Thermodynamics of the N_2/N^{3-} Redox Couple in a LiBr−KBr−CsBr Melt

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Nitrogen electrode reaction has been investigated in a LiBr−KBr−CsBr melt containing Li_3N. The reaction $N^{3-} \rightarrow \frac{1}{2}N_2 + 3e^-$ is confirmed by quantitative analysis of anodically evolved gas. The Nernst relation holds for the rest potential of Ni electrodes at a nitrogen gas pressure, p_{N_2}, of 0.05−1.0 atm and an anion fraction of the N^{3-} ions, $x_{N^{3-}}$, of 0.003−0.010 (anion fraction). Then, the standard formal potential of the N_2/N^{3-} couple, $E^{\circ\prime}_{N_2/N^{3-}}$, is evaluated to be 0.251 ± 0.009 V versus Li^+/Li (p_{N_2} = 1 atm, $x_{N^{3-}}$ = 1) at 673 K. The dependence of $E^{\circ\prime}_{N_2/N^{3-}}$ on the temperature (570−730 K) gives a linear relation, whose slope is $(-0.930 ± 0.117) \times 10^{-3}$ V K^{-1}. Thermodynamic quantities for the formation of Li_3N in the melt are also estimated.

Introduction

Nitride ions (N^{3-}) have been reported to exist stably in a molten LiCl−KCl system containing Li_3N.[1] In this system, the following redox reaction has been found.

$$\frac{1}{2}N_2 + 3e^- = N^{3-} \qquad (1)$$
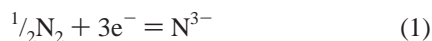
This electrode reaction involving nitrogen gas that has been considered to be inert is of great interest, since the reaction is specific in molten salts. Electrode reactions involving the N_2/N^{3-} redox couple are finding promising applications for thermoelectric converters, such as a Li−N_2 thermally regenerative fuel cell[2] and a N_2−N_2 thermogalvanic cell, and for material reforming as the electrochemical nitriding processes[3−8] and the electrolytic synthesis of ammonia.[8−10] To date, we have conducted thermodynamic and kinetic investigation and have reported the diffusion coefficient of the N^{3-} ions in the molten LiCl−KCl−Li_3N system.[1] For the above applications, it is important to optimize the operating temperature for providing optionalities of cell designs and operating conditions. Applying the above reaction at temperatures below 700 K would also be attractive from both viewpoints of energy consumption and actual manipulation. Nevertheless, nitrogen electrode reaction has not been investigated at temperatures below 700 K. Thus, we investigated the N_2/N^{3-} couple in LiCl−KCl−CsCl melts at temperatures of 600−730 K earlier.[11]

The aim of the present paper is to study the nitrogen electrode reaction at temperatures of 520−730 K by adopting new electrolytes having lower melting points. We have thus selected a LiBr−KBr−CsBr eutectic melt (mp 498 K[12]) as an electrolyte. First, the anodic reaction of the N^{3-} ions to nitrogen gas in this melt is discussed by means of electrochemical measurements combined with analysis of the evolved gas. The discussion of the stability of the N^{3-} ion in the melt is also made. Second, the equilibrium potential of the N_2/N^{3-} is obtained by using a nitrogen gas electrode. The thermodynamic quantities of dissolved Li_3N at temperatures around 600−700 K are calculated

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from the temperature dependence of the equilibrium potential. Thermodynamic evaluation is then carried out using these quantities.

Experimental Section

Experiments were conducted in an argon glovebox with a gas circulating purifier (MIWA MFG. Co., Ltd.). The eutectic mixture (LiBr/KBr/CsBr = 0.561/0.189/0.250, in mole fraction) was prepared from LiBr (99+%, Aldrich), KBr (99.0+%, Wako Pure Chemical Industries, Ltd.), and CsBr (99%, Mitsuwa Chemicals Co., Ltd.) in a high-purity alumina crucible (SSA-S, 99.5%, Al_2O_3, Nikkato Co., Ltd.) and dried in a furnace under vacuum at 423 K for at least 30 h. After that, it was melted at 673 K. Li_3N (99.5+%, Mitsuwa Chemicals Co., Ltd.) was added into the melt as a N^{3-} ion source. The anion fraction of the N^{3-} ions was regarded as being equal to the concentration of Li_3N added. A chromel−alumel thermocouple was used for the temperature measurement.

Experimental cell and gas lines used in this study are shown in our previous paper.[11] The working electrode was a Ni disk (99.7%, $\phi 6 \times 0.2$ mm, Nilaco Corp.) which was electrochemically polished before measurements. It was immersed just below the surface of the molten salt to minimize the thermal uncertainty. The reference electrode was an Al−Li alloy in the coexisting ($\alpha + \beta$) phase state prepared electrochemically from an Al wire (99.99%, $\phi 1 \times 5$ mm, Nilaco Corp.). The equilibrium potential of this electrode is determined by the following reversible reaction.[13]

$$Al(\alpha) + Li^+ + e^- = AlLi(\beta) \qquad (2)$$

The potential of this reference electrode was calibrated with reference to that of a Li^+/Li electrode, which was prepared by electrodepositing lithium metal on a Ni wire. In this paper, all potentials are shown in reference to this Li^+/Li electrode potential. The counter electrodes were a glassy carbon rod ($\phi 3$ mm, Tokai Carbon Co., Ltd.), which was used for the above potential calibration, and an Al plate (99.99%, Nilaco Corp.) for the investigation of the oxidation reaction of the N^{3-} ions.

The measurements were conducted using an electrochemical measurement system (Hokuto Denko Co., Ltd., HZ-3000)

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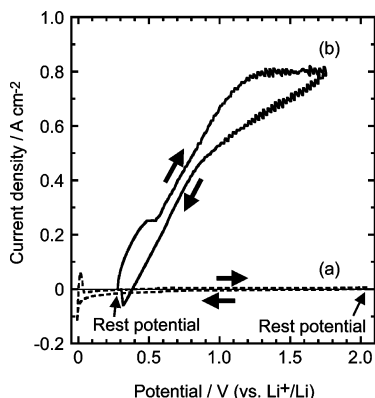*J. Phys. Chem. B, Vol. 109, No. 50, 2005* **23973**

Figure 1. Cyclic voltammograms for a Ni electrode in a LiBr−KBr−CsBr melt under a nitrogen gas atmosphere at 723 K (a) before and (b) after addition of Li$_3$N of 0.01 mole fraction. The scan rate is 0.5 V s^{-1}.

TABLE 1: Current Efficiency of Anodic Potentiostatic Electrolysis

electrolysis potential/V (vs Li$^+$/Li)	quantity of evolved gas/mol	quantity of electricity/C	current efficiency
0.34	1.96×10^{-3}	1220	0.9

controlled by a personal computer. The sampled gases were analyzed by a gas chromatograph (Shimadzu Co., Ltd., GC-8A, TCD detector). The rest potential of the N$_2$/N^{3-} was measured by the method described in detail earlier.[11]

Results and Discussion

Anodic Nitrogen Gas Evolution from the N^{3-} Ions. Figure 1 shows typical cyclic voltammograms for the Ni disk electrode in the LiBr−KBr−CsBr eutectic melt containing 0.01 mole fraction Li$_3$N at a scan rate of 0.5 V s^{-1}. After addition of Li$_3$N, anodic current was observed at more positive potentials than the rest potential of the Ni electrode of 0.3 V versus Li$^+$/Li. These currents indicate the following reaction due to the oxidation of the N^{3-} ions produced by the dissociation of Li$_3$N:

$$N^{3-} \rightarrow {}^{1}/_{2}N_2 + 3e^- \qquad (3)$$
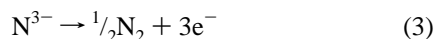
since the Br$^-$ ions do not discharge in this potential region.[13]

To confirm the above reaction, potentiostatic electrolysis was carried out at 723 K. The evolved gas obtained by potentiostatic anodization of the N^{3-} ions at a potential more positive than 0.3 V was analyzed by gas chromatography. As a result, the evolved gas was proved to be nitrogen gas. Assuming that all observed currents are ascribed to reaction 3, the current efficiencies are calculated to be around 100% (see Table 1). This result is reasonable, so that experimental error in measuring the amount of nitrogen gas can be negligible, taking into account that the solubility of nitrogen gas into the melt is very low.[14] The amount of nitrogen gas coming from the thermal decomposition of Li$_3$N was negligibly small compared to that from the electrolysis, since no nitrogen gas was detected before performing potentiostatic electrolysis. This shows that the N^{3-} ions are stable in the melt. Almost constant current during the electrolysis also supports the stability.

Evaluation of the Standard Formal Potential of the N$_2$/N^{3-} Redox Couple. The Nernst equation for reaction 1 should be expressed as

$$E_{N_2/N^{3-}} = E^{\circ}_{N_2/N^{3-}} + \frac{RT}{3F} \ln \frac{f_{N_2}^{1/2}}{a_{N^{3-}}} \qquad (4)$$
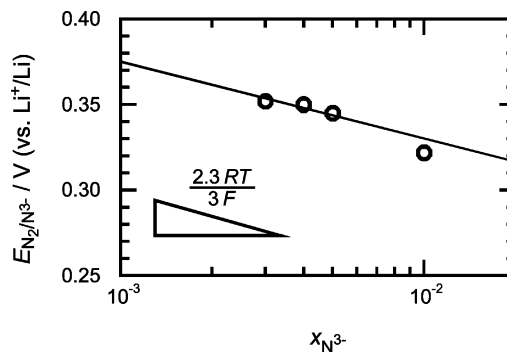

Figure 2. Relation between the rest potential of a Ni electrode and the anion fraction of the N^{3-} ion in a LiBr−KBr−CsBr−Li$_3$N melt at 673 K. p_{N_2} = 1.0 atm.

where f_{N_2} and $a_{N^{3-}}$ are the fugacity of nitrogen gas and the activity of the N^{3-} ions, respectively. $E^{\circ}_{N_2/N^{3-}}$ is the standard potential expressed with reference to the Li$^+$/Li potential in the melt. The other variables (R, T, and F) have their common meanings. Here, the standard state is defined as $f_{N_2} = 1$ and $a_{N^{3-}} = 1$. By using the fugacity coefficient of nitrogen gas, γ_{N_2}, and the activity coefficient of the N^{3-} ions, $\gamma_{N^{3-}}$, eq 4 is rewritten as

$$E_{N_2/N^{3-}} = E^{\circ}_{N_2/N^{3-}} + \frac{RT}{3F} \ln \frac{(\gamma_{N_2}p_{N_2})^{1/2}}{\gamma_{N^{3-}}x_{N^{3-}}} \qquad (5)$$

where p_{N_2} and $x_{N^{3-}}$ are the pressure of nitrogen gas and the anion fraction of the N^{3-} ions, respectively. $\gamma_{N^{3-}}$ is defined as unity in a pure liquid Li$_3$N ($x_{N^{3-}} = 1$). Here, it should be noted that the liquid Li$_3$N is a hypothetical state, since it does not exist under an atmospheric pressure. By using the standard formal potential, $E^{\circ\prime}_{N_2/N^{3-}}$, eq 5 can be expressed as

$$E_{N_2/N^{3-}} = E^{\circ\prime}_{N_2/N^{3-}} + \frac{RT}{3F} \ln \frac{p_{N_2}^{1/2}}{x_{N^{3-}}} \qquad (6)$$

where

$$E^{\circ\prime}_{N_2/N^{3-}} = E^{\circ}_{N_2/N^{3-}} + \frac{RT}{3F} \ln \frac{\gamma_{N_2}^{1/2}}{\gamma_{N^{3-}}} \qquad (7)$$

Thus, using eq 6, $E^{\circ\prime}_{N_2/N^{3-}}$ can be obtained from the relation between $E_{N_2/N^{3-}}$ and $\ln(p_{N_2}^{1/2}/x_{N^{3-}})$ in the experiments. In the following, $E^{\circ\prime}_{N_2/N^{3-}}$ was estimated by investigating the dependency of the rest potential of the nitrogen gas electrode on $x_{N^{3-}}$ and p_{N_2}.

The rest potential for the nitrogen gas electrode was measured in the LiBr−KBr−CsBr−Li$_3$N melt under a 1 atm nitrogen gas atmosphere at 673 K, when $x_{N^{3-}}$ was varied from 0.003 to 0.01 in anion fraction by the addition of Li$_3$N. Here, $x_{N^{3-}}$ was regarded as being equal to the concentration of Li$_3$N added. As shown in Figure 2, the rest potential linearly shifted to a negative direction with a logarithmic increase of $x_{N^{3-}}$. The data obtained are well described by the least-squares line having a theoretical slope of $-2.3RT/3F$ in eq 6. Next, the rest potential for the nitrogen gas electrode was measured in the LiBr−KBr−CsBr−Li$_3$N (0.003 mole fraction Li$_3$N added) melt at 673 K, when p_{N_2} was varied from 1 to 0.05 atm. The cell was preliminarily filled with a pure nitrogen gas at atmospheric pressure, and then, it was evacuated to reduce p_{N_2} to the specified pressure for every measurement. As shown in Figure 3, the rest potential linearly shifted to a negative direction with a logarithmic decrease of
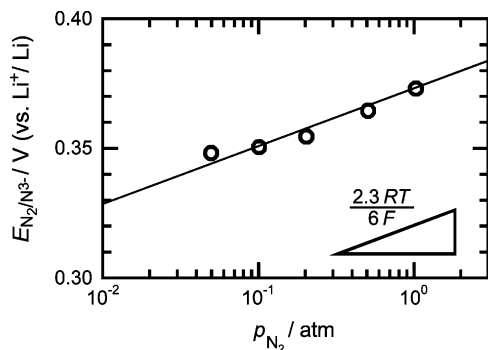
Figure 3. Relation between the rest potential of a Ni electrode and the pressure of the nitrogen gas over a LiBr−KBr−CsBr−Li$_3$N (0.003 mole fraction) melt at 673 K.
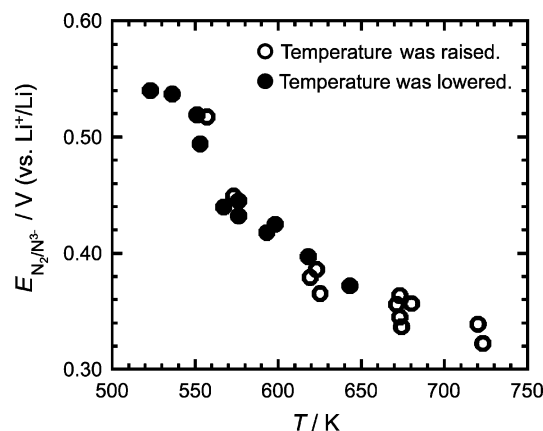

Figure 4. Relation between the equilibrium potential of the N$_2$/N^{3-} redox couple and the temperature in a LiBr−KBr−CsBr−Li$_3$N (0.005 mole fraction) melt under a 1 atm nitrogen gas atmosphere.

p_{N_2}. The data obtained are also well described by the least-squares line which has a theoretical slope of $2.3RT/6F$ in eq 6. As a result of these Nernstian plots, the equilibrium potential is found to be expressed by the following equation:

$$E_{N_2/N^{3-}} = (0.251 \pm 0.009) + \frac{RT}{3F} \ln \frac{p_{N_2}^{1/2}}{x_{N^{3-}}} \quad (\text{V vs Li}^+/\text{Li}) \quad (8)$$

The error value is the 95% confidence intervals. Since the Nernstian relation holds, it is reasonable to consider that the rest potential observed in this series of measurements corresponds to the equilibrium potential of the N$_2$/N^{3-} electrode represented as reaction 1 under these measured conditions. $E^{\circ\prime}_{N_2/N^{3-}}$ is calculated to be 0.251 ± 0.009 V versus Li$^+$/Li by extrapolating the fitted line to $\log(p_{N_2}^{1/2}/x_{N^{3-}}) = 0$.

Temperature Dependency of the Standard Formal Potential. The equilibrium potentials for the N$_2$/N^{3-} redox couple at the nitrogen gas electrode were measured in the LiBr−KBr−CsBr−Li$_3$N (0.005 mole fraction Li$_3$N added) melt under a 1 atm nitrogen gas atmosphere at various temperatures ranging from 520 to 730 K. The measurements were carried out during both raising and lowering of the temperature. Figure 4 shows the dependence of $E_{N_2/N^{3-}}$ on the temperature, which provides the relation between $E^{\circ\prime}_{N_2/N^{3-}}$ and the temperature as shown in Figure 5 using eq 6. The plots at temperatures in the range 570−730 K are fitted with a straight line by means of the least-squares method, which gives

$$E^{\circ\prime}_{N_2/N^{3-}}(T) = 0.877(\pm 0.074) - 0.930(\pm 0.117) \times 10^{-3}T$$

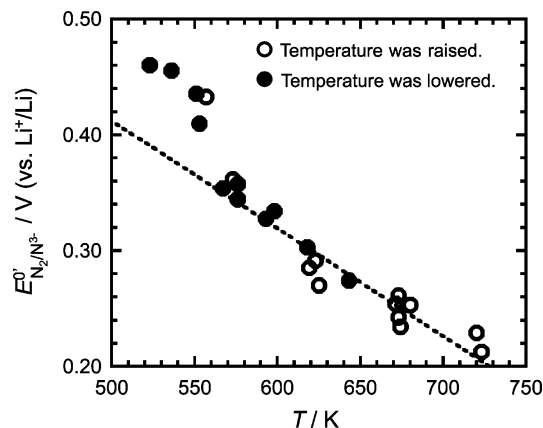$$(\text{V vs Li}^+/\text{Li}) \quad (9)$$

Figure 5. Relation between the standard formal potential of the N$_2$/N^{3-} redox couple and the temperature in a LiBr−KBr−CsBr−Li$_3$N melt.

Thermodynamic quantities of Li$_3$N dissolved in the LiBr−KBr−CsBr melt can be obtained from this relation. The discrepancy of the plots from the straight line is explained in terms of the change of the ionic interactions or the melt structure at temperatures near the melting point.

Thermodynamic Consideration. Since the above electrode potentials are expressed with reference to the Li$^+$/Li electrode in the LiBr−KBr−CsBr−Li$_3$N melt, a consideration of the concentration of the Li$^+$ ions in the melt is necessary to discuss the thermodynamic quantities of Li$_3$N. Assuming the activity coefficient of LiBr in the LiBr−KBr−CsBr eutectic melt ($x_{Li^+} = 0.561$) was nearly 1 on Raoult's law basis, the Li$^+$/Li potential is expressed as

$$E_{Li^+/Li} = E^{\circ}_{Li^+/Li} + \frac{RT}{F} \ln x_{Li^+} \quad (10)$$

where x_{Li^+} is the cation fraction of the Li$^+$ ions and $E^{\circ}_{Li^+/Li}$ is the standard potential of Li$^+$/Li. Since the Li$^+$/Li potential in the LiBr−KBr−CsBr eutectic melt ($x_{Li^+} = 0.561$) has been defined as zero, $E^{\circ}_{Li^+/Li}$ is expressed as

$$E^{\circ}_{Li^+/Li} = -\frac{RT}{F} \ln(0.561) \quad (11)$$

Generally, the standard free energy of the formation of Li$_3$N, ΔG°_f, is calculated from the relation

$$\Delta G^{\circ}_f = -3F(E^{\circ}_{N_2/N^{3-}} - E^{\circ}_{Li^+/Li}) \quad (12)$$

However, $E^{\circ}_{N_2/N^{3-}}$ cannot be obtained from the experimental results. Accordingly, ΔG°_f also cannot be obtained. We thus introduce the standard formal free energy of the formation of Li$_3$N, $\Delta G^{\circ\prime}_f$, as follows:[15]

$$\Delta G^{\circ\prime}_f = \Delta G^{\circ}_f - RT \ln \frac{\gamma_{N_2}^{1/2}}{\gamma_{N^{3-}}} \quad (13)$$

This is a similar concept to the standard formal potential in eq 7; that is, $\gamma_{N^{3-}}$ is defined as unity in an ideal pure liquid Li$_3$N. Using eqs 7, 11, and 12, eq 13 is rewritten as

$$\Delta G^{\circ\prime}_f = -3F(E^{\circ\prime}_{N_2/N^{3-}} - E^{\circ}_{Li^+/Li}) \quad (14)$$

$$= -3FE^{\circ\prime}_{N_2/N^{3-}} - 3RT \ln(0.561) \quad (15)$$

$\Delta G^{\circ\prime}_f$ is therefore obtained directly from the experimental data

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TABLE 2: Comparison of Thermodynamic Data for the Formation of Li$_3$N at 673 K^a

	T/K	ΔG_f°/ kJ mol^{-1}	ΔS_f°/ J mol^{-1} K^{-1}	ΔH_f°/ kJ mol^{-1}
the formal state in LiBr−KBr−CsBr (this study)	673	($\Delta G_f^{\circ\prime}$ =) −63.0 ± 2.7	($\Delta S_f^{\circ\prime}$ =) −284 ± 34	($\Delta H_f^{\circ\prime}$ =) −254 ± 23
the formal state in LiCl−KCl−CsCl[11]	673	($\Delta G_f^{\circ\prime}$ =) −46.4 ± 2.2	($\Delta S_f^{\circ\prime}$ =) −242 ± 69	($\Delta H_f^{\circ\prime}$ =) −212 ± 46
crystal[16]	673	−77.5	−145	−175

^{a} The error values are the 95% confidence intervals.

of $E_{N_2/N^{3-}}^{\circ\prime}$. In the same manner, both the standard formal entropy of the formation of Li$_3$N, $\Delta S_f^{\circ\prime}$, and the standard formal enthalpy of the formation of Li$_3$N, $\Delta H_f^{\circ\prime}$, can be defined and written as

$$\Delta S_f^{\circ\prime} = -\left(\frac{\partial \Delta G_f^\circ}{\partial T}\right)_p \tag{16}$$

$$= -\left(\frac{\partial \Delta G_f^\circ}{\partial T}\right)_p + \frac{\partial}{\partial T}\left(RT \ln \frac{\gamma_{N_2}^{1/2}}{\gamma_{N^{3-}}}\right)_p \tag{17}$$

$$= \Delta S_f^\circ + \frac{\partial}{\partial T}\left(RT \ln \frac{\gamma_{N_2}^{1/2}}{\gamma_{N^{3-}}}\right)_p \tag{18}$$

$$= 3F\left(\frac{\partial E_{N_2/N^{3-}}^{\circ\prime}}{\partial T}\right)_p + 3R \ln(0.561) \tag{19}$$

$$\Delta H_f^{\circ\prime} = \Delta G_f^{\circ\prime} + T\Delta S_f^{\circ\prime} \tag{20}$$

$$= \Delta G_f^\circ + T\Delta S_f^\circ + RT^2 \frac{\partial}{\partial T}\left(\ln \frac{\gamma_{N_2}^{1/2}}{\gamma_{N^{3-}}}\right)_p \tag{21}$$

$$= \Delta H_f^\circ + RT^2 \frac{\partial}{\partial T}\left(\ln \frac{\gamma_{N_2}^{1/2}}{\gamma_{N^{3-}}}\right)_p \tag{22}$$

where ΔS_f° and ΔH_f° are the standard entropy of the formation of Li$_3$N and the standard enthalpy of the formation of Li$_3$N, respectively. $\Delta S_f^{\circ\prime}$ is therefore obtained from the relation between $E_{N_2/N^{3-}}^{\circ\prime}$ and the temperature in the experiments. Then, $\Delta H_f^{\circ\prime}$ is evaluated from $\Delta G_f^{\circ\prime}$ and $\Delta S_f^{\circ\prime}$.

Accordingly, these thermodynamic quantities can be derived from the temperature dependency obtained in the foregoing section (eq 9), using these relational expressions. The linear relation between $E_{N_2/N^{3-}}^{\circ\prime}$ and the temperature shows that $\Delta S_f^{\circ\prime}$ can be regarded as being constant between 570 and 730 K. By using eq 19, $\Delta S_f^{\circ\prime}$ is calculated to be −284 ± 34 J mol^{-1} K^{-1}. Equation 15 directly gives a $\Delta G_f^{\circ\prime}$ value of −63.0 ± 2.7 kJ mol^{-1} at 673 K. Then, $\Delta H_f^{\circ\prime}$ is calculated to be −254 ± 23 kJ mol^{-1} at 673 K according to eq 20.

The formal thermodynamic quantities obtained are compared with literature data and those for the chloride melt reported earlier,[11] as shown in Table 2. The literature data are for the formation of crystalline Li$_3$N from liquid Li and gaseous nitrogen at 673 K that has been calculated by linear interpolation of the data at 600 and 700 K.[16] The positive deviation in $\Delta G_f^{\circ\prime}$ from ΔG_f° of the crystalline Li$_3$N is explained by the fact that the existing state of Li$_3$N in the molten salt deviates toward the liquid or gas state from the solid crystal state. The degree of

the deviation in $\Delta G_f^{\circ\prime}$ for the present case is smaller than that for the chloride melt. This indicates that the repulsive force between the Br$^-$ ion and the N^{3-} ion is smaller than that between the Cl$^-$ ion and the N^{3-} ion, which is reasonably explained by the smaller electrostatic force around the Br$^-$ ion due to its larger ionic radii. The negative deviation in $\Delta S_f^{\circ\prime}$ from ΔS_f° of the crystal can be understood in terms of the formation of an ordered local structure in the melt. The degrees of the deviation in $\Delta S_f^{\circ\prime}$ for the present case and the case for the chloride melt are likely to be the same order of magnitude, taking into account the error values. This indicates that a similar local structure is formed in both systems.

Conclusions

The results of quantitative analysis of anodically evolved gas from a LiBr−KBr−CsBr−Li$_3$N melt show that the oxidation of the N^{3-} ions proceeds to produce pure nitrogen gas almost quantitatively at potentials more positive than 0.3 V versus Li$^+$/Li according to the following reaction:

$$N^{3-} \rightarrow {}^1/_2 N_2 + 3e^- \tag{3}$$
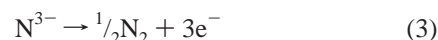
The Nernst relation holds for the rest potential of Ni electrodes at nitrogen gas pressure, p_{N_2}, and the anion fraction of the N^{3-} ions, $x_{N^{3-}}$, in the melt. The standard formal potential of the N$_2$/N^{3-} redox couple, $E_{N_2/N^{3-}}^{\circ\prime}$, is then evaluated to be 0.251 ± 0.009 V versus Li$^+$/Li (p_{N_2} = 1 atm, $x_{N^{3-}}$ = 1) at 673 K. The dependency of $E_{N_2/N^{3-}}^{\circ\prime}$ on the temperature (570−730 K) gives a linear relation, whose slope is −0.930 ± 0.117 mV K^{-1}. The formal thermodynamic quantities for the formation of Li$_3$N in the melt are $\Delta G_f^{\circ\prime}$ = −63.0 ± 2.7 kJ mol^{-1} at 673 K, $\Delta S_f^{\circ\prime}$ = −284 ± 34 J mol^{-1} K^{-1}, and $\Delta H_f^{\circ\prime}$ = −254 ± 23 kJ mol^{-1} at 570−730 K.

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