JOURNAL OF APPLIED ELECTROCHEMISTRY 25(1995) 48-53

Electrochemical formation of Pd–Li alloys in LiCl–KCl eutectic melts

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Received 31 January 1994; revised 8 June 1994

The aim of the present study is to provide fundamental information regarding the electrochemical formation of Pd–Li alloys and palladium-rare earth alloys in the molten LiCl–KCl system. Pd–Li alloy formation via deposition of lithium onto a palladium electrode in LiCl–KCl eutectic melts was investigated by cyclic voltammetry, open-circuit potentiometry and X-ray diffraction (XRD) analysis. Various phases of Pd–Li alloys, i.e. $LiPd_7$, $LiPd_2$, LiPd and Li_2Pd, form at 1.05, 0.64, 0.53 and 0.20 V vs Li^+/Li at 450° C, respectively. The electrochemical window of the molten LiCl–KCl system thus becomes narrow when palladium is used as a cathode.

1. Introduction

Pd–Li alloys are interesting materials worth investigating for their hydrogen absorbing properties, electrocatalytic properties, magnetic properties, etc. [1]. These properties are considered to depend significantly on the compositions of the alloys. However, using metallurgical methods for producing the alloys [1], it is difficult to control their compositions. This disadvantage may be overcome by applying electrochemical formation methods. For example, when a palladium electrode is cathodically polarized in LiCl–KCl eutectic melts, the electrochemical formation of Pd–Li alloys, whose compositions are determined by the applied potentials, occurs. To control the compositions, it is necessary to determine the relationship between the applied potential and the phases of the Pd–Li alloys formed.

Palladium-rare earth alloys are also promising materials worth studying for their superconductivity, magnetic properties [2] and hydrogen diffusion properties. In particular, such alloys are expected to find uses as new hydrogen diffusion membranes [3]. For example, a Pd–8%Y alloy has been shown to have improved permeability over the Pd–25%Ag alloy, which is currently in use as a conventional hydrogen diffusion membrane [4]. One of the most useful techniques for the formation of palladium–rare earth alloys, electrochemical processes using alkali halide solvents such as LiCl–KCl eutectic melts, will be possible when the method of electrochemical formation of Ni–Y intermetallic compounds in the molten LiCl–KCl system recently proposed by the authors [5] is applied. The advantages of such an electrochemical process are low working temperature and high alloy purity. However, when using platinum group metals as cathode, electrochemical formation of lithium alloy occurs at a considerably more noble potential compared to that of pure alkali metal deposition. Therefore, the electrochemical window of the solvent electrolyte is narrow. When a palladium electrode is used in the molten LiCl–KCl system, the electrochemical formation of Pd–Li alloy occurs as mentioned above. Thus, to control the electrochemical formation of palladium-rare earth alloys, it is important to determine previously the formation potentials of the various Pd–Li alloys.

To date there have been no reports of the electrochemical formation of Pd–Li alloys in molten salt systems.

The electrochemical formation reactions of Pd–Li alloys in LiCl–KCl eutectic melts was investigated in the present work.

2. Experimental details

A schematic representation of the apparatus used is shown in Fig. 1. The experiments were conducted in LiCl–KCl eutectic melts at 450° C. All chemicals were reagent grade (Wako Chemical Co., Ltd.). Materials were contained in a high purity alumina crucible (99.5% Al_2O_3; Nippon Kagaku Togyo Co., Ltd, SSA–S), and were dried under vacuum for more than 72 h at 200° C to remove water. The eutectic mixture was then melted under a dry argon atmosphere at 450° C. To remove residual water contamination further, pre-electrolysis was carried out with a terminal voltage of 2.5 V, using a platinum wire cathode and a glassy carbon rod anode. When the cathodic current density became less than $0.5\,mA\,cm^{-2}$, pre-electrolysis was terminated. A chromel–alumel thermocouple was used for temperature measurement.

The working electrodes were rectangular sheets of palladium (15 mm × 8 mm × 0.05 mm, The Nilaco Corporation, 99.95%) or nickel (15 mm × 8 mm × 0.2 mm, The Nilaco Corporation, 99.95%). The reference electrode was Li–Al alloy in the two phase

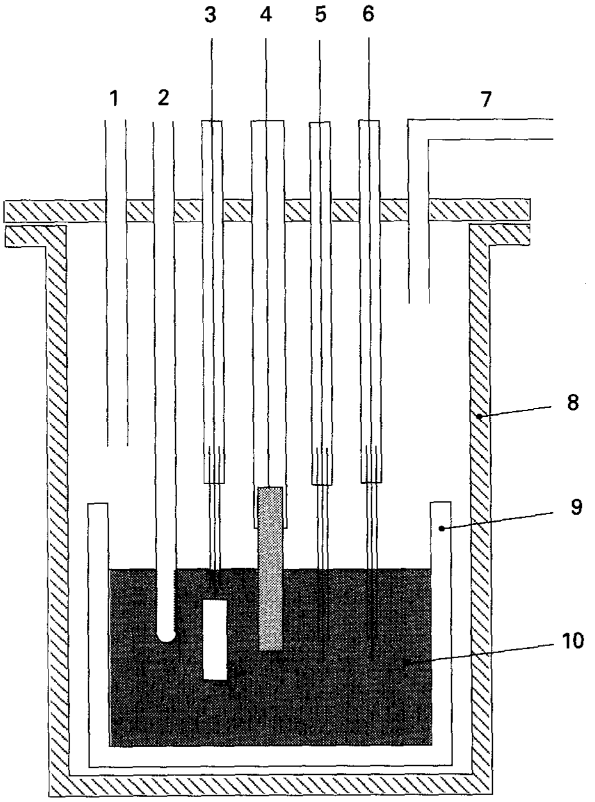

Fig. 1. Schematic representation of experimental apparatus. (1) Ar gas inlet, (2) thermocouple, (3) working electrode, (4) counter electrode, (5) reference electrode, (6) $\mathrm{Li}^+/\mathrm{Li}$ electrode (Ni wire), (7) Ar gas outlet, (8) Pyrex holder, (9) crucible and (10) LiCl–KCl eutectic melts.

$(\alpha + \beta)$ concentration region. The equilibrium potential of this electrode is determined by the following reversible reaction [6–8]:

$$\mathrm{Al}(\alpha) + \mathrm{Li}^+ + e^- \rightleftharpoons \mathrm{LiAl}(\beta)$$

The potential of this reference electrode was calibrated with reference to that of the $\mathrm{Li}^+/\mathrm{Li}$ electrode, prepared by electrodepositing lithium metal on a nickel wire [9]. All potentials are given with reference to this $\mathrm{Li}^+/\mathrm{Li}$ electrode potential. The counter electrodes were Li–Al alloy in the two phase $(\alpha + \beta)$ concentration region for cyclic voltammetry and glassy carbon for galvanostatic and potentiostatic electrolysis. The Li–Al alloy used as reference and counter electrodes were prepared electrochemically from an aluminum rod (70 mm × 5 mm diam. The Nilaco Corporation, 99.99%) in another cell.

Cyclic voltammetry and open-circuit potentiometry were applied to investigate the electrochemical behaviour of palladium.

Pd–Li alloy samples were prepared by potentiostatic electrolysis at 0.95, 0.70, 0.56, 0.30 and 0.08 V (samples 1–5, respectively), with charging times between 11.5 and 23 h. After electrolysis, the samples which were formed in the noble potential region (samples 1–3) were removed from the bath and washed with acetone. Their XRD patterns were then measured by a diffractometer. $\mathrm{Cu}K_\alpha$ (154.18 pm) line was used as an X-ray source. Because samples which were formed in the base potential region (samples 4 and 5) reacted easily with air, they were sealed with argon gas immediately after being removed from the bath. They were then ground into powder and sealed in capillaries in an argon glove box, and their XRD powder data were measured by the Debye–Scherrer method. All XRD data were compared with those calculated based on the reported structure and lattice constants of each Pd–Li intermetallic compound [1].

3. Results and discussion

3.1. *Cyclic voltammetry*

Figure 2(a) shows a typical cyclic voltammogram of the palladium electrode at 450° C (reversal potential = 0.15 V; scanning rate = $1\,\mathrm{mV\,s^{-1}}$). On the cathodic sweep, current began to flow at about 0.97 V, and there were five cathodic peaks (shoulders) where the current increased sharply at 0.97, 0.87, 0.62, 0.49 and 0.19 V (peaks 1–5). To investigate the peaks observed in the base potential region, the reversal potential was changed to 0 V and the scanning rate

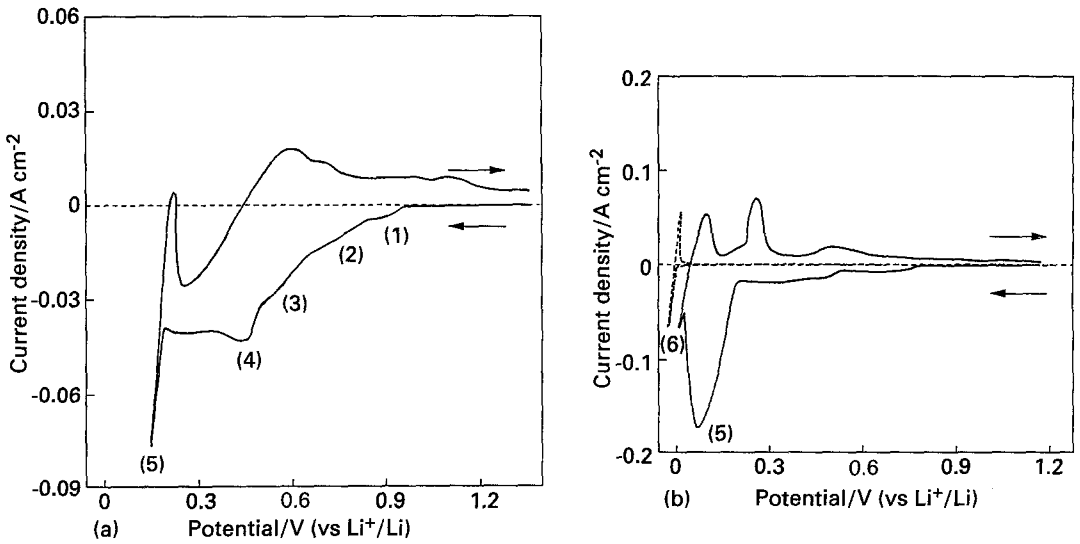

Fig. 2. Cyclic voltammograms of Pd (——) and Ni (- - - -) electrodes in LiCl–KCl eutectic melts at 450° C. Reversal potential: (a) 0.15 V and (b) 0 V. Scanning rate: (a) $1\,\mathrm{mV\,s^{-1}}$ and (b) $0.1\,\mathrm{mV\,s^{-1}}$. (1) Peak 1, (2) peak 2, (3) peak 3, (4) peak 4, (5) peak 5 and (6) peak 6.

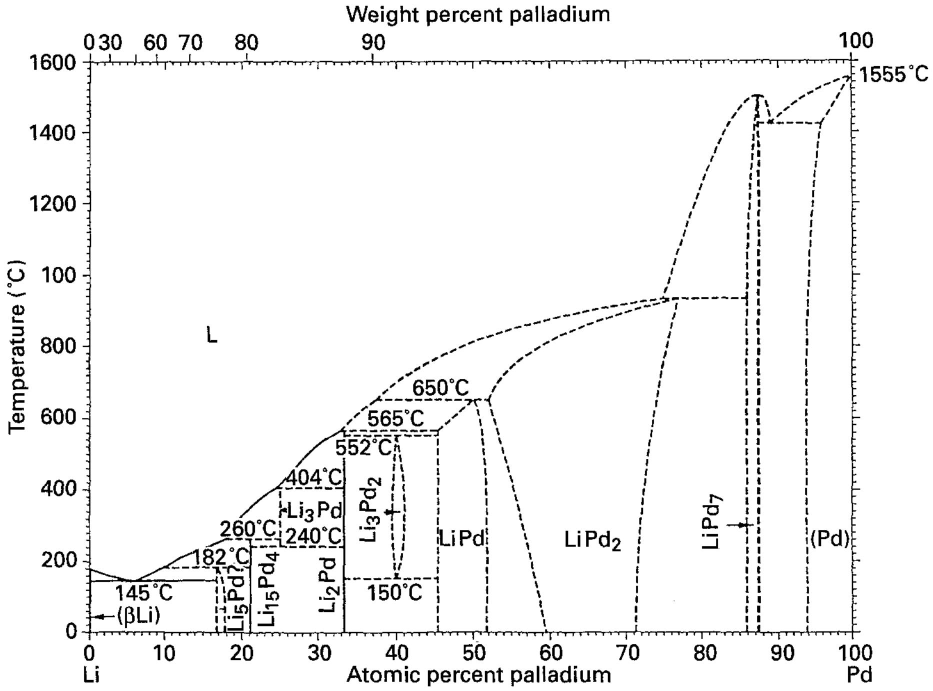

Fig. 3. Phase diagram of the Pd–Li system [1].

was lowered to 0.1 mV s^{-1}. The results are shown in Fig. 2(b). In this voltammogram, a sixth cathodic peak (peak 6) was observed, at which the current increased sharply at 0.06 V.

For comparison, the cyclic voltammogram of the nickel electrode at 450° C is also shown as a dotted line in Fig. 2(b). Because no alloys or intermetallic compounds can be formed between nickel and lithium at 450° C [10], only the peak of lithium deposition was observed.

According to the Pd–Li phase diagram [1] shown in Fig. 3, there were several intermetallic compounds and a liquid phase at 450° C. The above six cathodic peaks (peaks 1–6) in Fig. 2(a) and (b) were considered to be associated with the formation reaction of each Pd–Li alloy.

3.2. *Open-circuit potentiometry*

Open-circuit potentiometry was also carried out to investigate the electrochemical behaviour of the palladium electrode at 450° C. After galvanostatic electrolysis for 30 s at an electrolysis current density of 1 A cm^{-2}, the current was interrupted, and the open-circuit potential transient curve of the palladium electrode was measured. Figure 4 shows the results. There were five potential plateaux (plateaux 1–5) at about 1.05, 0.91, 0.64, 0.53 and 0.20 V,

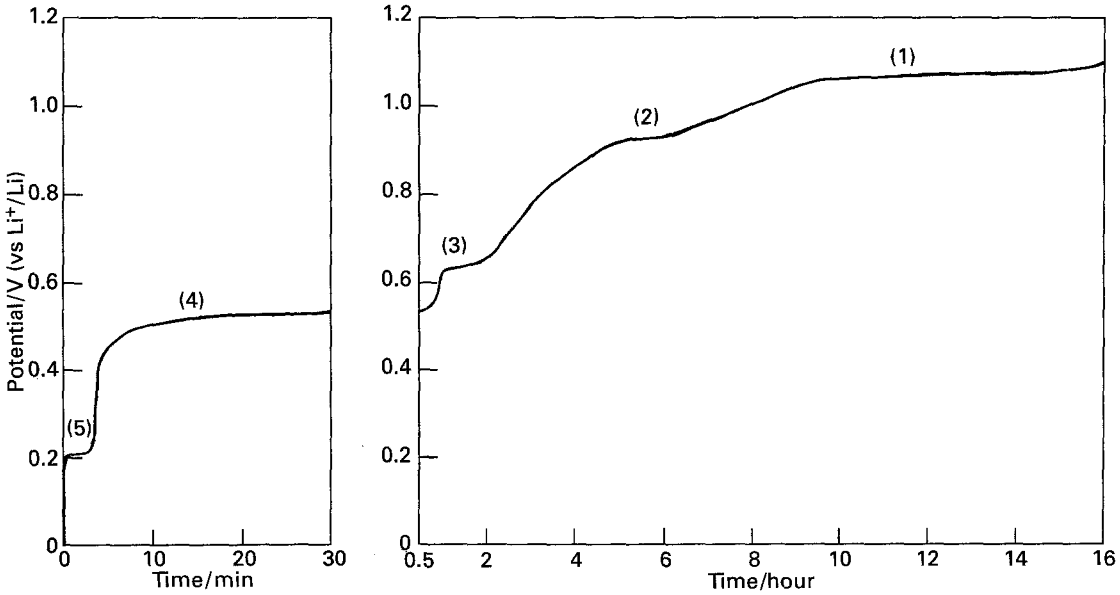

Figure 4. Open-circuit potential transient curve of palladium electrode in LiCl–KCl eutectic melts at 450° C, after galvanostatic electrolysis for 30 s at a current density of 1 A cm^{-2}. (1) Plateau 1, (2) plateau 2, (3) plateau 3, (4) plateau 4 and (5) plateau 5.

respectively. These five plateaux corresponded to the five cathodic peaks (peaks 1–5) shown in Fig. 2(a), respectively, each of which were considered to correspond to each coexisting phase state of the solid Pd–Li alloy.

3.3. *Characterization of electrochemically formed Pd–Li alloys, and reaction formulas*

Based on the results obtained by cyclic voltammetry and open-circuit potentiometry, potentiostatic electrolysis was conducted to form Pd–Li alloy samples with electrolysis potentials of 0.95, 0.70, 0.56, 0.30 and 0.08 V, respectively (samples 1–5). As an example, a cross-section SEM image of sample 2 is shown in Fig. 5, in which it can be seen that a surface layer of alloy was formed on the substrate Pd metal. Similar results were obtained with samples 1 and 3.

From the XRD pattern shown in Fig. 6, sample 1 (electrolysed at 0.95 V) was identified as $LiPd_7$. The XRD pattern of substrate Pd metal is also shown in Fig. 6. This result indicates that potential plateau 1 (1.05 V), shown in Fig. 4, corresponds to the following

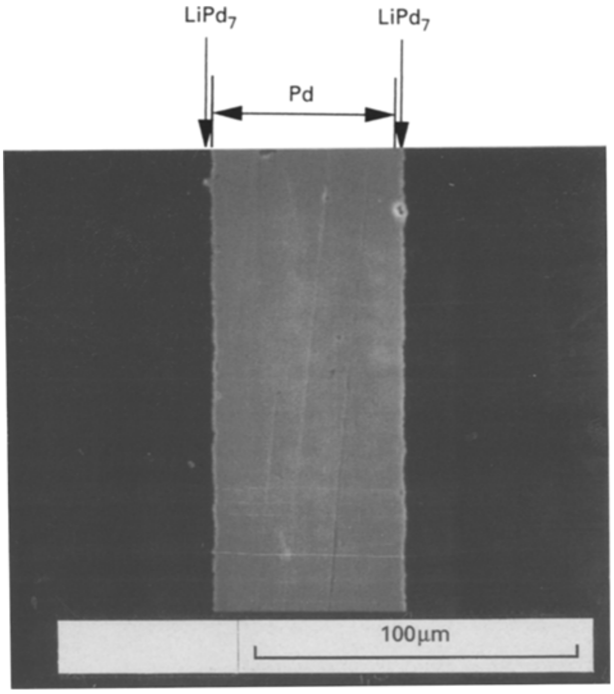

Fig. 5. Cross-section SEM image of sample 2 prepared at 0.70 V for 23 h at 450° C.

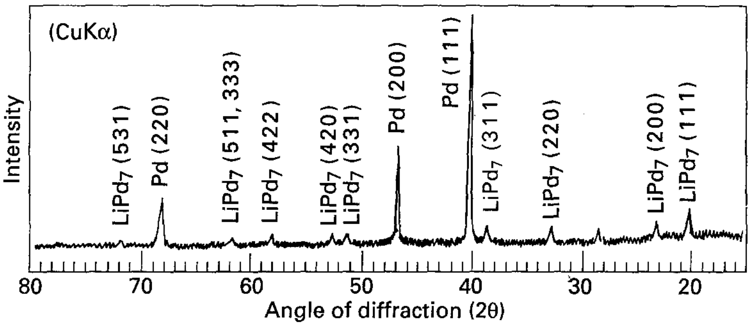

Fig. 6. XRD pattern of sample 1 prepared at 0.95 V for 21 h at 450° C. $LiPd_7$: cubic unit cell with $a = 766.0$ pm.

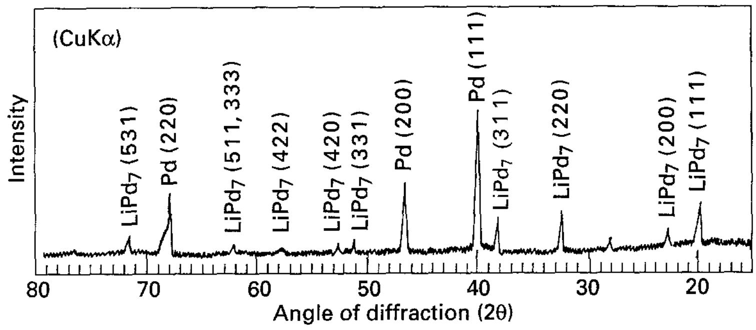

Fig. 7. XRD pattern of sample 2 prepared at 0.70 V for 23 h at 450° C. $LiPd_7$: cubic unit cell with $a = 766.0$ pm.

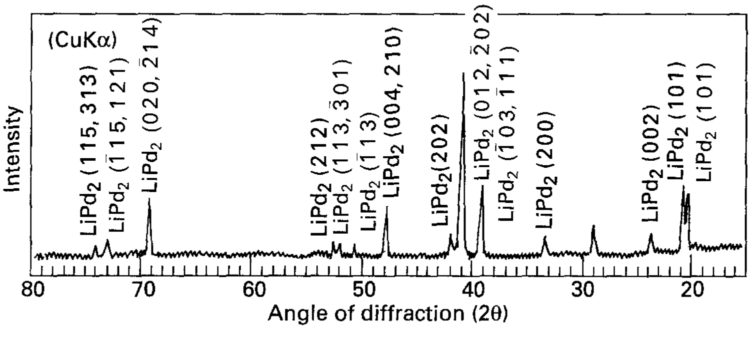

Fig. 8. XRD pattern of sample 3 prepared at 0.56 V for 12 h at 450° C. $LiPd_2$: monoclinic unit cell with $a = 537.1$ pm, $b = 272.5$ pm, $c = 765.8$ pm and $\beta = 91.09°$.

reaction:

$$7Pd + Li^+ + e^- \rightleftharpoons LiPd_7$$

The XRD pattern shown in Fig. 7 identifies sample 2 (electrolysed at 0.70 V) also as $LiPd_7$ and substrate Pd metal. This result suggests that potential plateau 2 (0.91 V) corresponds to the formation of a new metastable phase which has not been reported previously.

From the XRD pattern shown in Fig. 8 sample 3 (electrolysed at 0.56 V) was identified as $LiPd_2$. Therefore, potential plateau 3 (0.64 V) is considered to represent the following reaction:

$$2LiPd_7 + 5Li^+ + 5e^- \rightleftharpoons 7LiPd_2$$

The XRD data for sample 4 (electrolysed at 0.30 V) are shown in Table 1. Sample 4 was identified as LiPd, and the reaction at potential plateau 4 (0.53 V) can be expressed as

$$LiPd_2 + Li^+ + e^- \rightleftharpoons 2LiPd$$

Similarly, from the XRD data shown in Table 2, sample 5 (electrolysed at 0.08 V) was identified as Li_2Pd, and potential plateau 5 (0.20 V) is thus considered to correspond to the following reaction:

$$LiPd + Li^+ + e^- \rightleftharpoons Li_2Pd$$

In samples 4 and 5, the palladium sheet was completely alloyed, and it was noted that the volume of sample 5 became several times larger than that of the initial palladium sheet. It is also interesting to note that the current density of peak 5 in Fig. 2(b) is much larger than that of the other peaks, which indicates that the diffusion of lithium in Li_2Pd is faster than that in the other phases.

Besides the five solid intermetallic compounds, there is a liquid phase in the Pd–Li phase diagram (Fig. 3). Peak 6 in Fig. 2(b) is thus considered to correspond to the following reaction:

$$Li_2Pd + xLi^+ + xe^- \rightleftharpoons \text{liquid}$$

Table 1. X-ray powder data for sample 4 prepared at 0.30 V for 21 h at 450° C (CuKα 154.18 pm)

Intensity (S, M, W)	*d*/pm	*h k l for LiPd**
S	406.4	0 0 1
M	238.8	1 0 0
VS	206.2	1 0 1
S	155.7	1 0 2
M	137.4	1 1 0
M	131.1	1 1 1
M	119.2	2 0 0, 1 0 3
M	114.9	2 0 1
W	103.5	2 0 2
W	97.6	1 1 3
W	94.7	1 0 4
W	90.5	2 1 0
W	88.5	2 1 1

* Hexagonal unit cell with $a = 276.3$ pm, $c = 416.7$ pm.

Table 2. X-ray powder data for sample 5 prepared at 0.08 V for 11.5 h at 450° C (CuKα 154.18 pm)

Intensity (S, M, W)	*d*/pm	*h k l for Li_2Pd**
W	355.5	1 0 0
W	259.3	0 0 1
W	215.8	1 0 1
M	208.3	1 1 0
M	180.6	2 0 0
M	165.8	1 1 1
M	150.7	2 0 1
W	137.4	2 1 0
M	135.9	0 0 2
S	127.3	1 0 2
M	122.7	2 1 1
W	121.5	3 0 0
M	114.3	1 1 2
M	111.2	3 0 1
M	108.9	2 0 2
M	105.3	2 2 0
M	101.2	3 1 0
W	98.3	2 2 1
M	97.0	2 1 2
S	95.0	3 1 1

* Hexagonal unit cell with $a = 421.4$ pm, $c = 272.8$ pm.

The Pd–Li phase diagram shown in Fig. 3 also suggests the possibility of Li_3Pd_2 formation, which, however, was not identified in any samples under the present experimental conditions. This supports the results of Van Vucht and Buschow [11] who reported that Li_3Pd_2 does not exist.

To summarize the above experimental results and discussion, the plateau potentials and the corresponding reactions are listed in Table 3.

4. Conclusions

To provide fundamental information concerning the electrochemical formation of Pd–Li alloys and palladium-rare earth alloys in the molten LiCl–KCl system, electrodeposition of lithium on palladium was investigated by electroanalytical chemistry. The results of the present study can be summarized as follows:

(i) Electrochemical formation of various phases of Pd–Li alloys was achieved with cathodic polarization of the palladium electrode at various potentials in LiCl–KCl eutectic melts at 450° C.

(ii) The formation reactions and the corresponding

Table 3. Formation reactions and corresponding formation potentials of each type Pd–Li alloy in LiCl–KCl eutectic melts at 450° C

Reaction	*Equilibrium potential* /V (vs Li^+/Li)
$7Pd + Li^+ + e^- \rightleftharpoons LiPd_7$	1.05
$2LiPd_7 + 5Li^+ + 5e^- \rightleftharpoons 7LiPd_2$	0.64
$LiPd_2 + Li^+ + e^- \rightleftharpoons 2LiPd$	0.53
$LiPd + Li^+ + e^- \rightleftharpoons Li_2Pd$	0.20

formation potentials of each phase of Pd–Li alloy were determined as follows:

$$\begin{array}{ll} 7\mathrm{Pd} + \mathrm{Li}^+ + \mathrm{e}^- \rightleftharpoons \mathrm{LiPd}_7 & 1.05\,\mathrm{V\ vs\ Li^+/Li} \\ 2\mathrm{LiPd}_7 + 5\mathrm{Li}^+ + 5\mathrm{e}^- \rightleftharpoons 7\mathrm{LiPd}_2 & 0.64\,\mathrm{V\ vs\ Li^+/Li} \\ \mathrm{LiPd}_2 + \mathrm{Li}^+ + \mathrm{e}^- \rightleftharpoons 2\mathrm{LiPd} & 0.53\,\mathrm{V\ vs\ Li^+/Li} \\ \mathrm{LiPd} + \mathrm{Li}^+ + \mathrm{e}^- \rightleftharpoons \mathrm{Li}_2\mathrm{Pd} & 0.20\,\mathrm{V\ vs\ Li^+/Li} \end{array}$$

(iii) These results also provide useful information concerning the electrochemical window of the molten LiCl–KCl system, which is very important in considering the electrochemical formation reactions of palladium-rare earth alloys.

Acknowledgements

This work was carried out under support from the Tokyo Ohka Foundation for the Promotion of Science and Technology and a grant-in-aid from the Japanese Ministry of Education, Science and Culture. We thank Koji Yoshida of Kyoto University for the SEM measurements.

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