Minerals Engineering (SRCR '14 special issue) Revised version
--

Title: Enhanced dissolution of alkali metal platinates in dilute hydrochloric acid
by addition of calcium chloride

Author names: Ryo Kasuya^{*}, Takeshi Miki, Hisashi Morikawa, and Yutaka Tai

Affiliation: National Institute of Advanced Industrial Science and Technology (AIST),
2266–98 Anagahora, Shimo-Shidami, Moriyama-ku, Nagoya 463–8560,
Japan

^{*}Corresponding author. Tel.: +81 52 796 7595; fax: +81 52 796 7406

E-mail address: ryo-kasuya@aist.go.jp (R. Kasuya)

Abstract

To decrease the environmental load from current Pt recovery processes that use strong acids in combination with oxidizing agents, the dissolution of Pt in hydrochloric acid (HCl) by way of alkali metal platينات was examined. The alkali metal platينات, Li_2PtO_3 , Na_2PtO_3 , and a $(\text{Na,Li})_2\text{PtO}_3$ solid solution, were prepared by calcining mixtures of Pt black and the alkali metal carbonates (Li, Na) at 600–800°C in air. The dissolution of the resulting alkali metal platينات in HCl solutions was monitored by inductively coupled plasma–optical emission spectrometry. The results showed that Pt solubility approached 100% after choosing the appropriate calcination conditions. It was also found that by adding calcium chloride, the rate of Pt dissolution in dilute HCl significantly increased. The dissolution behavior of the alkali metal platينات was discussed based on the dissolution rates of the alkali metals and Pt ions, together with the crystal structures of the platينات.

Keywords: Platinum; Alkali metal; Double oxide; Calcium chloride; Hydrochloric acid;

Dissolution property

1. Introduction

Platinum group metals (PGMs) play important roles in various industrial applications, especially as environmental catalysts ([Bernardis et al, 2005](#)). In particular, their use as emission control catalysts for vehicles constitutes the largest segment of the PGMs market. The demand for PGMs is only expected to grow because of the rapid increases in motorization in developing nations and tightened exhaust emission regulations in developed countries ([Johnson Matthey Plc., 2013](#)). However, primary PGM resources are limited geographically and their production has not shown any significant increase in recent years. To stabilize the supply of PGMs, their recycling has become increasingly important.

PGMs are typically recovered after dissolution in aqueous solutions and subsequent metallurgical separation processes ([Shibata and Okuda, 2002](#)). However, PGMs in the metallic state barely dissolve in protic acids because the oxidation/reduction potentials of PGMs are more positive than that of hydrogen ([Barin and Knacke, 1973](#)). Therefore, strong acids containing oxidizing agents are used; these typically include aqua regia or a mixture of hydrochloric acid (HCl) and chlorine (Cl₂)

gas. In aqua regia, spontaneously generated compounds such as nitrosyl chloride (NOCl) and Cl_2 oxidize the PGMs (Kizilaslan et al, 2009). Despite their indispensable oxidizing powers, these species are highly corrosive and extremely toxic. Therefore, an ionization process for PGMs without toxic oxidizing agents would improve the safety of hydrometallurgical recovery.

To dissolve PGMs in a non-oxidative acid such as pure HCl, this study focused on dissolution via complex oxides. In our previous study, alkali metal platinates were successfully and simply synthesized by a procedure involving calcination of a mixture of Pt black and alkali metal salts. The obtained Li_2PtO_3 (Kasuya et al, 2013a, 2013b), Na_2PtO_3 , and $(\text{Na,Li})_2\text{PtO}_3$ solid solution (Kasuya et al, 2014) have the Na_2PtO_3 structure that is easily dissolved in HCl. In particular, nearly 100% Pt solubility was recorded by dissolving Li_2PtO_3 obtained at 600°C under appropriate dissolution conditions (Kasuya et al, 2013a, 2013b). This study focused on the dissolution of the alkali metal platinates using dilute HCl, which would further improve the safety profile of the recovery process. It was previously confirmed that the Pt solubility of Li_2PtO_3 decreased with decreasing HCl concentration (in the range 1–12 M) (Kasuya et al, 2013a). This is probably due to the inhibition of the formation of the Pt–Cl complex ion. Thus, in this study, the effect of chloride addition on the dissolution properties of

the alkali metal platinates has been investigated. Furthermore, the dissolution behavior of alkali metal platinates was characterized by monitoring the time dependence of the solubilities of the Pt and alkali metals.

2. Experimental

2.1. *Synthesis of alkali metal platinates*

The details of the preparation of Li_2PtO_3 , Na_2PtO_3 , and the $(\text{Na,Li})_2\text{PtO}_3$ solid solution are provided elsewhere ([Kasuya et al, 2013a, 2013b, 2014](#)). Basically Pt black (250.0 mg) and the alkali metal salts, lithium carbonate (189.4 mg Li_2CO_3) and/or anhydrous sodium carbonate (271.7 mg Na_2CO_3), were mixed in an agate mortar. For Li_2PtO_3 and Na_2PtO_3 , the feed ratio of Na and Li to Pt, $(\text{Na} + \text{Li})/\text{Pt}$, was fixed at 4.0 by atomic ratio. The $(\text{Na, Li})_2\text{PtO}_3$ solid solution was prepared with feed ratios of $(\text{Na} + \text{Li})/\text{Pt} = 3.0$, and $\text{Li}/(\text{Na} + \text{Li}) = 0.20$. The mixtures were calcined at 600 or 800°C for 1–20 hrs in an electric furnace in air.

2.2. *Dissolution of calcined samples in HCl solution*

The dissolution properties of the calcined samples in HCl were characterized as follows: One-tenth (by weight) of the prepared material was added to 3 M HCl solution (dil.) or 12 M HCl (conc.) in 20 mL flask equipped with a reflux condenser. The solution was stirred at 80°C for 5 min–9 hrs. Then, the flask was immediately cooled in an ice-water bath, and ice-cold ultrapure water (20 mL) was added to the suspension to disable further dissolution. For solid-liquid separation, the suspension was filtered through a PTFE filter (pore size, 0.1 μm) under reduced pressure. The obtained solid residue was dried at 110°C for 3 hrs in an oven. For comparison purposes, Pt black (25.0 mg) and Pt dioxide (PtO_2 , 29.1 mg) were also dissolved in conc. HCl at 80°C for 9 hrs. To investigate the effect of chloride addition, dil. HCl containing saturated anhydrous calcium chloride (CaCl_2 , 26 g) was used to dissolve the alkali metal platinates. The Cl^- concentration originating from CaCl_2 was ca. 16 mol/L under saturation conditions. Thus, the total Cl^- concentration was ca. 19 mol/L in the HCl– CaCl_2 solution.

2.3. *Characterization of calcined samples and solid residues*

The crystalline phases of the calcined samples and residues obtained after dissolution were analyzed using an X-ray diffractometer (XRD, Rigaku RINT 2000) equipped with a Cu K α radiation source (40 kV, 30 mA). The diffraction profiles were acquired over the 2θ range from 10° to 80°, with a step width of 0.02°. Detailed measurements in the 2θ range of 15°–25° with a step width of 0.01° were also performed to analyze the structures of the solid residues.

The concentrations of Pt, Na, and Li in the solution samples after the dissolution tests were determined using 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 pressure decomposition as follows ([Jackwerth and Gomišček, 1984](#)): a powder sample, either the calcined sample (1/10 of the total amount by weight) or residue, was added to conc. HCl (10 mL) in a PTFE vessel. This vessel was placed in a pressure casing made of stainless steel and heat treated. The decomposition conditions were 80°C for 9 hrs for Li₂PtO₃, whereas the other calcined samples and residues were treated at 180°C for 2 hrs in an oven. When unreacted Pt black was observed after this dissolution operation, conc.

HNO₃ (3.3 mL) was added to the vessel, and the resultant aqua regia mixture was further aged overnight at room temperature to dissolve the Pt. The Pt solubility of a sample was calculated based on its total Pt content evaluated by the above procedures.

The optical absorption spectra of the Pt-containing solution samples were measured using an ultraviolet-visible absorption spectrophotometer (UV-vis, JASCO V-530). The solutions obtained after the dissolution tests were diluted 250-fold with ultrapure water to adjust the absorbance into a measurable range before analysis.

3. Results and discussion

3.1. Preparation of the alkali metal platينات

The alkali metal platينات were synthesized by the calcination of Pt black and alkali metal salts. The XRD profiles of the obtained samples are displayed in [Fig. 1](#). After calcination of Pt black and Li₂CO₃ at 600°C for 1 hr, nearly 100% of the Pt was converted to Li₂PtO₃ ([Fig. 1\(a\)](#)). In contrast, the corresponding sodium salt was much less reactive. The major crystalline phase observed for the sample obtained from Pt

black and Na_2CO_3 was due to unreacted Pt, although small diffraction peaks for Na-Pt complex oxides were confirmed (Kasuya et al, 2013b). A higher calcination temperature (800°C) and longer time (20 hrs) were needed to complete the reaction between Pt black and Na_2CO_3 (Kasuya et al, 2014). The resultant compound was identified as Na_2PtO_3 (Fig. 1(b)). These results indicate that Li_2CO_3 is more reactive than Na_2CO_3 toward alkali metal platinate formation.

In terms of reducing the cost for the Pt recovery process, the use of the inexpensive Na salt would be favored. However, the formation of the Na-Pt complex oxide requires severe preparation conditions, compared with those of Li_2PtO_3 . Thus, we investigated the effect of adding a Li salt during the synthesis of Na-based platينات. By adopting the feed conditions of $\text{Li}/(\text{Na} + \text{Li}) = 0.20$ and $(\text{Na} + \text{Li})/\text{Pt} = 3.0$, nearly 100% Pt reacted after calcination at 800°C for 1 hr (Fig. 1(c)). The XRD profile of the sample using Li_2CO_3 and Na_2CO_3 (Fig. 1(c)) was similar to that of pure Na_2PtO_3 (Fig. 1(b)). Detailed XRD measurements revealed that the angle of the (002) diffraction peak ($2\theta = 17.0^\circ$) of the sample prepared using Li_2CO_3 and Na_2CO_3 was higher than that of pure Na_2PtO_3 ($2\theta = 16.8^\circ$) (Kasuya et al, 2014). Na_2PtO_3 and Li_2PtO_3 have layered crystal structures consisting of alternating layers of A^+ ($\text{A} = \text{Na}, \text{Li}$) and a mixture of PtO_6 octahedra and A^+ that stack along the c -axis (Urland and Hoppe, 1972; O'Malley

et al, 2008). The peak shift indicates a decrease in the interlayer distance in Na_2PtO_3 due to the substitution of Na^+ with smaller Li^+ . It is noteworthy that, based on the reported preparation conditions of Li_2PtO_3 with a Li/Pt ratio = 4.0, a reduction in the use of Li by 85% occurs if a $(\text{Na,Li})_2\text{PtO}_3$ solid solution is prepared instead of Li_2PtO_3 for the recovery of Pt.

3.2. *Dissolution properties of the alkali metal platinates*

To characterize the dissolution properties of the alkali metal platinates, the platinates were dissolved in HCl under various conditions. After dissolution of Li_2PtO_3 , Na_2PtO_3 , and the $(\text{Na,Li})_2\text{PtO}_3$ solid solution at 80°C for 9 hrs in conc. HCl, the Pt concentration in the liquid phase was determined through ICP-OES analysis. The resultant Pt solubilities are shown in Fig. 2, in addition to those of Pt black and PtO_2 for comparison purposes. Clearly, the synthesized alkali metal platinates are soluble in HCl, with Pt solubilities reaching 97–99%. In contrast, Pt black hardly dissolved in conc. HCl, exhibiting a Pt solubility of only 4.9%. The soluble fraction may result from oxide layers on the surface of the Pt black fine particles. Indeed, we confirmed that PtO_2 was soluble in HCl, with a Pt solubility of 97.5% (Fig. 2). These results imply that

crystalline phases containing oxidized Pt are soluble in HCl. The reaction between the alkali metal platinates and HCl can be written as follows.

The alkali metal platinates were soluble in conc. HCl, and almost 100% solubility was confirmed for Li_2PtO_3 . However, with respect to the safety of the dissolution process, it would be desirable to avoid using concentrated acid. Thus, we examined the dissolution of the prepared compounds in dilute HCl (3 M). In Japan, acid solutions containing less than 10% HCl (corresponding to 3 M HCl) are classified as dilute; and they are exempted from laws and regulations such as the Poisonous and Deleterious Substances Control Law ([Japan Soda Industry Association, 2006](#)). [Figure 3](#) shows the results after dissolution at 80°C for 9 hrs in dil. HCl.

3.3. *Effect of chloride addition*

The dissolution data and [Eq. \(1\)](#) led us to conclude that the addition of chloride into the HCl would facilitate the formation of Pt-Cl complex ions that would result in

increased Pt solubility. The enhancement of leaching by chloride addition has been reported in the acid dissolution of hematite, ilmenite, Ni laterites and Cu oxide (Das et al, 2013; Harris et al, 2006; Majima et al, 1980, 1985). Here, we investigated the effect of chloride on the acid dissolution of alkali metal platinates, using CaCl_2 as the Cl^- source due to its low toxicity and high solubility. Figure 3 also presents the Pt solubilities of the alkali metal platinates after dissolution tests using HCl- CaCl_2 solution at 80°C and 9 hrs. Clearly, chloride addition raised the Pt solubility of the alkali metal platinates. The highest Pt solubility, 99.8%, was obtained by dissolving Li_2PtO_3 in HCl- CaCl_2 solution. Thus, a near complete dissolution of Pt in dil. HCl was achieved.

To investigate the effect of chloride addition in detail, we monitored the time-dependence of Pt solubility. To clarify the dissolution behavior of the alkali metal platinates, the solubilities of alkali metals were also determined. The changes in the metal solubilities of Li_2PtO_3 , Na_2PtO_3 , and the $(\text{Na,Li})_2\text{PtO}_3$ solid solution are shown in Figs. 4–6, respectively. As shown in Figs. 4(a), 5(a), and 6(a), the Pt dissolution rate drastically increases after chloride addition. The Cl^- concentration in the HCl- CaCl_2 solution (ca. 19 mol/L) is much higher than that of conc. HCl (12 mol/L), and probably promotes accelerate the formation of Pt-Cl complex ions that result in the increased Pt solubility. Furthermore, chloride addition is expected to favour the formation of H_2O in

Eq. (1), because the activity of H^+/HCl is enhanced at a higher total Cl^- concentration (Das et al, 2013). The reaction between O^{2-} and H^+ involves the cleavage of the Pt–O bond, which will promote surface complexation between Pt^{4+} and Cl^- . Presumably, this facilitates the transfer of Pt into the solution.

The time dependence of the metals solubilities (Figs. 4–6) clarified that the alkali metals were initially leached into the HCl prior to Pt. As shown in Figs. 4(b) and 6(b)–(c), chloride addition did not significantly contribute to the dissolution of alkali metals for Li_2PtO_3 and the $(\text{Na,Li})_2\text{PtO}_3$ solid solution, and the initial dissolution of Na was suppressed for Na_2PtO_3 (Fig. 5(b)). From these results, we can conclude that the added chloride mainly enhances the dissolution of the Pt from the crystals, which is probably due to the facile complexation of Pt^{4+} and Cl^- ions.

3.4. Identification of Pt complex ions in HCl

To confirm the formation of the complex ion $[\text{PtCl}_6]^{2-}$ from dissolution, we measured the UV-vis spectra of solution samples obtained by dissolving the alkali metal platinates in HCl- CaCl_2 solution at 80°C for 9 hrs. The spectra obtained are displayed in Fig. 7. For comparison, the UV-vis spectrum of an aqueous solution of

hexachloroplatinate(IV) (H_2PtCl_6 ; Pt concentration: 2.30×10^{-5} mol/L) is also shown in the figure. The UV-vis spectra of the solution samples were quite similar in shape, exhibiting absorption maxima at 262 nm. The observed peak in the aqueous H_2PtCl_6 solution originates from the $[\text{PtCl}_6]^{2-}$ complex ion (Gerogieva and Andonovski, 2003). These results indicate that this ion is produced during the dissolution of the alkali metal platinates in HCl-CaCl_2 solution. It should be noted that Pt dissolution using aqua regia and HCl-Cl_2 also produces $[\text{PtCl}_6]^{2-}$; therefore, conventional separation and extraction techniques would be applicable after the dissolution process via the alkali metal platinates.

3.5. Structural changes of platinates after dissolution

Initially during the dissolution of the alkali metal platinates (Figs. 4–6), the alkali metals preferentially leached out, followed by the gradual dissolution of Pt in HCl . Thus, sample residues collected during the initial dissolution period should exhibit an A/Pt ratio lower than 2.0. To characterize the structural changes of the alkali metal platinates, the sample residues were analyzed by ICP-OES and XRD. The chemical compositions of the solid residues were determined after dissolving the alkali

metal platinates in dil. HCl–CaCl₂ solution at 80°C for 5 min. The ICP-OES measurements revealed that the A/Pt ratios of sample residues were much lower than 2.0, affording values of 0.18 (Li₂PtO₃), 0.25 (Na₂PtO₃), and 0.04 ((Na,Li)₂PtO₃ solid solution). The rapid leaching of A⁺ from the platinates is probably related to the ion-exchange reaction between A⁺ and H⁺ in HCl.

The XRD profiles of the solid residues are displayed in Fig. 8. Expanded XRD profiles of the residues are also displayed in Fig. 9. After dissolution, the diffraction peaks for Li₂PtO₃ (001) and Na₂PtO₃ (002) reflections shifted to higher angles, and the resulting diffraction peaks overlapped reflections from Li₂PtO₃ (010) and, Na₂PtO₃ (020) and (110) planes. The diffraction angles of the solid residues were $2\theta = 19.6^\circ$ (Li₂PtO₃), and $2\theta = 19.3^\circ$ (Na₂PtO₃ and (Na,Li)₂PtO₃ solid solution). The observed peak shift represents the decrease in the interlayer distances of A₂PtO₃ (A = Li, Na). The A/Pt ratios of the sample residues were lower than the stoichiometric ratio of 2.0, hence, the replacement of A⁺ by H⁺ is a possible explanation for the decrease in the platinate interlayer distances. Weak diffraction peaks due to Pt metal were observed in the residues of Na₂PtO₃ and the (Na,Li)₂PtO₃ solid solution (Figs. 8(b) and (c)). The

presence of unreacted Pt may be a reason for the incomplete dissolution in conc. HCl.

Further optimization of the preparation conditions will improve the Pt conversion rate.

4. Conclusions

The synthesis and dissolution of Pt-containing complex oxides in HCl were examined. The alkali metal platينات were prepared by calcining a mixture of Pt black and alkali metal salts in air. The alkali metal platينات obtained easily dissolved in HCl. The addition of CaCl_2 in the dil. HCl dramatically increased the Pt solubility, and nearly 100% dissolution was observed with Li_2PtO_3 . Pt dissolution via alkali metal platينات offers a much safer process than current methods because it does not require toxic oxidizing agents, harsh conditions, or highly concentrated acids.

Acknowledgments

This study was supported by a Grant-in-Aid for Challenging Exploratory Research, No. 23656566, The Naito Science & Engineering Foundation, and the Japan

Science and Technology Agency (JST) via the A-STEP feasibility study program, No.
AS251Z02844M.

References

- Bernardis, F.L., Grant, R.A., Sherrington, D.C., 2005. A review of methods of separation of the platinum-group metals through their chloro-complexes. *Reactive and Functional Polymers* 65 (3), 205-217.
- Johnson Matthey Plc., 2013. *Platinum 2013*. pp. 31.
- Shibata, J., Okuda, A., 2002. Recycling Technology of Precious Metals. *Journal of MMIJ* 118 (1), 1-8 [in Japanese].
- Barin, I., Knacke, O., 1973. *Thermochemical Properties of Inorganic Substances*. Springer-Verlag, New York, pp. 538.
- Kizilaslan, E., Aktaş, S., Şeşen, M.K., 2009. Environmentally safe recovery of platinum from scrap automotive catalytic convertors, *Turkish Journal of Engineering and Environmental Sciences* 33, 83-90.
- Kasuya, R., Miki, T., Tai, Y., 2013. Preparation of Li_2PtO_3 and its dissolution properties in hydrochloric acid. *Journal of the Ceramic Society of Japan* 121 (2), 261-264.

Kasuya, R., Miki, T., Morikawa, H., Tai, Y., 2013. Synthesis of alkali metal platينات and their dissolution behavior in hydrochloric acid. Journal of the Ceramic Society of Japan. 121 (10) 884-890.

Kasuya, R., Miki, T., Morikawa, H., Tai, Y., 2014. Synthesis of sodium platينات and their dissolution behaviors in hydrochloric acid: Effects of lithium carbonate addition on platinate formation. International Journal of Mineral Processing. 128 33-39.

Jackwerth, E., Gomišček, S., 1984. General aspects of trace analytical methods-VI. Acid pressure decomposition in trace element analysis. Pure Applied Chemistry. 56 (4) 479-489.

Urland, W., Hoppe, R., 1972. Zur Kenntnis der Oxoplatinate Na_2PtO_2 , Na_2PtO_3 , „ K_2PtO_3 ” und „ Rb_2PtO_3 ”. Zeitschrift für Anorganische und Allgemeine Chemie. 392 (1) 23-36 [in German].

O'Malley, M.J., Verweij, H., Woodward, P.M., 2008. Structure and properties of ordered Li_2IrO_3 and Li_2PtO_3 . Journal of Solid State Chemistry. 181 (8), 1803-1809.

Japan Soda Industry Association, 2006. Permanent Committee on Technology and Safety, *Safe Handling of Hydrochloric Acid*, , pp. 1.

Das, G.K., Pranolo, Y., Zhu, Z., Cheng, C.Y., 2013. Leaching of Ilmenite Ores by

Acidic Chloride Solutions. *Hydrometallurgy*. 133 94-99.

Harris, B., White, C., Jansen, M., Pursell, D., 2006. A New Approach to the High

Concentration Chloride Leaching of Nickel Laterites. *Proceedings of ALTA*

Nickel/Cobalt conference, ALTA Metallurgical, Perth, Western Australia, 20 pages.

Majima, H., Awakura, Y., Yazaki, T., Chikamori, Y., 1980. Acid Dissolution of Cupric

Oxide. *Metallurgical Transactions B* 11 (2) 209-214.

Majima, H., Awakura, Y., Mishima, T., 1985. The Leaching of Hematite in Acid

Solutions. *Metallurgical Transactions B* 16 (1) 23-30.

Gerogieva, M., Andonovski, B., 2003. Determination of Platinum(IV) by UV

Spectrophotometry. *Analytical and Bioanalytical Chemistry*. 375 (6) 836-839.

Figure caption

Fig. 1. XRD profiles of alkali metal platينات: (a) Li_2PtO_3 , (b) Na_2PtO_3 , and (c) $(\text{Na,Li})_2\text{PtO}_3$ solid solution. Calcination conditions were 600°C, 1 hr for pattern (a); 800°C, 20 hrs for pattern (b); and 800°C, 1 hr for pattern (c). A/Pt ratios are 4.0 for patterns (a) and (b), and 3.0 for pattern (c). Solid circles, solid diamonds, plus signs, and open diamonds indicate Li_2PtO_3 , Na_2PtO_3 , Li_2CO_3 , and Na_2CO_3 , respectively.

Fig. 2. Pt solubilities of alkali metal platينات after dissolution at 80°C for 9 hrs in conc. HCl.

Fig. 3. Pt solubilities of alkali metal platينات after dissolution at 80°C for 9 hrs in dil. HCl, and dil. HCl– CaCl_2 solutions.

Fig. 4. Time dependence of metal concentrations during dissolution of Li_2PtO_3 in dil. HCl and dil. HCl– CaCl_2 solutions at 80°C: (a) Pt and (b) Li.

Fig. 5. Time dependence of metal concentrations upon dissolution of Na_2PtO_3 in dil. HCl, and dil. HCl– CaCl_2 solutions at 80°C: (a) Pt and (b) Na.

Fig. 6. Time dependence of metal concentrations upon dissolution of $(\text{Na,Li})_2\text{PtO}_3$ solid solution in dil. HCl, and dil. HCl–CaCl₂ solution at 80°C: (a) Pt, (b) Na, and (c) Li.

Fig. 7. UV-vis absorption spectra of the solutions from (a) Li_2PtO_3 , (b) Na_2PtO_3 , and (c) the $(\text{Na,Li})_2\text{PtO}_3$ solid solution after dissolution in dil. HCl–CaCl₂ solution at 80°C for 9 hrs (diluted 250 times), and (d) H_2PtCl_6 aqueous solution (Pt concentration: 2.30×10^{-5} mol/L).

Fig. 8. XRD profiles of sample residues obtained after dissolution at 80°C for 5 min in dil. HCl–CaCl₂ solution: (a) Li_2PtO_3 , (b) Na_2PtO_3 , and (c) $(\text{Na,Li})_2\text{PtO}_3$ solid solution.

Fig. 9. Extended XRD profiles of sample residues obtained after dissolution at 80°C for 5 min in dil. HCl–CaCl₂ solution: (a) Li_2PtO_3 , (b) Na_2PtO_3 , and (c) $(\text{Na,Li})_2\text{PtO}_3$ solid solution.

Fig. 1. XRD profiles of alkali metal platinates: (a) Li_2PtO_3 , (b) Na_2PtO_3 , and (c) $(\text{Na,Li})_2\text{PtO}_3$ solid solution. Calcination conditions were 600°C , 1 hr for pattern (a); 800°C , 20 hrs for pattern (b); and 800°C , 1 hr for pattern (c). A/Pt ratios are 4.0 for patterns (a) and (b), and 3.0 for pattern (c). Solid circles, solid diamonds, plus signs, and open diamonds indicate Li_2PtO_3 , Na_2PtO_3 , Li_2CO_3 , and Na_2CO_3 , respectively.

Fig. 2. Pt solubilities of alkali metal platinates after dissolution at 80°C for 9 hrs in conc. HCl.

Fig. 3. Pt solubilities of alkali metal platinates after dissolution at 80°C for 9 hrs in dil. HCl, and dil. HCl–CaCl₂ solutions.

Fig. 4. Time dependence of metal concentrations during dissolution of Li_2PtO_3 in dil. HCl and dil. HCl- CaCl_2 solutions at 80°C : (a) Pt and (b) Li.

Fig. 5. Time dependence of metal concentrations upon dissolution of Na_2PtO_3 in dil. HCl, and dil. HCl- CaCl_2 solutions at 80°C : (a) Pt and (b) Na.

Fig. 6. Time dependence of metal concentrations upon dissolution of $(\text{Na,Li})_2\text{PtO}_3$ solid solution in dil. HCl, and dil. HCl- CaCl_2 solution at 80°C : (a) Pt, (b) Na, and (c) Li.

Fig. 7. UV-vis absorption spectra of the solutions from (a) Li_2PtO_3 , (b) Na_2PtO_3 , and (c) the $(\text{Na,Li})_2\text{PtO}_3$ solid solution after dissolution in dil. HCl-CaCl_2 solution at 80°C for 9 hrs (diluted 250 times), and (d) H_2PtCl_6 aqueous solution (Pt concentration: 2.30×10^{-5} mol/L).

Fig. 8. XRD profiles of sample residues obtained after dissolution at 80°C for 5 min in dil. HCl–CaCl₂ solution: (a) Li_2PtO_3 , (b) Na_2PtO_3 , and (c) $(\text{Na,Li})_2\text{PtO}_3$ solid solution.

Fig. 9. Extended XRD profiles of sample residues obtained after dissolution at 80°C for 5 min in dil. HCl – CaCl_2 solution: (a) Li_2PtO_3 , (b) Na_2PtO_3 , and (c) $(\text{Na,Li})_2\text{PtO}_3$ solid solution.