TITLE:
Electrochemical Formation of Pr-Ni Alloys in LiF-CaF2-PrF3 and NaCl-KCl-PrCl3 Melts

AUTHOR(S):
Yasuda, K.; Kondo, K.; Nohira, T.; Hagiwara, R.

CITATION:

ISSUE DATE:
2014-02-15

URL:
http://hdl.handle.net/2433/189438

RIGHT:
© 2014 The Electrochemical Society
Electrochemical Formation of Pr–Ni Alloys in LiF–CaF$_2$–PrF$_3$ and NaCl–KCl–PrCl$_3$ Melts

Kouji Yasuda, a,b∗ Katsuya Kondo, a Toshiyuki Nohira, a,b,∗, z and Rika Hagiwara a,b

a Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan
b Environment, Safety and Health Organization, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan

For the establishment of a process for the electrochemical recovery of rare earth elements from used magnet scraps, the electrochemical formation of Pr–Ni alloys in molten LiF–CaF$_2$–PrF$_3$ and NaCl–KCl–PrCl$_3$ salts at 1123 K and 973 K, respectively, was investigated. Cyclic voltammetry and open-circuit potentiometry indicated the formation of several phases of Pr–Ni alloys. Alloy samples were prepared by one- or two-step potentiostatic electrolysis using a Ni plate electrode at various potentials. Scanning electron microscopy observations and X-ray diffraction measurements confirmed the formation of Pr,Ni$_2$, Pr,Ni$_3$, Pr$_2$Ni$_7$, and Pr,Ni$_5$. The formation potential for each Pr–Ni alloy phase was determined from experimental results. In addition, the optimum electrolysis conditions for the separation of Nd, Dy, and Pr are discussed.

© 2014 The Electrochemical Society. [DOI: 10.1149/2.012407jes] All rights reserved.

Manuscript submitted February 28, 2014; revised manuscript received April 21, 2014. Published May 14, 2014. This paper is part of the JES Focus Issue on Electrochemical Processing and Materials Tailoring for Advanced Energy Technology.
Results and Discussion

Lif–CaF2 system.—Cyclic voltammetry.—The phase diagram of the Pr–Ni system\(^{17}\) (Fig. 1) shows four intermetallic compounds, namely, PrNi\(_2\), PrNi\(_3\), Pr\(_2\)Ni\(_7\), PrNi\(_5\), and a liquid alloy at 1123 K. It is expected that these Pr–Ni alloys are formed electrochemically. In this study, a Mo electrode was occasionally used for comparison with the Ni electrode, because no alloys exist in the binary Mo–Pr, Mo–Li, Mo–Ca, Mo–Na, and Mo–K systems at the present experimental temperatures according to their phase diagrams.\(^{18}\)

Figure 2 shows a comparison of the cyclic voltammograms for Mo and Ni wire electrodes in a molten LiF–CaF\(_2\)–PrF\(_3\) (0.50 mol\%) system at 1123 K. For the Mo electrode, only a single pair of redox peaks (B, B’\(^{18}\)) is observed around 0.2 V (vs. Li\(^+\)/Li) except for the redox peaks (A, A’) for Li deposition/dissolution. These peaks correspond to the deposition and dissolution of Pr metal. For the Ni electrode, a cathodic current (C) is observed from approximately 0.6 V, which suggests the formation of Pr–Ni alloys. Several anodic peaks/shoulders (C’) are observed at 0.3 V, 0.4 V, 0.6 V, 0.8 V, and 1.0 V in the anodic sweep, and are possibly caused by the dissolution of Pr from different Pr–Ni alloy phases.

Open-circuit potentiometry.—To determine the deposition potential of Pr metal, the measurement was conducted for a Mo electrode in a molten LiF–CaF\(_2\)–PrF\(_3\) (0.50 mol\%) at 1123 K. By using the same procedures as those employed in our previous studies on Nd and Dy in a LiF–CaF\(_2\) melt,\(^{8,9}\) the deposition potential of Pr was measured from the transient curve for the open-circuit potential after galvanostatic electrolysis at −3.0 A cm\(^{-2}\) for 10 s. The potential stays at 0.21 V for around 120 s, which corresponds to the Pr(III)/Pr potential.

Open-circuit potentiometry is suitable for determining the formation potential of RE–Ni binary alloys.\(^{7–12,19}\) Thus, open-circuit potentiometry was carried out for the Ni plate electrode after galvanostatic electrolysis at −0.15 A cm\(^{-2}\) for 10 min in the same melt. The same measurements were successively repeated thrice to obtain more distinct potential plateaus. Figure 3 shows the three successive open-circuit potentiograms obtained by this process. The potential shifts in the positive direction with time, owing to a decrease in the Pr concentration at the surface of the electrode as Pr atoms diffuse toward the inside of the plate. For the 2nd and 3rd measurements, potential plateaus are observed at 0.33 V, 0.42 V, 0.50 V, 0.82 V, and 1.00 V, which possibly correspond to the equilibrium states of two different Pr–Ni phases, as shown by Eq. 1.

\[
\text{Pr}_x\text{Ni} + (y - x)\text{Pr(III)} + 3(y - x)\text{e}^- \rightleftharpoons \text{Pr}_y\text{Ni} \quad [1]
\]

Figure 2. Cyclic voltammograms for Mo and Ni wire electrodes in molten LiF–CaF\(_2\)–PrF\(_3\) (0.50 mol\%) at 1123 K. Scan rate: 0.05 V s\(^{-1}\).
Figure 3. Open-circuit potentiograms for a Ni plate after galvanostatic electrolysis at -0.15 A cm$^{-2}$ for 10 min for 3 cycles in molten LiF–CaF$_2$–PrF$_3$ (0.50 mol%) at 1123 K. (a) Initial 120 min, and (b) the whole plots.

Table I. Electrolysis conditions for alloy samples prepared in molten LiF–CaF$_2$–PrF$_3$ (0.50 mol%) at 1123 K.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Step</th>
<th>Potential vs. Li$^+$/Li / V</th>
<th>Time / min</th>
</tr>
</thead>
<tbody>
<tr>
<td>(F-1)</td>
<td>1st step</td>
<td>0.20</td>
<td>90</td>
</tr>
<tr>
<td>(F-2)</td>
<td>1st step</td>
<td>0.25</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>2nd step</td>
<td>0.36</td>
<td>90</td>
</tr>
<tr>
<td>(F-3)</td>
<td>1st step</td>
<td>0.25</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>2nd step</td>
<td>0.60</td>
<td>90</td>
</tr>
<tr>
<td>(F-4)</td>
<td>1st step</td>
<td>0.25</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>2nd step</td>
<td>0.86</td>
<td>60</td>
</tr>
</tbody>
</table>

Figure 4. (a) A cross-sectional SEM image of and (b) a powder XRD pattern for sample (F-1) prepared by the potentiostatic electrolysis using a Ni plate electrode at 0.20 V for 90 min in molten LiF–CaF$_2$–PrF$_3$ (0.50 mol%) at 1123 K.
Equilibrium potential of Pr–Ni alloys.—From the results, the potential plateau at 0.33 V is ascribed to the following reaction:

$$2 \text{PrNi}_3 + \text{Pr(III)} + 3e^- \rightleftharpoons 3 \text{PrNi}_2$$  \[2\]

Considering the number of alloy phases appearing in the binary Pr–Ni phase diagram, the following reaction should exist:

$$3 \text{Pr}_2\text{Ni}_3 + \text{Pr(III)} + 3e^- \rightleftharpoons 7 \text{PrNi}_3$$  \[3\]

Although the formation of Pr$_2$Ni$_3$ could not be confirmed by XRD analysis of samples, the potential plateau at 0.42 V possibly corresponds to the above reaction. If this is the case, since the PrNi$_3$ phase was obtained at 0.60 V, the plateau at 0.50 V would correspond to the reaction given below:

$$\frac{7}{3} \text{PrNi}_3 + \text{Pr(III)} + 3e^- \rightleftharpoons \frac{5}{3} \text{Pr}_2\text{Ni}_7$$  \[4\]

The plateau at 0.82 V is attributed to the following reaction:

$$5 \text{Ni} + \text{Pr(III)} + 3e^- \rightleftharpoons \text{PrNi}_5$$  \[5\]

Finally, the plateau at 1.00 V is possibly derived from the impurities contained in the melt.

Table II lists the formation potentials of Nd–Ni alloys,$^8$ Dy–Ni alloys,$^9$ and Pr–Ni alloys in LiF–CaF$_2$–PrF$_3$ (0.30 mol%; RE = Nd or Dy; 0.50 mol%; RE = Pr) at 1123 K. For the Dy–Ni system, neither a potential plateau nor an XRD pattern was observed for the Dy$_2$Ni$_7$ phase.$^9$ The alloy formation potentials of the Pr–Ni system are almost equal to those of the Nd–Ni system. This result is attributed by the well-known striking similarity in the chemical properties of Nd and Pr. The Nd–Ni and Pr–Ni phases have more negative formation
potentials than the corresponding Dy–Ni phases, while the deposition potential of RE metals shows the opposite trend: Nd(III)/Nd (0.19 V), Dy(III)/Dy (0.16 V), and Pr(III)/Pr (0.21 V).

In a molten LiF–CaF2 system containing PrF3, NdF3, and DyF3, the effective potential range for the separation of Dy from Pr and Nd is expected to be between 0.34 V and 0.40 V. The thermodynamically stable phases in this potential range are PrNi3, NdNi3, and DyNi2. Further, it is expected that the formation rate of DyNi2 is considerably faster than those of PrNi3 and NdNi3 in this potential range. Thus, it is expected that the formation of DyNi2 would proceed preferentially to that of PrNi3 and NdNi3. Nd and Pr components are expected to remain in the molten salt, and they can be recovered as a Nd–Pr alloy afterward.

NaCl–KCl system.—Cyclic voltammetry.—As shown in Fig. 1, five intermetallic compounds, namely, PrNi, PrNi2, PrNi3, Pr2Ni7, PrNi5, and a liquid alloy exist in the Pr–Ni system at 973 K.17

Figure 8 shows a comparison of the cyclic voltammograms for Mo and Ni wire electrodes in a molten NaCl–KCl–PrCl3 (0.50 mol%) system at 973 K. For the Mo electrode, only a single pair of redox peaks (D, D′) is observed around 0.2 V (vs. Na+/Na). These peaks correspond to the deposition and dissolution of Pr metal. On the negative sweep for a Ni electrode, the cathodic currents (E) flow gradually from approx. 0.7 V and increase sharply from 0.4 V, possibly owing to the formation of Pr–Ni alloys. After the reversal of the sweep direction at 0 V, several anodic current peaks appear; this indicates the dissolution of Pr from the different Pr–Ni alloy phases.

Open-circuit potentiometry.—The deposition potential of Pr metal was determined to be 0.23 V by open-circuit potentiometry for a Mo electrode after galvanostatic electrolysis at −0.25 A cm−2 for 3 min in molten NaCl–KCl–PrCl3 (0.50 mol%) at 973 K; this procedure is the same as that employed in our previous studies.8,13

Subsequently, open-circuit potentiometry was carried out for the Ni plate electrode in order to examine the potentials of Pr–Ni alloy formation. Figure 9 shows the open-circuit potentiogram obtained after galvanostatic electrolysis at −0.03 A cm−2 for 3 min. Potential plateaus are observed at 0.38 V, 0.45 V, 0.52 V, and 0.78 V, which correspond to the coexisting states of different Pr–Ni phases. Here, the plateau potentials are determined as the values at which the differential coefficients of the open-circuit potentiogram become the local minima.

Preparation of Pr–Ni alloys and their characterization.—On the basis of the open-circuit potentiometry results, Pr–Ni alloy samples were prepared by the potentiostatic electrolysis using Ni plate electrodes at potentials between the plateaus observed in the open-circuit potentiogram: The conditions are summarized in Table III. A Pr–Ni alloy sample (sample (Cl-1)) was prepared by the potentiostatic electrolysis using a Ni plate electrode at 0.25 V for 40 min. Figure 10 shows (a) a cross-sectional SEM image of and (b) a powder XRD pattern for sample (Cl-1). An alloy layer with a thickness of around 100 μm is observed at both sides of the electrode. EDX analysis revealed

---

Table II. Formation reactions and corresponding potentials for RE–Ni alloys and RE metals in molten LiF–CaF2–REF3 at 1123 K (RE = Nd, Dy, and Pr). Concentrations of REF3 are 0.30 mol% for NdF3 and DyF3, and 0.50 mol% for PrF3.

<table>
<thead>
<tr>
<th>Formation reaction</th>
<th>RE = Nd</th>
<th>RE = Dy</th>
<th>RE = Pr (This study)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 Ni + RE(III) + 3 e− ⇌ RENi5</td>
<td>0.73</td>
<td>0.79</td>
<td>0.82</td>
</tr>
<tr>
<td>3 RENi5 + RE(III) + 3 e− ⇌ 3 RE2Ni7</td>
<td>0.49</td>
<td>-</td>
<td>(0.50)</td>
</tr>
<tr>
<td>5 RE Ni5 + RE(III) + 3 e− ⇌ 5 RENi3</td>
<td>-</td>
<td>0.57</td>
<td>-</td>
</tr>
<tr>
<td>3 RE2Ni7 + RE(III) + 3 e− ⇌ 7 RENi3</td>
<td>0.42</td>
<td>-</td>
<td>(0.42)</td>
</tr>
<tr>
<td>2 RENi3 + RE(III) + 3 e− ⇌ 3 RENi2</td>
<td>0.34</td>
<td>0.40</td>
<td>0.33</td>
</tr>
<tr>
<td>RE(III) + 3 e− ⇌ RE</td>
<td>0.19</td>
<td>0.16</td>
<td>0.21</td>
</tr>
</tbody>
</table>

---

Figure 8. Cyclic voltammograms for Mo and Ni wire electrodes in molten NaCl–KCl–PrCl3 (0.50 mol%) at 973 K. Scan rate: 0.05 V s−1.

Figure 9. Open-circuit potentiograms for a Ni plate electrode after galvanostatic electrolysis at −0.03 A cm−2 for 3 min in molten NaCl–KCl–PrCl3 (0.50 mol%) at 973 K.
the atomic composition to be Pr:Ni = 33:67 at% in the alloy layer. The XRD pattern shown in Fig. 10b confirms that the alloy is PrNi2 at the surface of the plate. The formation of PrOCl is also detected. Even at the potential of 0.25 V which was close to the deposition potential of Pr metal (0.23 V), only PrNi2 phase was observed when the electrolysis time was 40 min. According to the phase diagram of Pr–Ni system (Fig. 1), the Pr-richest compound “PrNi” is supposed to be obtained at 973 K. A similar phenomenon had been reported for the formation of Pr–Ni alloys in LiCl–KCl–PrCl3 at 723 K. Only the PrNi2 phase was detected for the sample prepared by the potentiostatic electrolysis using a thick Ni electrode (200 μm) at 0.50 V vs. Li+/Li for 30 min. Here, the potential was close to the deposition potential of Pr metal (0.47 V). On the other hand, PrNi phase was evidently obtained at 0.50 V by the longer time electrolysis (240 min) using a thin Ni electrode (50 μm). These results were explained by the process that the PrNi2 phase forms preferentially until the whole electrode becomes PrNi2 and the PrNi phase starts to form afterward. Thus, in the present NaCl–KCl system, the PrNi phase would also form by longer time electrolysis at 0.25 V.

Two-step electrolysis was carried out in the NaCl–KCl–PrCl3 melt. In this melt, a Pr-rich alloy was formed at 0.25 V (first step). Figure 11 shows the SEM and XRD results for the samples prepared at 0.42 V in the second step (sample (Cl-2)). A 120-μm-thick alloy layer with the composition Pr:Ni = 26:74 at% is observed. XRD analysis revealed this alloy to be the PrNi3 phase. Thus, the stable phase at 0.42 V is PrNi3. Figure 12 shows (a) a cross-sectional SEM image of and (b) a powder XRD pattern for sample (Cl-3) that was electrolyzed at 0.48 V in the second step. EDX analysis confirmed that the atomic composition of the surface region was Pr:Ni = 18:82 at%. As shown in Fig. 12b, a distinct Pr2Ni7 pattern is observed in the XRD analysis; this observation leads to the conclusion that Pr2Ni7 is the thermodynamically stable phase at 0.48 V. For sample (Cl-4) prepared at 0.70 V in the second step, a 100-μm-thick alloy layer is observed in the SEM image (Fig. 13a). According to EDX analysis results, the composition in this layer is Pr:Ni = 18:82 at%. XRD analysis (Fig. 13b) reveals the existence of the PrNi2 phase. Thus, PrNi2 is stable at 0.70 V. When the second electrolysis was carried at 1.00 V (sample (Cl-5)), as shown in Fig. 14, the whole electrode returned to pure Ni. Thus, the Pr–Ni alloy phase is no longer stable at 1.00 V.

Equilibrium potential of Pr–Ni alloys.— On the basis of the above-mentioned results, the formation potentials of Pr–Ni alloys in molten NaCl–KCl–PrCl3 (0.50 mol%) are determined as follows. The potential plateau at 0.38 V in Fig. 9 corresponds to the equilibrium between PrNi3 and PrNi2 (reaction 1). The plateau at 0.45 V is ascribed to the equilibrium reaction between Pr2Ni3 and PrNi3 (reaction 2). The potential plateaus at 0.52 V and 0.78 V correspond to the equilibrium reactions of PrNi5/Pr2Ni7 and Ni/PrNi5, respectively. The formation potentials of the Pr–Ni alloys and the deposition potential of Pr metal at 973 K are summarized in Table IV. The values for the Nd–Ni–Dy–Ni systems are also listed for reference.

In a molten NaCl–KCl system containing 0.50 mol% of PrCl3, NdCl3, and DyCl3, the effective potential range for the separation of Dy from Pr and Nd is expected to be between 0.39 V and 0.48 V. In this potential range, the thermodynamically stable phases are PrNi5, NdNi3, and DyNi2. Since the formation rate of DyNi2 is considerably faster than those of PrNi5 and NdNi3, it is expected that the formation of DyNi2 would proceed preferentially to those of NdNi3 and PrNi5. As a result, Pr(III) and Nd(III) ions are expected to remain in the molten salt, and they can be recovered as a Nd–Pr alloy afterward.

Comparison of LiF–CaF2 and NaCl–KCl–KCl systems.— Through the experimental results obtained in this study, the formation potentials of Pr–Ni alloys and the effective potential ranges for RE separation in molten LiF–CaF2 and NaCl–KCl–KCl systems have been clarified, as shown in Tables II and IV, respectively. In both these molten salts, the electrochemical behaviors of Nd and Pr were very similar. The separation of Nd and Pr by using the proposed molten salt electrochemical process was found to be difficult. However, this point is not significant because the recovered Nd–Pr alloy (didymium) can be directly used as a raw material for Nd–Fe–B magnets. Since Dy is very scarce and must be distributed at the grain boundaries of magnets, an effective separation ability of Dy from Nd and Pr is important. In this respect, the present molten salt electrochemical process has considerable potential for practical application.

Between LiF–CaF2 and NaCl–KCl molten salt systems, the former is advantageous from the standpoint of kinetics, as indicated in the voltammograms of Figs. 2 and 8. The formation current for RE–Ni alloys in molten LiF–CaF2 is higher than that in molten NaCl–KCl–KCl, which is probably due to the higher operating temperature for the former. The advantage of NaCl–KCl–KCl system is a wider potential region for the effective separation of Dy from Nd and Pr. In addition, its low corrosivity enables a wide selection of cell structure materials. To further optimize the electrolysis condition, the electrode behaviors in

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Step</th>
<th>Potential vs. Na+/Na / V</th>
<th>Time / min</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Cl-1)</td>
<td>1st step</td>
<td>0.25</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>2nd step</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>(Cl-2)</td>
<td>1st step</td>
<td>0.25</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>2nd step</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>(Cl-3)</td>
<td>1st step</td>
<td>0.25</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>2nd step</td>
<td>0.48</td>
<td>50</td>
</tr>
<tr>
<td>(Cl-4)</td>
<td>1st step</td>
<td>0.25</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>2nd step</td>
<td>0.70</td>
<td>55</td>
</tr>
<tr>
<td>(Cl-5)</td>
<td>1st step</td>
<td>0.25</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>2nd step</td>
<td>1.00</td>
<td>60</td>
</tr>
</tbody>
</table>

![Figure 10](130.54.130.237)
Figure 11. (a) A cross-sectional SEM image of and (b) a powder XRD pattern for sample (Cl-2) prepared by the potentiostatic electrolysis using a Ni plate electrode at 0.25 V for 42 min and subsequently at 0.42 V for 40 min in molten NaCl–KCl–PrCl₃ (0.50 mol%) at 973 K.

Figure 12. (a) A cross-sectional SEM image of and (b) a powder XRD pattern for sample (Cl-3) prepared by the potentiostatic electrolysis using a Ni plate electrode at 0.25 V for 40 min and subsequently at 0.48 V for 50 min in molten NaCl–KCl–PrCl₃ (0.50 mol%) at 973 K.

Figure 13. (a) A cross-sectional SEM image of and (b) a powder XRD pattern for sample (Cl-4) prepared by the potentiostatic electrolysis using a Ni plate electrode at 0.25 V for 40 min and subsequently at 0.70 V for 55 min in molten NaCl–KCl–PrCl₃ (0.50 mol%) at 973 K.

Figure 14. (a) A cross-sectional SEM image of and (b) a powder XRD pattern for sample (Cl-5) prepared by the potentiostatic electrolysis using a Ni plate electrode at 0.25 V for 40 min and subsequently at 1.00 V for 60 min in molten NaCl–KCl–PrCl₃ (0.50 mol%) at 973 K.
melted salts containing all the RE halides (RE = Nd, Dy, and Pr) should be investigated on the basis of the information obtained in this study.

**Conclusions**

The electrochemical formation of Pr–Ni alloys was investigated in molten LiF–CaF$_2$–PrF$_3$ (0.50 mol%) system at 1123 K and molten NaCl–KCl–RECl$_3$ (0.50 mol%) system at 973 K. The results obtained in this study are summarized as follows:

1. The potentials of Dy(III)/Dy were 0.21 V vs. Li$^+$/Li in the LiF–CaF$_2$ system and 0.23 V vs. Na$^+$/Na in the NaCl–KCl system.
2. The open-circuit potentiogram obtained after the galvanostatic electrolysis using a Ni electrode exhibited several potential plateaus corresponding to coexisting states of Pr–Ni phases.
3. The equilibrium reactions of Pr–Ni alloys and the corresponding potentials were determined by SEM/EDX and XRD analyzes of the prepared alloy samples.
4. The effective electrolysis potential ranges for the separation of Dy from Nd and Pr were suggested to be 0.34–0.40 V and 0.39–0.48 V in molten LiF–CaF$_2$ and NaCl–KCl, respectively.

**Acknowledgments**

A part of this study was supported by a grant-in-aid for Scientific Research from the Japanese Ministry of the Environment.

**References**