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Electrochemistry of nitrogen and nitrides in molten salts

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Abstract

Electrochemical behavior of nitrogen and nitrides in a molten LiCl–KCl–Li_3N system has been investigated from thermodynamic and kinetic point of view. Nitride ions are anodically oxidized to form nitrogen gas almost quantitatively on a nickel electrode according to the following reaction:

$$N^{3-} = \frac{1}{2}N_2 + 3e^-.$$

This is a reversible one-step three-electron reaction governed by a simple diffusion-controlled charge transfer process. The diffusion coefficient of nitride ion is estimated to be about 1.8×10^{-5} $cm^2\ s^{-1}$ at 723 K. On the other hand, nitrogen gas is cathodically reduced almost quantitatively to form nitride ions, the reaction of which is expressed as

$$\frac{1}{2}N_2 + 3e^- = N^{3-}.$$

The standard electrode potential of an N_2/N^{3-} couple, $E^0_{N_2/N^{3-}}$, at 723 K was found to be 0.382 V vs. Li^+/Li. Potential-pN^{3-} diagrams were constructed using $E^0_{N_2/N^{3-}}$ together with thermochemical data for elements relevant to the electrochemical reprocessing of nitride fuels. The obtained results also enable us to propose new processes such as the electrochemical formation of functional nitride films and the electrochemical synthesis of ammonia gas under ambient pressure.

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1. Introduction

A nitride fuel cycle system based on molten salt electrochemical reprocessing is a promising one from a viewpoint of the actinide confinement [1]. The main process of this fuel recycle, as schematically shown in Fig. 1, consists of the anodic dissolution of spent nitrides and the cathodic electrorefining in molten salts. For developing the above electrochemical processes, it is important to consider their feasibility from a thermodynamic point of view. We have thus proposed the potential-pN^{3-} diagrams [2], which are particularly useful, since the diagrams cover all conditions under which molten salts are normally used. The diagrams are conceptually similar to the potential-pH diagrams [3] and potential-pO^{2-} diagrams [4], that is, in the potential-pN^{3-} diagrams, the chosen composition variable is the concentration of nitride ion (N^{3-}) in the melt, which is expressed as its negative logarithm, pN^{3-}. For constructing this diagram, it is necessary to evaluate the standard electrode potential of a N_2/N^{3-} couple in molten salt system. Also, with the use of the nitrogen gas electrode reaction, we have

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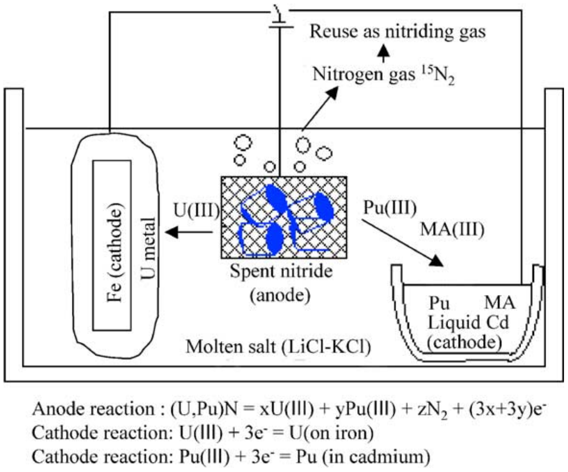

Fig. 1. Principle of spent nitride fuel reprocessing in molten salt system.

proposed the new electrochemical processes, e.g., the electrochemical formation of functional nitride film and the electrochemical synthesis of ammonia gas under ambient pressure, other than the electrochemical reprocessing of spent nitride fuels.

Against the background, we have thoroughly studied the electrochemical behavior of nitrogen and nitrides in molten salt from thermodynamic and kinetic points of view. By using the obtained thermodynamic data, the potential-pN^{3-} diagrams for various elements were constructed. Based on the obtained results, the above newly proposed electrochemical processes have been examined by using the cell containing nitrogen gas electrode as a cathode.

2. Experimental

All experiments were conducted in an argon atmosphere using a glove box with a continuous gas refining instrument. An electrochemically polished nickel plate (Nilaco Co., 99.99%, Ni) was used as a working electrode for investigating electrochemical behavior of nitride ions. A nickel wire (ϕ 1 mm or ϕ 0.1 mm, Nilaco Co., 99.99%, Ni) bundled type electrode covered with a high purity alumina tube (Nikkato Co., SSA-S, Al_2O_3) was used as a gas electrode. Mixed gas consisting of dried pure argon (Teisan Co., 99.998%) and dried pure nitrogen (Teisan Co., 99.998%) was supplied from the top of the gas electrode. The nitrogen gas partial pressure was controlled by variation of the gas flows. Reagent grade LiCl (Wako Co., 99.99%) and KCl (Wako Co., 99.99%) was dried under vacuum for more than 72 h at 473 K in order to remove water. The eutectic mixture (59 mol% LiCl, 41 mol% KCl) was then melted in a high purity alumina crucible. Lithium nitride (Mitsuwa Co., Li_3N, 99.8%) was used as a nitride ion source. Electrochemical measurements were conducted using a potentio/galvanostat (Hokuto Denko Co., HA-301) combined with a function generator (Hokuto Denko Co., HB-104).

3. Results and discussion

3.1. Electrochemical behavior of nitride ions [5]

The electrochemical behavior of nitride ions in an LiCl–KCl–Li_3N system on nickel electrode was studied by means of electrochemical measurements together with gas analysis. Fig. 2 shows typical cyclic voltammograms for nickel electrode in the LiCl–KCl eutectic melt containing 0.04 mol% Li_3N at various sweep rates ranging from 0.05 to 0.5 V s^{-1}. One anodic peak and a corresponding cathodic peak are observed. From these voltammetric data, the anodic currents are considered to be due to the oxidation of nitride ions. Thus, nitride ions in the melt are considered to be anodically oxidized to form nitrogen gas at potentials more positive than about 0.45 V, the reaction of which can be expressed as

$$N^{3-} = \frac{1}{2}N_2 + 3e^-. \qquad (1)$$

In order to confirm this, quantitative analysis of the generated gas obtained after potentiostatic anodic oxidation of nitride ions at various potentials ranging from 0.45 V to 0.85 V was conducted. The evolved gas

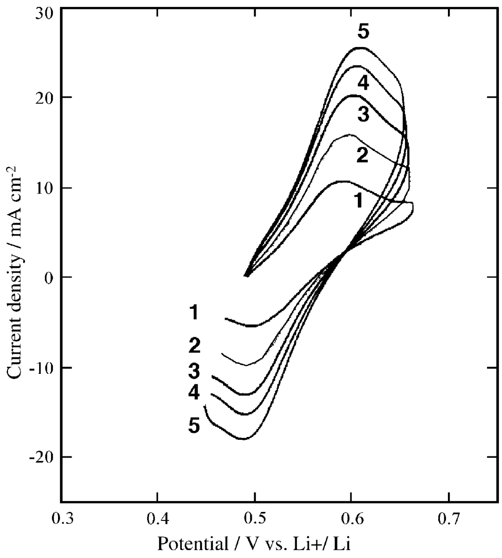

Fig. 2. Cyclic voltammograms for Ni electrode in LiCl–KCl containing 0.04 mol% Li_3N, scan rates: (1) 0.05, (2) 0.1, (3) 0.2, (4) 0.3 and (5) 0.5 V s^{-1} at 723 K.

obtained after potentiostatic anodic oxidation of nitride ions was mainly pure nitrogen gas. Provided that all observed currents were due to the reaction (1), the current efficiency was calculated to be around 100%. The results of quantitative analysis of anodically evolved gas showed that the oxidation of nitride ions proceeded to produce pure nitrogen gas almost quantitatively at potentials more positive than 0.45 V according to the reaction (1). The anodic peak potentials scarcely change with sweep rate as shown in Fig. 2, which indicates that the oxidation of nitride ions is very close to a reversible process. For a process with high reversibility, the following equation is available for estimating the number of electrons transferred:

$$|E_{\mathrm{pA}} - E_{\mathrm{pA/2}}| = 2.2\frac{RT}{nF}, \tag{2}$$

where E_{pA} is the anodic peak potential, $E_{\mathrm{pA/2}}$ is the anodic half-peak potential, R is the gas constant, T is the temperature, n is the number of electrons transferred and F is Faraday constant. By means of Eq. (2), the number of transferred electrons was estimated to be 3.0 ± 0.2, corresponding to the number of electrons in reaction (1). Fig. 3 shows that the anodic peak current varies linearly with the square root of the scan rate. Thus, the oxidation step is considered to be a simple diffusion-controlled charge transfer process. The diffusion coefficient of nitride ions in an LiCl–KCl eutectic melt was estimated from Fig. 3 according to the following relationships:

$$j_{\mathrm{pA}} = 0.4463nFC\left(\frac{nF}{RT}\right)^{1/2} v^{1/2}D^{1/2}, \tag{3}$$

where j_{pA} is the anodic peak current density, C is the bulk concentration of nitride ions, D is the diffusion coefficient, v is the scan rate and j_{pA} is the anodic current density. The diffusion coefficients of nitride ion in an LiCl–KCl–Li_3N system at 723 K were found to be $\sim 1.8 \times 10^{-5}\ \mathrm{cm^{-2}\ s^{-1}}$.

3.2. Electrochemical reduction of nitrogen gas

3.2.1. Equilibrium potential of the nitrogen gas electrode [6]

Considering the results of the electrochemical behavior of nitride ions, one can expect that nitrogen gas can be electrochemically reduced to produce nitride ions under moderate condition by using a nitrogen gas electrode in a molten chloride system, the reaction of which can be expressed as

$$\frac{1}{2}N_2 + 3e^- = N^{3-}. \tag{4}$$

The electrochemical reduction of nitrogen gas in an LiCl–KCl–Li_3N system has been thus studied with the use of a nickel wire bundled type nitrogen gas electrode. Fig. 4 shows the relationship between nitrogen gas partial pressure and the rest potential of the gas electrode. The potential shifts linearly to a more positive value as the nitrogen gas pressure increases. The Nernstian relationship between rest potential and the nitrogen partial pressure shows that the rest potential measured here is certainly the equilibrium potential corresponding to the reaction (4), that is, the slope in Fig. 4, 0.024 V/decade, corresponds to the theoretical value of a three-electron reaction at 723 K. Fig. 5 shows the relationship between the concentration of nitride ion and the rest potential of the gas electrode under constant nitrogen partial pressure of 1 atm. The potential varies linearly with the concentration of nitride ion. The slope, 0.048 V/decade, is also corresponding to the theoretical value of a three-electron reaction at 723 K. Assuming that the activity coefficient of nitride ion is almost unity at linear

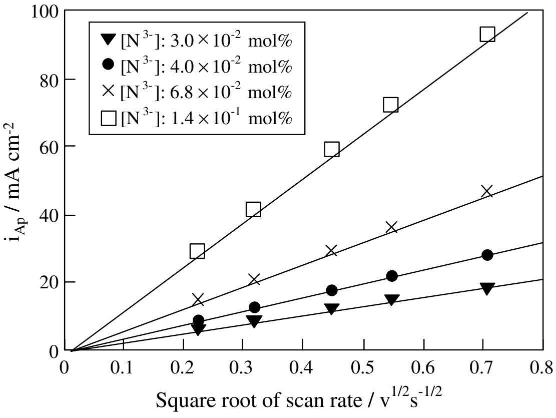

Fig. 3. Variations of anodic peak current densities with square roots of potential scan rates.

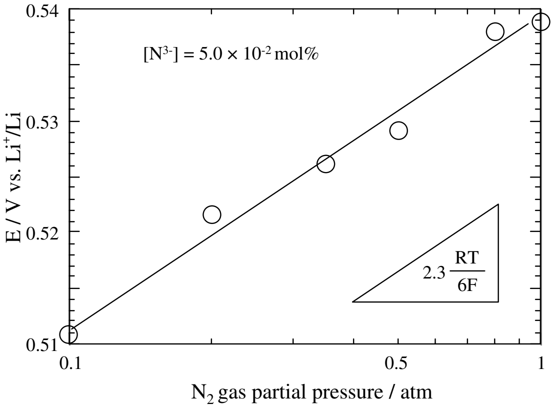

Fig. 4. The relationship between rest potential of the gas electrode and nitrogen partial pressure in LiCl–KCl containing 0.05 mol% Li_3N at 723 K. Gas electrode: three nickel wires (ϕ 1 mm) tied up in a bundle.

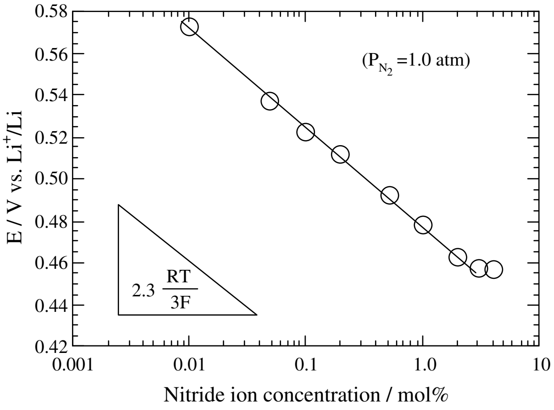

Fig. 5. The relationship between rest potential of the gas electrode and nitride ion concentration in LiCl–KCl–Li_3N melts at 723 K. Gas electrode: three nickel wires (ϕ 1 mm) tied up in a bundle. $PN_2 = 1$ atm.

region, the value of standard electrode potential at 723 K, $E^0_{N_2/N^{3-}}$, was estimated to be 0.382 V vs. Li^+/Li by extrapolating the line of linear part to the point of 100 mol%. Therefore, the equilibrium potential of the gas electrode at 723 K is given by the following Nernstian equation:

$$E = 0.382 + \frac{RT}{6F}\ln(P_{N_2}) - \frac{RT}{3F}\ln(a_{N^{3-}})\text{V vs. } Li^+/Li \text{ at 723 K.} \tag{5}$$

3.2.2. Polarization of the nitrogen gas electrode

It was confirmed, by the cathodic polarization curves of nitrogen gas electrode together with quantitative analysis of evolved gas, that the reduction of nitrogen gas quantitatively proceeded to form nitride ions according to the reaction (4). Considering practical use, it is necessary to develop nitrogen diffusion gas electrode with good polarization characteristics, that is, the reaction (4) efficiently proceeds with higher current density at small overpotential. Polarization characteristics have been studied concerning the shape and electrode material of the electrode. At the present stage, the gas diffusion electrode consisting of porous nickel shows excellent polarization characteristics, as shown in Fig. 6.

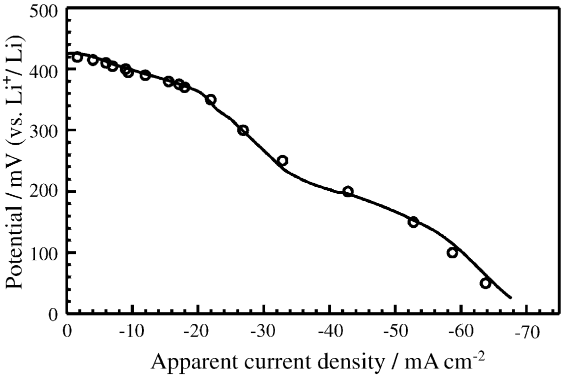

Fig. 6. Cathodic polarization curves of N_2 gas electrodes of sintered Ni in molten LiCl–KCl–Li_3N (0.5 mol%) at 723 K. Gas flow rate 2.5 ml min^{-1}.

3.3. Potential-pN^{3-} diagram in LiCl–KCl

3.3.1. Drawing method of potential-pN^{3-} diagram

There are a number of possible electrochemical and/or chemical reactions that need to be considered. For simplicity, only trivalent metal ions are taken into consideration

$$\frac{1}{2}N_2 + 3e^- = N^{3-}, \tag{4}$$

$$M(III) + 3e^- = M, \tag{6}$$

$$MN + 3e^- = M + N^{3-}, \tag{7}$$

$$MN = M(III) + N^{3-}. \tag{8}$$

The electrode potentials and equilibrium constants corresponding to the above equations can be expressed as follows:

$$E_{N_2/N^{3-}} = E^0_{N_2/N^{3-}} + \frac{2.303RT}{6F}\log P_{N_2} + \frac{2.303RT}{3F}pN^{3-}, \tag{4'}$$

$$E_{M(III)/M} = E^0_{M(III)/M} + \frac{2.303RT}{3F}\log[M(III)], \tag{6'}$$

$$E_{MN/M,N^{3-}} = E^0_{MN/M,N^{3-}} + \frac{2.303RT}{3F}pN^{3-}, \tag{7'}$$

$$= \frac{\mu^0_{MN} - \mu^0_{N^{3-}}}{3F} + \frac{2.303RT}{3F}pN^{3-}, \tag{7''}$$

$$K_{sp} = [M(III)][N^{3-}], \tag{8'}$$

where [M(III)] is the concentration of trivalent metal ion in cation fraction and $[N^{3-}]$ represents the nitride ion concentration in anion fraction. pN^{3-} is defined as

$$pN^{3-} = -\log[N^{3-}]. \tag{9}$$

K_{sp} represents the solubility product of MN. In order to construct the potential-pN^{3-} diagram, it is necessary to determine the standard electrode potential and the solubility product corresponding to reactions 4,6,7 and 8, respectively. $E^0_{N_2/N^{3-}}$ at 723 K has already been evaluated to be 0.382 V vs. Li^+/Li from the equilibrium potential measurement of nitrogen gas electrode in previous section. $E^0_{M(III)/M}$ is available from literature [7]. $E^0_{MN/M,N^{3-}}$ is determined using the values of $\mu^0_{N^{3-}}$ and μ^0_{MN}, since $\mu^0_{N^{3-}}$ is evaluated from the value of $E^0_{N_2/N^{3-}}$ and μ^0_{MN} is available from literature [8,9]. K_{sp} is derived from Eq. (10) using the values of $E^0_{MN/M,N^{3-}}$ and $E^0_{M(III)/M}$

$$E^0_{MN/M,N^{3-}} = E^0_{M(III)/M} + \frac{RT}{3F}\ln K_{sp}. \tag{10}$$

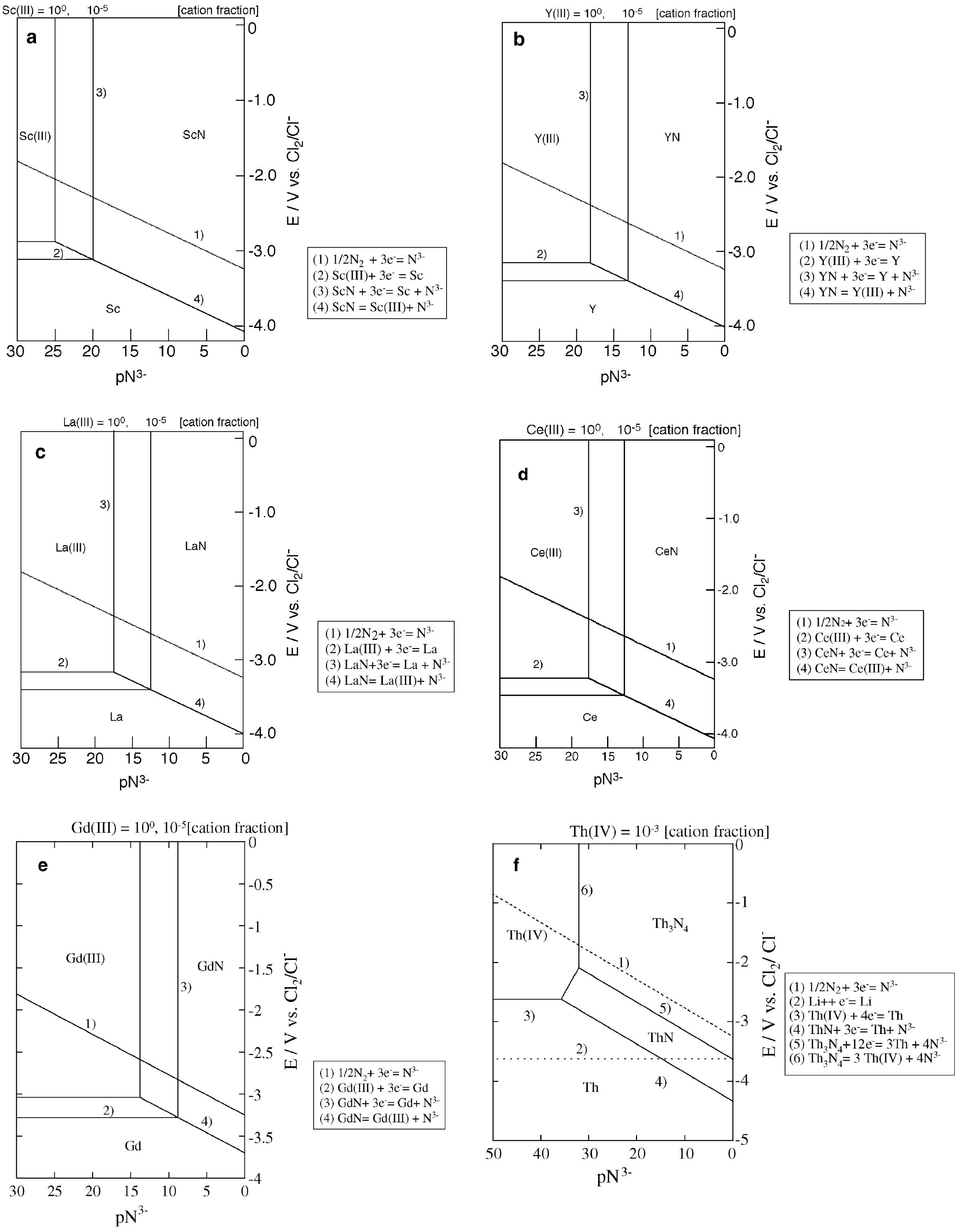

Fig. 7. Potential-pN^{3-} diagrams for (a) Sc–N system, (b) Y–N system, (c) La–N system, (d) Ce–N system, (e) Gd–N system, (f) Th–N system, (g) U–N system, (h) Np–N system and (i) Pu–N system in a molten LiCl–KCl system at 723 K.

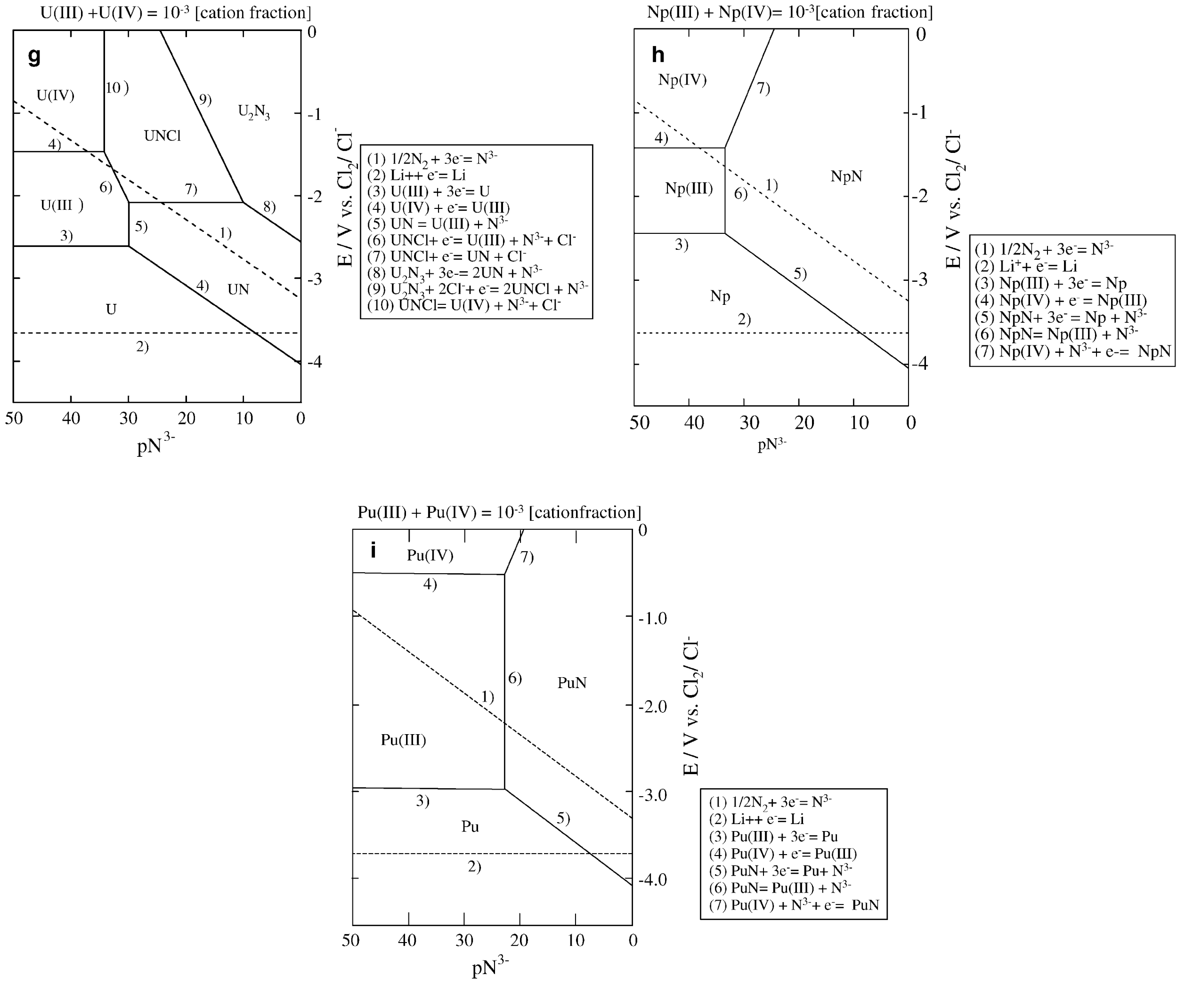

Fig. 7 (*continued*)

As a convention, the potential zero is taken as the potential of a chlorine electrode (1 atm) in contact with an LiCl–KCl melt at unit chloride activity in anion fraction.

3.3.2. Potential-pN^{3-} diagram for lanthanide and actinide elements

By using the above drawing method, the potential-pN^{3-} diagrams of lanthanide and actinide elements can be constructed as shown in Fig. 7(a)–(i). Each line with a specified number corresponds to one of the reactions described in Fig. 7. The nitrogen partial pressure is chosen to be 1 atm. This potential-pN^{3-} diagram shows that MN_x (M: lanthanide (Sc, Y, La, Ce, Gd) and actinide (Th, U, Np, Pu) elements) is thermodynamically stable at the section denoted as MN_x in the diagram. The diagram enables us to consider the electrolytic conditions corresponding to the electrochemical reprocessing process of nitrides from a thermodynamic point of view. The solubility products of nitrides are summarized in Table 1.

Table 1
Solubility products of nitrides in an LiCl–KCl system at 723 K

Reaction (LiCl–KCl at 723 K)	($\log K_{sp}$)
ScN = Sc(III) + N^{3-}	−26.6
YN = Y(III) + N^{3-}	−19.8
LaN = La(III) + N^{3-}	−19.1
CeN = Ce (III) + N^{3-}	−19.2
GdN = Gd(III) + N^{3-}	−13.8
Th_3N_4 = 3Th(IV) + $4N^{3-}$	−32.1
UN = U(III) + N^{3-}	−33.0
UNCl = U(IV) + Cl^- + N^{3-}	−37.3
NpN = Np(III) + N^{3-}	−37.0
PuN = Pu(III) + N^{3-}	25.2

3.4. New electrochemical processes concerning nitrogen

We have proposed several new electrochemical processes involving nitrogen and its compounds based on the results of previous sections. This section describes the electrochemical formation of nitrides and the electrochemical synthesis of ammonia under moderate condition, processes of which have recently been developed in our laboratory.

3.4.1. Electrochemical formation of nitrides

By using the anodic oxidation of nitride ion on a metal electrode, electrochemical formation of nitride (MN_x) could be achieved according to the consecutive reactions:

$$xN^{3-} \rightarrow xN + 3xe^- \tag{11}$$

$$M + xN \rightarrow MN_x \tag{12}$$

where, M represents so far, Ti, Zr, Fe, Al, Co, Cr, Ga, Zn and stainless steel [10–16]. In these experiments, however, Li_3N was used as nitride ion source, which is difficult to handle under ambient atmosphere. Furthermore, from a practical point of view, lithium metal will be accumulated in the melt by the continuous addition of Li_3N, if the cathodic reaction is not available for its removal and recovery. This is not desirable for industrial use, where continuous operation is necessary. Therefore, it is necessary to develop a novel process without adding Li_3N as a nitride ion source. As shown in Fig. 8, this process can be achieved by using the nitrogen gas electrode as a cathode. In order to confirm this, long-term nitriding of titanium with use of a nitrogen gas electrode was conducted successively for three periods in the same melt; each nitriding procedure consisted of potentiostatic anodic oxidation at 1.0 V for 10 h. A new titanium electrode was exchanged between each period. For comparison, the same potentiostatic electrolysis was carried out without supplying nitrogen gas. The sample obtained at the third period was analyzed by XPS, respectively. The formation of nitride was confirmed only in the case of using a nitrogen gas electrode as a cathode. These results show that continuous electrochemical formation of nitride without adding Li_3N can be achieved by using nitrogen gas electrode [6].

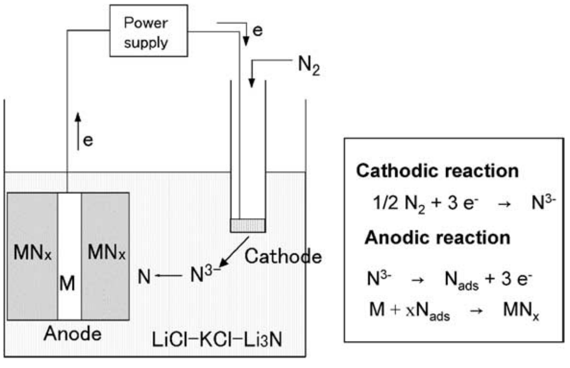

Fig. 8. Schematic representation of electrochemical formation process of nitride in molten salt system by using nitrogen gas electrode as a cathode.

3.4.2. Electrochemical synthesis of NH_3

Nitrogen fixation as ammonia is a very important chemical process because a wide variety of important chemical products are prepared from ammonia, including fertilizers, nitric acid, urea and amines. In the near future, it is expected that ammonia will be synthesized as the selective reductant of NO_x in small-scale and on every site of NO_x emission, such as ships and stationary facilities. Furthermore, ammonia is expected to be utilized as a hydrogen storage and transportation medium. However, at present, ammonia is synthesized by the Harber–Bosch process in large-scale at high temperature (~750 K) and high pressure (~10 MPa) and it is still difficult to synthesize ammonia at lower temperature and under atmospheric pressure. From the background, the authors have developed the novel ammonia synthesis method at lower temperature ($\leqslant$673 K) and under atmospheric pressure, which uses electrochemical reactions in molten salts as shown in Fig. 9. The principle is as follows: The electrolyte is molten alkaline halides containing nitride ions. The cathode is a nitrogen gas electrode and the anode is a hydrogen gas electrode. On the cathode, nitrogen gas is reduced to nitride ions according to the reaction (4). On the anode, nitride ions are oxidized and react with hydrogen gas to synthesize ammonia according to the following reaction:

$$N^{3-} + \frac{3}{2}H_2 \rightarrow NH_3 + 3e^- \tag{13}$$

The total reaction is expressed as

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3 \tag{14}$$

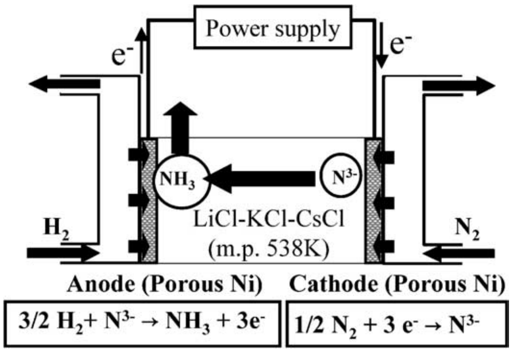

Fig. 9. Schematic representation of electrochemical synthesis of ammonia gas under ambient pressure.

Since the Gibbs energy change of reaction (14) is 15.9 kJ mol^{-1}, the theoretical electrolysis voltage is calculated to be 0.05 V at 600 K. Ammonia was successfully synthesized by using an experimental cell with high current efficiency under atmospheric pressure and at lower temperatures than the Haber–Bosch process [17]. It was confirmed from quantitative analysis that nitride ions, which were produced by the reduction from nitrogen gas at the cathode, was anodically oxidized and reacted with hydrogen to produce ammonia at the anode with quite high current efficiency (∼72%), when anodic electrolysis of hydrogen gas electrode was conducted at 0.7 V in LiCl–KCl–CsCl containing 0.1 mol% Li_3N at 673 K [17].

4. Conclusions

The results obtained throughout the present study are summarized as follows:

(1) In molten chloride systems, nitrogen gas is cathodically reduced almost quantitatively to form nitride ions, the reaction of which is expressed as

$$\frac{1}{2}N_2 + 3e^- = N^{3-}$$

The value of standard electrode potential, $E^0_{N_2/N^{3-}}$, at 723 K was found to be 0.382 V vs. Li^+/Li.

(2) Nitride ions are anodically oxidized to form nitrogen gas almost quantitatively on nickel electrode according to the following reaction:

$$N^{3-} = \frac{1}{2}N_2 + 3e^-$$

This is a reversible one-step three electron reaction governed by a simple diffusion-controlled charge transfer process. The diffusion coefficient of nitride ion was determined to be 1.8×10^{-5} cm^2 s^{-1} at 723 K.

(3) The concept and the drawing method of potential-pN^{3-} diagram were described. By using the value of standard electrode potential of a nitrogen gas electrode, $E^0_{N^2/N^{3-}}$, together with thermodynamic data, the potential-pN^{3-} diagrams of lanthanide and actinide elements can be constructed. With the use of the diagram, it is possible to consider the feasibility of the electrochemical processes related to nitrogen and its compounds in a LiCl–KCl system from a thermodynamic point of view.

(4) By utilizing the electrochemical reaction of nitrogen and its compounds in molten chloride, new processes such as the electrochemical formation of functional nitrides films and the electrochemical synthesis of ammonia gas under ambient pressure are able to be developed, which do not require high temperature and complicated apparatus.

However, the studies on electrochemistry of nitrogen and nitrides in molten salt systems are still at early stages and now are being further continued. Through intensive and systematic studies, molten salt electrochemical processes related to nitrogen and nitrides will become a key technology in the future.

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