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Cathode properties of layered structure Li_2PtO_3

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Abstract

Li_2MO_3 (M: transition metal), which has a similar layer structure to $LiCoO_2$, is interesting for use as another layered rocksalt-type oxide cathode for Li-ion batteries. We found that Li_2PtO_3 in Li_2MO_3 system is the first full 4 V class cathode material among 5d metal compounds. We investigated the electrochemical, structural and kinetic characteristics of the 4 V region. The volumetric capacity of the 4 V plateau on discharge is comparable to that of $LiCoO_2$. Moreover, the reversibility of the structural change in the 4 V region was confirmed by X-ray diffractometry.

Keywords: Lithium-ion cell; Intercalation; Layered rocksalt; Cathode

1. Introduction

Of the rocksalt-type ternary oxides, $LiCoO_2$ and $LiNiO_2$ with an α-$NaFeO_2$ [1] type structure have been most intensively studied for use as 4 V cathode materials in practical Li ion batteries. They have a layered rocksalt superstructure with alternate cationic (111) planes of Li and M which occupy the octahedral sites of a cubic close packing of oxygens. The two dimensional Li diffusion paths between the oxygen layers allow the reversible electrochemical extraction of lithium with fast electrode kinetics.

Other layered rocksalt-related oxides Li_2MO_3 also have the similar structure to α-$NaFeO_2$ as shown in Fig. 1 and could be expected to have similar electrode kinetics to $LiCoO_2$ and $LiNiO_2$. All Li_2MO_3 compounds reported so far, except Li_2ZrO_3 can be represented as $(Li^+)_{3a}$-$(Li^+_{1/3}M^{4+}_{2/3})_{3b}O_2$ [2]. Of these potential cathode materials, most attention has been directed to Li_2MO_3 with Mo [3], Ru [4], Ir [5], Mn [6] and Pt [7] as M. Because the pentavalent or hexavalent state of M retains the charge neutrality and the layer structure at a fully charged state, $Li_{2-x}M^{+(4+x)}O_3$. In fact, they can all with the exception of Li_2MnO_3, reversibly deintercalate Li from the initial composition.

This paper describes the electrochemical, structural and kinetic characteristics of Li_2PtO_3 and introduces Li_2PtO_3 as the first 4 V cathode material providing 100 mA h/g from among the 5d transition metal compounds.

2. Experimental

Li_2PtO_3 was prepared by firing a 1:1 molar ratio mixture of reagent grade lithium carbonate (Kanto Chemical, 99%) and platinum black (Furuuchi Chemical, 99.98%) at 800°C for 1 day in air. Products thus obtained were identified by X-ray powder diffractometry (XRD, Rigaku Rotaflex) with monochromated CuKα radiation.

The electrochemical cathode performance was evaluated in coin-type lithium cells (23 mm in diameter and 2 mm thick). The Li_2PtO_3 working electrode was fabricated by mixing the obtained Li_2PtO_3 powder, acetylene black (Denki Kagaku) and PTFE Teflon binder (Daikin) in a weight ratio of 70:25:5, respectively. The electrolyte was a solution of 1 M $LiPF_6$ dissolved in a 50/25/25 vol.% (v/o) mixture of 1,2-dimethyl carbonate (DMC), propylene carbonate (PC) and ethylene carbonate (EC), respectively. This electrolyte has often been used for high voltage cathodes, because of its resistance to oxidation [8]. The cells were galvanostatically cycled between voltage limits of 3.5 and 4.5 V at a current density of 0.5 mA/cm^2 using a computer-controlled cycler system.

Structural changes in the cathode during the charge/discharge cycle were measured by XRD. After reaching potential equilibrium, each cathode pellet was adequately rinsed with dimethyl carbonate and dried in vacuum.

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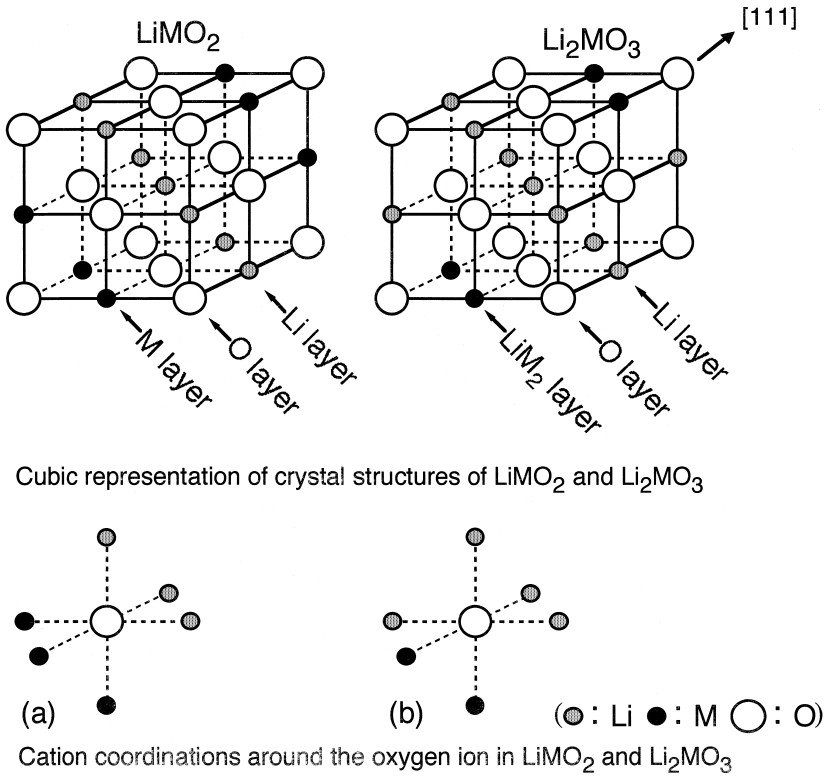

Fig. 1. Cubic representation of $LiMO_2$ and Li_2MO_3 layered rocksalt structure. (a) is the only possible coordination of the oxygen atoms in layered rocksalt $LiMO_2$ and only the configuration in (b) is geometrically possible for layered rocksalt Li_2MO_3 except Li_2ZrO_3.

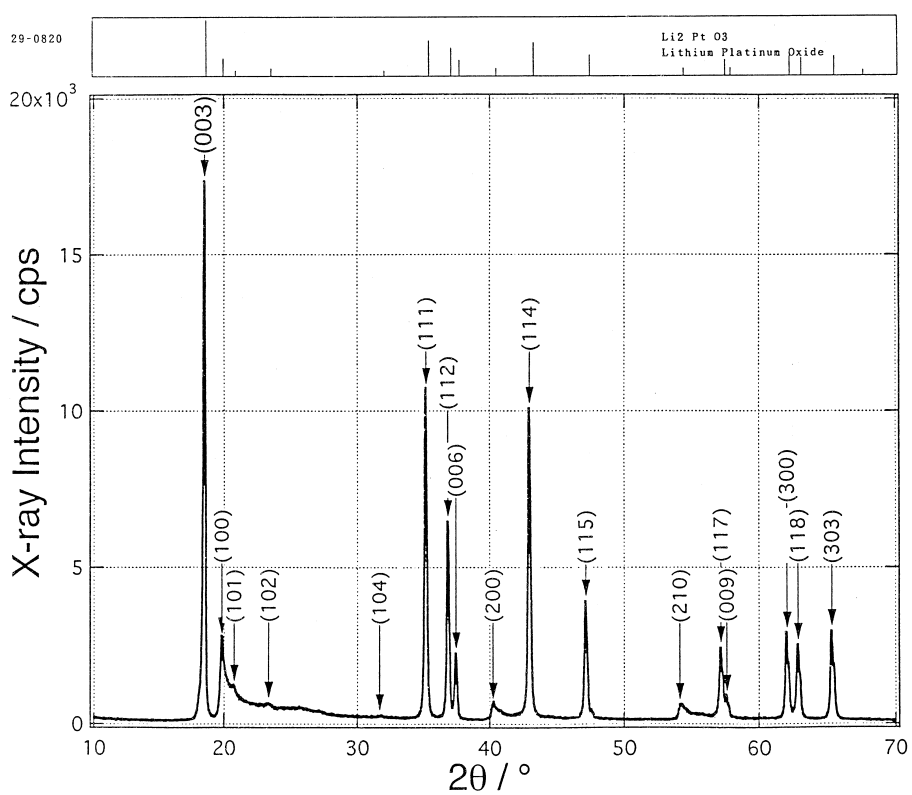

Fig. 2. XRD profile of Li_2PtO_3 with CuKα radiation.

3. Results and discussion

3.1. Identification of Li_2PtO_3

The X-ray diffraction patterns of the yellow Li_2PtO_3 powders we obtained could be indexed to a hexagonal unit cell ($P3_1$; $a = 5.17$ Å, $c = 14.42$ Å) as shown in Fig. 2. All the peaks match those given for Li_2PtO_3 in the JCPDS powder diffraction card No. 29-0820 well with no extra peaks.

3.2. Electrochemical properties of Li_2PtO_3

The charge/discharge curve of $Li_{2-x}PtO_3$ is shown in Fig. 3 with the congener. The lithium ions can be removed up to $x = 1.2$ from $Li_{2-x}PtO_3$ by charging to 4.5 V. The discharge curve after oxidative lithium extraction exhibits a 4 V region, which is very similar to that of $LiCoO_2$ and $LiNiO_2$. Li_2PtO_3 have a relatively large irreversible capacity at the 1st cycle in the same manner as Li_2IrO_3 and Li_2RuO_3. However, after the 1st cycle, the charge and discharge curves are very similar to each other and the polarization ($V_{charge}-V_{discharge}$) is less than 0.5 V at a rate of 0.5 mA/cm^2. The rechargeable capacity in the 4 V region is about 100 mA h/g. Although the gravimetric capacity is smaller than that of $LiCoO_2$, as shown in Fig. 4, the volumetric capacity (764 mA h/cm^3) exceeded that of $LiCoO_2$, because the density of Li_2PtO_3 is 1.5 times that of $LiCoO_2$.

The rechargeability of the 4 V region was electrochemically confirmed in various voltage ranges in the $Li/Li_{2-x}PtO_3$ cell as shown in Fig. 5. After charging to 5.0 V, the 4 V region disappeared in the discharge curve. This undoubtedly caused by cathode degradation or electrolyte oxidation breakdown. However, there seem to be no serious problems in the cell on charging to 4.6 V. Between 3.5 and 4.5 V, the specific capacity of the 4 V region slowly decreases and then remains stable for at least 50 cycles.

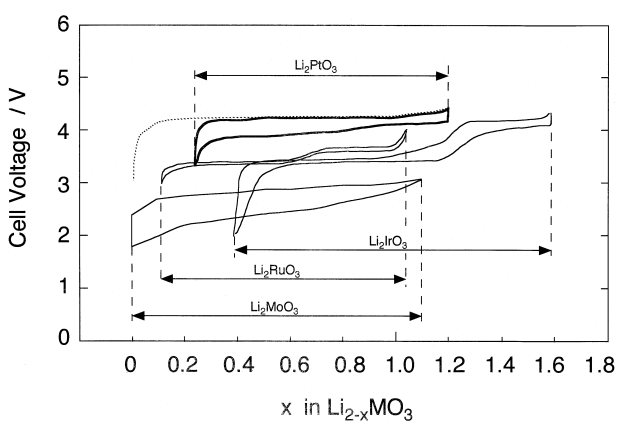

Fig. 3. Charge–discharge profiles of several $Li_{2-x}MO_3$ cathodes. The Li/Li_2PtO_3 cell was cycled at a rate of 0.5 mA/cm^2 between 3.5 V and 4.5 V; Li_2PtO_3: 100 mA h/g, Li_2IrO_3: 130 mA h/g [5], Li_2RuO_3: 160 mA h/g [4], Li_2MoO_3: 180 mA h/g [3]. Dotted line shows first charge.

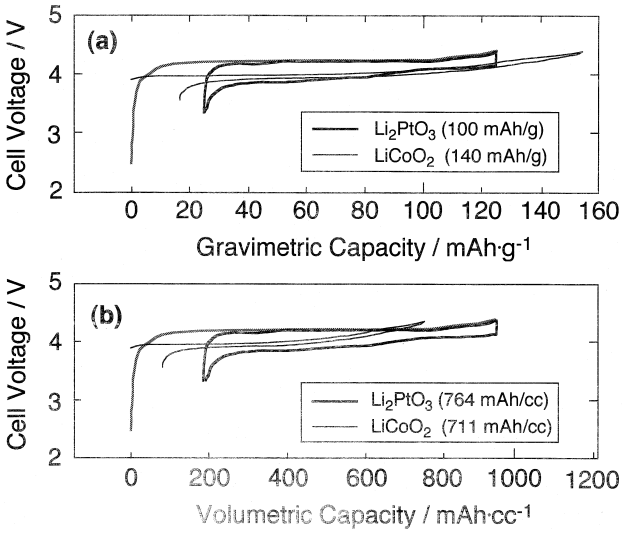

Fig. 4. Specific capacities of $Li/LiCoO_2$ and Li/Li_2PtO_3 cell; comparison of (a) gravimetric capacity, and (b) volumetric capacity.

3.3. Structural properties of Li_2PtO_3

In order to investigate the rechargeable mechanism in the 4 V region, we used XRD to measure the structural changes in the $Li_{2-x}PtO_3$ cathode pellets on charging up to $x = 1.2$. Fig. 6 shows the behavior of the ($00c$) and ($a00$) peaks of Li_2PtO_3 during the initial charging process. The variation in the lattice parameters and unit cell volume were independently calculated from Fig. 6(a) to (b). As x in $Li_{2-x}PtO_3$ increases from 0 to 1.2, the interlayer spacing decreases slightly and the intralayer distance increases a little as shown in Fig. 7. In addition, some distinct peaks which are probably caused by a lithium depleted phase can be seen at $2\theta = 18.1°$, 21.3°, 34.1°, 41.5° and 47.9° for $x > 0.8$ in $Li_{2-x}PtO_3$ and this phase disappears reversibly

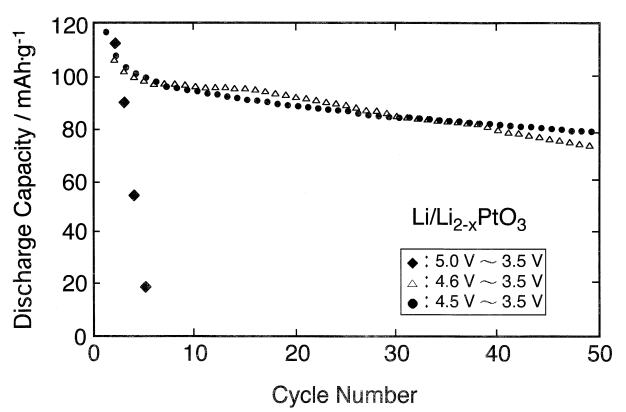

Fig. 5. Cyclability of Li/Li_2PtO_3 cell at a rate of 0.5 mA/cm^2 in various voltage ranges; ●: between 3.5 and 4.5 V, Δ: between 3.5 and 4.6 V, and ◆: between 3.5 and 5.0 V.

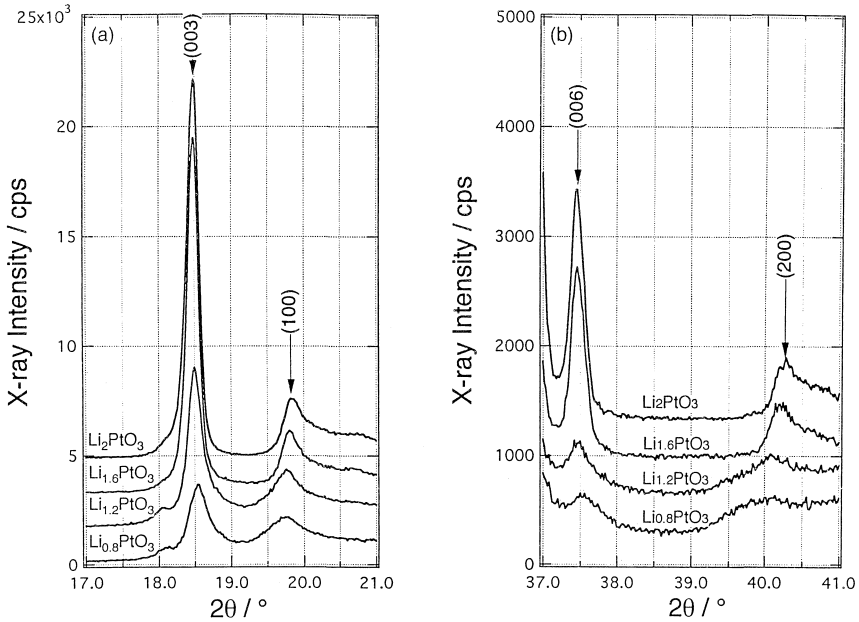

Fig. 6. Behavior of (00c) and (a00) Bragg diffraction peaks of $Li_{2-x}PtO_3$ during charging up to $x = 1.2$; (a) (003) and (100) peaks, (b) (006) and (200) peaks.

on discharge. The interlayer spacing is usually decreased by lithium extraction on charging in layered transition metal dichalcogenides such as $Li_{1-x}TiS_2$, while it increases on charging in layered rocksalt oxides such as $Li_{1-x}CoO_2$ as a result of the strong ionicity of the M–O bonds. The behavior of the Li_2PtO_3 system is intermediate because the Pt–O bonds have a higher covalency than the Co–O bonds in $LiCoO_2$. The relatively mild repulsion between adjacent oxygen layers in $Li_{2-x}PtO_3$ makes the layer structure with an empty van der Waals gap more thermodynamically stable than in $LiMO_2$. This leads to a suppression of the unit cell volume change ratio, $\Delta V/V$, to less than 1.5% during the cycling process, as shown in Fig. 7(c) and enlarges the reversible intercalation composition limit, for example $x < 1$ in $Li_{1-x}TiS_2$ and $x < 1.2$ in $Li_{2-x}PtO_3$,while $x < 0.5$ in $Li_{1-x}CoO_2$.

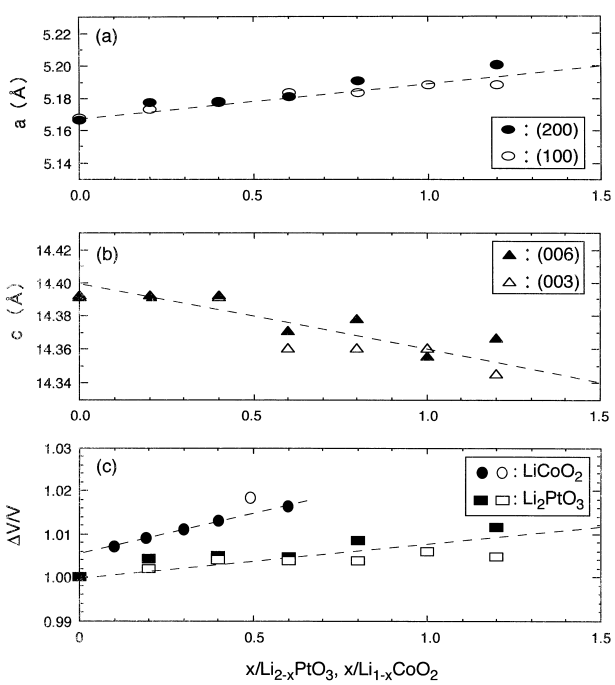

Fig. 7. Variations in unit cell with Li extraction from Li_2PtO_3; (a) a-lattice parameter variation: the open and solid ovals were calculated from (100) and (200) peak shifts, respectively, (b) c-lattice parameter variation: the open and solid triangles were calculated from (003) and (006) peak shifts, respectively, and (c) unit cell volume variation compared to that of $LiCoO_2$ [9]: the open and solid circles show hexagonal and monoclinic phases of $LiCoO_2$, respectively.

The XRD profiles of Li_2PtO_3 cathode pellets after 100th cycle are compared with that of the initial pellet in Fig. 8. The broad peaks around $2\theta = 26°$ in the XRD profile were caused by the Mylar films in which the pellets

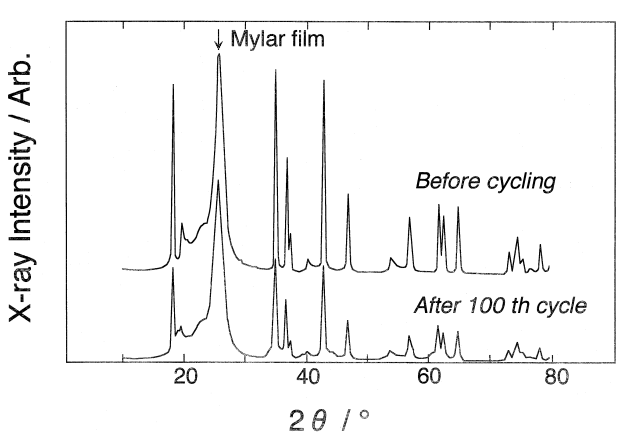

Fig. 8. XRD profiles of Li_2PtO_3 cathode pellet; top: before cycling, bottom: after 100th cycle.

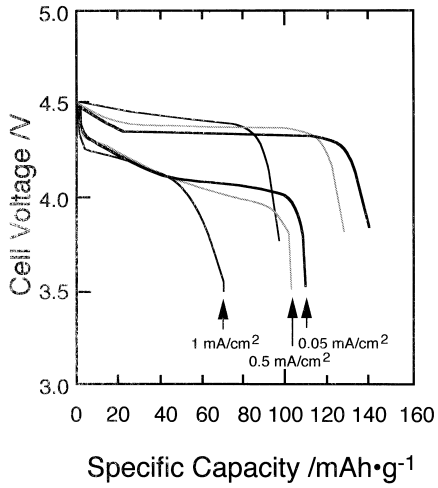

Fig. 9. Rate capability of $Li/Li_{2-x}PtO_3$ cell; thick line: 0.05 mA/cm^2 (1.1 mA/g), dotted line: 0.5 mA/cm^2 (10 mA/g), thin line: 1.0 mA/cm^2 (19 mA/g).

were wrapped to protect them from moisture. The comparison of the two XRD diffraction profiles revealed no significant degradation in any specific peaks. Even after the 100th cycle, Li_2PtO_3 still retained a basal layered rocksalt structure in the 4 V region, although the crystallinity of the 100th cycle cathode is lost a little.

3.4. Kinetic properties of Li_2PtO_3

The rate capability of $Li_{2-x}PtO_3$ is shown in Fig. 9. It reveals a relatively small overpotential in the charged state $x > 0.5$ in $Li_{2-x}PtO_3$.

4. Conclusion

We undertook the electrochemical delithiation of Li_2PtO_3 in the hope of finding a cathode performance similar to that of layered rocksalt oxide $LiCoO_2$. We found that $Li_{2-x}PtO_3$ has a 4 V region vs. Li^0/Li^+ over a wide composition range of $x(0.2 < x < 1.2)$. To date, $Li_{2-x}PtO_3$ is a unique 4 V cathode with a volumetric capacity comparable to that of $LiCoO_2$ even among 5d transition metal compounds. Much cathode research has been directed to the first-row 3d transition metal oxides which have high energy densities by weight. Although 5d transition metals are neither light nor inexpensive, this good result with Li_2PtO_3 encourages us to look for novel cathode materials among the 4d and 5d transition metal oxides. This is because the disadvantages of 4d and 5d transition metal oxide cathodes, their heaviness and expense, should not be critical in terms of applications such as solid state microbatteries.

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