Synthesis of alkali metal platinates and their dissolution behavior in hydrochloric acid

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To decrease the environmental load due to current Pt dissolution processes that use strong acids in combination with oxidizing agents, the synthesis and dissolution of alkali metal platinates in hydrochloric acid (HCl) were examined. The alkali metal platinates were prepared by calcinating mixtures of Pt black and the alkali metal carbonates (Li, Na, K) at 600–800°C in air. Li2PtO3 powder was obtained through the calcination of a Pt black and Li2CO3 mixture at 600°C. The formation of Na2PtO3 and Na2PtO4 was confirmed upon the calcination of Pt black and Na2CO3 at 600–800°C; however, unreacted Pt also remained in the calcined samples. The calcination of Pt black and K2CO3 did not yield any Pt-containing oxides, even at 800°C. These results indicated that Li2CO3 was the most active reagent among the examined alkali metal carbonates for the formation of alkali metal platinates. The dissolution of the resulting Li2PtO3 in conc. HCl was monitored by inductively coupled plasma–optical emission spectrometry. The results showed that Li ions leached into HCl prior to the Pt, and the solubilities of the metals increased with decreasing calcination temperature. The dissolution behavior of Li2PtO3 was discussed based on the crystal size and anisotropy of the crystal. A Pt dissolution process by way of these platinates is expected to benefit the establishment of recovery processes for PGMs with low environmental loads.

Key-words: Platinum, Alkali metals, Double oxide, Li2PtO3, Hydrochloric acid, Dissolution property

1. Introduction

Platinum group metals (PGMs) play important roles in various industrial applications, especially as environmental catalysts. However, the supply of PGMs is unstable because the global distribution of PGM production sites is limited and subject to geopolitical disruption. Thus, Japan, the United States, and the European Union have classified the PGMs as critical materials because of their economic importance and their supply risks. Since the demand for PGMs is expected to increase in the foreseeable future, the recovery of PGMs from scrap materials has become increasingly important.

The hydrometallurgical recovery of PGMs typically consists of dissolution, separation, and purification processes. Among these, dissolution is a key step, because the subsequent separation and purification processes, such as solvent-extraction, co-precipitation, and ion-exchange methods, are designed for PGMs in solution. However, PGMs in the metallic state cannot be oxidized by the hydrogen ions in acids, because the standard reduction potentials of PGMs are more positive than that of hydrogen. Thus, the dissolution of PGMs does not proceed in non-oxidizing acids such as HCl. As a result, strong acids containing oxidizing agents are used to dissolve PGMs; these typically include aqua regia and HCl sparged with chlorine (Cl2) gas. At present, aqua regia, a traditional solvent that can dissolve PGMs, is mainly used in small scale dissolutions, i.e., laboratory experiments. The oxidizing power of aqua regia originates from the Cl2 and nitrosyl chloride (NOCl) that evolve upon mixing HCl and nitric acid. For industrial scale operations, PGMs are often dissolved in HCl sparged with Cl2 that is supplied from large gas containers; thus, Cl2 acts as the oxidizing reagent. In spite of their indispensable oxidizing powers, these oxidizing agents are highly corrosive and extremely toxic. Therefore, the dissolution of PGMs in a non-oxidative acid, for example pure HCl, would be very effective in terms of reducing environmental load.

In recent years, PGM pretreatments have been examined toward improving the dissolution of PGMs in HCl. Complex oxides which contain PGMs, such as Ca4PtO6, and PGM-containing perovskite-type multiple oxides, have been reported to be soluble in HCl. The PGMs in these complex oxides are oxidized, which may account for their solubility in HCl. However, the formation of these PGM-containing complex oxides can be complicated or require extended, very high treatment temperatures. For example, Ca4PtO6 was prepared through the oxidation of a Ca–Pt alloy at 900°C for 24 h, where the Ca–Pt alloy was produced via the treatment of Pt with Ca vapor at 800–900°C for 3 h. The formation of a perovskite-type multiple oxide that could absorb PGM vapors, La0.7Sr0.2Ba0.1ScO3−δ, needed more severe conditions: mixtures of the starting materials were calcined at 1350°C, followed by additional calcination at 1600°C for 20 h. Furthermore, heat treatment at 1525°C for 10 h was necessary to absorb Pt vapor in the perovskite-type multiple oxides. Thus, it would be desirable to prepare PGM-containing complex oxides using simple procedures and/or milder conditions.

In a previous report, we revealed that lithium platiniate, Li2PtO3, was obtained via the facile and direct calcination of Pt black and Li2CO3 at 600°C. Through dissolution experiments, we confirmed that the resulting Li2PtO3 was soluble in HCl at ambient temperatures. The Pt solubility increased with dissolution temperatures over the range 40–80°C, and the sample calcined at 600°C was almost completely dissolved after treatment in conc. HCl at 80°C for 9 h.
In this study, we examined the applicability of other alkali metal carbonates, Na2CO3 and K2CO3, in the synthesis of platinates. Given the cost of the alkali metal salts, the less expensive Na and K salts would be preferable to Li salts. We also focused on the dissolution behaviors of the alkali metal platinates. Thus, the time evolution of ion concentrations in solution and the structures of the solid residues were investigated in detail. Based on these results, factors related the dissolution rate of Pt and the dissolution mechanism of Li2PtO3 were discussed.

2. Experimental

2.1 Synthesis of alkali metal platinates

To prepare the alkali metal platinates, Pt black (250.0 mg, Wako Pure Chemical Industries) and the alkali metal salts were mixed in an agate mortar. The metal dispersion of Pt black, determined by the CO adsorption method, was 0.36%, which corresponded to a mean diameter of ca. 300 nm. We used the following salts: lithium carbonate (Li2CO3, 189.4 mg, Wako), sodium carbonate (Na2CO3, 271.7 mg, Wako), and hydrous potassium carbonate (K2CO3, 354.2 mg, Wako). The feeding ratio of the alkali metals ("A") to Pt, A/Pt, was 4.0. Mixtures of Pt black and Al2CO3 were mounted in alumina boats and placed in an electric furnace, except for that containing Li2CO3, which was mounted on gold foil to avoid reaction between the Li2CO3 and the alumina. The mixtures were calcined in air at temperatures from 500 to 800°C. The calcination time was fixed at 1 h unless otherwise stated. To clarify the effect of the oxygen in air upon the generation of alkali metal platinates, the preparation of Li2PtO3 under nitrogen flow (300 mL/min) was also examined.

2.2 Dissolution treatment of alkali metal platinates using HCl

To characterize the dissolution properties of the alkali metal platinates in HCl, a sample of the obtained powder (10% by weight of the obtained material, containing 25.0 mg Pt) was added to conc. HCl (20 mL, Wako) in a flask with a reflux condenser. The suspension was heated at 80°C in a water bath with stirring for a period that was varied from 5 min to 9 h. After this dissolution treatment, the flask was immediately placed in an ice water bath, and ice cold, ultrapure water (20 mL) was added to the suspension to quench further dissolution. The suspension was then filtered through a PTFE filter (pore size, 0.1 µm) under reduced pressure to separate the solution from the solid residue. The filtrate was retained and the residue was dried at 110°C for 3 h in an oven.

2.3 Characterization

The crystalline phases and crystallite sizes of Li2PtO3 were analyzed using an X-ray diffractometer (XRD, Rigaku RINT 2000) equipped with a Cu Kα radiation source (40 kV, 30 mA). The diffraction patterns were acquired over a 2θ range from 10 to 80° with a step width of 0.02°. To avoid moisture adsorption by platinates were obtained from N2 adsorption measurements using a flow-BET instrument (BELCAT, BEL Japan). After removal of excess alkali metal carbonate by washing with ultrapure water, the samples (ca. 0.3 g) were annealed at 300°C in a flow of He carrier gas prior to the measurements.

The concentrations of Pt and Li in the solution samples after dissolution treatment were determined by inductively coupled plasma–optical emission spectroscopy (ICP-OES, IRIS Advantage, Thermo Jarrell Ash Co.). The total metal contents of the calcined samples and residues were measured after complete dissolution using a pressure decomposition system, as follows. A powder sample, either the calcined sample (1/10 of the total weight) or the residue, was added to conc. HCl (10 mL) in a PTFE inner vessel. This vessel was placed in a pressure casing made of stainless steel. For the sample calcined at 600°C and its residue, the decomposition temperature and time were 80°C and 9 h, respectively. The samples calcined at 700 and 800°C, and their residues, were decomposed at 180°C for 2 h. The metal solubility of a sample was calculated based on its total metal content evaluated through the above procedures. Under the assumption that the Li content in the calcined Li2PtO3 crystal samples was twice that of Pt, the Li content due to unreacted Li2CO3 was evaluated as follows: (content of Li in solution sample) – (content of Pt in the decomposed sample) × 2.

3. Results and discussion

3.1 Preparation of the alkali metal platinates from different alkali metal carbonates

Alkali metal carbonates (A2CO3, A: Li, Na, K) were calcined with Pt black at 600°C, and their reactivities toward Pt were compared. The XRD profiles of the calcined samples are displayed in Figs. 1(a)–1(c). The diffraction peaks for the sample prepared using Li2CO3 were identified as those of Li2PtO3 and Li2CO3 (JCPDS No. 22-1141) [Fig. 1(a)]. The diffraction peaks of Li2PtO3 were indexed on the basis of monoclinic symmetry; the corresponding lattice constants have been previously reported. The lack of any peaks due to Pt black confirmed its complete reaction with Li2CO3. The residual Li2CO3, identified by the corresponding XRD peaks, was due to the excess loading of the reagent. The XRD pattern of the sample prepared with Na2CO3 [Fig. 1(b)] exhibited diffraction peaks originating from Na2Pt3O4 (JCPDS No. 6-534) and Na2PtO3 (JCPDS No. 27-774), whereas the main crystallite phases were identified as unreacted Pt (JCPDS No. 4-506) and Na2CO3 (JCPDS No. 19-1130). Oxide phases containing Pt were not confirmed for the sample calcined with K2CO3; only unreacted Pt and K2CO3 (JCPDS No. 16-820) were detected [Fig. 1(c)]. These results demonstrated that the reactivity order of A2CO3 toward Pt black was Li2CO3 > Na2CO3 > K2CO3.

![Fig. 1. XRD profiles of samples calcined at 600°C with (a) Li2CO3, (b) Na2CO3, and (c) K2CO3. The Miller indices of Li2PtO3 are labeled in pattern (a). Plus signs, solid diamonds, solid squares, white diamonds, white circles, and asterisks indicate the diffraction peaks due to Li2CO3, Na2Pt3O4, Na2PtO3, Na2CO3, K2CO3, and Pt, respectively.](image-url)
From these results, the formation of Li$_2$PtO$_3$ involving O$_2$ paths to Li$_2$PtO$_3$ by assuming different by-products, CO$_2$, CO, reaction paths were evaluated. First, we compared three reaction

$$
\text{Li}_2\text{CO}_3(s) + \text{Pt}(s) + \text{O}_2(g) \rightarrow \text{Li}_2\text{PtO}_3(s) + \text{CO}_2(g)
$$

$$
\text{Li}_2\text{CO}_3(s) + \text{Pt}(s) + 1/2\text{O}_2(g) \rightarrow \text{Li}_2\text{PtO}_3(s) + \text{CO}(g)
$$

$$
\text{Li}_2\text{CO}_3(s) + \text{Pt}(s) \rightarrow \text{Li}_2\text{PtO}_3(s) + \text{C}(s)
$$

The standard formation enthalpy $\Delta H_f$ of compounds (kJ/mol): Li$_2$PtO$_3$: $-1085.7$; Li$_2$CO$_3$: $-1215.9$; Li$_2$O: $-597.9$; LiOH: $-487.5$; CO$_2$: $-393.5$; CO(g): $-110.5$; H$_2$O(g): $-241.8$. $\Delta H_f$ of Li$_2$PtO$_3$ was estimated from the $\Delta H_f$ of Li$_2$O and PtO$_2$ [−80 (kJ/mol)].

To promote the formation of platinates containing Na and K, calcination at higher temperatures, 700 and 800°C, was examined. The XRD patterns of the samples calcined using Na$_2$CO$_3$ and K$_2$CO$_3$ are displayed in Figs. 2 and 3, respectively. For comparison, the XRD profiles of the samples calcined at 600°C are also included [Figs. 2(a) and 3(a)]. It is obvious from Fig. 2 that the formation of Na$_2$PtO$_3$ and Na$_2$PtO$_4$ was promoted by the increased calcination temperatures; however, unreacted Pt and Na$_2$CO$_3$ seemed to remain even after calcination at 800°C. Calcination of K$_2$CO$_3$ and Pt black at high temperatures did not yield any oxide phases containing Pt (Fig. 3).

Thus, the formation of Li$_2$PtO$_3$, Na$_2$PtO$_3$, and Na$_2$PtO$_4$ was experimentally confirmed, whereas K platinates could not be obtained under the present reaction conditions. The reactivity of an alkali metal salt may depend on the size of its metal ion.

### 3.2 Evaluation of the enthalpy changes in the formation of alkali metal platinates

To explore the differences in the formation conditions of the alkali metal platinates, the enthalpy changes $\Delta H_f$ of various reaction paths were evaluated. First, we compared three reaction paths to Li$_2$PtO$_3$ by assuming different by-products, CO$_2$, CO, and C, as shown in Table 1. Based on reported values,$^{20}$ the standard formation enthalpy $\Delta H_f$ of Li$_2$PtO$_3$ was calculated to be $-1085.7$ kJ/mol, using $\Delta H_f$ of Li$_2$O ($-597.9$ kJ/mol)$^{21}$ and PtO$_2$ ($-80$ kJ/mol)$^{22}$. The resulting $\Delta H_f$ of the reaction which yielded CO$_2$ as a by-product was a negative value, $-263.3$ kJ/mol, whereas positive values of $\Delta H_f$ were obtained for reactions generating CO ($23.8$ kJ/mol) and C ($130.2$ kJ/mol).

$$
\text{Pt} + \text{Li}_2\text{CO}_3 + \text{O}_2 \rightarrow \text{Li}_2\text{PtO}_3 + \text{CO}_2
$$

From these results, the formation of Li$_2$PtO$_3$, involving O$_2$ and CO$_2$ was concluded to be thermodynamically favored. To investigate the effect of oxygen upon the formation reaction, Pt black and Li$_2$CO$_3$ were calcined at 600°C under nitrogen flow. From the XRD measurements, a large portion of the sample was found to be unreacted Pt and Li$_2$CO$_3$, which indicated that the formation of Li$_2$PtO$_3$ was significantly suppressed by a lack of oxygen. It was, therefore, concluded both theoretically and experimentally that Li$_2$PtO$_3$ was generated via Eq. (1).

Next, we evaluated $\Delta H_f$ for the formation of Na and K platinates, assuming the paths involving O$_2$ and CO$_2$. The results are summarized in Table 2. As can be seen, the resulting $\Delta H_f$ of Li$_2$PtO$_3$ ([−263.3 kJ/mol]) was smaller than that of Na$_2$PtO$_4$ ([−326.2 kJ/mol]). Nevertheless, the yield of Li$_2$PtO$_3$ calcined at 600°C for 1 h [Fig. 1(a)] was almost 100%, which was much higher than that of the Na platinates prepared under the same conditions [Fig. 1(b)].

The enthalpy changes are important in terms of thermodynamic considerations, whereas the contributions of kinetic factors should affect the product yield and selectivity. In the formation of alkali metal platinates, Pt, the alkali metal salts, and oxygen in air are involved. To investigate the reactivity between Pt and oxygen, Pt black was calcined at 600°C in air. However, Pt oxide was not observed by XRD measurement. Judging from this result and the preceding considerations, the reactivity of the alkali metal salts toward Pt can be a key factor in the formation of alkali metal platinates. Since Li$^+$ is smaller than Na$^+$ and K$^+$, Li$^+$ may diffuse into the Pt lattice more easily. This could be the reason why Li$_2$PtO$_3$ was produced under milder conditions.

### 3.3 The effect of calcination temperature and time upon the formation of Li$_2$PtO$_3$

From a technological viewpoint, a low reaction temperature for alkali metal platinate synthesis would be desirable. However, even with the most reactive carbonate among those examined,
Li$_2$PtO$_3$ was clearly promoted with longer calcination times. The crystallite size of Li$_2$PtO$_3$ estimated from the (001) diffraction peaks increased with calcination temperature: values of 19, 31, and 71 nm were obtained for the samples calcined at 600, 700, and 800°C, respectively. No other peaks were observed. The crystallite sizes of the samples calcined at 600, 700, and 800°C. The Miller indices of Li$_2$PtO$_3$ are labeled in patterns (a) and (f). Plus signs and/or crosses indicate to effects complete reaction, Pt and Li$_2$CO$_3$ were calcined for 600 min. The solubilities of Pt and Li were plotted in Figs. 5(a) and 5(b), respectively. Figure 6 clearly indicates that the solubility of Pt increased almost linearly from 0.5 to 6 h for the sample calcined at 700°C. The Pt solubility was found to increase with decreasing calcination temperature. The effect of the dissolution temperature was also investigated using the sample obtained at 600°C. An enhancement of Pt solubility was confirmed upon increasing the dissolution temperature from 40 to 80°C. These results were based on solubility data obtained after a fixed treatment time of 9 h.

### Table 2. Standard formation enthalpies ($\Delta H_f^\circ$) of alkali metal platinates and the changes in enthalpy ($\Delta H_r^\circ$) during their formation under the present experimental conditions

| Chemical formulae of alkali metal platinates | Standard formation enthalpies of alkali metal platinates $\Delta H_f^\circ$ (kJ/mol) | Formation reactions of alkali metal platinates | Standard enthalpy change of reaction $\Delta H_r^\circ$ (kJ/mol) |
|------------------------------------------|----------------------------------|-----------------------------------------------|-----------------|
| Li$_2$PtO$_3$                            | $-1085.7$                        | Li$_2$CO$_3$(s) + Pt(s) + O$_2$(g) $\rightarrow$ | $-259.2$        |
| NaPt$_2$O$_4$                            | $-694.8$                        | $1/2$Na$_2$CO$_3$(s) + 3Pt(s) + 7/4O$_2$(g) $\rightarrow$ | $-326.2$        |
| Na$_2$PtO$_3$                            | $-933.9$                        | Na$_2$CO$_3$(s) + Pt(s) + O$_2$(g) $\rightarrow$ | $-196.4$        |
| K$_2$PtO$_3$                             | $-955.7$                        | K$_2$CO$_3$(s) + Pt(s) + O$_2$(g) $\rightarrow$ | $-198.3$        |

The standard formation enthalpy $\Delta H_f^\circ$ of compounds (kJ/mol): Li$_2$CO$_3$(s): $-1215.9$; Na$_2$CO$_3$(s): $-1130.7$; K$_2$CO$_3$(s): $-1151.0$; CO$_2$(g): $-393.5$.

Fig. 4. XRD profiles of samples obtained by calcination under the designated conditions using Li$_2$CO$_3$: (a) 500°C, 1 h; (b) 500°C, 12 h; (c) 500°C, 24 h; (d) 600°C, 1 h; (e) 700°C, 1 h; and (f) 800°C, 1 h. The Miller indices of Li$_2$PtO$_3$ are labeled in patterns (a) and (f). Plus signs and asterisks indicate the diffraction peaks due to Li$_2$CO$_3$ and Pt, respectively.

Li$_2$CO$_3$, the yield of Li$_2$PtO$_3$ was very low after calcination at 500°C for 1 h [Fig. 4(a)]. The dissolution properties of Li$_2$PtO$_3$ were expected to improve with decreasing calcination temperature because of the suppression of crystal growth. In contrast, the presence of unreacted Pt would decrease Pt solubility. Thus, to effect complete reaction, Pt and Li$_2$CO$_3$ were calcined for longer times at 500°C. From Figs. 4(a)–4(c), the formation of Li$_2$PtO$_3$ was clearly promoted with longer calcination times; however, Pt still remained even after 24 h. The diffraction peaks observed for the samples calcined at 600, 700, and 800°C [Figs. 4(d)–4(f)] were attributed to Li$_2$PtO$_3$ and excess Li$_2$CO$_3$; no other peaks were observed. The crystallite sizes of the samples calcined at 600–800°C were evaluated using the Scherrer equation. The crystallite size of Li$_2$PtO$_3$ estimated from the (001) diffraction peaks increased with calcination temperature: values of 19, 31, and 71 nm were obtained for the samples calcined at 600, 700, and 800°C, respectively.

It has been reported that Li$_2$PtO$_3$ can be synthesized by the calcination of Li$_2$CO$_3$ and Pt black at 800°C for 12 h or longer. Recently, it was reported that calcination of the same materials at 750°C for 12 h led to the formation of Li$_2$PtO$_3$. The Li$^+/Pt$ ratios in the reports were equal or used 5% excess Li$_2$CO$_3$ to the stoichiometric ratio of Li$_2$PtO$_3$. Because the melting point of Li$_2$CO$_3$ is 720°C, calcination above 720°C implies that melted Li$_2$CO$_3$ reacts with Pt black. In contrast, we found that Li$_2$PtO$_3$ could be synthesized in a solid-phase reaction at 600°C for 1 h, using an excess Li$^+/Pt$ ratio of 4.0.

### 3.4 Dissolution behavior of Li$_2$PtO$_3$ in HCl

In a previous report, samples prepared at 600–800°C were dissolved in HCl at 60°C to characterize the dissolution properties of Li$_2$PtO$_3$. The Pt solubility was found to increase with decreasing calcination temperature. The effect of the dissolution temperature was also investigated using the sample obtained at 600°C. An enhancement of Pt solubility was confirmed upon increasing the dissolution temperature from 40 to 80°C. These results were based on solubility data obtained after a fixed treatment time of 9 h.

To understand the dissolution behavior of Li$_2$PtO$_3$ in detail, observation of the time dependence of Pt and Li solubilities was required. Thus, the solubilities of Pt and Li after the immersion of the calcined samples were monitored between 0.5 and 9 h by ICP-OES. Figures 5(a) and 5(b) display the dissolution time dependence of Pt and Li solubilities for the samples calcined at 600, 700, and 800°C. The dissolution temperature was 80°C. Note that the contribution from Li due to unreacted Li$_2$CO$_3$, evaluated by the method described in section 2.3, was subtracted from the Li concentration raw data. Figures 5(a) and 5(b) indicate that Li leached into HCl prior to Pt in all the samples calcined at 600–800°C. Figures 5(a) and 5(b) also indicate that the solubilities of Pt and Li increased with decreasing calcination temperature. This is probably because the smaller crystallite or particle size of Li$_2$PtO$_3$ increased the total contact area between the Li$_2$PtO$_3$ particles and HCl. For the sample calcined at 600°C, the Pt solubility abruptly increased in the initial stage of dissolution, and then gradually increased after 1 h. In contrast, the Pt solubility increased almost linearly from 0.5 to 6 h for the sample calcined at 700°C. The Pt solubility was directly proportional in the dissolution period from 0.5 to 9 h for the sample calcined at 800°C. The Li solubilities [Fig. 5(b)] behaved differently. After dramatically increasing in the initial stage of dissolution, however, further increases in the solubilities abruptly decreased at around 1 h and became almost zero at 9 h, regardless of the solubility values.

To investigate the metal dissolution behaviors over shorter time periods, Li$_2$PtO$_3$ samples were dissolved in HCl at 80°C for 5 to 60 min. The solubilities of Pt and Li were plotted in Figs. 6(a) and 6(b), respectively. Figure 6 clearly indicates that the solubility of Li was always higher than that of Pt, which supports the faster leaching of Li than Pt.

The standard formation enthalpy $\Delta H_f^\circ$ of compounds (kJ/mol): Li$_2$CO$_3$(s): $-1215.9$; Na$_2$CO$_3$(s): $-1130.7$; K$_2$CO$_3$(s): $-1151.0$; CO$_2$(g): $-393.5$.

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3.5 Structural change of Li$_2$PtO$_3$ due to a dissolution treatment

The dissolution studies of Li$_2$PtO$_3$ confirmed the faster leaching of Li than Pt, especially in the initial stages (Fig. 6). Thus, the Li$^+$/Pt ratio of the residues in the initial stage of dissolution was expected to be lower than 2.0. To investigate changes in the Li$^+$/Pt ratio and the structure of Li$_2$PtO$_3$ after dissolution treatment, ICP and XRD measurements were obtained for residues collected after HCl treatment at 80°C for 5 min. The ICP results revealed that the Li$^+$/Pt ratios in the residues calcined at 600, 700, and 800°C were 0.43, 0.62, and 1.28, respectively. Although the Li$^+$/Pt ratios in the residues increased with calcination temperature, the obtained values were less than 2.0, which is the stoichiometric ratio of Li$_2$PtO$_3$.

The crystal structures of the residues were characterized by XRD analysis (Fig. 7). A shift of the (001) diffraction peak toward a higher diffraction angle was observed for the residues calcined at 600°C [Fig. 7(a)] and 700°C [Fig. 7(b)]. The (001) and (020) diffraction peaks overlapped one another in the residues calcined at 600 and 700°C. Li$_2$PtO$_3$ is a layered compound consisting of alternating layers of Li$^+$ and a mixture of Li$^+$ and Pt$^{4+}$ that stack along the c-axis (Fig. 8). The shift of the (001) diffraction peak to a higher diffraction angle suggested a decrease in the interlayer distance. Since the Li$^+$/Pt ratio of the residues was lower than the stoichiometric ratio of Li$_2$PtO$_3$, 2.0, the replacement of Li$^+$ by H$^+$ could be the reason for the decrease in the interlayer distance of Li$_2$PtO$_3$. The partial exchange of Li$^+$ for the smaller H$^+$ is consistent with a decrease in the interlayer distance.

The XRD pattern of the residue obtained from the sample calcined at 800°C [Fig. 7(c)] exhibited separate peaks for the (001) and (020) diffractions. However, the intensity of the (001) diffraction peak was markedly decreased. The decrease in this (001) peak intensity could be related to a randomization of the...
layered structure induced by the selective leaching of Li. This structural change may be related to the ion-exchange reaction between Li\(^+\) and H\(^+\).

From these results, a decrease in calcination temperature was found to promote the leaching of metals, especially Li\(^+\). In the next section, we will discuss factors that determine the dissolution properties in terms of the particle properties and crystal structure of Li\(_2\)PtO\(_3\).

### 3.6 Factors determining the dissolution properties of Li\(_2\)PtO\(_3\)

The dissolution rate of Li\(_2\)PtO\(_3\) should increase with the total contact area between the Li\(_2\)PtO\(_3\) particles and HCl, assuming that the dissolution rate is constant for all crystal planes. Thus, we compared the dissolution rates of the samples prepared at different calcination temperatures with their specific surface areas and crystallite sizes.

The apparent dissolution rates of Pt, represented by the rate at 5 min from the beginning of HCl treatment at 80°C, BET surface areas, and crystallite sizes are summarized in Table 3. The apparent dissolution rate of Pt increased with decreasing calcination temperature. However, a significant difference was not observed in the specific surface areas between the samples calcined at 600 and 700°C. In contrast, the crystallite sizes estimated from the (001) diffraction peak were significantly different: 19 and 31 nm for the samples calcined at 600 and 700°C, respectively. These results suggested that the apparent dissolution rate of Pt was affected by the crystallite size rather than the specific surface area of Li\(_2\)PtO\(_3\).

Because Li\(_2\)PtO\(_3\) has a layered structure (Fig. 8), we also examined the anisotropy of the crystal by evaluating the relative crystallite sizes of Li\(_2\)PtO\(_3\) (001) to Li\(_2\)PtO\(_3\) (131), \(D_{(001)}/D_{(131)}\); the (001) diffraction reflects the growth of the crystal along the c-axis, while the (131) diffraction represents isotropic growth of the crystal. The \(D_{(001)}/D_{(131)}\) ratio decreased from 1.3 to 1.1 with increasing calcination temperature from 600 to 700°C, whereas the value for the sample calcined at 800°C was maintained at 1.1 (Table 3). The \(D_{(001)}/D_{(131)}\) value of 1.1 corresponded to that of large crystallites which were prepared via calcination at 800°C for 24 h in air. Judging from these results, crystal growth in the \(ab\) plane could be suppressed in the samples calcined at 600°C, compared to the samples obtained at 700 and 800°C. The samples calcined at 700 and 800°C exhibited the same \(D_{(001)}/D_{(131)}\) ratios, which indicated that the difference in their dissolution properties (Figs. 5 and 6) was due to specific surface area or crystallite sizes.

In the preparation of Li\(_2\)PtO\(_3\), a decrease in crystallite size and enhancement of anisotropic crystal growth along the c-axis were achieved when we decreased the calcination temperature. A decrease in the calcination temperature also resulted in the faster leaching of Li and acceleration of the subsequent leaching of Pt. The obtained results indicate that the crystallite size and anisotropy of the crystal dominate the dissolution properties of Li\(_2\)PtO\(_3\). From the dissolution results and the crystal structure, the Li\(^+\) layer along the \(ab\) plane probably experiences rapid leaching. The dissolution properties of Li\(_2\)PtO\(_3\) depend on the exposed area of the crystal planes perpendicular to the \(ab\) plane, which we can conclude to be the most important factor for the dissolution of Li\(_2\)PtO\(_3\).

### 4. Conclusions

Alkali metal platinates were synthesized by the calcination of Pt black and alkali metal carbonates. The order of reactivity was Li\(_2\)CO\(_3\) > Na\(_2\)CO\(_3\) > K\(_2\)CO\(_3\). The optimum calcination temperature for Li\(_2\)PtO\(_3\) was 600°C, with respect to the preparation and dissolution of the compound in HCl. The dissolution treatments of Li\(_2\)PtO\(_3\) showed that Li leached into the solution prior to Pt. The exposed area of the crystal planes perpendicular to the \(ab\) plane could be a principal factor determining the dissolution properties of Li\(_2\)PtO\(_3\).

### Acknowledgements

This study was supported by a Grant-in-Aid for Challenging Exploratory Research, No. 23656566.

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