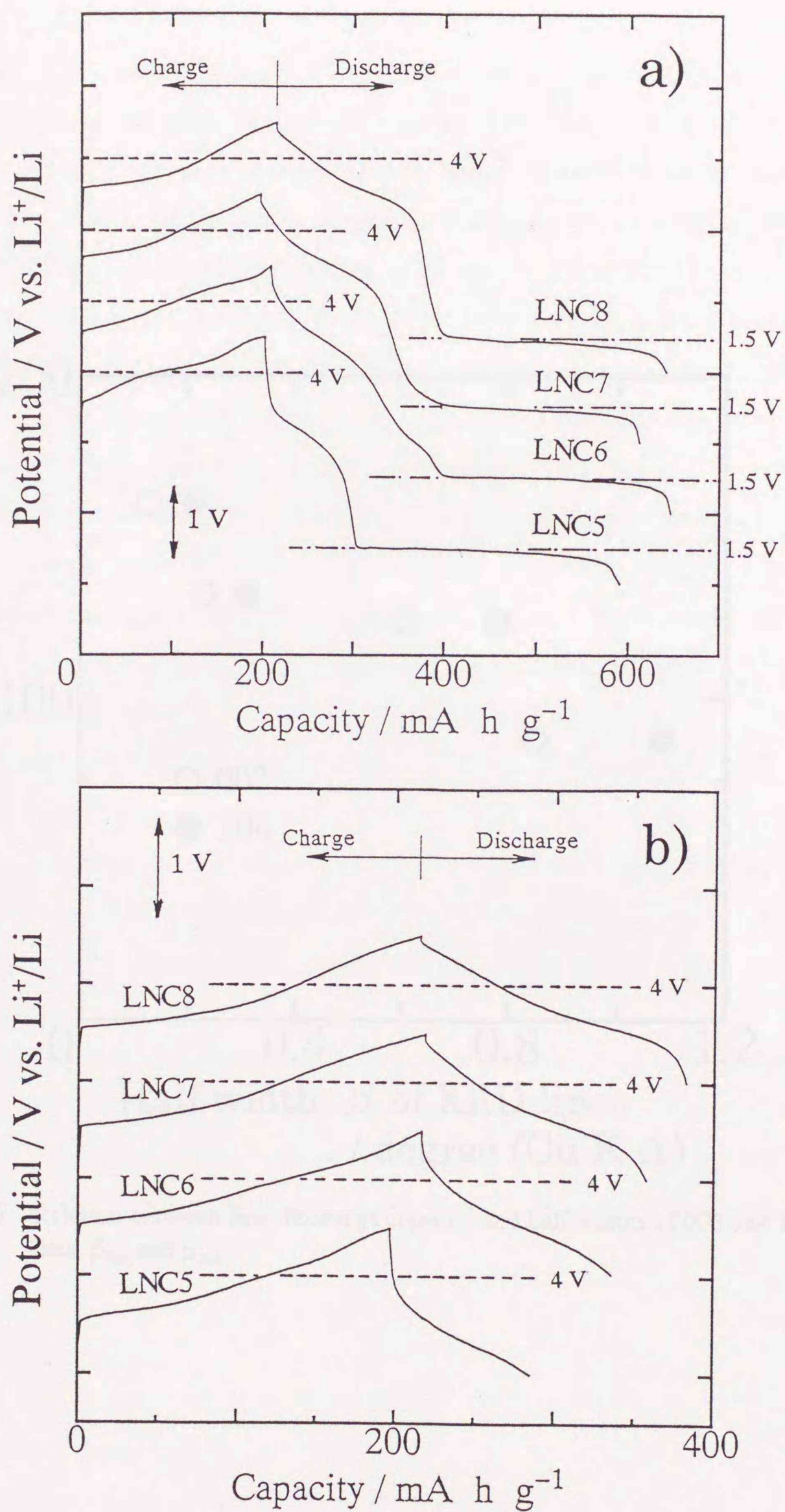


Fig. 3.5 First charge-discharge curves down to 1.0 V a) and 3.0 V b) of the samples, where each curve is shifted up sequentially by 1.0 V for easier view.

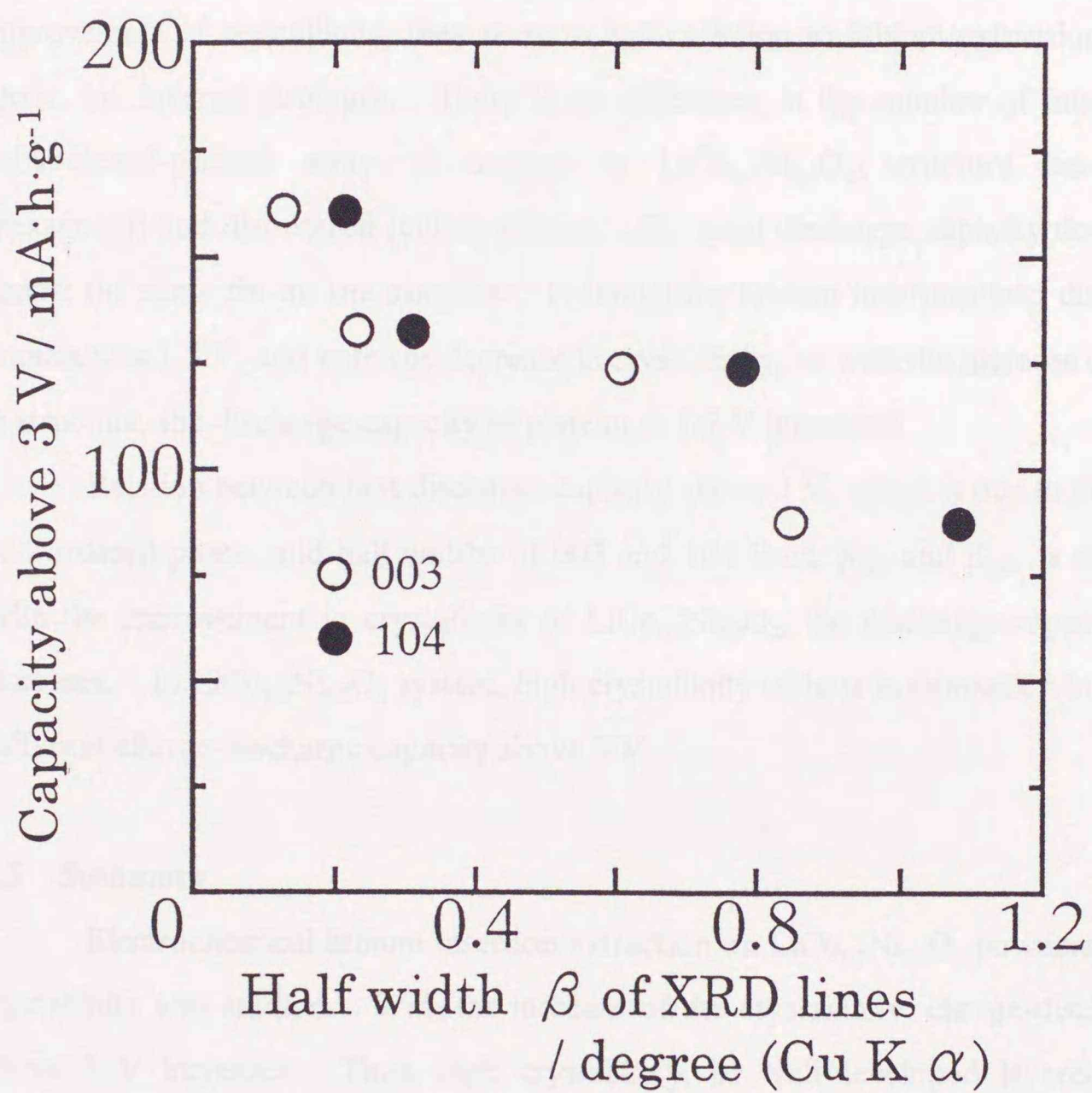


Fig. 3.6 Relation between first discharge capacity and half widths of 003 and 104 lines, β_{003} and β_{104} .

the formation of cubic rock-salt domain (disordered phase), may occur. Because the charge plateau at around 4.2 V is observed only in the samples LNC5 and LNC6, the reaction at 4.2V seems to be related to lithium extraction reaction from the cubic rock-salt structure (disordered phase) domains. Because of the disordered structure, diffusion of lithium ions seemed to be disturbed and the largest polarization at the inverse point of current direction from charge to discharge was observed in sample LNC5, and the polarization decreased with the increase in heating temperature. Since charge plateau below 4.0 V and gradual potential change region between 4.0 and 4.5 V increases with the improvement of crystallinity, they seem to have relation to lithium extraction from ordered phase, i.e. layered structure. There is no difference in the number of interstitial sites in cubic-closed-packed array of oxygen in $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ structure between ordered (hexagonal) and disordered (cubic) phases. So, total discharge capacity down to 1.0 V is almost the same for all the samples. Potential for lithium insertion into disordered phase domain was 1.5 V, and with the decrease in crystallinity, or with the increase of disorderness in structure, the discharge capacity of plateau at 1.5 V increased.

Relation between first discharge capacity above 3 V, which is due to lithium insertion into ordered phase, and half widths of 003 and 104 lines, β_{003} and β_{104} , is shown Fig. 3.6. With the improvement in crystallinity of $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$, the discharge capacity above 3 V increases. In $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ system, high crystallinity of host is demanded in order to get a sufficient charge-discharge capacity above 3 V.

3.5 Summary

Electrochemical lithium insertion/extraction on $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ powders with different crystallinity was studied. With the increase of the crystallinity, charge-discharge capacity above 3 V increases. Thus, high crystallinity, or well-developed layered structure, is necessary to get a high performance of the electrode in 4 volt rechargeable lithium ion batteries.

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Chapter 4

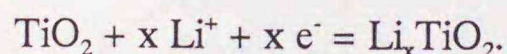
Anatase type TiO_2

4.1 Introduction

Titania (TiO_2) has different crystallographic modifications, such as rutile, anatase, brookite, and amorphous. Three crystal structures differ in the mutual connection between chains consisting of edge-shared Ti-O octahedra with some distortion. The construction in anatase is shown in Fig. 4.1. Ti-O octahedra share their edges to make a zigzag chain. The chains are also connected by sharing edges as shown in Fig. 4.1. The resultant structure belongs to the space group of $I4_1/amd$ and has three dimensional channels where lithium ions can diffuse through and also be accommodated.

Lithium insertion/extraction on rutile, anatase, and brookite powders has been studied, and anatase powders showed the best electrochemical performance, the largest capacity and the highest discharging potential, among the three crystal types [1,2]. Anatase powders are very attractive material because of the possibility of their various applications, such as membrane in dye-sensitized solar cell [3,4], electrodes for lithium batteries [5,6], and electrochromic windows [7,8]. Lithium insertion/extraction reaction on anatase is utilized in the latter two applications i.e., electrodes for batteries and electrochromic devices, and has been studied since 1970's.

Lithium insertion/extraction reaction on TiO_2 is expressed as follows;



For the anatase-type TiO_2 , in the composition range $0 < x < 0.5$ of Li_xTiO_2 , lithium ions are inserted through three dimensional channels and accommodated randomly in vacant octahedral sites of ccp oxygen array [3,4]. Because the octahedral site is distorted, lithium ion is displaced from the center of the octahedron and, as a result, the nearest neighbor oxygen atoms are five. The anatase TiO_2 skeleton is maintained during lithium insertion, and then inserted lithium ions are reversibly extracted [5-8]. Crystallographic unit cell parameters for anatase and $\text{Li}_{0.5}\text{TiO}_2$ are compared in Table 4.1 [4-6]. The lattice parameters expand from 0.3784 to 0.38082 nm and 0.40768 nm in the direction of a and b axes, respectively, but shrinks from 0.9515 to 0.90526 nm along the c axis. On lithiation, tetragonal symmetry of anatase changes to orthorhombic one in Li_xTiO_2 .

In the present chapter, lithium insertion/extraction on anatase-type TiO_2 with different crystallinity and morphology was investigated. The powders of anatase-type TiO_2

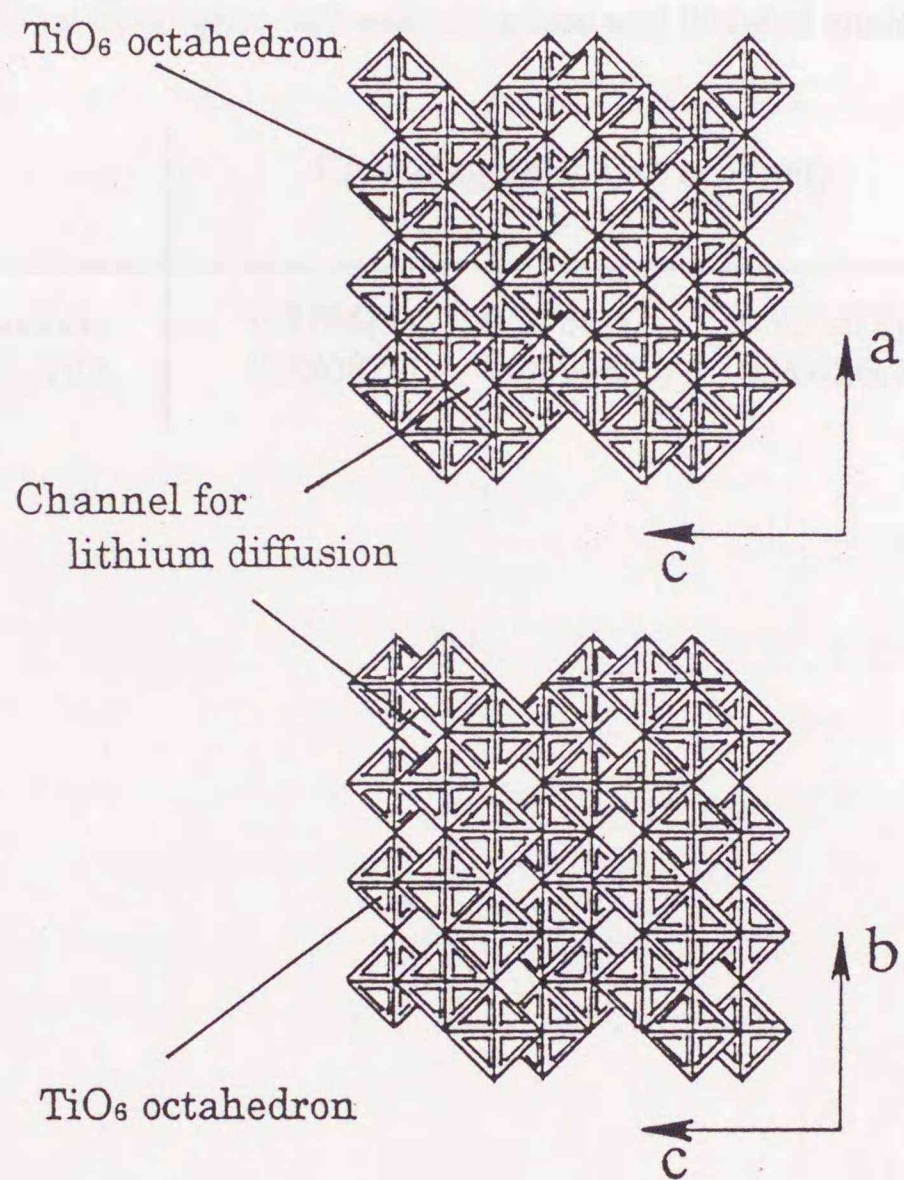


Fig. 4.1 Construction of Ti-O octahedra in anatase.

Table 4.1 Crystallographic unit cell of anatase and lithiated anatase, $\text{Li}_{0.5}\text{TiO}_2$.

	Crystallographic unit cell (nm)		
	a	b	c
Anatase	0.3784(1)	0.3784(1)	0.9515(2)
$\text{Li}_{0.5}\text{TiO}_2$	0.38082(1)	0.40768(1)	0.90526(4)

were synthesized under hydrothermal conditions from amorphous TiO_2 prepared by hydrolysis of titanium tetraisopropoxide. The original amorphous TiO_2 and reagent grade anatase were also employed as samples. For all of the samples, the first discharge capacity down to 1.6 V was about $170 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$, which corresponds to the composition of $\text{Li}_{0.5}\text{TiO}_2$, but different potential changes with lithium insertion ranges were observed; a plateau at 1.75 V and gradual potential decrease from 2.5 to 1.75 V. In the samples prepared by using hydrothermal technique, the powder particles consisted of crystallite of anatase covered with amorphous TiO_2 , and in their first discharge curves, the plateau region was thought to be due to lithium insertion into crystalline anatase phase and gradual potential region was thought to correspond to lithiation into amorphous TiO_2 . Crystallinity of the samples had an effect on a flatness of the plateau at 1.75 V, and the increase in the lattice strain, ϵ , seemed to lead to the decrease in flatness of the plateau.

4.2 Experimental

Anatase-type TiO_2 powders were prepared as follows; reagent grade titanium tetraisopropoxide (75 cm^3) was diluted with reagent grade 1-propanol to a total volume of 500 cm^3 . By adding this solution into 1500 cm^3 water, white precipitates were obtained. The precipitates were isolated by a centrifuge and dried in a vacuum dryer at around 20°C . The white powders obtained were found to be amorphous in structure and to contain 5-20 wt.% water (hereafter TA). Anatase-type TiO_2 powders were prepared by hydrothermal treatment of these TA powders. After increasing the pressure up to 15 MPa, the autoclave was heated to an appropriate temperature with a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$. During heating, the pressure in the bomb was kept constant at 15 MPa. Preparation conditions for each sample are listed in Table 4.2 with sample code. The details of the preparation procedure were reported in the literature [9]. Starting amorphous titania (TA) and also a reagent grade TiO_2 with anatase structure (TR) were also employed for lithium insertion/extraction reactions.

XRD measurements with Ni-filtered $\text{Cu K}\alpha$ radiation were performed on the samples with a scanning speed of $2^\circ\cdot\text{min}^{-1}$ for measuring over all patterns and that of $0.1^\circ\cdot\text{min}^{-1}$ for measuring half width of diffraction peaks. From the half width of diffraction peaks (101, 200, 105, and 211 peaks were used), lattice strain, ϵ , and crystallite size, L , were

Table 4.2 Preparation conditions of the samples.

Sample Code	Preparation Conditions
TA	Hydrolysis of titanium tetraisopropoxide.
T350W	Hydrothermal treatment at 350 °C, 15 MPa, 48 h with addition of water of 10 cm ³ .
T350	Hydrothermal treatment at 350 °C, 15 MPa, 48 h without addition of water.
T100W	Hydrothermal treatment at 100 °C, 15 MPa, 1 h with addition of water of 10 cm ³ .
TR	Reagent from Kanto Kagaku Co.Ltd.

determined. Procedure of calculation using Hall's equation was described in the section 2.2.2.

UV-VIS absorption spectra were measured on the samples by using a diffuse reflectance attachment with a scanning speed of $5 \text{ nm} \cdot \text{min}^{-1}$. From the peak position of the first derivative of the absorption spectra, the absorption edge was determined.

Particle morphology and microstructure of the samples were examined under scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM observation was carried out with an acceleration voltage of 25 kV. Because anatase powders are electrical insulator, sample powders mounted on a copper holder were coated with gold by sputtering. For TEM observation, sample powders were dispersed in methanol and were deposited on a Ni grid with carbon film.

All electrochemical tests were performed in a glove box filled with argon gas. Discharge curves down to 0.5 V (vs. Li^+/Li) and discharge-charge curves in a potential range between 1.6 and 3.6 V (vs. Li^+/Li) were measured with a constant current of $10 \text{ mA} \cdot \text{g}^{-1}$. After the cell was settled for 12 hours, rest potential of the cathode against Li^+/Li was recorded. Fabrication method for the conventional two electrode cell, the composite cathode and the anode were described in the section 2.3.3.

4.3 Results

4.3.1 Structural characterization

The XRD patterns of the TiO_2 samples are shown in Fig. 4.2. The sample TR shows sharp diffraction lines characteristic of anatase phase, which reveals the highest crystallinity of the present samples used. Three TiO_2 powders prepared under hydrothermal conditions show only the diffraction lines of anatase phase, but the broadness of diffraction lines depends strongly on preparation condition; much broader on the sample treated at 100°C (sample T100W) than those at 350°C (sample T350W). The sample TA shows no diffraction peak indicating amorphous.

Crystallite size, L , and lattice strain, ϵ , calculated from the half widths using Hall's equation are summarized in Table 4.3. Because there is no peak in the XRD pattern of sample TA, its crystallite size and lattice strain were not possible to be determined, but it is reasonably supposed that the crystallite size is much smaller and the lattice strain is markedly larger than other samples used. Sample TR has the largest crystallite size among the

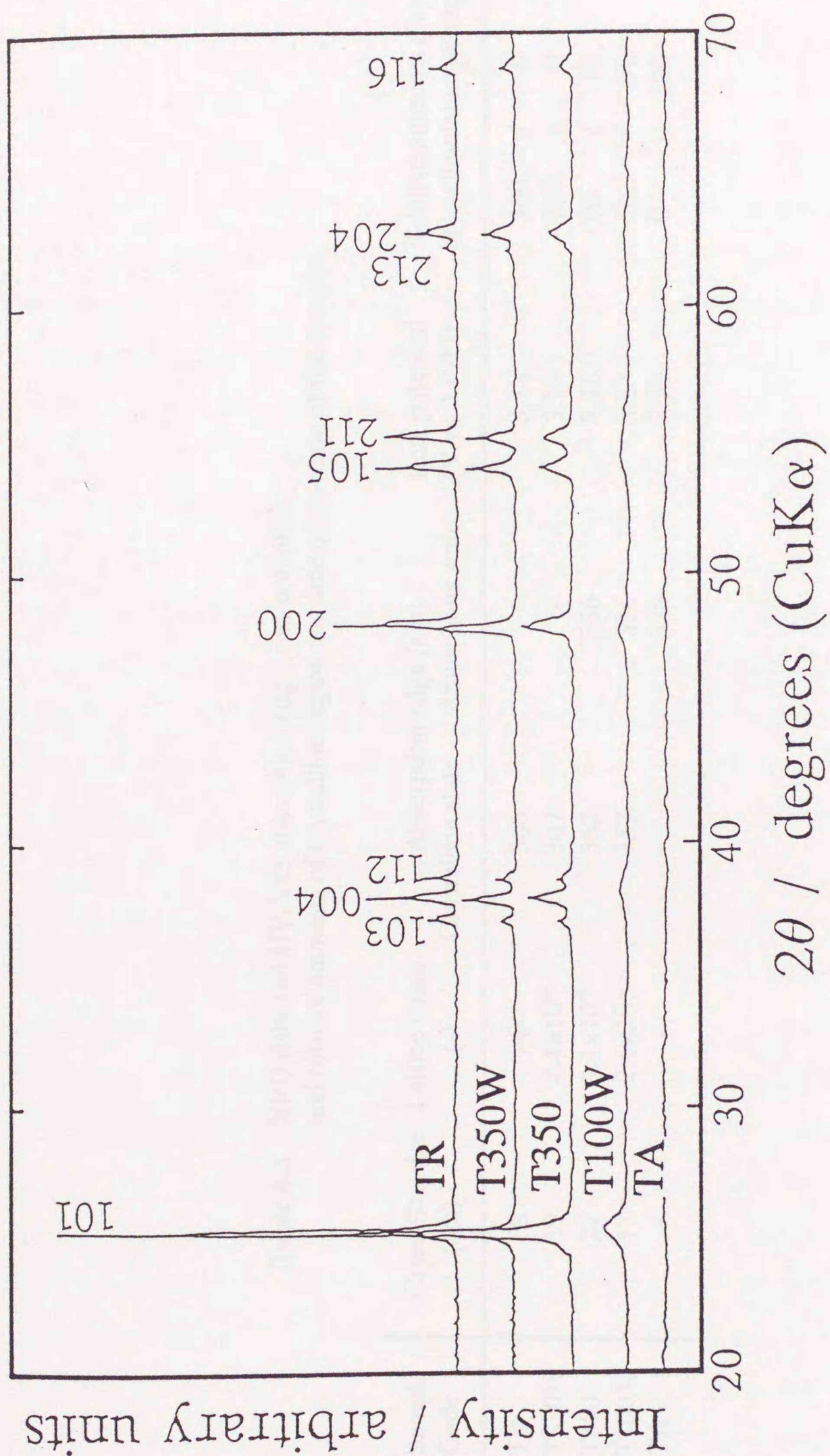


Fig. 4.2 The XRD patterns of the samples.

Table 4.3 XRD data and UV-VIS absorption edge, rest potential, and relative amounts of crystalline region and amorphous one of the samples.

Sample Code	Crystallite size (nm)	Lattice strain (-)	Absorption edge (nm)		Rest potential (V vs. Li ⁺ /Li)	Relative amounts (%) crystalline/amorphous	
			Crystalline state	Amorphous state			
TR	68	≈0	366	-	3.18	100	/ 0
T350W	59	4.4×10 ⁻⁴	367	-	3.19	100	/ 0
T350	27	9.1×10 ⁻⁴	362	336	3.18	90	/ 10
T100W	17	2.6×10 ⁻²	357	336	3.23	50	/ 50
TA	-	-	-	336	3.39	0	/ 100

samples used, and there is almost no strain in the crystallite of sample TR. Sample T100W shows a relatively small crystallite size and large lattice strain. As the two samples heated at 350 °C, T350 and T350W, are compared, an addition of excess water during hydrothermal treatment assists the crystallization of sample, because the latter has a larger crystallite size and smaller lattice strain than the former.

Fig. 4.3a) shows the UV-VIS absorption spectra of the samples. The absorption edge of these powders seems to shift toward shorter wavelength, and to widen with the decrease of crystallinity determined by XRD measurements. The first derivatives of UV-VIS absorption spectra are shown in Fig. 4.3b). The absorption edge of these samples was determined from apparent peak positions. The values observed are listed in Table 4.3. Sample TA in amorphous state has a single peak at 336 nm, and samples TR and T350W in crystalline anatase state have a single peak at 366 nm. However, samples T350 and T100W have two peaks, and the position may be assigned to those for amorphous titania (336 nm) and for crystalline anatase (366 nm). This suggests that these two samples prepared under hydrothermal conditions are constituted of two phases with amorphous and crystalline states, though only anatase phase was detected on XRD pattern. In the samples prepared under hydrothermal conditions, an absorption edge related to crystalline anatase shifts to shorter wavelength linearly with the decrease in crystallite size and this is known as blue shift [10].

The SEM photographs of samples are shown in Fig. 4.4. For sample TR, the particle size is about 0.1 μm . The particle size of sample T350W is not uniform; the largest is about 0.5 μm and the smallest below 0.1 μm . For samples T350, T100W, and TA, uniform particle size below 0.1 μm is observed.

The bright field images of samples T350W, T350, T100W, and TA are shown in Fig. 4.5. In sample T350W, polygonal particles, which are not uniform in size, are observed, and some of them grow beyond 0.1 μm . Particles of sample T350 are constructed with two regions; polygonal particles with the size of about 70 nm and featureless regions which are almost transparent to electron beam, the latter appearing to cover the former (Fig. 4.5b). In sample T100W, polygonal particles, whose size is about 20 nm, are also covered with transparent regions (Fig. 4.5c). These three samples were concluded to be anatase-type structure from their XRD patterns. Combining with the result of UV-VIS absorption spectra, however, the polygonal particles and the transparent regions are reasonably

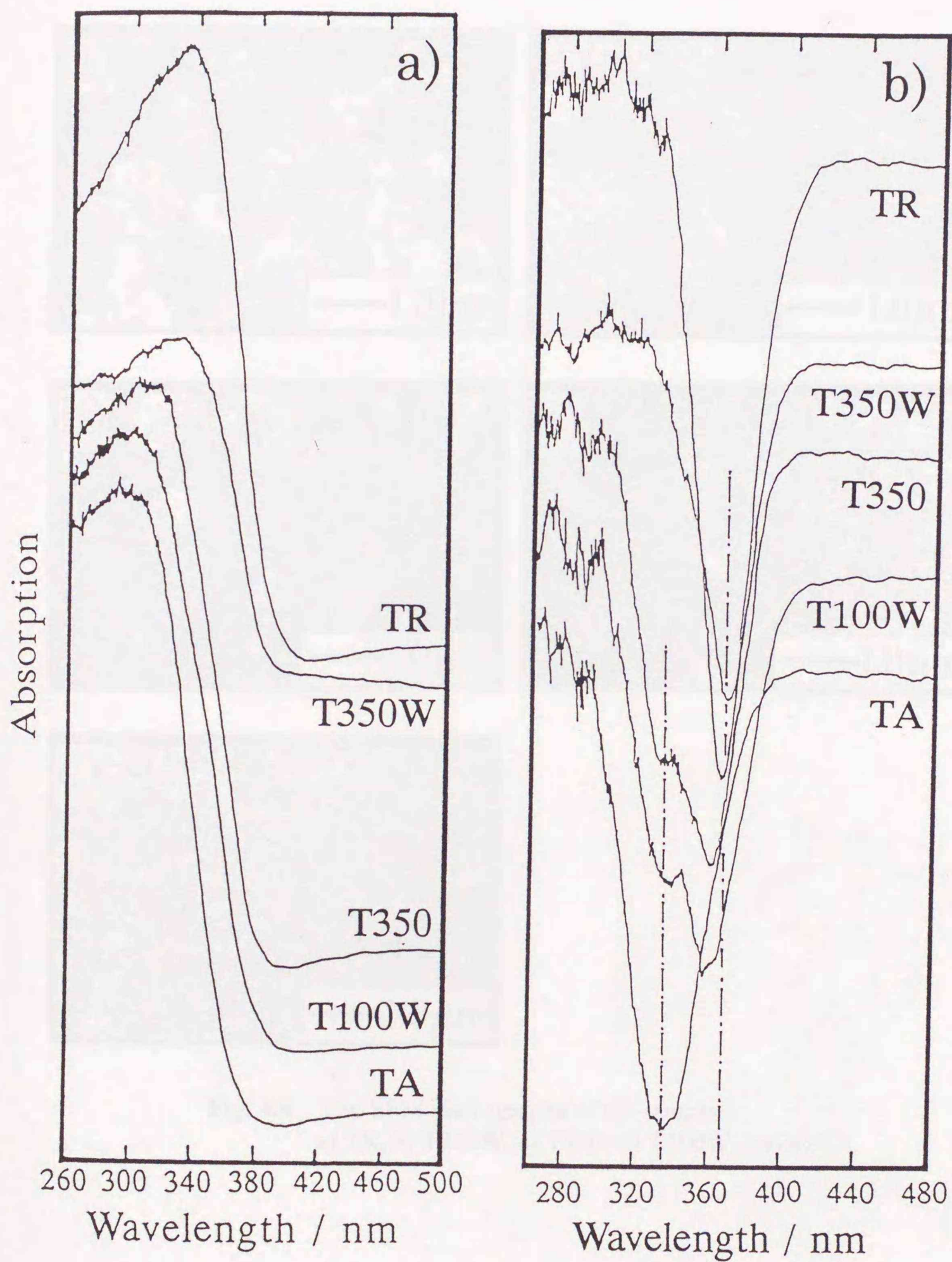


Fig. 4.3 The UV-VIS absorption spectra a) and the first derivatives of UV-VIS absorption spectra b) of the samples.

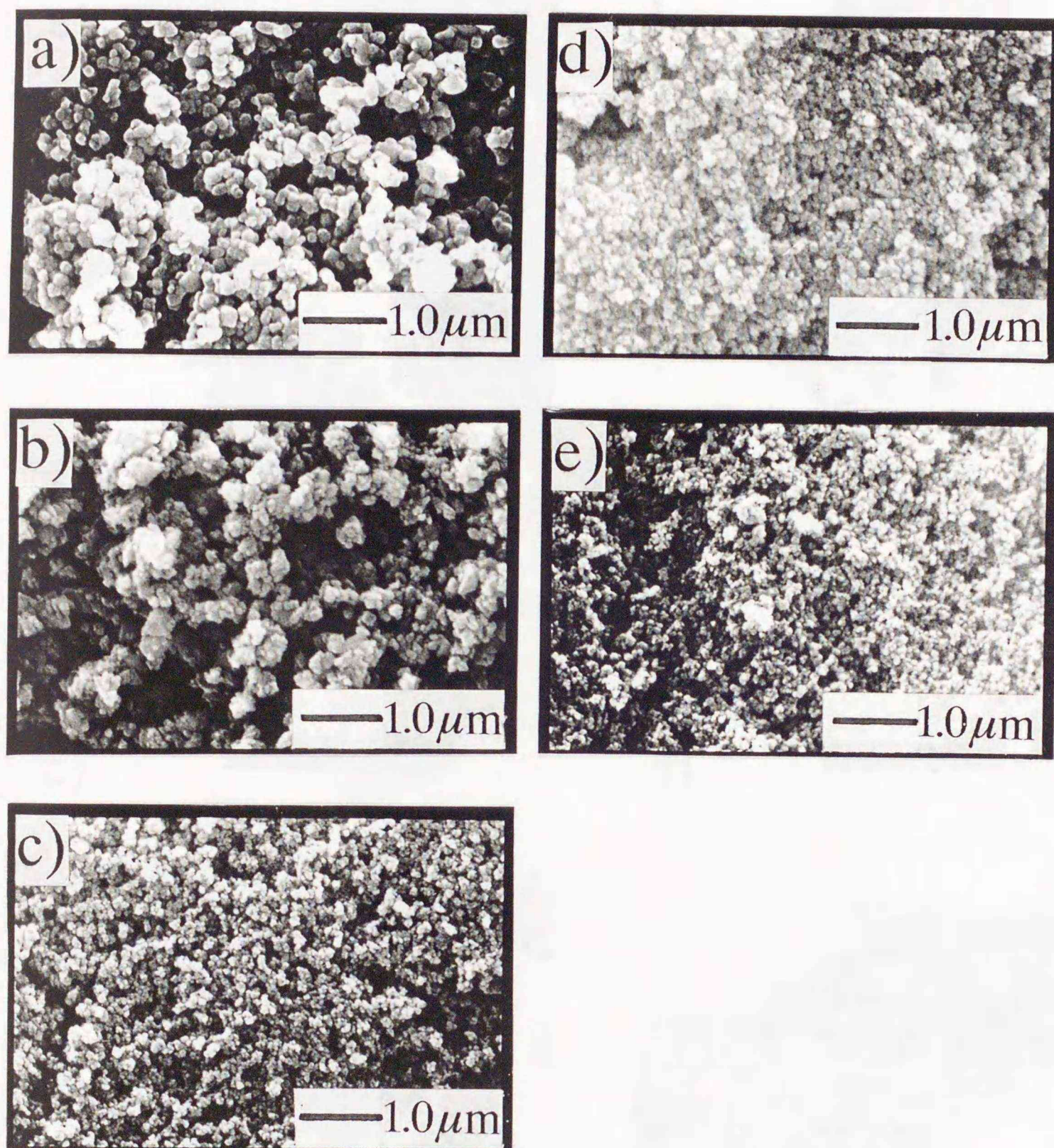


Fig. 4.4 The SEM photographs of the samples.
 a) TR, b) T350W, c) T350, d) T100W, and e) TA.

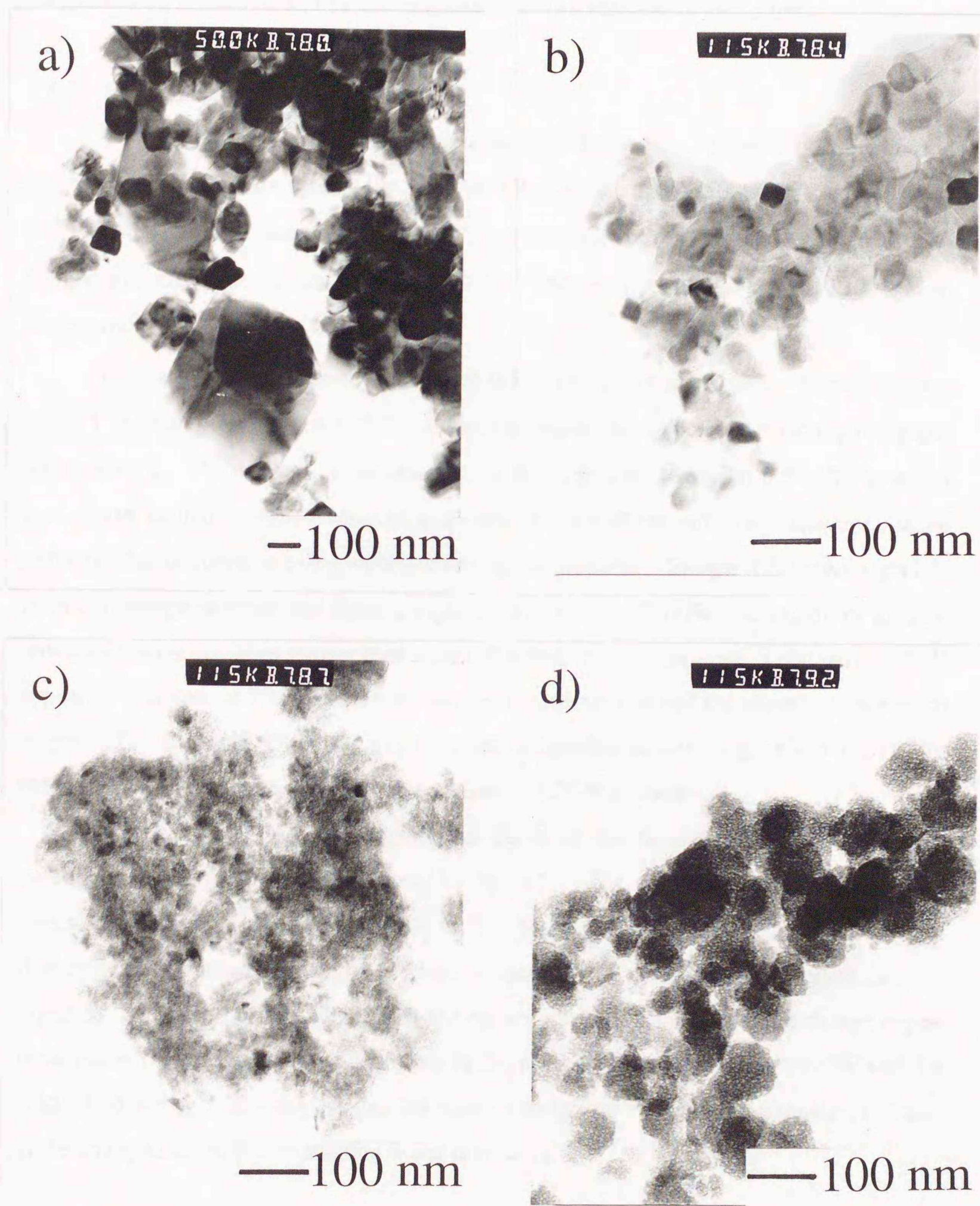


Fig. 4.5 The bright field images of samples.
a) T350W, b) T350, c) T100W, and d) TA.

supposed to be anatase crystallites and amorphous TiO_2 , respectively. In sample TA, its particle size is in the range 20 to 100 nm, and its shape is featureless, no polygonal shape particles being observed, and its electron diffraction pattern shows only a halo.

4.3.2 *Electrochemical performance*

The rest potential of the samples are listed in Table 4.3. There is no difference in the value of rest potential among the samples, TR, T350W, and T350, which have relatively small lattice strain, ϵ , smaller than 1.0×10^{-3} , and the value of rest potential is about 3.18 V. Sample TA shows the highest value of 3.39 V. The rest potential of sample T100W with lattice strain of 2.6×10^{-2} is 3.23 V.

Discharge curves of samples down to 0.5 V are shown in Fig. 4.6. Capacity down to 0.5 V is about $400\text{--}500 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ for all samples, except for sample TA which shows about $800 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$. The amount of lithium inserted down to 1.6 V is about 0.5 Li/ TiO_2 , which was said to be that reversibly inserted and extracted, for all the samples. However, shape of the discharge curves are very different among the samples. Sample TA shows a gradual potential change without any plateau region. For sample T100W, the region of gradual potential change becomes shorter than sample TA and, as a consequence, a plateau at 1.75 V appears. For sample T350, the former becomes much shorter and the latter becomes much longer. For samples T350W and TR, a capacity of gradual potential region above 1.75 V is very small, even negligible, and long flat plateau at 1.75 V is observed.

The changes in the discharge-charge curve of the samples with cycling between potentials of 1.6 and 3.6 V are shown in Fig. 4.7. If it is taken into account that the crystallinity changes from TR (Fig. 4.7a) to TA (Fig. 4.7e) in turn, capacity loss during the first cycle of discharge and charge is found to increase with the decrease in crystallinity of samples. It has to be pointed out that the capacity in the gradual potential change region observed in the discharge curve decreases in the charge curve for samples T100W and TA (Figs. 4.7d and e). This implies that the main capacity loss is due to the trapping of lithium in the amorphous regions containing water molecules.

4.4 Discussion

Samples TR and T350W are comprised of anatase type TiO_2 powders, whose particle size is about 100 nm, and lattice strain, ϵ , is relatively small as below 1.0×10^{-3} .

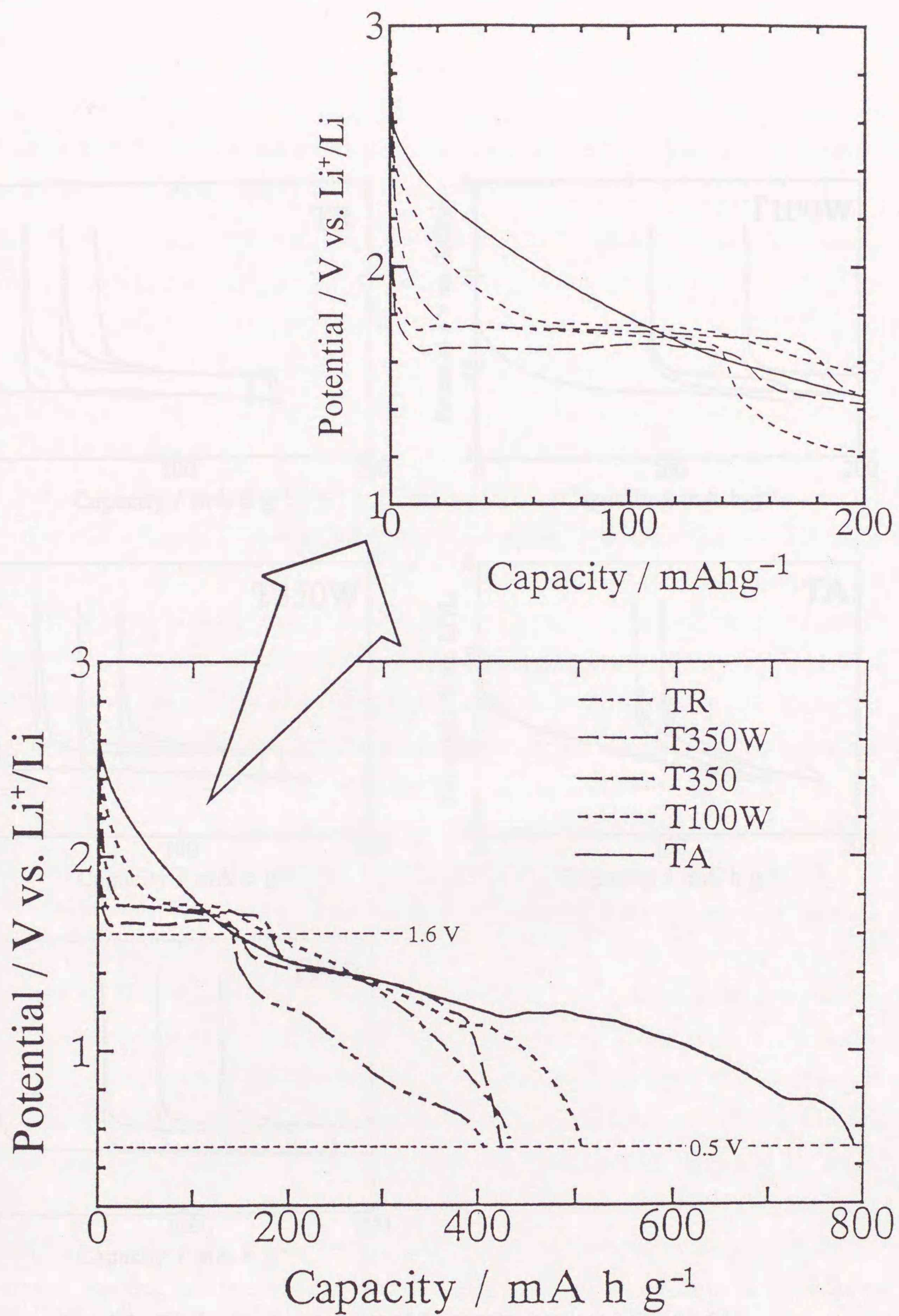


Fig. 4.6 Discharge curves of the samples down to 0.5 V vs. Li⁺/Li.

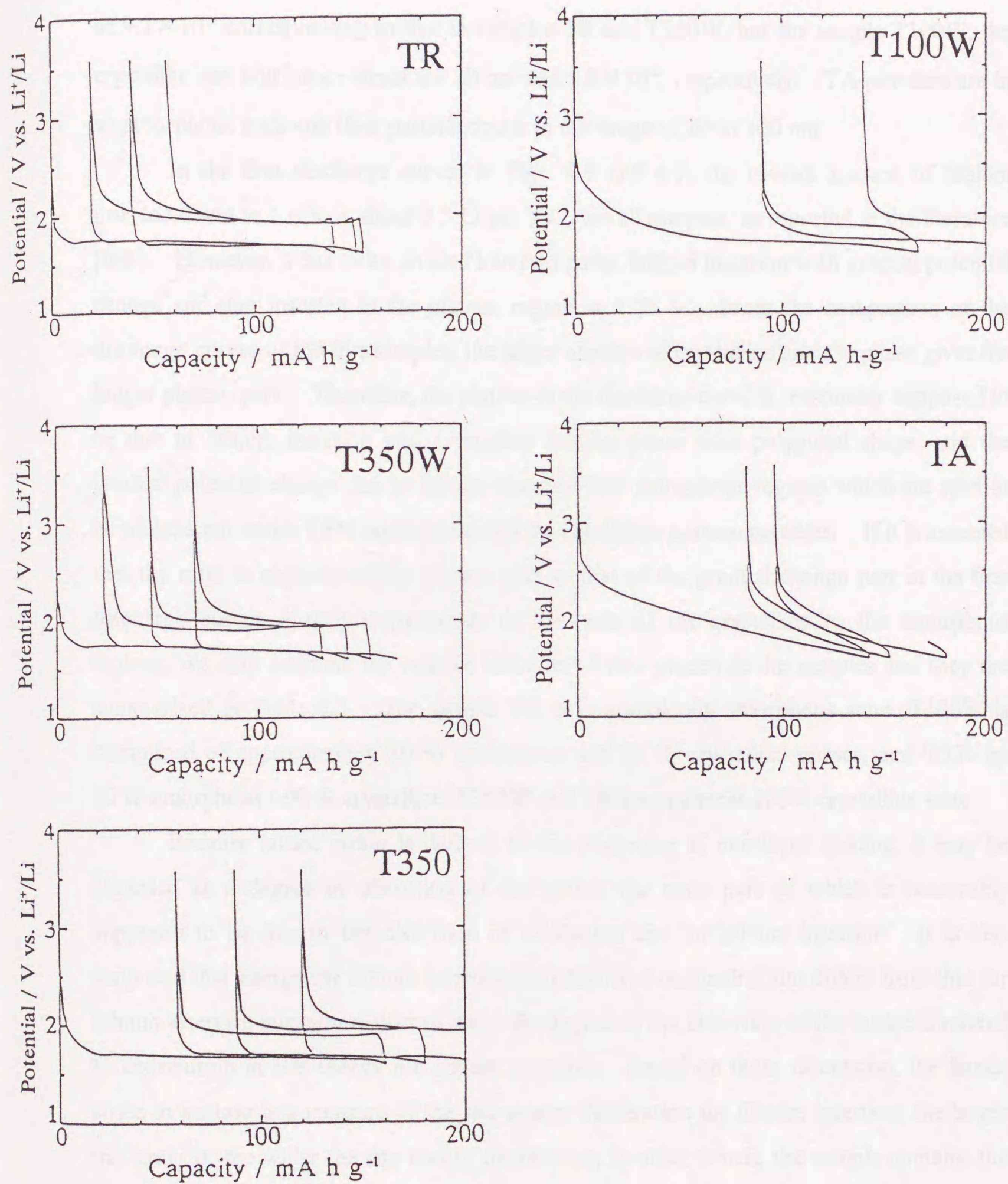


Fig. 4.7 Discharge-charge curves of the samples between 1.6 and 3.6 V.

From the results of XRD pattern, UV-VIS absorption spectra, and TEM photographs, the particles of samples T350 and T100W are found to be anatase-type crystallites covered with amorphous TiO_2 . Crystallite of sample T350, whose size is about 70 nm, has a lattice strain of 9.1×10^{-4} corresponding to that in samples TR and T350W, but for sample T100W, the crystallite size and lattice strain are 20 nm and 2.6×10^{-2} , respectively. TA powders are in an amorphous state and their particle size is in the range of 20 to 100 nm.

In the first discharge curves in Figs. 4.6 and 4.7, the overall amount of lithium inserted down to 1.6 V is about 0.5 Li per TiO_2 for all samples, as reported in the literature [6-8]. However, it has to be divided into two parts; lithium insertion with gradual potential change and that inserted in the plateau region at 1.75 V. From the comparison of the discharge curves of the five samples, the larger amount of crystalline anatase phase gives the longer plateau part. Therefore, the plateau in the discharge curve is reasonably supposed to be due to lithium insertion into crystalline anatase phase with polygonal shape, and the gradual potential change due to lithium insertion into amorphous regions which are seen to be transparent under TEM and surrounded the crystalline anatase particles. If it is assumed that the ratio in capacity of the plateau part to that of the gradual change part in the first discharge curves directly corresponds to the ratio of the crystalline to the amorphous regions, we may estimate the relative amounts of two phases in the samples and they are summarized in Table 4.3. The sample TA is in completely amorphous state. T100W is comprised of approximately 50 % amorphous and 50 % crystalline phases, and T350 by 10 % amorphous / 90 % crystalline. T350W and TR are in almost 100% crystalline state.

Because lattice strain is defined as the scattering in interlayer spacing, it may be regarded as a degree of distortion of the lattice, the main part of which is reasonably supposed to be due to the distortion of octahedral site for lithium insertion. It is also supposed that energy for lithium insertion into distorted octahedral site differs from that for lithium insertion into non-distorted site. So degree of the distortion of the lattice is related to distribution in site energy for lithium insertion. Based on these discussion, the lattice strain in anatase is a measure of the site energy distribution for lithium insertion; the larger the strain is, the wider the site energy distribution, in other words, the sample contains the more distorted octahedral sites. Rest potential is thought to be chemical potential of lithium in the host structure, or a site energy for lithium ions. The samples TR, T350W, and T350 have very small lattice strain, below 1×10^{-3} , which means they have homogeneous

site energy for lithium insertion. This consideration is consistent with their flat plateau at 1.75 V (Fig. 4.7a, b, and c), which corresponds to lithium insertion into crystalline anatase. For sample T100W, lattice strain is 2.6×10^{-2} and rest potential is 3.23 V. These values are higher than those of samples TR, T350W, and T350. This indicates that there is a larger distribution of site energy for lithium insertion in this sample than that of other three samples, which appears on the discharge curve in Fig. 4.7d as the decrease in a flatness of the 1.75 V plateau. For sample TA, rest potential is the highest among the samples, 3.39 V, and lattice strain is thought to be relatively large compared with other samples. So, the site energy distribution is thought to be broad, and lithium ions are inserted and extracted at wider potential range as shown in Fig. 4.7e.

Sample TA has an amorphous structure containing water. Because of the reaction between water molecules and lithium ions inserted, and its less compact structure than crystalline one, sample TA shows a comparatively large discharge capacity down to 0.5 V of about $800 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$. For all five samples discharged down to 0.5 V, almost all the lithium ions inserted are impossible to be extracted.

4.5 Summary

From the present work, the following conclusions are obtained:

1. The two titania samples prepared under hydrothermal conditions (T350 and T100W) were composed of both amorphous and crystalline regions. In their particles, the crystalline particles with polygonal shape seemed to be covered with amorphous TiO_2 .
2. Lithium insertion into the amorphous region took place with gradual potential change in the potential range from 2.5 V to 1.75 V, and lithium was inserted into the crystalline region with a plateau around 1.75 V. The ratio of the amorphous region to the crystalline region was determined by that of the amount of lithium inserted in those two potential ranges.
3. Value of lattice strain and rest potential seems to represent a distribution degree of site energy for inserted lithium ions.

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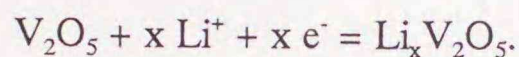
Chapter 5

Crystalline V_2O_5

5.1 Introduction

Crystalline vanadium pentoxide (V_2O_5) has a quasi-layered structure as shown in Fig. 5.1. Each layer is built up from VO_5 square pyramids along crystallographic ab-plane, sharing their edges and corners. While four distances of vanadium-oxygen bonds which form bottom square are 0.177, 0.188, 0.188, and 0.202 nm, the apical one is very short (0.154 nm) and corresponds to a double bond [1,2]. The layers are piled up along the c axis of the orthorhombic cell with weak sixth vanadium-oxygen bonds, whose bond length is 0.281 nm. Because of the presence of the sixth V-O bonds, structure of crystalline V_2O_5 has channels along the b-axis rather than layer structure with two dimensional gaps.

Study for lithium insertion/extraction reaction on V_2O_5 in order to develop electrodes for lithium batteries and electrochromic devices started from 1970's [3-9]. Lithium insertion and extraction reaction on V_2O_5 is expressed as follows;



Lithium ions are inserted not from ab-plane (basal plane) but from edge plane (ac-plane), and are thought to diffuse through channels along the b axis [10]. Schematic potential change curve of V_2O_5 down to 1.0 V (vs. Li^+/Li) with lithium insertion is shown in Fig. 5.2. There are four plateaus at 3.4, 3.2, 2.5, and 2.0 V, and their capacities are $\Delta x = 0.5, 0.5, 1.0$, and 1.0, respectively. Detailed structural change of V_2O_5 with lithium insertion and extraction has been studied by means of X-ray diffraction (XRD) [11-13], electron paramagnetic resonance (EPR) [14-16], X-ray absorption (XRA) [17], 7Li -nuclear magnetic resonance (7Li -NMR) [18]. Stability diagrams for $Li_xV_2O_5$ ($0 < x < 2$) around room temperature proposed by several authors are shown in Fig. 5.3 [16]. Although composition range of each phase differs among the diagrams mainly due to a difference in experimental conditions, such as current density and V_2O_5 sample used, it has been clearly shown that host structure changes in the order of α -, ϵ -, δ -, and γ - $Li_xV_2O_5$ phases with lithium insertion. Fig. 5.4 shows schematic representation of the structures of V_2O_5 and ϵ -, δ -, and γ - $Li_xV_2O_5$ phases [15]. The α -phase, though its structure is not shown in Fig. 5.4, has almost the same structure of pristine V_2O_5 except for slightly wider interlayer spacing between the layers of V-O square pyramids. In ϵ - and δ -phases, both widening of the spacing between V-O

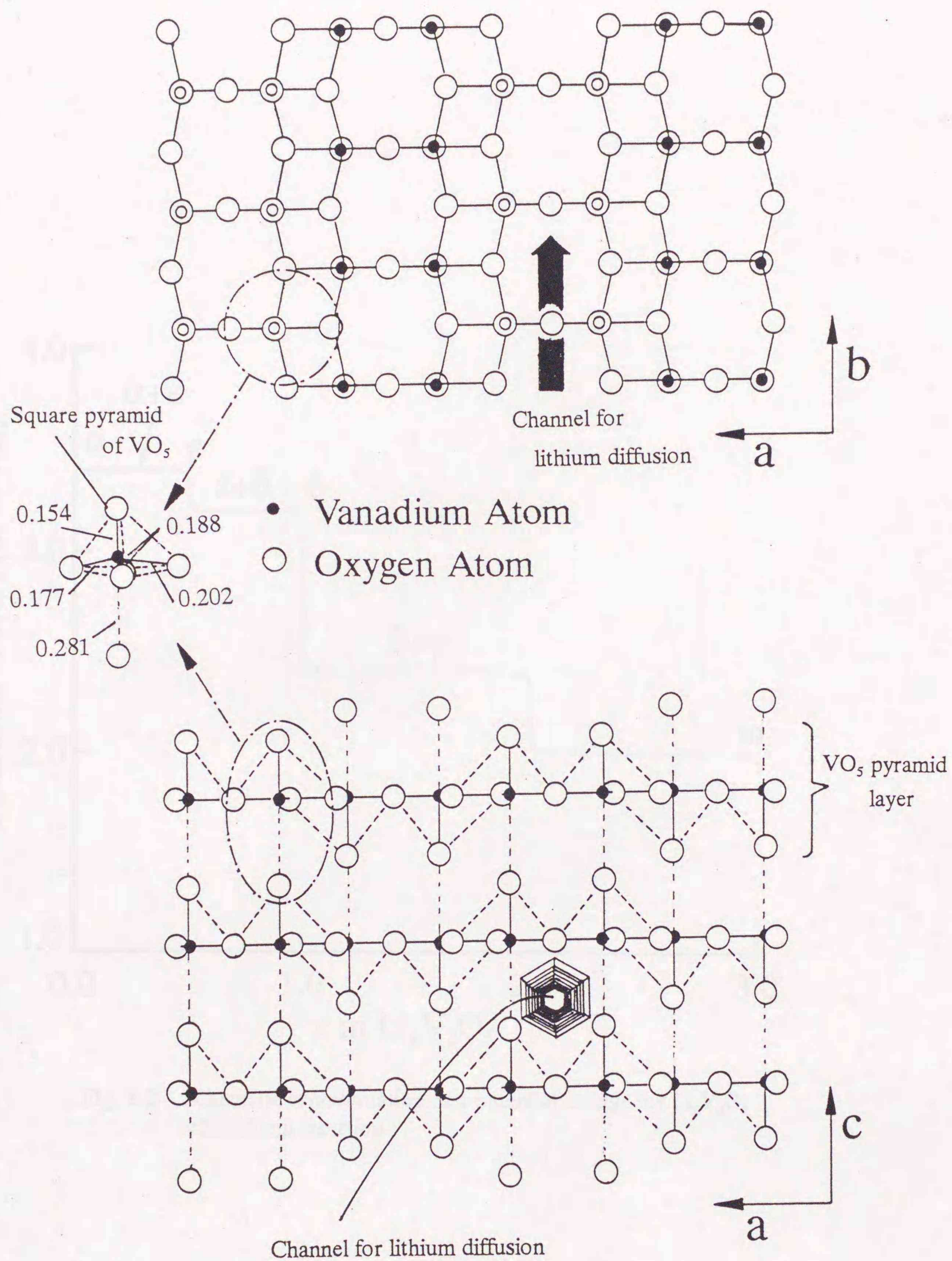


Fig. 5.1 Construction of V-O linkage in V_2O_5 structure.

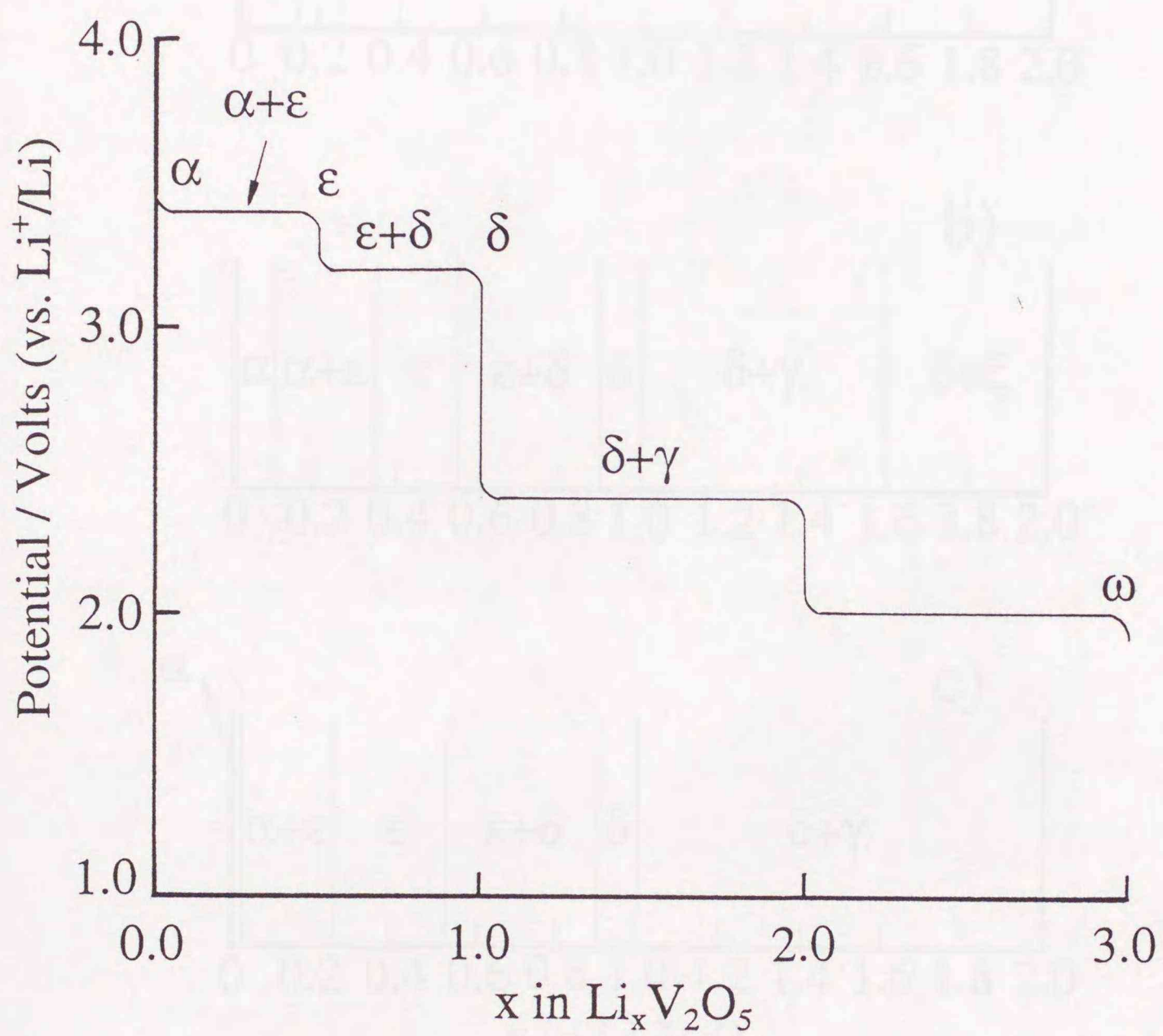


Fig. 5.2 Schematic representation of a potential change for $\text{Li}_x\text{V}_2\text{O}_5$ with lithium insertion.

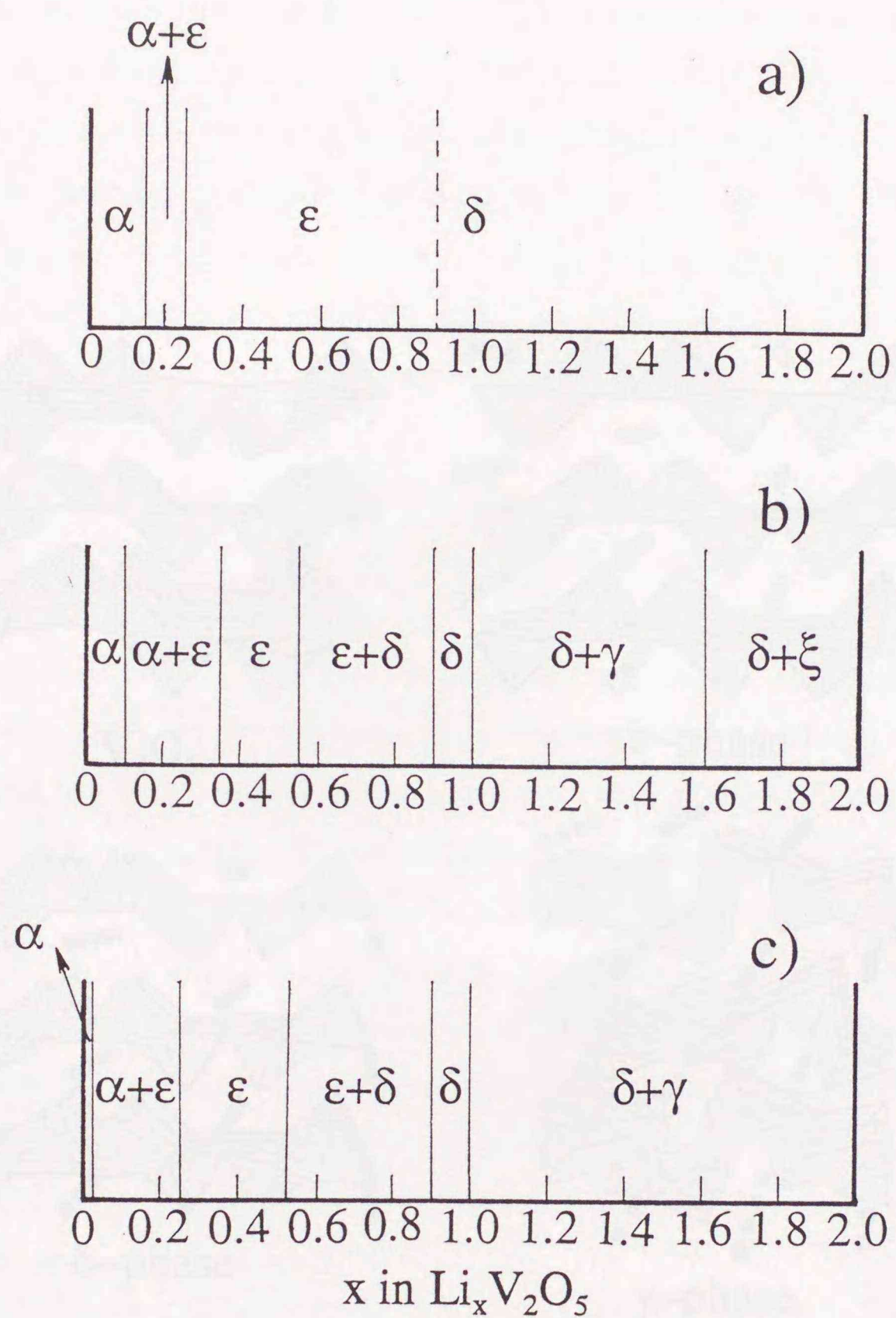


Fig. 5.3 Stability diagrams for $\text{Li}_x\text{V}_2\text{O}_5$ ($0 < x < 2$) phases as determined by several authors: a) Ref. [5.11]; b) Ref. [5.36]; and c) Ref. [5.15].

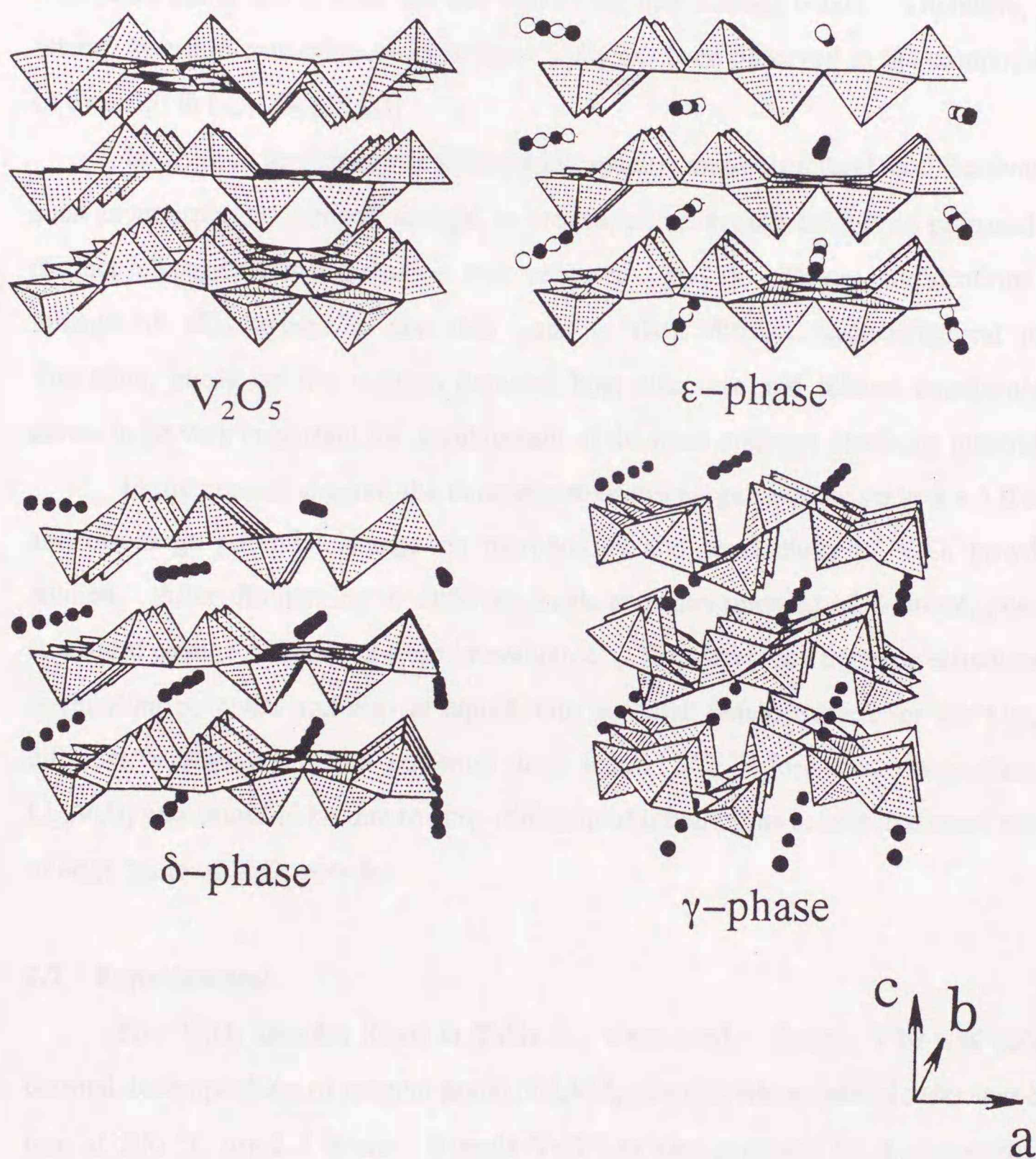


Fig. 5.4 Schematic representation of the structures of V_2O_5 and the ϵ -, δ -, and γ -phases. Open and closed circles represent vacant and occupied sites for lithium ions.

layers and puckering of V-O sheets by the rotation of pyramids, resulting in the increase of c-parameter and the shrinkage of a-parameter, respectively, occur, but the V_2O_5 skeleton is maintained as shown in Figs. 5.4b and c. The degree of puckering of V-O sheets increases from α - to δ - through ϵ -phases. By further insertion of lithium above $x = 1.0$, layer puckering becomes more pronounced than in the δ -phase and, as a consequence, the VO_5 pyramids alternate up and down: the structure is named γ -phase (Fig. 5.4). The structural change from δ - to γ -phase causes the destruction of composite cathode because of pronounced distortion of structure and also of expansion along c-axis. Therefore, reversible lithium insertion/extraction on crystalline V_2O_5 has been observed in the composition range of $0 < x < 1.0$ in $Li_xV_2O_5$ [19,20]

In order to improve reversibility and capacity, many structural modifications of V_2O_5 , such as amorphous, xerogel, aerogel, α -bronze, and β -bronze have been prepared and their distinct electrochemical behavior was reported [21-33]. These modifications differ in linkage of VO_5 pyramids, and this leads to their distinct electrochemical properties. Therefore, study on the relation between host structure and lithium insertion/extraction seems to be very important for development of the most effective electrode material.

In the present chapter, the dependence of discharge capacity up to $x = 1.0$ above 3 V and discharge potential change on morphology and crystallinity of V_2O_5 powders were studied. After discharging to different levels and then opening of a circuit, potential and structural change of samples were investigated. The difference between structures at non-equilibrium potential and also at equilibrium potential was observed for the samples with different crystallinity. The potential drop below 3 V before the composition reached $Li_{1.0}V_2O_5$ was found to be due to slow diffusion of lithium ions in host and small surface area of edge plane of V_2O_5 powders.

5.2 Experimental

Five V_2O_5 samples listed in Table 5.1 were used. Sample V30 was prepared by thermal decomposition of reagent grade NH_4VO_3 powder, whose particle size was below 60 μm , at 300 °C for 1.5 hours. Sample V65 was also prepared by decomposition of the NH_4VO_3 powder at 600 °C for 1.5 hours and then followed by heating at 650 °C for 7 hours. Flaky crystals of V_2O_5 with about 180 μm , sample VS, were synthesized using B_2O_3 flux by

Table 5.1 Specific surface area and X-ray data of V_2O_5 samples.

Sample Code	Specific Surface Area ($m^2 \cdot g^{-1}$)	Lattice Parameters (nm)			Intensity Ratio I_{001}/I_{110}	Rest Potential (V)
V30	11.8	1.151	0.3564	0.4376	1	3.58
V65	1.5	1.152	0.3562	0.4372	2	3.50
VS	1.2	1.151	0.3566	0.4363	362	3.52
VS3	10.4	1.151	0.3564	0.4368	13	-
VS6	23.0	1.151	0.3564	0.4368	2	-

slow cooling with a rate of about $1.7 \text{ K}\cdot\text{min}^{-1}$ from 750°C . Samples VS3 and VS6 were obtained by grinding VS sample in an agate mortar for 30 and 60 minutes, respectively.

Specific surface area of these five samples was measured by means of an adsorption of nitrogen gas at the liquid nitrogen temperature. XRD measurements were performed on the pristine samples and the lithiated ones by using $\text{Cu K}\alpha$ radiation. Lattice parameters of the pristine V_2O_5 samples used were determined from 020, 601, 021, 412, 710, and 321 diffraction lines by referring to the internal standard of crystalline Si powders. The intensity ratio of 001 peak to 110 peak, I_{001}/I_{110} , depends strongly on the preferred orientation of V_2O_5 crystals in a X-ray sample holder, so that it was adopted as a measure of extension of VO_5 square pyramid sheets, i.e., [001] plane. UV-VIS absorption spectra of samples were recorded by diffuse reflectance mode with a scanning speed of $5 \text{ nm}\cdot\text{min}^{-1}$.

Two electrode cell with composite cathode and anode for electrochemical measurements was fabricated in the same way as described in Section 2.3.3. Rest potential of the cathode was measured after the cell was assembled and settled for 12 hours, before the measurements of discharge-charge performance. Potential changes with time during discharging and charging at a constant current of $10 \text{ mA}\cdot\text{g}^{-1}$ were recorded. All these electrochemical tests were carried out in the glove box filled with argon gas.

Structure of the samples discharged down to different depth was investigated by means of XRD. Immediately after discharging down to certain depth, the cathode was taken out from electrochemical cell and its XRD pattern was measured without rinsing (sample in non-equilibrium). Potential of the discharged cathode was traced after the circuit was opened, and after reaching the equilibrium potential, structure of samples was also studied by XRD (sample in equilibrium).

5.3 Results

5.3.1 Effect of heating temperature

a) structural characterization

Specific surface area of V30, V65, and VS is summarized in Table 5.1. The higher the treatment temperature, the smaller the surface area. Sample V30 has about 10 times larger surface area than samples V65 and VS.

The XRD patterns of V30, V65, and VS are shown in Fig. 5.5. Diffraction peaks become broader with the decrease in heating temperature. The results indicate that sample

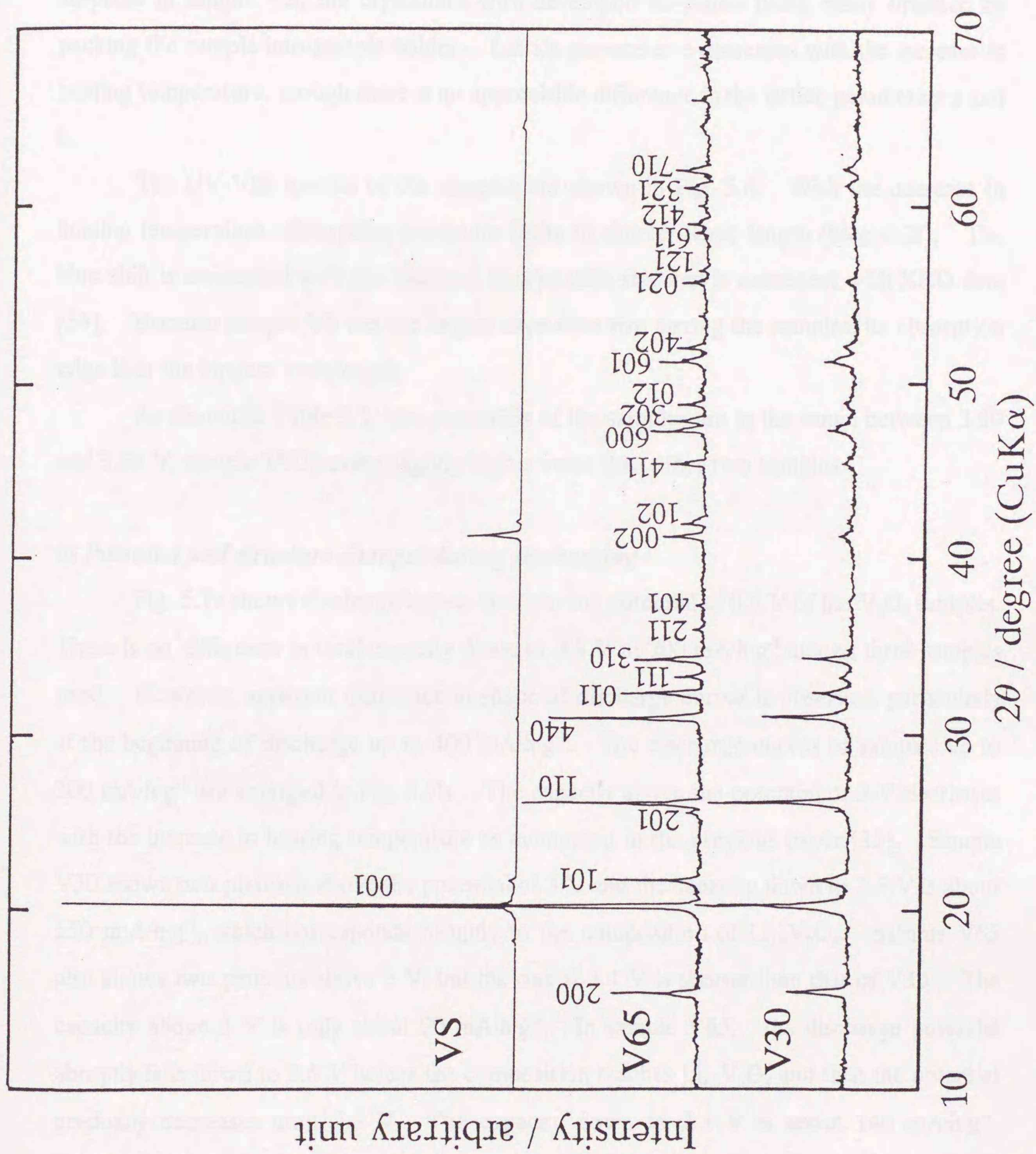


Fig. 5.5 The X-ray powder patterns of the V_2O_5 samples.

V30 has the smallest crystallite size among three samples. Diffraction patterns of sample VS shows a sharp and strong 00 l peaks and relatively weak peaks 200, 101, 110, and 440, indicating strong orientation of ab-planes. Intensity ratio, I_{001}/I_{110} and lattice parameters of V30, V65, and VS are also listed in Table 5.1. The intensity ratio I_{001}/I_{110} of sample VS is much larger than that of samples V30 and V65. This indicates an enhanced development of ab-plane in sample VS, the crystallites with developed ab-planes being easily oriented by packing the sample into sample holder. Lattice parameter c decreases with the increase in heating temperature, though there is no appreciable difference in the lattice parameters a and b .

The UV-VIS spectra of the samples are shown in Fig. 5.6. With the decrease in heating temperature, absorption maximum shifts to shorter wave length (blue shift). The blue shift is concerned with the decrease in crystallite size and is consistent with XRD data [34]. Because sample VS has the largest crystallite size among the samples, its absorption edge is at the longest wavelength.

As shown in Table 5.1, rest potentials of the samples are in the range between 3.50 and 3.58 V, sample V30 having slightly higher value than other two samples.

b) Potential and structure changes during discharging

Fig. 5.7a shows discharge curves down to the potential of 0.5 V of the V_2O_5 samples. There is no difference in total capacity down to 0.5 V of 700 mA·h·g⁻¹ among three samples used. However, apparent difference in shape of discharge curves is observed, particularly at the beginning of discharge up to 400 mA·h·g⁻¹. The discharge curves of samples up to 300 mA·h·g⁻¹ are enlarged in Fig. 5.7b. The capacity above the potential of 3 V decreases with the increase in heating temperature as mentioned in the previous paper [35]. Sample V30 shows two plateaus above the potential of 3 V and the capacity down to 2.5 V is about 150 mA·h·g⁻¹, which corresponds roughly to the composition of $Li_{1.0}V_2O_5$. Sample V65 also shows two plateaus above 3 V, but the one at 3.4 V is shorter than that of V30. The capacity above 3 V is only about 90 mA·h·g⁻¹. In sample V65, the discharge potential abruptly falls down to 2.5 V before the composition reaches $Li_{1.0}V_2O_5$ and then the potential gradually decreases until 2.3 V. The capacity down to 2.3 V is about 140 mA·h·g⁻¹. Sample VS shows no obvious plateau above 3 V and the capacity down to 3 V is only 40

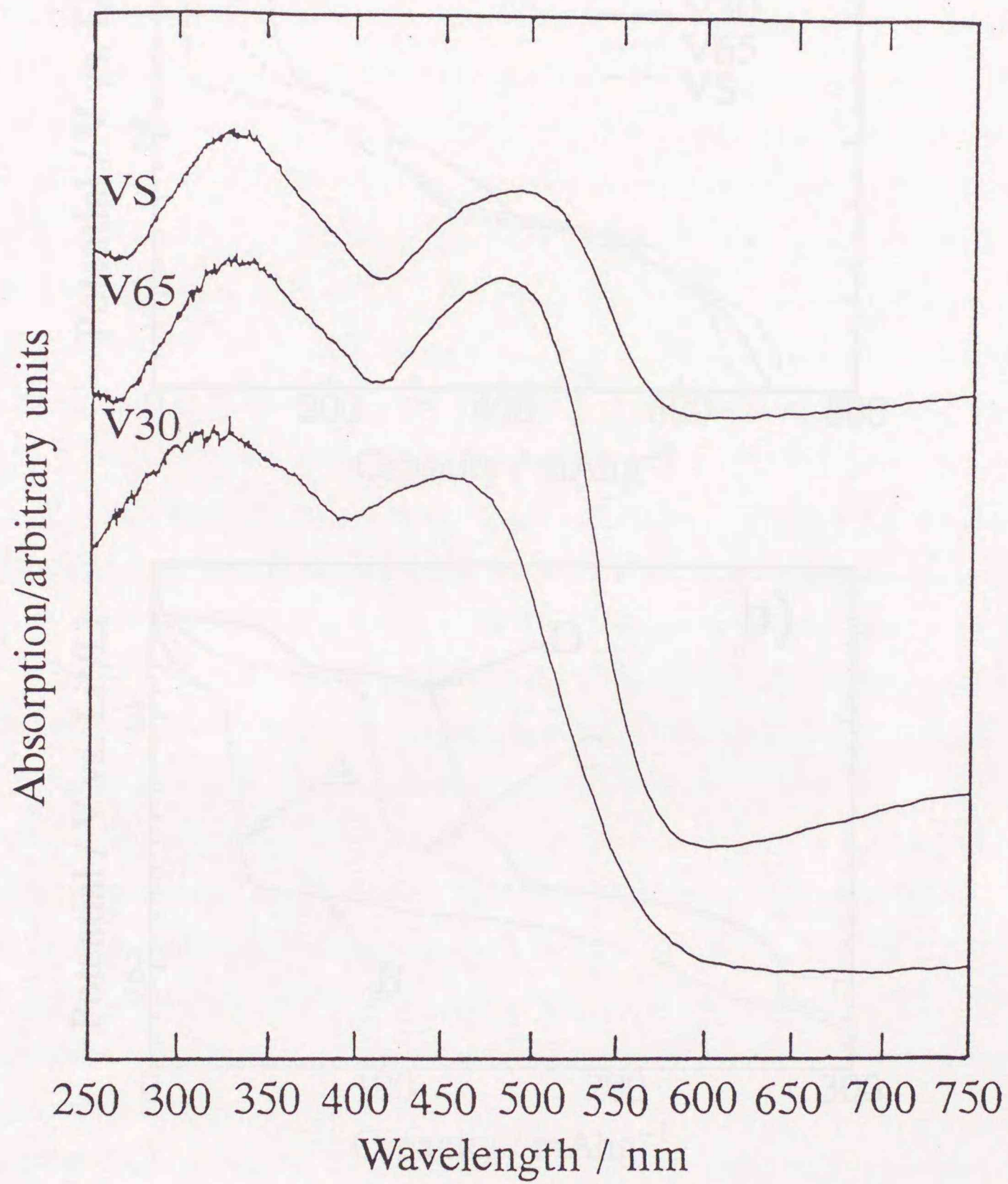


Fig. 5.6 The UV-VIS spectra of the V_2O_5 samples.

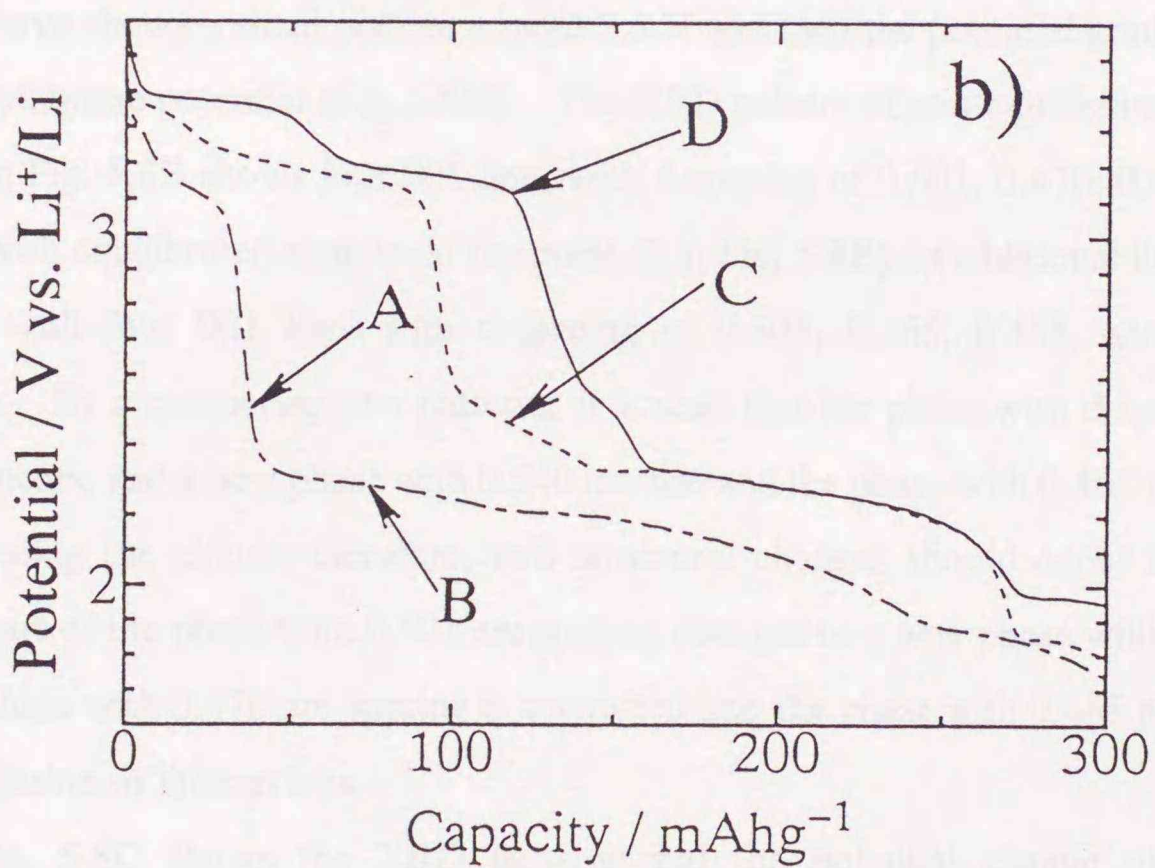
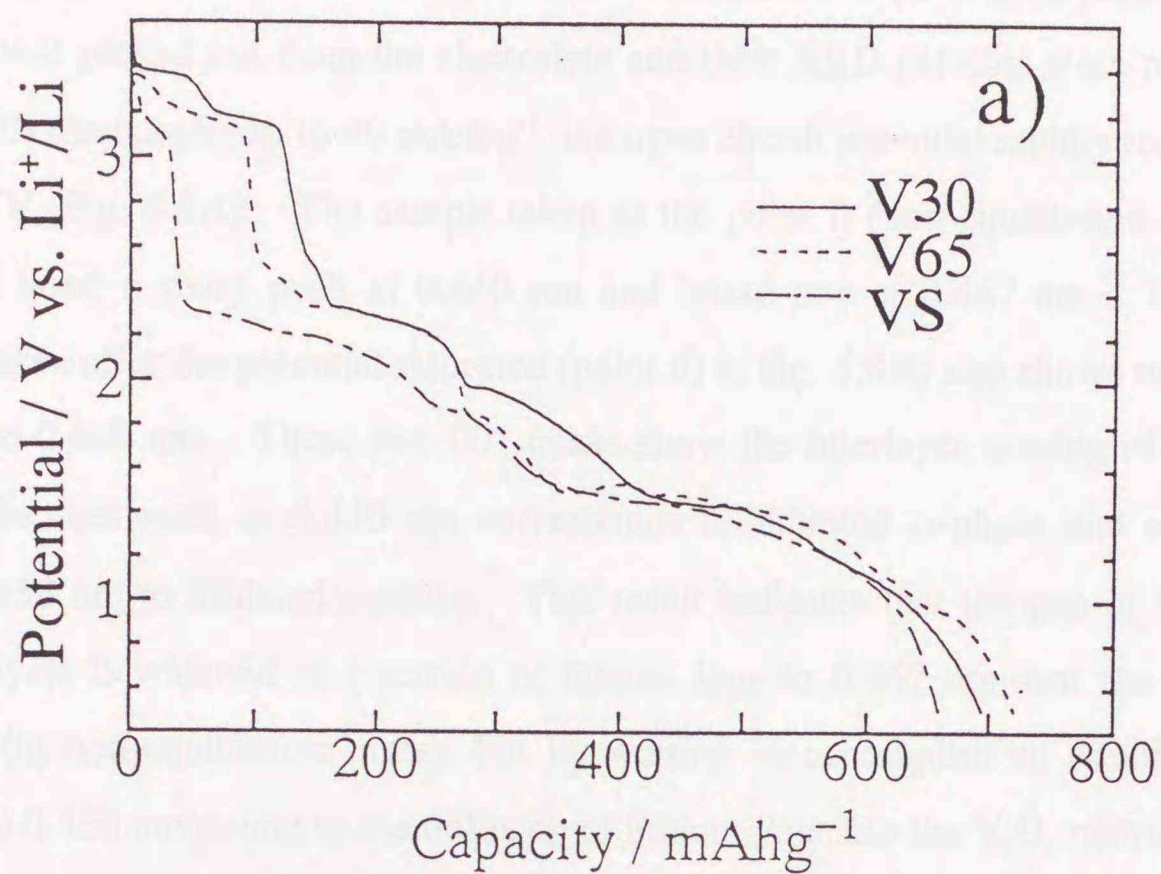


Fig. 5.7 The discharge curves of V_2O_5 samples down to 0.5 V (vs. Li^+/Li) a) and up to 300 $mAhg^{-1}$ b).
The symbols A-D are referred to following Fig. 3A-D.

$\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$. The discharge potential drops to about 2.3 V and then decreases gradually down to 2.2 V, the capacity down to 2.2 V being about $120 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$.

The changes of potential after discharging down to different depths A to D are recorded (Fig. 5.8) as shown in Fig. 5.7b. At different steps in each potential curve, the cathode was picked out from the electrolyte and their XRD patterns were measured. For sample VS discharged up to $40 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$, the open circuit potential rapidly recovers to reach above 3 V (Fig. 5.8A). The sample taken at the point i) (non-equilibrium sample) shows two 001 lines; a sharp peak at 0.440 nm and broad one at 0.467 nm. The equilibrium sample taken after the potential saturated (point ii) in Fig. 5.8A) also shows two 001 lines, at 0.440 and 0.448 nm. These two 001 peaks show the interlayer spacing of VO_5 pyramids sheets, the first peak at 0.440 nm corresponds to lithiated α -phase and second peak at 0.467-0.458 nm to lithiated ϵ -phase. This result indicates that the gap of V-O pyramidal square layers is widened by insertion of lithium ions to 0.467 nm near the surface of the cathode (in non-equilibrium state), but by waiting to accomplish an equilibrium the gap shrinks to 0.458 nm owing to the diffusion of lithium ions into the V_2O_5 matrix.

For VS sample discharged up to $75 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ (point B in Fig. 5.7b), the potential change curve shows a small plateau around 2.5 V and then the potential gradually increases to the equilibrium potential (Fig. 5.8B). The XRD pattern of non-equilibrium sample at the point i) in Fig. 5.8B shows four 001 lines with d-spacing of 0.501, 0.470, 0.455, and 0.440 nm, but with equilibrated sample (at the point ii) in Fig. 5.8B) an additional line at 0.540 nm together with four 001 lines with d-spacing of 0.501, 0.465, 0.455, and 0.440 nm is observed. By a comparing two patterns, it is seen that the phase with d-spacing of 0.470 nm disappears, and a new phase with 0.540 nm line and the phase with 0.465 nm are formed. After opening the circuit, therefore, two structural changes should occur in the lithiated V_2O_5 ; a part of the phase with 0.501 nm spacing changes to a new phase with 0.540 nm line and the phase with 0.470 nm spacing is converted into the phase with 0.465 nm spacing due to the diffusion of lithium ions.

Fig. 5.8C shows the XRD patterns and the potential change of sample V65 discharged up to $120 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ at the potential of 2.5 V (point C in Fig. 5.7b). The potential increases gradually after opening the circuit, much slower compared with sample VS discharged down to the same potential (Fig. 5.8A). There is no difference in XRD

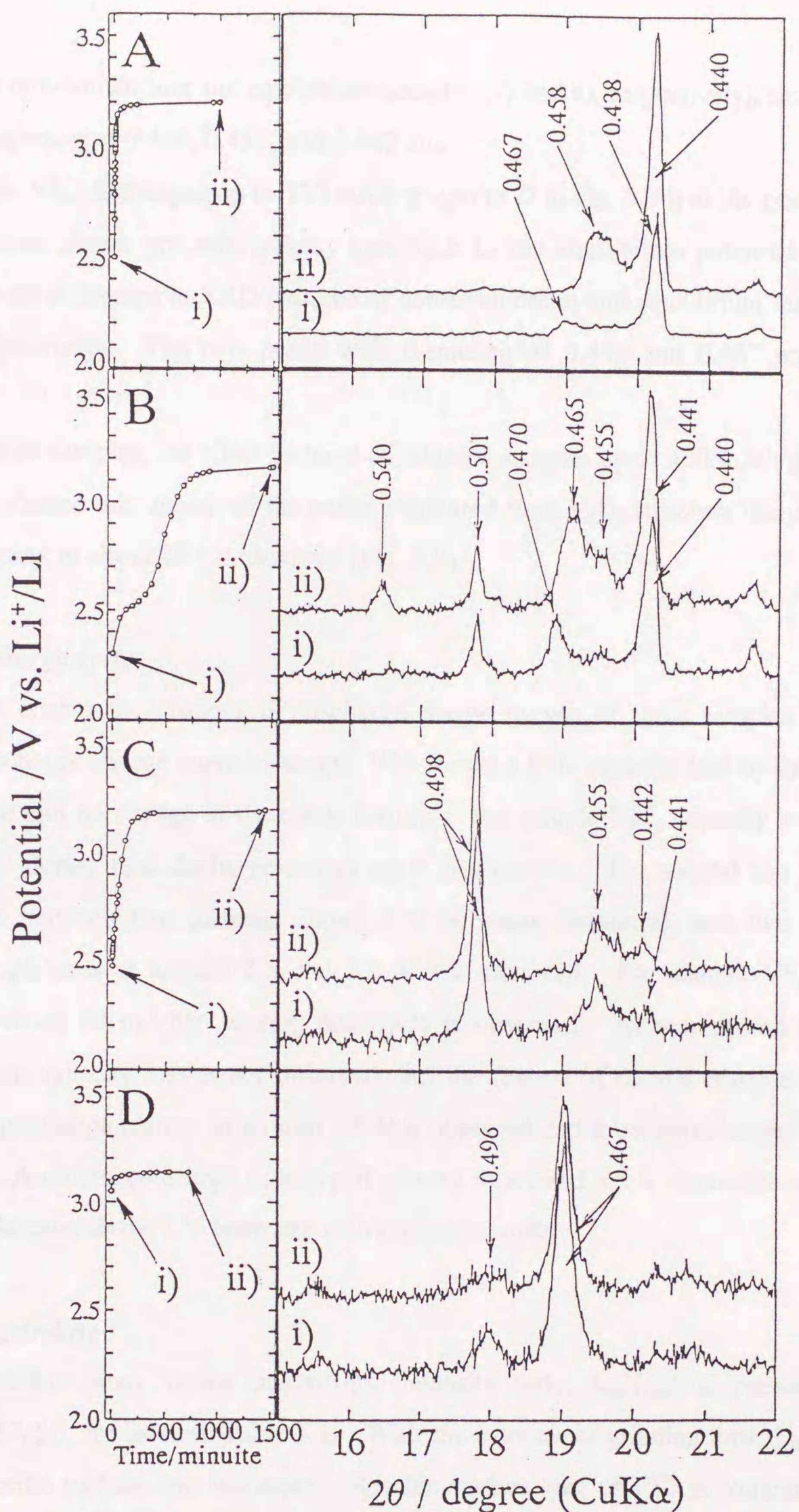


Fig. 5.8 The X-ray powder patterns and the potential changes after opening circuit of discharged samples. The numbers indicated are d-spacing in nano meter unit.

A) sample VS discharged up to $40 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$,

B) sample VS discharged up to $75 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$,

C) sample V65 discharged up to $120 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$,

D) sample V30 discharged up to $120 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$.

The symbols i) and ii) are corresponding with each other in potential change curve and X-ray powder patterns.

patterns between non-equilibrium and equilibrium samples (i) and ii), respectively), showing 001 lines with d-spacing of 0.498, 0.455, and 0.442 nm.

For sample V30 discharged up to $120 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ (point D in Fig. 5.7b) at the potential of 3.15 V, the open circuit potential quickly gets back to the equilibrium potential (Fig. 5.8D). There is no difference in XRD patterns of non-equilibrium and equilibrium samples (i) and ii), respectively). The two peaks with d-spacing of 0.496 and 0.467 nm are observed.

For the three samples, the XRD patterns of lithiated samples up to $400 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ are measured and confirmed that almost all the peaks originated from V_2O_5 structure disappear, and that a broad peak at about 18° is observed (Fig. 5.9).

c) Discharge-charge cycles

Fig. 5.10. shows the changes of discharge-charge curves of three samples with cycling. The discharge-charge curve of sample V30 shows a little capacity loss by cycling at least up to fifth and no change in the curve feature. For sample V65, capacity loss of about $20 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ during first discharge-charge cycle is observed. For second and third cycles, difference between two plateaus above 3 V becomes distinctive, and two new discharge-charge plateaus at around 2.5 and 3.5 V are observed. For sample VS, the capacity loss of about $50 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ during first cycle is observed. At second and third cycles, a significant capacity loss is not observed, but the feature of curves changes with cycling; a discharge-charge plateau at around 3.5 V is observed and it becomes longer with cycling number. A discharge-charge capacity of plateau at around 2.5 V decreases and a capacity of two plateaus above 3 V increases with cycling number.

5.3.2 Effect of grinding

Specific surface area, lattice parameters, intensity ratio, I_{001}/I_{110} , of pulverized samples, VS3 and VS6, are listed in Table 5.1. With the increase of grinding time, I_{001}/I_{110} decreases and specific surface area increases. Specific surface area of VS3 is comparable to that of V30, where lithium ions are fully inserted up to the composition of $\text{Li}_{1.0}\text{V}_2\text{O}_5$ at above 2.5 V, but the intensity ratio I_{001}/I_{110} of VS3, as a measure of extension of VO_5 square pyramid layers, is still ten times larger than that of V30. For sample VS6, the specific surface area and the intensity ratio I_{001}/I_{110} are two times larger than those of V30. The c-

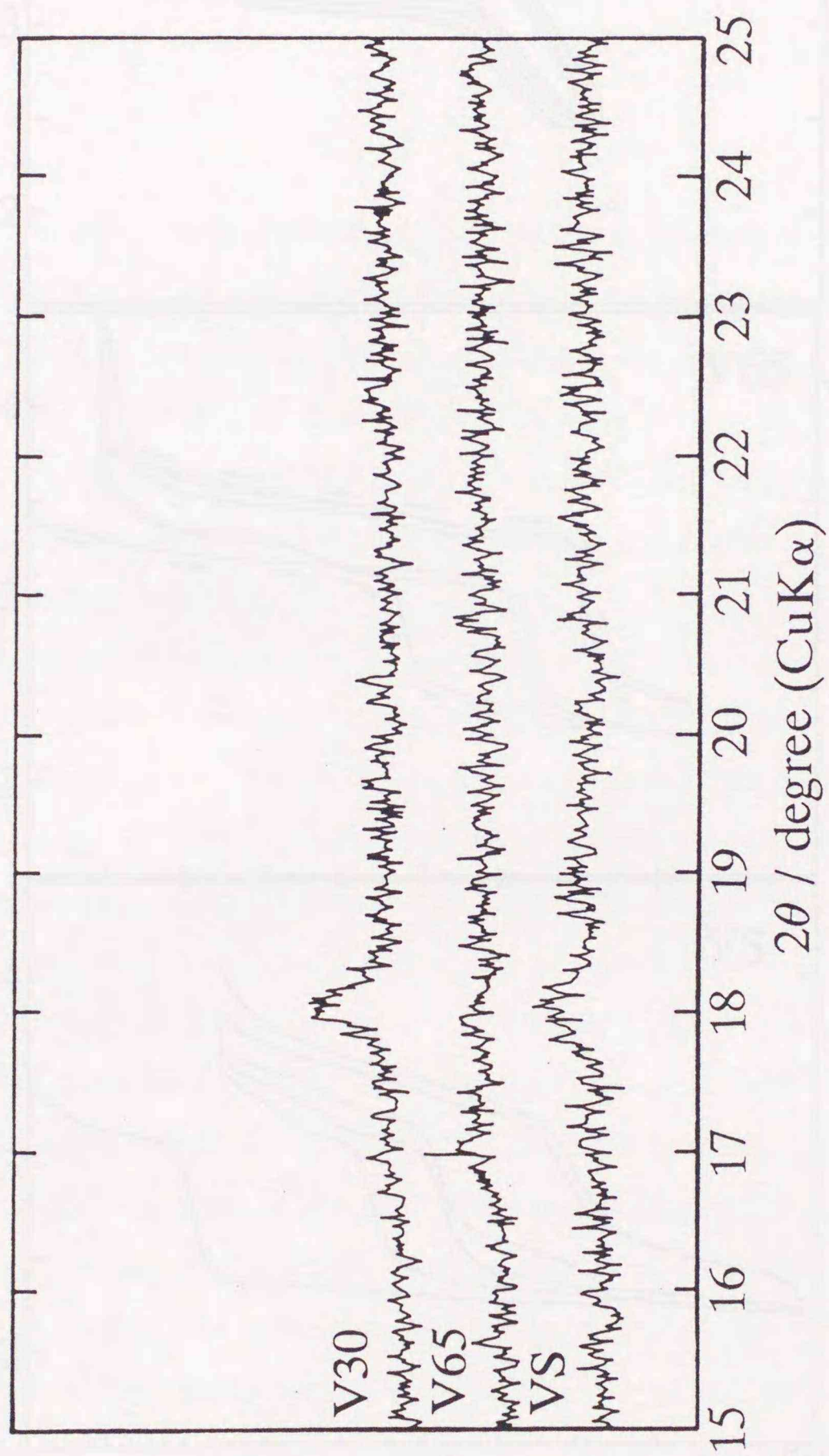


Fig. 5.9 XRD patterns of V_2O_5 samples discharged up to $400\text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$.

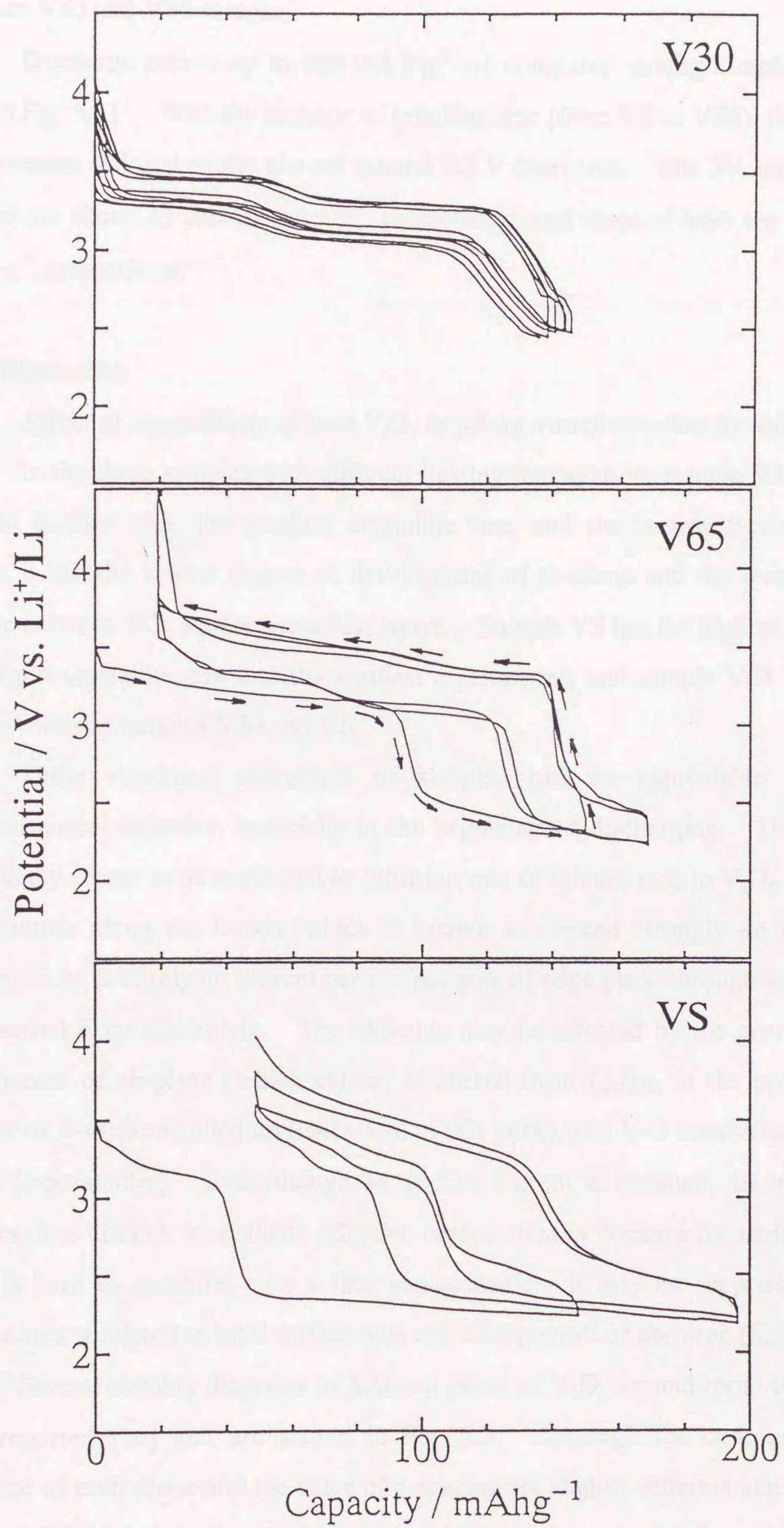


Fig. 5.10 The discharge-charge curves of V_2O_5 samples.

parameter of ground samples is larger than that of VS, but there is no difference in the value between VS3 and VS6 samples.

Discharge curves up to $400 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ are compared among samples VS, VS3, and VS6 in Fig. 5.11. With the increase of grinding time (from VS to VS6), the capacity above 3V increases and that of the plateau around 2.3 V decreases. The 3V and 2.3V capacities of VS3 are about 75 and $50 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$, respectively, and those of VS6 are about 110 and $0 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$, respectively.

5.4 Discussion

5.4.1 Effect of crystallinity of host V_2O_5 in phase transformation by lithiation

In the three samples with different heating temperature, sample V30 has the largest specific surface area, the smallest crystallite size, and the largest c-parameter, in other words, it has the lowest degree of development of ab-plane and the weakest V-O bonds linkage between VO_5 square pyramidal layers. Sample VS has the highest crystallinity, i.e., the largest crystallite size and the smallest c-parameter, and sample V65 is located at the middle between samples V30 and VS.

These structural characters of samples had an appreciable effect on their electrochemical behavior, especially in the beginning of discharging. This effect of host crystallinity seems to be attributed to diffusion rate of lithium ions in V_2O_5 structure, i.e., in the channels along the b-axis, which is known to depend strongly on effective current density, more precisely on current per surface area of edge plane through which lithium ions are inserted from electrolyte. The diffusion may be affected by the crystallinity, such as enlargement of ab-plane (which can be estimated from I_{001}/I_{110} in the present work), the number of V-O sheets piled up (half width of 001 peak), and V-O bond strength linking VO_5 sheets (c-parameter). Even though an applied current is constant, $10 \text{ mA}\cdot\text{g}^{-1}$, for every samples, it is difficult to evaluate effective current density because the surface area of edge plane is hard to measure. As a first approximation, it may be supposed that the edge surface area is related to total surface area and enlargement of ab-plane (I_{001}/I_{110}).

Several stability diagrams of lithiated phase of V_2O_5 around room temperature have been reported [16] and are shown in Fig. 5.3. Although the composition ranges of existence of each phase and the value of c-spacing are slightly different among the diagrams reported [11-13,16] as discussed in section 5.1, it is the same in all reports that the phase

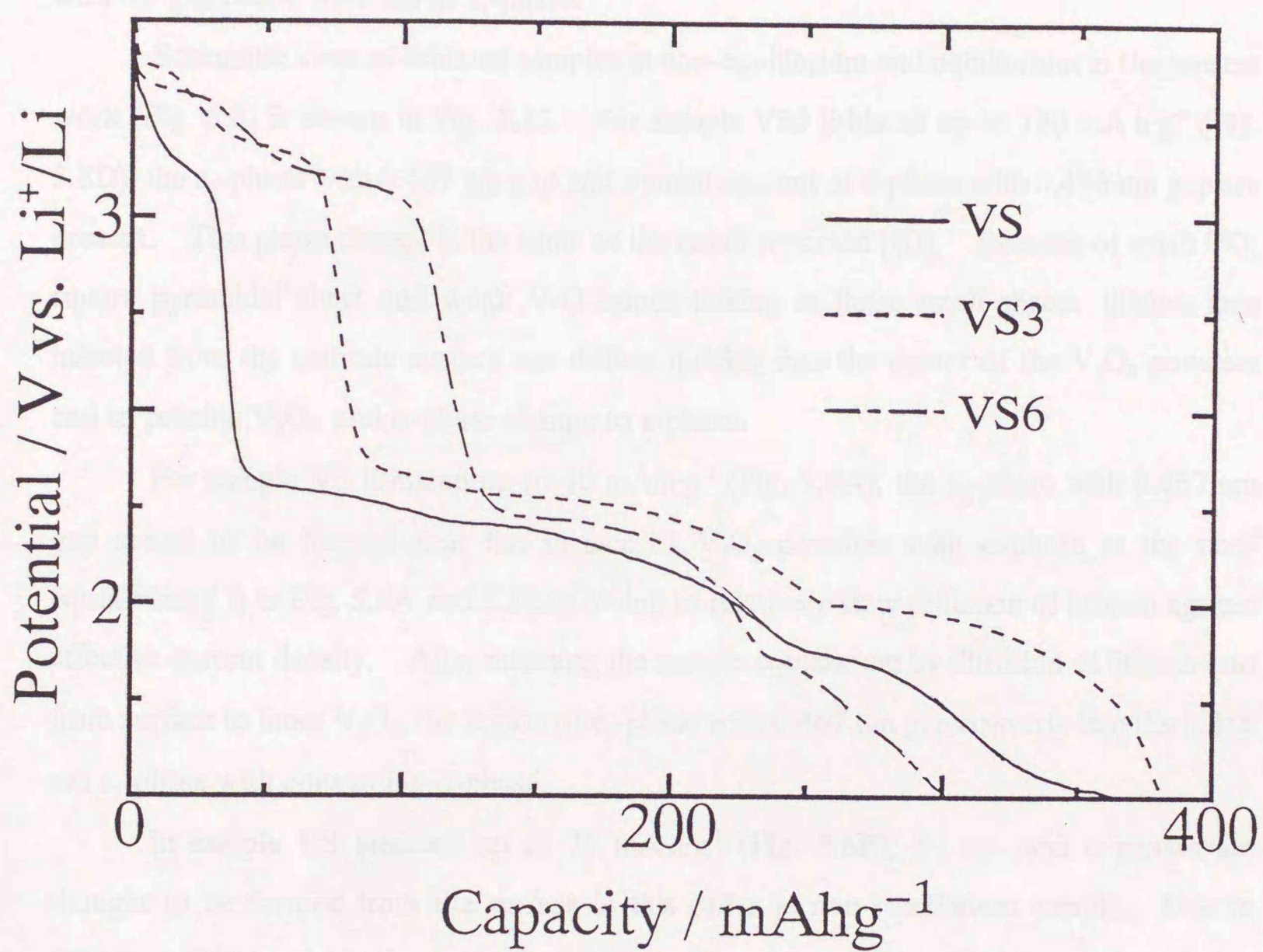


Fig. 5.11 The discharge curves of ground V_2O_5 samples.

changes from pristine V_2O_5 to α -, ϵ -, δ -, and γ -phase in order, and V_2O_5 skeleton is maintained up to δ -phase. Pecquenard et al. [15,16] reported that a part of γ -phase dissolves into electrolyte in the form of VO_2^+ ions during lithium insertion in the range of $1.0 < x < 2.0$. From these reports, the lithiated phases with 0.44, 0.45-0.47, and 0.50 nm gap are attributed to α -, ϵ -, and δ -phase, respectively, and the phase with 0.54 nm spacing is assigned to γ -phase. The ϵ -phase with 0.47 nm gap is named as ϵ_2 -phase and the phase with the gap below 0.47 nm as ϵ_1 -phase.

Schematic view of lithiated samples at non-equilibrium and equilibrium in the present work (Fig. 5.8) is shown in Fig. 5.12. For sample V30 lithiated up to $120 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ (Fig. 5.8D), the ϵ_2 -phase with 0.467 nm gap and a small amount of δ -phase with 0.496 nm gap are present. This phase change is the same as the result reported [20]. Because of small VO_5 square pyramidal sheet and weak V-O bonds linking in these small sheets, lithium ions inserted from the cathode surface can diffuse quickly into the center of the V_2O_5 powders and so pristine V_2O_5 , and α -phase change to ϵ -phase.

For sample VS lithiated up to $40 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ (Fig. 5.8A), the ϵ_2 -phase with 0.467 nm gap seems to be formed near the surface of V_2O_5 powders with α -phase at the non-equilibrium (i) in Fig. 5.8A and 5.12A) owing to relatively slow diffusion of lithium against effective current density. After attaining the sample equilibrium by diffusion of lithium ions from surface to inner V_2O_5 , the region of ϵ_2 -phase with 0.467 nm gap converts into the 0.458 nm ϵ_1 -phase with consuming α -phase.

In sample VS lithiated up to $75 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ (Fig. 5.8B), δ -, ϵ_2 -, and α -phases are thought to be formed from the surface in this order in non-equilibrium sample. Due to diffusion of lithium ions, the ϵ_2 -phase changes to the ϵ_1 -phase with consuming α -phase, and a part of δ -phase converts into γ -phase. Disappearance of ϵ_2 -phase may be explained to be due to very slower diffusion rate of lithium during the structural change from δ -phase to ϵ_2 -phase compared with that during change from ϵ_2 - to ϵ_1 -phase with a wide range of gaps of 0.465-0.455 nm. This implies that the stability of ϵ_2 -phase is lower than that of δ -phase and ϵ_1 -phase. The finding may be concerned with a partial molar entropy change with lithium concentration in lithiated phase of V_2O_5 reported by Pereira-Ramos et al. [36]. According to them, the partial molar entropy is minimum at $x = 0.3$ in $Li_xV_2O_5$, or ϵ_1 -phase with 0.45 nm gap, but it increases with the increase in the concentration until the composition of $x = 0.5$, or ϵ_2 -phase with 0.467 nm gap, and then gradually decreases until the composition of x

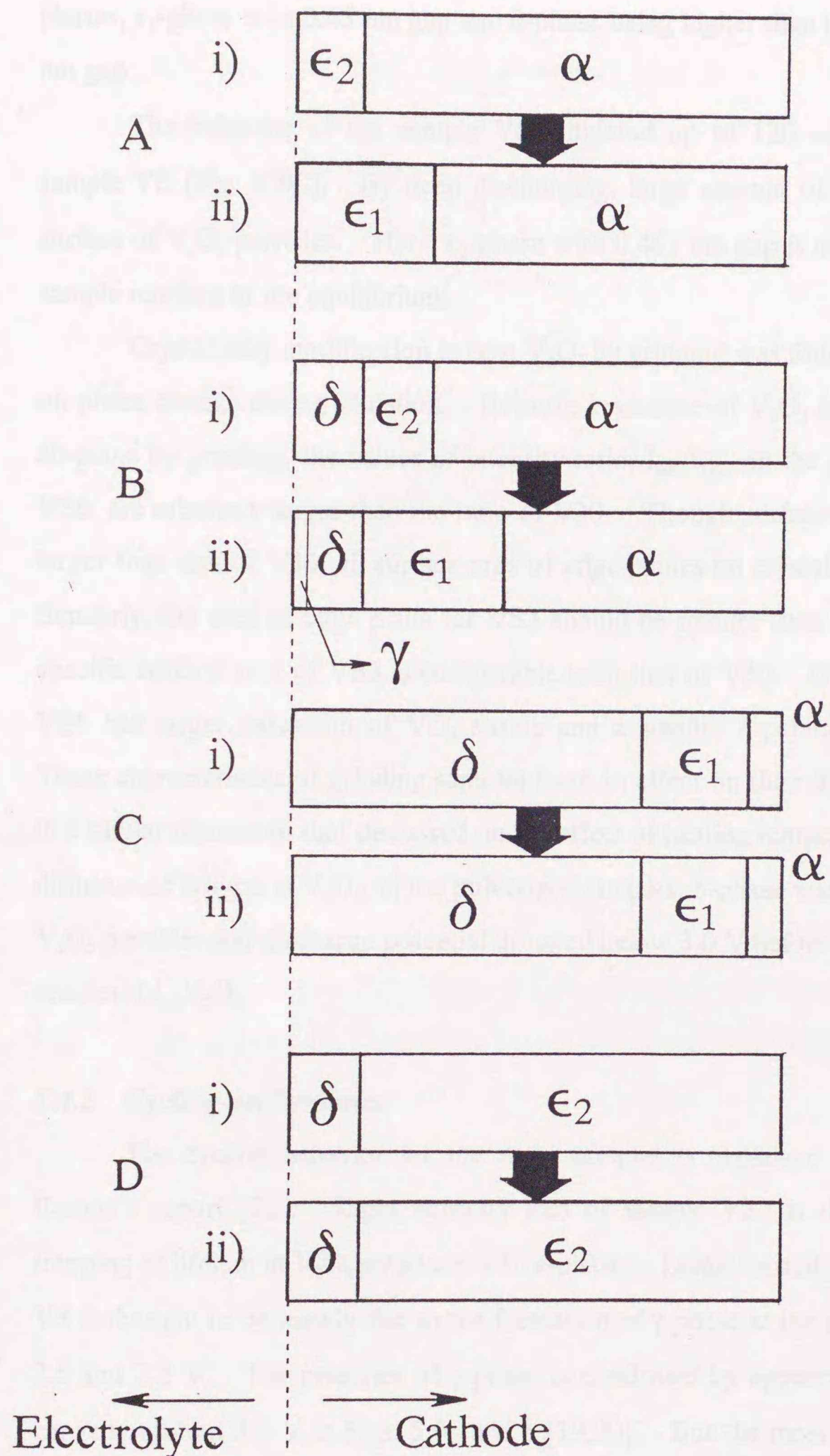


Fig. 5.12 Schematic view of lithiated samples at non-equilibrium i) and equilibrium ii). The symbols A-D are referred to Fig. 3A-D. ϵ_1 is ϵ -phase with the interlayer spacing of 0.47 nm and ϵ_2 is ϵ -phase with the interlayer spacing below 0.47 nm.

= 0.9, or δ -phase. These entropy variation is caused by the ordering of lithium ions in these phases, ϵ_1 -phase with 0.45 nm gap and δ -phase being higher than that in ϵ_2 -phase with 0.467 nm gap.

The behavior of the sample V65 lithiated up to $120 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ resembles that of sample VS (Fig. 5.8C). By deep discharging, large amount of δ -phase is formed at the surface of V_2O_5 particles. Here, ϵ_2 -phase with 0.467 nm gap is not observed even after the sample reached to the equilibrium.

Crystallinity modification in host V_2O_5 by grinding was found to have the same effect on phase change during lithiation. Because crystallite of V_2O_5 is cleaved mainly along its ab-plane by grinding, the values of intensity ratio, I_{001}/I_{110} , on the ground samples, VS3 and VS6, are relatively larger than the ratio of V30. Though surface area of VS6 is two times larger than that of V30, all surface area of edge planes on crystallites may not be so large. Similarly, the area of edge plane for VS3 should be smaller than that of V30, whereas the specific surface area of VS3 is comparable with that of V30. Grinding samples VS3 and VS6 has larger extension of VO_5 sheets and a smaller c-parameter than those of V30. These characteristics of grinding samples have an effect on their discharge curve (Fig. 5.11) in a similar manner to that discussed on the effect of heating temperature. Because of slow diffusion of lithium in V_2O_5 , in the pulverized samples, δ -phase was formed at the surface of V_2O_5 particles and discharge potential dropped below 3.0 V before the lithium concentration reached $\text{Li}_{1.0}\text{V}_2\text{O}_5$.

5.4.2 Cycling performance

The cycling behavior for the three samples is explained on the basis of Pereira-Ramos's report [32]. Slight capacity loss of sample V30 is thought to be caused by trapping of lithium in V_2O_5 structure with ϵ -phase. Large capacity loss of samples V65 and VS is thought to be mainly due to the formation of γ -phase at the potential plateau between 2.5 and 2.2 V. The presence of γ -phase is confirmed by appearance of charge-discharge capacity around 3.5 V in Figs. 5.9b and c [19,20]. But the most of lithium in the γ -phase can not be extracted because of poor electrical contact in the composite cathode due to large structural change of lithiated V_2O_5 . For samples VS and V65, the increase of 3V-capacity seems to be caused by destruction of large crystallites during the cycling (chemical grinding). Resulting small crystallites can lead to an easy diffusion of lithium as shown V30.

5.5 Summary

From the present work, the following conclusions are derived:

1. Total capacity down to 0.5 V is almost the same and about $700 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ among the samples with different crystallinity.
2. Effect of crystallinity on discharge potential especially on the early stage of discharge up to $400 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ was observed. Because, in the sample with high crystallinity, stacking and extension of VO_5 pyramids were developed and diffusion of lithium in V_2O_5 was very slow, δ - and γ -phases were formed near the surface. Therefore, in the samples with high crystallinity, discharge potential was dropped below 3.0 V before the composition reaches $\text{Li}_{1.0}\text{V}_2\text{O}_5$.
3. Structural change from δ -phase to ϵ_2 -phase with 0.47 nm gap during discharge is very slow compared with that from ϵ_2 -phase with 0.47 nm gap to ϵ_1 -phase with 0.45 nm gap.
4. V_2O_5 powders with high specific surface area, and small intensity ratio I_{001}/I_{110} , and large c-parameter, or with low crystallinity were better for cathode materials in lithium batteries.

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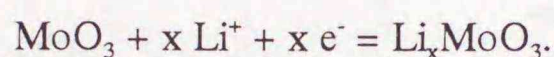
Chapter 6

Crystalline MoO₃

6.1 Introduction

Molybdenum trioxides (α -MoO₃) has a layered structure, as shown in Fig. 6.1, where Mo-O octahedra share their edges to make zigzag chain S along the a-axis and these zigzag chains connect with each other at corners of Mo-O octahedron to make a sheet in ac-plane. The sheets pile up along the b-axis with van der Waals force. Resultant structure belongs to the space group of D_{2h}¹⁶ of orthorhombic system with the lattice constants of a=0.3966, b=1.388, and c=0.3703 nm.

Lithium insertion into and extraction from the van der Waals gaps of α -MoO₃ have been studied since 1970's in order to investigate the possibility for cathode materials in lithium batteries [1-5] and electrochromic windows [6,7]. The reaction is expressed as;



α -MoO₃ has known to have wide composition range of $0 < x < 1.5$ in Li_xMoO₃ for reversible lithium insertion and provides high energy density of 670 W·h·kg⁻¹ [1-5]. Li_xMoO₃ shows some electronic conductivity and high Li⁺ mobility even at room temperature [8].

Molybdenum trioxide has some crystal forms, such as amorphous MoO₃ and β -MoO₃, and molybdenum bronze, and solid solutions with other transition metal oxides, such as MoO₃-V₂O₅, and MoO₃-WO₃ systems, are also known. For these materials, distinct electrochemical behavior has been reported [9-14].

In the present chapter, electrochemical lithium insertion/extraction was studied on three α -MoO₃ samples prepared at different temperatures with different crystallinity. The structural change during lithium insertion/extraction was followed by means of XRD measurements. The crystal structure of pristine MoO₃ was irreversibly converted into distorted one, accompanied by the increase in interlayer spacing of the van der Waals gap from 0.69 to 1.20 nm at the first discharge plateau of 2.8 V. The expansion of interlayer spacing with lithiation was up to 1.24 nm and larger than that reported previously, for which one of possibilities was shown to be the co-insertion of organic electrolyte molecules. No dependence of electrochemical behavior on crystallinity of MoO₃ was observed.

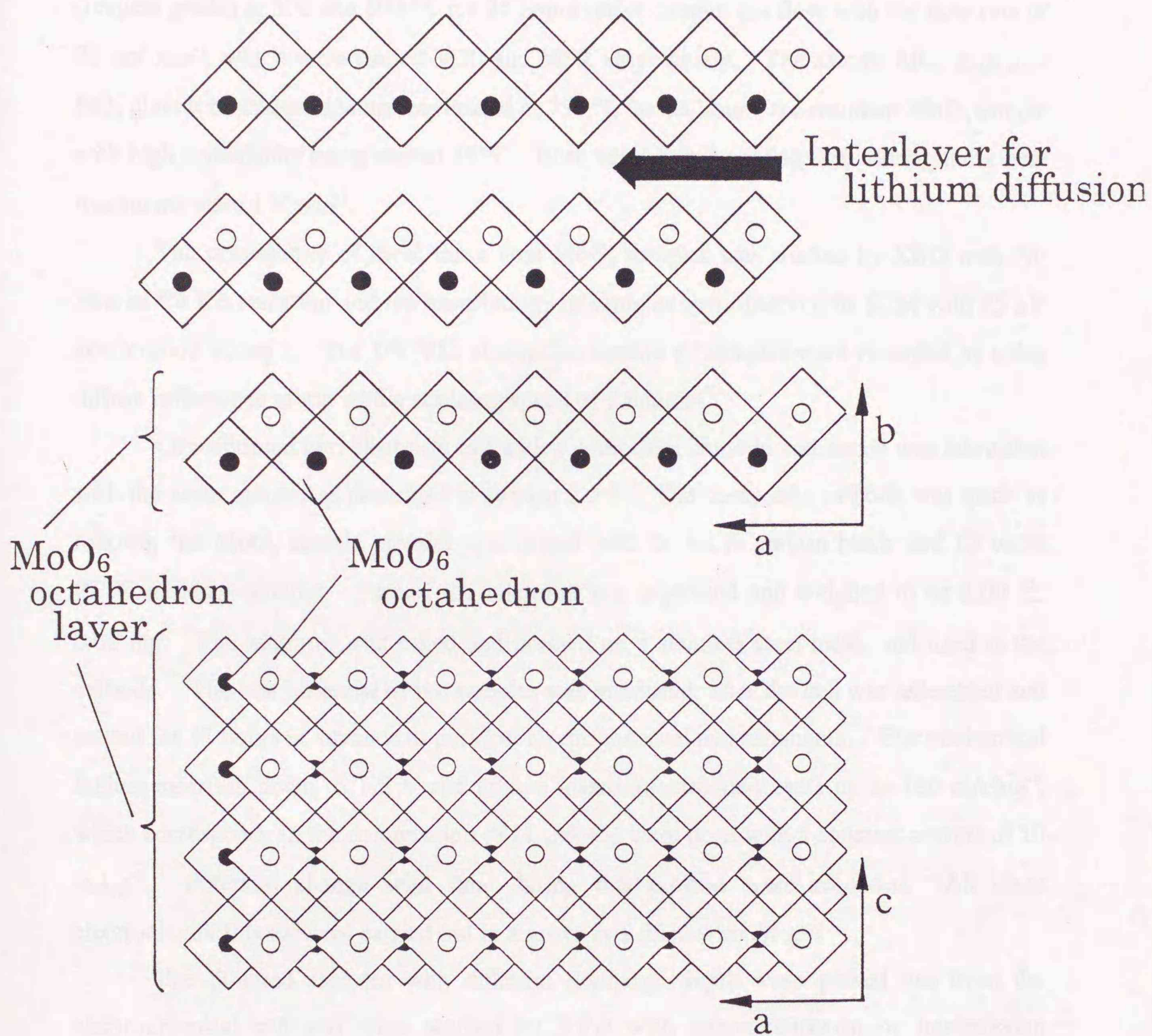


Fig. 6.1 Construction of MoO_6 octahedra in α - MoO_3 .

6.2 Experimental

MoO₃ samples were prepared by thermal decomposition of (NH₄)₆Mo₇O₂₄ powder (reagent grade) at 300 and 600 °C for 24 hours under oxygen gas flow with the flow rate of 20 cm³·min⁻¹, which were named M30 and M60, respectively. The sample M60 kept in a SiO₂ glass tube under vacuum was heated at 750 °C for 24 hours, the resultant MoO₃ sample with high crystallinity being named M75. Both heating and cooling rates during these heat treatments were 1 K·min⁻¹.

The crystallinity of these three host MoO₃ samples was studied by XRD with Ni-filtered Cu K α radiation and the morphology of samples was observed by SEM with 25 kV acceleration voltage. The UV-VIS absorption spectra of samples were recorded by using diffuse reflectance mode with a scanning speed of 5 nm·min⁻¹.

Conventional two electrode cell with a composite cathode and anode was fabricated with the same manner as described in section 2.3.3. The composite cathode was made as follows; the MoO₃ sample powder was mixed with 10 wt.% carbon black and 10 wt.% PTFE molding powder. Part of the mixtures was separated and weighed to be 1.00 $\pm$ 0.03 mg. The mixtures was rolled and pressed on a stainless steel mesh, and used as the cathode. The rest potential of the samples was measured, after the cell was assembled and settled for 12 hours in advance to perform electrochemical measurements. Electrochemical lithium insertion down to 1.5 V and lithium insertion/extraction cycle up to 180 mA·h·g⁻¹, which corresponds to the composition of Li_{1.0}MoO₃, were done with a constant current of 10 mA·g⁻¹. Potential change with time during this process were recorded. All these electrochemical tests were carried out in a grove box filled with Ar gas.

The lithiated samples with different discharge depth were picked out from the electrochemical cell and were studied by XRD with either reflection or transmission arrangement for incident X-ray beam. The thin composite cathode pressed onto stainless steel mesh without rinsing was stuck on an X-ray sample holder by adhesion tape. Because the XRD pattern recorded on the cathode containing pristine MoO₃ with reflection mode showed only 0*k*0 lines and the pattern recorded with transmission mode showed only *h*0*l* lines, the particles of MoO₃ in the composite cathode tend to be orientated by making their b-axes preferentially perpendicular to the surface of the cathode. Therefore, XRD pattern observed by reflection arrangement gives the structural information mainly on the stacking

of Mo-O octahedron layers along the b-axis and that by transmission arrangement on the connection of Mo-O octahedron in their layers along the ac-planes.

6.3 Results

6.3.1 Characterization of pristine samples

The powder patterns of the pristine MoO_3 samples are shown in Fig. 6.2. With the increase in heating temperature, diffraction peaks become sharp and $0k0$ lines get strong in comparison with other hkl lines. From these patterns, lattice parameter, b , which corresponds to the twice of interlayer spacing of Mo-O octahedron layers stacked along b-axis, was determined as a measure of the width of van der Waals gap and listed in Table 6.1. Intensity ratio between 040 and 101, I_{040}/I_{101} , was also calculated (Table 6.1) as a parameter of the preferred orientation of particles with anisotropic shape in an X-ray sample holder, which depended strongly on the size of Mo-O octahedron layers. The layers with the large size were easier to be orientated and so gave the higher value of I_{040}/I_{101} . With the increase in heating temperature, interlayer spacing slightly decreases, i.e. the van der Waals gap slightly narrows, and the I_{040}/I_{101} ratio drastically increases, i.e., Mo-O octahedron layers greatly grow.

The color of sample M30 was gray, but those of samples M60 and M75 were light yellow. Since MoO_3 single crystal is reported to have anisotropy in color, ab-plane being black and both bc and ac-planes light yellow [15], sample M30 is reasonably supposed to have the largest fraction of ab-plane (perpendicular planes to Mo-O octahedron layers) on the surface of their particles among three samples. The color of the samples is consistent with the expectation from X-ray I_{040}/I_{101} ratio.

The SEM photographs of the samples used are shown in Fig. 6.3. Sample M30 consists of small particles, the size of which is about 1 μm . In sample M60, however, flat platy-particles are observed, the largest one being about 10 μm , and in sample M75, most of particles have long flat stick-shape with the length of more than 100 μm . Large stick-shaped anisotropic crystals in sample M75 are reasonably supposed to be formed through vapor phase in glass tube during the heat treatment at 750 °C. The crystal planes with large area observed in samples M60 and M75 are reasonably supposed to correspond to ac-plane. The present SEM photograph observation is consistent with XRD results and sample color.

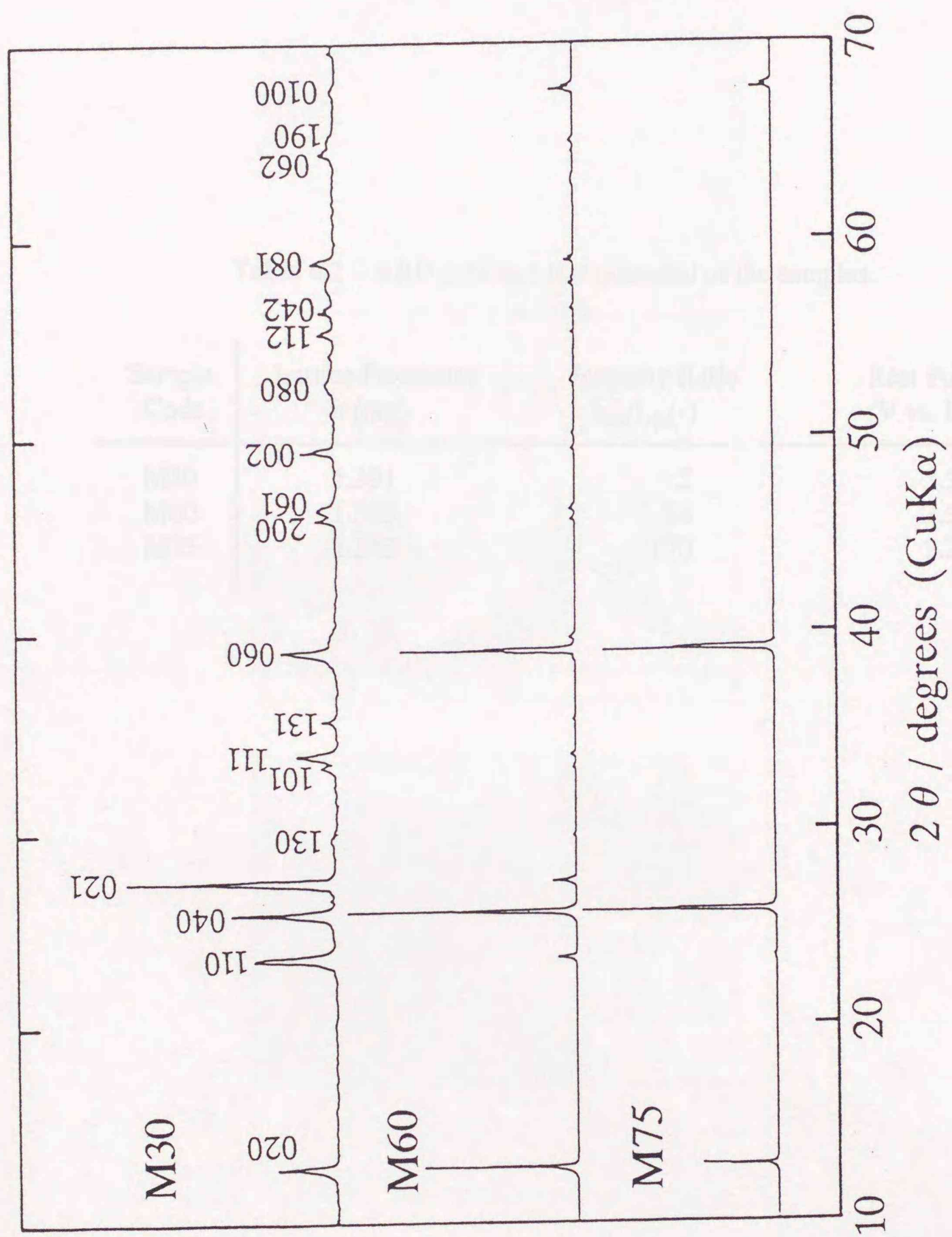


Fig. 6.2 The XRD patterns of the samples.

Table 6.1 XRD data and rest potential of the samples.

Sample Code	Lattice Parameter b (nm)	Intensity Ratio $I_{040}/I_{101}(-)$	Rest Potential (V vs. Li ⁺ /Li)
M30	1.391	2	3.39
M60	1.385	34	3.31
M75	1.383	1170	3.29

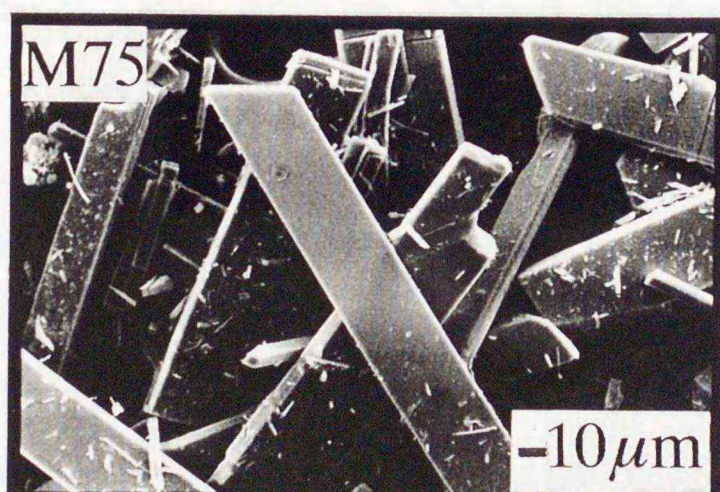
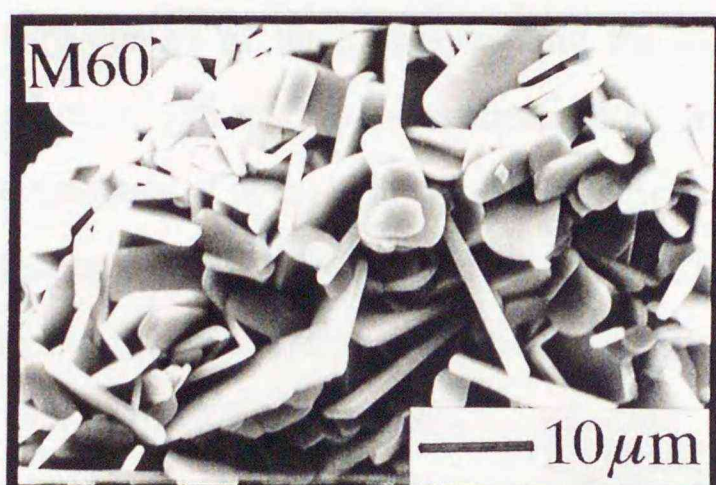
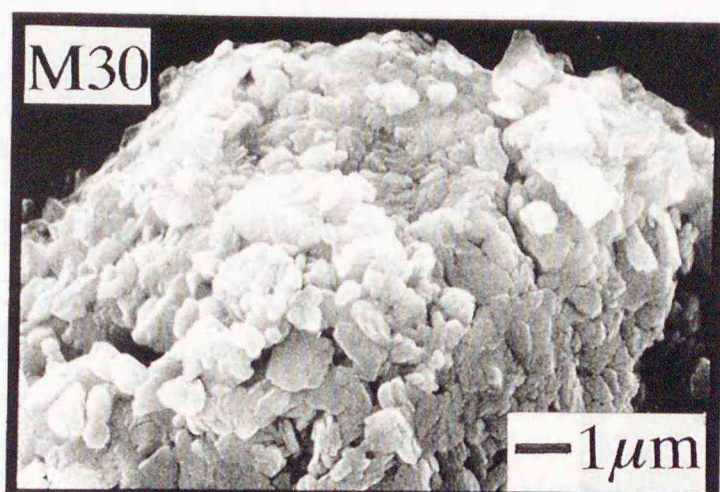


Fig. 6.3 The SEM photographs of the samples.

Fig. 6.4 shows the UV-VIS absorption spectra of the samples. Absorption maximum shifts to shorter wavelength with the decrease in treatment temperature, as is known as blue shift on absorption edge. The blue shift is thought to be concerned with the decrease in particle size of MoO_3 [16]. Sample M30 has the smallest particle size among three samples and therefore its absorption edge lies at the shortest wavelength (blue shift).

The rest potential of samples, which represents site energy for lithium insertion, is also summarized in Table 6.1 with XRD data. Marked difference is not observed among three samples, but it appears that the higher the treatment temperature the somewhat higher the rest potential.

6.3.2 Structural change during first lithium insertion process

The discharge curves of three samples and the changes of XRD patterns during lithium insertion reaction (discharge) on sample M60 are shown in Fig. 6.5a) and b), respectively. The symbols of A to H in the XRD patterns are referred to the symbols on discharge curve of sample M60. From the position of 020 line for pristine MoO_3 and 030 one for lithiated MoO_3 , the interlayer spacing of Mo-O octahedron layers is calculated and listed on the right side of the XRD patterns.

There is no difference in the feature of discharge curve among three samples. These three discharge curves show two plateaus, the first one at about 2.8 V with the capacity of about $50 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$, and the second one at the potential range from 2.4 to 2.0 V with the capacity of $200 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$.

At the first plateau, pristine MoO_3 with the interlayer spacing of 0.69 nm coexisted with a new lithiated MoO_3 phase with the spacing of 1.175 nm, as shown in XRD pattern B in Fig. 6.5b. With the increase in lithium ions inserted, the diffraction lines of pristine MoO_3 become gradually weak and the new broad $0k0$ lines grow up which are continuously shifting to lower diffraction angle side. At the end of this first plateau (point C in Fig. 6.5a), the interlayer spacing of the new phase becomes 1.20 nm. Then, the spacing of the new phase continues to widen until the beginning of the second plateau (point D in Fig. 6.5a) and reaches about 1.24 nm (pattern D in Fig. 6.5a). In the second plateau, the spacing of lithiated MoO_3 decreases gradually with lithium insertion down to 1.115 nm (point H in Fig. 6.5a). Change in the interlayer spacing with concentration of lithium in MoO_3 is shown in Fig. 6.6. Pristine MoO_3 completely disappeared at the composition of $\text{Li}_{0.2}\text{MoO}_3$ (Fig. 6.6a). Interlayer spacing of the lithiated MoO_3 continues to increase up to 1.24 nm around

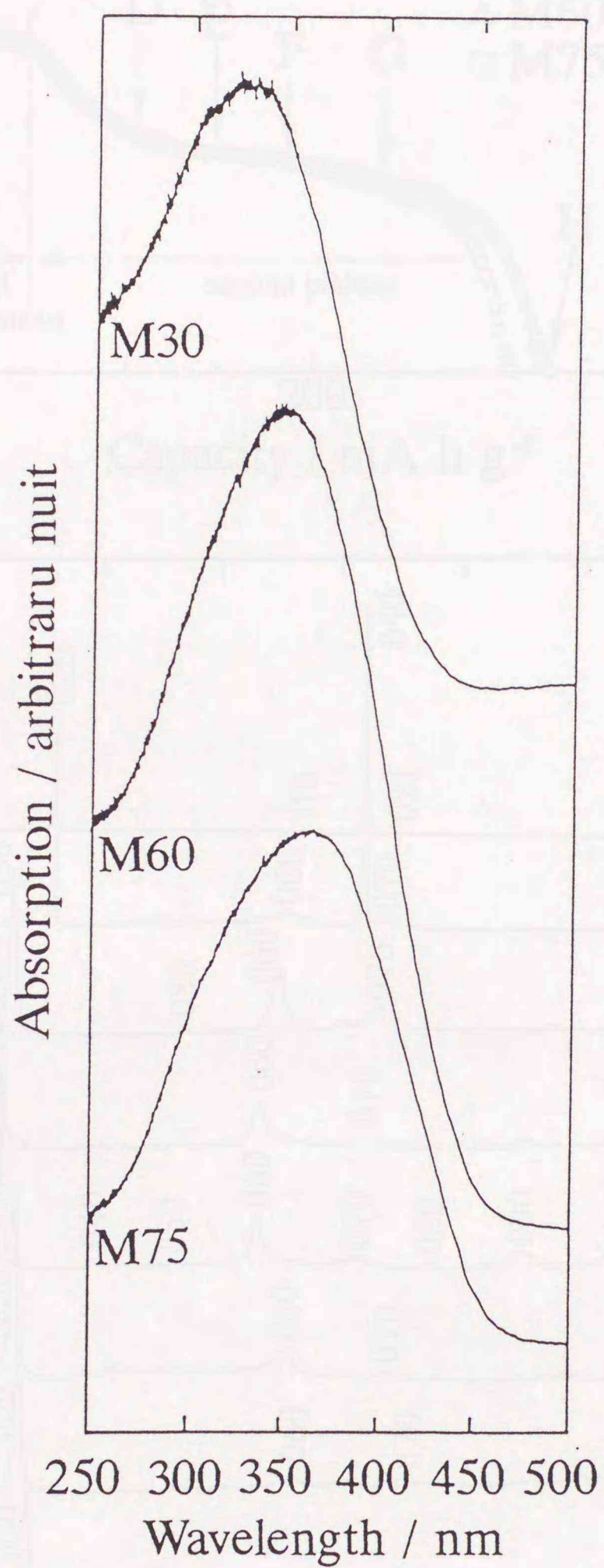


Fig. 6.4 The UV-VIS spectra of the samples.

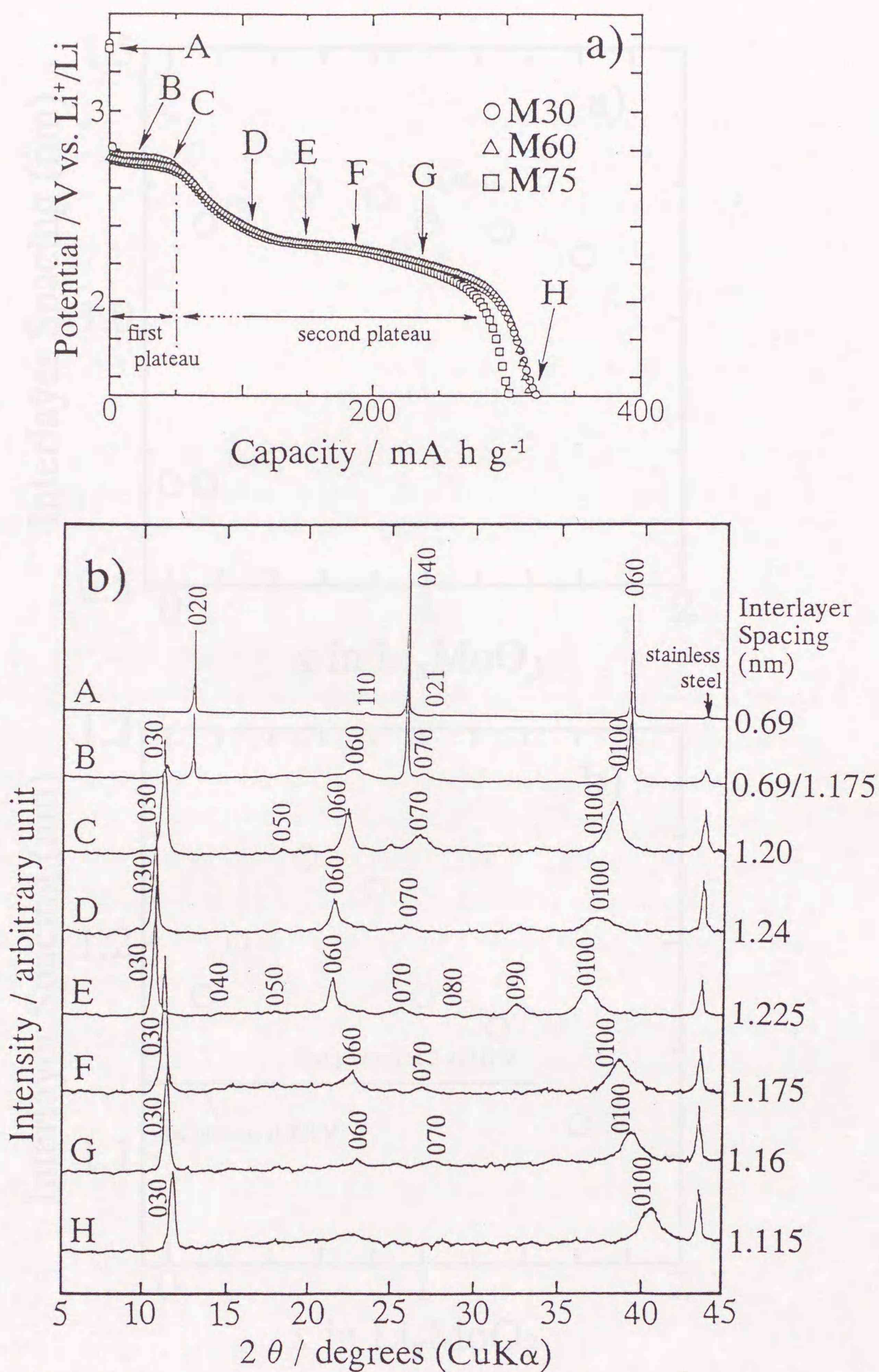


Fig. 6.5 First discharge curves down to 1.5 V of the samples a) and changes of the XRD patterns during lithium insertion for sample M60 b). Symbols A-H are corresponding with each other in discharge curves and XRD patterns.

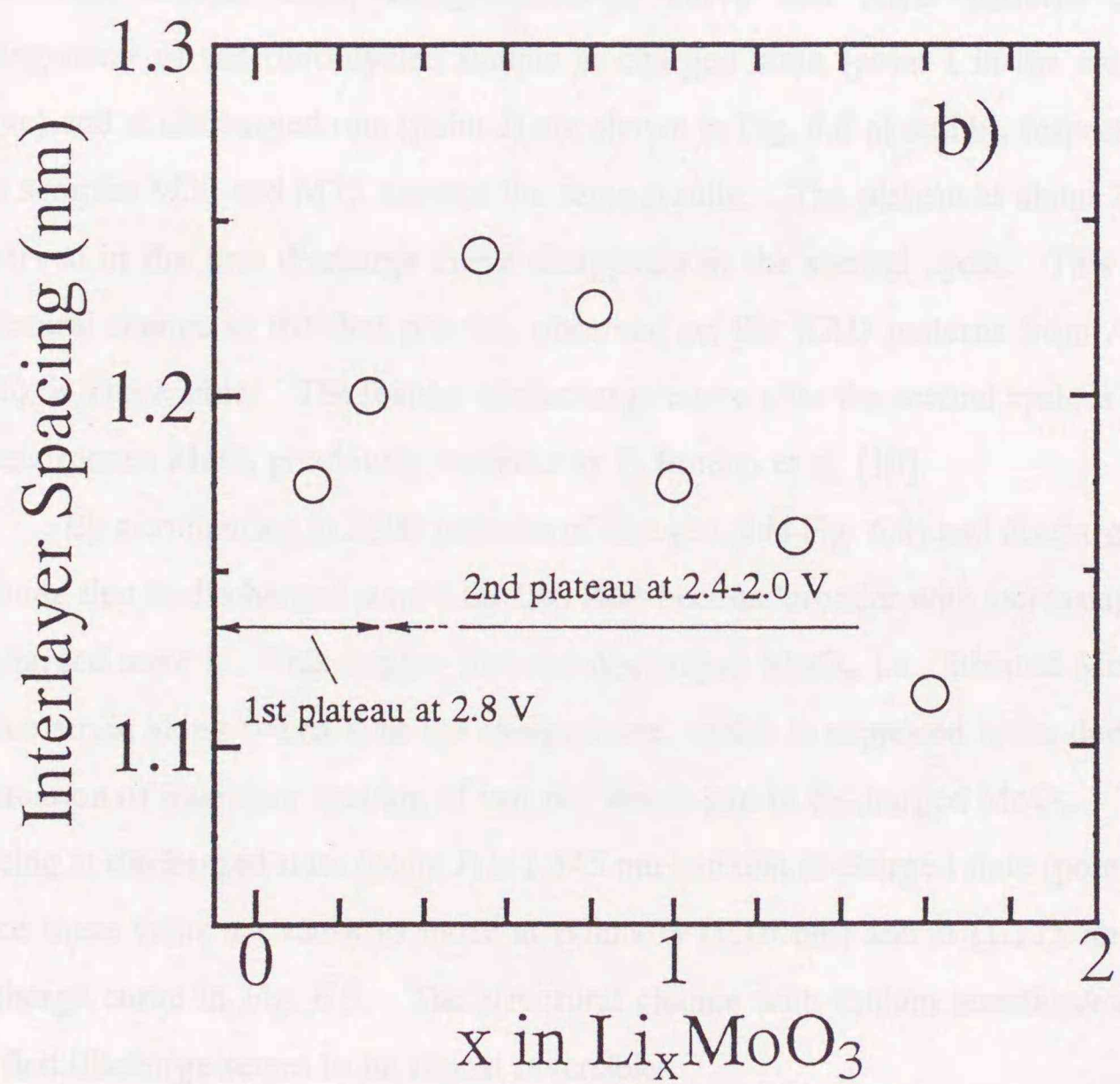
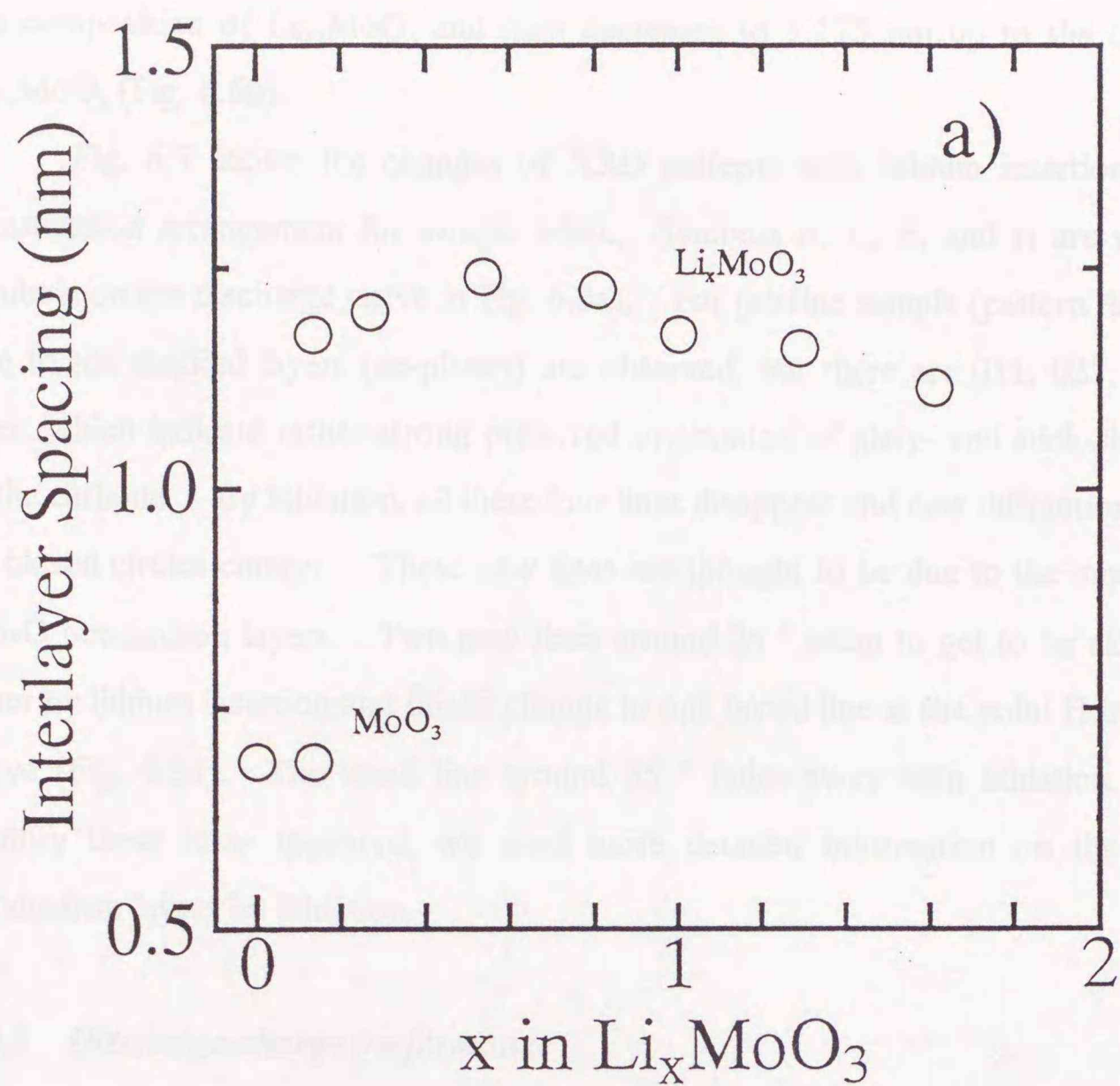


Fig. 6.6 Change of interlayer spacing of Li_xMoO_3 with lithium composition a) and enlarged one in the range between 1.1 and 1.3 nm.

the composition of $\text{Li}_{0.5}\text{MoO}_3$ and then decreases to 1.175 nm up to the composition of $\text{Li}_{1.6}\text{MoO}_3$ (Fig. 6.6b).

Fig. 6.7 shows the changes of XRD patterns with lithium insertion measured by transmission arrangement for sample M60. Symbols A, C, E, and H are referred to the symbols on the discharge curve in Fig. 6.5a). For pristine sample (pattern A), no $0k0$ lines due to the stacked layers (ac-planes) are observed, but there are 011, 021, 101, and 111 lines, which indicate rather strong preferred orientation of platy- and stick-shaped particles in the cathode. By lithiation, all these four lines disappear and new diffraction lines denoted by closed circles emerge. These new lines are thought to be due to the inner structure of Mo-O octahedron layers. Two new lines around 25° seem to get to be closer with each other by lithium insertion and finally change to one broad line at the point H in the discharge curve (Fig. 6.5a). The small line around 35° fades away with lithiation. In order to identify these lines appeared, we need more detailed information on the distortion of octahedron layers by lithiation.

6.3.3 Discharge-charge performance

For sample M60, charge-discharge curve and XRD patterns in reflectance arrangement of the third-cycled sample at charged state (point I in the charge-discharge curve) and at discharged one (point J) are shown in Fig. 6.8 a) and b), respectively. Other two samples M30 and M75 showed the same results. The plateau at about 2.8 V which is observed in the first discharge curve disappears in the second cycle. This indicates that structural change at the first plateau, observed on the XRD patterns from A to C in Fig. 6.5b), is irreversible. The feature of discharge curve after the second cycle is similar to that of amorphous MoO_3 previously reported by F. Bonino et al. [10].

By a comparing in XRD patterns of charged (I in Fig. 6.8) and discharged state (J), it is found that in discharged state J the $0k0$ lines become broader with increasing k index than in charged state I. This implies that the discharged MoO_3 , i.e., lithiated MoO_3 , has more lattice strain along b-axis than the charged one, which is supposed to be due to the larger fluctuation of interlayer spacing of van der Waals gap in discharged MoO_3 . The interlayer spacing at discharged state (point J) is 1.145 nm and that at charged state (point I) 1.185 nm. Since these value are close to those at points G (1.16 nm) and B (1.175 nm) on the first discharge curve in Fig. 6.5. The structural change with lithium insertion/extraction after the first discharge seems to be almost reversible.

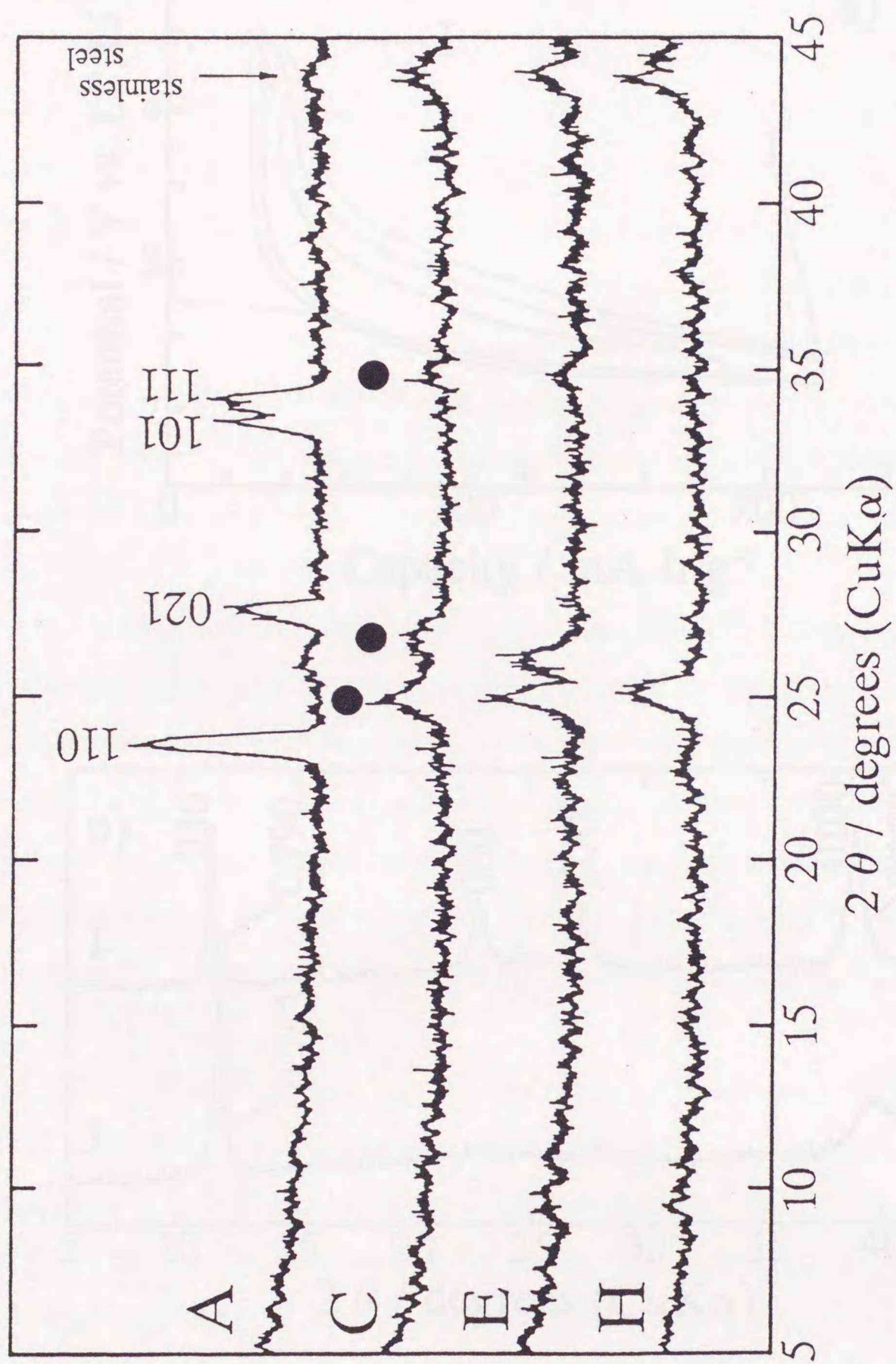


Fig. 6.7 The XRD patterns of lithiated M60 samples measured by transmission arrangement. Closed circles are unknown peaks. Symbols A, C, E, and H correspond to those in Fig. 6.5.

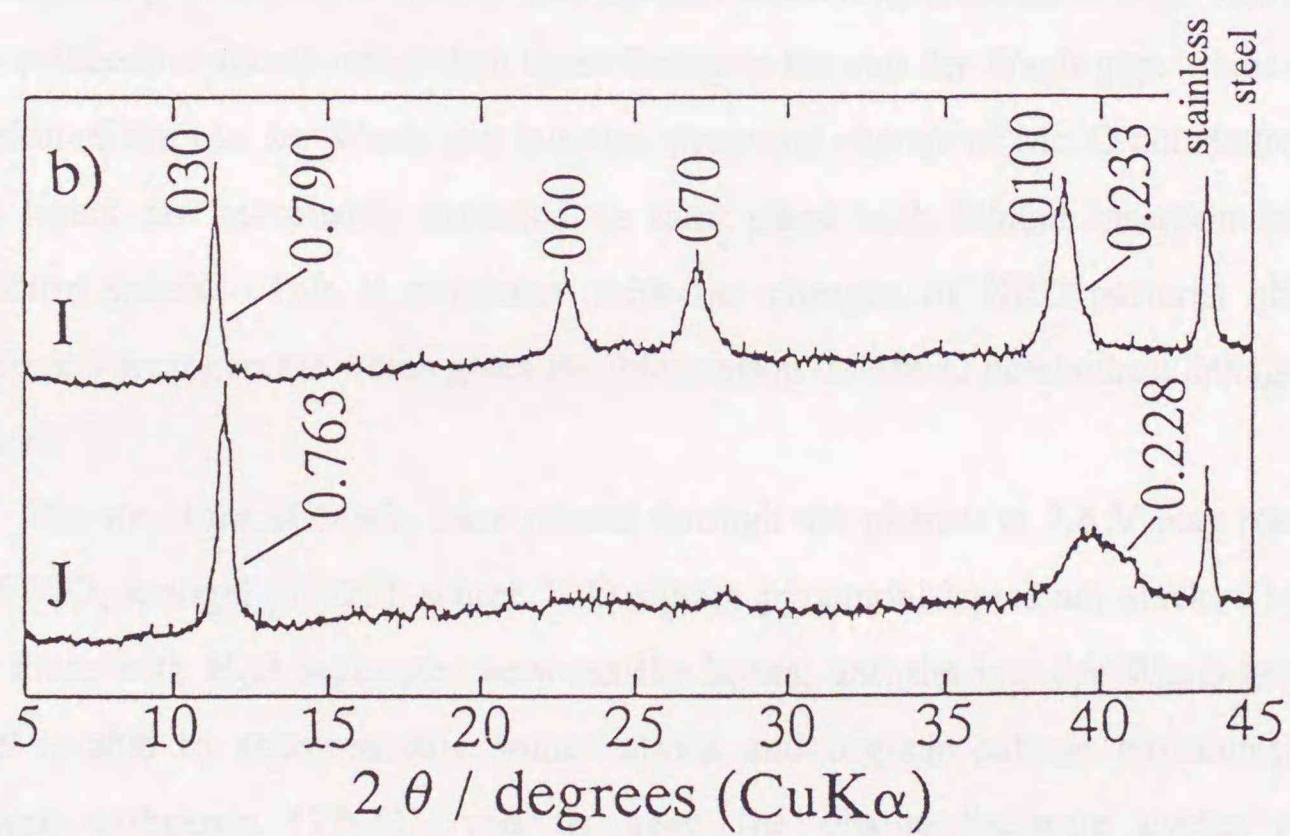
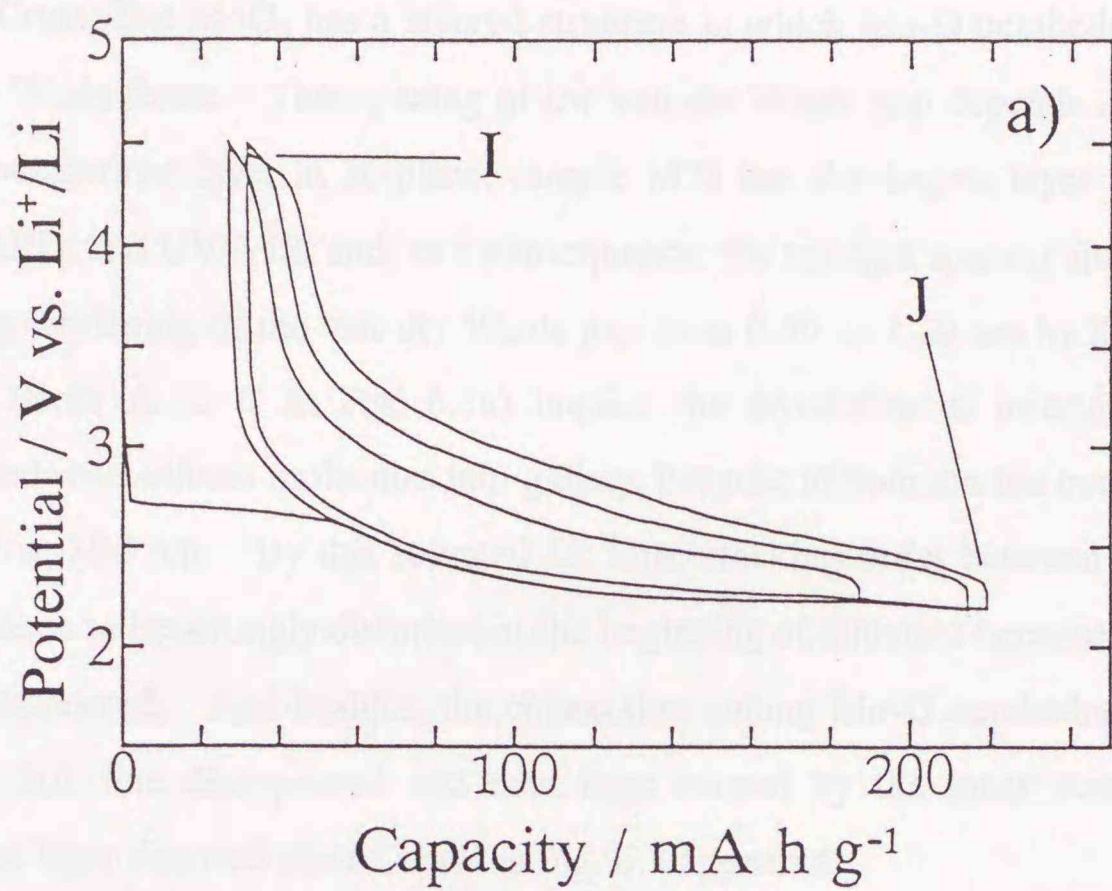


Fig. 6.8 Discharge-charge curve of sample M60 and the XRD patterns of charged I) and discharged J) M60 samples.

6.4 Discussion

Crystalline MoO_3 has a layered structure in which Mo-O octahedron layers stack by van der Waals force. This spacing of the van der Waals gap depends on the extension of Mo-O octahedron layer in ac-plane; sample M75 has the largest layer size, as proved by SEM, XRD, and UV-VIS, and, as a consequence, the smallest spacing among three samples. The large widening of the van der Waals gap from 0.69 to 1.20 nm by lithiation at the first plateau (from A to C in Fig. 6.5a) implies the possibility of insertion of lithium ions associated with solvent molecules into gallery, because lithium ion has been known to have a size below 0.08 nm. By this solvated Li^+ ions, stacking order between Mo-O octahedron layers seems to be strongly disturbed at the beginning of lithiation because 110, 021, and 111 lines disappeared. And besides, the connection among Mo-O octahedra may be distorted, because 101 line disappeared and new lines caused by the inner structure of the new deformed layer denoted closed circle in Fig. 6.7 appeared.

Senoh et al. [12] pointed out from the changes in FTIR spectra during lithiation that in the beginning of lithiation lithium ions interact with oxygen atoms at edge sharing part in Mo-O octahedron sheets rather than those facing to the van der Waals gap. Not only large expansion of the van der Waals gap but also structural change of Mo-O octahedron linkage in the layers are reasonably expected to take place with lithium insertion into Mo-O octahedron sheets. This is consistent with the changes of XRD patterns observed in transmission arrangement which gives the information on Mo-O octahedron linkage in layers (Fig. 6.7).

The structure of MoO_3 once passed through the plateau at 2.8 V may resembles to that of V_2O_5 xerogel [17-20], where V-O square pyramidal layers are stacked by van der Waals force with H_2O molecules between the layers, and the van der Waals gap in V_2O_5 xerogel is able to accommodate some cations and organic solvent molecules, such as propylene carbonate [17-20], and to keep the charge-discharge cycles reversible. Therefore, there is no effect of host MoO_3 crystallinity on electrochemical performance.

The reason for shrinkage of van der Waals gap with further insertion of lithium above $150 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$, as shown in Fig. 6.5, could not be cleared in the present work. If solvated lithium ions are also inserted during the second plateau, the gap has to be either expanded further or kept constant. So solvent molecules are not thought to be inserted into the gap at the second plateau.

First discharge capacity down to 1.5 V and discharge-charge cycle performance up to about $190 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$, which corresponds to the composition of $\text{Li}_{1.0}\text{MoO}_3$, are all the same among three samples. After the second cycle, potential change with lithium insertion/extraction reaction shown in Fig. 6.8 is very similar to that reported on an amorphous MoO_3 [10]. This result indicates that layered structure of MoO_3 is not necessarily needed for lithium insertion/extraction reaction, and that lithium ions are held in particular part of Mo-O octahedron linkage.

Based upon the above discussion, a scheme of lithium insertion into crystalline MoO_3 is shown in Fig. 6.9. Symbols A-H correspond to those in Fig. 6.5a). At the first plateau at 2.8 V in the first discharge curve (Fig. 6.5a), the van der Waals gap is widened by the insertion of solvated lithium ions. Lithium ions inserted into the van der Waals gaps are accommodated in the sites in Mo-O octahedron layers (Fig. 6.9B) and the solvent molecules are left behind. At the end of this plateau, pristine MoO_3 completely disappeared (Fig. 6.9C). This process contains irreversible structural change in octahedron sheets (Fig. 6.7) and the 2.8 V plateau is not observed after the second cycle of discharge-charge (Fig. 6.8a). At the second plateau at 2.4-2.1 V, solvent molecules are not inserted, but lithium ions inserted further more diffuse among solvent molecules in the gap and are accommodated in the certain sites in the layers, which gives small shrinkage of the gap and strong distortion of octahedron layers (Fig. 6.9C to H). This structural change seems to be reversible and so the discharge-charge cycle is also reversible as shown in Fig. 6.8.

6.5 Summary

Lithium insertion/extraction reactions on three $\alpha\text{-MoO}_3$ samples with different crystallinity were studied. Since the first lithium insertion into pristine MoO_3 caused a strong distortion in structure even though started from a highly crystalline host, all three samples gave the same electrochemical performance afterward, which was similar to that of an amorphous MoO_3 , in other words, no effect of crystallinity of starting MoO_3 on electrochemical performance. The spacing of the van der Waals gap in $\alpha\text{-MoO}_3$ was widened from 0.69 to 1.24 nm and the inner structure of the Mo-O octahedron layers was also changed by lithiation.

From the structural change studied mostly on sample M60, a scheme for the lithium insertion into MoO_3 was discussed. A possibility on the insertion of solvated lithium ions

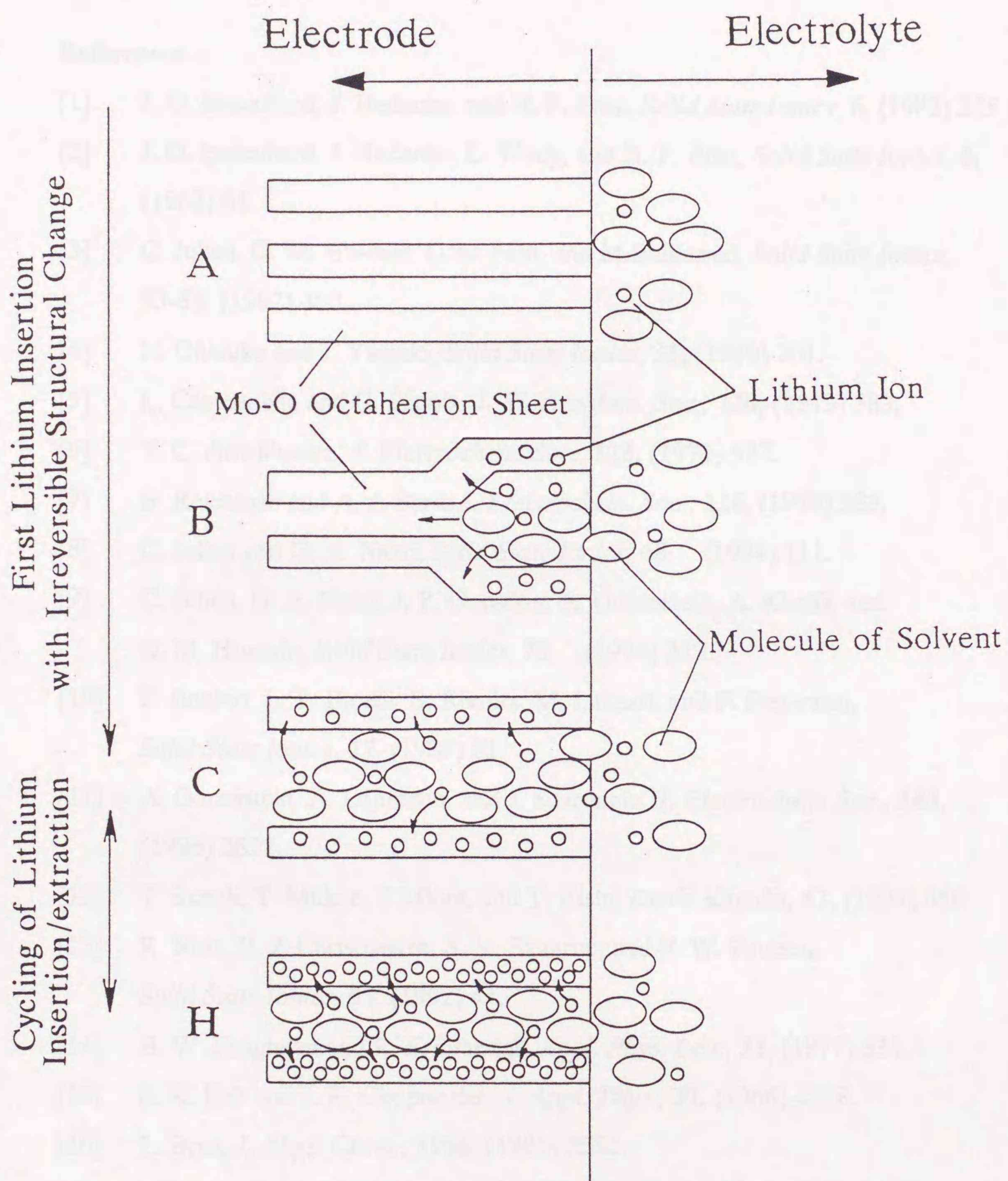


Fig. 6.9 A schematic view of lithium insertion into MoO_3 . Symbols A-H are corresponding to those in Fig. 6.5.

into the gap was expected by a large expansion of the van der Waals gap with lithiation at 2.8 V plateau and an accommodation of inserted lithium ions in certain sites of Mo-O octahedron sheets was supposed from XRD studies.

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7.1. Descriptive Statistics: Frequency Distributions and Graphs

Chapter 7 contains material on frequency distributions and graphs. It is one of the first chapters in the book and is intended to provide a foundation for the more advanced topics that follow. The chapter is divided into two main sections: frequency distributions and graphs. The first section discusses the importance of frequency distributions in summarizing data and the various methods for constructing them. The second section discusses the various types of graphs that can be used to display frequency distributions, including histograms, bar charts, and pie charts. The chapter concludes with a discussion of the relationship between frequency distributions and probability distributions.

The first section of the chapter discusses the importance of frequency distributions in summarizing data. It begins by defining a frequency distribution as a table that shows the number of times each value of a variable occurs in a sample. It then discusses the various methods for constructing frequency distributions, including the use of class intervals and the use of relative frequencies. The second section of the chapter discusses the various types of graphs that can be used to display frequency distributions. It begins by discussing histograms, which are bar charts in which the bars are adjacent to each other. It then discusses bar charts, which are similar to histograms but with gaps between the bars. Finally, it discusses pie charts, which are used to display the relative frequencies of the categories of a variable.

The chapter concludes with a discussion of the relationship between frequency distributions and probability distributions. It begins by defining a probability distribution as a table that shows the probability of each value of a variable occurring. It then discusses the various methods for constructing probability distributions, including the use of the normal distribution and the use of the binomial distribution. The chapter concludes by discussing the relationship between frequency distributions and probability distributions, noting that as the sample size increases, the frequency distribution of a variable approaches the probability distribution of the variable.

7.2. Inferential Statistics: Estimation and Hypothesis Testing

This section of the chapter discusses the various methods for estimating the parameters of a population and for testing hypotheses about the population. It begins by discussing the various methods for estimating the population mean, including the use of the sample mean and the use of the confidence interval. It then discusses the various methods for testing hypotheses about the population mean, including the use of the t-test and the use of the F-test. The section concludes with a discussion of the relationship between estimation and hypothesis testing, noting that the two are closely related and that the results of one can be used to inform the other.

Chapter 7

Discussion and conclusions

7.1 Synthesis of lithium containing transition metal oxides via dicarboxylates

Lithium containing transition metal oxides are mainly prepared by firing of mechanical mixtures of lithium compound and transition metal one [1-4]. Because lithium oxide, Li_2O , evaporates from the reaction system during heating above 600°C , it is hard to control the composition of resultant compound. It is very important to adjust the composition of electrode materials, since the deviation from the stoichiometric composition has an obvious effect on electrochemical lithium insertion/extraction reaction, such as cycle retention and capacity [5-8]. Therefore, many preparation methods, such as alcoholate method [9], complex salt method [10], ultrasonic spray decomposition [11], etc., were reported. Synthesis method of lithium containing transition metal oxides from lithium-transition metal-dicarboxylates was suggested and demonstrated in the present work.

In order to study about the effect of dicarboxylic acid on the synthesis of LiMn_2O_4 powders, four dicarboxylic acids, oxalic, malonic, succinic, and tartaric acid, were selected. On the basis of the results of XRD, FTIR, DTA-TG-MAS, the structure of the precursor, i.e., lithium-manganese-dicarboxylates, was proposed. Oxalate and succinate has a chain like structure in which lithium and manganese ions are linked by dicarboxylate ions. Malonate and tartrate is mixtures of lithium-manganese complex salt and manganese dicarboxylate. In the complex salt, two dicarboxylate ions connect to manganese ion as bidentate to be complex ion, and charge balance of the complex salt is achieved by proton and lithium ion. The four precursors decompose and convert to LiMn_2O_4 phase above 300°C .

The present method is not suitable for industrial manufacture, because the price of these dicarboxylic acid and ethanol is so expensive that the total cost of this method should be more higher than that of a conventional method, in which mechanical mixtures of manganese oxide and lithium carbonate are heated. But it is useful for obtaining sample powders with a low crystallinity in laboratory scale without any by-product.

7.2 Crystallinity of the samples

Transition metal oxides are known to have different crystal structures and in each structure type to have a wide range of crystallinity from single crystal to amorphous state through polycrystalline powders with various size and morphology. Each structure type

has their thermodynamically stable temperature-pressure region which is shown as phase diagram for each oxide. However, the crystallinity in each structure type depends strongly on the preparation conditions, particularly in polycrystalline powders.

In order to develop electrochemically active electrode materials for batteries, particularly for lithium ion batteries, the selection of structure type is one of the important factors, because it governs the amount of lithium which can be inserted and extracted, and also the diffusion rate of lithium ion in the structure which is strongly related to the maximum current density obtained during charge and discharge of the batteries. From this point of views, various investigations have been carried out on the materials with layered structure, such as $\text{Li}(\text{Co},\text{Ni})\text{O}_2$, MoO_3 , MoS_2 , TiS_2 , and graphite, and on the insertion into and extraction from the gallery of their layered structure [12-18]. Vanadium pentoxides V_2O_5 has also been studied because of its pseudo-layered structure [19]. However, it has been shown that manganese dioxides MnO_2 , which have been extensively used as cathode materials in primary lithium batteries, and almost all the transition metal oxides show lithium insertion/extraction through three dimensional channels in the host structure [20-22]. In the spinel-type LiMn_2O_4 , which is extensively studied in the present work from its preparation to batter performance, lithium ions in the host can be extracted and inserted through its three-dimensional networks of lithium and vacant sites [23].

For these oxide electrodes, their crystallinity is also expected to have important effect on their electrochemical performance, because it may govern the occupancy of lithium in preferential sites and also diffusion of lithium through structure. In order to understand this effect, it is necessary to obtain a wide range of crystallinity on each oxide. This is one of the reasons why there have not been so many works on this effect. To study this effect, one of the ways is to prepare first the oxide with low degree of crystallinity and then anneal at different high temperatures to get different crystallinity.

Lithium containing transition metal oxides, LiMn_2O_4 and $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$, were prepared by a novel method, i.e., thermal decomposition of lithium and transition metal dicarboxylates at low temperature as 300 °C. The method developed in the present work enabled the preparation of these samples with low degree of crystallinity because mixing in atomic scale between lithium and transition metals was achieved at the stage of the precursors, lithium and transition metal dicarboxylates [24,25]. The lithium containing transition metal oxide powders were formed at a mild condition without any by-product. Starting from these samples, we obtained the sample powders with higher crystallinity by heating to higher temperatures.

For LiMn_2O_4 samples, crystallinity of the sample was characterized by lattice parameter, a_0 , and lattice strain, ϵ , which were determined by XRD measurements. Lattice parameter increases and lattice strain decreases with the increase in heating temperature and these changes seemed to be due to improvement of cation distribution in spinel structure and the decrease of mean oxidation state of manganese ion. Crystallinity of $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ samples was evaluated by half width of XRD lines. The half widths of 003 and 104 lines, which corresponded to development of stacking thickness and extension of the layers, respectively, seemed to increase with the increase of disturbance of cation distribution, or the increase of disorder rock-salt type cubic $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ domains.

For lithium containing transition metal oxides, the decrease of crystallinity causes not only the decrease of crystallite size but also imperfection of cation distribution. Thus the decrease of the crystallinity leads to change in the structural skeleton of host.

TiO_2 powders prepared by hydrothermal treatment of amorphous TiO_2 powders were proved to be comprised from amorphous and crystalline anatase regions, though they were reported to be a single phase of anatase type structure [26]. The crystallinity of anatase regions decreased and the amount of amorphous region increased with the decrease in heating temperature. In the crystalline region, lattice strain, ϵ , increased and crystallite size, L , decreased with the decrease in heating temperature.

For V_2O_5 and MoO_3 powders, which were prepared by thermal decomposition of corresponding ammonium salts, NH_4VO_3 and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$, crystallite size (extension of layers consisting of square pyramidal VO_5 and octahedral MoO_6) increased and interlayer spacing decreased with the increase in heating temperature.

On these three transition metal oxides, TiO_2 , V_2O_5 , and MoO_3 , the decrease of crystallinity caused the decrease of crystallite size and the increase of lattice strain, but the construction of TiO_6 octahedra, VO_5 pyramids, and MoO_6 octahedra did not change with the decrease of crystallinity. In other words, structural skeleton of host maintained in the low crystalline samples, even in the amorphous state short range ordering of the construction being thought to be held.

7.3 Electrochemical performance of the samples

Rest potential of the oxide, which was measured in the electrochemical lithium cell, increased with the decrease of the crystallinity. Rest potential is thought to be chemical potential of lithium ions in the host structure and the chemical potential is closely related to site energy for lithium insertion/extraction [27-32]. The decrease of crystallinity is caused

by the introduction of various imperfections into structure, such as disorder of cation distribution, cation and oxygen vacancies, etc., and these imperfections make the distribution of site energy for lithium insertion/extraction broader and more stable sites for lithium. Therefore, rest potential tends to increase with the decrease of crystallinity for all the five samples.

Electrochemical performance of the cathode of the present transition metal oxides is classified into two groups, as summarized in Fig. 7.1, with charge-discharge curves, on the basis that whether the crystallinity of these oxides affects to the performance or dose not. Lithium containing transition metal oxides, LiMn_2O_4 and $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$, showed a pronounced effect of crystallinity on the first charge-discharge capacity at around 4 V, which is related to lithium extraction/insertion on 8a sites in spinel structure and 3b sites in ordered rock-salt type structure, respectively. The decrease of crystallinity of host, or the increase of the disturbance in cation distribution, gave rise to the decrease of the capacity. This indicates that high crystallinity, perfect crystal structure, is demanded in order to get a theoretical capacity, $148 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ for LiMn_2O_4 and $274 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ for $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$.

The effect of crystallinity on charge-discharge capacity was reported on carbon materials [33,34]. Theoretical discharge-charge capacity of graphite is $372 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$, and that of carbon materials decreases linearly with the decrease of graphitization degree, P_1 , which is one of the parameters for crystallinity of carbon materials and relates to the ratio of the hexagonal stacking of graphite layers. Lithium ions are accommodated in the crystallographic sites in graphite structure and are not able to be accommodated in the sites of turbostratic structure (disordered stacking) [34].

For these materials, such as graphite and lithium containing transition metal oxides, a certain crystal structure is necessary to lithium insertion/extraction.

On the other three transition metal oxides, TiO_2 , V_2O_5 , and MoO_3 , the first discharge capacity was independent from the crystallinity of the host. For MoO_3 powders, any effect of the crystallinity of host on electrochemical performance was not observed. The first discharge curve of TiO_2 powders prepared under hydrothermal conditions showed gradual decrease of potential from 3.0 to 1.75 V and a plateau at around 1.75 V, which are corresponding to lithium insertion into amorphous and crystalline regions, respectively. The capacity down to 1.6 V, or capacity of the gradual potential decrease plus that of plateau region, was almost the same among the samples used. For V_2O_5 samples, the first discharge potential change up to $400 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ was strongly affected by host morphology, extension of VO_5 layer, but the total capacity down to 0.5 V was almost the same among the

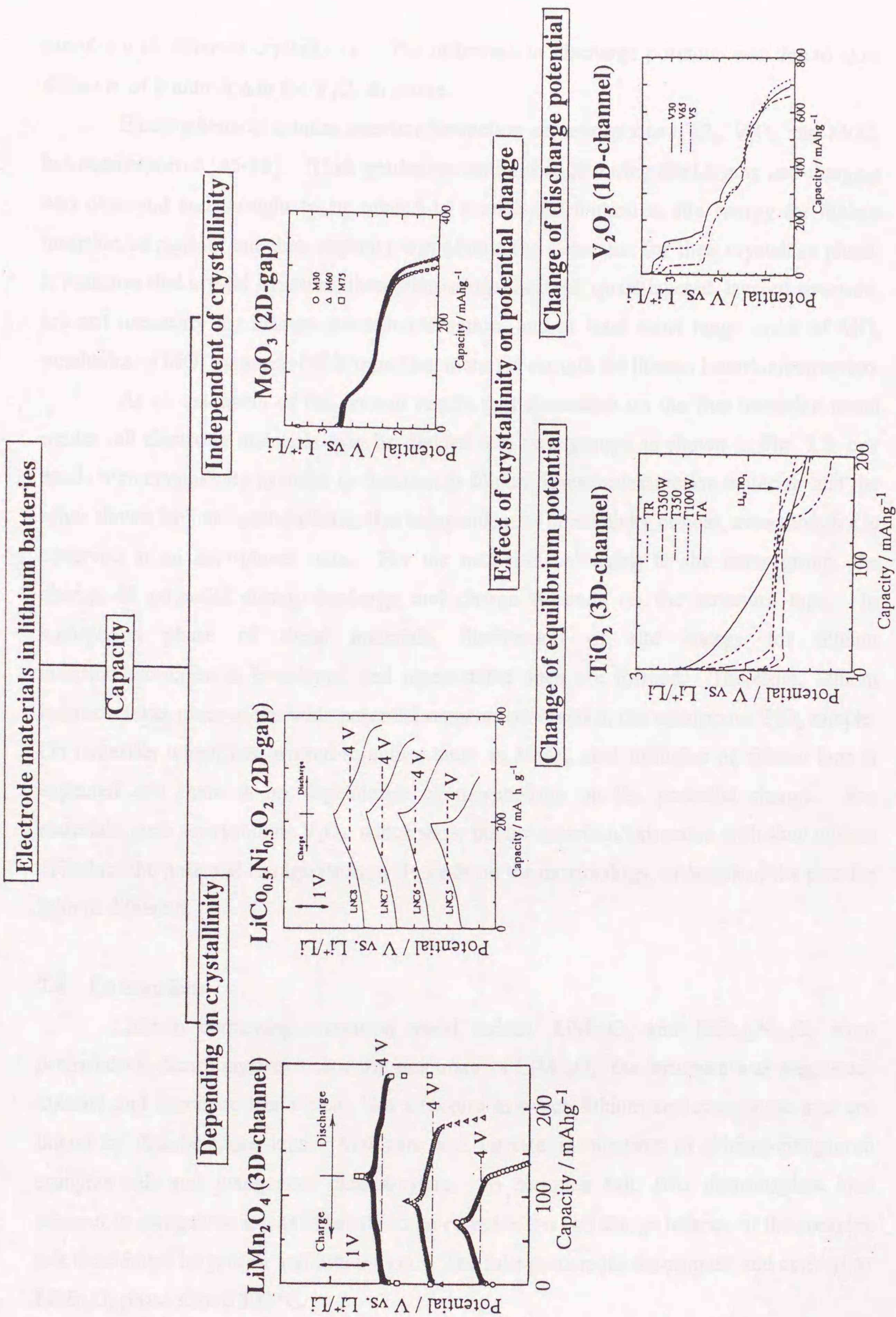


Fig. 7.1 Classification of electrode materials used.

samples with different crystallinity. The difference in discharge potential was due to slow diffusion of lithium ion in the V_2O_5 structure.

Electrochemical lithium insertion/extraction on amorphous TiO_2 , V_2O_5 and MoO_3 has been reported [35-38]. Their gradual potential change during discharging and charging was observed and thought to be related to a wide distribution in site energy for lithium insertion/extraction, but their capacity was almost the same that for their crystalline phase. It indicates that crystal structure, three dimensional anatase, quasi-layered, layered structure, are not necessary for lithium insertion/extraction, and at least short range order of MO_6 octahedra or MO_5 pyramids (M is transition metal) is enough for lithium insertion/extraction.

As an extension of the present results and discussion on the five transition metal oxides, all electrode materials may be divided into two groups as shown in Fig. 7.2; one needs high crystallinity in order to function as lithium insertion/extraction materials and the other shows lithium insertion/extraction independent of crystallinity of host, even though it is observed in an amorphous state. For the materials belonging to the latter group, the change of potential during discharge and charge depends on the structure type. In amorphous phase of these materials, distribution of site energy for lithium insertion/extraction is broadened and more stable sites are formed. Therefore, lithium insertion takes place in the wide potential range as observed in the amorphous TiO_2 sample. On materials which has layered structure such as MoO_3 , first diffusion of lithium ions is expected and there is no dependence of morphology on the potential change. For materials, such as crystalline V_2O_5 , which show lithium insertion/extraction with slow lithium diffusion, the potential change strongly depends on the morphology, or length of the pass for lithium diffusion.

7.4 Conclusions

Lithium containing transition metal oxides, $LiMn_2O_4$ and $LiCo_{0.5}Ni_{0.5}O_2$ were prepared via dicarboxylates. For the precursor of $LiMn_2O_4$, the structure was suggested: Oxalate and succinate has a chain like structure in which lithium and manganese ions are linked by dicarboxylate ions. Malonate and tartrate is mixtures of lithium-manganese complex salt and manganese dicarboxylate. In complex salt, two dicarboxylate ions connect to manganese ion as bidentate to be complex ion and charge balance of the complex salt is achieved by proton and lithium ion. The four precursors decompose and convert to $LiMn_2O_4$ phase above 300 °C.

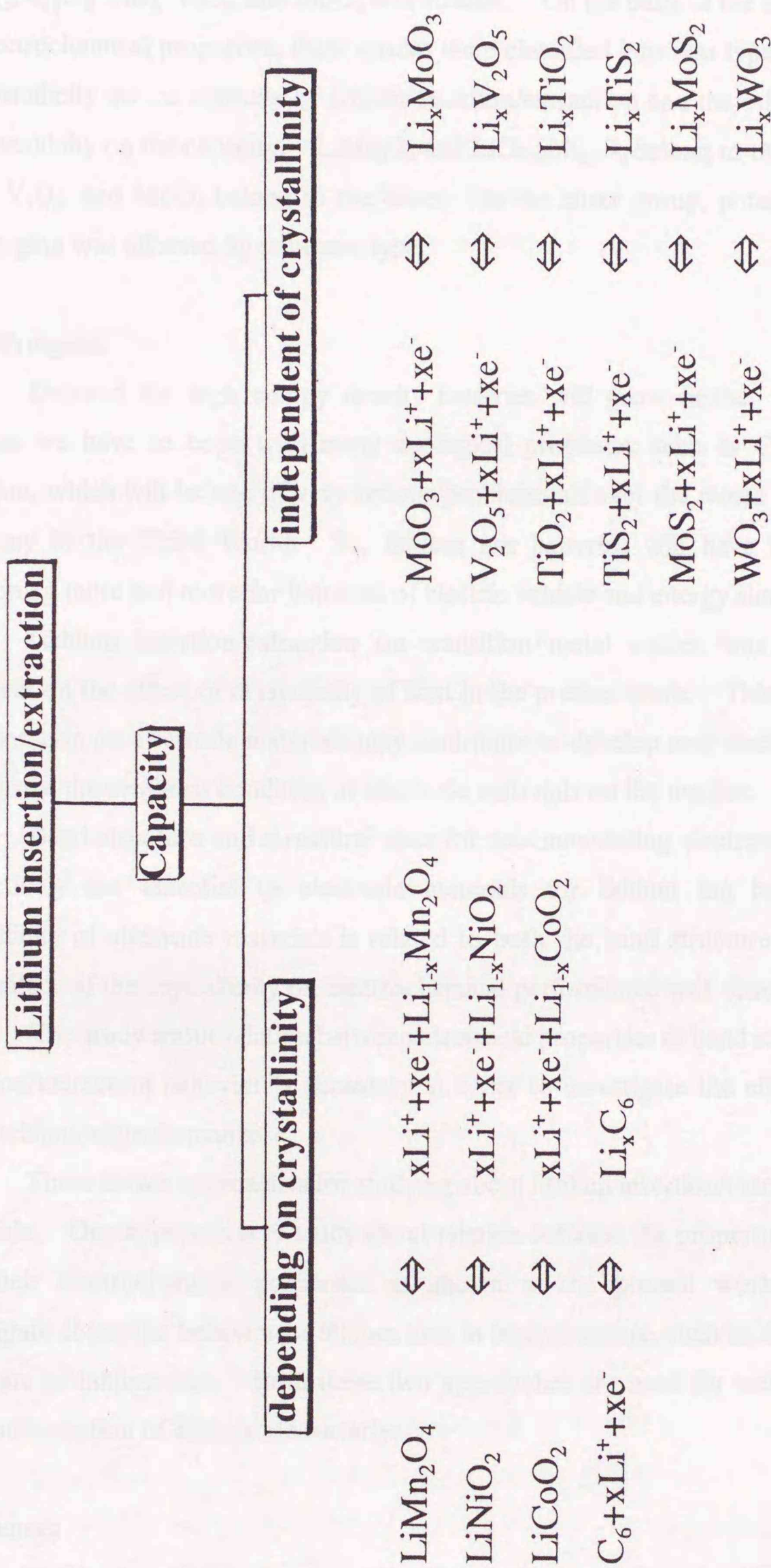


Fig. 7.2 Classification of lithium insertion/extraction reactions.

Lithium insertion/extraction of the five transition metal oxides, LiMn_2O_4 , $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$, TiO_2 , V_2O_5 , and MoO_3 was studied. On the basis of the effect of crystallinity on electrochemical properties, these oxides were classified into two types; one shows effect of crystallinity on the capacity of lithium insertion/extraction and the other shows no effect of crystallinity on the capacity. LiMn_2O_4 and $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ belong to the former group and TiO_2 , V_2O_5 , and MoO_3 belong to the latter. In the latter group, potential change during discharging was affected by structure type.

7.5 Prospect

Demand for high energy density batteries will grow further in the 21 century, because we have to cope with many ecological problems, such as CO_2 , NO_x , and SO_x emission, which will be one of very serious problems all over the world with the growth of economy in the Third World. So, lithium ion batteries will have been studying and developing more and more for batteries of electric vehicle and energy storage system.

Lithium insertion/extraction on transition metal oxides was discussed putting emphasis on the effect of crystallinity of host in the present work. This kind of systematic consideration on electrode materials may contribute to develop new electrode materials and to improve the synthesis condition of electrode materials on the market.

Band structure and structural sites for accommodating electrons and lithium ions, respectively are essential to electrode materials for lithium ion batteries. Because crystallinity of electrode materials is related to both the band structure and the structural sites, effect of the crystallinity on electrochemical performance was observed in the present thesis. The study about relation between electronic properties as band structure and lithium insertion/extraction behavior is necessary in order to investigate the effect of host on the electrochemical performance.

There is two approaches for studying about lithium insertion/extraction on electrode materials. One approach is to study about relation between the properties of host materials and their electrochemical properties as shown in the present work. Another is to investigate about the behavior of lithium ions in host structure, such as diffusion coefficient and state of lithium ions. Both these two approaches are need for well understanding of electrode reaction of lithium ion batteries.

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